UNIVERSITI
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PETRONAS

‘’Effect of Temperature And Aging Time Factor On Wettability Alteration During Surfactant Flooding Process’’

By

Atefeh Zamani

17850

Dissertation submitted in partial fulfilment of the requirements for the degree of Study (Hons)

(Petroleum Engineering)

FYP II, May 2015

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

ATEFEH ZAMANI

Abstract

About half of world’s known oil reserves are in carbonate reservoirs (Roehl 1985). However, many carbonate reservoirs (about 80%) are mixed-wet or oil-wet (Downs, 1989). Hence the efficiency of water flooding is very low as the rock surface is oil wet. In such cases using surfactant flooding has been suggested many times as an advantageous replacement for secondary recovery (Seethepalli et al 2004, Lu et al 2014). Surfactant flooding is an efficient approach for oil recovery from the carbonate reservoirs by a recovery of up to 70% Oil in Place or OOIP (Austad et al 1997, Standnes, et al 2003, Lu et al 2014). As the rock surface prefers oil, spontaneous imbibition does not occur in the reservoir, so break through time decreases and water cut approaches sooner, increasing water production while decreasing the beneficial oil production. In this study Dodecyl Trimethyl Ammonium Bromide or in abbreviation form DTAB is used as the surfactant element for wettability alteration from hydrophobic to hydrophilic in the limestone cores, to find the impact of temperature and aging time. It is observed that DTAB surfactant’s optimum workability is at T=80°C and for surfactant concentration 1.5 W%. The results show that in lower temperatures also the best result is gained for a higher concentration.

Acknowledgment

My appreciations to God, for making this opportunity possible for me to undertake my studies in UTP and secondly to my parents without whose support and resources this experience would not have been made possible for me. This FYP owns its improvement and completion from the first day to my supervisor, Mr. Muhammad Luqman B Hasan, whose strong support impacted my work to take it as serious as possible, and whose guidance was my candle all the way from the very start to the very end, and then to my coordinators Mr. Titus Ntow Ofei and Mr. Asif Zamir whose coordination during FYP1 and FYP2 was a big dedication to improving this FYP work in a comfortable manner. My everlasting gratitude to Dr Mohammed Idrees Ali, who was my examiner during FYP1 and FYP2, with the questioning of whom I was encouraged for betterment of my project.

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Abbreviations and Nomenclatures

DOE (Design OF Experiment)

EOR (Enhanced oil recovery)

Interfacial Tension (IFT)

Dodecyl Trimethyl Ammonium Bromide (DTAB)

Oil/Brine/Rock (OBR)

United States Bureau of Mines (USBM)

Oil Oringinally In Place (OOIP)

Cetyl Trimethyl Ammonium Bromide (CTAB)

Total Dissolved Solid (TDS)

Response Surface Method (RSM)

Central Composite Design (CCD)

Analysis of Variance (ANOVA)

Chapter 1 Introduction

1.1 Background of Study

Surfactant flooding is an Enhanced Oil Recovery method for wettability alteration and lowering interfacial tension (IFT) between injected water and reservoir oil towards improving oil recovery in oil wet or mixed wet reservoirs. Surfactant can act in several ways to contribute to enhanced oil recovery (EOR):

1) Lowering interfacial tension between the oil trapped in small pores and the water surrounding those pores in order to mobilize the oil.

2) Altering the matrix wettability toward water wet (Imbibition process).

After primary recovery in the reservoir, water flooding is the usual way to push the oil in front of the water towards the production wells but in oil wet or mixed – wet rocks ability of the matrix to imbibe the water is poor. In this condition break through occurs very soon and the water oil ratio is too high, thereby production cost increases dramatically and there is a chance of abandoning the well. Although the real potential of the reservoir is still high with 50 – 70% of the original oil still in place.

In such cases, chemical enhanced oil recovery is applied using surfactant flooding to reduce the IFT, change the wettability, increase the spontaneous imbibition of water injected and finally for improving oil recovery.

Surfactant based EOR is receiving attention because the technique have had great potential for mobilizing residual oil in reservoirs (Barnes, et al., 2012). Since water flooding is applicable best for highly permeable layers in the water-wet reservoirs, the recovery factor for carbonate reservoirs is low because injected water sweeps only the high-permeability layer, leaving the low-permeability layer behind.

By altering the wettability in this condition and using spontaneous imbibition process the oil recovery can be improved, thus wettability is a very important factor in oil recovery processes, because it has strong impact on the distribution, location and flow of oil and water in the reservoir during production (Anderson, 1986b; Anderson, 1986a). Understanding the mechanisms behind wettability alteration could help improving its performance. Of the factors contributing to wettability alteration are surfactant concentration and temperature impact on it. Choosing the right temperature and concentration window not only can save expenses, but also helps improve the process performance, on which not a lot of researches are available.

1.2 Problem Statement

Primary recovery of oil utilizes the natural energy in the reservoir but production is often limited to about 15% of original oil in place. Secondary recovery mechanism, like water flooding, increases oil recovery to only about 30% of original oil in place. After water flooding, as much as 60% of the original oil is still left trapped in the pores in the reservoir due to high capillary pressure from water.

Water flooding efficiency in oil wet reservoirs is low because the wettability causes the rock surface to naturally prefer oil over water. Hence rock won’t show spontaneous imbibition characteristics and water is not adsorbed by the rock surface naturally. This speeds up breakthrough time, decreasing oil production and increasing water production from the well as the water cut achieves sooner. As about half of world’s known oil reserves are in carbonates and many carbonate reservoirs (about 80%) are mixed-wet or oil-wet in the case for which water flooding does not dedicate enough to oil production recovery, while surfactant flooding is a solution to that problem.

Different carbonate reservoirs are located in different parts of the world, with different temperatures but the impacts of temperature alteration has not been studied enough in previous researches. That is why the impact of an effective temperature is important for an advantageous surfactant flooding, which on one hand will help define a beneficial reactivity window of the applied surfactant, and on the other hand helps reduce costs of surfactant purchase as an expensive material.

1.3 Objective

To find the impact of temperature and aging time on surfactant flooding to define a suitable range of workability for surfactant flooding using DTAB in carbonate reservoirs.

1.4 Scope of the Study

This paper focuses on the impact of temperature on wettability alteration as it has been suggested by many researchers that temperature alteration can improve wettability (Wang and Gupta, 1995; Morrow et al., 1986; Chimienti et al, 1999, Graue et al., 1998., Zhou et al., 1995., Xie and Morrow, 2001; Xie et al, 2005; Tie and Morrow, 2005).

On the other hand many previous works showed that water-wet reservoirs have higher recovery (Donaldson and Thomas, 1966; Owens and Archer, 1971), while also some researches oppose the idea that strongly water-wet reservoirs have higher recovery (Richardson et al., 1955; Amott, 1959; Denekas et al., 1959; Treiber et al. (1972) .

In this study a crude oil sample is used to investigate the effect of the understudied surfactant on wettability alteration. The core plug used is synthesised limestone core plugs. The surfactant that will be used is Dodecyl Trimethyl Ammonium Bromide (DTAB) with chemical formula $C_{12}H_{25}N\text{-}(CH_3)\text{-}Br$ purchased from Sigma company. To achieve the objectives of this research following methods and equipment are used:

1. To design the experiment, Design Expert application is used.
2. Contact angle measurements for surveying wettability alteration is done using Camera part of IFT 700 Tensiometer, in a method called sessile drop method, available in UTP reservoir studies lab located in Block 15.
3. AutoCAD software is used for measuring the angles of the photos produced by IFT 700 camera.

Chapter 2 Literature review

2.1 Wettability

Wettability is defined as “the tendency of a fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Anderson, W.G., 1986a.). Wettability is considered as a key parameter in oil recovery studies because it can affect the fluid location, fluid flow, residual oil saturation and distribution in rocks (Anderson, W.G., 1986a. and 1986b). Wettability is the indicator of remaining residual oil saturation in the rock pores after secondary recovery. There are 3 main wettability defined for a rock. Water-wet, oil-wet, and mixed wet.

Number one factor effecting oil recovery in a reservoir is its tenancy towards water wet state. Wettability determines the stability of the oil film in the reservoir surface (Zhichu 2003). Surface adsorption means operate the hydrophobicity alteration method in such a way to increase water adsorption on the reservoir rock’s surface.

On the other hand out of the many factors influencing wettability is temperature. According to previous studies, temperature alteration, directs rock wettability to be more water-wet (Wang & Gupta, 1995).

2.1.1 Water-wettability

Water wettability is the status when the rock surface has a tendency toward water adsorption. Most of sand stones are water-wet for which water flooding recovery is high.

2.1.2 Oil-wettability

Oil wettability is defined as the status when the surface of the rock has tendency to adhere oil rather than water, oil-wettability is either a natural tendency due to rock’s formation characteristic, or it can occur at the last stages of a reservoir’s life when reservoir is facing depletion. Water flooding is not a god option in these cases.

2.1.3 Mixed-wettability

Mixed wettability is a condition caused due to complex OBR interactions which was firstly developed in the 1970’s. This term is used in cases where the wettability is not continuous or is inhomogeneous. There is a different between intermediate wetting and mixed wetting; a rock with intermediate wetting does not have strong desire to adsorb water over oil, but a mixed wet condition is a neutral wetting condition where the rock prefers either of oil or water.

