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# **The Effects of Surface-Active Chemicals on Wettability of Conventional and Unconventional Formations**

**Bachelor thesis**

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## ***The Effects of Surface-Active Chemicals on Wettability of Conventional and Unconventional Formations***

### **Anotace:**

Tato studie je přehledovým článkem, který zkoumá, jak povrchově aktivní chemikálie (SAC) v surové ropě ovlivňují smáčivost rezervoárů. Aby byl určen vliv přirozeně se vyskytujících SACs, obvykle se nacházejících v surové ropě, na smáčivost pískovcových a vápenatých hornin při různých salinitách a teplotách, byla v této práci provedena revize literatury nejnovějšího stavu výzkumu. Smáčivost se vztahuje k relativní náchylnosti rezervoárových hornin k oleji nebo vodě. Smáčivost rezervoáru ovlivňuje jak účinnost postupů týkajících se obnovy oleje, tak rozložení tekutin v rezervoáru. Bohužel, ještě není známo, jak chemické látky regulují smáčivost některých rezervoárů. Teplota, chemie tekutin a mineralogie hornin ovlivňují smáčivost látky. Pro simulaci olejové fáze byl použit čistý dekan a SACs. Čtyři skupiny SACs, které byly zkoumány, jsou aromatické, kyslík obsahující, síru obsahující a dusík obsahující SACs. Tato studie odhaluje, že je nezbytné popsat surovou ropu, slanou vodu a rezervoárové horniny přesně, aby bylo možné pochopit, proč snížená salinita vody zvyšuje obnovu oleje v některých rezervoárech, ale ne v ostatních. Tím je umožněna účinná modifikace chemie vstříkované vody k zvýšení obnovy oleje a zlepšení smáčivosti. Celkový vliv na podmínky, buď olejově mokré nebo vodou mokré, byl ukázán jako více závislý na teplotě, než na salinitě vody. Při snižování salinity kvůli dusíkatým SACs, nekyselým sírovým SACs a krátkým kyslíkovým SACs se smáčivost vápenatých hornin přesunula směrem k podmínkám, kdy jsou mokré vodou. Při snižování salinity slané vody se SACs, kyselé sírové SACs a aromatické látky upravovaly smáčivost uhlikatých hornin k olejově mokré podmínkám.

### **Annotation:**

This study is a review article that investigates how surface-active chemicals (SAC) in crude oil impact the wettability of reservoirs. In order to determine the impact of naturally occurring SACs usually found in crude oil on wettability of sandstone and carbonate rocks at a range of salinities and temperatures, a review of the state-of-the-art literature has been done in this thesis. Wettability refers to a reservoir rock's relative susceptibility for oil or water. Both the efficiency of oil recovery procedures and the distribution of fluids in a reservoir are affected by the wettability of the reservoir. Unfortunately, it is yet unknown how chemical agents regulate the wettability of certain reservoirs. Temperature, fluid chemistry, and rock mineralogy all influence the wettability of a substance. Pure decane and SACs were combined to simulate the oleic phase in order to identify the effects of certain SACs. The four SAC groups being studied

are aromatic, oxygen-containing, sulfur-containing, and nitrogen-containing SACs. This study discovers that, it is essential to describe crude oil, brine, and reservoir rock exactly in order to comprehend why low salinity waterflooding boosts oil recovery in some reservoirs but not others. order to determine the impact of naturally occurring SACs usually found in crude oil on wettability of sandstone and carbonate rocks at a range of salinities and temperatures, a review of the state-of-the-art literature has been done in this thesis. This enables the efficient modification of injection water chemistry to increase oil recovery and improve wettability. Overall impacts toward either oil-wet or water-wet conditions were shown to be more reliant on temperature than brine salinity. As salinity decreased as a result of nitrogen SACs, non-acidic sulfur SACs, and short-chained oxygen SACs, the wettability of carbonate rocks moved toward circumstances where they were wet with water. As the salinity of the brine decreased, SACs, acidic sulfur SACs, and aromatics modified the wettability of carbonates to oil-wet conditions. It was postulated that differences in how SACs respond to salt are one of the reasons why low salinity waterflooding works in certain reservoirs but not in others.

**Keywords:**

Surface active chemicals

Enhanced Oil recovery

Part-Per-Million

Enhanced Oil recovery

Modified Floating Technique

I declare that I have prepared the bachelor's thesis myself and that I have stated all the used information resources in the thesis.

In Olomouc, May 27, 2022

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Yousif Al-Shaaya

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## **List of Abbreviations**

SACs: Surface Active Chemicals

EOR: Enhanced Oil Recovery

MFT: Modified Floating Technique

PPM: Parts -Per -Million

DDDC: Dual Drop Dual Crystal

IFT: Interfacial Tension

OOIP: Original Oil In Place

GC-MS: Gas Chromatography - Mass Spectrometry

NIST: National Institute of Standards and Technology.

DCM: Diluted in Dichloromethane

AN: Acid Number

BN: Base Number

USBM: The United States Bureau of Mines

NMR: Nuclear Magnetic Resonance

DI: Deionized (water)

SAIL: Surface-Active Ionic liquid

## **1.Introduction**

It is difficult for the oil and gas industry to maximize oil recovery from current hydrocarbon reserves in order to meet the rising global energy demand. Currently, the average worldwide field recovery by waterflooding is 35 percent, leaving 60 to 70 percent of the oil in place (Shell, 2016). This is a substantial opportunity for enhanced oil recovery (EOR) techniques. EOR technologies attempt to mobilize crude oil by lowering interfacial tension (IFT) and/or modifying wettability to a favourable wetting state. The concept of modifying and engineering the injected water's chemistry has emerged as a promising EOR technique, referred to by various names such as "low salinity waterflooding" (Lager et al., 2008), "designer waterflooding" by Shell (Ligthelm et al., 2011), and "advanced ion management" by ExxonMobil (Gupta et al., 2011). Wettability, which results from the equilibrium of surface forces between oil and water interactions with the rock's surface, describes the reservoir rock's relative preference for oil or water. According to the findings of this study, oil chemistry, water chemistry, rock form and mineralogy, temperature, and degree of wetness all influence a rock's position on the wettability continuum. At the grain level, wettability is homogenous, meaning that it is either water-wet or oil-wet. Reservoir-scale wettability is heterogeneous or fractionally moist (Al-Hashmi, 2014). According to fractional wettability, a portion of the rock is oil-wet and the other portion is water-wet. Two forms of heterogeneous/fractional wettability are mixed and speckled/spotted/dalmatian wettability. It is also proposed that mixed-wettability, in which oil-wetted surfaces constantly pass through larger pores while tiny pores remain water-wetted and oil-free. Speckled, spotted, or dalmatian wettability refers to continuously wet surfaces with patches of occasionally oil-moist surfaces, and vice versa (Zhang et al., 2019). Understanding the distribution of fluids inside a reservoir necessitates familiarity with wettability. It is also necessary for the development of more effective and efficient oil recovery methods. Wettability, however, has proven to be a hard geochemical issue due to the fact that it is governed by a multitude of reservoir parameters. Standard wettability measurement techniques are limited by the time (days to weeks) and costs (thousands of dollars) necessary to conduct a single experiment, which exacerbates the problem. This presents a considerable bottleneck for laboratory experiments. Consequently, it is unknown which chemical mechanisms determine the wettability of certain reservoirs (Zhao, et. al., 2019). Understanding how oil surface active chemicals (SACs) impact a reservoir's ability to retain water in carbonate and sandstone is the goal of this study.

## **1.1 Aims of Study**

The study aims at providing insight into how SACs can alter the wettability of reservoir rocks and influence oil recovery, based on a review of the state-of-the-art literature. Also, aims at providing insights into the mechanisms behind wettability alteration and damage mitigation using the mixed surfactant solution. The study evaluates the effectiveness of the solution through laboratory experiments, including contact angle measurements, interfacial tension measurements, and core flooding experiments. The study also aims to investigate the impact of the mixed surfactant solution on the reservoir rock properties, such as permeability, porosity, and mineralogy. The study assesses the stability of the wettability alteration and the potential for long-term damage mitigation using the mixed surfactant solution. The study ultimately aims to provide a better understanding of how SACs present in crude oil can alter reservoir wettability and contribute to improved oil recovery. This information could have important implications for the oil and gas industry, as it may help to optimize oil recovery strategies by accounting for the impact of SACs on reservoir wettability. The findings of the study could have significant implications for the oil and gas industry, as they may help to develop more effective strategies for enhancing oil recovery from tight gas sandstone reservoirs while mitigating damage caused by aqueous phase trapping.

## 2.Theory and Background

### 2.1.1 Oil-Formation adhesion dynamic

As shown in **Figure (1)**, wettability is an indicator of the equilibrium between cohesive and adhesive forces. "Cohesive" and "adhesive" are terms used to describe the way materials stick together. "Cohesive" refers to the tendency of particles or molecules within a substance to stick together. This internal attraction between the particles or molecules allows the substance to maintain its shape and form. For example, water molecules are cohesive, which is why they form droplets and have surface tension. "Adhesive," on the other hand, refers to the ability of a substance to stick to other substances. This can occur through physical or chemical bonding. For example, glue is an adhesive substance because it can bond two surfaces together, creating a strong connection. The terms "cohesive" and "adhesive" are often used together to describe the way substances interact. For example, in the case of tape, the adhesive layer sticks to a surface (adhesion), while the layers of the tape stick together (cohesion). Understanding cohesive and adhesive properties is important in many fields, such as material science, chemistry, and engineering, as they can affect the behavior and performance of materials in various applications (Busireddy et al., 2004). To improve oil recovery in oil-wet reservoirs, surfactants or other chemicals can be used to alter the wettability of the rock surface and make it more water-wet. This process is called wettability alteration. By changing the wetting properties of the rock surface, it is possible to increase the displacement of oil by water and improve recovery. Overall, the wetting properties of a surface can have a significant impact on oil recovery in reservoirs. Understanding and manipulating these properties is an important area of research in petroleum engineering. Oil-rock adhesion is presumably regulated at the molecular level by electrostatic (and van der Waals) interactions (Buckley et al., 1989; Dubey & Doe, 1993), Electrostatic interactions are governed by aqueous chemistry, petroleum chemistry, rock mineralogy, and temperature. The interaction of charged oil and mineral surfaces causes electrostatic forces (Busireddy & Rao, 2004; Israelachvili, 2011). Due to the separation of polar molecules of  $N_2$  and  $O_2$  at the oil-water interface, the oil surface is charged. Mineral surfaces are charged because broken, unsaturated bonds hydrate at the mineral-water interface. The effects of electrical interaction might be either repellent, attractive, or both. According to (Hirasaki,1991), Three factors have historically made it difficult to establish a quantitative relationship between electrostatics and wettability and oil recovery: (1<sup>st</sup> ) multiple electrostatic mechanisms can operate simultaneously, making it impossible to determine the individual contributions; (2<sup>nd</sup>) experimental and field data from cores are the sum of chemical

and physical processes, making it difficult to isolate the specific chemical role of surface charge; and (3<sup>rd</sup>) surface charge measurement techniques have not been able to distinguish the chemical role of surface charge (Brady et al., 2015).

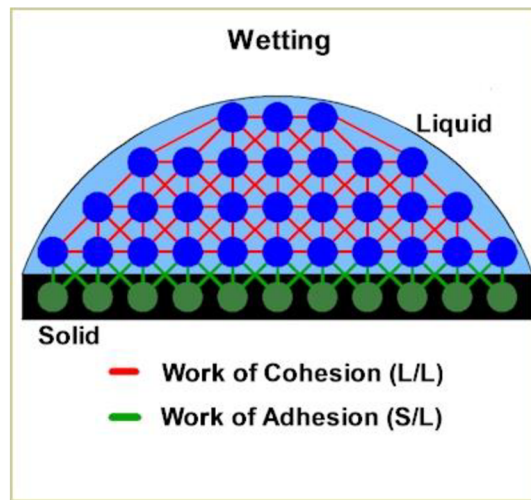


Figure (1): *equilibrium between cohesive and adhesive forces (Manshad et al., 2017).*

The Surface active compounds, known as SACs, are what govern wettability and recovery by reacting electrostatically with the rock surface. SACs are composed mostly of nitrogen bases and carboxylic acids when they are connected to non-polar hydrocarbon chains or rings. This study evaluates a newly developed wettability testing technique by analysing the effect of particular SACs on oil adhesion to carbonate and sandstone minerals (Liu et al., 2018).

