

**Mechanism and influence of wettability alteration using
Gemini surfactants in carbonate EOR**

BY

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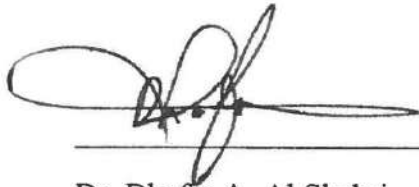
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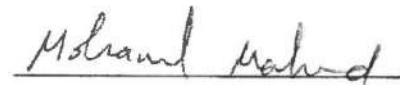
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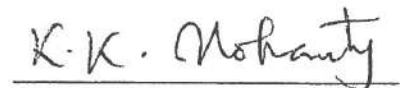
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|人生如碧野，立一茫茫身。

秦风兴楚水，落日黯浮尘。

慕贤来万里，怀旧尽孤樽。

长歌不快意，谁与游纷纭。 |

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LIST OF ABBREVIATIONS

EOR	:	enhanced oil recovery
IFT	:	interfacial tension
WA	:	wettability alteration
DI	:	deionized water
SW	:	seawater
DTPA	:	diethylene triamine penta acetic acid
DSD	:	ethylene diamine tetra acetic acid di-sodium salt dihydrate
EDTA	:	ethylene diamine tetra acetic acid
GLDA	:	glutamic acid diacetic acid
TSSH	:	ethylene diamine tetra acetic acid tetra-sodium salt hydrate
ZS	:	zwitterionic surfactant
VES	:	viscoelastic surfactant
GS	:	gemini surfactant

|

ABSTRACT

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Thesis Title : [Mechanism and influence of wettability alteration using Gemini surfactants in carbonate EOR]

Major Field : [Petroleum Engineering]

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Half of the world proved oil reserves are in carbonate formations. However, carbonate formations are mostly oil-wet and naturally fractured. A large amount of oil remains in the rock matrix after secondary recovery, substantially limiting the economic potential. There are different materials that can alter rock wettability, improving the oil recovery. Wettability alteration and IFT reduction are widely considered two of the most important mechanisms in enhanced oil recovery (EOR). Surfactants, applied initially for IFT reduction purpose, are found to induce wettability alteration. The performance depends on their molecular structures, and the formation fluids compositions. Among all surfactants, cationic surfactants generally have the strongest and irreversible wettability alteration performance in oil-wet carbonate rock. Gemini surfactants, as a novel type of surfactant, reduce IFT much more efficiently than conventional surfactants. Combining the advantages, cationic gemini surfactants are potential materials for the optimal performance in both wettability alteration and IFT reduction, implying favorable EOR outcomes.

This study focuses on 14 locally synthesized cationic gemini surfactants. The wettability alteration performance of studied surfactants and the influencing factors are studied, reflecting the wettability alteration performance of the studied surfactants, and the

relationship between surfactant molecular structure and the performance. Some other chemicals, including five chelating agents, and a zwitterionic surfactant, were also studied regarding their wettability alteration performance in deionized water, synthetic seawater, and diluted synthetic seawater solutions. From the studied materials, four cationic gemini surfactants, the zwitterionic surfactant, and chelating agent DTPA were selected for spontaneous imbibition tests, reflecting the relative importance of interfacial tension (IFT) reduction and wettability alteration in the imbibition oil recovery. The 14 cationic gemini surfactants' wettability alteration performance varied widely from weak to strong. Surfactants with one phenyl group in the spacer performed the best that changed oil-wet rock to water-wet conditions. Unsaturation in the spacer and salinity in the solution have a strong negative impact. Other features, including spacer length, and count-ion, showed less significant influences. With the addition of the chelating agent into gemini surfactant solutions, the salinity tolerance, and wettability alteration performance is significantly improved. Spontaneous imbibition results indicate that for oil-wet carbonate rock when wettability alteration happens, both enhancing wettability alteration, and alleviating IFT reduction, can increase and accelerate the oil recovery. Though permeability had a significant impact on imbibition process, it was more auspicious when IFT reduction became the main driving force.

ملخص الرسالة

الاسم الكامل: DENG XIAO

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التخصص: **Petroleum Engineering**

تاريخ الدرجة العلمية: PhD

CHAPTER 1

INTRODUCTION

1.1 Background

Half of the world proved oil reserves are in carbonate formations. However, carbonate formations are mostly oil-wet and naturally fractured. These fractures make it difficult to apply a large pressure gradient through the matrix to overcome the capillary forces ¹. As a result, a large portion of the original oil in place (OOIP) may be left behind after water flooding ^{2,3}. Different enhanced oil recovery (EOR) methods have been studied and applied, especially when oil prices increase rapidly in recent years. A study done by Manrique et al. analyzed 1507 international EOR projects and found that much more EOR applications have been done in sandstone rather than in carbonate. Considering the proven reserves in different lithologies, the application of EOR methods has great potential in carbonate reservoirs.

Oil-wet state of the rock surfaces has proved to be induced by organic adsorption ⁴⁻⁷, which depends strongly on the conditions such as pH, salinity, and properties of the oil ⁸. One of the most accepted explanations was given by Buckley et al. ⁷. They believed that four possible mechanisms induce organic adsorption in carbonate rocks, which include: polar interactions, surface precipitation, acid/base interactions, and ion binding ⁷. Under the combined contribution of different mechanisms, the surface-active material moves from the oil/water interface and adsorbs onto the rock surface, forming a monolayer lipophilic structure that renders carbonate rock oil wetness ^{4,5}.

Among all organics that render carbonate rock oil-wetness, fatty acids and carboxylate anions have proved to be the most important ^{6,9,10}. Carbonate rock is positively charged by nature. Negative ions from formation fluid are adsorbed onto calcite surface, in which fatty acids and carboxylate polymers are believed to be the dominating components ⁹. Experimental studies have shown that those components have a high affinity towards carbonate and their adsorption tends to be a very fast process ^{11,12}, which is irreversible ^{4,5,13}. Thomas et al. attributed this irreversible adsorption to a combined effect of the increased affinity towards carbonate brought by carboxylate groups and the additional stability provided by a long, straight chain of fatty acids ⁵. The experiments taken by Wu et al. have shown that within these naphthenic acids, an increase in alkyl chain length reduces their adsorption but increases the ultimate oil-wetness ¹⁴. They concluded that the induced oil-wetness was not directly related to the adsorption of naphthenic acids, but depended on their molecular structure instead ⁵. Since the acid number (AN) of oil is closely related to the number of fatty acids and carboxylate anions, it can be used to estimate the degree of oil-wetness of aged chalk ¹⁵. Natural petroleum base is believed to form complexes with carboxylates in the oil and prevent them from covering rock surfaces ¹⁶. Generally, oil wetness increases with the increase in AN ^{7,15}. There is no direct relation between the amount of asphaltenes and rock wettability, although the asphaltene amount is usually related to AN ¹¹. Researchers hold different opinions about the influence of temperature on the wettability of aged carbonate. Thomas et al. suggested that increased temperature could alleviate this oil-wetness induced by the organic material coating due to enhanced aqueous solubility of organic adsorbates ⁴. Zhang and Austad, however, argued that the effect of temperature is a minimum ¹⁵.

The removal of adsorbed organic material will change rock surface condition and thus influence its wettability. Wettability alteration has been recognized as an important mechanism that enhances

the oil recovery from carbonate reservoirs by changing the wettability of rock toward water-wet conditions. There are different types of wettability modifiers including surfactants, nanoparticles, salts, and alkalis. Among them, surfactants and alkalis are observed to reduce IFT significantly meanwhile.

Gemini surfactants are a novel type of surfactant having two head groups and two tail groups and a spacer group. Their structures are very much like two conventional surfactant molecules connected by a spacer group. Gemini surfactants are found to effectively change oil-wet surface to water-wet conditions ^{17,18,19}. In sandstone formations, gemini surfactants can induce contact angle reduction of 140~40 ²⁰, 110~10 ¹⁹ as well as higher imbibition recovery than conventional surfactants ^{18,20}. Promising results are also found in carbonate rock cases in a few studies. Qi et al. observed that carbonate samples treated by gemini surfactants changed from intermediate-wet to strongly water-wet ²¹. Ghosh and Mohanty observed that mineral calcite plates treated by cationic gemini surfactant changed from oil-wet to intermediate-wet ^{22,23}. Due to these encouraging results and their outstanding properties compared to conventional surfactants, gemini surfactants can be good EOR material for oil-wet carbonate rocks. However, since the study on wettability alteration efficacy of gemini surfactants is limited, further investigation of the WA mechanism and performance of gemini surfactants is needed.

To help explain the mechanisms behind the wettability alteration induced by surfactants, a series of the experimental study were conducted. Different parameters including temperature, rock porosity, and permeability, fluid salinity and salt compositions, surfactant molecular structure, surfactant treatment time, and surfactant concentrations were studied. Aside from the cationic surfactants, other chemical EOR materials, including a zwitterionic surfactant, and five chelating agents, were also studied regarding their wettability alteration and IFT reduction potential.

1.2 Problem statement and research objectives

Gemini surfactants are relatively novel materials for wettability alteration (WA). A good understanding of their mechanisms and application efficacy is required. Gemini surfactants have novel molecular structures and micellar behavior. The current understanding of wettability alteration induced by conventional surfactants may not apply in gemini surfactant cases. There is related work yet to be done:

There are only a few papers that discussed the relative importance of IFT reduction over wettability alteration in carbonate EOR. There is no experimental work on this topic yet. However, a better understanding of this topic could be very helpful.

There are only a few papers of experimental work that present the wettability alteration performance of gemini surfactants in carbonate reservoirs. No discussion on the relationship between surfactant structure and properties has been proposed. The influence of surfactant concentration is not discussed either.

Due to the lack of knowledge on the mentioned aspects, the main objectives are listed below:

1. The relative importance of WA over IFT reduction on carbonate rock EOR;
2. WA performance of gemini surfactants in carbonate rocks. In this part, influencing factors such as concentration and brine composition are to be discussed;
3. The relationship between gemini surfactants' structure and their properties.

With the results of those objectives, this study is meant to provide further knowledge about the wettability alteration by gemini surfactants and a better understanding of whether IFT reduction or WA is more important in the carbonate EOR process.

1.3 Measurement techniques

1.3.1 Contact angle measurement

There are different contact angle measurement techniques. The sessile drop method is mostly used, in which a drop of fluid settles on the surface of the substrate. A camera is used to capture the angle between the solid/liquid interface and the tangent to the liquid/vapor interface, which is considered as contact angle ²⁴. In our study, it was conducted using the Theta Attension Tensiometer from Biolin Scientific. The accuracy of this instrument is $\pm 0.1^\circ$.

1.3.2 Spontaneous imbibition experiment

Spontaneous imbibition and coreflooding are helpful techniques to link wettability alteration directly to enhanced oil recovery. By different core flooding experiments using different EOR fluids, or by further increased oil recovery after changing injected EOR fluid, we can link oil recovery directly to studied EOR fluids and thus have an assessment of them according to oil recovery. Spontaneous imbibition experiment links wettability alteration directly to oil recovery. Imbibition recovery can be obtained as an assessment of the EOR performance of different fluids. Besides, imbibition experiment results can also be analyzed to help explain different oil recovery from core flooding experiments. When combined, these two experiments can be applied to obtain a reliable assessment of the EOR performance of different fluids and also to reflect on the mechanism behind increased oil recovery.

The imbibition experiment is conducted by immersing oil-saturated cores inside prepared EOR fluid in the Amott cells for some time. If the EOR fluid successfully changed rock to water-wet, capillary pressure will drive the EOR fluid inside and displace the oil. Besides, the oil may also be produced by gravity from the upper surface of the core. Measure the produced volume of oil and compare different cases, the recovery differences are results of wettability alteration differences. Imbibition experiment is widely applied to study wettability alteration since no extra pressure is supplied so the oil production is closely related to wettability alteration.

1.3.3 SEM

Scanning Electron Microscope (SEM) can provide direct visualization of inter-granular fluid distribution in rock. SEM imaging shows directly how the additives affect rock surfaces, proves the efficacy of that treatment, and helps explain the mechanism. In addition, SEM is used to provide the core-scale to-pore-scale surface images of rock samples. In a word, SEM can be used as a qualitative method that detects wettability change and helps to understand the mechanisms.

1.3.4 Spinning drop method

The spinning drop method is widely used in measuring the interfacial tension (IFT) between oil and water. In our study, it was conducted using the instrument provided by Kruss. The measuring range of this instrument is 10^{-6} to 2000 mN/m. The resolution is 10^{-6} mN/m.

1.4 Thesis arrangement

This thesis is arranged into three main parts:

1. Chapter 1 as the introduction part;

2. Chapter 2 and Chapter 3 as the literature review part. Chapter 2 focuses on the wettability modifiers in carbonate reservoirs. Chapter 3 focuses on the relative contribution of IFT reduction and wettability alteration;
3. Chapter 4 to Chapter 7 as the experiments, results, and conclusions part. Chapter 4 studies the locally synthesized cationic gemini surfactants. Chapter 5 studies other chemicals, including five chelating agents and a zwitterionic surfactant, as potential chemical EOR materials for carbonate reservoirs. Chapter 6 studied the performance of the mixture combining chelating agent DTPA and our locally synthesized cationic gemini surfactant GS8. Contact angle results given in Chapters 4, 5, and 6 reflect on the wettability alteration performance of different materials. Chapter 7 combines the results obtained from Chapter 4 to Chapter 6 with spontaneous imbibition results to reflect on the relative contribution of IFT reduction and wettability alteration. |

|CHAPTER 2

LITERATURE REVIEW 1: WETTABILITY MODIFIERS FOR CARBONATES

2.1 Introduction

Half of the world proved oil reserves are in carbonate formations. However, carbonate formations are mostly oil-wet and naturally fractured. These fractures make it difficult to apply a large pressure gradient through the matrix to overcome the capillary forces ¹. As a result, a large portion

of the original oil in place (OOIP) may be left behind after water flooding ^{2,3}. Different enhanced oil recovery (EOR) methods have been studied and applied, especially when oil prices increase rapidly in recent years like is shown in Figure 1(a). A study done by Manrique et al. analyzed 1507 international EOR projects and found that much more EOR applications have been done in sandstone rather than in carbonate, as is shown in Figure 1(b) ²⁵. Considering the proven reserves in different lithologies, the application of EOR methods has great potential in carbonate reservoirs.

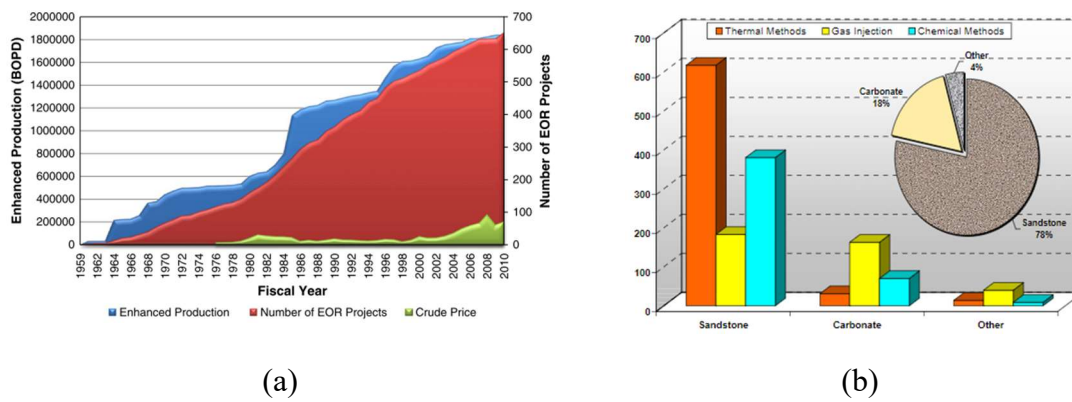


Figure 1 (a) EOR projects & enhanced production trend ²⁶; (b) EOR field projects by lithology.

Many studies have shown that wettability alteration can increase recovery significantly in carbonate reservoirs ^{14,27-29}. Wettability alteration is found to be one of the most important mechanisms that increase recovery ³⁰. Oil-wet state of the rock surfaces has proved to be induced by organic adsorption ⁴⁻⁷, which depends strongly on the conditions such as pH, salinity, and properties of the oil ⁸. One of the most accepted explanations was given by Buckley et al. ⁷. They believed that four possible mechanisms induce organic adsorption in carbonate rocks, which include: polar interactions, surface precipitation, acid/base interactions, and ion binding ⁷. Under the combined contribution of different mechanisms, the surface-active material moves from the oil/water interface and adsorbs onto the rock surface, forming a monolayer lipophilic structure that renders carbonate rock oil wetness ^{4,5}.

Among all organics that render carbonate rock oil-wetness, fatty acids and carboxylate anions have proved to be the most important ^{6,9,10}. Carbonate rock tends to have a positively charged surface under common formation pH values. Negative ions from formation fluid are adsorbed onto calcite surface, in which fatty acids and carboxylate polymers are believed to be the dominating components ⁹. Experimental studies have shown that those components have a high affinity towards carbonate and their adsorption tends to be a very fast process ^{11,12}, which is irreversible ^{4,5,13}. Thomas et al. attributed this irreversible adsorption to a combined effect of the increased affinity towards carbonate brought by carboxylate groups and the additional stability provided by a long, straight chain of fatty acids ⁵. The experiments taken by Wu et al. have shown that within these naphthenic acids, an increase in alkyl chain length reduces their adsorption but increases the ultimate oil-wetness ¹⁴. They concluded that the induced oil-wetness was not directly related to the adsorption of naphthenic acids, but depended on their molecular structure instead ⁵. Since the acid number (AN) of oil is closely related to the amount of fatty acids and carboxylate anions, it can be used to estimate the degree of oil-wetness of aged chalk ¹⁵. Natural petroleum base is believed to form complexes with carboxylates in the oil and prevent them from covering rock surface ¹⁶. Generally, oil wetness increases with the increase in AN ^{7,15}. There is no direct relation between the amount of asphaltenes and rock wettability, although asphaltene amount is usually related to AN ¹¹. Researchers hold different opinions about the influence of temperature on the wettability of aged carbonate. Thomas et al. suggested that increased temperature could alleviate this oil-wetness induced by the organic material coating due to enhanced aqueous solubility of organic adsorbates ⁴. Zhang and Austad, however, argued that the effect of temperature is a minimum ¹⁵.

As wettability alteration keeps gaining attention, several review works have been reported. Purswani et al. studied the applications and mechanisms of chemically tuned waterflooding, which

involves carefully controlled injection fluid salinity and salt composition ³¹. Negin et al. studied different kinds of nanoparticles and discussed their effect on wettability ³². Olayiwola et al. studied the wettability alteration induced by nanoparticles with low salinity water and surfactant in both sandstone and carbonate rocks.³³. Kazemzadeh et al. reported a comprehensive review on the use of nanoparticles in EOR processes ³⁴. Bartels et al. conducted a review on low salinity waterflooding, highlighting the influence of different scales, in which wettability alteration was discussed. Mohammed and Babadagli did a review on the wettability alteration materials and methods for both sandstone and carbonate ³⁵.

This chapter focuses on carbonate reservoirs and studies the potential of different wettability modifiers. Four main categories of wettability modifiers which include surfactants, nanoparticles, salts, and alkalis are discussed. Various techniques that have been used to evaluate the performance of wettability modifiers and underlying mechanisms are also described in this review. This review identified potential cost-effective wettability modifiers for carbonate reservoirs.

2.2 Wettability alteration techniques

This section discusses commonly used wettability measurement techniques. The most widely used techniques including contact angle measurement, Amott test, and USBM are described. Apart from that, some novel techniques are also described.

2.2.1 Conventional techniques

2.2.1.1 Contact angle measurement

There are different contact angle measurement techniques. The sessile drop method is mostly used, in which a drop of fluid settles on the surface of the substrate. A camera is used to capture the

angle between the solid/liquid interface and the tangent to the liquid/vapor interface, which is considered the contact angle ²⁴. Rock wettability is assessed according to criteria based on obtained contact angle values as given in Table 1.

Table 1 Rock Wettability and Contact Angle ³⁶.

Type	Contact angle (°)
Strongly water-wet	0-30
Water-wet	30-70
Intermediate-wet	70-110
Oil-wet	110-150
Strongly oil-wet	150-180

2.1.1.2 Amott-Harvey test

Amott-Harvey test is composed of two spontaneous imbibitions and two forced displacement processes. Imbibition oil saturation S_{oi} , total oil saturation S_{ot} , imbibition water saturation S_{wi} , and total water saturation S_{wt} are obtained from displaced phase volume and total pore volume ³⁷. Amott-Harvey Index I_{AH} , the wettability assessment, is defined in Equation 2.1:

$$I_{AH} = \left(\frac{S_{wi}}{S_{wt}} \right) - \left(\frac{S_{oi}}{S_{ot}} \right) \quad (2.1)$$

Based on the index, a rock wettability assessment can be made according to the criteria listed in Table 2.

Table 2 Rock Wettability and Amott-Harvey Index ³⁷.

Type	Amott-Harvey Index
Water-wet	0.3~1

Mixed-wet	-0.3~0.3
Oil-wet	-1~-0.3

2.1.1.3 USBM

USBM goes through the same process as the Amott-Harvey test. Its wettability index, I_{USBM} , is defined upon two parameters: the area under the oil-drive curve, A_o , and the area under the water-drive curve, A_w ³⁷.

$$I_{USBM} = \log \left(\frac{A_o}{A_w} \right) \quad (2.2)$$

Mostly, the index value is in the range of -2~2 ³⁸. Similarly, rock wettability is assessed according to the index values given in Table 3.

Table 3 Rock Wettability and USBM Index ³⁷.

Type	USBM index
Water-wet	>0
Mixed-wet	~0
Oil-wet	<0

2.2.2 Novel techniques

Although conventional techniques are the most widely used methods, they have shortcomings that limit their application. Contact angle measurements are taken on the rock surface, while wettability on the rock surface can be different from that inside the matrix ³⁹. Amott test and USBM both give a value that describes the overall wettability of a rock sample. However, they fail to directly show the wettability state on the pore scale. Besides, the Amott test has limited accuracy in neutral wetting conditions ³⁸. Some other techniques have been reported in the literature that can be used

to assess the wettability alteration quantitatively. Besides, some commonly used techniques that can reflect the mechanisms behind wettability alteration are also mentioned in this section.

2.2.2.1 Chromatographic study

The chromatographic study is a quantitative wettability test technique³⁸. This test checks the chromatographic separation between SCN^- and SO_4^{2-} as two tracers in chalk. The chromatographic separation takes place in water-wet regions. Since SO_4^{2-} has a high affinity toward chalk while SCN^- does not. The effluent will show a difference between the concentrations of the two tracers (see Figure 2), which is closely related to the water-wet area, A_{wett} , in rock. Taking the area of a completely water-wet sample, A_{heptane} , as a reference, a new wetting index, $W_{\text{chromatographic}}$, can be derived from the results according to Equation 3.

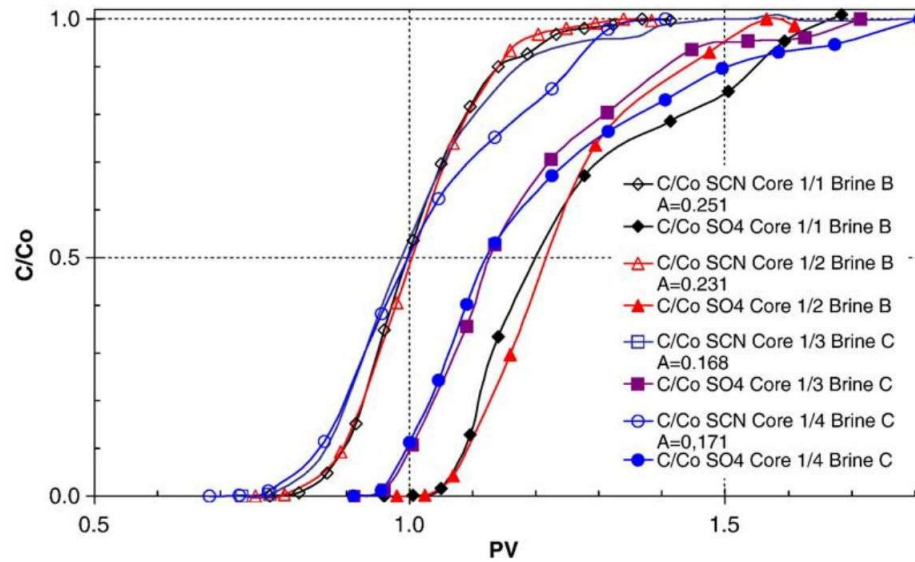


Figure 2 Typical effluent concentration plot result³⁸.

$$W_{I_{\text{chromatographic}}} = \frac{A_{\text{wett}}}{A_{\text{heptane}}} \quad (2.3)$$

2.2.2.2 Flotation test

The flotation test is based on the concept that lesser wetted particles are easier to float^{14,40}. As shown in Error! Reference source not found., there are a one-phase flotation test and a two-phase separation test. In one phase flotation test, wettability can be assessed by dividing the volume of the floating grains by the total volume¹⁴. In the two-phase separation test, wettability can be assessed by dividing the volume of grains in either phase by the total volume.

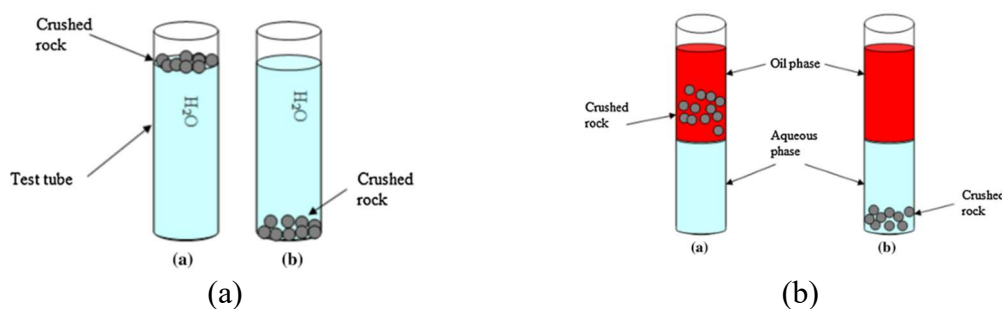


Figure 3 Typical flotation test (Left) and separation test (Right) results, (a) oil-wet and (b) water-wet in both cases⁴⁰.

The advantage of the flotation test is its extreme convenience. This test requires no core or plug, no smooth surface, and provides an overall description of the rock wetting state.

2.2.2.3 NMR

Carbonate rock is very heterogeneous even on a small scale. Correlations that describe sandstone can hardly apply to carbonate rock. It is especially helpful to have information about liquid distribution inside the carbonate rock matrix. Nuclear Magnetic Resonance (NMR) works by agitating the hydrogen proton that is abundant in both water and oil and detecting their response to the magnetic fields. Their response shows the existence of hydrogen protons, in petroleum engineering case, the existence of water and oil. On the other hand, water has a different relaxation time (T2) than oil. These two phases can be differentiated by their relaxation time, obtaining

information about residual saturations. Compared to fluid in bulk, fluid in contact with rock surface has a shorter relaxation time. For partially saturated pores, the relaxation rate of the non-wetting phase is dominated by fluid in bulk while that of the wetting phase is dominated by the fluid on the surface. In this way, the obtained relaxation time information can be translated into saturation and wettability index. There are several different wettability indexes based on NMR. An example of those indexes is developed by Chen et al.,⁴¹. This technique provides a way to utilize NMR data for wettability description and has been shown to correlate well with the Amott-Harvey test result. It should be noticed that this technique is based on the assumption that the rock sample is neutral to water-wet.

2.2.2.4 Micro-CT

Micro-CT or X-ray computed microtomography (μ -CT), is a visualization tool that can provide pore-scale images of the rock plugs as shown in Error! Reference source not found.⁴². Direct assessment of the pore-size distribution and the locations of remaining phases, such as aqueous and oil phases, can be obtained⁴². Analysis of generated tomograms provides information about phase residual and pore-scale contact angles on rock grains. Based on that, the wettability assessment will be obtained. Furthermore, the obtained images can also be analyzed to provide a more realistic pore structure in numerical models and micro-models.

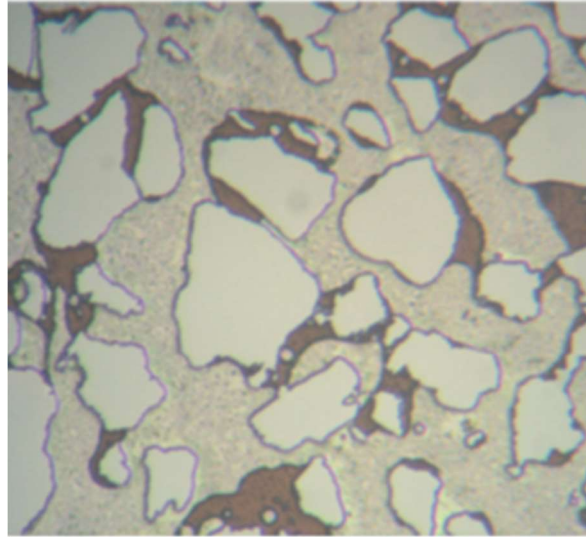


Figure 4 An example of Micro-CT image ⁴³.

2.2.2.5 SEM

Scanning Electron Microscope (SEM) can provide direct visualization of intergranular fluid distribution in rock. SEM is applied for wettability evaluation from the core-scale to pore-scale ¹⁰. In addition, SEM is used to provide the core-scale to pore-scale surface images of rock samples. Surface images before and after EOR treatment, as shown in Error! Reference source not found., can help to prove the efficacy of that treatment and explain the mechanism of wettability alteration. In a word, SEM can be used as a qualitative method that detects wettability change and helps to understand the mechanisms.

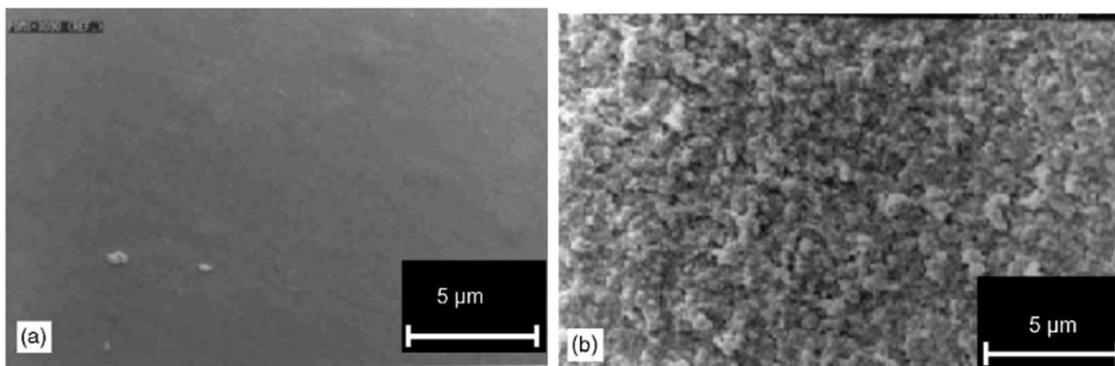


Figure 5 SEM images of surface modification before and after treatment ⁴⁴.

2.2.2.6 Infrared Spectroscopy

The infrared (IR) spectrum or Fourier Transform Infrared (FTIR) spectrum is used to determine components in a system based on their chemical bonding as given in Table 4. Different bonds give different wavenumber in IR. By analyzing the distribution of peaks over wavenumber and their corresponding height, as shown in Figure 6Error! Reference source not found., the components on sample surfaces and possible mechanisms in surface wettability change can be identified. The changes in peaks before and after EOR treatment indicate the mechanism and efficacy of wettability alteration⁴⁴. This technique is widely used in surfactant characterization and wettability alteration mechanism studies.

Table 4 Functional adsorbate groups and corresponding adsorption band⁴⁵.

Adsorption band (cm⁻¹)	Functional group
3400-3100 (broad band)	Stretching vibration of the phenol O-H bonds (the bands are broadened due to hydrogen bonding)
3300-2500	Broad -OH stretching vibration when a hydrogen bond is present, -OH associated (carboxylic acids)
3100	Stretching vibration of C-H bonds of aromatic compound
3000-2800	Stretching vibration of the alkyl C-H bonds (CH ₃ and CH ₂)
2805-2780	N-CH ₃ (aliphatic amines), CH ₃ Asym. Stretching vibration
2975-2950	Asym. C-H stretching vibration in R-CH ₃
2955-2920	Asym. CH ₂ stretching vibration in -OCH ₂ -
1800-1700	Stretching of the carbonyl groups C=O bonds (COOH)
1600	Stretching of the C=C bonds of conjugated and aromatic compounds
1500	Bending vibration of the O-H bond
1450-1370	Bending of the alkyl C-H bonds

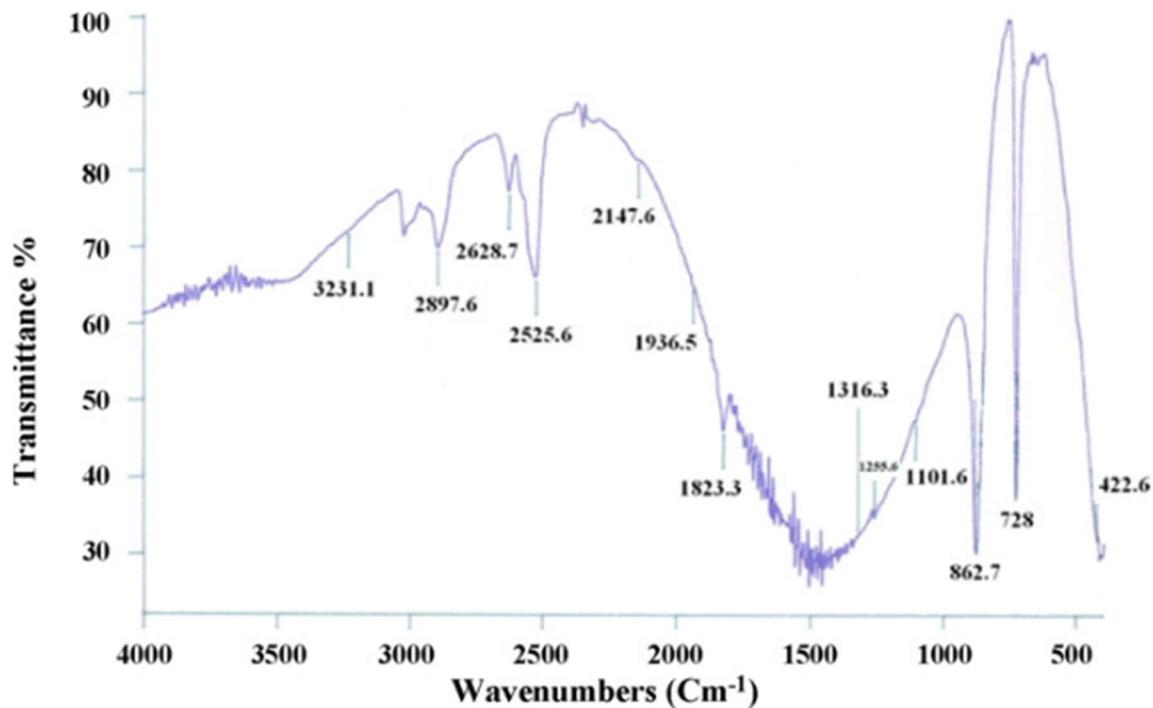


Figure 6 An example of FTIR result ⁴⁵.

2.2.2.7 TGA

Thermogravimetric analysis (TGA) monitors the mass change of a sample with increasing temperature ⁴⁵. Based on the relative strength of different bonds between rock surfaces and adsorbates, mass loss at different temperatures is related to the mass of the adsorbed component. For example, in Figure 7, aged wet dolomite has its weight loss occurs in a staged manner, indicating physical desorption (110-230 °C), decomposition of chemisorbed stearic acid (~380 °C), and degradation of dolomite mineral (>600 °C). In this way, adsorption type and amount on rock surface can be obtained. This analysis is commonly used to help explain the mechanism of wettability alteration and assess the improvement brought by the EOR method.

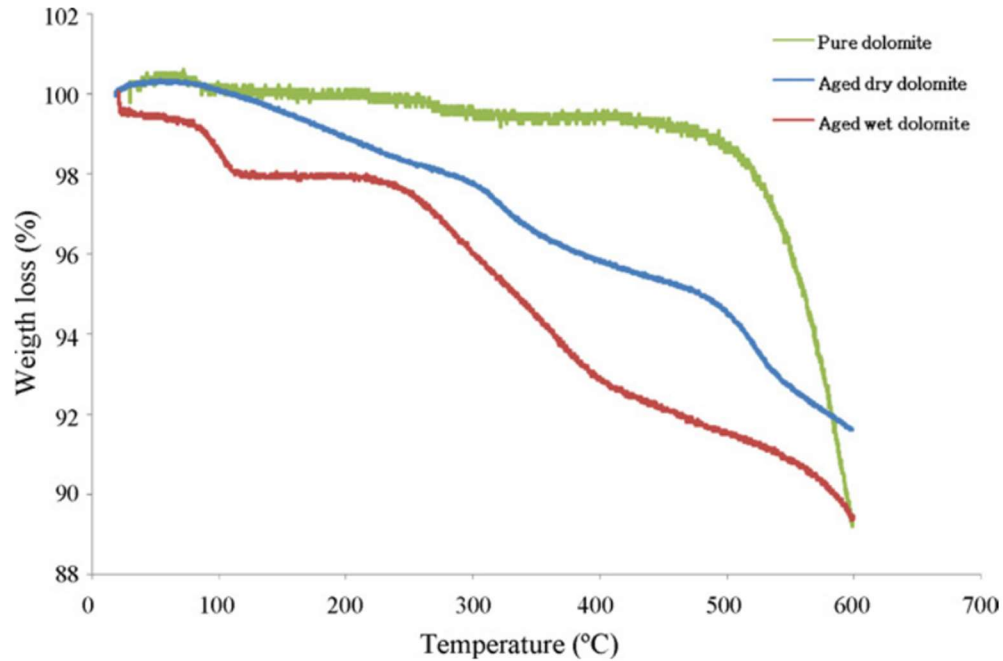


Figure 7 An example of TGA result ⁴⁵.

2.2.2.8 AFM

Atomic force microscopy (AFM) measures the force distance between a tip and the surface tested. By repeating the measurement until the whole surface of the sample is covered, we can obtain the image of that surface, soft or hard, dry or wet ⁴⁶. The difference in force-distance can be translated into compositional changes on the rock surface and thus is closely related to wettability ⁴⁶. For example, in Figure 8, (c) and (d) have smaller force distances and smoother surfaces, indicating adsorption of surfactant ⁴⁵. AFM is a convenient technique for showing the changes on sample surfaces, thus is commonly used to study the adsorption of materials such as surfactants, nanoparticles, organic materials, and so on. It is commonly used to help reflect wettability alteration mechanisms.

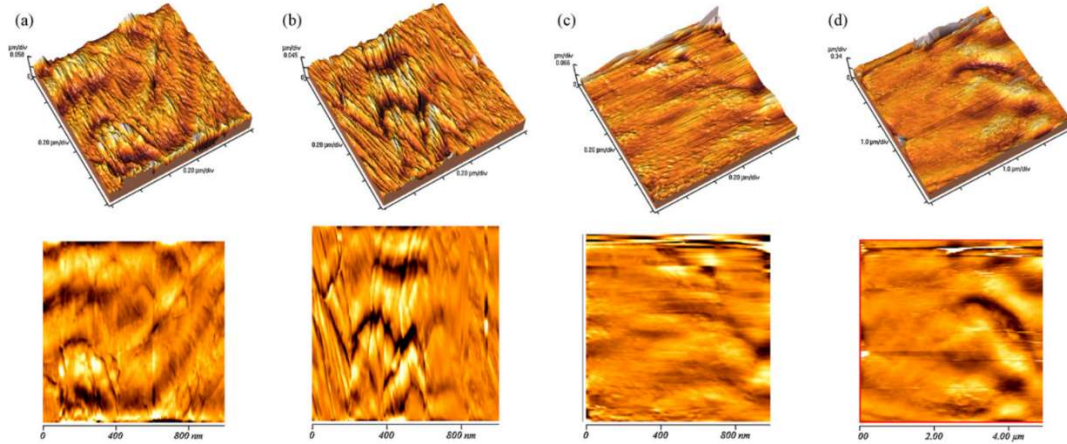


Figure 8 An example of AFM surface images ⁴⁵.

Among the techniques discussed, three provide wettability indexes that are convenient for comparison, including chromatographic study, flotation test, and NMR. The flotation test is the fastest and most convenient technique among those three. However, it requires that the rock sample is crushed into fine powders and has no extended cases in reservoir temperature or other types of rocks rather than chalk. Micro-CT technique provides pore-scale wettability information. Four techniques provide qualitative results about wettability change, including SEM, Infrared, TGA, and AFM. TGA is a destructive technique that is less repeatable than the other three techniques. Besides, it provides mass change information that supports surface changes and indicates adsorption types behind these changes. Infrared-based techniques are more precise in reflecting different adsorption types. SEM and AFM give direct images of rock surfaces that clearly show surface change.

2.3 Wettability modifiers

Materials that can modify the wetting state of rock surfaces are called wettability modifiers. Different modifiers will have different properties and thus induce a different reaction in the formation. Modifiers for specific formations should be carefully selected according to the nature

of formation rock, oil properties, formation pH, temperature, and salinity. There are four main categories of wettability modifiers in carbonate rock including surfactants, nanoparticles, salts, and alkalis.

2.3.1 Surfactants

Surfactants are surface-active molecules that have hydrophilic heads and lipophilic tails (Figure 9Error! Reference source not found.). Based on the different charges of the head, surfactants can be divided into cationic, anionic, nonionic, and zwitterionic surfactants ⁴⁷.

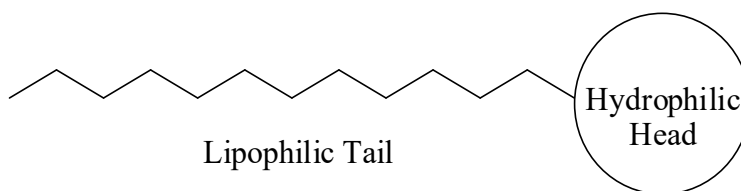


Figure 9 Schematic diagram of conventional surfactant.

Gemini surfactants are relatively new and have more than one head and tail linked by a spacer group (Figure 10). Surfactants have long been used to lower the interfacial tension between the oil and brine phases in surfactant flooding, thus improving oil recovery. Aside from that, they can also modify rock wettability ^{48,49}. It has also been suggested of applying to drilling fluid to reduce carbonate formation damage and keep reservoir rock water-wet ⁵⁰.

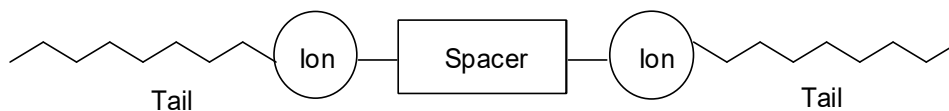


Figure 10 Schematic diagram of gemini surfactant.

There are four fundamental properties of surfactants namely: critical micelle concentration (CMC), Krafft temperature, hydrophilic-lipophilic balance (HLB), and cloud point (CP). Critical micelle concentration is the concentration of surfactant above which micelles start to form at specific conditions ³⁶. CMC can be measured by surface tension versus concentration of the surfactants ⁵¹

(Figure 11) because an increase in surfactant concentration above CMC will not bring major changes in surface tension. The electrical conductivity test can also be used to measure CMC value

52.

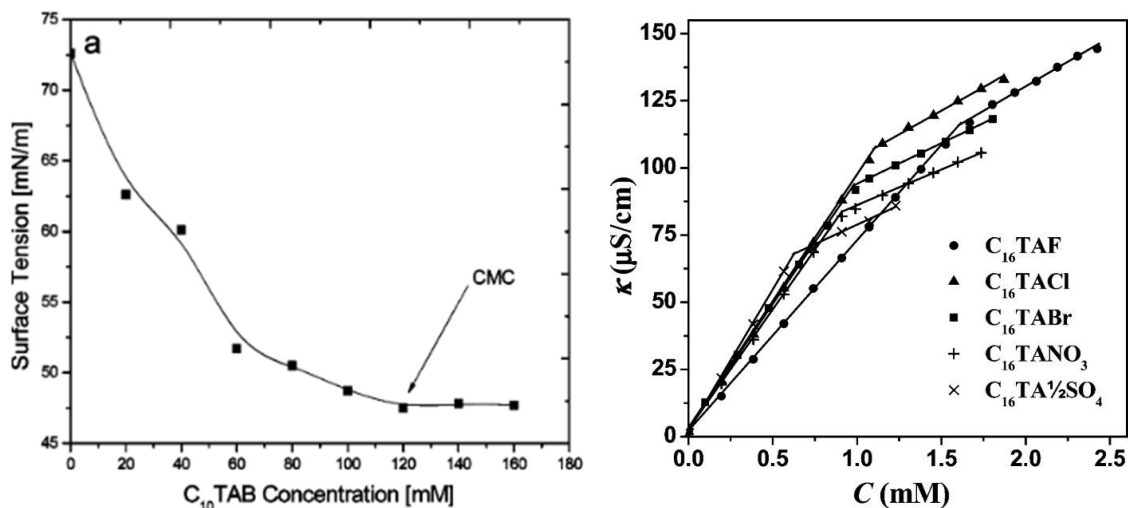


Figure 11 CMC Measured by Surface Tension⁵³ and Electrical Conductivity⁵².

The Krafft temperature is the minimum temperature that micelle can form³⁶. HLB is a value describing the degree of hydrophilicity or lipophilicity. HLB equals 1 means completely hydrophobic; HLB around 40 means completely hydrophilic³⁶. Surfactants for oil displacement usually have HLB values within a range of 6-9⁵⁴. A proper HLB value ensures favored partitioning of surfactants between oil and aqueous phases that achieve optimal contact angle⁵⁵.

Cloud point (CP) is also an important value of surfactants. It is the temperature at which the solid phase begins to form in surfactant solution⁵⁶. From its definition, a surfactant should be reconsidered when the reservoir temperature is higher than the cloud point. Although the cloud-point phenomenon can sometimes be observed in other types of surfactant systems^{57,58}, it is generally more influential in nonionic surfactants.

CMC, the Krafft temperature, HLB values, and CP are closely related to the surfactant structure. Experiments on cationic surfactants from the C_n TAB family taken by Kumar et al. reveal that more carbon atoms in the molecule lead to a significantly decreased CMC value ⁵³. A longer carbon chain of surfactant generally means more hydrophobicity ⁵⁹, thus smaller HLB, as well as larger Krafft temperature ⁶⁰ and lower CP ⁶¹.

The wettability alteration using surfactants depends on several factors like contact time, surfactant concentration, salinity, pH, temperature, rock mineral, and oil compositions. Generally, the contact angle reduces with an increase in contact time, sharply at first and slowly afterward. The effect of temperature on wettability change induced by surfactants can be mixed. Firstly, a lifted temperature may give rise to surfactant stability problems. Secondly, temperature influences surfactant adsorption. Thirdly, the lifted temperature can reduce the contact angle directly because of enhanced aqueous solubility of organic materials ⁴. Fourthly, the temperature has a significant impact on IFT (interfacial tension). Lastly, temperature influences the diffusion efficiency of surfactants. When these parameters change, surfactant performance will undergo an apparent change. One of the common issues limiting the application of surfactants is their poor performance under harsh conditions.

These days, researchers are developing novel surfactants in favor of better oil recovery. Many of them find new surfactants with better performance that can modify the rock surface wettability significantly while improving interfacial performance ^{39,40,62,63}. Numerical simulation has now been widely used in the wettability study using surfactants. For example, simulation results show that, when surfactants alter the rock wettability to a water-wet state, an increased IFT would be favored for increased recovery, though oil recovery increases with decreased contact angle irrespective of IFT. Simulation results also showed that the contribution of wettability alteration

could increase recovery ⁶⁴, especially for low permeability reservoirs ^{65,66}. There are also studies on the effect of surfactant molecular structure. For example, regression results on anionic and nonionic surfactants show that larger hydrophobes are needed under high temperature or high oil EACN (equivalent alkane carbon number) conditions ⁶⁷. A developed correlation relates to optimal salinity with the number of EO, PO groups, and hydrophobe size was given by Solairaj et al. based on the regression study ⁶⁷.

In general, surfactants have a long history of application in enhanced oil recovery. Besides improving oil/water interfacial tension, they can also alter rock toward water-wet conditions. To obtain optimal wettability change, the underground environment and surfactant system itself should be carefully examined.

In the following subsections, different types of surfactants that have been used for wettability alteration are discussed.

2.3.1.1 Cationic surfactant

Cationic surfactants are surfactants with positively charged heads. The most commonly used cationic surfactants in EOR are quaternary ammonium salts ⁶⁸. Table 5 shows typical cationic surfactants and their corresponding effect on carbonate rock wettability. Cationic surfactants have been proved to be more effective than anionic, nonionic, and zwitterionic surfactants in wettability modification of carbonate surface ^{2,45} by adsorbing onto rock surface ^{45,53}. They can modify oil-aged calcite toward a more water-wet state even in hard brines and high temperatures ³. As shown in Figure 12, they are believed to form ion pairs with adsorbed carboxylate group ($-\text{COO}^-$) on the rock surface ¹². This ion-pair is suggested to be stabilized by electrostatic force and hydrophobic interactions ¹². The product will not dissolve in the aqueous phase. It will either be trapped in

surfactant micelles or dissolved in oil phase ⁶⁹. This irreversible desorption of organic materials leads to irreversible wettability modification on carbonate surface ^{12,53,70,71}.

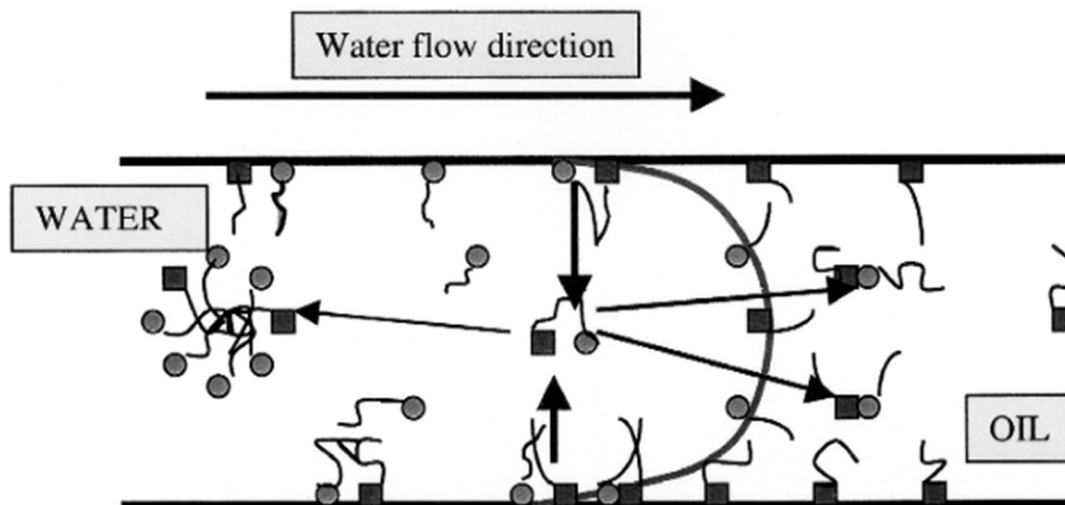


Figure 12 Wettability alteration mechanism of cationic surfactants. Circles are surfactants, squares are surface-active organic materials in the oil ¹².

Generally, higher cationic surfactant concentrations lead to more water-wetness on treated rock samples. An increased surfactant concentration significantly induced higher imbibition recovery, which indicated more water-wetness (Entry 4-6 in Table 5). However, Entry 6,8 seems to give a curious comparison, where faster but reduced recovery is observed with increased surfactant concentration. This recovery drop is explained that although the rock surface is changed to more water-wet by higher surfactant concentration, part of the desorbed oil is trapped in an increased number of micelles inside the aqueous phase, thus reducing oil phase recovery ¹².

Higher hydrophobicity makes cationic surfactants easier to form ion pairs with adsorbed organic materials. However, higher hydrophobicity reduces the CMC value of surfactant, resulting in the presence of a smaller amount of surfactant monomers, which will impair the desorption efficiency ¹². As a result, a cationic surfactant as a wettability modifier must have a molecular structure that gives proper HLB value. One way to increase its hydrophobicity is by increasing the length of the

carbon chain in the tail. The experiments taken by Standnes and Austad showed that imbibition recovery increased and then decreased with increasing carbon chain length, indicating the existence of an optimal hydrophobicity level. Besides, functional groups inside a molecule will affect each other. In their experiments, surfactants with a methyl group bonded to a nitrogen atom had a larger influence on wettability than surfactants with a benzyl group bonded ¹² (Figure 13).