In the case of both oil-wet and mixed-wet reservoirs, since oil is adhered to the rock surface, disturbing oil flow, lowering S_{or}, which opens a continuous path for water-flow, which reduces water breakthrough time and so that the more water injected to the reservoir from the injection wells, the more water is produced from the production well; this way the oil recovery reduces as water saturation increase continuously.
The figure 1 shows the differences between the wetting statuses.

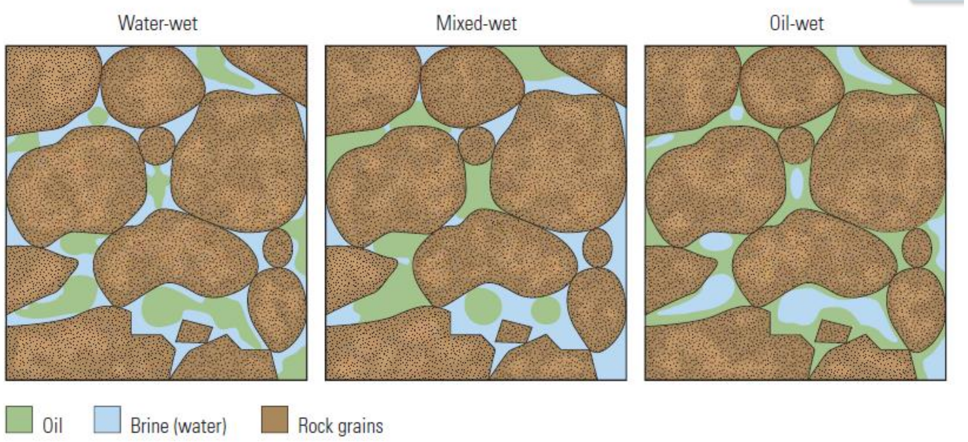


Figure 1. Wetting condition in pores with similar oil and water saturations.[60]

As it can be seen from the figure1 , in case of water-wet rock, oil traps in middle of pores while water adheres to surfaces, whereas for oil-wet condition, water traps in the middle and oil adheres to surfaces. In a mixed-wet case, oil is able to displace some water from the pores and is adsorbed to the surfaces.

2.2 Spontaneous Imbibition

Imbibition is the process of absorbing a wetting phase into a porous rock. Spontaneous imbibition is the natural ability of the porous media to adsorb the wetting without applying pressure which is an important water drive mechanism since it motivates water mobilisation. In this case study as after applying the surfactant flood, forced imbibition occurs during which the wetting phase (water) displaces the non-wet phase (oil), sweeping the oil from the reservoir which increases reservoir productivity (Xie et al., 2001).

2.3 Wettability Alteration

As a reservoir depletes, wettability changes as the remaining oil is pushed back to the capillary pressure pores, a process implied by capillary pressure force. In order to understand this phenomena, oil/brine/rock (OBR) relationship should be known. Especially in case of carbonate reservoirs which are usually naturally fractured, studying OBR behaviour is even of more importance. This point is where imbibition and wettability cross. In naturally fractured reservoirs imbibition occurs as a natural process, but as time passes by and the OBR equilibrium in the reservoir is disturbed. Wettability changes from water wet to oil wet which decreases water mobility, so spontaneous imbibition which is a beneficial element to oil recovery eliminates. In order to return the imbibition to the production cycle, wettability needs to be changed toward water wet.

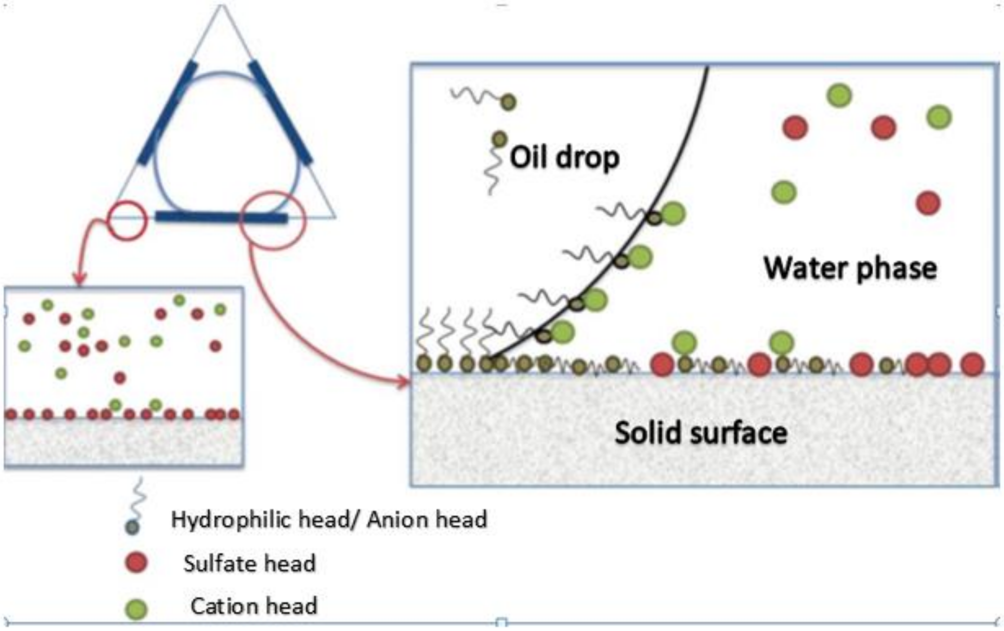


Figure 2. OBR interaction.[44]

As per the figure 2 , considering a small portion of the surface where all existing phases are at equilibrium. The surfactant acts as a bridge between the 2 phases of oil and water, from one head (Anion tail) the surfactant connects to oil and from the other side it is connected to water phase. Also the sulphate, molecules react with the solid surface.

As the water saturation increases oil saturation decreases, and since water is less viscous than oil so water mobility is higher in water wet reservoirs, giving a better flow distribution to water phase in the reservoir, sweeping a larger area. Although in case of carbonates which are oil-wet, all this process is opposite. In this case also OBR interactions are the determining factor which on the other hand in a detailed overview are themselves controlled by particle adsorption between polar oil components and rock surface (Denekas et al., 1959, Lowe et al., 1973; Cuiec, 1984; Buckley, 2002). The attempt is to break the strong OBR chains in oil-wet reservoirs. This cannot be done unless appropriate chemicals are applied a method which is known as chemical flooding.

2.4 Wettability Measurement/Contact Angle Method

Contact angle measurements for surveying wettability alteration is done using Camera part of IFT 700 Tensiometer, in a method called sessile drop method , available in UTP reservoir studies lab located in Block 15. This method have been suggested by many researches and firms as a quantitative assessment method, such as the following: (Newcombe et al., 1955; Leach et al., 1962; Treiber et al., 1972; Chilingar and Yen, 1983), United States Bureau of Mines (USBM) method, Donaldson et al., 1969.

Figure 3. IFT-700 Tensiometer equipment

In contact angle method a single brine drop is placed on the surface of the sample using a needle, and using computer and a strong camera a photo is taken which later on is used to asset the wettability. In this study the angles were measured each 1, 6.5 and 12 hours for different samples as per suggested by DOE software used in the experiment simulation, to find an optimum aging time.

According to definition if the measured angle between the drop and the rock is lower than 90 ° the surface is wettable. If the angle is equal to 90° the surface has mixed-wet characteristics and if the angle is more than 90° the surface is non-wet.

Figure 4. Contact angle image [online image] retrieved May 23, 2015, from www.biolinscientific.com

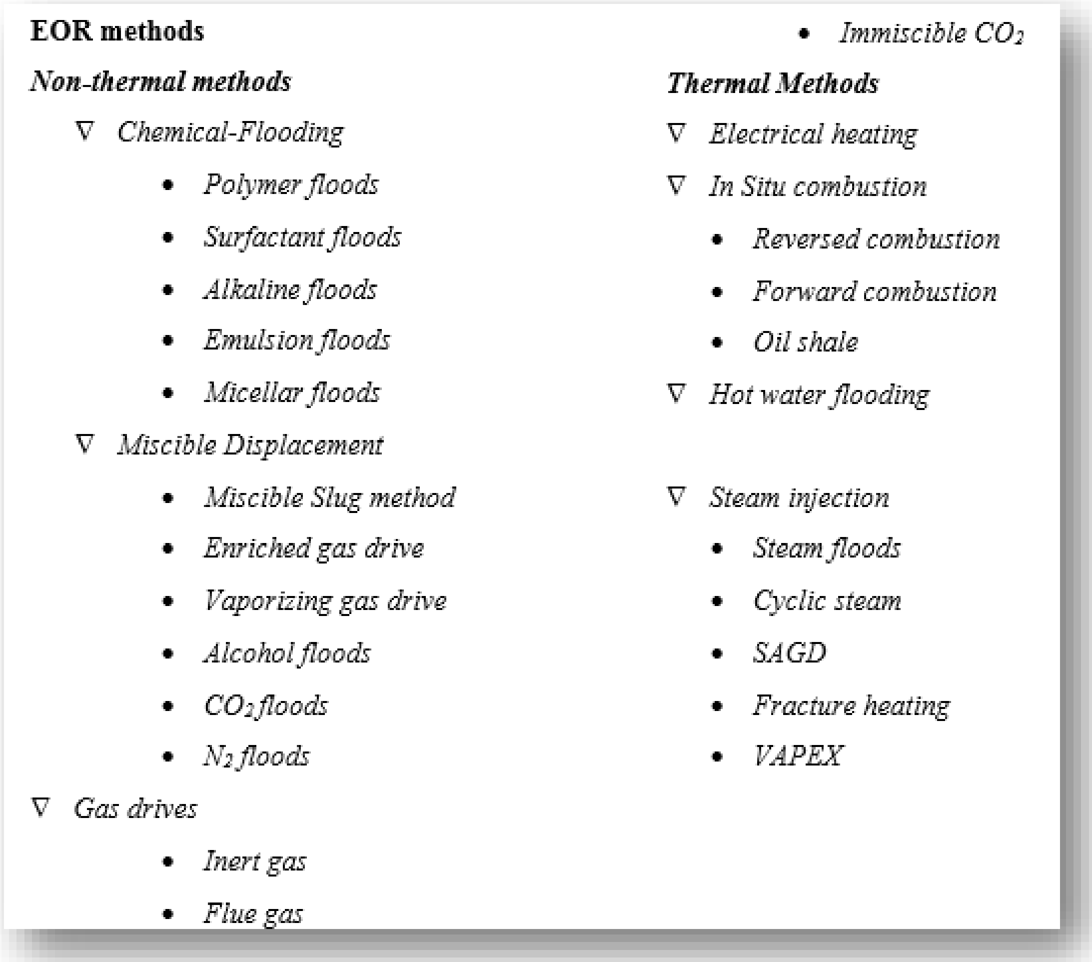
Figure 5. From Left To Right Hydrophilic Condition Increases

