

**AN INVESTIGATION OF GEMINI SURFACTANT
ADSORPTION ON CARBONATE ROCKS**

BY

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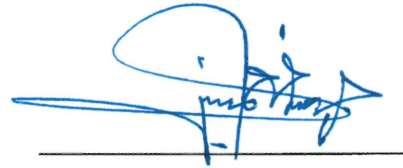
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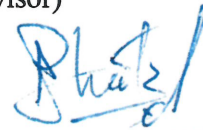
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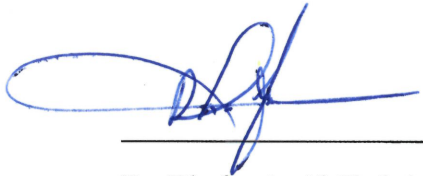
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Dedication

I dedicate my work to my parents, my lovely wife, and my siblings.

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LIST OF ABBREVIATIONS

The list of abbreviations is as follows:

cEOR	:	Chemical enhanced oil recovery
CMC	:	Critical micelle concentration
CPC	:	Cetylpyridinium chloride
CTAB	:	Cetyltrimethylammonium bromide
DI	:	Deionized water
ELSD	:	Evaporative Light Scattering Detector
EOR	:	Enhanced Oil Recovery
EDTA	:	Ethylenediaminetetraacetic acid
FTIR	:	Fourier-transform infrared spectroscopy
GS12	:	Inhouse synthesized cationic Gemini surfactant
HPLC	:	High-Performance Liquid Chromatography
HTHS	:	High temperature and high saline
IEP	:	Isoelectric point
IFT	:	Interfacial tension
LSW	:	Low Salinity Water
MAE	:	Mean absolute error
MSE	:	Mean squared error
M	:	Mass of the dry core sample in g
MB	:	Methylene blue

N	:	Total number of collected effluent samples
PV	:	Pore volume in cc
PZC	:	Point of Zero Charge
pH	:	power of hydrogen
RF	:	Random Forest
SEM	:	Scanning electron microscope
XGBoost	:	eXtreme Gradient Boosting
XRD	:	X-Ray Diffraction
XRF	:	X-ray fluorescence
Symbols		
α_r	:	Constant in Redlich-Peterson adsorption isotherm in L/mg
α_s	:	Sips Model constants in L/mg
α_E	:	Initial adsorption rate in Elovich Model in $mg/g \text{ min}$
b_T	:	Temkin constant related to sorption heat in J/mol
β_r	:	An exponent in Redlich-Peterson adsorption isotherm that ranges between 0 and 1
β_s	:	Sips model exponent
		Desorption constant linked with the extent of surface coverage
β_E	:	and activation energy for chemisorption in the Elovich kinetic model in g/mg

C^0	:	Concentration of the surfactant before adsorption (initial concentration) in ppm
C	:	Concentration of the surfactant after adsorption in ppm
C_a	:	Calcite percentage, %
C_i	:	Surfactant concentration of the effluents collected at a different time period in ppm
C_e	:	Adsorbate's equilibrium concentration in mg/L
C_p	:	Constant term in Intra particle diffusion model
D	:	Dolomite percentage, %
F	:	Feldspar percentage, %
I	:	Illite percentage, %
K_{HE}	:	Henry's adsorption constant in L/g
K_L	:	Langmuir constant in L/mg
K_F	:	Freundlich adsorption capacity in L/mg
K_m	:	Temkin isotherm constant in L/g
K_R	:	Redlich-Peterson isotherm constant in L/g
k_s	:	Sips Model constants in L/g
K_D	:	Hill isotherm constant
K_1	:	First order constant in 1/min
K_2	:	Second order constant in g/mg min

K_p	:	Equilibrium rate constant of Intra particle diffusion model in mg/g min
$M_{adsorbate}$	:	Molecular weight of the adsorbate
m_R	:	Mass of the powdered rock in g
$1/n$	:	Adsorption intensity in the Freundlich adsorption isotherm
n_H	:	Hill cooperativity coefficient of the binding interaction
q_{SH}	:	Maximum uptake of Hill isotherm in mg/g
q_e	:	Adsorbed amount at equilibrium in mg/g
q_m	:	Maximum amount of adsorbed surfactant in mg/g
q_t	:	Adsorption at time t in mg/g
Q	:	Quartz percentage, %
R	:	Universal gas constant in J/mol K
R^2	:	Coefficient of determination
T	:	Temperature in K
t	:	Time in min
V	:	Total volume of injected surfactant solution in L
V_i	:	Volume of the effluents collected at different time period in L
V_s	:	Surfactant solution volume in mL
Greek symbols		
ΔG	:	Change in Gibbs free energy of adsorption
Γ_{static}	:	Surfactant's static adsorption in mg/g-rock

$\Gamma_{dynamic}$	:	Dynamic adsorption in mg/g-rock
ν_{N-H}	:	N-H stretching vibration
ν^s_{C-H}	:	Symmetric vibrations of the CH ₂ groups
ν^{as}_{C-H}	:	Asymmetric vibrations of the CH ₂ groups
Υ_{CMC}	:	Surface tension at the CMC
ζ	:	Zeta potential

ABSTRACT

Full Name : Shams Kalam

Thesis Title : An investigation of Gemini surfactant adsorption on carbonate rocks

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Surfactant adsorption has been a great challenge for surfactant-based chemical enhanced oil recovery (cEOR) techniques as it adversely affects the overall economics and efficiency of a cEOR project. This research focuses on reducing adsorption of an in-house, synthesized, cationic, Gemini surfactant (GS12) on some reservoir rock minerals as well as two Saudi dolomite rock outcrops. GS12 is tolerant of high reservoir temperatures and exhibits excellent solubility in high salinity brines due to the proper placement of ethoxy units between the hydrophilic head and hydrophobic tail group of the surfactant molecule. This study's findings show very promising techniques to reduce adsorption of this novel surfactant on various reservoir rock types.

Rock characterization was carried out using X-Ray Diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) techniques. High-performance liquid chromatography (HPLC) integrated with an evaporative light scattering detector (ELSD) were utilized to measure surfactant adsorption. Both static and dynamic adsorption tests were conducted.

The adsorption mechanism of GS12 was first investigated. It is proposed that an interdigitated bilayer forms on carbonate rocks whereas in sandstone rock a non-interdigitated bilayer forms. Investigating GS12 adsorption on individual minerals revealed that clay minerals showed more negative effects as compared to silicate minerals (quartz and K-feldspar). Carbonate minerals (calcite and dolomite) showed very little adsorption.

To reduce GS12 adsorption on carbonate rocks three strategies were investigated. (1) Methylene blue (MB) - A novel adsorption inhibitor – was tested. Adding 500ppm MB to the GS12 solution caused a reduction of about eight times to the surfactant's adsorption on the Saudi dolomite samples. It is proposed that MB molecules form a bridge between the cationic GS12 and the negative binding sites of the adsorbents, resulting in electrostatic repulsion, which consequently reduces surfactant adsorption. (2) The impact of rock's point of zero charge (PZC) was analyzed. Adding 1% formic acid lowered the surfactant solution's pH below PZC, resulting in GS12 adsorption reduction due to electrostatic repulsion. Such addition also decreased GS12 static adsorption values on Guelph dolomite, Guff dolomite, and Indiana limestone to 0.16, 0.14, and 0.13 mg/g-rock, respectively. The dynamic adsorption of GS12 on Indiana limestone was reduced to 0.041 mg/g-rock. (3) The effect of low salinity water (LSW) was investigated as well. By expanding the electric double layer, the static and dynamic adsorption of GS12 on Indiana limestone was reduced to 0.18 and 0.11 mg/g-rock, respectively, using ten times diluted Arabian Gulf water to prepare the GS12 solution.

ملخص الرسالة

الاسم الكامل : شمس كلام

عنوان الرسالة : تحقيق في امتصاص عناصر السطح الفعالة الثنائية على الصخور الكربونية

التخصص : هندسة النفط

تاريخ الدرجة العلمية : سبتمبر 2022

يعد إمتزاز الفاعل النشط السطحي (فنس) من أكبر التحديات التي تواجه طرق الإستخلاص المعزز الكيميائي للزيت المستندة على حقن محاليل الفنس، حيث أنه يؤثر سلبا على إقتصاديات و كفاءة مثل مشاريع الإستخلاص هذه. يتمحور هذا البحث حول تخفيض إمتزاز فنس من نوع جمناي موجب القطبية تم إبتكاره في الجامعة على بعض معادن صخور المكامن إضافة إلى عينات من نتوءين سعوديين لحجر الدولومايت. يتميز هذا الفنس بتحملة لدرجات الحرارة العالية كما يظهر ذوبانية ممتازة في الأجاجات مرتفعة الملوحة نظرا للتموضع المناسب لوحدات الإثوكسي بين الرأس المحب للماء و الذيل الكاره للماء في جزيء الفنس. و تظهر هذه الدراسة أساليب واعدة لخفض إمتزاز هذا الفنس البديع على مختلف أنواع صخور المكامن.

تم توصيف الصخور بواسطة تقنيات إنحراف الأشعة السينية و إستشعاع الأشعة السينية و التحليل الطيفي لدون الحمراء بواسطة إبدال فوربييه و المسح الألكتروني الميكروسكوبي. كذلك إستخدمت كروماتوغرافيا السوائل ذات الأداء العالي مدمجة مع كاشف للتبخر الضوئي المشتت لقياس إمتزاز الفنس. كما أجريت قياسات كلا من الإمتزاز الساكن و المتحرك.

تم في البدء التحقيق في آلية إمتزاز الفنس. و يقترح أن طبقة مزدوجة ذات بنية تصابعية تتكون على الصخور الكربونية بينما الطبقة المزودجة التي تتكون على الصخر الرملي لا تكون كذلك. و بالتحقيق في إمتزاز الفنس على معادن منفردة كشف أن معادن الطين أبدت تأثيرات سلبية اكبر بالمقارنة مع المعادن السيلكونية كالكوارتز و فلبسبار البوتاسيوم. أما على المعادن الكربونية كالكلسايت و الدولومايت فكان الإمتزاز ضئيلا.

و لقد إتبعنا ثلاث إستراتيجيات لتقليل إمتزاز الفنس على الصخور الكربونية. (1) تم إختبار الميثيلين الأزرق، و هو مثبت بديع للإمتزاز. و بإضافة الميثيلين الأزرق بتركيز 500 جزء في المليون لمحلول الفنس تم خفض إمتزاز الفنس على عينات الدولومايت السعودي بواقع ثمان مرات. و لذا يقترح أن جزيئات الميثيلين الأزرق تنشئ جسرا بين الفنس موجب القطبية و بين المواقع سالبة القطبية على السطح الصلب مما يحدث تنافرا كهربيا ساكنا، و الذي بدوره يخفض من إمتزاز الفنس. (2) تم تحليل وقع نقطة الشحن الصفري للصخور. فإضافة حمض النمليك (الفورميك) بتركيز 1% تم خفض الرقم الهيدروجيني لمحلول الفنس إلى دون نقطة الشحن الصفري مما أدى إلى خفض إمتزاز الفنس نتيجة للتنافر الكهربائي الساكن. كما أدت هذه الإضافة إلى تقليص الإمتزاز الساكن للفسن على حجر دولومايت دولف و حجر دولومايت غف و حجر انديانا الجيري إلى 0.16 و 0.14 و 0.13 مغ/غم على التوالي. (3) تم أيضا التحقيق في تأثير الماء منخفض الملوحة. فبتوسعة الطبقة الكهربائية المزدوجة تم خفض كلا من الإمتزاز الساكن و المتحرك للفسن على حجر انديانا الجيري إلى 0.18 و 0.11 مغ/غم على التوالي و ذلك بإستخدام مياه الخليج العربي مخففة عشر مرات لتحضير محلول الفنس.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Oil recovery mechanisms are broadly classified as primary, secondary, and tertiary recovery methods. Approximately one-third ($1/3$) of the oil present in the subsurface can be recovered using primary and secondary recovery methods. To unlock the remaining oil from the reservoir, tertiary recovery methods are employed, known as Enhanced Oil Recovery (EOR) techniques. Several EOR methods were developed to recover more oil, namely gas injection, chemical methods, and thermal methods [1]. A classification of EOR methods is presented in Figure 1. Several EOR techniques have been investigated and applied during the last 50 years. Figure 2 is based on 1507 global EOR projects, which shows that most of the EOR techniques have been applied in sandstone formations. The application of EOR in carbonates has been a great interest because more than fifty percent of the world's proven reserves of hydrocarbon are found in carbonates [2–4].

Several types of research have been conducted in the domain of chemical EOR (cEOR) in the past 60 years [5]. The use of surfactant, polymer, alkali, and/or a mixture of these

compounds are discovered to be effective chemical EOR methods to recover residual oil [6–8]. Chemical EOR processes have been widely applied globally, such as in Austria, China, Canada, France, Germany, and the US [9]. The consumption and cost of chemicals used in the EOR method depend on the reservoir's characteristics and the type of chemical EOR method employed. Surfactant flooding is believed as broadly employed and the most efficient EOR technique [10,11]. Several researchers have investigated it because of many interesting properties such as; reducing oil/water interfacial tension, wettability alteration, and foam-generation ability [2,6,12–22]. Besides those advantages, there are some challenges associated with surfactant-based cEOR depending on oil reservoir conditions. Surfactant adsorption is one of the problems since it accounts for the surfactant mass loss during the flooding process through porous media, which is directly related to the economics and efficiency of the whole cEOR process [16,23–25]. Hence surfactant adsorption must be reduced to prevent surfactants' chromatographic retardation, making the cEOR process economically feasible. The desired surfactant to be used must have the lowest possible oil/water interfacial tension, wettability-alteration ability, and negligible or minimum adsorption.

The primary reasoning behind surfactant adsorption is the electrostatic attraction between rock surfaces and surfactants. Understanding the rock surface chemistry and surfactant structure is very important in the surfactant selection criteria during surfactant flooding. It becomes critical information in surfactant adsorption studies. The following sub-sections

present the necessary information about different kinds of reservoirs and surfactants that exist in nature.

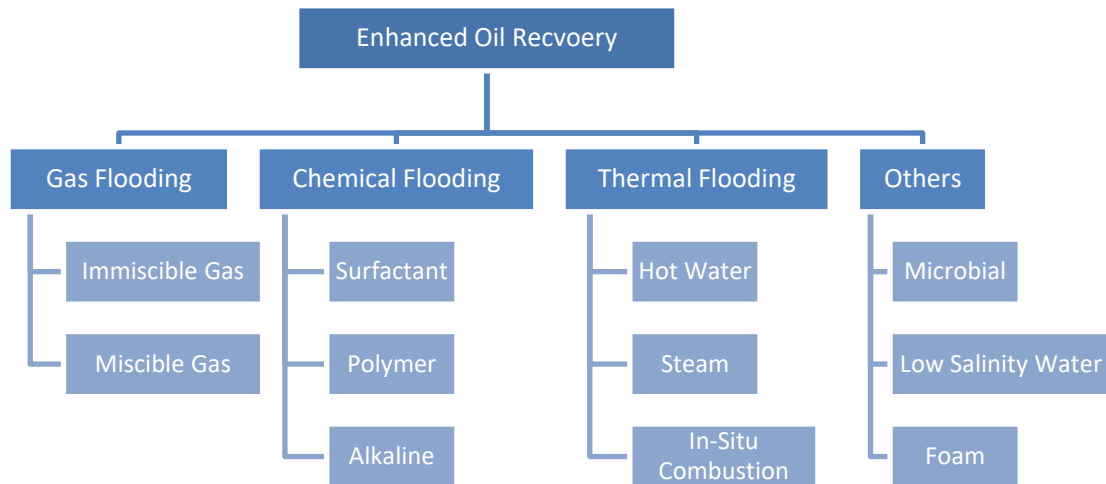


Figure 1: Classification of EOR techniques

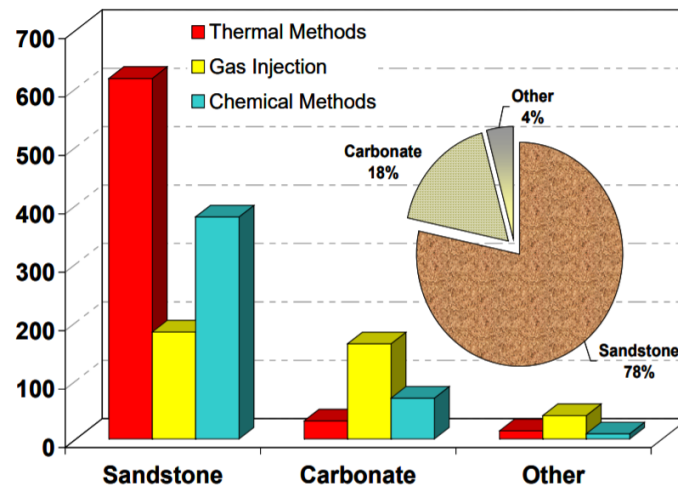


Figure 2. Classification of EOR projects by lithology (published by the permission of the publisher) [26]

1.1.1 Reservoir Types

Porous media is classified into either sandstone or carbonate reservoirs. Sandstone formations are negatively charged, while the surface charge on the carbonate rock surface is positive at typical reservoir conditions [27].

The sandstone type belongs to silica, composed of silicon (Si) and oxygen (O). Si and O tend to combine to form silica tetrahedrons. A single silica tetrahedron unit contains four oxygens and one silicon atom and holds a net charge of -2 (Si^{+4} plus 4O^{-2}). It is believed that there are negative charges on the silica surface for a wide pH range [28]. Isoelectric point (IEP) is the pH at which a molecule is electrically neutral. IEP of silica ranges from 1.7 to 3.5 [29]. The understanding of carbonate rock is complex, unlike sandstone. Most carbonate rocks are either oil-wet or mixed wet, naturally fractured, and heterogeneous [30,31]. Complex pore structures are found in carbonates, and a broad range of heterogeneity exists, such as layers, microporosity, vugs, and natural fractures [12]. Calcite and dolomite belong to the carbonate family having similar structures [32,33]. The solubility of calcite and dolomite is higher than that of silicate and oxides because of their nature of salt-type minerals [32]. Some authors believe that minerals' surface charge also depends on the equilibrium pH of the solution. It concludes that more hydroxy anions are present in the solution at high pH leading to the net negative surface charge. In contrast, the presence of hydrogen cations at low pH leads to a net positive surface charge [34]. The two types of reservoirs, namely sandstone, and carbonates, possess negative and positive surface charges. The rock surface charge helps in the selection of the surfactant type, which is discussed in the following sub-section.

1.1.2 Surfactant Types

Surfactants' structure plays a vital role in analyzing their behavior [35]. The basic system comprises two components: a hydrophilic head part and a hydrophobic tail part. The oil-soluble element (hydrophobic tail) may consist of a long chain hydrocarbon, while the water-soluble element (hydrophilic head) may be nonionic, anionic, cationic, and amphoteric. Surfactants are classified based on the hydrophilic head group. Nonionic surfactants have no charge on the hydrophilic head part, while cationic and anionic surfactants possess positive and negative charges on the hydrophilic head group, respectively [6]. Both positive and negative charges are found at the hydrophilic head group of amphoteric surfactants [6]. They are anionic in alkaline solution and behave like cationic in the solution of acid [36]. The structure of each surfactant type is shown in Figure 3. Surfactants can also be classified on other bases such as monomeric or Gemini. Surfactants can show viscoelastic properties as well, and such surfactants are called viscoelastic surfactants (VES). Gemini surfactants comprise two covalently linked traditional surfactants by a spacer. Geminis can have various sub-categories of cationic and anionic surfactants [37]. In contrast, viscoelastic surfactants have the dual nature of lowering the interfacial tension and enhancing sweep efficiency [38,39].

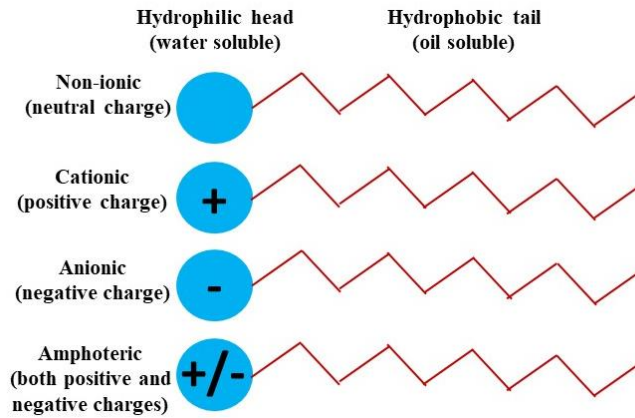


Figure 3: Surfactant structures

Anionic surfactants are extensively utilized in the cEOR technique mostly for sandstone reservoirs because of several reasons such as low adsorption capability, cost-effectiveness, interfacial tension (IFT) reduction, and high-temperature stability [40]. Surfactant adsorption has been a significant problem as it directly deals with chemical EOR economics. Numerous studies have been conducted to reduce surfactant adsorption in both sandstone and carbonate reservoirs [16,23–25,27,41–43]. Carbonates are getting more attention in recent times because of their complexity and the possibility of having 50% and above oil reserves in the world. Due to positive charges on the surface of the carbonate under reservoir conditions, cationic surfactants are most attractive causing lower surfactant adsorption [44–46].

1.2 Literature Survey

An extensive literature review has been conducted for adsorption studies in carbonates. This section presents the adsorption mechanisms and strategies adopted to reduce it in carbonates.

1.2.1 Surfactant Adsorption Mechanism

The mechanism behind surfactant retention includes adsorption, phase trapping, and precipitation [9,27,41–43,47]. Novosad reported that the three most important mechanisms for surfactant retention are: (1) adsorption of surfactant at the interface of solid and liquid, (2) unfavorable phase behavior might lead to the trapping of surfactant in the immobile oil phase, and (3) low solubility of surfactant in the reservoir brines may cause surfactant precipitation [48]. This study is focused on surfactant adsorption on carbonate rocks.

Electrostatic attraction and van der Waals interactions between the reservoir rock surface and the surfactant are the prime adsorption mechanisms [6]. Figure 4 illustrates the adsorption mechanism of surfactants on a rock surface. The surfactant adsorption at the interface is influenced by the characteristics of both solid substrates and the solution. There are numerous other mechanisms for the adsorption of surface-active molecules from aqueous solution on the subsurface rocks, such as hydrophobic bonding, exchange of ions, dispersion forces, ion association, pi-electrons polarization [49–52]. Anionic, cationic, and other classes of surfactants behave differently on various types of rocks.

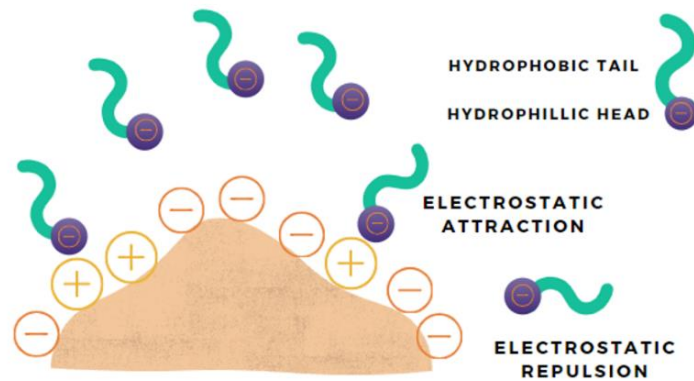


Figure 4: Surfactant adsorption mechanism on a rock

Since carbonates contain a positive charge at the surface, the injection of cationic surfactants in the carbonate rocks may lead to negligible adsorption [34]. The negligible adsorption of cationic surfactants on the carbonate rock surface requires purity [16]. The presence of impurities like silica and/or clay in carbonates may significantly increase cationic surfactant adsorption [16]. An experimental study shows adsorption of cationic cetyl pyridinium chloride (CPC) and anionic sodium dodecyl sulfate (SDS) surfactants on natural carbonate rock with and without CO₂ [16]. Adsorption of cationic surfactant on carbonate surface is a function of silicon occurrence inside carbonate (electrostatic attraction between negative charge of silica/clay and positively charged cationic surfactant). The effect of CO₂ will be discussed later in the adsorption reduction section. Anionic surfactant adsorption on Indiana limestone was studied [53]. The adsorption reasoning was the electrostatic attraction between the negatively charged anionic surfactant and the positively charged mineral surface.

Rosen and Li studied cationic Gemini surfactant adsorption on limestone, which was higher than that of conventional surfactants [54]. The possible reason for higher absorption is the enhanced hydrophobicity between the Gemini surfactants' hydrophobic chains [54]. The effect of anionic Gemini and conventional surfactants on the limestone surface has also been discussed. In the case of anionic Gemini surfactant, one hydrophilic head part adsorbs on the calcium site, while the second hydrophilic head part is positioned in the direction of the aqueous phase. In contrast, electrostatic interaction with the calcium sites is the adsorption mechanism for conventional anionic surfactants. Nonionic surfactants are mainly used as cosolvents. Unlike ionic surfactants, hydrogen bonding is the primary mechanism behind nonionic surfactants' adsorption [55].

Table 1 illustrates the summary of surfactant adsorption mechanisms for numerous surfactant and rock types, as reported by several researchers. In summary, the injected surfactant must be consistent with the reservoir rock and reservoir conditions, such as high temperature and high saline environment, and adsorption as low as possible. Systematic injection strategies must be adopted to tackle the adsorption problem, which will be described in the following section.

Table 1: Reported mechanisms of surfactant adsorption

Entry	Surfactant Type	Rock/Mineral Type	Key Findings	References
1	Anionic	Limestone	Electrostatic interaction with the calcium sites.	[54]
2	Anionic	Carbonate	Electrostatic attraction between opposite charges.	[34]
3	Anionic	Indiana limestone	Electrostatic attraction between anionic surfactant (negatively charged) and positively charged mineral surface	[53]
4	Cationic	Carbonate	Coulombic interactions (repulsive) between like-charged surface and surfactant.	[34]
5	Cationic	Natural carbonate	Electrostatic attraction between the negative charge of silica/clay present in carbonate as an impurity and positively charged cationic surfactant	[16]
6	Cationic	Synthetic calcite	- Silicon and aluminium are not found in synthetic calcite. - Electrostatic repulsion is dominant.	[16]
7	Anionic Gemini	Limestone	- One hydrophilic head part adsorbs on the calcium site. - The second hydrophilic head part is positioned in the direction of the aqueous phase.	[54]
8	Cationic Gemini	Clay	- One hydrophilic head is adsorbed on the clay (opposite charged). - The second hydrophilic head is positioned in the direction of the aqueous phase.	[56]
9	Cationic Gemini	Clay	Adsorption is mainly by ion exchange.	[54]
10.	Cationic Gemini	Limestone	Electrostatic interaction and hydrophobic bonding.	[54]

1.2.2 Surfactant Adsorption Reduction

Reducing surfactant adsorption is very important for a chemical EOR process' economic feasibility because surfactant adsorption causes the massive usage of chemicals employed in the flooding process [57,58]. Several attempts have been made to reduce surfactant

adsorption. Carbonates are still challenging because of their complexity. This section is dedicated to the adsorption reduction strategies applied by numerous researchers for different surfactants on carbonates.

