THE INFLUENCE OF PRESSURE AND SALINITY ON SURFACTANT PERFORMANCE IN ALTERING ROCK WETTABILITY

By

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(9862)

Dissertation submitted in a partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
Petroleum Engineering

MAY, 2011

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CERTIFICATION OF APPROVAL

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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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ABSTRACT

In the past time, surfactants were used to increase oil recovery by lowering the interfacial tension between fluids of a multiphase reservoir. Later on, many researchers have focused on how to use surfactants to alter the oil wet reservoirs to water wet reservoirs to increase their ultimate recoveries. However, the influence of pressure and temperature on surfactant's performance in altering the wettability of a reservoir is currently not clearly known. The objective of this experimental study is to investigate the influence of different pressures, ranging from 14.7 psi-5000 psi and salinities, ranging from 3000-35000 ppm NaCl, on the surfactant's performance in altering the wettability of a rock. A synthetic brine, Sodium Deodecyl Sulphate surfactant, a selected crude oil and a Berea sandstone core sample was used in this study. The core was trimmed to 16 slices, each of 0.8-1.0 mm thickness and left to saturate for 20 days in 16 combinations of brine-surfactant concentrations. The experiment was conducted using the IFT 700 at constant temperature 70°C. It measured the wettability of the rock slice sample, by means of the sessile up method, where an oil droplet was risen to the core slice in the brine-surfactant phase and subsequently its contact angle measured. Contact angle expresses wettability. The sample's wettability change when pressure and salinities are changed has been evaluated. The study found that as salinity increases, the surfactant's performance decreased in changing the rock wettability from water-wet to weak water-wet, but after a certain point, further increase of salinity results in the increase of wettability to become more water-wet. On the other hand, there was a general increase in effectiveness of surfactant on rock wettability as pressure increased. The outcome of this study was achieved, which was to observe at which optimum pressure and salinity the surfactant is most effective in achieving better wettability.

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1.0 INTRODUCTION

1.1 Background of Study

The main task of a petroleum reservoir engineer is to produce oil and gas reservoirs with maximum economic rate and reaching ultimate recovery.

The ultimate recovery is heavily dependant on the capillary pressure and relative permeability behaviour of a sedimentary reservoir. These two parameters on the other hand are related to the reservoir wettability.

Reservoirs wettability varies from fully water wet to fully oil wet. The preferred wetting condition for a better ultimate recovery of oil/gas from a reservoir is water-wet. This study will look at ultimate recovery from the perspective of a water drive mechanism as the primary drive; or water-flooding as a secondary or tertiary recovery mechanism. The importance of maintaining a water-wet condition in a field under water drive has been discussed by many authors (Coley, Marsden and Calhoun 1956; Kinney and Nielsen 1951). These authors have shown that oil recovery, as a function of the water injected (using water-flooding as an Enhanced Oil Recovery, EOR option), is greater from water-wet cores than from oil-wet cores.

Thus, it is always favourable to have water-wet reservoirs. However this is not the case for all reservoirs. Most of the world's oil reservoirs are found in sedimentary rocks, where 60% of the world's oil and 40% of the world's gas reserves are in carbonate reservoirs (Bai 2009; Roehl and Choquette 1985). Carbonate reservoirs are typically more oil-wet than sandstone reservoirs (Chilingar and Yen 1983).

Most (80% of) carbonate reservoirs, which contain fractures are mixed to oil wet (Anderson 1986; Downs and Hoover 1989) making waterflooding recoveries very low (Tabary and Bazin 2007). Most sandstone reservoirs have mixed wettability, i.e. the oil is in contact with mineral surfaces to a limited degree (Dullien *et al.*, 1990). Thus, similarly, poor recoveries are also observed from oil-wet sandstone reservoirs. Waterflooding as an enhanced oil recovery (EOR) option is often performed to increase the recovery efficiency of these reservoirs.

In oil-wet reservoirs, oil recovery from waterflooding relies on the spontaneous imbibition of water to expel oil from the matrix into the fracture system. The spontaneous imbibition process is least efficient in strongly oil-wet rocks where the capillary driving force is weak. Therefore waterflooding oil recoveries are low in these reservoirs.

To increase recoveries in fractured, oil wet reservoirs, spontaneous imbibition can be promoted, by the use of surfactants (Zhang *et al.* 2006). Oil-water interfacial tension (IFT) reduction and wettability alteration are the causes that enhance spontaneous imbibition (Tabary and Bazin 2007; Bai 2009; Zhang *et al.* 2006; Hirasaki, Miller and Puerto 2008; Salehi, Johnson and Liang 2008; Wu *et al.* 2006).

This study will contribute to the knowledge of the use of surfactants in EOR, in terms of how its effectiveness in altering a reservoir's wettability is influenced by salinity and pressure.

1.2 Problem Statement

Ultimate recoveries of oil in oil-wet and mix-wet reservoirs are much lower than water-wet reservoirs. Surfactants are currently being studied for their uses in altering reservoirs' wettability from oil-wet/ mixed-wet to water-wet reservoirs. However;

The influence of pressure and salinity on surfactant's performance in altering the wettability of a reservoir is not known.

1.3 Objectives and Scope of Study

The objectives of this study were:

- To investigate the influence of pressure on surfactant performance on rock wettability.
- To investigate the influence of salinity on surfactant performance on rock wettability.

The scopes of study included:

- Conducting research on the theory and definition of terms related to the study.
- Conducting experiments to see the effectiveness of a surfactant in altering the wettability of a core sample when two parameters are varied, i.e. pressure and salinity.

1.4 Relevancy of Study

This study will produce a general relationship the between two independent variables (pressure and salinity of a surfactant) and a dependant variable (the wettability of a water-oil-rock system).

This relationship will give an idea on how these two independent variables will increase or decrease the recovery efficiency of a reservoir utilizing surfactant injection as an EOR option.

1.5 Feasibility of Study

Previously, surfactants were used to create low interfacial tensions (IFTs) between brine and oil. This results in the increase of spontaneous imbibition (Salehi *et al.* 2006). For significant oil recovery, many orders of magnitude reduction in IFT is required (Ayirala 1996). So, large quantities of surfactants are required for this purpose. According to Ayirala (1996), these surfactants are expensive.

Currently, more studies are dedicated for another approach for surfactant use. Low cost surfactants can be used at a moderate concentration to alter the wettability of the rock itself (Ayirala 1996), instead of the need to create ultra-low IFTs such as in the first approach.

From the results of this study, the knowledge of how salinity and pressure affects the performance of a surfactant, may help reservoir engineers determine the optimal pressure and salinity conditions for the maximum performance of a surfactant in changing a reservoir's wettability.

By this determination, the cost for surfactant applications can be reduced further.

The literature review will be covered in the next section, followed by the description of the experimental methodology in the following part, as well as the current progress. The results will be then discussed. The conclusions of the study are summarized in the last section.

2.0 LITERATURE REVIEW

2.1 Wettability Definition

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids (Tarek 2001). The fluid with the higher affinity toward the solid surface is called the wetting phase, the other fluid is the non-wetting phase.

Wettability is very important in oil recovery processes and has a strong impact on distribution, location and flow of oil and water in reservoir during production (Anderson 1986).

When the system is in equilibrium, the wetting phase will completely occupy the smallest pore and be in contact with a majority of the rock surface, if the saturation of wetting fluid is sufficiently high. The non-wetting fluid will occupy the centers of the larger pores and will form globules that extend over several pores (Tiab 2004). The fluid, which occupies the larger pores have high relative permeability as compared to the fluid occupying the smaller pores.

2.2 Wettability Classification

In a porous medium containing two immiscible fluids (oil and water), the wettability of fluid/rock system can range from strongly water-wet to strongly oil-wet.

A rock sample that imbibes only water spontaneously is said to be *strongly water-wet*. In this case water occupies the small pores and contacts the majority of the rock surface (Anderson 1986; Derahman and Zahoor 2008). The one that imbibes only oil spontaneously is called *strongly oil-wet*. Oil occupies the smaller pores and spreads over the majority of the rock surface, while the water occupies the larger pores.

When the rock has no strong preference for either oil or water, the system is said to be *neutral (or intermediate) wettability* (Tiab 2004). Besides strong and neutral wettability, there are two different types of wettability such as *fractional wettability*, and *mixed wettability* (Anderson 1986).

Fractional wettability (or Dalmation wetting) implies spotted heterogeneous wetting of the surface (Brown and Fatt 1956). Mixed wettability commonly refers to the condition where the smaller pores are occupied by water and are water wet, but the larger pores of the rock are oil wet and a continuous filament of oil exists throughout the core in the larger pores.

Because the oil is located in the larger pores of the system in a continuous path, oil displacement from the rock occurs even at very low oil saturation. That is why the residual oil saturation of mixed-wettability rocks is unusually low.

2.3 Wettability Measurement Techniques

To-date, different methods have been proposed and used for representing wettability (Amott 1959; Anderson 1986; Donaldson *et al.* 1969).

They include quantitative methods such as *contact angle measurements* (Young, 1805), *imbibition and forced displacement from a core (Amott)* (Amott 1959), and *USBM wettability method, which uses centrifugal displacement to determine the average wettability of a core* (Donaldson *et al.* 1969). By representing the wettability in a quantitative way, it is possible to interpret the type of wettability existing or the types of wettability co-existing within a reservoir.

The contact angle measures the wettability of a specific surface, while the Amott and USBM methods measure the average wettability of a core (Anderson 1986). In this study, the author utilizes the contact angle measurement as a means of the quantitative determination of the wettability of a brine-oil-rock system.

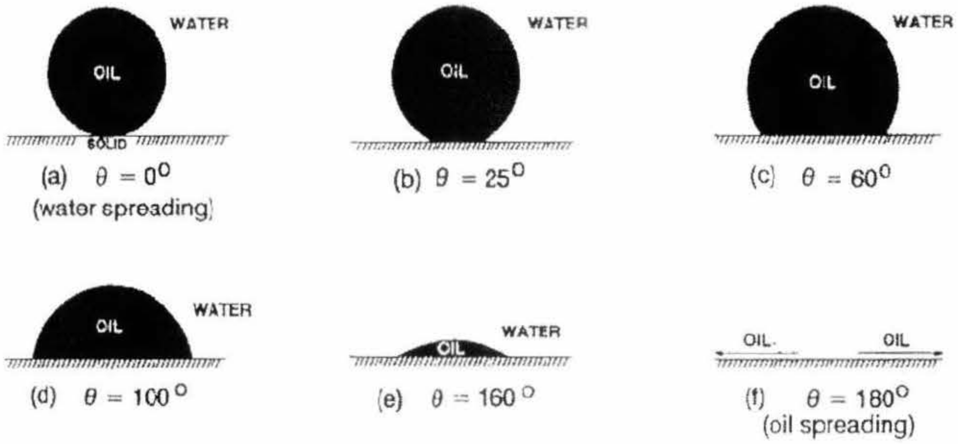


Figure 1: Idealized examples of contact angles and spreading (Morrow 1990)

When oil and water are placed together on a surface (Figure 1), a curved interface between the oil and water is formed, with a contact angle at the surface that can range from 0-180°. By convention, the contact angle, θ, is measured through the water. According to Anderson (1986), when θ is;

- 0° and 60-75°, the system is defined as water wet
- 180° and 105-120°, the system is defined as oil-wet
- 60-75° and 105-120°, a system is neutrally or intermediately wet

Several methods are available in determining contact angle: tilting plate method, sessile drop method, vertical rod method, tensionmetric method, cylinder method and capillary rise method (Anderson 1986). The most common method employed in the petroleum industry, and in this study, is the sessile drop method.

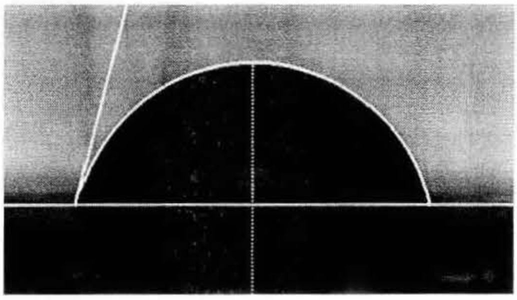


Figure 2: An illustration of the sessile drop method

The contact angle is measured by using the sessile drop method (Figure 2). A liquid-droplet is dropped on a cleaned and polished area of a solid (example: a drop of oil inside water). Then, the contact angle is measured optically with a video system.

2.4 Surface/ Interfacial Tension

The above section decribed the term wettability, which relates to the interaction between fluids and rock. In this section, the interaction between the fluids (oil-water) will be elaborated instead.

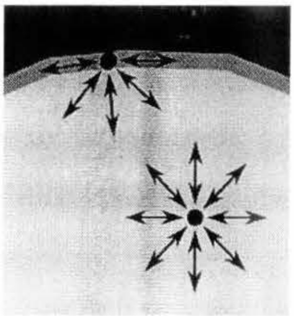


Figure 3: Diagram of the forces on two molecules of a fluid interfacing with another fluid (Snacks 2010)

When two immiscible fluids (gas-liquid) or (liquid-liquid) are in contact, the fluids are separated by a well-defined interface, which is only a few molecular diameters in thickness. Surface tension results from an imbalance of molecular forces in a fluid. At the surface of the fluid, the fluid molecules are attracted to each other and exert a net force pulling themselves together. High values of the surface tension means the molecules tend to interact strongly. Lower values mean the molecules do not interact as strongly.

Surface/ interfacial tension is described as a measurement of energy on the surface of one fluid surrounded by another immiscible fluid which allows it to behave like an elastic sheet (denoted by the purple interface layer in Figure 3). When a liquid interfaces with a gas to produce this effect, it is referred to as surface tension (ST).

When this effect is found between two liquid phases (such as in oil-water), it's referred to as interfacial tension (IFT). The ST and IFT can be measured using the pendant drop method. They have the dimensions of force per unit length (Newtons/meter or Dynes/cm).

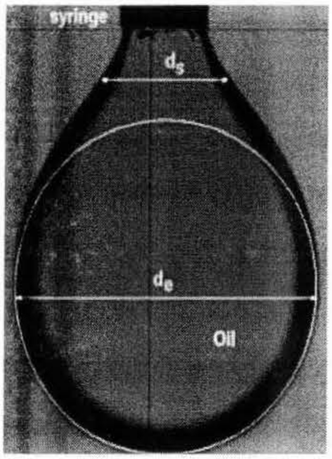
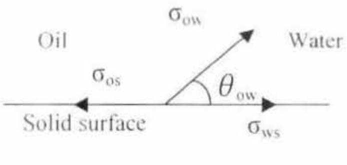


Figure 4: An illustration of the sessile drop method

Using the pendant drop method (Figure 4), the geometry of a drop is analysed optically. A drop is generated from the end of a capillary needle in a bulk fluid at reservoir conditions (Pressure and Temperature). With a calibrated and accurate video lens system, the complete shape of the drop is analysed with software. Then, the Laplace equations of the analysis are solved numerically over its complete shape to get the ST/IFT.

In this study, the ST/IFT is can be correlated qualitatively to the wettability of a water-oil-rock system using Young's equation (Young, 1805) below:



$$\cos\theta = \frac{\sigma_{os} - \sigma_{ws}}{\sigma_{ow}}$$

Figure 5: Illustration of the parameters from Young's equation and Young's equation (Dijke & Sorbie)

As can be seen, by assuming that σos and σws is constant when the ST/IFT, σow is lowered, we know that the contact angle is lowered and thus a water-oil-rock system becomes more water-wet.

2.5 Factors that Determine the Wettability of a Rock

The interaction between a rock surface and a fluid such as oil and water determines its wetting characteristics, whether it is water-wet or oil-wet. From thermodynamic, all surfaces try to reach to their lowest possible surface energy in a specific fluid phase (Stumm 1992). The lowest surface energy of sandstone in most oil-water rock systems is when the quartz from sandstone is in contact with the formation water. This means that quartz is preferentially water-wet (Schlangen *et al.* 1995). However, there are other factors that can determine the wettability of a rock.

