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Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization: Master of Science in Petroleum Engineering Reservoir Engineering	Fall semester, 2010 Open access
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Faculty supervisor: Jostein Kolnes Laboratory supervisor: Ola Ketil Siqveland	
Title of thesis: Evaluation of experimental methods to determine wettability	
Credits (ECTS): 30	
Keywords: Carbonate reservoirs Contact angle Spontaneous imbibition Surfactants (cationic) Wettability alteration	Pages: 27 + frontpage + enclosures: none Stavanger, Jan 3 rd , 2011 date/year

Evaluation of experimental methods to determine wettability

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Abstract

Two methods to evaluate the wettability of carbonates have been investigated: Aqueous cationic surfactant solutions contact angles on oil-wet calcite crystals, and imbibition time of surfactant drops into oil-wet outcrop chalk slices, both immersed in n-decane during measurements. The procedure to measure contact angles offered good repeatability, and the results were according to theory. However, the effectiveness of the surfactants was ordered differently depending on which pure carboxylic acid was used to create oil-wet crystals, and it would perhaps be desirable to use crude oil instead. The repeatability in the imbibition experiments was poor, and water and/ or brine often imbibed faster than surfactants, this was attributed to weakly oil-wet chalk slices. Ignoring water and brine, the effectiveness of the surfactants were ordered like in Amott-tests reported by Standnes and Austad (2000). Overall in both experiments, C12TAB and C14TAB were the most effective wettability modifiers. In the imbibition experiments, oil expulsion from the chalk slices was also observed.

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1. Introduction

1.1. Background

The purpose of this study was to develop simple and fast experimental methods to investigate surfactant-induced wettability alteration on carbonates. Contact angles on calcite crystals and imbibition time into outcrop chalk plates were measured. The two methods were compared to each other, and to spontaneous imbibition (SI) experiments (Amott-tests) performed by Standnes and Austad (2000).

1.2. Wettability

Wettability is defined by Anderson (1986a) as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids”. The reservoir rock may be water-wet, oil-wet, or neutral-wet if both fluids have equal affinity for the rock surface. The wettability may be non-uniform; various types of fractional wettability exists where isolated areas are

water-wet and oil-wet, mixed wettability is a special case where the oil- and water-wet areas are each continuous (Anderson, 1986b; Milner, 1996; Standnes, 2001).

On a smooth surface, wettability can be evaluated by contact angles. The contact angle θ_c depends on the oil-solid interfacial tension (IFT), σ_{os} , water-solid IFT, σ_{ws} , and oil-water IFT, σ_{ow} , as described by Young's equation,

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cdot \theta_c. \quad (1.1)$$

With water (with or without dissolved surfactant) as the reference fluid, the surface is water-wet when $\theta_c < 90^\circ$, oil-wet when $\theta_c > 90^\circ$, and neutral-wet when $\theta_c = 90^\circ$. The concept is illustrated in Fig. 1.1. Several authors have defined an intermediate-wet area around $\theta_c = 90^\circ$, with various cut-off values (Standnes, 2001).

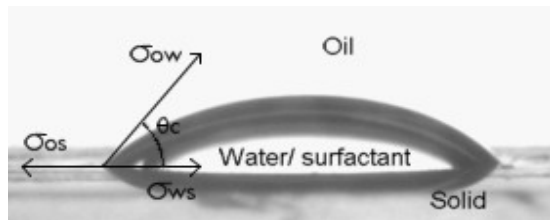


Figure 1.1. A water/ surfactant drop on a solid surface immersed in oil. The surface is water-wet.

In porous media, the wettability of the rock and performance of wettability modifiers can be measured on core plugs in Amott-tests. The core is water-wet if it spontaneously imbibe water, oil-wet if it spontaneously imbibe oil, neutral-wet if neither fluid is imbibed, and mixed-wet if both fluids are imbibed spontaneously (Standnes, 2001).

Correlations between contact angle and core plug measurements have been observed, but results from different wettability tests will usually exhibit great scatter (Standnes, 2001). Standnes (2001) states that "(...) contact angles are a useful guide to evaluate relatively large changes in wettability induced by crude oils or surface-

active materials for example, but they cannot be used to quantitatively predict SI or displacement efficiencies in porous media".

1.3. Spontaneous imbibition

SI of injected water (the term water includes brine) can enhance recovery from naturally fractured water-wet carbonate reservoirs. When water is the wetting phase, the capillary pressure,

$$p_c = p_{\text{non-wetting phase}} - p_{\text{wetting phase}}, \quad (1.2)$$

is positive. Injected water will spontaneously imbibe into the pores, increasing the water saturation and displacing the oil. The increasing water saturation will increase the pressure in the water phase, decreasing the capillary pressure. SI will take place for as long as the capillary pressure is larger than zero (Milner, 1996), even if the reservoir is highly fractured (Høgnesen, 2005).

SI will not take place in neutral- to oil-wet reservoirs, due to the very small or negative capillary pressure in Eq. 1.2 (Milner, 1996; Standnes, 2001). In fractured reservoirs, enhanced oil recovery (EOR) projects may be difficult, as injected fluids will prefer to move along the fractures due to the higher porosity and permeability compared to the pores, resulting in poor sweep efficiency. Høgnesen (2005) listed several options. The capillary barrier can be overcome by viscous or gravity/ buoyancy forces by injecting water or gas, forcing imbibition. The barrier itself can be reduced by lowering the IFT by injecting surfactants or near-miscible gas. Altering the wettability by injecting surfactants may remove the barrier entirely, as it will change the sign of the capillary pressure. The latter option is then the most desirable, as it will allow for SI to take place.

1.4. Wettability modifiers in crude oil

Carbonate rocks are naturally water-wet (Høgnesen, 2005); the surface possesses higher affinity for water than for oil. When crude oil migrates from a source rock and invades an originally water-filled reservoir, the capillary pressure increases and can exceed the force barrier which keeps the water-wetting film in place. As the water-wetting film becomes ultra-thin and ruptures, the wetting molecules are displaced and replaced by surface-active polar components in the oil, which adsorb irreversibly onto the rock surface, effectively altering the wettability towards oil-wet (Milter, 1996).

Historically, the slightly polar, heavy components asphaltenes and resins are known to alter the wettability towards oil-wet (Standnes, 2001), but during the last two decades the importance of acidic components in the crude oil have been emphasized (Standnes, 2001). The contents of these acids are not directly related to the asphaltene contents (Skauge et al., 1999), but they are present in all crude oils (Standnes, 2001). This study applies carboxylic acids dissolved in n-decane to alter the wettability of carbonate rock towards oil-wet.

Carboxylic acids consists of one or more carboxyl groups attached to a hydrocarbon chain of various length. The carboxyl group is polar, negatively charged, while the hydrocarbon chain is neutral. The surface of carbonates is positively charged below pH 8 to 9 (Pierre et al., 1990; Wesson and Harwell, 2000). The negatively charged carboxyl groups adsorb onto the positively charged carbonate rock surface when the water-wetting film is displaced. Similarly, positively charged basic components are known to alter the wettability of sandstones, which are negatively charged on the rock surface (Standnes, 2001).

To illustrate the importance of carboxylic acids, Milter (1996) showed that,

by measuring the contact angle, a calcite crystal aged in the carboxylic acid stearic acid dissolved in dodecane became oil-wet, while Ekofisk crude oil only altered the wettability slightly. Pure dodecane altered the wettability the least.

The acid number (AN) is a measurement of the contents of acidic components in crude oil. The unit is mg KOH/ g oil; the mass of potassium hydroxide required to neutralize 1 g of oil. It is presented without a unit in this text. AN = 1 corresponds to a concentration of 0.013 M in a solution containing only a single type of acid, as with the carboxylic acids used in this study. To further illustrate the importance of acidic components, Standnes (2001) performed SI measurements of brine into cores saturated with various oils with various acid numbers (AN), and showed that the rate of SI decreased with increased AN. In other words, the cores saturated with the highest AN were the most oil-wet. A core saturated with an oil with AN = 1.04 had not imbibed brine at all after 80-90 days at 40°C.

It is unknown if the length of the hydrocarbon chain of the carboxylic acids is important for the initial wettability alteration from water-wet to oil-wet. Zhang and Austad (2005), confirm the importance of AN, and state that temperature had little effect on the oil-wetting process. Milter (1996) however states that aging cores in oil at elevated temperature is more effective, and imbibition tests showed that the cores became more oil-wet the longer they had been aged; wettability alteration was still ongoing after 125 days at 80°C.

According to Buckley and Liu (1998) there are two different mechanisms determining how strongly the acids adsorb to the surface. With initial water saturation they adsorb by acid-base interactions, while with no initial water they adsorb by polar binding. Usually they would adsorb stronger with initial water saturation (Buckley, 1996).

To alter the oil-wet carbonates back to water-wet, the carboxylic acids and other

polar components must be desorbed from the rock surface, and transported away.

1.5. Surfactants

Surfactants are amphiphilic molecules, consisting of a hydrophilic head group and a hydrophobic hydrocarbon chain of various length. The head group may be non-ionic, cationic, anionic, or zwitter-ionic. The surfactants applied in this study are of the quaternary ammonium type, cationic surfactants with general formula $R-N(CH_3)_3^+Br^-$ where R is the hydrocarbon chain, abbreviated CnTAB, where n is the length of the hydrocarbon chain while TAB is short for trimethyl-ammoniumbromide.

Typically surfactants have been injected into oil reservoirs to mobilize residual/trapped oil by decreasing oil-water IFT, which reduces the effect of capillary forces while promoting the influence of gravity forces (Høgnesen 2005). In a non-fractured reservoir, strong capillary forces will trap oil (Standnes, 2001), in this case a low IFT is desirable to reduce the capillary forces. In the case of wettability alteration and SI in fractured carbonate reservoirs, a low IFT is not desirable (Milter, 1996), as the SI process is enhanced by capillary forces. Ultimate recovery under low IFT conditions (low capillary forces) can be very high as less oil is trapped when the drainage is mainly governed by gravity forces, but this process may be too slow to be economic (Standnes, 2001; Milter, 1996). According to Høgnesen et al. (2006), injecting a cationic surfactant as applied in this study into a fractured carbonate reservoir would most likely result in a totally gravity-driven drainage process due to low IFT, even though increased water wetness increases the capillary forces.

Surfactants partition as monomers into the bulk water solution, and at the oil-water interface. The accumulation at the interface decreases the oil-water IFT. Increasing the surfactant concentration in the bulk above

the critical micelle concentration (CMC), leads to formation of micelles in the bulk water solution. Micelles are spherical or cylindrical aggregates of surfactant molecules with the hydrophilic head groups pointing outwards, while the hydrophobic hydrocarbon chains point to the center of the micelle. Increasing the surfactant concentration further will only result in higher micelle concentration, and the IFT remains near constant beyond CMC (Standnes, 2001). CMC of a given surfactant-system depends on various parameters. CMC of ionic surfactants will usually decrease by decreasing temperature (Zana, 1990); increasing salinity (Standnes, 2001); and increasing the hydrocarbon chain length (Mørk, 1997).

