

SURFACTANT SELECTION FOR ENHANCED OIL RECOVERY BASED ON
SURFACTANT MOLECULAR STRUCTURE IN UNCONVENTIONAL LIQUID
RESERVOIRS

A Thesis

by

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ABSTRACT

Experimental observations and field applications have revealed that surfactants have significant potential to enhance oil recovery in unconventional liquid reservoirs (ULR). The objectives of this study are to determine the effect of surfactant molecular structure on wettability alteration and to evaluate the performance of surfactant formulation in enhanced oil recovery (EOR). A comprehensive workflow is proposed for surfactant selection including surfactant screening, a novel surfactant stability test, and spontaneous imbibition experiments. The mechanism of wettability alteration is investigated for different surfactant structures.

Contact angle (CA) and interfacial tension (IFT) were measured for crude oil and oil-saturated samples from the Eagle Ford and Wolfcamp formations using various surfactant formulations. A workflow to test surfactant stability was proposed to evaluate the duration of wettability alteration. Surfactants having great wettability alteration were utilized to perform Surfactant Assisted Spontaneous Imbibition (SASI) to assess their performance in improving oil recovery. Wettability was measured on a glass slide using different surfactants to further understand the mechanism of wettability alteration on a smooth surface. A systematic analysis was performed to demonstrate the correlation between surfactant performance and molecular structure.

The primary recovery mechanism of surfactant EOR in ULR is highly influenced by wettability alteration, IFT reduction, and the retention time of surfactant on the rock surface. IFT and contact angle measurements were performed with anionic, cationic,

nonionic, and zwitterionic surfactants to evaluate the effectiveness of these surfactants. Results indicate that both hydrophilic head and hydrophobic tail have significant effects on wettability alteration. Surfactants with longer tails could effectively alter the wettability of rock from oil-wet to more water-wet and reduce the IFT to lower range. Surfactant stability tests demonstrate that surfactants with greater stability are more favorable for spontaneous imbibition. The performance of nonionic surfactants is governed by the number of Ethylene Oxide (EO) groups. In this study, nonionic surfactants generally have better performance than ionic surfactant. It is attributed to that nonionic surfactants have higher adsorption density and more stable adsorption layer than ionic surfactants. At reservoir temperature, some nonionic surfactants reach cloud points that obscure CA measurements. The stability test provides a method to assess the wettability of rock using those nonionic surfactants.

The proposed selection method is validated by the results of surfactant screening, stability tests, and SASI experiments. This work provides a more definitive interpretation of the surfactant molecular structure on rock-fluid interactions in ULR.

DEDICATION

To my loving parents, Longmei Chen and Yongsong Chen, for inspiring me and showing the path that brought me here. Thank you for your unconditional love and support.

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All work conducted for this thesis was completed by the student independently.

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NOMENCLATURE

| | |
|--------|-----------------------------|
| bopd | Barrels of oil per day |
| CA | Contact angle |
| CAPB | Cocamidopropyl betaine |
| CT | Computed tomography |
| d | Days |
| DAC | Dimethyl Amine Chloride |
| DW | Distilled water |
| EO | Ethylene oxide |
| EOR | Enhanced oil recovery |
| gpt | Gallon per thousand gallons |
| h | Hours |
| IFT | Interfacial tension |
| IOS | Internal Olefin Sulfonate |
| lbm/ft | Pound per feet |
| mN/m | Millinewton per meter |
| NMR | Nuclear magnetic resonance |
| OOIP | Original oil in place |
| P_c | Capillary pressure |
| POS | Propylene Oxide Sulfate |
| PW | Produced water |

| | |
|---------------|--|
| ppm | Parts per million |
| r | Pore radius |
| SARA | Saturates, Asphaltenes, Resins & Aromatics |
| SASI | Surfactant assisted spontaneous imbibition |
| surf | Surfactant |
| TAC | Trimethyl Amine Chloride |
| TDS | Total dissolved solids |
| ULR | Unconventional Liquid Reservoir |
| USBM | U.S. Bureau of Mines |
| wt% | Weight percent |
| ° | Degrees |
| °F | Fahrenheit degrees |
| θ | Contact angle |
| σ | Interfacial Tension |
| μL | microliter |

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1. INTRODUCTION AND LITERATURE REVIEW

Unconventional liquid reservoirs (ULR) have been attracting the attention of many researchers, service companies, and operators since the early 2000s. The U.S. Energy Information Administration (EIA 2020) estimates that tight oil produced from ULR accounts for more than half of the total U.S. crude oil production. The reservoir rock in ULR is characterized by low porosity and ultra-low permeability. Hence, the recovery factors for shale reservoirs are typically low even though a significant volume of hydrocarbons has already been produced by primary depletion (Zhang, Adel, et al. 2019). Enhanced oil recovery (EOR) techniques including the addition of surfactant into the completion fluid and/or the use of surfactant for EOR along with gas injection are required to achieve a higher oil recovery in ULR.

This section is oriented to overview the prospects for surfactant EOR and its applications to ULR. Fundamentals of surfactant molecular structure are reviewed along with the molecular interactions. Wettability alteration by surfactant adsorption as well as their effects on oil recovery are described. Lastly, the parameters in consideration for surfactant selection are summarized to highlight the complexity of an EOR project design.

1.1. Enhanced Oil Recovery

1.1.1. EOR methods in conventional reservoirs

In conventional reservoirs, the oil recovery processes are categorized into three different stages: primary, secondary, and tertiary (known as EOR) stage. The primary and

secondary recovery techniques depend on the natural energy of the reservoir and the pressure differential between the reservoir and the producing well connected to the surface (Satter and Iqbal 2016). Enhanced oil recovery functions by altering rock wettability and fluid mobility to reduce the residual oil saturation of the reservoir.

EOR methods applied in conventional reservoirs include the five main types listed in **Fig. 1**: thermal recovery, miscible (gas injection), mobility control, chemical injection, and microbial enhanced oil recovery (MEOR) (Alamooti and Malekabadi 2018). Thermal EOR raises the reservoir temperature with the introduction of heat energy into the reservoir. The wettability of the reservoir rock is also shifted, influenced by the temperature (Kovscek 2012). This enhances the possibility of obtaining additional oil recovery during the thermal EOR operations.

Chemical EOR is considered the most promising EOR method due to its high efficiency, economic feasibility, and reasonable cost (Levitt and Pope 2008). The U.S. Department of Energy (2010) estimates that chemical techniques account for about one percent of U.S. EOR production. Chemical EOR in conventional reservoirs involves the use of surfactants, polymers, alkaline, and emulsion. Chemicals are added into the completion fluid to increase the effectiveness of fluid penetration. Polymer flooding is a chemical EOR method that utilizes large molecular size polymers to increase oil recovery. Water soluble polymers decrease the water-oil mobility ratio thereby improving sweep efficiency during water flooding (Al-Shakry et al. 2018).

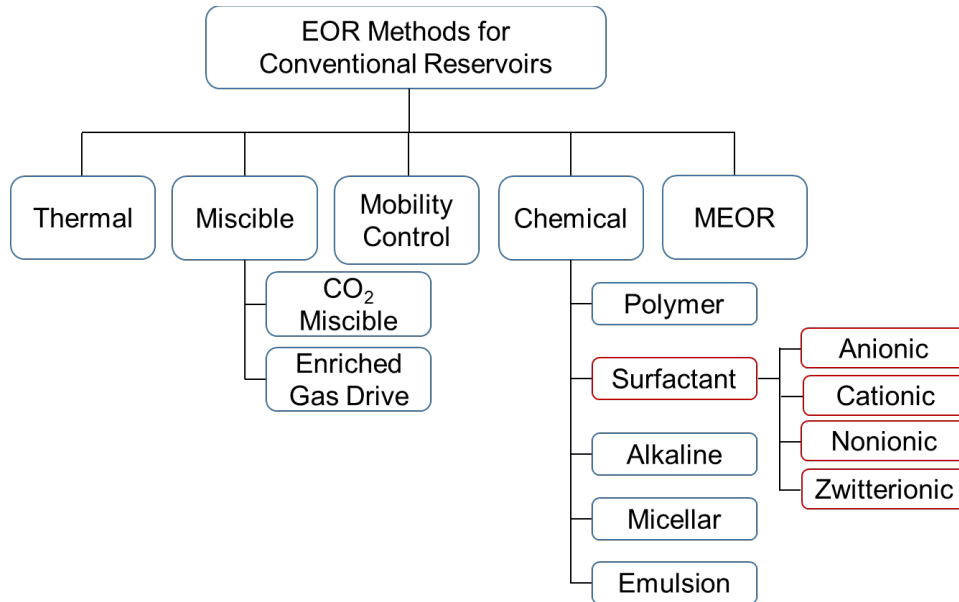


Figure 1. Classification of EOR methods for conventional reservoirs.

1.1.2. EOR methods in unconventional reservoirs

The matrix permeability of ULR is several orders of magnitude lower than conventional reservoirs. This increases the uncertainty on the storage capacity of rock and the possibility of EOR. Effective EOR techniques are essential for recovery from unconventional reservoirs because of the ultra-low permeability and poor efficiency of primary and secondary recovery.

Surfactant, carbon dioxide, natural gas, and low salinity water (LSW) listed in **Table 1** are promising EOR methods in unconventional liquid reservoirs (Alfarge et al. 2017). Gas injection utilizing one of several components such as: carbon dioxide, natural gas, and ethane enriched gas has the potential to recover 30-50% of OOIP from oil-saturated shale cores under miscible conditions (Adel et al. 2018). Incremental oil recovery could be achieved by gas injection through multi-contact miscibility, oil swelling

and molecular diffusion. In the experimental and numerical study with the Eagle Ford formation (Zhang, Saputra, et al. 2019), combination of gas injection with surfactant EOR resulted in further oil recovery increase. This revealed the potential of achieving a higher ultimate oil recovery with the hybrid EOR methods.

Table 1. EOR methods for ULR and the mechanisms.

| EOR Methods for ULR | Functional Mechanisms |
|--|--|
| Chemical Methods <ul style="list-style-type: none"> • Surfactant • Surfactant + Alkaline | <ul style="list-style-type: none"> ▪ Wettability alteration ▪ Interfacial tension reduction |
| Miscible Gas Injection <ul style="list-style-type: none"> • CO₂ • Natural gas • Enriched gas | <ul style="list-style-type: none"> ▪ Multiple contact miscibility ▪ Oil swelling ▪ Diffusion |
| Low Salinity Waterflooding | <ul style="list-style-type: none"> ▪ Clay swelling and shale cracking ▪ Wettability alteration |

In unconventional reservoirs, polymers have their limitations due to the large molecular size and small pore size. Surfactant EOR is a promising technique in ULR, functioning by altering rock surface wettability and reducing oil and water interfacial tension. The alkaline EOR method is based on the reaction between the alkali agent and organic acids to produce in situ surfactant and therefore alter the wettability (Sheng 2011). Surfactants are typically injected into the reservoir along with the synthetic brine. The alkali in the brine affects the effectiveness of surfactant EOR by modifying the adsorption of surfactant molecules.

1.1.3. Surfactant EOR

The effect of surfactants on EOR in unconventional liquid reservoirs has been studied in the previous investigations (Saputra and Schechter 2018, Alhashim et al. 2019, Alvarez et al. 2014). Observations of the laboratory studies on the Bakken, Wolfcamp and Eagle Ford formations indicate that surfactants have the capability of enhancing oil recovery by altering capillary forces and promoting imbibition. However, most of these studies were performed without specific information of the molecular structure of the surfactants tested. Through a systematic surfactant selection process, this study evaluates the performance of various surfactants with their specified molecular structures and choose the best surfactant formulation for optimal performance in field operations. We rely on contact angle and spontaneous imbibition to evaluate the efficacy of selected surfactants.

In general, the surfactant EOR technique is promising to achieve a higher oil recovery from unconventional reservoirs. Developing surfactant EOR technique and designing optimum surfactant formulation requires comprehension of the solubility and adsorption behavior of the surfactant. This study is designed to reveal the potential of surfactant EOR through the surfactant selection process. The workflow is based on improved understanding of the influence of the head group and tail group on contact angle and SASI thereby gaining a deeper understanding the role of surfactant molecular structure in altering wettability and the potential for using this information for EOR project design.

1.2. Molecular Structure of Surfactant

Surfactants with the proper formulation have been recognized to have the capability of altering wettability, reducing IFT, and improving oil recovery in ULR (Alvarez et al. 2017, Zhang et al. 2018). Surfactants have a characteristic molecular structure consisting of a hydrophilic head and a hydrophobic tail, which is known as an amphiphilic structure. This amphiphilic structure is the key to understand the behavior of surfactant in the rock-oil-aqueous systems.

The solution behavior of the surfactant is dominated by its molecular structure (Shinoda 1983, Kon-No and Kitahara 1971). In the rock-oil-aqueous systems, surfactant molecules tend to concentrate at the interface of two phases (oil-water or solid-water), orienting the hydrophilic heads towards the polar phase and the hydrophobic tail towards the non-polar phase. Hydrophobicity of the oil-water interface and the rock surface are both reduced. This enables the surfactant to reduce interfacial tension of oil and water, and alter the wettability through surfactant adsorption on the rock surface (Rosen and Kunjappu 2012).

1.2.1. Electric charge of surfactants

Based on the electric charge of a functional group on the hydrophilic head, surfactants are categorized into four types, including anionic, cationic, nonionic, and zwitterionic. The molecular structure of the different types of surfactants is shown in **Fig. 2**. The head group of anionic surfactant is negatively charged, and the head of cationic surfactant is positively charged. Nonionic surfactant carries no charge, and zwitterionic

surfactant carries both positive and negative charges. The electric charge carried by ionic surfactants could modify the surface charge of solids due to the adsorption of surfactant molecules on the solid surface (Goloub et al. 1996).

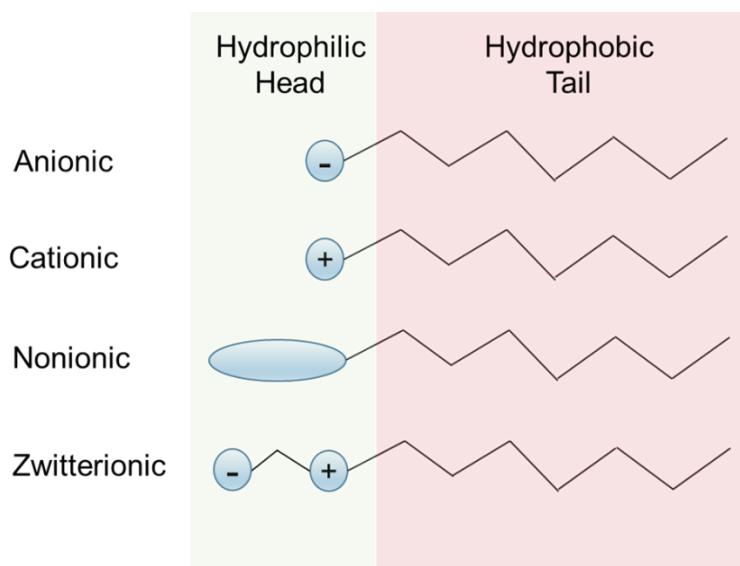


Figure 2. Amphipathic structure of the different types of surfactant head groups.

The electric charge of anionic surfactants is carried by polar groups at the head including sulfate ($-\text{SO}_4^-$), sulfonate ($-\text{SO}_3^-$), phosphate ($-\text{PO}_4^-$), and carboxylates ($-\text{COO}^-$). Carboxylates are the most common surfactants because they could be easily produced from fats and comprise a large majority of common soaps. Alkylbenzene sulfonates and alkyl sulfates are commonly used for wettability alteration of a solid surface due to their high polarity. The positive charge of cationic surfactants is typically carried by nitrogen atoms as a constituent of amine groups. Hydrogen atoms of ammonia (NH_3) are substituted by alkyl or aryl, forming the hydrophobic tail adjacent to the head group. Based on the number of substituents, amines are categorized as a primary amine, secondary amine,

tertiary amine, and quaternary amine. Zwitterionic surfactants, otherwise known as amphoteric surfactants, have both cationic and anionic charged centers. The cationic part is similar to cationic surfactants, based on the nitrogen atom of amines. The anionic groups can be sulfonates or carboxylates as in the betaines. A betaine is any neutral chemical compound consisting of a cationic group such as quaternary ammonium and an anionic group such as carboxylates. Head groups of the nonionic surfactants are mostly composed of ethylene oxide (EO) or ethoxylated alcohols.

1.2.2. Hydrophobicity of surfactants

The hydrophobic tail is a hydrocarbon, fluorocarbon (Dong et al. 2007) or siloxane (a methylated siloxane hydrophobe) (Hill 1997). The number of carbon atoms in the tail typically varies from 5 to 30. Carbon atom numbers out of this range are unfavorable for the amphiphilic structure of surfactant. Molecules with a larger carbon atom number (>40) are mostly oil soluble and have low solubility in aqueous solutions.

The molecular shape of the tail can be straight alkyl chain or containing aromatic groups. Khalil and Saadoon (2015) studied the effect of the presence of benzene ring in the hydrophobic chain. The aromatic group is less hydrophobic than alkyl groups with the same atoms number due to the π system on the ring. The results indicated that the benzene ring reduce the hydrophobic interactions and increase the solubility of surfactants. In the study with alkylbenzene sulfonate (Dick et al. 1971), it was found that the hydrophobic interactions per carbon decrease for branched surfactants compared to straight-chain molecules. As a result, the adsorption of linear alkyl benzene sulfonates is greater than

branched chain surfactants on the solid surface. Lin et al. (1974) investigated the effect of branched chain on the hydrophobicity of the tail. Identification of the actual number of methyl and methylene groups in the chain was proposed based on the micelle and hemimicelle formations. The effective number of $-\text{CH}_2-$ groups of ionic and nonionic surfactants are affected by the total carbon number and the position of the anionic group. Due to the branched structure of the tail, the effective carbon number is approximately 80% of the actual number. Presumably, the hydrophobicity of the tail is less compared to the linear chain that has the same actual carbon number.

Hydrophobicity is used to describe the physical property of a hydrophobic or lipophilic molecule that is repelled from water in the aqueous system (Ben-Naim 2012). The hydrophobicity of a surfactant molecule varies with the surfactant tail length and the polarity of the head group. Hydrophilic-lipophilic balance (HLB) was proposed to evaluate the hydrophilic and hydrophobic groups of surfactants (Davies 1957, Griffin 1954). The Davies method is shown in **Eq. 1**, where n is the number of $-\text{CH}_2-$ groups in the molecule.

$$\text{HLB} = \sum (\text{hydrophilic group numbers}) - n (\text{group number per } \text{CH}_2 \text{ group}) + 7 \quad \dots (1)$$

HLB group number of lipophilic group $-\text{CH}_2-$ is -0.475 , group $-\text{O}-$ is $+1.3$, and derived group $-(\text{CH}_2-\text{CH}_2-\text{O})-$ is $+0.33$, and group $-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O})-$ is -0.15 . The HLB value of a molecule is calculated with the number of hydrophobic/hydrophilic groups and the

group number. This equation indicates that the hydrophobicity of the surfactant molecule increases with increased hydrocarbon chain length in the hydrophobic tail.

1.2.3. Rock-surfactant interactions

The behavior of surfactant molecules in the rock-oil-water system is dominated by the rock-surfactant interactions as well as the oil-water interactions. There are three major types of rock-surfactant interactions including electrostatic interactions, hydrophobic interactions, and hydrogen bonds.

Electrostatic interactions can be attractive or repulsive forces depending on the electric charge of the surfactant head and the surface charge of the rock. Electrostatic interactions dominate the performance of ionic surfactants because they are typically greater in magnitude than hydrophobic interactions and hydrogen bonds. The surface of shale rock can carry both positive and negative charges. The clay minerals are negatively charged due to the isomorphous substitution of silicon atoms by aluminum or magnesium atoms (Perrott 1977). Carbonate minerals including calcite and dolomite carry a positive charge due to preferential hydrolysis of surface calcium and carbonate ions (Somasundaran and Agar 1967). The charge of the minerals is also influenced by the pH of the aqueous system. The function groups of the minerals often contain oxygen or nitrogen, two atoms that can be protonated or deprotonated to become charged. The change in the concentration of hydrogen ions affects the surface charge of the minerals.

Hydrophobic interactions are short-range attractive forces describing the preference of nonpolar hydrocarbon chains to interact with other nonpolar molecular

surfaces and exclude water molecules (Motiejunas and Wade 2006). Hydrophobic interactions of the surfactant tails are affected by their hydrophobicity (Okuzaki and Osada 1994), higher hydrophobicity leading to stronger hydrophobic interactions. Rock surface is induced to hydrophobic by the adsorbed hydrophobic components from the crude oil. Surfactant molecules are attracted to the rock surface due to hydrophobic interactions between the tail groups and rock surface. Kumar and Mandal (2018) synthesized a series of betaine-based zwitterionic surfactants having the chain length of 12, 14, 16, and 18 carbons. It was found the increase in carbon chain length increased the affinity for micelle formation due to increase in the hydrophobicity of the tail. As the chain length increased, the critical micelle concentration (CMC) decreased and IFT between oil and surfactant solution decreases. The larger hydrophobic tail length was found to be more effective in altering the rock surface wettability due to increased hydrophobic interactions.

Hydrogen bonds form between hydrogen atoms of the surfactant hydrocarbon tail and oxygen atoms of a surface mineral group. The adsorption of nonionic surfactant on hydrophilic surface occurs mainly through hydrogen bonding. Nonionic surfactants have the capability of altering the wettability of a hydrophilic surface to more water-wet. Hydrogen bonds increase with increased hydrocarbon chain length. Hydrogen bonds form between oxygen atoms of the surfactant head groups and hydrogen atoms of the water molecules as well. The EO-based nonionic surfactants are water soluble through hydrogen bonds (Takamura and James 2015).

The intensity of rock-surfactant interactions depends on the charge density of the rock/surfactant and the chain length of the surfactant tail. For instance, the increase in

negative charge density of rock surface leads to increase in the attractive forces between the surface and cationic surfactants, and thereby promotes surface adsorption. Alila et al. (2005) investigated the adsorption of four cationic surfactants with different chain length on a solid-liquid surface. The adsorption isotherms of the surfactants tested were measured using a depletion method. The amount of adsorbed surfactant was calculated with the initial surfactant concentrations and the amount of free surfactant in the supernatant determined by potentiometric titration. It was observed that when the chain length increased from 12 to 18 carbon atoms, the hydrophobic interactions between surfactant molecules increased. Thereby the adsorption density increased and the surface charge was more positive. This literature suggested that the correlation of adsorption density with the chain length was associated with a progressive transition from monolayer to bilayer aggregates. The hydrophobic interactions of C_{18} were sufficient to counterbalance the electrostatic repulsive forces and bilayer surfactants formed, In contrast, the hydrophobic interactions of C_{12} are not sufficient, and only monolayer was supposed to form.

1.2.4. Cloud point of nonionic surfactant

Nonionic surfactant carries no charge, thus electrostatic interactions between the surfactant molecules and the rock surfaces are negligible. EO groups function as a hydrophilic part of the nonionic surfactant. The HLB value is a measure of the EO content in nonionic surfactants. An HLB value is equal to the molecular weight percent of the hydrophilic group divided by 5 using the Griffin method. Hence, the HLB value of one nonionic surfactant molecule is proportional to the EO content. The hydrophobicity of

nonionic surfactants decreases with increased EO number in the hydrophilic head. As EO number increases, hydrophobic interactions of the surfactant decreases and hydrogen bonds increases. Hence, the solubility of nonionic surfactant increases with increased EO number. Hydrogen bonds decrease with increasing temperature, and therefore the solubility of nonionic surfactants decreases with the increased temperature.

A critical feature of nonionic surfactants, in contrast to other types of surfactants, is that their solubility decreases significantly with increasing temperature (Lindman et al. 2016). The surfactant solution starts to scatter light strongly in a well-defined range of temperature on heating. The turbidity of the solution increases sharply when the temperature reaches the cloud point of the surfactant, which obscures the measurement of CA and IFT. Cloud point is a crucial parameter for the evaluation of nonionic surfactants (Mukherjee et al. 2011) and should be determined before surfactant assessment. Cloud points of nonionic surfactants are dominated by the average number of EO groups in the hydrophilic head. Adsorption of ethoxylated nonionic surfactants on carbonate minerals increases with increasing temperature (Jian et al. 2016). At high temperature in the reservoir, nonionic surfactants could effectively alter the rock wettability to water-wet through dense adsorption of surfactant molecules. Nonionic surfactants with high cloud points are promising candidates for EOR projects.

Briefly, the behavior of surfactants in the rock-oil-aqueous system is dominated by the rock-surfactant interactions which rely on the molecular structure of surfactants. The electric charge and hydrophobicity are essential properties of the surfactant. Different

charge and hydrophobicity of the surfactants will lead to different surfactant performance in wettability alteration and oil recovery process.

1.3. Effect of Surfactant on Wettability Alteration

1.3.1. Wettability of rock surface

Wettability is defined as the affinity of an immiscible fluid for a specific solid in the existence of other immiscible fluids (Craig 1971). Wettability can be measured by the Amott-Harvey index, U.S. Bureau of Mines (USBM), nuclear magnetic resonance (NMR) and contact angle methods. The Amott-Harvey Index method is based on spontaneous imbibition, involving the measurement of the amount of fluids imbibed by a rock sample. The USBM method is similar but takes into account intermediate-wet states. The NMR is a qualitative indication of fluid affinity, measuring the volume of matrix fluid with the relaxation of hydrogen atoms.

The contact angle is a quantitative measure of the wettability, as well as the Amott-Harvey and USBM methods (Thyne 2015). The contact angle is defined by the tangent to the oil-water interface at the intersection point with the flat and smooth rock. In the rock-oil-water system, the rock is treated as water-wet when the CA between water and solid goes from 0° to 75° , intermediated-wet from 75° to 105° , and oil-wet from 105° to 180° (Anderson 1986).