These main factors include anything that may change the surface energy of a rock surface, including: petroleum composition effects, pH alteration, clay percentage, feldspar percentage, the presence of surfactants, salinity, and pressure and temperature change (Barclay and Worden 2000). In this study we will utilize surfactants to alter wettability.

By adding surface-active agents (surfactants) to a water–oil–rock system the wetting preference of the sandstone rock surface can be altered by changing the surface energy between the sandstone surface and the non-wetting fluid. By this way, a rock wettability can be altered by the addition of surfactants. These surfactants are usually polar compounds which have the capability of changing the energy of a surface.

2.6 Wettability Alteration by Surfactants

A surfactant is a polar compound, consisting of an amphiphilic molecule, with a hydrophilic part (anionic, cationic, amphoteric or nonionic) and a hydrophobic part (Sah 2003). Surfactant, derived from "surface acting agent", is a wetting agent used to lower the IFT of an oil-water mixture allowing improved wetting (by a more preferred wetting phase, water) (Retrieved from http://www.ramehart.com/glossary.htm#Surface_Tension on 25th August 2010).

There are a number of mechanisms for surfactant adsorption such as electrostatic attraction/repulsion, ion-exchange, chemisorption, chain-chain interactions, hydrogen bonding and hydrophobic bonding. The nature of the surfactants, minerals and solution conditions as well as the mineralogical composition of reservoir rocks play a governing role in determining the interactions between the reservoir rock and externally added surfactants and their effect on wettability (Babadagli 2003).

2.7 Sodium Dodecyl Sulfate

Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$), also called sodium lauryl sulfate, is a negatively charged surfactant (an anionic wetting agent that reduces and lowers the surface tension of a liquid and the tension between two liquids).

From the below figure, it can be seen that in aqueous form, the polar part of the molecule (consisting of the chain and the SO_4 end) has an amphiphilic part (the chain end) and the hydrophilic part (the SO_4 end).

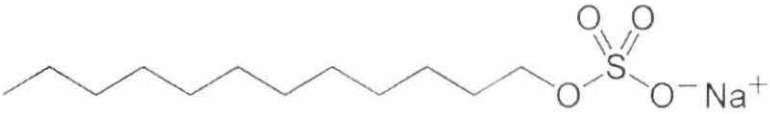


Figure 6: The molecular illustration of sodium dodecyl sulfate

3.0 RESEARCH METHODOLOGY

The main objective of this project was to experimentally study the effect of pressure and salinity on the effectiveness of surfactant on rock wettability.

3.1 Key Milestones and Elaboration

Figure 6 below describes the overall milestones and general flow of this project.

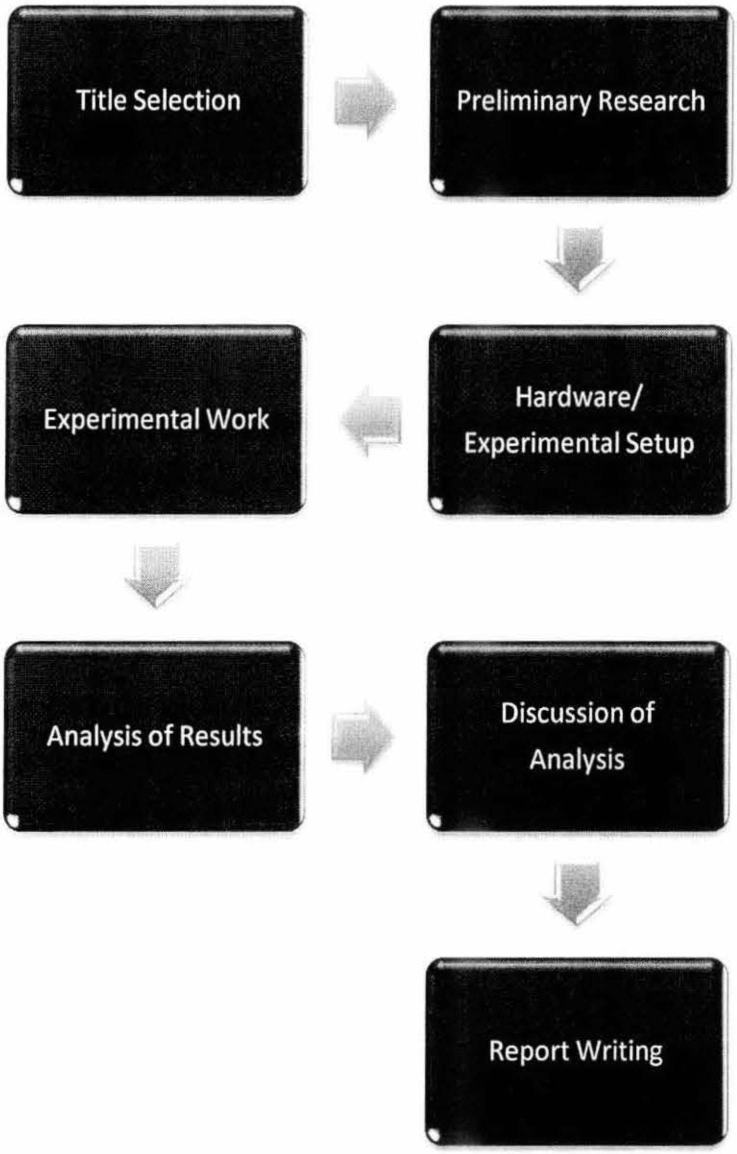


Figure 7: Flowchart Representation of Project Key Milestones

Table 1: Elaboration on the Key Milestones

Steps	Activity
Title Selection	Selection of the most appropriate final year project title.
Preliminary Research	The performing of initial ground work in obtaining information regarding the project and its elements like fundamental theories and concepts, hardware, software and other verifications. Also included critical literature survey to enhance knowledge about advances and previous studies regarding wettability and surfactants, among others. Initial tools/equipments that are required were identified.
Hardware / Experimental Setup	The selection and design of experimental apparatus, materials, and procedures and learned how to operate hardware. Involved booking for the use of hardware in the lab. Involved the purchasing of surfactants (or other items, if necessary). Cable termination, instrument setup and PC/Laptop initializations were done in this milestone.
Experimental Work	A surfactant, an oil sample, water was selected for this experiment to produce a simulation of a water-oil-rock system. The two independent variables, pressure and salinity of the system has been manipulated using the IFT 700 and manual preparation, respectively. Their changing effect on the contact angle of the water-oil-rock system was monitored and measured using the IFT 700. Results were then recorded and tabulated.
Analysis of Results	The tabulated contact angle was used to calculate, quantitatively the wettability of the water-oil-rock system that was experimented on. The pressure and salinity change with the wettability change of the core was plotted onto a series of graphs. The curves provided an illustration of their relationships.
Discussion of Analysis	The results were discussed and compared to literature. They were studied to conclude which conditions of salinity and pressure is the most optimal in changing the wettability of a reservoir for the particular water-oil-rock system. Determination if the objectives were met.
Report Writing	Compilation of all research findings, literature reviews, experimental works and outcomes into a final report.

3.2 Research Methodology/ Project Activities

3.2.1 Preparation of Brine and Surfactant Mixtures

1) Sixteen (16) brine-surfactant mixtures with different concentration combinations, 1 liter each, has been prepared by dissolving Sodium Chloride (NaCl) and Sodium Doedcyl Sulfate ($CH_3(CH_2)_{11}OSO_3Na$) in distilled water. The mixtures were prepared using a heater-mixer.

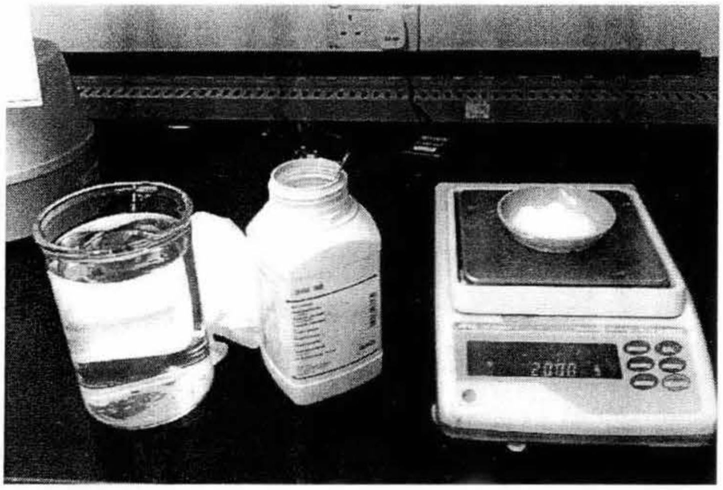


Figure 8: Sodium Chloride and Sodium Deodcyl Sulphate mass measurement using a digital weighing machine

The brine-surfactant mixtures were prepared according to mass amounts specified in the table below:

Table 2: The sixteen combinations of brine-surfactant mixtures that has been prepared

	SDS (0.0g)	SDS (0.5g)	SDS (1.5g)	SDS (3.5g)
NaCl (3.0g)	NaCl 3000ppm, SDS 0ppm	NaCl 3000ppm, SDS 500ppm	NaCl 3000ppm, SDS 1500ppm	NaCl 3000ppm, SDS 3500ppm
NaCl (5.0g)	NaCl 5000ppm, SDS 0ppm	NaCl 5000ppm, SDS 500ppm	NaCl 5000ppm, SDS 1500ppm	NaCl 5000ppm, SDS 3500ppm
NaCl (20.0g)	NaCl 20000ppm, SDS 0ppm	NaCl 20000ppm, SDS 500ppm	NaCl 20000ppm, SDS 1500ppm	NaCl 20000ppm, SDS 3500ppm
NaCl (35.0g)	NaCl 35000ppm, SDS 0ppm	NaCl 35000ppm, SDS 500ppm	NaCl 35000ppm, SDS 1500ppm	NaCl 35000ppm, SDS 3500ppm

3.2.2 Measurement of Core Properties

1) The Berea sandstone core was dried by leaving it in an oven, set at 50-60 degrees Celcius for 1 day, from 8:20am, 09/02/2011 to 8:20am, 10/02/2011 (Figure 9).

Figure 9: The core sample was dried using an oven

2) The length and diameter of the core was measured using a vernier scale.

3) The Poroperm apparatus was used to measure the porosity and permeability of the core sample for a number of six times and the average measurements were recorded.

3.2.3 Slicing of Core

1) The core was sliced into 16 slices using the core trimming machine, each ranging from 0.8-1.0 mm thickness (Figure 10).

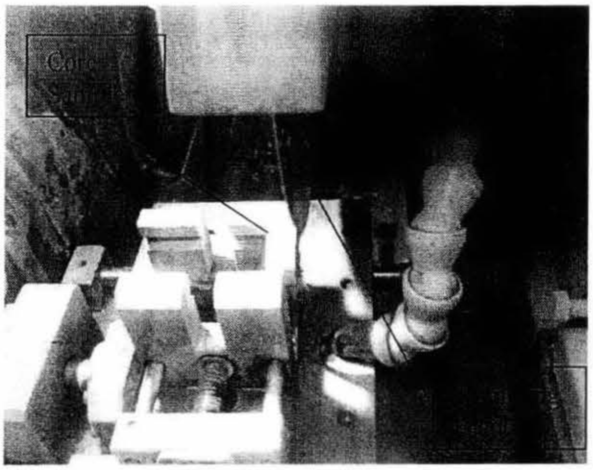


Figure 10: The core sample was sliced using the core trimming machine

3.2.4 Measurement of Contact Angle (with the Sessile Up Method)

1) The 16 core slices were saturated and aged in the brine-surfactant mixtures of 0ppm SDS (NaCl 3000ppm,SDS 0ppm; NaCl 5000ppm,SDS 0ppm; NaCl 20000ppm,SDS 0ppm; NaCl 35000ppm,SDS 0ppm) for 20 days. Each core slice was placed in a plastic container containing 100ml of one mixture. The saturation and aging was done at atmospheric pressure and room temperature.

Figure 11: The core slices were saturated and aged in the brine-solution mixtures at atmospheric pressure and room temperature for 20 days

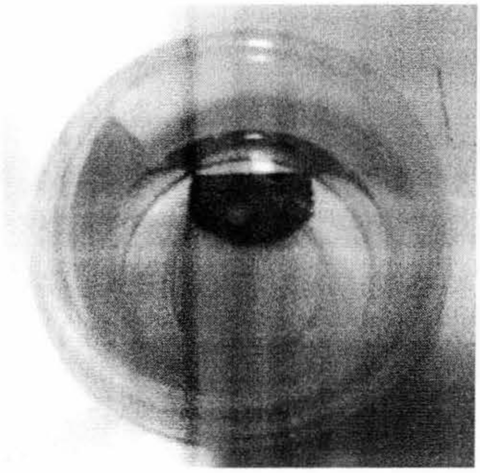


Figure 12: A close-up view of a core slice being saturated and aged in a plastic container containing 100ml of one mixture

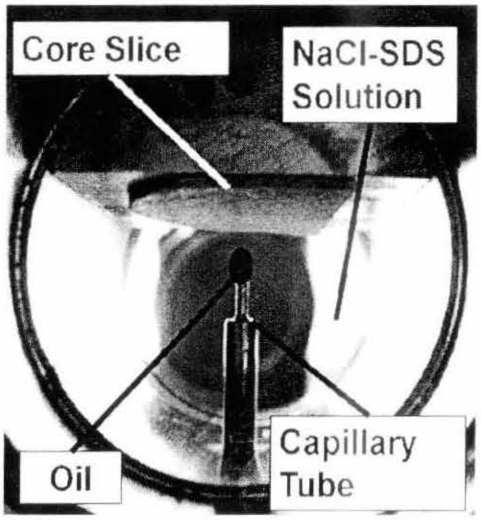


Figure 13: The sessile up experimental setup

Note: The following methodology details the procedures used for the measurement of contact angle.

2) The capillary nozzle of the IFT700 was cleaned using compressed air and was screwed to the bottom of the IFT700 viewing cell.

3) The line was connected to the screwed capillary nozzle.

4) One of the cell's window nuts was unscrewed and the cell was cleaned using compressed air.

5) The core slice that has been saturated and aged with NaCl 3000ppm, SDS 0ppm for 20 days was mounted onto a holder in a horizontal position. The core slice holder was then placed in the core chamber.

6) The cell was closed by re-screwing the window nut.

7) The Vacuum Pump and Supply Line (which will feed the associated brine-surfactant mixture into the cell) was connected to the cell.

8) The Vacuum Pump was started to obtain a vacuum state in the cell. The valve was closed and the Vaccum Pump was turned off.

9) The valve from the Supply Line was opened and the view cell was filled with NaCl 3000ppm, SDS 0ppm mixture. Some fluid was left to drain at the top of the cell to remove any air bubbles.

10) The valve was closed once view cell is full.

11) The temperature of the cell was set to 70 °C.

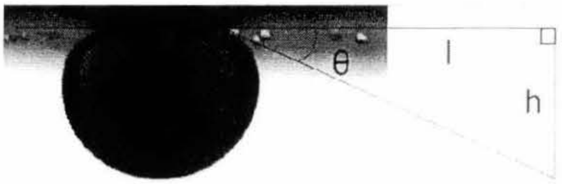
12) The pressure of the cell was set to 200 psia using the IFT700 Pressure Handpump.

13) A drop of crude oil was released from the capillary nozzle into the cell (Figure 13) so that it rises and touches the bottom of the core slice. The drop was released using the IFT700 Droplet Handpump.

14) The cell was then set aside with all the valves closed to age for a predetermined time of 30 minutes for the oil-brine-rock system to reach equilibrium.

15) Camera focus was adjusted so that the tip of the needle image is visibly sharp. The camera viewing angle was adjusted so that the needle image is vertical. Camera focus was adjusted to get a clear image of the oil bubble at the bottom of the core slice.