Mixing aqueous surfactant solutions with oil when the surfactant concentration is above CMC will result in one of the following outcomes: An oil-in-water microemulsion and an excess oil phase, a Type II(+) system; a water-in-oil microemulsion of inverted micelles and an excess water phase, a Type II(+) system; and excess water and oil phases with a surfactant-rich phase in the middle, a Type III system. The surfactant systems applied in this study are Type II(-) systems (Standnes, 2001).

By electrostatic interaction between the positively charged head groups of the cationic surfactants and the negatively charged carboxyl groups of the carboxylic acids, the cationic surfactant monomers have the ability to desorb the organic material from the rock surface as surfactant-carboxylic acid ion-pairs (Austad et al., 1998; Khan and Marques, 1997; Standnes, 2001), and as such alter the wettability towards water-wet. Hydrophobic interaction between the hydrocarbon chains stabilize the ion-pairs (Standnes and Austad, 2000). At surfactant concentrations above CMC, Standnes and Austad (2000) showed that the imbibition rate was nearly independent of concentration, indicating that only the

monomers are active in the desorption process.

The desorbed components must also be transported away from the rock surface. The ion-pairs are not soluble in water. Standnes and Austad (2000) proposed two transport mechanisms. The desorbed materials are 1) solubilized in the water phase by forming mixed micelles or 2) transported to the oil phase as clusters of ion-pairs (where they may aggregate into inverted micelles). The desorption and transport mechanisms are illustrated in Fig. 1.2. SI experiments showed that when the surfactant concentration was below CMC, little imbibition took place. Contact angles were also much larger below CMC compared to above CMC, further indicating that importance of the presence of micelles in the surfactant solution. In addition to solubilizing desorbed materials, it was also believed that the micelles would supply monomers to the rock surface (Standnes, 2001). The partitioning of surfactants into the oil phase was also measured (Standnes and Austad, 2000). The partitioning into the oil phase increased in the presence of carboxylic acids, or by increasing AN when crude oils were applied, supporting the theory that ion-pairs are formed and transported into the oil phase. Further arguments can be obtained in the mentioned paper.

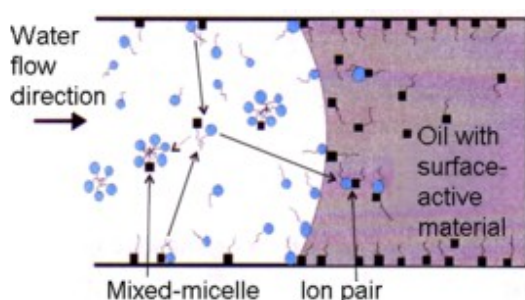


Figure 1.2. Illustration of the desorption and transport mechanisms for cationic surfactants (Standnes, 2001). The blue circles are surfactant head groups, and the black squares are carboxylic acid head groups.

Increasing the temperature during the imbibition experiments from 40°C to 70°C results in a significant increase in the SI rate (Standnes and Austad, 2000).

Certain anionic surfactants will also alter the wettability of the rock (Standnes and Austad, 2000). The hydrophobic section of anionic surfactants with one or more ethoxy-groups (EO-groups) in the hydrophilic section, an oxygen molecule attached to a hydrocarbon chain of length 2, have the ability to interact with the hydrophobic section of the carboxylic acids, forming a bilayer with the EO-group pointing outwards. The surface then becomes weakly water-wet, but the wettability is reversible as the hydrophobic bonding is weak. SI was non-uniform and slow. Of the surfactants studied by Standnes (2001), the best anionic EO-surfactant was much less effective than the best cationic surfactants. Anionic surfactants without ethoxy-groups did not seem to alter the wettability at all (Standnes and Austad, 2000). Anionic surfactants were not applied in this study.

2. Experimental

2.1. Materials

Carboxylic acids dissolved in n-decane were used to create oil-wet surfaces. The acids are presented in Table 2.1.

Table 2.1. Carboxylic acids tested.

Carboxylic acids	HC-chain	Name
$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	10	Decanoic acid
$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	12	Lauric acid
$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	14	Myristic acid
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	18	Stearic acid

The n-decane was supplied by two manufacturers, Merck and Fluka, of purity larger than or equal to 94%, and 95%, respectively. The surfactants were dissolved

in synthetic sea water (SSW) of pH 8.04. The surfactants are presented in Table 2.2, and the composition of SSW in Table 2.3.

Table 2.2. Cationic surfactants tested, with CMC values from Mukerjee and Mysels (1971). Note that CMC values were measured when the surfactants were dissolved in DW. The CMC values in SSW are slightly lower. The CMC values were measured at 25°C, except C14TAB which was measured at 30°C.

Surfactant	Abbreviation	CMC in DW at 25C [wt.%]
n-C ₁₀ -N(CH ₃) ₃ ⁺ Br ⁻	C10TAB	1.9
n-C ₁₂ -N(CH ₃) ₃ ⁺ Br ⁻	C12TAB	0.43
n-C ₁₄ -N(CH ₃) ₃ ⁺ Br ⁻	C14TAB	-
n-C ₁₆ -N(CH ₃) ₃ ⁺ Br ⁻	C16TAB	0.03

Table 2.3. Ion composition and Total Dissolved Solid (TDS) of FW and SSW.

Ion	FW [g/L]	SSW [g/L]
Cl ⁻	42.46	28.36
Na ⁺	15.73	0.97
Ca ²⁺	9.26	4.38
Mg ²⁺	0.61	0.57
SO ₄ ²⁻	-	0.22
HCO ₃ ⁻	-	10.35
K ⁺	-	0.01
TDS	68.06	44.86

Artificial formation water (FW) of pH 7.78 was used to age calcite crystals before oil-wetting with carboxylic acids, the composition is presented in Table 2.3.

C10TAB and C16TAB were supplied by Fluka, C12TAB by Sigma, and C14TAB by VWR. All carboxylic acids were supplied by Merck. n-heptane from Merck of purity larger than 99% was used to rinse crystals.

2.2. Contact angle experiments

Carbonate rock as limestone/ chalk are primarily made up from calcite minerals, CaCO₃, and smooth, horizontal calcite crystals were used as the wetting surface in the contact angle measurements.

(1) The crystals were wet-polished with waterproof silicon carbide P4000 paper. To remove grease, they were cleaned with toluene and rinsed with n-heptane. n-heptane does not have an effect on wettability (Standnes, 2001).

(2) The crystals were aged in FW for 1 h at 20°C, to simulate the fluids in contact with a reservoir rock. The special interest was to leave a layer of salts present in FW on the crystals. When removed from the FW bath, the remaining water was removed with a Teflon plate. Letting the water evaporate would leave too much salt on the surface, while gently letting it absorb into a piece of paper would possibly leave too little.

(3) The crystals were then aged in a carboxylic acid for 1 h at 20°C. When removed from the acid bath, they were rinsed with n-heptane to remove excess acid which had not adsorbed to the calcite surface.

(4) Finally, the crystals were placed in one glass cell each. The cells were filled with n-decane. The contact angles were measured on static sessile drops of distilled water (DW), SSW, or surfactants, at specific time intervals. Four to six drops of volume 2 μL were generated at the needle at deposition speed 50 μL/min, and deposited on the surface when they had grown to their complete volume. Drop placement is illustrated in Fig. 2.1.

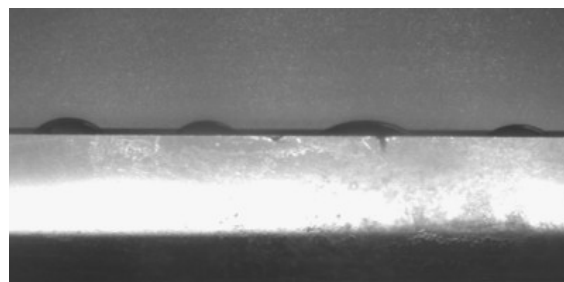


Fig 2.1. Four drops deposited on a crystal.

The left and right angles were measured with a Krüss DSA100 goniometer, and in some cases with a semi-circle, and the

contact angle for each drop is presented as the mean value of those two angles. Crystals which were reused were re-polished on all surfaces to remove surface-active materials.

2.3. Imbibition experiments

Outcrop chalk from Stevns Klint in Denmark was used in the imbibition experiments. Hjuler and Fabricius (2009) determined that the flooding properties of Stevns Klint were comparable to those of most reservoir chalks; their conclusion seems to be based mostly on the specific surface area of $1.7 \text{ m}^2/\text{g}$ being comparable to that of most reservoir chalks. They determined the average porosity to 53.4%, and the Klinkenberg permeability to 8.1 mD.

(1) The chalk was cut into horizontal slices of dimensions 5-8 mm in height and width, and 10-20 mm in length.

(2) The slices were dried at 105°C before being placed in a vacuum pump, then saturated in n-decane or carboxylic acid solutions at pressures between 10^{-1} and 10^{-2} mbar.

(3) The slices were rinsed in n-decane to remove excess carboxylic acid molecules on the surface, and placed in glass cells which were filled with n-decane.

(4) A $5 \mu\text{L}$ water or surfactant drop was generated on the chalk surface at $80 \mu\text{L}/\text{min}$, because DW and SSW drops would not wet the surface if generated on the needle before being deposited. The time the drop required to completely imbibe was measured.

2.4. Uncertainties

The contact angles were measured using the software included with the goniometer if possible. By visual inspection, the uncertainty in any single measurement seemed very small under optimal lighting, less than $\pm 1^\circ$. In the cases where it was possible to observe that the calculations were a little off, angles were more often overestimated than underestimated. When

measuring several drops deposited on one crystal, the lighting occasionally had to be alternated from drop to drop to result in a satisfactory measurement. As such the uncertainty increases to perhaps $\pm 1^\circ - 2^\circ$ because the contact angles of a specific drop are not measured under identical conditions in each measurement.

In some cases contact angles had to be measured manually using a semi-circle, because the software could not produce a curve fit for a particular drop/ angle. The uncertainty was perhaps $\pm 2^\circ - 3^\circ$, especially if computer measurements and manual measurements are combined in any given data set, mixing two sets of interpretations. This rarely happened, but there were a few times when the contact angles during the course of the experiment decreased below the optimal range for the software to calculate.

The time a drop needed to imbibe into chalk plates were measured from the second the drop was generated on the surface and until it disappeared. The timer was started manually, and the uncertainty is within a second.

The uncertainties discussed here, which are based on experience, not a statistical analysis, are not considered beyond this point. The range spanned by for example five drops in one experiment is always larger than the equipment uncertainty. This is discussed in the following chapter.

3. Results and discussion

3.1. Contact angles

3.1.1. General observations

This subsection discusses some general observations and important parameters which will be used when discussing contact angles measured on different systems. A C12TAB/ lauric acid system is used as an example.