Anionic surfactant adsorption in carbonates is typically higher than in sandstones because of the dominant positively charged surface and the presence of divalent ions. The use of alkali alters the calcite surface charge from positive to negative by increasing pH and reducing the adsorption of anionic surfactants on carbonates [59]. Most of the carbonates contain iron-bearing minerals (IEP = 9.7). This IEP is considered very high, therefore, to introduce enough negative charges, the pH must go beyond the IEP by no less than two units of pH. Due to positive charges on the carbonate rocks surface under reservoir conditions, cationic surfactants are most attractive, causing lower surfactant adsorption. In addition, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) have been a great challenge in the use of sacrificial agents to reduce adsorption.

There are very few adsorption studies for carbonates reported in the literature to date [24]. Estailades limestone belongs to the carbonate family, does not contain gypsum, possesses a lower degree of heterogeneity, and is mainly calcite (99.5 wt%). Reported surfactant retention values in Estailades limestone are 0.58 mg/g-rock [60], 0.34 mg/g-rock [43] and 0.30 mg/g-rock [61]. Surfactant retention in a 20 mD reservoir carbonate core was greater than 1.38 mg/g-rock [62]. Surfactant retention in Lavoux limestone was reported in the range of 0.38 to 1.9 mg/g-rock [63]. Sodium hydroxide was investigated for carbonates to reduce surfactant retention. Reported surfactant retention in Indiana limestone using sodium hydroxide is 0.14 mg/g-rock [24,53]. The study indicates that sodium hydroxide

can significantly decrease anionic surfactant retention in carbonates containing anhydrite or gypsum [24]. However, sodium carbonate cannot be used for carbonate rocks as most carbonates contain anhydrite or gypsum, leading to the precipitation of calcium carbonate [64]. Therefore, alternatives must be tested to reduce surfactant retention in carbonates. The alkali ammonia does not react with anhydrite usually present in carbonate rocks and is considered highly tolerable for divalent ions [65,66]. A recent study shows the use of ammonia, sodium hydroxide as well as Diisopropylamine (DIPA) with ethylene oxide (EO) combined with it to improve the pH and advance the low retention of surfactant [64]. Another study shows that reduction of surfactant retention by using ammonia was not clearly observed for carbonates [67].

Sodium Polyacrylate was explored as a sacrificial agent for the adsorption studies of anionic surfactants on rocks containing anhydrite [68,69]. Sodium Polyacrylate decreased the adsorption of some anionic surfactants on several outcrops such as Carlpool dolomite, industrial calcite, kaolinite, Berea sandstone, and Indiana limestone. The reported sacrificial agent was found to be more effective upon comparison with several chemicals such as disodium EDTA, sodium carbonate, glycolic acid, glyceric acid, sodium alginate as polymers, pectin from citrus peel, polyethyleneglycol, and sodium metaborate. The reduction of anionic surfactant adsorption by sodium polyacrylate is more effective for clays and carbonates as compared to sandstone [69]. In addition, a few strategies were also evaluated in this study, including the effect of the molecular weight of sodium polyacrylate, divalent ions concentration, salinity, and the effect of temperature. Results showed that increasing the molecular weight of Sodium Polyacrylate may reduce the adsorption up to

a certain extent. On the other hand, increasing the salinity leads to a large amount of adsorption except for dolomite. Similar behavior was observed for the increase of divalent ions concentration. Adsorption of anionic surfactant can be reduced in the presence of sodium polyacrylate at different temperatures without precipitation [70].

The use of polymers either as a co-injection or pre-flushing may also considerably reduce the surfactant adsorption [71]. Some authors investigated the impact of a nanoparticle Zirconium Oxide (ZrO_2) for the adsorption studies of dodecyl trimethylammonium bromide (cationic surfactant) and sodium dodecyl sulfate (anionic surfactant) on carbonates [72]. It was found that the adsorption of dodecyl trimethylammonium bromide on carbonates in the presence of ZrO_2 nanoparticles is because of nanostructures formation. Also, the adsorption rate of cationic surfactant is higher than anionic.

Adsorption studies were also conducted for cetylpyridinium chloride (cationic surfactant) and sodium dodecyl sulfate (anionic surfactant) on carbonates in the presence of 1 atm CO_2 [16]. As discussed earlier, the adsorption of cationic surfactant on natural carbonate is mainly due to silicon and aluminum (interaction between positively charged cationic surfactant and negative sites in silica). The presence of 1 atm CO_2 decreases the adsorption level compared to 1 atm air for the cationic surfactant in natural carbonate, while no adsorption of cationic surfactant was found on synthetic carbonate. In the case of anionic surfactant, the surfactant solution is acidified by the addition of CO_2 , which releases more divalent ions from the synthetic carbonate surface, resulting in anionic precipitation surfactant. Similar behavior was observed for natural carbonate, which shows that

precipitation of the anionic surfactant is independent of the natural carbonate rock's impurities.

There are some special types of interesting surfactants, such as Gemini and viscoelastic surfactants. A few authors have investigated Gemini surfactants' adsorption and compared it with the traditional surfactants [54,56]. Rosen and Li reported negligible adsorption of anionic Gemini on sand [54]. Adsorption of Gemini surfactants at the interface of silica and aqueous solution was studied [73]. The effect of spacer sizes ranging from 2 to 12 on surface excess was analyzed. The largest surface excess was noticed at the smallest size of the spacer.

Li et al. investigated the impact of salinity, calcium ions, pH value, and temperature on viscoelastic surfactant adsorption in porous media [39]. A lower amount of adsorption was observed on the quartz surface as compared to montmorillonite and kaolinite. The adsorption was slightly decreased for the temperature ranges of 60 to 80 degrees Celsius. Another study shows a lower amount of adsorption of a viscoelastic surfactant on powdered calcite at higher temperatures [74]. However, an increase in calcium and sodium ions concentration results in the rise of adsorption [39]. The effect of an increase in pH values on VES adsorption on quartz is insignificant, whereas, for Kaolinite and Montmorillonite, a rise in pH values increases the surfactant adsorption [39]. A few studies have been found regarding the adsorption reduction strategies of those special kinds of surfactants.

In brief, carbonates contain mainly positive charges on the surface, making cationic surfactants most attractive resulting in lower surfactant adsorption. However, both anionic

and cationic surfactants have been investigated for carbonates. Fewer studies have been found on cationic surfactants as compared to others. The presence of impurities like silica and/or aluminium, gypsum and/or anhydrite are the major challenges associated with carbonate formations. Some studies have been conducted to overcome the problems arising from gypsum/anhydrite in carbonates such as the use of ammonia, sodium hydroxide, diisopropylamine, 10 ethylene oxide, etc. On the other hand, the occurrence of a minute amount of silica and/or aluminium inside carbonates may result in cationic surfactants' adsorption. Some researchers have tried CO₂ to tackle this problem. It is imperative to study the rock characterization before selecting any surfactant and additional chemicals for adsorption reduction. Table 2 summarizes the chemicals and strategies examined by numerous investigators to reduce surfactant retention in carbonates.

Table 2: Summary of various studies emphasizing the key finding(s) for retention reduction of ionic surfactants on carbonates

Entry	Type Surfactant	Rock/Mineral Type	Influencing Factor(s)	Key Finding(s)	References
1	Anionic Surfactant	Indiana Limestone	NaOH	0.3 weight percent of NaOH improves the pH to 12.6 and helps in reducing the anionic surfactant adsorption on limestone. - NaOH can be used to increase the pH of limestones consisting of anhydrite or gypsum.	[24,53]
2	-	Carbonate core	Ammonia, sodium hydroxide,	DIPA-10EO can be used for carbonates having anhydrite without precipitation.	[64]

			and DIPA-10 EO	Surfactant retention was decreased	
3	-	Carbonates	Ammonia	The reduction of surfactant retention by using ammonia was not clearly observed for carbonates.	[67]
4	-	Carbonate core containing gypsum	Ammonia	Low surfactant retention for ASP core flood in carbonates containing gypsum.	[66]
5	Dodecyl trimethylammonium bromide (Cationic), Sodium Dodecyl Sulfate (Anionic)	Carbonate	Nanoparticle (Zirconium Oxide)	- The adsorption of Dodecyl trimethylammonium bromide on carbonates in the presence of ZrO₂ nano particle is because of nanostructures formation. - The adsorption rate of cationic surfactant is higher than anionic.	[72]
6.	Amphoteric Surfactant and Sulfonated Polyacrylamide	Carbonates	Polymers	The use of polymers either as a co-injection or pre-flushing might reduce the surfactant adsorption considerably.	[71]
7	Cetylpyridinium chloride (Cationic)	Natural Carbonate	Mineral Composition and CO ₂	- Adsorption of cationic surfactant on natural carbonate is mainly due to silicon and aluminum (interaction between positively charged cationic surfactant and negative sites in silica). - It can be deduced that the higher the silicon and/or aluminum content inside natural carbonate, the higher	[16]

				will be the adsorption of cationic surfactant. The presence of 1 atm CO₂ decreases the adsorption level as compared to 1 atm air.	
8	Cetylpyridinium chloride (Cationic)	Synthetic Carbonate	Mineral Composition	An insignificant amount of adsorption was observed on synthetic calcite because of the absence of silicon and aluminum.	[16]
9	Sodium Dodecyl Sulfate (Anionic)	Synthetic Carbonate	CO ₂	The surfactant solution is acidified by CO₂, which releases more divalent ions from the carbonate surface, resulting in the precipitation of anionic sodium dodecyl sulfate.	[16]
10	Sodium Dodecyl Sulfate (Anionic)	Natural Carbonate	CO ₂	Similar behavior was observed for natural carbonate, which shows that precipitation of the anionic surfactant is independent of the carbonate rock's impurities.	[16]
11	Anionic Surfactant	Carlpool dolomite, industrial calcite, kaolinite, Berea sandstone, and Indiana limestone	Sodium Polyacrylate as a successful sacrificial agent, Effect of molecular weight of Sodium Polyacrylate, divalent Ions, brine	- Sodium Polyacrylate was investigated as an effective sacrificial agent compared to others (glycolic acid, polymers (sodium alginate), sodium carbonate, glyceric acid, disodium EDTA, sodium metaborate, and polyethyleneglycol). - Higher the molecular weight of Sodium Polyacrylate, the lower will be the adsorption up to a certain extent.	[68,70]

			salinity, and temperature	- Higher salinity leads to a large amount of adsorption except for the case of dolomite. - An increase in divalent ions concentration increases the adsorption except in dolomites.	
12	Anionic Gemini	Sand	-	No adsorption	[54]
13	Gemini Surfactants	Silica	Spacer Sizes	The largest surface excess was observed at the smallest size of the spacer.	[73]
14	Anionic Viscoelastic Surfactant (VES)	Quartz, Montmorillonite, and Kaolinite	Temperature, Calcium Ions, Salinity, Concentration, and pH	- Less adsorption of VES was noticed on the quartz surface as compared to other minerals. - VES adsorption on the minerals was slightly lowered at 60-80 degrees Celsius. - An increase in sodium ions concentrations increases adsorption. - The influence of calcium ions is consistent with that of sodium ions. - Negligible effect of the rise in pH on the adsorption of VES on quartz. - A rise in pH increases the surfactant adsorption on Kaolinite and Montmorillonite.	[39]
15	Viscoelastic Surfactant	Calcite	Temperature	Static adsorption is reduced at a higher temperature.	[74]

1.3 Adsorption Isotherms

1.3.1 Henry's Isotherm

It is a one-parameter model and the most basic adsorption isotherm. It proposes a linear relationship between the adsorbed amount and the adsorbate's bulk concentration, as presented by Eq. (1) [75].

$$q_e = K_{HE} C_e \quad (1)$$

where q_e is the adsorbed amount at equilibrium in mg/g, K_{HE} is Henry's adsorption constant in L/g, and C_e is the adsorbate's equilibrium concentration in mg/L.

Henry's model can be used when the coverage ratio of the adsorption sites is minimal. It approximates the data trend only at low solute concentrations. Hence, it shows monolayer adsorption at initially low adsorbate concentrations. This simplest model is invalid at high concentrations of surfactant.

1.3.2 Langmuir Isotherm

Langmuir isotherm was initially developed for gas-solid interaction but is also used for various adsorbents [76]. It is an empirical model based on kinetic principles, i.e., the surface rates of adsorption and desorption are equal with zero accumulation at equilibrium conditions [77]. Based on the following assumptions: (a) monolayer adsorption, (b) homogeneous sites, (c) constant adsorption energy, and (d) no lateral interaction between the adsorbed molecules, the Langmuir isotherm can be written as;

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_m is the maximum amount of adsorbed surfactant in mg/g and K_L is the Langmuir constant in L/mg.

The monolayer assumption requires identical adsorption sites and only one molecule can be adsorbed at each site. There is no more adsorption in a site once a surfactant molecule has occupied it. This model converts to Henry's model at very low concentrations ($K_L C_e \ll 1$).

1.3.3 Freundlich Isotherm

Unlike Langmuir isotherm, this empirical model can be used for multilayer adsorption on heterogeneous sites [78]. It assumes that the adsorption heat distribution and affinities towards the heterogeneous surface are non-uniform [79]. The mathematical model can be shown as;

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F is the adsorption capacity in L/mg and $1/n$ is the adsorption intensity or surface heterogeneity. When $0 < 1/n < 1$, adsorption is considered favorable. Unfavorable adsorption occurs when $1/n > 1$ and is irreversible at $1/n = 1$.

Freundlich isotherm describes multilayer adsorption and assumes exponential decay in the energy distribution of adsorbed sites. However, it is not valid for a large range of adsorption data [80].

1.3.4 Temkin Isotherm

Temkin model, which presumes a multilayer adsorption process, considers interactions between the adsorbent and the adsorbate [81] but it ignores very small and very large concentration values [79]. The non-linearized form of the Temkin isotherm is expressed by;

$$q_e = \frac{RT}{b_T} \ln(K_m C_e) \quad (4)$$

where R is the universal gas constant in J/mol K, T is the temperature in K, b_T is the Temkin constant related to sorption heat in J/mol, and K_m is the Temkin isotherm constant in L/g.

1.3.5 Redlich-Peterson Isotherm

This three-parameter adsorption isotherm possesses the characteristics of both the Langmuir and the Freundlich isotherms, and so does not exhibit ideal monolayer adsorption behavior [82]. Being a hybrid version, the Redlich-Peterson isotherm can be used in both homogeneous and heterogeneous systems. The mathematical form of the model is given by Eq. (5).

$$q_e = \frac{K_r C_e}{1 + \alpha_r C_e^{\beta_r}} \quad (5)$$

where K_R is the Redlich-Peterson isotherm constant in L/g, α_r is a constant in L/mg, and β_r is an exponent that ranges between 0 and 1. At low concentrations ($\beta \sim 1$), the model approaches Langmuir isotherm and at high concentrations ($\beta \sim 0$) it approaches Freundlich isotherm.

1.3.6 Sips Isotherm

Sips suggested an equation that combines the Freundlich and Langmuir isotherms after recognizing the issue of a continual rise in the adsorbed quantity with an increase in concentration in the Freundlich equation. This results in an equation that shows a finite limit at high concentrations [80]. Sips model is the most appropriate, three-parametric isotherm used for monolayer adsorption of surfactant. It can be used for heterogeneous systems and is valid for localized adsorption without adsorbate-adsorbate interactions [83]. The mathematical form is

$$q_e = \frac{k_s C_e^{\beta_s}}{1 + \alpha_s C_e^{\beta_s}} \quad (6)$$

where β_s is a model exponent and α_s and k_s are model constants in L/mg and L/g, respectively.

Sips model does not follow Henry's law at low concentrations of adsorbate since it approaches Freundlich isotherm. On the other hand, it shows the monolayer adsorption behavior of the Langmuir model at a high concentration. The parameters of the model are controlled by temperature, pH, and change in concentration [84].

1.3.7 Hill Isotherm

Hill adsorption model was developed from non-ideal competitive adsorption (NICA) isotherm [85]. It demonstrates the binding of various species onto homogeneous substrates. In this model, adsorption is considered a cooperative phenomenon, with the adsorbate

binding ability at one site on the adsorbent may influence other binding sites on the same adsorbent. The mathematical form can be presented as:

$$q_e = \frac{q_{SH} C_{eq}^{n_H}}{K_D + C_{eq}^{n_H}} \quad (7)$$

where q_{SH} is the maximum uptake of Hill isotherm in mg/g, n_H shows the Hill cooperativity coefficient of the binding interaction, K_D is the Hill isotherm constant. The binding is considered negative, non-cooperative, or positive, when $n_H < 1$, $n_H = 1$, or $n_H > 1$, respectively.

1.4 Adsorption Kinetics

1.4.1 Pseudo-First Order

Lagergren developed the pseudo-first order kinetic equation in 1898 to assess the kinetics of liquid and solid phase adsorption [86]. The occupancy rate of adsorption sites is thought to be proportional to the number of available sites [87].

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (8)$$

where t is the time in min, q_t shows adsorption at time t in mg/g, q_e represents adsorption at equilibrium time in mg/g, and K_1 is the first order constant in 1/min.

1.4.2 Pseudo-Second Order

This model is based on the adsorption capacity of the solid phase, useful to find the type of reaction and rate constant [88]. It does not describe the adsorption controlled by diffusion.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where K_2 is the second order constant in g/mg min.

1.4.3 Intra Particle Diffusion

It considers the adsorption process due to the diffusion mechanism [89].

$$q_t = K_p t^{1/2} + C_p \quad (10)$$

Where K_p is the equilibrium rate constant of the Intra particle diffusion model in mg/g min and C_p is the constant.

1.4.4 Elovich Model

It is used to determine chemisorption adsorption kinetics [87].

$$q_t = \frac{1}{\beta_E} \ln(\alpha_E \beta_E) + \frac{1}{\beta_E} \ln(t) \quad (11)$$

where α_E is the initial adsorption rate in mg/g min and β_E is the desorption constant linked with the extent of surface coverage and activation energy for chemisorption in g/mg.

1.5 Problem Statement and Research Gap

The amount of surfactant loss caused by adsorption during flooding through reservoir rock is still a challenge in surfactant-based cEOR techniques. Reducing surfactant adsorption is very important for a chemical EOR process' economic feasibility because surfactant adsorption causes the enormous consumption of chemicals employed in the flooding process. Gemini surfactants are a special class of surfactants that show unique properties, such as good water solubility, low critical micelle concentration, high efficiency in reducing oil/water interfacial tension, unusual micelle structures, aggregation behavior, and interesting rheological properties [90]. Carbonates contain more than 50% of the world's oil reserves. Cationic surfactants are attractive candidates for cEOR in carbonates. Very few studies have been conducted on cationic Gemini surfactants, mainly for clays and sands. Adsorption of cationic Gemini surfactants in carbonates has not been explored, especially for local Saudi carbonate outcrops. This research work aims at investigating the adsorption mechanism and adsorption reduction strategies for a cationic Gemini surfactant on carbonate rocks including Saudi carbonate outcrops.

1.6 Research Objectives

The ultimate objective of this research was to reduce the adsorption of a cationic Gemini surfactant on carbonates, including a Saudi outcrop. The key objectives are summarized as follows:

- 1- Investigation of the adsorption mechanisms of a cationic Gemini surfactant in different types of rocks.

- 2- Investigate the behavior of surfactant adsorption on individual minerals.
- 3- Inspect different chemicals to reduce surfactant adsorption.

1.7 Research Methodology

The methodology of this study is summarized as follows:

- 1- Rock characterization using standard techniques, such as XRD (X-Ray Diffraction), XRF (X-ray fluorescence), FTIR (Fourier-transform infrared spectroscopy), and SEM (scanning electron microscope).
- 2- Static adsorption tests using powdered rock samples for an in-house synthesized cationic Gemini surfactant.
- 3- Dynamic adsorption tests using core flooding for an in-house synthesized cationic Gemini surfactant.
- 4- High-Performance Liquid Chromatography (HPLC) for determining remaining surfactant concentration after adsorption tests

CHAPTER 2

ADSORPTION MECHANISMS OF A NOVEL CATIONIC GEMINI SURFACTANT ONTO DIFFERENT ROCKS

Abstract

The need to reduce surfactant adsorption on rock surfaces has been a difficult task in chemical enhanced oil recovery, as it directly impacts the economics of the project. This requires a comprehensive insight into the adsorption mechanism on rocks. The adsorption mechanism of an in-house cationic Gemini surfactant on different rocks has been studied in this work. The novel surfactant is compatible with high temperature and high salinity environments. All experiments were conducted at room temperature and in deionized water. Adsorption in sandstone rocks was found significantly higher than that in carbonates because of the high density of negative charges. The differences in the quantity of adsorbed surfactant can be explained by different layer structures. It is proposed that an interdigitated bilayer is formed on carbonate rocks, whereas a non-interdigitated bilayer is formed in sandstone rock samples. The maximum and minimum adsorption values were found around 9 mg/g-rock and 1 mg/g-rock in sandstone and carbonates, respectively. Scanning electron microscopy showed that the surface of sandstone rocks was rougher after the adsorption of Gemini surfactant, whereas no substantial variation in the morphology of

carbonates was found. Similarly, the Fourier transform infrared spectroscopy showed the symmetric and asymmetric vibration of the CH₂ groups in the post adsorption analysis of sandstone, but not in carbonates. Adsorption isotherm modeling was also conducted to investigate the adsorption mechanism of Gemini surfactant on different rocks. All rocks follow a Hill isotherm, showing that the adsorption process is cooperative. However, better curve fitting was obtained using a Redlich-Peterson isotherm in sandstone, whereas both the Langmuir and Redlich-Peterson isotherm performed better for carbonates. The experimental results confirm the formation of interdigitated and non-interdigitated bilayer of the employed surfactant, which explains its adsorption behavior in different rocks and how this adsorption follows different adsorption models in different rocks.

2.1 Introduction

Primary and secondary drive mechanisms recover about one-third of oil from the subsurface [22,46]. Oil recovery from the primary drive mechanism is due to the reservoir's natural pressure, whereas, in the secondary drive mechanism, water injection is carried out to further recover oil and maintain reservoir pressure as well [45]. Tertiary oil recovery or enhanced oil recovery (EOR) techniques are employed to unlock the remaining oil potential. Chemical enhanced oil recovery (cEOR) is one type of EOR techniques in which surfactants are commonly used for numerous purposes, such as oil/water interfacial tension (IFT) reduction, foam generation, and wettability alteration [8,19,22,91].

A surfactant is typically a long-chain molecule with a hydrophilic (water-soluble) head and a hydrophobic (oil soluble) tail group. Surfactants are categorized based on the charge on

the hydrophilic head portion. Generally, they can be non-ionic (no charge), anionic (negative charge), cationic (positive charge), and amphoteric (both negative and positive charges). The most-reported surfactants employed in EOR are ethoxylated and propoxylated sulfates and sulfonates (anionic surfactants) [90]. There are several challenges associated with surfactant-based EOR techniques, including compatibility with harsh reservoir conditions (high salinity and high temperature), attaining ultra-low IFT, wettability alteration, and reduction of adsorption on rocks. Adsorption of surfactants on rocks is the most critical issue since it directly affects the economics and efficiency of a surfactant-based EOR technique [92]. Several studies have been reported on surfactant adsorption [93–106]. High adsorption causes surfactant chromatographic retardation during its transport through the reservoir. Hence understanding the adsorption mechanism is essential to reduce surfactant adsorption.

Oil reservoirs are categorized as sandstone or carbonate depending on the prevalent mineral in the rock. A significant amount of quartz (silica, SiO_2) is present in sandstone that contains a negative charge across a broad range of pH (the point of zero charge (PZC) is 1.7 to 3.5) [29]. Anionic surfactants inhibit adsorption in sandstone reservoirs because of electrostatic repulsion. However, the presence of clay minerals (kaolinite, Illite, etc.) in sandstone may lead to some degree of adsorption since clay possesses heterogeneous surface charges [107]. On the other hand, the main constituents of carbonates are calcite and/or dolomite. Calcite is composed of alternate layers of calcium (Ca^{2+}) and carbonate ions (CO_3^{2-}), while dolomite is formed by alternate layers of calcium (Ca^{2+}), magnesium

(Mg^{2+}), and carbonate ions (CO_3^{2-}). Carbonates are generally considered positively charged, but the presence of some impurities like silica may influence their surface chemistry [108]. Some studies show that natural carbonates may contain a slight negative charge [16,108]. A low amount of cationic surfactant adsorption was found in carbonates as compared to anionic surfactants [16,34]. Therefore, cationic surfactants are preferred in carbonates. In summary, the electrostatic attraction between the surfactant and the oppositely charged surface is the main mechanism of surfactant adsorption on rocks. To reduce surfactant adsorption, researchers have reported techniques, such as the addition of sacrificial agents, the selection of salt-tolerant surfactants, etc. [16,34,69,70,92].