2.5 Primary, Secondary and Tertiary Recovery (EOR)

There are three main oil recovery methods classifications namely primary, secondary and tertiary methods.

Primary oil production methods include using the natural energy of the reservoir such solution gas (dissolved gas) method, gas cap (gravity drainage) method and water flux, while secondary means include water flooding and gas injection. The aim of the implying secondary methods is to maintain pressure by injecting a high pressure fluid to the reservoir. Although applying both methods leave almost 67% of the oil unrecovered.

Tertiary or Enhanced Oil Recovery (EOR) methods have been developed using the newest technologies and advances in the industry just in recent years as a backup for oil recovery. The sub-category of EOR methods consist of a large group thermal or non-thermal processes. A list of all available EOR methods can be found as per below:



EOR methods

Non-thermal methods

- ∇ *Chemical-Flooding*
  - *Polymer floods*
  - *Surfactant floods*
  - *Alkaline floods*
  - *Emulsion floods*
  - *Micellar floods*
- ∇ *Miscible Displacement*
  - *Miscible Slug method*
  - *Enriched gas drive*
  - *Vaporizing gas drive*
  - *Alcohol floods*
  - *CO_2 floods*
  - *N_2 floods*
- ∇ *Gas drives*
  - *Inert gas*
  - *Flue gas*
  - *Immiscible CO_2*

Thermal Methods

- ∇ *Electrical heating*
- ∇ *In Situ combustion*
  - *Reversed combustion*
  - *Forward combustion*
  - *Oil shale*
- ∇ *Hot water flooding*
- ∇ *Steam injection*
  - *Steam floods*
  - *Cyclic steam*
  - *SAGD*
  - *Fracture heating*
  - *VAPEX*

Figure 6. EOR methods

As the oil based industry are growing day by day, oil demand is also increasing. According to estimation the oil demand growth is 2-3% annually, reaching to up to 50% till the year 2035, so that the importance of being able to support such plea is being felt more and more.

On the other hand there is the constraints of oil exploration and drilling expenses which is one important limit on the way of producing new wells. As carbonates form half of the world's total reservoirs, and as many of the existing fields have reached or are reaching their decline phase, it seems more convenient to focus on producing the existing reservoirs to their potentials, which in the case of carbonates is recovering the 50% remaining OOIP using newer methods (e.g. EOR). In this research study surfactant flooding method is applied for carbonate reservoirs. As it can be seen from figure 6, surfactant flooding is a sub-category of chemical flooding. It is of mention that EOR will keep up the production phase from carbonates to provide oil for another 80 years.

2.6 Surfactant

Surfactant stands for Surface Active Agents. In definition Surfactants are wetting agents that reduce interfacial tension (IFT) of a liquid phase. Surfactants get adsorbed by the surface of the two liquids in a two phase system (oil-water), forming a separative layer (boundary) between the two phases, which causes the IFT between the surfaces of the immiscible fluids to decrease. Though this effect is not the only impact of surfactants, and they also are widely used as wettability alteration factors in oil recovery process.

Surfactants are amphiphilic, e.g. they have two different heads, a polar head and a non-polar head. The polar head is water-soluble and since water is also a polar molecule it is hydrophilic, and the non-polar head is hydrocarbon soluble and since HC is also a non-polar molecule this head is hydrophobic. This natural characteristic gives the surfactant to be physically attracted (e.g. adsorbed) to both water and HC in a reservoir, which apparently can be used to change the wettability of the reservoir.

In general there are two main surfactant classes based on their water-dissolution characteristics, ionic and non-ionic. Ionic structures are divided into two categories, anionic and cationic surfactants.

2.6.1 Ionic Surfactants

If solved in water, the reaction between the water molecules and the surfactant produces ion atoms.

2.6.1.1 Anionic Surfactants

If dissolved in water, this category produces an amphiphilic (neutral) head and a cation head. Some of the most common examples are: detergents, foams, soaps, dispersants, and wetting agents. This category have been used by Standnes and Austad, 2000a, Ronaldo et al., 2006; Golabi et al., 2009 .

2.6.1.2 Cationic Surfactants

If dissolved in water, this group of surfactants produces an amphiphilic cation head and an anion head. Usually the anion head is a halogen (e.g. F, Cl, Br, I, and At elements). Some of the most common examples are natural fatty amine salts and quaternary ammoniums, Cationic surfactants are more abundant than the anionic group. This group of surfactants have been used by Tabatabal et al., 1993; Xie et al., 2004, Golabi et al., 2009 and Golabi et al, 2012, Zhang and Austad (2005)

Current study is an experimental work on the impact temperature and aging time factor in surfactant flooding in the understudied carbonate rocks (limestone). On the other hand this study is also a of nano technology in EOR in the past decade, looking at its contributions as a potential EOR solution in reservoir engineering. The four main categories which will be looked at are the nano particles functions on IFT reduction, wettability alteration, and its subsequent impact on permeability and retention phenomena in porous media.

2.6.2 Non-ionic Surfactants

If dissolved in water, non-ionic surfactants do not produce any ions, since the hydrophilic head will not react with the water molecules due to low adsorption desire between the molecules. One example is polyethylene glycol oxide. This category have been introduced by Chen et al., 2000; Golabi et al., 2009.

2.7 Surfactant Flooding

Surfactant flooding is a type of Enhanced Oil Recovery (EOR), sub-category of chemical flood, using surfactant agent. Surfactant is used to mobilize the trapped oil in the reservoir where water flooding is not applicable. This method helps improve wettability in the reservoir for a more efficient recovery. (Seethepalli, 2004; Liu et al., 2004; Sheng, 2010, Heidari et al, 2014). Surfactant flooding changes reservoir's natural characteristics in the direction of producing the trapped through IFT reduction and wettability alteration. To achieve this, a suitable surfactant element is essential. In the case of this examination DTAB is that agent. According to Adibhatla (2006) using either dilute anionic and non-ionic surfactants reservoir recovery increase up to 60% in case of their understudied fractured oil-wet carbonate core samples, Delshad et al (2006) also verify the same results.

2.8 Micelle

Micelle is accumulation of surfactant's molecule disperse in the liquid phase. In other words, when the hydrophilic head of the surfactant connects to the surrounding water molecules and the hydrophilic head is connected to the surrounding non-polar (oil) molecules, a structure is developed which is called micelle.

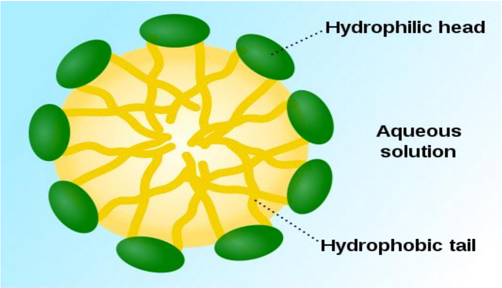


Figure 7. Micelle formation [68]

2.9 Breakthrough Time

In the reservoir, breakthrough time is the time period between injecting a phase into the reservoir and producing the same phase. After breakthrough occurs, injection is stopped since it won't increase the oil recovery any more. The more breakthrough time is delayed the more chemicals are adsorbed.

2.10 Water-Cut

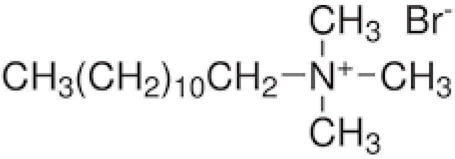
The ratio of the produced water to the total volume of produced liquids is called water-cut.

2.11 Aging Time

The time period of sleeping the sample core plugs in the surfactant is called the aging time.