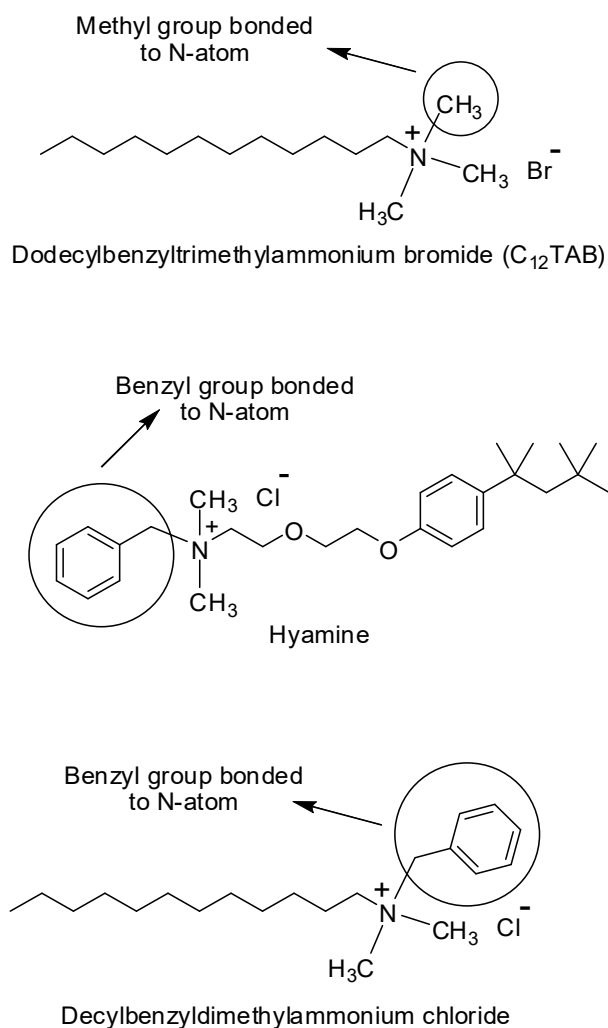


Figure 13 Illustration of methyl and benzyl groups in cationic surfactants.

Experiments show that an optimal salinity exists for cationic surfactants to have the smallest contact angle ⁵³. Two possibly functioning mechanisms are proposed. Increased salinity leads to increased repulsive electrostatic forces that prevent the aqueous phase from spreading. Besides,

increased salinity reduces the solubility of surface-active material in the aqueous phase. Due to these two mechanisms, there exists an optimum salinity that breaks a balance and gives optimum wettability alteration effect ⁵³.

Results are showing increased oil recovery in surfactant solution imbibition brought by lifted temperature, such as Entry 6,7 and 8,9 in Table 5. However, these increases could be explained by reduced oil viscosity or reduced IFT, not necessarily by improved wettability change brought by surfactants.

The adsorption of cationic surfactants is very low due to the abundance of Ca^{2+} ions in the aqueous phase that leads to a positively charged surface ¹². This adsorption can be further reduced by increasing multivalent cations' concentration ⁷². It is found to be well described by the Langmuir and the Freundlich isotherms ⁵³.

In summary, cationic surfactants are good wettability modifiers for oil-wet carbonate rock because they can form an ion-pair connection with organic materials and desorb them from rock surfaces irreversibly. They can turn carbonate rock into strongly water-wet and achieve high recovery, especially under high temperatures. However, attention should be made to their stability under high temperature and high salinity conditions. Adsorption of cationic surfactants is relatively low in carbonate reservoirs due to the presence of Ca^{2+} ions that can help to reduce adsorption and alter rock surface charge.

Table 5 Wettability alteration of cationic surfactants.

Entry	Surfactant	Conc. (wt%)	Rock	Water type	Temp (°C)	Contact angle change before-after treatment (°)	Oil recovery %	Ref
1	C8TAB	4.0	Chalk	Brine	40	NG	3	Standnes and Austad, 2000 ¹²
2	C10TAB	2.5	Chalk	Brine	40	NG	60	Standnes and Austad, 2000 ¹²
3	C12TAB	0.13	Chalk	Brine	40	NG	5	Standnes and Austad, 2000 ¹²
4	C12TAB	0.2	Chalk	Brine	40	NG	7	Standnes and Austad, 2000 ¹²
5	C12TAB	0.4	Chalk	Brine	40	NG	24	Standnes and Austad, 2000 ¹²
6	C12TAB	1.0	Chalk	Brine	40	NG	60	Standnes and Austad, 2000 ¹²
7	C12TAB	1.0	Chalk	Brine	70	NG	70	Standnes and Austad, 2000 ¹²
8	C12TAB	5.0	Chalk	Brine	40	NG	56	Standnes and Austad, 2000 ¹²
9	C12TAB	5.0	Chalk	Brine	70	NG	70	Standnes and Austad, 2000 ¹²

10	C16TAB	1.0	Chalk	Brine	40	NG	16	Standnes and Austad, 2000 ¹²
11	Hyamine	0.2	Chalk	Brine	40	NG	8	Standnes and Austad, 2000 ¹²
12	ADMBACl	0.5	Chalk	Brine	40	NG	8	Standnes and Austad, 2000 ¹²
13	C12TAB	1.0	Limestone	FW,SW	50	NG	45	Ravari et al., 2011 ²
14	Dodigen 5462	0.5	Limestone	FW, SW	50	NG	55	Ravari et al., 2011 ²
15	DTAB	1	Calcite	FW	92	NG	72	Sharma and Mohanty, 2013 ⁷³
16	Arquad 50	C- 0.2	Calcite	FW	100	No change	NG	Sharma and Mohanty, 2013 ⁷³
17	Arquad 50	T- 0.2	Calcite	FW	100	No change	NG	Sharma and Mohanty, 2013 ⁷³
18	DTAB	1.0	Carbonate	Brine	25	Intermediate-wet-66	NG	Seethepalli et al., 2007 ⁷⁴
19	C10TAB	0.4	Limestone	Brine	25	NG	12	Wu et al., 2008 ¹⁴
20	C12TAB	0.4	Limestone	Brine	25	NG	48	Wu et al., 2008 ¹⁴
21	C10TPPB	0.4	Limestone	Brine	25	NG	62	Wu et al., 2008 ¹⁴

22	C12TPPB	0.4	Limestone	Brine	25	NG	52	Wu et al., 2008 ¹⁴
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*Oil recovery data comes from spontaneous imbibition experiments, which reflects wettability change in the rock matrix

*Concentration values without unit are of default unit (wt%);

*DW: deionized water; FW: formation water; SW: seawater; NG: not given.

2.3.1.2 Anionic surfactant

Anionic surfactants have negatively charged heads (Figure 14). Widely used anionic surfactants include alkylbenzene sulfonates, alpha-olefin sulfonates, sulfates, ether sulfates, carboxylates, isethionates, and phosphate surfactants ⁷⁵. Table 6 shows typical anionic surfactants and their corresponding effect on carbonate rock wettability.

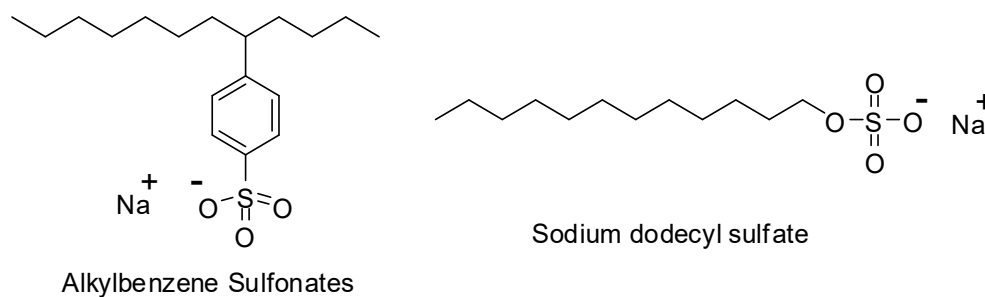


Figure 14 Examples of anionic surfactants.

Generally speaking, anionic surfactants are less effective in rendering carbonate rock water-wetness compared to other types of surfactants ⁴⁵. As shown in Figure 15, they are believed to form a layer over the adsorbed organic layer by hydrophobic interaction, forming a double-layer structure on rock surface ¹². Since hydrophobic interaction is a relatively weak connection, the desorption of carboxylates, and thus the wettability alteration, induced by anionic surfactants is probably completely reversible ¹².

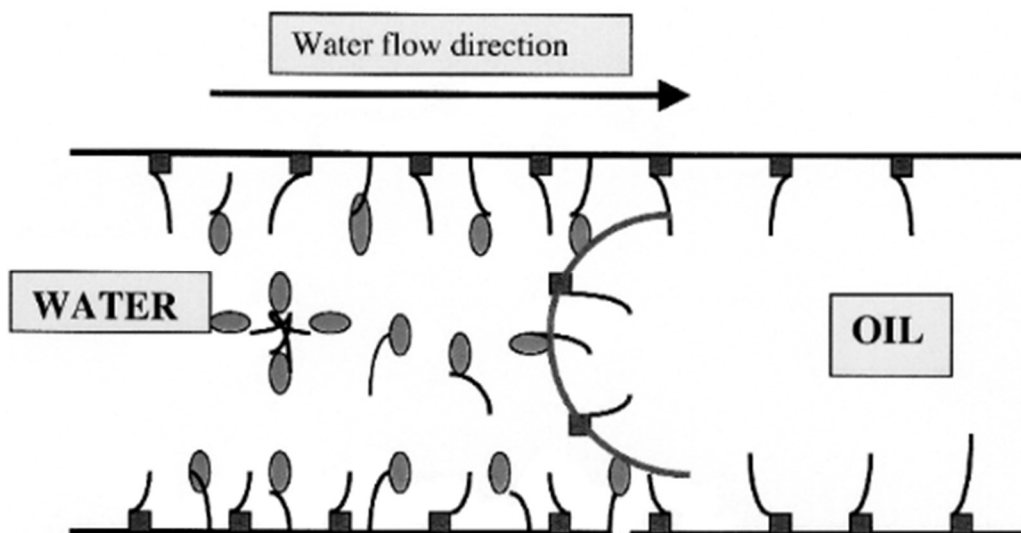


Figure 15 Wettability alteration mechanism of anionic surfactants. Ellipses are surfactants, squares are organic materials ¹².

There are results obtained by Alvarez et al. showing that increased concentration leads to reduced contact angle between the anionic surfactant system and carbonate rock surface ⁷⁶. There are also results obtained by Gupta and Mohanty showing the existence of optimal concentrations at a given formation environment of anionic surfactant Alf-38 and B27 ⁵⁵. This difference may be induced by different concentration ranges (0.2-2 gpt and 0-0.6 wt%), possible different salinity values, or different kinds of anionic surfactants. Similar optimal concentration has not yet been observed in other types of surfactants and the mechanisms behind need further investigation.

From the Alf surfactants series (Entry 12,14,15,21-23) listed in Table 6, it is clear that molecular structures also have a significant influence on anionic surfactants' performance. It is found that increasing the number of EO groups can increase the temperature tolerance of anionic surfactant ²⁹ and the extent of wettability alteration induced ^{12,55}. Sulfate has better multivalent ion tolerance than sulfonates and is more widely used under low temperatures ⁷⁷. Under high temperatures, sulfonates become a better choice because they have better temperature tolerance than sulfate ²⁹.

Anionic surfactants seem to have the potential to modify carbonate wettability to strongly water-wet only under low brine salinity, especially low divalent-ion concentrations such as Mg^{2+} and Ca^{2+} ³. Multivalent cations can interact with anionic surfactant and cause possible precipitation, reducing its wettability alteration effect in carbonate⁷². As a result, the presence of a sequestration agent can improve the wettability modification effect of anionic surfactants significantly with the presence of multivalent cations³. Experiments taken by Gupta and Mohanty showed that there existed an optimal salinity for each surfactant concentration because salinity influences surfactant partitioning between oil and aqueous phases⁵⁵. They also found that as salinity increased, the optimal surfactant concentration decreased and the optimal contact angle increased²⁸. Besides, the optimal salinity for the anionic surfactant to have the best wettability alteration performance decreased or remained unchanged when the temperature increased⁷⁸. Optimal salinity has also been well correlated with natural soap/surfactant model ratio⁷⁹. The temperature increase is observed to reduce the contact angle between the anionic surfactant system and carbonate rock surface⁷⁸.

Compared to cationic surfactants, anionic surfactants have significantly higher adsorptions on carbonate rock⁷². Adibhatla and Mohanty found the adsorption process of anionic surfactants to be dependent on pH, salinity, and temperature. As pH increases, adsorption decreases; as salinity decreases, adsorption decreases. The addition of alkali can reduce the adsorption of the studied anionic surfactant. The relationship between adsorption and temperature differs between enthalpy-driven and entropy-driven adsorption⁸⁰.

In summary, the application of anionic surfactants in carbonate reservoirs could be expensive due to high adsorption. Besides, anionic surfactants generally change carbonate wetting state from strongly oil-wet to intermediate-wet conditions, because their wettability modification comes from

a reversible hydrophobic interaction with organic materials. However, with carefully designed molecular structures and some additives like alkali, the wettability modification effect of anionic surfactants can be as good as commonly used cationic surfactant systems. For example, a surfactant system of guerbet alkoxy carboxylates with internal olefin sulfonates (IOS) as cosolvent showed good results in IFT reduction and wettability alteration and obtained excellent oil recovery from extremely fractured HTHS carbonate reservoir ⁸¹. In the presence of Na_2CO_3 , some anionic surfactants are also found to be as good as the cationic surfactants in modifying wettability ⁷⁴.

Table 6 Wettability alteration of anionic surfactants.

Entry	Surfactant	Conc. (wt%)	Rock	Water type	Temp (°C)	Contact angle change before-after treatment (°)	Oil recovery %	Ref
1	S-150	0.5	Chalk	Brine	40	NG	20	Standnes and Austad, 2000 ¹²
2	B 1317	0.5	Chalk	Brine	40	NG	10	Standnes and Austad, 2000 ¹²
3	S-74	0.5	Chalk	Brine	40	NG	6	Standnes and Austad, 2000 ¹²
4	APES	1.0	Chalk	Brine	40	NG	5	Standnes and Austad, 2000 ¹²
5	Cropol	0.5	Chalk	Brine	40	NG	1	Standnes and Austad, 2000 ¹²
6	Akypo	0.5	Chalk	Brine	40	NG	0.5	Standnes and Austad, 2000 ¹²
7	Gafac	0.5	Chalk	Brine	40	NG	0	Standnes and Austad, 2000 ¹²
8	SDS	0.1	Chalk	Brine	40	NG	0	Standnes and Austad, 2000 ¹²
9	SDS	0.23	Limestone	Brine		NG	NG	Ahmadi et al., 2015 ⁴⁰

10	AV-70	0.1	Calcite	FW	100	Oil-wet to intermediate-wet	NG	Sharma and Mohanty, 2013 ⁷³
11	AV-150	0.1	Calcite	FW	100	Oil-wet to intermediate-wet	NG	Sharma and Mohanty, 2013 ⁷³
12	Alf 68	0.05	Limestone	Brine	25	Oil-wet70	40	Gupta et al., 2009 ²⁹
13	DF	0.05	Limestone	Brine	25	Oil-wet-155	NG	Gupta et al., 2009 ²⁹
14	Alf 38	0.05	Limestone	Brine	25	Oil-wet -32	60	Gupta et al., 2009 ²⁹
15	Alf 35	0.05	Limestone	Brine	25	Oil-wet -62	62	Gupta et al., 2009 ²⁹
16	B 27	0.05	Limestone	Brine	25	Oil-wet -133	NG	Gupta et al., 2009 ²⁹
17	TX	0.3	Limestone	Brine	25	Oil-wet -127	NG	Gupta et al., 2009 ²⁹
18	4-22	0.05	Carbonate	Brine	25	intermediate-wet -140	NG	Seethepalli et al., 2007 ⁷⁴
19	5-166	0.05	Carbonate	Brine	25	intermediate-wet -87	NG	Seethepalli et al., 2007 ⁷⁴
20	SS-6656	0.05	Carbonate	Brine	25	intermediate-wet -68	NG	Seethepalli et al., 2007 ⁷⁴

21	Alf 65	0.05	Carbonate	Brine	25	intermediate-wet -67	NG	Seethepalli et al., 2007 ⁷⁴
22	Alf 63	0.05	Carbonate	Brine	25	intermediate-wet -84	NG	Seethepalli et al., 2007 ⁷⁴
23	Alf 33	0.05	Carbonate	Brine	25	intermediate-wet -95	NG	Seethepalli et al., 2007 ⁷⁴

*Oil recovery data comes from spontaneous imbibition experiments, which reflects wettability change in the rock matrix

*Concentration values without unit are of default unit (wt%).

*DW: deionized water; FW: formation water; SW: seawater; NG: not given.

2.3.1.3 Zwitterionic surfactant

Zwitterionic surfactants are also called amphoteric surfactants. They have both positive and negative charges on their heads and remain electrically neutral (Figure 16). Ammonium and pyridinium ions are examples of positive parts and the negative parts can be phosphate, carbonate, sulfonate, or sulfate ⁵¹. Due to their special structural properties, they are compatible with other surfactants ⁸². Table 7 shows typical zwitterionic surfactants and their corresponding effect on carbonate rock wettability.

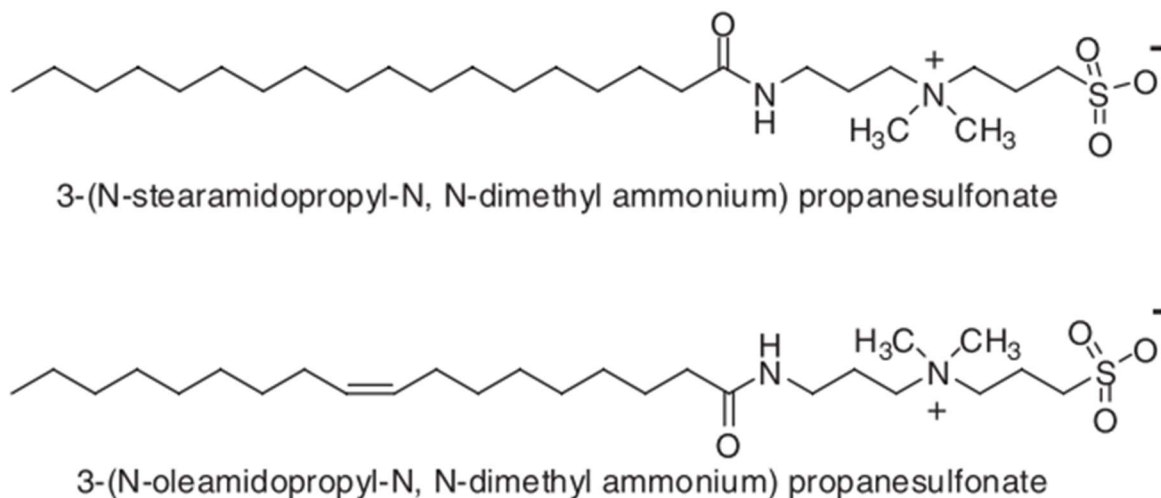


Figure 16 Examples of zwitterionic surfactants ⁸³.

Due to its high cost, zwitterionic surfactants were less investigated in the past ^{47,84}. Therefore, the mechanism of wettability alteration is not well addressed. Some suggested that the wettability alteration process in carbonate rock induced by zwitterionic surfactants is rapid due to amphoteric charges on the heads ⁸⁵. A few experiments have shown that this type of surfactant can modify originally oil-wet carbonate rock toward strongly water-wet ^{84,86}.

For zwitterionic surfactants, it is observed that increased concentration leads to reduced contact angles on carbonate rock surface ⁸⁷. The molecular structure influences the properties of

zwitterionic surfactants. For example, saturated alkyl and unsaturated alkyl chains in the tail give different properties to zwitterionic surfactants with the same head groups ⁸³. Generally, as the separation between different charges in the head part increases, the CMC value of this surfactant increases as well ^{44,88}.

Contact angle measurements after surfactant post-flush and zwitterionic surfactant solution treatment show an increased and then decreased contact angle value with increasing temperature, indicating a mixed influence of temperature on wettability alteration induced by zwitterionic surfactants ⁸⁹. The adsorption of zwitterionic surfactants on carbonate rock surfaces is suggested by Alvarez et al. to be driven by electrostatic and hydrophobic interactions as well as different micellar systems ⁹⁰. It is observed to increase with increased surfactant concentration ⁹¹. The adsorption of zwitterionic surfactants in seawater on limestone is found to follow a monolayer Langmuir tendency. In the connate water system, however, a doubled adsorption is observed. The difference is explained by different concentrations of divalent ions (Ca^{2+} and Mg^{2+}) in different aqueous systems ⁹⁰, indicating that brine composition and salinity have an influence on zwitterionic surfactant adsorption on carbonate rocks. In the connate water system, adsorption decreases after maximum value with increased surfactant concentration. Alvarez et al. attributed this phenomenon to the transition of surfactants from micelles to vesicles which had lower adsorption ⁹⁰. Because most of the zwitterionic surfactant adsorption is an exothermic process, temperature increase leads to adsorption decrease ^{89,90}.

In summary, zwitterionic surfactants are found to have excellent tolerance toward high salinity and temperature ^{47,51,83,92}. They have relatively low adsorption on carbonate rock and the adsorption further reduces with increased temperature or salinity ⁹⁰. Due to their special structure, they are good co-surfactant with other surfactants and contribute to salinity and temperature

tolerance in the system. Zwitterionic surfactants are also able to alter oil-wet carbonate rock to water-wet. But their application is limited by the high cost.

Table 7 Wettability alteration of zwitterionic surfactants.

Entry	Surfactant	Conc. (wt%)	Rock	Water type	Temp (°C)	Contact angle change before-after treatment (°)	Oil recovery %	Ref
1	HABSA	3000ppm	Carbonate	Brine	25	150-76	NG	Souraki et al., 2019 ⁸⁷
2	NX-2760	1000 mg/L	Carbonate	FW	80	137-46	NG	Ahsaei et al., 2019 ⁸⁶
3	NX-1510	1000 mg/L	Carbonate	FW	80	137-37	NG	Ahsaei et al., 2019 ⁸⁶
4	TR-880	1000 mg/L	Carbonate	FW	80	137-57	NG	Ahsaei et al., 2019 ⁸⁶
5	OCT-2	0.2	Carbonate	Brine	75	155-67	NG	Ahsaei et al., 2019 ⁹³
6	OCT-2	0.2	Carbonate	SW	75	NG	70	Ahsaei et al., 2019 ⁹³

7	OCT-3	0.2	Carbonate	Brine	75	132-58	30	Ahsaei et al., 2019 ⁹³
8	OCT-3	0.2	Carbonate	SW	75	NG	26	Ahsaei et al., 2019 ⁹³

*Oil recovery data comes from spontaneous imbibition experiments, which reflects wettability change in the rock matrix

*Concentration values without unit are of default unit (wt%).

*DW: deionized water; FW: formation water; SW: seawater; NG: not given.

2.3.1.4 Nonionic surfactant

Nonionic surfactants do not have charged hydrophilic heads and do not ionize in the aqueous phase. The temperature has a significant influence on nonionic surfactant solution stability. As mentioned before, the cloud point phenomenon is most observed in this type of surfactant. Figure 17 shows two examples of nonionic surfactants. Table 8 shows typical nonionic surfactants and their corresponding effect on carbonate rock wettability.

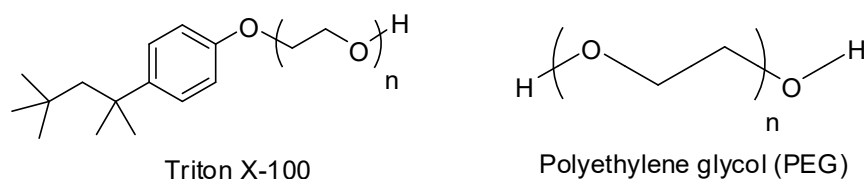


Figure 17 Examples of nonionic surfactants.

The mechanism of nonionic surfactant-induced wettability change can be the formation of a bilayer structure between the oil-wet rock and aqueous phase as was believed by Standnes et al. based on its reversible nature ⁷¹. Another mechanism hypothesis is proposed as a “coating and sweeping” process by Das et al.. In the beginning, there is an oil coat covering the rock surface. When surfactant solution is introduced, the surfactant-water combination moves into micro defects of that “coat” and sweeps it ⁹⁴. According to the enhanced wettability modification induced by nonionic surfactants with more EO groups, Souayah et al. suggested the formation of hydrogen bonds between EO group in surfactant and carboxyl or hydroxyl group in oil components to be another mechanism aside from the bilayer model mentioned previously ⁹⁵. However, experimental results from Sharma and Mohanty show that increased EO groups lead to decreased water-wetness of treated calcite samples ⁷³. Those two opposite conclusions may be induced by different molecular structures, thus different HLB values of surfactants. Jarrahian et al. observed that the

adsorption of surfactant reduced the zeta potential of rock surface ⁴⁵. They proposed a mechanism that the adsorption of surfactant released stearic acid on the rock surface and changed the wettability, as shown in Figure 18.

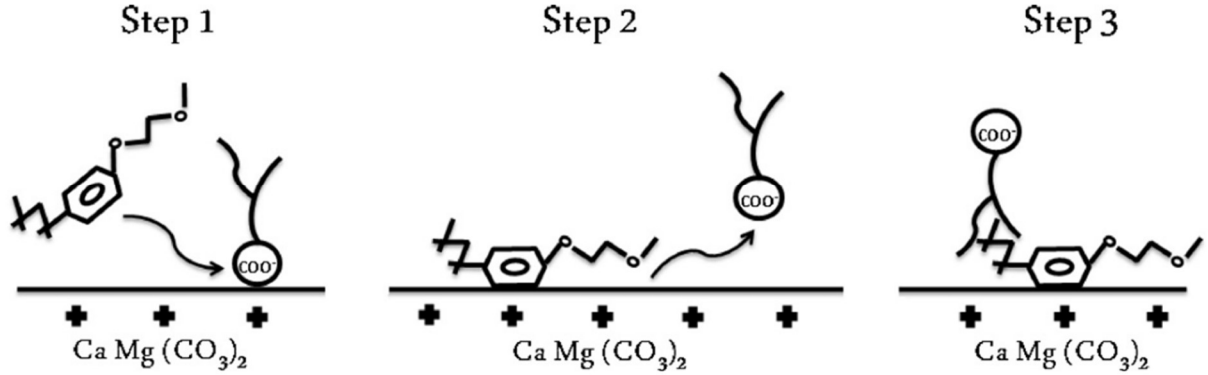


Figure 18 The procedure proposed for nonionic surfactant treatment ⁴⁵.

An increased concentration of nonionic surfactants can lead to the reduction of contact angle to some extent. After that, no major wettability alteration is induced by surfactant addition ^{39,45}. The molecular structure is also an important factor in nonionic surfactant properties. Wettability modification induced by nonionic surfactants has been proved to depend heavily on surfactant molecular structure. Higher hydrophobicity of surfactant is found to lead to more water-wetness after surfactant processing ⁹⁴. Gupta et al. proposed a relation between the number of EO groups (P) and CP (cloud point) of nonionic surfactants ²⁹:

$$\frac{P - P^0}{CP} = a + b(P - P^0) \quad 2.4$$

Where a, b, and P^0 are three constants.

Temperature is observed to have a positive effect in reducing the contact angle between nonionic surfactant solution and carbonate rock surface ^{50,78,94}. From Table 8, nonionic surfactants generally can only alter oil-wet carbonate to intermediate-wet, except in the case when the

temperature is high (90 °C). Entry 2,3 and 4,5 and 13,14 in Table 8 show the positive effect of temperature. The optimal salinity for the nonionic surfactant to have the best wettability alteration performance is found to decrease or remain unchanged when the temperature increases⁷⁸.

Adsorption of nonionic surfactant can be described by equilibrium adsorption models such as linear, Langmuir⁹⁶, Temkin, and Freundlich⁹⁷ model. It can be significantly reduced by either pre-flushing or co-injecting polymer⁹⁸. It is found to be influenced by clay content in carbonate as well. Generally the more clay content, the more hydroxyl groups on the rock surface, and the more adsorption⁹⁹. The higher the surfactant concentration, the more adsorption of nonionic surfactant⁹⁷.

In summary, commonly used nonionic surfactants are not good wettability modifiers for oil-wet carbonate rocks due to their poor stability and limited effect of wettability alteration under reservoir conditions.

Table 8 Wettability alteration of nonionic surfactants.

Entry	Surfactant	Conc. (wt%)	Rock type	Water type	Temp (°C)	Contact angle change before-after treatment (°)	Oil recovery %	Ref
1	TDA 30EO	<0.2	Calcite	FW	80	Oil-wet to intermediate-wet	NG	Sharma and Mohanty, 2013 ⁷³
2	15S	0.1	Limestone	Brine	25	Oil-wet -145	NG	Gupta et al., 2009 ²⁹
3	15S	0.1	Limestone	Brine	90	Oil-wet -20	50	Gupta et al., 2009 ²⁹
4	NP	0.1	Limestone	Brine	25	Oil-wet -118	NG	Gupta et al., 2009 ²⁹
5	NP	0.1	Limestone	Brine	90	Oil-wet -75	NG	Gupta et al., 2009 ²⁹

6	Tergitol S-3	15-	0.4	Limestone	Brine	25	NG	12	Wu et al., 2008 ¹⁴
7	Tergitol S-7	15-	0.4	Limestone	Brine	25	NG	23	Wu et al., 2008 ¹⁴
8	Tergitol S-40	15-	0.4	Limestone	Brine	25	NG	6	Wu et al., 2008 ¹⁴
9	Igepal 530	CO-	0.4	Limestone	Brine	25	NG	52	Wu et al., 2008 ¹⁴
10	Neodol	25-7	0.4	Limestone	Brine	25	NG	7	Wu et al., 2008 ¹⁴
11	Triton 100	X-	1	Carbonate	Brine	25	150-60	NG	Amirpour et al., 2015 ³⁹
12	Cedar		2	Carbonate	Brine	25	150-80	NG	Amirpour et al., 2015 ³⁹
13	PEG		7% vol	Carbonate	Drilling fluid	25	1-18 (oil)	NG	Amirpour et al., 2015 ³⁹

14	PEG	7% vol	Carbonate	Drilling fluid	80	1-40 (oil)	NG	Kiani et al., 2018 50
15	EA	3500 ppm	carbonate	Brine	25	133-107	NG	Standnes et al., 2002 ⁷¹

*Oil recovery data comes from spontaneous imbibition experiments, which reflects wettability change in the rock matrix

*Concentration values without unit are of default unit (wt%).

*DW: deionized water; FW: formation water; SW: seawater; NG: not given.

2.3.1.5 Gemini surfactant

Gemini surfactants have more than one head group and more than one tail linked by a spacer ⁷⁵. The spacer can be located between heads or between tails (Figure 19). There are different types of spacers (Figure 20). For the same number of carbon atoms per hydrophilic head, gemini surfactants have much lower CMC ^{100,101} and better oil solubility ¹⁰⁰ than conventional surfactants. The most widely studied gemini surfactants are usually referred to as *m-s-m* type, while *m* is the number of carbon atoms of the alkyl chain, *s* is the number of carbon atoms of the spacer ³⁶. Most studies on gemini surfactants focus on their IFT reduction potential and rheology. They are about 3 orders of magnitude more efficient in reducing IFT and more than 2 orders of magnitude in forming micelles ¹⁰².

To obtain the anticipated properties of gemini surfactants, the molecular structure has to be optimized by adjusting polarity and hydrophobicity. Polarity can be added by ester, ether, amide, sulfide, and cyclodextrin groups. Hydrophobicity can be added by some fluorine groups or introduced by dehydroabietylamine derivative ⁷⁵. Their oil solubility (and hence hydrophobicity) increases as hydrocarbon chain length increases ¹⁰⁰. However, according to the hypothesis proposed by Menger and Littau, higher hydrophobicity doesn't ensure lower CMC for gemini surfactants due to self-coiling ¹⁰². They also proposed that Gemini surfactants with long tails tended to undergo more complex processes than micelle $\rightleftharpoons$ monomers equilibria in conventional surfactants ¹⁰². Salt tolerance is found to increase as the carbon atom number in the spacer increases ¹⁹. There exists an optimal spacer length for the lowest IFT ¹⁰³. Depending on the charges on its heads, gemini surfactants can also be classified as anionic, cationic, and zwitterionic gemini. The degree of asymmetry, which describes how different two parts are there on the sides of the spacer, also has a significant influence on the properties of gemini surfactants ⁷⁵.

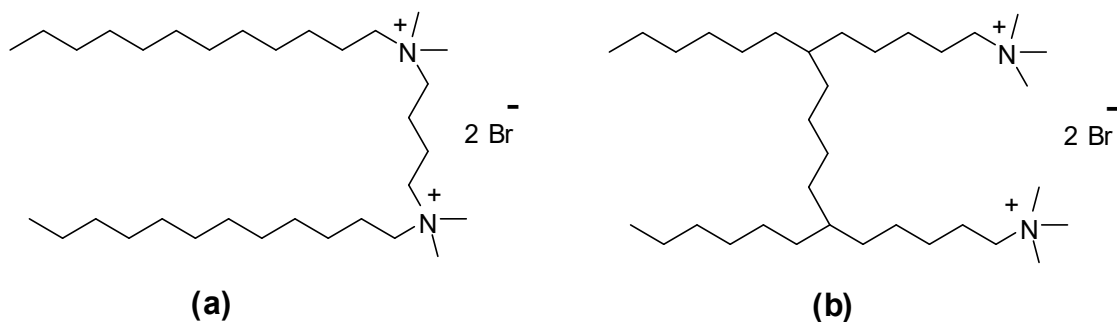


Figure 19 Gemini surfactants with spacer located between heads (a) and between tails (b).

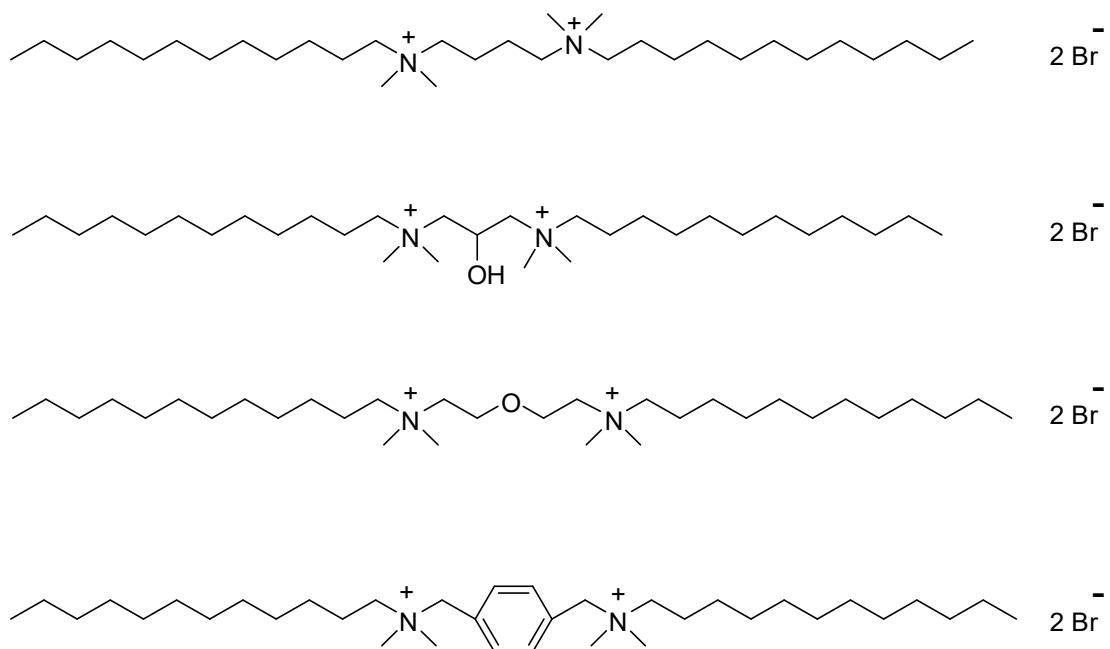


Figure 20 Examples of different spacers in gemini surfactants.

Gemini surfactants have been proven to be effective in changing oil-wet surface to water-wet^{17,104}. In sandstone formation, contact angle reduction of 140~40²⁰, 110~10¹⁹ as well as higher imbibition recovery than conventional surfactants^{18,20} are observed. The extent of how much can gemini surfactants change carbonate rock wettability and the related mechanisms are discussed in only a few papers. Qi et al. observed contact angle results showing carbonate changing from intermediate-wet to strongly water-wet after treatment by gemini surfactants²¹. Ghosh and Mohanty observed the wetting state of mineral calcite plates changed from oil-wet to intermediate-wet by gemini cationic surfactants^{22,23}. Due to these encouraging results and their outstanding

properties compared to conventional surfactants, gemini surfactants can be good wettability modifiers for oil-wet carbonate rocks. Adsorption of gemini surfactants is found to be captured by the Langmuir model and is dependent on the condition and structure. Higher salinity, as well as longer alkyl chains and spacer groups, lead to higher adsorption ¹⁰⁵.

Further investigation of gemini surfactants on the wettability of carbonate rocks is needed. However, based on the outstanding interfacial properties and micellization behavior, as well as their performance on other types of surfaces, gemini surfactants can be very efficient wettability modifiers for carbonate rocks.

2.3.1.6 Natural surfactants

In the above sections, surfactants are categorized either by the charge(s) on the head group(s) or by molecular structure. It is also common to categorize surfactants by their origins, namely natural surfactants and synthesized surfactants. Strictly speaking, natural surfactants are surfactants that can be obtained directly from natural origins including plants and animals by separation processes such as extraction, precipitation, and distillation. Throughout the production, no organic synthesis should be involved. However, only a few surfactants, such as lecithin, meet this strict requirement. A much more general definition is commonly used that a surfactant is considered a natural surfactant if one of its main building blocks, head group or tail, is obtained from the natural source. In this review, the general definition is used ¹⁰⁶.

Compared to synthesized surfactants, natural surfactants can have advantages in lower cost, less environmental impact, and better local availability. Due to those advantages, natural surfactants have been an important topic recently. In 2001, Krister Holmberg did a review on three types of natural surfactants, i.e. surfactants produced from bacteria and yeast, surfactants based on either

sugar or an amino acid as a polar head group, and surfactants based on either fatty acid or sterol as the hydrophobic tail. In his review, the origins, molecular structures, and properties of these most popular types of natural surfactants were discussed. He concluded that the latter two types of natural surfactants showed great promise ¹⁰⁶. Torres et al. compared the solutions surface tension between a group of synthesized surfactants and three nonionic natural surfactants, guar gum, locust bean gum, and rhamnolipid ¹⁰⁷. They concluded that the tested natural surfactants gave promise in the EOR process, especially rhamnolipid. Ahmad and Shadizadeh studied the adsorption of a natural surfactant derived from the leaves of a plant called *Zyziphus spina-christi* on carbonate ¹⁰⁸, shale-sandstone ¹⁰⁹, and the influence of nano-silica ¹¹⁰. Ahmad et al. proposed a new natural surfactant prepared by simply milling the leaves of mulberry trees down to micro-size and mixing those micro-particles with distilled water. They found this new surfactant to be efficient in lowering IFT between oil and water aside from other advantages including ease of preparation, environmental friendliness, and low cost ¹¹¹. Pal et al. proposed a nonionic gemini surfactant derived from sunflower oil. They found that the proposed surfactant had favorable salt and hardness tolerance and good foaming performance, showing potential for EOR purpose ¹¹².

There are also studies on the wettability effect of natural surfactants on carbonate rocks. In the study of a natural surfactant derived from roots of *Glycyrrhiza Glabra*, Ahmad et al. found the surfactant had an intermediate wettability effect which contributed to increased oil recovery ⁴⁰. The study taken by Standnes and Austad showed that a natural tertiary ammonium surfactant derived from coconut palm was very efficient in wettability alteration from completely oil-wet to more water-wet ⁶³. A natural surfactant (Cedar) showed strong wettability alteration efficiency in the study done by Sofla et al. ¹¹³.

In a word, natural surfactants have advantages like lower cost and higher environmental friendliness and have been proposed as alternatives for synthesized surfactants in the EOR process. They are intensely studied these years. Besides their potential in lowering IFT and forming foam and emulsions, their influence on wettability also contributes to increased oil recovery.

Among all kinds of surfactants, cationic surfactants are relatively effective in the wettability alteration of carbonate rock while weak in reducing IFT. Anionic surfactants, however, show strong potential in reducing IFT, while weak in wettability alteration, and endure high surfactant retention in the carbonate reservoir. Zwitterionic surfactants have good performance but their application is limited by the high cost. Nonionic surfactants tend to have moderate wettability alteration. Some encouraging experimental results have shown the potential of natural surfactants in wettability modification. The most potential type of surfactant as a wettability modifier is the gemini surfactant. Gemini surfactants can reach ultra-low IFT and have very low adsorption in carbonate reservoirs. Although further study on their wettability effect on carbonate rock is needed, their performance in sandstone and other types of surfaces implies their successful application in carbonate rock.

2.3.1.7 Field applications & economic evaluation

Research interest in surfactant-based chemical EOR has been growing very rapidly since many existing reservoirs have gone into the mature phase while hydrocarbon demand keeps increasing rapidly. A keyword search of “surfactant EOR” in the Web of Science database shows a spike in publications from 15 articles in 2009 to 150 articles in 2019. The same keyword search in Google Scholar shows a spike from 647 in 2009 to 2380 in 2019. Besides the rapidly growing research interest, surfactant-based EOR techniques have been considered robust EOR techniques for field application. Microemulsion generation as well as foam generation and stabilization used to be the

primary reason for surfactant application in EOR. Recently, the potential of surfactants to modify rock wettability has also been recognized as a contributor to incremental oil recovery ¹¹⁴. Conventional techniques including surfactant flooding, alkali-surfactant flooding, and alkali-surfactant-polymer (ASP) flooding have been widely used in sandstone reservoirs and are also attracting attention recently for their potential in carbonate reservoirs ¹¹⁴. A few field applications in carbonate reservoirs can be found in the literature, as shown in Table 9.

Among those field cases, wettability modification due to surfactant contributed to part of the increased recovery in Yates field case ¹¹⁵. The incremental oil recovery in the case of the Cottonwood Creek field is believed to be primarily induced by wettability change since the surfactant they used could not reduce IFT significantly ¹¹⁶. Both cases show the importance of a good understanding of how surfactant would modify carbonate rock wettability.

To achieve wide adoption of surfactant EOR techniques in fields, several technical problems need to be solved. For example, Ca^{2+} and Mg^{2+} ions usually have high concentrations in carbonate formation brine. These divalent ions could form sulfonates with typical commercial surfactants that either precipitate or partition into oil phase ¹¹⁷. Besides, brine salinity and hardness also have an impact on the performance of surfactants, as mentioned in the above sections. Furthermore, some surfactants are toxic and dangerous for workers and the environment, which to a large extent limits the field application of surfactants.

Apart from technical problems, surfactant flooding suffers low-cost effectivity since synthetic surfactants are usually costly. On the other hand, surfactant retention in the reservoir also adds to the quantity of consumed surfactant and thus the cost. As mentioned in the anionic surfactant section, the addition of alkali can reduce the adsorption of anionic surfactants since it changes the

pH value of the formation brine. However, the addition of alkali could induce other problems like scaling, the negative effect of viscosity, and the production of very stable foams ⁸⁰. Many researchers nowadays work on natural surfactants that are less expensive and eco-friendly. Some work to find less expensive synthetic surfactants ¹¹⁸. Some look for ways to reduce the price of surfactant through local production and large quantity production. For example, Guo et al. reported that the surfactant price has been reduced to about 10,000 RMB/ton in Daqing oilfield, China. They also did an estimation of the ASP cost (30-45 USD/bbl) and weak alkali ASP cost (27 USD/bbl) ¹¹⁹. Some researchers and engineers look for methods that help optimize EOR processes based on economic evaluation. For example, Odi et al. applied an ensemble-based method to EOR optimization ¹²⁰. Rommerskirchen et al. concluded that EOR optimization should consider both chemical prices and their performance ¹²¹.

Due to the high cost of surfactants, surfactant-based EOR techniques could be risky to apply in fields. Among different types of surfactants, anionic surfactants are generally less expensive than cationic surfactants ¹²². Zwitterionic surfactants are expensive compared with other types of surfactants ⁶⁸. Economic evaluation is widely used to assess the risk of the project and optimize the surfactant EOR technique for specific field conditions. The most important factors include the cost of surfactants, the cost of water flooding, environmental impacts, formulations, oil price, and estimated incremental oil recovery. An evaluation was done in 1993 for dilute surfactant flooding which had been proven in the laboratory to recover 80-90% of the residual oil after waterflooding at a low concentration (1%). A negative conclusion was obtained due to the limitation of facilities, chemical volume requirements, and associated technical cost per barrel. In that case, the chemical cost alone was about \$20/bbl ¹²³. Alkaline flooding is characterized for low operational costs. ASP is a cost-effective process ¹²². Reported ASP projects in the USA in 1988 and 1994 were all

profitable ¹²⁴. By numerical simulation, the cost per barrel of incremental oil for ASP application in Sabriyah Lower Burgan was obtained to be \$28.63, \$10.42, and \$10.95 for pilot sizes of 2.2, 5.4, and 60 MMbbl respectively. Corresponding rates of return were up to 14% ¹²⁵.

Table 9 Surfactant-based chemical EOR field applications in carbonate reservoirs ¹¹⁴.

Entry	Field	Year	Chemicals used	Oil recovery	Ref
1	Wichita County Regular reservoir, Texas, USA	1975	Surfactants: petroleum sulfonates + alkyl ether sulfate Polymers: polyacrylamide	22.0 %OOIP	Leonard, 1984 ¹²⁶
2	Wesgum field, Arkansas, USA	1980	Surfactants: petroleum sulfonates + alkyl ether sulfate Polymers: polyacrylamide	26.7 %OOIP	Leonard, 1986 ¹²⁷
3	Bob Slaughter Block Lease, Texas, USA	1980	Surfactants: alkyl ether sulfates and Witco petroleum sulfonate, alkyl aryl ether sulfates, synthetic sulfonate	12.0 %OOIP	Adams and Schievelbein, 1986 ¹²⁸
4	Cambridge Minnelusa, Wyoming, USA	1993	Surfactant: Petrostep B-100 Alkali: Na ₂ CO ₃ Polymer: Alcoflood 1175A	36.0 %OOIP	Vargo et al., 2000 ¹²⁹
5	Yates field, Texas, USA	1998	Surfactants: nonionic ethoxy alcohol (Shell 91-8) and anionic ethoxy sulfate (Stepan CS-460)	15.0 %OOIP	Yang and Wadleigh, 2000 ¹³⁰ , Chen et al., 2000 ¹¹⁵
6	Mauddud reservoir, Bahrain	1999	Surfactants: Not given, Alkali: Na ₂ CO ₃	10-15 %OOIP	Zubari and Sivakumar, 2003 ¹³¹

7	Cottonwood Creek field, Wyoming, USA	1999	Surfactant: nonionic polyoxyethylene alcohol (POA)	10.4 %OOIP	Weiss et al., 2006 ¹¹⁶
8	Semoga field, Indonesia	2009	Surfactants: nonionic surfactants	5800bbl accumulated production over 3 months	Rilian et al., 2008 ¹³²

2.3.2 Nanoparticles

Nanoparticles refer to particles smaller than 100 nm and compose of a core and a thin shell, as shown in Figure 21. The chemical nature of the shell will determine the solubility of that nanoparticles into either of the 2 types: 1. lipophobic and hydrophilic nanoparticles (LHP) that are easier to dissolve in a polar solvent; 2. hydrophobic and lipophilic nanoparticles (HLP) that dissolve in non-polar solvents. The shell generally composes of 3 separate regions: tail group, hydrocarbon chain, and active head group ^{133,134}. Due to the importance of the shell, surface modification is usually taken on nanoparticles to obtain favored properties, such as hydrophobicity ¹³⁵. The small sizes of nanoparticles enable them to diffuse into reservoir pores ¹³⁶. They can be reinjected without a major change in performance ¹³⁷. However, nanoparticles have to be applied with caution if a high concentration is needed in the low-permeability reservoir in case they block the pore network and impair recovery ¹³⁴. Table 12 shows typical nanofluids and their corresponding effect on carbonate rock wettability.

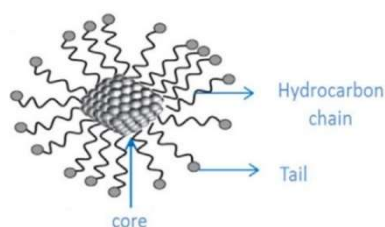


Figure 21 Typical nanoparticle structure ^{133,134}.

The isoelectric point is an important indicator of the surface charge of nanoparticles. It is, by definition, the pH value at which the object has no electric charge. At a pH above this point, the object will have a positive surface charge and vice versa. Experiments show that pH is an important factor in wettability change ¹³⁸. When preparing nanofluids, it is common to add chemicals for pH value control ¹³⁹. Dolomite rock has an isoelectric point 2-3 units lower than that of limestone rock, indicating that dolomite has a more positive surface charge and is thus more attractive to negatively

charged materials. As a result, negatively charged nanoparticles, uncoated SiO₂ for example, reaches better wettability alteration performance on dolomite than limestone ¹⁴⁰.

Changing pH results in changed surface charges (Table 10Error! Reference source not found.). As a generally accepted case, the surface charge of rock dominates wettability. SiO₂ particles can reduce the pH of the solution. Al₂O₃ nanoparticles can slightly increase pH. SiO₂ nanofluid is much more effective in wettability alteration than Al₂O₃ nanofluid ¹³⁸.

Table 10 Carbonate rock surface charge and pH value ¹⁴¹.

pH value	Carbonate rock surface charge
>9	Negative
=9	Isoelectric point
<9	Positive

Due to the high surface area to particle size ratio, nanoparticles have relatively high surface energy, making them easy to aggregate in solution ¹³⁵. The stability of nanofluids is one of the most critical screening criteria for their application. Zeta-potential analysis can be used to measure the stability based on Table 11.

Table 11 Zeta potential value and nanofluid stability ¹⁴¹.

Zeta-potential (mV)	Stability level
>60	High stability
30~60	Good stability
10~30	Relative stability
<10	Weak stability
0	Instability

2.3.2.1 Nanofluids preparation

Experimentally used nanofluids are usually prepared by adding nanoparticles into the water, magnetic stirring, and sonication process ¹⁴². To keep nanoparticles solution stable, materials called “dispersion agents” are usually added. Commonly used dispersing agents include surfactants, small molecules, inorganic electrolytes, and polymers ¹⁴². The properties of nanofluids are significantly influenced by chemicals added such as surfactants and acids. With different additives, nanofluids can have very different performances in wettability alteration or even fail in changing wettability ¹³⁹. A mixture of nanoparticles and surfactants can result in a significant change in surfactant surface activity due to strong interaction between nanoparticles and surfactant molecules ¹³⁶. Recently, a new type of nanofluid has been proven to improve carbonate recovery remarkably without surfactant and stabilizer ¹⁴³.

2.3.2.2 Types of nanoparticles

There are different nanoparticles, including zirconium dioxide (ZrO_2), calcium carbonate (CaCO_3), titanium dioxide (TiO_2), magnesium oxide (MgO), aluminum oxide (Al_2O_3), cerium oxide (CeO_2), silicon dioxide (SiO_2), and carbon nanotube (CNT). Among them, SiO_2 , TiO_2 , ZrO_2 , CNT, and CaCO_3 are shown to have the potential for wettability alteration on carbonate rocks. CaCO_3 and SiO_2 have been proved to have the best salinity tolerance. Between them, SiO_2 outperformed CaCO_3 in recovery improvement from carbonate but cost a longer time to take effect ¹⁴⁴.

Silica (SiO_2) nanoparticles can modify the wettability of oil-wet calcite to strongly water-wet by adsorbing on the rock surface, with a minimum effective concentration of 1-2 wt% ¹³⁷. Different observations are proposed by researchers about whether this adsorption is reversible or not. Arain et al. found that this adsorption is mostly reversible and easy to get washed off by solvent such as

deionized water ¹³⁵, while Al-anssari et al. found that this adsorption is mainly irreversible ¹³⁷. These conflicting results might be induced by an insufficient exposure time to solvent applied in the experiment taken by Al-anssari et al., where silica nanofluid had a higher concentration (2 wt%). Uncoated silica nanoparticles are negatively charged and thus are naturally attracted by positively charged carbonate rock ¹⁴⁰. With their adsorption onto the rock surface, part of the positive charge on the rock surface is neutralized and previously adsorbed organic materials are desorbed. Their interaction with the carbonate surface leads to partial desorption of organic materials by competitive adsorption ^{138,142}. However, uncoated silica nanoparticles aggregate rapidly over time and the average particle size was observed to grow up to 1000 nm in the first 40 minutes. Hybrid (coated by silane agent) silica nanofluid showed a small average particle size increase and improved stability ¹³⁵. Another mechanism that enhances wettability modification is proposed that silica nanoparticles gradually form a wedge film in the three-phase contact area and lead to the generation of structural disjoining pressure due to the coexistence of electrostatic repulsion and Brownian motion between nanoparticles. When this structural disjoining pressure increases above oil droplet adhesion, oil droplets on the rock surface start peeling off, resulting in a more water-wet surface and higher oil recovery ¹⁴².

Most metallic oxide nanoparticles, such as zirconium oxide nanoparticles, are hydrophilic in nature. Their adsorption onto a carbonate surface will render strong water-wetness to originally oil-wet rock. Researchers proposed a wettability alteration mechanism that metallic oxide nanoparticles move and gather by the formation of wedge film, and then the oil drop is peeled. Free imbibition tests revealed the strong capability for oil recovery from oil-wet carbonate of metallic oxide nanoparticles ¹⁴⁵.

Bare Fe_3O_4 nanoparticles show clearly good hydrophilicity. Shalbafan et al. took experiments to study the performance of differently coated Fe_3O_4 NPs¹⁴¹. EDTA or SLS-coated Fe_3O_4 nanoparticles are more stable and hydrophilic than bare Fe_3O_4 NPs. Increased concentration (0~0.9 wt%) of coated Fe_3O_4 nanofluid results in reduced and then increased contact angles, suggesting an optimal concentration of 0.2 wt% and 0.3 wt% for EDTA or SLS coated nanoparticles respectively. EDTA-coated Fe_3O_4 nanoparticles can alter wettability at low concentrations, while SLS-coated Fe_3O_4 nanoparticles achieve better stability and oil recovery enhancement. The contact angle didn't stabilize until after 48 hours of exposure time. Reducing the salinity (0~30000 pm) leads to a decrease in contact angle. Pressure (1~35 bar) has a negligible effect on the wettability effect of nanoparticles. Temperature increase leads to contact angle reduction. Changes in pH affect rock surface charge and affect the attraction of rock surface towards nanoparticles, resulting in different wetting state¹⁴¹.