### **2.1.2 Forces that influence Oil-Formation interactions.**

The van der Waals force, which frequently results from molecular-scale polarization between particles, is attractive and acts between two materials as shown in **Figure (2)**. Despite being weaker than electrostatic or hydrogen bonding interactions, this force is always present. As the oil and mineral double layers approach one another, electrostatic forces will interact. Coulomb's law controls the interaction between two charged substances when they come near together in a vacuum (Danov et. al., 2010). The Debye length, which is inversely related to the square root of the electrolyte concentration, is the distance at which the electrical field near a charged surface decays practically exponentially. (Cai et al., 2015)

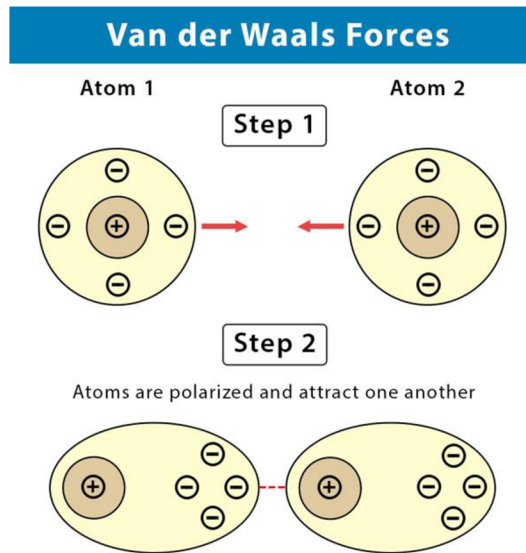


Figure (2): *van der Waals forces* (Chemistry Learner., Acc., 2023).

While van der Waals and electrostatic forces are long-range interactions, structural forces occur at a distance of less than 5 nm. These forces are generated when two surfaces meet at a distance of a few orders of molecular diameter (Gregory, 1975;1981). Surface interactions cannot be described by continuum theories of attractive van der Waal and repulsive double layer forces (Israelachivili, 2011).

### 2.1.3 Effects of Mineralogy, Chemistry and Salinity:

All reservoir rocks are originally moist with water. Water-rich sandstone and carbonate reservoirs are buried. The nature of rock also impacts how the various polar compounds can change rock wettability. Sandstones and carbonates are two common types of sedimentary rocks, and they differ in their mineral composition. Sandstones are composed primarily of sand-sized mineral grains, which are typically quartz, feldspar, and rock fragments. The exact mineral composition of sandstones can vary depending on the source of the sediment that formed them. For example, sandstones formed from beach deposits may have a higher percentage of shell fragments, while sandstones formed from volcanic ash may have a higher percentage of volcanic glass. In addition to the mineral grains, sandstones may also contain cementing material that binds the grains together. This cementing material can be composed of a variety of minerals, including calcite, silica, iron oxide, and clay minerals. The type and amount of cementing material can affect the strength and durability of the sandstone. Carbonates, on the other hand, are composed primarily of calcium carbonate ( $\text{CaCO}_3$ ) minerals,



such as calcite and aragonite. These minerals are typically formed from the shells and skeletons of marine organisms, such as corals, mollusks, and foraminifera. Carbonates may also contain other minerals, such as dolomite, which is a calcium-magnesium carbonate mineral. The mineral composition of carbonates can affect their properties, such as their porosity, permeability, and hardness. For example, dolomite is generally less soluble than calcite, which can make dolomite-rich rocks more resistant to weathering and erosion. Overall, the mineral composition of sedimentary rocks such as sandstones and carbonates can provide clues about the environment in which they were formed, as well as their physical and chemical properties (Jennings et al., 2017). Despite reservoir solution chemistry, sandstone surfaces are anionic while limestone surfaces are cationic. "anionic" refers to a negatively charged surface, while "cationic" refers to a positively charged surface. Sandstone surfaces are said to be anionic, meaning they have a net negative charge, whereas limestone surfaces are cationic, meaning they have a net positive charge. The clay minerals present in sandstones have both negatively charged faces and positively charged edges when wet. The negatively charged basal plane clay groups in sandstones interact with the positively charged surface groups of oil through electrostatic interactions, leading to oil adherence. The amount of charged oil surface groups depends on the oil's chemistry and history, as well as the composition of the connate fluid. On the other hand, the amount of negatively charged basal plane clay groups is set by lattice composition, such as pH, brine salinity, and brine composition (Fathi, et al., 2010). The smaller particle size, plate-like structure, and much higher surface areas of clay minerals cause them to commonly predominate the reactive surface area observed by oil. They have positively charged edges and negatively charged faces when wet. Oil adherence is likely mediated by electrostatic interaction between positively charged oil surface groups and negatively charged clay basal planes in sandstones containing clays such as illite or smectite (Fathi, S.J et al., 2010). The quantity of charged oil surface groups is based on the history of the oil and the chemistry of the oil and the connate fluid, whereas the amount of negatively charged basal plane clay groups is set by lattice composition (e.g. pH, brine salinity, brine composition). The production of electrostatic "bridges" and oil adhesion, which raises the degree of oil wetting, should be supported by the presence of high numbers of nitrogen bases and calcium-terminated carboxyl groups (Alotaibi et al., 2011). Reducing calcium-terminated carboxyl groups and nitrogen bases makes the formation more water-wet, improving oil mobility and recovery (Ferno et al., 2011). Precipitation and dissolution alter carbonate rock surface chemistry. Calcium and carbonate ions governed the surface potential of calcite, not hydrogen and hydroxide ions.

The aqueous chemistry however with the pH, ion concentration, and salinity of the pore water impact the oil and mineral surface charge and, subsequently, the system wettability (Donaldson et al., 1969). Temperature also impacts how wettable a material is in relation to water chemistry. Several organizations have achieved enhanced oil recovery from sandstone and carbonates by modifying the chemistry of floods (Gamage et al., 2011).

The surface charge of crude oil and reservoir rock is regulated by brine composition and salinity, which in turn determines the system's subsequent wettability (Jun Lu et al., 2014). Brines are naturally occurring solutions that are high in salt content. They are commonly found in areas such as salt pans, salt lakes, and underground reservoirs. The composition of brines can vary widely depending on their source and location. However, some of the most common ions found in brines include sodium ( $\text{Na}^+$ ), chloride ( $\text{Cl}^-$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), sulfate ( $\text{SO}_4^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ), potassium ( $\text{K}^+$ ), iron ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ), manganese ( $\text{Mn}^{2+}$ ), strontium ( $\text{Sr}^{2+}$ ), barium ( $\text{Ba}^{2+}$ ), lithium ( $\text{Li}^+$ ), and boron ( $\text{B}(\text{OH})_4^-$  and  $\text{BO}_3^{3-}$ ) (Kharaka et al., 2003). These ions can have significant impacts on the properties of brines, such as their density, viscosity, and electrical conductivity. For example, the presence of calcium and magnesium ions can lead to scaling and other forms of mineral build-up, which can be problematic for oil and gas production operations. Conversely, lithium and boron ions are sometimes extracted from brines for use in batteries and other industrial applications. Overall, the composition of brines is an important consideration for many industries, including oil and gas, mining, and agriculture. By understanding the types and concentrations of ions present in a particular brine, companies can better predict and manage any potential challenges or opportunities that may arise. Ions like sulfate, calcium, and magnesium can attach to mineral surfaces, changing the surface charge and perhaps affecting polar oil adsorption (Nandwani et al., 2017). Brine salinity and composition affect charged oil component concentration at the oil-water contact. This affects oil surface charge. Ions can also form complexes with polar oil components, changing their solubility in the oil phase (Al-Adasani, et al., 2012).

Additionally, some companies have undertaken in-depth studies on the influence of brine salinity on wettability. The University of Wyoming's Morrow group started this research on low-salinity brines' effects on wettability and oil recovery (Surdam et al., 2013). This research has made oil and gas companies aware of how injected water chemistry may affect oil recovery. Most researchers believe low salinity brines improve wettability and oil output. However, a substantial number of study teams have revealed that low salinity water injection has no appreciable influence on oil recovery. Low salinity waterflooding in Wyoming's Powder River

Basin fields was evaluated. They found no difference in recovery between the 24 fields that received low salinity water and the 22 that received mixed or formation water. In 32 of these 46 fields, injected water salinity was considerably decreased, whereas in the remaining 10 fields it was only marginally reduced (Hadia et al., 2013). Salinity decrease and oil recovery were unrelated. (Boussour et al., 2009) tested a reservoir core sample with low salinity waterflooding but found no increased oil recovery.

#### **2.1.4 Influence of Oil chemistry and Temperature**

Oil is a complex mixture of hydrocarbons, which are compounds made up of carbon and hydrogen atoms. The principal compounds in crude oil are typically long chains of hydrocarbons, ranging from methane (CH<sub>4</sub>) to heavy, complex molecules with hundreds of carbon atoms. These hydrocarbons can be classified into different groups, including alkanes, alkenes, and aromatics, based on their molecular structure.

In addition to hydrocarbons, crude oil also contains small amounts of other elements, such as sulfur, nitrogen, and oxygen. These elements can form compounds known as heteroatoms, which are often found in the form of sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and carbon monoxide (CO) during the burning of oil. The composition of crude oil can vary widely depending on its source and the conditions under which it was formed. Refining processes are used to separate crude oil into different fractions based on their boiling points and chemical properties, which are then used to produce a wide range of petroleum-based products, including gasoline, diesel fuel, and lubricating oils (Speight, J. G. 2014). Oil chemistry has a major impact on the wettability of a system. BN (base number) and AN (acid number) are two important measurements used in the oil industry to determine the acidity and basicity of crude oil and other petroleum products. The acid number (AN) is a measure of the number of acidic compounds in the oil, such as carboxylic acids, phenols, and naphthenic acids. The AN is typically expressed in milligrams of potassium hydroxide (KOH) required to neutralize one gram of oil. Higher AN values indicate higher levels of acidic compounds, which can contribute to corrosion, fouling, and other problems in oil processing equipment. The base number (BN), on the other hand, is a measure of the number of basic compounds in the oil, such as alkaline earth metal salts and basic nitrogen compounds. The BN is also expressed in milligrams of KOH required to neutralize one gram of oil. Higher BN values indicate higher levels of basic compounds, which can help neutralize acidic compounds and prevent corrosion in oil processing equipment (Bera et al., 2019). In terms of wettability of oil, BN and AN can play a role in determining the surface properties of rock and other surfaces in contact with the oil.

Acidic compounds can contribute to the formation of polar surfaces that are more likely to be wetted by water, while basic compounds can contribute to the formation of non-polar surfaces that repel water. The balance between acidic and basic compounds can affect the overall wettability of the oil and its ability to flow through rock formations. The base number (BN), which is frequently much higher than the acid number (AN), is a measurement of the crude oil's basic composition. Acid number (AN) is a measure of crude oil's acidic content (Punternvold et al., 2007). Since naphthenic acids in crude oil possess the highest surface adsorptive capabilities, they may function as "anchor" molecules for other surface-active components also present in crude oil (Standnes & Austad, 2003). Due to the negative disjoining pressure, the thin water layer that forms between the negatively charged oil-water interface and the positively charged chalk surface becomes unstable, and the oil may make contact with the chalk surface. Carboxylates from the oil may stick to the chalk's surface and diminish its wetting ability (Thomas 1993). Thus, AN could determine the water's moisture content. Increasing AN increases the possibility of carboxylates clinging to the chalk surface and decreases the rock's capacity to absorb water. Additionally, steric acid was shown to promote oil-wetting. As the AN increases, water humidity decreases. (Punternvold et al., 2008) examined the influence of basic components on the wetting properties of chalk using oil with a constant AN of 0.5mg KOH/g oil and varying AN/BN ratios between 0.24 and 4.6. They used the basic chemical benzyl amine and discovered that when the base content increased to approximately four times the acid concentration, the water wetness decreased (Emerson, ZI., 2007).

