Physico-Chemical and Micromodel Investigation of Low-Tension Waterflooding in Tight Reservoirs

by

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Abstract

The existing controversies in the exact mechanism responsible for improved oil recovery during low-tension water flooding in rocks have portrayed the chemical enhanced oil recovery technique to be risky, hence less exploited in the field.

This study evaluates experimentally, the effect of brine ionic composition, salinity and surfactant type on improved oil recovery in five different rocks - Botucatu outcrop sandstone, Indiana limestone outcrop core, Silurian dolomite outcrop core, Slave point reservoir core, and Evie shale. Commercially available surfactants (Nonylphenol ethoxylate, Sodium Olefin Sulfonate, and Dodecyl Trimethyl Ammonium Bromide) at 1% surfactant concentration in Sodium chloride, Calcium Chloride, and Synthetic formation brines at varying salinities ranging from 0 ppm, and 200,000 ppm is used for this study.

Initially, fluid-fluid analyses were conducted via phase behavior, oil-brine electrokinetic, and interfacial tension measurements to understand the effect of the varying components on the oil-brine system. Based on the observed trend from the fluid-fluid analyses, a new brine was designed to further reduce the oil-brine interfacial tension with the non-ionic surfactant. Also, rock-fluid studies were conducted via rock-brine electrokinetic measurements, single phase spontaneous imbibition tests and micromodel flooding with specially designed and fabricated homogeneous and fractured micromodel which are representative of the rocks studied. Based on the understanding of rock-brine electrokinetic interaction in the outcrop carbonate cores, a newly designed brine was prepared and evaluated for an increased wettability alteration potential with the slave point reservoir core. The Single-phase spontaneous imbibition and micromodel flooding experiments were conducted to determine the dominating mechanism involved in recovery and correlate the rock-brine electrokinetic results with porous media experiments.

Results indicate that the non-ionic surfactant although not able to alter wettability favorably, can reduce interfacial tension better than the other two surfactants. The non-ionic surfactant in the newly designed brine reduced the interfacial tension better than the base case scenario in the original synthetic formation brine. It was also observed that the wettability alteration potential in the newly designed brine was better compared to the original synthetic formation brine in the slave point core which implies that a common trend exits in similar carbonate cores.

Single-phase spontaneous imbibition experiments with the Silurian dolomite core showed that expansion of the electrical double layer (EDL), rock dissolution and multi-component ion exchange are responsible for favorable wettability alteration, with the EDL mechanism occurring first. For the Evie shale core, the illite content of the rock and pore connectivity could have a significant impact on the imbibition results which could further explain the unusual imbibition profile observed during imbibition.

In less heterogeneous rocks such as sandstones, the homogenous micromodel flooding results show that ion effect dominates recovery compared to the interfacial tension values. Contrarily, for heterogeneous or fractured rocks such as carbonates, the interfacial tension reduction plays a dominant role in improved oil recovery, especially for surfactants that are not able to alter wettability favorably.

This study adds to the body of knowledge for surfactant slug design in rocks, suggests the dominant oil recovery mechanism in the analyzed rocks and projects the possibility of sodium ions as potential determining ions.

Preface

This thesis is an original work by Benedicta Nkenchor Nwani. All sample preparations, conducted experiments, and data analyses presented in this thesis are the independent work of the author, Benedicta Nkenchor Nwani.

The Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analysis for the Botucatu sandstone rock was done by a visiting Ph.D. candidate, Alana Almeida Da Costa and published in literature while that for the slave point formation core was done by Dr. Imran Ul-haq. The information of the X-Ray Diffraction (XRD) analysis for the Evie shale used was done by Mingxiang Xu, Mojtaba Binazadeh, Ashkan Zolfaghari, and Hassan Dehghanpour, which is also published in the literature. The X-Ray Diffraction (XRD) analysis for the Indiana limestone core was gotten from Maubert, and his team as published in a Society of Petroleum Engineers (SPE) conference proceeding while that of the Silurian dolomite was acquired from a Society of Petroleum Engineers (SPE) published conference proceeding by Hassan Mahani and his team. The zwitterionic surfactant used in for the fractured micromodel experiment was synthesized by Zifan Zhang.

The homogeneous photomask used for the fabrication of the homogeneous micromodel was designed by the author Benedicta Nkenchor Nwani while the micromodel manufacturing was done with the help of University of Alberta nanofabrication department staff at the University of Alberta Nanofabrication facility. The fractured photomask used in the fabrication of the fractured micromodel was designed by Mudit Chordia and fabricated at the University of Alberta Nanofabrication facility.

Dedication

Dedicated to Almighty God, Our Mother of Perpetual Help and my patron saint, St. Anthony of Padua who has made all things possible for me.

To my ever supportive, loving and caring parents, Chief Christopher Azuka Nwani, Mrs. Fidelia Ugochuckwu Nwani, all your sacrifices, and prayers have paid off. To my siblings who stood by me from the onset, Barrister Juliet Ijeawele Okolo (Ph.D.) (Nee Nwani), Cynthia Onyekachukwu Nwani, Judith Uchechukwu Nwani (ACCA), Victoria Chekwubechukwu Nwani and my Nephew, Ikenna Emmanuel Ogochukwu Okolo. I appreciate you all and words are not enough to express exactly how I feel and I hope I can pay back all of your good deeds and sacrifices.

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My heartfelt gratitude goes to my supervisor, Dr. Japan Trivedi, for his patience, challenging and believing in me while being there to guide me through this work. I feel very privileged to have obtained this Master's degree under your mentorship. I really cannot thank you enough.

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I would also like to thank the Niger Delta Development Commission (NDDC) and the Canada First Excellence Research Fund via the University Of Alberta Future Energy Systems (FES) for funding this research.

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I am also immensely grateful to my research group members; Jose Leonardo Guevara Urdaneta (my confidant), Najmudeen Sibaweihi, Azad Madhar, Jestril Ebaga Ololo, Salomao Chissonde, Viralkumar Patel, Zifan Zhang, Carolina Arambula, Rajan Patel and Loreana Morales Fornerino for their support in the cause of my program.

Finally, I am thankful to Dr. Ngozi Okonjo Iweeala for her inspiration.

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Chapter 1 : Introduction

The increase in energy demand has led to extensive research and development on economically, environmentally, and technically feasible ways of improving the ever-growing energy demand. Most of the energy demand is the demand for oil. Most oil reservoirs are depleted while others are technically challenging to produce from thereby requiring advanced techniques such as Enhanced Oil recovery mechanisms in recovering trapped oil. ***Figure 1-1*** shows the stages of oil recovery in petroleum reservoirs. The first, second and third stages are primary, secondary and tertiary recovery mechanisms respectively.

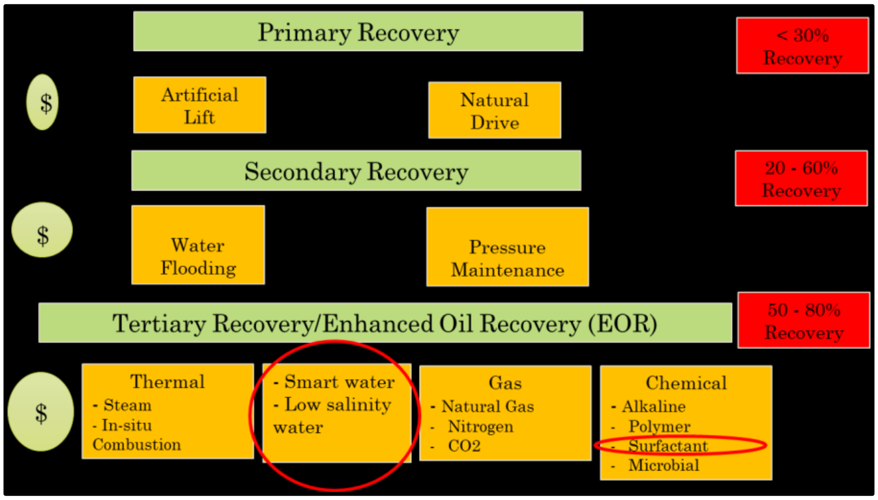


Figure 1-1: Recovery Mechanisms

1.1 Background on Low Salinity water and Surfactant Flooding

The concept of low salinity water involves the alteration of the chemical equilibrium in the reservoir through the injection of low salinity brine for an improved oil recovery via different mechanism. Surfactants are also known as surface acting agents and are chemicals that get adsorbed on or concentrate at a surface or a fluid-fluid interface when they are present at relatively low concentrations (Rosen & Kunjappu, 2012). They are amphiphilic molecules that contain both a polar and a non-polar component (Hydrophilic and hydrophobic portions respectively). The hydrophobic (lipophilic/non-polar/hydrocarbon) portion of the surfactant which can either be a straight or branched chain is often referred to as the tail group while the hydrophilic (polar) part is the head group of the surfactant. Surfactants reduce the interfacial tension that exists between an interface to ultra-low values of about 0.001 mN/m. Such ultra-low IFT values overcome the capillary forces responsible for oil trapping (Wu et al.,2010). The two means in which IFT is reduced with surfactants is through adsorption at the interface and formation of micelles (Li et al., 2000). Various kinds of surfactants exist and include; anionic, cationic,non-ionic, zwitterionic, Gemini surfactants, etc.

Trapping of mobilized oil in the reservoir after low salinity water flooding necessitates the use of surfactant EOR methods. Low salinity water flooding, which is a promising oil recovery technique in its research and developmental stages is a promising oil recovery mechanism. (Tang & Morrow, 1997) have reported improved oil recovery with low salinity water flooding. (Tang, Guo-Qing & Morrow, 1999) studied the necessary conditions required for positive low salinity water effect to be seen in sandstones. These include; The presence of a significant clay fraction, presence of connate water and also exposure to crude oil which creates a mixed-wet condition. In carbonate rock, however, this mechanism is different as they do not contain a significant amount of clay minerals since they are mainly composed of calcium carbonate (chalk and limestone) and dolomite. They may also include some evaporate rocks such as gypsum or anhydrite which are hydrated and non-hydrated calcium sulfate minerals respectively. Following the works of (Tang & Morrow, 1999), other researches have dug deeper into the low salinity mechanism to reproduce and explain the low salinity water and surfactant effect (LSE). Mechanisms attributed to low salinity effect include the following;

- Osmotic pressure (Buckley & Morrow, 1990)
- Clay swelling and migration of fines (Barnaji et al., 2016; Lebedeva & Fogden, 2011; Loahardjo et al., 2007)
- Multi-component ion exchange (Alagic & Skauge, 2010; Haagh et al., 2017; Pouryousefy et al., 2016; Tang & Morrow, 1999; Wei et al., 2017; Xie, Saeedi, et al., 2016),
- Increase in pH (Aksulu et al., 2012; Austad et al., 2010; RezaeiDoust et al., 2011),
- Expansion of the electrical double layer (Buckley et al., 1998; Ligthelm et al., 2009; Nasralla & Nasr-El-Din, 2014; Wei et al., 2017)
- Reduction of the interfacial tension between oil and water (Wei et al., 2017)
- Interfacial viscoelasticity (Alvarado et al., 2014; Wang, X. & Alvarado, 2016)
- Change of surface charge (Mahani et al., 2015; Rezaei et al., 2006; Zhang, P. & Austad, 2006a)
- Calcite or anhydrite dissolution (Hiorth et al., 2010; Yousef et al., 2011) (Al-Shalabi et al., 2015; Zaretskiy, 2012)

1.1.1 Osmotic Pressure Effects

Osmotic pressures are generated due to the differences in the chemical potential of a solution across a membrane. (Buckley & Morrow, 1990) in their adhesion test on a smooth glass surface to characterize the interaction between various crude oil and injected brine at different salinity (NaCl brine; 0.01 M, 0.1 M and 1.0M) have reported that there is a threshold pH during low salinity water flooding where there is no oil adsorption on the rock, and the osmotic pressure gradient is one of the mechanisms that causes a positive low salinity effect. Most of the threshold pH values reported for the various oil tested ranged from 5 to 7 and greater than 8 for California oil. The osmosis between low-salinity water flooding and high connate water can create extra pressure, which facilitates the desorption of oil from pores. The positive effect of low salinity water flooding in shale via osmotic pressure effect was reported by (Fakcharoenphol et al., 2014) who performed imbibition experiment in preserved middle Bakken core using both high salinity (280,000 PPM for five days) and low salinity KCl brines (20,000 ppm for six days), where the core was first imbibed in the high salinity brine and then the low salinity brine. There was more oil recovery in the low salinity brine compared to the high salinity brine due to the osmotic pressure gradient as a result of salinity contrast. Injecting low salinity brine in shales with high smectite content causes clay swelling and reduced permeability. This was not the case for the Bakken core because it contains more illite and the KCl brine used is a clay swelling inhibitor. The experiments confirm that chemical osmosis induces counter-current flow during low salinity water flooding which improves oil recovery.

1.1.2 Multi-component ion exchange (MIE)

Different ions have different affinities on the rock surface. In this sense, multi-valent and divalent cations are strongly adsorbed on the rock surface. These multivalent cations form organometallic complexes with the oil by bonding to the resins and asphaltenes (polar compounds) present in the oil phase, which in turn promotes the oil wetness of rocks. MIE as a low salinity effect is supported by (Lager et al., 2008a) after analyzing the effluent brine composition from North slope cores after flooding with low salinity brine. Their analysis showed that there was a decrease in divalent ion concentration (Mg^{2+} and Ca^{2+}) compared to the composition of these ions in the injected brine, which suggests an exchange at the rock surface. (Jerauld et al., 1997; Jerauld et al., 2006) have stated that the degree of oil recovery by MIE is dependent on the amount of clay content present on the mineral surface. Low salinity brine injection makes these multivalent cations accessible through the expansion of the electrical double layer, which then causes desorption of the oil from the rock, hence favorable wettability alteration due to the replacement of complex cations on the rock surface with uncomplex ones.

The mechanism for MIE during low salinity water flooding in sandstone and carbonates are different due to the little or absence of clay contents in the rock, which then affects the way oil is adsorbed on the rock. Generally, eight different mechanisms for the adsorption of oil on the mineral surface has been proposed by the extended DLVO theory (Arnarson & Keil, 2000) and they are: Cation bridging, Anion exchange, Cation exchange, Ligand exchange, Van der Waals interactions, hydrogen bonding, water bridging and Protonation of which only four (Cation bridging, Cation exchange, water bridging, and Ligand bonding) are affected by the cation exchange during low salinity water flooding.

Cation bridging is typically weak adsorption that occurs between the polar functional group present in the oil and the cations which are exchangeable on the mineral surface while cation exchange occurs when there is a replacement of exchangeable metal cations which are bounded on the clay mineral with quaternary nitrogen or heterocyclic ring. Ligand binding is the direct interaction between the multi-valent cations and the carboxylate group present in the oil which is a stronger interaction than cation bridging. Water bridging occurs in the presence of solvated cations such as magnesium, in which water solvates the exchangeable cations and the polar functional group present in the oil (Lager et al., 2008).

For carbonates, the adsorption strength of the organic material attached to the rock is stronger which makes it challenging to remove the oil from the rock by mere solvation or reduction of the brine ionic strength but by increasing the surface reactivity of potential determining ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-} at high temperatures by MIE mechanism in line with that described by (Lager et al., 2008; Thomas et al., 1993). Hence for carbonates, wettability alteration occurs at typically higher salinity such as seawater salinity when compared with sandstones.

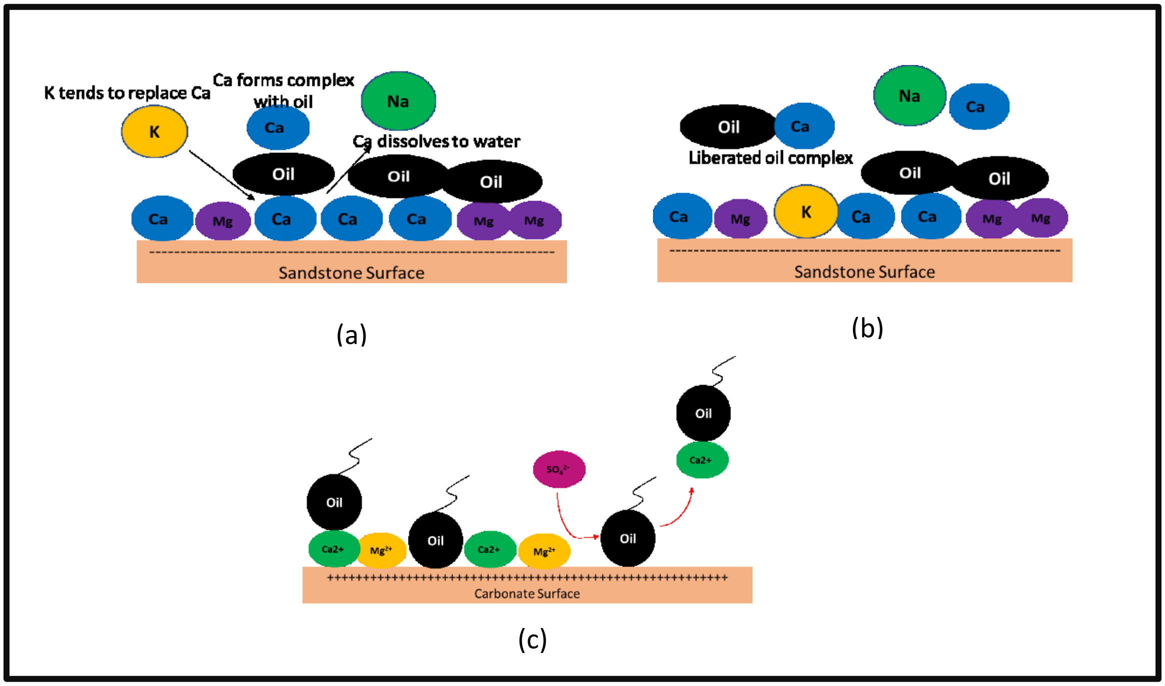
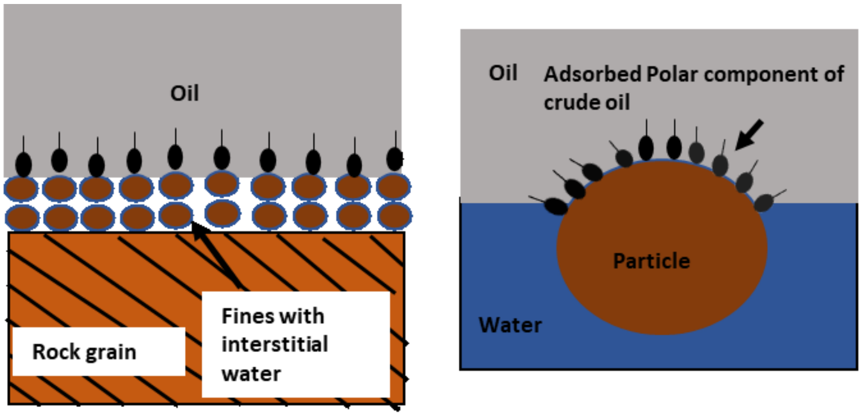


Figure 1-2: Oil recovery mechanism in sandstone utilizing low salinity flooding (a,b)- Oil recovery by MIE in sandstone (c) oil recovery mechanism by MIE in carbonates

1.1.3 Clay swelling and fines migration

From (Tang & Morrow, 1999), in contact with freshwater, clay tends to hydrate and swell, which causes the dispersion of both clay and silt in the formation. This leads to the mobilization of clay and silt into high permeability paths and causes clogging in smaller pores of the high permeability paths. These high permeability paths become less permeable which in turn leads to a uniform waterflood performance. Clays present in these reservoirs are typically kaolinite and illite. Destabilization of these oil/mixed wet clay particles from the pore walls results in favorable wettability alteration towards more water-wet conditions. The process of clay swelling and fines migration is shown in ***Figure 1-3*** - ***Figure 1-5***



Adsorption onto potentially mobile fines at low initial water saturation

Mobilized particle at oil-water interface

Figure 1-3: Adsorption of polar components from crude oil to form mix-wet fine

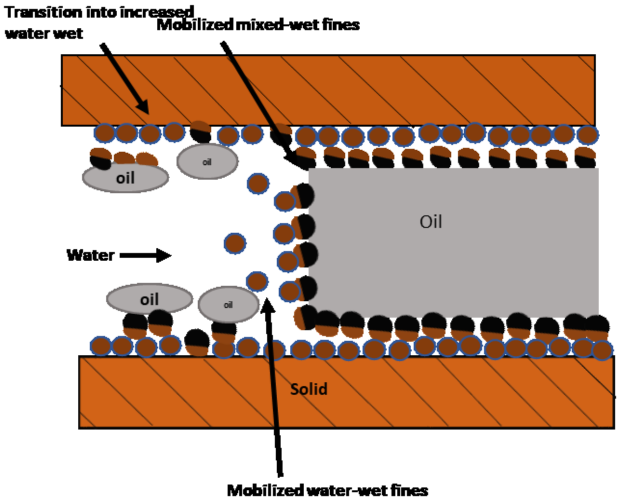


Figure 1-4: Partial stripping of mixed wet fines from pore walls during waterflooding

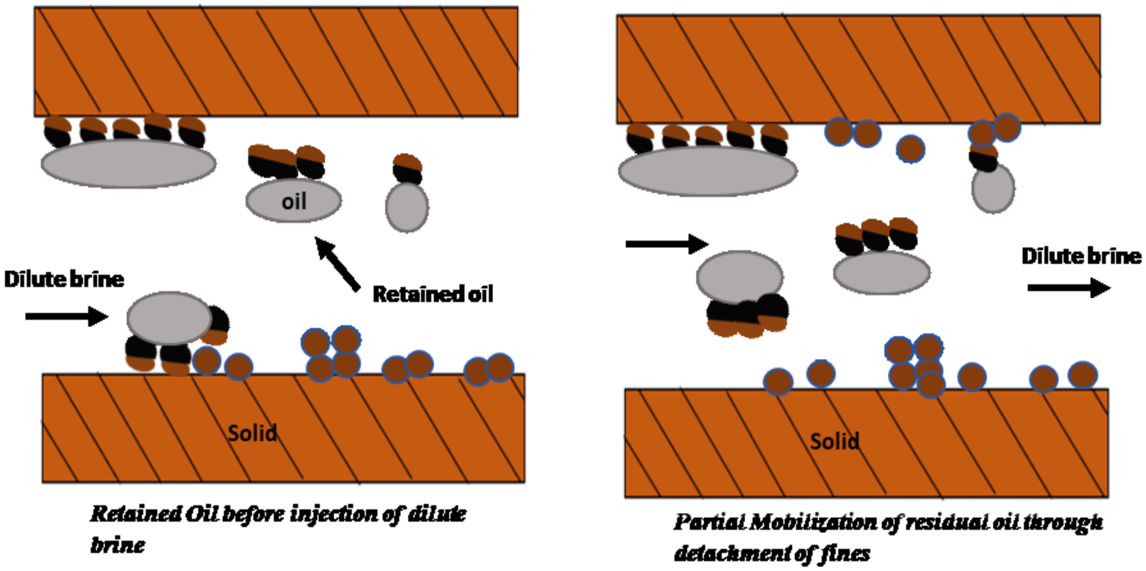


Figure 1-5: Mobilization of trapped oil

1.1.4 pH increase and Carbonate Dissolution

pH increase is a mechanism that has been attributed to the positive low salinity water flooding observed in laboratory studies (Lager et al., 2008b; McGuire et al., 2005; Tang & Morrow, 1999). pH increase in effluent water is due to two factors: Carbonate dissolution and cation exchange. The mechanism of mineral dissolution was proposed by (Hiorth et al., 2010). The authors established a surface complexation model (SCM) and a correlation between the oil recovery factor and expected mineral dissolution. The developed chemical model was tested in the spontaneous imbibition results of (Austad et al., 2007; Zhang & Austad, 2006; Zhang et al., 2007) and results suggested that the dissolution of calcite could increase water wetness mainly if the dissolution occurs at the same point where oil is desorbed from the rock. (Yousef et al., 2012) used observation from Nuclear magnetic resonance (NMR) that showed there was an improvement in the micro and macropore connectivity after injecting low salinity water (dilute seawater) in anhydrite ($CaSO_4$) containing carbonate rock. They suggested that the presence of anhydrite in the carbonate rock will lead to the generation of in-situ sulfate ions (SO_4^{2-}) which is a potential determining ion, important for wettability alteration. (Yousef et al., 2010) further confirmed that anhydrite dissolution is a mechanism for wettability alteration in carbonate rocks. After flooding the anhydrite containing carbonate rock with 35 pore volume (PV) of de-ionized water, it was observed from the analysis of the effluent brine concentration that the concentration of SO_4^{2-} and Ca^{2+} were equal and constant, thereby suggesting that the source of the ions is from rock dissolution. (Pu et al., 2010) investigated the low salinity water flooding mechanism in carbonate rock (dolomite) containing anhydrite and their results are indicative that in addition to anhydrite dissolution or dissolution of other minerals leads to the release of adsorbed organic material from the rock, hence wettability alteration. Contrarily, various studies have observed no increase in oil recovery in carbonate rocks from anhydrite dissolution. (Nasralla et al., 2014) believe from their geochemical model that calcite dissolution is not a significant mechanism for low salinity water flooding after analyzing the calcite dissolution from four different brines, in which two (25 times diluted seawater and 100 times diluted seawater) was supposed to lead to calcite dissolution due to their negative calcite saturation index. The increase in the calcium concentration was insignificant which demonstrates a minimal contribution of calcite dissolution in the low salinity effect. More so, the authors noted that calcite dissolution will reach rather quickly in the reservoir close to the injector and will not cause further dissolution far away from the injector.

Carbonate dissolution is presented in the following chemical reactions;

$$CaCO_3(s) \leftrightarrow\ Ca^{2+}(aq) + {CO_3}^{2-}(aq)$$

$$CO_3^{2-}(aq) \leftrightarrow\ HCO_3^{-}(aq) + OH^{-}(aq)$$

Carbonate dissolution is associated with an increase in pH. The magnitude of pH increase is dependent on the carbonate content of the rock. In turn, dissolution of carbonate occurs when the carbonate rock is not fully equilibrated with calcium ions. Dissolution leads to the deposition of negatively charged hydroxyl ions on the rock surface. The reaction shown above occurs at a fast rate.

(Den et al., 2015; Nasralla et al., 2015) have demonstrated both experimentally and numerically that calcite dissolution occurs very quickly in porous media experiments. This implies that no more mineral dissolution occurs as the flood front advances deeper into the reservoir.

Cation exchange occurs at a faster rate compared to carbonate dissolution. The cation exchange capacity is dependent on the amount of clay minerals present in the rock, and it is an interaction between the clay surface and the brine present. The reservoir pH is usually acidic between 4 and 7 due to the presence of dissolved acid gases such as CO_2 and H_2S present in the reservoir brine. It has been suggested by (Austad et al., 2010) that at the pH of 5, there is an adsorption of clay minerals by acidic and protonated basic components from the crude oil, and cations present in the reservoir brine such as calcium ions. Injecting low salinity brine in this scenario leads to the mineral surface exchanging hydroxyl (OH^-) ions present in reservoir brine with the cations previously adsorbed on the mineral surface thereby leading to an increase in pH. There is a fast reaction between the hydronium (H^+) ions and the adsorbed acidic and protonated basic material which causes wettability alteration to more water-wet conditions due to the desorption of the organic component from clay.

(McGuire et al., 2005) have suggested that there is a generation of in-situ surfactant with an increase in pH which causes saponification, wettability alteration and the reduction of interfacial tension between oil and water. However, it has been suggested by (Ehrlich & Wygal Jr, 1977) that saponification will only occur if the acid number of the crude oil is greater than 0.2mg KOH/g of oil. ***Figure 1-6*** shows the proposed mechanism for mineral dissolution, while ***Figure 1-7*** shows effect of pH on oil mobilization.

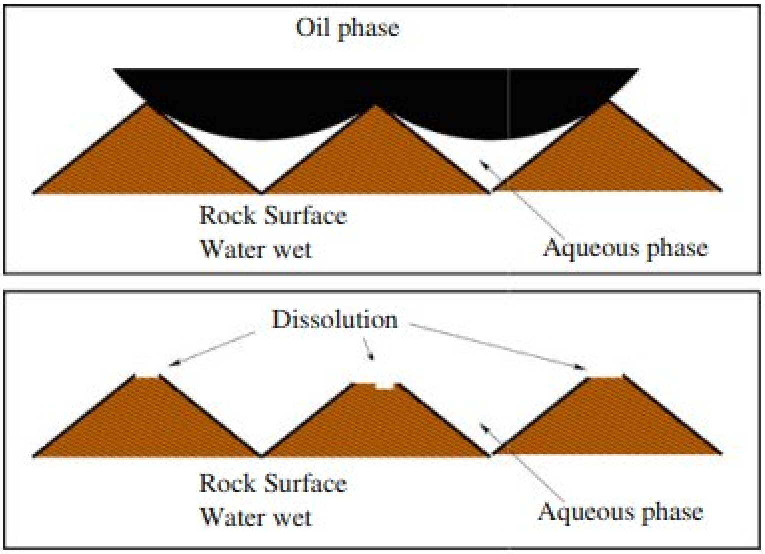


Figure 1-6: Proposed mechanism for mineral dissolution

(Hiorth et al., 2010)

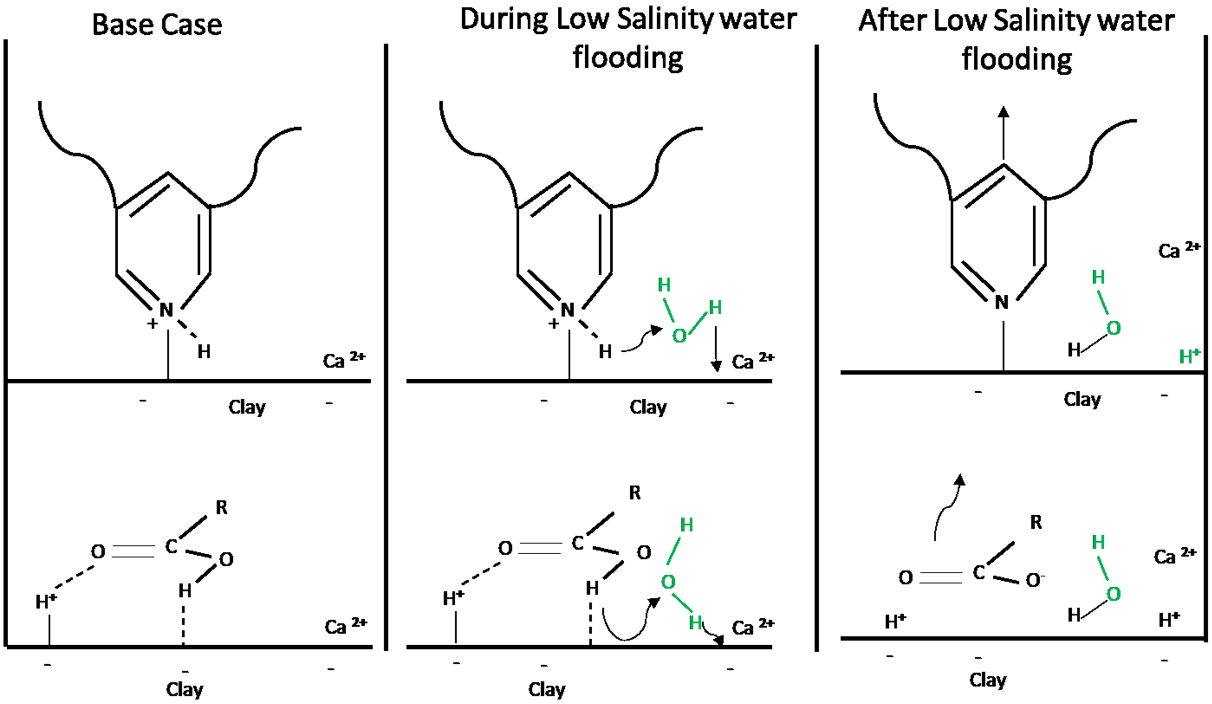


Figure 1-7: Proposed mechanism for low salinity water flooding at a reservoir pH of 5 Upper: Desorption of basic material. Lower: Desorption of acidic material

modified after (Austad et al., 2010)

1.1.5 Expansion of the Electrical Double Layer

The expansion of the electrical double layer is one of the low salinity effects. (Nasralla & Nasr-El-Din, 2014) studied the effect of EDL expansion via zeta potential, contact angle and core flood experiments on (mica surface – muscovite for contact angle and Berea sandstone for zeta potential and core flood) to investigate the dominancy of the EDL on oil recovery. Correlation of their experimental work shows that the EDL expansion dominates other low salinity effect mechanism during secondary oil recovery mode, as core flooded with 5,000 ppm NaCl, which gave a bigger EDL, a more negative zeta potential and at a higher pH (5.9) yielded about 8% more oil recovery than the same salinity (5000 ppm) with $CaCl_2$ which had a lesser EDL, lower pH (5.5) and a positive zeta potential value closer to zero.

1.1.6 Reduction of Interfacial tension between oil and water

Low salinity water flooding results in saponification, depending on the acid number of the oil. The in-situ surfactant generated during this process helps in the reduction of interfacial tension depending on the brine composition. (Buckley & Morrow, 1990) has noted that high salinity brine containing potential determining ions such as Magnesium and calcium ions can cause precipitation of the surfactants, thereby reducing their ability to generate in-situ surfactant. (Wei et al., 2017) conducted a comprehensive study on the crude oil brine and rock interactions using packed glass beads in a micro model flooded with both low (0.21 wt %, 0.105 wt.% and 0.021 wt% diluted from high salinity synthetic brine) and high salinity synthetic brine (2.1 wt % and 4.2 wt %). Their results show that the low salinity brine was able to reduce the interfacial tension by order of magnitude 10^{-1} compared to the high salinity brine. However the interfacial tension reduction is not enough to overcome the capillary forces that cause oil trapping. Furthermore, the emulsions prepared with the low salinity brine were more stable and heavier than those produced during high salinity, and this was attributed to the salting in effect that occurs during low salinity water flooding. In their studies, up to 7% of the oil recovered during the low salinity injection was attributed to hydrocarbon stabilization and expansion of the electrical double layer.

1.1.7 Interfacial Viscoelasticity

(Alvarado et al., 2014) performed double wall ring interfacial rheometry, direct visualization on micro-fluidic devices and core flood on Berea sandstone to investigate the effect of injected water chemistry on oil recovery. Their results show that the interfacial viscoelasticity increases as the brine salinity is decreased, irrespective of the cations or anions present in the brine. Analysis from their visualization in micromodel shows that the increased viscoelasticity reduces snap –off, hence leading to a more continuous oil phase (oil bank) at low salinity. Their core flood result is also consistent with the interfacial viscoelasticity, ie higher oil recovery was seen with higher interfacial viscoelasticity which occurs at low salinity. (Garcia-Olvera et al., 2016) have found the build-up of a viscoelastic interface to be dependent on the acids and asphaltene content of the crude oil.

1.1.8 Surface charge Alteration

Surface charge alteration is studied through zeta potential measurements. Most liquids comprise of anions and cations which are negatively and positively charged respectively. Suspending a solid particle in these charged liquids results in an attractive force between the liquids and the solid particles. The distribution of the ions around the particle varies. The ions closer to the surface of the particle are strongly bonded to it in the **Stern/inner layer** (a monolayer of stationary counterions which is less than the amount of ions required to neutralize the surface charge) while those further away from the particle are loosely attached to it in the **Outer/Diffuse Layer/Gouy-Chapman layer**. A notional boundary exists within the diffuse layer known as the '**Slipping plane.'** Ions within the slipping plane move together with the particles while ions further from the slipping plane does not. Hence, the potential at the slipping plane is the Zeta Potential. For a given mineral or oil surface, the surface charge is dependent on the degree of acid/base dissociation reaction which is, in turn, dependent on the pH at the surface. For some brine compositions, both, the charges at the oil-brine and mineral-brine will be the same, thereby resulting in the stabilization of the water film thickness, hence favorable wettability alteration. If the charges are different, then there is a collapse of the water film thickness which could lead to less water-wet conditions (Buckley et al.,1989). The schematics for this phenomenon is shown in ***Figure 1-8***

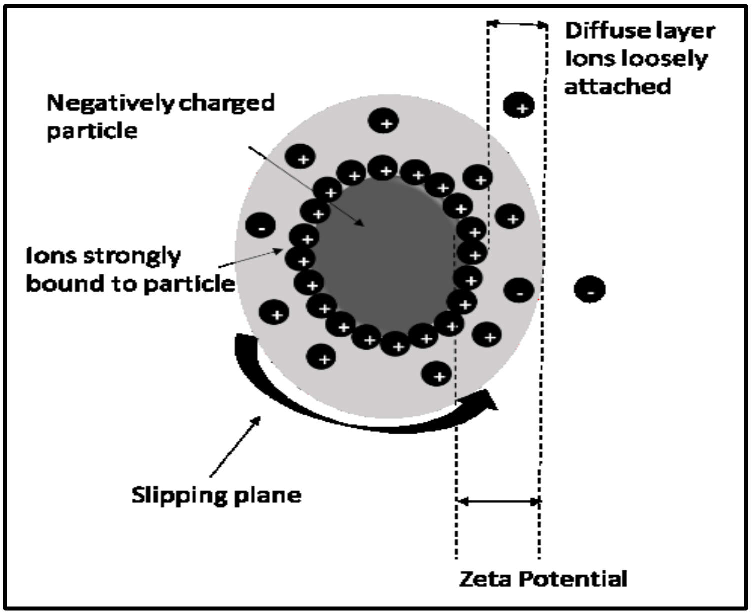


Figure 1-8: Zeta Potential

As the particles move, a force of attraction brings them close together, and as they come very close together, there is a born force of repulsion that tends to separate the particles. For the particles to be stabilized, an osmotic force must be applied. The osmotic force of water brings about the force of dispersion stability that dilutes the region and separate the particles (causes a repulsive force) as shown in ***Figure 1-9***. Addition of salts (high salinity brine) does not bring enough osmotic gradient for the particles to be stabilized unlike in low salinity brine where the bond is broken, and particles stabilized due to a higher osmotic pressure gradient. One of the ways of keeping particles in suspension is by electrostatic stabilization of the electrical double layer, which occurs when a counter ion is added to the particle.

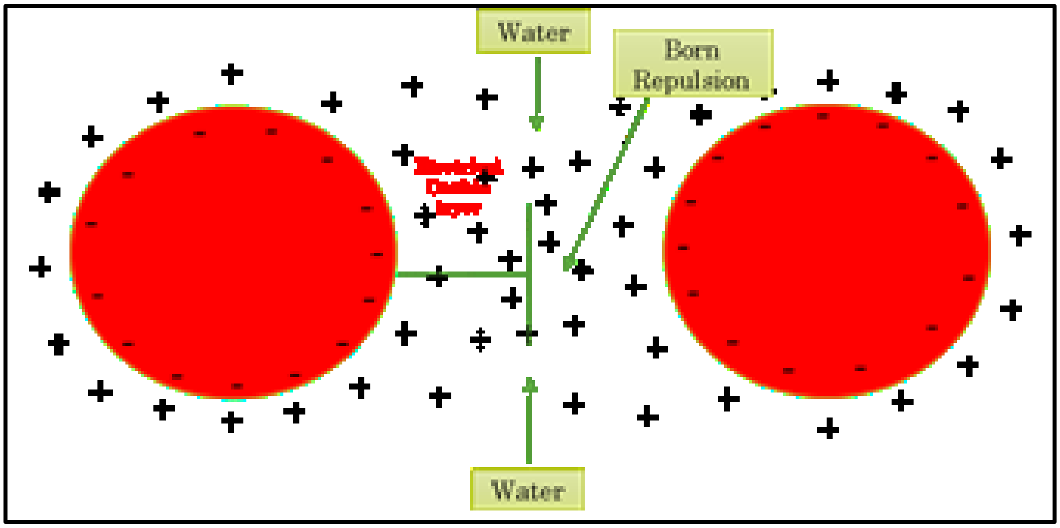


Figure 1-9: Salinity effect on colloidal Stabilization

(Alotaibi et al., 2011; Alotaibi & Yousef, 2017; Mahani et al., 2015; Mahani et al., 2017) have proposed wettability alteration in carbonate rocks to be caused by the alteration of surface charge which in turn leads to the expansion of the electrical double layer (EDL) as a result of the creation of electrostatic repulsion between the rock/brine and the brine/oil interfaces. As previously cited, formation brine and seawater brine causes carbonate dissolution and mineralogical changes over specific temperature ranges. This causes the rock strength to have different hydrostatic yield point. Brines have chemical reactions which form complexes either with the bulk solutions or with the rock surface. The ions that are usually present in the formation brine are; H^+, Ca^{2+}, HCO_3^-, H_2O, Na^+, Mg^{2+}, Cl^- and SO_4^{2-}.

In the aqueous phase, several ions are formed (Hiorth et al., 2010) as shown in the following reactions;

$$CO_3^{2-} \leftrightarrow HCO_3^- - H^+$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$CaSO_4{}^O \leftrightarrow Ca^{2+} + SO_4{}^{2-}$$

$$MgSO_4{}^O \leftrightarrow Mg^{2+} + SO_4{}^{2-}$$

$$CaHCO_3{}^+ \leftrightarrow Ca^{2+} - HCO_3{}^-$$

These reactions are typically controlled by the chemical processes taking place at the interface between the mineral lattice and the bulk solution.

At the rock interface, the hydrolysis reaction of carbonate rock generates surface charge. pH determining ions (H^+ and OH^-) ions are potential determining ions for many solids. Hence, surface charge is pH-dependent and can either have positive or negative values. A high pH will favor an excess concentration of negative species such as CO_3^{2-} and HCO_3^-, whereas a low pH will favor the excess concentration of positive species such as; Ca^+, $CaHCO_3^{+,}$ and $CaOH^+$.

(Mahani et al., 2015) measured the zeta potential of reservoir limestone rocks from the middle east at three brine salinities. Their results showed a swift declining trend of zeta potential from positive values with the formation brine to negative values for both seawater and seawater diluted

25 times. The change in surface charge from positive in the formation water to negative in seawater and low salinity brine, coupled with the negatively charged oil dispersed in the various brines resulted in the expansion of the electrical double layer which was proposed to be the reason for the observed wettability alteration on the limestone rocks.

(Mahani et al., 2015) aimed at understanding the mechanism of low salinity flood in carbonates (limestone and dolomite) with detailed contact angle measurements as a function of salinity and their results show that wettability alteration is dependent on the electrokinetic processes that occurs at the rock-brine and oil-brine interfaces whereby a wettability change was only observed when the zeta potential of the oil and carbonate rocks in the low salinity brine is lower (more negative) than the zeta potential in the formation water, suggesting that the electro-kinetic processes influencing the electric charges in the carbonate-water-oil interface are likely to be responsible for a less oil-wet state and therefore subsequent detachment from the surface. Their study also showed that low salinity effect could be observed even without rock dissolution since the brine will equilibrate with minerals from the rock as the displacement front advances in the reservoir. The potential mechanism proposed by the researchers is shown in ***Figure 1-10***. At first, there is diffusion of low salinity brine into the three-phase contact line, after which the alteration of surface charges at both the rock brine and brine rock interfaces occur. In the third stage, there is a decrease in the attractive force (ie an increase in the repulsive force) between both surfaces, as caused by surface charge change and EDL expansion. Finally, the contact angle recesses to less oil-wet conditions.

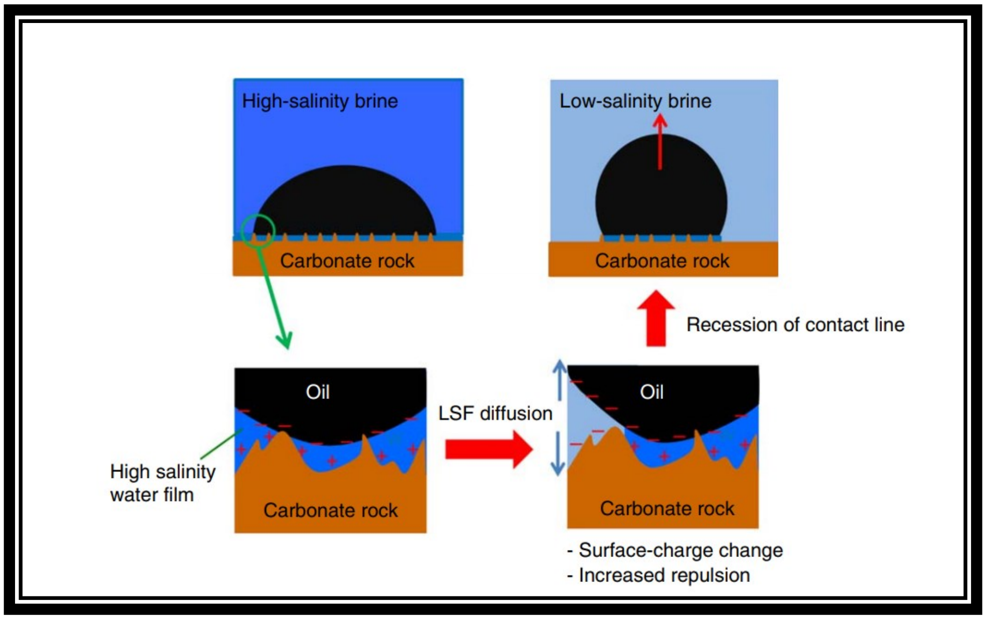


Figure 1-10: Proposed mechanism of wettability alteration by low salinity water flooding in carbonate

(Mahani et al., 2015)

(Chen et al., 2014) conducted zeta potential measurements of limestone in high salinity formation brine of salinity greater than 220,000 ppm and a low $CaCl_2$ salinity brine of 0.1 wt.%. They observed a continuous decrease in the zeta potential with an increase in pH from 5 to 11. The reason for this was attributed to the changes in the concentration of H^+ and OH^- ions and concomitant dissolution of the rock used in their experiment. However, the mineral composition of the rock used in their analysis contained 18% of quartz and clay minerals which tend to have negative zeta potential at higher pH and depending on how they cover the carbonate surface; they can affect the effective surface charge of the carbonate rock.

(Alotaibi et al., 2011) investigated the effect of clay minerals present in sandstone particles on zeta potential in three different brines – De-ionized water, aquifer water with a salinity of 5436 ppm and seawater with a salinity of 54680 ppm. Their results are indicative that clay minerals are negatively charged with these salinity ranges investigated as shown in ***Figure 1-11***

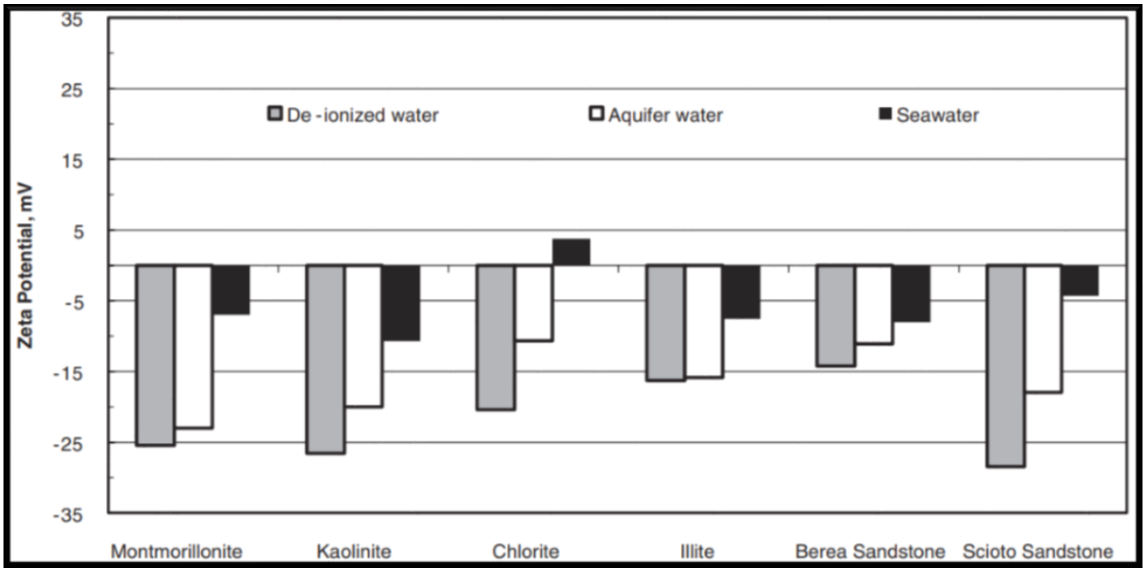


Figure 1-11: Zeta potential of clay minerals and sandstone

(Alotaibi et al., 2011)

Contrary to the work of (Chen et al., 2014) , (Alotaibi et al., 2011) measured the zeta potential of carbonate rocks – limestone and dolomite particles in different brines of various ionic composition containing both monovalent and divalent ions such as Na^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} at different pH values and their results indicates that the zeta potential values of the rocks became more positive as the pH increased from 3 to 12. The addition of specific ions such as SO_4^{2-} induced a more negative zeta potential value. The differences in both researchers work were attributed to the combined effect of rock mineralogy and brine composition with change in pH.

