



NTNU – Trondheim
Norwegian University of
Science and Technology

Partitioning of surfactants between the water and oil phases and relations to enhanced oil recovery methods

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Submission date: June 2014

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Preface

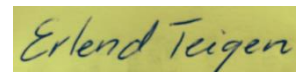
This master thesis has been conducted during the spring of 2014, at NTNU Gløshaugen, Trondheim. All experiments related to the thesis have been done in the Uglestad Laboratory.

I'm grateful to Professor Gisle Øye for valuable feedback through the process. I especially want to thank my co-supervisor Thomas Tichelkamp for introducing me to the new instruments and helping me with problems related to the experiments and theoretical background.

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

Place and date: Trondheim - 10.06.2014

Signature:



Abstract

The focus in this master thesis has been to investigate how a varying $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction affects the interfacial tension of a surfactant/brine - dodecane/toluene interface. It has also been investigated how the same systems are affected by a varying oil phase composition, stretching from pure- dodecane to toluene. Measurements regarding the pure dodecane phase have been performed during the project thesis in the autumn of 2013.

Series in which model oil composition was richest in dodecane start off with high IFT values at lower calcium content and experience a decrease followed by a rise, as calcium content increases. IFT for systems where toluene was the most abundant component in the oil phase rose as calcium fraction in the system was increased. Series with equally mixed oil phases or 75/25 wt. % in favor of either dodecane or toluene showed IFT values that were clearly influenced by both components.

Experiments proved that an increase of dodecane fraction relative to toluene in the model oil phase moved the minimum IFT point(s) towards higher calcium mole fractions. This behavior was expected from the EACN theory. Some values in the series conducted proved hard to measure, therefore a decrease in overall ionic strength proved useful in terms of finding the minimal interfacial tension for some of the dodecane/toluene series.

The IFT value of the dodecane/brine and toluene/brine systems showed not to be affected by an increasing calcium mole fraction when surfactant was removed from the aqueous solution. This indicates that the observed changes in IFT in systems where surfactant is used, is clearly an effect of interactions between surfactants and cations.

The optimal outcome has been to get a more mechanistic understanding of the oil-water interface, and the results can be used to model how a varying $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction affects the interfacial tension of an aqueous-oil system. Experimental results match exceptionally well with what is expected behavior from the EACN theory, and can be of high interest to further research related to combined surfactant- and low salinity flooding in relation to EOR.

Sammendrag

Målet i denne oppgaven har vært å undersøke hvordan en varierende $\text{Ca}^{2+}/\text{Na}^{+}$ molfraksjon påvirker overflatespenningen mellom vann og olje i et surfaktant/saltvann - dodekan/toluene system. Det har også blitt undersøkt hvordan de same systemene påvirkes av ulik sammensetning i oljefasen, som har blitt variert fra ren- dodekan til toluene. Eksperimenter gjort med ren dodekan ble utført under spesialiseringsprosjektet, høsten 2013.

I seriene med modeloljesammensetning dominert av dodekan var overflatespenningen høy for lavere kalsium molfraksjoner, mens den gradvis falt til et minimum når $\text{Ca}^{2+}/\text{Na}^{+}$ molfraksjonen økte, for så å stige igjen når molfraksjonen av kalsium ble enda høyere. I systemene der model olje fasen inneholdt mest toluene ble det observer en gradvis økning i overflatespenningen med økt kalsium innhold i vannløsningen. Overflatespenningen for systemer med lik oljesammensetning (50/50 wt. %) eller gradvis dominert av den ene komponenten (75/25 wt. %) viste seg å være påvirket av begge de rene komponentene.

Eksperimenter viste at en økt fraksjon av dodekan i modeloljefasen gradvis forskjøv minimum overflatespenning(er) mot høyere molfraksjon av kalsium. Denne trenden var på forhånd forventet fra EACN teorien. Noen verdier viste seg å være vanskelige å måle, derfor ble ionestyrken senket i et forsøk på å finne et absolutt minimum for utvalget av $\text{Ca}^{2+}/\text{Na}^{+}$ molfraksjoner.

For systemer uten surfaktant viste det seg at overflatespenningen for verken toluene/saltvann eller dodekan/saltvann systemene ble påvirket av en økende molfraksjon av kalsium. Dette indikerer at den observerte endringen i overflatespenning i systemer der surfaktant benyttes, åpenbart er en effekt av interaksjoner mellom surfaktanter og kationer.

Det optimale resultater har vært å få en mer mekanistisk forståelse for olje-vann grenseskiktet, og resultatene oppnådd kan brukes til å modelere hvordan en varierende $\text{Ca}^{2+}/\text{Na}^{+}$ molfraksjon påvirker overflatespenningen til et vann-olje system. Eksperimentelle resultater oppnådd passer godt overens med hva som var forventet fra EACN teorien, og kan være veldig relevante for videre forskning knyttet til kombinert surfaktant og lav-salinitet operasjoner innen EOR.

Abbreviations

EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
AOT	Aerosol OT (sodium bis(2-ethylhexyl) sulfosuccinate)
LoSal	Low Salinity
CMC	Critical Micelle Concentration
CPP	Critical Packing Parameter
SVT	Spinning Drop Video Tensiometer
milliQ	“Ultrapure” water
EACN	Equivalent Alkane Carbon Number
ACN	Alkane Carbon Number

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1. Theoretical Background

1.1 Steps of oil recovery

Enhanced oil recovery (EOR) generally refers to oil recovery over and above that obtained through the natural energy of the reservoir. Within the broad definition there are a huge variety of processes, including among others waterflooding, hydrocarbon injection and micellar-polymer flooding. Oil recovery processes have been classified into three levels, including primary, secondary and tertiary. The means that are taken in order to extract the oil from the reservoir decide to which classification a certain method belong, and will be described in the sections below.¹

1.1.1 Primary recovery

During the primary recovery step, the driving force mainly comes from the pressure difference between the reservoir and the surface. Since the natural pressure in the reservoir is much higher than the atmospheric pressure plus the hydrostatic pressure between the reservoir and the surface, no additional pressure needs to be applied in order to extract the oil. Usually less than 15 % of the total oil is recovered during the primary recovery phase.²

1.1.2 Secondary recovery

During the secondary recovery stage, the reservoir pressure itself does not suffice in order to recover the oil. In order to maintain or to restore the pressure in the reservoir, injection of water or gas is necessary.²

1.1.3 Tertiary recovery

The remaining oil trapped after the two first recovery phases is the target of EOR, and the combined oil production from both the primary and secondary recovery phases is generally less than 40 % of the original oil in place. Thus, the potential target for EOR does often exceed the reserves that can be produced by conventional methods, and makes research related to EOR methods of high interest.¹ The different EOR procedures are divided into three main categories: miscible, thermal and chemical methods.²

When the injected fluid is gas rather than water, the interfacial tension between the oil and the injected fluid is drastically lowered. Displacement methods do among others include injection of hydrocarbon gas, which leads to a lower viscosity and therewith mobilization of oil trapped

in the pores of the reservoir rock. Also CO₂ injection has since the 1950s been a subject to wide research, due to its ability to both swell the oil and lower the oil's viscosity.^{1,2}

The thermal displacement methods are all about reducing the viscosity of the crude oil, which is done either by injection of hot fluids or by the so-called in-situ combustion method. The crude oil undergoes both physical and chemical changes due to the effects of the heat supplied, and is thus mobilized. One method often applied is the injection of hot water/steam, which represented 72 % of the total enhanced oil recovery for the USA in 1988.³ The in-situ combustion method involves combustion of oil components inside the reservoir (air is supplied), and therewith mobilizes the heavier oil components. The effects of the thermal processes do among other vary with crude oil composition and temperature.

Chemical Flooding is the last main group of processes, and involves polymer, surfactant and alkaline flooding, as shown in Figure 1.1 below.⁴ Adding polymers to the injection water increases the viscosity of the water, and hence increases its sweep efficiency in the reservoir. Due to water having a higher permeability in the porous rock, the increased viscosity allows a higher recovery in the porous rock. The history of alkaline chemical usage dates back to the early 1920s, when it was believed that flooding the reservoir with alkaline solutions like sodium carbonate and caustic soda would enhance the oil recovery.² Although mechanisms were not understood completely at that time, the hypothesis of changed wettability and lower IFT between oil and water was well established. Modern research points towards a saponification effect (more known as formation of surfactant), as the base formed surfactants with the natural acidic substances in the crude, and hence caused a reduction in the IFT.² Selection of alkaline chemicals for use in different reservoirs is never easy, due to the variations in the chemical systems, meaning an absolute classification is obviously difficult. The alkaline effect is also strongly related to the pH in the reservoir.²

Surfactant- and low-salinity flooding are two methods related to the tertiary oil recovery phase. They're both of high relevance for the experiments that have been carried out in this thesis, and will thus be explained in the upcoming sections more comprehensively.

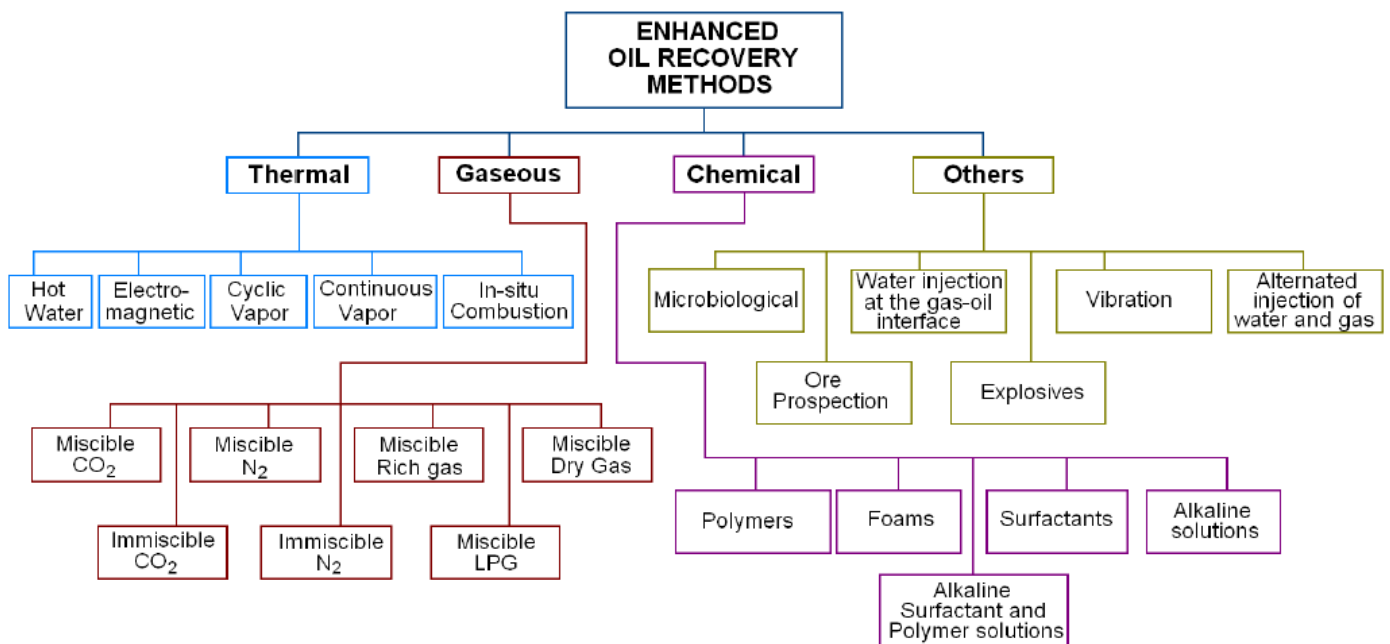


Figure 1.1: Classification of different EOR methods.⁴

1.2 Surfactant injection in EOR

1.2.1 General about surfactants

A surface active agent, more known as a surfactant, has the tendency to adsorb at interfaces, hence lowering the interfacial tension between two phases. The result of a surfactant adsorption is lowering the free energy of the interface. Surfactants have a molecular structure that consists of a hydrophilic head group and a hydrophobic tail. It is this very structure of the molecule that ensures its high affinity to interfaces, and thereby reducing the interfacial tension between the two immiscible phases. The interfacial tension can be described either in terms of a force or as an energy, the two most common ways of expressing the interfacial tension are shown by Equations 1.1 and 1.2 below.³

$$\gamma = \left(\frac{dG}{dA} \right)_{T,P} \quad (1.1)$$

$$\gamma = F/2L \quad (1.2)$$

Where γ in the first case represents the increase in surface free energy [J/m^2], which can be related to force per length as [$\text{J/m}^2 = \text{N/m}$], in the latter equation above.

For a two component system having constant temperature, the following Equation 1.3 applies.³

$$d\gamma = - \sum^i \Gamma_i d\mu_i \quad (1.3)$$

Here Γ_i represents the surface excess of the component i , and $d\mu_i$ is the change in chemical potential of component i . The equation above is commonly known as Gibbs' equation of adsorption, it does however only apply to a simple 2-component system. For a surfactant/brine-oil system we see that a higher adsorption of surfactants at the interface leads to a lower interfacial tension. The ability to adsorb at the interface depends on many different factors, among others surfactant structure and surfactants affinity to a specific surface, which again are controlled by fluid characteristics.

It is usual to distinguish between 4 different types of surfactants, the classification is related to the properties of the hydrophilic head group. The four main groups are: anionic, cationic, non-ionic and zwitter-ionic.³

The anionic surfactants is by far the largest group and stands alone for some 73 % of the total world consumption.³ Such surfactants are used in the everyday life, as they are cheap and easy to fabricate, and almost every detergent derives from an anionic surfactant. Though depending on the head group properties, most anionic surfactants generally have the ability to lower the IFT and at the same time be relatively stable and robust. These very properties mentioned above, make the anionic surfactants of high interest for the EOR industry.

The second largest group in terms of consumption is the non-ionic surfactants, which constitute 21 % of all surfactant usage on world basis.³ Although being more robust and more tolerant to high salinity water solutions, they do not have the ability to lower the IFT to the same extent as the anionic, and are therefore of lesser interest in relation to EOR. Both cationic (6%) and zwitter-ionic (< 1 %) surfactants stand for very little of the total world consumption, they are also too expensive to be used in an EOR operation.³

1.2.2 CMC and Self-Assembly

Equation 1.3 above shows that a higher adsorption of surfactants at the interface will lower the interfacial tension between the two immiscible fluids. By increasing the surfactant

concentration more surfactant molecules will be available for adsorption at the interface, but at some point, the so-called critical micelle concentration is reached. At this point, no change in interfacial tension is observed, and adding more surfactant molecules to the mixture will not further lower the IFT. This happens because the surfactant monomers will from this point on start self-assembling into micelles, resulting in a constant surfactant monomer concentration. Many factors influence when CMC is reached, the nature of the surfactant itself is of course at prime essence, but also the solvent, temperature and electrolytes present will influence when the value is reached.³ Figure 1.2 below shows a sketch of the CMC behavior.

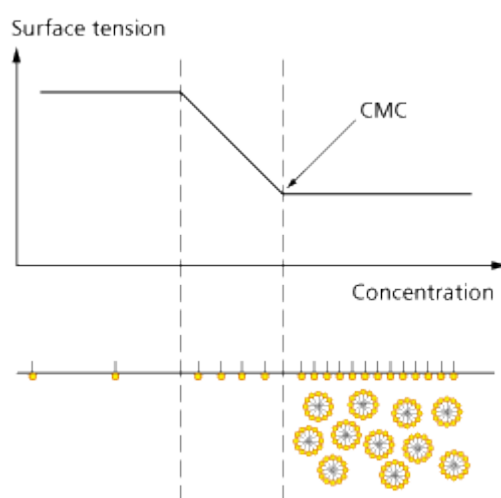


Figure 1.2: Illustration of the critical micelle concentration (CMC) phenomena.⁵

1.2.3 Critical packing parameter (CPP)

The packing parameter gives information about how surfactants will arrange on the interface. The value is defined as the ratio between the chain volume, head group size and length of the hydrocarbon tail according to Equation 1.4 below. Figure 1.3 shows how a change in CPP will alter the preferred surfactant arrangement towards another domain.

$$CPP = \frac{V_t}{a_h l_t} \quad (1.4)$$

Where: V_t is the volume of the surfactant's hydrocarbon tail

a_h is the size of the head group

l_t denotes the length of the hydrocarbon tail

CPP simply describes the balance of the interactions between the hydrophobic moieties and the polar part of the surfactant. The CCP value increases with increasing salinity, as the effective charge of the surfactants polar head is to some extent shielded, which reduces the area of the head group. To form spherical micelles, the critical packing parameter cannot exceed the value $1/3$.⁶

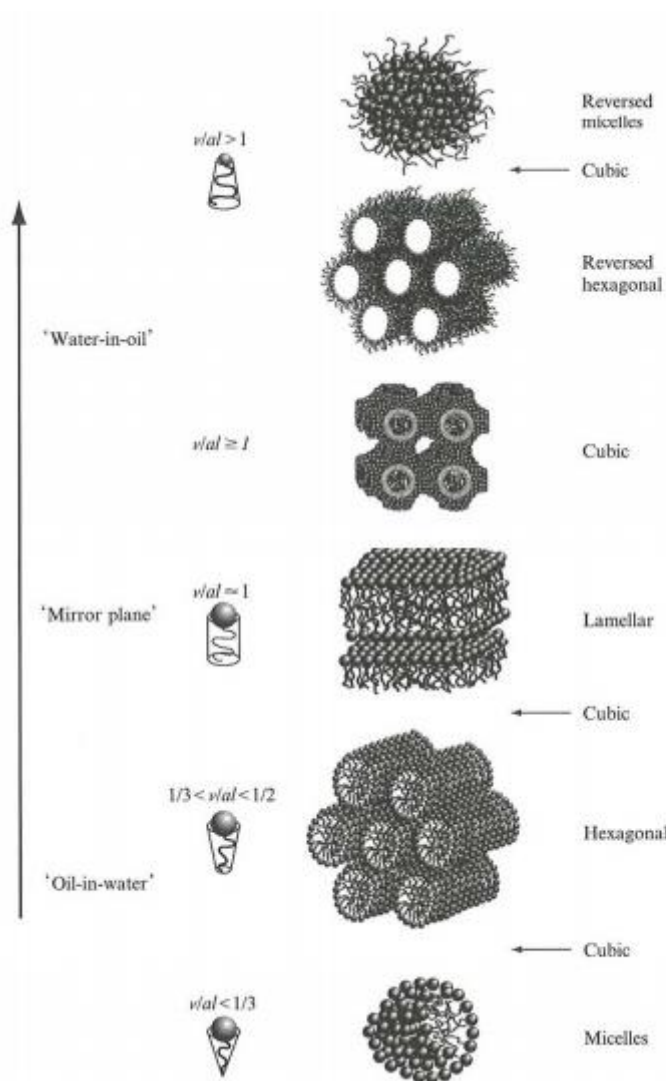


Figure 1.3: Preferred surfactant arrangement on the interface with changing CPP value.⁷

It has been observed that exchanging even small amounts of sodium- with calcium ions effectively lowers the optimal salinity in surfactant solutions disproportionate to ionic strength and molarity of the electrolyte.⁸ Because the degree of protonation of the surfactant head group also alters its effective area (low pH high CPP), IFT and phase behavior are strongly dependent on the solutions pH.⁸

1.2.4 Surfactant Flooding and wettability alternation

Injecting surfactants into the reservoir to mobilize residual oil, and thus enhance the oil recovery is mentioned in the introduction part in the tertiary oil recovery section. Lowering the interfacial tension between the oil and the aqueous phase increases the recovery of displaced oil. In order to project the effect of surfactant flooding, the capillary number N_c (Equation 1.5) is used to define the ratio between the viscous and capillary forces acting on the immobile oil layers.⁹

$$N_c = \frac{\eta v}{\gamma} \quad (1.5)$$

The three parameters involved in the capillary number are the velocity v , viscosity η and the capillary IFT forces. It is known that an increase in the capillary number would improve the oil recovery.⁶ Increasing the injection speed would risk fracturing the reservoir rock and therewith cause plugging of pores, meaning that increased plugging over time could lead to a reservoir breakdown. Hence velocity is not considered to be a parameter that can be changed particularly in order to enhance the oil recovery.^{9,10}

In surfactant flooding the goal is to lower the interfacial tension, and by doing so, increasing the capillary number. The surface tension between water and rock highly depends on the wettability of the rock, which again can be related to pore-size distribution.⁶

In relation to the enhanced oil recovery process, it is distinguished between a water-wetted and an oil-wetted system. The overall agenda is to increase the water wettability in the system, which will mobilize the oil-layers, and by doing so release the oil-layers bound to the rock surface. Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. Although contact angles are almost universally accepted as a basic measure of wettability, their application to reservoir systems are limited, because measurements are not done directly on reservoir rock surfaces. The difference is caused by the mineralogical complexity of the reservoir rocks, meaning the wettability differs all over on the rock surface.¹

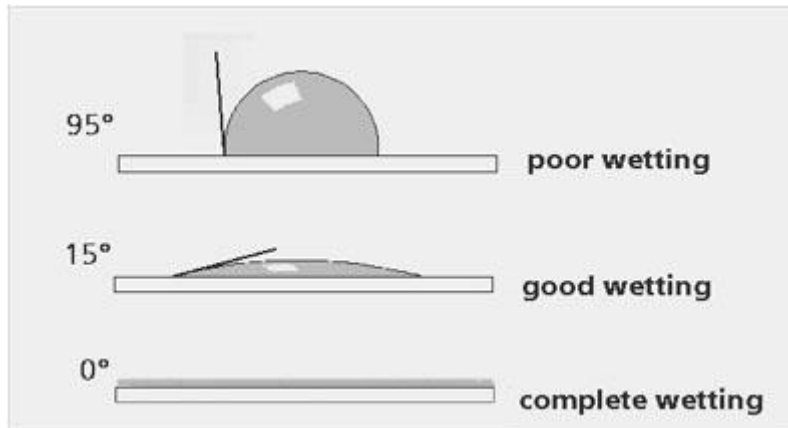


Figure 1.4: Illustration of the contact angle and wettability principles.¹¹

Altering the wettability in the reservoir rock towards a more water-wetted system has been shown to enhance the oil recovery.⁶ By changing the wettability, other characteristics are affected, among them the capillary pressure, electrical properties and relative permeability.² Several studies have been conducted to see how the presence of surfactants alters the wettability. Anionic surfactants have the tendency to alter the wetting angle of an oil-brine-dolomite system in both directions. Surfactants in enhanced oil recovery operations are mostly used to change the wettability from an oil-wetted to a water-wetted system, but initially weakly water-wetted systems can also move towards a more oil-wetted system when anionic surfactants are added. Non-ionic surfactants do not change the wettability to the same extent, as the ionic ones do.¹²

1.2.5 Emulsions and Microemulsions

When performing a surfactant flooding operation, there are several criteria that need to be fulfilled in order for the process to be successful. First of all, the surfactant slug should be a single-phase micellar solution. The ability to solubilize oil or other hydrophobic substances in the interior of the micelles, and by so doing form microemulsions, is an important property of the single-phase micellar solution. A micro emulsion system is thermodynamically stable, and is ideal for transport through the reservoir and towards the production well, as no oil is lost in the process. The different microemulsion-systems shown in Figure 1.5 below, were all defined by Winsor.¹³

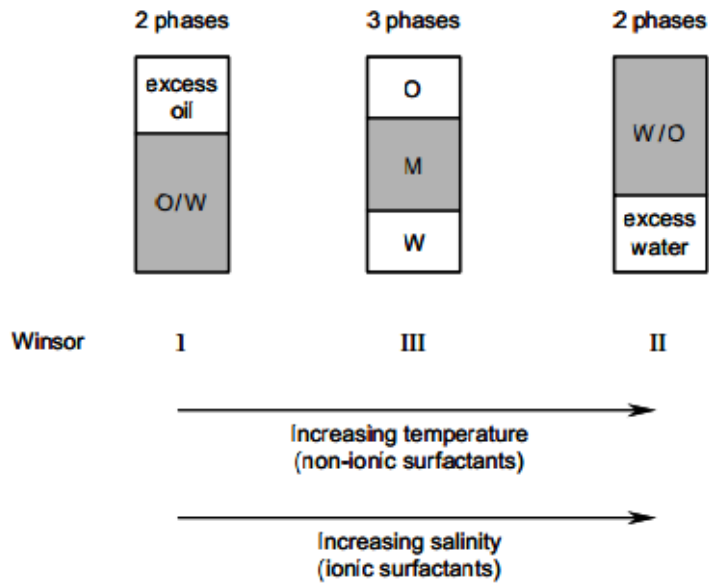


Figure 1.5: Winsor classification, Winsor I and II systems feature an excess oil- and water phase, respectively. While in the three phase system, the bi-continuous phase (M) is in equilibrium with both the excess- oil and water.¹³

A Winsor I system is defined as a system where the oil content exceeds the solubility capacity of the micelles, and hence an oil phase arise in equilibrium with the micro emulsion. The Winsor II system holds excess water, hence a water phase is in equilibrium with the micro emulsion.^{6,13}

The Winsor 3 system is considered ideal and consists of two excess phases in equilibrium with a bi-continuous micro emulsion phase in the middle. Because of the low viscosity and ability to mobilize the oil, the Winsor 3 system is assumed to be the ideal micro emulsion system for surfactant flooding. However, adjusting the salinity and surfactant concentration to obtain such a system is complicated. A further increase would tip the system towards a Winsor 2 system, which would lead to loss of surfactant and trapping of w/o emulsions in the reservoir rock, which could jeopardize the profitability of the operation.⁶

1.2.6 Aerosol OT

Aerosol OT also known as “sodium bis(2-ethylhexyl) sulfosuccinate”, is an anionic surfactant, and the only surfactant that has been used in this project thesis. It has a molecular weight of 444,5 g/mol, and is not considered a dangerous chemical for humans, but may be irritant for eyes, lungs and skin.¹⁴ Figure 1.4 shows the chemical structure of the Aerosol OT molecule, where the negative charge sits on the “sulfonate” group.

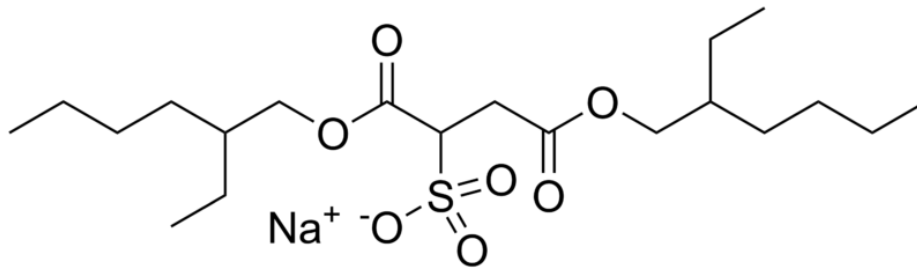


Figure 1.6: Chemical structure of the Aerosol OT molecule.¹⁴

1.3 Low Salinity Water Flooding

It is well documented through many years of research that low salinity (LoSal) waterflooding may give improved oil recovery. Several factors are suggested to explain the LoSal effect, including destabilization of oil layers on the rock surface, multicomponent ion exchange and fine migration. However, there is no consensus of the key factor that can explain the results.

Back in 1997, Tang and Morrow reported how low-salinity waterflooding could enhance the crude oil recovery from Berea sandstone cores.¹⁵ Since then, the interest in research related to the low-salinity effect has increased rapidly, as laboratories and organizations are trying to explain the LoSal behavior.¹⁶ Tang and Morrow's research did among others show that having a low degree of salinity in both formation water- and injected- water, would lead to an increase in the overall recovery of crude oil, when compared to tests having higher brine salinities. Decreasing the overall salinity also showed to change the reservoir's wettability towards a more water wet state.¹⁵

Further research by Tang and Morrow in 1999 claimed that necessary conditions for observing the LoSal effect in Berea-sandstone cores were the following.¹⁶

- Significant clay fraction
- Presence of connate water
- Exposure to crude oil to create mixed-wet conditions

These conditions do however only apply to the type of sandstones that were investigated during the research period, although other sandstones fulfilled the conditions mentioned above, no LoSal effect was observed. The cause of such significant differences has yet to be identified.

Based on his earlier research, Tang later discovered that the composition of the rock highly influenced the effect of low-salinity flooding experiments.¹⁷ The cores used during the flooding experiments were rich in clay, and when injecting water having a salinity of 10 % of the total reservoir salinity, he proved to increase the recovery. Rock fines were however observed in the effluent water stream. The rock fines in the core later showed to be essential in terms of explaining the behavior, as the oil recovery gradually increased when more rock fines were removed from the core. When all rock fines had been washed out of the core, no further change in the oil recovery was observed due to change in salinity.

In order to further investigate this behavior, all rock fines were in the next experiment removed from the core prior to the flooding. The core was then flooded with brines having different salinities. This time, however, the recovery rate was not dependent on the salinity of the brine, and results were fairly similar to the highest recovery results, obtained from the previous experiment. The research series showed that low salinity water only improved the oil recovery when loose fines were present on the rock surface. It is believed that the polar oil components adsorbed on the fines get mobilized when the fines loosen, and hence reducing the total oil saturation in the core.¹⁷

The results lead to development of the so called multiple ion exchange (MIE) mechanism theory, studied by Lager et al.¹⁸ Divalent ions like calcium and magnesium have the ability to bind to negatively charged surfaces of carboxylic nature, present in larger oil compounds. By injection of LoSal water, exchanging of divalent ions with monovalent ones like sodium may occur, resulting in desorption of acidic oil components and adjacent adsorbed oil layers, hence increasing the recovery. By this Lager claimed that the fines mobilization was rather an effect of MIE than a requirement for increasing the oil recovery, as previously stated by Tang and Morrow in 1997.

Lager did in 2008 publish a new article, in which he stated that injection of low-saline water into a mineral reservoir would lead to an increase in pH.¹⁹ The increase in pH would happen because H^+ ions were adsorbed and therewith replacing other ions on the mineral surface. Lager additionally claimed that the increase in pH was caused by dissolution of carbonates in the reservoir. Building on Lager's research, Austad et al. mentioned that low salinity flooding can cause desorption of oil layers from the clay.²⁰ Especially is the exchange between calcium by H^+ in the water important, as OH^- ions are formed and therewith increasing the pH. The increased pH may lead to a lowering of the interfacial tension, as oil components released

from the clay could be surface active, and hence start moving towards an interface. Figure 1.7 illustrates the proposed mechanism.

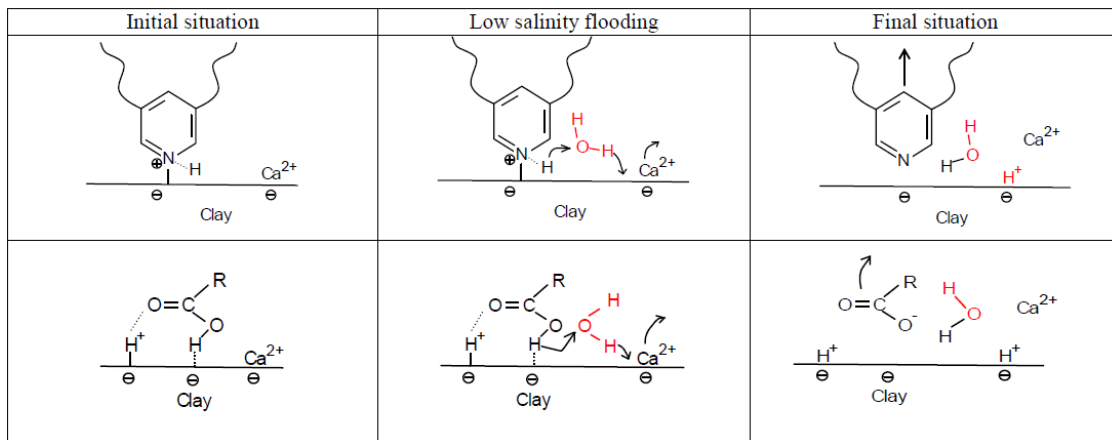


Figure 1.7: Proposed mechanism for LoSal effects.²⁰

In spite of the growing interest in the low salinity effect, a consistent mechanistic explanation to the phenomena has not yet emerged. Neither of the mechanisms mentioned above can be said to fully describe the effect. It should also be mentioned that back in 2004, the first field evidence of reduction in residual oil recovery during a reservoir LoSal test was provided, indicating that many mechanisms are in play at the same time.¹⁶ As earlier mentioned it is not quite easy to explain the LoSal effect, the complexity of minerals, crude oils, and aqueous compositions and their interactions among themselves, are all contributing to the confusion related to the actual mechanism of a LoSal injection. However, the variety of circumstances under which the LoSal effect is observed clearly suggests that more than one mechanism may be in play.

1.3.1 Electrical Double Layer

An electrically charged surface will influence the distribution of adjacent ions in a polar medium. Ions of opposite charge (counter-ions) will be attracted to the surface, whereas similar charges (co-ions) will be repelled. A spread distribution of counter-ions around the charged particles or oil droplets will serve as a shield, as they will repel each other, and thus stabilize the charged particles or oil droplets in an emulsion. A more dense distribution around the charged surface does not serve as a shield to the same extent, and thereby allows the charged particles to come closer and may cause coagulation, hence destabilization of the dispersion. The ionic distribution depends on many parameters, most easily understood by looking at Equation 1.6 below.³

$$\kappa = \left(\frac{2e^2 N_A C_{el} z^2}{\varepsilon} \right)^{1/2} \quad (1.6)$$

The parameter κ expresses the effect of both ion- concentration and charge, the other parameters are given in the symbol list. The value κ^{-1} indicates the extension of the electrical double layer, meaning that a lower value of κ leads to higher extension of the double layer. A higher concentration of electrolytes along with a high valency would lead to a more dense distribution around the charged particle, and by doing so destabilize the dispersion.

