Screening of selected surfactants to alter wettability for EOR applications

By

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14615

Dissertation Submitted in Partial Fulfillment of the Requirements
For the Bachelor of Engineering (Hons)
(Petroleum)

January 2015

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Petroleum Engineering program

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Approved by:

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January 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.

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PEDRO ANGLAZE CHILAMBE

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NOMENCLATURE

AOS- Alpha olefin sulfonate

IFT- Interfacial Tension

EOR- Enhanced oil recovery

SDS- Sodium dodecyl Sulfate

ABSTRACT

Enhanced oil recovery is a very important activity in the production of oil from reservoirs which have reached residual oil and are in need of secondary recovery methods to extract the hydrocarbons. These reservoirs to be produced require water flooding or gas injection to assist in its production. This project looks at reservoirs that are oil wet and there for when water is injected into the reservoir, which can be recovered by the use of solvent or surfactants also known as surface active agents to alter the wettability of the rocks and allow for the process of imbibition to occur and for the oil in the reservoir to be produced. There is a lot of research in the industry about the selection and optimization of surfactants but there is still a gap to cover more areas about this topic. Therefore, it is important to do more research to add to what is known about the use of surfactants in EOR applications. This project studies suitable surfactants to alter wettability, and optimize them to get the optimum alteration of wettability. The optimized surfactant showed high activity towards the alteration of wettability. The project also finds the recovery attainable by the selected surfactant.

CHAPTER 1

Introduction

1.1 Background

As a lot of the oil and gas resources reduce to residual oil saturation, close to the point of no possible primary recovery, Enhanced oil recovery methods have become the go to method to increase the recovery factor of these reservoirs which require specialized and tailored solutions to produce the remaining oil.

Surfactants assist in the displacement of oil where water flooding or gas injection is necessary for enhanced oil recovery. Wettability is a factor that affects the flow behaviour and when altered, imbibition moves out the oil, because capillary pressure changes from negative to positive. Wettability alteration in reservoir rock formation is an important factor in improving the effectiveness of water flooding operations, as there is a desire to export more oil from the reservoir to the surface.

Capillary and gravity forces are functions of wettability, interfacial tension, density differences and pore radius and are mainly what is responsible for the imbibition process. Capillary imbibition in the principle method for producing hydrocarbons due to the reduced pore size, and hydraulic fractures improve the performance of the matrix-fracture interaction to recover oil from the matrix.

The various chemicals that can be used to alter wettability are measured by checking the contact angle, measuring the interfacial tension and the magnitude of penetration and also by doing spontaneous imbibition experiments to show the effectiveness of the performance of the chemical. In this project we will specifically look at Selected, anionic surfactants and experimentally compare their effects on wettability alteration. These surfactants are said to lower contact angle and interfacial tension according to (Johannes O. Alvarez, 2014) experimental work, and in this project we will attempt to use a different methodology to verify the findings and the theory behind the alteration of wettability by the use of these chemicals.

1.2 Problem Statement

One of the difficulties we face when stimulating wells is the selection of appropriate and effective chemicals to create an effective and desired outcome. In the case of recovering residual oil or in improving enhanced oil recovery, screening chemicals to find those that give the best results is an ongoing development which must always be tackled to keep recovering more difficult unconventional resources, from difficult reservoirs to operate in. The existence of many chemicals to perform this recovery, means that many solutions must be analyzed to assist in increasing the knowledge of the effects of various concentrations of certain surfactants. Therefore more research is required to find out the best chemicals for improving wettability for enhanced oil recovery.

1.3 Objectives and Scope of Study

The main objective of this project will be to;

- Research chemicals used to alter wettability, anionic surfactants.
- Investigate the surfactant interactions on sandstone surface sample and determined wettability alteration by measuring of the contact angles.
- Study water flooding improvement with the most suitable surfactant on the recovery of oil after pre-surfactant treatment.

CHAPTER 2

Literature Review

Wettability

Wettability, according to Rosen, (Rosen, 2012) or the process known as wetting is a displacement of one fluid from another’s surface, or from the surface of a solid. For the screening and optimization of surfactants to alter the wetting phase of an oil and gas reservoir rock, we must first understand the basic fundamentals of wettability and the forces that are involved in the attraction between fluid contacts and surface contact as well. Wettability is a crucial factor in remaining or residual oil saturation, capillary pressure and relative permeability curves (Hirasaki, 1991).

Hirasaki (Hirasaki, 1991) also states that system wettability is determined by the multiple existences in pore spaces of mineral rock, brine, oil and or gas contact angles, meaning that a complete study of wettability requires a description of the contact angles between these substances as boundary conditions for fluid distribution on the measured surface. Agreeing with Hirasaki (Hirasaki, 1991) is Morrow (Morrow, 1990) that says that reservoir wettability depends on what he referred to as complex interface boundary conditions, that act within the pores.

One important factor for enhanced oil recovery is to alter the activation energy to alter wettability through a chemical reaction.

Therefore, it is understood that in general wettability is the tendency of fluid/fluid or fluid/solid to attract to one another due to ionic forces between these substances. So to alter wettability, a chemical reaction to weaken this bond must occur.