Gemini surfactants belong to a unique class of surfactants that contain molecules of two conventional surfactants linked by a spacer [109]. The hydrophobic spacer is usually at or close to the head group, which enhances the hydrophobicity of Gemini surfactants as compared to that of conventional surfactants [73]. This special characteristic makes Gemini surfactants act like two surfactants in one and, hence, enhances their performance. They possess the ability to form aggregates at a much lower concentration leading to lower critical micelle concentration (CMC) as compared to the monomeric types. The lower CMC helps decrease IFT efficiently [110]. Gemini surfactants have gained a lot of attention due to their outstanding properties and significant research has been conducted in the past decade [7,8,111–119]. However, most of these studies are related to the Gemini surfactants' solution properties; their adsorption behavior on rock surfaces is relatively uncommon [120,121] and not well understood. Since Gemini surfactants possess interesting properties in comparison with the conventional monomeric types, their

adsorption behavior on rock surfaces is an interesting area of research. The adsorption of a cationic Gemini surfactant (hexyl- α,ω -bis(dodecyldimethylammonium bromide)) on silica surface and the effect on wettability were studied [121]. This investigation showed that by the increase of surfactant concentration, surfactant adsorption takes place in a sequence starting from no aggregates to circular islands, followed by the formation of semicontinuous islands, and finally the formation of a two-bilayer structure. In addition, the investigation claims that wettability depends on the surfactant aggregates morphology. Another study showed that the ionic, liquid-type, imidazolium Gemini surfactant forms a bilayer on a silicon surface [122]. Bilayer adsorption behavior of a cationic Gemini surfactant (C₁₂-C₄-C₁₂) on the silica surface was also investigated by Zhou and Somasundaran [123]. A most recent study by Gao et al. showed that branched cationic Gemini surfactants (Gemini C₃ and C₆) form a more compact adsorption film on quartz surfaces instead of the formation of a bilayer [120]. This is due to the bending of the flexible spacer chain. All the investigations related to the adsorption of cationic Gemini surfactants mentioned above were conducted on a quartz surface; their adsorption on carbonates is rarely studied. Nanoparticles are also getting a lot of attention in the cEOR process [124–128]. The primary aim of this study is to investigate the adsorption mechanism of a newly synthesized cationic Gemini surfactant (GS12) onto different types of rocks.

The in-house synthesized surfactant contains two lipophilic tails and two hydrophilic head groups connected by a spacer. The chemical structure of GS12 was carefully designed to achieve a surfactant that is more suitable for high temperatures and high salinity environments. For instance, the amide group [-NH-C(O)-] in GS12 exhibits enormous

advantages compared to the conventional amine group such as better thermal stability, low CMC, low Krafft points, and less adsorption onto reservoir rocks, and enhanced surfactant performance under harsh reservoir environments. Similarly, the surface/interface properties can be improved by increasing the spacer length. Therefore, a spacer with 12 carbons was selected to achieve better physicochemical properties. The solubility of the surfactant in normal and high salinity brine is one of the most important properties of any surfactant selected for oilfield application. The solubility of GS12 in normal and high salinity brine was achieved by adding a proper number of ethoxy groups between lipophilic tails and lipophilic head groups. The resulting solubility enhancement was attributed to the hydrogen bonding between the oxygen of the ethoxy group (-CH₂-CH₂-O-) and hydrogen of the water molecule (H-O-H).

In this work, the adsorption mechanism of an inhouse synthesized cationic Gemini surfactant, which was engineered to be tolerant to high temperatures and salinities, on different types of rocks including sandstone and carbonate was investigated. A systematic approach has been employed to achieve the research goals. Mineralogical and elemental analyses of rock samples were carried out using XRD (X-Ray Diffraction) and XRF (X-Ray Fluorescence), respectively. Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy were employed to observe the changes in rock surface morphology and surfactant spectrum on the rock surface before, and after, adsorption, respectively. Static adsorption tests were conducted, and the supernatants were analyzed using HPLC (high-performance liquid chromatography) for the surfactant

concentration determination. Adsorption isotherm modeling was also performed using standard adsorption isotherms.

2.2 Materials and Methods

2.2.1 Gemini Surfactant

The chemical structure of the surfactant employed in this study is shown in Figure 5 [129]. Better surface properties and reduced absorption in rocks are obtained by increasing the spacer length [130]. The surfactant is quaternary ammonium (Br^- counter ions) Gemini surfactant with a longer spacer (C12) and a hydrophobic tail (C12), abbreviated as GS12. The unusual nature of this type of surfactant is the presence of ethoxy units in the chemical structure. The conventional quaternary ammonium Gemini surfactants without ethoxy groups show poor solubility in high salinity brine. However, this surfactant is compatible with high reservoir temperatures and exhibits excellent solubility in low salinity and high salinity brine due to the proper placement of ethoxy units between the hydrophilic head and hydrophobic tail group. In a recent publication [129], the surface properties of GS12 were measured by the Wilhelmy plate technique. The CMC and surface tension at the CMC (γ_{CMC}) in deionized water (DI) at 30 °C is 8.26×10^{-6} mol/L (15.5 ppm) and 39.55 mN/m, respectively. The structure of the micelles formed is expected to be rod-like, as Gemini surfactants with longer spacer form rod-like micelles (B. Sekhon, 2004). All experiments in this work were conducted in DI at ambient temperature.

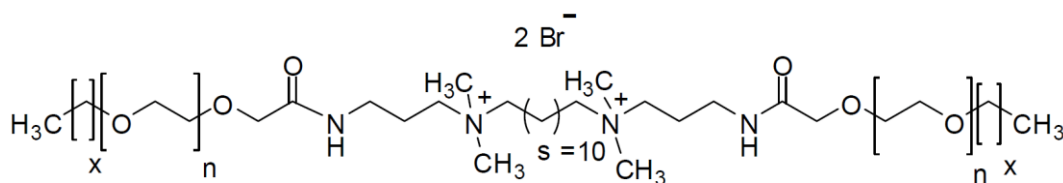


Figure 5: Structure of the quaternary ammonium Gemini surfactant (GS12) [129]

2.2.2 Adsorbents

The adsorbents used in this study are sandstone (Gray Berea, Scioto, and Berea Buff), calcite, and natural carbonate (Indiana limestone). Rock samples were crushed to powder and then sieved using a sieve shaker to ensure uniform particle size.

2.2.3 Rock Characterization

XRD (X-Ray Diffraction) and XRF (X-Ray Fluorescence) were conducted on the rock powder for the mineralogical and elemental analysis, respectively. XRD patterns of the samples were acquired utilizing Empyrean X-ray diffraction from Malvern Panalytical. XRF was performed on the adsorbents employing the M4-Tornado X-ray fluorescence from Bruker.

The FTIR analysis was conducted using the Inventio-S from Bruker. The spectrum wave number ranges from 400 to 4000 cm^{-1} . The signal-to-noise ratio and resolution were 55,000:1 and 1.4 cm^{-1} , respectively. After the adsorption experiments, the rock samples were dried at 60 °C before FTIR analysis. The rock morphology was studied using a Helios NanoLab G3 UC Scanning Electron Microscope at 15 kV accelerating voltage before and after static adsorption experiments.

2.2.4 Zeta Potential Measurement

Zeta potential (ζ) measurement was carried out using the Anton Paar Litesizer 500 having a size range of ~ 3.8 nm to ~ 100 μ m. Samples were left for at least 24 hours in vials and then centrifuged using a Hermle Z326K centrifuge at a minimum of 2000 rpm for 2 minutes to obtain a clear supernatant for zeta potential measurements. The average of twenty measurements was reported as the sample's zeta potential.

2.2.5 Static Adsorption Test

Static adsorption was determined using 1 g of powdered rock samples in 15 ml of surfactant solution with several concentrations (100 – 1500 ppm). The mixture was agitated on a linear shaker for 24 hours at room temperature. The mixtures were then centrifuged at a minimum of 3000 rpm for 30 min, and the supernatant was filtered using a 0.45 μ m filter. The supernatant liquid (filtrate) was analyzed for the residual surfactant concentration using HPLC (high-performance liquid chromatography). Static adsorption values were calculated using Eq. (12).

$$\Gamma_{\text{static}} = V_s \left(\frac{C^0 - C}{m_R} \right) * 10^{-3} \quad (12)$$

where Γ_{static} (mg/g-rock) signifies the extent of surfactant's static adsorption on the rock surface, C^0 (mg/L or ppm) and C (mg/L or ppm) are concentrations of the surfactant at pre and post-adsorption, respectively, V_s (mL) represents the surfactant solution volume, and m_R (g) is the mass of the powdered rock.

2.2.6 HPLC Analysis

The HPLC analyses were performed on an Agilent 1290 Infinity II equipped with a 1260 Infinity II evaporative light scattering detector (ELSD). The ELSD is considered a universal sensor for a variety of surfactants [131,132]. The residual surfactant concentration of GS12 after the static adsorption experiments on rock powder was obtained from a calibration curve that correlates the ELSD peak area with known concentrations of GS12. By correlating the GS12 concentration with the initial concentration it is possible to determine how much GS12 was adsorbed on the rock during the experiment. HPLC measurements were repeated three times and the average values were reported.

2.2.7 Adsorption Isotherm Models

Please see section 1.3 for the description of adsorption isotherm models.

2.3 Results and Discussion

2.3.1 Characterization of Crushed Rock Samples

2.3.1.1 XRD and XRF

XRD and XRF tests were conducted to analyze the constituents of powdered rock samples as shown in Table 3 and Table 4, respectively. Table 3 presents the mineralogy of each rock sample. Sandstone rock samples, such as Gray Berea, Scioto, and Buff Berea contain a significant amount of quartz along with clay contents and some impurities. On the other hand, carbonate rock samples, namely Indiana limestone contain 99.2% calcium carbonate along with some impurities. Moreover, calcite is 99.8% pure along with 0.2% silica. XRF

results (Table 4) show a significant amount of Si in sandstone and Ca in carbonates, which confirms the XRD results.

Table 3: XRD analysis of rock samples

Minerals	Gray Berea	Scioto	Buff Berea	Calcite	Indiana Limestone
Calcite, %	0	0.1	0.4	99.8	99.2
Dolomite, %	13.2	0	0.3	0	0.1
Quartz, %	40.2	59.5	48	0	0.2
Kaolinite, %	12.4	8.9	17.9	0	0.1
K-feldspar, %	19.1	9.9	18.2	0	0
Plagioclase, %	7	9.7	4.7	0	0
Illite, %	6.6	11.3	10.2	0	0.1
Alunite, %	0	0	0	0	0.3
Gypsum, %	0	0.1	0.1	0	0
Stishovite, %	0	0	0	0.2	0
Others, %	1.5	0.5	0.2	0	0

Table 4: XRF analysis of rock samples

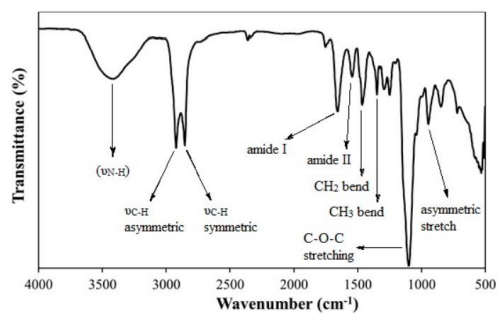
Element	Gray Berea	Scioto	Buff Berea	Calcite	Indiana Limestone
Mg, %	0.23	0.22	0	0.06	0.45
Al, %	3.57	5.89	3.72	0.29	0.3
Si, %	80.03	75.63	82.14	0.02	0.41
K, %	6.48	8.39	7.79	0.00	0
Ca, %	3.8	0.29	1.45	99.19	98.15
Mn, %	0.16	0.05	0.12	0.16	0.06
Fe, %	4.53	6.78	3.56	0.00	0.25
Ti, %	0.81	1.62	0.89	0.00	0.01
Others, %	0.4	1.13	0.32	0.27	0.37

2.3.1.2 FTIR Spectroscopy

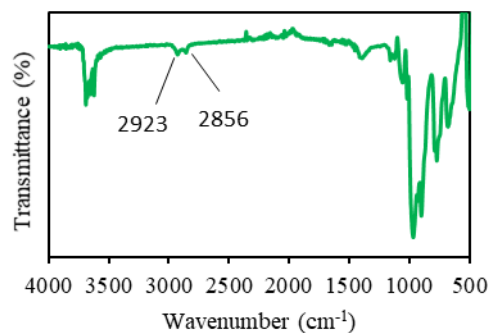
FTIR measurements were conducted on the different rock samples following the adsorption experiments of GS12 at 1000 ppm surfactant concentration. To analyze the post-adsorption effect, the FTIR was blanked using the corresponding pre-adsorption rock powders. Figure 6(a) shows the FTIR spectra of GS12 [129] while Figure 6(b-f) show FTIR data of Gray

Berea, Scioto, Buff Berea, Calcite, and Indiana limestone, respectively. The fingerprint region in an IR spectrum is defined as the area between the wavenumber of 400 cm^{-1} and 1500 cm^{-1} . It generally has a lot of peaks and noises, which makes identifying individual peaks difficult. Therefore, the functional group region (NH), as well as the aliphatic region (CH₂), were analyzed in this study.

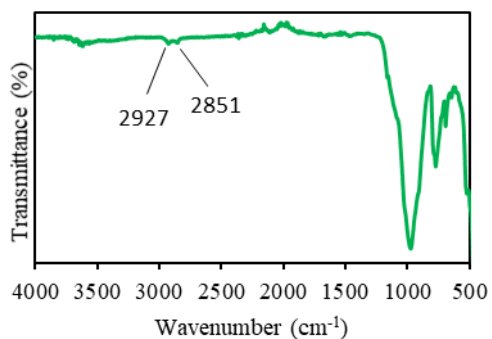
Figure 6(a) illustrates that the signals at 3412 cm^{-1} , 2855 cm^{-1} , and 2921 cm^{-1} correspond to the N-H stretching vibration ($\nu_{\text{N-H}}$) and symmetric ($\nu^{\text{s}}_{\text{C-H}}$) and asymmetric ($\nu^{\text{as}}_{\text{C-H}}$) vibrations of the CH₂ groups, respectively, in the functional group region [129]. As revealed by Figure 6(b-d), similar bands of $\nu^{\text{s}}_{\text{C-H}}$ and $\nu^{\text{as}}_{\text{C-H}}$ were seen in Gray Berea, Scioto, and Buff Berea, respectively, consistent with GS12 spectra. On the other hand, bands of $\nu^{\text{s}}_{\text{C-H}}$ and $\nu^{\text{as}}_{\text{C-H}}$ were not observed in the case of carbonates (calcite and Indiana limestone) as shown in Figure 6(e-f), respectively. However, a band of $\nu_{\text{N-H}}$ was found in the zoomed view of Figure 6(e-f) for calcite and Indiana limestone, respectively, which shows a little amount of GS12 adsorption. Table 5 presents the values of $\nu_{\text{N-H}}$, $\nu^{\text{s}}_{\text{C-H}}$, and $\nu^{\text{as}}_{\text{C-H}}$ peaks found in the rock samples due to surfactant adsorption.



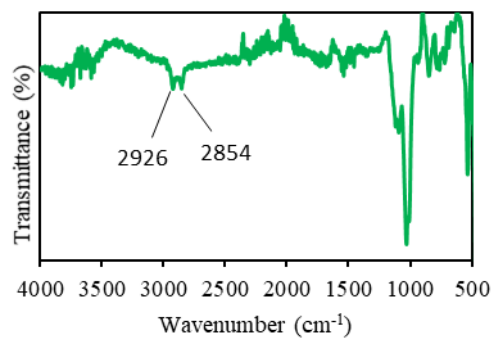
(a) FTIR spectra of GS12 [129]



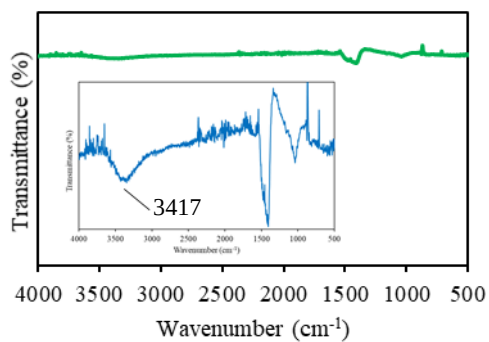
(b) Gray Berea



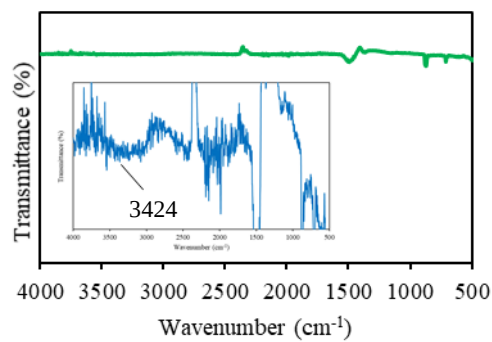
(c) Scioto



(d) Buff Berea



(e) Calcite



(f) Indiana limestone

Figure 6: FTIR spectra for (a) GS12 [129], (b) Gray Berea, (c) Scioto, (d) Buff Berea, (e) calcite, and (f) Indiana limestone

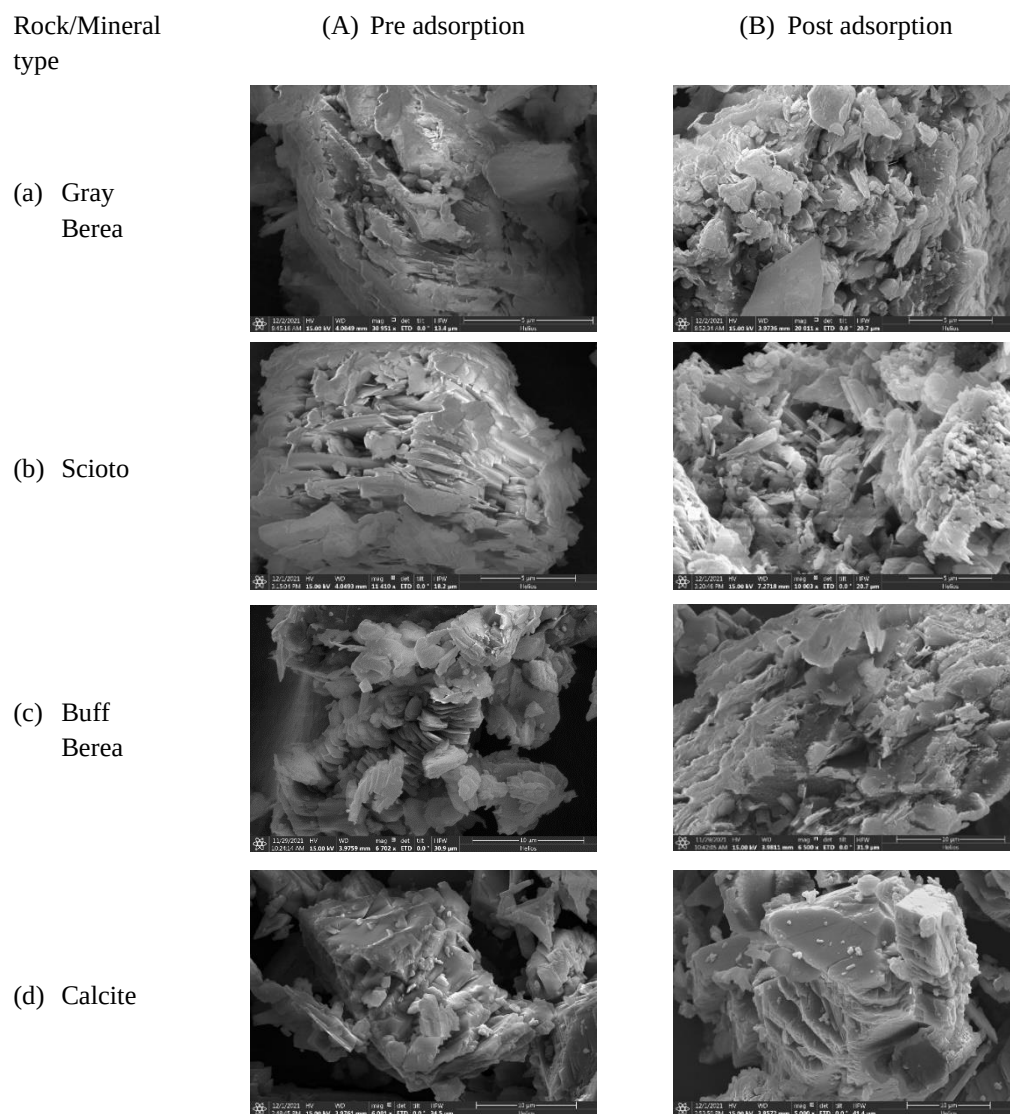
Table 5: FTIR spectral data of all samples

Sample	$\nu_{\text{N-H}} (\text{cm}^{-1})$	$\nu^{\text{s}}_{\text{C-H}} (\text{cm}^{-1})$	$\nu^{\text{as}}_{\text{C-H}} (\text{cm}^{-1})$
GS 12 [129]	3412	2855	2921
Gray Berea	-	2856	2923
Scioto	-	2851	2927
Buff Berea	-	2854	2926
Calcite	3417	-	-
Indiana Limestone	3424	-	-

2.3.1.3 SEM Microscopy

SEM examination of the microscopic morphology of the rock surfaces before and after the static adsorption experiments. This analysis only allows enlarged observation of the localized area found on the surface of the particles and cannot encompass the whole surface of particles present in the samples. However, locations showing particles of similar dimensions and shapes (approximately) were selected to investigate changes in surface morphology as a result of adsorption. The analyzed samples were treated at 1000 ppm for static adsorption; all SEM micrographs are presented in Figure 7. Figure 7A(a-c) show the pre-adsorption SEM observations for Gray Berea, Scioto, and Buff Berea, respectively. All sandstone rock samples show smooth surface and lamellar structure before adsorption. Figure 7B(a-c) present post adsorption SEM images of those samples. After GS12 adsorption, the surface turned rougher, and floc emerged. This suggests that GS12 was adsorbed on the sandstone rock samples, altering the surface morphology and resulting in loss of surfactant concentration. On the other hand, no significant changes were observed in the morphology of the carbonate group (calcite and Indiana limestone) before and after

adsorption as depicted in Figure 7A(d-e) and Figure 7B(d-e), respectively, which suggests low adsorption of GS12 onto those samples. Static adsorption results in this study also showed maximum surfactant adsorption of ~ 1 mg/g-rock in both calcite and Indiana limestone.



(e) Indiana
Limestone

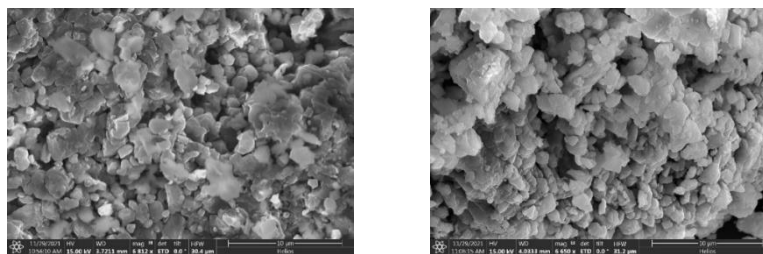


Figure 7: (A) Pre adsorption SEM images and (B) Post adsorption SEM images for (a) Gray Berea (5 μ m), (b) Scioto (5 μ m), (c) Buff Berea (10 μ m), (d) calcite (10 μ m), and (e) Indiana limestone (10 μ m).

2.3.2 Surface Charge of Crushed Rock Samples

The rock surface charge is a key parameter to investigate adsorption mechanisms. The Zeta potential of all rock samples suspended in deionized water was determined as shown in

Figure 8. An average of twenty measurements has been reported. The pH values shown in Figure 8 were not adjusted with either acid or base, which implies the natural interactions between aqueous solution and rock surface. The net negative charge in DI water found in sandstone rocks before static adsorption experiments as shown in

Figure 8 are mainly due to the presence of silica and clay particles. Figure 8 shows that all sandstone rock samples exhibit high pH values ($\sim$ 7 to 8) when suspended in DI water. These findings are consistent with past studies, that sandstone is negatively charged above pH 2–3 [133,134]. On the other hand, both calcite and Indiana limestone also showed negative zeta potential when suspended in DI water, which is in agreement with the literature [135–137]. The possible reasoning for the slight negative charge is the presence of impurities such as quartz and/or clays. The magnitude of the zeta potential in Indiana

limestone was found to be slightly higher than that of calcite because of its higher content of silica and clay minerals. Some researchers assume that calcite dissolution may be attributed to the negative zeta potential [138,139]. The sandstone rock samples are more negatively charged in comparison with carbonate rocks because of very high content of quartz. Similar studies have been reported in the literature, i.e., natural carbonates carry a slight negative charge [16,108,140,141]. In general, carbonate rocks are positively charged, but the influence of silica impurities and clay particles may alter the surface chemistry of carbonates, which should not be ignored in surfactant adsorption studies.

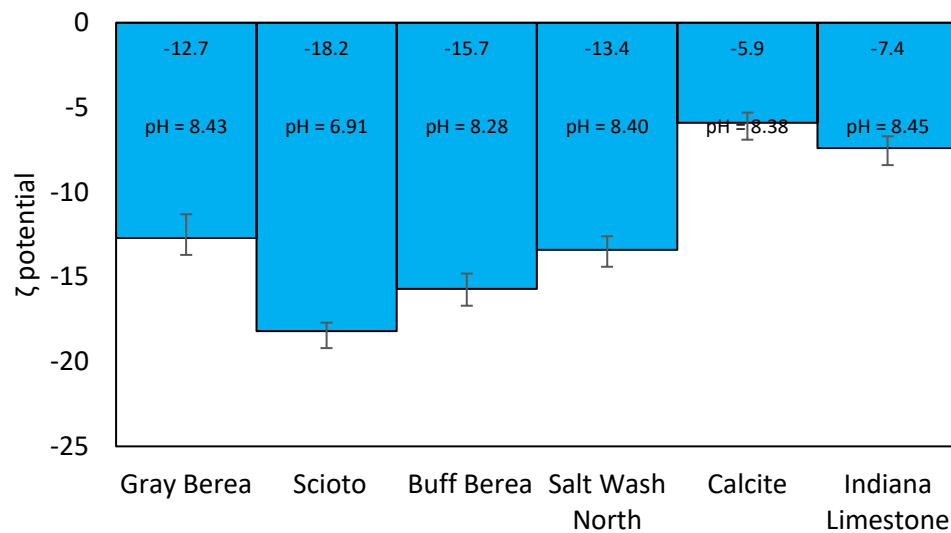


Figure 8: Zeta potential of all rock samples in deionized water. Data points show pH values and the average of twenty measurements of zeta potential.