Experiments on ZrO_2 nanofluid (0.05~0.10 g/ml) and calcite surface taken by Karimi et al. indicate the existence of optimal concentrations that provide the smallest contact angle. The mixture of ZrO_2 nanofluid and nonionic surfactant imbibed rapidly into the carbonate core and reached 40% oil recovery in half a day. ZrO_2 nanoparticles can change carbonate from strongly oil-wet to strongly water-wet. It changes wettability by adsorbing and forming nanostructured ribbons. This process requires at least 2 days¹⁴⁵.

MgO nanoparticles seem to perform differently from other types of nanoparticles under changing environmental parameters. For MgO nanofluid, it is suggested by Nahid et al. to have proper contact time, temperature, and nanoparticle concentration to ensure the desired nucleation rate. MgO nanoparticles form different nano-structures on carbonate rock due to different nucleation rates, thus resulting in different rock surface roughness. Below that desired value, an increase in

each of these three parameters has a positive effect on wettability alteration. Above that value, it goes adversely. Temperature increases may either strengthen or impair the wettability effect of MgO nanoparticles, depending on the composition of the nanofluid. However, by using the composition of the best wettability alteration performance, increased temperature resulted in further contact angle reduction. A treatment time of 3 days is the most satisfying choice. Longer than 3 days, some disorder on the nanostructured surface could happen that increase contact angle. They suggested that different treatment times resulted in different nucleation rates, which in turn led to different crystal structures on rock surfaces ¹³⁹.

A mixture of different kinds of nanoparticles can also bring interesting properties. For example, a mixture of 30% NiO/SiO₂ showed the self-cleaning property (heavy oil been conveniently removed) which was not observed separately in NiO nor SiO₂ case. The suggested mechanism attributes this property to the high energy level of nanoparticles mixture that enables them to penetrate the layers of oil, lightening and dispersing heavy oil into solvent by forming hydrogen bonds with asphaltenes ¹³⁶.

2.3.2.3 Influencing factors

Several important parameters influence the wettability effect of nanoparticles, including particle size, contact time, nanoparticle concentration, temperature, and salinity.

Nanoparticle size can influence wettability alteration and oil recovery from the carbonate reservoir. Silica nanoparticles of smaller size (11-14 nm) were observed to lead to smaller contact angles and higher recovery compared to larger ones (30-40 nm). Researchers believed that this improvement brought by size difference was because smaller particles can be transported better through porous media. Besides, by dissolving into a solution, nanoparticles also aggregate. Thus the average size

of nanoparticles in water is usually much bigger than the average size of nanopowder ¹⁴⁶. This average size difference was also proved by the study of Arain et al. ¹³⁵. In their experiments, however, the difference in nanoparticle sizes didn't induce a difference in recovery. The size range of their experiment was 5-10 nm and 20-25 nm, which was relatively small and might be the reason for the different phenomena.

Increased contact time inside nanofluid leads to more water-wet rock surfaces ^{140,142}. It is observed that wettability modification induced by different types of nanoparticles were slow changes that take at least 2 days to stabilize ^{141,142,145}. However, there are also results showing that the adsorption of silica nanoparticles is a fast process. Al-anssari et al. found that 3 hours is enough for silica nanofluid. They observed that most of the wettability modification happened during the first 1 hour ¹³⁷. Abbas and Hadi also observed that the wettability modification happened in about 1 hour ¹⁴⁷. This difference might be caused by different nanoparticle types and concentrations. The nanoparticles studied by Shalbafan et al. ¹⁴¹ and Karimi et al. ¹⁴⁵ were Fe₃O₄ and ZrO₂ respectively. The concentration of silica nanoparticles studied by Al-anssari et al. and Abbas&Hadi was 2 wt% and 0.4 wt%, much higher than 0.1 wt% which was used in the study of Hou et al ¹⁴².

Increased nanoparticle concentration has a positive influence on wettability alteration toward water-wet conditions ^{136,140,142}. For example, an increased concentration of silica nanoparticles (from 0 to 0.8 wt%) improved the wettability modification effect ¹⁴⁸. However, Al-anssari et al. found that after concentration reached a threshold value, this positive influence became insignificant. They suggested controlling the nanofluid concentration at the corresponding threshold value from an economic perspective ¹³⁷. Some observed that increased concentration (3 wt%) led to increased contact angle, which was explained by the enhanced precipitation of acids on rock surface ¹³⁸. The oil recovery results obtained by Maghzi et al. showed decreased recovery

after silica nanoparticle concentration went beyond 3 wt% ¹⁴⁹. Those results suggest the existence of a concentration limit beyond which increased concentration leads to an impaired wettability modification effect.

Temperature leads to different wettability results in carbonate rock treated with nanoparticles. Shalbafan et al. found that increased temperature rendered more water-wetness to carbonate rock treated with Fe₃O₄ nanoparticle solution. They suggested this effect of temperature to be due to the reduction in IFT and oil viscosity ¹⁴¹. The experiments taken by Arain et al. showed that temperature lower than 50°C had little effect on silica nanoparticle adsorption. As the temperature increased from 50°C to 70°C, bare silica nanoparticle adsorption was reduced while hybrid silica nanoparticle adsorption was enhanced. They suggested that this difference was due to the surface charge difference of nanoparticles and surface charge of carbonate rock changing from positive to negative along with increased temperature ¹³⁵. Generally, increased temperature leads to more aggregation of nanoparticles due to enhanced Brownian motion while changing the surface charge of carbonate rock, thus resulting in different adsorption behavior under different conditions.

Salinity has a relatively negative effect on nanofluids. An increase in salinity reduces nanofluid stability, especially under low nanoparticle concentrations ¹⁵⁰. Entry 1,3 and 2,4 as well as 6 and 7,8 in Table 12, nanoparticles have poor wettability alteration performance under high salinity conditions, especially at low concentration ¹³⁸. A study on Fe₃O₄ shows that reduced brine salinity induces reduced contact angle due to better stability and wettability modification effect of nanoparticles ¹⁴¹. However, impaired stability doesn't necessarily lead to impaired wettability modification. For example, it is observed that the addition of NaCl can decrease silica nanoparticles' stability but improve the wettability modification because sodium ions compress the electric double layer ^{140,142}. Al₂O₃ nanoparticles are observed to have a better wettability effect

in deionized water rather than brine. They tend to precipitate very fast in high salinity water ¹³⁸. It is suggested that the presence of electrolyte neutralizes part of the zeta potential and decreases the electrostatic repulsion forces among nanoparticles as well as between nanoparticles and rock surface, resulting in more and faster adsorption of nanoparticles onto carbonate surface ¹⁴⁰. Enhanced adsorption can lead to enhanced wettability modification as was observed by Nazari et al. in SiO₂, TiO₂ nanofluid cases with salinity increased from 30000 ppm to 120000 ppm ¹⁴⁴. On the other hand, partial agglomeration would happen among nanoparticles, leading to an irregularly coated rock surface due to adsorption which indicates reduced wettability modification ¹³⁷. There seems to be a threshold electrolyte concentration value. Below this value, little aggregation happens among nanoparticles with surface charge. Above this value, however, average particle size increases sharply and adsorbs onto rock surface ¹⁴⁰. Depending on the different coating, increased salinity may have the opposite effect on interfacial behavior. For example, for NiO/SiO₂ nanocomposite, increased salinity seems to have a positive effect on PEG 6000 coated nanocomposite while a negative effect on polydimethylsiloxane coated nanocomposite concerning interfacial behavior ¹³⁶.

In summary, nanoparticles can change the wettability of carbonate rocks from strongly oil-wet to water-wet at relatively low concentrations. It is important to ensure the stability of nanofluid under reservoir conditions, especially high salinity. Temperature's influence on the performance of nanoparticles differs according to different temperature ranges and different kinds of nanoparticles. Pressure has a negligible effect on nanoparticle behavior ^{135,141}.

Table 12 Wettability alteration of nanoparticles.

Entry	nanoparticle	Surfaces modification	Conc. (wt%)	Rock	Water type	Temp (°C)	Contact angle change before-after treatment (°)	Oil recovery %	Ref
1	30% NiO/SiO ₂	PEG 6000	8 v/v%	Carbonate	DW	80	170-40	NG	Dahkaee et al., 2019 ¹³⁶
2	30% NiO/SiO ₂	Polydimethylsiloxane	8 v/v%	Carbonate	DW	80	170-60	NG	Dahkaee et al., 2019 ¹³⁶
3	30% NiO/SiO ₂	PEG 6000	8 v/v%	Carbonate	SW	80	170-105	NG	Dahkaee et al., 2019 ¹³⁶
4	30% NiO/SiO ₂	Polydimethylsiloxane	8 v/v%	Carbonate	SW	80	170-80	NG	Dahkaee et al., 2019 ¹³⁶
5	SiO ₂	Uncoated	500mg/L	Dolomite	Brine	25	166-60	NG	Aghajanzadeh et al., 2019 ¹⁴⁰
6	SiO ₂	Uncoated	500mg/L	Limestone	Brine	25	166-66	15 (nanofluid) 18 (nanofluid + 50000)	Aghajanzadeh et al., 2019 ¹⁴⁰

								mg/L NaCl)	
7	SiO ₂		0.05	Calcite	Brine	25	140-76	20 (nanofluid + 0.10 wt% NaCl)	Hou et al., 2019 ¹⁴²
8	SiO ₂		0.05	Calcite	Brine	25	NG	17 (nanofluid + 0.05 wt% NaCl)	Hou et al., 2019 ¹⁴²
9	SiO ₂		0.10	Calcite	Brine	25	140-57	NG NaCl)	Hou et al., 2019 ¹⁴²
10	MgO		50g/L	Carbonate	Solution with surfactants and acid	70	180-70	NG	Khiabani et al., 2019 ¹³⁹
11	Fe ₃ O ₄	SLS	0.3	Limestone	Solution	25	140-20	NG	Shalbafan et al., 2019 ¹⁴¹
12	Fe ₃ O ₄	SLS		Limestone	Solution	25	NG	20	Shalbafan et al., 2019 ¹⁴¹
13	Fe ₃ O ₄	EDTA	0.2	Limestone	solution	25	140-23	NG	Shalbafan et al., 2019 ¹⁴¹

14	SiO ₂		0.1	Calcite	Solution	25	69.7-58.1	NG	Rezaei et al., 2019 ¹³⁸
15	SiO ₂		2	Calcite	Solution	25	69.7-28.8	NG	Rezaei et al., 2019 ¹³⁸
16	SiO ₂		3	Calcite	Brine	25	69.7-16	NG	Rezaei et al., 2019 ¹³⁸
17	ZnO/SiO ₂ nanocomposite	Xanthan	2000ppm	Carbonate	Low salinity solution	25	132.62- 34.08	19.28	Ali et al., 2019 ¹⁵⁰
18	SiO ₂		0.4	Limestone	Brine	22	167-146	NG	Haeri et al., 2019 ¹⁴⁸
19	SiO ₂		0.4	Limestone	Brine with surfactant 2000ppm	22	167-98	NG	Haeri et al., 2019 ¹⁴⁸

*Oil recovery data comes from spontaneous imbibition experiments, which reflects wettability change in the rock matrix

*Concentration values without unit are of default unit (wt%).

*DW: deionized water; FW: formation water; SW: seawater; NG: not given.

2.3.3 Salt

Electrolytes have been proved to be efficient wettability modifiers. Among all electrolytes, potential determining ions (PDI) play an important role in the wettability alteration process ¹⁵¹. PDI are ions that determine the zeta potential. Generally, they are ions that can dissolve from or precipitate onto the rock surface. For carbonate rocks, the most influencing PDI are SO_4^{2-} , Mg^{2+} , and Ca^{2+} . Water carefully treated with potential determining ions is known as smart water and is applied for improved recovery ⁷⁰. Seawater is also considered a “smart EOR fluid” that reduces the contact angle of carbonate in formations that have low initial salinity ^{152–154}.

2.3.3.1 Different electrolytes and corresponding mechanisms

As one of the PDI for carbonate rock, sulfate (SO_4^{2-}) plays a dominant role in changing rock surface wetting state under high temperature ⁵⁵. Adsorption of sulfate onto chalk can change the surface charge and desorb attracted carboxylic materials ¹⁵¹. Under higher temperatures, sulfate has a stronger affinity towards carbonate surface ^{16,151,152,154,155}. This is because sulfate is solvated by hydrogen bonds in water. A part of these bonds is broken under high temperature, giving rise to a higher affinity towards carbonate surface ¹⁵³. An increase in sulfate concentration is proven to lead to an increase in recovery ¹⁵⁵. However, experiments taken separately by two groups (Gupta and Mohanty, Abdallah and Gmira) showed that sulfate was not able to obtain significant wettability change unless magnesium ions were introduced ^{28,156}. The presence of Ca^{2+} can also promote the effect of sulfate as a wettability modifier ¹⁵¹. At high salinity hard brine conditions, sulfate is not

suitable as a wettability modifier due to possible CaSO_4 precipitation ¹⁵². Besides the implementation in wettability alteration, sulfate seems to have other effects on carbonate that contribute to additional recovery ¹⁵⁵.

Mg^{2+} seems not able to change wettability alone ²⁸. Karimi et al. proposed the possible mechanisms behind wettability modification induced by Mg^{2+} as follows: the addition of Mg^{2+} can increase rock surface zeta potential to more positive, substitute Ca^{2+} on the rock surface, desorb attached carboxylate group, form complexes between carboxylate group and Mg^{2+} , resulting in irreversible desorption of lipophilic groups on rock surface ⁷⁰. The synergic effect has been observed between Mg^{2+} and surfactants on contact angle changes ⁷⁰. At low temperatures, Mg^{2+} is highly hydrated in water. Increased temperature causes dehydration, reduced solubility of Mg^{2+} , less ion-pair between Mg^{2+} and SO_4^{2-} and thus higher activity of Mg^{2+} . Under high temperatures, Mg^{2+} is so active that it was observed to replace Ca^{2+} on rock surface ¹⁵³. By replacing Ca^{2+} or in other words, adsorbing onto the carbonate surface, the presence of Mg^{2+} was observed to modify carbonate wettability to a more water-wetting state ^{70,156}.

Results are showing that the addition of Ca^{2+} can also lead to an increase in oil recovery ^{28,154,156,157}.

Ca^{2+} ions are suggested to react with adsorbed organic materials and desorb them from carbonate rock surface ¹⁵⁶. Although Ca^{2+} ions can alter carbonate rock wettability alone, higher concentration and temperature are favored for a major change in wettability ⁵⁵.

The ratio between ions also influences wettability modification, as observed in the experiment taken by Zhang and Austad ¹⁵⁴. As the Mg^{2+}/Ca^{2+} ionic ratio increases, surface dissolution increases, and thus wettability alteration is improved. The ratio between SO_4^{2-} and Ca^{2+} is related to the zeta potential of the rock surface. As the SO_4^{2-}/Ca^{2+} ionic ratio increases, significant surface change happens mainly because of the desorption of carboxylic materials with the change of zeta potential.

Salinity increase will reduce the optimal surfactant concentration while suppressing the extent of wettability modification under optimal condition ²⁸ and it can reach a salinity level where no wettability modification is induced by specific surfactants ²⁹. For specific oil and surfactant systems, under a given surfactant concentration, there is an optimal salinity for wettability alteration and vice versa ²⁸. Apart from their influence on surfactant performance, Salinity also has a significant effect on nanofluid stability. The experiment taken by Nazari et al. showed that an optimal salinity existed in the wettability effect of $CaCO_3$ nanoparticles but not in that of SiO_2 and TiO_2 nanoparticles ¹⁴⁴.

2.3.3.2 Influencing factors

Rock mineral composition has a considerable influence on the wettability alteration effect of electrolytes. The effect of sulfate on wettability is much larger in chalk than in dolomite ¹⁵⁸, indicating that major mineral difference results in different sulfate performance as a wettability modifier. Minor mineral contents also influence that. There is a so-called “low-salinity effect” that

reduction of brine salinity leads to increased recovery in carbonate formations due to surface charge and possible dissolution ¹⁵⁹. In the experiment taken by Austad et al., it turned out that low-salinity brine contributed to tertiary oil recovery only when there was anhydrite inside the rock material, whose amount had a great impact on the recovery. They believed that sulfate came out of anhydrate and modified the wetting state of rock ¹⁶⁰. Oil composition also has an effect. Experiments have shown that the recovery efficiency of brine injection with carefully prepared salt composition depends partly on oil composition ¹⁵⁵. It is observed that these mentioned three kinds of ions have better performance at high temperatures ²⁸. pH is also an important factor. It is observed that instead of rendering water-wetness, sulfate changes carbonate surface to slightly more oil-wet at pH larger than 7 ⁹. No such phenomenon is reported in the cases of Mg^{2+} and Ca^{2+} . In general, salts or electrolytes can affect carbonate rock wettability either directly by influencing the surface charge or indirectly by influencing the performance of other wettability modifiers. Among all electrolytes, three PDI including sulfate, magnesium, and calcium ions are the main functioning ions. Among these three, sulfate turns out to be the dominating one in wettability modification. It has a strong affinity toward carbonate surfaces, especially under high temperatures and with the presence of the other two kinds of ions. Mg^{2+} and Ca^{2+} are less effective. For a given reservoir and surfactant injection program, there exists an optimal salinity that helps achieve the lowest contact angle.

2.3.4 Alkalies

The application of alkali in the EOR process has been investigated since 1917¹⁶¹. It creates an in-situ surfactant that lowers the IFT and changes the wettability of rock, resulting in a much lower cost than the surfactant flooding process¹⁶¹. It is usually used in a synergic effect with surfactant and polymers to form the ASP flooding process in EOR cases^{162,163}. Alkali can be used to modify the brine pH and improve the wettability performance of surfactants⁷⁹ by shifting the surface charge of carbonate^{1,29}. A combined system of alkali and surfactant showed better wettability modification performance than alkali alone in recovery¹⁶⁴. The addition of alkali into surfactant solutions tends to significantly reduce surfactant consumption^{13,79,165} and extend surfactant application into harsh condition reservoirs^{163,164}.

Commonly used alkalies include Na_2CO_3 , NaOH , and NaHCO_3 ¹⁶⁶. Considering ion composition in brine, strong alkalies, such as Na_2CO_3 , NaOH and KOH are not suitable for high salinity with hard brines due to precipitation issues. NaHCO_3 can be considered under such condition²⁹.

2.4 Challenges and prospects

Most of the commercial surfactants for oilfield applications are expensive. Surfactant retention, especially of anionic surfactants, significantly reduces the profit of increased incremental oil recovery induced by surfactants. Many researchers now turn their interest to natural surfactants in pursuit of lower costs. Some researchers have investigated additives or conditions that reduce

surfactant retention. Surfactant stability issues under high temperature high salinity conditions limit their application in such reservoirs. New solution systems are proposed to improve their performance under harsh conditions. Gemini surfactants have shown promising results in wettability alteration on sandstone rocks and other types of rock surfaces. Further investigation of their application on carbonate rock is required. Natural surfactants have shown their advantages in lower cost and better eco-friendliness.

Nanoparticles are relatively novel materials for wettability alteration. They can substitute surfactants in the solution in the aspect of wettability change of rock. They can also be used alone for wettability modification. Relatively lower cost is one of the major advantages of nanoparticles. To date, a high concentration of nanoparticles in injection fluid is not recommended for low permeability formations because it may block the pores. The stability problem is also a limiting issue for nanoparticles, especially in high salinity formation. Researchers are studying the effect of different coatings, different solution compositions, or different nanoparticle compositions (nanocomposite) to develop types of nanofluids that form monolayer nanostructure on rock surfaces under formation conditions. On the other hand, the mechanism of how nanoparticles attach reversibly or irreversibly to the rock surface is not yet clear.

Selected salts are added into injection fluid for improved compatibility with formation brine. They tend to have a better wettability effect under high temperature conditions and with the presence of some specific minerals like anhydrate. Alkali can modify the formation fluid pH and influence the

zeta potential of the rock surface. They are also added to create in-situ surfactants in ASP EOR processes. However, the application of alkali faces problems like scaling, the negative effect of viscosity, and the production of very stable foams that costs more to handle. Besides, it is important to know how alkalis influence the stability and wettability effect of other wettability modifiers.

2.5 Conclusions

The global petroleum reserves distribution in carbonate reservoirs provides a huge economic potential for enhanced oil recovery from carbonate reservoirs by wettability modification in the originally mixed-wet to oil-wet carbonate rock. Materials that have long been used (surfactants, salt, alkali) or novel (nanoparticles) showed their effect on the wetting state individually or in combination with each other. Surfactants can render low or ultra-low IFT and water-wetness at the same time. Within all types of surfactants, cationic surfactants and gemini surfactants seem to be most applicable. Gemini surfactants show good wettability alteration potential and outstanding interfacial and physicochemical properties. Specific electrolytes, especially potential determining ions of the carbonate rock have a strong influence on rock surface properties and thus influence wettability directly. Alkalis can create in-situ surfactant and also modify carbonate rock wettability by modifying the zeta potential of rock surface. It promotes some surfactants' effect on wettability and IFT while extending their tolerance toward temperature and salinity. Nanoparticles are relatively novel materials for mobility control and strong wettability alteration can be achieved by nanoparticles. It changes the wetting state of carbonate rock by partly irreversible adsorption.

CHAPTER 3

LITERATURE REVIEW 2: RELATIVE CONTRIBUTION OF

WETTABILITY ALTERATION AND INTERFACIAL

TENSION REDUCTION IN EOR

3.1 Introduction

World energy consumption is increasing rapidly in recent years. From 2009 to 2017, annual energy consumption increased by 18%. Among all types of resources, oil is the most important primary energy resource. The consumption of oil stands for around 34% of the total energy consumption. From 2009 to 2017, oil consumption increased by 12.5%. In 2018, a further increase of 1.40 MMbbl/day of crude oil consumption was observed. The long-term consumption increase indicates even higher demand in the future. However, a large portion of oil production comes from mature and declining giant oilfields ¹⁰⁸. To meet future demand, oil producers must either produce more oil from oilfields or develop new reservoirs. EOR techniques are developed for this purpose. Chemical EOR (cEOR) achieves higher oil recovery by injecting certain chemicals. Various chemicals such as polymers, surfactants, salts, and alkalis are applied in oilfields. Novel materials like nanoparticles and nanocomposites have also shown potential. Most of these materials alter oil-water interfacial tension or rock wettability or both.

Interfacial tension (IFT) is an assessment of the energy that keeps the two-phase interface to stabilize the separation. The two-phase interface becomes easier to break when IFT is reduced. Studies on surfactants show that effective surfactants can reduce IFT significantly and mix two phases to form a microemulsion phase ^{81,167}.

Wettability is an assessment of rock preference towards oil and water. In oil-wet formation, the rock favors oil more than water. A large amount of oil adheres to the rock surface and becomes residual oil after waterflooding. In water-wet formation, the rock favors water more than oil. Oil occupies the center of pores and pore throats. In intermediate-wet or mixed-wet formation, the conditions are more complicated. Rock wettability can be altered either by removing the rock surface materials or covering the rock surface with other materials ^{4,12,13}. Important factors affecting wettability include oil composition ^{168,169}, rock mineralogy ¹⁷⁰, rock surface morphology ¹⁷¹, formation temperature and pressure ¹⁷², formation fluid pH ^{16,173}, and so on.

There are several different methods for rock wettability assessment, such as contact angle measurement ²⁴, Amott-Harvey test ³⁷, USBM ³⁷, flotation test ⁴⁰, NMR-based wettability indices ⁴¹, and chromatographic study ³⁸. Contact angle measurement is the most convenient method and is widely used for wettability assessment.

Both IFT and wettability strongly affect oil recovery. IFT reduction is the most applicable way to increase the capillary number by 3~4 orders to make oil flow much easier. WA can significantly increase residual oil production since the oil phase adhering to the rock surface or trapped in pore

centers becomes mobilized and displaced during WA ^{68,174}. However, different cEOR materials have varying impacts on IFT and wettability. Polymers take effect mainly by increasing the viscosity of water injected. In this way, the sweeping efficiency is improved. Novel polymers also showed good performance in WA ¹⁷⁵. Surfactants are very effective materials designed and applied for IFT reduction. Researchers report that many surfactants affect both IFT and wettability, and their performance differs significantly among different types of surfactants ^{176–179}. Table 13 is a general summary of their effect on carbonate rocks. Injection water formulations with salts designed to increase oil recovery are often called "smart water". Salts take effect mainly by affecting the wettability of rock ^{180,181}. Alkaline create in-situ surfactants and lift pH to a higher value that alters rock wettability ^{112,182,183}. Nanoparticles also alter wettability and slightly modify IFT simultaneously ^{184,185}. As a result, if we know the optimal IFT value and wettability condition, the impact on IFT and wettability can be used as the criteria for EOR material selection.

Table 13 Impact of different types of surfactants on IFT and wettability in oil-wet carbonate rocks.

Surfactant types	Impact	Mechanism(s)
Cationic	Strong WA, weak IFT reduction	Forming ion-pairs with organic materials to irreversibly alter rock wettability
Anionic	Weak WA, strong IFT reduction	Form a layer that shows a preference towards the water on top of organic materials on the rock surface to reversibly alter rock wettability.

		Significantly reducing interfacial energy, thus reducing IFT to the ultralow range.
Zwitterionic	Strong WA, strong IFT reduction	Not well addressed.
Nonionic	Moderate impact on wettability and IFT	Forming a double-layer structure between an oil-wet rock and an aqueous phase.

Generally, IFT reduction and WA are considered two main mechanisms for EOR. However, conflicting conclusions about the effect of IFT and WA are presented in the literature. For example, ultralow IFT is reported not favored in liquid-rich shales¹⁸⁶ but is reported to obtain higher oil recovery from fractured oil-wet carbonate cores⁵⁵. WA to water-wet condition increased oil recovery from oil-wet carbonate cores¹⁸⁷ while WA to intermediate-wet condition obtained the highest oil recovery from water-wet sandstone cores¹⁸².

These conflicts may come from two main difficulties in the experimental study of the effect of IFT reduction and WA. Firstly, most EOR materials change IFT and wettability simultaneously, making it difficult to study their impact separately¹⁸⁸. Some studies suggest the relationship between wettability alteration and IFT reduction^{188–190}, which implies that studying their effect separately could be impossible. The second difficulty lies in maintaining the same experimental conditions. IFT and rock's wettability are influenced by many factors such as pH, salinity, nature of the rock surface, brine ionic composition, and temperature^{19,113,191–194}. For example, an increased temperature enhanced the water-wetness of carbonate rock surface^{71,195} while reducing IFT. Besides, there are no identical natural cores. Even when the experiments are conducted in

the same core, the restored saturation and wettability might differ. That difference weakens the confidence in the conclusions drawn.

Considering the difficulties in experiments, numerical simulation becomes a good option since it is much easier to separate the effect of IFT and WA and control other factors in numerical models. Besides, experiments are mostly limited to a core scale, while numerical models can be upscaled to a reservoir scale. The disadvantage of numerical modeling is that it is hard to capture the physical or chemical nature and the complexity of the process by modeling. For example, Darcy's law is widely used to describe the flowing behavior inside reservoirs. It is sufficient in describing the flow of the continuous phase, but it fails to describe the transport of scattered phases ¹⁹⁶. In the EOR process, the residual oil can be scattered, introducing errors into numerical models using Darcy's law. To ensure that the simulation reflects real processes, researchers usually compare their modeling results with experimental results. When they match well, the models are validated and considered qualified for further studies. Then, by changing the IFT and wettability parameters in those validated models, they manage to study the separate effect of IFT reduction and WA on oil recovery. In other words, both experiments and numerical simulations have limitations in providing valuable knowledge about the connection between IFT and wettability with oil recovery. By combining information from both experimental and simulation studies, we can get a more comprehensive understanding of the impacts and relative contribution of IFT reduction and WA for different situations.

The relative contribution of IFT reduction and WA is frequently mentioned in the literature. For example, the experimental studies conducted by Iman et al.¹⁹⁷, and Xu et al.¹⁹⁸ show how the coupled effect works out in real cases. The simulation studies conducted by Shen et al.¹⁹⁹ and Sheng²⁰⁰ provide valuable insights into the interplay of the two mechanisms. However, the discussions on this topic are limited to specific materials or conditions. Besides, there is no comprehensive review on this topic till now. Our work considered different factors including rock types, residual oil categories, initial IFT magnitude, initial wetting state, and formation permeability to comprise a comprehensive review that explains the relative contribution of IFT reduction and WA under different conditions.

In this chapter, we reviewed numerical simulations and experimental studies focused on the effect of IFT reduction and WA on the EOR process. Conflicting results and conclusions are compared and discussed to reflect on the mechanisms behind them. Before discussing IFT and WA's relative contribution, it is crucial to understand different residual oil categories. Section 2 discusses the categorization of residual oil.

3.2 Categories of residual oil

The residual oil formation process is dominated by rock structure, wettability, fluid properties, displacement situation, and initial water contents^{196,201,202}. There are different categories of residual oil. Guo et al.¹⁹⁶ defined five different categories: isolated oil droplet, oil film, residual oil in dead ends, residual oil in pore throats, and cluster residual oil¹⁹⁶. Zhang et al.²⁰² classified

the residual oil into four typical categories: oil film that adheres to the pore walls, residual oil in dead ends, residual oil in pore throats (referred to as oil ganglia), and residual oil at pore corners²⁰². Fang et al.²⁰³ classified the residual oil in low permeability reservoirs into five categories: oil film, residual oil in blind ends, columnar, residual oil cluster and trapped oil drops²⁰³. All of these categorizations are based on residual oil locations and forms.

Wettability is found to be the key factor in determining the residual oil distribution¹⁹⁶. From the aspect of amount, Guo et al.¹⁹⁶ found that all categories of residual oil are widely distributed in an oil-wet porous medium. However, in a neutral-wet/water-wet medium, it is difficult to find oil film or residual oil in pore throats. They also observed that residual oil cluster and residual oil in dead ends are significantly reduced¹⁹⁶. From the aspect of the location, in water-wet rocks, oil droplets locate at the center of pores due to the capillary snap-off mechanism²⁰¹, while in oil-wet rocks, the isolated oil droplets attach to the pore walls due to rock preference toward the oil phase¹⁹⁶. In oil-wet rock, the residual oil clusters have a flatter sheet-like structure and fill the small pores. However, in water-wet rock, the residual oil clusters tend to occupy the centers of the wider pores²⁰⁴ as shown in **Figure 22**.

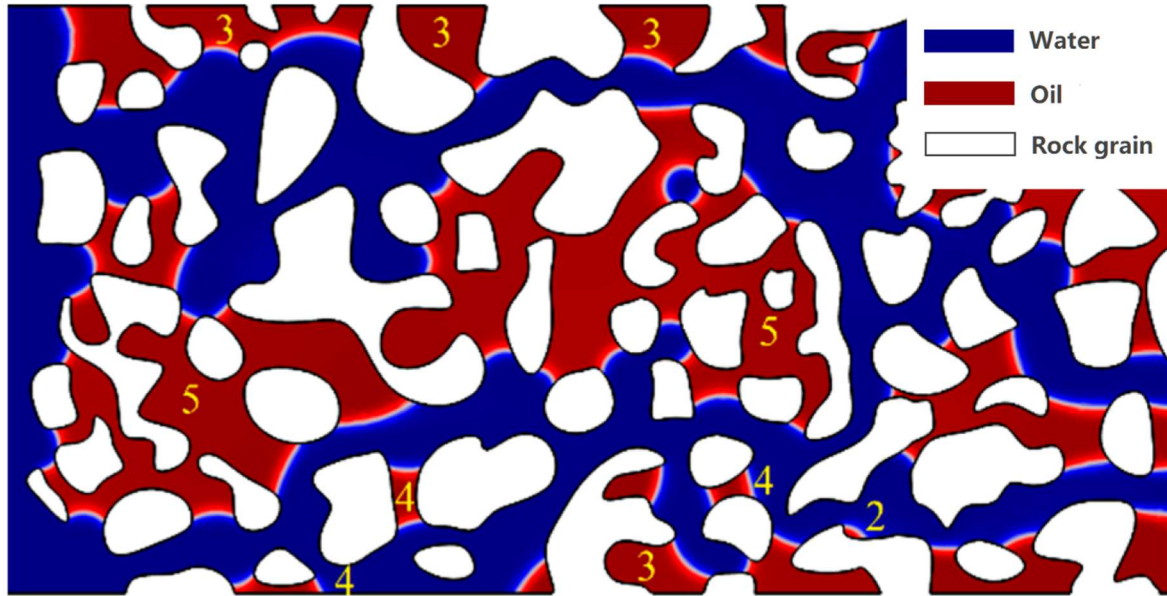


Figure 22 Residual oil distribution in the oil-wet rock (1) isolated oil droplets; (2) oil film; (3) residual oil in dead ends; (4) residual oil in pore throats; and (5) residual oil cluster 196 (Image reused with permission of the rights holder, MDPI, 2019).

The oil displacement by water flooding involves different forces. The four major forces to consider during the surfactant solution imbibition process include pressure gradient generated by fluid injection, gravity, capillary force, and viscous force ⁶⁵. Other forces can also play an important role when the system meets specific conditions. For example, when there is a high salinity contrast between the injected fluid and formation brine, the effect of osmotic pressure becomes significant ^{205,206}. The pressure gradient generated by fluid injection is determined by the pressure difference between injection and production wells and their distance on a large scale. The heterogeneity of the formation has a significant effect on its distribution. Gravity force is determined by the density difference between the injected water phase and the oil phase. It is an important natural drainage mechanism throughout oil recovery. Capillary force is determined

by the interfacial activities between rock, oil, and injected fluid. Its magnitude and direction can be modified by the EOR method to help recover residual oil. Viscous force is the force between residual oil and the fluid flowing past the oil. Generally, EOR methods are designed to enhance or mitigate one or more of the forces to mobilize the residual oil. For example, the selective formation plugging method blocks high permeability zones to increase the pressure gradient exposed to low permeability zones²⁰⁷. Wettability modifiers such as surfactants alter rock to water-wet condition to reverse the capillary force's direction. In this way they help drain the oil out. Forces involved in oil displacement and their related EOR methods are illustrated in Table 14. Different EOR approaches change the four major forces differently. As a result, the difference in residual oil amount and location calls for different EOR approaches. To design an optimal EOR program, it is essential to know the residual oil distribution and how IFT and WA affect residual oil. In thesis, the residual oil is classified into five categories based on its locations and forms: oil film, dead end oil, pore throat oil, residual oil clusters and trapped oil droplets. In the following subsections, detailed descriptions are given for each category of residual oil.

Table 14 Forces involved in oil displacement and their related EOR methods.

Forces	The role in oil displacement	Related EOR method(s)
Pressure gradient	The main driving force in the waterflooding stage. It will not play	EOR methods including selective plugging and the addition of polymers can help alleviate the viscous fingering phenomenon. In such cases, the pressure

generated by fluid injection	an important role in the EOR stage unless the flow pattern is changed.	gradient exerted on lower permeability zones is increased. Improvement in sweeping efficiency leads to residual oil recovery ^{207,208} .
Gravity force	Generally, a positive driving force during oil production. On the other hand, it may also induce gravity override and decrease the oil recovery in gas flooding.	Many methods such as SEGD, WAG, and GAGD involve gas injection and possibly IFT reduction to enhance the gravity force ^{2,209} . In the gas flooding process, techniques like foaming and in-situ gas generation can be applied to eliminate the gravity override problem ²¹⁰ .
Capillary force	A negative force that holds residual oil inside the formation.	By alternating the wettability, the negative force can be turned into positive and helps the imbibition of injection fluid to displace residual oil inside ^{68,174} .
The viscous force between water and oil	A positive force that helps recover oil in all stages.	Increasing the injection velocity can enhance the viscous force. It involves the interplay between the viscous force and capillary force ^{211,212} . Increasing the injection fluid viscosity can help to exert viscous force on residual oil ²⁰² .

3.2.1 Oil film

In oil-wet rock, the thin layer of oil that adheres to the pore and pore throat walls after waterflooding is called oil film, as is shown in the micro-model image in Figure 23. The oil film is formed by the attraction between the oil-wet rock surface and the oil phase.

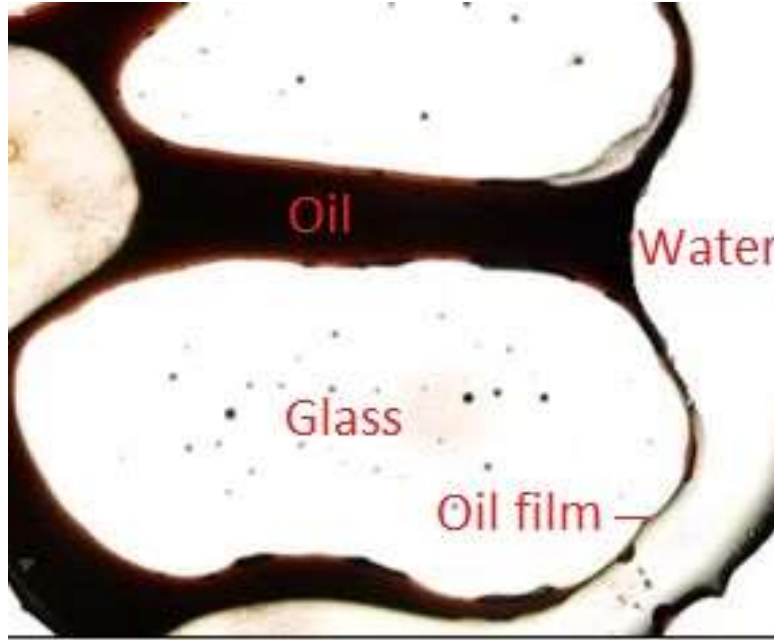


Figure 23 Oil film in oil-wet micromodel ²¹³.

The removal of the oil film is studied from a stress and energy point of view. From a stress point of view, Zhang et al. ²⁰² suggested yield stress that characterizes oil film by the following equation:

$$\text{if } \tau \leq \tau_y \quad \gamma = 0 \quad (3.1)$$

$$\text{if } \tau > \tau_y \quad \tau - \tau_y = \eta_p \gamma \quad (3.2)$$

In these two equations, τ and τ_y are shear stress and yield stress respectively, γ represents the shear rate. Based on the equation, shear stress should exceed the value of yield stress to mobilize the oil film ²⁰².

From an energy point of view, Israelachvili proposed Equation 3.3 which describes the work of adhesion in the oil film removal process ⁸. In the EOR process, the removal of oil film involves the separation of the attached oil phase from pore walls.

$$W_{ows} = \gamma_{ow}(1 - \cos\theta) \quad (3.3)$$

In Equation 3.3, W_{ows} is the work of adhesion. θ is the wetting angle between the tangent line of the interface and the water-rock interface. γ_{ow} is the interfacial energy on the interface between oil and water. For liquid-liquid interfaces, interfacial energy equals interfacial tension. Based on Equation 3.3, changes in IFT and wettability directly affect this work of adhesion, indicating that IFT reduction and WA towards water-wet conditions help the recovery of oil.

3.2.2 Dead-end oil

Dead ends refer to pore bodies that connect with other pores from only one side. Figure 24 illustrates the distribution of dead-end oil. The polymer flooding test reported in Guo et al. 's study showed that although polymer flooding significantly reduced the formation of other categories of residual oil, the dead-end oil was still widely distributed ¹⁹⁶. Jamaloei and Kharrrat also observed that dead-end oil distributed widely even after dilute surfactant flooding ²¹⁴. They observed that in a water-wet medium, a small volume of residual oil can remain in dead ends located away from the direction of water streamlines ²¹⁴. Zhang et al. conducted micromodel flooding experiments which showed that dead-end oil required more soaking time to recover than residual oil in other locations ²¹⁵. In a word, the mobilization of dead-end oil is relatively hard because of the connectivity of the pores.

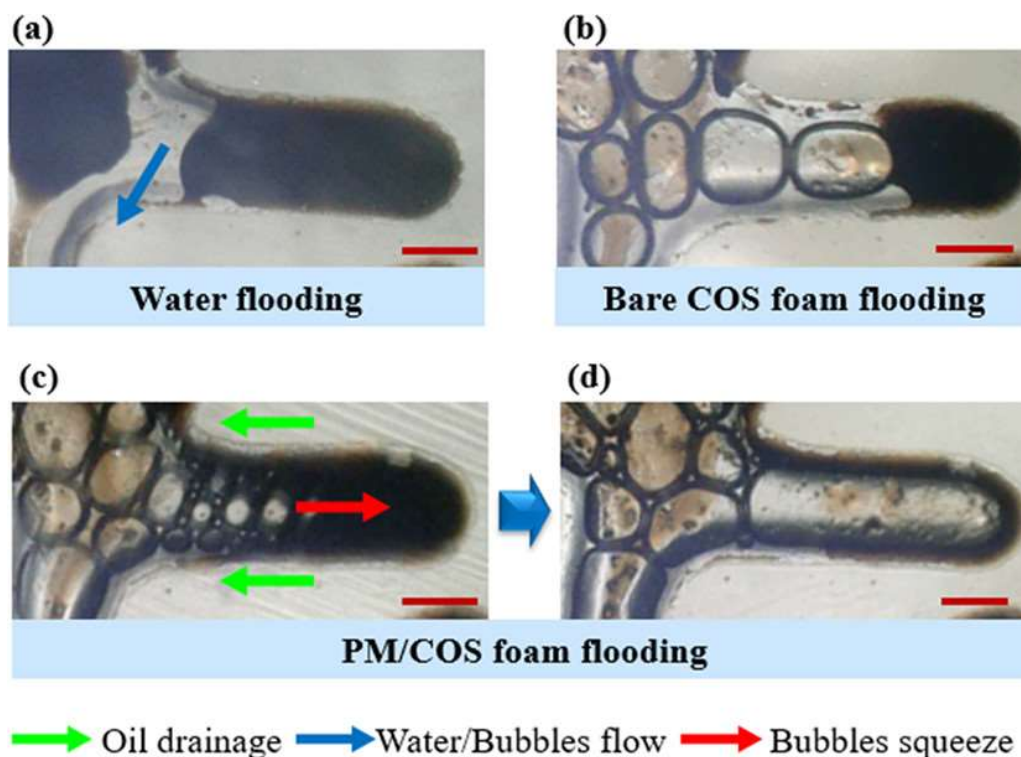


Figure 24 Dead-end oil and its recovery from water flooding, CO₂ foam flooding, and CO₂ foam flooding stabilized by particulate matter (PM) 216 (Image reused with permission of the rights holder, ACS publications, 2020).

The pressure gradient generated by fluid injection fails to directly displace dead-end oil because those pores are blocked from one side. The recovery of dead-end oil usually involves foams to increase the viscosity of injection fluid. When injected fluid flows over the open side of a dead-end, a vortex is developed at the opening. This vortex disturbs the stable condition of residual oil and exerts a viscous force on it. Besides, researchers also find that viscoelastic polymers can develop deeper vortex that contacts more oil and is of greater stress. Under such conditions, the vortex disperses the residual oil into smaller oil drops and moves those drops from the dead ends to the main channels^{202,217}. Lv et al.²¹⁶ observed that aqueous CO₂ foam flooding successfully

displaced oil in dead ends by scrubbing ²¹⁶. Qian et al. suggested nanoparticle-stabilized foam for the recovery of dead-end oil ²¹⁸. The changes in IFT and wettability can also play their roles in this process. Sohrabi et al. observed that IFT reduction made gas and oil phases more miscible. As a result, the gas flow carried more residual oil out from dead ends ²¹⁹. Seyyedi et al. ²²⁰ observed that diffusion of CO₂ into the oil reduced the IFT significantly, resulting in oil recovery from dead ends ²²⁰. Yekeen et al. concluded from flooding experiments that emulsion stability and viscosity, IFT reduction, and WA played important roles in dead-end oil recovery ²²¹. These results indicate that IFT reduction, WA, and viscous force enhancement are possible mechanisms for the recovery of dead-end oil.

Dead-end oil recovery by viscoelastic polymers relates to the viscoelastic effect that improves micro displacement efficiency and adds to the swept volume ²⁰². Three dimensionless numbers, Deborah number (De), Elasticity number (El), and Weissenberg number (Wi) can be applied to describe the viscoelastic effect ^{222–224}. Deborah number is the ratio between the relaxation time and the residence time in the flow. Elasticity number is the ratio of elastic to inertial stresses independent of kinematic processes. Elasticity number can be represented by the ratio between Weissenberg number and Reynolds number (Re). Weissenberg number is the dimensionless strain rate ²²³. Deborah number is widely used in viscoelastic effect assessment from experiment data or as input in numerical models. Azad and Trivedi reported that a lower Deborah number referred to a stronger viscoelastic effect which would increase the residual oil recovery ²²².

3.2.3 Pore throat oil

The oil film is formed mainly due to rock wettability and is widely distributed. Dead-end oil exists in places hardly swept by waterflooding. These two categories of residual oil will not block the flowing of water through pore or pore throats. Residual oil in pore throats, however, occupies all the space inside the pore throat and thus preventing water from flowing through. Similar to oil film, the formation of pore throat oil is also found to be influenced by rock wettability and capillary forces ¹⁹⁶. Besides, a lack of pressure gradient on both openings of the pore throats may also induce the forming of pore throat oil, as shown in Figure 25 (a) ²¹⁶. In oil-wet rocks, capillary force may stop water from entering pore throats, leaving oil inside the pore throats intact, as shown in Figure 25 (b).

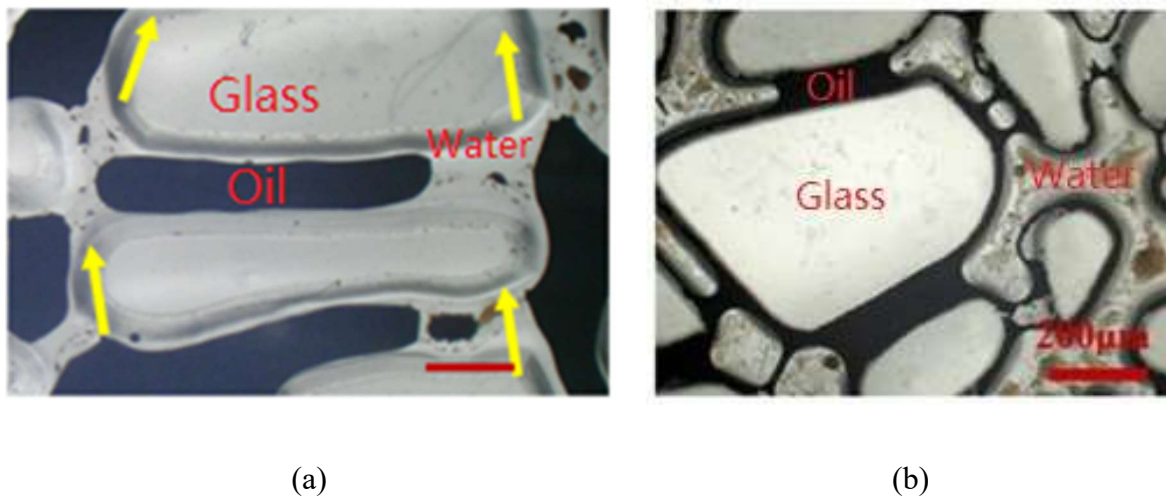


Figure 25 Pore throat oil in water-wet (left) and oil-wet (right) medium in micromodels ²¹⁶.

In water-wet rocks, to displace pore throat oil, it is important to increase the microscopic sweep efficiency. Foam flooding, polymer flooding, and viscoelastic fluid flooding may be applied.

The pressure difference generated by capillary pressure can be represented by Equation 3.4: To displace the oil in the rock matrix, the pressure distribution should satisfy this condition: $p_w + \Delta p > p_o$.

$$\Delta p = \frac{2\gamma_{ow}\cos\theta}{r_c} \quad (3.4)$$

In this equation, Δp is the capillary pressure across the interface. γ_{ow} is interfacial tension on the interface between oil and water. θ is the contact angle. r_c is the radius of the pore throat. From this equation, the capillary pressure depends on IFT, contact angle, and the radius of the pore throat. The average pore throat radius is closely related to rock permeability. If not considering the influence of heterogeneity, high permeability rock theoretically has a larger average pore throat radius. Since wettability is one of the main factors in the residual oil forming process, changing rock wettability can help recover pore throat oil ¹⁹⁶. When rock is altered to a water-wet condition, the negative capillary force that kept oil inside will change its direction to positive. According to Equation 3.4, when the direction of the capillary force becomes positive, the pressure difference starts helping the imbibition of water to pore throats, thus helping oil displacement. In such a condition, water starts to enter the pore throats from the pore throat walls to the center and expel the oil phase. Equation 3.4 also indicates that IFT reduction helps to produce pore throat oil by reducing the magnitude of the negative capillary force. When capillary force is reduced, less pressure difference is required to displace the residual oil in oil-wet pore

throats. In such a condition, water starts to enter the pore throats from the center of the pore throats and expel the oil phase. Another recovery method involves vortices. Similar to dead-end oil, the flowing of water over the opening of the pore may create a vortex that exerts a viscous force on the oil phase inside the pore throats ²⁰².

In a word, IFT reduction, WA to water-wet condition, viscous force enhancement, and microscopic sweep efficiency improvement are possible mechanisms for the recovery of pore throat oil.

3.2.4 Residual oil clusters

Residual oil clusters are continuous oil phases occupying several pores or even a large block of the rock matrix, as shown in Figure 26. They are believed to be formed mainly because of reservoir heterogeneity and are normally located in low permeability zones in addition to water fingering due to viscosity contrast. Due to heterogeneity, water prefers to flow through the predominant pathways formed in high permeability zones. In low permeability zones near the predominant pathways, the oil is thus difficult to be swept ¹⁹⁶. In a naturally fractured, oil-wet reservoir, for example, the low permeability rock matrix surrounded by high permeability fractures can contain a large number of residual oil clusters after waterflooding ¹⁶⁴.

All four driving forces mentioned before can be enhanced to displace residual oil clusters. Fang et al. ²⁰³ found that increased displacement pressure gradient helped oil recovery from residual

oil clusters. They also found that polymer flooding could enhance the viscous force and help oil displacement ²⁰³. Lu et al. found that IFT reduction enhanced the gravity effect while WA to water-wet condition changed capillary force from negative to positive. The combined effect of these two mechanisms helped displace the residual oil from an extremely vuggy and heterogeneous core. Capillary and gravity forces are the two main driving forces that help injected aqueous phase imbibe into low permeability formation.

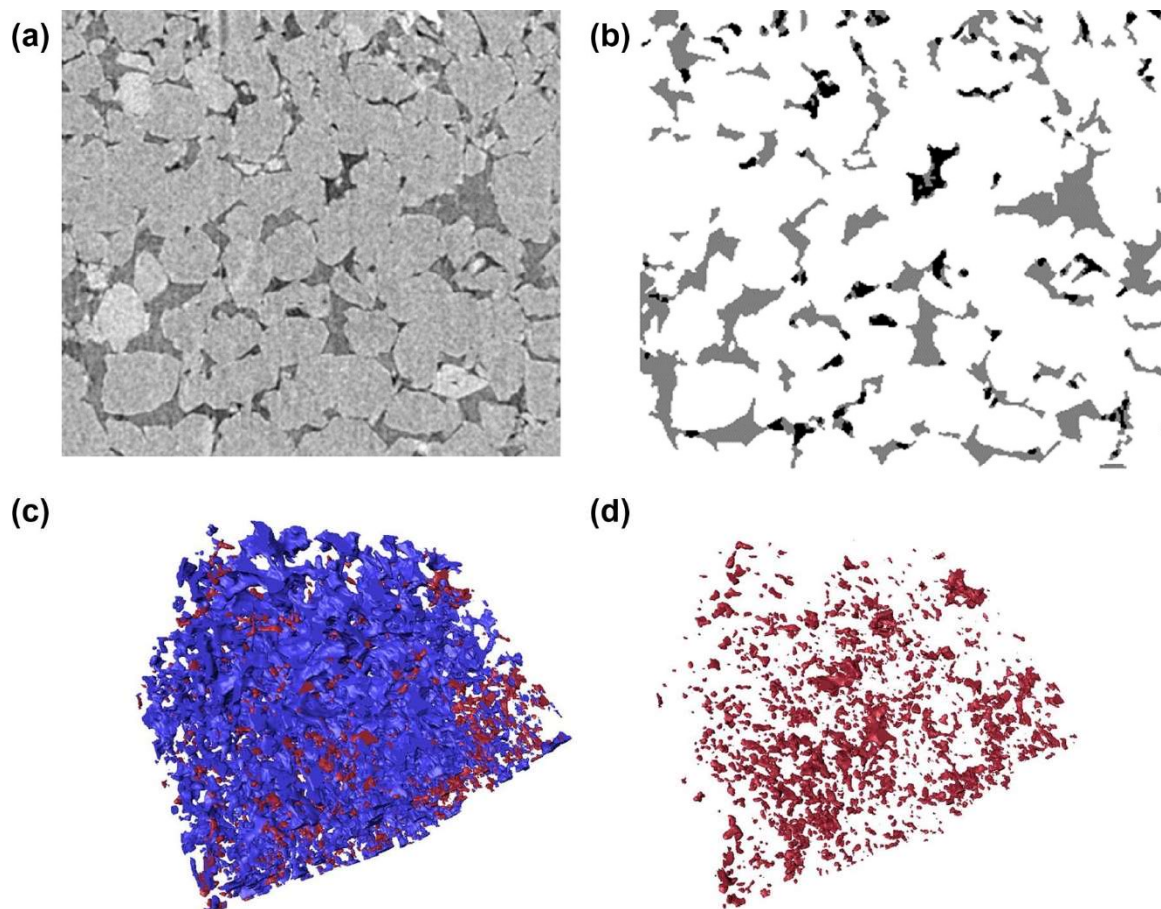


Figure 26 Residual oil clusters: gray and black parts in (a,b), red parts in (c,d) ²⁰⁴.