Contact Angle

The effects on this parameter will be the primary screening criteria for selection of the most suitable type of surfactant to alter wettability. The contact angle is the angle of the macroscopic surface curvature of the fluid droplet when extrapolated to zero thickness (Hirasaki, 1991). It is where two fluid surfaces or fluid/solid surfaces intersect. The angle measurement is taken from the solid surface towards the aqueous phase, (in the case of oil and gas, it is read from the oil through to the gas phase). It is important to make the readings of a contact angle using a smooth and flat surface because the roughness of a sample surface affects the measurement of this parameter (Schlumberger, 2014).

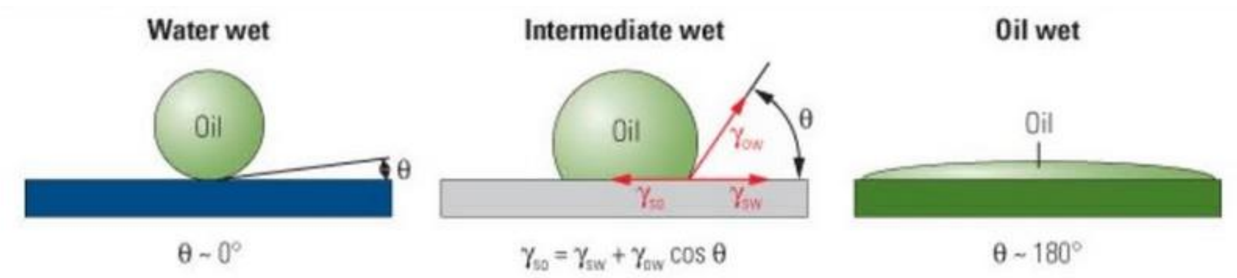

Figure 1 Contact angle

Experimentally, the contact angle is measured by applying a droplet of fluid (oil in this case) on a mineral surface. On figure 1, we see on the left image, that for a determination of wettability of a water wet surface, a drop of oil (green) will become surrounded by water (which is at 180˚ to the surface) when it enters into contact with a water wet surface, and will have a contact angle that is close to zero (Schlumberger, 2014). The opposite occurs with the drop when it is on an oil wet surface, where it will have a contact angle of approximately 180˚ which we see on the right of figure 1 according to Schlumberger's oil field glossary (Schlumberger, 2014). In the case of an intermediate wet surface it will form a bead as it does on a water wet surface, but in this case will be at angles approximately at 90˚ according to (Hirasaki, 1991), at this point we have what is called adhesional wetting where the oil droplet has a tendency to spread over a wider area of the surface with which it comes into contact with as argued by (Rosen, 2012).

Adapting further from Rosen (Rosen, 2012), for oil and mineral surfaces, the contact angle for a surface with intermediate wetting can be found by computing the surface tension between solid and the oil, which is found by adding the surface tension of the mineral solid and the water phase, to the surface tension of the water and oil phase and considering the direction of these vector forces. The equation that describes this is called Young's equation.

$$\gamma_{so} = \gamma_{sw} + \gamma_{ow} \cos \theta \tag{1}$$

The contact angle is an important indicator when it comes to identifying the alteration of wettability due to surfactant and other chemicals used to switch wettability. It is when this angle is changed that we can see the changes in the forces that are holding the surfaces together, so it is a good physical indicator of what is happening on the surface of the rocks.

Surfactant Chemicals

The surfactant chemicals that will be used in this project to alter wettability and that will go through the screening of which surfactant causes the best mode of alteration are chemicals studied by Mohamed (Mohamed, 2011).

To understand surfactant chemicals, first we must understand the basic chemistry behind these organic amphiphilic compounds. They are composed of long chains that contain both, head-section hydrophilic (attracts water) and long tail section hydrophobic (repels water) components (Furse, 2011). Surfactants are usually classified into anionic (negatively charged hydrophilic head), non-ionic (no charge) and cationic (positively charged hydrophobic head) types. An example of a common surfactant 4-(5-Dodecyl) benzenesulfonate can be seen in figure 2 bellow.

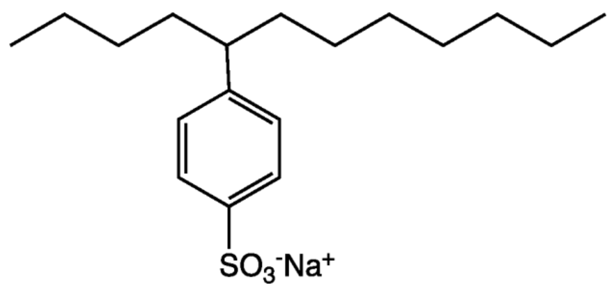

Figure 2 4-(5-Dodecyl) benzenesulfonate

It is these properties of attraction of water, which favours oil wetting, and repelling water which favours water wetting of the mineral surfaces.

The mechanism of the reaction that surfactants have at the water and oil interfaces, in an oil wet situation where a water flooding is occurring with surfactant, is that the surfactant entering an oil wet rock, will stick its tail out on to the oil interface and its head will point away from the oil interface but into the oil interface, and usually these particles tend to form a bond with other particles there for forming a ball called a micelle, where the connet water will be shielded by these particles where the head of the surfactants will be holding to the water.

