# The Impact of Temperature on the Effectiveness of Surfactant to Change the Wettability

By

# ZAHIDAH BT ABDUL RAHIM

(11737)

.

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum Engineering)

JAN 2011

#### ACKNOWLEDGEMENT

Words can hardly express my sense of gratitude to my supervisor, Mr Ali F.Mangi Alta'ee from petroleum engineering department. His wide knowledge and logical way of thinking have been of great value for me. Mr ali patiently guided me through the study process, never accepting less than my best efforts. His understanding, encouraging and personal guidance have provided a good basis to complete the experiment.

This dissertation could not been written without the kind of mr riduan from core analysis lab petroleum engineering department, who guided me during my experimental works. His presence is also to ensure everyone's safety and helped in solving the mechanical and operational problems while using the Interfacial Tension 700 (IFT 700) tool.

I wish to express my warm and sincere thanks to all my friends who devoted their valuable time and helped me in all possible ways towards successful completion of this work. I owe my most sincere gratitude to my parents and my whole family whose honest support and obstinate love give me energy to complete this work successfully and gave me untiring help during my difficult moments. They have always wanted the best for me and i admire my parent's determination and sacrifice to put me through UTP. Thanks is a very small word for this.

I thanks to all those who have contributed directly or indirectly to this work.

# ABSTRACT

Utilization of surfactants is one of the methods for wettability alteration of reservoir rock, from oil wet into water wet by reducing the interfacial tension. Studying of wettability alteration mechanism using surfactants has been emphasized by researches. Later on, many researchers have focused on surfactants capability of tolerating on a condition created by increasing temperature to increase their ultimate recoveries. However the wettability of porous media is difficult to observe directly during the injection of the surfactant process. Many differ in opinion among researchers for the exact temperature on the effectiveness of surfactant and contact angle to recover the oil. Therefore, experimental study needs to be performed to observe the changes in contact angle at the optimum temperature. The objective of this experimental study is to investigate the impact of different temperatures, ranging from 50°C-120°C on the surfactant's performance in altering the wettability of a rock. In this study, sessile up method for contact angle measurement have been made using Berea sandstone core sample, Dulang crude oil in the presence of Sodium Dodecyl Sulfate (SDS) surfactant at pressure 200 psia and constant salinity of 5000ppm. The experiment is being conducted using the Interfacial Tension 700 (IFT700) tool and measured the contact angle. The changes in contact angle when temperatures are increasing have been evaluated. The contact angle is found to decrease from  $110^{\circ}$  to  $48^{\circ}$  as the temperature increase. The wettability has been enhanced and changed from oil wet to water wet means contact angle decreasing as temperature increases, leading to increase the oil recovery.

# CERTIFICATION OF APPROVAL

# Impact of the Temperature on the Effectiveness of Surfactant to Change the Wettability

By

Zahidah Abdul Rahim

A project dissertation submitted to the Petroleum Engineering Programme University Teknologi PETRONAS In partial fulfillment of the requirement for the Bachelor of Engineering (Hons) Petroleum Engineering

pproved b ALLE-MANGIALTA EE

Locurer Geoscience & Petroleum Engineering Department Universiti Teknologi PETRONAS Bandar Seri Iskandar, 31750 Tronoh, Perak Darul Ridzuan, Malaysia. (Ali F. Mangi Alta'ee)

# 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 originality work contained here have not been undertaken or done by unspecified sources or persons.

۷

(Zahidah Abdul Rahim)

# **TABLE OF CONTENTS**

Abstract	ü
1 INTRO	DUCTION 1
1.1 Ba	ckground of Study 1
1.2 Pro	blem Statement
1.2.1	Problem Identification
1.2.2	Significant of the project
1.3 Ob	jective
1.4 Sco	ope of Study
2 LITERA	ATURE REVIEW
	dies on temperature effect on wettability alteration using surfactant by IFT ntact angle measurement
2.2 Stu	dies on wettability alteration using surfactant5
2.3 Stu	dies on wettability measurement method
2.3.1	Contact angle measurement
2.3.2	Amott method
2.3.3	USBM method 11
3 METHO	DDOLOGY 12
3.1 Res	earch methodology 12
3.1.1	Reagent Selection
3.1.2	Surfactant Solution Preparation
3.1.3	Core Properties Measurement
3.1.4	Core Slicing/ Trimming
3.1.5	Saturation Duration
3.2 Exp	perimental Setup 17
3.2.1	: Determine Drop Orientation
3.2.2	: Instrument Setup 18

3.2	2.3 : Fluid Loading	18
3.2	2.4 : Drop Dispense	19
3.2	2.5 : Temperature Increasing	19
3.2	2.6 : Aging Time	19
3.3	Contact Angle Measurement	20
3.4	Equipment and tool	21
3.5	Key Milestone	22
3.6	Gantt Chart	23
4 RE	ESULTS AND DISCUSSION	25
4.l	Contact Angle Calculation	25
4.2	Wettability determination	25
5 CC	ONCLUSIONS AND RECOMMENDATIONS	30
5.1	Conclusions	30
5.2	Recommendations	30
REFER	ENCES	31

# LIST OF FIGURES

Figure 2.1 : Consecutive images of the process of detachment of a hexadecane drop from a glass plate immersed in solutions of anionic surfactant (Kolev <i>et al.</i> , 2003)
Figure 2.2 : A contact angle of liquid sample (Retrieved from http://en.wikipedia.org/wiki/Contact angle)
Figure 2.3 : Contact angle wettability (Retrieved from http://en.wikipedia.org/wiki/Contact angle)
Figure 2.4 : Oil droplet surrounded by water
Figure 3.1 : Surfactant Solution Preparation
Figure 3.3 : Cores was Saturated with Brine more than 10 days
Figure 3.4 : Bubble sitting beneath solid surface captive by other missible 17
Figure 3.5 : A drop lying on the solid surface
Figure 3.6 : Syringes, Cuvet and Needles 19
Figure 3.7 : Contact Angle Calculation
Figure 3.8 : IFT 700
Figure 3.9 : Gantt Chart during FYP1 23
Figure 3.10 : Gantt Chart during FYP2 24
Figure 4.1 : Contact Angle vs temperature for 0ppm and 500ppm surfactant concentration
Figure 4.2 : Contact Angle Vs Temperature for ranging from 0ppm-3500ppm surfactant concentration