2.12 Dodecyl Trimethyl Ammonium Bromide (DTAB)

The chemical formula is as followed. DTAB is widely used as an efficient surfactant. DTAB was selected for the purpose of this experiments since it is stable in aqueous solution at high temperatures.



$$CH_3(CH_2)_{10}CH_2-\overset{\overset{\Large CH_3\ \ Br^-}{|}}{\underset{\underset{\Large CH_3}{|}}{N^+}}-CH_3$$

Figure 8. DTAB chemical formation [69]

Dodecyltrimethylammonium Bromide, $C_{12}TAB$ or DTAB, is a cationic surfactant. DTAB is an amphiphilic chemical surfactant which is used in this project for wettability alteration in order to increase imbibition of the water into the rock matrix. Some of DTAB features are summarized as per the table 1 below.

Table1. Chemical characteristic of DTAB

Chemical formulation	$C_{15}H_{34}BrN$
Linear formulation	$CH_3(CH_2)_{11}N(CH_3)_3Br$
Description	Cationic ammonium surfactant
Molecular weight	308.34 g/mol
Melting temperature	246^oC
Color	White, or slightly yellow
State	Solid (powder)
Solubility	0.1M at 20^oC in water

DTAB is described as a quaternary ammonium cationic surfactant in the formula of which nitrogen cation is attached to four organic radicals (hydrocarbon family) and a negative bromine ion that neutralizes the positive charge of the nitrogen. From the other side being an amphiphilic chemical, DTAB has a lipophilic end which desorbs water molecules and a hydrophilic end which adsorbs the water molecules. The lipophilic or hydrophobic head is the long-chain organic radical, and the hydrophilic or lipophobic end is the part containing the Nitrogen atom. The DTAB used in this project is purchased from Sigma-Aldrich at 25^oC the and with a purity of approximately 99% according to the purchase details.

One of DTAB characteristic is its ability of spontaneously imbibing into limestone at high salinities, while when ameliorating the process at low temperatures (Hognesen et al. 2005). According to Austad et al. (1997) DTAB improves spontaneous imbibition of water in an almost oil-wet chalk rock improving the recovery by up to 70%, in other similar study by Sharma et al. (2011) the recovery is reported up to 72% OIP.In newer studies by Lane and Aderibigbe. (2013), it was shown that shale adsorbs DTAB through cationic exchange process and hydrophobic bonding. According to studies undertaken by Nguyen, and Sadeghi, (2011) applying DTAB helps break the alkali/surfactant/polymer or ASP emulsion formation at room temperature (25^oC). In other study by Seethepalli et al (2004) DTAB applied to change wettability in oil-wet carbonates successfully altered the wettability status to water- wet state.

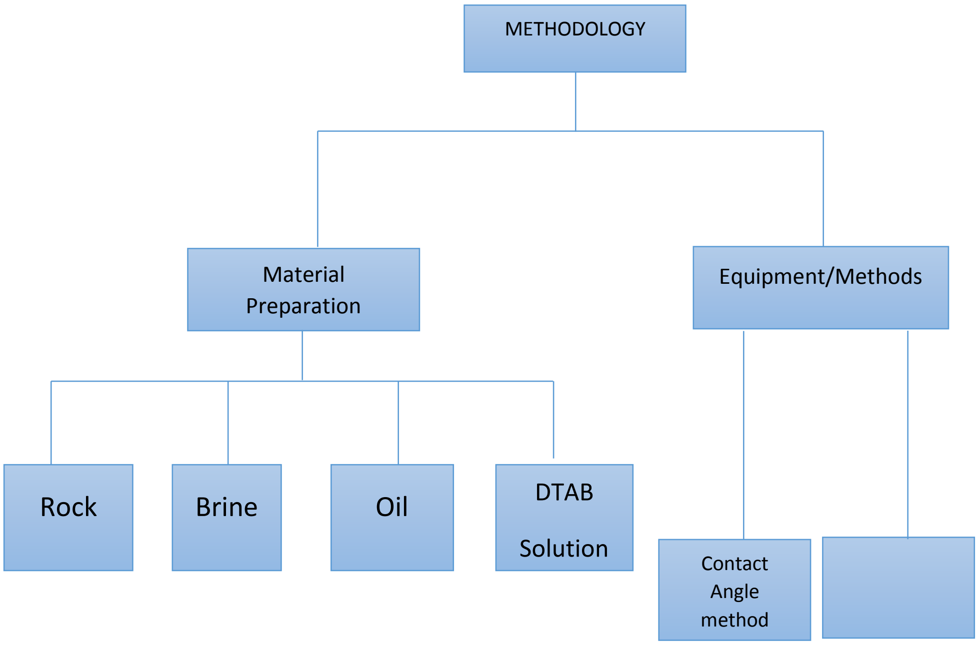
According to Sharma and Mohanty.(2011) cationic surfactants such as Cetyl Trimethyl Ammonium Bromide (CTAB), Dodecyl Trimethyl Ammonium Bromide (DTAB), Arquad C-50 and Arquad T-50are stable at high temperatures (100 ^oC). According to Standness and Austad (2000, 2003) cationic surfactants, such as DTAB induce imbibition in the originally wet- chalk core samples and so show up to 70% oil recovery in concentrations above (~1 wt. %).

Chapter 3 Methodology

3.1 Methodology

The methodology of the experiment is as per below. The steps include material preparation and wettability calculation method.

Figure 9. Methodology graph



3.2 Preparing Chemical Solutions and Formation Brine

Cationic surfactant with 1.5 Wight % and salts at different concentration will be dissolved in distilled water to prepare the chemical solutions. The synthetic formation brine is formed by adding formation water components to pure water at the same concentration in the lab.

3.3 Core Sample Cutting

The understudied core samples were received from Kocurek Industries, Inc. as a whole carbonate roll. The samples had to be cut and prepared accordingly for the sake of the experiment procedure. To do so, the cutting and grinding equipment is Block 15 core lab were used. The cutting procedure is per below:

1. Core plugs were cut out from the original core roll using GEOCUT Geological Cutter machine (core plug diameter 1.5 inch, length 3inch).

Figure 10. GEOCUT, Geological Cutter machine

2. Each core plug was cut 2 times, one time cross-sectional across the length of the plugs and one time radial across the radius to make half circle core slices. The reason for such cutting is that the contact angle measurement equipment (IFT 700) can only accept half circle slices (diameter of 1.5 inch) also all samples have same thickness (2 mm (0.079 inches) to eliminate possible width factor effect in further steps during oil-wetting.

Figure 11. Core Slice

3.4 Sample Preparation

The actual samples which will be used in the contact angle measurement experiment are the core slices. In order to make oil-wet core plugs to simulate oil-wet carbonate rock, the following steps are required:

3.4.1 Core Slice Prepration

1. Washing Core slices

To wash the core slices Soxhlet distillation extraction method was performed. The Soxhlet Extrator apparatus has been used for washing samples for almost 35 years upon invention. The device is made up of four parts, including a heater, a boiling flask, a chamber and a condenser as per figure 12 below. This device uses a solvent to clean the core slices and the cleanness of the core slices is determined by the color of the solvent after interaction to the sample. The samples will be placed in the chamber and the solvent placed in the boiling flask will be vaporized using theater. Then the solvent will be condensed in the condenser unit at the topper side of the device then the hot solvent liquid will run through the chamber where it pours into the chamber immersing the core samples, and finally cleaning them by dissolving and extracting the hydrocarbons inside the core slices. Then the solvent will be guided to the boiling flask again to be redistilled, and the cleaned solvent will re-enter the cycle again. This process will be repeated until the colour of the solvent indicates there is no more dirt (hydrocarbon) inside the core slices. The solvent used in extractor apparatus was toluene.

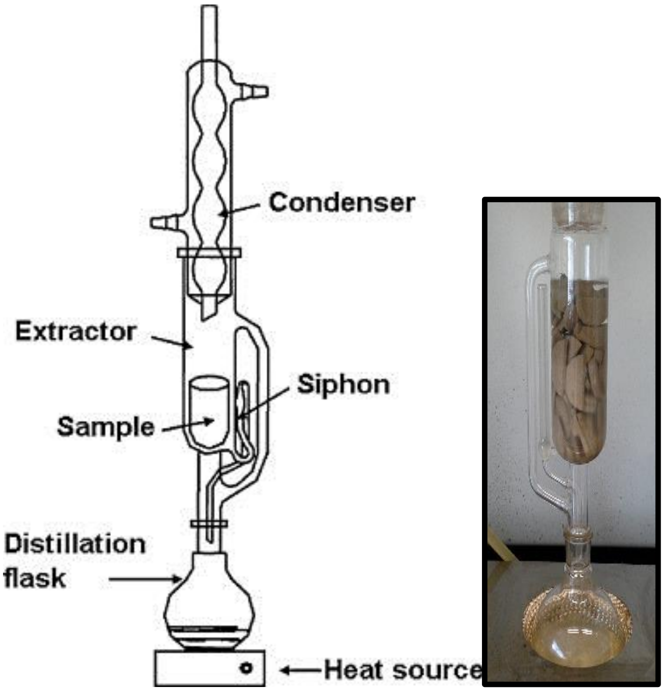


Figure 12. The configuration of Soxhlet extractor apparatus (left), Core Slices in Sochlet Extrator chamber filled with toluene (right)

2. Grinding and Polishing core slices

In this stage in order to remove any possible imperfection on the surface and making the most possible similar condition for the test samples a grinder machine is used. FORCIPOL 300 - 1V grinding and polishing machine was used for this process. Using different disks with different hardness, the samples are grinded. For the sake of the experiment to avoid damages to the core surfaces, a smooth disk was used. This is important since the aim is to eliminate irrelative external factors for contact angle measurements.

