Surfactant enhanced oil recovery by wettability alteration in sandstone reservoirs

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SURFACTANT ENHANCED OIL RECOVERY BY WETTABILTY ALTERATION IN SANDSTONE RESERVOIRS

by

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ABSTRACT

Recovering more oil from existing oil reservoirs using enhanced oil recovery methods holds the key for meeting future energy demands. Even though wettability is a cornerstone in oil recovery, few studies have focused on increasing oil recovery in sandstone reservoirs through wettability alteration. The objective of this thesis is to prove that altering the wettability of a sandstone rock to preferentially water-wet condition will reduce the remaining oil saturation and thus increase the percentage of recovered oil.

Two commercial surfactants were selected after studying both the phase behavior and the interfacial properties of 30 surfactants with oil and 1.00% sodium chloride brine systems. Both surfactants then were tested for their ability to alter the wettability of sandstone rocks. This alteration was measured based on the contact angles of different surfactant solutions on oil-treated glass chips. In all cases, the surfactant solutions were able to alter the wettability of the oil-treated glass chips from weakly water-wet to strongly water-wet. The ability of both selected surfactants to increase the percentage of recovered oil then was examined using oil-treated sands. The oil recovery tests from both oil-wet and water-wet sand showed that both surfactants can change the wettability of oil-wet sand to water-wet and increase oil recovery. Both surfactants also were shown to significantly improve oil recovery from oil-wet sandstone through spontaneous imbibition. Considering that up to half of all sandstone reservoirs are possibly oil-wet, the results of this work could enhance oil recovery from oil-wet, water-flooded, mature sandstone reservoirs.
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<tr>
<td>$N_c$</td>
<td>Capillary Number</td>
</tr>
<tr>
<td>$V$</td>
<td>Darcy velocity</td>
</tr>
<tr>
<td>$M$</td>
<td>Mobility ratio</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
</tr>
<tr>
<td>$\gamma_{ow}$</td>
<td>Oil-Water Interfacial Tension</td>
</tr>
<tr>
<td>$\gamma_{os}$</td>
<td>Interfacial-free energy between solid and oil</td>
</tr>
<tr>
<td>$\gamma_{ws}$</td>
<td>Interfacial-free energy between solid and water</td>
</tr>
<tr>
<td>$r$</td>
<td>Capillary pore radius</td>
</tr>
<tr>
<td>$p_c$</td>
<td>Capillary pressure</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>Density of oil</td>
</tr>
<tr>
<td>$\rho_d$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular velocity</td>
</tr>
<tr>
<td>$D$</td>
<td>Drop minor axis semi diameter</td>
</tr>
<tr>
<td>EO</td>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>PO</td>
<td>Propylene oxide</td>
</tr>
<tr>
<td>HLB</td>
<td>Hydrophilic-lipophilic balance</td>
</tr>
<tr>
<td>S.S.</td>
<td>Surfactant solution</td>
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<td>IFT</td>
<td>Interfacial tension</td>
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1. INTRODUCTION

1.1. CATEGORIES OF OIL RECOVERY

Historically, oil recovery has been divided into three categories, primary, secondary and tertiary recovery. Primary recovery results in recovering 5-30% of the original oil in place (OOIP) (Farouq & Stahl, 1970). Secondary recovery usually is implemented after primary production declines and recovers up to 20-35 % of the OOIP. Tertiary recovery, or enhanced oil recovery (EOR), can increase the percentage of oil recovery to 30-60% or more. The recovery profile of a conventional reservoir is shown in Figure 1.1.

![Figure 1.1. Recovery Profile of a Conventional Reservoir](www.CANOPETRO.com, 2012)

1.2. SIGNIFICANCE OF ENHANCED OIL RECOVERY

In order to address the need for EOR, the definition of oil reserves must be determined. Reserves refer to the amount of oil that can be produced from a reservoir
under existing economics and with available technology, which is given by the following material balance equation.

\[
\text{Present reserves} = \text{Past reserves} + \text{Additions to reserves} - \text{production from reserves} \quad (1)
\]

In order to maintain oil reserves, large fields must be discovered, new wells drilled, or other techniques implemented to increase the percentage of recovery from known reservoirs. The probability of finding large fields is declining, making the need to increase the percentage of recovery from known reserves the practical solution; this can be accomplished by applying EOR methods.

1.3. FACTORS INFLUENCING REMAINING OIL SATURATION

EOR implies a reduction of the remaining oil saturation. Three major factors influence the remaining oil saturation in a reservoir.

The first factor is the capillary number (Nc), defined as \( N_c = \frac{v \mu}{\sigma \cos \theta} \), where \( v \) is the Darcy velocity (m/s), \( \mu \) is the displacing fluid viscosity (Pa.s), \( \sigma \) is the interfacial tension (IFT) (N/m) and \( \theta \) is the contact angle. The capillary number affects the microscopic pore-level oil displacement. The second factor is the mobility ratio (M), defined as \( M = \frac{\lambda_D}{\lambda_d} \), where \( \lambda_D \) is the mobility of the displacing fluid and \( \lambda_d \) is the mobility of the displaced fluid. \( \lambda = \frac{k}{\mu} \), where \( k \) is the effective permeability (md) and \( \mu \) is the viscosity (cp). A value of \( M > 1 \) is considered unfavorable as it indicates that the mobility of the displacing fluid is higher than that of the displaced fluid. The mobility ratio affects the macroscopic displacement efficiency. Reservoir heterogeneity is the third major factor that can influence the remaining oil saturation. Reservoirs can contain impermeable lithological divisions and heterogeneous porosity/permeability distribution that notably affect the fluid flow path and distribution. Other factors also
may influence the remaining oil saturation, such as the well bore structure and well pattern.

1.4. METHODS OF ENHANCED OIL RECOVERY

With a few minor exceptions, all EOR falls distinctly into one of four categories: thermal, gas, chemical, and others. This study focuses on wettability alteration methods, one of the techniques of chemical recovery.

1.4.1. Chemical Recovery. Although chemical EOR is not used widely except in China, this method holds promise for future improvements in oil production, especially in mature and waterflooded fields. Chemical EOR can be classified into three categories, polymer, surfactants and alkaline agents; in addition, combinations of the three categories can be used, such as alkali-polymer (AP), surfactant-polymer (SP) and alkali-surfactant-polymer (ASP).

Chemical recovery has been tested in a limited number of fields. Micellar polymer flooding was used in light and medium crude oil reservoirs until the early 1990s. Although it showed promising results, the high concentrations and cost of surfactants and co-surfactants, combined with the low oil prices during the mid-1980s, limited its use. Surfactant-induced wettability alteration has been studied intensively for the past 50 years as a promising method by which to reduce the remaining oil saturation in reservoirs. This method continues to undergo much laboratory investigation (Wang et al., 2011). Developments in ASP technology and surfactant chemistry have focused renewed attention on chemical EOR in recent years.
1.5. SCOPE OF THE RESEARCH

Wettability is a major factor controlling the location, flow, and distribution of the fluids in a reservoir (Anderson, 1987). Many investigations of wettability and its effects on oil recovery have concluded that there exists favorable reservoir wettability for operators to recover maximum crude oil from subterranean reservoirs (Dandina et al., 1992).

Studies suggest that reservoirs cover a wide range of conditions, from strongly oil-wet to weakly water-wet. Carbonate reservoirs are often mixed-wet to oil-wet because of the positive zeta potential of the rock surface (Sharma et al., 2001). A handful of studies have suggested that sandstone reservoirs vary from water-wet to oil-wet (Wang et al., 2011). Also, in high saline environments, it is very possible for clay particles lining the pores of sandstone reservoirs to be extremely hydrophobic. The hydrophobic properties of clay can cause local oil wetness in sandstone reservoirs (Clementz, 1982). Tiab and Donaldson (1996) suggested that up to 50% of sandstone reservoirs are oil-wet.

The objective of this thesis is to examine the effect of altering the wettability of sandstone reservoirs to preferentially water-wet condition on oil recovery. First, different commercial surfactants were screened using phase behavior screening and a spinning drop tensiometer apparatus. After selecting the best surfactant candidates, the advanced goniometer was used to test the ability of the selected surfactants to alter the rock’s wettability. An oil recovery test with oil-wet and water-wet sand and a spontaneous imbibition test were performed in order to evaluate the ability of the selected surfactants to increase oil recovery.
1.6. THESIS OVERVIEW

The first section introduces the concept of enhanced oil recovery and the significance of using EOR in oil fields. Chemical EOR is explained, as are the major factors manipulating the remaining oil saturation. Finally, the objective of this work is outlined.