Apart from the capillary force, the gravity force is another main driving force. A three-regime oil displacement model (shown in Figure 27) was proposed to describe the spontaneous imbibition

process in high permeability limestone core ²: (1) Regime 1, the main driving force is capillary force; (2) Regime 2, both gravity and capillary force contributes to the oil recovery; (3) Regime 3, gravity becomes the main driving force. The oil recovery rate decreases from regime 1 to regime 3. Depending on the rock, fluids, and pressure conditions, one or two regimes may not appear in the curve. For example, as core height decreases, regime 3 may become negligible due to the weakened effect of gravity ². When EOR materials applied lack the ability to induce strong wettability alteration and thus strong capillary force, regime 1 and regime 2 may disappear ⁸⁴. As a result, the contribution of capillary force and gravity can be distinguished from the spontaneous imbibition curve. Besides, the driving forces can be distinguished by observing where the oil comes out of the sample. Capillary force drives the oil out from all surfaces of the rock sample. Gravity drives oil out mainly from the top surface ²²⁵.

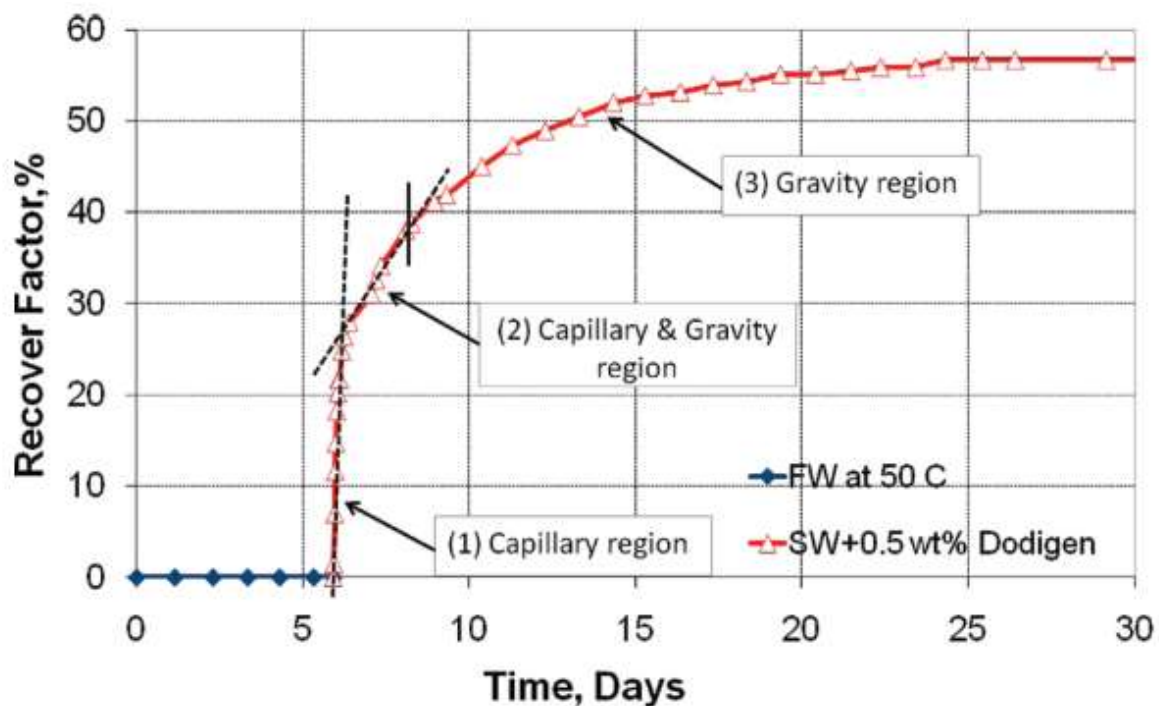


Figure 27 The three regimes of spontaneous imbibition ².

The bond number can be used to assess the relative importance of gravity and capillary force. It is the ratio between gravity and capillary force. There are different definitions. Here we adopt the one from Pennell et al. 's work ²²⁶ that considers both IFT and wettability. It is expressed in Equation 3.5.

$$N_B = \frac{kk_{rw}\Delta\rho g}{\gamma_{ow}\cos\theta} \quad (3.5)$$

In the equation, N_B is the bond number. $\Delta\rho$ represents the difference in the densities of the water phase and oil phase. g represents the gravity coefficient. k represents rock permeability. k_{rw} represents the water relative permeability.

A larger bond number indicates that gravity plays a dominating role and Regime 3 will account for most of the increased oil recovery. A smaller bond number indicates that capillary force is the dominant driving force and Regime 1 will account for most of the increased oil recovery. IFT reduction enhances gravity force in oil-wet conditions. WA towards the water-wet condition reverses the capillary force direction. Either of them can help displace residual oil clusters. The introduction of materials such as surfactants, alkalis, and nanoparticles can change the IFT and wettability of rock. Apart from IFT reduction and WA, increasing injection fluid viscosity by injecting foams ²²⁷ or adding polymers, or reducing oil viscosity by hot water injection are also effective EOR mechanisms for residual oil clusters ²²⁸.

3.2.5 Trapped oil droplets

The four categories of residual oil described above distribute more in oil-wet rocks. In water-wet rocks, water flooding can leave some oil behind in the pores due to the capillary snap-off mechanism. In porous media, the nonwetting phase flows through the center of pores and throats. At locations where the aspect ratio is large, the nonwetting phase may be cut into discontinuous droplets at the narrow pore throats by the wetting phase. In a water-wet rock case, the nonwetting phase is the oil phase. Due to a relatively high IFT, the oil droplets inside the pores cannot deform or disperse to flow through the pore throats. Injected aqueous fluid flows around the droplets and forms the continuous phase, reducing the pressure gradient exposed to the oil droplets. The residual oil exists at the center of the pores in form of oil droplets, as shown in the micro-model image in Figure 28. In such a case, the positive capillary force prevents the residual oil from flowing out^{201,229}. The formation mechanism of trapped oil indicates that either reducing IFT or reversing the wettability towards intermediate-wet conditions will reduce the number of trapped oil droplets.

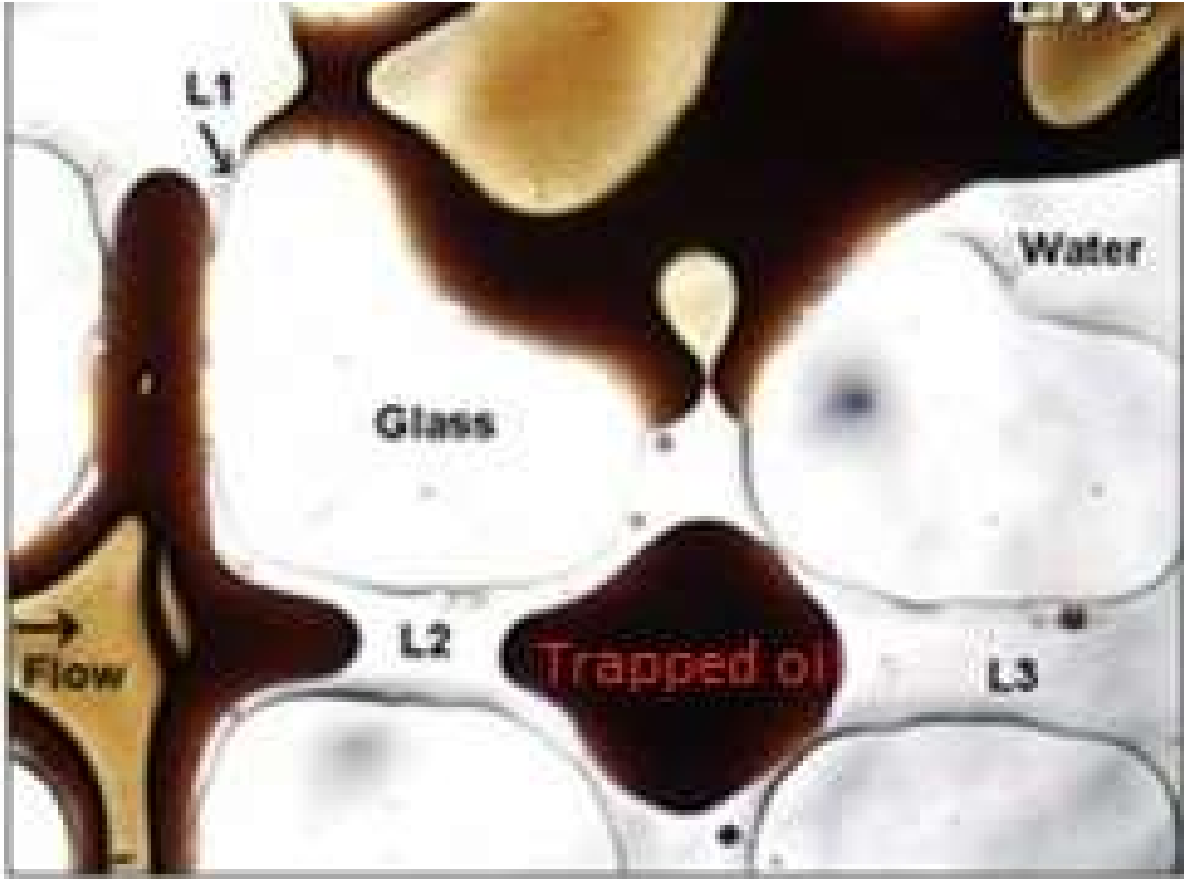


Figure 28 Trapped oil droplet ¹⁸³.

The trapping number can be used to reflect on possible recovery mechanisms for trapped oil droplets. The definition given by Pennell et al. (Equation 3.6, 3.7, 3.8) considers viscous force, gravity force, and capillary force ²²⁶. For one single pore, there exists a critical trapping number value above which the trapped oil droplet starts to produce. Although equations listed here are not validated by some experimental work ²³⁰ and there are other different definitions ²²⁹, they provide an understanding of how wettability and IFT affect trapped oil droplets.

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B \sin\alpha + N_B^2} = \frac{2kk_{rw}\beta}{r_n d_b} \quad (3.6)$$

$$N_{Ca} = \frac{q_w \mu_w}{\gamma_{ow} \cos \theta} \quad (3.7)$$

$$N_B = \frac{k k_{rw} \Delta \rho g}{\gamma_{ow} \cos \theta} \quad (3.8)$$

In this equation system, N_{Ca} is the capillary number. It reflects the relative magnitude of viscous force over capillary force. N_B is the bond number. It reflects the relative magnitude of gravity force to capillary force. α is the angle between pore orientation and horizontal axis. r_n and β are representative of the average pore characteristics of the medium. d_b is the characteristic globule "length". q_w is the Darcy velocity of the water phase in the direction of the pore orientation. μ_w is the water phase dynamic viscosity.

Under different conditions, the trapping number can be simplified accordingly. In the spontaneous imbibition process, the trapping number approximately equals the bond number since the Darcy velocity of the injection phase is relatively small. Equation 3.9 can be used as a simplified form of the trapping number. In core flooding and forced imbibition experiments, the Darcy velocity may be high enough to make the capillary number the dominant term. The trapping number can be simplified to Equation 3.10.

$$N_T \approx N_B = \frac{k k_{rw} \Delta \rho g}{\gamma_{ow} \cos \theta} \quad (3.9)$$

$$N_T \approx N_{Ca} = \frac{q_w \mu_w}{\gamma_{ow} \cos \theta} \quad (3.10)$$

Based on both equations, IFT reduction and WA towards water-wet conditions will increase the trapping number, thus helping to produce trapped oil droplets.

Franklin proposed an equation that relates the saturation of residual oil with capillary and bond numbers. The Franklin equation was found to have a good match with experimental data ^{231,232}.

His definition is given below:

$$S_{or} = 0.02 + 0.0505 \log \left(\frac{0.01227}{N_c + 0.5N_B} \right) \quad (3.11)$$

$$N_B = \frac{\Delta \rho g k}{\gamma_{ow}} \quad (3.12)$$

In his definition, the bond number is not related to rock wettability. The capillary number he used is defined by Equation 3.7. Based on his equation, IFT reduction and WA towards water-wet conditions will increase the capillary number. IFT reduction will increase the bond number.

When the capillary number or/and the bond number are increased, the residual oil saturation decreases. Both IFT reduction and WA will help produce residual oil. In this aspect, the Franklin equation agrees with the trapping number equation given by Pennell et al. ²²⁶.

Lebedeva observed that more water-wet medium was prone to oil trapping ⁴². Standnes ⁷¹ suggested that gravity-driven imbibition was less likely to form trapped oil droplets than capillary-driven imbibition ⁷¹. Tetteh et al. ¹⁸⁰ suggested that IFT reduction suppressed the capillary snap-off phenomenon by affecting surface elasticity ¹⁸⁰. Schechter suggested that to recover trapped oil droplets in pores that contain initial water saturation, the inverse Bond number should be much lower than 0.04, which indicates a relatively negligible capillary force

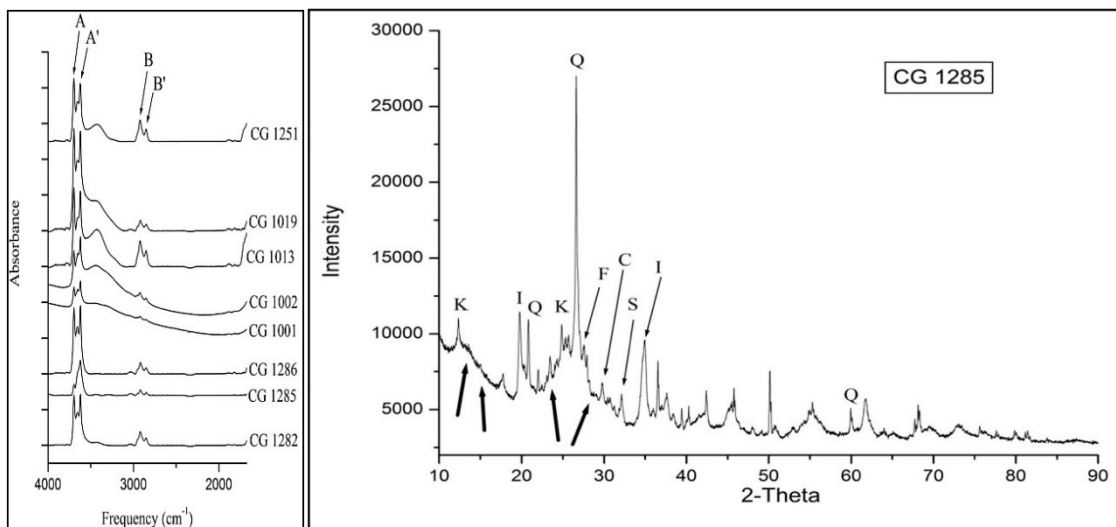
²³³. Chen and Mohanty observed that when the inverse Bond number decreased below 0.5, the saturation of trapped oil reduced sharply ²²⁹.

3.2.6 Rock types and residual oil categories

The main wetting conditions of carbonate reservoirs are found to be oil-wet (65%) or strongly oil-wet (15%) ³⁶. Sandstone reservoirs, however, are mainly water-wet ²³⁴. A possible explanation for the wettability difference is that the main minerals of carbonate rock, namely calcite and dolomite, tend to be positively charged in natural conditions while the main mineral of sandstone, namely quartz, tends to be negatively charged ^{113,153}. The organic materials in oil components that adhere to rock surfaces are negatively charged. As a result, the positively charged calcite and dolomite tend to attract negatively charged organic materials and thus become oil-wet ²³⁵. Calcite and dolomite make up a large portion of carbonate while only a small portion in sandstone. As a result, carbonate reservoirs are more often found to be oil-wet than sandstone reservoirs.

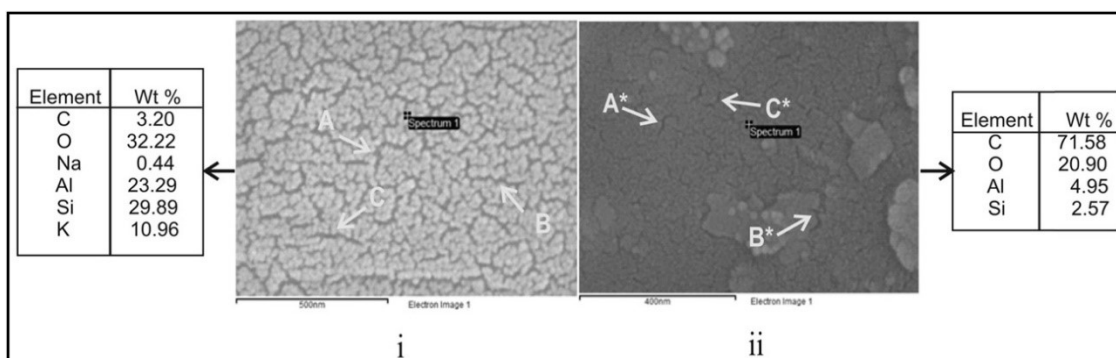
There are various methods to reflect on the mineral composition of rock to help understand the wettability and residual oil amount and distribution. Figure 29 shows the results from four different methods. Fourier transform infrared spectrometry (FTIR) records the absorbance of infrared radiation, as shown in Figure 29 (a). Different chemical structures give different resulting spectrums. Based on the spectrums, the chemical structures in the rock sample can be obtained. X-ray powder diffraction (XRD) gives different results when different crystalline

materials are involved. It is widely used to determine the mineral composition of rock samples, as shown in Figure 29 (b). Scanning Electron Microscope (SEM) reflects the microstructure and morphology of the materials. When combined with other techniques like energy dispersive X-ray (EDX), SEM can be used to recognize different materials on the sample surface, as shown in Figure 29 (c). Thin section samples are also widely used to show the mineral composition of rocks, as shown in Figure 29 (d).

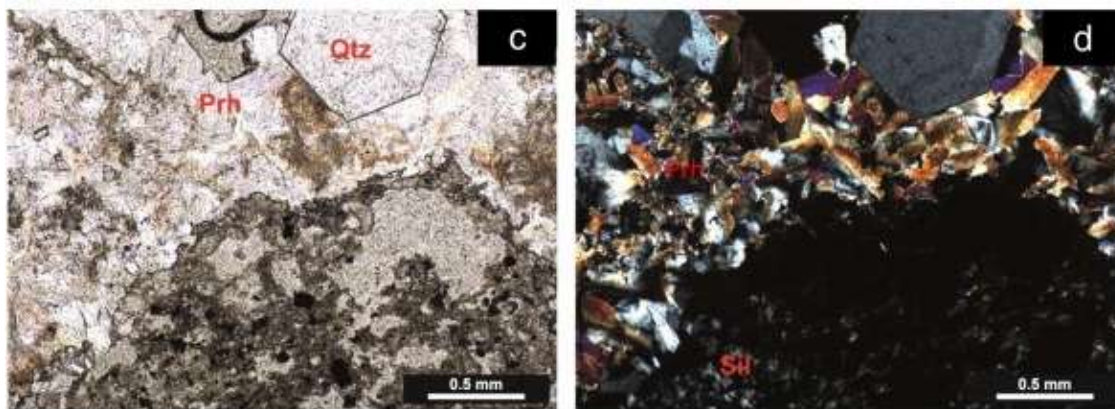


(a)

(b)



(c)



(d)

Figure 29 Methods that help to understand rock wettability and residual oil distribution. (a) FTIR showing kaolinite and aliphatic C-H stretching ²³⁶; (b) XRD diagram showing various mineral phases ²³⁶; (c) SEM image showing minerals (i) and organic materials (ii) as indicated from EDX results ²³⁶; (d) Thin section optical photomicrograph of rock sample ²³⁷.

The mineral composition and statistical wettability data indicate that the amount of residual oil in carbonate reservoirs is higher than in sandstone reservoirs on average. A recent statistical study showed that the average primary and secondary recovery factor is higher in sandstone reservoirs than in carbonate reservoirs ²³⁸. Carbonate and sandstone reservoirs also have a difference in heterogeneity. Most of the carbonate reservoirs are very heterogeneous and have complex pore structures ^{23,81,194}. A large number of carbonate reservoirs are naturally fractured ⁸¹. As a result, a large portion of residual oil remains as the residual oil clusters in the matrix of heterogeneous carbonate reservoirs, especially in intermediate-wet or oil-wet reservoirs ⁴⁵. In sandstone reservoirs, all categories of residual oil can be found in oil-wet and intermediate-wet formations. Water-wet sandstone formations contain mainly trapped oil droplets ¹⁸³ and a relatively small amount of residual oil clusters and dead-end oil, as illustrated in the studies of Fang et al. ²⁰³ and Iglauder et al. ²⁰⁴.

3.2.7 Summary

The residual oil is dominated by pore distribution, wettability, fluid properties, displacement situation, and initial water content. In oil-wet reservoirs, oil film, dead-end oil, pore throat oil, and residual oil clusters are widely distributed and have relatively higher amounts. In neutral-wet or water-wet reservoirs, oil film and pore throat oil are difficult to find. The amount of dead-end

oil and residual oil clusters significantly decreased. Trapped oil is widely distributed in water-wet reservoirs. The different amounts and locations of residual oil categories under different wettability call for different EOR approaches. IFT reduction and WA both play essential roles in the recovery of all categories of residual oil through their impact differs for different categories of residual oil, as shown in Table 15. A comparably higher heterogeneity of carbonate reservoirs suggests that the residual oil clusters in carbonate reservoirs are more significant than in sandstone reservoirs. Sandstone reservoirs are mostly water-wet. As a result, trapped oil droplets are more significant in sandstone.

Table 15 The effect of IFT reduction and WA for different oil categories.

Residual oil	IFT reduction	WA towards water-wetness	EOR methods
Oil film	Positive	Positive	Any method that helps the removal of an oil film from pore walls.
Dead end oil	Positive	Positive	Foams; near miscible CO ₂ ; viscoelastic polymers.
Pore throat oil	Positive	Positive	Foams, polymers, viscoelastic fluids, surfactants, nanoparticles, and so on.
Oil clusters	Positive	Positive	Mainly by imbibition and gravity force.
Trapped oil droplets	Positive	Negative	Materials that reduce the inverse Bond number: polymers that increase water viscosity and surfactants that reduce IFT significantly.

3.3 Effect of IFT and WA on residual oil recovery

To understand the effect of IFT change and WA on residual oil, numerical simulations and experiments are widely conducted. The commonly conducted experiments in studying IFT and

WA's effect are spontaneous imbibition and core flooding experiments. The potential of applied EOR material is assessed by measuring oil production obtained in the experiments. As has been mentioned before, researchers usually match numerical simulations to experiments to make sure the simulations reflect real processes. Many numerical simulation studies build models that represent spontaneous imbibition and core flooding processes.

In a spontaneous imbibition experiment, core plugs are saturated and aged in oil with irreducible saturation of brine. Saturated core plugs are then put inside Amott cells and kept in a static state. In Amott cells, the core plugs are surrounded by EOR fluids. The core plugs and liquids are under no extra pressure except gravity. The effective EOR fluids will start imbibing into the core plugs and displace oil ²³⁹. The expelled oil will float upwards to the top of Amott cells where its volume can be measured by the graduations marked on the container surface. The oil volume will increase and reach a plateau in the end. By measuring the oil volume over time, we will know how much and how fast can the EOR fluid displace oil inside the core. With prior knowledge of core porosity and initial water saturation, the recovery factor (RF) can be calculated by dividing the expelled oil volume by the original oil in place (OOIP).

In spontaneous imbibition experiments, core shape and size are very important parameters.

Among cores of the cylindrical, square prism, and triangular prism shapes, the cylindrical core has the highest imbibition rate while the triangular core has the lowest. The length of the core is also found to affect the imbibition rate. Yildiz et al. ²⁴⁰ observed that when the cores were placed

horizontally, shorter cores had a higher imbibition rate than longer cores. They defined the shape factor as the ratio between all open surfaces area and the bulk volume. The imbibition rate was higher when the shape factor was higher. The spontaneous imbibition test represents oil production by counter-current imbibition better when all surfaces are open to the surrounding fluid. If part of the surface is blocked, the imbibition rate will decrease since the shape factor decreases ²⁴⁰.

Besides, the way how core samples are placed in the imbibition cell is also critical. When the cylindrical core is put horizontally, the effect of gravity on pressure distribution is negligible. If put vertically, however, the effect of gravity should be considered. Zahasky et al. suggested that when the viscous front stabilization forces and capillary forces were much larger than gravity force, the core could be placed horizontally. When gravity force was relatively strong, or the nonwetting phase viscosity was high, the core might be necessary to be oriented vertically ²⁴⁰. Sheng observed that when the core was placed vertically, increased core height enhances the effect of gravity force ²⁰⁰.

To mimic the real condition in the EOR process, some researchers use water or brine as the surrounding phase at the first stage ^{241,242}. After the oil production reaches a plateau for water, they change the surrounding water with EOR fluid at the second stage ^{71,93}. If the EOR fluid is effective, the oil will again start to produce. The incremental oil recovery is the volume of

produced oil in the second stage. In this case, the imbibition is mainly driven by the enhanced or modified effect of capillary force and/or gravity.

Some researchers start spontaneous imbibition experiments with EOR fluids at the first stage. In this case, the produced oil should not be regarded as incremental oil because part of the oil may also be produced without using EOR materials. Spontaneous imbibition experiments conducted in this way mimic the processes where EOR materials or fluids are applied in the secondary recovery process.

In core flooding experiments, the core plugs are saturated and aged in oil with irreducible saturation of brine. Injection fluid is then pressured by pumps to enter the core plugs and displace the oil. In the literature, there is another experiment called forced imbibition ²⁴³. In most cases, forced imbibition experiments are conducted with pumps. To study the effect of WA, the injection fluids used are mostly wettability-reversal fluids and thus will induce the imbibition process. Under such conditions, the forced imbibition experiment and core flooding experiment have little difference.

Similar to spontaneous imbibition experiments, some core flooding experiments go through water flooding and then EOR fluid flooding ¹⁶⁰ while some core flooding experiments start with EOR fluids ²⁴⁴. In the previous case, the oil produced with EOR fluids is from residual oil after waterflooding. In the latter case, however, the produced oil should not be regarded as residual oil.

From the experiments' descriptions, we can see that the major difference between the two experiments is whether the experiment involves extra pressure. Core flooding affects the pressure gradient created by pumps to mimic the flooding process in the real field. This pressure gradient is not included in spontaneous imbibition experiments. Despite this main difference, both the spontaneous imbibition experiment and the core flooding experiment reflect the EOR program's efficiency.

Experimental studies observe that IFT reduction and WA happen simultaneously in most cases. The increased oil recovery is usually a result of the combined effect of IFT and WA. It is nearly impossible to quantify their contribution to oil recovery separately. However, It is essential to study their impact separately as well as simultaneously. There are materials such as some surfactants that induce significant WA and IFT reduction at the same time. Some materials only generate significant changes in either IFT or wettability. For example, silica nanoparticles are reported to induce significant WA while very slightly affecting IFT. As a result, it is also necessary to know the effect of IFT reduction and WA separately.

There are four ways to study the effect of either IFT reduction or WA alone. Firstly, a lot of simulation studies managed to analyze their effect separately. Secondly, many studies in which IFT reduction and WA happened simultaneously are also indicative of their separate effect. For example, surfactant A and surfactant B obtained comparable IFT reduction. On the other hand, surfactant A resulted in a much lower contact angle than surfactant B. If the oil recovery using

surfactant A is much higher than using surfactant B, we can infer that enhanced WA contributes to increased oil recovery. Thirdly, when only one EOR material is tested. If IFT changed a little bit while the contact angle changed significantly, we could also conclude that the main contributing factor was WA instead of IFT. Fourthly, when a spontaneous imbibition test is conducted, the main driving mechanism can be obtained by observing from which surface the oil produces. Oil production only from the top surface indicates that gravity dominates oil production. The effect of capillary pressure change is negligible. IFT reduction rather than WA is the main contributing factor. Oil production both from the top and side surfaces indicates that positive capillary pressure plays a dominating role. WA rather than IFT reduction is the main contributing factor.

In the following sections, we start with discussions about the contribution of IFT reduction and WA separately. After that, the coupled effect of IFT reduction and WA is discussed. Since permeability is also an essential factor determining IFT reduction and WA's performance, we also talked about the influence of permeability. In the end, the relative contribution of IFT reduction and WA on EOR is discussed considering different conditions.

3.3.1 Effect of IFT reduction on residual oil recovery

There are materials, such as some types of anionic surfactant, which can reduce the IFT to very low values. However, their WA performance is found to be slightly and completely reversible ¹².

This section discusses the effect of IFT reduction when no significant WA is induced. It starts

with a mechanism discussion of how IFT reduction helps displace residual oil. After that, simulation and experimental results are gathered to determine how IFT reduction alone affects residual oil recovery in different wettability cases.

IFT reduction affects residual oil from three aspects: work of adhesion, capillary force, and interface elasticity. According to Equation 3.3, IFT reduction can reduce the work needed to remove oil film from the oil-wet rock surface ²⁴⁵. According to Equation 3.7, the capillary number is determined by Darcy velocity, viscosity, IFT, and contact angle. IFT between the water phase and oil can be reduced by 3~4 orders of magnitude by introducing surfactants.

Compared with modifications in the other three factors, IFT reduction is the most applicable way to increase the capillary number by 3~4 orders to make oil flow much easier ²⁴⁶. Besides, when IFT is reduced, the oil/water interface's elasticity is changed, making it easier to mix the two phases ¹⁸⁰. Concerning the previously mentioned mechanisms, IFT reduction has long been regarded as a practical EOR approach.

Many studies suggest that IFT reduction alone increases oil recovery. The simulation conducted by Kowalewski et al. kept the wettability parameters constant and reduced the input IFT. They found that a gradual IFT reduction alone could increase oil recovery from strongly water-wet core ²⁴⁷. They also conducted spontaneous imbibition experiments on several cores. By setting a core 8 that was believed not to undergo wettability modification as the control group, they concluded that IFT reduction was the main mechanism that induced the increased oil recovery in

core 7 in their paper ²⁴⁷. The simulation conducted by Lu et al. showed that IFT reduction alone could improve oil recovery for oil-wet rocks ⁸¹. The latter conclusion was confirmed by the experimental results obtained by Najafi et al. ²⁴⁸. He suggested that WA was not significant for a quick core flood process. The reason for the oil recovery increase in the quick core flood test was IFT reduction. Sheng concluded from simulation results that WA played an important role only when IFT was high. From his results, for oil-wet rocks, the recovery factor increased when IFT was reduced with and without WA ²⁰⁰.

Due to a difference in residual oil categories in different wettability conditions, increased oil recovery's main mechanism differs. Here the effect of IFT reduction is discussed according to three different wettability cases: oil-wet, intermediate-wet, and water-wet.

Case 1: Effect of IFT reduction in oil-wet rocks

In oil-wet rocks, the main categories of residual oil are dead-end oil, pore throat oil, oil film, and oil clusters. According to Equation 3.4, when the rock wettability is not altered, the capillary force will stay negative and prevent the water phase's entrance into pores and pore throats. By reducing IFT, the negative capillary force is reduced. The entrance of the injection fluid becomes easier. The injection fluid will enter pores and pore throats and displace the oil phase inside.

Besides, the reduction of IFT will reduce the work of adhesion and help the displacement of the oil phase away from the rock surface ^{29,65,93,187,200,229,245,249}. As long as the oil phase is mobilized and leaves the rock surface, it becomes easier to be displaced. In a word, in oil-wet rocks, IFT

reduction increases oil recovery by helping the desorption of residual oil and the entrance injection fluid into pores and pore throats.

Case 2: Effect of IFT reduction in intermediate-wet rocks

In intermediate-wet rocks, the main residual oil category may diverse from case to case. If the wetting state of the rock is not changed, IFT reduction may have a slight effect on oil recovery. It takes effect by reducing adhesion work and changing the interface elasticity to help produce oil.

Case 3: Effect of IFT reduction in water-wet rocks

In water-wet rocks, the main category of residual oil is trapped oil droplets. When IFT is reduced, the oil/water interface elasticity is weakened. Some oil droplets may deform from a more sphere shape to a bar shape. Some oil droplets may break into smaller droplets. After deformation and breakup, it becomes easier for oil droplets to move through narrow pore throats. As a result, IFT reduction mitigates the capillary snap-off effect and helps displace the oil phase.

250,251 .

A few studies suggest the opposite effect of IFT reduction in water-wet rocks. For example, the core flooding tests reported by Newcomb et al. suggested that increased IFT led to increased oil recovery in water-wet sand packs ²⁴⁹. This is because the experiments started from unflooded samples instead of from samples containing residual oil. In samples that haven't gone through secondary recovery, increased IFT enhances the positive capillary force to displace more oil,

thus increasing the oil recovery. Nowadays, many studies found that applying EOR materials in secondary flooding will increase potential oil recovery more than applying EOR materials after secondary flooding^{21,252}. The oil phase in that case cannot be considered residual oil. It is very important to notice the difference between applying EOR materials in secondary flooding and tertiary flooding. Table 16 summarized cases in which IFT reduction induced major changes in capillary pressure and thus obtaining incremental oil recovery.

In a conclusion, if no WA is involved, IFT reduction contributes to oil recovery in all wettability conditions. The wetting state of rock will influence the main functioning EOR mechanism. For oil-wet rock, IFT reduction takes effect mainly by reducing the negative capillary force that blocks the injection fluid entrance. In intermediate-wet rock, IFT reduction takes effect mainly by helping the desorption of oil and the mixing between oil and water. In water-wet rock, IFT reduction takes effect mainly by reducing the positive capillary force and weakening the interface elasticity to help the flowing of captured oil droplets.

Table 16 Cases of capillary pressure change induced mainly by IFT reduction.

No.	EOR Material	k (mD)	Initial IFT; Final IFT (mN/m)	Initial CA; Final CA (°)	Capillary Pressure ratio (Final/Initial)	Incremental RF (%OOIP)	Comment	Ref.
1	n-hexylamine (0.1 mol/L)	85~465	47; 1.1	120; 120	0.39	8.2	Negative capillary pressure was reduced by IFT reduction.	187
2	Simulation	122	0.049; 0.0088	Unchanged Oil-wet	0.18	40		200
3	Simulation	150	30; 0.001	Unchanged Oil-wet	0.00003	90		65
5	GD70 (0.05 wt%)	45	Not given; 2.493	Not given; 121.2	Unknown; -0.258×106 mN/m2	35 (not incremental)		245
6	Simulation	19.9	0.01; 30	70; 70	3000	25		29
7	Simulation	19.9	1; 0.01	140; 140	0.00033	50		29
8	F-68 (1000 ppm)	11000	35.8; 1.2	162; 154	0.03	5.5		249
9	Biosurfactant	1.16	26; 3	Unchanged water-wet (quick flooding tests)	0.12	9.85	Positive capillary pressure that holds residual oil as trapped oil droplets was reduced by IFT reduction.	251
10	Twice diluted seawater	314.79	15; 11	105; 100	0.49	8	Both IFT reduction and WA reduced the negative capillary pressure.	252

3.3.2 Effect of WA on residual oil recovery

There are materials, such as some nanoparticles, that can significantly change the rock wettability while only inducing slight changes in IFT¹⁸⁵. This section discusses the effect of WA on residual oil recovery when no significant IFT reduction takes place. Simulation and experimental results are gathered to determine how WA alone affects residual oil recovery in different wettability cases and the corresponding mechanisms behind it.

The contribution of WA to residual oil recovery has long been recognized since the 1960s²⁵³. In recent years, WA is becoming a focused research area. Studies show that good WA performance coupled with moderate IFT reduction can result in more significant oil recovery than moderate WA performance coupled with IFT reduction to ultralow values^{12,74,79,113,254,255}. These studies indicate that WA also has vast potential in EOR.

Results and conclusions from previous studies reflect that WA's effect on residual oil recovery is closely related to the initial wettability condition. Due to the difference in residual oil categories in varying wettability conditions, increased oil recovery's primary mechanism differs. Here the initial wetting state of rock is divided into two separate cases: intermediate-wet/oil-wet and water-wet.

Case 1: Effect of WA in initially oil-wet or intermediate-wet rocks

In initially intermediate-wet/oil-wet rock, altering the rock to water-wet using various cEOR materials generally is found to increase oil recovery^{12,182,196,200,248,249,253}. The study conducted by Hou et al. observed comparable IFT values and different contact angle values for five kinds of surfactants. Recovery results from spontaneous imbibition tests showed that surfactant that reached the lowest contact angle (SDS, 38.1°) achieved the

highest oil recovery (around 60%)²⁵⁶. Jiang et al. observed that nanofluid inducing significant WA but negligible IFT reduction increased the oil recovery¹⁸⁵. Rania et al. observed that with IFT reduction of 1.57 mN/m from 14.49 to 12.92 mN/m (which is a minor change) and contact angle change from 165° to 103° (which is a moderate modification from strongly oil-wet to intermediate-wet condition), the incremental oil recovery achieved 19% OOIP²⁵⁷. Wang et al. observed that by changing the limestone sample from oil-wet to strongly water-wet condition alone, oil recovery was significantly increased (around 20%)²⁴³. Simulation results also suggest that turning oil-wet rock to water-wet condition increases oil recovery in the spontaneous imbibition process regardless of the IFT value^{65,258,259}.

The positive effect of WA from intermediate-wet/oil-wet to water-wet is a combined effect of capillary force change, adhesion reduction, and an increase in oil relative permeability. The capillary force is either negligible or negative at the original state that prevents injection fluid from entering pore throats. Residual oil adheres to the pore walls and pore throat walls. When the wettability is altered to water-wet, capillary force becomes positive which helps the imbibition of fluid, which helps the displacement of oil⁷¹. As a result, WA causes a decrease in negative forces and an increase in positive forces, thus enabling the displacement of oil. When the contact angle is reduced, the oil will move away from pore walls and pore throat walls due to the reduced work of adhesion according to Equation 3.3. In this way, residual oil that was adsorbed on rock surfaces becomes mobilized. Furthermore, WA to water-wet increases oil relative permeability^{80,81,229,245}. When the rock surface is changed from intermediate-wet/oil-wet to water-wet condition, it will favor water more than oil. The water phase will cover the

rock surface. The oil phase tends to locate at the center of the pores or pore throats. As a result, it becomes much easier to form flowing paths for the oil phase since the friction between the oil and rock surfaces is largely eliminated.

Many studies observed that the materials changing wettability more achieved higher oil recoveries^{20,76,256,260}. Based on these results, we may conclude that stronger WA performance leads to increased oil recovery. However, it may not always be favorable to alter the wetting condition to extremely water-wet conditions. A study conducted by You et al. suggested the existence of an optimal extent of WA, in other words, an optimal contact angle. They found that when the contact angle decreases below the optimal value, the water phase tended to spread along the rock's pore surface and formed a water film. At this point, the driving force acting on the oil phase is significantly reduced, resulting in trapped oil droplets inside pores and pore throats²⁶¹. This mechanism is also referred to as the capillary snap-off mechanism⁴². Their observation showed a transition of mobilized residual oil from other categories that distribute widely in oil-wet rocks to trapped oil droplets that distribute mainly in water-wet rocks. The transition of residual oil categories settles the mobilized oil phase down and negatively affects residual oil production. This is because high positive capillary force can capture oil droplets and hold them inside pores. In a conclusion, WA alone can result in significant recovery factor improvement from intermediate-wet/oil-wet rocks. There seems to exist an optimal WA extent that reaches a positive capillary force to help the entrance of injection fluid while on the other hand avoiding too much of capillary snap-off phenomenon that will negatively affect residual oil production.

Case 2: Effect of WA in initially water-wet rocks

In initially water-wet rocks, however, enhancing the water-wetness may result in lower oil recovery. On the contrary, changing the rock wettability to less water-wet or intermediate-wet conditions will increase the oil recovery^{182,247,250,251}. This is because, in initially water-wet rocks, the main residual oil category is the trapped oil. For this category of residual oil, increasing the positive capillary force will further enhance the capillary snap-off mechanism and make it more difficult to displace trapped oil. Only by reducing the magnitude of a capillary force or by reversing its direction can we mitigate the mechanism to displace more oil. If the rock surface is changed to the oil-wet condition, some trapped oil will adhere to the rock surface and form other residual oil categories. This transition of residual oil categories will also demobilize the oil phase and negatively affect residual oil production. It should be avoided in order not to impair oil recovery. There are cases where WA managed to increase oil recoveries due to other mechanisms. Gong et al.¹⁸³ reported an oil recovery increase when the water-wet micromodel became oil-wet during alkaline flooding. They believed that induced WA improved the sweeping efficiency by blocking water channels. In most cases, a change from strongly water-wet to less water-wet or intermediate-wet condition is recommended.

In initially intermediate-wet/oil-wet rocks, changing its wettability towards water-wet increases oil recovery; for initially water-wet rocks, changing its wettability towards intermediate-wet increases oil recovery. The difference in WA directions is due to the difference in the main residual oil categories. For initially oil-wet rocks, residual oil exists mainly in dead ends, pore throats, and as oil film and residual oil clusters. These categories of residual oil remain in the formation due to the attraction between rock

surfaces and oil. Altering the wettability to water-wet reduces the attraction and helps the oil phase to desorb from rock surfaces. For initially water-wet rocks, the main residual oil category is trapped oil droplets. Trapped oil droplets stay in the center of the pores and pore throats and are kept inside formation by the capillary snap-off mechanism. Changing the wettability towards intermediate-wet reduces the capillary force and helps the oil droplets to move through pore throat necks ¹⁸³.

In summary, for initially intermediate-wet/oil-wet rocks, WA from intermediate-wet/oil-wet to water-wet conditions contributes to residual oil production regardless of IFT value. For initially water-wet rocks, WA from strongly water-wet towards less water-wet or intermediate-wet leads to increased oil recovery. WA affects residual oil production mainly by affecting the work of adhesion and capillary force. When the contact angle is reduced, the work of adhesion is reduced so that it becomes easier to mobilize residual oil. Capillary force change, however, has a two-fold effect on residual oil production. On the one hand, WA can reduce or even reverse the capillary force that retains residual oil inside the rock to help produce residual oil. On the other hand, strong WA might induce the category-transition of residual oil and thus impairing production. Generally, more robust WA performance in both directions leads to higher oil recovery. There exist an optimal WA extent where the category-transition of residual oil is not significant and the oil recovery is the highest.

3.3.3 The coupled effect of IFT reduction and WA

Previous sections discussed the effect of IFT reduction and WA on residual oil recovery separately. In real EOR processes, however, IFT reduction and WA happen simultaneously most of the time. In such a situation, IFT reduction and WA also affect each other's influence on residual oil recovery. Studies suggest that IFT reduction could even be one of the mechanisms that induce WA ^{189,239,262,263}. It is imperative to understand the coupled effect of IFT reduction and WA under different conditions to help design EOR processes.

In the coupled effect, WA is one of the dominant factors determining how and to what extent IFT reduction will affect oil recovery. As discussed in section 3.1, IFT reduction is favored in all wettability conditions when studied separately. When WA is considered, however, the effect of IFT reduction becomes more complicated.

Many studies observed a positive effect of IFT reduction when the wetting state of rock changes from oil-wet to water-wet ^{187,264,265}. Researchers find that when IFT reduction and WA are combined in oil-wet rocks, the effect on oil recovery is higher than either of them alone. This is often referred to as the synergic effect between IFT reduction and WA ^{81,93,181,229,261,266}. Chen and Mohanty suggested that this is because lower IFT helps to produce trapped oil ²²⁹. Roustaei et al. ²⁶⁴ and Joonaki & Ghanaatian ¹⁷⁴ also suggested this idea. You et al. suggested that the wedge-film structure and the spreading force could be formed to promote water phase imbibition into low permeability rocks ²⁶¹. Xu et al. found that in preferentially oil-wet sandstones, the combined effect of WA and IFT reduction induced by surfactant and nanoparticles achieved higher oil recovery than nanoparticles alone which induced only strong WA performance ²⁴³. Singh and Mohanty

found that surfactant composition failed to alter wettability and achieved very low oil recovery⁸⁴. Moradi et al. observed that at comparable WA from oil-wet to water-wet, a lower IFT led to higher oil recovery¹⁸¹. According to these studies, when the rock is changed from oil-wet to water-wet condition, IFT reduction have a positive effect on oil recovery.

However, opposite observations are also obtained. In the imbibition tests conducted by Seethepalli et al., higher IFT values led to higher oil recoveries. In their study, surfactants Alf-35, Alf-38, and Alf-68 managed to alter the rock wettability from oil-wet to water-wet. Alf-35 or Alf-38 solutions had higher IFT values than Alf-68 solutions. The oil recoveries obtained by Alf-35 and Alf-38 were about 20% higher than that of Alf-68⁷⁴. The imbibition tests conducted by Roustaei showed that silica nanoparticles could slightly increase IFT and change rock surface from oil-wet to strongly water-wet. The observed oil production was significantly increased in this case²⁶⁷. Alvarez and Schechter observed that anionic surfactants obtained much more significant IFT reduction than nonionic surfactants while their WA performance was comparable. Nonionic surfactants, however, achieved higher oil recovery in imbibition experiments¹⁸⁹. The core flooding tests conducted by Roustaei and Bagherzadeh obtained a similar conclusion¹⁴⁷. According to these studies, when the rock is changed from oil-wet to water-wet conditions, IFT reduction may have a negative or negligible²²⁹ effect.

The confusing effect of IFT reduction when oil-wet rocks change to water-wet conditions results from two oppositely acting mechanisms. On the one hand, for initially oil-wet rocks, when the rock wettability is altered from oil-wet to water-wet, the direction of capillary force is reversed from negative to positive. In this case, a stronger capillary

force is favorable since it helps the entrance of the water phase into the rock matrix^{29,65,249}. As a result, many researchers observe that IFT reduction harms recovery. They recommended maintaining the IFT values in such cases. On the other hand, the positive capillary force could also induce the snap-off phenomenon of the oil phase and traps the oil droplets inside pores, especially in rock with a high aspect ratio. As discussed in section 3.2, the mobilized oil moves to the pore centers when the rock becomes water-wet. When IFT is high, both capillary force and oil/water interface elasticity are strengthened. Oil droplets are more likely to be trapped inside pores under such conditions²⁶¹. On the contrary, IFT reduction weakens the capillary force and makes the deforming of oil droplets easier, thus helping the residual oil production. In such a condition, the forces that hold the oil droplets are weakened while the mixing of oil and the aqueous phase becomes easier. As a result, the effect of gravity or viscous forces is strengthened to become the main driving force to produce residual oil^{71,80,81,264}.

In a word, when the rock is changed from oil-wet to water-wet condition, IFT reduction has a complex effect. IFT modification in such a case should consider the magnitude of the capillary force, the aspect ratio, and other driving mechanisms including gravity and viscous forces.

When the rock is changed from oil-wet or water-wet to intermediate-wet, the magnitude of capillary force becomes negligible. IFT reduction slightly adds to oil recovery by reducing the work of adhesion and helps to mix the two phases. Saha et al. observed that emulsification, saponification, and wettability alteration to intermediate-wet were the main mechanisms for alkaline flooding oil recovery in the water-wet sand pack. IFT reduction alone didn't contribute as much but was necessary for emulsification¹⁸². Due to

mitigated capillary force, the oil recovery is observed to be less sensitive to IFT values under this condition ^{180,249}.

For initially intermediate-wet rocks, if the wetting state is changed to water-wet, the effect of IFT reduction is reported to be positive ¹⁸⁴. If the wetting state is changed to oil-wet, which may rarely happen, IFT reduction may be favorable because the magnitude of negative capillary force will be reduced. It also helps to mix the oil and water phase.

For initially water-wet rock, if the wetting state is altered to oil-wet, the effect of IFT reduction may be favored due to two reasons. Firstly, reduced work of adhesion reduces the chances that the mobilized oil phase adheres to pore and pore throat walls again. Secondly, reduced oil/water interface elasticity eases the mixing of two phases, thus helping residual oil production.

In conclusion, WA affects the effect of IFT reduction. Both the initial wetting state and the resulting wetting state should be considered before making any IFT modification decisions. The effect of IFT reduction on EOR recovery considering WA is summarized in Table 17.

Table 17 Effect of IFT reduction on residual oil recovery.

Initial wetting state of rock	Resulting wetting state of rock	Effect of IFT reduction on EOR recovery
Oil-wet	Oil-wet	Positive
Oil-wet	Intermediate-wet	Slightly positive
Oil-wet	Water-wet	Complex
Intermediate-wet	Intermediate-wet	Slightly positive
Intermediate-wet	Water-wet	Positive
Water-wet	Water-wet	Positive
Water-wet	Intermediate-wet	Slightly positive

From the opposite point of view, the influence of WA on IFT reduction's effect may also be understood as the influence of IFT reduction on WA's effect on residual oil recovery. For example, if the rock is initially oil-wet and IFT is significantly reduced, WA to the water-wet condition may not contribute more oil recovery. If rock is water-wet and IFT is increased, WA towards intermediate-wet becomes necessary to reduce the positive capillary force that holds residual oil droplets inside pores.

According to Equation 3.4, IFT reduction reduces the magnitude of the capillary force. Since WA affects residual oil recovery mainly by affecting the capillary force. If the magnitude of the capillary force is reduced by IFT reduction, capillary force change induced by WA will be limited to a smaller range. As a result, IFT reduction reduces the extent that WA may affect oil recovery. Sheng concluded that WA was important only when IFT was high based on simulation results²⁰⁰. Ravari et al. 's experimental study also suggested that significant IFT reduction retarded the effect of WA and made gravity the main driving force in oil-wet rock².

3.3.4 Influence of permeability on the coupled effect

Permeability is an important factor for residual oil both in its formation and displacement. From the formation aspect, oil in lower permeability zones is easier to be left behind due to fingering. From the displacement aspect, it is more difficult for EOR materials to enter lower permeability zones to take effect on the residual oil. Many studies report that the cumulative oil recovery from EOR is reduced in low permeability cores, confirming low permeability's negative effect on EOR efficiency^{80,258,268}.

Researchers find that the effect of capillary force is enhanced in lower permeability zones⁶⁵. This observation can be understood by the definitions of the bond number and the capillary number. According to Equation 3.8, when permeability is small, the bond number is small. A small bond number indicates that capillary force gains more significance over the gravity force. At a constant injection pressure and a lower permeability, the flow rate is also lower. According to Equation 3.7, a lower flow rate reduces the capillary number. A reduced capillary number indicates that capillary force gains more significance over viscous force. As a result, in lower permeability zones, the capillary force's dominance in oil displacement is enhanced.

Due to the close connection between WA and capillary force, WA's effect is amplified in lower permeability zones. Adibhatla and Mohanty found that when IFT was kept high, surfactants that induced WA reached a much higher recovery rate in lower permeability zone⁶⁵. Li et al. did a series of flooding experiments in both oil-wet and water-wet sand packs. They observed that in oil-wet sand packs, a higher permeability zone gave higher oil recovery. In water-wet sand packs, however, the lower permeability zone gave higher oil recovery²⁶⁴. Their study indicated that WA in lower permeability formations would

be more beneficial than in higher permeability formations. The study conducted by Alvarez and Schechter also showed that for ultra-low permeability unconventional fluid reservoir cores, the importance of capillary force was enhanced ¹⁸⁹. In a word, WA has a stronger effect in lower permeability zones.

Adibhatla and Mohanty emphasized that WA's significant effect was obtained when IFT was kept high ⁶⁵. This is because IFT reduction reduces the magnitude of the capillary effect. When the capillary effect is helping oil displacement, IFT reduction harms it.

Raveri et al. found that C₁₂TAB and Dodigen acted as good in WA. Dodigen reached lower IFT (0.34 mN/m) than C₁₂TAB (0.67 mN/m). Results from spontaneous imbibition showed that C₁₂TAB achieved higher oil recovery than Dodigen, indicating the negative effect of IFT reduction ². Thus in lower permeability zones where WA plays an important role, IFT reduction may impair residual oil recovery ^{21,65}. In higher permeability zones, the impact of gravity and viscous forces is enhanced. IFT reduction leads to increased oil recoveries due to gravity and viscous forces ².

3.3.5 Summary

The most commonly used experiments to study IFT reduction and WA effects are spontaneous imbibition and coreflooding tests. Most of the cases reported in the literature involve the coupled effect of IFT reduction and WA. However, there are cases where only one of them takes place. As a result, it is necessary to know the effect of IFT reduction and WA separately and simultaneously.

If no WA is involved, IFT reduction increases oil recovery in all wettability cases. In oil-wet and water-wet rocks, its effect is significant due to the reduced magnitude of

capillary force. In intermediate-wet rocks, however, IFT reduction impact slightly the residual oil recovery due to reduced work of adhesion and interface elasticity.

If no IFT reduction is involved, the effect of WA differs between different wettability cases. In intermediate-wet/oil-wet rocks, WA toward water-wet increases residual oil recovery due to reversed capillary force direction. Studies are suggesting that there may exist an optimal WA extent for maximum residual oil recovery. Over that extent, some mobilized residual oil may again be retained inside the rock. However, in water-wet rocks, WA toward less water-wet or intermediate-wet increases residual oil recovery since it is the positive capillary force that holds oil droplets as residual oil in this case.

When both IFT reduction and WA are involved, the initial and resulting wettability determines how and to what extent IFT reduction will affect oil recovery. When oil-wet rock changes to the water-wet condition, the optimal IFT modification should consider the capillary force's magnitude, the aspect ratio, and other driving mechanisms, including gravity and viscous forces.

WA's effect is more significant in lower permeability rocks where capillary force is usually the main driving force. However, in higher permeability rocks, capillary force is usually not as dominant as in lower permeability rocks. As a result, the effect of IFT reduction is more significant in higher permeability rocks. Table 18 summarizes the recent publications related to the increment in oil recovery with different surfactant types such as gemini surfactant, amino acid-based surfactant, carboxy betaine, and many naturally occurring surfactants.