# LIST OF TABLE

Table 3.1 : Amount of Surfactant concentration, SDS, NaCl, and distilled water	14
Table 3.2 : Core Properties Measurement	15
Table 3.3 : Core Slices with Different Surfactant Concentration	16
Table 3.4 : Aging time studies of IFT studies	20
Table 3.5 : Key Milestone	22
Table 4.1 : Visual images of oil bubble for contact angle measurement (0ppm and         500ppm surfactant concentration)	26
Table 4.2 : Visual image of oil bubble for contact angle measurement (1500ppm and         3500ppm surfactant concentration)	28

# **CHAPTER 1**

#### **1** INTRODUCTION

#### 1.1 Background of Study

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 Ahmad, 2001). When these immiscible fluids are in contact, the active forces are exists. This existence of these forces gives rise to fundamental properties such as interfacial tension and wettability. Because of these attractive forces, the wetting phase tends to occupy the smaller pores of the rock and the nonwetting phase occupies the more open channels. For a water wet reservoir, water occupies the small pores and most of the rock surface is in contact with water. When the rock has no strong preference for either oil or water then it is an intermediate wet reservoir. In an oil wet reservoir, oil covers most of the rock surface and small pores. The wettability of reservoir rocks to the fluids is important in that the distribution of the fluids in the porous media is a function of wettability (Dandekar, 2006).

Many different methods have been proposed for measuring the wettability of a rock/fluid system. They consist of quantitative methods such as Contact angles, imbibitions and forced displacement (Amott) method and United States Bureau of Mines (USBM) method. Quantitative methods are direct measurement methods, where the wettability is measured on actual rock samples using reservoir fluid samples and the reported the wettability in terms of wettability index, signifying the degree of water, oil wetness, or intermediate wetness. 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). Primarily the ability of surfactant to reduce the interfacial tension (IFT) and altering wettability it is viable option being explored today. The surfactant comes from the term surface-active agent.

en de la

#### 1.2 Problem Statement

#### 1.2.1 Problem Identification

Wettability of porous media is difficult to observe directly during the injection of the surfactant process. Many differ in opinion among researchers for the exact temperature on the effectiveness of surfactant and contact angle to recover the oil. Previous study on wettability alteration showed that, advancing angle measured was decreasing during surfactant injection (135°-139°) compared to initial advancing angle (152°) measured before surfactant injection (Xu *et al.*, 2005) .Contact angle decreases as temperature increases (Standnes and Austad, 2000). Decreasing trend IFT from 40.1 mN/m at 28°C to 35.7 mN/m at 70°C as the temperature increase for 0.005Mole Stearic Acid (SA) in n-decane/water system (Hamouda and Karoussi, 2008). Therefore, experimental study needs to be performed to observe the changes in contact angle as the temperature increases.

#### 1.2.2 Significant of the project

This project is very important in order to observe the changes in contact angle as the temperature increases during surfactant injection in the core sample surface. The changes of contact angle will be measured throughout the experiment process. This study will investigate a relationship between two dependent variables which are temperature and contact angle. There has been considerable effort to study surfactant ability in order to recover the remaining oil. Surfactant can be used to create ultra low IFT between surfactant bank and remaining oil thus increase the remaining oil mobility (Salehi *et al.*, 2006). This project may help to bring out the idea on how this relationship of these two dependent variables will increase or decrease the recovery efficiency of a reservoir utilizing surfactant injection as an EOR option.

# 1.3 Objective

The objective of this project is to study experimentally the impact of temperature on the surfactant ability to change the wettability.

#### 1.4 Scope of Study

There are extensive areas of studies for the effect of temperature on the effectiveness of surfactant to change the wettability. In this project, the study will be looking into measurement of the initial wettability on the core samples saturated in brine without surfactant. Then, this study focuses on changes of the contact angle by apply a variation of temperature on the surfactant as well as to perform better wettability in core sample. This involves knowledge in wettability, measurement on contact angle, and the effective of temperature on better wettability changes.

# **CHAPTER 2**

#### **2** LITERATURE REVIEW

# 2.1 Studies on temperature effect on wettability alteration using surfactant by IFT and/or Contact angle measurement.

Hamouda and Karoussi (2008) studied the effect of the temperature on oil recovery by measured the interfacial tension (IFT) and contact angle. In order to examine the trend and the effect of these ions in salt water, the IFT measurements are performed with 0.005Mole concentration of stearic acid (SA) in n-decane /water containing 0.1Mole concentration of Sodium Sulfate or Magnesium Chloride. Indeed interfacial tension experiments show the expected decreasing trend IFT from 40.1 mN/m at 28°C to 35.7 mN/m at 70°C as the temperature increase for 0.005Mole concentration of Stearic Acid (SA) in n-decane/water system.

Standnes and Austad (2000) measured the advancing and receding contact angles as a function of temperature for modified calcite surfaces with 0.005Mole concentration of Stearic Acid (SA) dissolved in decane. The result showed that the contact angle decreases with temperature which is indicate that the calcite surface is becoming more water- wet as a function of temperature.

Hjelmeland and Larrondo (1986) studied that temperature can have an effect in reducing the IFT between crude oil and an aqueous sulfonate system. The result showed that temperature was found to have a large effect on the wetting characteristics. At low temperature, the solid phase exhibited oil-wet behavior, whereas at higher temperatures it exhibited water-wet behavior.

Wang and Gupta (1995) reported that contact angle measurements at reservoir conditions. Their experimental results included contact angle measurements for crude oil-brine-quartz system over a pressure range of 200 to 3000 psig and temperature range of 72.5°F to 200°F. The quartz mineral surface was used to represent the

sandstone. The result showed the contact angle decreases as the temperature increasing.

#### 2.2 Studies on wettability alteration using surfactant

Wu *et al.*, (2008) studied the application of surfactants on the mechanisms responsible for enhanced oil recovery from carbonate reservoirs. This study used naphthenic acids dissolved in decane as a model oil to make calcite surfaces more water-wet. Results indicate this flotation test is a useful rapid screening tool to identify better EOR surfactants for carbonates.

Xu *et al.*, (2005) studied the wettability altering capability of the surfactants. In this experiments, the fractured Yates dolomite reservoir, Yates crude oil, synthetic brine and an anionic ethoxy sulphate surfactant have been used. The experiment has been conducted at Yates reservoir conditions of 700 psi and 82° F. The contact angles have been measured using the Dual-Drop Dual Crystal (DDDC) technique. The results showed that the advancing angle measured was decreasing during surfactant injection  $(135^{\circ}-139^{\circ})$  compared to initial advancing angle  $(152^{\circ})$  measured before surfactant injection.

