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The effect of calcium/sodium ratio on the dynamic adsorption of sodium dodecyl benzene sulfonate (SDBS) onto water/air interfaces. Evaluation of critical micelle concentrations, diffusion coefficients and molecular areas

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By

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Preface:

This thesis is a continuation of the previous specialization project done in 2015 as a part of the course of Industrial Colloid Chemistry (TKP4) at NTNU.

The task was to look at the CMC, surface excess, minimum surface area, diffusion coefficient (boh before and after CMC) for different $\frac{CaCl_2}{NaCl} - ratio$ with the use of SDBS as the surfactant, where the ionic strength was kept constant at 20mM and the temperature kept at 25 °C. Five different $\frac{CaCl_2}{NaCl} - ratio$ was chosen, 0, $\frac{1}{117}$, $\frac{1}{57}$, $\frac{1}{17}$ and $\frac{1}{12}$. With at least nine different surfactant concentrations was used to localize the CMC. As well with three parallels.

All of the practical work was performed at Ugelstad Laboratory, NTNU, from January 2016 to June 2016, under supervision of Professor Gisle Øye.

There were some issues with the measurements with the maximum bubble pressure tensiometer, where the value of the surface tension dropped at a certain surface age. This issue was fixed by coating the capillary with *silanization solution I* to make it hydrophobic.

Every Monday there was a meeting where the results for the previous week was introduced, at those meetings, Gisle Øye (Professor), Kancir Eugenie (PhD Candidate) Yinghong Gao (PhD Candidate), Muhammad Awais Ashfaq Alvi (PhD Candidate) and Marcin Dudek (PhD Candidate) participated, and feedback was given.

Last, I like to give a special thanks to Sirsha Patatunda, Sulalit Bandyopadhyay and Sebastien Charles Simon for some discussion and briefing about the results.

Trondheim 06.06.2016

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  Arnt Ove Jektvik Olsen

Summary:

Evaluation on how the $\frac{CaCl_2}{NaCl} - ratio$ would affect the CMC, diffusion coefficients and surface excess, by using maximum bubble tensiometer.

The CMC values for brines whit constant ionic strength of 20 mM and constant temperature at 25°C, and $\frac{CaCl_2}{NaCl} - ratio$ of 0, $\frac{1}{117}$, $\frac{1}{57}$, $\frac{1}{17}$ and $\frac{1}{12}$ was determined with maximum bubble pressure method along with regression. Addition the value of minimum area pr molecule for the different brine was also calculated, which show that it decreases with higher $\frac{CaCl_2}{NaCl} - ratio$ for the 3 first ratios.
Diffusion coefficient was found with the same data by using short time approximation of *Ward and Tordai equation*. And also tested by comparing the model with the measured values where the solutions with high concentration of SDBS didn't fit well with the model.

The CMC for the brine with $\frac{CaCl_2}{NaCl} - ratio$, 0, $\frac{1}{117}$, $\frac{1}{57}$, $\frac{1}{17}$ and $\frac{1}{12}$, with an ionic strength of 20 mM and temperature at 25°C was found to be to be 0.566 (±0.042)mM, 0.403(±0.007)mM, 0.318(±0.006)mM, 0.262(±0.0.47)mM and 0.238(±0.004)mM. The surface tension is also lower after CMC with the increase of the $\frac{CaCl_2}{NaCl} - ratios$ for the first three $\frac{CaCl_2}{NaCl} - ratios$.

Content

1   Introduction:

In most of today's oil rig there is used *inject water* to pump oil out of the reservoirs. To increase the amount of oil pumped out, there is also added surfactant into this water. The function of the surfactant is to lower the surface tension of the water, witch lead to more oil getting pumped out. Before proceeding farther into the process that consists of 3-phase gravity separator, hydrocyclone, flotation, pumps etc. But the water also consists of many other components witch can and will affect the behavior of the surfactant, behaviors like CMC, surface excess and diffusion coefficient. One thing that can affect the surfactants is different ions, and maybe even the ratios of different ions. By studying what happens with the surfactant at different ions ratios, will give a better understanding of how the surfactant will behave, witch again can be used to improve the oil process itself, both in increasing the oil recovery and reduction in operating cost.

Every part of the process is heavily dependent on the interfacial tension. And by study how can manipulate the properties of the interfacial tension and the mechanism, there is a big efficacy gain by understanding and improving the oil recovery.

Therefore, will this thesis be looking at how the ratios of $CaCl_2$ and NaCl will affect CMC, surface tension, surface excess, minimum area pr molecule and diffusion coefficient.

2   Theory:

This chapter will cover some topic of the theory of *Colloid and Polymer Chemistry*, mostly to what is relevant to this thesis. It will go throe crude oil, surface tension, the measurement method, surfactants diffusions and critical micelle concentration.

2.1   Crude Oil:

The crude oil consists of a complex mixture of hydrocarbons and hetero compounds. Even with today's technology it is hard to identify all the components that exist in the feedstock. Therefore, it is normal to characterize the crude oil by:

- Gravity
- Aniline point
- Boiling range
- Hydrogen content
- Heteroatom content (like sulfur and nitrogen)

Another way the crude oil can be characterized is by defining the different type of hydrocarbons that are present, such as paraffins, naphtenes, aromatics and etc.

The crude oil can very quiet a lot depending on where the crude oil originates from, an example of this is shown in Table 1.[1]

Table 1. An example of how the crude oil can vary from place to place.[1]

Crude source	Bombay High, India	Taching, China	Arabia Heavy, Saudi Arabia	California, USA
LV % yield of 240-540 °C VGO	26	37	24	24
API gravity	28	31	22	14
Mass spec. Group type, LV %				
Paraffins	46	37	17	1
Naphthenes	23	47	25	42
Aromatics	31	16	58	57
Sulfur, wt%	0.5	0.1	3.0	1.0
Nitrogen, ppm	410	690	150	6470

Another method to described crude oil can be based on their polarizability and polarity, this method is called SARA [2]. Here the crude oil is divided into something called SARA fractions, which split up the crude oil into four fractions, saturates, aromatics, resins and asphaltenes. The first fraction, saturates consist of nopolar material including linear, branched, and cyclic saturated hydrocarbons. The second fraction, aromatics, consist of one or more aromatic rings, which make it more polarizable. While resins and asphaltenes all has polar

substituents. What distinguishes resins and asphaltenes is that the asphaltenes are insoluble in an excess of heptane and pentane, while resins don't.[2]

An overview of the different fraction is showed in the Figure 1 below:

- A and E: highest saturate content
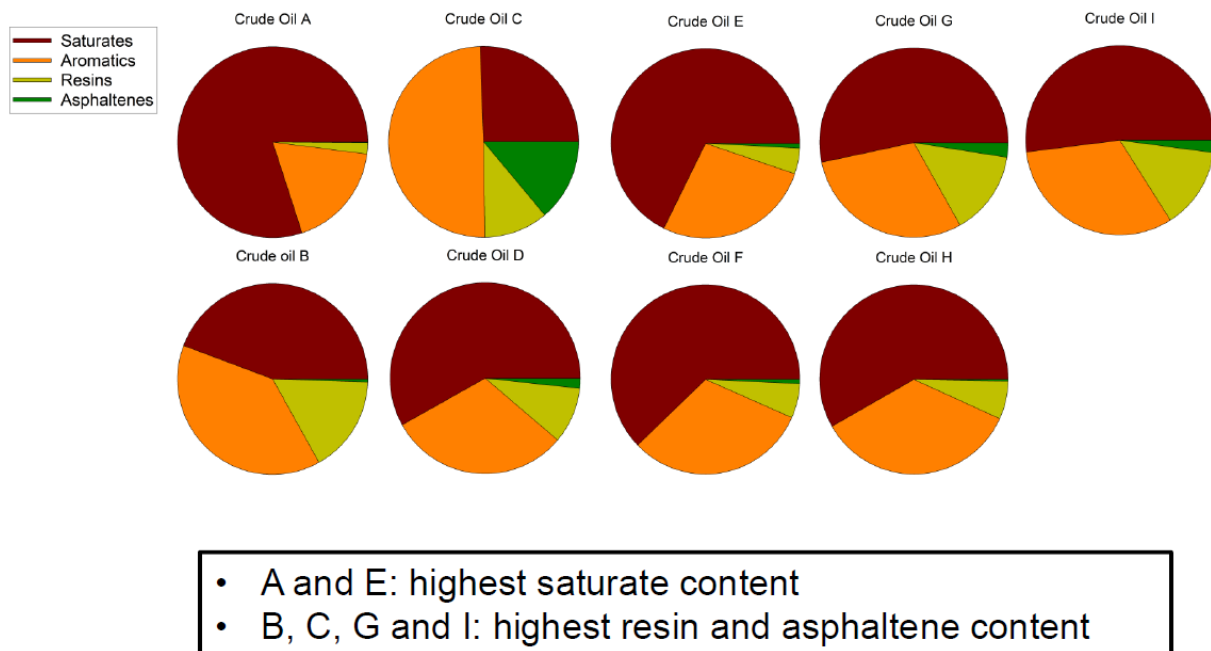- B, C, G and I: highest resin and asphaltene content

Figure 1. An illustration of the component of different crude oil types, red is the amount of saturates, orange is the amount of aromatics, yellow is amount of resins and green is the amount of asphaltenes..[3]

2.2 Surface Tension:

Surface tension is a force that tends to lower the surface area, and that is result that comes from the intermolecular interactions that are short range in macroscopic terms. Example is that a liquid molecule has a negative side/charge and a positive side/charge, and those molecule tend to structural itself so that the negative side/charge and the positive side/charge of each molecule can make a "bond", and what the surface tension do is to lower the amount of "broken bonds" as much as possible.[4]

Since surface tension is a force that try to lower the surface area, then the SI-unit for surface tension, γ, is N/m.

There are many ways to measure surface tension, some are; tilted plate method, Wilhelmy plate technique, capillary rise technique, maximum bubble-pressure method, drop-weight method and ring method.

As mention earlier, the SI-unit for surface tension is N/m, this mean that surface tension also can be viewed as an energy, J/m^2, or surface free energy.

If keep the pressure and temperature constant, the surface tension can be defined as the change in Gibbs free energy per surface area, as seen in the equation below (Eq.1).

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,p} \qquad \text{(Eq.1)}$$

One of the most famous equations when it comes to surface tensions, then it is *Laplace equation*(Eq.2), which was derived in 1805. [4]

$$\Delta p = \gamma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad \text{(Eq.2)}$$

2.3 Produced Water:

Produced water consists of a mix of organic and inorganic materials, and some factors that can influence this mixture can be such as the geological location of the field, its geological formation, lifetime of the reservoirs. Some type of hydrocarbon products that are being produced can also affect the physical and chemical properties of the produced water. The main compounds in produced water are as follow:[5]

- Dissolved and dispersed oil compounds
- Dissolved formation minerals
- Production chemical compounds
- Production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes)
- Dissolved gases

The produced water characteristic can also be affected by the operational condition, and chemicals used in the process facilities.[5]

2.3.1 Dissolved and dispersed oil compounds:

The oil itself consists of a mixture of different hydrocarbons like benzene, toluene, naphthalene etc. The factor that affect the amount of dissolved and suspended oil that are present in produced water is:[5]

- Oil composition
- pH, salinity, TDS (total dissolved solids), temperature
- Oil/water ratio
- Type of quantity of oilfield chemicals
- Type and quantity of various stability compounds (waxes, asphaltenes, fine solids)

2.3.2 Dissolved formation minerals:

The inorganic dissolved compounds in produced water are radioactive materials, heavy metals, cations and anions. These components affect the produced water chemistry when it comes to buffering capacity, salinity and scaling of different equipment's and pipelines.[5]

2.3.3 Production chemical compounds:

Throughout the oil and gas process, different types of chemicals are added into the process to prevent different operational problems. The chemicals that get added can be corrosion inhibitors, scale inhibitors, biocides, emulsion breaker, antifoam and other water treatment chemicals.[5]

2.3.4 Production solids:

The components consist of many different materials like formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes.[5]

2.3.5 Dissolved gases:

These components are mainly CO_2, O_2 and H_2S.[5]

2.4 Surfactant:

Surfactant is a molecule that can affect the surface tension in a solution dramatically. Surfactant consists of a hydrophilic "head" and a hydrophobic "tail".

The surfactant is primary classification basis on the charge of the polar head group. Classes as anionic, cationic, non-ionic and zwitterionics. Where the zwitterionic contains both anionic and cationic charge. [6]

2.4.1 Anionic:

The polar groups that are found in the anionic are carboxylate, sulfate, sulfonate and phosphate. The anionic surfactants constitute about 60 % of the total surfactant production worldwide. One of the main reasons for the popularity for this surfactant is the low cost to manufacture the surfactant.

A short polyoxyethylene chain between the hydrocarbon and the anionic group gives the surfactant a greater tolerance toward salt. While a short polyoxypropylene chain between the hydrocarbon and the anionic group will increase the solubility in organic solvents.

Anionic surfactants are also quite sensitive toward hard water.[6]

2.4.2 Cationic:

Most of the cationic surfactants are based nitrogen carrying the cationic charge, amine and quaternary ammonium-based products are common. They cannot be used as high pH.

Cationic surfactants adsorb strongly to many surfaces, and their main uses are related to *in situ* surface modification. In general, cationic surfactants will not be compatible with anionic surfactants, but there are some exceptions. [6]

2.4.3 Non-Ionic:

This surfactant doesn't have a polyether or a polyhydroxyl unit as the polar group.

Unlike the anionic surfactant, this surfactant is not sensitive toward hard water, they are the second largest surfactant among the other surfactant class, and they are compatible with other surfactants type. The non-ionic become less water soluble at high temperature.[6]

2.4.4 Zwitterionic surfactants:

Zwitterionic contain both positive charged and negative charged, where the positive charge mostly consist of ammonium, while the negative charge can vary.

This surfactant type is the smallest surfactant class, but still is compatible with all of them. Most of them have shown very low skin and eye irritation, and therefore is quite suited for personal care products like shampoos.[6]

2.5 Diffusion:

Diffusion is a value that tells how fast particles (molecule, ions, bacteria, dye etc.) spread out. One driving force can be the concentration gradient, where molecule goes from high concentration to love concentration, until the system has reached a steady state.[7]

Here the diffusion is the transport of monomer(surfactant) to the surface. When the monomer is at the subsurface it will follow one of two models. The first model is called *diffusion controlled*, this model assumes that the rate-controlling step is the diffusion between the bulk and the subsurface, and the adsorption to the surface is very fast. The second model is called the *mixed kinetic-diffusion*, this model assumes that the rate-controlling step is the transport of monomer to the surface. Where it is a adsorption barrier that prevent the adsorbing of the monomer.[8]

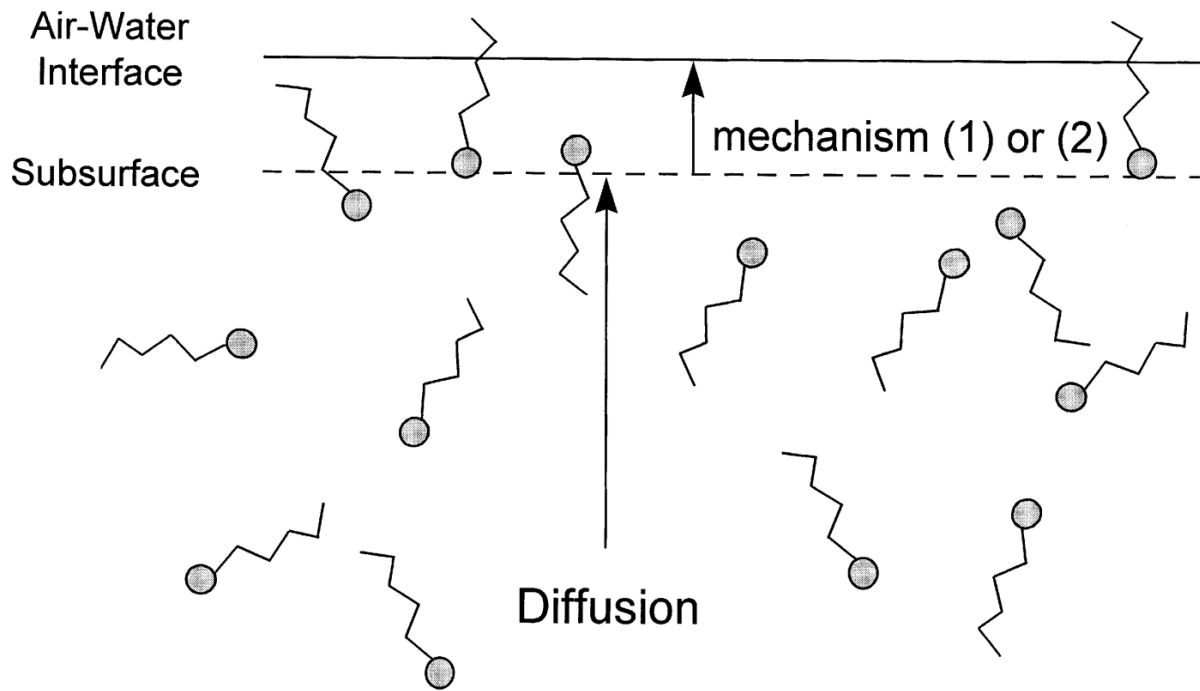An illustration of both models are shown in Figure 2 below.

Figure 2. Figure illustrates how monomer transport to the surface, where the monomer first goes to the subsurface, and then it will either follow 1 of the two models. Either instantaneously adsorb to the surface (diffusion control), or pass through a potential barrier to adsorb(mixed kinetic-diffusion)[8]

2.6   Critical Micelle Concentration:

Critical micelle concentration, short CMC, is the concentration of the surfactant where micelle starts to form. The formation of micelle is an alternative mechanism than adsorption at the interfaces to be able to reducing the free energy of the system. The micelle can be viewed as a reservoir for the surfactant, what is important to know is that the surface tension won't reduce anymore above the CMC. An illustration of how the surfactant behaves and starts to form micelle is shown in the Figure 3. [6]
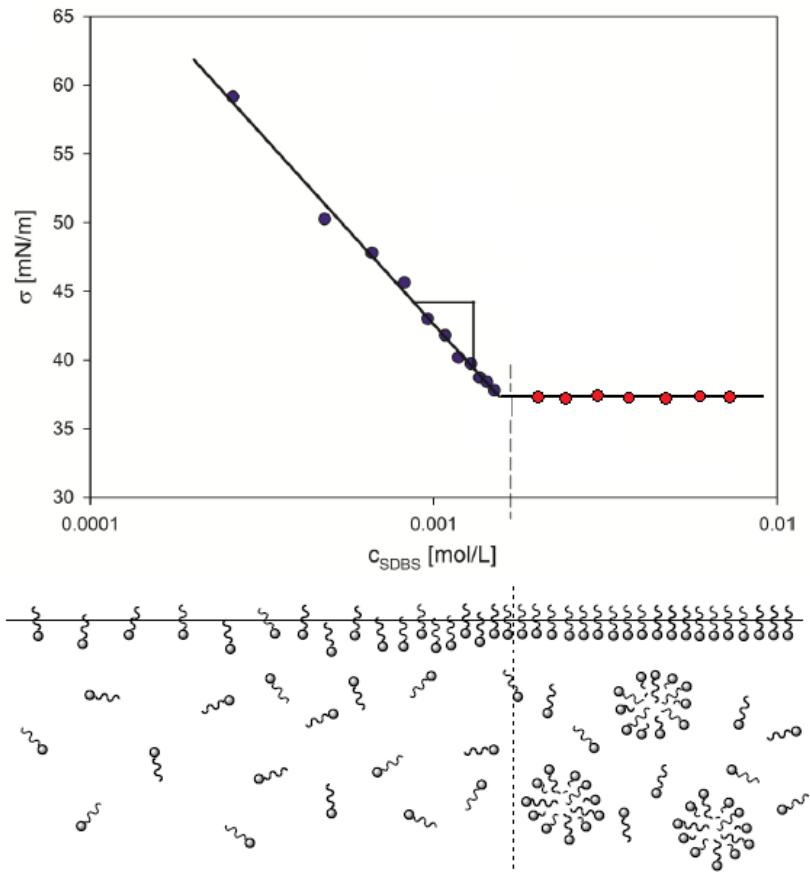
Figure 3. Illustration of how increasing the concentration of the surfactant will affect the surface tension and how the surfactant will structure itself in the solutions, and start to form micelles. [9]

2.1 Maximum Bubble pressure:

Maximum Bubble pressure is a method that is used to measure surface tension as a function of surface age, where the surface age is the time from where the bubble format (minimum pressure) until the bubble detach (maximum pressure, and where the bubble has formed a half sphere).[10]

The formation of the bubble is caused by an air flow going through the capillary, the maximum bubble pressure tensiometer start with a high air flow to measure the surface tension for low surface age, and for each measurement it will reduce the air flow to measure the surface tension or a higher surface age. The equation the is used to calculated the surface tension is (Eq.3):[11]

$$\gamma = \frac{(P_{max} - P_0)R}{2} \qquad \text{(Eq.3)}$$

Where γ is the surface tension, P_{max} is the maximum pressure inside the bubble (point C on Figure 4), P_0 is the hydrostatic pressure in the capillary, R is the radius of the bubble.

Figure 4 show an example how the maximum bubble pressure tensiometer function.
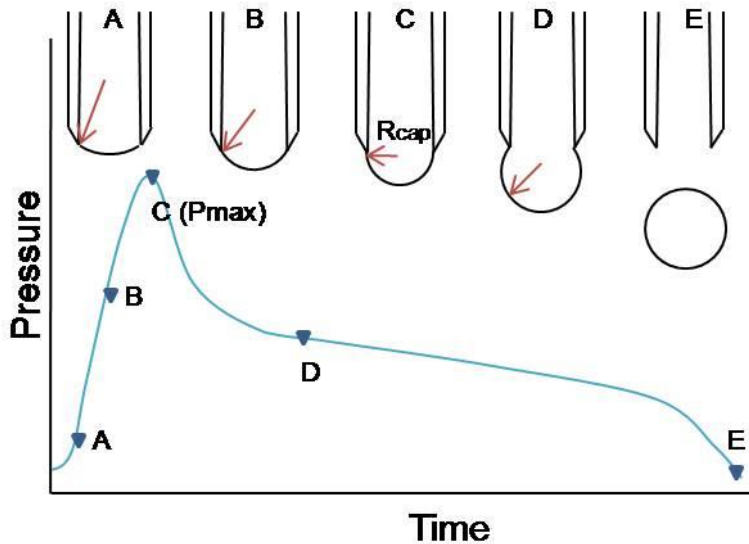
Figure 4. An illustration over how the maximum bubble pressure tensiometer function. At point A and B is where the bubble start to form and the pressure start to increase. Point C is where the bubble has become a half sphere, which also is where the pressure is the highest. Point D is where the bubble start to detach itself from the capillary as the pressure is reducing as well. Point E is where the bubble has completely detached itself from the capillary.

The rang of this method when it comes to the surface age goes from 5 ms up to 200 second. This method is great for measurement at low surface age, but if want to measure at higher than 200 second then other technic should be consider, like drop pressure, drop volume, pendant drop, plate tensiometry or ring tensiometry.[11]

3   <u>Material and practical method :</u>

The practical consist of preparation of the brine (Chapter 3.1), using the density meter (Chapter 3.2) and maximum bubble pressure tensiometer (Chapter 3.3). Along with some regression for the result, but the regression will be talked about much more in the Result chapter (Chapter 4.4)

3.1   **Preparation of brine:**

3.1.1   Equipment's and chemicals:
- Volumetric flask (5000 ml)
- Weight (10 mg – 320g)
- Bottles (100 ml, 2000 ml)
- NaCl
- $CaCl_2 \cdot 2\ H_2O$
- SDBS

3.1.2   Procedure:

The necessary amount of NaCl and $CaCl_2$ (to make different molar $\frac{CaCl_2}{NaCl} - ratios$; 0, $\frac{1}{117}$, $\frac{1}{57}$, $\frac{1}{17}$ and $\frac{1}{12}$)was put in a volumetric flask (5000 ml) and dilute to mark, where the ionic strength was kept constant (20 mM), the solution (2000 ml) then get transferred into bottle along with enough SDBS to make the highest concentration of the SDBS. Then the solution was put on a shaker (4+ hours), before making three parallel sets of lower concentration of SDBS, where the pure brine was used as diluent. Then getting placed on the shaker again (4+ hours).

3.2   **Density measurment:**

3.2.1   Equipment's and chemicals:
- Density Meter, Anton Paar, DMH 5000
- Tetrahydrofurar
- Toluene
- Petroleum Ether
- Injector (5 ml)

3.2.2 Procedure:

The settings for density meter are set on constant temperature, 25°C. Each $\frac{CaCl_2}{NaCl} - ratios$ solutions for all the SDBS concentration are injected into the density meter where all air-bubbles are removed from the injector to determent the density for the solution, followed by a cleaning procedure after each measurement. The density is needed for the bubble pressure tensiomter.

3.3 Bubble Pressure Tensiometer

3.3.1 Equipment's and chemicals:
- Bubble Pressure Tensiometer, Krüss, BP100-Mk1, serial no: 20005010.
- capillary (glass, SH3120 , ~ 0.2 mm)
- Toluene

3.3.2 Procedure

The diameter of the capillary was measured with *capillary measurement*. This data is required for the bubble pressure measurements, along with the density of each $\frac{CaCl_2}{NaCl} - ratios$ solutions for all the SDBS concentration. The run time (Surface Age) for the measurements was set to go from 10ms to 200 seconds. The capillary and the bowl were cleaned between each measurement.

4 Results:

The results are split up into results from the Maximum bubble pressure (Chapter 4.1), Regression for the equilibrium surface tension (Chapter 4.2), Critical micelle concentration (Chapter 4.3), Estimating the n-value (Chapter 4.4), Surface Excess (Chapter 4.5), Diffusion coefficient (Chapter 4.6) and Model vs measured value (Chapter 4.7)

4.1 Maximum Bubble Pressure:

One example of the results with the bubble pressure tensiometer is showed in the graph below (Figure 5), the rest of the results is shown in the Appendix 1 (Figure 15 to Figure 29).
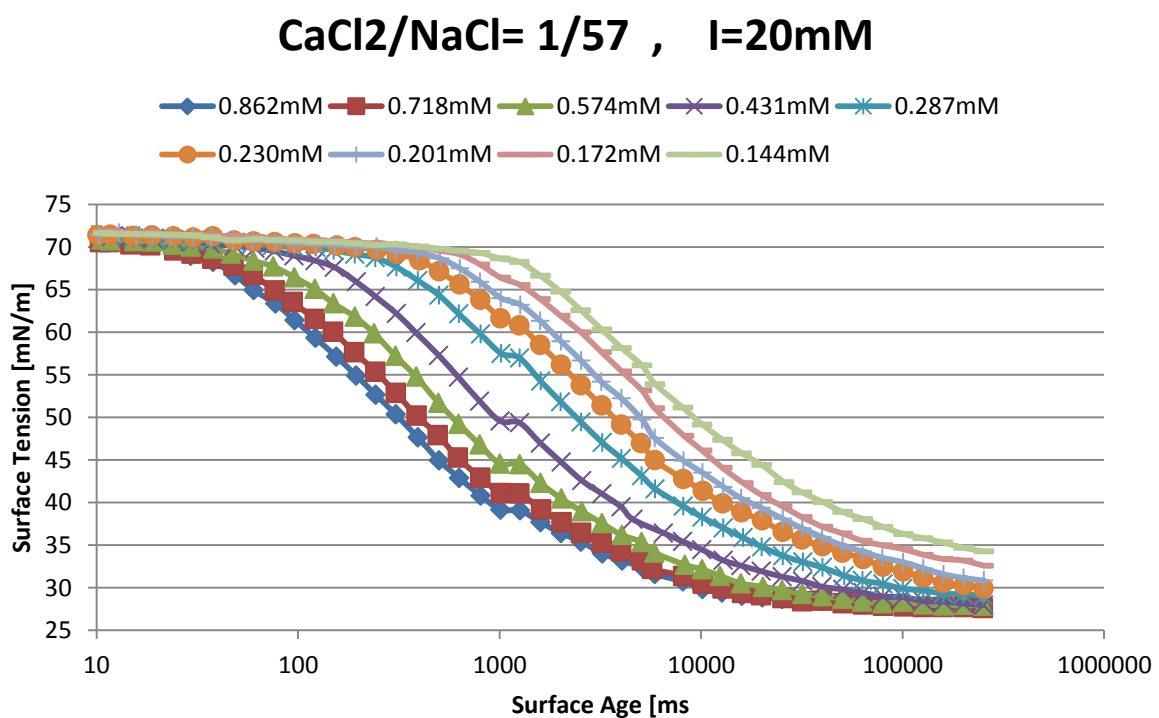
Figure 5. Plot for surface tension over surface age gotten from the maximum bubble pressure tensiometer for different concentration of SDBS. Ionic strength kept at 20 mM, temperature at 25 °C. The CaCl2/NaCl ratio is 1/57

4.2 Regression for the surface tension equilibrium:

Sigmaplot(v.13.0) was used for the regression, regression was done on all of the data from the maximum bubble pressure tensiometer since some of the solutions didn't reach the equilibrium when it came to the surface tension. There was the solution with lowest concentration of surfactant that didn't reach the equilibrium.

The equation that was used to find the equilibrium surface tension was exponential decay with 7 parameters seen below (Eq.4).

$$\gamma(t) = \gamma_{eq} + a \cdot e^{-b\sqrt{t}} + c \cdot e^{-d\sqrt{t}} + g \cdot e^{-h\sqrt{t}} \qquad \text{(Eq.4)}$$

The γ_{eq} is the surface tension at equilibrium, while t is the surface age. The parameters a, b, c, d, g and h are all constants, while t is the time measured in seconds.

This equation has no physical connection to any real models, the reason it was used was to achieve γ_{eq} that was most trustworthy, where the measured data fitted to the value that was measured. Some data had to be cut out to make the fitting possible to the exponential decay formula, since a few of the data didn't fit the start of the measured to the exponential decay equation (Eq.4). Unforcedly, the lower the surfactant concentration was, the more data points had to be cut out to make the fitting good.

4.3 **Critical Micelle Concentration:**

The data from the regression was used to find the CMC for each of the different $\frac{CaCl_2}{NaCl}-$ $ratios$.

The overview of all the CMC is shown in the Table 2 below while an example of one of the ratios for the CMC plot is shown in Figure 6. Rest of the salt ratios is shown in appendix 2 (Figure 30 to Figure 34). Figure 7 show a plot of CMC based on the salt ratios.

Table 2. Data of the CMC for each CaCl2/NaCl-ratios, both in ppm and mM.

$\frac{CaCl_2}{NaCl}$-ratio	Cons. of SDBS [ppm]	Cons. of SDBS [mM]
0	197 (± 14)	0.566 (± 0.042)
$\frac{1}{117}$	140 (±2.6)	0.403 (±0.007)
$\frac{1}{57}$	110 (± 2)	0.318 (± 0.006)
$\frac{1}{17}$	91 (± 16)	0.262 (±0.047)
$\frac{1}{12}$	83 (± 1.4)	0.238 (± 0.004)
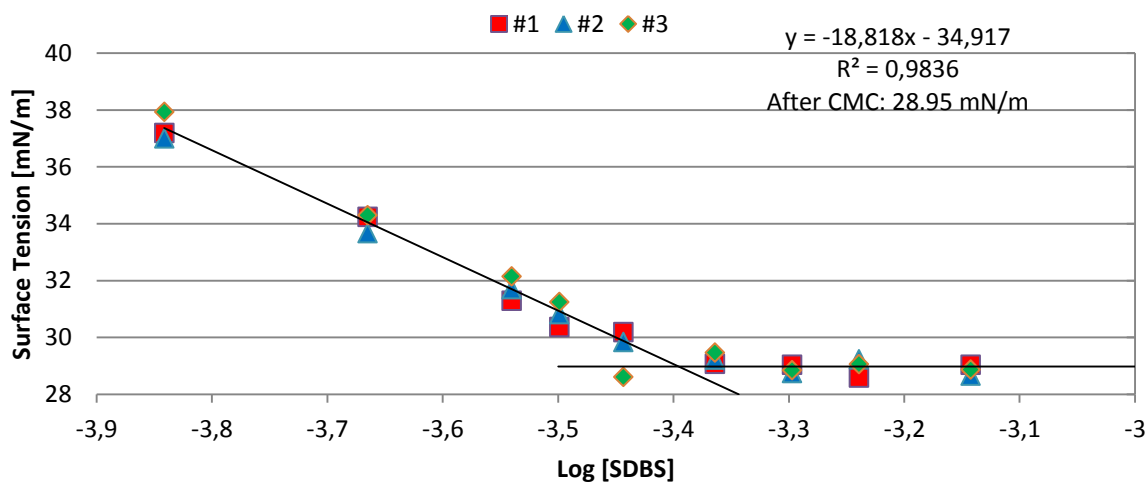
Figure 6. Plot for the CMC for CaCl2/NaCl = 1/117 with ionic strength of 20 mM and temperature of 25°C. The red square is the first parallel, the blue triangle is the second parallel, the green square is the third parallel.
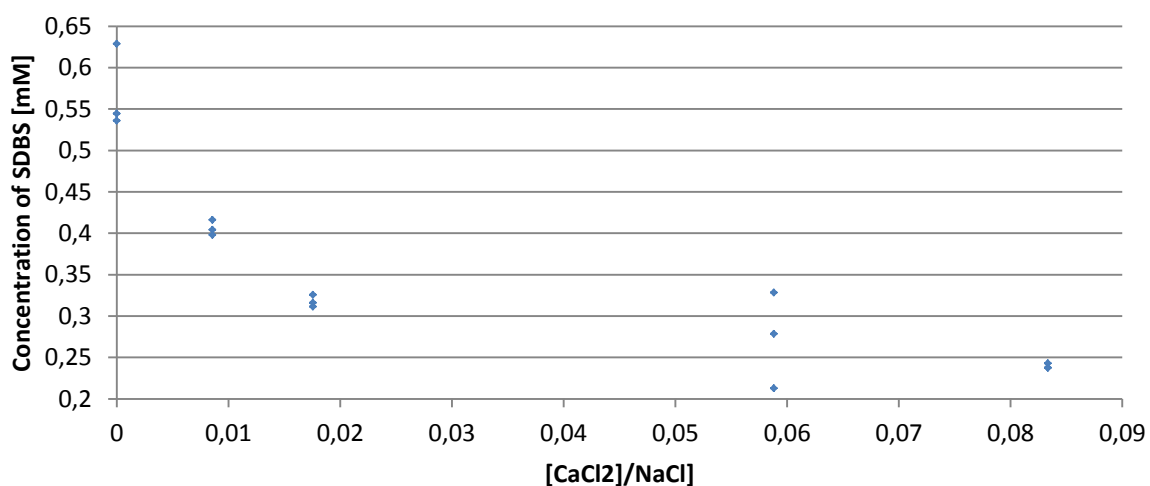

Figure 7. Plot over the CMC for different CaCl2/NaCl-ratios with 3 parallels on each ratios, where the ionic strength was kept constant at 20 mM and the temperature kept constant at 25 °C.
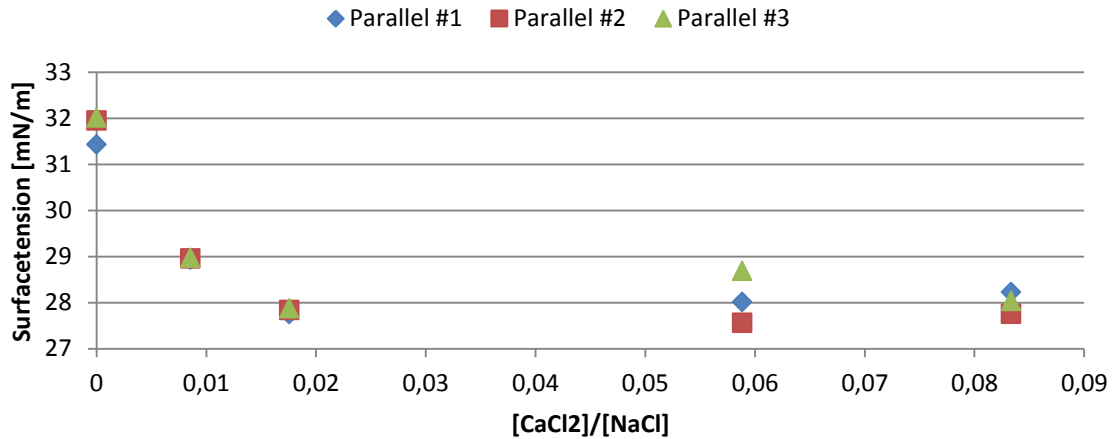
Surface tension after CMC

Figure 8. Graph show how the surface tension after CMC changes with the change of $CaCl_2$/NaCl-ratios, where the ionic strength is 20 mM, the temperature is 25 °C. With 3 parallels. The blue square is the first parallel, the red square is the second parallel, the green triangle is the third parallel.

4.4 Estimating the n-value:

The n-value is driven from the Gibbs adsorption isotherm equation (Eq.5)[12, 13]

$$d\gamma = \sum_i \Gamma_i d\mu_i \qquad (Eq.5)$$

Where $d\gamma$ is the change in interfacial tension, Γ_i is how much of component i has adsorbed per unit area, also called surface excess, $d\mu_i$ is the change in chemical potential of component i . The equation (Eq.6) is for the chemical potential:[12]

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (Eq.6)$$

And the change in chemical potential is given by deriving that equation(Eq.6) into(Eq.7):[12]

$$d\mu_i = RT \, \mathrm{d}\ln a_i \qquad (Eq.7)$$

Where μ_i is the chemical potential of component i, μ_i^0 is the reference point of chemical potential of component i, R is the gas constant, 8,314 J/(K mol), T is the temperature in K and the a_i is the activity coefficient of component i.

Electrolyte #1:	$NaCl \rightarrow Na^+ + Cl^-$	(Eq.8)
Electrolyte #2:	$CaCl_2 \rightarrow Ca^{+2} + Cl^-$	(Eq.9)
Surfactant:	$NaDBS \rightarrow Na^+ + DBS^-$	(Eq.10)
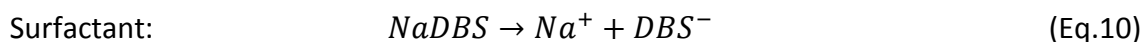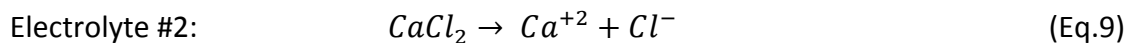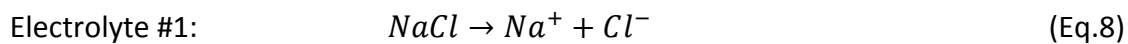
Where NaCl and $CaCl_2$ are the two electrolyte and NaDBS (SDBS) is the anionic surfactant. Combining Gibbs adsorption isotherm (Eq.5) and the equation for change in potential (Eq.7) energy for this system, give (Eq.11):

$$-\frac{d\gamma}{RT} = (\Gamma_{\text{Na}^+} d \ln a_{Na^+}) + (\Gamma_{\text{Ca}^{2+}} d \ln a_{Ca^{2+}}) + (\Gamma_{Cl^-} d \ln a_{Cl^-}) + (\Gamma_{DBS^-} d \ln a_{DBS^-}) \qquad \text{(Eq.11)}$$

With electro neutral means that (Eq.12):[12, 13]

$$\Gamma_{Na^+} + \Gamma_{Ca^{2+}} = \Gamma_{Cl^-} + \Gamma_{DSB^-} \qquad \text{(Eq.12)}$$

Assuming that the concentration of NaCl is much higher than $CaCl_2$ and NaDBS (SDBS), than can neglect the affect from $\Gamma_{Ca^{2+}}$ and Γ_{DBS^-}. And by changing the concentration of NaDBS will keep the concentration of Cl⁻ at constant, therefore make $d\mu_{Cl^-} = 0 \rightarrow \ln a_{Cl^-} = 0$. Giving equation (Eq.12):

$$-\frac{d\gamma}{RT} = \Gamma_{\text{Na}^+} d \ln a_{Na^+} \qquad \text{(Eq.13)}$$

With a small concentration of the surfactant NaDBS in the presence of NaCl means that a_{Na^+} is much higher than a_{DSB^-}, but $d(\ln a_{Na^+})$ is still the same as $d(\ln a_{DBS^-})$ since the variations of the concentration is still the same when add surfactant. This will give the final equation (Eq.14):

$$\Gamma = -\frac{1}{nRT} \cdot \frac{d\gamma}{(d \ln a_{X^-})} \qquad \text{(Eq.14)}$$

Where n is equal to 1.[13]

4.5 Surface Excess and Minimum Area pr molecule:

The surface excess was calculated based on the slope close to the CMC with equation (Eq.14) where activity coefficient is equal of the concentration of SDBS, since the concentration is small, this will give (Eq.15).[13]

$$\Gamma = -\frac{1}{nRT} \cdot \left(\frac{\partial \gamma}{\partial \ln c}\right) \qquad \text{(Eq.15)}$$

Where Γ is the surface excess at equilibrium in mol/m^2, R is the gas constant 8.314 J/(mol K), T is the temperature in kelvin, which is 298.15 (±1) K, n-value is either 1 or 2, dependent on the solution and the surfactant. It is 1 when there is a non-ionic surfactant, neutral molecules or ionic surfactant in the presence of excess electrolyte. The n-value is 2 for 1:1 ionic surfactant where assume electrical neutrality of the interface. In this case the n-value is in this case 1 as mention in Chapter 4.4. And last it is $\left(\frac{\partial \gamma}{\partial \ln c}\right)$, which is the slope close to the CMC.[8]

The minimum area pr molecule is calculated with equation (Eq.65). [14]

$$A_{min}^{a/w} = \frac{1}{N_A \Gamma} \qquad \text{(Eq.16)}$$

Where $A_{min}^{a/w}$ is the minimum area pr molecule in m^2/molecule, N_A is the Avogadro constant, $6.002140 \cdot 10^{23} mol^{-1}$. Γ is as mention earlier the surface excess in mol/m^2.

The average value of the surface excess and minimum are pr. molecule can be found in Table 3 and an illustration is shown in Figure 9 and Figure 10 below.

Table 3. Data for the slope close to the CMC, surface excess and minimum area pr molecule for each CaCl2/NaCl-ratios where the ionic strength is kept constant at 20 mM and temperature is kept constant at 25 °C.

$\frac{CaCl_2}{NaCl}$-ratio	$\left(\frac{\partial \gamma}{\partial \ln c}\right)$ [N/m]	Γ [mol/m^2]	Minimum Area pr molecule [nm^2]
0	-0.0067693	$2.731 (\pm 0.074) \cdot 10^{-6}$	0.608 ($\pm$0.074)
$\frac{1}{117}$	-0.00881727	$3.557 (\pm 0.110) \cdot 10^{-6}$	0.467 ($\pm$0.017)
$\frac{1}{57}$	-0.0089606	$3.615 (\pm 0.057) \cdot 10^{-6}$	0.459 ($\pm$0.007)
$\frac{1}{17}$	-0.0056958	$2.298 (\pm 0.800) \cdot 10^{-6}$	0.723 ($\pm$0.216)
$\frac{1}{12}$	-0.0044959	$1.814 (\pm 0.024) \cdot 10^{-6}$	0.916 ($\pm$0.036)

Surface Excess vs Salt-ratio
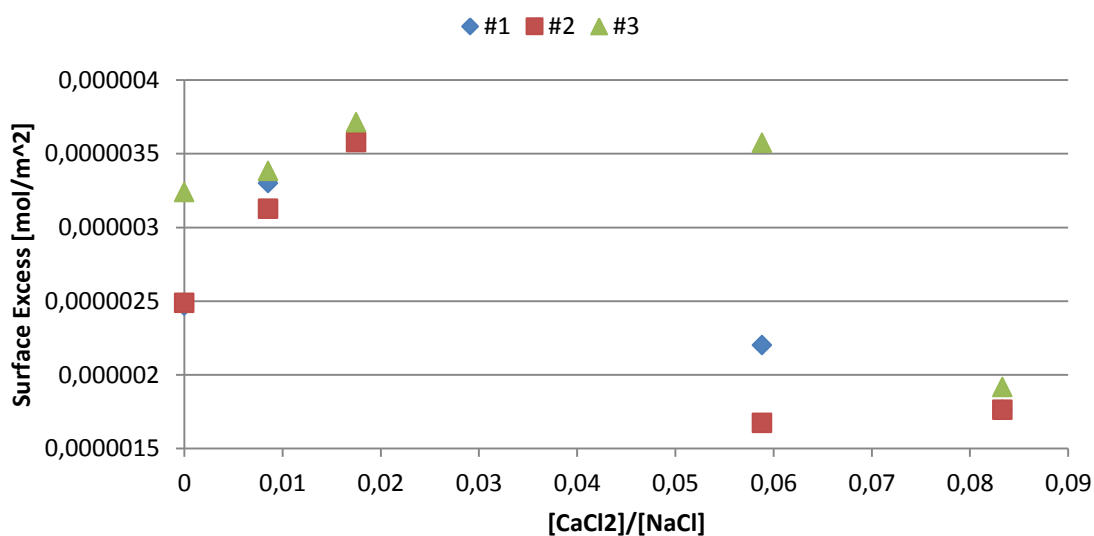
Figure 9. Plot of the surface excess vs CaCl2/NaCl2-ratio with 3 parallels, where the ionic strength is kept constant at 20 mM and the temperature is kept constant at 25 °C. The blue square is the first parallel, the red square is the second parallel, the green triangle is the third parallel.

Minimume Area pr molecule vs Salt-ratio

◆ #1 ■ #2 ▲ #3
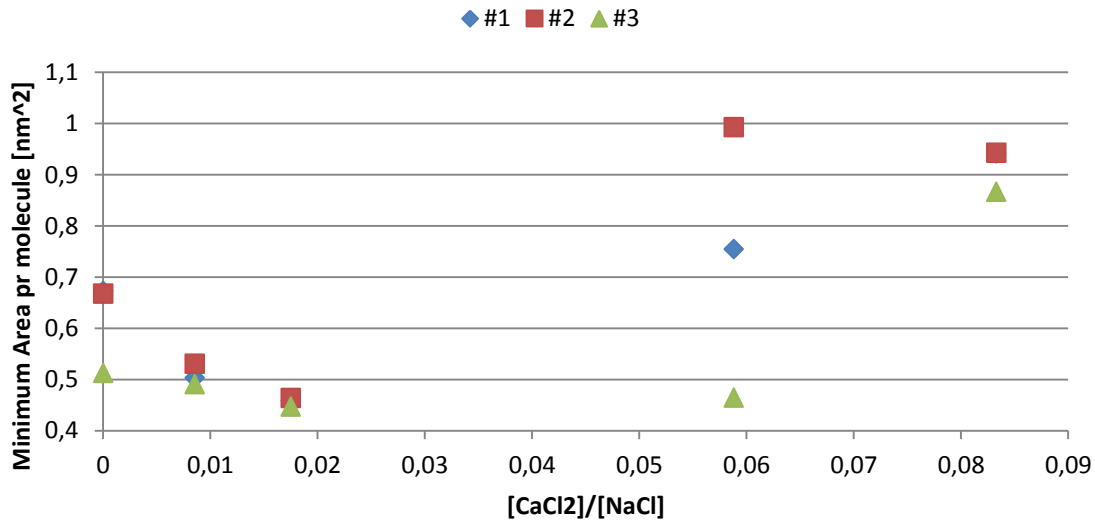
Figure 10. Plot of the minimum are pr molecule vs CaCl2/NaCl-ratio with 3 parallels, where the ionic strength is kept constant at 20 mM and the temperature is kept constant at 25 °C. The blue square is the first parallel, the red square is the second parallel, the green triangle is the third parallel.