2.3.3 Adsorption Mechanism of GS12 in Various Rocks

2.3.3.1 Static Adsorption

Figure 9 shows static adsorption of cationic GS12 onto several rocks, namely, Gray Berea, Scioto, Buff Berea, calcite, and Indiana limestone, as a function of equilibrium concentration. It is obvious that adsorption in all rocks increases with the increase in surfactant concentration until saturation is reached, after which an adsorption plateau is observed. The type of electrostatic attraction between the cationic GS12 and the negative sites of the rocks (sandstone and carbonate) constitutes the adsorption mechanism. Sandstone rock samples (Gray Berea, Scioto, and Buff Berea) exhibited a large amount of adsorption as compared to carbonate rocks (calcite and Indiana limestone) because of the presence of a higher percentage of silica and clay minerals (higher density of negative charges). The surfactant adsorption was observed to increase until a concentration of ~500 ppm whereafter an adsorption plateau was observed in all rock samples. The highest amount of adsorption (~9 mg/g-rock) seen in Scioto is due to the rock's relatively large content of quartz (59.5%) and Illite (11.3%). Gray Berea and Buff Berea exhibited similar behavior, reaching an adsorption plateau at ~4 mg/g-rock.

It is assumed that a small presence of silica and/or clay minerals in carbonates resulted in the adsorption of cationic GS12. However, the amount adsorbed was very low as compared to that in sandstone. This low adsorption level is attributed to the repulsive force between the positively charged surfactant head groups and calcium cations present in carbonates. The adsorption plateau in both calcite and Indiana limestone was observed at around 1

mg/g-rock, but it was slightly higher in the natural carbonate (Indiana limestone) than in calcite due to the presence of larger silica content and clay minerals. The adsorption of cationic surfactants, such as cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) onto natural carbonates due to silica impurities has been reported in the literature [16,108]. It can thus be deduced that significant adsorption of GS12 may occur in carbonate rocks with a large silica and clay content. As shown in Table 6, the adsorption level of cationic GS12 on different rocks was in the order of Scioto > Buff Berea > Gray Berea > Indiana Limestone > Calcite.

Figure 10 illustrates this study's proposed mechanism of GS12 adsorption onto sandstone and carbonate substrates. The schematic on the left shows the non-interdigitated bilayer in sandstone, whereas an interdigitated bilayer is assumed to be formed in carbonates (right schematic). The surfactant adsorption on a surface having a monolayer with all surfactants heads up would be similar to that of fully interdigitated surfactants alternating with head up and down [142]. The development of a fully developed bilayer on the sandstone surface, as opposed to an interdigitated bilayer on the carbonate surface, is explained by a very high density of negative charges on the former. Self-assembling of solid-supported cationic Gemini surfactant aggregates into interdigitated bilayer stacks has been revealed using electron density profiles calculations along the normal to the bilayers [143]. Mivehi et al. conducted an analogous study on the adsorption of cationic Gemini surfactants onto silica and gold in which the formation of an interdigitated bilayer on gold and a non-interdigitated double layer on silica was proposed [142]. Double-tailed surfactants, namely phospholipids, may also form an interdigitated bilayer [144,145]. A most recent study

demonstrated the formation of the interdigitated bilayer of cationic Gemini surfactant on nanoparticles [146].

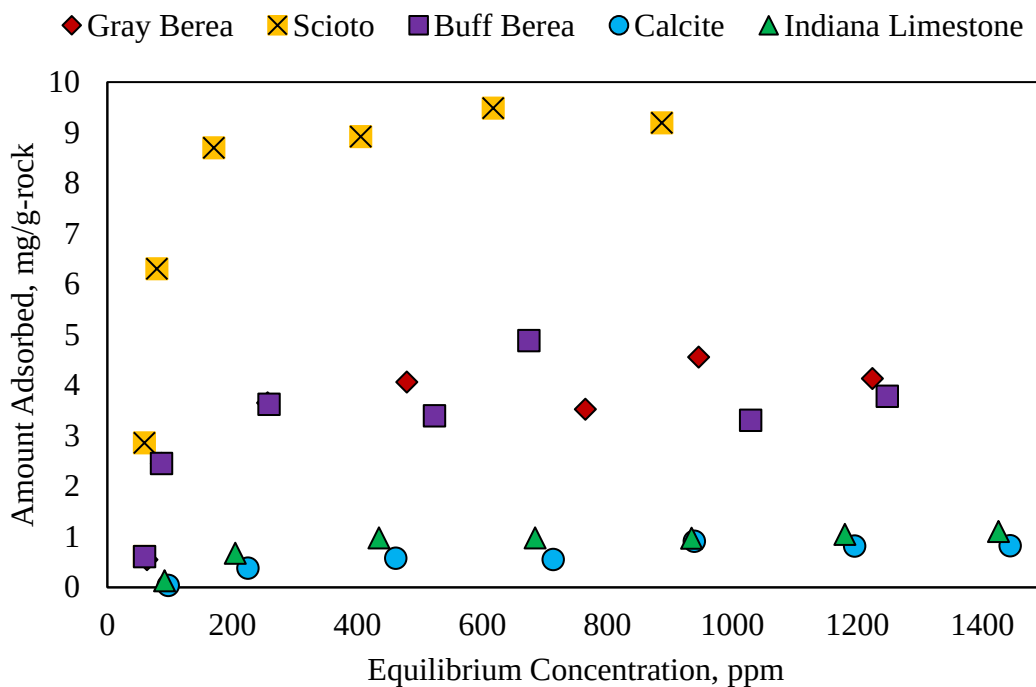


Figure 9: Single measurement of static adsorption of cationic GS12 onto different crushed rocks

Table 6: Range of adsorbed amount for cationic GS12 in the plateau region

Category	Substrate	Adsorbed amount in the plateau region, mg/g-rock
Sandstone	Gray Berea	3.52 - 4.55
	Scioto	8.69 – 9.48
	Buff Berea	3.31 – 4.88
Carbonate	Calcite	0.89 – 0.90
	Indiana Limestone	0.97 - 1.11

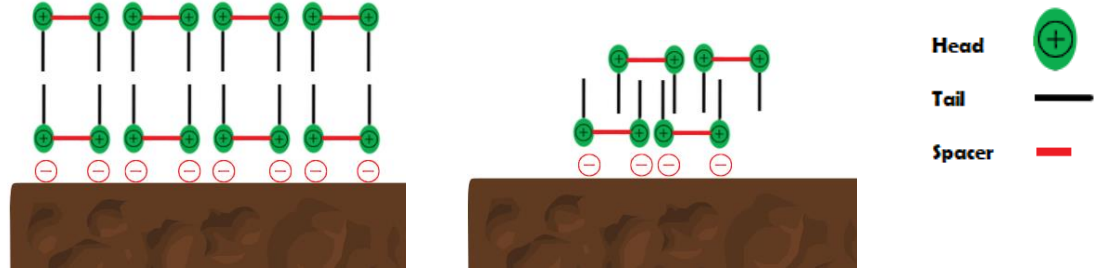


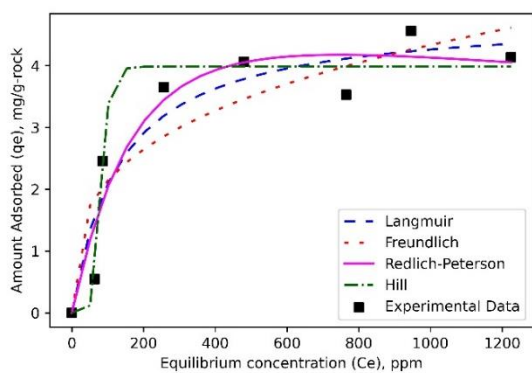
Figure 10: Proposed GS12 adsorption mechanism. Left, non-interdigitated bilayer in sandstone; right, interdigitated bilayer in carbonate

2.3.3.2 Adsorption Isotherm Modeling

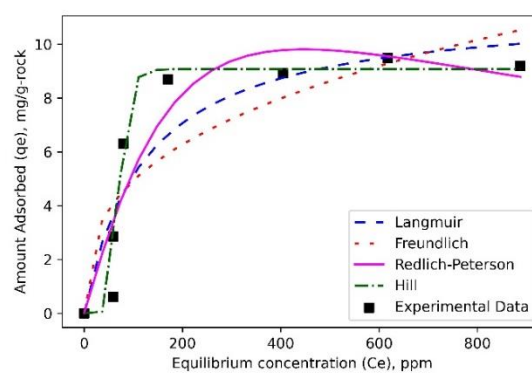
For further investigation, the GS12 adsorption behavior was studied using isotherm modeling. Langmuir, Freundlich, Redlich-Peterson, and Hill adsorption models were used to fit the adsorption data. A non-linear, least-squares, curve-fitting technique was employed using the Levenberg-Marquardt algorithm. Figure 11 (a-e) presents the curve fitting results for Gray Berea, Scioto, Berea Buff, calcite, and Indiana limestone, respectively, using Langmuir, Freundlich, Redlich-Peterson, and Hill adsorption models. Error metrics of mean absolute error (MAE), mean squared error (MSE), and coefficient of determination (R^2) were used to evaluate the performance of the adsorption models. Model parameters and error metrics for each model are reported in Table 7. The highest R^2 and the lowest MAE and MSE were obtained using Hill adsorption isotherm for all rock types. This suggests that the adsorption of GS12 onto different rocks is a cooperative phenomenon and the substrates are homogenous (fine rock powder). In addition, n_H is greater than unity for all cases, which shows that binding has positive cooperativity.

In the case of sandstones (Gray Berea, Scioto, and Berea Buff), better error metrics (high R^2 and low error) were obtained with the Redlich-Peterson model as compared to Langmuir and Freundlich. This validates the non-interdigitated bilayer adsorption of cationic GS12 onto powdered sandstone rock samples. In contrast, better curve fitting was obtained using both Langmuir and Redlich-Peterson isotherms in the case of carbonates (Calcite and Indiana limestone). This supports the interdigitated bilayer adsorption of GS12 in powdered carbonate rocks. Recalling that the surfactant adsorption on a substrate having a fully interdigitated bilayer with alternating head up and down would be similar to that of a monolayer with all surfactants head up [142]. Interdigitated bilayer adsorption results in a lower amount of adsorption as compared to non-interdigitated bilayer adsorption. This is consistent with the well-known fact that cationic surfactants adsorb more on sandstones than on carbonates [92].

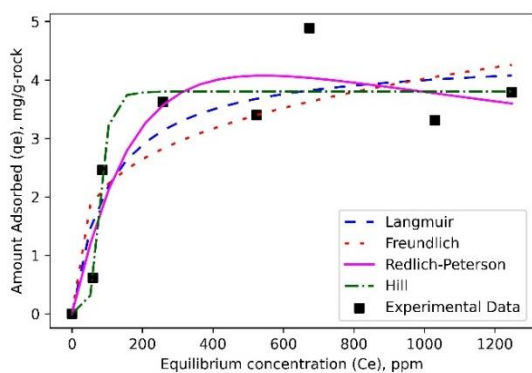
Adsorption of cationic GS12 in carbonates was found to be reasonably low (~ 1 mg/g-rock), confirming the potential of this novel cationic Gemini surfactant as a candidate for the cEOR in those rocks. However, this is not the case with sandstones where adsorption was found significantly high. The maximum adsorption value found in sandstone was around 9 mg/g-rock in Scioto. Alternatively, anionic surfactants are preferred in sandstone reservoirs in cEOR due to a lower degree of adsorption [9,92,101]. Although cationic GS12 is not desirable in sandstone reservoirs for cEOR techniques, a recent study showed that the adsorption layer formed by this type of surfactant on a rock surface can be utilized in inhibiting the reaction rate between acid and rock in reservoir stimulation [147]. Therefore, GS12 can be used in several oilfield applications.



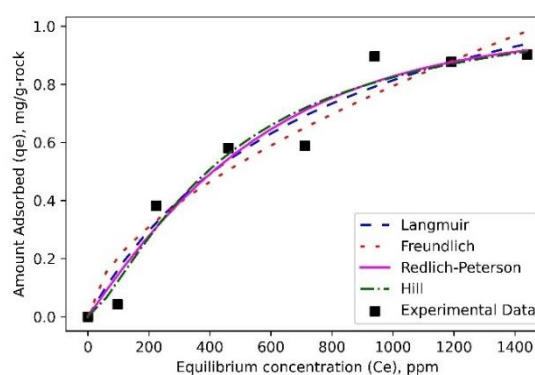
(a) Gray Berea



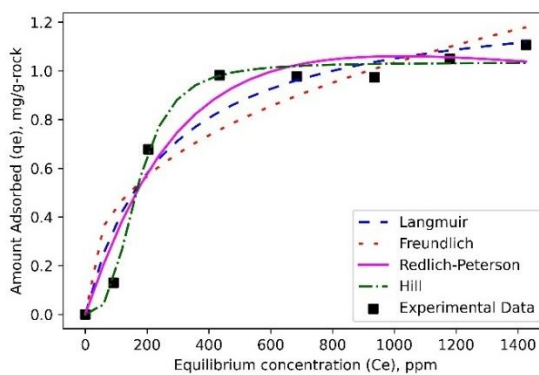
(b) Scioto



(c) Berea Buff



(d) Calcite



(e) Indiana Limestone

Figure 11: Adsorption isotherm modeling for all rocks

Table 7: Adsorption isotherm parameters and error metrics for all rocks

Rock type		Langmuir		Freundlich		Redlich-Peterson		Hill	
Gray Berea	Model parameters	K_L	0.0076	K_F	0.5204	K_R	0.026	q_{SH}	3.9861
		q_m	4.8181	n	3.2598	α_r	0.0008	n_H	7.5186
						β_r	1.2734	K_D	2.23E+14
	Error metrics	MAE	0.4305	MAE	0.5458	MAE	0.359	MAE	0.1991
		MSE	0.2667	MSE	0.4277	MSE	0.2271	MSE	0.0849
		R^2	0.8969	R^2	0.8347	R^2	0.9123	R^2	0.9672
Scioto	Model parameters	K_L	0.0082	K_F	0.9953	K_R	0.0629	q_{SH}	9.0779
		q_m	11.3912	n	2.8779	α_r	0.0002	n_H	7.6395
						β_r	1.5359	K_D	1.45E+14
	Error metrics	MAE	1.1066	MAE	1.4626	MAE	0.9738	MAE	0.4133
		MSE	2.3284	MSE	3.3915	MSE	1.7683	MSE	0.3589
		R^2	0.8346	R^2	0.7591	R^2	0.8744	R^2	0.9745
Berea Buff	Model parameters	K_L	0.0095	K_F	0.6654	K_R	0.0248	q_{SH}	3.8019
		q_m	4.4191	n	3.8406	α_r	0.0003	n_H	5.9588
						β_r	1.4341	K_D	1.87E+11
	Error metrics	MAE	0.5336	MAE	0.6156	MAE	0.4475	MAE	0.2722
		MSE	0.3997	MSE	0.6044	MSE	0.2933	MSE	0.2018
		R^2	0.8348	R^2	0.7502	R^2	0.8787	R^2	0.9166
Calcite	Model parameters	K_L	0.0013	K_F	0.0139	K_R	0.0015	q_{SH}	1.091
		q_m	1.4446	n	1.7087	α_r	0.0001	n_H	1.3821
						β_r	1.389	K_D	4.54E+03
	Error metrics	MAE	0.0576	MAE	0.0701	MAE	0.0541	MAE	0.0507
		MSE	0.0052	MSE	0.0076	MSE	0.0049	MSE	0.0046
		R^2	0.9557	R^2	0.9351	R^2	0.9582	R^2	0.9609
Indiana Limest one	Model parameters	K_L	0.004	K_F	0.0794	K_R	0.0036	q_{SH}	1.0337
		q_m	1.3164	n	2.6917	α_r	0.0001	n_H	3.0766
						β_r	1.4042	K_D	7.00E+06
	Error metrics	MAE	0.0729	MAE	0.1075	MAE	0.0696	MAE	0.0258
		MSE	0.0105	MSE	0.0204	MSE	0.0075	MSE	0.0014
		R^2	0.9364	R^2	0.8766	R^2	0.9547	R^2	0.9918

2.4 Conclusions

In this study, the adsorption mechanism of a novel, cationic, Gemini surfactant (GS12) onto different sandstone and carbonate rock samples was investigated using static adsorption experiments, and adsorption isotherm modeling, FTIR, and SEM studies. The following are the main conclusions:

1. Adsorption of GS12 on sandstone rocks was found significantly higher than that of carbonates. This is because the density of negative charges is very high in sandstone rock than in carbonates.
2. The presence of a little quantity of impurities, such as silica and clay minerals in carbonates may lead to the adsorption of cationic GS12.
3. The variation in the quantity of the surfactant adsorbed is believed to be due to the adsorbed layer structure. It is proposed that an interdigitated bilayer is formed on carbonate rocks, whereas a non-interdigitated bilayer in sandstone rock samples.
4. Better error metrics were obtained using Redlich-Peterson isotherm in sandstone, whereas both Langmuir and Redlich-Peterson isotherm performed better in carbonates. All rocks follow the Hill model, depicting that the adsorption process is cooperative.
5. FTIR and SEM observations confirm the proposed adsorption behavior of the surfactant in both sandstone and carbonate rock samples.
6. The maximum adsorbed amount on different rocks was in the order Scioto > Buff Berea > Gray Berea > Indiana Limestone > calcite.

CHAPTER 3

STATIC ADSORPTION OF A NOVEL CATIONIC GEMINI SURFACTANT: A MINERALOGICAL STUDY

Abstract

Surfactants are deemed an advantageous chemical in enhanced oil recovery (EOR) because of their potential of lowering the interfacial tension and modifying the wettability. However, the surfactant loss by adsorption on the rock surface is one of the major shortcomings of surfactant-based flooding techniques. The static adsorption of an inhouse synthesized cationic Gemini surfactant (GS12) is investigated as a function of mineral type, salinity, and concentration. Both clay and non-clay minerals have been examined. Surfactant adsorption was increased continuously by the increase of concentration till 1000ppm and then an adsorption plateau was observed in all minerals except montmorillonite and kaolinite. It was found that clay minerals may cause more detrimental effects as compared to silicate minerals and carbonate minerals showed the least adsorption. The maximum amount of surfactant adsorbed on the mineral surface was in the order of montmorillonite > kaolinite > Illite > K-feldspar > quartz > dolomite > calcite. Lower adsorption of GS12 was detected because of the presence of multivalent ions (Ca^{2+} and Mg^{2+}). Methylene blue (MB) has been revealed as a novel adsorption inhibitor for

cationic GS12 in carbonate formation. MB adsorbs on the negative binding sites of both clay and non-clay minerals. Therefore, an electrostatic repulsion takes place between the cationic dye (MB) and cationic GS12, leading to the reduction of GS12 adsorption on the rock/mineral surface. Only the addition of 100ppm of MB in the surfactant solution at the highest concentration (1500ppm) reduced GS12 adsorption on quartz surface to 0.67 mg/g-rock. This study will help in designing the chemical EOR process using GS12 on carbonate formation containing silica and clay minerals as impurities.

3.1 Introduction

Surfactants have been used in various domains, namely, pharmaceuticals, industrial and household cleaning, paper, plastics, food, textiles, petroleum industry, and so on [148–151]. In the oil and gas industry, surfactants are mainly used in enhancing oil recovery by either decreasing the interfacial tension between oil and water and/or altering the wettability. One of the main challenges associated with surfactant-based chemical enhanced oil recovery (cEOR) processes is the surfactant adsorption on the rock surface [151,152]. An undesirable amount of surfactant adsorption may lead to an uneconomical and inefficient cEOR process. Therefore, surfactant adsorption must be reduced to prevent chromatographic separation of the employed surfactants, leading to an effective cEOR process.

Several factors affect surfactant adsorption, such as surfactant charges, mineral type, salinity, temperature, pH, etc. [6,92,153,154]. The well-documented mechanism behind the adsorption of ionic surfactants is the electrostatic attraction between the opposite charges

of surfactant and the reservoir rock surface [9,92]. Reservoir rocks, such as sandstone and carbonates consist of a variety of minerals. Each mineral carries a specific charge(s). The composition of sandstone reservoirs depends on the sedimentology of the reservoir formation and usually contains a large portion of quartz (silica, SiO_2) and a little quantity of other silicate and carbonate minerals [16,140]. The quartz crystal comprises silica tetrahedra with the silicon ions positioned in the center and the oxygen ions sited at the corner [155]. The silica tetrahedron has a net charge of -4 . Another most famous silicate mineral is K-feldspar which consists of a ring of four tetrahedral units (three silicon tetrahedral and one aluminum tetrahedron) [155]. On the other hand, carbonate reservoirs mainly contain calcite (CaCO_3), magnesite (MgCO_3), or dolomite ($\text{CaMg}(\text{CO}_3)_2$) [138,156,157]. They may contain a little amount of silicate and clay minerals as well. Montmorillonite, Kaolinite, and Illite are the most common types of clay minerals usually found in both sandstone and carbonates. The presence of clay minerals may lead to significant surfactant adsorption in both sandstone and carbonate reservoirs [16,107,158]. An understanding of clay minerals' structure is essential to investigate the surfactant adsorption mechanism. Generally, clay minerals are made up of two fundamental crystal sheets (silica tetrahedral sheet and alumina octahedral sheet) arranged differently [159]. The basic structural unit of montmorillonite consists of an alumina octahedral sheet sandwiched between two silica tetrahedral sheets to form a single layer and hence known as a 2:1 mineral. Montmorillonite mineral is formed by many such structural units joined together by van der Waals forces. It can accommodate oppositely charged molecules between the layers and that is why it is an expandable clay mineral. Kaolinite is a 1:1

mineral comprised of one silica tetrahedral sheet and one alumina octahedral sheet. The structural units of Kaolinite minerals are joined together by a hydrogen bond. The basic structural unit of Illite is similar to that of montmorillonite and hence it is also a 2:1 mineral. There is an isomorphous substitution of silicon ions by aluminum ions. The potassium ions occupy the space between the basic structural unit. Unlike montmorillonite, the clay minerals kaolinite and Illite are non-expandable [160].

The surfactant used in the cEOR process must be compatible with the harsh reservoir conditions, such as high temperature and high salinity with the minimum adsorption capacity. Several studies have been conducted on surfactant adsorption [151,152,154,161–166]. The newly synthesized ethoxylated quaternary ammonium Gemini surfactant (GS12) showed excellent results in terms of solubility at 214,000 ppm salinity and 90 degrees Celsius temperature [129]. Deng et al. conducted a study on the wettability alteration of carbonate rock using a series of cationic Gemini surfactants [115]. The findings show that the inclusion of the phenyl ring in the spacer improves the wettability alteration. A study was conducted to investigate the physicochemical properties of a series of cationic Gemini surfactants [112]. It was found that ultra-low IFT was obtained using a longer spacer length. Therefore, a spacer with 12 carbons was chosen to attain better physicochemical properties of GS12. The effect of adsorption of a non-ionic surfactant on different minerals has been studied [166]. It was shown that the adsorption capacity of surfactant depends on the mineral content in the order of illite > feldspar > montmorillonite > kaolinite. Khan and co-authors recently studied the dynamic adsorption of a Gemini surfactant on Indiana limestone [167]. The study shows that higher surfactant retention was obtained at higher

surfactant concentration and lower flow rates. The reported surfactant retention was 0.42 mg/g-rock. A most recent study shows the adsorption mechanisms of a cationic Gemini surfactant onto different categories of rocks, including sandstone and carbonate [164]. It was reported that an interdigitated bilayer and a non-interdigitated bilayer were formed on carbonate and sandstone rock samples, respectively. Most of the adsorption studies of Gemini surfactants were conducted on either sandstone or carbonate. Since a reservoir rock contains different types of minerals, therefore, the influence of individual minerals needs to be investigated. Herein, the adsorption behavior of a novel cationic Gemini surfactant onto different minerals has been studied. The studied minerals are calcite, dolomite, quartz, K-feldspar, montmorillonite, kaolinite, and illite. Furthermore, methylene blue (MB) – a well-known cationic dye has been used to reduce the GS12 adsorption. MB is easily available and has been widely used in various fields, such as dyeing, paint, biomedical applications, textile, pharmaceutical, paper, printing, medicine, and food industries [168–172]. In the oil and gas industry, it has been used for rock swelling estimation, a tracer for anionic surfactants, titration for surfactant concentration determination, and so on [173–175]. To the best of our knowledge, its use as an adsorption inhibitor in the cEOR process has not been investigated. In addition, soft computing tools were applied to predict the surfactant adsorption in terms of mineral composition, maximum adsorption capacity, and concentration of Gemini surfactant.

Firstly, the rock characterization was carried out using XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy). The Zeta potential of minerals in an aqueous solution was found to determine the net surface charge of the minerals in an aqueous solution. Static

adsorption tests were conducted, and the supernatants were examined utilizing high-pressure liquid chromatography (HPLC) to determine surfactant adsorption. The effect of salinity has been studied, including monovalent ions, divalent ions, and seawater. An interesting effect of methylene blue as an adsorption inhibitor has been presented in this research. Lastly, the application of soft computing tools has been presented.

3.2 Materials and Methods

3.2.1 Cationic Gemini Surfactant (GS12)

The chemical structure of the Gemini surfactant (GS12) used in this study is shown in Figure 12. GS12 is compatible with a high temperature and high saline (HTHS) environment and has a very low critical micelle concentration (CMC), equal to ~15.5ppm [129]. The details of the chemical structure elucidation of this surfactant can be found in our preceding report [129,164].

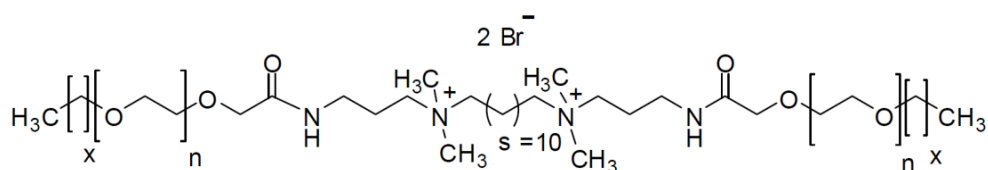


Figure 12: Structure of the cationic Gemini surfactant (GS12) [129]

3.2.2 Adsorbents

Adsorbents employed in this study are minerals, including white quartz, calcite, dolomite, K-feldspar, K10-montmorillonite, kaolinite, and Illite. The chemical formula of the employed minerals is shown in Table 8.