Section 2, which contains the background and a review of the literature pertaining to recovering oil by altering wettability, is intended as a refresher on the effect of reservoir wettability on oil recovery. It also explains the methods used to measure wettability. Surfactants and their behavior in solution are defined and classified. This section also explains the mechanism of wettability alteration in both sandstone and carbonate reservoirs.

Section 3 details the laboratory screening methods performed to select candidate surfactants. Phase behavior and IFT measurement experiments and results are presented.

Section 4 evaluates the performance of selected candidate surfactants to both alter the wettability of sandstone rock and increase oil recovery. A series of laboratory experiments are performed and results are presented.

Section 5 summarizes the conclusions arrived at through this research.
2. BACKGROUND AND LITERATURE REVIEW

2.1. SURFACTANTS

2.1.1. Definition and Classifications. Surface active agents are amphiphilic, usually organic compounds with a chemical structure that consists of two different molecular components, known as hydrophilic and hydrophobic groups (see Figure 2.1). A hydrophilic group is a water-soluble component. A hydrophobic group is a water-insoluble component. In the standard surfactant terminology, the soluble component, or hydrophilic group, is called the “head,” and the hydrophobic group is called the “tail.” The head and tail surfactants attack the interface between two immiscible surfaces, thus decreasing the interfacial forces between the two surfaces.

![Surfactant Chemical Structure](http://conf.sej.org/pollution-environmental-health/, 2011)

Surfactants can be classified into four main categories according to the composition of their head (see Figure 2.2)
2.1.1.1 Anionic surfactants. Anionic surfactants are the most commonly-used surfactants. They dissociate in water into an amphiphilic anion and a cation. The cation is general, either an alkaline metal (Na+, K+) or a quaternary ammonium. Anionic surfactants account for approximately 50% of surfactants produced worldwide.

2.1.1.2 Nonionic surfactants. Nonionic surfactants are the second most commonly-used surfactants. Nonionic surfactants do not ionize in aqueous solution. The hydrophilic group consists of non-dissociable types, such as alcohol, phenol, ether, ester, or amide. The lipophilic group consists of the alkyl or alkylbenzene type, the former coming from naturally-occurring fatty acids.

2.1.1.3 Cationic surfactants. Cationic surfactants dissociate in water into an amphiphilic cation and an anion, most often of the halogen type. These surfactants are, in general, more expensive than anionic surfactants because of the high-pressure
hydrogenation reaction required during their synthesis. Cationic surfactants are often of great commercial importance, such as in corrosion inhibition.

2.1.1.4 Amphoteric or zwitterionic surfactants. Amphoteric surfactants, such as betaines and sulfobetaines, exhibit both anionic and cationic dissociation.

2.1.2. Behavior of Surfactants in Solution. When introducing a surfactant into a solution, the surfactant initially will partition the interface until the surface area covered by surfactant increases and the surface energy decreases. At that point, the surfactant will begin to aggregate into micelles. The surfactant concentration in the solution above which micelles form is called the critical micelle concentration (CMC), as shown in Figure 2.3. Prior to reaching the CMC, the system’s free energy is reduced by lowering the energy of the interface. After reaching the CMC, the system’s free energy will continue to decrease by minimizing the area of the hydrophobic parts of the surfactant that makes contact with water.

Figure 2.3. Micelle Formation in Surfactant Solution (http://people.maths.ox.ac.uk/griffit4/micelle_schematic.jpg)
2.1.3. Effect of Surfactants on Oil Recovery in Oil Reservoirs. Two techniques are applied to inject surfactant into reservoirs, the first of which is known as surfactant flooding. This technique uses separate injection and production wells. Oil recovery improvement occurs by reducing both IFT and capillary forces in the formation. Surfactant flooding will decrease the residual oil saturation and is applied primarily in sandstone reservoirs.

In a successful displacement process the injected surfactant slug must achieve an ultra-low IFT in order to mobilize the residual oil and create an oil bank in which both oil and water flow continuously (Bourrel & Schechter, 1988). This ultra-low IFT must be maintained at the moving displacement front in order to prevent mobilized oil from being trapped by capillary forces. Long term surfactant stability at reservoir conditions is also necessary for a successful displacement process.

In the second technique, known as huff-n-puff, a single well is used both as an injector for the surfactant solution and as a producing well. Generally, surfactants can decrease the residual oil saturation near the well bore. When applied in carbonate reservoirs, surfactants can be imbibed into the carbonate matrix, which will favorably alter the matrix wettability to the point at which oil recovery can be improved. First, surfactants are injected into the formation through a single well. This is followed by a soaking period. Production from the same well then takes place.

Early research on surfactant use in EOR focused on the injection of microemulsions into reservoirs. These microemulsions contained high concentrations of surfactant, cosolvent, and oil (Gogarty et al., 1968). While technically successful, this
approach was not economically practical at that time due to both high chemical costs and low oil prices.

Later work focused on reducing the amount of chemical required and emphasized low concentration aqueous surfactant solutions with an added polymer for mobility control. Austad and Milter (2000) provide an overview of up to 2000 cases of surfactant flooding developments.

Surfactant flooding methods were first developed for sandstone reservoirs. The fact that oil recovery from fractured carbonate reservoirs can be increased by both surfactant-induced wettability alteration and spontaneous water imbibition draws a great deal of attention to the application of surfactant flooding to oil-wet carbonate reservoirs. Both wettability alteration and IFT reduction will enhance oil expulsion from the carbonate rock matrix into fractures, thus increasing oil recovery.

2.2. WETTABILTY DEFINITION AND CLASSIFICATION

Wettability is one of the major factors that controls both the distribution and flow of fluids in the pores of a reservoir (Anderson, 1986). Wettability can be described as the preference of a solid to contact either a liquid or a gas in what is known as the wetting phase, as depicted in Figure 2.4.

![Figure 2.4. Wettability of a Drop of Liquid on a Solid Surface](image-url)
Wettability generally can be classified as either homogeneous or heterogeneous. In a homogeneous system, the reservoir rock has the same molecular affinity for either oil or water and can be water-wet, oil-wet or intermediate-wet. In a heterogeneous system, the reservoir rock shows a different affinity for either oil or water across distinct rock sections of the reservoir. Heterogeneous wettability is classified as either fractional or mixed. In fractional wettability, the reservoir exhibits local areas that are strongly oil-wet while most of the reservoir is water-wet. This phenomenon occurs when reservoir rock contains variable minerals. In a mixed-wet system, small pores are filled with water (water-wet), and larger pores are filled with oil (oil-wet). Low residual oil saturation exists in a mixed-wet system.

2.3. RESERVOIR WETTABILITY

Almost all minerals in a natural, clean state exhibit water-wet behavior. Certain components, primarily heavy asphaltene and the resin fractions of crude oil, can alter the wettability of the original water-wet rock (Dubey, 1989).

Components carrying a charged group, such as an acid or a base, significantly affect wettability during the formation of the reservoir (Cuiec, 1984). Additional significant components include oil and mineral composition (Buckley et al., 1998), water solubility of polar oil components (Anderson, 1986; Kaminsky & Radke, 1998), capillary pressure and thin film forces (Melrose 1982; Hirasaki, 1991). Temperature, salinity, pressure and initial water saturation can affect the degree of wettability alteration as well.

Buckley et al. (1998) proposed four different mechanisms by which polar components from crude oil are adsorbed to mineral surfaces. These mechanisms include polar interactions, which occur in the absence of a water film between oil and solid,
surface precipitation of asphaltenes, which occurs when the oil is a poor solvent for the heavy crude components. An acid/base interaction that takes place between liquid/liquid and solid/liquid interfaces is also one of the mechanisms for the adsorption process. Ion binding, in which divalent or multivalent ions in the brine can bridge the mineral surface to an oil/brine interface, is the final mechanism by which polar components from crude oil are adsorbed to mineral surfaces.

2.4. WETTABILITY MEASUREMENTS

As one of the most significant properties controlling oil recovery, the reservoir wettability must be studied sufficiently. Measuring the wettability of an oil/water/rock system is not an easy task. Different measurement methods can yield different results. A variety of methods has been proposed to measure the wettability of a system. These methods can be classified as either quantitative or qualitative. The contact angle, modified Amott test, and U.S. Bureau of Mines (USBM) methods are all examples of quantitative methods used to measure the wettability of a system. Capillary pressure curves, reservoir logs, and imbibitions rates are examples of qualitative methods.