16) Initial image of the sample was obtained and the contact angle was calculated using trigonometric functions illustrated by Figure 14. The initial contact angle was recorded.



Contact Angle Calculation

1. A right angled triangle was drawn with the hypotenuse line being the contact angle line
2. The contact angle θ was calculated with the formula:

$$\theta = \tan^{-1}(h/l)$$

Figure 14: Contact angle calculation

17) Procedures 14-16 are to be repeated for pressures 200psi, 500psi, 1000psi, 3000psi, 5000psi.

18) Procedures 2-17 are to be repeated for the other 3 brine-surfactant mixtures containing 0ppm SDS (i.e. NaCl 5000ppm, SDS 0ppm; NaCl 20000ppm, SDS 0ppm; NaCl 35000ppm, SDS 0ppm)

19) Procedures 1-18 are to be repeated for the other 12 brine-surfactant mixtures containing 500ppm SDS, 1500ppm SDS and 3500ppm SDS.

3.3 Equipments and Tools

Figure 15: The IFT 700

The main equipment that is to be used in this study is the IFT 700, manufactured by Vinci Technologies. The IFT will be used to determine at reservoir conditions:

- Contact angle between liquid and solid interfaces using sessile drop method.

The pendent drop method and sessile drop method has been described in the introductory section of this document. The technical specifications of the IFT 700 are:

IFT standard measurement	: 0.1 to 72 mN/m
Temperature	: Ambient to 180°C
Temperature accuracy	: 0.1 °C
Pressure	: 700 bar (10,000psi)
Wetted parts	: Stainless steel
Power supply	: 220 VAC 50 Hz

Other equipments used in this experiment are the digital weighing machine, heater-mixer, oven and the core trimming machine.

3.4 Key Milestones

There were two semesters in the completion of this project: the research semester and the experimental work semester. All activities were completed as per the Gantt Charts below:

FINAL YEAR 1st SEMESTER (JULY 2010)

No.	Detail/ Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
1	Project title selection and start	■						Mid-semester break								
2.	Preliminary research work		■	■	■	■	■									
3.	Preliminary report submission						■									
4.	Study on fundamental concepts related to the project				■	■	■									
5.	Study on effect of pressure change on the surfactant's effectiveness on wettability change				■	■	■		■	■						
6.	Submission of progress report									■						
7.	Seminar (optional)					■										
8.	Study on effect of salinity change on the surfactant's effectiveness on wettability change									■	■	■	■	■	■	
9.	Preparation of interim report													■	■	
10.	Submission of interim report														■	
11.	Oral presentation															■

Figure 16: The Gantt Chart for the Research Semester

FINAL YEAR 2nd SEMESTER (JAN 2011)

No.	Detail/ Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
1	Finalizing experiment methodology	■						Mid-semester break								
2.	Gathering and booking of equipments and reagents		■													
3.	Preparation of SDS-NaCl mixtures			■												
4.	Measurement of core sample properties and slicing of core sample				■											
5.	Aging of core sample in SDS-NaCl mixtures					■	■									
6.	Commencement of experimental work using IFT700 and preparation of progress report								■	■						
7.	Submission of progress report									■						
8.	Experimental work using IFT700									■	■					
9.	Seminar/ Poster exhibition											■	■			
10.	Submission of final report												■			
11.	EDX													■		
12.	Oral presentation														■	
13.	Delivery of Report to External Examiner															■

Figure 17: The Gantt Chart for Experimental Work Semester

4.0 RESULTS AND DISCUSSION

The measurements of the Berea sandstone core properties are as of the below:

Table 3: The measurements of properties of the core sample

Core Properties					**Dimensions**		
	Porosity, %	Grain Density, (g/cc)	Kair,(mD)	K∞,(mD)	L,(mm)	D,(mm)	Weight,(g)
Initial reading	14.3	2.67			51.24	38.08	131.907
Reading 1	14.605	2.647	20.062	17.098			
Reading 2	14.773	2.652	20.24	17.183			
Reading 3	14.853	2.655	20.432	17.212			
Reading 4	14.844	2.654	20.317	17.567			
Reading 5	14.897	2.656	20.315	17.655			
Reading 6	14.929	2.657	20.385	17.527			
Average	14.817	2.654	20.292	17.374			

From the above, it can be deduced that the sample is of low porosity and poor permeability.

The snapshots that were taken from the sessile up experiment for all sixteen brine-oil-rock-surfactant systems and the calculation of their respective contact angles can be found in the APPENDIX. Those results are summarized in the Tables 4-7 below:

Table 4: Summary of Contact Angle Results for 0ppm SDS solutions

	3000 ppm NaCl	**5000** ppm NaCl	**20000** ppm NaCl	**35000** ppm NaCl
200 psi	51.17	103.37	49.94	36.87
500 psi	50.06	97.24	46.51	35.88
1000 psi	47.29	94.84	46.40	34.82
3000 psi	39.61	93.75	45.37	34.35
5000 psi	26.79	93.50	43.41	32.57

Table 5: Summary of Contact Angle Results for 500ppm SDS solutions

	3000 ppm NaCl	**5000** ppm NaCl	**20000** ppm NaCl	**35000** ppm NaCl
200 psi	40.36	47.76	44.56	32.25
500 psi	41.03	48.18	40.60	35.89
1000 psi	37.80	45.81	35.62	30.75
3000 psi	27.64	36.36	29.90	23.84
5000 psi	26.24	35.40	27.85	23.43

Table 6: Summary of Contact Angle Results for 1500ppm SDS solutions

	3000 ppm NaCl	**5000** ppm NaCl	**20000** ppm NaCl	**35000** ppm NaCl
200 psi	24.23	45.73	35.88	42.65
500 psi	21.14	42.19	34.79	39.42
1000 psi	19.74	40.54	32.17	34.16
3000 psi	15.59	38.50	31.76	33.02
5000 psi	14.85	38.13	27.67	27.18

Table 7: Summary of Contact Angle Results for 3500ppm SDS solutions

	3000 ppm NaCl	**5000** ppm NaCl	**20000** ppm NaCl	**35000** ppm NaCl
200 psi	20.56	32.97	30.30	49.14
500 psi	19.89	22.67	28.71	47.56
1000 psi	19.02	21.80	27.84	47.49
3000 psi	18.85	20.04	17.43	44.10
5000 psi	17.99	17.97	13.69	37.44

4.1 The Influence of Pressure on the Performance of Surfactant on Rock Wettability

Four graphs of contact angle θ versus pressure graphs were plotted based on results from Tables 4-7, each for 0 ppm SDS, 500 ppm SDS, 1500 ppm SDS, 3500 ppm SDS solutions:

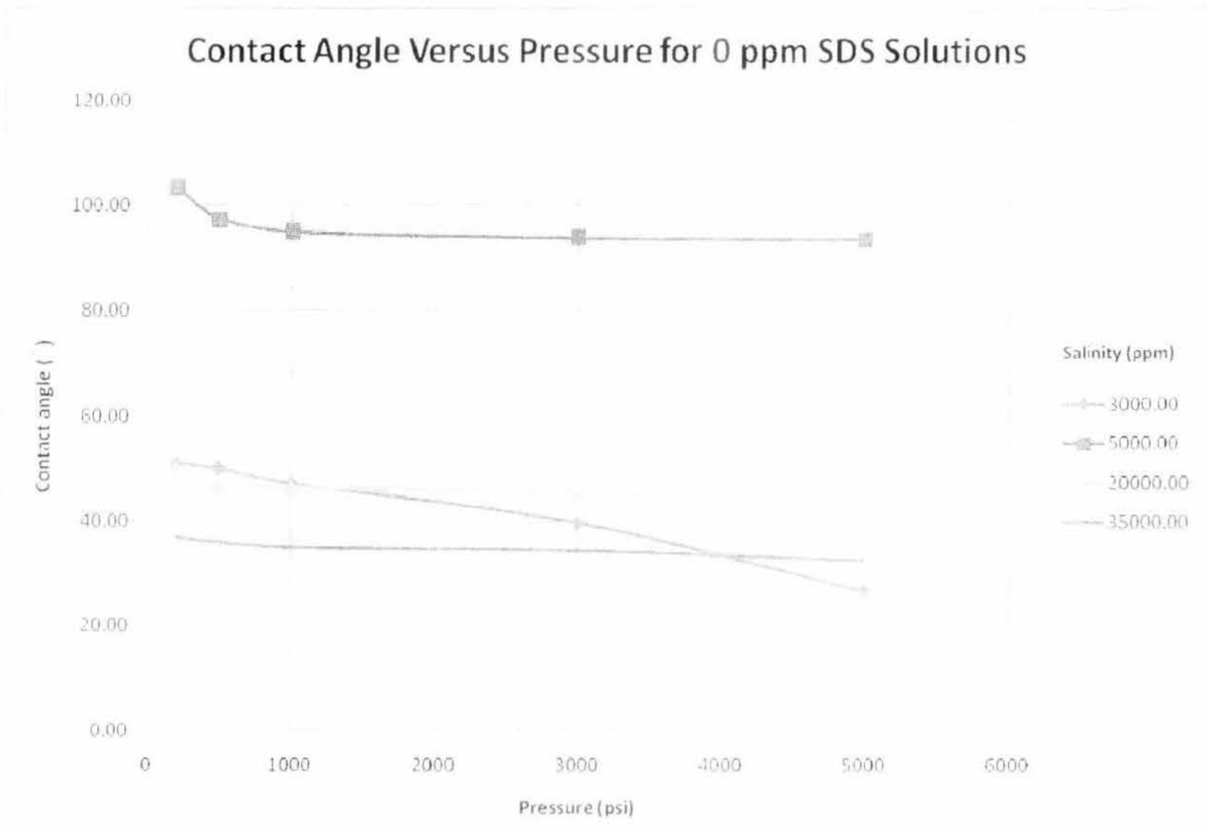


Figure 18: Contact angle versus pressure graph for 0ppm SDS solutions

Figure 18 is an illustration of the original wettability of the rock at various pressures as there is no SDS present in the system. It can be observed that the original wettability of the rock has a weak relationship with pressure, compared to that of salinity (Discussed further in Section 4.2). The trend shows that as pressure increases, the original wettability of the Berea sandstone approaches a slightly more water-wet nature.