Table 8: Chemical formula of minerals

Mineral	Chemical formula
Calcite	CaCO_3
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
White quartz	SiO_2
K-Feldspar	KAlSi_3O_8
K10- Montmorillonite	$(\text{K}_{0.25} \text{Na}_{0.118} \text{Ca}_{0.022})(\text{Al}_{1.06} \text{Fe}_{0.206} \text{Mg}_{0.166})(\text{Si}_{7.39} \text{Al}_{0.61})\text{O}_{20} (\text{OH})_4$
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Illite	$(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{AL})_4\text{O}_{10}[(\text{OH})_2, \text{H}_2\text{O}]$

3.2.3 Rock Characterization

XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy) were carried out for the minerals to determine the mineral composition and surface morphology. Empyrean X-ray diffraction from Malvern Panalytical was used to acquire XRD patterns. Helios NanoLab G3 UC Scanning Electron Microscope at 20 kV accelerating voltage was used for SEM analyses.

3.2.4 Preparation of Surfactant Solutions and Synthetic Seawater

A standardized 1000 mL container was used to make the stock surfactant solution. 2g of surfactant was dissolved in 1000ml of deionized water using a magnetic stirrer to make a 2000ppm concentrated surfactant solution. The stock solution was then diluted to different

desired concentrations (1750ppm, 1500ppm, 1250ppm, 1000ppm, 750ppm, 500ppm, 250ppm, and 100ppm). Synthetic seawater was made using the composition displayed in Table 9.

Table 9: Seawater composition

Salt	mg/L (ppm)
NaHCO ₃	165.25
Na ₂ SO ₄	6339.02
NaCl	41172.35
CaCl ₂ .2H ₂ O	2387.13
MgCl ₂ .6H ₂ O	17644.12
Sea water salinity	67707.86

3.2.5 Surface Charge Determination

The net surface charge of the minerals in an aqueous solution was determined using a zeta potential meter (ζ). The Anton Paar Litesizer 500 having a size range of ~ 3.8 nm to ~ 100 μ m was acquired for this purpose. Samples were shaken in a linear shaker for at least 24 hours in vials and then centrifuged using Hermle Z326K at a minimum of 3000 rpm for 3 minutes to achieve a clear supernatant.

3.2.6 Static Adsorption Experiments

Static adsorption tests were conducted using 1g of powdered rock/mineral samples in 15ml of surfactant solution at various concentrations. The rock-fluid mixture was made in 25ml vials and put in a linear shaker for 24hr to agitate at room temperature. After static adsorption, the surfactant solutions were centrifuged at a minimum of 3000 rpm for 30 minutes. After centrifugation, the liquid was filtered using a 0.45 μ m filter. The supernatant

liquid was examined for the equilibrium surfactant concentration using HPLC (high-performance liquid chromatography). Static adsorption can be determined using Eq. (13).

$$\Gamma_{\text{static}} = V_s \left(\frac{\Delta C}{m_R} \right) * 10^{-3} \quad (13)$$

where Γ_{static} is the amount of surfactant adsorbed on the rock surface in mg/g-rock, $\Delta C = C^0 - C$, C^0 and C are concentrations of the surfactant before and after adsorption, respectively in ppm, V_s shows the volume of the surfactant solution in mL, and m_R represents the mass of the powdered rock/mineral samples.

3.2.7 Soft Computing Tools

After generating the data set experimentally, soft computing tools were used to build the digital model for surfactant adsorption prediction. The error metric used in this study consists of R^2 and RMSE. The data set was divided into training and testing with a ratio of 80:20. XGBoost and Random Forest were utilized in the training data set to forecast the surfactant adsorption in terms of mineral composition, and maximum adsorption capacity, and surfactant concentration. The remaining 20% of the data set was employed to test the model. The hyperparameter tuning was carried out using K-fold cross-validation integrated with an exhaustive grid search technique as shown in Figure 13. In K-Fold cross-validation, the data set is divided into K segments: one segment is used for validation and the remaining K-1 segments are combined to be used for training purposes. This process is iterated K times, and the average error of each iteration is reported. In this way, each sample

in the dataset is being tested. This may help in reducing the overfitting issue in the training process. We have used 5 folds as demonstrated in Figure 13.

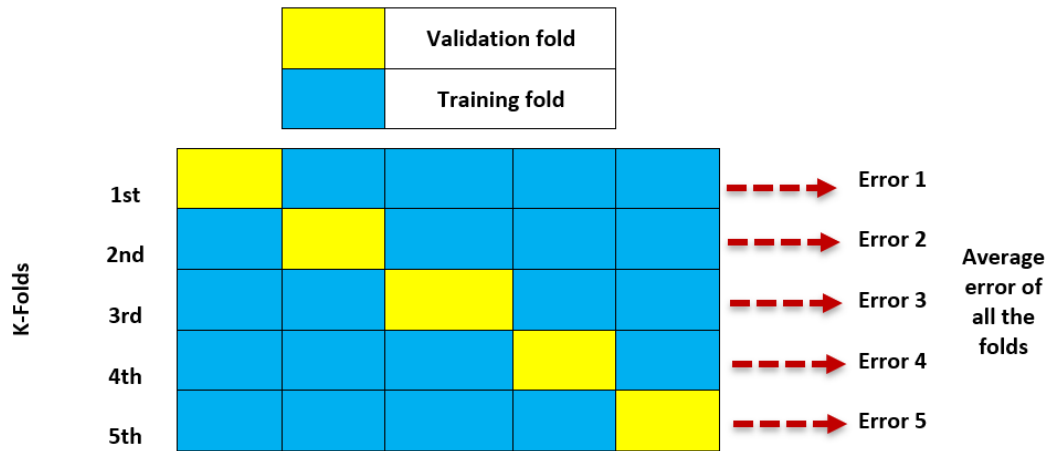


Figure 13: K-Fold cross-validation technique

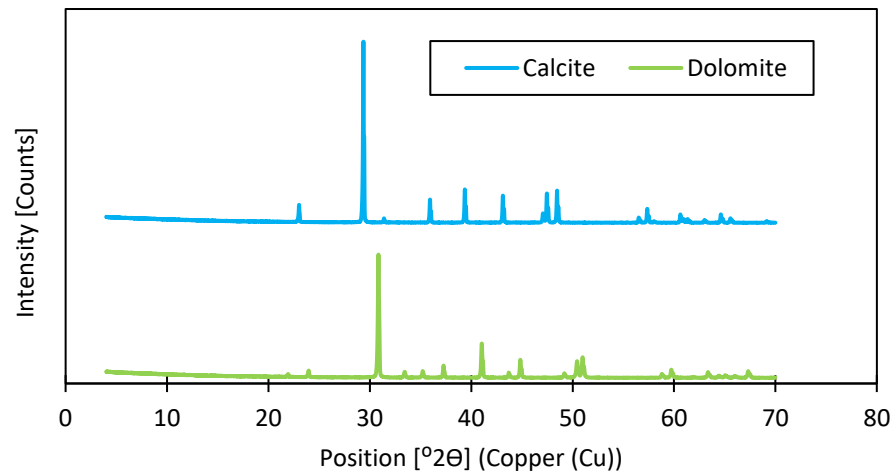
3.3 Results and Discussion

3.3.1 Characterization of Adsorbent Samples

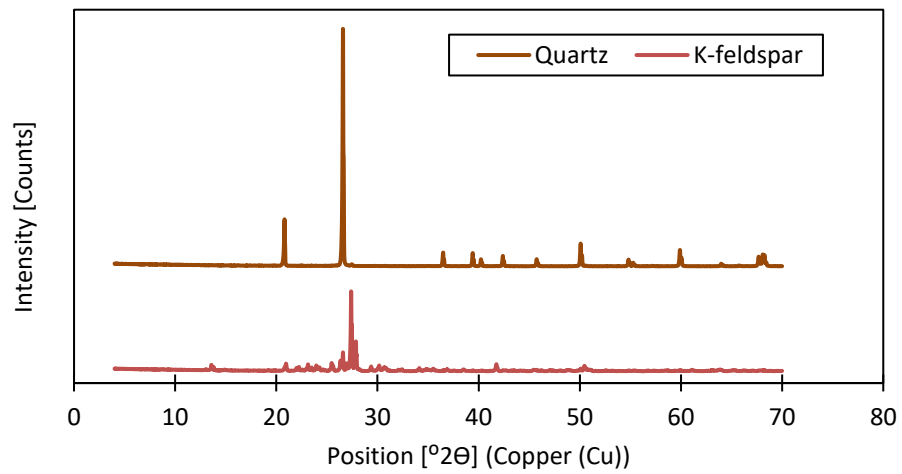
3.3.1.1 X-Ray Diffraction

X-Ray Diffraction (XRD) analysis was conducted on carbonate, silicate, and clay minerals as shown in Figure 14 (a), (b), and (c), respectively. The 2θ peaks at ~ 29.38 and ~ 30.87 correspond to calcite and dolomite, respectively as shown in Figure 14 (a). On the other hand, Figure 14(b) shows the peaks at $^{\circ}2\theta$ of ~ 26.6 and ~ 27.56 for quartz and feldspar, respectively. The 2θ peaks at ~ 19.82 , ~ 5.89 , and ~ 12.36 in the diffractogram are related to Illite, montmorillonite, and kaolinite, respectively as illustrated in Figure 14(c). The

XRD pattern of the Illite shows that it contains Illite clay mineral as a major phase along with quartz as a minor phase.



(a) Carbonate minerals



(b) Silicate minerals

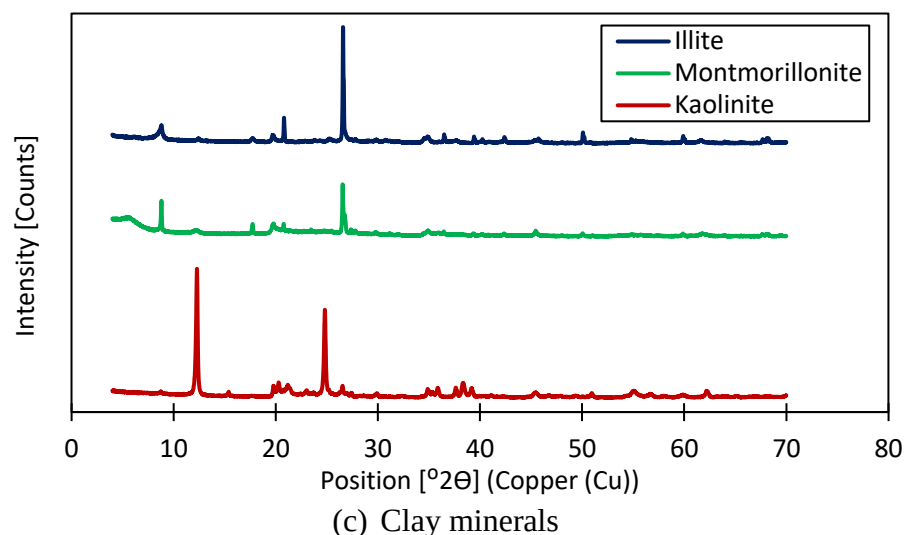


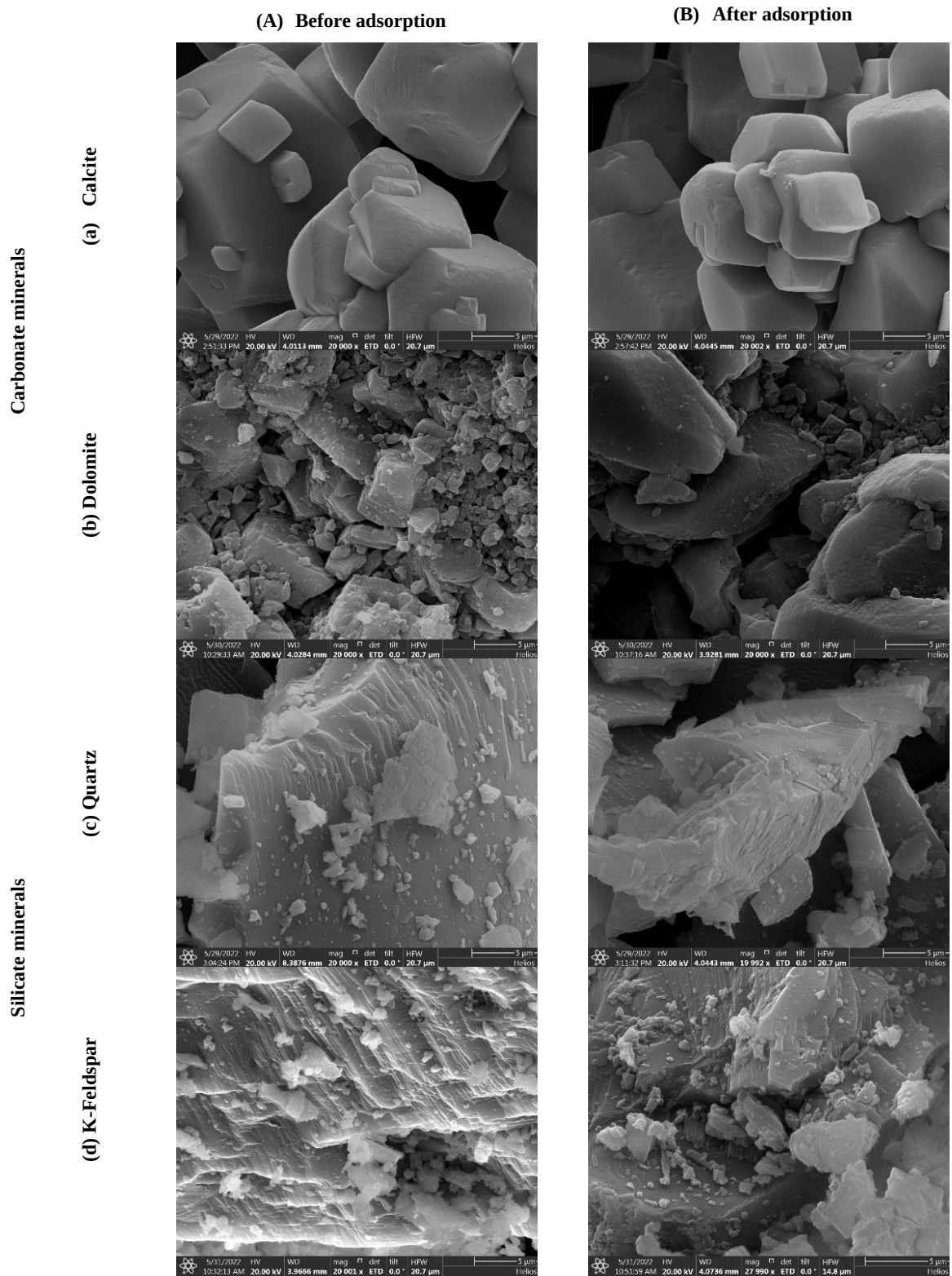
Figure 14: XRD peaks for (a) carbonate minerals, (b) silicate minerals, and (c) clay minerals

3.3.1.2 Scanning Electron Microscopy

SEM studies of minerals help in the analysis of surface characteristics, such as texture, morphology, and roughness. These properties impact the mineral surface's adsorption capacity and film thickness of the adsorbate particle [176]. Therefore, SEM micrographs were captured of all minerals before and after adsorption. These measurements were conducted at 20 kV and 5 μm resolution.

Figure 15A(a-d) and Figure 15B(a-d) show SEM micrographs of non-clay minerals (calcite, dolomite, quartz, and K-feldspar), before and after adsorption, respectively. Whereas Figure 15A(e-g) and Figure 15B(e-g) present SEM micrographs of clay minerals (montmorillonite, kaolinite, Illite), before and after adsorption, respectively. The SEM images show that the structure of non-clay minerals is less porous as compared to that of

clay minerals. Since calcite has negligible surfactant adsorption in this study, therefore, no change in the rhombohedral shape of calcite crystal was observed. Dolomite particles were found well sorted before and after adsorption. The quartz surface was not changed before and after chemical treatment using a surfactant. These findings show that the adsorption in these minerals was not significant as compared to others. K-feldspar SEM image shows a lamellar structure with a regular inclination in Figure 15A(d). The surface of K-feldspar after surfactant adsorption was found rough as displayed in Figure 15B(d). The SEM micrograph of montmorillonite shows a smooth surface and undulated flexible sheets before adsorption. Whereas kaolinite and Illite SEM images show tightly stacked layered structures before adsorption. After adsorption of GS12, the surface of montmorillonite, kaolinite, and Illite became rougher, and the number of pores was enhanced. Montmorillonite after the adsorption tests seems to be swollen because of its inherent expandable property upon interaction with water. The emergence of flocs is also visible in Figure 15B(e).



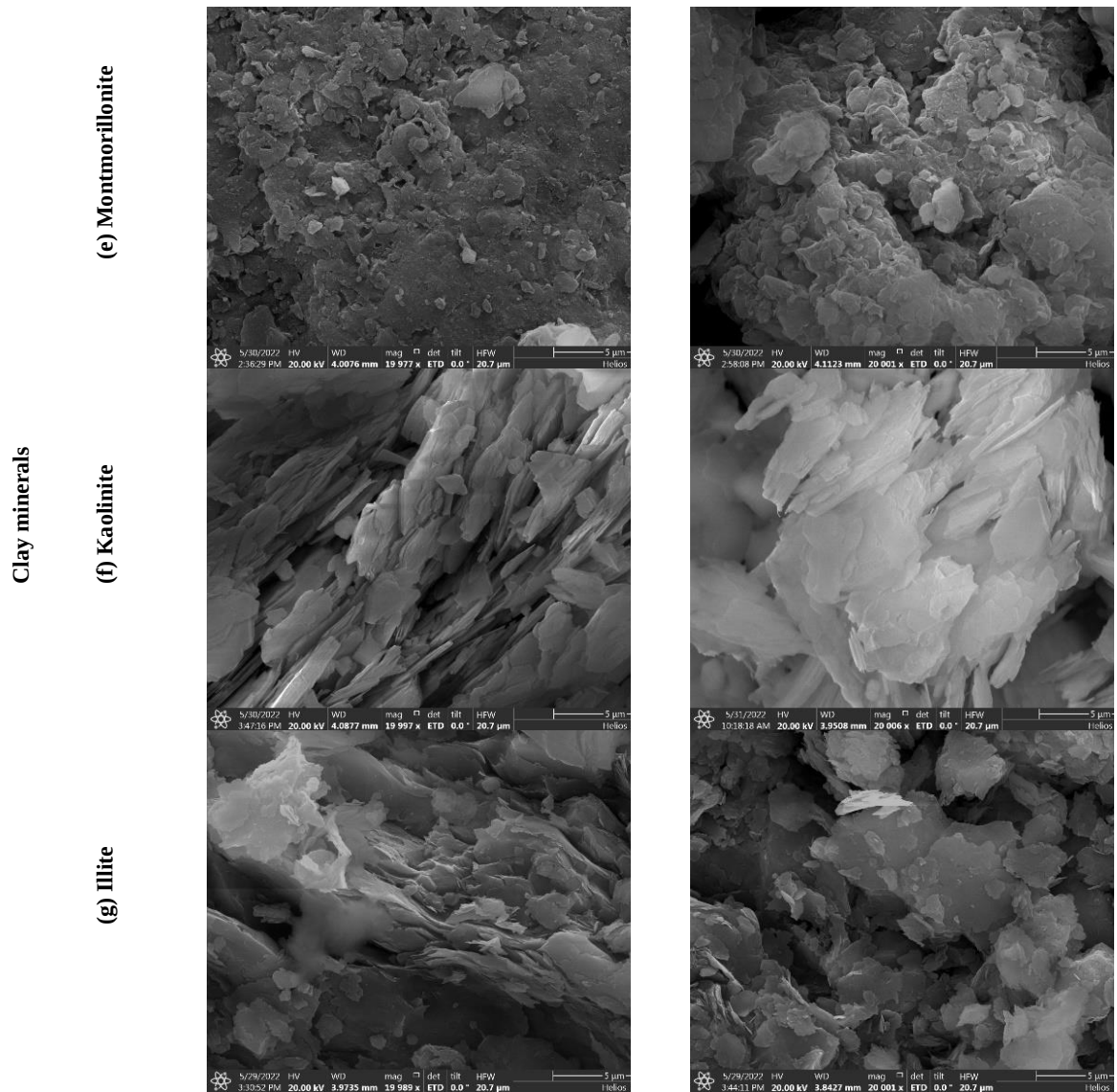


Figure 15: SEM analysis of all minerals before and after adsorption

3.3.2 Mineral Surface Charge

The rock surface charge is a crucial parameter that needs to be considered in adsorption studies. When a mineral particle is suspended in an aqueous solution, it obtains a surface charge owing to preferential dissolution or hydrolysis of surface species [156]. The zeta potential of all minerals suspended in deionized water (DI) was estimated, as shown in

Figure 16. The pH values displayed in Figure 16 were not tweaked with either acid or base, which suggests the natural interaction of minerals in the aqueous solution.

Figure 16(a) presents the net negative charge of non-clay minerals in DI water. The surface charge of calcite and dolomite (carbonate minerals) in water is supposed to be positive at a pH below ~9 [156,177]. But the carbonate minerals' surface charge can be altered by the concentrations of potential determining ions, namely, CO_3^{2-} , Ca^{2+} , and/or Mg^{2+} [178]. The higher concentration of CO_3^{2-} ions make the surface charge more negative, and the higher density of Ca^{2+} and Mg^{2+} ions result in a more positive surface charge [179]. Calcite mineral showed a net weak negative charge in DI water, which may result due to the calcite dissolution (desorption of Ca^{2+} ions from the calcite crystal) [136,138,139]. However, the magnitude of the zeta potential of other non-clay minerals (dolomite, quartz, and K-feldspar) was found much higher than that of calcite in DI water. A higher negative zeta potential of dolomite may result due to the higher concentration of CO_3^{2-} ions. Quartz and K-feldspar showed higher negative zeta potential as compared to carbonate minerals due to the presence of silica particles. Silica particles bear very less or no charge at a pH of around 2 [180]. With the increase in pH, the silanol groups dissociate on the silica surface, resulting in the increased negative surface charge density [180]. As shown in Figure 16, the pH values of quartz and K-feldspar in the DI water were around 8.26 and 6.95, respectively (much higher than 2), resulting in a higher net negative charge. Figure 16(b) presents the zeta potential of clay minerals (montmorillonite, kaolinite, and Illite). All of them showed

a higher net negative surface charge in DI water. The montmorillonite used in this study was K10-montmorillonite, which shows negative zeta potential at all pH values [181].

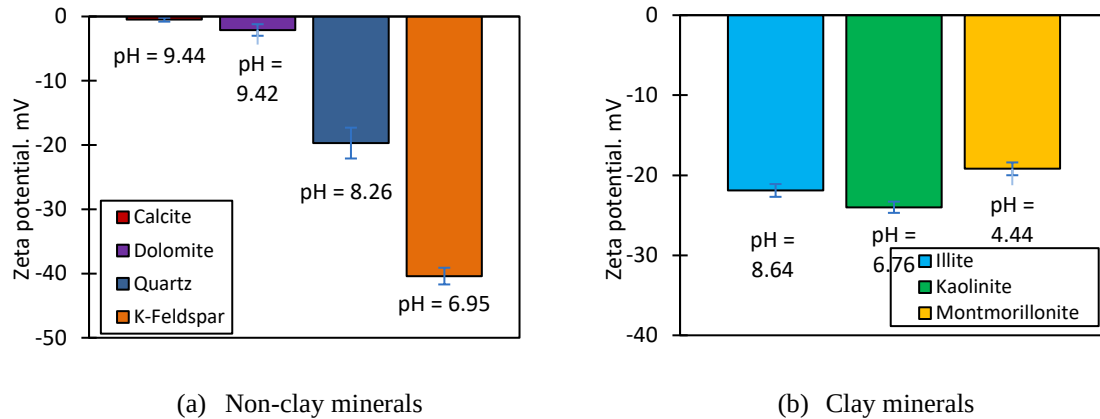


Figure 16: Zeta-potential of minerals in deionized water (a) for non-clay minerals, and (b) for clay minerals

3.3.2 Adsorption Study

3.3.2.1 Effect of Minerals on Surfactant Adsorption Capacity

Figure 17 presents the adsorption isotherms of GS12 on both clay and non-clay minerals. In the case of non-clay minerals (Figure 17(a)), the adsorption of cationic GS12 on the carbonate minerals (calcite and dolomite) was found the lowest. This is due to the lower density of net negative charge as discussed in the previous section. The adsorption of GS12 on silicate minerals was found higher than that of carbonate minerals. K-feldspar showed a significantly higher amount of surfactant adsorption as compared to quartz and other carbonate minerals. Adsorption increases gradually on calcite, dolomite, and quartz surface till 1000ppm surfactant concentration and then levels off, exhibiting the adsorption plateau. Whereas the adsorption of GS12 on K-feldspar increased sharply till 1000ppm and then

the adsorption plateau was observed. The GS12 adsorption values in the plateau region of calcite, dolomite, quartz, and K-feldspar were 0.58, 1.14, 2.16, and 8.11 mg/g-rock, respectively. Hence, the maximum amount adsorbed on non-clay minerals was in the order K-feldspar > quartz > dolomite > calcite. This shows that the presence of little quantity of silicate minerals (K-feldspar and quartz) in the carbonate reservoir rock will exhibit a significant amount of adsorption of cationic GS12.

Figure 17(b) illustrates the adsorption behavior of GS12 on the three most famous clay minerals (montmorillonite, kaolinite, and Illite). Cationic GS12 adsorbs on the negative sites of these clay minerals. The adsorption plateau was not observed on both montmorillonite and kaolinite until 1500ppm surfactant concentration (~100 times of CMC). However, Illite exhibited an adsorption plateau at 1000ppm surfactant concentration. Since montmorillonite is an expandable clay mineral (2:1 layered structure), it may be assumed that the cationic GS12 was intercalated between the sheets of montmorillonite, resulting in a very higher degree of adsorption. On the other hand, Illite layers (2:1 mineral) are strongly bonded together with a high charge density through the interlayer K^+ cation [159]. Therefore, cationic GS12 cannot be intercalated between the Illite layers, reaching an adsorption plateau upon saturation. In the case of kaolinite (1:1 layered structure), there is a strong hydrogen bonding between layers, GS12 cannot penetrate the interlayer space, resulting in negligible swelling behavior. The amount of GS12 adsorption at 1500ppm on clay minerals was found in the order of montmorillonite > kaolinite > Illite. Hence, the presence of a small quantity of any of the clay minerals in reservoir rock will result in a significant amount of cationic GS12 adsorption.