Nonetheless, it has been demonstrated that temperature has a significant effect on wettability. (Rao, 1999) revealed that when the temperature rises, sandstone reservoirs become normally more oil-wet and carbonate reservoirs become typically more water-wet. When water is pumped into a reservoir, the temperature changes, causing oil-wet surface particles to separate and leaving a water-wet surface. One result is that wettability changes during oil displacement by water and that oil displacement by water may vary with respect to its wettability. Various results may explain the wettability behaviour in sandstones, where systems grow more water-wet as temperature decreases, utilizing Rao's arguments and other comparable conclusions, but they do not account for the observed behaviour in carbonates (Sondergeld et al., 2006). In addition, research has demonstrated that decarboxylation of carboxylic substances happens at elevated temperatures and that carbonate may accelerate this process. Due to the decrease in AN, this action decreases the acid number AN to base number BN ratio and increases the oil-wetness of the system (Al-Anssari, et. al., 2017).

### 2.2.1 Sandstone formation-wettability dynamic

Sandstone reservoirs are composed of negatively charged quartz and clays. Due to their significant negative charge and large surface area, clays have a tendency to absorb cationic SAC components from crude oil. In the past decade, low salinity waterflooding in sandstone reservoirs has gained considerable attention (Morrow & Buckley, 2011). Multiple laboratory and field investigations have demonstrated that altering the composition of the brine may greatly boost oil recovery (10–30% of OOIP “Original oil in place”) (Aladasani et al., 2014). This technique is extensively utilized because it is cost-efficient, water is easily accessible, it is straightforward to implement on-site, and it is excellent in replacing light to medium gravity crude oils. In the laboratory and in the field, injecting low-salinity brine into carbonate and sandstone reservoirs has been shown to boost waterflood efficiency (Myint & Firoozabadi, 2015). Coreflooding investigations on sandstone cores proved the advantages of adopting low salinity water injection in secondary mode rather than tertiary mode by producing 6 to 20% more oil. The low salinity effect is believed to be caused by a variety of factors. In all low salinity waterflooding processes, the adhesion of oil SACs to the rock surface is stated. In order to establish forecasts for low salinity waterflooding, the role of SAC adhesion must be quantitatively evaluated and comprehended (Robertson, 2010; Hadia et al., 2013). **Figure (3)** shows pore space of oil-wet and water-wet porous rocks.

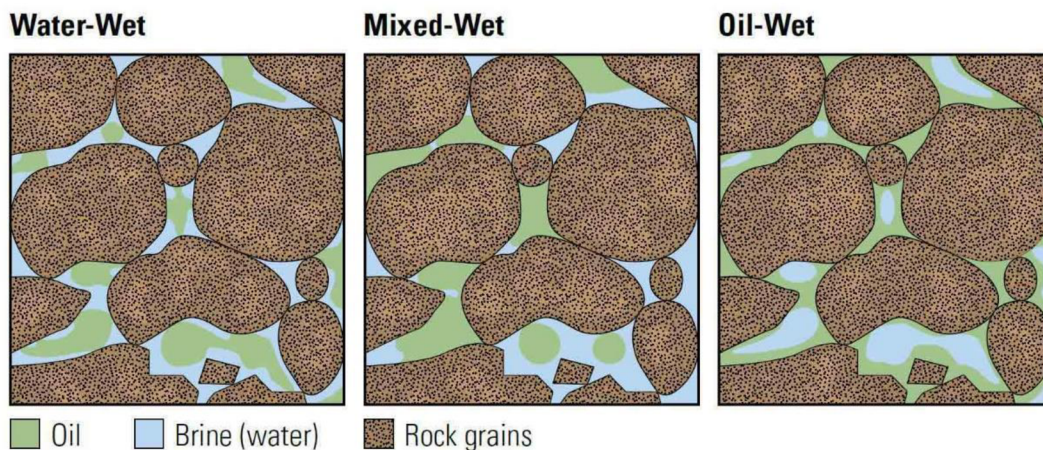


Figure (3): pore space of oil-wet and water-wet porous rocks (Hirasaki et al., 2011).

According to (Winoto et al., 2012), the mobility of tiny particles, notably kaolinite, can greatly affect the sensitivity of oil recovery to salt. They concluded that the idea that heavy polar components of crude oil adsorb onto particles and pore walls to create mixed wetness might explain a range of facts about oil recovery and wettability. Clay fines are aged when in contact with and exposed to crude oil, resulting in the formation of mixed-wet particles. Since the fines



movement revealed the underlying surfaces, increasing the water-wetting of the system, the development of oil droplets on these clays would contribute to the system's transformation into a more water-wetting system. In the presence of high salinity brine, clays stay undisturbed and maintain their oil-wet condition, resulting in decreased displacement efficiency. In the presence of low salinity water, clay particles will detach from the surface of the pores. Unfortunately, clay migration can plug pore throats and reduce permeability while fluid is moving (Saboorian-Jooybari, et al., 2019).

### **2.2.2 Salinity and Migration in Sandstone formations**

(McGuire et al., 2005) reported a pH increase with low salinity injection in Sandstone and North Slope field samples. The North Slope field is an oil field located on the North Slope of Alaska, USA. It is one of the largest oil fields in North America and has been a major source of crude oil production since the 1970s. The field is primarily composed of sandstone reservoirs that are overlain by impermeable shale formations. In the context of the provided reference, the North Slope field is mentioned as one of the field samples used in a study on the effects of low-salinity water injection on reservoir rocks. The study found that injecting low-salinity water can cause an increase in pH and a drop in interfacial tension (IFT) in sandstone and North Slope field samples. The increase in pH was attributed to the exchange of hydrogen ions with adsorbed sodium ions in the water. The pH increase resulting from low-salinity water injection can have a significant effect on the zeta potential of the rock, which can in turn affect the adsorption of organic molecules on clay surfaces. This information is relevant for understanding the mechanisms of enhanced oil recovery (EOR) processes, such as low-salinity water flooding and alkaline flooding, which can be used to increase the recovery of oil from reservoirs like the North Slope field (McGuire et al., 2005). Low-salinity processes resembling alkaline floods may be caused by an increase in pH and a drop in IFT. It has been proposed that this increase in pH is the result of hydrogen ions in the water exchanging with sodium ions that have been adsorbed (Hadia et al., 2013). A moderate variation in the bulk pH of the rock can have a considerable effect on its zeta potential. Zeta potential is a measure of the electrical charge that develops at the interface between a solid surface, such as a rock or clay particle, and a fluid. In the context of enhanced oil recovery (EOR), the zeta potential of the reservoir rock is an important factor that affects the wettability of the rock and the adsorption of organic molecules on its surfaces. A moderate variation in the pH of the rock can have a significant effect on its zeta potential. As the pH of the fluid increases, hydrogen ions in the water may exchange with adsorbed sodium ions on the rock surface, resulting in a change in the electrical charge at the

interface. This change in zeta potential can in turn affect the adsorption of organic molecules on clay surfaces, which can impact the efficiency of EOR processes. The information on zeta potential is relevant in understanding the mechanisms of EOR processes, such as low-salinity water flooding and alkaline flooding, which can be used to increase the recovery of oil from reservoirs like the North Slope field. The increase in pH resulting from low-salinity water injection can cause changes in the zeta potential of the rock, which can impact the wettability of the rock and alter the interactions between the rock and fluids (Hadia et al., 2013). When the pH rises, organic molecules may be absorbed from clay surface. **Figure (4)** shows Electric double layer model.

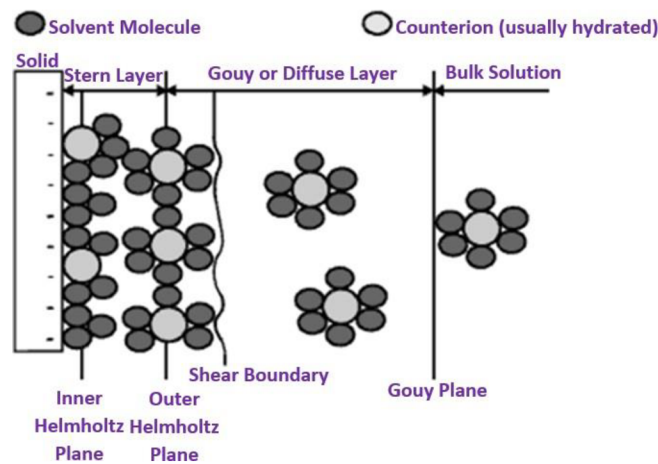


Figure (4): *Electric double layer model (Davis et al., 1978), modified.*

According to (Austad et al., 2010), the following elements are critical for low salinity effects in sandstones: (1) rock mineralogy (such as clay properties, type and quantity); (2) crude oil chemistry (such as SACs) and (3) aqueous chemistry (e.g. brine composition and pH). According to the suggested method, polar components and active cations must be adsorbed onto clay first. The adsorption and desorption windows of clays vary. Clay minerals having a high cation exchange capacity are often helpful for researching the influence of low salinity. Clay minerals with a high cation exchange capacity are those that can exchange cations with the surrounding solution. Examples of such clay minerals include smectite and Illite. Smectite is a type of expandable clay mineral that has a high cation exchange capacity due to the presence of negatively charged layers that can absorb positively charged ions. Illite, on the other hand, is a non-expandable clay mineral that also has a high cation exchange capacity. Other clay minerals that may exhibit high cation exchange capacities include kaolinite, vermiculite, and chlorite, depending on their specific properties and composition. In the context of enhanced oil

recovery, the cation exchange capacity of clay minerals is important because it affects their ability to adsorb and desorb active ions and organic molecules (Austad et al., 2010). As mentioned in the previous paragraph, the adsorption and desorption windows of clays can vary, and clay minerals with a high cation exchange capacity are often useful in studying the effects of low salinity. When low salinity brine is injected into a reservoir, it can displace adsorbed cations on the surface of the clay minerals, which can lead to an increase in pH and the desorption of organic molecules. Understanding the cation exchange capacity of clay minerals can help in predicting the efficiency of low salinity EOR processes and in designing effective strategies for increasing oil recovery from reservoirs. At a pH of around 5 in the reservoir, organic material, active cations, and protons initially balance-adsorb onto the clay minerals. A typical acid-base interaction occurs between  $\text{OH}^-$  and the adsorbed acid and protonated base, which promotes the desorption of organic molecules. The oil recovery rate increases as the water's moisture content increases (Al Harrasi, et al., 2012). Due to calcium ions being replaced by hydrogen ions on the surface of the clay, injection of low salinity brine would result in the desorption of adsorbed cations, elevating the pH along the water-clay interface. Due to the fact that the rock is already saturated with water, the low salinity EOR impact will be negligible if there is little organic material adsorption and an abundance of active ion adsorption. As long as the concentration of active ions is low enough to promote considerable desorption from the clay surface, the composition of the injected low-saline water may not be critical. (AlRatrouf, et al., 2018).

### **2.2.3 Carbonate formation-wettability dynamic**

According to (Chilingar and Yen1983), 15% of the 161 carbonate rocks investigated were highly oil-wet, 65% were oil-wet, 12% were intermediate-wet, and 8% were water-wet. In fractured and low-permeability carbonate reservoirs, oil displacement from matrix blocks by spontaneous imbibition of the injection fluid is the major driving factor for achieving high oil recovery (Haugen, 2016). The adverse wetting state of carbonates limits the spontaneous absorption of water (and ejection of oil) into the matrix due to negative capillary pressure. The spontaneous imbibition of wettability-altering water into fractured reservoirs of chalk, limestone, and dolomite is a key secondary oil recovery technology (carbonate reservoirs). Under water-wet to mixed-wet conditions, the strategy appears to be rather effective. By modifying the wettability of the rock surface to a more favourable water-wet state, the capillary pressure can be increased to promote spontaneous imbibition into oil-wet carbonate matrices and improve oil recoveries. To do this, one must first know the relationship between wettability



and SACs. Carbonates in brines with pH values near to neutral have positively charged and weakly basic surfaces. Due to the carboxylic acids in the oil, the contact between rock and brine is positively charged, whereas the interaction between oil and brine is negatively charged. Due to the electrostatic attraction caused by opposing charges on the oil/brine and mineral/brine surfaces, the brine coating tends to weaken, and the oil may come into direct contact with the mineral surface (Fjelde, et al., 2017).