1.4 Combined low salinity and surfactant injection in EOR

A new generation of EOR methods come from combining techniques to make the overall process more efficient and minimize the loss of chemicals during the recovery process. The combination of surfactant- and low-salinity flooding has recently shown to be of high interest, as the combination may feature reduced capillary forces and avoids re-trapping of destabilized oil. By combining these two techniques, it has through extensive research been observed that the combined process may exceed the recovery that either of the techniques applied.²¹ One major advantage of keeping the salinity at a low level when using surfactants is diminishing problems occurring at high water hardness, like potential formation of anisotropic phases i.e. liquid crystals and lamellar phases.⁶

1.5 Equivalent alkane carbon number

The chemical composition of crude oil is complex, and every component contributes to how the oil-phase interacts with injected water in the reservoir. The idea behind the equivalent alkane carbon number (EACN) concept is to be able to predict the interfacial tension values of complex hydrocarbon - aqueous/surfactant systems. The EACN number for a pure substance is calculated based on the longest continuous carbon chain, where also branches along this very chain (i.e. a methyl or ethyl group) count for the total EACN number.²² A straight chained dodecane molecule has an ACN value of 12. For a straight chain alkane like dodecane, EACN essentially becomes alkane carbon number (ACN) since there are no atoms in between. A benzene ring however, counts as zero, making the methyl group on the toluene molecule the only contributor to the average EACN number, hence toluene has an EACN value of only 1. By increasing the fraction of dodecane relative to toluene in a mixture, the

EACN number gradually moves towards a higher EACN value. The classification of EACN values for certain hydrocarbon molecules derives from systematic experiments.²²

Observations have resulted in Equation 1.7 which can be used to calculate the average EACN value, but only for binary mixtures of alkanes, alkyl benzene and alkyl cyclohexanes.²²

$$EACN_{avg} = \sum_i (EACN)_i X_i \quad (1.7)$$

Where $EACN_{avg}$ is the EACN for the mixture, $EACN_i$ represents the EACN values for the individual components, and X_i denotes the mole fraction of each component.

In example can this theory be used to predict that a crude mixture having an average EACN of 5,5 is expected to yield a minimum interfacial tension against a certain surfactant solution with constant salinity that gives low interfacial tensions against oil phases of similar chemical structure as pentane and hexane. The EACN value, at which the lowest interfacial tension is observed, is called the N_{min} value.²³ This concept is very useful because, given an oil of known EACN, those surfactants that process the similar N_{min} values can be screened out as the ones that most likely were to exhibit ultra-low interfacial tensions against the oil in question, and consequently be the most effective surfactant to use in a surfactant-flooding operation.²³

Figure 1.6 below illustrates the very principle of the EACN scale. As more hexadecane (ACN = 16) is added to the mixture it can be observed how the interfacial tension varies with increasing EACN-number, when both surfactant and salinity is kept constant throughout the experimental series.

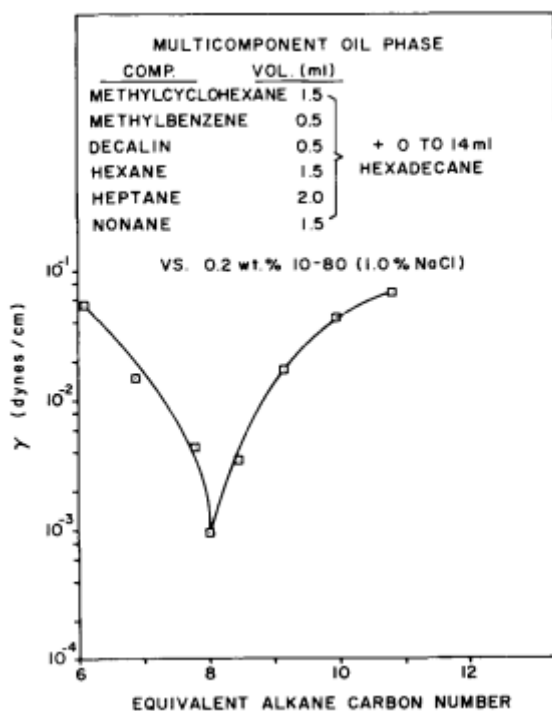


Figure 1.6: Interfacial tensions for variations in the composition of a multicomponent oil phase against an aqueous 0,2 wt. % TRS 10-80 and 1,0 wt. % NaCl.²²

Studies also indicate that there is a direct linear correlation between surfactant average equivalent weight and the EACN for the oil phase.²² This means that AOT (EACN =8), which is the surfactant used in every experiment in this thesis would yield the lowest interfacial tension against an oil phase having an average EACN number of 8.

This matter has been put to the test as AOT and SBDS with an EACN number of 8 and 12, respectively, were in aqueous solutions tested against a heptane model oil phase under similar conditions that will be used in the experiments in this thesis. Heptane has an ACN value of 7 and experiments in an aqueous solution with a mole fraction of 1/45 $\text{Ca}^{2+}/\text{Na}^{+}$ performed, showed that the interfacial tension at the water-oil interface yielded much lower IFT than those reported with SDBS and heptane. Values reported showed 0,004 mN/m for the AOT/Brine-Heptane system at 60 °C, which can be reported as “ultralow” interfacial tensions.⁸

2. Experimental

2.1 Measuring interfacial tension

Controlling the interface is essential when stabilizing an emulsion. Lowering the interfacial tension would essentially mean to allow the dispersed phase to coagulate, while increasing the interfacial tension between two phases prevents coagulation and stabilizes the system. Controlling this parameter is of prime essence when running a huge oil recovery operation, where the difference between stable emulsion and separated systems can affect the profitability of the operation to a high extent.

Measuring the interfacial tension can be done by many different methods. The classification of different measuring methods shown in Figure 2.1 below are done by Drelich et al in 2002.²⁴ What separates the different methods from each other is how quickly the first interfacial measurements can be taken (described by an example in the next sentence) and how low interfacial tensions that can be measured. In cases where it is desirable to collect data as soon as possible, due to rapid changes in IFT early on in the experimental period, the maximum bubble pressure method would be a suitable choice. On the other hand, if it is desirable to measure extremely low IFT, the spinning drop would be a better choice, as it can measure ultralow IFT (10^{-6} mN/m).²⁵

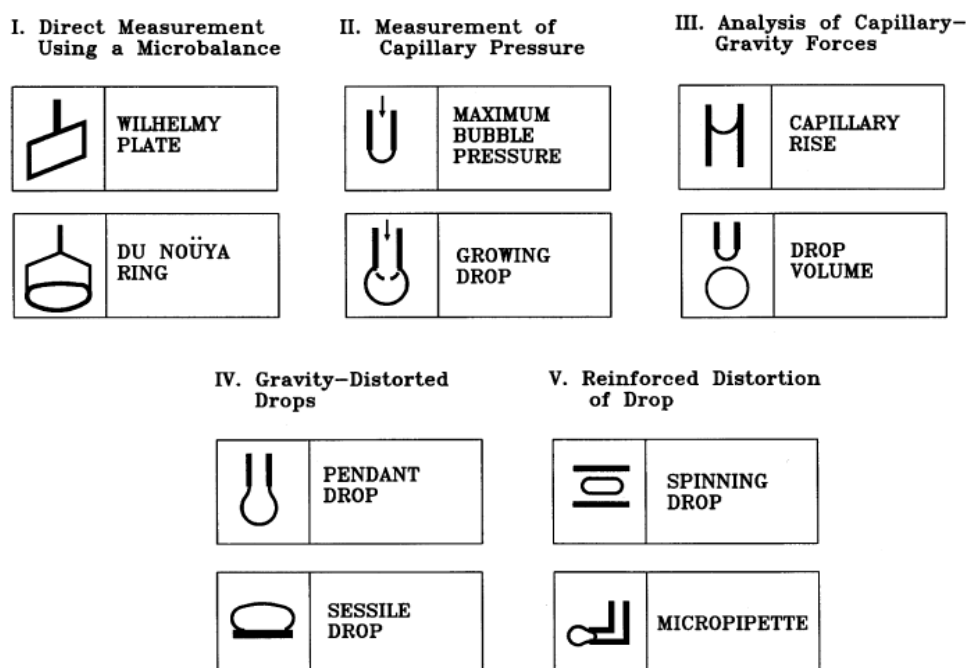


Figure 2.1: Classification of techniques for interfacial tension measurements.²⁴

There are many theoretical ways of calculating the interfacial tension between two immiscible fluids. Some equations give more precise results for a specific measuring method, while others are more general. However, the change in drop curvature is always at prime essence when calculating the change in interfacial tension. Bernard Vonnegut did in 1942 propose the spinning drop method for determining surface- and interfacial tensions.²⁶ In this method, two immiscible fluids with known densities are spun around a horizontal axis in a capillary. The elongation of the bubble stops when the forces acting on it (surface tension and centrifugal forces) are balanced. This gave rise to the Vonnegut equation (Equation 2.1) which made it possible to express the total energy of the bubble and solve it for the equilibrium shape with minimum energy. Another well-known equation for measuring the interfacial tension is the Laplace-Young (Equation 2.2), both are shown below.²⁶

$$\gamma = \frac{\Delta\rho\omega^2R^3}{4} \quad (2.1)$$

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad (2.2)$$

Where γ is the interfacial tension, R_1 and R_2 are radii of curvature, ΔP is the pressure difference across a curved interface, ω is the rotation speed, R denotes the radius of the cylindrical part of the drop body and $\Delta\rho$ is the density difference between the two fluids.

The following Figure 2.2 shows the principle behind the spinning drop method, and how the shape of the drop is affected while increasing the rotation speed of the capillary. However, Vonnegut's equation will not give correct results if the drop isn't of center-cylindrical proportions, and can thus not be applied in every situation.²⁷ The equations used in the SVT tensiometer derive from the Laplace Young Equation, where effects from gravitational- and centrifugal forces have been cooperated into the equation (Equation 2.3).

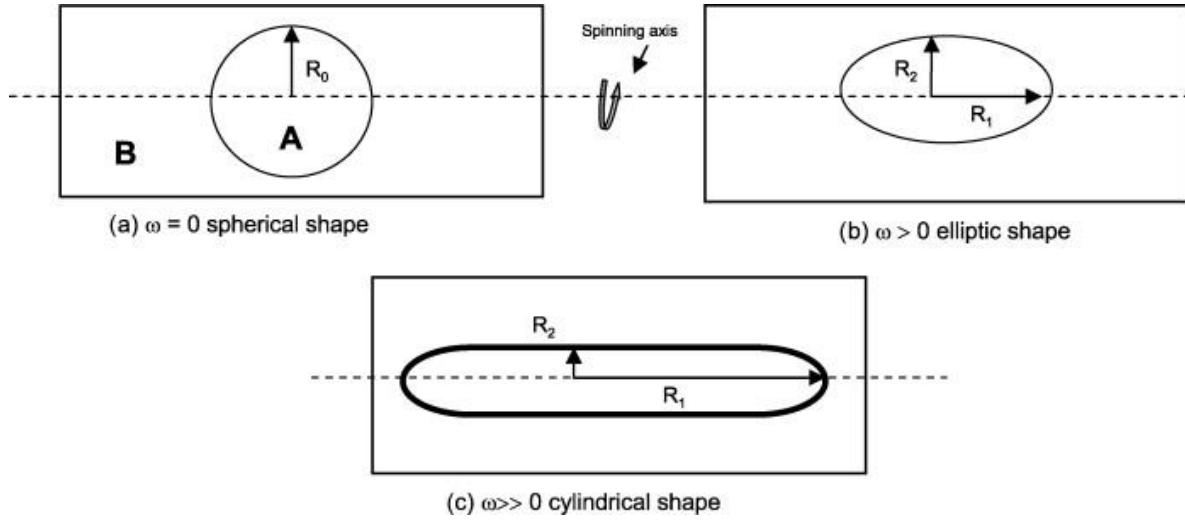


Figure 2.2: Drop shape is affected by increasing centrifugal forces.²⁶

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R_0} + \Delta\rho\omega^2\lambda^2 \quad (2.3)$$

The term $\Delta\rho\omega^2\lambda^2$ represents the centrifugal forces acting on the volume element, λ is the potential distance, i.e the drop's displacement from the axis of rotation caused by the gravitational field, R_0 is the radius of the drop when $\omega = 0$ and $\Delta\rho$ is the density difference between the two fluids.

In an article published by Chan et al. in 2003, it was claimed that the dimensions of the drop had to have a length/diameter ratio larger than 4 in order for the Vonnegut equation to be reliable.²⁷ Equation 2.3 above does not require any specific drop shape in order to calculate the interfacial tension, and can thus be used more universally.

2.2 Experimental procedure - Preparation

The main objective in this project thesis has been to see how different cationic compositions influence the interfacial tension of a surfactant/brine-oil system. Both the brine and the surfactant solution were prepared to a double concentration, and later equal volumes of each were mixed in order to get the desired concentration. The brine/surfactant mixture, also known as the aqueous solution was then transferred into the capillary with a syringe, subsequently followed by the oil phase, which also was injected by a syringe into the capillary. The overall ionic strength was kept constant at all time, while the mole fraction of calcium to sodium was the varying parameter along with a changing model oil composition. Calculations related to constant ionic strength were done according to Equation 2.4 below.

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (2.4)$$

Where I denotes the ionic strength, c_i is the concentration of ion i , and z_i^2 is the valency of ion i squared.³

The two chemicals which have served as the oil-phase in the experiments performed in this thesis are dodecane and toluene. An important aspect of using model oil instead of crude oil is the fact that the surfactant will be the only surface active component in the mixture. Acidic components in the crude have surface active properties, which will influence the measured IFT and make any trend harder to comprehend. Every test was performed at 60 °C, a heating cabinet was used to preheat the solutions prior to the injection in the capillary.

2.2.1 Preparation of the salt and surfactant solutions

The surfactant solution was prepared by dissolving solid Aerosol OT (Alfa Aesar, > 96 %) surfactant in ultra-purified (milliQ) water. The surfactant concentration used in every measurement was 2,47 mM.

Brine solutions were made by dissolving sodium chloride (Merck, > 99,5 %) and calcium chloride (Merck, > 98 %) in milliQ water. The mole fraction $\text{Ca}^{2+}/\text{Na}^+$ was varied between zero and six percent in every series, calculated by Equation 2.5.²⁸

$$X_{\text{Ca}^{2+}} = \frac{n_{\text{Ca}^{2+}}}{n_{\text{Ca}^{2+}} + n_{\text{Na}^+}} \quad (2.5)$$

All mixtures were made to the same ionic strength of 40 mM, so that the ionic strength of the brine/surfactant mixture would yield 20 mN/m. In series where ionic strength was 5 mM, the brine solution was merely diluted twice before being mixed with the surfactant solution. All IFT values over the different $\text{Ca}^{2+}/\text{Na}^+$ mole fractions measured in this thesis are shown in Appendix A1.

2.2.2 Density measurements

Knowing the exact density difference between the two immiscible fluids is essential in order to get a good measurement of the interfacial tension. All aqueous solutions was in advance believed to have the same density, and therefore only extreme values were tested ($\text{Ca}^{2+}/\text{Na}^+$ mole fraction of 0, 1/25, 1/16). All samples were preheated to 60°C prior to being measured in the Anton Paar DMA 4100 density meter. Two or more parallels were done in order to

ensure precision, and the overall average values are shown in the Table 2.1 below. A complete list for all samples is shown in the Appendix A1, Table A4.

Table 2.1: Densities for individual surfactant/brine and dodecane/toluene mixtures. *Measured during the specialization project in the autumn of 2013.

Samples at 60 °C	Average density [g/cm ³]
Aerosol OT/Low Salinity, [I] = 20 mM, C _{AOT} = 2,47 mM	0,9840*
Aerosol OT/Ultralow Salinity [I] = 5 mM, C _{AOT} = 2,47 mM	0,9830
Dodecane	0,7196*
Dodecane - Toluene (90 - 10 wt. %)	0,7238
Dodecane - Toluene (75 - 25 wt. %)	0,7314
Dodecane - Toluene (50 - 50 wt. %)	0,7680
Dodecane - Toluene (25 - 75 wt. %)	0,7820
Dodecane - Toluene (10 - 90 wt. %)	0,8155
Toluene	0,8289

2.2.3 Preparation of model oil sample

Different model oil compositions stretching from pure- dodecane (KeboLab, > 99 %) to toluene (VWR, > 99,5 %) were tested in these experiments. Compositions in wt. % and densities at 60°C are shown in Table 2.1 above.

2.2.4 Measuring IFT by spinning drop tensiometer

Both the aqueous solution and the oil phase were injected into the capillary by syringes. The aqueous solution first, followed by preferably a single drop of model oil. The capillary (shown in Figure 2.3) can hold about a 2 mL solution. Preventing air-bubbles from entering the mixture is essential in order to get reliable measurements, as the air-bubbles may interfere directly with the oil drop when spun around the horizontal axis. Closing the capillary so no air gets locked in is therefore essential, which may be challenging when dealing with low interfacial tension values.



Figure 2.3: Capillary used for measurements in the spinning drop tensiometer.

The rotation speed was adjusted to give the drop the desired shape, typically ovoid. Figure 2.4 shows an image of the program used, and also how the drop shape looked like when measurements were done. After stabilizing the drop by changing the tilt angle of the capillary, a calibration of the drop image was necessary. Density values were also inserted, and the computer program reads the camera pixels and calculates the exact drop size. This results in a reliable measurement of the change in interfacial tension over time, based on Equation 2.3.

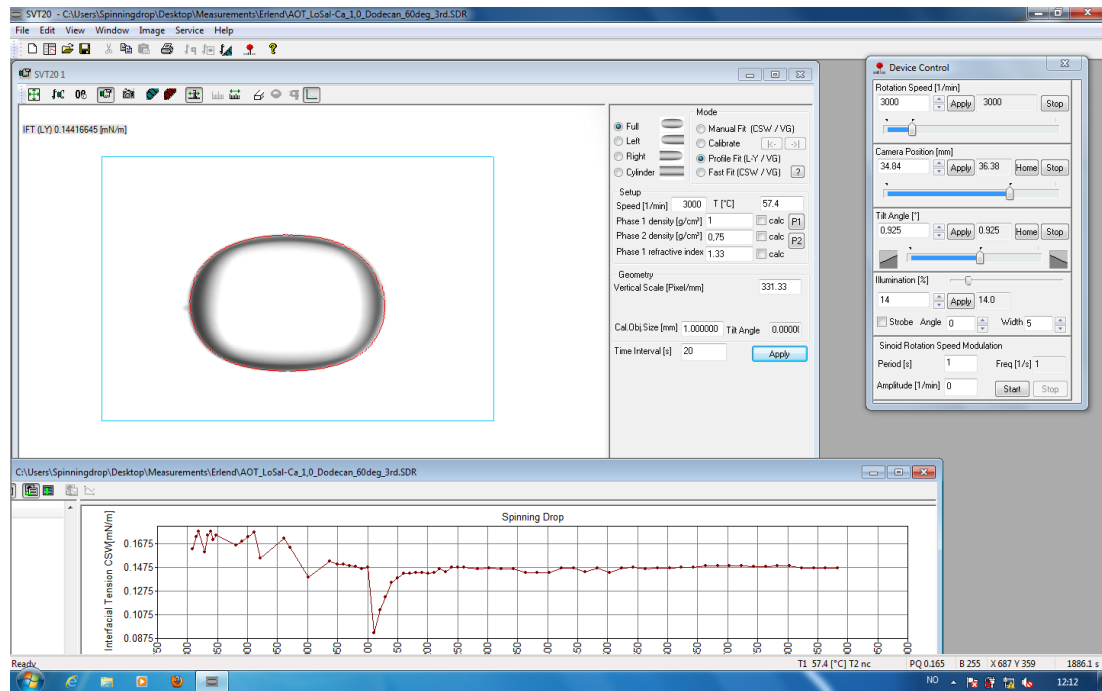


Figure 2.4: Picture showing the program interface.

Time spent on each sample depends on how fast it reaches equilibrium, meaning some samples have to run for a longer time than others. The average time it takes for a drop to reach equilibrium is usually less than one hour. In example are values displayed in Figures 3.1 - 3.5, which are presented in the result part, all the average values at equilibrium from IFT vs. time measurements. In cases where more than one parallel was run, the values displayed in the result part are the average of the two or more equilibrium values obtained. Standard deviation has been calculated according to the following formula.

$$s = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - x_{average})^2} \quad (2.6)$$

Where s denotes the standard deviation, N is the number of parallels run, x_i is the average interfacial tension value for parallel i , $x_{average}$ is the overall average interfacial tension value measured.

3. Results

3.1 Effect of calcium ions on IFT in AOT/Brine-Dodecane/Toluene systems

The minimum IFT-value measured was just below 0,01 mN/m. This value was taken from the pure dodecane series at a $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction of 1/25, but was not the only low value measured, as values close to 0,01 mN/m were found in every series. In addition did all series but the two richest in dodecane have immeasurable values, due to even lower interfacial tensions than the lowest measured. The highest value measured was found at 1/16 mole fraction $\text{Ca}^{2+}/\text{Na}^{+}$ for the pure toluene series, yielding a value of 1,68 mN/m. Exact values for all series are shown in Appendix A1, Table A1.

Figuratively shown by the following logarithmic graphs for some of the series measured (Figures 3.1 - 3.5), it can be seen that the minimum IFT value(s) measured is gradually moving towards the one of pure dodecane, as dodecane fraction in wt. % increases. The dashed lines imply that interfacial tension was not measurable for the following (range) of mole fractions. Series where model oil composition was 90/10 wt. % dodecane/toluene and 10/90 wt. % dodecane/toluene did not differ much from the pure model oil series, and are thus only shown in Appendix A2. Collective graphs of all series in one diagram proved to be very disorderly, and are thus only shown in Appendix A2, A61.

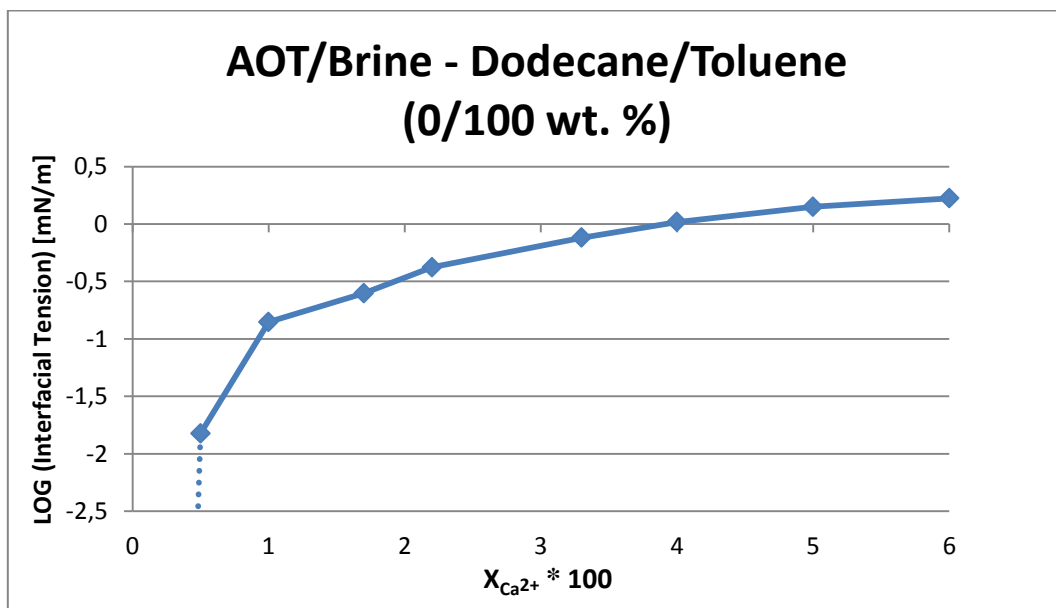


Figure 3.1: Logarithmic IFT of AOT/Brine - Dodecane/Toluene (0/100 wt. %) with different $\text{Ca}^{2+}/\text{Na}^{+}$ mole fractions, at 60°C.

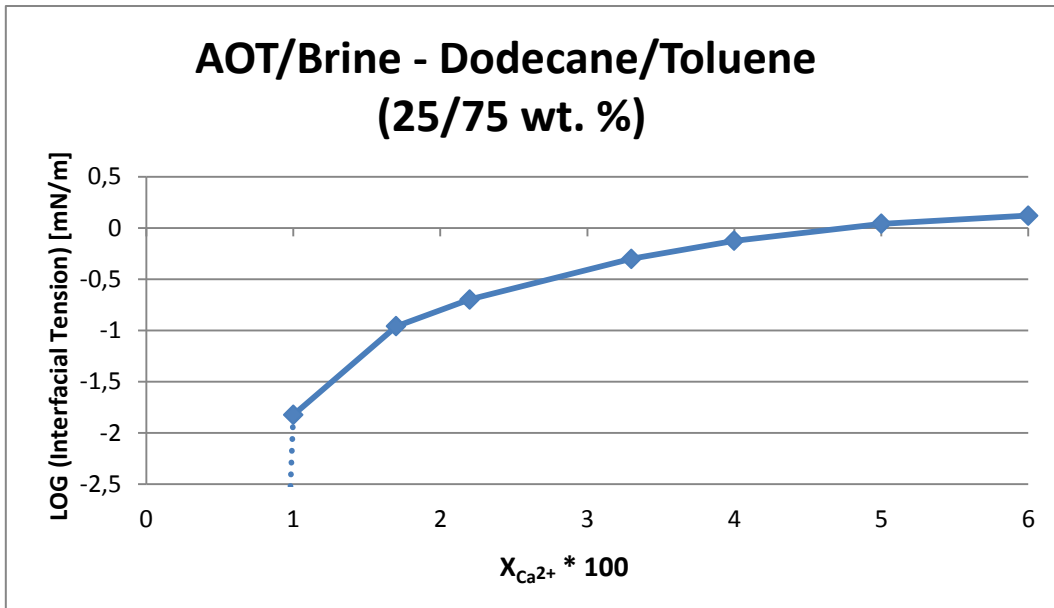


Figure 3.2: Logarithmic IFT of AOT/Brine - Dodecane/Toluene (25/75 wt. %) with different Ca^{2+}/Na^+ mole fractions, at 60°C.

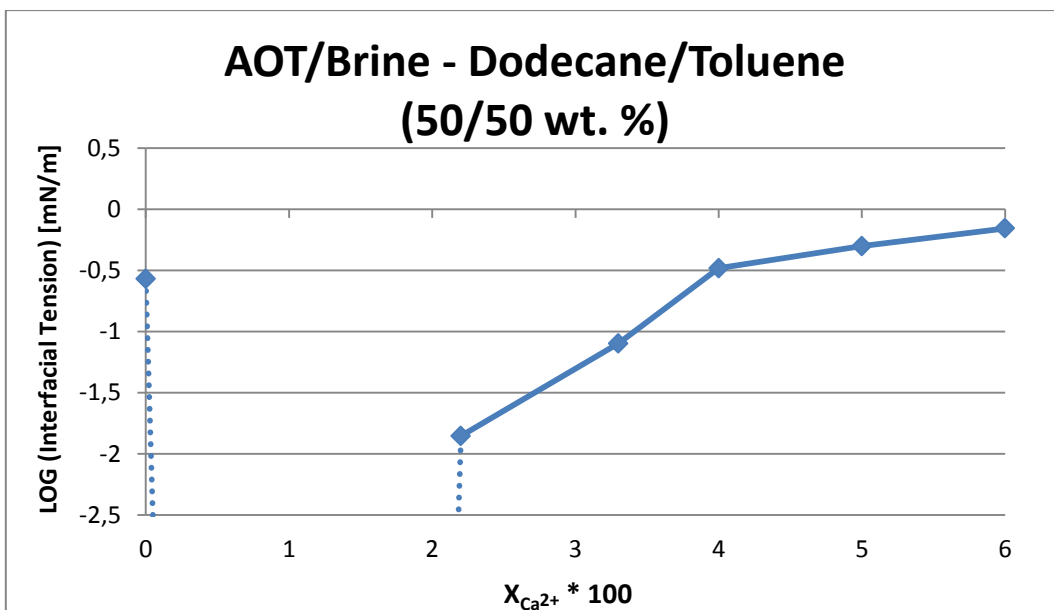


Figure 3.3: Logarithmic IFT of AOT/Brine - Dodecane/Toluene (50/50 wt. %) with different Ca^{2+}/Na^+ mole fractions, at 60°C.

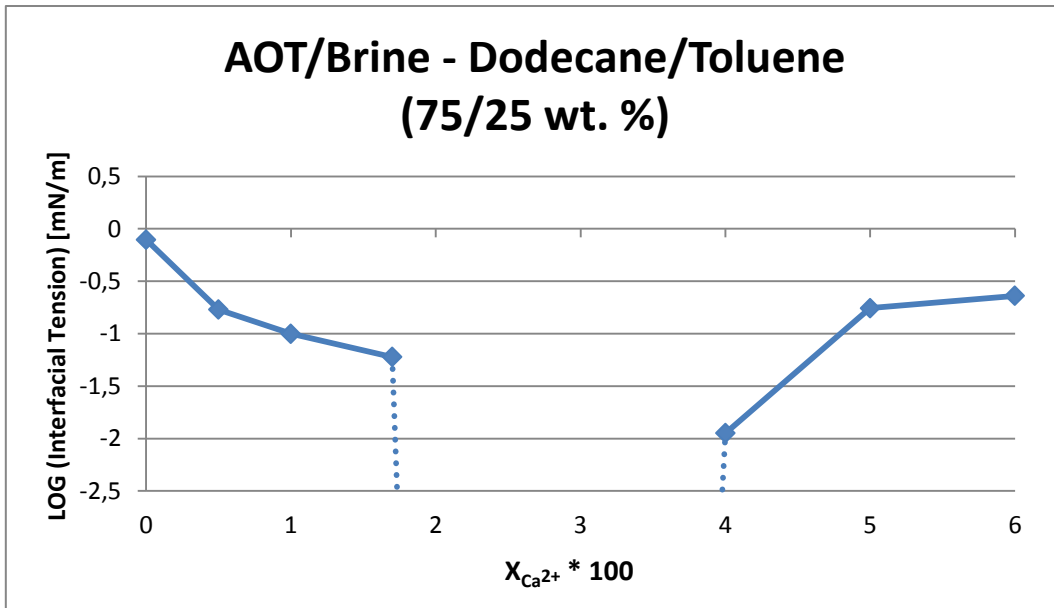


Figure 3.4: Logarithmic IFT of AOT/Brine - Dodecane/Toluene (75/25 wt. %) with different Ca^{2+}/Na^{+} mole fractions, at 60°C.

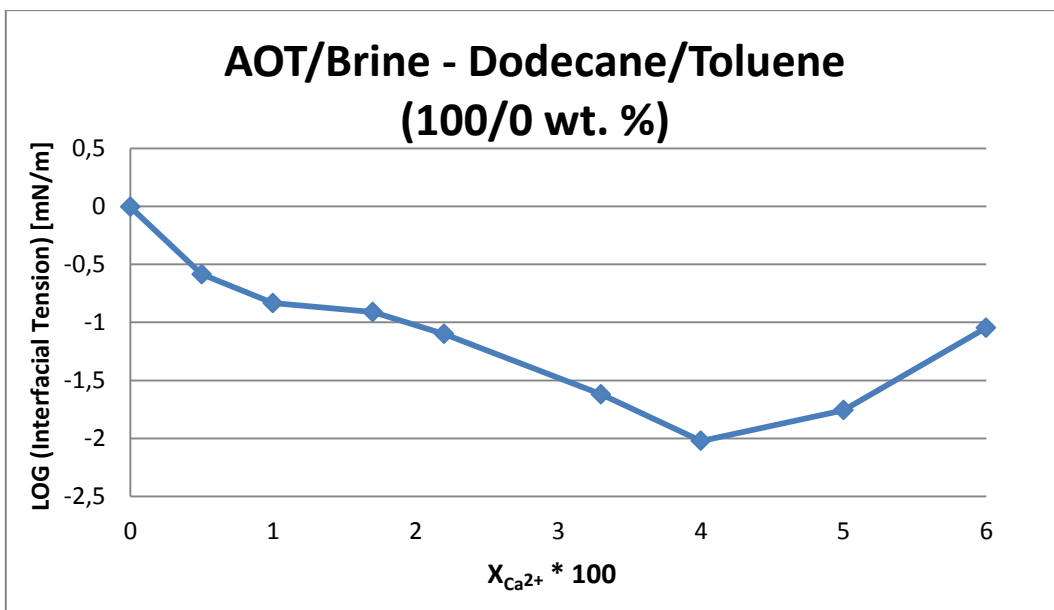


Figure 3.5: Logarithmic IFT of AOT/Brine - Dodecane/Toluene (100/0 wt. %) with different Ca^{2+}/Na^{+} mole fractions, at 60°C.

As earlier mentioned, the values used in Figures 3.1 and 3.5 are equilibrium values obtained from interfacial tension versus time measurements. Figures 3.6 - 3.8 below are examples of such measurements, the rest are shown in Appendix A2.