Table 18 Effect of IFT reduction and WA in spontaneous imbibition experiments.

References	Experiments	Name of Surfactant	Increment in oil recovery	Major Player
Nowrouzi et al. ¹⁹⁷	IFT, CA, and oil recovery coreflooding	Saponin extracted from Anabasis Setifera plant-based surfactant	70%	Ultra-low IFT 1.066 mN/m and WA.
Ganie et al. ²⁶⁹	IFT	Lignin	59 – 67 %	Low IFT (0.5-1.0)
Kiani et al. ²⁷⁰	IFT and oil recovery coreflooding	iC18S	72%	Low IFT
Kumar and Mandal ⁵¹	IFT, WA, and sand pack oil recovery coreflooding	Carboxybetaine	31%	Ultra-low IFT and WA
Madani et al. ²⁷¹	IFT, WA, and oil recovery coreflooding	Surfactants based on Amino acid	60.0%	Low IFT and WA
Moradi et al. ¹⁸¹	IFT, WA, and oil recovery coreflooding	Tribulus Terrestris	64%	Ultra-low IFT 13.5 mN/m and WA
Pal et al. ²⁷²	IFT	Sunflower oil-based dicationic surfactant	Not given	Low IFT
Pal et al. ²⁷³	IFT, WA, and oil recovery coreflooding	Coconut oil-based anionic surfactant	20.05%	Ultra-low IFT and WA
Pal et al. ¹⁹	IFT, WA, and oil recovery coreflooding	Dicationic surfactant	29-35%	Ultra-low IFT and WA
Pillai et al. ²⁷⁴	IFT and oil recovery coreflooding	Imidazolium ionic liquids	32%	Ultra-low IFT and WA
Rostami et al. ²⁷⁵	IFT, WA, and oil recovery coreflooding	Surfactants based on Amino acid	12%	Low IFT
Saxena et al. ²⁷⁶	IFT, WA, and oil recovery coreflooding	Soap-nut-based surfactant	28%	Ultra-low IFT 2.013 x10-2 mN/m and WA
Saxena et al. ²⁷⁷	IFT, WA, and oil recovery coreflooding	Mahua oil-based anionic surfactant	20%	Ultra-low IFT and WA

Song et al. 278	IFT and WA	Double chain carboxyl betaines surfactants	Not given	Ultra-low IFT 0.01 mN/m and WA
Yan et al. 279	IFT and WA	Double-Chain SingleHead sulfobetaine surfactant	Not given	Ultra-low IFT and WA

3.4 Conclusions

The residual oil can be divided into five categories depending on the forms and locations: oil film, dead-end oil, pore throat oil, residual oil clusters, and trapped oil droplets. When studied alone, IFT reduction and WA have different effects on each residual oil category. When IFT reduction and WA are combined, which is the usual case, their influence on residual oil recovery becomes complex. Several conclusions are drawn based on the mechanism study and review discussions.

1. IFT reduction alone helps the mobilization of all categories of residual oil. WA alone helps mobilize oil film, dead-end oil, pore throat oil, and residual oil clusters. WA from water-wet to intermediate-wet helps the mobilization of trapped oil droplets.
2. IFT reduction alone increases recovery in all wettability cases. In initially intermediate-wet/oil-wet rocks, WA to water-wet alone increases recovery. In initially water-wet rocks, WA to less water-wet or intermediate-wet alone increases residual oil recovery.
3. The coupled effect of IFT reduction and WA is more complicated since the changes in IFT and wettability influence each other. WA becomes a factor determining how and to what extent IFT reduction will affect oil recovery. In most WA processes, IFT reduction is favorable. However, when the rock is changed to water-wet, IFT reduction

may negatively affect residual oil recovery. The optimum IFT modification should consider the capillary force magnitude, the aspect ratio, and other driving mechanisms, including gravity and viscous forces. IFT also influences to what extent WA will affect residual oil recovery. If the IFT is reduced to ultralow values, the effect of WA becomes negligible.

4. In lower permeability rocks, the effect of WA on residual oil recovery is enhanced. As the permeability of rock increases, the relative importance of IFT reduction also increases.

As a result, to decide optimal IFT and wettability modifications for EOR purposes, it is essential to know the amount of each oil category, the initially wetting state, the magnitude of the capillary force, the aspect ratio, and the impact of gravity and viscous forces.

CHAPTER 4

WETTABILITY ALTERATION OF LOCALLY SYNTHESIZED CATIONIC GEMINI SURFACTANTS ON CARBONATE ROCK

4.1 Introduction

Carbonate formations are usually fractured compared to sandstone formations. The injected fluids tend to flow through the interconnected fractures while passing by the low permeability rock matrix ⁷⁷. Besides, carbonate reservoirs are found to be mostly oil-wet ²³⁴. Capillary pressure in the oil-wet condition is negative, which prevents the displacement of oil. As a result, a large amount of oil is left behind inside the rock matrix.

Enhanced oil recovery (EOR) for carbonate reservoirs is crucial to meet the increasing oil demand. Two main mechanisms can be utilized for EOR in carbonate formations: Interfacial tension (IFT) reduction ⁵⁵ and wettability alteration (WA) ⁶⁹. IFT reduction decreases the magnitude of capillary pressure and the work of adhesion ⁸. WA from oil-wet to water-wet conditions, on the other hand, changes the direction of capillary pressure from negative to positive ²⁸⁰. Positive capillary pressure reduces the pressure difference needed for residual oil recovery. Besides, when rock is changed from oil-wet to water-wet, the relative permeability of oil increases ²⁸¹, making it easier to form flowing paths for oil.

Researchers have observed encouraging incremental oil recovery induced by the synergic effect of IFT reduction and WA, both in simulations and experiments ^{181,229}.

Surfactants have long been applied to effectively reduce IFT by up to 3~4 orders ⁶⁸. Some surfactants are also effective in altering rock wettability. Showing potential in both IFT reduction and WA, surfactants are intensively studied for their EOR implication. Depending on the charge(s) of the surfactant head group(s), they can be divided into cationic, anionic, zwitterionic, and nonionic surfactants. For carbonate rock, cationic surfactants are found to have the strongest WA performance due to the ion-pairing behavior between positively charged surfactant heads and negatively charged organic matter ¹². Furthermore, the adsorption of cationic surfactant is the least compared to other types due to the electronic expelling force between positively charged head groups and positively charged carbonate rock surface ⁷². Combining both advantages, cationic surfactants can be efficient EOR materials for oil-wet carbonate reservoirs.

Gemini surfactants are surfactants with two head groups and two tail groups. The name “gemini surfactant” was first proposed by Menger and Littau ¹⁰² since a monomer of gemini surfactant looks like two monomers of conventional surfactant connected by a spacer group. The unique structure renders gemini surfactant outstanding interfacial behavior. Scientists find that gemini surfactants reach ultralow IFT faster and at much lower concentrations compared to conventional surfactants ³⁶. Apart from that, some gemini surfactants also show good WA performance ^{17,19}.

The outstanding properties have attracted the focus of researchers on developing various EOR strategies based on gemini surfactants. Possible EOR strategies include the synthesis

and application of cost-effective, environmental-friendly bio-based gemini surfactants, the combination of gemini surfactants and polymers to enhance the viscosity and elasticity of the EOR fluid, the development of gemini type-ionic liquids that exhibit improvements in the stability, cost-efficiency and biocompatibility, the application of gemini surfactants as the stabilizing agents in microemulsions or nanoemulsions, and the utility of gemini surfactant foams as efficient EOR fluids ²⁸².

This study focuses on the WA performance of some locally synthesized cationic gemini surfactants in carbonate rock. Contact angle measurement tests were conducted to study different factors that may influence surfactants' WA performance, including (1) surfactant treatment time; (2) concentration; (3) spacer length; (4) unsaturation in the spacer; (5) functional groups in the spacer; (5) counter-ions; and (6) salts.

4.2 Experimental study

4.2.1 Materials

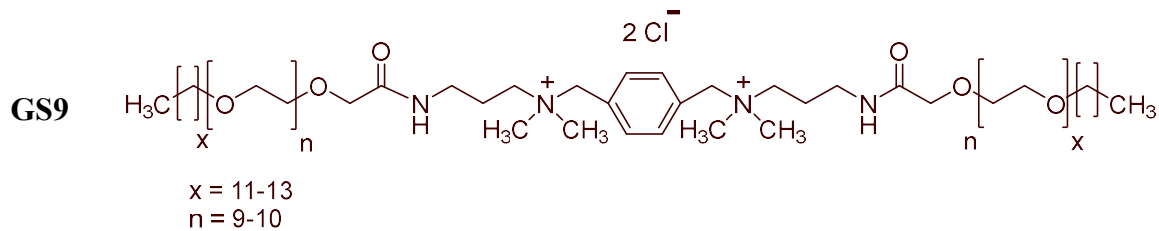
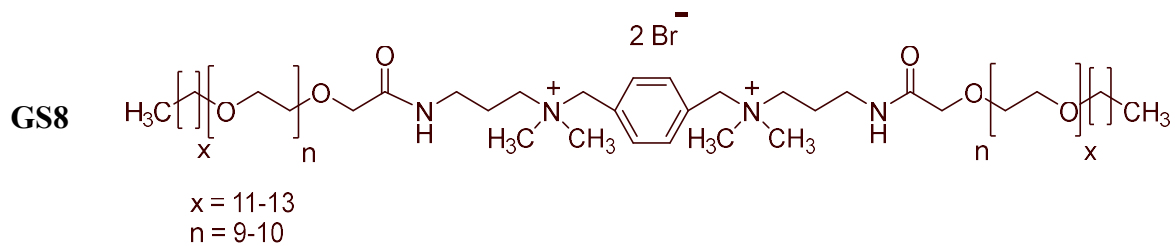
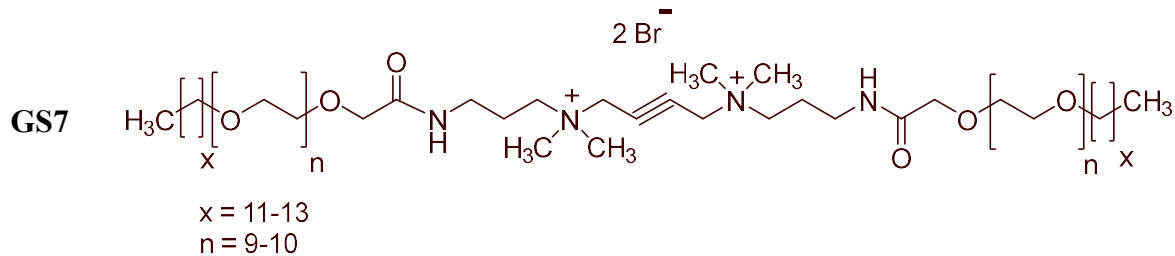
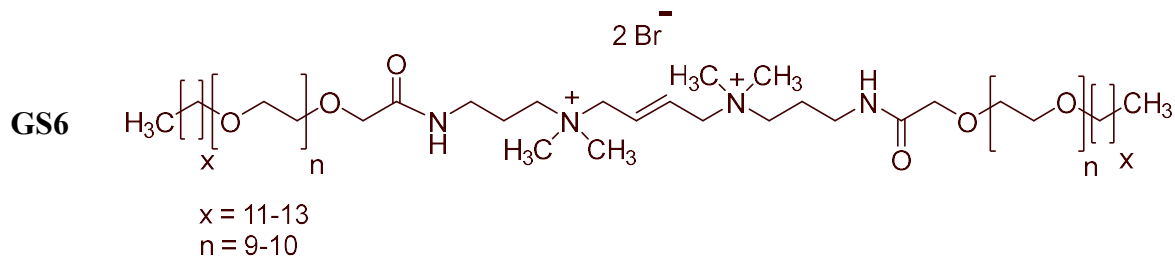
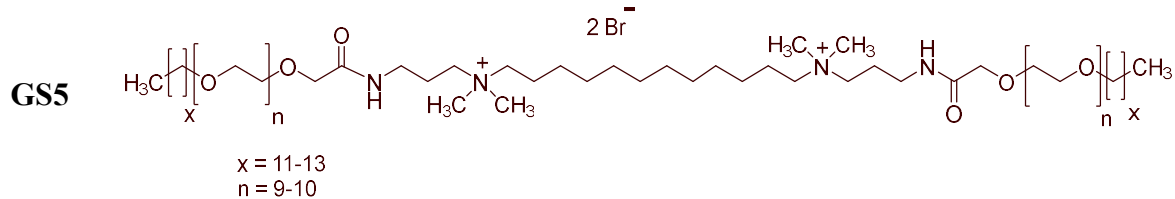
Indiana limestone cores were used in this study. They had an average porosity of 15.1% and permeability around 10mD. XRD results showed that these core samples contained 100% calcite. They were cut into substrates (diameter 1 inch, thickness 3~4 mm) for contact angle measurements and plugs (diameter 1.5 inches, height around 2 inches) for spontaneous imbibition tests. After cutting, their surfaces were polished using sandpaper of particle size P500. Fragments were collected for SEM imaging.

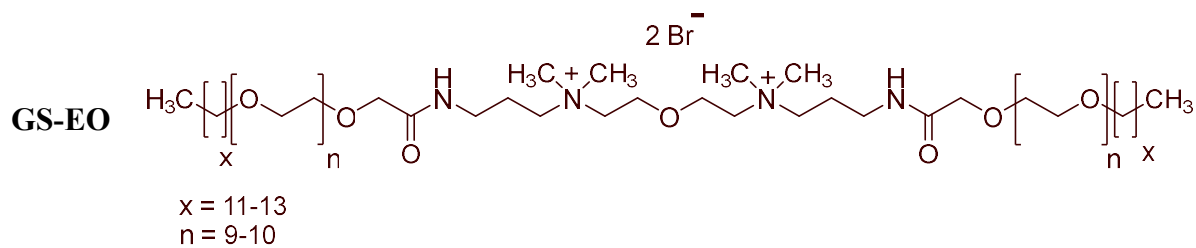
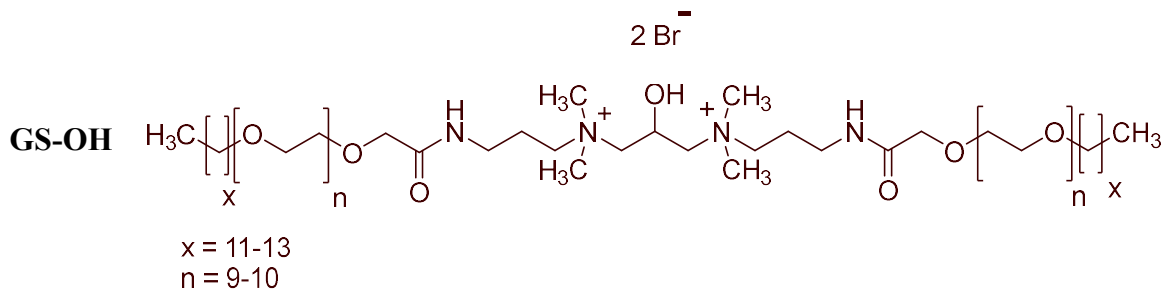
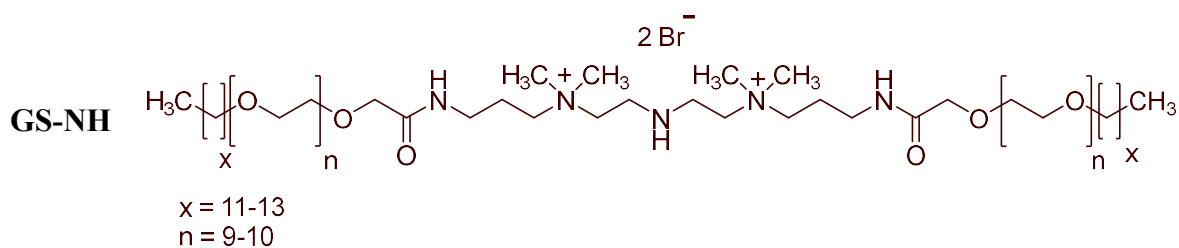
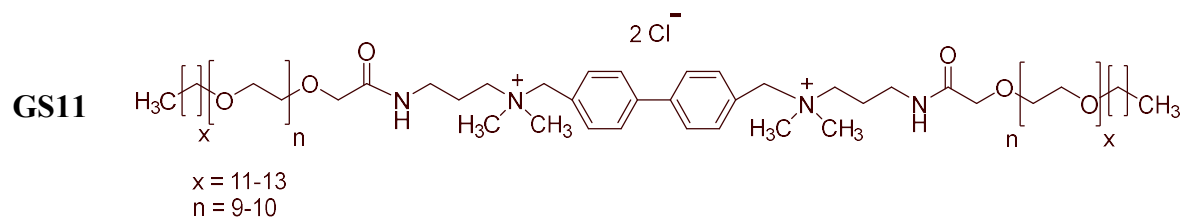
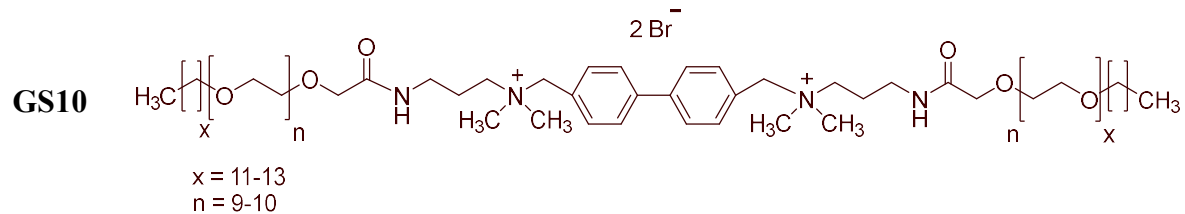
Filtered crude oil (API 31.07) was used. The seawater and diluted seawater were prepared in the lab using deionized water (DIW) and salts provided by Sigma-Aldrich.

The target materials of this study, 14 kinds of locally synthesized ethoxylated quaternary ammonium gemini surfactants, consist of the same head groups and tail groups. The only two differences among them are the structure of the spacer and counter-ions. Table 19 summarizes the structure of tested surfactants.

Table 19 The molecular structure of tested surfactants.

Name	Structure
GS1	$x = 11-13$ $n = 9-10$
GS2	$x = 11-13$ $n = 9-10$
GS3	$x = 11-13$ $n = 9-10$
GS4	$x = 11-13$ $n = 9-10$





4.2.2 Contact angle measurement

The contact angle is a convenient and commonly used method in the assessment of wettability. The relation between contact angle value and wettability is roughly described in Table 20. Core flooding and spontaneous imbibition experiments are widely applied to relate the interface behavior of surfactants with oil recovery. Compared with flooding tests, spontaneous imbibition emphasizes the impact of WA²⁰⁰. This study combined contact angle measurement and spontaneous imbibition to study cationic gemini surfactants' WA performance and how their WA performance affects oil recovery.

Table 20 The relation between contact angle value and wettability.

contact angle value (°)	wettability
0-30	Strongly water-wet
30-70	Water-wet
70-110	Intermediate-wet
110-150	Oil-wet
150-180	Strongly oil-wet

In this study, Indiana limestone substrates were firstly cleaned with toluene and dried. Then they were immersed in oil and kept at a 90°C for oil-aging. After oil-aging, the initial contact angle values were measured. Then surfactant solution treatment was conducted by dipping oil-aged samples inside solutions for 1.5 days. In the end, the final contact angle values were measured.

Contact angle measurements were conducted at room conditions (~22°C, 1 atm) using the Attension Tensiometer provided by Biolin scientific, as schematically shown in Figure 30.

In a single measurement, values from both sides of the oil drop should be obtained and averaged to represent the wettability of the spot where the oil drop is located on the rock surface. Then another oil drop was created to contact with another spot of the same substrate to obtain another averaged CA (contact angle) value that represented the corresponding new spot. The CA values measured on two spots were averaged to represent the overall wettability of the rock sample. Samples were divided into groups. The error bars shown in the figures and standard deviation (SD) in the tables represent the difference between values obtained from two rock substrate samples in the same group.

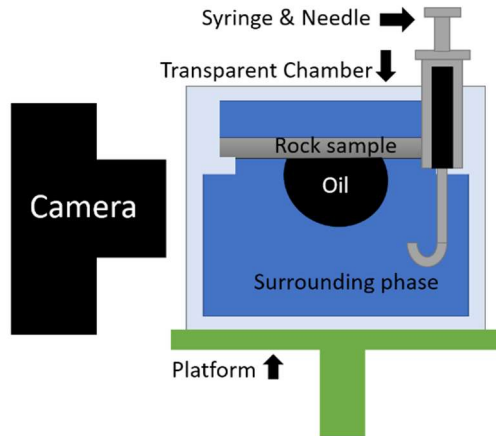


Figure 30 Contact angle measurement instrument.

4.2.3 Scanning electron microscope study

Scanning Electron Microscope (SEM) provides the core-scale to pore-scale surface images of rock samples. It is also widely used for the direct visualization of intergranular fluid distribution in rock. In our study, SEM was applied to provide images of the surfaces at a scale of 30~40 μm . The difference between images before and after EOR treatment can help prove the efficacy of that treatment and explain the mechanism of wettability alteration.

4.3 Results and discussions

4.3.1 Preparation test: required oil aging time

The Indiana limestone samples used in our study were by nature under water-wet conditions. To study the WA performance of surfactants, samples needed to be oil-aged. It is very important that all oil-aged samples have comparable initial oil-wetness. As the temperature, pressure, and oil were kept the same for all samples, aging time and sample heterogeneity were the only two factors that might result in differing wetness.

This preparation test showed the tendency of carbonate rock to become oil-wet after contacting oil. An appropriate aging time can be obtained from its result. Twelve substrates were divided into six groups, each with a different aging time ranging from 0.5 days to 16 days. Table 21 summarizes the measurement results. After only half a day's aging, the contact angle values became mostly more than 150° , which indicated strong oil-wetness. Previous results from 116 substrates showed that before oil-aging, the substrates had CA ranging from 5° to 49° . The average CA value before oil-aging is 26.15° , which indicates strong water-wetness. As a result, half a day's aging is enough to alter carbonate rock substrates' wetting state from a strongly water-wet condition to a strongly oil-wet condition. Increasing the aging time over 0.5 days seemed to have no further effect.

Table 21 Effect of oil aging time on carbonate rock wettability.

Aging time (days)	Sample 1	Sample 2	Average CA	SD
0.5	152.43	155.80	154.11	1.68
1	146.69	153.54	150.12	3.42
2	139.28	153.63	146.46	7.18
4	153.56	153.66	153.61	0.05
8	155.60	146.06	150.83	4.77
16	152.25	151.94	152.10	0.16

In a word, carbonate rock has a strong tendency to become oil-wet or strongly oil-wet after contacting oil at a lifted temperature. Substrates can be altered from strongly water-wet to strongly oil-wet in 0.5 days by contacting oil at 90°C.

4.3.2 Preparation test: required surfactant solution volume

To lower the consumption of the surfactant solutions, the other preparation test was conducted. Twelve substrates were divided into 6 groups, two substrates each. At least 20 ml of solution was required to fully immerse both substrates and ensure that both substrates are equally treated. The surfactant volume values of the six groups were set as 20, 40, 60, 80, 100, and 120 ml. GS3 of concentration 0.05 wt% was used in this test.

Figure 31 shows that GS3 has relatively good WA performance that alters oil-aged surface wettability from strongly oil-wet to intermediate-wet or water-wet conditions, regardless of the surfactant solution volume.

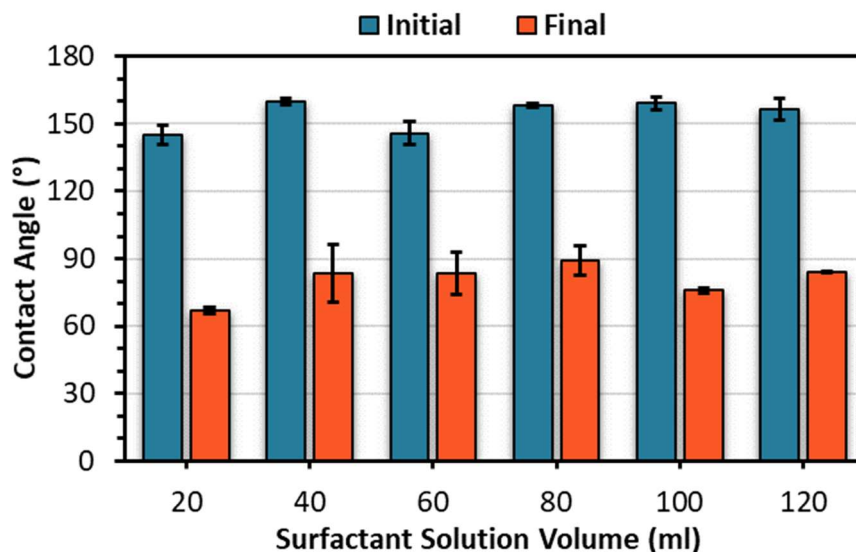


Figure 31 Influence of surfactant solution volume on WA performance.

Table 22 summarizes the CA value difference between the initial state and final state (CA difference = Initial – Final). It shows that volume increase from 20 to 120 ml did not affect the WA performance of GS3.

Table 22 Relation between surfactant solution volume and CA difference.

Surfactant solution volume (ml)	20	40	60	80	100	120
CA difference (°)	77.94	76.60	62.62	69.23	83.29	72.45

In a word, 20 ml surfactant solution is enough for the surfactant solution treatment process.

This volume was applied in the following tests.

4.3.3 Influence of surfactant treatment time

Time is a factor that influences the WA extent. If time is too short, surfactants can not fulfill their WA potential. This test divided substrates into groups that underwent different surfactant treatment times, which is the time of immersion inside surfactant solutions. The surfactant solution used was GS3 of concentration 0.05 wt%.

From Figure 32, while the initial CA values were in the range of strongly oil-wetness, the final CA seemed to decrease rapidly as the treatment time increased from 0.5 days to 1.5 days. As the treatment time increased further over 1.5 days, the final CA seemed to reduce slowly or stabilize. Table 23 summarizes the CA differences. When the treatment time is longer than 1.5 days, it shows a relatively stable CA difference in the range of 60° to 80°, which accord with the results obtained in previous tests that GS3 has good WA performance for oil-wet carbonate rock.

In a word, GS3 fulfills its WA performance after about 1.5 days of treatment. This surfactant treatment time was applied in the following tests.

Table 23 Relation between surfactant treatment time and CA difference.

Time (Days)	0.5	1	1.5	2	3	6	9	12
CA difference (°)	28.54	43.89	67.40	60.49	69.70	75.25	66.17	48.55

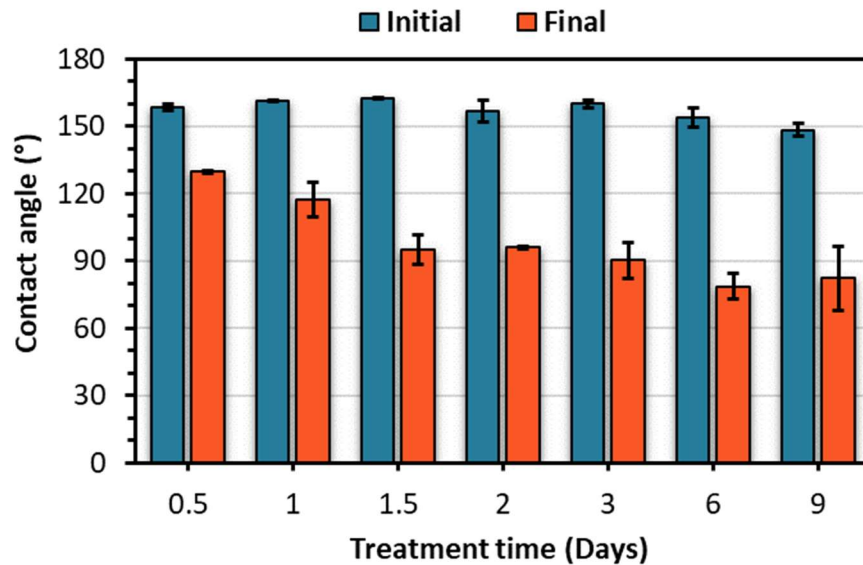


Figure 32 Influence of treatment time on WA performance.

4.3.4 Influence of surfactant concentration

Concentration is an important parameter in both the effectiveness aspect and the economic aspect. A low concentration may lead to insufficient performance. A high concentration may enhance the performance of the surfactant solution but leads up to higher costs. There should also be a threshold concentration for WA, which means the lowest concentration value at which the surfactant fulfills its WA potential.

To study the threshold concentration for the gemini surfactants, GS3 surfactant solutions with 9 different concentrations ranging from 0.002 to 0.50 wt% were tested. The CMC of GS3 at 30°C in DIW is 1.068×10^{-6} mol/L or 1.935×10^{-3} g/L, which is close to 0.002 wt%. Results are shown in Figure 33. The CA differences along with increasing concentration are summarized in Table 24.

Table 24 Relation between surfactant concentration and CA difference.

Conc. (wt%)	0.00	0.01	0.02	0.03	0.04	0.05	0.10	0.30	0.50
	2								
CA difference (°)	-5.74	-	30.2	35.0	31.5	53.0	59.0	41.0	50.4
)		6.81	0	0	9	8	1	4	2

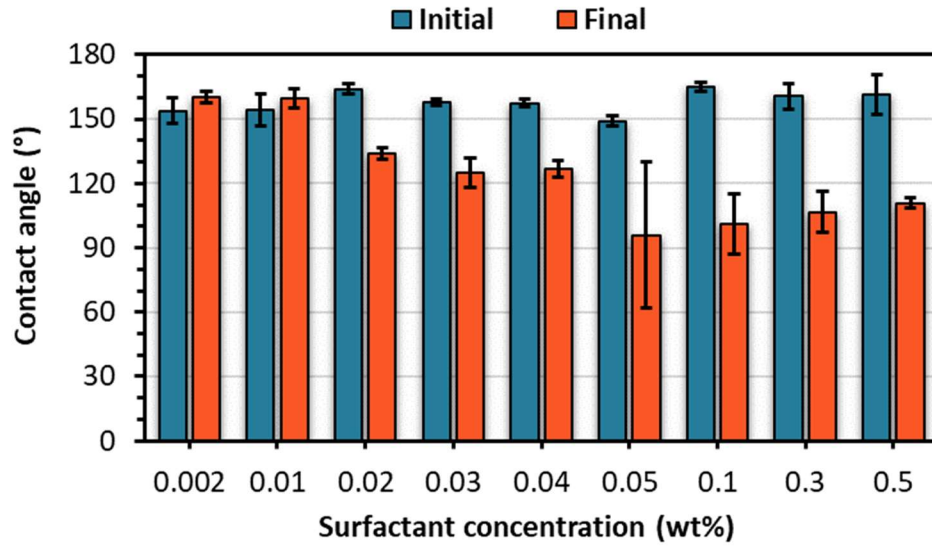


Figure 33 Influence of surfactant concentration on WA performance.

The negative contact angle differences shown in Table 24 seemed counterintuitive because they indicate enhanced oil-wetness. As has been proven in previous tests, GS3 surfactant solution reduces oil-wetness. We would rather understand the negative CA differences as consequences of substrate heterogeneity and measurement error. At a concentration that is 5 times the CMC value, GS3 failed to alter the wettability of the rock. This observation may indicate that micelles are necessary for cationic surfactant-induced WA. As suggested by Standnes et al., cationic surfactant molecules form ion-pair with the negative charge carboxylic groups on organic molecules and desorb them from rock surfaces ¹². When they form ion pairs, they turn their hydrophilic groups towards each other and their hydrophobic groups outwards. Thus, the ion-pair complex shows an overall hydrophobicity and is unstable inside the water phase. To achieve a stable state, it may either move into the oil phase or surfactant micelles ¹². During surfactant treatment, the amount of oil was very small compared to the aqueous phase. As a result, surfactant micelles were necessary to stabilize the ion-pair complex and thus promote the reaction between surfactant monomers

and the adsorbed organic matter. This explains why WA only happened at concentrations much higher than the CMC value.

When the concentration increased over 0.01 wt%, surfactant solution started having a tangible effect on rock wettability gradually. At a concentration of 0.05 wt%, the WA performance reached its largest extent. 0.05 wt% seemed to be the threshold concentration for GS3 to fulfill its WA potential.

Above 0.05 wt%, concentration increase did not enhance the WA performance. One possible explanation for this observation relates with the electrostatic state of the rock surface. Carbonate rock which contains mainly calcite has a positively charged surface by nature. When the rock contacts oil, the negatively charged organic matter starts to adsorb on the rock surface. This adsorption increases the oil-wetness. On the other hand, it also neutralizes the positive charges and weakens the attraction between the rock surface and organic matter. When cationic surfactant molecules desorb this organic matter, the positive charge increases, leading to a stronger attraction between the rock surface and organic matter. As a result, the removal of the organic matter becomes more and more difficult. At a certain point, the surfactant solution achieves its optimal WA performance and will not remove any more organic matter.

Another possible explanation relates to the micellization process. At low concentrations over CMC, surfactant monomers in aqueous liquids form one-layer micelles with hydrophilic head groups towards the outside hydrophobic and tail groups towards the inside, as shown in Figure 34 (c). However, as the concentration increases, the shape and structure of micelles start to change. They may change from globular micelles to elongated

rodlike micelles ²⁸³. They may also change from one-layer micelles to two-layer vesicles, as shown in Figure 34 (d). These vesicles are made up of monomer pairs shown in Figure 34 (b). In these vesicles, hydrophilic head groups are positioned both outside and inside ²⁸⁴. This transition from micelles to vesicles has been reported to reduce the concentration of monomers ⁹⁰. Reduced concentrations lead to the reduced reaction between monomers and the organic absorbance on the rock surface. This transition could be an explanation for the slightly weakened WA performance when concentration increased from 0.05 wt% to 0.50 wt%.

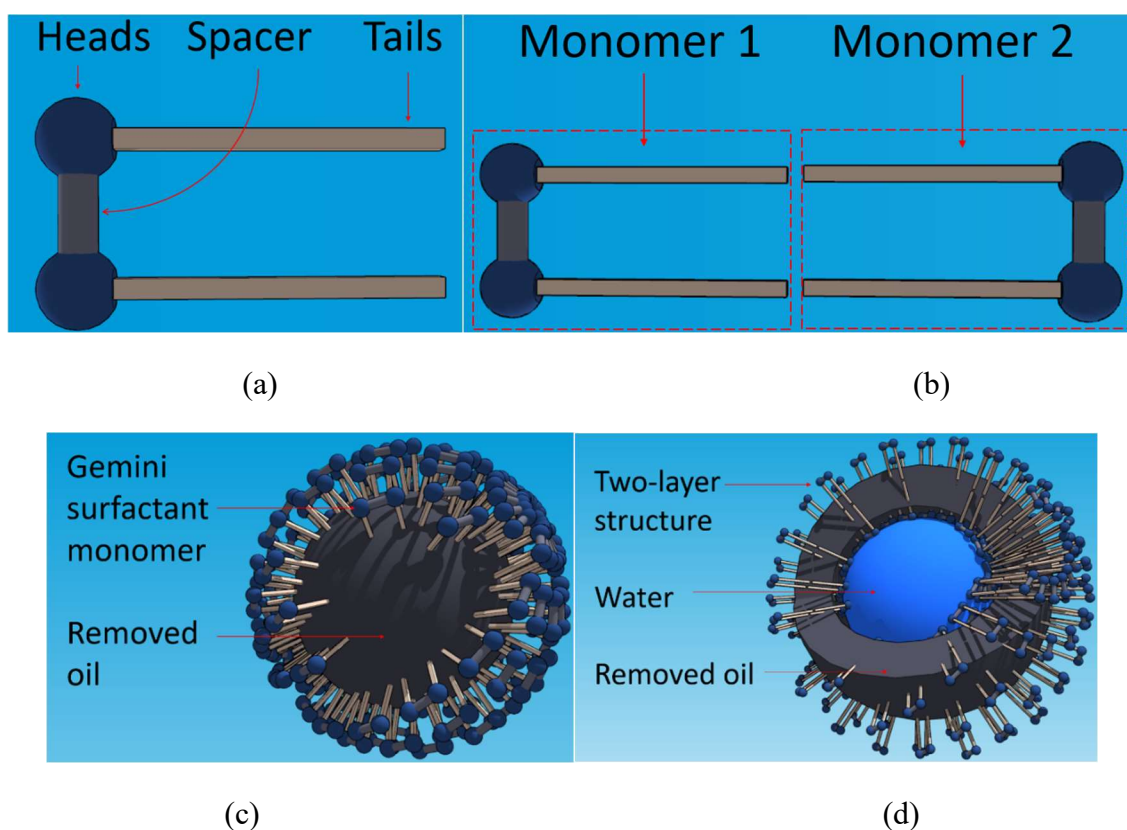


Figure 34 Illustration of possible micelle to vesicle transition (a) monomer (b) a pair of monomers (c) micelle (d) vesicle.

4.3.5 Influence of surfactant molecular structure

4.3.5.1 Straight carbon chain spacer: chain length

Five surfactants GS1 to GS5 were selected for this test. All have saturated straight carbon chains as the spacer groups. The only difference among them is the length of the carbon chain. In other words, the number of carbon atoms in the spacer. Their solutions were prepared at a common concentration of 0.05 wt%. Oil-aged rock substrates were treated in the solutions for 1.5 days. The initial and final CA are shown in Figure 35 I. The CA differences are given in Table 25.

The range of CA difference in Table 25 is narrow, from 41° to 55°, indicating that the difference in WA performance among these five surfactants is insignificant. Changes in the spacer carbon chain length in the range of [4, 12] have negligible influence on WA.

Table 25 Relation between straight carbon chain length of the spacer and CA difference.

Carbon chain length	4	6	8	10	12
CA difference (°)	41.45	46.31	49.31	54.98	45.56

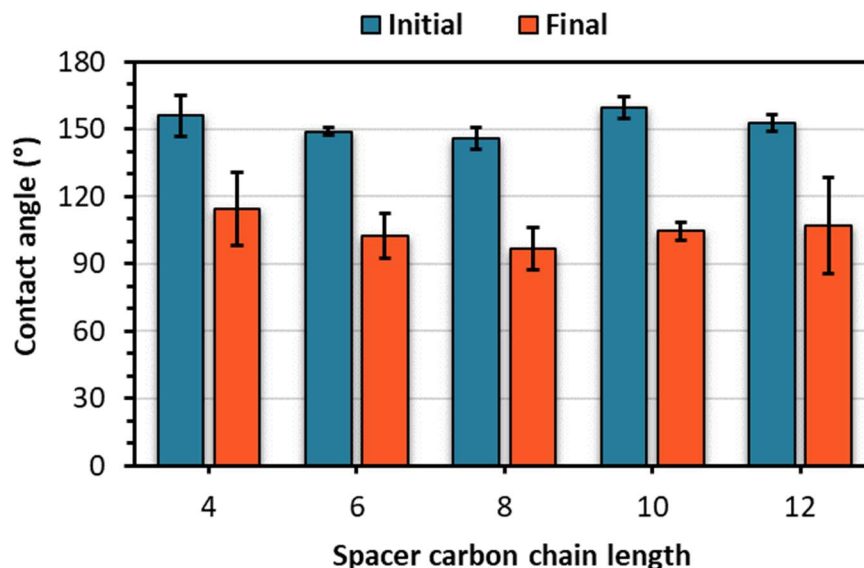


Figure 35 Influence of straight carbon chain length of the spacer on WA performance.

4.3.5.2 Straight carbon chain spacer: unsaturation

Three surfactants GS1, GS6, and GS7 were selected. Double bond equivalent (DBE) is used to describe the unsaturation of organic molecules. All three surfactants have 4 carbon atoms in the spacer and share almost the same structure except that GS1 has a saturated straight carbon chain spacer (DBE = 0), while GS6 has a double bond (DBE = 1) and GS7 has a triple bond (DBE = 2) in the spacer. Their solutions were prepared at a common concentration of 0.05 wt%. Oil-aged substrates were treated in the solutions for 1.5 days.

Results shown in Figure 36 and Table 26 indicate that as unsaturation increased, the surfactant WA performance became weaker. GS1 has a saturated spacer and changed the rock to intermediate-wet condition. GS6 and GS7 have unsaturated spacers and changed the rock only to less oil-wet conditions.

In a word, unsaturation in the spacer impaired the WA performance of cationic gemini surfactants that have a straight carbon chain as the spacers. A probable explanation is that

unsaturation in the spacer affects the HLB of the surfactant, leading to a different aggregation behavior, as well as a different ion-pair formation behavior with the adsorbed organic matter.

Table 26 Relation between unsaturation of the spacer and CA difference.

DBE	0	1	2
CA difference (°)	60.95	22.66	20.59

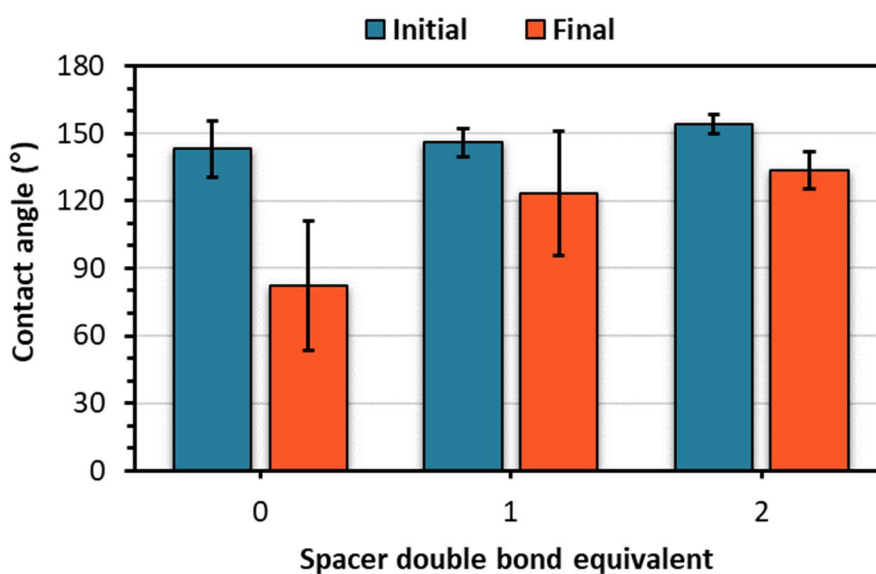


Figure 36 Influence of unsaturation of the spacer on WA performance.

4.3.5.3 Functional groups in the spacer

Five surfactants GS8, GS10, GS-EO, GS-NH, and GS-OH were selected. The involved functional groups are described in Table 19. The surfactant solutions were prepared at a common concentration of 0.05 wt%. Oil-aged substrates were treated in the solutions for 1.5 days.

From the results shown in Table 27 and Figure 37, we obtain a sequence of the surfactants by their WA performance: GS8 > GS-OH > GS-EO $\approx$ GS-NH > GS10. Based on that, a

sequence that describes the influence of functional groups can be organized as: one phenyl group > -OH- group > -NH- group $\approx$ -EO- group > two phenyl groups. The CA difference ranged from 38° to 82°, indicating that the functional group has a significant impact on surfactant WA. GS8 showed good WA performance by changing rock to water-wet. According to the CA differences in Table 25, Table 26, and Table 27, GS8 has the strongest WA performance.

Table 27 Relation between functional groups in the spacer and CA difference.

Functional group	Phenyl	2 Phenyl	-EO-	-NH-	-OH
CA difference (°)	82.05	38.25	48.12	46.45	55.86

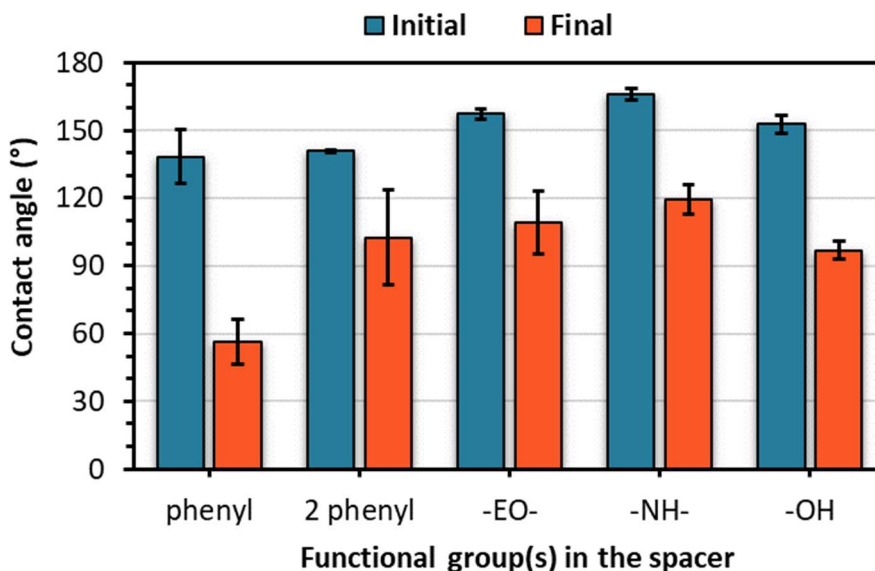


Figure 37 Influence of functional groups in the spacer on WA performance.

4.3.5.3 Counter-ion

Table 28 summarized the structural differences between GS8 to GS11 as well as their corresponding differences between initial and final CA values. From Figure 38, surfactants having one phenyl group in the spacer showed better WA performance than surfactants having two phenyl groups in the spacer. Comparing the results of GS8 and GS9, Br⁻ showed

a better influence on WA performance than Cl^- . However, this difference was not observed in the comparison between GS10 and GS11. In a conclusion, Br^- has a positive influence on the WA performance of surfactants as compared to Cl^- . The influence of counter-ion is less significant than the influence of functional groups in the spacer.

Table 28 Relation between counter-ions and CA difference.

Surfactant	group	Counter-ion	CA DIFF
GS8	phenyl	Br^-	82.04884
GS9	phenyl	Cl^-	69.09843
GS10	2 phenyl	Br^-	38.24547
GS11	2 phenyl	Cl^-	39.10581

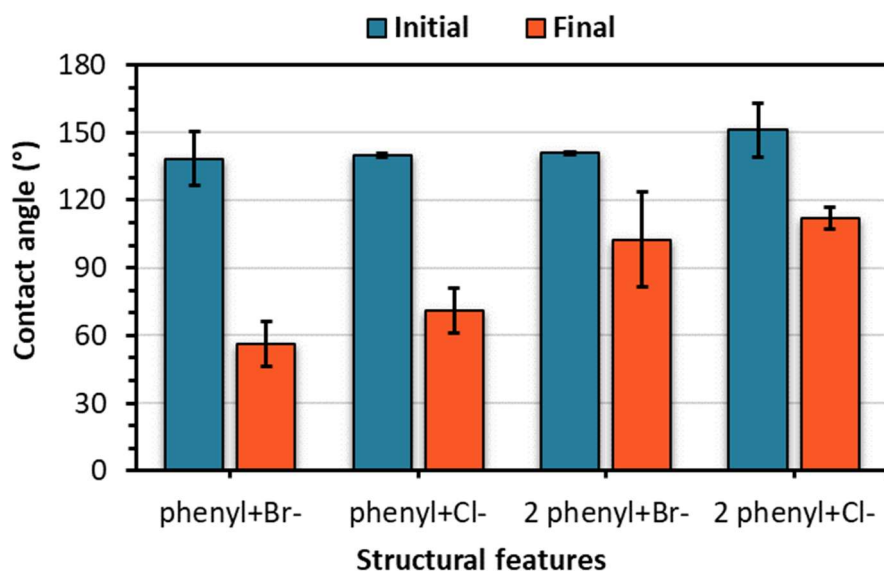


Figure 38 Influence of counter-ions on WA performance.

4.3.6 Influence of salts

Salinity and hardness are important factors that affect the performance of surfactants. Many surfactants that have poor or moderate salt tolerance can only modify the IFT and wettability to a favored extent at low salinity. Increased salinity can lead to consequences including precipitation²⁸⁵, increased adsorption²⁸⁶, different aggregation behavior²⁸⁷, and so on. Researchers have reported the existence of optimal salinity for varying surfactant concentrations to achieve the best WA performance²⁸. Besides, divalent ions have a stronger effect on rock wettability^{31,151} and surfactant performance⁹⁰ than monovalent ions, making hardness an important parameter to consider.

Recently, the application of seawater or diluted seawater has shown its EOR potential in both lab experiments and field studies especially in carbonate reservoirs^{30,288}. This test focuses on salt concentrations related to seawater. Different salt water was prepared. The compositions are given in Table 29. They were lab-prepared seawater, diluted seawater, and salt solutions that had the same or diluted concentrations compared to the same salt in seawater. The DIW group was set as the control group with no salinity. All these solutions contained surfactant GS3 with a concentration of 0.05 wt%.

Table 29 Salt compositions of different surfactant solutions.

Group Name	CaCl ₂ (mol/L)	MgCl ₂ (mol/L)	Na ₂ SO ₄ (mol/L)	NaCl (mol/L)	GS3/GS8 (wt%)
DIW	0	0	0	0	0.05
¼SW	0.07970169	0.03885248	0.00091197	0.64359172	0.05
½SW	0.15940339	0.07770497	0.00182394	1.28718344	0.05
SW	0.31880677	0.15540994	0.00364789	2.57436687	0.05
½CaCl ₂	0.15940339	0	0	0	0.05
CaCl ₂	0.31880677	0	0	0	0.05
3/2CaCl ₂	0.47821016	0	0	0	0.05
2CaCl ₂	0.63761355	0	0	0	0.05
½MgCl ₂	0	0.07770497	0	0	0.05
MgCl ₂	0	0.15540994	0	0	0.05
3/2MgCl ₂	0	0.2331149	0	0	0.05
2MgCl ₂	0	0.31081987	0	0	0.05
½Na ₂ SO ₄	0	0	0.00182394	0	0.05
Na ₂ SO ₄	0	0	0.00364789	0	0.05
3/2 Na ₂ SO ₄	0	0	0.00547183	0	0.05
2 Na ₂ SO ₄	0	0	0.00729577	0	0.05
½NaCl	0	0	0	1.28718344	0.05
NaCl	0	0	0	2.57436687	0.05
3/2NaCl	0	0	0	3.86155031	0.05
2NaCl	0	0	0	5.14873374	0.05

From Table 30 and Figure 39, as concentration increased, Na_2SO_4 had no effect or slightly positive effect on WA, while NaCl , MgCl_2 , and CaCl_2 had an overall negative effect on WA performance of GS3. Among them, MgCl_2 seemed to have a positive effect at lower concentrations (1/2). Then the effect became negative as concentration increased. NaCl had a negligible effect at lower concentrations (1/2 and 1) and changed the WA performance of GS3 from good to moderate at higher concentrations (3/2 and 2). CaCl_2 had a negative effect at lower concentrations and changed the WA performance of GS3 from good to poor at higher concentrations (3/2 and 2).

Table 30 Relation between salt concentrations compared to seawater and CA difference.

Relative concentration	0	1/2	1	3/2	2
NaCl CA reduction (°)	68.51	77.88	70.45	14.44	43.88
Na₂SO₄ CA reduction (°)	68.51	81.87	89.52	67.17	87.88
MgCl₂ CA reduction (°)	68.51	100.19	60.36	23.42	52.59
CaCl₂ CA reduction (°)	68.51	66.68	34.23	7.40	40.80

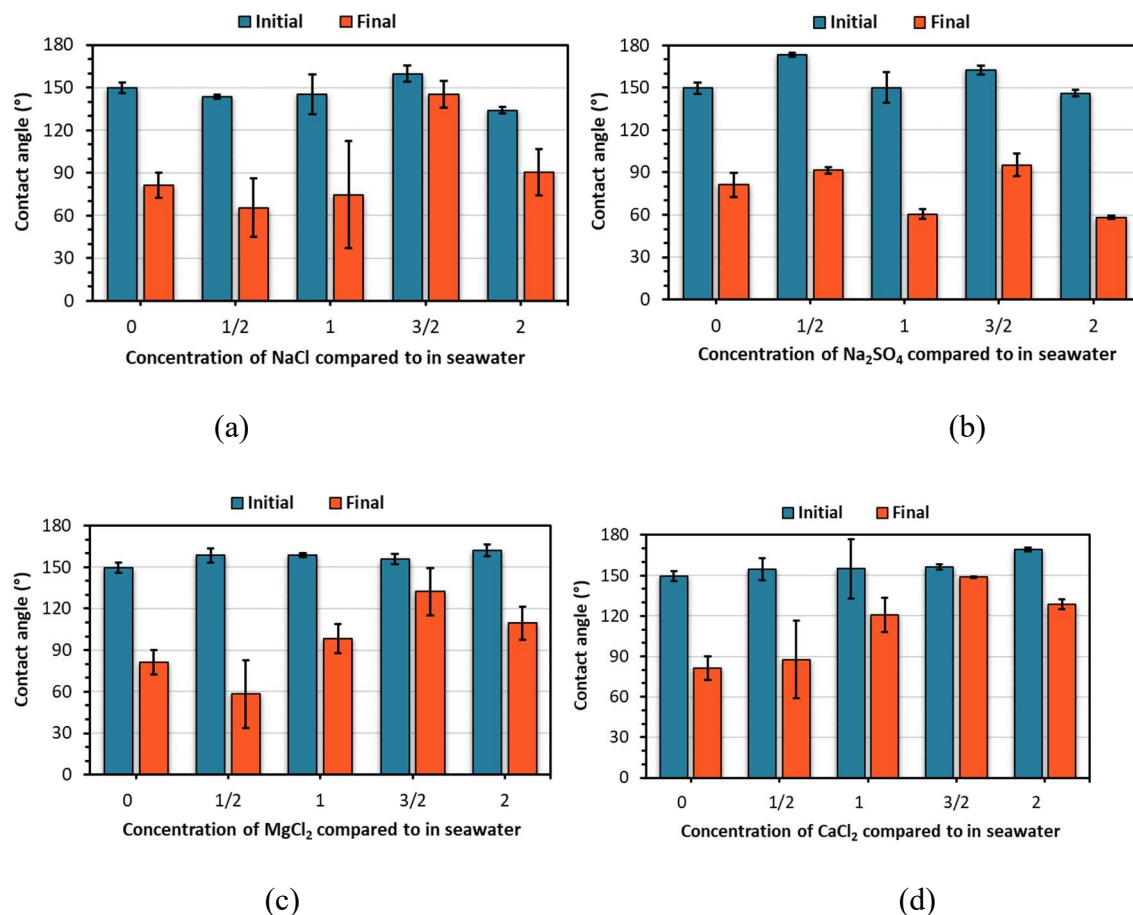


Figure 39 Influence of salt concentrations on WA performance (a) NaCl (b) Na₂SO₄ (c) MgCl₂ (d) CaCl₂.