The influence of low salinity water injection in carbonate reservoirs has not been examined as thoroughly as in sandstone reservoirs (Jia et al., 2019). Low salinity waterflooding of sandstone reservoirs modifies their wettability due to the presence of clay. Only a few field-scale low-salinity waterflood projects have been reported, including those at the Ekofisks and Valhall oil fields. The Ekofisk and Valhall oil fields are located in the North Sea, which is a large body of water between the coasts of Norway, Denmark, the UK, and other European countries. These oil fields are known for their production of crude oil and natural gas, and have been subject to various enhanced oil recovery (EOR) techniques to increase their production rates. The low salinity waterflooding project was implemented in these fields as a pilot study to evaluate the potential of this technique for increasing oil recovery. The Ekofisk field in particular has been studied extensively for its unique geology, including the fractured chalk reservoir that was the focus of the low salinity waterflooding project. The success of this project has led to further research and development of low salinity waterflooding as a viable EOR technique (Johansen et al., 2016). The discovery of an abnormally significant oil recovery by injecting saltwater into the fractured Ekofisk chalk reservoir of the North Sea aroused interest in modifying the water chemistry in the injected water (Al-Shalabi et al., 2014).

#### **2.2.4 Effects of Rock Dissolution and Salinity**

Increased oil recovery due to changing brine chemistry of injection water has been connected to increased wettability of carbonates (Prathibha Pillai et al., 2018). Fundamental findings from laboratory tests and real-world settings reveal that altering the water's chemistry improves oil mobility underflow and imbibition, indicating that the water's wettability has altered. The bulk of observed data attributed increased oil recovery to wettability shifting to a more water-wet or mixed-wet state. As wettability modification options, decreasing the total salinity of the injected water and adding potential determining ions are proposed (Al-Attar, et. al., 2013). However, there is limited consensus on a single basic mechanism behind the impact of low salinity. This is due to the complex interaction between crude oil, brine, and rock, as well as a number of contradicting experimental findings. Therefore, either there are many mechanisms in play or

the optimal method for enhancing oil recovery using chemically modified water has not yet been identified (Gao, H.,2020).

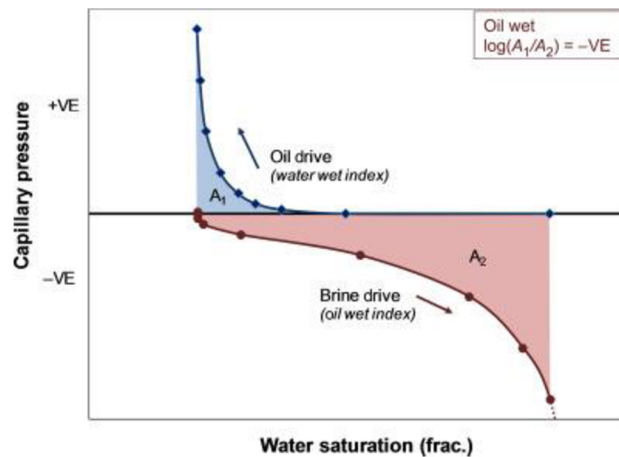
Calcium carbonate from the rock dissolves and reaches equilibrium with the low-salinity brine as a result of the brine's lower calcium concentration. As the calcium carbonate dissolves, the components of the adsorbed oil are liberated, leaving the rock surface moist. During carbonate dissolution, an excessive quantity of  $\text{OH}^-$  will increase the pH. In Middle Eastern reservoir limestone core flooding tests, (Gupta et al., 2011) observed that soft water dissolved a small amount of rock, desorbing a portion of the oil, and changing the wettability towards a more water-wet state. In carbonate core flooding investigations conducted under reservoir conditions, (Yousef et al., 2012) investigated pore coupling and revealed that microscopic anhydrite dissolution was responsible for the link between micro and macro pores (Yue Wang et al., 2015). Utilizing geochemical modelling to evaluate the concept of rock dissolution, concluded that chemical dissolution of calcite appears to be the primary factor.

### 3. Methods:

In this chapter, we go through the various methods used in either calculating wettability or understanding the nature of what alters wettability in general.

#### 3.1. Amott and USBM

Amott and USBM (The United States Bureau of Mines) tests are the most prominent quantitative methods for assessing wettability status. Both methods yield an estimate of the macroscopic average wettability of the rock-oil-brine system. Some of the methods used to measure wettability include the US Bureau Method (USBM), permeability/saturation relations, wire-line logs, imbibition rates, production performance, capillary pressure curves, relative permeability curves, microscope examination, flotation, nuclear magnetic resonance (NMR), displacement capillary pressure, dye adsorption, and capillary metric methods (Amott, 1959; Donaldson et al., 1969; Sharma & Wunderlich, 1987). Shown in **Figure (5)**.



**Figure (5):** Amott and USBM method. (Amott, 1959)

Capillary pressure is typically measured in units of pressure, such as psi (pounds per square inch), Pa (Pascals), or bar. Water saturation is typically measured as a fraction or percentage, with no units, but it can also be expressed in volumetric terms as a fraction or percentage of the pore space filled with water (e.g., 0.25 or 25%). Capillary pressure is the difference in pressure between two fluids in contact with a solid surface due to the surface tension at the interface between the fluids. In the context of the Amott and USBM charts, capillary pressure is used to

describe the relationship between the water saturation (the fraction of the rock pore space occupied by water) and the pressure required to displace the water from the rock pores. The Amott chart is used to determine the capillary pressure by injecting a series of fluids (water, oil, and mercury) into a rock sample and observing how they flow through it. By measuring the capillary pressure, the Amott chart can help determine the fluid flow characteristics of the rock, which is important for assessing its suitability for oil and gas production.

The USBM chart, on the other hand, does not directly measure capillary pressure. Instead, it uses measurements of the rock's permeability and porosity to determine its capillary pressure curve, which is then used to determine the water saturation at various pressure levels. The USBM chart can help classify rocks as sandstones, shales, or carbonates based on their permeability and porosity, which can help predict their fluid flow characteristics and suitability for oil and gas production.

In summary, capillary pressure is an important parameter used in both the Amott and USBM charts to describe the relationship between water saturation and pressure in rock samples. The Amott chart directly measures capillary pressure, while the USBM chart uses measurements of permeability and porosity to derive the capillary pressure curve.

### **3.2 Contact angle**

The contact angle method is a widely used technique for measuring wettability in the petroleum industry. The contact angle is the angle formed between a fluid droplet and a solid surface at the point where the droplet meets the surface. It is commonly used to determine the degree of wettability of a surface, which is the tendency of a fluid to spread over or be absorbed by the surface (Al-Kaabi, 2014).

In this method, a small droplet of the test fluid is placed on the surface of a solid sample, such as a rock or a mineral. The contact angle is then measured using a goniometer, which is a device that can accurately measure angles. The contact angle is determined by measuring the angle between the tangent to the droplet at the point where it meets the surface and the surface itself. The contact angle method is most accurate when applied to pure fluids and synthetic cores, as the properties of natural rocks can vary widely due to their heterogeneous mineral composition. The method is efficient and has the advantage of allowing direct testing of wettability in reservoir conditions (Pinczewski et al., 2015). However, it has some limitations, including the hysteresis induced between the water-advancing and water-retreating angles. Surface

roughness, heterogeneity, and immobility can also contribute to contact angle hysteresis, which can affect the accuracy of the measurement.

In summary, the contact angle method is a useful technique for measuring wettability in the petroleum industry. It has some limitations, but it is a reliable and efficient method that can be used to directly test wettability in reservoir conditions (Rossen, 2011). Contact angle method Shown in **Figure (6)**.

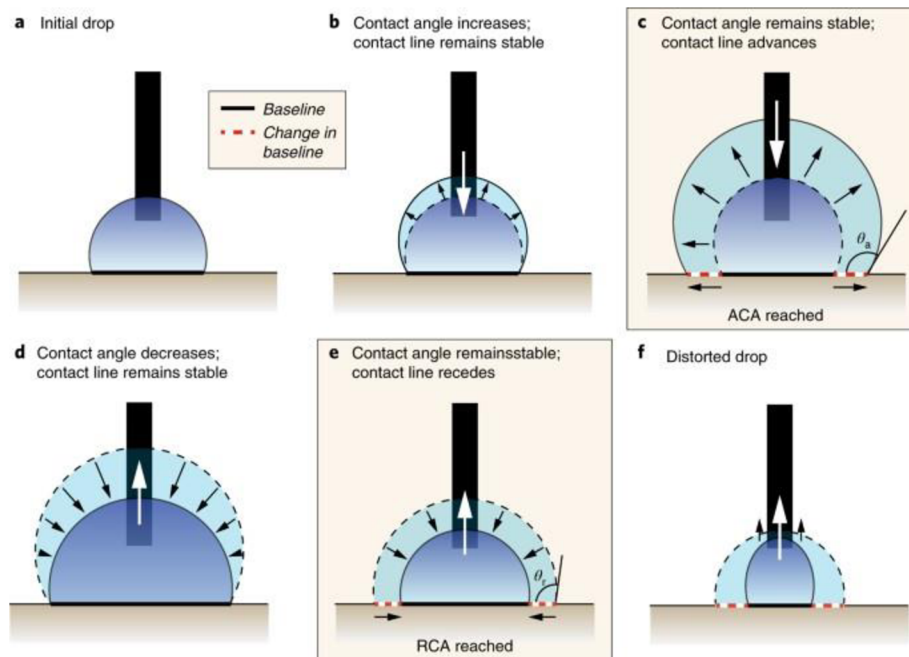


Figure (6): *Contact angle method (Tribonet,. Acc 2023)*.

Changes in the equilibrium contact angle and the kind of hysteresis, both of which are essential for determining the oil saturation, can be caused by changes in surface variations of comparable magnitude. Brown and Fatt (1956) advocated discarding the concept of a reservoir rock contact angle. Due to the heterogeneous mineral composition of the bulk of reservoir rocks, each has a distinct surface chemistry and the ability to adsorb surface active components from reservoir fluids.

### 3.3 DDDC method.

The dual drop dual crystal technique was developed by (Rao and Girard, 1996). Two droplets of crude oil (A) are put on parallel, polished rock surfaces that are supported by the horizontal and vertical arms of an optical cell. Before measuring the advancing and retreating contact angles in relation to aging time, the water film between the crude oil sessile droplets and mineral crystal surfaces is drained with the aid of buoyancy forces to achieve adhesion equilibrium. By inverting the bottom crystal (A B), there are three different behaviours for the oil drop. In

example B1, the oil drop remains adhered to the bottom crystal owing to adhesion. In case B2, a portion of the oil drop floats away due to buoyancy. In cases B1 and B2, the higher crystal is lowered such that the two oil droplets can combine (C). In example B3, the upper crystal is lowered to contact with the surface where the oil drop from the lower crystal was located. The advancing and retreating contact angles are determined by laterally moving the bottom crystal (D). The water advancing contact angle explains the wettability and rock/oil adhesion, whereas the water receding contact angle governs the spreading behaviour of reservoir fluids (Rao and Girard, 1996) **Figure (7)**.

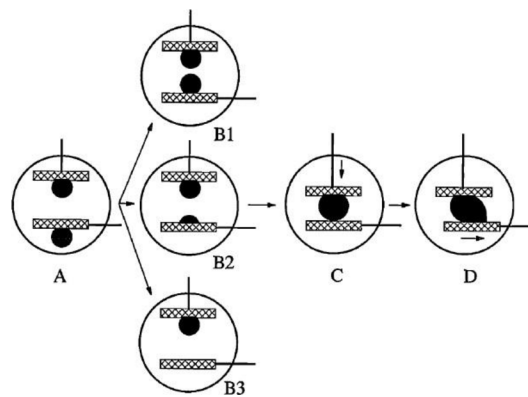


Figure (7): DDDC method depiction (Rao and Girard, 1996)

Two droplets of crude oil are placed on parallel, polished rock surfaces that are supported by the horizontal and vertical arms of an optical cell. Before measuring the advancing and retreating contact angles in relation to aging time, the water film between the crude oil sessile droplets and mineral crystal surfaces is drained with the aid of buoyancy forces to achieve adhesion equilibrium.