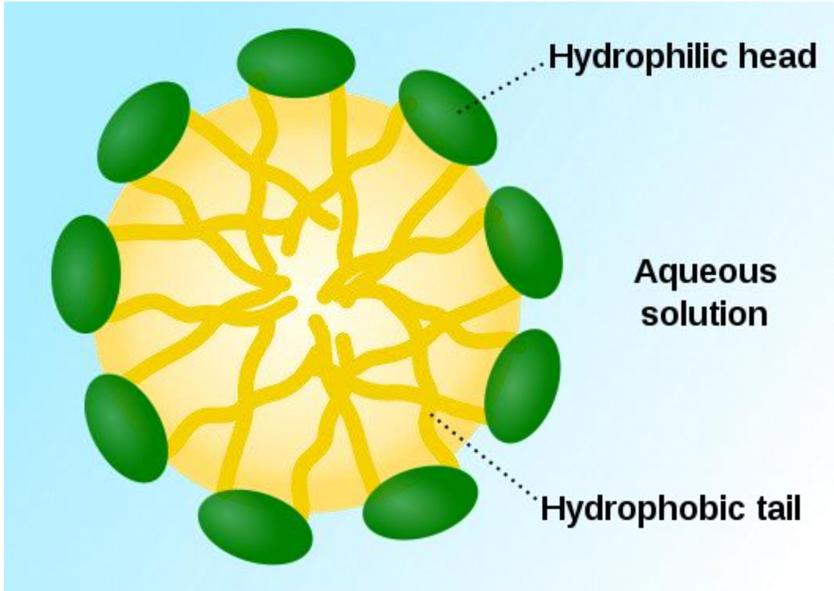

Figure 3 Schematic of surfactant behaviour in aqueous solution with oil emulsion called a micelle.

When water floods the rock, the scenario is reverted as there is more water being absorbed into the rock and therefore now the surfactant heads turn around and the tails form an inverse bubble now shielding the oil into a bubble form which in turn loses its attachment to the rock and allows for the process of imbibition to occur. What happens during this process is that as the bubble is formed, the angle of contact of the oil to the solid surface is reduced until there is little interfacial tension between the fluid and the rock, allowing it to be displaced more easily.

Figure 4 Effect of surfactant on oil wet shale in aqueous solution (Imbibition) from oil wet to water wet.

According to Johannes (Johannes O. Alvarez, 2014) cationic surfactants seem to have a very low effect on the alteration of wettability in unconventional liquid reservoirs, in the case of shale rock for example, according to Mohamed (Mohamed, 2011) the cationic surfactants have a high adsorption capacity towards the anionic clay surfaces like illite clay ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$) due to their opposite charges which attract, allowing the surfactant to be absorbed more easily . He goes on to say that Non-ionic surfactants attract chemicals due to their electro negativity making it a good type of surfactant, and that anionic is a good type of surfactant due to its stability and resistance to retention. Cationic and nonionic surfactants are usually good candidates to alter the oil-wet rock towards more water-wet, but not efficient to reduce oil-water IFT (Cationic surfactants has no tendency to low the IFT).

Anionic surfactants are very efficient to lower the IFT to ultra-low level, but do not effectively alter the wettability.

The chemicals we will experiment with which were reviewed by Mohamed (Mohamed, 2011) and other commercial surfactants are; Anionic- Sodium dodecyl sulfate (SDS or NaDS) and anionic Alpha Olefin Sulfonate (AOS).

These surfactants have shown positive results in other rock types, such as dolomite, limestone, and calcite crystals. This is a positive indication that there is a highly likeable chance that they will at least cause some reaction with the liquid content in the tight sandstone surfaces, and that they might bring a positive result.

CHAPTER 3

Methodology

3.1 Research Methodology

For the research of this project, previous works and attempts at the alteration of wettability will be analysed and studied in order to guide this project, and provide a sound basis of the technical work that will be necessary to achieve the desired objectives. The research will include, revision of literature, consultation with experts in the field of chemical EOR and books written about Surfactant chemistry.

Laboratory research will also be a key part of this experiment as it will be the activity which will determine which of the surfactants are suitable for wettability alteration, and will be the chemicals deemed eligible for optimization.