Zhang *et al.*, (2006) investigated the controlling mechanisms and variables of improved the oil recovery using surfactant. He found the use of alkaline surfactant is able to alter wettability of calcite from intermediate-wet to water-wet. The presence of sodium carbonate also significantly reduces the anionic surfactant adsorption.

Jarrahin *et al.*, (2010) studied on a wettability alteration of reservoir rock using surfactants. In this experiment, model oil is prepared by adding Stearic Acid in n-heptane. Calcite surface as solid surfaces was saturated in 2 different conditions which are with stearic acid in n-heptane and without Stearic Acid in n-heptane and aged for 2 days. Afterward, a drop of water was placed on the calcite surface. The results showed the contact angle decreases from  $110^{\circ}$  to  $28^{\circ}$ .

Kolev *et al.*, (2002) carried out experiments on detachment of oil drops from glass substrates in solutions of an anionic surfactant. In this experiment, it use surfactant C14/C16-alfa-olefin-sulfulate (AOS) sodium salt with a concentration was 0.3molar Mole and dissolved in 0.1Mole concentration of Natrium Chloride (NaCI), deionized water to form surfactant solution. Pure hexadecane was used as the oil phase and dry glass slides used as substrates. Then, a drop of hexadecane was placed on the upper side dry glass slide. Afterwards, the surfactant solution was carefully poured into the vessel until completely immersing the oil drop in the solution. Consecutive video frames of such drops are digitized and the time dependencies of the contact angle are determined. All experiments were carried out at the ambient room temperature, 22°C. The experimental images of a drop at different stages of spontaneous detachment shows as Figure 2.1 below. It is visible that initially the drop has an approximately spherical shape. With elapsed time the contact angle decreases and the drop becomes slightly elongated under the action of buoyancy. At the final stage (t= 878s) a neck is formed. Next, the drop detaches very fast.

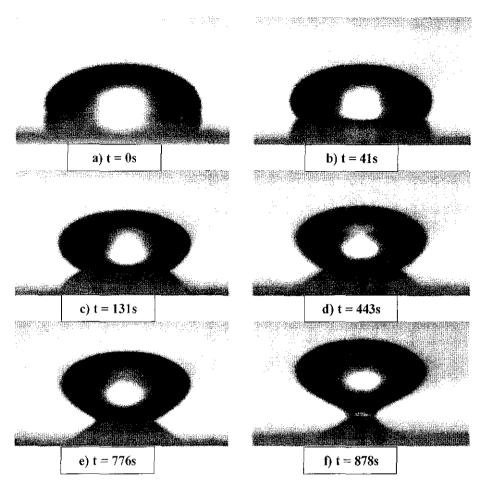


Figure 2.1 : Consecutive images of the process of detachment of a hexadecane drop from a glass plate immersed in solutions of anionic surfactant (Kolev *et al.*, 2003)

Vijapurapu and Rao (2003) studied effect of brine dilution and surfactant addition on spreading and adhesion behavior of Yates crude oil on dolomite surfaces. Spreading and adhesion have been characterized through measurements of oil-water interfacial tension (IFT) and contact angles. Surfactant has ability to alter wettability in addition to reducing IFT. They saturated the core sample in the brine with different surfactant concentrations ( 0ppm, 500ppm, 1500ppm, 3500ppm) .For the Yates reservoir rock-fluids system, an Ethoxy Alcohol surfactant altered the strongly oil-wet nature (advancing angle of 158°) to water-wet (advancing angle of 39°) at a concentration of 3500 ppm.

#### 2.3 Studies on wettability measurement method

#### 2.3.1 Contact angle measurement

The contact angle is the angle at which a liquid and vapor interface meets a solid surface. The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young's relation. When a droplet of liquid rests on the surface of a solid, the shape of the droplet is determined by the balance of the interfacial liquid/vapor/solid forces. The contact angle plays the role of a boundary condition (Retrieved from http://en.wikipedia.org/wiki/Contact angle). It can write an equation that must be satisfied in equilibrium (known as the Young Equation):

 $\gamma_{LG} \cos \theta_c = \gamma_{SG} - \gamma_{SL}$ 

where :  $\gamma_{LG} = Iiquid$ -gas interfacial tension

 $\theta_c = Contact angle$ 

 $\gamma_{SG}$  = solid-gas interfacial tension

 $\gamma_{SL}$  = solid-liquid interfacial tension

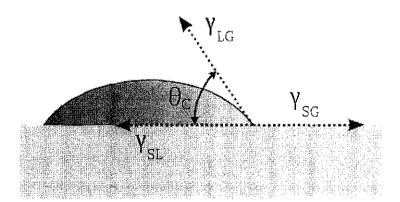


Figure 2.2 : A contact angle of liquid sample (Retrieved from http://en.wikipedia.org/wiki/Contact angle)

The common methods of contact angle measurement employed in petroleum industry are sessile drop method. This methods required the mineral crystal to be tested is mounted in a contaminant free test cell made of inert mineral. Sessile drop method only need a single flat, polished mineral crystals. Quartz and calcite crystals are commonly used in place of sandstone and limestone respectively. Figure 2.3 showed the sessile drop measurement. In this case the water droplet was surrounded by oil. For a water wet, the surface is in contact with water and the contact angle was less than 90°. In an oil wet, the surface is in contact with less water and the contact angle was more than 90° (Retrieved from http://en.wikipedia.org/wiki/Contact angle).

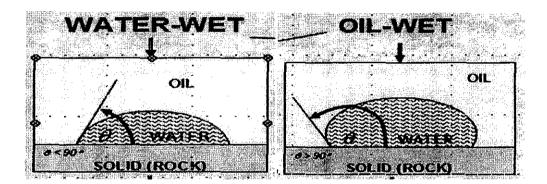


Figure 2.3 : Contact angle wettability (Retrieved from http://en.wikipedia.org/wiki/Contact angle)

Sometimes the contact angle was measured differently when the oil droplet was surrounded by water which is measured the contact angle of water (more dense fluid) not the oil. From Figure 2.4, for strong oil wet, the surface is in contact with oil and the contact angle of water was more than  $90^{\circ}$ . In a less oil wet, the surface is in contact with more water than oil. So the contact angle was less than  $90^{\circ}$ .