4.6   Diffusion Coefficient (Linearization):

The Ward and Tordai equation (Eq.17) was used to find the diffusion coefficient, with a short time approximation.[8]

$$\Gamma(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} - 2\sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} c_s \, d\left(\sqrt{t-\tau}\right) \qquad \text{(Eq.17)}$$

This approximation will eliminate the last term of the equation and give the following equation (Eq.18):

$$\Gamma(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} \qquad \text{(Eq.18)}$$

By taking a modified Henry isotherm equation (Eq.19)[8]

$$\gamma_0 - \gamma = nRT\Gamma \qquad \text{(Eq.19)}$$

and putting it together with the short time approximation of the Ward and Tordai equation (Eq.18) will give the following equation (Eq.20):

$$\gamma_{t\to 0} = \gamma_0 - 2nRTc_0 \sqrt{\frac{D}{\pi}} \cdot \sqrt{t} \qquad \text{(Eq.20)}$$

24

CaCl$_2$/NaCl = 1/117 , I = 20 mM , 0.144mM SDBS

The linearization
y = -2,6884x + 71,851
R² = 0,8517

Measured   ■Data point used for linearization

Surface Tension [mN/m]

Surface Age [Sec^0.5]
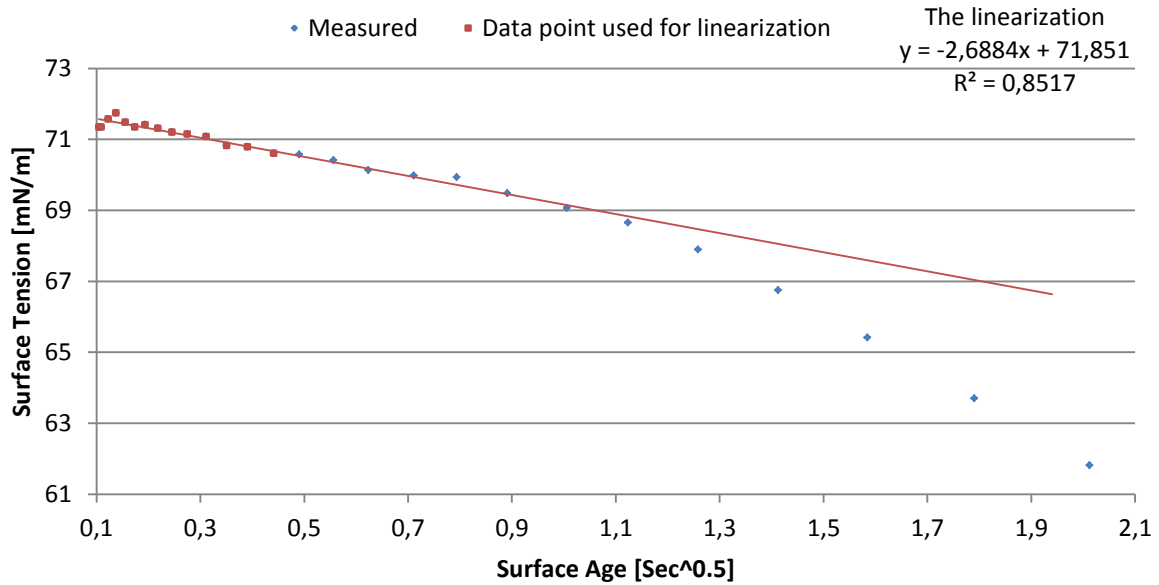
Figure 11. Example of the linearization for the CaCl2/NaCl-ratio of 1/117,ionic strength of 20 mM, temperature of 25°C and 0.144mM SDBS. The blue dots is the measured data, and the red dots is the values that was used for the linearization.

By taking the data from the bubble pressure tensiometer with the surface tension on the y-axis and square root of the surface age on the x-axis make the linearization possible (as seen in Figure 11 above).

The linearization was done mostly in the range of 10 ms to 250 ms , depending on the accuracy of the linearization. And the equation is as follow:

$$\gamma = \gamma_0 + a \cdot \sqrt{t} \qquad \text{(Eq.21)}$$

$$y = b + ax \qquad \text{(Eq.22)}$$

Where the slope, a, is as follow:

$$a = -2nRTc_0\sqrt{\frac{D}{\pi}} \qquad \text{(Eq.23)}$$

And the diffusion coefficient was calculated by:

$$D = \left(\frac{a\sqrt{\pi}}{-2nRTc_0}\right)^2 \qquad \text{(Eq.24)}$$

The D is the diffusion coefficient, with the unit m²/s, n in in this case is 1 as mention in Chapter 4.4. R is the gas constant that is 8.314 J/(K*mol). T is the temperature which was

298.15 (±1) K for all the solutions. C_0 is the concentration of the free surfactant with the SI-unit of mol/m³ $\left(= \frac{1000mol}{l}\right)$, meaning that should use CMC-value for the concentration above CMC.[8]

Graphical illustration of all the linearization for all the $\frac{NaCl_2}{NaCl} - ratios$, for the different SDBS concentrations is shown in Appendix 3 (Figure 35 to Figure 67) along with the value of the slope. The value of the diffusion coefficient is shown in Appendix 6 (Table 4 to Table 8). A graph showing the diffusion coefficient for some selected SDBS concentration for the different $\frac{CaCl_2}{NaCl} - ratios$ is shown in Figure 12, while an illustration of the diffusion coefficient close to the CMC is shown in Figure 13. Graph of all the diffusion coefficients can be seen in Appendix 4 (Figure 68 to Figure 72).
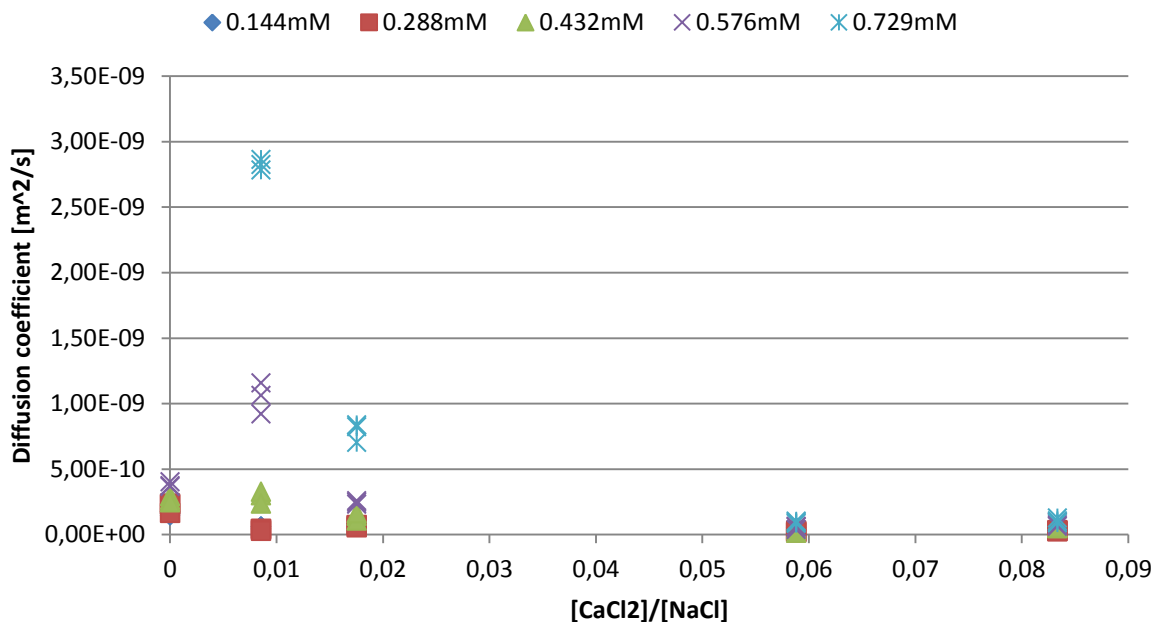
Figure 12. Plot showing diffusion coefficient with variations of CaCl₂/NaCl-ratios for different concentration of SDBS concentration (with three parallels), 0.144mM (Blue squares), 0.288mM (Red squares), 0.432mM (Green triangle), 0.576mM (Purple X) and 0.729mM (Blue star). The ionic strength is kept constant at 20mM and temperature at 25°C.
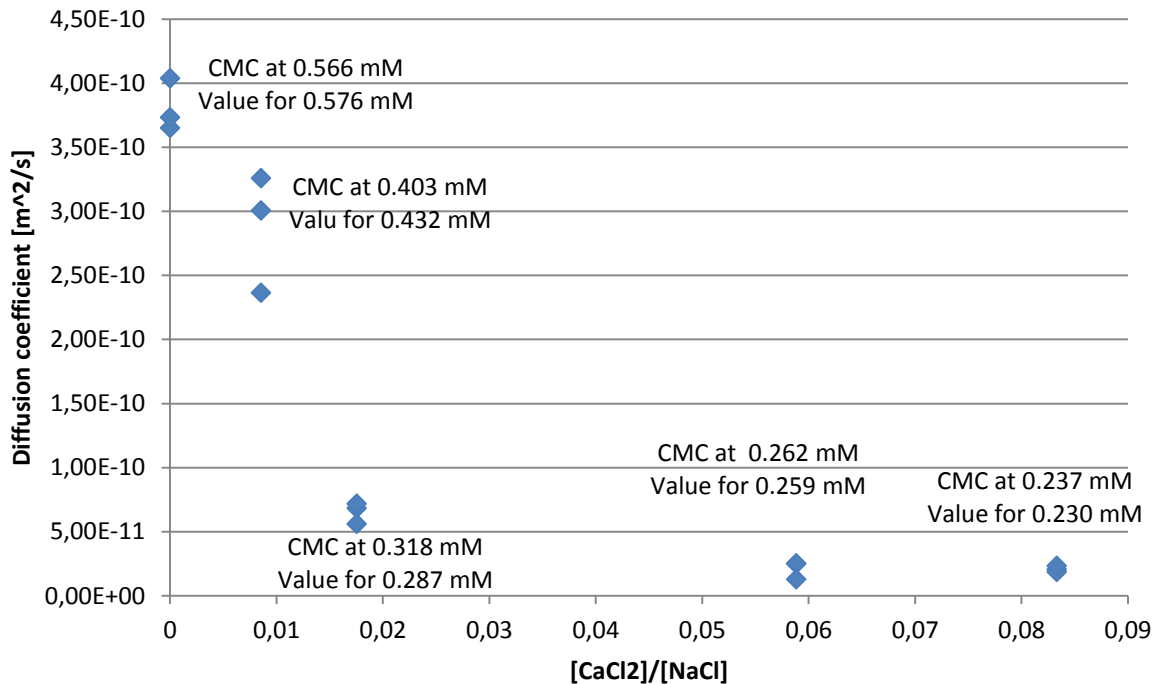
Figure 13. Diffusion coefficient close to the CMC for different CaCl₂/NaCl-ratios with three parallels, where the ionic strength is at 20 mM and temperature at 25°C. The value used in this plot wasn't directly on the CMC, but the closes value was used.

4.7 Model vs measured values:

The diffusion coefficients value was used into the equation for Ward and Tordai with short time approximation and compared to the measured value of the surface tension. An example of one model is shown in Figure 14 below. And rest of the models is shown in Appendix 5 (Figure 73 to Figure 97). The time, t_d, shows the time where the model start to differ more than 1 mN/m compared to the measured value. An overview of these values is shown in Appendix 6 (Table 4 to Table 8).
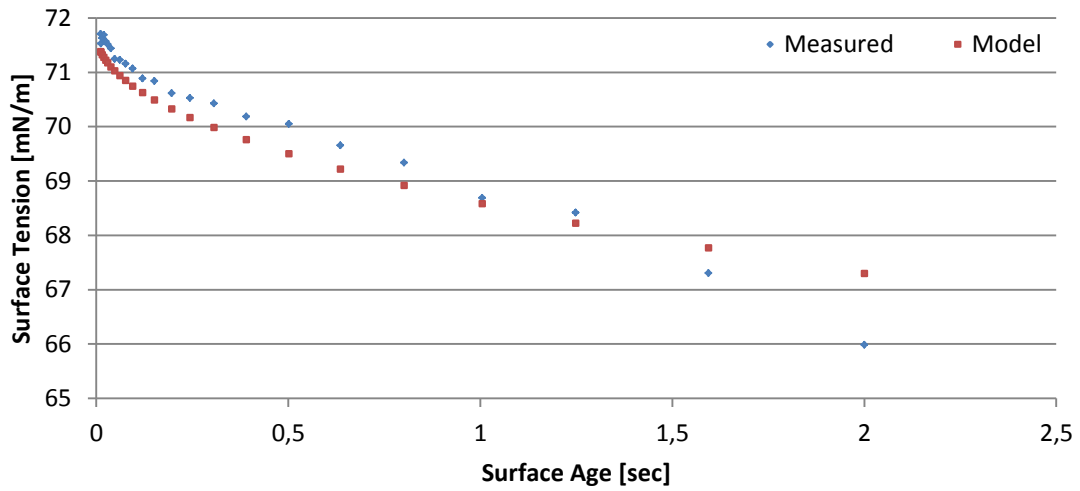
Figure 14. Plot of the measured value (Blue dots) of the surface tension over surface age, compared to the model (red dots) with the calculated diffusion coefficient for CaCl$_2$/NaCl-ratio of 1/117 with ionic strength of 20 mM, temperature of 25 °C and 0.144 mM SDBS. The last dots is where the differ between the measured value and the model is greater than 1 mN/m.

5 Discussion:

The discussion start off with discussion on the surface tension equilibrium value and the CMC values (Chapter 5.1), then go over discussion on the linearization for the diffusion coefficients (Chapter 5.2), discussion of the model (Chapter 5.3), then over to surface excess and minimum area pr molecule (Chapter 5.4), and last finish off with discussion what could be done different and what could do next (Chapter 5.5).

5.1 Equilibrium value from bubble pressure tensiometer and CMC:

Many of the measurement done with the bubble pressure tensiometer didn't reach the equilibrium constant, especially on the solution that had less than 0.288 mM SDBS. Therefor regression had to be done with all the value, just to make sure that all the value has been treated similar. Since the regressions aren't a value that has been measured, rather estimated, it means that it is some uncertainties with those values. This will affect the value of the CMC. Now that is said, when it comes to the value to each of the $\frac{CaCl_2}{NaCl} - ratios$, it does show a decrease in the CMC with the increase of the $\frac{CaCl_2}{NaCl} - ratios$ which is correct to the theory when it comes CMC for when adding electrolyte[14, 15].

In the report *Adsorption of linear alkyl benxene sulfonates on oil-water interface:Effects of Na$^+$,Mg^{+2} and Ca^{2+}ions* show that having NaCl has almost no effect on the CMC when there is 1.2 mM of Ca^{2+}ions in the solutions, even having as much as 46.4 mM NaCl.[15]

The CMC value for the $\frac{CaCl_2}{NaCl} - ratios$, 0 , $\frac{1}{117}$, $\frac{1}{57}$, $\frac{1}{17}$ and $\frac{1}{12}$ was estimated to be 0.566(±0.042) mM, 0.403(±008) mM, 0.318(±0.006) mM, 0.262(±047) mM and 0.237(±0.004) mM. In Thomas paper, it was found that the CMC for pure water was at 1.69mM [9, 16], which is higher than with electrolyte.

Another thing that is worth noticing is that the surface tension after the CMC also seem to be lowered by the increased $\frac{CaCl_2}{NaCl} - ratio$ with the exception of the two highest, but that is most likely caused from some dissociation issue when the concentration of CaCl$_2$ is too high (1 mM and 1.33 mM), especially when getting closer to the CMC (See Figure 8).

5.2 Diffusion Coefficient (Linearization):

The linearization on all the $\frac{CaCl_2}{NaCl} - ratios$ had most of the accuracy value (The R^2) above 0.94, with some exception with an accuracy value as low as 0.81. But with three parallels it will give quite clear indication of what the slope value should be. The solutions with the highest concentration of surfactant had fewer data points on their linearization compared to the solutions with lower concentration of surfactant, since the surface tension decreased earlier with high surfactant concentration (See Appendix 1, Figure 15 to Figure 29). So the number of data point used in the linearization varies between 10 to 18 points. But this still give a good linearization.

One thing that can notice is that the diffusion coefficient increase drastically after the CMC, so the diffusion coefficient also has to be evaluated with testing the model.

Another thing that is worth noticing is that for the $\frac{CaCl_2}{NaCl} - ratios, \frac{1}{117}, \frac{1}{17}$ and $\frac{1}{12}$ is that the diffusion coefficient is decreasing when getting closer to the CMC (Figure 69, Figure 71 and Figure 72) that corresponds to the report *Surfactant Diffusion Near Critical Micelle Concentrations*. [17]The value of the diffusion coefficient before CMC vary between the rang of $1.275*10^{-11}$ m^2/s to $2.924*10^{-10}$ m^2/s for all the $\frac{CaCl_2}{NaCl} - ratios$. And looking at the value from *Dynamic adsorption of sodium dodecylbenzene sulphonate and dowfroth 250 onto the air–water interface* [18] show that the value of diffusion coefficient for SDBS concentration below CMC is around the range of 10^{-10} for pure water.

When look at the diffusion coefficient after the CMC, it is clear that it increased quite much, where it increases much quicker for the lower $\frac{CaCl_2}{NaCl} - ratios$ (See Figure 68 to Figure 72), by looking at the diffusion coefficient close to CMC, it is a clear decreasing in diffusion coefficient with the increase $\frac{CaCl_2}{NaCl} - ratios$ (Figure 13), the same can be seen with looking for the diffusion coefficient for the same SDBS concentration, where it also decreases the diffusion coefficient with the increase $\frac{CaCl_2}{NaCl} - ratios$ (Figure 12). It was some uncertainty if should use 1 or 2 for the n-value, but with testing it on the minimum area pr molecule, it show that it is most likely to be 1 for all the $\frac{CaCl_2}{NaCl} - ratios$. Because when try out n=2 (seen in Appendix 7 (Figure 98)), it show an increase in minimum are pr molecule when add CaCl$_2$ into the solution, which does not make sense.

5.3 Model and measured values:

When a model was made with the calculated diffusion coefficient, and compared with the measured value of the surface tension, there was some that fitted decent within a short time range, and some that didn't fit at all. The one that didn't fit at all was the one with the highest concentration of the surfactant, and only one in the brine, $\frac{CaCl_2}{NaCl} = 0$. This can indicate the *long time contribution* from *Ward and Tordi equation*(Eq.17) is more important for the solutions with higher SDBS concentrations. By only doing the long time approximation of *Ward and Tordai equation* could give a better model for the solutions with high concentration of the surfactant, but that would most likely give bad model for the low concentration of the surfactant, so should keep both part to increase the time, t$_d$.

5.4   Surface excess and Minimum Area pr Molecule:

For the first three $\frac{CaCl_2}{NaCl} - ratios$ show that the minimum area pr molecule decreases with the increasing of CaCl$_2$, which is correct as shown in the report *Positional Isomers of Linear Sodium Dodecyl Benzene Sulfonate:Solubility, Self-Assembly, and Air/Water Interfacial Activity* [14]. When comes to the surface excess and minimum area pr molecule for the two highest $\frac{CaCl_2}{NaCl} - ratios$ there was some issue when it came to dissociation, where the solutions was blurry close to the CMC and above. The CaCl$_2$ concentration (1 mM and 1.33mM) at those ratios made the CaCl$_2$ interact with the surfactant witch lead to higher minimum area pr molecule. In the report, *Adsorption of linear alkyl benzene sulfonates on oil–water interface:Effects of Na$^+$, Mg^{2+}and Ca^{2+}ions*, [15] they used solutions with 1.2 mM Ca^{+2}, the surfactant that was used in that report was LAS (linear alkyl benzene sulfonates), which also is a similar anionic surfactant.

When comparing the value from *Positional Isomers of Linear Sodium Dodecyl Benzene Sulfonate: Solubility, Self-Assembly, and Air/Water Interfacial Activity* which has value around 0.50 nm^2/molecule in a solution of 10 mM NaCl with LAS as surfactant, we can see that the value our report get ain't too far away, which is around 0.608 nm^2/molecule for a solution with 20 mM NaCl. But what the other report show is that the minimum area pr molecule decreases with the increase concentration of NaCl.

Even changing the n-value from 1 to 2 will not make any more sense of the plot (Figure 10), an illustration is shown in Appendix 7 (Figure 98) how the area increase when go from pure NaCl to a mix of NaCl and CaCl$_2$, which does not make sense. This is also an indicator that using n=1 is correct when it comes to the diffusion coefficient.

5.5   Further work / What could do different:

In the future there may be an idea to include crude oil into the same measurements, test out the ratio between different salt (like BaCl$_2$, MgCl$_2$ or SrCl$_2$), where the ratio with the new salt is the same ratio with the salts done in this task.

Since the maximum bubble pressure tensiometer didn't reach equilibrium on many of the analysis, there could also be an option to try another method to measure the surface tension, but still need to do the maximum bubble pressure method to find the kinetics of the surfactants, since the maximum bubble pressure tensiometer is able to measure a surface age as low as 10 ms.

Try out *long time approximation of Ward and Tordai equation*, or maybe even another model to see if give the same diffusion coefficient for the low concentration, and maybe it can give a better model for the one with high concentration of the surfactant.

6 Conclusion:

Increasing the ratio of $\frac{CaCl_2}{NaCl}$, while keeping the ionic strength and temperature constant will lower the CMC. The CMC for the $\frac{CaCl_2}{NaCl} - ratios$, 0, $\frac{1}{117}$, $\frac{1}{57}$, $\frac{1}{17}$ and $\frac{1}{12}$ was determent to be 0.566(±0.042) mM, 0.403(±008) mM, 0.318(±0.006) mM, 0.262(±047) mM and 0.237(±0.004) mM. The surface tension is also lower after CMC with the increase of the $\frac{CaCl_2}{NaCl} - ratios$ for the first three $\frac{CaCl_2}{NaCl} - ratios$.

Short time approximation was a good model for the low concentration of SDBS. The *long time contribution* from *Ward and Tordi equation* seem to be more important for the higher concentration of SDBS.

Diffusion coefficient decreases when getting closer to CMC for $\frac{CaCl_2}{NaCl} - ratios$, $\frac{1}{117}$, $\frac{1}{17}$ and $\frac{1}{12}$.

While it increase drastically after CMC for all the $\frac{CaCl_2}{NaCl} - ratios$. Diffusion also decreases with the increase $\frac{CaCl_2}{NaCl} - ratios$.

Minimum are pr molecule decreases when increasing the ratio of $\frac{CaCl_2}{NaCl} - ratio$ for the 3 first ratios, while it couldn't be determined for the two highest ratios because of dissociations issues.

7   Reference List:

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Calum J. Drummond, *Positional Isomers of Linear Sodium Dodecyl Benzene Sulfonate: Solubility, Self-Assembly, and Air/Water Interfacial Activity.* Publicer: Langmuir, 2006.
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16.   Tichelkamp, T., et al., *Interfacial Tension between Low Salinity Solutions of Sulfonate Surfactants and Crude and Model Oils.* 2014.
17.   Alan Siderius, Stacey Kolisnek Kehl, and D.G. Leaist, *Surfactant Diffusion Near Critical Micelle Concentrations.* Solution Chemistry, 2002. **31**.
18.   C.M. Phan, A.V. Nguyen , and G.M. Evans, *Dynamic adsorption of sodium dodecylbenzene sulphonate and dowfroth 250 onto the air–water interface.* Elsevier, 2004.

Appendix:

$$\frac{CaCl_2}{NaCl} = 0 , \qquad I = 20 \ mM , \ T = 25°C$$
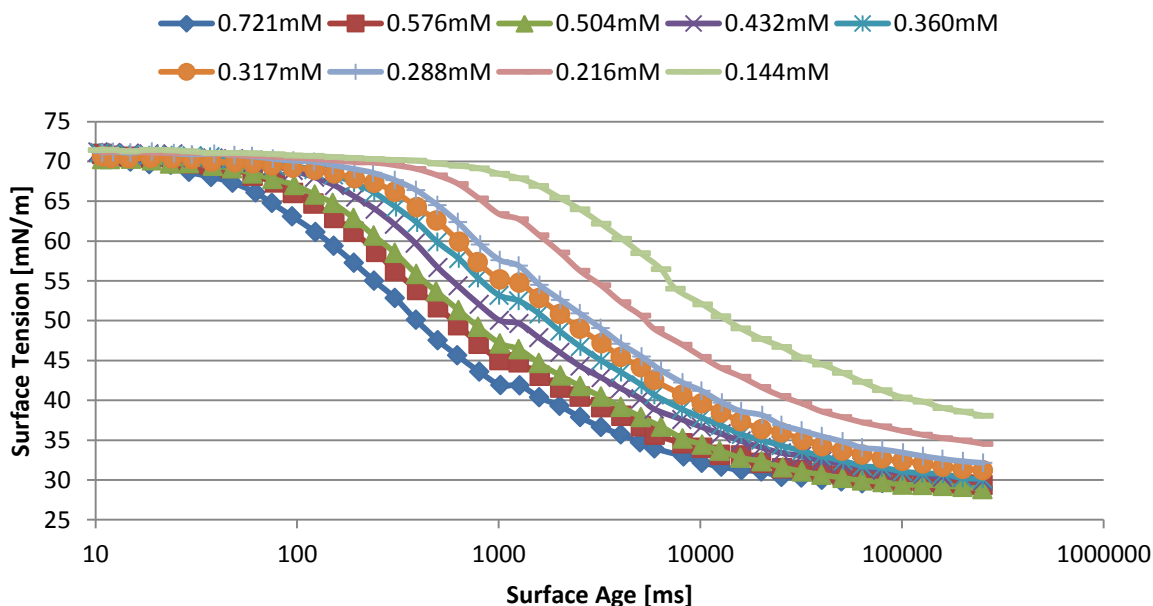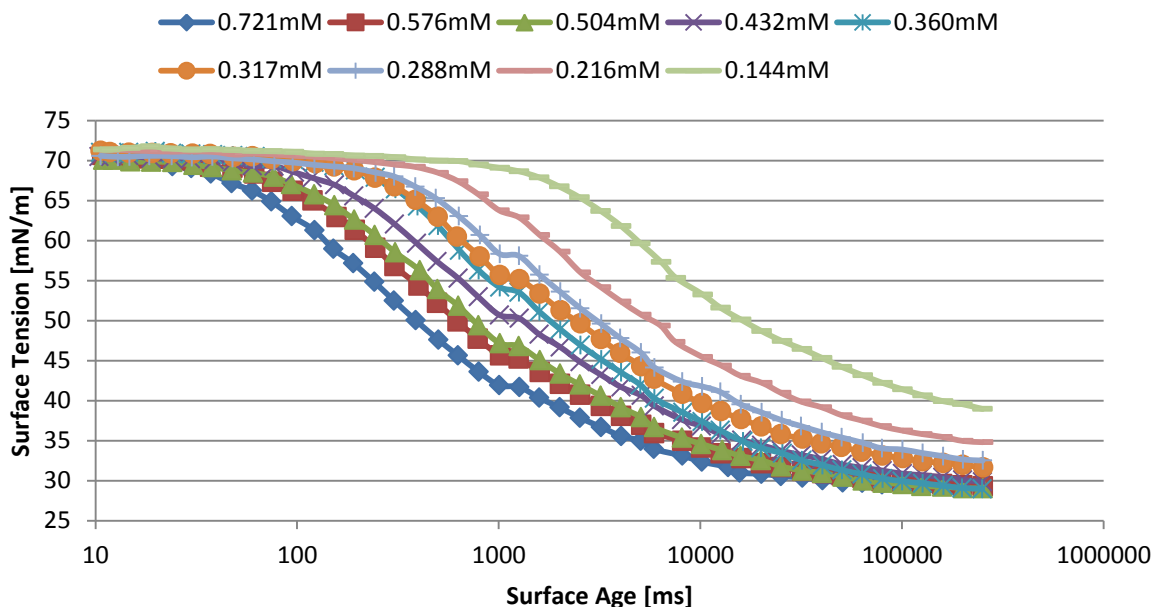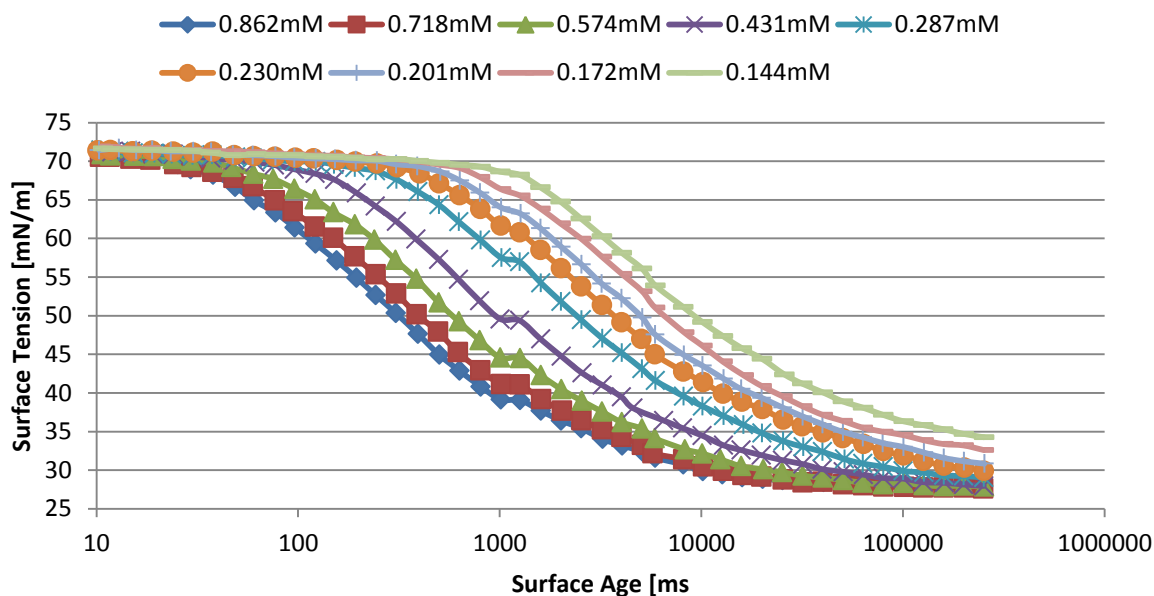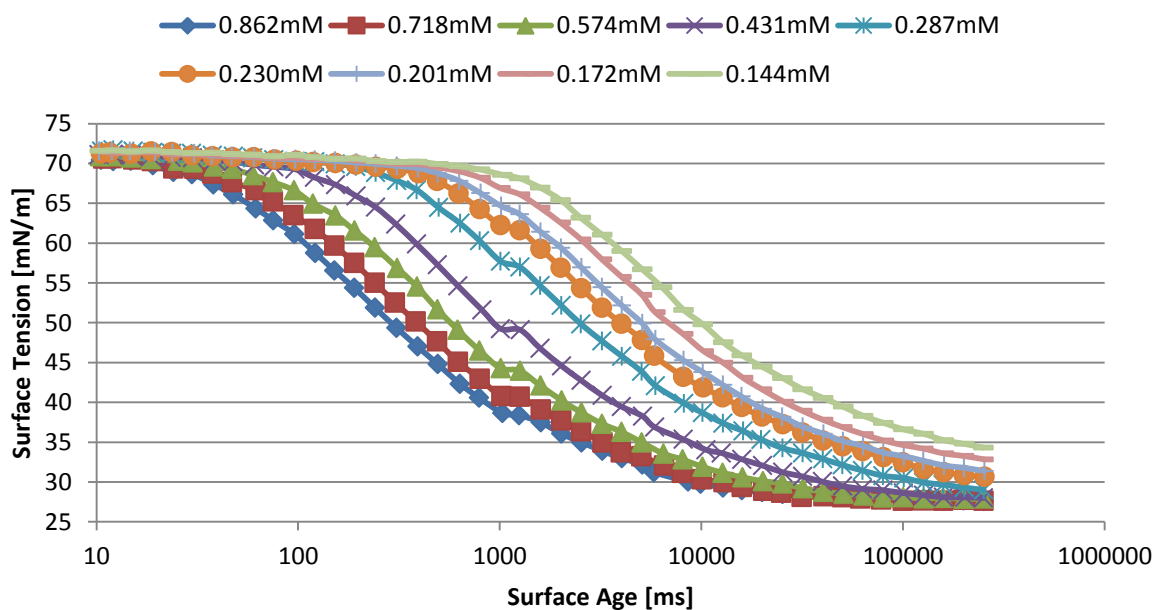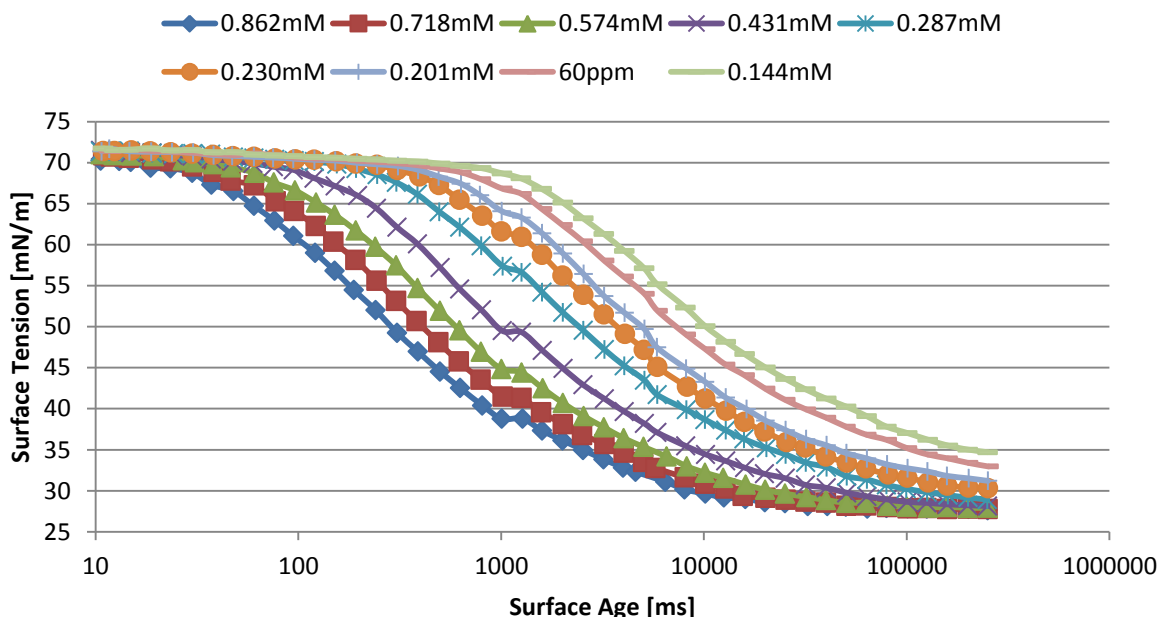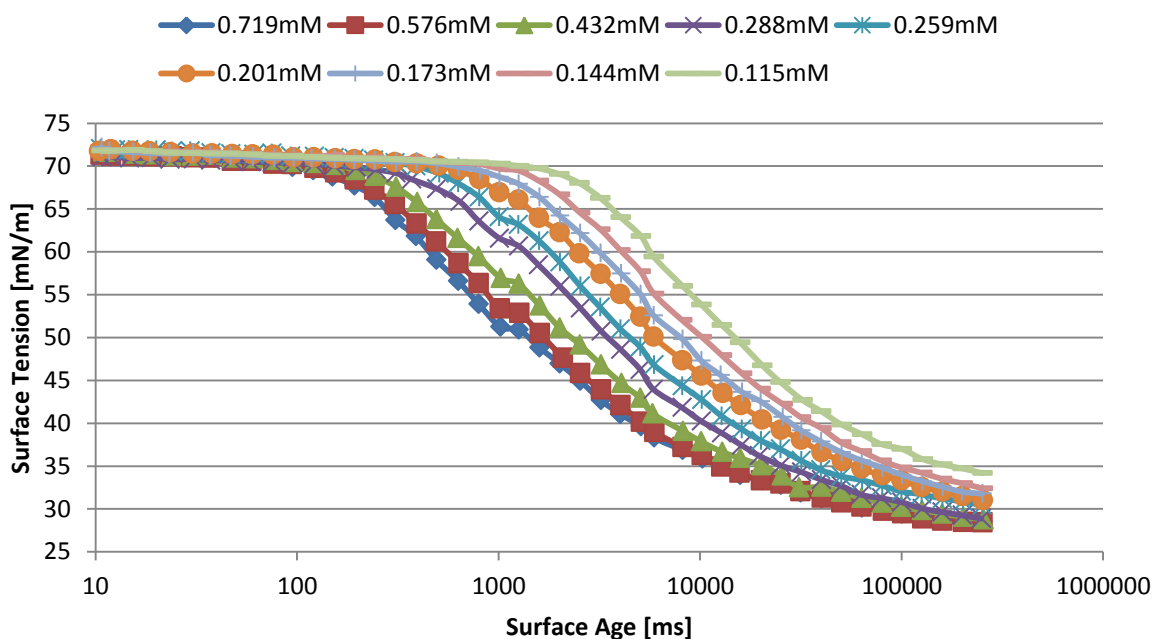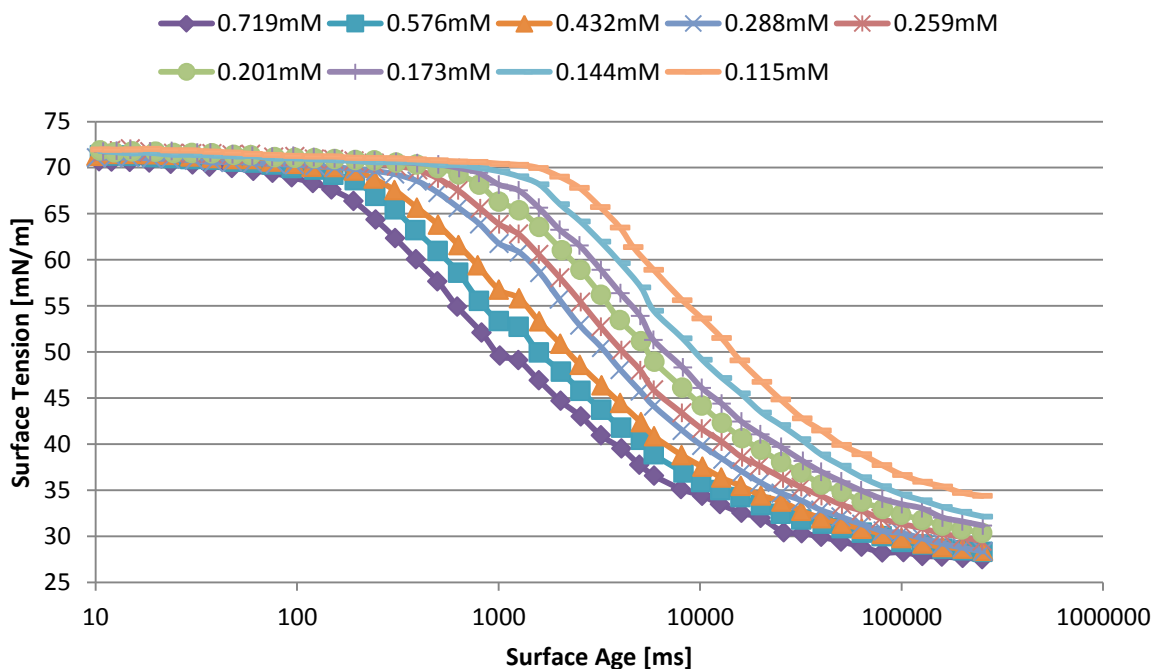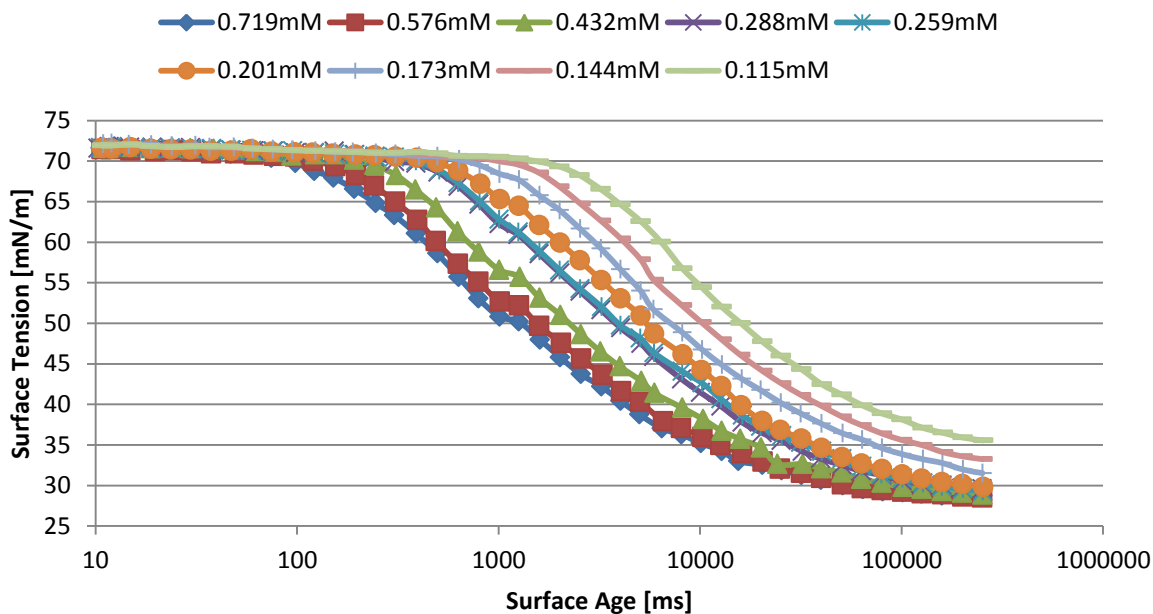
Parallel #1

Figure 15. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the first parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 0

Parallel #2
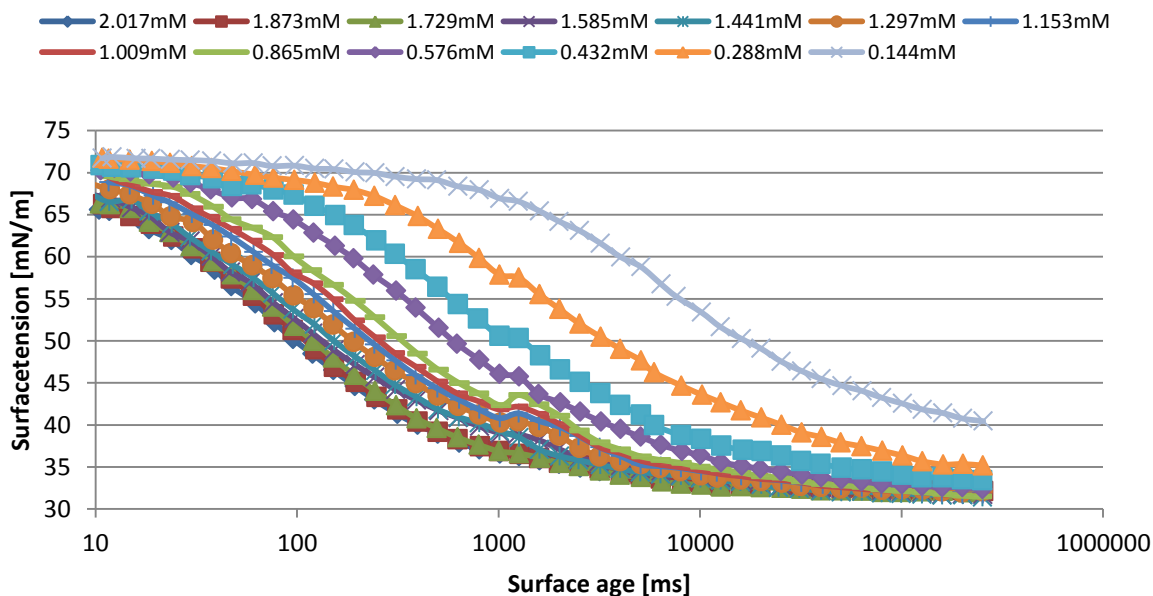
Figure 16. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the second parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 0
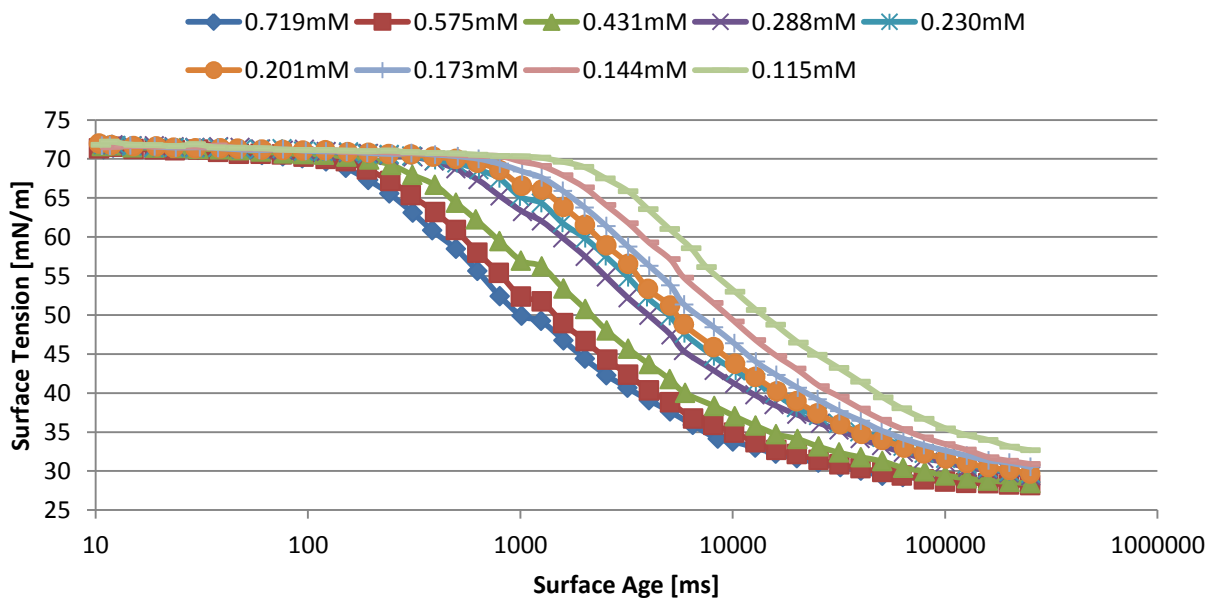
Parallel #3
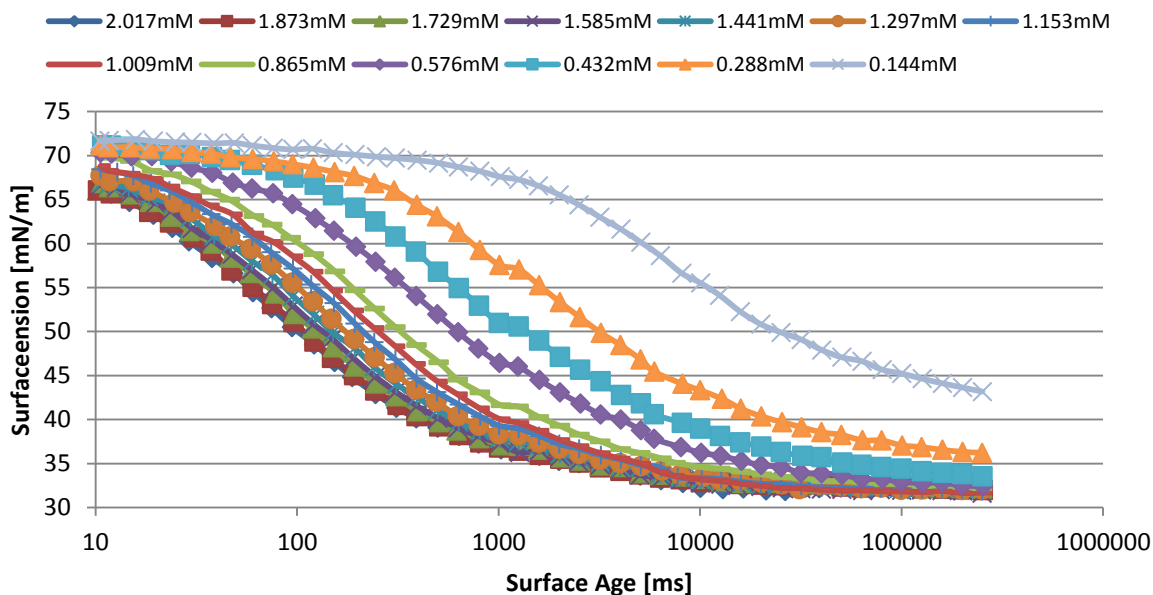
Figure 17. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the third parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 0