The bottom crystal is then inverted to observe the behavior of the oil drop, which can result in three different cases: (1) the oil drop remains adhered to the bottom crystal owing to adhesion; (2) a portion of the oil drop floats away due to buoyancy; and (3) the upper crystal is lowered to contact with the surface where the oil drop from the lower crystal was located

The advancing and retreating contact angles are determined by laterally moving the bottom crystal. The water advancing contact angle explains the wettability and rock/oil adhesion, whereas the water receding contact angle governs the spreading behavior of reservoir fluids. The DDDC method is useful for understanding the interactions between crude oil droplets and

rock surfaces, which can be important in the study of reservoir properties and oil recovery processes.

### 3.4 X-Ray Diffraction Technique

To ascertain the mineral compositions of the rocks utilized in this experiment, X-ray diffraction (XRD) was employed. By causing an x-ray beam to diffract in particular directions due to the crystal's crystalline atoms, XRD is used to determine the atomic and molecular structure of a crystal. The density of electrons within the crystal may be seen in three dimensions by measuring the angles and intensities of these diffracted beams. The mean locations of the atoms in the crystal, as well as their chemical bonds and a number of other properties, are then calculated using the produced electron density. **Figure (8)** depicts the Panalytical Empyrean XRD apparatus utilized in this experiment. For a repeatable and precise diffraction pattern, sample preparation is essential. Graininess, micro-absorption, texture, sample height displacement, surface roughness, and sample transparency are issues linked to subpar sample preparation (Cui, Q., et al., 2019). The mineral composition of rocks can have a significant impact on their wettability. This is because the surface properties of minerals, such as surface energy, surface charge, and surface roughness, can influence the way fluids interact with the rock surface. For example, minerals with higher surface energies are generally more hydrophilic and have lower contact angles with water, while minerals with lower surface energies are more hydrophobic and have higher contact angles with water

XRD is commonly used in wettability research to determine the mineral composition of rocks and understand how it affects their wettability. Several studies have used XRD to investigate the relationship between mineral composition and wettability. For example, Cui et al. (2019) used XRD to analyse the mineral composition of sandstone samples and found that minerals such as quartz and feldspar were associated with higher contact angles and lower wettability. Similarly, Mousavi et al. (2017) used XRD to analyse the mineral composition of carbonate rocks and found that calcite and dolomite were associated with higher wettability.

Other studies have also used XRD in combination with other techniques such as contact angle measurements and scanning electron microscopy (SEM) to gain a more complete understanding of the relationship between mineral composition and wettability. For example, Yang et al. (2017) used XRD, contact angle measurements, and SEM to analyse the mineral composition and surface morphology of shale samples and found that the surface roughness and mineral composition were important factors affecting wettability.



Figure (8): XRD instrument (Cui, Q., et al., 2019)

There is a set sample preparation and loading protocol for the XRD, however there are certain small but important specifics that vary depending on the type of material being tested. Thus, it is crucial.

### 3.5 Gas Chromatography Technique

Gas chromatography (GC) is a widely used technique for the separation and identification of complex mixtures of volatile organic compounds. The technique involves separating individual compounds from a mixture based on differences in their physical and chemical properties, such as boiling point, vapor pressure, and polarity. The separated compounds are then identified and quantified by a detector, such as a flame ionization detector (FID) or mass spectrometer (MS). In the context of studying the compounds present in oil that can affect wettability, GC can be used to identify and quantify specific hydrocarbons and other organic compounds in the oil that interact with the rock surface. These compounds can include paraffins, olefins, naphthenes, and aromatics, which are known to have different effects on wettability (Pillai et al. 2018).

The first step in using GC to analyse oil samples is to extract the hydrocarbons and other organic compounds from the oil matrix. This is typically done by dissolving the oil sample in a suitable



solvent, such as hexane or dichloromethane. The extracted compounds are then separated by GC using a stationary phase, such as a silica gel or a polar stationary phase, that selectively interacts with the compounds based on their physical and chemical properties. The separated compounds are detected and quantified by a detector, such as an FID or MS, which measures the amount of each compound as it elutes from the GC column. The FID measures the amount of carbon atoms in each compound and provides a response that is proportional to the concentration of the compound. The MS, on the other hand, identifies the specific mass-to-charge ratio of each compound and provides a unique spectrum that can be used to identify the compound (Li et al., 2019).

By analysing the composition of the oil using GC, it is possible to determine the types and concentrations of the different hydrocarbons and other organic compounds that affect wettability (Mohammadi et al., 2021). This information can be used to better understand the behaviour of oil on the rock surface and to optimize oil recovery processes. Several papers have used GC to study the compounds present in oil that affect wettability, including "Wettability alteration of oil-wet sandstone by surfactant flooding: Mechanisms and influencing factors" by Prathibha Pillai et al. (2018), and "Assessing the effectiveness of alkali-surfactant-polymer flooding for EOR: Wettability alteration and oil recovery" by Haidong Wei et al. (2019). Gas Chromatograph schematic is shown in **Figure (9)**.

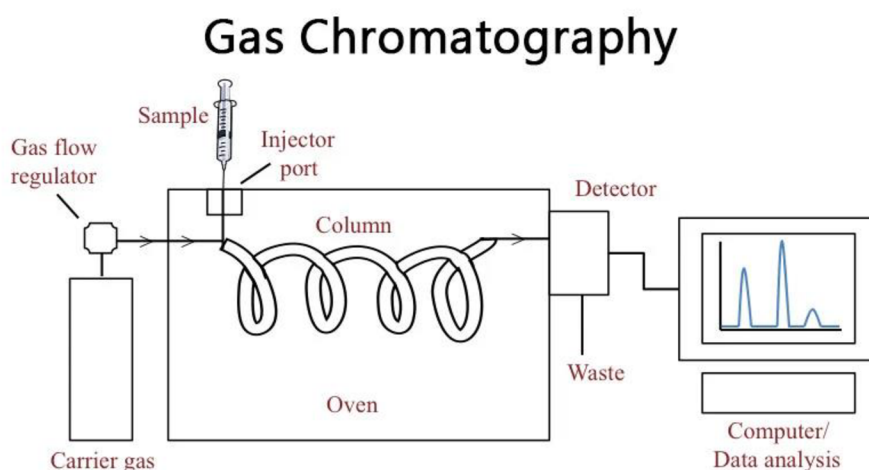


Figure (9): *Gas Chromatograph schematic (Microbe Notes. Acc., 2023).*

A Varian CP-3800 gas chromatograph and a Varian Saturn 2200 Ion Trap mass spectrometer were used to examine the GCMS samples (Agilent). The temperature program for the samples' splitless injection was as follows: beginning temperature of 40°C, hold for 6min, increase to 240°C at a rate of 40/min, hold for 10min, ramp to 280°C at 20/min, hold for 5min, total run

duration of 73min. The temperature of the injector was always 2000. Helium was the carrier gas, flowing continuously of 1 ml per minute. 1900 volts was the electron multiplier voltage. The NIST library search was used to confirm the spectra- (Prathibha Pillai et al, 2018).

## **4. Case Studies**

The following is a detailed dissection of all the approaches, methods and experiments done by different authors with different approaches. In this chapter we will compare and understand the methods to then discuss our findings and conclusion.

### **4.1 The Role of Surface Active Compounds in Crude Oil on Reservoir Wettability.**

**(Mwangi, PM., 2017)**

Mwangi\_(2017) aimed to investigate the role of surface active compounds (SACs) in crude oil on reservoir wettability, and to determine the potential of using SACs to enhance oil recovery. The study aimed to contribute to the existing literature on the topic and provide experimental evidence to support the hypothesis that SACs can significantly alter wettability in reservoirs. In order to achieve these aims, the study conducted a comprehensive literature review on the topic of SACs and wettability alteration in reservoirs. They did this conducting a literature review by searching and analyzing various published articles, books, and conference proceedings related to the physicochemical properties of SACs, their interactions with reservoir rocks and fluids, and their potential for enhanced oil recovery. From the review, they synthesized and summarized the key findings and conclusions regarding the role of SACs in altering wettability and enhancing oil recovery. The authors also discussed the limitations of previous studies and identified areas for further research.

The study also conducted laboratory experiments to investigate the effects of SACs on wettability. The experiments involved measuring the contact angles of different crude oils on different types of rock surfaces, with and without the presence of SACs. The study also conducted interfacial tension measurements to determine the effects of SACs on oil-water and oil-rock interfaces. The researchers took reservoir rock samples and exposed them to crude oil with varying levels of SACs. To do this, they likely took a certain volume of crude oil and mixed in different concentrations of SACs to create different samples. Since 92% of the rock component is water-wet (quartz and feldspar) and 8% is clay, sandstone is called water-wet. The 8% of sandstone that floats are caused by the interaction between the weak polar charge in decane and the charge on the clay particles. The composition of sandstone includes minerals such as quartz and feldspar, which are hydrophilic or water-loving, meaning they have a natural

affinity for water. Hence, 92% of the rock component is considered water-wet. The remaining 8% of the sandstone composition consists of clay minerals, which are generally more hydrophobic or oil-loving, meaning they repel water. However, in the presence of nonpolar liquids such as decane, some clay minerals may become partially hydrophilic and contribute to the water-wettability of the rock. This is because the weak polar charge on the clay particles can interact with the nonpolar decane, resulting in a water-wet surface. This review included studies on the physicochemical properties of SACs, their interactions with reservoir rocks and fluids, and their potential for enhanced oil recovery.

In the study, gas chromatography (GC) and differential dynamic contact angle (DDDC) were used to analyze the chemical composition of the crude oil samples and the wettability of the reservoir rock samples, respectively. Gas chromatography (GC) is an analytical technique used to separate and analyze components of a mixture. In the study, GC was used to determine the chemical composition of the crude oil samples, including the type and concentration of surface-active compounds (SACs) present in the oil.

Differential dynamic contact angle (DDDC) is a technique used to measure the wettability of a solid surface by a liquid. In the study, DDDC was used to measure the contact angles between the crude oil and the rock surface at different temperatures and concentrations of SACs. The contact angles were used to determine the wettability of the reservoir rock, with lower contact angles indicating a more water-wet surface. By measuring the contact angles at different conditions, the researchers were able to investigate the effect of SACs and temperature on the wettability of the reservoir rock.

Next, they measured the contact angle between the oil and the rock surface. The contact angle refers to the angle between the surface of the rock and the interface between the rock and the crude oil. A smaller contact angle indicates that the crude oil is more likely to spread out and adhere to the rock surface, indicating a more water-wet surface. The researchers used cylindrical core samples of sandstone from a reservoir. They cleaned and dried the samples before placing them in a cell designed to mimic reservoir conditions. The cell had two sections, one for the rock sample and one for the crude oil.

The crude oil used in the experiments was obtained from the same reservoir as the rock samples. Different levels of SACs were added to the oil, ranging from 0.5% to 5%. The samples were then left for several days to allow the oil to saturate the rock samples.

After the saturation period, the contact angle between the oil and the rock surface was measured using the sessile drop method. This involved placing a droplet of oil on the rock surface and measuring the angle formed between the oil droplet and the rock surface. A contact angle goniometer was used for the measurements. The contact angles between the oil and the rock surface were measured at each temperature, and the results showed that as the temperature increased, the contact angle decreased even further, indicating a greater shift towards a more water-wet surface. This suggests that the SACs present in the crude oil become more active at higher temperatures, resulting in greater wettability alteration. The researchers repeated the experiments at different temperatures ranging from room temperature to 80°C. They observed that as the temperature increased, the wettability alteration also increased. This was attributed to the increased activity of the SACs at higher temperatures, which caused greater adsorption onto the rock surface and a stronger reduction in the contact angle.

The results of the experiment showed that as the level of SACs in the oil increased, the contact angle decreased. This means that the rock surface became more water-wet as the amount of SACs in the oil increased.