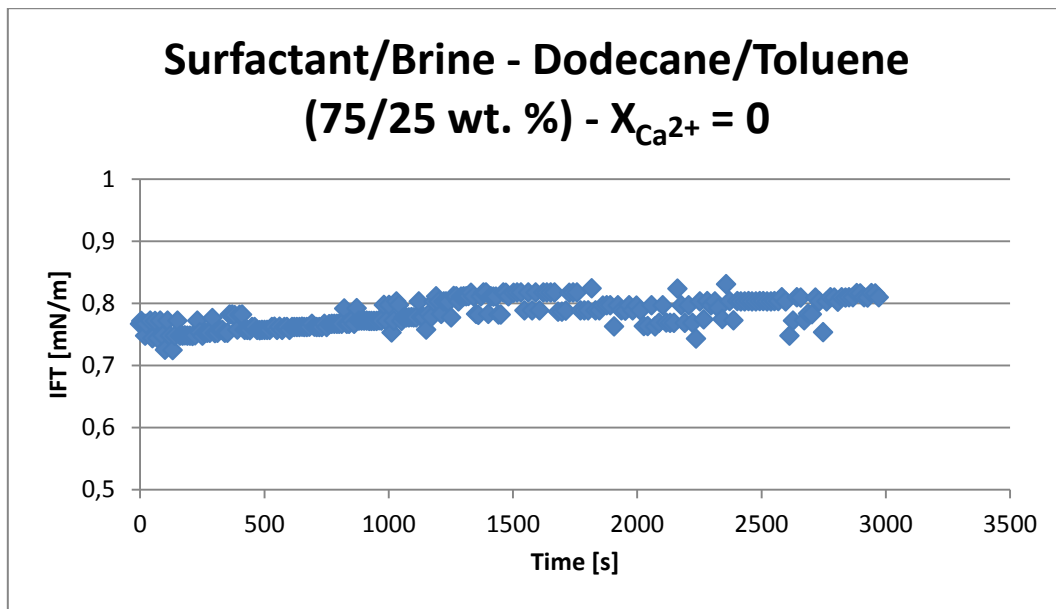


Figure 3.6: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 0. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (75/25 wt. %). Temperature is 60°C.

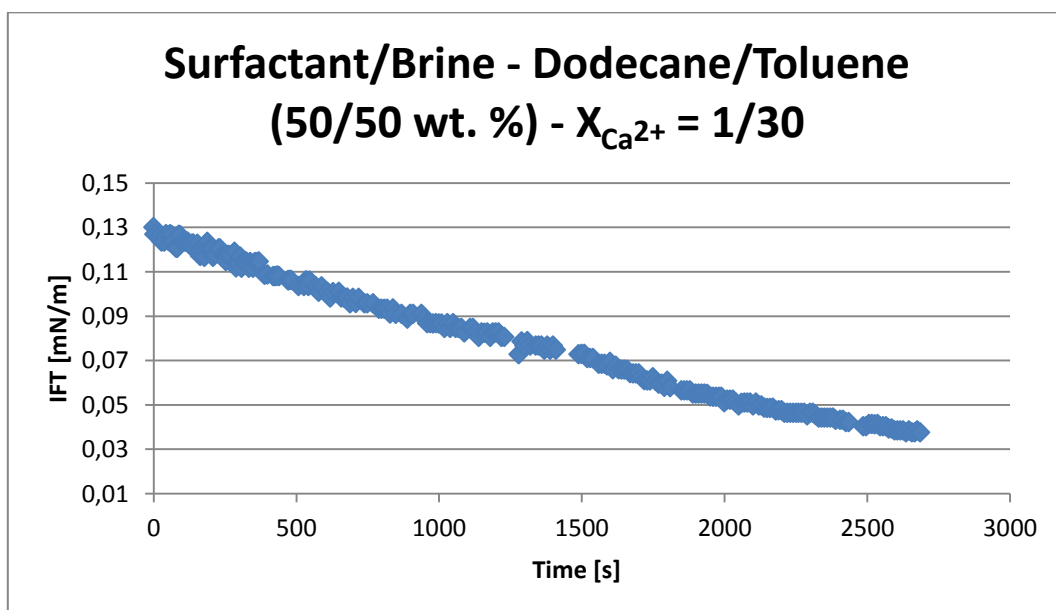


Figure 3.7: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.

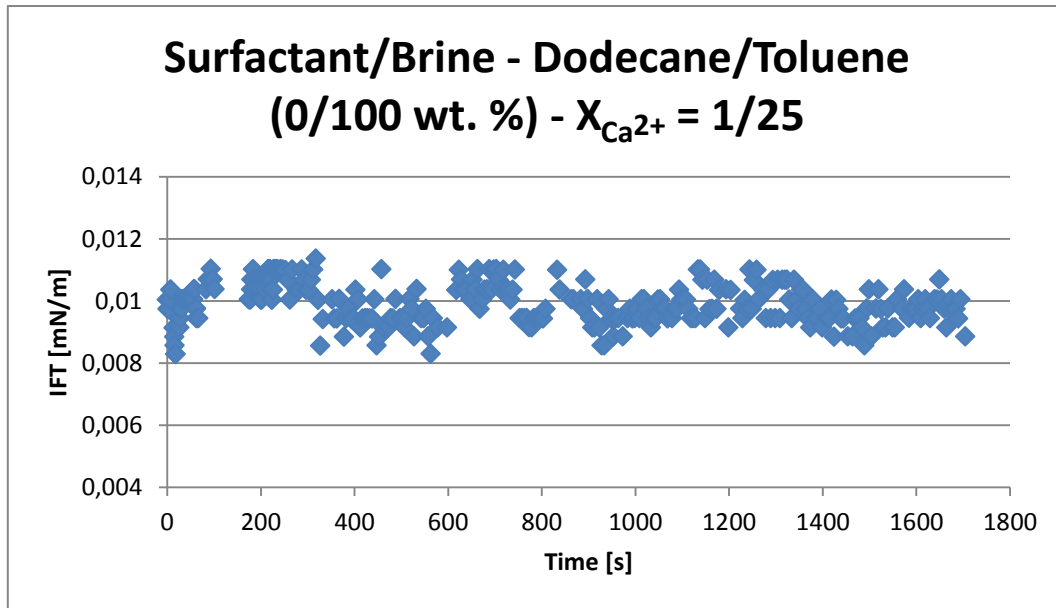


Figure 3.8: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.

In example is the equilibrium value for the measurement shown in Figure 3.8 estimated to be just a bit lower than 0,01 mN/M. Average value in Figure 3.7 has been estimated on the basis of other equilibrium values in the same series.

3.2 Effect of calcium ions on IFT in Brine-Dodecane and Brine-Toluene systems

As reported in the specialization project, the interfacial tension of a brine-dodecane system at 60°C showed not to be affected as the calcium concentration was increased. Values for the brine-dodecane system varied from 31,7 - 32,1 mN/m. Neither the IFT of the brine-toluene system showed any significant dependency on calcium content, and interfacial tension was measured to values between 21,75 and 21,9 mN/m, also at 60 °C. This trend is shown in Figure 3.9, presented below. The interfacial tension versus time measurements that were used to obtain the displayed values are shown in Appendix A3, Figures A71 - A76.

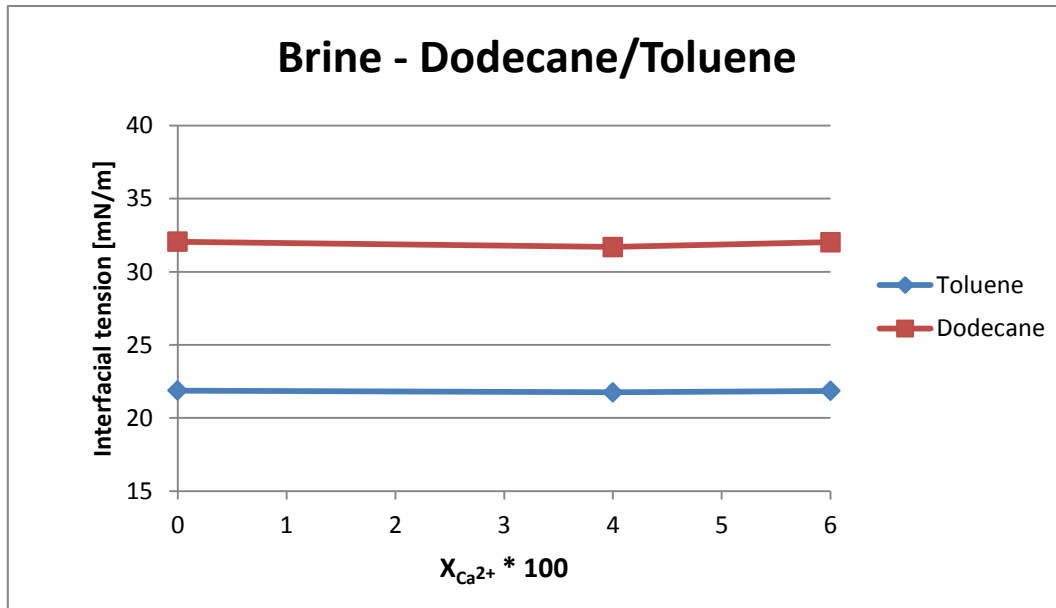


Figure 3.9: Interfacial tension of Brine-Dodecane- and Brine-Toluene mixtures with different Ca^{2+}/Na^{+} mole fractions, at 60°C.

3.3 Effect of salinity on IFT in AOT/Brine-Dodecane/Toluene systems

In an attempt to find the minimum IFT value in the series of the equally mixed oil phases, the brine solution was diluted from 20 mM to 5mM. Both mixtures had a surfactant concentration of 2,47 mM. In the 20 mM series the minimum interfacial tension value was found somewhere between Ca^{2+}/Na^{+} mole fractions of 1/200 and 1/60, but no minima could be confirmed due to very low interfacial tensions. Figure 3.10 shows that the minimum value for the 5 mM series was found at a mole fraction of 1/60 Ca^{2+}/Na^{+} , yielding a value of 0,12 mN/m.

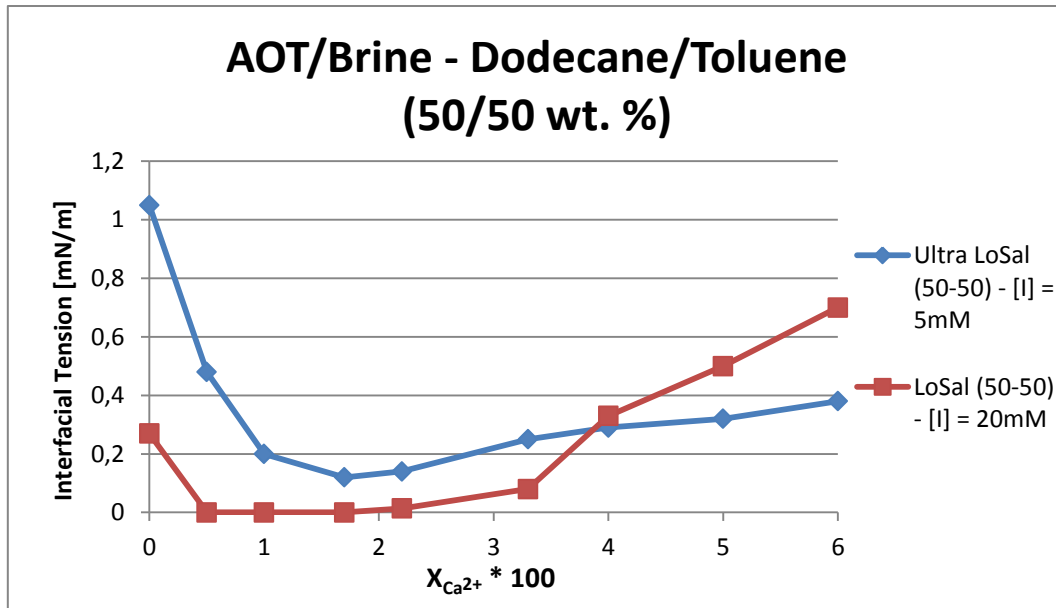


Figure 3.10: Measurement of interfacial tension for two similar systems with different salinity. The Ultra LoSal system has an ionic strength of 5 mM, while the LoSal system has an ionic strength of 20mM. Temperature is 60°C.

3.4 Effect of model oil composition on IFT in relation to the EACN scale, in AOT/Brine - Dodecane/Toluene systems

The average EACN number was calculated according to Equation 1.7.

Table 3.1: EACN and IFT minimum for each series measured. *Minimum found from the ultra-low salinity series.

Dodecane wt. %	Toluene wt. %	EACN _{avg}	Ca ²⁺ / Na ⁺ mole fraction at minimum IFT range [mol/mol]
100	0	12,0	1/25
90	10	10,1	1/25
75	25	7,8	1/45 - 1/30
50	50	4,9	1/200 - 1/60 (1/60)*
25	75	2,7	0 - 1/200
10	90	1,6	0 - 1/200
0	100	1,0	0

The Aerosol OT molecule has an EACN value of 8, according to the theory presented in Section 1.5. It is expected that the minimum interfacial tension value for any mixture of dodecane and toluene is to be found when the oil-mixture also has an EACN value of 8.

Figure 3.11 illustrates this by comparing IFT variations for three different model oil compositions with different EACN value on a varying $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction axis. Dashed lines imply that interfacial tension in the following region was too low to be measured.

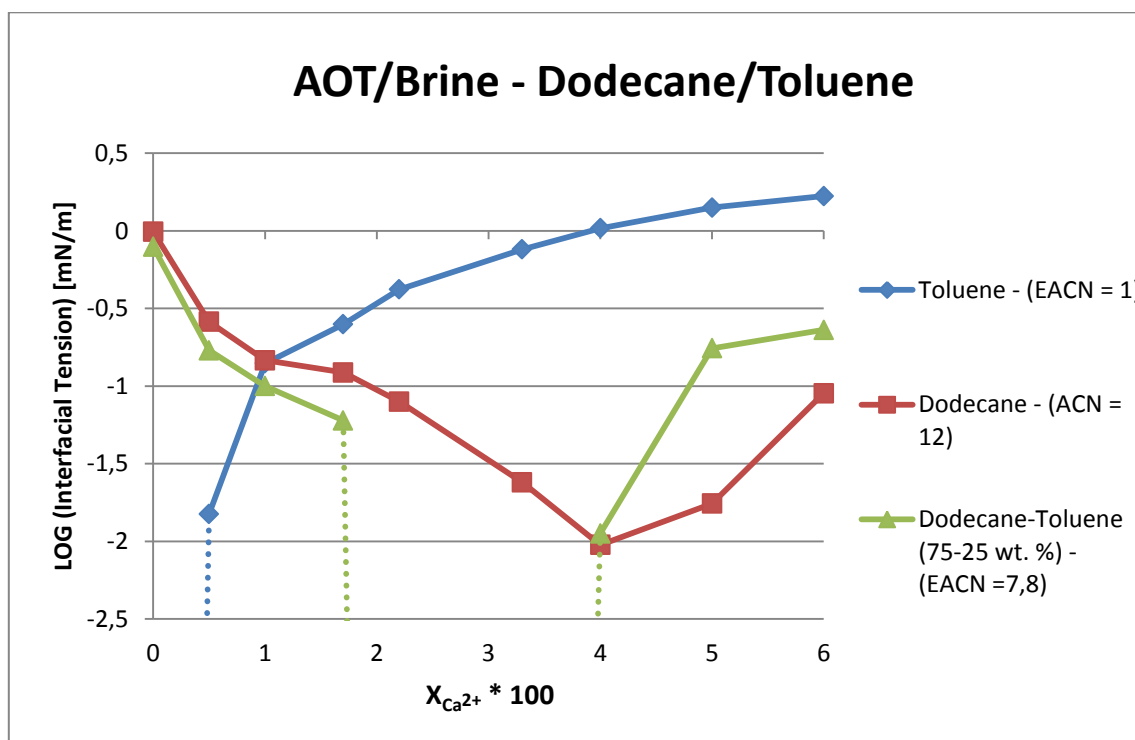


Figure 3.11: Interfacial tension varies with oil-phase composition. Dashed lines indicate that the interfacial tension was too low to be measured in the region.

Exact IFT minimum values were not found for all series. It can, however, be confirmed that the section of minimum values observed in every series gradually moves towards the minimum value found in the pure dodecane series, when gradually more dodecane is added to the oil phase. Figure 3.11 above shows the observed trend for pure dodecane, pure toluene and a 75 - 25 wt. % mixture in favor of dodecane. Minimum IFT values measured were found at mole fractions 0 $\text{Ca}^{2+}/\text{Na}^{+}$ for pure toluene, 1/25 $\text{Ca}^{2+}/\text{Na}^{+}$ for pure dodecane, and somewhere between 1/45 - 1/30 $\text{Ca}^{2+}/\text{Na}^{+}$ for the 75-25 wt. % mixture.

4. Discussion

4.1 Effect of calcium ions on IFT in AOT/Brine-Dodecane/Toluene systems

An important aspect of these experiments is that AOT is the only surface active component in the system, which makes it easier to comprehend any trend. Crude oils have a large number of surface active components. A mixture of dodecane and toluene has been used to model crude oil in these experiments.

One of the mentioned disadvantages with the spinning drop method is that it takes time before one first can start measuring, due to the time-consuming adjustments that have to be done before starting each experiment. During this period of time, many surfactant molecules migrate to the interface and cause a rapid decrease in interfacial tension over time. For all IFT vs. $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction graphs is this decrease not shown. However, in Figures 3.6- 3.8 and those presented in Appendix A2, the change in interfacial tension over time is shown. Here some decrease can be observed, due to the fact that some surfactants still are migrating to the surface and gradually moving towards equilibrium. However, if compared to the initial interfacial tension, which would be of the same order as values displayed in Figure 3.9, the decrease observed during the experiment itself is minor in comparison to the rapid drop that happens before the first measurements are registered.

Measurements for series with model oils rich in toluene and with low calcium content showed to be dominated by pure toluene properties and proved hard to measure, due to low IFT. Systems with low calcium content and an oil phase dominated by pure dodecane on the other hand, were all measurable and showed pretty high IFT. The highest IFT-values were measured for systems rich in toluene at higher calcium mole fractions, while dodecane dominated systems for the same mole fractions proved to yield fairly low interfacial tensions in comparison.

The trend observed is quite interesting. Figuratively shown by the logarithmic graphs for the 20 mM ionic strength series in Figures 3.1 - 3.5, it can be seen that the minimum IFT value(s) measured are gradually moving towards the one of pure dodecane, as dodecane fraction in wt. % increases. In spite of not being able to measure IFT at all points, the trend is pretty clear according to what would be expect from the EACN-theory presented in section 1.5. This behavior will be further discussed in the light of the EACN-theory in section 4.4.

First of all it is clear that a changing model oil composition affects the interfacial tension between the model oil and the aqueous phase, but there is also a second determining factor. Calcium content in the aqueous phase clearly influences the surfactant packing density on the interface, and hence the interfacial tension of the system, according to the CPP parameter presented in section 1.2.3. Calcium ions are divalent and have thus thinner double layers than sodium ions, meaning they can come closer to each other before the repulsion forces start acting. For the series where dodecane is the most abundant component in the model oil phase it is seen that the presence of calcium ions between the polar anionic surfactant head-groups allows a more dense packing of surfactants on the interface, as the normally high repulsion between the anionic surfactant head groups is shielded by positive charges. This is not observed for toluene in the range of cationic mole fractions investigated, and will be further discussed.

By comparing the trends for the pure- toluene and dodecane systems with increasing calcium content, it is clear that they are at different stages in the trend development. To make this clearer it is observed that the pure dodecane system starts off with a high interfacial tension followed by a significant drop and a raise as the calcium content increases for the following range of mole fractions of $\text{Ca}^{2+}/\text{Na}^{+}$ investigated. This is not the case for the pure toluene system, as interfacial tension merely rises as calcium fraction increases in the system. It is therefore likely to believe that the same type of trend could be observed for pure toluene, as for pure dodecane, but rather at lower salinities which have not been investigated in this thesis. This also means that a lower interfacial tension value for the pure toluene may exist at lower salinities, than those levels that have been investigated in this thesis. Based on Figures 3.1 - 3.2 there is therefore reason to believe that all the series with a model oil fraction of 75 wt. % toluene or more could have a lower minimum interfacial tension value outside the range of cationic mole fractions investigated in this thesis.

Essentially the results tell us that surfactant packing density in the pure toluene system would be higher at lower salinities, as the surfactant head groups require less shielding from cations to pack densely. The same type of trend is observed when the model oil consists of only dodecane, but in this case is a higher concentration of calcium required in order to obtain a minimum interfacial tension. Whether or not this is caused by the higher polarity of the toluene molecule or if it is merely a result of molecule structure is not going to be speculated, but it is safe to say that oil-surfactant-water interactions greatly depend on the oil phase regarding to observed interfacial tension of the system. Based on the experiments performed

in this thesis, there is reason to believe that a lower interfacial tension can be measured with pure toluene serving as model oil, when every condition but the ionic strength remains the same. This is believed logic to assume since every value for the pure dodecane-system was measurable, which was not the case for pure toluene systems. At higher $\text{Ca}^{2+}/\text{Na}^{+}$ mole fractions it is likely to believe that aggregates between the surfactant and calcium ions are formed at the interface. This results in surfactant migration to the bulk oil phase, which essentially means that fewer surfactant molecules arrange on the interface, hence a higher interfacial tension for the system.⁸

In the span of measurements that have been done through this thesis, some values proved to be impossible to measure, due to very low interfacial tensions. In some cases the oil drop merely dissolved into smaller drops right after being injected, and those drops were way too small for the camera used in the spinning drop tensiometer to use for measuring. This was especially the case for systems where toluene was the most abundant compound in the model oil phase, where the interfacial tension was too low to be measured.

Many of the single measurements like the one presented in Figure 3.7 and also some in the Appendix A2 show how the interfacial tension simply refuses to stabilize, and gradually makes its way towards the lower IFTs as time passes by. This trend was mostly observed in series where toluene was the dominating compound in the model oil phase. These oil drops rich in toluene had the tendency to gradually elongate despite of lowering the capillary rotation speed. Some did even divide into so small drops that measuring no longer was possible, which made stabilization and precise results difficult to obtain. In order to get credible results, the equilibrium values that are plotted in the collective graphs have been chosen from the same time period (i.e 2000 seconds after sample was started) and also considered relative to other measurements for the current series.

In order to get a phase inversion into a Winsor 3 system which is ideal for transportation of oil from the reservoir to the production well, ultralow interfacial tensions at specific salinities are required. Though ultralow IFTs were obtained at different salinities, the methods used in this thesis do not allow us to conclude if a phase inversion ever took place.

Densities for the aqueous solutions were only measured for the extreme values ($\text{Ca}^{2+}/\text{Na}^{+}$ mole fractions were 0, 1/25 and 1/16). All samples were in advance believed to have the same density, due to very little change in composition between each of them. The density measurements are shown in the Appendix A1. Based on the measured densities, any real

deviation from the density used in the calculations would be of such a small magnitude, that it would have no significant effect on the results presented.

Standard deviation has only been calculated for the dodecane series performed during the specialization project in 2013. Calculated discrepancies proved too small to even be noticed on the wide scale figures both then and now, and have not been accounted for in the construction of the different diagrams in the result part.

The results can be used to model how a changing $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction affects the interfacial tension of an aqueous-oil system, and is of high interest to further research related to combined surfactant- and low salinity flooding in relation to EOR.

4.2 Effect of calcium ions on IFT in Brine-Dodecane and Brine-Toluene systems

It was in advance expected that in the absence of surfactant molecules, a varying $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction would not influence the interfacial tension significantly. Along with varying model oil composition, are the interactions at the interface between anionic surfactant head groups and cations the reason for the observed change in interfacial tension. In this series the cations have no strong affinity to the interface, and hence a variation in calcium content should not influence the interfacial tension of the system.

Figure 3.9 shows that the interfacial tension for neither the dodecane- nor the toluene system is affected by an increasing $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction. As toluene is the more polar component, it was expected to yield the lowest interfacial tension against the aqueous non-surfactant phase. This implies that the observed changes in IFT in systems where surfactant is used, is clearly an effect of surfactant-cationic interactions. The Brine-Dodecane measurements have been done during the specialization project in the autumn of 2013.

The actual difference between the extreme values obtained in both series equal to 1,25 % and 0,57 % for the dodecane-brine- and toluene-brine system, respectively. The discrepancy is not considerably high. The observed difference in IFT in Figure 3.9 is considered insignificant, and the small variation in measured value is therefore rather more likely to be a coincidence than an actual effect of a varying calcium mole fraction.

4.3 Effect of salinity on IFT in AOT/Brine-Dodecane/Toluene systems

Since it was not possible to find a minimum IFT for the AOT/Brine - Dodecane/Toluene (50/50 wt. %) series, a second series with a lower salinity was performed in order to find a minimum value. There is reason to believe that the minimum IFT value found in the ultra-low

salinity series would have been found at the same $\text{Ca}^{2+}/\text{Na}^+$ mole fraction in the low salinity series, if they were measurable. This is based on the trend that is observed in previous sections, where it is clear that the minimum observed IFT value gradually moves towards higher calcium mole fraction, as dodecane wt. % increases in the model oil phase. By looking at Figure 3.10 we observe that salinity affects the IFT values measured, however, both systems behave the exact same way regarding the trend, which amplifies the likelihood of the two series having the same IFT-minima. Results showed that a mole fraction of 1/60 $\text{Ca}^{2+}/\text{Na}^+$ gave the minimum IFT value in the series.

Despite this being a digression from the original series where the ionic strength was 20 mM, the result obtained proved useful in relation to finding a minimum interfacial tension value in the EACN scale investigations. It would, however, have been much work to complete a second series with ionic strength of 5 mM, as the series with model oil phase dominated by toluene potentially could have a minimum interfacial tension outside the range of calcium mole fractions investigated throughout this thesis.

4.4 Effect of model oil composition on IFT in relation to the EACN scale, in AOT/Brine-Dodecane/Toluene systems

It is apparent from Figure 3.11 that the behavior of the dodecane/toluene (75/25 wt. %) system is greatly influenced by the trends from the two pure model oil systems, along the changing calcium mole fraction scale. As previously said is it shown by the logarithmic graphs for the 20 mM ionic strength series in Figures 3.1 - 3.5, that the minimum IFT value(s) measured are gradually moving towards the one of pure dodecane, as the dodecane (which has a much higher EACN-value than toluene) fraction in wt. % increases.

It is very interesting to see that the two series with model oil composition of 50- and 75 wt. % dodecane, each having an EACN number of 4,9 and 7,8, respectively, showed to yield similar results as reported in earlier published material.²⁷ Both mixtures have EACN values fairly close to the one of pure heptane, which has an ACN value of 7. According to previous work done in this field it is expected that measured interfacial tension for both systems would be in the vicinity of what was found for pure heptane against an aqueous AOT/Brine solution under the exact same conditions. The reported value for a mole fraction of 1/45 $\text{Ca}^{2+}/\text{Na}^+$ has previously be mentioned to be 0,004 mN/m, which can be reckoned as an “ultralow” IFT-value.⁸ In this thesis, the minimal interfacial tension for the equally mixed model oil phase was found at a $\text{Ca}^{2+}/\text{Na}^+$ mole fraction of 1/60, while it was found somewhere between a

$\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction of 1/45 and 1/30 for the 75/25 wt. % dodecane/toluene model oil mixture.

As previously mentioned was the value reported found under the exact same conditions as are used in this experimental series, as surfactant concentration, ionic strength, pH and temperature were the same.²⁷ For the 50/50 wt. % dodecane/toluene model oil system at a $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction of 1/45, the measured value was reported to 0,014 mN/m, which is pretty close to the one for the pure heptane system. Although IFT for the system with model oil phase consisting of 75-25 wt. % dodecane/toluene proved too low to be measured at $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction of 1/45, it is still likely to believe that if a value were to be measured, it would be lower than 0,014 mN/m, and even closer to the one for pure heptane system. That is based on the fact that the EACN number for the 75/25 wt. % model oil mixture in favor of dodecane lies closer to the one of pure heptane, hence a lower interfacial tension is expected than the one for the 50/50 wt. % model oil system.

Results obtained from experiments correlates with previous observations, which also have been noted in section 1.5. Despite missing some values due to not being able to measure some samples, does the trend seem to match previous work done by other researchers quite well, and serve as a good base for further experiments related to the EACN scale.^{8,22,23}

5. Conclusion

From the experimental results it can be observed that a variation in oil mixture composition causes the series to respond differently to the change in $\text{Ca}^{2+}/\text{Na}^+$ mole fraction. Calcium content in the aqueous phase clearly influences the surfactant packing density on the interface, and hence the interfacial tension of the system, according to the CPP parameter. Series where model oil composition was richest in dodecane started off with high IFT values at low calcium mole fractions and experienced a decrease followed by a rise, as calcium content increased. IFT for systems where toluene was the most abundant component in the oil phase merely rose as calcium fraction in the system was increased.

As more dodecane was added to the oil-phase, the minimum IFT point(s) gradually moved towards higher $\text{Ca}^{2+}/\text{Na}^+$ mole fractions. According to the EACN scale theory this is assumed behavior for the series as the average EACN number increases. Also IFT values found in this thesis correlated well with previous experimental observations under the same conditions.

Neither the IFT of toluene nor dodecane showed to be affected by increasing calcium content when surfactant was removed from the aqueous solution. This indicates that the observed changes in IFT in systems where surfactant is used, is clearly an effect of interactions between surfactants and cations.

By lowering the ionic strength it proved easier to find a minimum IFT value for the current series. The overall trend in the ultra-low salinity series matched the trend for the same series with higher salinity. Values found did also match the expected alternation in minimum interfacial tension according to the EACN theory.

The results can be used to model how calcium mole fraction and oil composition affect the interfacial tension of an aqueous-oil system. Experimental results match expected behavior from the EACN theory well, and can be of high interest to further research related to combined surfactant- and low salinity flooding in relation to EOR.

List of symbols

Symbol	Units	Description
γ	mN/m	Interfacial tension
dG	J	Change in free energy
dA	m ²	Change in surface area
F	N	Force
L	m	Length
d γ	mN/m	Change in interfacial tension
Γ_i	mol/m ²	Surface excess of component <i>i</i>
d μ_i	J	Change in chemical potential of component <i>i</i>
CPP	-	Critical packing parameter
V _t	m ³	Volume of surfactant's hydrocarbon tail
a _h	m ²	Area of surfactant's head group
l _t	m	Length of Surfactant's hydrocarbon tail
N _c	-	Capillary number
η	kg/ms	Viscosity
v	m/s	Velocity
κ	m ⁻¹	Parameter expressing the effect of ionic concentration and valency
e	C	Electron charge (Constant)
N _A	mol ⁻¹	Avogadro's number
C _{el}	mol/m ³	Bulk concentration
z	-	Valency/Ionic charge
ϵ	F/m	Permittivity
c _i	mol/m ³	Concentration of component <i>i</i>
EACN	-	Equivalent alkane carbon number
EACN _{avg}	-	Average equivalent alkane carbon number
X _i	-	Mole fraction
N _{min}	mN/m	Minimal interfacial tension
n _i	mol	Moles of compound <i>i</i>

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Appendices

Appendix A1 - Tabled experimental values

All values are at equilibrium. Measurements with more than one parallel have been averaged and are displayed as one value in the Table A1 below. Surfactant concentration are in all series 2,47 mM, ionic strength is 20 mM and the temperature is 60 °C. Pure dodecane measurements have been taken from the specialization project finished in the autumn of 2013. In cases where IFT values have been reported with two stars (**) was the interfacial tension not measurable by the spinning drop tensiometer used, due to low IFTs. Standard deviation has not been accounted for in the graphic presentations.

Table A1: Data collected from different Surfactant/Brine - Dodecane/Toluene series. * Single measurement, ** Not measured due to too low interfacial tensions

Molefraction Ca ²⁺ /Na ⁺ [mol/mol]	IFT [mN/m] D-T (100-0)	IFT [mN/m] D-T (90-10)	IFT [mN/m] D-T (75-25)	IFT [mN/m] D-T (50-50)	IFT [mN/m] D-T (25-75)	IFT [mN/m] D-T (10-90)	IFT [mN/m] D-T (0-100)
0	0,9875	0,9	0,79	0,27	**	**	**
1/200	0,26	0,275	0,17	**	**	**	0,015
1/100	0,1465	0,12	0,1	**	0,015	0,03	0,14
1/60	0,1225	0,115	0,06*	**	0,11	0,17	0,25
1/45	0,0795	0,08	**	0,014	0,2	0,25	0,42
1/30	0,024	0,03	**	0,08	0,5	0,65	0,76
1/25	0,0095	0,013	0,01125	0,33	0,75	0,7	1,04
1/22	0,045	-	-	-	-	-	-
1/20	0,0175	0,03	0,175	0,5	1,1	1,225	1,41
1/16	0,09	0,1	0,23	0,7	1,32	1,4	1,675

The next series was only performed for the equally mixed model oil phase (50/50 wt. % dodecane/toluene). All values are at equilibrium and are displayed as one value in the Table A2. Surfactant concentration is 2,47 mM, ionic strength is 5 mM and the temperature is 60°C.

Table A2: Data collected from Surfactant/Brine - Dodecane/Toluene (50/50 wt. %) ultralow salinity series.

Molefraction Ca ²⁺ /Na ⁺ [mol/mol]	0	1/200	1/100	1/60	1/45	1/30	1/25	1/20	1/16
IFT [mN/m] U.LS (50-50)	1,05	0,48	0,2	0,12	0,14	0,25	0,29	0,32	0,38

The following table A3 shows detailed experimental information collected from the brine-dodecane/toluene series. In cases where more than 1 parallel was run, only the average value is shown in Table A3. The noted interfacial tension values are at equilibrium. Ionic strength is 20 mM and the temperature was 60°C.

Table A3: Data collected from the brine-dodecane series

Molefraction Ca ²⁺ /Na ⁺ [mol/mol]	0	1/25	1/16
Brine-Dodecane Series - IFT [mN/m]	32,06	31,7	32,02
Brine Toluene Series - IFT [mN/m]	21,88	21,75	21,85

All samples were preheated to 60°C prior to being measured in the Anton Paar DMA 4100 density meter, exact values are shown in Table A4.

Table A4: Density measurements of samples at 60 °C. * Densities measured during the specialization project in the autumn of 2013.

