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A study of the formation mechanism of calcium naphtenate deposits by using the axisymmetric drop shape analysis technique

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Preface

This report was done as a Master thesis. This project is a continuation of three previous master theses on the subject, by Estefania Blanco Manotas in 2017 [1], Kyllian Goirand in 2017 [2] and Mohd Faidzul Hakim Mohd Adnan in 2016 [3]. The experimental work was done at Uglestad laboratory fall and winter 2017/2018. The project was done under supervisor Sébastien Simon and professor Johan Sjöblom.

I would like to thank Sébastien Simon for his cooperation and help to do the experiments, help discussing the results and writing this report. I want to thank Bicheng Gao for helping me with the extraction of ARN from deposits. Finally I want to thank professor Johan Sjöblom for letting me take this project and all the people working at Ugelstad Laboratory that have helped me this year.

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

Sondre W. Tofte

Abstract

New batches of ARN were extracted with a yield of 7-8% and with a purity of 92-93%. The axisymmetric drop shape analysis (ADSA) technique was used on different samples of ARN, xylene and asphaltenes to study the dilational interfacial rheology. The results from the experiments confirm that ARN cause the calcium napthenate gel formation when the carboxylate groups in ARN react with calcium ions from the buffer. A strong gel is formed for 2.5μM ARN with a long exchange time (5400 seconds) and the adsorption layer of ARN is being reorganized. The presence of asphaltenes in a mixture of ARN and asphaltenes prevents gel formation. A buffer with pH 6 and 7 can be used with a concentration of 25 μM ARN, but for a buffer with pH 8 the concentration is at the limit of what can be studied at 9 μM-10 μM ARN.

7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene was found to have different interfacial tension during the adsorption. This could be a result of pollution. A new procedure with more thorough cleaning was created to prevent pollution of asphaltenes. Asphaltenes are able to desorb gel that is already formed, even when the gel was strong at high ARN concentration (10 μM) and after coalescence. Coalescence with ARN is increasing the gel formation significantly. This may be caused by a new adsorption layer, probably multilayer formation. The time to desorb the formed gel is increased when the ARN concentration is increased because the gel is stronger. The axisymmetric drop shape analysis (ADSA) technique can be used with an ARN concentration of 10 μM for pH 8 with a contracted volume to look at the gel formation during coalescence. Pictures of the drop and the interfacial tension values during the experiments show that the shape often is hard to control after contraction for 10.0 μM ARN, but the shape is controlled properly for 7.5 μM ARN. The interfacial tension is calculated to be significantly lower when the shape is longer. The axisymmetric drop shape analysis (ADSA) technique is hard to use for contraction with higher concentration of ARN because the shape of the drop is hard to control. The profile error from the software can be used to determine if the drop got a good shape after contraction.

Table 1: List of abbreviations

Abbreviation	Meaning
SINTERFACE	Equipment that measures the interfacial tension
BA	Benzoic acid
NA	Naphthenic acids
TAN	Total acid number
MW	Molecular weight
IFT	Interfacial tension
ADSA	Axisymmetric drop shape analysis
ARN	Tetrameric acid
ASP	Asphaltenes
XYL	Xylene
ARN-xylene	ARN in pump 1 and xylene in pump 2
NMR	Nuclear magnetic resonance
CCD	Charge coupled device

Table 2: List of symbols

Symbol	Meaning
M_{ARN}	Molar mass of ARN
M_{BA}	Molar mass of Benzoic acid
m_{BA}	mass of Benzoic acid
m_{ARN}	mass of ARN
$Area_{2.11->2.30ppm}$	Area between 2.11 and 2.30ppm
$Area_{8.1ppm}$	Area at 8.1ppm
γ	interfacial tension
dW	amount of work
dA	amount of area
F	force
ldx	dimension of distance
s	arc length
x	horizontal coordinate
z	vertical coordinate
R_0	curvature radius
Θ	the angle of the tangent to the profile
$\Delta\,\rho$	density difference
g	acceleration of gravity
$\Delta\,\gamma$	the dilational stress of an adsorbed layer
γ^0	the initial value of interfacial tension
E_0	coefficient of dilatational surface elasticity
α	surface deformation
$\eta_{'}$	coefficient of dilatational surface viscosity
$\alpha^{'}$	rate of surface deformation.
ΔA	area perturbation
$i2\pi\,\omega\,\eta$	imaginary part related to viscosity.
$\hat{E}$	inverse Fourier transform of E
A_0	reference surface area
$\tilde{A}$	amplitude of the area oscillation
γ_0	equilibrium reference interfacial tension
$\tilde{\gamma}$	amplitude of the interfacial tension
φ	phase shift
$E(\omega)$	complex viscoelastic modulus
E'	the elastic modulus
E''	the viscous modules
μ	micro

Contents

1 Introduction

1.1 Problem

Naphthenic acids are acids that can be found in crude oil. They can cause different problems in crude oil production. For example the acids can react with calcium from the water phase and create calcium napthenate deposit. Calcium napthenate deposit slows down the flow of crude oil. The shut down to clean the deposits can be very expensive. Calcium napthenate formation starts as a gel formed by a chemical reaction between tetrameric acids (ARN) and water containing calcium. The gel can then grow or react with other compounds to form large deposits [3].

1.2 Solution

The properties and rhelogy of dynamic interface were studied between ARN, asphaltenes or a mixture of ARN + asphaltenes and a calcium buffer at different pH, time, volume and concentration values. This was done to look at the effect of time, pH, volume and concentration on the formation of calcium napthenate deposit. To study if the solvent asphaltenes could desorb gel already formed. New procedures were used to mimic the effect of drops coalescing.

This project is a continuation of three previous master theses on the subject, by Estefania Blanco Manotas in 2017 [1], Kyllian Goirand in 2017 [2] and Mohd Faidzul Hakim Mohd Adnan in 2016 [3].

1.3 Goal

1.3.1 Extraction of ARN

The first part of the thesis was to prepare the samples. Extraction of ARN from deposits takes a long time and was the first part of the thesis. Because this is a continuation of previous theses there were some ARN left, but new samples of ARN were made because it will be needed later. Because the concentration of ARN needed was very low, only the old sample was used.

1.3.2 Dilational interfacial rheology

The main goal of the report is to look at the dilational interfacial rheology of different samples of ARN, asphaltenes and xylene to look at the gel formation at the interface. To look at the dilational interfacial rheology a technique called axisymmetric drop shape analysis was done using an equipment called SINTERFACE. With this technique the interfacial tension (IFT) of a drop can be measured by looking at the shape of the drop. For a drop of a liquid inside another liquid the shape is determined by interfacial and gravity forces. Oscillation of the samples were done to see if gel was formed. Many experiments were done with different settings and procedures. For most experiments more than one parallel were done to confirm the result.

2 Theory

2.1 Naphthenic acids in crude oil

Crude oil is unrefined petroleum that is found in nature. Crude oil contains a mixture of different molecules. Most of them are hydrocarbons and the rest are organic compounds of sulfur, oxygen, nitrogen and metallic constituents. Crude oil can be divided into fractions of the four hydrocarbon groups saturates, aromatics, resins and asphaltenes (SARA), where asphaltenes have the highest polarity and saturates have the lowest polarity [4].

Naphthenic acids (NA) are acids that can be found in crude oil. NA are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids. NA are amphibic, the carboxylic part is hydrophillic and the hydrocarbon part is hydrophobic. The chemical structure for naphthenic acids can be seen in figure 1. The chemical formula for naphthenic acids are $C_nH_{2n+z}O_2$, where n indicates the carbon number and z is zero if the molecule is a fatty acid, or negative depending on the number of condensed and/or aromatic rings. There can be a lot of different NA in crude oil which gives the different crude oil different chemical and physical properties [4].

PHs affect the properties of NA. Increasing pH will make the carboxylic acids dissociate which makes it more soluble in water. When the crude oil is produced there will be a pressure drop. The pressure drop creates gases like CO_2, which increase the pH and this makes NA dissociated. Naphthenic acids cause corrosion problems in crude oil transportation. "Sweet" corrosion from naphthenic acids can lead to pitting which penetrates the mass of the metal [5].

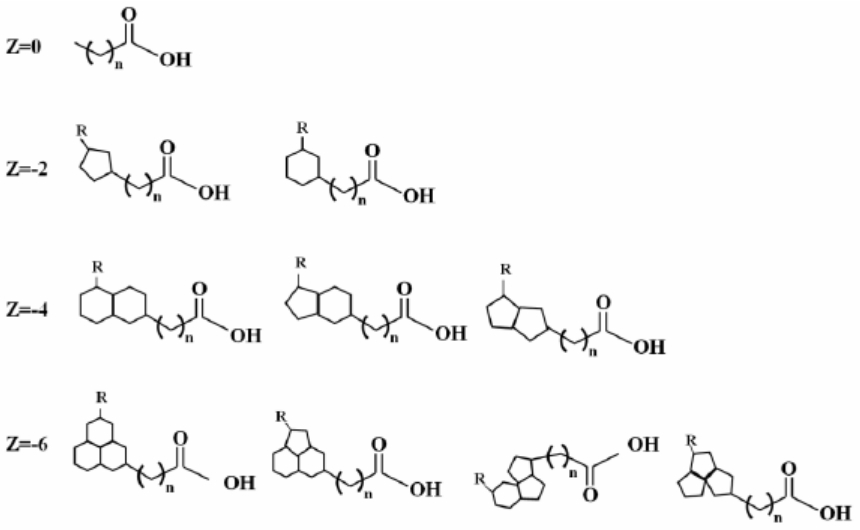

Figure 1: Structure of naphthenic acids [4]

2.2 Tetrameric acid or ARN

ARN is a weak acid that was discovered by Statoil and ConocoPhillips [6]. ARN is a naphthenic acid and consists of 4-protic carboxylic acids with 4-8 unsaturated rings in the hydrocarbon skeleton. ARN forms in oil in water emulsions at water cuts from 10 to 90% in volume. The structure of the ARN $C_{80}H_{142}O_8$ with a molar mass of 1231 g/mole, can be seen in figure 2 [7].

ARN is amphiphilic and can therefore act as a surfactant, the ability to act as a surfactant depends on the pH. The emulsion is stabilized by increasing the pH. This is probably because the

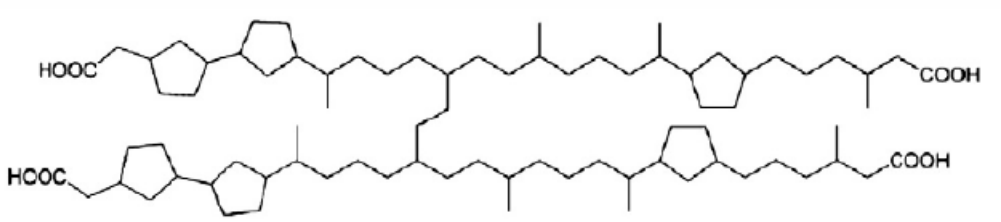

Figure 2: Structure of the ARN $C_{80}H_{142}O_8$

increase in electrostatic repulsions between droplets when the carboxylic acid groups are ionized. Addition of salts like *NaCl* makes ARN more oil soluable. Therefore, increasing the *NaCl* concentration decreases the stability by decreasing the electrostatic repulsions. [6]

Crude oil contains many different acids, and ARN is a small amount of the total acids. The amount of naphtenic acids are usually significantly higher than ARN. Because of the presence of naphtenic acids and asphaltenes the elasticity and viscosity of oil and water mixtures are decreased. This slows down, removes or prevents the gel formation. This could be because at least one naphtenic molecule goes between two ARN molecules and prevents the calcium ions to connect and form a cross linked network [8].

2.3 Asphaltenes

Asphaltenes are the part of crude oil that is insoluble in n-alkane, but soluble in aromatic solvents like toluene. Asphaltenes are the main cause of organic deposits. Asphaltenes are surface active, and create a stable emulsion in oil and water phases at different stages in oil production. [3].

2.4 Calcium naphthenate gel formation

Oil containing ARN reacts with water containing calcium and forms a calcium naphthenate film at the interface. The reaction only occurs if the pH is high enough. Ionized carboxylic acid groups react with calcium ions by cross-linking. The reaction between ARN and calcium is considered to be the first step in the calcium naphtenate deposit formation process [3]. The second step in the formation process is coalescing between the drops. The third step in the process is the growth of the deposit with other structures. To study the formation of calcium naphtenate deposit a large amount of ARN is needed. There is a significant amount of ARN in organic deposits.

2.5 Extraction of ARN from calcium naphthenate deposit

The needed amount can be isolated from the deposit by using an ion exchanger [3]. The purity of ARN using this method is not always that high because it extracts all the carboxylic acids. To calculate the purity of ARN a method have been developed where ARN is esterfied into aromatic ester to be detected by HPLC [3]. BP10 and Pe10 are molecules that are made to mimic the properties of ARN. They can be detected easier than ARN due to presence of chromophore[3].

2.6 Nuclear magnetic resonance (NMR)

To test the purity of the obtained TA a purity test was done using Nuclear magnetic resonance (NMR) analysis. The NMR method is described in [9]. The purity of TA is the calculated using

equation 1 and assuming M_{ARN} is 1230 $\frac{g}{mol}$, M_{BA} is 122.12 $\frac{g}{mol}$, the masses are measured before the experiment and the Areas are obtained from NMR.

$$P = 50\frac{m_{BA}Area_{2.11->2.30ppm}M_{ARN}}{M_{BA}Area_{8.1ppm}m_{ARN}} \tag{1}$$

2.7 Interfacial tension

Interfacial tension is the tension between two liquids. There are attractive forces between the liquids, this force is caused by molecules in the liquids. This phenomenon can be illustrated in figure 3. The interaction between the molecules at the interface is the interfacial tension. The interfacial tension (γ) can be defined as equation 2.

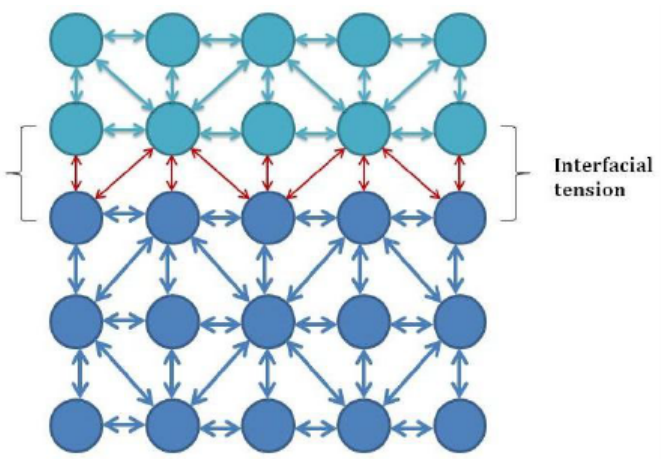

Figure 3: Interfacial tension between two liquids

$$dW = \gamma dA \tag{2}$$

Where dW is the amount of work (mJ), γ is the interfacial tension ($\frac{mJ}{m^2}$) and dA is the amount of area (m^2). The interfacial tension can also be defined as equation 3.

$$dW = Fdx = 2\gamma ldx \tag{3}$$

Where F is the force (mN) and ldx is the dimension of distance (m).

2.8 Dilational interfacial rheology

The dilational interfacial rheology can be analyzed using a technique called axisymmetric drop shape analysis (ADSA) where the interfacial tension of a drop can be measured by looking at the shape of the drop. For a drop of a liquid inside another liquid the shape is determined by interfacial and gravity forces. The gravity forces make the shape of the drop vertical and the interfacial tension make the drop spherical. The relation between Laplace pressure, interfacial tension and surface curvature can be described by Gauss Laplace equations. The equations can be seen in equation 4, 5, 6. The drop is rapidly analyzed by using charge coupled device (CCD) cameras and using software to fit the shape to Gauss Laplace equation. An example of an analyzed drop is shown in figure 4.

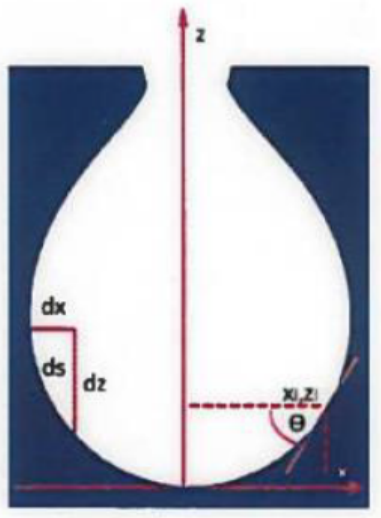

Figure 4: Example of a drop analyzed using Gauss Laplace equation

$$\frac{dx}{ds} = cos(\Theta) \tag{4}$$

$$\frac{dz}{ds} = sin(\Theta) \tag{5}$$

$$\frac{d\theta}{ds} = \frac{2}{R_0} - \frac{\Delta\rho g z}{\gamma} - \frac{sin(\Theta)}{x} \tag{6}$$

Where
s is the arc length (m)
x is the horizontal coordinate
z is the vertical coordinate
R_0 is the curvature radius from the drop apex (m)
Θ is the angle of the tangent to the profile
$\Delta\ \rho$ is the density difference ($kg/m3$)
g is the acceleration of gravity ($m/s2$)
γ is the interfacial tension (mN/m)

2.9 Use of coaxial capillary

For all experiments a coaxial capillary apparatus was used. The use of capillary apparatus is shown in figure 5 and 6 [3]. An emerging drop is formed at the capillary at equilibrium with a bulk concentration of surface active molecules. The composition and volume of the drop is controlled during the experiments with the inlet and outlet of the pumps. Contraction of the volume of the drop can be used to mimic coalescence and oscillation can be done to look at the elasticity of the sample.

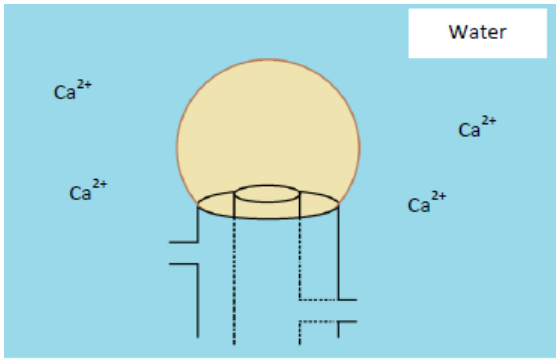

Figure 5: The figure shows an oil phase drop under exchange. Oil phase is added via inlet and removed via outlet simultaneously to control the volume and composition of the drop

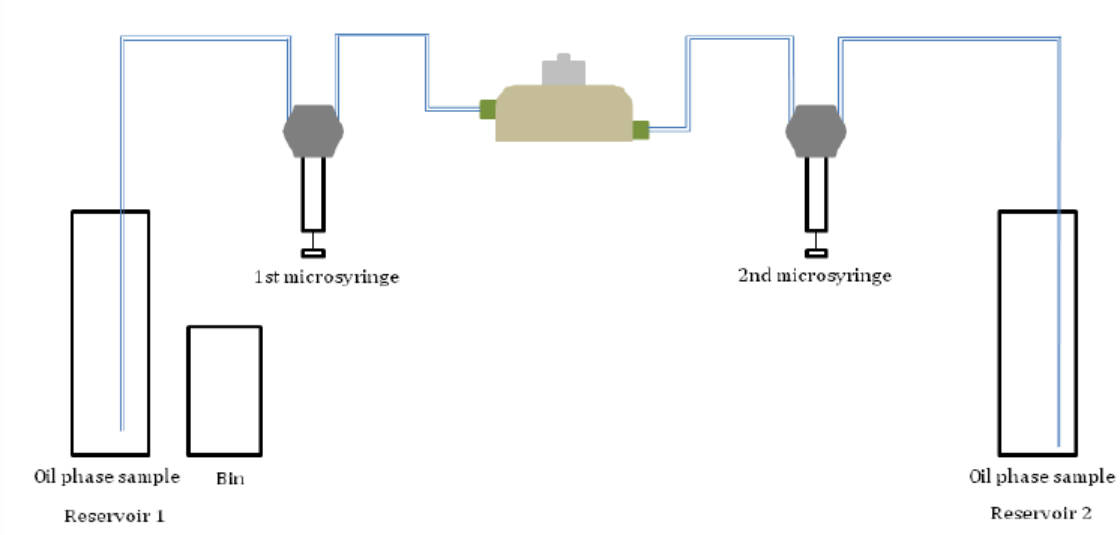

Figure 6: An example of the settings for an Asphaltenes-Asphaltenes experiment. The samples are pumped into the micro syringe and added to the coaxial capillary to control the volume and composition of the drop

2.10 Viscoelastic modulus

Viscoelastic modulus is a model that can be used to show the relationship between the surface modification of an interfacial layer and the related interfacial tension. The dilational stress of an adsorbed layer $\Delta\ \gamma$ can be defined as the variation of the interfacial tension γ from its initial value γ^0 shown in equation 7.

$$\Delta\gamma = \gamma(t) + \gamma^0 \tag{7}$$

The related surface deformation is the expansion/contraction of the surface area (A). The dilational viscoelasticity can be written as the sum of equations 8 that describes the elastic behavior, and 9 that describes the viscous behavior.

$$\Delta\gamma = E_0\alpha + \eta\alpha^{'} \tag{8}$$

E_0 is coefficient of dilatational surface elasticity α is the surface deformation η is the coefficient of dilatational surface viscosity $\alpha^{'}$ is the rate of surface deformation. The complex viscoelastic modulus E can be written as equation 9.

$$E = \frac{\Delta\gamma A_0}{\Delta A} = E_0 + i2\pi\omega\eta \tag{9}$$

Where ΔA is the area perturbation and i2π ω η is an imaginary part related to viscosity.

Area modification on the interface can according to Fourier formalism be described as a superposition of harmonic components in the domain of frequency. The adsorbed layer can be written as equation 10.

$$\Delta\gamma = \int_0^t \hat{E}(\tau)\alpha(t-\tau)d\tau \tag{10}$$

Where $\hat{E}$ is the inverse Fourier transform of E.

The method used to analyze the dilational interfacial rheology is called oscillating drop. Harmonic compression and expansion is done on the drop. Equation 11 describes the harmonic deformation on the drop.

$$A = A_0 + \tilde{A}sin(2\pi\omega\eta) \tag{11}$$

Where A_0 is the reference surface area and $\tilde{A}$ is the amplitude of the area oscillation.

The harmonic response of the interfacial tension γ can be written as equation 12.

$$\gamma = \gamma_0 + \tilde{\gamma}sin(2\pi\omega\eta + \varphi) \tag{12}$$

Where γ_0 is the equilibrium reference interfacial tension, $\tilde{\gamma}$ is the amplitude of the interfacial tension, φ is the phase shift between the area perturbation and the response of the interfacial tension. We can combine the equations and write the complex viscoelastic modulus $E(\omega)$ as equation 13.

$$E(\omega) = \frac{\tilde{\gamma}A_0}{\tilde{A}}exp(i\varphi) \tag{13}$$

All values in equation 13 can be calculated using the axisymmetric drop shape analysis. The viscoelastic modulus can be divided into two equations, the elastic modulus E' seen in equation 14 and the viscous modules E'' seen in equation 15 shows the viscous energy in the system. The elastic modulus E' is proportional with the surface deformation, it characterizes the energy stored in the system in elastic form [10]. The E' value can be used to look at the gel formation of a sample. High elastic modulus indicates high gel formation.

$$E' = E*(\omega)cos(\varphi) \tag{14}$$

$$E'' = E*(\omega)sin(\varphi) = 2\pi\omega\eta \tag{15}$$

3 Methods

3.1 List of chemicals

The chemicals used can be seen in table 3.

Table 3: List of chemicals

Product	Purity	Orgin
Toluene(Analar Normapur)	99,8% Purity	Sigma-Aldrich
1 M HCl solution	Prepared from ampoule	Merck
MQ water	Ultra pure Conductivity 18.2 MΩ.cm	MQ system (laboratory)
$NaCO_3$	99 %	VWR
$NaHCO_3$	$>$ 99.5 %	Sigma-Aldrich
$CaCl_2$	$>$ 99% Purity	Sigma-Aldrich
$NaCl$	99.5%	Merck
ARN	97%	From previous experiment
MES	99.5% Purity	Sigma-Aldrich
MOPS	99.5% Purity	Sigma-Aldrich
Borax decahydrate	99,5% Purity	Sigma-Aldrich
Xylene	$>$ 98,5% Purity	VWR
Chloroform	99.4%	Merck
Crude oil	Production chemical free	Grane oil field
Hexane	98%	VWR
Benzoic acid	99.5%	Merck
d-Chloroform with 0.05% TMS	99.96%	Sigma-Aldrich

3.2 List of equipment

The equipment used can be seen in table 4. All the equipment used was found and used at Uglestad laboratory.

Table 4: List of equipment

Product	Origin
Shaker	H5501 digital IKAWERAE
Vacuum pump	——
Magnetic stirrer	——
PH meter	——
0.2 micro m PTFE filter	Sigma-Aldrich
Sonication bath	——
SINTERFACE PAT-1M	——
Turbovap	——

3.3 Tetra Acid Extraction from Deposits

3.3.1 Preparation of 1M HCl

A prepared concentrated solution of 1M HCl was added into a 1L volumetric flask. Then MQ water was added until the total mix had 1L in total.

3.3.2 Preparation of $NaCO_3$ + $NaHCO_3$ Buffer

185.9313g $NaCO_3$ was added to a 2L volumetric flask with a magnet on a stirrer, MQ water was added slightly under the 2L mark and the mixture was dissolved using the magnet for one hour. 21.0422g of $NaHCO_3$ was then added to the dissolved mix using a spoon with approximately 1g $NaHCO_3$, and the $NaHCO_3$ was always dissolved before the next amount was added. The sample was left on the stirrer for 30 minutes. The magnet was then removed and MQ water was added to the 2L mark, and the magnet was added again. The sample was stored on the stirrer.

3.3.3 Sample preparation

10g Napthenate deposit was crushed with a mortar and added to a 500mL Schott flask, this was done for 6 samples. The exact masses can be seen in table 9 in appendix. Then 235 mL of toluene was added to the samples. The samples were then put on a shaker for 2 days. Out of the 6 deposits 3 samples were made (1+2), (3+4) and (5+6).

The samples were removed from the shaker and stored for 1 hour. Toluene was removed using a vacuum pump. 235mL Toluene was added to the deposit. The samples were put back on the shaker. This procedure was done 3 times. After the removal of Toluene for the 3rd time 100 mL 1M HCl and 235 mL toluene was added to the 3 samples. The samples were put on a shaker. The 3 samples were stored in a 2L schott flask. The toluene phase was removed using a vacuum pump and stored in the schott flasks. 235mL Toluene was added and the samples were put back on shaker. The samples were washed with toluene 3 times, and the toluene phase was stored.

3.3.4 Ion exchanger

750mL of buffer solution was poured over 10g of the Ion exchanger Sephadex with a filter of pH 7 under carefully manual stirring. A vacuum pump was used to remove the rest. The same procedure was done for 750mL distilled water, then for 250mL methanol, but the pump was not used for the methanol. The sephadex was transferred to the sample of stored toluene rinsing it with methanol and toluene if needed. The mixture was put on a stirrer with a flying magnet for at least 12 hours with aluminum foil on top. The exact mass of Sephadex and the time can be seen in table 10 in Appendix.

3.3.5 Filtration of Ion exchanger

The filtration was done to remove the non-polar phase. Black ribbon filter paper was used on a Bûchner funnel, the filter was made wet with toluene, the vacuum pump was started. The stirred sample was then poured over the filter. The beaker was rinsed with 20mL toluene and left on the filter for 5 minutes before starting the pump to remove the rest. The rinsing was done 3 times with 20mL toluene. Then the same method was done 3 times for 21 mL total of a mixture with 14 mL toluene and 7 mL methanol. The sephadex was transferred back into the beaker, the funnel and the filter was washed with equal amount toluene and methanol. The non-polar phase is then

filtrated using blue ribbon round filter. The bottle was cleaned with equal amount methanol and toluene. The filter and funnel was rinsed to make sure all the sephadex was transferred back to the beaker. 250mL Methanol, 250mL Toluene and 32,5mL 1M Formic acid (formic acid in toluene) was added to the sample. The sample was then put back on stirring for 24 hours. This method was used for all 3 parallels.

3.3.6 Extraction of polar phase

After the samples had been stirring for 24 hours they were taken off the shaker. The sample was filtered with black ribbon filter and rinsed with 21mL of toluene/methanol (14/7 mL) the pump was started after 5 minutes. The rinsing was done 3 times. The polar phase was then filtered through blue ribbon and stored. The filter was rinsed with toluene and methanol. 250mL Methanol, 250mL of Toluene and 5mL of formic acid was added. The sample was covered with aluminum foil and stirred for 24 hours. The next day the samples were filtered using the same method for black then blue ribbon filter. The filter and the ion exchanger were thrown in the thrash in the fume-hood and the filtrate was stored for evaporation. This method was used for all 3 parallels.

3.3.7 Evaporation

The filtrate was evaporated using turbovap. The small amount of filtrate left after evaporation was transferred to 40mL screw cap vials. The evaporation equipment was rinsed with Toluene and transferred to the vial. The mass of the vials and time of measurement was noted to make sure the sample was completely dry. The obtained yield of ARN can be seen in table 5. The obtained TA yields were fairly similar for all samples, but under the assumed value of approximately 15 % . The equation used to calculate the TA yield can be seen in equation 5.

Table 5: Yield of ARN

Sample	Mass deposits	Mass ARN recovered	Yield extraction
1	9.9g	1.6817g	8.45%
2	10.0g	1.6817g	8.45%
3	10.0g	1.4825g	7.49%
4	9.8g	1.4825g	7.49%
5	9.9g	1.4887g	7.52%
6	9.9g	1.4887g	7.52%

$$Yield_{TA(1+2)} = \frac{m_{screwcapwithcap+TA} - m_{emptyscrewcapwithcap}}{m_{deposit1} + m_{deposit2}} \tag{16}$$

To test the purity of the obtained mass a TA purity test was done using NMR analysis described chapter 2.6. 3 samples (1+2 3+4 and 5+6) were made with 70mg TA, 40mg Benzoic acid 99.5% and 1.5g d-Chloroform with 0.05% TMS, the exact masses can be seen in table 11 in Appendix. The samples were then sent for NMR analysis. The results from the NMR analysis can be seen in figure 80 - 82 in appendix.

The conclusion of the NMR analysis of the old and the new samples can be seen in table 6. This show that the samples have a very high purity of ARN, especially the sample that was used for the dilational interfacial rheology analysis.

Table 6: Results from NMR analysis on the ARN used and the ARN obtained

Sample	Purity
5+6 Old sample	97%
1+2 New sample	92%
3+4 New sample	93%
5+6 New sample	93%

3.3.8 Preparation of Buffer for dilational interfacial rheology measurements

4240mg Borax and 1300mg of 10mM $NaCl$ were added with MQ water to a 1L Schott flask to a total mass of 1000g. A magnet was added and the sample was left on a stirrer. 1.47g 20mM $CaCl_2$ was added with MQ water to a 0.1L Schott flask to a total mass of 100g. A magnet was added and the sample was left on a stirrer. A mixture of Calcium solution and buffer was created using 90g of the calcium solution and 810 of the Borax buffer(8pH).

A pH meter was calibrated using calibration samples of 7 and 4 pH. The Borax solution was put on the stirrer at the pH meter. 1M HCl solution was added to the Borax solution until the pH was 8.00. The exact masses for the different samples can be seen in figure 12 and 13 in Appendix.

3.3.9 Preparation of ARN solution for dilational interfacial rheology measurements

All samples were made using TA 5+6 B6 11.11.2015 from Bicheng as the fully protonated ARN solution. First a 500 μM ARN solution was made. 30 mg of the fully protonated ARN solution was added to a 60mL screw-capped tube, then xylene was added to a total mass of 42.3g. The sample was shaken over night. The exact mass can be seen in table 14 in Appendix.

A 0.2 micro M PTFE filter was used to filtrate the 500 μM solutions after shaking over night. After filtration the sample was added to a 250mL Schott bottles, the mass depends on the concentration (2.925g for 7.5 μM ARN), the sample was completed by adding xylene to a total mass of 195 g. The mass of ARN after filtration and the total mass after addition of xylene can be seen in table 15 in Appendix.

3.3.10 Preparation of Asphaltenes for dilational interfacial rheology measurements

Crude oil was put in the heating cabinet at 60C for 1 hour, then shaken to make it homogeneous. Two 1L Schott flasks were used. 20.06 g crude oil and 800mL Hexane was used for sample 1. 20.0g and 800 mL of Hexane were used for sample 2. The samples were left on a stirrer over night.

A bag was filled with nitrogen, for asphaltene storage. Hexane was used for cleaning. The mass of the filter was measured before the experiment. A 2L filtration flask and a vacuum pump with a filter was used to remove the asphaltenes from the sample. The crude oil sample was put in a sonication bath for 30 minutes. The filter was made wet by washing it with hexane before use. The filter was in the center. A magnet holder was used to keep the magnet in the flask. After the asphaltenes were removed it was stored in the nitrogen bag. The Asphaltenes mass was measured two times for both samples to make sure they were dry. The Crude oil was assumed to have 2.5% yield of asphaltenes. The yield of the collected asphaltenes can be seen in table 7. The yield of both samples were slightly over the assumed yield of 2.5%.

First a 1 g/L asphaltenes solution were made. 30mg of asphaltenes were added to a 40 mL screw-capped tube, the sample were completed with xylene to a total mass of 26g. The tube were

Table 7: Yield of asphaltenes

Batch	Mass used crude oil	Obtained mass asphaltenes	Yield (%)
1	20.06g	0.5493g	2.74%
2	20.00g	0.6193g	3.10%

then put on sonication bath for 30 min and put on a shaker over night. The exact masses for all prepared samples can be seen in figure 16 in appendix.

The next day 12g of the 1g/L asphaltenes sample were added to a 40mL screw-capped tube, the sample were completed with xylene to a total mass of 30g. The sample were then put on sonication bath for 10 minutes before use. A microscope was used on the first samples to see if they were pure. The exact mass for the 0.4g/L asphaltenes solution can be seen in figure 17 in Appendix.

3.3.11 Preparation of Mixture of ARN and asphaltenes for dilational interfacial rheology measurements

To prepare 2 batches with a mixture of ARN and asphaltenes the first 2 batches of 2.5 μM ARN and 0.4 g/L asphaltenes were used. 0.24g of 2.5 μM ARN and 18.8g of 0.4 g/L asphaltenes were added to a 60 mL screw-capped tube, then xylene was added to a total mass of 47g. The mixture was put on sonication for 10 minutes before use. The exact masses for both prepared samples can be seen in figure 18 in appendix.

3.4 Calibration of SINTERFACE

Before the SINTERFACE equipment was used with the prepared samples, it was tested to check if it was properly calibrated. Three tests with a hook using a pendant drop of water with constant volume of 15 μL for a total time of 600 sec were done. The calibration constant was noted in the calibration book in the laboratory. Then the equipment was tested three times with pure xylene. Both pumps were cleaned 100 times with xylene and a test was done for an emerging bubble of pure xylene with a coax capillary, oscillation, a constant volume of 15μL and a total time of 3600 sec. Then the same procedure with xylene in pump 1 and water in pump 2 water (ARN-water) were done once. These experiments was done as part of the training on how to use the equipment. The results were compared to the reference values of 72.3 mN/m for water and xylene and for 36 mN/m for xylene at 20 degrees. The results from the calibration can be seen in figure 108 - 110 in appendix. The equipment was found to be properly calibrated. Pump 1 and 2 were replaced before the first experiment with the prepared samples was stared.

3.5 Use of the SINTERFACE equipment

For all experiments the fume hood was always turned on and the samples were covered with aluminum on top. The pumps were cleaned with xylene 20 times and then with the samples 20 times. If air bubbles were noticed in the pumps they were removed. The cuvette was cleaned with acetone then distilled water, then acetone, then toluene, and then acetone again. After the cuvette was cleaned the cuvette was placed inside the SINTERFACE and 20mL of buffer was added to the cuvette with a pipette. The wet part of the capillary was cleaned very carefully with a tissue before it was added to the cuvette. A drop of solvent was created from pump 2 and then a drop was created with pump 1. The camera settings were checked to be fine. The lights were turned

off before the experiment was started. For experiments with exchange, the hose going to pump 1 was moved from the sample to the trash after the exchange was started.

The setup used for the experiments using the axisymmetric drop shape analysis technique can be seen in figure 7. An example of how the values were chosen on the computer can be seen in figure 111 - 114. The pumps to the right are connected to the used sample and the capillary. A cuvette is filled with the buffer and placed in the equipment. Then the capillary is placed on top of the cuvette and pumps are used to create and control the drop inside. The camera is used to look at the shape of the drop, and the computer screen is used to show the drop and the results during the experiment.

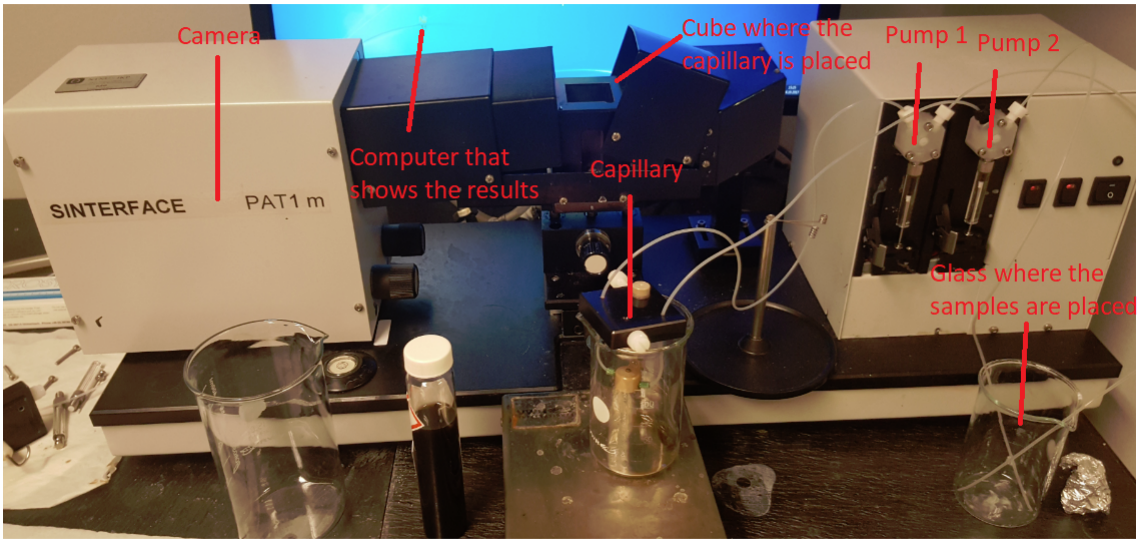

Figure 7: Picture of the setup used for all experiments

3.5.1 Analyzing the oscillation

For all experiments there were an oscillation part that was done to study the gel formation. For all experiments the oscillation was done in 5 periods of 100, 80, 60, 40 and 20 sec. The E′ and E″ was obtained by fitting with the last period (20 seconds).