Most measurements were performed on two specific crystals, referred to as crystals A and B. Fig. 3.1.1 shows the results from an example experiment, in this case for C12TAB (1 wt.%) drops on a crystal aged in lauric acid (AN = 19.23/ 0.25 M). Each curve represents the mean value of left and right contact angles, abbreviated CA in all figures and tables, for one drop over a period of 70 minutes. Five drops were deposited on this crystal.

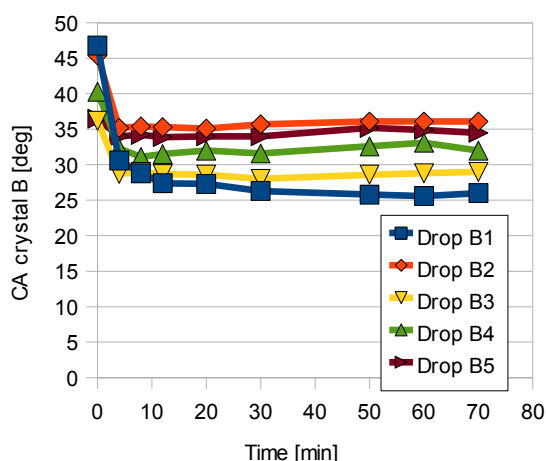


Figure 3.1.1. Measurements of five C12TAB (1 wt.%) drops on crystals aged in lauric acid (AN = 19.23/ 0.25 M) as a function of time, deposited on crystal B.

During the first few seconds, a rapid decrease was observed. The contact angles recorded at time 0 in Fig. 3.1.1 are not the contact angles upon immediate contact with the crystal surface as they would be difficult to measure when several drops were deposited on the same crystal, but measured when the decrease is no longer easily visible on the monitor, typically 20 – 40 seconds after the drops were deposited. As such, measurements at time 0 should not be paid much attention. After this, a more gradual decrease occurred until the contact angles entered apparent equilibrium, typically after 4 – 12 minutes.

Long-term experiments revealed that this apparent equilibrium is not entirely stable. Fig 3.1.2 shows the contact angles for the given system after nearly three days (66

hours). Each drop had the contact angles reduced by another 15°, calculated as the difference between the value obtained at the start of the apparent equilibrium region and three days, not the from the very start of the experiment. While no measurements were recorded between 70 minutes and 66 hours on the system in Fig. 3.1.2, measurements on other systems, often performed after 20 hours instead of three days, suggest that the decrease in contact angles after reaching apparent equilibrium is indeed fairly linear, with a rate of 3 – 5° pr. day. However, at one point it must start to flatten out, but experiments were not run for more than three days. This long-term effect was not expected to be important in the imbibition process. The results in this study are calculated from the apparent equilibrium region usually between 12 and 70 minutes. Even so, stability may be an important parameter in evaluating the developed procedure, and certainly better stability is practical during experiments.

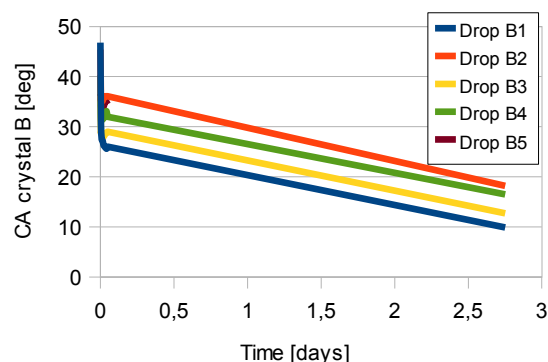


Figure 3.1.2. C12TAB (1 wt.%) drops on crystals aged in lauric acid (AN = 19.23/ 0.25 M), drops placed on crystal B. Reduction of contact angle values is still ongoing after reaching apparent equilibrium. The contact angles on drop B5 could not be measured after 66 hours, because the drop had deformed. No measurements were performed along the straight lines.

It is also worth noting that drops did not approach a common contact angle. The initial spacing in contact angles for all the drops are preserved even after 66 hours. This happened more often than not; curves

rarely crossed each other, except occasionally during the first four minutes.

The final contact angle for a given system was reported as the mean value of all drops at all measured times during the first 30 – 60 minutes after reaching apparent equilibrium, rounded to the nearest integer. In the example above, it was then the mean value of five drops measured at times 12, 20, 30, 50, 60, and 70 minutes from the deposition of the drops; the average of 60 left and right contact angle measurements.

It may be argued that, as the apparent equilibrium region is not completely stable, the results between for example 12 and 60 minutes should not be included in the same mean value. However, comparing with the long-term results, the contact angle should be reduced by approximately $0.2^\circ / \text{h}$ in this region, an accuracy which is far below the expected measurement accuracy. It was often observed that the contact angles measured on a given drop increased and decreased slightly during the apparent equilibrium region, indicating that measurements could be averaged over a short time as no trend was observed within this time.

A simple empirical method was applied to quantify the scatter and repeatability of an experiment. The range is reported as the largest difference between the two drops with the highest and lowest contact angles at any time in the apparent equilibrium region during a given experiment. A smaller range indicates that the measurements of individual drops deposited on one crystal are packed closely together, indicating small scatter and uncertainty in the estimated mean value. The resulting contact angle in the example experiment presented in Fig. 3.1.1 was then 31° , with a range of 11° . A range of 11° is acceptable, and most experiments shared approximately that same value. Standnes (2001) reported a repeatability of $\pm 3^\circ$, but the measurements were carried out in air, not in n-decane.

The same experiment was also performed on crystal A. The mean values from crystals A and B were shifted by approximately 3° , as shown in Fig. 3.1.3. The two averages approached the same value, 15° , after 66 hours (not shown in figure), this, as previously seen, did not happen in all experiments.

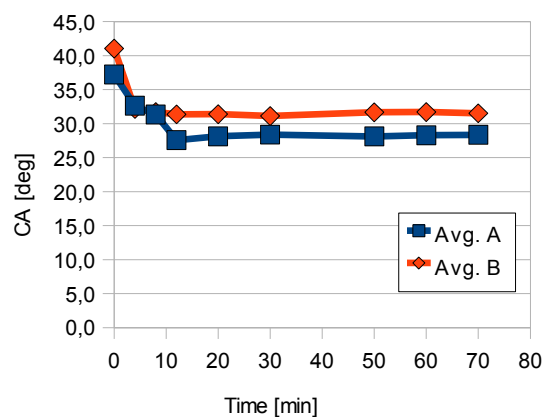


Figure 3.1.3. C12TAB (1 wt.%) drops on crystals aged in lauric acid (AN = 19.23/ 0.25 M), averages of drops placed on crystals A and B.

The deviation was small enough to consider the crystals equal, and most experiments were carried out only on one crystal, but both crystals were in use for efficiency, hence the importance of showing that the two crystals give similar results; i.e. experiments with C12TAB performed only on crystal A can be compared to experiments with C14TAB performed only on crystal B given the same carboxylic acid was used. The shift can be attributed to the quality of the polishing job, typically crystal A would have a slightly clearer finish than crystal B. A few other experiments were also performed on both crystals, and the deviations were similar to the one in this example.

A more accurate way to show that the two crystals can be considered equal is shown in Fig. 3.1.4. All individual drops are shown, where the blue curves represents contact angles measured on crystal A, and red curves contact angles measured on

crystal B. The results from the C12TAB – lauric acid experiments performed on crystals A and B overlap reasonably well, indicating good repeatability. The total range, the difference between the largest and smallest values from either experiment, increased slightly compared to the range reported for measurements on crystal B.

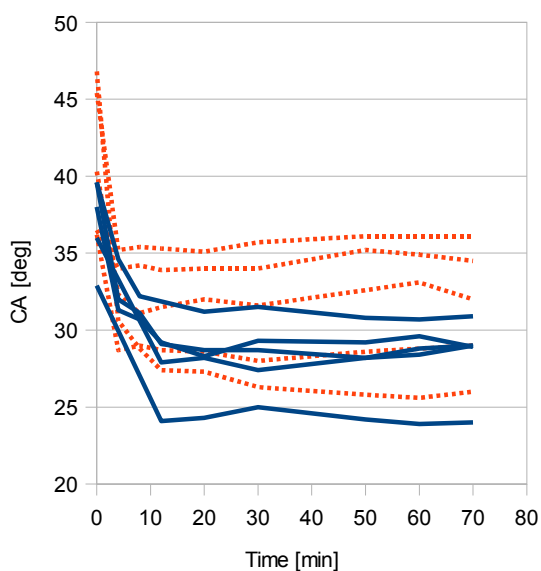


Figure 3.1.4. C12TAB (1 wt.%) drops on crystals aged in lauric acid (AN = 19.23/ 0.25 M), drops placed on crystals A (blue/ full lines) and B (red/ dotted lines). The figure shows that the measurements carried out on both crystals overlap, and the total range is approximately 12°. Good repeatability is indicated.

When two experiments were carried out with, for example, two different surfactants applying the same carboxylic acid, on any two crystals as they have been showed to give very similar results, whether the results overlap or not tells whether the results can be considered truly different or not. If the averages were shifted for example 7°, and there was no overlap, it can be said with a high degree of certainty that applying the two surfactants results in different degrees of wettability alteration. However, if there is a substantial amount of overlap, it may not be so certain that one surfactant really is better than the other. Of course, it is also

possible that the surfactants result in similar degree of wettability alteration.

In summary, the uncertainty of the mean value and the repeatability of an experiment on a given system is evaluated by the range spanned by all the measurements during the experiment, and whether or not the results overlap with results from a repeated experiment.

3.1.2. Polishing method

The following three subsections discusses how the procedure in subsection 2.2. was developed. The main focus was to achieve good repeatability.

The quality of the polishing job seems to be of high importance, especially considering repeatability of the experiments. During the very first experiments, the crystals were soft-polished on a rotating cloth, applying a polishing-powder of unknown substance dissolved in DW. This was discontinued in fear of leaving powder residue on the surface. When measurements of the same system on two different crystals were performed, the average values calculated from each crystal were shifted far apart, in one case as much as 60°, and there was no overlap between the results from the two crystals. Although the range during each measurements on each crystal was as normal, these experience showed no repeatability between measurements on different crystals, and no information could be learned. Overlap of results from two crystals was first achieved when the crystals were polished with P4000 paper. However, the first P4000 paper was already worn out from the start, effectively useless. New P4000 papers were eventually acquired, resulting in even better overlap. An example of the latter is shown in Fig. 3.1.4, and all other experiments which were performed on both crystals where the procedure in subsection 2.2. was followed, with new P4000 paper, experienced similar or better overlap, indicating good repeatability.

Another problem encountered when using the polishing powder was that the drops would not always reach apparent equilibrium, a steady decrease in contact angles could often be observed for a few hours. This became especially evident when the long-term stability was investigated; the contact angles were reduced as much as 20° during one day, not counting the initial reduction during the very first minutes. Apparent equilibrium was usually reached after 12 - 20 minutes when the crystals were polished with worn-out P4000 paper, and during one day after this region the contact angles were only reduced 1 – 10°. With new P4000 paper, apparent equilibrium was usually reached after 2 – 8 minutes, and never later than 12 minutes. Long-term stability was 3 – 5° / day.