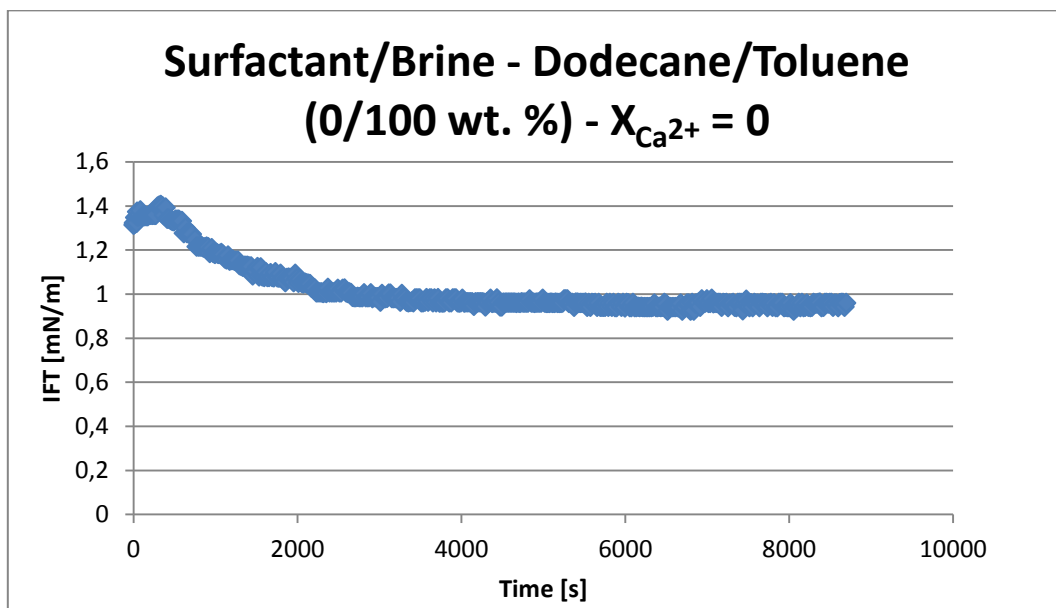
Sample	Density [g/cm ³]
Low Salinity: Aerosol OT/Brine, Ca ²⁺ /Na ⁺ mole fraction = 0	0,9840*
Low Salinity: Aerosol OT/Brine, Ca ²⁺ /Na ⁺ mole fraction = 1/25	0,9840*
Low Salinity: Aerosol OT/Brine, Ca ²⁺ /Na ⁺ mole fraction = 1/16	0,9838*
Ultra-low salinity: Aerosol OT/Brine, Ca ²⁺ /Na ⁺ mole fraction = 0	0,9828
Ultra-low salinity: Aerosol OT/Brine, Ca ²⁺ /Na ⁺ mole fraction = 1/25	0,9831
Ultra-low salinity: Aerosol OT/Brine, Ca ²⁺ /Na ⁺ mole fraction = 1/16	0,9831
Brine, Ca ²⁺ /Na ⁺ mole fraction = 0	0,9839*
Brine, Ca ²⁺ /Na ⁺ mole fraction = 1/25	0,9838*
Brine, Ca ²⁺ /Na ⁺ mole fraction = 1/16	0,0938*

Dodecane	0,7196*
Dodecane - Toluene (90 - 10 wt. %)	0,7238
Dodecane - Toluene (75 - 25 wt. %)	0,7314
Dodecane - Toluene (50 - 50 wt. %)	0,7680
Dodecane - Toluene (25 - 75 wt. %)	0,7820
Dodecane - Toluene (10 - 90 wt. %)	0,8155
Toluene	0,8289

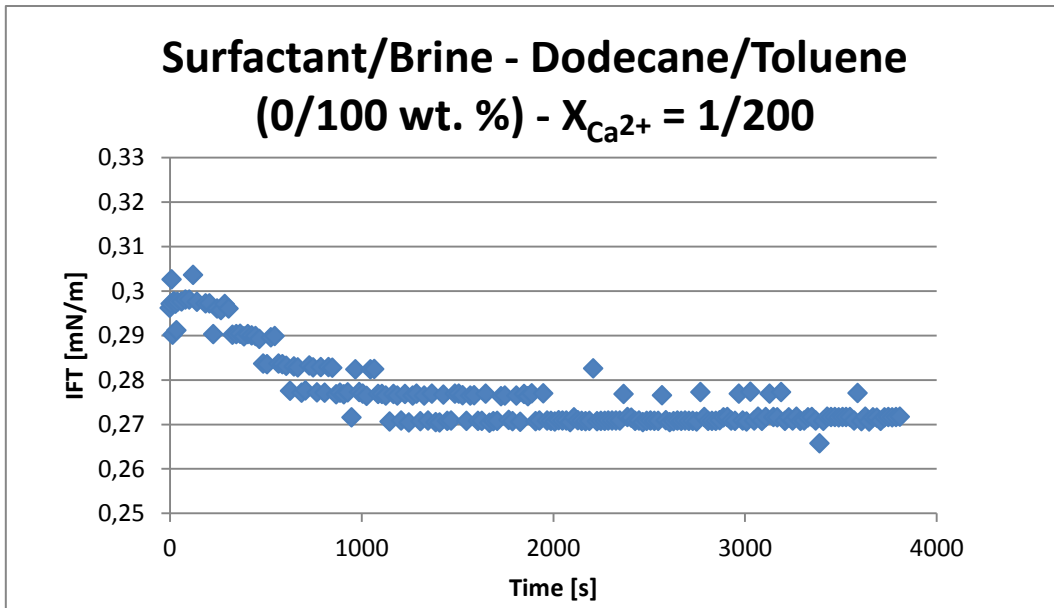
Appendix A2 - IFT vs. time measurements for [I] = 20 mM series and collective graphs

The following Figures (A1 - A53) show the graphed values of the interfacial tension versus time, at different $\text{Ca}^{2+}/\text{Na}^{+}$ mole fractions for the Surfactant/Brine-Dodecane/Toluene series. Ionic strength was 20 mM and surfactant concentration was 2,47 mM. All measurements were conducted at 60°C, and are the basis for all of the combined graphs presented in the chapter 3. AOT is the surfactant that has been used in every series conducted. Only one parallel is shown for each ratio, equilibrium values for the other parallel(s) are averaged and shown in Appendix A1, Table A1. Values for the pure dodecane series have been taken from the specialization project finished in the autumn of 2013.

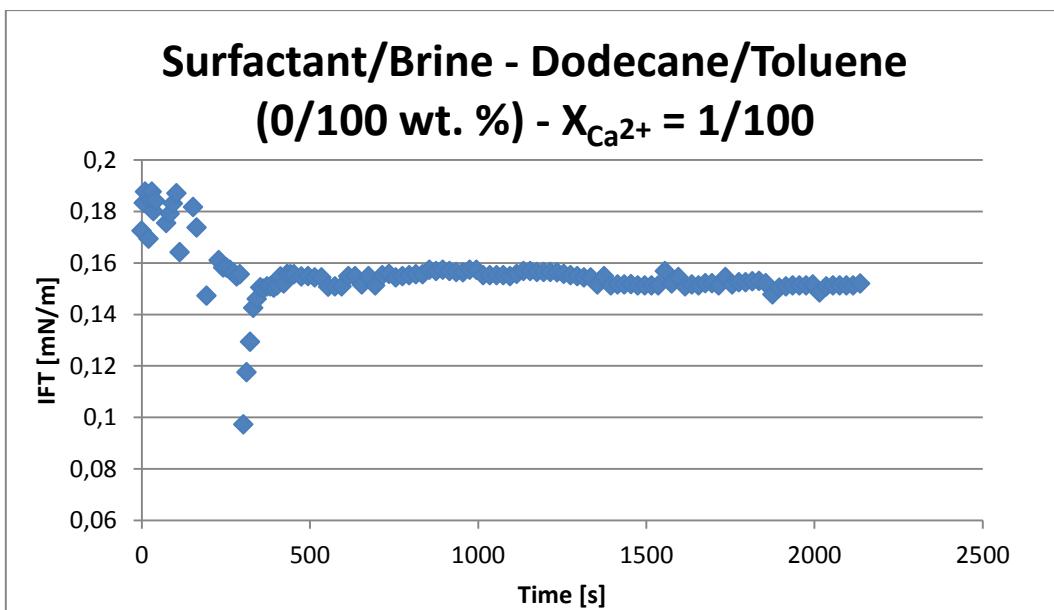
Surfactant/Brine - Dodecane/Toluene (100/0 wt. %):



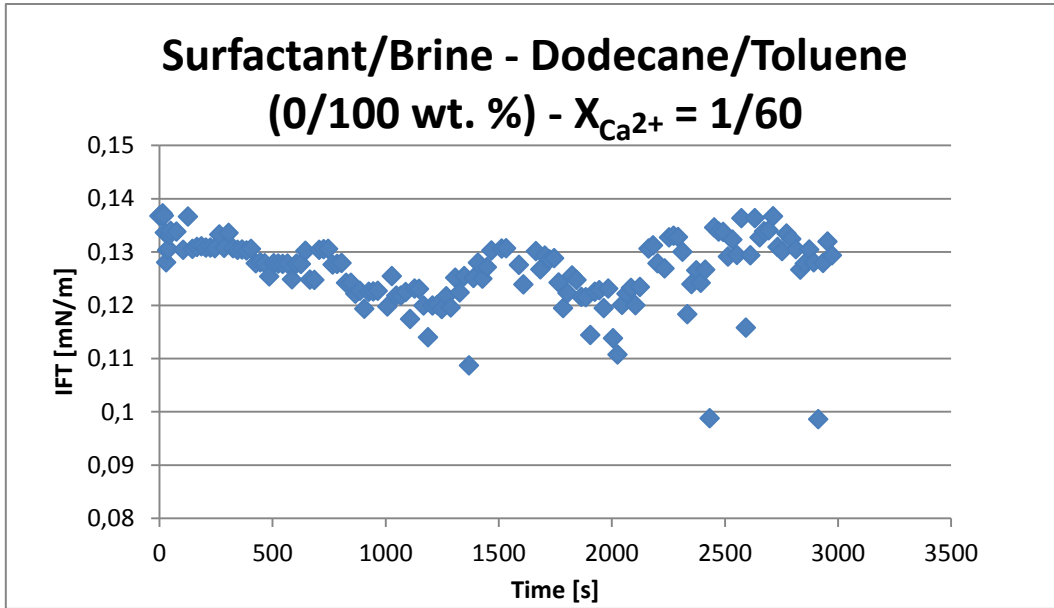
A1: Interfacial tension vs. time, for a $\text{Ca}^{2+}/\text{Na}^{+}$ mole fraction of 0. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.



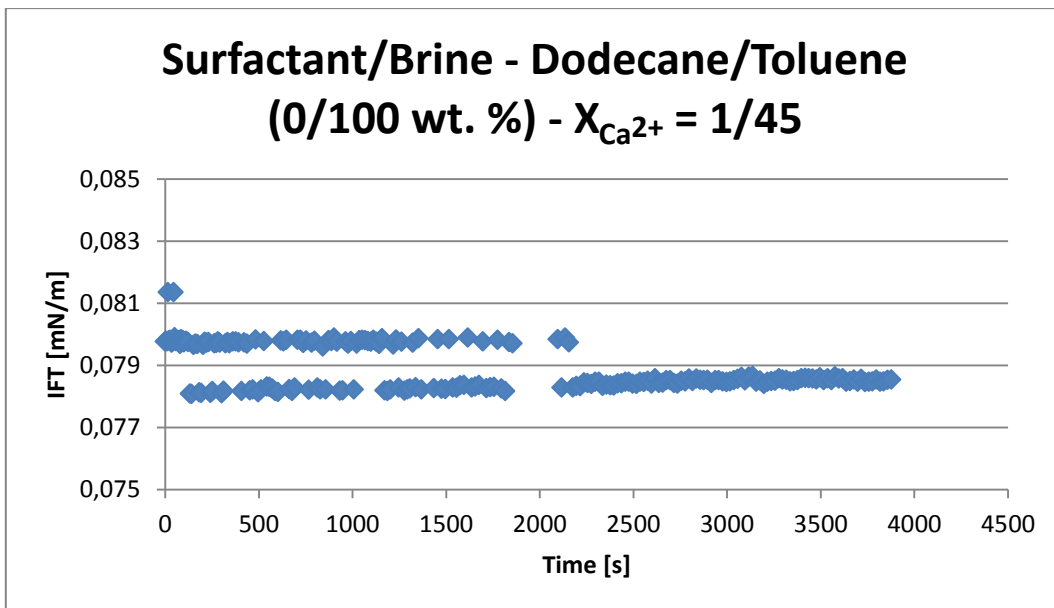
A2: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/200. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.



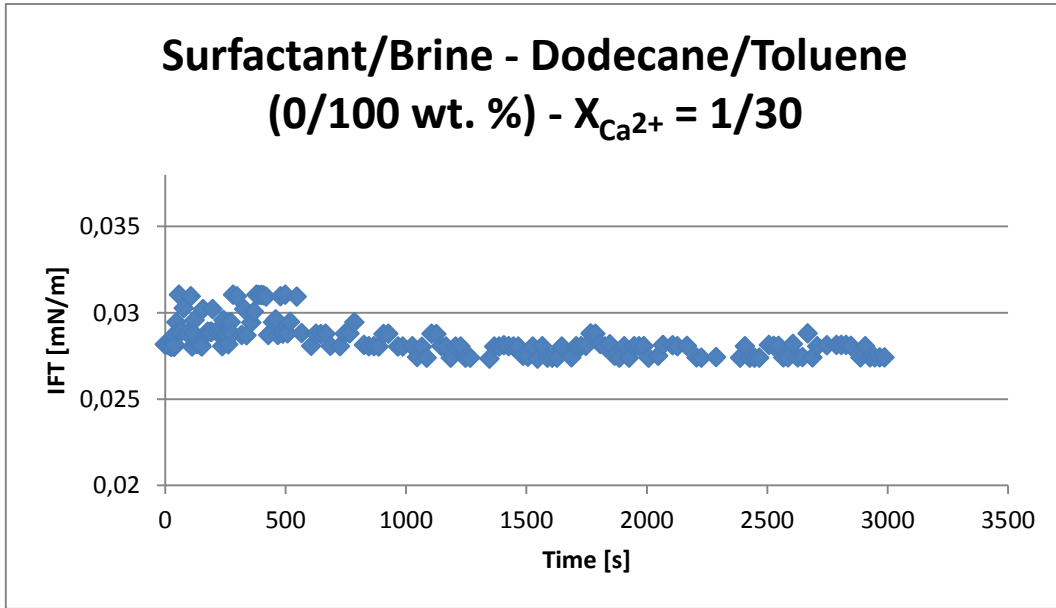
A3: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.



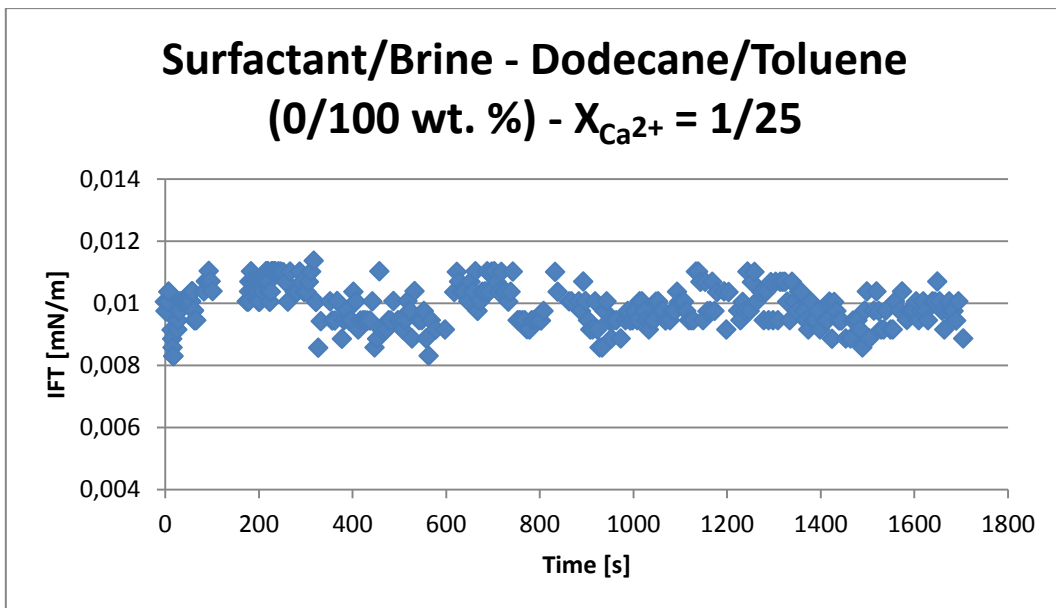
A4: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/60. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C..



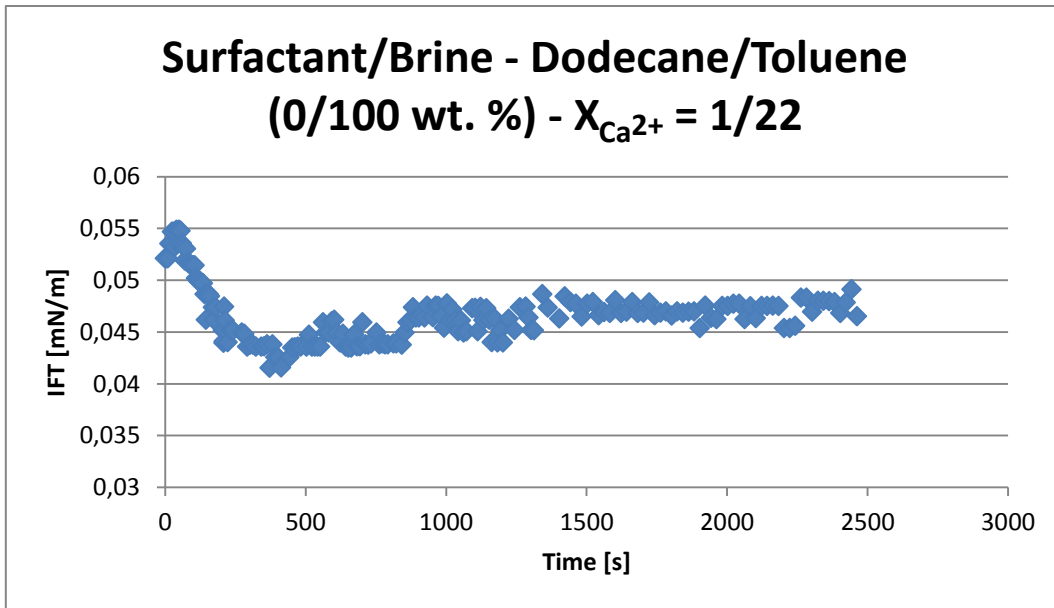
A5: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C..



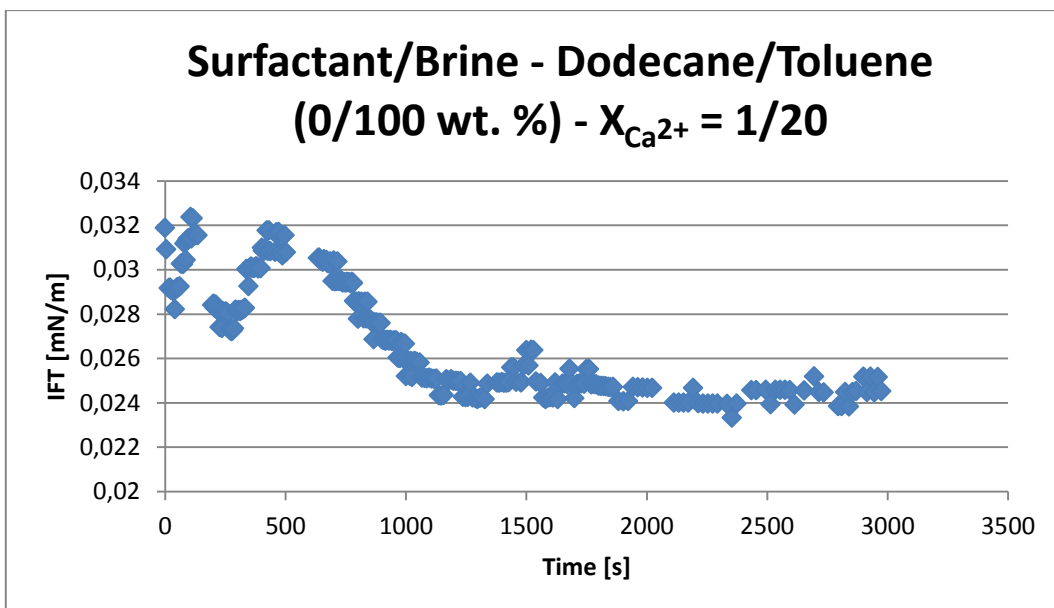
A6: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.



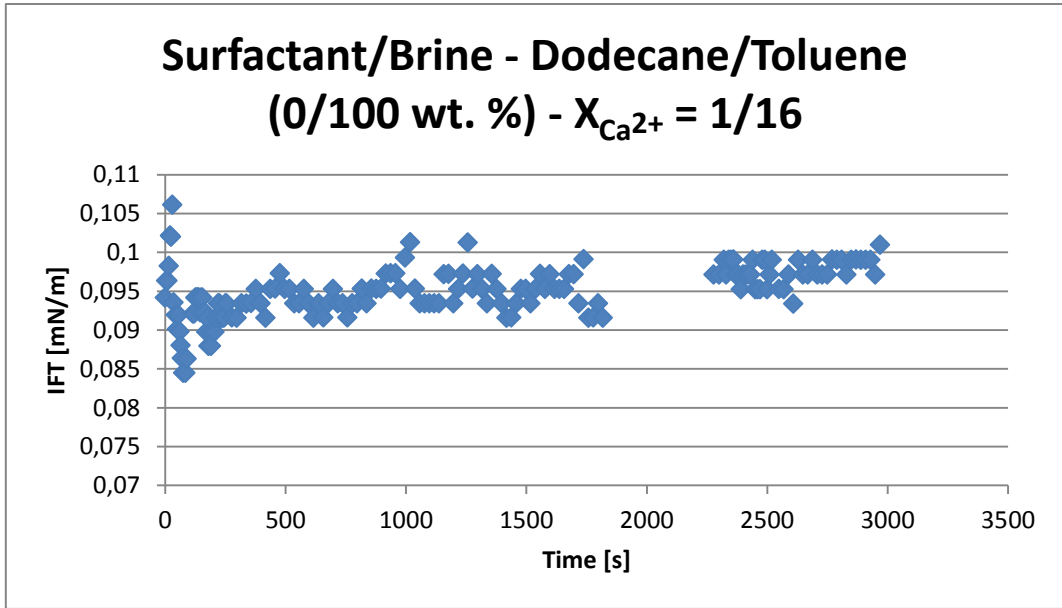
A7: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.



A8: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/22. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.

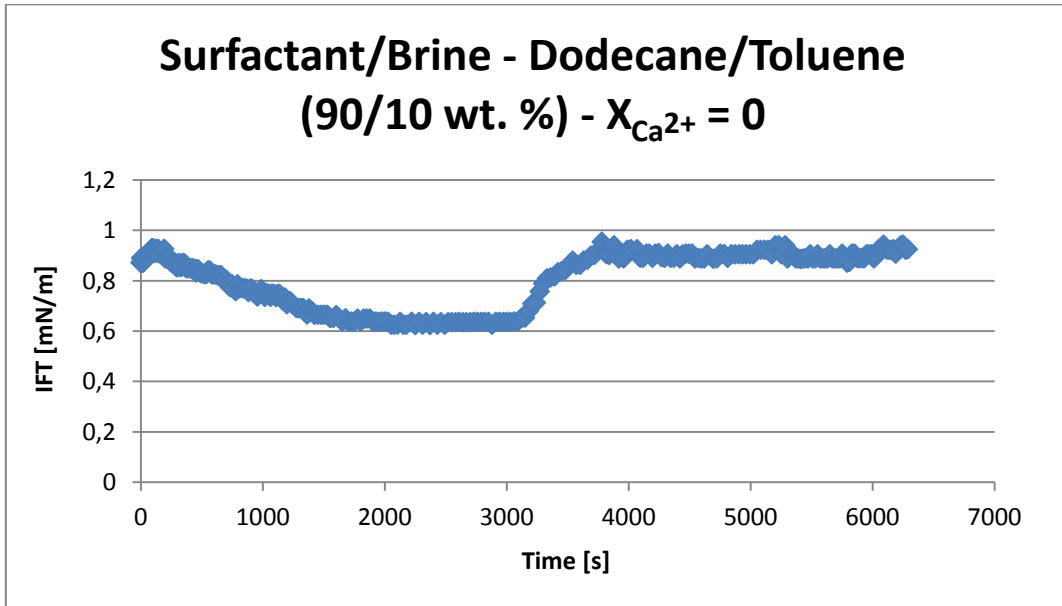


A9: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.

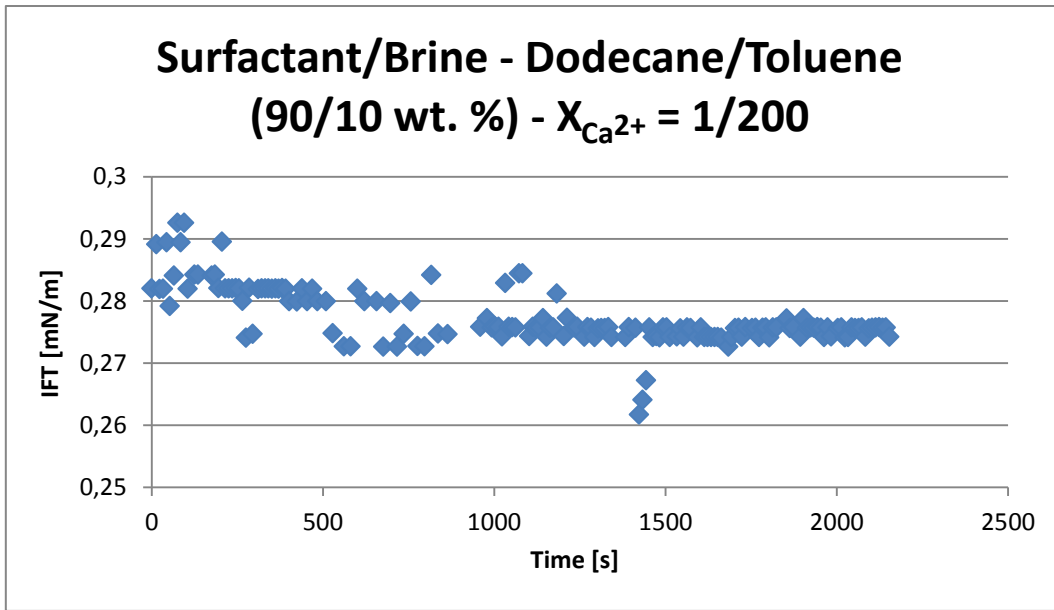


A10: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (100/0 wt. %). Temperature is 60°C.

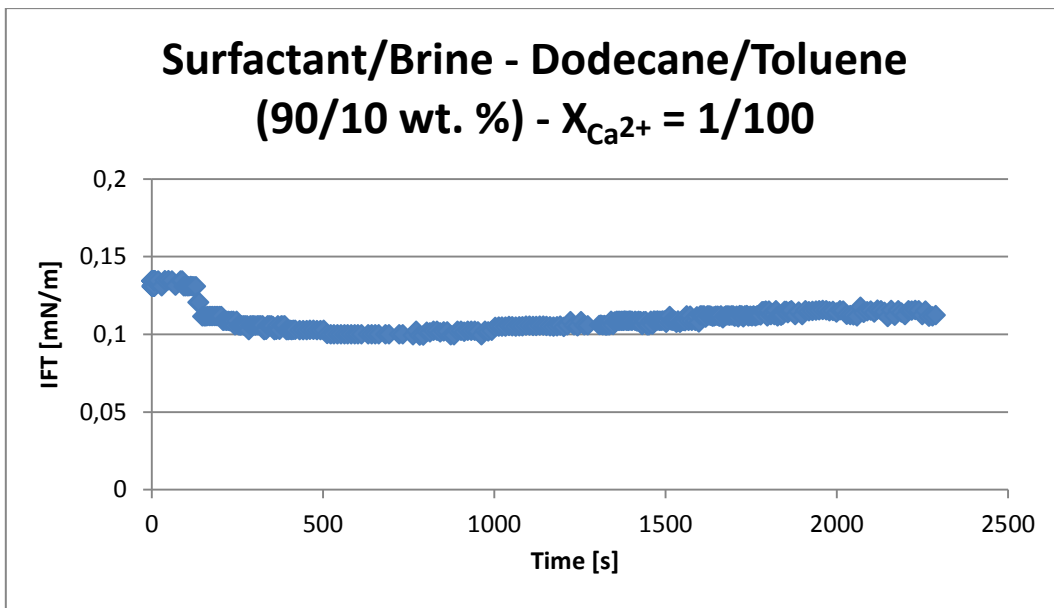
Surfactant/Brine - Dodecane/Toluene (90/10 wt. %):



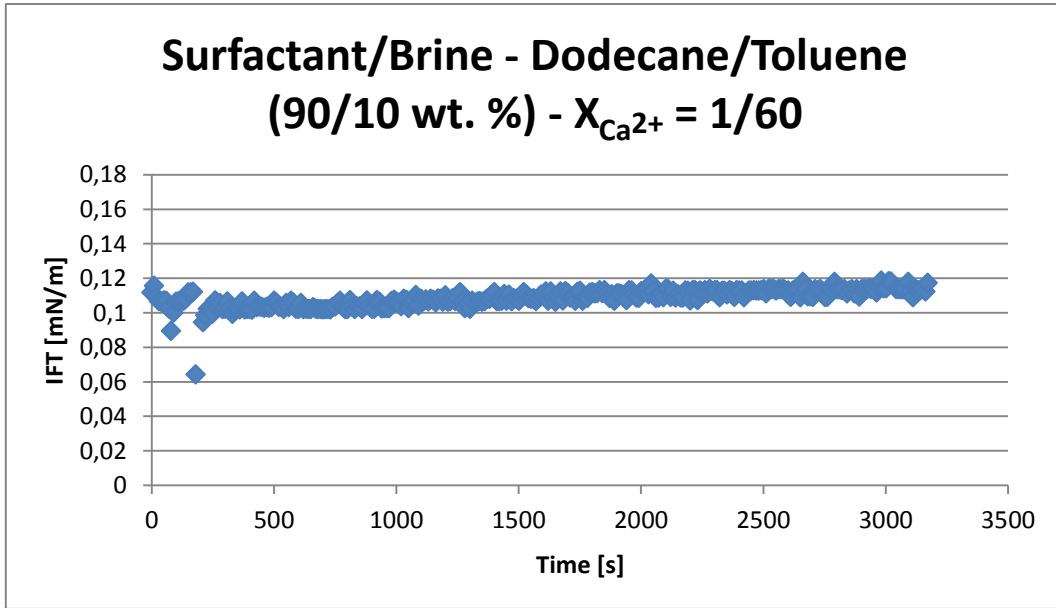
A11: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 0. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.



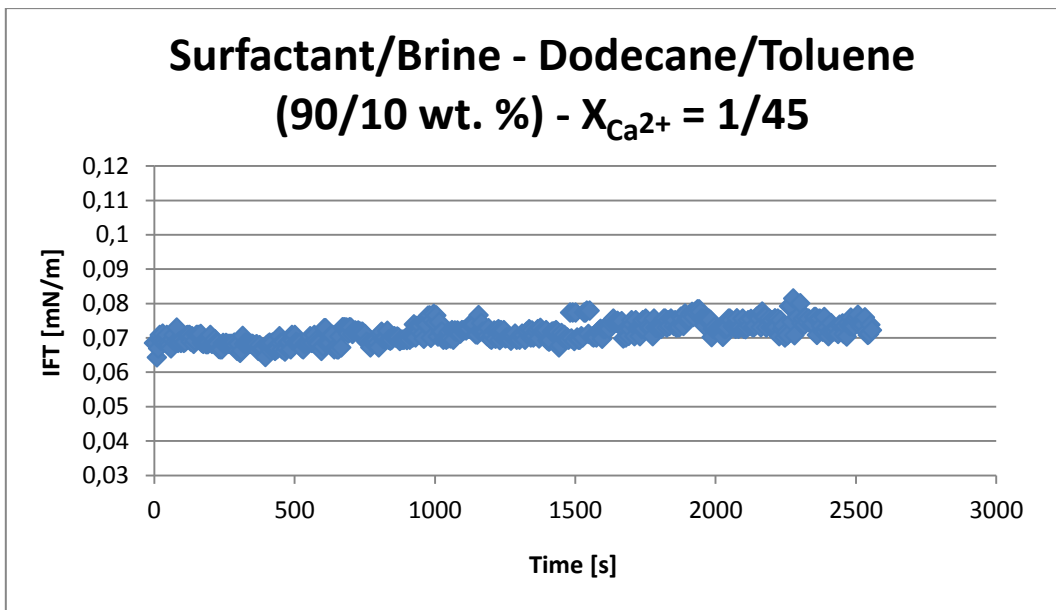
A12: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/200. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.



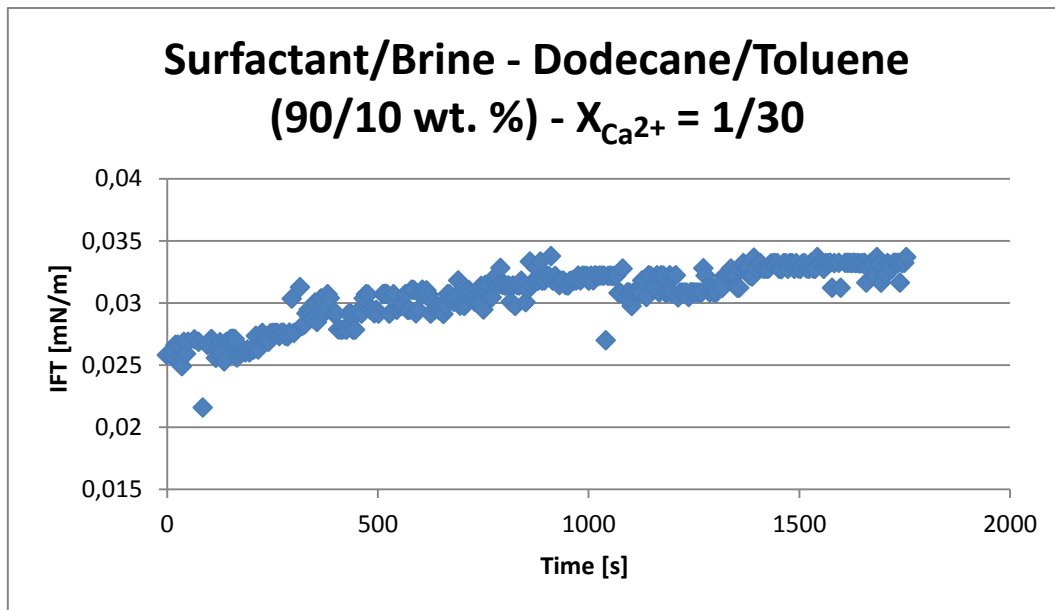
A13: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.