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \, , \qquad I = 20 \, mM \, , \; T = 25°C$$
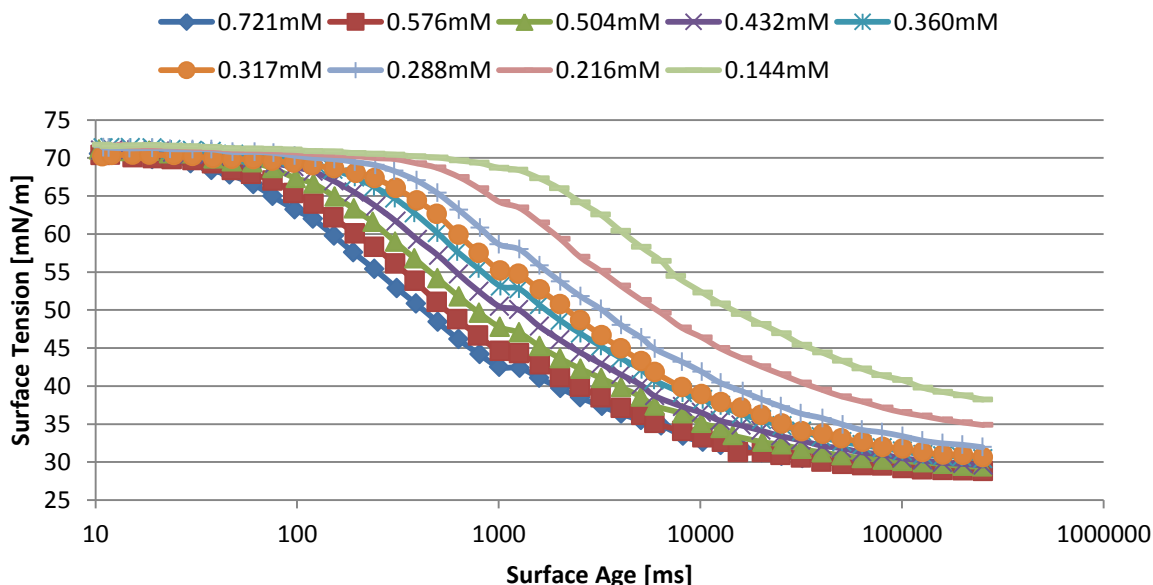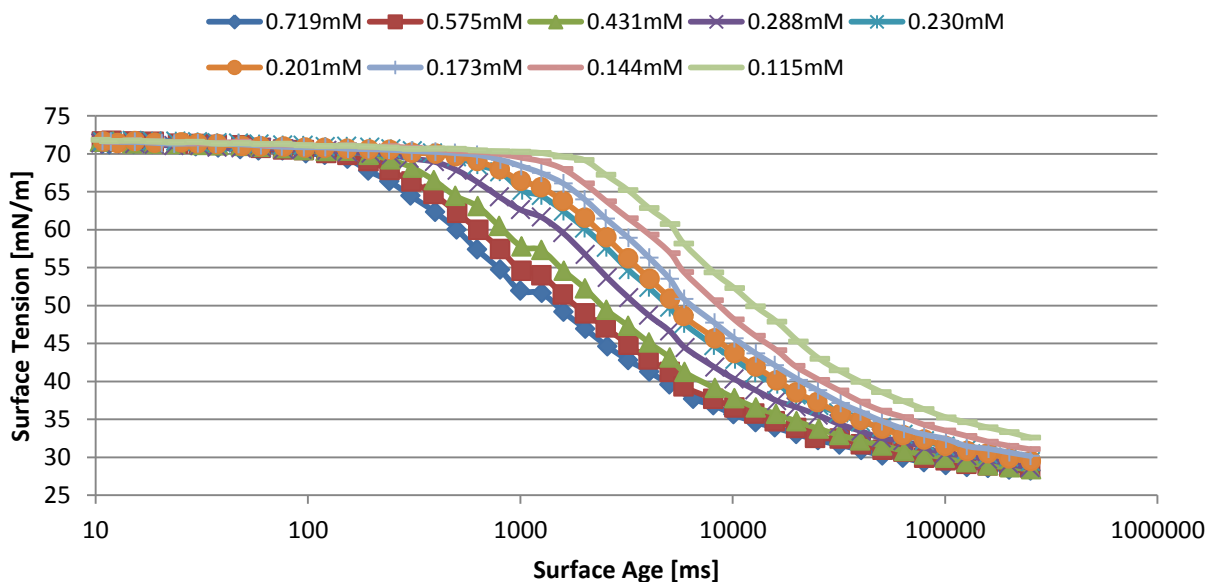
Parallel #1

Figure 18. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the first parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/117

Parallel #2

Figure 19. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the second parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/117
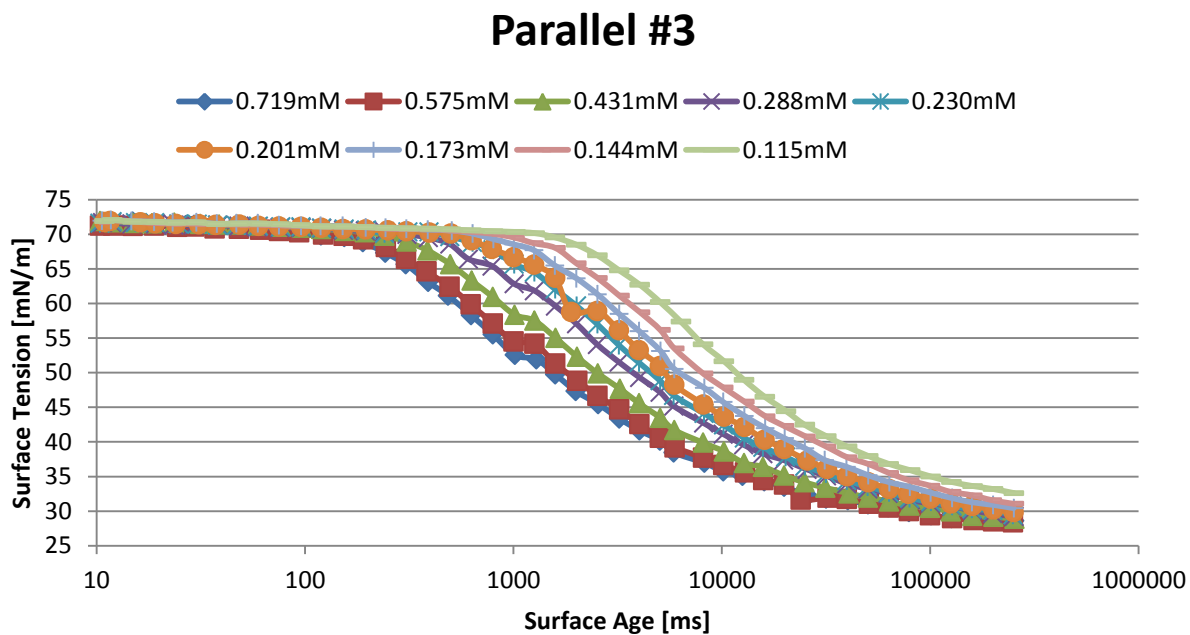
Parallel #3

Figure 20. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the third parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/117

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \, , \qquad I = 20 \; mM \, , \;\; T = 25°C$$

Parallel #1

Figure 21.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the first parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/57

Parallel #2

Figure 22.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the second parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/57

Parallel #3

Figure 23. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the third parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/57

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} , \qquad I = 20 \ mM , \ T = 25°C$$

Parallel #1

Figure 24. Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the first parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/17

Parallel #2

Figure 25.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the second parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/17

Parallel #3

Figure 26.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the third parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/17

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \ , \qquad I = 20 \ mM \ , \ T = 25°C$$

Parallel #1

Figure 27.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the first parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/12

Parallel #2

Figure 28.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the second parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/12

Parallel #3

Figure 29.Measurement done with the maximum bubble pressure tensiometer. Plot show surface tension over surface age for different SDBS concentration, for the third parallel. Ionic strength 20 mM, 25 °C and Xca/Na = 1/12

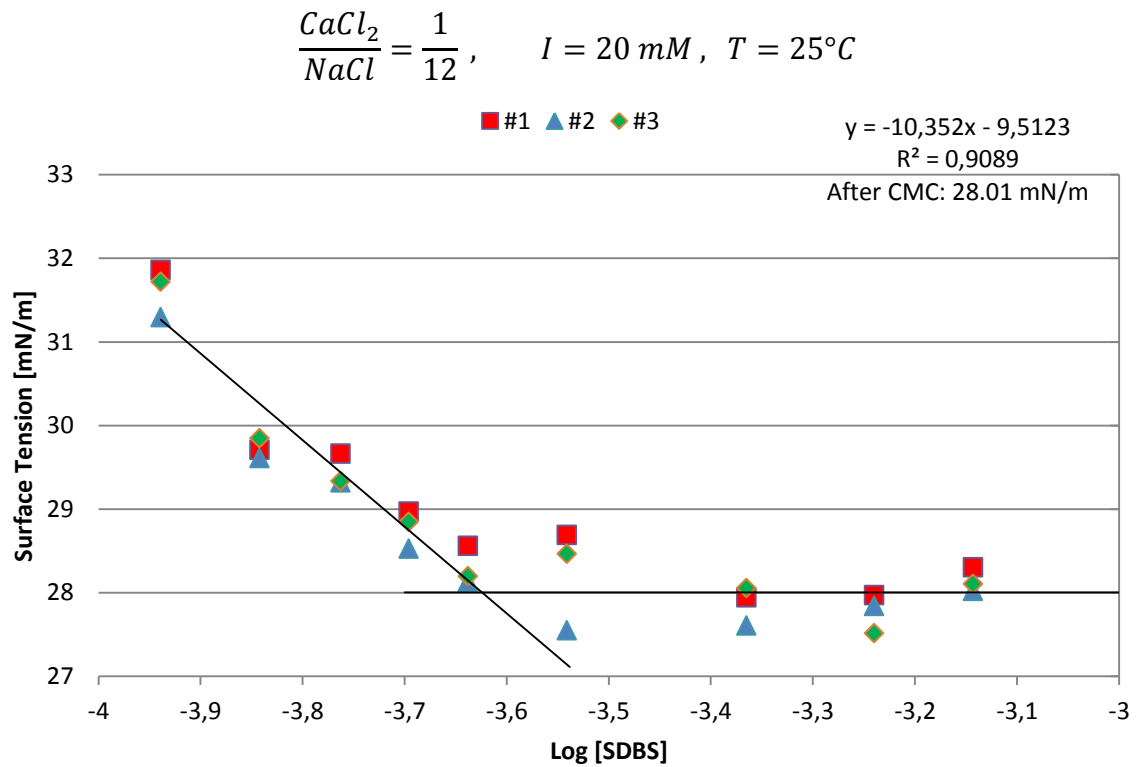$$\frac{CaCl_2}{NaCl} = 0 \, , \qquad I = 20 \; mM \, , \;\; T = 25°C$$
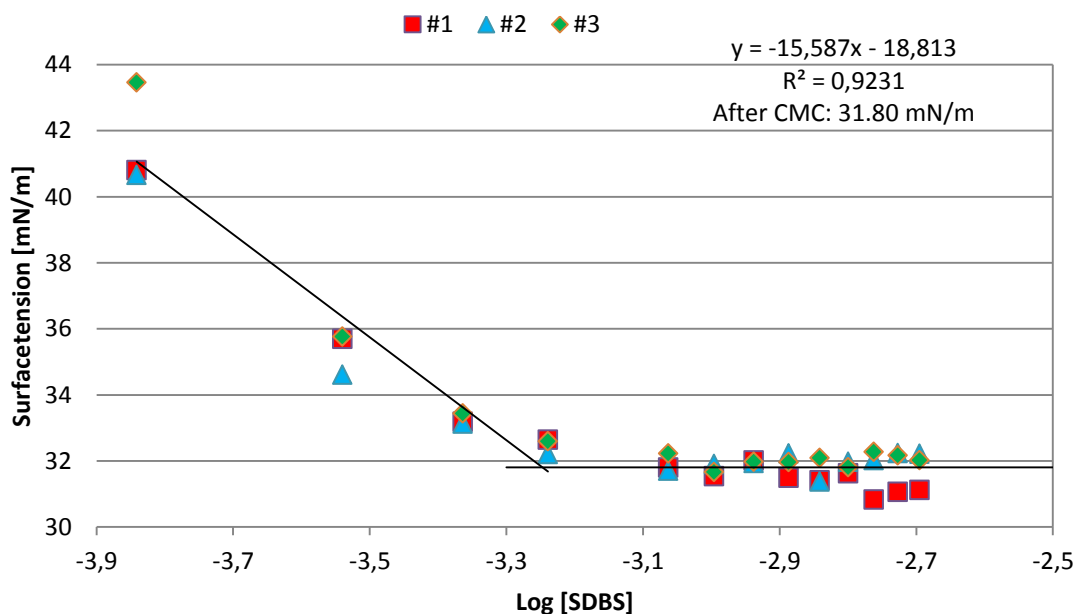
Figure 30. Graph showing the change in surface tension with the change of logarithm of the concentration of SDBS, where the breakpoint is the CMC. The red squares is the first parallel, the blue triangles is the second parallel, and the green squares is the third parallel. The ionic strength is at 20 mM, temperature is at 25°C and the CaCl$_2$/NaCl-ratio is 0.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \, , \qquad I = 20 \; mM \, , \;\; T = 25°C$$
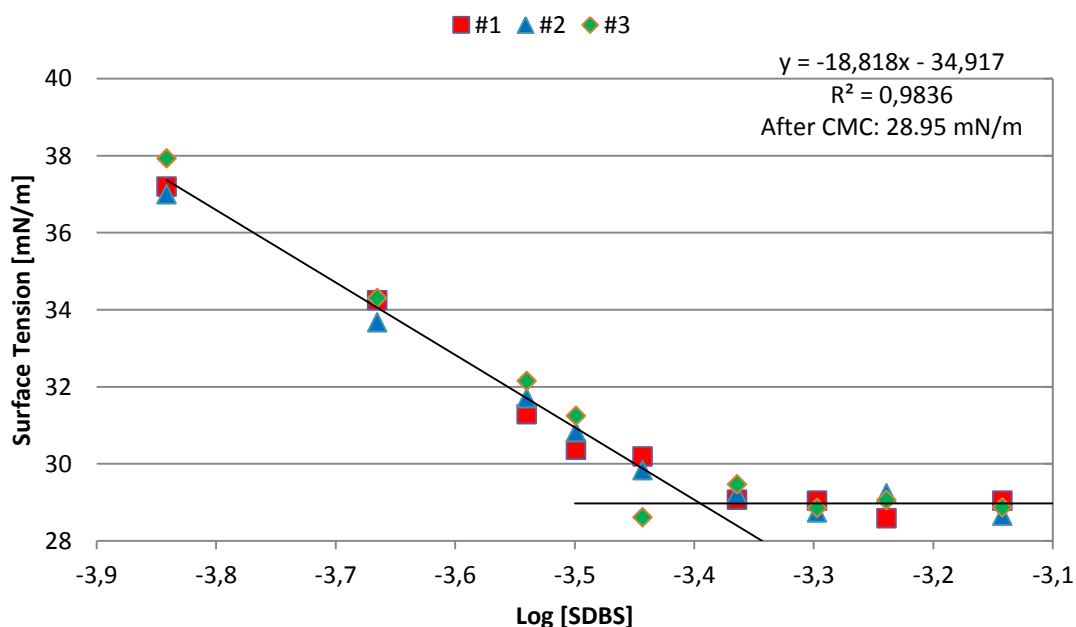
Figure 31. Graph showing the change in surface tension with the change of logarithm of the concentration of SDBS, where the breakpoint is the CMC. The red squares is the first parallel, the blue triangles is the second parallel, and the green squares is the third parallel. The ionic strength is at 20 mM, temperature is at 25°C and the CaCl$_2$/NaCl-ratio is 1/117.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57}, \qquad I = 20\ mM,\ \ T = 25°C$$

■ #1　▲ #2　◆ #3
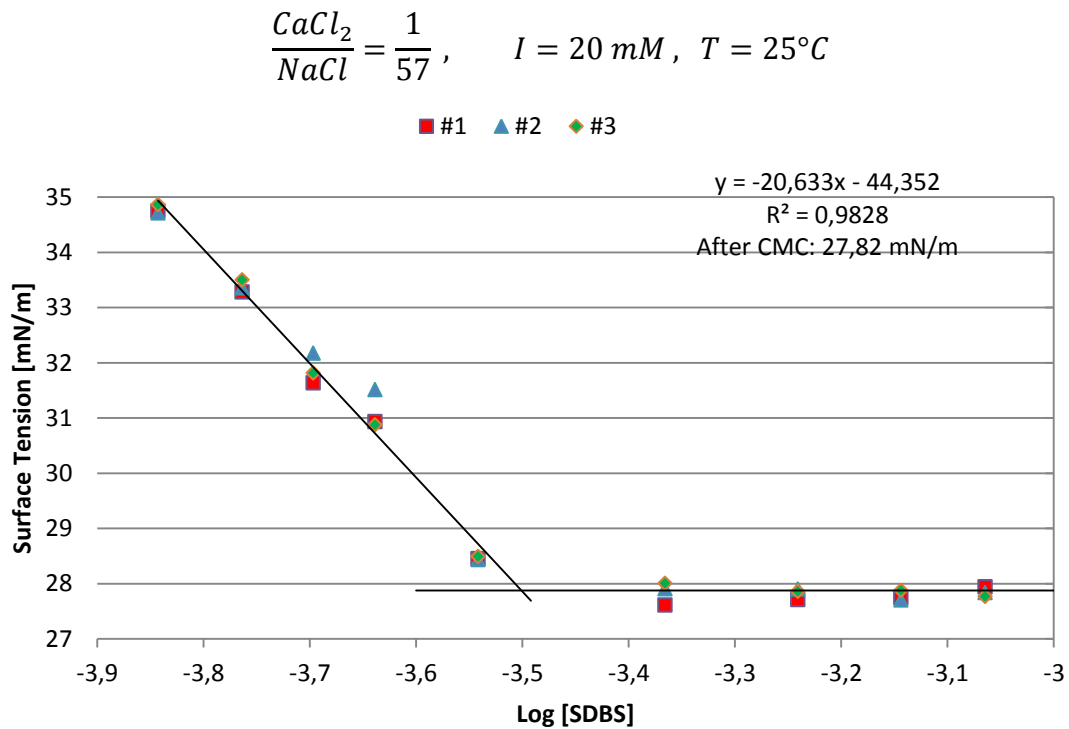
Figure 32. Graph showing the change in surface tension with the change of logarithm of the concentration of SDBS, where the breakpoint is the CMC. The red squares is the first parallel, the blue triangles is the second parallel, and the green squares is the third parallel. The ionic strength is at 20 mM, temperature is at 25°C and the CaCl$_2$/NaCl-ratio is 1/57.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17}, \qquad I = 20\ mM,\ \ T = 25°C$$

■ #1　▲ #2　◆ #3
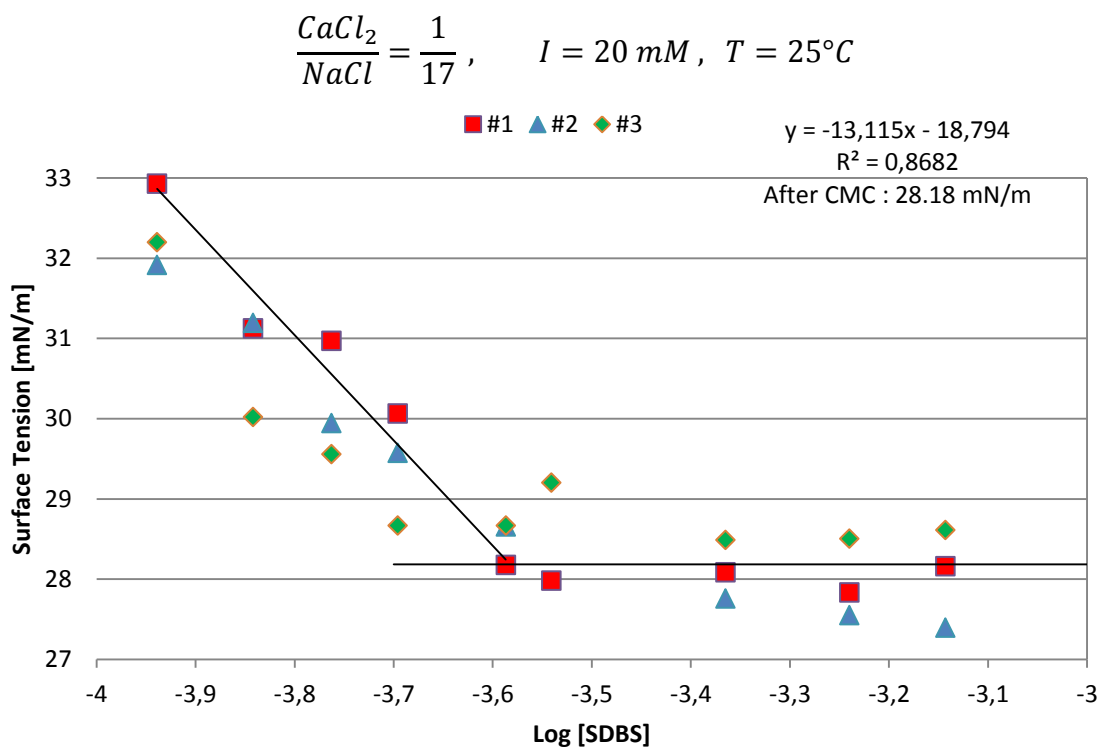
Figure 33. Graph showing the change in surface tension with the change of logarithm of the concentration of SDBS, where the breakpoint is the CMC. The red squares is the first parallel, the blue triangles is the second parallel, and the green squares is the third parallel. The ionic strength is at 20 mM, temperature is at 25°C and the CaCl$_2$/NaCl-ratio is 1/17.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \; , \qquad I = 20 \; mM \; , \;\; T = 25°C$$

Figure 34. Graph showing the change in surface tension with the change of logarithm of the concentration of SDBS, where the breakpoint is the CMC. The red squares is the first parallel, the blue triangles is the second parallel, and the green squares is the third parallel. The ionic strength is at 20 mM, temperature is at 25°C and the CaCl$_2$/NaCl-ratio is 1/12.

$$\frac{CaCl_2}{NaCl} = 0 \, , \qquad I = 20 \ mM \, , \ T = 25°C \, , \qquad Parallel \ \#1$$

| 2.017mM	1.873mM	1.729mM	1.585mM
y = -64,198x + 70,057	y = -78,684x + 72,923	y = -68,186x + 72,269	y = -69,426x + 73,231
R² = 0,9701	R² = 0,9923	R² = 0,9897	R² = 0,9872
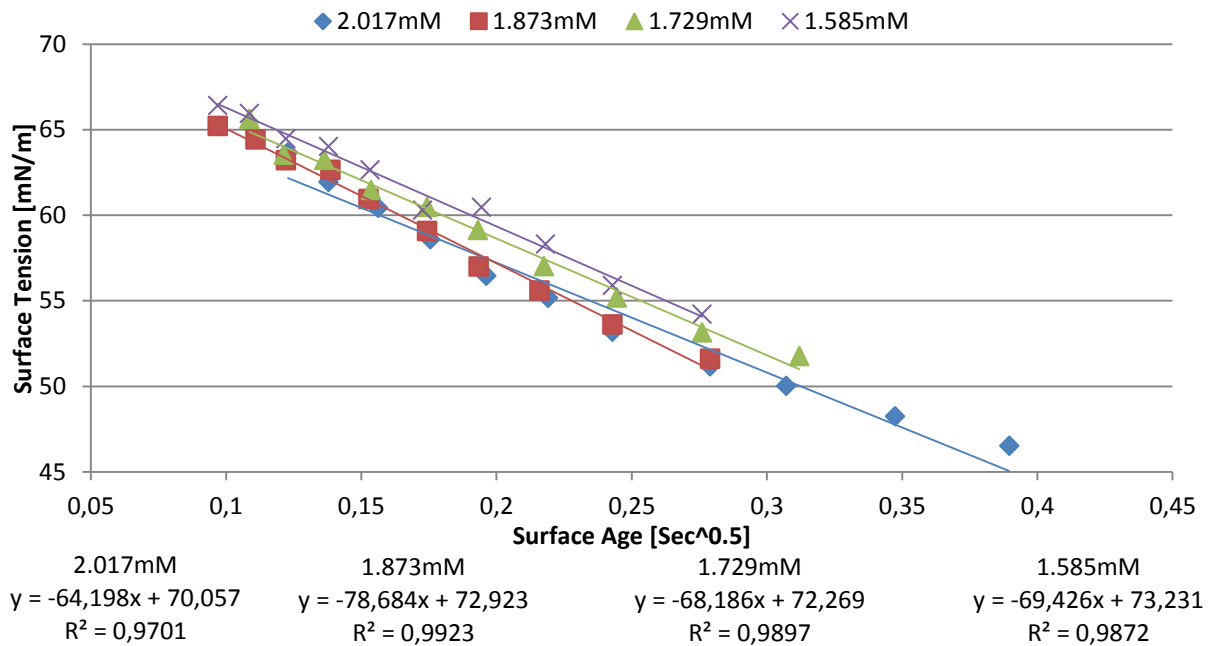
Figure 35. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 2.017mM (Blue squares), 1.873mM (Red squares), 1.729mM (Green triangles) and 1.585mM (Purple X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.


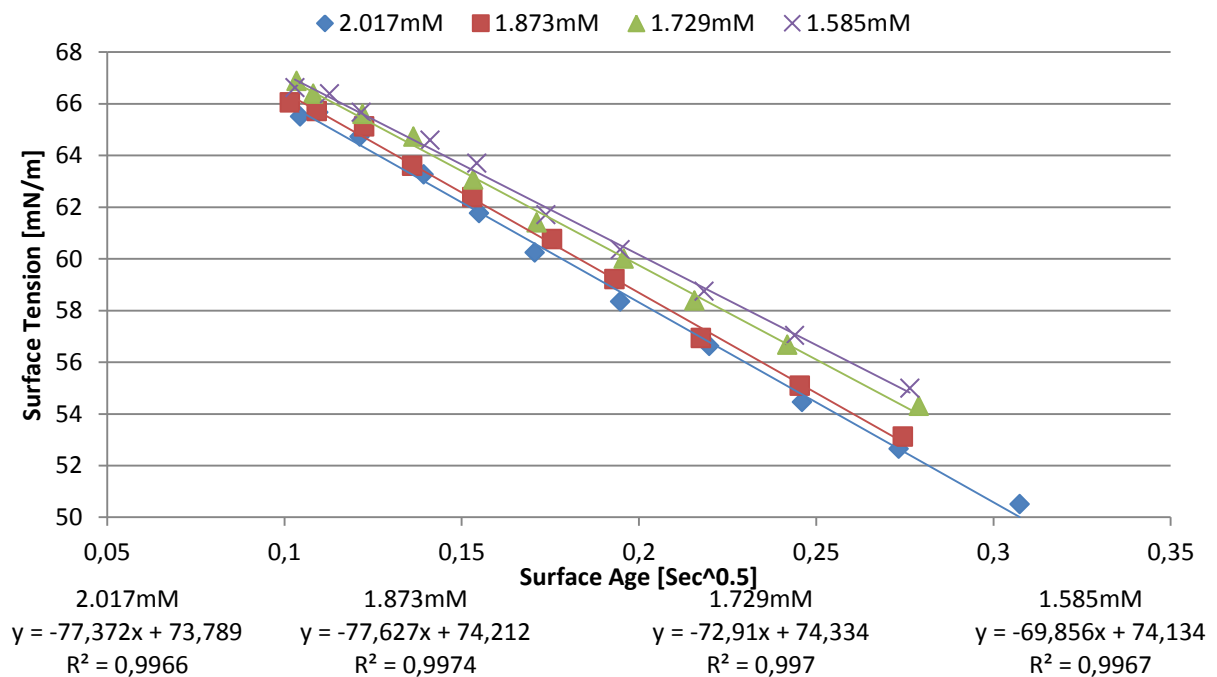| 1.441mM	1.297mM	1.153mM	1.009mM
y = -62,213x + 73,139	y = -57,273x + 73,005	y = -55,539x + 74,99	y = -47,297x + 74,252
R² = 0,9954	R² = 0,9902	R² = 0,9898	R² = 0,9907
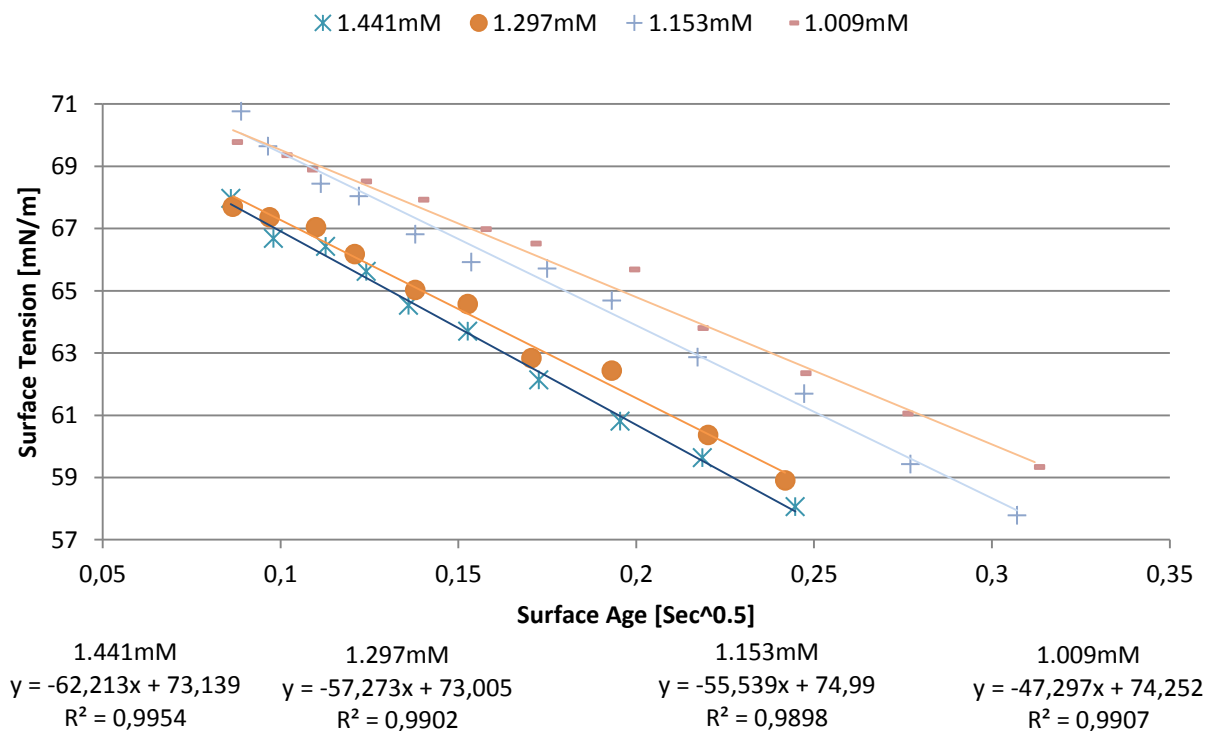
Figure 36. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 1.441mM (Blue star), 1.297mM (Yellow circle), 1.153mM (Blue plus) and 1.009mM (Tan rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
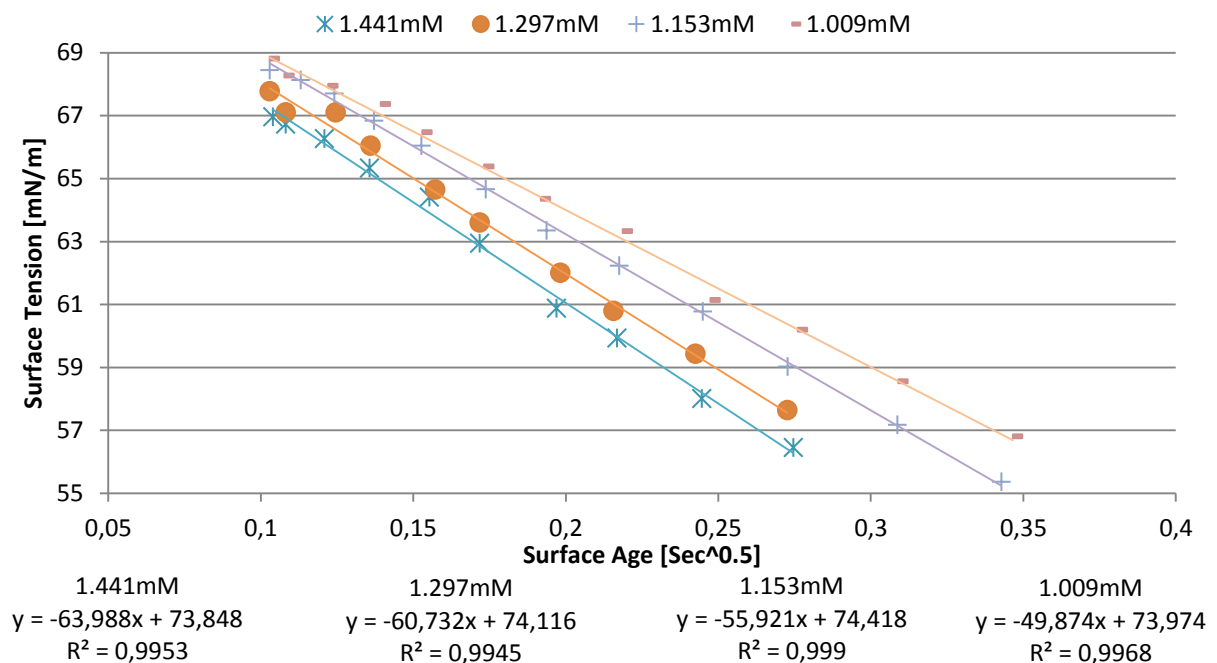
$$\frac{CaCl_2}{NaCl} = 0, \qquad I = 20\ mM, \quad T = 25°C, \qquad Parallel\ \#2$$

0.865mM	0.576mM	0.432mM	0.288mM	0.144mM
y = -46,901x + 74,957	y = -30,588x + 74,742	y = -20,673x + 74	y = -12,405x + 73,232	y = -5,3381x + 72,262
R² = 0,9977	R² = 0,9968	R² = 0,9991	R² = 0,9921	R² = 0,9912
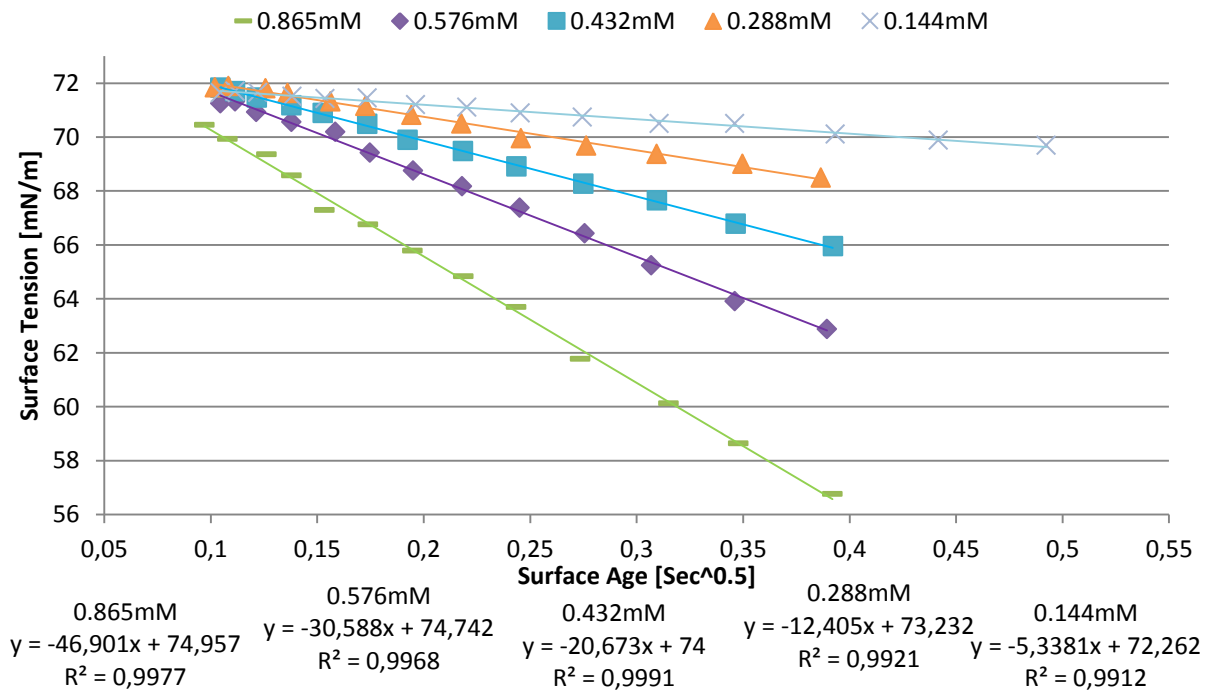
Figure 37. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.865mM (Green rectangle), 0.576mM (Purple square), 0.432mM (Blue square), 0.288mM (Yellow triangle) and 0.144mM (Blue X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.


2.017mM	1.873mM	1.729mM	1.585mM
y = -77,486x + 73,791	y = -76,842x + 74,283	y = -74,212x + 74,222	y = -74,39x + 74,727
R² = 0,9969	R² = 0,9992	R² = 0,9966	R² = 0,9948
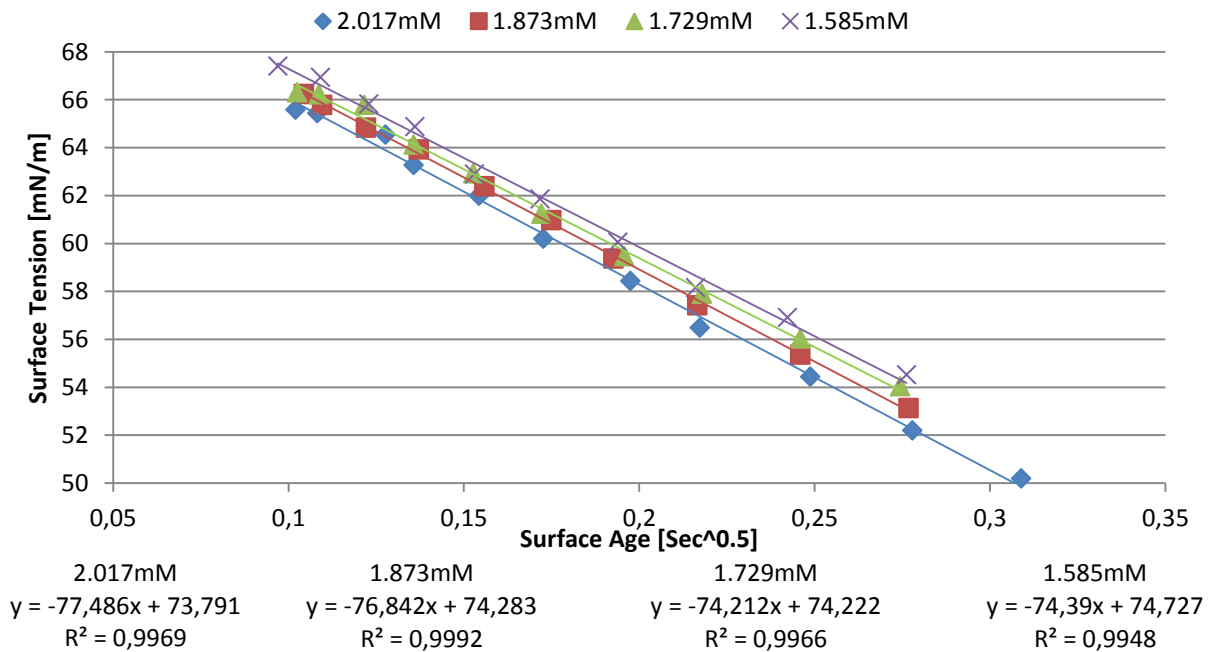
Figure 38. Graph showing the second parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 2.017mM (Blue squares), 1.873mM (Red squares), 1.729mM (Green triangles) and 1.585mM (Purple X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
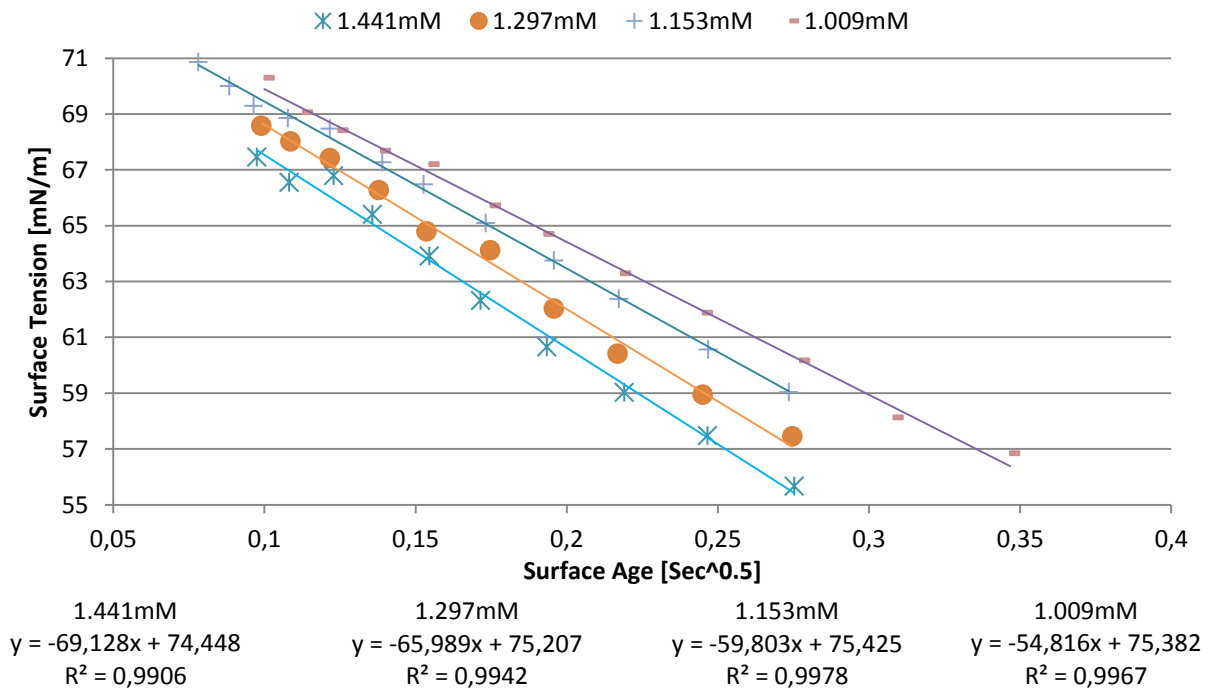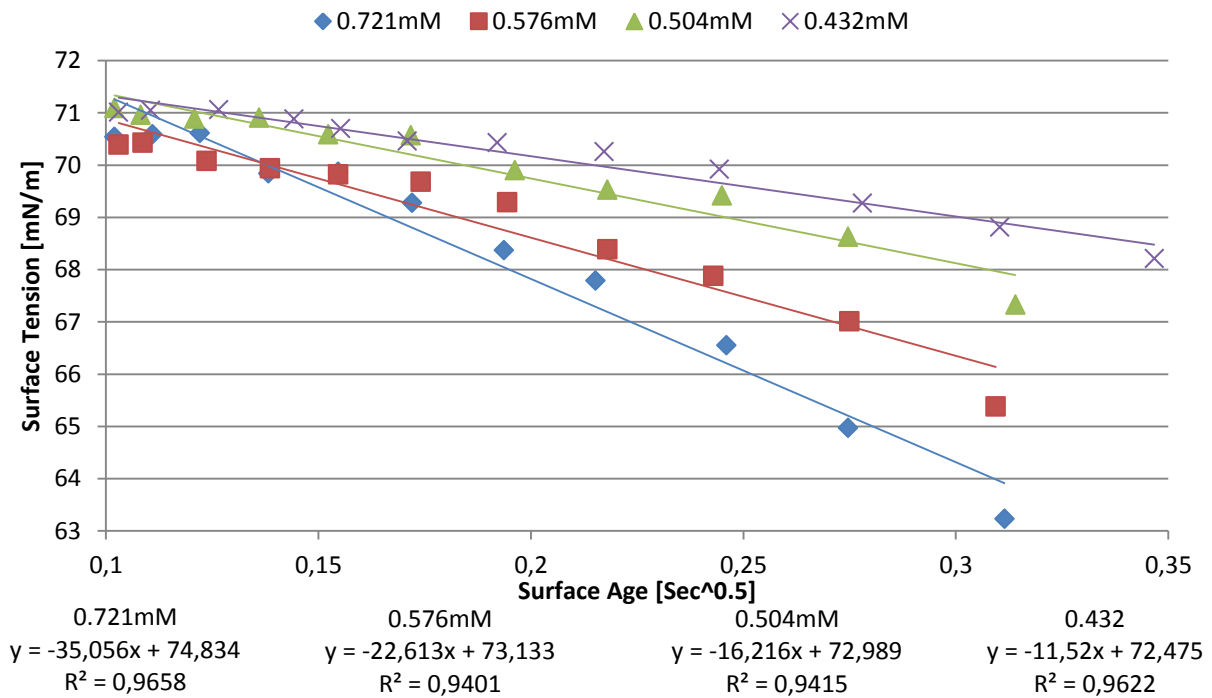
Figure 39. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 1.441mM (Blue star), 1.297mM (Yellow circle), 1.153mM (Blue plus) and 1.009mM (Tan rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
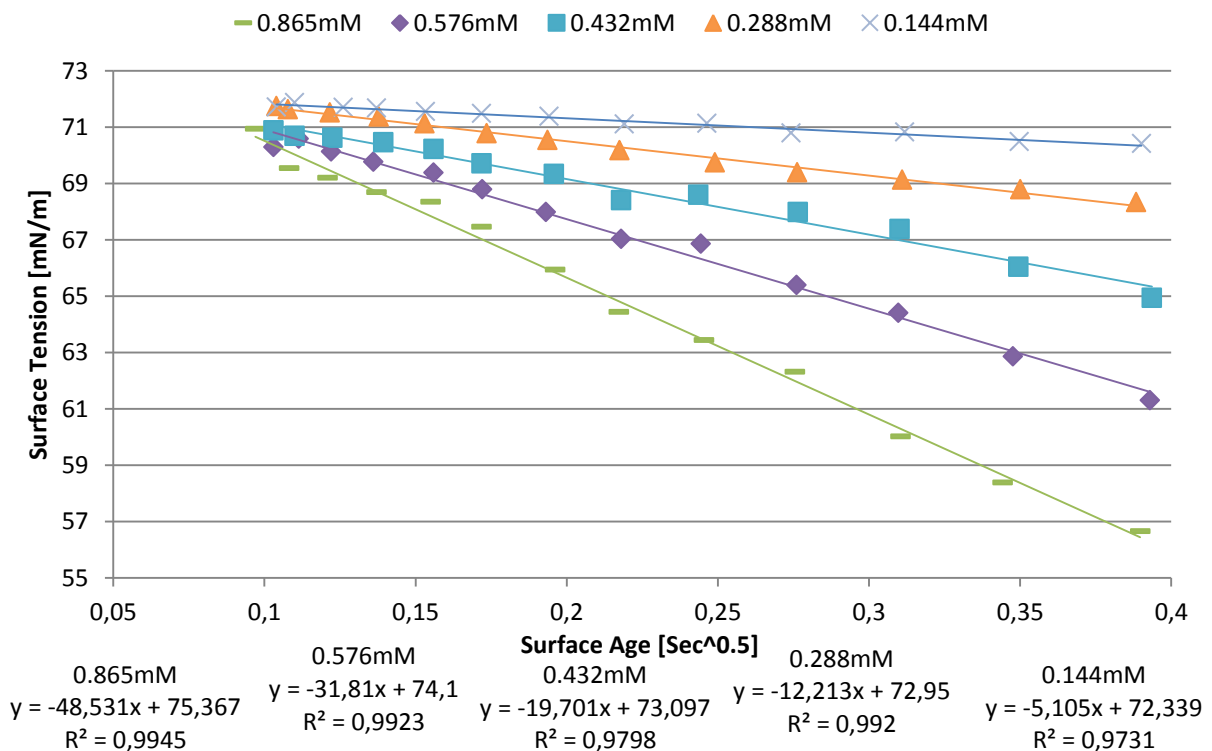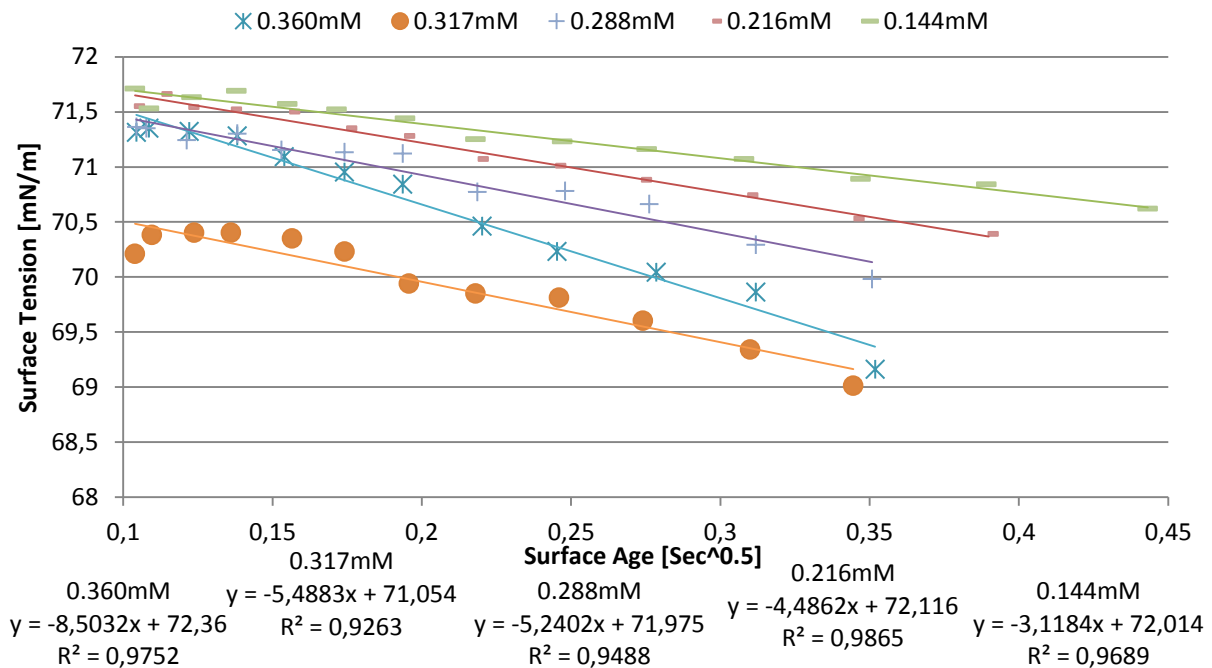