Figure 13. FORCIPOL 300 -1V grinding and polishing machine

3.4.2 Aging Process

Aging is defined as causing the same conditions as in the reservoir for the core samples. In order to produce fine oil-wet samples, two stages must take place. From the fact that the reservoir rock is initially filled with formation water which is displaced by oil later, the same will be done to the core samples. E.g. the samples will firstly be saturated by brine and later on by oil. The process is as per below.

1. Saturation with Formation water (brine)

In this stage the core slices are aged, immersing in brine for a duration of 5 days at 80°C in an oven (pre-migration state).

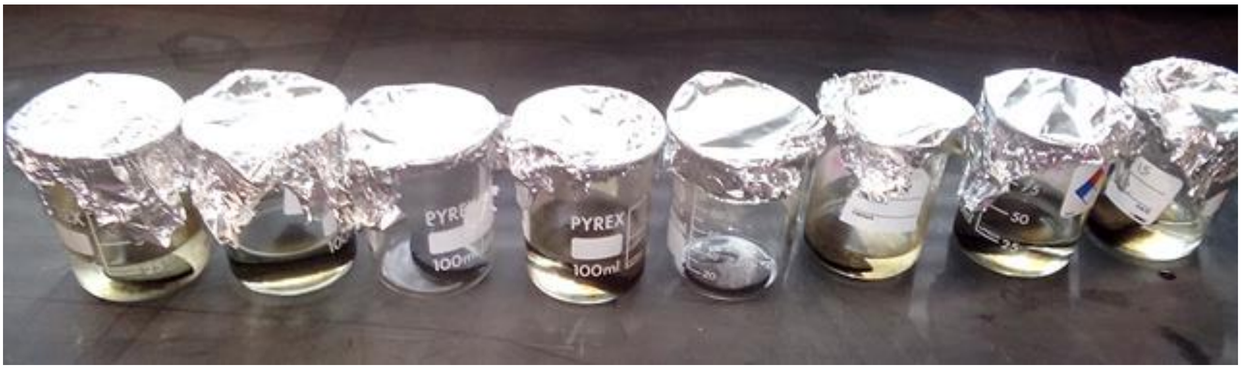


Figure 14. Core Slices immersed in different formtaion brines

2. Saturation with Oil

In this stage the core slices were aged using oil. The previous water saturated core samples were immersed in oil (ANGSI crude oil) and were made oil-wet at 80°C for 5 days in an oven. The oil will consequently displace the water phase causing oil-wetness conditions in the rocks (oil migration condition).

3.5 Preparation of Brines and Chemical Solutions

In order to prepare the liquid samples used in the experiment (e.g. brine and DTAB) simple chemistry concept is used. For brine solutions complexity is more since the brine used in the experiment is the A synthesized seawater which contains different chemical compositions. In this experiment as for saving the chemicals, the aim was to produce half a litre brine. The synthesized brine sample consists of the following salts with the concentration as defined.

Table2. Seawater Composition

Brine Composition	**Concentration gr/L**	**Concentration (ppm)**
NaCl	100	100,000
KCl	1	1,000
Na_2SO_4	50	50,000
$CaCl_2$	20	20,000
$MgCl_2$	50	50,000
$MgSO_4$	5	5,000
Total Dissolved Solid (TDS)	226	

The most suitable method to avoid chemical interaction between the ions while producing the right concentration of the solutions needed is to make liquid samples of each salt and then mix the liquids together in relation to their respective concentrations.

Solution making steps are as per follow:

1. Define the concentration of each sample needed.
2. Measure the correct mass amount of each salt using the digital balance equipment. In order to avoid chemicals interactions between the samples to be weighted on the same surface of the balance it is important to avoid chemical's direct touch to the surface; so that firstly the mass of a piece of paper is measured and then the desired amount of each chemical is added to it using a spoon until reach right mass.
3. Using a pipette and based on table 2 the right concentrations of each solution is added to a balloon slowly.
4. Distilled water is added to the previous balloon until reached desired volume (1L). The concentration of the product brine solution is 50,000ppm.
5. Work space is cleaned and all equipment are washed out and left to dry.

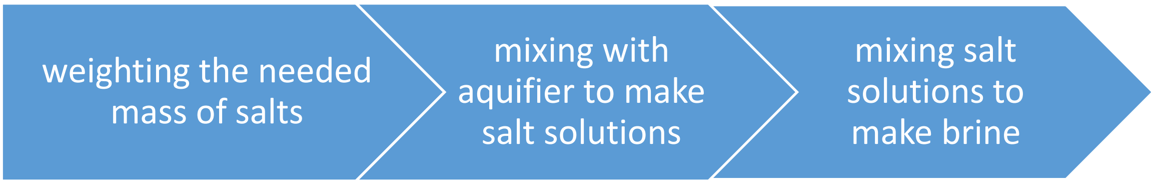


Figure15. Solution making summery

Calculations. In this experiment, 1L of brine with concentration of 50,000(ppm) was produced using salt solutions of 100,000ppm. To find the volume of the salt to mix with distilled water to produce such brine the following formula was applied which relates the concentration and volume of mixture of liquids before and after mixing.

$$V_1C_1 = V_2C_2 \longrightarrow V_{2=\frac{V_1C_1}{C_2}} \qquad \text{(Equation.1)}$$

V_1 and C_1 being the volume and concentration of the solution before mixing

V_2 and C_2 being the volume and concentration of the product mixture (brine)

A clear example would be brine preparation using 100,000ppm NaCl to produce a NaCl concentration of 20,000ppm in 50 millilitres solution. For this case then C_1= 100,000ppm, C_2=20,000ppm, V2=50ml, so to find V_2 applying the above formula we'll have:

$$V_1 = \frac{20{,}000\text{ppm X } 50\text{ml}}{100{,}000\text{ppm}} = 10\text{ml}$$

As for other components:

Table 3. Amount of Brine Components To Be Mixed

Brine Composition	V2
NaCl	10ml
KCl	1000ml
Na_2SO_4	20ml
$CaCl_2$	50ml
$MgCl_2$	20ml
$MgSO_4$	200ml

The same method is used for preparing DTAB solution. The volume-concentration correlation formula was also used to determine the amount of DTAB to be dissolved into the chemicals solutions. From the DTAB solution of 10gr/L, the aim is to produce 25ml of DTAB solutions of 0.3, 0.9, 1.5 gr/L in order of appearance. The value 25 ml is chosen based on necessity and the required concentrations are as per DOE the DTAB volumes used were as per below:

Table 4. DTAB Solution Prepration

DTAB solution concentration gr/L	**Required volume of DTAB**
0.3	1.35 ml
0.9	3.6 ml
1.5	6 ml

The calculated amount of DTAB is added to brine solution previously made to produce 25 ml of surfactant.

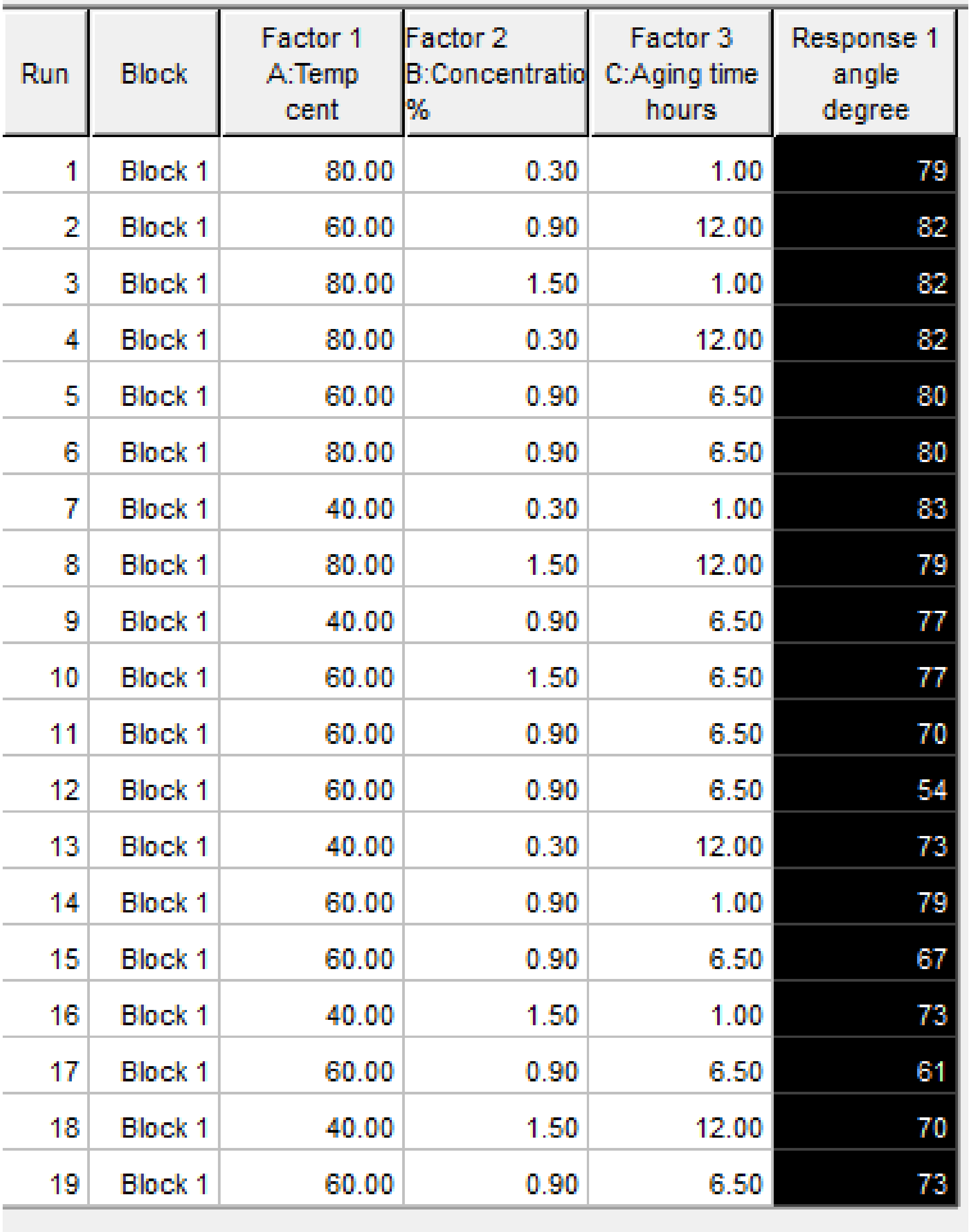
3.6 Design Of Experiment (DOE)