The shape of liquid droplets in a multi-phase system is determined by interfacial tension or surface tension. A droplet of oil in water is pulled into a spherical shape by the imbalance of cohesive forces on the surface layer. When a fluid system contains

surfactant, the surfactant may partition into the oil phase from the aqueous phase (Wade et al. 1978). Low interfacial tensions occur when the surfactant molecules reduce differential forces between sides of the interface. The CA of an oil droplet on a solid surface in water is given by the Young equation, which is presented in **Eq. 2**:

$$\cos \theta_Y = \frac{\sigma_{so} - \sigma_{sw}}{\sigma_{ow}} \quad \dots (2)$$

where, θ_Y is the Young CA, σ_{so} is the surface tension of the solid and oil, σ_{sw} is the surface tension of the solid and water, and σ_{ow} is the IFT of oil and water. The correlation between surface tension and contact angle is illustrated in **Fig. 3**. When the surface tension of the solid and oil is less than the surface tension of solid and water, the solid surface is oil-wet. Once σ_{so} is altered to be greater than σ_{sw} by surfactant, the rock surface is altered to be water-wet.

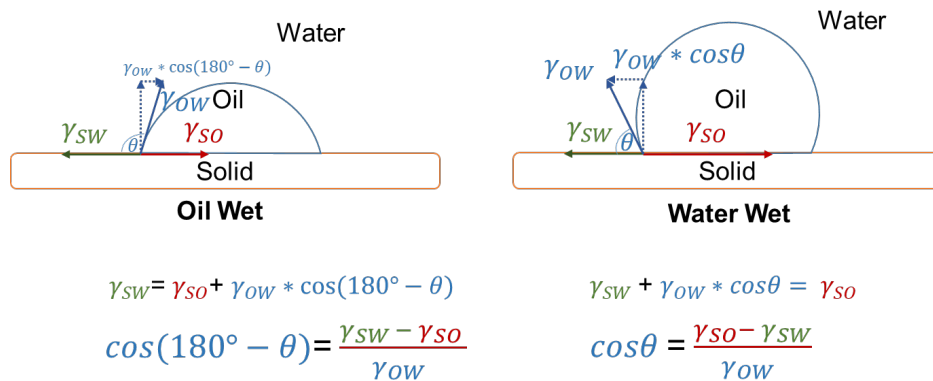


Figure 3. Correlation of surface tension and contact angle in a rock-oil-water system. Young equation is explained with the shape of oil droplet in contact with solid surface.

Wettability is one of the significant factors that influence oil recovery from reservoirs (Donaldson et al. 1969). Most of the reservoir rock initially has a high affinity to water. In the conventional reservoirs, surfaces of the reservoir rock are induced to oil-wet by crude oil, with the hydrophobic components in the oil adsorbed on the rock surface (Morrow et al. 1986). Zhou et al. (1996) investigated the interrelationship of wettability, aging time, and oil recovery with Berea Sandstone cores. Based on the Amott wettability index results, water-wetness of the core decreased as aging time increased and rate of spontaneous imbibition was sensitive to wettability. Graue et al. (2002) performed a systematic aging study on chalks. Core plugs were aged at high temperature with crude oil for different aging periods. A consistent wettability change from strongly water-wet to intermediate-wet with increased aging time was observed. Imbibition rate and final oil saturation decreased with increasing aging time. As aging proceeds, presumable polar molecules adsorb from the crude oil onto the rock surface rendering the surface more oil wet. Different crude oil led to different wettability of the chalk in the experiments. The crude oil containing a higher fraction of heavy components was more efficient in altering the wettability. In the unconventional plays, the hydrocarbon bearing source rock functions as the reservoir rock. Hydrocarbons formed in the tight rock modified the surface to oil-wet. In experimental work, it is necessary to achieve an original oil-wet condition through an aging process. The effect of aging process on unconventional cores are studied in this thesis and will be further investigated in future work.

1.3.2. Wettability alteration with surfactant

Different interpretations have been proposed for the mechanism of wettability alteration with surfactants (Hou et al. 2015, Standnes and Austad 2000). The adsorption of surfactants on rock surfaces is recognized as the key driver (Ataman et al. 2016). The surfactant molecules adsorb on the rock surface in the form of the layer due to rock-surfactant interactions. The wettability alteration on the rock surface depends on the volume of adsorbed surfactant molecules (Das et al. 2018) and also the surfactant adsorption mechanism (Somasundaran and Zhang 2006). Wettability of rock can be altered to more hydrophilic or hydrophobic depending on the orientation of the adsorbed surfactant molecules (Guo et al. 2018).

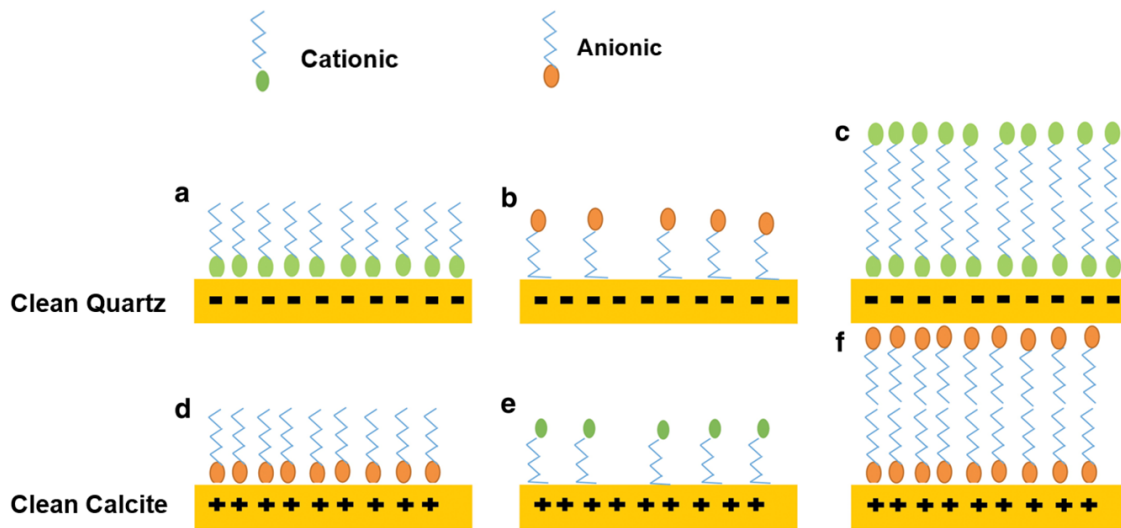


Figure 4. Schematic diagram of adsorption mechanism of (a) cationic surfactant on clean quartz, (b) anionic surfactant on quartz, (c) cationic surfactant on quartz (double layer formation), d) anionic surfactant on calcite, e) cationic surfactant on calcite, and f) anionic surfactant on calcite (reprinted from Zhou et al. (2016)).

The model from Zhou et al. (2016) describing the adsorption layer of surfactant molecules on clean quartz and calcite is illustrated in **Fig. 4**. The cationic surfactant molecules have strong electrostatic attractions between their positively charged head groups and the negatively charged quartz surface. This results in strong adsorption of the head groups on the quartz surface. This type of adsorption mechanism leads to the hydrophobic tail orienting to the aqueous phase at low surfactant concentration and alters the surface more oil-wet. As the adsorption density of cationic surfactant increases at higher concentrations, the surface is altered to water-wet due to the formation of a double layer. The double layer formation develops as the hydrophobic interactions of the tail increase and the hydrophilic head groups orient towards the aqueous phase. On the positively charged calcite surface, there are repulsive forces between the head groups and the surface. Cationic surfactant adsorbs through weak hydrophobic interactions, altering the surface to slightly more hydrophilic. The situation is completely opposite for anionic surfactants where the negatively charged head groups are attracted by positively charge calcite surface while repelled by negatively charge quartz. The adsorption of nonionic surfactant is due to hydrophobic interactions and hydrogen bonds. This is a simplified model characterizing the adsorption of ionic surfactants on electric charged minerals. It is beneficial for understanding the complicated wettability alteration on shale rock using various surfactants studied in this work.

The ion-pair formation mechanism was also proposed for the wettability alteration with surfactant. It was observed that cationic surfactants imbibed into oil-wet carbonate cores and improved oil recovery (Strand et al. 2003). The saturated chalk cores were

immersed into the cationic surfactant dodecyltrimethyl ammonium bromide ($C_{12}TAB$) solutions. The ultimate oil recovery with 1.0 wt% cationic surfactant and 1.0 wt% salinity was as high as 80% after imbibition for 80 days. Sulfate in the fluid was observed to alter the wettability of calcite, dolomite, and magnesite to more water-wet and promote the imbibition as well. This mechanism illustrated in **Fig. 5** suggests that the positively charged heads of cationic surfactants interact with the negatively charged compounds, mainly carboxylates, in the crude oil (Austad and Standnes 2003). The sulfate in the aqueous system modified the surface charge so that the cationic surfactant could remove strongly-adsorbed carboxylic compounds. The oil molecules desorb from the rock surface due to the ion-pairing with the surfactant molecules, and thus the oil-wet rock surface returns to water-wet.

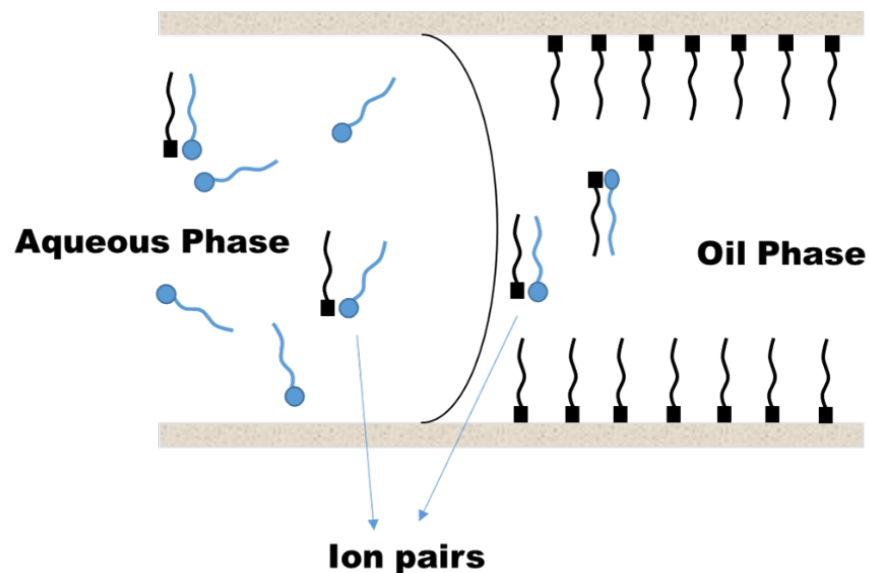


Figure 5. Schematic of wettability alteration by ion pairs (reprinted from Standnes (2001)). Surfactant forms ion pairs with oil molecules and results in oil repulsion.

Wettability alteration on different types of solid surfaces with various surfactant additives was investigated in many publications. Zdziennicka et al. (2009) evaluated the wettability of acid-cleaned quartz with nonionic, anionic, and cationic surfactants and its correlation with the surface free energy of quartz. The system was composed of quartz, air, and aqueous solution containing surfactants. The surface free energy consists of two components, surface tension and work of adhesion, describing the potential of surfactant molecules to adsorb on the quartz-water interface. The shape of contact angle vs. concentration curves for nonionic and anionic surfactants was similar to those of surface tension versus concentration. Contact angle and surface tension decreased with increased surfactant concentration. The change of contact angle vs. concentration in the case of cationic surfactants were different with anionic and nonionic surfactants. Contact angle increased with increased concentration at low cationic surfactant concentration. There was a maximum contact angle corresponding to a critical concentration, above which contact angle decreased with the increased surfactant concentration. Based on the surface free energy calculation, the cationic surfactant was more possible to adsorb on the quartz-water surface compared to anionic and nonionic surfactants. The correlation between surface tension and adhesion work was complicated for anionic surfactant. This indicated that double layer of cationic surfactant was formed at the quartz-water interface.

Zhang et al. (2006) assessed the wettability of the crude oil on calcite plate by measuring the water advancing contact angle. Clean calcite plate was preprocessed with sodium chloride brine, and aged in the crude oil for 24-80h. Initial state of the oil-brine-calcite system was strongly oil-wet. Wettability of the calcite was altered to intermediate-

wet or water-wet by addition of anionic surfactant. It also observed that the adsorption of anionic surfactant on calcite was significantly reduced by the presence of sodium carbonate. This was consistent with the contact angle measurements that the surfactant led to less wettability alteration with sodium carbonate in the brine. This study confirmed that surfactants had the ability to alter the wettability of carbonate minerals through adsorption of surfactant molecules, and the adsorption density was influenced by ions in the aqueous phase.

Ma et al. (2013) investigated the adsorption volume of cationic surfactant and anionic surfactant on different minerals. Residual surfactant concentration of surfactant on the surface was determined by potentiometric titration. The adsorption of the cationic surfactant on synthetic calcite was negligible compared with the anionic surfactant. In contrast, high adsorption of cationic surfactant and negligible adsorption of anionic surfactant on silica were observed. Both the cationic and anionic surfactant could adsorb on the surface of kaolin, one typical clay mineral. The electric charge on this mineral surface depends on pH, and an increase in pH reduced the adsorption of the anionic surfactant. Adsorption of the cationic and anionic surfactant was also measured on natural carbonates including dolomite and calcite. The adsorption volume of the cationic surfactants depended on the silicon composition in the carbonate samples. Only when the silicon composition was low, the cationic surfactant had a significantly lower adsorption than the anionic surfactant.

In order to verify the effect of quartz and clay minerals on the adsorption of cationic surfactant, one surfactant was studied on its adsorption on natural carbonate

minerals (Cui et al. 2014). The surfactant (ethoxylated amine) is a nonionic surfactant at high pH, however, switches to cationic at low pH and become soluble with high salinity brine. The adsorption of this surfactant on calcite was low at low pH conditions. When the silica or clay content in the carbonate formation increased, the surfactant adsorption increased significantly. It was observed that the adsorption of this surfactant decreased with increased cations due to the competition for the negatively charged silica sites.

Kathel and Mohanty (2013) studied the wettability alteration of initially intermediate-wet, tight, fractured sandstone reservoirs using different surfactants. Eight anionic surfactants (alkyl ether sulfates and internal olefin sulfonates) and three nonionic surfactants were tested. The aqueous system was a mixture of surfactant and brine containing 13.2% TDS. In the contact angle measurements, anionic surfactants a large number (>20) of ethoxy groups altered the rock surface to water-wet at the concentration of 0.10 wt%. Ultimate oil recovery as high as 68% of OOIP was obtained in the spontaneous imbibition experiments performed on the tight oil-wet/intermediate-wet sandstone reservoir cores. Anionic surfactant with 27 EO and thirteen carbon atoms in the tail possessed the best performance. Recovery factors in the diluted formation brine (TDS 6.6%) were higher than those in the original formation brine. This work suggested that the main recovery mechanism was the capillary-pressure-gradient driven counter-current imbibition due to wettability alteration.

Most of the studies presented previously were on the wettability alteration in conventional reservoirs. Surfactants were also confirmed to have the capability of altering wettability in unconventional reservoirs. Wang et al. (2012) altered the wettability of the

Bakken shale cores from initially oil-wet to water-wet using four surfactant formulations: dimethyl amine oxide, ethoxylated alcohol, internal olefin sulfonate, and linear olefin sulfonate. The surfactant consistently imbibed to recover significantly more oil than brine alone. A maximum EOR values, 25% OOIP, was achieved through the spontaneous imbibition experiments. It was observed that the addition of 0.2% alkaline provided higher oil recovery than 0.1% alkaline. This study suggests that surfactants, added into brine or produced water, have the potential to alter wettability and promote imbibition in unconventional reservoirs.

1.3.3. Driving forces for oil recovery

Capillary forces provide the dominant driving force for spontaneous imbibition in unconventional reservoir systems. The very small pore throat radii in ULR naturally would result in high capillary forces. If the imbibing fluid can be properly designed, then the rate and recovery of a surfactant EOR huff n' puff could presumably be optimized. The Young-Laplace equation (**Eq. 3**) relates capillary pressure (P_c) to IFT (σ), contact angle (θ), and pore radius (r).

$$P_c = \frac{2\sigma \cos\theta}{r} \quad \dots (3)$$

Surfactant additives could modify the value of capillary forces by altering the IFT of oil-water and wettability of the rock and consequently improving oil recovery. It must

be recognized that the addition of surfactant results in lowered IFT which would reduce the capillary driving force. However, alteration of the CA from an oil-wet to the water-wet state would counterbalance the reduction in IFT. There is some credibility to the idea that lowering the IFT would also result in improvement of relative permeability which would also counterbalance the effect of lowered capillary forces.

Alvarez et al. (2017) constructed the capillary pressure curve from history matching of the laboratory results. Capillary pressure curve endpoints were calculated from the measured IFT and CA values. A history match method was used to build the capillary pressure profile throughout the saturation change. Higher positive capillary pressures were indicated with additive cationic surfactant. The intersection point at the capillary pressure equal to zero for the surfactant was further to the right compared with the water curve indicating a reduction in the residual oil saturation. This difference was attributed to be the effect of wettability alteration. Spontaneous imbibition ceased when the driving capillary force is equal to zero. The capillary pressure curves were generated with initial water saturation, boundary condition, and the final recovery factors. The surfactant that resulted in greater wettability alteration had higher capillary pressure.

Besides capillary forces, osmotic pressure was considered to have the capability to enhancing oil recovery from fracture shale reservoirs. Fakcharoenphol et al. (2014) suggested that the fine-grained shale could function as a semi-permeable membrane. Low and high salinity experiments were performed using a core from the Bakken formation. The core was first submerged in high salinity solution (TDS 28.2%), and only a few oil droplets were produced. The core was then replaced into another cell containing 2% TDS

KCl brine. Significantly more oil drops formed on the core surface, indicating osmotic forces caused flow of water into the pore space. This experimental study proposed that the osmotic pressure caused by salinity difference could promote counter-current flow of oil and improve oil recovery.

In summary, wettability alteration of solid surface is mainly due to the adsorption of surfactant molecules. It was confirmed in experimental study that surfactant could adsorb on the surface of quartz, calcite, natural carbonates, and clay minerals. The adsorption volume depends on the surfactant type and the mineralogy. Various surfactant formulations were verified to alter the wettability of fractured sandstone, carbonate, and shale reservoirs, and promote imbibition recovery by increased capillary pressure as a result of wettability alteration.

1.4. Parameters of Surfactants Selection

1.4.1. Formulation of the surfactant

The effects of the hydrophilic head and hydrophobic tail on wettability alteration are essential in the surfactant selection. The electric charge on the head dominates the type and intensity of electrostatic interactions. The polarity of the head group affects the solubility behavior of the surfactant. Hydrophobicity of the tail depends on the number of carbon atoms and the structure (benzene ring or branched tail). The total polarity of the surfactant molecule is a counterbalance of the head group hydrophilicity and the tail group hydrophobicity. Hence, in the design of surfactant formulation, a long carbon chain is

always adjacent to a high polarity head group. For instance, if the head of a nonionic surfactant is composed of 30 or more EO groups, the tail is likely to be octylphenol or nonylphenol with a large carbon number.

Wang et al. (2019) proposed a design of extended surfactant formulation for an ultrahigh salinity oil field based on the hydrophilic lipophilic deviation (HLD) approach. The concept of HLD is expressed by **Eq. 4**, where S is the brine salinity, EACN is the equivalent alkane carbon number of the oil, K is the slope of salinity as a function of alkane carbon number (ACN), α_T is the temperature coefficient, ΔT is the different between the formulation temperature and the reference temperature, C_c is a characteristic parameter of surfactant, and $f(A)$ is a function of alcohol type and concentration. Various surfactants were screened with a micro-emulsion study and an optimum formulation was proposed for the high salinity reservoir EOR. The tertiary recovery was 67% in the sand pack flooding experiments at reservoir conditions.

$$\text{HLD} = \ln(S) - K \times \text{EACN} - \alpha_T \times \Delta T + C_c - f(A) \quad \dots (4)$$

The HLB and HLD values are proper methods to predict the behavior of surfactant. The HLD, especially, is a measure of all the parameters that influence the effectiveness of the surfactant. The correlation between the wettability, oil recovery, and the HLB/HLD value has yet to be revealed. This will provide guidance for the surfactant EOR design in future work.

1.4.2. Surfactant concentration

The concentration of surfactant is an important parameter for its EOR effectiveness. A sharp exponential IFT decline was observed with the increase of surfactant concentration until an inflection point referred to as critical micelle concentration (CMC) (Karnanda et al. 2013). Ahmadi and Shadizadeh (2013) performed an experimental study on the adsorption of a nonionic surfactant on carbonate minerals. Adsorption of surfactant on the rock was determined by batch equilibrium tests on crushed core in a centrifuge tube. The surfactant concentrations in aqueous phase was determined by the conductivity method. Conductivity of solutions was a function of the surfactant concentration. Volume of surfactant adsorbed was calculated with the difference between surfactant concentrations before and after adsorption. The results shown in **Fig. 6** indicated that the magnitude of adsorption density in the surface of carbonate rocks increases as the surfactant concentration increases.

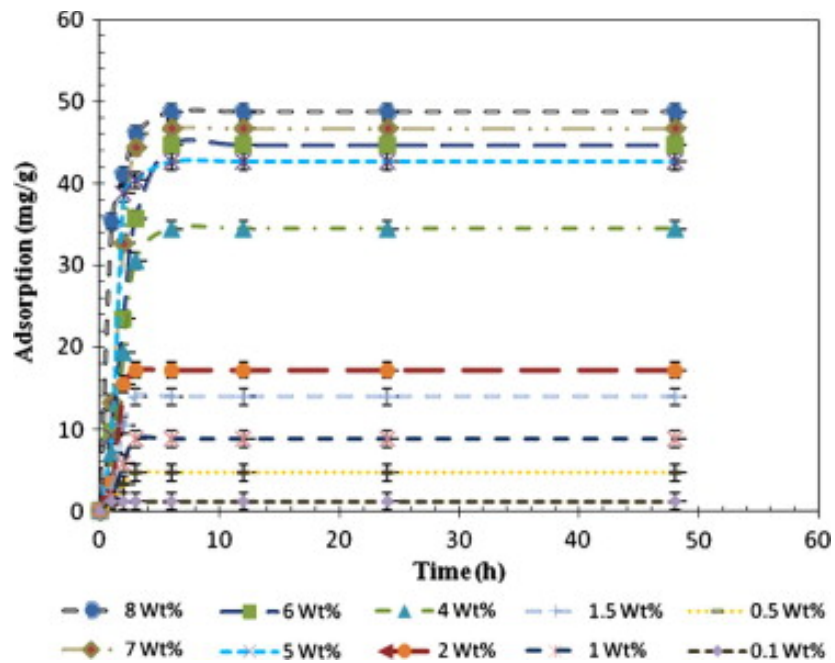


Figure 6. Adsorption of surfactant vs. Time for different surfactant concentration (reprinted from Ahmadi and Shadizadeh (2013)). Adsorption of surfactant increased with increasing surfactant concentration.

As surfactant concentration increases, the mechanism of surfactant adsorption changes. At low surfactant concentration, the adsorption of ionic surfactants is dominated by the electric charge and the adsorption of nonionic surfactants depends on the hydrogen bonds. As concentration increases, lateral interactions or hydrophobic interactions will appear between the adsorbed surfactant molecules and drive surfactant molecules to aggregate (Belhaj et al. 2020). A high concentration is beneficial for the performance of surfactants for EOR. However, the cost of surfactant increases which implies there must be an optimum surfactant concentration to achieve the necessary wettability alteration for improved recovery.

1.4.3. Brine salinity

The chemistry of brine can also alter the wettability of the rock surface with the ion-mineral interactions. Rezaei Gomari and Hamouda (2006) investigated the effect of water composition and pH on the wettability of calcite surfaces by measuring contact angle of a calcite/n-decane system. The results indicated that sodium ions have a negligible effect, however, the presence of magnesium and sulfate ions converted the calcite surface to more water-wet with a pH of 7. Above a pH of 7, the sulfate ions altered the surface to slightly more oil-wet whereas the magnesium increased the water-wetness.

Ions in the brine influence the electrostatic and hydrophobic interactions of surfactant molecules. Ions also affect the solubility of surfactants. The salinity of brine modifies the surfactant effectiveness by enhancing or reducing the adsorption of surfactant. Some investigators (ShamsiJazeyi et al. 2014, Bera et al. 2013) report increased adsorption with increasing salinity while others (Cui et al. 2014, Yekeen et al. 2019) report reduced adsorption is observed with increasing salinity. Alkali-surfactant flooding, as an EOR method, could lead to improved recovery by reducing the interfacial tension of oil and water, and entrapping oil droplets (Bryan and Kantzas 2007). Low salinity water (2-4 wt%) huff n' puff improves oil production from tight oil reservoirs by altering wettability thus modifying capillary pressure. Also, surfactant plus low salinity aqueous phase huff n' puff could further enhance oil recovery due to the synergistic effect of wettability alteration by surfactants and additional IFT reduction (Teklu et al. 2018). However, it was also observed high salinity water (up to 30 wt%) leads to a low oil

recovery efficiency. Thus, the salinity level also has to be optimized for selection of surfactant for EOR.

1.4.4. Rock mineralogy

The mineralogy of the reservoir rock affects the adsorption of surfactant molecules. Due to electrostatic interactions, cationic surfactants tend to adsorb on the silica sites of the rock surface and anionic surfactants tend to adsorb on the carbonate sites. Saxena et al. (2019) carried out an adsorption analysis of one anionic surfactant on sandstone, carbonate and bentonite. The adsorption profiles obtained by UV spectroscopy and conductivity was analyzed by fitting with adsorption isotherms such as Langmuir, Freundlich, Temkin, and Redlich-Peterson models. The results demonstrated that the anionic surfactant showed the least adsorption on sandstone rock surface. Bentonite, a highly porous material, adsorbed the highest volume of surfactant.

Mehana et al. (2018) investigated the effect of mineralogy on slick water spontaneous imbibition in shale. It was found that the carbonate/clay content ratio had a significant effect on the imbibed volume, although the correlation between carbonate/clay ratio and imbibed volume was nonlinear. The imbibed volume was maximized at a ratio of 1.5, where the carbonate is 50% more than the clay. This study is beneficial for understanding the difference in ultimate oil recovery caused by rock mineralogy. In general, cationic surfactants have better performance in high carbonate content reservoirs such as in chalk. The repulsive forces ensure that only monolayer can form with hydrophilic head groups orienting towards the aqueous phase. The rock surface is always

altered to more water-wet and oil recovery would be increase. Anionic surfactants, in contrast, would have better performance in cores with high clay content compared to carbonate formations. The carbonate/clay ratio has no significant effect on the behavior of nonionic surfactants. Molecular size of nonionic surfactant is typically large, thereby pore size or porosity of the reservoir is a key parameter for the oil recovery with nonionic surfactants.