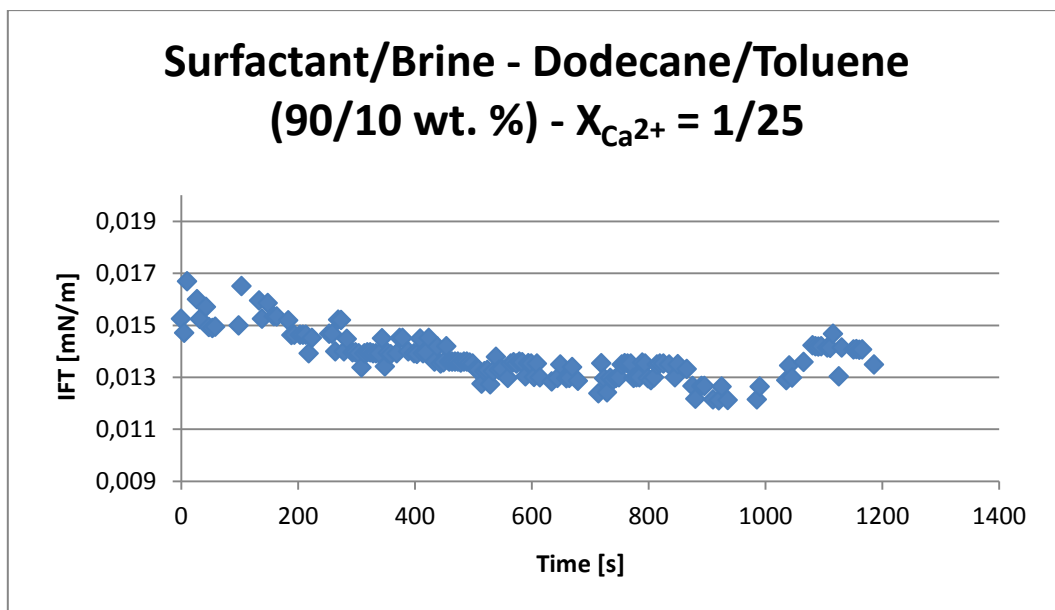
A14: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/60. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.



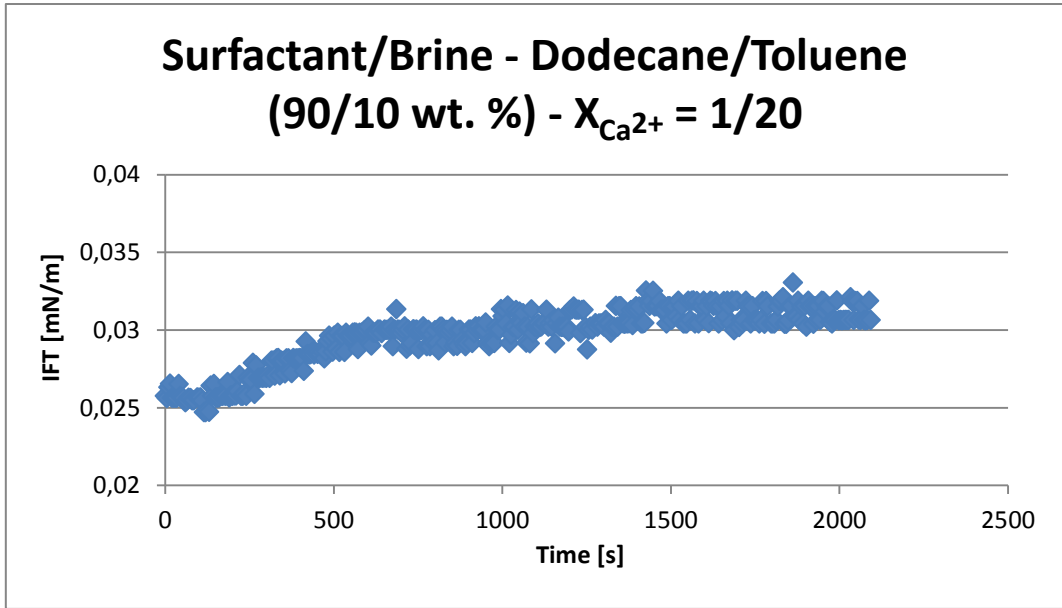
A15: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.



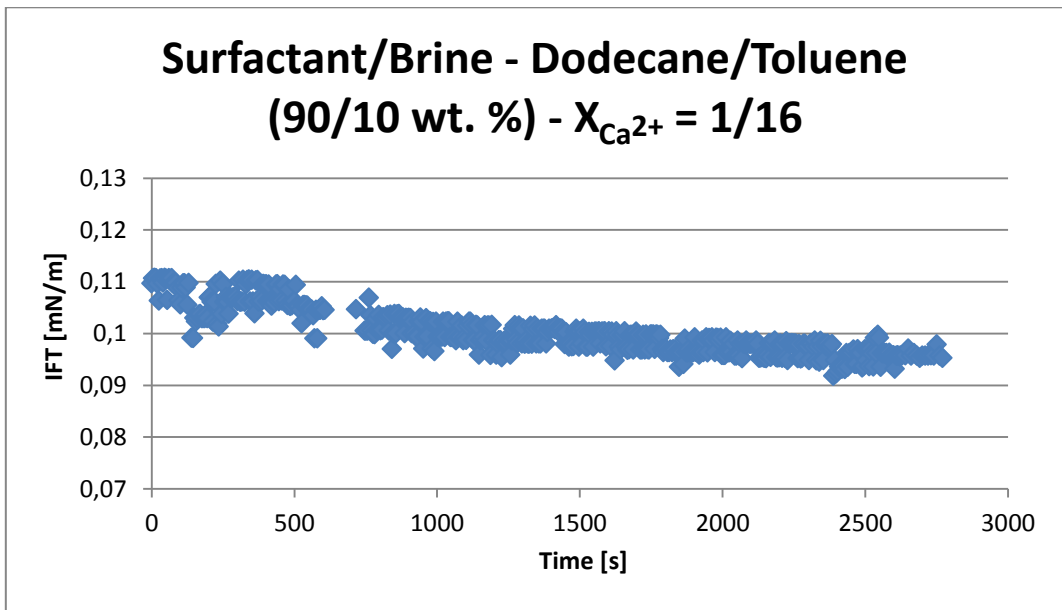
A16: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.



A17: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.

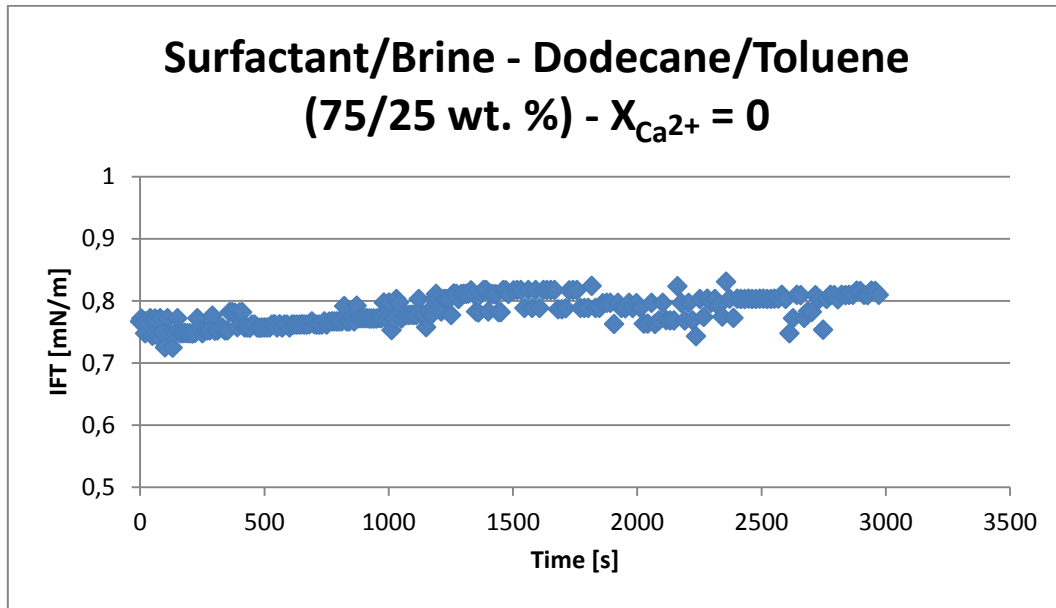


A18: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.

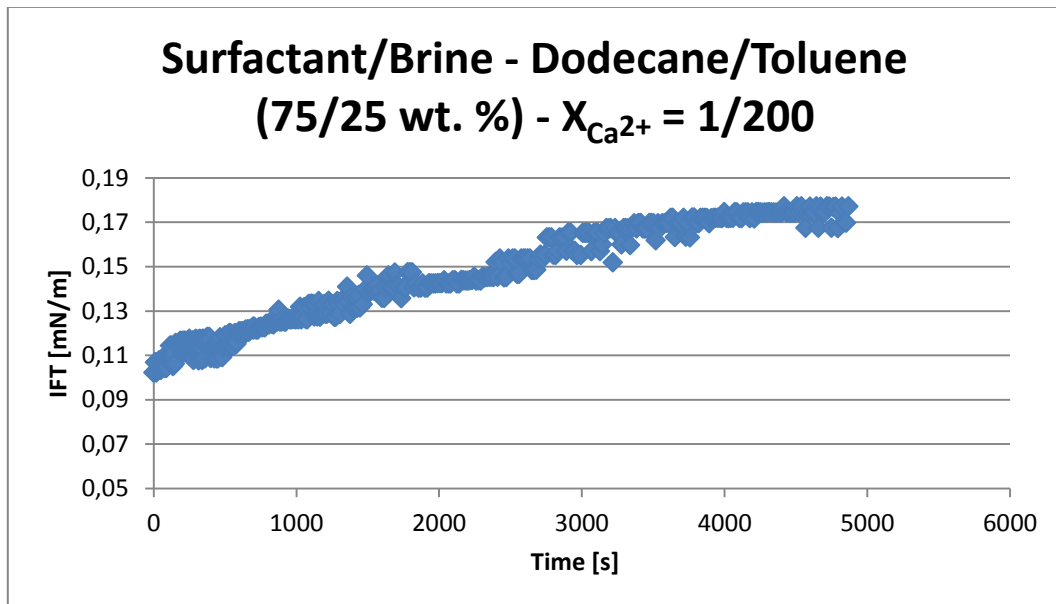


A19: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (90/10 wt. %). Temperature is 60°C.

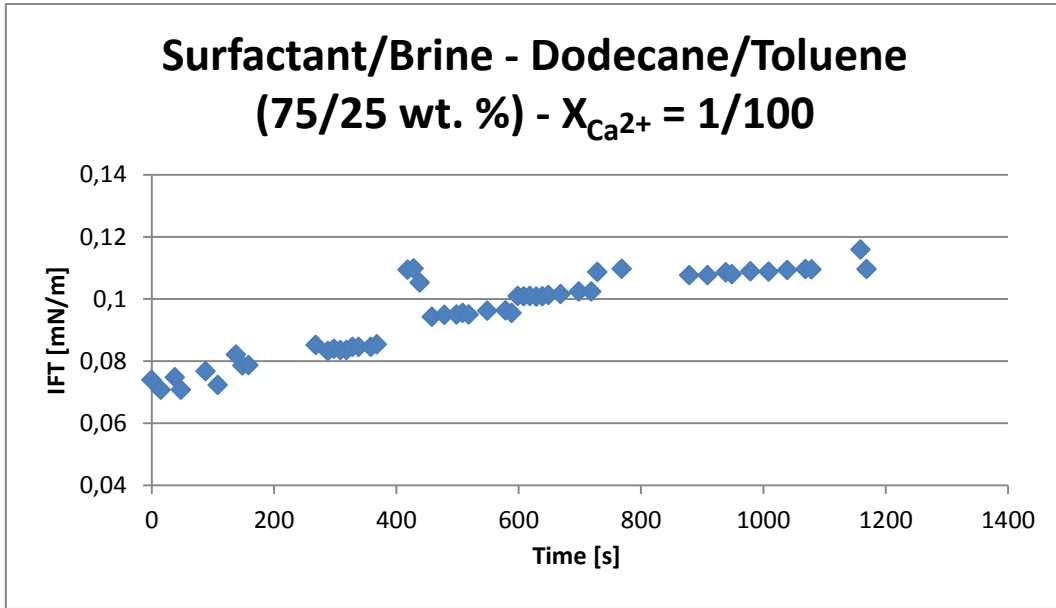
Surfactant/Brine - Dodecane/Toluene (75 - 25 wt. %):



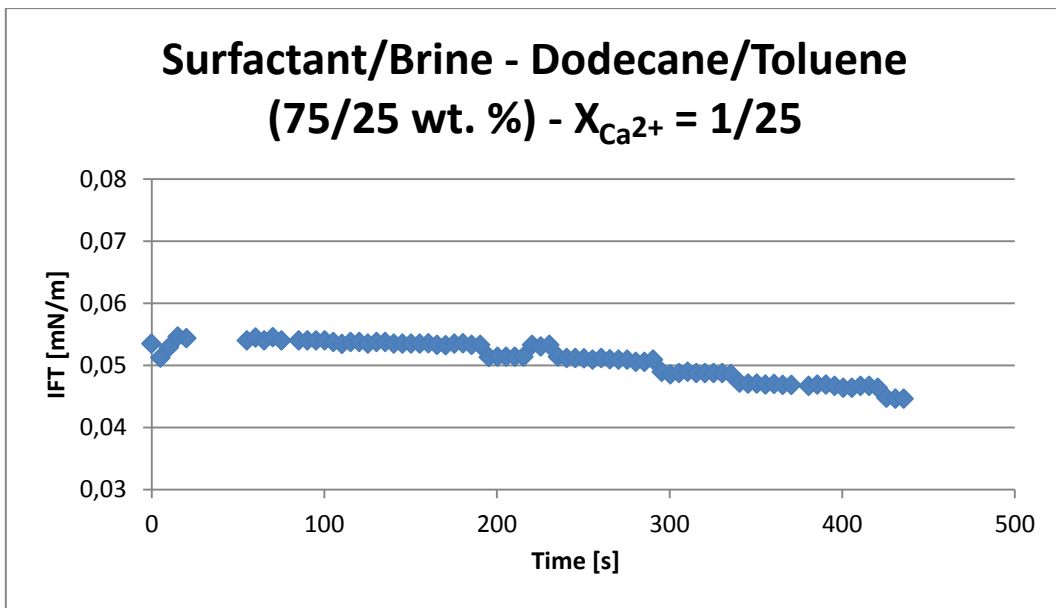
A20: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 0. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (75/25 wt. %). Temperature is 60°C.



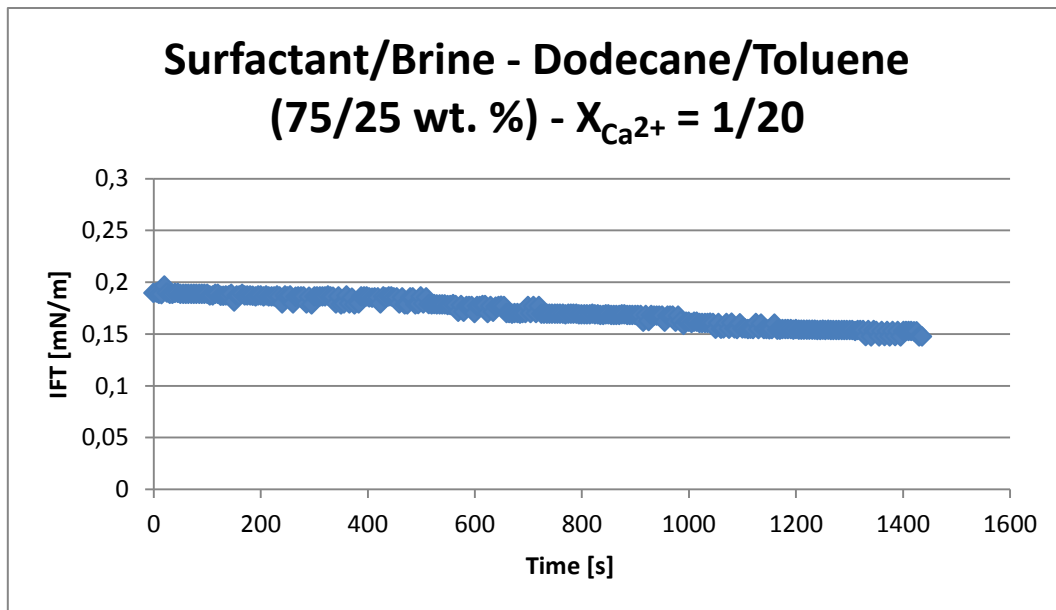
A21: Interfacial tension vs. time, for 0,5 mole % Ca^{2+}/Na^{+} ratio. Both ionic strength and surfactant concentration are 2,47 mM and the model oil composition is Dodecane-Toluene (75 - 25 wt. %). Temperature is 60°C.



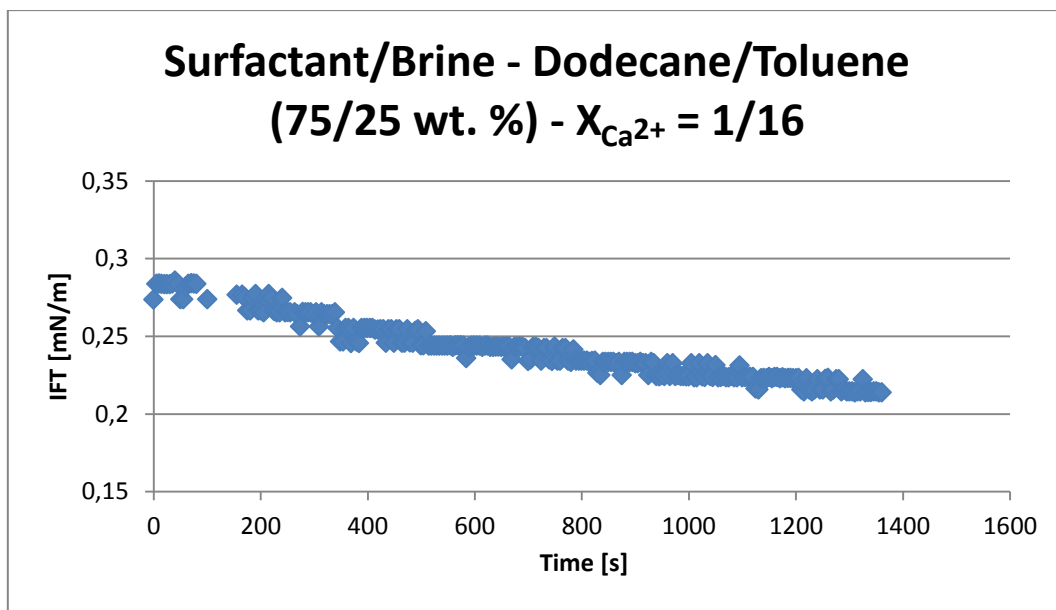
A22: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (75/25 wt. %). Temperature is 60°C.



A23: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (75/25 wt. %). Temperature is 60°C.

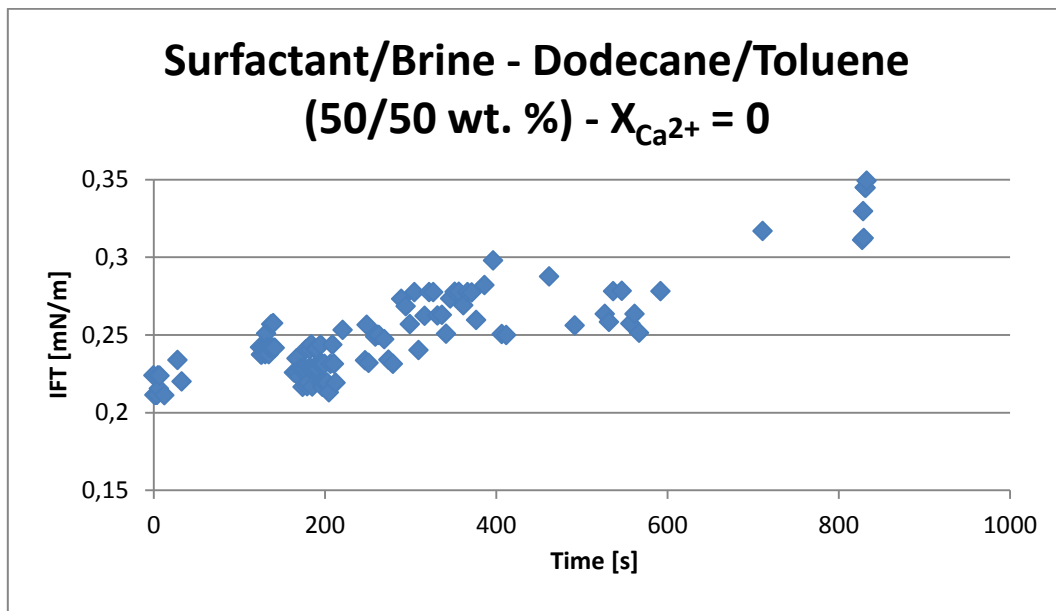


A24: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (75/25 wt. %). Temperature is 60°C.

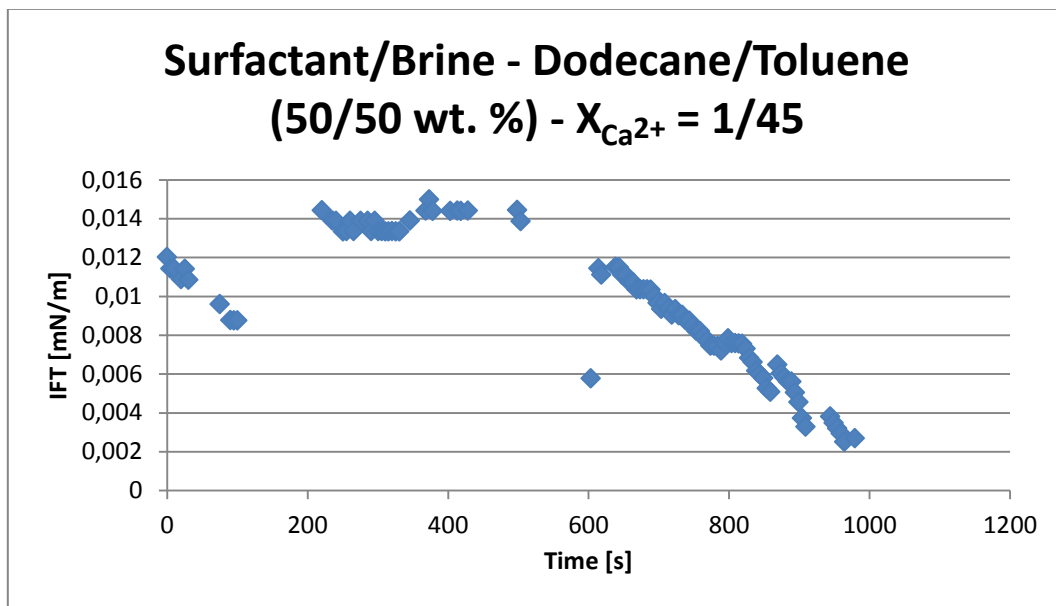


A25: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (75/25 wt. %). Temperature is 60°C.

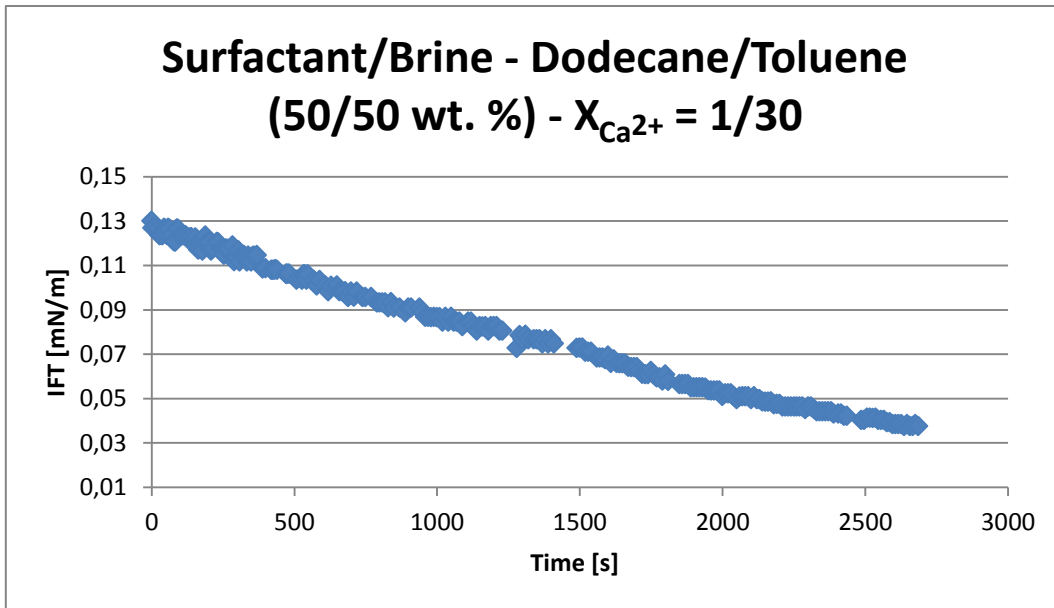
Surfactant/Brine - Dodecane/Toluene (50 - 50 wt. %):



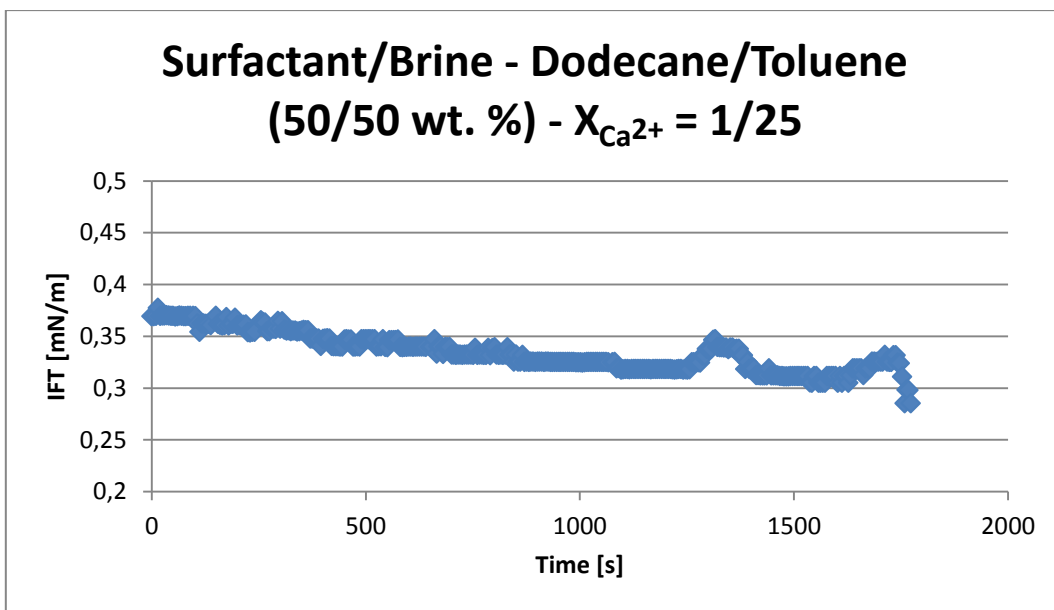
A26: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 0. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



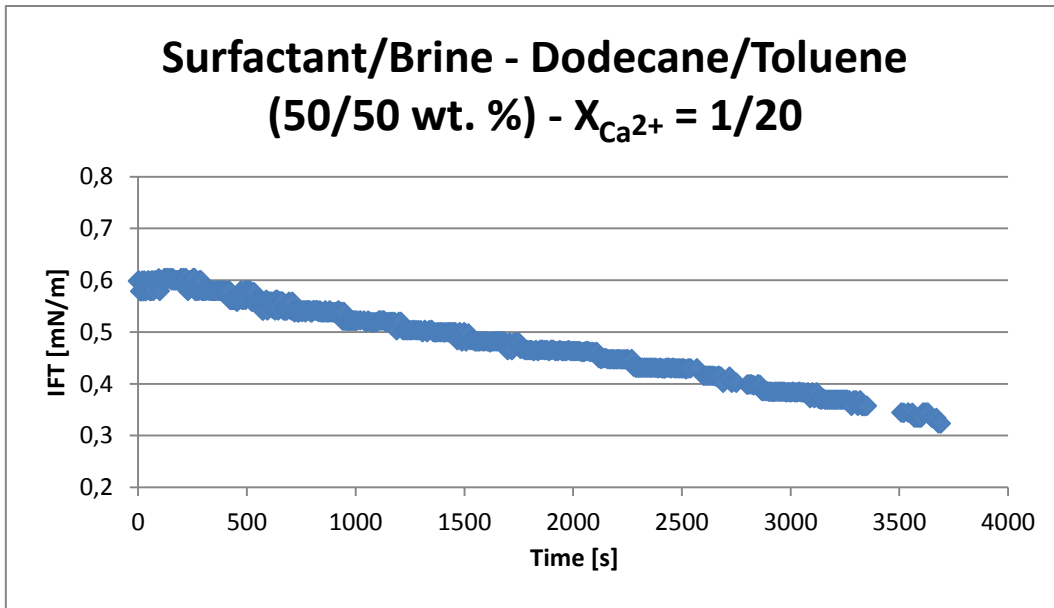
A27: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



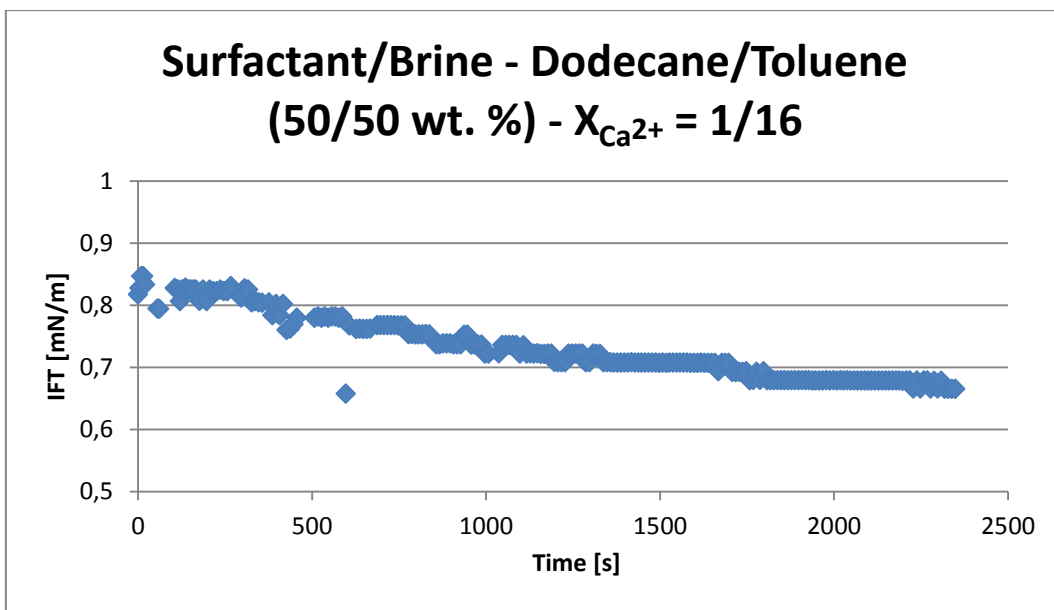
A28: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



A29: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.

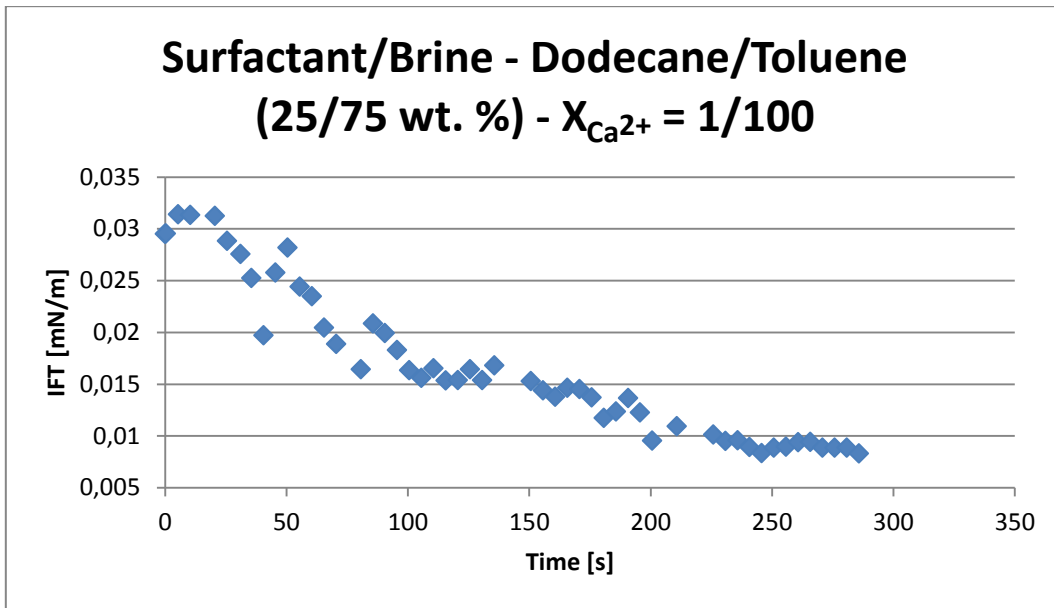


A30: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.