(Alotaibi & Yousef, 2017) measured the zeta potential of pure calcite at a fixed brine salinity of 5761 ppm with different ionic composition. They concluded that smart water, sodium chloride, and sodium sulfate solutions provide negative zeta potential needed for the electrostatic repulsion which is responsible for the expansion of the electrical double layer.

This study focuses more on the surface charge alteration since it is more feasible in the field scale as there is seen to be buffering effect and equilibration in a real-life scenario which makes calcite dissolution non-feasible.

1.2 Correlation between zeta Potential and Wettability

In the work of (Jackson & Vinogradov, 2012), different oil types were used for the zeta potential measurements at the oil-brine interface. The zeta potential was plotted against the amott wettability index after spontaneous imbibition and core flood experiments. It was observed that with three of the oils- Oil B, C and D with an acid number, base number and asphaltene content of 0.2, 1.77 and 2.9 for oil B, 0.05, 0.4 and 0.1 for oil C and 0.2, 1.2 and 2.3 for oil D respectively, the zeta potential becomes increasingly negative with a decreasing amott wettability index (ie as the samples become more oil-wet). While for oil A with an acid number, base number and asphaltene % of 0.15, 0.8 and 0.05 %, the zeta potential becomes increasingly positive with a decreasing Amott wettability index (ie samples are more water-wet). In an attempt to further investigate the influence of aging on wettability and zeta potential (Jackson & Vinogradov, 2012) measured the zeta potential of strongly water-wet carbonate rock and observed positive values. After aging the rock in crude oil, however, the zeta potential became negative, and the conclusion was that for an oil aged core, the zeta potential on the rock surface reflects that at the oil-brine interface, while for water-wet or unaged rocks, the zeta potential seen reflects that at the mineral-brine interface.

From the literature cited, it is evident that there still exists ambiguity on the factors that cause low salinity effects. This is even more evident in the successful and unsuccessful cases highlighted in chapter two of this work.

1.3 Definition of Terms

1.3.1 Electrical Double Layer (EDL)

The electrical double layer is two parallel layers of charge that surround an object/particle when exposed to a fluid. Surface charges of the particle, together with counter ions and other electrolytes make up the electrical double layer. The thickness of the double layer governs the extent of repulsion forces, and it is a function of the surface charge density, electrolyte concentration in the water phase and the valence of the ions with a charge opposite to the surface charge as described by the DLVO theory (Verwey, 1947).

1.3.2 Debye Length (K^{-1}, nm)

This is the measure of the thickness of the double layer. It is also known as 'electrostatic screening length' which is inversely proportional to the valence/concentration of the counterions, thereby making the debye length a function of the concentration of the salt (electrolyte). For a mixture of salt, the debye length is a function of the brine ionic strength, I. The equation for debye length calculation is given in **equation 1**

$$K^{-1} = \left(\frac{\varepsilon_o * \varepsilon_r * K_B * T}{2000 * e^2 * I * N}\right)^{0.5} \qquad \textbf{equation 1}$$

Where;

ε_o = Permittivity of free space (= 8.854 * 10^{-12} Fm^{-1})

ε_r = Relative permittivity of liquid (or dielectric constant) (For water = 80.103)

K_B = Boltzmann's constant (= $1.38 * 10^{-23}$ JK^{-1})

T = Temperature in Kelvin

E = electronic charge in columbs (= $1.6022 * 10^{-19}$ C)

N = Avogadro's number (= $6.022 * 10^{23}$ mol^{-1})

I = Ionic concentration (mol/L)

The ionic concentration which is the only user input variable is calculated with **equation 2**

$$I = {}^{1}\!/_{2} \sum C_i Z_i^2 \qquad \textbf{equation 2}$$

Where

C_i = Molar concentration of the particular species (mol/L)

Z_i = Valence of the ion (+ve for cations and –ve for anions)

The relationship between debye length and salt concentration is presented in ***Figure 1-12***

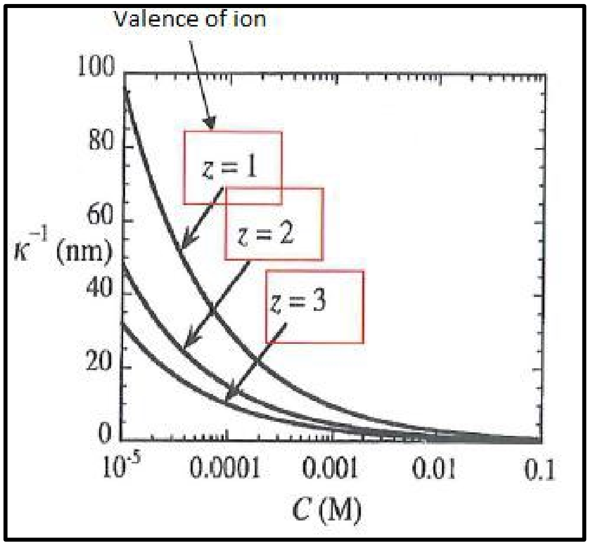


Figure 1-12:Debye length as a function of salt concentration and valence of ion

(Berg, 2010)

1.3.3 Disjoining Pressure

The disjoining pressure is the pressure that tends to separate different interfaces trying to come together at a contact line. The pressure occurs as a result of intermolecular or interionic forces; namely: Van der Waals, electrostatic and hydration forces. The electrostatic force may either be attractive or repulsive or a combination of both. For stability and water-wet conditions, then there must be a positive disjoining pressure while a negative disjoining pressure leads to less water-wet conditions (Skauge et al., 2007). The disjoining pressure depends on factors such as brine salinity and pH, rock mineral composition and the crude oil composition (Hirasaki, G. J., 1991).

1.3.4 DLVO (Deryagn, Landu, Vervey and Overbeek) Theory

The DLVO theory is a definitive theory for electrostatic stabilization, named after the originators Deryagin and Landau (1941) and later Verwey and Overbeek (1948). This theory calculates the repulsive potential energy in the case of electrostatic stabilization, and when combined with attractive potential energy, the calculations enable a quantitative theory of colloidal stability to be formulated. The theory states that the stability of a colloidal particle is as a result of the diffuse layer rather than the stern layer.

1.3.5 DLVO Theory Assumptions

- Ions in the electrical double layer are point charges
- There is no specific adsorption of ions at the particle surface
- As the particles approach each other, the electrostatic potential at the surface is constant

In practical systems, the second assumption is violated. The DLVO theory has limitations in high salinity brine as there are other forces apart from the van der Waal, electrostatic and hydration forces which become increasingly important in the stabilization of the water film thickness. ***Figure 1-13*** illustrates the DLVO theory.

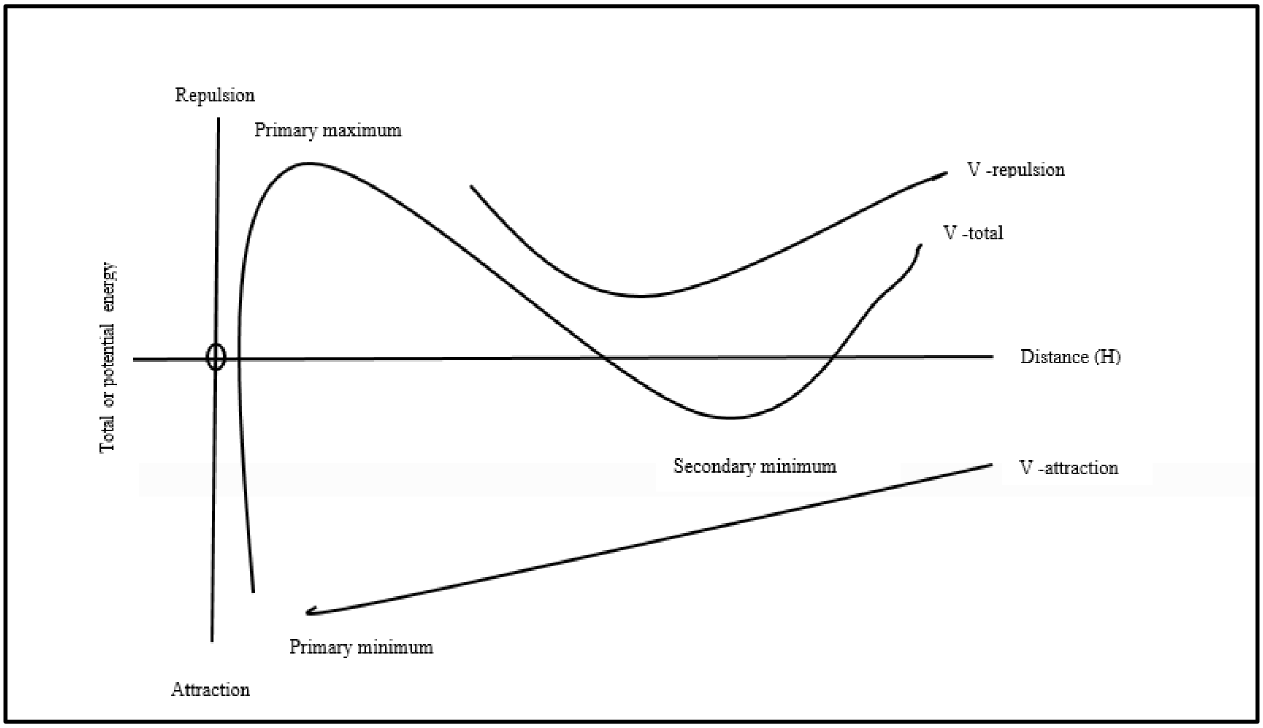


Figure 1-13: DLVO Theory

DLVO Theory

The DLVO theory is used to model the movement of particles and their attraction or repulsion

$V_T = V_A + V_R + V_S$

V_T = Total energy potential between particles

V_A = Attraction between particles due to van der Waals

V_R = Repulsion between particles due to Electric Double Layer- EDL

V_S = Steric repulsion between particles (Polymer coatings). This is usually ignored because it is not associated with zeta potential measurements.

At the secondary minimum, the particles are slightly below the neutral area, ie the zero areas and at that point, the flocculated aggregate can easily be dispersed.

At the primary maximum, the repulsion is greater than the attraction, and the particles are going to be dispersed.

At the primary minimum, we start having hard aggregate, and it will be challenging to get the particles re-dispersed, ie the force of attraction is greater than the force of repulsion. Increasing the zeta potential of dispersion means increasing the area of our primary minimum.

Zeta potential is the potential in mV measured at a distance from the surface of the particle, known as the slipping plane. It is a measure of the magnitude of electrostatic repulsion/attraction between suspended particles. Larger size of electrostatic repulsion/ attraction results in the higher stability for an emulsion. Adding acid to an emulsion causes a reduction in the magnitude of zeta potential until it finally becomes neutralized or even positive. The opposite effect is seen when an alkali is added. When an alkali is added, the magnitude of the negative zeta potential increases, like the effect seen in low salinity.

1.4 Research Aims

Since crude-oil/water/rock interactions can lead to significant variations in the displacement efficiency of water floods, the broad objective of this study is to understand, evaluate and rank the performance of three different classes of surfactants in sandstone and unconventional reservoirs (carbonate and shale) based on zeta potential measurements, favorable wettability alteration and interfacial tension (IFT) reduction capabilities under varying brine conditions (ionic composition, valency and salinity) which therefore provides more insight to resolve the controversies involving the crude-oil-brine (COBR) interactions that leads to an improved oil recovery in low tension water flooding. This work aims to eliminate the bottle-neck of designing an efficient surfactant system which can be favorably replicated in-field pilot tests for similar reservoirs by addressing how the zeta potential of rocks such as Indiana limestone, Silurian dolomite, Botucatu sandstone and Evie Shale in different ionic strength, composition, surfactant, and pH affects oil recovery. Moreso, proposed salinities for improved oil recovery are addressed.

1.5 Order of Thesis

Chapter 2 gives a literature review of some laboratory and field tests that have been done to see the effects of influencing parameters in the subject area. It also uncovers the research gaps, problem statement and research questions.

In chapter 3, the experimental procedure/methodology that was used in this work is explained. For example, bine/surfactant solution preparation, phase behavior, zeta potential, interfacial tension measurements, and low-tension waterflooding with micromodel is shown. All experiments are conducted in ambient temperature and pressure.

Chapter 4 presents and discusses the collated experimental results, starting with the fluid-fluid analysis, which is followed by the rock-fluid analysis and then micromodel flooding results.

In chapter 5, an overall conclusion and further research areas/recommendations are given.

Chapter 2 : Literature Review

Low salinity water flooding is an emerging enhanced oil recovery mechanism still in its research and development stages. It generally involves the destabilization of the oil adhered to the rock surface for more water-wet conditions (McGuire et al., 2005; Rivet et al.,2010; Tang, G. Q. & Morrow, 1997). In surfactant flooding, the surfactant is added to the injection brine to reduce the Interfacial tension (IFT) by increasing the capillary number (Taber, 1969). The capillary number, N_c, is a dimensionless ratio of viscous to capillary forces. During low salinity water flooding, the salinity of the injected water usually ranges from 2 ppm to 3000 ppm (Morrow & Buckley, 2011b) while salinities up to 5000 ppm has shown a favorable low salinity effect (Alagic & Skauge, 2010). Low salinity effect which should lead to an improved oil recovery is however not always observed which implies that there are more than one contributing mechanisms (Morrow & Buckley, 2011). Favorable wettability alteration is however considered by many researchers to be the leading cause of positive low salinity effect.

Low salinity water and surfactant flooding (LSS), otherwise known, as low-tension water flooding is a hybrid mechanism that could have a synergetic effect of both wettability alteration observed by low salinity water flooding and interfacial tension reduction found in surfactant flooding alone (Alagic & Skauge, 2010; Spildo et al., 2012). (Spildo et al., 2012) showed a better oil recovery from low salinity and surfactant flooding in intermediate wet cores compared to the low salinity brines alone.

2.1 Successful Low Salinity Flooding Cases – Laboratory Studies

(Tetteh et al., 2017) performed some low salinity water flood in both aged and unaged Indiana limestone cores. In both cores, there was an improvement in oil recovery between 2.5% and 9%.

The authors further investigated the fluid-fluid interactions that occur during low salinity water flooding through Fourier Transform Infrared spectroscopy (FTIR), Environmental scanning electron micro-spectroscopy (ESEM) imaging and thermal gravimetric analysis (TGA). Their results showed that low salinity effect is observed in both low salinity brine and seawater brine (2005 ppm and 32895 ppm respectively). The FTIR, ESEM and TGA analysis showed that low salinity brine improves the oil recovery by changing the composition of the Lasing Kansas City - LKC crude oil used in their experiments. The low salinity brine causes the formation of a micro-dispersion within the oil phase whereas no changes in the oil composition were observed with the use of formation water. Further investigation showed that the micro-dispersion was however not formed at salinities above 6000 ppm. Lowest IFT values were gotten with the seawater as compared to the case of the formation and low salinity water. They, therefore, attributed the low salinity effect seen in the seawater to be as a result of a higher dilational elasticity and reduced snap off during the core flood experiments with the seawater brine. Again, these hypotheses were backed up with the observation from the FTIR, ESEM and TGA analysis.

(Fathi et al., 2010) studied the effect of temperature, salinity, and ion composition on the oil recovery in chalk cores with porosity ranging between 45% and 47%. Oil recovery increased by 10 % when imbibition temperature was 110ºC and 120ºC in seawater brine depleted in NaCl, compared to seawater alone. The water-wet fraction of the chalk rock was 29% in seawater depleted in NaCl brine compared to ordinary seawater which had an 11 % water-wet fraction in the imbibition studies. A four times increase in the amount of NaCl brine reduced the oil recovery by 5% while 10,000 ppm diluted seawater did not lead to additional oil recovery. During forced displacement with seawater, there was no observed additional oil recovery. The authors attributed the incremental oil recovery to the relative concentrations of active and non-active ions present in the injected brine, hence oil recovery.

(Zhang et al., 2007) studied the effect of low salinity brine injection using three different oils of different viscosities in unconsolidated sandstone cores of permeability in the range of 600mD. Both high salinity and low salinity brine of 29,690 ppm and 1479 ppm respectively containing monovalent and divalent ions, and two concentrations of NaCl brine of 8000 ppm and 1500 ppm salinities were injected. Cores were saturated with both crude oil and mineral oil. The low salinity brine of 1479 ppm resulted in recovered between 7 – 14% of the original oil in place while the 8000 ppm resulted in no additional oil recovery in tertiary mode. Switching to 5000 ppm NaCl brine salinity resulted in an additional 5% oil recovery. Oil recovery from the mineral oil was insignificant compared to the crude oil.

(Agbalaka et al., 2009) investigated the impact of brine salinity, temperature, and wettability on oil recovery using Berea and shaley sandstones from Milne Point Unit (MPU). The Berea sandstone had porosity values between 18 and 20% and absolute permeability between 0.0888 and 0.2682 μm^2 (90 mD – 290 mD) while the Miline sandstone's porosity and absolute permeability values range from 16 – 26% and 0.000918 – 0.19 μm^2 (0.93 mD – 194 mD) respectively. Three synthetic NaCl brines of different salinities were used in their study – High salinity (4 % NaCl) and low salinities (2% and 1%). Cores were initially flooded with the high salinity brine and then low salinity brine at low and high temperatures (between 80 °C and 82°C) followed by the low salinity brine injection for the Berea sandstone. Meanwhile, for MPU, the cores are flooded to re-establish connate water saturation to re-calculate Amott Harvey wettability index at both ambient and high temperature with the varying brine salinities. There was incremental oil recovery with decreasing brine salinity and increasing temperature. Overall oil recovery ranged between 62% and 87%, while the residual oil saturation was decreased from 39% to 15%. However, with a decrease in brine salinity, early water breakthrough is seen with less than one pore volume of brine injection, and it was attributed to the wettability of the sandstones which are already water wet.

(Tang & Morrow, 1997) investigated the effect of temperature, salinity and connate water on oil recovery in Berea sandstone. Their results indicate that the oil recovery gotten during low salinity water flooding is dependent on the salinity difference between the connate brine and injected brine. Low salinity water resulted in an additional 6% recovery in high salinity brine (24,168 ppm) while there was no change in recovery when a high salinity brine was injected in a core containing a low salinity brine of 241.68 ppm salinity. No incremental oil recovery was also seen in the case where a low salinity brine was injected in a core that was already saturated with low salinity brine. In the case where the invaded brine was of low salinity, in a high saline core, the oil recovered was 56%, while for the case where a high salinity brine invaded the core saturated with a low saline brine, the oil recovered was 80% of the original oil in place (OOIP). This also proves the impact of osmotic pressure gradient on a successful low salinity oil effect.

2.2 Successful Field Trials of Low Salinity Water Flood

(McGuire et al., 2005) carried out field trials of single-well chemical tracer test (SWCTT) in two Alaska sandstone rocks. The SWCTT wells were drilled in the Borealis Field of the Prudhoe Bay Unit, one in the Kuparuk sand and the other in the other in the Ivishak sand. The Kuparuk sand had an average porosity of 16% and a reservoir temperature of 150^{o}F. Before the tracer test was carried out, the well was under production for ten days with an average daily production of 650 BOPD and a zero water cut. High and low salinity brines of 23,000 ppm, and 2500 ppm respectively were injected. Residual oil saturation for the high salinity case was 0.21 ± 0.02 while that of the low salinity flood was 0.13 ± 0.02.

The Ivishak sand has a porosity of 22% and a reservoir temperature of 217^{o}F. Before the SWCTT test, the well produced an average of 400 BOPD with a water injection of 150 BWPD. Injection of low salinity water further reduced the residual oil saturation from 0.19 ± 0.03 seen with high salinity water to 0.15 ± 0.03. Similarly, positive low salinity effects were seen in the single-well chemical tracer test (SWCTT) for the Endicott Kekiktuk sand, which signifying positive low salinity effects for the Alaska North slopes with possible incremental oil recoveries between 6 to 12 %. Based on their observations and laboratory results from previous studies on sandstones, the authors further concluded that the changes that occur in the reservoir fluids, fluid-rock interaction and wettability during low salinity water flooding is similar to those that occur during alkaline and surfactant flooding. The increase in oil recovery was also attributed to an increase in pH from the reservoir pH of 7 - 8 to values at 9 as observed during the low salinity waterflooding process. According to the authors, the cause of the pH increase is the increase in the hydroxyl ions, which are generated by the reactions of the low salinity brine with the minerals that are native to the reservoir and also due to the elimination or lack of the presence of high concentration of dissolved chemicals that would have been generated during a typical conventional water flooding. A high pH value causes the generation of in situ surfactants.

(Seccombe et al., 2010) demonstrated that there is a positive low salinity effect in a tertiary mode in an inter-well field trial, similar to core flood experiments and single-well tests in the Endicott field which is a sandstone reservoir in the North Slope Alaska. Initial oil saturation was 95%. Two risks of low salinity EOR were evaluated - The impact of mixing of reservoir water with the low salinity brine or other mechanisms that may cause an adverse low salinity effect and the risk of viscous fingering reducing the oil recovery from the low salinity waterflood. The reduced salinity waterflood effect was observed after three months, where the oil recovery began to increase, and the ion composition of produced water showed a reduced salinity. The high salinity brine injection swept 59 % of the original oil in place while the low salinity brine swept an additional 10 % (scaled for clay content) after a total of 1.6 pore volume of the low salinity brine injection. Their simulation results showed that there would be no adverse mixing effect or viscous fingering. The authors believe that the low salinity waterflood was the cause of the additional oil recovery because the incremental oil recovery came at the breakthrough time of the low salinity water injection and analysis of produced water showed no traces of PDI. There was a good correlation between the incremental oil recovery and laboratory core flood experiments, and finally, after scaling for clay content, the core flood experimental recovery matched the results for the pilot test.

(Webb et al., 2003) performed a log-inject-log analysis to test the low salinity phenomenon on a well drilled in a clastic reservoir that comprises of complex series of the tidal, estuary, deltaic, valley fill and shoreface sands interbedded with semi-continuous shales. The porosity of the sands ranges between 20 and 30%. Low salinity waterflood recovery gave between 10 % (at middle perforation – 50 % at top perforation) During the injection of low salinity water, the flow rate of 0.5 bbls/min was low to avoid cross-flow (by allowing for pressure equilibrium/stabilization) and to ensure that the additional oil recovery is as a result of the low salinity brine. Initially, 10 -15 Pore volume of 220,000 ppm high salinity brine was followed by 120,000 ppm medium salinity brine containing mainly NaCl brine and then 3000 ppm of low salinity brine containing PDI's (Ca^{2+}, Mg^{2+} and HCO_3^-). After the injection of the low salinity brine, the residual oil saturation was 50% in the top perforation and 10-20% in the middle and bottom perforation. As stated by the authors, although there was an increase in oil recovery, the mechanism of this positive low salinity brine effect was not fully understood.

(Robertson, 2007) showed that there is a positive low salinity effect in three units of minnelusa formation fields (West Semlek reservoir, North Semlek reservoir, and the Moran reservoir) comprising of white cemented sandstone loosely cemented by carbonate and anhydrite, having porosity and permeability values of 16.2 % and 50 - 657 mD respectively. Formation brine salinities of the units are 60,000 ppm, 42,000 ppm, and 128,000 ppm respectively while the injected low salinity brine was 10,000 ppm, 3304 ppm, and 7948 ppm respectively. Their results show positive low salinity effect where the oil recovery increases with an increase in salinity ratio (ratio of the salinity of the injected to formation fluid).

(Lager et al., 2008) Confirmed a positive low salinity effect in inter-well and tracer test between one injector and two producers in the Alaskan field. The chemical analysis of the produced water was a pointer to show that the low salinity effect was as a result of multi-component ion exchange between the adsorbed crude oil components, cations in the in situ brine and the clay minerals. Analysis of the produced water showed that it contained less magnesium ion, which indicates ion exchange between the injected brine and reservoir rock. Other factors such as fine migration and pH variation were ruled out of the possible causes of improved oil recovery since fine migration results in the blockage of pores, hence reduced injectivity. The injectivity was constant during the low salinity flood, ruling out possible fine migration while pH did not increase significantly. Injected low salinity brine is 2,600 ppm, whereas, the reservoir brine salinity was 16,000 ppm. Residual oil saturation was reduced by 10 % when the injected brine was switched from high salinity to low salinity brine.

In the Omar field test and concurrent experiments, (Vledder et al., 2010), noted that the laboratory model showed additional recoveries within the range of what was expected and observed in the field tests. The increase in the ultimate recovery factor in the field was between 5 % - 15 %, whereas, the laboratory tests which modeled the waterflood showed an additional recovery between the range of 9 % - 23 %, which indicates an overlap of the expected results and serves as a pointer to the fact that laboratory models could help achieve an estimation of waterflood performance on a field scale.

2.3 Unsuccessful Low Salinity Waterflooding Cases

(Rivet et al., 2010) evaluated the effect of injected brine salinity and cation composition on oil recovery rate, residual oil saturation and relative permeability in six outcrops Berea cores and two oil reservoir cores in 21 different brine salinities with varying cation concentration. Parallel and serial water floods were conducted in the cores. For the parallel water flood, the cores were cut from the same block of Berea formation while the water flood was conducted in similar but separate cores. However, for the serial water flood, the waterflood experiments were conducted one after the other in the same cores in order to eliminate the effect of differences in mineralogical composition. The effect of Na^+ and Ca^{2+} ions were investigated for the high salinity injection. In addition to the ions studied during high salinity injection, Li^+ ions were also investigated for the low salinity case. In one of the parallel experiments, the sodium and calcium content in both the high and low salinity brines were of the same ratio. The first parallel waterflood injection was done in five Berea cores whereby one of the cores was flooded in secondary mode with Na^+ and Ca^{2+} ions contained in the high salinity. Low salinity brine injection containing Na^+ and Ca^{2+} ions was done in tertiary mode. Low salinity flooding was done in the other four cores with brine containing

Na^+ and Ca^{2+} ions alone, Na^+ ions alone, Ca^{2+} ions alone and Li^+ ions alone in secondary mode. The highest recovery of about 58% OOIP was gotten in the case where low salinity brine containing sodium and calcium ions were flooded in secondary mode while the other low salinity brines which were flooded in secondary mode resulted in a higher oil recovery than the previous case where it was flooded in tertiary mode where no additional oil recovery was observed after 50% of the OOIP was recovered by the high salinity brine flooded in tertiary mode.

Contrary to the work of (McGuire et al., 2005) who attributed the increase in oil recovery to be as a result of an increase in pH values, the effluent pH gotten from the low salinity brine which gave the highest oil recovery was the lowest at about 7.6 while the low salinity brine which resulted in the lowest oil recovery had the most elevated effluent pH at the end of the flood.

The oil recovery sensitivity to the injected brine cation was attributed to cation exchange mechanism. The affinity binding for clay present in a core to cation is in the following order; $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > Mg^{2+} > Ca^{2+} > Sr^+ > Ba^{2+} > H^+$ (Lake, 1989) . It was therefore suprising that the recoveries from low salinity brine containing Lithium was not similar to the low salinity brine containing sodium.

In one of the serial waterflood using the same core, the core was flooded with various brines similar to the parallel water flood descried above. Four different flooding sequence was carried out, in which after each flooding sequence, the high salinity brine connate water saturation was restored before the next flooding sequence. The first flood was done with high salinity brine in secondary mode and then low salinity brine in tertiary mode, after restoring the connate water saturation, the next flooding sequence was with low salinity brine in tertiary mode, the third sequence was the same as the first, while the fourth sequence was the same as the second. After four pore volume

(PV) of injection, the highest oil recovery was gotten from the third sequence of flood where the high salinity brine was first injected in secondary mode before the low salinity brine while the lowest oil recovery was gotten from the first sequence. Similarly in terms of pH, the highest oil recovery was obtained when the effluent pH was the lowest after 4 PV of brine injection. Again, none of the low salinity brine recovered incremental oil. In the two other serial experiments carried out, low salinity and high salinity brine recoveries were the same for one, while for the other, the low salinity brine resulted in a higher oil recovery compared to the high salinity brine. The concentration of the high and low salinity brine used in the studies are 30510 ppm and 1140 ppm respectively. The results show that cores which are already water wet due to the low clay content show no significant improvement in recovery during low salinity water injection.

(Skrettingland et al., 2011) in their work conducted both laboratory and field test to investigate the low salinity effect for the upper Statford formation in the Snorre field. The low salinity core flood experiments resulted in a 2 % incremental oil recovery. A single-well chemical tracer test (SWCTT) was then conducted to replicate the positive core flood results on a field scale but did not show any significant change in the residual oil saturation. The conclusion therefore drawn by the authors is that the wetting state of the Snorre field is very close to optimum for seawater injection, which eliminates the need for low salinity water flooding.

(Zhang, Y. & Morrow, 2006) investigated the effect of low salinity on various crude oil and Berea sandstone combinations and their results show that the low salinity brine injection is not successful in all cases as recovery from one of the cores was similar for both high and low salinity cases which were unexpected. This was further tested by injecting distilled water to obtain a higher salinity contrast, and the results showed that the recovery from the distilled water was similar to both the high and low salinity brine. Even more surprisingly, the sharp increase in pressure drop did not have an effect on oil recovery during the distilled water injection. The authors attributed this to the release of kaolinite clay during the start of the injection of freshwater which causes permeability damage. Doubling the salinity of the connate water and then injecting low salinity brine resulted to even lower oil recovery compared to the case where the injection was done at the original brine salinity thereby debunking the effect of osmotic pressure gradient as a contributory mechanism to the low salinity effect. The concentration of the high and low salinity brines were 15140 ppm and 151.4 ppm respectively and the authors' attributed oil recovery response to be dependent on the overall rock properties.

(Nasralla et al., 2011) conducted eight high pressure, high temperature (500 psi, 100° C) water-flood experiments on Berea sandstone rock at varying salinity values ranging from de-ionized water, 5000 ppm to 174,000 ppm in both secondary and tertiary modes, using two different oil types to investigate the low salinity effect and the effect of crude oil composition on low salinity effect. The cores were saturated with formation brine at connate water saturation ranging between 31.23 % and 39.81% while the remaining pore volume was saturated with oil. Four of the cores were used for each of the crude oil. In all experiments, injecting de-ionized water in tertiary mode resulted in no additional recovery and the authors attributed this to the change in wettability towards more water-wet state with the injection of higher salinity brine in secondary mode before freshwater injection. However, injecting low salinity water such as aquifer water and de-ionized water in secondary mode resulted in at least 65% and 70% incremental oil recovery for aquifer water and de-ionized water respectively for the two crude oil types investigated. The incremental oil recovery gotten in the low salinity cases contradicts the work of (Zhang & Morrow, 2006). The salinity of the aquifer water, seawater and formation water used for the experiments are 5436 ppm, 54680 ppm and, 174156 ppm respectively.

From all the cited literature, it is evident that there is still a contradiction on the mechanism that causes low salinity effect in both sandstones and carbonate rocks. Surprisingly, even low salinity water flooding has been extensively applied in sandstones which are thought to be less complicated than carbonates, the low salinity mechanism remains a mystery. Moreso, no account was taken to study the effect of chemical additives such as surfactants on low salinity water flooding. The next section thereby describes the low salinity and surfactant flooding processes.

2.4 Low Salinity Water and Surfactant Flooding

Surfactants are utilized to reduce the Interfacial tension (IFT) and improve wettability alteration. Chemical Enhanced oil recovery with sandstones have been explored extensively (Manrique et al., 2010), while more work needs to be done in carbonates. Carbonate rocks are of primary interests since they contain more than half of the world's oil reserves (Choquette & Roehl, 1985; Klemme & Ulmishek, 1991). Some chemical flooding that has been applied to various fields including fields in Canada are shown in ***Table 2-1*** and

Table 2-2

Table 2-1: Chemical flooding in various fields

(Kamal et al., 2017)

Country	Field	Formation Type	Surfactant

USA	Cretaceous Upper Edwards	Carbonate	PetroStep-B 100
	The cottonwood creek	Carbonate	Polyoxyethylene glycol
	Yates Field	Carbonate	Non-ionic ethoxy alcohol
	Tanner	Sandstone	ORS-41
China	Daging	Sandstone	Petroleum Sulfonate,Lignosulfonate, alkyl benzenesulfonate,petroleum carboxylate, biosurfactant
	Karamay	Sandstone	Petroleum sulfonate
India	Viraj	Sandstone	Petroleum Sulfonate
	West Kiehl	Sandstone	Petrostep B-100
Indonesia	Minas	Sandstone	Petroleum Sulfonate
Argentina	Chihuido de la sierra negra		SS-6066
Germany	Bramberge	Sandstone	Olefin sulfonate

Table 2-2: Some Chemical enhanced oil recovery in Alberta Canada

Source: (https://aer.ca/documents/reports/ercb-eor-report1.pdf)

Field name	**Producing formation**	**Primary recovery factor (%)**	**Enhanced Recovery factor**	**Type**
Entice	Ellerslie	10	25	ASP flood
Mooney	Bluesky	7	12	ASP flood
Suffield	Glauconitic	10	25	ASP flood

Taber	Glauconitic	18	38	ASP flood
Taber South	Mannville GRP	10	42	ASP flood
Countess	Glauconitic	10.5	36	Polymer flood
Edgerton	Woodbend	6	3	Polymer flood
Provost	Manville Upper	3	12	Polymer flood
Suffield	Manville Upper	15	20	Polymer flood
Vokiing-Kinsella	Wainwright	14	35	Polymer flood
Wildmere	Lloydminster SS/Sparky	11	12	Polymer flood
Wrentham	Sunburst SS	15	30	Polymer flood
Wrentham	Manville Lower	15	30	Polymer flood

2.4.1 Mechanism of Wettability Alteration with Surfactants

As observed by (Standnes & Austad, 2000), cationic surfactants are able to alter the wettability of low permeability oil-wet chalk rocks towards the more water-wet state. For the cationic surfactant, they have proposed the mechanism of wettability alteration due to the electrostatic interaction between the cationic surfactant and the adsorbed anionic material from the crude oil, in which the adsorbed material at the interface between oil, water and rock will be desorbed by the formation of an ion pair between the negatively charged adsorbed material (carboxylic group of the oil) and the surfactant. The ion pair is stabilized by both electrostatic interactions and hydrophobic interactions and it is insoluble in the water phase but soluble in the oil phase as a 1.1 complex.

component and the positively charged cationic head, which can strip off the oil component on the rock, hence, altering wettability towards more water-wet state. Their results show that anionic surfactants with EO-Sulfonate groups are not able to alter wettability of chalk rocks in an irreversible way since it is difficult for the anionic surfactant to desorb negatively charged oil component from the chemical/electro-static point of view. They proposed that anionic surfactants thereby alter wettability through the hydrophobic interactions with the adsorbed crude oil component. In general, anionic surfactants generate weak capillary forces through hydrophobic interaction between the tail of the surfactant and the negatively charged adsorbed group (Standnes & Austad, 2000). The minor oil displacement by ethoxylated sulfonate observed with anionic surfactant was attributed to the formation of a water-bi layer between the carbonate surface and the oil. (Kumar et al., 2005) proposed wettability alteration with anionic surfactant in positively charged oil-wet AP Mica plates to be through IFT reduction, whereby the gravitational force exceeds the capillary pressure, thereby promoting imbibition and micellar solubilization of adsorbed organic components surfactants. This layer of adsorbed surfactant with the hydrophilic head groups covering the originally oil-wet rock surface could then change the wettability to more water-wet conditions. ***Figure 2-1*** and ***Figure 2-2*** illustrates the wettability alteration mechanisms by cationic and anionic surfactants.

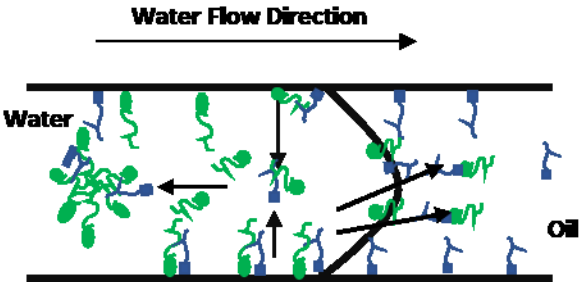


Figure 2-1: Illustration of the suggested mechanism of wettability alteration with cationic surfactants in a pore. Circles cationic surfactants and squares are anionic surface-active organic material in the crude oil Modified after

(Standnes & Austad, 2000)

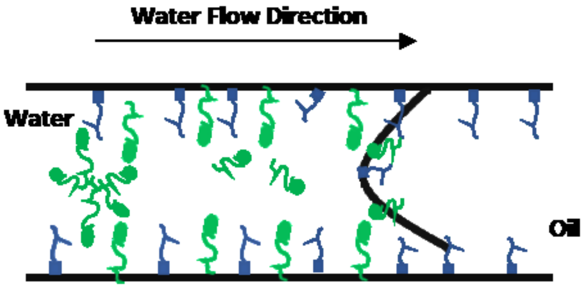


Figure 2-2: Illustration of the suggested mechanism of wettability alteration with anionic surfactants in a pore. Circles anionic (EO- sulfonates) surfactants and squares are organic carboxylate material in the crude oil Modified after

(Standnes & Austad, 2000)

In the previous literature, the effect of increasing electrical double layer, ion type, wettability alteration has been seen for both successful and unsuccessful low salinity water flooding cases in sandstones and carbonate rocks. In this section, a literature review is given for the effect of surfactant in low salinity waterflood.

2.4.2 Effect of Surfactant on Recovery

Low salinity waterflood cannot contribute significantly to IFT reduction. IFT reduction is needed for the mobilization of residual oil and creation of oil bank from the oil ganglia. Maintaining the low IFT at the displacement front is essential during flooding so that mobilized remaining oil is not retrapped. Low salinity flood operating at higher IFT/higher capillarity leads to the entrapment of the mobilized oil as oil ganglia (Johannessen & Spildo, 2013). The displacement efficiency will become lower in this case which can be understood by comparing the oil recovery results of low saline flooding done at low capillarity with high capillarity.

(Spildo et al., 2012) reported that injection of low saline water with 3002 ppm as a follow-up slug to seawater (with 36494 ppm) doesn't reduce residual oil saturation (S_{or}) by more than 0.01 in three different sandstone cores. However, low salinity surfactant (LSS) flooding carried out using anionic surfactant reduced the oil saturation by more than 0.1 in those cores. The authors emphasize the importance of low capillarity for preventing oil entrapment during the low salinity flooding. Surfactant flooding will also be benefitted from when combined with low salinity flooding as surfactant retention was reported to be lower in the low salinity environment when compared with high salinity (Alagic & Skauge, 2010; Spildo et al., 2012).

Most of the previous work that has advocated the efficacy of surfactant smart water flood was performed in the low saline range (Alagic & Skauge, 2010; Spildo et al., 2012). Contrarily, few studies reported that seawater and optimal saline water injection could lead to higher oil recovery than low saline injection (Johannessen & Spildo, 2013). For example. (Johannessen & Spildo, 2013) diluted the 36431-ppm North Sea water and reported that anionic surfactant flooding with Alcohol Propoxyl sulfate (APS) having propoxy group ranging from 7 to 13 and Internal olefin sulfonate (IOS) conducted at optimal salinity (15503 ppm) gave higher recovery in the Berea sandstone than the low salinity water and surfactant (LSS) flooding conducted at low salinity (2584 ppm). Some researchers conclude that injecting seawater will result in the higher oil recovery than injecting any other water in chalk carbonate (Austad et al., 2005; Strand et al., 2006; Zhang, P. & Austad, 2006b; Zhang et al., 2007). The question arises at which salinity that the surfactant flood should be combined with, during smart water-surfactant flood.

Most of the LSS studies were conducted using an anionic surfactant. Particularly for positively charged carbonate rocks, negatively charged anionic surfactants are not preferred due to the possible adsorption. Cationic surfactant, non-ionic surfactant (Han et al., 2013; Ma et al., 2013), zwitterionic surfactants (Kamal et al., 2015) and viscoelastic surfactants (Azad & Sultan, 2014) have been evaluated for chemical EOR applications in carbonate formations. Therefore, it is vital to consider various classes of surfactant when investigating their hybrid oil recovery application in carbonate formation. (Yousef et al., 2011) pointed out that lowering the salinity further down from seawater salinity does not result in drastic reduction in IFT. This indicates that surfactant in seawater may give lower IFT, as ultra-low IFT is normally seen at relatively higher salinity (Green & Willhite, 1998; Healy et al., 1976) Ultra-low IFT and higher capillary number is a prerequisite for any recovery experiments that involve the forced displacement. Carbonate reservoirs with a permeability of 35 mD have been subjected to forced displacement experiments by (Yousef et al., 2011). Carbonate formations such as chalk with the permeability ranging from 5.5 to 6.2 mD, limestone with the permeability ranging from 3.9 to 56.5 mD, dolostone with the permeability ranging from 10.8 to 235md are subjected to imbibition experiments (Romanuka et al., 2012). For imbibition-based recovery, wettability alteration may be more important in early times (Sheng, James J., 2013). Therefore, an EOR researcher attempting to find an optimal surfactant for oil recovery applications in carbonate formation must have preliminary knowledge about both the IFT reduction and wettability alteration potential of different classes of surfactant at various salinities.

(Chandrasekhar, 2013) reported that modified seawater containing Mg^{2+} and So_4^{2-} ions in the diluted seawater changes the wettability of carbonate from oil-wet to water-wet.

(Johannessen & Spildo, 2013) performed in their experiments with oil aged Berea sandstone core plugs using Alcohol Propoxyl sulfate (APS) with propoxy group ranging from 7 to 13 and Internal olefin sulfonate (IOS) in seawater of various salinities (36431 ppm, 15503 ppm and 2584 ppm) to compare the performance of low and optimal salinity water and surfactant injection of which optimal salinity water and surfactant results in an ultra-low IFT value compared to the former case. Their results were indicative that the low salinity and optimal salinity recoveries were comparable; however, optimal salinity water flooding had higher surfactant adsorption, thereby making low salinity water and surfactant flooding which gave a capillary number two orders lower than the optimal salinity better. Phase behavior experiments at varying water-oil ratio were carried out with a 3: 1 ratio blend of APS-IOS and a total surfactant concentration of 3.3 wt%, for selecting the surfactant and salinity which gives a Winsor type III microemulsion at high salinity (optimal salinity) and a Winsor type I microemulsion at low salinity. The surfactant retention on the rock measured by dynamic retention measurement which involves the saturation of a dry core with surfactant solution followed by chase water and then measuring the effluent surfactant concentration by potentiometric titration showed a 0.39 mg/g and 0.24 mg/g of Rock for the optimal salinity and the low salinity cases. Oil recovery from both cases was also similar with the LSS case giving a high recovery that would be expected in the capillary number relationship, while the recovery for the OSS was similar to would have been gotten with the capillary number relationship. This is a pointer that wettability alteration plays more role in oil recovery compared to the reduction in interfacial tension. The low salinity water and surfactant (LSS) flooding performs better compared to the optimal salinity water and surfactant (OSS).

(Alagic & Skauge, 2010) also confirmed low surfactant retention in low salinity waterflood of 0.5 wt % NaCl, using an anionic surfactant in Berea sandstone cores. Oil recovery seen in the LSS flood was over 90% and was attributed to the combination of wettability alteration and the reduction of the oil-brine interfacial tension. The low salinity water and surfactant flooding were done in tertiary mode after flooding with seawater containing potential determining ions with a salinity of 36321 ppm. The composition of the low salinity injection slug was 0.5 wt.% NaCl, 1.0 wt.% Internal olefin sulfonate and 1.0 wt% isoamyl alcohol (IAA).

(Martavaltzi et al., 2012) studied the effect of various ions and their concentration on the wettability of Indiana limestone outcrop core as well as the effect of surfactant addition on the wettability of calcite crystal samples with the aim of providing guidelines for the design of injection brines for enhanced oil recovery. The wettability alteration behavior was studied using a sessile drop contact angle method on the rock after equilibrating with different brine solutions and on the calcite crystal with $CaCl_2$ brine and various surfactant solutions. The oil used in their study was a model oil made from 1.5 wt. % naphthenic acid in decane, while the formation brine was a mixture of salts: NaCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4. Commercially available nonionic surfactants containing various ethoxylate groups ranging from 10 to 50 were used. Also, secondary alcohol ethoxylate nonionic surfactants were also used for their study. All surfactants used has a cloud point above 100 ^oC. For the contact angle measurement, the Indiana limestone rock was aged with the model oil for 200 hours at 100 ^oC after equilibrating with the formation brine. After aging, the samples were immersed in different brine solutions (0.01M $CaCl_2$, 1M $CaCl_2$, 5M $CaCl_2$, 0.01 M $MgCl_2$, 1M $MgCl_2$, 5M $MgCl_2$, 0.01 M Na_2SO_4, 1M Na_2SO_4) to test the effect of ions and salinity on wettability alteration. To isolate the effect of each interaction (brine or oil with the solid surface), contact angle of a reference sample after only equilibrating in formation brine and of another after only aging in oil was measured. The contact angle procedure that was done on the Indiana limestone and the calcite plate was similar except that the calcite plate was immersed in different surfactant solutions (0.01M $CaCl_2$ + 0.4 wt% Surfactant), with all the surfactants being 100% active except the Nonyl Phenol Ethoxylate (NP 50) with 70 wt.% activity. Their results are indicative that the reference rock which was only equilibrated in formation brine but not aged was weekly water wet, with a contact angle of 51^o while that which was aged in the model oil for ten days was oil-wet, having a contact angle of 138^o. Immersion of the sample equilibrated formation brine and aged with model oil with a low salinity brine of 0.01 M $CaCl_2$ dropped the contact angle from 138° to 34°, indicating a more water-wet state. When the sample was immersed in the same salinity for $MgCl_2$ brine the contact angle only dropped to 104°. The other brine salinities and ions used had a negative effect on the wettability alteration, with 1M Na_2SO_4 increasing the contact angle to as much as 168°. The authors stated that sulfate ions are not able to alter the wettability of carbonates significantly in the absence of divalent cations such as Ca^{2+} and Mg^{2+}. Moreso, Magnesium ions alone are not able to alter the wettability of calcite crystals. In the calcite plate, the contact angle of the plate equilibrated in formation brine and then immersed in de-ionized water was 12° and then when it was aged with the model oil and then immersed in de-ionized water, the contact angle was 155°. When aged sample was immersed in 0.01 M $CaCl_2$, the contact angle dropped to 34°. All surfactant solutions were able to change the wettability of the calcite plate towards more water-wet conditions better than the 0.01 M $CaCl_2$ brine except the Nonylphenol ethoxylate with 10 EO groups and the secondary alcohol with 30 EO groups which resulted in contact angles of 45° and 155° respectively. The authors explained that the non-ionic surfactants of homologous series NP and 15-S which was used in their study could only alter wettability at temperatures above 80°. Since their experiments were carried out at room temperature and pressure, it was therefore not surprising that the non-ionic surfactant could not alter wettability of the calcite plate significantly.