1.4.5. Oil composition

Hundreds of organic compounds are contained in crude oil. These complex molecules can be generally summarized into two categories, polar and nonpolar compounds. The nonpolar compounds are composed of carbon and hydrogen. The polar compounds contain nitrogen, sulfur, and oxygen besides hydrocarbon. Oil polarity has an effect on the solution behavior of oil in aqueous system, hence affects the oil-water IFT and wettability of the crude oil on the solid surface.

Tang and Morrow (1997) studied the effect of crude oil composition on wettability and waterflood recovery. Light components were removed by evacuation of the crude oil and then hexane was added to modify the oil composition. Reduction in average molecular weight of the crude oil led to greater water-wetness and changed the imbibition rate. Base on the imbibition recovery, the wettability was altered to less water-wet by the addition of hexane or heptane. It is consistent with the notion that nonpolar molecules increased the hydrophobicity of the rock and alter the surface to more oil-wet.

1.4.6. Effect of temperature

The effectiveness of surfactant is influenced by temperature, especially for nonionic surfactants. As temperature increases, the intensity of hydrogen bonds decrease, thus the solubility of nonionic surfactants decreases significantly. At higher temperature, intensity of hydrophobic interactions among surfactant molecules would increase. In addition, the oil viscosity decreases with increasing temperature. The temperature effects on surfactant imbibition in carbonate cores was studied by Gupta and Mohanty (2007). Contact angle was measured on calcite plates with 28.2 API oil. Anionic and nonionic surfactant were examined and surfactants were mixed with brine at various salinity. Both surfactants altered the oil-wet calcite plates to water-wet. It was observed that the final contact angle decreases with the increase in temperature for all the surfactants. The oil recovery in spontaneous imbibition was consistent with the contact angle results. High recoveries (above 60% OOIP) were achieved for surfactants at the concentration of 0.1 wt% in the tight carbonate cores.

In this work, the correlation between surfactant structure regard to wettability alteration and production enhancement was investigated in unconventional shale cores. The results from experiments demonstrate that nonionic surfactants with larger EO numbers have higher cloud points and but yet better effectiveness for EOR. Compared with ionic surfactants, the nonionic surfactants have better performance on enhanced oil recovery in shale reservoirs. The effects of surfactant concentration and brine salinity on wettability are discussed to comprehensively analyze the parameters that should be

considered in the design of EOR projects based on molecular structure of the surfactant molecule.

1.5. Field Cases of Surfactant EOR

Surfactant EOR has been applied in conventional reservoirs since the late 1990s and success was achieved in several pilot trials. As unconventional shale oil resources are becoming increasingly important hydrocarbon supplies, enhancing oil recovery from ULR using surfactants is one of the obvious choices. A few cases were reported over the last few years. Fields cases with conventional reservoirs and unconventional formations are analyzed to describe the prospect of surfactant EOR.

1.5.1. The Yates Field in Texas

The Yates Field in the Permian Basin of west Texas is a massive naturally fractured, dolomite reservoir. It is a conventional reservoir with average matrix porosity and permeability of 15% and 100md respectively. Chen et al. (2000) investigated surfactant imbibition with Yates rock and pilot tests at in the Yates reservoir. The density of the Yates dead crude oil was 0.874 g/cc. Initial wettability of the Yates core was measured to be oil-wet using the USBM index method. Three imbibition fluids were used including the synthetic brine, 0.35% nonionic ethoxyl alcohol (C₉-C₁₁ with 8EO), and 0.35% anionic ethoxy sulfate (C₁₂ + 3EO + -SO₄⁻) solutions mixed with synthetic brine. It was observed in wettability evaluation that both surfactants altered Yates rock surfaces from strongly oil-wet to moderately oil-wet. In the single-well and multi-well huff-n-puff

performed with dilute surfactant in 1998, 0.3-0.4% nonionic surfactants were injected into one well over a period of three to four days. The well was shut in for a brief period of time. The oil production increased over 30 bopd per day, with a water-oil-ratio reduction. The concentration of dilute surfactant produced back was about 25% of what was injected, which indicated adsorption/loss of surfactant in the reservoir.

1.5.2. The Cottonwood Creek Field in Wyoming

Xie et al. (2005) performed imbibition experiments on core plugs from the dolomite reservoirs at Cottonwood Creek Field. Permeability of the cores from Cottonwood Creek field ranges from 0.2md to about 130md, and porosities from approximately 9.5% to 18%. The Cottonwood Creek oil samples includes 31.2% saturates, 43.1% aromatic, 25.7% resins, and 2.3% asphaltenes. Cationic surfactant cocoalkyl-trimethyl ammonium chloride at the concentration of 0.05% and nonionic surfactant polyoxyethylene alcohol at the concentration of 0.075% were used in the imbibition tests. A comparison of cationic and nonionic surfactant was performed. The nonionic surfactant was more effective in improving oil recovery. A shift in wettability to more water-wet was observed and the incremental oil recovery ranged from 2% to 10% of the OOIP.

Weiss et al. (2006) conducted field tests at the Cottonwood Creek field to determine to effectiveness of surfactant EOR. Initial acid pretreatment was carried out to remove iron sulfide from the wellbore to reduce surfactant adsorption. Initial concentration of the nonionic surfactant was 0.075%, and was increased to 0.15% to allow for surfactant loss. Single-well surfactant treatments were performed at 23 wells. Although

70% of the treatments were failures, several wells showed significant increase in the oil rate. The minimum amount of surfactant for a successful treatment was reported to be 60 lbm/ft of perforated interval according to this literature.

1.5.3. The Wolfcamp Formation

Porosity of the Wolfcamp formation varies from 4% to 12%, and permeability is as low as 10mD (Blomquist 2016). Rising productivity in the Wolfcamp play has been driven by horizontal drilling and completions optimization. Jones et al. (2016) carried out an experimental and field study on surfactant EOR in the Wolfcamp formation in Reagan County, Texas. It was oriented to evaluate the effectiveness of weak emulsifying surfactants (WES). The WES has the capability of creating reverse oil-in-water emulsion, solubilizing oil and reducing IFT of oil and water. The Wolfcamp rock samples contained 30% quartz, 20% calcite, and 10% dolomite on average. The surfactant selection process was composed of an emulsion tendency study and crushed sample analysis. The formation rock was crushed and screened to 100 size mesh, and then saturated with corresponding oil at high temperature. Fracture fluids mixed with various surfactants were pumped through the column twice. The evaluation of the surfactant performance was based on the second pass that extracted the trapped oil. A set of 163 wells in the Wolfcamp was studied, among which 43 used the weak emulsifying surfactant and the rest did not. Accounting for the bias caused by lateral length, proppant, and artificial lift, the wells treated with the WES outperformed wells without WES. Incremental oil recovery in the Wolfcamp benches varied from 13% to 41%, and it was higher than the laboratory results. The study

suggested that the WES functioned by mobilizing the trapped oil in the pores and improving the overall relative permeability.

In another field study of surfactant EOR the Wolfcamp A formation of the Permian Basin performed by Bidhendi et al. (2019), two wells were treated with one surfactant labeled as PROE I. According to contact angle in the lab, this surfactant altered the contact angle the Wolfcamp rock from 130° to 60° at the concentration of 0.10 wt%. In the field study, the surfactant was injected at a concentration of 0.1% along with fresh injection water (TDS~0.4%). After the treatment, the wells were shut-in for two weeks before production. The trial demonstrated approximately 39% increase above the average type curve for the area after 180 days. This study proposed that wettability alteration is the key driver for improving oil recovery. The salinity of the formation brine, oil properties, mineralogy of the reservoir, and the intensity of natural fractures were regarded as the factors that had significant effect on the performance of surfactant.

1.5.4. The Eagle Ford formation

The Eagle Ford is a carbonate-dominated formation, calcite content ranging from 40 to 90%, and quartz content ranging from 10 to 30% (Tian et al.). The Eagle Ford shale is the most active shale play in the world and the largest single economic development in the history of Texas (Tunstall et al. 2013). The formation produces variable amount of gas, condensate and oil.

The effectiveness of the weakly emulsifying surfactant was also evaluated in the Eagle Ford field study (He et al. 2014), comparing with the non-emulsifying surfactant

(NES). In the experimental study, a WES was injected into the nano-fluidic chip with 4% KCl to displace the contained crude oil. Results indicated that the WES yielded higher oil recovery compared with the control fluid bearing no surfactant. The WES was more effective in surface cleanup compared to the NES. A group of 45 wells were separated in two areas in the Eagle Ford shale. Production data in terms of 30 and 90 days was gathered for these two different areas, respectively. The production data was normalized accounting for lateral lengths and fracturing stages. Production results indicated that wells treated with WES exhibited enhanced recovery compared to those treated with NES.

Mohanty et al. (2019) studied the effectiveness of a chemical blend consisting of a surfactant, an organic solvent, and an oxidization agent with trials in the Eagle Ford formation. Contact angle measurements were performed on the aged shale surface. In the formation brine (TDS 12%), the CA was approximately 179° . The measured CA in the low salinity brine (TDS 0.2%) was 150° , still oil-wet. The addition of 0.5% anionic surfactant into the 0.2% brine modified the CA to 50° , and final CA with the addition of the chemical blend was 33° . In the fracture-core experiments, 15% of OOIP was produced. Several lateral wells in the Eagle Ford liquid reservoirs located at South Texas were treated with the blend. A volume of 3,000 to 20,000 bbl of blend solution was pumped in followed by a shut-in period. The cumulative incremental oil was 20,000 bbl, showing a strong well performance. This study suggested that the wettability alteration of the fracture face had the potential to promote imbibition and reduce capillary end effect.

In summary, most of the pilot cases in conventional and unconventional reservoirs revealed that surfactant has the capability of improving oil production in the field. Wettability alteration of the rock surface observed in the laboratory is a key driver for the incremental oil recovery. With the proper selection of surfactant, a higher ultimate oil recovery could be achieved through this process

2. METHODOLOGY

Experiments are performed for the evaluation and selection of surfactants following a systematic workflow which is presented in **Fig. 7**. Interactions of rock, crude oil, and aqueous phase including surfactant and ionic species are involved in the assessment of ULR rock wettability. Surfactants are screened with contact angle and interfacial tension measurements, then evaluated with a novel surfactant stability test, and finally validated with spontaneous imbibition experiments. This study seeks to investigate the interactions of fluids and ULR rock with surfactant additives and their effect on oil recovery.

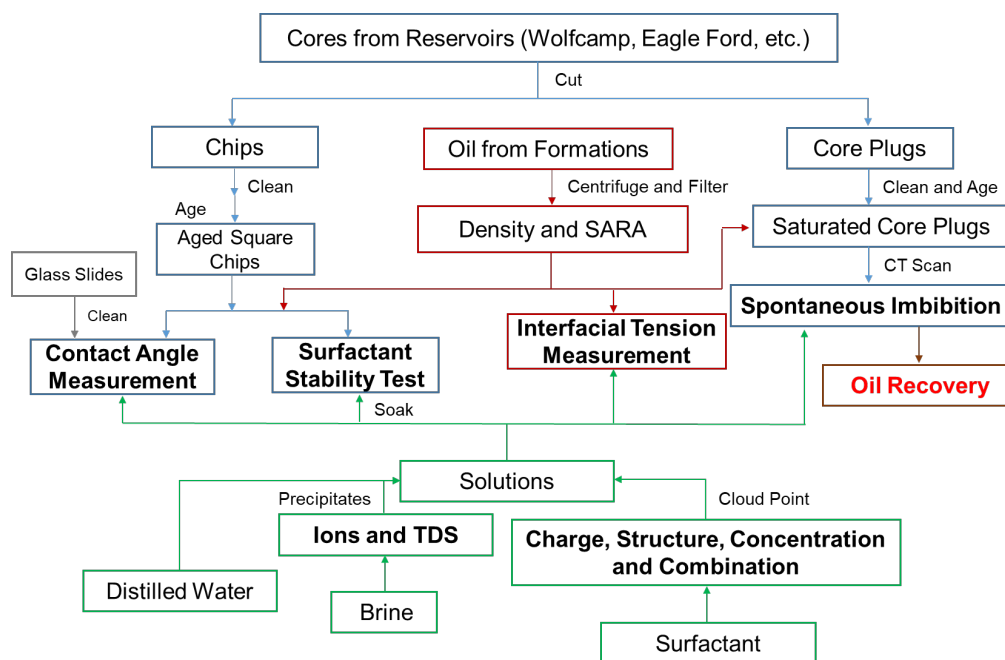


Figure 7. Comprehensive workflow of surfactant selection. Rock sample is shown in blue frames, oil in red, and aqueous solution in green.

With this systematic workflow, we oriented to choose a surfactant candidate for field EOR applications. This surfactant selection workflow suggests that an effective surfactant should have the capability of altering the rock surface to water-wet, reducing IFT, forming a stable layer on the rock surface, and thereby leading to higher oil recovery from ULR core.

2.1. Rock and Oil Properties

Rock samples were retrieved from the Eagle Ford and Wolfcamp wells for the surfactant selection study. Sidewall cores from different depths of the Eagle Ford interval were prepared for CA measurements and stability tests. Mineralogical composition by x-ray diffraction analysis (XRD) of the core from the Eagle Ford and Wolfcamp rock is shown in **Fig. 8**. Calcite was found to be the most abundant constituent of Eagle Ford rock with an average greater than 60%. Some quartz and clay minerals were also observed from the XRD results. Core plugs from the Wolfcamp formation with less carbonate content were utilized for further analysis of CA measurements. Quartz content was found to be approximately 60% in the Wolfcamp rock sample from XRD results. The wettability of clean quartz glass slides was also assessed for the evaluation of surfactant performance on different solid surfaces.

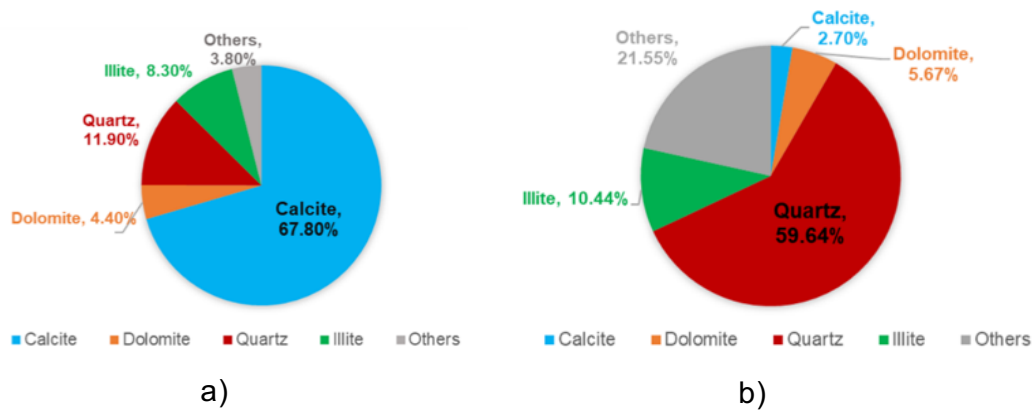


Figure 8. Mineral composition of the (a) Eagle Ford and (b) Wolfcamp rock sample tested in the study.

In preparation, cores collected from the target area were cut into 1-inch diameter core plugs for spontaneous imbibition experiments as well as square chips for CA measurements. Core plugs and chips were cleaned, dried, and then aged with crude oil obtained from the corresponding formation to restore the original reservoir condition. The glass slides were cleaned but not aged in oil to retain the water-wet condition. Solids in the oil affect the repeatability of the measurements. Thus, crude oil was centrifuged and filtered to discard sand and water suspended in the sample. Density and Saturates, Asphaltenes, Resins & Aromatics (SARA) were measured for the composition and properties of the crude oil.

The density of crude oil is a function of the temperature. The reservoir temperature of Eagle Ford presented in this study is approximately 200°F. Ambient pressure contact angle is not possible above the boiling point of water and is not practical for temperatures above 170°F thus all CA and IFT measurements for the Eagle Ford samples were performed at 170°F. The density of the Eagle Ford crude oil was used with 0.8452 g/cc at

170°F. The reservoir temperature of Wolfcamp is lower than the Eagle Ford reservoir, and the lighter Wolfcamp oil was used with a density of 0.7719 g/cc at 150°F. API gravity at 60°F for Eagle Ford and Wolfcamp oil are 28.3 and 43.5, respectively.

SARA measurement was performed for the Eagle Ford black oil, where the values for saturates, asphaltenes, resins & aromatics are 33.98%, 2.33%, 14.73%, and 48.97% respectively. The SARA values for the Wolfcamp light oil are 68.41% saturates, 0.22% asphaltenes, 7.84% resins, and 23.53% aromatics. The SARA test results are summarized in **Fig. 9**. Saturates are nonpolar fractions in the crude oil, resins are slightly more polarizable, and resins and asphaltenes are polar fractions. The Eagle Ford oil has more polar compounds than the Wolfcamp oil sample.

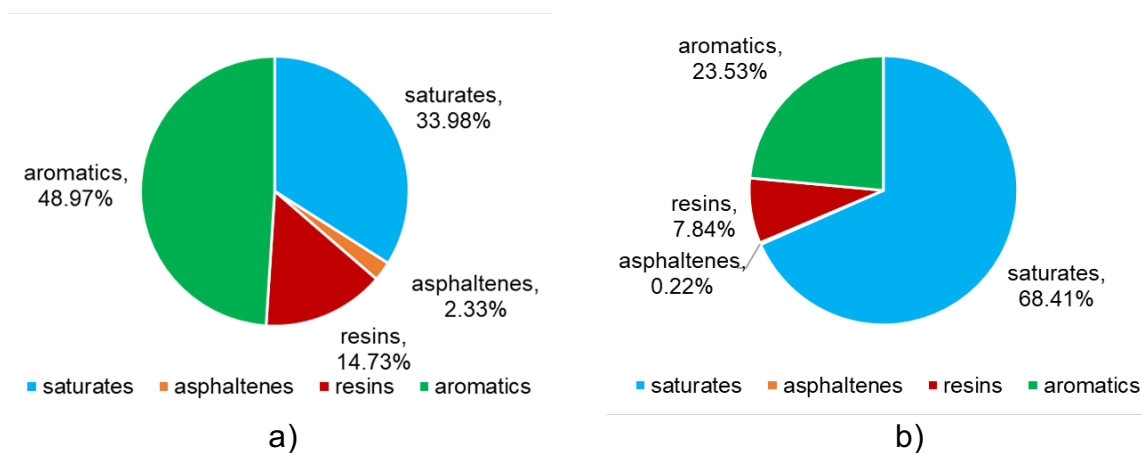


Figure 9. SARA of the (a) Eagle Ford oil and (b) Wolfcamp oil.

2.2. Surfactants and Brine

Surfactants with different functional head groups and hydrocarbon tail groups were tested in surfactant screening, stability tests, and spontaneous imbibition experiments.

First, surfactants were pre-screened with CA and IFT measurements in distilled water (DW) to investigate the trend of surfactants behavior. The concentration of surfactants is measured in weight percent (wt%). Then, select surfactants were tested in produced water (PW) from the corresponding well. The produced water from the Eagle Ford contains total dissolved solids (TDS) of approximately 11%. Brines were mixed with the produce water recipe but diluted (50/50) to TDS of 6%. The ions content in the 6% brine is described in **Fig. 10**. The calcium and sodium ions concentration was also modified to investigate the effect of Ca/Na ratio on rock wettability and surfactant performance.

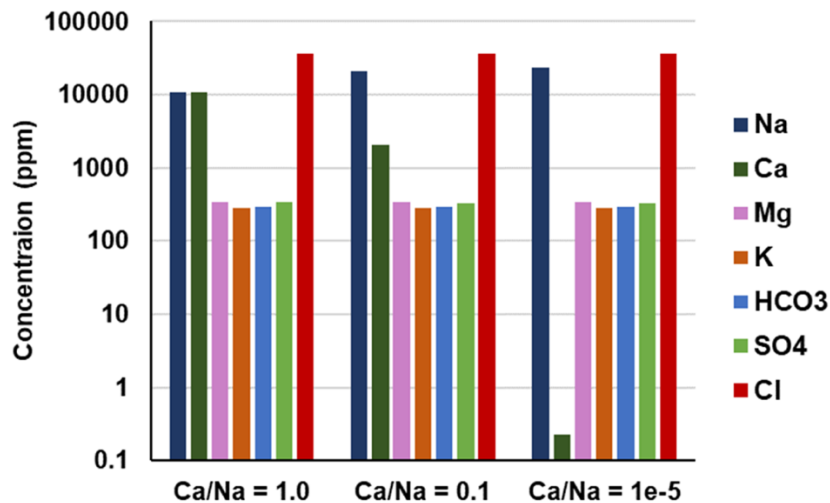


Figure 10. Ions content of the 50/50 brines. TDS = 6%.

Fig. 11 Illustrates the molecular structure of the surfactants tested in this study. Abbreviations of surfactants are used in the following sections for convenience. Typical functional groups for cationic surfactants are Dimethyl Amine Chloride (DAC) and Trimethyl Amine Chloride (TAC). Surfactant C-1 has a DAC head and double tails. Two

typical anionic surfactants are Internal Olefin Sulfonate (IOS) and Propylene Oxide Sulfate (POS). The carbon atom numbers of the ionic surfactant tails range from C₁₀ to C₂₆. Nonionic surfactants are characterized by the Ethylene Oxide (EO) group. The EO number of nonionic surfactants ranges from 2 to 40. One typical zwitterionic surfactant is the Cocamidopropyl betaine (CAPB), which contains a long hydrocarbon chain. Most surfactants have straight hydrocarbon chains, while surfactants N-7 and N-8 have aromatic tails. Molecular structure including electric charge and tail length, the concentration of the surfactant, and salinity of the solution were assessed for the performance of surfactant on wettability alteration.

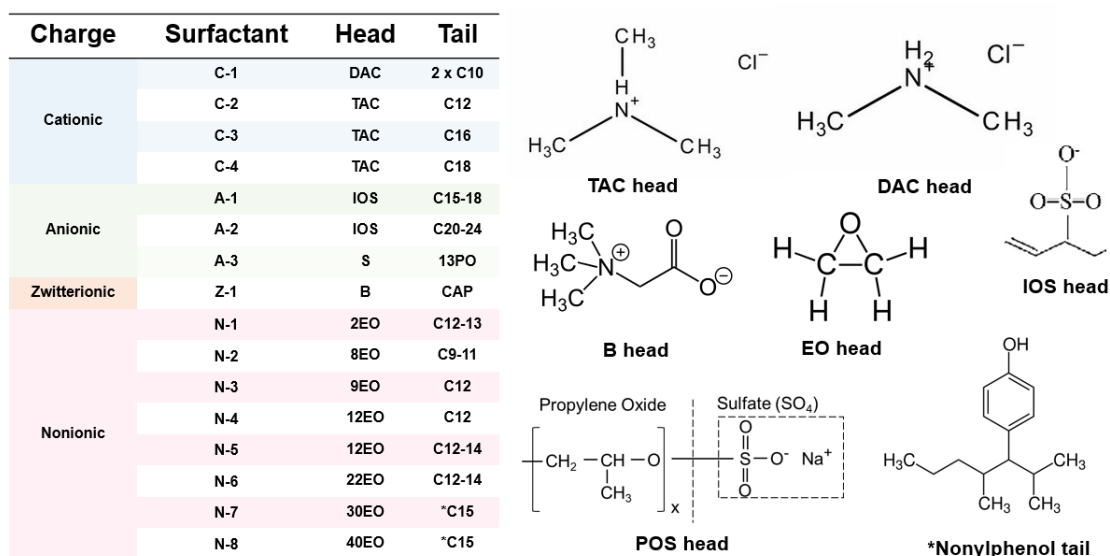


Figure 11. Molecular structure of the surfactants tested in the study.

Interactions of bicarbonate anions with magnesium and calcium cations lead to precipitates in the brine, which increases the solution turbidity and obscures

measurements. These precipitate could cause deviations in surfactant performance and final oil recovery. To match the turbidity of the synthetic brine, the concentration of bicarbonate ions was modified. Salts were mixed in the water with a different mass of sodium bicarbonate. The brines were agitated for 12 hours, then the brine containing excess bicarbonate slowly became cloudy. The visual cloudiness of the brines is presented in **Fig. 12**, and turbidity of the solution increases with increased HCO_3^- concentration. Final sodium bicarbonate content was determined as 400ppm (0.04%) referring to the cloudiness inflection point.

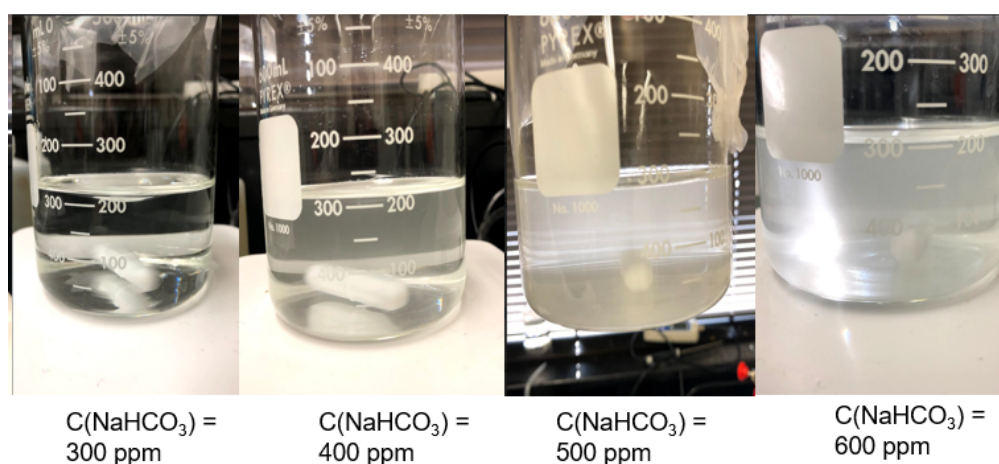


Figure 12. Turbidity of brine increases with increasing bicarbonate concentration.