The methods most widely used in determining the wettability of an oil/water/rock system are the contact angle, Amott test and USBM. The contact angle measures the wettability of a liquid drop on a solid surface but does not consider the heterogeneity of the reservoir or surface roughness. The Amott test and USBM measure the average wettability of a core. As a result, they are applied when studying reservoir properties.

2.4.1. Contact Angle. The contact angle method is the most widely-used method for measuring the wettability between a pure fluid and an artificial core. Wettability in an
oil/water/rock system can be explained by the contact angle of a drop of water on a solid surface, as shown in Figure 2.5.

The relation between the surface energies and the contact angle are explained by Young’s equation:

\[
\gamma_{ow} \cos \theta = \gamma_{os} - \gamma_{ws}
\]  

(2)

The contact angle measures through denser fluid, so in a water/oil/rock system, the contact angle is measured through water. When \( \theta \) is between 0 and 60 to 75° in such a system, it is defined as water-wet. When \( \theta \) is between 180 and 105 to 120°, the system is defined as oil-wet. In the range of a 75 to 105° contact angle, the system is neutral-wet (Anderson, 1986).

Many methods have been used to measure the contact angle, including both the static and dynamic sessile drop method, tilting plate method, dynamic Wilhelmy method and others. Additional methods are explained in (Anderson, 1986).

2.4.1.1 Static sessile drop method. A contact angle goniometer is used to measure the contact angle between a pure liquid drop and a solid surface. A high-resolution camera is used to capture the profile of a pure liquid on a solid surface and the
angle formed between the liquid/solid interface and the liquid/vapor interface. Software is then used to analyze the captured drop profile.

### 2.4.1.2 Dynamic sessile drop method

The same measurement apparatus used in the static sessile drop method is used in the dynamic sessile drop method, but with modifications. A common variation of this method takes place in two steps. The first step involves measuring the largest contact angle that can be formed on the liquid/solid interface without increasing the three-phase line. The contact angle is measured by adding a volume of liquid dynamically. The measured angle is defined as the advancing angle. In the second step, volume is removed from the liquid surface in order to form the smallest possible angle without decreasing the three-phase line. The angle measured in this step is referred to as the receding angle. The difference between the largest and the smallest angle is the contact angle hysteresis.

### 2.4.1.3 Dynamic Wilhelmy method

The dynamic Wilhelmy method requires homogeneous properties and uniform geometries for both sides of the solid surface, as well as a precision force scale. The dynamic Wilhelmy method involves immersing a solid plate in a liquid with a known IFT and measuring the force acting on the plate. As result of this method’s complexity, it is not widely used.

### 2.4.2. Amott Wettability Measurements

The Amott wettability is a macroscopic average wettability measurement for a solid/fluid system. It involves measuring the amount of both spontaneous and forced imbibitions for a rock sample. The Amott wettability is used as a standard measurement for comparing the wettability of different core samples.
2.4.3. USBM (U.S. Bureau of Mines) Method. Like the Amott method, the USBM method is a macroscopic average wettability measurement for a solid/fluid system. The difference between these two methods is that the USBM considers the work required to conduct a forced fluid displacement, while the Amott method does not.

2.4.4. Imbibition Rates. Imbibition is widely used as it reveals the wettability of an oil/water/rock system using a simple apparatus.

Spontaneous imbibition is the displacement of a wetting phase for a non-wetting phase in a porous media. In a water-wet oil/water/rock system, the water is the displacing fluid, and the oil is the displaced fluid. The most important factor affecting the imbibition rate is capillary pressure.

The imbibition rate is extremely important in a water-drive reservoir because it can either advance or hinder water movement, thus affecting areal sweep. Imbibition rate measurements provide information about the dynamic IFT and wetting phenomena. The imbibition rate also is used in both Amott and USBM wettability measurements.

2.5. OIL RECOVERY THROUGH RESERVOIR WETTABILITY ALTERATION

Studies have confirmed that wettability directly affects the percentage of oil recovered from a reservoir. It has been proven that there is a favorable reservoir wettability at which maximum oil recovery can be achieved; therefore, intensive studies have been conducted in the area of increasing oil recovery through surfactant-induced wettability alteration.

2.5.1. Wettability Alteration of Carbonate Reservoirs. Nearly 50% of all known reserves are in carbonate reservoirs (Smith, 2010). Spontaneous imbibition, the displacement of one fluid by another immiscible fluid through capillary action, is a key
method for recovering oil in carbonate reservoirs. Under the influence of water injection, or aquifer drive, the consequent recovery of oil from the rock matrix, if it exists, depends primarily on the spontaneous imbibition of water, which is a relatively slow process, especially when the rock has low permeability.

Due to initially being oil-wet or less water-wet, water flooding in carbonate reservoirs will not displace the oil within the matrix, resulting in low oil recovery from carbonate rock. Imbibition is driven by surface energy through the action of capillary pressure. This capillary pressure can be written as:

\[ p_c = \frac{2\sigma \cos \theta}{r} \]  

(3)

where \( p_c \) is the capillary pressure, \( \sigma \) is the oil-water IFT, \( \theta \) is the contact angle, and \( r \) is the capillary pore radius. If \( p_c \) is positive or \( \theta \) is less than 90, spontaneous imbibition will occur, and oil will automatically be drained out of pores by water. So, altering the wettability of carbonate reservoirs to preferentially more water-wet conditions will favorably affect oil recovery by enhancing the spontaneous imbibition process.

Buckley and Leveret (1942) published one of the first papers on the effect of wettability on oil recovery. Since then, studies have continuously debated the optimum wettability that provides maximum oil recovery. Recently, EOR methods based on chemically-induced wettability alteration have gained a great deal of attention (Wu, 2008). Austord and colleagues (2000) performed a series of studies on oil-wet chalk cores, investigating the effect of different surfactant solutions on oil recovery. A cationic surfactant, dodecyl trimethyl ammonium bromide (DTAB), was tested at concentrations higher than their critical micelle concentration. DTAB yielded an oil recovery of 70\% OOIP by imbibing water into originally oil-wet cores. It was observed that the imbibition
rate was directly proportional to the system’s temperature and inversely proportional to the connate water saturation. It also was observed that most of the anionic surfactants tested were not able to desorb adsorbed organic carboxylates. Some of the tested anionic surfactants increased oil recovery from the oil-wet chalk at a slower rate than the cationic surfactants.

Standnes et al. (2002) investigated oil recovery from oil-wet reservoir cores at room temperature. Aqueous solutions of a nonionic surfactant (ethoxylated alcohol, EA) and a cationic surfactant (C12TAB) were used in the experiments. Different core lengths of 5 cm and 30 cm with an initial water saturation of 17-33% and permeability of 45 mD were tested. In general, the C12TAB was more efficient than the EA in terms of the amount of spontaneous oil expelled from the cores. For the 5 cm core experiments, approximately 40-45% of OOIP was recovered using C12TAB versus an average recovery of 10% using EA. The imbibition of EA solution into the 30 cm core was less than 5%, but a large improvement was achieved when switching to a C12TAB solution. Contact angle measurements on oil-wet calcite crystals confirmed that C12TAB was much more efficient than EA in altering wettability toward more water-wet conditions.

Seethepalli et al. (2004) suggested that anionic surfactants (SS-6656, Alfoterra 35, 38, 63, 65, and 68) can alter the wettability of the calcite surface to intermediate-wet or water-wet conditions. The anionic surfactants altered the wettability even better than the cationic surfactant DTAB with Texas crude oil in the presence of sodium carbonate.

Zhang et al (2004) reported the wettability alteration of a calcite surface from originally oil-wet to intermediate or preferential water-wet conditions with alkaline/anionic surfactant systems.
Mohahanty et al. (2004) reported more than 50% OOIP recovery using different anionic surfactants on aged outcrop limestone core plugs. Wettability was considered an important contribution in the oil recovery process.

Bryant and colleagues (2004) studied induced wettability alteration through the adsorption and removal of amine sulfates with known molecular structures on mica surfaces that were exposed to decane solutions of the surfactant brine. Low PH conditions that promote protonation of the surface amine groups produced the greatest wettability alteration. Above a PH of 8 or 9, no adsorbed surfactant molecule remained on the mica surface.

Xie et al. (2005) observed that injecting surfactant solution after ceasing production using brine can lead to the recovery of an additional 5-10% of OOIP. The additional oil recovery was due to the increased water wetness of the core.