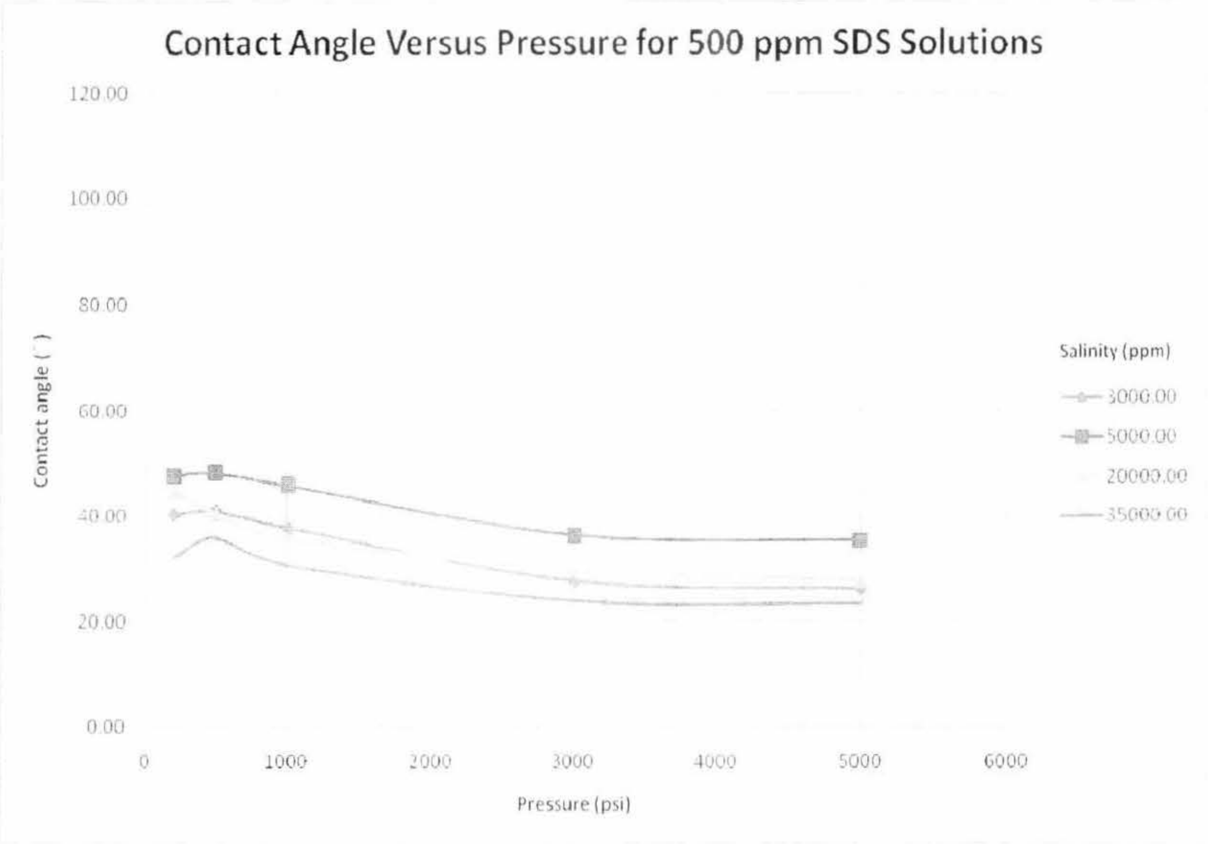


Figure 19: Contact angle versus pressure graph for 500ppm SDS solutions

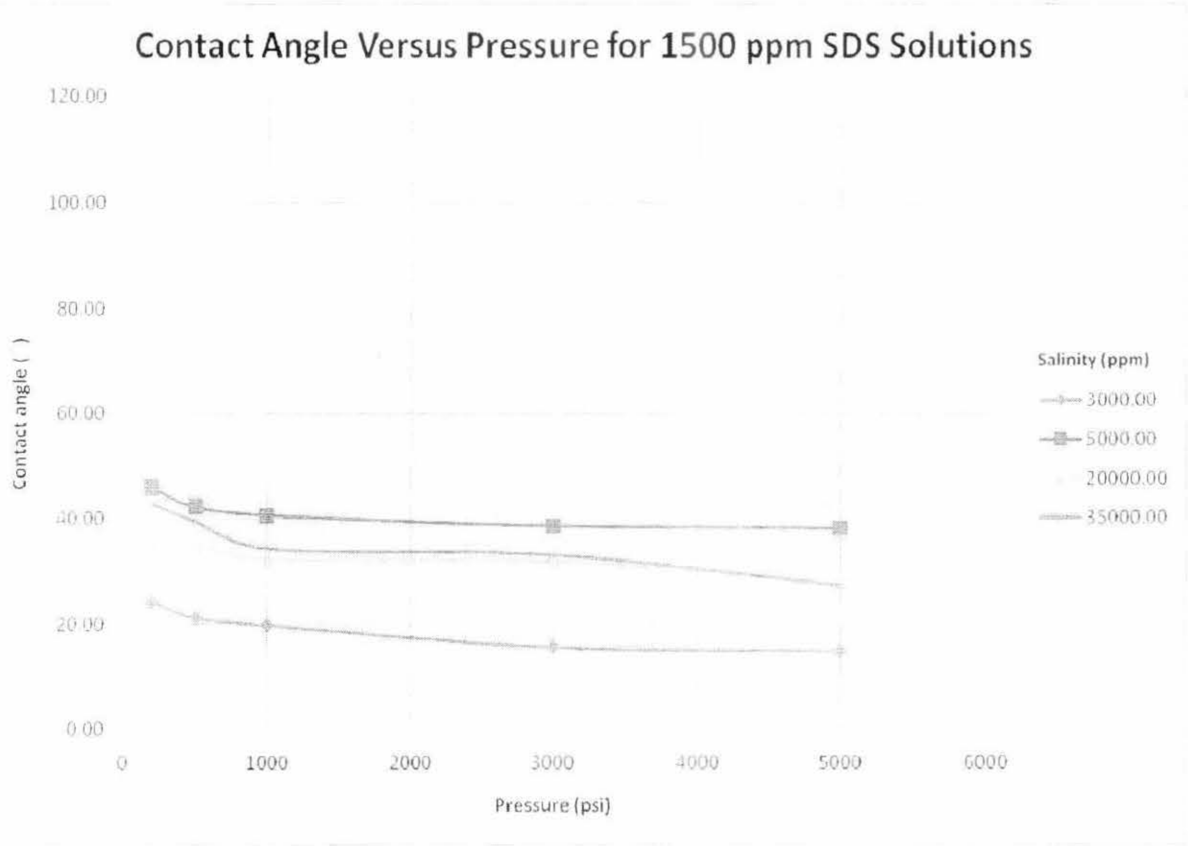


Figure 20: Contact angle versus pressure graph for 1500ppm SDS solutions

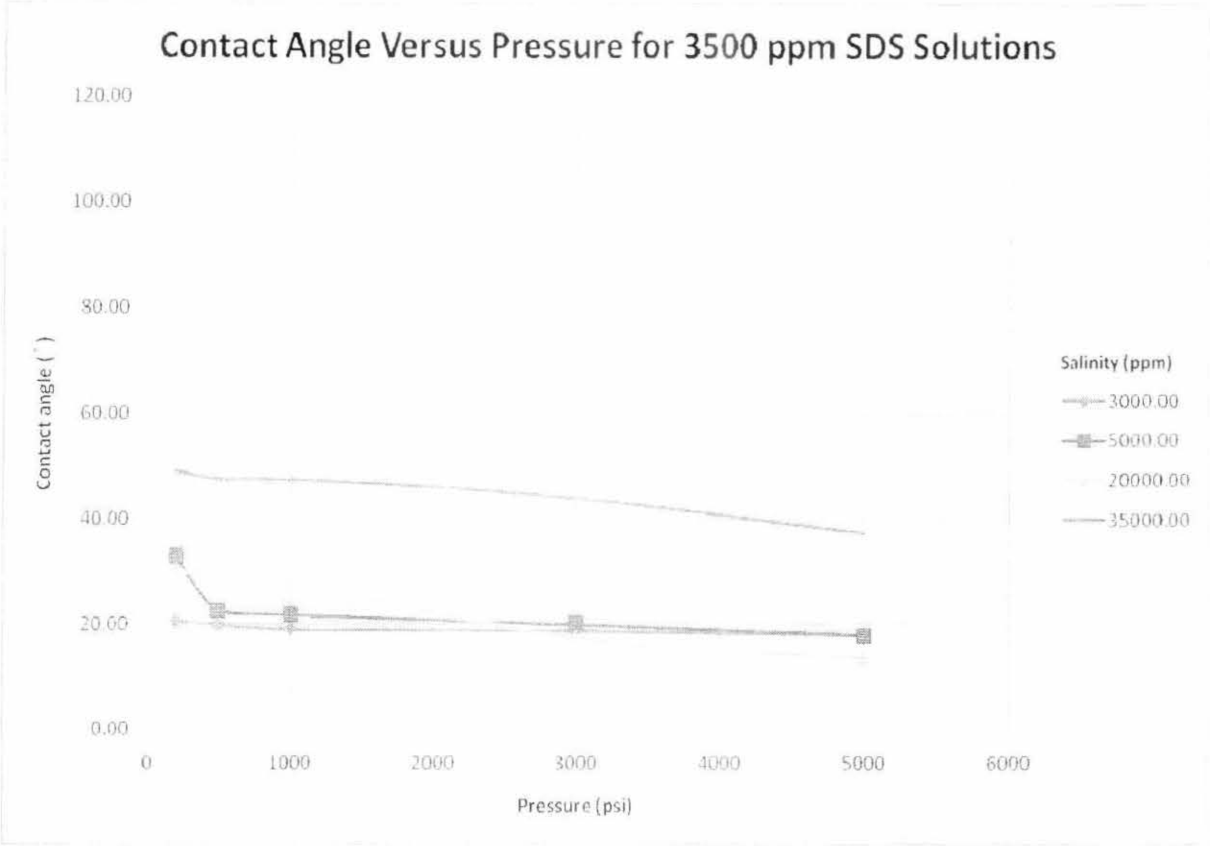


Figure 21: Contact angle versus pressure graph for 3500ppm SDS solutions

Figures 19, 20 and 21 shows the relationship between wettability and pressure with presence of surfactant SDS in three concentrations – 500, 1500 and 3500 ppm SDS. From these figures it is suggested that the concentration of SDS does not affect the extent of wettability change with relation to pressure. For example, for both 1500 and 3500 ppm SDS (at salinity 5000 ppm NaCl), when pressure is increased from 3000 to 5000 psi, the contact angle changes from 36.36°- 35.40° and 20.04°- 17.97°, respectively. The change in contact angles are approximately the same and are not affected by the concentration of SDS.

For all concentrations of Brine-SDS, it can be observed that there is a reduction in contact angle (wettability approaches a more water-wet nature) as pressure increases. An increase in pressure leads to the compression of the oil droplet. The compression results in the change of the droplet's shape, causing the decrease in its contact angle to the rock surface. It can be illustrated in Figure 22.

Figure 22: A figure depicting a higher contact angle for a low pressure system (left) and a lower contact angle for a high pressure system (right) due to compression of an oil droplet.

The below mentioned literature can give an understanding of the associated observations.

Wang and Gupta (1995) presented IFT data for crude oil and two different brine systems in a pressure and temperature range of 14.7 to 10000 psia and 70 to 200°F respectively. Trend lines fitted to the data indicated an increase in the IFT with increasing pressure. However a fair amount of scatter in the plots indicates the absence of any clear trend. An increase in IFT means the wettability has been altered to a more water-wet state (Wang and Gupta 1995).

Jennings and Newman (1971) conducted a similar study to investigate the effect of temperature and pressure on the IFT of benzene-water and n-decane-water using the pendant drop method and reported that IFT increased with the increasing pressure and decreased with increasing temperature, respectively. It also devoids any particular trend (Jennings and Newman 1971).

Hocott (1938) reported that the IFT between water and reservoir crude oil samples increase with pressure until the saturation pressure is reached, and then slowly decreased with pressure.

In summary, the change of IFT and contact angle (and thus the wettability) with pressure is largely influenced by the composition of fluids in a rock-oil-water system. If the oil is of a more compressible type, then the contact angle will very greater when pressure is changed. The presence of SDS does not affect the extent of wettability change when pressure is increased.

4.2 The Influence of Salinity on the Performance of Surfactant on Rock Wettability

Four graphs of contact angle θ versus salinity graphs were plotted based on results from tables 4-7, each for 0 ppm SDS, 500 ppm SDS, 1500 ppm SDS, 3500 ppm SDS solutions:

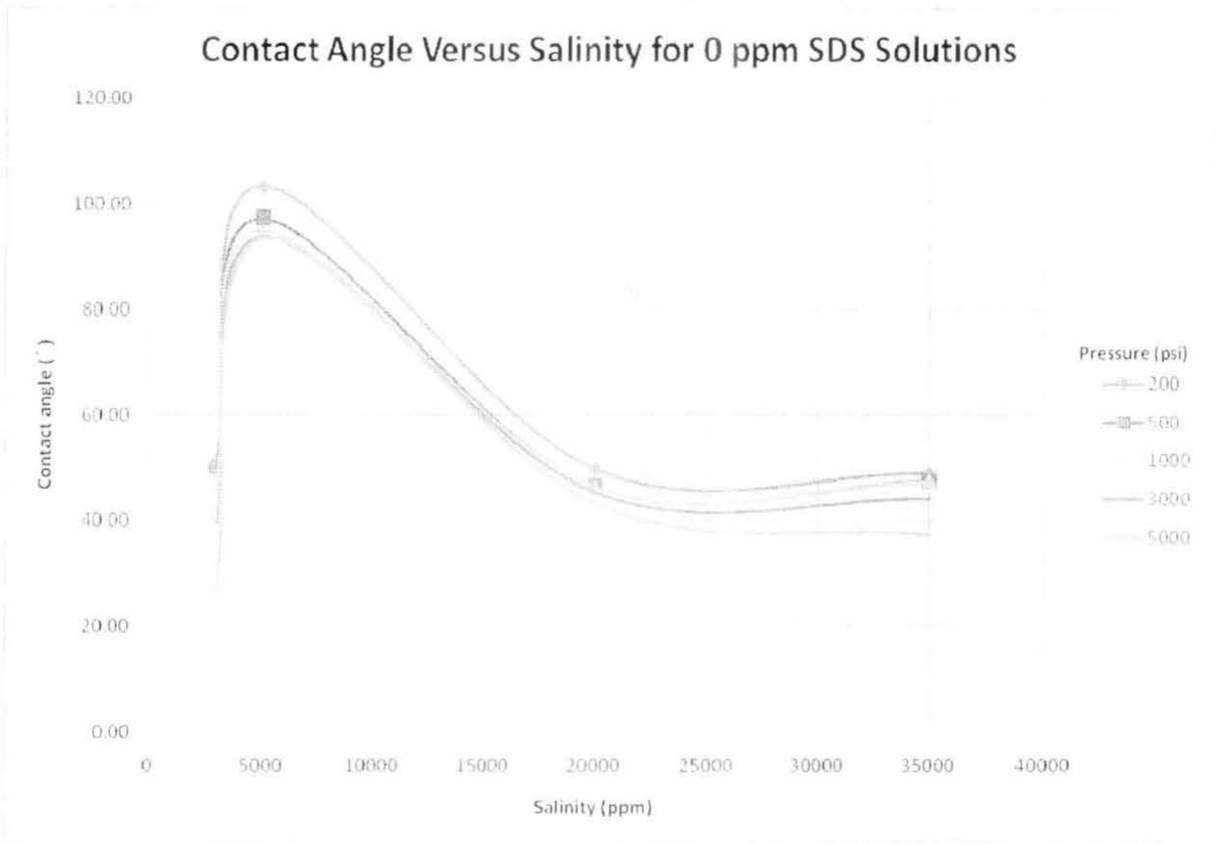


Figure 23: Contact angle versus salinity graph for 0ppm SDS solutions

Figure 23 is an illustration of the original wettability of the rock at various salinities as there is no SDS present in the system. The figure suggests that salinity has a more profound effect on wettability compared to pressure. It can be observed that the rock is water-wet (Contact Angle < 75°) for both low salinity (3000 ppm NaCl) and high salinity (20000, 35000 ppm NaCl) systems. However the rock wettability was altered to oil-wet (Contact Angle > 90°) when the salinity was intermediate at 5000 ppm NaCl.