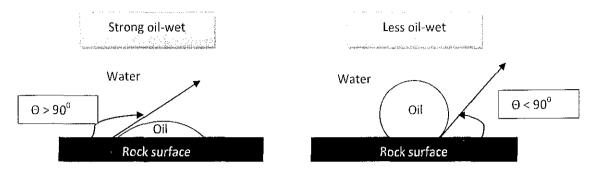


Figure 2.4 : Oil droplet surrounded by water

#### 2.3.2 Amott method

Amott method is one of the most widely used empirical wettability measurement s for reservoir cores in petroleum engineering. The method combines two spontaneous imbibitions measurements and two forced displacement measurements. This method recognizes the fact that wetting fluid will generally imbibe spontaneously into a core, displacing the nonwetting fluid. The wetting fluid is forced to imbibe some more by using centrifugal (Anderson, 1986). The most important parameters to be measured in Amott method are:

- \* Amount of oil displaced by spontaneous imbibitions of water, Vosp.
- $\bullet$  Amount of oil displaced by force imbibitions of water,  $V_{ot}$
- \* Amount of water displaced by spontaneous imbibitions of oil, V<sub>wsp.</sub>
- Amount of water displaced by force imbibition of oil, V<sub>wt</sub>.

The parameters measured above are used in the following calculation of displacement by water ratio  $\delta_w$  and displacement by oil ratio  $\delta_o$ .

$$\delta_{w} = \frac{V_{osp}}{V_{wt}} \qquad \qquad \delta_{o} = \frac{V_{wsp}}{V_{ot}}$$

# 2.3.3 USBM method

USBM method was developed by Donaldson *et al* (1969) and also designed to measure the average wettability of a core sample. The entire wettability test is conducted in a centrifuge apparatus which used to place the core sample and displaced the fluid. The wettability of the core sample was determined if the  $I_{\text{USBM}} > 0$ , the core is water-wet and when  $I_{\text{USBM}} < 0$ , the core is oil-wet. Whereas a near zero value of  $I_{\text{USBM}}$  it indicates neutral wettability (Dandekar, 2006).

# **CHAPTER 3**

# **3 METHODOLOGY**

#### 3.1 Research methodology

#### 3.1.1 Reagent Selection

The following reagents are used in this experiment:

a) Salt solution (brine) of 5000ppm from chemical engineering lab is prepared by dissolving 5g of natrium chloride, NaCI in 1 liter distilled water.
Increasing in oil recovery from laboratory coreflood studies is achieved by waterflooding using low salinity water, compared with injection of high salinity water. The reasons for this improved oil recovery are thought to be due to effective wettability changes, controlled removal of clay constituents or intentional injection of water containing low concentrations of total dissolved solids into the reservoir. Normally, salinity of less than 5000ppm is implemented (McGuire *et al.*, 2005)

Webb *et al.*, (2008) compared the high and low salinity of the injection brine to the crude oil for waterflood recovery. The injection brines were simulated the formation brine for high salinity waterfloods (salinity of 15,000ppm to 200000ppm) and low salinity brine(less than 5000ppm) for low salinity corefloods. All brines, both high and low salinity were used for waterflood tests. As the results, it has proven that low salinity of injection brine improved the waterflood characteristics.

- b) Dulang Crude oil
- c) Anionic surfactant (Sodium Dodecyl Sulfate) supplied by Chemical Engineering laboratory.

Sodium Dodecyl Sulfate with two different surfactant concentrations for 0ppm and 500ppm is dissolved in brine was prepared. The experiment was repeated for the 1500ppm and 3500ppm surfactant concentration to investigate the affect of surfactant concentration to the changes in contact angle.

Table 3.1 showed according to amounts listed to produce surfactant solution. This range of concentration is chosen because it is used in the field operations (Ayirala, 1996).

Many studies use the same range of concentrations in their experiments. For example, Vijapurapu and Rao (2003) studied effect of brine dilution and surfactant addition on spreading and adhesion behavior of Yates crude oil on dolomite surfaces. Spreading and adhesion have been characterized through measurements of oil-water interfacial tension (IFT) and contact angles. They saturated the core sample in the brine with different surfactant concentrations (0ppm, 500ppm, 1500ppm, 3500ppm). For the Yates reservoir rock-fluids system, an Ethoxy Alcohol surfactant altered the strongly oil-wet nature (advancing angle of 158°) to water-wet (advancing angle of 39°) at a concentration of 3500 ppm.

#### d) One sandstone core sample

Berea sandstone core sample is sliced to provide surfaces for contact angle measurements in this experiment. Berea sandstone is widely familiar by petroleum industry since the past 30 years for the purpose of studying surfactant efficiency. Jadhunandan and Morrow (1995) were studied that wettability can be varied in Berea Sandstone by changing the condition for adsorption from crude oil.

## 3.1.2 Surfactant Solution Preparation

Four surfactant solutions over constant salinity of 5000ppm of each surfactant concentration are prepared by dissolving Natrium Chloride (NaCl) and surfactant, Sodium Dodecyl Chloride (SDS) in distilled water according to amounts specified in Table 3.1 and Figure 3.1 below:

Surfactant	0	500	1500	3500	Total amount
concentration, ppm					
Sodium Dodecyl	0	0.5	1.5	3.5	5.5
Chloride , g					
Natrium Chloride, g	5	5	5	5	20
Distilled water, liter	1	1	1	1	4

Table 3.1 : Amount of Surfactant concentration, SDS, NaCl, and distilled water



1 liter

Figure 3.1 : Surfactant Solution Preparation

# 3.1.3 Core Properties Measurement

The core sample properties were measured using poro perm (CoreEval 30) device. Firstly, measured the dimension of the core and then left the core dried in the oven at  $60^{\circ}$ C for 1 day. Porosity and permeability was determined as shown in Table 3.2 below:

Core propert	ies	dimensio					
					ns		
	Porosi	Grain	Kair,(m	K∞,(md	L,(mm)	D,(m	Weight,(
	ty, %	Density,	d)	)	1	m)	g)
		(g/cc)					
Initial	14.3	2.67			51.24	38.08	131.907
reading							
Reading 1	14.605	2.647	20.062	17.098			L
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			

Table 3.2 : Core Properties Measurement

# 3.1.4 Core Slicing/ Trimming

The core trimming device is used to cut the core sample into thin slices. Four slices of core were cut with diameter of about 1mm and were made to provide solid surfaces for the contact angle determination with drop of oil using sessile up orientation.