3.6 Procedures

3.6.1 Procedure 1: With exchange, then relaxation and finally oscillation

This procedure can be divided into three steps. First an exchange part where the volume is regulated to control the composition. During the exchange the volume is changed by 1μL every 7 sec, to manage this different max volumes was used for different exchange times, the values of the exchange time and max volume can be seen in table 8.

Table 8: Settings for the maximum volume for all experiments with exchange

Exchange time(sec)	Max volume (μL)
720	103
2700	387
5400	774

The next part is a relaxation part, it was done to stabilize the system. The last part was an oscillation part started after 1200 seconds. The different steps and the change in volume for this procedure can be seen in figure 8.

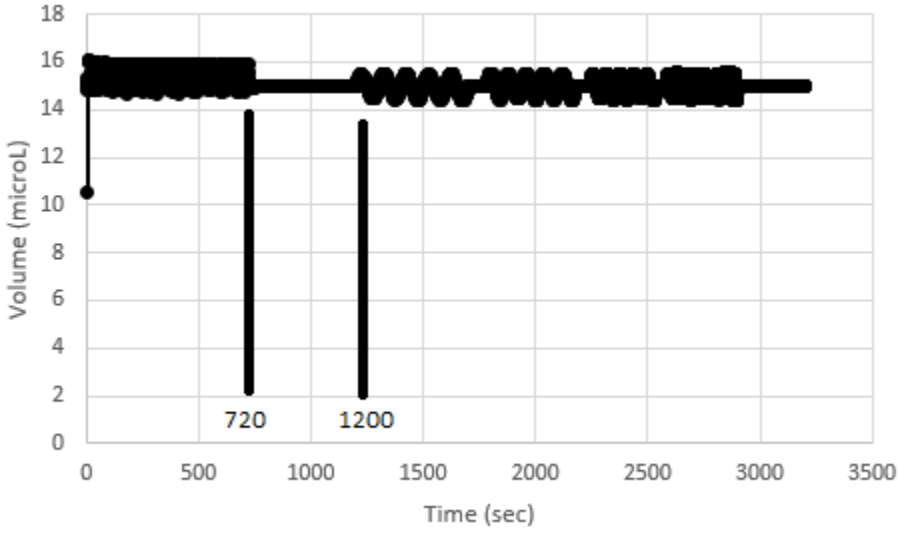

Figure 8: The different steps for this procedure with an exchange part where the volume is regulated to control the composition. A relaxation part that was started after 720 seconds to stabilize the system, and finally oscillation part started after 1200 seconds to study the gel formation

3.6.2 Procedure 2: With one hour of adsorption, then exchange, then relaxation and finally oscillation

This procedure can be divided into four steps. First a part where the ARN is adsorbed and gel is formed. Then an exchange part, a relaxation part and an oscillation part at the end. The different steps and the change in volume for this procedure can be seen in figure 9.

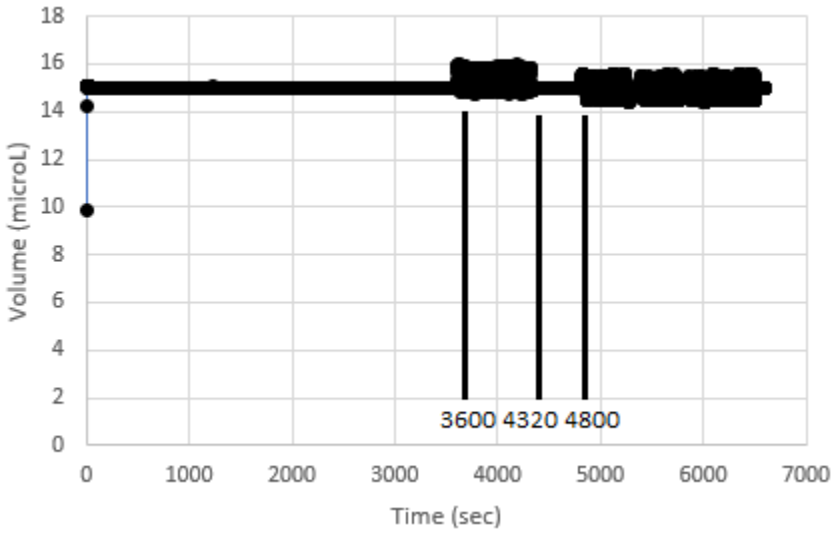

Figure 9: This procedure started with a part where the ARN was adsorbed, then an exchange part that was started after 3600 seconds where the volume is regulated to control the composition. A relaxation part that was started after 4320 seconds to stabilize the system, and finally oscillation part started after 4800 seconds to study the gel formation

3.6.3 Procedure 3: With increased cleaning

This procedure use the same settings as, the procedure with one hour of adsorption, then exchange, then relaxation and then oscillation, but with a new cleaning procedure. Previously the pumps was cleaned with xylene and the used sample 20 times between the experiments. This time the pumps were cleaned with chloroform 50 times, then xylene 50 times and then with the used sample 50 times.

Before the experiment was started a drop from pump 2 was made, then a drop from pump 1 was made. For the experiments with ARN-asphaltenes four additional drops of ARN (from pump 1) were made before the experiment was started, to prevent pollution of the asphaltene drop from pump 2.

3.6.4 Procedure 4: Small drop of asphaltenes and with the drop of asphaltenes sucked in

This procedure use the same settings as, the procedure with one hour of adsorption, then exchange, then relaxation and then oscillation and with cleaning with chloroform. This time one experiment where done with the asphaltenes drop was sucked in before start, and one experiment where only a small drop of asphaltenes was created.

3.6.5 Procedure 5: For mimicing coalescence

This procedure can be divided into four steps. First a part where the ARN is adsorbed, then a part where the volume of the drop is decreased from 25 μL to 15 μL at 3600 seconds, a relaxation part after the volume decrease and an oscillation part at the end. The different steps and the change in volume for this procedure can be seen in figure 10.

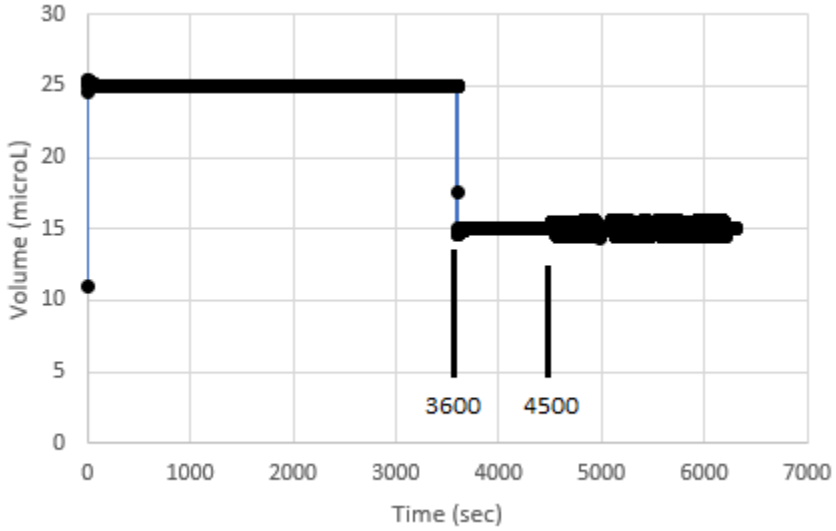

Figure 10: This procedure started with a part where the ARN was adsorbed, then the volume was decreased from 25 μL to 15 μL after 3600 seconds. A relaxation part to stabilize the system from 3600 to 4500 seconds, and finally an oscillation part started after 4500 seconds to study the gel formation

3.6.6 Procedure 6: For exchange after coalescence

This procedure can be divided into six steps. First a part where the ARN is adsorbed, then a part where the volume of the drop is decreased from 25 μL to 15 μL at 3600 seconds, a relaxation part after the volume decrease, then exchange, then relaxation again and finally oscillation part at the end. The different steps and the change in volume for this procedure can be seen in figure 11.

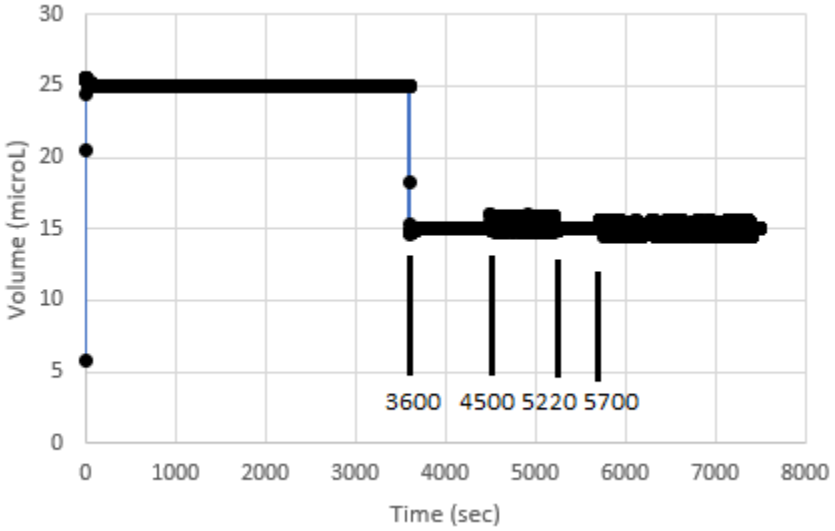

Figure 11: This procedure started with a part where the ARN was adsorbed, then the volume was decreased from 25 μL to 15 μL after 3600 seconds. A relaxation part to stabilize the system from 3600 to 4500 seconds, then exchange from 4500 to 5220 seconds, then relaxation again and finally an oscillation part started after 5700 seconds to study the gel formation

4 Results and discussion

4.1 Influence of the exchange on interfacial tension

4.1.1 Goal

Determine the interfacial conditions for ARN, asphaltenes and a mixture of ARN and asphaltenes. To observe the development of the system for longer exchange time.

4.1.2 Solution

Study the dilational interfacial rheology of 2.5 μM ARN, 0.4g/L asphaltenes and a mixture of ARN and asphaltenes with an exchange time of 720, 2700 and 5400 sec. The procedure used is with exchange, relaxation and oscillation. The procedure is described in chapter 3.6.1 Procedure 1.

4.1.3 Interfacial tension

For this section 3 parallels were done to make sure the experiments follow the same trend. Only one of the parallels are shown in the figures. All experiments can be seen in figure 83 - 91 in Appendix. The results for ARN, asphaltenes and a mixture of ARN and asphaltenes with an exchange time of 720, 2700 and 5400 sec can be seen in figure 12, 13 and 14. From the figures it is possible to see that the interfacial tension is getting slightly lower with time for asphaltenes and the mixture of ARN and asphaltenes.

The figures for ARN show that the interfacial tension is decreasing more rapidly, a plateau after approximately 500, 2000 and 4200 seconds can be seen for ARN. The plateaus are probably a result of reorganization in the adsorption layer. A reorganization in the adsorption layer could be explained by three reasons: A) ARN is changing the conformation (mean molecular area at the interface). B) Reorganization to leave more COO- at the interface to react with calcium ions. C) Reorganization to create a multilayer. More experiments using different techniques like ellipsometry can be done to determine an explanation to the reorganization in the adsorption layer. The behaviour of the mixture of ARN and asphaltenes is more similar to asphaltenes than ARN. The results show no sign of reorganization in the adsorption layer for asphaltenes and the mixture of ARN and asphaltenes.

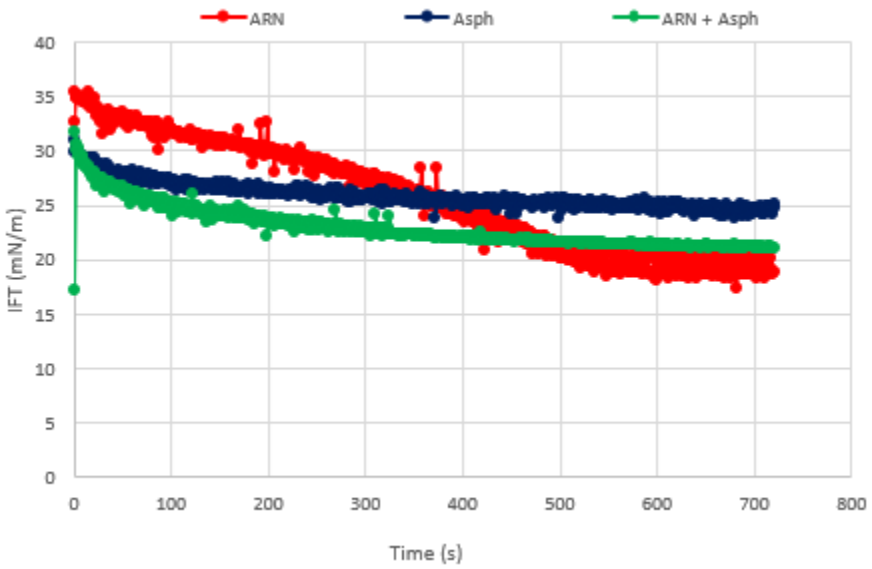

Figure 12: Comparison of the exchange for the experiments done for 2.5 μM ARN, asphaltenes and a mixture of 2.5 μM ARN and asphaltenes with an exchange time of 720 sec

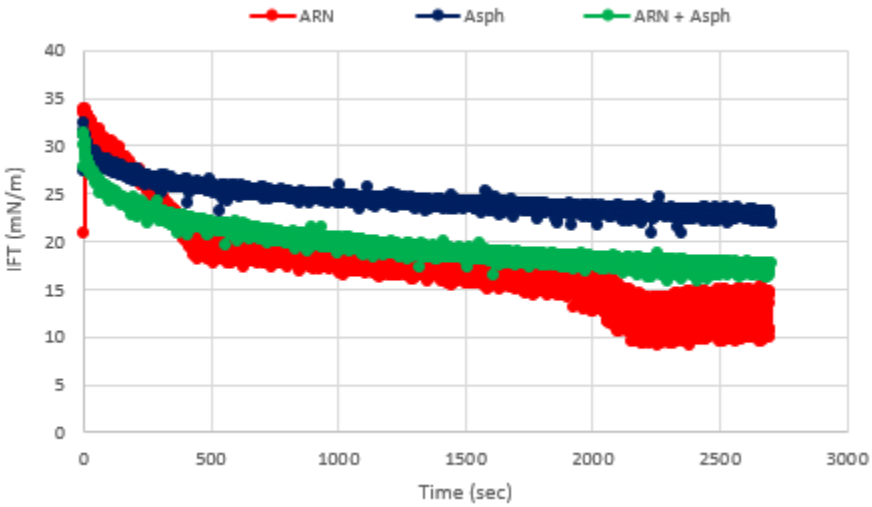

Figure 13: Comparison of the exchange for the experiments done for 2.5 μM ARN, asphaltenes and a mixture of 2.5 μM ARN and asphaltenes with an exchange time of 2700 sec

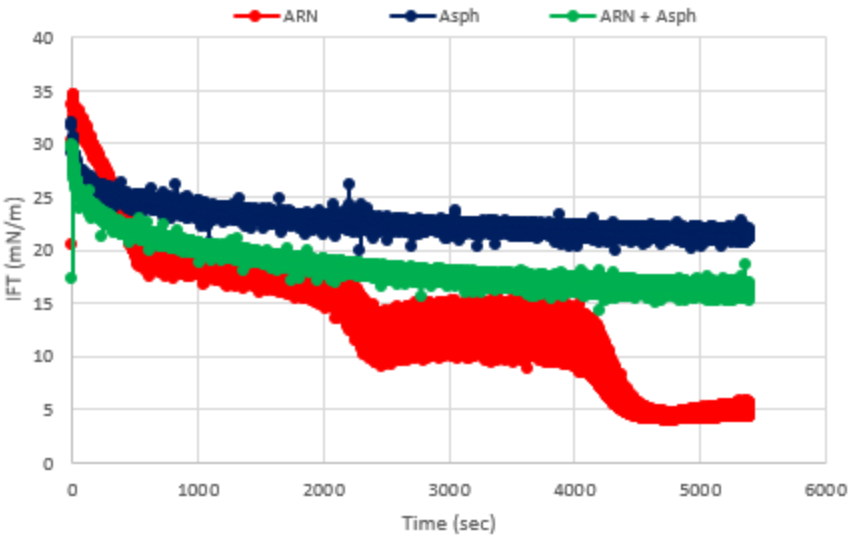

Figure 14: Comparison of the exchange for the experiments done for 2.5 μM ARN, asphaltenes and a mixture of 2.5 μM ARN and asphaltenes with an exchange time of 5400 sec

4.1.4 Oscillation

The oscillation experiments were done because E' is an indication of gel formation. The results for E' and E'' with an exchange time of 720, 2700 and 5400 sec can be seen in figure 15, 16 and 17. For pure ARN the value is high for longer times. By looking at the values of E' for ARN at all 3 times it is possible to see that a total time of 3200 sec is not enough to form a strong gel, but at 7880 sec the gel formation is a lot higher. For the mixture of ARN and asphaltenes the E' value is low for all times. This could be a result of asphaltenes is desorbing the ARN and the gel is not formed in the presence of asphaltenes. The results show E' is highest for ARN and lower for ARN-asphaltenes for all times. This is because the presence of asphaltenes prevent the gel formation. Asphaltenes do not cause gel formation, therefore the value for asphaltenes is always low.

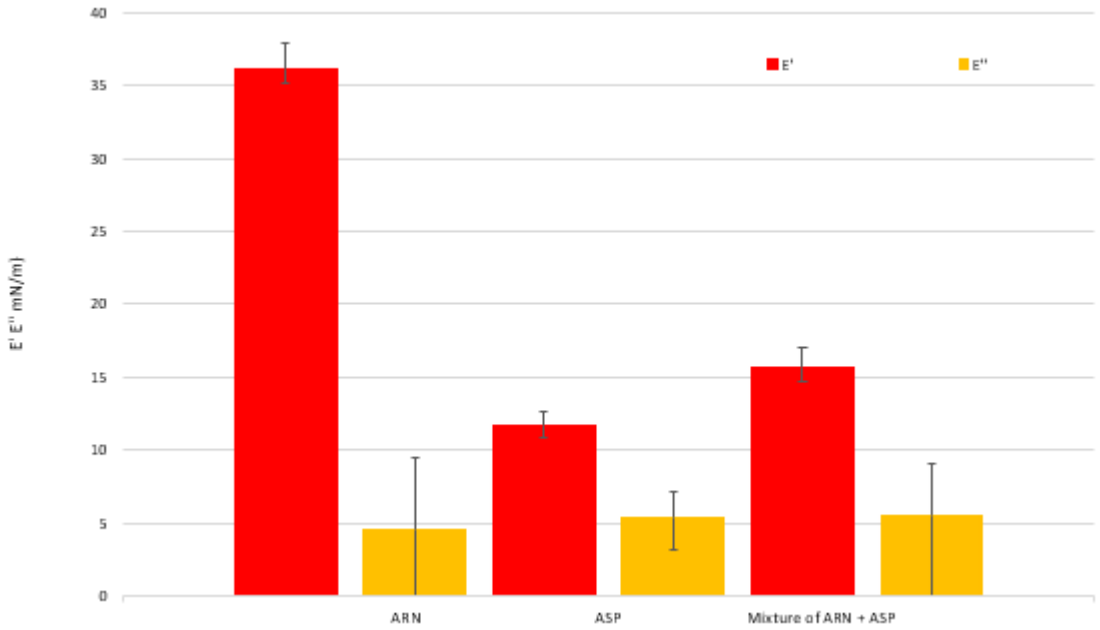

Figure 15: Comparison of E′ and E″ for the experiments done for 2.5 μM ARN, asphaltenes and a mixture of 2.5 μM ARN and asphaltenes with an exchange time of 720 sec

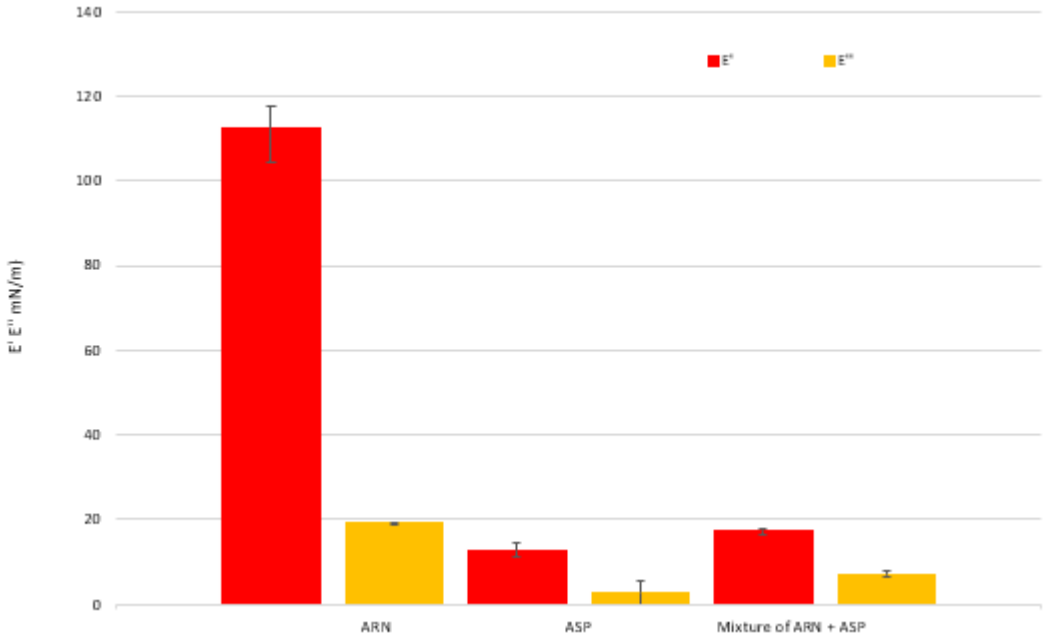

Figure 16: Comparison of E′ and E″ for the experiments done for 2.5 μM ARN, asphaltenes and a mixture of 2.5 μM ARN and asphaltenes with an exchange time of 2700 sec

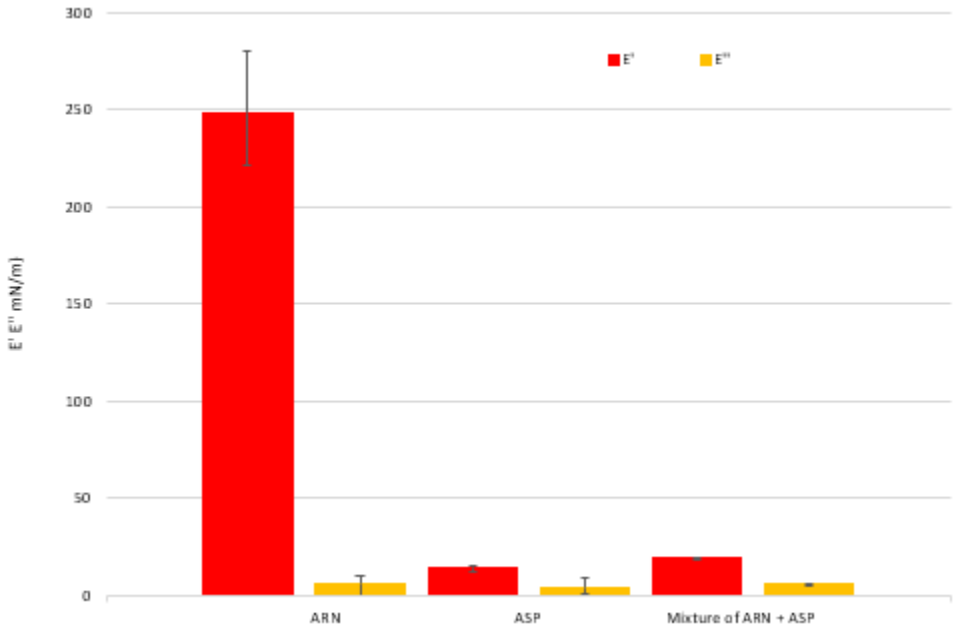

Figure 17: Comparison of E′ and E″ for the experiments done for 2.5 μM ARN, asphaltenes and a mixture of 2.5 μM ARN and asphaltenes with an exchange time of 5400 sec

4.1.5 Conclusion

A strong gel is formed for experiments for 2.5μM ARN with an exchange time of 5400 seconds, but 720 seconds is not enough to create a strong gel for 2.5μM ARN. The adsorption layer of ARN is being reorganized for experiments with longer time. The behaviour of the mixture of ARN and asphaltenes is very similar to the behavior of asphaltenes, and the presence of asphaltenes in the mixture prevents gel formation.

4.2 Influence of the Amplitude on oscillation fit

4.2.1 Goal

Determine the best amplitude value to achieve a good fit for the oscillation curve.

4.2.2 Solution

Study the fit of the last period of oscillation of experiments done with different amplitude values. Three different amplitude values were chosen for the three parallels done for 2.5 μM ARN with an exchange time of 5400 sec shown in figure 14 used to calculate the E' and E" values shown in figure 17.

4.2.3 Amplitude

The results of the last period with an amplitude of 3.5% , 3.0% and 2.5% can be seen in figure 18, 19 and 20. For all values the fit of the curve was OK, the fit at the top and bottumn of the curve where slightly off the fit sometimes. The curve was not a perfect sinus curve, but the results where the same for all amplitude values, which shows that a small change in the amplitude does not have a large impact on the fit of the curve.

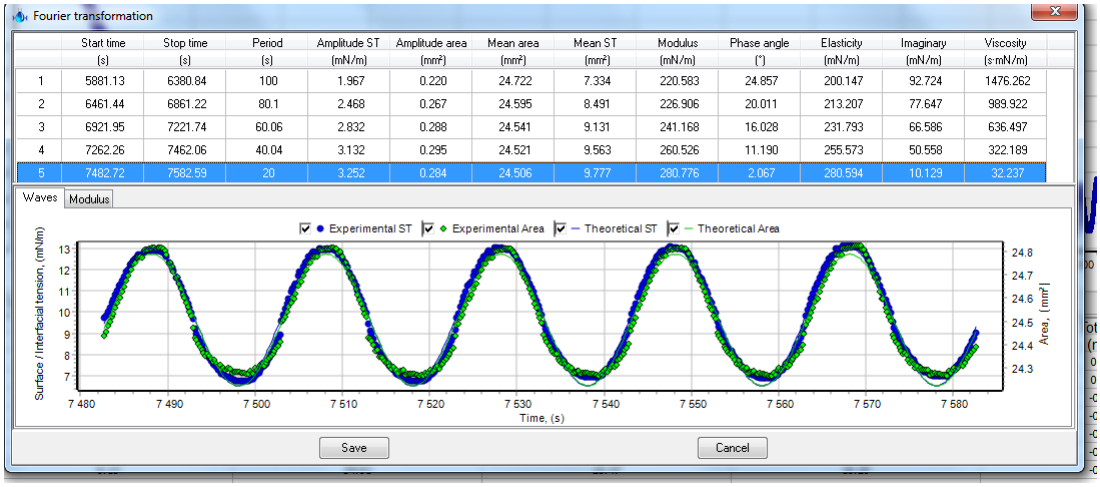

Figure 18: The fit of the curve for the last period of oscillation for the experiment with an amplitude value of 3.5%

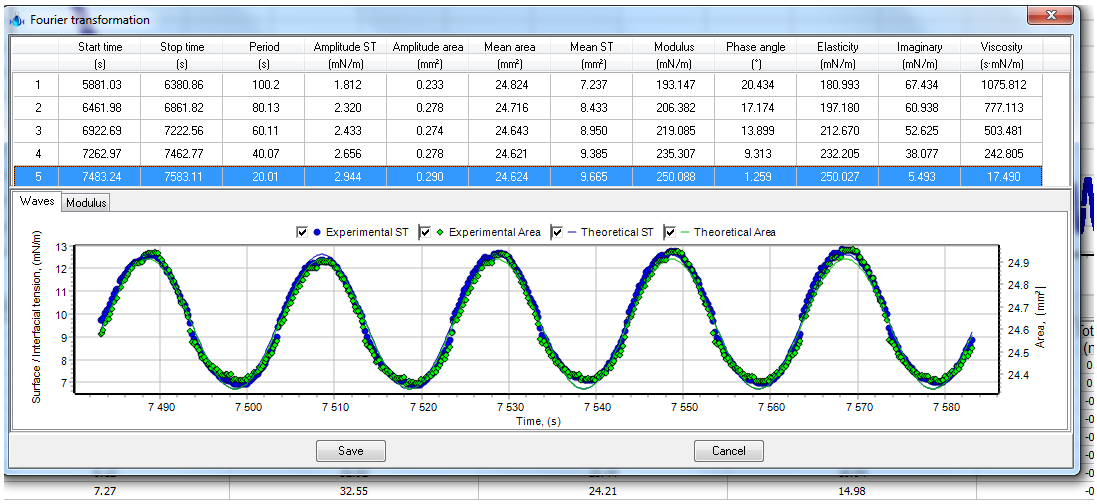

Figure 19: The fit of the curve for the last period of oscillation for the experiment with an amplitude value of 3.0%

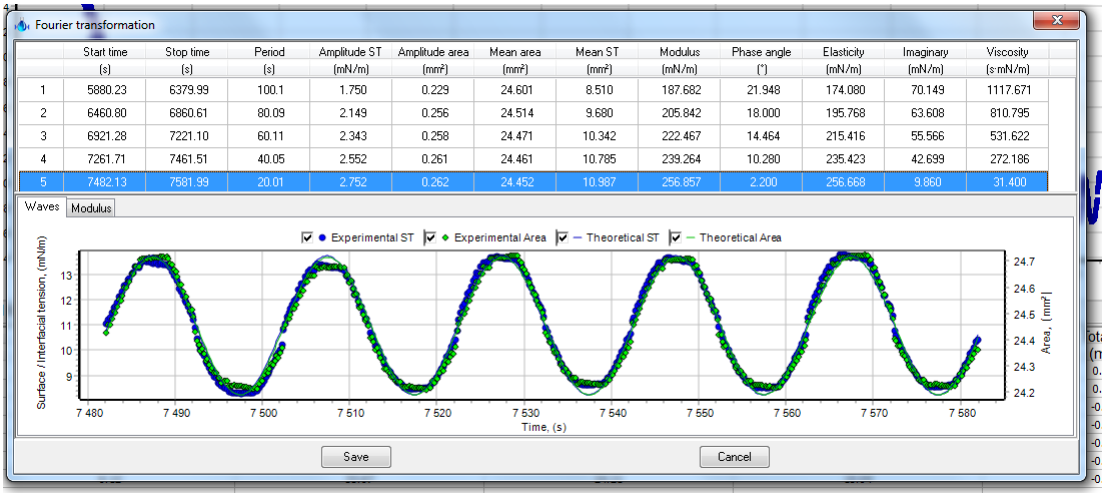

Figure 20: The fit of the curve for the last period of oscillation for the experiment with an amplitude value of 2.5%

4.2.4 Oscillation

The E′ and E″ of the experiments with an amplitude of 3.5% , 3.0% and 2.5% can be seen in figure 21. All E′ values were very high. The change in amplitude did not result in a significant difference on the E′ and E″ values.

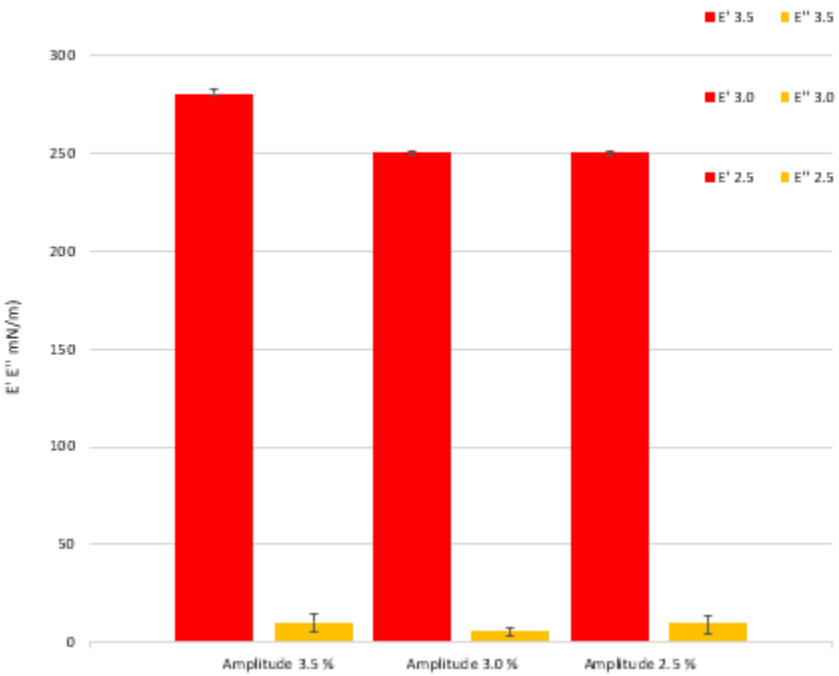

Figure 21: Comparison of E′ and E″ for an amplitude value of 3.5% , 3.0% and 2.5%

4.2.5 Conclusion

The change in amplitude did not result in a significant difference in the fit of the curves or E′ + E″ values. Therefore, the rest of the experiments were done with the same amplitude value (3.5%).

4.3 Influence of the pH on interfacial tension

4.3.1 Goal

To determine the highest possible pH value of the buffer when using the axisymmetric drop shape analysis (ADSA) technique.

4.3.2 Solution

Study the dilational interfacial rheology of 25 μM ARN using buffers with pH values 6, 7 and 8. The procedure used is with exchange, relaxation and oscillation. The procedure is described in chapter 3.6.1 Procedure 1.

4.3.3 Interfacial tension

The results for pH 6, 7 and 8 can be seen in figure 22, 23 and 24. From the figures for pH 6 and 7 it can be observed that the interfacial tension could be properly measured, but for pH 8 the results were bad because the drop falls down when the interfacial tension gets too low. New drops were formed during the experiment and gave bad interfacial tension values. The axisymmetric drop shape analysis (ADSA) technique can therefore not be properly performed with a concentration of 25 μM ARN and a pH 8 buffer.

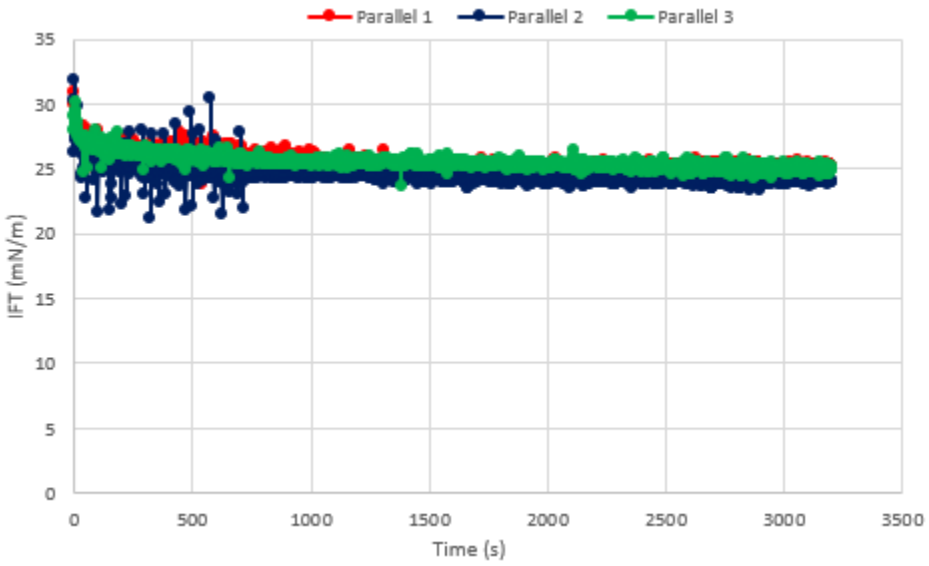

Figure 22: Experiments done for 25μM ARN with a pH 6 buffer

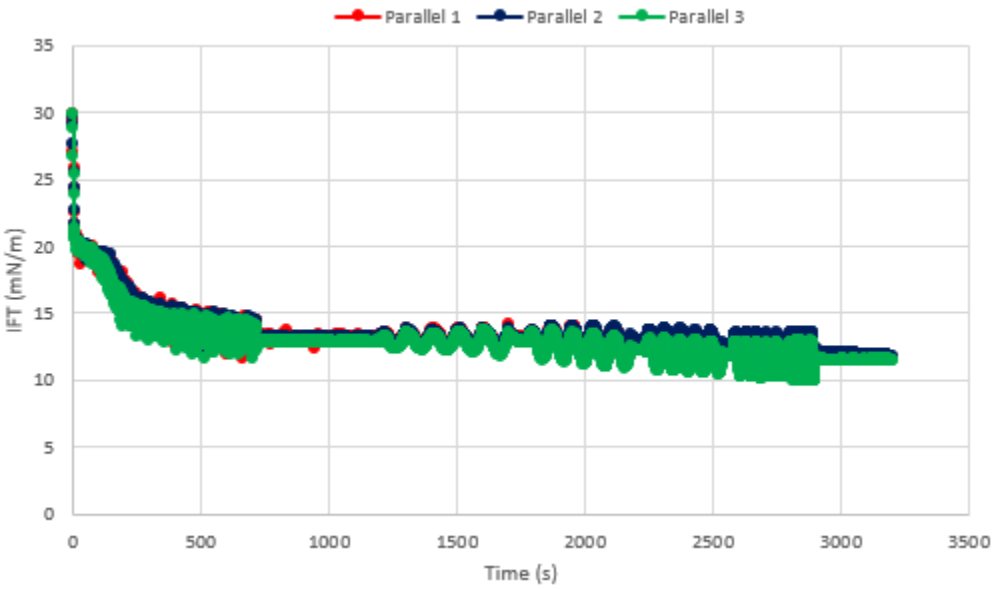

Figure 23: Experiments done for 25μM ARN with a pH 7 buffer

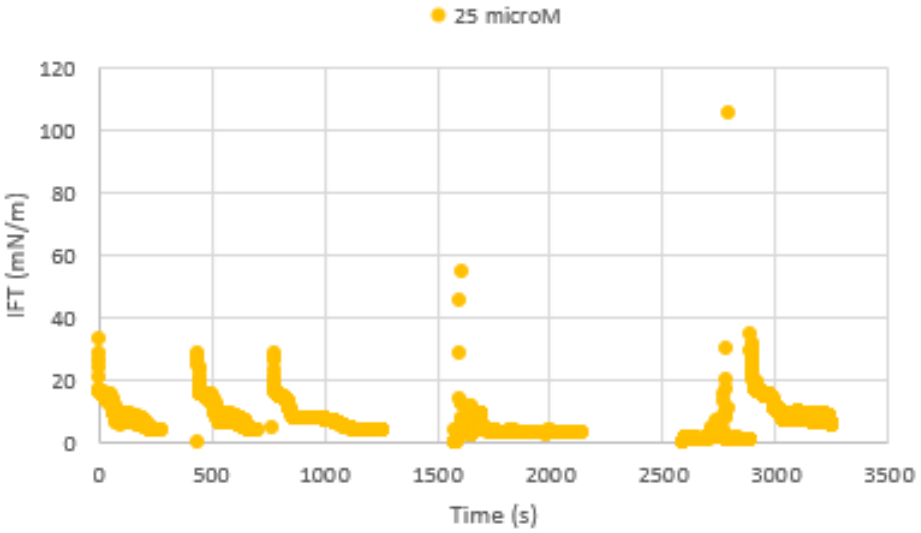

Figure 24: The experiment done for 25μM ARN with a pH 8 buffer

4.3.4 Oscillation

The results from the oscillation for pH 6 and pH 7 can be seen in figure 25. Because the drop was falling down for pH 8 the oscillation could not be done for pH 8. The figure show gel is formed for pH 7, but not for pH 6.