2.5.2. Wettability Alteration of Sandstone Reservoirs. Sandstone reservoirs are more complex than carbonate reservoirs. The wettability of sandstone reservoirs may vary widely from strongly water-wet to strongly oil-wet states. Neutral or intermediate wettability is also common (Wang et al., 2011)

Sandstone reservoirs usually undergo waterflooding. Oil recovery during waterflooding is a function of wettability, fluid distribution, pore geometry, saturation, saturation history, and oil/water viscosity ratio. Wettability affects waterflooding by controlling the flow and spatial distribution of fluids in a porous medium.

Several laboratory waterfloods show oil recovery decreasing with decreasing water-wetness. This finding is consistent with the intuitive concept that the strong wetting preference of the rock for water yields the most efficient oil displacement. On the other
hand, a number of cases of better recovery for weakly water-wet and intermediate wetting conditions have been reported. Rathmell et al. (1973) found in their waterflooding experiments in 7 ft-9 ft long Berea cores that as the cores became less water-wet or altered toward intermediate wettability, both the breakthrough and oil recovery increased. These results can be explained on the basis of weak capillary forces in weakly water-wet or intermediately water-wet cores (Wang, 2011).

Studies conducted by Rao et al. (2006) indicate that the surfactant-induced wettability alteration process appears beneficial for field implementation in oil-wet reservoirs. In these reservoirs, the surfactants can induce wettability alterations to either less oil-wet or less water-wet states, thus improving oil recovery. In initially water-wet reservoirs, the surfactant-induced wettability alteration process is beneficial only if the surfactant induces either mixed wettability or intermediate wettability. This process is detrimental for improved oil recovery if the surfactant induces oil wetness. Thus, the surfactant type, rock mineralogy, and surfactant concentration are significant in determining the profitable success of this process in the field.

Improper determination of a reservoir’s original wettability can lead to poor decisions for EOR field applications using surfactants. Hence, the surfactant must be chosen carefully depending on the initial reservoir wettability in order to maximize the benefits.

2.5.3. Summary

- Efforts to enhance oil recovery through wettability alteration methods have been active in recent years. However, many basic questions have been ambiguous up until now.
Major factors affecting oil recovery using surfactant treatments are the wetting characteristic, rock mineralogy, porosity, permeability, pore heterogeneity, matrix boundary conditions, saturation, oil/water IFT, gravity, capillary number, surfactant type, surfactant adsorption property, surfactant molecular diffusion coefficient, etc. (Wang et al., 2011). Every factor should be evaluated individually in order to achieve maximum oil recovery from reservoirs.

Technical interest in wettability alteration is expected to continue in the coming years.
3. SURFACTANT SCREENING

3.1. INTRODUCTION

30 commercial surfactants were tested to select the best candidate. First, phase behavior screening was used as a quick and effective method by which to identify favorable surfactant formulations. This involved observing the equilibrium time, microemulsion viscosity, oil and water solubilization ratio, and IFT. Then, the spinning drop test was used to measure the IFT for the different oil/brine/surfactant systems as a supplement to the phase behavior test.

3.2. IDENTIFY PROMISING SURFACTANT EOR FORMULATIONS

This study was performed under ambient temperatures; different kinds of surfactants (i.e., anionic, cationic and nonionic surfactants) were investigated. The following steps were taken to identify promising surfactant EOR formulations:

- Use knowledge of surfactant chemistry and commercial surfactant production capabilities to identify potential surfactant test candidates.

- Acquire samples from surfactant companies and screen the acquired surfactants using the phase behavior experiment.

- Observe the viscosity of the oil/surfactant/brine microemulsion in order to avoid high-viscous phases.

- Determine the IFT for oil/brine/surfactant systems using a spinning drop tensiometer.
3.2.1. Identify Potential Surfactant Test Candidates. Extensive research on surfactants has established a clear relationship between the surfactant structure and the reservoir fluid properties (Bourrel & Schechter, 1988; Aoudia et al., 1995). For instance, an increased hydrophobe length for surfactants is accompanied by both a decreased optimal salinity and an increased solubilization ratio. Furthermore, adding weakly hydrophobic function groups, i.e., propylene oxide (PO) will increase the range of the ultra-low IFT region. In contrast, adding ethylene oxide (EO) groups increases both the hydrophilic properties and the optimal salinity.

So, the degree of both propoxylation and ethoxylation can be used to alter the surfactant to a given crude oil, temperature, and salinity (Aoudia et al., 1995; Wu et al., 2005; Jayanti et al., 2002; Levitt, 2006; Hirasaki et al., 2006).

Varying the number of PO groups and EO groups will cause the surfactant to exhibit varying ratios of the hydrophilic-lipophilic balance (HLB). The HLB can be used to identify the surfactant properties. As described by Griffin (1949, 1954), an HLB value less than 10 indicates strong hydrophobic properties, while a value greater than 10 indicates strong hydrophilic properties. An HLB value from 11 to 14 indicates good wetting agent properties. Based on previous information and prior work in this field, 30 different surfactants were selected to undergo the phase behavior screening.

3.2.2. Phase Behavior Screening. After identifying potential surfactant candidates, surfactant samples were acquired from chemical companies. The process of screening 30 surfactants using the Winsor phase behavior method was performed using different surfactant solutions and pure hydrocarbon (i.e., decane). Clarity of interfaces is just one advantage of using pure hydrocarbon for the initial screening.
3.2.2.1 **Winsor phase behavior.** The formation of separate, thermodynamically stable phases when surfactant, oil and brine are mixed was first illustrated by Winsor (1954). Winsor phase behavior is a distinction among the three phase behaviors of oil, water and surfactant systems when they form a microemulsion, as Figure 3.1 illustrates.

![Figure 3.1. Winsor Phase Behavior](www.owlnet.rice.edu)

3.2.2.2 **Effect of salinity on phase behavior.** A transition in phase behavior can be caused by altering a variable such as the salinity, surfactant structure, temperature, or equivalent alkane carbon number (EACN) of the oil.

The salinity of the brine phase is an important parameter influencing which type of Winsor phase behavior occurs. At low salinity, Type I, or oil-in-water, microemulsions occur; these are characterized by coexistence with an excess brine phase. At very high
salinity, Type II, or water-in-oil, microemulsions are formed, which are characterized by coexistence with an excess oil phase. A narrow intermediate range exists between the Type I and Type II regions in which oil and water microemulsions are formed as a middle phase and coexist with both excess oil and excess water phases. These are referred to as Type III microemulsions. The salinities at which the transition occurs between Type I and Type III behavior is referred to as the lower critical salinity, and the salinity of the transition between Type III and Type II is referred to as the upper critical salinity.

3.2.2.3 Optimal solubilization ratio and optimal salinity. The salinity at which equal volumes of oil and water are solubilized in the microemulsion is defined as the optimal salinity. The ratios \( V_o/V_s \) and \( V_w/V_s \) increase and decrease with salinity, respectively. When these ratios are plotted, the intersection point within the Type III salinity range is the optimum solubilization ratio at the optimum salinity.

Optimal salinity also has been defined as the salinity at which the IFT between the microemulsion and water equals the IFT between the microemulsion and oil; it is typically the same or nearly the same as the optimal salinity for equal solubilization. The optimal salinity lies approximately at the midpoint between the lower critical salinity and the upper critical salinity.

The optimum solubilization ratio corresponds to the lowest IFT, which is the desired condition for mobilizing oil in EOR. Optimum solubilization ratios for specified oils will vary for different surfactants and their mixtures. However, a high optimum solubilization ratio is not sufficient to yield acceptable behavior and high oil recovery. The absence of viscous phases such as gels, liquid crystals and macroemulsions and short equilibration times are equally important.
Healy & Reed (1974) developed an empirical correlation between the solubilization ratios and IFT between the microemulsion and each excess phase. Later, Huh (1979) derived a theoretical relationship between the solubilization ratio and IFT. A simplified form of his theory predicts that the IFT ($\sigma$) is inversely proportional to the square of the solubilization ratio ($S^2$).

$$\sigma = \frac{C}{S^2}$$

In this equation, $C$ is approximately $0.30$ dynes/cm, and the solubilization ratio ($s$) is defined as the volume of solubilized oil or water divided by the volume of surfactant on a 100% active basis. The solubilization ratio is much more easily and accurately measured over time than IFT and therefore serves as a useful surrogate for measuring IFT directly.