As observed in Section 3.5.3, GS8 showed the strongest WA performance among all 14 surfactants. Since GS8 could be a promising EOR material for carbonate rock, its WA performance in seawater and diluted seawater was also tested. The results were compared with those of GS3 in Table 31 and Figure 40.

As the salinity increased, both surfactants had their WA performance impaired. GS3 had poor WA performance while GS8 had a moderate WA performance in seawater. In solutions with the same salinity, GS8 had better performance than GS3. This observation accords with the observation that GS8 is stronger than GS3 in WA.

Table 31 Relation between diluted seawater and CA difference of GS3 and GS8.

Relative seawater salinity	0	1/4	1/2	1
GS3 contact angle reduction (°)	68.51	44.60	40.34	34.64
GS8 contact angle reduction (°)	82.05	76.94	63.50	53.99

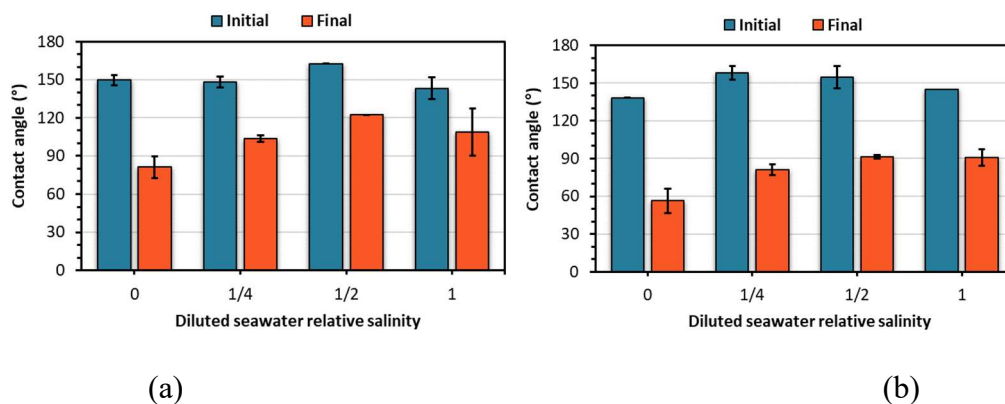


Figure 40 Influence of diluted seawater on WA performance (a) GS3 (b) GS8.

In summary, for surfactant solutions prepared using seawater or diluted seawater, the influence of concentration differed for different salts. Na_2SO_4 had no effect or slightly positive effect on the WA performance of GS3. NaCl and CaCl_2 had an overall increasing negative effect. MgCl_2 had a positive effect at a lower concentrations and a negative effect at higher concentrations. The combined effect of all salts in seawater and diluted seawater turned out to be negative. The WA performance of GS3 was changed from good in DIW to poor in seawater. GS8 remained a better wettability modifier than GS3 at all tested diluted seawater salinities. As the salinity increased, its WA performance was changed from good in DIW to moderate in seawater.

4.3.7 The wettability alteration mechanism of cationic gemini surfactants

A widely accepted explanation of the WA process brought by cationic surfactants suggests that they alter rock wettability by irreversibly removing the organic materials. In our study, SEM images of differently treated sample surfaces were taken and shown in Figure 41.

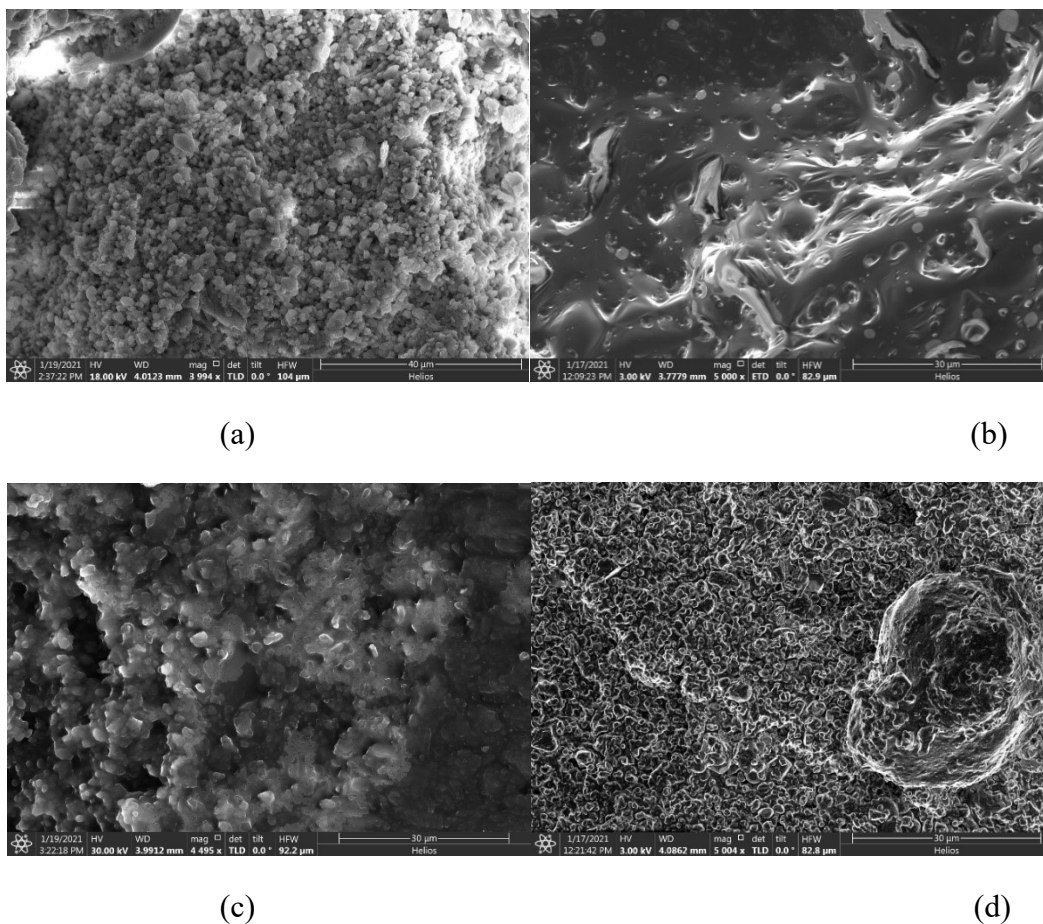


Figure 41 SEM results (a) before oil-aging (b) after oil-aging (c) soaked by DIW (d) treated with a surfactant.

Compared to the image before oil-aging (Figure 4.12(a)), the rock surface after oil-aging (Figure 41(b)) looks much smoother. Only some edges of larger particles can be seen. Small particles were covered under a dark film-like material. This dark film-like material was the attached oil that rendered sample surface oil-wetness. After being soaked by DIW (Figure 41(c)), the oil film on the surface became partly removed. One possible explanation

is related to buoyancy. During the treatment by DIW, the density difference between oil and water formed the buoyancy that removed loosely adsorbed oil, leaving behind the oil phase that strongly adhered to the sample surface. The remaining oil phase formed the thin oil film that was distributed mostly between particles of the rock minerals. When the sample was treated with cationic gemini surfactant (Figure 41(d)), more oil was removed from the sample surface. Compared to the sample soaked with water, smaller particles can be clearly distinguished. In a conclusion, surfactant seemed to further remove the oil film and promotes the exposure of rock particles to the aqueous phase, thus restoring rock water-wetness.

In a word, the tested cationic gemini surfactants alter oil-wet carbonate rock wettability by removing the organic adsorbent on the rock surface.

4.4 Conclusions

It is reported that cationic surfactants have better wettability alteration performance and less adsorption in carbonate rock ¹². Cationic gemini surfactants are potential high-efficiency EOR materials for carbonate reservoirs. This chapter is based on the results from contact angle measurements and spontaneous imbibition experiments of 14 locally synthesized cationic gemini surfactants. It adds to the understanding of their wettability alteration performance and the influences of factors including required reaction time, surfactant concentration, molecular structure, and salts.

The following conclusions are drawn:

1. The tested cationic gemini surfactants alter oil-wet carbonate rock wettability by removing the organic adsorbent on the rock surface.
2. The cationic gemini surfactant GS3 whose spacer consists of a straight carbon chain of 8 carbon atoms has good wettability alteration performance in oil-wet carbonate rock. At a concentration of 0.05 wt%, it managed to alter the rock surface to a water-wet condition in 1.5 days.
3. For surfactants whose spacer consists of a straight carbon chain, an increase in carbon atom number from 4 to 12 in the spacer had negligible influence. When unsaturation was introduced, the wettability alteration performance of surfactants was significantly impaired.
4. Functional groups in the spacer have a significant influence on the wettability alteration performance. Among tested surfactants, surfactants with one phenyl group in the spacer showed the best performance. Surfactants with either -EO-, -NH- or -OH group in the spacer showed moderate performance. Surfactants with two phenyl groups in the spacer showed the weakest performance.
5. Counter-ion had a less significant influence. Surfactants with Br^- had better wettability alteration performance than surfactants with Cl^- .
6. The influence of salts on surfactant wettability alteration performance differs. Na_2SO_4 had no effect or slightly positive effect on the performance of GS3. NaCl and CaCl_2 had a negative effect that became severer as concentration increased. MgCl_2 had a positive effect at a lower concentrations and a negative effect at higher concentrations.

7. The combined effect of all salts in seawater and diluted seawater turned out to be negative that impaired the wettability alteration performance of GS3 from good to poor. The surfactant GS8 which has one phenyl group in the spacer remained a better wettability modifier than surfactant GS3 at all tested diluted seawater salinities. As the salinity increased, its performance was also impaired from good to moderate.

CHAPTER 5

WETTABILITY ALTERATION OF CARBONATE ROCK

BY CHELATING AGENTS AND VISCOELASTIC

SURFACTANTS: SYNERGETIC IMPACT

5.1 Introduction

Wettability alteration (WA) is an important mechanism in EOR. Carbonate reservoirs are often oil-wet and naturally fractured. During waterflooding, the injected fluid tends to flow through high permeability zones such as the connected fractures or high permeability zones, leaving relatively low permeability rock matrix unflooded ⁷⁷. As a result, a lot of oil remains in the rock matrix. When the rock is modified to water-wet condition, the capillary pressure changes from a negative force, that prevents the displacement of oil, to a positive force that promotes the displacement of oil ⁸⁰. The positive capillary pressure has an especially important impact in the lower permeability zones ⁶⁵. The injected liquid tends to enter the unflooded low permeability zone by spontaneous imbibition, thus increasing the recovery factor.

A wide variety of materials, including surfactants, nanoparticles, salts, alkalis, and so on, can be applied to modify carbonate rock wettability conditions ¹⁷⁶. Among them, surfactants are the most studied materials. A synergic effect is observed in several studies showing the interfacial tension (IFT) reduction mechanism and WA can be combined to

increase oil recovery ^{81,181}. Numerical simulations and several experiments, however, suggest keeping the magnitude of IFT as high as possible to obtain a strong positive capillary pressure ^{74,200,229}. Surfactants reduce the IFT between two phases. Viscoelastic surfactants (VES) are surfactants that exhibit viscoelasticity. Compared to conventional surfactants, VES provides high viscosity. VES alone can obtain IFT reduction and mobility control at the same time, which was done previously by combining polymers and surfactants ⁶⁸. Apart from the aforementioned advantages, the wettability alteration potential of some VES was proven to be an important contributor to incremental oil recovery ²⁸⁹.

A major concern in the application of VES is the retention of surfactants. Studies have shown that the retention of VES is considerably impacted by pore radius, VES concentration, displacing velocity, and salinity. Salinity affects the partitioning of surfactants ²⁹⁰. There is sometimes an optimal salinity for a surfactant to reduce the IFT, generate the microemulsion phase ²⁹¹, as well as to alter rock wettability ^{28,53}. Low salinity waterflooding has been proposed as a wettability alteration and oil recovery scheme by many researchers ^{30,288}. However, as salinity increases, an adverse effect on the performance of surfactants is observed. As salinity increases, VES retention increases significantly ²⁹². For high-temperature, high-pressure reservoirs, a newly proposed EOR technique suggests combining VES and chelating agents ²⁹³. Chelating agents are chemical compounds that form complexes with metal ions ²⁹⁴. Formation brine usually has high salinity and hardness. Many EOR materials, such as surfactants, become less effective in high salinity conditions ^{295,296}. Chelating agents can be applied alongside these materials to fulfill their EOR potential by capturing the metal ions ^{293,297}. Experimental studies by Chen

and Mohanty showed that adding chelating agents enhanced the WA performance of surfactants ²⁹⁸. Yao et al. confirmed this enhancement from their study on 338 imbibition test results from over 50 publications ²⁹⁹.

Chelating agents themselves are found to cause WA on different types of rock as well. Alarifi et al. found that DTPA (diethylene triamine penta acetic acid) made the zeta potential of sandstone rock more negative, indicating that the rock treated by DTPA became more water-wet ³⁰⁰. Pratama and Babdagli observed that chelating agents promoted auspicious WA and IFT reduction in the sandstone/heavy-oil/steam system ³⁰¹. Janjua et al. observed additional oil recovery by injecting chelating agent solution into carbonate rock after flooding with seawater and viscoelastic surfactant solution ²⁹³. Studies conducted by Chen and Mohanty ²⁹⁸, Hassan and Al-Hashim ³⁰² both observed rock dissolution caused by chelating agents. Hassan and Al-Hashim observed that chelating agents managed to change the zeta potential of carbonate rock to a more negative condition, indicating stronger water-wetness ³⁰³.

EDTA is probably the most implemented chelating agent in oil fields ³⁰⁴. It has been widely applied in well stimulation ^{305,306} and formation damage removal ³⁰⁶. Recently, some new applications of EDTA were proposed. Mahsa et al. used EDTA to coat nanoparticles ¹⁴¹. Mahmoud and Abdelgawad used EDTA as the EOR material for both sandstone and carbonate ³⁰⁷. DTPA has good stability at a temperature up to 400°F at high pH ³⁰⁰. GLDA is developed by LePage et al. ³⁰⁸. GLDA showed very promising stimulation properties, including better solubility in HCl, better biodegradation level (>60%), and good thermal stability. EDTA, DTPA, and GLDA are amino polycarboxylic acids. The ionization of amino polycarboxylic acids is a stepwise process depending on the pH, as shown in Figure

42. At low pH, chelating agents react with the CO_3^{2-} ions on the carbonate rock surface. At high pH, however, they react with the Ca^{2+} ions on the rock surface³⁰⁴.

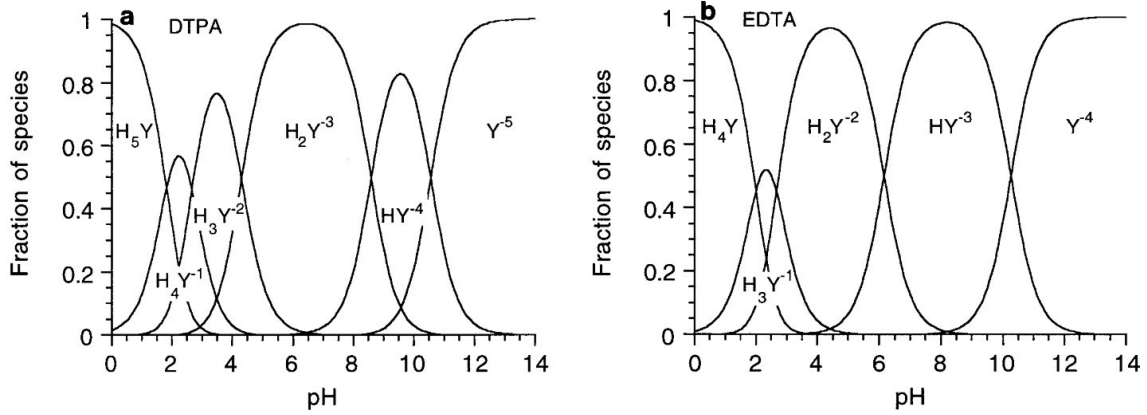


Figure 42 Distribution of ionic species of (a) DTPA and (b) EDTA at 25°C³⁰⁴.

A lack of study about the wettability alteration performance of VES is found in the literature. Previous studies involving the WA potential of chelating agents on carbonate rock applied zeta potential measurement, which is a qualitative rather than quantitative technique. In this study, contact angle measurement that quantitatively reflects the wettability change. The WA performance of VES, different chelating agents, and the combined VES+CA compositions, can thus be assessed and compared based on contact angle results.

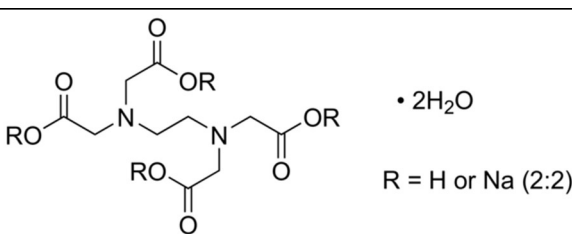
5.2 Materials and Experimental

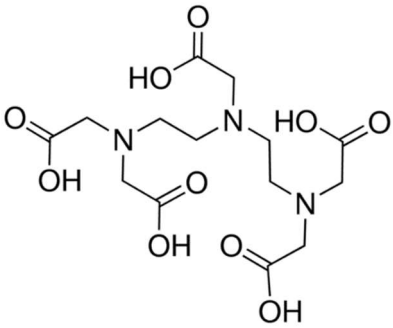
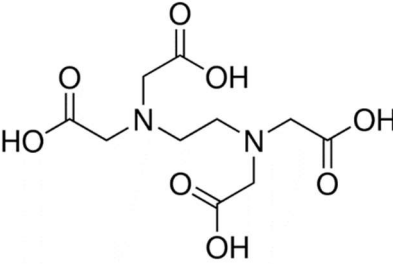
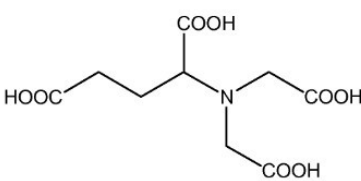
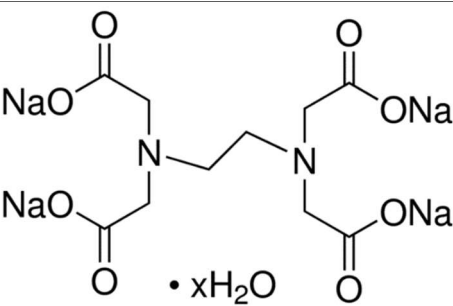
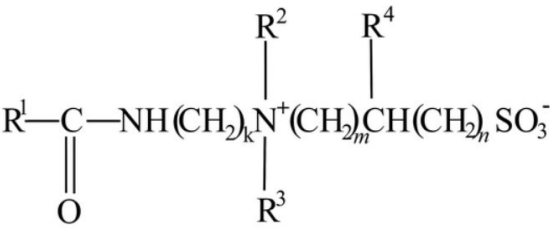
The rock used in the study was relatively tight Indiana limestone (porosity 14.6%, permeability around 10 mD). XRD study was conducted. Results showed a 100% calcite mineral composition. To conduct contact angle measurements, the rock samples were processed into slices with 1-inch diameter and 3~4 mm thickness. Surfaces of the rock

slices were smoothened using P500 sandpaper. The oil used in the study was filtered crude oil (API 31.07).

The viscoelastic surfactant (VES) used in this study is the AGA-97, 40~45 wt% of erucamidopropyl sulfobetaine provided by AkzoNobel. Diethylene triamine penta acetic acid (DTPA) and Glutamic acid diacetic acid (GLDA) was provided by a local service company. Ethylene diamine tetra acetic acid (EDTA, assay 99.4~100.6%), Ethylene diamine tetraacetic acid disodium salt dihydrate (DSD, assay 99.0~101.0%), and Ethylene diamine tetra acetic acid tetra-sodium salt hydrate (TSSH, assay $\geq 99.0\%$), were purchased from Sigma-Aldrich. Information on the studied chelating agents is included in Table 32. Fredd and Fogler observed that at a pH higher than 8, the dissolution rate of calcite by EDTA and DTPA did not change along with the increasing pH ³⁰⁴. In our study, the pH values of the chelating agent solutions were modified by adding KOH so that the 3 wt% solutions had a pH of around 11. 0.3 wt% solutions had a pH of around 9~10.

Table 32 The structures of the studied chelating agents and viscoelastic surfactant ³⁰⁹.

Short name	Full name	Structure
	Molecular weight (g/mol)	
DSD	ethylene diamine tetra acetic acid disodium salt dihydrate	
	372.24	
DTPA	diethylene triamine penta acetic acid	

	393.35	
EDTA	ethylenediamine tetra acetic acid	
	292.24	
GLDA	glutamic acid diacetic acid	
	351.13	
TSSH	ethylenediamine tetra acetic acid tetra-sodium salt hydrate	
	380.17 (anhydrous basis)	
VES	erucamidopropyl sulfobetaine	

Synthetic seawater and diluted synthetic seawater were prepared according to Table 33.

Table 33 Composition of synthetic seawater and diluted synthetic seawater.

Concentration (g/L)	SW	3/4SW	2/4SW	1/4SW
NaHCO ₃	0.165	0.12375	0.0825	0.04125
Na ₂ SO ₄	6.339	4.75425	3.1695	1.58475
NaCl	41.172	30.879	20.586	10.293
CaCl ₂ .2H ₂ O	1.802	1.3515	0.901	0.4505
MgCl ₂ .6H ₂ O	8.266	6.1995	4.133	2.0665
TDS	57.745	43.30875	28.8725	14.43625

For contact angle measurement, the Theta Attension Tensiometer from Biolin Scientific was used. As shown in Figure 43, the rock sample and the fluids were contained in a transparent chamber. The chamber was placed on a platform of the Theta Attension Tensiometer. The position and height of the platform were controlled by the control system. A computer imaging system and a camera were attached to capture the interface and obtain the contact angle values from photos. A syringe holder was installed on top of the instrument to hold the syringe filled with oil. During a measurement, an oil drop was generated from the syringe. It grew larger and eventually left the tip of the syringe needle. The oil drop floated in the water and contacted the bottom surface of the rock sample. After the contour of the oil drop stabilized, the contact angle was obtained. Rock samples were cleaned with toluene for 4 days and dried in the oven at around 50°C with air flush for 3 days. Then they were put inside crude oil in a container. The container was kept at 120°C for 4 days of oil-aging. After oil-aging, samples were taken out from the oil. Contact angle measurements were conducted. The obtained results were labeled as “initial contact angle” as they represent the wetting state before treatment. After the initial contact angle measurements, the samples were treated with different chelating agent solutions by soaking them inside these solutions for 4 days. All solutions had the same mass 60 g (about 60 ml). After that, samples were taken out from the solutions. Contact angle measurements were

conducted. The obtained results were labeled as “final contact angle” as they represent the wetting state after treatment. The results were categorized into different wetting conditions according to Table 34.

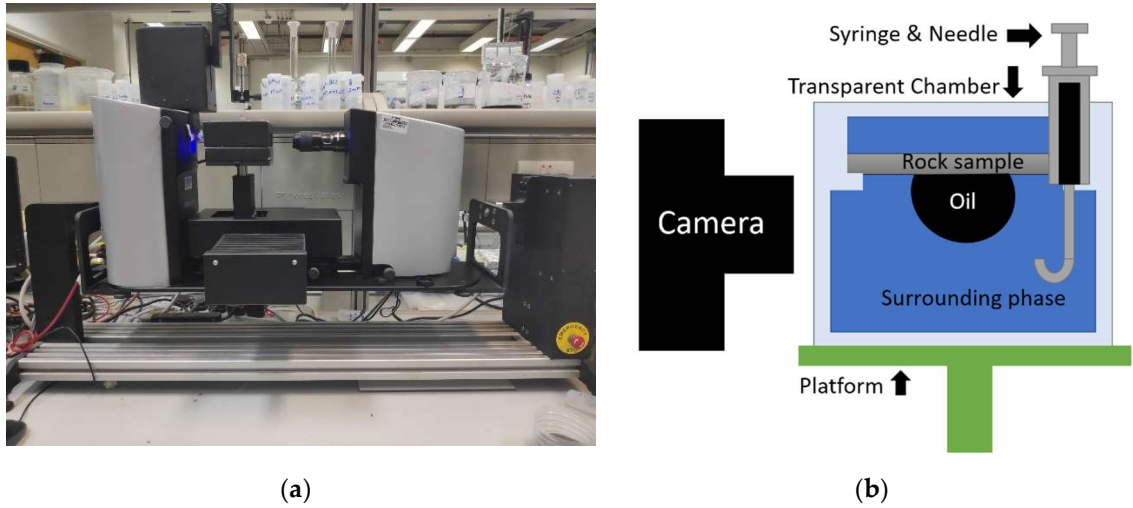


Figure 43 Contact angle measurement (a) the instrument; (b) an illustration of how contact angle is captured ³¹⁰.

Table 34 The relation between rock surface wettability and contact angle value.

Type	Contact angle (°)
Strongly water-wet	0-30
Water-wet	30-70
Intermediate-wet	70-110
Oil-wet	110-150
Strongly oil-wet	150-180

In the following context, several abbreviations will be used to represent a type of solution. “CA+DI” represents the chelating agent in a deionized water solution. “CA+SW” represents the chelating agent in synthetic seawater solution. “CA+diluted SW” represents the chelating agent in diluted synthetic seawater solution. “VES+SW” represents VES in

synthetic seawater solution. “VES+CA” represents the combination of chelating agent and VES in synthetic seawater solution. Table 35 summarizes all the concentration values involved in this study for VES and studied chelating agents. A previous study conducted by Hassan et al. suggested that 3 wt% EDTA was the optimal chelating agent concentration that can enhance oil recovery without inducing formation damage by mineral dissolution³⁰². Another study by Hassan et al. found 5 wt% to be the threshold concentration of EDTA below which no severe mineral dissolution takes place³⁰³. In our study, the concentration of chelating agents was limited to 3 wt% to avoid severe mineral dissolution.

Table 35 Concentration values of different chemicals involved in the study.

	DTPA (wt%)	EDTA (wt%)	DSD (wt%)	TSSH (wt%)	GLDA (wt%)	VES (wt%)
CA+DI	0.04, 0.1, 0.2, 0.3, 0.5, 0.8, 1, 2, 3	0.1, 0.3, 0.5, 0.8, 1, 3	0.1, 0.3, 0.5, 0.8, 1, 3	0.1, 0.3, 0.5, 0.8, 1, 3	0.1, 0.3, 0.5, 0.8, 1, 3	0
CA+SW	0.4, 1, 2, 3, 4	0.3, 1, 3	0.3, 1, 3	0.3, 1, 3	0.3, 1, 3	0
CA+diluted SW	0.4	0	0	0	0	0
VES+SW	0	0	0	0	0	0.1, 1, 2
VES+CA	0.3, 1, 3	0.3, 1, 3	0.3, 1, 3	0.3, 1, 3	0.3, 1, 3	0.3

5.3 Results and discussion

Sample surfaces were strongly oil-wet after oil-aging. The initial contact angles were above 150°. After treating them with different solutions, the wettability status varied. In this study, the difference between the initial contact angle (after oil-aging) and the final contact

angle (after soaking treatment), as described by Equation 5.1, is considered the quantitative reflection of the wettability alteration. They are referred to as “contact angle differences” in this thesis.

$$\text{Contact angle difference} = \text{Initial contact angle} - \text{Final contact angle} \quad (5.1)$$

5.3.1 Wettability alteration by chelating agents in deionized water

This section discusses the WA performance of different CA+DI solutions. The concentrations of different CA can be found in the 1st row of Table 35. Results are shown in Figure 44.

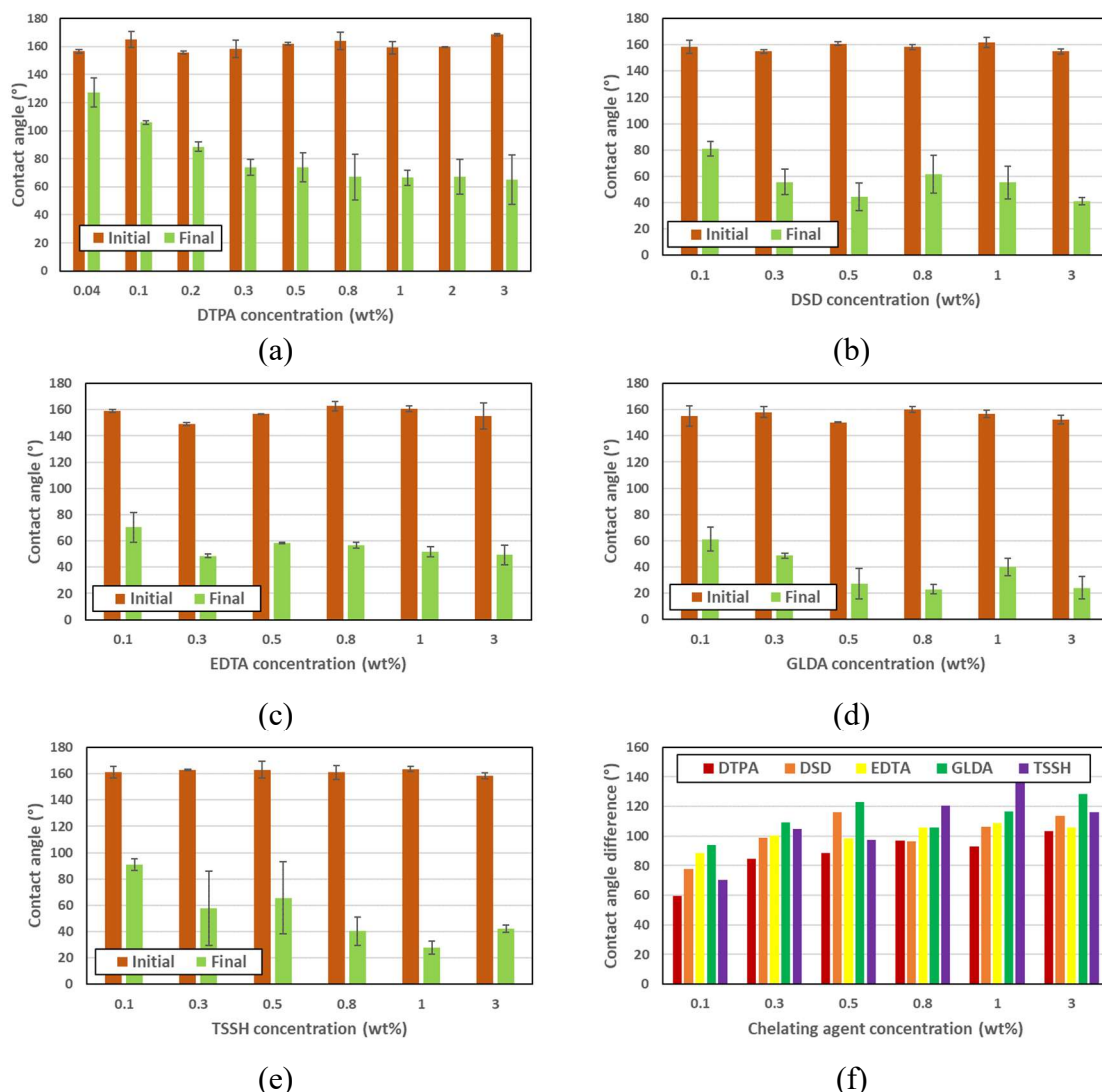


Figure 44 Wettability alteration performance of the chelating agent in deionized water solutions. (a~e) Contact angle before (Initial) and after (Final) soaking treatment in CA+DI solutions (a) DTPA (b) DSD (c) EDTA (d) GLDA (e) TSSH. (f) the contact angle difference induced by chelating agents in deionized water solutions at 6 different concentrations.

Figure 44 (a~e) shows that all studied chelating agents have strong wettability alteration performance with no salts in the solutions. The aged samples had strong oil-wetness (contact angle values larger than 150°) as an initial state. After the soaking treatment, however, the samples became intermediate-wet (at lower concentrations), water-wet, and strongly water-wet (at higher concentrations), conditions. From the results of DTPA, when the concentration of DTPA increased, the wettability alteration performance was enhanced.

When the concentration reached a threshold value (0.3 wt%), however, the influence of concentration increase became negligible. A similar trend can also be found in other chelating agents. The threshold concentration differs among the tested chelating agents. The WA performance of DSD and EDTA seemed to stabilize at a concentration of around 0.3 wt%. For GLDA, the threshold concentration locates in the range of 0.3~0.5 wt%. For TSSH, the threshold concentration is higher, at around 0.8 wt%. Figure 44 (f) summarizes the contact angle differences induced by DTPA, DSD, EDTA, GLDA, and TSSH. The tested chelating agents have comparable wettability alteration performance. GLDA and TSSH seem to be slightly stronger than the other three. DTPA has relatively weaker WA performance as compared to the other four.

At high pH, chelating agents alter carbonate rock wettability by surface complexation³⁰⁴. Chelating agents comprise negatively charged carboxylate groups. They are attracted to the positively charged carbonate surface and start complexation with calcite ions on the surface. The adsorption of chelating agents neutralizes the positive charges on the surface, leading to decreased adsorption of hydrophobic matter.

5.3.2 Wettability alteration by chelating agents in synthetic seawater

This section discusses the WA performance of different CA+SW solutions. The tested concentrations of different CA can be found in the 2nd and 3rd row of Table 35.

Figure 45 shows the WA performance of DTPA (0.4 wt%) in diluted synthetic seawater solutions. As the dilution ratio increased, the WA performance was impaired. This trend can be explained by the relation between the dilution ratio and salinity. As the dilution ratio increased, the salinity and hardness increased, and the concentration of active metal ions

became higher. Chelating agents form complexes with metal ions. A higher concentration of metal ions led to higher consumption of metal ions, resulting in a lower concentration of chelating agents that contributed to the WA.

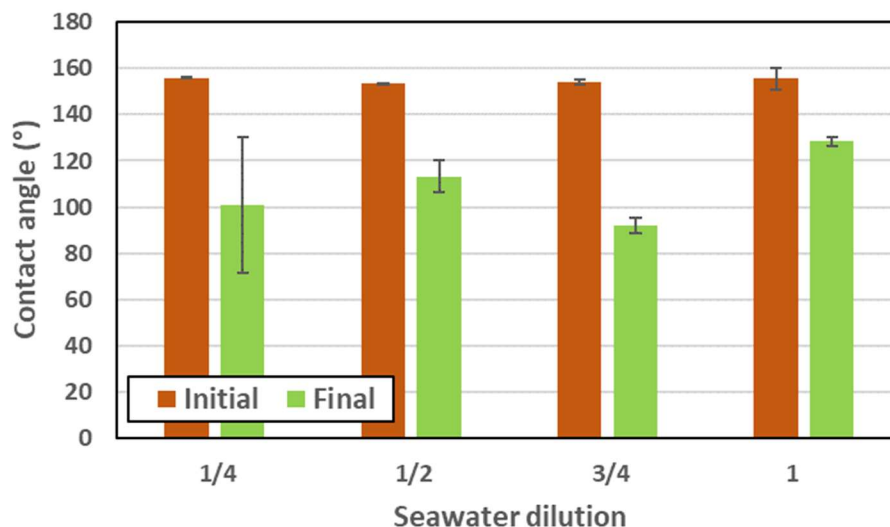


Figure 45 Contact angle before (Initial) and after (Final) soaking treatment in DTPA (0.4 wt%) + diluted SW solutions.

Figure 46 shows the result of all chelating agents dissolved in synthetic seawater. Figure 46 (a~e) shows that when dissolved in synthetic seawater, the wettability alteration performance of all chelating agents became weaker than when they were dissolved in DI water. The increased salinity and hardness negatively affected their wettability alteration performance. By increasing the concentration of chelating agents, the wettability change was enhanced, except for TSSH which showed no improvement as its concentration increased from 0.3 wt% to 3 wt%.

The studied chelating agents showed different salinity tolerance regarding wettability alteration. The salinity tolerance was assessed based on contact angle differences at the same concentration. For example, at 3 wt%, TSSH resulted in negligible contact angle change. DSD, however, changed the rock surface from strongly oil-wet (152.1°) to

intermediate-wet (91.2°). Figure 46 (f) summarizes the contact angle differences induced by all chelating agents at tested concentrations. The salinity tolerance of other chelating agents can be compared straightforwardly from Figure 46 (f). The salinity tolerance decreases in the order: DTPA $\approx$ EDTA > GLDA > DSD > TSSH.

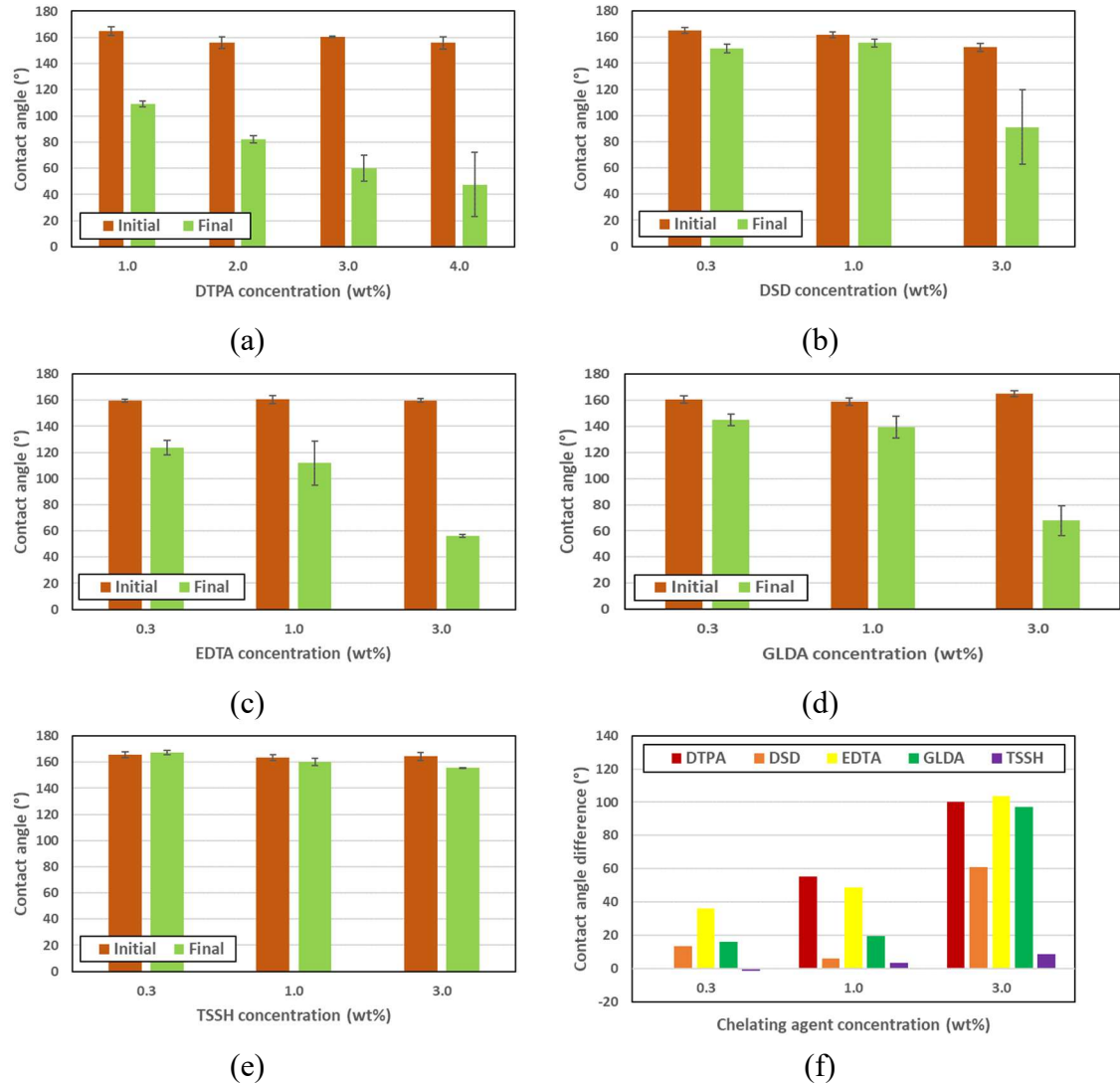


Figure 46 Wettability alteration performance of the chelating agent in synthetic seawater solutions. (a~e) Contact angle before (Initial) and after (Final) soaking treatment in CA+SW solutions (a) DTPA (b) DSD (c) EDTA (d) GLDA (e) TSSH. (f) the contact angle difference induced by all chelating agents in synthesized seawater solutions at 3 different concentrations.

Comparing the wettability alteration performance of chelating agents in DI water and synthetic seawater, a much higher concentration is required in seawater solutions to obtain

significant wettability alteration obtained in DI water solutions. In DI water solutions, at a concentration in the range of 0.3~0.5 wt%, all chelating agents altered rock surface to water-wet condition. In synthetic seawater solutions, DTPA, EDTA, and GLDA altered rock surface to water-wet condition at a much higher concentration, 3 wt%. The other two chelating agents, DSD and TSSH, suffered from significant performance loss.

The wettability alteration performance became quite different among DSD, TSSH, and EDTA, while DSD and TSSH are basically ionized EDTA. This difference could be due to the molar concentration difference and the different salt types. Compared to EDTA, DSD and TSSH have higher molar mass. At the same weight concentration, DSD and TSSH have lower molar concentrations, resulting in weaker wettability alteration performance compared to EDTA. Another possible explanation relates to the adsorption behavior. Hassan et al. observed that salt type affected the adsorption behavior of GLDA. The adsorption increased in this sequence: $\text{Na}_4\text{-GLDA} < \text{K}_4\text{-GLDA} < \text{Ca}_2\text{-GLDA}$ ³¹¹. Here in our study, DSD is partially ionized EDTA, with 2 hydrogen ions replaced by sodium ions. TSSH is fully ionized EDTA, with all 4 hydrogen ions replaced by sodium ions. When the solution pH was modified to around 12 by adding KOH, EDTA became fully ionized with all 4 hydrogen ions replaced by potassium ions. DSD was fully ionized with all 4 hydrogen ions replaced by 2 sodium ions, and 2 potassium ions. TSSH was fully ionized with all 4 hydrogen ions replaced by 4 sodium ions. In DI water solutions, the difference in wettability alteration was not obvious. However, EDTA had better performance than DSD and TSSH at the concentration of 0.1 wt%. In seawater solutions, chelating agents were largely consumed by the metal ions. The difference in wettability alteration became significant.

5.3.3 Wettability alteration by VES in synthetic seawater

VES was dissolved in synthetic seawater at three different concentrations: 0.1 wt%, 1 wt%, and 2 wt%. The contact angle results are shown in Figure 47. Only small contact angle changes were observed in the concentration range of 0.1 wt% to 2 wt%. The tested VES has negligible wettability alteration performance on oil-wet carbonate rock.

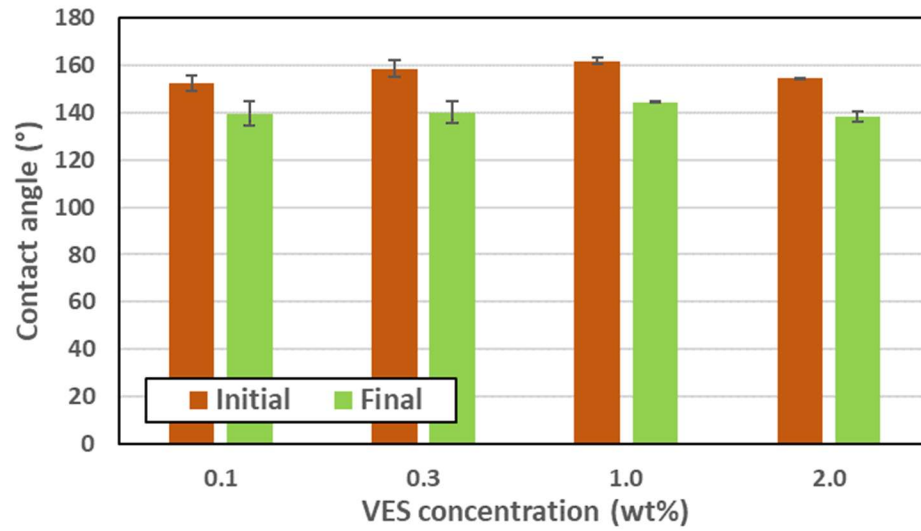


Figure 47 Contact angle before (Initial) and after (Final) soaking treatment in VES+SW solutions.

The small contact angle reduction might be due to IFT reduction. Equation 5.2 shows the connection between work of adhesion, IFT, and wettability. In the equation, $W_{adhesion}$ is the work of adhesion, which is the work needed to remove adhered oil in our case. γ_{ow} is the IFT between oil and water. θ is the contact angle.

$$W_{adhesion} = \gamma_{ow} (1 - \cos\theta) \quad (5.2)$$

When IFT decreases while wettability change is small, the work of adhesion decreases. The work needed to remove the adsorbed oil is reduced. Oil removal becomes easier. A small part of oil could be removed by buoyancy, exposing the rock surface to the water, thus slightly changing the surface wettability. The positive effect of IFT reduction on WA

can be found in the studies conducted by Alvarez and Schechter ³¹², Liu et al. ²³⁹, and Yassin et al ²⁶³.

5.3.4 Wettability alteration by chelating agents + VES in synthetic seawater

This section discusses the WA performance of different VES+CA solutions. The concentrations of different CAs were 0.3 wt%, 1 wt%, and 3 wt%. The concentration of VES is 0.3 wt% for all solutions.

Figure 48 (a~e) shows the results of each chelating agent. Like in the results of CA+SW solutions, the negative effect of increased salinity and the positive effect of concentration increase are both observed in all chelating agents except TSSH. Figure 48 (f) summarizes the contact angle differences induced by all chelating agents. Among them, DTPA showed the best overall WA potential in combination with VES in synthetic seawater. DSD, EDTA, and GLDA were not as good as DTPA but better than TSSH, especially at higher concentrations.

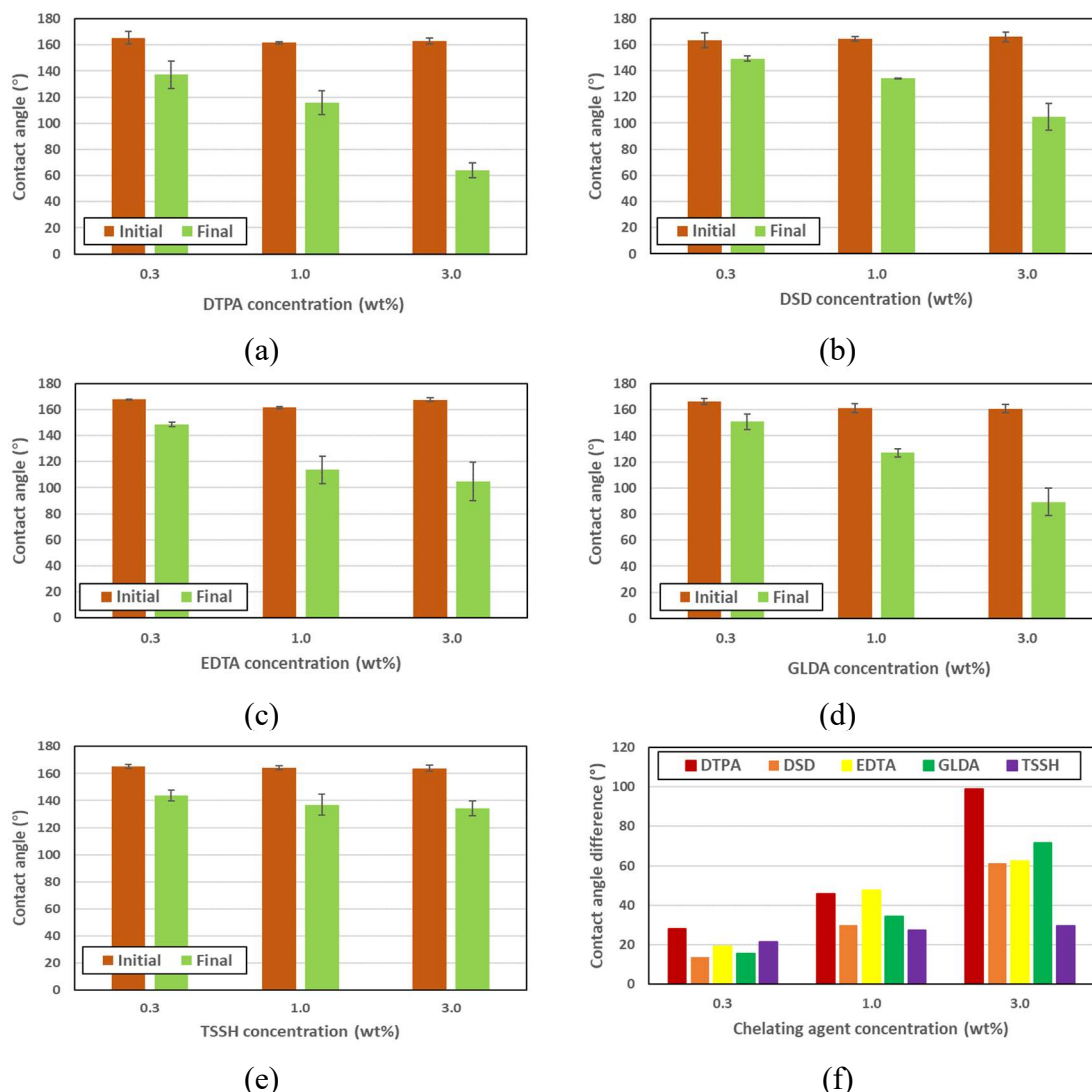


Figure 48 Wettability alteration performance of chelating agent combined with VES in synthetic seawater solutions. (a~e) Contact angle before (Initial) and after (Final) soaking treatment in VES+CA solutions (a) DTPA (b) DSD (c) EDTA (d) GLDA (e) TSSH. (f) the contact angle difference induced by all chelating agents combined with VES in synthesized seawater solutions at 3 different concentrations.

At a concentration of 0.3 wt%, VES alone was observed to induce a contact angle difference of 18.5°. The oil-wetness of the treated rock surface was slightly reduced. When chelating agents were added at high concentrations (1 wt% and 3 wt%), however, significant WA improvement was observed. Figure 49 shows the contact angle differences obtained in VES solution (0.3 wt%) and VES+CA in synthetic seawater solutions. When no chelating agent was added (red bars), VES alone (0.3 wt%) slightly reduced the oil-

wetness of the rock surface. At low concentrations (0.3 wt%, orange bars), chelating agents have a negligible impact on the WA performance. This accords with the observation in Section 4.2. Salts in the solutions consumed the added chelating agent. At 1 wt% and 3 wt% (yellow and green bars), added chelating agents significantly improved the WA performance.

Containing both VES and chelating agents, the combined VES+CA solutions combine the advantages of VES (IFT reduction and mobility control) and chelating agents (wettability alteration and salinity tolerance). DTPA is the strongest among all tested five chelating agents in improving the WA performance in VES+CA solutions. The WA performance improvement decreases in the order: DTPA > EDTA $\approx$ GLDA > DSD > TSSH. This sequence accords well with the salinity tolerance sequence obtained in previous sections.

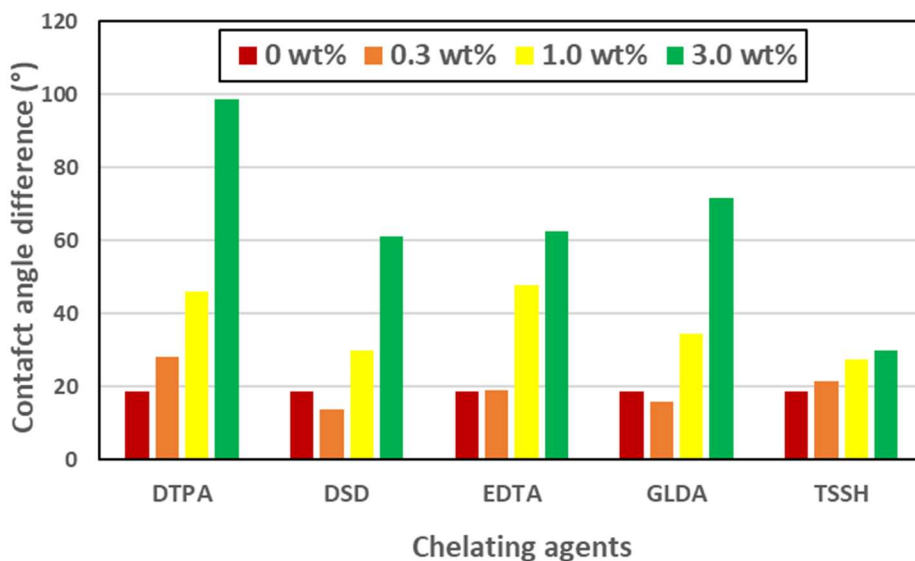


Figure 49 Wettability alteration performance of VES and VES+CA solutions.