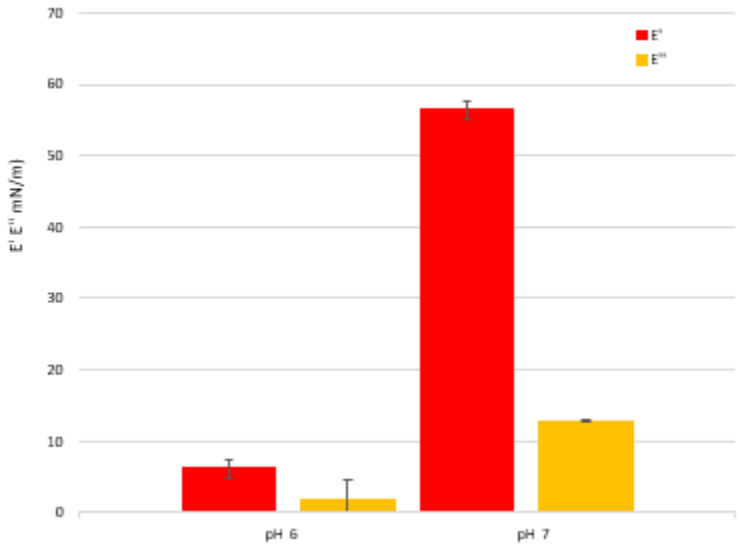

Figure 25: Comparison of E′ and E″ for an pH 6 and pH 7 for 25μM ARN

4.3.5 Conclusion

A buffer with pH 6 and 7 can be used with a concentration of 25 μM ARN, but for a buffer with pH 8 the axisymmetric drop shape analysis (ADSA) technique could not be done because new drops were formed during the experiment and gave bad interfacial tension values as a result of too high ARN concentration.

4.4 Influence of concentration of ARN on interfacial tension

4.4.1 Goal

To determine the highest possible concentration of ARN when using the axisymmetric drop shape analysis (ADSA) technique.

4.4.2 Solution

Study the dilational interfacial rheology with a pH 8 buffer using ARN concentrations of 25 μM, 15 μM, 10 μM and 9 μM. The procedure used is with exchange, relaxation and oscillation. The procedure is described in chapter 3.6.1 Procedure 1.

4.4.3 Interfacial tension

Because the axisymmetric drop shape analysis (ADSA) technique could not be done with a buffer of pH 8 and a concentration of 25 μM, two new experiments were done for 15 μM and 10μM ARN, to find the highest possible concentration. The results of the experiments for all 3 concentrations can be seen in figure 26.

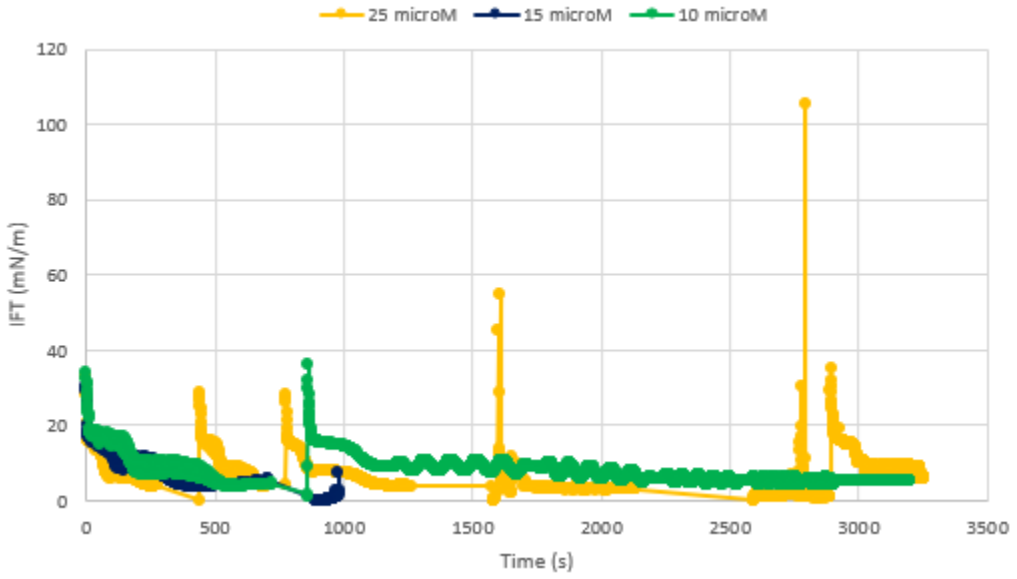

Figure 26: Experiments done for 25μM ARN, 15μM ARN and 10μM ARN with a pH 8 buffer

The interfacial tension values are not good for any of the ARN concentrations used. Because the drop is falling off. This indicates that the experiment can not be done for a concentration of 10 μM ARN at pH 8. New experiments were done for 10 μM and 9 μM ARN to determine if the experiment could not be done at 10 μM earlier because of pollution. The results from the experiments done for 10 and 9 μM ARN with a pH 8 buffer can be seen in figure 27. Here the interfacial tension is measurable and the drop did not fall off during the experiments.

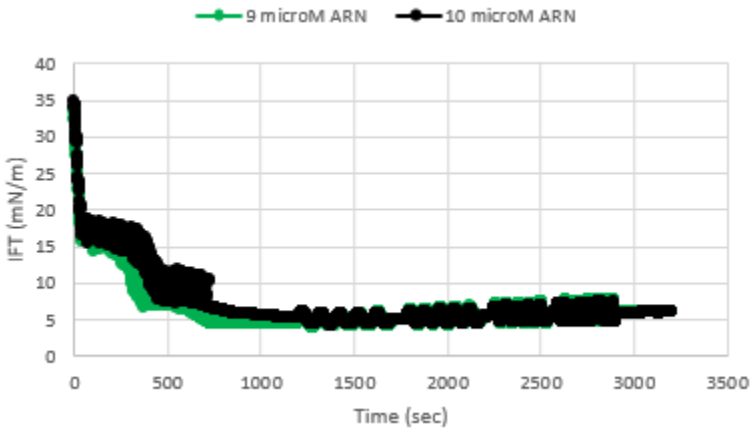

Figure 27: Experiments done for 10 and 9 μM ARN with a pH 8 buffer

4.4.4 Oscillation

The results from the oscillation of 10 μM and 9 μM ARN with a pH 8 buffer can be seen in figure 28. For 10 μM and 9 μM we can see some very high E″ values and very high errors. This could be a because of the assumptions for calculating the elasticity is not met and the pressure is not Laplace anymore. To look at the calculation of the E′ and E″ values the fit of the last period was analyzed.

Figure 28: Figure of E′ and E″for 10 μM and 9 μM ARN with a pH 8 buffer

4.4.5 Fit of the last period

The results of the last period of the experiments with 10 μM and 9 μM for both stocks can be seen in figure 29 - 32. For the first experiment with 10 μM ARN, the fit of the last period and the E′ + E″ values are good, but for the second stock of 10 μM ARN and both stocks of 9 μM ARN have a very bad oscillation fit and the E′ + E″ values are not valid. Because of the inconsistent fit of the last period, the axisymmetric drop shape analysis (ADSA) technique is difficult to use with an ARN concentration of 9 μM or higher, for pH8. From previous experiments we already know the fit and E′ + E″ values are consistent at 2.5 μM, 5.0 μM and 7.5 μM.

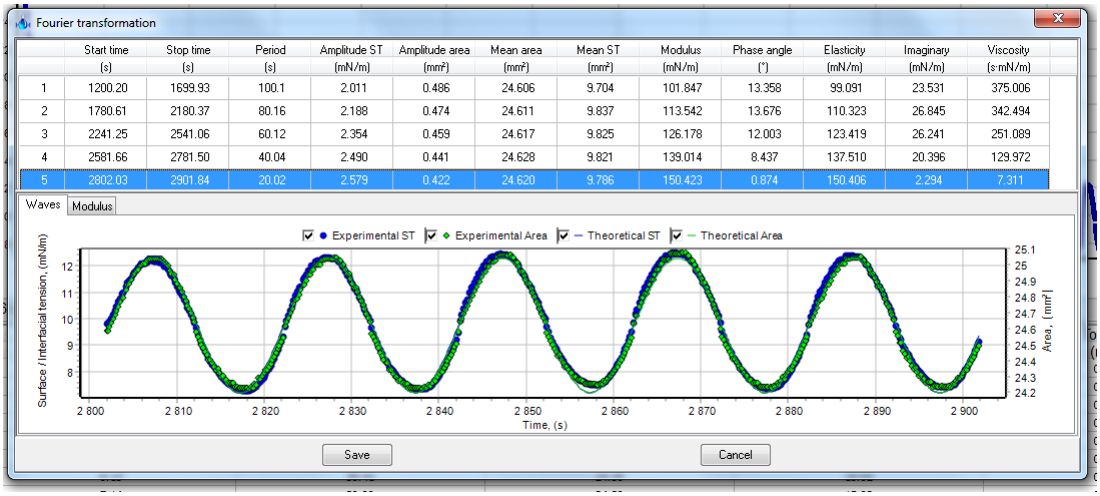

Figure 29: The fit of the curve for the last period of oscillation for the first stock with 10 μM

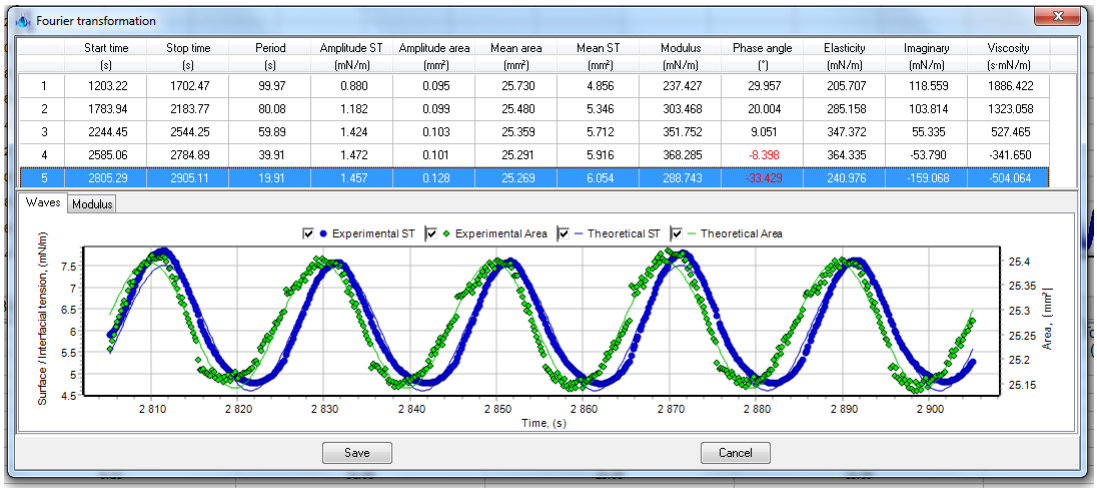

Figure 30: The fit of the curve for the last period of oscillation for the second stock with 10 μM

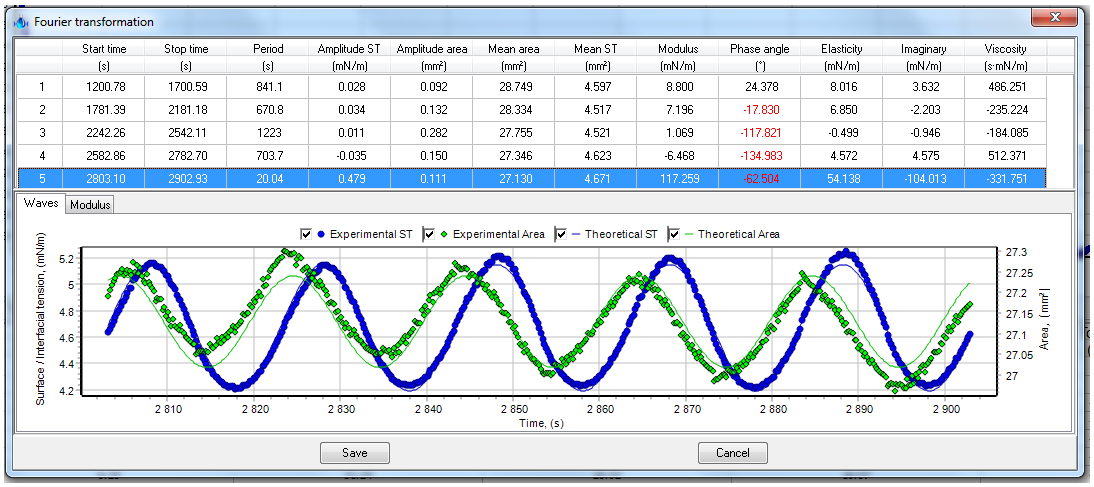

Figure 31: The fit of the curve for the last period of oscillation for the first stock with 9 μM

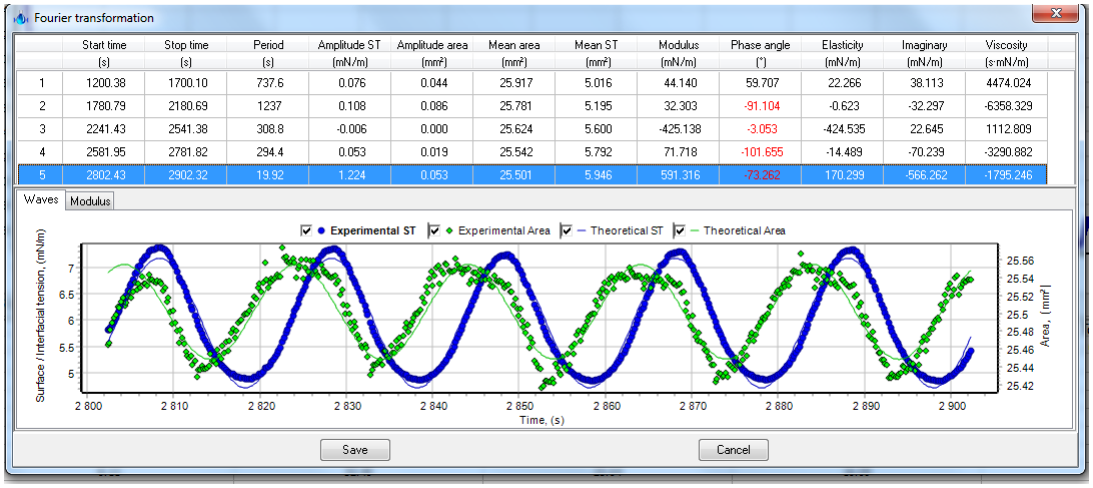

Figure 32: The fit of the curve for the last period of oscillation for the second stock with 9 μM

4.4.6 Conclusion

For 10 μM and 9 μM ARN with a pH 8 buffer the drop is hard to control, because the concentration is at the limit of what can be studied. Only one of the four experiments at 10 μM or 9 μM ARN could perform oscillation and calculate the gel formation properly because the gel is too strong to oscillate.

4.5 Determining if asphaltenes can desorb gel already formed

4.5.1 Goal

To check if asphaltenes can desorb gel that is already formed.

4.5.2 Solution

Study the dilational interfacial rheology with a new procedure where 7.5 μM ARN is first desorbed for one hour. The procedure with one hour of adsorption, then exchange, then relaxation and finally oscillation at the end. The procedure is described in chapter 3.6.2 Procedure 2.

4.5.3 Interfacial tension

To determine if asphaltenes can desorb gel already formed, experiments for 7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene were done with one hour of adsorption before the exchange. The results of the experiments with and exchange time of 720 seconds, 2700 seconds and 5400 seconds can be seen in figure 33, 34 and 35. Three parallels were done for 7.5 μM ARN-asphaltenes, 7.5 μM ARN-xylene and xylene-asphaltenes, all figures can be seen in Appendix figure 92 - 101. From the figures it is possible to see a significant change in the interfacial tension before the exchange is started for 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes. Because the same batches was used and the exchange was not started yet, the interfacial tension was expected to be fairly similar before the exchange. An explanation to the different results could be pollution. To determine if the system was clean, experiments with xylene-xylene were done. The system was found to be clean, the result of xylene-xylene can be seen in figure 107 in appendix.

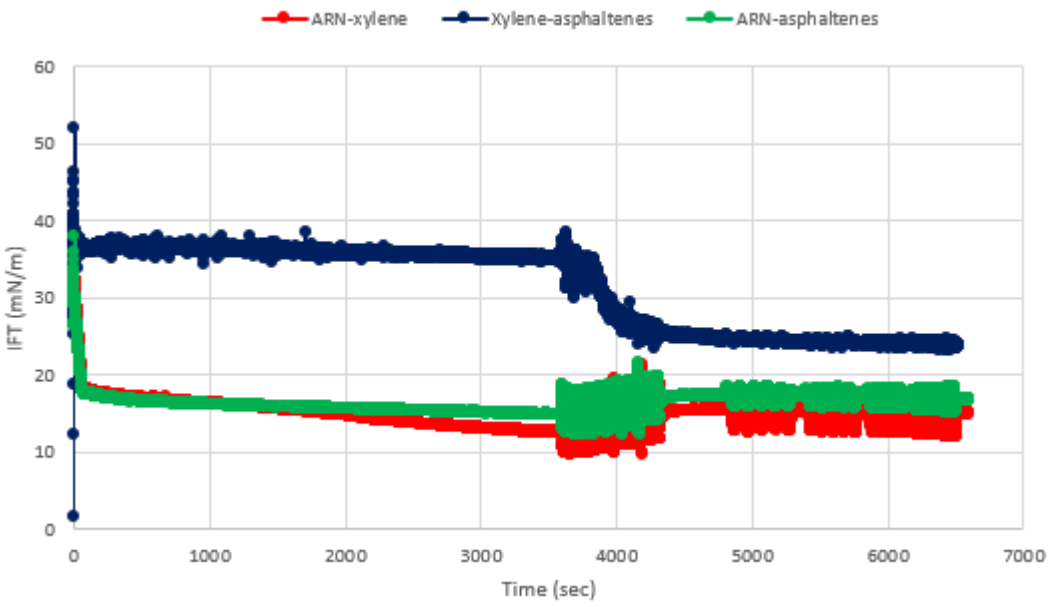

Figure 33: Comparison of 7.5 μM ARN-xylene, Xylene-asphaltenes and 7.5 μM ARN-asphaltenes with an exchange time of 720 sec started after one hour

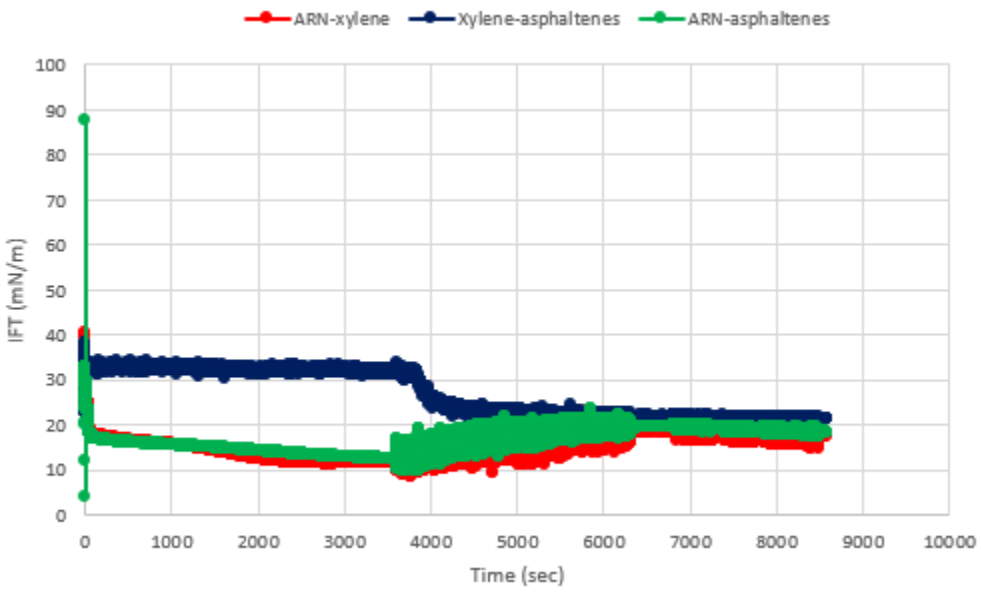

Figure 34: Comparison of 7.5 μM ARN-xylene, Xylene-asphaltenes and 7.5 μM ARN-asphaltenes with an exchange time of 2700 sec started after one hour

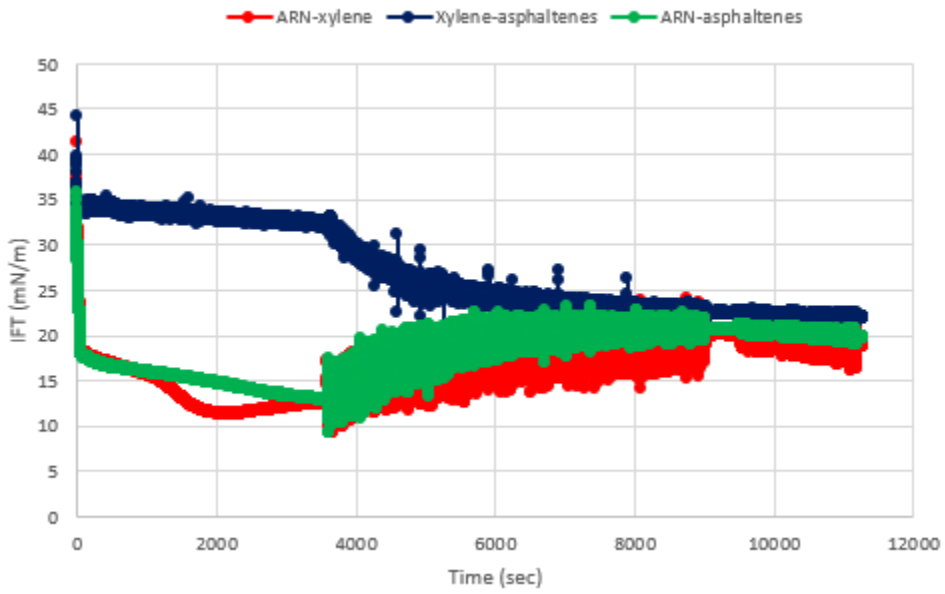

Figure 35: Comparison of 7.5 μM ARN-xylene, Xylene-asphaltenes and 7.5 μM ARN-asphaltenes with an exchange time of 5400 sec started after one hour

4.5.4 Oscillation

Oscillation for 7.5 μM ARN-asphaltenes and 7.5 μM ARN-XYL for 720, 2700 and 5400 seconds can be seen in figure 36, 37 and 38. From the figures it is possible to see that gel is formed for 7.5 μM ARN-XYL for all times, and that the E' value is low for 7.5 μM ARN-asphaltenes for all times. Which means there is no gel formed with 7.5 μM ARN-asphaltenes because the asphaltenes solution is desorbing the gel that is already formed. The pH of the buffer was measured after the experiments and did not change significantly.

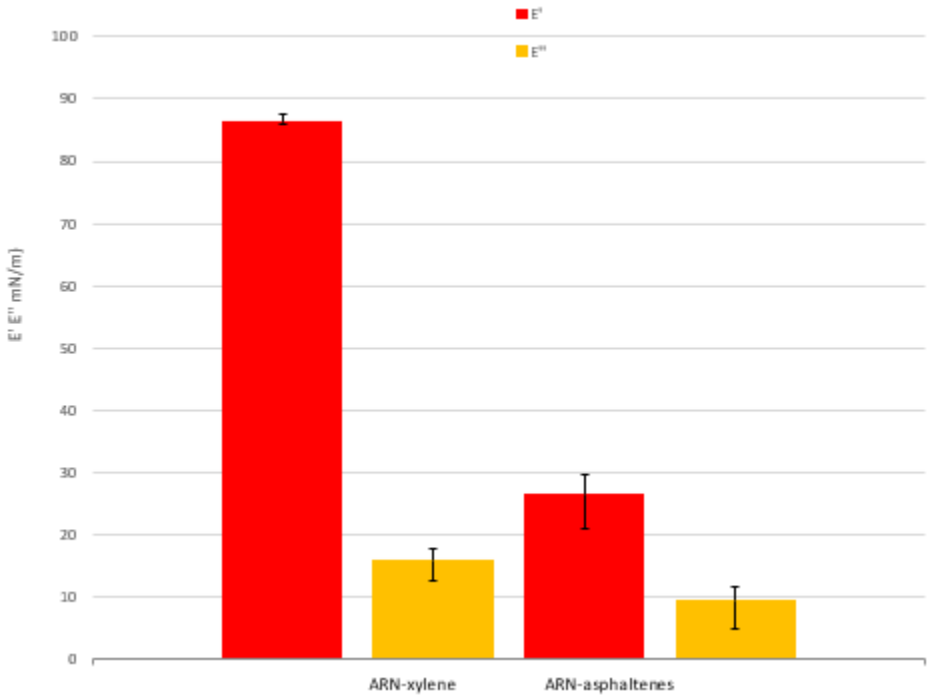

Figure 36: Comparison of E' and E'' for 7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene with an exchange time of 720 sec

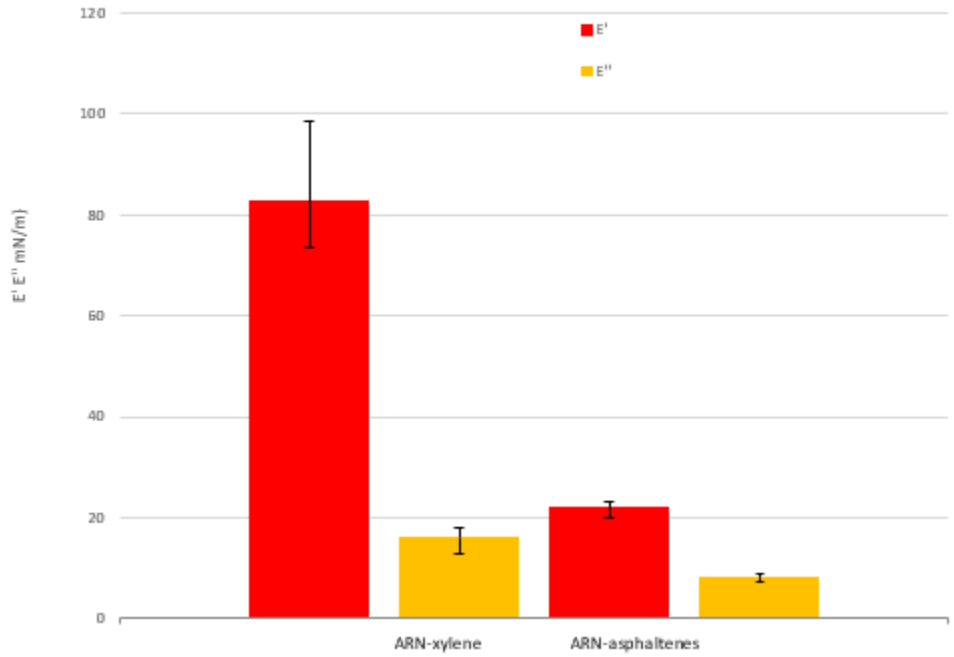

Figure 37: Comparison of E′ and E″ for 7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene with an exchange time of 2700 sec

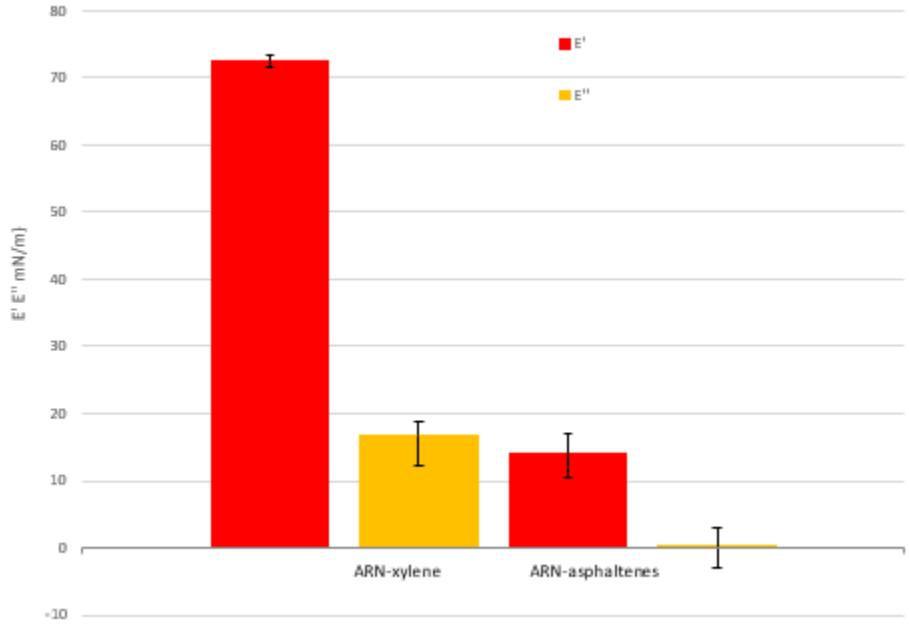

Figure 38: Comparison of E′ and E″ for 7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene with an exchange time of 5400 sec

4.5.5 Conclusion

7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene have different interfacial tension during the first hour with adsorption. This could be a result of pollution. Asphaltenes are desorbing the gel that is already formed.

4.6 Influence of asphaltenes pollution on ARN adsorption

4.6.1 Goal

To find a better procedure and to check if the different interfacial tension values obtained from previous experiments were a result of pollution in the pump or the drop of asphaltenes created before the experiment was started.

4.6.2 Solution

Study the dilational interfacial rheology with the same procedure, where 7.5 μM ARN is first desorbed for one hour, but this time with increased cleaning between the experiments to prevent pollution. The procedure is described in chapter 3.6.3 Procedure 3. Experiments where also done where the asphaltenes drop was sucked in before start, and one experiment where only a small drop of asphaltenes was created. The procedure for a small drop and with asphaltenes sucked in is described in chapter 3.6.4 Procedure 4.

4.6.3 Interfacial tension

Because the experiments from chapter 4.5 had different results of 7.5 μM ARN-XYL and 7.5 μM ARN-asphaltenes before one hour, two new parallels were done for both samples to check if the experiments follow this trend, or if the results were caused by pollution. This time the procedure was changed, the samples were cleaned with chloroform and xylene before the experiment. The results of the first parallel with 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes can be seen in figure 39. The trend was the same as previously, the interfacial tension was higher for 7.5 μM ARN-asphaltenes before one hour.

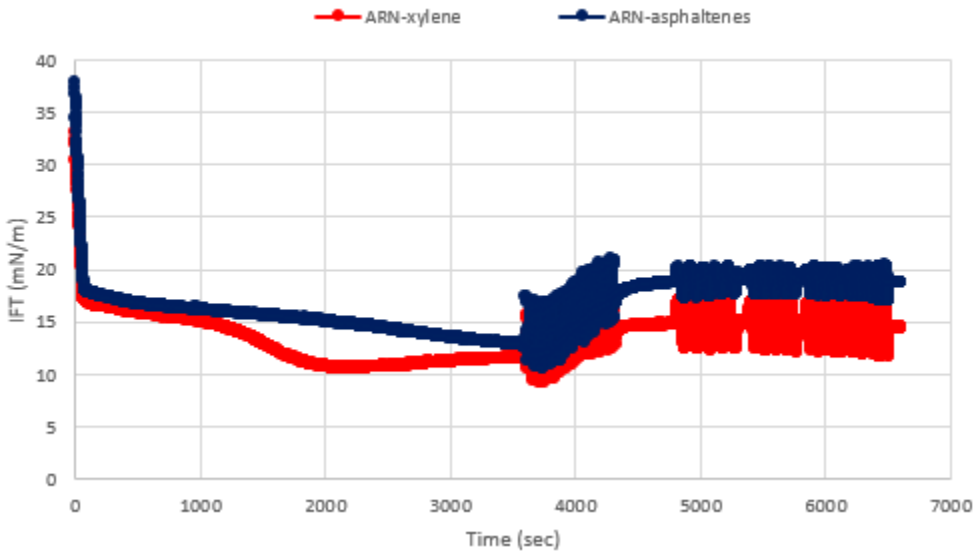

Figure 39: Comparison of the first parallel of the new samples of 7.5 μM ARN-XYL and 7.5 μM ARN-asphaltenes with an exchange time of 720 sec without removing 4 ARN drops before the experiment where started

For the second parallel four drops of 7.5 μM ARN were added before the experiment was started to prevent the pollution of asphaltenes. The results of the second parallel with 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes can be seen in figure 40. The figure show the IFT got slightly lower compared to parallel one, but the interfacial tension is still higher for 7.5 μM ARN-asphaltenes than 7.5 μM ARN-xylene. An explanation to this could be that the one drop of asphaltenes that is formed before the experiment is started, is influencing the result significantly, even with additional cleaning with ARN droplets.

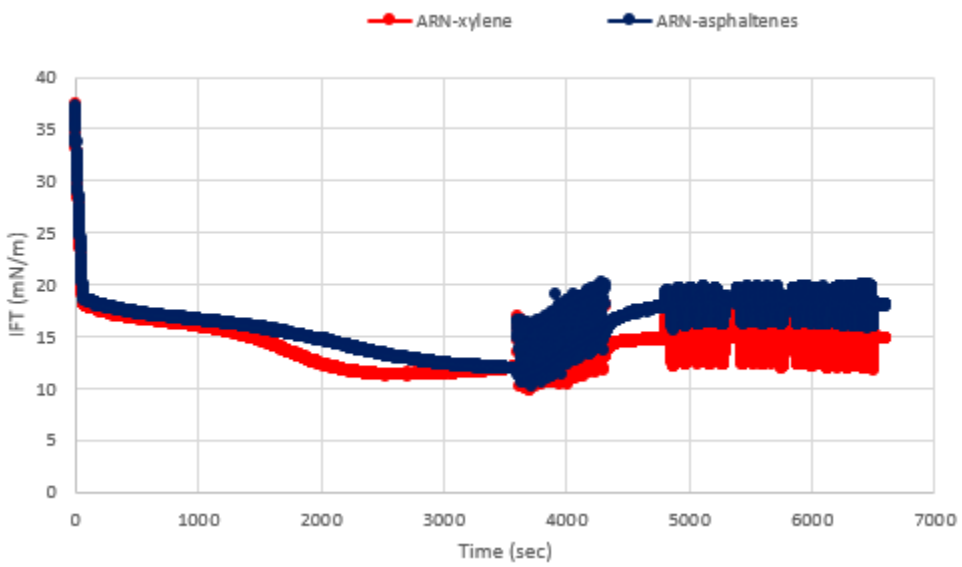

Figure 40: Comparison of the second parallel of the new samples of 7.5 μM ARN-XYL and 7.5 μM ARN-asphaltenes with an exchange time of 720 sec with removing 4 ARN drops before the experiment where started

4.6.4 Comparison of experiments with different procedures

To check if the new cleaning procedure improved the results, the interfacial tension of the samples using the new procedure was compared to the interfacial tension of the samples using the old procedure. The comparison can be seen in figure 41. All ARN-asphaltenes experiments had higher interfacial tension than ARN-xylene during the adsorption. From the figure it is possible to observe that the cleaning with chloroform + ARN drops have the lowest interfacial tension, then the cleaning with chloroform without ARN drops and then the 3 parallels with the old procedure. Even if the concentration of the new and old samples are not exactly the same, the result indicates that the cleaning procedure has been improved.

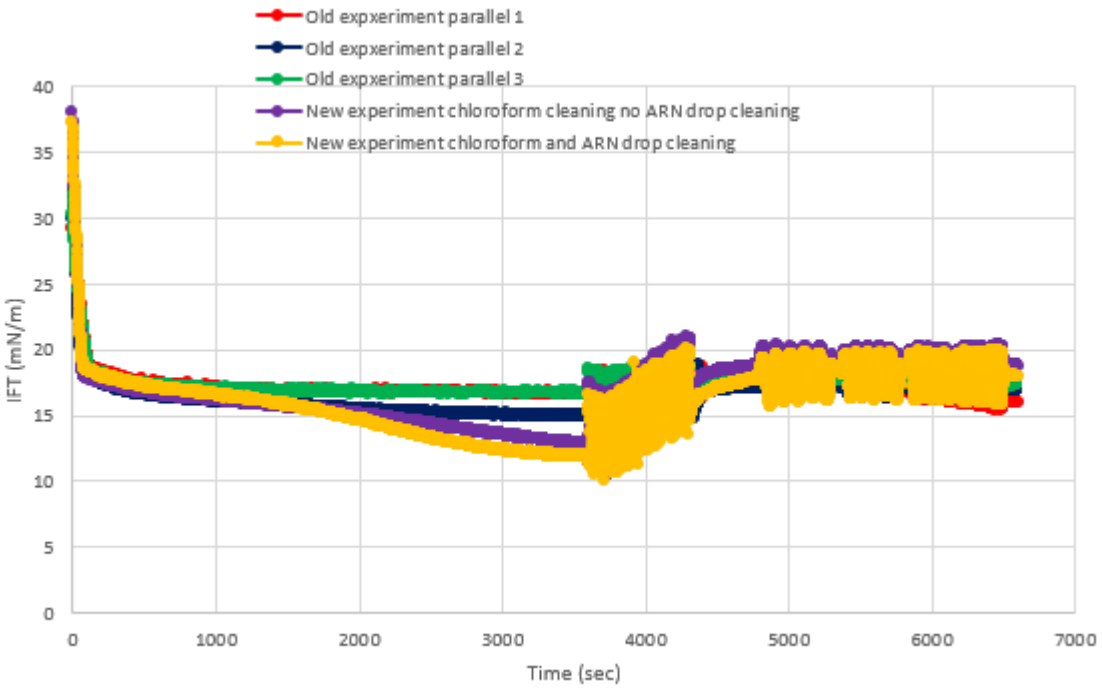

Figure 41: Comparison of the old samples of 7.5 μM ARN-asphaltenes and 7.5 μM ARN-asphaltenes with an exchange time of 720 sec started after one hour with the new samples. One of the new samples was done with cleaning of 4 ARN drops and one of the samples was done without, but both new samples were cleaned with chloroform

4.6.5 Experiments with asphaltene drop sucked in and with a small drop of asphaltenes

The results of the experiments where the asphaltenes drop was sucked in before start, and the experiment where only a small drop of asphaltenes was created can be seen in figure 42 and 43. Comparing the plot of the two new experiments to the data for 7.5 μM ARN - asphaltenes and 7.5 μM ARN - xylene, it is possible to observe that the data is very similar to the data for 7.5 μM ARN - asphaltenes.