(Karimi et al., 2016) studied the effects of ions on oil recovery in oil-wet limestone as well as the impact of low salinity brine containing magnesium and sulfate ions on wettability alteration and oil recovery. The effect of 0.5 wt.% dodecyl trimethyl ammonium bromide (DTAB) on wettability alteration on these low salinity brines were also studied using contact angle, spontaneous imbibition, and interfacial tension measurements. Their contact results was done on Iceland spar crystal which after attaining initial water saturation with formation brine and aging in crude oil at 75°C for 10 days and their results are indicative that both magnesium and sulfate ions can act as wettability modifying agents for oil-wet calcite and all the low salinity brines modified for variations in magnesium and sulfate ions changed the wettability of the oil-wet calcite towards more water-wet state. The contact angle of the plate after aging in crude oil was 149 o, indicating an oil-wet state. The use of 196010 ppm formation brine diluted 100 times for contact angle measurements resulted in a slight wettability alteration to a value of 146°. When 12160 ppm of brine containing sulfate ions were used, the contact angle decreased further to 89° whereas with 46190 ppm of brine containing magnesium ions, the contact angle was 61°, contact angle reduced further to 47° in brine 56390 ppm of brine containing significant amount of calcium and magnesium ions, indicating that there is a synergetic effect for favorable wettability alteration in the presence of both sulfate and magnesium ions. In the presence of the 0.5 wt % cationic surfactant, the 100 times diluted formation brine resulted in a contact angle of 69°, indicating that the cationic surfactant is a good favorable wettability alteration modifier. The authors attributed this to the ion pair formation between cationic surfactant and adsorbed carboxylate on the surface desorption of oil, with the ion pairs being stabilized by both hydrophobic and electrostatic interactions. With the same concentration of cationic surfactant in the brine containing sulfate ions, the cationic surfactant altered the wettability further from 89° to 59°. When the cationic surfactant was added to the brine containing magnesium ions, there was a significant decrease in contact angle from 61° to 16°, suggesting that both cationic surfactant and magnesium ions are active in the removal of the adsorbed carboxylate group from the calcite plate. Treating the calcite plate with the cationic surfactant and the brine containing magnesium and sulfate ions caused a wettability alteration from 47° to 5° The cationic surfactant also had a favorable impact on the wetting state of the Indiana limestone. Their spontaneous imbibition results done on Indiana limestone after attaining initial water saturation and aging in crude oil at 75 °C for 45 days are indicative that mineral dissolution, salting in effect and electrical double layer expansion are responsible for the increase in oil recovery during spontaneous imbibition of diluted brine. With formation brine, the oil recovery was 8% of the original oil in place (OOIP), whereas with the 100 times diluted formation brine, the oil recovery was 58% of the OOIP. The authors attributed this to the low salinity effect whereby the salt content of the aqueous phase influences the partitioning of the organic compounds between water and oil and inorder to solubilize the organic chemical in the aqueous phase, a structure around the hydrophobic part of the organic molecule should be formed via hydrogen bonds of water molecules. According to the authors, there is a strong interaction between water dipoles and small ions in the aqueous phase that improves the cohesive energy in water. The presence of ions in water thereby leads to a breakup of the water structure around the organic material, therefore, the partition equilibrium of the organic chemical shifts towards the oil phase as the salinity of the water increases. referred to as a salting-out effect (Endo, Pfennigsdorff, & Goss, 2012). Hence, the solubility of the aqueous phase can be improved by the removal of salt from the water, otherwise known as the salting in effect, which enhances the desorption of carboxylate materials from the rock surface. The salting in effect gives an increase in the solubility of polar species in brine, thereby affecting the oil-water IFT. The oil recovery in the brine containing magnesium ions was 56% of the OOIP that containing sulfate ion was 65% of the OOIP while that containing both sulfate and magnesium ions resulted in a 75% OOIP. The spontaneous imbibition and contact angle results for the brine containing magnesium ions are not very consistent as spontaneous imbibition result shows that this brine results in the lowest oil recovery, whereas the worst-case scenario for contact angle is the formation brine diluted 100 times and they attributed this to the difference in salinity with both brines, which reduces the EDL in the case of the brine containing magnesium. Also, the authors stated that the mineral dissolution in the case of the brine containing magnesium ions must have been to a lesser extent as shown by the final pH (after spontaneous imbibition) which was more acidic (6.5), while the 100 times diluted brine had a final pH of 7.1. Their initial pH values were 6.1 and 5.8 respectively. When cationic surfactant was mixed with formation brine and then used as the imbibing fluid, there was a 56% oil recovery as against the 8% oil recovery seen with the formation brine alone. With the 100 times diluted brine in the cationic surfactant, oil recovery was 82% of the OOIP as against the 58% with the diluted brine alone. The oil recovery with the cationic surfactant contained in the brine with magnesium resulted in 77% of the OOIP as against the 56% offered in the same scenario in the absence of surfactant, while 91% of the OOIP was recovered with the cationic surfactant contained in the brine with sulfate ions as against the 65%. The mechanism explained for this case was the formation of ion pairs between the cationic surfactant and the adsorbed carboxylate group on the rock, whereby the ion pairs, adsorbed carboxylate molecules as well and the surfactant molecules desorb from the rock, causing the rock surface to be more positively charged, therefore influencing a strong electrostatic force of attraction between the sulfate molecules and the positively charged rock. With the cationic surfactant in the brine containing both magnesium and sulfate ions, oil recovery was increased to 95% as against the 75% observed in the same case without surfactant, which is in line with the contact angle results. They attributed the high oil recovery of the brine containing the cationic surfactant, magnesium and sulfate ions to be as a result of multi-component ion exchange between the magnesium, sulfate, rock and carboxylic component of the oil, whereby the positively charged magnesium ions react with the rock containing negatively charged organic component, thereby causing a partial desorption of the oil from the rock and making the rock less negatively charged, which results in a stronger force of attraction between the sulfate ions and the rock, causing more wettability alteration towards more water-wet state.

In comparison to the brine containing magnesium ions, sulfate ion brines were better in wettability alteration. During spontaneous imbibition experiments, the initial and final IFT values were measured with and without surfactant. In the absence of surfactant, the IFT values were high, between the range of 23.5 mN/m and 48.6 mN/m, whereas, in the presence of DTAB, the initial and final IFT values were in the range of 8.6 mN/m and 3.8 mN/m. This implies that both wettability alteration and interfacial tension reduction contributes to oil recovery.

2.4.3 Surfactant Assisted Flooding with Micromodel

(Mejia et al., 2019) analyzed oil mobilization with the use of surfactants in a fractured oil-wet micromodel. Tridecyl alcohol propoxy sulfate, internal olefin sulfonate, and phenol ethylene oxide were used as the surfactants in NaCl brine at an optimal salinity of 44,000 ppm. Horizontal and vertical micromodel flooding was carried out. In the horizontal flooding, the effect of gravity was minimized by placing the micromodel horizontally on a flat surface with a minute 23-micrometer hydrostatic head height. Whereas, in the vertical micromodel flooding, the gravity effects were included. Images were taken every twenty-four hours for the static experiments with negligible gravity effects and every ten or fifteen minutes for the experiments with gravity-driven imbibition. In the case where no surfactant was contained in the imbibing brine for the horizontally placed micro model, no oil recovery was gotten even after thirty-one days of injection. This was attributed to the non-connectedness of the pore throat features as a result of glass imperfections during micromodel fabrication that may have prevented the diffusion of micelles into the brine. A high inverse bond number was calculated which indicated a capillary driven imbibition. With surfactant solution which gave ultra-low IFT values, 60% of the oil was recovered after 31 days of soaking in the brine, leaving behind some oil ganglia. The authors attributed the increase in oil recovery to be as a result of the diffusion of solubilized oil since capillary and gravity forces were low in that scenario as indicated by the small inverse bond number.

For the vertically placed micromodel with a hydrostatic head of 5 cm, with a 44,000 ppm NaCl brine, some of the oil was recovered with the displacement occurring from the bottom, where the oil-water pressure difference is at its peak. After 15 hours of soaking, oil was recovered from the sides, while after 45 hours of soaking, 3.3% of the initial oil was recovered. Even though the gravity effect contributed to recovery, the capillary pressure calculated was still two orders of magnitude larger than the capillary pressure by the hydrostatic head, hence a low recovery. In the case where surfactant solution was added at optimal salinity, 30% of the oil was recovered after 150 minutes whereas, after 7.9 hours of imbibition, 74% of the oil was recovered. As noted by the authors, the introduction of surfactants reduces the capillary forces to values two orders of magnitude lower than the pressure head from the water column.

The results of their experiments show that wettability alteration and solubilization can recover the same amount of oil from the matrix at a rate slower than solubilization/IFT reduction, gravity/IFT reduction and vicious cross flow whereby the viscous crossflow recovers same amount of oil in hours, gravity/IFT reduction in days and then solubilization and IFT reduction in weeks. Hence, surfactant flooding in fractured carbonate rocks has a different time scale.

(Broens & Unsal, 2018) studied the flow dynamics and emulsification kinetics required to solubilize and mobilize non-aqueous phase liquids by in situ emulsification. A micro model, n-decane, NaCl brine, and internal olefin sulfonate anionic surfactant was used for the study. The micromodel was designed to have both conductive and stagnant dead-end channels in a single pore system to isolate the different possible transport mechanisms and how they transit. In the conductive pathways, the surfactant was carried with flow while localized flow dynamics controlled the emulsification. Whereas in the stagnant zone, chemical concentration gradient controlled the driving forces of mass transfer. The micromodel experiment was visualized under fluorescence light where the oil was amber color, the microemulsion was red, and the water phase was black.

In the base case experiment with de-ionize water which had an IFT value of 43mN/m with the n-decane, no emulsification occurred due to the absence of surfactant and the water began to imbibe into the dead-end channels, displacing no oil until after twelve hours in which one third of the oil in the dead-end channel was recovered. With the surfactant solutions having ultra-low IFT values with NaCl at salinities ranging between 1.6 wt % and 2.0 wt% at different flow rates between 1nL/min to 100 nL/min, emulsification was seen in the dead-end channels and the main channels and a convective flow stream was also observed at the entrance of the dead-end channels. In brief, the oil recovery was controlled by the emulsification characteristics of the surfactant, oil and water system, surfactant delivery rate and pore geometry.

(Xu, K. et al., 2017) developed a 2.5 D micro model to better represent 3D systems compared to the conventional 2 D micromodels to identify capillary snap off and the formation of isolated residual oil. Visualization of the generated microemulsion possible with the use Tween surfactant solutions with ultra-low IFT of $8.5 * 10^{-4}$ mN/m was also illustrated. The generated microemulsion with the surfactant flooding solubilized trapped oil (octane) and reduced capillary trapping while moving together with the aqueous phase, hence resulting in a more water-wet system.

(Alzahid et al., 2019) studied the phase behavior of brine (4.5 – 5.75 % NaCl), polymer (Sulfonated hydrolyzed polyacrylamide-HPAM) Winsor type surfactant (Alkyl ether sulfate) in an oil-wet micromodel at various capillary numbers and viscosity ratios. The zeta potential of the different microemulsion phases was also measured. In the case of water displacing oil, there was observed viscous fingering due to a decrease in capillary number unlike in the case of polymer displacing oil. In the displacement with the formulation with a Winsor type II - microemulsion, an increase in flow rate improved the oil recovery, whereas the opposite was the case for the Winsor type III and II+ microemulsion, thereby making viscous fingering to occur at only high flow rates. The highest oil recovery for the Winsor type III microemulsion at 5% NaCl brine salinity at the lowest capillary number, whereas the highest oil recovery for the Winsor type II- was achieved at the highest capillary number. The dependence of the oil recovery on capillary number was attributed to how close to unity the measured viscosity is since the increase in capillary number could result in either a stable displacement or a viscous fingering. The Winsor type III microemulsion resulted in the least negative value of -15.6 mV while the Winsor type II – and Type II + had zeta potential values of -30.5 and -35.20 mV respectively. The authors explained that the zeta potential values suggest the stability of the microemulsion phase in which the type III being the lowest was least stable and formed micellar and bicontinuous structures as observed by their phase behavior studies whereby the type II – and II+ showed better stability for many weeks.

(Tagavifar et al., 2017) studied the dynamics of microemulsion formation at the pore scale using a 2.5 D micromodel to understand the coupling between phase change and bulk flow. The effect of each phase during the flooding process on the bulk flow rate was analyzed with the use of anionic surfactants – Tridecyl alcohol propoxy sulfate and internal olefin sulfonate in 30500 ppm NaCl brine. The microemulsion was formed via liquid-liquid nucleation or spontaneous emulsification at low low flow rate, while mechanical mixing was responsible for the microemulsion formation at high flow rate. The microemulsion was formed initially by diffusion-driven nucleation of the microemulsion film at discrete locations when the surfactant solution initially comes in contact with the oil and then later on by continuous interfacial mass transfer on emulsion droplets.

In all the literature analyzed, microemulsion formation was responsible for oil recovery in the visualized micromodel. It is, however, important to determine the comparative effectiveness of wettability alteration and interfacial tension reduction on oil recovery as seen in the next section.

2.4.4 Dominant Mechanism between Wettability Alteration and IFT reduction in cores and micromodels

It is still not very specific as to which mechanism between wettability alteration and IFT reduction plays a dominant role in oil recovery. Surfactants can reduce IFT in several ways, including the adsorbing at the oil-water interface or forming mixed micelles (Li et al., 2000). As a general rule of thumb, the IFT value must be reduced to 0.001 mN/m to overcome the capillary forces that are holding the oil in the reservoir (Wu et al., 2010). As a result of reduction of IFT to ultra-low values of 0.001 mN/m, there is a subsequent increase in capillary number by about three orders of magnitude. SP or ASP floods with ultra-low IFT values do not give the highest oil recovery as expected as cited in the following studies.

(Bataweel & Nasr-El-Din, 2012) performed chemical flooding such as surfactant-polymer (SP), low tension polymer (LTPF) and alkaline surfactant polymer (ASP) flooding on Berea sandstone rock in order to evaluate the performance of organic alkali (sodium salt of polyaspertic acid) in scale prevention using high salinity brine of 172,000 ppm, anionic (internal olefin sulfonate) and amphoteric (betaine based) surfactants at a temperature of 95ºC. Their results show that in the ASP flooding, the amphoteric surfactant, although resulted in the lowest interfacial tension value did not give the highest oil recovery compared to the anionic surfactant. It was also observed that there was a quicker rate of oil production in the anionic surfactant compared to the amphoteric surfactants and this was attributed to a better chemical propagation in the core.

(Yu et al., 2010) investigated using physical simulation, emulsion, and visual experiments the reason for differences in oil recovery gotten with low and ultra-low IFT values in the ranges of 10^{-2} mN/m and 10^{-3}mN/m respectively. The physical simulation experiment was done with two parallel homogeneous cores which were saturated and aged for 12 hours with crude oil after saturating with low salinity brine of 865 mg/L. Brine was continually injected until water cut reached 0.98 after which 0.3 pore volume of polymer surfactant slug was injected into the cores. In their emulsion experiments, a mixture of the polymer/surfactant with oil was done while the volume of the emulsion formed was recorded over time. Two parallel glass plates were used for the visualization experiments, where the space between the plates was filled with sand and the edges of the plates sealed. Similar flooding sequence conducted in the simulation experiment was also carried out in the glass plates. Their results showed that the highest oil recovery was not gotten in the ultra-low IFT case and there is no direct correlation between ultra-low IFT and recovery, but there exists an optimal IFT which is higher than the ultra-low IFT case that gives high oil recovery. The authors attributed the better oil recovery observed in the case of the low IFT to be as a result of Jamin effect that is induced by grains in emulsions with low IFT which improves sweep efficiency since more water is imbibed into low permeability areas. (Wang et al., 2010) also performed similar experiments with similar findings where the low IFT surfactant polymer flooding resulted in higher oil recovery compared to the ultra-low case. The reason for this was also attributed to the Jamin effect.

There are cases where a high IFT resulted in higher oil recoveries for surfactants that are able to change wettability favorably to water-wet conditions (Karimi et al., 2016). Under water wet conditions, a low IFT results in a gravity-driven water flooding process, while a high IFT results in a capillary driven flooding process (Gupta et al., 2008). At the same time, water flooding process is not able to imbibe the matrix in fractured oil-wet reservoirs (Gupta et al., 2008). The leading forces which govern oil recovery for fractured-oil wet rocks are capillary and gravity forces. Imbibition of an oil-wet rock in brine without surfactant results in a negative capillary pressure which is larger than the gravity head, hence opposing the imbibition of brine into the rock, while the gravity force favors imbibition of the brine into the rock from the bottom. Presence of a surfactant solution into the imbibing water reduces the IFT and capillary pressure. If the surfactant is able to reduce IFT without altering wettability to more water-wet conditions, capillary force still opposes spontaneous imbibition of the brine while the gravity force becomes more extensive and improves imbibition, hence recovering oil by co-current imbibition of surfactant solution at the bottom and oil recovery at the top of the core, which is a slow process. For surfactants that can alter wettability to water-wet conditions, capillary pressure becomes positive, and both gravity and capillary forces favor spontaneous imbibition of the surfactant solution which results in higher oil recovery, from both the sides and top of the core (counter-current flow). This means that even if the surfactant is not able to reduce the IFT to ultra-low values but is able to alter wettability towards the more water-wet state, gravity and capillary forces dominates resulting in a higher oil recovery compared to when only either of the forces dominates due to the synergetic effect of both forces on oil recovery. The effect of capillary forces and gravity forces on imbibition is given in ***Figure 2-3***

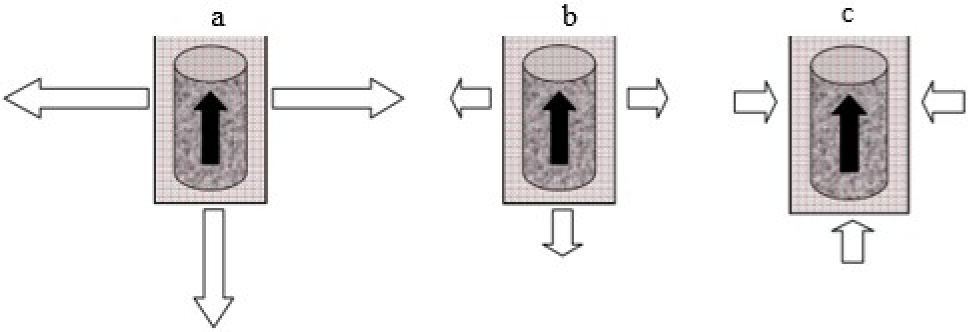


Figure 2-3: Capillary forces (white arrows) and gravity forces (black arrows) for (a) brine imbibition (b) Surfactant imbibition in an oil-wet case (c) Surfactant imbibition in a water-wet case

(Gupta et al., 2008)

(Gupta et al., 2008) in their work with the aim of identifying the factors that affect oil recovery rate in oil-wet fractured carbonate reservoir. The parameters investigated were;

- The extent of wettability alteration
- Increase in IFT of a given water-wet condition
- Increasing Temperature
- Increasing fracture density
- Effect of pressurizing gas saturated fractured reservoirs

Imbibition experiments using anionic and non-ionic surfactants on oil-wet Texas Cordava limestone samples with crude oil from a West Texas fractured carbonate field and contact angle wettability test with calcite plate measured by a goniometer plate using both the field oil and model oil comprising of 1.5wt% cyclohexane pentanoic acid in n- decane. For the contact angle test, the plates were first saturated with brine and then model oil for one day at room temperature for aging, while with the field oil, the aging was done at 90°C for two days. For the spontaneous imbibition experiments, the authors saturated the core with brine and then with oil to connate water saturation, while the oil-saturated cores were aged for 60 days at 80°C for the field oil and 20 days at room temperature for the model oil. Imbibition was done at optimal salinity while oil production was monitored as a function of time. Core immersed in the anionic surfactant resulted in a 40% increase in OOIP with a contact angle of 40° whereas, core saturated with the non-ionic surfactant recovered 20% OOIP with a contact angle of 109° after 20 days. The effect of surfactant concentration on oil recovery was also studied. When surfactant concentration was increased from 0.25 wt% to 0.5 wt% at optimal salinity in the anionic surfactant solution the contact angle increased from 47° to 120° which indicates a more oil-wet condition.

Moreso, Simulation results were carried out to determine the effect of IFT on oil recovery and their results show that for a 60 % oil recovery, when wettability is altered to water wet, surfactant with IFT of 1mN/m will take 3 days while that with 0.001 mN/m will take 20 days to recover such amount of oil. They attributed this to the high capillary forces generated with the surfactants which alter wettability to water wet conditions, which is favorable for surfactant imbibition. Also, the inverse bond number (ratio of the capillary to gravity forces) was used to determine the processes that are gravity dominated and those that are capillary dominated. For an inverse bond number greater than one, the process is capillary driven and oil is recovered through counter-current imbibition, whereas, an inverse bond number less than one indicates that the process is gravity driven and oil is recovered through co-current imbibition. Form their study; the authors stated that one of the ways to improve oil recovery is to maintain a high IFT while altering the wettability to water-wet conditions. The other factors which were investigated to affect oil recovery are fracture density/matrix size, pressurization of gas saturated carbonate reservoir and temperature effect. Their results show that an increase in matrix size and gas saturation yields a decrease in the oil recovery rate while a decrease in the temperature reduces the oil recovery as there is less desorption of the carboxylic and naphthenic acid component from the rock at lower temperatures.

(Babadagli, 2005) in their oil recovery experiments observed a decrease in the oil recovery with an increase in the bond number for various imbibition experiment carried out in naturally fractured sandstone and carbonate cores (limestone, dolomitic limestone and chalk) with various anionic (Diol) and non-ionic (t-octyphenoxypolyethoxyethanol and ethoxylated nonylphenol) concentrations ranging from 0.01 % to 1 % in 3% NaCl brine in order to identify various recovery mechanisms. Observation showed that the oil recovery for low IFT surfactant solution in the sandstone rock was lower compared to high IFT brine solution at early time, while at a later time, the lower IFT solution resulted in the highest ultimate recovery. In non-ionic surfactant, one of the limestone rock was seen to be a capillary dominated oil recovery while the was not, and this was attributed to the wettability and adsorption characteristics on the limestone. The recovery from the chalk was seen to be gravitationally dominated at high anionic surfactant (0.1%, one dyne/cm) concentration which is above the 0.05 % critical micelle concentration and yielded a higher oil recovery than the brine case with an IFT of 16 dyne/cm. A lower anionic surfactant concentration below the critical micelle concentration, (0.01 %, 7dyne/cm) in the chalk, however, resulted in a smaller recovery than the brine case with an IFT of 16 dyne/cm, while the recovery from the non-ionic surfactant was very effective and independent of surfactant concentration. A correlation between the inverse bond number and ultimate recovery showed that as the inverse bond number increases, the ultimate recovery reduces, which is contrary to the work of (Gupta et al., 2008)

(Standnes & Austad, 2000) have shown in a series of experiments with both anionic and cationic surfactant that oil recovery from oil-wet chalk cores with the use of surfactants such as dodecyl tri-methyl ammonium bromide (DTAB) is quite effective in oil recovery as they have been seen to recover up to 70% OOIP through imbibition at a surfactant concentration of 1 wt. %. The mechanism of imbibition proposed with the use of cationic surfactant is the formation of ion pairs by the interaction between the surfactant and the adsorbed organic carboxylate from the crude oil, in which dissolution of the ion pair in the oil phase and micelles causes wettability alteration to water-wet conditions which I turn leads to counter-current imbibition of brine due to capillary pressure. The imbibition rate was seen to increase with an increase in temperature, while it decreases with connate water saturation. The interfacial tension between the oil and surfactant solution was high (> 0.1 mN/m) and not to ultra-low values. The tested anionic surfactants showed that they were not able to desorb the adsorb organic carboxylates. Ethoxylated sulfonates can displace oil by spontaneous imbibition of brine, while oil was displaced by a propoxy sulfate when the buoyancy force exceeded the capillary force caused by low interfacial tension values of 0.08 mN/m. They observed a slower recovery with the use of anionic surfactants compared to the cationic surfactants. Their contact angle results showed that the air-water contact angle on the surfactant-adsorbed calcite was between 12^{o} to 28^{o} with the cationic surfactants while the anionic surfactant was between 39 ^{o} and 63 ^{o}. No water-oil contact angle was measured for these surfactants.

(Chen et al., 2000) performed dilute (0.35 wt.%) surfactant imbibition test for carbonate cores from the Yates field with anionic and non-ionic surfactant, with the use of computerized tomography (CT Scans) were to monitor the imbibition process. CT scans indicated that high imbibition is possible due to counter-current flow which occurs at the beginning of the imbibition while gravity-driven flow (co-current) occurred at later stages. Implying that at the beginning of the imbibition process, wettability alteration plays more role in oil recovery. Spinler et al. conducted spontaneous imbibition and adsorption tests with a surfactant that was an ammonium salt of ethoxylated and sulfated alcohols at very low concentrations (∼0.05 wt%) and a high reservoir temperature (∼131 °C). It was found to be effective in improving imbibition in North Sea chalk cores, and adsorption was low.

(Hirasaki et al., 2004) studied different ethoxylated and propoxylated sulfates in the presence of a low concentration potential determining ions (∼0.3 M Na_2CO_3). They found that interfacial tension (IFT) can be lowered to ultralow levels ($\sim10^{-3}$ mN/m), wettability can be changed to intermediate wettability, and imbibition can be improved (>35% OOIP) by the use of very dilute anionic surfactant/ alkali solutions.

2.5 Problem Statement/ Importance of Research

Chemical Enhanced Oil Recovery is an attractive option for a variety of fields. In comparison to the additional oil recovery that could be attained (15% - 20%), the capital expenditure is limited. Since this process involves the understanding of the crude oil brine and rock interactions, then oilfields should be evaluated accordingly because not all chemical enhanced oil recovery methods can be applied in the same way to different fields. The western Canadian Sedimentary basin, for example, boasts of a variety of oil resources such as unconsolidated heavy oil deposits, consolidated carbonate/sandstone medium/light oil, and ultra-tight oil reservoirs. Even though low tension water flooding has been applied extensively in sandstones, the mechanism governing the additional oil recovery remains a mystery. Carbonate rocks are even of major interest since they contain over 50% of the world’s oil reserves and are characterized as oil/mixed wet in nature together with shales which have extremely low porosity and permeability leading to a limited injected fluid imbibition in these rocks.

For an improved oil recovery in rocks, an alteration of the chemical equilibrium which typically exists in the crude-oil-brine and rock system via wettability alteration or interfacial tension reduction must be achieved. Various researchers have shown that the wettability of a solid surface is affected by multiple parameters such as; brine salinity, brine ionic composition, surface chemistry, pressure, temperature and surface roughness while the interfacial tension is affected Salinity, temperature, surfactant concentration, surfactant type, surfactant purity and the nature of the hydrocarbon phase (Green & Willhite, 1998). It is still however unclear as to which mechanism dominates for an improved oil recovery which this work addresses.

The synergetic effect of smart water and surfactant flooding, therefore, should give favorable wettability alteration towards more water-wet conditions and ultra-low interfacial tension values. Smart water and surfactant flooding have been employed over the years as an EOR mechanism and have produced negligible results in some cases. This can be attributed to the limited understanding of the complex crude-oil-brine and rock interactions that take place during the process. Limited knowledge of the process could lead to reservoir damage, an increase in non-productive time and high cost. With a proper design of this complex hybrid process, taking into account various influencing parameters such as the electro-kinetic effect, injection brine salinity, and brine ionic composition, these problems/challenges could be mitigated, leading to a zero non-productive time and a better reservoir development and management.

2.6 Research Questions

1. How does the zeta potential change under the influence of different brine salinities and ionic composition at both the oil-brine and brine-rock interfaces?
2. What is the effect of surfactant addition on the Crude Oil Brine and Rock (COBR) interaction?
3. Can the results from the roc-brine zeta potential measurements be generalized for different rock types or unconventional plays such as tight carbonate rocks and shale? Is there any trend?
4. For an improved oil recovery during low salinity water/low tension water flooding, does the result from the rock-brine zeta potential correlate to porous media experiment? Is there any trend?
5. Can the results from the Oil-brine zeta potential be correlated to the Interfacial Tension results?
6. For a better oil recovery which mechanism plays a dominant role in the different kinds of sedimentary rocks studied?
7. What is the optimum slug composition that will result in the highest oil recovery in the rocks studied?

2.7 Hypothesis

The problems associated with low salinity water flooding in rocks limit the implementation of the technique in the field. In sandstone reservoirs, for example, this process leads to fine migration which could either be beneficial or harmful to the overall process. Similarly, in the case of carbonate reservoirs which are known to behave differently due to their heterogeneities and complex nature, there could be mineral dissolution and precipitation of which pore blockage is inevitable in the latter case. The addition of surfactant to the injected brine makes the process even more complicated due to the complex rock-fluid, and fluid-fluid interactions, coupled with the surrounding environment would affect the surfactant compatibility and performance. For tighter rocks with poor petrophysical properties such as shales, the technique has to be implemented even more carefully to prevent formation damage. There would, therefore, be an optimal slug composition for these systems and a similar trend which applies to these kinds of rocks to prevent the stated risks. This is only possible if the mechanism of the process is well understood, thereby serving as a guide for a successful surfactant slug design.

Chapter 3 Methodology and Approach

The method used in this work can be divided into three sections as shown in the workflow in

Figure 3-1

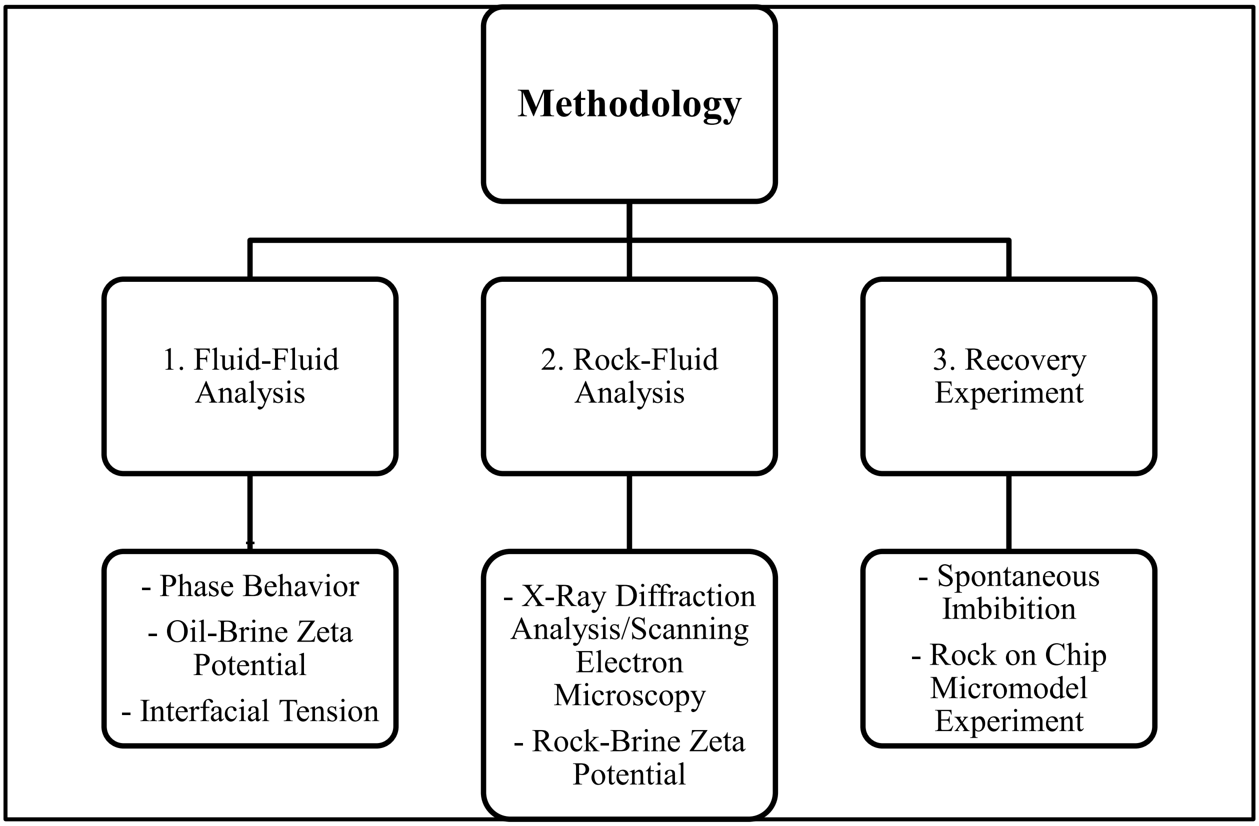


Figure 3-1: Workflow

3.1 Fluid-Fluid Analysis

Seven different brine types are used - NaCl brine, $CaCl_2$ brine KCl brine, and four different synthetic formations brine. The first synthetic formation brine has similar brine composition as a North American carbonate reservoir under investigation while the second has similar brine composition as that in the shale formation being studied and then the third and the fourth formation brines are the newly designed brines for optimal performance in terms of wettability alteration and IFT reduction for the carbonate and shale formations respectively. The KCl brine was however evaluated only for the shale formation because KCl is a significant salt in the original brine composition of the shale formation studied. The brine salinities investigated ranges from low to high salinities of 0 ppm, 5000 ppm, 10,000 ppm, 25,000 ppm, 50,000 ppm, 100,000 ppm, and 200,000 ppm.

The three broad classes of surfactants –anionic, cationic and non-ionic surfactants were studied, and the surfactants were chosen based on cost and compatibility with most of the brines. Even though the three broad classifications of surfactants chosen reduces the interfacial tension compared to what is applicable with conventional water flooding, literature shows that these surfactants do not reduce IFT to ultra-low values; hence the ability of the surfactants to reduce the IFT to ultra-low values were not taken into consideration for the selection criteria. The three surfactant selected and their properties are shown in ***Table 3-1;***

The three surfactants used were:

- Non-ionic – Nonylphenol Ethoxylate with 9 Ethoxy groups provided by Huntsman (denoted as S1)
- Anionic: Sodium olefin sulfonate Provided by Stepan (Denoted as S2)
- Cationic- Dodecyl trimethyl ammonium bromide with 99 percent purity as provided by Alfa Aesar (Denoted as S3)

Table 3-1: Properties of the selected surfactant

Surfactant	CMC (ppm)	Structure	Mol. Weight (g/mol)	Density g/ml	Activity (%)

S1	48	$(C_2H_4O)_9C_{15}H_{24}O$	638	1.06	99 - 100
S2	301	$C_{14}H_{27}NaO_3S$	315	1.062	39.1
S3	3083.41	$C_{15}H_{34}BrN$	308.341	1.1566	99

3.1.1 Solubilization Ratios

Water solubilization ratio is plotted when a Winsor type II or III micro-emulsion is achieved, while the oil solubilization ratio is plotted when a Winsor type I or III micro-emulsion is achieved. Phase behavior test seeks to establish the salinity where a Winsor type III microemulsion is largest (ie the maximum volume oil and water solubilized per volume of surfactant). If V_o is the volume of oil in the microemulsion phase, then V_s is the volume of active surfactant matter. When the oil and water solubilization ratios are plotted, the intersection point within the type III salinity range is the optimum solubilization ratio at the optimum salinity. The optimum solubilization ratio corresponds to the point of lowest IFT.

3.1.2 Salinity Scan Test – Phase behavior test

Oil was added to the aqueous surfactant solutions to see if a micro-emulsion is formed, how long it took (if formed), the equilibration time and the type of microemulsion formed.

The phase behavior experiments were performed in 20 mL test tubes. The crude-oil was first filtered with a filter paper to get rid of the impurities in the oil and the oil-brine ratio used for the experiment was 50:50 and a surfactant concentration of 1% with varying brine salinity from 0ppm, to 200,000 ppm in Sodium chloride brine, Calcium chloride brine and in the original synthetic formation brine. Surfactant adsorption increases with an increasing surfactant concentration up until the critical micelle concentration (CMC) after which it remains constant. Surfactant concentration at or above the CMC is desirable since it leads results in low IFT values. (Bortolotti et al., 2009; Kamal et al., 2017) Therefore, a surfactant concentration of 1% is used for this study since it is above the CMC for all the surfactants. The aqueous phase of the experiment consisted of the surfactant solution. No effect of pressure on the phase behavior as analyzed since pressure has a negligible effect on phase behavior (Sheng, James, 2010) After injecting oil and surfactant solution; the sample was shaken for about one minute and then left to stand until there was a stable phase boundary.

Once the surfactant solution was added into the test tubes, sufficient time is allowed for all the fluid to drain down the sides of the tubes. Fluid levels were recorded before the addition of oil, and the measurements were marked on a record sheet. The test tubes used were not graduated and to compensate for that, the tubes were manually graduated by gradually injecting various defined volumes of fluid into an empty test tube with a syringe and marking the volume on the tube. The tubes empty tube and tubes filled with oil/surfactant solution were placed side by side on an equally leveled platform to determine the fluid levels. The mixtures were left to stand for several days to observe any changes. The top and bottom interfaces were recorded as the scan transitioned from an oil-in-water to a water-in-oil micro-emulsion. The initial readings were taken at the beginning of the experiments and after that at increasing time intervals until equilibration was reached or the experiment deemed unessential for continued observation.

For the crude oil used in this study, the top interface around the over the optimum region was difficult to see.

3.1.3 Solubilization ratio Curves

The solubilization ratio curves a plotted in Excel. It is worthy of note that the solubilization ratio curves only have two solubilization ratios per salinity for a Winsor type III microemulsion. While in the cases of types I and II micro-emulsion, only oil or water solubilization curves are available (i.e. water solubilization curve for Winsor type II and oil solubilization curve for Winsor type I) per salinity.

3.1.4 Oil Brine Zeta Potential Measurements

The sample preparation for measuring the zeta potential of the oil-brine interface was done using the procedure reported by (Mahani et al., 2015). The oil-brine ratio used for the zeta potential at the oil-brine interface was 1:5, prepared by mixing 2 mL of oil with 10 mL of brine solution in a flat bottom vial tube and agitated in an ultra-sonic sonicator bath for 20 minutes to ensure that there is a dispersion of the oil phase in the brine phase. The brine-rock and oil-brine mixtures were left to equilibrate for 3 hours and 24 hours respectively before zeta potential measurements were carried out.

Since zeta potential results are dependent on the surrounding conditions, (Cicerone, Regazzoni, & Blesa, 1992a; Thompson & Pownall, 1989a) extreme care was taken to ensure that there was little or no atmospheric CO_2 present in the sample by completely sealing up the polystyrene cuvette which held 0.75 mL of the sample and ensuring that no bubbles were present in the measuring sample. For repeatability of results, a minimum of two measurements was made, with each having a minimum of three runs, which consists of 100 cycles per run.

3.1.5 Interfacial Tension Measurement

The interfacial tension was measured with a site100 spinning drop tensiometer by KRÜSS, which is capable of measuring ultra-low IFT values of up to 10^{-6} mN/m. The brine and surfactant (1% w/v for cationic surfactant and 1vol% for the other two surfactants) were mixed to the desired salinities after which the IFT measurement was made between the aqueous and oleic phases. The analysis was carried out at a temperature of 20°C and atmospheric pressure. The spinning drop equipment has a capillary tube filled with the aqueous phase and a drop of oil-injected with a syringe and rotated at different rotational speed until a constant value of IFT was gotten. The tensiometer has a maximum speed of 15,000 rpm and can be rotated at temperatures above 0°Cand below 100° CThe software uses the Vonnegut equation shown in ***equation 3***

$$\gamma = \frac{r^3 \omega^2 (\rho_H - \rho_L)}{4}$$ **equation 3**

Where;

γ = Interfacial tension between the phases mN/m

r = drop radius (m), determined by the software

ω = angular frequency of rotation (radian/s), was continuously changed to get a uniform IFT

ρ_H = Density of the heavy phase (kg/m^3), a measured parameter

ρ_L = Density of the light phase (kg/m^3), a measured parameter

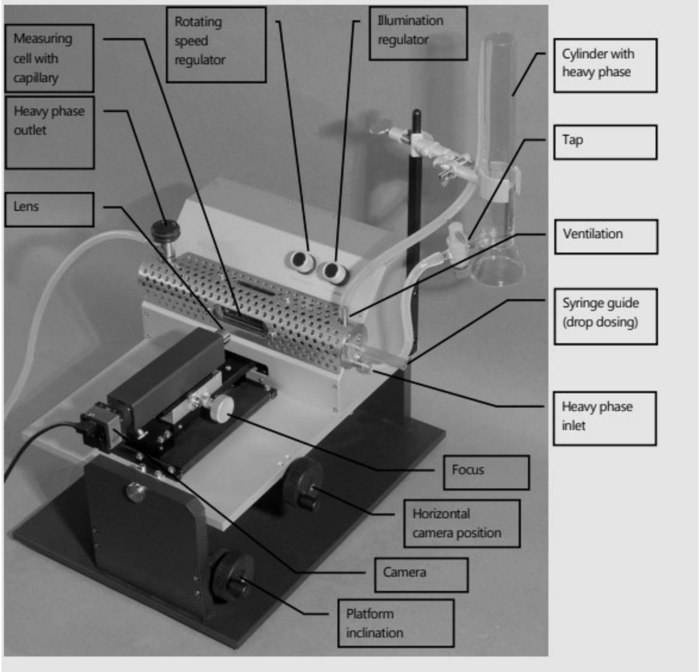


Figure 3-2: Kruss SITE 100 Tensiometer

Source: Manual Kruss SITE 100 Tensiometer

3.2 Rock- Fluid Analysis

3.2.1 Rock-Brine Zeta Potential Measurement

The Malvern zeta sizer Nano ZSP, model ZEN 5600 was used to measure the zeta potential for the various crushed rock particles. The temperature range of the instrument is between 0-degree Celcius and 90-degree Celcius. The zeta sizer Nano ZSP instrument, model ZEN5600 has the capability of measuring particle size, zeta potential, and molecular weight. The recommended diameter for an accurate size measurement is between 0.3 nanometers to 10 micrometer, while the size range for zeta potential measurement is between 3.8 nm to 100 micrometer and has the capability of measuring a molecular weight between 342 to 2 x 10^7 Daltons. It is capable of measuring particle diameter ranging between 0.3nm to 10 micrometers. In this study, the measurement principle for the particle size and zeta potential alone are given since the molecular weight was not measured.

The Optical configuration of the zeta sizer nanosystem for zeta potential measurement is shown in ***Figure 3-3***.

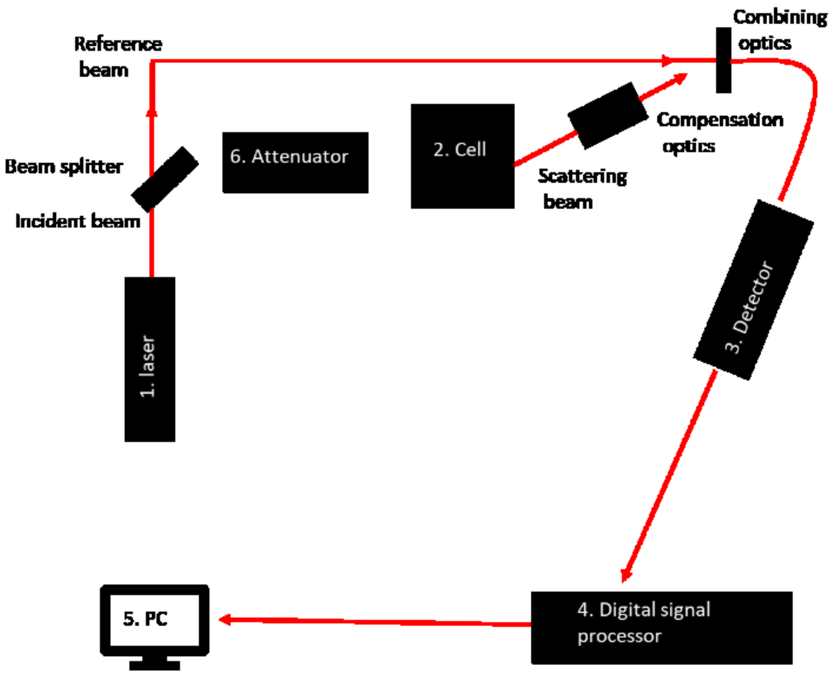


Figure 3-3: Optical configuration of the zeta sizer nano

3.2.1.1 Cell Type

The DTS1070 folded capillary cell shown in ***Figure 3-4*** is primarily designed for zeta potential measurements but could also for size measurements. The disposable cuvette (cell) is made from polycarbonate with gold plated electrodes. The minimum sample volume the cell can hold is 0.75 mL and suitable for temperatures below 70°C.

Figure 3-4: Zeta potential cell (DTS 1070)

The cells are first rinsed severally with alcohol (ethanol or methanol) and then with de-ionized water several times before loading the sample into the cell. Alcohol rinsing is done before the first measurement only.

3.2.1.2 Quality Check for Zeta Potential measurement

For quality checking, the expert advice and the zeta quality reports were used. The expert advice report gives an insight into the mean count rate while the quality report gives an insight into the quality of the results.

At least three measurements were taken to ensure repeatability, consistency, and accuracy of the generated results. For an accurate result, the count rate should be consistent to a reasonable extent. Increasing count rate from successive measurement signifies particle aggregation while a decreasing count rate from successive measurement signifies either particle sedimentation or dissolution. Random count rate from successive measurements signifies particle instability due to aggregation or breakup.

For the zeta quality report, a warning is given for any measurement that falls outside specified limits and reasons for this is also displayed in the notification. For example, flare from the capillary walls caused by bubbles or noise can bring about results falling outside specified limits. If none of the tests fails, however, the report shows ‘Results meets quality criteria.’

3.2.1.3 Rock-Brine Zeta Potential Sample Preparation

The zeta potential was measured at the brine-rock interfaces at a temperature of 20ºC with the Malvern zeta sizer Nano equipment. The equipment uses the Laser Doppler Velocimetry (LDV) technique to measure the electrophoretic mobility of the suspensions being tested while the zeta potential is calculated from the Smoluchowski model. The pH of the samples used for the zeta potential measurements was unaltered to replicate the actual reservoir conditions as close as possible and to prevent any external influence of acid or bases on the zeta potential results.

The sample preparation for the zeta potential measurement at the rock-brine interface was done according to the procedure of (Nasralla & Nasr-El-Din, 2014). The rock was crushed using fine-grit sandpaper for all samples to ensure that they have the same particle size. 0.1 g of the rock powder which represents 1 % of the solution was mixed in a 10 mL brine solution and agitated with an ultrasonic sonicator for one minute. Samples were allowed to equilibrate for at least two hours before zeta potential measurements were made.

Five different kinds of rocks are analyzed in this study – Botucatu Sandstone rock, Indiana Limestone outcrop core, Silurian dolomite outcrop core, slave point formation rock, and Evie shale.

3.2.2 Rock Mineralogy

The rock mineralogy for Botucatu sandstone, Indiana limestone, Silurian dolomite, slave point formation, and Evie shale are shown here;

3.2.2.1 Botucatu sandstone rock

The Botucatu formation is located in the Parana Basin in Northeastern Brazil and comprises mostly of eolic sandstone, containing mainly quartz, kaolinite and illite with trace amount of calcium, iron, and Titanium. ***Figure 3-5*** shows the scanning electron microscopy results for the Botucatu sandstone rock while ***Table 3-2*** shows its elemental composition from scanning electron microscope (SEM) and Energy-dispersive X-ray (EDX) Spectroscopy.