In order to investigate the effect of temperature on wettability alteration, the experimental setup was modified by conducting the tests at different temperatures. The reservoir rock samples were again exposed to crude oil with varying levels of SACs, but this time the tests were conducted at different temperatures ranging from room temperature to 90°C. Samples were sourced from three different types of rocks commonly found in reservoirs: sandstone, shale, and carbonate. Specifically, they used four different types of sandstones (Berea, Gray Berea, Kirby, and Bandera), one type of shale (Mancos shale), and three types of carbonates (Austin chalk, Indiana limestone, and Silurian dolomite).

To prepare the rock samples for their experiments, they ground and sieved them into five different sizes ranging from less than 53  $\mu\text{m}$  to greater than 206  $\mu\text{m}$ . They used the 105-206  $\mu\text{m}$  grain size distribution for their experiments. To prevent contamination, they thoroughly cleaned their equipment including the mortar, pestle, and sieves using a specific procedure involving air blasting, rinsing with DI water and acetone, and using rock powder to scrub the surface of the equipment to pick up any contamination. The researchers wanted to ensure that their experimental results were not affected by any external contaminants.

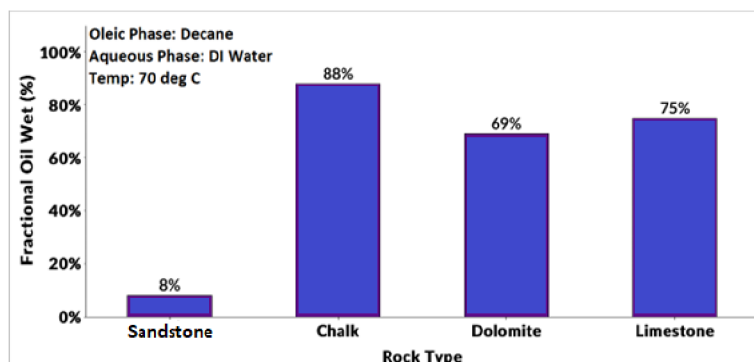


Figure (10): *Rock samples baseline conditions. (Mwangi, 2017)*

As indicated in **Figure (10)**, baseline conditions were determined by measuring the wettability of each rock in the presence of decane and deionized water. Decane is a hydrocarbon alkane with the formula ( $C_{10}H_{22}$ ) with 75 structural isomers. Between the carbon and hydrogen atoms of decane, a dipole moment provides a mild polar charge. This charge is strong enough to interact with the opposing charge on the rock surface in the presence of DI water.

The mortar, pestle, and sieves were thoroughly cleaned in order to prevent contamination. To do this, the following steps were taken: blast the equipment with 100 psi air inside a fume hood until all loose powder is removed; rinse with deionized water; rinse with acetone; and dry with air; then, crush a small quantity of the target rock into a fine powder; use the powder to scrub the equipment's surface in an effort to remove any contamination that may have become stuck to the surface. The equipment is then ready for use after the possibly contaminated powder has been decanted. (Mwangi, 2017).

This experiment employed model oils mixes of pure decane and surface-active compounds to replicate the oleic phase in order to separate the impacts of specific SACs. A model oil can only loosely match natural petroleum since it is a complicated brew of organic components. Model oils, however, are a helpful tool for separating the impacts of various SACs on wettability. Aromatic, oxygen-bearing, sulfur-bearing, nitrogen-bearing, and a natural condensate sample are the four types of SAC that were examined. The SACs used in this investigation are listed in **Table (1)**.

Table (1): Surface active compounds used by (Mwangi, PM., 2017)

Surface Active Compounds (SAC)	Label	Chemical compound	Chemical Formula	MW (g/mol)
	O1	Acetic acid (short	$CH_3COOH$	60.05

Oxygen-bearing SAC		chain)		
	O2	Myristic acid (long chain)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CO OH	228.37
	O3	Naphthenic acids (long chain)	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	126.15

Table(1) Cont'd

Surface Active Compounds (SAC)	Label	Chemical compound	Chemical Formula	MW (g/mol)
Sulfur-bearing SAC	S1	Dibenzothiophene	C <sub>12</sub> H <sub>8</sub> S	184.26
	S2	Di-n-Butyl Sulfide	C <sub>8</sub> H <sub>18</sub> S	146.29
	S3	1-Tetradecanethiol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> SH	230.45
Nitrogen-bearing SAC	N1	Carbazole	C <sub>12</sub> H <sub>9</sub> N	167.20
	N2	Quinoline	C <sub>9</sub> H <sub>7</sub> N	129.16
	N3	Pyridine	C <sub>5</sub> H <sub>5</sub> N	79.10
Condensate	Cond	Condensate		
Non-reactive organic medium	Dec	Decane	C <sub>10</sub> H <sub>22</sub>	142.28

The condensate was provided by a significant oil corporation (Shell). This fluid is transparent, and its specific gravity, density, and viscosity at 20 degrees Celsius are 60°API, 0.8 g/cm<sup>3</sup>, and 1.03 cp, respectively. Deionized water was used for baseline experiments, and then various salts were added to create chemically distinct brines in order to separate the specific impacts of brine composition on wettability.

The majority of the carbonate rocks are oil-wet, before transferring the rock to the oleic phase. Consequently, the initial wettability is often water-wet, and the presence of the oleic phase may or may not encourage contact with the rock surface decane binds to a significant proportion of carbonate rocks, namely 88% of chalk (Ca<sub>0.845</sub>Mg<sub>0.155</sub>CO<sub>3</sub>), 75% of dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), and 69% of limestone (CaCO<sub>3</sub>). The observed binding of decane to carbonate rocks is due to

the interaction between the dipole moment of decane and the positively charged carbonate rock surfaces. These interactions are mild, but as salinity increases, electrostatic forces become more widespread and powerful. (Liu, et al., 2018). The final findings and conclusions were:

- Surface active compounds (SACs) present in crude oil can significantly alter the wettability of reservoir rocks, which can affect oil recovery.
- As the level of SACs in the crude oil increased, the contact angle between the oil and rock surface decreased, indicating a shift towards a more water-wet surface.
- Higher temperatures increased the activity of SACs and resulted in greater wettability alteration.
- Asphaltenes had the most significant effect on wettability alteration, followed by resins and then aromatics.

The conclusion of the study is that surface active compounds (SACs) present in crude oil can significantly alter reservoir wettability, which in turn affects enhanced oil recovery. The study found that the level and type of SACs present in the crude oil can affect wettability alteration, with asphaltenes having the most significant effect. Additionally, the study found that higher temperatures can increase the activity of SACs and lead to greater wettability alteration.

The study suggests that SACs can be used to alter wettability and enhance oil recovery, but further research is needed to fully understand the mechanisms involved. The findings have important implications for the oil industry, as understanding the role of SACs in wettability alteration can inform enhanced oil recovery strategies and improve the efficiency of oil production.

Overall, the study suggests that SACs can be used to alter wettability and enhance oil recovery in reservoirs, but more research is needed to fully understand the mechanisms involved.



#### **4.2 A formulation based on a cationic surface-active ionic liquid and an anionic surfactant for enhanced oil recovery at a carbonate reservoir. (Somoza et al., 2021).**

The researchers synthesized a novel cationic surface-active ionic liquid (SAIL) and combined it with an anionic surfactant to form a mixed surfactant system. The system was tested for its ability to reduce the interfacial tension between oil and water, and its effectiveness in improving oil recovery from carbonate rocks was evaluated. The results showed that the mixed surfactant system had a low interfacial tension, which could help to mobilize trapped oil in the reservoir. The system also showed good stability in high salinity and high-temperature conditions, which are common in carbonate reservoirs.

The aims were to develop an innovative formulation for enhanced oil recovery (EOR) in carbonate reservoirs by synthesizing a novel cationic surface-active ionic liquid (SAIL) and combining it with an anionic surfactant to form a mixed surfactant system.

The literature review provides an overview of the current methods for EOR in carbonate reservoirs, including surfactant flooding, which involves the injection of surfactants to reduce the interfacial tension between oil and water and improve oil recovery. The article also discusses the challenges associated with EOR in carbonate reservoirs, such as high salinity and high-temperature conditions. The literature review in the article provides a comprehensive overview of the current methods for enhanced oil recovery (EOR) in carbonate reservoirs, with a particular focus on surfactant flooding. Surfactant flooding is a widely used EOR technique that involves the injection of surfactants into the reservoir to reduce the interfacial tension between oil and water and improve oil recovery.

The article discusses the challenges associated with EOR in carbonate reservoirs, including the unique properties of carbonate rocks that make them more difficult to recover oil from compared to other types of reservoirs. Carbonate rocks have a complex pore structure, and the oil is often trapped in small, isolated pockets, making it difficult to recover using traditional EOR methods. Moreover, carbonate reservoirs typically have high salinity and high-temperature conditions, which can cause surfactants to become less effective or even destabilize, reducing their ability to reduce interfacial tension and mobilize trapped oil. These challenges must be considered when developing new EOR formulations for carbonate reservoirs. To address these challenges, the researchers in the study developed a novel mixed surfactant system based on a cationic surface-active ionic liquid (SAIL) and an anionic

surfactant. The system was designed to have good stability in high salinity and high-temperature conditions, which are commonly found in carbonate reservoirs. researchers in this study used contact angle measurements to evaluate the wettability of the carbonate rocks and determine the effectiveness of the mixed surfactant system in improving oil recovery. However, without more information, it is not possible to confirm whether contact angle measurements were integrated into the study shown in **Figure (11)**.

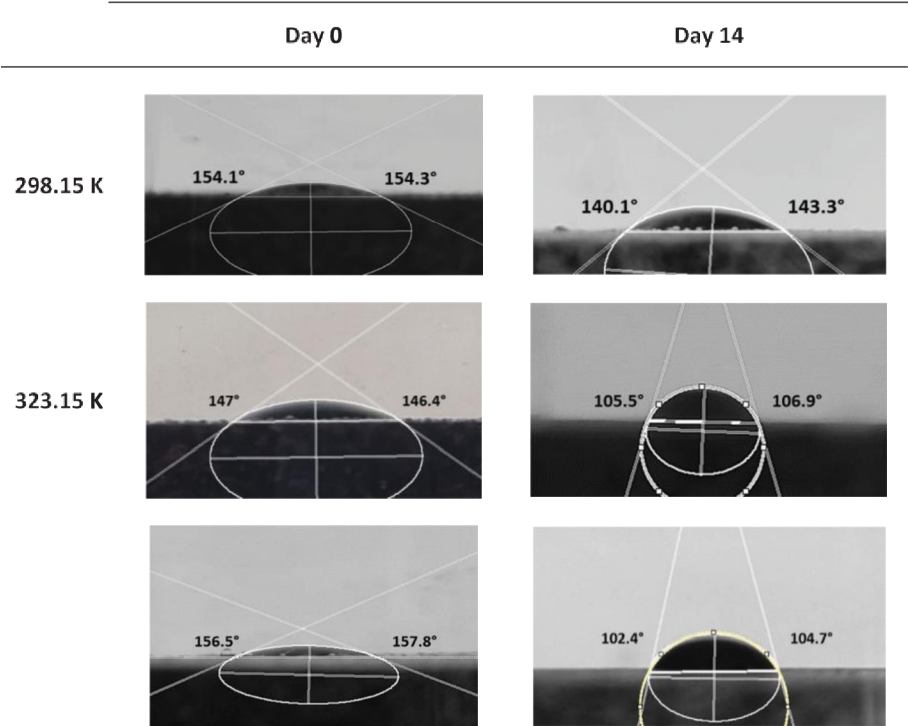


Figure (11): Contact angle measurements in oil-wet rock before and after treatment with the surfactant formulation at different temperatures. (Somoza et al., 2021).

In the study, the researchers synthesized a novel cationic surface-active ionic liquid (SAIL) and combined it with an anionic surfactant to form a mixed surfactant system. The synthesis process involved a series of chemical reactions to produce the desired cationic SAIL compound. The researchers then characterized the chemical and physical properties of the SAIL and mixed it with the anionic surfactant to create the surfactant system. They used a base oil sample shown in **Table (2)**,

Table (2): Crude oil main properties (provided by supplier), (Somoza et al., 2021).