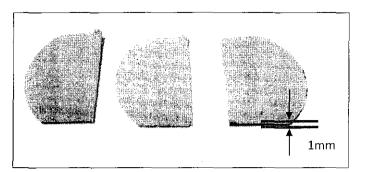


Figure 3-2 : Core Slicing

# 3.1.5 Saturation Duration

The saturation duration of published studies of surfactant effect on rock wettability, range from one day to ten days. All the four core slices are saturated in the surfactant solution of different Sodium Dodecyl Sulfate concentrations (0ppm, 500ppm, 1500ppm, 3500ppm) more than 10 days.

Morrow *et al.*, (1999) performed a study on wettability characterization from spontaneous imbibitions measurements. They saturated the core sample with brine and allowed to equilibrate for ten days. Besides that, Zhou *et al.*, (2000) was studied the interrelationship of wettability, initial water saturation, aging time, and oil recovery by spontaneous imbibitions and water flooding. The dry core samples were vacuumed and saturated with the surfactant solution and left immersed for about ten days to establish ionic equilibrium between the rock constituents and the brine. This Table 3.3 below showed the core slices for each different surfactant concentration:

Core Slices	Sodium Sulfate Dodecyl (SDS) concentration, ppm
Core 1	0ppm SDS
Core 2	500ppm SDS
Core 3	1500ppm SDS
Core 4	3500ppm SDS

Table 3.3 : Core Slices with Different Surfactant Concentration

Figure 3.3 below showed the picture of core when it was saturated with brine more than 10 days:

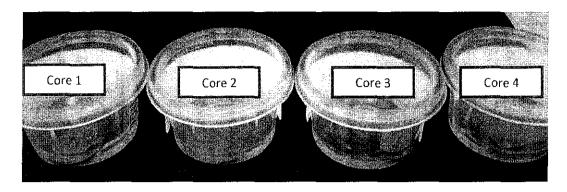


Figure 3.2 : Cores was Saturated with Brine more than 10 days

# 3.2 Experimental Setup

# 3.2.1 : Determine Drop Orientation

There are two drop orientations for sessile method namely:

1) Sessile up method or sessile bubble

This orientation is selected from user if oil drop is injected from the bottom, so that oil drop will float up in the brine and rest at the rock slice bottom.

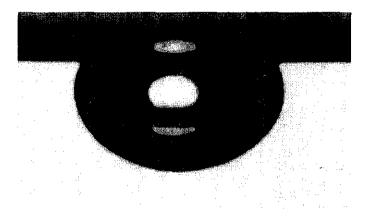


Figure 3.3 : Bubble sitting beneath solid surface captive by other missible

2) Sessile down method or sessile drop

This orientation is selected from user if water drop is injected from the top, so that water drop will sit on the core slice surrounded by oil

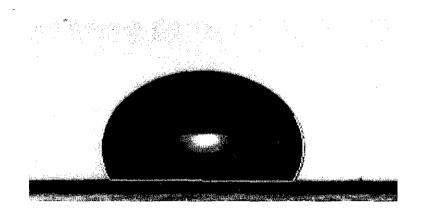


Figure 3.4 : A drop lying on the solid surface

Since the back light is not bright enough to give the view of the water drop surrounded by oil, the first orientation is selected for this experiment.

#### 3.2.2 : Instrument Setup

- Core slice is mounted on a holder so it may be held in horizontal position.
   Double sided tape is used to place the core slice on the holder.
- 2) The core slice holder is placed in the core chamber.
- 3) Test fluids (oil and brine) are placed in syringes that will be attached to the inlet ports on the device, IFT 700. These ports are connected to the sample chamber through tubing lines.

#### 3.2.3 : Fluid Loading

The software requires some external parameters to be supplied such as needle size (internal/external diameter) and fluid densities.

- 4) Syringes are attached to the inlet ports.
- 5) Brine is fed into the chamber until it is full.

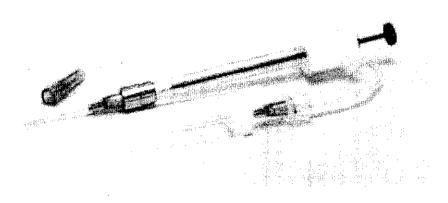


Figure 3.5 : Syringes, Cuvet and Needles

# 3.2.4 : Drop Dispense

- 6) Oil drop is formed at the tip of the needle and release
- 7) That oil drop will float up in the brine and rest at the rock slice bottom.
- 8) Initial live video image of the sample is obtained. Camera focus is adjusted, so that the tip of the needle image is visibly sharp. The camera viewing angle is adjusted so that the needle image is vertical on the computer screen. Camera focus is adjusted to get a clear image of the oil bubble at the bottom of the core slice.

# 3.2.5 : Temperature Increasing

- 9) Temperature was found to have a large effect on the wetting characteristics. In this experiment, the temperatures were increasing for about 50°C, 70°C, 90°C, and 120°C for each of different surfactant concentration respectively.
- 10) The initial wettability was determined by measured the contact angle of less dense fluid without surfactant (0ppm).

#### 3.2.6 : Aging Time

Aging time is duration of absorption of surfactant solution at the interface to reach equilibrium for contact angle measurement. Measurement of IFT is normally performed when the immiscible fluids are assumed to be in equilibrium. As in the case of liquid-liquid-solid system, the equilibrium between the IFT will also enable the contact angle to be measured. The aging time of IFT studies were presented as shown in Table 3.4 below:

Researchers	Fluid tested for dynamic IFT	Aging time
Hassan et al .(1953)	Propane, n-butane, n-pentane, n-	2 minutes
	hexane, n-octane, i-octane, and	
	benzene against water	
Jasper et al. (1970)	Benzene and water	5 minutes
McCaffey (1972)	n-dodecane and water	10 minutes
Hjelmeland et al. (1986)	Oil and brine	30 sec to 20
		minutes

Table 3.4 : Aging time studies of IFT studies

# 3.3 Contact Angle Measurement

Contact angles are measured by fitting a mathematical expression to the shape of the drop and then calculating manually using simple trigonometry. Where angle  $\theta$ , is obtained from the inverse of tangent a to b, tan<sup>-1</sup> (a/b).