3.2.2.2 Carbonate Core

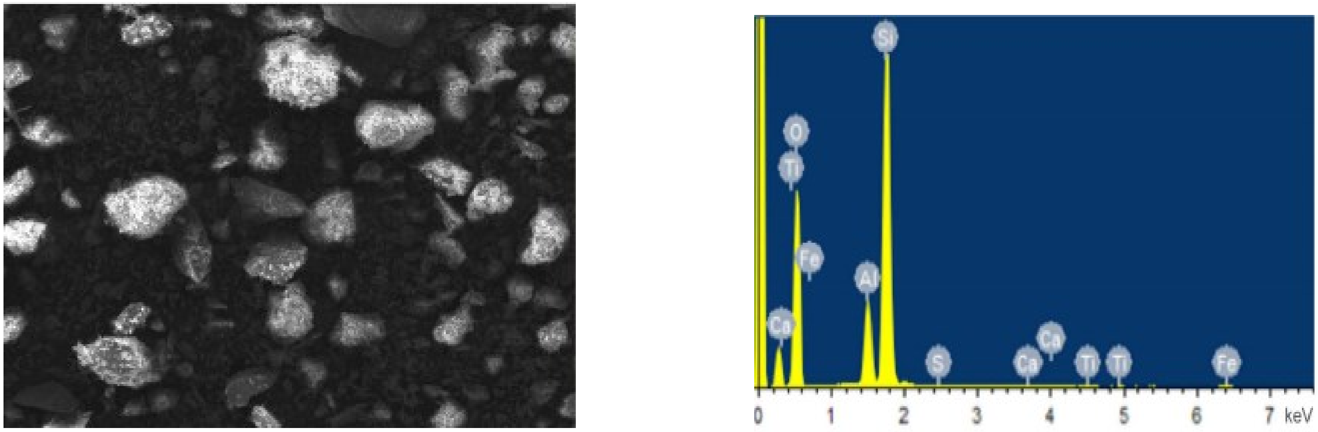
The slave point carbonate formation is located on the western Canadian sedimentary basin in northern Alberta. The slave point formation from the middle Devonian period is characterized to have between light yellowish-brown to dark brown limestone interbedded with finely crystalline dolomite and a thin lamina of shale. The formation extends from the southern northwest territory into the northeastern British Columbia and northern Alberta. The play has low porosity values between 4 to 9 % and an average in-situ permeability of ± 0.5mD (Glass, 1990). The elemental composition of the Slave point core is given in table ***Table 3-4*** while ***Figure 3-6*** shows the SEM/EDX images.

The XRD analysis for the Indiana limestone and Silurian Dolomite outcrop cores were gotten from (Maubert et al., 2018) and (Mahani et al., 2015) respectively.

3.2.2.3 Evie Shale

The Evie shale is one of the subsurface members of the Horn River formation. Others are the Muskwa and Otter Park. The Horn River formation is a stratigraphic unit of Devonian age in the western Canadian sedimentary basin, located in North-Eastern British Columbia and extend to the Northwest Territories. The formation generally comprises of dark argillaceous limestone, calcareous to siliceous shale, often bituminous (Reynolds & Munn, 2010). The Xray diffraction (XRD) analysis of the Evie shale is given in ***Table 3-3*** which was gotten from (Xu et al., 2018).

3.2.2.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Spectroscopy of Botucatu sandstone rock



a

b

Figure 3-5: Scanning electron microscopy results for Botucatu sandstone

(Almeida et al., 2018)

Table 3-2: SEM/EDX Elemental composition for Botucatu sandstone

(Almeida et al., 2018)

Element	Weight (%)	Atomic (%)
O	60.06	72.68
Al	6.90	4.95
Si	31.65	21.82
S	0.16	0.10
Ca	0.19	0.09

Ti	0.13	0.05
Fe	0.92	0.32

3.2.2.5 X-ray Diffraction (XRD)-Analysis

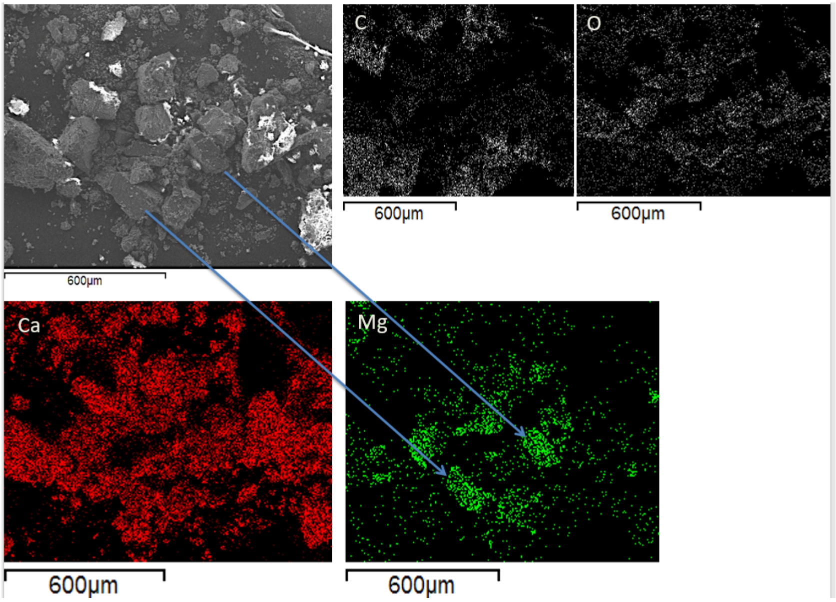
The XRD analysis for the outcrop carbonate cores – Indiana limestone and Silurian dolomite and Evie shale are shown in the table ***Table 3-3***;

Table 3-3: XRD Analysis for carbonates (Indiana limestone and Silurian Dolomite) and Evie shale

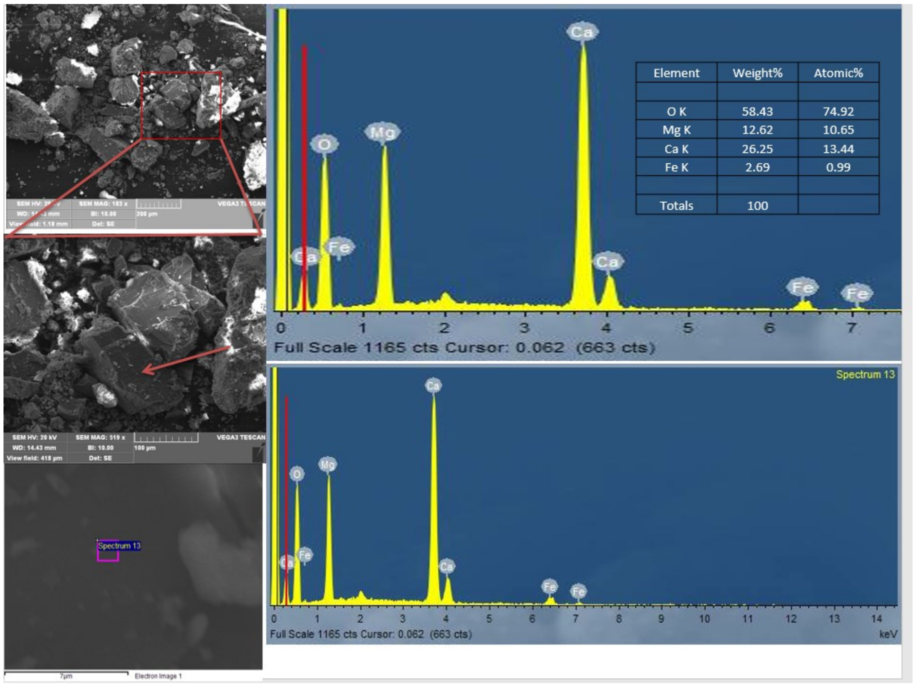
Indiana Limestone	**Mineral Content**	**Weight %**
	Quartz	0.9
	Calcite	97.7
	Fe- Dolomite	0.2
	Halite	0.6
	Illite and Mica	0.6
	Total	**100.0**
Silurian Dolomite	**Mineral Content**	**Weight %**
	Quartz	1.0
	Calcite	0.0
	Dolomite	99.0
	Halite	0.0
	Illite and Mica	0.0
	Total	**100.0**
Evie Shale	**Mineral Content**	**Weight %**
	Quartz	51.9
	Calcite	13.3
	Dolomite	2.6
	Plagioclase	5.7
	Pyrite	3.0
	K-feldspar	4.9
	Illite/Smectite	6.6
	Illite+Mica	12.0
	Total	**100.0**

Table 3-4: SEM and EDX elemental analysis of Slave point reservoir core

Element	**Weight (%)**	**Atomic (%)**
O	58.43	74.92
Mg	12.62	10.65
Ca	26.25	13.44
Fe	2.69	0.99
Total	100	100



a. Elemental mapping of slave point core at a depth of 1565.52 m


Element	Weight%	Atomic%
O K	58.43	74.92
Mg K	12.62	10.65
Ca K	26.25	13.44
Fe K	2.69	0.99
Totals	100	

b. SEM/EDX Elemental composition of slave point core at a depth of 1565.52 m

Figure 3-6: SEM/EDX analysis of slave point core

The SEM/EDX analysis of the slave point core shows that it comprises mainly of calcite and dolomite with more calcite compared to dolomite and traces of iron.

3.2.2.6 Porosity and Permeability Measurement

The permeability of the Indiana limestone was measured with an unsteady state permeameter and also with mineral oil using a core flood apparatus at 20ºC while the porosity was measured with synthetic formation brine using the weight method The porosity of the Silurian dolomite core is measured with brine while the permeability was measured with an unsteady state permeameter containing mainly inert nitrogen gas. The permeability values measured with mineral oil was calculated using the Darcy equation while that with the unsteady state permeameter was computed using the tiny permeability correlation as shown in ***equation 4***

$$T = -0.8206 * log_{10}(K) + 12.8737 \qquad \textbf{equation 4}$$

Where;

T = TinyPermII value

K = Permeability (mD)

Table 3-5: Rock Properties

	Permeability (mD) in air	Permeability (mD) in mineral oil	Permeability in brine (mD)	Porosity (%)
Botucatu Sandstone	262	-	4.78	28.3
Indiana Limestone	268.883	2.345	-	17
Silurian Dolomite	6.663	-	-	17
Slave Point Formation	0.91	-	-	6.2
Evie Shale	0.000384	-	-	5

The permeability for the Botucatu sandstone, Evie shale and slave point core are taken from literature. The porosity and permeability of the Botucatu sandstone measured with 5,000 ppm of similar brine composition of the basin's formation water are 28.3% and 4.78mD respectively (Almeida et al., 2018) while the air permeability has been reported to be 262 mD (Cardoso & de Carvalho Balaban, 2015). The porosity and permeability values for the slave point formation were taken from (Quirk et al., 2014). The Evie shale porosity and permeability are measured with a helium porosimeter and a pulse decay permeameter respectively (Xu et al., 2018).

3.2.3 Imbibition/RecoveryExperiment

3.2.3.1 Single Phase Spontaneous Imbibition Measurement

To fully understand the results from the zeta potential results at the rock-brine interface, single-phase spontaneous imbibition experiments were carried out with Amott cells. The imbibition was done using three Silurian dolomite rocks and NaCl at salinities of 5,000 ppm, 25,000 ppm and 50,000 ppm in the anionic surfactant. The outcrop cores were cut to the same dimension of 1 mm in thickness and 2 inches diameter. The steps followed for the imbibition are highlighted below;

- The 2 inches diameter cores were cut to 1-inch thickness with dicing saw and water
- The cores were dried at 100-degree Celcius for 48 hours
- Cores were put under vacuum for three days to remove excess air in the core
- Cores were then weighed after vacuum and values were recorded
- Cores were imbibed in surfactant solution of 5,000 ppm, 25,000 ppm and 50,000 ppm NaCl brine salinity with the anionic surfactant using the Amott cell

- Imbibition was done with all faces open (AFO) since this is the case applicable in reality, especially in fractured carbonate rocks. AFO promotes counter-current imbibition which is a slower process compared to co-current imbibition.
- The change in volume and weight was recorded over one month, and imbibition profile with time was plotted for the three salinities.
- Schematics of the amott spontaneous imbibition cell used is shown in ***Figure 3-7***

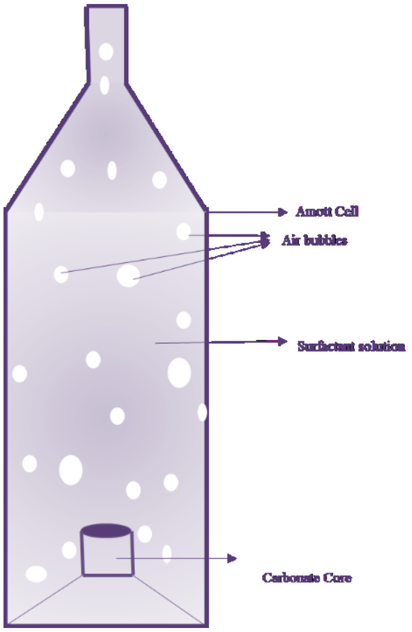


Figure 3-7: Single-phase spontaneous imbibition

For the flooding step, micromodels were used and details of the micromodel design representing a homogeneous porous structure together with the fabrication procedure are given herein.

3.2.3.2 Micro-model Experimental Design with KLayout

An essential step in the micro model design is the fabrication of the critical components of the rock such that it replicates the pore network of a reservoir/core in reality. Based on this, a two Dimensional pore throat network was designed using KLayout which is a Graphic Data System

(GDS) and Open Artwork System Interchange Standard (OASIS) file format for a chip design engineer that allows the engineering view, edit and create GDS and OASIS files such as chip designs from the scratch. Since the single-phase imbibition was done for the carbonate core, micro-model was therefore designed to be homogeneous in order to represent a sandstone rock.

3.2.3.3 Pore Network Design for Rock on Chip

Regular, homogenous network design was done based on scanning electron microscope (SEM) images of the Botucatu sandstone rock. The pore channels are 60 µm wide and 60 µm deep with a matrix size of 40 µm. The length of the chip is 7cm, with a width of 1 cm in order to fit into the chip holder. The diameter of the inlet and outlets ports are 0.2 cm each. The conceptualized flow map for the ROC is shown in ***Figure 3-8***

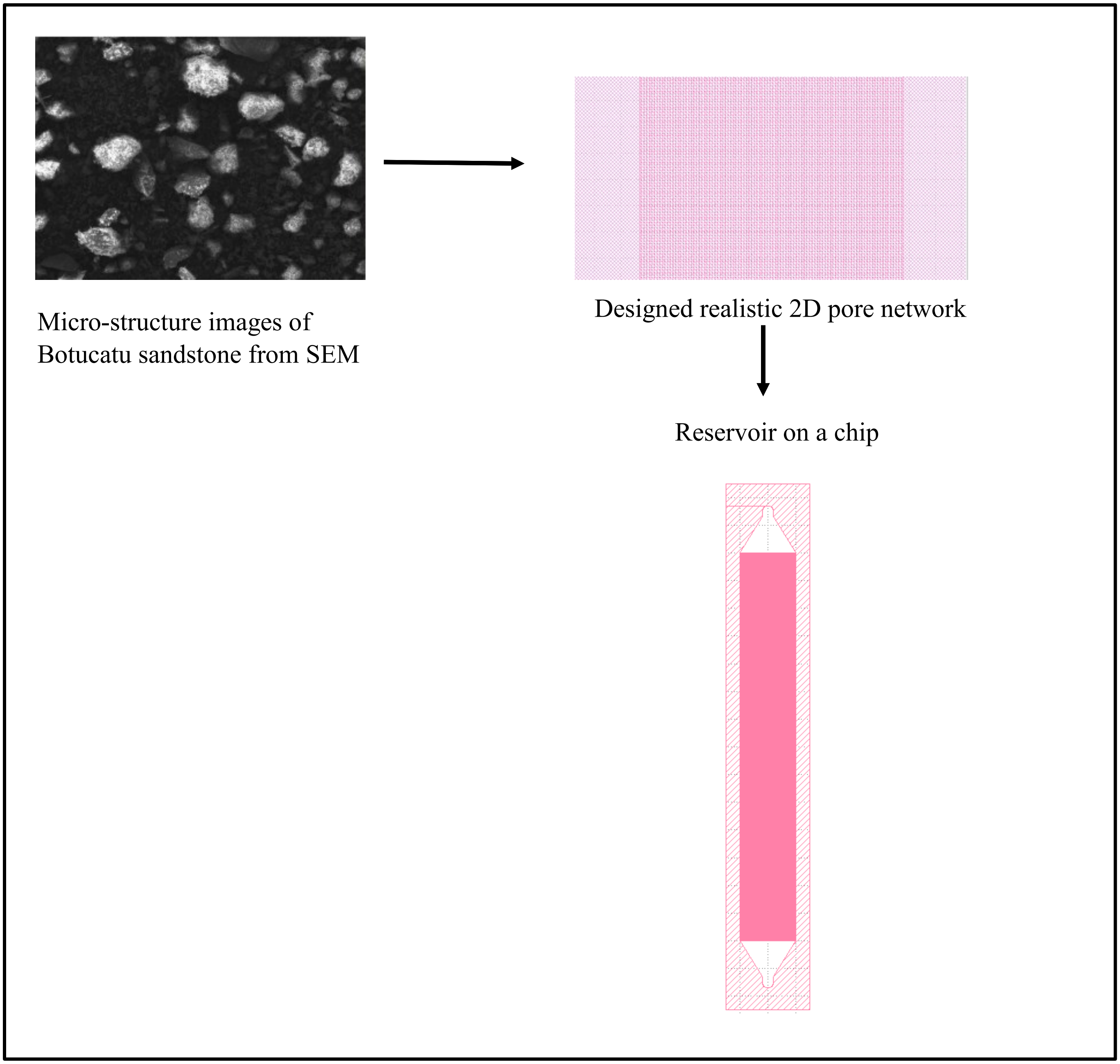


Figure 3-8: Designed conceptualized flow-map for 'Reservoir-on-a-chip' (ROC)

The micro-model fabrication was done at the University of Alberta nanoFAB 1000 deposition area (clean room) while the chip dicing was done in the same facility but at the 10,000 deposition area.

Figure 3-9: Fabricated homogeneous micromodel

3.2.3.4 Micro-Model Flooding

Two micromodel floodings were carried out to represent homogeneous sandstone rocks and heterogeneous carbonate rocks. The chip used for the heterogeneous micromodel flooding was already available in the lab, while fabrication was done for the homogeneous sandstone rock.

- The image of the microchip/micro model is taken with a Canon camera with a 5X zoom, capable of capturing 200µm feature.
- With the assumption of a zero initial water saturation, oil was used to saturate the chip using a Chemyx Nexus 6000 syringe pump, with a range of flow rate between 1.666667e-8 mL/min to 200 mL/min.
- The homogeneous chip was used to represent a water-wet sandstone; therefore no oil aging was done before the brine flooding while for the fractured chip which represents a fractured carbonate rock, oil aging was done in an oven at a temperature of 80°C for two days in order to represent an oil-wet carbonate rock.
- Brine injection was done at a flow rate of 0.0016mL/min at the chosen surfactant slug salinity until no more oil is recovered from the chip.

- Images of the flooding process were taken within several minutes for the homogenous chip while for the fractured chip, the images were taken after several hours since the process is slower for the fractured chip.
- Images of the chip were then processed using the Fiji Image J software in order to calculate the oil saturation over time as a means of determining the optimal surfactant slug for the different rock types and ranking the mechanism responsible for improved oil recovery.
- For the homogeneous chip, the flooding was done with 10,000 ppm and 50,000 ppm Sodium chloride and calcium chloride brines in the absence of surfactant since the chip is already water wet and also in the presence of 10,000 ppm Sodium chloride and calcium chloride brine with the anionic surfactant to evaluate the effect of additional wettability alteration on oil recovery.
- To investigate the actual magnitude of zeta potential at the oil-brine and brine rock interfaces and the effect of brine ionic composition on sweep efficiency, flooding was done in the homogeneous chip using the following procedure;
- Flooding pictures were taken every minute to observed the changes with oil saturation over time. After flooding with 50,000 ppm, the chip was cleaned with toluene and de-ionized water then dried for two hours at 60ºC in an oven after which it was reused for others.
- For the calcium chloride brine, the same flood process which was done for the NaCl brine was applied to the calcium chloride brine but with a new micromodel.
- For the heterogeneous fractured chip, in order to identify the impact of ultralow IFT and low IFT on wettability alteration and oil recovery, the flooding was done with the non-ionic surfactant in 100,000 ppm synthetic formation brine surfactant and also with a chembetaine zwitterionic surfactant in 100,000 ppm synthetic formation brine. Both floods

with the non-ionic and zwitterionic surfactant was done for two days each to analyze the impact of ultra-low IFT on oil recovery from matrix (Since the zwitterionic surfactant resulted in an ultra-low IFT) compared to the non-ionic surfactant which only reduces the IFT by an order of 2 compared to what will usually be obtained in a system without surfactant. Experimental set up for the micromodel flooding is shown in ***Figure 3-10***

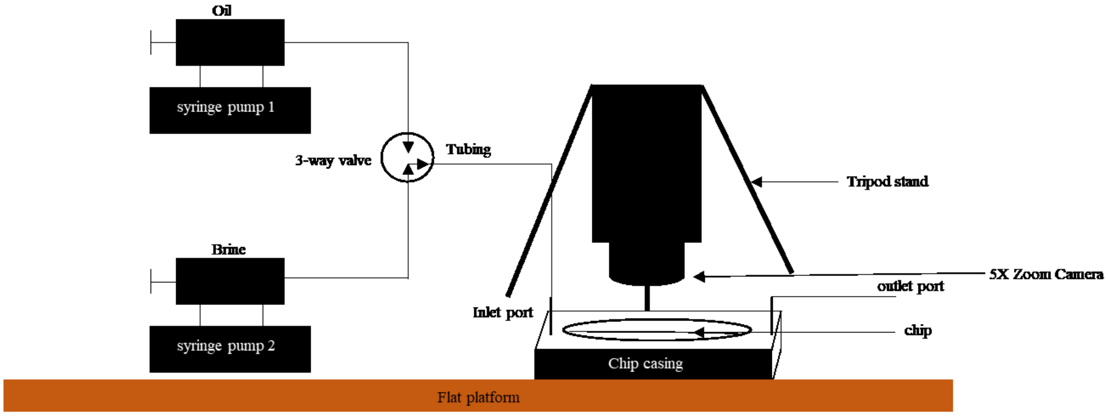


Figure 3-10: Experimental set up for micromodel flooding

3.2.3.5 Image Processing/ Analysis

An open-access software, Image J was used for the segmentation and processing of the images. Image stacks were first converted to an 8-bit and thresholded using the Automatic threshold method. Pixel intensity was adjusted by ±3% to ensure robustness of the segmentation. Oil saturations were then calculated by dividing the number of pixels containing oil with the total number of pixels in the images.

3.2.4 Brine and Surfactant Solution Preparation

To confirm the contribution of various ions in brine on wettability alteration and IFT reduction, three different brines – NaCl, $CaCl_2$ and Synthetic formation brine were synthetically made by the dissolution of the salts in de-ionized water and stirred for miscibility. The synthetic formation brine composition used is similar to that of an actual reservoir. The initial concentration prepared for each brine was 200,000 ppm and was further diluted to the desired salinities for phase behavior, zeta potential, IFT, and rock on-chip (ROC) experiments. Chemical composition of the synthetic formation brine is shown in ***Table 3-6*** while the brine properties at 20ºC and 14.7 psi are given in ***Table 3-7***. The same procedure used for the brine preparation is also used for the surfactant solution preparation except that in the case with the surfactant, 1% surfactant concentration is added.

Table 3-6: Chemical composition of the synthetic formation brine (200,000 ppm in 200 mL solution)

Composition	% Concentration	Mass of salt (g)
NaCl	62	24.8
$CaCl_2.2H_2O$	19.63	7.852
Na_2SO_4	1.95	0.78
$MgCl_2.6H_2O$	16.3	6.52
$NaHCO_3$	0.12	0.048
Total	100	40

Table 3-7: Brine properties

Brine Salinity (mg/L)	Density (g/ml)		
	NaCl	$CaCl_2.2H_2O$	SFMB
200,000	1.0820	1.0700	1.1276
100,000	1.0267	1.0145	1.029
50,000	1.0197	1.0106	1.0020
25,000	0.9869	0.9894	0.9965
10,000	0.9820	0.9740	0.9860
5,000	0.9737	0.9692	0.9725
De-ionized water	0.975	0.975	0.975

3.2.5 Oil Properties

Crude oil from a carbonate reservoir in North America was used for this study. The measured and chemical properties of the crude oil are listed ***Table 3-8*** and ***Table 3-9***. The oil was filtered to remove impurities.

Table 3-8: Measured Oil properties

Property	20°C	38°C
Density (g/cm^3)	0.84179	-
Viscosity (cP)	-	1.065
°API	36.46	-

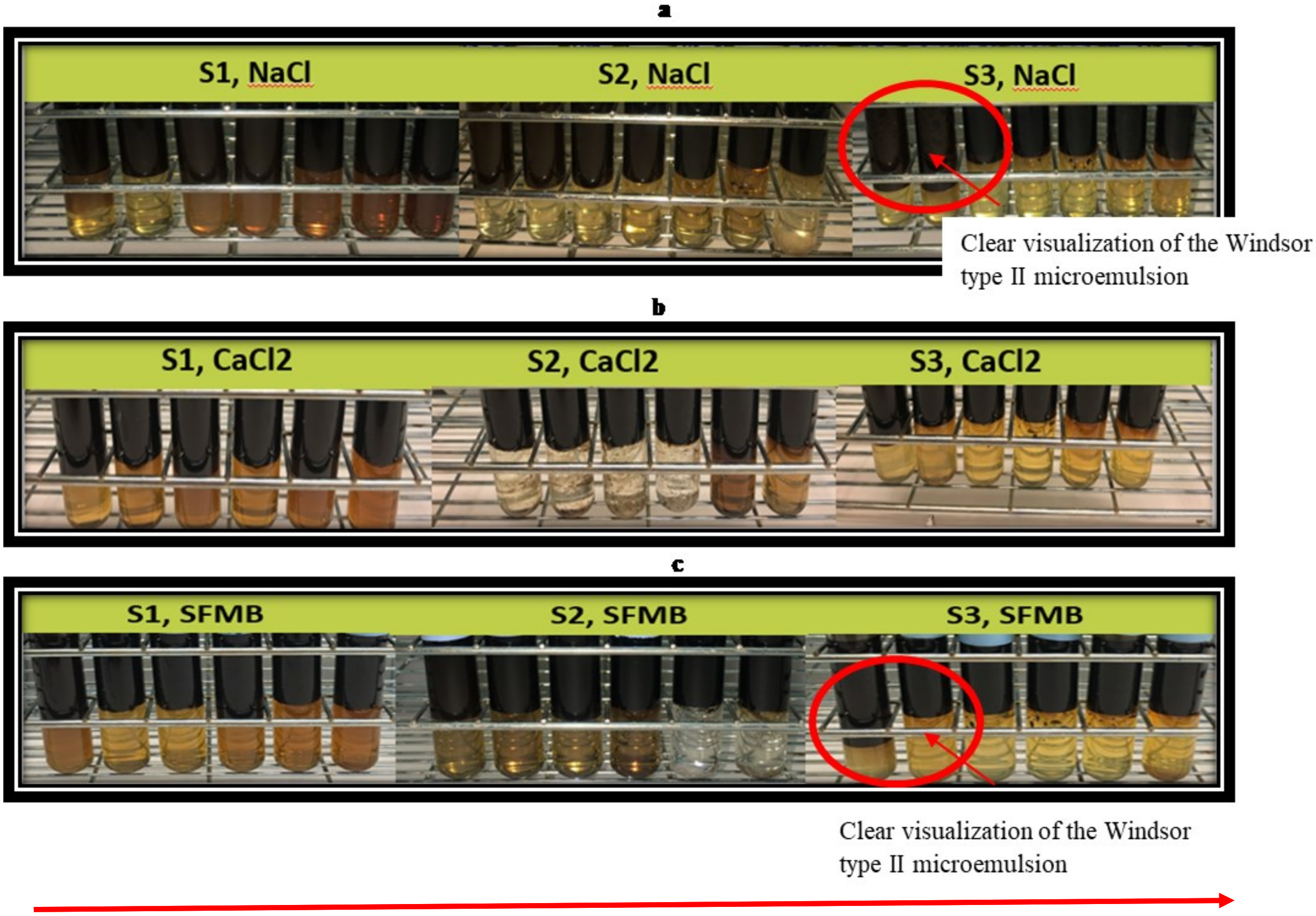
Table 3-9: Chemical oil properties

Component	N_2	CO_2	H_2S	C1	C2	C3	IC4	C4	IC5	C5	C6+	Total
Mole Fraction	0.0326	0.0068	0	0.2352	0.0498	0.0654	0.0175	0.0472	0.022	0.0246	0.4989	1

Chapter 4 : Results and Discussion

4.1 Phase Behavior Measurements with Surfactant Systems

The phase behavior test was done using the three different surfactants at varying brine ionic type and concentration. None of the surfactants gave a Winsor type III microemulsion, which is an indication of the surfactants inability to reduce the Interfacial tension to ultra-low values. The phase behavior experiments are presented in ***Figure 4-1***.



Clear visualization of the Windsor type II microemulsion

Clear visualization of the Windsor type II microemulsion

Figure 4-1: Phase behavior results for different brine and surfactant combinations (a) Increasing salinity from 0 ppm to 200,000 ppm (b) and (c), increasing salinity from 5000 ppm to 200,000 ppm

As observed from the phase behavior experiments, there is no clear microemulsion for all the surfactant systems except with the NaCl and synthetic formation brines where the cationic surfactant is present and results in a Winsor type II microemulsion at low salinities between 0 ppm and 5000 ppm for the NaCl brine and 5000 ppm and 10,000 ppm for the synthetic formation brine. The color of the brine solution in the NaCl and surfactant 1 (S1) otherwise known as the non-ionic surfactant Nonyl Phenol Ethoxylate) changes to a dark brownish color compared to the case with other surfactants which implies more surfactant and oil dissolution in the water phase, forming a Winsor type I microemulsion. This phenomenon is even more prominent at higher salinities. With the anionic surfactant, there is a Winsor type I microemulsion, whose IFT levels are expected to be higher than those of the non-ionic surfactant due to less brownish color in the brine phase.

The non-ionic surfactant dissolves more in the brine phase in the calcium chloride brine at salinities between 25,000 ppm and 200,000 ppm. Higher IFT values with this brine and surfactant are expected at salinities between 5,000 ppm and 10,000 ppm due to less brine dissolution at those salinities. Unlike the case of NaCl brine, no clear Winsor type II microemulsion is observed with the cationic surfactant present in the $CaCl_2$ brine, and the water phase is slightly brownish. This means that compared to the case where the cationic surfactant is present in the NaCl brine, the IFT with the $CaCl_2$ brine is likely going to be lower.

With the synthetic formation brine, a Winsor type I microemulsion is observed with the non-ionic and anionic surfactants. However, with the anionic surfactant, the IFT is likely to be highest at salinities between 100,000 ppm and 200,000 ppm since there is no oil in water microemulsion seen at those salinities. With the cationic surfactant in the synthetic formation brine, a Winsor type II micro-emulsion is seen at salinities between 5000 ppm and 10,000 ppm, indicating higher IFT values at those salinities.

From these qualitative phase behavior analysis with the surfactants, it can then be concluded that in NaCl brine, the non-ionic surfactant will result in the lowest IFT which is even less with an increase in salinity, while the cationic surfactant will result in the highest IFT especially at low salinities between 0 ppm and 10,000 ppm.

In general, the cationic surfactant is likely going to cause surfactant retention and reduced oil production, especially at low salinities at the concentrations used. In terms of compatibility, the anionic surfactant is not compatible with the $CaCl_2$ brine at high salinities since it precipitates even from 10,000 ppm $CaCl_2$ brine which can, therefore, cause pore blockage in the reservoir.

For the phase behavior analysis, only the cationic surfactant in NaCl and synthetic formation brine (SFMB) solutions showed clear Windsor type II micro-emulsion at salinities between 0 and 5000 ppm for NaCl and between 0 and 10,000 ppm for the synthetic formation brine, the oil solubilization ratio (V_o/V_s) is plotted as shown in ***Figure 4-2*** for only the cationic surfactant in both brines. It is also assumed in this case that Winsor type II microemulsion is gotten at higher salinities since the lower salinity brines already have a Winsor type II phase behavior. It should also be noted that since there is no Winsor type III microemulsion, both oil and water solubilization ratios cannot be gotten.

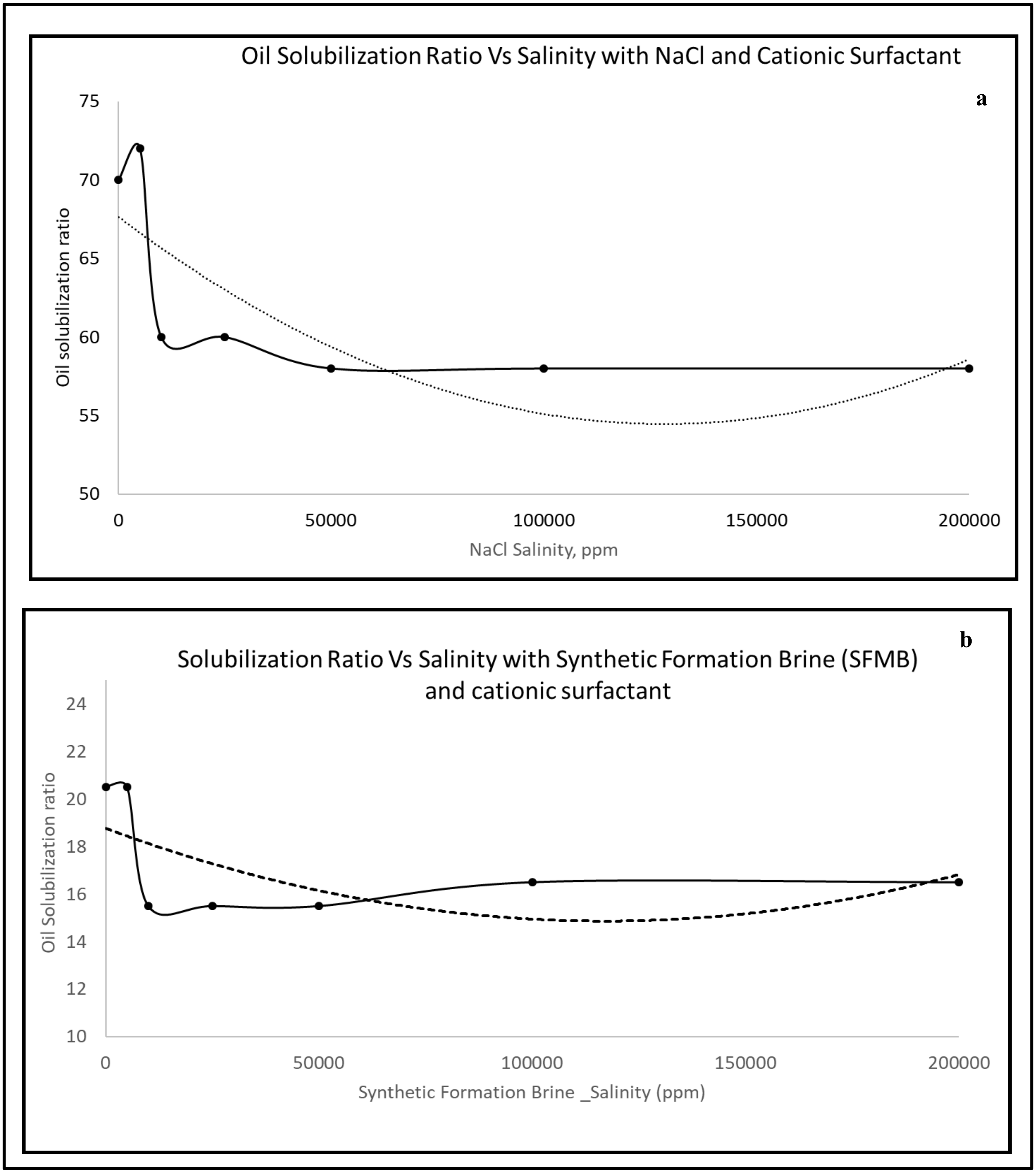


Figure 4-2: Oil solubilization ratio for the cationic surfactant with NaCl brine and Synthetic formation brine (SFMB)

The results presented in ***Figure 4-2 (a,b)*** show the oil solubilization ratio with the cationic surfactant. In NaCl brine, the oil solubilization is less at 50,000 ppm. Therefore the lowest IFT with NaCl and cationic surfactant system is expected to be at 50,000 ppm. In the case of the cationic surfactant in the synthetic formation brine, the lowest IFT is expected between 25,000 ppm and 100,000 ppm.

The results correlate to the work of (Wegner, J. & Ganzer, 2017) where phase behavior analysis was done on one wt. % anionic surfactant with a sulfate head group and 8 propoxy groups in varying NaCl brine salinities between 2.2 wt.% and 3.6 wt% where no Winsor type III microemulsion was gotten. Since no middle phase microemulsion was seen in all cases, and the microemulsion in the oil/water phase for most of the surfactant systems were not clearly observed, it was therefore difficult to determine the solubilization parameter or optimal salinity. More so, the results are consistent with the work of (Austad, T. & Milter, 1997) who performed phase behavior studies with 1wt. % cationic surfactant (DATB) and 1 wt.% anionic surfactant (propoxy-ethoxy-sulfate) in synthetic formation brine concentration of 44.93 g/l and n-heptane with density and viscosity values of 0.684 g/ml and 0.4 cP respectively. Their results show that the anionic surfactant resulted in a Winsor type I microemulsion, with an IFT value of 0.02 mN/m while the cationic surfactant partitions into the oil phase forming a Winsor type II microemulsion with an IFT of 1mN/m. (Alvarez, Saputra, & Schechter, 2017) also performed phase behavior experiments with five different surfactants – Two anionic surfactants containing alcohol and proprietary sulfonate, one non-ionic surfactant (alcohol oxyalkylate), one nonionic-cationic surfactant (ethoxylated isodecyl alcohol + Quaternary ammonium compound) and one Complex nanofluid (CnF ; Isopropyl alcohol + Citrus terpenes +proprietary compound) 2 gallons per thousand gallons (gpt) surfactant concentration in an equal volume of Bakken oil (0.7936 g/mL and 37.3° API at

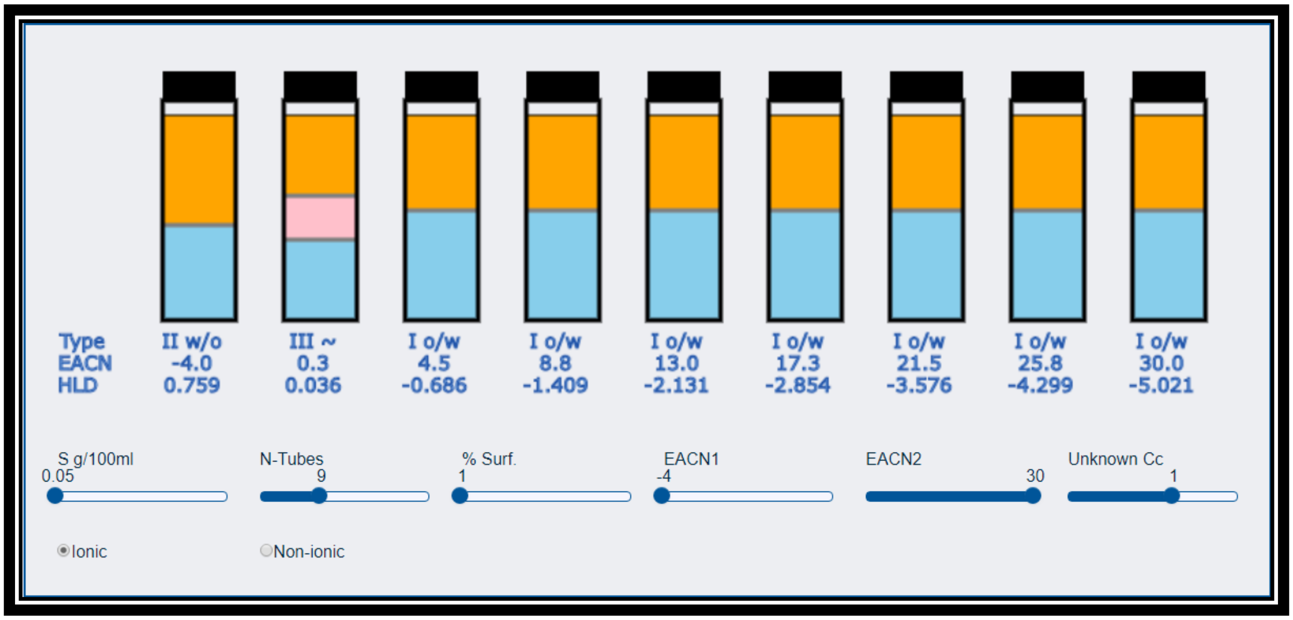
82ºC) and 4 wt % Potassium Iodide brine. One of the anionic surfactant, CnF, and the non-ionic cationic surfactant did not show any visible micro-emulsion at both the oil and water phase. The other anionic surfactant resulted in a Windsor type I micro-emulsion which was observed by a mere change in color of the brine phase. The non-ionic surfactant was not capable of moving all of the oil in the brine phase and resulted in a sub-optimal separation.

Microemulsion phase behavior is a property of the system and not necessarily the property of the surfactant, making the hydrophilic-lipophilic Difference (HLD) of the surfactant more important in characterizing micro-emulsion phase behavior rather than the hydrophilic-lipophilic balance (HLB) which only considers the surfactant and not the whole system. The HLD is dependent on factors such as the salinity, temperature, and equivalent alkane number (EACN) of the oil (Abbott, 2017). This means that it is possible to obtain Winsor type II micro-emulsion even at lower salinities depending on the parameters mentioned previously. The same authors have stated that for a balanced system, resulting in the Windsor type III micro-emulsion observed at optimal salinity; then it implies an HLD of 0 while for HLD values greater than 0, a Windsor type II microemulsion is seen while an HLD less than 0 results in a Windsor type I micro-emulsion. The HLD equation is presented in ***equation* 5**

$$HLD = Cc - k.EACN - \alpha.\Delta T + f(S)$$ **equation 5**

Where Cc = Characteristic curvature of the surfactant, k = EACN Scaling factor = 0.17, α = constant for surfactant depending on temperature difference (0.01 for anionics, -0.06 for ethoxylates and 0 for sugar-based surfactants), ΔT = Temperature difference from 25ºC, f(S) = Salinity term (g NaCl/100mL). Salinity is 0.13S for non-ionic and S for ionic.

Determination of the likely phase behavior types from the HLD has been established based on varying EACN, salinity and surfactant type (here) and is therefore presented in this work.



Type	II w/o	III ~	I o/w	I o/w	I o/w	I o/w	I o/w	I o/w	I o/w
EACN	-4.0	0.3	4.5	8.8	13.0	17.3	21.5	25.8	30.0
HLD	0.759	0.036	-0.686	-1.409	-2.131	-2.854	-3.576	-4.299	-5.021

S g/100ml 0.05

N-Tubes 9

% Surf. 1

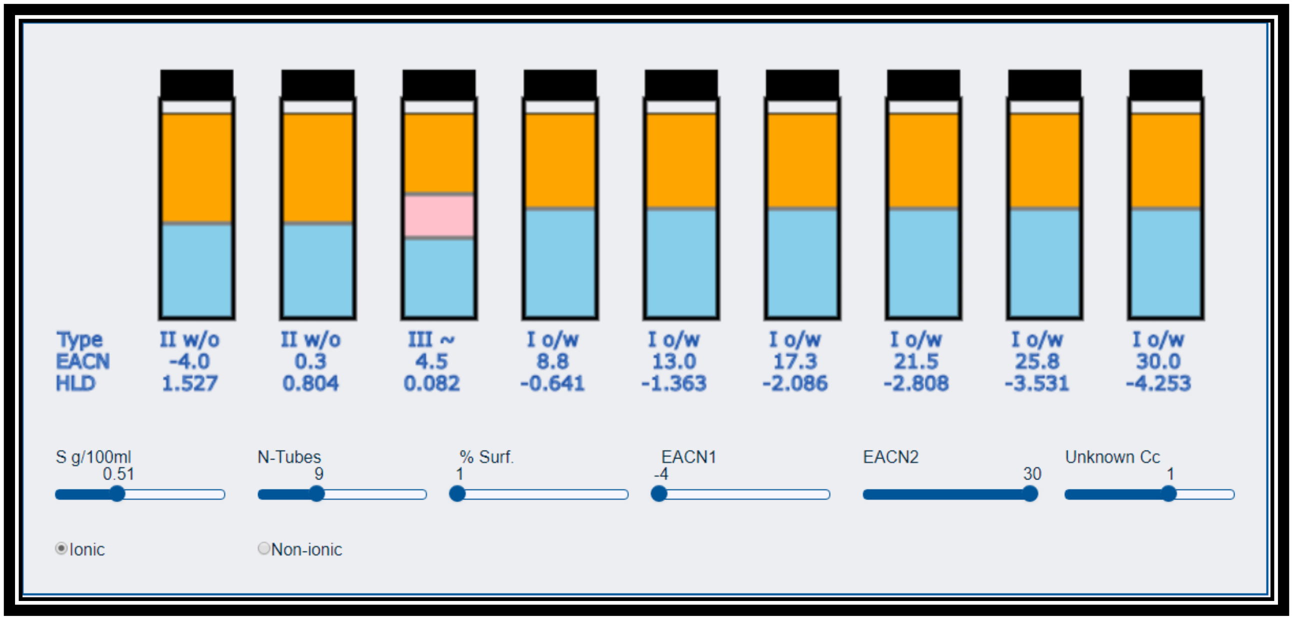
EACN1 -4

EACN2 30

Unknown Cc 1

● Ionic ○ Non-ionic

Figure 4-3: Phase behavior based on HLD and EACN for 0 ppm brine



Type	II w/o	II w/o	III ~	I o/w	I o/w	I o/w	I o/w	I o/w	I o/w
EACN	-4.0	0.3	4.5	8.8	13.0	17.3	21.5	25.8	30.0
HLD	1.527	0.804	0.082	-0.641	-1.363	-2.086	-2.808	-3.531	-4.253

S g/100ml 0.51

N-Tubes 9

% Surf. 1

EACN1 -4

EACN2 30

Unknown Cc 1

● Ionic ○ Non-ionic

Figure 4-4: Phase behavior based on HLD and EACN for 5000 ppm NaCl brine

Figure 4-3 shows phase behavior with de-ionized water based on varying HLD and EACN in ionic surfactant while ***Figure 4-4*** shows those for 5000 ppm NaCl brine. The results imply that a Winsor type II microemulsion can be gotten at lower salinities.

This implies that the EACN of the oil used is between -4 and 4.5. Assuming and EACN of 4.5, a Windsor type III microemulsion may have been gotten with the salinity.

In addition, comparing the HLB values for the three surfactants analyzed, using the William Griffin method, the HLB value of the cationic surfactant is the lowest, which indicates its water-in-oil or Windsor type II emulsion formation compared to the other surfactants analyzed. The non-ionic surfactant, having an HLB value of 12.413, is the highest of the HLB values for the three surfactants used in this work.

The phase behavior test is however not enough to understand the reactions of the surfactant at the oil brine interface hence a more quantitative measurement such as IFT is conducted and compared with the phase behavior results.

4.2 Zeta Potential Measurement at the Oil Brine Interface

To further understand the phenomena occurring at the fluid-fluid interface, the results for the zeta potential at the oil-brine interface are presented with the same surfactant and brine combination used in the phase behavior experiments.