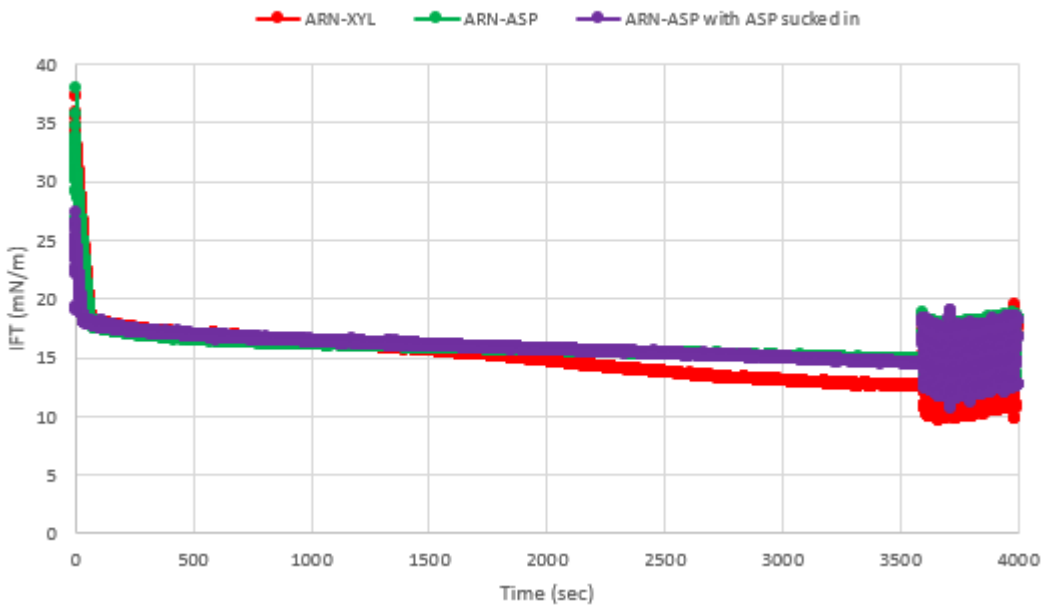

Figure 42: Comparing the experiment where asphaltenes was sucked in before the experiment was started to 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes

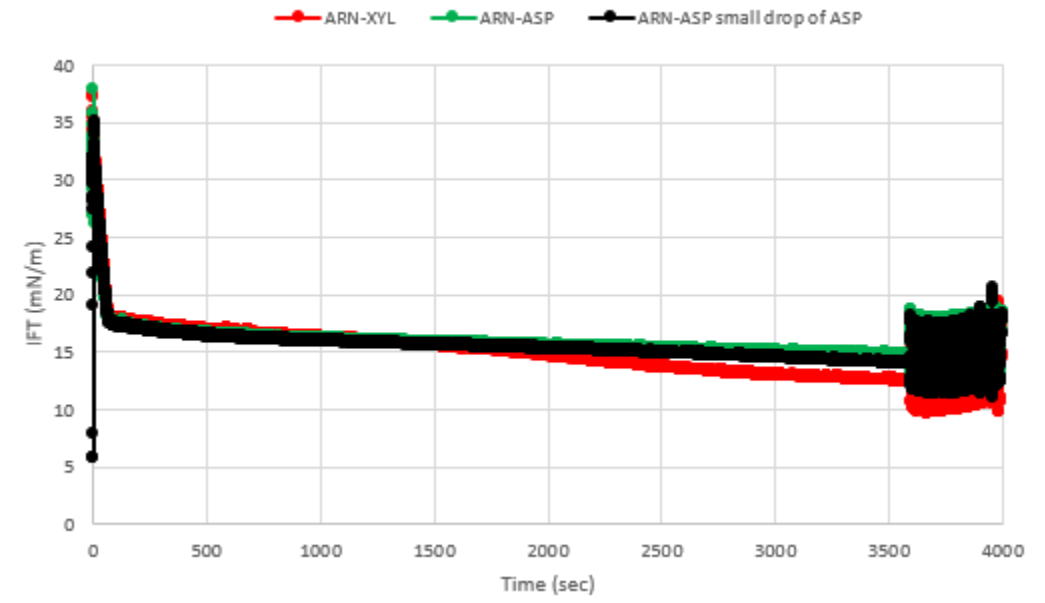

Figure 43: Comparing the experiment where only a small drop of asphaltenes was created before the experiment to 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes

4.6.6 Conclusion

The new procedure with more thorough cleaning show an improvement in the result, but it follows the same trend as previously during the adsorption of 7.5 μM ARN-XYL and 7.5 μM ARN-asphaltenes. The new experiments where a smaller asphaltene drop is formed before the experiment where started and the experiment where the asphaltenes drop was sucked in before the experiment where started could not explain why 7.5 μM ARN - asphaltenes and 7.5 μM ARN - xylene have different interfacial values during the adsorption. The difference could therefore not be proven to be a result of pollution by the samples in the pumps or by the procedure used before the experiment where started.

4.7 Influence of the exchange on interfacial tension after adsorption

4.7.1 Goal

Determine the interfacial conditions for ARN and asphaltenes after adsorption.

4.7.2 Solution

Study the dilational interfacial rheology of 7.5 μM ARN - xylene, xylene - 0.4g/L asphaltenes and 7.5 μM ARN - 0.4g/L asphaltenes with an exchange time of 720, 2700 and 5400 sec. The procedure used is with one hour of adsorption, then exchange, then relaxation, then oscillation and with the new cleaning procedure. The procedure is described in chapter 3.6.3 Procedure 3.

4.7.3 Interfacial tension

The data comparing the interfacial tension of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 0, 720, 2700 and 5400 sec can be seen in figure 44, 45, 46 and 47. All figures show that xylene-asphaltenes have an interfacial tension of approximately the expected value of 35 mN/m for pure xylene before the exchange, the interfacial tension is then reduced after the exchange is started. This trend was expected and indicates that the system is clean and pollution is not influencing the system significantly. For all exchange times 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes are fairly similar, but the interfacial tension is always slightly lower for 7.5 μM ARN-xylene.

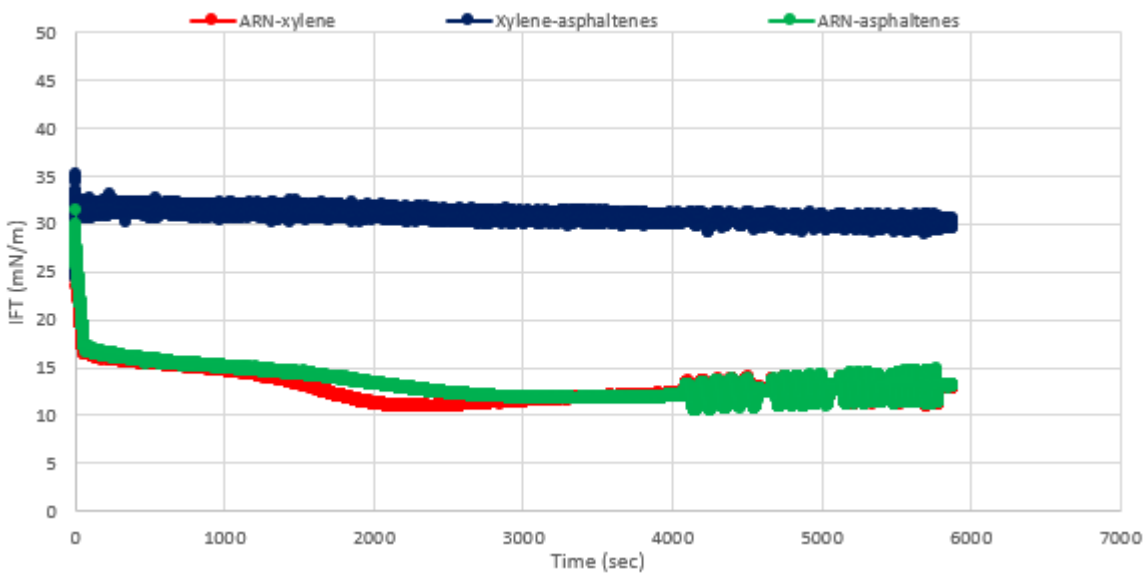

Figure 44: Comparing the interfacial tension of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes without exchange

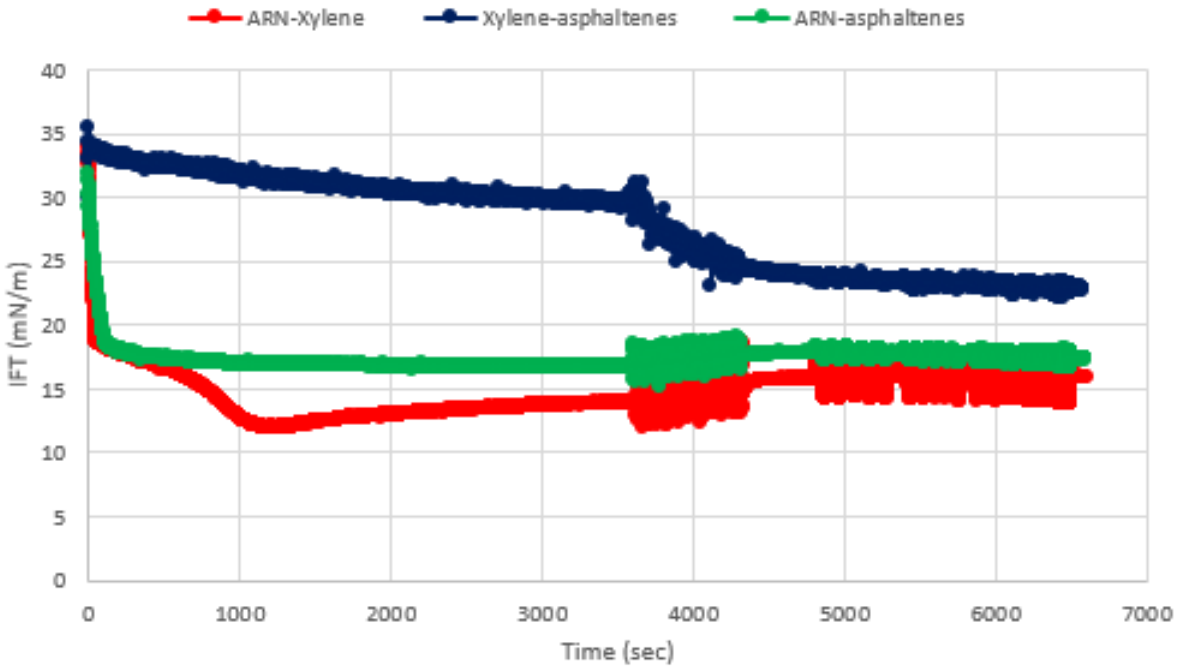

Figure 45: Comparing the interfacial tension of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 720 sec

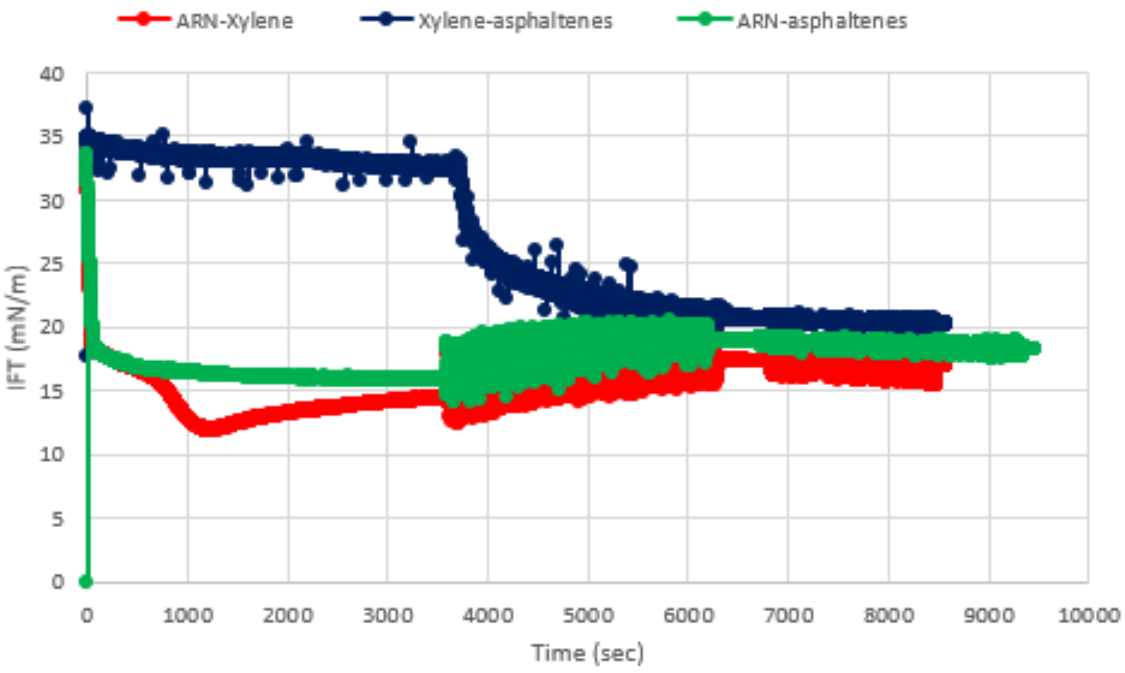

Figure 46: Comparing the interfacial tension of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 2700 sec

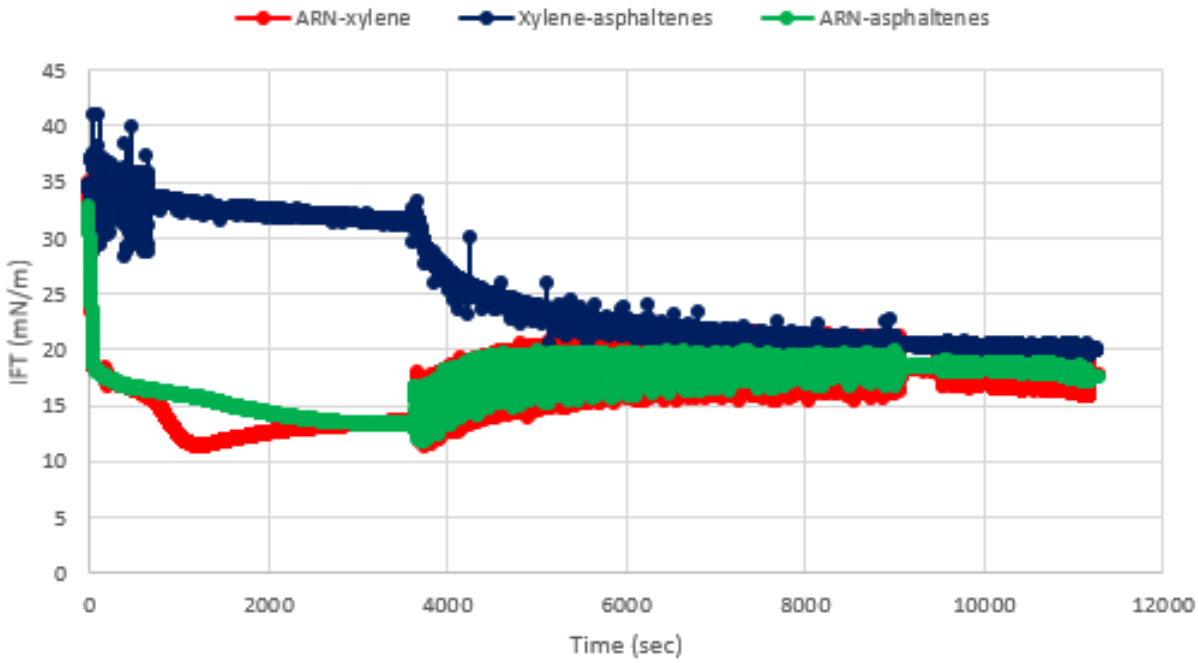

Figure 47: Comparing the interfacial tension of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 5400 sec

4.7.4 Oscillation

The data comparing E′ and E″ of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 0, 720, 2700 and 5400 sec can be seen in figure 48, 49, 50 and 51. The figure for without exchange shows that the gel formation for 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes is the same. The asphaltenes can not desorb gel without exchange. The 3 figures with exchange show that asphaltenes are desorbing the gel, and that the desorbed amount is increasing with exchange time.

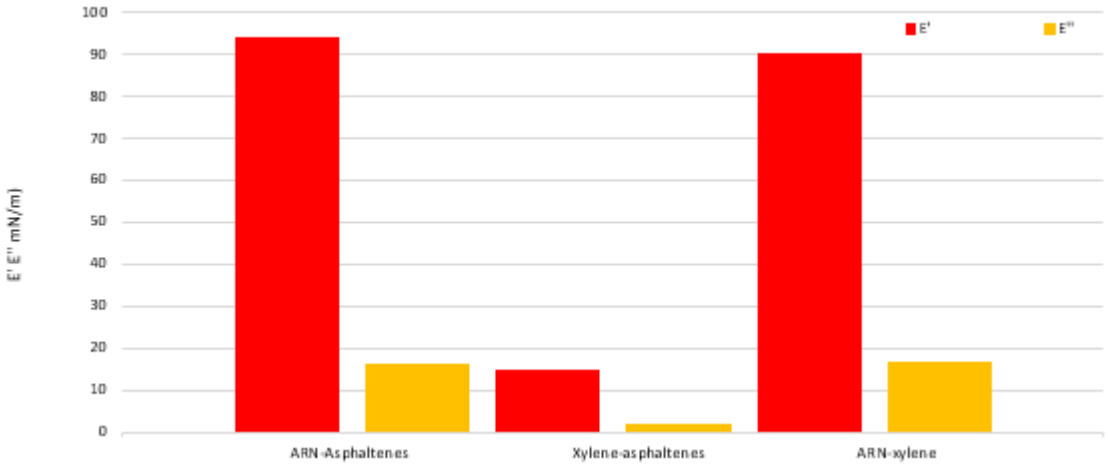

Figure 48: Comparing the E′ and E″ of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes without exchange

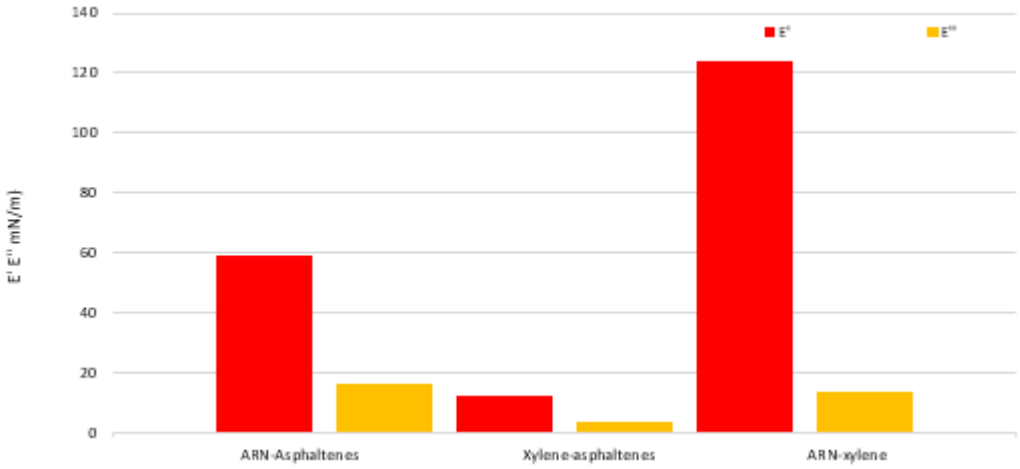

Figure 49: Comparing the E′ and E″ of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 720 sec

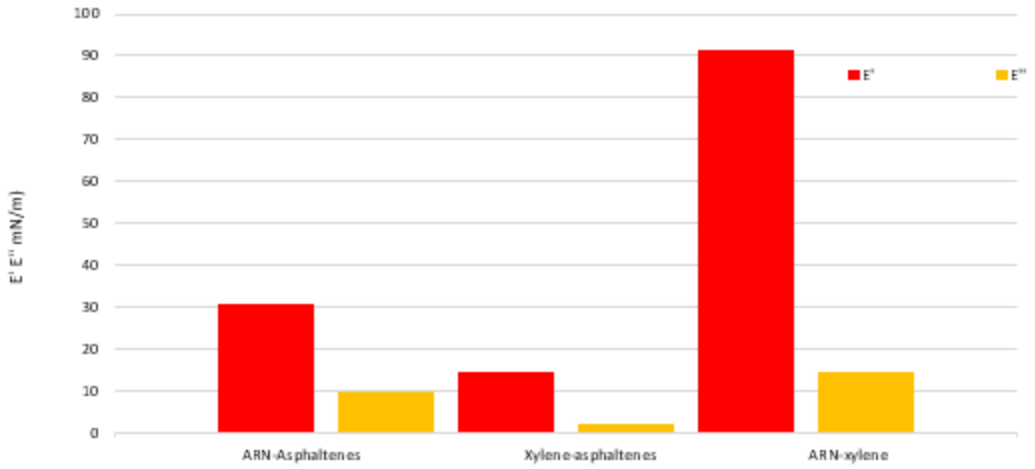

Figure 50: Comparing the E′ and E″ of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 2700 sec

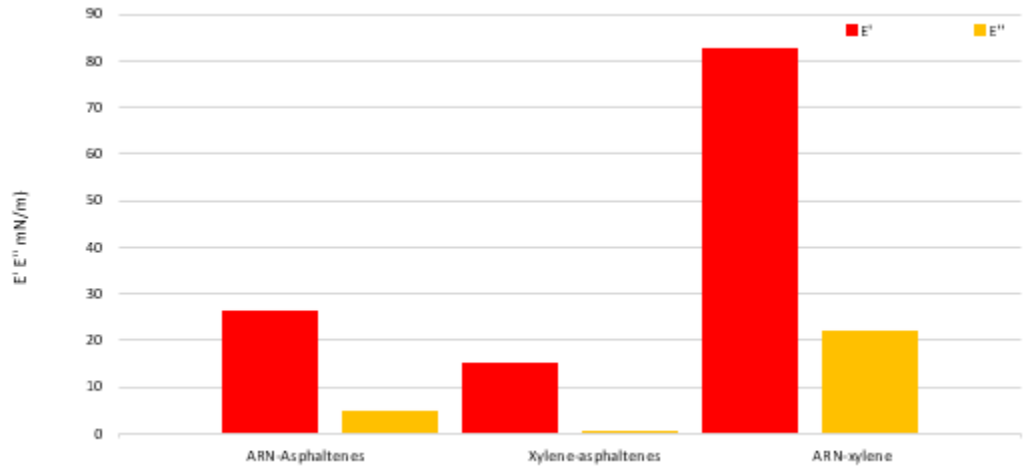

Figure 51: Comparing the E′ and E″ of xylene-asphaltenes, 7.5 μM ARN-xylene and 7.5 μM ARN-asphaltenes with an exchange time of 5400 sec

4.7.5 Conclusion

Asphaltenes are desorbing the gel already formed after exchange and the desorbed amount is increasing with exchange time.

4.8 Influence of coalescence on ARN

4.8.1 Goal

Determine the effect of coalescence on interfacial conditions for ARN.

4.8.2 Solution

One of the important steps in calcium napthenate deposit formation is when two drops with ARN go together, this is called coalescence. To mimic the process of coalescence experiments where done with a contracted volume from 25 μL to 15 μL after one hour. The total area of one big drop is lower than for the two drops that made it, this procedure mimics the coalescence process because both cases will have a decrease in area. The procedure used for for coalescence is described in chapter 3.6.5 Procedure 5.

4.8.3 Interfacial tension

In this section the dilational interfacial rheology of 2.5, 5.0 and 7.5 μM ARN with a constant volume and with contracted volume from 25 μL to 15 μL after one hour without exchange was studied. At least two parallel experiments were done. The results from stock 3 with an ARN concentration of 2.5 μM, 5.0 μM and 7.5 μM can be seen in figure 52, 53 and 54. All results from the stocks can be seen in figure 103, 104 and 105.

From the figures it is possible to observe that the interfacial tension is significantly decreased after the contraction. The interfacial tension is then increased during the relaxation. The interfacial tension is decreasing with increasing ARN concentration.

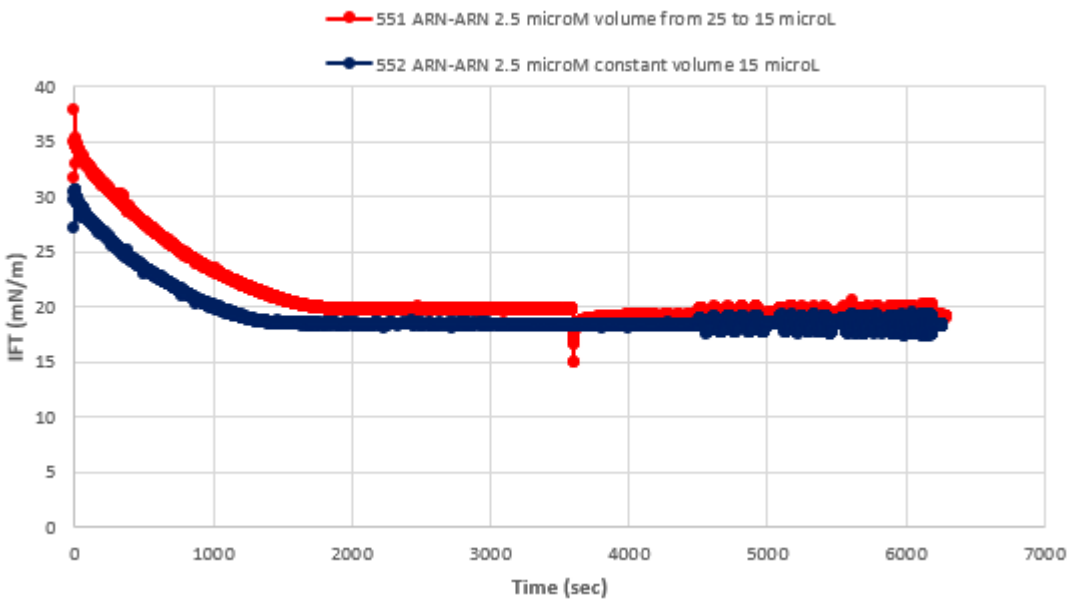

Figure 52: Comparison of the interfacial tension for 2.5 μM ARN with contracted volume from 25 to 15 μL after one hour and to an experiment with volume constant at 15 μL

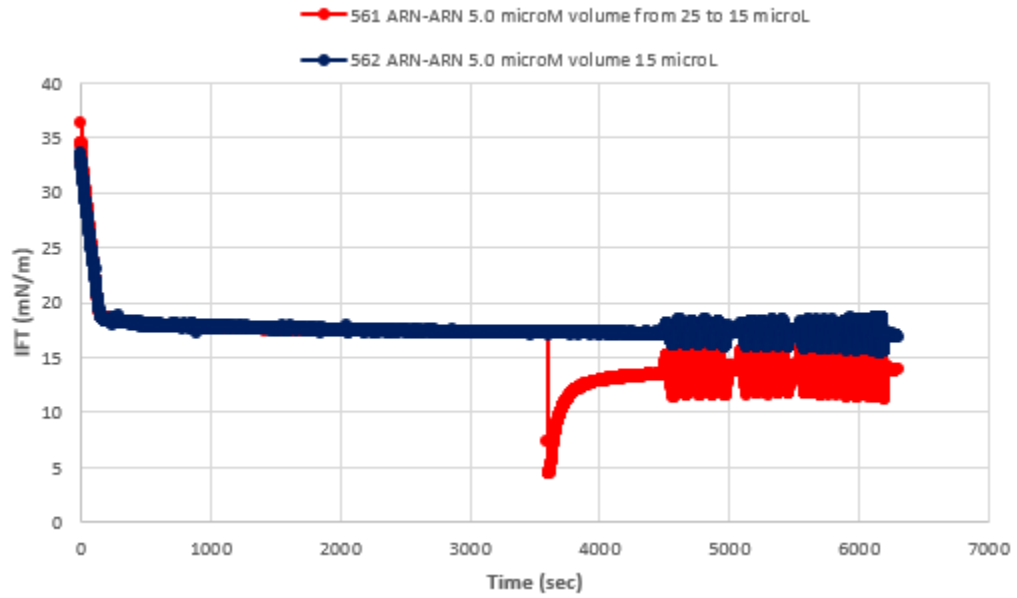

Figure 53: Comparison of the interfacial tension for 5.0 μM ARN with contracted volume from 25 to 15 μL after one hour and an experiment with volume constant at 15 μL

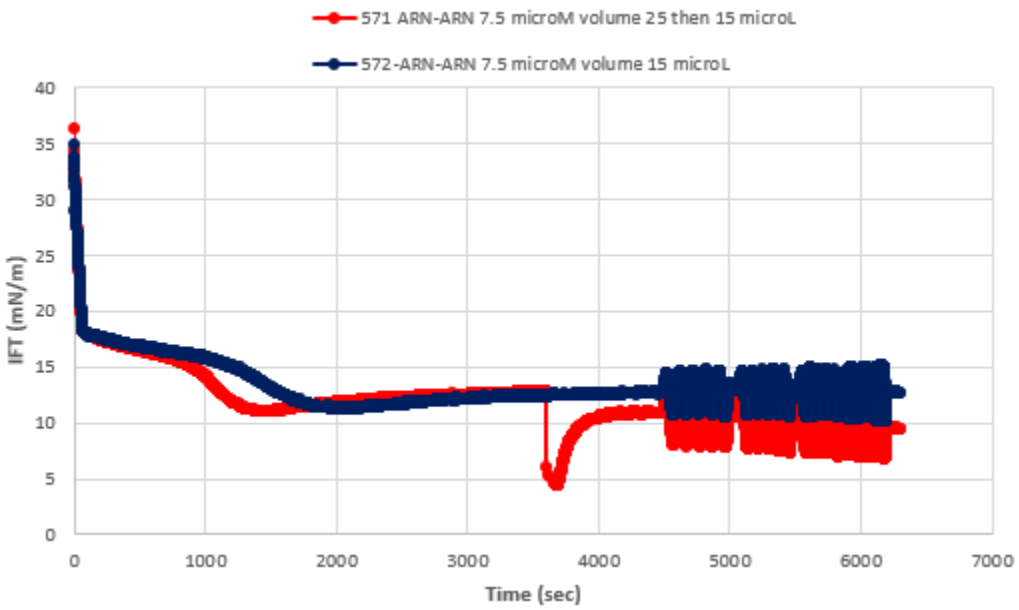

Figure 54: Comparison of the interfacial tension for 7.5 μM ARN with contracted volume from 25 to 15 μL after one hour and an experiment with volume constant at 15 μL

4.8.4 Oscillation

Comparison of E′ and E″ for 2.5 , 5.0 and 7.5 μM ARN can be seen in figure 55, 56 and 57. The results show that there is not formed a strong gel for 2.5 muM ARN, but gel is formed for 5.0 and 7.5 muM. Significantly more gel is formed when the volume is decreased after one hour for both stocks of 5.0 and 7.5 μM ARN. This show that coalescence will increase the gel formation.

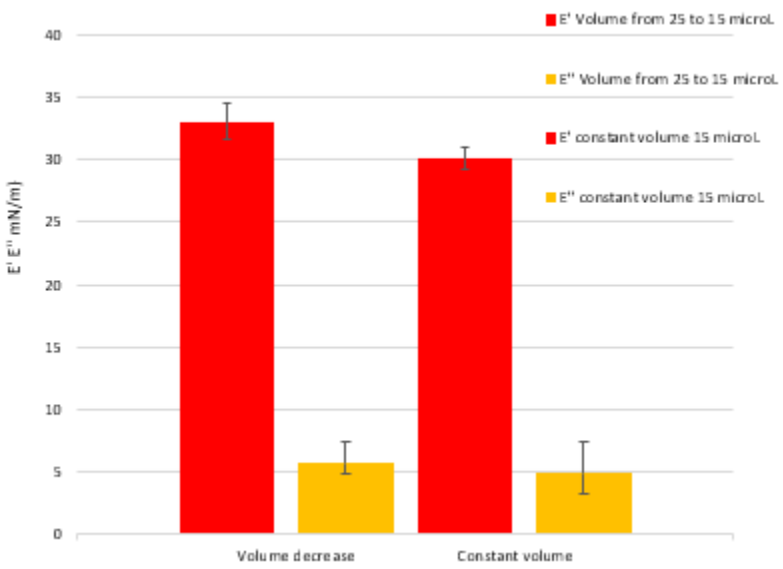

Figure 55: Comparison of the E′ and E″ for 2.5 μM ARN with contracted volume from 25 to 15 μL after one hour and an experiment with volume constant at 15 μL

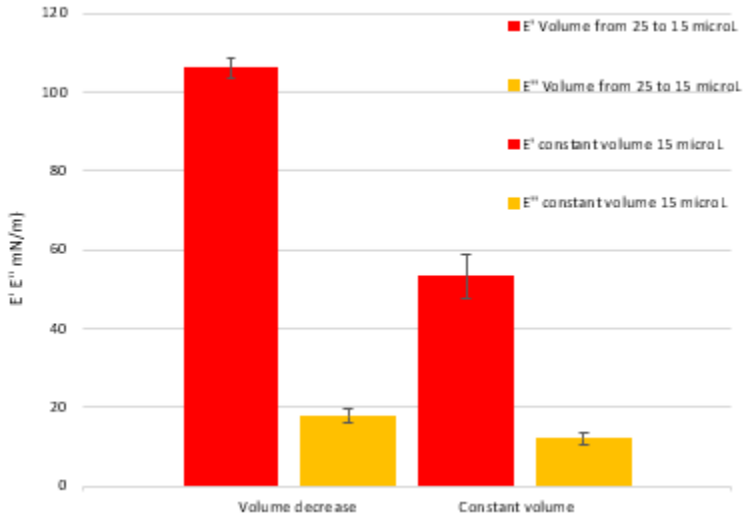

Figure 56: Comparison of the E′ and E″ for 5.0 μM ARN with contracted volume from 25 to 15 μL after one hour and an experiment with volume constant at 15 μL

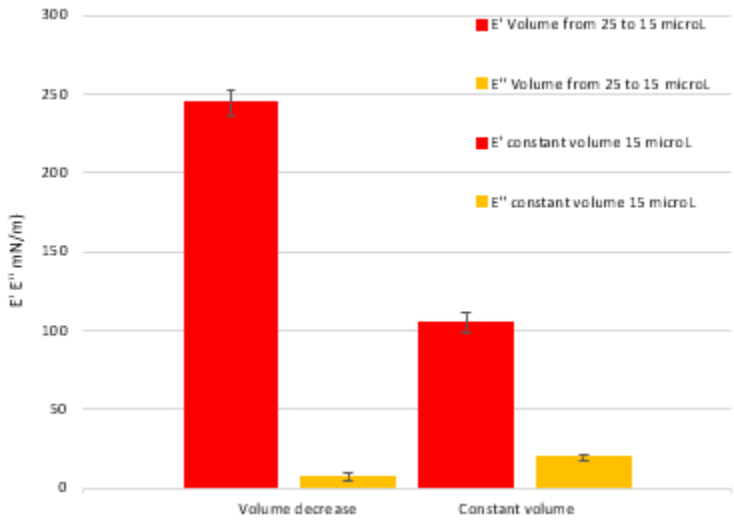

Figure 57: Comparison of the E′ and E″ for 7.5 μM ARN with contracted volume from 25 to 15 μL after one hour and an experiment with volume constant at 15 μL

4.8.5 Conclusion

Coalescence with ARN is increasing the gel formation significantly. This may be caused by a new adsorption layer, probably multilayer formation.

4.9 Influence of coalescence on asphaltenes

4.9.1 Goal

Determine the effect of coalescence on interfacial conditions for asphaltenes.

4.9.2 Solution

In this section the dilational interfacial rheology of asphaltenes with a constant volume and with a contracted volume from 25 μL to 15 μL after one hour without exchange was studied. The procedure used for for coalescence is described in chapter 3.6.5 Procedure 5.

4.9.3 Interfacial tension

To look at the behavior of asphaltenes with changing volume two experiments were done where the volume was decreased from 25 to 15 μ L, and two experiments where the volume was constant at 15 μ L. The interfacial tension for asphaltenes can be seen in figure 58. The other parallel can be seen in figure 106 in appendix, both stocks follow the same trend. From the plot of interfacial tension it is possible to observe a small decrease in interfacial tension right after the contraction, then the interfacial tension is increasing slightly afterwards. This behavior in the interfacial tension is due to the contraction is causing a small effect on the asphaltenes, and the asphaltenes does not desorb.

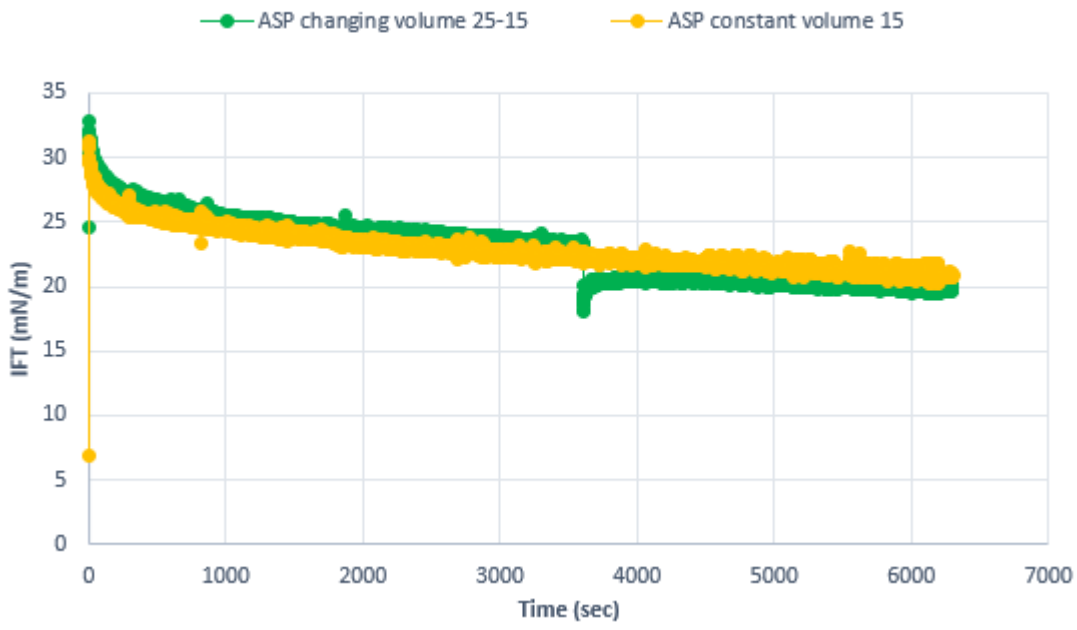

Figure 58: Plot of interfacial tension of asphaltenes with changing volume from 25 to 15 μ L and constant volume at 15 μ L

4.9.4 Oscillation

The E′ and E″ can be seen in figure 59. The tests show the same trend for asphaltenes with decreasing volume and for constant volume. From the figure it is possible to observe that the contraction does not have an effect on the rheological properties of asphaltenes.