Figure 40. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.865mM (Green rectangle), 0.576mM (Purple square), 0.432mM (Blue square), 0.288mM (Yellow triangle) and 0.144mM (Blue X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = 0, \qquad I = 20\ mM, \quad T = 25°C, \qquad Parallel\ \#3$$

2.017mM
y = -77,372x + 73,789
R² = 0,9966

1.873mM
y = -77,627x + 74,212
R² = 0,9974

1.729mM
y = -72,91x + 74,334
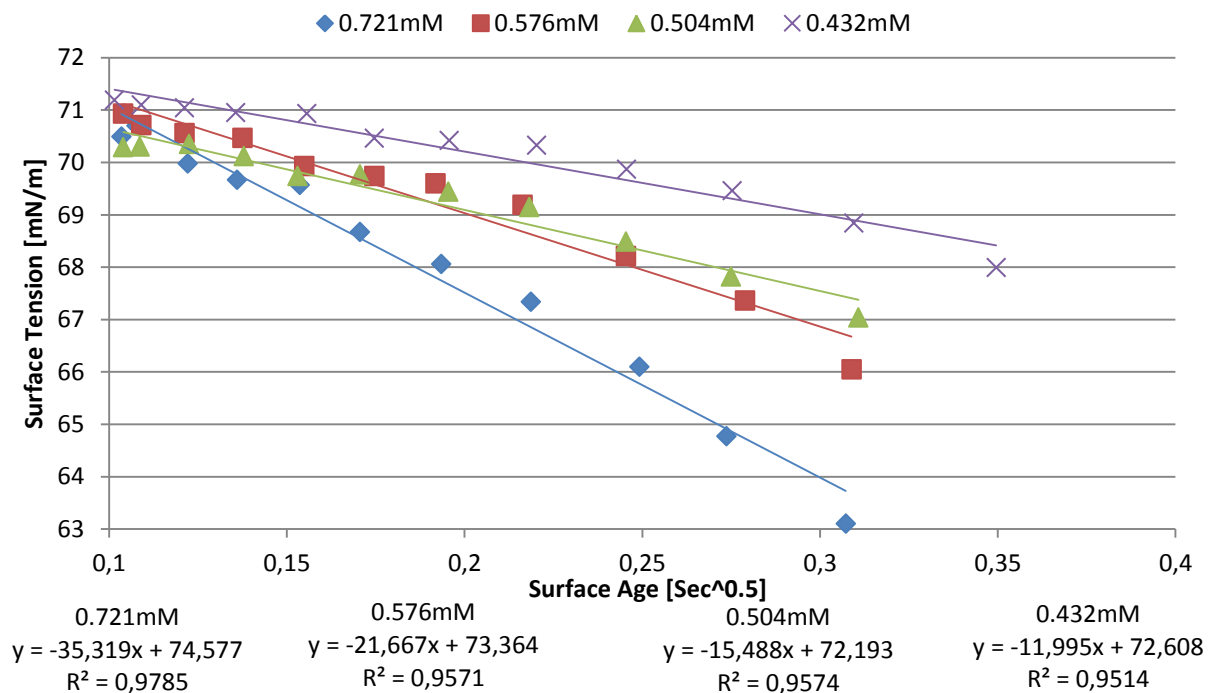R² = 0,997

1.585mM
y = -69,856x + 74,134
R² = 0,9967

Figure 41. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 2.017mM (Blue squares), 1.873mM (Red squares), 1.729mM (Green triangles) and 1.585mM (Purple X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
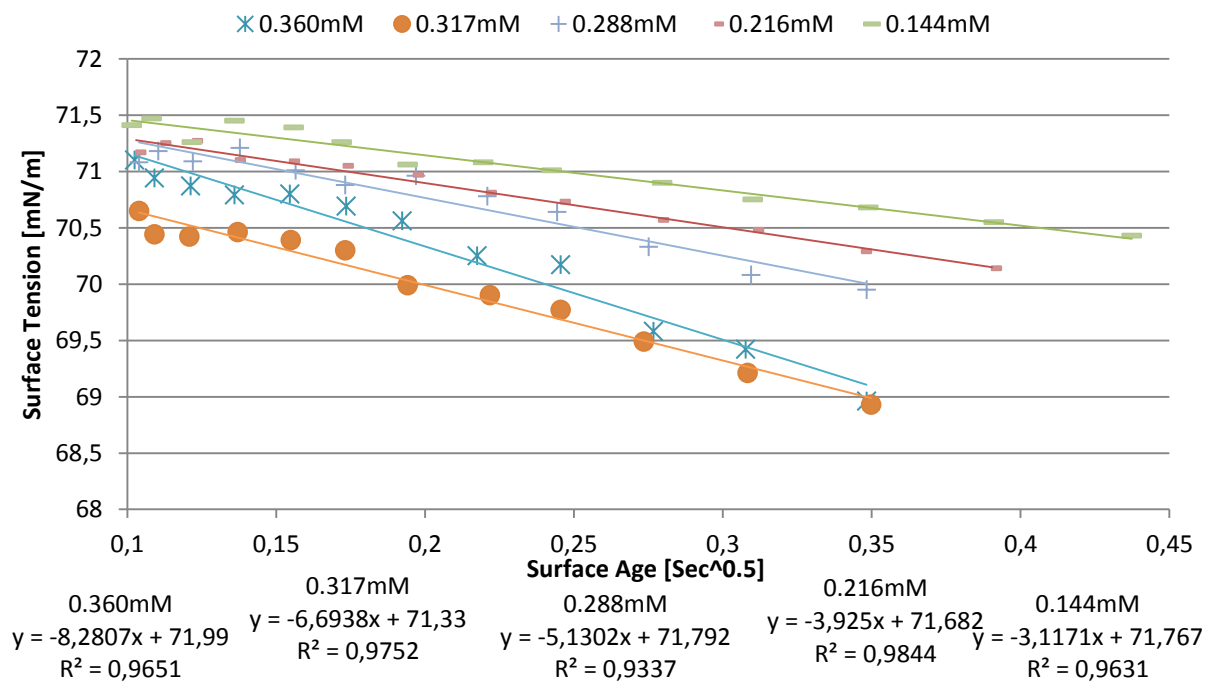

1.441mM
y = -63,988x + 73,848
R² = 0,9953

1.297mM
y = -60,732x + 74,116
R² = 0,9945

1.153mM
y = -55,921x + 74,418
R² = 0,999

1.009mM
y = -49,874x + 73,974
R² = 0,9968

Figure 42. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 1.441mM (Blue star), 1.297mM (Yellow circle), 1.153mM (Blue plus) and 1.009mM (Tan rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
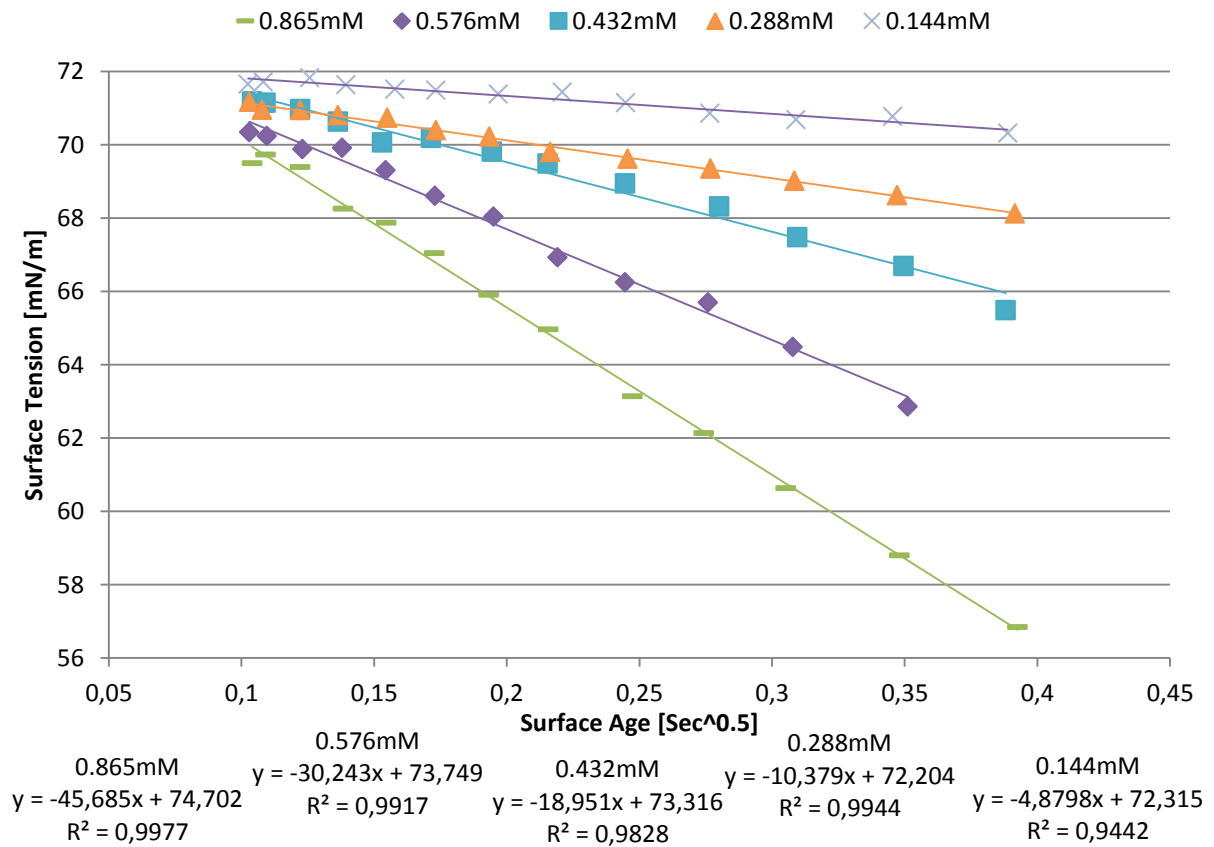
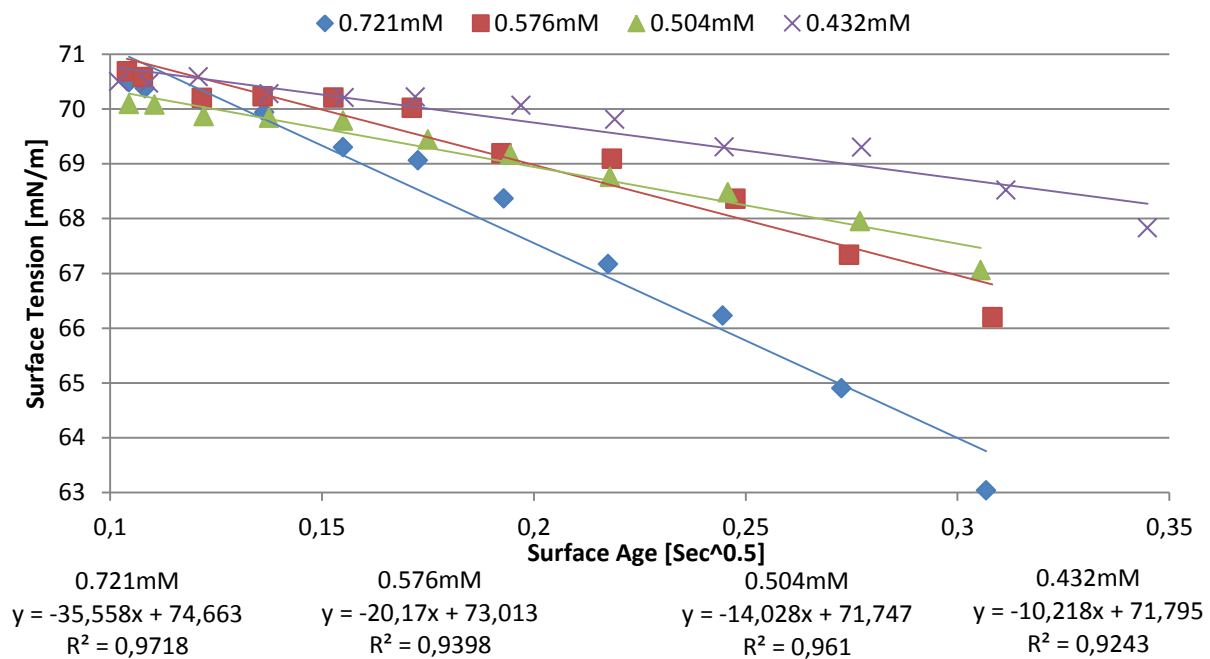**Figure 43. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 0, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.865mM (Green rectangle), 0.576mM (Purple square), 0.432mM (Blue square), 0.288mM (Yellow triangle) and 0.144mM (Blue X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.**
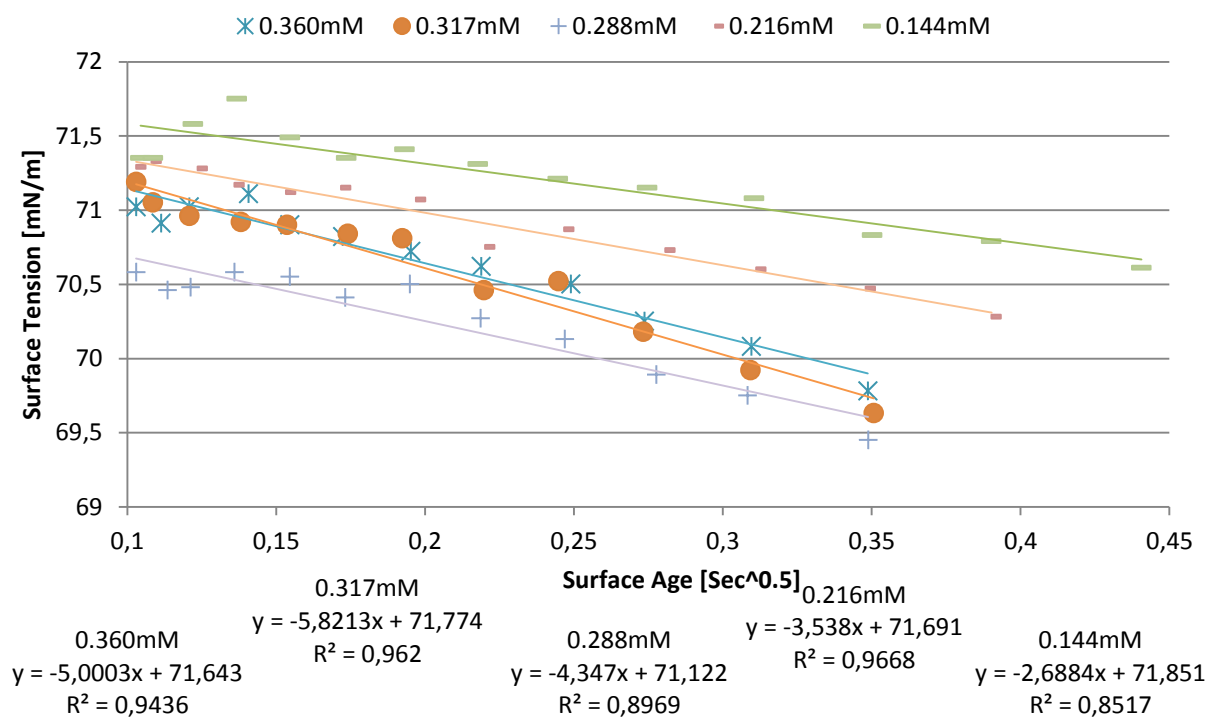
$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \ , \qquad I = 20 \ mM \ , \ T = 25°C \ , Parallel \ \#1$$

0.721mM   0.576mM   0.504mM   0.432mM

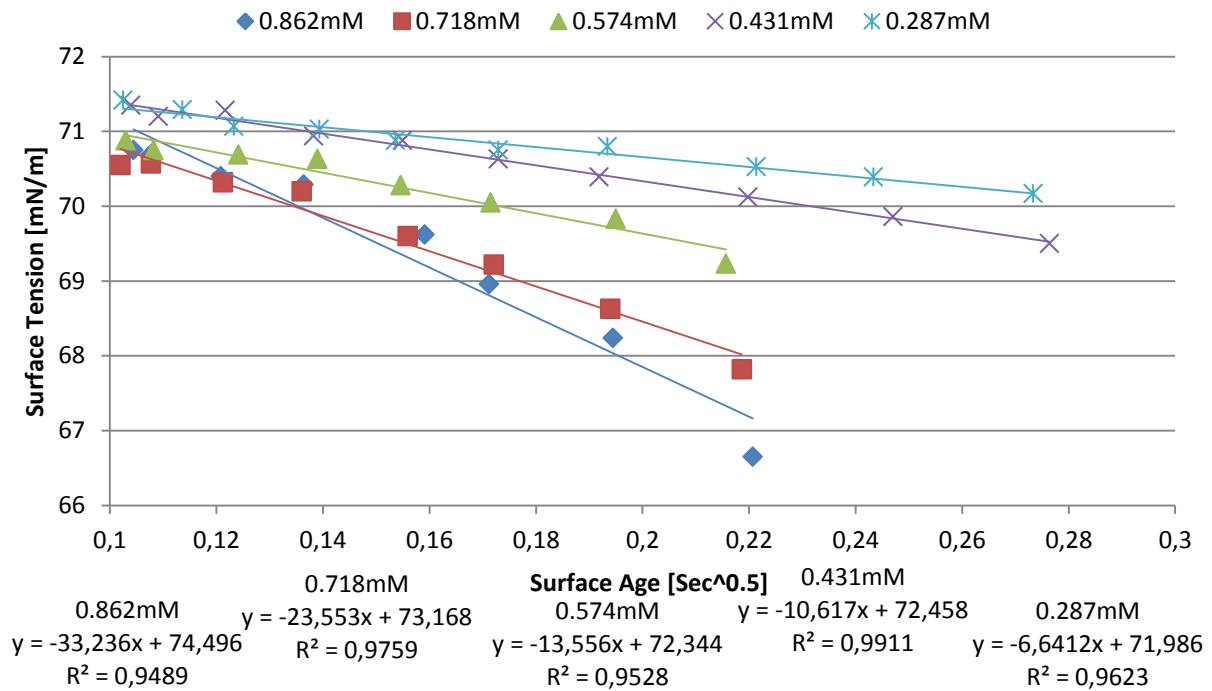| 0.721mM	0.576mM	0.504mM	0.432
y = -35,056x + 74,834	y = -22,613x + 73,133	y = -16,216x + 72,989	y = -11,52x + 72,475
R² = 0,9658	R² = 0,9401	R² = 0,9415	R² = 0,9622

Figure 44. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/117, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.721mM (Blue squares), 0.576mM (Red squares), 0.504mM (Green triangles) and 0.432mM (Purple X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

0.360mM   0.317mM   0.288mM   0.216mM   0.144mM

0.360mM	0.317mM	0.288mM	0.216mM	0.144mM
y = -8,5032x + 72,36	y = -5,4883x + 71,054	y = -5,2402x + 71,975	y = -4,4862x + 72,116	y = -3,1184x + 72,014
R² = 0,9752	R² = 0,9263	R² = 0,9488	R² = 0,9865	R² = 0,9689

Figure 45. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/117, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.360mM (Blue star), 0.317mM (Yellow circle), 0.288mM (Blue plus), 0.216mM (Tan rectangle) and 0.144(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
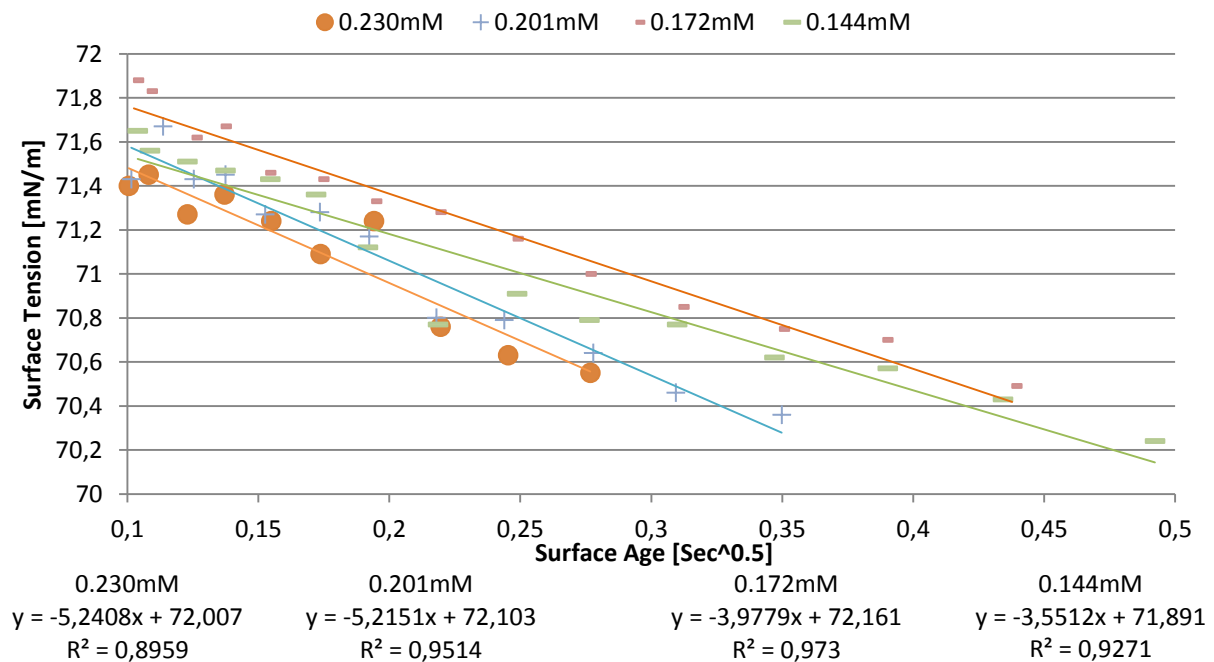
$$\frac{CaCl_2}{NaCl} = \frac{1}{117}, \qquad I = 20 \ mM, \ T = 25°C, Parallel \ \#2$$

0.721mM
y = -35,319x + 74,577
R² = 0,9785

0.576mM
y = -21,667x + 73,364
R² = 0,9571

0.504mM
y = -15,488x + 72,193
R² = 0,9574

0.432mM
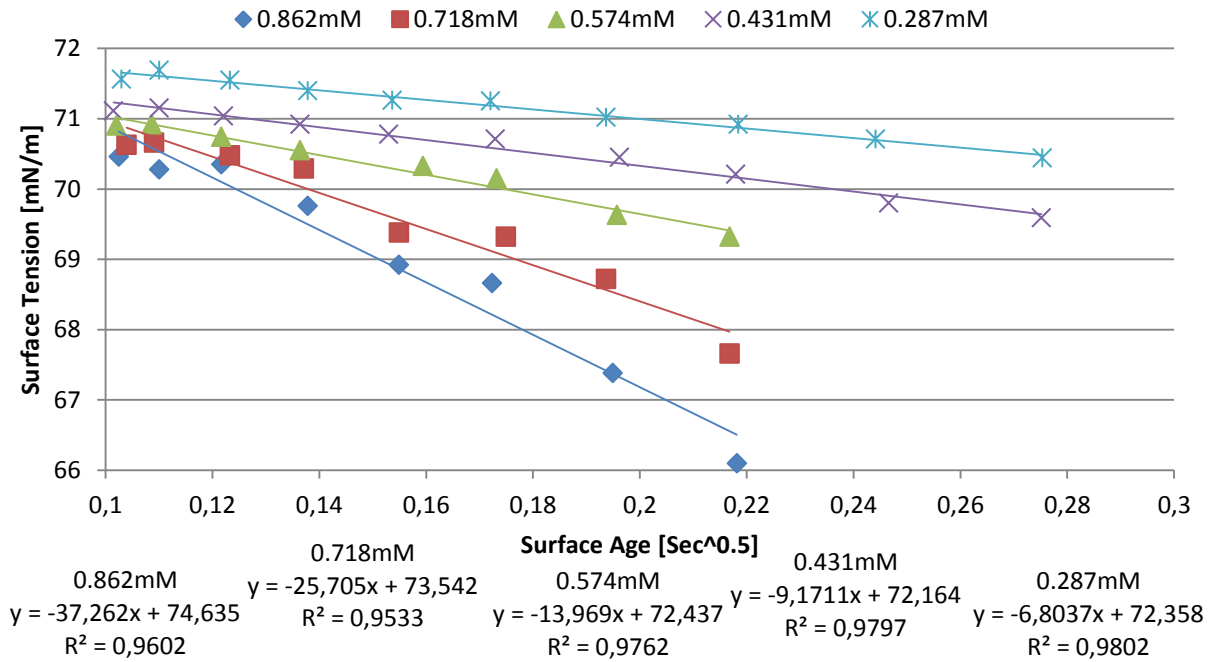y = -11,995x + 72,608
R² = 0,9514

Figure 46. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 1/117, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.721mM (Blue squares), 0.576mM (Red squares), 0.504mM (Green triangles) and 0.432mM (Purple X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
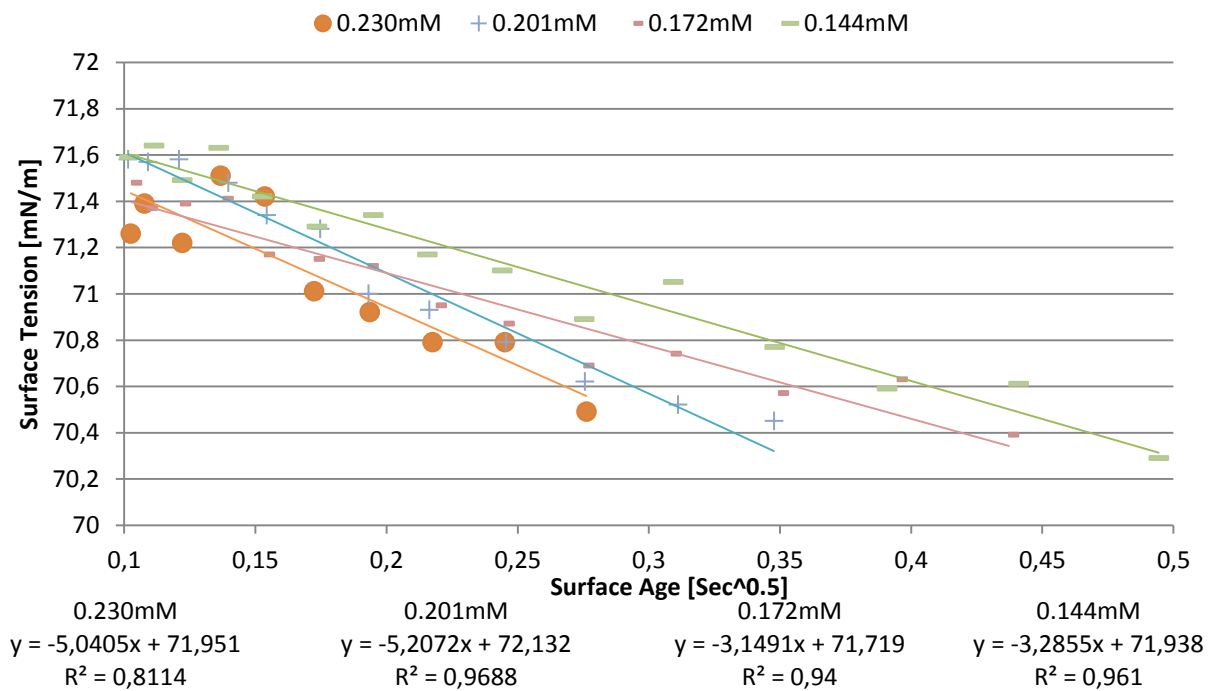

0.360mM
y = -8,2807x + 71,99
R² = 0,9651

0.317mM
y = -6,6938x + 71,33
R² = 0,9752

0.288mM
y = -5,1302x + 71,792
R² = 0,9337

0.216mM
y = -3,925x + 71,682
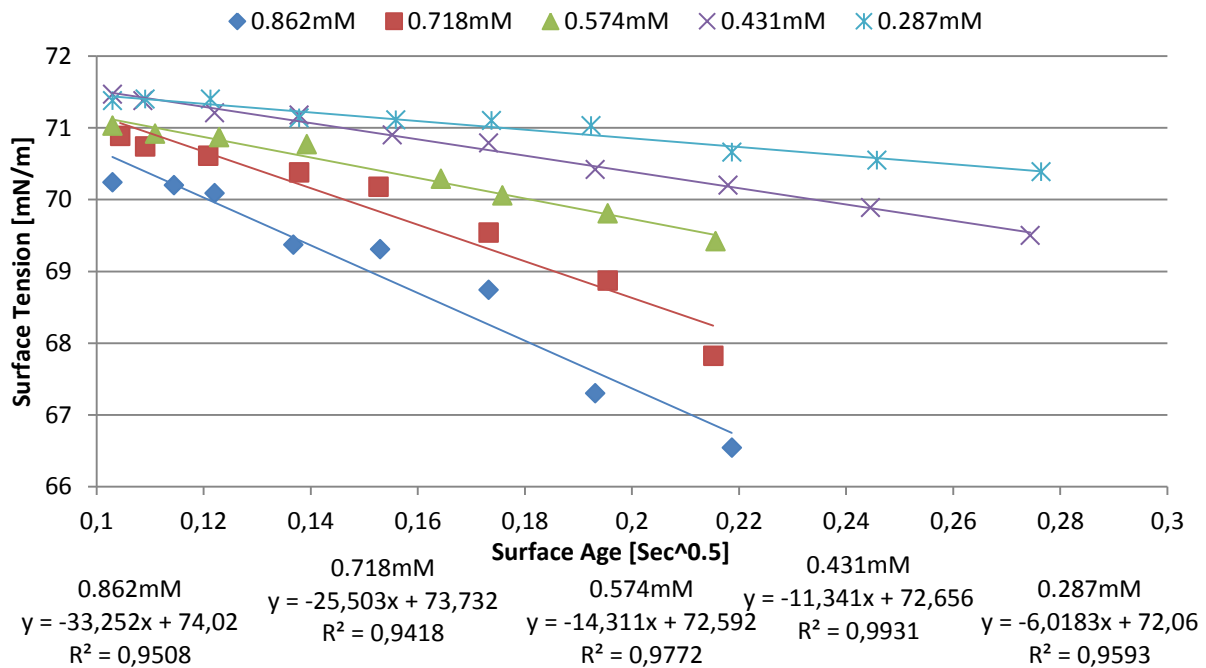R² = 0,9844

0.144mM
y = -3,1171x + 71,767
R² = 0,9631

Figure 47. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 1/117, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.360mM (Blue star), 0.317mM (Yellow circle), 0.288mM (Blue plus), 0.216mM (Tan rectangle) and 0.144(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \ , \qquad I = 20 \ mM \ , \ T = 25°C \ , Parallel \ \#3$$

0.721mM	0.576mM	0.504mM	0.432mM
y = -35,558x + 74,663	y = -20,17x + 73,013	y = -14,028x + 71,747	y = -10,218x + 71,795
R² = 0,9718	R² = 0,9398	R² = 0,961	R² = 0,9243

Figure 48. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/117, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.721mM (Blue squares), 0.576mM (Red squares), 0.504mM (Green triangles) and 0.432mM (Purple X). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
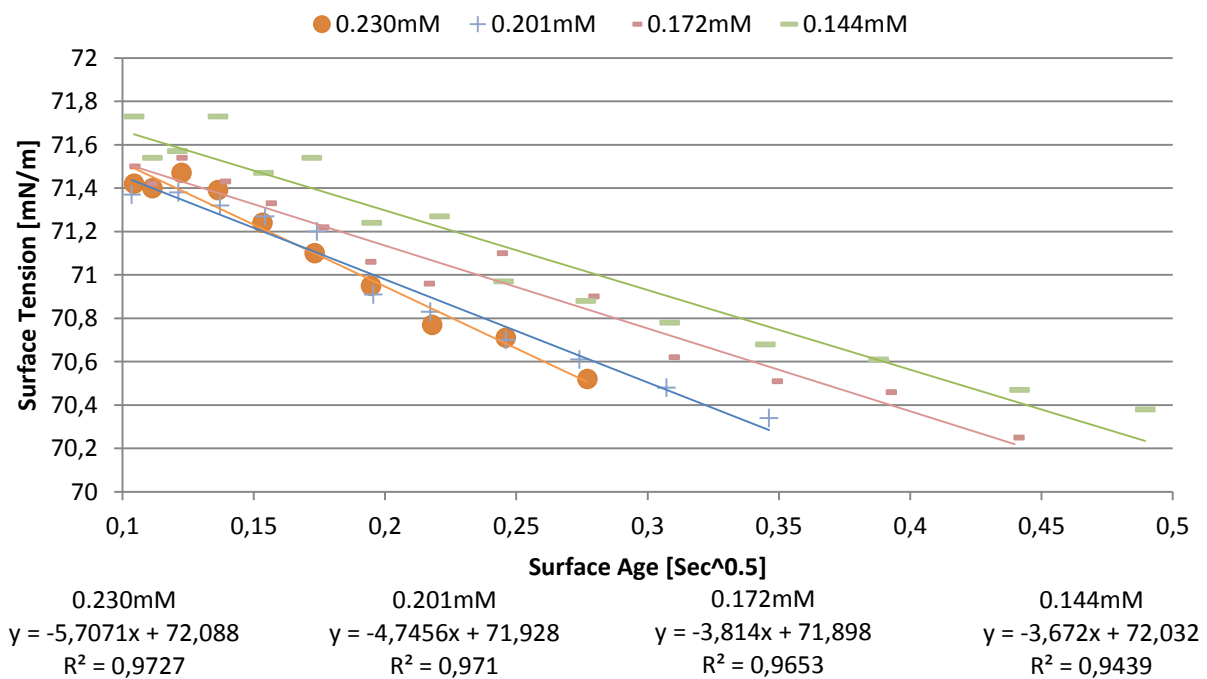

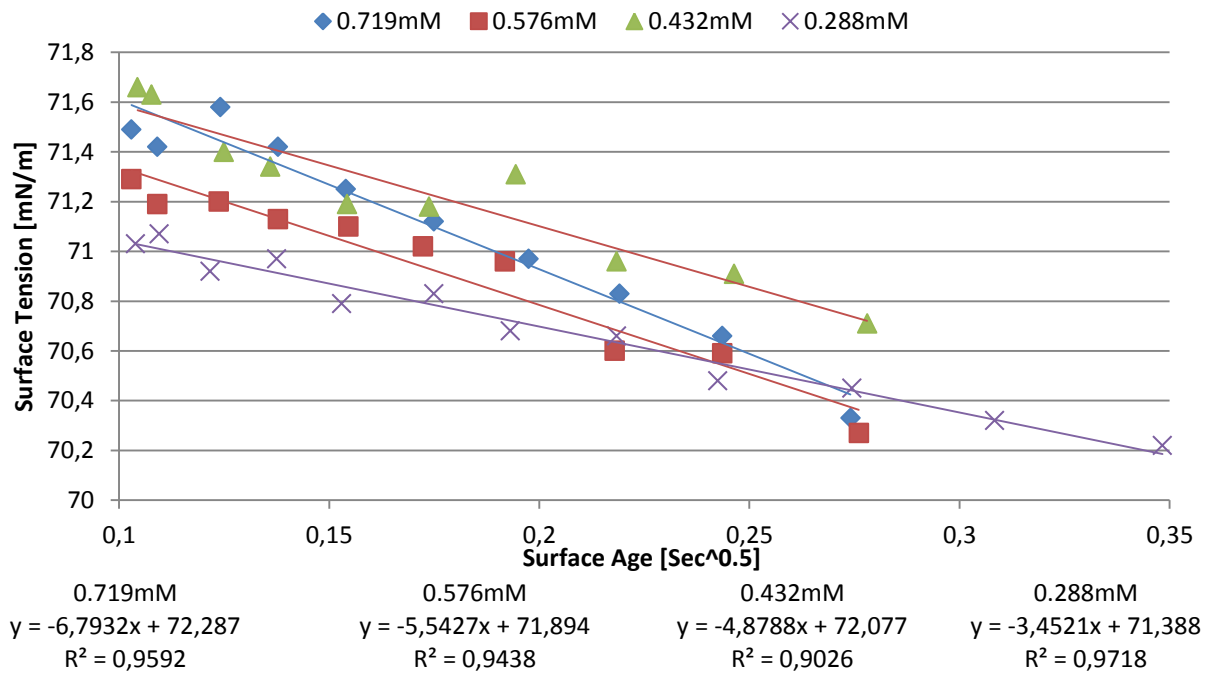| 0.360mM	0.317mM	0.288mM	0.216mM	0.144mM
y = -5,0003x + 71,643	y = -5,8213x + 71,774	y = -4,347x + 71,122	y = -3,538x + 71,691	y = -2,6884x + 71,851
R² = 0,9436	R² = 0,962	R² = 0,8969	R² = 0,9668	R² = 0,8517

Figure 49. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/117, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.360mM (Blue star), 0.317mM (Yellow circle), 0.288mM (Blue plus), 0.216mM (Tan rectangle) and 0.144(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
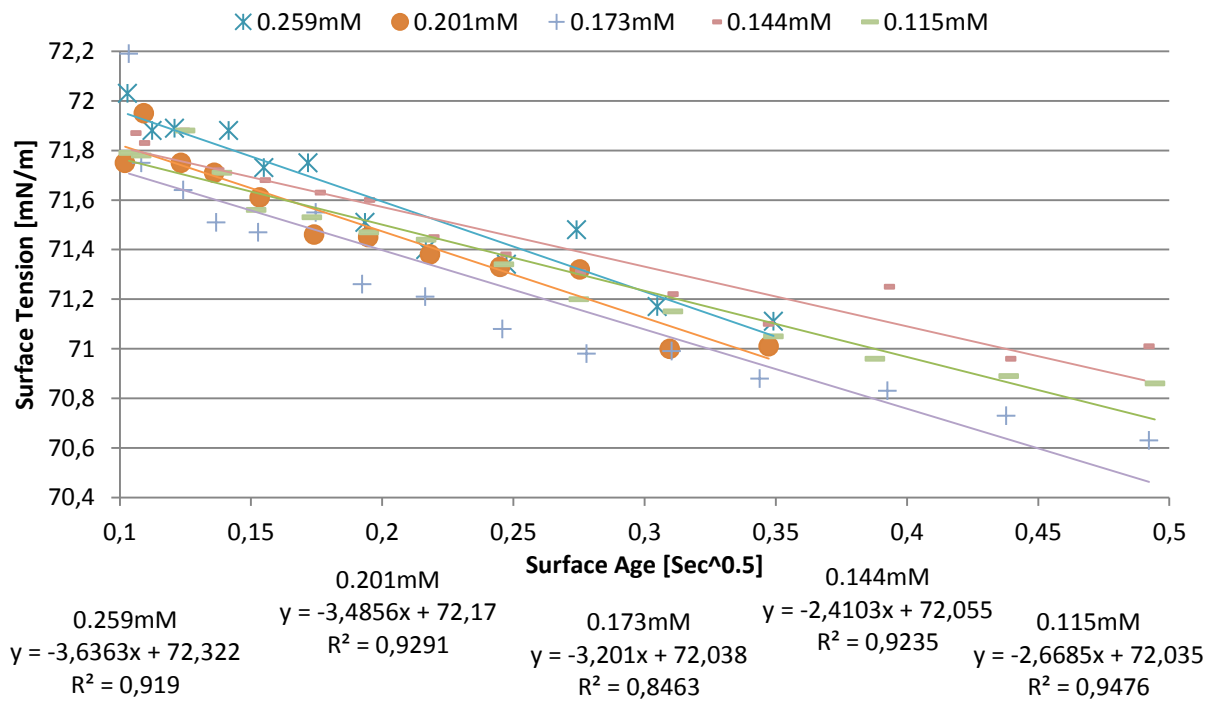
$$\frac{CaCl_2}{NaCl} = \frac{1}{57}\,, \qquad I = 20\ mM\,,\ T = 25°C\,, Parallel\ \#1$$