2.3. Contact Angle and IFT Measurements

Wettability of the rock surface is determined by the contact angle measurement. The captive bubble method was applied for CA measurements on the Dataphysics OCA15 Pro apparatus by submerging rock chips into surfactant solutions. The experimental setup is shown in **Fig. 13** and **Fig. 14**. The rock chip was placed on a plate holder in the glass cuvette with the temperature-stabilized solution. The volume of the solution in the cuvette

is about 60ml. Crude oil was dispensed bottom-up through a 500 μL syringe and a J-shaped needle. Then the oil droplet was brought up to the bottom surface of the rock chip, forming an oil bubble in contact with the surface. The angles of the oil-water interface with rock were measured by enhanced video-image digitization technique and converted to achieve the defined CA values. The solution was heated to a certain temperature with a heating device on the apparatus. To achieve consistency and repeatability of the measurements, seven to ten trials for each sample were performed.

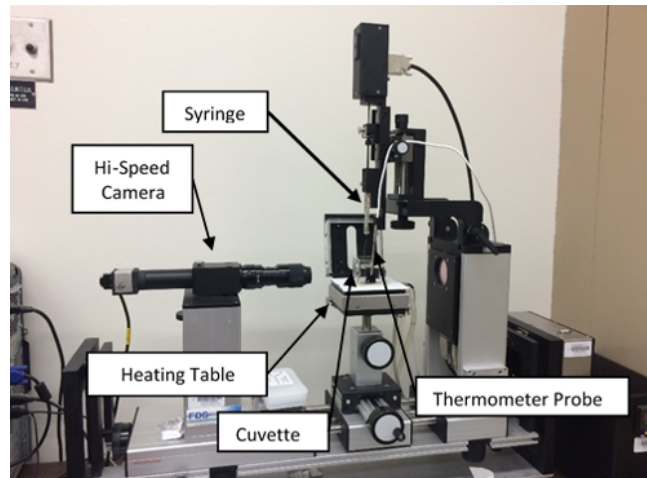


Figure 13. Dataphysics OCA15 Pro apparatus for CA and IFT measurements.

Core samples were cut carefully into square chips to fit the holder inside the device and polished to achieve a smooth surface. They were submerged in toluene for two days and in methanol for one day to remove any impurities. The chips were dried in vacuum for one day and then aged in the crude oil at a high temperature until reservoir conditions have been restored. The solution used for CA and IFT measurement was distilled water, brine, or mixture of surfactant with DW/brine. The solution was agitated for 15 minutes

before the measurements to ensure that the surfactant was completely mixed in the aqueous phase.

IFT measurements were performed by the pendant drop method with the Dataphysics OCA15 Pro apparatus to determine the strength of the capillary force in the imbibition process. The crude oil was dispensed through the syringe and needle that was submerged in aqueous solutions of surfactants. The experiment was recorded with a digital camera. The image of when the drop was about to leave the needle was analyzed to calculate the IFT. The shape and size of oil were matched to the Young-Laplace equation by the device software automatically.

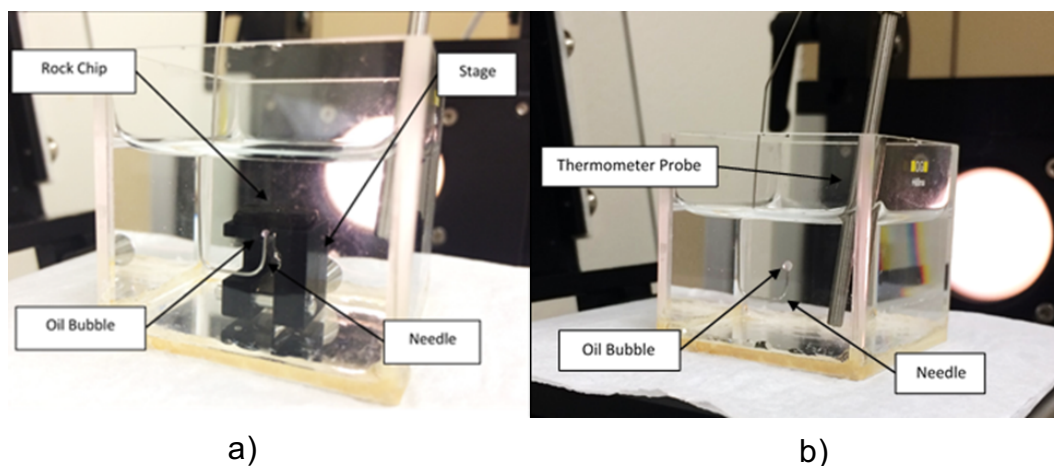


Figure 14. Setup for (a) contact angle and (b) interfacial tension measurement.

The density difference of the oil droplet and ambient phase was used in the Young-Laplace equation for the calculation of IFT. The density of oil was measured in Anton Paar DM 4100 M density meter at atmospheric pressure. The oil density is a linear function

of temperature. The value of oil density at high temperature could be obtained through a density versus temperature function.

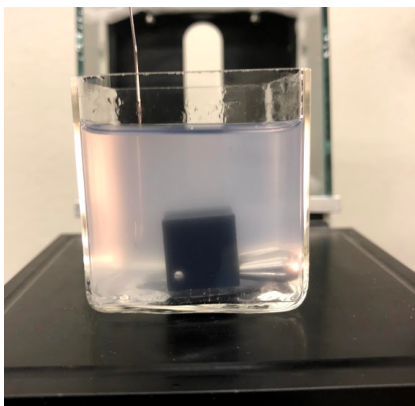


Figure 15. Example of turbid solution that obscures measurement of CA.

CA and IFT measurements require that the light from the apparatus passes through the solution in the cuvette and be captured by the digital camera. The cloudy phenomenon of surfactants shown in **Fig. 15**, however, scatters the light strongly and obscures the CA and IFT measurements. To avoid measuring cloudy solutions, a novel surfactant stability test was proposed.

2.4. Surfactant Stability Test

In this study, the actual wettability of the rock surface is defined by the contact angle of rock chip measured in distilled water or brine without surfactant additives. Common contact angle measurement is performed in surfactant solutions for the screening process. In most cases, the rock chip is soaked in the solution contained in the cuvette for ten minutes during the entire test. The adsorbed surfactant layer can temporarily alter the

wettability of the rock surface. However, when the rock chip is taken out from the surfactant solution and then measured in water without surfactant, the actual wettability of the rock surface is observed to return to an oil-wet condition. The short soak time is not sufficient for surfactant molecules to form a stable layer on the surface, causing the actual wettability of the rock surface not entirely altered from oil-wet to water-wet. To ensure wettability alteration is retained through EOR operations, it is recommended to perform a stability test for surfactant performance evaluation.

In this study, the surfactant stability describes the retention of surfactant molecules on the rock surface when the concentration of surfactant decreases significantly. In EOR operations, surfactants are injected with mixed completion fluid into fractures. As the surfactant is adsorbed on the rock surface or diluted by the reservoir fluid, the surfactant concentration in the aqueous phase decreases. If the surfactant is unstable, the surfactant molecules will desorb from the rock surface and diffuse into the aqueous phase. The wettability of rock would then return to oil-wet as initially induced by crude oil. Through the stability test, we suggest that effective surfactants can not only alter the rock surface into the water-wet region, but also form a stable layer on the rock surface.

The workflow for the surfactant stability test is presented in **Fig. 16**. This test consists of two soak periods, 1) soak in the surfactant solution and 2) soak in distilled water or brine. The chips used for stability tests were aged in crude oil for typical CA measurements to restore original wettability. Then the aged rock chip was immersed in a specific surfactant solution for two days. During the soak period, surfactant molecules adsorb on the rock surface and penetrate into the rock matrix. As surfactant molecules

construct a hydrophilic layer, oil in the rock was expelled from the matrix. Then, the contact angle of the soaked chip was measured in distilled water/brine. An oil-wet condition indicates surfactant has been displaced from surface and is ineffective for wettability alteration, while a water-wet condition suggests the surfactant could be an EOR candidate.

In the second soak period, the rock chip was immersed in the DW/brine for another two days. The contact angle was then measured again in DW/brine. For surfactants with high stability, the wettability of the rock is altered to water-wet and the contact angle between the two soak periods varies by less than 5°. If the variation of contact angle is greater than 5°, this surfactant cannot lead to continuous oil recovery once its concentration decreases in the hydraulic fractures or reservoir matrix.

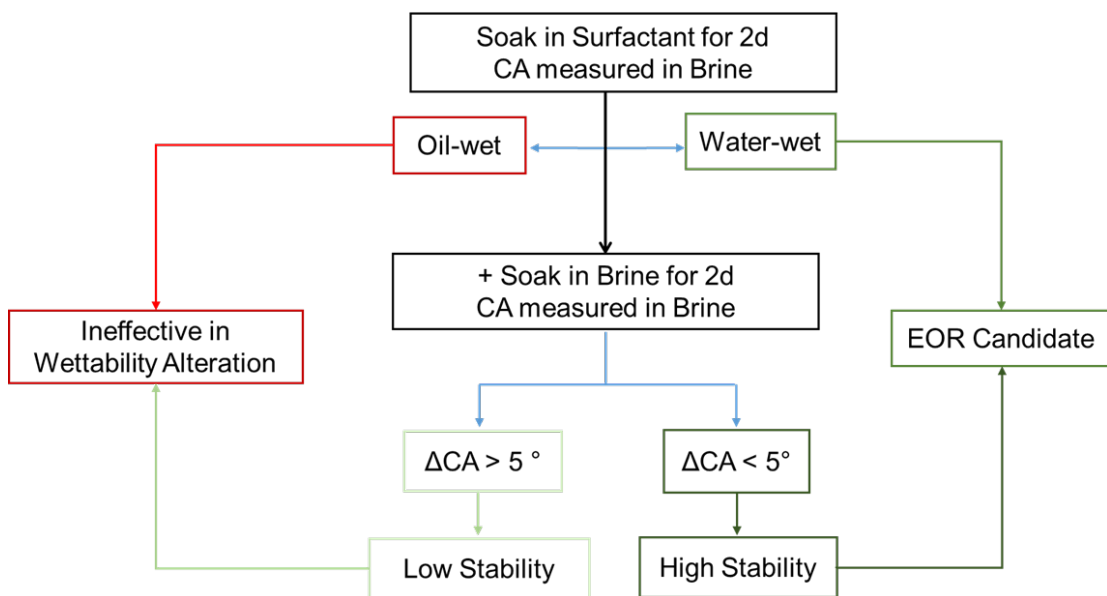


Figure 16. Workflow of stability test and criteria for surfactant stability.

In the surfactant stability test, the soak time in the surfactant solutions was determined from a preliminary analysis with Wolfcamp rock chips. Several aged chips with the same initial wettability were soaked in the same surfactant solution for various times in different containers. The soak time for these tests was set to 1h, 6h, 1d, 2d, 4d, 6d, and 10d. Based on the preliminary study, we observed that the wettability of the chip was altered to water-wet after two days of soak with different surfactants. Results of anionic surfactant A-3 and nonionic surfactant N-2 are shown in **Fig. 17**. Longer soak time does not help wettability alteration. Two days of soak in DW/brine were added to the stability test to accelerate the detachment of surfactant molecules and shorten the experimental time.

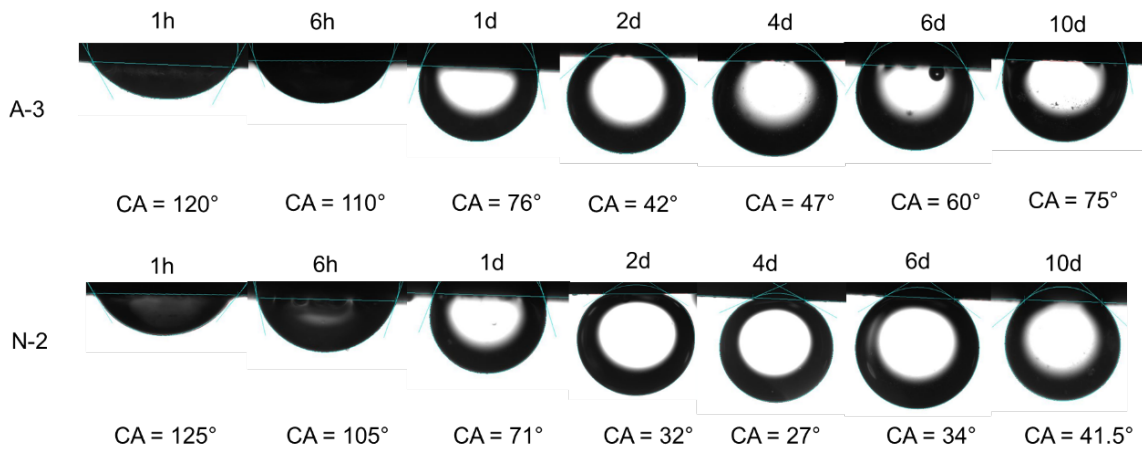


Figure 17. Contact angle variation of Wolfcamp chips soaked in surfactants.

The stability of the surfactant is a significant parameter for the evaluation of surfactant performance. Presumably, the longer the surfactant layers exist on the rock surface, the higher the incremental oil production. Surfactant stability is crucial for the

real potential of surfactant EOR operations. The surfactant stability test is a direct method to investigate the effect of surfactants on wettability alteration, avoiding the impact of interfacial tension. In the basic experimental procedure, the contact angle is measured in a surfactant solution. This could lead to a bias for the understanding the true potential of wettability alteration.

In addition, the surfactant stability workflow provides a method to assess wettability, which cannot be determined through CA measurement alone. For nonionic surfactants with a low cloud point temperature, stability test would also be applied for performance evaluation. Rock chips are aged in cloudy surfactant solution shown in **Fig. 18** while all CA measurements are performed in brine. There is no need for consideration of solution turbidity. This makes it possible for cloudy surfactants to be screened and broadens the surfactant selection range.



Figure 18. Eagle Ford chips soaked in cloudy surfactant solutions during the test.

2.5. Spontaneous Imbibition Experiments

Spontaneous imbibition is the final step for experimental data gathering and validation of results obtained from preliminary surfactant screening and stability tests. The experiment was performed in a modified Amott Cell shown in **Fig. 19**, containing about 500ml aqueous solution. The Amott cell consists of a core-holder base and a glass jar with a graduated measuring scale at the top to measure oil recovery with time. Core plugs from the Eagle Ford formation were cleaned in toluene for two weeks and in methanol for one week, and then dried in a vacuum for one more week. In order to saturate the cores and measure original oil in place (OOIP), the aging process in the crude oil was carried out at reservoir temperature for more than six weeks.

Saturated cores were weighed with an analytical balance before being transferred into the Amott cells. The Amott cells were filled with selected surfactant solutions, and placed in an oven to bring up the temperature to 200°F. The core was immersed in surfactant solution and the aqueous phase imbibed into the core matrix by capillary forces. Oil was expelled out from the core and collected in the graduated cylinder. The time-lapse volume of oil produced was recorded to build an accurate oil production curve. The imbibition experiments ended when the production curve reaches a plateau. The base case was performed with brine, and the results with surfactant solutions were compared to investigate the potential of surfactant additives.



Figure 19. Amott Cell placed in the oven at the reservoir temperature.

Computed Tomography (CT) scan as a non-destructive imaging technique is utilized to visualize the penetration of fluid into the shale cores. It uses x-rays to produce tomographic images of specific areas of the cores with a Toshiba Aquilion TSX-101A CT scanner. The Amott cell is placed in the CT scanner shown in **Fig. 20** and scanned as the imbibition experiments proceed. The difference in density between aqueous and oil phases leads to a difference in CT numbers. Time-lapse images obtained from the CT scan provide an internal view of fluid movement during the imbibition process.

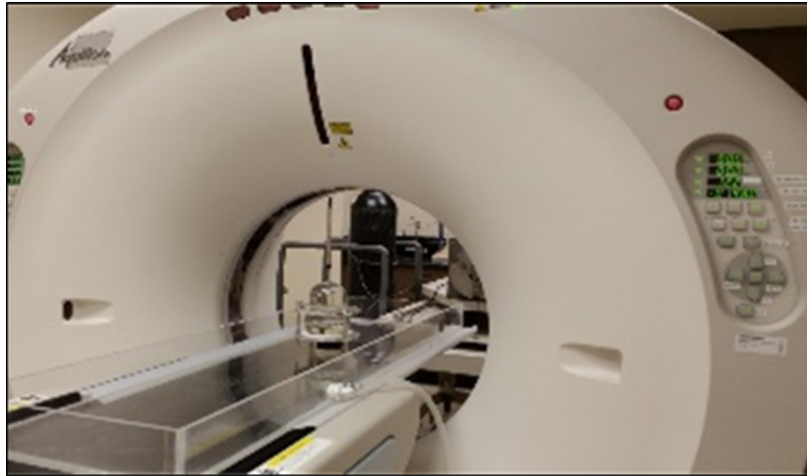


Figure 20. CT scanner used for the scan of core samples. The core sample was placed in a Amott cell and scanned as the imbibition experiments proceed.

3. WETTABILITY AND IFT ALTERATION BY SURFACTANT

The completed surfactant selection process consists of the surfactants screening, surfactant stability tests, and spontaneous imbibition experiments. These experiments were designed to evaluate the performance of surfactants in altering rock-oil wetting properties and improving oil recovery in the lab as a preliminary step to select a candidate for an EOR project.

In this section, the effects of surfactant additives on the rock wettability and oil-water interfacial tension are investigated. Contact angle and IFT measurements were performed on different rock and oil samples retrieved from the Eagle Ford and Wolfcamp formations. Also, wettability on glass slides was assessed with different surfactants. These experiments serve as a screening process for the surfactants tested in this study. The results were analyzed by comparing the final wettability or IFT with its initial state. Surfactants are distinguished based on their capability of altering the wettability and enhancing the imbibition mechanism.

3.1. Contact Angle Results

3.1.1. Wettability alteration of the Eagle Ford rock

Cores retrieved from the unconventional reservoirs were cut into square and flat chips for CA measurements. The wettability of six cores from different depths of the Eagle Ford formation was studied. The contact angle was measured in distilled water and recorded periodically through the aging process. Original wettability of the clean bare

chips without oil/water saturation was in the water-wet region. The rock chips were then aged in the corresponding crude oil to restore reservoir conditions. During the aging process, the wettability of the rock chips was gradually altered to oil-wet or intermediate-wet. Presumably, wettability alteration was induced by the adsorption of polar compounds within the crude oil. Hydrophobic groups of the oil compounds oriented towards the aqueous phase. This increased the hydrophobicity of the rock surface and altered it to oil-wet.

A stable oil-wet condition was achieved for rock samples through submersion in the crude oil for various times under high temperature, which is presented in **Fig. 21**. Wettability of chips 2-2 and 3-1 were stable over a three-week period during the aging process, while the wettability of the chips 1-1 and 1-2 was not stable until the fifth week. Chips marked as 1-3, 2-2 & 3-1 were chosen for further CA measurements due to their high repeatability and coverage of the contact angle range.

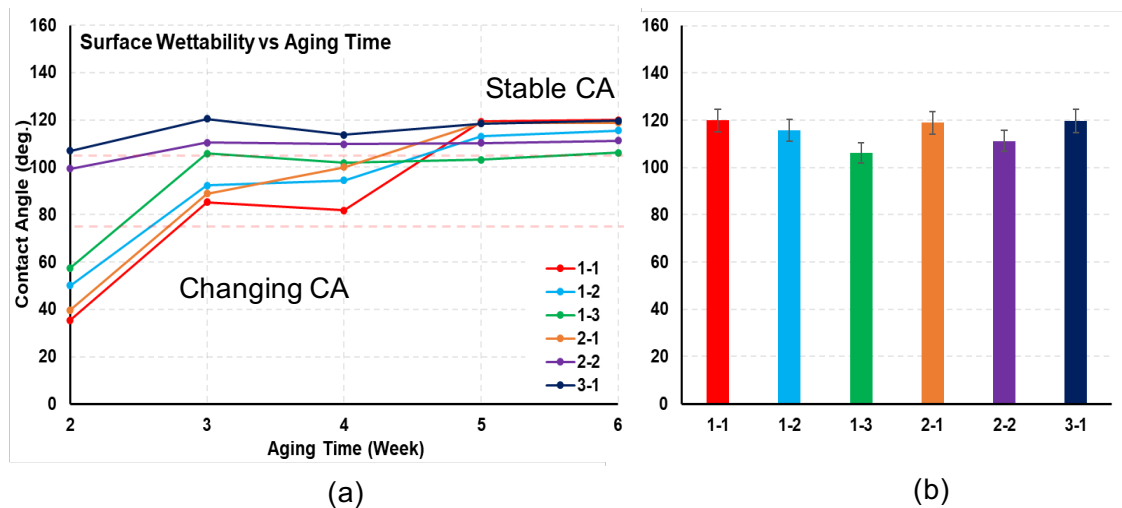


Figure 21. (a) CA changing over 6-week time frame and (b) final CA for each sample.

First, the surfactants were pre-screened with a fluid system that mixed surfactant additives in distilled water. The CA measurements were performed at concentrations of 0.05 wt%, 0.10 wt%, and 0.20 wt% surfactant on select Eagle Ford rock chips. Multiple CA measurements were conducted on the same rock chip, and the reported CA values were averaged from all the measurements to minimize error. Surfactants with different head and tail groups were tested, and the results are shown in **Fig. 22**. The results demonstrate that the electric charge of the surfactant head group has a significant effect on the performance of surfactant in wettability alteration.

All three rock chips were observed to be more oil-wet with anionic surfactants compared to the initial condition. For instance, the initial CA of chip 1-3 is about 106°, while the final CA with the anionic surf A-3 is large as 150° at the concentration of 0.20 wt%. Surfactant A-2 has the same head group as surf A-1 but a longer tail, leading to more oil-wet behavior than surf A-1. Cationic surfactants altered the chips to more oil-wet at the lower concentration (0.05 wt%), and more water-wet at the higher concentration (0.20 wt%). When the concentration is high, cationic surfactants with longer carbon chains generally show better wettability alteration than cationic surfactants with shorter carbon chains. At a concentration of 0.02 wt%, the final CA of chip 1-3 with surf C-2 (C₁₂) is 120°, and with surf C-4 (C₁₈) is 75°. Nonionic surfactants with medium EO numbers (10-20) and large EO numbers (20-50) have high cloud points, which enables the CA to be measured at 170°F. These nonionic surfactants could effectively alter the wettability to water-wet at a concentration of 0.20 wt%. Surfactants with large EO numbers, such as surf N-6 and surf N-7, have better performance than surfactants with less EO numbers.

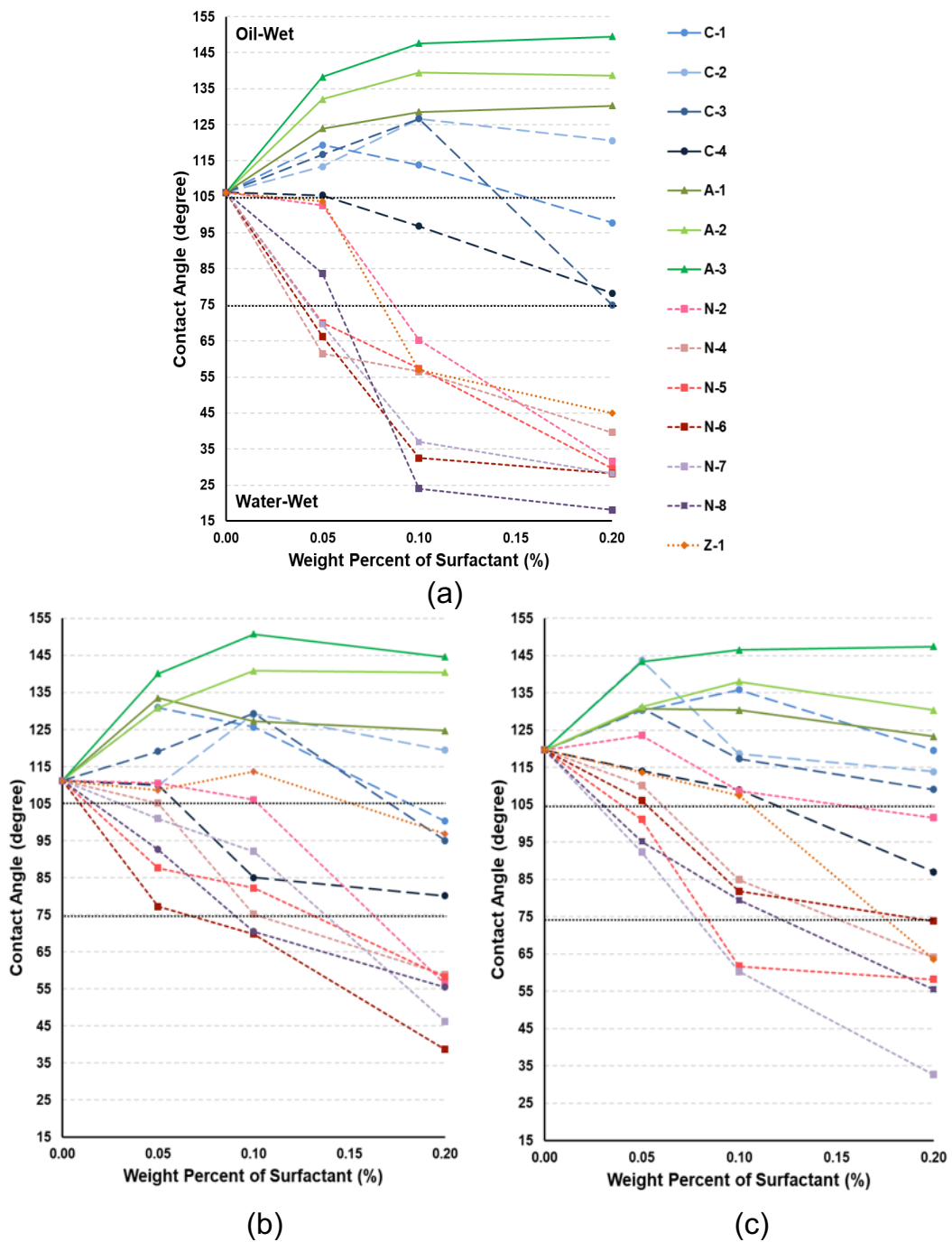


Figure 22. Wettability alteration of the chosen three Eagle Ford chips (a) 1-3 (b) 2-2 and (c) 3-1. Chip 1-3 was retrieved from the top of Eagle Ford interval, and chips 2-2 and 3-1 were retrieved from the bottom of Eagle Ford interval.