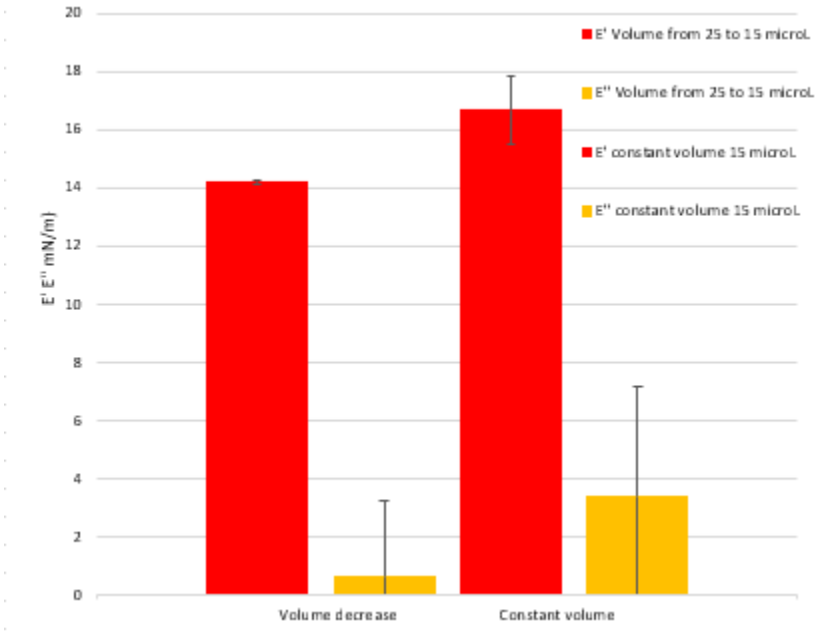

Figure 59: E′ and E″ for asphaltenes with changing volume from 25 to 15 μ L and constant volume at 15 μ L

4.9.5 Conclusion

Contraction have a very small effect on the rheological properties of asphaltenes.

4.10 Influence of exchange on interfacial tension during the coalescence process

4.10.1 Goal

Determine the interfacial conditions for ARN-asphaltenes during the coalescence process.

4.10.2 Solution

Study the dilational interfacial rheology of 7.5 μM ARN - 0.4 g/L asphaltenes, with contraction and an exchange time of 720, 2700 and 5400 sec. The procedure used for exchange after coalescence is described in chapter 3.6.6 Procedure 6.

4.10.3 Interfacial tension

The interfacial tension for both stocks of 7.5 μM ARN - 0.4 g/L asphaltenes, with contraction and an exchange time of 720, 2700 and 5400 sec can be seen in figure 60, 61, 62 and 63.

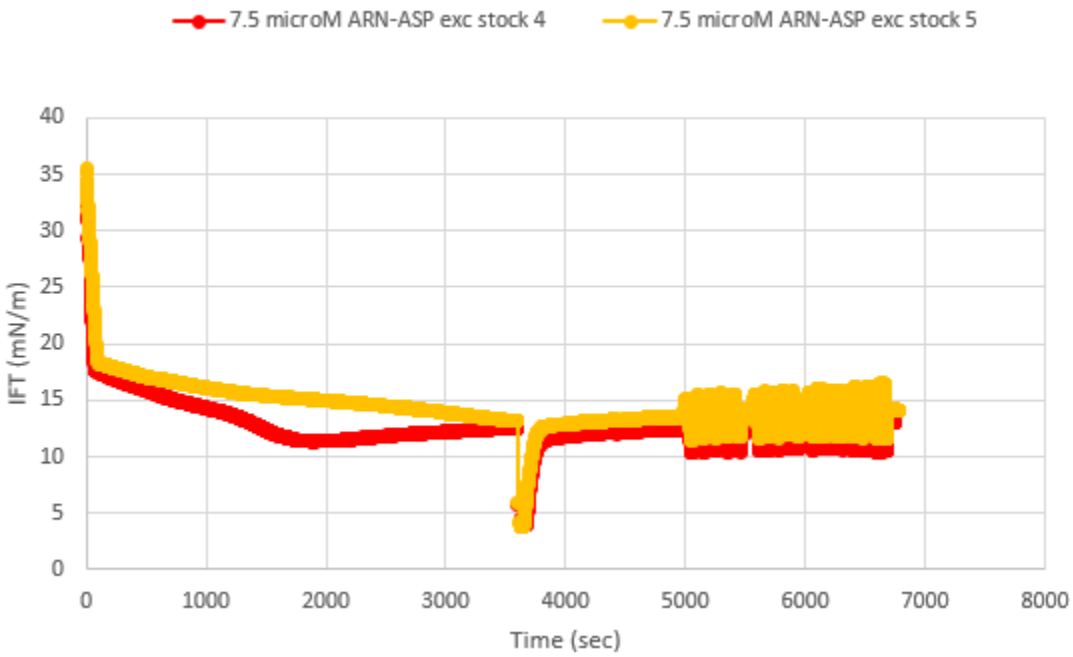

Figure 60: Plot of both stocks of the IFT vs time of samples with 7.5 μM ARN-asphaltenes, contraction and no exchange

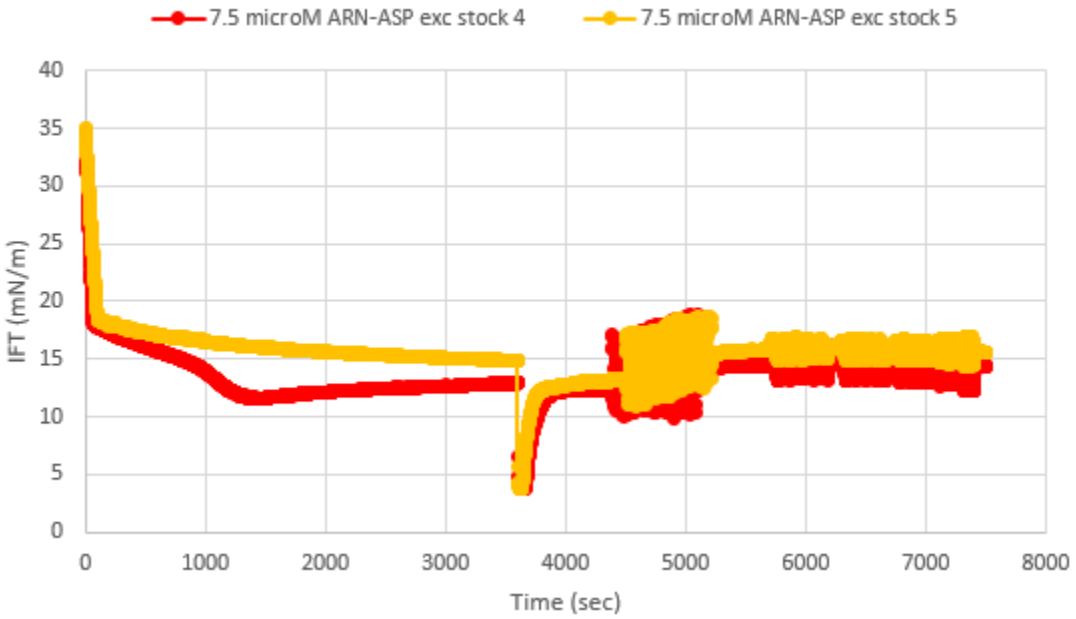

Figure 61: Plot of both stocks of the IFT vs time of samples with 7.5 μM ARN-asphaltenes, contraction and an exchange time of 720 sec

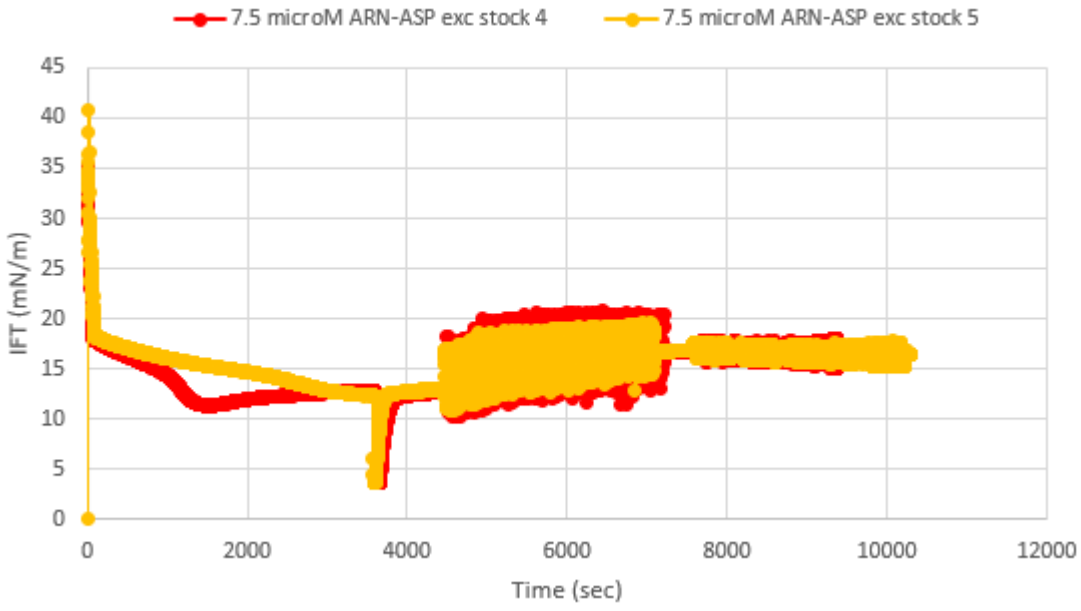

Figure 62: Plot of both stocks of the IFT vs time of samples with 7.5 μM ARN-asphaltenes, contraction and an exchange time of 2700 sec

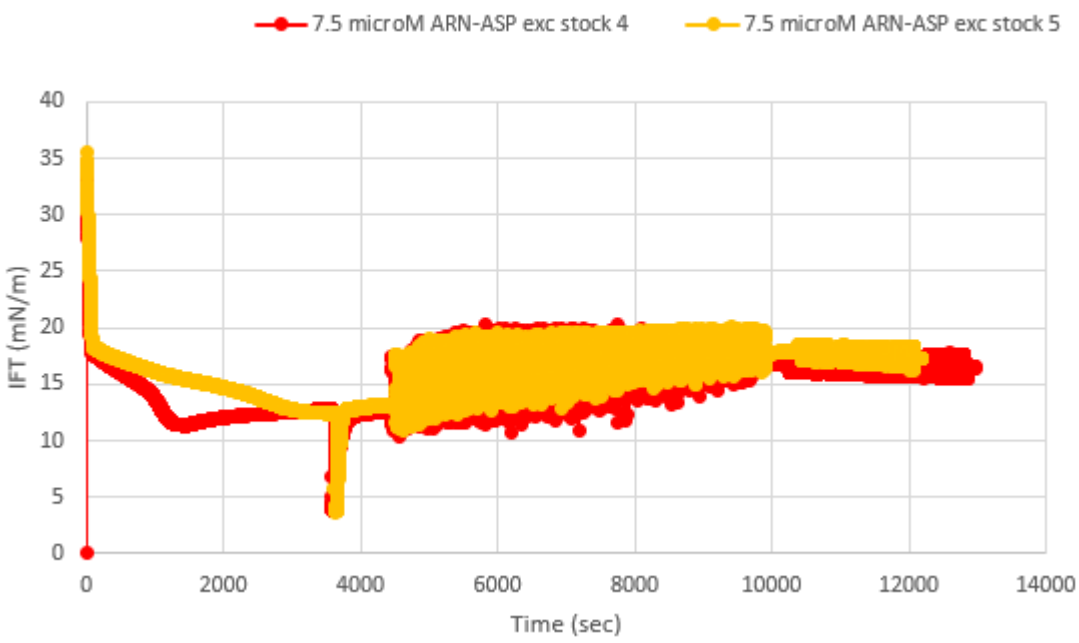

Figure 63: Plot of both stocks of the IFT vs time of samples with 7.5 μM ARN-asphaltenes, contraction and an exchange time of 5400 sec

4.10.4 Oscillation

The E′ and E″ of 7.5 μM ARN-asphaltenes with reduced volume from 25 to 15 μL with an exchange time of 5400 sec, 2700 sec, 720 sec and no exchange can be seen in figure 64. The figure shows that the gel formation is significantly higher without exchange compared to with high exchange time. The asphaltenes are able to desorb the gel formed even after coalescence.

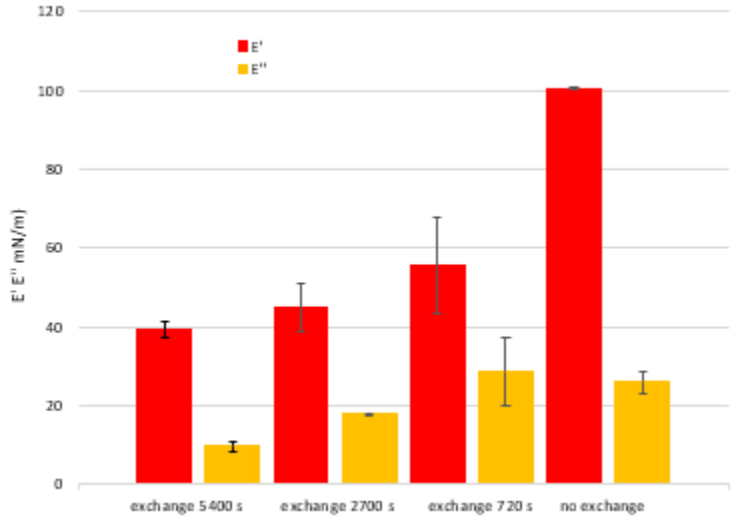

Figure 64: E′ and E″ of 7.5 μM ARN-asphaltenes with reduced volume from 25 to 15 μL with an exchange time of 5400 sec, 2700 sec, 720 sec and no exchange

4.10.5 Conclusion

Asphaltenes are able to desorb the gel formed after coalescence.

4.11 Influence of ARN concentration on interfacial tension in the coalescence process with exchange with asphaltenes

4.11.1 Goal

To determine the the axisymmetric drop shape analysis (ADSA) technique can be used for higher concentration of ARN when analyzing coalescence.

4.11.2 Solution

Study the dilational interfacial rheology of 10 μM ARN - 0.4 g/L asphaltenes, with an exchange time of 720, 2700 and 5400 sec. The procedure used for exchange after coalescence is described in chapter 3.6.6 Procedure 6.

4.11.3 Interfacial tension

The interfacial tension for both stocks of 7.5 and 10 μM ARN - 0.4 g/L asphaltenes, with contraction and an exchange time of 720, 2700 and 5400 sec can be seen in figure 65, 66, 67 and 68. From the figures it is possible to observe that the interfacial tension is very low for 10 μM ARN (especially the first stock) during the relaxation after the compression, but after the exchange is started the interfacial value increases. This could be because the shape could not be properly controlled with an ARN concentration of 10 μM ARN. The shape was analyzed more in the next sections.

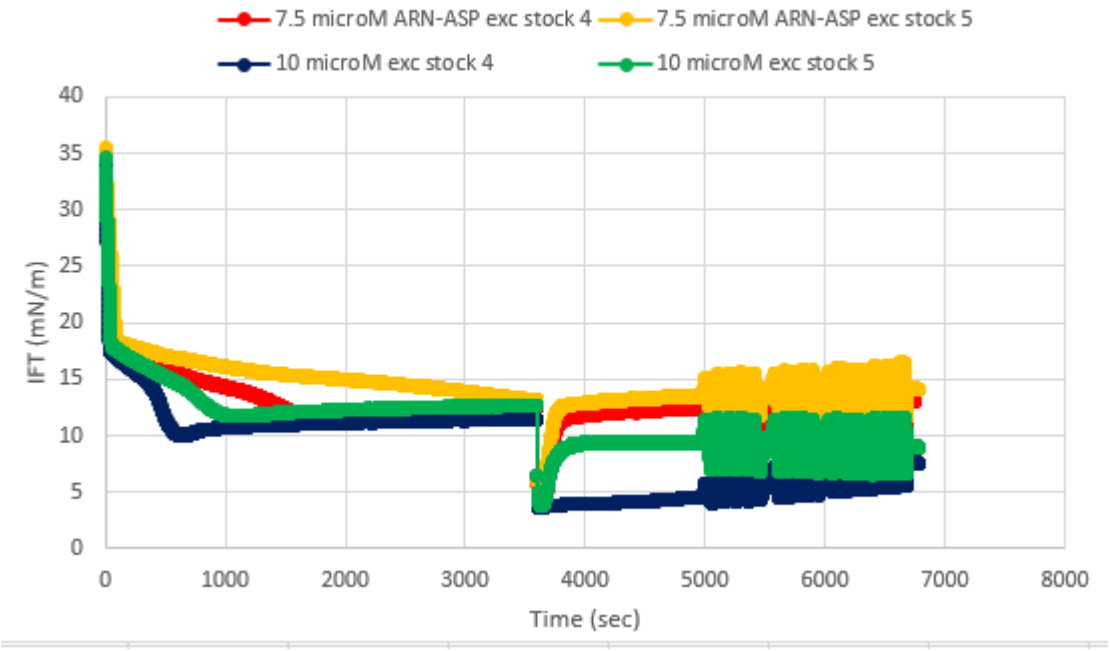

Figure 65: Plot of both stocks of the IFT vs time of samples with 7.5 and 10 μM ARN-asphaltenes, contraction and no exchange

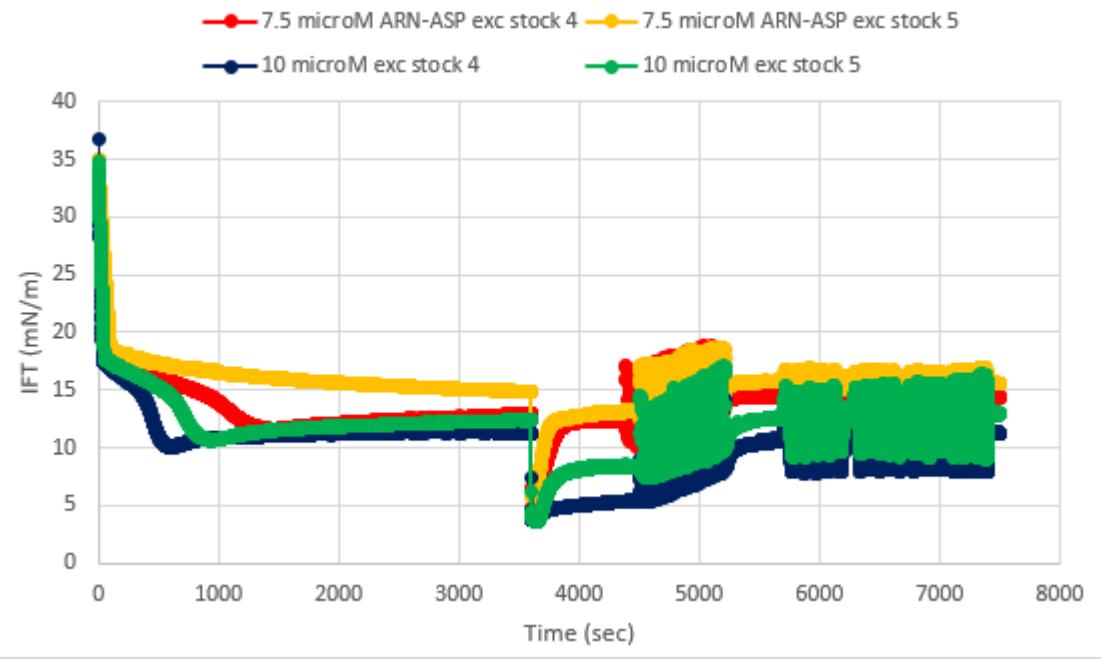

Figure 66: Plot of both stocks of the IFT vs time of samples with 7.5 and 10 μM ARN-asphaltenes, contraction and an exchange time of 720 sec

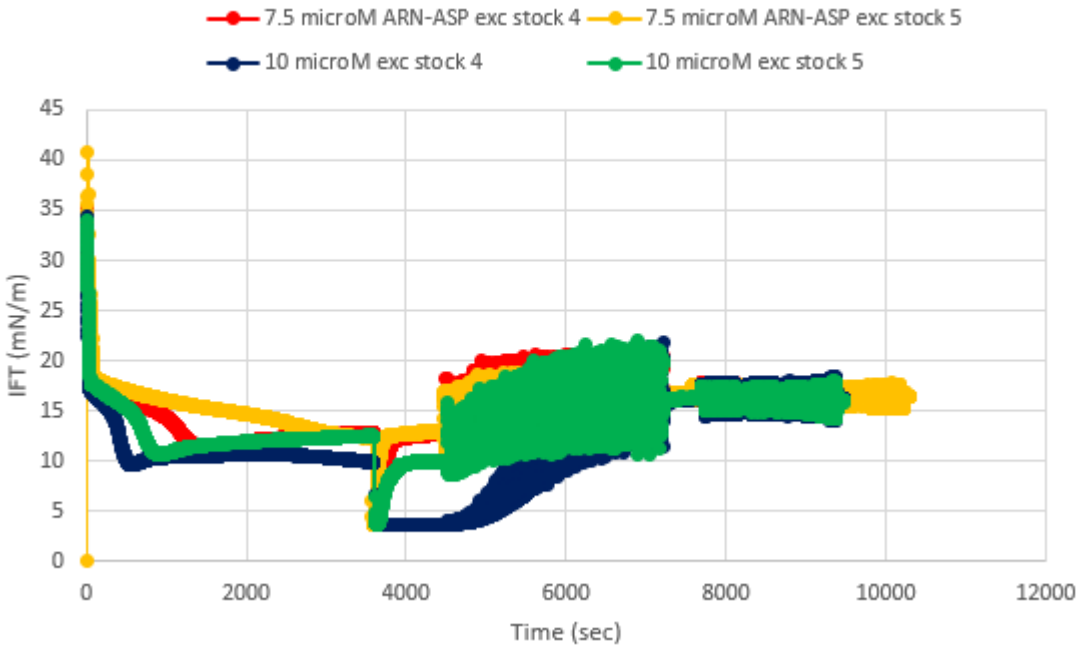

Figure 67: Plot of both stocks of the IFT vs time of samples with 7.5 and 10 μM ARN-asphaltenes, contraction and an exchange time of 2700 sec

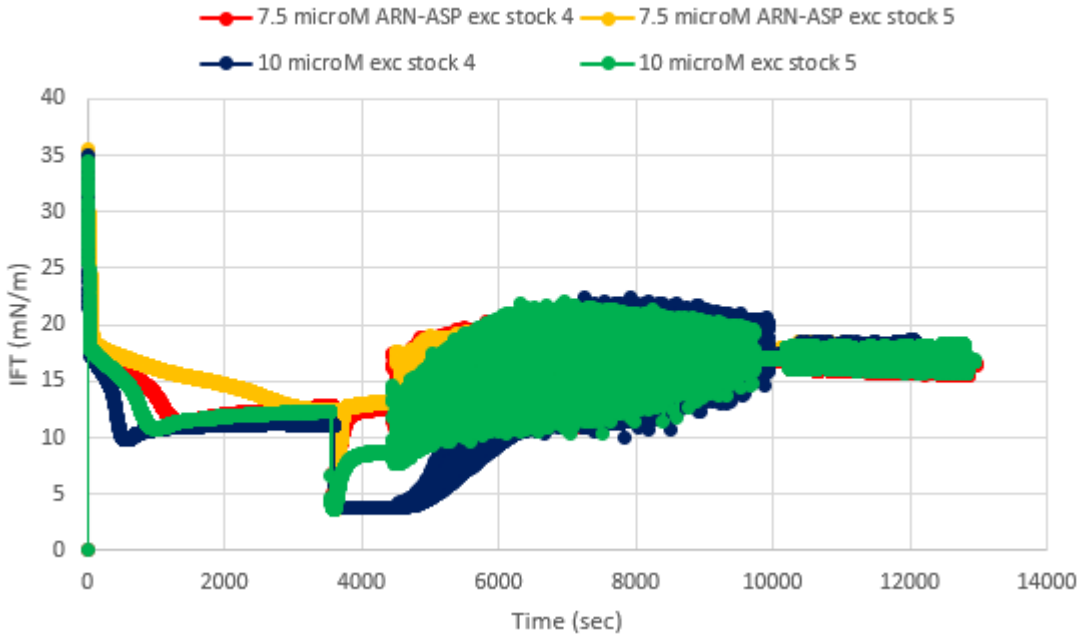

Figure 68: Plot of both stocks of the IFT vs time of samples with 7.5 and 10 μM ARN-asphaltenes, contraction and an exchange time of 5400 sec

4.11.4 Oscillation

The results of E′ and E″ for 10 μM ARN-asphaltenes with volume decreased from 25 to 15 μL for no exchange, 720 seconds exchange, 2700 seconds exchange and 5400 seconds exchange can be seen in figure 69. From the plot we can see that the gel formation is decreasing with exchange time because asphaltenes are still able to remove the formed gel, even with higher ARN concentration. The E′ values are still very high after 720 sec of exchange with 10 μM ARN-asphaltenes, but not for 7.5 μM ARN-asphaltenes from figure 64. This shows that the time to desorb the formed gel is increased because the gel formed is increased for higher ARN concentration.

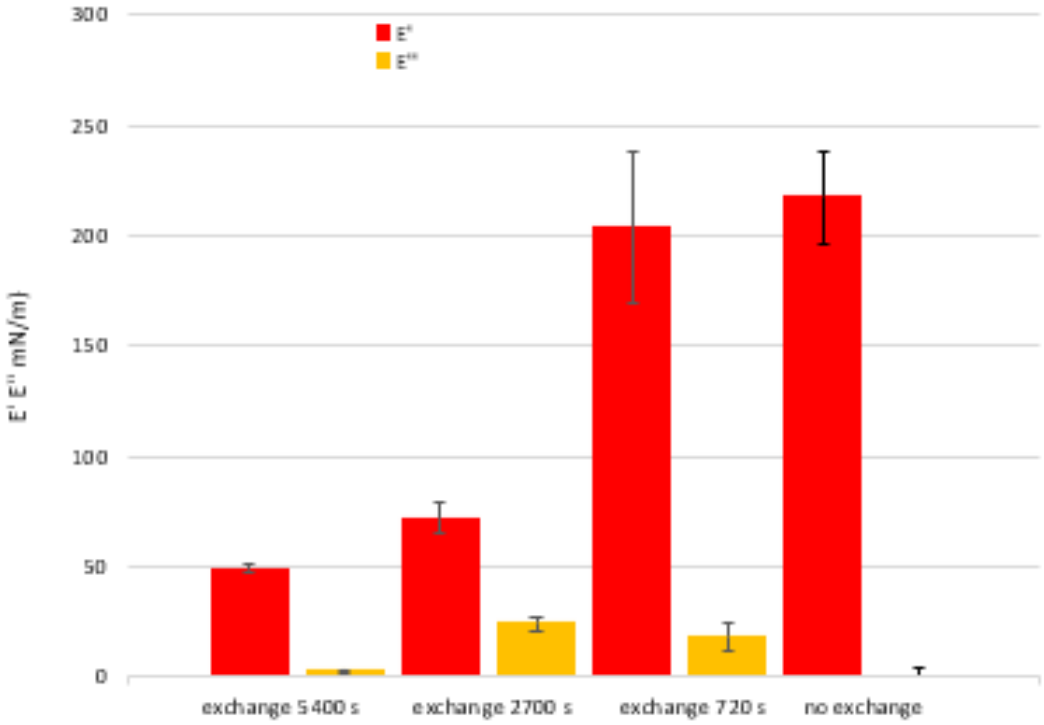

Figure 69: E′ and E″ of 7.5 μM ARN-asphaltenes with reduced volume from 25 to 15 μL with an exchange time of 5400 sec, 2700 sec, 720 sec and no exchange

4.11.5 Fit of the last period

The results of the last period of the experiments with an exchange time of 720 seconds with both stocks of 10 and 7.5 μM ARN can be seen in figure 70, 71, 72 and 73. For all four experiments the E′ and E″ values were good. The results indicate that the axisymmetric drop shape analysis (ADSA) technique can be used with an ARN concentration of 10 μM for pH8 with a decreasing volume to look at the gel formation during coalescence.

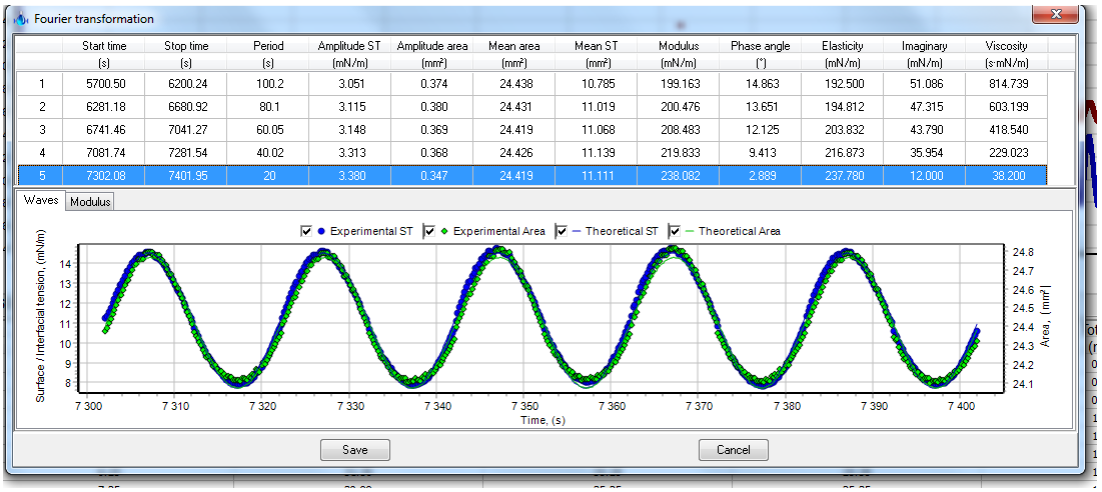

Figure 70: The fit of the curve for the last period of oscillation for the first stock with 10 μM for a decreasing volume after one hour and an exchange time of 720 sec

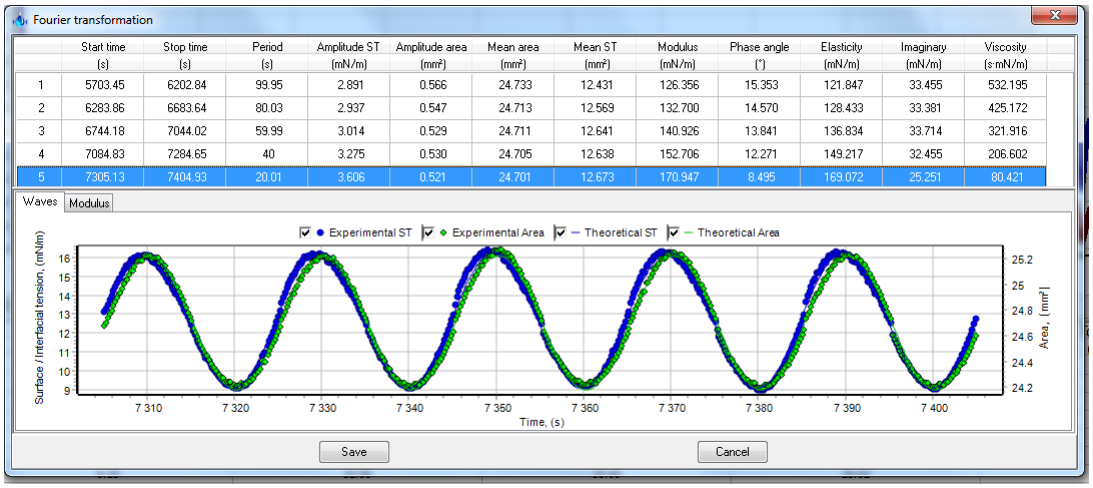

Figure 71: The fit of the curve for the last period of oscillation for the second stock with 10 μM for a decreasing volume after one hour and an exchange time of 720 sec

4.11.6 Conclusion

Asphaltenes are still able to remove the formed gel, even with higher ARN concentration. The time to desorb a large the formed gel is increased when the ARN concentration is increased because the gel formed is increased. The axisymmetric drop shape analysis (ADSA) technique can be used with an ARN concentration of 10 μM for pH8 with a decreasing volume to look at the gel formation during coalescence.

4.12 Influence of the drop shape

4.12.1 Goal

Determine the consequence of compressing the drop volume during the experiments with high ARN concentration.

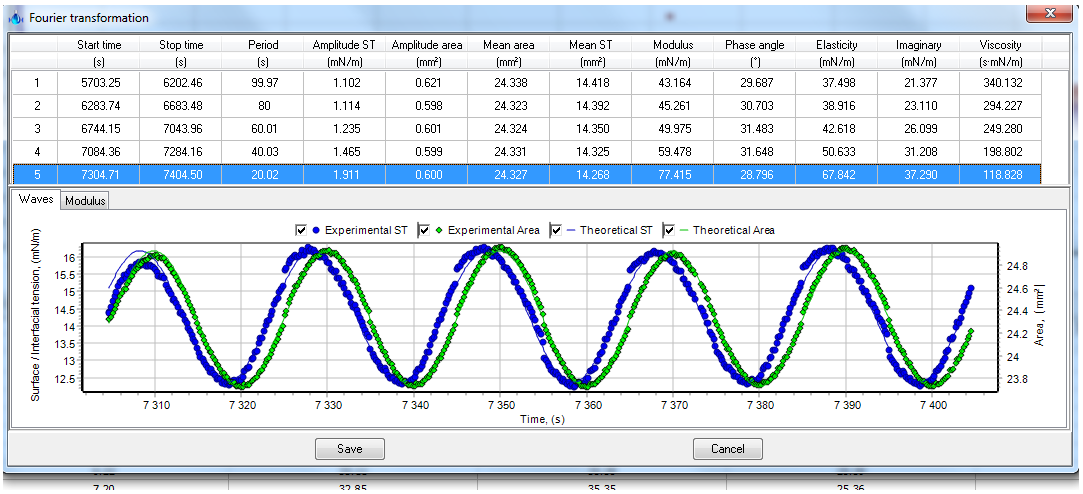

Figure 72: The fit of the curve for the last period of oscillation for the first stock with 7.5 μM for a decreasing volume after one hour and an exchange time of 720 sec

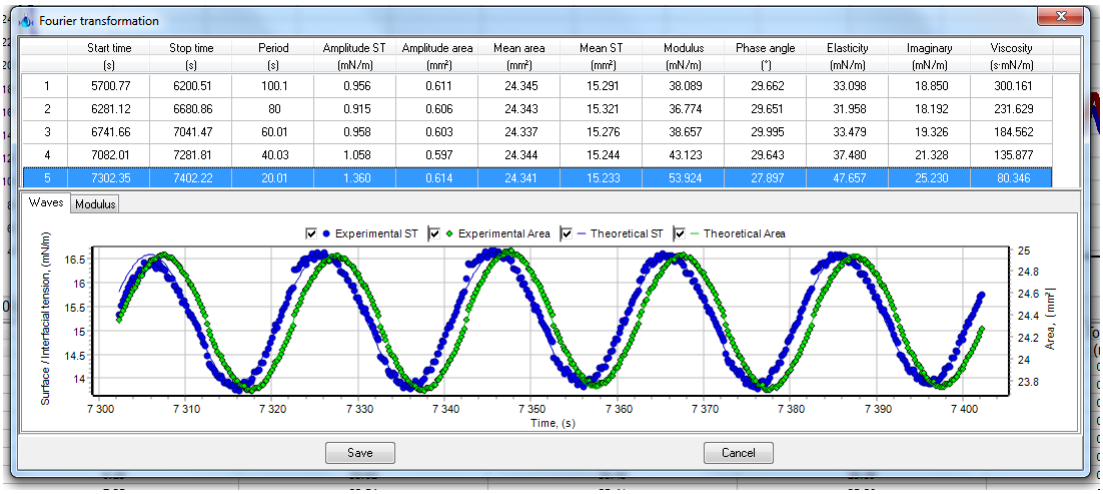

Figure 73: The fit of the curve for the last period of oscillation for the second stock with 7.5 μM for a decreasing volume after one hour and an exchange time of 720 sec

4.12.2 Solution

Study the development of the shape during the last experiments with 7.5 and 10 μM ARN, by taking pictures of the drop during the experiments.

4.12.3 Analyzing the shape

When an experiment with 10 muM were done, the drop was noticed to have a longer shape than normal when the exchange was started. Therefore, pictures of the drop shape were taken for the remaining experiments. The shape of the drop for the experiment with the first stock of 10 μM ARN-Asphaltenes and the second stock of 7.5 μM ARN-Asphaltenes with an exchange time of 720 seconds can be seen in figure 74 and 75. The experiment for 10.0 muM ARN-asphaltenes with exchange the second stock and the experiment for 10.0 muM ARN-asphaltenes without exchange with the first stock with shape development of the drop can be seen in figure 76 and 77.

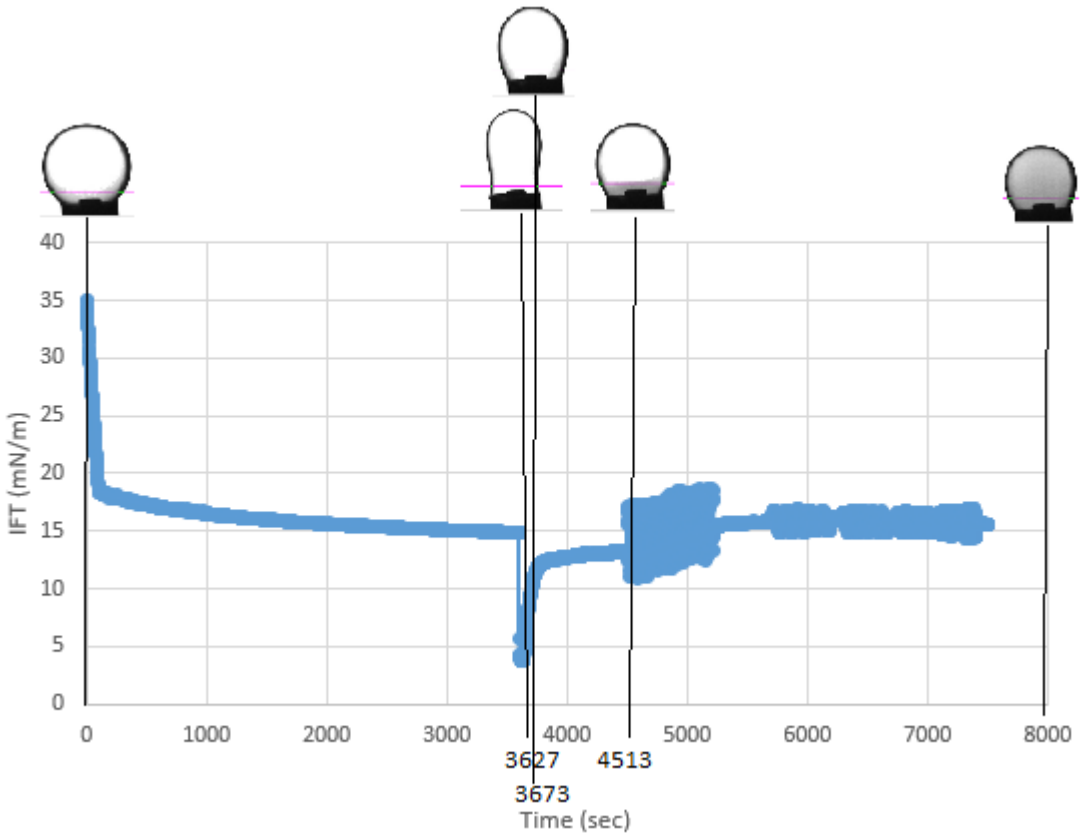

Figure 74: Experiment with pictures of the drop during the experiment with the second stock of 7.5 μM ARN-Asphaltenes with an exchange time of 720 seconds. Pictures were taken at the start of the experiment, 27 seconds after the contraction, during the relaxation, after the start of the exchange and at the end of the experiment.