The new P4000 paper had a larger effect on the values of the contact angles than expected. Experiments were conducted on the C12TAB – lauric acid system, and the results are presented in Table 3.1.1. Using new paper resulted in a 19° decrease in contact angles, with no overlap between the experiments using new and old papers to polish the crystals.

Table 3.1.1. C12TAB (1 wt.%) drops on crystals aged in lauric acid (AN = 19.23/ 0.25 M), comparison of P4000 papers.

Paper	Avg. CA
Worn	49°
New	30°

The different methods applied to polish the crystals did not seem to have a large effect on the size of the range during measurements of contact angles on drops on one single crystal. The range was usually 8 – 12° for all methods. P4000 paper was used to polish the crystals used in all presented results, unless otherwise is specified.

3.1.3. Drop volume and deposition

There are three important parameters to consider when depositing a drop: Deposition speed, drop volume, and whether to generate the drop directly on the surface, or generate it on the needle and deposit it when it has grown to its complete volume. In initial experiments, the drops were generated directly on the surface. This occasionally lead to the drops being deformed, growing only in one direction from the needle. The result was a drop with very different left and right angles. Depositing the drop after it had been generated on the needle seemed to result in more uniform drops. Also in initial experiments, the drop volume was 5 µL, and the deposition speed was around 150-200 µL / min. At this time, drops with an abrupt change in curvature just above the solid-liquid contact was frequently observed, making it impossible to measure the contact angles. Reducing the drop volume to 2 µL, reducing the deposition speed, and generating the drop on the needle resulted in drops being deformed less frequently. Also, 5 µL C16TAB fell off the needle before the full volume had grown, because of low IFT between C16TAB and n-decane.

Whether the decline in the occurrence of such drops is the result of the reduction of drop volume, change of deposition method, or change of polishing method, or a combination of all, is unknown. There are too many variables involved to form a conclusive answer. All drop and deposition parameters in the presented results are as described in subsection 2.2, unless otherwise is specified.

The drop volume also had an effect on the actual values of the contact angles, assuming measurable drops were deposited. Experiments performed on water drops surrounded air showed that varying the drop volume from 1 to 10 µL had little effect (Thomsen and Bilke-Krause, undated). However, the influence of gravity is

increased when the IFT is decreased, as experienced when measuring contact angles on surfactant drops in n-decane. Experiments were performed with C12TAB (1 wt.%) and lauric acid (AN = 19.23/ 0.25 M), varying the drop volume between 2 and 5 μL , resulting in contact angles of 31° and 49° , respectively, without any overlap. Other experiments also indicated the importance of the drop volume, but other variables were also involved or the repeatability was poor, so they are not reported here.

3.1.4. Cell fluid

Initially, surfactant drops were attempted deposited while the crystal was still immersed in the carboxylic acid in step (3) in subsection 2.2. This proved impossible, because the surfactants would not form drops at the syringe needle when the needle was submerged in n-decane containing acids at concentrations of 0.1 M nor 0.01 M, or AN = 7.69 and 0.77, respectively, instead the surfactant would flow out from the needle like water from a tap, leaving a long, flat puddle on the crystal surface. This was attributed to low IFT, because DW and SSW drops were deposited easily. This was also the reason the crystals were rinsed with n-heptane after being removed from the acid bath, only very small amounts of acid in the n-decane could result in failure.

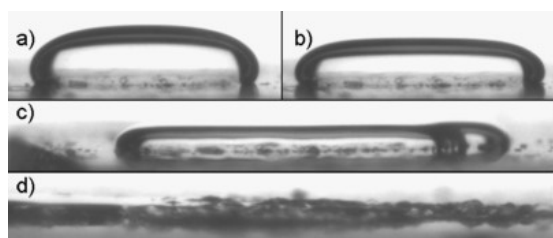


Figure 3.1.5. C10TAB (0.1 wt.%) drop on crystal aged in lauric acid (AN = 0.77/ 0.01 M), while the crystal was still immersed in the acid. The pictures show the drop a) shortly after being deposited, b) after 2 minutes, c) after 5 minutes, and d) after 48 minutes. Usually the drops would not be formed like in a) and b) at all, but puddles like in c) or d) were formed instantly.

Drops formed immersed in carboxylic acids on a few occasions for low concentrations of surfactant and acid, the result is illustrated in Fig. 3.1.5. Contact angles were close to 180° for as long as they could be measured. However, in almost all cases puddles like in Fig. 3.1.5 c) formed the moment the surfactants came in contact with the crystal. If left for several hours, a white substance, appearing to be a solid, was formed in a reaction between the surfactant and acid where the puddle had been.

When carboxylic acids were added to cells where good surfactant drops had originally been formed on crystals immersed in only n-decane, the surfactant drops would usually deform into puddles shortly after the acid was added. In some cases drops reformed from the puddles, covered in a white substance which appeared to be solid. Some examples are presented in Fig. 3.1.6.

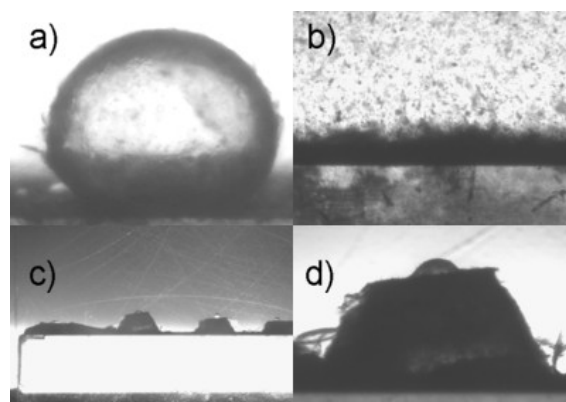


Figure 3.1.6. The result of dissolving acid in the cell filled with n-decane during measurements. First the surfactant drops turned into puddles, but drops reformed after a few days. All pictures were taken five days after acid was added. Picture a) shows a reformed drop covered in white solid from surfactant-carboxylic acid reactions, b) shows the amount of solid in the cell when it was shaken, c) shows a different system of re-formed “drops” after acid-addition, d) shows a close-up of c).

Proper drops were formed when the crystals were moved to new glass cells and immersed in n-decane after having aged in carboxylic acid. It was investigated whether or not the decane purity had an effect on contact angles, and it seemed to be of some

importance. n-decane of purity $\geq 95\%$ and purified n-decane, using the same 95% n-decane as base, were compared. Two systems were investigated.

(1) Crystals A and B were used, and both experiments were performed on both crystals. The crystals were polished with the worn-out P4000 paper, cleaned with toluene and n-heptane, and put into cells and immersed in the desired decane. To avoid other variables, the crystals were not aged in FW nor any carboxylic acids. Four DW drops of 5 μL each were deposited on each crystal. The results are presented in Table 3.1.2. The range was approximately 20° in all four separate experiments, the purity of the n-decane had no influence on the range.

Table 3.1.2. Results from the investigation into the importance of decane purity. DW drops were deposited on two crystals immersed in 95% n-decane, then repeated immersed in purified n-decane. The crystals were not aged in FW nor any carboxylic acids.

Decane	Avg. A	Avg. B	Tot. Avg.	Overlap
95%	77°	89°	83°	Poor
Purified	81°	77°	79°	Very good

The large range may have been a result of poor quality of the polishing job. The P4000 paper was used for the first time during these experiments, and were not as clear as in later experiments when more experience had been gained. As seen in Table 3.1.2, the total averages were separated by only 4° . All four experiments completely overlap, the contact angles of all eight DW drops deposited in the purified n-decane environment are completely contained between the largest and smallest values of the drops deposited in the 95% n-decane environment. As such, the decane purity seemed to have little or no effect on the final reported contact angles. Purified n-decane lead to much better overlap between the results from drops measured on crystals A and B compared to 95% n-decane, but later experiments with 95% n-decane have

achieved much better overlap than what was achieved in this case.

(2) C12TAB drops (1 wt.%, 2 μL) were deposited on crystals aged in lauric acid (AN = 19.23/ 0.25 M). The procedure in subsection 2.2. was followed, except purified n-decane was used in one experiment. Crystal A was used in both experiments. The results are presented in Table 3.1.3. The average contact angles were shifted 12° , with no overlap. It seems decane purity clearly had an effect on the reported contact angles, but it should be mentioned that the worn-out P4000 paper was used to polish the crystals, which may have lead to uneven quality of the polishing job, which would explain much of the deviation.

Table 3.1.3. Results from the investigation into the importance of decane purity. C12TAB (1wt.%) drops were deposited on crystals aged in FW and lauric acid (AN = 19.23/ 0.25 M), and immersed in 95% or purified n-decane during measurements.

Decane	Avg. CA	Range
95%	49°	16°
Purified	61°	7°

While using purified n-decane in the cells during measurements decreased the range slightly, and resulted in better overlap between the same experiments performed on different crystals in the first case reported above, it was decided to use 95% n-decane. As stated, good overlap was later achieved using 95% n-decane.

3.1.5. Effect of formation water

The procedure in subsection 2.2. was followed with C12TAB (1 wt.%) as the surfactant, and the crystals were aged in lauric acid (AN = 19.23/ 0.25 M). The experiment was performed on crystals A and B. The experiment was repeated on both crystals, this time the crystals were not aged in FW. They were aged in lauric acid

immediately after polishing. The results are presented in Table 3.1.4.

Table 3.1.4. Results from experiments where the crystals were and were not aged in FW. Crystals were aged in lauric acid (AN = 19.23/ 0.25 M) in both cases, and C12TAB (1 wt.%) drops were deposited.

FW	CA	Range	App. Eq.	Long-t. Stbl.
A	28°	7°	12 min	4° / 20h
B	31.5°	10°	12 min	5° / 20h
Total	30°	13°	-	-
Overlap	Good			
No FW	CA	Range	App. Eq.	Long-t. Stbl.
A	50.5°	17°	4 min	3.5° / 20h
B	43°	7.5°	4 min	0.5° / 20h
Total	47°	17°	-	-
Overlap	Very good			

The results are shifted 17° with no overlap in results from FW and no-FW experiments. Aging the crystals in FW clearly had a large effect in reducing the contact angle significantly. The layer of deposited salts may reduce the ability of the carboxylic acids to adsorb onto the calcite surface, and/ or form a surface for the aqueous surfactant solutions to spread on. Rapid decrease in contact angles have been observed on crystals on which too much salt was deposited. The layer of salts deposited when using the Teflon plate to remove excess FW was often uneven. A better method to remove excess FW should perhaps be found. It would also have been interesting to see the effect of aging the crystals in DW instead of FW, this however was unfortunately not investigated.