Achieving ultra-low IFT on the order of $10^{-3}$ dynes/cm is necessary to mobilize the residual oil saturation in reservoir rocks and to reduce the oil saturation towards zero under typical pressure gradients in oil reservoirs. However, additional conditions must be satisfied for surfactantflooding to be both efficient and practical under reservoir conditions. In order to transport surfactant solutions at low pressure gradients (~1 psi/ft) encountered in typical oil reservoirs, highly viscous phases must be avoided.

3.2.2.4 Experimental procedures. Phase behavior screening experiments were performed to evaluate the phase behavior of surfactant/oil/water mixtures at 1.00 wt% NaCl and 2,000 ppm surfactant solution. 7.00 ml of surfactant solution and 7.00 ml of synthetic oil (decane) were pipetted, as shown in Figure 3.2. The pipettes then were inverted several times to facilitate mixing. Phase behaviour was observed and recorded
over time. If the formation of macroemulsions appeared to inhibit mass transfer, the pipettes sometimes were agitated again.

The phase behavior of the surfactant system was evaluated using the following mostly qualitative criteria:

- How fast the emulsions break after gentle mixing and form a microemulsion in equilibrium with oil and/or brine
- The absence of macroemulsions

![Figure 3.2. Surfactant/Oil/Water Mixtures in test tubes](image)

**3.2.3. Interfacial Tension Measurements.** As mentioned previously, a theoretical relationship between the solubilization ratio and IFT is an easy and accurate way to measure IFT. This research employed a spinning drop tensiometer as a supplement to screen surfactants.

**3.2.3.1 Experimental procedures.** The same 30 surfactants selected for the phase behavior screening test were tested in the IFT test in order to evaluate their ability to reduce the IFT between the synthetic oil and the surfactant solution. All of the surfactant
solutions were prepared with brine (1 wt. %) at 0.20 wt. % concentration, and the test was conducted at 25 °C. Each sample was prepared with 7.00 ml of surfactant solution and 7.00 ml of synthetic oil (decane). The dynamic IFT values between the synthetic oil and surfactant solutions were measured by the spinning drop tensiometer using image acquisition and analysis software, as shown in Figure 3.3.

![Figure 3.3. Spinning Drop Tensiometer Apparatus](image)

The principle behind the spinning drop method used to measure IFT is the formation of a long oval drop of oil in the water under the effect of centrifugal force, gravity, and IFT. Its major axis is L and minor axis is D. When L/D ≥4, the IFT is obtained from:

$$\gamma = 3.42694 \times 10^{-7} (\rho_h - \rho_d) \omega^2 D^3$$  \hspace{1cm} (5)

where \((\rho_h - \rho_d)\) is the density difference between oil and water, \(\omega\) is the angular velocity, and D is the drop minor axis semi diameter.

When L/D <4, Equation 5 is modified as:
\[ \gamma = 2.74156E - 3 \frac{(\rho_h - \rho_d)\omega^2}{C} \]  

(6)

where \( C \) is the correction factor, which is related to L/D and obtained from tables.

3.2.4 Results and Discussion. In this section both Phase behavior and interfacial tension measurements are presented. Two anionic surfactants were selected as potential surfactant test candidates for surfactant-enhanced oil recovery.

3.2.4.1 Phase behavior results. After preparing the samples and keeping the pipettes at room temperature for the solution to reach equilibrium, three different phase behaviors of oil, water and surfactant systems (i.e., Winsor Types I, II and III) were formed, as shown in Figure 3.4. The screening process identified both Alfoterra 145-4S and Alfoterra 145-8S as high-performance EOR surfactants under the required brine/oil conditions. Both surfactants formed stable microemulsions. The microemulsion had low-viscosity properties as well. Figure 3.5 shows the two most promising surfactant candidates.

3.2.4.2 Interfacial tension measurements results. The spinning drop tensiometer apparatus results supported the phase behavior screening outcome by identifying both Alfoterra 145-4S and Alfoterra 145-8S as high-performance EOR surfactants under the required conditions. Figure 3.6 shows the IFT values for the most promising surfactants. Table 3.1 shows the IFT results for all of the screened S/O/W systems.

The best IFT result among the nonionic surfactants was 0.16 mN/m for Tomadol® 45-13 with an HLB of 14.40 and 13.00 moles of EO. The anionic surfactant Alfoterra® 145-8S (8 moles PO) showed an ultra-low IFT of less than 0.001 mN/m.
For a series of nonionic surfactants at a constant salinity (1 wt. %) and constant surfactant concentration (0.2 wt. %), increasing the number of moles of EO was accompanied by a decrease in the IFT value. It was also observed that when the HLB exceeded 14.50, the IFT value increased even if the number of moles of EO increased, as shown in Figures 3.7. through 3.11. The HLB results for nonionic surfactants match Griffin’s method (1954). Griffin’s method indicates that a nonionic surfactant with an HLB in the range of 11 to 14 is a good wetting agent, meaning that these surfactants can significantly reduce surface and interfacial tension and facilitate the spreading of a fluid over a surface.

Figure 3.4. Different Phase Behaviors for O/W/S Systems
Table 3.1. Description and IFT Measurements for Surfactants Investigated

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Chemical Description</th>
<th>HLB</th>
<th>IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodol® 1-5</td>
<td>Linear C11 primary alcohol with 5 moles of ethylene oxide (EO)</td>
<td>11.20</td>
<td>0.241</td>
</tr>
<tr>
<td>Neodol® 1-7</td>
<td>Linear C11 primary alcohol with 7 moles of ethylene oxide (EO)</td>
<td>12.80</td>
<td>0.227</td>
</tr>
<tr>
<td>Neodol® 1-9</td>
<td>Linear C11 primary alcohol with 9 moles of ethylene oxide (EO)</td>
<td>13.90</td>
<td>0.200</td>
</tr>
<tr>
<td>Neodol® 25-7</td>
<td>Linear C12-C15 primary alcohol with 7 moles of EO</td>
<td>12.30</td>
<td>0.532</td>
</tr>
<tr>
<td>Neodol® 25-9</td>
<td>Linear C12-C15 primary alcohol with 9 moles of EO</td>
<td>13.1</td>
<td>0.203</td>
</tr>
<tr>
<td>Neodol® 25-12</td>
<td>Linear C12-C15 primary alcohol with 12 moles of EO</td>
<td>14.40</td>
<td>0.168</td>
</tr>
<tr>
<td>Tomadol® 45-7</td>
<td>Linear C14-C15 primary alcohol with 7 moles of EO</td>
<td>11.60</td>
<td>0.235</td>
</tr>
<tr>
<td>Tomadol® 45-13</td>
<td>Linear C14-C15 primary alcohol with 13 moles of EO</td>
<td>14.40</td>
<td>0.158</td>
</tr>
<tr>
<td>Tergitol® 15-S-3</td>
<td>C12-14 secondary alcohol ethoxylate with 3 moles of EO</td>
<td>8.30</td>
<td>0.438</td>
</tr>
</tbody>
</table>
Table 3.1. Description and IFT Measurements for Surfactants Investigated Cont.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Description</th>
<th>IFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tergitol® 15-S-9</td>
<td>C12-14 secondary alcohol ethoxylate with 9 moles of EO</td>
<td>13.30</td>
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<tr>
<td>Tergitol® 15-S-12</td>
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<td>C12-14 secondary alcohol ethoxylate with 20 moles of EO</td>
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<td>Igepal® CO-530</td>
<td>Ethoxylated nonylphenol with 5 moles of EO</td>
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<tr>
<td>Tergitol® NP-10</td>
<td>Ethoxylated nonylphenol with 10 moles of EO</td>
<td>13.20</td>
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<tr>
<td>Triton® X-405</td>
<td>Ethoxylated octylphenol with 40 moles of EO</td>
<td>17.60</td>
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<tr>
<td>Calamide® CW-100</td>
<td>Modified coconut diethanolamide</td>
<td>0.309</td>
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<tr>
<td>Calamide® CWT</td>
<td>Modified coconut amidesoap superamide</td>
<td>0.313</td>
</tr>
<tr>
<td>Calamide® F</td>
<td>Vegetable oil diethanolamide</td>
<td>0.146</td>
</tr>
</tbody>
</table>
| Calsoft® LAS-99            | Benzensulfonic acid, C10-C16 alkyl derivitives                             | Acid | 0.280  
| Calimulse® EM-99           | Benzensulfonic acid, C10-C16 alkyl derivitives                             | Acid | 0.442  
| Calimulse® PRS             | Benzensulfonic acid, dodecyl branched                                       | Acid | 0.336  
| Ethomeen® C/12             | Bis(2-hydroxyethyl)cocoalkylamines                                         | 12.20| 0.461  
| Ethomeen® S/12             | Bis(2-hydroxyethyl)soyaalkylamines                                         | 10.00| 0.501  
| Aerosol® MA-80             | Sodium dihexyl sulfosuccinate, isopropanol and water                       | Anionic | 1.282  
| Alfoterra® 23              | Branched alcohol propoxylate sulfate with 3 moles of PO                     | Anionic | 0.303  
| Alfoterra® 48              | Branched alcohol propoxylate sulfate with 8 moles of PO                     | Anionic | 0.137  
| Tomadol® 600               | C10-C16 ethoxylated alcohol                                                 | 10.60| 0.403  
| Tomadol® 901               | C9-C11, C10-C16 ethoxylated alcohols                                       | 12.10| 0.578  
| Alfoterra® 145-4S          | Branched alcohol propoxylate sulfate with 4 moles of PO                     |       | 0.032  
| Alfoterra® 123-4S          | Branched alcohol propoxylate sulfate with 4 moles of PO                     |       | 0.989  
| Alfoterra® 145-8S          | Branched alcohol propoxylate sulfate with 8 moles of PO                     |       | 0.001  