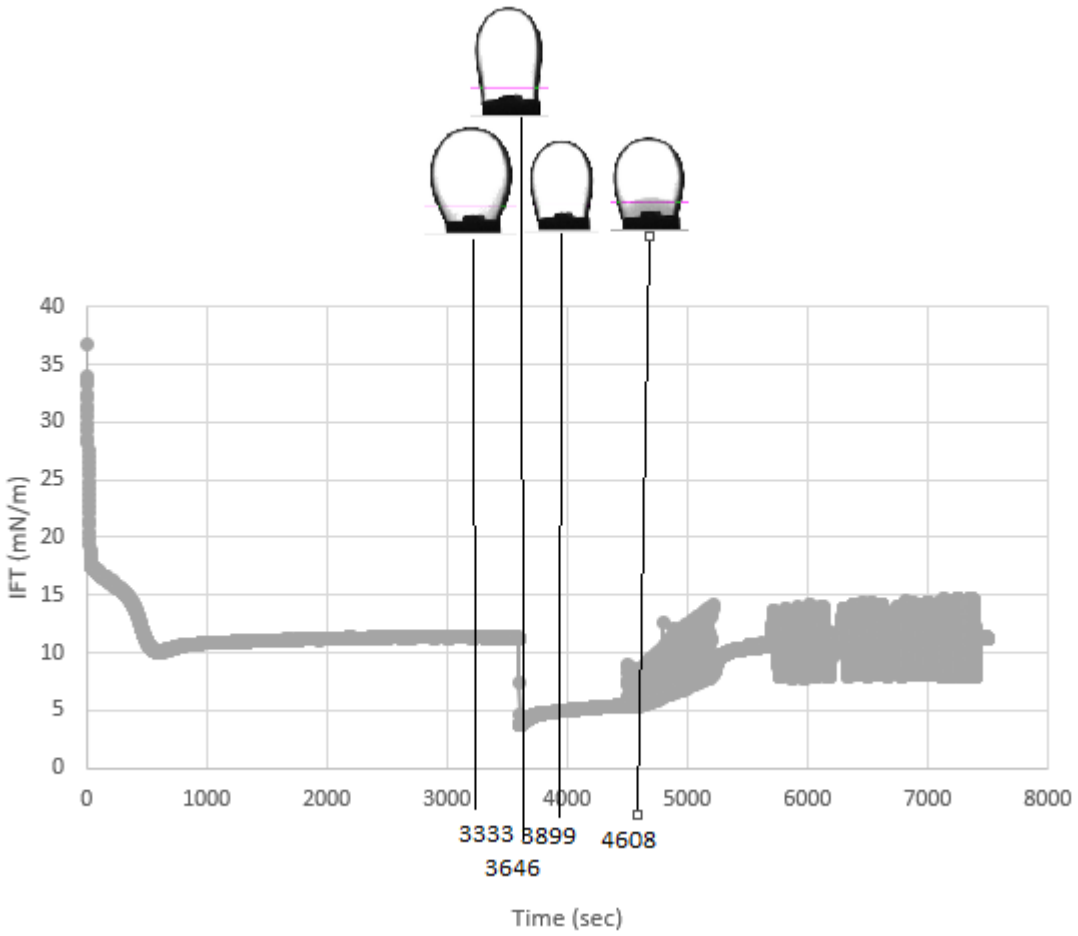

Figure 75: Experiment with pictures of the drop during the experiment with the first stock of 10 μM ARN-Asphaltenes with an exchange time of 720 seconds. Pictures were taken before the contraction, 46 seconds after the contraction, during the relaxation, after the start of the exchange and at the end of the experiment.

For the figure with 7.5 μM ARN-Asphaltenes the picture at 3627 seconds show what happens during the contraction. The picture at 3673 seconds show the drop was quickly adjusted to a good shape. From the picture of 10 μM ARN-Asphaltenes it is possible to see that the shape of the drop is longer during the relaxation, and the shape is not adjusted enough after the contraction. From the figures it is possible to observe that the experiment with the second stock of 10.0 μM ARN-Asphaltenes with an exchange time of 5400 seconds got a nice shape during the relaxation after the contraction (4375 sec), but 10.0 muM ARN-asphaltenes without exchange 10.0 muM with the first stock have a longer shape during the relaxation after the contraction (4531 sec). When the shape of the drop is longer the calculations of the interfacial tension is not correctly done, because the assumption of the shape is not completely true. The calculated interfacial tension values are significantly lower when the drop got a longer shape. This can be observed by comparing the relaxation after the contraction for all four figures.

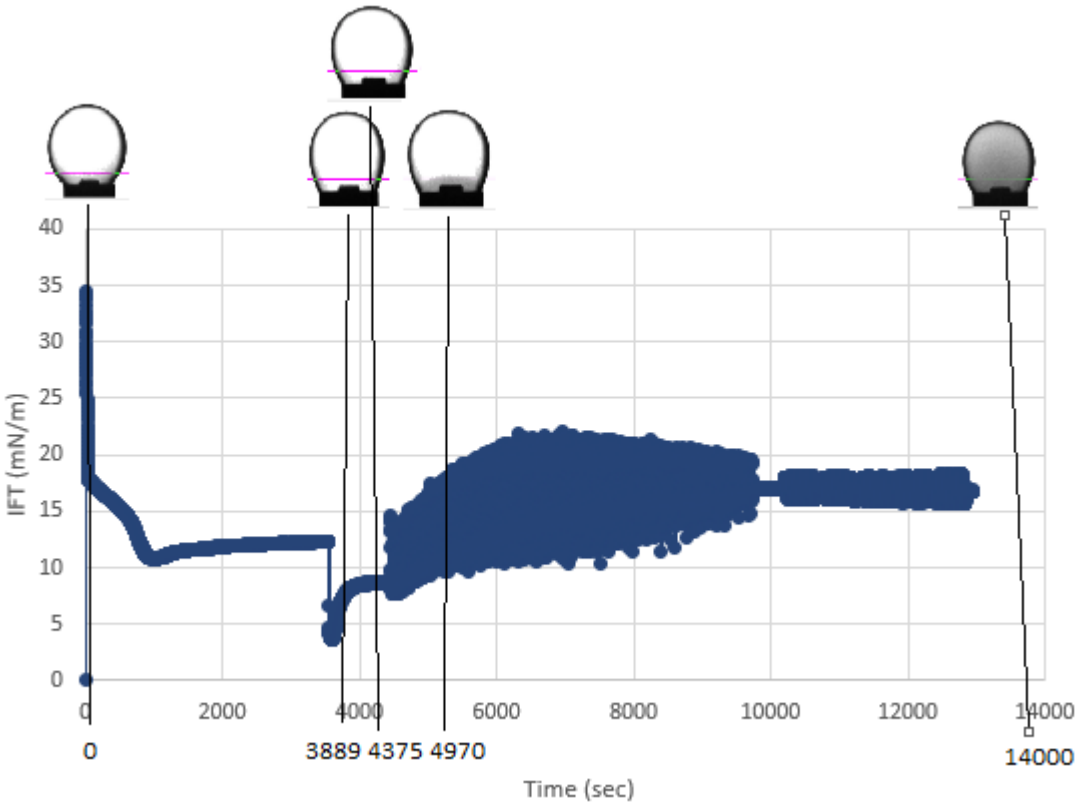

Figure 76: Experiment with pictures of the drop during the experiment with the second stock of 10.0 μM ARN-Asphaltenes with an exchange time of 5400 seconds. Pictures were taken at the start of the experiment, 289 seconds after the contraction, during the relaxation, after the start of the exchange and at the end of the experiment.

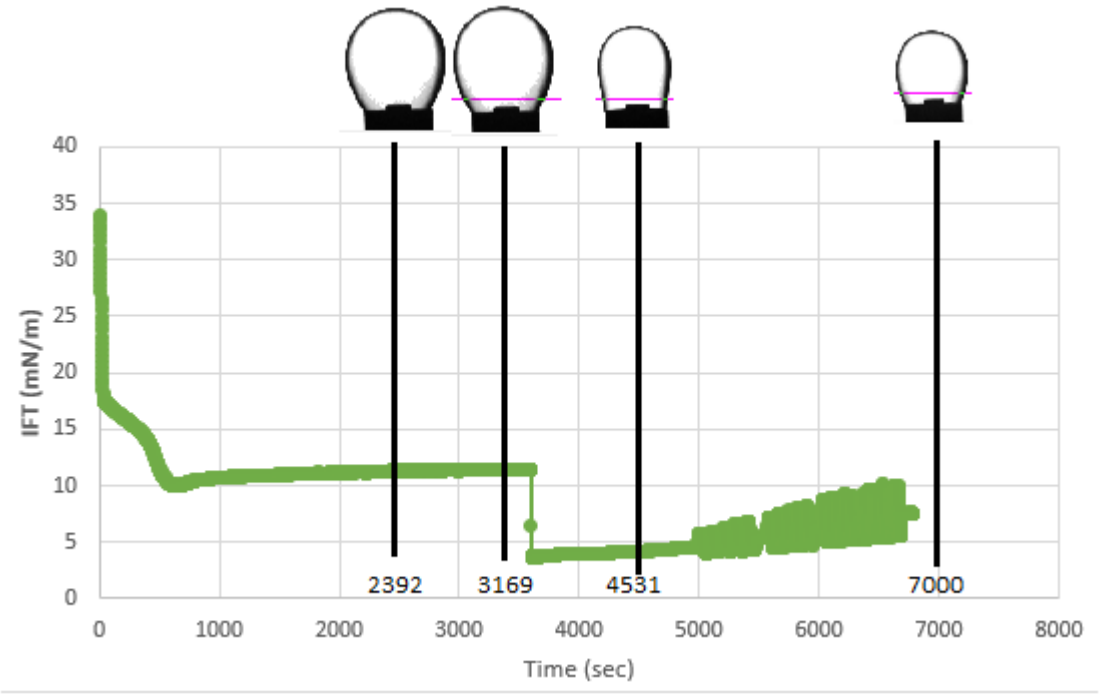

Figure 77: Experiment with pictures of the drop during the experiment with the first stock of 10.0 μM ARN-Asphaltenes with no exchange. Pictures were taken before the contraction, during the relaxation and at the end of the experiment

4.12.4 Conclusion

The pictures of the drop and the interfacial tension values show that the shape often is hard to control after contraction for 10.0 μM ARN, but the shape is controlled properly for 7.5 μM ARN. The interfacial tension is calculated to be significantly lower when the shape is longer. This indicates that the axisymmetric drop shape analysis (ADSA) technique is hard to use for contraction with higher concentration of ARN.

4.13 Errors during coalescence experiments

4.13.1 Goal

Determine how compressing volume and exchange influence the errors and to check if the profile error could be used to indicate a difference of the shape.

4.13.2 Solution

Study the development of the calculated errors by the software, during the experiments with 7.5 and 10 μM ARN - asphaltenes with and without exchange.

4.13.3 Analyzing the Errors

For the experiment with the first stock of 10 microM ARN-asphaltenes, exchange time 5400 sec and compressing volume after one hour the shape of the drop was noticed to be long. Therefore, the profile error of the experiments with exchange time 5400 sec was analyzed. The profile error is the error in measuring the interfacial tension using the shape of the drop. The plots of profile error as a function of time for the 4 experiments with exchange time of 5400 sec can be seen in figure 78 and a zoomed in version can be seen in figure 79. From the plot we can see a few very high profile error values at 3600 sec because of the compression. High profile error values can be seen towards the end of the exchange for all experiments. The most notable result from the plots is that the profile error values for the experiment with the long shape (10 microM ARN-asphaltenes with the first stock) is high at 4500 seconds when the exchange was started. This is because the bad shape is adjusted to the right shape when the exchange has started. The profile error during the relaxation before the exchange is started is low even for the experiment with a bad shape.

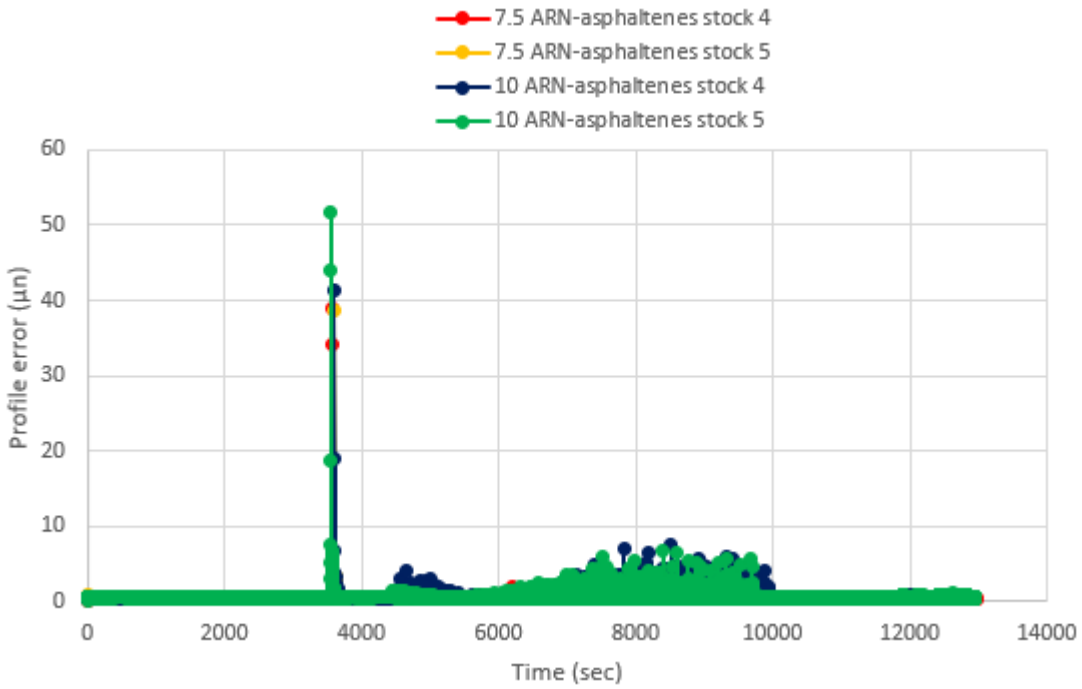

Figure 78: Error as a function of time for the experiments with exchange and a volume that was decreased from 25 to 15 μL

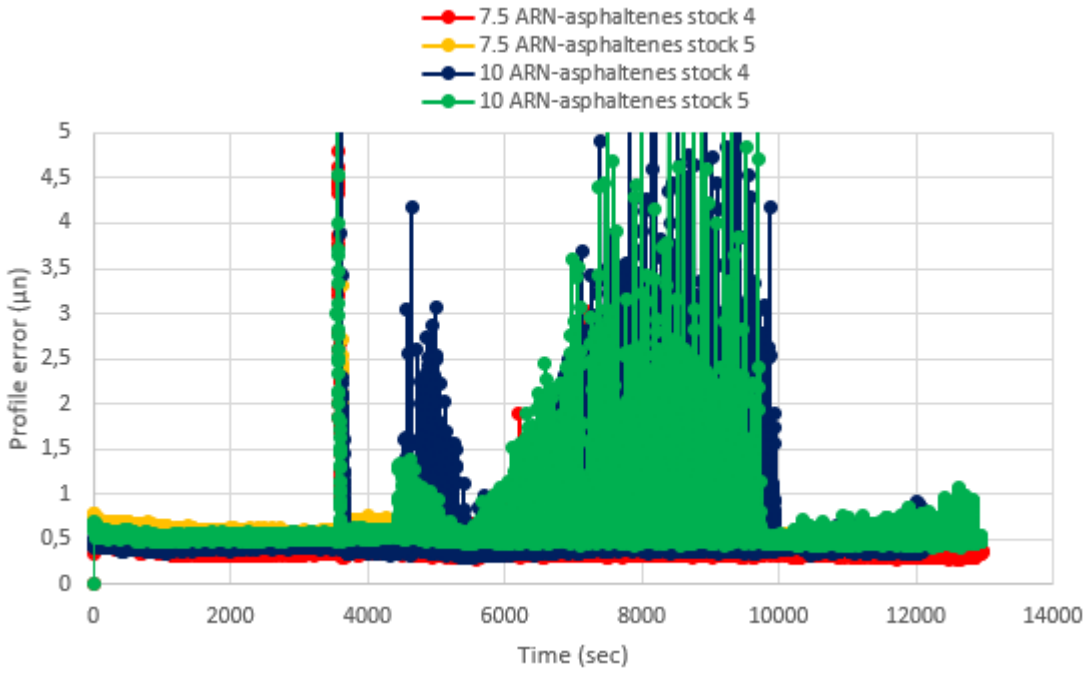

Figure 79: Zoomed in on the error as a function of time for the experiments with exchange and a volume that was decreased from 25 to 15 μL

4.13.4 Conclusion

For the experiment with 10 μM ARN and a bad shape the profile error is high when the shape is adjusted after the exchange is started. Therefore, the profile error can be used to determine if the drop got a good shape after contraction. The experiment with a bad shape after contraction have good values before contraction and after some time of exchange. Therefore, the interfacial data before contraction can be trusted and the E′ and E″ values obtained from oscillation can be trusted.

5 Conclusion

New batches of ARN were extracted with a yield of 7-8% and with a purity of 92-93%. To study the dilational interfacial rheology the axisymmetric drop shape analysis (ADSA) technique was used with a coaxial capillary to study the interfacial tension and dilatational interfacial viscoelastic values for many experiments with ARN, xylene and asphaltenes. The results from the experiments confirm that ARN cause the calcium napthenate gel formation when the carboxylate groups in ARN react with calcium ions from the buffer.

5.1 Influence of ARN concentration on the gel formation at the interface

A strong gel is formed for experiments for 2.5μM ARN with an exchange time of 5400 seconds, but 720 seconds is not enough to create a strong gel for 2.5μM ARN. The adsorption layer of ARN is being reorganized for experiments with longer time. The behaviour of the mixture of ARN and asphaltenes is very similar to the behavior of asphaltenes, and the presence of asphaltenes in the mixture prevents gel formation. The change in amplitude did not result in a significant difference in the fit of the curves or E' values. Therefore, the rest of the experiments were done with the same amplitude value.

A buffer with pH 6 and 7 can be used with a concentration of 25 μM ARN, but for a buffer with pH 8 the axisymmetric drop shape analysis (ADSA) technique could not be done because the drop fell off and new drops were formed during the experiment and gave bad interfacial tension value as a result of too high ARN concentration. For 10 μM and 9 μM ARN with a pH 8 buffer the drop is hard to control, the concentration is at the limit of what can be studied with the (ADSA) technique. Because the gel is strong at 9 μM and 10 μM it is difficult to oscillate.

5.2 Desorption of ARN at the interface by the solvent asphaltenes

7.5 μM ARN-asphaltenes and 7.5 μM ARN-xylene have different interfacial tension during the first hour with adsorption. This could be a result of pollution. The new procedure with more thorough cleaning show an improvement in the result, but it follows the same trend as previously during the adsorption of 7.5 μM ARN-XYL and 7.5 μM ARN-asphaltenes. The new experiments where a smaller asphaltene drop is formed before the experiment was started and the experiment where the asphaltenes drop was sucked in before the experiment was started could not explain why 7.5 μM ARN - asphaltenes and 7.5 μM ARN - xylene have different interfacial values during the adsorption. The difference could therefore not be proven to be a result of pollution by the samples in the pumps or by the procedure used before the experiment was started. Asphaltenes are able to desorb the gel that is already formed. Asphaltenes are desorbing the gel already formed after exchange and the desorbed amount is increasing with exchange time.

5.3 Experiments done to mimic coalescence conditions, then study of desorption by asphaltenes under coalescence conditions

Coalescence with ARN is increasing the gel formation significantly. This may be caused by a new adsorption layer, probably multilayer formation. Contraction have a very small effect on the rheological properties of asphaltenes. Asphaltenes are still able to remove the formed gel, even with higher ARN concentration. The time to desorb the formed gel is increased when the ARN concentration is increased because the gel is stronger. The axisymmetric drop shape analysis

(ADSA) technique can be used with an ARN concentration of 10 μM for pH8 with a decreasing volume to look at the gel formation during coalescence.

The pictures of the drop and the interfacial tension values show that the shape often is hard to control after contraction for 10.0 μM ARN, but the shape is controlled properly for 7.5 μM ARN. The interfacial tension is calculated to be significantly lower when the shape is longer. This indicates that the axisymmetric drop shape analysis (ADSA) technique is hard to use for contraction with higher concentration of ARN. The profile error is high when the shape is adjusted after the exchange is started. Therefore, the profile error can be used to determine if the drop got a good shape after contraction. For the experiment with 10 μM ARN and a bad shape the profile error is high when the shape is adjusted after the exchange is started. Therefore, the profile error can be used to determine if the drop got a good shape after contraction. The experiment with a bad shape after contraction have good values before contraction and after some time of exchange. Therefore, the interfacial data before contraction can be trusted and the E' and E" values obtained from oscillation can be trusted.

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6 Appendix

6.1 Preparation of samples

Table 9: Crushed naphtenate deposit

Sample	Deposit(g)	Toluene
1	9.9	235
2	10.0	235
3	10.0	235
4	9.8	235
5	9.9	235
6	9.9	235

Table 10: Sephadex and time

Sample	Sephadex(g)	Collected Toluene	Time stirring(hours:minutes)
1+2	10.0270	1450	21:35
3+4	10.0060	1450	21:50
5+6	10.0710	1450	24:15

Table 11: Exact mass used for the ARN samples sent to purity test

Sample	TA(mg)	Benzoic acid(mg)	d-Chloroform(g)
1+2	72.4mg	45.0mg	1.5173g
3+4	70.8mg	43.8mg	1.5219g
5+6	71.8mg	42.6mg	1.4959g

Table 12: Exact mass for buffer preparation part 1

Sample	Mass Borax	Mass Na_Cl	Total mass	$CaCl_2$H2O	Total mass
Buffer1	4240.6mg	1301.0mg	1000.1g	1.4670g	100.0g
Buffer3	4242.9mg	1302.6mg	1001.9g	1.4617g	100.0g
Buffer4	4245.0mg	1306.2mg	1000.0g	1.4620g	100.5g
Buffer5	4235.5mg	1299.1mg	1000.0g	1.4696g	100.0g
Buffer6	4194.8mg	1301.4mg	999.2g	1.4618g	100.1g

Table 13: Exact mass for buffer preparation part 2

Sample	Ca2+ buffer	Total mass with Borax buffer	Adjusted final pH
Buffer1	90.0g	910.0g	8.00
Buffer3	89.8g	899.9g	8.00
Buffer4	90.0g	810.0g	8.01
Buffer5	90.0g	901.2g	8.00
Buffer6	90.1g	903.5g	7.99

Table 14: Exact mass of fully protonated ARN and xylene used to prepare new ARN samples

Sample	Mass fully protonated ARN(mg)	total mass completed with xylene(g)
ARNS1	31.4mg	42.77g
ARNS2	32.0mg	43.89g
ARNS3	30.1mg	42.30g
ARNS4	34.9mg	42.34g
ARNS5	32.8mg	42.25g
ARNS6	33.6mg	42.28g
ARNS7	31.2mg	42.30g
ARNS8	31.6mg	42.30g
ARNS9	30.6mg	42.30g
ARN10	29.6mg	42.30g
ARN11	30.7mg	42.30g
ARN12	31.3mg	42.40g
ARN13	28.6mg	42.36g

Table 15: Exact mass and concentration of the used ARN sample created with newly prepared 500 μM ARN and xylene

Sample	Concentration	Mass 500 μM ARN	From stock	Total mass	Final concentration (M)
ARN1	2.5	0.9969g	ARNS1	196.8g	2,62E-06
ARN2	2.5	0.9862g	ARNS2	195.4g	2,59E-06
ARN3	25	9.85g	ARNS3	195.1g	2,53E-05
ARN4	25	9.83g	ARNS4	195.6g	2,92E-05
ARN5	15	5.8539g	ARNS5	196.2g	1,50E-05
ARN6	20	7.7972g	ARNS3	195.1g	2,01E-05
ARN7	10	4.8833g	ARNS3	194.2g	1,26E-05
ARN8	12.5	5.8600g	ARNS3	195.8g	1,50E-05
ARN9	7.5	2.9112g	ARNS5	199.7g	7,98E-06
ARN10	7.5	2.9413g	ARNS6	195.5g	8,43E-06
ARN11	7.5	2.9262g	ARNS6	194.8g	8,42E-06
ARN12	10	3.9046g	ARNS7	201.2g	1,01E-05
ARNS15	9	3.5217g	ARNS8	195.8g	9,45E-06
ARNS16	7.5	2.9262g	ARNS9	194.8g	7,66E-06
ARNS17	7.5	2.9451g	ARNS9	194.7g	7,56E-06
ARNS18	2.5	1.0270g	ARNS9	195.0g	2.69E-06
ARNS19	5.0	1.9917g	ARNS9	195.2g	5.20E-06
ARNS20	2.5	0.9830g	ARNS10	195.0g	2.49E-06
ARNS21	2.5	0.9891g	ARNS11	194.9g	2.60E-06
ARNS22	5.0	1.9775g	ARNS10	194.9g	5.00E-06
ARNS23	5.0	1.9667g	ARNS11	195.0g	5.16E-06
ARNS24	7.5	2.9389g	ARNS10	194.9g	7.44E-06
ARNS25	7.5	2.9263g	ARNS11	196.0g	7.64E-06
ARNS26	2.5	0.9493g	ARNS12	193.5g	2.55E-06
ARNS27	2.5	0.9468g	ARNS13	195.0g	2.36E-06
ARNS28	7.5	2.9715g	ARNS12	195.1g	7.93E-06
ARNS29	7.5	2.9934g	ARNS13	194.9g	7.31E-06
ARNS30	10	3.9047g	ARNS12	195.0g	1.04E-05
ARNS31	10	3.9337g	ARNS13	195.6g	9.57E-06

Table 16: Exact mass of asphaltenes and xylene to create a 1 g/L asphaltenes sample

Sample	Mass of asphaltenes	Total mass completed with xylene	Concentration (g/L)
ASPF1	0,0311g	24.1g	1,19 g/L
ASPF2	0,0332g	26.1g	1,10 g/L
ASPF3	0,0322g	26.1g	1,07 g/L
ASPF4	0,0297g	26.4g	0,98 g/L
ASPF5	0,0291g	26.0g	0,97 g/L
ASPF6	0,0300g	26.0g	1,00 g/L
ASPF7	0,0292g	26.0g	0,97 g/L
ASPF8	0.0297g	26.0g	0,99 g/L
ASPF10	0.0286g	26.0g	0.95 g/L
ASPF11	0.0287g	26.0g	0.96 g/L

Table 17: Exact mass of 1 g/L asphaltenes and xylene to create a 0.4 g/L asphaltenes sample

Sample name	Mass of ASPF sample	total mass completed with xylene	Concentration (g/L)
ASP1	12,05g	30,07g	0,448 g/L
ASP2	11,85g	30,03g	0,436 g/L
ASP3	12,05g	30,07g	0,429 g/L
ASP4	12,01g	30,03g	0,390 g/L
ASP5	12,08g	30,09g	0,389 g/L
ASP6	12,10g	29,95g	0,404 g/L
ASP7	12,12g	29,99g	0,393 g/L
ASP8	12,00g	30,00g	0,396 g/L
ASP9	12.06g	30,00g	0,398 g/L
ASP10	12.02g	30.07g	0.381 g/L
ASP11	12.00g	30.02g	0.382 g/L

Table 18: Exact mass of ARN sample and asphaltenes sample used to create a mixture of ARN and asphaltenes

Name of sample	Mass 2.5 μM ARN of sample	Mass asphaltenes(0.4 g/L) of sample	Total mass completed with xylene
Mixture1	0.2372g ARNS1	18.7488g ASP1	46.866g
Mixture2	0.2415g ARNS2	18.8015g ASP2	47.913g

6.2 NMR of the extracted ARN samples

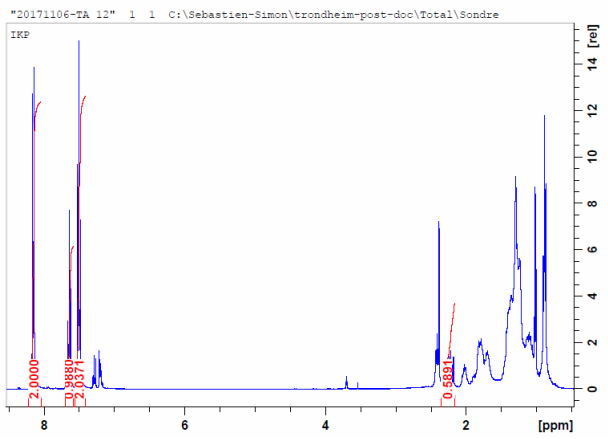

Figure 80: The result from the NMR for sample 1+2

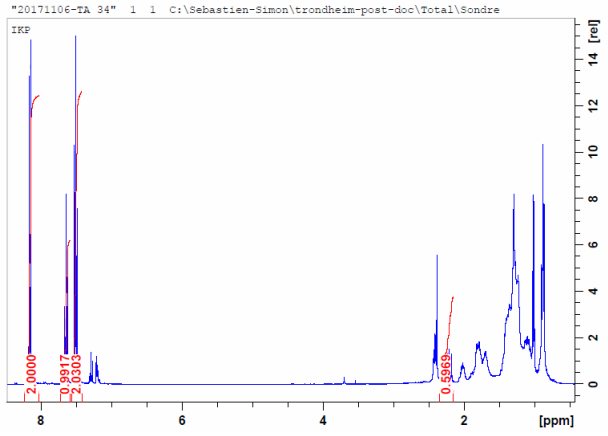

Figure 81: The result from the NMR for sample 3+4

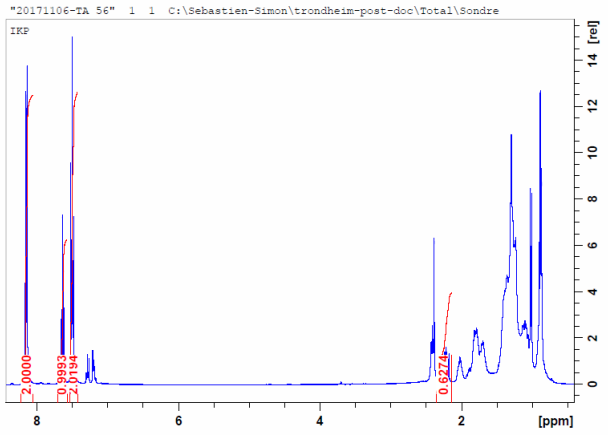

Figure 82: The result from the NMR for sample 5+6

6.3 Settings

Table 19: SINTERFACE experiments

Sample name	Sample	Oscillation time (sec)	Total time (sec)	Max volume (μL)	Amplitude (%)
1.1	7.5 μM ARN1	1200	3200	103	3.5
1.2	7.5 μM ARN1	1200	3200	103	3.5
1.3	7.5 μM ARN2	1200	3200	103	3.5
2.1	7.5 μM ARN2	3180	5180	387	3.5
2.2	7.5 μM ARN2	3180	5180	387	3.5
2.3	7.5 μM ARN1	3180	5180	387	3.5
3.1	7.5 μM ARN1	5880	7880	774	3.5
3.2	7.5 μM ARN1	5880	7880	774	2.5
3.3	7.5 μM ARN1	5880	7880	774	3.0
3.4	7.5 μM ARN1	5880	7880	774	3.0
3.5	7.5 μM ARN2	5880	7880	774	3.0
4.1	ASP1	1200	3200	103	3.5
4.2	ASP1	1200	3200	103	3.5
4.3	ASP1	1200	3200	103	3.5
4.4	ASP2	1200	3200	103	3.5
5.1	ASP2	3180	5180	387	3.5
5.2	ASP2	3180	5180	387	3.5
5.3	ASP1	3180	5180	387	3.5
6.1	ASP1	5880	7880	774	3.5
6.2	ASP1	5880	7880	774	3.5
6.3	ASP2	5880	7880	774	3.5
7.1	MIX1	1200	3200	103	3.5
7.2	MIX1	1200	3200	103	3.5
7.3	MIX2	1200	3200	103	3.5
8.1	MIX2	3180	5180	387	3.5
8.2	MIX2	3180	5180	387	3.5
8.3	MIX1	3180	5180	387	3.5
9.1	MIX1	5880	7880	774	3.5
9.2	MIX1	5880	7880	774	3.5
9.3	MIX2	5880	7880	774	3.5

Table 20: SINTERFACE experiments

Sample name	Sample	Oscillation time (sec)	Total time (sec)	Max volume (μL)	pH
10.1	25 μM ARN3	1200	3200	103	6
10.2	25 μM ARN3	1200	3200	103	6
10.3	25 μM ARN4	1200	3200	103	6
11.1	25 μM ARN4	1200	3200	103	7
11.2	25 μM ARN4	1200	3200	103	7
11.3	25 μM ARN3	1200	3200	103	7
12.1	25 μM ARN3	1200	3200	103	8
13.1	15 μM ARN4	1200	3200	103	8
13.2	10 μM ARN4	1200	3200	103	8

Table 21: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Oscillation time (sec)	Total time (sec)	Max volume (μL)
14.1	7.5 μM ARN5	XYL	4800	6600	103
14.2	7.5 μM ARN6	XYL	4800	6600	103
14.3	7.5 μM ARN6	XYL	4800	6600	103
15.1	7.5 μM ARN5	XYL	6780	8580	378
15.2	7.5 μM ARN6	XYL	6780	8580	378
15.3	7.5 μM ARN6	XYL	6780	8580	378
16.1	7.5 μM ARN5	XYL	11280	9480	774
16.2	7.5 μM ARN6	XYL	11280	9480	774
16.3	7.5 μM ARN6	XYL	11280	9480	774
17.1	7.5 μM ARN5	XYL	5880	4080	-
17.2	7.5 μM ARN5	XYL	5880	4080	-
17.3	7.5 μM ARN5	XYL	5880	4080	-
18.1	7.5 μM ARN5	ASP1	4800	6600	103
18.2	7.5 μM ARN6	ASP2	4800	6600	103
18.3	7.5 μM ARN6	ASP2	4800	6600	103
19.1	7.5 μM ARN5	ASP1	6780	8580	378
19.2	7.5 μM ARN5	ASP1	6780	8580	378
19.3	7.5 μM ARN6	ASP2	6780	8580	378
20.1	7.5 μM ARN5	ASP1	11280	9480	774
20.2	7.5 μM ARN5	ASP1	11280	9480	774
20.3	7.5 μM ARN6	ASP2	11280	9480	774
21.1	XYL	ASP1	4800	6600	103
21.2	XYL	ASP2	4800	6600	103
21.3	XYL	ASP2	4800	6600	103
22.1	XYL	ASP1	6780	8580	378
22.2	XYL	ASP2	6780	8580	378
23.1	XYL	ASP1	11280	9480	774
23.2	XYL	ASP2	11280	9480	774

Table 22: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Oscillation time (sec)	Total time (sec)	Max volume (μL)
24.1	10 μM ARN	10 μM ARN	3200	1200	103
24.2	10 μM ARN	10 μM ARN	3200	1200	103
25.1	9 μM ARN	9 μM ARN	3200	1200	103
25.2	9 μM ARN	9 μM ARN	3200	1200	103

Table 23: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Oscillation time (sec)	Total time (sec)	Max volume (μL)
30.1	7.5 μM ARN	XYL	6600	4800	103
30.2	7.5 μM ARN	XYL	6600	4800	103
31.1	7.5 μM ARN	asphaltenes	6600	4800	103
31.2	7.5 μM ARN	asphaltenes	6600	4800	103
32.1	7.5 μM ARN	XYL	8580	6780	387
32.2	7.5 μM ARN	XYL	8580	6780	387
33.1	7.5 μM ARN	asphaltenes	8580	6780	387

Table 24: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Oscillation time (sec)	Total time (sec)	Max volume (μL)
40.1	7.5 μM ARN	XYL	6600	4800	103
40.2	7.5 μM ARN	asphaltenes	6600	4800	103
40.3	XYL	asphaltenes	6600	4800	103

Table 25: SINTERFACE experiments

Sample	Pump 1	Pump 2	Exchange time (sec)	Max volume (μL)	Comment
41.1	7.5 μM ARN	XYL	720	103	Suck in asphaltenes
41.2	7.5 μM ARN	asphaltenes	720	103	redo 40.1
41.3	XYL	asphaltenes	720	103	Small drop of asphaltenes

Table 26: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Oscillation time (sec)	Total time (sec)	Max volume (μL)
42.1	7.5 μM ARN	XYL	8580	6780	387
42.2	7.5 μM ARN	XYL	11280	9480	774
43.1	7.5 μM ARN	asphaltenes	8580	6780	387
43.2	7.5 μM ARN	asphaltenes	11280	9480	774
44.1	XYL	asphaltenes	8580	6780	387
44.2	XYL	asphaltenes	11280	9480	774

Table 27: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Total time (sec)	description
45.1	7.5 μM ARN	asphaltenes	5880	no exchange
45.2	XYL	XYL	5880	no exchange
45.3	7.5 μM ARN	XYL	5880	no exchange
45.4	XYL	asphaltenes	5880	no exchange