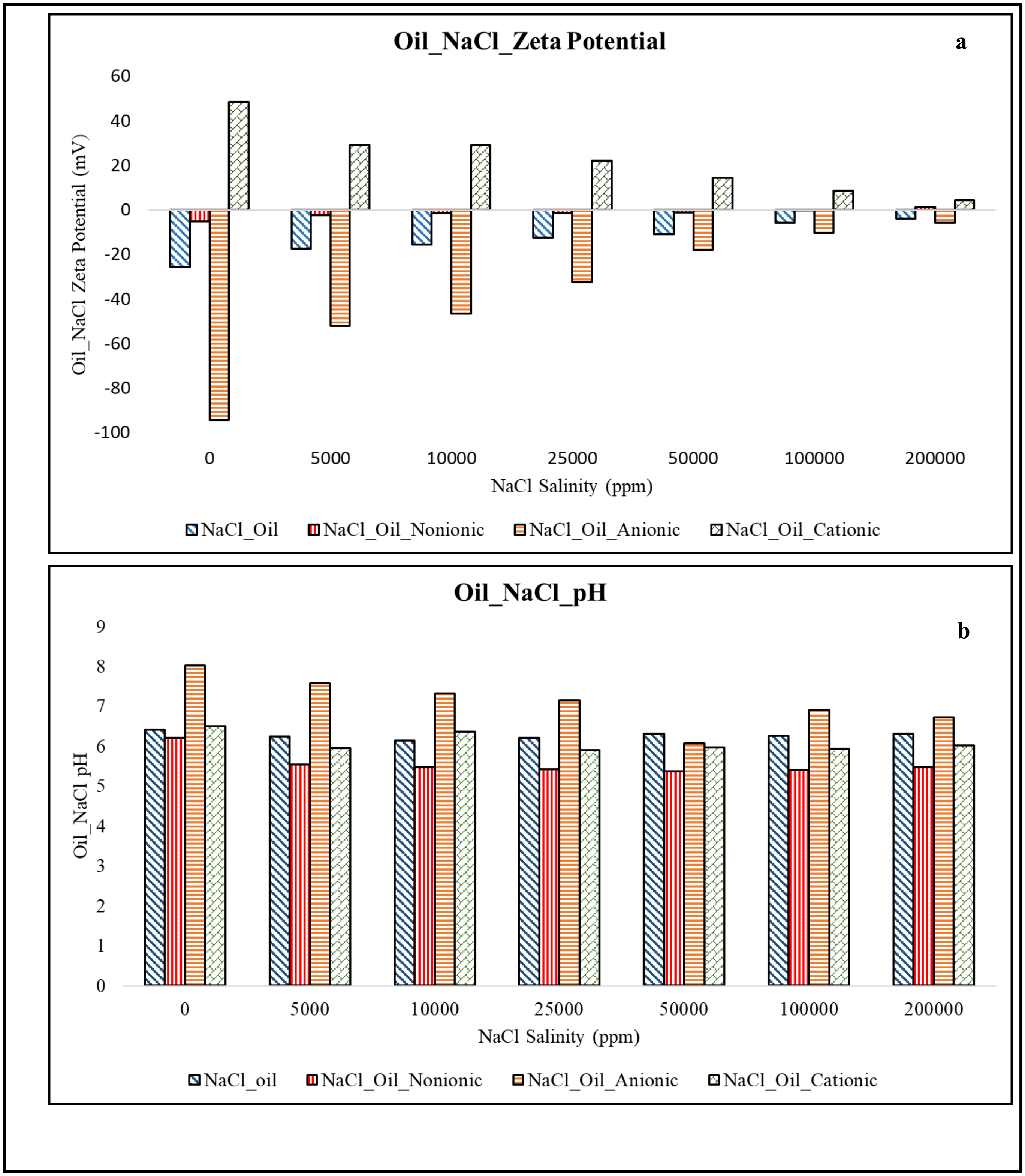


Figure 4 - 5 (a,b) 1; (a) Oil_NaCl zeta potential, (b) Oil_NaCl pH

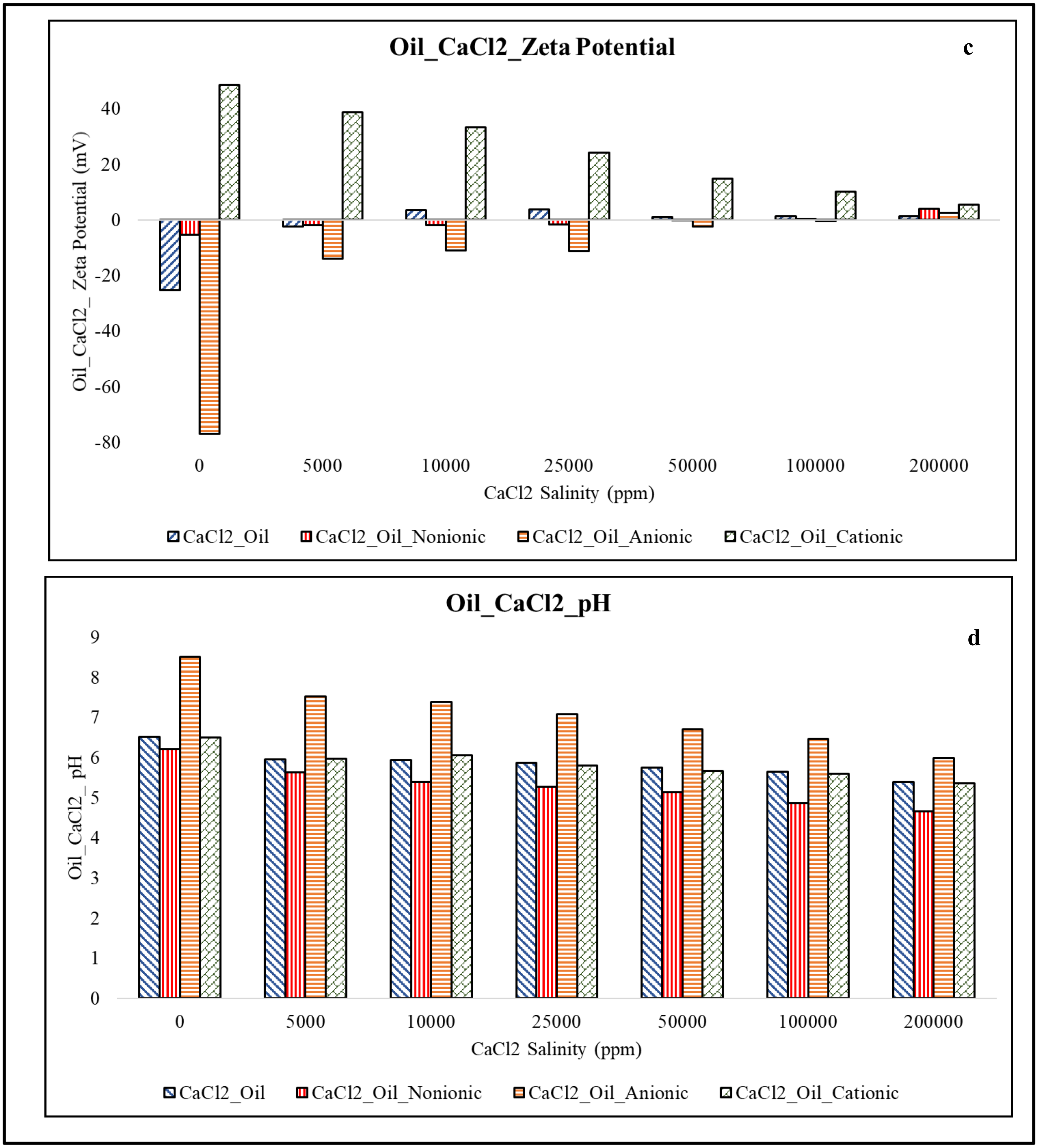


Figure 4 -5 (c,d) 1; (c) Oil_CaCl2 Zeta Potential (d) Oil_CaCl2 pH

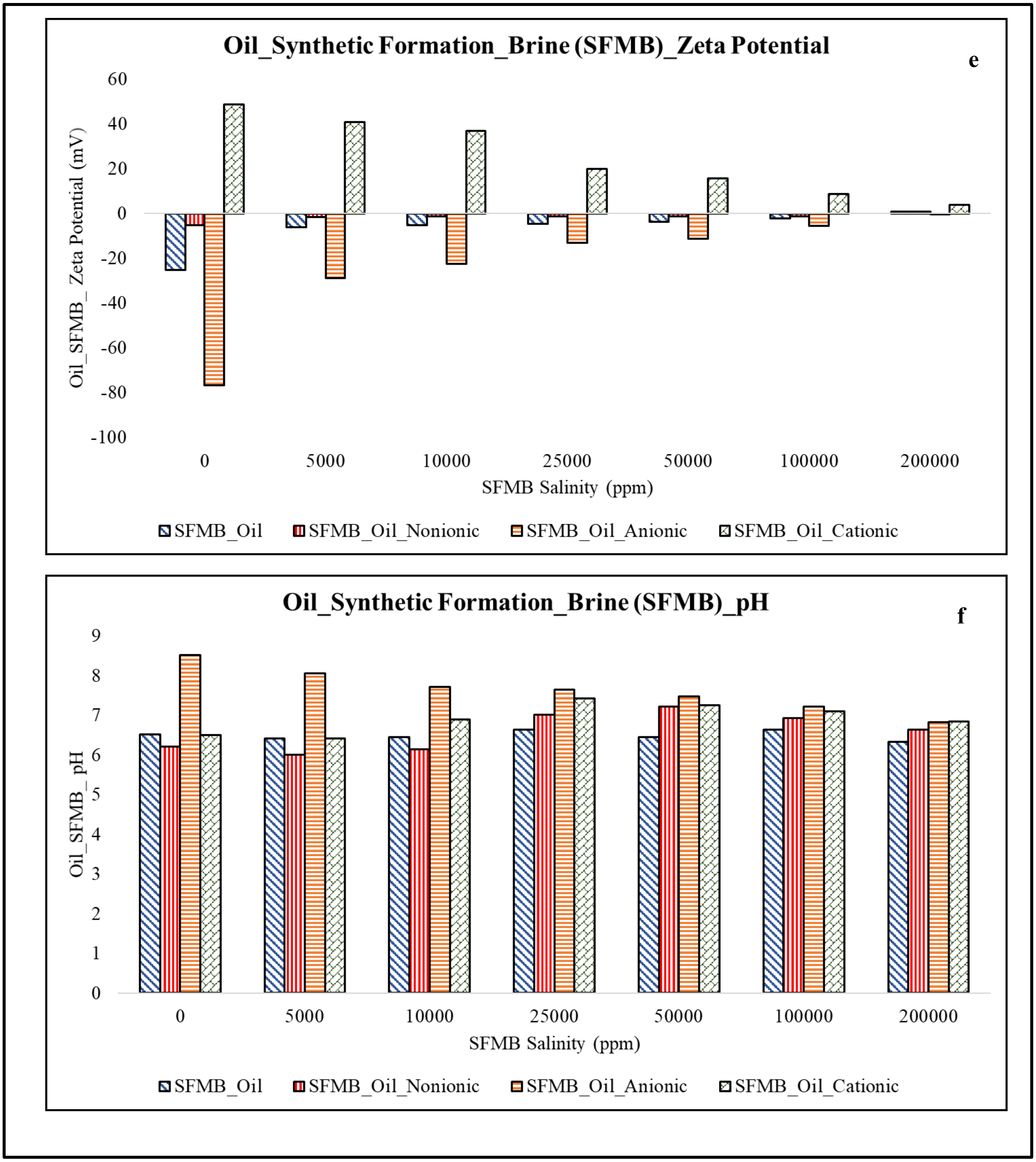


Figure 4 - 5 (e,f) 1: (e) Oil_Synthetic formation brine zeta potential, (f) Oil_synthetic formation brine pH

Figure 4-5: Zeta Potential and pH results at the oil-brine interface

Figure **4 - 5 (e,f)** ***1*****: (e) Oil_Synthetic formation brine zeta potential, (f) Oil_synthetic formation brine pH**

Figure ***4-5*** (**a, c and e)** shows the results for zeta potential and pH in NaCl brine, $CaCl_2$ brine and Synthetic formation brine (SFMB). The oil-brine zeta potential results show a reduction in the zeta potential magnitude with salinity with all the brine and surfactant systems analyzed. This is an indication that at higher salinities, there is a strong van der Waals attractive force between the oil and brine which may be an indication of reduced IFT values compared to the low salinity cases. In the absence of surfactant in NaCl and SFMB, the zeta potential values are negative at the oil-brine interface. These negative charges are due to the presence of negatively charged carboxylic acids present in the oil. In $CaCl_2$ brine alone, the oil exhibits positive charges at salinities between 10,000 ppm and 200,000 ppm which is likely due to the presence of an increasing concentration of divalent cations at higher salinities. This could have an effect on the overall wettability alteration depending on the charges at the rock brine interfaces at the salinities being considered. As noted by (Jackson, et al., 2016), wettability alteration will occur when the signs of charges at both the oil-brine interface and the brine-rock interface are the same.

In the presence of the non-ionic surfactant in all the brines studied, the zeta potential values are only slightly negative and even closer to zero at salinities between 0 ppm and 100,000 ppm then becomes positive at 200,000 ppm. This is an indication of Vander Waals force of attraction present at the oil and brine interfaces in the presence of the non-ionic surfactant. This is a further indication, similar to the results obtained from the phase behavior experiments that the non-ionic surfactant can reduce the IFT better than the other surfactants. The anionic surfactant dissociates and deposits its negatively charged ions at the oil-brine interface which increases the magnitude of negative charges compared to the base case without surfactant. The excess negative charges results in a bigger EDL compared to the case with the non-ionic surfactant, hence an increased IFT value due to further separation of the oil and brine phases. The magnitude of the negative charges with the anionic surfactant is however reduced in the $CaCl_2$ brine because of the presence of divalent cations which counters the negative charges from the anionic surfactant. With the cationic surfactant, the charges at the oil-brine interface are positive and even more positive in the presence of calcium chloride brine compared to the other brines due to the ionization of the cationic surfactant which results in positive charges and also due to the presence of the positively charged head group of the cationic surfactant. Again, these are qualitative results and can only be verified with more quantitative results such as IFT measurements.

The pH results are presented in **Figure *4* - 5 (e,f) *1*: (e) Oil_Synthetic formation brine zeta potential, (f) Oil_synthetic formation brine pH**

Figure *4-5* ***(b, d, and f)***. Only the anionic surfactant affects the pH values drastically to alkaline values compared to the base case scenario without surfactant. The highly alkaline pH values observed with the anionic surfactant is due to the nature of the surfactant which ionizes partly at a pH as low as 2. From the base case, however, the pH is greater than 2, hence there is expected to be complete ionization of the anionic surfactant. Another possible mechanism could be that after the ionization of the anionic surfactant, the negatively charged head bonds to the CO group present in the carboxylic acid as COOH, while replacing the OH^- group. In this process, therefore, OH^- ions are released which then increases the pH of the solution to more alkaline values. This is however not the case for the non-ionic surfactant due to its high degree of hydrophilicity as a result of the Ethoxy (EO) group present which has a strong hydrogen bond with water, thereby having less effect on the release of OH^- ions present in the COOH of the oil, hence resulting in an acidic environment. The cationic surfactant although has an impact on the zeta potential at the oil-brine interface, does not have an effect on the pH at the interface when compared to the base case scenario without surfactant. This is a pointer to show that the cationic surfactant may be better at wettability alteration and not IFT reduction.

In brief, the phase behavior and oil-brine zeta potential measurements are somewhat consistent.

4.3 Interfacial Tension Results

The interfacial tension between oil and brine is affected by various parameters such as;

- Addition of polymers
- Surfactant concentration
- Molecular structure of the surfactants
- Presence of Alkali
- Presence of co-surfactant
- Salinity
- Temperature

There may be causes when the operators can use only specific brine such as the produced water or formation water. It is therefore essential to study the effect of different surfactants on each brine. Also, it is crucial in a scientific perspective to study the interfacial behavior of each surfactant with different brines. Therefore, the relevant results are discussed separately as;

a) Effect of surfactant type on the IFT with various brine salinities and ionic composition

b) Effect of brine type on IFT with different surfactants

From the oil-brine zeta potential and phase behavior experiments, only four brine salinities were chosen for the interfacial tension measurements which cover the ranges of salinities studied (low salinity, seawater salinity, and high salinity). The salinities chosen are 5,000 ppm, 25,000 ppm, 50,000 ppm, and 100,000 ppm brine salinities for all the brine types and surfactant combination. For the Evie shale, the interfacial tension measurement was not done with the KCl brine since it is a monovalent ion and the results are likely to be very similar to that of the NaCl. This is because cations in brine have an electrostatic effect on the distribution orientation of the polar components in the oil, which is in the following magnitude; $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ (Le Calvez et al.2001b)

4.3.1 Effect of Surfactant on the Interfacial Tension in Various Brine Salinities and Ionic Composition

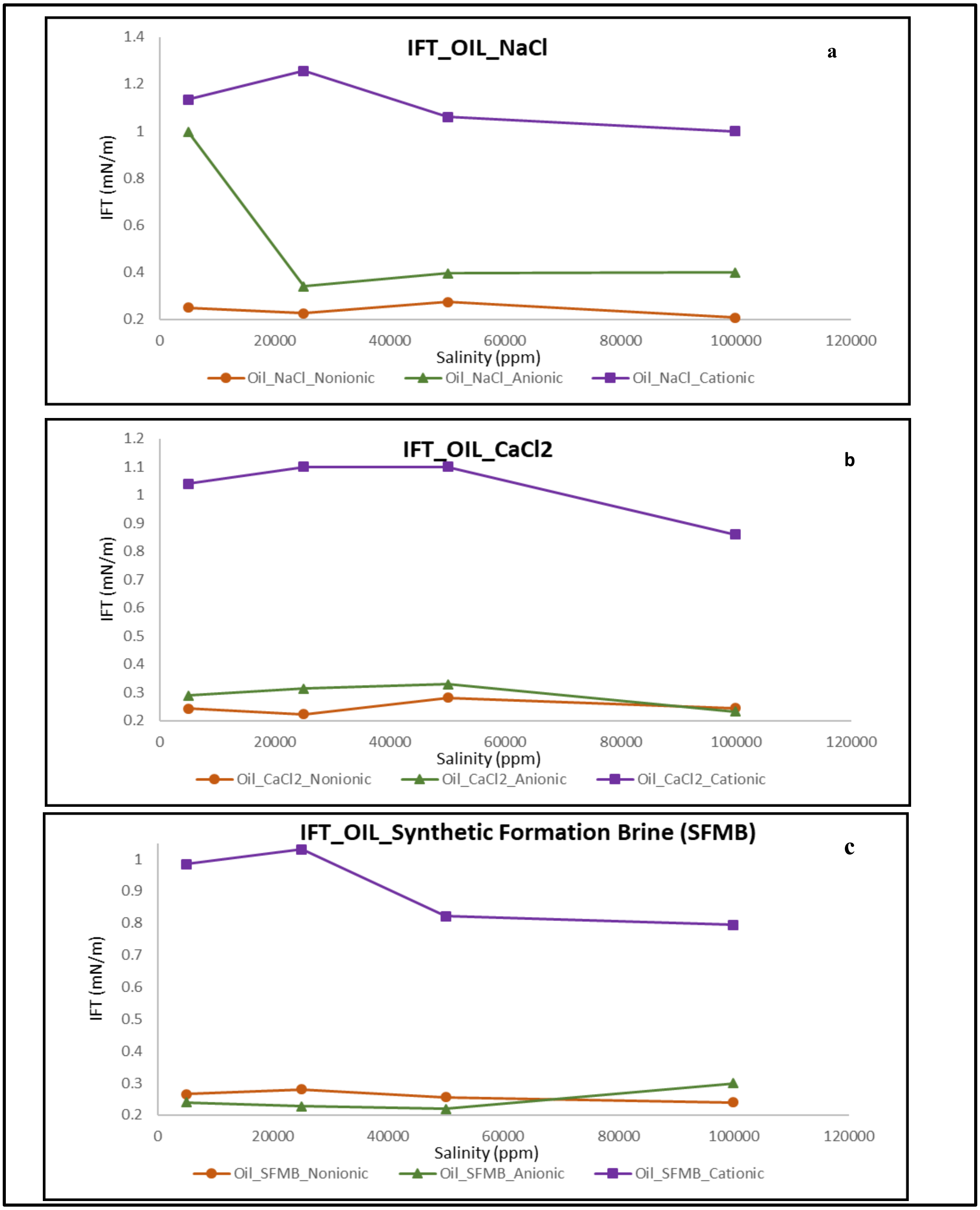
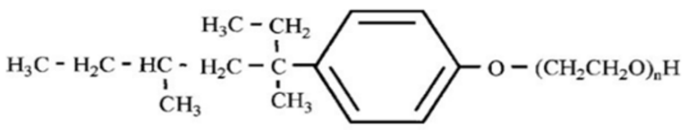


Figure 4-6: Effect of surfactant types on interfacial tension in various brine salinities and ionic composition

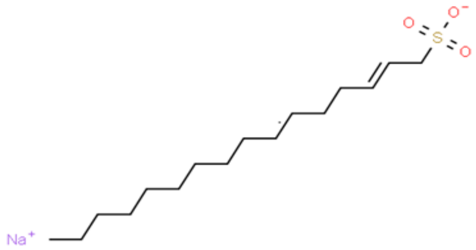
Figure 4-6 ***(a)*** shows the IFT values of all the three surfactants in the presence of NaCl. All surfactants result in lower IFT values at high salinities compared to the low salinity cases. As expected based on the phase behavior and oil-brine zeta potential results, the non-ionic surfactant gives lower IFT values at all salinities compared to both the ionic surfactants. The cationic surfactant results in the highest IFT values at all the salinities investigated. At 5000 ppm, the IFT of anionic surfactant is relatively high and then decreases at other salinities. This is due to the less dissolution of oil in the water phase as seen by the color of the brine at that salinity. A similar trend was observed by (Kathel & Mohanty, 2013) who reported that IFT decreases for an anionic surfactant with increasing salinity with formation brine. This trend was attributed to the competition between the high saline brine and surfactant for aqueous solubilization whereby the surfactant is moved towards the oil-brine interface at higher salinities, which results in a lower IFT at higher salinities. ***Figure 4-6 (b)*** shows the IFT results of the $CaCl_2$ brine and oil with the surfactants studied. Similar to ***Figure 4-6 (a)***, the lowest IFT is observed with non-ionic surfactant in $CaCl_2$ brine while with the anionic surfactant, the IFT values continually increase at lower salinities after which it decreases at high salinity of 100,000 ppm. This decrease in IFT at 100,000 ppm could be because of the high concentration of calcium ions, which has a strong binding affinity with the polar components in the crude oil, which could lead to better emulsification. (Le Calvez, Blaudez, Buffeteau, & Desbat, 2001a) studied the binding effect of different cations with polar species present in crude oil and their results show that the affinity for Ca^{2+} ions to the polar component present in the brine is strongest compared to the other cations studied hence a lower IFT. Again, the competition for solubilization between the surfactant and the ions in the high salinity brine for aqueous solubilization pushes the surfactant towards the oil-brine interface. In comparison to ***Figure 4-6 (a)*****,** it is observed that the IFT value at 5,000 ppm is higher in the case of anionic surfactant in NaCl brine. The ability of divalent ions in reducing the IFT when compared to the monovalent ions has been reported by (Lashkarbolooki, Ayatollahi, & Riazi, 2014a; Tetteh, Joel, Janjang, & Barati, 2018).

Figure 4-6 (c) shows the results for IFT with synthetic formation brine and surfactant solutions. With the non-ionic surfactant, the IFT continually decreases as the salinity increases, which again corresponds to the phase behavior experiments. However, for the anionic surfactant, the IFT reduces continually between 5,000 ppm and 50,000 ppm after which it increases at 100,000 ppm salinity, as seen by the very clear solution observed in the phase behavior measurements at 100,000 ppm. The cationic surfactant shows a continuous decrease in IFT with an increase in salinity except at 25,000 ppm, which gives the highest salinity and corresponds to the brightest brownish color of brine from the phase behavior experiment. The optimal salinity for IFT reduction, in this case, is at 100,000 ppm for the non-ionic and cationic surfactants. However, for the anionic surfactant, the optimal salinity for IFT reduction is at 50,000 ppm. Comparing this result with the case of NaCl and $CaCl_2$ brines in the anionic surfactant, it shows that when the anionic surfactant is present in a brine containing a high concentration of NaCl, IFT increases at a very high salinity- 100,000 ppm in this case. The IFT values are high in the low salinity regions because there is less divalent cation concentration, thereby the binding effect of the surfactant to the oil is reduced.

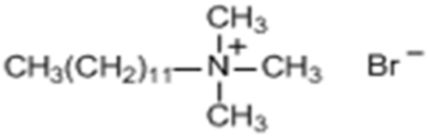
Apart from the presence of ions, the molecular structure of the surfactant plays a part in the interfacial tension. It has been noted by various researchers (Yang, J., Qiao, Li, & Cheng, 2005) that the surfactants which have more methyl group in their outer most hydrocarbon chain structure compared to CH_2 group will have a lower IFT because the interfacial energy of CH_2 is more than CH_3. The nonylphenol ethoxylate surfactant has more methyl structure in their outer most hydrocarbon chain group compared to the other ionic surfactants; hence it can reduce the IFT better that the other surfactants. The molecular structure of the surfactants is given in ***Figure 4-7***



a: Non-ionic Surfactant: Nonyl Phenol Ethoxylate



b. Anionic surfactant: Sodium olefin sulfonate



$$CH_3(CH_2)_{11}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N^+}}-CH_3 \quad Br^-$$

c. Cationic surfactant: Dodecyl trimethyl ammonium bromide

Figure 4-7: Molecular structure of surfactants used

It is worthy of note that while the non-ionic and anionic surfactant reduces the IFT by an order of two, compared to values between 10mN/m and 30mN/m that would usually be obtained in the absence of surfactant, the cationic surfactant only reduces the IFT by a magnitude of order one.

4.3.2 Effect of brine Type on IFT with different surfactants

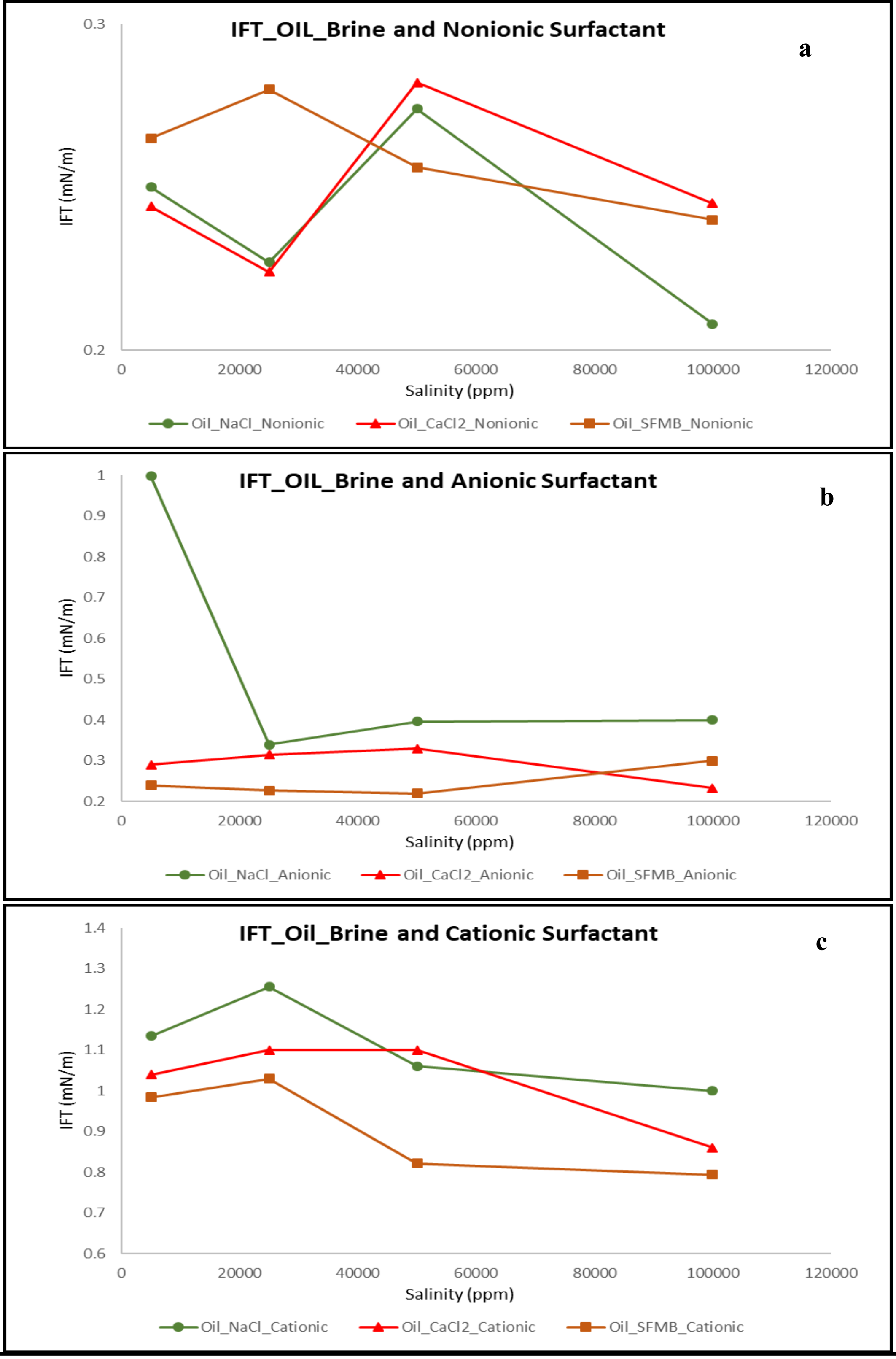


Figure 4-8: Effect of brine type on IFT with different surfactants

The effect of ionic composition in NaCl (BX), $CaCl_2$ (BY)and synthetic formation (BZ) brines are shown for non-ionic surfactant ***Figure 4-8 (a)***, anionic surfactant ***Figure 4-8 (b)*** and cationic surfactant ***Figure 4-8 (c).***

Figure 4-8 (a) shows the IFT values of the non-ionic surfactant at various salinity in different brines. The IFT trend for NaCl and $CaCl_2$ brines is very similar at all salinity ranges tested, yielding almost the same values at salinities between 5000 ppm, and 50,000 ppm. The IFT with NaCl brine is lower than that with $CaCl_2$ brine at salinities between 50,000 ppm and 100,000 ppm, which implies that the non-ionic surfactant is more compatible with monovalent cations at high salinity for a better IFT reduction.

Figure 4-8 (b) and ***Figure 4-8 (c)*** show the IFT values in the three brine with the anionic and cationic surfactants respectively. Compared to the other two brines, the IFT values are lowest in the presence of the synthetic formation brine at all salinities for both surfactants except in the case where the anionic surfactant is present in 100,000 ppm $CaCl_2$ brine which results in the lowest IFT. The IFT trend observed in both surfactants with the brines tested are similar, where the divalent cations give a lower IFT compared to the monovalent cations. Cations in brine have an electrostatic effect on the distribution orientation of the polar components in the oil, which is in the following magnitude; $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ (Le Calvez, Blaudez, Buffeteau, & Desbat, 2001b). This means that the polar components in the brine are more bonded with Calcium ions compared to magnesium, sodium, and potassium which results in a lower IFT with calcium ion compared to sodium ions. The cations move the polar component in the oil phase closer to the interface, thereby reducing the free energy at the interface. As the salinity reduces further, the assembled oil component at the interface will be dissolved in the brine phase (salting in effect), thereby increasing the Interfacial tension, compared to high salinity cases.

Some salinities show a spike in IFT which is not within the trend observed by other salinities. For example with the non-ionic surfactant in NaCl brine, there is a reduction of IFT at increasing brine salinity except at 50,000 ppm, where the IFT is highest. This behavior could be attributed to the non-monotonic behavior of IFT with salinity, as shown by various researchers. (Chávez-Miyauchi, Firoozabadi, & Fuller, 2016; Lashkarbolooki et al., 2014; Lashkarbolooki, Ayatollahi, & Riazi, 2014b; Lashkarbolooki, Riazi, Ayatollahi, & Hezave, 2016; Xu, W., 2005).

As expected, the results for the phase behavior experiments are in line with the IFT results and oil-brine zeta potential results. For instance, with the anionic surfactant present in $CaCl_2$ brine, whereby limited oil dissolution in the brine phase is seen at salinities between 5000 ppm and 50,000 ppm, which indicates a high IFT, the IFT values are indeed higher at those salinities compared to the case of 100,000 ppm. Moreso, with the cationic surfactant present in NaCl and the synthetic formation brine which showed Windsor type II micro-emulsion at low salinities, the results indeed show that the IFT values are higher at those low salinities compared to higher salinities of 50,000 ppm and 100,000 ppm. The non-ionic surfactant, which does not show nay Winsor type II micro-emulsion gives low IFT values compared to the other cases.

Even though in most of the cases, the non-ionic surfactant gave the lowest IFT compared to the other surfactants, however, these values are not to ultra-low values.

The high IFT values given by the cationic surfactant compared to the other surfactants may be attributed to the working principle of the cationic surfactant. According to (Standnes & Austad, 2000) Since there is a formation of ion-pair between the negatively charged component in the crude oil and the surfactant, which is insoluble in water, it is then reasonable to see that the cationic surfactant results in the highest IFT value which makes the IFT values consistent with the phase behavior studies.

The behavior of the non-ionic surfactant in the two ions analyzed was studied, and the findings are summarized below;

- The interfacial tension is lowest with the nonionic surfactant compared to the other surfactant types in NaCl brine
- The non-ionic surfactant results in the lowest IFT values in $CaCl_2$ brine compared to the other surfactant types
- The non-ionic surfactant is compatible with high salinity brines compared to the other surfactants used

Based on the highlighted factors, an optimized synthetic formation brine composition was designed to further reduce the interfacial tension with the non-ionic surfactant to check if ultra-low IFT values can be observed. The newly designed brine composition for IFT reduction is given in ***Table 4-1***.

Table 4-1: Newly designed brine for IFT reduction with the non-ionic surfactant

Salts	Optimized SFMB (S1) (%)
NaCl	81.63
$CaCl_2.2H_2O$	-
$MgCl_2.6H_2O$	16.3
Na_2SO_4	1.95
$NaHCO_3$	0.12

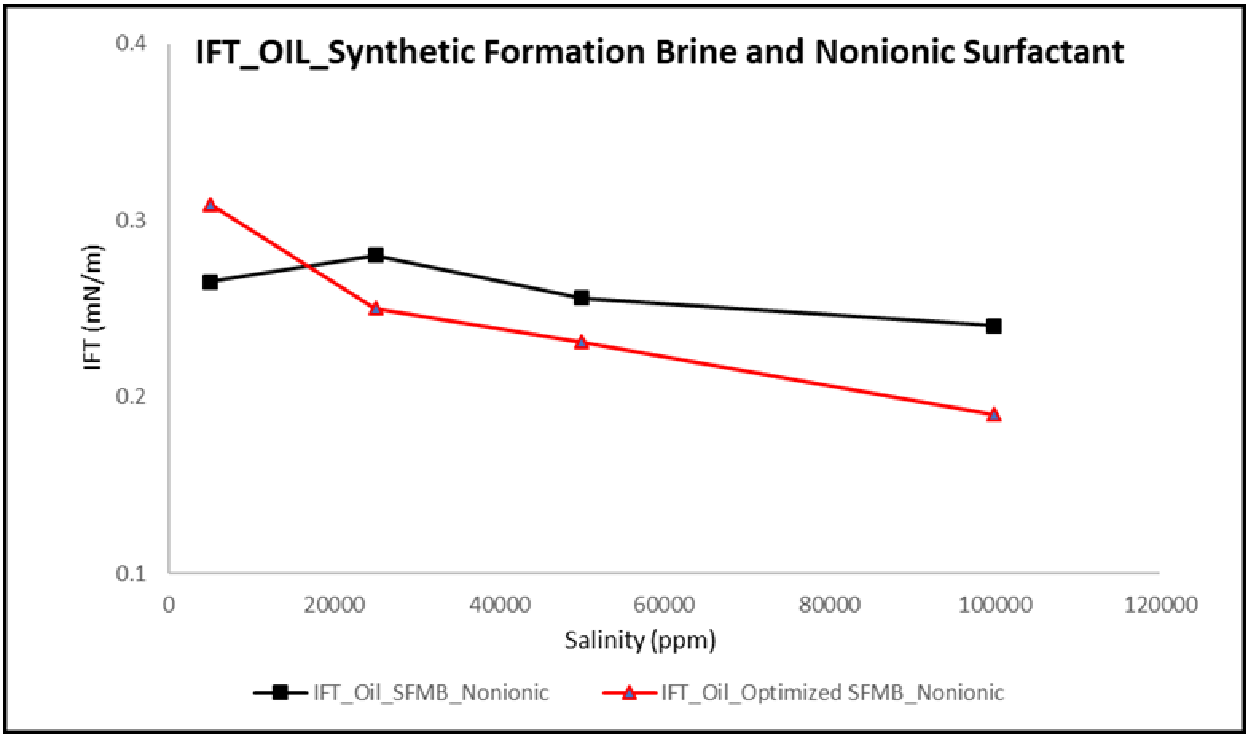


Figure 4-9: IFT results with the newly designed synthetic formation brine in the non-ionic surfactant

Figure 4-9 shows the comparison for the IFT results with the newly designed synthetic formation brine and the originally used synthetic formation brine. The newly designed brine reduces IFT further with the non-ionic surfactant compared to the base case scenario with the original synthetic formation brine present in the non-ionic surfactant. It is however seen that similar to the previous case where the IFT is highest at 5000 ppm; it still remains high at the same salinity for the optimized case. The reason for this may be attributed to the less cation present at lower salinities, whereby with an increase in the cation (sodium ion) concentration, the IFT reduces further.

4.4 Zeta Potential at the Rock-Brine Interface

4.4.1 Sandstone Rock

The zeta potential and corresponding pH results with the Botucatu sandstone rock is shown in

Figure 4-10

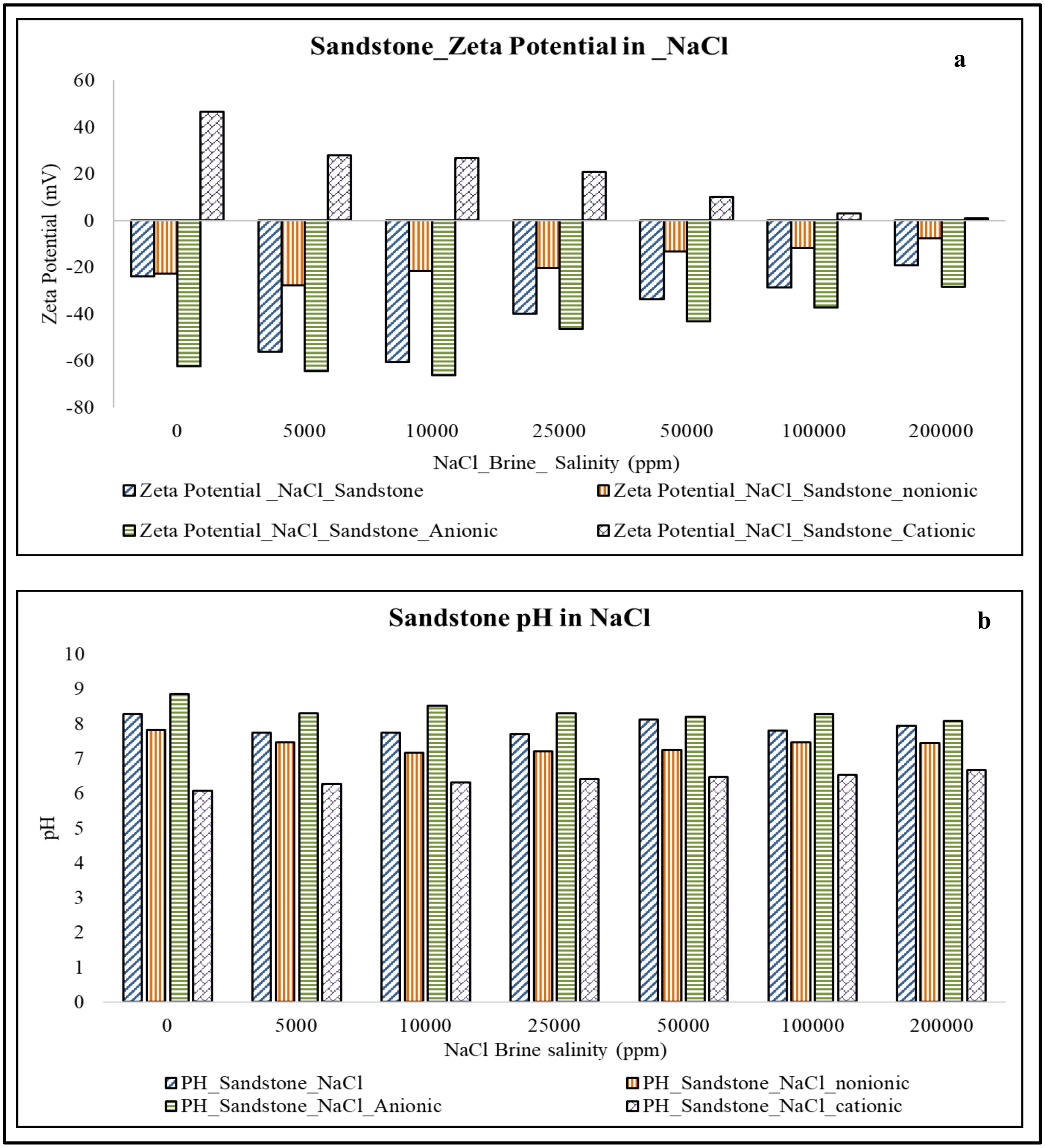


Figure 4 -10 (a,b) 1: (a) Sandstone Zeta Potential in NaCl brine (b) Sandstone pH in NaCl brine

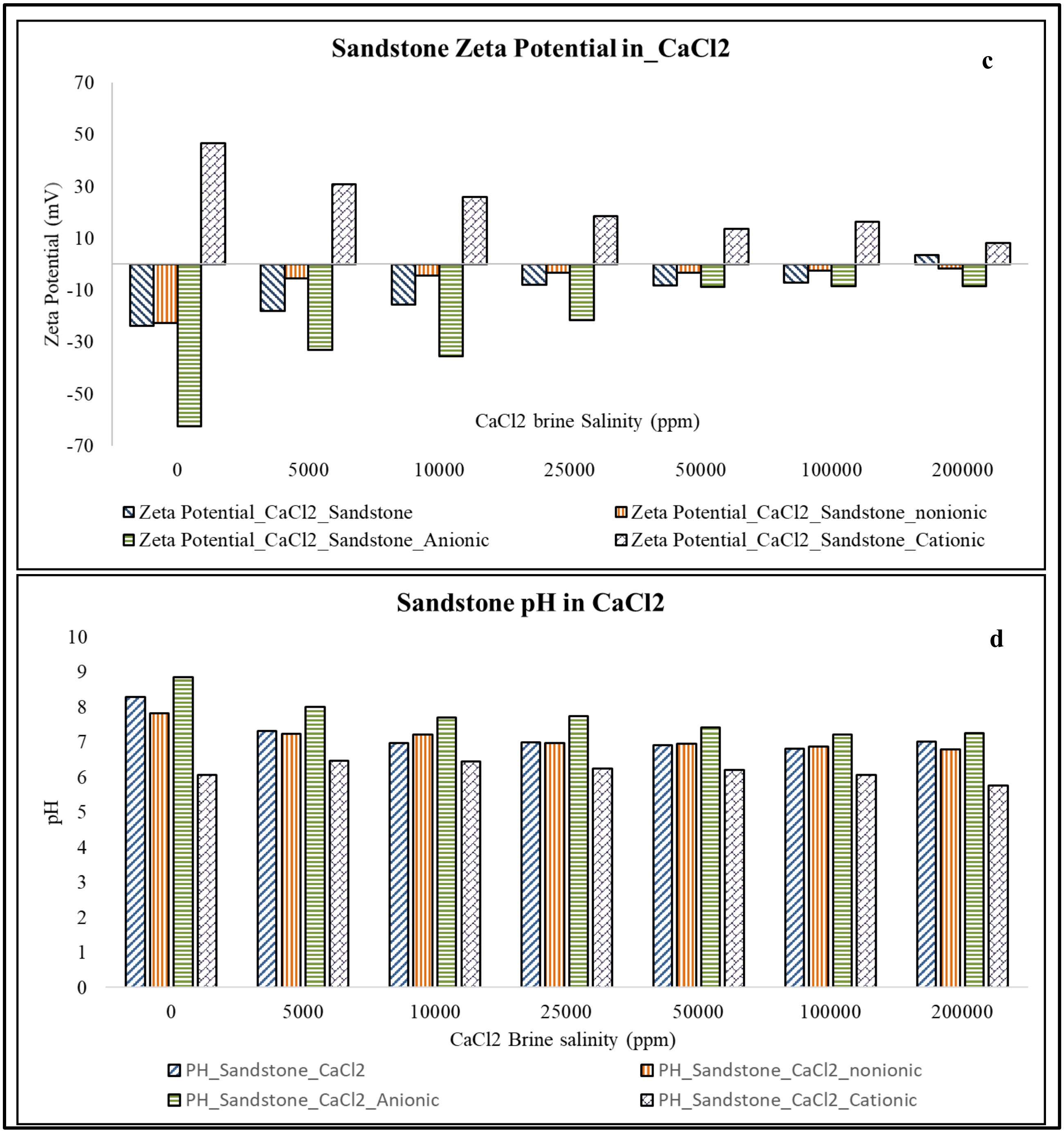


Figure 4 -10 (c,d) 2: (c) Sandstone Zeta Potential in CaCl2 brine (d) Sandstone pH in CaCl2 brine

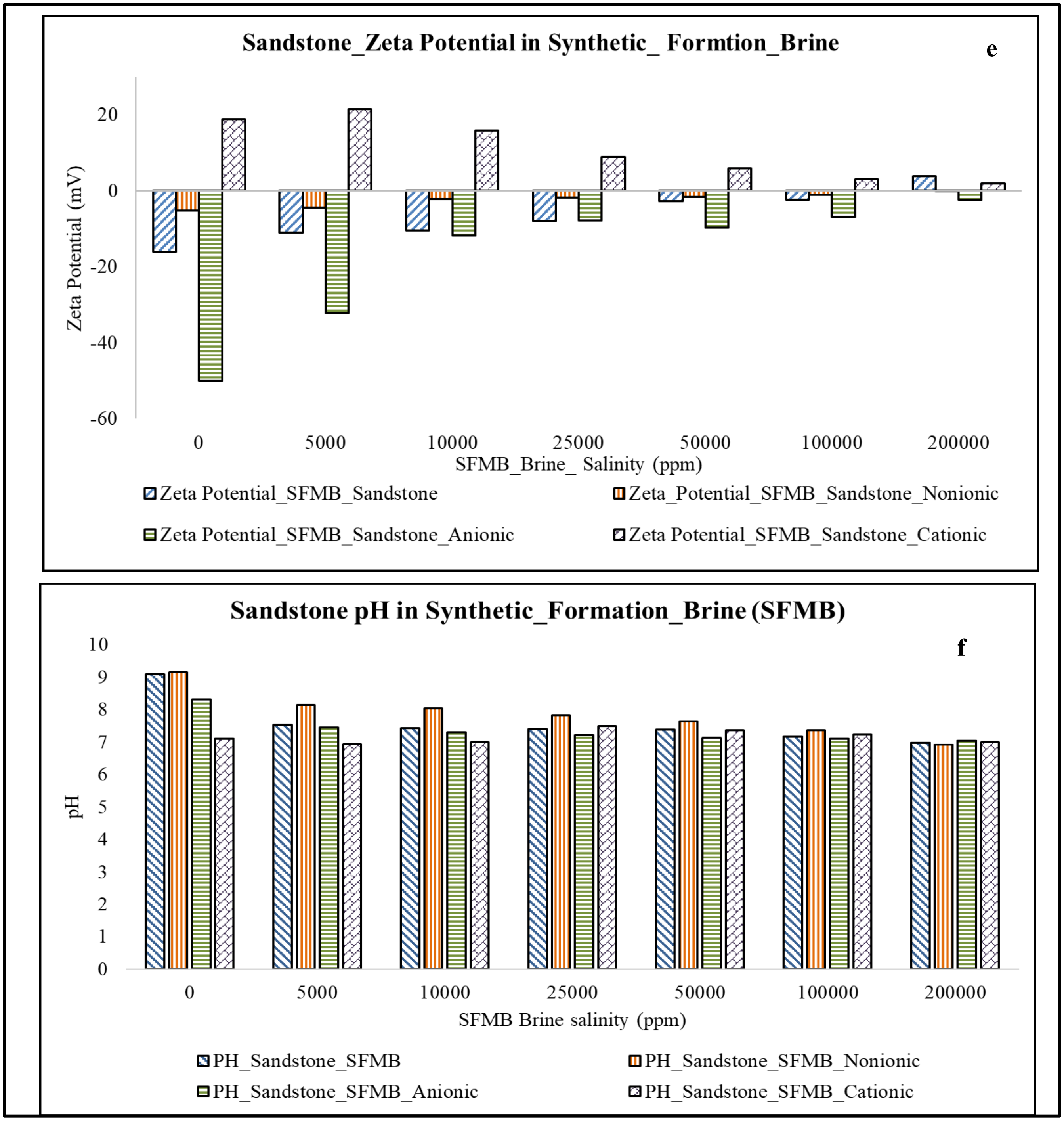


Figure 4 -10 (e,f) 1; (e) Sandstone Zeta Potential in synthetic formation brine, (f) sandstone pH in synthetic formation brine

Figure 4-10: Zeta Potential and pH measurements with Botucatu sandstone

Figure 4-10 shows the zeta potential, and pH values for Botucatu sandstone rock in the presence and absence of surfactants in three different brine ionic compositions and varying concentrations ranging from 0 ppm to 200,000 ppm. In terms of the sign of the charges, the surfactant gives similar charge effect in all brines studied. The Botucatu sandstone rock is negatively charged in the absence of surfactant for all three brines. This could be attributed to the quartz and clay content of the rock. (Alotaibi et al., 2011) investigated the effect of clay minerals present in sandstone particles on zeta potential in three different brines – De-ionized water, aquifer water with a salinity of 5436 ppm and seawater with a salinity of 54680 ppm. Their results are indicative that clay minerals are negatively charged with these salinity ranges investigated. Hence their results correlate to those in this work. In the NaCl brine shown in

Figure 4-10 (a) the magnitude of the zeta potential is largest at 10,000 ppm brine salinity which indicates that wettability alteration towards more water-wet conditions is more favorable at that salinity due to a bigger EDL formed around the rock particles. In the $CaCl_2$ brine shown in figure

Figure 4-10 (b)**,** the negative magnitude of the zeta potential values reduces with an increase in salinity, where it becomes positive at 200,000 ppm in the absence of surfactant. Compared to the case of NaCl, the negative magnitude of zeta potential values are smaller in $CaCl_2$ due to the presence of divalent calcium ions.