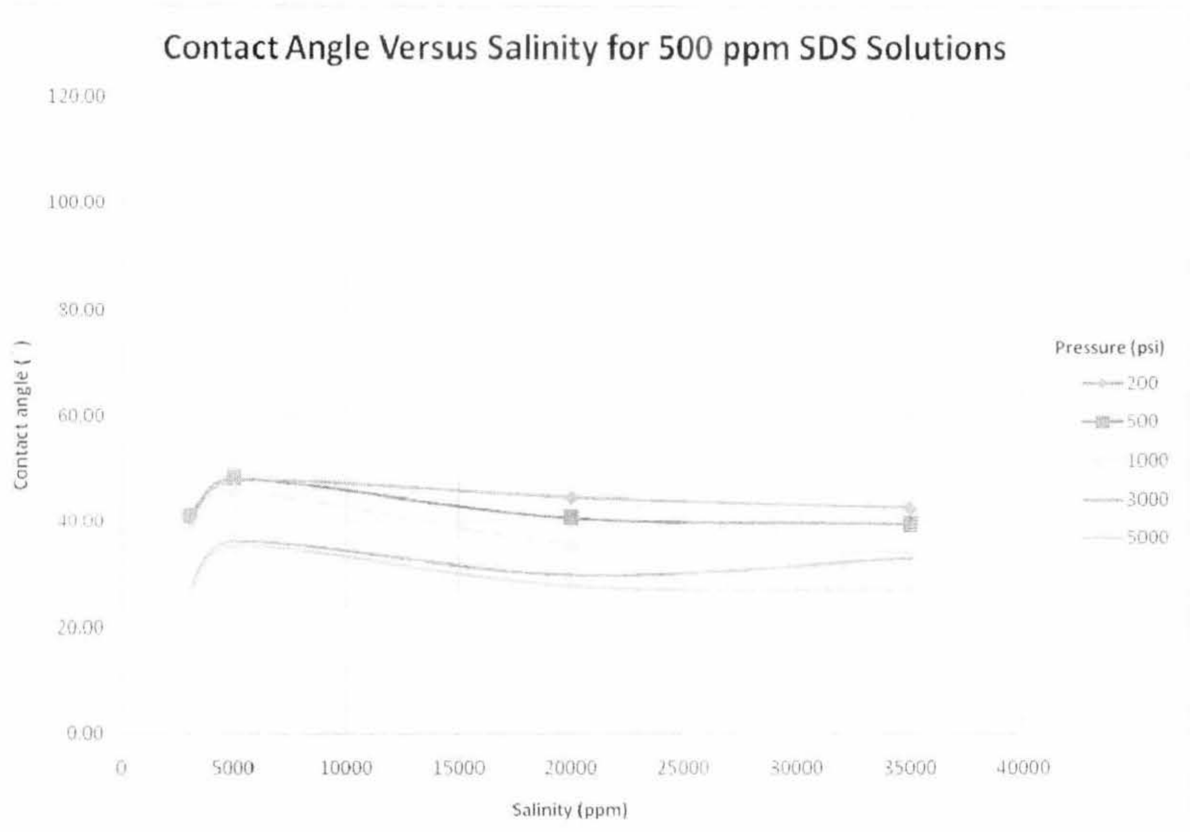


Figure 24: Contact angle versus salinity graph for 500ppm SDS solutions

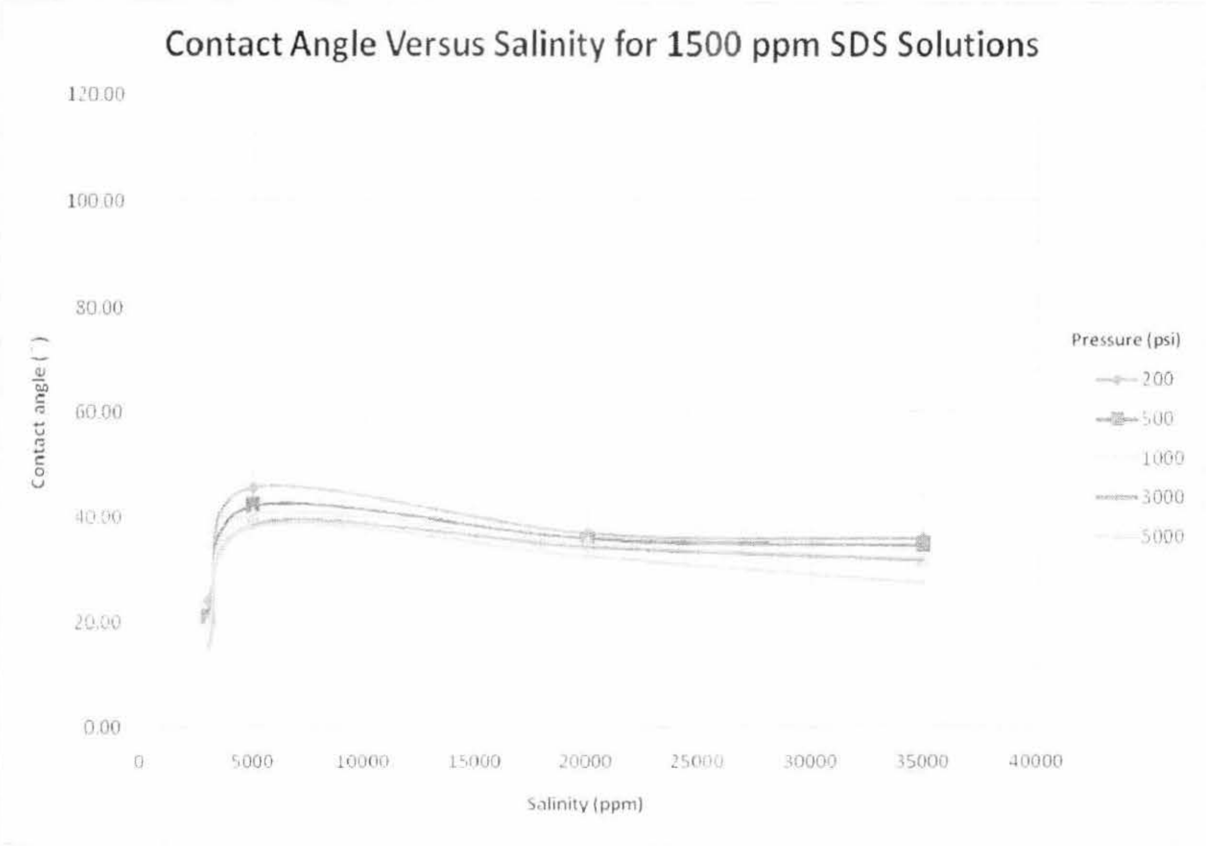


Figure 25: Contact angle versus salinity graph for 1500ppm SDS solutions

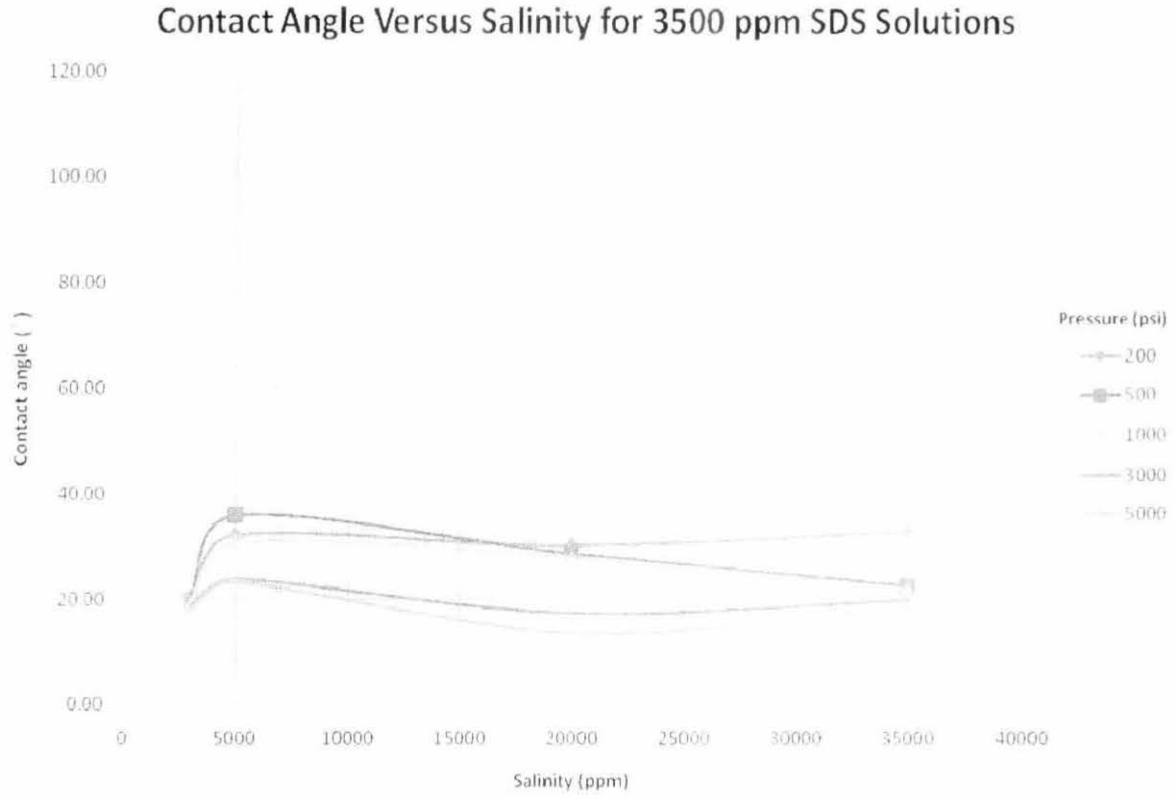


Figure 26: Contact angle versus salinity graph for 3500ppm SDS solutions

Figures 24-26 illustrates the relationship between wettability and salinity with the presence of surfactant SDS. For all SDS concentrations, as salinity increases from 3000 ppm NaCl to 5000 ppm NaCl, there is an increase in the contact angle (rock surface becomes less water-wet). A continued increment of salinity to 20000 ppm NaCl and 35000 ppm NaCl returns the contact angle to a lower value (rock surface becomes more water-wet).

As the salinity increases, it is observed that the extent of the maximum wettability alteration decreases for a surfactant.

A similar behaviour can be observed in literature.

Vijapurapu and Rao (1996) evaluated the effects of brine dilution and surfactant addition on the spreading and adhesion behaviour of an oil-brine-rock system.

The oil and brine was Yates oil and brine and the rock used was dolomite. Oil-water IFT is measured using Computerized Axisymetric Drop Shape Analysis (CASDA) and dynamic (water advancing and receding) contact angles are measured using the Dual-Drop-Crystal (DDDC) technique. Their results indicated that the initial oil-wet nature of the oil-brine-rock system was changed to intermediate wettability simply by diluting the reservoir brine with deionized water. However with further dilution of reservoir brine, it resulted in the increase of IFT (return of intermediate wettability back to the initial oil-wet nature) (Vijapurapu and Rao 1996).

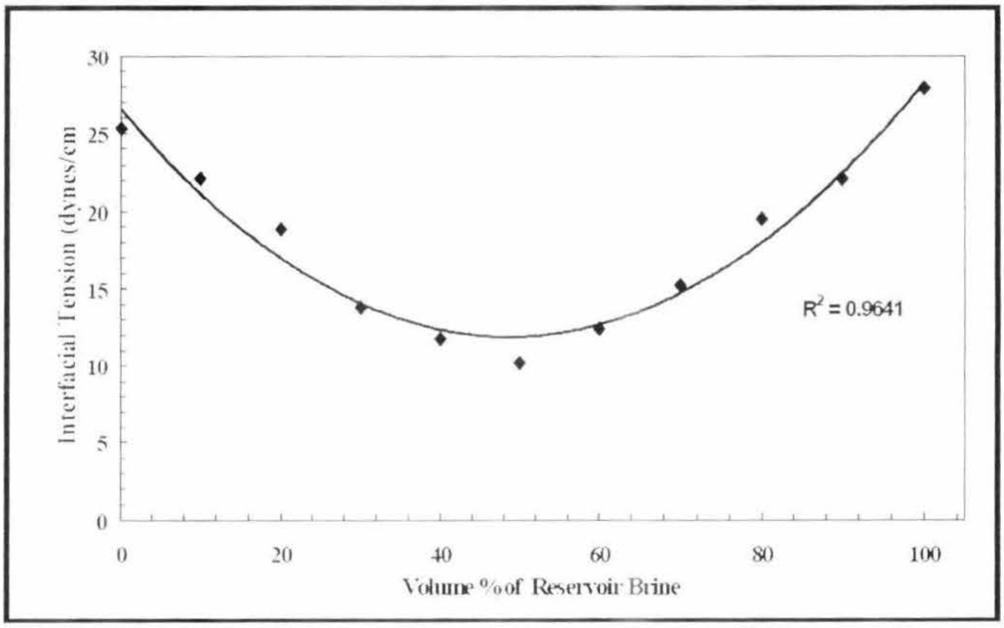


Figure 27: Effect of brine dilution on IFT between brine and crude oil (Vijapurapu and Rao 1996)

Bagci *et al.* (2001) reported that the IFT of an oil-brine system decreased then increased by increasing salinity of NaOH and $NaSiO_4$ brines.

Gupta and Mohanty (2008) studied the oil recovery from initially oil-wet fractured carbonate reservoirs by wettability alteration with dilute surfactants and electrolyte solutions. They found that there exists an optimal chemical concentration for varying salinity. They also found that there is an optimal salinity for varying surfactant concentration at which the wettability alteration is the maximum for a surfactant. As the salinity increases, the extent of the maximum wettability alteration decreases for a surfactant, but the surfactant concentration decreases for the maximum wettability alteration (Gupta and Mohanty 2008).

According to Leja (1982) the salinity and pH of brine affect wettability because they change the charge on the rock surface and fluid interfaces, which in turn can affect the adsorption of surfactants. It is generally accepted that adsorption of polar compounds such as surfactants onto the rock surface has a significant effect on its wettability (Anderson 1986). Positively charged, cationic surfactants will be attracted to negatively charged surfaces, while negatively charged anionic surfactants will be attracted to positively charged surfaces.

The more attraction there is, the more the wettability is changed. However, the salinity also influences with this attraction (and wettability of a rock) as explained in Section 2.5. This explains how salinity change has affect wettability in this study.

In literature, *Zhang et al.* (2004) reported a reduction of anionic surfactant adsorption and good oil recovery is the aqueous surfactant solution is at high pH and has an optimal salinity for the specific reservoir conditions.

Another study conducted by Barnes *et al.* (2008) investigated the properties of two families of anionic surfactants (internal olefin sulfonates and branched C16, 17 alcohol based alkoxy sulfonates) are described for chemical flooding of oil reservoirs at high temperatures and/or high salinities. The results obtained relate to oil/water IFT behaviour and produced the 'operating window' of the surfactants in terms of their optimal salinity. From the results shown from this study, there are different optimal salinities for different surfactants (Barnes *et al.* 2008).

In this study, there is an unusual behaviour of wettability change at high salinity 35000 ppm NaCl, particularly at high concentration of SDS at 3500 ppm SDS. From Figure 23 (3500 ppm SDS), it can be observed that as salinity was changed from 20000 ppm to 35000 ppm NaCl, the contact angle increases slightly, making a weaker water wet rock. This pattern has not been observed in literature.

For lower concentrations of SDS (500 and 1500 ppm SDS) we can see that the extent of wettability change is smaller between 20000-35000 ppm NaCl salinity, as compared to 5000-20000 ppm NaCl salinity. In other words, it can be said that the effect of SDS in changing rock wettability becomes weaker as salinity increases.

It is also found that for low ppm surfactant (0 ppm and 500 ppm SDS), the most water-wet condition is obtained with the lowest salinity at 3000 ppm NaCl. On the other hand, the wettability is most water-wet at high salinity 35000 ppm NaCl for higher ppm surfactant concentrations (1500 ppm and 3500 ppm SDS). This pattern, too, is not found in literature.

5.0 CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

This study has produced a general relationship between two independent variables (pressure and salinity of a surfactant) and a dependant variable (the wettability of a water-oil-rock system). This study has proven that:

- As salinity was increased, the surfactant's performance first decreases. The rock wettability initially changes from water-wet to weak water-wet, but after a certain salinity, further increment of salinity resulted in the increase of surfactant performance. The rock wettability reverts to a more water-wet state. This shows that there is an optimum salinity for the best wettability.
- There was a general increase in effectiveness of surfactant on rock wettability as pressure was increased. As pressure increased, the oil-water-rock system became more water-wet. However the effect of pressure change is much less significant compared to salinity change.

The above results of this experimental study have given an idea on how salinity and pressure will increase or decrease the recovery efficiency of a reservoir utilizing surfactant injection as an EOR option.

5.1 Recommendation

As a recommendation for future works, a more modern technique to measure wettability such as the DDDC (Dual-Drop-Dual-Crystal) technique where dynamic (water advancing and receding) contact angles are measured instead of traditional contact angle. It involves the equilibration of two parallel solid surfaces immersed in reservoir brine with two crude oil drops placed on them before creating the advancing and receding interfaces. Reasons are:

- In reservoir engineering, what is generally concerned is the moving of oil out of the reservoir by pushing it with injected water. Hence, advancing angles have been accepted as a better measure of reservoir wettability.
- The DDDC technique differs from the traditional contact angle methods by overcoming their limitations. By exposing both the upper and lower crystal surfaces in a similar manner to crude oil, the dissimilarity of the modified sessile drop method is overcome. By keeping the drop volume constant throughout the experiment, the problem (encountered in the sessile drop technique) of increase in contact angle with decreasing drop volume is eliminated (Rao 2002).
- Another advantage of the DDDC technique is that it accelerates the achievement of the oil–brine–crystal equilibrium during the initial aging of the two drops on the two surfaces because of the destabilizing influence of the buoyancy force on the wetting water film. This results in considerably shorter run times than the traditional methods (Rao 2002).

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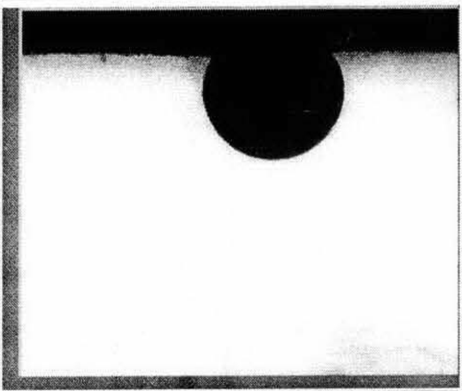
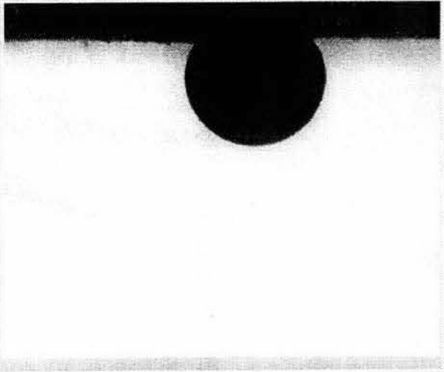
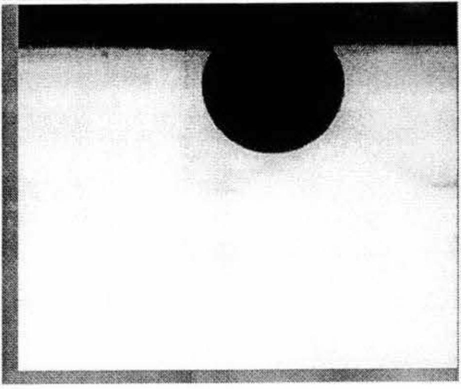
7.0 APPENDIX

Table A1: Contact angle calculation for the various pressures for NaCl 3000ppm SDS 0ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 3000ppm, SDS 0ppm	200				51.17
	500				50.06
	1000				47.29