It is also worth noticing how quickly the drops stabilized when the crystals were not aged in FW, and also the increased long-term stability. Such stability was first observed when DW drops were deposited on crystals which had not been aged in carboxylic acid solutions, only in n-decane, and it was attributed to the absence of acids. Those crystals were not aged in FW, but this was given little importance at the time. At this time it seems that not aging the crystals

in FW was the most important variable responsible for increased stability. DW and SSW drops were also generally more stable than surfactant drops.

3.1.6. Establishing oil-wet crystals

DW and SSW contact angles were below 90°. When drops reached apparent equilibrium, the contact angles were typically 60° – 80°. In some cases the contact angles were above 90° for a short time immediately after the drops made contact with the calcite surface, but most often they were not. It appeared that the crystals were only intermediate-wet to slightly water-wet. Water contact angles above 90° were only observed when the crystals were still immersed in carboxylic acid solution during measurements. The results were 164° for DW and 163° for SSW, clearly oil-wet, but surfactant drops could not be placed in a carboxylic acid environment because of low IFT, so this procedure could not be used. It did, however, demonstrate that a slightly different system can lead to a completely different interpretation of wettability.

Standnes et al. (2002) also performed measurements on crystals immersed in n-decane, and contact angles above 130° were observed for brine drops. Standnes' procedure was slightly different. The crystals were aged in carboxylic acids dissolved in n-heptane, and then aged in brine or a surfactant solution. DW drops were deposited on the crystals. With this procedure it could be possible to perform measurements while the crystals were immersed in carboxylic acid solution, as no surfactant drops would have to be deposited. If so, it is suggested to use lower concentration acid during measurements than during aging. The downside is that the immediate effect of the surfactants cannot be observed.

Still, a significant wettability alteration was observed when using surfactants

compared to DW or SSW drops. Two examples are shown in Fig. 3.1.7.

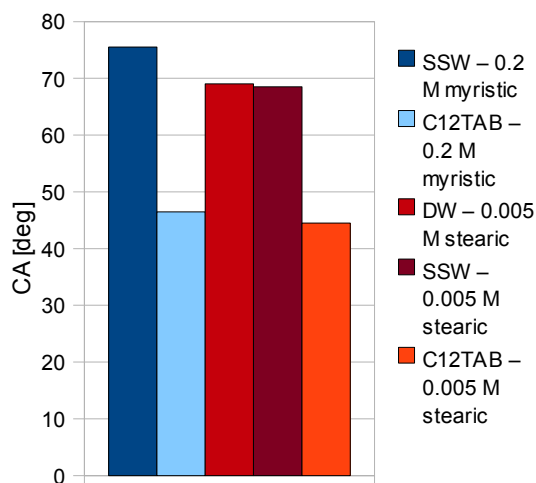


Figure 3.1.7. Water and C12TAB (1 wt.%) drops deposited in two different systems, one where the crystals were aged in myristic acid (AN = 15.38/ 0.2 M), and one where the crystals were aged in stearic acid (AN = 0.38/ 0.005 M). Only results where the same acid were used can be compared to each other, as different drop volumes and different quality P4000 papers were used.

It was observed that DW and SSW resulted in almost identical contact angles, both in the experiments with stearic acid shown in Fig. 3.1.7, and in the previously mentioned experiments with carboxylic acid still in the cell while measuring. Brines are generally better wettability modifiers than DW, particularly dependent on concentration of SO_4^{2-} -ions together with Mg^{2+} or Ca^{2+} -ions, but the effect decreases with decreasing temperature (Austad et al., 2009; Høgnesen, 2005). The low temperature during experiments and the low concentration of SO_4^{2-} -ions in SSW may explain the results.

3.1.7. Effect of acid chain length

It was investigated how the acid chain length, the hydrophobic nature, affected the surfactants' ability to desorb the acid. C12TAB (1 wt.%) was used in all experiments. Unfortunately, some crystals

were polished with the worn-out P4000 paper, and some with the new P4000 paper. Previous results have shown that these measurements cannot be compared, and the results are separated in two parts. Table 3.1.5 and Fig. 3.1.8 present the result from the crystals polished with the worn-out paper, and Table 3.1.6 and Fig. 3.1.9 present the results from crystals polished with the new paper. The procedure described in subsection 2.2. was followed in all experiments, except for the quality of the P4000 paper.

Table 3.1.5. The effect of acid chain length at comparable acid concentrations, results from crystals polished with the worn-out P4000 paper. C12TAB (1 wt.%) was used as surfactant. 0.2 and 0.25 M relate to AN = 15.38 and 19.23, respectively.

Acid	Avg. CA	Range
Decanoic (0.25 M)	38°	8°
Lauric (0.25 M)	49°	16°
Myristic (0.2 M)	33°	4°

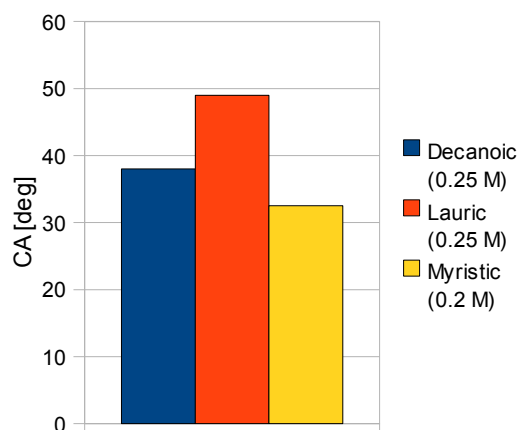


Figure 3.1.8. The effect of acid chain length at comparable acid concentrations, results from crystals polished with the worn-out P4000 paper. C12TAB (1 wt.%) was used as surfactant.

It was believed that the desorption of carboxylic acids would decrease as the hydrocarbon chain increase, and the contact angles would increase as a result. Comparing Figs. 3.1.8 and 3.1.9 using lauric acid as calibration reference, this was partly observed. Stearic acid, with a hydrocarbon

chain of length 18, resulted in the highest contact angles even if the concentration was several orders of magnitude lower than lauric acid, with a hydrocarbon chain of length 12, clearly demonstrating the importance of the chain length. This was also observed by Standnes and Austad (2003). Lauric acid in turn resulted in a higher contact angle than decanoic acid, with a hydrocarbon chain of length 10. However, myristic acid, with hydrocarbon chain of length 14, resulted in the smallest contact angle, where the results only slightly overlapped with the results using decanoic acid.

Table 3.1.6. The effect of acid chain length, results from crystals polished with the new P4000 paper. The concentrations are not comparable, but it is clearly illustrated that stearic acid is harder to desorb. C12TAB (1 wt.%) was used as surfactant. 0.25 and 0.005 M relate to AN = 19.23 and 0.38, respectively.

Acid	Avg. CA	Range
Lauric (0.25 M)	30°	13°
Stearic (0.005 M)	45	9°

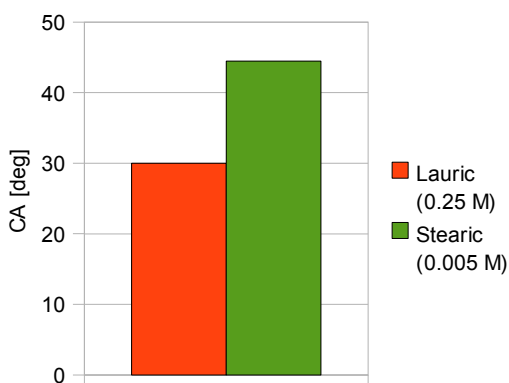


Figure 3.1.9. The effect of acid chain length, results from crystals polished with the new P4000 paper. C12TAB (1 wt.%) was used as surfactant.

3.1.8. Effect of acid concentration

The effect of acid concentration was investigated using C12TAB (1 wt.%) and lauric acid solutions of varying concentration. The procedure in subsection 2.2. was followed, and new P4000 papers

were used in all measurements. The results are presented in Table 3.1.7, and graphically in Fig. 3.1.10.

Table 3.1.7. The effect of acid concentration. C12TAB (1 wt.%) was used as surfactant, and lauric acid was used as crystal wettability modifier. 0.25, 0.1, and 0.01 M relate to AN = 19.23, 7.69, and 0.77, respectively.

Acid concentration	Avg. CA	Range
0.25 M	30°	13°
0.1 M	31°	9°
0.01 M	25°	5°

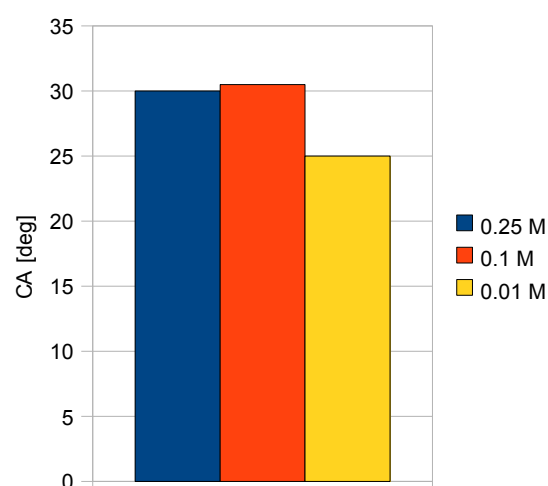


Figure 3.1.10. The effect of acid concentration, presented graphically. C12TAB (1 wt.%) was used as surfactant.

The concentration seemed to be of little importance, in contrast to imbibition experiments where increasing AN resulted in a larger decrease in the imbibition rate. The contact angles measured on the crystal aged in 0.25 M lauric acid overlapped strongly with the two other experiments. 0.1 M and 0.25 M concentrations are probably too close to each other to have a measurable effect. The results indicate that any of the acid concentrations fully saturate the crystal in carboxylic acid, but perhaps even lower concentrations would result in smaller contact angles. The acid concentration may have had a stronger influence on the contact angles had it been possible to form

surfactant drops while the crystals were still dissolved in carboxylic acid. Kolnes et al. (2008) observed a stronger dependence of acid concentration on brine drops deposited on crystals immersed in hexanoic acid dissolved in n-decane.

3.1.9. Effect of surfactant chain length

Four surfactants, C10TAB, C12TAB, C14TAB, and C16TAB, all 1 wt.%, were compared to each other, on crystals aged in lauric acid (worn-out P4000 paper was used) and stearic acid (new P4000 paper was used). Unfortunately, it was discovered too late that the concentration of C10TAB was below the CMC value. It is still included in the results as it performed better than expected in the stearic acid system. The results from the stearic acid system is presented in Table 3.1.8 and Fig. 3.1.11.

Table 3.1.8. Contact angles for various surfactants. Stearic acid (AN = 0.38/ 0.005 M) was used as crystal wettability modifier. All surfactant concentrations were 1 wt.%.

Surfactant	Avg. CA	Range
SSW	69°	22°
C10TAB (below CMC)	46°	10°
C12TAB	45°	9°
C14TAB	32°	13°
C16TAB	50°	9°

In the case where stearic acid was used, three of the surfactants gave very similar contact angles. It was observed that C12TAB and C10TAB resulted in the same contact angle, even though the C10TAB concentration was below CMC. The CMC value in this system could have been reduced if some desorbed stearic acid molecules formed mixed micelles with C10TAB surfactant molecules (Scamehorn, 1986; Standnes and Austad, 2003). The theory is based on Standnes and Austad's (2003) observations of that C10TAB above and below CMC resulted in similar contact

angles when stearic acid was used as crystal wettability modifier.