In addition, the concentration of surfactant solution affects the final CA. As the surfactant concentration increases, the adsorption of surfactant molecules on the oil-water interface and the solid surface increases. CA with nonionic surfactants decreases monotonically with increased surfactant concentration. The smallest CA (greatest wettability alteration), about 18° and shown in **Fig. 23**, was achieved on the surface of chip 1-3 with 0.20 wt% surfactant N-8. The small CA enables oil to move in the reservoir matrix and fractures with less flow resistance. With cationic surfactants, the rock surface was altered to more oil-wet at low surfactant concentration and more water-wet at high surfactant concentration. A relatively high concentration is required to achieve a water-wet condition, which results in enhancing the production of crude oil from the matrix to production well in the reservoir scale.

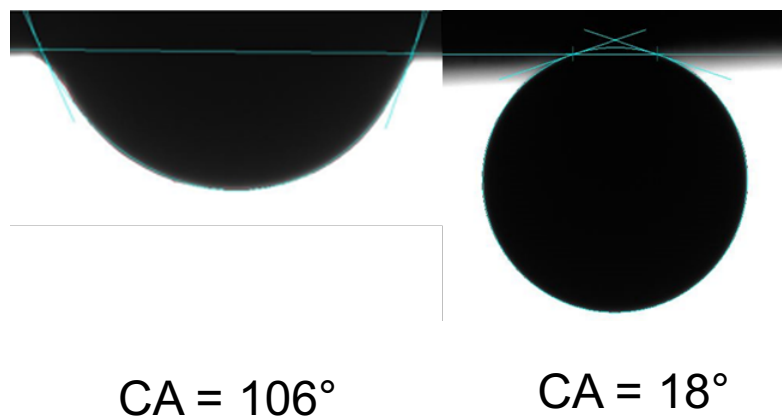


Figure 23. initial CA and the smallest CA achieved in the measurements.

Select chips from different depths of the Eagle Ford formation were tested. We observed that the final CAs of the chips were strongly affected by the initial CAs of the chips. In most cases, the rock chip having a larger initial CA also leads to a larger final CA with the same surfactants. More significant wettability alteration occurred on the chip from a shallower depth. Based on the above observations, it can be concluded that nonionic surfactants generally lead to smaller contact angles thus more significant wettability alteration, than ionic surfactants for the Eagle Ford shale rock.

3.1.2. Wettability alteration of Wolfcamp rock

The effect of electric charge carried by surfactant head group on rock wettability has been reported in Eagle Ford measurements. Rock chips from the Wolfcamp formation were tested to investigate the role of the tail group. The results of ionic surfactants at different concentrations are presented in **Fig. 24**. The initial state of the Wolfcamp chip is intermediate-wet, with a CA of 97° . Three different surfactant concentrations were tested on the Wolfcamp rock chip, which are 0.2, 1, and 2 gallons per thousand gallons (gpt).

In contrast to the CA measurements with the Eagle Ford rock, most of the anionic and cationic surfactants tested have the ability to alter the wettability of the Wolfcamp rock surface from initial intermediate-wet to more water-wet. Surfactant A-3 leads to the smallest CA at the concentration of 2gpt. Compared to cationic surfactants, anionic surfactants altered the wettability to more water-wet. In general, the anionic surfactant with a longer tail leads to smaller CA.

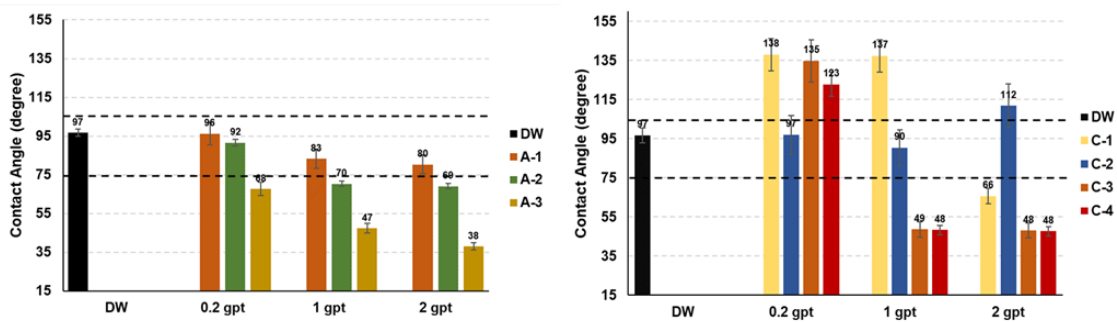


Figure 24. Wettability alteration of Wolfcamp chip with anionic and cationic surfactants.

Wettability alteration of the Wolfcamp rock using cationic surfactants was similar to the Eagle Ford cases. Most of the cationic surfactants were observed to alter the rock surface to more oil-wet at lower concentration. Surfactants with a long tail could effectively alter the surface to water-wet at higher surfactant concentrations. However, cationic surfactant C-2 with the shortest tail cannot alter the surface to water-wet, even at very high concentrations (e.g. 8 gpt). Similar to anionic surfactants, the longer carbon chain of cationic surfactant is beneficial for achieving water-wet conditions.

Nonionic and zwitterionic surfactants were also tested for the Wolfcamp rock. The final CA with surfactant Z-1 is 46° at a concentration of 1 gpt. Surfactant N-2 altered CA of the chip to 36.5° , which is more water-wet than the surface tested with cationic and anionic surfactants. Images of the CA results with ionic and nonionic surfactants is presented in **Fig 25**. It is also true with the Wolfcamp rock that nonionic surfactants would have better performance than ionic surfactants in wettability alteration.

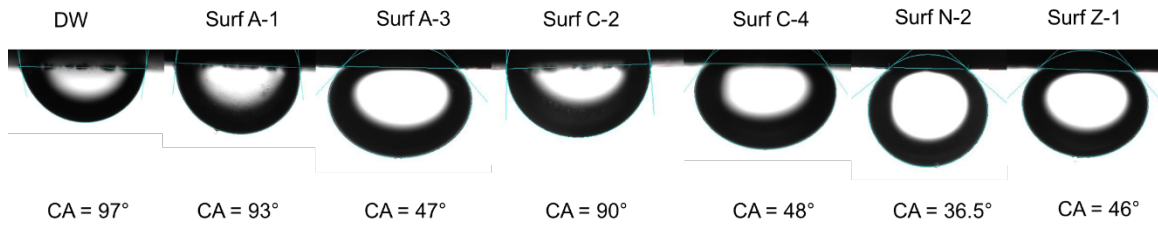


Figure 25. CA results with ionic and nonionic surfactants at the concentration of 1gpt.

3.1.3. Wettability alteration on a glass slide

CA measurements were also performed with clean glass slides and the Eagle Ford heavy oil for the assessment of surfactants on uniform solid surfaces in order to understand the mechanism of wettability alteration. The quartz glass slide is not saturated with oil and the initial state of the surface is water-wet. To have a detailed classification of water-wet conditions, the surface is defined as strongly water-wet with CA from 0° to 30°, and moderately water-wet with CA from 30° to 75° (Fanchi 2002). The surface of the glass slide is moderately water-wet with an initial CA of 47° as shown in **Fig. 26**.

The results with cationic surfactants tested are summarized in **Fig. 26**. All cationic surfactants altered the water-wet glass slides to oil-wet at low concentrations (e.g. 1gpt). Cationic surfactants with long-chain altered the glass slide back to water-wet at high concentrations, which is consistent with the CA results on rock chips. Surfactant C-3 and C-4 could even alter the surface into the strongly water-wet region. Surfactant C-2 with the shortest tail was not observed to have the ability to alter the glass slide to water-wet.

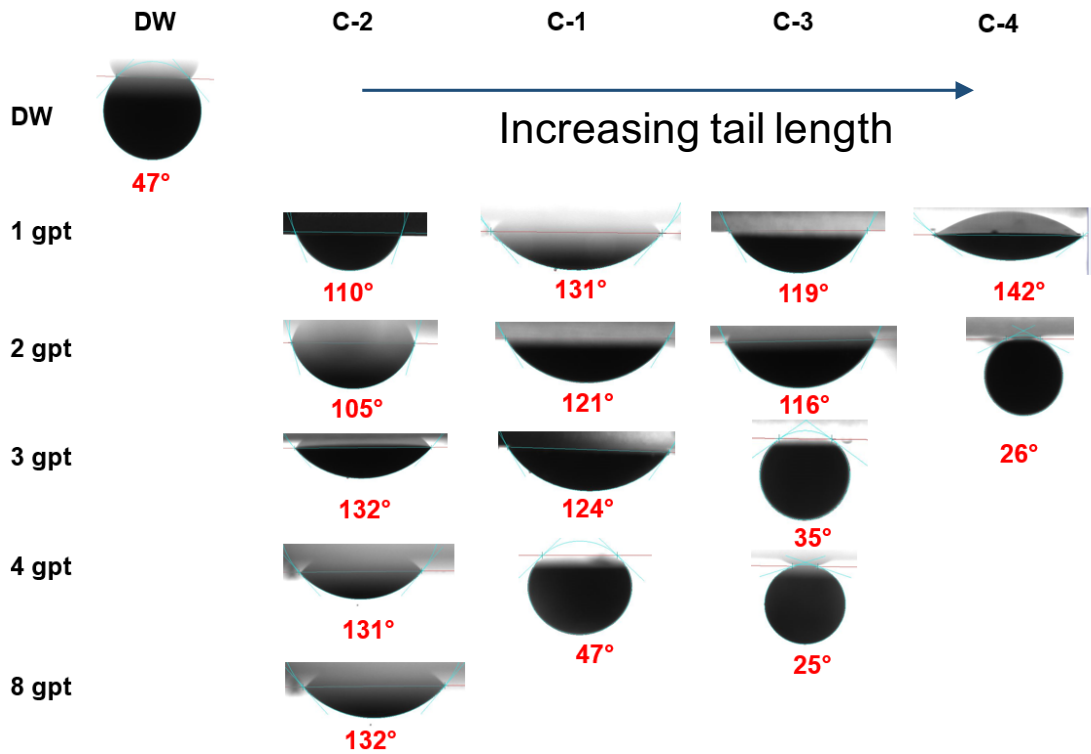


Figure 26. Wettability alteration of glass slides with cationic surfactants.

Contact angle results of glass slides with anionic and nonionic surfactant additives are presented in **Fig. 27**. With anionic or nonionic surfactant, the surface of the glass slide was altered to water-wet. Surfactant A-1 results in the lowest CA on glass at approximately 20 degrees. This indicates that surfactants not only has the ability to alter oil-wet surface to water-wet but also alters moderately water-wet surface to strongly water-wet. Based on the observations of three different solid surfaces, we can conclude that the performance of surfactants in wettability alteration depends on both the head charge and the tail length of the surfactant molecules in addition to the net charge of the solid surface.

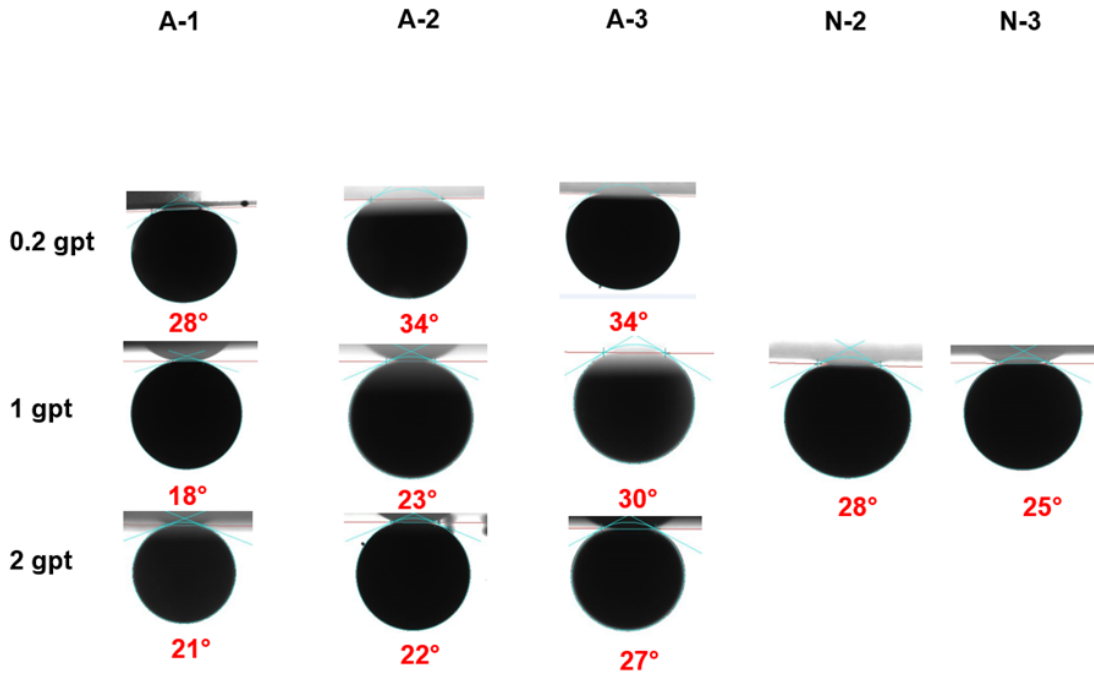


Figure 27. Wettability alteration of glass with anionic and nonionic surfactants.

Three types of solid surfaces with different initial wettability conditions, oil-wet, intermediate-wet, and moderately water-wet, were assessed with surfactants. One type of surfactant possesses different performance in the Eagle Ford, Wolfcamp, and glass slide cases. This emphasizes the importance of rock/oil properties from a specific formation in the evaluation of surfactants. Optimum production could be obtained only if surfactants are assessed with the samples from the target zone. A proper surfactant has the potential to alter rock surface to water-wet and consequently improve oil recovery in shale reservoirs. However, an improper surfactant selection may negatively affect reservoir performance. This work demonstrates the importance of judicious selection of surfactants based on 1) oil type 2) surface type 3) surfactant head group and 4) surfactant tail group.

3.2. Interfacial Tension Results

Interactions of crude oil and water with surfactant additives in the aqueous system were investigated through IFT measurements. Surfactants are well known for reducing the interfacial tension between oil and water phases, which is also confirmed in this study. Oil-water IFT is an important parameter to understand during EOR applications in unconventional reservoirs. According to the Young-Laplace equation (**Eq. 3**), IFT is directly proportional to capillary pressure. The initial IFT and the possible IFT reduction is fundamental for incremental oil recovery by spontaneous imbibition as a reduction in IFT implies lowered capillary pressure and thereby reduced imbibition.

Initial IFT of Eagle Ford oil and distilled water was measured to be 39.65 mN/m. Surfactants lead to remarkable IFT reduction in all tests. The IFT reduction results with different surfactants are summarized in **Fig. 28**. Oil-water IFT decreases as the surfactant concentration increases. Nonionic surfactant N-4 was observed to have the largest IFT reduction, with a final IFT of 1.89 mN/m at the concentration of 0.20 wt%. In general, nonionic surfactants have greater IFT reduction compared to ionic surfactants, and cationic surfactants exhibit less IFT reduction than anionic surfactants. For cationic and anionic surfactant tests, a longer tail results in greater IFT reduction. This trend of surfactant behavior is described with detailed IFT values in **Table 2**. For instance, IFT of the Eagle Ford oil and water with the addition of 0.20 wt% cationic surfactant C-2 (C_{12}) is 17.17 mN/m, and IFTs with 0.20 wt% cationic surfactant C-3 (C_{16}) and C-4 (C_{18}) are 5.70 mN/m and 5.57 mN/m respectively. Zwitterionic surfactant Z-1 with a long hydrocarbon tail also resulted in greater IFT reduction. Although minimum variation of

IFT was observed in all nonionic surfactant cases, a larger EO number was observed to result in higher IFT value. Surfactant N-8 with the largest EO number (40) leads to the highest IFT value among nonionic surfactants.

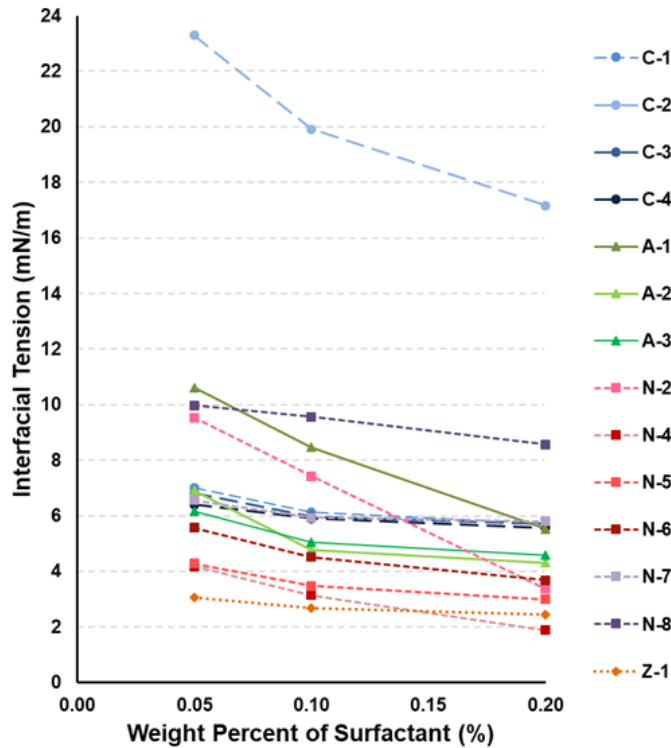


Figure 28. Interfacial tension reduction of the Eagle Ford oil and water. Cationic surfactants are shown in blue lines, anionic surfactants are shown in green lines, and nonionic surfactants are shown in red lines.

The final IFT is determined by forces differential on the oil-water interface. Surfactant molecules, with the amphiphilic structure, align themselves on the oil-water interface lowering IFT. Surfactants that can penetrate into the oil phase and reduce the forces differential can lead to significant IFT reduction. Theoretically, high IFT results in large capillary pressure when the contact angle is less than 90 degrees based on the Young-

Laplace equation. However, the reduction of IFT can be beneficial as it would reduce the flow resistance of fluid through the pores. A relatively moderate IFT is desirable for the design and execution of surfactant EOR applications.

Table 2. IFT (mN/m) reduction with different surfactants for Eagle Ford oil at 170°F.

| Wt% | C-2 | C-1 | C-3 | C-4 | A-1 | A-2 | A-3 |
|--------------|--------------|-------------|-------------|-------------|--------------|-------------|-------------|
| 0.05% | 23.29 | 7.01 | 6.81 | 6.41 | 10.62 | 6.92 | 6.16 |
| 0.10% | 19.91 | 6.13 | 5.98 | 5.91 | 8.47 | 4.77 | 5.06 |
| 0.20% | 17.17 | 5.72 | 5.70 | 5.57 | 5.53 | 4.31 | 4.58 |
| Wt% | N-2 | N-4 | N-5 | N-6 | N-7 | N-8 | Z-1 |
| 0.05% | 9.53 | 4.18 | 4.29 | 5.57 | 6.56 | 9.97 | 3.05 |
| 0.10% | 7.43 | 3.14 | 3.48 | 4.52 | 5.93 | 9.56 | 2.67 |
| 0.20% | 3.37 | 1.89 | 2.99 | 3.69 | 5.80 | 8.57 | 2.44 |

3.3. Effect of Salinity

In practice, surfactants are typically injected into the reservoir after mixing with produced water for a completion fluid. Interactions between the ions in the PW and the surfactant molecules affect the performance of surfactant additives. Salinity affects the solubility of both oil and surfactants. Aqueous systems with different salinity levels and ionic content are utilized for the evaluation of surfactants in the section. The recipe of the mixed brine used in this study was composed of the average brine data from the Eagle Ford wells. The produced water (PW) has a salinity of 11% which can be mixed with distilled water (DW) to reach a level of 60,000 ppm (6%). The effects of salinity on the solution behavior and wettability alteration of surfactant are discussed.

3.3.1. Effect of salinity on cloud point

One feature of nonionic surfactants is the phase separation resulting in a cloud point, especially at high reservoir temperature. The surfactant solution becomes cloudy due to the solubility decreasing with increased temperature. The mixture starts to phase-separate, which reduces the effectiveness of surfactants. A high cloud point is favorable for practical applications to ensure that the surfactant would behave reservoir conditions as observed in laboratory behavior. Cloud points of two nonionic surfactants were tested with DW, PW, and mixed brines at atmospheric pressure. Ionic content, such as Ca/Na ratio, was also modified to investigate its effect on wettability. The result presented in **Fig. 29** indicates that the cloud point of surfactant decreases significantly with increased salinity. In DW, the cloud points of those two surfactants with large EO numbers are higher than the boiling point of water. In the 6% mixed brines, cloud points are about 200°F, which is close to the reservoir temperature. In the original PW retrieved from the field, the cloud points of those two surfactants are much lower than the reservoir temperature. We also observed the cloud point of surfactant increases with an increased Ca/Na ratio. The difference of cloud point with various Ca/Na ratio is minor, which is negligible in practice. The cloud point of surf N-6 is higher than surf N-7 in the corresponding salinity test due to the more hydrophobic nature of the tail of surf N-7.

With a high salinity, ionic surfactant solutions can also turn cloudy at high temperatures. In general, the cloud point of ionic surfactant is higher than that of nonionic surfactants. In many applications, surfactants are mixed to maintain the physical properties of the solution and to achieve high solubility. Adding ionic surfactant to nonionic

surfactant could raise its cloud point by forming mixed aggregates (Li et al. 2009). This approach was not taken due to, as previously shown, the negative effect of ionic surfactants on the wettability alteration performance.

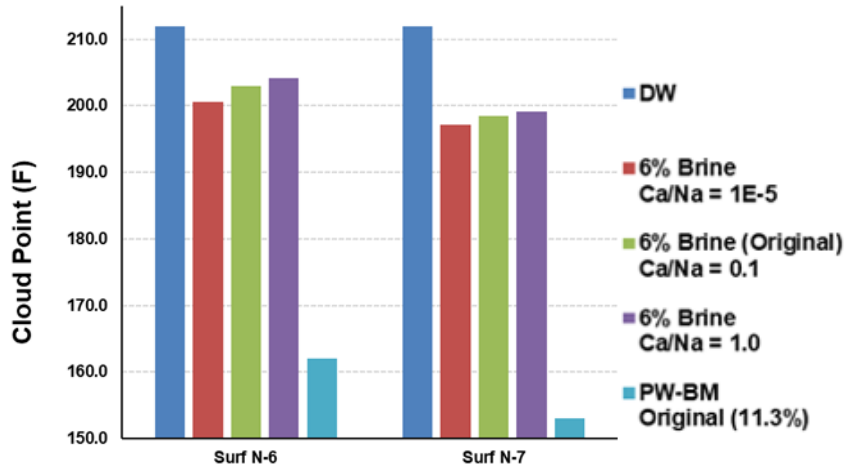


Figure 29. Cloud points of nonionic surfactants tested with distilled water, produced water and mixed (50/50) brine.

3.3.2. Effect of salinity on wettability

Contact angle measurements were performed in brines mixed with select nonionic surfactants at a concentration of 0.20 wt% on the Eagle Ford chips, and the results are shown in **Fig. 30**. Produced water was diluted to 6% to be compared with synthetic brine (salinity 11.3%). In the aqueous systems without surfactant additives, the rock surface is more water-wet in the 6% brine compared to distilled water. This indicates that ions, interacting with rock minerals and oil compounds, could alter the wettability of rock surface to more water-wet. However, the effect is reversed for the original PW where the rock is observed to be more oil-wet than when diluted with PW (6%). For the rock samples

from the lower part of the Eagle Ford interval, the surface is more oil-wet in the synthetic brine than in DW.

The performance of surfactants on wettability alteration was assessed in fluid systems with different salinity levels and ionic contents. Within the brine/PW surfactant tests, contact angles are greater than those measured with DW. In the lower part of the Eagle Ford, rock surface was intermediate-wet in the PW with surfactant additives. Based on CA results, salinity reduces the performance of surfactants on wettability alteration. The results indicate that the CA is slightly affected by the Ca/Na ratio in the brine although no clear trend was observed in CA measurements. The surf N-6 leads to similar final CA among the 50/50 (6%) cases, all in the water-wet region. Hence, the parameter that should be addressed for PW injection is the total salinity level or TDS. Overall, the performance of surf N-6 is better than surf N-7 in brine, even though surf N-7 exhibits better performance in DW. The efficacy of surf N-7 is more sensitive to salinity, which is consistent with cloud point results. Surf N-8 with a greater EO number was also tested in brine, however, its performance was worse than surf N-7.

Based on the experimental results, we can conclude that high salinity is unfavorable for wettability alteration on the rock surface. Solubility and efficacy of surfactants decrease with increased salinity. Thus, it is recommended that produced water used for surfactant operation should be diluted to an optimum salinity if possible.

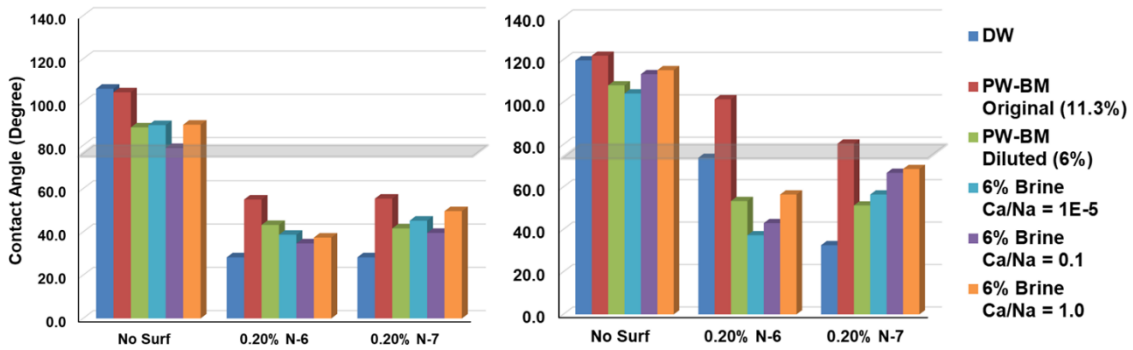


Figure 30. Effect of salinity on contact angle measurements of the left) top and right) bottom Eagle Ford intervals with surfactants.