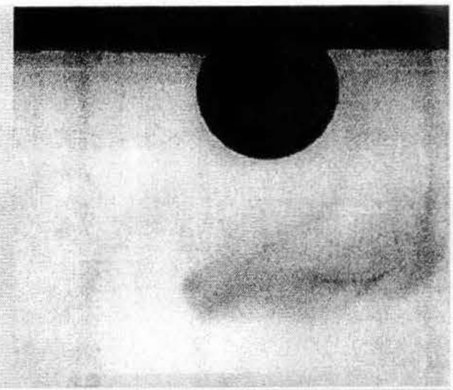
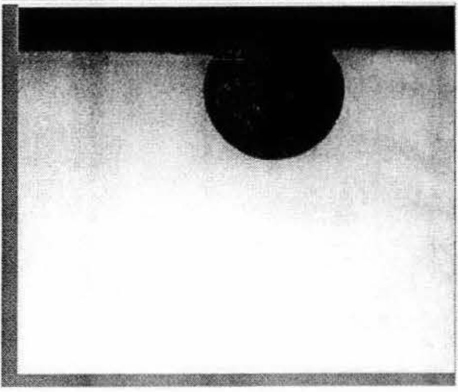
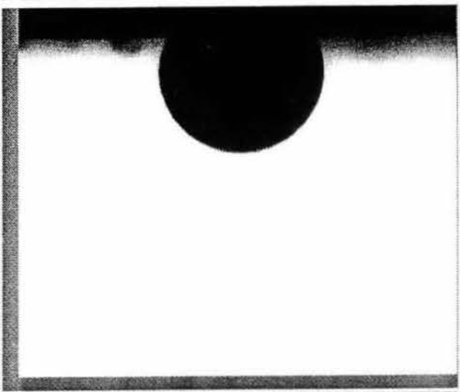
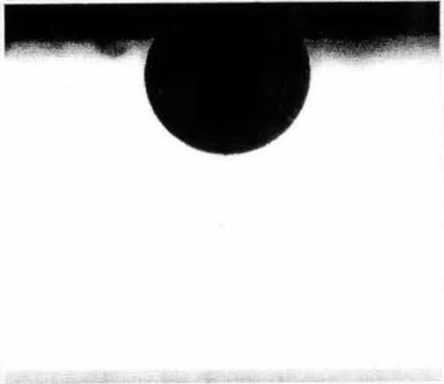
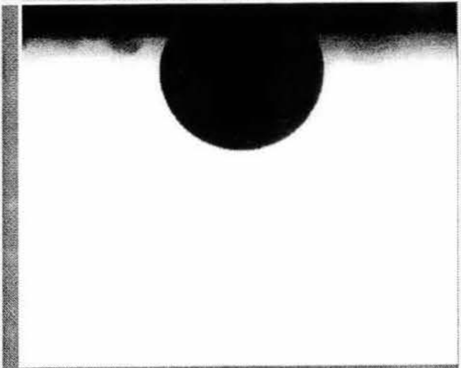
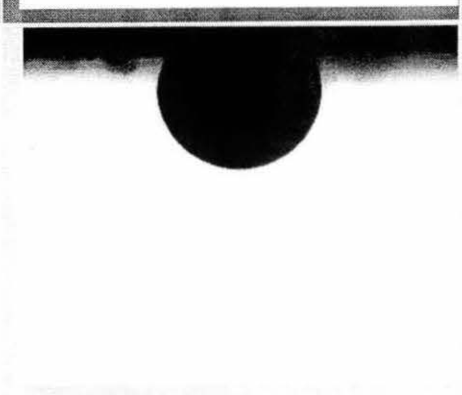
	3000				39.61
	5000				26.79

Table A2: Contact angle calculation for the various pressures for NaCl 3000ppm SDS 500ppm solution

SDS-NaCl Concentration	**Pressure (psi)**	**Image**	**Ratio h/l**	**tan-1(h/l)**	**Contact Angle, θ (°)**
NaCl 3000ppm, SDS 500ppm	200		1.24	40.36	40.36
	500		1.19	41.03	41.03
	1000		1.08	37.80	37.80
	3000		0.83	27.64	27.64

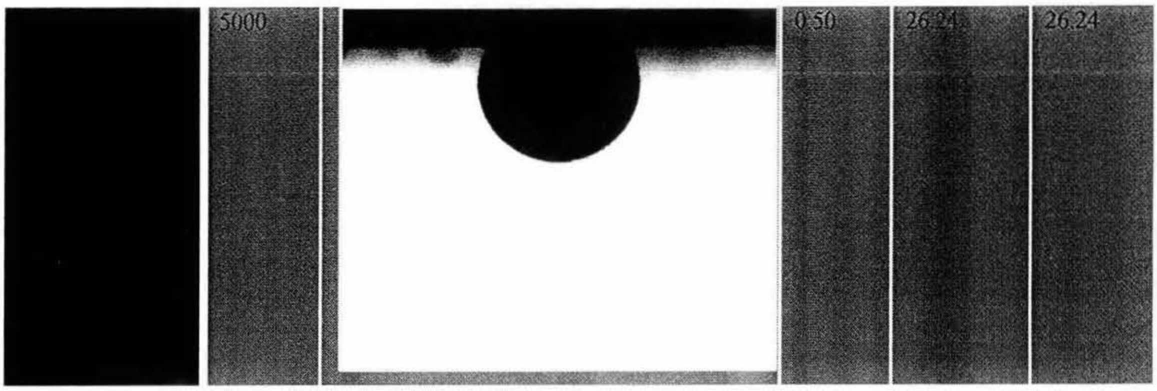
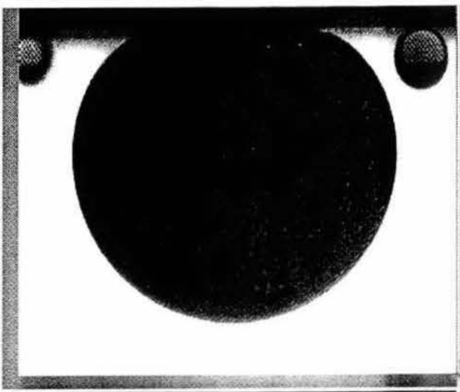
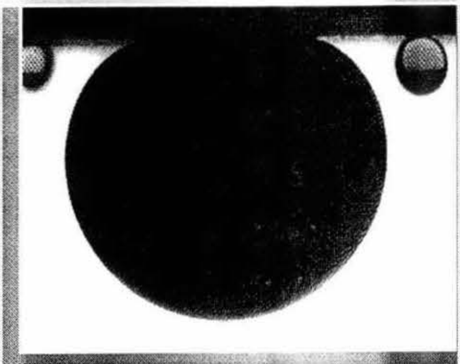
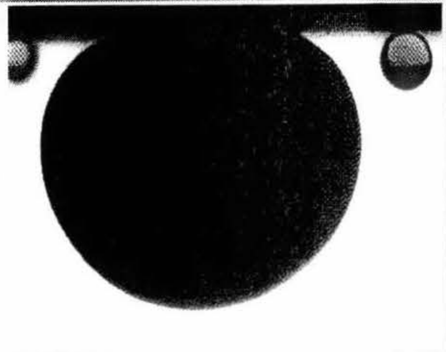

5000
0.50
26.24
26.24

Table A3: Contact angle calculation for the various pressures for NaCl 3000ppm SDS 1500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 3000ppm, SDS 1500ppm	200		0.45	24.23	24.23
	500		0.39	21.14	21.14
	1000		0.36	19.74	19.74
	3000		0.28	15.59	15.59

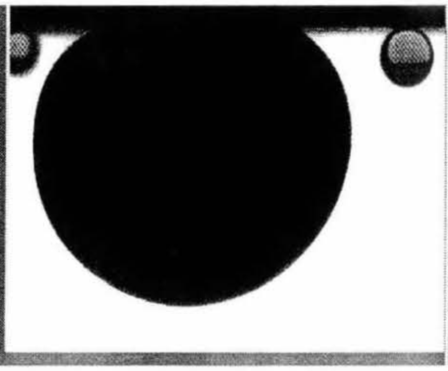
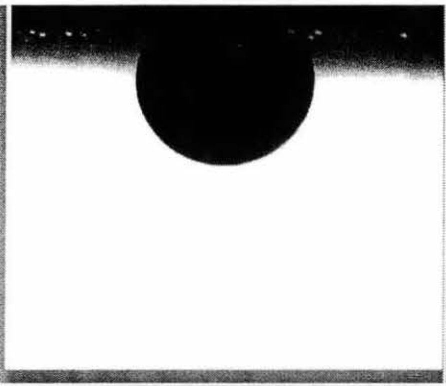
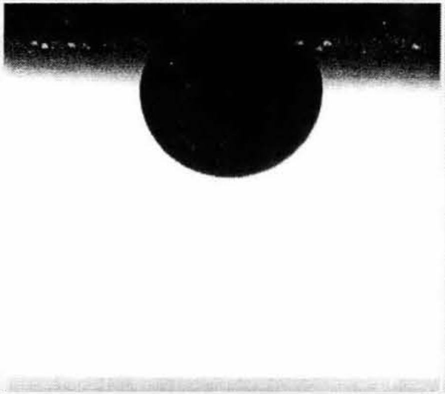
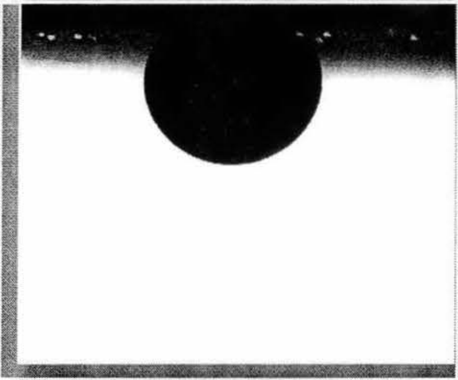
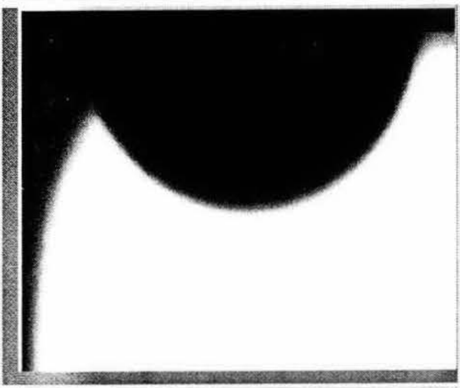
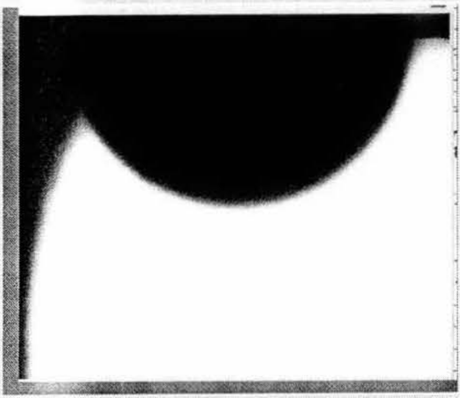
	5000		0.27	14.85	14.85

Table A4: Contact angle calculation for the various pressures for NaCl 3000ppm SDS 3500ppm solution

SDS-NaCl Concentration	**Pressure (psi)**	**Image**	**Ratio h/l**	**tan-1(h/l)**	**Contact Angle, θ (°)**
NaCl 3000ppm, SDS 3500ppm	200		0.38	20.56	20.56
	500		0.36	19.89	19.89
	1000		0.34	19.02	19.02
	3000		0.34	18.85	18.85

	5000		0.32	17.99	17.99

Table A5: Contact angle calculation for the various pressures for NaCl 5000ppm SDS 0ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 5000ppm, SDS 0ppm	200		4.21	76.63	103.37
	500		7.87	82.76	97.24
	1000		11.81	85.16	94.84
	3000		15.26	86.25	93.75

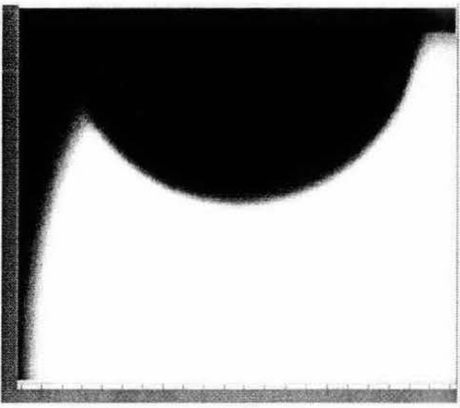
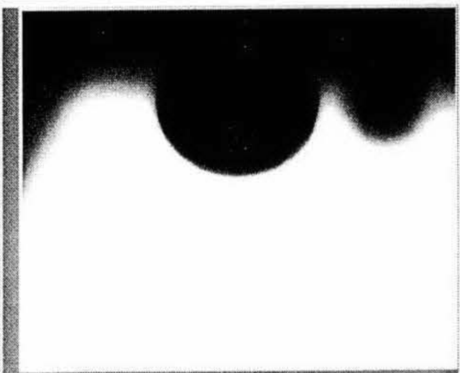
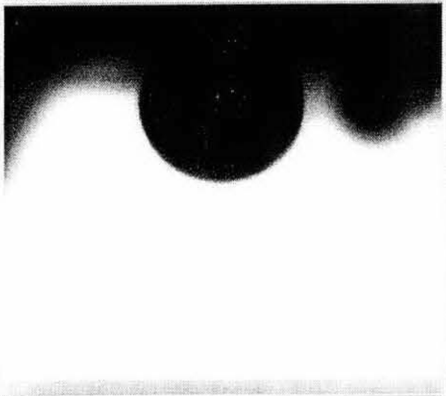
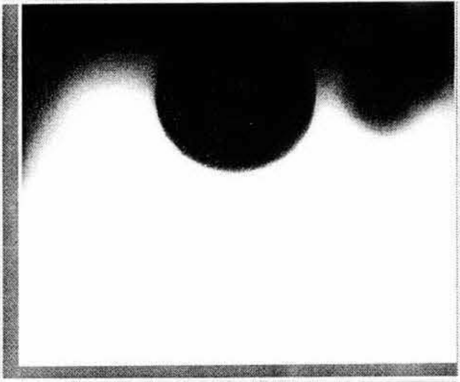
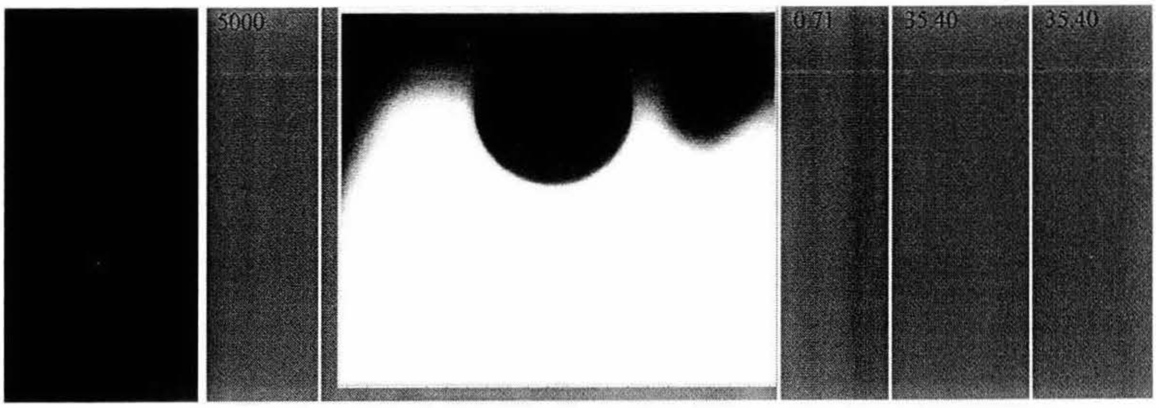
[redacted]	5000		16.35	86.5	93.50