0.862mM
y = -33,236x + 74,496
R² = 0,9489

0.718mM
y = -23,553x + 73,168
R² = 0,9759

0.574mM
y = -13,556x + 72,344
R² = 0,9528

0.431mM
y = -10,617x + 72,458
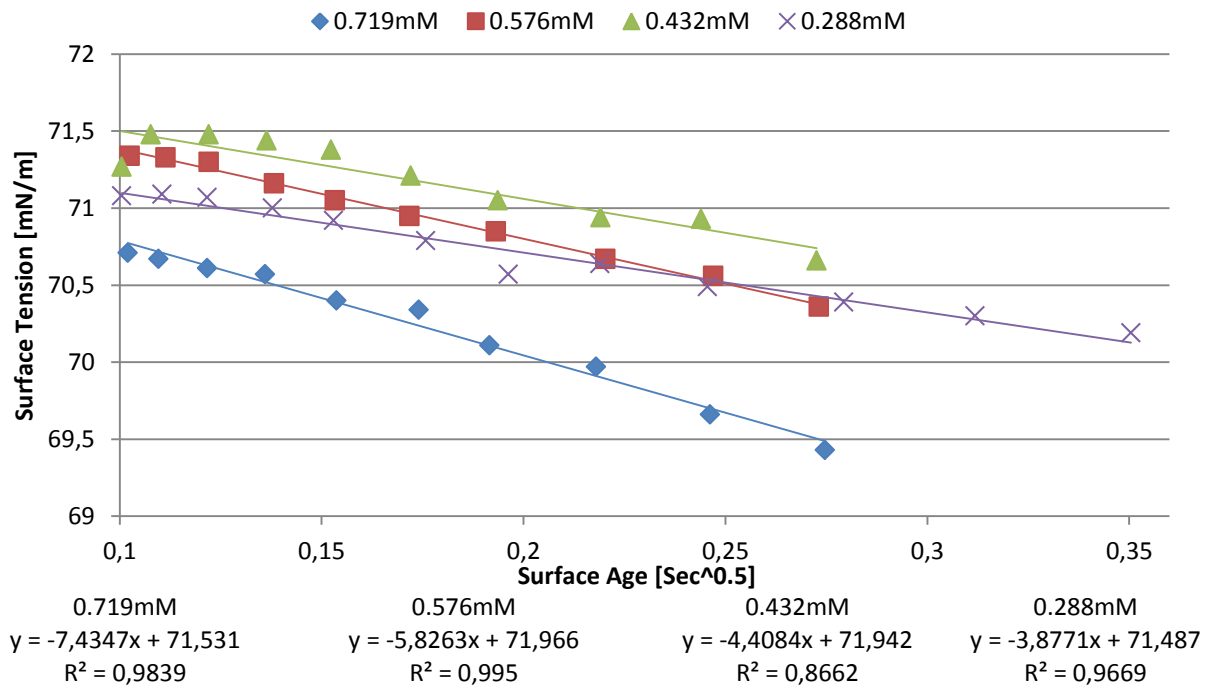R² = 0,9911

0.287mM
y = -6,6412x + 71,986
R² = 0,9623

Figure 50. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/57, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.862mM (Blue squares), 0.718mM (Red squares), 0.574mM (Green triangles), 0.431mM (Purple X) and 0.287mM (Blue star). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

0.230mM
y = -5,2408x + 72,007
R² = 0,8959

0.201mM
y = -5,2151x + 72,103
R² = 0,9514

0.172mM
y = -3,9779x + 72,161
R² = 0,973

0.144mM
y = -3,5512x + 71,891
R² = 0,9271

Figure 51. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/57, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.230mM (Yellow circle), 0.201mM (Blue plus), 0.172mM (Tan rectangle) and 0.144(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
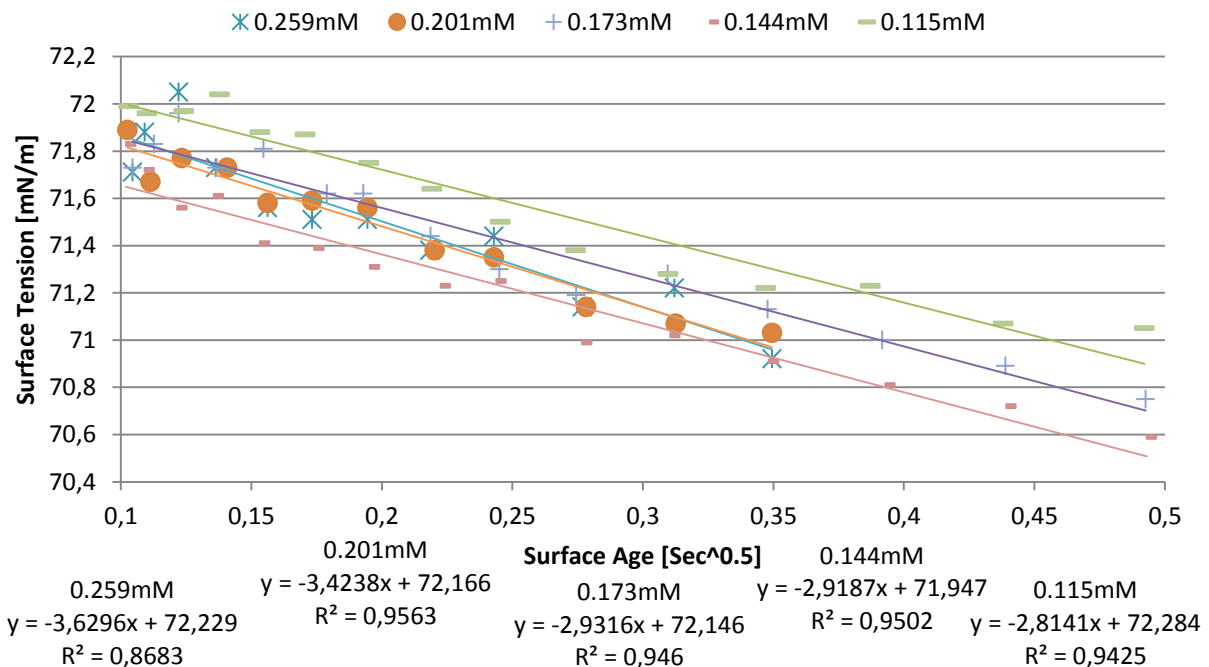
$$\frac{CaCl_2}{NaCl} = \frac{1}{57} , \qquad I = 20 \ mM , \ T = 25°C , Parallel \ \#2$$

0.862mM
y = -37,262x + 74,635
R² = 0,9602

0.718mM
y = -25,705x + 73,542
R² = 0,9533

0.574mM
y = -13,969x + 72,437
R² = 0,9762

0.431mM
y = -9,1711x + 72,164
R² = 0,9797
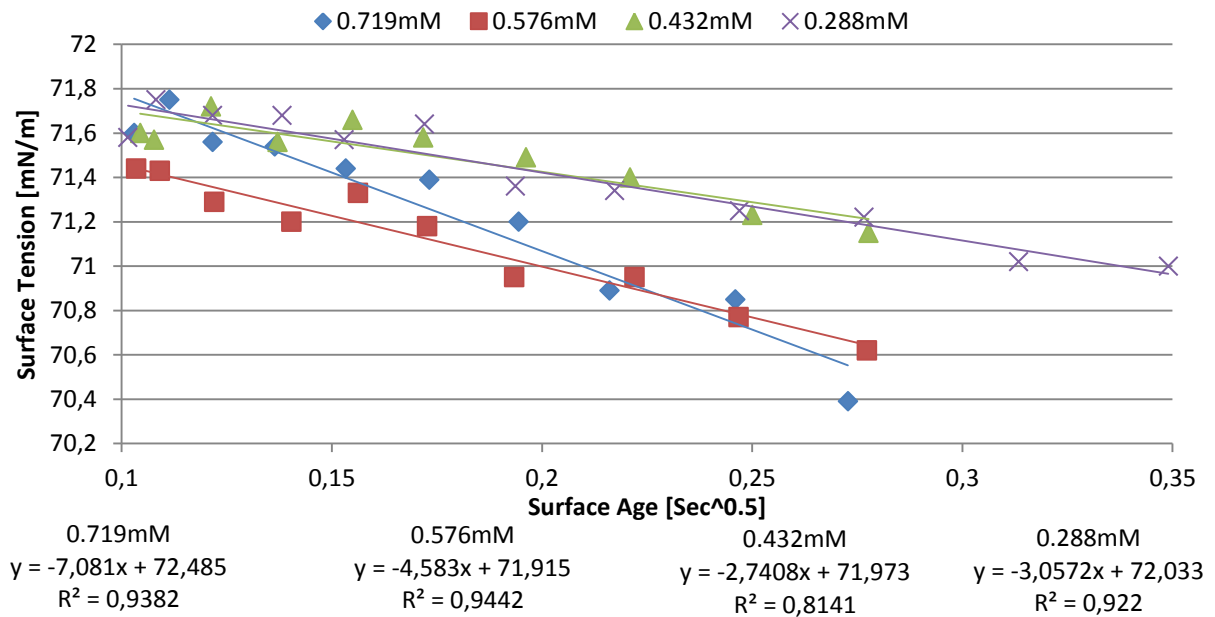
0.287mM
y = -6,8037x + 72,358
R² = 0,9802

Figure 52. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 1/57, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.862mM (Blue squares), 0.718mM (Red squares), 0.574mM (Green triangles), 0.431mM (Purple X) and 0.287mM (Blue star). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
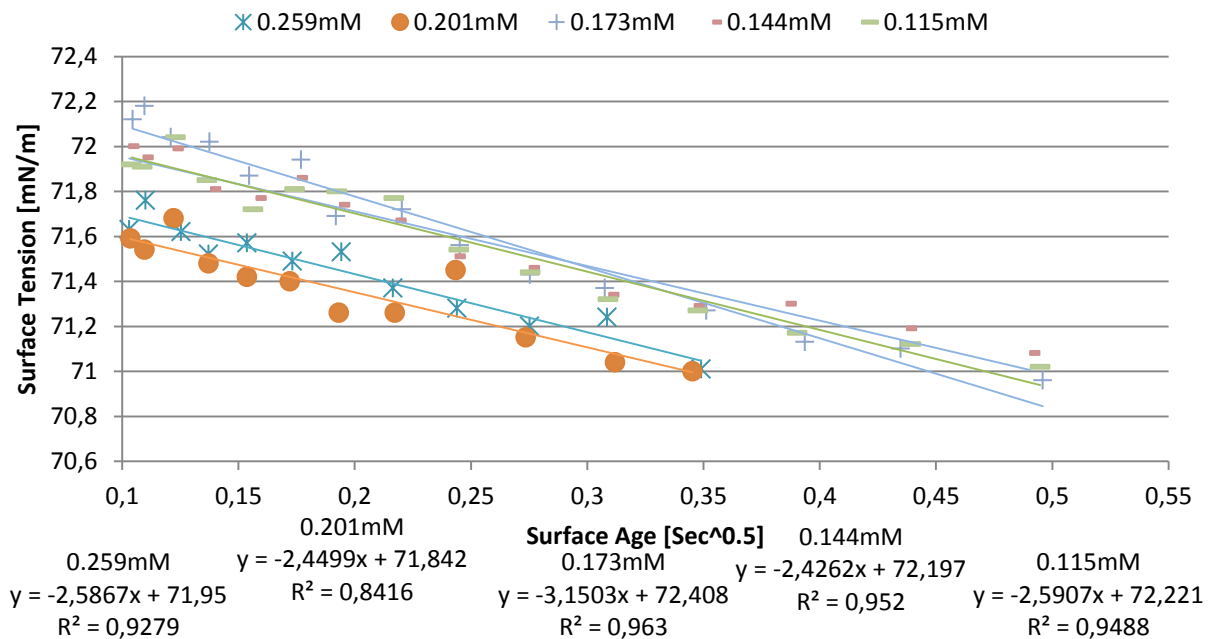

0.230mM
y = -5,0405x + 71,951
R² = 0,8114

0.201mM
y = -5,2072x + 72,132
R² = 0,9688

0.172mM
y = -3,1491x + 71,719
R² = 0,94

0.144mM
y = -3,2855x + 71,938
R² = 0,961

Figure 53. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 1/57, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.230mM (Yellow circle), 0.201mM (Blue plus), 0.172mM (Tan rectangle) and 0.144(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} , \qquad I = 20\ mM ,\ T = 25°C , Parallel\ \#3$$

0.862mM
y = -33,252x + 74,02
R² = 0,9508

0.718mM
y = -25,503x + 73,732
R² = 0,9418

0.574mM
y = -14,311x + 72,592
R² = 0,9772

0.431mM
y = -11,341x + 72,656
R² = 0,9931

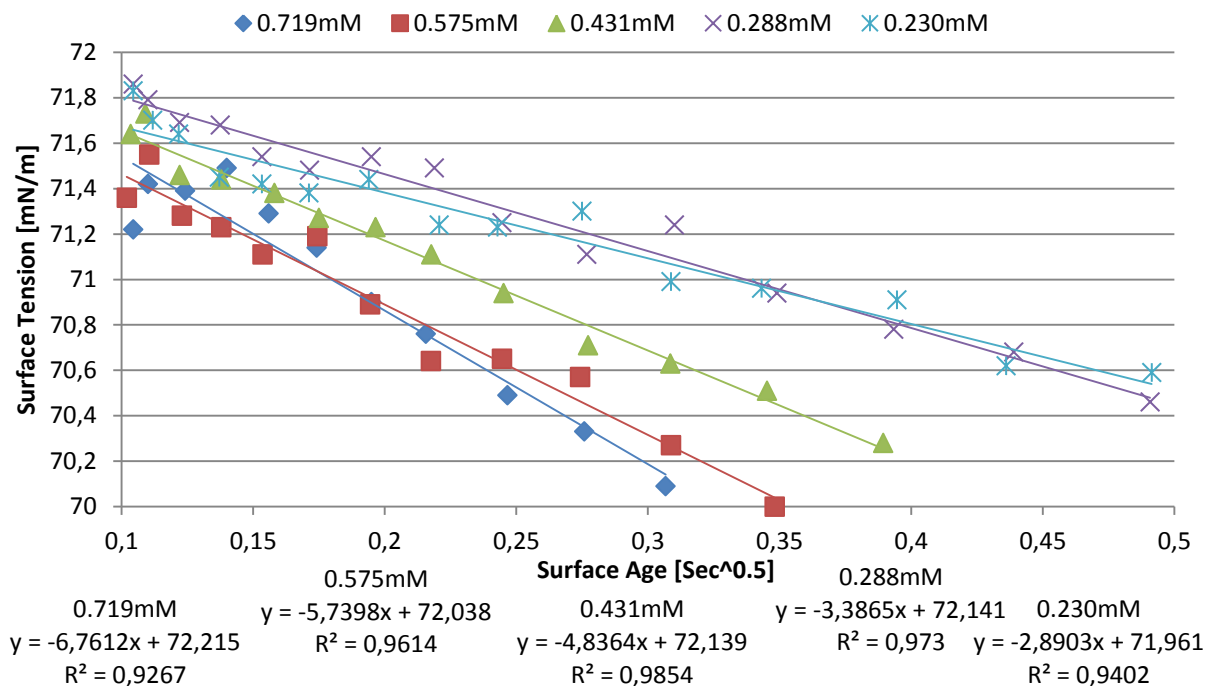0.287mM
y = -6,0183x + 72,06
R² = 0,9593

Figure 54. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/57, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.862mM (Blue squares), 0.718mM (Red squares), 0.574mM (Green triangles), 0.431mM (Purple X) and 0.287mM (Blue star). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
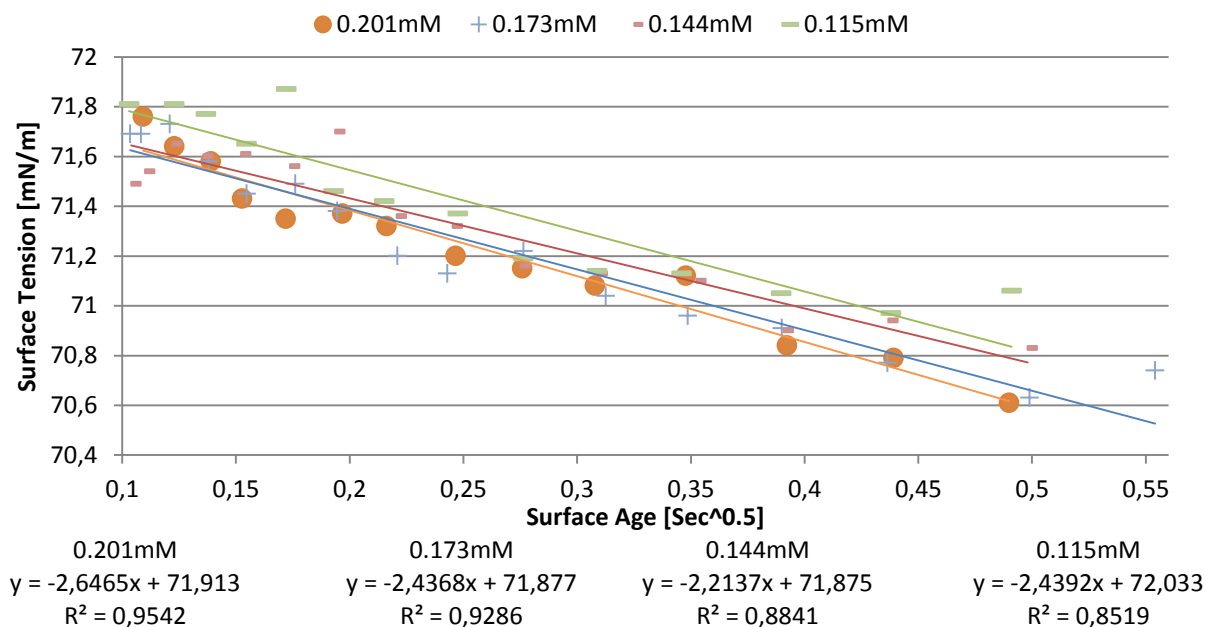

0.230mM
y = -5,7071x + 72,088
R² = 0,9727

0.201mM
y = -4,7456x + 71,928
R² = 0,971

0.172mM
y = -3,814x + 71,898
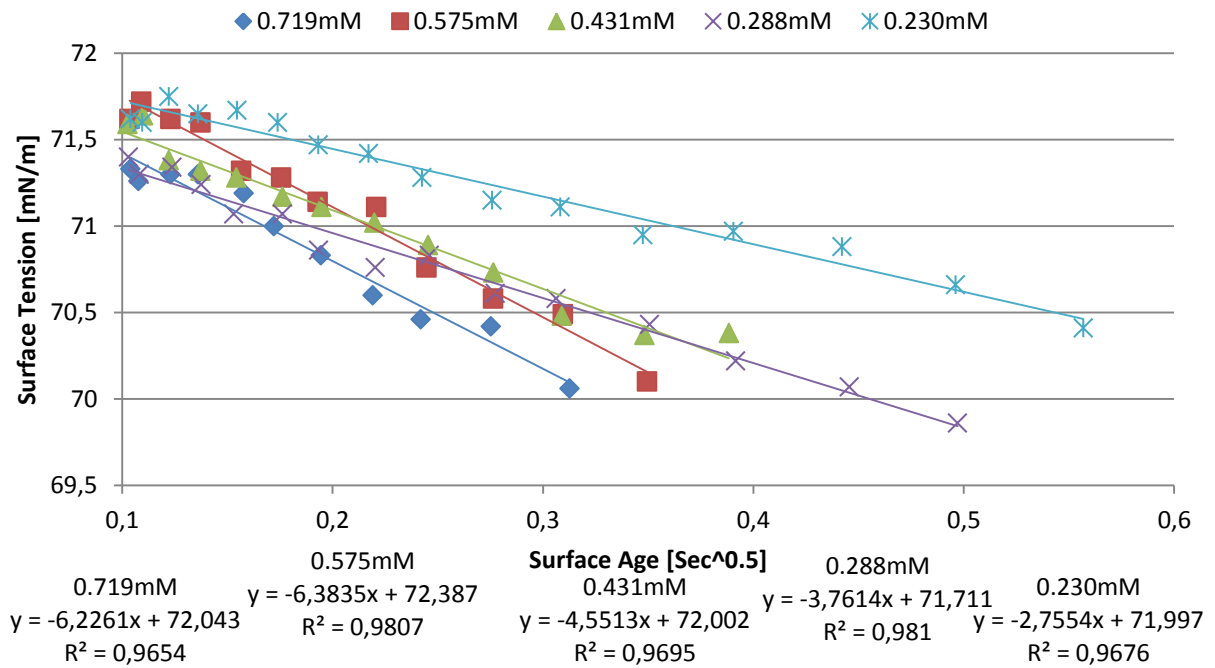R² = 0,9653

0.144mM
y = -3,672x + 72,032
R² = 0,9439

Figure 55. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/57, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.230mM (Yellow circle), 0.201mM (Blue plus), 0.172mM (Tan rectangle) and 0.144(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} , \qquad I = 20 \; mM , \; T = 25°C , Parallel \; \#1$$

0.719mM
y = -6,7932x + 72,287
R² = 0,9592

0.576mM
y = -5,5427x + 71,894
R² = 0,9438

0.432mM
y = -4,8788x + 72,077
R² = 0,9026

0.288mM
y = -3,4521x + 71,388
R² = 0,9718

Figure 56. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/17, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.719mM (Blue squares), 0.576mM (Red squares), 0.432mM (Green triangles) and 0.288mM (Purple X) . With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
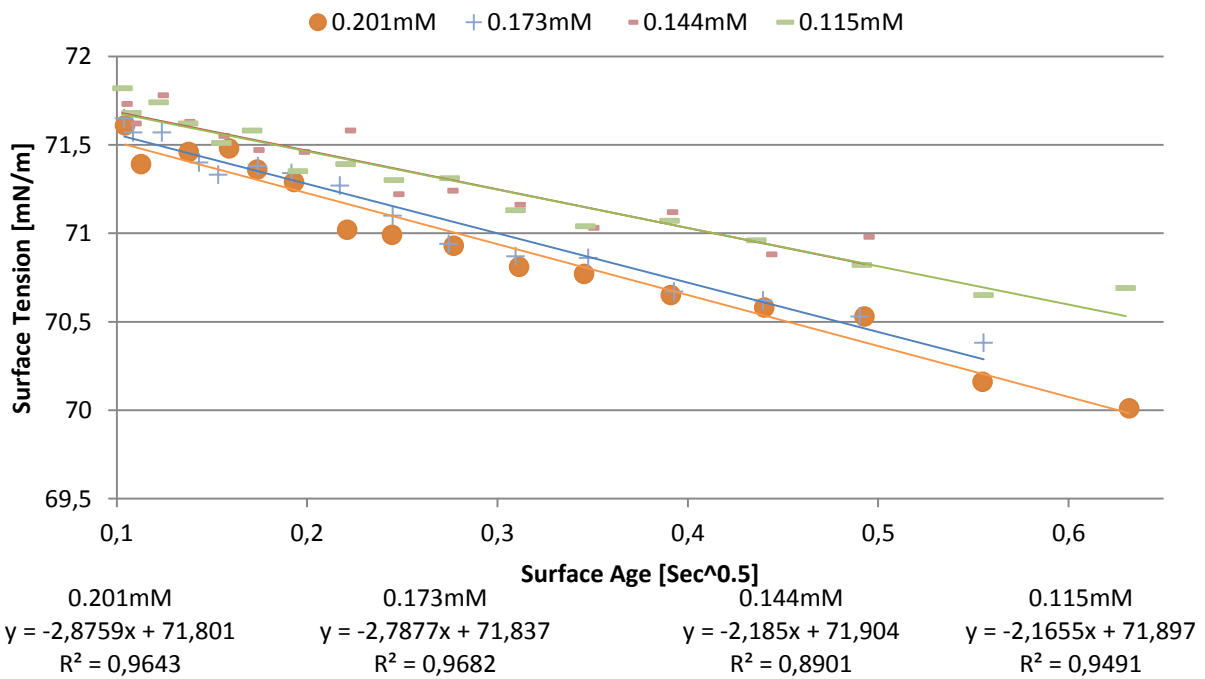

0.259mM
y = -3,6363x + 72,322
R² = 0,919

0.201mM
y = -3,4856x + 72,17
R² = 0,9291

0.173mM
y = -3,201x + 72,038
R² = 0,8463

0.144mM
y = -2,4103x + 72,055
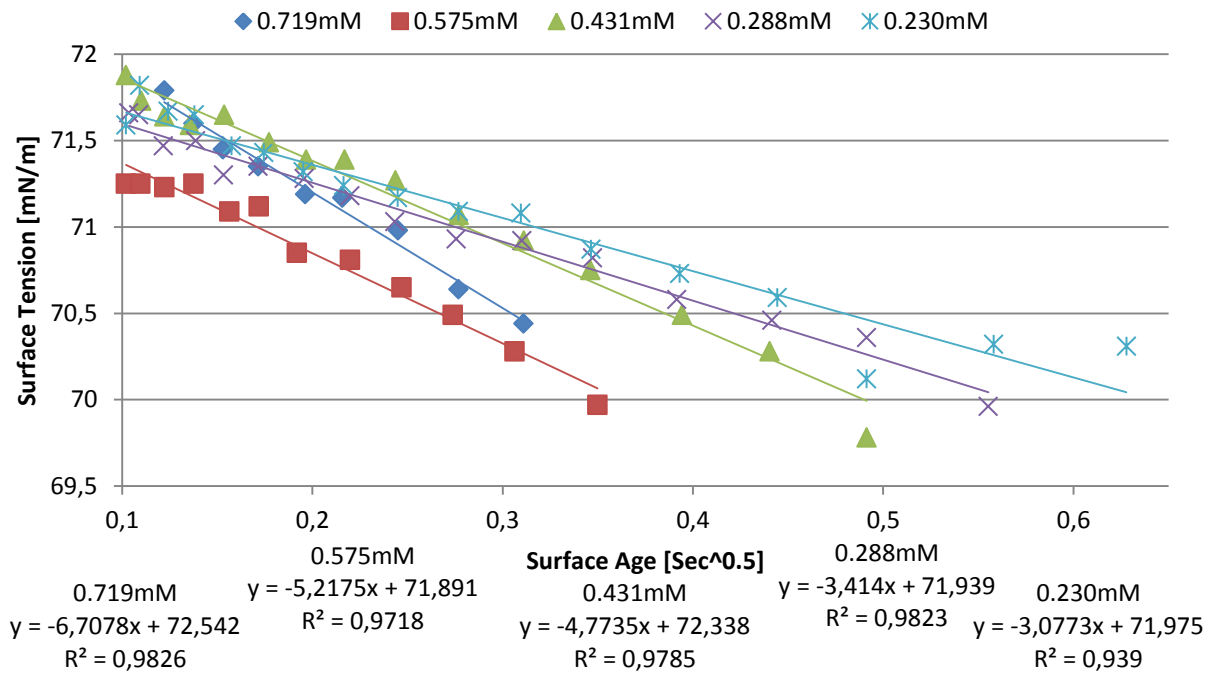R² = 0,9235

0.115mM
y = -2,6685x + 72,035
R² = 0,9476

Figure 57. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/17, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.259mM (Blue star), 0.201mM (Yellow circle), 0.173mM (Blue plus), 0.144mM (Tan rectangle) and 0.115(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.
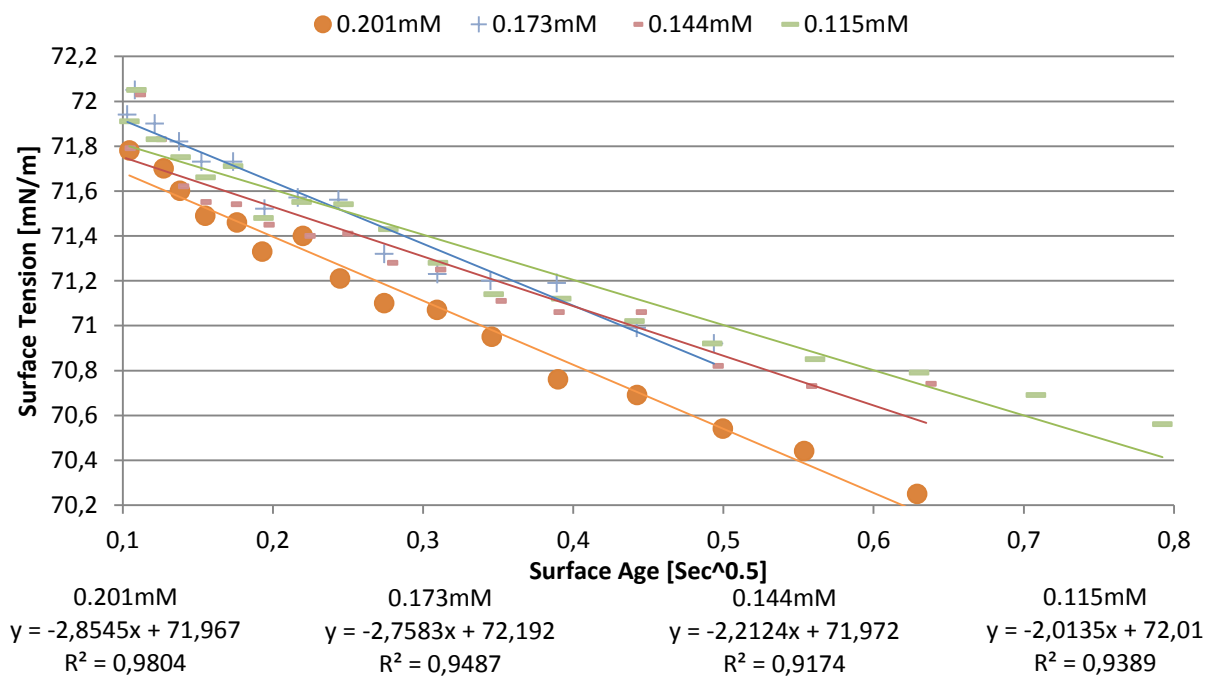
$$\frac{CaCl_2}{NaCl} = \frac{1}{17}, \qquad I = 20\ mM,\ T = 25°C, Parallel\ \#2$$

0.719mM
y = -7,4347x + 71,531
R² = 0,9839

0.576mM
y = -5,8263x + 71,966
R² = 0,995

0.432mM
y = -4,4084x + 71,942
R² = 0,8662

0.288mM
y = -3,8771x + 71,487
R² = 0,9669

Figure 58. Graph showing the second parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/17, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.719mM (Blue squares), 0.576mM (Red squares), 0.432mM (Green triangles) and 0.288mM (Purple X) . With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

0.259mM
y = -3,6296x + 72,229
R² = 0,8683

0.201mM
y = -3,4238x + 72,166
R² = 0,9563

0.173mM
y = -2,9316x + 72,146
R² = 0,946

0.144mM
y = -2,9187x + 71,947
R² = 0,9502

0.115mM
y = -2,8141x + 72,284
R² = 0,9425

Figure 59. Graph showing the second parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/17, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.259mM (Blue star), 0.201mM (Yellow circle), 0.173mM (Blue plus), 0.144mM (Tan rectangle) and 0.115(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17}, \qquad I = 20 \ mM, \ T = 25°C, Parallel \ \#3$$

0.719mM
y = -7,081x + 72,485
R² = 0,9382

0.576mM
y = -4,583x + 71,915
R² = 0,9442

0.432mM
y = -2,7408x + 71,973
R² = 0,8141

0.288mM
y = -3,0572x + 72,033
R² = 0,922

Figure 60. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/17, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.719mM (Blue squares), 0.576mM (Red squares), 0.432mM (Green triangles) and 0.288mM (Purple X) . With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

0.259mM
y = -2,5867x + 71,95
R² = 0,9279

0.201mM
y = -2,4499x + 71,842
R² = 0,8416

0.173mM
y = -3,1503x + 72,408
R² = 0,963

0.144mM
y = -2,4262x + 72,197
R² = 0,952

0.115mM
y = -2,5907x + 72,221
R² = 0,9488

Figure 61. Graph showing the third parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/17, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.259mM (Blue star), 0.201mM (Yellow circle), 0.173mM (Blue plus), 0.144mM (Tan rectangle) and 0.115(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12}, \qquad I = 20\ mM\ ,\ T = 25°C\ ,Parallel\ \#1$$

0.719mM
y = -6,7612x + 72,215
R² = 0,9267

0.575mM
y = -5,7398x + 72,038
R² = 0,9614

0.431mM
y = -4,8364x + 72,139
R² = 0,9854

0.288mM
y = -3,3865x + 72,141
R² = 0,973

0.230mM
y = -2,8903x + 71,961
R² = 0,9402

Figure 62. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/12, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.719mM (Blue squares), 0.575mM (Red squares), 0.431mM (Green triangles), 0.288mM (Purple X) and 0.230mM (Blue star) . With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

0.201mM
y = -2,6465x + 71,913
R² = 0,9542

0.173mM
y = -2,4368x + 71,877
R² = 0,9286

0.144mM
y = -2,2137x + 71,875
R² = 0,8841

0.115mM
y = -2,4392x + 72,033
R² = 0,8519

Figure 63. Graph showing the first parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/12, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.201mM (Yellow circle), 0.173mM (Blue plus), 0.144mM (Tan rectangle) and 0.115(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} , \qquad I = 20\ mM ,\ T = 25°C , Parallel\ \#2$$

◆ 0.719mM　■ 0.575mM　▲ 0.431mM　✕ 0.288mM　✳ 0.230mM

0.719mM
y = -6,2261x + 72,043
R² = 0,9654

0.575mM
y = -6,3835x + 72,387
R² = 0,9807

0.431mM
y = -4,5513x + 72,002
R² = 0,9695

0.288mM
y = -3,7614x + 71,711
R² = 0,981

0.230mM
y = -2,7554x + 71,997
R² = 0,9676

Figure 64. Graph showing the second parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/12, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.719mM (Blue squares), 0.575mM (Red squares), 0.431mM (Green triangles), 0.288mM (Purple X) and 0.230mM (Blue star) . With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

● 0.201mM　＋ 0.173mM　▬ 0.144mM　▬ 0.115mM

0.201mM
y = -2,8759x + 71,801
R² = 0,9643

0.173mM
y = -2,7877x + 71,837
R² = 0,9682

0.144mM
y = -2,185x + 71,904
R² = 0,8901

0.115mM
y = -2,1655x + 71,897
R² = 0,9491

Figure 65. Graph showing the second parallel of linearization for short time approximation of CaCl₂/NaCl-ratio of 1/12, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.201mM (Yellow circle), 0.173mM (Blue plus), 0.144mM (Tan rectangle) and 0.115(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12}, \qquad I = 20\ mM, \quad T = 25°C, Parallel\ \#3$$

0.719mM
y = -6,7078x + 72,542
R² = 0,9826

0.575mM
y = -5,2175x + 71,891
R² = 0,9718

0.431mM
y = -4,7735x + 72,338
R² = 0,9785

0.288mM
y = -3,414x + 71,939
R² = 0,9823

0.230mM
y = -3,0773x + 71,975
R² = 0,939

Figure 66. Graph showing the third parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 1/12, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.719mM (Blue squares), 0.575mM (Red squares), 0.431mM (Green triangles), 0.288mM (Purple X) and 0.230mM (Blue star). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

0.201mM
y = -2,8545x + 71,967
R² = 0,9804

0.173mM
y = -2,7583x + 72,192
R² = 0,9487

0.144mM
y = -2,2124x + 71,972
R² = 0,9174

0.115mM
y = -2,0135x + 72,01
R² = 0,9389

Figure 67. Graph showing the second parallel of linearization for short time approximation of CaCl$_2$/NaCl-ratio of 1/12, ionic strength of 20mM and temperature 25°C, for different SDBS concentrations, 0.201mM (Yellow circle), 0.173mM (Blue plus), 0.144mM (Tan rectangle) and 0.115(Green rectangle). With square root of surface age along the x-axis and surface tension on the y-axis. Along with the equation of the linearization with the accuracy constant, R.

$$\frac{CaCl_2}{NaCl} = 0, \qquad I = 20\ mM,\ T = 25°C$$
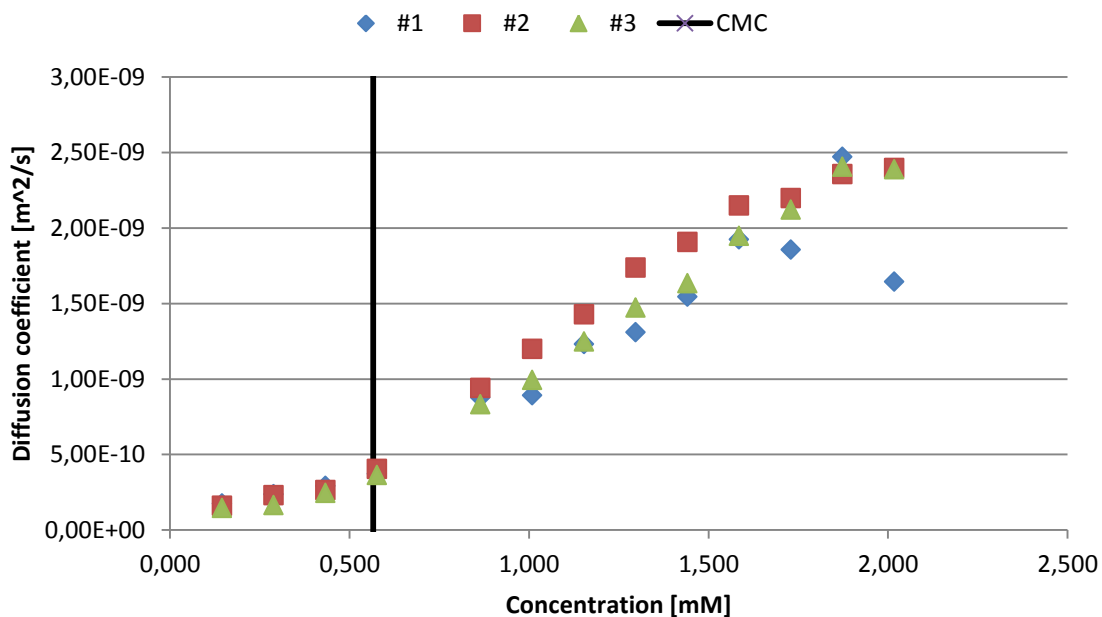
Figure 68. Plot showing the diffusion coefficient for different concentration of SDBS, with ionic strength of 20 mM, temperature is 25 °C and CaCl$_2$/NaCl-ratio is 0. The blue squares is the first parallel, the red squares is the second parallel, and the green triangle is the tird parallels. The black line show the estimated CMC.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117}, \qquad I = 20\ mM,\ T = 25°C$$
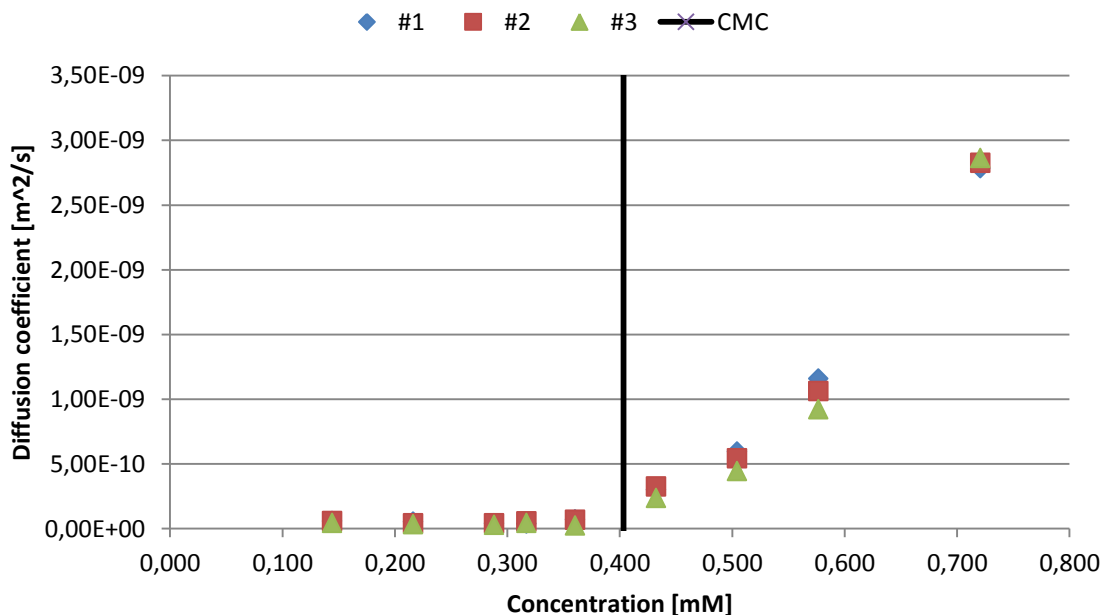
Figure 69. Plot showing the diffusion coefficient for different concentration of SDBS, with ionic strength of 20 mM, temperature is 25 °C and CaCl$_2$/NaCl-ratio is 1/117. The blue squares is the first parallel, the red squares is the second parallel, and the green triangle is the tird parallels. The black line show the estimated CMC.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57}, \qquad I = 20\ mM,\ T = 25°C$$
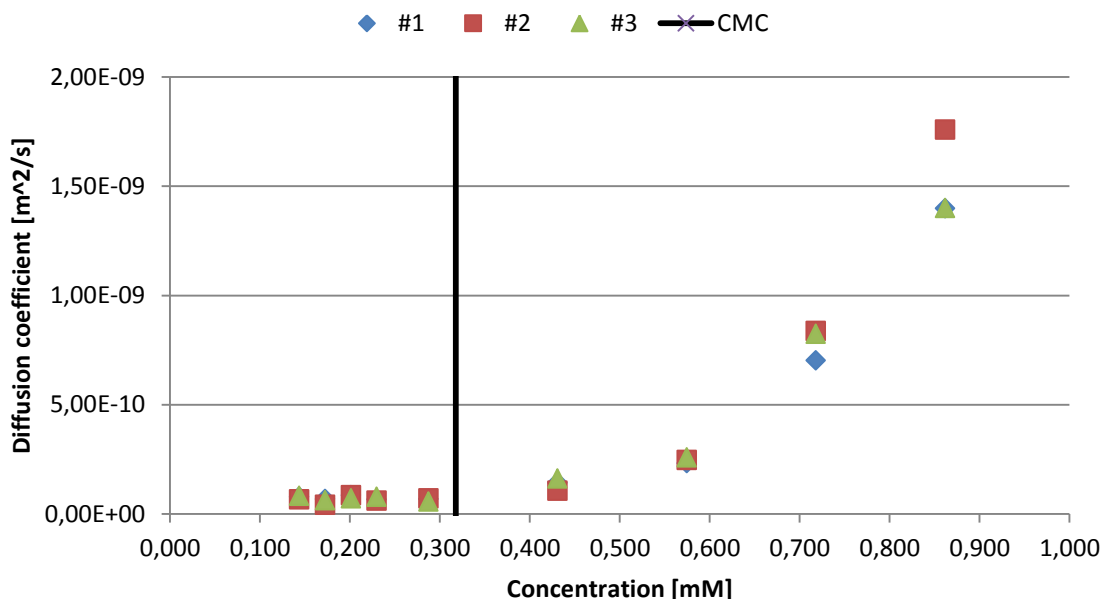
Figure 70. Plot showing the diffusion coefficient for different concentration of SDBS, with ionic strength of 20 mM, temperature is 25 °C and CaCl$_2$/NaCl-ratio is 1/57. The blue squares is the first parallel, the red squares is the second parallel, and the green triangle is the tird parallels. The black line show the estimated CMC.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17}, \qquad I = 20\ mM,\ T = 25°C$$
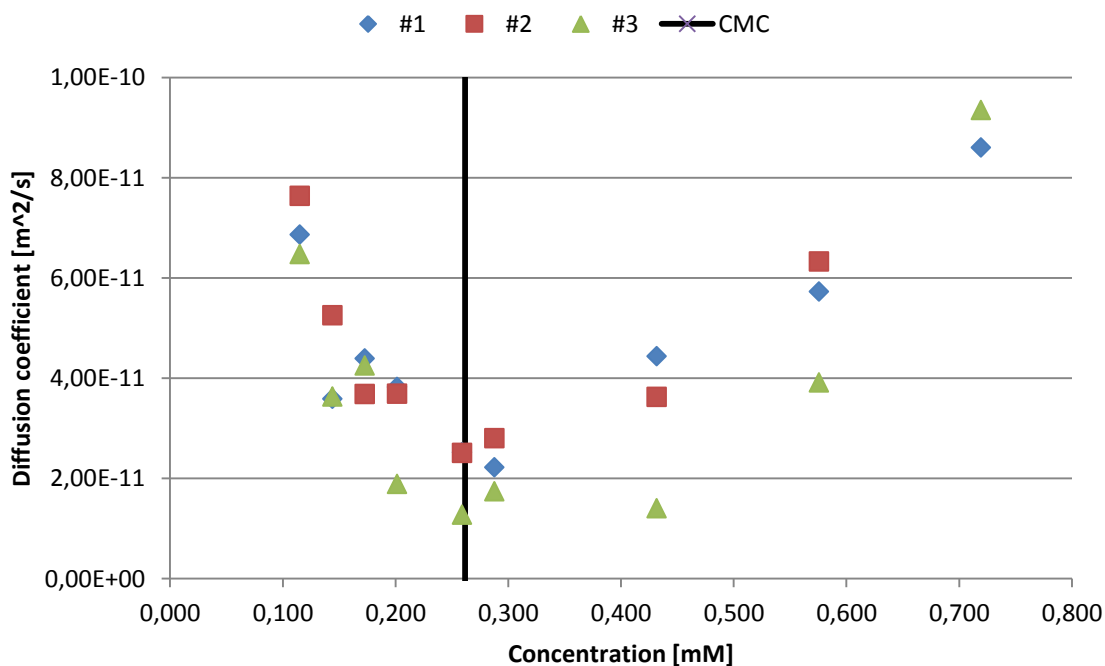
Figure 71. Plot showing the diffusion coefficient for different concentration of SDBS, with ionic strength of 20 mM, temperature is 25 °C and CaCl$_2$/NaCl-ratio is 1/17. The blue squares is the first parallel, the red squares is the second parallel, and the green triangle is the tird parallels. The black line show the estimated CMC.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} , \qquad I = 20 \ mM , \ T = 25°C$$
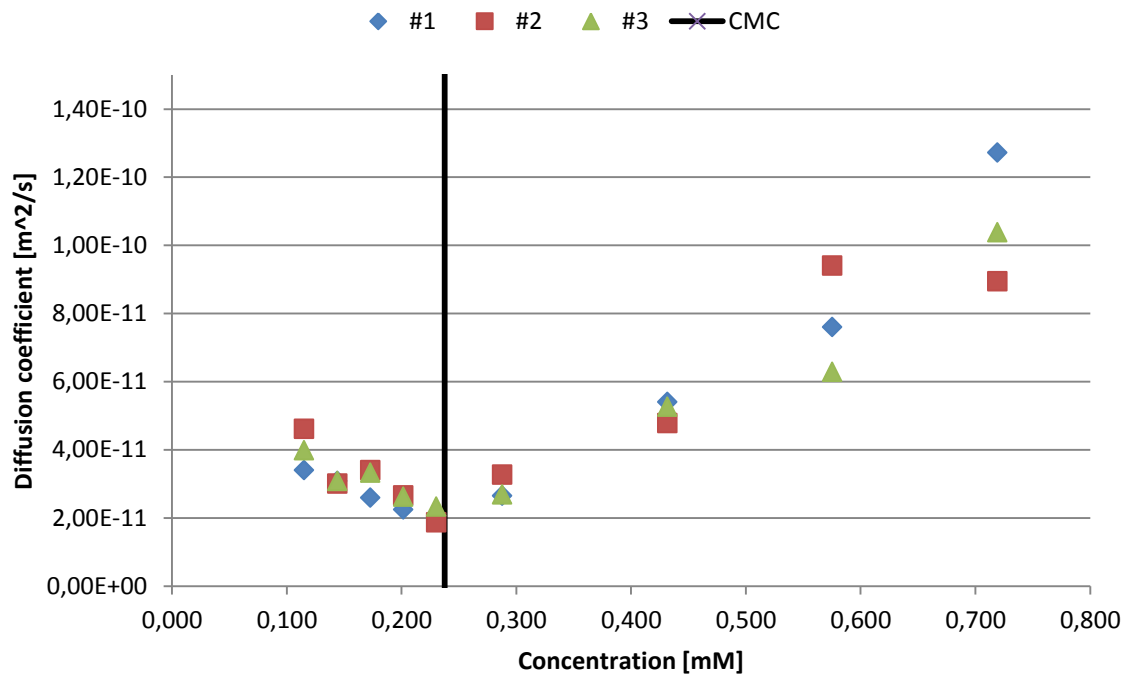
Figure 72. Plot showing the diffusion coefficient for different concentration of SDBS, with ionic strength of 20 mM, temperature is 25 °C and CaCl$_2$/NaCl-ratio is 0. The blue squares is the first parallel, the red squares is the second parallel, and the green triangle is the tird parallels. The black line show the estimated CMC.