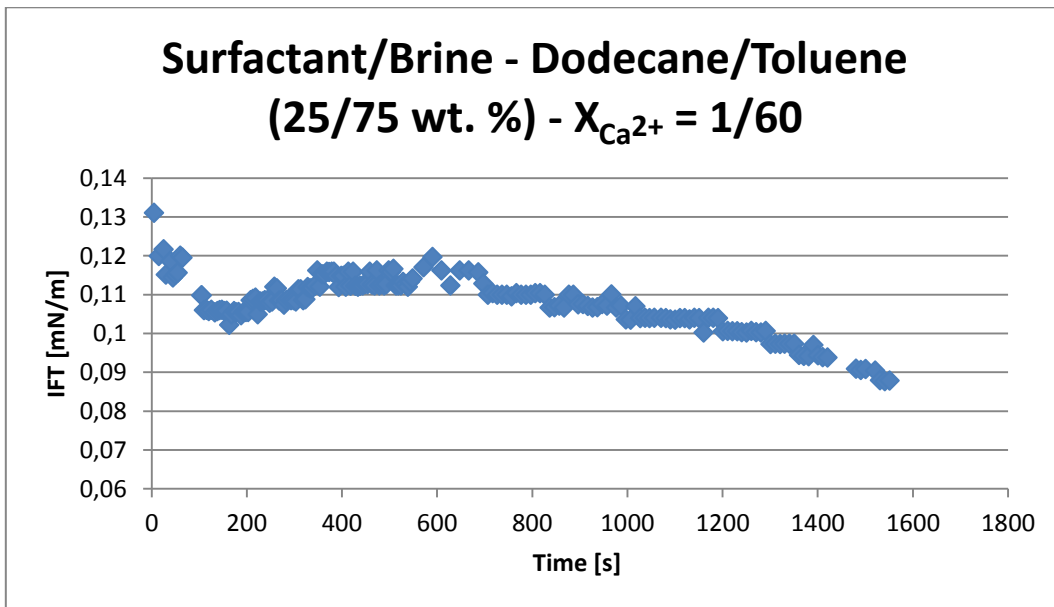


A31: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.

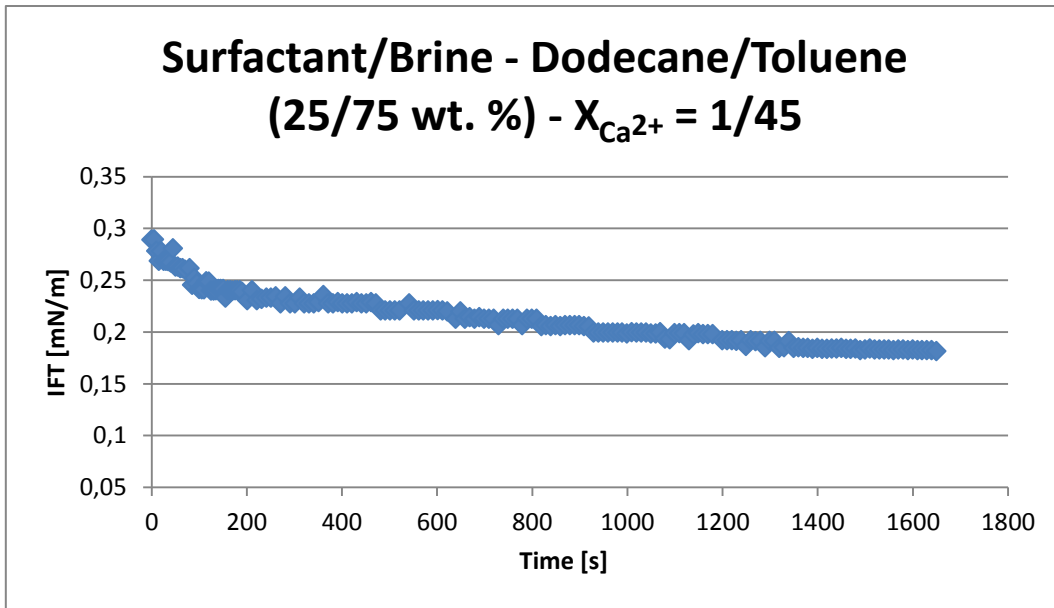
Surfactant/Brine - Dodecane/Toluene (25/75 wt. %):



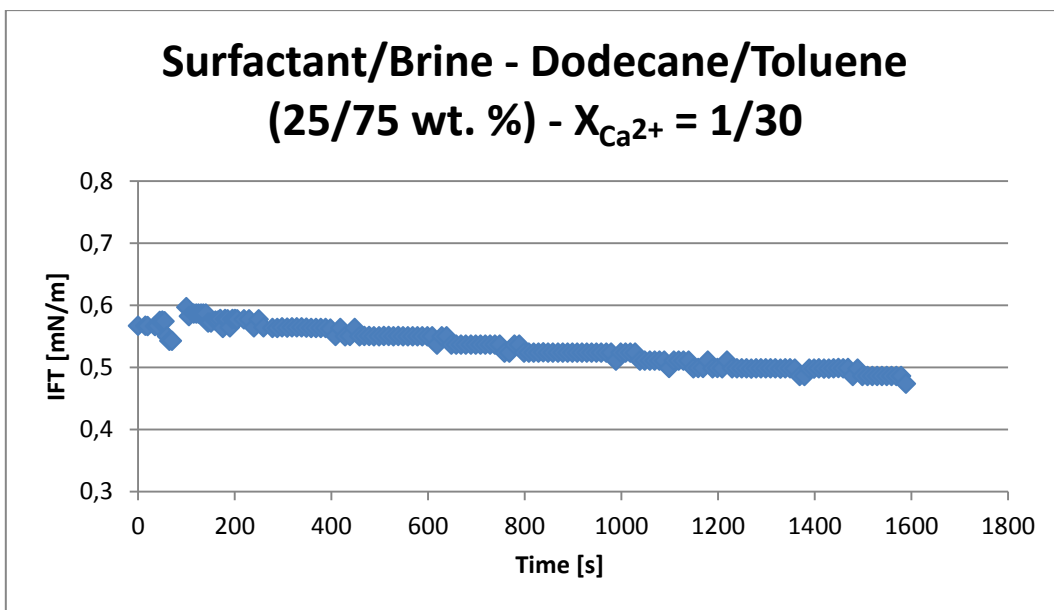
A32: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.



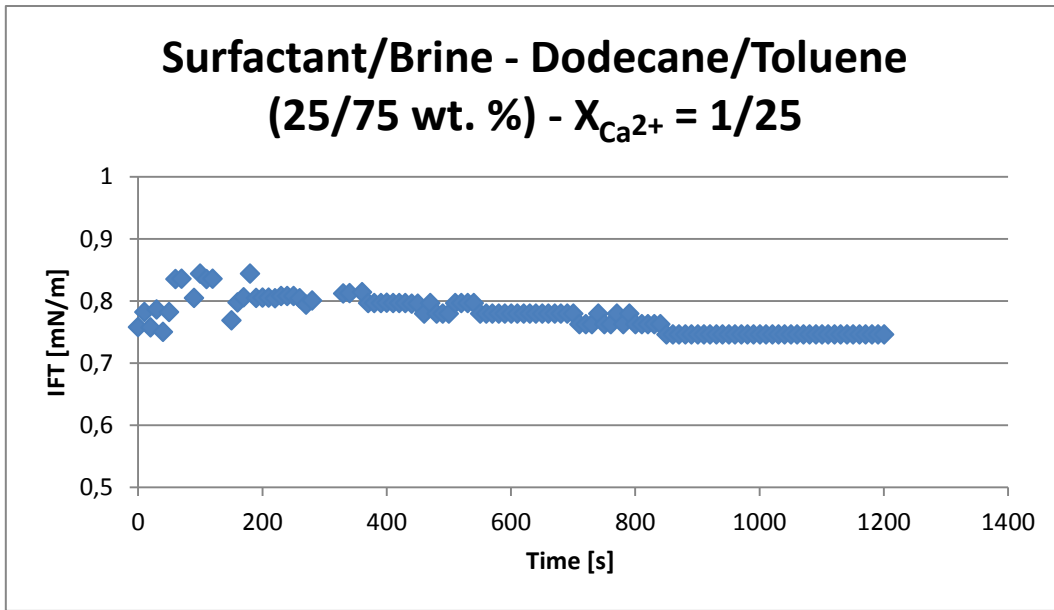
A33: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/60. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.



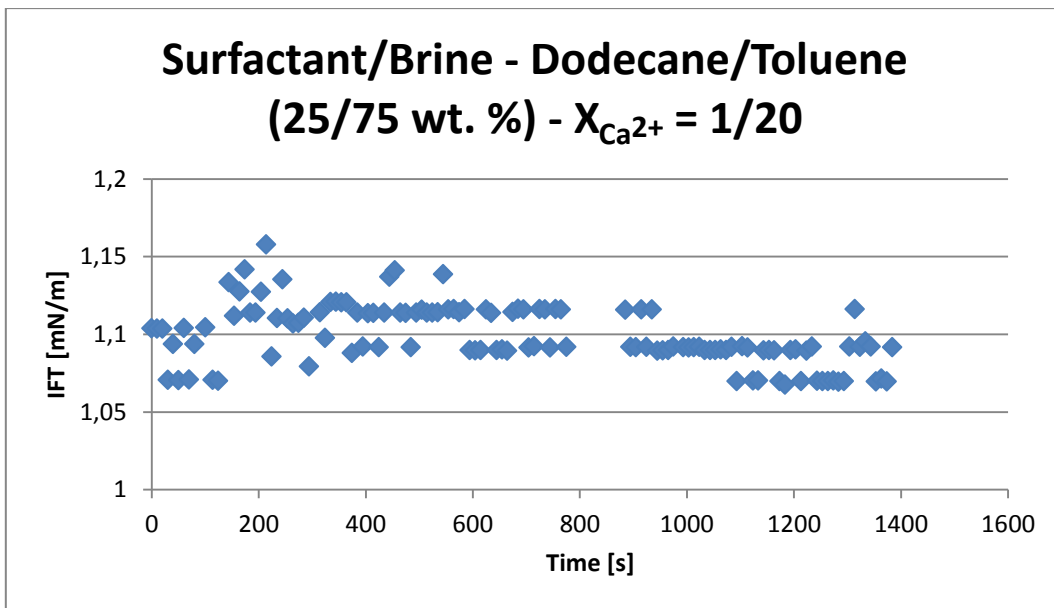
A34: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.



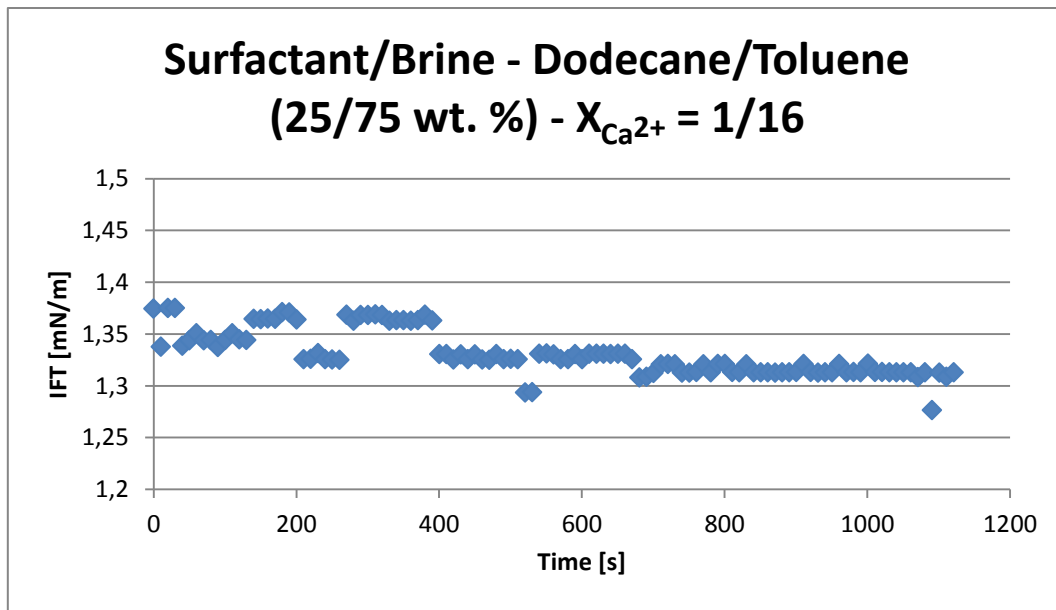
A35: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.



A36: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.

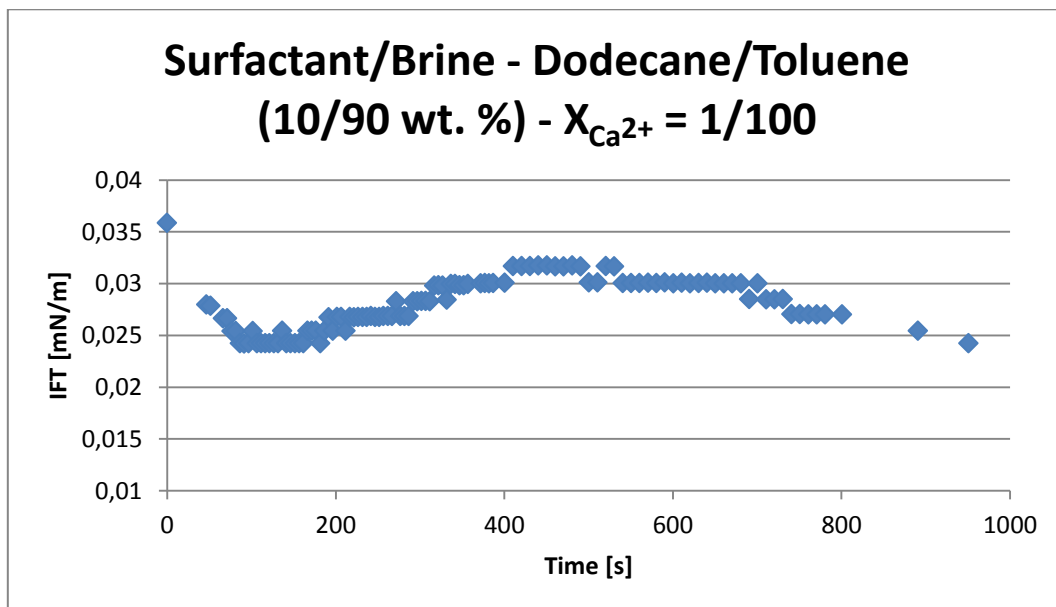


A37: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.

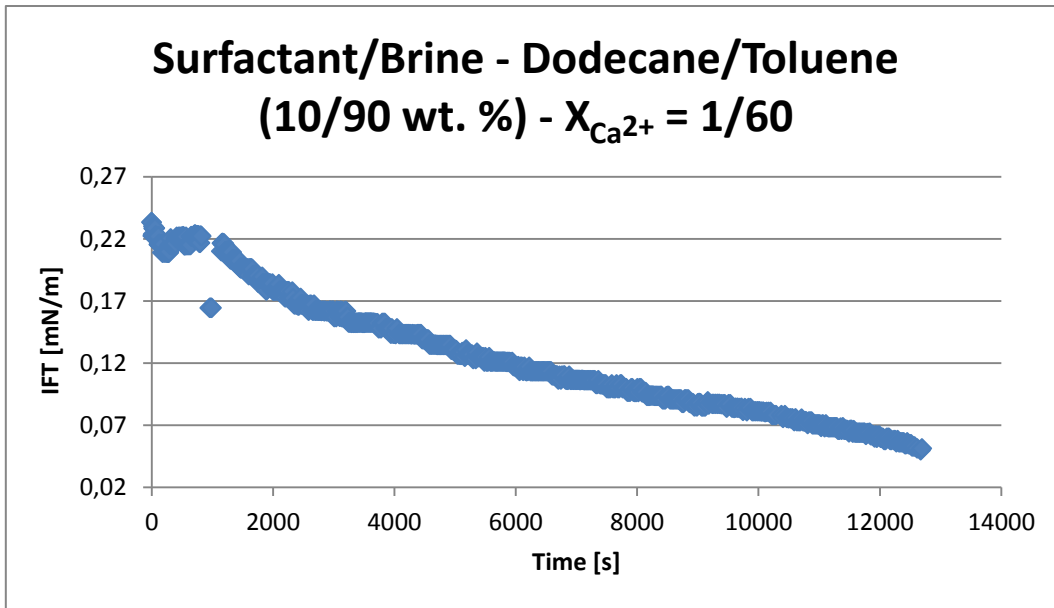


A38: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (25/75 wt. %). Temperature is 60°C.

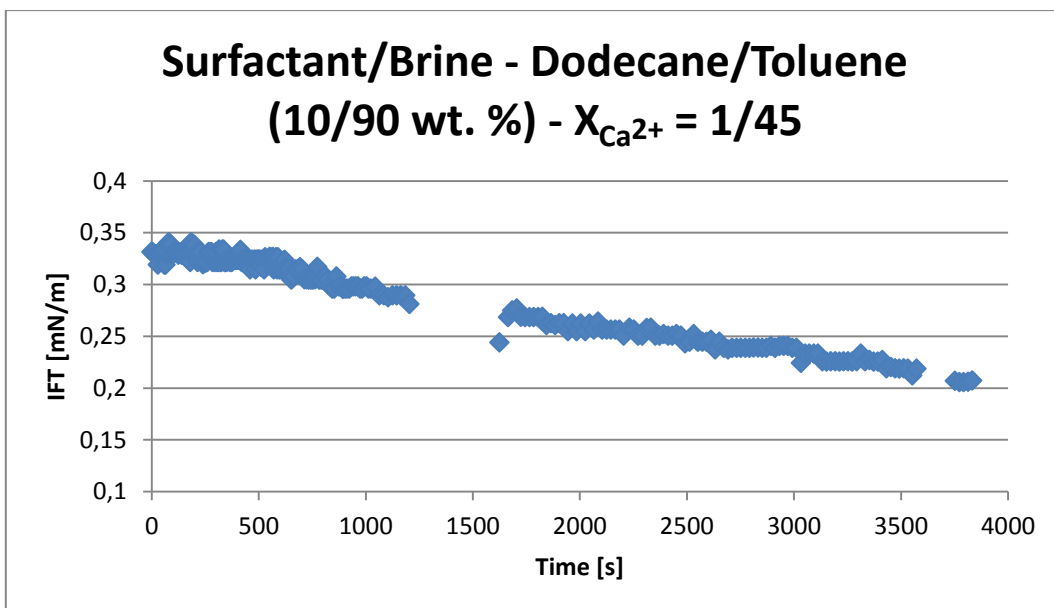
Surfactant/Brine - Dodecane/Toluene (10/90 wt. %):



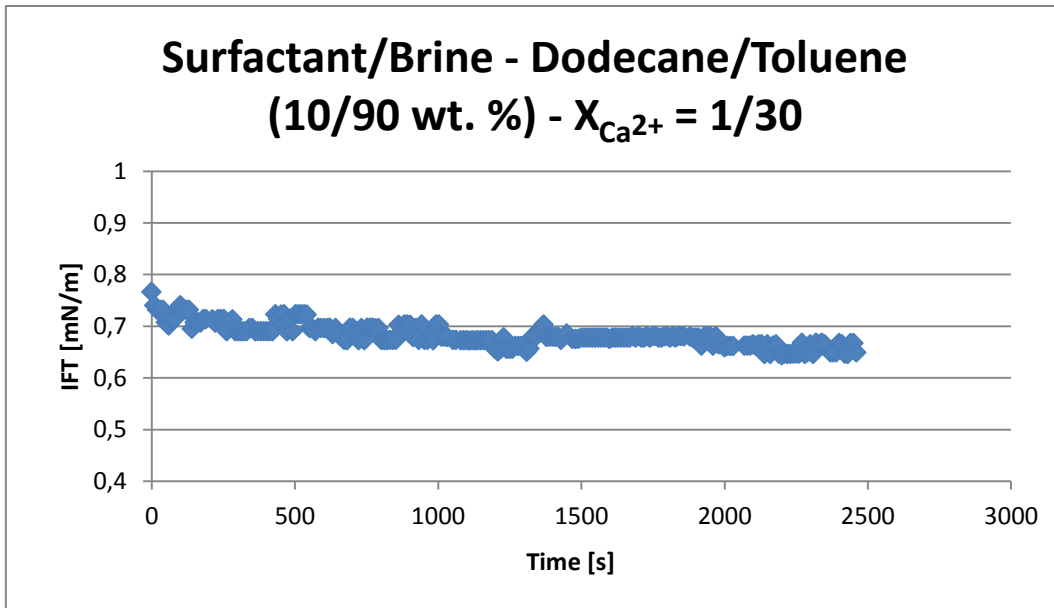
A39: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.



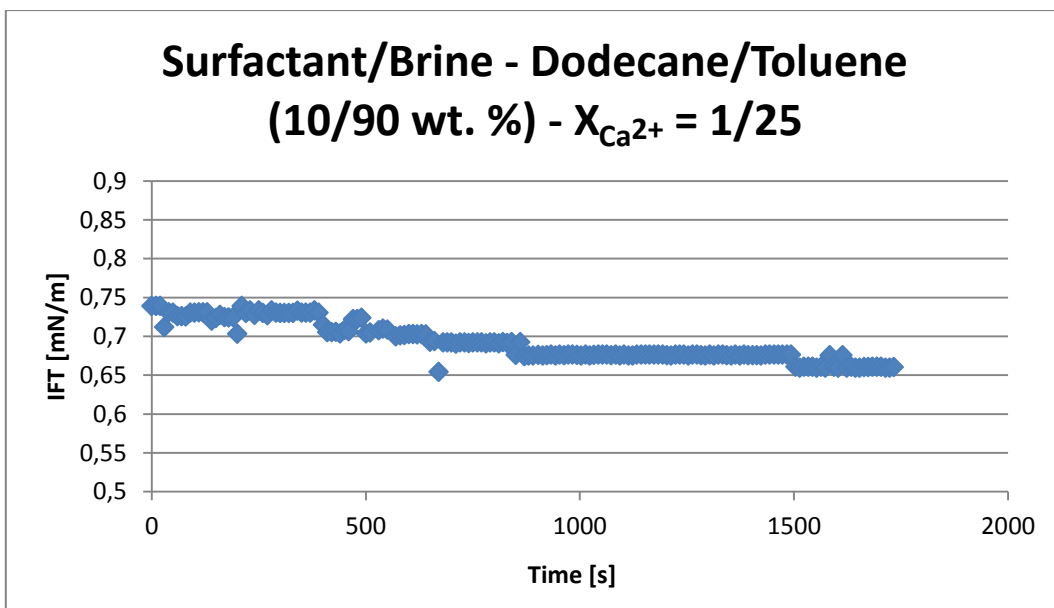
A40: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/60. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.



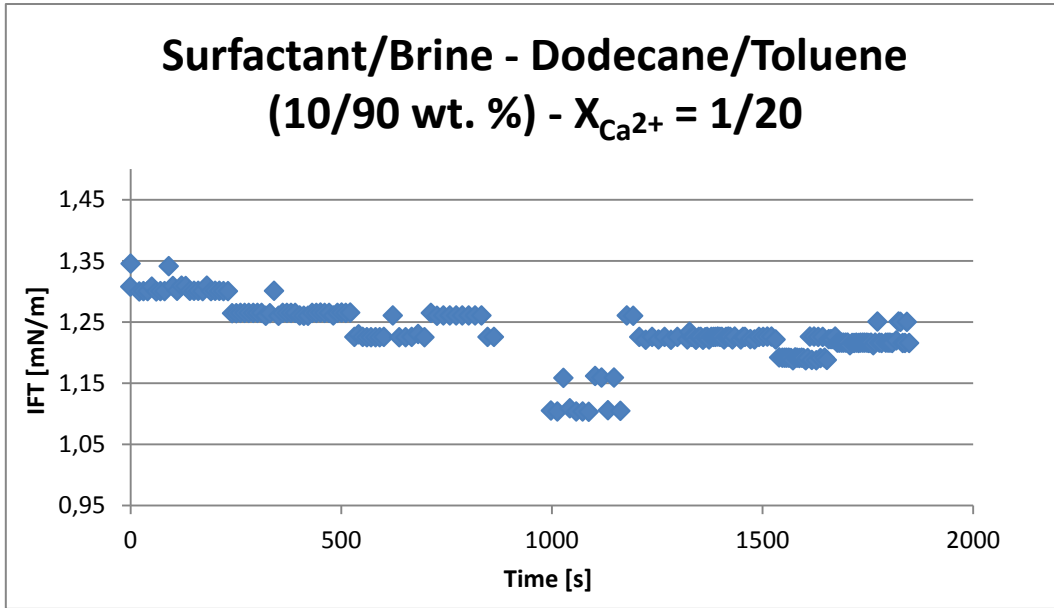
A41: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.



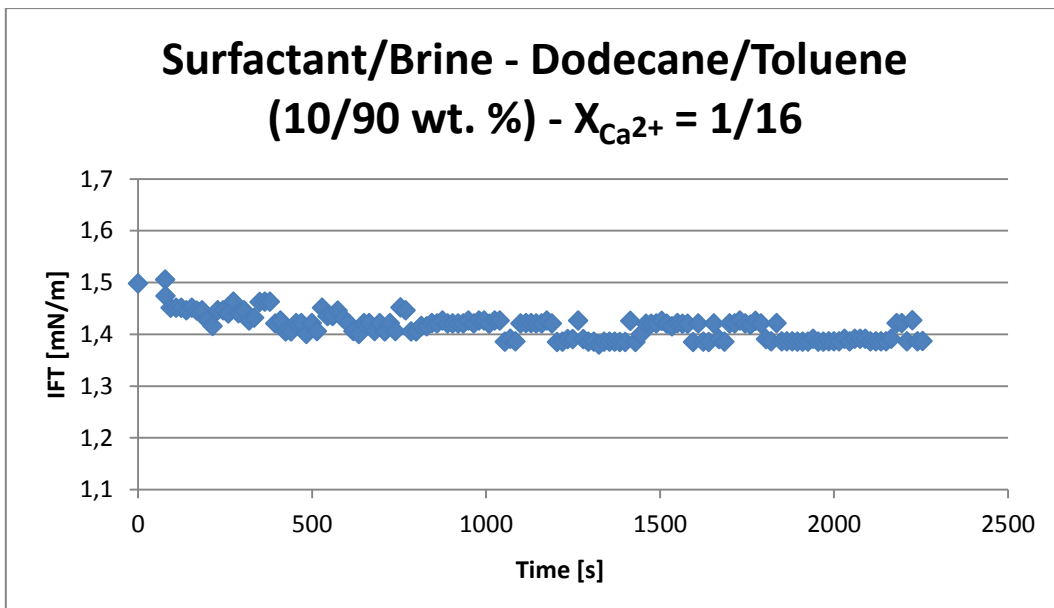
A42: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.



A43: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.

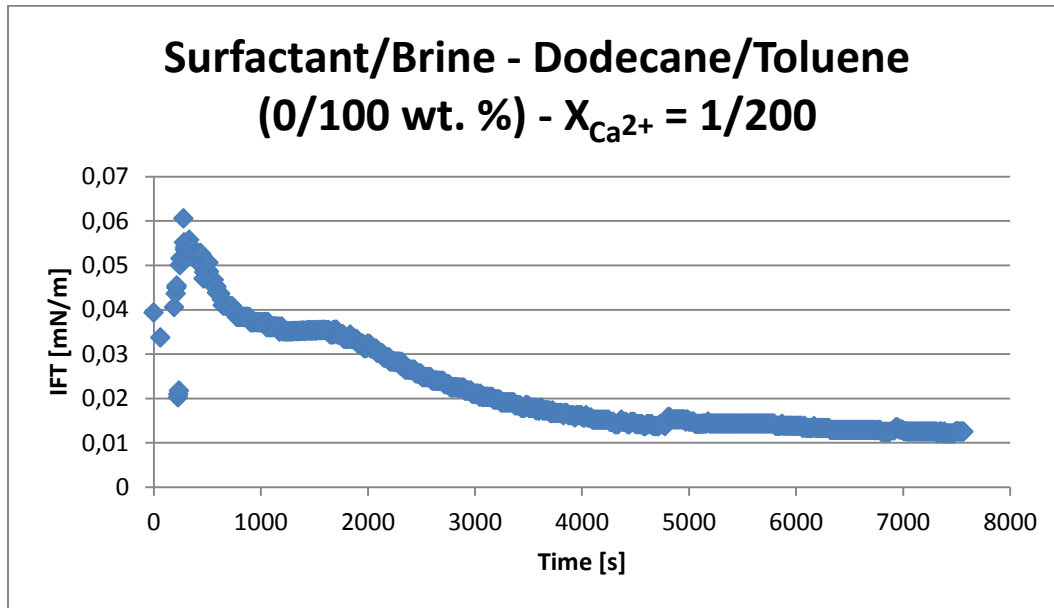


A44: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.

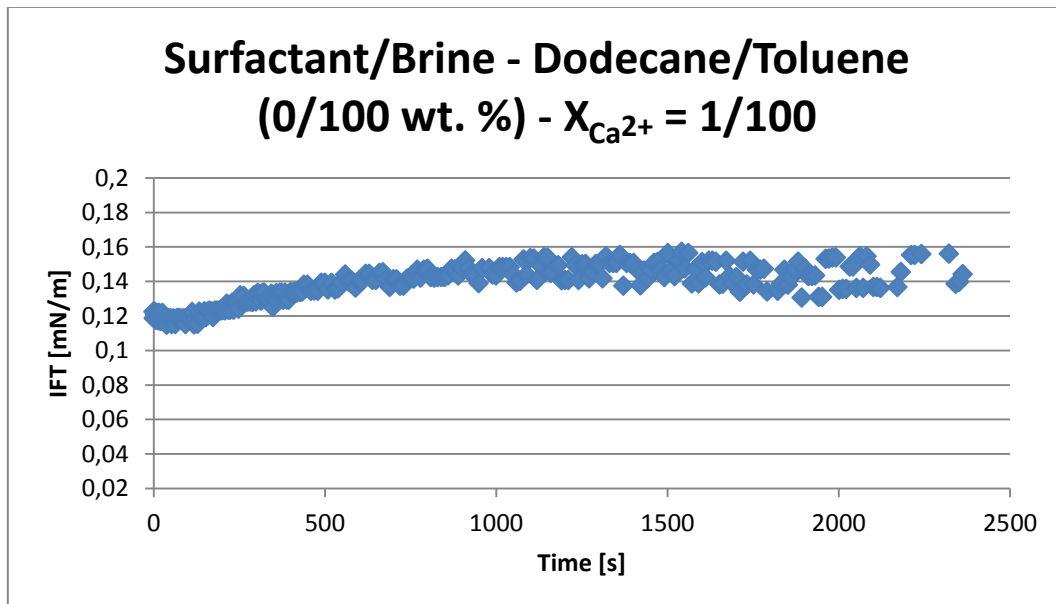


A45: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (10/90 wt. %). Temperature is 60°C.

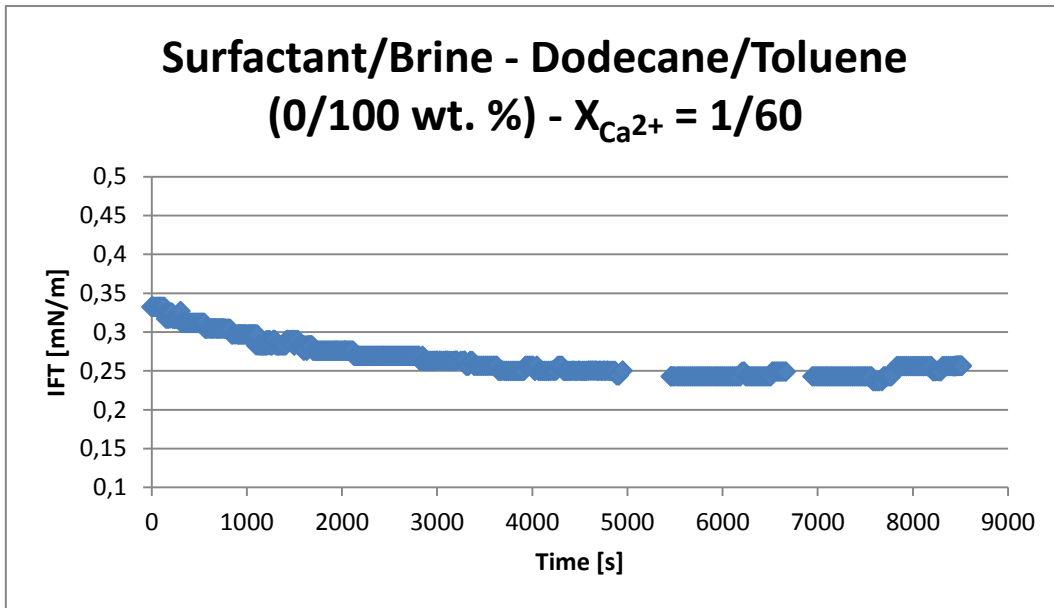
Surfactant/Brine - Dodecane/Toluene (0/100 wt. %):



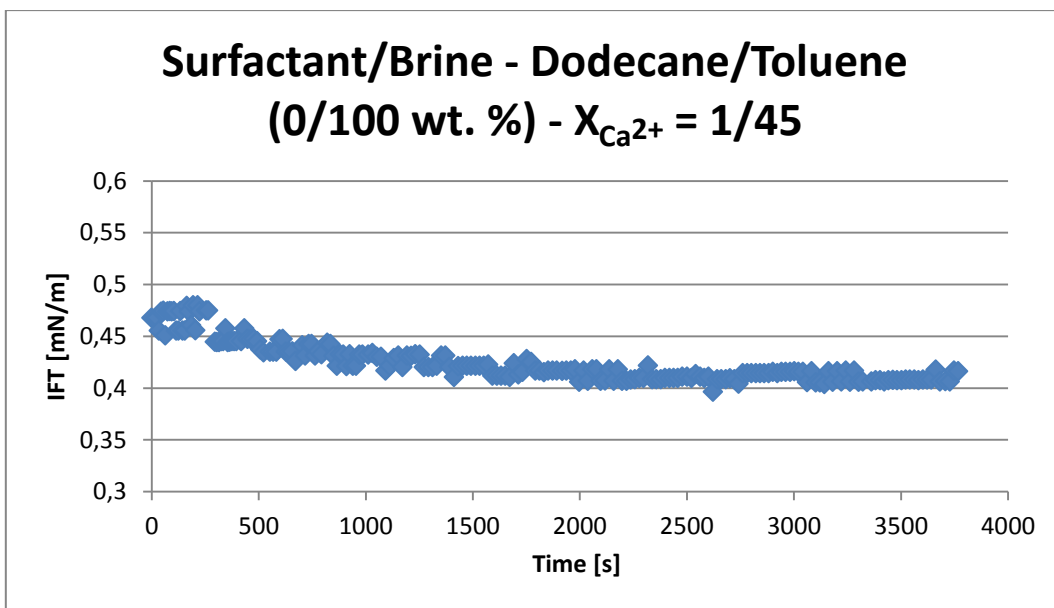
A46: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/200. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.