Figure 4-10 (c) shows the zeta potential results with the synthetic formation brine (SFMB) which shows a reducing magnitude of zeta potential value with salinity.

In the presence of non-ionic surfactant in all cases, shown in

Figure* 4-10 *(a, c, e) the magnitude of the negative zeta potential reduces even further, which indicates that there is an adverse effect of the non-ionic surfactant on wettability alteration in the Botucatu sandstone rock. Non-ionic surfactants are stabilized by steric repulsion in a colloidal suspension. Colloidal stabilization, in the form of steric repulsion, is provided by oligomeric or polymeric entities that are attached to the surface either by chemical bonding or adsorption (Birdi, 2015). The extent of steric stabilization of colloidal particles is dependent on the solubility of the hydrophilic part of the stabilizing moieties (Romero-Cano, Martın-Rodrıguez, Chauveteau, & De Las Nieves, F J, 1998). Non-ionic surfactants are generally not soluble in water; however, the presence of EO group increases their hydrophilicity via hydrogen bonding with the aqueous phase which implies a weak form of steric stabilization, hence a smaller double-layer compared to the ionic surfactants.

In all brines shown in

Figure* 4-10 *(a, c, e), the ionic surfactant (anionic and cationic) results in a negatively charged and positively charged rock particles respectively due to the ionization of the surfactants into negative and positive charges. The EDL in the case of ionic surfactants is bigger compared to the case of a non-ionic surfactant. This implies that if flooding is to be done with the ionic and non-ionic surfactants, better wettability alteration will be observed in the case with the ionic surfactants especially at 10,000 ppm NaCl brine concentration. It is however not guaranteed that 10,000 ppm NaCl brine will result in the highest oil recovery compared to other brines since improved oil recovery is governed by other factors apart from wettability alteration as measured by the EDL size. The big magnitude of positive charges, especially at low salinities observed in the case of the cationic surfactant, could represent either an increase in the EDL size or cationic surfactant adsorption on the negatively charged sandstone rock as observed in the base case without surfactant. In $CaCl_2$ brine, the magnitude of negative zeta potential reduces in the presence of anionic surfactant, while it increases in the presence of cationic surfactant. Again, the reduction in the magnitude of negative charges in the presence of the $CaCl_2$ brine may be as a result of the excess positively charged divalent calcium ions present in the $CaCl_2$ brine. The binding affinity for clay present in a core to cation is in the following order; $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > Mg^{2+} > Ca^{2+} > Sr^+ > Ba^{2+} > H^+$, which implies that Ca^{2+} ions will have more impact in reducing the negative charges of the rock.

The pH results are presented in

Figure 4-10 (b,d,f). For the pH results, in the NaCl brine, In

Figure 4-10 (b) the pH values are at alkaline levels in all cases except when the cationic surfactant is present whereby the pH values become acidic. Depending on the acid number of the crude oil, alkaline pH values could lead to in-situ surfactant generation.

With the calcium chloride brine in

Figure 4-10 (d), pH values are at alkaline levels at low salinities between 0 ppm and 5000 ppm in the absence of surfactant, while they become acidic from 10,000 ppm. With the non-ionic surfactant, pH values are alkaline between 0 ppm and 10,000 ppm and become acidic at higher brine salinities. For the anionic surfactant, the pH values are alkaline in all cases while for the cationic surfactant, pH values are also acidic, similar to the case with NaCl.

With the synthetic formation brine in

Figure 4-10 (f), pH values are alkaline between 0 ppm and 100,000 ppm, however, they get closer to acidic pH at 200,000 ppm. In the presence of the non-ionic surfactant, the pH values are alkaline at all salinities except at 200,000 ppm, while in the case of the anionic surfactant, pH values are alkaline. In the case of cationic surfactants, the pH values are only slightly alkaline. The slightly alkaline pH values seen in the cationic surfactant with the synthetic formation brine may be as a result of the combined effect of other ions present in the brine.

The best combination that can be used for flooding for maximum wettability alteration effect would be with 10,000 ppm NaCl brine in the presence of the anionic surfactant since the zeta potential and pH magnitude are largest at that salinity. 10,000 ppm NaCl without surfactant and 10,000 ppm NaCl with the anionic surfactant is therefore used for flooding with the homogeneous micromodel.

4.4.2 Carbonate Rock

The zeta potential experiments were carried out to determine the effect of surfactant on the size of the electrical double layer, relative to the rock type, at varying brine ionic composition and strength. Three different carbonate rocks are used – Indiana limestone, Silurian Dolomite and slave point formation core. Since high salinity brines have more ions and different chemistry compared to low salinity brine, their chemical reactions with carbonate particles are expected to be dramatically different. In sandstone reservoirs, for example, clay controls the interaction in low salinity water (Alotaibi, Azmy, & Nasr-El-Din, 2010; Zhang & Austad, 2006) whereas, in carbonate reservoirs, the salinity effect is more pronounced.

4.4.2.1 Zeta Potential with Indiana Limestone

The brines, salinity ranges and surfactant types used in the case of the Botucatu sandstone rock is also used here.

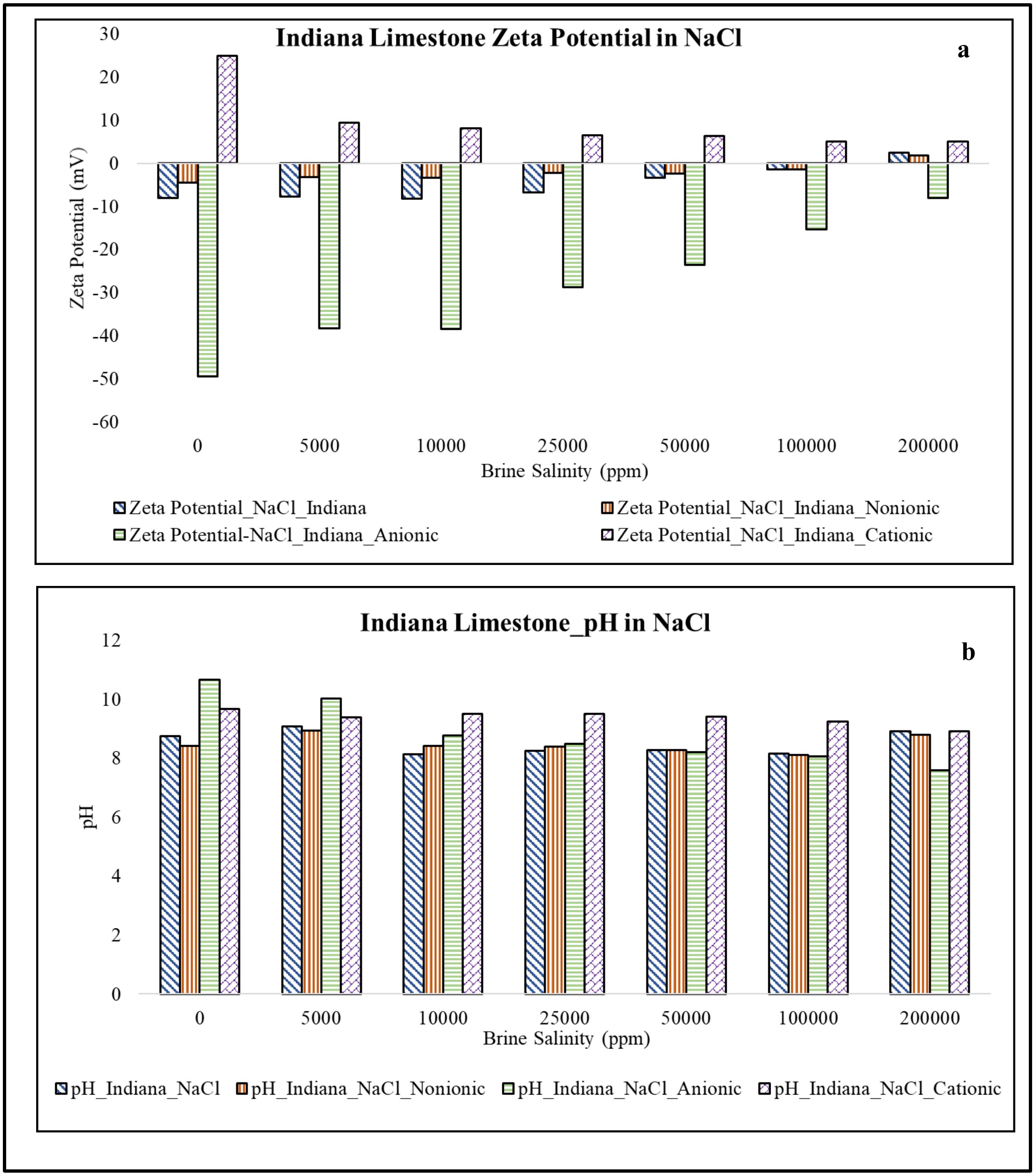


Figure 4 -11 (a,b) 1; (a) Indiana limestone zeta potential in NaCl brine (b) Indiana limestone pH in NaCl brine

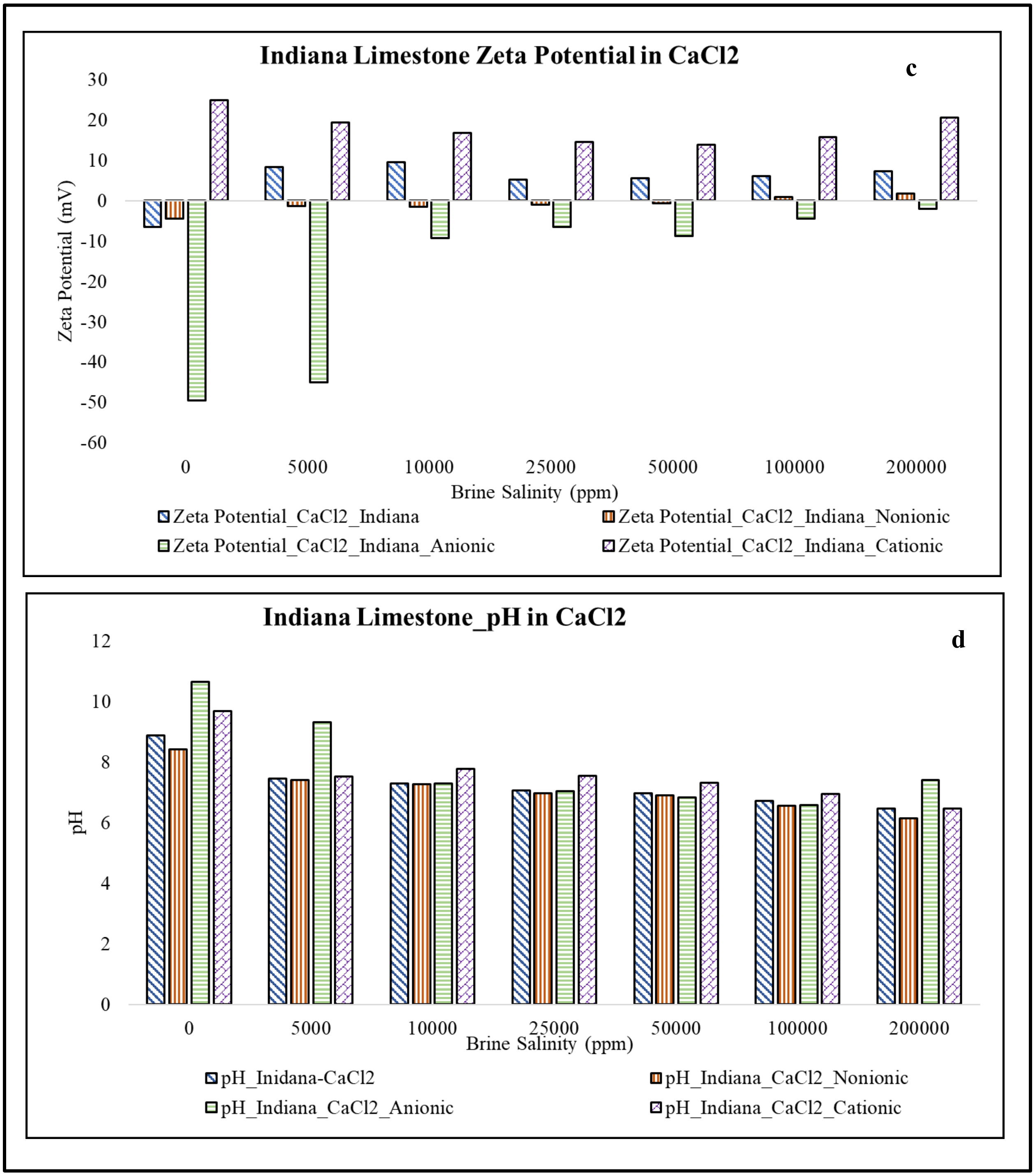


Figure 4 - 11 (c, d) 1; (c) Indiana limestone zeta potential in CaCl2 brine (d) Indiana limestone pH in CaCl2 brine

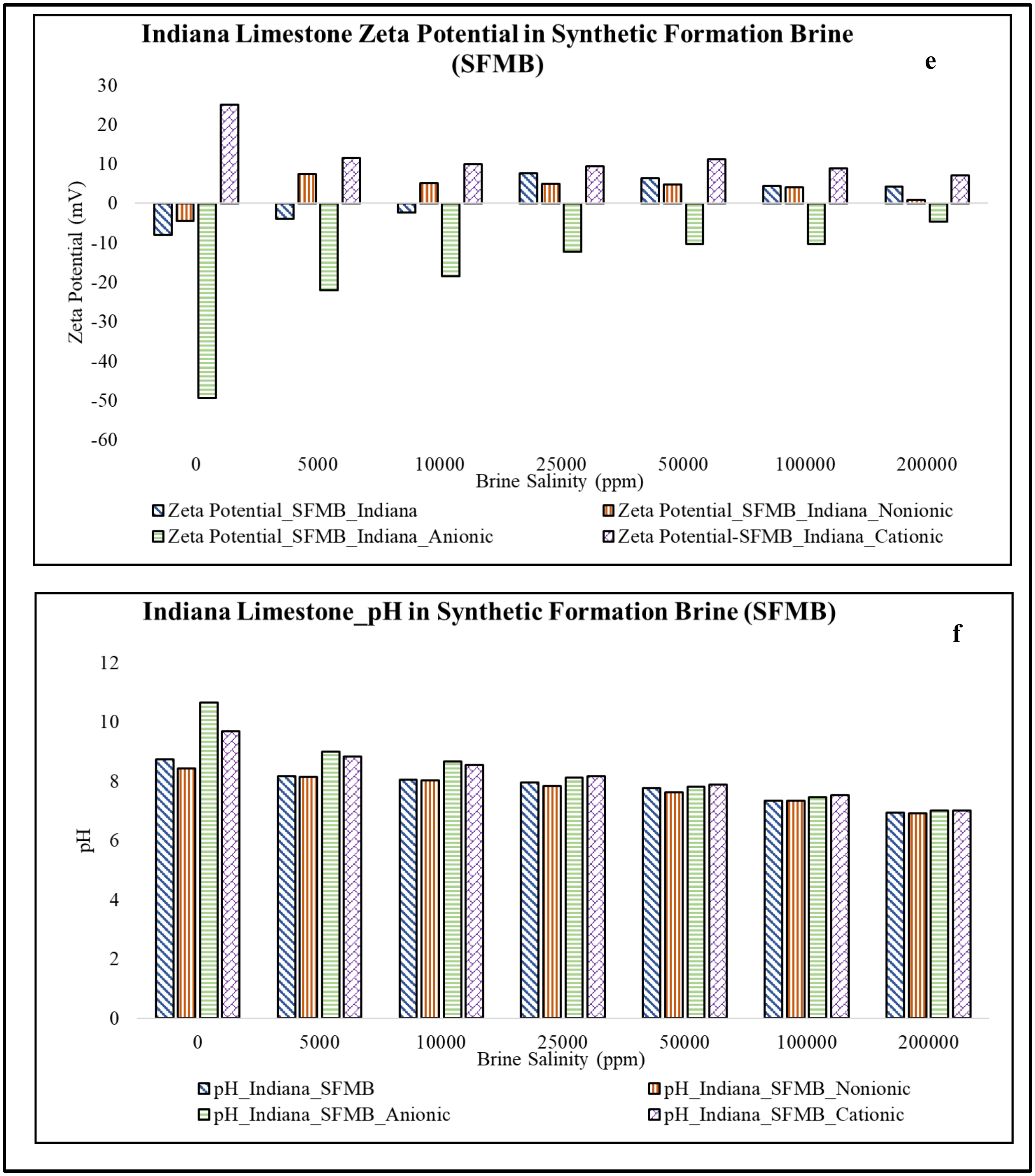


Figure 4 - 11 (e,f) 1; (e) Indiana limestone zeta potential in synthetic formation brine, (f) Indiana limestone pH in synthetic formation brine

Figure 4-11: Zeta Potential and pH values for Indiana limestone

NaCl Brine

Figure 4-11 (a) shows the plot for zeta potential at the Indiana limestone and NaCl brine interface with varying brine salinity and surfactant type. In the absence of surfactant, the zeta potential at the rock-brine interface is negatively charged at salinities between 0 ppm and 100,000 ppm, while it becomes positive at 100,000 ppm in NaCl brine. In general, carbonate rocks are known to be positively charged at reservoir pH but can be changed depending on various factors such as the presence of PDI, pH, rock mineralogy and the isoelectric point of the carbonate rock which varies with salinity, temperature, and presence of surfactant. The varying isoelectric point of carbonate rock reflects the dynamics of the electrostatic/ionic interactions at the interface. According to (Mahani et al., 2017) there are two factors that affect the zeta potential at the rock-brine interface, and they are;

- Regulation of surface charge due to the adsorption of potential determining ions (PDI's)
- Ionic strength

Other factors are;

- Calcite dissolution
- Presence of surfactant
- Rock mineralogical composition
- Isomorphic substitution
- pH

The zeta potential results are, therefore discussed according to the factors highlighted above.

Potential Determining ions (PDI's)

Models have been developed to explain how the surface charges are generated according to the type of surface complexes that are made up from the spatial arrangement of partially solvated ions which form dynamically at the surface. Various potential determining ions have been identified, and they are; H^+, OH^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, $Ca^{2+,}$ and Mg^{2+}. These ions form charged surface complexes upon adsorption on the calcite surface. These surface complexes are then responsible for the charges at the mineral surface and can be studied through a surface complexation model (SCM). The SCM requires detailed geochemical reactions that occur at the rock brine interface. An SCM is a chemical model that describes the reactions occurring at the interface of the mineral and solution and simulates the chemical equilibrium. These reactions have equilibrium (stability) constants which are similar to analog reactions in the bulk solution. The SCM, therefore, gives an insight into the causes of the changes observed at the rock interface.

In terms of improved oil recovery, (Brady, Patrick V. & Krumhansl, 2012; Brady, Patrick Vane, Krumhansl, & Mariner, 2012) have used SCM to validate the theories of wettability alteration while giving an insight to the coordination of the polar functional group present in the crude oil and the mineral which leads to the desorption of the adsorbed oil on clay and calcite.

Na^+ and K^+ have been identified as indifferent cations since they are said not to have an effect on the surface charge of the rock. From the results in ***Figure 4-11 (a)*** it is obvious that the charge of the Indiana limestone is negative even without the addition of salt i.e. in the presence of de-ionized water, whereby the zeta potential value is -8.01mV. (Alotaibi et al., 2011) has reported a zeta potential value of -11.2 mV for limestone particles suspended in de-ionized water at a neutral pH while (Smani, Blazy, & Cases, 1975a) reported a zeta potential value of -15mV for calcite in de-ionize water. This could mean that NaCl may be a PDI and reacts with the rock since the positive magnitude of the zeta potential decreases with an increase in salinity. In the same brine and at salinities between 0 ppm and 100,000 ppm, the zeta potential value is negative and becomes positive at a salinity of 200,000 ppm. Other factors could be responsible for the surface charges observed. One of which is the nature of the carbonate rock used or the pH. The effect of pH is explained in the pH section. The change in pH is, however not very consistent with the change in the charges observed at the rock-brine interface. For example, at 200,000 ppm brine salinity in NaCl brine alone where the zeta potential is positive, the pH values are at alkaline levels which further project sodium ions as potential determining ions. In terms of pH, Similar results were obtained by (Zhang & Austad, 2006) who investigated the effect of Mg^{2+}, $Ca^{2+,}$ and SO_4^{2-} on the zeta potential of chalk in equilibrium with 0.573 M of NaCl brine containing various concentrations of Mg as $MgCl_2$ and SO_4 in the form of Na_2SO_4. Their result showed a negative zeta potential in pure NaCl brine solution which became increasingly positive with the addition of Ca^{2+} or Mg^{2+} ions, while it became increasingly negative with an increasing concentration of SO_4^{2-} ions at a constant pH of 8.4. The negative zeta potential value with the NaCl brine was attributed to alkaline pH levels, which results in the deposition of OH^- ions on the rock surface.

Ionic strength (EDL) with NaCl brine

A reduction in the ionic strength causes an increase of the EDL, which in turn increases the absolute magnitude of the zeta potential. There is a linear relationship between zeta potential and ionic strength at a constant surface charge (Adamson, Chilingar, & Beeson, 1963) shown in ***equation* 6**

$$pI = -log_{10}(I) \qquad \textbf{equation 6}$$

Where ‘I’ is the brine ionic strength. The equation is consistent with the results seen in the case of NaCl brine at all salinities, in which the EDL reduces as the salinity increases.

Presence of Surfactant

Zeta potential values beyond -30mV and +30mV depicts a stable water film, hence a bigger EDL and favorable wettability alteration towards more water-wet conditions. Therefore, it implies that even though the wettability alteration improves compared to the base case without surfactant, there is a reduced wettability alteration in the presence of non-ionic and cationic surfactant at all salinities in the NaCl brine, while the anionic surfactant proves to be more efficient in wettability alteration at salinities between 0 ppm and 10,000 ppm. The anionic surfactant outperforms the other two surfactants at all salinities investigated while the non-ionic surfactant performs least in terms of wettability alteration. The unfavorable wettability alteration with the non-ionic surfactant is attributed to the mechanism of stabilization of the rock particles with the surfactants. Colloidal stabilization in the form of steric repulsion is provided by oligomeric or polymeric entities that are attached to the surface either by chemical bonding or adsorption; for example, nonionic surfactants (Birdi, 2015). The extent of steric stabilization of colloidal particles is dependent on the solubility of the hydrophilic part of the stabilizing moieties (Romero-Cano et al., 1998). Non-ionic surfactants with hydrophilic EO group are generally not soluble in brine, but there exists a strong hydrogen bond between the hydrophilic EO group and brine, which implies a weak form of steric stabilization, hence a smaller double layer potential compared to the ionic surfactants. For small values of double-layer potential (zeta potential), the London-van der Waals Potential appears to prevail for all particle distances and the particles become attracted to each other, leading to flocculation.

Electro-statically stabilized dispersion may arise in a variety of ways such as; adsorption of potential determining ions (for example anionic and cationic surfactants), ionization of ionogenic groups (for example carboxylic acids), presence of lattice defects in the disperse phase such as clay. This implies that electrostatic stabilization is the main mechanism for colloidal stability with ionic surfactants. Bigger zeta potential magnitude as observed in the case of ionic surfactants results in stabilized colloidal particles prevents agglomeration (Verwey, 1947). The poor performance of non-ionic surfactant in altering the wettability of calcite plates to water-wet conditions has also been observed by (Martavaltzi et al., 2012).

Calcite Dissolution

One of the factors which can affect the magnitude and sign of the zeta potential values is the method used in sample preparation which could lead to the dissolution of calcite. During the agitation of the samples, the samples were exposed to acidic atmospheric CO_2. In contact with the sample, calcite dissolution is expected to occur, making the total system become alkaline, hence releases some hydronium ions which in turn increases pH to alkaline levels and yields a negatively charged surface. Calcite dissolution also occurs when the brine is not fully equilibrated with calcium ions.

Rock mineralogical composition

The rock mineralogical composition affects the charge density observed. From the XRD analysis of the Indiana limestone rock, it is seen that the rock contains some quartz and clay minerals which contribute to the negative charges observed with NaCl brine. (Chen et al., 2014) Conducted zeta potential measurements in high salinity formation brine of salinity greater than 220,000 ppm and a low $CaCl_2$ salinity brine of 0.1 wt.%. They observed a continuous decrease in the zeta potential with an increase in pH from 5 to 11. The reason for this was attributed to the changes in the concentration of H^+ and OH^- ions and concomitant dissolution of the rock used in their experiment. However, the mineral composition of the rock used in their experiment contained 18% of quartz and clay minerals which tend to have negative zeta potential at higher pH and depending on how they cover the carbonate surface; they can affect the effective surface charge of the carbonate rock.

Isomorphic Substitution

An isomorphic substitution that occurs between similar size ions will result in the properties/charges of the replacing ions being transferred to the rock lattice (Kronberg et al., 2014). Since Na^+ and Ca^{2+} ions are of similar size, less dense Sodium ions in the brine replace more dense calcium ions present in the limestone rock. The positive charges of the calcite are thereby reduced due to charge density differences. If the isomorphic substitution does occur in the rock, then the SCM theory becomes contradicted since Na^+ ions are known to be indifferent ions, therefore should not react with the rock exchange site.

pH Results with NaCl

The results for pH vs Salinity for Indiana limestone in various NaCl with and without surfactant are presented in ***Figure 4-11 (b,d, and f)***. In all cases, the pH values are at alkaline levels, which could be an indication of calcite dissolution due to the absence of calcium ions in the brine and also due to the method of sample preparation which could have caused the dissolution of atmospheric CO_2 in the sample, thereby leading to the release of hydroxyl ions which is reflected in the negative sign of the zeta potential value.

Even though the pH values are at alkaline levels in the absence of surfactant and with the non-ionic surfactant, zeta potential values are still positive at 200,000 ppm, thereby implying the impact of high salinity. Hence, at a very high salinity such as 200,000 ppm, the sign on the limestone rock is mainly dependent on the ionic strength of the brine and not the pH value. Similarly, the cationic surfactant results in alkaline levels of pH with the NaCl brine in Indiana limestone even though the zeta potential remains positive. Therefore, alkaline pH values which release OH^- ions do not solely determine the surface charge on the rock in the presence of cationic surfactant. The positive rock charge in the case is due to the positive charges from the head group of the cationic surfactant, which results from the ionization of the cationic surfactant in the NaCl brine. Other factors such as additives, brine ionic composition and salinity must be taken into consideration. This is in line with the explanation given by (Mahani et al., 2017) who has stated that the sensitivity of pH to zeta potential decreases at high salinities such as formation brine salinity because at high salinities, the EDL is densely populated with PDI's such as Ca^{2+}, $Mg^{2+,}$ and SO_4^{2-} which compete for surface binding sites and the concentration of these ions is much larger than the concentration of H^+ and OH^-. Therefore, the PDI's have a stronger influence on the zeta potential.

Generally, anionic surfactants are known to cause adsorption on the calcite surface due to the reaction between the positive charges present in the rock and the negatively charged head group of the surfactant. In this case, there is likely to be minimal adsorption of anionic surfactant because as the pH increases, the limestone surface becomes more negative as it crosses the point of zero charge (PZC) where the adsorption of anionic surfactant is reduced. Although it is difficult to determine the PZC for carbonates since the value changes with salinity, a generally accepted value for the PZC of limestone is at 9.2 while that of dolomite is about 7.4 (Gupta et al., 2008). Analyzing the pH values given by the anionic surfactant in the Indiana limestone, it is seen that all the values are above 9.2 except at 200,000 ppm, which has a pH of 8.91. This implies that less anionic surfactant adsorption is expected at salinities below 200,000 ppm of NaCl brine. Similarly, various researchers (Chilingar & Haroun, 2014; Mielczarski, Schott, & Pokrovsky, 2006; Van Cappellen, Charlet, Stumm, & Wersin, 1993) have reported different charge for the zeta potential of carbonate rocks (Calcite and Dolomite) in monovalent ions such as NaCl brine. Their observations show that below the isoelectric point (IEP), these rock particles become positively charged while the reverse is the case for a pH above their IEP.

Based on the pH results, Na^+ ions may be considered a PDI;

Inference for Carbonate Rocks –Why Sodium may be regarded as a Potential determining ion

The presence of Sodium ions, which have been found to be indifferent may be beneficial in the low salinity effect in two ways;

- Rock Dissolution
- Saponification of fatty acid (carboxylic acid)

The presence of sodium ions alone especially in a limited amount in the brine may lead to rock dissolution since the brine is not equilibrated with calcite. Again, for the surface complexation model, there seem not to be a viable reason why the sodium ions will not react with the $>CO_3^{2-}$ exchange site present in the limestone rock, just like every other divalent cation, known as PDI would react. The reaction of Sodium with the $>CO_3^{2-}$ exchange site would lead to H^+ ions, bringing about an acidic environment which will further lead to the dissolution of the rock. One of the products likely to be formed is Sodium carbonate (Na_2CO_3), which is a weak base, hence leading to saponification, making the system alkaline. Depending on the acid number of the crude oil, in-situ surfactants could be generated as a result of the saponification reaction.

Again, the generation of the alkali, a sacrificial agent could result in less anionic surfactant adsorption. Furthermore, sodium is compatible with the anionic surfactant and does not form a precipitate which can cause pore blockage in the rock like the divalent cations.

In brief, the rock dissolution from the use of Na^+ ions will lead to the generation of alkali making the rock negatively charged due to saponification reaction which will lead to a higher repulsive force with the negatively charged oil-brine interface. In the presence of anionic surfactant, this repulsive force is even bigger, hence bottle-neck of anionic surfactant adsorption may be reduced with the addition of Na^+ ions.

The proposed reactions with the mineral and oil phase are therefore shown below;

Some of the $>CO_3^{2-}$ rock exchange site are protonated at a pH between 6.5 -7 (within the range of reservoir pH), to form CO_3H^o with no charge, while the other $>CO_3^{2-}$ exchange site could form a surface complex of $>CO_3Na^+$

$$> CO_3H^O + Na^+ \leftrightarrow CO_3Na^+ + H^+$$

Reaction with the crude oil

$$Na_2CO_3(aq) + 2CH_3COOH\ (aq) \leftrightarrow 2CH_3COONa\ (aq) + CO_2(g) + H_2O(l)$$

$$Alkali + Carboxylic\ acid \leftrightarrow salt\ (sodium\ carboxylate) + gas + water$$

Saponification of fatty acids involves any reaction between an alkali with the acid that produces soap, which are salts of fatty acids. The saponification reaction may occur slowly since the base and acid are weak however it will still occur.

It has been noted however that rock dissolution can also result in the precipitation of Ca^{2+} and Mg^{2+} ions. However, (Mahani, Keya, Berg, & Nasralla, 2015) did not observe any sign of precipitation and concluded that the formation of surface charge is faster than precipitation.

$CaCl_2$ brine

Since Ca^{2+} ions are considered to be PDI's, then the SCM reaction at the Indiana limestone surface can be written. The SCM reaction is complex but can however be viewed as the calcite/limestone surface as having two exchange sites; $>Ca^{2+}$ and $>CO_3^{2-}$ (> indicates they are surface complexes) for which all surface complexes for calcite are defined in terms of two master hydration species; $>CaOH$ and $>CO_3H^o$ according to the standard used by (Stipp & Hochella Jr, 1991). The results for the zeta potential in the presence of $CaCl_2$ brine is shown in ***Figure 4-11 (c)***

Presence of PDI

In the absence of surfactant, the zeta potential is negative at 0 ppm and becomes positive at increasing salinities. This shows that calcium ions are indeed potential determining ions since they are able to alter the charge of the rock from negative values seen in the case of de-ionized water to positive values unlike the case with the NaCl brine where the zeta potential values are negative from 0 ppm to 100,000 ppm.

Various authors have reported different charges for pure calcite suspended in calcium chloride brine. The charge of zeta potential of calcite in calcium chloride brine is positive at the pH range between 7 and 12 in the work of (Cicerone, Regazzoni, & Blesa, 1992b; Thompson & Pownall, 1989b). They attributed the surface charge to be due to the concentration of calcium ion in the brine. Contrary to that, various authors (Douglas & Walker, 1950; Smani, Blazy, & Cases, 1975b) have reported negative charges in the same condition at pH ranging between 5.5 and 12. The surface charge could be positive or negative depending on the suspension concentration, vigorous shaking and the presence of atmospheric CO_2. (Berlin & Khabakov, 1961) suggests that the nature of the surface charge is dependent on the nature of the sample ie if the calcite surface is from biogenic (composed of calcareous fossils), non-biogenic (crystalline or natural origin), synthetic or Iceland spar (pure crystalline or double spar origin) origin. For example, in an open system natural calcite suspended in $CaCl_2$ brine,the zeta potential is positive whereas in closed system with synthetic calcite suspended in $CaCl_2$ brine, zeta potential is negative.

Other researchers (Mishra, 1978; Smallwood, 1977; Yarar & Kitchener, 1970) are, however of the opinion that the surface charge is dependent on the calcium and carbonate concentrations. (Madsen, 1996) is of the opinion that the difference in charges observed is likely due to the experimental condition or the nature of the carbonate material used.

Ionic Strength effect/EDL

EDL is biggest at 10,000 ppm brine salinity in the absence of surfactant. This does not follow the brine ionic strength and EDL relationship presented previously in **equation 1**

This could be as a result of the presence of more calcium ions which is a potential determining ion in the case of 10,000 ppm. The magnitude of the zeta potential values at salinities above 10,000 ppm is lower due to the presence of more ions which suppresses the EDL.

Calcite Dissolution

Calcite dissolution is expected to occur only at low salinities between 0 and 5000 ppm, where the brine is likely not to be fully equilibrated with calcium ions, coupled with the atmospheric CO_2 which could induce dissolution when in contact with the solution. This could be confirmed from the pH results. At higher salinities, however, there will be reduced calcite dissolution since the brine is fully equilibrated with calcium ions.

Presence of Surfactant

The EDL is reduced with the use of the non-ionic surfactant as in previous cases. The anionic surfactant results in negatively charged rock while the cationic surfactant results in a positively charged rock due to the charges seen at the head group of each of the surfactants during ionization in brine. It should, however, be noted that for the case of the anionic surfactant in $CaCl_2$ brine, the EDL is smaller compared to the case of the anionic surfactant in NaCl brine. The reason for this could be due to the presence of positively charged Ca^{2+} ions which counteracts the negatively charged head group of the anionic surfactant thereby reducing the magnitude of the EDL. Hence for the anionic surfactant in $CaCl_2$ brine, the EDL is only stable at 0 ppm and 5,000 ppm, while at other salinities, the EDL decreases significantly compared to the NaCl case. This implies that the anionic surfactant is not able to alter wettability significantly at a wide range range of salinity in the presence of $CaCl_2$ brine. Moreso, due to the incompatibility of the anionic surfactant with high divalent ion concentration, there could be pore blockage. The cationic surfactant results in positive values of zeta potential whose magnitude is higher when compared to the NaCl case. This could be attributed to the presence of divalent calcium ions and the presence of positively charged cationic surfactant. In brief, with $CaCl_2$ brine, the cationic surfactant outperforms the other two surfactants used especially at salinities between 10,000 ppm and 200,000 ppm.

Isomorphic Substitution

Isomorphic substitution is likely not going to occur in this case since the calcium ions present in the brine is same as those present in the rock. The role of the Calcium ions, in this case, is, therefore, to increase the calcium ion concentration to an optimum level where calcium present in the brine forms organometallic complexes with the adsorbed oil on the rock surface, hence causing desorption of the oil from the rock.

pH for $CaCl_2$ brine

The pH results will be evaluated based on the SCM. At low salinities, the brine is not fully equilibrated with calcium ions; hence mineral dissolution is expected to occur, which releases OH^-, reflected by high pH values of 8.74 and 7.45 at very low salinities of 0 ppm and 5000 ppm respectively. With an increase in the $CaCl_2$ brine concentration, the pH becomes more acidic, which can be explained via the SCM. The surface complexation formed in the case of calcite particles suspended in calcium chloride brine will be; For the $>Ca^{2+}$ site: $> CaOH$, $> CaOH_2^+$ and $> CaO^-$, while for the $> CO_3^{2-}$ site will be $> CO_3Ca^+$ and $> CO_3H^o$. The possible reactions are shown below;

$$> CO_3H^o + Ca^{2+} \leftrightarrow CO_3Ca^+ + H^+$$

$$> CaOH \leftrightarrow CaO^{-} + H^{+}$$

As seen in the equation, more hydrogen ion is being released in the presence of Calcium, thereby contributing to the positive charges seen and more acidic pH. In the presence of surfactant, the charge is affected.

Synthetic Formation brine

The zeta potential values for the synthetic formation brine is represented in ***Figure 4-11 (e)***. The synthetic formation brine is a combination of different salts diluted in de-ionized water in which the percentage concentration of NaCl is highest compared to the other salts. The behavior of the synthetic formation brine is therefore similar to the case of NaCl, although there are slight variations due to the presence of potential determining ions such as Ca^{2+}, $Mg^{2+,}$ and SO_4^{2-} ions present in the brine. For the formation brine composition, the possible surface complexes formed on the on the $>Ca^{2+}$ site would be $> CaOH$, $> CaOH_2^{+}$, $> CaO^{-}$, $> CaSO_4$, $> CaCO_3^{-}$ and $> CaHCO_3^{o}$ while on the $>CO_3^{2-}$ site, the surface complexes forme are; $> CO_3Ca^{+}$, $> CO_3Mg^{+}$ and $> CO_3H^{o}$. This holds for the Indiana limestone used for these studies since it contains mainly calcite.

Potential Determining Ions

In the absence of surfactant and at salinities between 25,000 ppm and 200,000 ppm, the zeta potential values are positive compared to the case of NaCl brine, where they are mainly negative. The positive values could be attributed to the presence of PDI in the form of Ca^{2+} and Mg^{2+} ions. At lower salinities between 0 and 10,000 ppm however, the zeta potential values are negative which is similar to the case of NaCl brine. However, comparing the magnitude of the zeta potential in NaCl and that in the synthetic formation brine, it is observed that the latter case is smaller due to the presence of other PDI's such as SO_4^{2-} present in the form of Na_2SO_4 and HCO_3^- present in the form of $NaHCO_3$.

Ionic Strength/EDL

In the absence of surfactant, apart from de-ionized water which contains no ions, the EDL is biggest at 25,000 ppm. This could be a pointer to show that the optimum salinity with the synthetic formation brine where wettability alteration is expected to be at its best is at 25,000 ppm, which is typically seawater salinity. Similar to the previous cases, the EDL reduces in the presence of non-ionic surfactant, whereas, in the cationic and anionic surfactant, there is an increase in the EDL compared to the base case without surfactant. For the ionic surfactant, the EDL values are between those observed in NaCl and $CaCl_2$ brine.

Calcite Dissolution

Calcite dissolution is expected to occur at lower salinities between 0 ppm and 10,000 ppm, where the brine is not fully equilibrated with calcium ions coupled with the presence of atmospheric CO_2 which could cause the solution to become more alkaline. The degree of calcite dissolution is expected to decrease with an increase in salinity, which is observed in the pH values, in which the pH becomes more acidic with an increase in the brine salinity.

Presence of Surfactant

The effect of surfactant is similar to the previous cases analyzed, whereby the non-ionic surfactant has a negative effect on the magnitude of the EDL with the same reasons as discussed previously. The anionic surfactant results in a bigger EDL between 0 and 25,000 ppm when compared to the cationic surfactant. The reverse is the case at salinities between 50,000 ppm and 200,000 ppm due to the presence of increasingly positively charged ions from the brine at higher salinities and the ionization of the

Isomorphic Substituitom/SCM/pH

The isomorphic substitution, SCM, and pH effect are discussed together. Various ions are present in the of which only the PDI's will be able to react at the rock exchange site. For limestone containing mainly calcite ($CaCO_3$), the exchange sites are $>Ca^+$ and $>CO_3^{2-}$ ions. The surface reactions based on the salts present in the brine used are as follows;

S/N	Brine Component	Surface reaction	Ions released
1	$CaCl_2.2H_2O$	$> CO_3H^o + Ca^{2+} \leftrightarrow CO_3Ca^+ + H^+$	H^+
2	$MgCl_2.6H_2O$	$> CO_3H^o + Mg^{2+} \leftrightarrow CO_3Mg^+ + H^+$	H^+
3	$NaHCO_3$	$> CaOH + {CO_3}^{2-} + 2H^+ \leftrightarrow CaHCO_3{}^O + H_2O$	-
4	Na_2SO_4	$> CaH_2O + {SO_4}^{2-} \leftrightarrow {CaSO_4}^- + H_2O$	-
5	Na_2SO_4	$> CaOH + {SO_4}^{2-} \leftrightarrow {CaSO_4}^- + OH^-$	OH^-
6	H_2O	$> CaOH + H^+ \leftrightarrow CaH_2O^+$	-
7	H_2O	$> CO_3H^o \leftrightarrow {CO_3}^- + H^+$	H^+

The various ions released during SCM contributes to the different charges seen in the case of the synthetic formation brine, coupled with the brine salinity.

With values from the rock-brine interface alone, the wettability alteration capability of the brine is not very conclusive. (Jackson et al., 2016) provided a strong correlation between the zeta potential measurement on the calcite surface with wettability alteration leading to improved oil recovery. As they noted, wettability alteration in calcite rock occurs when the same surface charge polarity is measured at the oil/brine and calcite brine interfaces. This leads to a positive contribution of the electrostatic forces to the total disjoining pressure, which leads to the desorption of the oil from the rock surface.

Theoretical Debyle Length

The theoretical debye length calculated with ***equation one*** is plotted and represented in ***Figure 4-12*** for the three different brines used at the salinities investigated. The molar concentration of each brine at the varying salinities were calculated based on the salinity and the ions present in the brine. The debye length shows an increasing EDL with a reduction in salinity for all the brines used. The calculated debye length using the debye length equation should not be relied upon since it only takes into account the effect of brine ionic strength and not other factors such as PDI, rock type, additives such as surfactants or surface complexation reactions that occur at the rock exchange site. For example, the calculated debye length shows that the EDL in the case of NaCl brine is bigger than that of $CaCl_2$ brine, which is the exact opposite observed in the zeta potential results, especially with Indiana limestone rock.