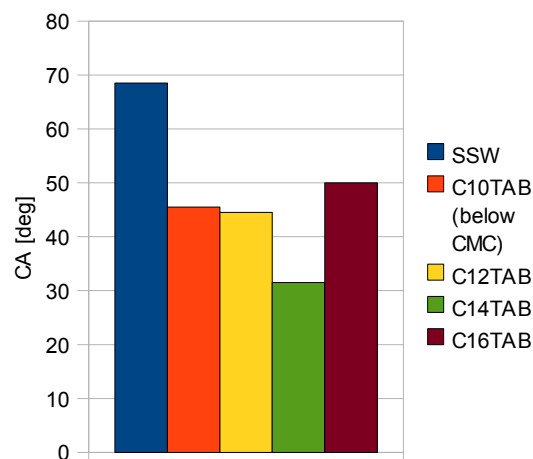


Figure 3.1.11. Contact angles for various surfactants. Stearic acid (AN = 0.38/ 0.005 M) was used as crystal wettability modifier. All surfactant concentrations were 1 wt.%.

The surfactants were ordered C14TAB < C12TAB ≈ C10TAB (below CMC) < C16TAB, where C14TAB resulted in the smallest contact angles. C16TAB contact angles were a little higher than C12TAB and C10TAB, but the contact angles measured on individual drops almost completely overlap, so a definite distinction of the surfactants cannot be made.

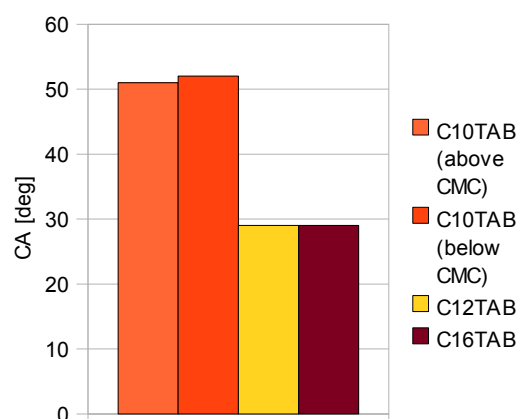


Figure 3.1.12. Standnes and Austad's (2003) contact angle results. Stearic acid was used as crystal wettability modifier, but the procedure was slightly different compared to this study: Aged in acid – aged in surfactant – DW drops deposited surrounded in air.

Standnes and Austad (2003) measured contact angles surrounded in air, otherwise their procedure was as described in subsection 3.1.6. The surfactants were ordered slightly differently, $C16TAB \approx C12TAB < C10TAB$ (below CMC) $\approx C10TAB$ (above CMC), as can be seen in Fig. 3.1.12 (the numerical values themselves may not be comparable to the results in this study, due to the different procedure). Observe that in Standnes and Austad's experiments, C16TAB resulted in the lowest contact angles.

Some surfactant and water drops from the study involving stearic acid are shown in Fig. 3.1.13.

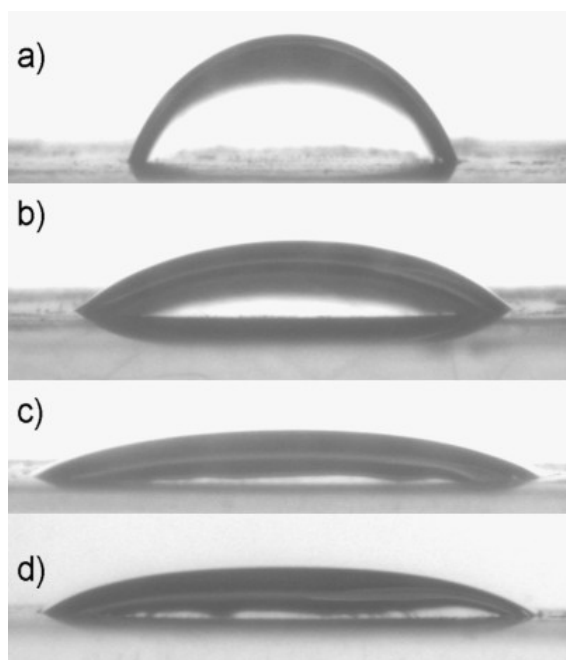


Figure 3.1.13. Four example drops from the stearic acid experiment. The pictures were taken after approximately 20 hours, and the contact angles observed at this time are a little lower than presented in Table 3.1.8 due to slight long-term instability. The drops are a) DW, b) C12TAB, c) C14TAB, and d) C16TAB.

The results from the lauric acid system are presented in Table 3.1.9 and Fig. 3.1.14. The surfactants were better separated when lauric acid was used as crystal wettability modifier, only a slight overlap between C16TAB and C14TAB was observed.

C10TAB (below CMC) was much less effective in this case, the behavior observed with stearic acid was not observed. This was also observed by Standnes and Austad (2003). This study and Standnes and Austad (2003) observed the same order of the surfactants, except Standnes and Austad did not perform measurements with C14TAB, they were ordered $C16TAB < C14TAB < C12TAB \ll C10TAB$ (below CMC).

Table 3.1.9. Contact angles for various surfactants. Lauric acid (AN = 19.23/ 0.25 M) was used as crystal wettability modifier. All surfactant concentrations were 1 wt.%.

Surfactant	Avg. CA	Range
C10TAB (below CMC)	73°	27°
C12TAB	49°	16°
C14TAB	44°	10°
C16TAB	37°	9°

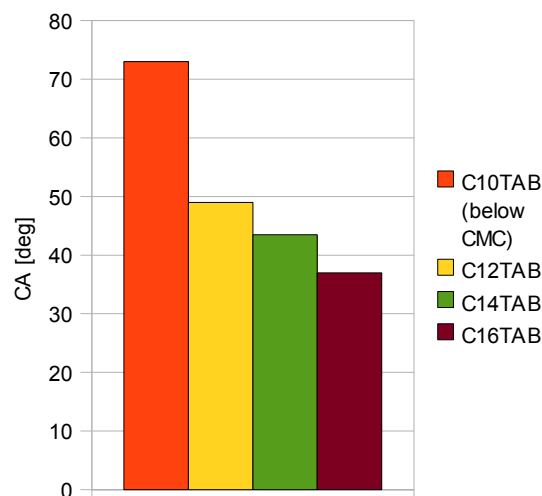


Figure 3.1.14. Contact angles for various surfactants. Lauric acid (AN = 19.23/ 0.25 M) was used as crystal wettability modifier. All surfactant concentrations were 1 wt.%.

Except for the slightly higher value of C16TAB contact angles when stearic acid was used, the surfactants' ability to desorb carboxylic acids increase with increasing hydrocarbon chain. Standnes and Austad (2000) proposed that surfactants with the longer hydrocarbon chains interact stronger with the adsorbed acids. For example,

C8TAB showed little hydrophobic interaction with adsorbed acids, both in contact angle and SI experiments (Standnes, 2001). However, the CMC value decreases with increasing hydrocarbon chain. The most effective surfactant is probably the surfactant which best balances the CMC value and length of the hydrocarbon chain (Standnes and Austad 2000).

Amott-test imbibition experiments with crude oil (AN = 1.73) by Standnes and Austad (2000) ordered the surfactants C12TAB \approx C10TAB > C16TAB, where C16TAB resulted in the slowest SI rate/smallest wettability alteration. All surfactants were above CMC. This is comparable to the contact angle results in the stearic acid case presented in this study (although it would be interesting to see how C14TAB ranked in SI experiments), but different to the lauric acid case. This showed that contact angles in a simplified system of individual carboxylic acids cannot be used to predict how surfactants will be ordered in SI experiments where crude oil has been used to alter the wettability of chalk cores, at least not with the current model developed in this study.

Standnes and Austad (2003) also performed contact angle measurements on crystals aged in in the same crude oil, and the surfactants were ordered C12TAB < C16TAB < C10TAB, where C12TAB resulted in the smallest contact angles/ best wettability alteration. Just a few degrees separated C10TAB and C16TAB. Even when the same crude oil was used as crystal wettability modifier, the surfactants were ordered a little differently to the SI experiments, but at the very least C12TAB was identified as the most effective surfactant in both types of experiments.

3.1.10. Effect of surfactant concentration

It was observed that, in accordance with most SI and contact angle measurements performed by Standnes (2001), surfactants

at concentrations below CMC resulted in poorer wettability alteration compared to the same surfactants at concentrations above CMC. The measurements were performed on a C12TAB/ lauric acid system, and the results are presented in Table 3.1.10.

Table 3.1.10. The effect of surfactant concentration. Lauric acid (AN = 19.23/ 0.25 M) was used as crystal wettability modifier.

Concentration	Avg. CA	Range
C12TAB 0.1 wt.%	39°	14°
C12TAB 1 wt.%	30°	13°

3.2. Imbibition time

3.2.1. General observations

It was first investigated whether contact angles and imbibition time could be measured simultaneously on the chalk slices. This was unsuccessful, because both surfactant and water drops resulted in similar contact angles around 150° when the slices were immersed in n-decane. This was not necessarily a bad thing, because the surface area available for imbibition was the same regardless of fluid. If a surfactant spread out more than water, the imbibition time would also be a function of the contact area. Only C16TAB spread out over a slightly larger area, but as a result the height of the drops decreased, and contact angles were still above 150°. Different contact angles on surfactants and water were observed when the drops were deposited on slices surrounded in air, but this procedure was not pursued.

It was first attempted to saturate the slices with 0.01 M (AN = 0.77) and 0.001 M (AN = 0.077) lauric acid, but neither water nor C12TAB imbibed after three days. DW and C12TAB drops imbibed in 12 and 10 minutes, respectively, when the slices were surrounded in air, but this procedure was as previously stated not pursued. A significant amount of evaporation would also take place during 10 minutes. Imbibition when the

slices were immersed in n-decane took place at concentrations 10^{-4} M ($AN = 7.7 \cdot 10^{-3}$) and lower. It was also attempted to saturate the slices in Naphthenic acid ($AN \approx 1$) from Acros, because it should be weaker adsorbed to the chalk, but again no water nor surfactant would imbibe. Lower AN may have given better results.

It was investigated if depositing a drop on one side of the slice, and let it imbibe, would affect the time a drop placed on the other side imbibed in. The slice was simply flipped 180° inside the n-decane cell. In most cases, this led to much faster imbibition on the second side, often as much as two to three times as fast. Interestingly, C12TAB drops placed on both sides usually imbibed in approximately the same time in almost all experiments, but this property was not shared by the other surfactants. All presented results are from measurements performed on the first drop deposited on a slice, as all slices were immersed in n-decane during measurements.