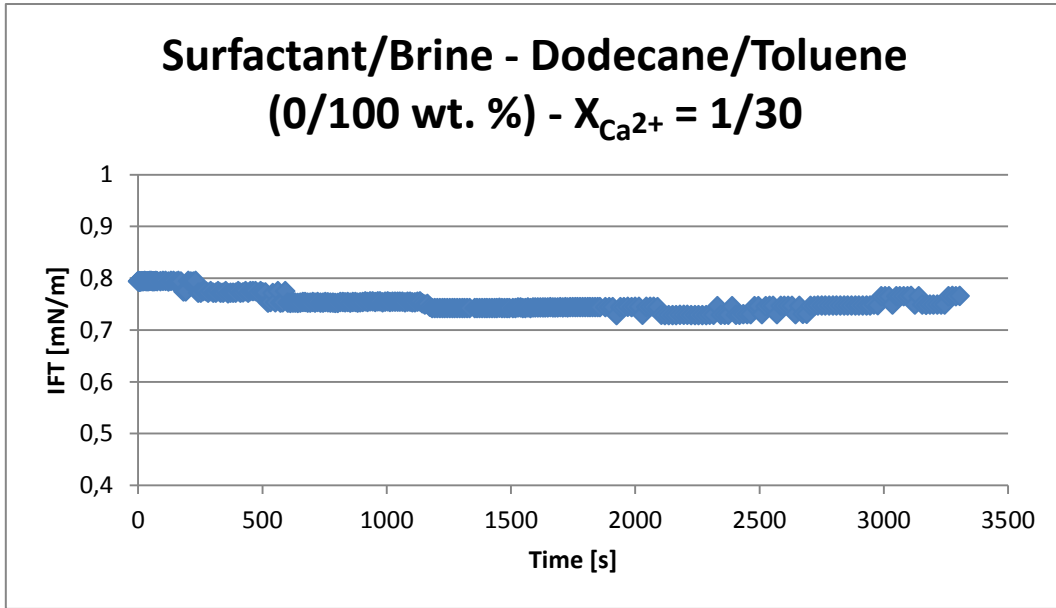
A47: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.



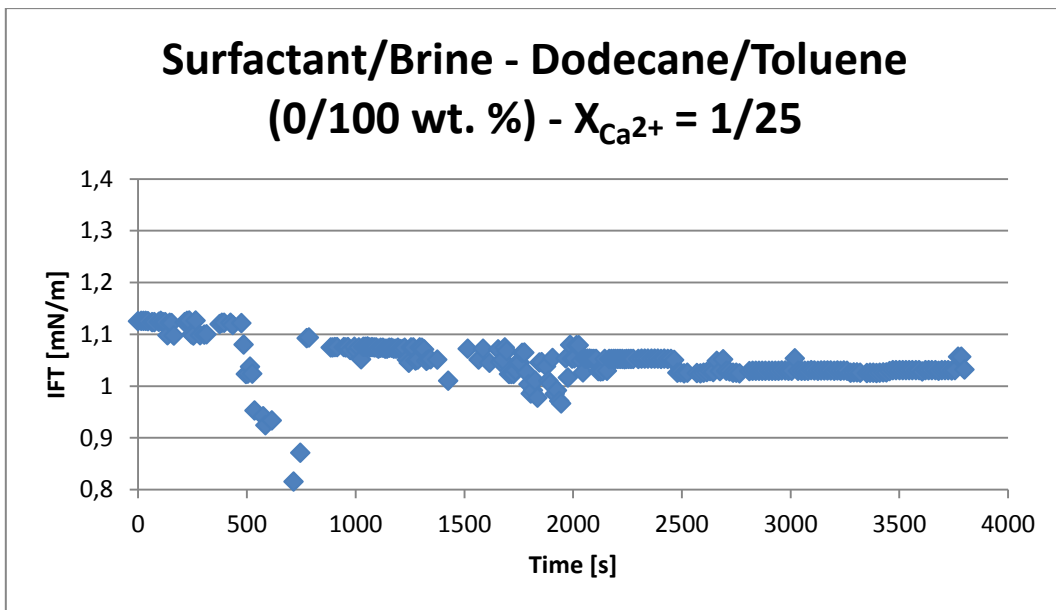
A48: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/60. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.



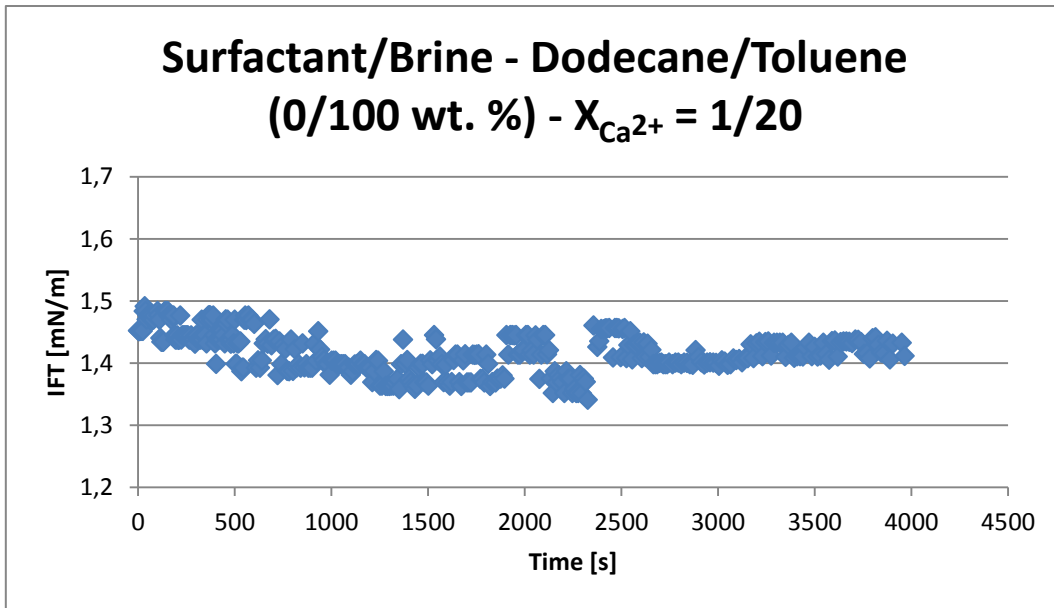
A49: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.



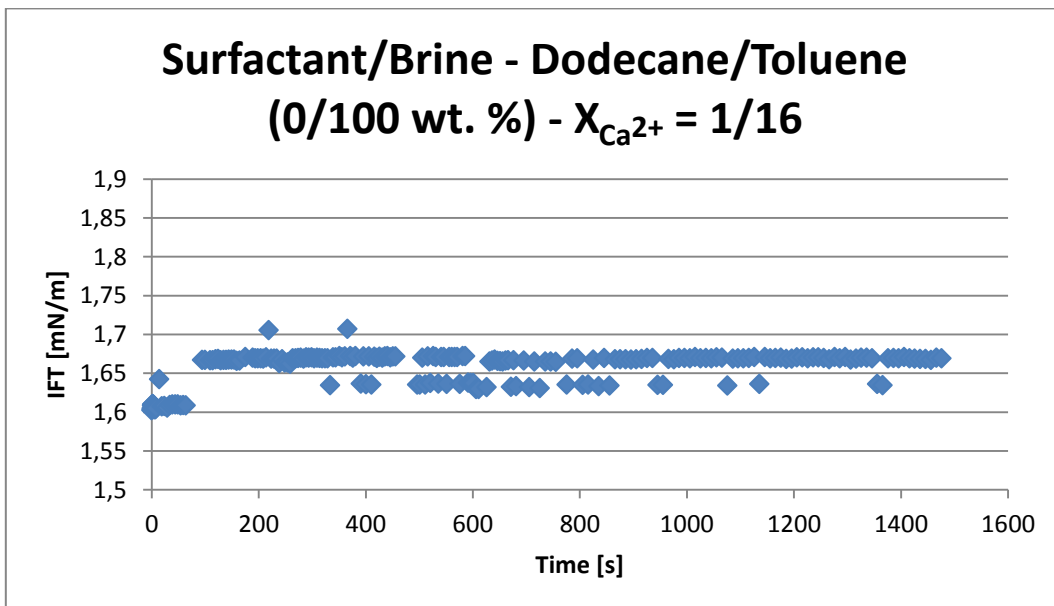
A50: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.



A51: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.



A52: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.

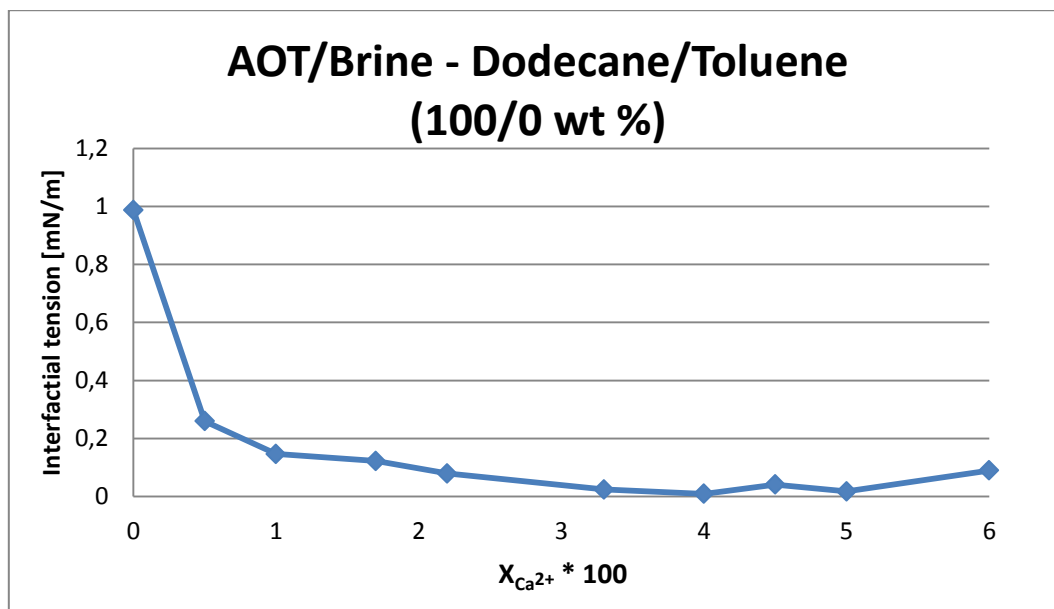


A53: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 20 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (0/100 wt. %). Temperature is 60°C.

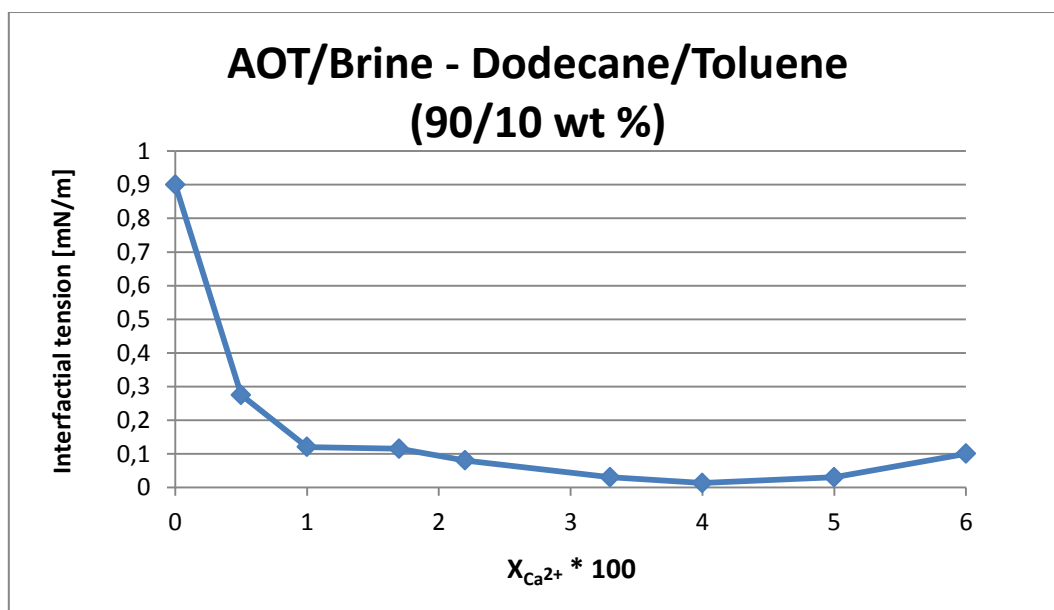
Collective graphs

Following Figures A54 - A60 are graphic presentations of change in IFT-value with increasing cationic ratio. The marked dots are equilibrium values taken from the single

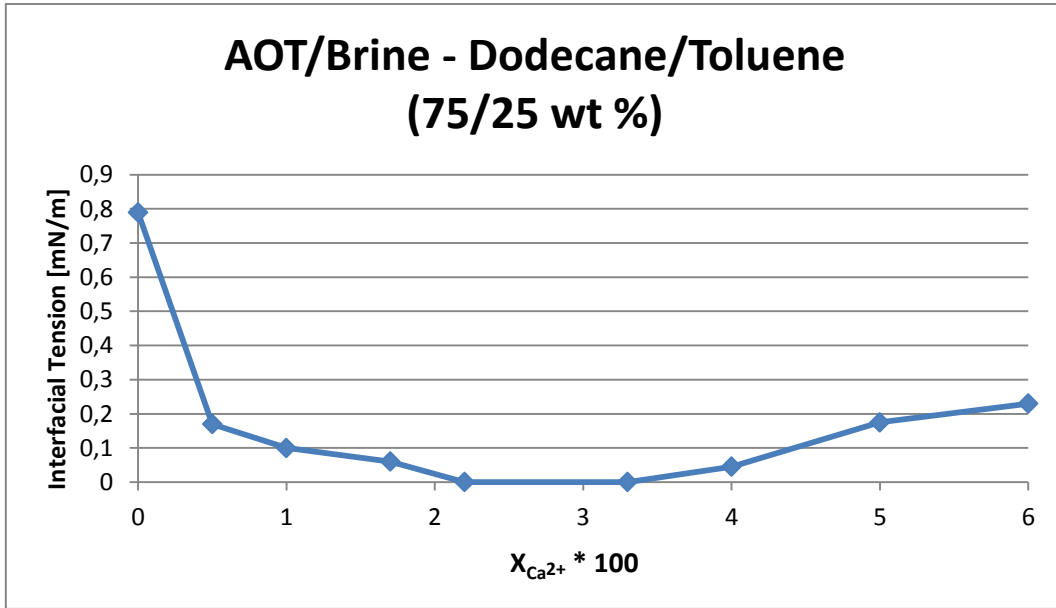
measurements Appendix (A1 - A53) from their respective series, presented above. Exact measurements have all previously been presented in Table A1. Figures A54-A60 have all been cooperated into a single diagram in Figure A62.



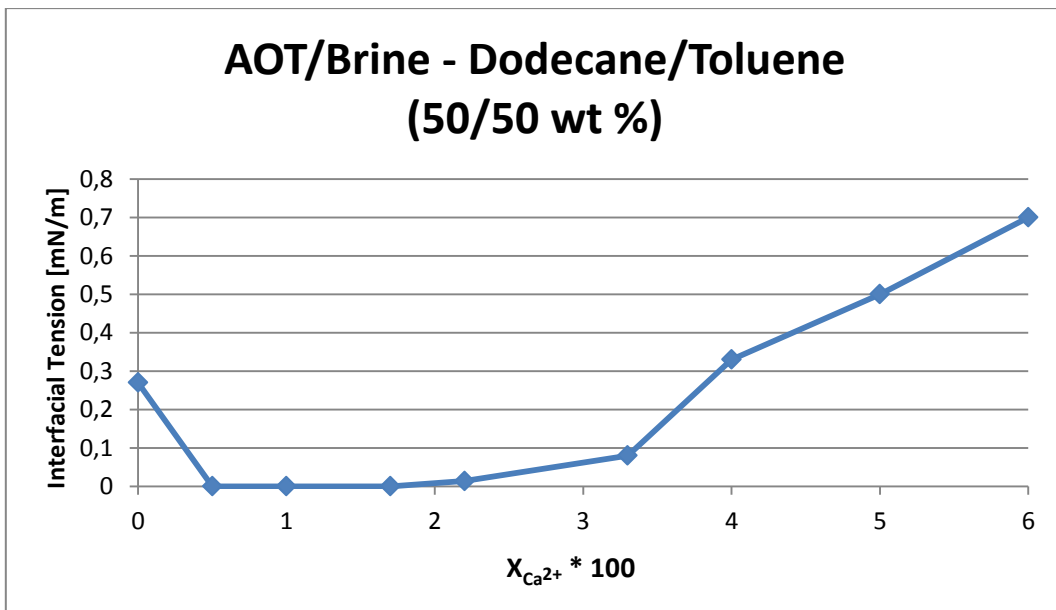
A54: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (100/0 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



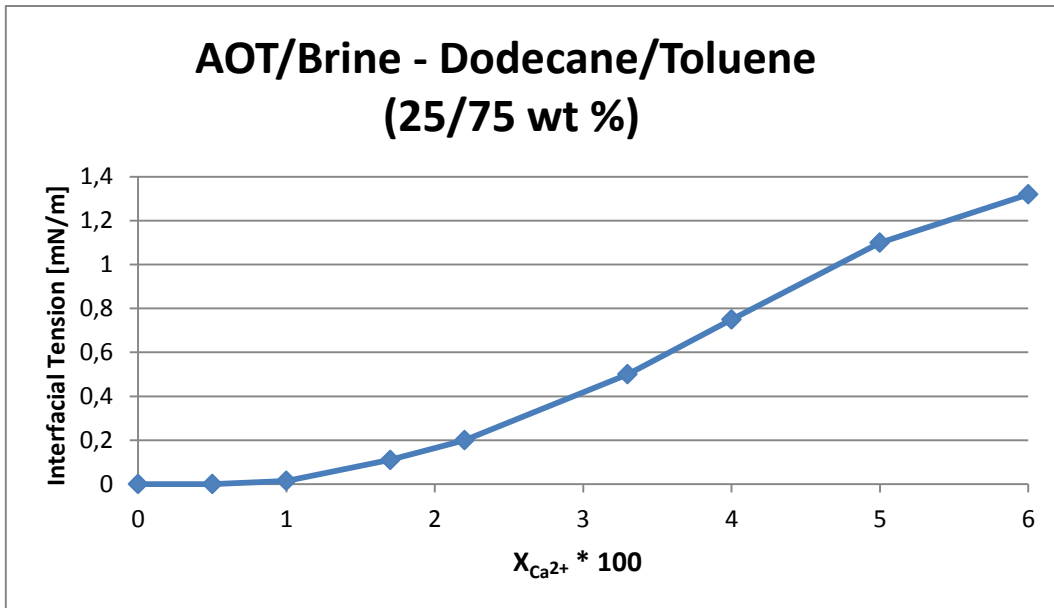
A55: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (90/10 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



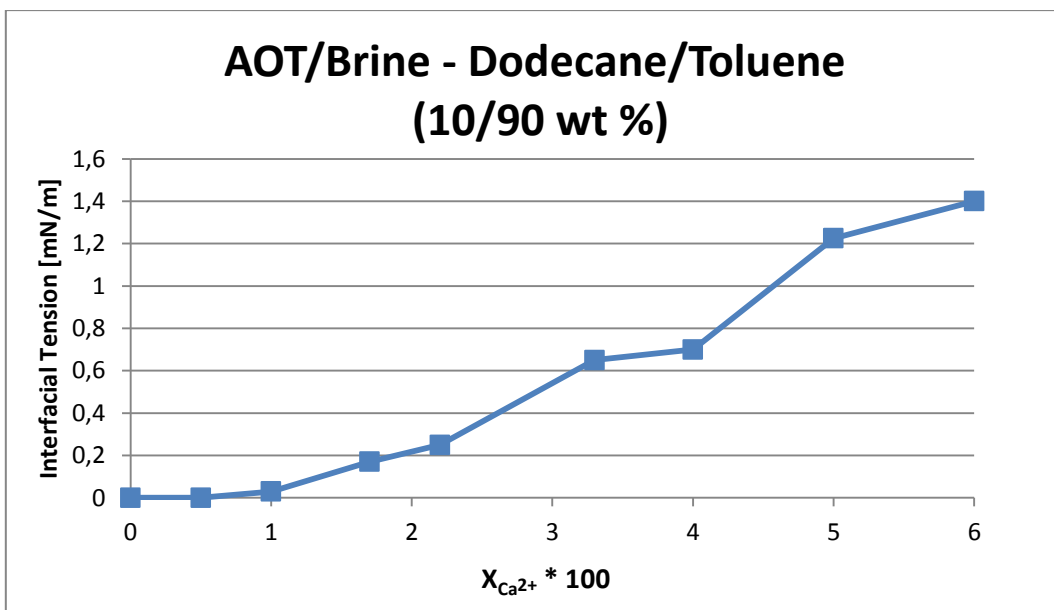
A56: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (75/25 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



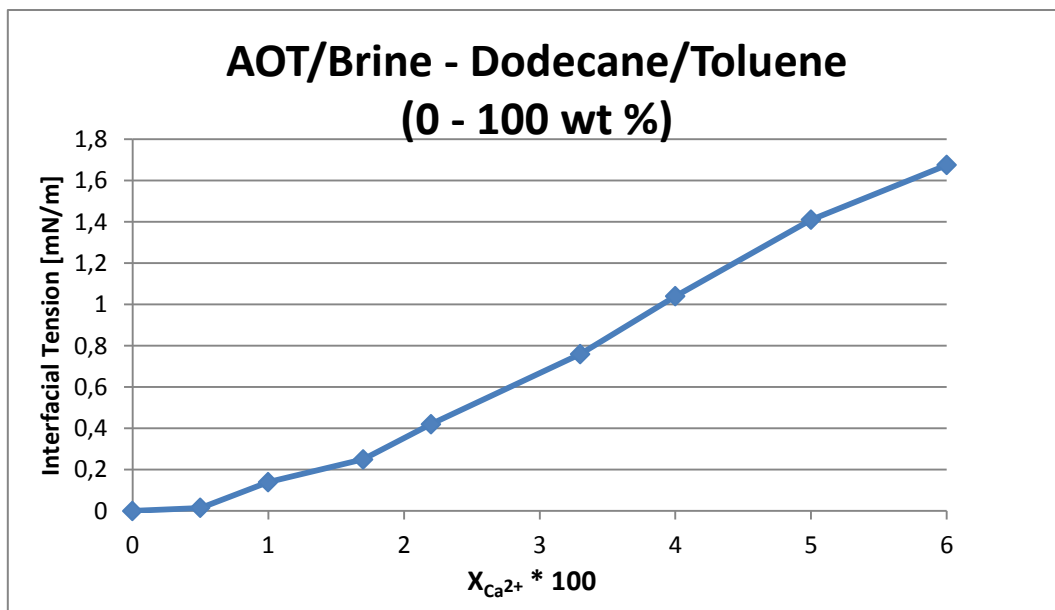
A57: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (50/50 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



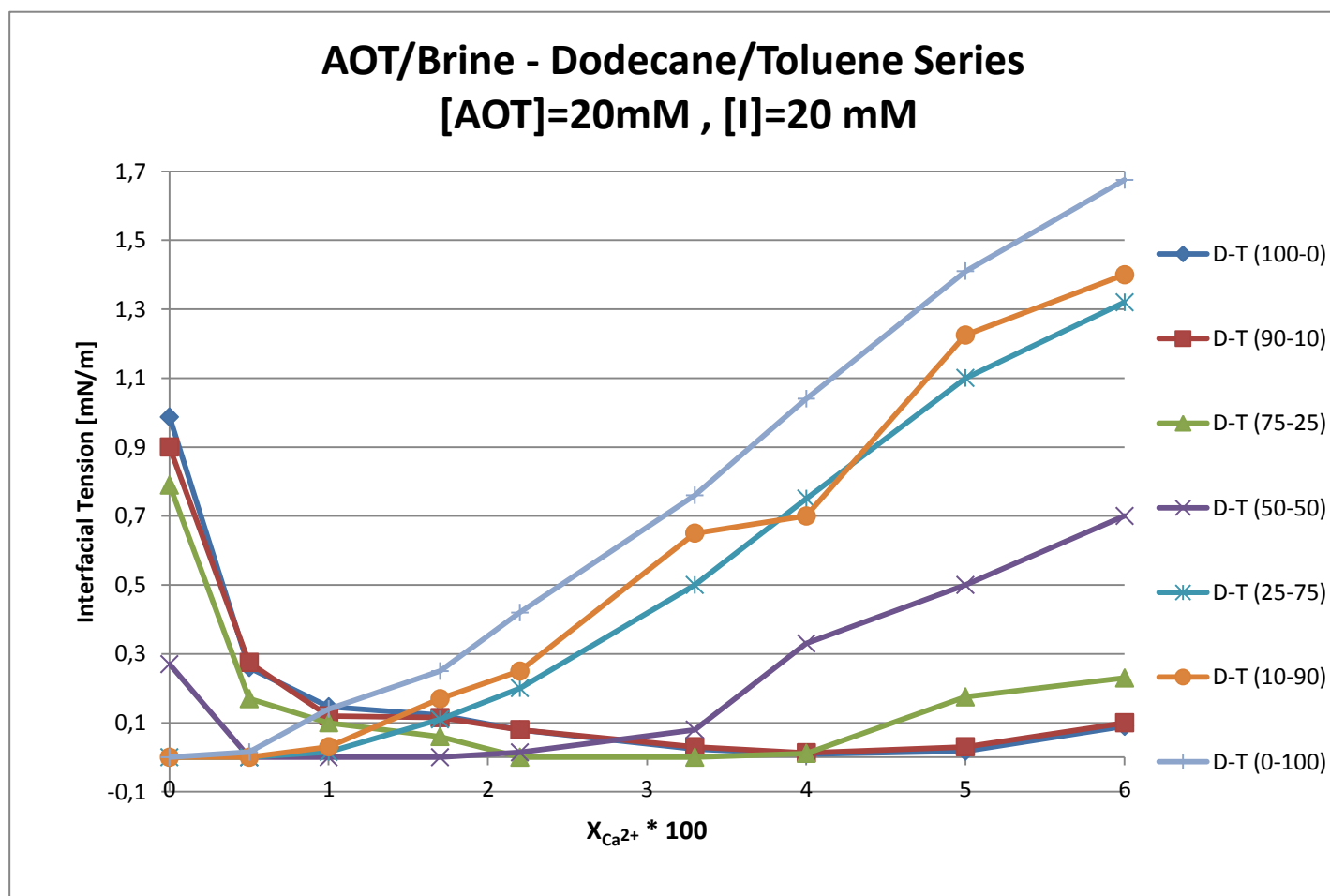
A58: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (25/75 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



A59: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (10/90 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



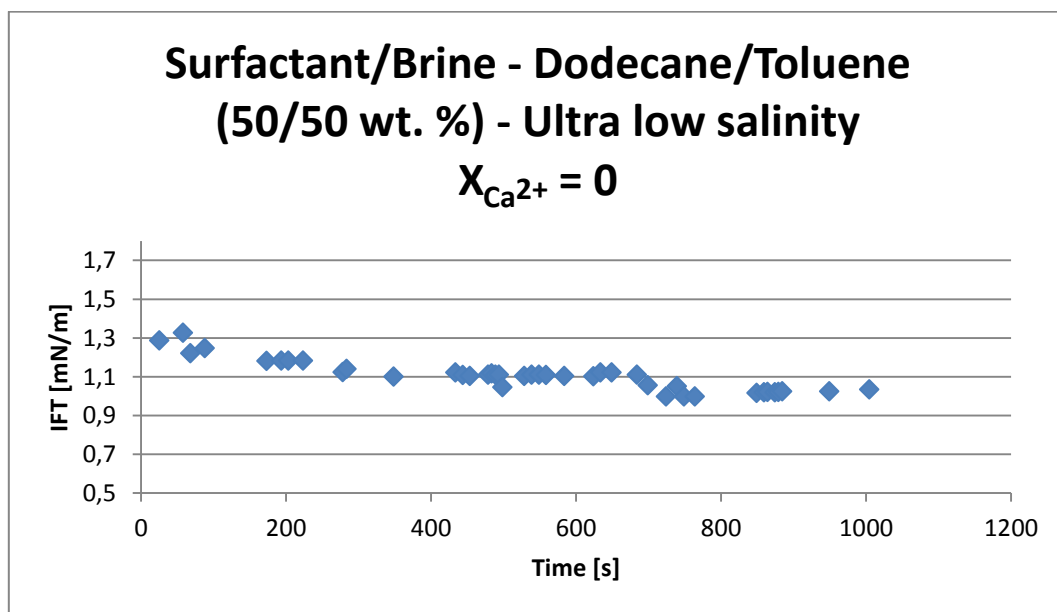
A60: Graph showing the change in IFT of AOT/Brine - Dodecane/Toluene (0/100 wt. %) system with different Ca^{2+}/Na^{+} mole fractions, at 60°C



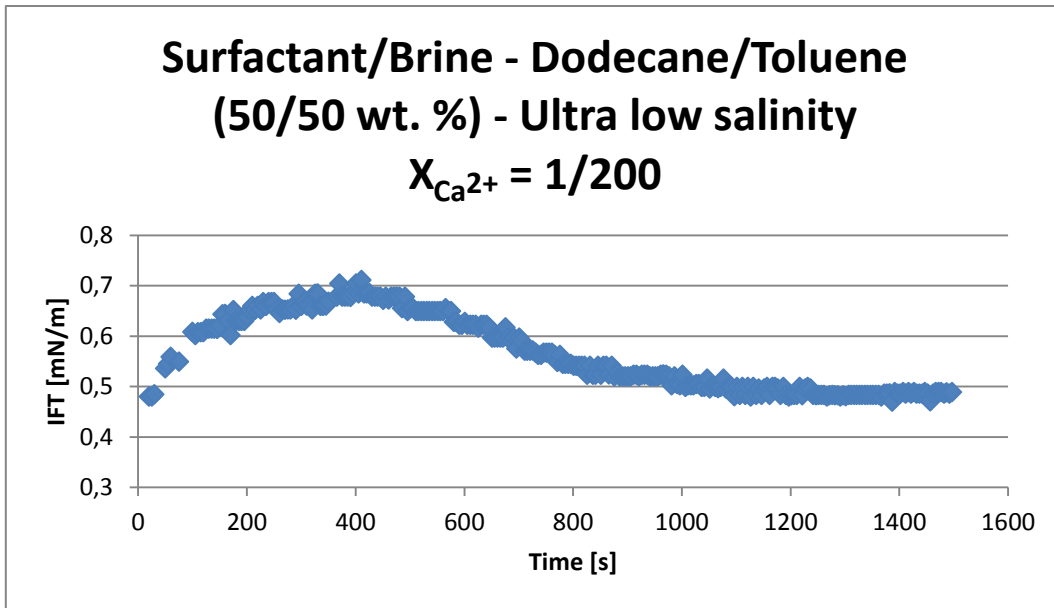
A61: Collective graph of all series measured with ionic strength of 20 mM. Surfactant concentration is 2,47 mM and temperature is 60°C. D and T denote dodecane and toluene, respectively, while the numbers behind represent wt. % of each.