3.2 Project Activities

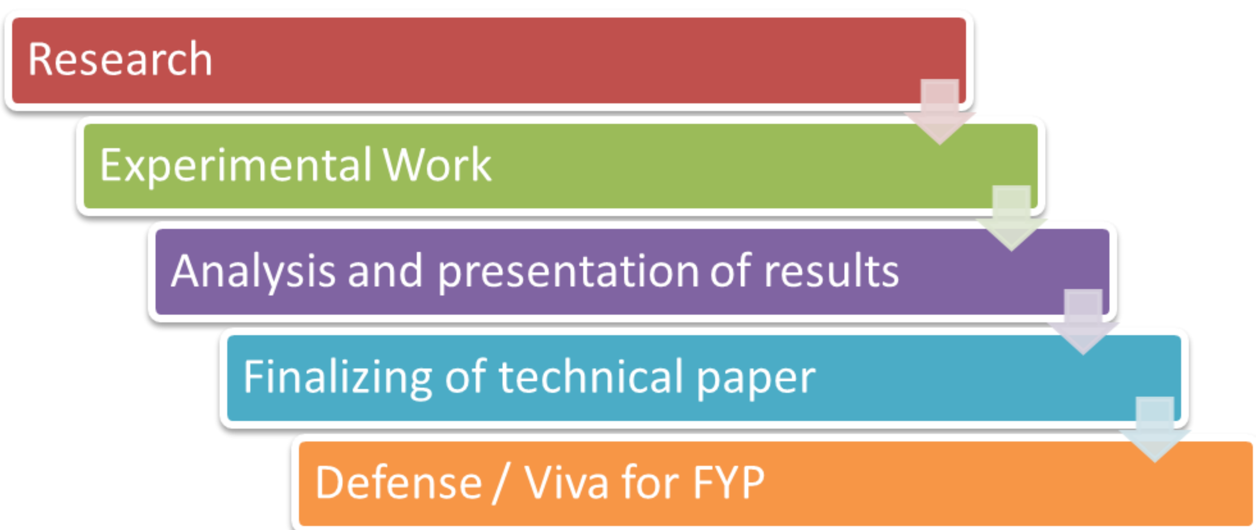

Figure 5 Project Flow chart

3.3 Key Milestones

	Key Milestones	
1	Submission of Extended proposal defense	sem1/week 6
2	Submission of interim draft report	sem1/week 13
3	Submission of interim report	sem1/week 14
4	Preliminary lab results	sem2/week 7
5	Submission of progress report	sem2/week 8
6	Pre-sedex	sem2/week 11
7	Draft report submission	sem2/week 12
8	Submission of Dissertation soft bound	sem2/week 13
9	Submission of technical paper	sem2/week 13
10	Oral presentation	sem2/week 14
11	Submission of Dissertation Hard bound	sem2/week 15

Figure 6 Key Milestones

3.4 Project Gantt chart

Table 1 Gantt Chart FYP1

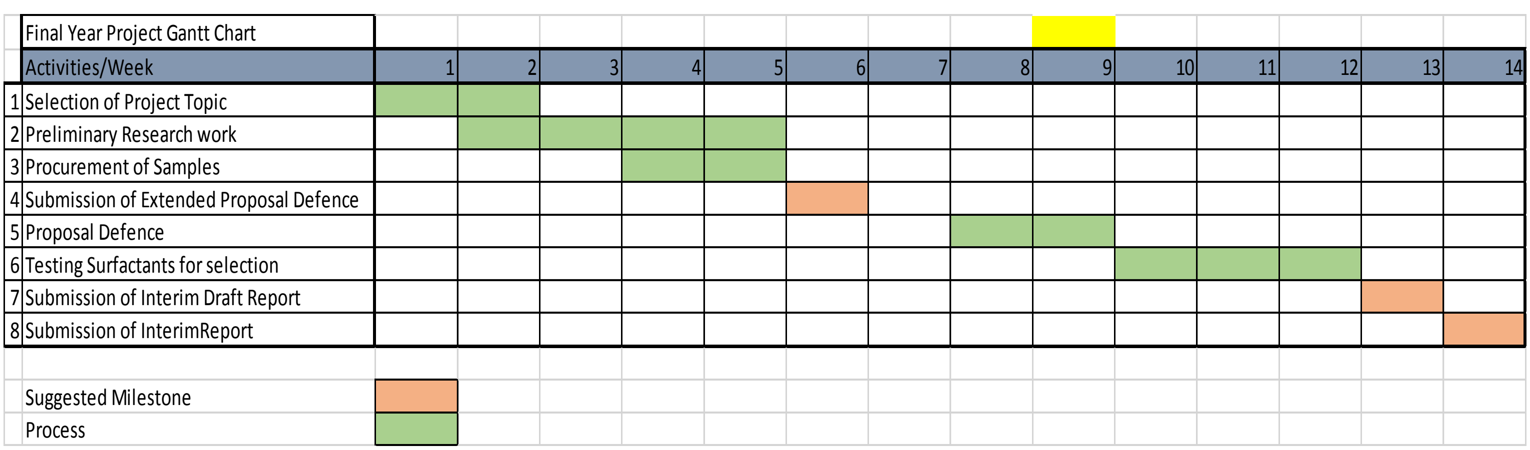

Table 2 Gantt Chart FYP2

	Final Year Project Gantt Chart															
	Activities/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Contact angle measurements (LAB)															
2	Selection of Best Surfactants (LAB)															
3	Optimization and alterations to Surfactants (LAB)															
4	Contact angle measurements II (LAB)															
5	Preliminary LAB Results															
6	Submission of Progress Report															
7	Project Work Continues															
8	Pre Sedex															
9	Draft report submission															
10	Submission of Dissertation Soft Bound															
11	Submission of Technical Paper															
12	Oral Presentation															
13	Submission of Project Dissertation Hard Bound															
	Suggested Milestone															
	Process															

3.5 Experimental

Sample Preparation

Core Sample Preparation

Core Samples are to be washed in methanol and dried at 80 degrees Celsius in an oven for 4 days. Then they must be removed from the oven, and brought to room temperature, and kept in a beaker.

These core samples must then be dimensioned using a Vernier calliper, to get the diameter and length of the core in millimetres. Finally the core sample must be weighed, and mass recorded in grams.

Thin Slice for IFT700

Two rock samples must be cut to dimensions of 30*35mm for use in the IFT700. Firstly it must be sanded using 1000-500 mesh sand paper to create a smooth surface; it will then be rinsed with deionized water and dried for 5 minutes at a 100˚C. This thin slice was then induced to oil wet by soaking the slice in crude oil for 14 days at 60˚C then it was cleaned in solvent to avoid asphaltene formation, and then soaked in mineral oil.