Design of Experiment (DOE) is a real-life experiment simulator used in process optimization, basics of which are probability studies. DOE is designed to produce experiment conditions for the parameter defined to it and their variability ranges, suggesting the number of experiments required to gain significant results which reduces the error of the work and also reduces cost of the experiment in a timely manner. After the results from the suggested experiments are introduced to the program, DOE uses probability studies to produce other data which could have been gained doing more tests manually, this way it actually predicts more responses using available lab data.

There are different options in DOE software, used for different purposes, in the case of this experiment, Response Surface Method (RSM) with a Central Composite Design (CCD) was used as it is used in cases where the variables are continuous. In this method Y (response) is a function of x (variable/s) in such a manner that $Y = F(X_1, X_2, \ldots, Xi) + \varepsilon$, ε being the error factor.This formula is applicable only and only if the variables are independent. The aim of this formulation is to estimate the optimum response/ responses. In this study the experiment variables are temperature and aging time and the response to be captured from the experiment is the contact angle.

In table 5 the experiment design can be found together with the responses from conducting the test. Upon completion of all the test runs, the experiment response, angle, will be matched with the results from a quadratic model using regression analysis to eliminate the less accurate responses.

Table 5. DOE and Responses Table

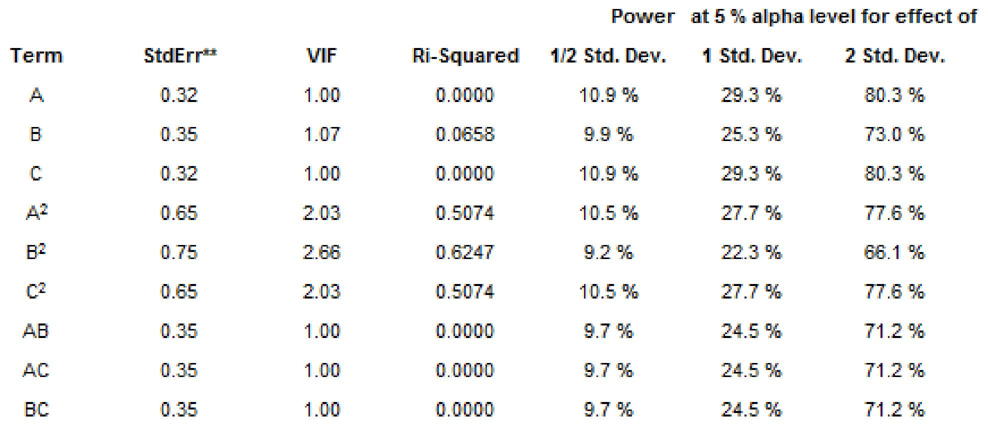


Run	Block	Factor 1 A:Temp cent	Factor 2 B:Concentratio %	Factor 3 C:Aging time hours	Response 1 angle degree
1	Block 1	80.00	0.30	1.00	79
2	Block 1	60.00	0.90	12.00	82
3	Block 1	80.00	1.50	1.00	82
4	Block 1	80.00	0.30	12.00	82
5	Block 1	60.00	0.90	6.50	80
6	Block 1	80.00	0.90	6.50	80
7	Block 1	40.00	0.30	1.00	83
8	Block 1	80.00	1.50	12.00	79
9	Block 1	40.00	0.90	6.50	77
10	Block 1	60.00	1.50	6.50	77
11	Block 1	60.00	0.90	6.50	70
12	Block 1	60.00	0.90	6.50	54
13	Block 1	40.00	0.30	12.00	73
14	Block 1	60.00	0.90	1.00	79
15	Block 1	60.00	0.90	6.50	67
16	Block 1	40.00	1.50	1.00	73
17	Block 1	60.00	0.90	6.50	61
18	Block 1	40.00	1.50	12.00	70
19	Block 1	60.00	0.90	6.50	73

Data analysis for a set of independent variables and one response is undertaken a strong probabilistic model called the regression model. Using this model, a variance is calculated for each of the data set based on which the next probable response value will be estimated. It is obvious that not all values will be accepted, but those that are within the acceptable rangeability.

Based on this analysis, the dependency of each of the factors to one another is determined as in a table such as below (table 6):

Table 6. Dependency of Variables



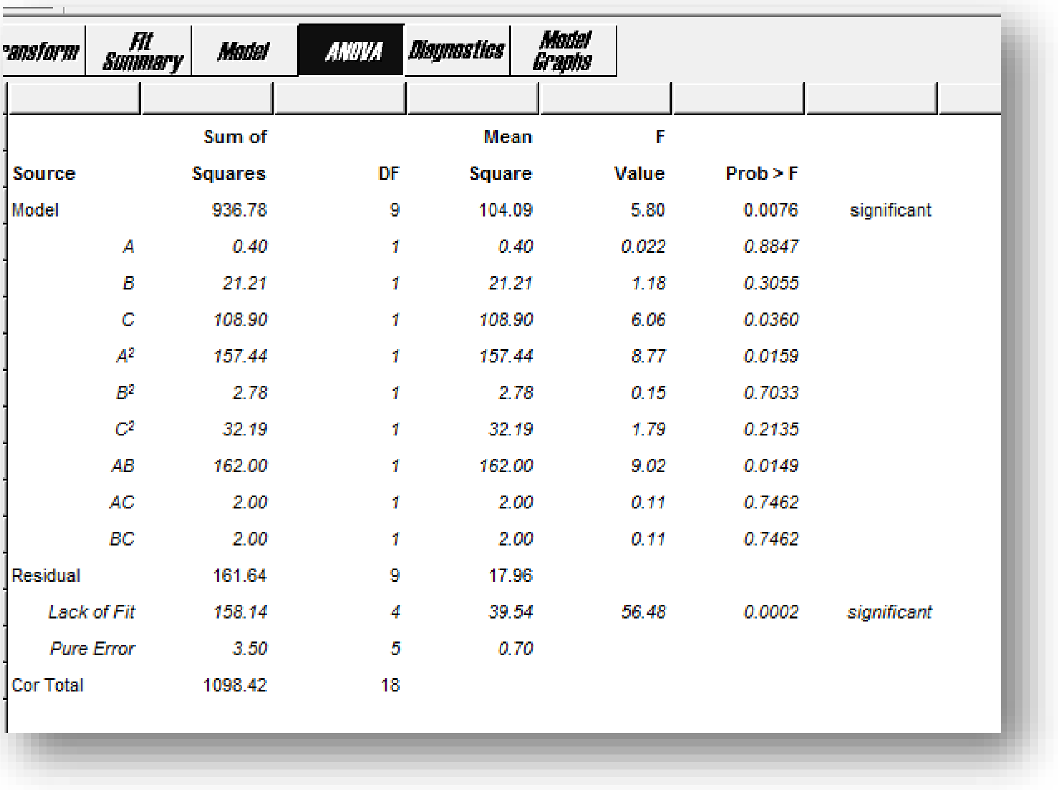
				Power	at 5 % alpha level for effect of	
Term	StdErr**	VIF	Ri-Squared	1/2 Std. Dev.	1 Std. Dev.	2 Std. Dev.
A	0.32	1.00	0.0000	10.9 %	29.3 %	80.3 %
B	0.35	1.07	0.0658	9.9 %	25.3 %	73.0 %
C	0.32	1.00	0.0000	10.9 %	29.3 %	80.3 %
A^2	0.65	2.03	0.5074	10.5 %	27.7 %	77.6 %
B^2	0.75	2.66	0.6247	9.2 %	22.3 %	66.1 %
C^2	0.65	2.03	0.5074	10.5 %	27.7 %	77.6 %
AB	0.35	1.00	0.0000	9.7 %	24.5 %	71.2 %
AC	0.35	1.00	0.0000	9.7 %	24.5 %	71.2 %
BC	0.35	1.00	0.0000	9.7 %	24.5 %	71.2 %

Applying Analysis of Variance (ANOVA) the error term which determines responses rangeability is found. ANOVA analysis consider an equal for all variance value for all the models. This variance distribution is called the homogeneity assumption. The software will indicate the insignificant models which reject homogeneity, eliminating the less possible responses, leaving the accurate results only. The following table 7 indicate ANOVA analysis. Picking up the best model cases introduced by the software can be done manually.