$$\frac{CaCl_2}{NaCl} = 0, \qquad I = 20\ mM, \ T = 25°C, \qquad 0.144 mM\ SDBS$$

Parallel #1
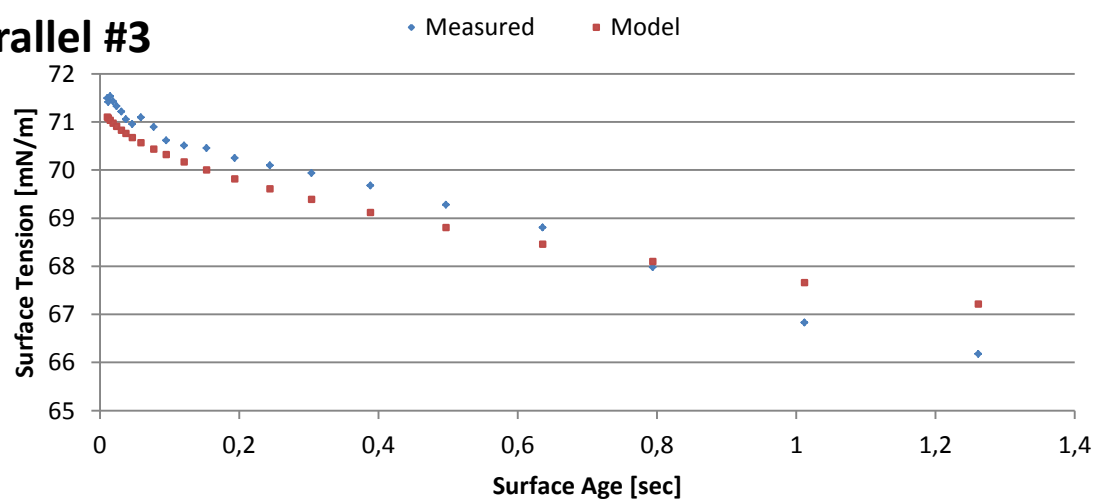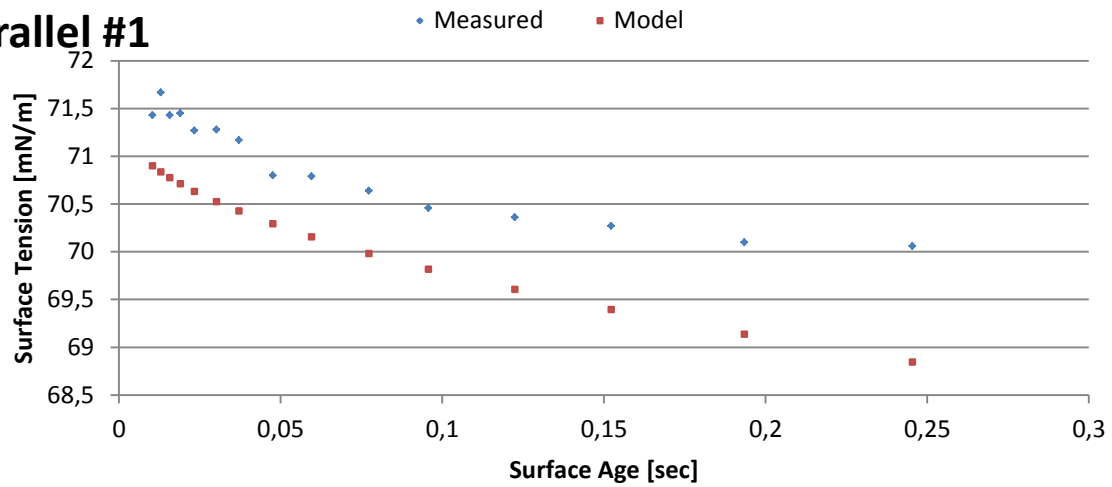

Parallel #2
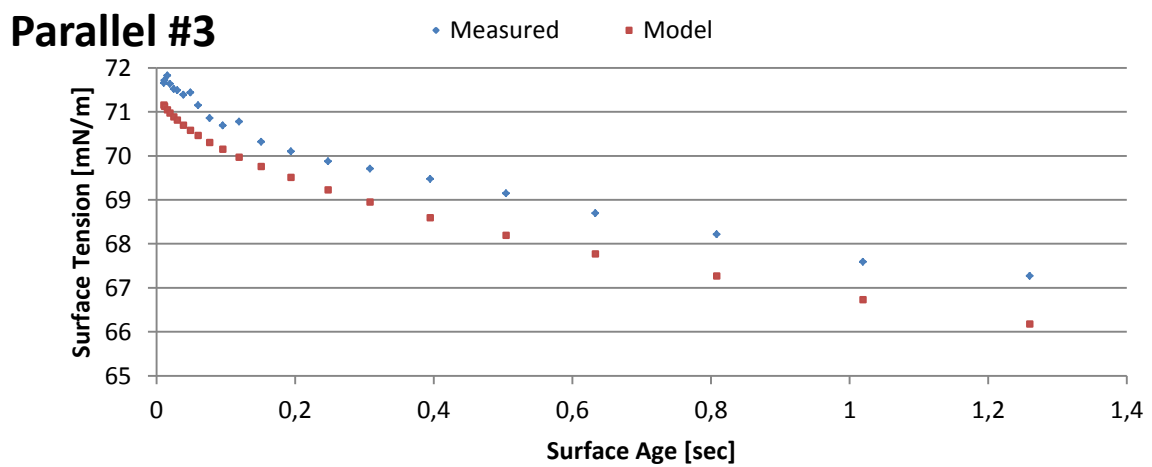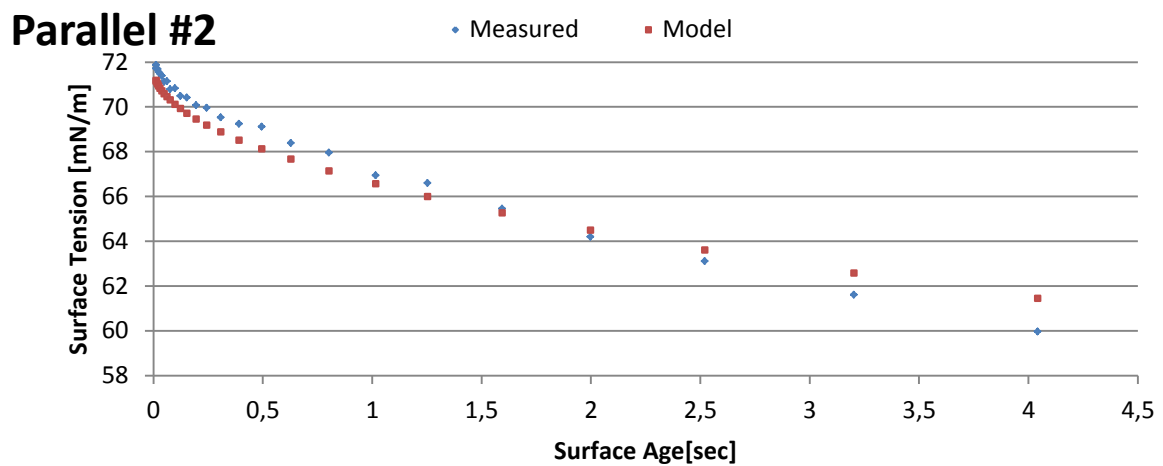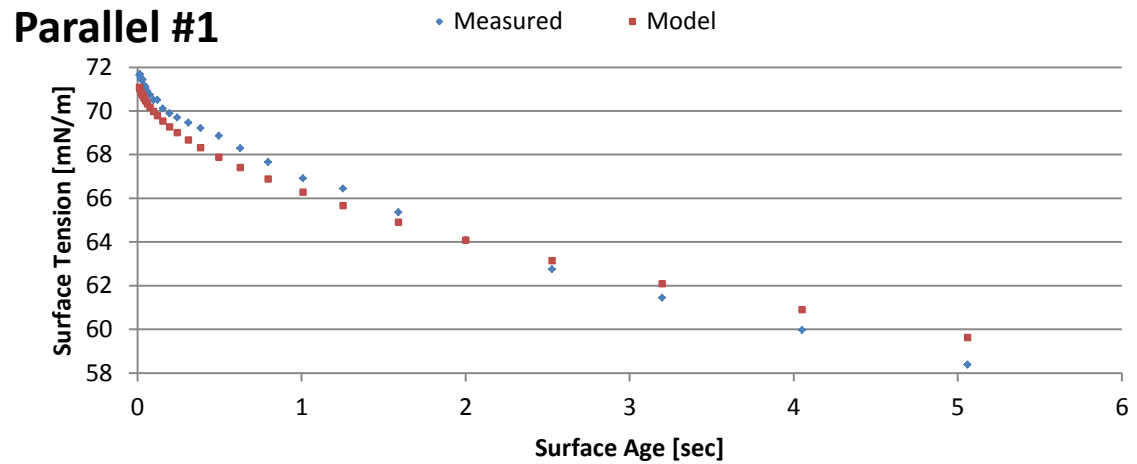
Parallel #3

Figure 73. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 0 and the concentration of SDBS is 0.144 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \; , \qquad I = 20 \; mM \; , \;\; T = 25°C \; , \qquad 0.144mM \; SDBS$$
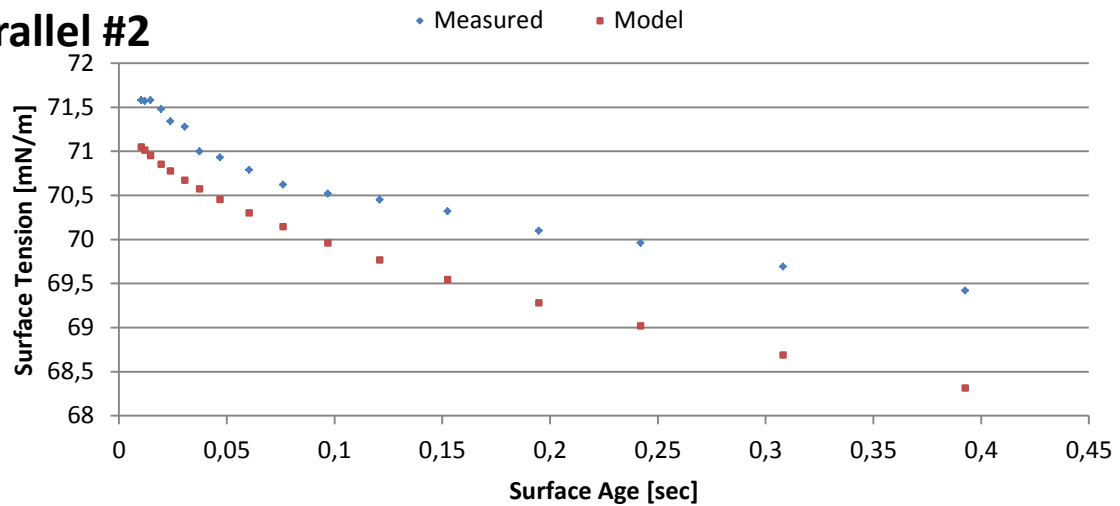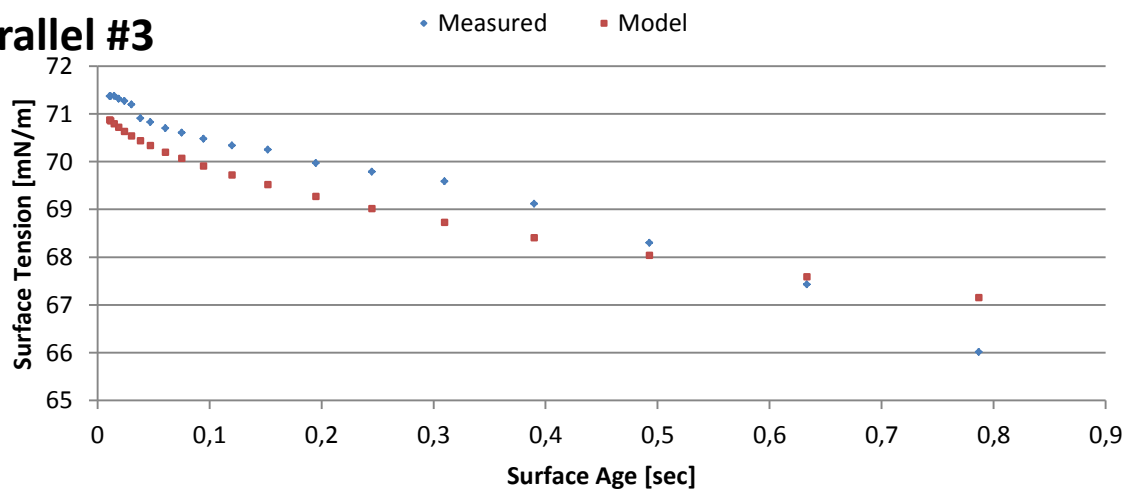
Parallel #1

Parallel #2
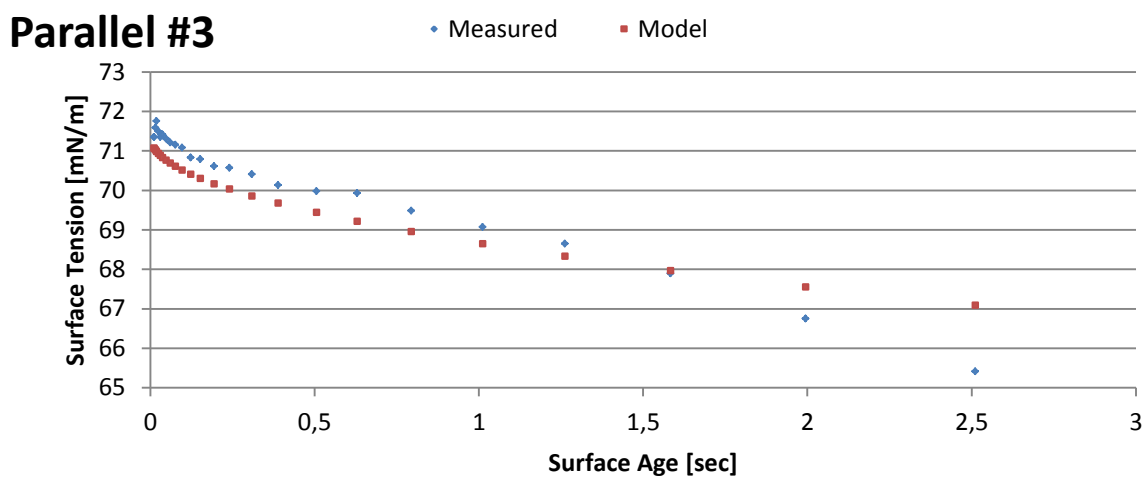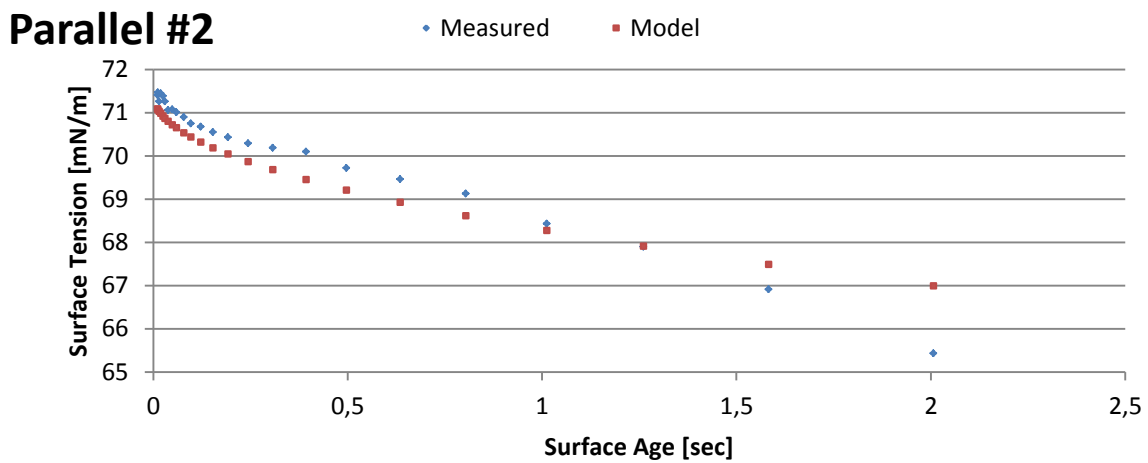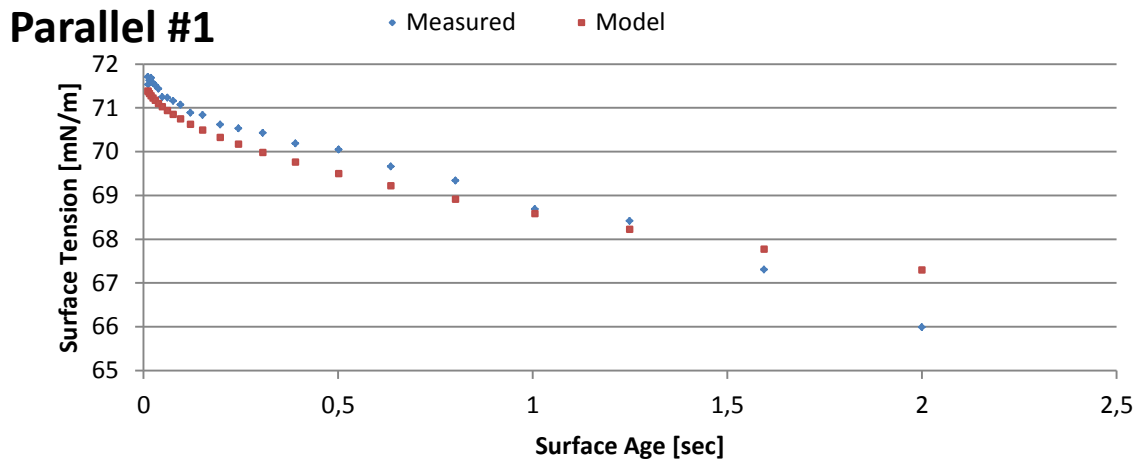
Parallel #3

Figure 74. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/117 and the concentration of SDBS is 0.144 mM. The last dots is where differ is more than 1 mN/m

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \ , \qquad I = 20 \ mM \ , \ T = 25°C \ , \qquad 0.216 mM \ SDBS$$
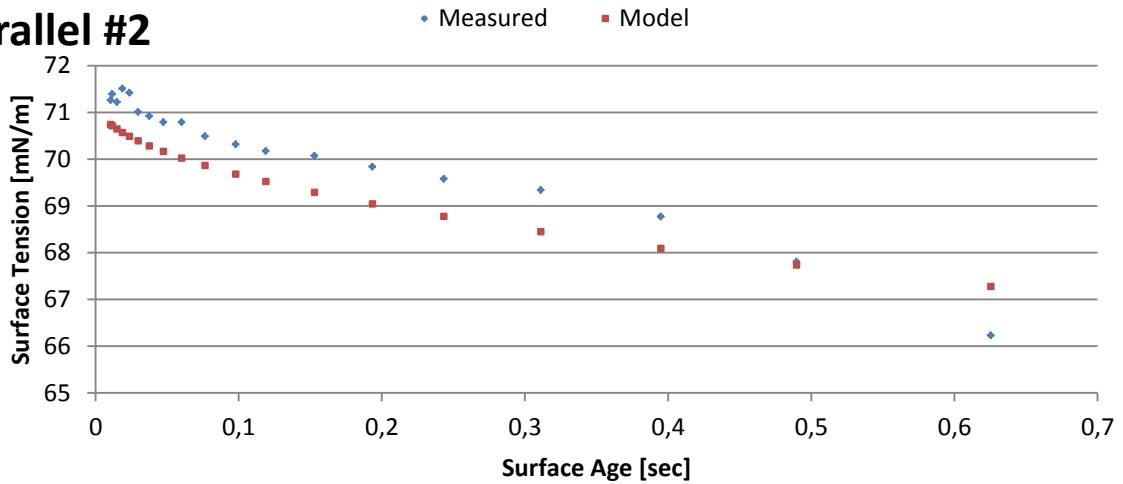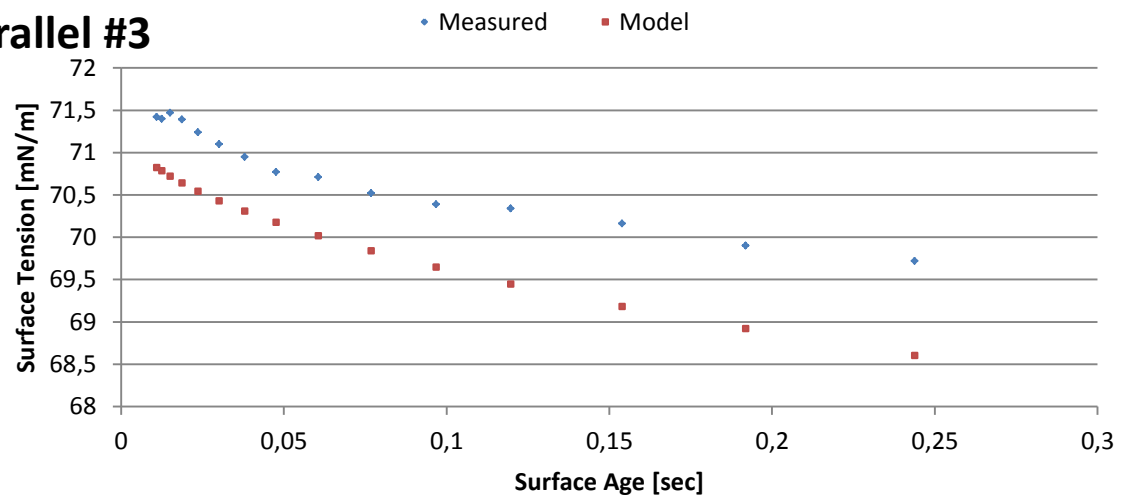
Parallel #1
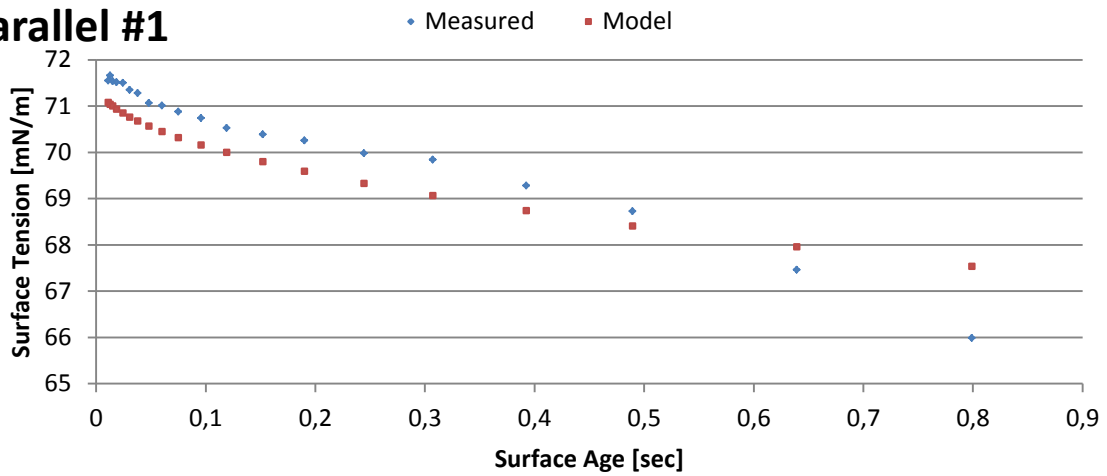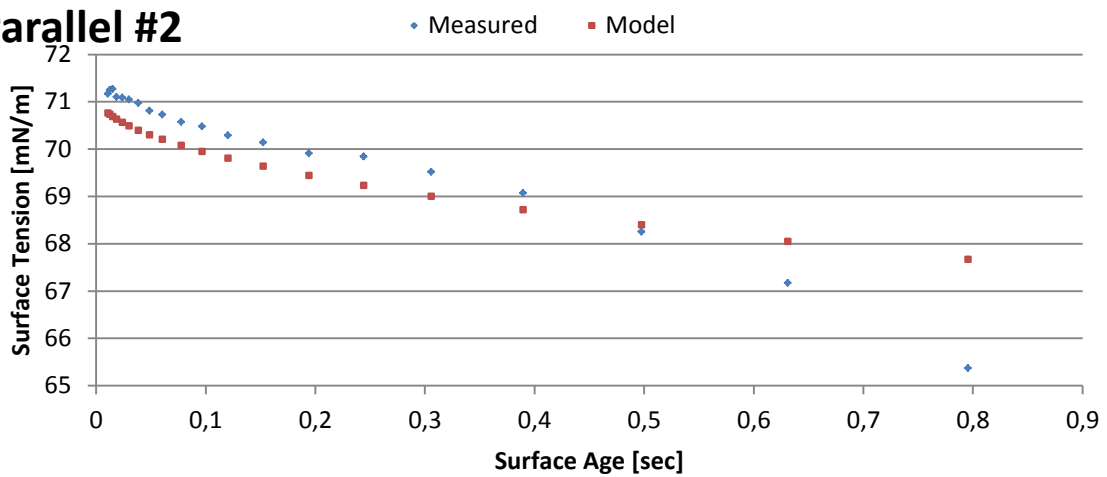
Parallel #2
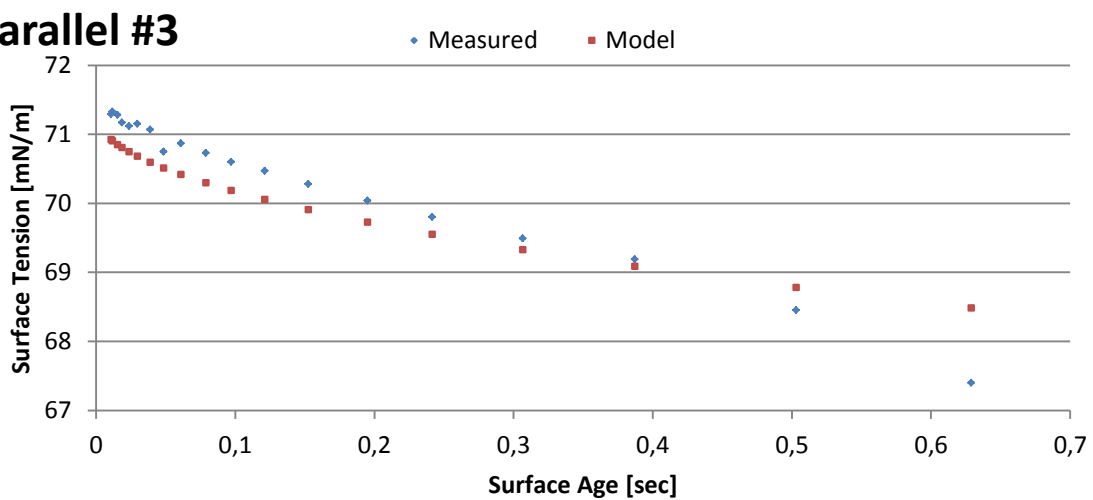
Parallel #3

Figure 75. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/117 and the concentration of SDBS is 0.216 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} , \qquad I = 20 \; mM , \;\; T = 25°C , \qquad 0.288 mM \; SDBS$$
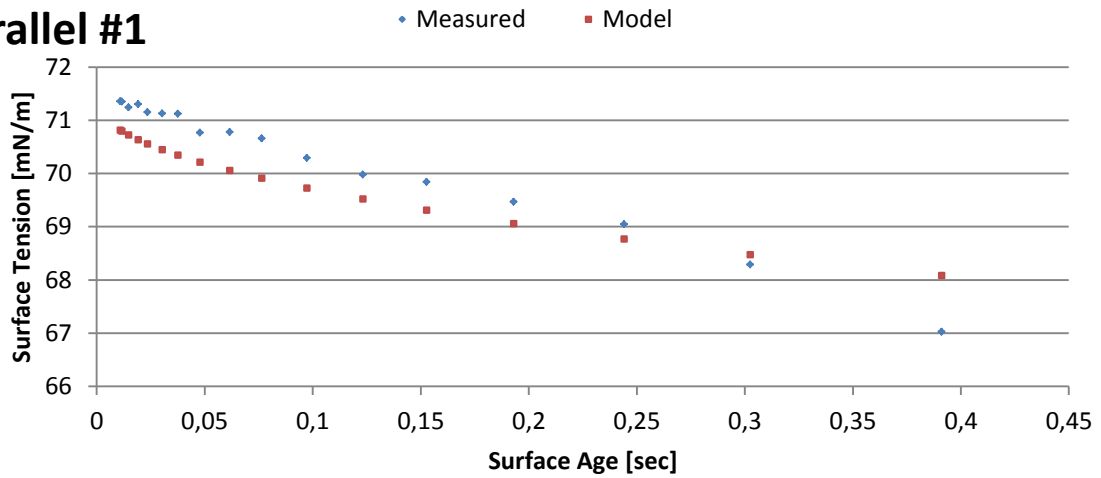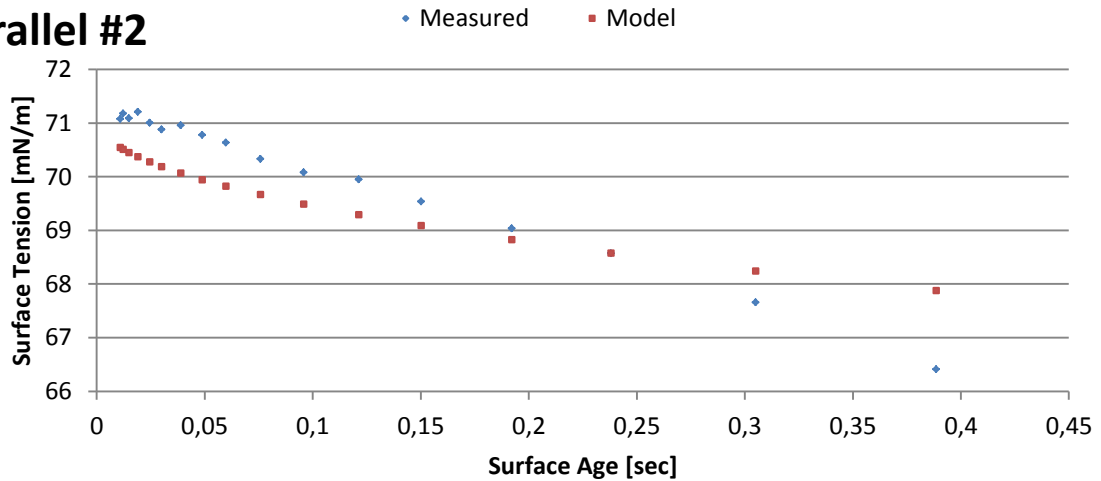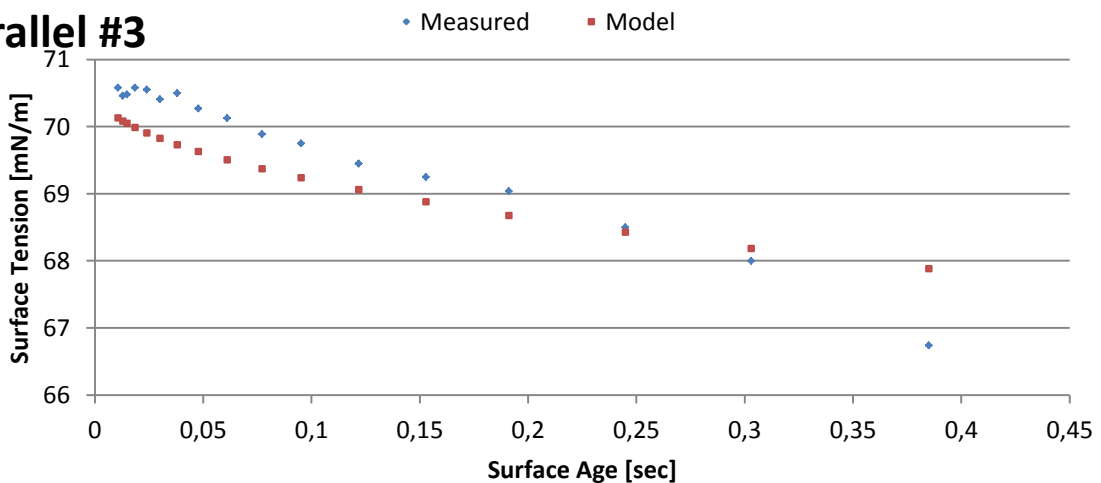
Figure 76. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl₂/NaCl-ratios is 1/117 and the concentration of SDBS is 0.288 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} \; , \qquad I = 20 \; mM \; , \; T = 25°C \; , \qquad 0.317 mM \; SDBS$$
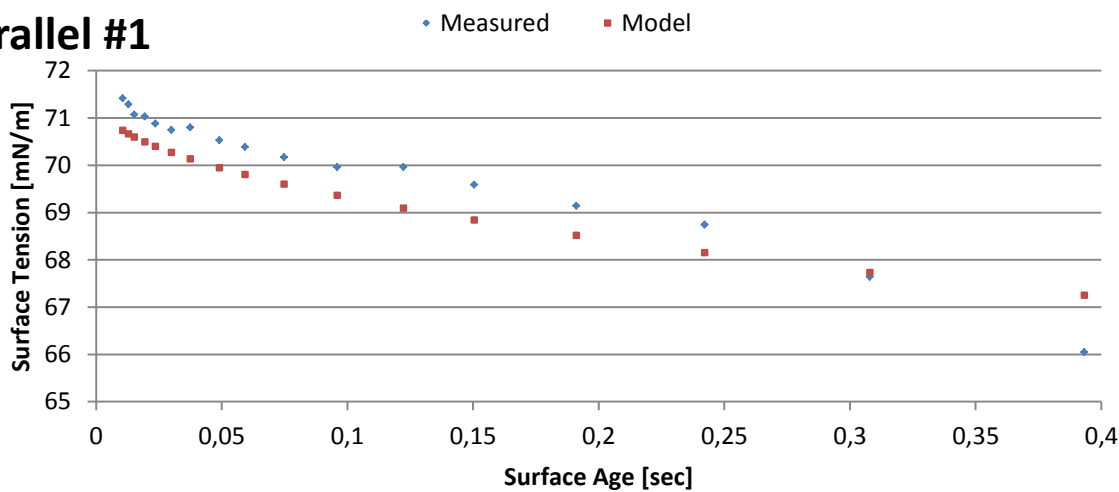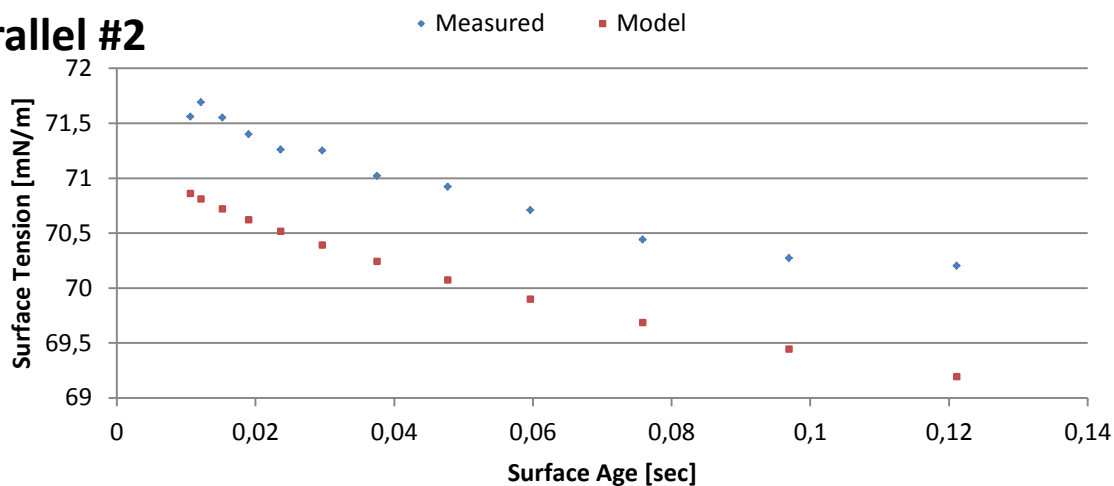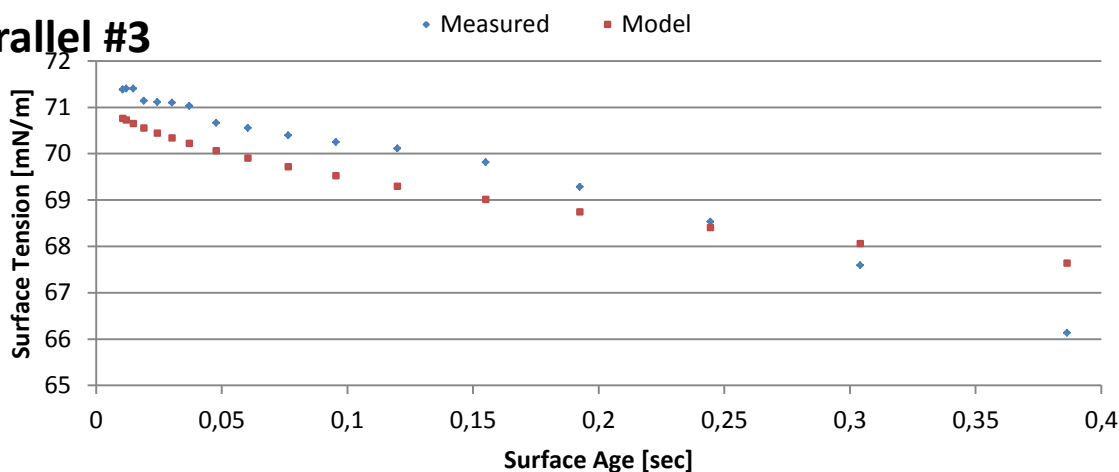
Parallel #1
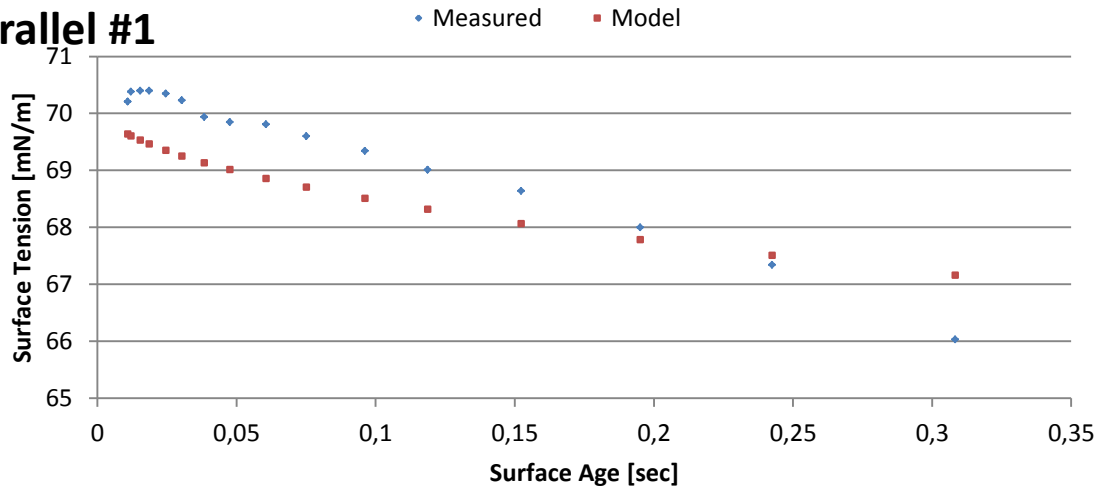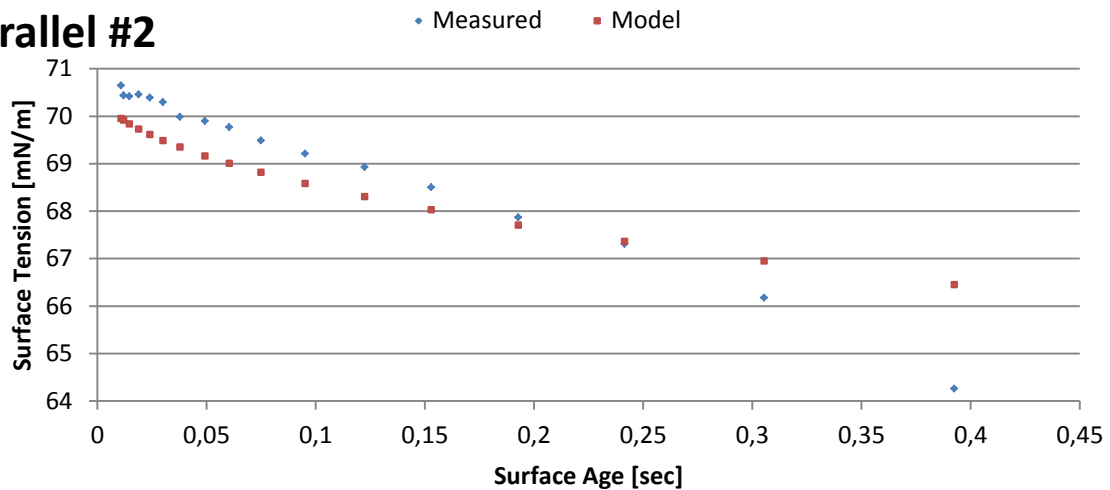
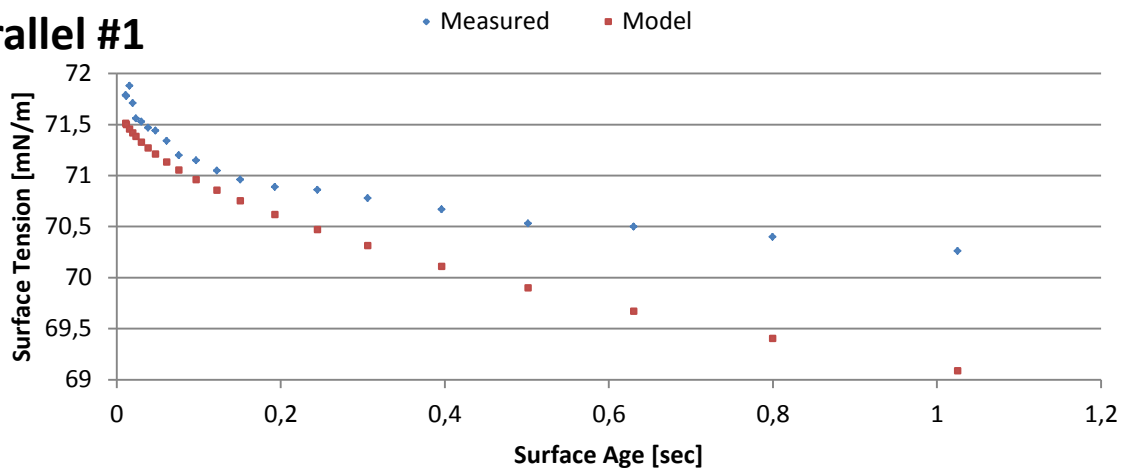

Parallel #2
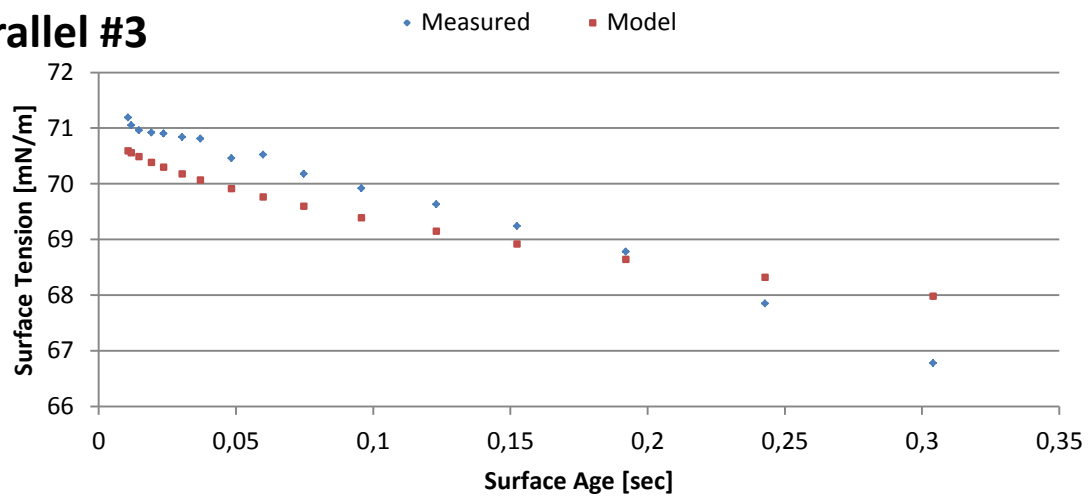
Parallel #3

Figure 77. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl₂/NaCl-ratios is 1/117 and the concentration of SDBS is 0.317 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{117}\ , \qquad I = 20\ mM\ ,\ \ T = 25°C\ , \qquad 0.360 mM\ SDBS$$