Table 28: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Total time (sec)	Volume	stock solution in pump 1
501	7.5 μM ARN	7.5 μM ARN	6300	25 then 15 μL	1
502	7.5 μM ARN	7.5 μM ARN	6300	constant 15 μL	1
511	2.5 μM ARN	2.5 μM ARN	6300	25 then 15 μL	1
512	2.5 μM ARN	2.5 μM ARN	6300	constant 15 μL	1
521	5.0 μM ARN	5.0 μM ARN	6300	25 then 15 μL	1
522	5.0 μM ARN	5.0 μM ARN	6300	constant 15 μL	1
531	2.5 μM ARN	2.5 μM ARN	6300	25 then 15 μL	2
532	2.5 μM ARN	2.5 μM ARN	6300	constant 15 μL	2
541	5.0 μM ARN	5.0 μM ARN	6300	25 then 15 μL	2
542	5.0 μM ARN	5.0 μM ARN	6300	constant 15 μL	2
551	2.5 μM ARN	2.5 μM ARN	6300	25 then 15 μL	3
552	2.5 μM ARN	2.5 μM ARN	6300	constant 15 μL	3
561	5.0 μM ARN	5.0 μM ARN	6300	25 then 15 μL	3
562	5.0 μM ARN	5.0 μM ARN	6300	constant 15 μL	3
571	7.5 μM ARN	7.5 μM ARN	6300	25 then 15 μL	3
572	7.5 μM ARN	7.5 μM ARN	6300	constant 15 μL	3

Table 29: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Total time (sec)	volume	stock solution in pump 1
581	2.5 μM ARN	2.5 μM ARN	6300 sec	25 then 15 μL	4
582	2.5 μM ARN	2.5 μM ARN	6300 sec	15 μL	4
591	2.5 μM ARN	2.5 μM ARN	6300 sec	25 then 15 μL	5
592	2.5 μM ARN	2.5 μM ARN	6300 sec	15 μL	5
601	asphaltenes	asphaltenes	6300 sec	25 then 15 μL	1
602	asphaltenes	asphaltenes	6300 sec	15 μL	1
611	asphaltenes	asphaltenes	6300 sec	25 then 15 μL	2
612	asphaltenes	asphaltenes	6300 sec	15 μL	2

Table 30: SINTERFACE experiments

Sample name	Pump 1	Pump 2	Total time (sec)	volume	stock solution in pump 1
621	7.5 μM ARN	asphaltenes	12180 sec	25 then 15 μL	4
622	7.5 μM ARN	asphaltenes	6780 sec	25 then 15 μL	4
631	7.5 μM ARN	asphaltenes	12180 sec	25 then 15 μL	5
632	7.5 μM ARN	asphaltenes	6780 sec	25 then 15 μL	5
641	10 μM ARN	asphaltenes	12180 sec	25 then 15 μL	4
642	10 μM ARN	asphaltenes	6780 sec	25 then 15 μL	4
651	10 μM ARN	asphaltenes	12180 sec	25 then 15 μL	5
652	10 μM ARN	asphaltenes	6780 sec	25 then 15 μL	5
661	7.5 μM ARN	asphaltenes	9480 sec	25 then 15 μL	4
671	7.5 μM ARN	asphaltenes	9480 sec	25 then 15 μL	5
681	7.5 μM ARN	asphaltenes	7500 sec	25 then 15 μL	4
691	7.5 μM ARN	asphaltenes	7500 sec	25 then 15 μL	5
701	10 μM ARN	asphaltenes	9480 sec	25 then 15 μL	4
711	10 μM ARN	asphaltenes	9480 sec	25 then 15 μL	5
721	10 μM ARN	asphaltenes	7500 sec	25 then 15 μL	4
731	10 μM ARN	asphaltenes	7500 sec	25 then 15 μL	5
741	7.5 μM ARN	asphaltenes	7500 sec	25 then 15 μL	5