3.3.3. Effect of salinity on interfacial tension

Interfacial tension of the Eagle Ford oil and water was measured with selected nonionic surfactants, and the results are shown in **Fig. 31**. The oil and water IFT decreases with increased salinity for both brine and surfactant cases. This indicates that the surfactant and salinity modify IFT in the same direction. TDS is the main parameter for the effect of brine, although IFT is slightly affected by the Ca/Na ratio in the brine. At each salinity level, oil and water IFT with surf N-6 is lower than surf N-7, which is the same as previous results in DW, where a larger EO number leads to higher IFT.

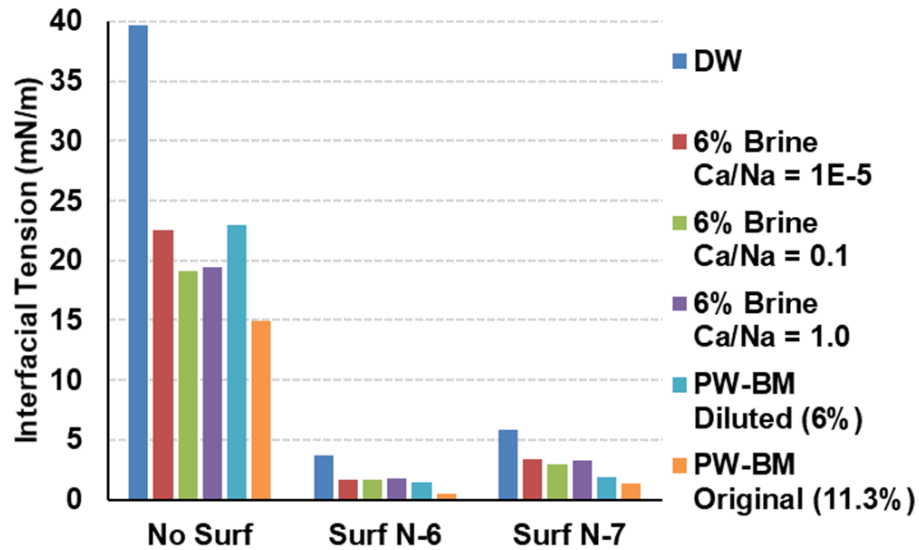


Figure 31. Effect of salinity on surfactants performance in IFT reduction.

The effect of the salinity and surfactant on the shape of an oil droplet in the aqueous system is summarized in **Fig. 32**. IFT reduction by surfactants is achieved due to their amphiphilic nature. The IFT reduction with brine is due to the presence of the cations at the negative oil-water interface (Rostami et al. 2019). Electrostatic interactions between the aqueous phase and the oil phase increases as the ion concentration increases. The shape of the oil droplet is maintained by the tension at the interface between oil and water. With ions and surfactant molecules in the aqueous phase, and the volume of oil in one droplet decreases significantly. This is favorable for oil to be expelled out from the rock matrix with lower resistance.

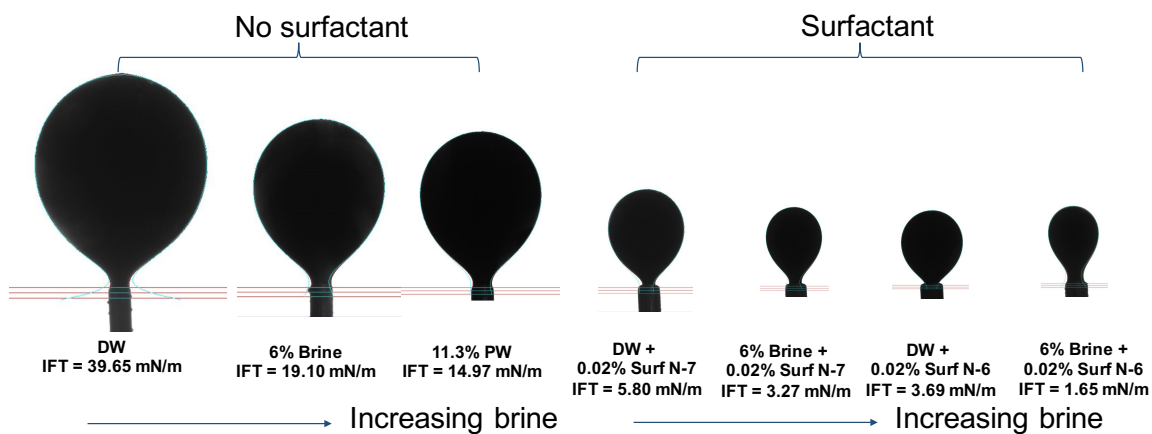


Figure 32. Shape of oil droplet with changing salinity and addition of surfactant.

4. SURFACTANT STABILITY TEST

The importance of testing the stability of adsorbed surfactant on rock surface has been explained in the methodology section. The surfactant that can form a stable layer of surfactant molecules on the rock surface can lead to prolonged wettability alteration and oil recovery. Thus, wettability alteration of the rock surface is retained even though the surfactant concentration in the completion fluid gradually decreases. This novel surfactant evaluation method works as an additional step in selecting surfactant EOR candidates. In this section, the stability of ionic and nonionic surfactants was tested with brine on the Eagle Ford chips. The results were analyzed to understand the behavior of different surfactant molecules' influence on the rock-oil-water wettability.

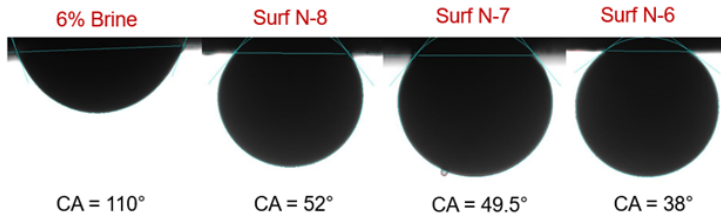
4.1. Stability Test Results

The surfactant stability tests were performed with twelve Eagle Ford chips retrieved from the same depth. The initial contact angle of those chips in the 6% brine is around 110° . Surfactants were mixed with brine at a concentration of 0.20 wt%. The newly proposed surfactant stability test consists of two soak periods. These oil-wet chips were first soaked in different aqueous solutions for two days. The contact angle was measured in brine with no surfactant additive to assess the actual wettability of the solid rock surface. A comparison of the CAs in surfactant screening and stability tests is plotted in **Fig. 33**. Results demonstrate that the wettability of the rock chips has been altered through the first soak period, and the performance of different surfactants varies.

In the base case with only brine, the contact angle is slightly changed. Without surfactant additives, soaking in brine for two days has no significant effect on the rock surface condition. The rock surface was altered to water-wet after two days of soak using nonionic surfactants N-6, and N-7 with large EO numbers. Surfactant N-6 leads to the smallest CA, indicating it would have the greatest effectiveness in wettability alteration and enhanced oil recovery. CA of surf N-8 was about 70°, greater than the CA with surf N-6 and N-7, which demonstrates that its effectiveness is lower although it has a larger EO number. For nonionic surfactant N-2 & N-4 with intermediate EO numbers, cationic surfactant C-4, and zwitterionic surfactant Z-1, the surface of the samples is more water-wet than the base case although remaining in the intermediate-wet region. In contrast, for nonionic surfactant N-1 with a low EO number and the anionic surfactant A-3, the rock surface wettability was altered to more oil-wet than the initial state.

In the aqueous system, surfactant molecules tend to concentrate on the interface of polar and nonpolar phases due to hydrophobic interactions. The orienting of the hydrophilic heads towards water increases its affinity to water. In contrast, exposure of the hydrophobic tails of these surfactant molecules to the aqueous phase could increase the hydrophobicity of the rock surface as observed in some cases. The wettability alteration of these rock chips indicates that the surfactant could form a layer covering the rock surface by adsorption of surfactant molecules.

Surfactant screening CA measured in surfactant solution:



Stability test CA measured in brine

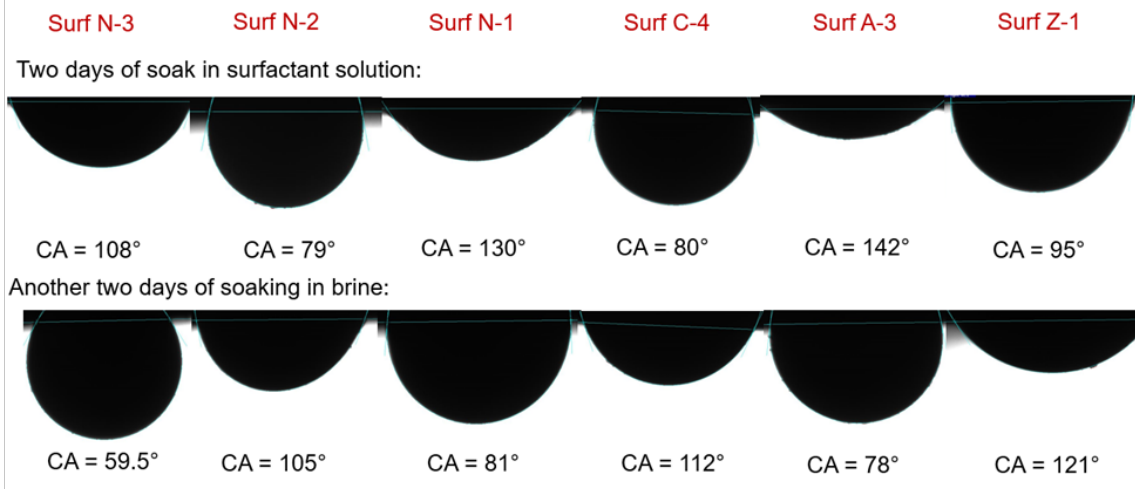
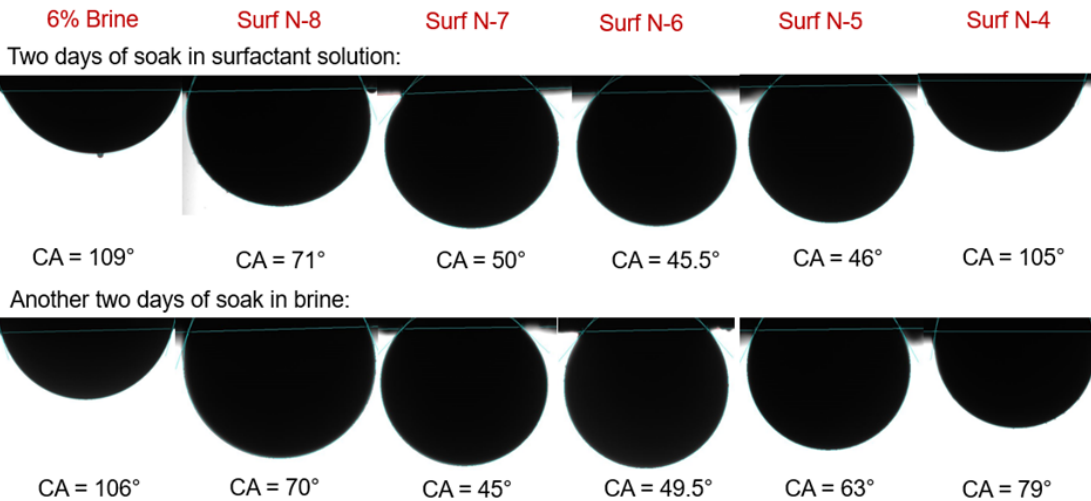


Figure 33. Contact angle of chips in the stability tests. First row: results of CA measurements in the surfactant screening; second row: CA results of the first soak period; third row: CA results of the second soak period; fourth and fifth row: results for different surfactants.

After completing the previous CA measurements, the once-soaked chips were then immersed into brine separately for another two days. The rock surface is covered with surfactant molecules, while the aqueous system is depleted in surfactant. During the second brine soak period, surfactant molecules could desorb from the rock surface due to the concentration difference. Finally, the contact angles of the chips were measured again in brine, and the captured images of the contact angle are also presented in **Fig. 33**. The CA of surf N-5 case increased up to 17 degrees after this soak. In contrast, the variation of CAs of surf N-6 and N-7 are within 5 degrees. This indicates the stability of the surf N-6 and N-7 is high, and surf N-5 has low stability. Nonionic surfactants with medium EO numbers show significant CA variation during those two soak periods, although the direction of CA change may be different. In the surfactant soak period, the chips in cases of surf N-1 and A-3 had been previously altered to oil-wet. However, the final CAs of N-1 and A-3 were smaller than the brine case due to the detachment of surfactant molecules along with the expulsion of oil molecules. This is recognized as a behavior of surfactant caused by low stability. The correlation of EO number with contact angles measured in the two soak periods is plotted in **Fig. 34**. A minimum contact angle is observed with 20-30 EO groups, which suggests that there exists an optimum EO number that results in longer duration of stable films.

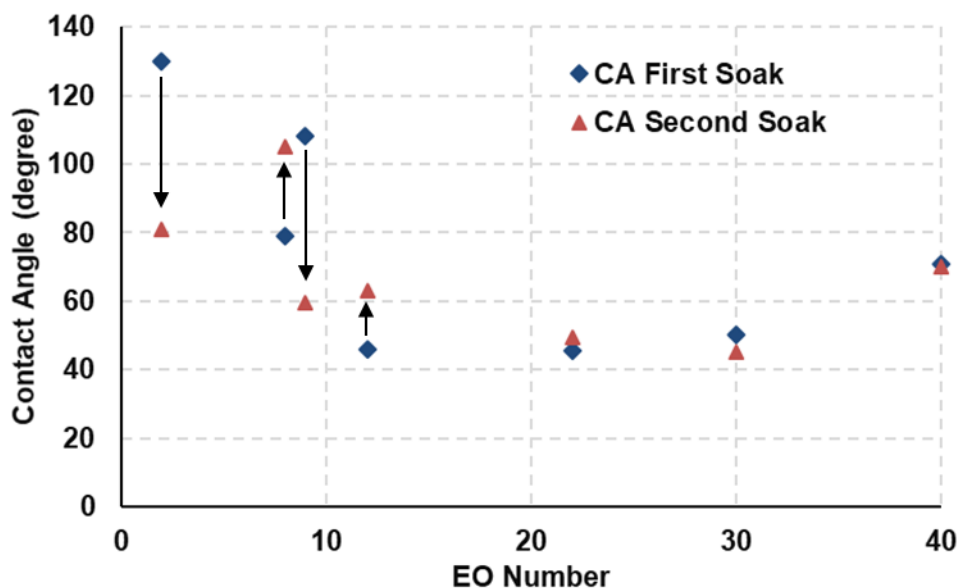


Figure 34. Correlation of CA with EO number. CA results of the first soak period are shown in blue rectangular, and CA results of the second soak period are shown in red triangle. CA could increase or decrease between two periods.

4.2. Application of Stability Test

The surfactant stability test is one of the surfactant evaluation methods, based on the retention of surfactant layers on the rock surface. In many studies, more than one surfactant has the capability to alter the wettability to water-wet. This test provides another level of scrutiny to quantify the influence of wettability alteration. Greater film stability implies nonionic surfactants can be optimized based on molecular structure for EOR applications.

Most of the results in the stability tests are consistent with the CA measurement results obtained during the surfactant screening. At high temperatures and high salinity, most nonionic surfactants are cloudy. In this study, cloud points of surf N-1, N-2, N-3, N-4, and N-5 are lower than the reservoir temperature. The cloudy solution scatters light

strongly, making it impossible to capture the shape of an oil droplet with a camera. It is also reasonable to assume the effectiveness of surfactants for wettability alteration diminish above the cloud point. In common CA measurements, those cloudy surfactants have to be tested at a lower temperature, but temperature has an effect on wettability and results in experiment error. In the stability test, rock chips are soaked in surfactant solutions at reservoir temperature, while the CA is measured in DW or brine and the shape of oil is always clearly visible. The stability test enables the CA measurement of those nonionic surfactants directly and the assessment of their performance in wettability alteration. This stability test also has potential for high pressure and ultra-high temperature tests, where the temperature exceeds 300°F. Almost every surfactant reaches the cloud point when the salinity level is high as well. The rock samples are soaked in the surfactant solutions at high pressure and ultra-high temperature, while the CA measurements could be performed under conditions that are favorable for experimental practice. Although surfactant begins to phase separate above cloud point and its efficacy diminishes, this method allows the measurement of actual surfactant effectiveness in wettability alteration.

5. SPONTANEOUS IMBIBITION EXPERIMENT

The effectiveness of surfactants in altering wettability and reducing IFT in unconventional reservoir rock and oil was discussed in the previous sections. The spontaneous imbibition experiments were performed to address the validity of the findings and qualitatively investigate the capability of select surfactants imbibing into ULR cores. In this study, spontaneous imbibition experiments functioned as the last laboratory step in the workflow for surfactant selection.

The aged cores from the Eagle Ford formation were immersed in aqueous solutions mixed with brines and the select surfactants. The experimental temperature was set to the reservoir temperature, to evaluate wettability alteration via associated oil recovery. CT scan method was used to visualize penetration of fluids in the cores.

5.1. Oil Production Curves of Spontaneous Imbibition Experiments

The volume of produced oil from the cores was measured on the top of the Amott Cells and converted to recovery factor by normalization to the initial oil volume. OOIP in these Eagle Ford cores was calculated by mass difference and density of oil at room temperature. Seven cores retrieved from the top of the Eagle Ford interval and four cores from the bottom of the Eagle Ford interval were used for imbibition experiments. The OOIP of the top seven core plugs is similar at approximately 1.65 cc. The porosity of these cores is around 5%, while the porosity of the plugs at the bottom of the interval is lower. The OOIP of the bottom plugs is about half of the plugs from the top of the interval.

First, seven core plugs from the top Eagle Ford interval were utilized for the surfactant evaluation in the spontaneous imbibition experiments. The base case was the 50/50 brine with a TDS of 6% with no surfactant and a corresponding CA of 106° . Results with surfactants were compared with the base case to assess the incremental oil recovery caused by surfactant additives. The produced water with a high salinity level was also tested to investigate the effect of salinity. Four nonionic surfactants with different EO numbers were tested at 0.20 wt% for their effectiveness of improving oil recovery. One experiment with surfactant N-6 at 0.10 wt% was performed to investigate the effect of surfactant concentration. Oil production curves from these spontaneous imbibition experiments are presented in **Fig. 35**.

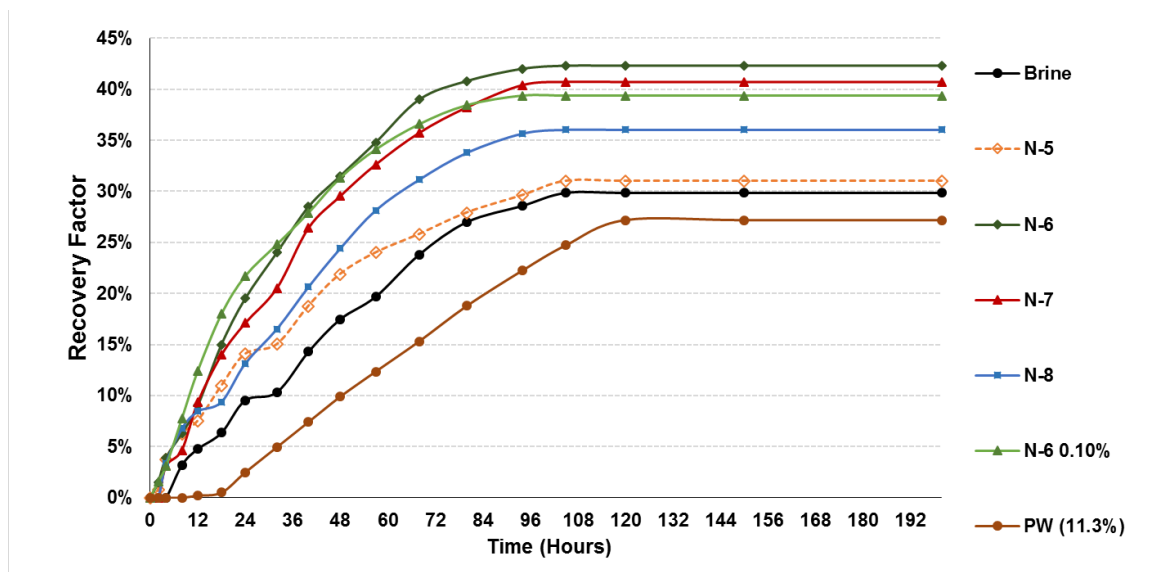


Figure 35. Production curves plotted with the spontaneous imbibition experiments results on cores retrieved from the top of Eagle Ford interval.

Oil recovery curves reached plateaus after four days of the imbibition process for all cases. For the base case scenario with only brine and no surfactant involved, about 30% of OOIP was produced from the spontaneous imbibition experiment. This result is consistent with the CA and IFT measurement that brine has remarkable IFT reduction and alters the wettability of rock to more water-wet from the initial condition. IFT of oil and water in brine was about half of the IFT in DW. CA decreased by approximately 15° in the 6% brine compared to DW. The recovery factor for the PW is lower than the base cases. The rock surface is more oil-wet in the PW than the 6% brine according to the previous CA measurements. This addresses the importance of the dilution of produced water with freshwater.

Adding proper surfactant into the aqueous phase always results in higher oil recovery compared to the base case. The highest ultimate oil recovery was achieved by using surf N-6, which is 42% of OOIP. Half of the oil production was during the first day, and 30% of OOIP was recovered within the first two days. More EO groups attached to the surfactant head does not result in greater recovery. This indicates that the EO group is most favorable in a certain range and surf N-6 has the optimum molecular structure for this particular oil/water/rock system tested in this study.

Surfactant N-6 was also tested at a lower concentration. The final recovery factor is lower than the higher concentration test, although faster recovery was observed at early time. Experimental results demonstrate that a higher concentration of surfactants leads to larger IFT reduction, more significant wettability alteration, and higher ultimate oil

recovery. An optimum concentration could be determined considering the balance of the production and the cost.

Spontaneous imbibition experiments were also performed using the core plugs from the bottom Eagle Ford interval to understand the effect of the rock properties. The 6% brine remained as the base case. One test with anionic surfactant A-1 was included additionally to verify the effect of the anionic surfactant on the wettability of Eagle Ford rock. The results are included in **Fig. 36**, compared with the previous experiments. The porosity of these cores retrieved from deeper depth is lower, and oil penetrated into these core plugs was less than the top Eagle Ford cores in the aging process. CA measurement results indicate that the wettability of the bottom Eagle Ford rock is more oil-wet than the top rock with and without surfactant. Lower recovery factors were achieved for these low-porosity cores compared with previous experiments. In the base case scenario, only 10% of OOIP was produced. Although the mechanism for the effect of rock properties on oil recovery is not clear, the performance of surfactant additives is consistent with different cores. The recovery factor with surfactant N-6 was twice as high as the base case. Nonionic surfactant N-7 leads to an increase in oil recovery, less than surf N-6. The recovery factor of the core plug with anionic surfactant was lower than the base case, which is consistent with the CA measurement.

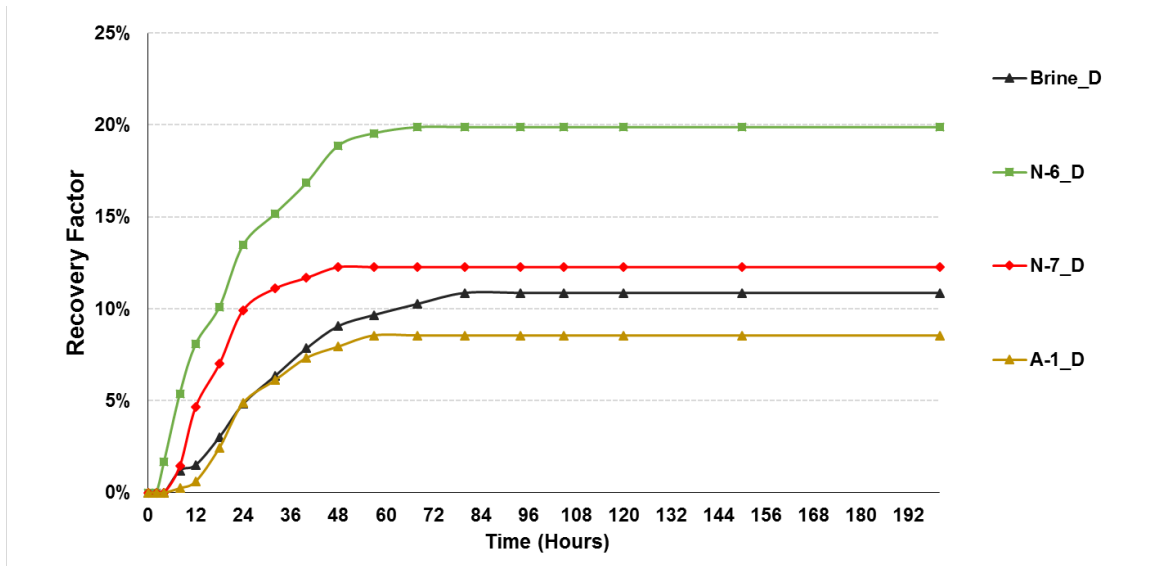


Figure 36. Production curves of spontaneous imbibition experiments on the lower porosity cores from the bottom of Eagle Ford interval.

5.2. Correlation between recovery factor and contact angle

During the imbibition experiments, we observed black oil was expelled out of the rock and attached on the rock surface for a while, which is presented in **Fig. 37**. Then, the oil droplets gathered and detached from the rock surface slowly with buoyancy force. The contact angle of the oil droplet and core surface was larger than 90° for the base case, and CAs decrease to lower than 90° with surfactant additives. Therefore, the oil droplets need a longer time to detach from the rock surface for the base case. Wettability alteration can improve ultimate oil recovery and increase the production rate. We also observed that the black oil preferred to be produced along with the bedding planes and fractures of the core plugs. Bedding planes and micro-fractures have higher conductivity than the matrix, which provide high flow paths for surfactant invaded into core plugs and oil extract out of cores. We believe these observations infer concurrent imbibition is the primary recovery

mechanism as aqueous phase imbibes in smaller pore throats associated with lower permeability portions of the rock. The oil is expelled through the more permeability features. This observation is contrary to the concept countercurrent imbibition where oil flows in the opposite direction of the aqueous phase. Thus, these observations have implications on the relevance of experiments conducted by scaling off oil faces of the core and measuring oil recovery from the same face that aqueous phase is allowed to imbibe.