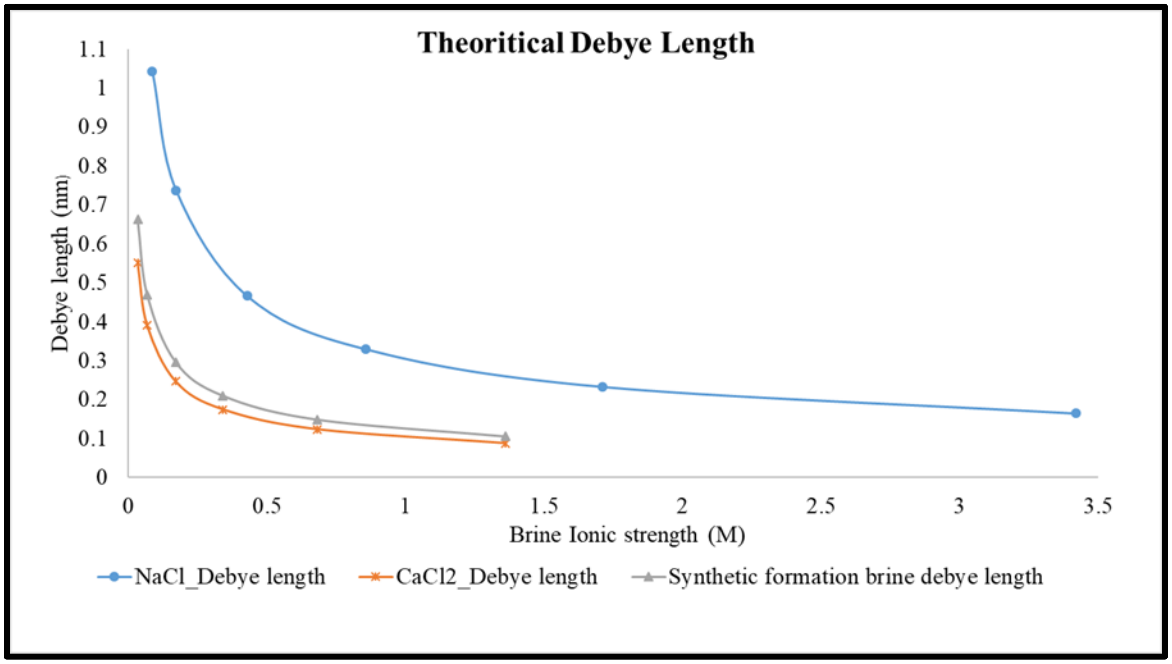


Figure 4-12: Graphical representation of calculated Debye Length for various brine and ionic strength

4.4.2.2 Zeta Potential with Silurian Dolomite

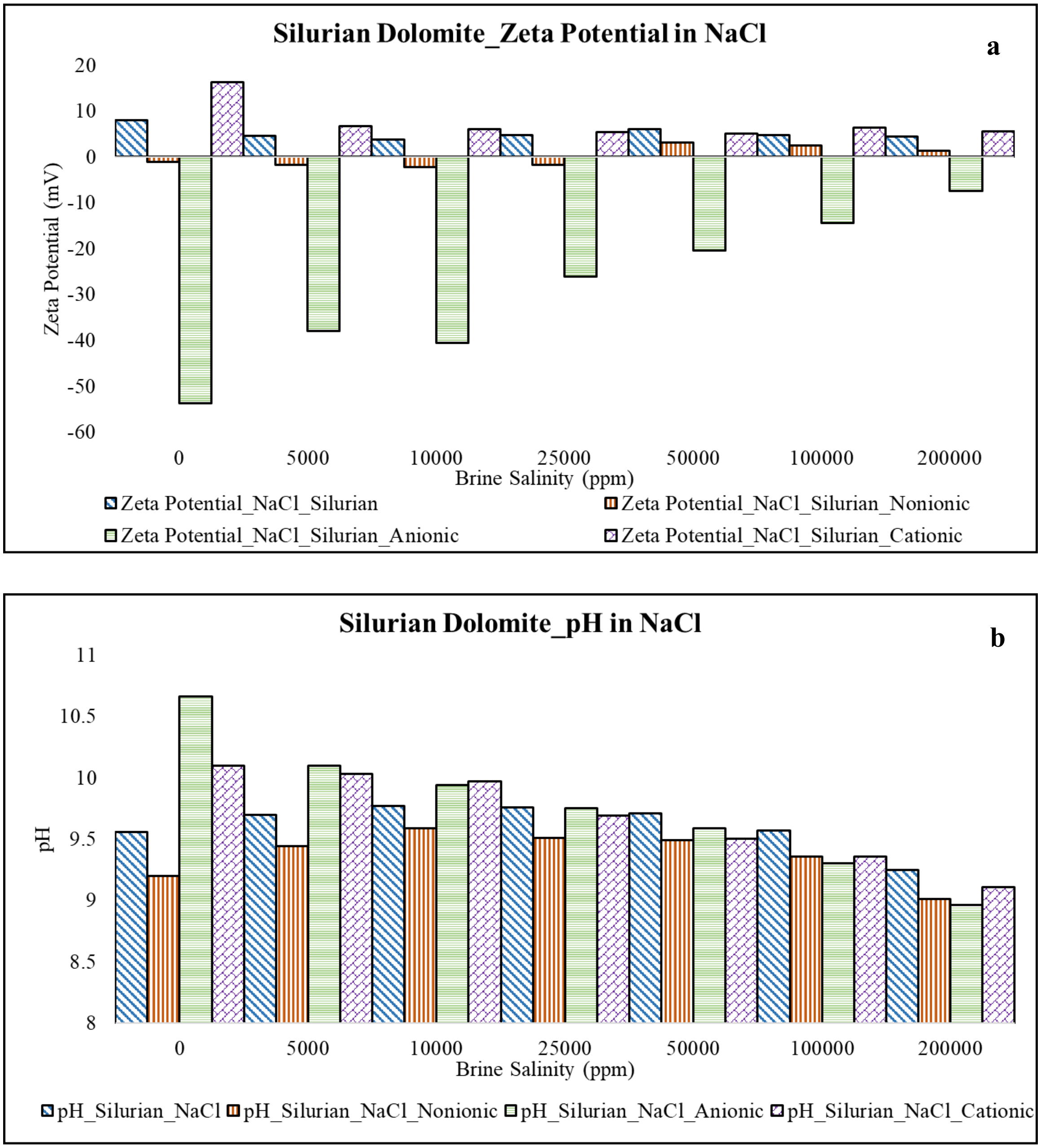


Figure 4 - 13 (a,b) 1; (a) Silurian Dolomite zeta potential in NaCl brine (b) Silurian Dolomite pH in NaCl brine

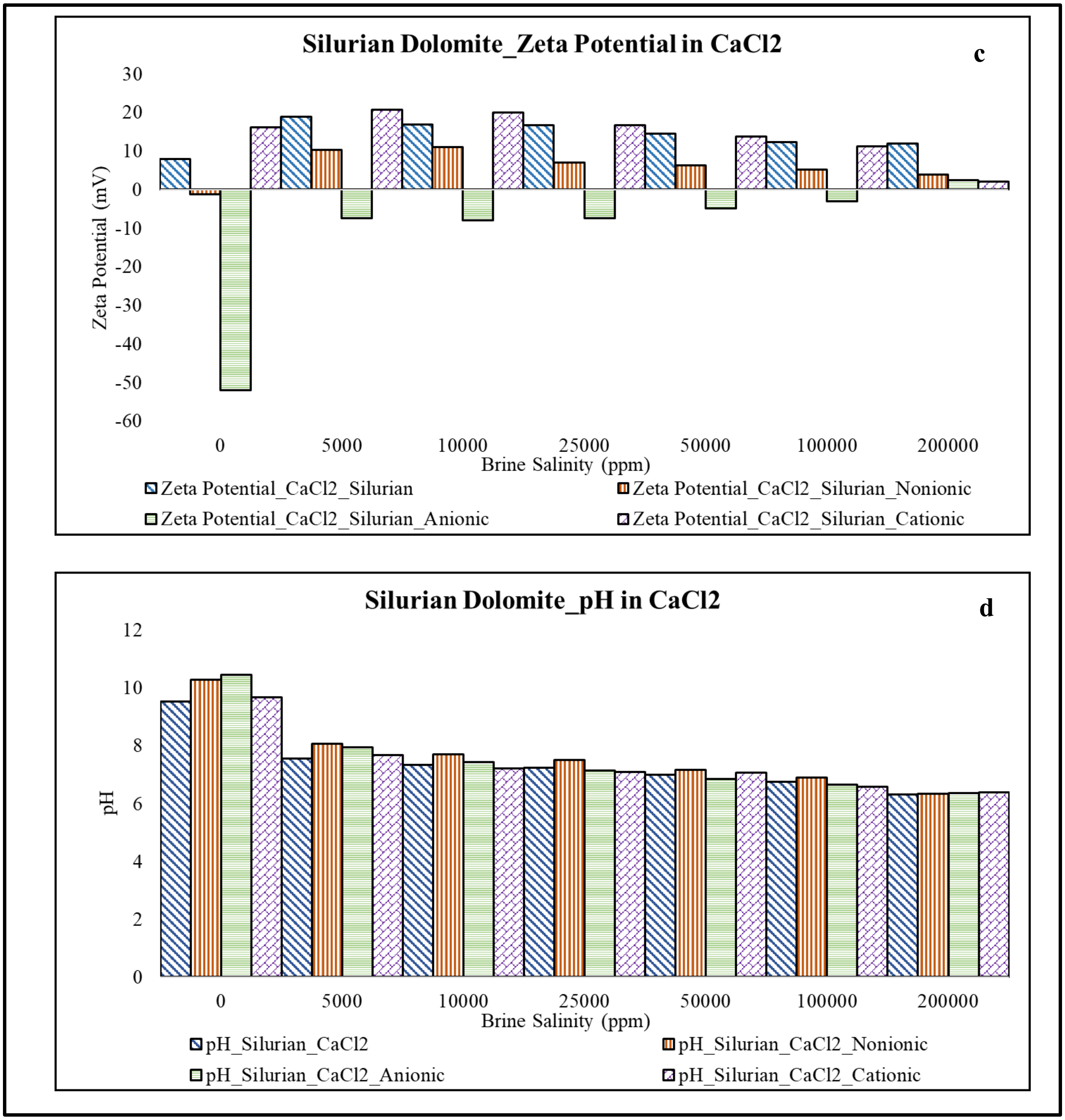


Figure 4 - 13 (c, d) 1; (c)Silurian Dolomite Zeta Potential in calcium chloride brine (d) Silurian dolomite pH in Calcium chloride brine

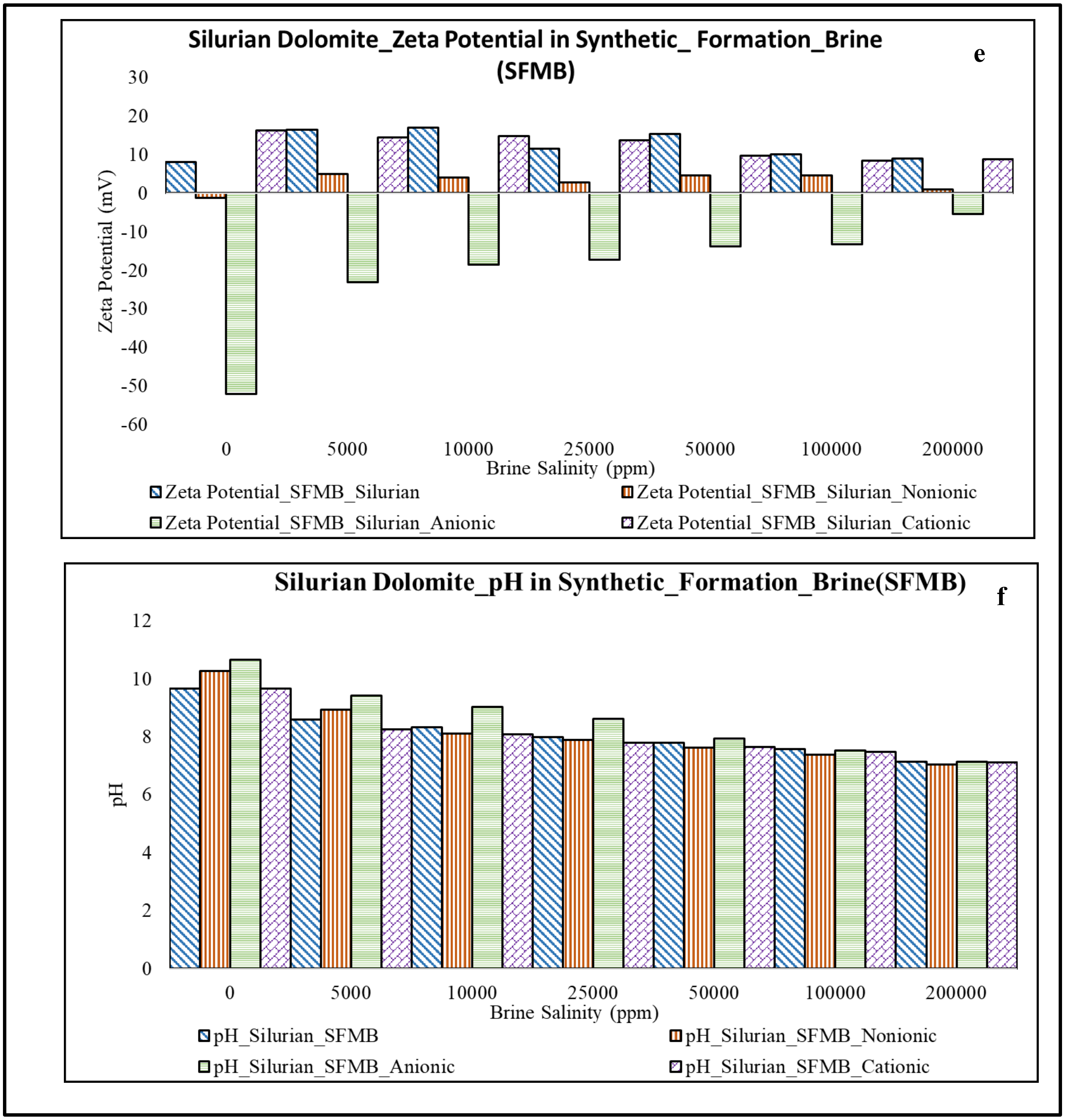


Figure 4 - 13 (e,f) 1; (e) Silurian dolomite zeta potential in synthetic formation brine (f) Silurian dolomite pH in synthetic formation brine

Figure 4-13: Zeta Potential and pH results for Silurian dolomite

The zeta potential and pH results for the Silurian Dolomite rock are given in ***Figure 4-13***. The trend observed in the case of the Indiana limestone rock, especially in the presence of surfactant is similar to the dolomite with some little difference. Dolomite particles exhibit more positive zeta potential at all brine ionic composition and strength compared to the Indiana limestone rock. The zeta potential value in the case of 200,000 ppm synthetic formation brine is +8.97 mV which correlates to the work of (Mahani et al., 2015) who reported a zeta potential value of +9 mV in the formation water with a brine salinity of 179,855 ppm for Silurian dolomite with the same mineralogical composition as the one used in this study.

(Van Cappellen et al., 1993) has attributed the more positive zeta potential value to the fact that dolomite contains an equal amount of calcium and magnesium ions which leads to an increased density of adsorption sites of 8 sites per $(nm)^2$ for potential determining ions instead of the usual five sites per $(nm)^2$. This implies that there is a higher number of sorption sites on dolomite as compared to limestone results in the build-up of higher positive charges at the dolomite/brine interface. The authors further stated that the surface charge density of dolomite rocks prevents a large influence of brine ionic strength on it.

In terms of EDL, (Mielczarski et al., 2006) has shown that the double layer capacitance also known as the amount of electrical charges stored by the means of double-layer effect for dolomite is larger than that of calcite by 10 F/m^2, whereby that of dolomite is 25 F/m^2 and calcite is 15 F/m^2 at a NaCl ionic strength of 0.01 M. The conclusion drawn from their work is that the EDL is thin, highly structured and non-diffuse and therefore can accommodate high charge densities.

The pH trend observed in the case of Indiana limestone is also very similar to the Silurian dolomite.

Based on the results from the Indian limestone and Silurian dolomite rocks, the following conclusions can be drawn about carbonate rocks

- In both carbonate rocks, the electrical double layer is smaller in NaCl brine alone and with NaCl brine containing the non-ionic surfactant.
- In both rocks, $CaCl_2$ ions increase electrical double layer compared to NaCl brine
- The non-ionic surfactant is likely to alter wettability better with $CaCl_2$, and synthetic formation brines in Silurian Dolomite than Indiana Limestone.
- Potential of wettability alteration is higher with the ionic surfactants tested compared to the non-ionic surfactant.
- For wettability alteration, anionic surfactant performs better with monovalent cations such as NaCl compared to divalent cations such as $CaCl_2$
- There is less wettability alteration with the Cationic surfactant and NaCl compared to the $CaCl_2$ brine
- Dolomite particles have a more positive zeta potential value compared to the limestone particles, and this could lead to wettability differences in both rocks.
- The results cannot be generalized for all carbonate rocks, but there seem to be a trend in their behavior

4.4.2.3 Zeta Potential In slave point formation Core

The common patterns observed in the response of the two carbonate rocks subjected under the same experimental conditions were used to design a new brine which optimizes for wettability alteration in the synthetic formation brine with the non-ionic and the cationic surfactants in an actual tight carbonate rock – Slave point formation. Optimization was not done for the anionic surfactant because even though it seems to result in a bigger electrical double layer, their adsorption on carbonate rocks may be an issue which then makes it uneconomical to be used in cEOR

The slave point formation core was used because it contains predominantly calcite (limestone) and dolomite with a trace of shale as seen from the SEM/EDX elemental analysis in ***Table 3-4***. The calcite and dolomite contents of the rock is a good representation of the combination of Indiana limestone and Silurian dolomite core initially studied. The brine composition designed for wettability alteration is shown in ***Table 4-2***.

Table 4-2: Synthetic formation brine for wettability alteration

Salts	SFMB (%)	Optimized SFMB (S1) (%)	Optimized SFMB (S2) (%)	Optimized SFMB (S3) (%)
NaCl	62	22.63	62	22.63
$CaCl_2.2H_2O$	19.63	59	19.63	59
$MgCl_2.6H_2O$	16.3	16.3	16.3	16.3
Na_2SO_4	1.95	1.95	1.95	1.95
$NaHCO_3$	0.12	0.12	0.12	0.12

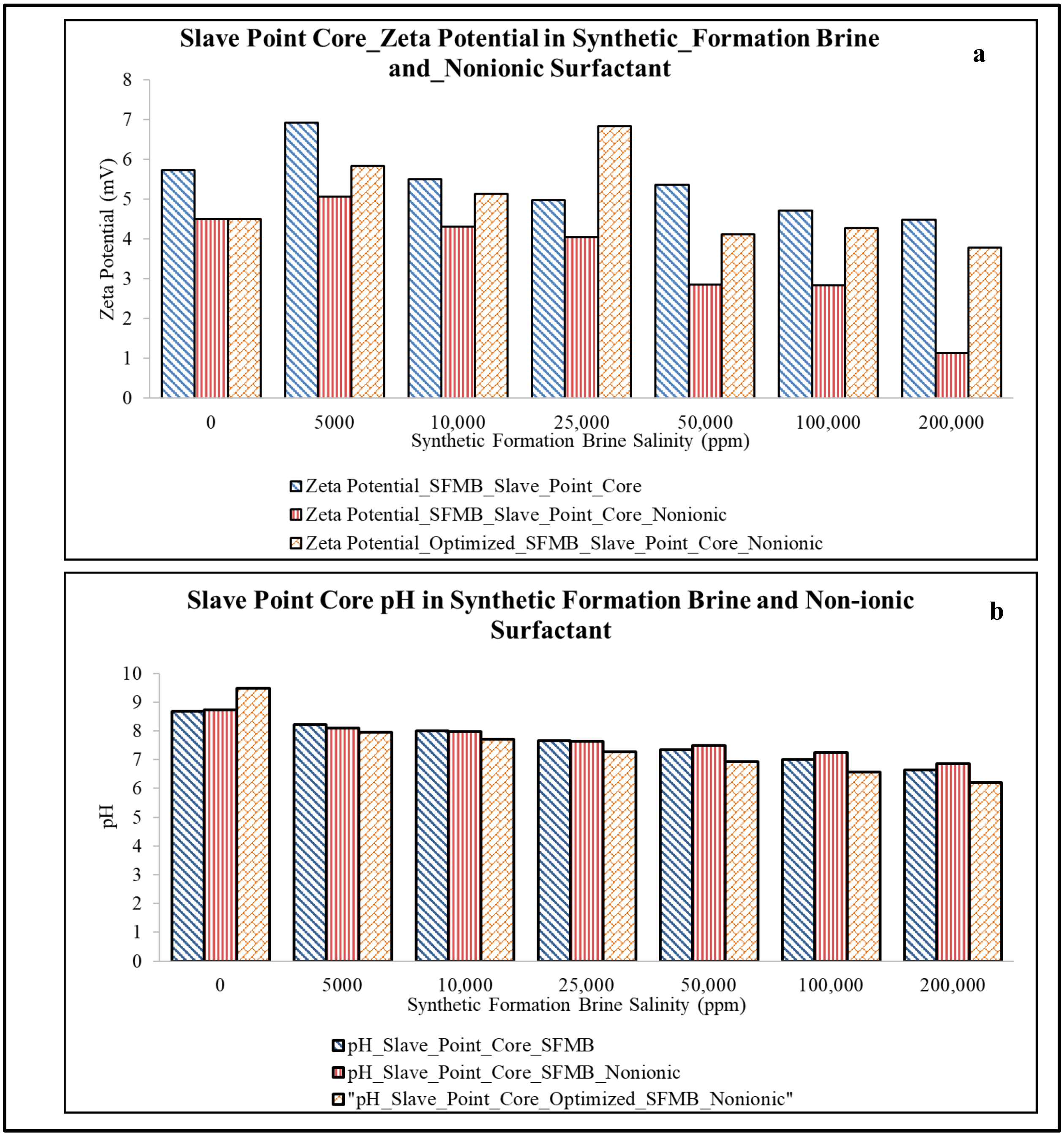


Figure 4-14 (a,b) 1; (a) Slave point core zeta potential in synthetic formation brine and nonionic surfactant (b) Slave point core pH in synthetic formation brine and non-ionic surfactant

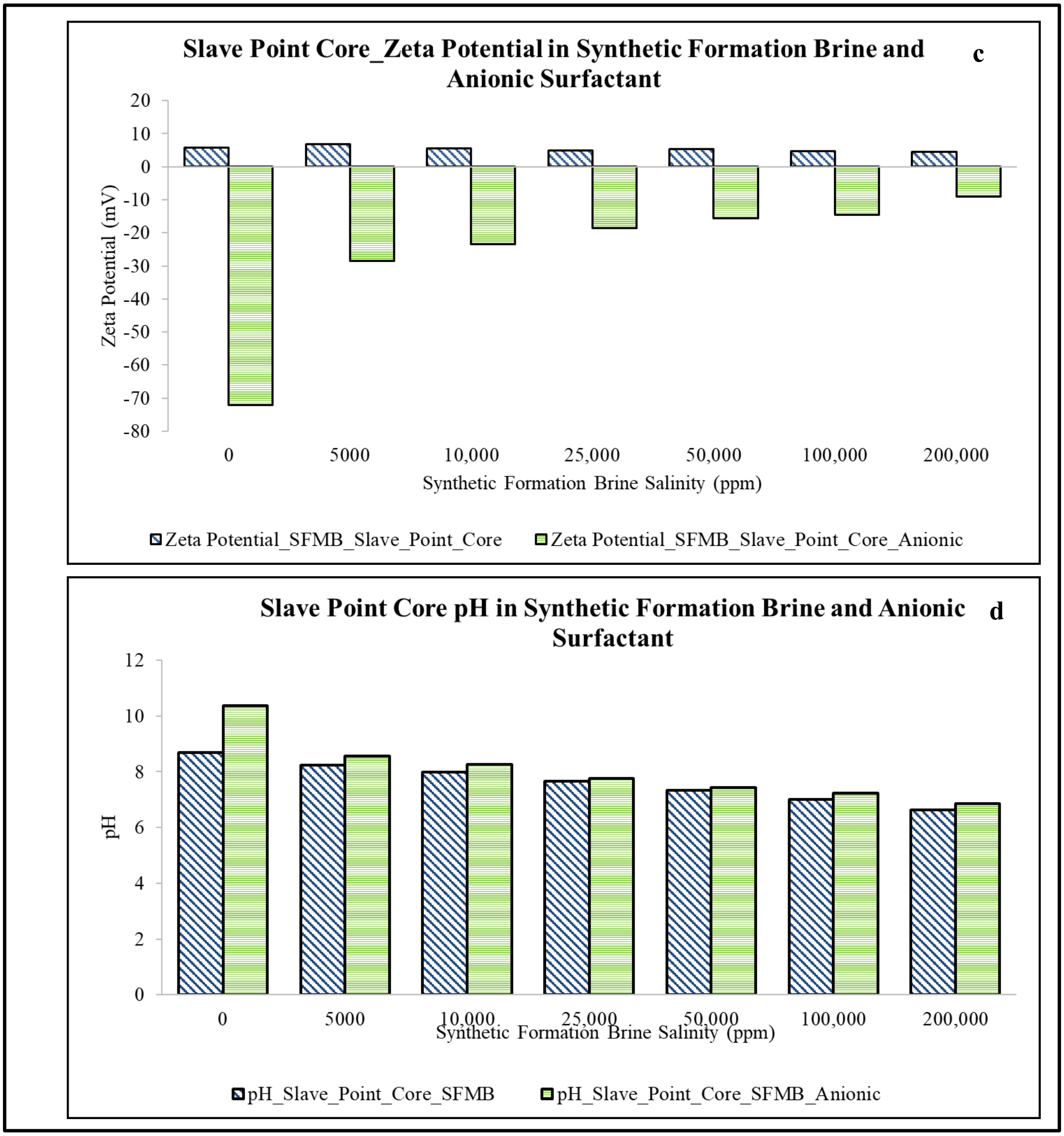
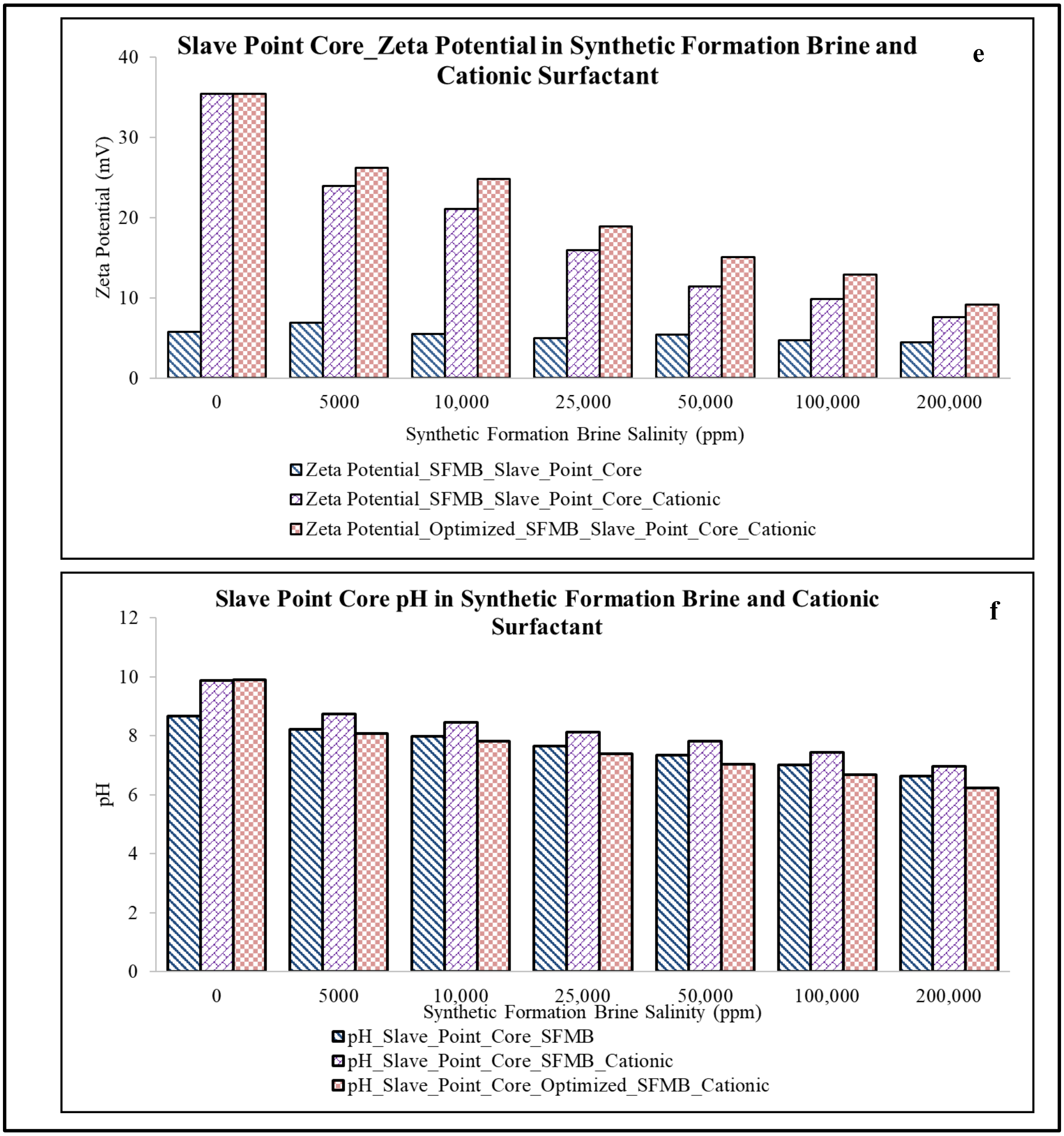


Figure 4 - 14 (c,d) 1; (c) Slave point core zeta potential in synthetic formation brine and anionic surfactant (d) Slave point core pH in synthetic formation brine and anionic surfactant


Slave Point Core_Zeta Potential in Synthetic Formation Brine and Cationic Surfactant

Slave Point Core pH in Synthetic Formation Brine and Cationic Surfactant

Figure 4 - 14 (e,f) 1: (e) Slave point core zeta potential in synthetic formation brine and cationic surfactant (f) Slave point core pH in synthetic formation brine and cationic surfactant

Figure 4-14: Zeta potential and pH results in slave point core

Figure 4-14 (a, c and e) show the results for the zeta potential values in the slave point core measured with the original synthetic formation brine and the newly designed synthetic formation brine for wettability alteration. In all the cases with the slave point core in the synthetic formation brine, the electrical double layer increases in the optimized brine compared to the base case scenario without surfactant in the original synthetic formation brine. The better performance of the newly designed brine compared to the original formation brine serves as a pointer that there is a similar trend of wettability alteration in different carbonate rocks subjected under the same experimental conditions - since the formation brine was designed based on the learnings from the initial two carbonate cores used – Indiana limestone and Silurian Dolomite. Similar to the initial outcrop cores used, the non-ionic surfactant has an adverse effect on the magnitude of the electrical double layer compared to the base case without surfactant. However, the presence of non-ionic surfactant in the optimized brine performs better compared to the case where the non-ionic surfactant is present in the original formation brine. Results are indicative that a better understanding of the rock-fluid interaction for carbonate rocks have been gotten. Therefore, the effect of the ionic composition of injected brine can never be overemphasized for favorable wettability alteration. The pH values presented in ***Figure 4-14 (b, d, and f)*** are mostly at alkaline values.

4.4.3 Zeta Potential measurements in the Evie Shale Formation

The Evie brine composition of the Evie formation typically contains NaCl and KCl brine.

Therefore results for these brine composition are shown in ***Figure 4-15***.

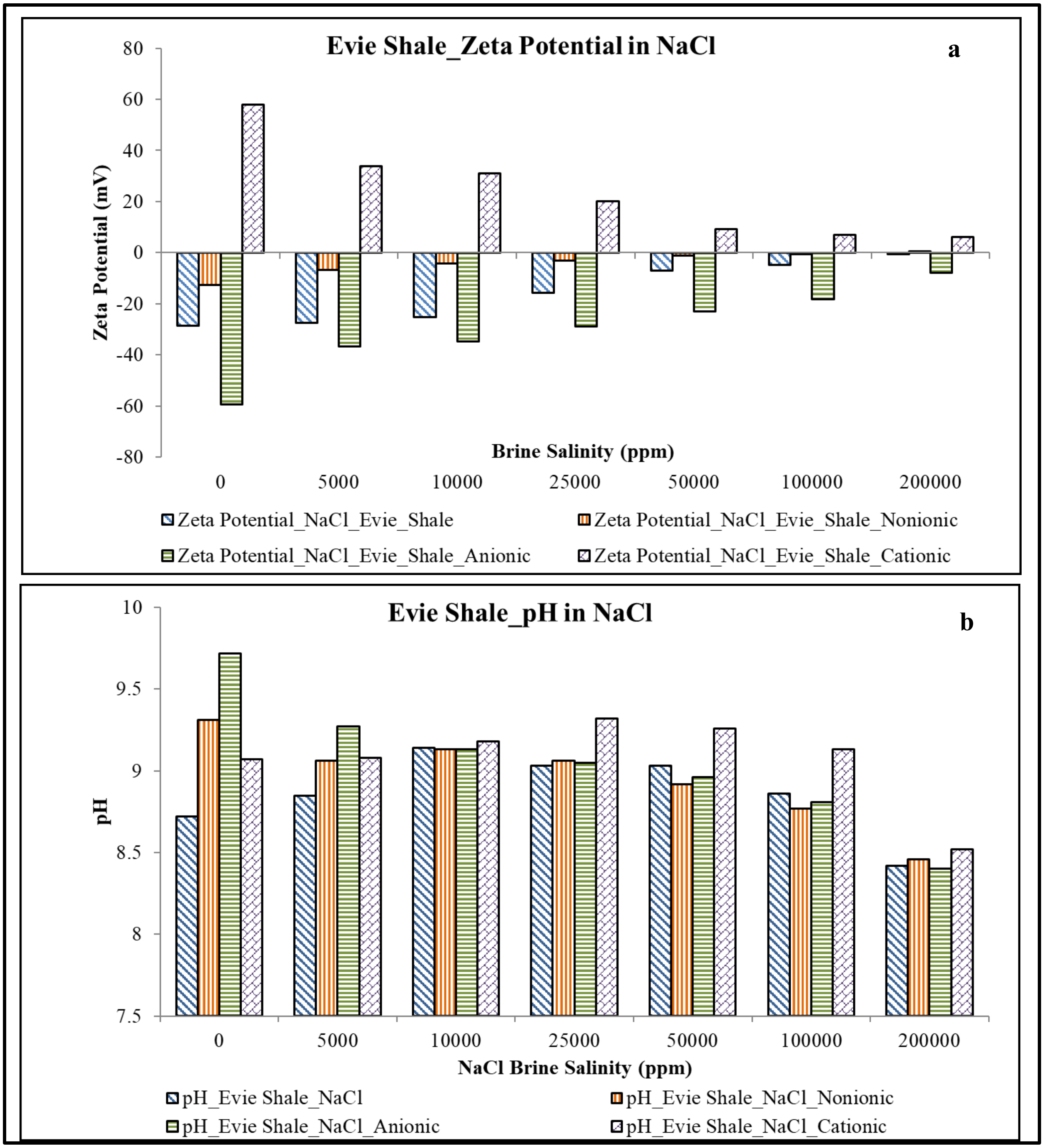


Figure 4-15 (a,b) 1; (a) Evie shale zeta potential in NaCl brine (b) Evie shale pH in NaCl brine

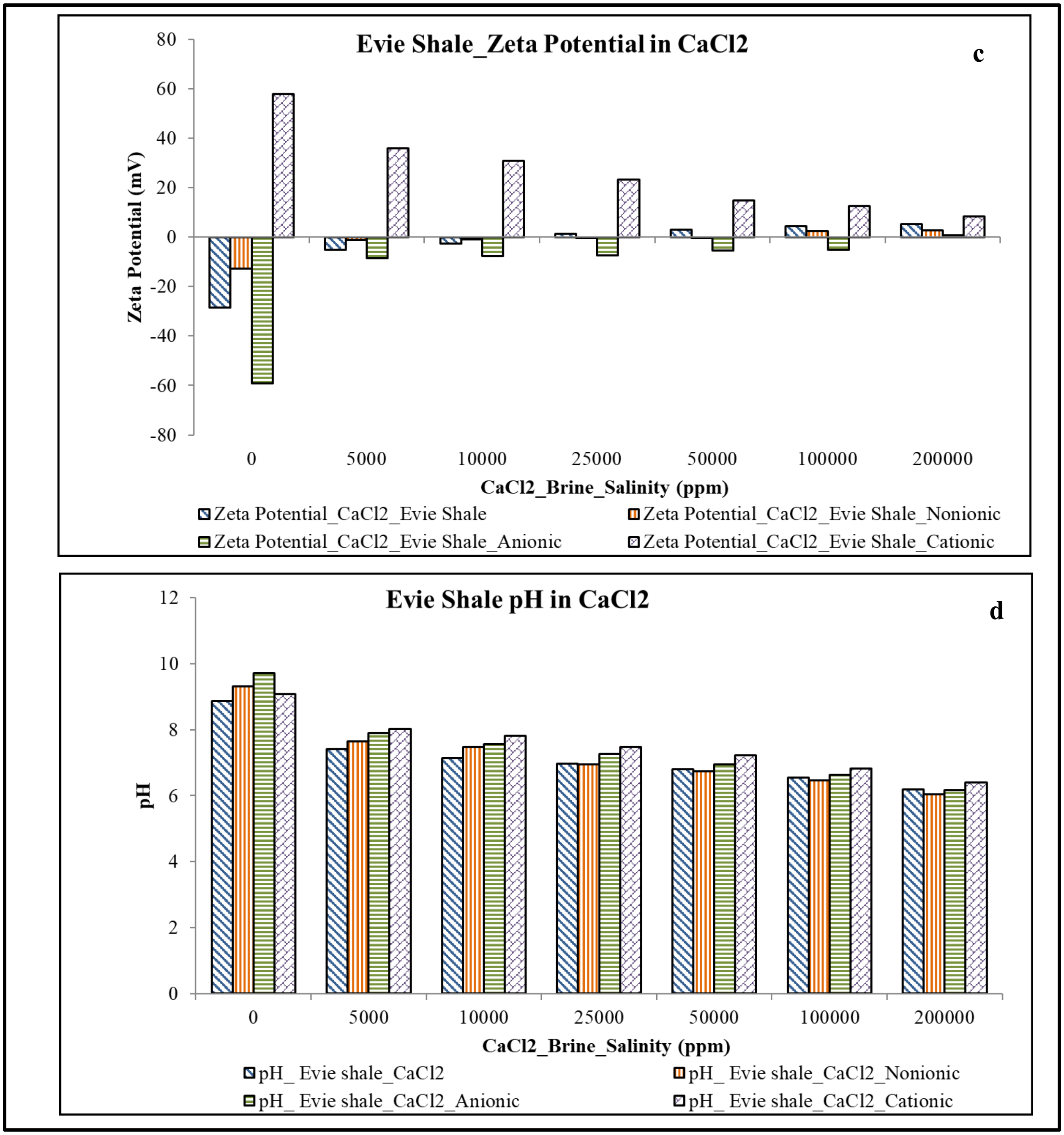


Figure 4- 15 (c,d) 1; (c) Evie shale zeta potential in $CaCl_2$ brine (d) Evie shale pH in $CaCl_2$ brine

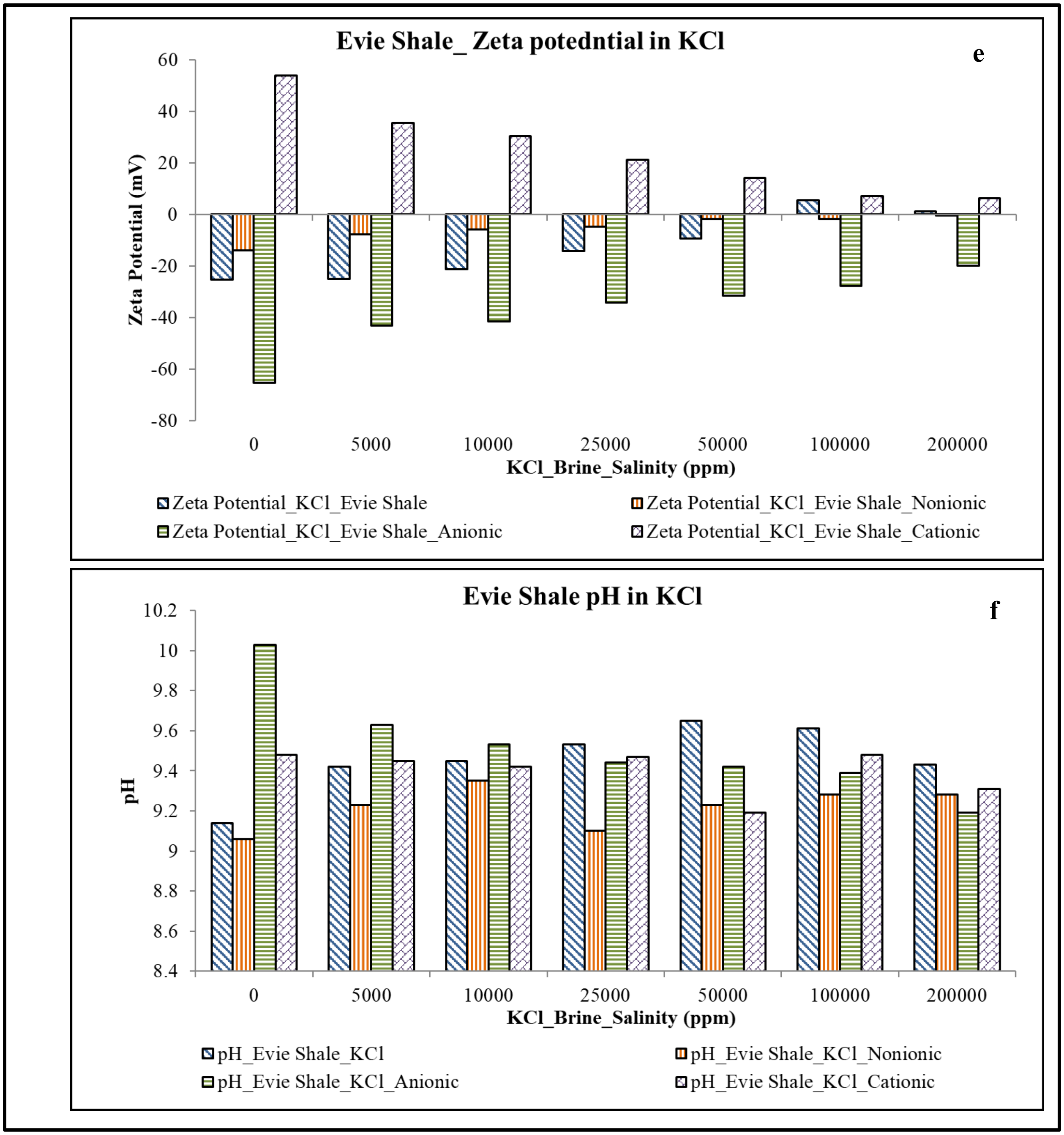


Figure 4 - 15 (e,f) 1:(e) Evie shale zeta potential in KCl brine (f) Evie shale pH in KCl brine

Figure 4-15: Zeta Potential and pH results for Evie shale

A similar trend observed with the NaCl brine in the Indiana limestone rock is also seen in the Evie formation with NaCl. The absolute magnitude of zeta potential in the absence of surfactant is bigger in the Evie formation compared to the Indiana limestone rock, especially at lower salinities. Notably, the zeta potential values are more negative in the Evie formation, which could be due to the mineralogical composition of the rock. The mineralogy of the Evie formation contains more clay minerals which are negatively charged than the carbonate rocks studied. Since the Evie formation brine is predominantly a mixture of NaCl and KCl, the zeta potential values for the case with KCl was also measured. The results show very similar trends and values for the zeta potential in NaCl since they are both monovalent ions with similar binding affinity with clay minerals as presented previously. To determine the effect of potential determining ions on the zeta potential of shale rock, the calcium chloride brine was also used. Similar to the Indiana limestone cores analyzed initially, the negative magnitude of the zeta potential is reduced in $CaCl_2$ brine alone and with the anionic surfactant. The balance of the excess positive charges from the calcium ions and the negative charges from the clay minerals may be the cause of the reduction of the negative magnitude of the zeta potential. The cationic surfactant results in positive charges as usual due to the combined effect of the calcium cation and the positively charged head group of the surfactant. Again, the non-ionic surfactant reduces the magnitude of the electrical double layer compared to the other two surfactants, which is a similar result observed in the case with the other carbonate cores. In all the rocks studied, the non-ionic surfactant is therefore screened out for wettability alteration since it results in a smaller and unstable water film as presented by the EDL. (Lan et al., 2015) performed imbibition experiments on both intact and crushed shale samples with de-ionized water, two weight % KCl brine, and kerosene. For the crushed sample, both vertical and horizontal imbibition were carried out. Their imbibition experiments did not correlate to the contact angle results for the intact sample as there was more KCl brine imbibition whereas the contact angle results showed that the core is oil-wet. For the crushed rock, the spontaneous imbibition experiments showed that the kerosene imbibed more than the de-ionized water used. The authors attributed these differences to be due to the hydrophobic and hydrophilic pore connectivity as confirmed by SEM images. This, therefore, makes it difficult to explain the zeta potential results, since a bigger EDL may not necessarily result in more brine imbibition. However, there are other possible mechanisms that could govern the process such as the oil type used. The presence of a polar component in oil enhances oil wetness compared to the use of refined oil such as kerosene.

4.5 Single Phase Spontaneous Imbibition Results

A Single-phase spontaneous imbibition experiment was carried out using the Amott cell to verify/interpret the zeta potential results observed in the carbonate cores. Three brine salinities with different range of zeta potential values were chosen for this; 5,000 ppm, 25,000 ppm and 50,000 ppm NaCl brine in the anionic surfactant. The results are presented in ***Figure 4-16***;

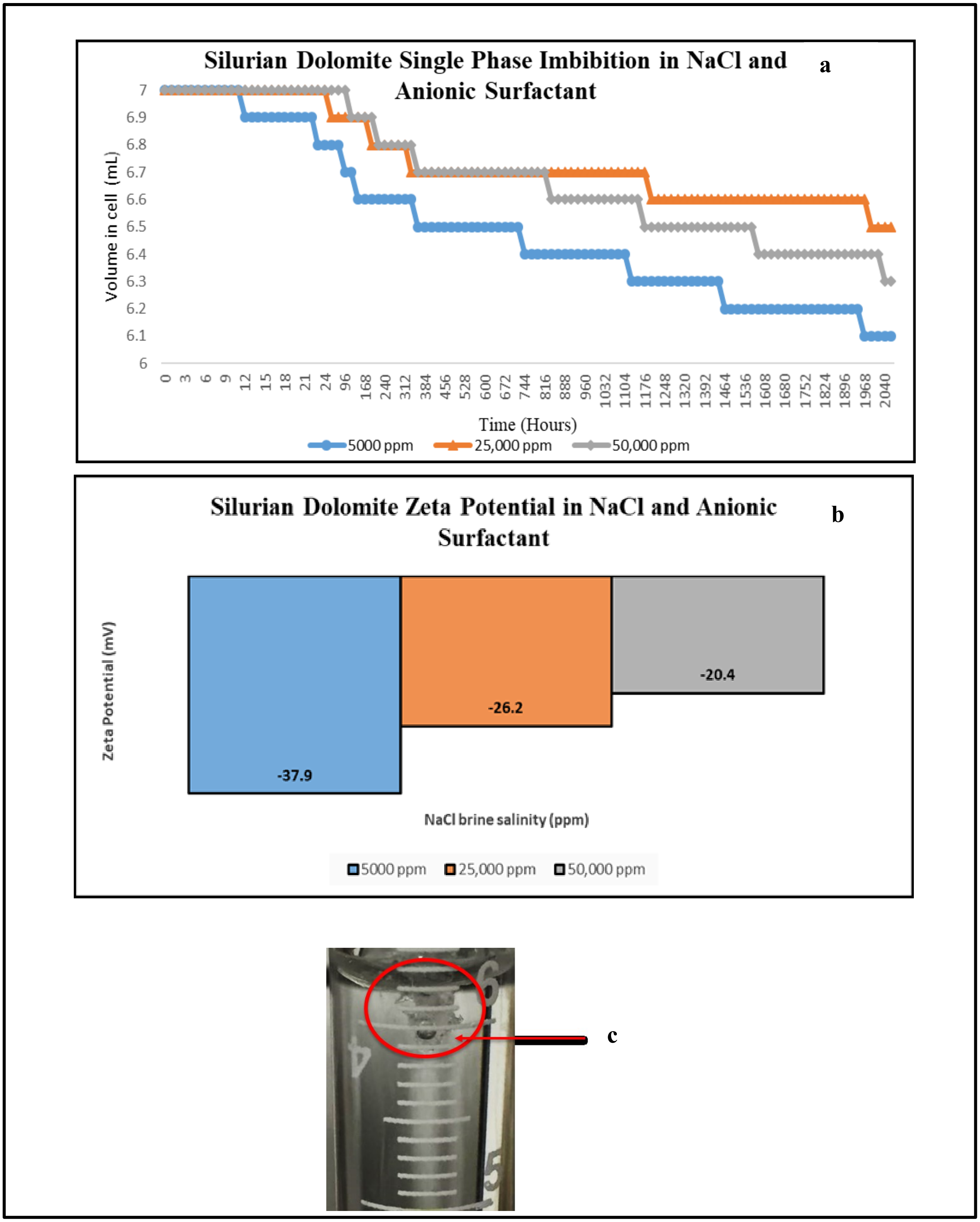


Figure 4-16: Single-phase spontaneous imbibition for Silurian dolomite

The results from ***Figure 4-16*** show that the zeta potential results are representative of the single-phase spontaneous imbibition experiments initially, especially for the higher salinity surfactant solutions (i.e. 25,000 ppm and 50,000 ppm). As seen in ***Figure 4-16 (a)**,* more surfactant solution is imbibed into the Silurian dolomite core at 5000 ppm throughout the process, and this could be attributed to the expansion of the electrical double layer as shown in the zeta potential results. Moreso, as seen in ***Figure 4-16 (c)***, rock dissolution and precipitation occur in the 5,000 ppm brine after 1464 hours which may have contributed to more brine imbibition throughout the whole process. There was however no observed rock dissolution and precipitation at 25,000 ppm and 50,000 ppm brine salinities.