Property	Value
API	33.0
Density at 288.15 K (g/cm <sup>3</sup> )	0.8600
Viscosity at 293.15 K (cSt)	10.3
Acidity (mgKOH/g)	0.06
Saturates (%)	61
Aromatics (%)	33
Resins (%)	4.6
Asphaltenes (%)	1.4
Carbon residue (%)	4.53

To evaluate the effectiveness of the mixed surfactant system for enhanced oil recovery (EOR) in carbonate reservoirs, the researchers tested the system for its ability to reduce the interfacial tension between oil and water. The interfacial tension was measured using a tensiometer, which is a device that can determine the force required to separate two liquids. In addition, the researchers conducted tests on carbonate rocks to evaluate the effectiveness of the mixed surfactant system in improving oil recovery. The tests were conducted under high salinity and high-temperature conditions to evaluate the stability of the mixed surfactant system.

The stability of the system was evaluated using several methods, including measuring the surface tension over time and observing the formation of any precipitates or emulsions. The results showed that the mixed surfactant system had a low interfacial tension, indicating its potential to mobilize trapped oil in the reservoir. The system also demonstrated good stability in high salinity and high-temperature conditions, suggesting its potential as an effective EOR agent for carbonate reservoirs. Carbonate reservoirs are known to have high salinity and high-temperature conditions, which can pose challenges for surfactant-based enhanced oil recovery (EOR) methods. High salinity can cause surfactants to become less effective, while high temperatures can destabilize surfactant molecules, reducing their ability to reduce interfacial tension and mobilize trapped oil. Therefore, these challenges must be considered when developing new EOR formulations for carbonate reservoirs. The researchers address these challenges by developing a novel mixed surfactant system based on a cationic surface-active ionic liquid (SAIL) and an anionic surfactant. The mixed surfactant system was designed to have good stability in high salinity and high-temperature conditions, which are commonly found in carbonate reservoirs.

To test the stability of the mixed surfactant system, the researchers conducted laboratory experiments under high salinity and high-temperature conditions. The stability of the system was evaluated using several methods, including measuring the surface tension over time and observing the formation of any precipitates or emulsions. The results showed that the mixed surfactant system had good stability under high salinity and high-temperature conditions, suggesting its potential as an effective EOR agent for carbonate reservoirs. The stability of the system was likely due to the unique properties of the cationic SAIL, which can form stable micelles in high salinity and high-temperature environments.

The findings of the study indicated that the mixed surfactant system based on the cationic SAIL and anionic surfactant has potential as an effective EOR agent for carbonate reservoirs. The tests showed that the mixed surfactant system had a low interfacial tension, which could help to mobilize trapped oil in the reservoir. Additionally, the mixed surfactant system showed good stability in high salinity and high-temperature conditions, which are common in carbonate reservoirs. The stability of the system was attributed to the unique properties of the cationic SAIL, which allowed it to form stable micelles even in high salinity and high-temperature environments. This stability was critical to the effectiveness of the mixed surfactant system as an EOR agent, as it allowed the system to maintain its ability to reduce interfacial tension and mobilize trapped oil in challenging reservoir conditions. Overall, the study demonstrated the potential of the mixed surfactant system based on the cationic SAIL and anionic surfactant as an effective EOR agent for carbonate reservoirs, and provided valuable insights into the development of surfactant-based EOR methods for challenging reservoir conditions. The challenges of using traditional anionic linear alkylbenzene sulfonate (LAS) surfactants for enhanced oil recovery (EOR) in carbonate rocks. These surfactants have been found to be unsuitable for use alone because they exhibit poor stability and high adsorption when used in carbonate reservoirs. In other words, they tend to break down or become less effective in these environments, reducing their ability to reduce the interfacial tension between oil and water and mobilize trapped oil.

To address these challenges, the researchers in the study developed a new mixed surfactant system based on RECOLAS 158, a type of LAS obtained from the petrochemical industry, and a T2EG (two ethylene glycol units) surface-active ionic liquid (SAIL). The mixed surfactant system was designed to have improved stability and effectiveness in carbonate reservoirs compared to traditional anionic LAS surfactants. The overall test results are shown in **Figure (12)**.

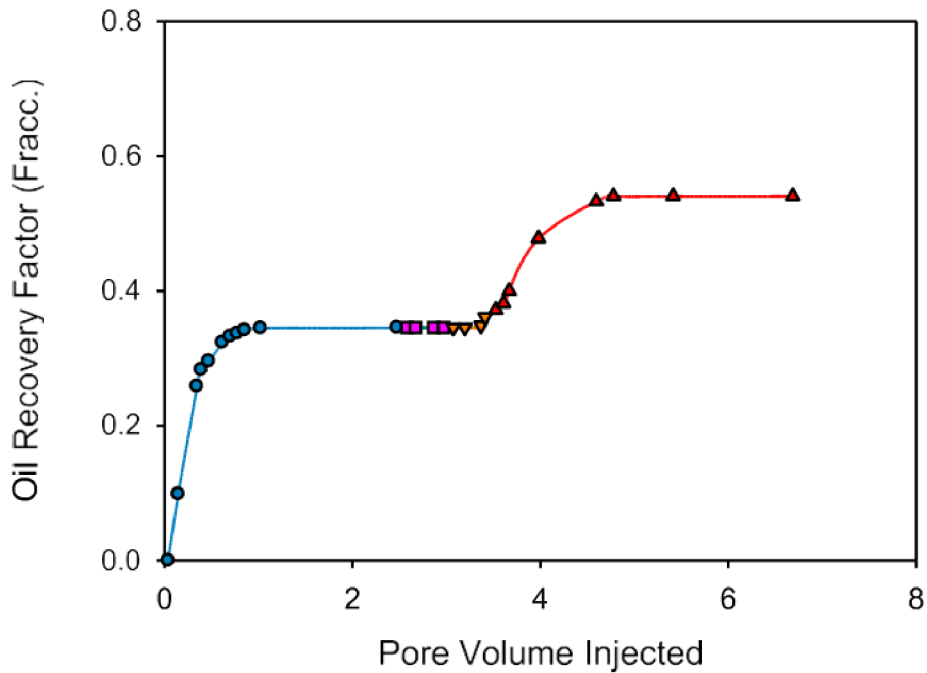


Figure (12): Core Flooding test 2. ● Water flooding (0.05 mL/min) ■ Surfactant flooding (0.025 mL/min) ▼ Polymer Flooding (0.025 mL/min) ▲ Polymer Flooding (0.05 mL/min). (Somoza et al., 2021).

The researchers concluded that the mixed surfactant system based on RECOLAS 158 and T2EG SAIL has the potential to be an effective EOR agent for carbonate reservoirs. The studies presented in the article provided evidence for the system's low interfacial tension and good stability in high salinity and high-temperature conditions, suggesting that it could help to mobilize trapped oil in these challenging environments.

The study concluded that the mixed surfactant system based on the cationic SAIL and anionic surfactant has potential as an effective EOR agent for carbonate reservoirs. The system was found to have a low interfacial tension, which could help to mobilize trapped oil in the reservoir. Additionally, the system showed good stability in high salinity and high-temperature conditions, which are common in carbonate reservoirs.

The study also highlighted the challenges associated with EOR in carbonate reservoirs, particularly the high salinity and high-temperature conditions that can make surfactant-based EOR methods less effective. To address these challenges, the researchers developed a novel

mixed surfactant system based on a cationic SAIL and anionic surfactant that was specifically designed to have good stability in high salinity and high-temperature environments.

Overall, the study provided valuable insights into the development of surfactant-based EOR methods for challenging reservoir conditions, and demonstrated the potential of the mixed surfactant system based on the cationic SAIL and anionic surfactant as an effective EOR agent for carbonate reservoirs.

#### **4.3 Impact of surface roughness, surface charge, and temperature on sandstone wettability alteration by nanoparticles. (Zhang et al., 2019).**

The study provides an overview of the importance of wettability alteration in oil recovery processes and the potential of nanoparticles for achieving this. The authors note that wettability alteration can improve oil recovery efficiency by reducing the capillary forces that trap oil in the reservoir rock. The introduction highlights that traditional methods of wettability alteration, such as chemical injection, can be costly and have negative environmental impacts. Nanoparticles, on the other hand, have the potential to be more effective and environmentally friendly. The authors then review the existing literature on wettability alteration and the use of nanoparticles in this process. The literature review highlights the potential of nanoparticles for altering the wettability of oil reservoirs and improving oil recovery efficiency. The authors note that nanoparticles can alter wettability through various mechanisms, including changing the surface charge of the rock, reducing the contact angle between the rock and water, and altering the interfacial tension between the oil and water phases.

The main aim of this study was to investigate the impact of surface roughness, surface charge, and temperature on the wettability alteration of sandstone using nanoparticles. Specifically, the study aimed to determine the optimal conditions for altering the wettability of sandstone using different types of nanoparticles, including silica, titanium oxide, and aluminium oxide. The main aim was to investigate how the wettability of sandstone can be altered using nanoparticles, and how different factors such as surface roughness, surface charge, and temperature affect this process. The authors used different types of nanoparticles, including silica, titanium oxide, and aluminium oxide, and aimed to determine the optimal conditions for achieving wettability alteration. Sandstone is a common type of reservoir rock in oil fields, and its wettability is an important factor that affects oil recovery efficiency. By altering the wettability of sandstone, capillary forces that trap oil in the rock can be reduced, making it easier to recover the oil.

The authors of this study focused on three key factors that can affect the wettability alteration of sandstone using nanoparticles: surface roughness, surface charge, and temperature. Surface roughness refers to the texture of the sandstone surface, and the authors hypothesized that rougher surfaces might provide more surface area for nanoparticle attachment and therefore result in more effective wettability alteration. Surface charge refers to the electrical charge of the sandstone surface, and the authors hypothesized that nanoparticles with a similar charge could interact more strongly with the surface and lead to more effective wettability alteration. Temperature can also affect the wettability alteration process, as changes in temperature can alter the interfacial tension between the oil and water phases, which in turn can affect the wetting behaviour of the sandstone. To investigate these factors, the authors conducted experiments using different types of nanoparticles and varying surface roughness, surface charge, and temperature. The authors measured the contact angle between the sandstone surface and water before and after nanoparticle treatment, which provided a measure of the wettability of the sandstone. Overall, the study aimed to provide insights into how different factors can affect the wettability alteration of sandstone using nanoparticles, and to determine the optimal conditions for achieving this. By understanding the mechanisms underlying this process, the authors hoped to provide a foundation for the design of more effective and efficient nanoparticle-based wettability alteration processes in the future.

The authors reviewed the existing literature on wettability alteration and the use of nanoparticles in oil recovery processes. The literature review highlighted the potential of nanoparticles for altering the wettability of oil reservoirs and improving oil recovery efficiency. The authors also noted that the effectiveness of nanoparticles in wettability alteration depends on various factors, including the size, shape, and surface properties of the particles. In their literature review, the authors of this study surveyed the existing research on wettability alteration and the use of nanoparticles in oil recovery processes. The authors noted that there is growing interest in the use of nanoparticles for wettability alteration, as these tiny particles have the potential to alter the properties of the reservoir rock in ways that traditional chemical methods cannot.

The literature review highlighted the potential of nanoparticles for improving oil recovery efficiency by altering the wettability of oil reservoirs. The authors pointed out that reducing the capillary forces that trap oil in the rock can make it easier to recover more of the oil, which can be especially important in cases where conventional recovery methods have been exhausted. Nanoparticles can alter wettability through a variety of mechanisms, such as changing the

surface charge of the rock, reducing the contact angle between the rock and water, and altering the interfacial tension between the oil and water phases.

However, the authors also noted that the effectiveness of nanoparticles in wettability alteration can depend on various factors, such as the size, shape, and surface properties of the particles. For example, smaller nanoparticles may be more effective at penetrating the pores of the rock and altering the surface properties, while larger particles may be more likely to get trapped in the pore throats and be less effective. The shape of the particles can also affect their interaction with the rock surface, with elongated particles potentially being more effective at penetrating the pores than spherical particles. In addition to size and shape, the surface properties of the nanoparticles can also affect their ability to alter wettability. The authors noted that nanoparticles with a high surface area-to-volume ratio, such as those with porous or rough surfaces, may be more effective at interacting with the rock surface and altering its properties. The surface charge of the nanoparticles can also affect their interaction with the rock surface, with particles that have a similar charge to the surface being more likely to adhere to it. Overall, the literature review provided important context for the study and highlighted the potential of nanoparticles for wettability alteration in oil recovery processes. By considering the factors that can affect the effectiveness of nanoparticles in this process, the authors were able to design more targeted experiments to investigate the impact of surface roughness, surface charge, and temperature on sandstone wettability alteration by nanoparticles.