It may be concluded that if a carbonate formation contains even a little quantity of silicate and/or clay minerals, a higher degree of cationic GS12 adsorption will take place. These findings are consistent with previous studies [16,164,165]. The impact of clay minerals was observed even worse than silicate minerals (quartz and K-feldspar) in this study. The negative effect of both clay and non-clay minerals on the behavior of surfactant adsorption was found in the order of montmorillonite > kaolinite > Illite > K-feldspar > quartz > dolomite > calcite as presented in Figure 18. The adsorption values range from 0.58 to 22.39 mg/g-rock at 1500ppm surfactant concentration for calcite and montmorillonite, respectively.

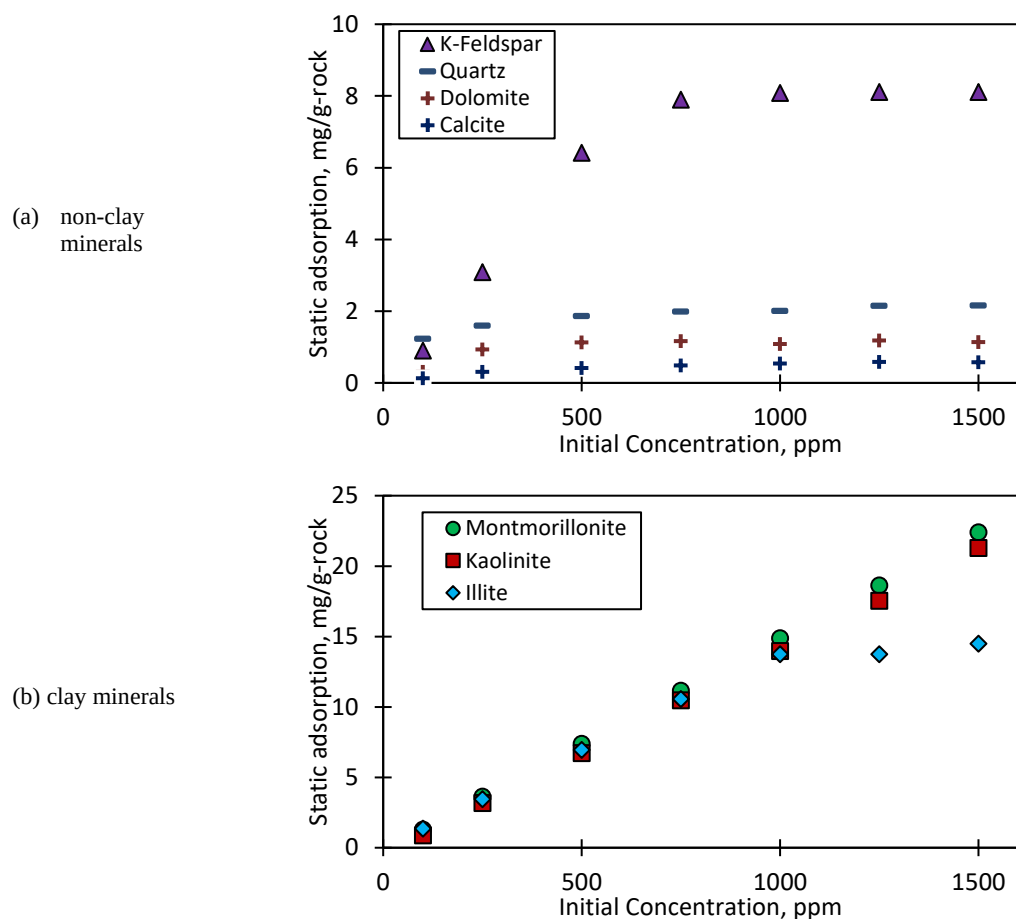


Figure 17: Surfactant adsorption isotherms for (a) non-clay minerals and (b) clay minerals

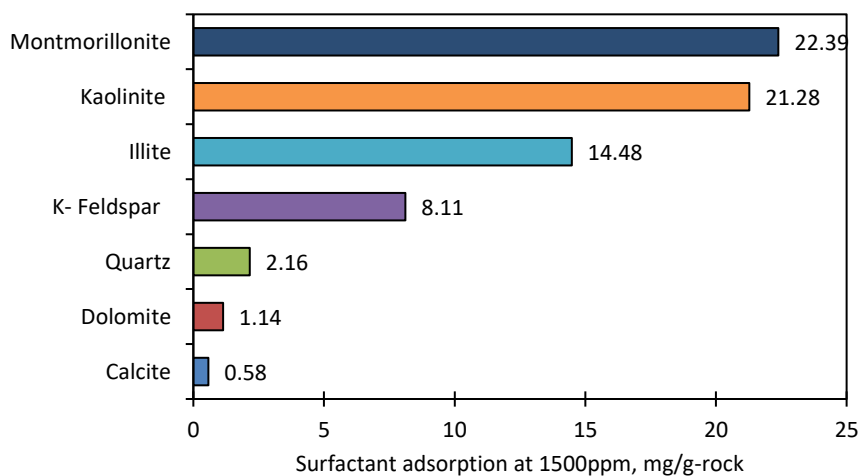


Figure 18: Surfactant adsorption of each studied mineral at 1500ppm concentration.

3.3.2.2 Effect of Salinity

The effect of salinity in terms of monovalent ions, divalent ions, and synthetic seawater was analyzed. The experiments were conducted at 1000ppm surfactant concentration with a variety of different salts of fixed molarity (0.1 M) as shown in Table 10. Figure 19(a) illustrates the effect of monovalent cation (Na^+) on the surfactant adsorption of GS12. The decrease of surfactant adsorption was found negligible in most of the minerals by using little concentration of NaCl as compared to that in DI water. This is consistent with the previous findings that monovalent cation (i.e., Na^+) does not impact the adsorption of a cationic surfactant on a silica surface [165]. However, the adsorption of cationic GS12 can be reduced by adding divalent cations (Ca^{2+} , Mg^{2+}) to the surfactant solution. Figure 19(b) and (c) show the effect of CaCl_2 , and MgCl_2 on the adsorption of GS12 on several minerals, respectively. The adsorption of GS12 on calcite, dolomite, quartz, K-feldspar, and Illite in the presence of CaCl_2 and MgCl_2 was found lower than that in DI water. This may be attributed due to the attraction of cationic salt ions on the negative binding sites of these minerals. However, similar results were not obtained in the case of montmorillonite and kaolinite due to the presence of a high density of negative binding sites. In addition, montmorillonite is an expandable clay mineral that can accommodate cations and swells. Figure 19(d) shows the comparative analysis of NaCl, CaCl_2 , and MgCl_2 . The impact of divalent cations (Ca^{2+} and Mg^{2+}) was found higher than that of monovalent cations (Na^+) due to higher ionic strength. Cui and co-authors also reported that the adsorption of a cationic surfactant on natural carbonate minerals can be reduced by adding multivalent cations [165]. The GS12 adsorption tests on different minerals were also conducted at high

salinity (67,708 ppm) as shown in Figure 20. The effect of high saline seawater was analyzed at 1500ppm surfactant concentration. Adsorption of GS12 was reduced in calcite, dolomite, quartz, K-feldspar, and Illite due to the attraction of cations present in the seawater on the negative binding sites of these minerals. However, the same was not true in the case of montmorillonite and kaolinite. These findings show that if a real reservoir rock contains a little amount of clay minerals, especially montmorillonite and kaolinite, a large degree of cationic GS12 adsorption may be expected on the reservoir rock surface even in the high saline condition.

Table 10: Concentration of the employed salts

Salt	Concentration, M (mol/L)	Concentration, ppm (mg/L)
NaCl	0.1	5,845
CaCl ₂ .2H ₂ O	0.1	14,690
MgCl ₂ .6H ₂ O	0.1	20,320

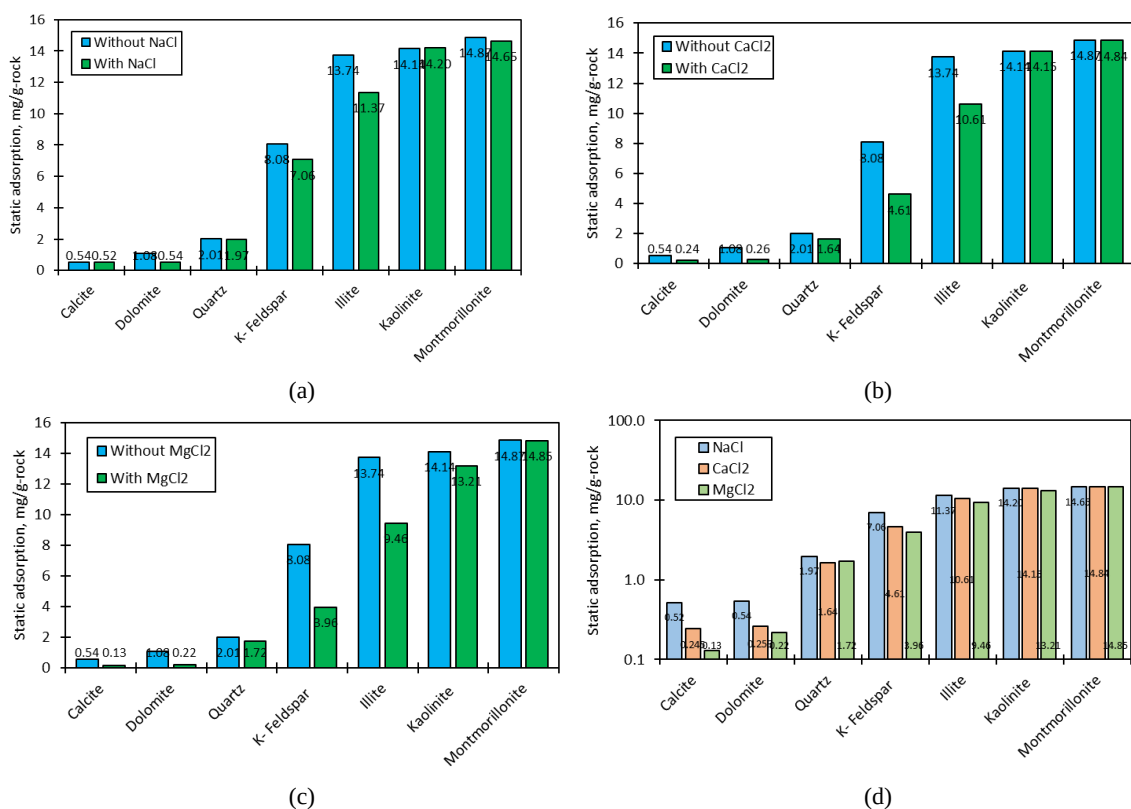


Figure 19: Surfactant adsorption at 1000ppm with different salts: (a) 0.1M NaCl, (b) 0.1M CaCl₂, (c) 0.1M MgCl₂, and (d) comparison of the studied salts.

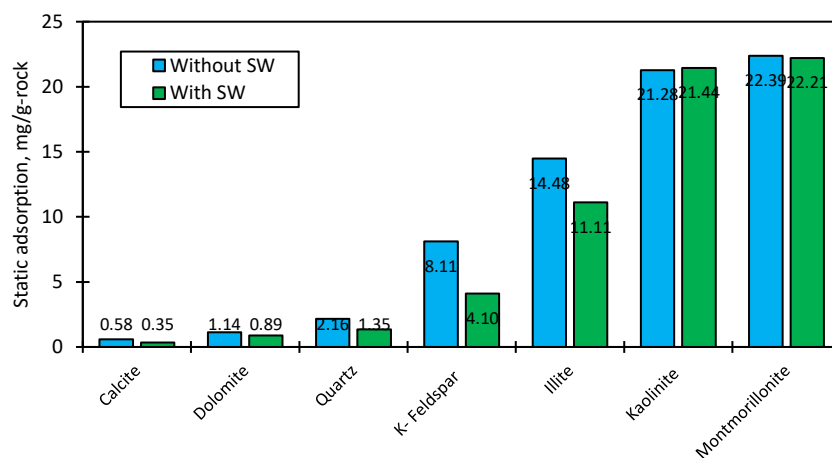


Figure 20: Effect of seawater (SW) on surfactant adsorption at 1500 ppm

3.3.2.3 Methylene Blue as an Adsorption Inhibitor

Methylene blue (MB) has been investigated as an adsorption inhibitor for a novel cationic Gemini surfactant in this study. Only 100ppm of MB was added to the surfactant solution at the highest surfactant concentration of 1500ppm. Results show that adsorption of cationic GS12 was significantly reduced to 0.32 and 0.67 mg/g-rock in dolomite and quartz, respectively as shown in Figure 21. This indicates that if natural dolomite rock contains impurities of quartz, the adsorption of cationic GS12 can be significantly reduced. Furthermore, calcite also showed little adsorption (~0.45 mg/g-rock) by using 100ppm of MB in GS12 solution at 1500ppm, making GS12 useful in limestone reservoirs containing quartz as an impurity. The GS12 adsorption in K-feldspar and Illite upon using MB was also reduced to 3.79 and 11.18 mg/g-rock, respectively. However, reduction in GS12 adsorption on the surface of montmorillonite and kaolinite was found negligible. Past studies show that montmorillonite and kaolinite have a high affinity toward MB [160,182]. Therefore, more quantities of MB may be required to adsorb on clay minerals to reduce the adsorption of GS12. Figure 22 shows the adsorption reduction of GS12 at 1500ppm concentration on clay minerals at different concentrations of methylene blue. The adsorption was significantly reduced in Illite and kaolinite by using 500ppm MB. The percentage of adsorption reduction in Illite and kaolinite was 59.05% and 80.26%, respectively. However, more concentration of MB may be required for montmorillonite to reduce the GS12 adsorption.

Figure 23 presents a cartoon showing the proposed adsorption reduction mechanism of GS12 using MB. MB adsorbs on the negative binding sites of both clay and non-clay

minerals, therefore, repelling cationic GS12, leading to the reduction of cationic GS12 adsorption. Figure 24 shows the pictures of vials taken after the static adsorption tests on all studied minerals. The color intensity of MB was decreased from Figure 24(a) to (d) corresponding to the static adsorption tests on montmorillonite, kaolinite, Illite, and K-feldspar, respectively. Figure 24(a) showed a clear solution, which confirms the highest amount of MB adsorption on montmorillonite among all studied minerals. This may be attributed to the inherited expandable property of montmorillonite. On the other hand, Figure 24(e) to (f) show a relatively dark color solution after the static adsorption tests of quartz, dolomite, and calcite, respectively. This confirms that 100ppm of MB solution was enough to reduce the surfactant adsorption of GS12 on quartz, dolomite, and calcite.

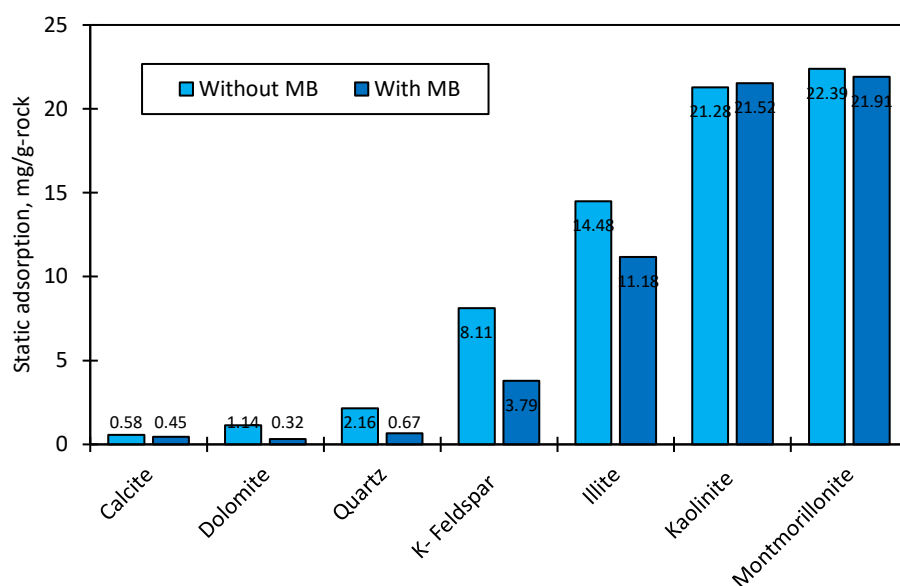


Figure 21: Application of methylene blue (100 ppm) as an adsorption inhibitor for several minerals

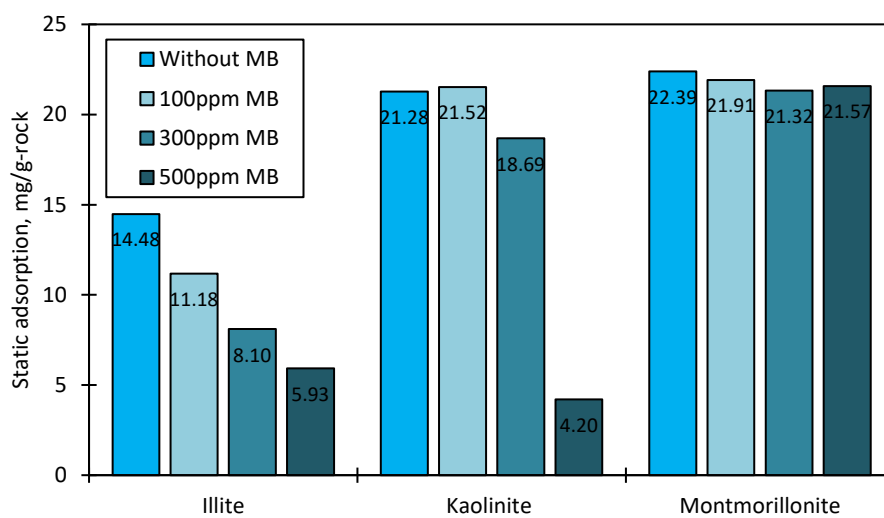
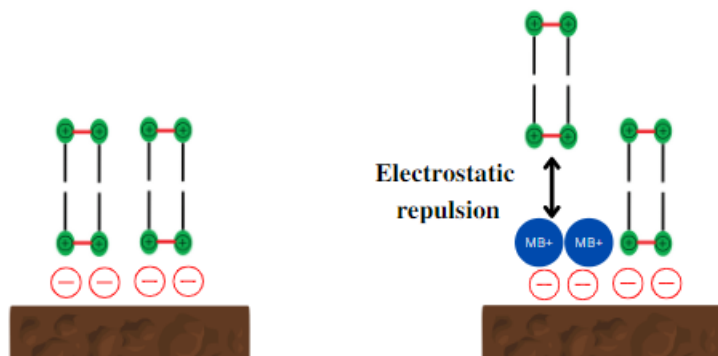
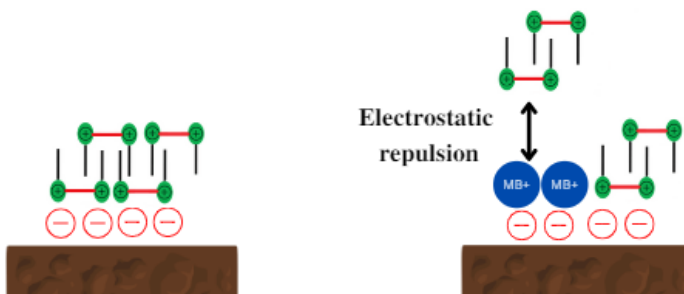


Figure 22: GS12 (1500ppm) Adsorption reduction on clay minerals at different concentrations of methylene blue



(a) Non-interdigitated bilayer adsorption mechanism in silicate/clay minerals without MB^+ [164]

(b) Adsorption reduction mechanism in silicate/clay minerals with MB^+



(c) Interdigitated bilayer adsorption mechanism in carbonate minerals without MB^+ [164]

(d) Adsorption reduction mechanism in carbonate minerals using MB^+

Figure 23: Proposed adsorption reduction mechanism using methylene blue

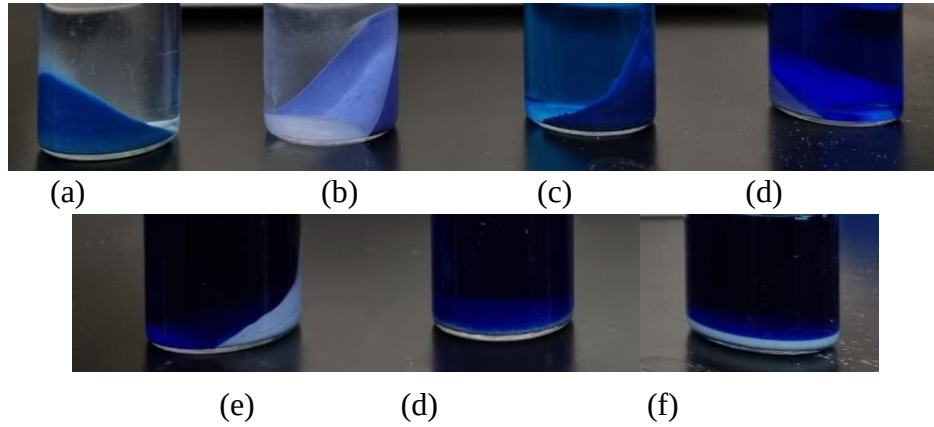


Figure 24: (a) Montmorillonite, (b) Kaolinite, (c) Illite, (d) K-Feldspar, (e) Quartz, (f) Dolomite, and (f) Calcite

3.3.2 Application of Soft Computing Tools

3.3.2.1 Data Analytics

The experimental dataset was divided into an 80:20 ratio for training and testing, respectively. The training data set was statistically analyzed using a correlation heatmap and statistical parameters as shown in Figure 25 and Table 11, respectively. The maximum adsorption capacity was determined by taking the average of the adsorption values at the plateau region, which showed the highest correlation coefficient as shown in Figure 25. The minimum and maximum adsorption values found were 0.1268 mg/g-rock and 14.4849 mg/g-rock, respectively. All minerals used in this study are 100% pure except Illite which contains 70% Illite and 30% quartz content. The target is to develop the model as follows;

$$\Gamma_{\text{static}} = f(C_e, q_m, C, D, Q, F, I) \quad (14)$$

where, C_e is the equilibrium concentration, ppm, q_m shows maximum adsorption capacity, mg/g-rock, C_a is the calcite percentage, %, D is the dolomite percentage, %, Q is the quartz

percentage, %, F is the Feldspar percentage, %, I is the Illite percentage, %, and Γ_{static} shows surfactant adsorption from static tests, mg/g-rock.

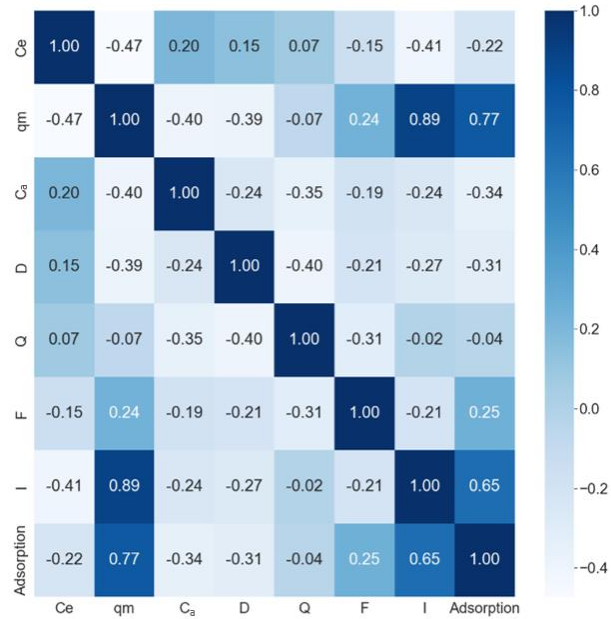


Figure 25: Correlation heatmap of the training data

Table 11: Statistical analysis of the training data

	Minimum	Maximum	Mean	Standard Deviation	Skewness	Kurtosis
Ce, ppm	10.3263	1461.5405	488.6186	476.9064	0.8168	-0.5795
qm, mg/g-rock	0.5684	13.9906	5.0265	5.3401	0.9082	-0.9203
C, %	0	100	17.8571	39.0021	1.7751	1.2339
D, %	0	100	21.4286	41.7855	1.4727	0.1762
Q, %	0	100	31.4286	42.0506	0.9609	-0.8579
F, %	0	100	14.2857	35.6348	2.1587	2.8592
I, %	0	70	15	29.2499	1.4727	0.1762
Γ , mg/g-rock	0.1268	14.4849	3.385	4.1097	1.6401	1.7129

3.3.2.2 Soft Computing Models: XGBoost and Random Forest

Random Forest is an ensemble learning algorithm that builds numerous decision trees in the training process. It forecasts the average prediction of trees for regression problems.

On the other hand, XGBoost (eXtreme Gradient Boosting) works under the gradient boosting framework. Both tools were tested on the training data set to develop the model. Input parameters used in this study were C_e , q_m , C_a , D , Q , F , and I , while surfactant adsorption is the output.

Hyperparameters of the applied algorithms were tuned using K-fold cross-validation integrated with an exhaustive grid search approach. Although the grid search approach takes a lot of time in running the model, however, it covers all possible combinations of the ranges of input parameters. The optimized hyperparameters obtained after tuning are reported in Table 12. The performance comparison of XGBoost and RF is described in the subsequent section.

Table 12: Hyperparameter tuning of the applied AI models

AI Tool	Hyperparameter	Range	Tuned hyperparameter
XGBoost	n_estimators	1000, 3000, 5000	5000
	max_depth	2, 4, 6	2
	learning_rate	0.1, 0.2, 0.3	0.3
	min_child_weight	3, 6, 9	3
	gamma	0	0
	subsample	1	1
	colsample_bytree	1	1
	alpha	0	0
	lambda	1	1
RF	n_estimators	1000, 3000, 5000	3000
	max_depth	2, 4, 6	4
	min_samples_split	2, 4, 6	4
	min_samples_leaf	2, 4, 6	2

3.3.2.3 Performance Comparison of XGBoost and Random Forest

The performance of Random Forest and XGBoost has been compared by using error metrics and a scatter plot as shown in Table 13 and Figure 26. Reported results were obtained using optimized hyperparameters. Results showed that XGBoost outperformed random forest. The error metric comprising R^2 and RMSE showed good agreement with the unseen data. Figure 26(a) and (b) show scatter plots for training and testing data, respectively. For XGBoost, most of the points lie on a 45-degree line, showing the robustness of the proposed model. The developed model can be used to predict surfactant adsorption by using mineral composition, maximum adsorption capacity, and surfactant concentration. It will save a substantial amount of time in running the time-taking experiments and will help to provide a good quick approximation of surfactant adsorption.