In ***Figure 4-16 (a)***, between 25,000 ppm and 50,000 ppm, there comes a time at 360 hours (15 days) whereby the imbibition of the high salinity brine is more than that at 25,000 ppm. The reason for this may be due to the bigger EDL shown by the zeta potential results in ***Figure 4-16 (b)*** and fewer sodium ions for multi-ion exchange in the case of 25,000 ppm brine. Whereas for 50,000 ppm brine, there is more multi-ion exchange that occurs between the brine and the rock as a result of the presence of excess sodium ions. Therefore at an early time, more imbibition occurs as a result of the size of the EDL, whereas at a later time, multi-ion exchange component between the brine and the rock plays a more important role in imbibition. This also serves as a pointer to show that there should be a reconsideration of Sodium ions as potential determining ions and not indifferent ions as reported in literature.

This can serve as a guide in field applications to know when brine salinity should be changed during flooding. In brief, for field applications, the magnitude of the zeta potential values reflects the wettability alteration capability of the surfactant slug used only at an early time especially when there is no rock dissolution and precipitation to further increase brine imbibition. It should also be noted that there is a possibility of getting an adverse effect of rock dissolution and precipitation which has the potential of causing pore blockage and reduced imbibition after a certain time. It is therefore advisable to switch to higher salinities after some time in order to mitigate pore blockage caused by mineral precipitation and lower salinities. From the results, it is therefore confirmed that the non-ionic surfactant would not be able to alter wettability favorably towards more water-wet conditions in these kinds of rocks due to the unstable zeta potential value.

4.6 Micromodel Flooding Results

4.6.1 Homogeneous Micromodel

The first stage of the micromodel flooding experiment was with the homogeneous chip to evaluate the influence of the actual magnitude of zeta potential values at both the brine-sandstone rock and oil-brine interfaces on oil recovery/sweep efficiency and to further investigate the effect of brine ionic composition on sweep efficiency. The brines used in flooding are presented in ***Table 4-3***

Table 4-3: Brines used in flooding with the Homogeneous micromodel

Salinity (ppm)	Brine	Surfactant	Conc. (%)	ZP Botucatu Sandstone (mV)	ZP_Oil-brine (mV)	IFT (mN/m)
10,000	NaCl	None	-	-60.6	-15.5	13
50,000	NaCl	None	-	-33.8	-11.1	20
10,000	NaCl	S2	1	-66.4	-46.5	0.7
10,000	$CaCl_2$	None	-	-18.1	+3.44	13
50,000	$CaCl_2$	None	-	-8.2	+1.11	17.1
10,000	$CaCl_2$	S2	1	-35.5	-11.1	0.4

The 50,000 ppm NaCl brine alone and 10,000 ppm $CaCl_2$ brine in the anionic surfactant has a similar magnitude of zeta potential at both the oil-brine and brine rock interfaces alone; therefore any difference in results will only be as a result of significant differences in the interfacial tension from the surfactant used.

All experiments were carried out until no more oil additional oil is swept from the micromodel. For all the experiments carried out, there was no extra oil recovered after less than 30 minutes of flooding. Therefore the results shown here are up to a maximum of thirty minutes.

Initially, the image of the chip saturated with oil is loaded. The images were processed using 8 bits, and an auto threshold is applied to normalize the histogram count, which was used in the calculation of oil and brine saturation in the chip. Images were processed in Red Green and Blue mood (RGB) as it was seen to give better results compared to the binary processing.

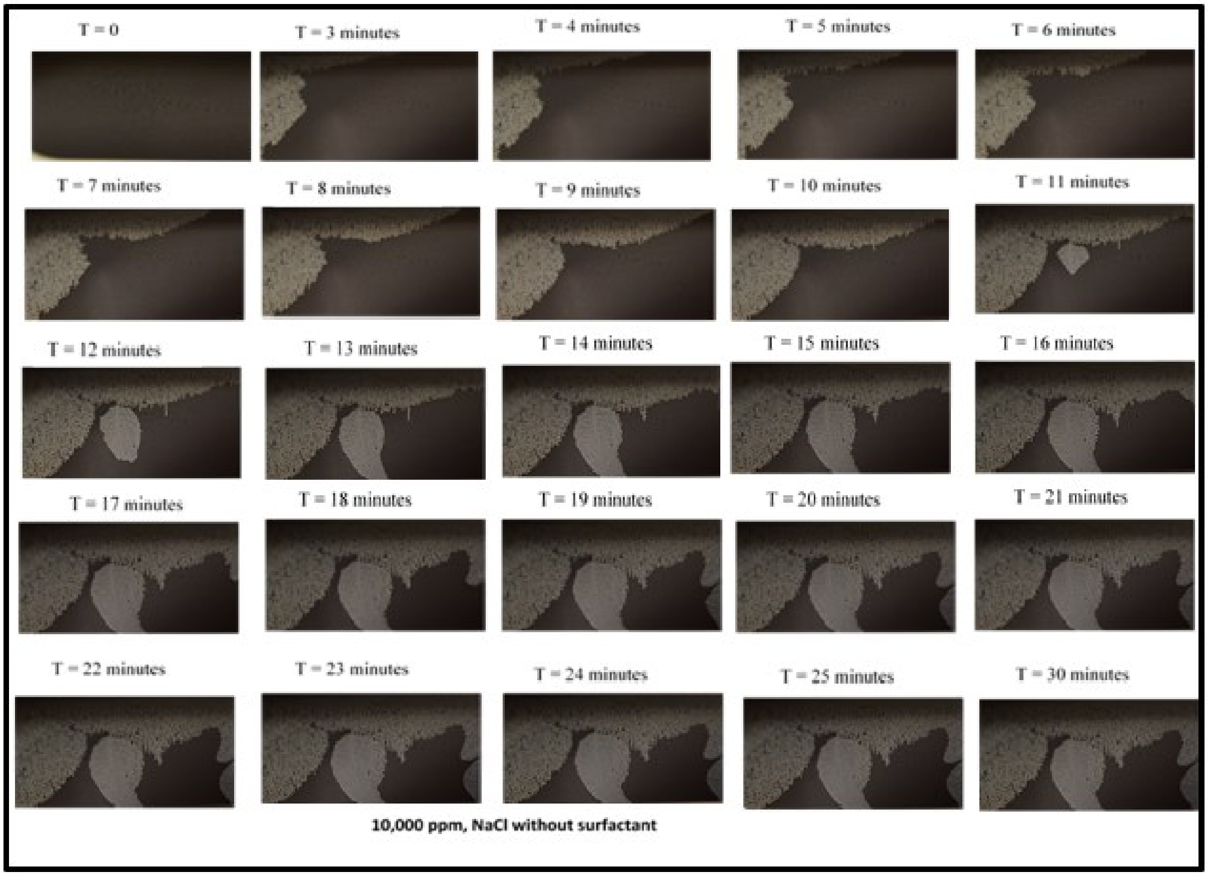


Figure 4-17: Flooding results with 10,000 ppm NaCl brine in the homogeneous micromodel

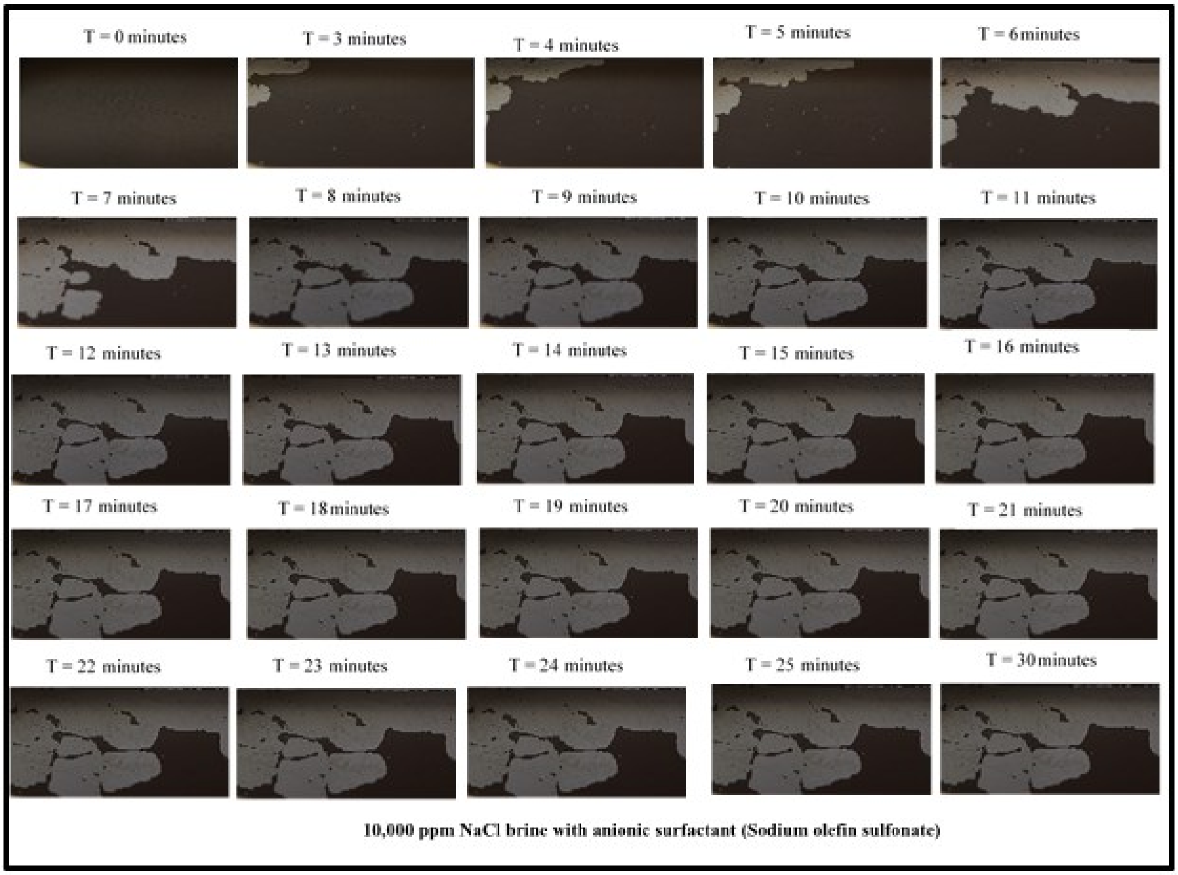


Figure 4-18: Flooding results with the homogeneous micromodel in 10,000 ppm NaCl brine and anionic surfactant

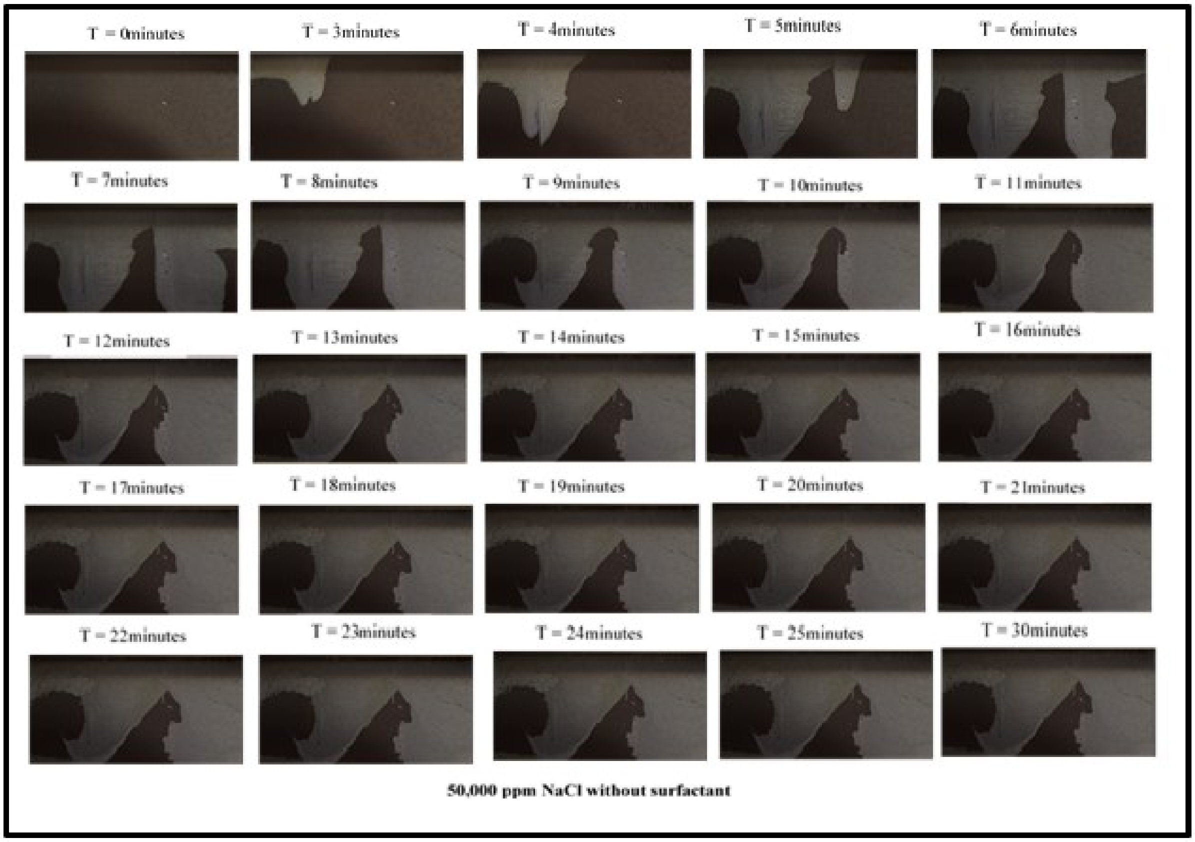


Figure 4-19: Flooding results with the homogeneous micromodel in 50,000 ppm NaCl brine

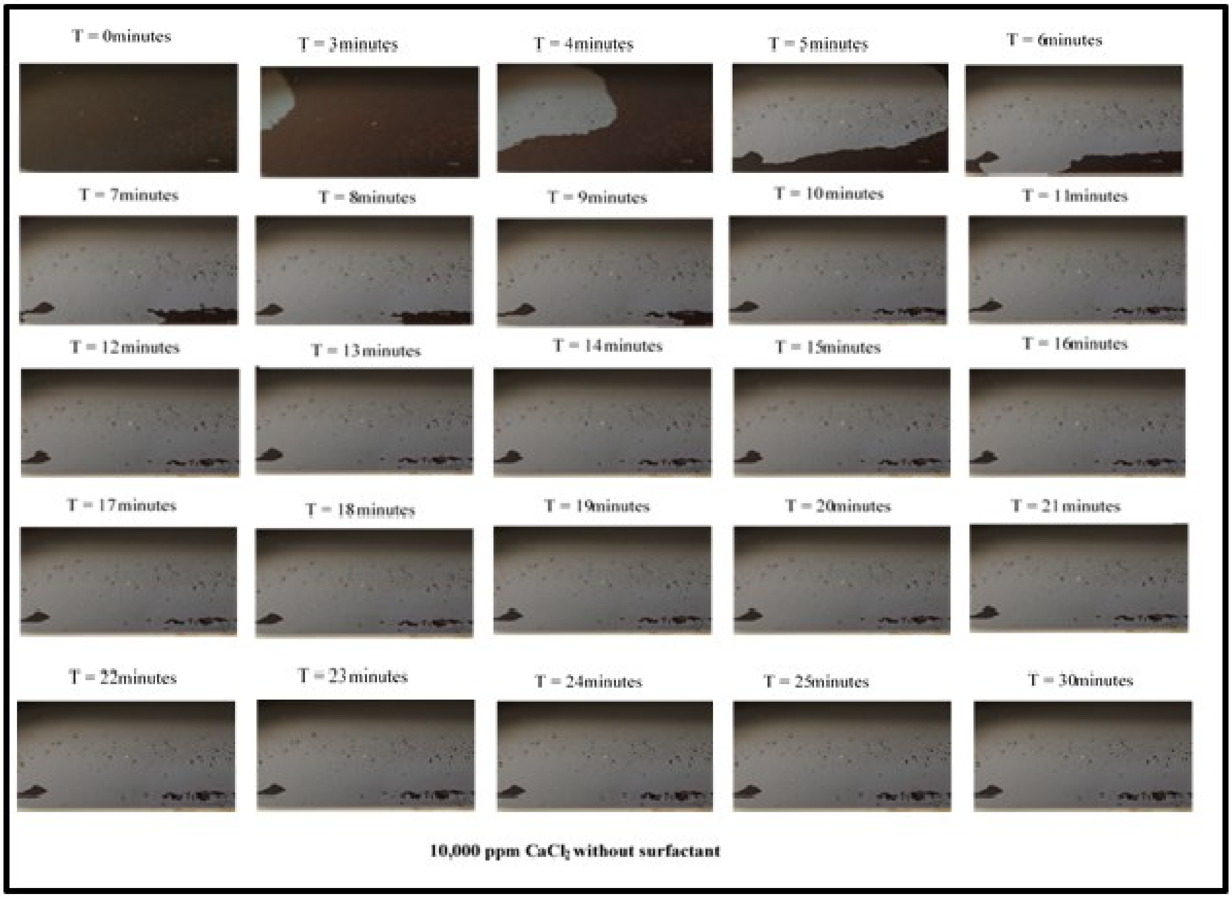


Figure 4-20: Flooding results with the homogeneous micromodel in 10,000 ppm CaCl2 brine

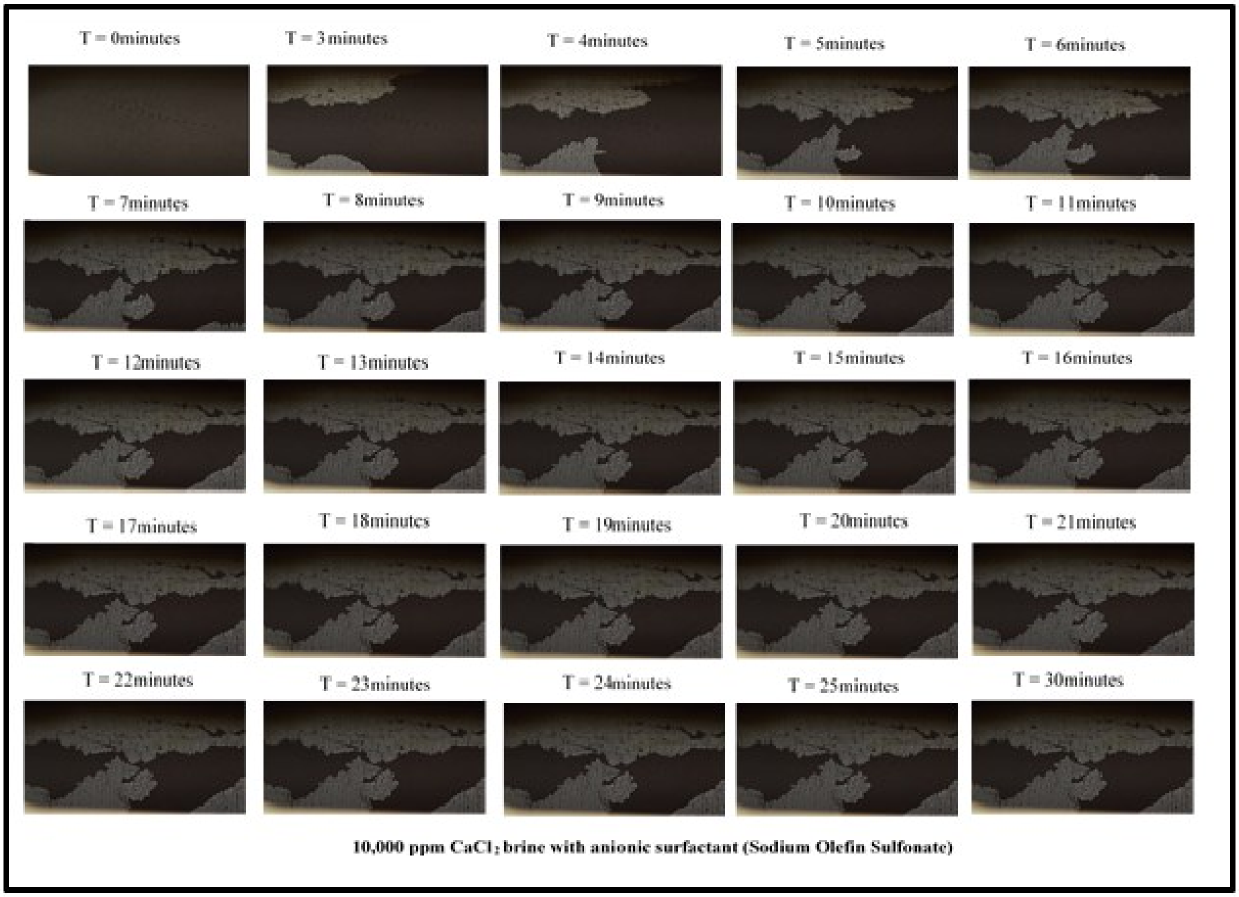


Figure 4-21:Flooding results in 10,000 ppm CaCl2 brine and anionic surfactant with the homogeneous micromodel

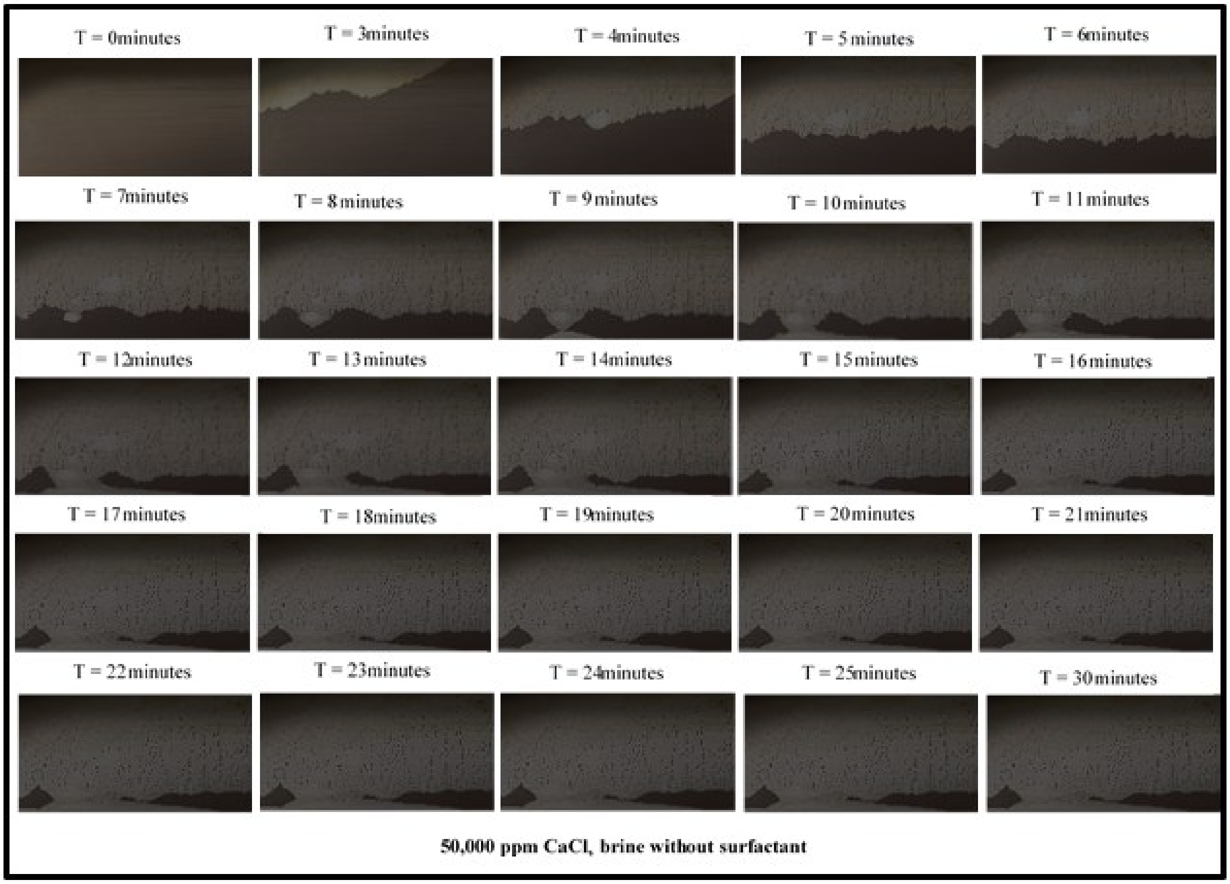


Figure 4-22: Flooding results with 50,000 ppm $CaCl_2$ brine with the homogeneous micromodel

Table 4-4: Summary of experimental results from the homogeneous micromodel

Salinity (ppm)	Brine	Surfactant	Conc. (%)	ZP Botucatu Sandstone (mV)	ZP_Oil-brine (mV)	IFT (mN/m)	% of swept oil	Time (mins)
10,000	NaCl	None	-	-60.6	-15.5	13	49.98	19
10,000	NaCl	Anionic	1	-66.4	-46.5	0.7	85.29	12
50,000	NaCl	None	-	-33.8	-11.1	20	68.54	15
10,000	$CaCl_2$	None	-	-18.1	+3.44	13	98.46	11
10,000	$CaCl_2$	Anionic	1	-35.5	-11.1	0.4	51.26	12
50,000	$CaCl_2$	None	-	-8.2	+1.1	17.1	78.23	17

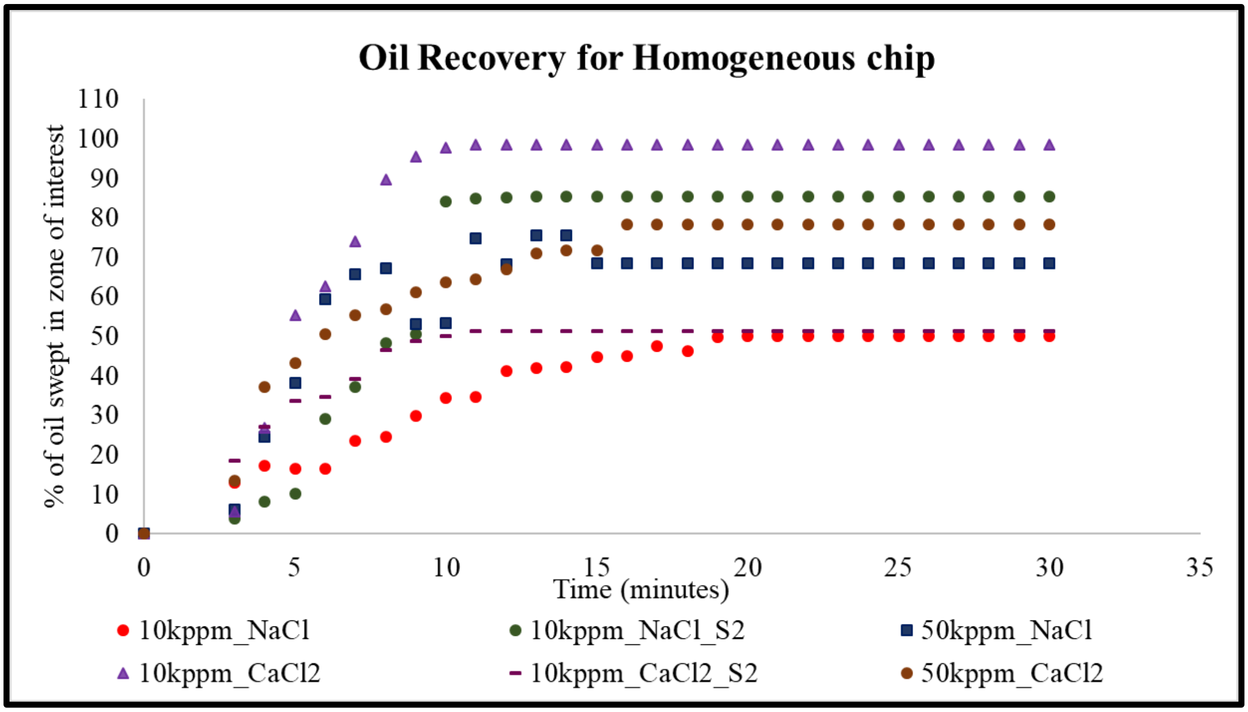


Figure 4-23: Oil recovery for the different brine and surfactant combinations

Figure 4-23 shows the oil saturation change with time in different brine and surfactant solutions with the aim analyzing the influence of the actual magnitude of zeta potential at the crude-oil-brine and rock interfaces on oil recovery, the influence of brine ionic composition on sweep efficiency and the dominant mechanism involved in oil recovery.

What is the influence of the actual magnitude of zeta potential at both the oil-rock and rock-brine interface on oil recovery?

In NaCl brine at low salinities where the zeta potential at both interfaces is highly negative, results show that the oil recovery is dependent on the magnitude of the zeta potential sign and magnitude at both interfaces. However, the degree to which this affects oil recovery is not proportional to the magnitude of the zeta potential sign. The difference in zeta potential magnitude at the oil-brine and rock brine interfaces with pure NaCl brine and anionic surfactant is of a large degree, with more of the difference coming from the values at the oil-brine interface whereby the negative magnitude is bigger for the case with anionic surfactant. The oil recovery difference in both cases is therefore significant whereby in the presence of anionic surfactant in NaCl brine, the oil recovery is 85.29% while that of pure NaCl alone results in 49.98%. The 50,000 ppm NaCl brine surprisingly results in a higher oil recovery than the 10,000 ppm NaCl brine even though the lower salinity brine has a bigger magnitude of zeta potential at both interfaces and even a smaller IFT value. This may be because the sodium ions present in the case of 10,000 ppm are not enough to affect the interfacial viscoelasticity that is required for an efficient oil sweep, as observed in the oil saturation pictures. The results are therefore a pointer to show the importance of sodium ions which have long been recognized as indifferent ions that will have little or no effect on oil recovery. Hence, Sodium ions may be considered to be a potential determining ion (PDI).

In $CaCl_2$ brine, however, the wettability alteration does not necessarily depend on the signs at both interfaces but salinity, the presence of Calcium ions which is a PDI and additives such as surfactant As seen in the case of 10,000 ppm Calcium chloride brine alone where the zeta potential at both interfaces has negative charges, the swept oil volume is 98.46%, whereas in the same brine with anionic surfactant, the oil recovered is 51.26% even with a more significant magnitude of zeta potential at both interfaces and a lower IFT value compared to the base case. The anionic surfactant used is not compatible in the presence of divalent cations such as calcium and in fact forms precipitates, which could have blocked some of the pored in the homogeneous chip and reduced the sweep efficiency. The results from the 50000 ppm $CaCl_2$ brine confirms even further that there must have been pore blockage in the low salinity case with anionic surfactant. In the case of 50,000 ppm Calcium chloride brine, the swept volume is 78.23% even though the zeta potential signs at both interfaces are different, coupled with a higher IFT value compared to the case of 10,000 ppm Calcium chloride and anionic surfactant.

Comparing the case of 10,000 ppm $CaCl_2$ brine and 50,000 ppm $CaCl_2$ brine alone, the oil recovery is bigger in the case of 50,000 ppm $CaCl_2$ brine because calcium ions increase water hardness and therefore reduces the foaming properties of the surfactant which is needed for better propagation of the surfactant in the micromodel. Even though calcium ions are considered to be potential determining ions, there must be a threshold value to which it can be used in order to prevent clogging the porous medium due to scale formation, hence reducing oil recovery.

In brief, the wettability alteration and oil recovery do not always correspond to the magnitude and signs of the zeta potential at the oil-brine and rock brine interfaces. The concentration and type of ion present in the brine is important in recovery and should not be overlooked.

What is the influence of brine ionic composition on sweep efficiency?

The Calcium chloride brine results in a higher recovery when compared to the sodium chloride brine except in the case where anionic surfactant is present in the Calcium chloride brine. This may be attributed to the strong binding affinity that exists between calcium ions and oil, thereby increasing the viscoelasticity effect in oil and reducing snap off as confirmed by the oil recovery pictures. In the case of sodium chloride brine, snap off is seen compared to the case of calcium chloride brine. This reduced snap off effect results in an additional 48.48% of oil recovery for 10,000 ppm when compared to a similar salinity for the NaCl brine. The proposed mechanism for an improved oil recovery in this case is that the some of divalent calcium ions present in the brine undergoes multi-component ion exchange with the negatively charged adsorbed oil on the micromodel and displaces it, while the increased viscoelasticity caused by the interaction of calcium ions and oil improves the sweep efficiency and reduces snap off.

Which mechanism Plays a more critical role between wettability alteration and IFT reduction on oil recovery?

Further analysis of the results shows that the highest recovery was not obtained at the lowest IFT. In fact, for the case of NaCl and $CaCl_2$ brines, the highest oil recoveries were at high IFT values. Even though the magnitude of the zeta potential at both the oil-brine and rock-brine interfaces is not always related to wettability, the ion type and concentration present in the brine affects its wettability alteration capabilities. The table below shows a ranking of the mechanisms considered to be dominant for the experiments.

Table 4-5: Ranking of improved oil recovery mechanism

Salinity (ppm)	Brine	Surfactant	Total zeta potential Ranking (mV)	IFT Ranking	Ranking of swept oil	Ranking of Mechanism
10,000	NaCl	None	2	3	6	Ion effect (less sodium ions)
10,000	NaCl	Anionic	1	5	2	Both
50,000	NaCl	None	4	1	4	Wettability
10,000	$CaCl_2$	None	5	3	1	Ion effect
10,000	$CaCl_2$	Anionic	3	6	5	Both
50,000	$CaCl_2$	None	6	2	3	Ion effect

Ranking

Swept oil: 1 = highest oil recovered and 6 = lowest oil recovered

Total Zeta Potential: 1 = biggest and 6 = lowest

IFT: 1 = biggest and 6 = smallest

The ranking is done based on the stability of the total zeta potential values and the IFT values. As noted earlier, a more stable film will be gotten when the zeta potential is beyond ±30mV. On this basis, comparing the case of For the NaCl brine where both mechanisms play a role, the oil recovery remains lesser compared to the case of Calcium chloride where only ion effect plays a role in oil recovery. A similar observation is also seen in the case of 50,000 ppm which gives the third largest recovery where ion effect seems to be more dominant and counteracts the less favorable wettability alteration and higher IFT. Moreso, in the case which gives the 5th largest oil recovery, even though both mechanisms seems to be favorable enough based on the parameters analyzed, the oil recovery is still low due to the incompatibility of the calcium ions with the anionic surfactant. Again this shows the important on ion effect on oil recovery. In the case which gives the fourth largest oil recovery where wettability alteration seems to be more dominant, the oil swept is still significantly less than the cases where ion effect is more dominant.

In all of the cases analyzed, none of them has IFT to be a dominant recovery mechanism. Therefore for improved oil recovery in a homogeneous rock, more attention should be given to the ion effect, then wettability effect before IFT.

4.6.2 Micromodel Flooding with Heterogeneous Fractured Chip

With the fractured heterogeneous chip which represents a typical carbonate formation, micromodel flooding was done with 100,000 ppm, synthetic formation brine with both non-ionic surfactant (Nonylphenol ethoxylate) and zwitterionic surfactant. The images are shown;

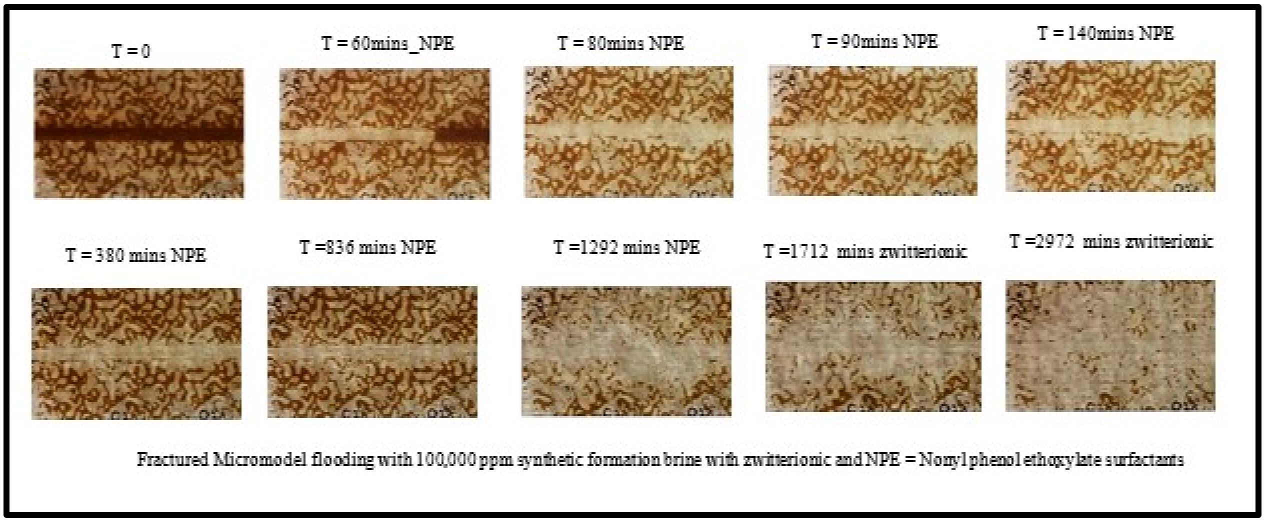


Figure 4-24: Micromodel flooding with fractured micromodel

Surfactant	**Synthetic formation Brine Concentration (ppm)**	**Surfactant Concentration (%)**	**IFT (mN/m)**	**Zeta Potential brine-Limestone (mV)**	**Zeta Potential oil-brine (mV)**	**% of oil swept**	**Time (Hours)**
Nonyl-Phenol-Ethoxylate	100,000	1	0.24	+ 4.07	-1.23	77	1292
Carboxybetaine based Zwitter Ionic(C_{16}DmCB)	100,000	0.025	0.004	-3.79	-3.38	97	1800

Figure 4-25: Results of IFT and zeta potential for the surfactant solutions in oil and rock

From ***Figure 4-25,*** it can be observed that initially, the surfactant slug can sweep the oil in the fracture completely before imbibing into the matrix. With the non-ionic surfactant in which the IFT is not at ultra-low values, the brine injected is only minimally able to displace the oil from the matrix whereas, in the case of the zwitterionic surfactant with ultra-low IFT, the brine imbibition in the matrix is significantly improved.

This shows that for a fractured rock such as carbonates, the IFT should be reduced to ultra-low values in order to allow for brine imbibition in the tight matrix. Even though the camera used was not able to visualize adequately the phenomena that causes the efficient sweep, it will be assumed that the formation of a Winsor type III microemulsion as seen in the work of (Broens & Unsal, 2018; Tagavifar et al., 2017; Xu et al., 2017) is responsible for the efficient matrix sweep, due to the ultra-low IFT values from the zwitterionic surfactant. The non-ionic surfactant with a low IFT value was able to recover about 77% of oil while the zwitterionic surfactant with an ultra-low IFT value recovered an additional 20% as shown in ***Figure 4-26***

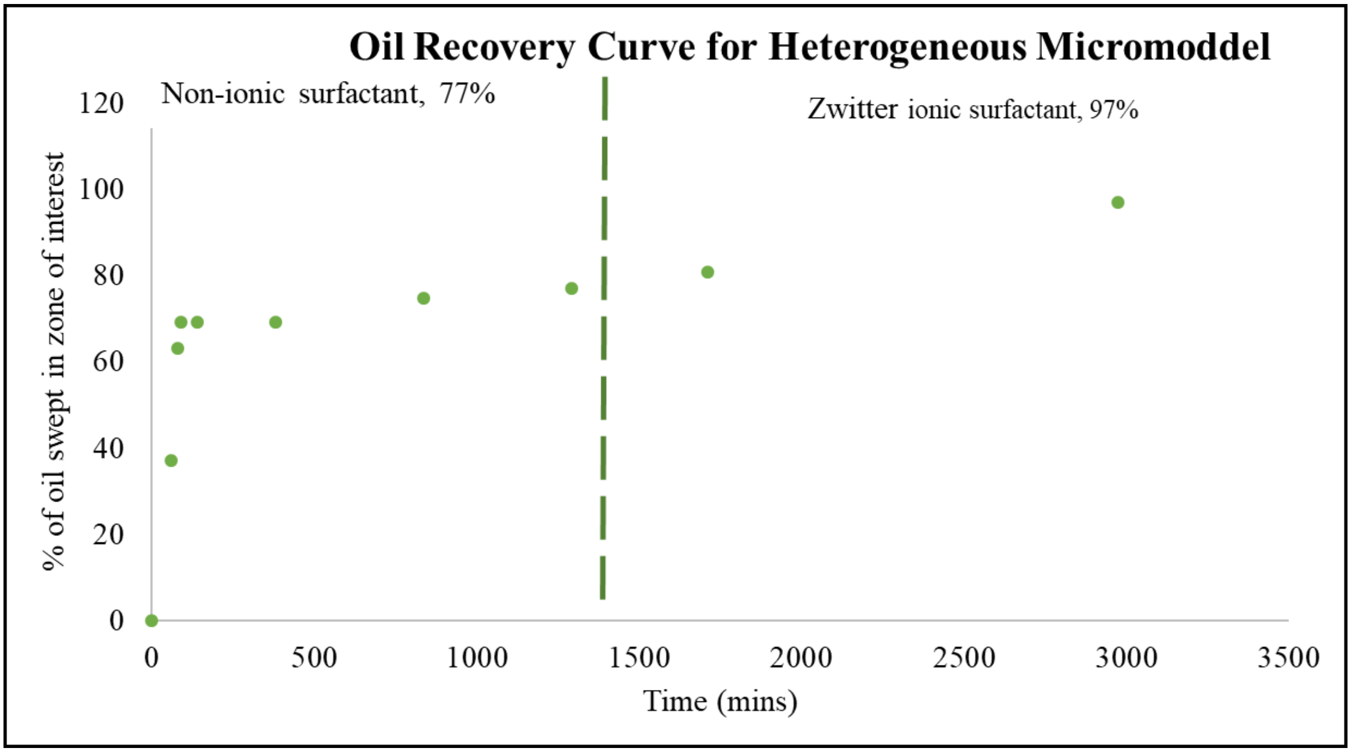


Figure 4-26: Oil recovery curve for fractured micromodel

Chapter 5 : Conclusions and Recommendations

5.1 Conclusions

From the analysis of the results, surfactant screening has been done based on the ability of the different surfactants to both alter wettability and reduce the interfacial tension at the oil-brine interface. Results are indicative that the non-ionic surfactant performs better for IFT reduction compared to wettability alteration. The answers to the initial research questions can then be summarized below based on the experiments conducted;

1. **How does electro-kinetic effect change under the influence of different brine salinities and ionic composition at both the oil-brine and brine-rock interfaces?**

Generally, the absolute magnitude of the zeta potential reduces with an increasing brine salinity due to the increase in Van der Waals force of attraction. This could imply a reduction in wettability alteration potential, depending on the other mechanisms involved. A similar trend is observed at the oil-brine interface.

2. **What is the effect of surfactant addition on the Crude Oil Brine and Rock (COBR) interaction?**

The charge seen at the oil-brine interface and brine rock interface is the same as the charge of the head group of the surfactant. The non-ionic surfactant reduces the EDL compared to the other two ionic surfactants analyzed. This reduction in EDL could be attributed to the fact that non-ionic surfactants stabilize colloids by steric repulsion which is weaker than the electrostatic repulsion from ionic surfactants.

3. **Can the results from the electrokinetic interaction be generalized for different rock types or unconventional plays such as tight carbonate rocks and shale?**

There is a general trend observed for the outcrop carbonate rocks used which were tested with a newly designed brine in the salve point core. Moreso, the surfactant effect on the charges of all the rocks analyzed are very similar.

4. **How can the results from the electro-kinetic effect be correlated with Porous media experiments? Is there any trend?**

Results from the single-phase spontaneous imbibition experiments show that the electro-kinetic results can be correlated to porous media experiments at an early time and only when one mechanism is active (which is usually not the case). For example, when the anionic surfactant is present in 5000 ppm NaCl brine, wettability alteration due to the EDL expansion and rock dissolution resulted in higher imbibition. However in the case of 25,000 ppm and 50,000 ppm brine, after some days, the imbibition of 50,000 ppm brine was more than the 25,000 ppm brine, due to the presence of more sodium ions in the 50,000 ppm case. Sodium ions which have been noted to be an indifferent ion may then be re-evaluated as a PDI.

5. **Can the results from the Oil-brine electrokinetics be correlated to the Interfacial Tension results?**

By studying the fluid-fluid interaction behavior of various surfactants with zeta potential and IFT, it could be concluded that one cannot use the zeta potential tool solely to measure the interfacial property especially in the case of anionic surfactants. Even for cationic and non-ionic surfactants, more experiments need to be done with various classes of non-ionic and cationic surfactants to ascertain if the trends are similar. However, generally, with an increase in the brine salinity, the magnitude of the zeta-potential at the oil-brine interface reduces which corresponds to a reduction in IFT.

6. **For a better oil recovery which mechanism plays a dominant role? Wettability alteration or IFT reduction?**

In less heterogeneous reservoirs such as sandstones, the effect of ion plays a bigger role than the IFT effect in oil recovery while for the heterogeneous fractured micromodel, the reduction of IFT to ultra-low values is necessary for brine imbibition in tight matrix.

7. **What is the optimum slug composition that will result in the highest oil recovery (not considering surfactant adsorption)?**

Based on this study, the optimum slug composition to be injected are as follows;

Sandstone: 10,000 ppm CaCl2 brine without surfactant or 10,000 ppm NaCl brine in Anionic surfactant

Carbonate: 5000 ppm NaCl brine with anionic surfactant

For the shale, more analyses need to be done since various factors could affect the oil recovery/imbibition from Shale. However based on the electrokinetic results alone and with the assumption that only one mechanism plays a dominant role in imbibition, then the optimal slug would be 5,000 ppm, 10,000 ppm NaCl or KCl brine in the anionic or cationic surfactant. Same brine salinity can also be used with the $CaCl_2$ brine but with only the cationic surfactant.

5.2 Recommendations/Future Work

The anionic surfactant even though it results in a bigger electrical double layer which is an indication of wettability alteration, may have high adsorption on the carbonate rocks thereby making it uneconomical to be used. The adsorption of the anionic surfactants should be tested at various salinities and surfactant concentration in order to determine which combination results in economical adsorption of less than 1 mg/g of rock, with a favorable wettability alteration.

The experiments should be conducted at a higher temperature and pressure, similar to what is applicable in reality to see if there will be a change of the results because the non-ionic surfactant even though has a good tolerance for high salinity may not be tolerant at high temperature due to the breakage of the hydrogen bond between brine and the surfactant at high temperature, which leads to a turbid solution. This should be checked as it might have a big impact on the IFT results. Again, an increase in temperature has an impact on the phase behavior of the anionic surfactant as observed in literature. As observed in literature, increase in temperature causes the anionic surfactant phase behavior to move from type II to Type III and then Type I. The temperature, salinity and brine composition where the type III micro-emulsion occurs should be studied. This can change the conclusions drawn about the non-ionic surfactant, which seems to give the lowest IFT at the temperature studied.

For the micro-model experiment, it should be conducted with a layer of beds of the actual rock in order to take into account the effect of the mineralogy of the rock on oil recovery. Alternatively, the same experiments cold be conducted on consolidated cores with micro-computed tomography (CT) scan. It is also recommended that for more representative cases, the results should be upscaled to actual reservoir conditions.

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