5.3.5 Influence of temperature on the wettability alteration by chelating agents + VES in synthetic seawater

Temperature is an important factor in chemical reactions, surface properties, and fluid stability. In the formation, the temperature is much higher than at room temperature. As mentioned in previous sections, “Initial” refers to the contact angle after the oil-aging process, and “Final” refers to the contact angle after soaking treatment. In this section, samples soaked in VES+CA solutions were soaked again but at different temperatures: 22°C and 80°C, following the process shown in Figure 50. After soakage, solutions at different temperatures were cooled down to the same temperature 22°C. Contact angle measurements were conducted. In the results, “22°C extended” refers to the contact angle measured after the samples were soaked again for 4 days at 22°C, and “80°C extended” refers to the contact angle measured after the samples were soaked again for 4 days at 80°C.

Figure 51 (a) shows that extended soaking at room temperature (22°C) further reduced the oil-wetness of sample surfaces. Figure 51 (b) shows that extended soaking at a high temperature (80°C) further reduced the oil-wetness of sample surfaces. This observation suggests that the wettability alteration brought by VES+CA solutions is a gradual process that requires more than 4 days to fulfill its potential.

Figure 51 (c) compares the contact angle differences in both cases. Here, the “extended contact angle difference” is the difference between “Final” and “22/80 °C extended”, as described by Equation 5.3. Results show a significant improvement at 80°C as compared to at 22°C, indicating that the wettability alteration performance of VES+CA solutions could be enhanced at reservoir temperature.

$$\begin{aligned} \text{Extended contact angle difference} \\ = \text{Final contact angle} - 22/80^\circ\text{C extended} \end{aligned} \quad (5.3)$$

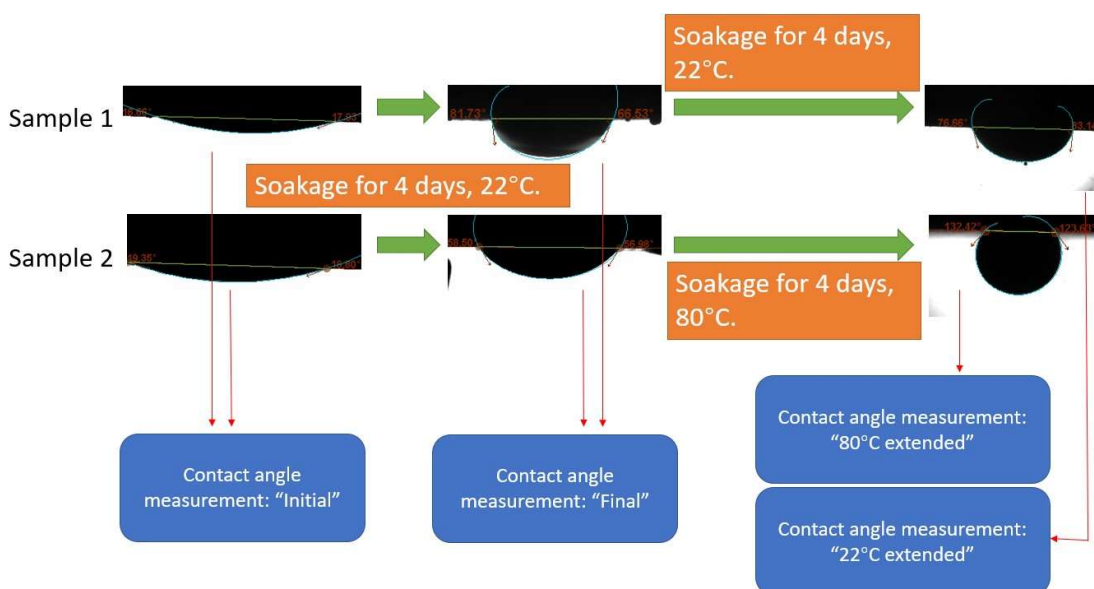
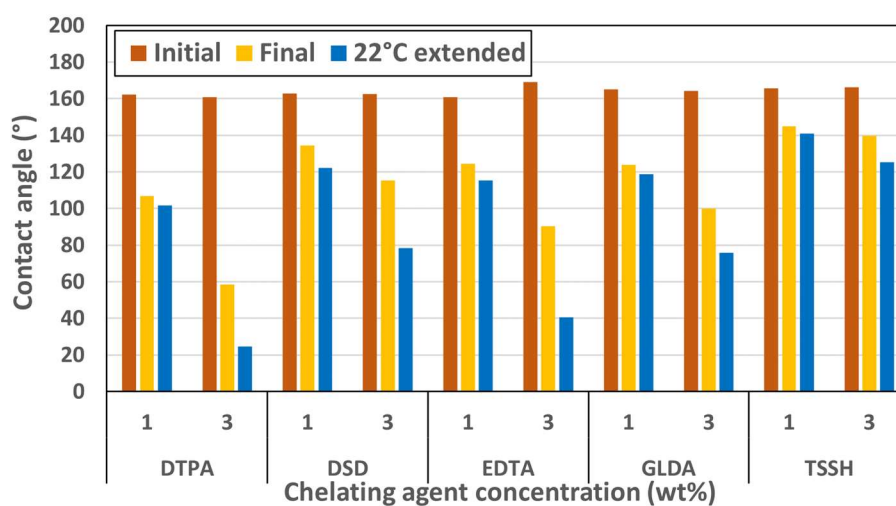
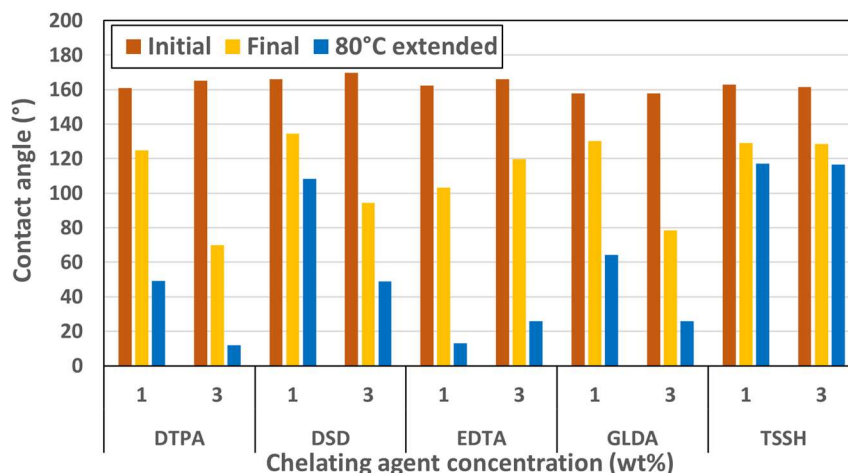


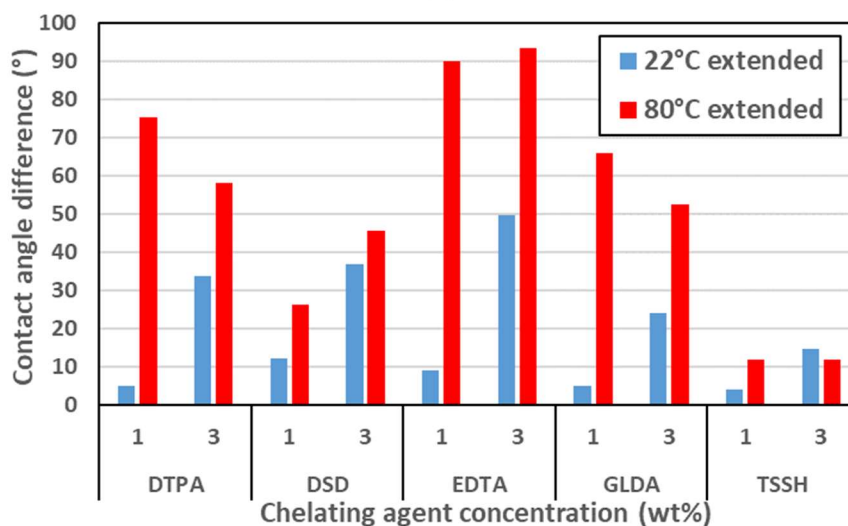
Figure 50 An illustration of the experiment process.



(a)



(b)



(c)

Figure 51 Contact angle difference after extended soakage in VES+CA solutions at (a) 22°C (b) 80°C (c) comparison.

5.4 Conclusions

Viscoelastic surfactants have promising potential for EOR applications due to their advantage in combining IFT reduction and mobility control. This study uses contact angle measurement to quantitatively assess and compare the wettability alteration performance of five chelating agents, including DTPA, DSD, EDTA, GLDA, and TSSH, in deionized

water, and synthetic seawater. The synergetic effect of chelating agents and VES on wettability alteration was studied. The following conclusions are drawn:

1. In deionized water solutions, all tested chelating agents have strong wettability alteration performance. Oil-wet or strongly oil-wet Indiana limestone samples became water-wet or strongly water-wet. GLDA and TSSH showed slightly stronger wettability alteration performance than DSD, EDTA, and DTPA.
2. In synthetic seawater or diluted synthetic seawater, metal ions consume part of the chelating agent molecules in the solution, significantly impairing the wettability alteration performance as compared to deionized water solutions of the corresponding chelating agent. This negative effect of salinity becomes stronger as salinity increases.
3. Increasing the chelating agent concentration enhances the wettability alteration performance of the seawater system. When the concentration is low, increasing the concentration leads to significant improvement in wettability alteration; when the concentration reaches a threshold value, increasing the concentration only slightly helps the wettability alteration. The threshold concentration value differs for different chelating agents. For the same chelating agent, increased salinity leads to a higher threshold concentration value.
4. The tested viscoelastic surfactant slightly reduces the oil-wetness of oil-wet Indiana limestone samples. This small wettability change might be a result of IFT reduction. The addition of chelating agents significantly improves the wettability alteration performance. DTPA is the strongest among all tested chelating agents in the

wettability alteration aspect. The rock surface treated with 3.0 wt% DTPA + 0.3 wt% VES solution was changed from strongly oil-wet (163.0°) to water-wet (64.2°).

5. Compared to VES alone, the addition of chelating agents grants the EOR fluid stronger salinity tolerance and significantly better wettability alteration performance. The wettability alteration brought by VES+CA solutions is a gradual process that requires a specific time to fulfill its potential. The wettability alteration performance of VES+CA solutions can be enhanced at lifted temperatures.

CHAPTER 6

WETTABILITY ALTERATION ON CARBONATE

ROCK BY THE MIXTURE OF GEMINI SURFACTANT

AND CHELATING AGENT

6.1 Introduction

Surfactants reduce the interfacial tension (IFT). They and are widely applied in EOR. There are also other mechanisms aside from IFT reduction that contributes to incremental oil recovery in surfactant flooding ^{166,218}. Wettability alteration (WA) is another key mechanism ^{3,27}. When the rock is changed to water-wet, the capillary pressure is changed from to positive, thus helping the oil displacement. Some surfactants are found to form a microemulsion phase between oil and water ^{313,314}. The microemulsion phase helps mobility control and increases the micro-scale sweep efficiency significantly. Viscoelastic surfactants provide surprisingly high viscosity, thus helping mobility control ⁶⁸.

Gemini surfactant is a novel type of surfactant that has two hydrophilic head groups and two hydrophobic tail groups ³⁶. The two monomers can be connected by the spacer (a functional group or a chemical bond ³¹⁵) at the head groups or the tail groups. When the head groups are identical and the tail groups are the same, the gemini surfactant is called a symmetric dimeric surfactant ⁷⁵. The primary advantage of gemini surfactants is their high efficiency in reducing IFT ^{316,317}. They are found to have much lower critical micelle

concentration (CMC) and reach ultralow IFT faster than conventional surfactants. They are also found to have better rheological properties than conventional surfactants ³¹⁸. A previous study conducted by the authors showed that a group of locally synthesized amido-amine-based cationic gemini surfactants ³¹⁹ could combine IFT reduction and WA to help produce oil from oil-wet carbonate formation ³²⁰. Besides, the developed group of Gemini surfactants showed excellent heat stabilities, salt tolerance, and foaming properties ^{178,321}, indicating huge potential for EOR in harsh conditions ³²². One of the studied gemini surfactants is selected to be used in this study. Its structure is given in Table 36.

Salts has an impact on surfactants' behavior. The ions of salts can affect the surfactant solubility ^{113,323,324}, the critical micelle concentration (CMC), micellization behavior of a cationic surfactant with high solubility mismatch: Composition, temperature, and salt effects ³²⁵, the IFT between oil/water ³²⁶, foam stability ³²⁷, and the wettability alteration ability of the surfactant ⁵³. High salinity is a challenge in EOR because of the stability issue and performance loss of chemicals under harsh conditions. Researchers have been searching for surfactant and surfactant combinations that perform well in high salinity environments.

The other way to accommodate surfactants in high salinity conditions is to adopt materials alongside surfactants that stabilize or enhance surfactants' performance. Chelating agents are compounds that are efficient in forming complexes with metal ions ²⁹⁴. In high salinity, high hardness formation brine, applying chelating agents can sequester metal ions, preventing them from negatively affecting the surfactants ^{293,297}. Chen and Mohanty observed significant improvement in surfactant-induced WA after adding chelating agent 2.5% EDTA ²⁹⁸. More comprehensive evidence is provided by Yao et al., confirming this

enhancement by summarizing 338 imbibition experiments ²⁹⁹. Apart from enhancing the WA by surfactants, chelating agents alone showed WA potential on different rocks ^{293,300,302,303}. Alarifi et al. observed that adding DTPA resulted in a more negative zeta potential on sandstone rock, indicating stronger water-wetness ³⁰⁰. Hassan and Al-Hashim applied the same method and found that 5 wt% EDTA induced stronger water-wetness on carbonate rock ³⁰³. Contact angle experiments conducted by Pratama and Babdagli showed that DTPA achieved promising WA and IFT reduction in a sandstone/heavy-oil/steam system ³⁰¹. Core flooding conducted by Janjua et al. showed additional oil recovery during DTPA injection into carbonate ²⁹³. The WA potential of chelating agents and their indication in EOR has been proven by multiple experimental techniques.

The chapter evaluates the effect of a chelating agent on the performance of gemini surfactants as wettability modifiers in high salinity conditions for carbonate reservoirs. The WA performance of a locally developed cationic gemini surfactant (GS8), and a commonly used chelating agent (DTPA), as well as the mixture between GS8 and DTPA, were tested. Two spontaneous imbibition tests were compared to reflect on the relative importance between IFT reduction and WA.

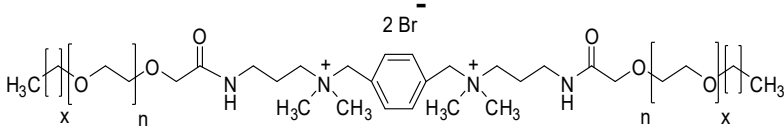
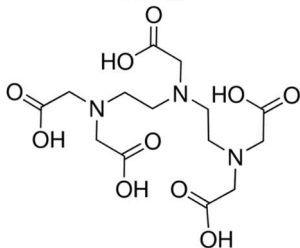
6.2 Materials

Crude oil (API 31.07) is used in the experiments. The rock samples used are Indiana limestone (porosity 14.6%) and Guelph dolomite. Core samples were cut into small slices (1 in diameter, 3~4 mm thickness) and two Indiana limestone core plugs (1.5 in diameter,

2 in length). XRD results show that Indiana limestone is 100% calcite (CaCO_3) and Guelph dolomite is 100% dolomite ($\text{CaMg}(\text{CO}_3)_2$).

The gemini surfactant used is a locally synthesized cationic gemini surfactant, GS8. The chelating agent is diethylene triamine penta acetic acid (DTPA) provided by Nouryon, Saudi Arabia. Information on GS8 and DTPA is included in Table 36. Salts, including NaCl , NaHCO_3 , Na_2SO_4 , MgCl_2 , and CaCl_2 , are provided by Sigma-Aldrich.

Table 36 The structure of the gemini surfactant and chelating agent.

Short name	MW (g/Mol)	Structure
GS8	1811.8	 (GS8)
DTPA	393.35	 (DTPA)

* $x=11\sim13$, $n=9\sim10$

Solutions were prepared according to Table 37. There are 4 groups: GS8 group, DTPA group, mixture group, and mixture modified group. Each group contains 7 solutions that differ in salt type while having the same concentration of GS8 (0.05 wt%, 2.76×10^{-4} M) and/or DTPA (0.025 M). In solutions that contain only one type of salt, the salt concentration is 0.1 M. In solutions that contain all five types of salts, the salt concentrations are modified to composite synthetic seawater (SW). In each group, there is

one solution containing no salt (the first one), which was used to reflect on the WA performance of the studied EOR materials in deionized (DI) water.

Table 37 Composition of the studied solutions (unit: Molar/L).

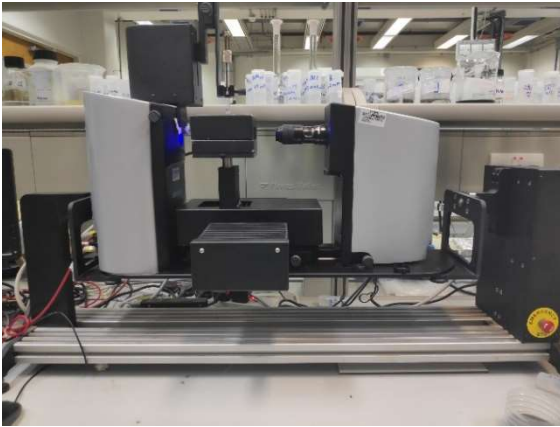
Group	Solution Code	Salt type	Na Cl	NaHC O₃	Na₂S O₄	Mg Cl₂	CaCl₂	GS8	DTP A
GS8 group	1-1	DI	0	0	0	0	0	2.76×10 ⁻⁴	0
	1-2	NaCl	0.1	0	0	0	0	2.76×10 ⁻⁴	0
	1-3	NaHC O ₃	0	0.1	0	0	0	2.76×10 ⁻⁴	0
	1-4	Na ₂ S O ₄	0	0	0.1	0	0	2.76×10 ⁻⁴	0
	1-5	MgCl ₂	0	0	0	0.1	0	2.76×10 ⁻⁴	0
	1-6	CaCl ₂	0	0	0	0	0.1	2.76×10 ⁻⁴	0
	1-7	SW	0.705	0.002	0.045	0.087	0.016	2.76×10 ⁻⁴	0
DTPA group	2-1	DI	0	0	0	0	0	0	0.025
	2-2	NaCl	0.1	0	0	0	0	0	0.025
	2-3	NaHC O ₃	0	0.1	0	0	0	0	0.025
	2-4	Na ₂ S O ₄	0	0	0.1	0	0	0	0.025
	2-5	MgCl ₂	0	0	0	0.1	0	0	0.025
	2-6	CaCl ₂	0	0	0	0	0.1	0	0.025
	2-7	SW	0.705	0.002	0.045	0.087	0.016	0	0.025
Mixture group	3-1	DI	0	0	0	0	0	2.76×10 ⁻⁴	0.025
	3-2	NaCl	0.1	0	0	0	0	2.76×10 ⁻⁴	0.025
	3-3	NaHC O ₃	0	0.1	0	0	0	2.76×10 ⁻⁴	0.025
	3-4	Na ₂ S O ₄	0	0	0.1	0	0	2.76×10 ⁻⁴	0.025

	3-5	MgCl ₂	0	0	0	0.1	0	2.76× 10 ⁻⁴	0.02 5
	3-6	CaCl ₂	0	0	0	0	0.1	2.76× 10 ⁻⁴	0.02 5
	3-7	SW	0.7 05	0.002	0.045	0.08 7	0.01 6	2.76× 10 ⁻⁴	0.02 5
Mixture modified group	Mix	SW	0.7 05	0.002	0.045	0.08 7	0.01 6	2.76× 10 ⁻⁴	0.02 5
	Mix_DT PA+	SW	0.7 05	0.002	0.045	0.08 7	0.01 6	2.76× 10 ⁻⁴	0.07 6
	Mix_DT PA-	SW	0.7 05	0.002	0.045	0.08 7	0.01 6	2.76× 10 ⁻⁴	0.01 1
	Mix_Bot h+	SW	0.7 05	0.002	0.045	0.08 7	0.01 6	5.52× 10 ⁻⁴	0.07 6
	Mix_Bot h-	SW	0.7 05	0.002	0.045	0.08 7	0.01 6	8.28× 10 ⁻⁵	0.01 1

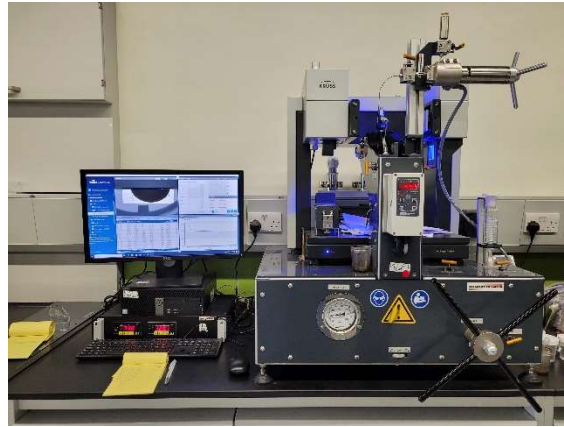
6.3 Experiments

Static contact angles were measured on the surface of rock slices using the Theta instrument provided by Biolin (room temperature 22°C, 1 atm) and Kruss & Eurotechnica (high temperature, high pressure). The difference between contact angles before and after treatment is used to represent the WA performance. Real-time wettability change is studied under reservoir conditions for limestone and dolomite.

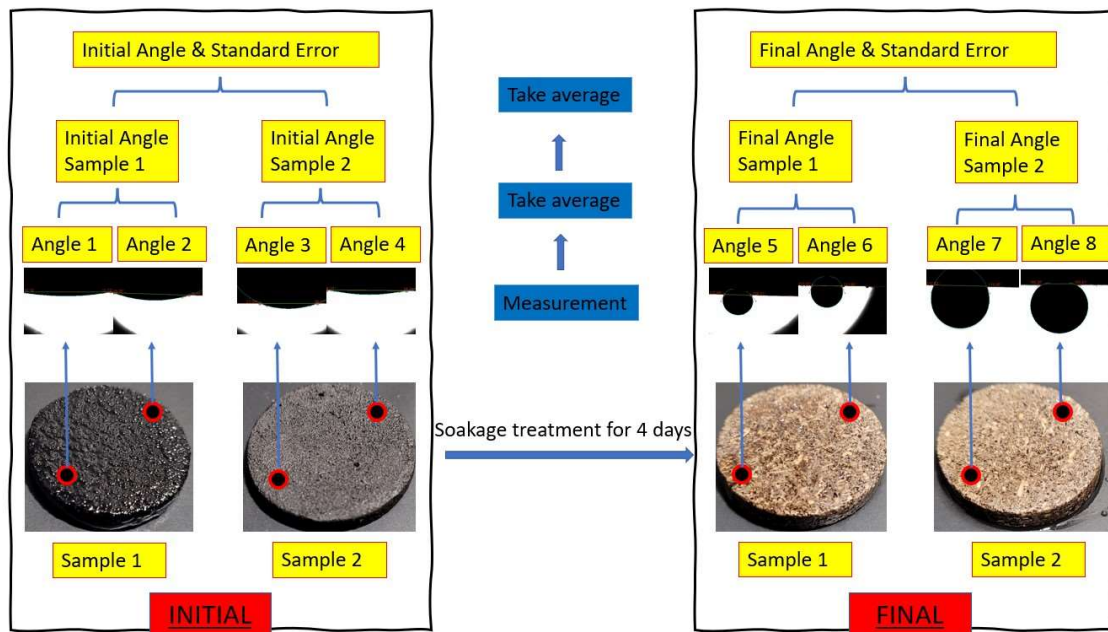
Rock samples were cleaned and dried. Then they were oil-aged by immersing them in crude oil (4 days, 120°C). After aging, the initial contact angle values were measured which reflected the wettability status of the surface right after the aging process. The samples were then soaked in different solutions for 4 days under ambient conditions. For each solution, 2 samples were treated. The mass of all types of solutions was kept at 60g (about 60 ml). When the soakage treatment was finished, the final contact angle values were measured which reflected the wettability status of the surface after solution treatment. The contact angle study process and related instruments are shown in Figure 52.



(a)



(b)



(c)

Figure 52 Instruments and process (a) Biolin ambient contact angle instrument; (b) Kruss & Eurotechnica HTHP contact angle instrument; (c) Contact angle study process.

Contact angle refers to the angle between the tangent of the oil/water interface and the rock surface. Table 38 is an example of how contact angle relates to surface wetness.

Table 38 A classification of rock wettability according to water contact angle.

Type	Contact angle (°)
Strongly water-wet	0-30
Water-wet	30-70
Intermediate-wet	70-110
Oil-wet	110-150
Strongly oil-wet	150-180

6.4 Results and discussion

6.4.1 Wettability alteration by gemini surfactant

In this section, rock samples were treated by the “GS8 group” solutions given in Table 37. Ambient contact angle results are shown in Figure 53. The samples in all solutions were strongly oil-wet in the beginning. After treatment, the oil-wetness was reduced. When there was no salt in the solution (“DI” in Table 37), the wettability condition was changed from strongly oil-wet to an intermediate-wet condition. NaCl, NaHCO₃, Na₂SO₄, MgCl₂, and CaCl₂ showed a negative effect on the WA by GS8. The negative effect decreases in the order: CaCl₂ > Na₂SO₄ > NaCl $\approx$ NaHCO₃ $\approx$ MgCl₂. The WA performance of GS8 was suppressed by CaCl₂ of 0.1M. In synthetic seawater, the concentrations of all salts except NaCl are lower than 0.1M. The negative effect of CaCl₂ was not as strong as in the 0.1M CaCl₂ solution. However, the greatly increased NaCl concentration strengthened the negative effect of NaCl. As a result, the WA on the samples treated by SW was weaker than that of samples treated with other solutions except for the 0.1M CaCl₂ solution.

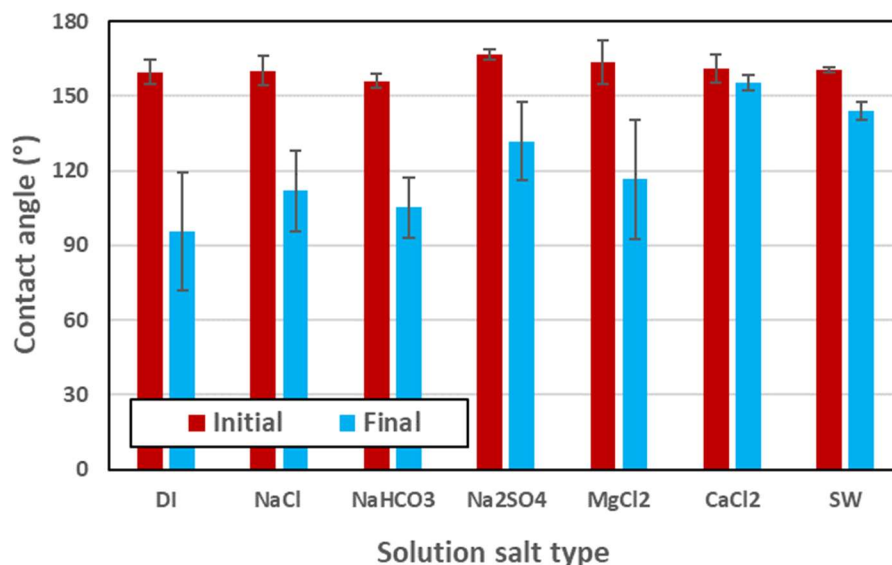


Figure 53 Influence of salts on gemini surfactant (GS8) wettability alteration performance.

A possible mechanism of WA on oil-wet carbonate rock by cationic surfactant, the ion-pair mechanism, was proposed by Standnes et al.¹². On oil-wet carbonate rock surfaces, the organic molecules with negatively charged carboxylate groups¹⁶ adhere to the rock surface under electrostatic force. When cationic surfactants are added, the positively charged head groups form ion pairs with the negatively charged carboxylate groups in the organic molecules. Due to the hydrophobicity, the ion pairs could not stay stable inside the water phase unless becoming wrapped by surfactant micelles. When salts are added, surfactant molecules move from the bulk solution to the interface. The partitioning of surfactant into the oil phase also increases with increasing water salinity. As a result, removing organic molecules becomes harder due to reduced surfactant concentration in the bulk fluid. Besides, the amount of surfactant micelles in the bulk fluid is also reduced. Overall, the addition of salts negatively impacts the wettability alteration of cationic surfactants²⁸. Although of the same molar concentration, salts with multivalent ions (Na_2SO_4 , MgCl_2 , and CaCl_2) generate solutions of around three times higher ionic potential

than salts with only monovalent ions (NaCl, NaHCO₃). As a result, salts with multivalent ions had a more severe impact on the wettability alteration of GS8.

6.4.2 Wettability alteration by the chelating agent

In this section, rock samples were treated by “DTPA group” solutions, listed in Table 37. Ambient contact angle results are shown in Figure 54. The samples in all solutions were strongly oil-wet in the beginning. After treatment, the oil-wetness was reduced. When there was no salt in the solution (“DI” in Table 37), the wettability condition was altered from strongly oil-wet to water-wet condition. At a concentration of 0.1 M, NaCl, NaHCO₃, Na₂SO₄, and MgCl₂ showed a small negative effect on the WA by DTPA. CaCl₂ seemed to have a slightly positive effect. This phenomenon might be related to the higher adsorption capacity of chelating agents when the counter-ion is Ca²⁺³¹¹. SW has a much higher salinity (57745 ppm) than 0.1 M salt solutions, resulting in higher consumption of chelating agents, which impaired the WA.

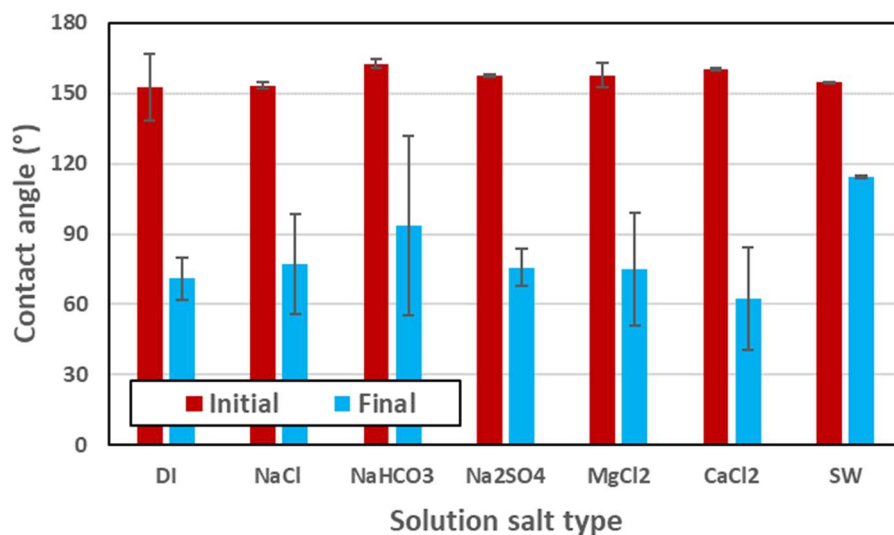


Figure 54 Influence of salts on chelating agent (DTPA) wettability alteration performance.

In this study, a test was conducted to reflect on the impact of pH on the WA performance of DTPA. pH was modified by adding HCl and KOH into 0.025M DTPA solutions in DI water, resulting in three solutions of pH 3.669, 7.434, and 11.405. The contact angle results of samples treated by DTPA solutions of different pH are shown in Figure 55. The WA performance of DTPA is better at lower pH.

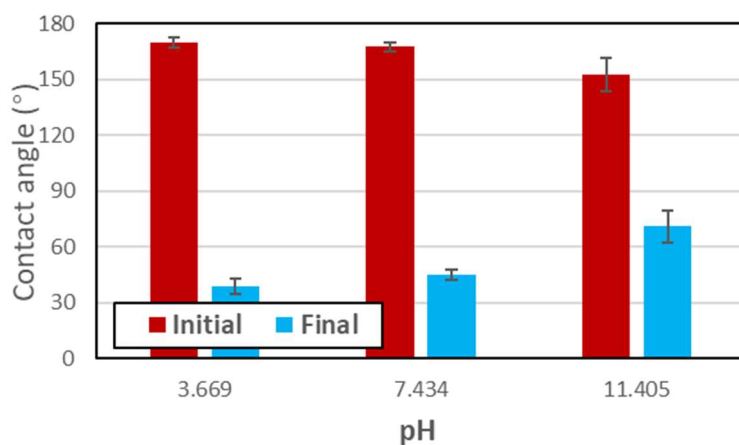


Figure 55 Influence of pH on chelating agent (DTPA) wettability alteration performance.

Gas bubbles were observed on the surface of samples when pH was low, as shown in Figure 56. When it was high, no gas bubble was generated. These bubbles were generated from

the reaction between DTPA and carbonate, namely mineral dissolution. Combining the contact angle results and the bubbles observed, we can conclude that both the WA by DTPA and calcite mineral dissolution caused by DTPA are strengthened at low pH.

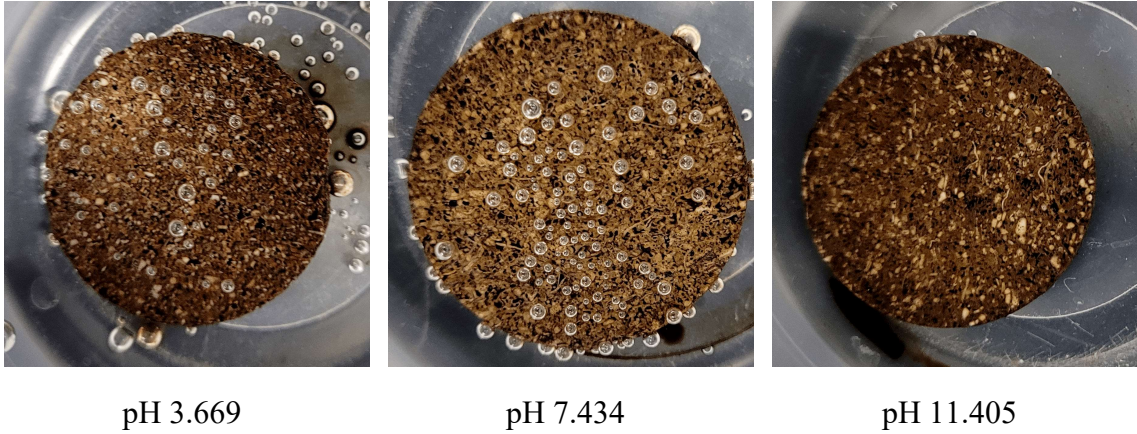


Figure 56 Gas bubbles generated by DTPA and limestone at different pH.

6.4.3 Wettability alteration by the mixture of gemini surfactant and chelating agent

In this section, rock samples were treated with “mixture group” and “mixture modified group” solutions in Table 37. Ambient contact angle results of samples treated by “mixture group” solutions are shown in Figure 57. The samples in all solutions were strongly oil-wet in the beginning. After treatment, the oil-wetness was reduced. When there was no salt in the solution (“DI” in Table 37), the wettability condition was changed from strongly oil-wet to water-wet condition. NaHCO_3 , Na_2SO_4 , MgCl_2 , and CaCl_2 showed a negative effect on the WA by GS8. The negative effect decreases in the order: $\text{CaCl}_2 \approx \text{MgCl}_2 > \text{NaHCO}_3 \approx \text{Na}_2\text{SO}_4$. SW has the strongest negative effect on the WA by the mixture. In SW, the mixture managed to change the wettability of strongly oil-wet samples to intermediate-wet conditions, better than GS8 or DTPA alone.

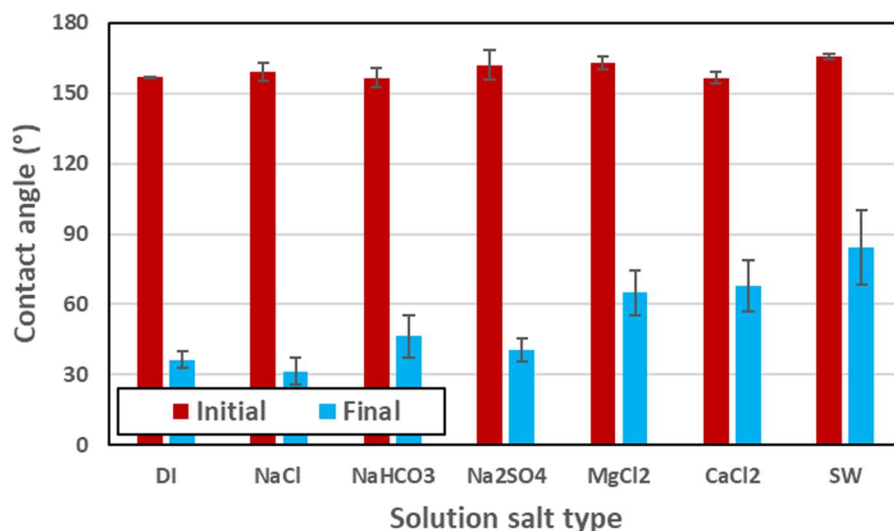


Figure 57 Influence of salts on the mixture of gemini surfactant and chelating agent (DTPA) wettability alteration performance.

The contact angle results of samples treated by “mixture modified group” solutions are shown in Figure 58. Here, the “Mix” solution has the same composition as solutions 3-7 in Table 37, which is 0.025 M DTPA dissolved in SW. Compared to “Mix”, “Mix_DTPA+” and “Mix_Both+” had higher DTPA concentrations. “Mix_DTPA-” and “Mix_Both-” had lower DTPA concentrations compared to “Mix”. “Mix_Both+” had a higher GS8 concentration than “Mix”. “Mix_Both-” had a lower GS8 concentration than “Mix”. When the concentration of GS8 was kept the same, increased DTPA concentration led to enhanced WA performance. “Mix_Both+” had stronger WA performance than “Mix_DTPA+”, indicating that adding GS8 can further enhance the WA performance of the mixture. “Mix_Both-” had a weaker WA performance than “Mix_DTPA-”, indicating that reducing GS8 concentration will impair the WA performance of the mixture. “Mix_Both+” provided the best WA performance among all tested solutions. The oil

recovery implication of the “Mix_Both+” composition was tested in a spontaneous imbibition experiment.

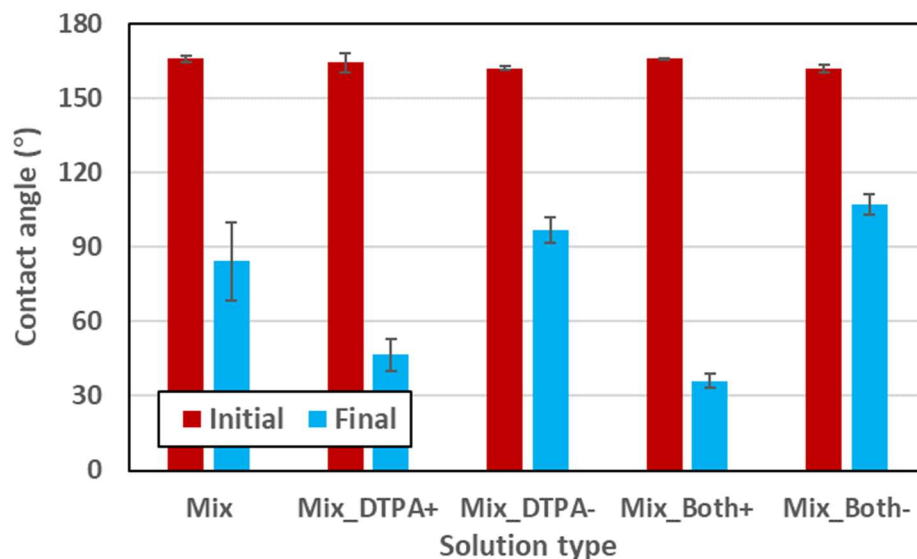
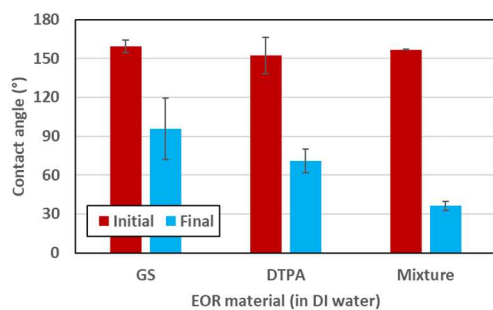


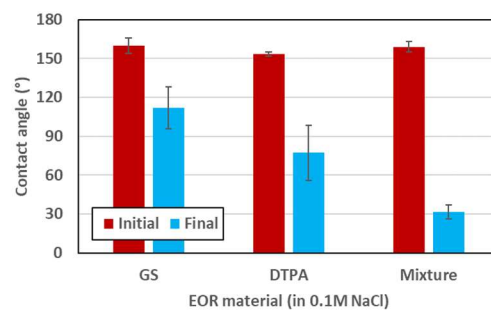
Figure 58 Influence of concentration on the mixture of gemini surfactant and chelating agent (DTPA) wettability alteration performance.

6.4.4 WA performance of GS8, DTPA, and their mixture: comparison

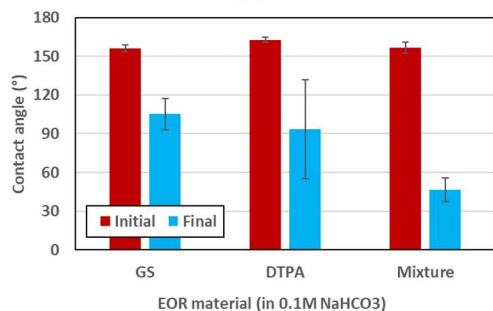
Figure 59 (a-g) compares the WA performance of GS8, DTPA, and the mixture in solutions of the same salt types. For WA by GS8, CaCl_2 has a strongly negative impact. For WA by DTPA, CaCl_2 has a positive impact. When GS8 and DTPA were combined, the WA performance of the mixture outperformed GS8 and DTPA solutions in all cases except the one with CaCl_2 . The mixture of GS8 and DTPA is a wettability modifier solution that has moderate to good WA performance in all types of salt solutions and high salinity conditions.



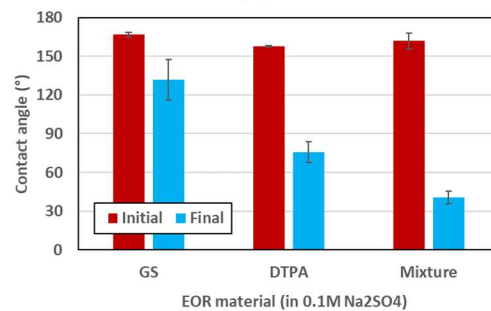
(a)



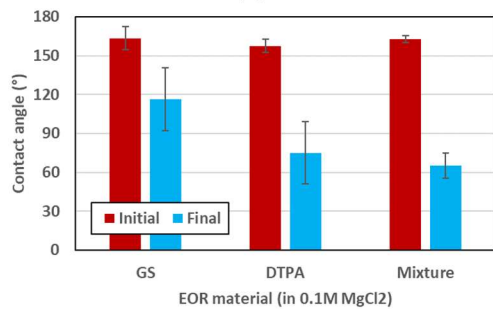
(b)



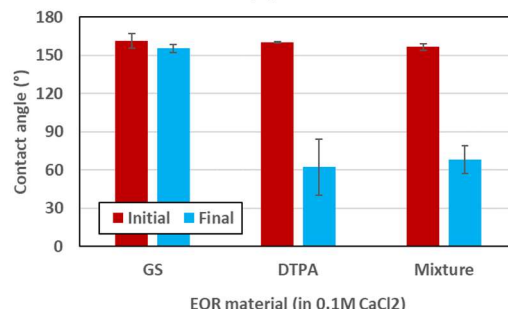
(c)



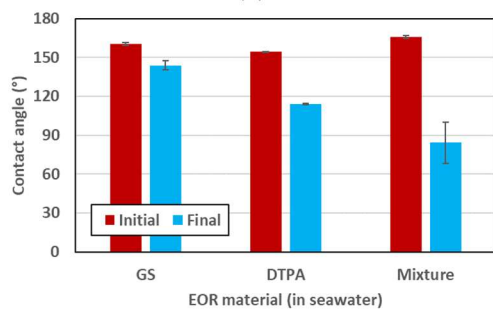
(d)



(e)



(f)



(g)

Figure 59 Wettability alteration by GS8, DTPA, and the mixture in solutions of different salt types.

6.4.5 Real-time wettability alteration induced by the GS8 + DTPA + SW

solution under reservoir condition

In this part, rock slices were placed inside GS8 (5.52×10^{-4} M) + DTPA (0.025 M) + SW solutions and kept at reservoir conditions (92 ± 2 °C, 200 ± 7 bar). Figure 60 is an illustration of the typical oil/water/rock contact scenario which shows the shape and location of each phase in an image taken during the experiment.

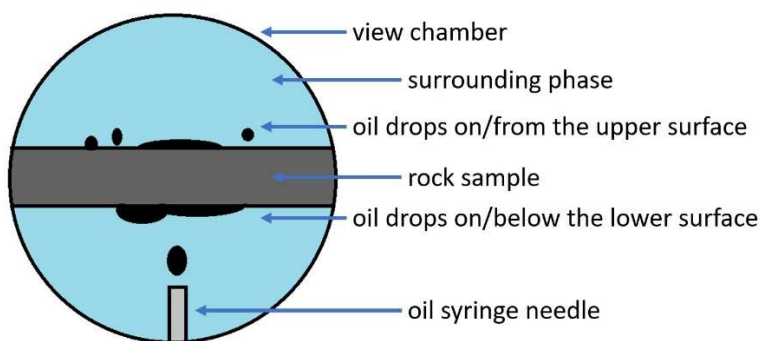


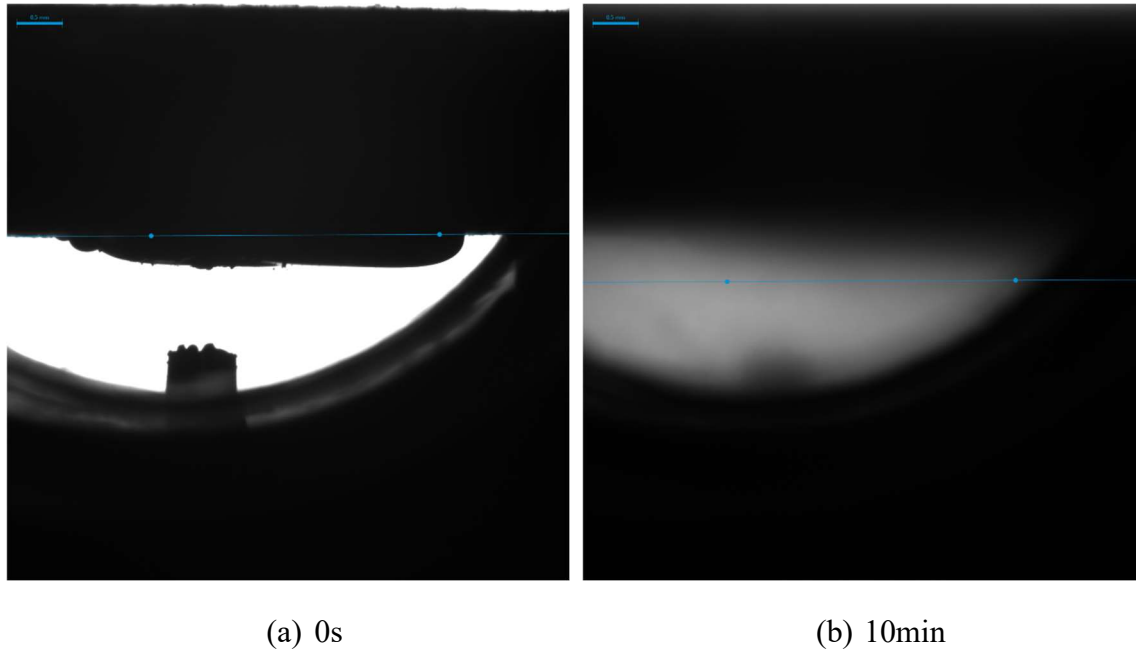
Figure 60 An illustration of the oil/water/rock contact scenario.

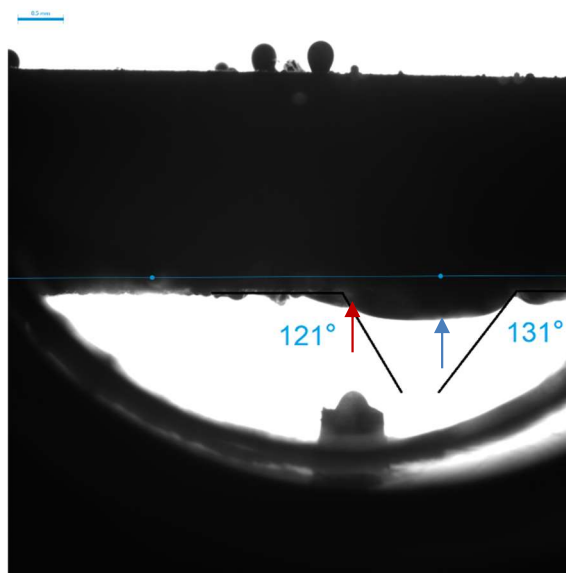
6.4.5.1 Guelph dolomite

A Guelph dolomite slice was oil-aged. After that, it was placed inside GS8 + DTPA + SW solution at reservoir condition (92 ± 2 °C, 200 ± 7 bar). The real-time wettability change and the spreading oil drop are shown in Figure 61. Compared to conventional surfactants, gemini surfactants are faster in reducing the IFT. Oil drop spreading happened when IFT was reduced. After 10 min, the image blurred (Figure 61 (b)) because of the rapid reaction between dolomite and DTPA. After 3h, the image became clear again (Figure 61 (c)). On the upper surface of the sample, oil drops emerged and left due to the combined effect of gravity and WA. Figure 61 (c-f) shows small oil drops leaving the upper surface of the

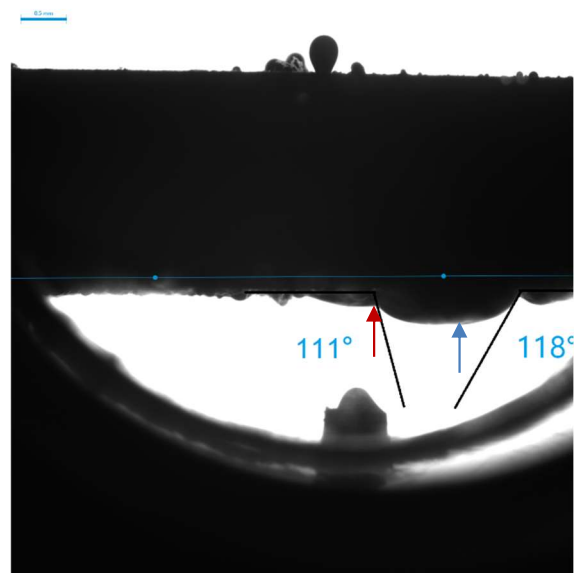
sample continuously. Most of the drops emerged from the crack across the sample (Figure 62).

On the bottom surface, two oil drops can be found (Figure 61 (c-f)), pointed by the red arrow (Drop 1) and blue arrow (Drop 2), respectively. Drop 1 vanished gradually. A possible explanation for the vanishing of Drop 1 is that it penetrated the sample through the crack. Drop 2 grew larger in height and smaller in horizontal span (diameter). The increase in height and decrease in diameter resulted in the smaller oil/rock contact angle, indicating reduced oil-wetness. After 12 h, the shape of Drop 2 became stable. The software fails to detect the angles when two drops overlap. The contact angle change of Drop 2 was manually measured.

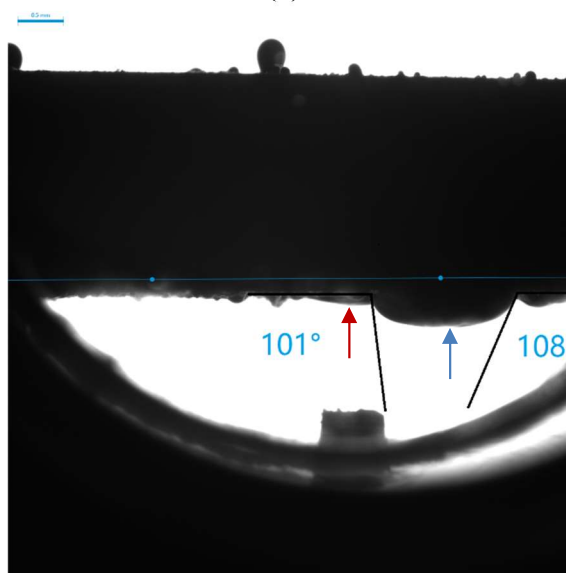




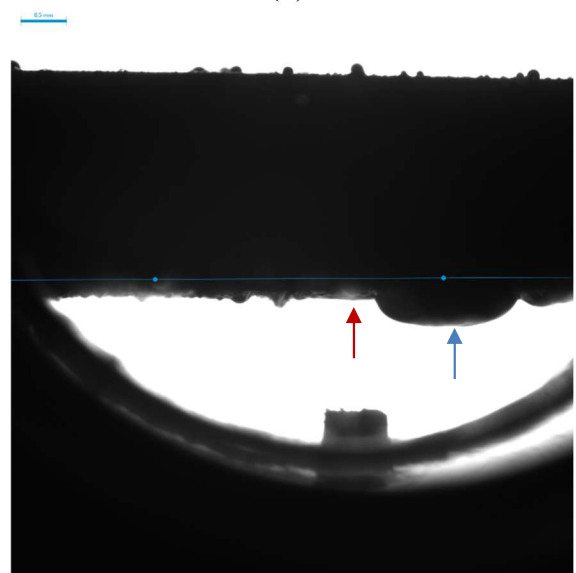
(c) 3h



(d) 7h



(e) 12h



(f) 17h

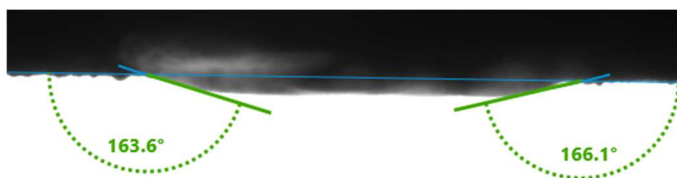
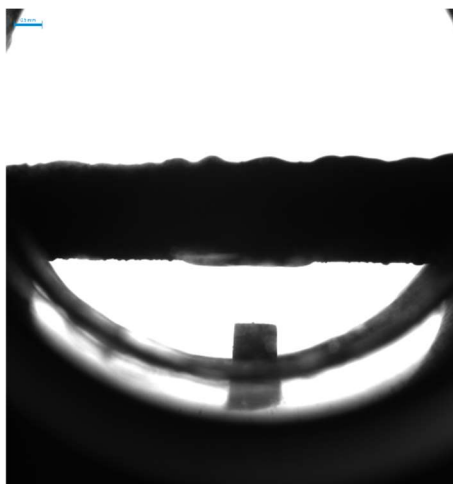
Figure 61 Real-time wettability alteration by GS8 + DTPA + SW solution on Guelph dolomite.