Surfactant Sample preparation

For the Surfactant solutions, AOS and SDS must be used in various concentrations, and in mixture. The first samples of AOS and SDS separately, will be prepared in 0.25 0.5 and 1% concentration of surfactant in a 1000ml solution. Followed by a 0.5 AOS and 0.5 SDS ratio mixture in 0.25 0.5 and 1% concentration in a 1000ml solution.

Surfactant A – SDS.

Surfactant B- AOS.

Surfactant C – 0.5AOS +0.5SDS.

Mineral Oil and Diesel Preparation

The density and viscosity of these fluids and the API gravity must be measured

Porosity and Permeability Test

Poroperm

The poroperm is an equipment that is composed of a porosimeter and a permeameter, which are used to determine the properties and or parameters of plug sized core samples at a confined ambient pressure. The poroperm will yield results from calculations for porosity and permeability using the software that accompanies the equipment.

In this equipment the core sample is pressurized, and flowed with fluid, to give directly measured values of, Gas permeability in mD, pore volume and core length and diameter. Calculations for, klinkenberg parameters, inertial co-efficient, grain density, grain volume, bulk volume and porosity will be made and provided by the software.

This experiment will assist in understanding the conditions of the various samples that will be used in the experiment, its porosity and permeability, in order to further analyse the conditions within which the surfactant will operate.

Contact Angle Measurements

IFT700

With the use of the IFT700, a thin slice of a rock sample will be inserted into the IFT 700, One normal testing will be made to check the contact angle of oil on the rock sample without the use of surfactant, and another experiment will be ran with the use of surfactant. The Experiment will aim to capture an image of the drop of oil in pressurized fluid at the point at which it reacts with the rock surface.

These images will be used to measure the contact angle manually, to verify the effects of each surfactant solution.

Core Flooding (Imbibition Test)

3-Phase Core Flooding Equipment

In this experiment, an oil saturated core will be flooded with water, gas, with and without surfactant to compare and analyse the effect of the surfactant on the wettability of the rock, and to analyse how the displacement of oil occurs with and without the use of surfactant EOR to determine the effect of the use of surfactant chemicals to alter wettability. This Displacement if possible will be conducted at high pressure, High temperature.

CHAPTER 4

Results and Discussion

<u>Porosity and Permeability Test</u>

The aim of the poroperm test was to gather the values of porosity and permeability of core samples to be used in the experimentation for the testing of the effects of surfactants to alter wettability.

Four core samples of barrier sandstone were used, and tested. These core samples in general showed moderate permeability and moderate porosity, considering that ranges of permeability in oil and gas reservoirs vary from tens to hundreds of Millidarcy and that minimum porosity to produce hydrocarbons is considered 8% and can range up to about 30% in sandstone.

These samples therefore show good reservoir characteristic, and are good samples for general representation of tight sandstone reservoirs when analysed against known ranges of the values that are common around the world.

The sample 100md, failed testing and showed no results for porosity and permeability, therefore it will not be used in the following experimentation procedures as the next step involves the testing of the surfactant chemicals ability to change the wettability using the IFT 700 to measure the contact angle and interfacial tension.

With the pore volume in the ranges of 13-14.5cc, we will be saturating the cores with close to 11ml of diesel and mineral oil for the core flooding.

Table 3 Poroperm result

Core Sample ID	Length (mm)	Width (mm)	Weight (g)	Permeability (Md)	Porosity (%)	Pore Volume (cc)
1	74	35.5	187.73	54.598	18.51	13.61
2	72	35.5	176.32	46.92	20.23	14.62
3	69	35,5	177.2	24.328	19.944	13.62

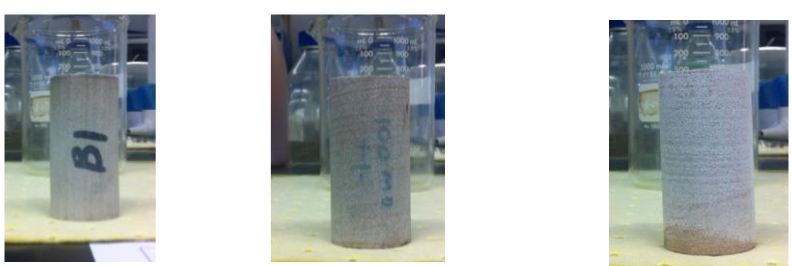

Figure 7 Sandstone Core Samples

Interfacial Tension Measurements

The results for this experiment were obtained by dropping an oil droplet in an external brine phase pressurised at 1500psi and at 90 degrees Celsius. A surfactant drop was injected, held at the tip of the needle and computer readings were recorded of the interfacial tension between the two fluids, different concentrations of the surfactants were used to get these results. Surfactant A being SDS, Surfactant B being AOS and Surfactant C being the mixture of the two at 0.5 concentration of each.

A lower interfacial tension is the main goal in the interacting properties of a fluid-fluid surface which is important to understand which surfactant will work best with the fluids in the reservoir.

From the results obtained for the interfacial tension measurements in figure 8 to 11 for various surfactant concentrations, it was seen that a higher concentration tends to be more effective in achieving a low surface tension. This because a higher concentration means that there is a higher amount of negative charges to react with the surface of the fluid and allow for higher micelle generation.