Parallel #3
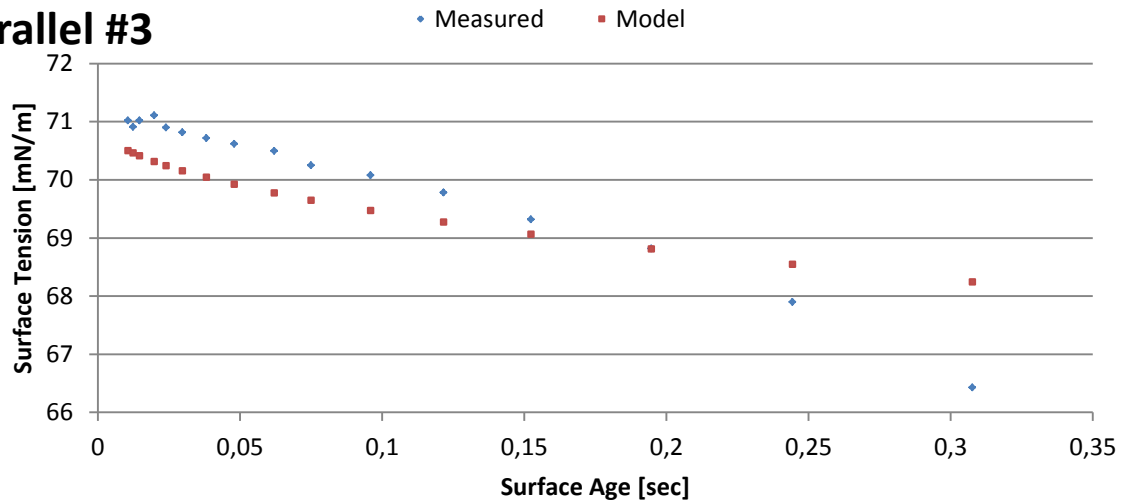
Figure 78. The graph show the measured value (Blue dots) and the model (Red dots) for one parallel, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/117 and the concentration of SDBS is 0.360 mM. The last dots is where differ is more than 1 mN/m. The first two parallels didn't have a good model.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \, , \qquad I = 20 \; mM \, , \; T = 25°C \, , \qquad 0.144 mM \; SDBS$$
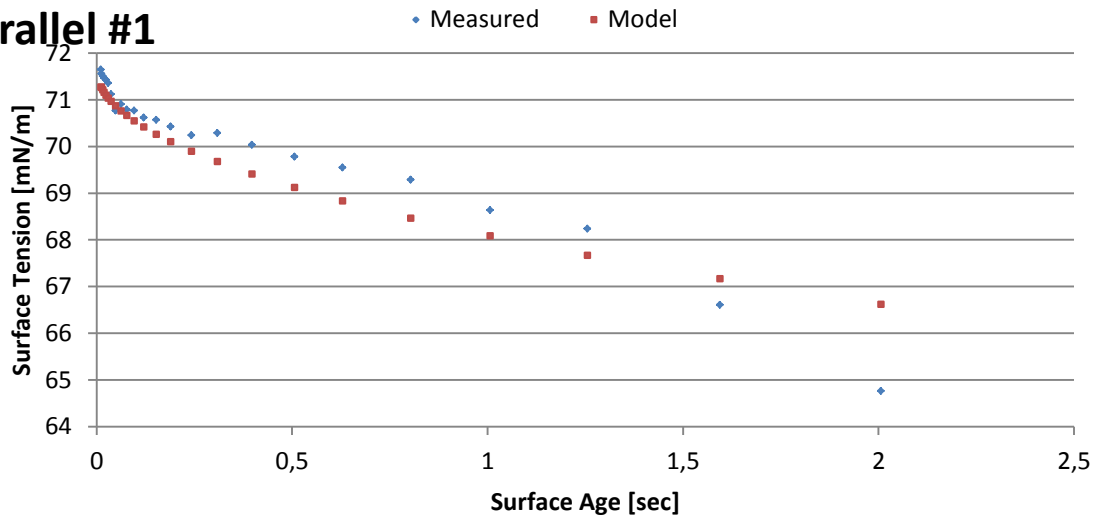
Parallel #1
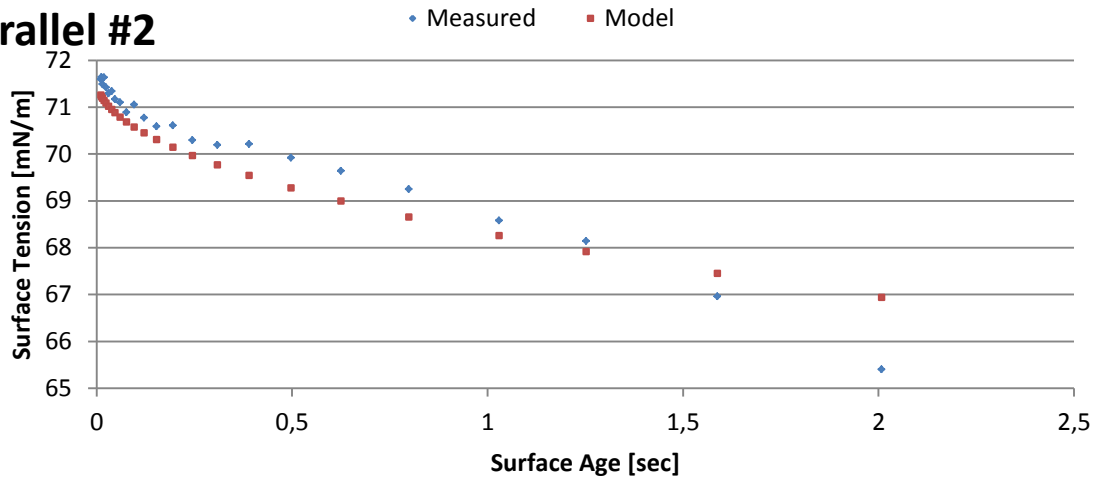
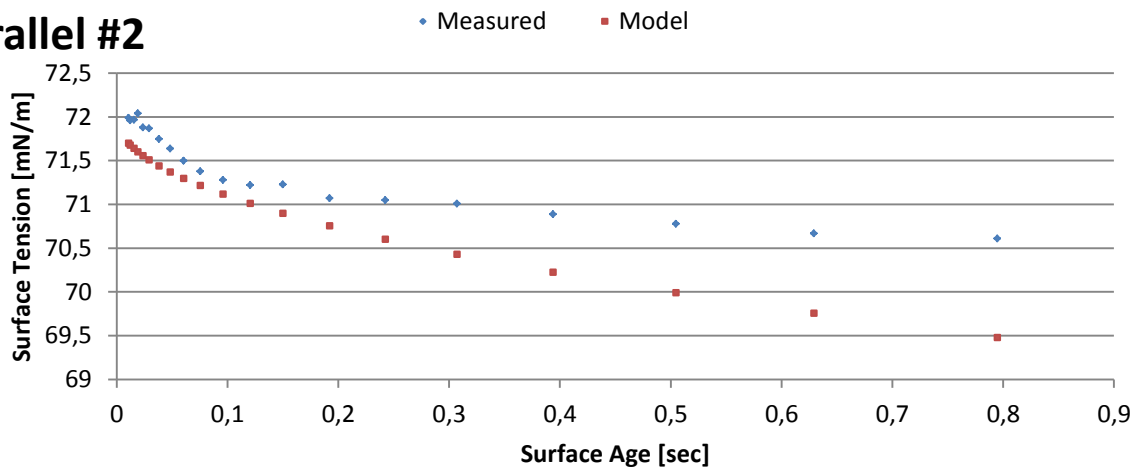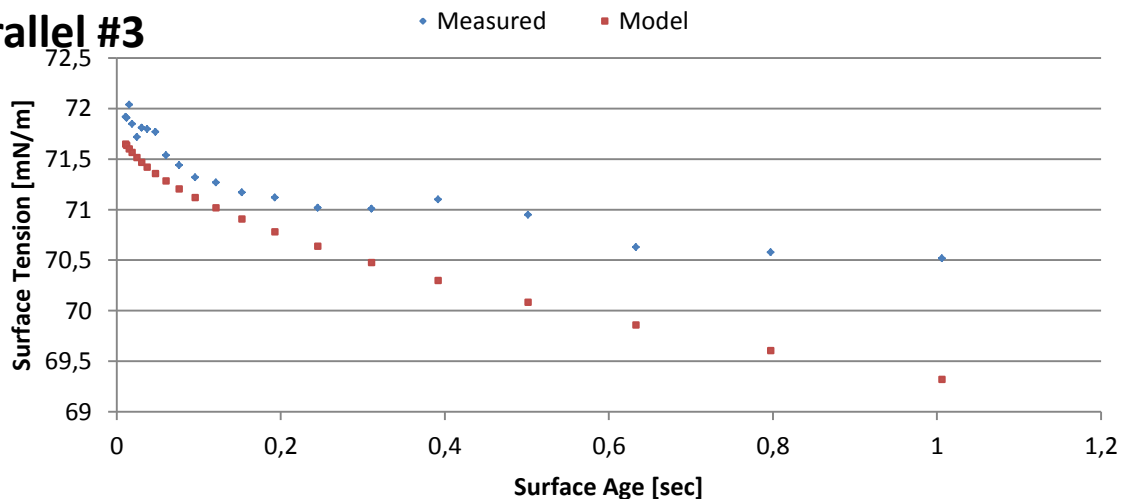## Parallel #2
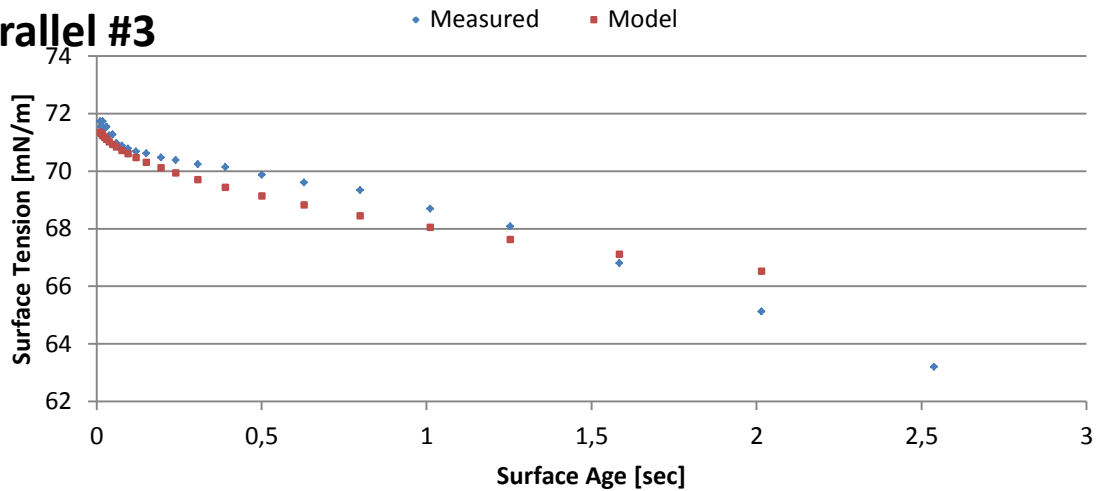
Parallel #3

Figure 79. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/57 and the concentration of SDBS is 0.144 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \ , \qquad I = 20 \ mM \ , \ \ T = 25°C \ , \qquad 0.172 mM \ SDBS$$

Parallel #1
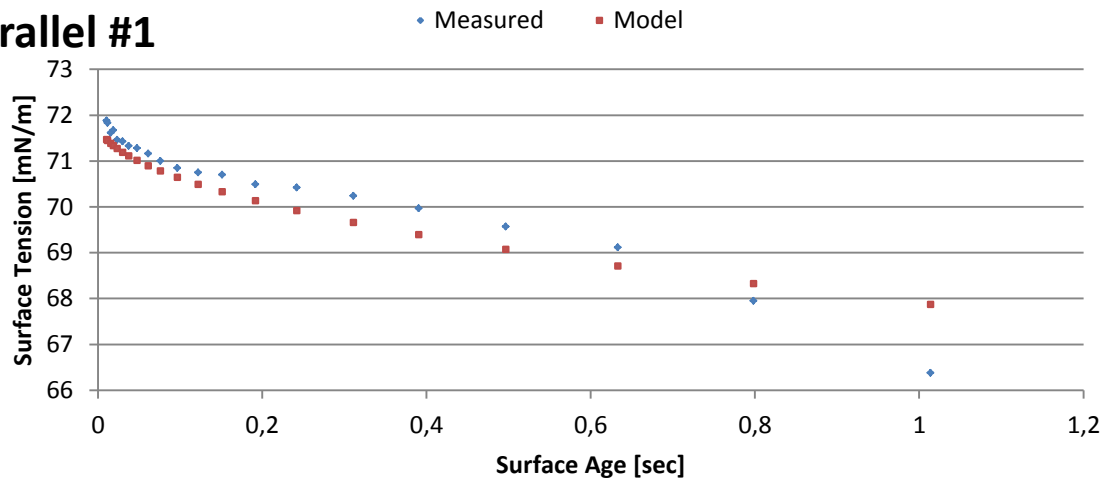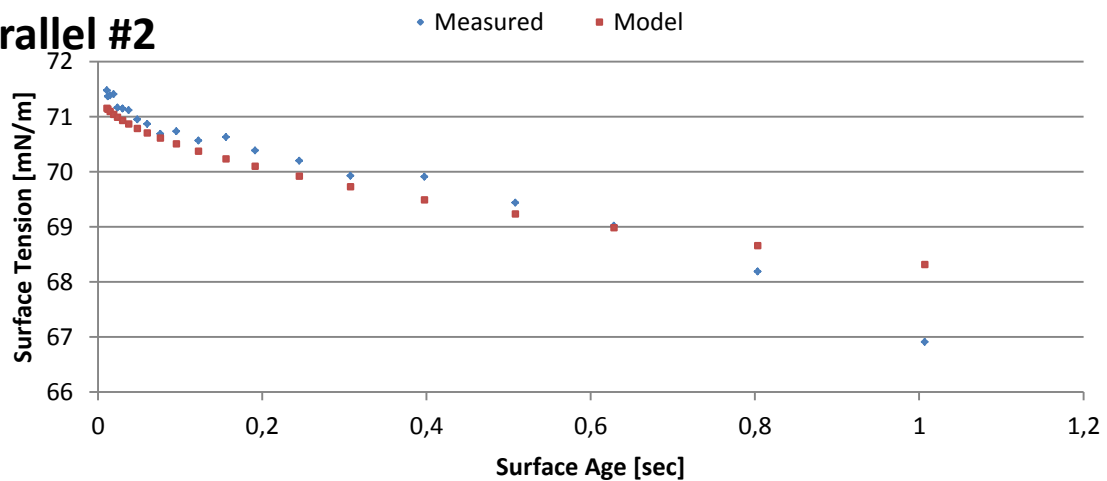
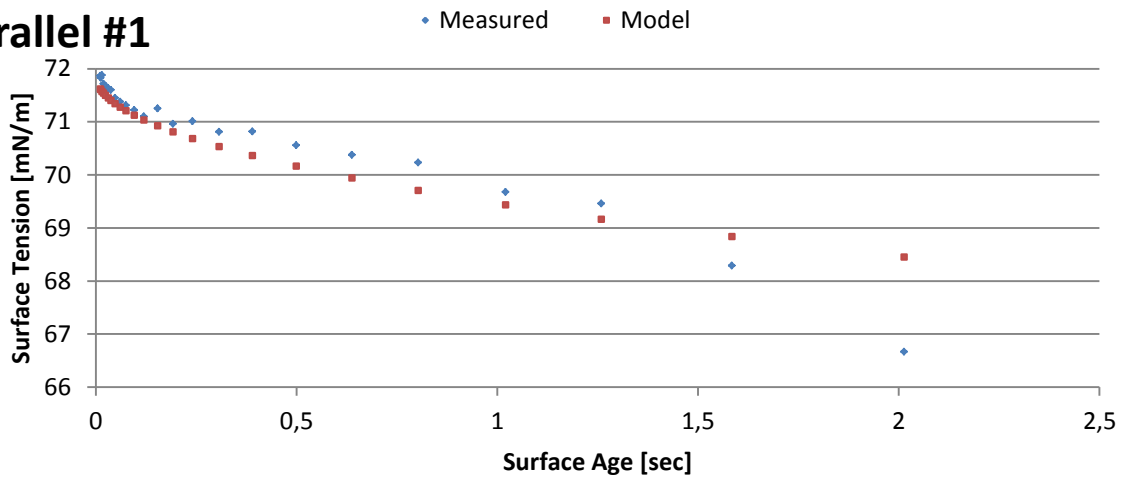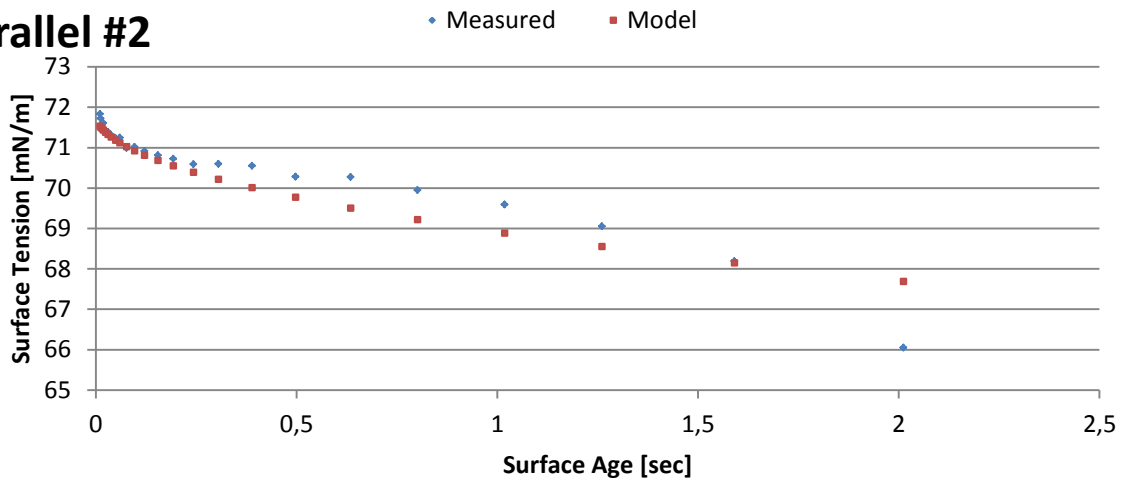

Parallel #2

Parallel #3

Figure 80. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/57 and the concentration of SDBS is 0.172 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \ , \qquad I = 20 \ mM \ , \ \ T = 25°C \ , \qquad 0.201 mM \ SDBS$$

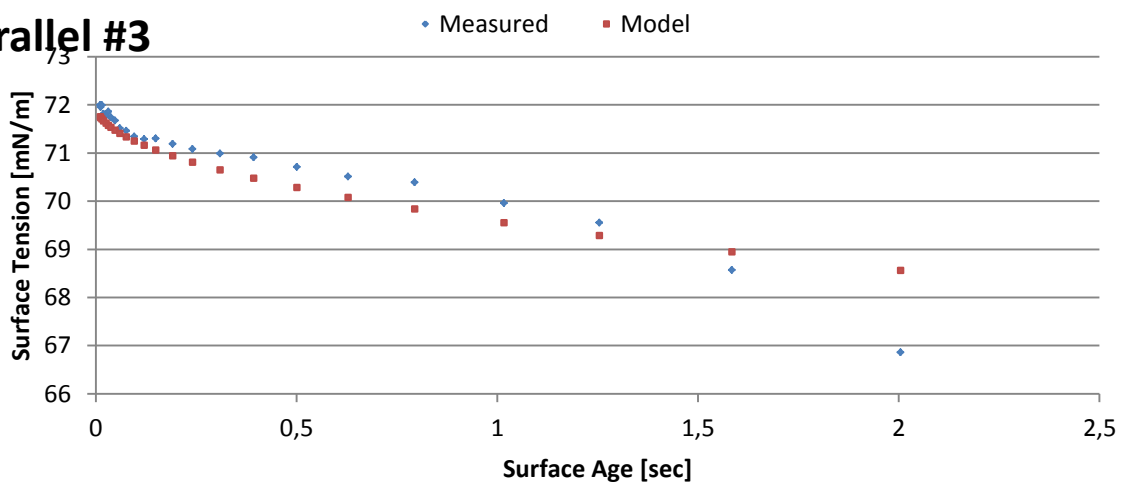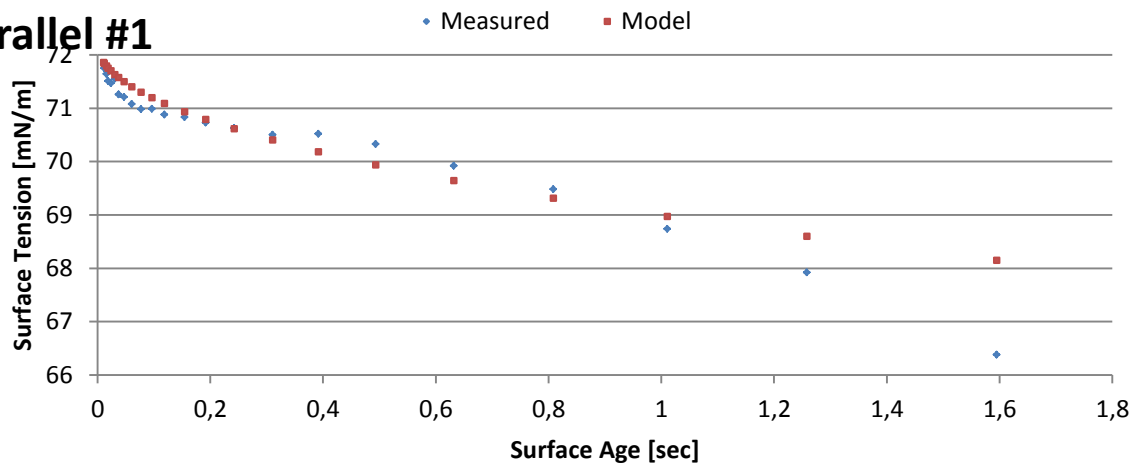## Parallel #1

Parallel #2

Parallel #3

Figure 81. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/57 and the concentration of SDBS is 0.201 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \, , \qquad I = 20 \, mM \, , \; T = 25°C \, , \qquad 0.230 mM \, SDBS$$
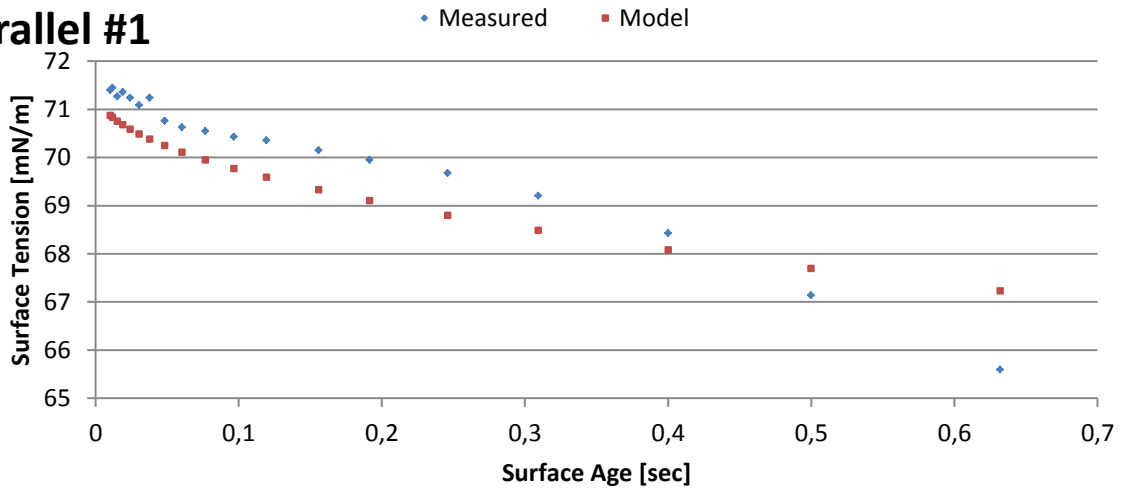
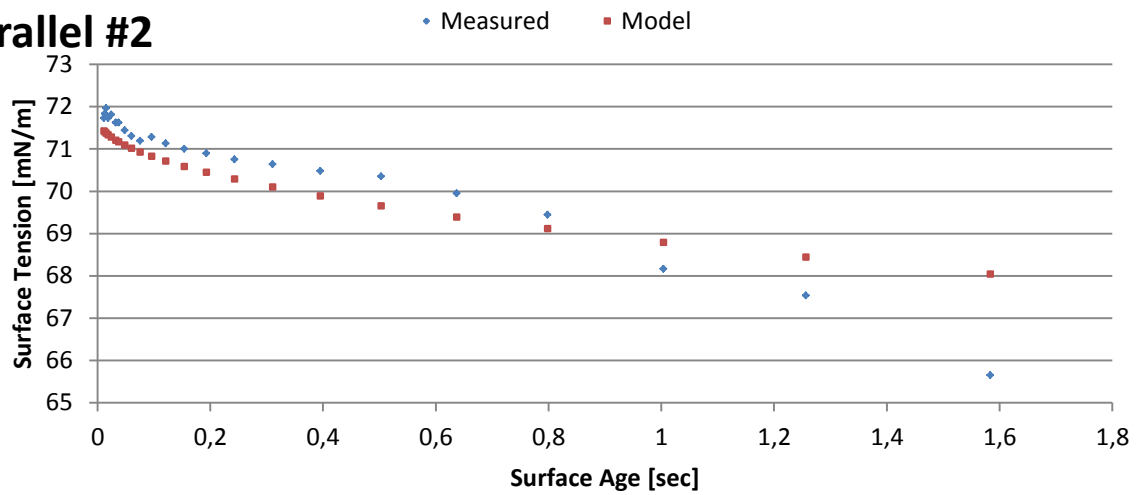## Parallel #1

Parallel #2

Parallel #3

Figure 82. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/57 and the concentration of SDBS is 0.230 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \ , \qquad I = 20 \ mM \ , \quad T = 25°C \ , \qquad 0.287 mM \ SDBS$$

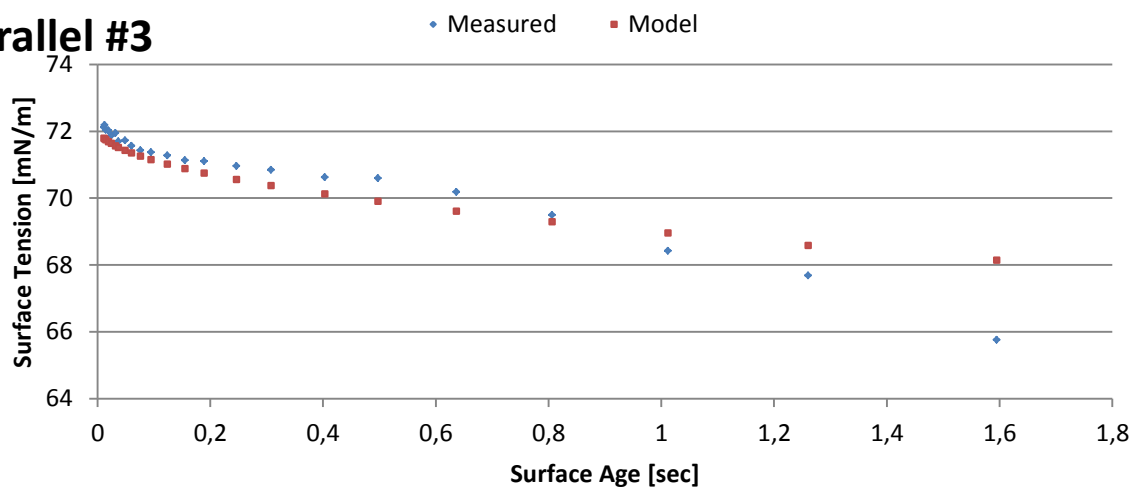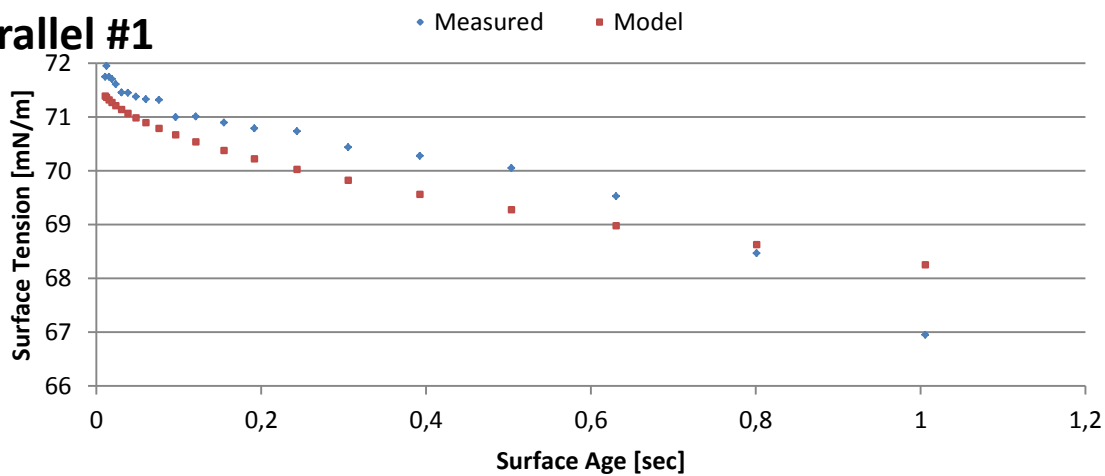## Parallel #1

Parallel #2

Parallel #3

Figure 83. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl₂/NaCl-ratios is 1/57 and the concentration of SDBS is 0.287 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} \; , \qquad I = 20 \; mM \; , \quad T = 25°C \; , \qquad 0.115 mM \; SDBS$$

Parallel #1
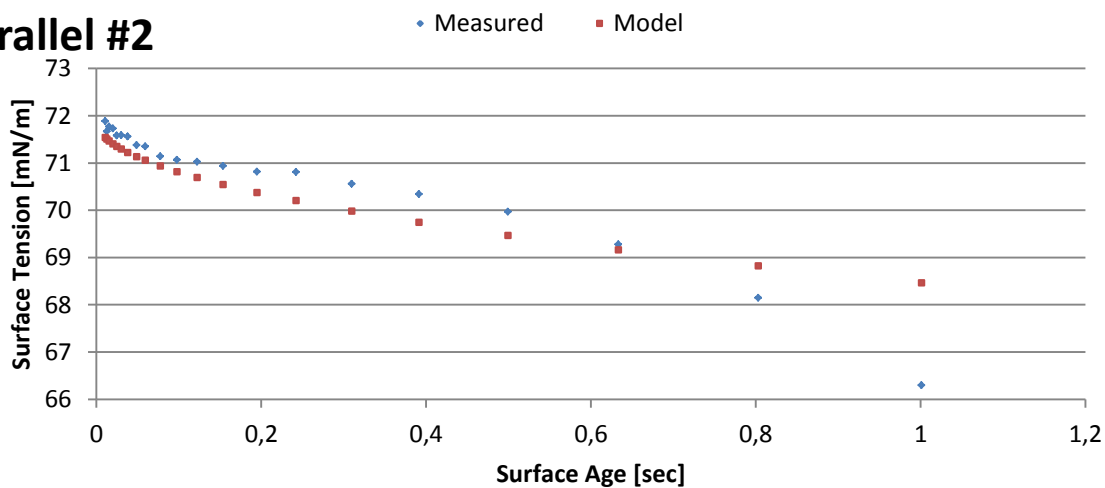

Parallel #2

Parallel #3

Figure 84. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/17 and the concentration of SDBS is 0.115 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} \ , \qquad I = 20 \ mM \ , \quad T = 25°C \ , \qquad 0.144 mM \ SDBS$$

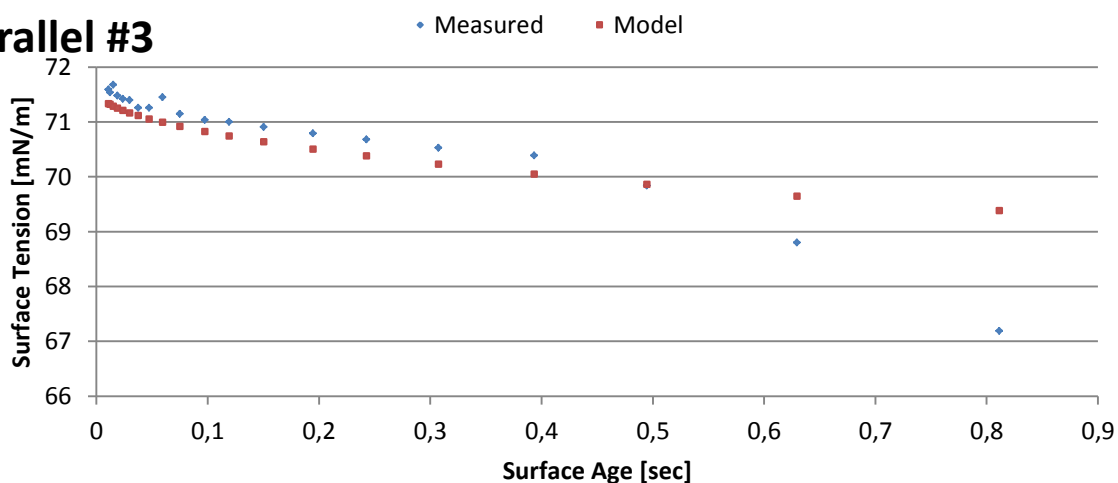## Parallel #1

Parallel #2

Parallel #3

Figure 85. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/17 and the concentration of SDBS is 0.144 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} \ , \qquad I = 20 \ mM \ , \quad T = 25°C \ , \qquad 0.173mM \ SDBS$$

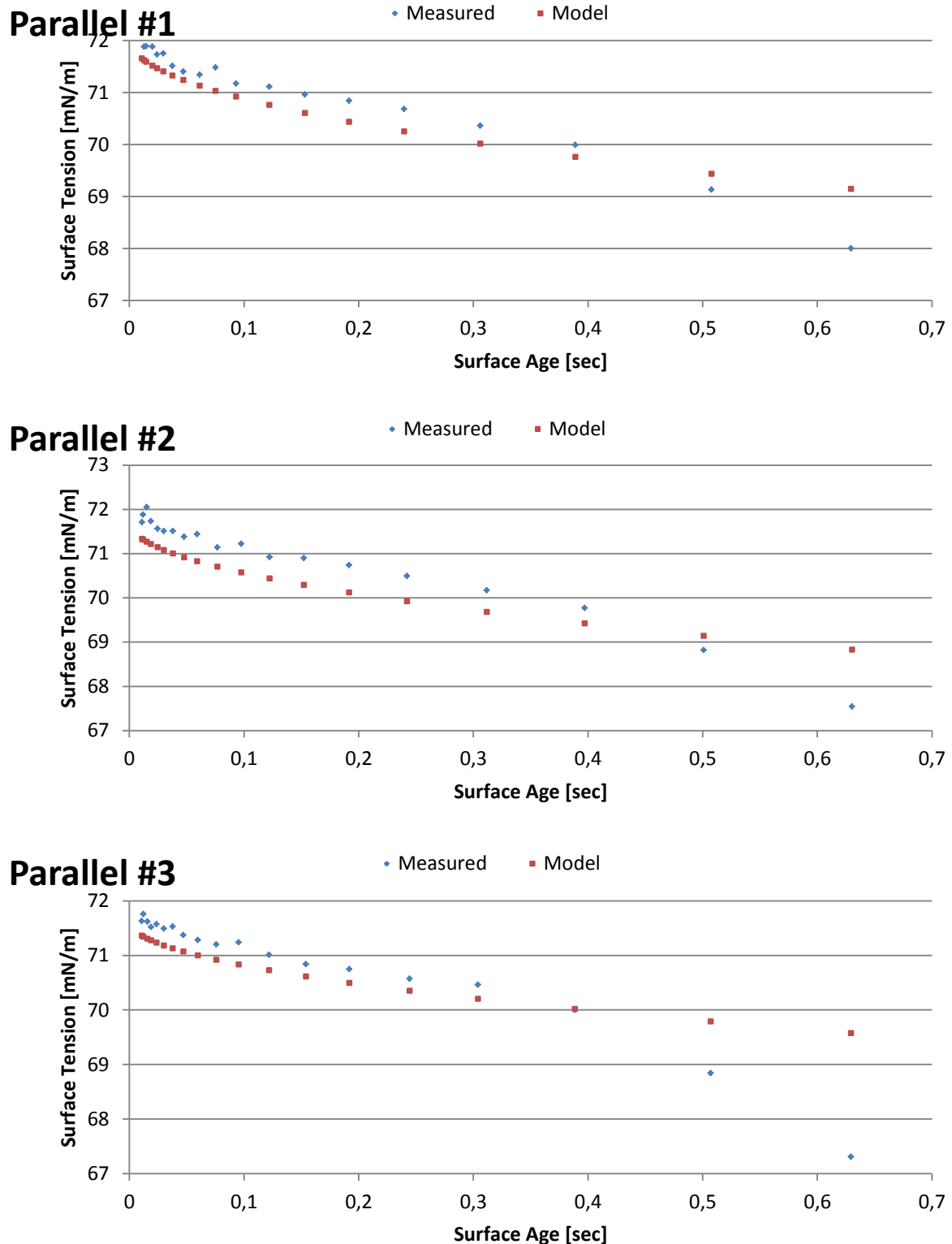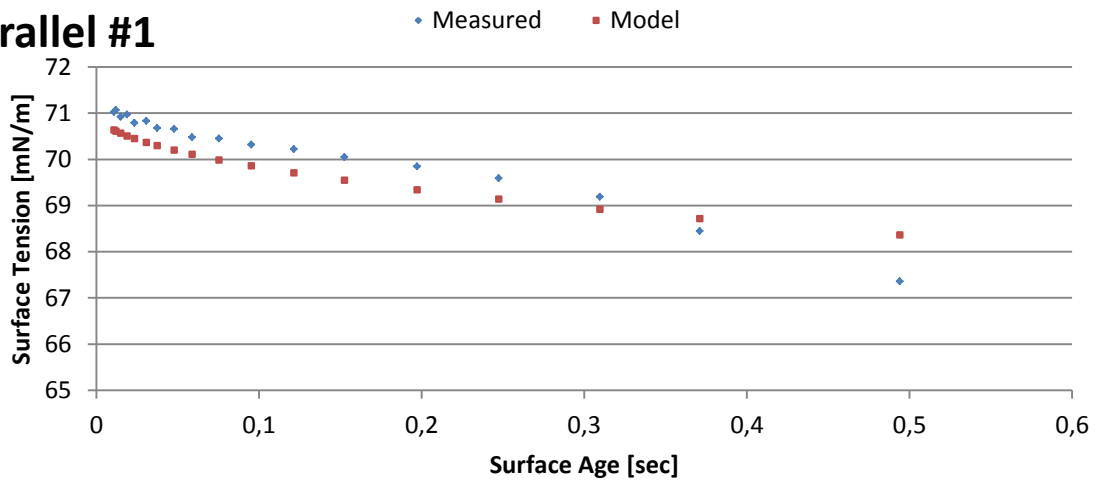## Parallel #1

Parallel #2

Parallel #3

Figure 86. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/17 and the concentration of SDBS is 0.173 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17}\,, \qquad I = 20\ mM\,, \quad T = 25°C\,, \qquad 0.201 mM\ SDBS$$
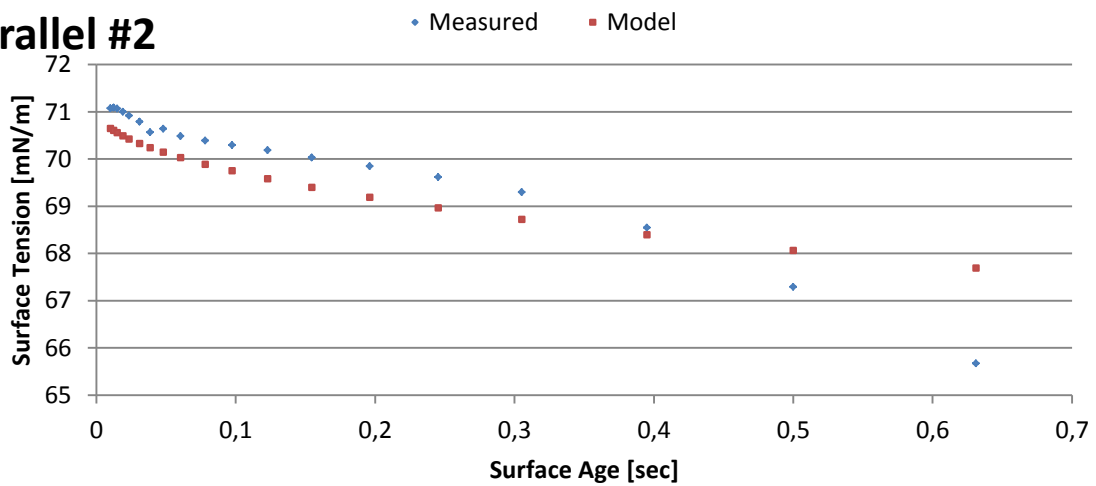

Figure 87. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/17 and the concentration of SDBS is 0.201 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} \ , \qquad I = 20 \ mM \ , \quad T = 25°C \ , \qquad 0.259 mM \ SDBS$$

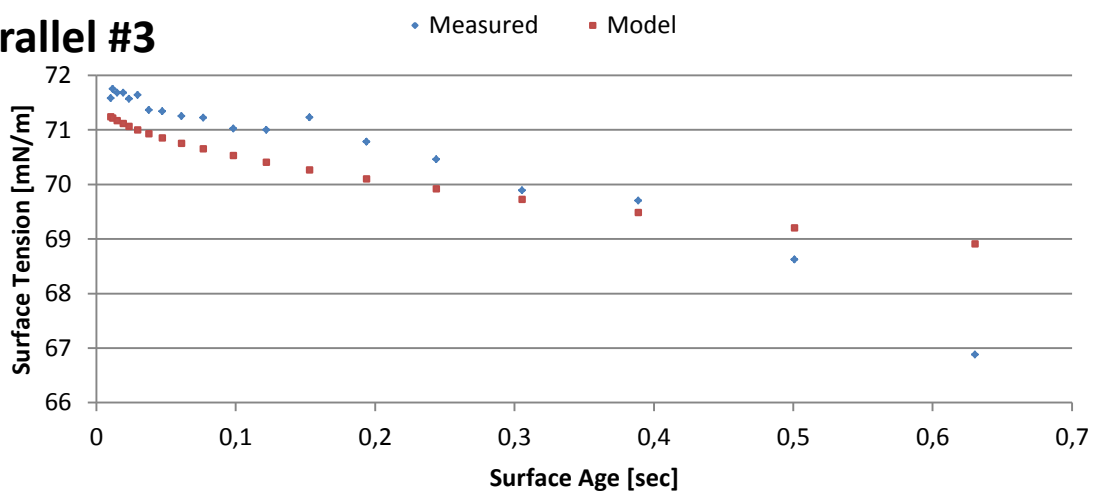## Parallel #1

Parallel #2

Parallel #3

Figure 88. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/17 and the concentration of SDBS is 0.259 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17}\ , \qquad I = 20\ mM\ , \quad T = 25°C\ , \qquad 0.288mM\ SDBS$$

Figure 89. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl₂/NaCl-ratios is 1/17 and the concentration of SDBS is 0.288 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} \; , \qquad I = 20 \; mM \; , \;\; T = 25°C \; , \qquad 0.432mM \; SDBS$$
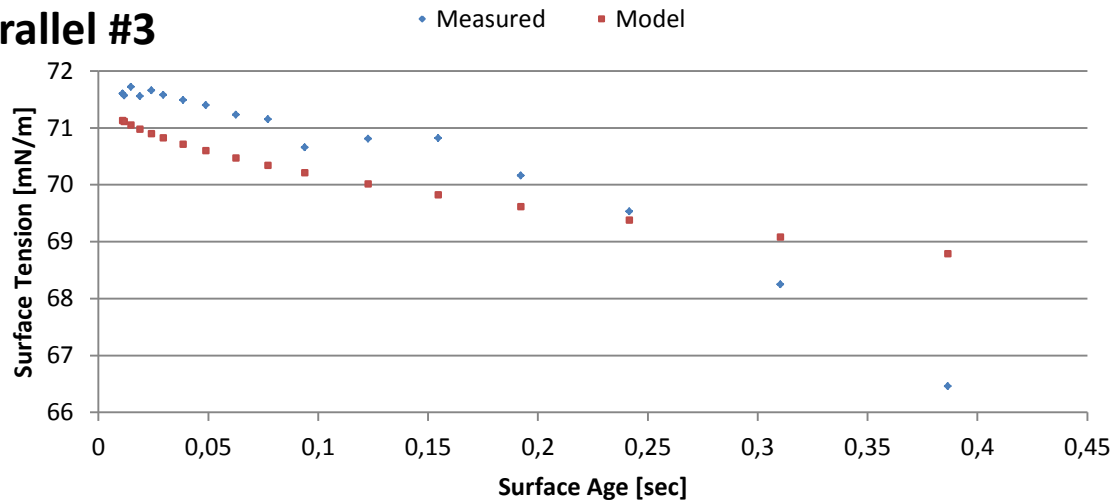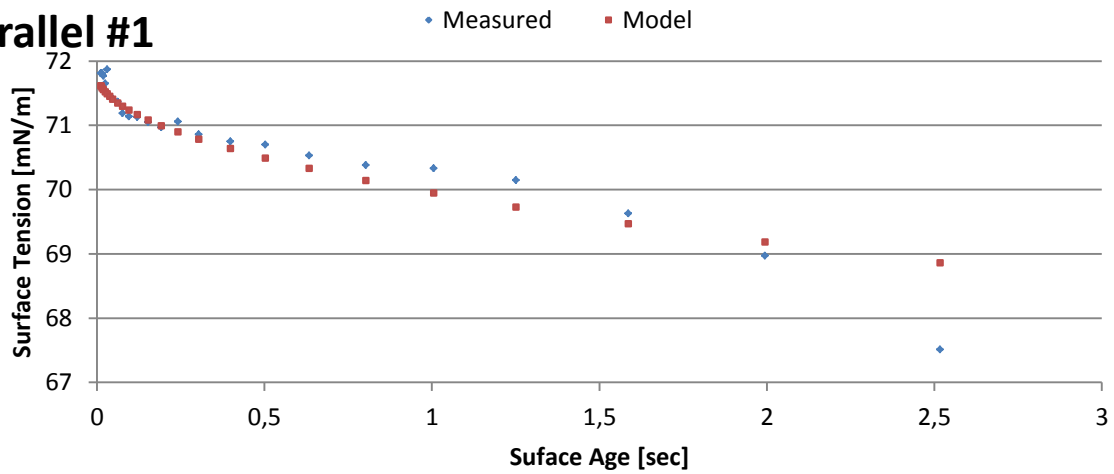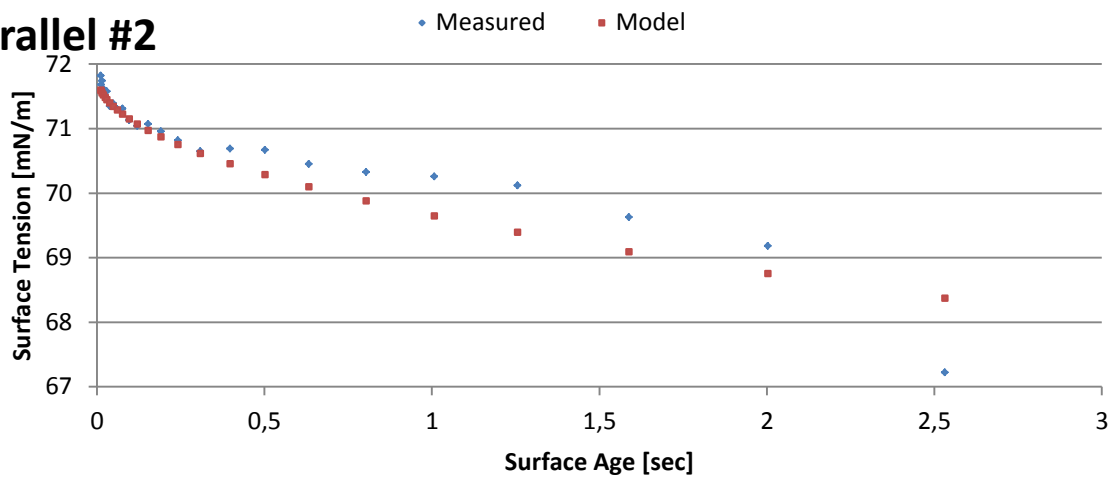
Parallel #3