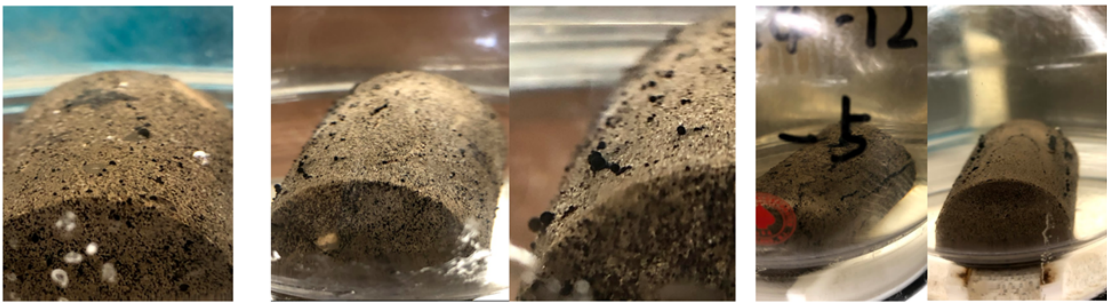


Figure 37. Observations of oil droplets expelled from core samples during spontaneous imbibition experiments.

The results obtained from contact angle measurements and spontaneous imbibition experiments are plotted in **Fig. 38**. The oil recovery results from cores imbibition are consistent with the wettability evaluation on the rock surface. The surfactant that leads to lower contact angle results in higher oil recovery. Surf N-6 was measured to alter the rock surface into the most water-wet condition and was stable in the stability test. This confirms that nonionic surfactant N-6 is effective in oil recovery and a suitable candidate for EOR projects. This emphasized the validity of the surfactant selection workflow.

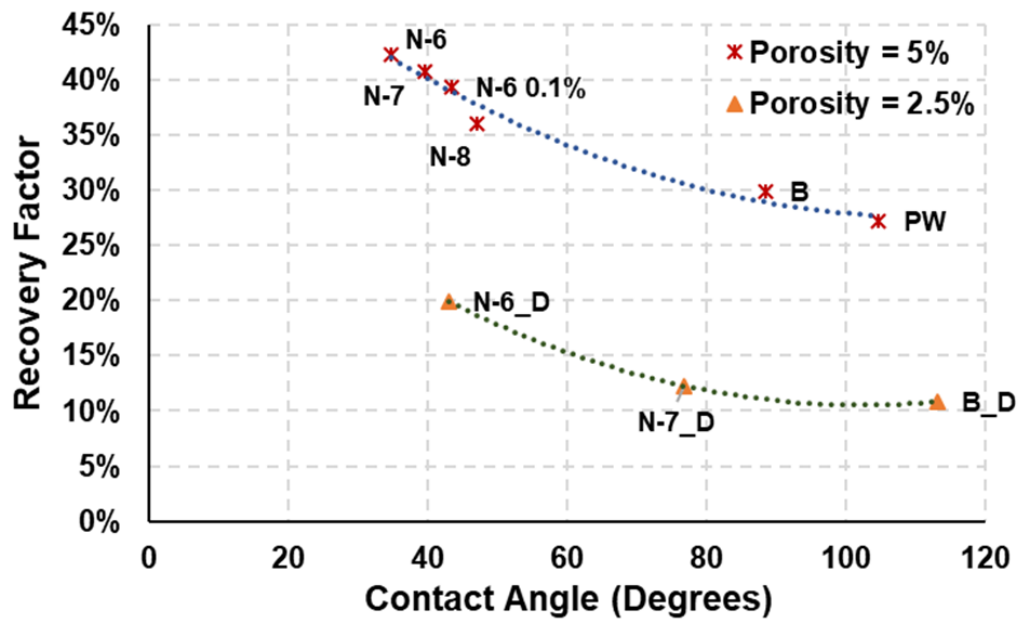


Figure 38. Correlation between contact angle and recovery factor.

5.3. CT Scan Results

CT number is related to the density of the scanned sample with the higher the CT number, the greater the density. Higher CT number demonstrates high water saturation and is shown as a brighter color, while lower CT number indicates higher oil saturation shown as reddish color. A compilation of periodic CT images obtained from imbibition experiments is presented in **Fig. 39**. A time-lapse 2D cross section at the same location showing increasing water saturation is presented. A general color shift from red to green was observed in the process, which indicates an increase in water saturation and movement of water into the core plugs. The trend of fluid moving along the bedding plane was also shown in the images.

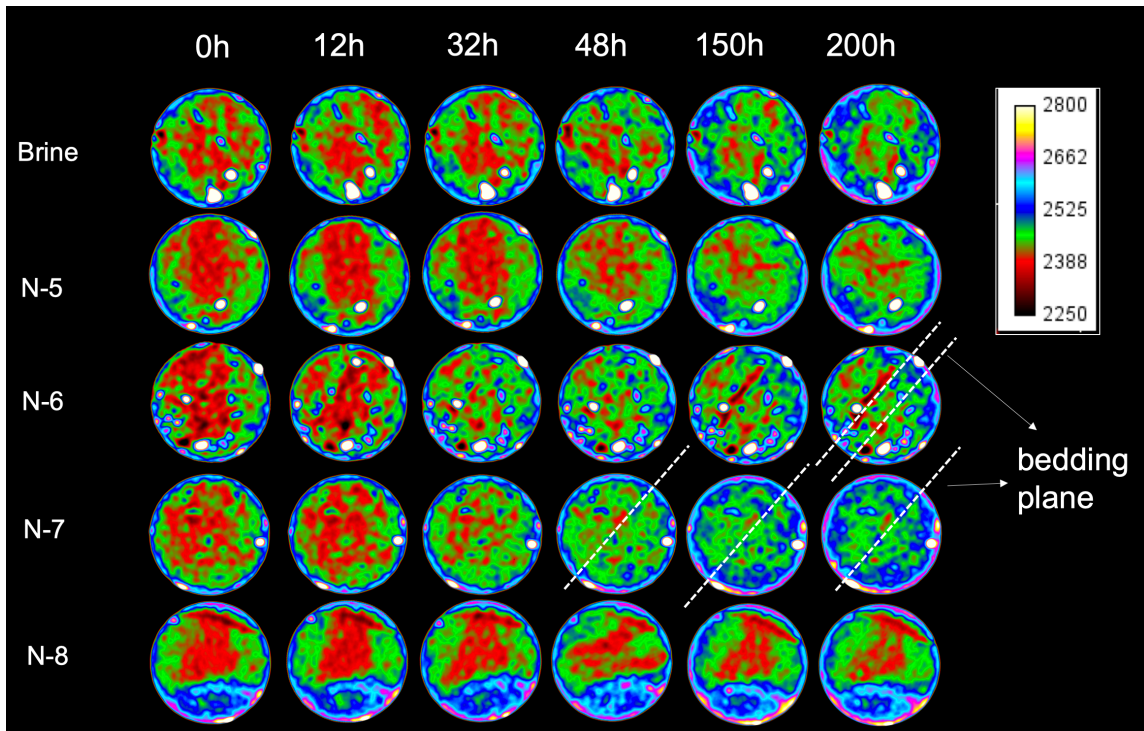


Figure 39. Periodic CT scan slides of core plugs during imbibition experiments.

5.4. Osmotic Pressure

Osmotic pressure (Π) is a measure of the tendency of a solution to transfer solvent by osmosis and defined by **Eq. 5** from Marine and Fritz (1981),

$$\Pi = \frac{RT}{V} \ln \left(\frac{a_1}{a_2} \right) \quad \dots (5)$$

where a_1 , a_2 are water activities of low-salinity brine and high-salinity brine. Water activity for fresh water is 1.0, R is gas constant, T is temperature in °K, and V is molar volume in liter/g-mol.

After the spontaneous imbibition process was completed, the core immersed in the 6% brine was transferred to another Amott Cell containing 6% brine + 0.20 wt% surfactant N-6. No oil was expelled out the core for a period of one week. The capillary pressure reaches a value of zero at final oil recovery after imbibition ceases. Although it was confirmed that surfactant has the capability of altering wettability and recovery factor is greater with surfactant, the surfactant cannot imbibe into the rock matrix without driving forces.

Similarly, the core submerged in the 11% produced water was transferred to an Amott Cell containing 6% brine. The surface of the core was gently wiped before the transfer in order to ensure no residual oil remained on the surface. Oil drops were expelled out and retained on the core surface within two hours. The oil drops on the core surface are shown in **Fig. 40**. The oil expulsion finished in two days and approximately 0.01cc oil (1% OOIP) was produced in this process.

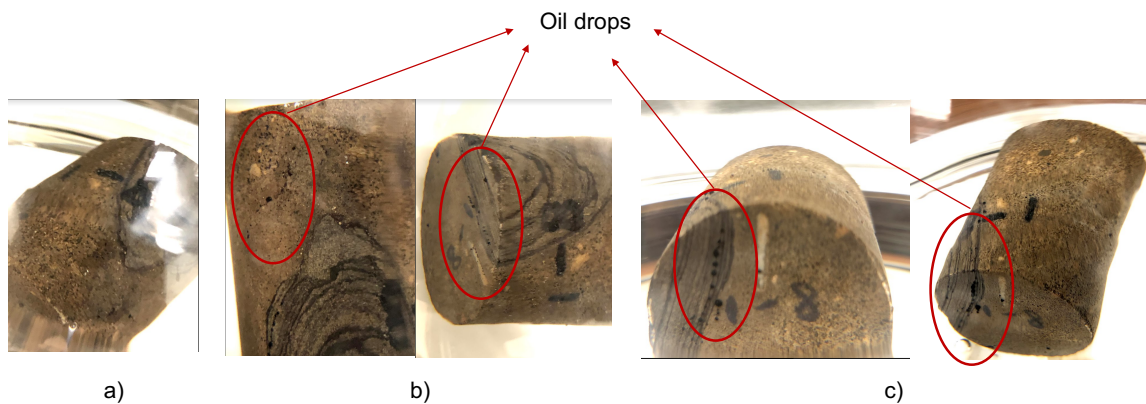


Figure 40. Oil drops on the core surface at a) 1h, b) 2h, and c) 1d after changing the salinity from PW to 6% brine.

This core was then transferred to another Amott Cell containing DW plus 0.20 wt% surfactant N-6 after 7 days of soak in the 6% brine. Approximately 0.005cc more oil was produced with the distilled water and surfactant in 24h period. It can be argued that the salinity inside the core was higher than the aqueous solution, and the composition of fluid inside the core was gradually changed by the osmotic pressure. Although the oil volume produced in this process was much less than that in the imbibition process, the osmotic pressure provides one possible method to drive the surfactant into the rock and alter the matrix wettability.

6. MECHANISM ANALYSIS OF WETTABILITY ALTERATION

The mechanism of wettability alteration on the rock surface is discussed in this section with the results from experiments. It is a summary of experimental observations and an interpretation of the surfactant molecular structure on the rock-fluid interaction in ULR. The effects of surfactant formulation, surfactant concentration, and brine salinity on wettability alteration and oil recovery factor were investigated in the experiments. Understanding the behavior (adsorption and desorption) of surfactants in the rock-oil-water system provides direction for further experimental design. The effectiveness of various surfactants was explained based on experimental results, seeking to unveil the real potential of surfactants in EOR.

6.1. IFT Reduction with Surfactant

The mechanism of oil-water IFT reduction with surfactant is straightforward. Surfactants have characteristic amphiphilic structure and are soluble both in polar and nonpolar media. Their solubility depends on the balance between the hydrophilic and hydrophobic groups (Torstensson and Hult 1992). Surfactant molecules tend to concentrate at interfaces between media of different polarities due to this dual nature. Surfactant molecules could penetrate into the oil phase and adsorb on the oil-water interface, with the hydrophilic heads aligning towards the aqueous phase. Hydrophobicity of the oil surface is reduced by the surfactant molecules, and the forces between the water

molecules and molecules on the interface are increased. The reduction of interfacial tension due to the adsorption and orientation of surfactants is illustrated in **Fig. 41**.

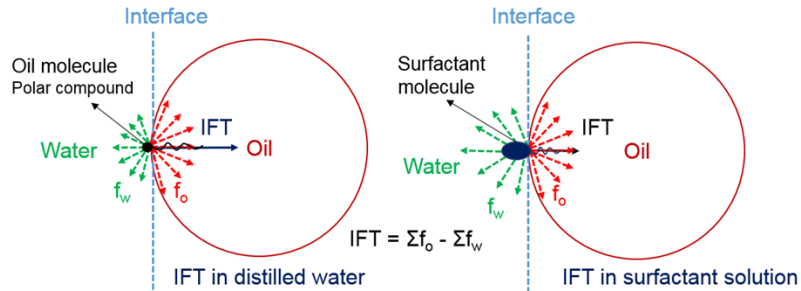


Figure 41. Mechanism of IFT reduction with surfactant. f_o is the force between oil molecule and the molecule on the interface, and f_w is the force between water molecule and the molecule on the interface.

The partition coefficient defined in **Eq. 6** is used to describe the penetration of surfactant molecules into the oil phase at equilibrium (IUPAC 1997). In this equation, K_D is the equilibrium constant, C_{oil} is the concentration of surfactant in the oil phase, and C_{aq} is the surfactant concentration in the aqueous phase. The partition coefficient is also a measure of the hydrophobicity of a chemical substance in addition to HLB and HLD values as discussed in the introduction section.

$$K_D = \frac{C_{oil}}{C_{aq}} \quad \dots (6)$$

According to the experimental and calculated partition coefficients results (Crook et al. 1965), the partition coefficient of nonionic surfactants decreases as the ethylene

oxide (EO) chain length increases. Nonionic surfactants with larger EO numbers are less hydrophobic and fewer surfactant molecules can penetrate into the oil phase. This is consistent with the IFT results in this study that nonionic surfactants with larger EO numbers lead to higher oil-water IFT. In addition, electrostatic repulsions between the negatively charged oil surface and the surfactant heads obscure the penetration of ionic surfactant molecules from bulk solution to the solid surface. This is the reason that ionic surfactants generally lead to less IFT reduction for the Eagle Ford heavy oil.

6.2. Surfactant Adsorption and Wettability Alteration

Polar compounds in the crude oil, resins, and aromatics, have a similar molecular structure. Some polar compounds consist of a polar group and nonpolar groups. The polar groups of oil compounds have electrostatic interactions with the rock surface. This leads to adsorption of oil on the rock surface and penetration of oil into the rock matrix. Meanwhile, the hydrophobic groups increase the hydrophobicity of the rock surface and induce an oil-wet condition. Due to hydrophobic interactions, surfactant molecules adsorb on the rock surface forming a surfactant layer, orienting themselves in an energetically favorable way. Similarly, surfactant molecules also adsorb on the hydrophobic oil surface, reducing oil-water IFT.

Without surfactant contained in the aqueous system, the surfaces of the rock and the oil are both hydrophobic. Strong attractions between the oil and rock surface lead to low rock-oil surface tension. The shape of oil droplet is maintained because the attractions between oil molecules are greater than the forces between oil and rock surface. The

spherical shape of the oil droplet cannot be maintained by forces differential and oil droplet spreads out on the surface once it contacts the rock. Therefore, the contact angle of oil in contact with the rock is larger than 90 degrees. With surfactants in the aqueous phase, in contrast, the rock surface is covered by the layer of adsorbed surfactant molecules. The hydrophobic tails tend to orient towards the nonpolar surface, and the hydrophilic heads of surfactant orient towards the polar phase. The rock surface is altered to hydrophilic or water-wet with the adsorbed surfactant layer. The surface tension of oil and the rock is large due to the repulsive forces between the oil droplet and the hydrophilic surface. The oil droplet could maintain its spherical shape on the rock surface, and thus contact angle with surfactant additives is smaller than 90 degrees. The whole simplified process of wettability alteration with oil molecules and surfactant molecules is illustrated in **Fig. 42**.

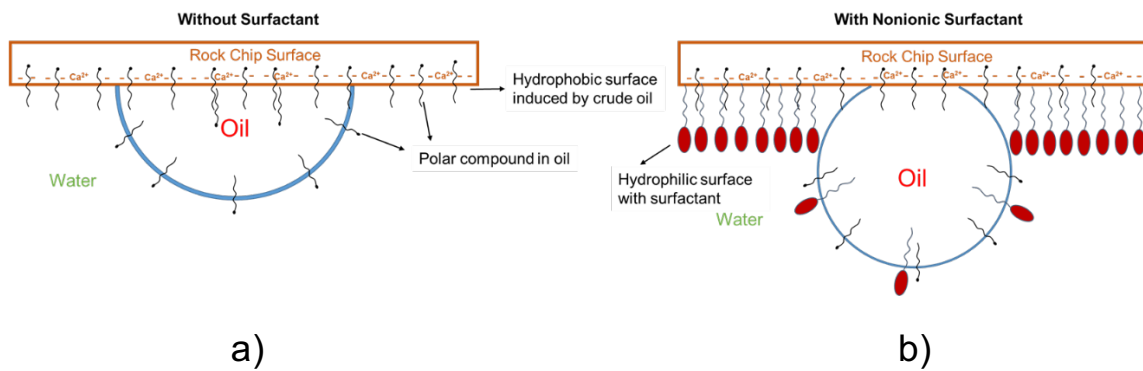


Figure 42. Schematics of contact angle forming on the rock surface. In a) polar components from oil interact with positively charged calcite allowing oil to spread. b) surfactant tails interact by hydrophobic mechanism with crude oil molecules allow charged head group to orient away from surface thereby creating oil repulsion.

6.3. Wettability Alteration with Different Surfactant Molecular Structure

Surfactant molecules aggregate in the solid-liquid system due to hydrophobic interactions. With only hydrophobic interactions and no other type of interactions, surfactant molecules tend to form a dense layer on the rock surface. However, the molecular distance between surfactant molecules increases due to electrostatic interactions and hydrogen bonds. Head groups of ionic surfactants are carrying the same-type electric charge, and repulsive forces exist between the head groups. In the aqueous system, oxygen atoms of EO groups in the hydrophilic heads of nonionic surfactants form hydrogen bonds with hydrogen atoms in water molecules. The hydrophilic heads tend to attract water molecules instead of other surfactant molecules. This affinity increases the molecular distance of nonionic surfactants.

In addition, the surface of the shale rock carries both positive and negative charges. The molecular distance of ionic surfactants increases due to the electrostatic repulsive forces between the head groups and the like-charged sites on the rock surface as well. These lead to a low adsorption density of surfactant molecules and exposure of the hydrophobic tails. At low surfactant concentrations, as shown in **Fig. 43**, heads of cationic surfactants are attracted to the rock surface with the electrostatic interactions between the positively charged heads and the negatively charged minerals. The rock surface is covered with monolayer surfactant molecules. The hydrophobic tails orient towards the aqueous phase and the surface is oil-wet. At high concentrations, a double layer of surfactant molecules forms due to high intensity hydrophobic interactions. The rock surface is then altered to water-wet, with the hydrophilic functional groups contacting the aqueous phase.

This is consistent with the surfactant behavior described in the two-step adsorption model (Zhu and Gu 1991, Tabor et al. 2010). Surfactants are adsorbed as individual molecules in the first layer on the solid surface through electrostatic attractions in the first step. Then, adsorption increases as hemi-micelles or bilayers form through hydrophobic interactions in the second step. Nonionic surfactants, however, were measured to have an S-type adsorption isotherm, indicating only one-step formation (Gu and Zhu 1990). Nonionic surfactants were measured to form monolayer on the rock surface. This trend of surfactant is more significant on quartz glass slides, which carry the negative surface charge. Nonionic and anionic surfactant can only form monolayer on the surface of glass slides and alter it to more water-wet. In contrast, cationic surfactants have two step adsorption due to the electrostatic attractions. The surface of the glass slides was altered to oil-wet by the low concentration cationic surfactants.

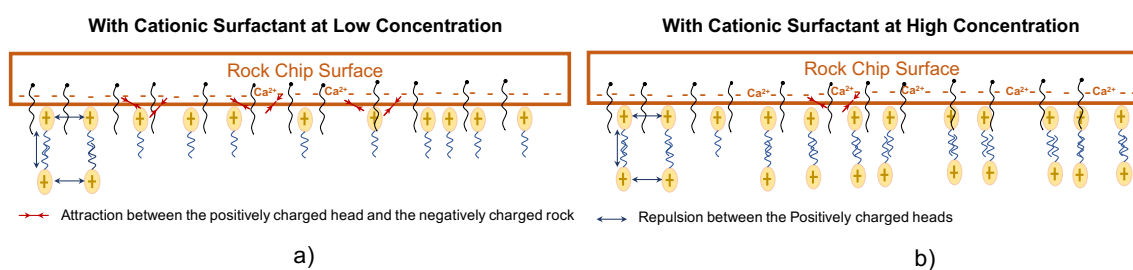


Figure 43. Schematic of cationic surfactant molecules adsorption at a) low concentrations forming monolayer and b) high concentration forming bilayer.

On the clean glass slide surface, illustrated in **Fig. 44**, anionic surfactant molecules are adsorbed due to hydrophilic interactions. The repulsive forces between the negatively-charged surface and negatively-charged heads ensure that the hydrophilic heads always

orient towards the aqueous phase. Thus, the glass slide was altered to strongly water-wet with an anionic surfactant. Whereas on the surface of carbonate shale rocks, the negatively-charged heads are attracted by the positively charged calcite or dolomite. The rock surface could be altered to oil-wet. The surface cannot be altered to water-wet unless double layers form when strong hydrophobic interactions prevails over the electrostatic interactions at high surfactant concentrations. On the surface of siliceous shale rock, quartz and clay minerals are the most abundant constituents. Attraction forces between the surface and the head groups are not significant. Wettability of the rock surface can be altered to water-wet with low concentration anionic surfactants.

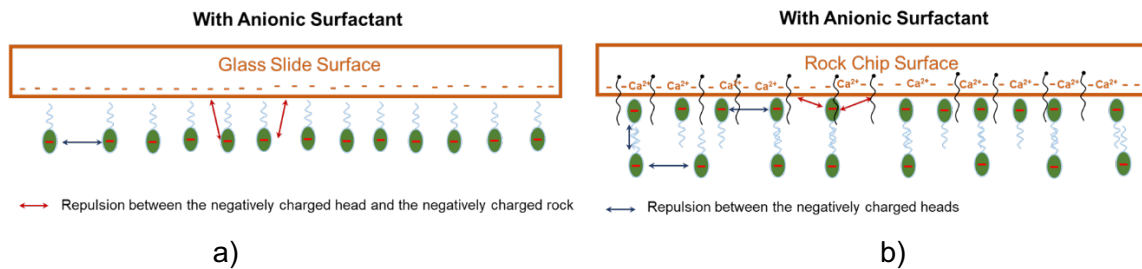


Figure 44. Schematic of anionic surfactant molecules adsorption on a) clean glass slide and b) aged shale rock chip.

Head groups of nonionic surfactants carry no charge which causes no electrostatic repulsion between surfactant molecules and rock surfaces. Nonionic surfactant molecules can align on the surface with shorter molecular distance. Adsorption density of nonionic surfactants is typically higher than ionic surfactants. Therefore, nonionic surfactants would have the most stable layer on the surface. This mechanism explains the superiority of the nonionic surfactants compared to ionic surfactant in altering rock wettability.

6.4. Desorption of Surfactant Molecules

Surfactant loss in the aqueous phase due to the adsorption on the porous media of the reservoir is a concern in surfactant EOR. Surfactant desorption from the rock surface due to the concentration difference weakens the effectiveness of the injected surfactant. Gogoi (2011) studied the adsorption and desorption of surfactant by measuring and calculating the volume of surfactant injected and surfactant in the effluent after flooding in a porous core sample. Alkaline-surfactant solution was injected in the core followed by an extended waterflood process. The normalized surfactant concentration versus PV of fluid produced curve demonstrated that surfactant adsorbed first and then part of it desorbed into the water phase during the extended waterflood.

The surfactant stability test was proposed to investigate the duration of wettability alteration in consideration of surfactant desorption. Based on the surfactant stability test, after the soak period in surfactant solution, the surfactant layers retain on the rock surface when contact angle measurements are performed in distilled water or brine. It is probably because that the surfactant molecules have penetrated into the rock matrix and bonded tightly with minerals. In the cases with high stability surfactant, the rock surface remained water-wet and the variation of CA was negligible. This is an indication that surfactant molecules did not significantly desorb from the rock. The water-wet condition lasted for a long period, and therefore continuous high oil recovery would be achieved with high stability surfactant.

7. CONCLUSIONS

This study presents a systematic workflow for the selection of surfactant formulations for wettability alteration. The workflow consists of three parts; 1) surfactants screening, 2) stability tests, and 3) spontaneous imbibition experiments. The validity of this workflow is addressed by the experimental results and mechanism analysis. The novelty of this study is a proposed workflow of the surfactant stability test to supplement the common contact angle measurement, enabling evaluation of cloudy nonionic surfactants as well. Based on the experimental results we conclude:

1. Both head charge and tail structure have a significant effect on the performance of surfactants in the wettability alteration of shale rock. Ionic surfactants with longer carbon chains generally lead to lower IFT and smaller CA or more water-wet surface.
2. Nonionic surfactants examined were observed to have better performance than ionic surfactants for wettability alteration. The adsorbed nonionic surfactant layer has a more stable structure than ionic surfactants. An optimum EO number exists for the nonionic surfactant to have the highest stability and maximum recovery improvement.
3. Higher surfactant concentration results in larger IFT reduction and smaller contact angle. A relatively high concentration is necessary to alter the rock into the water-wet region. Recovery factor of the surfactant in the spontaneous imbibition experiments also increases with increasing surfactant concentration.

4. The same surfactants were observed to have different performances on different formation samples. For instance, anionic surfactants altered Wolfcamp rock to more water-wet, but altered Eagle Ford rock to more oil-wet.
5. Water-wet surface of clean glass slide was altered to oil-wet by cationic surfactant at low concentration, and back to water-wet at high surfactant concentration. The surface could be altered to more water-wet by anionic and nonionic surfactants.
6. The salinity of brine has effects on rock wettability and surfactants performance, resulting in lower IFT and larger CA in brine than in distilled water. The cloud point of nonionic surfactant increases with increased salinity.
7. Stability tests demonstrate that surfactants with high stability have a continuous effect on wettability alteration. The water-wet condition of the rock surface is durable when the surfactant concentration decreases in bulk solution.
8. Nonionic surfactant N-6 possesses the best performance with the highest recovery factor of 42% OOIP from spontaneous imbibition experiment, which is consistent with the surfactant screening and stability tests.
9. Imbibition was observed to occur into the center of the core as observed from the CT images of all test core plugs, and oil expulsion was observed along the bedding planes and micro-fractures.
10. The optimum surfactant must be assessed with specified oil and rock samples for EOR project designing.