Appendix A3 - IFT vs. time measurements for [I] = 5 mM series

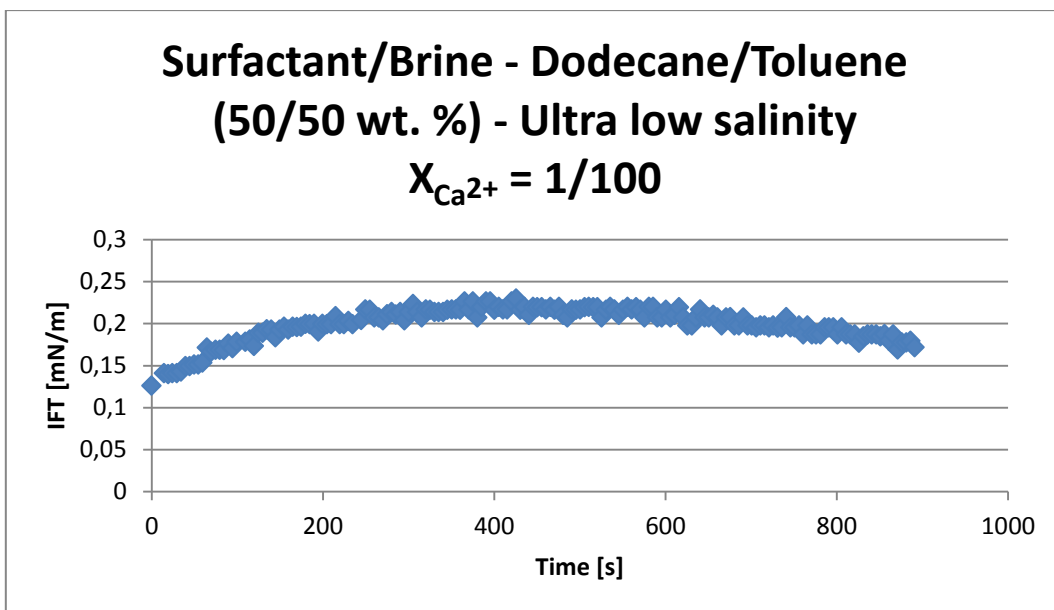
The following Figures (A62 - A70) show the graphed values of the interfacial tension versus time, at different relative cationic ion ratios for the ultralow salinity Surfactant/Brine - Dodecane/Toluene (50/50 wt. %) series. Ionic strength has been reduced to 5 mM, and surfactant concentration was still 2,47 mM. All measurements were conducted at 60°C. AOT is still the surfactant used. Only one parallel is shown for each ratio, average equilibrium value for each sample is shown in Appendix A1, Table A2.



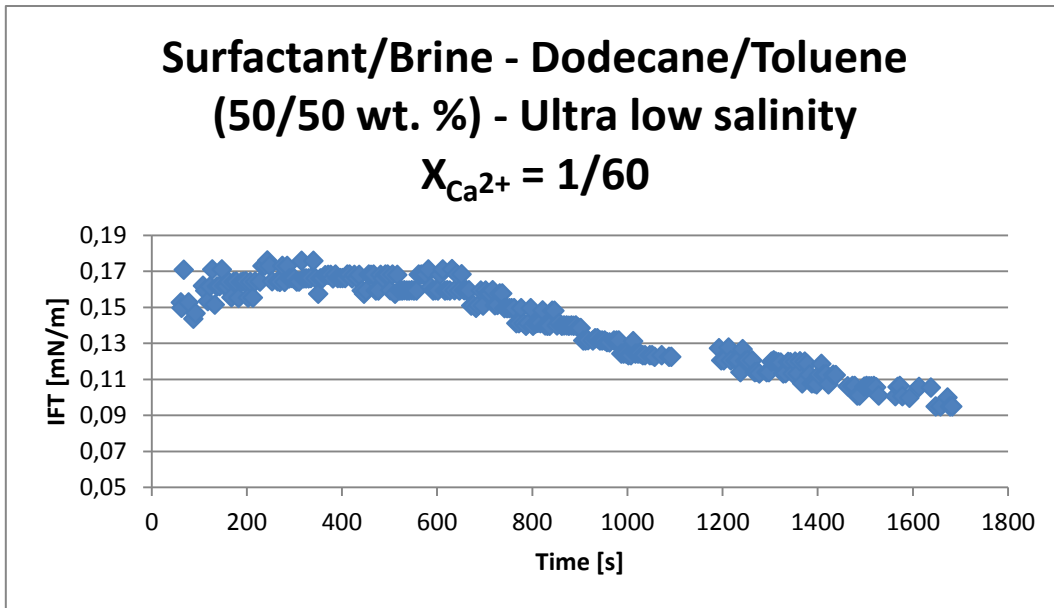
A62: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 0. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



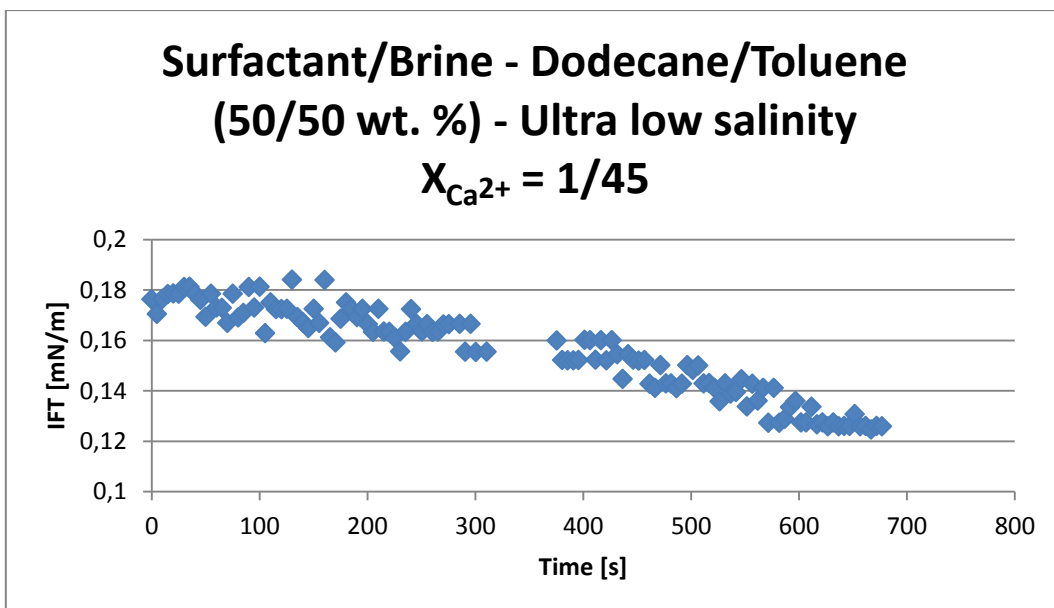
A63: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/200. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



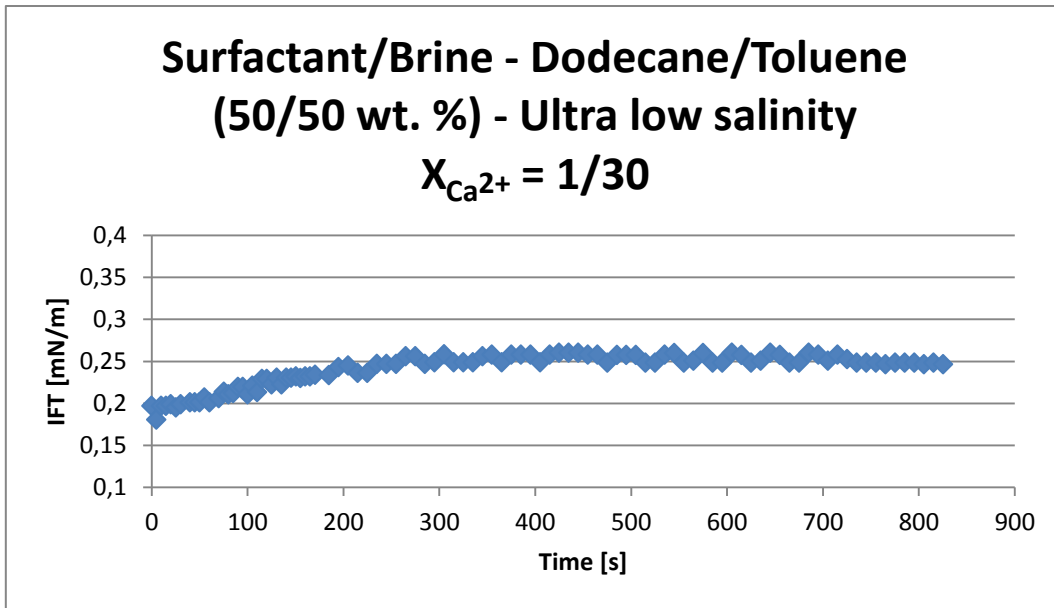
A64: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/100. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



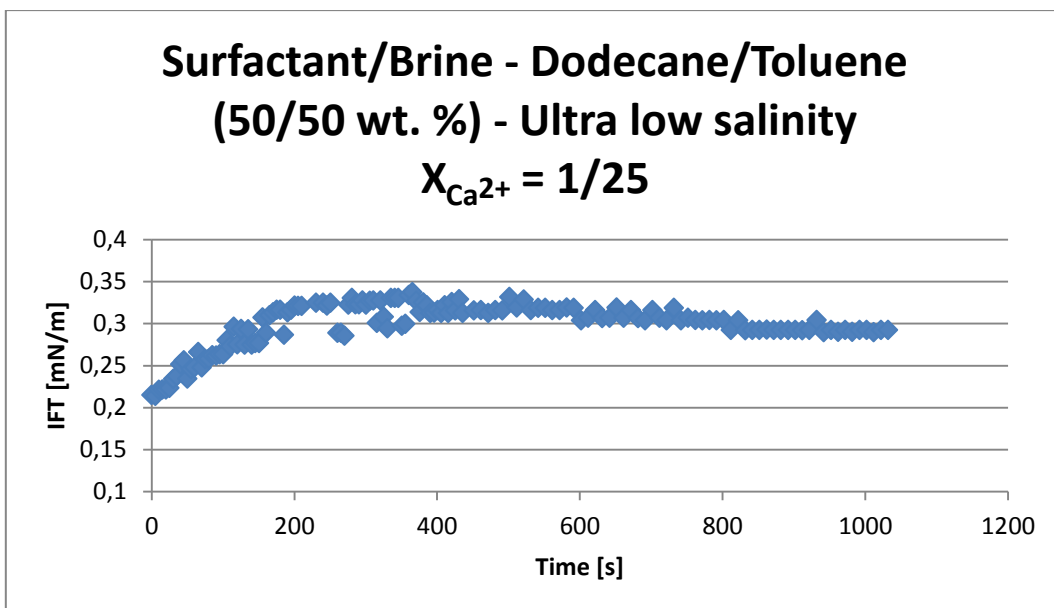
A65: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/60. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



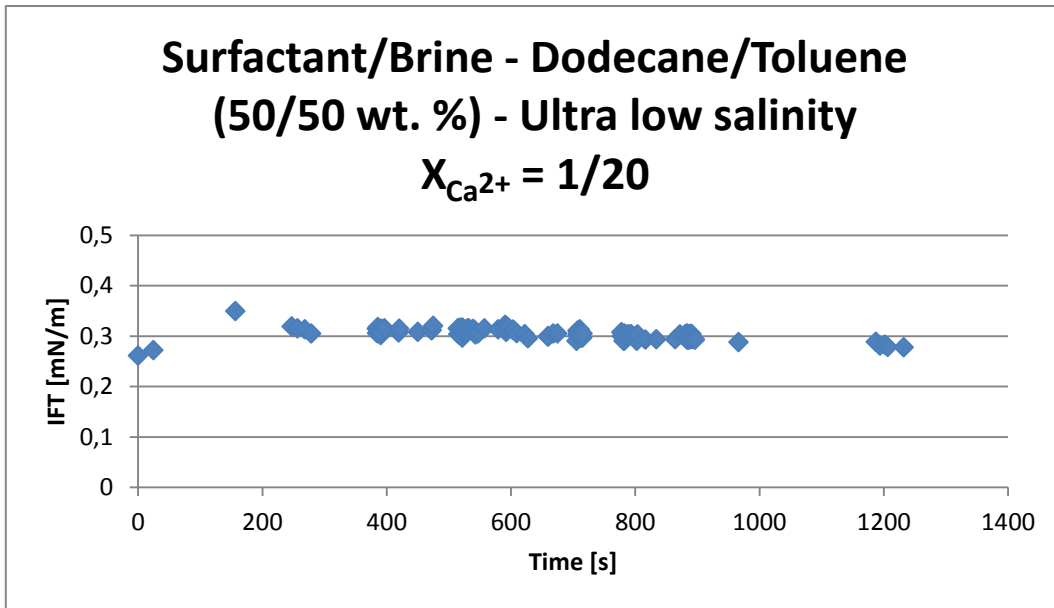
A66: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/45. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



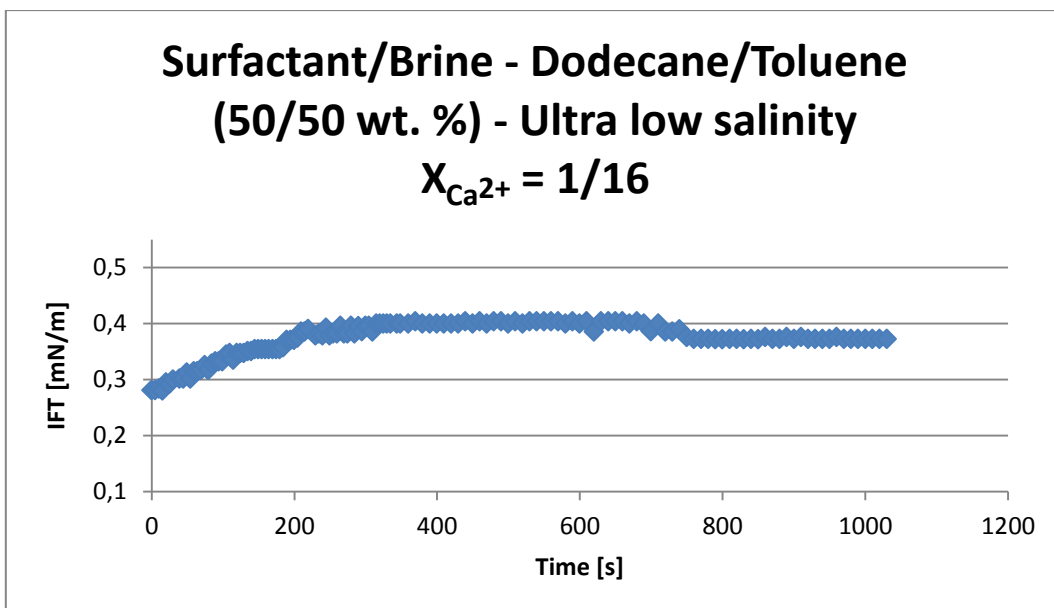
A67: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/30. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



A68: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/25. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.



A69: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/20. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.

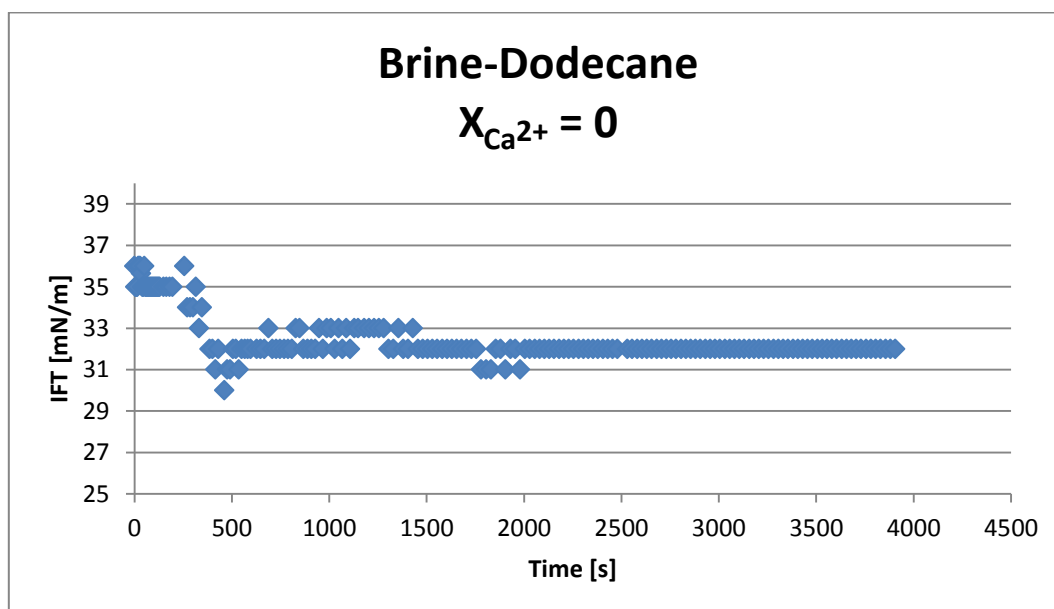


A70: Interfacial tension vs. time, for a Ca^{2+}/Na^{+} mole fraction of 1/16. Ionic strength is 5 mM and surfactant concentration is 2,47 mM. The model oil composition is Dodecane/Toluene (50/50 wt. %). Temperature is 60°C.

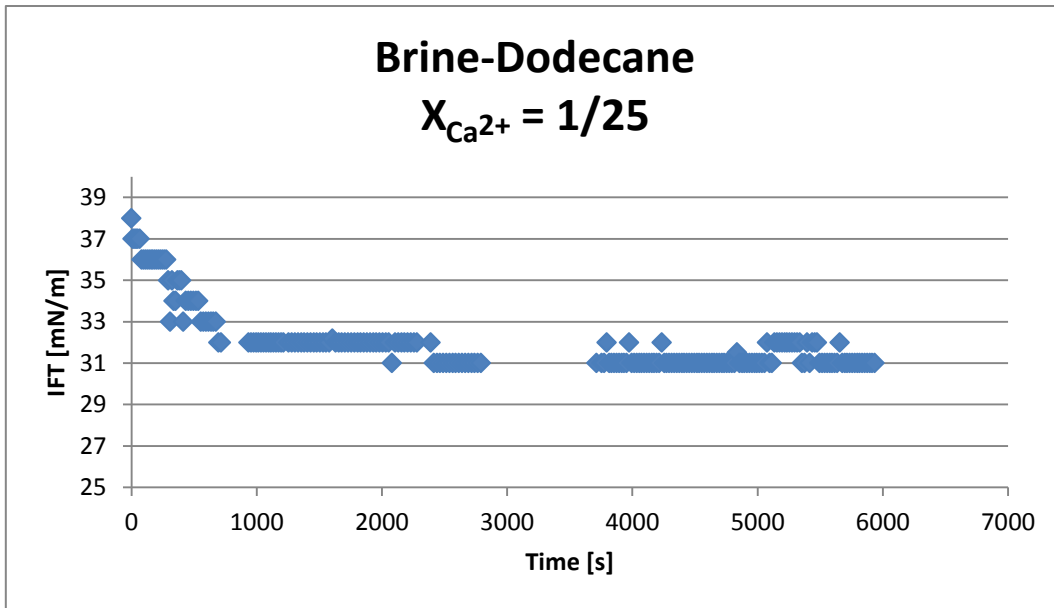
Appendix A4 - IFT vs. time for Brine-Dodecane and Brine-Toluene series

The following Figures (A71 - A76) show the graphed values of the interfacial tension versus time, at different relative cationic ion ratios for the Brine-Dodecane/Toluene series. All measurements were conducted at 60°C. Equilibrium values presented in the results are shown in Appendix A1, Table A3. Measurements from the Brine-Dodecane series were done during the specialization project in the autumn of 2013.

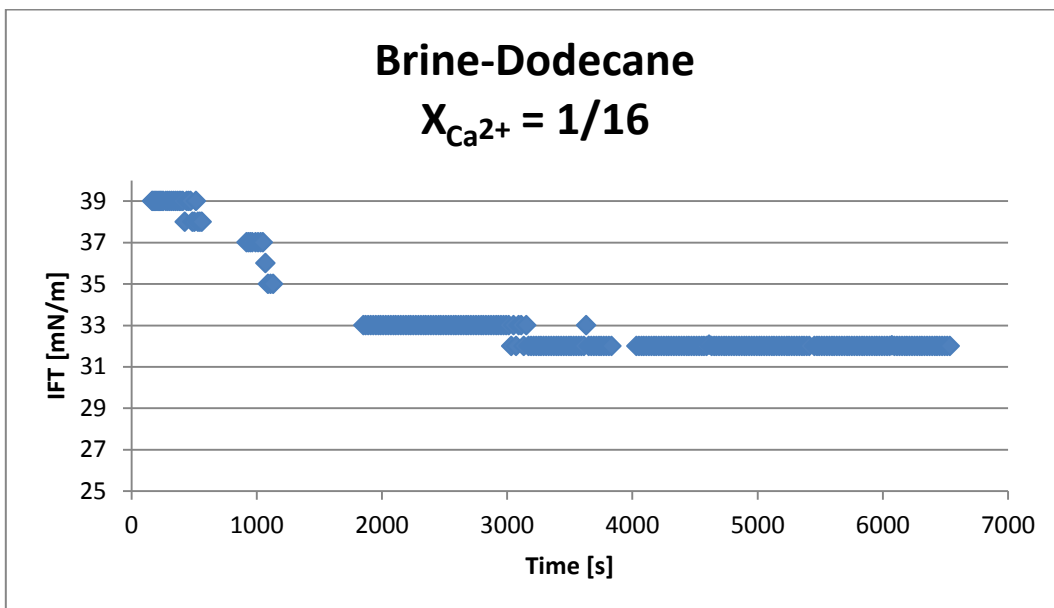
Brine-Dodecane Series



A71: Interfacial tension vs. time, for a mole fraction of 0 Ca^{2+}/Na^+ , at 60°C. Ionic strength is 20 mM

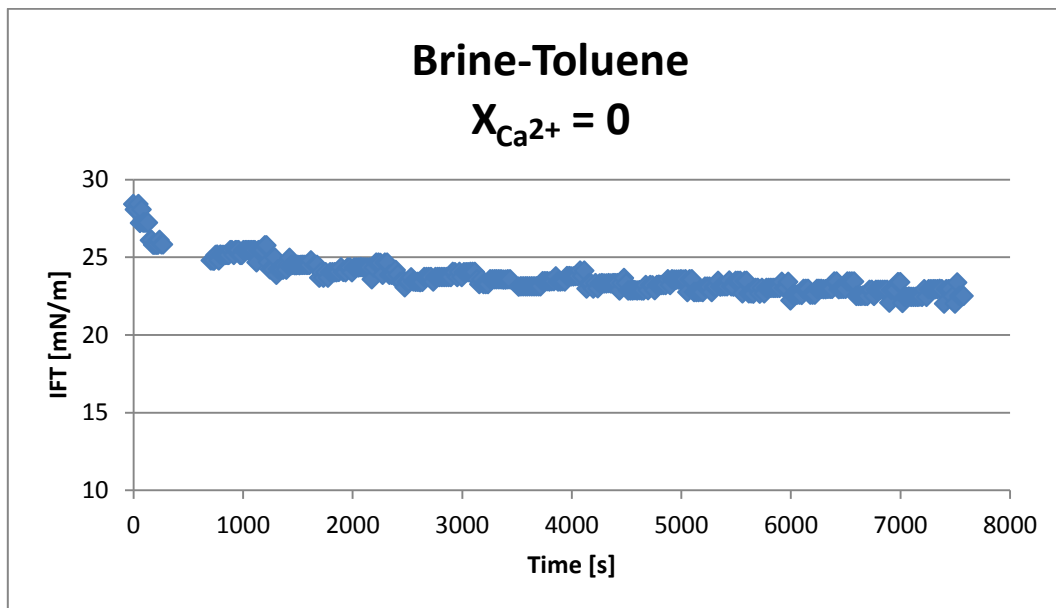


A72: Interfacial tension vs. time, for a mole fraction of 1/25 Ca^{2+}/Na^+ , at 60°C. Ionic strength is 20 mM

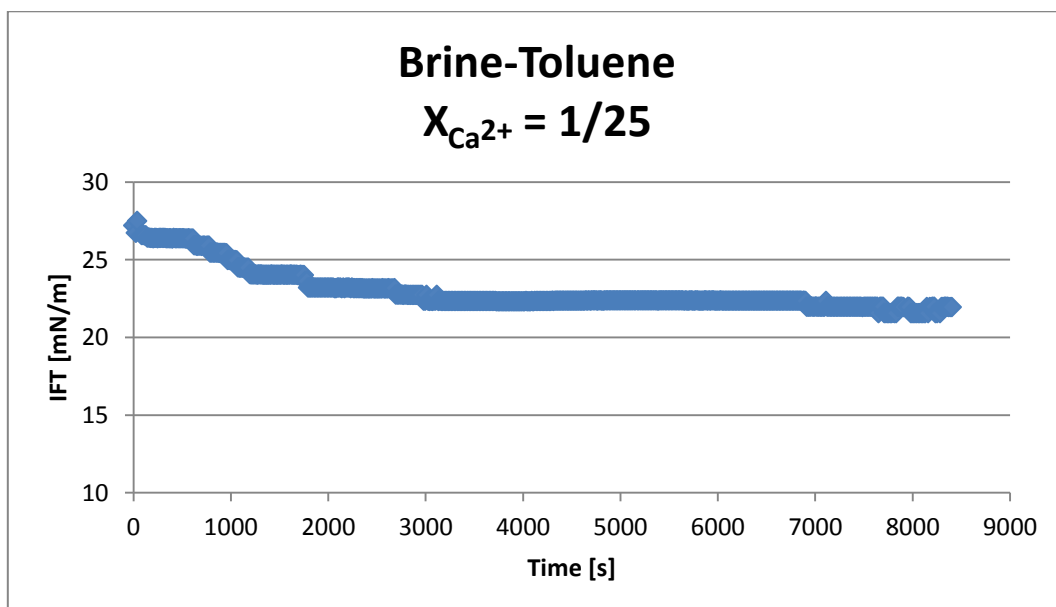


A73: Interfacial tension vs. time, for a mole fraction of 1/16 Ca^{2+}/Na^+ , at 60°C. Ionic strength is 20 mM

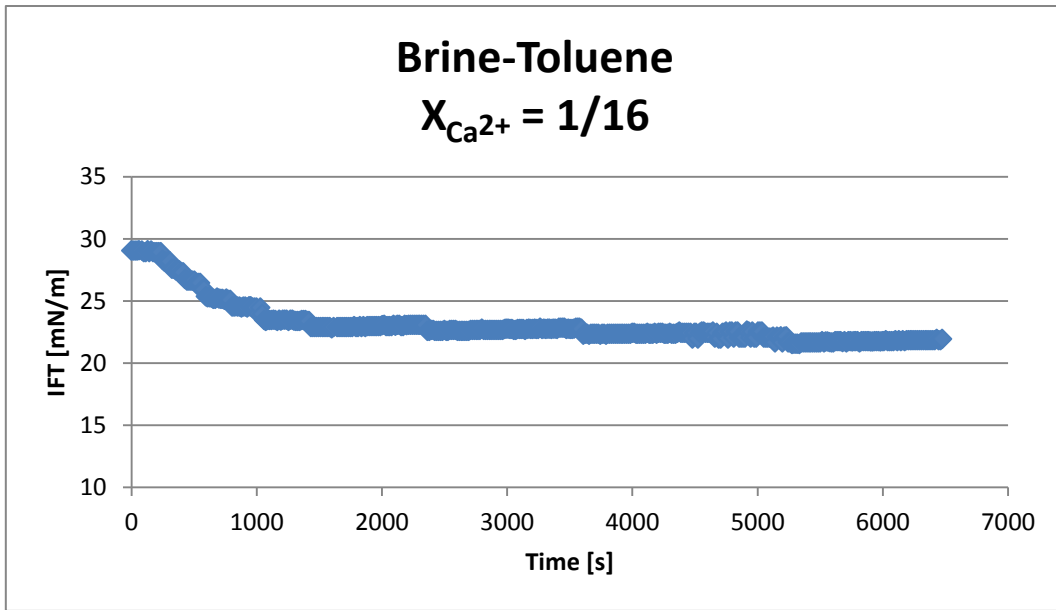
Brine-Toluene Series



A74: Interfacial tension vs. time, for a mole fraction of 0 Ca^{2+}/Na^{+} , at 60°C. Ionic strength is 20 mM



A75: Interfacial tension vs. time, for a mole fraction of 1/25 Ca^{2+}/Na^{+} , at 60°C. Ionic strength is 20 mM



A76: Interfacial tension vs. time, for a mole fraction of 1/16 Ca^{2+}/Na^{+} , at 60°C. Ionic strength is 20 mM

Appendix A5 - Risk Assessment

NTNU	Risk assessment			Prepared by	Number	Date
 HSE/JS				HSE section	HMSRV2603E	04.02.2011
		Approved by	Page	Replaces		
		The Rector	1 out of 3	01.12.2006		

Unit: Chemical Process Technology
Line manager: Edd Blekkan
Participants in the risk assessment (including their function): Erlend Teigen (Master student) and Thomas Tichelkamp (PhD)

Date: 05.03.2014

Activity from the identification process form	Potential undesirable incident/strain	Likelihood: Likelihood (1-5)	Consequence:			Risk value	Comments/status Suggested measures
			Human (A-E)	Environment (A-E)	Economy/material (A-E)		
Preparing organic solutions (dodecane and toluene)	Spilling can cause damage to hands/eyes. Danger upon inhalation. Harmful to health and flammable.	3	A	A	A	A3	Use protective goggles, nitril-gloves, and work in fume hood.
Preparing aqueous solutions (AOT and brine-solutions)	No hazards	3	A	A	A	A3	Use protective goggles and nitril-gloves
Starting the SVT-experiment. (Includes injection of both aqueous- an oil solution into the capillary by use of syringes)	Spilling can cause damage to hands/eyes. Danger upon inhalation. Harmful to health and flammable. Sting with needle	3	B	A	A	B3	Use protective goggles, nitril-gloves, and work in fume hood. Use safe disposal for needles.
Cleaning equipment (toluene and acetone)	Spilling can cause damage to hands/eyes. Danger upon inhalation. Harmful to health and flammable.	3	A	A	A	A3	Use protective goggles, nitril-gloves, and work in fume hood.

NTNU		Risk assessment		Prepared by	Number	Date
				HSE section	HMSRV2603E	04.02.2011
				Approved by	Page	Replaces
HSE/IKS			The Rector	2 out of 3	01.12.2006	



Likelihood, e.g.:

1. Minimal
2. Low
3. Medium
4. High
5. Very high

Consequence, e.g.:

- A. Safe
- B. Relatively safe
- C. Dangerous
- D. Critical
- E. Very critical

Risk value (each one to be estimated separately):

- Human = Likelihood x Human Consequence
 Environmental = Likelihood x Environmental consequence
 Financial/material = Likelihood x Consequence for Economy/material

Potential undesirable incident/strain

Identify possible incidents and conditions that may lead to situations that pose a hazard to people, the environment and any materiel/equipment involved.

Criteria for the assessment of likelihood and consequence in relation to fieldwork

Each activity is assessed according to a worst-case scenario. Likelihood and consequence are to be assessed separately for each potential undesirable incident. Before starting on the quantification, the participants should agree what they understand by the assessment criteria:

Likelihood

Minimal 1	Low 2	Medium 3	High 4	Very high 5
Once every 50 years or less	Once every 10 years or less	Once a year or less	Once a month or less	Once a week

Consequence

Grading	Human	Environment	Financial/material
E Very critical	May produce fatalities	Very prolonged, non-reversible damage	Shutdown of work >1 year.
D Critical	Permanent injury, may produce serious, serious health damage/sickness	Prolonged damage. Long recovery time.	Shutdown of work 0.5-1 year.
C Dangerous	Serious personal injury	Minor damage. Long recovery time	Shutdown of work < 1 month
B Relatively safe	Injury that requires medical treatment	Minor damage. Short recovery time	Shutdown of work < 1 week
A Safe	Injury that requires first aid	Insignificant damage. Short recovery time	Shutdown of work < 1 day

The unit makes its own decision as to whether opting to fill in or not consequences for economy/material, for example if the unit is going to use particularly valuable equipment. It is up to the individual unit to choose the assessment criteria for this column.

NTNU	Risk assessment			Prepared by	Number	Date
				HSE section	HMSRV2603E	04.02.2011
HSE/KS				Approved by	Page	Replaces
			The Rector	3 out of 3	01.12.2006	

Risk = Likelihood x Consequence

Please calculate the risk value for "Human", "Environment" and, if chosen, "Economy/materiel", separately.

About the column "Comments/status, suggested preventative and corrective measures":

Measures can impact on both likelihood and consequences. Prioritise measures that can prevent the incident from occurring; in other words, likelihood-reducing measures are to be prioritised above greater emergency preparedness, i.e. consequence-reducing measures.

NTNU	Kartlegging av risikofylt aktivitet				Utarbeidet av	Nummer	Dato
 HMS					HMS-avd.	HMSRV2601	22.03.2011
		Godkjent av	Side	Erstatler			
		Rektor	1 av 2	01.12.2006			

Unit: Chemical Process Technology
Head of unit: EddBlekkan

Date: 05.03.2014

Participants and their function: Erlend Teigen (Master student) and Thomas Tichelkamp (PhD)
Description::

ID nr.	Activity/process	Responsible	Existing documentation	Safety	Laws and regulations	Comments
1	Preparing organic solutions (dodecane and toluene)	E. Teigen T. Tichelkamp G. Øye	Laboratory guidelines	Use protective goggles, nitril-gloves, and work in fume hood.	Safetysheet for used chemicals. Working Environment Act, Chemical regulation, Laboratory and workshop manual for NTNU	
2	Preparing aqueous solutions (AOT and brine-solutions)	E. Teigen T. Tichelkamp G. Øye	Laboratory guidelines	Use protective goggles, nitril-gloves, and work in fume hood.	Safetysheet for used chemicals. Working Environment Act, Chemical regulation, Laboratory and workshop manual for NTNU	
3	Starting the SVT-experiment. (Includes injection of both aqueous- an oil solution into the capillary by use of syringes)	E. Teigen T. Tichelkamp G. Øye	Laboratory guidelines and procedure for SVT	Use protective goggles, nitril-gloves, and work in fume hood. Use safe disposal for needles.	Safetysheet for used chemicals. Working Environment Act, Chemical regulation, Laboratory and workshop manual for NTNU. Training for use of SVT by T. Tichelkamp	
4	Cleaning equipment (toluene and acetone)	E. Teigen T. Tichelkamp G. Øye	Laboratory guidelines	Use protective goggles, nitril-gloves, and work in fume hood.	Safetysheet for used chemicals. Working Environment Act, Chemical regulation, Laboratory and workshop manual for NTNU	