The most important information ANOVA can provide is model significant. If the probability value is less than the critical value (F), which can be defined by the user but automatically is set on 0.5, then the model is said to be significant. A significant model shows the variables impacted each other, otherwise the model is insignificant.

In another mathematical word, when the model is significant it shows that the means are different by a chance more than expected, or in other words, the treatment applied is not equally effective in all the runs. Based on this, the dependency of each variable and response is determined. As for this experiment, the model is significant as per the ANOVA below:

Table 7. ANOVA Analysis



Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	936.78	9	104.09	5.80	0.0076	significant
A	*0.40*	*1*	*0.40*	*0.022*	*0.8847*	
B	*21.21*	*1*	*21.21*	*1.18*	*0.3055*	
C	*108.90*	*1*	*108.90*	*6.06*	*0.0360*	
A^2	*157.44*	*1*	*157.44*	*8.77*	*0.0159*	
B^2	*2.78*	*1*	*2.78*	*0.15*	*0.7033*	
C^2	*32.19*	*1*	*32.19*	*1.79*	*0.2135*	
AB	*162.00*	*1*	*162.00*	*9.02*	*0.0149*	
AC	*2.00*	*1*	*2.00*	*0.11*	*0.7462*	
BC	*2.00*	*1*	*2.00*	*0.11*	*0.7462*	
Residual	161.64	9	17.96			
Lack of Fit	*158.14*	*4*	*39.54*	*56.48*	*0.0002*	*significant*
Pure Error	*3.50*	*5*	*0.70*			
Cor Total	1098.42	18				

The data distribution and variance is as per the graph below:

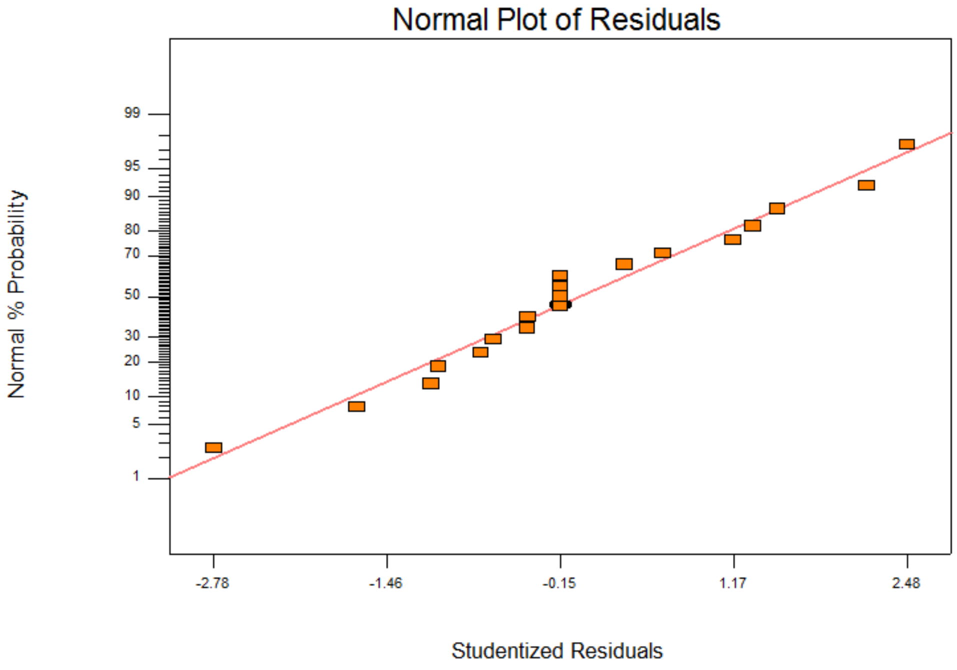
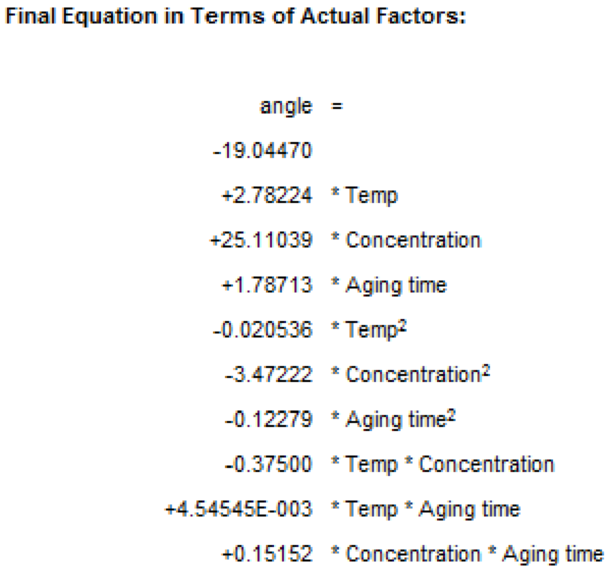


Figure 16. Normalized Response Distribution

Also the software will show the formulations based on which the response behaviour is predicted. Using this formula all other values for different cases of temperature, aging time and concentration are predicted, based on which the results discussion is. In this case angle is predicted by the following formulation in the software:



Final Equation in Terms of Actual Factors:

angle =
-19.04470
+2.78224 * Temp
+25.11039 * Concentration
+1.78713 * Aging time
-0.020536 * Temp^2
-3.47222 * Concentration^2
-0.12279 * Aging time^2
-0.37500 * Temp * Concentration
+4.54545E-003 * Temp * Aging time
+0.15152 * Concentration * Aging time

Figure 17. Response Formulation Prediction

Chapter 4 Results and Discussion

4.1 Results and Discussion

As per the results gained experimentally, and verified by DOE, the two experiment variables, aging time and temperature impact the angle by reducing it, which consequently caused a reduction of oil-wetness and increases water adsorption in the formation, which later on will dedicate to higher oil recovery. Comparing the angle reduction before and after aging in surfactant shows that the highest the temperature and the aging time is, for higher concentrations of surfactant, the angle reduction value is more. The results can be found as per table 8 below:

Table 8. Experimental Results Compared to Prediction Results

sample no	Temperature	Surf. Concentration	aging time	angle before	angle after	θ prediction	**Reduction percentage**
nom1.	60	0.9	6.5	83	79	85.11627218	4.819277108
nom2.	60	0.9	1	83	82	78.10212218	1.204819277
nom3	60	0.9	6.5	83	82	85.11627218	1.204819277
nom4	60	0.9	6.5	83	82	85.11627218	1.204819277
nom5	60	0.9	6.5	83	82	85.11627218	1.204819277
nom6	60	0.9	6.5	83	81	85.11627218	2.409638554
nom7	60	1.91	6.5	83	82	87.76258952	1.204819277
nom8	60	0.9	6.5	84	79	85.11627218	5.952380952
nom9	60	0.9	12	81	80	84.70162718	1.234567901
nom10	80	0.3	12	79	77	79.27903302	2.53164557
nom11	80	1.5	1	76	70	66.2445015	7.894736842
nom12	80	1.5	12	76	54	74.8440375	28.94736842
nom13	80	0.3	1	79	76	72.67956102	3.797468354
nom14	80	0.9	6.5	84	79	77.10118068	5.952380952
nom15	40	1.5	12	74	67	82.4454215	9.459459459
nom16	40	0.3	12	81	73	68.88041702	9.87654321
nom17	40	0.3	1	84	61	64.28094302	27.38095238
nom18	40	1.5	1	76	70	75.8458835	7.894736842
nom19	40	0.9	6.5	82	73	76.70256368	10.97560976

The following are the graphs showing the relationship of the factors and the response:

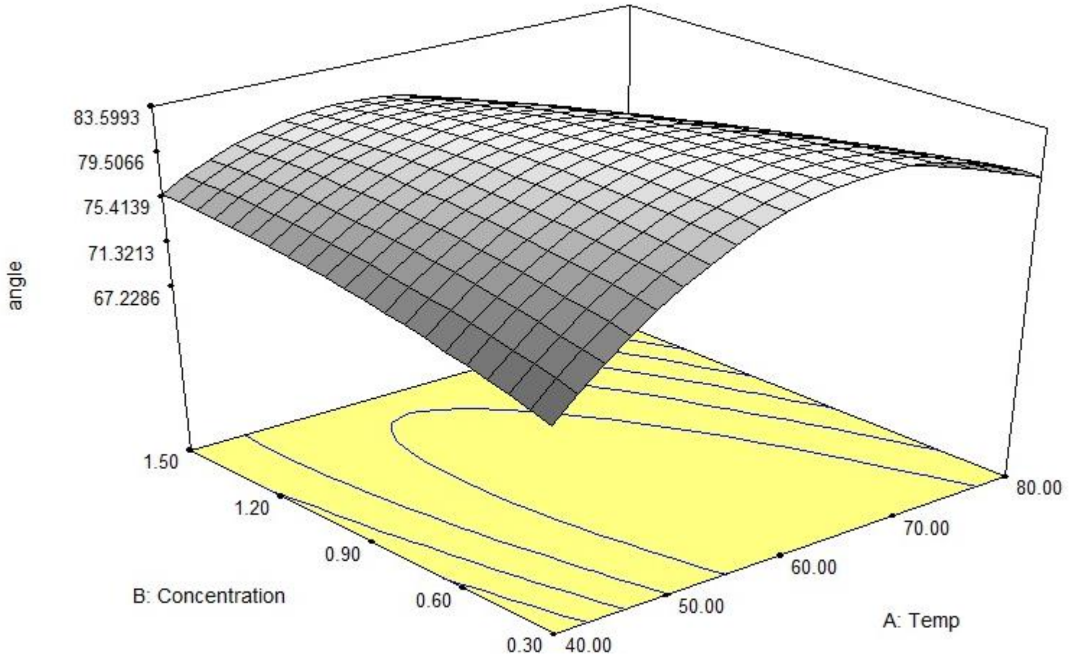


Figure 18. Variables and Response Relationship (3D)