Figure 90. The graph show the measured value (Blue dots) and the model (Red dots) for one parallel, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/17 and the concentration of SDBS is 0.288 mM. The last dots is where differ is more than 1 mN/m. The first two parallels didn't have a good model.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \; , \qquad I = 20 \; mM \; , \quad T = 25°C \; , \qquad 0.115mM \; SDBS$$
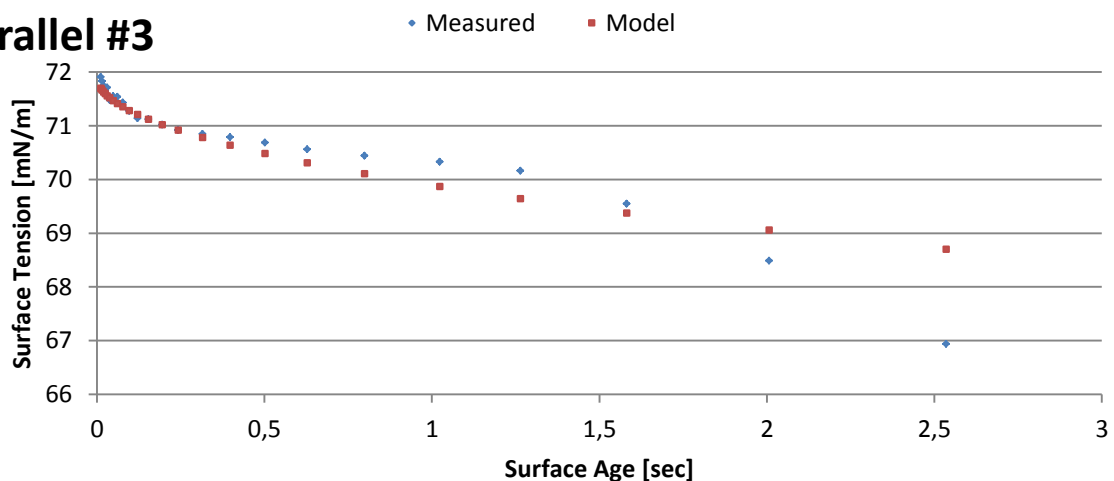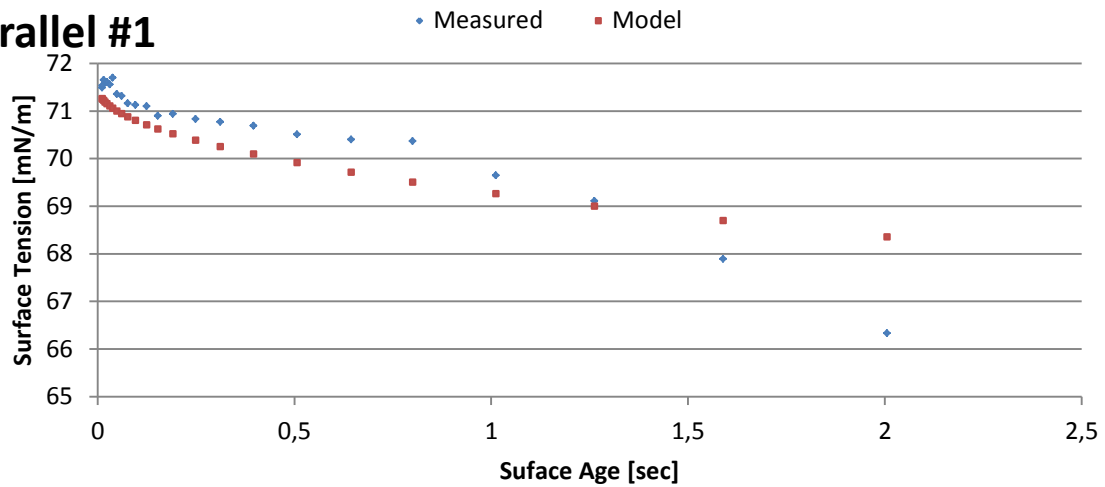
Parallel #1

Parallel #2

Parallel #3

Figure 91. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/12 and the concentration of SDBS is 0.115 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \ , \qquad I = 20 \ mM \ , \ \ T = 25°C \ , \qquad 0.144 mM \ SDBS$$

Parallel #1
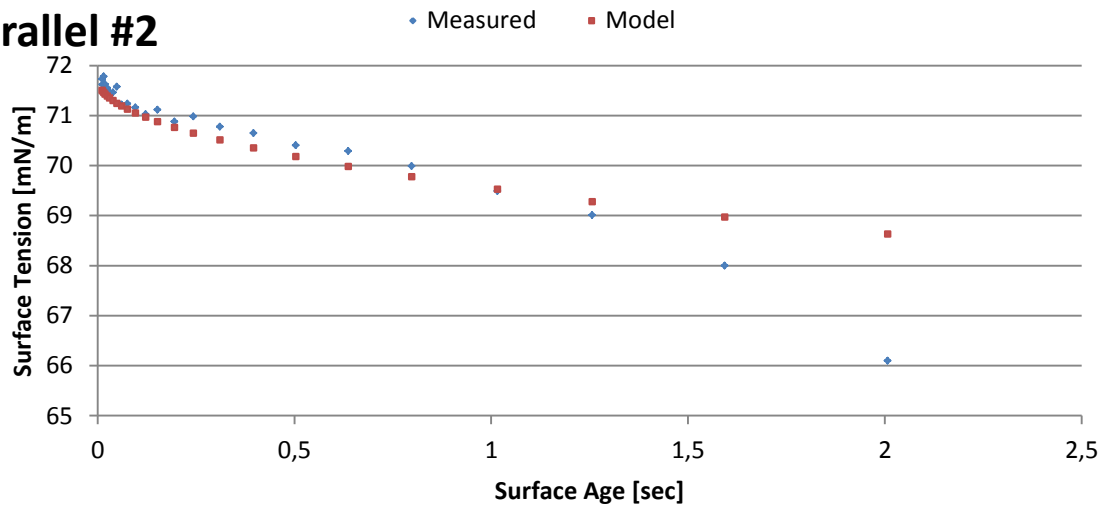

Parallel #2

Parallel #3

Figure 92. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/12 and the concentration of SDBS is 0.144 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12}\ , \qquad I = 20\ mM\ ,\ \ T = 25°C\ , \qquad 0.173 mM\ SDBS$$
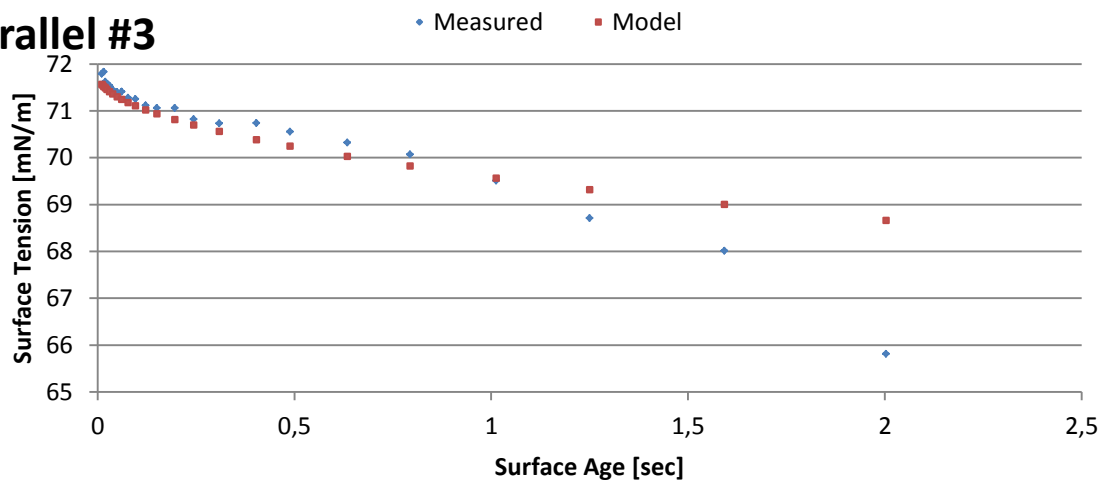
Parallel #1
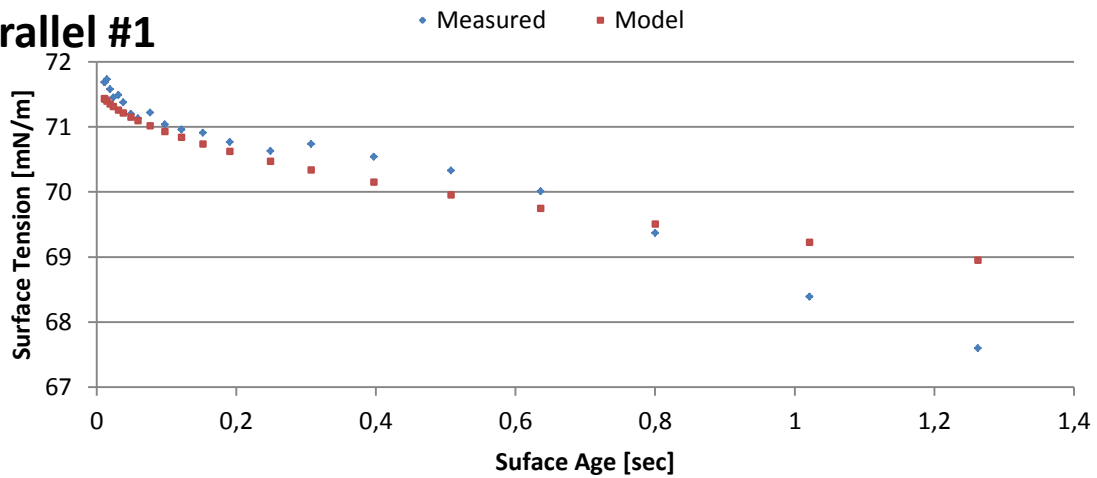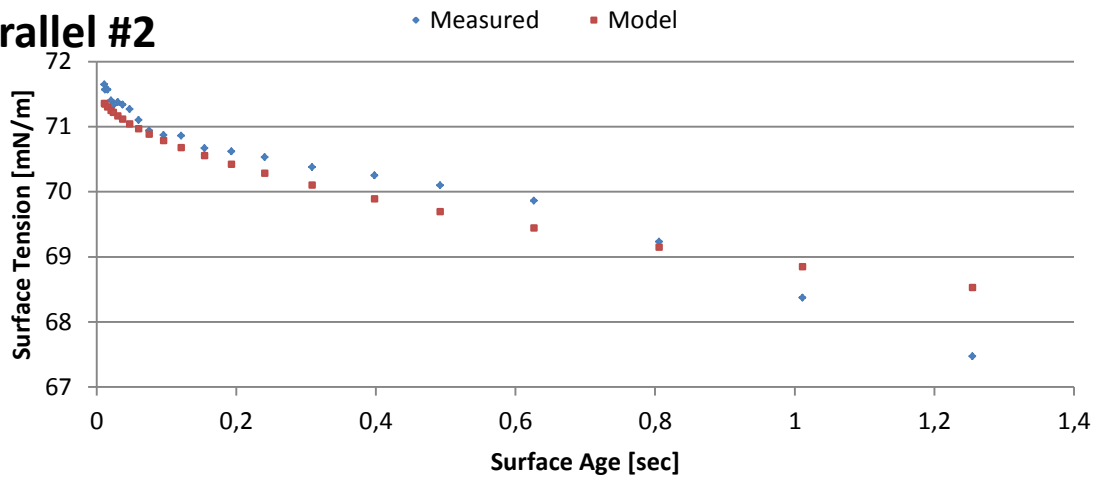

Parallel #2

Parallel #3

Figure 93. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl₂/NaCl-ratios is 1/12 and the concentration of SDBS is 0.173 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \ , \qquad I = 20 \ mM \ , \quad T = 25°C \ , \qquad 0.201 mM \ SDBS$$

Figure 94. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/12 and the concentration of SDBS is 0.201 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12}\ , \qquad I = 20\ mM\ ,\ \ T = 25°C\ , \qquad 0.230 mM\ SDBS$$

Parallel #1

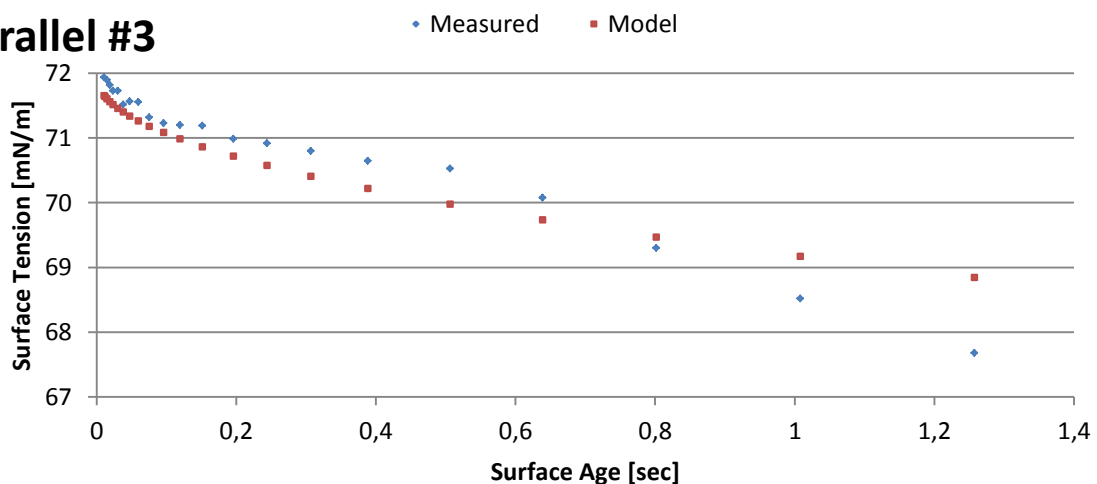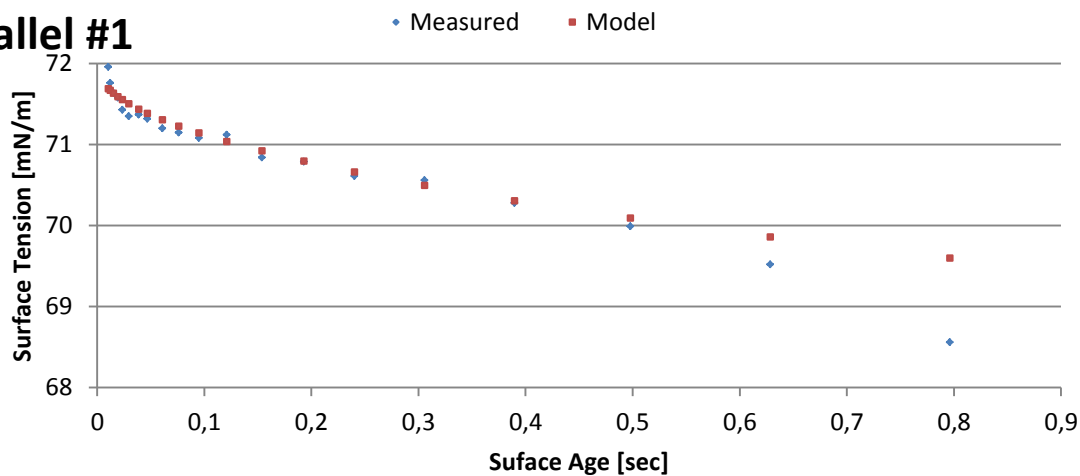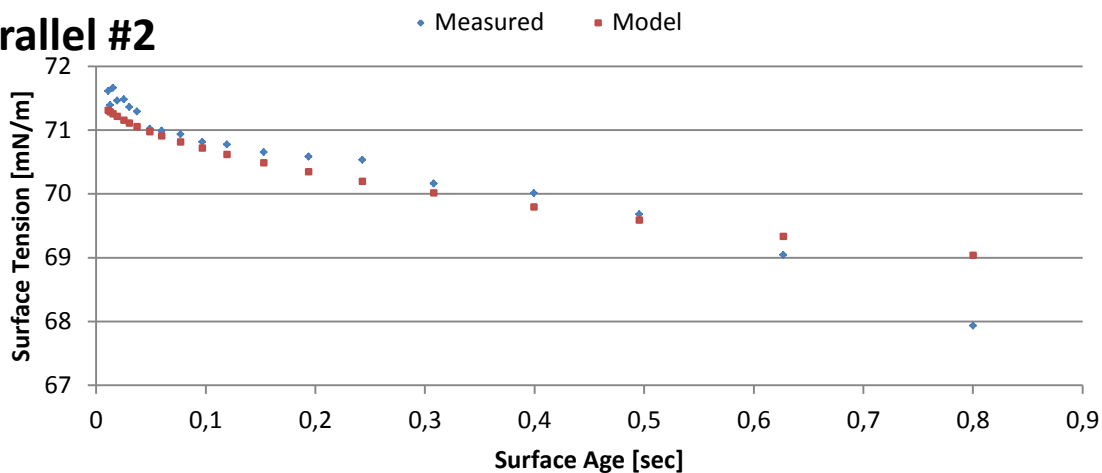# Parallel #2

Parallel #3

Figure 95. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/12 and the concentration of SDBS is 0.230 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \, , \qquad I = 20 \; mM \, , \;\; T = 25°C \, , \qquad 0.288 mM \; SDBS$$
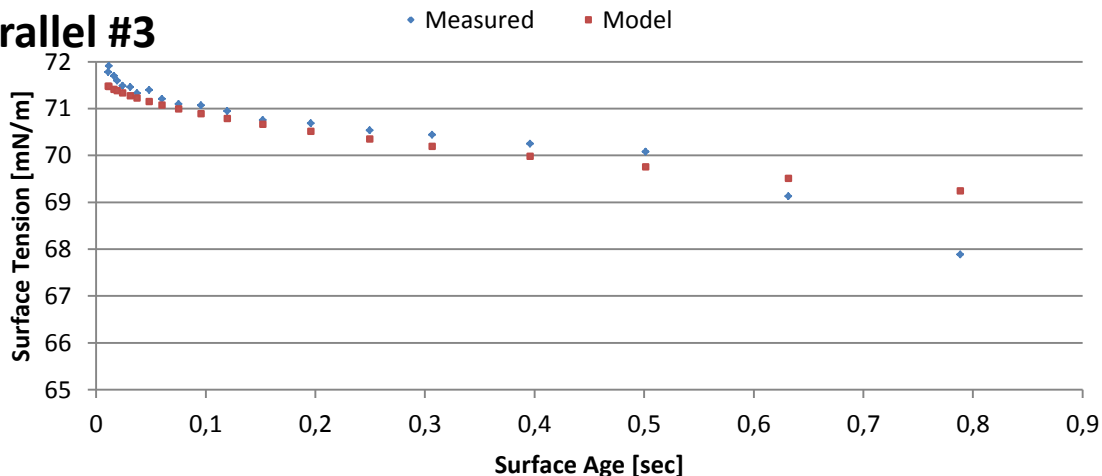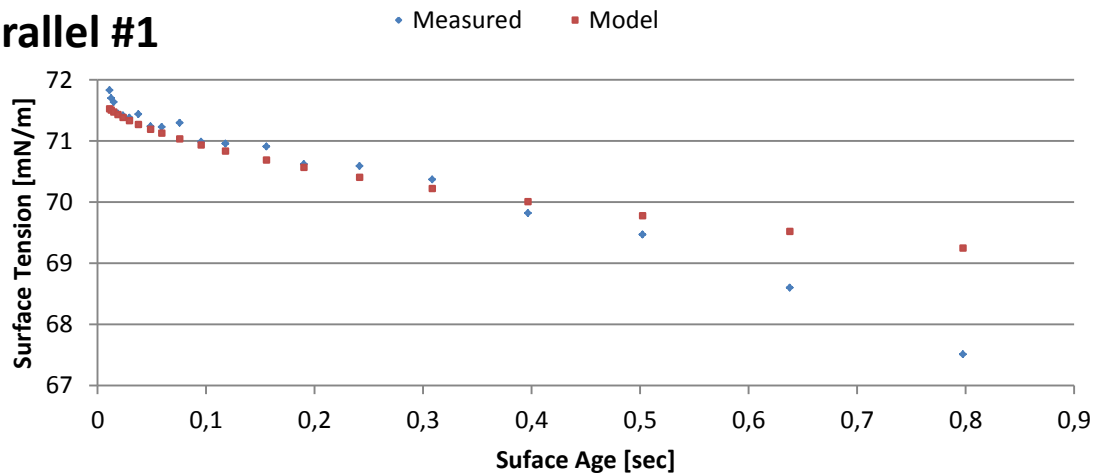
Parallel #1

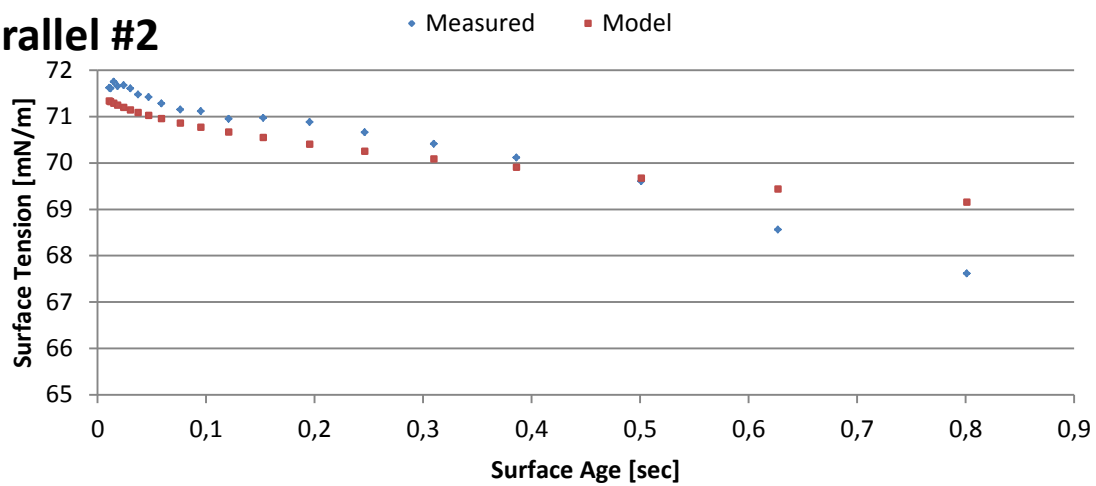## Parallel #2

Parallel #3

Figure 96. The three graphs show the measured value (Blue dots) and the model (Red dots) for the three parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/12 and the concentration of SDBS is 0.288 mM. The last dots is where differ is more than 1 mN/m.

$$\frac{CaCl_2}{NaCl} = \frac{1}{12} \ , \qquad I = 20 \ mM \ , \ T = 25°C \ , \qquad 0.431 mM \ SDBS$$

Parallel #2

Parallel #3

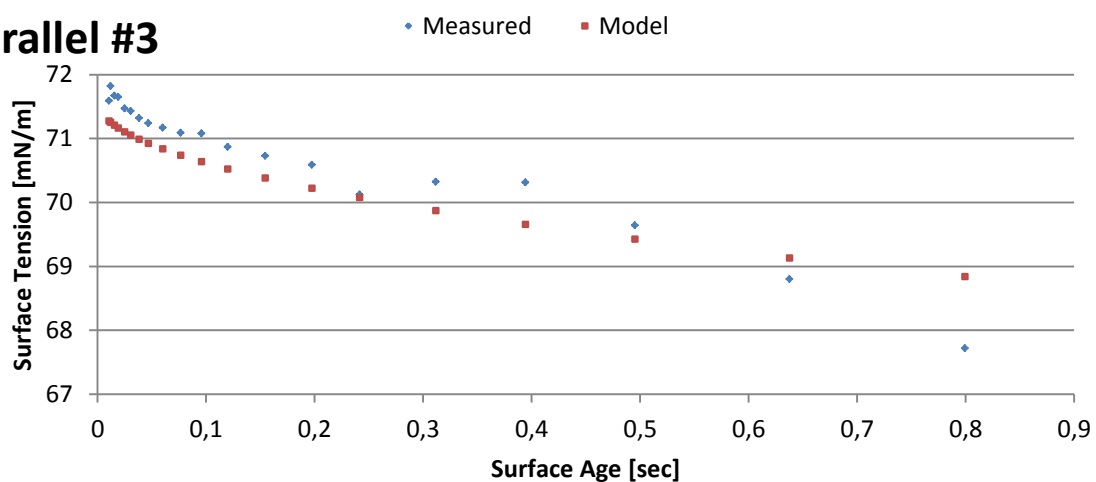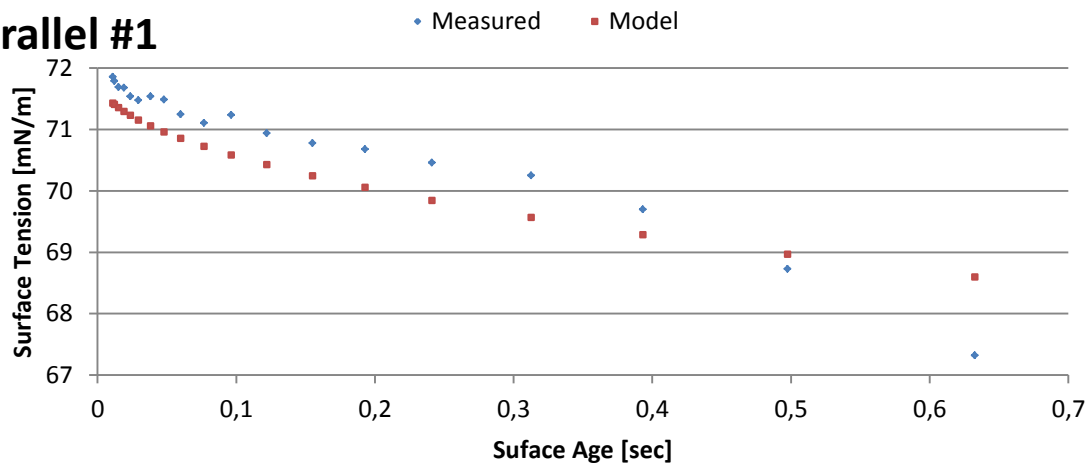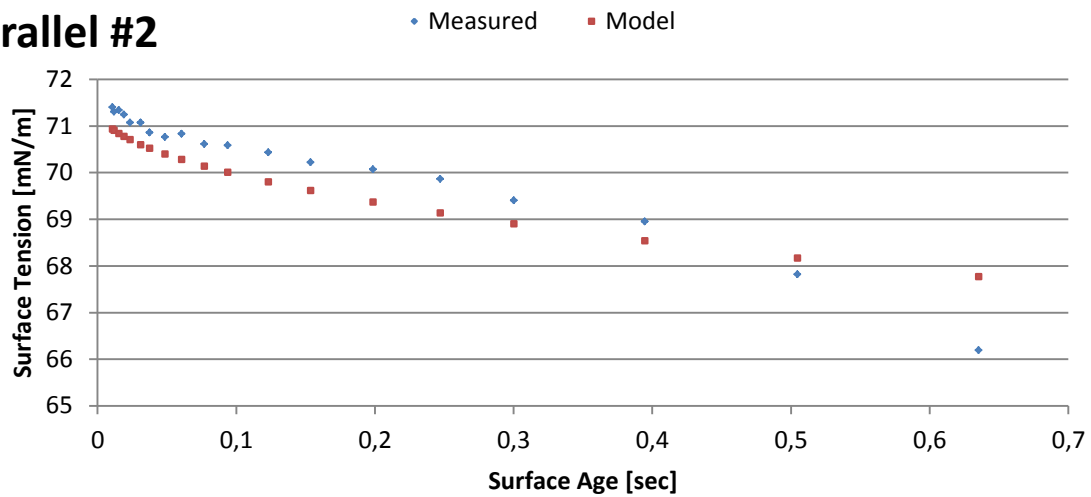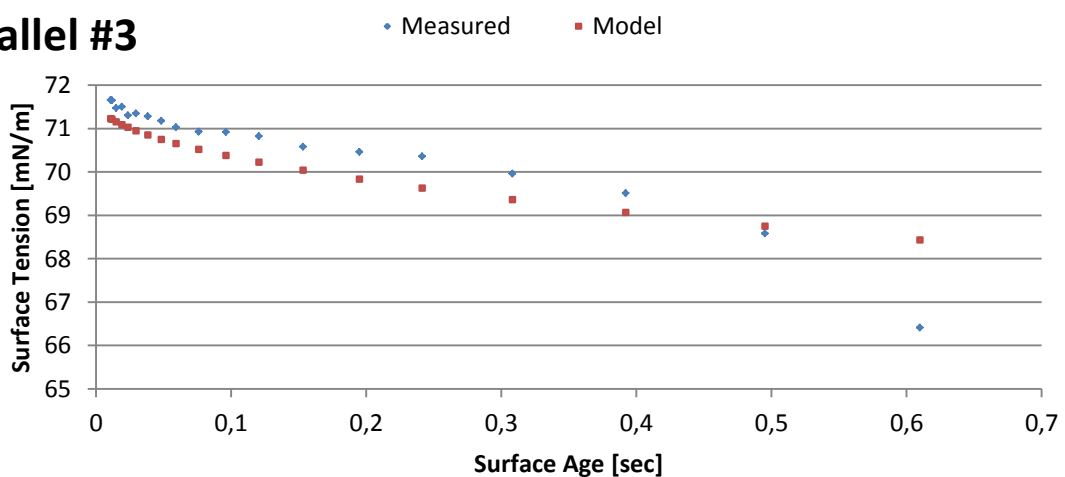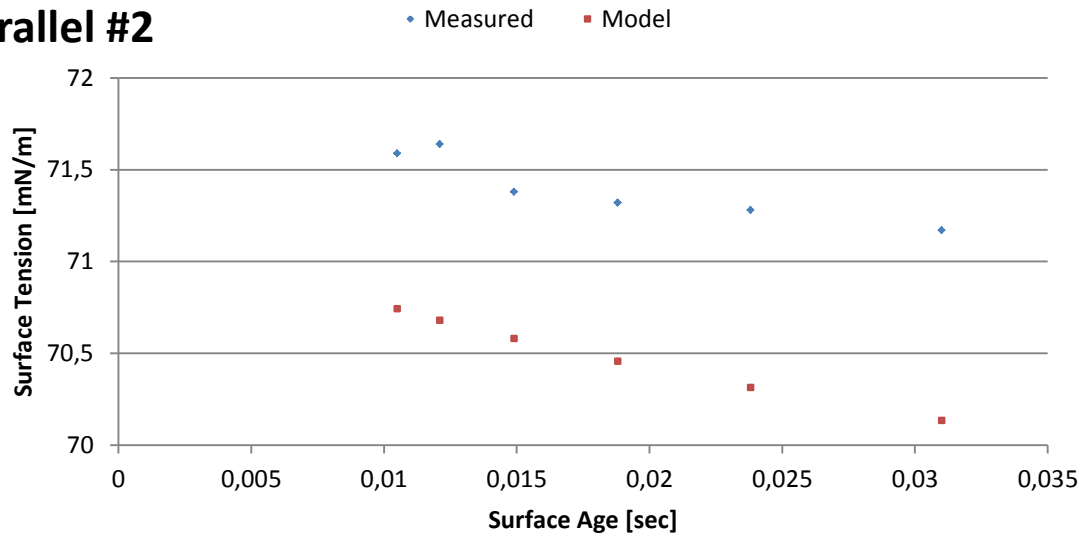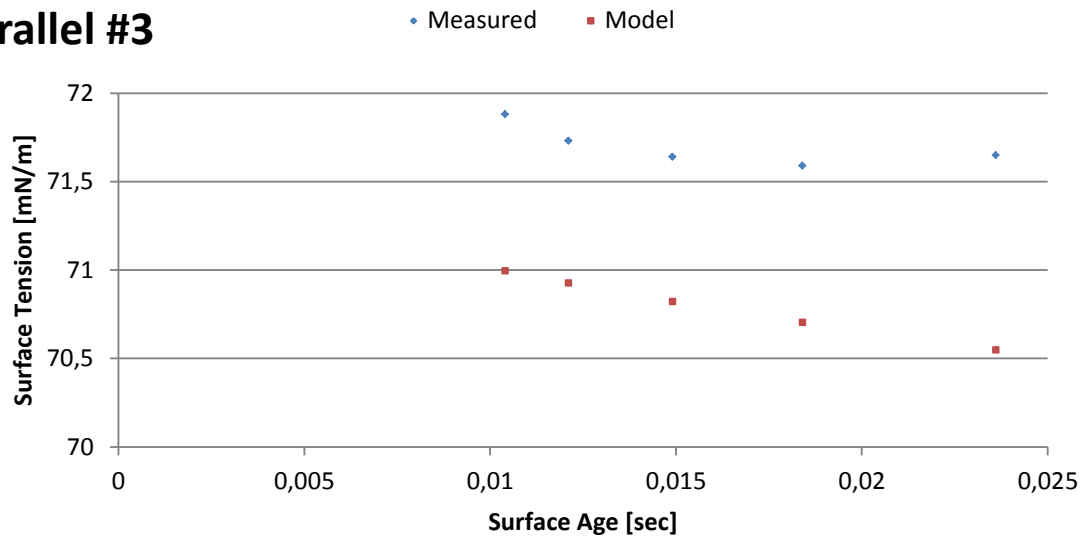Figure 97. The two graphs show the measured value (Blue dots) and the model (Red dots) for the two parallels, where the ionic strength is 20 mM, temperature is 25 °C, the CaCl$_2$/NaCl-ratios is 1/12 and the concentration of SDBS is 0.431 mM. The last dots is where differ is more than 1 mN/m. The first parallel didn't have a good model.

$$\frac{CaCl_2}{NaCl} = 0 , \qquad I = 20\ mM ,\ \ T = 25°C$$

Table 4. Data of the diffusion coefficient for different concentration of SDBS with constant ionic strength at 20 mM, constant temperature at 25 °C and CaCl$_2$/NaCl-ratio of 0. As well as the time,t_d, where the differ between the model and the measured surface tension is greater than 1 mN/m. The one without a time didn't have a good model. P1, P2 and P3 are each of the parallels.

[SDBS]	Diffusion Coefficient [m^2/s]			t_d [ms]		
[mM]	P1	P2	P3	P1	P2	P3
2.017	$1.645 \cdot 10^{-9}$	$2.396 \cdot 10^{-9}$	$2.389 \cdot 10^{-9}$	-	-	-
1.873	$2.471 \cdot 10^{-9}$	$2.357 \cdot 10^{-9}$	$2.405 \cdot 10^{-9}$	-	-	-
1.729	$1.856 \cdot 10^{-9}$	$2.198 \cdot 10^{-9}$	$2.122 \cdot 10^{-9}$	-	-	-
1.585	$1.924 \cdot 10^{-9}$	$2.150 \cdot 10^{-9}$	$1.948 \cdot 10^{-9}$	-	-	-
1.441	$1.545 \cdot 10^{-9}$	$1.907 \cdot 10^{-9}$	$1.634 \cdot 10^{-9}$	-	-	-
1.297	$1.309 \cdot 10^{-9}$	$1.738 \cdot 10^{-9}$	$1.472 \cdot 10^{-9}$	-	-	-
1.153	$1.231 \cdot 10^{-9}$	$1.427 \cdot 10^{-9}$	$1.248 \cdot 10^{-9}$	-	-	-
1.009	$8.929 \cdot 10^{-10}$	$1.199 \cdot 10^{-9}$	$9.928 \cdot 10^{-10}$	-	-	-
0.865	$8.780 \cdot 10^{-10}$	$9.401 \cdot 10^{-10}$	$8.330 \cdot 10^{-10}$	-	-	-
0.576	$3.734 \cdot 10^{-10}$	$4.039 \cdot 10^{-10}$	$3.651 \cdot 10^{-10}$	-	-	-
0.432	$2.924 \cdot 10^{-10}$	$2.655 \cdot 10^{-10}$	$2.457 \cdot 10^{-10}$	-	-	-
0.288	$2.369 \cdot 10^{-10}$	$2.296 \cdot 10^{-10}$	$1.658 \cdot 10^{-10}$	-	-	-
0.144	$1.754 \cdot 10^{-10}$	$1.605 \cdot 10^{-10}$	$1.466 \cdot 10^{-10}$	4049.8	3201.0	1019.3

$$\frac{CaCl_2}{NaCl} = \frac{1}{117} , \qquad I = 20\ mM ,\ \ T = 25°C$$

Table 5. Data of the diffusion coefficient for different concentration of SDBS with constant ionic strength at 20 mM, constant temperature at 25 °C and CaCl$_2$/NaCl-ratio of 1/117. As well as the time,t_d, where the differ between the model and the measured surface tension is greater than 1 mN/m. The one without a time didn't have a good model. P1, P2 and P3 are each of the parallels.

[SDBS]	Diffusion Coefficient [m^2/s]			t_d [ms]		
[mM]	P1	P2	P3	P1	P2	P3
0.721	$2.784 \cdot 10^{-9}$	$2.826 \cdot 10^{-9}$	$2.864 \cdot 10^{-9}$	-	-	-
0.576	$1.158 \cdot 10^{-9}$	$1.064 \cdot 10^{-9}$	$9.217 \cdot 10^{-10}$	-	-	-
0.504	$5.957 \cdot 10^{-10}$	$5.435 \cdot 10^{-10}$	$4.458 \cdot 10^{-10}$	-	-	-
0.432	$3.007 \cdot 10^{-10}$	$3.260 \cdot 10^{-10}$	$2.365 \cdot 10^{-10}$	-	-	-
0.360	$7.120 \cdot 10^{-11}$	$6.752 \cdot 10^{-11}$	$2.462 \cdot 10^{-11}$	-	-	244.3
0.317	$3.830 \cdot 10^{-11}$	$5.698 \cdot 10^{-11}$	$4.309 \cdot 10^{-11}$	242.4	305.4	242.7
0.288	$4.225 \cdot 10^{-11}$	$4.050 \cdot 10^{-11}$	$2.908 \cdot 10^{-11}$	302.5	305.0	30.3
0.216	$5.505 \cdot 10^{-11}$	$4.214 \cdot 10^{-11}$	$3.424 \cdot 10^{-11}$	639.2	630.8	503.0
0.144	$5.985 \cdot 10^{-11}$	$5.980 \cdot 10^{-11}$	$4.448 \cdot 10^{-11}$	1594.3	1582.6	1994.0

$$\frac{CaCl_2}{NaCl} = \frac{1}{57} \ , \qquad I = 20 \ mM \ , \ \ T = 25°C$$

Table 6. Data of the diffusion coefficient for different concentration of SDBS with constant ionic strength at 20 mM, constant temperature at 25 °C and CaCl₂/NaCl-ratio of 1/57. As well as the time,t_d, where the differ between the model and the measured surface tension is greater than 1 mN/m. The one without a time didn't have a good model. P1, P2 and P3 are each of the parallels.

[SDBS]	Diffusion Coefficient [m^2/s]			t_d [ms]		
[mM]	P1	P2	P3	P1	P2	P3
0.862	$1.400 \cdot 10^{-9}$	$1.759 \cdot 10^{-9}$	$1.401 \cdot 10^{-9}$	-	-	-
0.718	$7.029 \cdot 10^{-10}$	$8.372 \cdot 10^{-10}$	$8.241 \cdot 10^{-10}$	-	-	-
0.574	$2.328 \cdot 10^{-10}$	$2.472 \cdot 10^{-10}$	$2.595 \cdot 10^{-10}$	-	-	-
0.431	$1.428 \cdot 10^{-10}$	$1.066 \cdot 10^{-10}$	$1.630 \cdot 10^{-10}$	-	-	-
0.287	$6.834 \cdot 10^{-11}$	$7.173 \cdot 10^{-11}$	$5.613 \cdot 10^{-11}$	307.8	96.9	304.0
0.230	$6.650 \cdot 10^{-11}$	$6.152 \cdot 10^{-11}$	$7.887 \cdot 10^{-11}$	499.7	489.6	191.8
0.201	$8.601 \cdot 10^{-11}$	$8.575 \cdot 10^{-11}$	$7.122 \cdot 10^{-11}$	193.4	308.0	633.1
0.172	$6.811 \cdot 10^{-11}$	$4.269 \cdot 10^{-11}$	$6.262 \cdot 10^{-11}$	798.2	803.0	1011.8
0.144	$7.817 \cdot 10^{-11}$	$6.691 \cdot 10^{-11}$	$8.358 \cdot 10^{-11}$	1593.7	1587.3	1584.3

$$\frac{CaCl_2}{NaCl} = \frac{1}{17} \ , \qquad I = 20 \ mM \ , \ \ T = 25°C$$

Table 7. Data of the diffusion coefficient for different concentration of SDBS with constant ionic strength at 20 mM, constant temperature at 25 °C and CaCl₂/NaCl-ratio of 0. As well as the time,t_d, where the differ between the model and the measured surface tension is greater than 1 mN/m. The one without a time didn't have a good model. P1, P2 and P3 are each of the parallels.

[SDBS]	Diffusion Coefficient [m^2/s]			t_d [ms]		
[mM]	P1	P2	P3	P1	P2	P3
0.719	$8.608 \cdot 10^{-11}$	$1.031 \cdot 10^{-10}$	$9.353 \cdot 10^{-11}$	-	-	-
0.576	$5.730 \cdot 10^{-11}$	$6.332 \cdot 10^{-11}$	$3.918 \cdot 10^{-11}$	-	-	-
0.432	$4.440 \cdot 10^{-11}$	$3.625 \cdot 10^{-11}$	$1.401 \cdot 10^{-11}$	-	-	310.3
0.288	$2.223 \cdot 10^{-11}$	$2.804 \cdot 10^{-11}$	$1.743 \cdot 10^{-11}$	371.0	499.8	500.9
0.259	$2.520 \cdot 10^{-11}$	$2.511 \cdot 10^{-11}$	$1.275 \cdot 10^{-11}$	507.5	500.8	507.0
0.201	$3.827 \cdot 10^{-11}$	$3.693 \cdot 10^{-11}$	$1.891 \cdot 10^{-11}$	801.0	802.8	629.5
0.173	$4.393 \cdot 10^{-11}$	$3.685 \cdot 10^{-11}$	$4.255 \cdot 10^{-11}$	1258.2	1256.3	1260.4
0.144	$3.587 \cdot 10^{-11}$	$5.260 \cdot 10^{-11}$	$3.635 \cdot 10^{-11}$	1584.2	1590.6	1584.2
0.115	$6.870 \cdot 10^{-11}$	$7.640 \cdot 10^{-11}$	$6.475 \cdot 10^{-11}$	799.4	629.2	797.3

$$\frac{CaCl_2}{NaCl} = \frac{1}{12}\ , \qquad I = 20\ mM\ ,\ \ T = 25°C$$

Table 8. Data of the diffusion coefficient for different concentration of SDBS with constant ionic strength at 20 mM, constant temperature at 25 °C and CaCl$_2$/NaCl-ratio of 1/12. As well as the time,t$_d$, where the differ between the model and the measured surface tension is greater than 1 mN/m. The one without a time didn't have a good model. P1, P2 and P3 are each of the parallels.

[SDBS]	Diffusion Coefficient [m^2/s]			t$_d$ [ms]		
[mM]	P1	P2	P3	P1	P2	P3
0.719	$1.272 \cdot 10^{-10}$	$8.949 \cdot 10^{-11}$	$1.039 \cdot 10^{-10}$	-	-	-
0.575	$7.605 \cdot 10^{-11}$	$9.407 \cdot 10^{-11}$	$6.284 \cdot 10^{-11}$	-	-	-
0.431	$5.400 \cdot 10^{-11}$	$4.782 \cdot 10^{-11}$	$5.260 \cdot 10^{-11}$	-	23.8	18.4
0.288	$2.647 \cdot 10^{-11}$	$3.266 \cdot 10^{-11}$	$2.691 \cdot 10^{-11}$	497.4	504.5	495.2
0.230	$2.055 \cdot 10^{-11}$	$1.867 \cdot 10^{-11}$	$2.329 \cdot 10^{-11}$	638.0	627.0	637.5
0.201	$2.250 \cdot 10^{-11}$	$2.657 \cdot 10^{-11}$	$2.618 \cdot 10^{-11}$	628.3	626.8	631.5
0.173	$2.596 \cdot 10^{-11}$	$3.398 \cdot 10^{-11}$	$3.327 \cdot 10^{-11}$	1021.2	1011.0	1007.8
0.144	$3.086 \cdot 10^{-11}$	$3.006 \cdot 10^{-11}$	$3.082 \cdot 10^{-11}$	1589.2	1592.8	1591.8
0.115	$3.398 \cdot 10^{-11}$	$4.613 \cdot 10^{-11}$	$3.989 \cdot 10^{-11}$	1994.0	2003.1	2006.3

Minimume Area vs Salt-ratio

◆ #1 ■ #2 ▲ #3

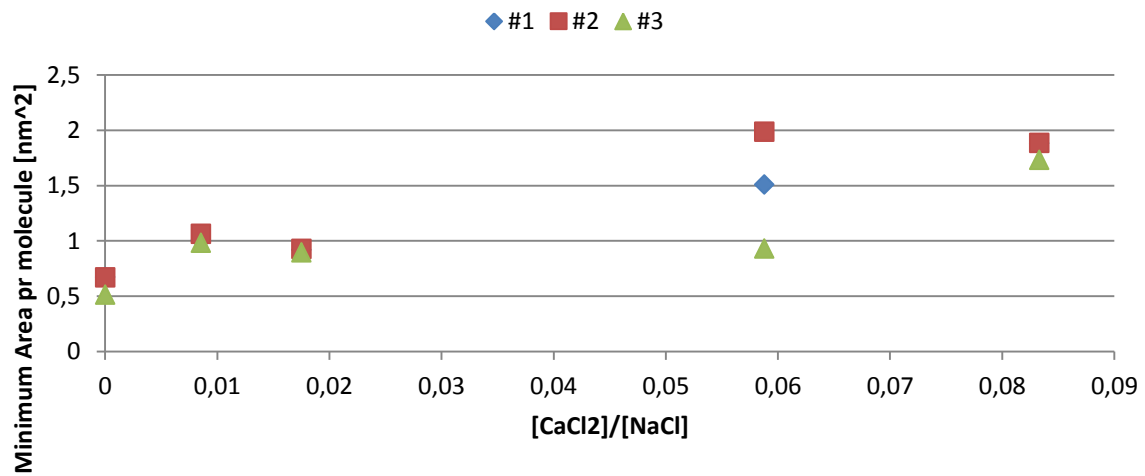**Figure 98.** Illustaration of the minimum area pr molecule with the change of $CaCl_2$/NaCl-ratios where the n-value for pure sodium is 1, and the n-value for the mix of NaCl and $CaCl_2$ is 2. This plot is only to illustrate that the n-value should be 1 for all the $CaCl_2$/NaCl-ratios. The blue square is the first parallel, the red square is the second parallel, the green triangle is the third parallel.