Figure 3.6. IFT Values for Best Surfactants at 1% wt Brine and 0.2% wt Surfactant Solution

Figure 3.7. Effect of Number of Moles of (EO) on IFT for Neodol® 1-N Series
Figure 3.8. Effect of Number of Moles of (EO) on IFT for Neodol® 25-N Series

Figure 3.9. Effect of Number of Moles of (EO) on IFT for Tergitol® 15-S-N Series
Figure 3.10. Effect of Number of Moles of (EO) on IFT for Igepal® CO-530, Tergitol® NP-10, and Triton® X-405 Surfactants

Figure 3.11. Effect of Number of Moles of (EO) on IFT for Tomadol® 45-N Series
4. EVALUATION OF WETTABILITY AND OIL RECOVERY USING PREFERRED SURFACTANT CANDIDATES FOR EOR

4.1. INTRODUCTION

In Section 3, more than 30 surfactants were considered as candidates for chemical enhanced oil recovery (EOR) applications. Results from the initial screening process performed in Section 3 revealed Alfoterra 145-4S and Alfoterra 145-8S as the preferred candidates for EOR. Surfactants were able to achieve both ultra-low interfacial tension (IFT) and stable emulsion at dilute concentrations without the addition of an alkaline agent or cosurfactant. In this section, the potential of both surfactants to alter the wettability of and increase the oil recovery from low-permeability sandstone reservoirs will be evaluated.

4.2. EXPERIMENTAL

The experimental section will cover both the materials used and the experimental procedures in this section.

4.2.1. Material. Oil and brine: A sample of heavy oil supplied by Mega West Company came from an oil field in Vernon County, western Missouri. Viscosity was measured to be 28,834 cp at 25 °C. The composition of synthetic brine used in the experiments was 1 wt. % sodium chloride and 99 wt. % deionized water.

Surfactant sample: The surfactant samples selected for this study were acquired from SASOL North America Inc. Alfoterra 145-4S is sodium salt of a monoalkyl C_{14-15} branched propoxy sulphate that contains 34.90 wt. % of active components. The surfactant has a density and viscosity of 1.01 g/ml and 4485 cSt, respectively, at 20°C. Alfoterra 145-8S is also a sodium salt of a monoalkyl C_{14-15} branched propoxy sulphate
that contains 32.40 wt. % of active components. The surfactant has a density and viscosity of 1.03 g/ml and 1600 cSt, respectively, at 20°C.

4.2.2. Experimental Procedures. This section illustrates the procedures for performed experiments. These experiments are intended to test the potential of both Alfoterra 145-4S and Alfoterra 145-8S as candidates for surfactant-enhanced oil recovery.

4.2.2.1 Preparation of synthetic brine. The composition of synthetic brine used for this study consisted of 30 grams of sodium chloride (NaCl) and 2970 grams of deionized water. Both sodium chloride salt and deionized water were mixed together in a beaker, and a magnetic stir bar was used to ensure that all of the salt completely dissolved in the solution. Then, 0.20M sodium hydroxide (NaOH) was added to adjust the brine to a 7.30 pH value.

4.2.2.2 Preparation of the surfactant solutions. The surfactant solutions were initially prepared at a 1.00 wt.% surfactant concentration. 14.30 g of Alfoterra 145-4S and 15.40 g of Alfoterra 145-8S (based on 100% pure surfactant) were put into two separate clean, dry bottles. Brine was then added to total 500 grams for each bottle. To ensure that the surfactants were completely dissolved in the brine, the bottles were placed on a shaker for 24 hours. Once completely dissolved the prepared surfactant solutions then were diluted to different concentrations of 0.01, 0.05, 0.10, 0.20, 0.25 and 0.50 wt%. The solutions were then left to shake for another 24 hours.

4.2.2.3 Preparation of the cores. Berea sandstone core plugs (1.00 cm in diameter and 2.50 cm in length) were cut from a 15.00 cm long Berea core. These core plugs were cleaned with methanol and dried in a heating oven at 60 °C. Both the porosity
and the permeability of the plugs then were measured. The core plugs had a porosity range of 10 to 15% and a permeability of 39.0 md.

4.2.2.4 Preparation of the oil sample. Oil used for imbibition testing was prepared by adding both 5.00 g of Missouri heavy oil and 95.00 g of decane to a beaker. The Missouri heavy oil was filtered by filter paper before being mixed with decane. Filtration was necessary to prevent any possible impurities dissolved in the oil from affecting the oil saturation process for the low-permeability sandstone cores. A magnetic stir bar then was used to ensure that all of the heavy oil was completely dissolved in decane.

4.2.2.5 Preparation of the oil-wet glass. Premium microscope glass slides were purchased from Fisher Scientific, and eight of them were dipped into a container filled with pure Missouri heavy oil to alter the wettability of the glass surface. The glass slides then were removed from the oil and left at room temperature for seven days to dry.

4.2.2.6 Interfacial tension measurements. Selected surfactants were tested for their ability to create ultra-low interfacial properties. Decane was used as an alternative to Missouri heavy oil. 7.00 ml of decane and 7.00 ml of different surfactant solutions were mixed in glass test tubes, which then were shaken for 5 minutes by hand at room temperature to create an oil/water emulsion. Then, the test tubes were placed in a rack for 14 days to allow the solutions to reach equilibrium. After reaching equilibrium, the IFT of oil/brine was measured using the Spinning Drop Tensiometer Model-500 (from Tamco, Inc.).

4.2.2.7 Contact angle measurements. The advanced goniometer, presented in Figure 4.1 was used to measure the contact angle for both surfactants. Different
surfactant concentrations of 0.01, 0.05, 0.10, 0.25, and 0.50 wt. % were used. The contact angle was measured on oil-treated glass slides representing sandstone samples. Each glass slide was used between four and five times. Each time, a droplet of liquid was applied to a different location of the chip under the same conditions. In our measurements, the specimens do not account for adsorption, surface roughness, material heterogeneity or presence of organic matter.

A drop of surfactant solution was deposited on a smooth, oil-treated glass slide. The angle between the solid surface and the tangent to the drop profile “at the drop edge” was measured using contact angle goniometry principles.

![Contact Angle Goniometer Instrument](www.ramehart.com/500.htm, 2012)

**4.2.2.8 Oil recovery through spontaneous imbibition testing.** Surfactants were evaluated for their ability to increase oil recovery from porous sandstone cores using spontaneous imbibition testing at room temperature.
4.2.2.8.1 **Core preparation.** An ink marker was used to mark sandstone cores from 1 to 11. The cores were weighed on a balance, and the exact weight for each sandstone core was recorded. The cores were placed into a 1000 ml Pyrex® flask to undergo a vacuum process because air trapped in the porous sandstone cores needed to be removed in order to ensure good oil recovery results.