There were few variables involved. Thickness of the slices, time dried (3 hours – 2 days), and vacuum pressure. No correlations were found for any of these parameters. Multiple slices were saturated at the same time, and performing measurements on all slices required several hours, meaning some slices were stored outside of vacuum longer than others, but still immersed in the n-decane or carboxylic acid. No effect of this was documented.

3.2.2. Imbibition results

Slices were saturated in 94% n-decane as reference, 10^{-5} M ($AN = 7.7 \cdot 10^{-4}$) lauric acid, and 10^{-4} M ($AN = 7.7 \cdot 10^{-3}$) lauric acid. Surfactant drops were all 1 wt.% unless otherwise specified. Very poor repeatability was observed. Within slices saturated at the same time, measurements on the same imbibition fluid varied up to several minutes. Figure 3.2.1 shows a dataset with representable scatter.

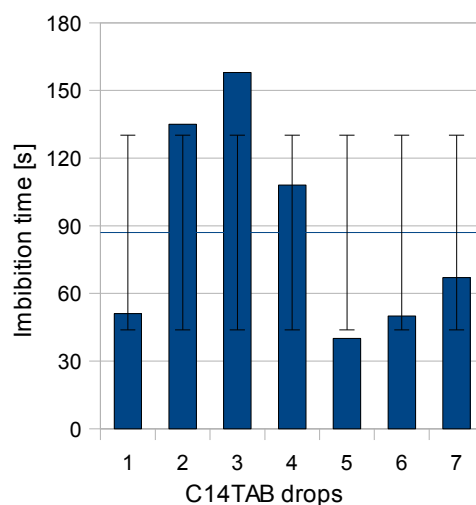


Figure 3.2.1. Typical scatter experienced, the mean value and standard deviation are indicated on the figure. The seven measurements were performed in one day on C14TAB drops deposited on chalk slices saturated in 10^{-5} M lauric acid.

Table 3.2.1. Results from the experiment on slices saturated in n-decane.

Fluid	Imb. Time [s]	Drops	Range [s]
DW	3	1	3
SSW	19	5	7 – 35
C12TAB	57	4	45 – 62
C14TAB	72	4	60 – 75

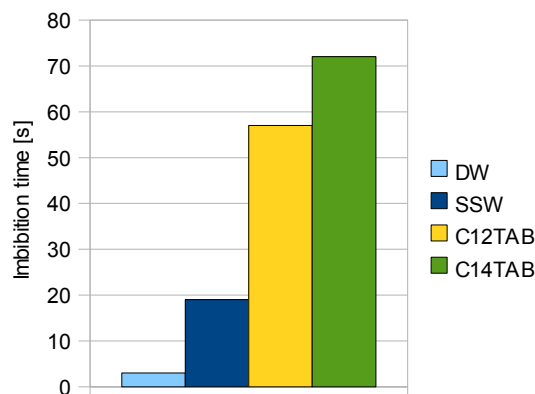


Figure 3.2.2. Results from measurements on slices saturated in n-decane presented graphically.

When the same experiment was repeated the next day, the results were often shifted several minutes from the previous results, and the order of the effectiveness of

surfactants and water was rearranged. DW or SSW drops often imbibed faster than surfactants.

The results from the slices saturated in n-decane are presented in Table 3.2.1 and Fig. 3.2.2. The range is represented by the shortest and longest imbibition time, to show how large the scatter is. The scatter was reasonably small in the n-decane measurements, except for SW drops. Surfactants seemed to inhibit imbibition when there was no acid dissolved in the n-decane. Since no wettability alteration was required, this makes sense if the imbibition is governed by capillary forces, as the reduced IFT caused by the surfactants decreases these forces.

Table 3.2.2. Results from the experiments on slices saturated in 10^{-5} M lauric acid. Surfactants and water are ordered by their effectiveness in each experiment. The different ordering of surfactants between experiments can easily be observed. The results are summarized in Table 3.2.3.

Fluid	Imb. Time [s]	Drops	Range [s]
Experiment 1			
C14TAB	65	2	59 – 71
C12TAB	174	2	154 – 193
SSW	275	2	212 – 337
Experiment 2			
C12TAB	71	4	47 – 90
C16TAB	74	2	73 – 75
C14TAB (below CMC)	100	1	-
SSW	103	7	34 – 255
Experiment 3			
DW	23	2	13 – 33
SSW	32	5	9 – 77
C12TAB	38	8	9 – 62
Experiment 4			
SSW	12	5	8 – 13
DW	13	3	11 – 16
C12TAB	40	6	33 – 55
C14TAB	54	5	29 – 100

The results from the slices saturated in 10^{-5} M lauric acid are presented in Table 3.2.2, and a total average in Table 3.2.3, which is also illustrated in Fig. 3.2.3. Poor

repeatability was observed in most experiments.

Table 3.2.3. Results from the experiments on slices saturated in 10^{-5} M lauric acid, mean values of all results presented in Table 3.2.2.

Imbibition fluid	Imbibition time [s]
DW	17
C14TAB	57
C12TAB	58
C16TAB	74
SSW	78
C14TAB (below CMC)	100

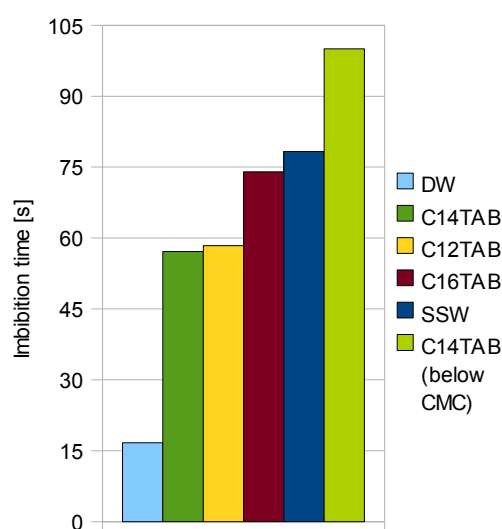


Figure 3.2.3. Results from the experiments on slices saturated in 10^{-5} M lauric acid, mean values of all results presented in Table 3.2.2.

The system may be very sensitive to small differences in concentration at low concentrations. The same lauric acid solution was not used in all experiments, new solutions were made as needed. This could explain the large scatter, but similar scatter was also observed in the experiments on slices saturated in 10^{-4} M lauric acid, and in those experiments the same solution was always used.

The results from the slices saturated in 10^{-4} M lauric acid are presented in Table 3.2.4, and a total average in Table 3.2.5, which is also illustrated in Fig. 3.2.4.

Table 3.2.4. Results from the experiments on slices saturated in 10^{-4} M lauric acid. Surfactants and water are ordered by their effectiveness in each experiment. The different ordering of imbibition fluids between experiments can easily be observed. The results are summarized in Table 3.2.5.

Fluid	Imb. Time [s]	Drops	Range [s]
Experiment 1			
C12TAB	100	4	71 – 134
SSW	184	3	152 – 218
DW	374	2	281 – 467
Experiment 2			
SSW	12	1	-
C12TAB	33	4	33 – 39
C14TAB	87	7	40 – 158
C16TAB	134	5	80 – 215
C10TAB (below CMC)	175	3	117 – 224
Experiment 3			
DW	199	9	9 – 900
Experiment 4			
SW	28	2	24 – 31
DW	161	3	12 – 325

Table 3.2.5. Results from the experiments on slices saturated in 10^{-4} M lauric acid, mean values of all results presented in Table 3.2.4.

Imbibition fluid	Imbibition time [s]
C12TAB	67
C14TAB	87
SSW	103
C16TAB	134
C10TAB (below CMC)	175
DW	215

It was observed that in many individual experiments, and partly in the two total summaries of all experiments, SSW and/ or DW imbibed faster than surfactants. At the lowest acid concentration, 10^{-5} M, DW outperformed SSW and all surfactants, which could mean the slices were only very weakly oil-wet. The results at the highest concentration, 10^{-4} M, were closer to the presented theory. DW imbibed slowest of all, indicating stronger oil-wetting, but it may still have been weak. SSW, which have the ability to alter the wettability itself, outperformed C16TAB and C10TAB, the

latter was below CMC. Surfactants reduce IFT, C16TAB the most of those tested, and imbibition time may have increased due to decreasing capillary forces. It made some sense that the surfactants which were outperformed by SSW were C16TAB and a surfactant at concentration below CMC, as these were shown to result in the weakest wettability alteration in Amott-tests performed by Standnes and Austad (2000). If it was possible for drops to imbibe at higher acid concentrations, there is a possibility that these two surfactants also had outperformed SSW, as the water would imbibe slower.

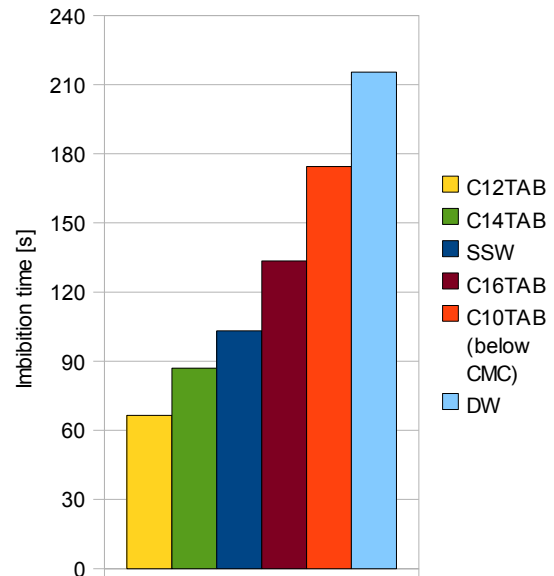


Figure 3.2.4. Results from the experiments on slices saturated in 10^{-4} M lauric acid, mean values of all results presented in Table 3.2.4.

Surfactants at concentrations below CMC imbibed slower than surfactants at concentrations above CMC, which is according to the presented theory.

The most effective surfactants were C12TAB and C14TAB at both acid concentrations while C16TAB was less effective, which is in accordance with SI experiments (Amott-tests) on chalk cores saturated in crude oil performed by Standnes and Austad (2000). However, in the contact

angle experiments on calcite crystals aged in lauric acid, C16TAB resulted in the smallest contact angles. This was also observed by Standnes and Austad (2003). C16TAB has a much lower CMC value than C12TAB and C14TAB, and as a result, a lower monomer concentration. Standnes and Austad's (2003) theory was that the monomer concentration was less important in static experiments such as contact angle measurements, compared to hydrophobic interaction. Having the longest hydrocarbon chain of the tested surfactants, C16TAB possesses the strongest hydrophobic interaction, but even in contact angle experiments the concentration must be above CMC to offer the most effective wettability alteration. This has been shown by both Standnes (2001) and in this study. In imbibition experiments however, both in the Amott tests as performed by Standnes and Austad (2000), and the simple experiments performed in this study, a balance between high CMC (high monomer concentration) and hydrophobic interaction is most effective, and the observed ordering of surfactants was as expected.