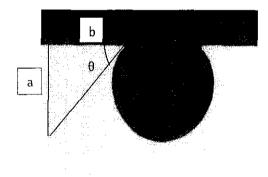


Figure 3.6 : Contact Angle Calculation

# 3.4 Equipment and tool

In this experiment the device, Interfacial Tension 700 (IFT700) device has been used to measure contact angles at elevated temperature. The picture of the device is shown in Figure 3.8. The central part of this system is core chamber, which has a design rating of 10000 psi at 180°C. The top one inside the core chamber is used to mount the core slice on a holder, while the bottom one has a needle to place on oil drop on the core sample surface. The other accessories are the image capturing system which includes a high-quality digital camera and a light source. It is connected to the computer, monitor and video recorder. The contact angles are measured by a captured of an oil drop shape.

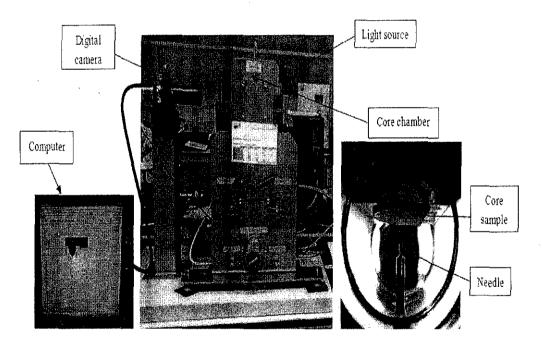


Figure 3.7 : IFT 700

# 3.5 Key Milestone

Table 3.5 : Key Milestone

	Week (2011)	Milestone
1	February 3- February 13	• Request for Chemicals (Sodium Dodecyl Sulfate, Natrium Chloride) approved by Chemical Engineering Lb Executive.
		<ul> <li>Laboratory use for chemical solutions preparation application approved by Chemical Engineering Lab Executive.</li> </ul>
2	February 14- February 20	• Laboratory and equipment use (IFT 700, poro-perm Core Eval 30, oven, core trimmer) application approved by Mechanical Engineering Lab Executive and Petroleum Engineering Department Technician.
3	February 21- February 28	<ul> <li>Surfactant solution preparation (Natrium Chloride + distilled water + Sodium Dodecyl Sulfate) completed.</li> </ul>
4	March 1-March 6	<ul> <li>Core properties measurement (measure porosity and permeability) completed.</li> </ul>
5	March 7-March 13	<ul> <li>Core trimming to slice the core as solid surfaces for contact angle measurement completed.</li> <li>Core slices saturation in surfactant solution for each different surfactant concentration commenced.</li> </ul>
6	March 14- March 20	<ul> <li>Mid-semester break</li> <li>Saturation of core slices continued.</li> <li>Progress report submitted (March 16).</li> </ul>
7	March 21- March 23	<ul> <li>Experimental setup for sessile up on IFT 700 was arranged.</li> <li>A test run is performed to confirm the operability of the arrangement.</li> </ul>
8	March 24- March 31	• Experiment commenced.
9	April 1- April 4	<ul> <li>Result analysis.</li> <li>Submission Final report( first draft) (April 5)</li> </ul>

# 3.6 Gantt Chart

A series of laboratory tests was conducted during this semester. A result of the tests was an analyzed the core samples wettability by measured the contact angle with varying temperature conditions. Figure 3.9 and 3.10 below is Gantt chart showing the timeline to complete the task.

	NAL YEAR 1 <sup>st</sup> SEMESTER ILY 10)													
No	Detaily Week		3	4	5	6		7	0	10	11	12	13	14
1	Topic selection													
2.	Preliminary research													
3.	Submission of Preliminary Report						break							
4.	Study on fundamental concept of wettability						nester							
5.	Study on effect of temperature on the surfactant						Mid-semester break							
6.	Submission of Progress Report													
7.	Seminar (optional)				-									
8.	Study on mechanisms of surfactant and the effect to the wettability										and the second second			
9.	Preparation for interim report													
10.	Submission of Interim Final Report													
11.	Oral presentation													

Figure 3.8 : Gantt Chart during FYP1

	VAL YEAR 2 <sup>nd</sup> SEMESTER N 2011)															
No	Detail/ Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
1	Finalizing experiment methodology															
2.	Gathering and booking of equipments and reagents															
3.	Preparation of SDS-NaCl mixtures							r break								
4.	Measurement of core sample properties and slicing of core sample					山東次の行動になった		Mid-semester break								
5.	Aging of core sample in SDS-NaCl mixtures				ALC: NO			M								
6.	Commencement of experimental work using IFT700 and preparation of progress report															
7.	Submission of progress report		T	T	T											
8.	Experimental work using IFT700		T		1	T				A DATES						
9.	Seminar/ Poster exhibition		T			1		1			102830	and the second se				
10.	Submission of final report															
11.	EDX															
12.	Oral presentation							1								

Figure 3.9 : Gantt Chart during FYP2

(Completed: Ongoing : )

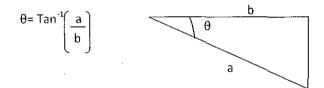
# **CHAPTER 4**

# 4 RESULTS AND DISCUSSION

#### 4.1 Contact Angle Calculation

Contact angle is measured once the oil drop is in equilibrium with brine, which is after the drop is in static condition. Water wet condition is when contact angle is less than  $90^{\circ}$ . Thus a smaller value of contact angle indicates a more water wet condition. Likewise, when contact angle is greater than  $90^{\circ}$  indicates oil wet conditions.

In this experiment, contact angle is calculated manually using simple trigonometry. Where angle  $\theta$  is obtained from the inverse of tangent a to b, tan<sup>-1</sup> (a/b).



#### 4.2 Wettability determination

A visual image at Table 4.1 below shows the result of the reduction in contact angle measurement as temperature and surfactant concentration increases. A plotted graph at Figure 4.1 showed that as the temperature increase the contact angle decreasing. It showed for each different surfactant concentration 0ppm and 500ppm. For 0ppm surfactant concentration contact angle decreases, ranging from 110°-100° and for 500ppm surfactant concentration contact angles decrease, ranging from 77°-55°. This decreasing trend of contact angle with increasing surfactant concentration as temperature increases indicates the wettability has changed from oil wet to become water wet. The wettability has been enhanced and changed from oil wet to water wet means contact angle decrease with increasing surfactant concentration as temperature increases with increasing surfactant concentration as temperature increases.