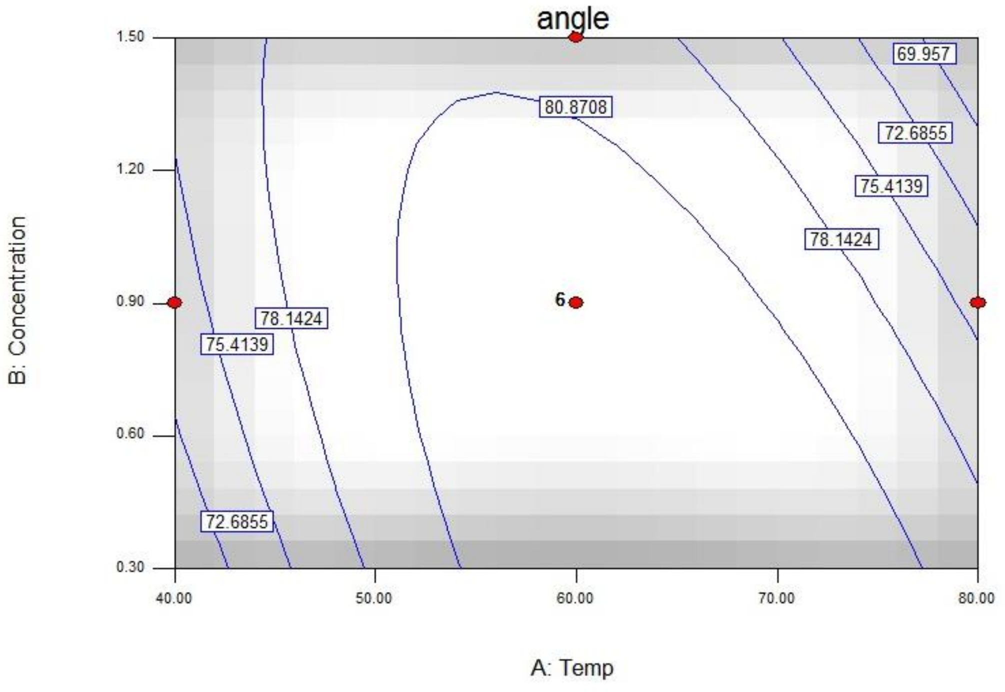


Figure 19. 2D Concentration-Temperature graph according to the graphs for a higher temperature and concentration values, the angle reduction is more, although the optimized temperature is at 60 degrees.

Some samples of the contact angles measured before and after applying surfactant are reported as follow:

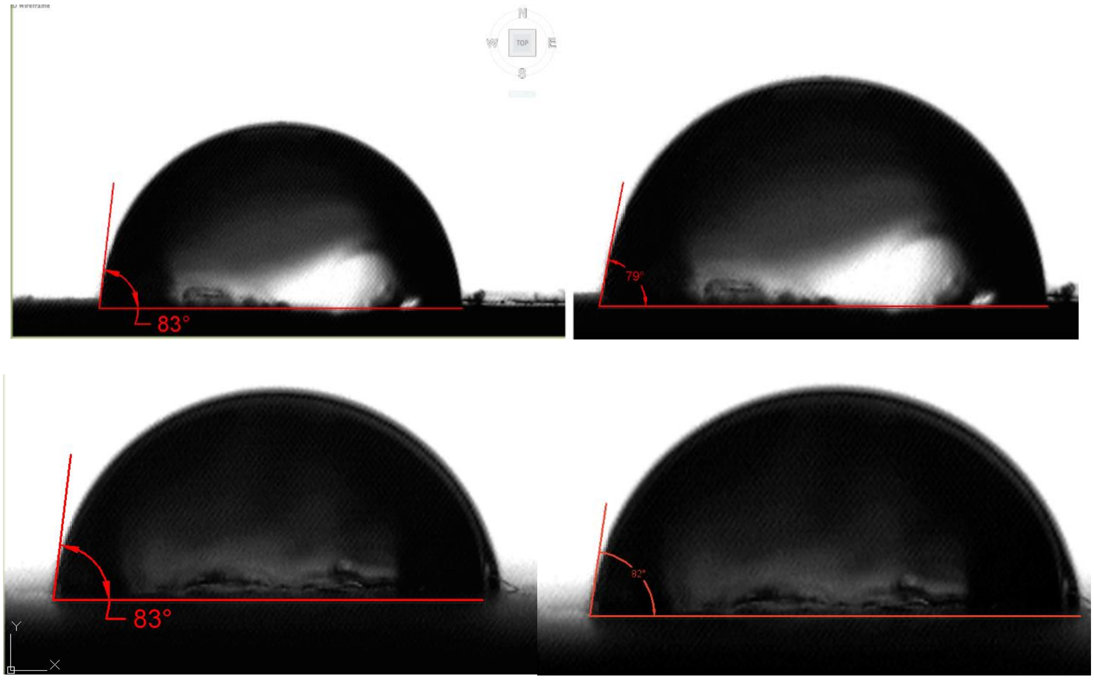


Figure 20. Left hand Side: Sample's Angle Reduction Before Applying Surfactant, Right Hand Side: Sample's Angle Reduction After Applying Surfactant

4.2 DTAB mechanism

As previously mentioned, spontaneous imbibition is the process responsible for adsorbing the wetting phase into the capillary pores which is adminned by capillary force. Applying surfactant decreases IFT, consequently reducing capillary pressure.

Reportedly by Austad investigation group on imbibition mechanism in chalk-formations, among the existing surfactants, DTAB in presence of sea water sulfate ions is the most effective to imbibe the wetting phase (Austad,et al. 1998, Standnes and Austad 2000; Milter and Austad 1996a, 1996b; Høgnesen et al. 2004, 2006). According to this investigation, the main mechanism of such effect is removal of the adsorbed naphthenic acids through ion pairing with the cationic surfactant. The bonding energy between crude oil which has a negative head, and the solid surface (carbonate rock) is much higher than that of crude oil and sandstone (Al Shalabi, et al, 2014). It is surfactant's responsibility to overcome the bonding energy as described in figure 21 below.

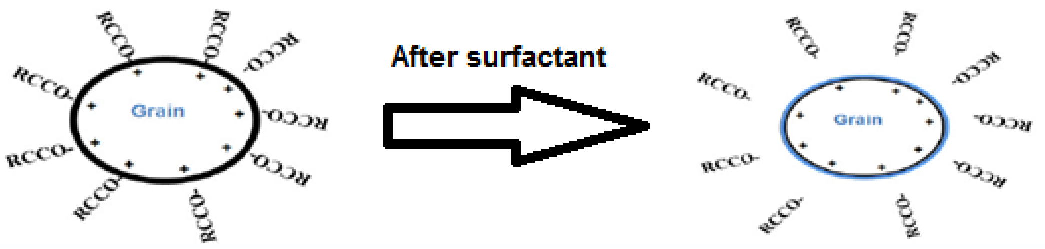


Figure 21. Surfactant Mechanism

In the above figure (figure 21), the left hand side shows the oil-grain interaction before introducing surfactant and the figure on the right side shows the same interaction after surfactant flooding. In the left hand side figure, carboxyl group is connected to grains, making the rock oil-wet. Rock grains are positively charged, attracting the negative head of the crude oil by strong bonds, while in the right hand side figure, after surfactant flooding, since the brine ions have higher electronegativity, they displace the carboxyl group, forming a seperative layer, which allows more crude oil production from the reservoir since the oil is no more bonded to the surface., consequently increasing water-adsorption and flow distribution in the matrix (Hirasaki and Zhang, 2004, Gupta, et al 2008).

Chapter 5 Conclusion and Recommendation

5.1 Conclusion and Recommendation

The objectives of the project have been met, as according to the conducted experiments, DTAB surfactant's optimum workability is at $T= 80\ °C$ and for surfactant concentration 1.5 W%. The results show that in lower temperatures also the best result is gained for a higher concentration.

As for recommendation it is suggested to conduct more studies on effect of salinity on DTAB solubility as DTAB although stable, but cannot be solved in high salinity brine, which limits its usage in case of high salinity reservoirs. In such cases though, the reservoir brine can be diluted by injecting low salinity brine prior to surfactant flooding.

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