The second observation that can be made from these results is that the mixture of the two anionic surfactants yields a lower interfacial tension than the other anionic surfactants alone, one reason why this maybe is that the amount of anions present is much higher when both surfactants are mixed together, meaning that its electrostatic forces are much higher than the stand alone surfactants and therefore it has a greater effect on reducing the interfacial forces between the surfaces.

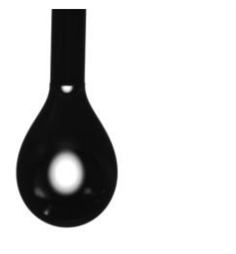

Figure 7 AOS 1wt% droplet

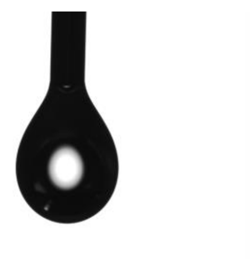

Figure 9 SDS 1 wt% droplet

Figure 10 0.5AOS+0.5SDS 1 wt% droplet

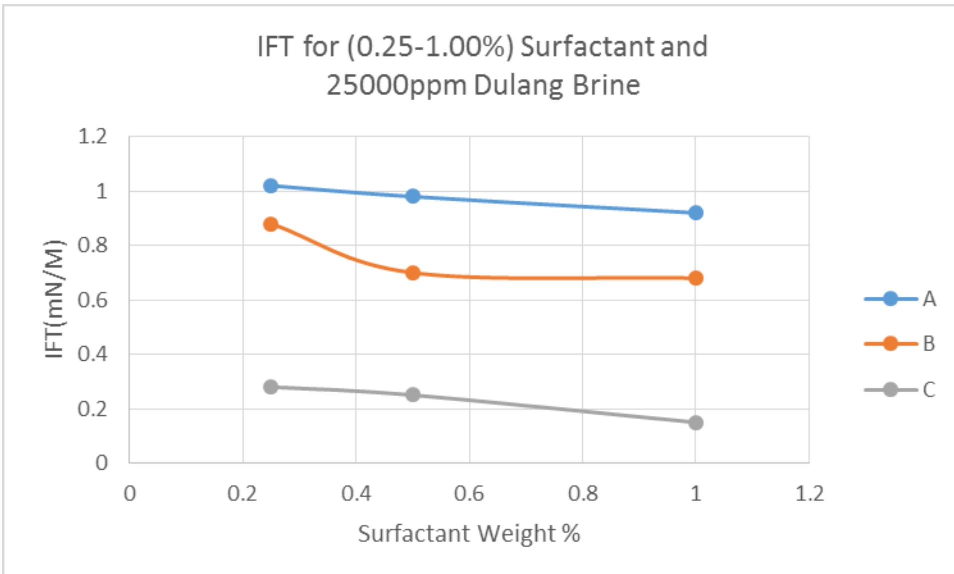

Figure 8 IFT Surfactant in brine and crude oil

Contact Angle

The contact angles were measured using the Interfacial tension meter (IFT700), which is composed of a chamber where two fluid phases, an injected phase and an external phase can be present and a rock sample can be placed within the chamber in the form of a slice.

The rock sample slice was placed in the first time before soaking in surfactant, and then placed after soaking with surfactant. An oil phase was injected in air at a pressure of 1500psia and 90 degrees Celsius and a bubble was dropped on the slice, and the angle between the rock and the bubble was measured manually from a screenshot of the computer image captured by the high resolution camera hosted by the equipment.

The contact angle measurements show that as the concentration of the AOS increases the contact angle of the oil droplet also increases, showing that at a higher concentration of AOS, 1wt% in this case, results in the highest alteration of wettability that can be achieved, this results backs up the results of interfacial tension which show that the higher concentration of AOS, the lower the interfacial tension achieved.

With this result we can also be sure that AOS, can be successful at reservoir conditions due to the pressure used and the temperature which closely match reservoir conditions. The alteration in the angle found, from practically a 180 degree angle of oil bubble, which happened as the rock was oil wet to a final 74 degree angle is what shows the wettability being altered as the adsorption of the oil towards the sandstone slice was reduced more and more as the concentration of the surfactant increased. This angle also according to (Schlumberger, 2014) is considered to be intermediate wet conditions, so the surfactant will not completely alter the wettability of the rock to water wet, which would happen as the contact angle reaches near a zero degree angle. This successfully covers one of the main objectives of this study.

Results from this experiment can be seen in figures 12 to 15.

Figure 12 Oil Without surface treatment

Figure 13 Oil drop with 0.25wt% AOS ϴ=52°

Figure 14 Oil drop with 0.50wt% AOS ϴ=68°

Figure 15 Oil drop with 1.00wt% AOS ϴ=74°

Core Flooding Experiment to measure oil recovery.

In this experiment , a benchtop permeability tool was used to do the simulation of recovery with a set up where fluid was injected from a measured beaker, through a pressurized pump at 3cc/min, through the core sample and out of a metallic pipe and into a test tube. The volume was collected measured against time and recorded to get the amount of volume produced. This volume was then turned into percentage to get the percentage of recovery of oil which is the desired out come in this experiment.

Looking at the trend in most of the results below from figure 16 to 18, we get an initial time up to about 500s where there was no oil produced as the differential pressure that held the core sample was still insufficient to pump the oil out of the core, once the differential pressure became enough, the oil began to be pumped out of the rock. This experiment was run until the confining pressure reached steady state, and the oil had stopped being produced, which explains the straight line which is seen towards the end of each result. The achieved steady state was kept on for between 20 to 30 minutes simply to guarantee that there was no more oil that the injected fluid could displace.