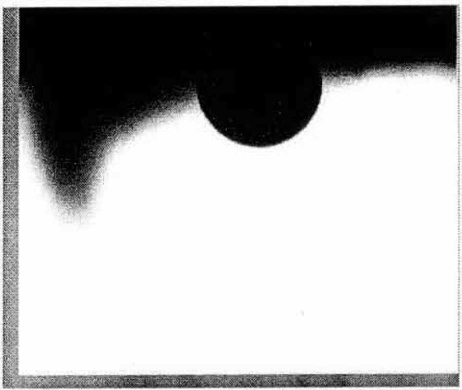
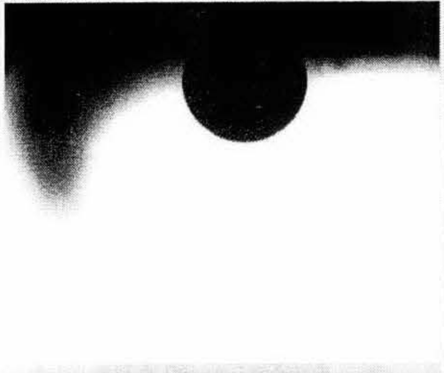
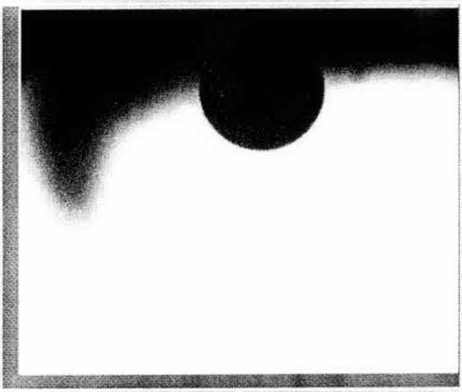
Table A6: Contact angle calculation for the various pressures for NaCl 5000ppm SDS 500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 5000ppm, SDS 500ppm	200		1.10	47.76	47.76
	500		1.12	48.18	48.18
	1000		1.03	45.81	45.81
	3000		0.74	36.36	36.36



5000
0.71
35.40
35.40

Table A7: Contact angle calculation for the various pressures for NaCl 5000ppm SDS 1500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 5000ppm, SDS 1500ppm	200		1.03	45.73	45.73
	500		0.91	42.19	42.19
	1000		0.86	40.54	40.54
	3000		0.80	38.50	38.50

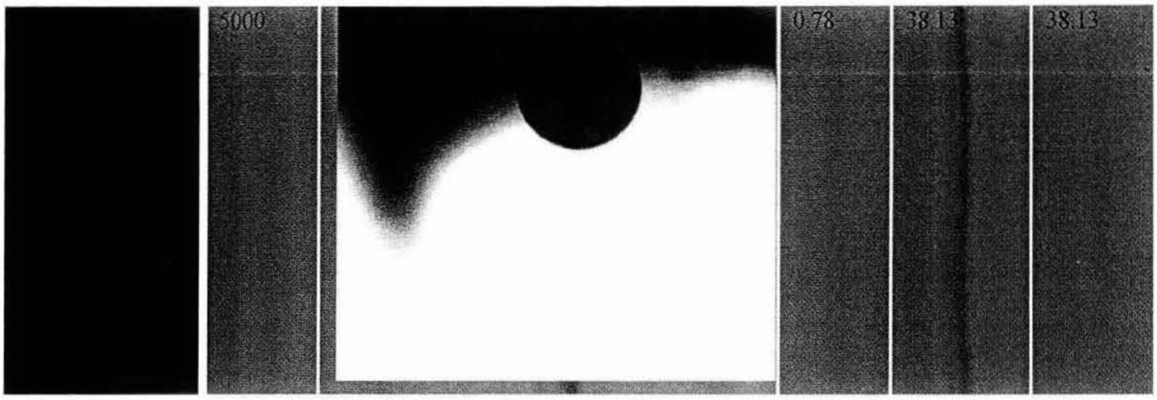
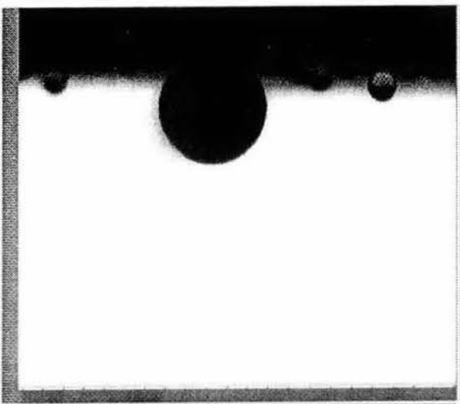
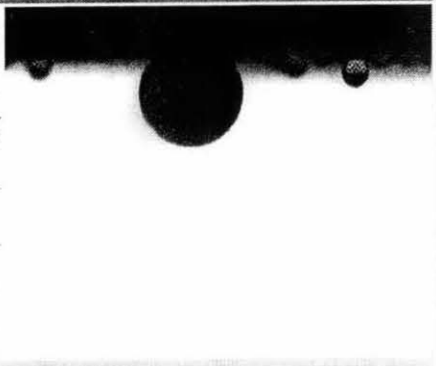
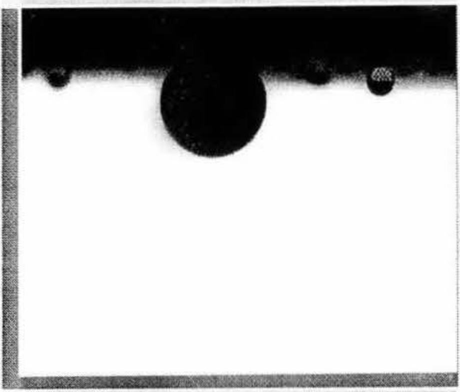

5000
0.78
38.13
38.13

Table A8: Contact angle calculation for the various pressures for NaCl 5000ppm SDS 3500ppm solution

SDS-NaCl Concentration	**Pressure (psi)**	**Image**	**Ratio h/l**	**tan-1(h/l)**	**Contact Angle, θ (°)**
NaCl 5000ppm, SDS 3500ppm	200		0.65	32.97	32.97
	500		0.42	22.67	22.67
	1000		0.40	21.80	21.80
	3000		0.36	20.04	20.04

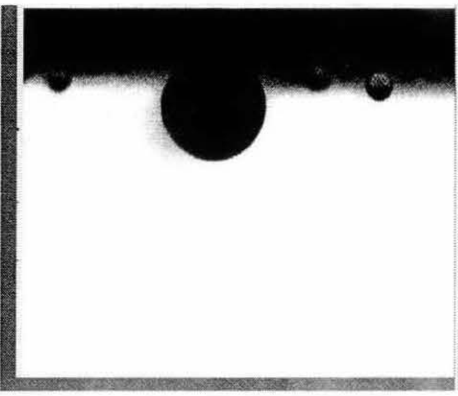
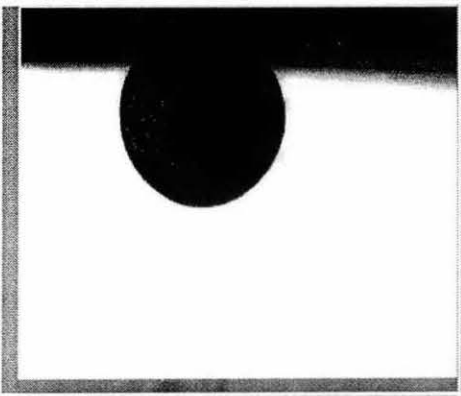
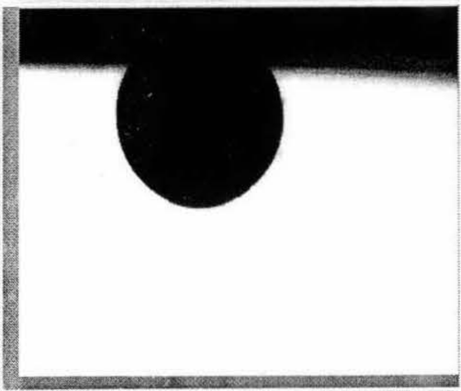
	5000		0.32	17.97	17.97

Table A9: Contact angle calculation for the various pressures for NaCl 20000ppm SDS 0ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 20000ppm, SDS 0ppm	200		1.19	49.94	49.94
	500		1.05	46.51	46.51
	1000		1.05	46.40	46.40
	3000		1.01	45.37	45.37

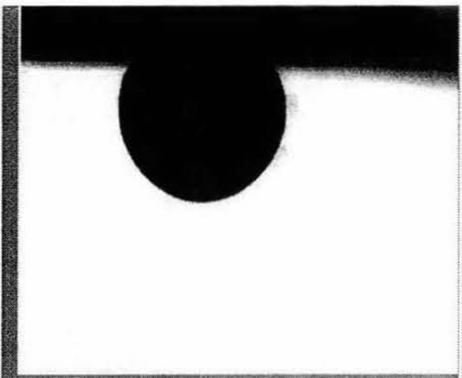
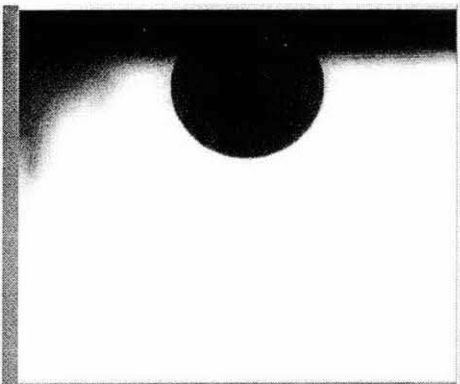
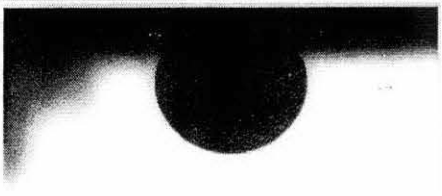
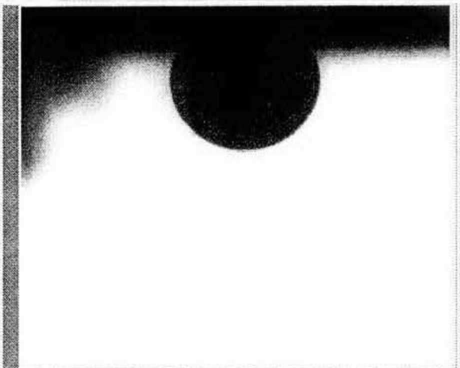
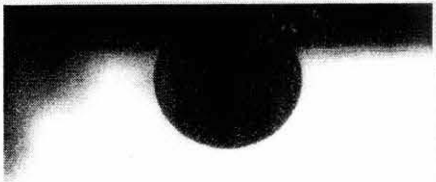
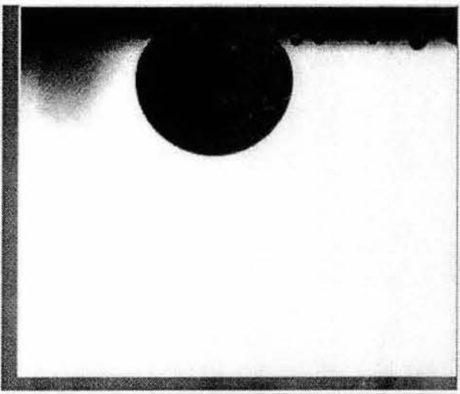
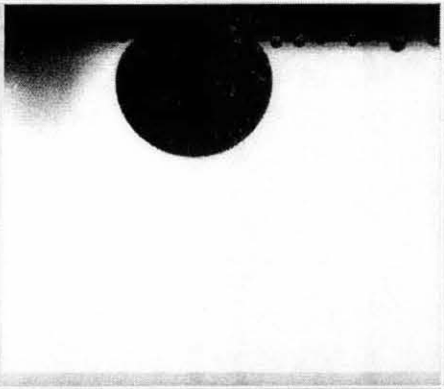
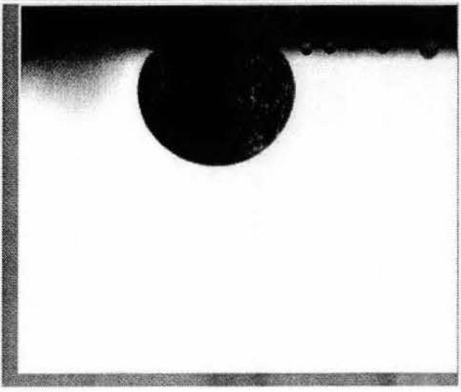
[redacted]	5000		0.95	43.41	43.41

Table A10: Contact angle calculation for the various pressures for NaCl 20000ppm SDS 500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 20000ppm, SDS 500ppm	200		0.98	44.56	44.56
	500		0.86	40.60	40.60
	1000		0.72	35.62	35.62
	3000		0.58	29.90	29.90

	5000		0.53	27.85	27.85

Table A11: Contact angle calculation for the various pressures for NaCl 20000ppm SDS 1500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 20000ppm, SDS 1500ppm	200		0.72	35.88	35.88
	500		0.69	34.79	34.79
	1000		0.63	32.17	32.17

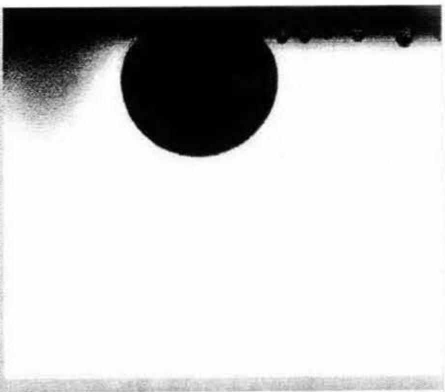
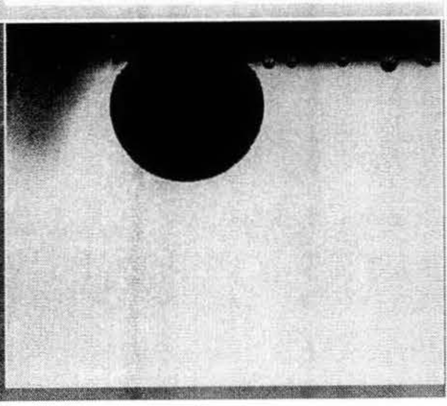
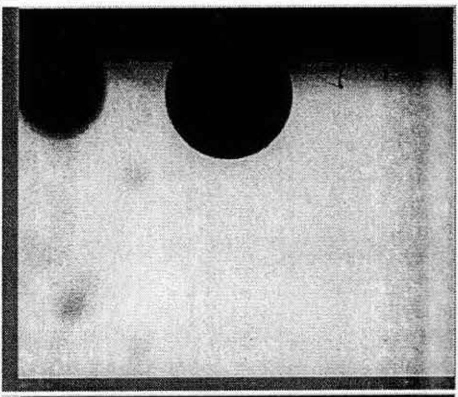
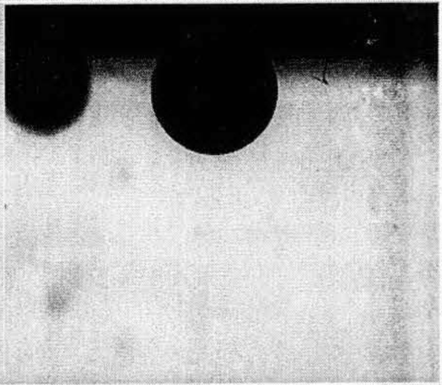
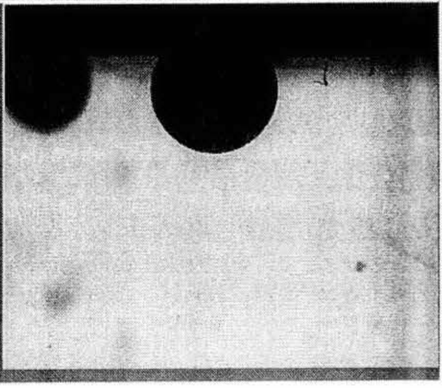
	3000		0.62	31.76	31.76
	5000		0.52	27.67	27.67

Table A12: Contact angle calculation for the various pressures for NaCl 20000ppm SDS 3500ppm solution

SDS-NaCl Concentration	**Pressure (psi)**	**Image**	**Ratio h/l**	**tan-1(h/l)**	**Contact Angle, θ (°)**
NaCl 20000ppm, SDS 3500ppm	200		0.58	30.30	30.30
	500		0.55	28.71	28.71
	1000		0.53	27.84	27.84