6.4 IFT vs Time for all parallels

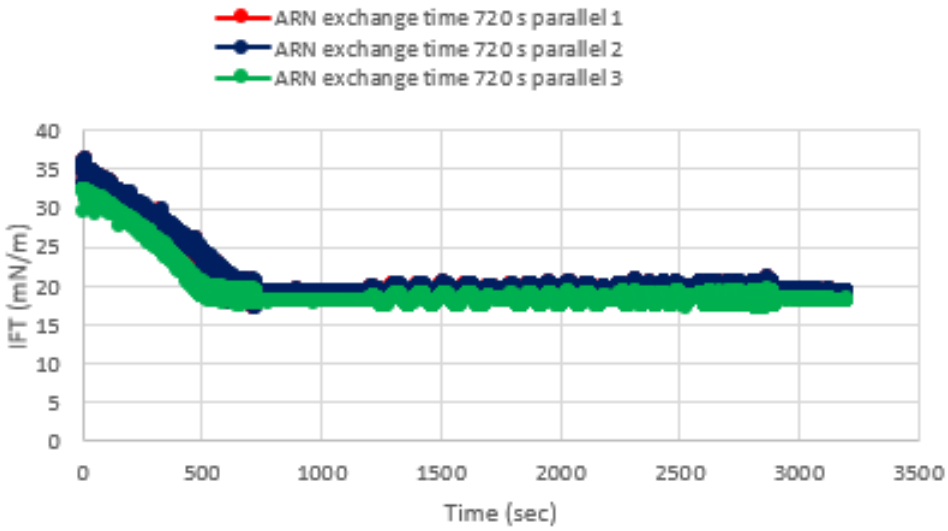

Figure 83: All 3 parallels for ARN-ARN exchange time 720 sec

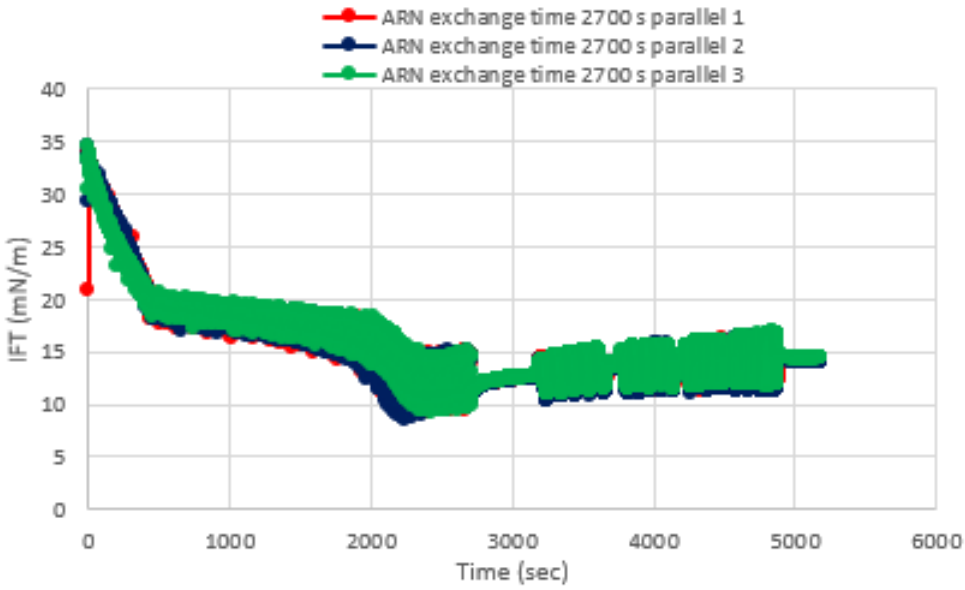

Figure 84: All 3 parallels for ARN-ARN exchange time 2700 sec

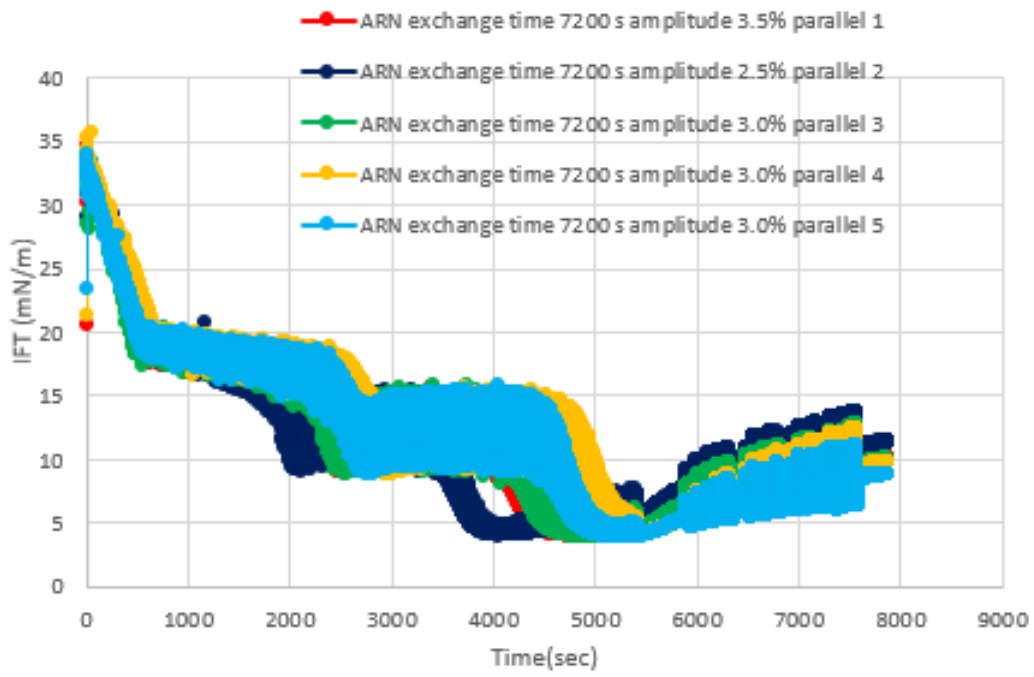

Figure 85: All 5 parallels for ARN-ARN exchange time 5400 sec

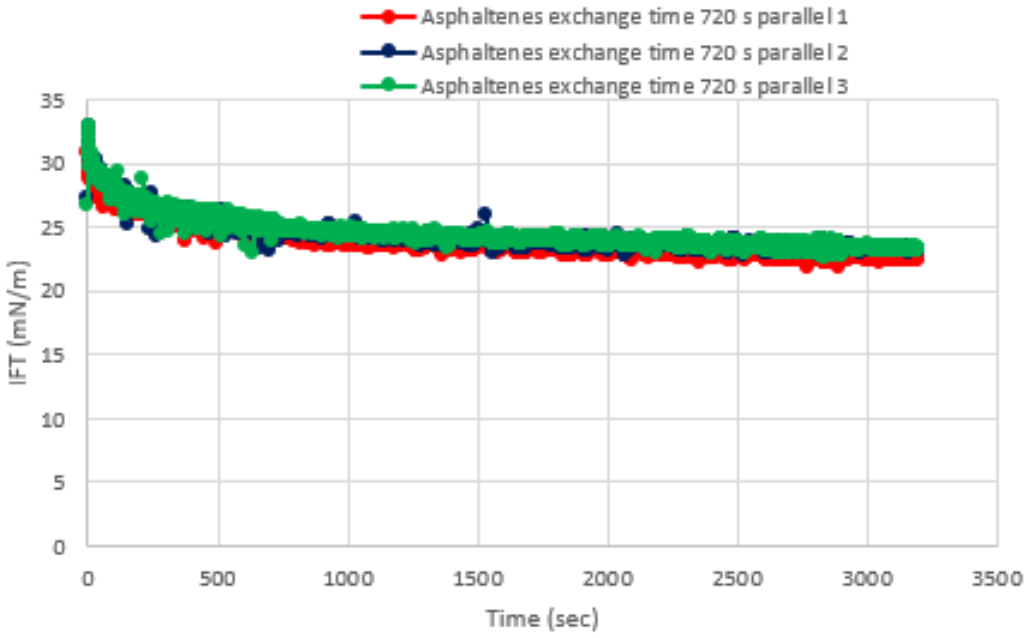

Figure 86: All 3 parallels for ASP-ASP exchange time 720 sec

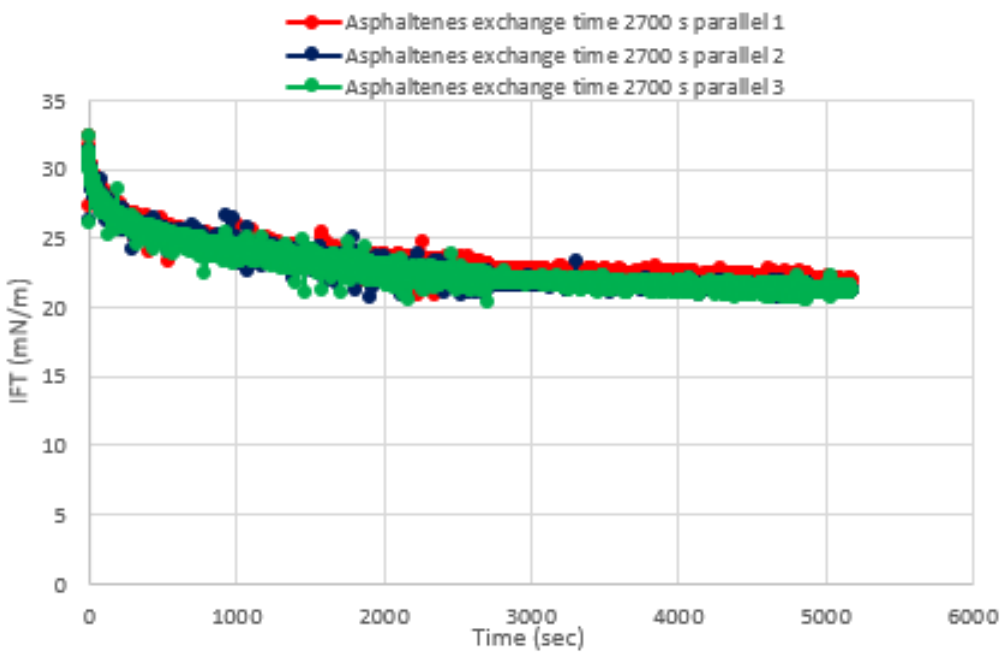

Figure 87: All 3 parallels for ASP-ASP exchange time 2700 sec

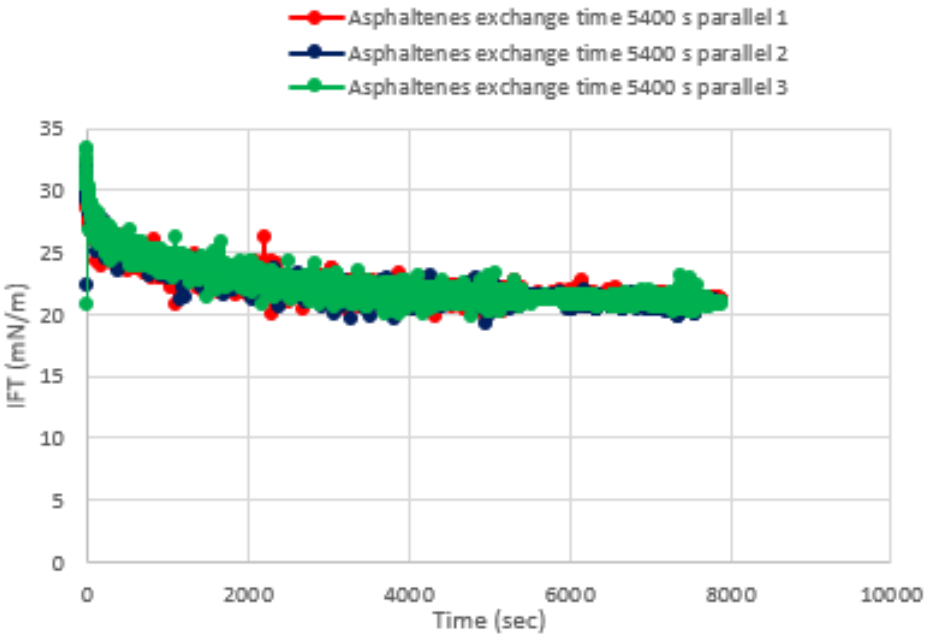

Figure 88: All 3 parallels for ASP-ASP exchange time 5400 sec

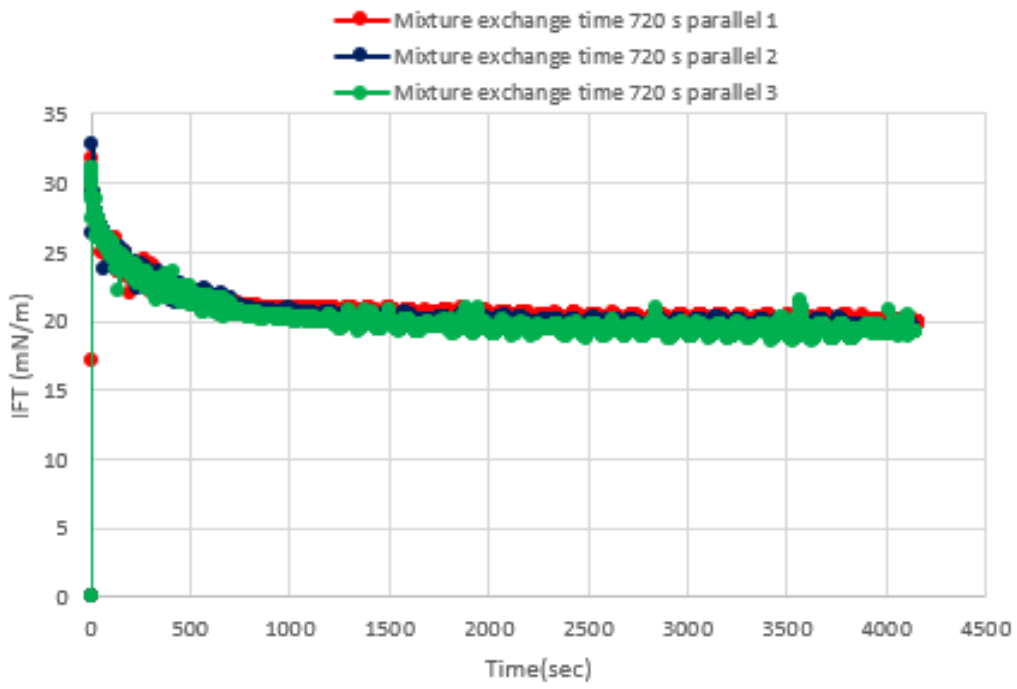

Figure 89: All 3 parallels for Mixture exchange time 720 sec

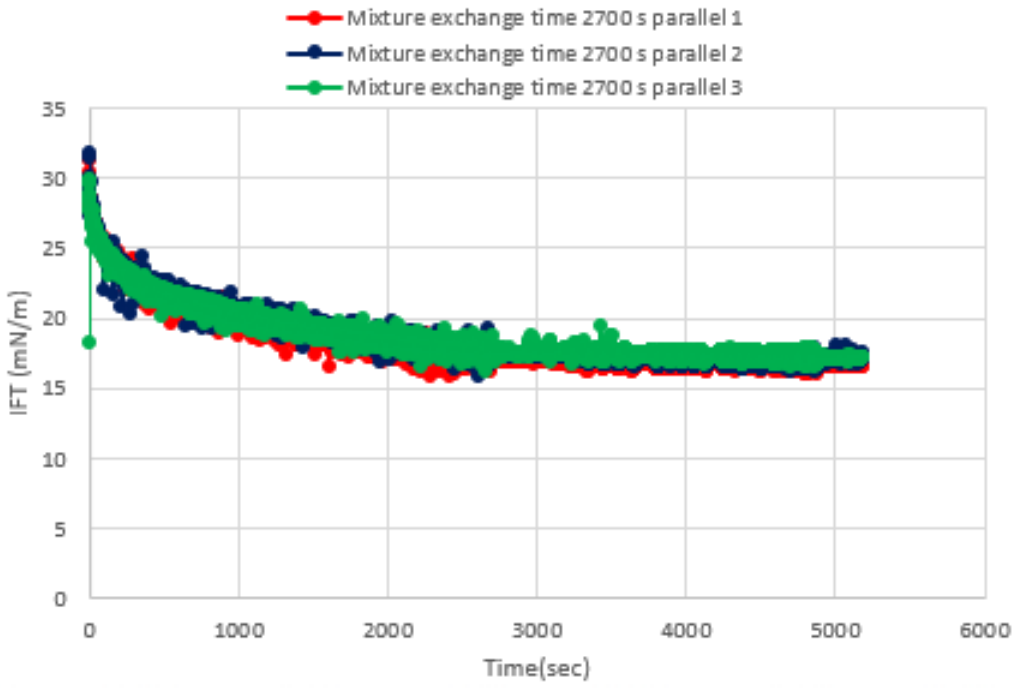

Figure 90: All 3 parallels for Mixture exchange time 2700 sec

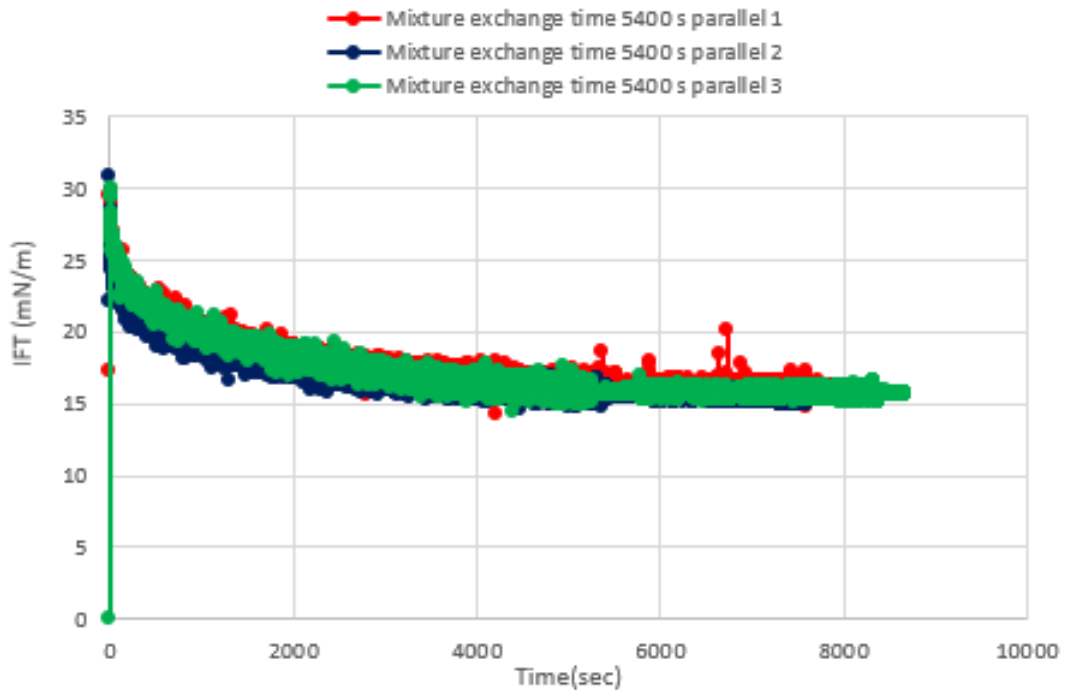

Figure 91: All 3 parallels for Mixture exchange time 5400 sec

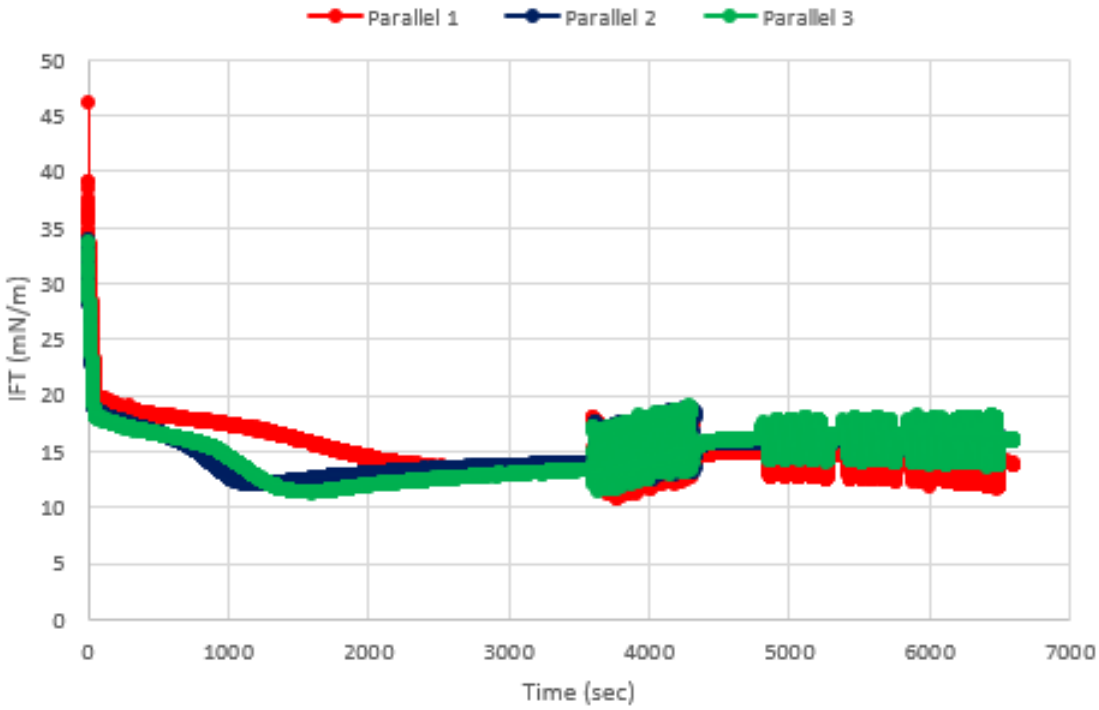

Figure 92: All 3 parallels for ARN-XYL exchange time 720 sec

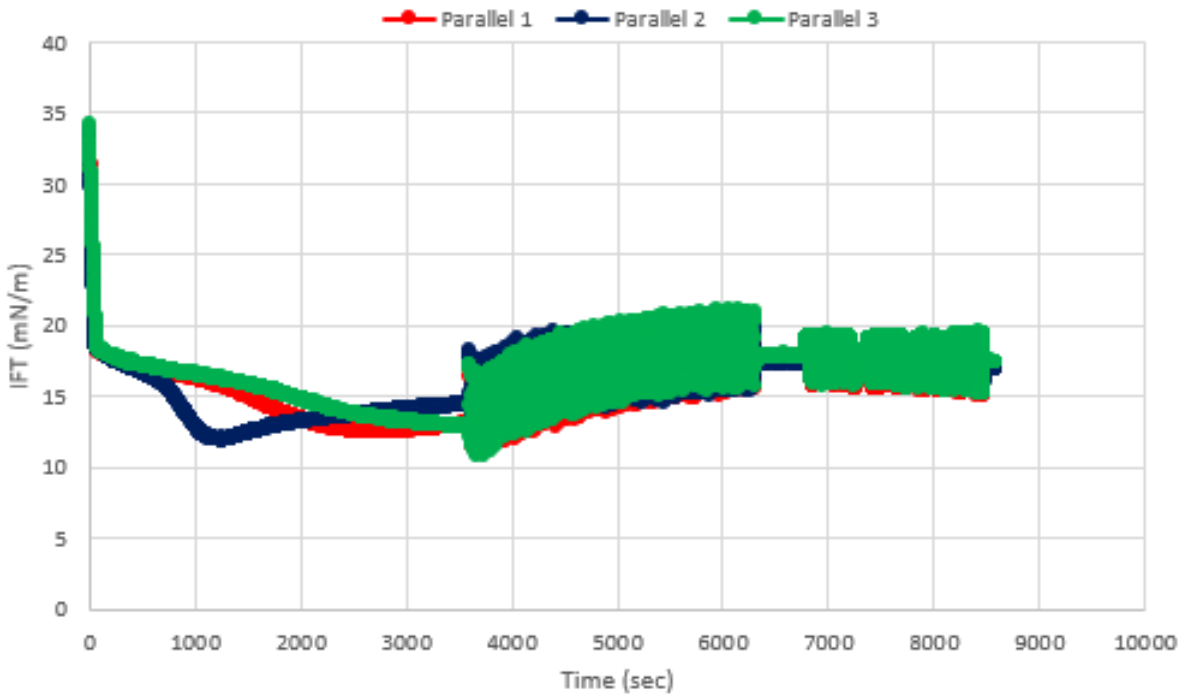

Figure 93: All 3 parallels for ARN-XYL exchange time 2700 sec

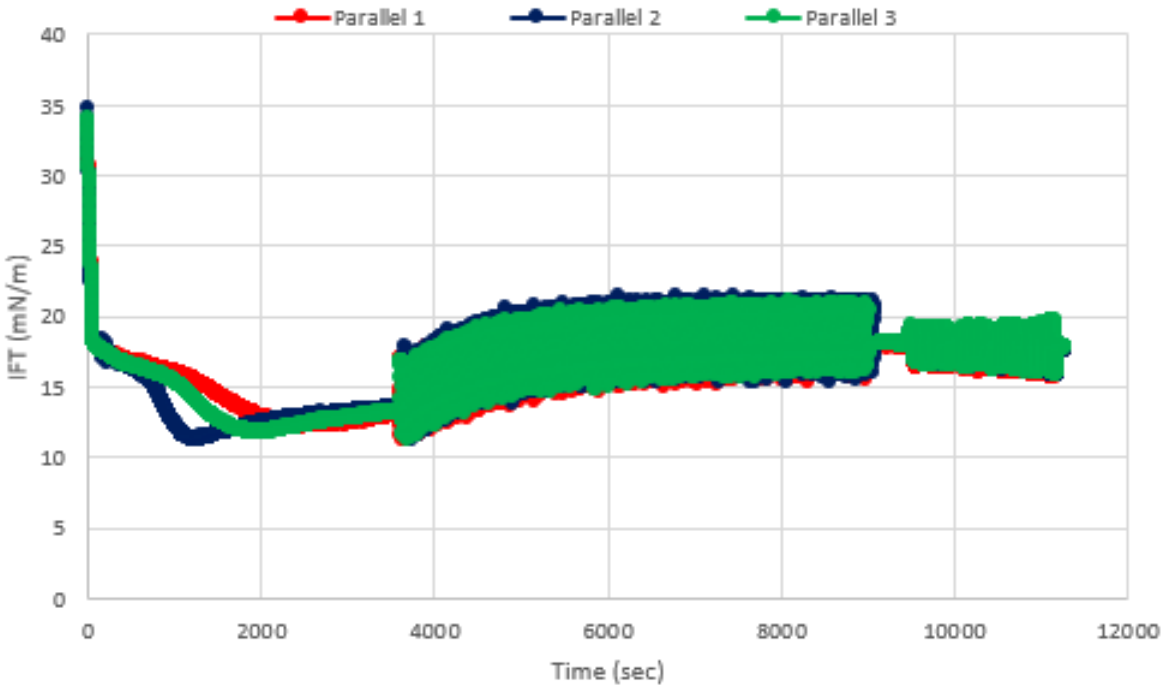

Figure 94: All 3 parallels for ARN-XYL exchange time 5400 sec

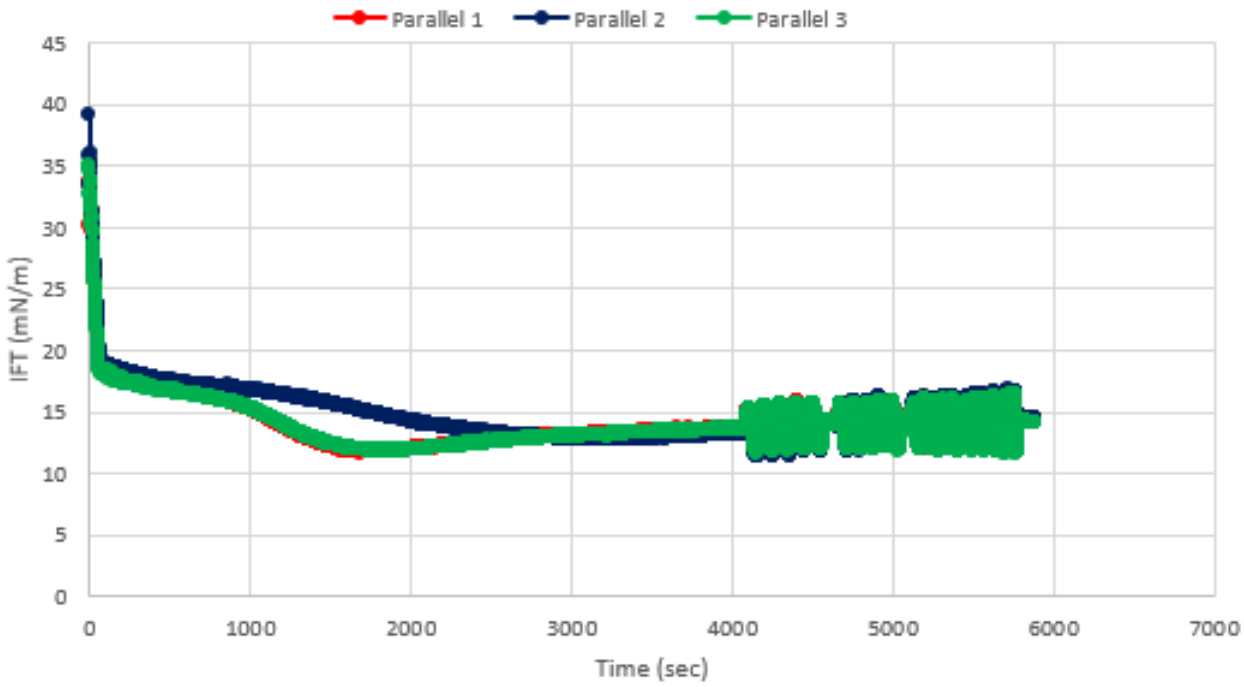

Figure 95: All 3 parallels for ARN-XYL no exchange

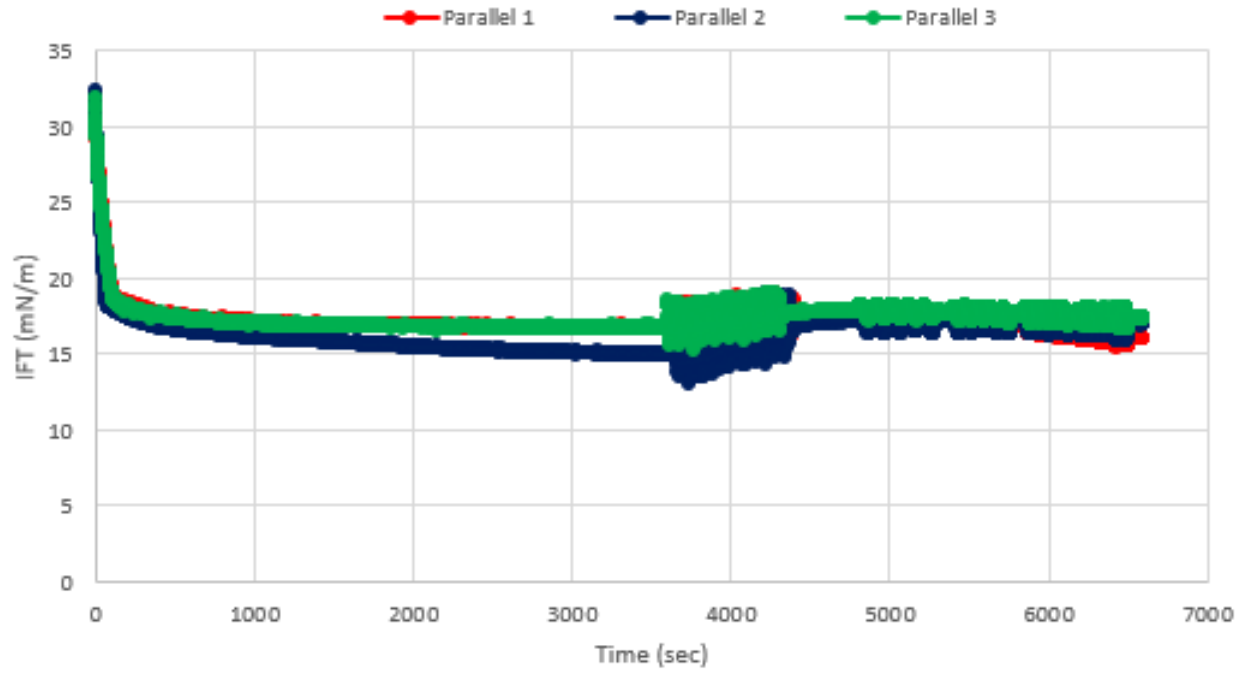

Figure 96: All 3 parallels for ARN-ASP exchange time 720 sec

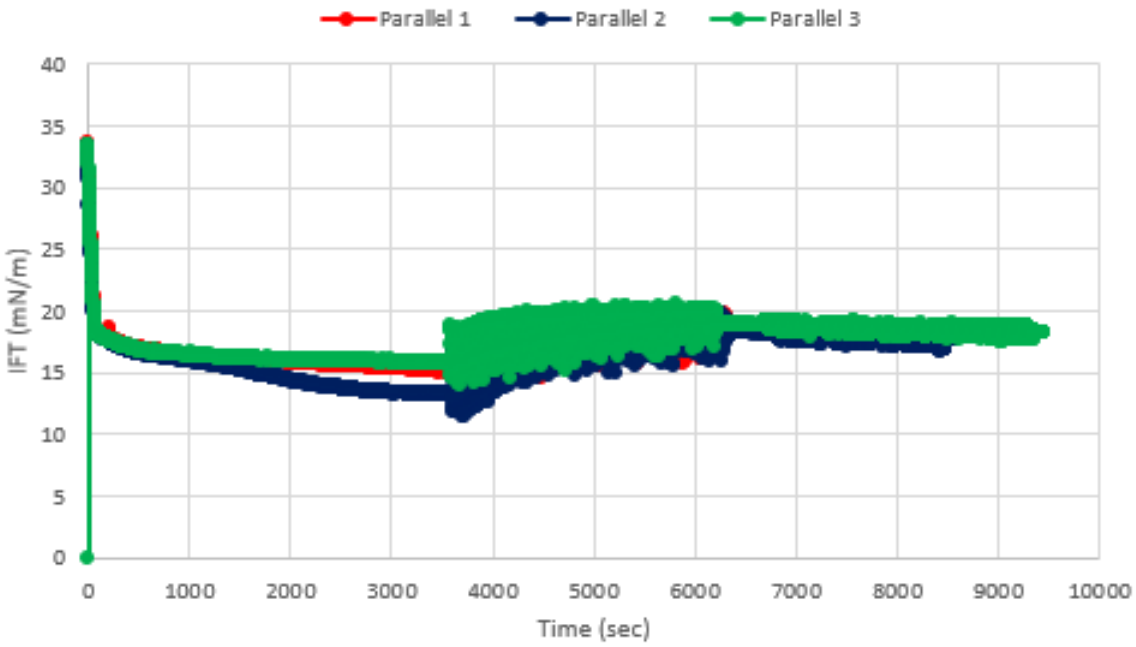

Figure 97: All 3 parallels for ARN-ASP exchange time 2700 sec

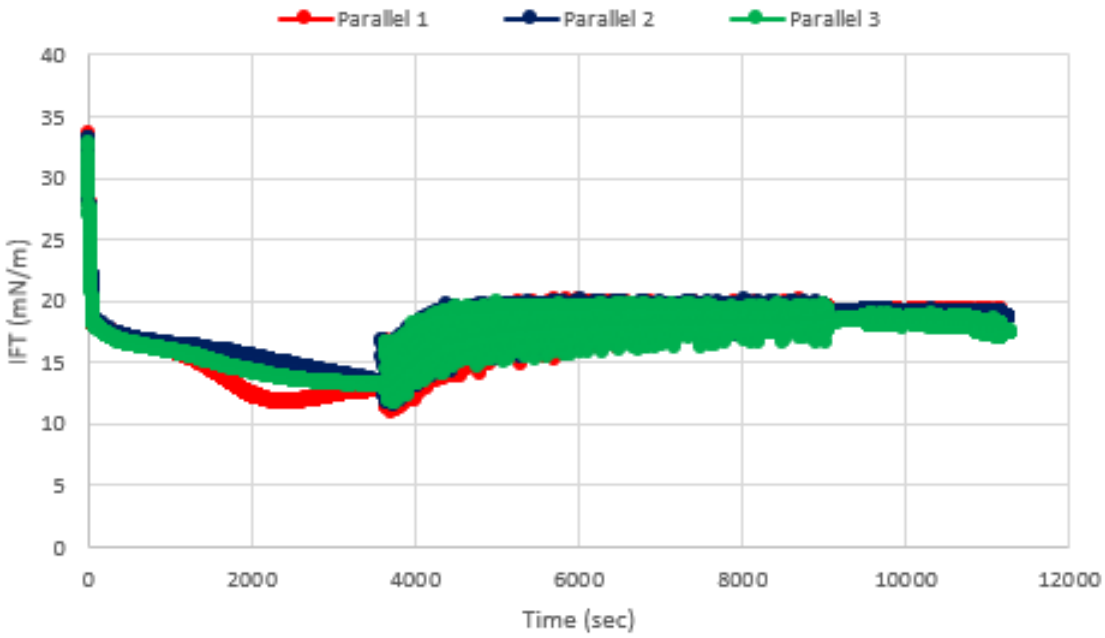

Figure 98: All 3 parallels for ARN-ASP exchange time 5400 sec

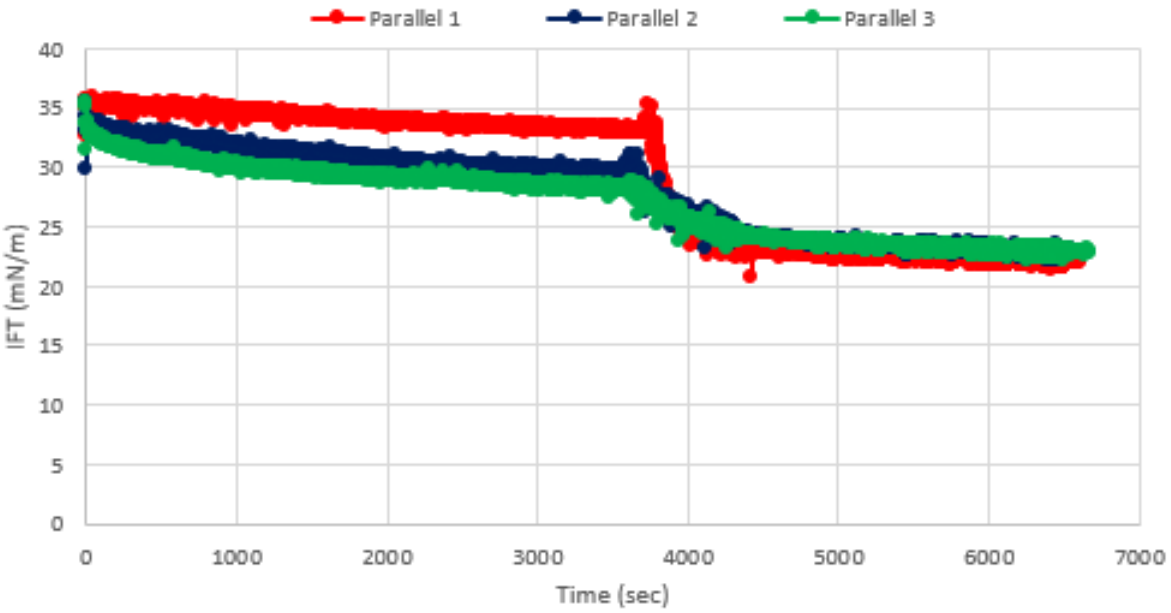

Figure 99: All 3 parallels for XYL-ASP exchange time 720 sec

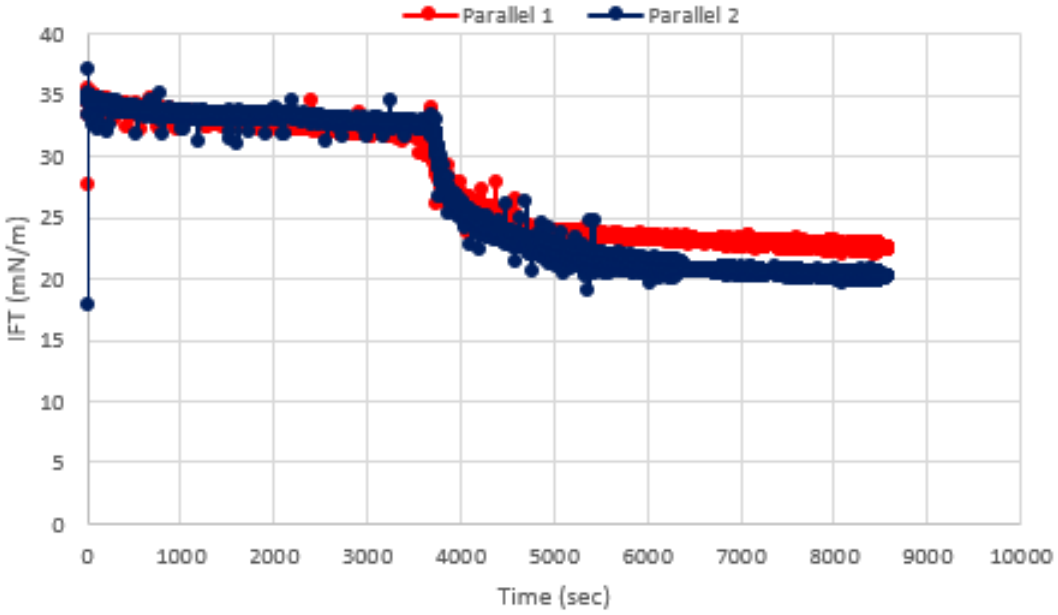

Figure 100: All 3 parallels for XYL-ASP exchange time 2700 sec

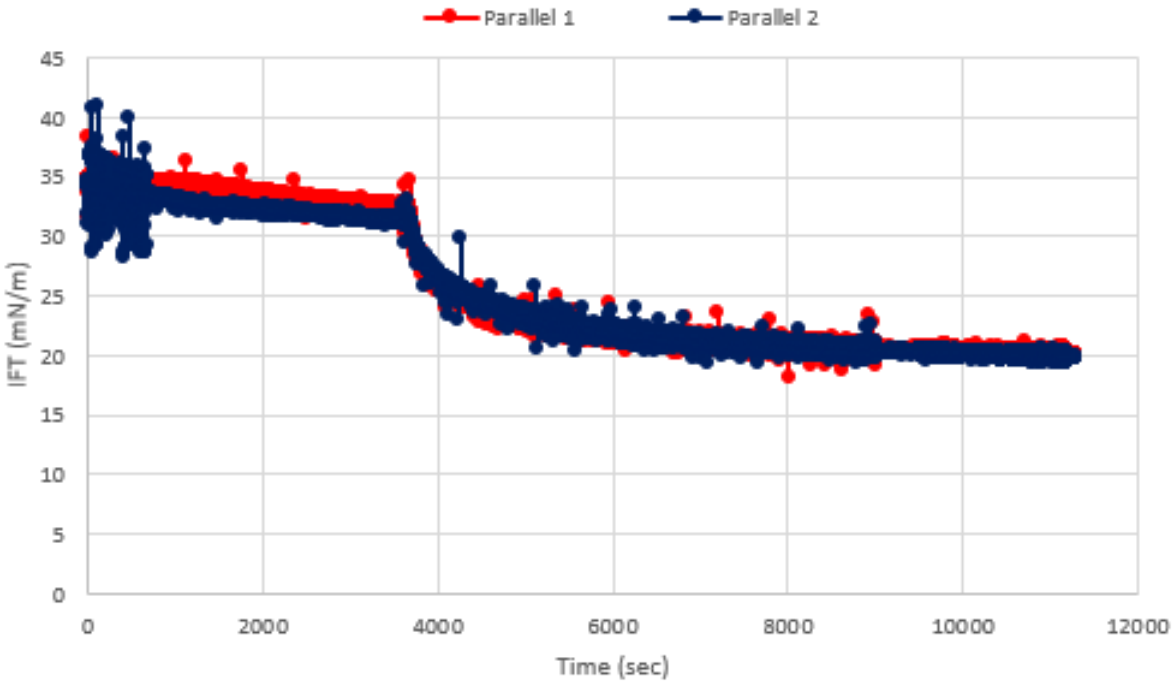

Figure 101: All 3 parallels for XYL-ASP exchange time 5400 sec

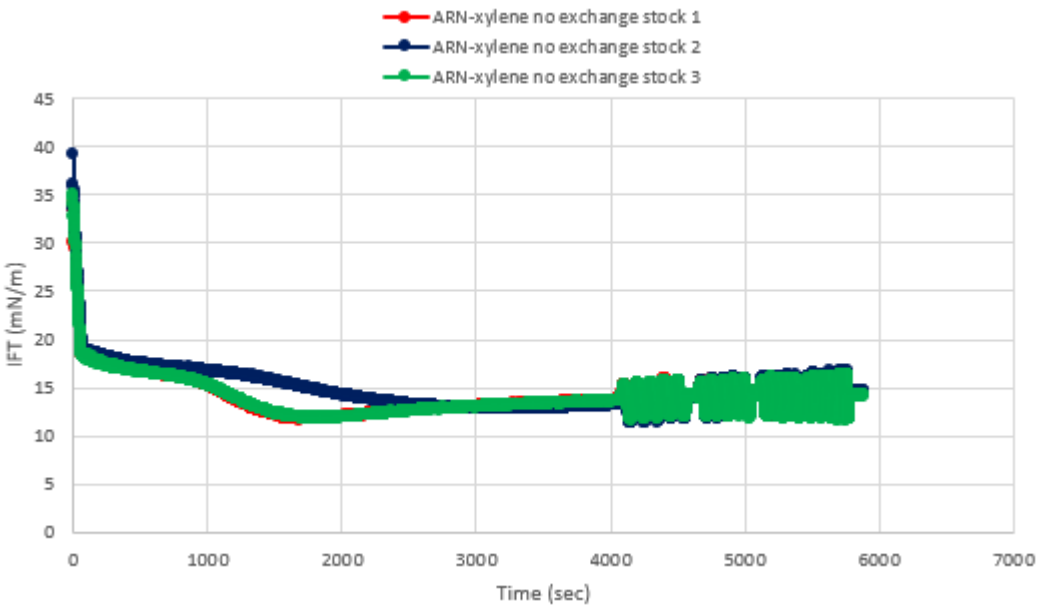

Figure 102: All 3 parallels for ARN-XYL no exchange

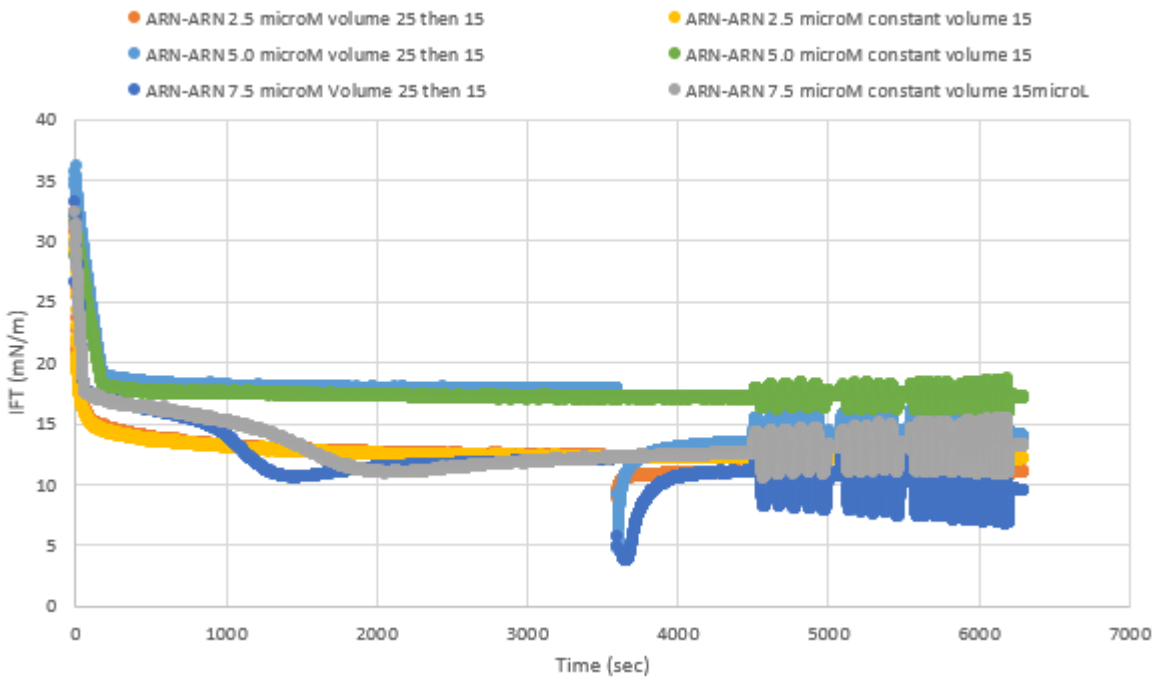

Figure 103: Plot of IFT as a function of time for stock 1 of ARN with concentration 2.5,5.0 and 7.5 μM, one parallel with volume changing from 25 to 15 μL after one hour and one with volume constant at 15 μL

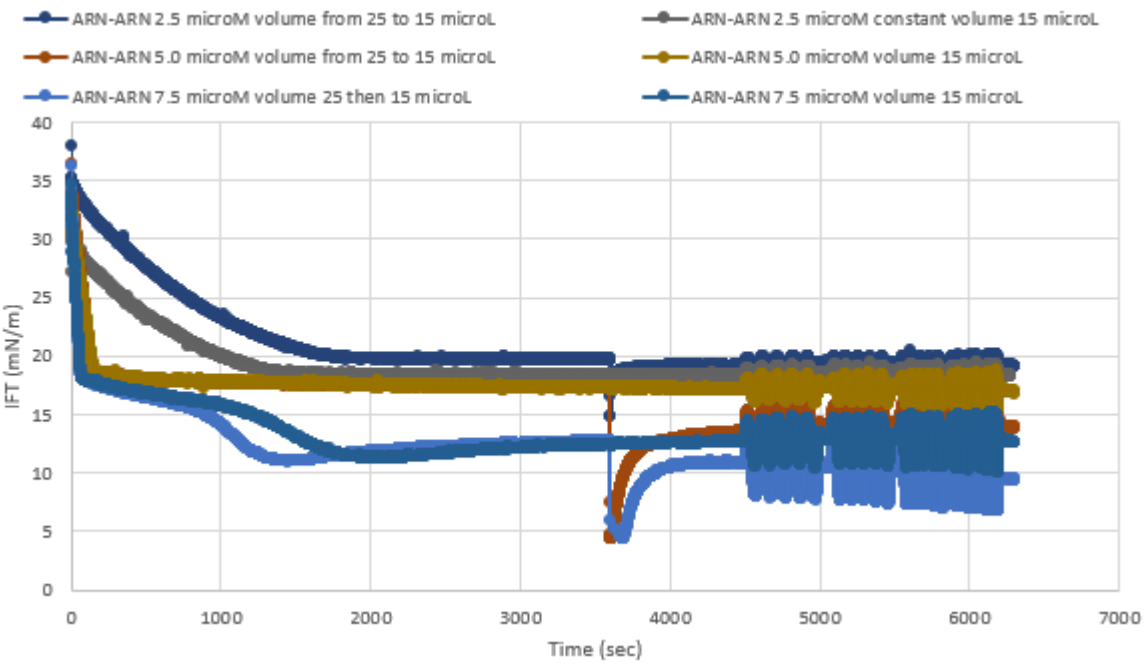

Figure 104: Plot of IFT as a function of time for stock 3 of ARN with concentration 2.5, 5.0 and 7.5 μM, one parallel with volume changing from 25 to 15 μL after one hour and one with volume constant at 15 μL

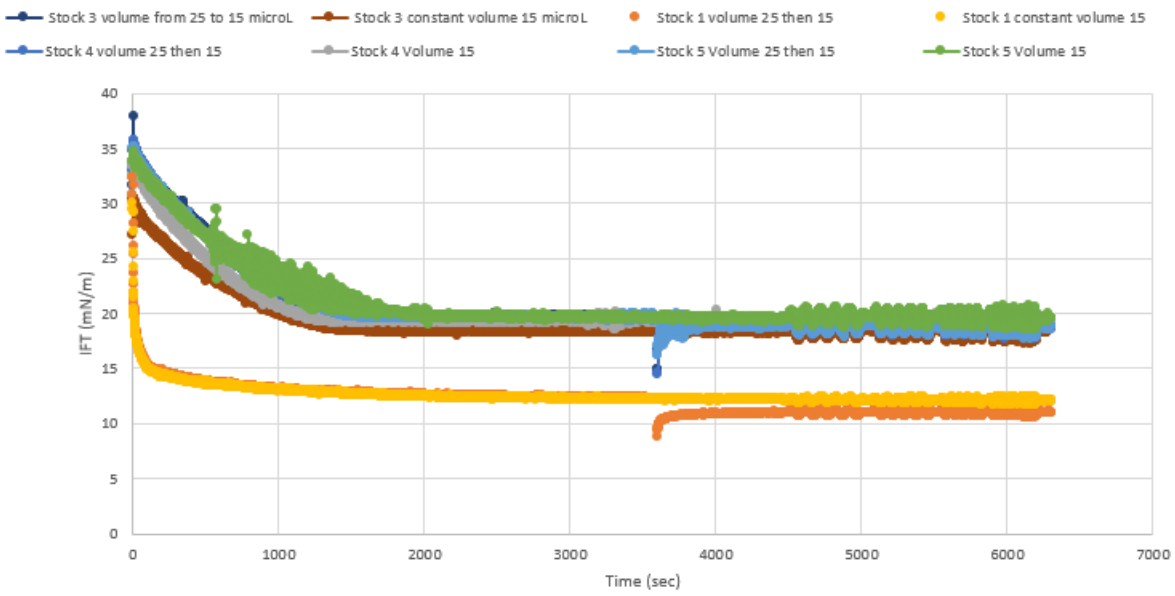

Figure 105: Result for all stocks of 2.5 *mu*M ARN with decreasing volume. The new stock 4 and 5 were done to confirm that the results from stock 1 could not be trusted

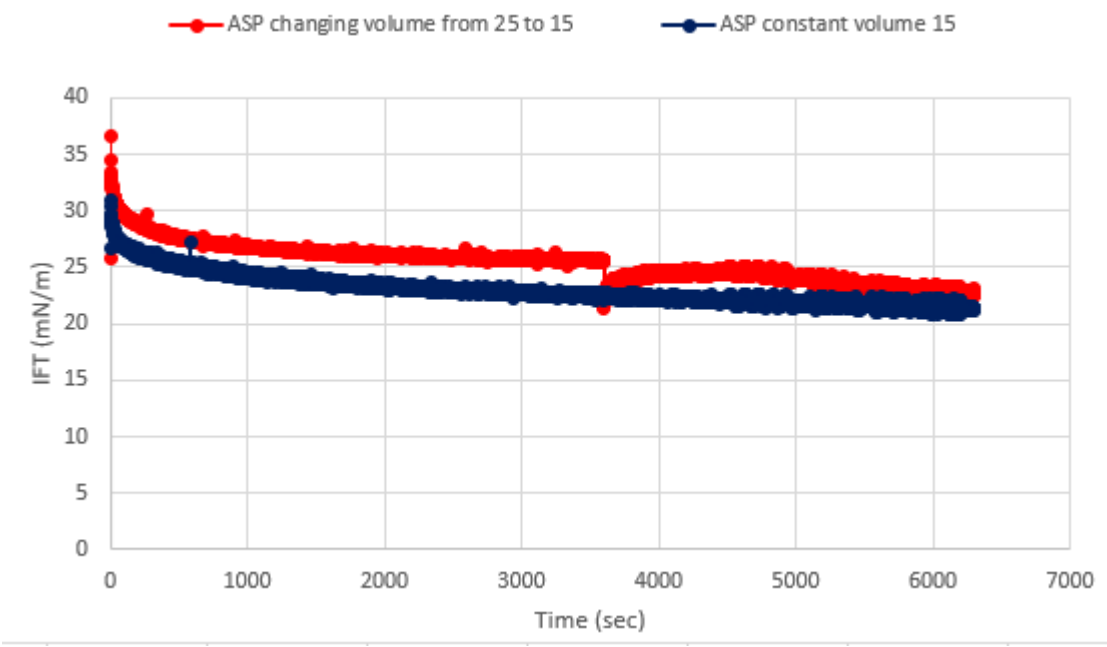

Figure 106: Plot of interfacial tension of asphaltenes for the second stock with changing volume from 25 to 15 μ L and constant volume at 15 μ L

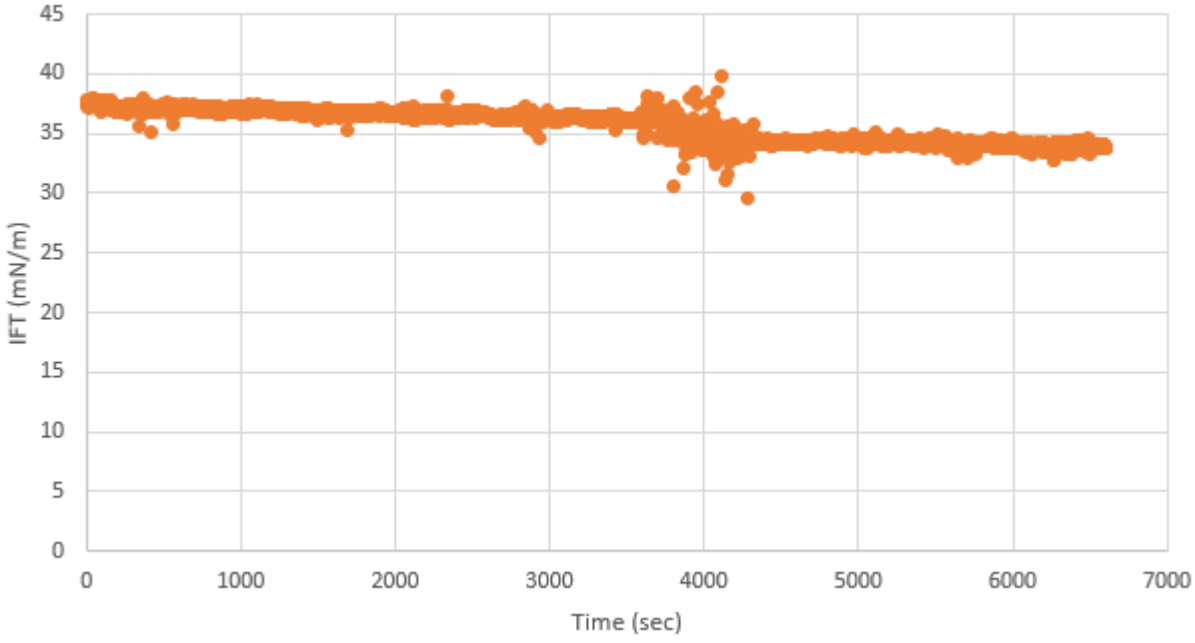

Figure 107: Experiment with pure xylene, done to see if the system was clean

6.5 Experiments done for calibration

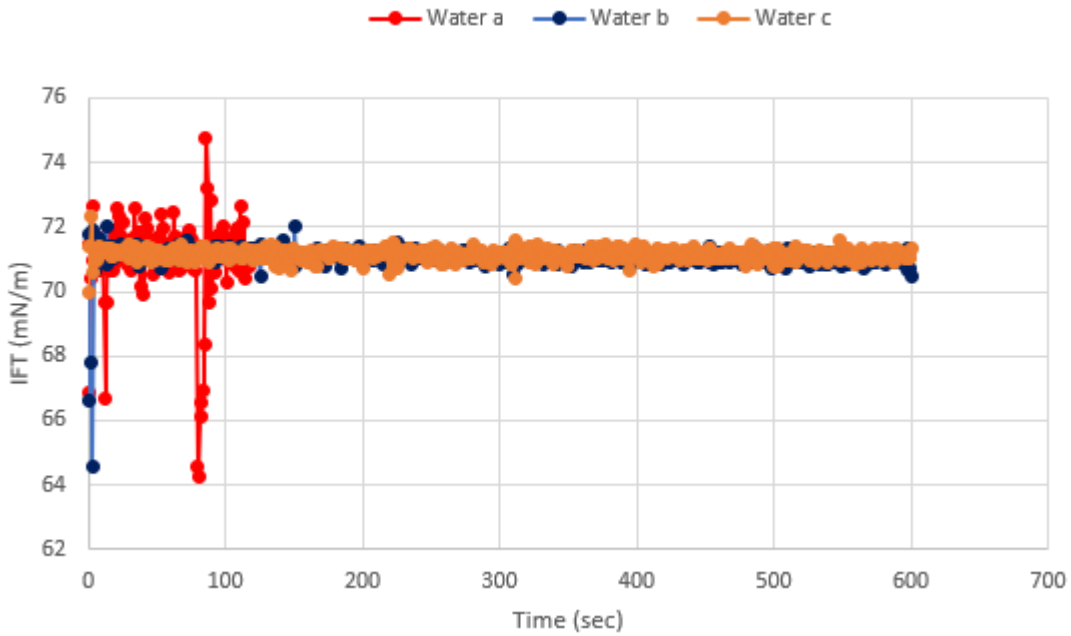

Figure 108: Interfacial tension of the experiments with water for calibration

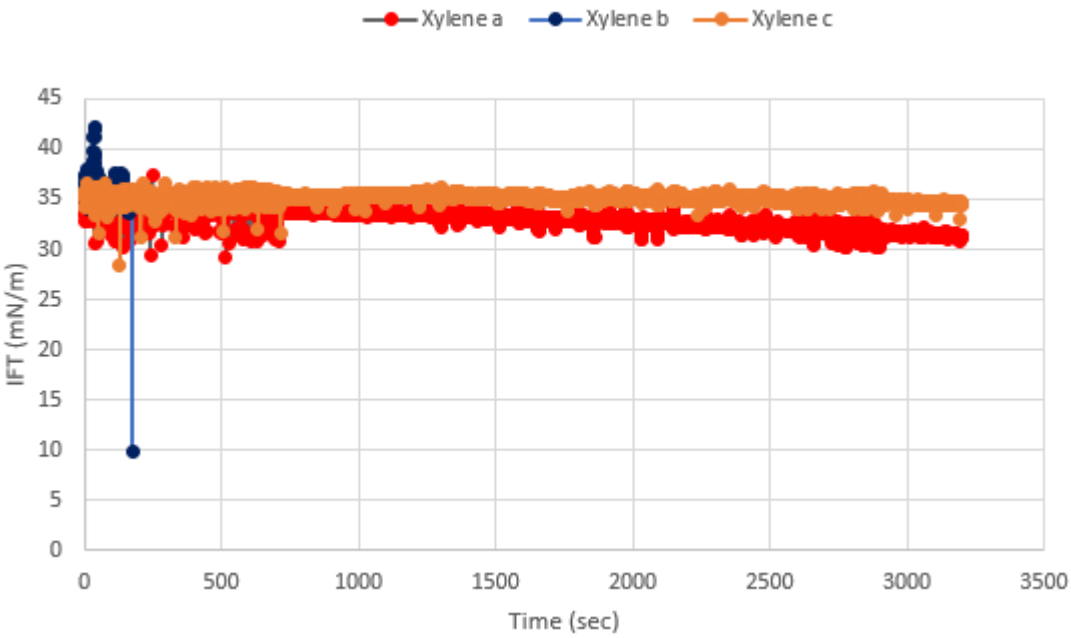

Figure 109: Interfacial tension of the experiments with xylene for calibration

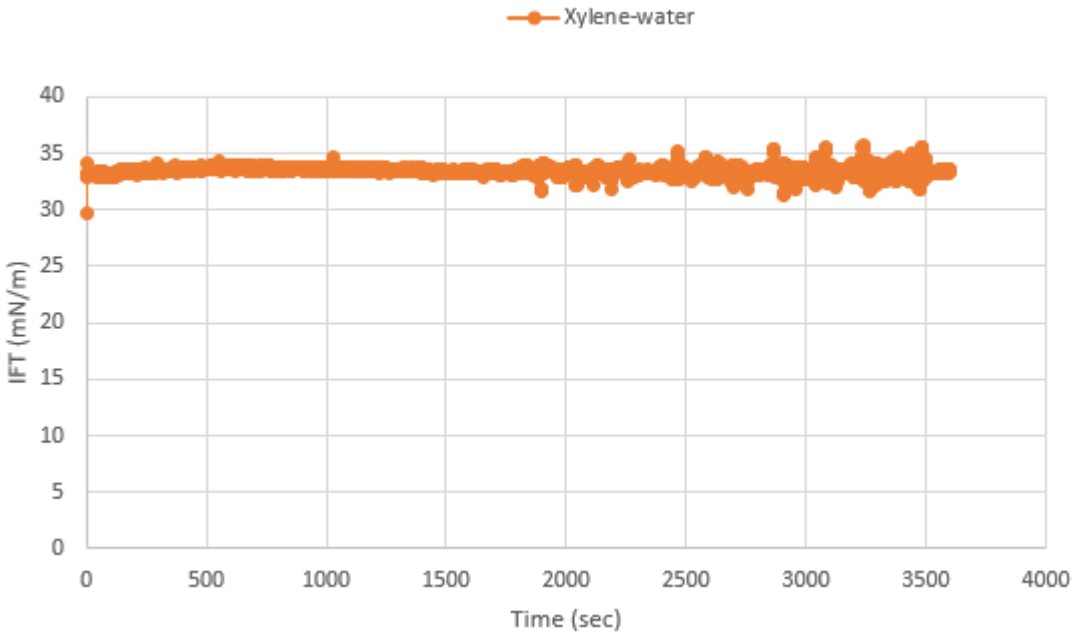

Figure 110: Interfacial tension of the experiments with xylene and water for calibration

6.6 Settings from SINTERFACE computer

The settings that were chosen on the computer for experiment with ARN-asphaltenes exchange 10.0 *mu*M stock 5, can be seen in figure 111 - 114.

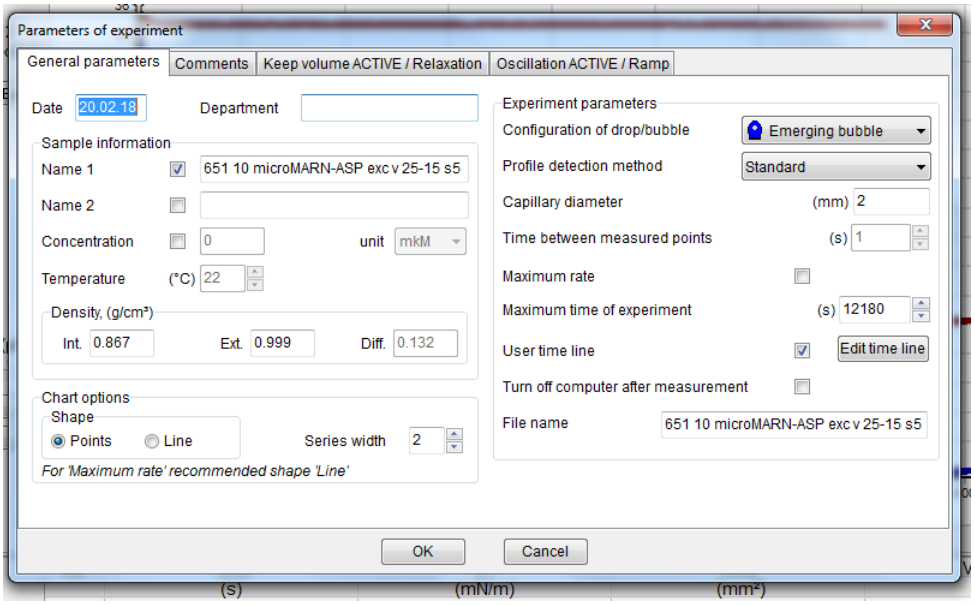

Figure 111: The setting used for experiment 651 ARN-asphaltenes exchange 10.0 *mu*M stock 5 part 1

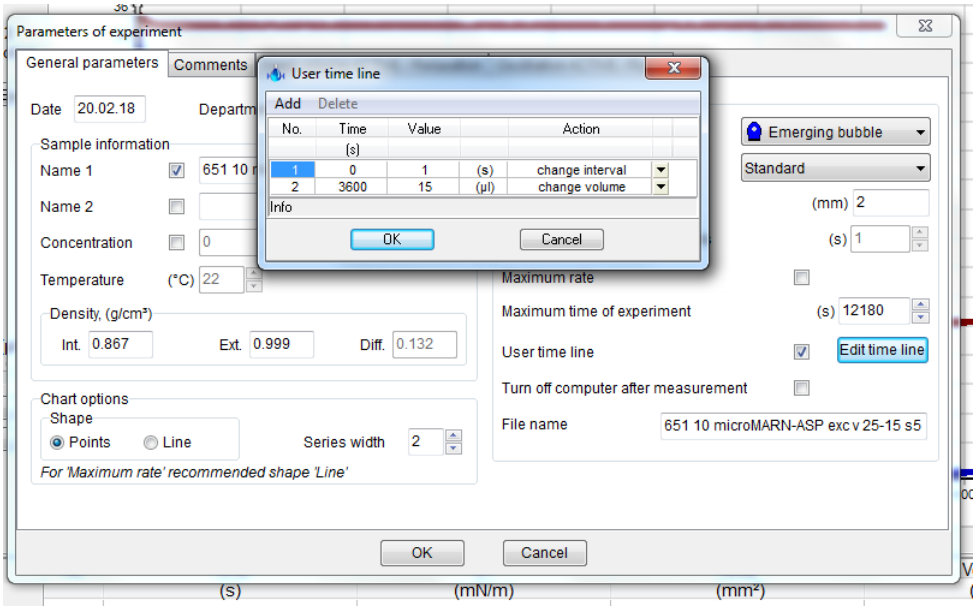

Figure 112: The setting used for experiment 651 ARN-asphaltenes exchange 10.0 *mu*M stock 5 part 2

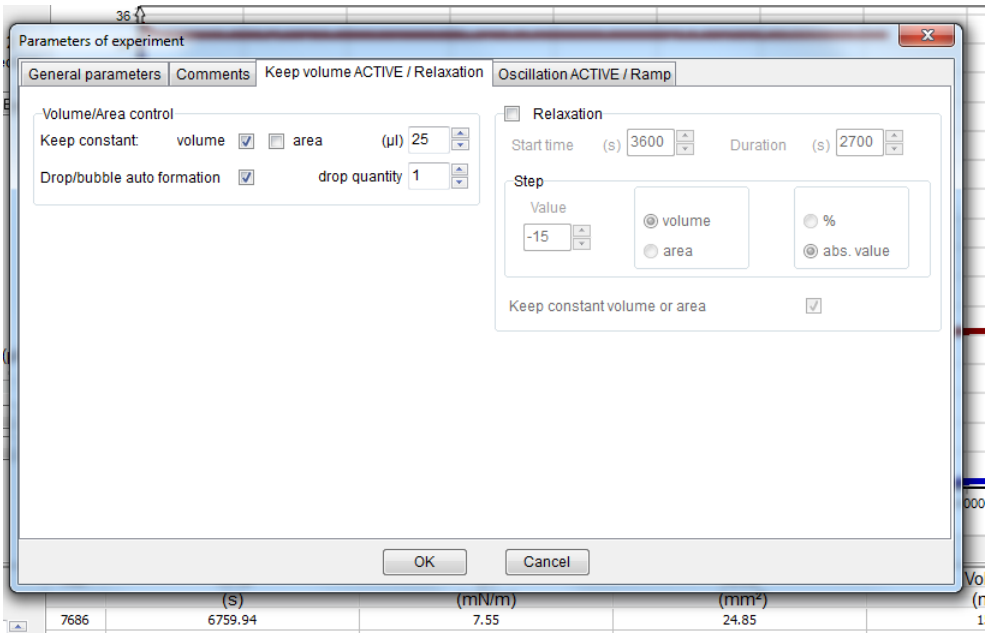

Figure 113: The setting used for experiment 651 ARN-asphaltenes exchange 10.0 *mu*M stock 5 part 3

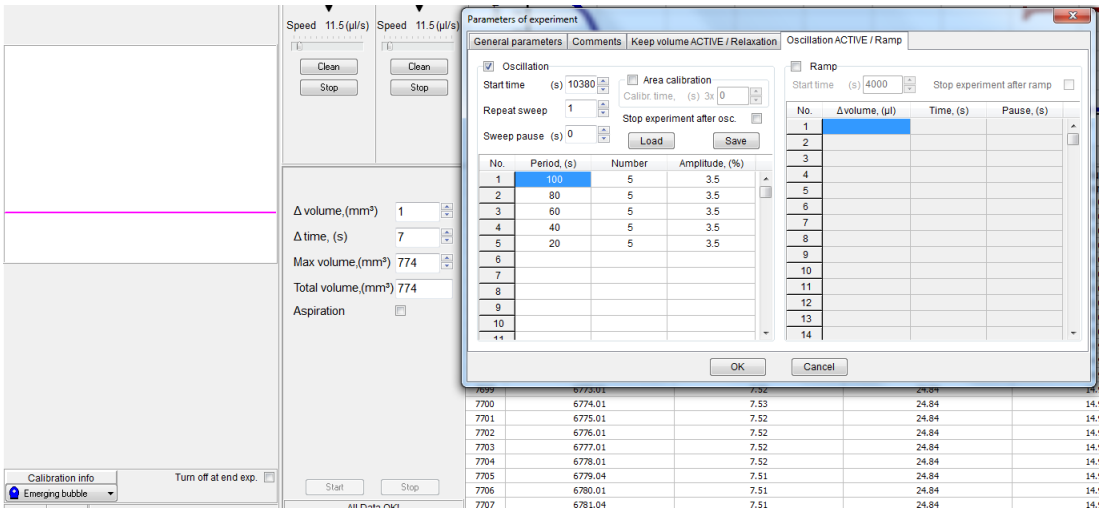

Figure 114: The setting used for experiment 651 ARN-asphaltenes exchange 10.0 *mu*M stock 5 part 4