REFERENCES

- Adel, Imad A., Tovar, Francisco D., Zhang, Fan et al. 2018. The Impact of MMP on Recovery Factor During CO₂ – EOR in Unconventional Liquid Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, USA. 2018/9/24/. <https://doi.org/10.2118/191752-MS>.
- Ahmadi, Mohammad Ali and Shadizadeh, Seyed Reza. 2013. Experimental investigation of adsorption of a new nonionic surfactant on carbonate minerals. *Fuel* **104**: 462-467. <https://doi.org/10.1016/j.fuel.2012.07.039>.
- Al-Shakry, Badar, Shiran, Behruz Shaker, Skauge, Tormod et al. 2018. Enhanced Oil Recovery by Polymer Flooding: Optimizing Polymer Injectivity. Presented at the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, Dammam, Saudi Arabia. 2018/8/16/. <https://doi.org/10.2118/192437-MS>.
- Alamooti, Amirhossein Mohammadi and Malekabadi, Farzan Karimi. 2018. Chapter One - An Introduction to Enhanced Oil Recovery. In *Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs*, ed. Alireza Bahadori, 1-40. Gulf Professional Publishing.
- Alfarge, Dheiaa, Wei, Mingzhen, and Bai, Baojun. 2017. IOR Methods in Unconventional Reservoirs of North America: Comprehensive Review. Presented at the SPE Western Regional Meeting, Bakersfield, California. 2017/4/23/. <https://doi.org/10.2118/185640-MS>.
- Alhashim, Hassan W., Zhang, Fan, Schechter, David S. et al. 2019. Investigation of the Effect of Pore Size Distribution on the Produced Oil from Surfactant-Assisted Spontaneous Imbibition in ULRs. Presented at the SPE Annual Technical Conference and Exhibition, Calgary, Alberta, Canada. 2019/9/23/. <https://doi.org/10.2118/195931-MS>.

- Alila, Sabine, Boufi, Sami, Belgacem, Mohamed Naceur et al. 2005. Adsorption of a Cationic Surfactant onto Cellulosic Fibers I. Surface Charge Effects. *Langmuir* **21** (18): 8106-8113. <https://doi.org/10.1021/la050367n>.
- Alvarez, J. O., Saputra, I. W. R., and Schechter, D. S. 2017. The Impact of Surfactant Imbibition and Adsorption for Improving Oil Recovery in the Wolfcamp and Eagle Ford Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA. 2017/10/9/. <https://doi.org/10.2118/187176-MS>.
- Alvarez, Johannes O., Neog, Anirban, Jais, Afif et al. 2014. Impact of Surfactants for Wettability Alteration in Stimulation Fluids and the Potential for Surfactant EOR in Unconventional Liquid Reservoirs. Presented at the SPE Unconventional Resources Conference, The Woodlands, Texas, USA. 2014/4/1/. <https://doi.org/10.2118/169001-MS>.
- Anderson, William G. 1986. Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. *Journal of Petroleum Technology* **38** (10): 1125-1144. <https://doi.org/10.2118/13932-PA>.
- Ataman, E., Andersson, M. P., Ceccato, M. et al. 2016. Functional Group Adsorption on Calcite: I. Oxygen Containing and Nonpolar Organic Molecules. *The Journal of Physical Chemistry C* **120** (30): 16586-16596. <https://doi.org/10.1021/acs.jpcc.6b01349>.
- Austad, Tor and Standnes, Dag C. 2003. Spontaneous imbibition of water into oil-wet carbonates. *Journal of Petroleum Science and Engineering* **39** (3): 363-376. <http://www.sciencedirect.com/science/article/pii/S0920410503000755>.
- Belhaj, Ahmed Fatih, Elraies, Khaled Abdalla, Mahmood, Syed Mohammad et al. 2020. The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review. *Journal of Petroleum Exploration and Production Technology* **10** (1): 125-137. <https://doi.org/10.1007/s13202-019-0685-y>.

- Ben-Naim, Arieh Y. 2012. *Hydrophobic interactions*: Springer Science & Business Media.
- Bera, Achinta, Kumar, T., Ojha, Keka et al. 2013. Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. *Applied Surface Science* **284**: 87-99.
<http://www.sciencedirect.com/science/article/pii/S0169433213013378>.
- Bidhendi, Mehrnoosh Moradi, Kazempour, Mahdi, Ibanga, Uwana et al. 2019. A Set of Successful Chemical EOR Trials in Permian Basin: Promising Field and Laboratory Results. Presented at the SPE/AAPG/SEG Unconventional Resources Technology Conference, Denver, Colorado, USA. 2019/7/31/.
<https://doi.org/10.15530/urtec-2019-881>.
- Blomquist, Peter K. 2016. Wolfcamp horizontal play, Midland Basin, West Texas. *Proc.*, AAPG Pacific Section and Rocky Mountain Section Joint Meeting, 2016.
- Bryan, Jonathan Luke and Kantzas, Apostolos. 2007. Enhanced Heavy-Oil Recovery by Alkali-Surfactant Flooding. Presented at the SPE Annual Technical Conference and Exhibition, Anaheim, California, U.S.A. 2007/1/1/.
<https://doi.org/10.2118/110738-MS>.
- Chen, H. L., Lucas, L. R., Nogaret, L. A. D. et al. 2000. Laboratory Monitoring of Surfactant Imbibition Using Computerized Tomography. Presented at the SPE International Petroleum Conference and Exhibition in Mexico, Villahermosa, Mexico. 2000/1/1/. <https://doi.org/10.2118/59006-MS>.
- Craig, Forrest F. 1971. *The reservoir engineering aspects of waterflooding*, Vol. 3: HL Doherty Memorial Fund of AIME New York.
- Crook, E. H., Fordyce, D. B., and Trebbi, G. F. 1965. Molecular weight distribution of nonionic surfactants: II. Partition coefficients of normal distribution and homogeneous p, t-octylphenoxyethoxy-ethanols (OPE's). *Journal of Colloid Science* **20** (3): 191-204.
<http://www.sciencedirect.com/science/article/pii/0095852265900103>.

- Cui, Leyu, Ma, Kun, Abdala, Ahmed A. et al. 2014. Adsorption of a Switchable Cationic Surfactant on Natural Carbonate Minerals. *SPE Journal* **20** (01): 70-78. <https://doi.org/10.2118/169040-PA>.
- Das, Soumik, Nguyen, Quoc, Patil, Pramod D. et al. 2018. Wettability Alteration of Calcite by Nonionic Surfactants. *Langmuir* **34** (36): 10650-10658. <https://doi.org/10.1021/acs.langmuir.8b02098>.
- Davies, JT. 1957. A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent. *Proc 2nd Intern Congr Surface Activity, Butterworths Scientific Publication, London* **426**.
- Department of Energy. 2010. Enhanced oil recovery. Retrieved from <https://www.energy.gov/fe/science-innovation/oil-gas-research/enhanced-oil-recovery>.
- Dick, S. G., Fuerstenau, D. W., and Healy, T. W. 1971. Adsorption of alkylbenzene sulfonate (A.B.S.) surfactants at the alumina-water interface. *Journal of Colloid and Interface Science* **37** (3): 595-602. <http://www.sciencedirect.com/science/article/pii/0021979771903377>.
- Donaldson, Erle C., Thomas, Rex D., and Lorenz, Philip B. 1969. Wettability Determination and Its Effect on Recovery Efficiency. *Society of Petroleum Engineers Journal* **9** (01): 13-20. <https://doi.org/10.2118/2338-PA>.
- Dong, Shuli, Li, Xin, Xu, Guiying et al. 2007. A Cationic Fluorocarbon Surfactant DEFUMACl and Its Mixed Systems with Cationic Surfactants: ¹⁹F NMR and Surface Tension Study. *The Journal of Physical Chemistry B* **111** (21): 5903-5910. <https://doi.org/10.1021/jp0705469>.
- Energy Information Administration 2020. How much shale (tight) oil is produced in the United States? Retrieved from <https://www.eia.gov/tools/faqs/faq.php?id=847&t=6>.

- Fakcharoenphol, Perapon, Kurtoglu, Basak, Kazemi, Hossein et al. 2014. The Effect of Osmotic Pressure on Improve Oil Recovery from Fractured Shale Formations. Presented at the SPE Unconventional Resources Conference, The Woodlands, Texas, USA. 2014/4/1/. <https://doi.org/10.2118/168998-MS>.
- Fanchi, John R. 2002. Chapter 7 - Measures of Rock-Fluid Interactions. In *Shared Earth Modeling*, ed. John R. Fanchi, 108-132. Woburn: Butterworth-Heinemann.
- Gogoi, Subrata Borgohain. 2011. Adsorption–Desorption of Surfactant for Enhanced Oil Recovery. *Transport in Porous Media* **90** (2): 589. <https://doi.org/10.1007/s11242-011-9805-y>.
- Goloub, Tatiana P., Koopal, Luuk K., Bijsterbosch, Bert H. et al. 1996. Adsorption of Cationic Surfactants on Silica. Surface Charge Effects. *Langmuir* **12** (13): 3188-3194. <https://doi.org/10.1021/la9505475>.
- Graue, A., Aspenes, E., Bognø, T. et al. 2002. Alteration of wettability and wettability heterogeneity. *Journal of Petroleum Science and Engineering* **33** (1): 3-17. <http://www.sciencedirect.com/science/article/pii/S0920410501001711>.
- Griffin, William C. 1954. Calculation of HLB values of non-ionic surfactants. *J Soc Cosmet Chem* **5**: 249-256.
- Gu, Tiren and Zhu, Bu-Yao. 1990. The S-type isotherm equation for adsorption of nonionic surfactants at the silica gel—water interface. *Colloids and Surfaces* **44**: 81-87. <http://www.sciencedirect.com/science/article/pii/016666229080189B>.
- Guo, Jianying, Zhang, Lei, Liu, Shengyu et al. 2018. Effects of hydrophilic groups of nonionic surfactants on the wettability of lignite surface: Molecular dynamics simulation and experimental study. *Fuel* **231**: 449-457. <https://doi.org/10.1016/j.fuel.2018.05.106>.
- Gupta, Robin and Mohanty, Kishore Kumar. 2007. Temperature Effects on Surfactant-Aided Imbibition Into Fractured Carbonates. Presented at the SPE Annual

Technical Conference and Exhibition, Anaheim, California, U.S.A. 2007/1/1/.
<https://doi.org/10.2118/110204-MS>.

He, Kai, Xu, Liang, Gao, Yuefeng et al. 2014. Validating Surfactant Performance in the Eagle Ford Shale: A Correlation between the Reservoir-on-a-Chip Approach and Enhanced Well Productivity. Presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA. 2014/4/12/.
<https://doi.org/10.2118/169147-MS>.

Hill, R. M. 1997. Siloxane surfactants. In *Specialist Surfactants*, ed. I. D. Robb, 143-168. Dordrecht: Springer Netherlands.

Hou, Bao-feng, Wang, Ye-fei, and Huang, Yong. 2015. Mechanistic study of wettability alteration of oil-wet sandstone surface using different surfactants. *Applied Surface Science* **330**: 56-64. <https://doi.org/10.1016/j.apsusc.2014.12.185>.

IUPAC, I., 1997. Compendium of chemical terminology. *the "Gold Book"*.

Jian, Guoqing, Puerto, Maura C., Wehowsky, Anna et al. 2016. Static Adsorption of an Ethoxylated Nonionic Surfactant on Carbonate Minerals. *Langmuir* **32** (40): 10244-10252. <https://doi.org/10.1021/acs.langmuir.6b01975>.

Jones, Marcus, Stratton, Jay, Newton, Robert et al. 2016. Case Study: Successful Applications of Weak Emulsifying Surfactants in the Wolfcamp Formation of Reagan County, TX. Presented at the SPE Liquids-Rich Basins Conference - North America, Midland, Texas, USA. 2016/9/21/.
<https://doi.org/10.2118/181771-MS>.

Karnanda, Wimpy, Benzagouta, M. S., AlQuraishi, Abdulrahman et al. 2013. Effect of temperature, pressure, salinity, and surfactant concentration on IFT for surfactant flooding optimization. *Arabian Journal of Geosciences* **6** (9): 3535-3544.
<https://doi.org/10.1007/s12517-012-0605-7>.

Kathel, P. and Mohanty, K. K. 2013. Wettability Alteration in a Tight Oil Reservoir. *Energy & Fuels* **27** (11): 6460-6468. <https://doi.org/10.1021/ef4012752>.

- Khalil, Rabah A. and Saadoon, Fadya A. 2015. Effect of presence of benzene ring in surfactant hydrophobic chain on the transformation towards one dimensional aggregate. *Journal of Saudi Chemical Society* **19** (4): 423-428.
<http://www.sciencedirect.com/science/article/pii/S1319610314000830>.
- Kon-No, Kijiro and Kitahara, Ayao. 1971. Solubility behavior of water in nonaqueous solutions of oil-soluble surfactants: Effect of molecular structure of surfactants and solvents. *Journal of Colloid and Interface Science* **37** (2): 469-475.
[https://doi.org/10.1016/0021-9797\(71\)90316-X](https://doi.org/10.1016/0021-9797(71)90316-X).
- Kovscek, A. R. 2012. Emerging challenges and potential futures for thermally enhanced oil recovery. *Journal of Petroleum Science and Engineering* **98**: 130-143.
- Kumar, Amit and Mandal, Ajay. 2018. Characterization of rock-fluid and fluid-fluid interactions in presence of a family of synthesized zwitterionic surfactants for application in enhanced oil recovery. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **549**: 1-12.
<http://www.sciencedirect.com/science/article/pii/S0927775718302711>.
- Levitt, David and Pope, Gary Arnold. 2008. Selection and Screening of Polymers for Enhanced-Oil Recovery. Presented at the SPE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA. 2008/1/1/. <https://doi.org/10.2118/113845-MS>.
- Li, Jing-Liang, Bai, Dong-Shun, and Chen, Bing-Hung. 2009. Effects of additives on the cloud points of selected nonionic linear ethoxylated alcohol surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **346** (1): 237-243.
<https://doi.org/10.1016/j.colsurfa.2009.06.020>.
- Lin, I. J., Moudgil, B. M., and Somasundaran, P. 1974. Estimation of the effective number of — CH₂ - groups in long-chain surface active agents. *Colloid and Polymer Science* **252** (5): 407-414. <https://doi.org/10.1007/BF01387966>.
- Lindman, Björn, Medronho, Bruno, and Karlström, Gunnar. 2016. Clouding of nonionic surfactants. *Current Opinion in Colloid & Interface Science* **22**: 23-29.
<https://doi.org/10.1016/j.cocis.2016.01.005>.

- Ma, Kun, Cui, Leyu, Dong, Yezi et al. 2013. Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. *Journal of Colloid and Interface Science* **408**: 164-172.
<http://www.sciencedirect.com/science/article/pii/S0021979713006462>.
- Marine, I. W., and S. J. Fritz, 1981, Osmotic Model to Explain Anomalous Hydraulic Heads, *Water Resources Research*, 17(1): 73–82.
- Mehana, Mohamed, Al Salman, Mohamed, and Fahes, Mashhad. 2018. Impact of Salinity and Mineralogy on Slick Water Spontaneous Imbibition and Formation Strength in Shale. *Energy & Fuels* **32** (5): 5725-5735.
<https://doi.org/10.1021/acs.energyfuels.7b03516>.
- Mohanty, Kishore K., Tong, Songyang, Miller, Chammi et al. 2019. Improved Hydrocarbon Recovery Using Mixtures of Energizing Chemicals in Unconventional Reservoirs. *SPE Reservoir Evaluation & Engineering* **22** (04): 1436-1448. <https://doi.org/10.2118/187240-PA>.
- Morrow, Norman R., Lim, Hau T., and Ward, Jill S. 1986. Effect of Crude-Oil-Induced Wettability Changes on Oil Recovery. *SPE Formation Evaluation* **1** (01): 89-103. <https://doi.org/10.2118/13215-PA>.
- Motiejunas, D. and Wade, R. C. 2006. Structural, Energetic, and Dynamic Aspects of Ligand–Receptor Interactions. *Comprehensive Medicinal Chemistry II* **4**: 193-212.
- Mukherjee, Partha, Padhan, Susanta K., Dash, Sukalyan et al. 2011. Clouding behaviour in surfactant systems. *Advances in Colloid and Interface Science* **162** (1): 59-79.
<https://doi.org/10.1016/j.cis.2010.12.005>.
- Okuzaki, Hidenori and Osada, Yoshihito. 1994. Effects of hydrophobic interaction on the cooperative binding of a surfactant to a polymer network. *Macromolecules* **27** (2): 502-506. <https://doi.org/10.1021/ma00080a025>.

- Rezaei Gomari, Sina and Hamouda, Aly. 2006. Effect of fatty acids, water composition and pH on the wettability alteration of calcite surface. *Journal of Petroleum Science and Engineering* **50**: 140-150.
- Rosen, Milton J and Kunjappu, Joy T. 2012. *Surfactants and interfacial phenomena*: John Wiley & Sons.
- Rostami, Peyman, Mehraban, Mohammad Fattahi, Sharifi, Mohammad et al. 2019. Effect of water salinity on oil/brine interfacial behaviour during low salinity waterflooding: A mechanistic study. *Petroleum* **5** (4): 367-374.
<https://doi.org/10.1016/j.petlm.2019.03.005>.
- Saputra, I. W. R. and Schechter, D. S. 2018. Comprehensive Workflow for Laboratory to Field-Scale Numerical Simulation to Improve Oil Recovery in the Eagle Ford Shale by Selective Testing and Modelling of Surfactants for Wettability Alteration. In *Unconventional Resources Technology Conference, Houston, Texas, 23-25 July 2018*, 2035-2056. Society of Exploration Geophysicists, American Association of Petroleum Geologists, Society of Petroleum Engineers.
- Satter, Abdus and Iqbal, Ghulam M. 2016. 11 - Primary recovery mechanisms and recovery efficiencies. In *Reservoir Engineering*, ed. Abdus Satter and Ghulam M. Iqbal, 185-193. Boston: Gulf Professional Publishing.
- Saxena, Neha, Kumar, Amit, and Mandal, Ajay. 2019. Adsorption analysis of natural anionic surfactant for enhanced oil recovery: The role of mineralogy, salinity, alkalinity and nanoparticles. *Journal of Petroleum Science and Engineering* **173**: 1264-1283.
<http://www.sciencedirect.com/science/article/pii/S0920410518309793>.
- ShamsiJazeyi, Hadi, Verduzco, Rafael, and Hirasaki, George J. 2014. Reducing adsorption of anionic surfactant for enhanced oil recovery: Part II. Applied aspects. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **453**: 168-175.
<http://www.sciencedirect.com/science/article/pii/S0927775714001617>.

- Sheng, James J. 2011. Chapter 10 - Alkaline Flooding. In *Modern Chemical Enhanced Oil Recovery*, ed. James J. Sheng, 389-460. Boston: Gulf Professional Publishing.
- Shinoda, K. 1983. Solution behavior of surfactants: The importance of surfactant phase and the continuous change in HLB of surfactant. *Proc.*, Frontiers in Colloid Science In Memoriam Professor Dr Bun-ichi Tamamushi, Darmstadt, 1983//, 1-7.
- Somasundaran, P. and Zhang, L. 2006. Adsorption of surfactants on minerals for wettability control in improved oil recovery processes. *Journal of Petroleum Science and Engineering* **52** (1): 198-212.
<https://doi.org/10.1016/j.petrol.2006.03.022>.
- Standnes, Dag C. and Austad, Tor. 2000. Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. *Journal of Petroleum Science and Engineering* **28** (3): 123-143.
[https://doi.org/10.1016/S0920-4105\(00\)00084-X](https://doi.org/10.1016/S0920-4105(00)00084-X).
- Standnes, Dag Chun. 2001. Enhanced Oil Recovery from Oil-Wet Carbonate Rock by Spontaneous Imbibition of Aqueous Surfactant Solutions.
- Strand, Skule, Standnes, Dag C., and Austad, Tor. 2003. Spontaneous Imbibition of Aqueous Surfactant Solutions into Neutral to Oil-Wet Carbonate Cores: Effects of Brine Salinity and Composition. *Energy & Fuels* **17** (5): 1133-1144.
<https://doi.org/10.1021/ef030051s>.
- Tabor, Rico F., Eastoe, Julian, and Dowding, Peter J. 2010. A two-step model for surfactant adsorption at solid surfaces. *Journal of Colloid and Interface Science* **346** (2): 424-428.
<http://www.sciencedirect.com/science/article/pii/S0021979710003383>.
- Takamura, K. and James, A. 2015. 13 - Paving with asphalt emulsions. In *Advances in Asphalt Materials*, ed. Shin-Che Huang and Hervé Di Benedetto, 393-426. Oxford: Woodhead Publishing.

- Tang, G. Q. and Morrow, N. R. 1997. Salinity, Temperature, Oil Composition, and Oil Recovery by Waterflooding. *SPE Reservoir Engineering* **12** (04): 269-276. <https://doi.org/10.2118/36680-PA>.
- Teklu, Tadesse Weldu, Li, Xiaopeng, Zhou, Zhou et al. 2018. Low-salinity water and surfactants for hydraulic fracturing and EOR of shales. *Journal of Petroleum Science and Engineering* **162**: 367-377. <http://www.sciencedirect.com/science/article/pii/S0920410517310148>.
- Thyne, Geoffrey. 2015. *A review of the measurement of wettability*.
- Tian, Yao, Ayers, Walter B., and McCain Jr, D. The Eagle Ford Shale play, south Texas: regional variations in fluid types, hydrocarbon production and reservoir properties. 2013, cp-350.
- Torstensson, Maria and Hult, Anders. 1992. Surface modification of polymers using surfactant monomers. *Polymer Bulletin* **29** (5): 549-556. <https://doi.org/10.1007/BF00296717>.
- Tunstall, Thomas Nelson, Oyakawa, Javier, Eid, H. et al. 2013. *Economic impact of the Eagle Ford Shale*: Institute for Economic Development, Center for Community and Business
- Wade, W. H., Morgan, James C., Schechter, R. S. et al. 1978. Interfacial Tension and Phase Behavior of Surfactant Systems. *Society of Petroleum Engineers Journal* **18** (04): 242-252. <https://doi.org/10.2118/6844-PA>.
- Wang, Dongmei, Butler, Raymond, Zhang, Jin et al. 2012. Wettability Survey in Bakken Shale With Surfactant-Formulation Imbibition. *SPE Reservoir Evaluation & Engineering* **15** (06): 695-705. <https://doi.org/10.2118/153853-PA>.
- Wang, Shuoshi, Chen, Changlong, Yuan, Na et al. 2019. Design of extended surfactant-only EOR formulations for an ultrahigh salinity oil field by using hydrophilic lipophilic deviation (HLD) approach: From laboratory screening to simulation.

Fuel **254**: 115698.

<http://www.sciencedirect.com/science/article/pii/S0016236119310506>.

Weiss, William W., Xie, Xina, Weiss, Jason et al. 2006. Artificial Intelligence Used to Evaluate 23 Single-Well Surfactant-Soak Treatments. *SPE Reservoir Evaluation & Engineering* **9** (03): 209-216. <https://doi.org/10.2118/89457-PA>.

Xie, Xina, Weiss, William W., Tong, Zhengxin J. et al. 2005. Improved Oil Recovery from Carbonate Reservoirs by Chemical Stimulation. *SPE Journal* **10** (03): 276-285. <https://doi.org/10.2118/89424-PA>.

Yekeen, Nurudeen, Padmanabhan, Eswaran, Idris, Ahmad Kamal et al. 2019. Surfactant adsorption behaviors onto shale from Malaysian formations: Influence of silicon dioxide nanoparticles, surfactant type, temperature, salinity and shale lithology. *Journal of Petroleum Science and Engineering* **179**: 841-854. <http://www.sciencedirect.com/science/article/pii/S0920410519304334>.

Zdziennicka, Anna, Szymczyk, Katarzyna, and Jańczuk, Bronisław. 2009. Correlation between surface free energy of quartz and its wettability by aqueous solutions of nonionic, anionic and cationic surfactants. *Journal of colloid and interface science* **340** (2): 243-248.

Zhang, Fan, Adel, Imad A., Saputra, I. W. R. et al. 2019. Numerical Investigation to Understand the Mechanisms of CO₂ EOR in Unconventional Liquid Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, Calgary, Alberta, Canada. 2019/9/23/. <https://doi.org/10.2118/196019-MS>.

Zhang, Fan, Saputra, I. W. R., Adel, Imad A. et al. 2018. Scaling for Wettability Alteration Induced by the Addition of Surfactants in Completion Fluids: Surfactant Selection for Optimum Performance. In *Unconventional Resources Technology Conference, Houston, Texas, 23-25 July 2018*, 971-987. SEG Global Meeting Abstracts, Society of Exploration Geophysicists, American Association of Petroleum Geologists, Society of Petroleum Engineers.

Zhang, Fan, Saputra, I. W. R., Adel, Imad A. et al. 2019. Numerical Investigation of EOR Applications in Unconventional Liquid Reservoirs through Surfactant-

Assisted Spontaneous Imbibition SASI and Gas Injection Following Primary Depletion. Presented at the SPE Annual Technical Conference and Exhibition, Calgary, Alberta, Canada. 2019/9/23/. <https://doi.org/10.2118/196055-MS>.

Zhang, leslie, Liu, Shunhua, Puerto, Maura et al. 2006. Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering* **52** (1): 213-226.
<http://www.sciencedirect.com/science/article/pii/S0920410506000684>.

Zhou, Letian, Das, Saikat, and Ellis, Brian R. 2016. Effect of surfactant adsorption on the wettability alteration of gas-bearing shales. *Environmental Engineering Science* **33** (10): 766-777.

Zhou, Xianmin, Morrow, Norman R., and Ma, Shouxiang. 1996. Interrelationship of Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibition and Waterflooding. Presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma. 1996/1/1/.
<https://doi.org/10.2118/35436-MS>.

Zhu, Bu-Yao and Gu, Tiren. 1991. Surfactant adsorption at solid-liquid interfaces. *Advances in Colloid and Interface Science* **37** (1): 1-32.
<http://www.sciencedirect.com/science/article/pii/000186869180037K>.