Core slice	Sodium · Dodecyl		Contact angle		·····
	Sulfate (SDS)	· · · · · · · · · · · · · · · · · · ·	Temperature <sup>o</sup> C		
	concentration, ppm	50°C	70°C	90°C	120°C
1	0 ppm	Θ = 110 deg	Θ = 108 deg		⊙ = 100 deg
2	500 ppm	⊕ = 70 deg	Θ = 67 deg	$\Theta = 59 \text{ deg}$	Ø = 55 deg

 Table 4.1 : Visual images of oil bubble for contact angle measurement (0ppm and 500ppm surfactant concentration)

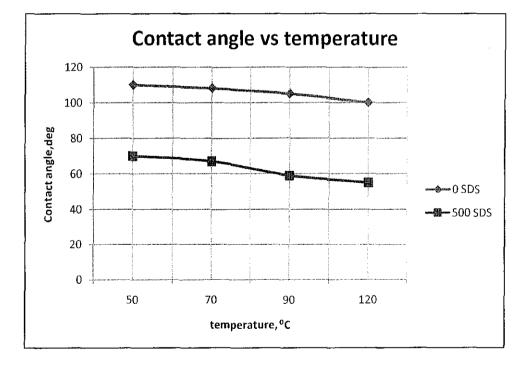


Figure 4.1 : Contact Angle vs temperature for 0ppm and 500ppm surfactant concentration

Temperature was found to have a large effect on the wetting characteristics. As temperature increase, it tends to increase the solubility of wettability altering compounds. Some compounds detached from the surface as temperature increase, hence result in a decrease in contact angle values and gives a good result in achieving good wettability.

Standnes and Austad (2000) measured the advancing and receding contact angles as a function of temperature for modified calcite surfaces with 0.005Mole concentration of Stearic Acid (SA) dissolved in decane. The result showed that the contact angle decreases with temperature which is indicate that the calcite surface is becoming more water- wet as a function of temperature.

Wang and Gupta (1995) reported that contact angle measurements at reservoir conditions. Their experimental results included contact angle measurements for crude oil-brine-quartz system over a pressure range of 200 to 3000 psig and temperature range of  $72.5^{\circ}F$  to  $200^{\circ}F$ . The quartz mineral surface was used to represent the sandstone. The result showed the contact angle decreases as the temperature increasing.

Hjelmeland and Larrondo (1986) studied that temperature can have an effect in reducing the IFT between crude oil and an aqueous sulfonate system. The result showed that temperature was found to have a large effect on the wetting characteristics. At low temperature, the solid phase exhibited oil-wet behavior, whereas at higher temperatures it exhibited water-wet behavior.

Afterwards, this experiment was repeated for the 1500ppm and 3500ppm surfactant concentration to investigate the affect of surfactant concentration to the changes in contact angle. Table 4.2 showed for the contact angle measurement as the surfactant concentration increasing. It is visible that from plotted Figure 4.2, when increase the surfactant concentration to 1500ppm and 3500ppm the contact angle still showed the decreasing trend as the temperature increases. For 1500ppm surfactant concentration

contact angle decreases, ranging from  $60^{\circ}-53^{\circ}$  and for 3500ppm surfactant concentration contact angles decrease, ranging from  $55^{\circ}-48^{\circ}$ .

Core slice	Sodium Dodecyl	Contact angle			
31100	Sulfate (SDS) concentration, ppm	50°C	Temperature <sup>o</sup> C 70 <sup>°</sup> C	90°C	120°C
ł	1500 ppm	$\Theta = 60 \text{ deg}$	Θ = 58 deg	⊙ = 57 deg	<ul><li>⊕ = 53 deg</li></ul>
2	3500 ppm	$\Theta = 55 \text{ deg}$	$\Theta = 54 \deg$	<ul><li>⊕ = 50 deg</li></ul>	<ul><li>Θ = 48 deg</li></ul>

 Table 4.2 : Visual image of oil bubble for contact angle measurement (1500ppm and 3500ppm surfactant concentration)

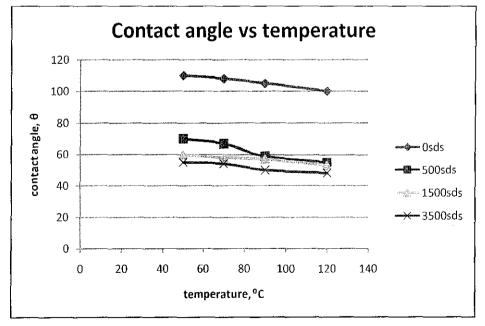


Figure 4.2 : Contact Angle Vs Temperature for ranging from 0ppm-3500ppm surfactant concentration

The purpose of increasing the surfactant concentration is to observe how many changes in contact angle and how affective it's for wettability alteration to become water wet. As expected, higher surfactant concentrations alter the wettability from oil wet to water wet. The decreasing trend of contact angle as surfactant concentration increases it indicates of wettability becoming water wet for each increasing temperature compared to initial wettability.

Alveskog *et al.*, (1998) studied on the influence of surfactant concentration, surfactant adsorption and interfacial tension between oil and aqueous phase. The anionic surfactants were used in the experiments with different concentration of surfactant. The core material was Berea Sandstone. The result showed that increased surfactant concentration results in a change in wettability from oil wet to water wet. The contact angle decreases with increasing surfactant concentration. These correspond to the driving factor which is the higher surfactant concentration the more surfactant absorption and lowered the IFT.

Zhang D.L *et al.*, (2006) investigated the effect of surfactant concentration and understand the controlling of mechanisms involve in surfactant on wettability alteration. The mechanism involved in surfactant are mainly wettability alteration and in IFT reduction. Anionic surfactant (Sodium Carbonate) used in the experiment and both wettability alteration and IFT reduction has been responsible for the increase in oil recovery. When Sodium Carbonate was increased from 0.45 to 1.2 mole concentration, contact angle decreasing ranging from 80° to 40°.

# CHAPTER 5

# 5 CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

As conclusions, the experimental result seems more reliable and conclusive. As temperature increase, the contact angle was decreased by increasing the surfactant concentration. The wettability has been enhanced and changed from oil wet to water wet which leading to increase the oil recovery. The result shows that the higher temperature the more absorption of surfactant is works in improving the wettability to water wet condition.