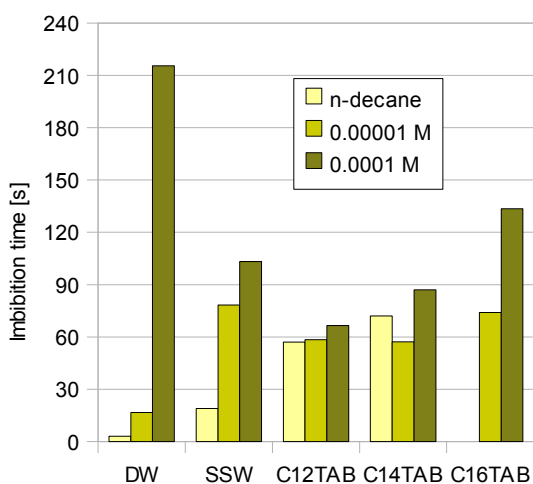


Figure 3.2.5. Increasing imbibition time as function of acid concentration.

All imbibition fluids imbibed slower as the acid concentration increased which is according to the presented theory, except in

one case, as seen in Fig. 3.2.5. This can be attributed to the large scatter observed.

3.2.3. Oil expulsion

Large oil bubbles usually formed inside the surfactant drops. This is shown in Fig. 3.2.6, which shows the entire imbibition process of a C12TAB drop. The bubbles stuck to the chalk surface, they were rarely observed to float to the top of the water/surfactant drops, and if they did, they did not penetrate the water-oil interface. When the surfactant was completely imbibed, the oil bubbles would often remain on the chalk surface for a short time before they burst. A thin membrane of carboxylic acids and surfactants seemed to protect the drops from immediately dissolving in the oil. The oil bubbles' total volume was less than the volume of the surfactant drops, and in some cases no oil bubbles were observed, so oil must also have been expelled in other directions.

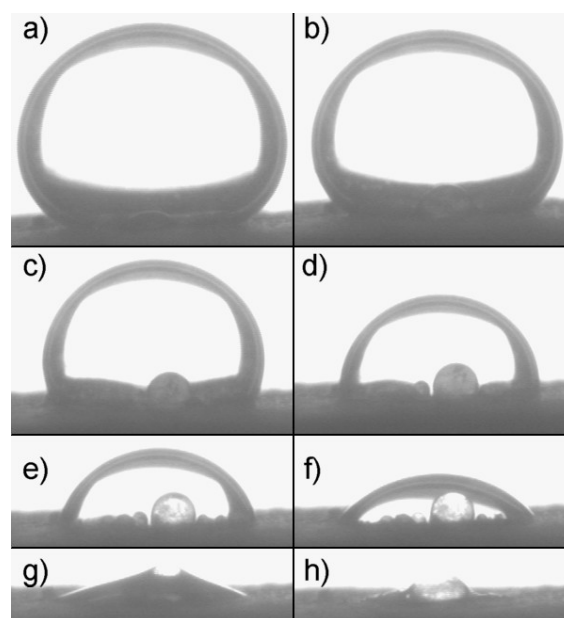


Figure 3.2.6. Imbibition of a C12TAB drop into chalk saturated in 10^{-5} M lauric acid. The drop imbibed in 29 seconds, the pictures show the drop after a) 2 seconds, b) 6 seconds, c) 14 seconds, d) 21 seconds, e) 24 seconds, f) 26 seconds, g) 28 seconds, and h) 29 seconds. The oil bubble burst in less than a second after the last shot was taken.

Oil was also expelled along the calcite-drop-decane contact. Microscopic bubbles were expelled around the drop, and attached to the drop surface where they aggregated into larger flakes on surfactant drops, which moved like a solid, or into looser bound structures on DW drops, as shown in Fig. 3.2.7. Large bubbles were rarely observed inside DW or SSW drops, in most cases only small bubbles along the drop surface were observed.

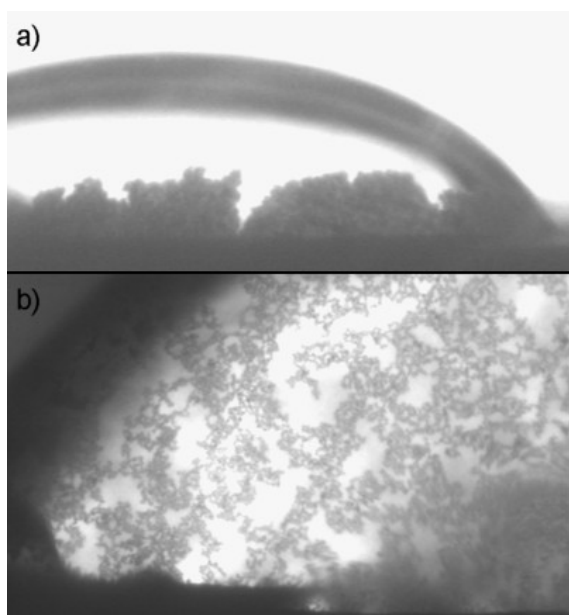


Figure 3.2.7. Structures formed on drop surfaces, a) C14TAB, chalk slice saturated in 10^{-5} M lauric acid, and b) DW, chalk slices saturated in 10^{-4} M lauric acid.

Various mixtures of n-decane, lauric acid, surfactants, and water were put in glass bottles and shaken. In surfactant-lauric acid systems a white, slightly rigid foam-like substance formed in the middle, the thickness seemed to increase with increasing surfactant concentration. An example is shown in Fig. 3.2.8. The oil-phase on top was completely clear, while the water phase in the bottom was muddy white indicating that some products in the middle phase were dissolved in the water-phase. In surfactants-decane, lauric acid-water, and decane-water systems, no foam was formed.

It is unknown if the formation of this substance in surfactant-acid systems had an effect on the imbibition experiments. No trace of it could be seen after a drop had imbibed. If formed along the surfactant-carboxylic acid contact inside the pores, it could perhaps inhibit imbibition, but the reason SSW and DW often outperform the surfactants is most likely related to weakly oil-wet chalk as previously described.

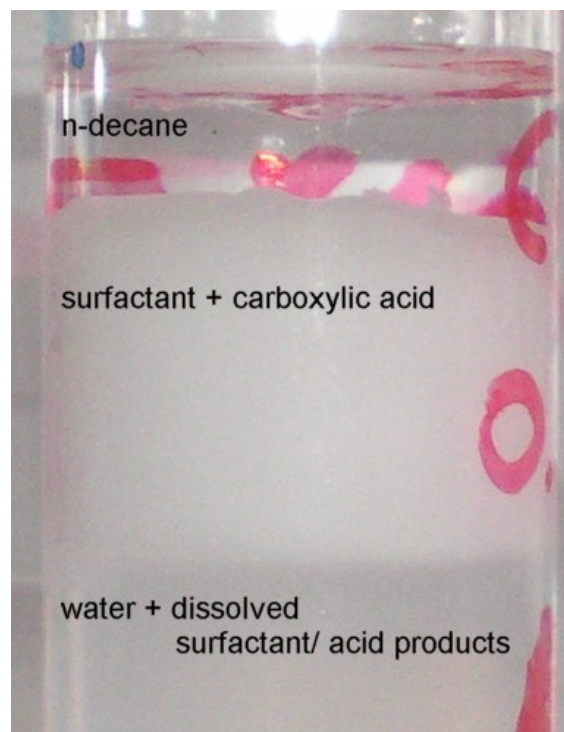


Figure 3.2.8. Mixture of C14TAB dissolved in DW and lauric acid dissolved in n-decane.

4. Conclusion

(1) The procedure to measure contact angles on oil-wet calcite crystals immersed in n-decane offered good repeatability, and it was possible to detect differences in wettability alteration induced by similar surfactants or similar carboxylic acids.

(2) Lower contact angles were obtained with increasing carboxylic acid concentration, although less than expected, and when the surfactant concentration was decreased below CMC, which is according

to theory. Increasing the acid chain length resulted in higher contact angles, except in one case. However, the effectiveness of the surfactants were ordered differently depending on which carboxylic acid was applied as crystal wettability modifier. Crude oil will probably give the most representable result if measurements are performed with a specific reservoir in mind.

(3) When lauric acid was used to oil-wet the calcite crystals, the surfactants were ordered C16TAB < C14TAB < C12TAB < surfactants below CMC. In the case of stearic acid, they were ordered C14TAB < C12TAB \approx C10TAB (below CMC) < C16TAB. The results are close to the ordering reported by Standnes and Austad (2003), with the exception of C16TAB in the stearic acid case performing worse. The results are otherwise comparable to the Amott-tests.

Compared to Standnes and Austad's (2003) Amott-tests, C16TAB ranked too high in one of the contact angle experiments. This was explained by that high surfactant monomer concentration (high CMC value) was less important than hydrophobic interaction in static experiments.

(4) Great care must be taken when polishing crystals, the crystals must appear identical to offer good repeatability. Other parameters like drop volume and deposition are also important, and results from experiments with slight deviations in the procedure may not be comparable to each other.

(5) The developed procedure to measure imbibition time into oil-wet outcrop chalk slices offered poor repeatability. According to theory, the imbibition time for each imbibition fluid increased as the carboxylic acid concentration increased, and when the surfactant concentration was decreased below CMC. However, water, including brine, occasionally imbibed faster than surfactants, which should not have been the case if the chalk slices were oil-wet. Very

low carboxylic acid concentration, 10^{-4} M (AN = $7.7 \cdot 10^{-3}$) lauric acid, was required for drops to imbibe at all, and the decrease in IFT caused by surfactants could explain why the least effective surfactants, C16TAB and surfactants below CMC, imbibed slower than SSW when the slices were only weakly oil-wet.

(6) In the imbibition experiments, the surfactants were ordered C14TAB \approx C12TAB < C16TAB < surfactants at concentrations below CMC, which is the same order observed in Standnes and Austad's (2000) Amott-tests (where crude oil was used instead of lauric acid), except Standnes did not perform experiments with C14TAB.

Nomenclature

A	One of two crystals mostly used
AN	Acid number [mg KOH/ g oil]
B	One of two crystals mostly used
CA	Contact angle (in tables and figures) [deg]
CMC	Critical Micelle Concentration [wt.%]
CnTAB	alkyl-trimethylammonium bromides
DW	Distilled water
EO	Ethoxy-group
EOR	Enhanced Oil Recovery
FW	Synthetic formation water
IFT	Interfacial tension [N/m]
P4000	Sandpaper, median particle diameter $\sim 3 \mu\text{m}$
P_c	Capillary pressure [Pa]
$P_{\text{non-wett. ph.}}$	Pressure in wetting phase, oil or water [Pa]
$P_{\text{wett. phase}}$	Pressure in non-wetting phase [Pa]
SI	Spontaneous imbibition
SSW	Synthetic sea-water
TDS	Total dissolved solid [g/L]
θ_c	Contact angle [deg]
σ_{os}	Oil-solid IFT [N/m]
σ_{ow}	Oil-water IFT [N/m]
σ_{ws}	Water-solid IFT [N/m]

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