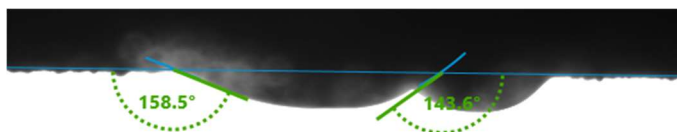
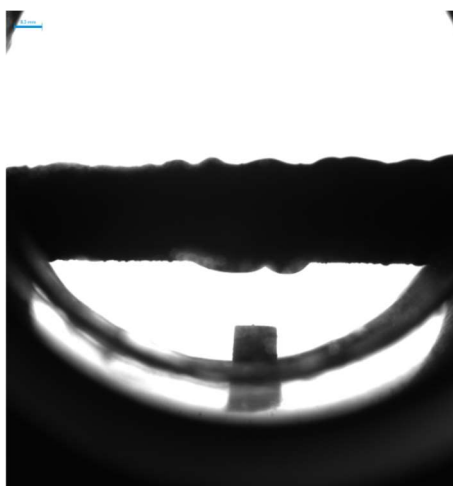
Figure 62 The crack across the Guelph Dolomite sample.

6.4.5.2 Indiana limestone

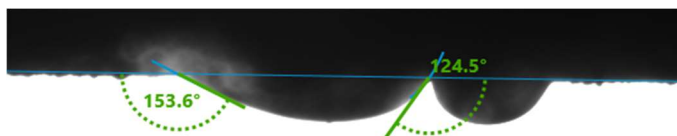
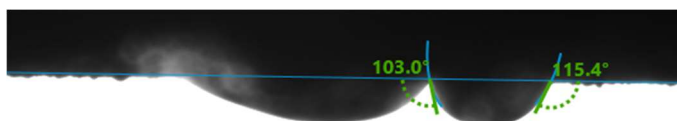
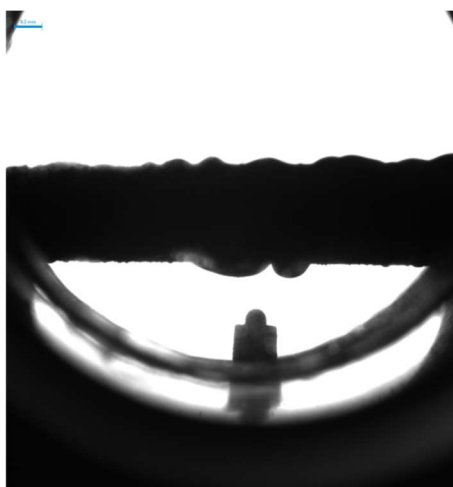
The real-time wettability change on Indiana limestone is shown in Figure 63. Though not shown here, the rapid reaction between limestone and DTPA also blurred the image in the beginning. After that, drops on the upper surface and bottom surface emerged. On the upper surface, the number and volume of the drops increased with time, indicating oil production under the combined effect of WA and gravity. Different from on Guelph Dolomite sample, oil drops were widely distributed on the upper surface of the Indiana limestone sample since Indiana limestone is relatively homogeneous and there was no crack on the sample surfaces. On the bottom surface, the contact angle of the two drops decreased due to WA. The volume of the two drops also decreased. This decrease is due to the penetration of oil from the bottom surface to the upper surface.



(a) 0s



(b) 20 min



(c) 1h

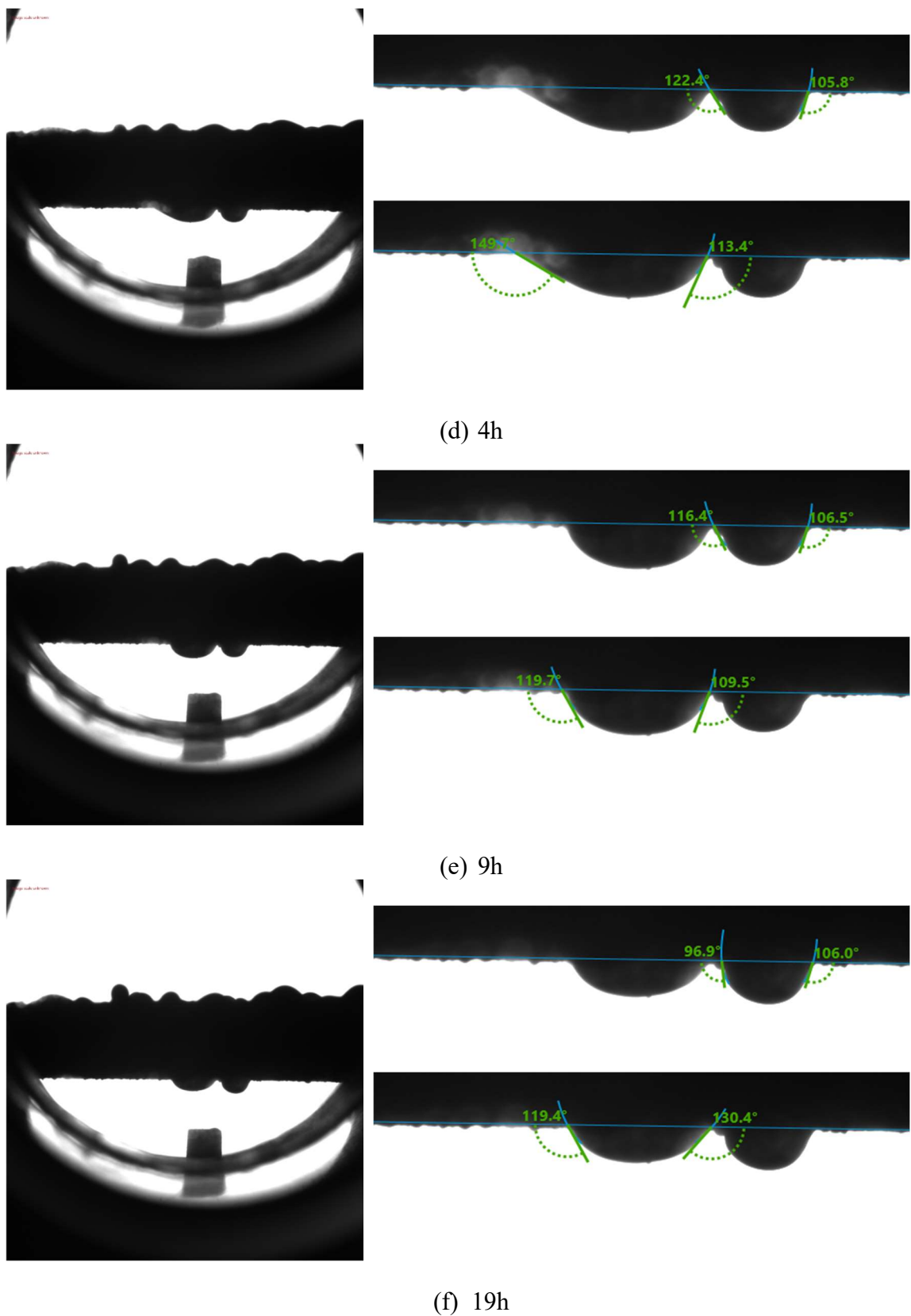


Figure 63 Real-time wettability alteration by GS8 + DTPA + SW solution on Indiana limestone.

The real-time drop shape changes on the bottom surface of both dolomite and limestone samples represent how the distribution of residual oil changes when WA happens. On an oil-wet surface, the oil drop spreads out. When WA happens, the oil-wetness of the surface reduces gradually. The diameter of the oil drop decreases, thus making it easier for removing the oil drop from the surface, exposing more area of the rock surface to the EOR fluid.

6.5 Conclusions

Salts, especially CaCl_2 , in the solution impairs the WA performance of the gemini surfactant. By combining gemini surfactant and chelating agents, the mixture can be a strong wettability modifier solution that performs well in all types of salt solutions and high salinity environments. This study tested the wettability alteration by a locally synthesized cationic gemini surfactant, GS8, by a widely used chelating agent, DTPA, and by the mixture between GS8 and DTPA. The following conclusions are drawn:

1. In deionized water solutions, GS8 is a good wettability modifier at a low concentration (0.05 wt%) as compared to conventional surfactants. Salts, especially CaCl_2 , harm the wettability alteration by GS8. In the solution of 0.1M CaCl_2 , GS8 failed to change the wettability.
2. DTPA is also a good wettability modifier for oil-wet carbonate rock. In salt solutions, the wettability alteration of DTPA is impaired due to the sequestration of DTPA by metal ions. In 0.1M CaCl_2 solution, however, the WA by DTPA seemed to be slightly enhanced.

3. By mixing GS8 with DTPA, the obtained solution has strong WA performance in all types of salt solutions. The WA performance of the mixed solution is better than GS8 or DTPA alone.

CHAPTER 7

RELATIVE CONTRIBUTION OF WETTABILITY

ALTERATION AND INTERFACIAL TENSION

REDUCTION IN EOR: AN EXPERIMENTAL STUDY

7.1 Introduction

Most of the carbonate reservoirs are oil-wet, or strongly oil-wet, and heterogeneous ^{28,36}. Under such conditions, the injected water during waterflooding tends to flow in high permeability channels. There is only a small pressure gradient on the rock matrix ¹. On the other hand, the lower permeability is usually related to a smaller average pore throat radius ^{328,329}, which in turn relates to stronger capillary pressure according to the Young-Laplace equation ^{189,330}. In an oil-wet rock matrix, the capillary pressure is negative ⁴⁶ which prevents water from entering the rock matrix. The small pressure gradient, and the stronger capillary pressure, combine to result in a large portion of oil left as residual oil in the rock matrix. The recovery of this residual oil has significant potential for increasing oil production. It has been an extensively studied enhanced oil recovery (EOR) topic ^{28,331,332}.

To recover this type of residual oil, either the pressure gradient should be increased, or the negative capillary pressure should be reduced. By applying EOR materials with better mobility control, such as polymers ⁶⁸, viscoelastic surfactants ^{202,333}, and foam ³³⁴, the pressure gradient exerted on the rock matrix can be increased, thus increasing the macro

sweep efficiency. By applying EOR materials that either reduce interfacial tension (IFT) or induce wettability alteration (WA), the capillary pressure is changed to less negative or even positive conditions ⁷⁸, thus releasing the trapped oil in the rock matrix, and increasing the micro sweep efficiency.

In the EOR applications, IFT reduction and WA usually happen at the same time. Surfactants are widely used EOR materials for IFT reduction. The WA potential of surfactants has gained a lot of attention. It is observed that cationic surfactants, in general, have strong and irreversible WA performance on oil-wet carbonate rock ¹². Under conditions like this, two mechanisms are combined to form a coupled effect on the oil recovery. However, there is confusion regarding the impact of IFT reduction when WA happens.

Some studies observed a positive impact of IFT reduction alongside WA. Alvarez and Schechter conducted spontaneous imbibition tests on 8 Bakken core samples (oil-wet or intermediate-wet, silicious, and carbonate) using different EOR materials. Results showed that a lower IFT led to faster oil recovery ¹⁸⁹. Li et al. conducted waterflooding experiments on 2D sandpacks (water-wet and oil-wet). They observed that the applied surfactant solution (NI) could alter the sandpack from oil-wet to water-wet while reducing IFT. Significant oil recovery was obtained ²⁶⁴. Lu et al. conducted both spontaneous imbibition and coreflooding experiments in oil-wet, fractured carbonate samples. The surfactant mixture was found to almost entirely remove the oil in the contact angle measurement, indicating a strong WA performance. It also implied an ultra-low IFT based on a solubility ratio of 16. Results showed a 33.3% imbibition oil recovery and a 65.9% incremental oil recovery by flooding. Sensitivity studies were conducted in numerical simulations using

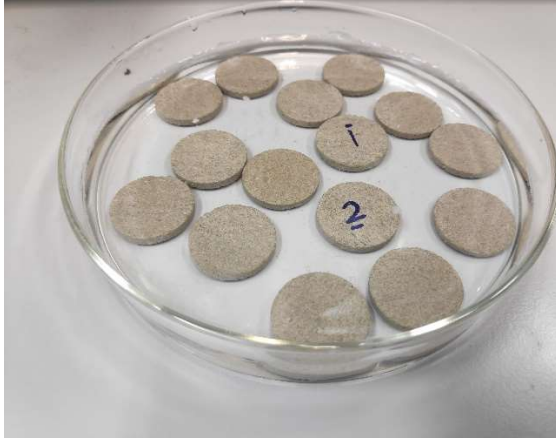
UTCHEM for corefloods. Results showed that combining IFT reduction and WA led to a faster and higher oil recovery than IFT reduction alone, or WA alone ⁸¹. Moradi et al. conducted coreflooding experiments in oil-wet carbonate samples. The tested surfactant obtained considerable IFT reduction. The seawater conditioned with sulfate (SW2.5S) obtained auspicious WA performance. The combination of surfactant+SW2.5S achieved higher oil recovery than surfactant alone, or SW2.5S alone ¹⁸¹. Chen and Mohanty conducted spontaneous imbibition experiments on oil-wet Silurian dolomite samples. They observed the oil recovery sequence from high to low: IFT reduction+WA > WA > IFT reduction ²²⁹.

Some other studies suggest a negative effect of IFT reduction alongside WA. Seethepalli et al. conducted spontaneous imbibition experiments on oil-wet carbonate samples (Iceland spar, limestone, marble, and dolomite plates). Surfactants Alf-35, Alf-38, and Alf-68, managed to revert the rock to water-wetness. In reducing IFT, Alf-68 was much stronger than Alf-35 and Alf-38. The oil recovery results showed that Alf-35 and Alf-38 recovered an extra 20% residual oil than Alf-68 ⁷⁴. In Roustaei's study, nanoparticles showed stronger WA and higher IFT than C₁₂TAB. The spontaneous imbibition oil recovery of nanoparticles was faster and higher than C₁₂TAB ²⁶⁷. Roustaei and Bagherzadeh found that SiO₂ nanofluid increased IFT and induced strong WA. It managed to nearly double the oil recoveries in coreflooding tests ¹⁴⁷. Alvarez and Schechter tested two types of surfactants: anionic and nonionic. They found that the WA performances had no big difference. However, anionic surfactants were much more efficient in reducing IFT. However, the imbibition recoveries by anionic surfactants were lower than by nonionic surfactants ¹⁴⁷.

A previous review work has suggested some understanding of this topic ³³⁵. This work aims at adding some understanding of the coupled effect of IFT reduction and WA through experimental approaches. The influence of permeability is also considered. Inspired by the studies mentioned above, IFT, contact angle, and oil recovery were measured, so to show the main factor in the oil recovery differences. EOR materials of different IFT reduction and WA performances were carefully selected for comparison purposes.

7.2 Materials

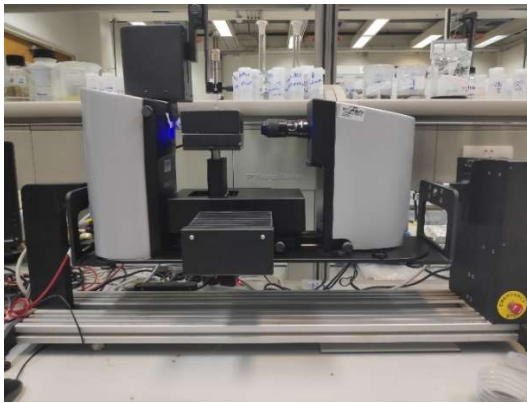
Indiana limestone outcrops are selected to represent carbonate rock. Rock sample substrates (1-inch diameter, 3~4 mm thickness) for static contact angle measurement, and rock sample plugs (1.5-inch diameter, 2-inch height) for spontaneous imbibition tests, are prepared. Rock substrates, as shown in Figure 64 (a), were prepared by cutting a relatively homogeneous limestone outcrop of brine permeability around 10 mD. The obtained raw substrates were then smoothened on the surface by using P500 sandpaper. The plugs, as shown in Figure 64 (b), were prepared by cutting limestone outcrops of low (~10 mD) and high permeabilities (~500 mD). XRD results showed 100% calcite in both low and high permeability Indiana limestone outcrops.



(a)



(b)



(c)



(d)



(e)



(f)

Figure 64 Contact angle measurement method (a) the rock sample substrates; (b) the rock sample plug; (c) the static contact angle measurement instrument; (d) the IFT measurement instrument; (e) Amott cells for spontaneous imbibition experiments; (f) the centrifuge instrument.

Filtered crude oil (API 31.07) was used. A zwitterionic surfactant AGA-97 and a chelating agent diethylene triamine penta acetic acid (DTPA) are used as EOR materials. By dissolving KOH in the chelating agent solution, the 3 wt% solution pH was modified to be around 11.

Four types of locally synthesized cationic gemini surfactants are used, including GS3, GS6, GS8, and GS-NH. All have the same tail groups and counter-ion (Br^-). The only difference lies in the spacer group. GS3 has a saturated straight carbon chain spacer of 8 carbon atoms. GS6 has a straight carbon chain spacer of 4 carbon atoms and a double bond. GS8 has a benzene ring group in the spacer. GS-NH has an amines group in the spacer.

The molecular structures of the studied chemicals are given in Table 39.

Table 39 The structures of studied chemicals ³⁰⁹.

Short name	Structure
DTPA	
ZS	$\text{R}^1-\text{C}(=\text{O})-\text{NH}(\text{CH}_2)_k\text{N}^+(\text{R}^2)(\text{R}^3)(\text{CH}_2)_m\text{CH}(\text{R}^4)(\text{CH}_2)_n\text{SO}_3^-$

GS3	$x = 11-13$ $n = 9-10$
GS6	$x = 11-13$ $n = 9-10$
GS-8	$x = 11-13$ $n = 9-10$
GS-NH	$x = 11-13$ $n = 9-10$

Salts provided by Sigma-Aldrich are used to prepare the synthetic seawater (SW) and the synthetic formation brine (FW). Compositions are given in Table 40.

Table 40 Synthetic seawater and synthetic brine compositions.

Concentration (g/L)	SW	FW
NaHCO ₃	0.165	0.487
Na ₂ SO ₄	6.339	0.518
NaCl	41.172	150.446
CaCl ₂ .2H ₂ O	1.802	52.724
MgCl ₂ .6H ₂ O	8.266	9.552
TDS	57.745	213.727

The studied EOR solutions are given in Table 41.

Table 41 The studied EOR solutions.

Short name	Composition
GS3	GS3 (0.05 wt%) in deionized water
GS6	GS6 (0.05 wt%) in deionized water
GS-NH	GS-NH (0.05 wt%) in deionized water
ZS+DTPA+SW	AGA-97 (0.3 wt%), DTPA (3.0 wt%) in synthetic seawater
GS8+DTPA+SW	GS8 (0.1 wt%), DTPA (3.0 wt%) in synthetic seawater

7.3 Experiments

7.3.1 Static contact angle

The static contact angle was measured on the Theta Tensiometer produced by Biolin Scientific, shown in Figure 64 (c). All measurements were taken at ambient conditions ($\sim 22^{\circ}\text{C}$, 1 atm). The instrument accuracy is $\pm 0.1^{\circ}$. This experiment follows the process below:

1. Clean the sample with toluene and dry it;
2. Sample oil aging by dipping the substrates in the crude oil at lifted temperature ($>90^{\circ}\text{C}$) for at least 7 days;
3. (Initial angle measurement) take the sample out from crude oil, clean flowing oil on the surface, and measure the contact angle;
4. Soak the sample in prepared EOR solution for the required time (1.5 days for GS3, GS6, GS-NH; 4 days for DTPA and AGA-97);
5. (Final angle measurement) take the sample out from the solution, flush the sample with DI water, and measure the contact angle.

The initial angle shows the initial wettability, which was the wettability right after oil-aging; the final angle shows the final wettability, which was the wettability after EOR treatment. By comparing the initial and final angles, the WA performance of the EOR materials can be obtained. Both the initial and final angles were measured in the oil/DI water/rock system to avoid the possible oil spreading problem and avoid the influence of IFT reduction on contact angle results as well.

Table 42 is a classification of rock surface wettability according to the contact angle value.

Table 42 Wettability and contact angle ³³⁶.

Type	Contact angle (°)
Strongly water-wet	0-30
Water-wet	30-70
Intermediate-wet	70-110
Oil-wet	110-150
Strongly oil-wet	150-180

7.3.2 Spinning drop method

In our study, the Spinning drop tensiometer provided by Kruss was used for IFT measurement at ambient conditions (~22°C, 1 atm), as shown in Figure 64 (d).

7.3.3 Spontaneous imbibition

The spontaneous imbibition experiment is a commonly adopted experiment for the EOR potential evaluation in highly heterogenous formations. In the spontaneous imbibition test,

no pressure is supplied. The main driving forces include gravity (buoyancy) and capillary pressure. It is a convenient method to relate EOR materials' IFT reduction and WA performance to oil recovery, as well as reflect on the recovery mechanisms. In this chapter, it was conducted using the Amott cells (suit core diameter, height) provided by Vinci Technologies, as shown in Figure 64 (e), at ambient conditions ($\sim 22^{\circ}\text{C}$, 1 atm). This experiment follows the process below:

1. Clean the sample with toluene and dry it;
2. Fully saturated the sample with synthetic brine by vacuuming;
3. Centrifuge the sample using the URC-628 centrifuge provided by Beckman Coulter, as shown in Figure 64 (f), with crude oil to establish oil and water saturations;
4. Dip the sample in crude oil at lifted temperature ($>90^{\circ}\text{C}$) for longer than 15 days;
5. Take out the sample, remove the oil on its surface, and put the sample in the Amott cell;
6. Fill the Amott cell with the prepared EOR solution;
7. Record oil production along with time. Calculate the oil recovery.

7.4 Results and discussion

Static contact angle results reflect the wettability alteration performance of the studied EOR materials. Spinning drop results show the IFT reduction performance. Spontaneous imbibition results relate the performance of the EOR materials to oil recovery.

7.4.1 Static contact angle results: wettability alteration

Wettability alteration attracts attention since capillary pressure can improve micro-sweep efficiency. Capillary pressure can be expressed according to Young-Laplace Equation, Equation 7.1, as shown below:

$$\Delta p = \frac{2\gamma_{ow}\cos\theta}{r_c} \quad (7.1)$$

In this equation, $\cos\theta$ is the term that relates contact angle to capillary pressure. The changed capillary pressure affects oil recovery in turn. So, wettability alteration performance can be defined using the initial and final angles, as shown by Equation 7.2:

$$WA = \cos\theta_{final} - \cos\theta_{initial} \quad (7.2)$$

In this equation, WA is wettability alteration, $\theta_{initial}$ is the initial contact angle, θ_{final} is the final contact angle. Since $\cos\theta$ lies in the range $[-1, 1]$, WA lies in the range $[-2, 2]$.

The initial, and final contact angles, and the WA , of the studied chemicals, are shown in Figure 65.

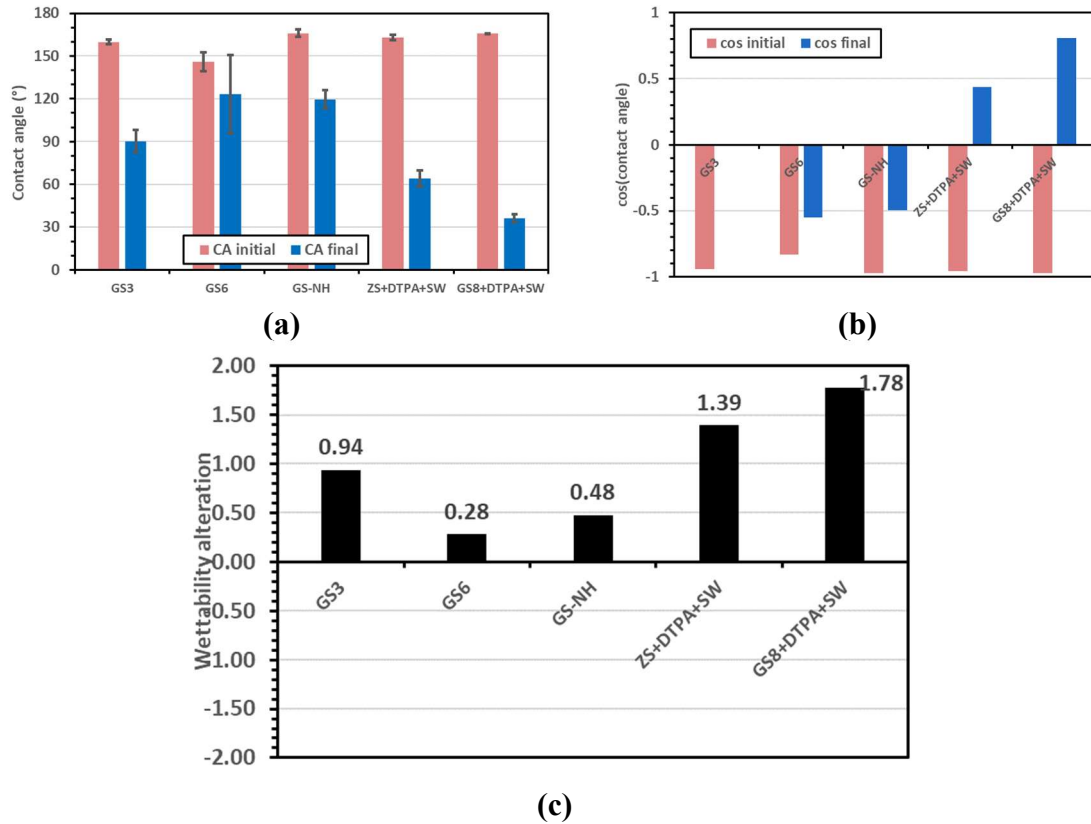


Figure 65 Contact angle results of the EOR solutions. (a) Contact angle before (Initial) and after (Final) soaking treatment; (b) $\cos\theta$ before and after soaking treatment; (c) wettability alteration.

The error in contact angle results can come from inherent sources (rock heterogeneity, surface smoothness) and experimental sources (oil drop size, optical angle deviation from horizontal, remaining oil phase on the rock surface, et al.). To obtain reliable evaluations of the WA performance, at least 2 substrates were treated by each EOR solution. At least 2 spots on each substrate were selected for measurement. The resulting initial and final angle values are the averages of the measurements. The error bars in Figure 65 (a) show the standard error of all the measurements for the same solution.

The initial angles are over or close to 150° , indicating that the original wettability of the oil-aged substrates was mostly strongly oil-wet. The final angles varied significantly from close to strongly water-wet condition (GS8+DTPA+SW, 36.0°) to oil-wet condition (GS6, 123.3°). Among five EOR solutions, GS8+DTPA+SW has the strongest WA performance.

GS6 has the weakest WA performance. The WA caused by GS3 was around 2 times the WA caused by GS-NH. The WA caused by GS8+DTPA+SW was around 1.28 times the WA caused by ZS+DTPA+SW. All solutions modified oil-wet samples toward the water-wet direction.

7.4.2 IFT measurement results

The IFT measurement results are shown in Figure 66.

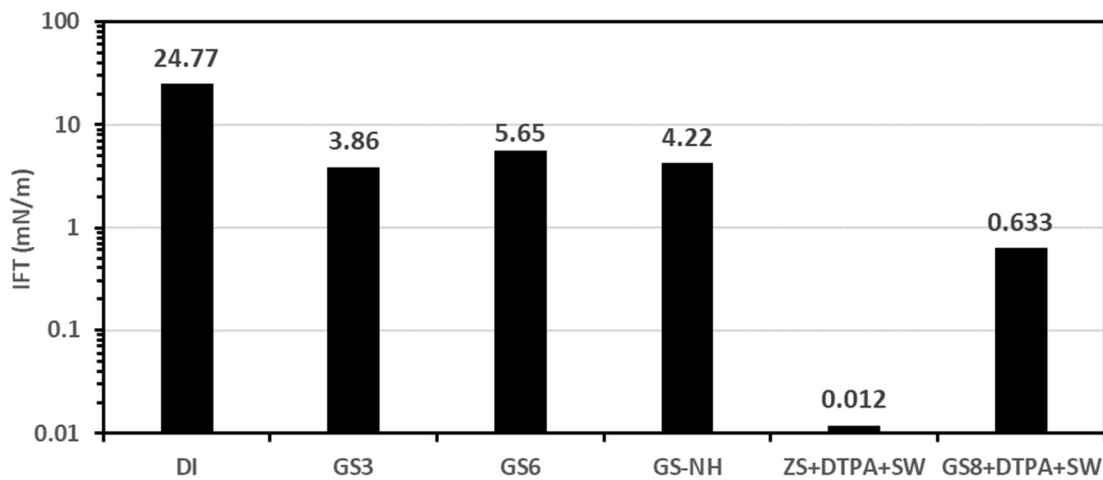


Figure 66 IFT between crude oil and the EOR solutions.

Among five EOR solutions, ZS+DTPA+SW reduced the IFT the most. GS6 reduced IFT the least. The IFT values obtained by GS3, GS6, and GS-NH, are comparable. The tested zwitterionic surfactant seemed to be very effective in reducing IFT. Regarding the resulting IFT, GS3, GS6, and GS-NH, are comparable. GS8+DTPA+SW is about 52 times higher than ZS+DTPA+SW.

7.4.3 Spontaneous imbibition results

Spontaneous imbibition were conducted on 8 Indiana limestone core plugs. The results from 4 comparison pairs reflect the oil recovery mechanisms.

Spontaneous imbibition reflects oil recovery mechanisms by the oil recovery curves and oil production on the plug surfaces. For imbibition driven mainly by buoyancy, the oil production comes mainly from the top surface of the core. For imbibition driven mainly by capillary force, the oil production comes from both top and side surfaces due to the counter-current flow of water and oil ^{337,338}. Buoyancy contributes to oil recovery at a relatively steady and slow rate, resulting in a nearly linear recovery curve. The oil recovery contribution of capillary force mainly comes at the beginning, resulting in a staged recovery curve ². Figure 67 is an illustration of the staged (capillary force dominant) imbibition recovery curve and the linear (buoyancy dominant) imbibition recovery curve.

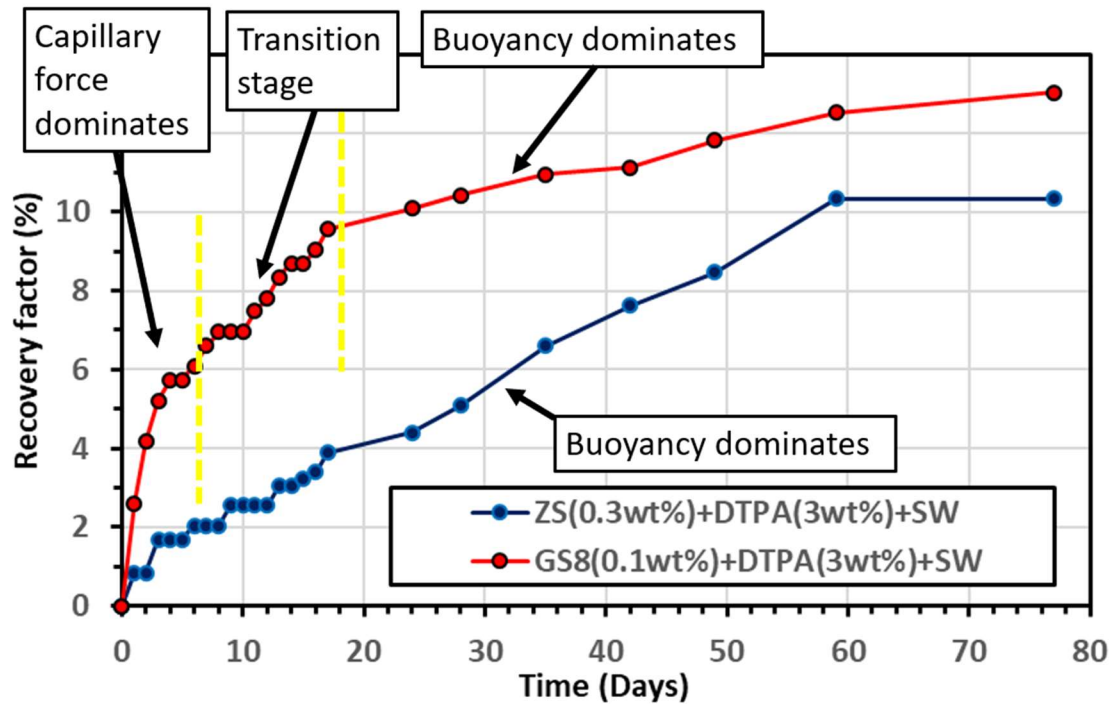


Figure 67 The relationship between driving mechanisms and the recovery curve shape.

Comparison 1: oil recovery contribution of wettability alteration

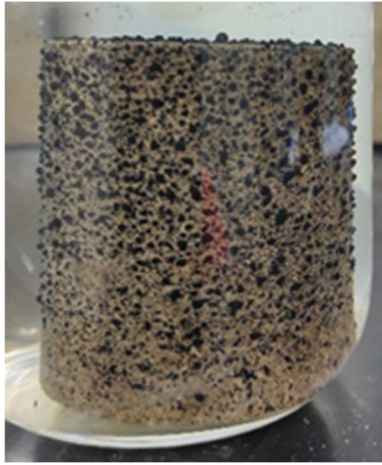
To study the contribution of WA, WA between two cases should be different, while IFT values should be comparable. The pair GS3 vs GS-NH satisfies this criterion. The IFT of

the GS3/oil system is 0.91 times that of the GS-NH/oil system. The WA of GS3 is about 2 times that of GS-NH. The main difference between GS3 and GS-NH is in WA. Detailed information on this comparison test is given in Table 43.

Table 43 Spontaneous imbibition details of GS3 vs GS-NH.

Test	Diameter (mm)	Height (mm)	ϕ	k (mD)	Soi	EOR	IFT (mN/m)	WA	Oil recovery
1	37.87	49.36	0.13	8.95	0.52	GS3	3.86	0.94	24.49%
2	37.87	48.03	0.12	8.81	0.57	GS-NH	4.22	0.48	19.55%

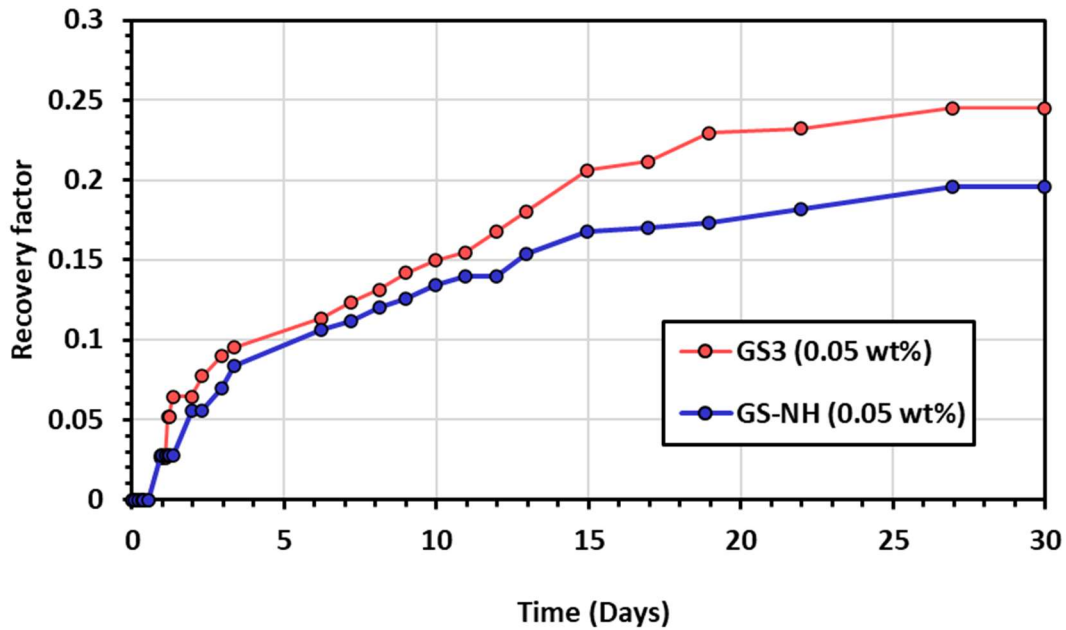
Table 43 shows that the two plugs used had similar properties and were centrifuged to comparable initial oil saturations. After treating them with GS3 and GS-NH in the Amott cells, the oil recovery curves were obtained and are shown in Figure 68.



(a)



(b)



(c)

Figure 68 Spontaneous imbibition GS3 vs GS-NH. (a) GS3 sample after 12 days; (b) GS-NH sample after 12 days; (c) oil recovery curves.

Both the staged shape of the recovery curves and the oil drops from the side surface on both plugs (Figure 68 (a,b)) that relate to counter current, indicate the important role of capillary force. In the condition that capillary force was the dominant driving force, GS3 obtained a higher and faster recovery than GS-NH, which corresponds to the fact that GS3 had stronger WA than GS-NH. This accordance supports the idea that when IFT values are

comparable, stronger wettability alteration leads to faster and higher oil recovery in the spontaneous imbibition test.

Comparison 2: oil recovery contribution of IFT reduction

To study the contribution of IFT reduction, IFT between two cases should be different, while WA values should be comparable. The pair GS8+DTPA+SW vs ZS+DTPA+SW satisfies this criterion. The IFT of the GS8+DTPA+SW/oil system is 53 times that of the ZS+DTPA+SW/oil system. The WA of GS8+DTPA+SW is about 1.28 times that of ZS+DTPA+SW. The main difference is in IFT. Detailed information is given in Table 44.

Table 44 Spontaneous imbibition details of GS8+DTPA+SW vs ZS+DTPA+SW.

Test	Diameter (mm)	Height (mm)	ϕ	k (mD)	Soi	EOR	IFT (mN/m)	WA	Oil recovery
3	38.08	50.86	0.15	7.44	0.66	GS8+DTPA+SW	0.633	1.78	13.04%
4	38.08	51.90	0.15	6.72	0.68	ZS+DTPA+SW	0.012	1.39	10.34%

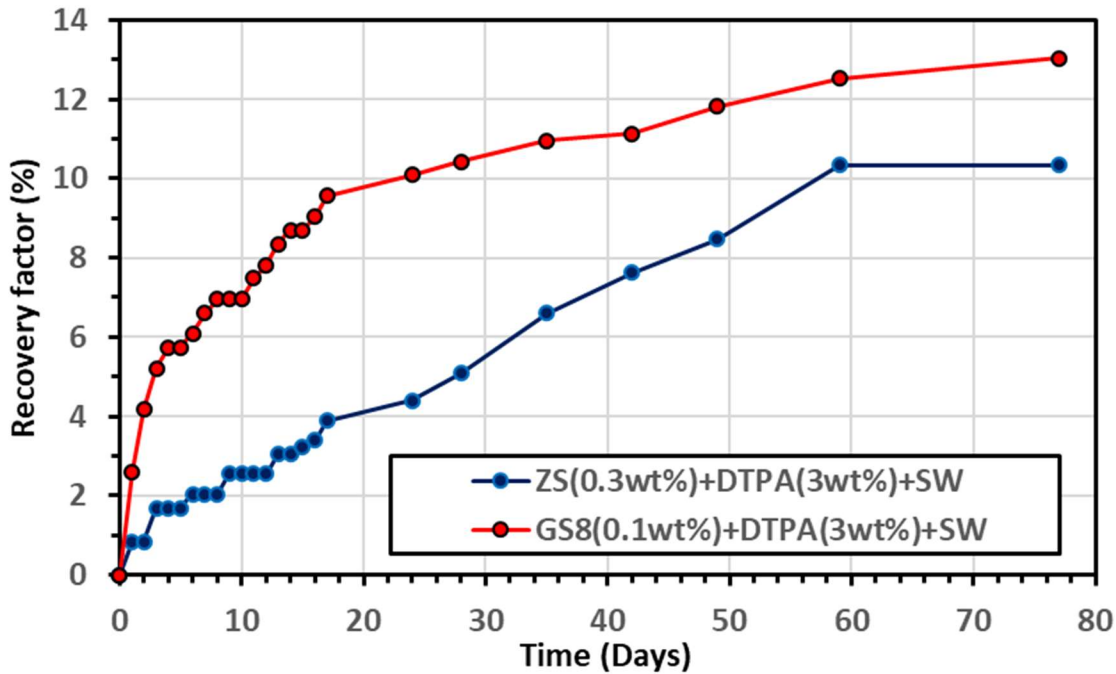


Figure 69 Spontaneous imbibition GS8+DTPA+SW vs ZS+DTPA+SW.

The staged shape of the GS8+DTPA+SW recovery curve in Figure 69 indicates the important role of capillary force. The nearly linear shape of the ZS+DTPA+SW recovery curve indicates the negligible role of capillary force. Though ZS+DTPA+SW had a comparable WA with GS8+DTPA+SW, the role of capillary force in oil recovery differed significantly.

According to Equation 7.1, IFT affects the magnitude of capillary force, while wettability affects the magnitude and direction of capillary force. In this comparison pair, both had positive capillary pressure as indicated in Figure 65 (b). However, due to the much lower IFT of ZS+DTPA+SW, the magnitude of capillary pressure was reduced to a very low value. The IFT of ZS+DTPA+SW was 0.012 mN/m that significantly enhanced the role of buoyancy while diminishing the oil contribution from the capillary force. As a result, capillary pressure was the dominant driving force in the GS8+DTPA+SW case, while buoyancy was the dominant driving force in the ZS+DTPA+SW case. This comparison

test supports the idea that when wettability alteration happens, a higher IFT is favored to maintain the magnitude of capillary pressure, increasing both the oil recovery and oil recovery rate.

Comparison 3: permeability's impact on buoyancy's recovery contribution

To study the impact of permeability on buoyancy's recovery contribution, an EOR solution that reduces the IFT but has negligible WA performance is required. GS6 satisfies this criterion. Detailed information is given in Table 45.

Table 45 Spontaneous imbibition details of GS6 in different permeability plugs.

Test	Diameter (mm)	Height (mm)	ϕ	k (mD)	Soi	EOR	IFT (mN/m)	WA	Oil recovery
5	37.87	50.10	0.15	7.56	0.73	GS6	5.65	0.28	17.66%
6	37.87	51.84	0.17	922	0.66				47.16%

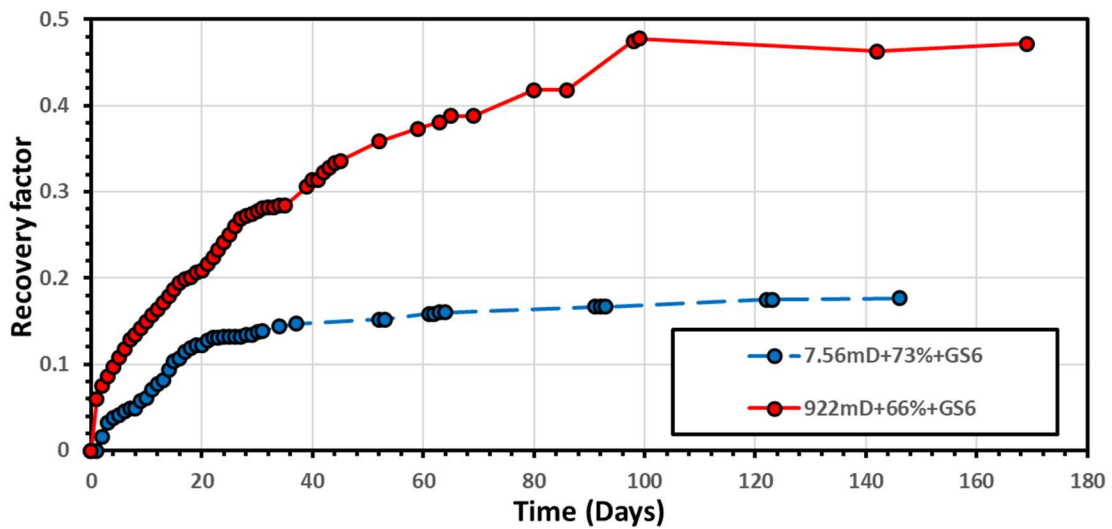


Figure 70 Impact of permeability on the spontaneous imbibition by GS6.

GS6 had negligible WA, the weakest among all five EOR solutions, as shown in Figure 65 (c). The rock substrates treated by GS6 were still oil-wet. IFT reduction was the main oil

recovery mechanism in the GS6 case. Buoyancy was the main driving force, which is also indicated by the nearly linear shape of the recovery curves (during the oil production period).

Figure 70 shows that, on the condition when IFT reduction was the oil main oil recovery mechanism, a higher permeability resulted in much higher and faster oil recovery. This observation can be explained by Darcy's equation and the relation between permeability with pore throat radius. Increased permeability led to a faster flow rate of oil inside the plug, resulting in a higher oil recovery rate. A higher permeability is usually related to a larger average pore throat radius. A larger pore throat radius, according to Equation 7.1, leads to a smaller magnitude of capillary pressure. Since substrates remained oil-wet after GS6 treatment, the capillary pressure was negative. The reduced magnitude of the negative capillary pressure led to less oil trapped by the capillary pressure, thus increasing the ultimate oil recovery. This comparison test supports the idea that when wettability alteration is negligible, a higher permeability improves the oil recovery and recovery rate.

Comparison 4: permeability's impact on the coupled effect

To study the impact of permeability on the coupled effect, an EOR solution that reduces IFT and changes wettability at the same time is required. GS3 satisfies this criterion. Detailed information is given in Table 46.

Table 46 Spontaneous imbibition details of GS3 in different permeability plugs.

Test	Diameter (mm)	Height (mm)	ϕ	k (mD)	Soi	EOR	IFT (mN/m)	WA	Oil recovery
1	37.87	49.36	0.13	8.95	0.52	GS3	3.86	0.94	24.49%
7	37.97	52.77	0.17	515	0.66				26.00%

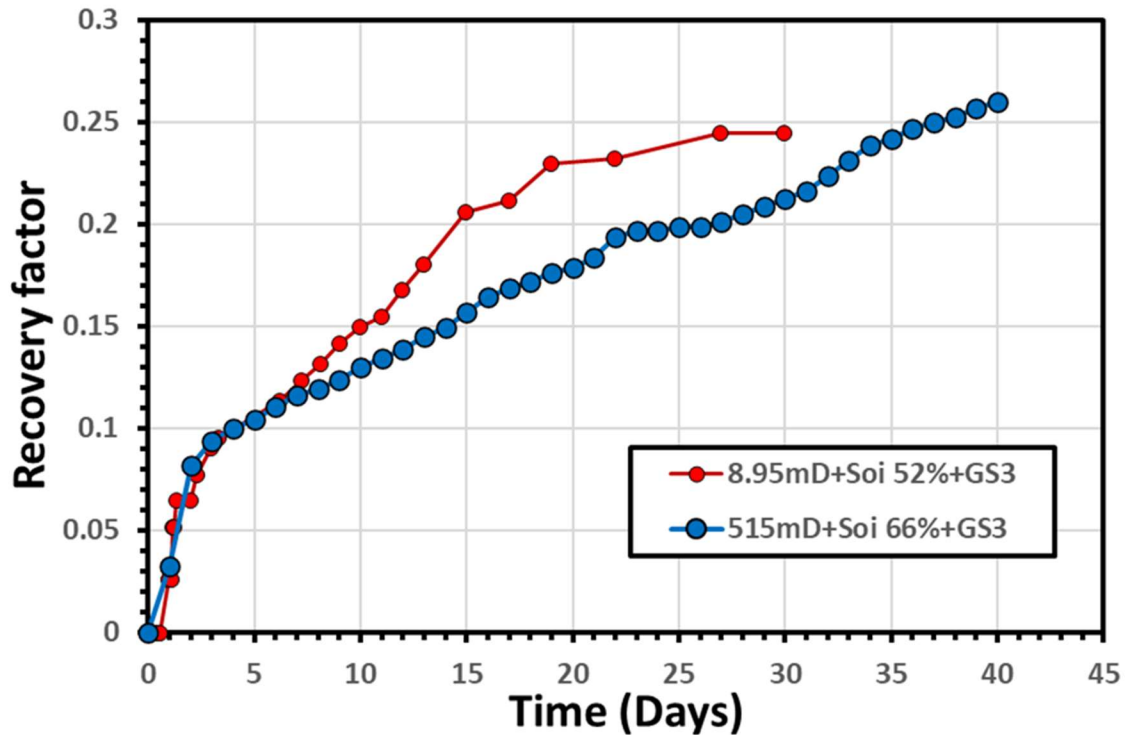


Figure 71 Impact of permeability on the spontaneous imbibition by GS3.

GS3 showed moderate IFT reduction and WA. The strongly oil-wet substrates were changed to intermediate-wet by GS3 treatment. Figure 71 shows that, in such conditions, a higher permeability resulted in higher ultimate oil recovery and a lower recovery rate in the beginning. This observation can be explained the relation between permeability with pore throat radius. As has been iterated in the previous comparison, a higher permeability diminishes the role of capillary pressure, thus reducing the oil recovery contribution from WA. As a result, in stages where capillary pressure was the, or one of the main driving force(s), the lower permeability sample had faster oil recovery than the higher permeability sample. On the other hand, when buoyancy played the dominant role, oil recovery was faster in the higher permeability sample than in the lower one, resulting in a further increase in oil recovery, and a higher continuing oil recovery.

This comparison test supports the idea that when wettability alteration happens, a higher permeability leads to a slower recovery rate in the beginning, but a faster recovery rate after that, and a higher ultimate oil recovery.

Further discussion: the balance between buoyancy and capillary force at the end of imbibition process

At the end of each imbibition process, no more oil is produced. There is a balance three forces: buoyancy, capillary force, and mechanical force. The mechanical force here prevents the residual oil from floating, either by the attraction between oil and rock, or by physical barriers. The capillary force here refers to the overall exertion of capillary pressure on the whole sample plug. Equation 7.3 describe the balance among the three forces.

$$P_c + \text{buoyancy} + F_{\text{mechanical}} = 0 \quad (7.3)$$

$$\text{buoyancy} = \Delta\rho g V_o \quad (2)$$

$$V_o = V * S_o \quad (3)$$

$$V = H * \pi * D^2 / 4 \quad (4)$$

Since the mechanical force here is a force on the opposite direction of buoyancy, the equation can be rewritten as Equation 7.4.

$$P_c + F_{\text{mechanical}} = -\text{buoyancy} \quad (7.4)$$

Thus we have Equation 7.5.

$$|P_c| \leq |\text{buoyancy}| \quad (7.5)$$

According to Equation 7.5, the overall capillary force has a magnitude bounded by buoyancy. According to the following equations, the buoyancy can be obtained.

$$buoyancy = \Delta \rho g V_o \quad (7.6)$$

$$V_o = V * S_o \quad (7.7)$$

$$V = H * \pi * D^2 / 4 \quad (7.8)$$

Oil density 0.87 g/ml. Brine density 1.15 g/ml. g 9.8 N/kg. The range of the overall capillary forces in the four comparisons can be quantitatively obtained, as given in Table 47.

Table 47 The range of the overall capillary force at the end of imbibition tests.

No.	H (mm)	D (mm)	k (mD)	Soi	RF (%)	So	IFT (mN/m)	WA	Pc ≤ (N)
1	49.36	37.87	8.95	0.52	24.49	0.39	3.86	0.94	5.95E-02
2	48.03	37.87	8.81	0.57	19.55	0.46	4.22	0.48	6.83E-02
3	50.86	38.08	7.44	0.66	13.04	0.57	0.633	1.78	9.06E-02
4	51.90	38.08	6.72	0.68	10.34	0.61	0.012	1.39	9.89E-02
5	50.10	37.87	7.56	0.73	17.66	0.60	5.65	0.28	9.29E-02
6	51.84	37.87	922	0.66	47.16	0.35	5.65	0.28	5.61E-02
7	52.77	37.97	515	0.66	26.00	0.49	3.86	0.94	8.03E-02

7.5 Conclusions

To recover residual oil left in the low permeability, oil-wet rock matrix, EOR materials that can either reduce the IFT, change the wettability toward water-wet conditions, or both, can be applied. Although the oil recovery contribution of IFT reduction or wettability alteration alone has already been well understood, the coupled effect between these two mechanisms still arises confusion in understanding. This work measured contact angle to evaluate the wettability. The spinning drop method was adopted to evaluate IFT reduction. Spontaneous

imbibition showed the oil recoveries of the studied EOR solutions and reflect on the oil recovery mechanisms.

Three conclusions are drawn:

1. When IFT values are comparable, stronger wettability alteration leads to faster and higher oil recovery in spontaneous imbibition;
2. When wettability alteration happens, a higher IFT is favored to maintain the magnitude of capillary pressure, increasing both the oil recovery and oil recovery rate;
3. The oil recovery contribution by IFT reduction is enhanced in high permeability conditions. The oil recovery contribution by wettability alteration is enhanced in lower permeability conditions.

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