#### 5.2 Recommendations

As recommendation for future works, Dandina Rao (2003) recommended the contact angle is measured using Dual -Drop Dual Crystal (DDDC) technique instead of the using the sessile up method. DDDC technique were resolved the some problem by using sessile up method. Some problem encounter during this experiment is air within the needle is trapped when the test chamber is being filled with brine/SDS which can cause the oil drop created contains smaller air bubble. This problem will affect the shape of oil drop. Besides that, Xu *et al.*, (2005) studied the wettability altering capability of the surfactants. In this experiments, the fractured Yates dolomite reservoir, Yates crude oil, synthetic brine and an anionic ethoxy sulphate surfactant have been used. The experiment has been conducted at Yates reservoir conditions of 700 psi and 82° F. The contact angles have been measured using the Dual-Drop Dual Crystal (DDDC) technique. The result showed that the advancing angle measured was decreasing during surfactant injection (135°-139°) compared to initial advancing angle (152°) measured before surfactant injection.

# REFERENCES

Alveskog P.L, Holt T. Torsaeter O. "The Effect of Surfactant Concentration on the Amott Wettability Index and Residual Oil Saturation", Journal of Petroleum Science and Engineering 20 (1998) 247-252, 1998.

Anderson, W. G., "Wettability Literature Survey – Part 2: Wettability Measurements", JPT, 1986, p. 1246-1262.

Ayirala S.C, "Surfactant Induced Relative Permeability Modification for Oil Recovery Enhancement", Master of Science in Petroleum Engineering, Thesis Louisiana State University and Agricultural and Mechanical College, 1996.

Dandekar A.Y, "Petroleum Reservoir Rock and Fluid Properties", ISBN-13, 2006.

Dandina N Rao, "Is There a Correlation Between Wettability from Corefloods and Contact Angle?" ,SPE 37234, this paper was prepared for SPE International Symposium on Oil Field Chemistry, Houston, Texas, 2003.

Donalson E.C, Thomas R.D, and Lorenz P.B, "Wettability Determination and its Effect on Recovery Efficiency, Journal of Petroleum Science and Engineering, 13-20,1969.

Hamouda A.A and Karoussi O.,"Effect of Temperature, Wettability and Relative Permeability on Oil Recovery from Oil-Wet Chalk", ISSN 1996-1073, 2008.

Hjelmeland OS, Larrondo LE – "SPE Reservoir Engineering, Experimental Investigation of the Effects of Temperature ,Pressure and Crude Oil Composition on Interfacial Properties",1986 - onepetro.org

http://en.wikipedia.org/wiki/Amott\_test

http://en.wikipedia.org/wiki/Contact angle

Jadhunandan P.P, Morrow N.R, "Effect of Wettability on Waterflood Recovery for Crude Oil/Brine/Rock System", SPE Reservoir Engineering, 1995.

Jarrahian KH, Sefti M.V, Ayotollahi Sh, Moghadam F, Moghadam A.M, "Study of Wettability Alteration Mechanism by Surfactants", SCA2010-38, this paper was prepared for presentation at the International Symposium of the Society of Core Analysis held in Halifax, Nova Scotia, Canada, 4-7 October, 2010.

Kolev V.L, Kochijashky I.I, Danov K.D, Kralchevsky P.A, Broze G., Mehreteab A., "Spontaneous Detachment of Oil Drops from Solid Substrates : Governing Factors", Journal of Colloid and Interface Science 257(2003) 357-363, 2003.

McGuire P.L, Chatham J.R, Paskvan F.K, Sommer D.M, Carini F.H, BP Exploration (Alaska) Inc, "Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope", SPE 93903, this paper was presented in SPE Annual Technical Conference and Exhibition, Anaheim, CA, U.S.A, 2005.

Miller C.A, Hirasaki G.J, "Recent Advances in Surfactant EOR", SPE 115386, this paper was presented in International Petroleum Technology Conference, Kuala Lumpur, Malaysia, 2008.

Morrow N.R, Zhang X., Zhou X.," Characterization of Wettability from Spontaneous Imbibitions Measurement", paper: 94-47, Journal of Canadian Petroleum Technology, 1999.

Salehi M, Johnson S, Bala G, "Wettability Alteration of Carbonate Rock Mediated by Biosurfactant Produced from High-Starch Agricultural Effluents", SPE 115386, this paper was presented in 9<sup>th</sup> International Symposium on Evaluation of Wettability and its Effect on Oil Recovery,2006.

Standnes DC, Austad T – "Journal of Petroleum Science and Engineering, Mechanism for Wettability Alteration from Oil-Wet to Water-Wet Using Surfactant", 2000.

Tarek Ahmad, "Reservoir Engineering Handbook, Houston, Gulf Professional Publishing", 2001.

Vijapurapu S.C, Rao D.N," Effect of Brine Dilution and Surfactant Concentration on Spreading and Wettability ", SPE 80273, this paper was presented in SPE International Symposium on Oilfield Chemistry, 2003.

Wang, W. and Gupta, A., "Investigation of the Effect of Temperature and Pressure on Wettability using Modified Pendant Drop Method", Proc. Society of Petroleum Engineers Annual Technical Conference and Exhibition. Oct 22–25, Dallas, Texas, SPE 30544, 1995.

Webb K, Lager A., Black C.," Comparison of High/Low Salinity Water/Oil Relative Permeability", SCA2008-38, this paper was prepared for presentation at the international symposium of the society of core analysis held in Abu Dhabi, UAE 29October-2 Novenber, 2008.

Wu Y, Shuler P.J, Blanco M, Tang Y and Goddard W.A, "An Experimental Study of Wetting Behaviour and Surfactant EOR in Carbonates with Model Compounds", SPE 99612, this paper was accepted for presentation at the 2006 SPE/DOE Symposium on Improved Oil Recovery Tulsa, 22-26 April 2006.

Xu W., Ayirala C., Rao D.N, "The Experimental Investigation of Oil Compositional and Surfactant Effects on Wettability at Reservoir Conditions", this paper was prepared for presentation at the International Symposium of Society of Core Analysis held in Toronto, Canada, 21-25 August 2005.

Zhang D.L, Liu S, Puerto M., Miller CA, Hirasaki G.J, "Wettability Alteration and Spontaneous Imbibitions in Oil-Wet Carbonate Formations", Journal of Petroleum Science and Engineering 52(2006)213-226, 2006.

Zhou X., Morrow N.R, Ma S.M.," Interrelationship of Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibitions and Waterflooding", SPE Journal Volume 5, 2000.