4.2.2.8.2 **Core vacuum apparatus set-up.** A vacuum pump, pressure gauge, and 1000 ml Pyrex® flask were all used to create a vacuum apparatus. The Pyrex® flask with sandstone cores was connected to the vacuum system (see Figure 4.2). Nalgene® PVC vacuum tubing (30 ~ 40 cm) was used to connect a bottle of 600 ml of prepared oil with the Pyrex® flask containing core samples. The tubing was closed with a tubing clip. Both the bottle and the tube on the oil side were filled with oil to remove air from that side. The end of this part of the tubing was put into the bottom of the bottle containing 600 ml of oil without any air re-entering the tubing.

![Figure 4.2. Vacuum System for Saturating Core Samples with Oil](image)

**Figure 4.2. Vacuum System for Saturating Core Samples with Oil**
After creating this apparatus, the vacuum pump was turned on. The reading on the pressure gauge quickly decreased from 0 MPa to -100 KPa (~ -1 atm). This low pressure was maintained for 4 hours to remove the air trapped in the sandstone cores. Once all air was removed, the vacuum tubing clip was opened very slowly to allow oil to flow into the Pyrex® flask and be sucked by the sandstone cores because of the reduced pressure in the vacuum system. Once all of the sandstone cores were covered in the flask, the vacuum pump was turned off. After 30 minutes, the Pyrex® flask was disconnected from the vacuum system and allowed to sit overnight. As a result, the sandstone cores were able to suck more oil at regular air pressure.

**4.2.2.8.3 Amott cell preparation.** The lower part of the Amott cells were labeled with the surfactant name on the outside of the container and numbered from 1 to 11. The container and its cover were weighed separately for each cell, and the data were recorded. The sandstone cores holding oil were carefully removed from the flask and placed in the Amott cell container with the same number. The total mass of the container and sandstone core holding oil was weighed. The mass (g) of oil sucked into this core equaled the total mass minus both the container mass and the dry core mass. The initial volume of the oil sucked into a sandstone core was then calculated by dividing the mass by the density of the oil (0.73 g/ml). This amount of oil was the target of oil recovery testing using imbibition.

A small amount of high-vacuum grease (Dow Corning®) was applied to the unpolished top part of the Amott cell surface. The cover and container were then assembled. The joint was slowly turned to ensure that the two parts connected thoroughly so that there would be no leakage after the cell was filled with surfactant solution.
Rubber bands were put on each side of the cells as a second protection to prevent leakage.

Surfactant solution was slowly added up to the 0 mark on the buret of each Amott cell with the corresponding label and number. After that, the total mass of each Amott cell containing a sandstone core and surfactant solution was weighed. The weight of the added surfactant solution was calculated as: Total weight - weight of empty Amott cell – sandstone core holding with oil.

Oil in the sandstone cores was displaced by the surfactant solution through gravity and/or the reduction of capillary force. Because the oil is less dense than the surfactant solution, the displaced (or recovered) oil rose and floated on the top of the buret. The volume of the floating oil was measured by taking the reading on the buret. During the first week, the reading was taken every day. After that, the reading was taken every two to three days until no more oil was recovered. The oil produced by imbibition in the Amott cells can be seen in Figure 4.3.

Figure 4.3. Imbibition of Oil in the Amott Cell
4.2.2.9 **Oil recovery test with both oil-wet and water-wet sand.** The performance of surfactants in enhancing heavy oil recovery from both oil-wet and water-wet sand was compared. Sand was purchased from the US Silica Company in Pacific, MO. Before the sand was used, it was washed with tap water several times until the water ran clear. The sand was then rinsed with distilled water three times before being placed into an oven at 90 °C. There, the sand dried for two days. Finally, the dry sand was separated using sieves, and the sand between 20 and 30 mesh was collected for testing.

Eleven water-wet sand samples were prepared by mixing 10.00 g of clean, dry sand and 1.25 g of synthetic brine. Then, 2.00 g of Missouri heavy oil was added to each sample. These sand-oil mixtures were warmed at 40 °C for 30 minutes to ensure that the heavy oil mixed with the sand thoroughly. 35.00 ml of the 10 surfactant solutions were then added separately to them. Brine was added to one sample to approximately the 40.00 ml mark on the bottle to compare oil recovery with and without surfactants.

In order to compare the performance of surfactants in enhancing heavy oil recovery from oil-wet and water-wet sand, 11 oil-wet sand samples were prepared in a similar fashion as described above, but without the addition of 1.25 g of formation water. Similarly, 35.00 mL of surfactant solutions were added separately to 10 samples, and 35 ml of brine was added to a separate sample as well.

The test tubes were shaken overnight at room temperature and then placed in a rack. The oil recovery from oil-wet and water-wet sand samples was observed.

4.2.3. **Results and Discussion** The results and discussion section will illustrate the effect of different surfactant solutions on the interfacial properties, wettability, sand
cleaning, and oil recovery from sandstone cores. These results will confirm the efficiency of both selected surfactants for surfactant-enhanced oil recovery.

4.2.3.1 Effects of surfactant concentration on interfacial properties. The IFT and the surfactant concentration in the brine-surfactant-oil system were measured and compared.

Alfoterra 14-4S: IFT results (see Table 4.1) for different surfactant solutions are illustrated in Figure 4.4. This experiment demonstrated that increasing the surfactant concentration in the solution to 0.25 wt% reduced the IFT to the ultra-low value of 0.001 mN/m. Increasing the concentration of the surfactant beyond the 0.25 wt% did not produce any significant effect on the IFT value. The phase behavior of the surfactant solutions are presented in Figure 4.5.

Table 4.1. IFT vs. Surfactant Concentration with Different Alfoterra 145-4S Solutions

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>100</th>
<th>250</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>2500</th>
<th>5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>IFT (mN/m)</td>
<td>0.437</td>
<td>0.383</td>
<td>0.3056</td>
<td>0.1929</td>
<td>0.032</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Alfoterra 145-8S: IFT results (see Table 4.2) for the different surfactant solutions are illustrated in Figure 4.6. The experiment demonstrated that increasing the surfactant concentration in the solution to 0.20 wt% reduced the IFT to the ultra-low value of 0.001 mN/m, increasing the concentration of the surfactant beyond the 0.20 wt% did not produce any significant effect on the IFT value. The phase behavior of the surfactant solutions are presented in Figure 4.7.
Table 4.2. IFT vs. Surfactant Concentration with Different Alfoterra 145-8S Solutions

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>100</th>
<th>250</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>2500</th>
<th>5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>IFT (mN/m)</td>
<td>0.744</td>
<td>0.593</td>
<td>0.488</td>
<td>0.312</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

4.2.3.2 Effects of surfactant solutions on wettability. The effects of surfactant concentration in the brine-surfactant-oil system on wettability have been investigated through contact angle measurements.

Alfoterra 145-4S: Contact angles for different surfactant solutions on oil-treated glass chips, with a comparison to the brine contact angle are presented in Figure 4.8. Figure 4.9 and 4.10 displays the results for the left and right contact angles for different surfactant solutions during the measurement process.

Alfoterra 145-8S: Contact angles for different surfactant solutions on oil-treated glass chips, with a comparison to the brine contact angle are presented in Figure 4.11. Figures 4.12 show an idealized example of the contact angle and the spreading of the liquid drop on the solid surface. Figure 4.13 display the results for the left and right contact angles for different surfactant solutions during the measurement process.

All of the surfactant solutions tested on the oil-treated glass resulted in the contact angle being reduced to zero, thus altering the weakly water-wet glass to strongly water-wet. Increasing the surfactant concentration in the surfactant solutions resulted in a reduced amount of time required for the contact angle to reach zero. These measurements were repeated at least three times and produced the same results, keeping in mind that contact angle results have an accuracy of ± 5 degrees.
4.2.3.3 Effects of surfactant solutions on oil recovery from sandstone cores.

The effects of wettability on oil recovery have been investigated through spontaneous imbibition experiments. In this research, tests were conducted with sandstone core plugs. These plugs ranged in porosity from 10 to 15%.

Alfoterra 145-4S: Results of oil recovery from cores through spontaneous imbibition for both the different surfactant solutions and the synthetic brine (see Table 4.3) are shown in Figure 4.14. All surfactant solutions, regardless of the surfactant concentration, showed a net oil recovery of 46% OOIP. These results indicate additional oil recovery of 27% OOIP when compared with recovery using synthetic brine. Increasing the surfactant concentration led to decreasing the required time to achieve maximum oil recovery.