To investigate the impact of surface roughness, surface charge, and temperature on sandstone wettability alteration by nanoparticles, the authors of the study conducted a series of experiments. They used different types of nanoparticles, including silica, titanium oxide, and aluminium oxide, and varied the surface roughness, surface charge, and temperature of the sandstone samples. The experiments were conducted in a custom-designed experimental setup that allowed the authors to measure the contact angle between the sandstone surface and water before and after nanoparticle treatment. The contact angle is a measure of wettability, with smaller contact angles indicating a more water-wet surface and larger contact angles indicating a more oil-wet surface. The authors used this measurement to assess the effectiveness of the nanoparticles in altering the wettability of the sandstone samples. In the experimental setup, the sandstone samples were first cleaned and dried, and then coated with the nanoparticles using a variety of methods, including immersion and injection. The authors varied the surface roughness of the sandstone samples by polishing them with different grades of sandpaper, and varied the surface charge by adjusting the pH of the nanoparticle suspension. To investigate the



impact of temperature on wettability alteration, the authors heated the sandstone samples to different temperatures using a custom-designed heating stage. The authors monitored the contact angle of the sandstone samples before and after nanoparticle treatment at different temperatures to determine the optimal temperature range for wettability alteration. By conducting experiments in a controlled environment and varying the relevant parameters, the authors were able to investigate the impact of surface roughness, surface charge, and temperature on sandstone wettability alteration by nanoparticles. The results of these experiments provided important insights into the mechanisms by which nanoparticles can alter wettability and identified optimal conditions for nanoparticle treatment to improve oil recovery efficiency. **Table (3)** shows initial conditions of synthetic surfaces.

Table (3): Average grain diameter ( $d$ ) and surface roughness ( $Ra$ ) of the synthetic surfaces. (Zhang et al., 2019).

Surface No.	Sieve size, $\mu\text{m}$	$d$ , $\mu\text{m}$	$Ra$ , $\mu\text{m}$
1	< 38	15.4	27.1
2	38–75	42.1	47.3
3	75–105	86.8	75.1

The results of the study showed that nanoparticles can effectively alter the wettability of sandstone by reducing the contact angle between the rock surface and water. Specifically, the study found that the addition of nanoparticles led to a decrease in the contact angle of the sandstone samples, indicating that the surface had become more water-wet. This effect was observed for all three types of nanoparticles studied, including silica, titanium oxide, and aluminium oxide. The study also found that the surface roughness and charge of the sandstone played a significant role in the wettability alteration process. Rougher surfaces showed a more significant response to the nanoparticles, likely due to the increased surface area available for nanoparticle attachment. In terms of surface charge, the authors found that changing the pH of the nanoparticle suspension could lead to changes in wettability alteration. The temperature of the system was found to be another important factor affecting the wettability alteration process. The authors observed that higher temperatures led to more significant changes in wettability, likely due to increased mobility of the nanoparticles and enhanced adsorption onto the sandstone surface. Finally, the study found that the effectiveness of the nanoparticles varied depending on the type of nanoparticle used. Silica nanoparticles showed the most significant

wettability alteration effect, likely due to their small size and high surface area, which allowed for more efficient attachment to the sandstone surface. Overall, the study provides important insights into the use of nanoparticles for wettability alteration in oil recovery processes. By identifying the key factors that affect wettability alteration, including surface roughness, surface charge, and temperature, the study highlights the importance of considering the surface properties and environmental conditions in the design of such processes. **Table (4)** shows the effects of wettability on surface roughness.

Table (4): Average grain diameter ( $d$ ), surface roughness ( $R_a$ ), measured contact angle ( $\theta_m$ ), surface roughness ratio ( $r$ ), and calculated contact angle ( $\theta_c$ ) for the synthetic surfaces.

Surface No.	$d$ , $\mu\text{m}$	$R_a$ , $\mu\text{m}$	$\theta_m$ , degree	$r$	$\theta_c$ , degree
1	15.4	27.1	108.6	2.68	96.9
2	42.1	47.3	118.7	1.91	104.5
3	86.8	75.1	133.1	1.53	116.6
4	133.2	129.0	138.3	1.72	115.7

Based on the experimental results, the authors concluded that the use of nanoparticles can effectively alter the wettability of sandstone and that this effect is influenced by the surface roughness, surface charge, and temperature of the system. The authors also found that the type of nanoparticle used plays a significant role in the effectiveness of wettability alteration. They found that the nanoparticles can reduce the contact angle between sandstone and water, which indicates a change in wettability. The effectiveness of the nanoparticles in altering wettability depends on various factors, including the type of nanoparticle used, the surface roughness and charge of the sandstone, and the temperature of the system. For example, rougher sandstone surfaces showed a more significant response to the nanoparticles, and higher temperatures led to more significant changes in wettability. The authors' conclusion highlights the potential of using nanoparticles for wettability alteration in oil recovery processes. By altering the wettability of the rock surface, the nanoparticles can improve the efficiency of oil recovery processes, leading to increased oil production and reduced costs. However, the authors note that the design of such processes must consider the surface properties and environmental conditions of the oil reservoir to achieve the best results.

## 5. Discussion

The relationship between subsurface chemistry, wettability, and oil recovery allows us to address one of the most fundamental challenges in petroleum engineering. This is a significant advancement that has the potential to significantly develop the field and enable us to accurately modify waterflood chemistry for maximum oil recovery.

By examining the influence of rock mineralogy (chalk, limestone, dolomite, and sandstone), surface active compounds (SACs), and temperature. To isolate the effects of particular SACs, the oleic phase of this experiment was represented by mixes of pure decane and a single SAC. The principal findings of this investigation were:

1. In the case of Sandstone, only the long-chained oxygen acids altered wettability by causing an increase in oil-rock adhesion as salinity declined. Therefore, among the studied SACs, long-chained oxygen SACs had the greatest effect on the wettability of Sandstone.
2. As their concentration grew, short-chained oxygen SACs, non-acidic sulfur SACs, and nitrogen SACs encouraged water-wet conditions in carbonate rocks. On the other hand, long-chained oxygen SACs and sulfur SACs with an acidic pH increased oil-rock adhesion. Organic acids exhibited a greater oil-wet shift than acidic sulfur SACs due to the fact that they are more acidic and, thus, more deprotonated under the experimental circumstances. Nitrogen and oxygen SACs must have had the biggest effect on the wettability of carbonates.
3. It was discovered that carbonates are more vulnerable to salt than sandstone. As brine salinity fell in the case of carbonate rocks, nitrogen SACs and short-chained oxygen SACs altered the wettability of the carbonate rocks towards water-wet conditions. In contrast, long-chained acid SACs, sulfuric acid SACs, and aromatics changed the wettability of carbonates towards oil-wet conditions. This disparity in SAC response to salinity has been suggested as one of the reasons why low salinity waterflooding is successful in certain reservoirs but not others. This study argues that the absence of a low salinity impact may also be attributable to a crude oil containing high levels of oil-wet promoting SACs with minimal sensitivity to salinity variation and/or low amounts of water-wet promoting SACs. In order for IOR operations relying on wettability modification to be effective, it is crucial to have a comprehensive understanding of the crude oil, brine, and rock mineralogy. This study suggests a further definition of crude

oils in which SACs may be discovered and measured according to their potential to promote oil-wetness or water-wetness

4. Temperature was discovered to influence the wettability of carbonate rocks. Low temperatures (25 °C) and higher temperatures (70 °C and 110 °C) resulted in considerable differences in the wettability of the rocks. The majority of the wettability change occurred at higher temperatures, and the difference between the two highest temperatures was little to nonexistent.

This study identified two fundamental features of wettability: microscale vs macroscale wettability and intrinsic versus situational wettability. Traditionally, wettability categories are often determined by the standard procedures for measuring wettability. Typically, these approaches test wettability at various scales. This has led to a great deal of uncertainty in the literature, particularly in the definition of heterogeneous wettability. I have discovered that scale must be taken into account while considering wettability. On a microscopic size (grain scale), wettability is uniform. On a large scale, wettability is heterogeneous because it represents the average wettability of all grains. Lastly, it is not an intrinsic quality of the rock surface to be water- or oil-wettable. Rather, it depends on the oil, water, rock, and temperature. These four criteria establish a distinct geochemical situation that results in a particular wettability state. Consequently, the wettability of a rock might range from water-wet to oil-wet depending on the existing geochemical situation. This makes a rock's wettability situational rather than an inherent property.

## **5.1 Recommendations**

1. I advise the development of an analytical method for identifying and quantifying surface-active chemicals in crude oils. Subsequently, these surface-active chemicals will be analyzed under various geochemical settings in order to compile a database relating their capacity to increase, decrease, or have no effect on the wettability of various rock types. This work aims to better define crude oils and give relevant and reliable information that can be utilized to construct accurate models for predicting wettability.
2. I discovered that both long-chained oxygen SACs and nitrogen SACs play a significant influence in carbonate rock wettability. To identify which of the two SAC groups has the greater influence on wettability, it is necessary to conduct a systematic research of the effects of mixing long-chained oxygen SAC (acids) that enhance oil-rock adhesion

with nitrogen SAC (bases) that improve water-wettability. This proposed study would emphasize the synergistic effects of the two groups, but more critically, it would identify the SACs that promote or inhibit oil-rock adhesion.

3. The effects of SACs on the wettability of sandstone and carbonate rocks in the presence of different brine salinities and temperatures were investigated. I suggest further this research by evaluating the impact of SACs in the presence of identified possible deciding ions, varying pH levels, and diverse sandstone and shale rock types. Additionally, I suggest researching more than three SACs per chemical group.
4. To gain a better understanding of how these SACs might alter wettability in a real reservoir, I suggest repeating these tests at pH settings typical of the reservoir and analyzing the influence of the basic SACs.
5. Finally, I suggest incorporating the data collected by this experiment in a model of surface complexation. A surface complexation model is a chemical model that mimics the chemical equilibrium and depicts the processes occurring at the interface of mineral and solution. The reactions result in the creation of surface complexes, which are ultimately responsible for the charges at the mineral surface and have particular equilibrium (stability) constants comparable to bulk solution reactions.

## 6. Conclusion

In conclusion, long-chained organic acids change the oil-wettability of all four rock types. The short-chained organic acids had no influence on the wettability of Sandstone, but they pushed the wettability of the three carbonate rocks toward water-wettability. Sulfur SACs had no influence on the wettability of sandstone. When present in large quantities, Dibenzothiophene (S<sub>1</sub>) and Di-n-butyl sulfide (S<sub>2</sub>) alter the wettability of carbonate rocks towards water-wet. 1-Tetradecanethiol (S<sub>3</sub>) has the opposite impact on the wettability of 1-tetradecanethiol. The tested nitrogen SACs had no influence on the wettability of Sandstone, however they changed the wettability of carbonate rocks towards water-wet. These studies also demonstrate that the sensitivity of SAC to concentration depends on the mineralogy of the rock. In the case of Sandstone, for instance, all SAC except for the long-chained acids had no influence on wettability regardless of the SAC content. The only SAC with concentration sensitivity was naphthenic acid. At the lowest concentration (1000 ppm), myristic acid moved the wettability of 100 percent of the rock towards oil-wettability; consequently, the sensitivity to concentration could not be identified. However, these findings also demonstrate the dynamic character of carbonate rock-oil-water systems. All SACs altered the wettability of carbonate rocks to some degree, particularly at 4000 ppm. For instance, as the quantity of acetic acid (O<sub>1</sub>), non-acidic sulfur compounds (S<sub>1</sub> & S<sub>2</sub>), and nitrogen SACs rose, the water content of carbonate rocks increased. For carbonate rocks, it is difficult to determine the concentration sensitivity of the long-chained acids since, at the lowest concentration, these acids completely oil-wet the rock.

## 7. References

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