Table 13: Performance comparison between Random Forest and XGBoost

Data type	Error metrics	Random Forest	XGBoost
Training	RMSE	1.267	0.2797
	R^2	0.9014	0.9952
Testing	RMSE	1.4863	0.433
	R^2	0.899	0.9914

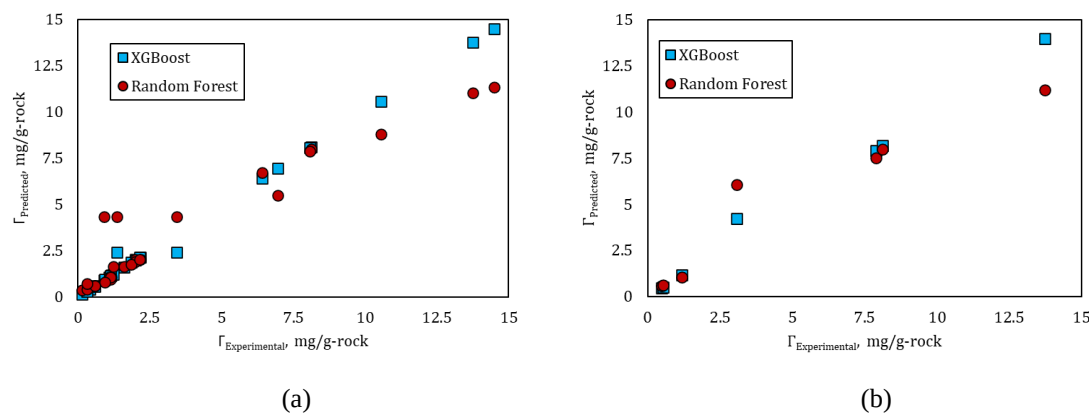


Figure 26: Scatter plot for (a) training data and (b) testing data

3.3.3 Conclusions

The static adsorption of a novel cationic Gemini surfactant on several minerals, including calcite, dolomite, quartz, K-feldspar, montmorillonite, kaolinite, and Illite has been investigated. The selected minerals are mostly found in both carbonate and sandstone reservoirs. Minerals characterization was conducted using XRD and SEM, and the surface charge was determined using a zeta potential meter. HPLC was employed to determine the surfactant adsorption using concentration differences before and after static adsorption tests. The effect of salinity on each mineral has been analyzed. MB has been used as a novel adsorption inhibitor for GS12. The major findings are listed below:

- 1- The type of mineral greatly affects GS12 adsorption. Clay minerals showed more negative effects as compared to silicate minerals (quartz and K-feldspar). Carbonate minerals (calcite and dolomite) showed very little amount of adsorption.
- 2- All minerals showed an adsorption plateau starting from 1000ppm except montmorillonite and kaolinite.

- 3- The maximum amount of surfactant adsorbed at 1500ppm was in the order of montmorillonite > kaolinite > Illite > K-feldspar > quartz > dolomite > calcite.
- 4- The reduction of surfactant adsorption using divalent ions (Ca^{2+} and Mg^{2+}) was found higher than that of monovalent ions (Na^{+}) because of higher ionic strength.
- 5- Only 100ppm of MB reduced GS12 adsorption on quartz surface to 0.67 mg/g-rock. Hence, a little addition of MB in the surfactant solution will help in the reduction of surfactant adsorption on carbonate reservoirs containing quartz as an impurity.
- 6- The percentage of adsorption reduction in Illite and kaolinite was 59.05% and 80.26%, respectively by using 500ppm MB in 1500ppm GS12 aqueous solution.
- 7- A novel intelligent model to estimate surfactant adsorption in terms of mineral composition, maximum adsorption capacity, and concentration of Gemini surfactant has been presented.

CHAPTER 4

REDUCING ADSORPTION OF A GEMINI SURFACTANT ON SAUDI CARBONATE

Abstract

Surfactant adsorption has been a great challenge for the surfactant-based chemical enhanced oil recovery (cEOR) techniques, as it directly reflects the overall efficiency of a cEOR project. The static adsorption of an inhouse synthesized cationic Gemini surfactant (GS12) has been investigated on Saudi dolomite outcrops as a function of concentration, time, salinity, and temperature. Three different types of outcrop samples taken from the Al-Lidam area (Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3) with an increasing percentage of silica and clay impurities were investigated. It was found that the higher the presence of silicate and clay minerals in Saudi dolomite outcrops, the higher will be the surfactant adsorption. The adsorption of GS12 was found to decrease at elevated temperatures and in a high saline environment, especially at very high concentrations of divalent salts (CaCl_2 and MgCl_2). In addition, a novel adsorption inhibitor - methylene blue has been proposed in this study, that reduced the surfactant adsorption significantly on Saudi dolomite outcrops. The GS12 adsorption on Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3 was reduced to 0.14 mg/g-rock, 0.48 mg/g-rock, and 2.31 mg/g-rock,

respectively, by the addition of 500ppm methylene blue in 1500ppm surfactant solution. Moreover, curve fitting was also performed to analyze the adsorption isotherm and kinetic data. Redlich-Peterson and Pseudo-second order models were found best to describe the adsorption isotherm and kinetics, respectively.

4.1 Introduction

Surfactants are most used in the chemical enhanced oil recovery (cEOR) techniques because of their ability to improve oil recovery by altering the wettability and/or lowering interfacial tension (IFT). Surfactant loss due to adsorption of surfactant on reservoir rock surface is the key issue that might make surfactant flooding uneconomical and inefficient [92]. Surfactant adsorption leads to a huge variation in reducing the desired IFT and changing wettability, making the cEOR process unfeasible. Studies show that surfactant adsorption densities must be lower than 1 mg/g-rock [183,184]. Therefore, reducing surfactant adsorption is crucial in making the cEOR process effective.

To date, most of the studies on surfactant adsorption reduction are dedicated to the anionic surfactants in sandstone reservoir rocks. Alkalis are most famous for reducing the anionic surfactant adsorption on sandstone rocks by increasing the pH [9,92]. Carbonate rocks are currently a great area of interest because they cover about 23% of the earth's crust and contain approximately 60% of the remaining oil [185,186]. Cationic surfactants are usually favored for carbonate reservoirs because of a smaller amount of adsorption. However, studies showed that the presence of impurities, such as silica and/or clay minerals in carbonate rocks may lead to a significant degree of surfactant adsorption [16,108,164].

Ahmadali and co-authors showed that the presence of divalent cations (Ca^{2+} and Mg^{2+}) dramatically reduces the adsorption of cationic surfactants on carbonates [34]. The addition of cations (lattice ions of the carbonate minerals) affects the mineral's surface charge, leading to the reduction of cationic surfactant adsorption in carbonates. Wang et. al studied sulfonated polyacrylamide polymer in reducing the adsorption of an amphoteric surfactant in carbonate reservoirs. It was observed that a polymer layer was formed on the surface of the rock, resulting in a decrease in active adsorption sites [71]. Ma et. al proposed that the adsorption of Cetylpyridinium Chloride (CPC) on natural carbonates can be reduced in the presence of 1 atm CO_2 in comparison with 1 atm of air [16]. The presence of CO_2 acidifies the surfactant solution, making the carbonate surface more positive, resulting in the reduction of CPC adsorption by electrostatic repulsion.

Most of the surfactants studied for the adsorption reduction on carbonates are conventional monomers. Gemini surfactants are relatively a novel class of surfactants containing two covalently linked traditional surfactants via a spacer. The spacer group can be rigid or flexible, hydrophobic or hydrophilic, the length of the hydrocarbon tails can be varied, and the polar group can be cationic, anionic, zwitterionic, and nonionic. This special class of surfactant has attracted many researchers because of its attractive properties, such as lower critical micelle concentration (CMC), good water solubility, unique micelles structures, ultra-low IFT, and so on [90,92,187]. Páhi et al. examined the adsorption behavior of Gemini surfactant and compared it with that of the conventional monomeric unit on sandstone. It was noted that the Gemini surfactant adsorption on sandstone was found low in comparison with monomeric units [188]. Zhao and co-authors studied the mechanism

of Gemini surfactant in inhibiting the acid-rock reaction rate [147]. By forming a monolayer on the rock surface, the cationic Gemini surfactant was able to prevent the acid-rock reaction. Yang and co-authors investigated the role of unsaturated double bonds on the adsorption behavior of cationic Gemini surfactants [189]. It was shown that the surfactant having the unsaturated double bonds on the hydrophobic chains shows better surface activity, while the adsorption kinetic process is mainly due to the mixed diffusion-kinetic model. Gao and M. Sharma conducted an interesting study of the adsorption behavior of anionic Gemini surfactants on Berea sandstone [187]. It was reported that the adsorption was increased by the increase of the alkyl chain length of the anionic Gemini surfactants having a fixed spacer. Lateral interactions between hydrocarbon chains increase by increasing the chain length. In addition, longer hydrocarbon tails decrease the solubility of the Gemini molecule in an aqueous solution, leading to the increase of adsorption density on the solid-water interface. The effect of spacer group length was also investigated. Results showed that shorter spacer length showed a smaller adsorption plateau because of the same reason. Dynamic adsorption of a cationic Gemini surfactant on Indiana limestone was studied recently [167]. Outcomes showed that decreasing surfactant concentration and increasing the flow rates will result in decreasing surfactant retention. Most recent research shows the adsorption mechanisms of a cationic Gemini surfactant onto sandstone and carbonate rocks [164]. It was proposed that a non-interdigitated bilayer and an interdigitated bilayer were formed on sandstone and carbonate rocks, respectively.

Adsorption studies of Gemini surfactants were conducted mainly on either sandstone or limestone. The adsorption behavior of cationic Gemini surfactant on local Saudi dolomite

has not been studied. In addition, an adsorption inhibitor for reducing the adsorption of cationic Gemini surfactant on carbonates remains unknown in the literature. Herein, the adsorption behavior of a novel cationic Gemini surfactant on Saudi dolomite rock acquired from Al-Lidam area has been studied. Firstly, the rock characterization was carried out using XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy). The net surface charge of the adsorbents in an aqueous solution was calculated using the Zeta potential measurements. Static adsorption tests were conducted, and the supernatants were examined using high pressure liquid chromatography (HPLC). Surfactant adsorption was calculated using the concentration difference. Adsorption isotherm modeling and kinetic modeling were conducted as well to explore the adsorption mechanism. The effect of salinity and temperature has been studied. More interestingly, a novel adsorption inhibitor – methylene blue has been proposed in this study.

4.2 Materials and Methods

4.2.1 Cationic Gemini Surfactant

The adsorbate studied in this research is a cationic Gemini surfactant that was prepared in two steps according to the method depicted in our preceding article. In the first step, the amidation of fatty acid (**5**) was done by reacting a 1:2 ratio of glycolic acid ethoxylate lauryl ether (**5**) (25 g, 36.23 mmol) and 3-(dimethylamino)-1-propylamine (**4**) (7.4 g, 72.46 mmol) in 100 mL 2-necked round bottom flask at 160 °C for 10 h. The residual amount of 3-(dimethylamino)-1-propylamine was removed by applying reduced pressure and the subsequent intermediate amide (**3**) was well characterized before the next step. In the

second step, the 100 mL 2-necked round bottom flask was charged with intermediate amide (3) (20 g, 25.84 mmol) and 1,12-dibromododecane (2) (3.85 g, 11.75 mmol) in 10 mL ethanol at 80 °C up to 48 h. The reaction was then stopped, and the subsequent crude product was purified by column chromatography using ethanol to acquire cationic Gemini surfactant (GS12) in viscous pale-yellow form (Figure 27) [129].

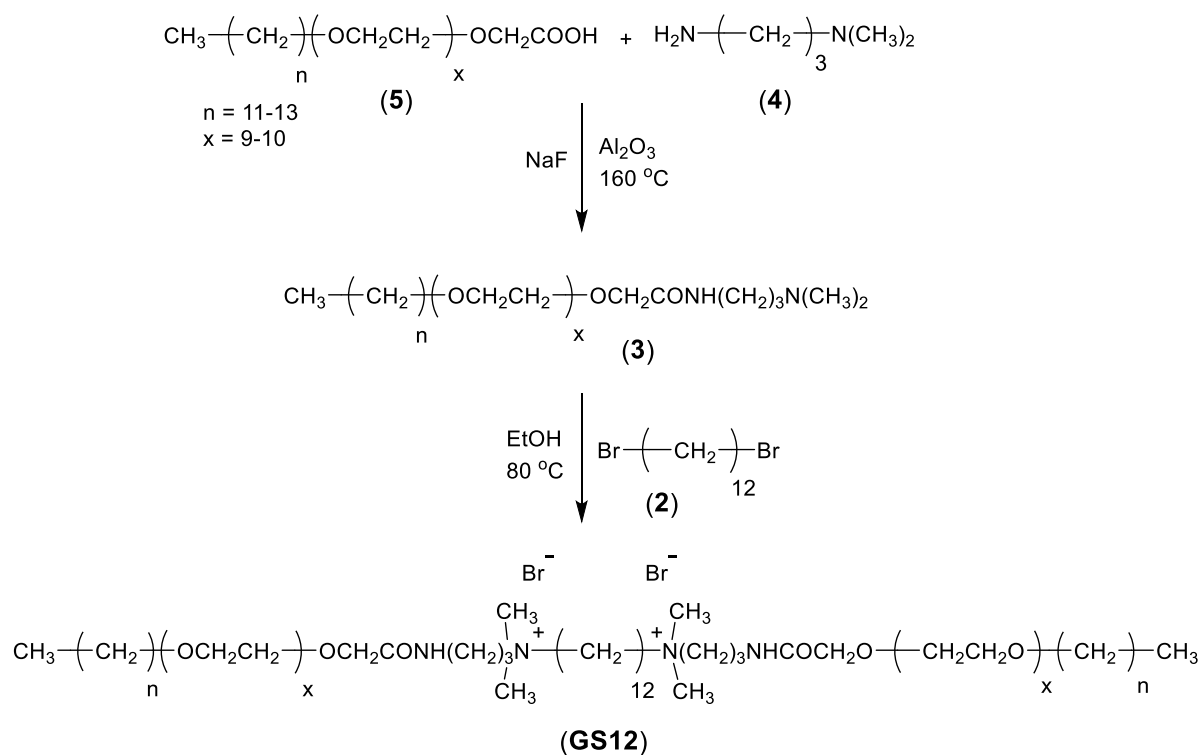


Figure 27: Synthesis of quaternary ammonium Gemini surfactant (GS12) [129]

4.2.2 Adsorbents

The outcrop rock samples were collected from the Al-Lidam escarpment area of the Eastern Province of Saudi Arabia, nearly 80 km to the west of Dammam city. It is situated between 26°15'30" N to 49°28'30" E and 26°14'15" N to 49°31'30" E [190]. Outcrops of the

Miocene Dam Formation are shown in the area and have a general strike NNW-SSE [190,191]. The geographical location on the map has been shown in Figure 28.

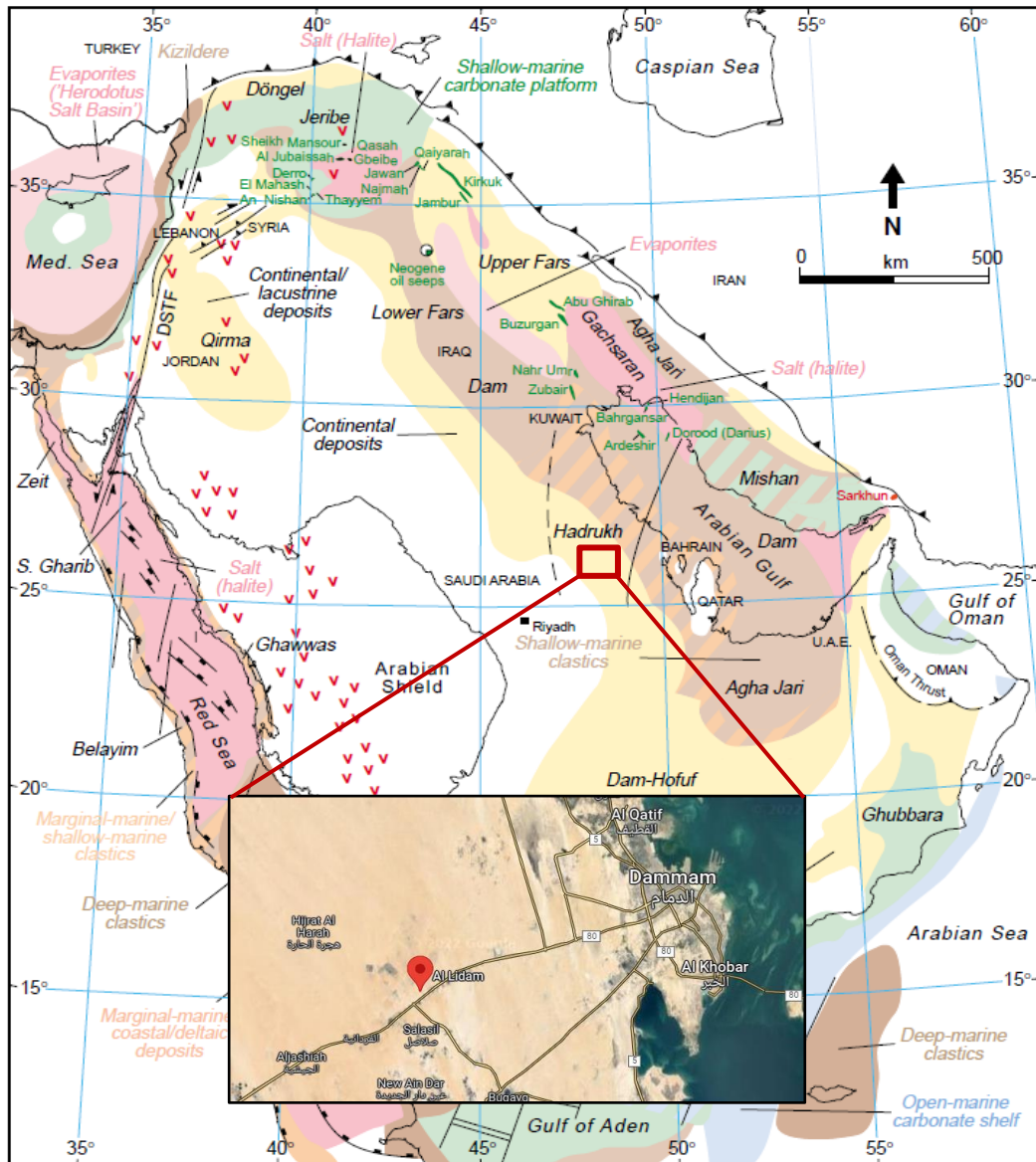


Figure 28: The Miocene paleofacies map with the study area location displayed in the red-bordered square (modified after [192])

4.2.3 Rock Characterization

XRD (X-Ray Diffraction) was conducted on the crushed samples of outcrops to determine the mineral composition. Empyrean X-ray diffraction from Malvern Panalytical was used to acquire XRD patterns. A morphological study of the outcrop samples was carried out using Helios NanoLab G3 UC SEM (scanning electron microscope).

4.2.4 Preparation of Solutions

2000ppm surfactant stock solution was made and then diluted to lower concentrations till 100ppm. The composition of synthetic seawater is displayed in Table 14. The concentrations of monovalent and divalent salts in ppm used in this study have been shown in Table 15.

Table 14: Seawater composition

Salt	mg/L (ppm)
NaHCO ₃	165.25
Na ₂ SO ₄	6339.02
NaCl	41172.35
CaCl ₂ .2H ₂ O	2387.13
MgCl ₂ .6H ₂ O	17644.12
Sea water salinity	67707.86

Table 15: Monovalent and divalent ions concentrations

Salt type	Concentration	
	ppm (0.1 M)	ppm (1 M)
NaCl	5845	58,450
CaCl ₂ .2H ₂ O	14,690	146,900
MgCl ₂ .6H ₂ O	20,320	203,200

4.2.5 Zeta Potential Measurements

The net surface charge of the adsorbents in an aqueous solution was quantified using a zeta potential meter. The Anton Paar Litesizer 500 having a size range of ~3.8 nm to ~100 μm was used for this purpose. A linear shaker was used to shake vials for at least 24 hours and then centrifugation was done using Hermle Z326K at a minimum of 3000 rpm for 3 minutes to attain a clear supernatant.

4.2.6 Static Adsorption

Static adsorption tests were carried out using a solid to liquid ratio of 1:15. Samples were agitated linearly using a linear shaker for 24hr at 25 degrees Celsius. The samples were centrifuged at a minimum of 3000 rpm for 30 minutes to separate liquid from solid. The supernatant liquid was filtered via a 0.45 μm filter before analyzing the surfactant concentration. The surfactant concentration after adsorption was determined utilizing HPLC (high-performance liquid chromatography) from Agilent technologies coupled with an evaporative light scattering detector (ELSD). A reversed-phase column - Acclaim™ surfactant plus was installed for the detection of a cationic Gemini surfactant. The mobile phases are 0.1 M ammonium formate modified to pH 4.50 using formic acid and acetonitrile.

Static adsorption can be computed using Eq. (14).

$$\Gamma_s = V_s \left(\frac{\Delta C}{m_R} \right) * 10^{-3} \quad (14)$$

where Γ_s is the amount of surfactant adsorbed on the rock surface in mg/g-rock, $\Delta C = C^0 - C$, C^0 and C are the surfactant concentrations before and after adsorption, respectively in ppm, V_s shows the volume of the surfactant solution in mL, and m_R is the mass of the powdered adsorbents.

4.2.7 Adsorption Isotherm Models and Kinetics

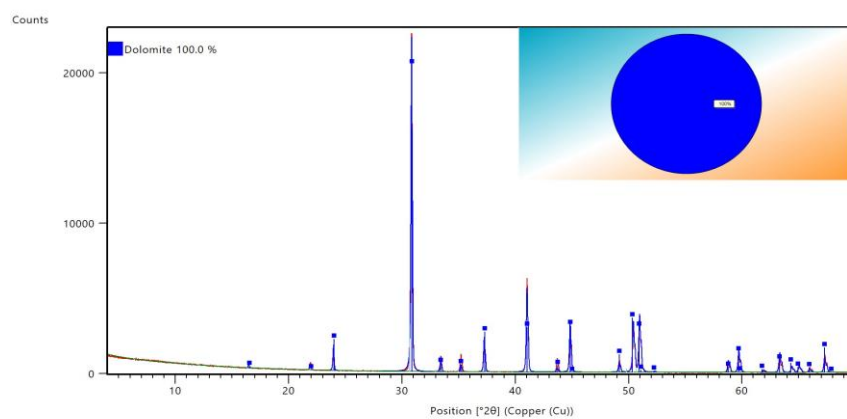
Please see sections 1.3 and 1.4 for the description of adsorption isotherm models and kinetics.

4.3 Results and Discussion

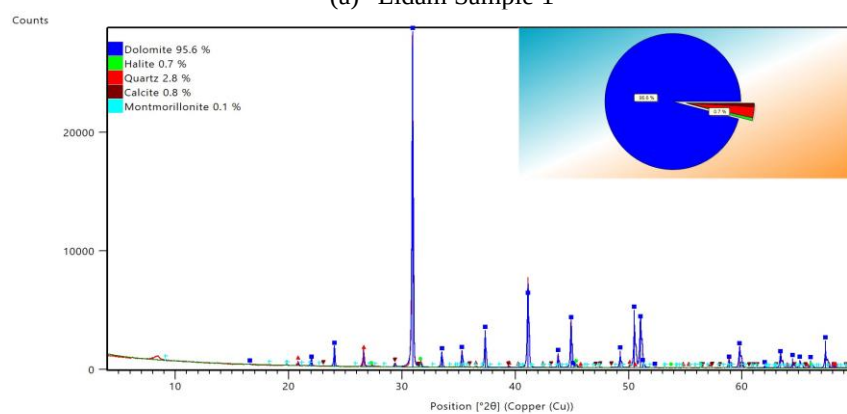
4.3.1 Characterization of Adsorbent Samples

4.3.1.1 X-ray Diffraction

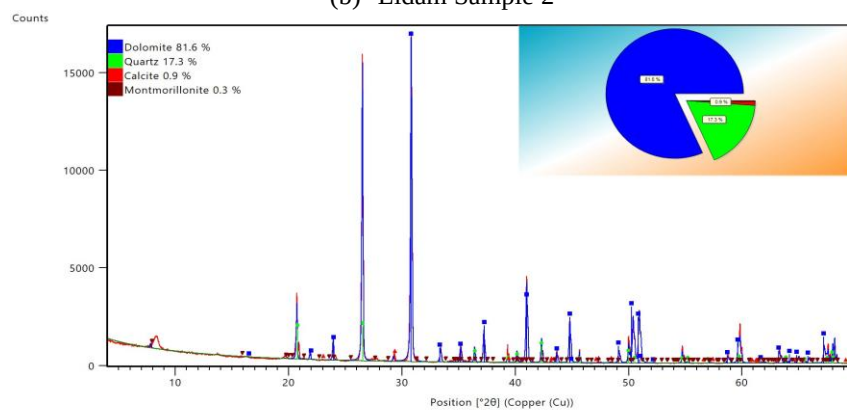
Outcrop samples taken from the Al-Lidam area were divided into three categories, namely Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3. XRD patterns of Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3 are shown in Figure 29(a) to (c), respectively. Figure 29(a) shows that Lidam Sample 1 is pure dolomite containing no impurities. However, Lidam Sample 2 and Lidam Sample 3 contain 95.6% and 81.6% dolomite, respectively. The percentage of quartz in Lidam Sample 2 and Lidam Sample 3 is 2.8% and 17.3%, respectively. and that of montmorillonite is 0.1% and 0.3%, respectively. The degree of outcrop's purity is in the order of Lidam Sample 1 > Lidam Sample 2 > Lidam Sample 3. The mineralogical composition of all adsorbents has been presented in Table 16.