**Table 4.3. Percentage of Oil Recovery vs. Time Using Different Alfoterra 145-4S Solutions**

<table>
<thead>
<tr>
<th>Day</th>
<th>Surfactant concentration in solution (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.50</td>
<td>10 %</td>
</tr>
<tr>
<td>0.75</td>
<td>14 %</td>
</tr>
<tr>
<td>1</td>
<td>18 %</td>
</tr>
<tr>
<td>2</td>
<td>18 %</td>
</tr>
<tr>
<td>3</td>
<td>19 %</td>
</tr>
<tr>
<td>4</td>
<td>19 %</td>
</tr>
<tr>
<td>14</td>
<td>19 %</td>
</tr>
</tbody>
</table>

Alfoterra 145-8S: Results of oil recovery from cores through spontaneous imbibition for both the different surfactant solutions and the synthetic brine (see Table
4.4) are shown in Figure 4.15. All surfactant solutions, regardless of the surfactant concentration, showed a net oil recovery of 47% OOIP. These results indicate additional oil recovery of 28% OOIP when compared with recovery using synthetic brine. Increasing the surfactant concentration led to decreasing the required time to achieve maximum oil recovery.

Table 4.4. Percentage of Oil Recovery vs. Time Using Different Alfoterra 145-8S Solutions

<table>
<thead>
<tr>
<th>Day</th>
<th>Surfactant concentration in solution (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>10 %</td>
</tr>
<tr>
<td>0.75</td>
<td>14 %</td>
</tr>
<tr>
<td>1</td>
<td>18 %</td>
</tr>
<tr>
<td>2</td>
<td>18 %</td>
</tr>
<tr>
<td>3</td>
<td>19 %</td>
</tr>
<tr>
<td>4</td>
<td>19 %</td>
</tr>
<tr>
<td>14</td>
<td>19 %</td>
</tr>
</tbody>
</table>

Results indicate that the major factor influencing oil recovery from tested Berea sandstone cores was the wettability alteration of cores to preferentially water-wet conditions.

4.2.3.4 Effects of surfactant solutions on sand cleaning. The ability of surfactant solutions to both alter the wettability of sand samples and increase oil recovery was investigated.

As shown in Figure 4.16, water-wet sand samples demonstrated oil recovery using synthetic brine; conversely, oil-wet sand samples demonstrated no oil recovery
using the same synthetic brine composition. These results support that wettability is a key factor in oil recovery.

Alfoterra 145-4S: Figure 4.17 shows oil recovery from water-wet sand samples using different surfactant concentrations. Higher recovery was observed when the concentration of surfactants in the solution was increased. These results indicate that reducing the IFT of the brine-oil-sand system increases oil recovery from water-wet sand samples. Figure 4.18 illustrate oil recovery from oil-wet sand samples using different surfactant concentrations. When oil-wet sand was altered to water-wet, oil recovery occurred. Increased oil recovery was observed when the concentration of surfactants in the solution increased. These results indicate that in addition to the effect of wettability alteration on oil recovery, achieving ultra-low IFT resulted in increased oil recovery by eliminating the unfavorable effect of the capillary retaining oil.

Alfoterra 145-8S: Figure 4.19 shows oil recovery from water-wet sand samples using different brine–surfactant concentrations. Higher recovery was observed when the concentration of surfactants in the solution was increased. These results indicate that reducing the IFT of the brine-oil-sand system increased the amount of oil recovered from water-wet sand samples. Figure 4.20 illustrate oil recovery from oil-wet sand samples using different brine-surfactant concentrations. When oil-wet sand was altered to water-wet, oil recovery occurred. Oil recovery increased when the concentration of surfactants in the solution increased. These results indicate that in addition to the effect of wettability alteration on oil recovery, achieving ultra-low IFT resulted in increased oil recovery by eliminating the unfavorable effect of the capillary retaining oil.
Results from sand samples show a combined effect of wettability alteration and IFT reduction on increasing the oil recovery.

4.2.3.5 Summary

- An ultra-low IFT of 0.001mN/m was achieved using both selected surfactants.
- Strong water-wet properties were attained using low concentrations of surfactant solutions.
- Low concentrations of surfactant solutions showed a high ability to increase oil recovery from sandstone cores through spontaneous imbibition.
- Surfactants showed a high ability to recover oil from oil-wet sand samples.
- Alfoterra 145-8S showed better performance using lower surfactant concentrations compared to Alfoterra 145-4S. A surfactant concentration of 0.2 wt% was successful in reaching an ultra-low IFT and maximum recovery from both sandstone cores and sand samples.
Figure 4.4. IFT vs. Surfactant Concentration with Different Alfoterra 145-4S Solutions

Figure 4.5. Phase Behavior of Alfoterra 145-4S/ Decane with Different Surfactant Solutions
Figure 4.6. IFT vs. Surfactant Concentration with Different Alfoterra 145-8S Solutions

Figure 4.7. Phase Behavior of Alfoterra 145-8S/Decane with Different Surfactant Solutions
Figure 4.8. Contact Angle Results for Alfoterra 145-4S Solutions Compared to Brine

Figure 4.9. Left and Right Contact Angles for Synthetic Brine Solution
Figure 4.10. Left and Right Contact Angles at (a) 100 ppm (b) 250 ppm (c) 500 ppm (d) 1000 ppm (e) 2500 ppm (f) 5000 ppm Alfoterra 145-4S Solutions
Figure 4.11. Contact Angle Results for Alfoterra 145-8S Solutions Compared to Brine

Figure 4.12. Idealized Examples of Contact Angle and Spreading of Alfoterra 145-8S Solutions on Oil Treated Glass Chips
Figure 4.13. Left and Right Contact Angles at (a) 100 ppm (b) 250 ppm (c) 500 ppm (d) 1000 ppm (e) 2500 ppm (f) 5000 ppm Alfoterra 145-4S Solutions
Figure 4.14. Percentage of Oil Recovery Using Different Alfoterra 145-4S Solutions

Figure 4.15. Percentage of Oil Recovery Using Different Alfoterra 145-8S Solutions
Figure 4.16. Oil Recovery from Both Oil-Wet and Water-Wet Sand Using Synthetic Brine

Figure 4.17. Oil Recovery from Water Wet Sand at Different Alforterra 145-4S Concentrations
Figure 4.18. Oil Recovery from Oil-Wet Sand at Different Alfoterra 145-4S Concentrations

Figure 4.19. Oil Recovery from Water-Wet Sand at Different Alfoterra 145-8S Concentrations
<table>
<thead>
<tr>
<th>0.01</th>
<th>0.025</th>
<th>0.05</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5 (wt %)</th>
</tr>
</thead>
</table>

Figure 4.20. Oil Recovery from Oil-Wet Sand at Different Alfoterra 145-8S Concentrations
5. CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSION

- Among the 30 surfactants studied, anionic surfactants (Alfoterra 145-4S and Alfoterra 145-8S) were found to be more efficient in lowering the IFT between oil and 1% NaCl brine.

- The wettability of the Berea sandstone surface can be altered from weakly water-wet to strongly water-wet using Alfoterra 145-4S and Alfoterra 145-8S.

- Altering the wettability of Berea sandstone cores to preferentially water-wet conditions is the major factor in increasing oil recovery from cores.

- Incremental oil recovery from oil-wet sand samples through treatments with Alfoterra 145-4S or Alfoterra 145-8S represents the combined effect of wettability alteration and IFT reduction.

- Alfoterra 145-8S showed better performance in increasing oil recovery using lower surfactant concentrations compared to Alfoterra 145-4S.

5.2. RECOMMENDATIONS

- Contact angle measurements for 1% wt brine on oil treated glass or quartz chips, using cationic, anionic and nonionic surfactants with known IFT, followed by a series of core flooding tests would explain the relation between IFT reduction, wettability alteration and oil recovery.

- Analysis using reservoir simulators is needed to check the feasibility of this process in the field.

- Pilot tests could confirm the ability of the surfactants to improve oil recovery at actual operation conditions.


Austad, T., & Milter, J. “Spontaneous imbibition of water into low permeable chalk at different wettabilities using surfactants,” SPE paper 37236 presented at the 1997 SPE Int. Symp. on Oilfield Chemistry, Houston, TX, 18-21 February.


VITA

Omar ElMofty was born September 17th, 1984 in New York City, New York, United States. He received his Bachelors degree in Chemical Engineering from Higher Technological Institute at 10th of Ramadan, Egypt on August 2007. He worked as a Field Production and Operation Engineer with Scimitar Production Egypt LTD in Egypt for two years. He received his M.S. in Petroleum Engineering from Missouri University of Science and Technology in Rolla, Missouri in May 2012.