The results attained from the simulation of oil recovery of Water flooding after the injection of surfactant shows that as stated above in the introduction, the surfactants do increase the recovery of oil and allow water flooding to remove on average another 18.5%. In the sample tested, the surfactant showed an overall recovery between 63%. Which is normal for a secondary recovery method which doesn't differ much from most of the papers used in this study which evaluate tight formations, and the cores being used being tight cores, similar results were expected. For this experiment only AOS, which showed the best performance was used for the testing ,
justifying the use on this surfactant. Results for this could be improved by the use of gas injection, or the use of SAG which tends to give a much higher recovery as a tertiary recovery method.

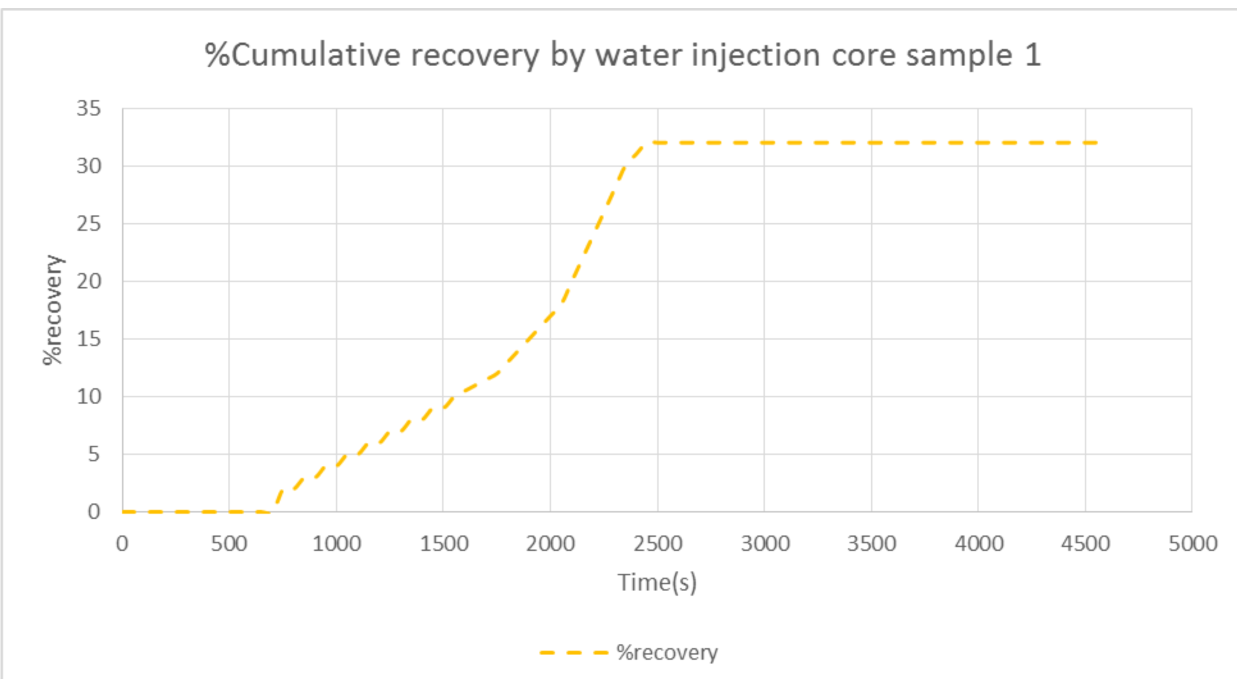

Figure 16 Cumulative recovery by water injection

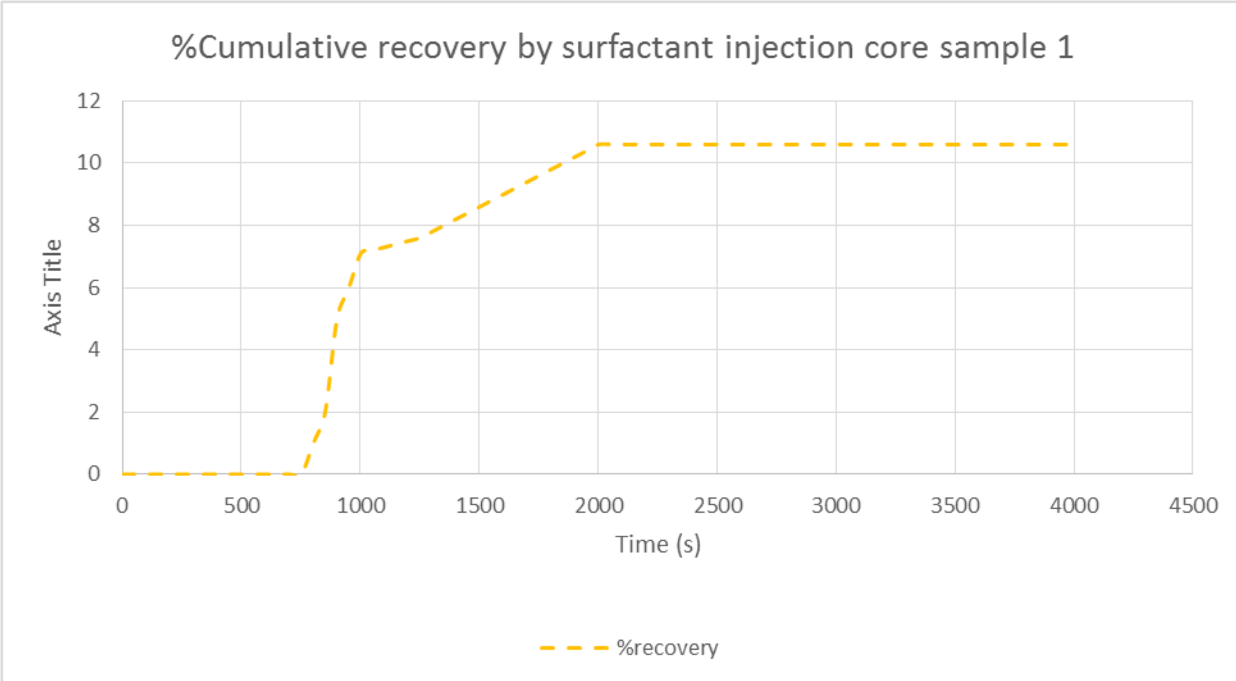

Figure 17 Cumulative recovery by surfactant

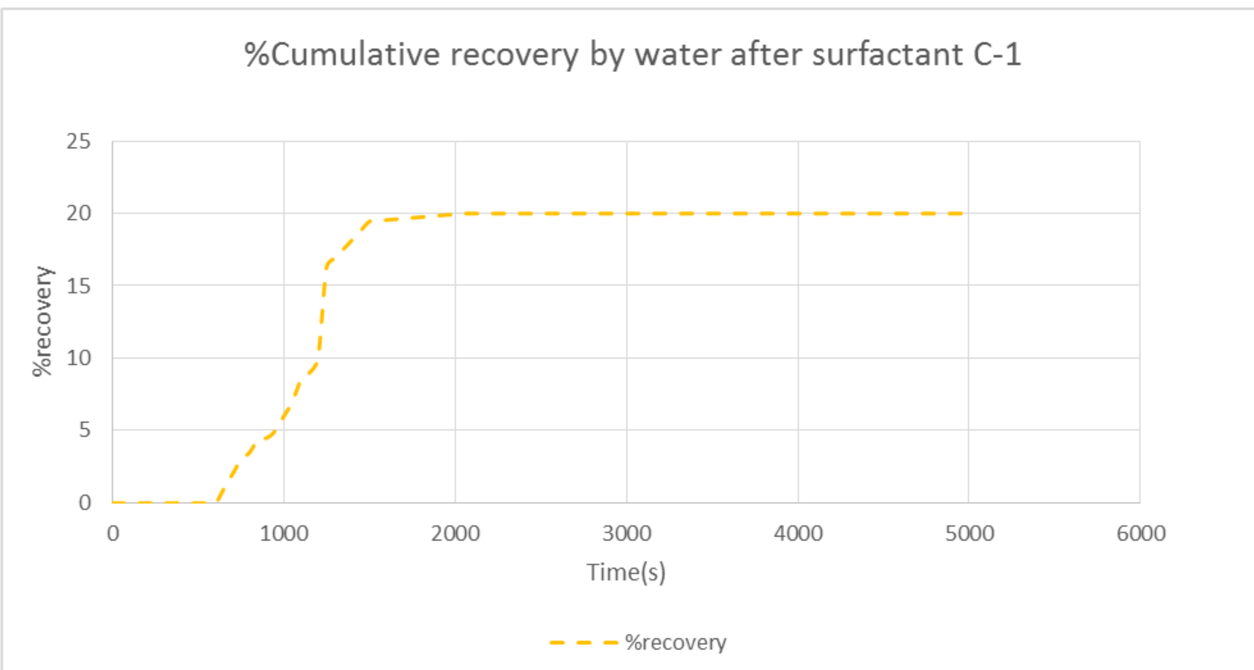

Figure 18 Cumulative recovery by water after surfactant

Table 4 Summary Core 1 Recovery

Core Sample 1	1%wt AOS	
Injected fluid	Recovery (%)	Cumulative Recovery (%)
Water	32	32
Surfactant	11	43
Water after Surfactant	20	63

CHAPTER 5

Conclusion and Recommendation

From the Experiments run, the studied surfactant between the 3 types of surfactants was the anionic type. This was chosen because cationic surfactants are easily adsorbed by oil wet induced sandstone and due to availability anionic surfactants were studied. Options created for the study were, AOS, SDS and the mixture of the two, from which AOS was seen as the more suitable surfactant for use due to its lower interfacial tension results and due to its higher stability. The contact angles for this surfactant were recorded and shown here in this report, which assisted in justifying the effect of the concentration of AOS in altering the wettability of the oil droplet on the induced oil wet surface.

Experimental core flooding, gave satisfactory results for the improvement of a secondary recovery method – water flooding, showing that the use of surfactant did improve the effectiveness of the recovery and in this case by 63% in total. This value may be improved and more oil may be recovered by the use of Gas injection.

The following recommendation for the project may help with future studies, which is more screening criteria could be studied to further develop better surfactant selection for use in recovery of oil in un-conventional shale oil reservoirs. Also the effect of the use of Gas injection with surfactants could be studied to further understand the increased potential for recovery.

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