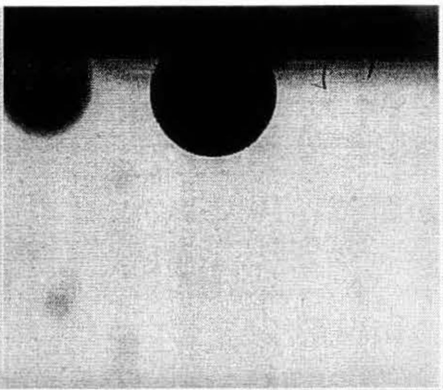
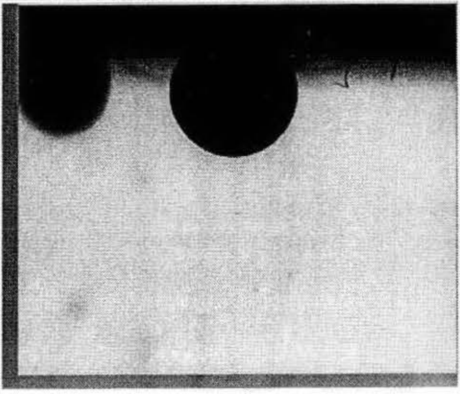
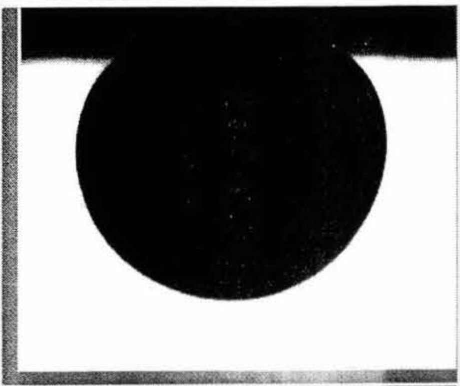
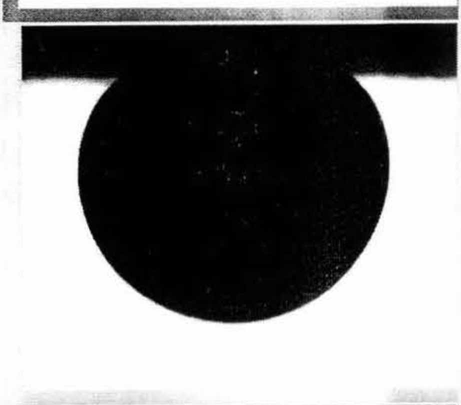
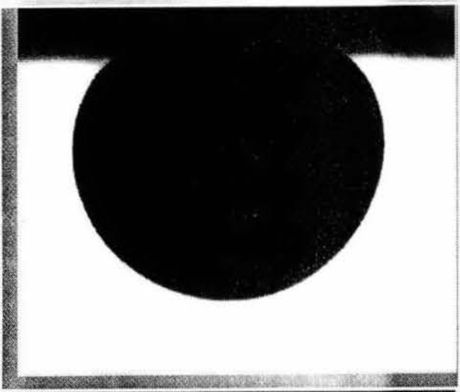
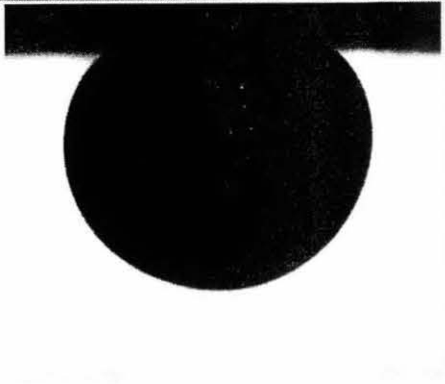
	3000		0.31	17.43	17.43
	5000		0.24	13.69	13.69

Table A13: Contact angle calculation for the various pressures for NaCl 35000ppm SDS 0ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 35000ppm, SDS 0ppm	200		0.75	36.87	36.87
	500		0.72	35.88	35.88
	1000		0.70	34.82	34.82
	3000		0.68	34.35	34.35

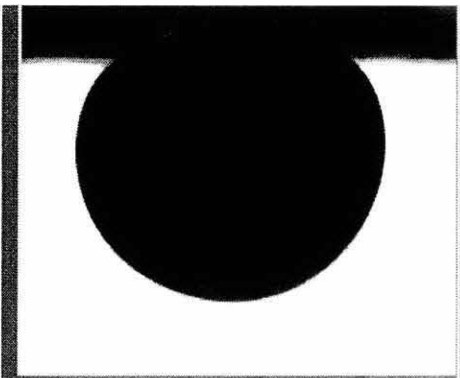
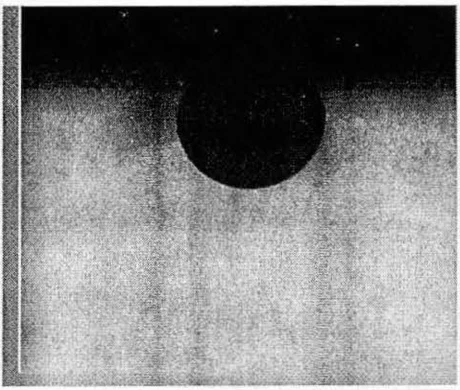
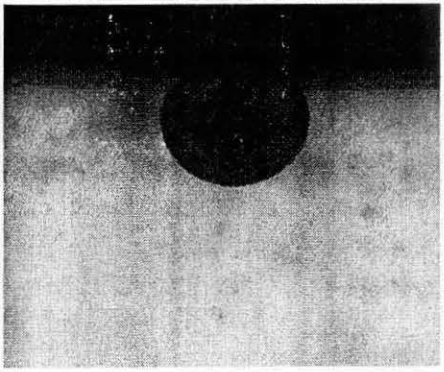
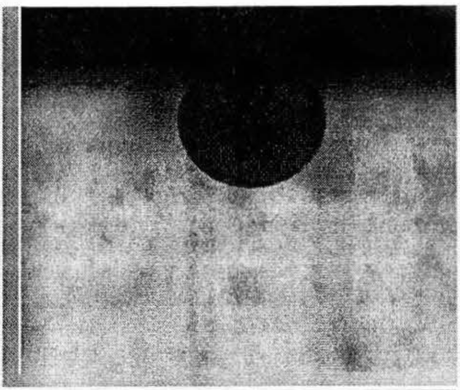
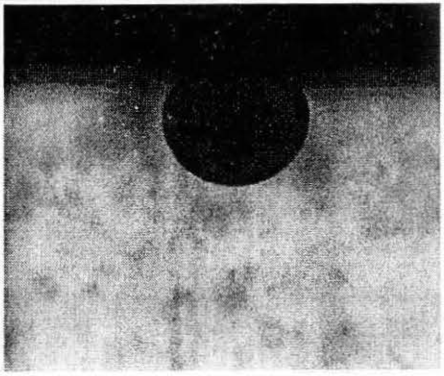
[illegible]	5000		0.64	32.57	32.57

Table A14: Contact angle calculation for the various pressures for NaCl 35000ppm SDS 500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 35000ppm, SDS 500ppm	200		0.63	32.25	32.25
	500		0.72	35.89	35.89
	1000		0.59	30.75	30.75
	3000		0.44	23.84	23.84

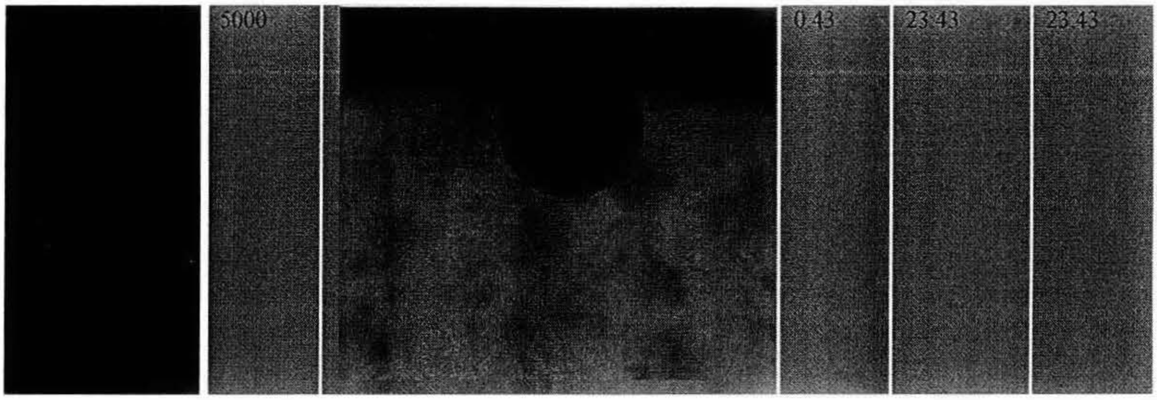
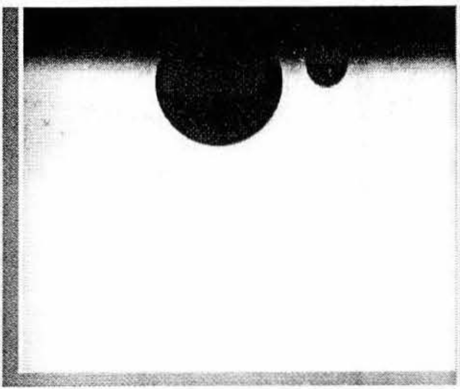
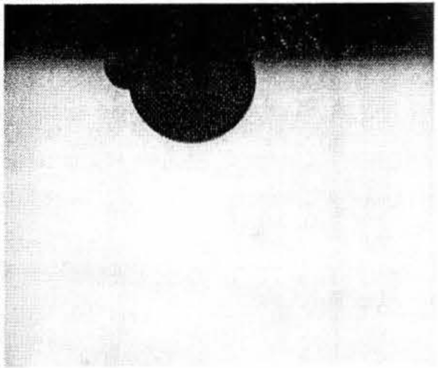
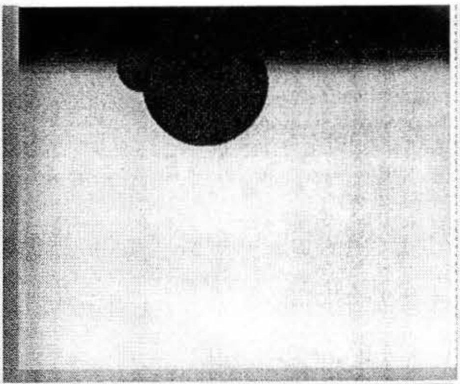
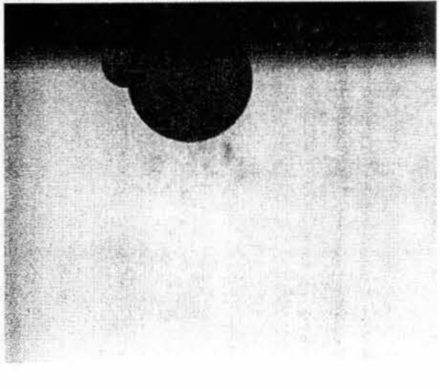

5000
0.43
23.43
23.43

Table A15: Contact angle calculation for the various pressures for NaCl 35000ppm SDS 1500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 35000ppm, SDS 1500ppm	200		0.92	42.65	42.65
	500		0.82	39.42	39.42
	1000		0.68	34.16	34.16
	3000		0.65	33.02	33.02

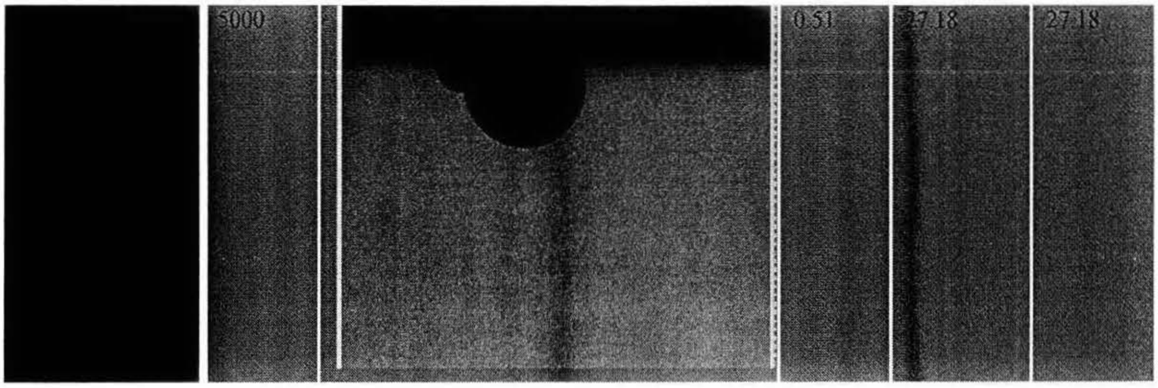
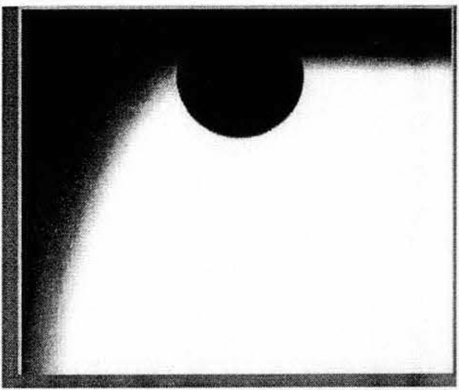
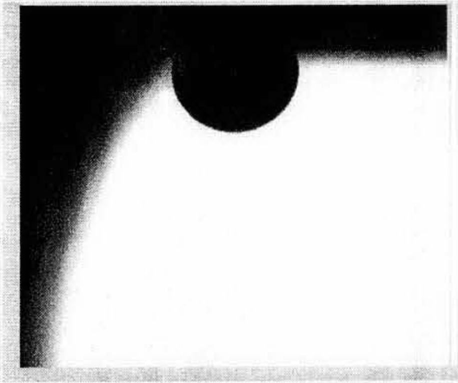
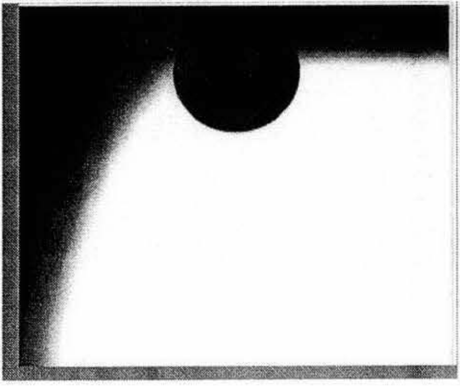
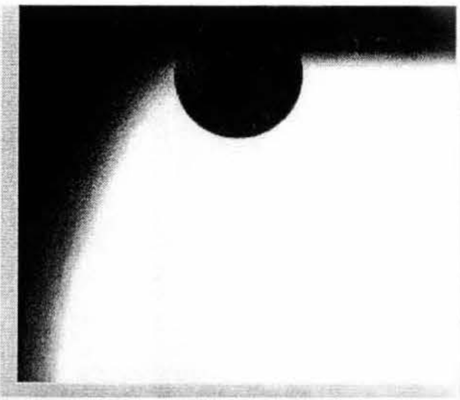
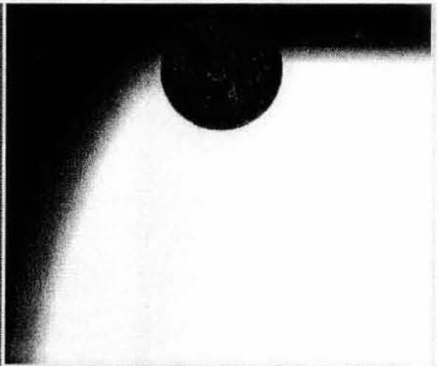

5000
0.51
27.18
27.18

Table A16: Contact angle calculation for the various pressures for NaCl 35000ppm SDS 3500ppm solution

SDS-NaCl Concentration	Pressure (psi)	Image	Ratio h/l	tan-1(h/l)	Contact Angle, θ (°)
NaCl 35000ppm, SDS 3500ppm	200		1.16	49.14	49.14
	500		1.09	47.56	47.56
	1000		1.09	47.49	47.49

	3000		0.97	44.10	44.10
	5000		0.77	37.44	37.44