(a) Lidam Sample 1



(b) Lidam Sample 2



(c) Lidam Sample 3

Figure 29: XRD patterns of (a) Lidam Sample 1, (b) Lidam Sample 2, and (c) Lidam Sample 3.

Table 16: Adsorbent composition

Minerals, %	Lidam Sample 1	Lidam Sample 2	Lidam Sample 3
Dolomite	100	95.6	81.6
Calcite	0	0.8	0.9
Quartz	0	2.8	17.3
Montmorillonite	0	0.1	0.3
Halite	0	0.7	0

4.3.1.2 Scanning Electron Microscopy

Scanning electron microscopy was conducted for the three adsorbents at different resolutions (50 μ m, 10 μ m, and 5 μ m) to analyze the rock morphology as shown in Figure 30. The decrease in dolomite purity level can be seen from top to bottom. The morphological images show that the degree of adsorbents' roughness increases as the impurities (quartz and montmorillonite) increases. A study shows that the carbonate rock displays a less porous structure in comparison with the surface of bentonite in SEM analysis [176]. This is consistent with our SEM investigation, i.e., as the amount of montmorillonite increases in the rock samples, the surface of the rock seems more porous.

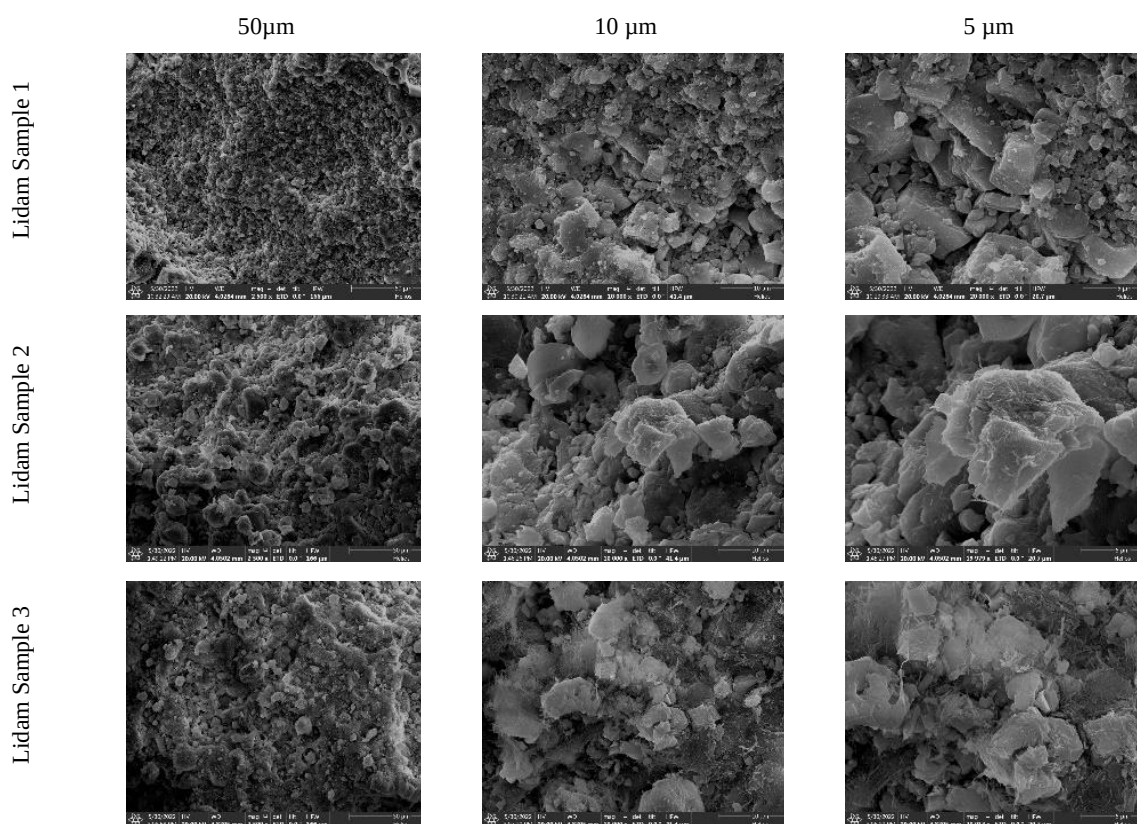


Figure 30: Scanning electron microscopy of adsorbents at different resolutions

4.3.2 Zeta Potential

The zeta potential of the three outcrop samples suspended in deionized water was measured, as shown in Figure 31. The pH of the solution was not adjusted until otherwise specified. The pH of all adsorbents was around 9, but the zeta potential was found different for the three adsorbents. All adsorbents showed negative zeta potential values, with the increasing magnitude due to an increase of impurities. The negative zeta potential of Lidam Sample 1 may result due to the higher concentration of CO_3^{2-} ions. The higher percentage of quartz and montmorillonite in the outcrop samples increases the number of negative sites, therefore increasing the magnitude of the zeta potential in the deionized water as

shown in Figure 31. The highest value of the negative zeta potential was found at -13.2 mV for Lidam Sample 3 in deionized water. Figure 32 presents the zeta potential of adsorbents suspended in the cationic GS12 surfactant solution at different concentrations. All samples at different surfactant concentrations exhibited a positive zeta potential, which shows the adsorption of cationic GS12 on the adsorbents. The magnitude of the zeta potential for Lidam Sample 2 was higher than that of Lidam Sample 1, signifying the higher degree of GS12 adsorption on Lidam Sample 2. The magnitude of the zeta potential increases with the increase of surfactant concentration, suggesting a higher amount of adsorption with the concentration increase.

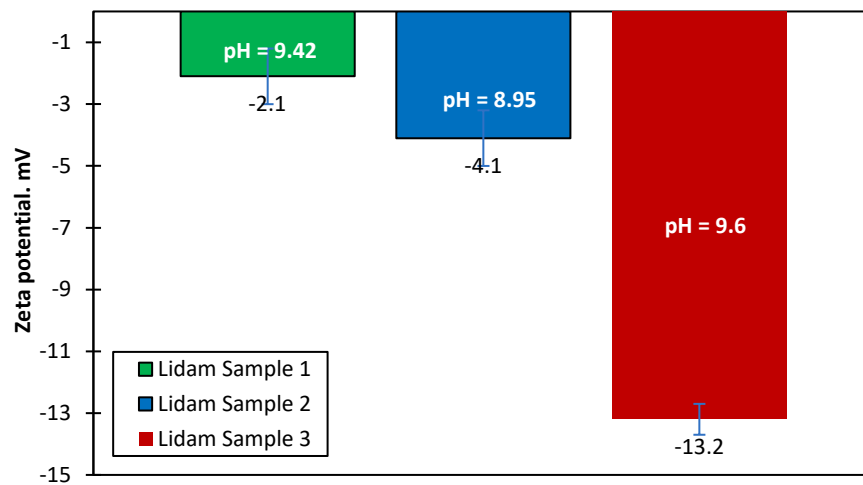


Figure 31: Zeta potential of adsorbents suspended in deionized water

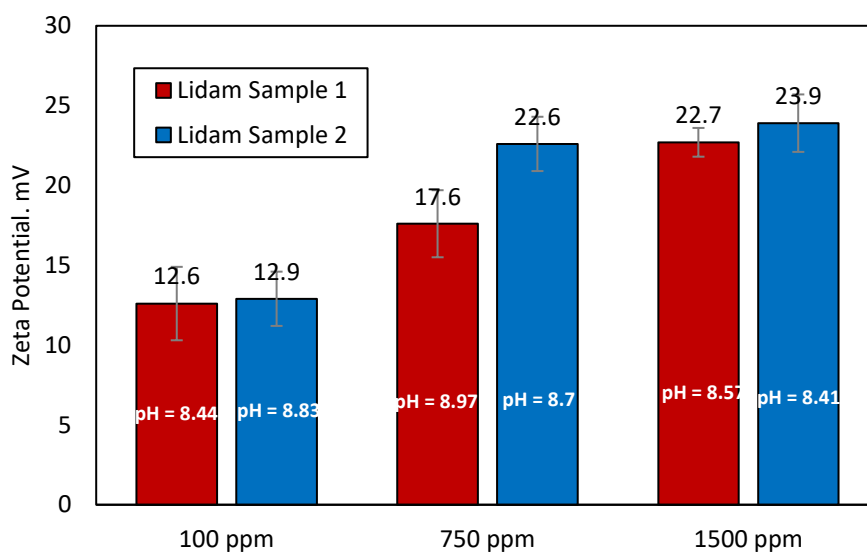


Figure 32: Zeta potential of adsorbents in surfactant solutions at different concentrations

4.3.3 Adsorption Kinetics

Investigating the impact of the adsorption time is crucial to ensure that static adsorption reaches equilibrium. The adsorption of GS12 on all adsorbents was studied at 750ppm and 1500ppm concentrations, as shown in Figure 33(a) and (b). The adsorption process was monitored for 48 hr. In the early stage, the adsorption rises gradually until 6 hr. After 24hr, the adsorption of GS12 (750ppm) reached equilibrium and remained at a constant value as shown in Figure 33a. However, at a higher concentration of GS12 (1500 ppm), the equilibrium time was found at ~6 hr. Herein, the solid-liquid interaction was kept at ~24hr to ensure surfactant adsorption achieving equilibrium in the subsequent experiments.

In order to get a deeper insight, adsorption kinetic modeling was conducted using pseudo-second order, intra-particle diffusion, and Elovich kinetic models. Corresponding model parameters and R^2 obtained via linear fitting for the three adsorbents were reported in Table

17. R^2 for intra-particle diffusion and Elovich kinetic models were found poor. However, R^2 for the pseudo-second order model was found excellent for all adsorbents. Figure 34(a) to (c) show the fitting of the pseudo-second order kinetic model at 750ppm and 1500ppm surfactant concentrations for the three adsorbents, respectively. Hence, among all applied kinetic models, it can be deduced that adsorption kinetics data follow the pseudo-second order model. Therefore, we can appropriately forecast the adsorption of GS12 on the studied Saudi outcrops over several concentrations and times using pseudo-second order model.

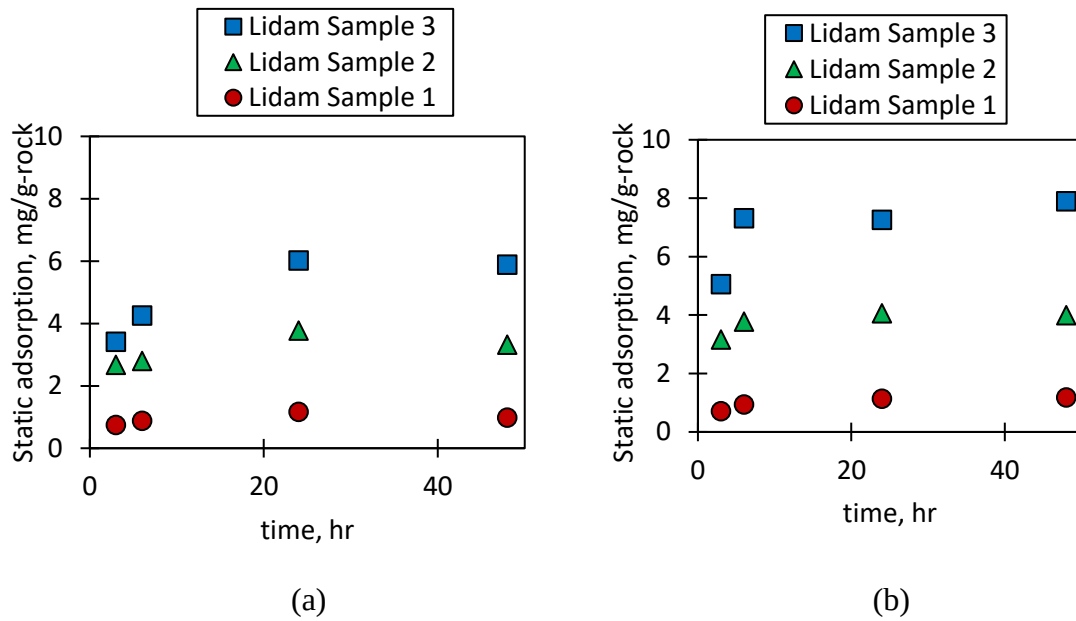
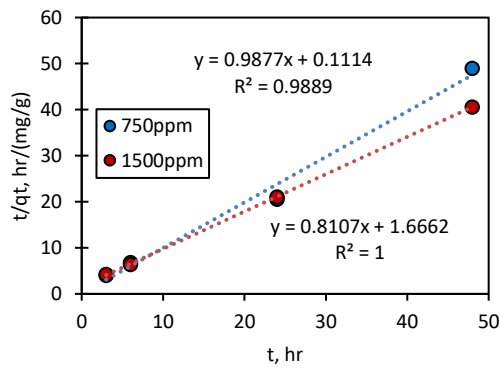


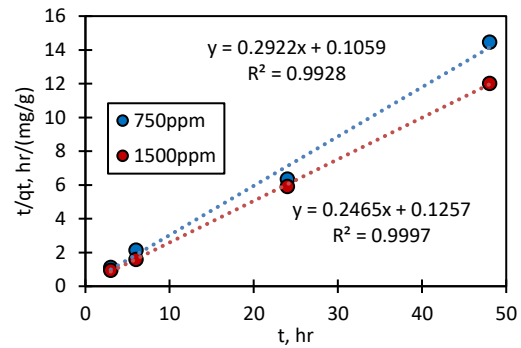
Figure 33: Surfactant adsorption on adsorbents as a function of time at different concentrations: (a) 750ppm and (b) 1500ppm

Table 17: Parameters of different adsorption kinetic models fitting

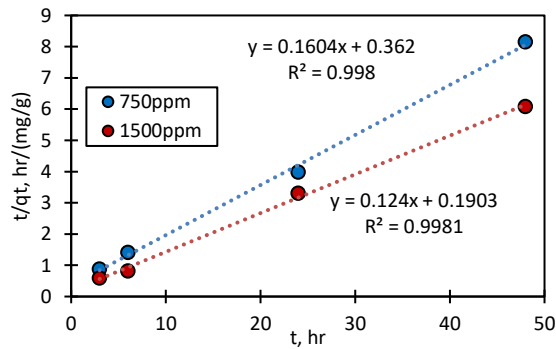
Adsorbent			Lidam Sample 1		Lidam Sample 2		Lidam Sample 3	
Surfactant concentration (ppm)			750	1500	750	1500	750	1500
Kinetic Model	Pseudo Second Order	K_2 (g/mg hr)	8.7572	0.3945	0.8062	0.4834	0.0711	0.0808
		q_e (mg/g)	1.0125	1.2335	3.4223	4.0568	6.2344	8.0645
		R^2	0.9889	1	0.9928	0.9997	0.998	0.9981
	Intra-particle diffusion model	K_p (mg/g hr)	0.0513	0.0839	0.1586	0.1345	0.4886	0.3994
		R^2	0.4639	0.8393	0.5514	0.6173	0.8323	0.576
	Elovich model	β (g/mg)	9.0416	6.0168	3.0534	3.5740	1.0324	1.2347
		α (mg/g hr)	45.6806	5.3956	398.6805	15315.3803	12.5813	328.9634
		R^2	0.6119	0.9349	0.6676	0.7579	0.9284	0.6721



(a) Lidam Sample 1



(b) Lidam Sample 2



(c) Lidam Sample 3

Figure 34: Fitting of Pseudo Second Order kinetic model for the three adsorbents

4.3.4 Adsorption Isotherms

The results of static adsorption experiments of GS12 on Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3 have been shown in Figure 35. The adsorption on all outcrop samples increases by increasing surfactant concentration. For the case of Lidam Sample 1, the adsorption increases gradually to ~400 ppm and then achieves an adsorption plateau at around 1 mg/g of rock. However, Lidam Sample 2 and Lidam Sample 3 attain the adsorption plateau at ~500 ppm. The adsorption values in the plateau region for Lidam Sample 2 and Lidam Sample 3 are ~4 and ~7 mg/g-rock, respectively. The GS12 adsorption on Lidam Sample 2 was found higher than that of Lidam Sample 1. This may be due to the presence of quartz (2.8%) and montmorillonite (0.1%) in Lidam Sample 2. Quartz and montmorillonite increase the number of negative binding sites and hence allowing more cationic GS12 molecules to adsorb on the rock surface. Lidam Sample 3 contains more impurities (quartz = 17.3% and montmorillonite = 0.3%) in comparison with Lidam Sample 2. Therefore, the adsorption of GS12 on Lidam Sample 3 was found higher than that of Lidam Sample 2. It may be concluded that if a carbonate formation contains even a slight quantity of silicate and/or clay minerals, a higher degree of cationic GS12 adsorption may take place. These conclusions are in line with previous studies [16,164,165]. In addition, the degree of adsorption will increase as the percentage of silicate and/or clay minerals increases. The amount of adsorption was in the order of Lidam Sample 1 < Lidam Sample 2 < Lidam Sample 3.

In order to study the adsorption process further, adsorption isotherm modeling was conducted using standard adsorption isotherm models, such as Henry, Langmuir,

Freundlich, and Redlich-Peterson. The Levenberg-Marquardt algorithm was used to perform a nonlinear least-squares curve fitting of the experimental data. Figure 36(a) to (c) present the curve-fitting for Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3, respectively, employing Henry, Langmuir, Freundlich, and Redlich–Peterson adsorption models. Coefficient of determination (R^2) was used to perform the model evaluation as shown in Table 18. Table 18 also shows the model parameters obtained after the curve fitting using different adsorption isotherm models. The lowest R^2 was obtained from Henry’s adsorption isotherm model and the highest R^2 was achieved using the Redlich-Peterson model for all adsorbents. The R^2 from the Langmuir model fitting was found comparable with the Redlich-Peterson model. Kalam et al. proposed that both Langmuir and Redlich–Peterson isotherms performed better in carbonates, depicting interdigitated bilayer adsorption mechanism of cation GS12 on carbonates that is equivalent to monolayer adsorption [164]. Another study showed that both Redlich-Peterson and Langmuir's adsorption isotherm models provided superior fits for the adsorption pattern of a soap-nut surfactant on different rock types, including carbonates, supporting the monolayer adsorption behavior [176]. The model performance was found in the order of Redlich-Peterson > Langmuir > Freundlich > Henry.

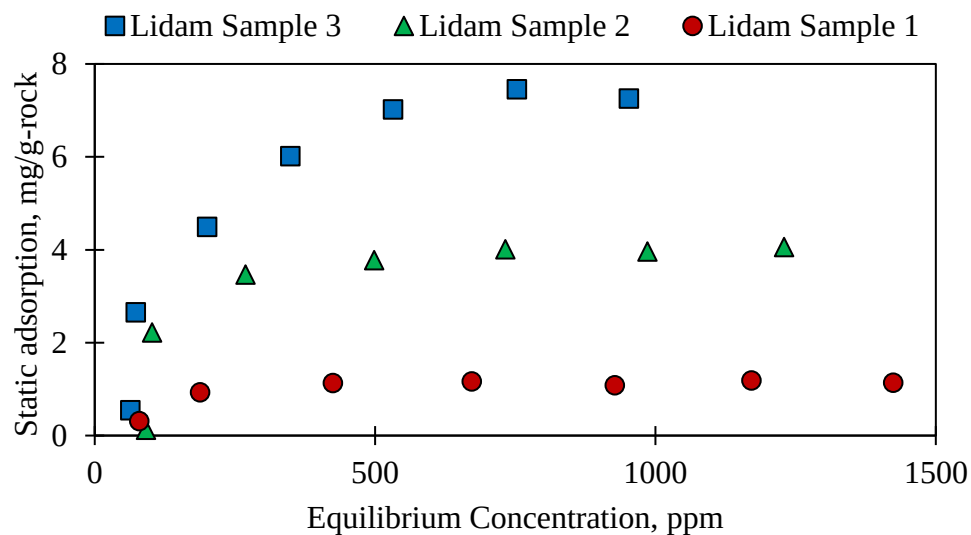


Figure 35: Static adsorption of GS12 on the three adsorbents

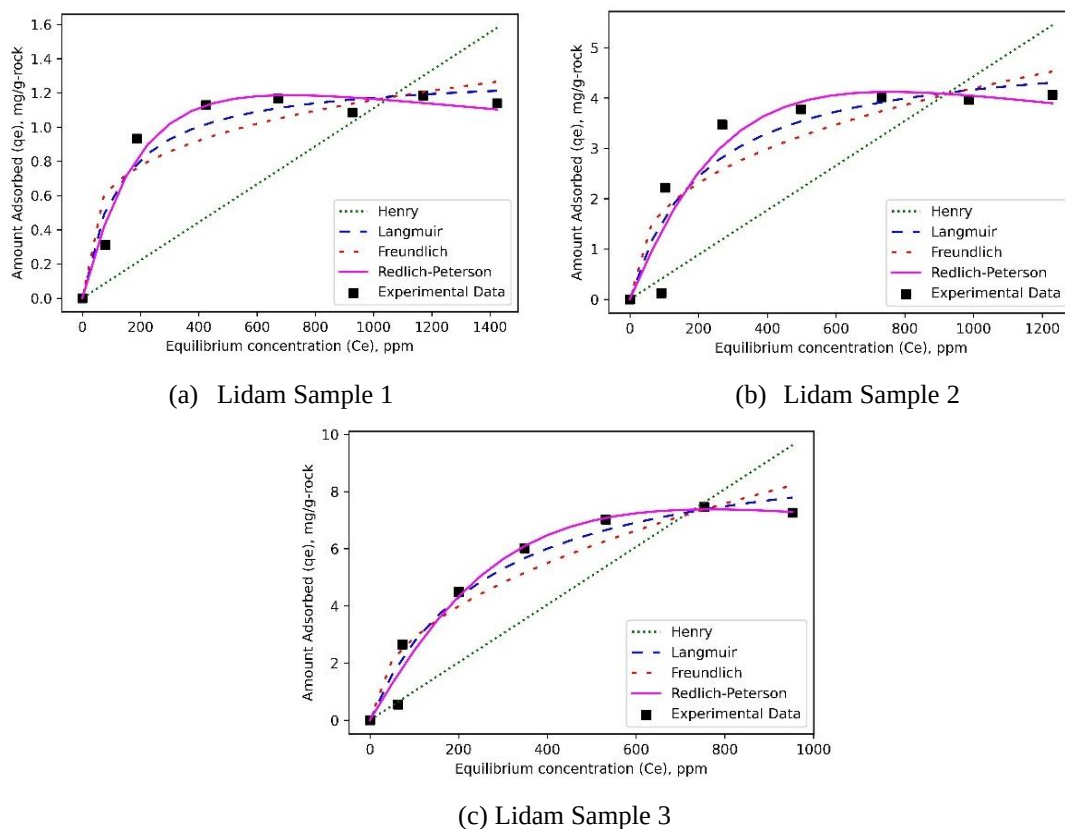


Figure 36: Adsorption isotherm modeling for all adsorbents

Table 18: Adsorption isotherm parameters for all adsorbents

Adsorbent	Henry		Langmuir		Freundlich		Redlich-Peterson	
Lidam Sample 1	K_{HE}	0.0011	K_L	0.0079	K_F	0.2061	K_R	0.0063
	R^2	0.0375	q_m	1.3193	n	4.0016	α_r	3.77E-04
			R^2	0.9403	R^2	0.8678	β_r	1.3573
							R^2	0.9714
Lidam Sample 2	K_{HE}	0.0044	K_L	0.0047	K_F	0.3262	K_R	0.0157
	R^2	0.3577	q_m	5.0504	n	2.7048	α_r	7.38E-05
			R^2	0.8638	R^2	0.8019	β_r	1.5307
							R^2	0.8919
Lidam Sample 3	K_{HE}	0.0101	K_L	0.003814	K_F	0.341681	K_R	0.026
	R^2	0.6219	q_m	9.935552	n	2.156742	α_r	4.65E-05
			R^2	0.9571	R^2	0.9107	β_r	1.5823
							R^2	0.9715

4.3.5 Effect of Salinity

The majority of standard EOR surfactants perform poorly in a high saline environment, often indicating precipitation upon the addition of Ca^{2+} and Mg^{2+} to their aqueous solutions [187]. The results are presented in Figure 37. Most notably, no solubility challenges were seen in these tests, even when the $CaCl_2$ and $MgCl_2$ concentrations went as elevated as 146,900 ppm (1M) and 203,200 ppm (1M), respectively.

Figure 37(a) presents the impact of seawater on the static adsorption of cationic GS12 on Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3. The adsorption was found to decrease for all adsorbents in comparison with that in deionized water. Since seawater contains several monovalent and multivalent salts, therefore it was crucial to explore the effect of individual salts on the adsorption of surfactant on dolomite rocks.

Figure 37(b) shows the effect of monovalent salt (NaCl) at 1000 ppm GS12 concentration. Both low salinity (5845 ppm or 0.1M) and high salinity (58,450 ppm or 1M) cases were analyzed. There exists an electric double layer at the adsorbent and adsorbate interface due to the unequal distribution of electrical charges [193]. At low salinity conditions, the electric double-layer between microparticles on a rock surface is expanded [194]. Expansion of the electric double-layer lowers the interfacial energy between fluid and rock [195], thereby reducing the surfactant adsorption on the rock surface. This mechanism has been observed for all studied rocks as shown in Figure 37(b). In contrast, the addition of a higher concentration of NaCl (58,450 ppm) results in increasing the surfactant adsorption on all rock samples. With the increase of the concentration of NaCl, the electrical double layer on the surface of the adsorbent is assumed to be compressed. Therefore, the repulsive forces between the surfactant and the rock reduce, leading to an increase in surfactant adsorption. On the other hand, the addition of divalent salts (CaCl_2 and MgCl_2) showed a reduction in surfactant adsorption for all adsorbents as shown in Figure 37(c) and (d). The higher the concentration of divalent salts in the surfactant solution, the more reduction of adsorption takes place. This may be due to the increase of rock surface charge by lattice ions (Ca^{2+} and Mg^{2+}) [34]. The sign of zeta potential was found positive for dolomite suspended in an aqueous solution containing CaCl_2 and MgCl_2 [196]. Consequently, repulsive forces between the surfactant and the rock surface increase, leading to adsorption reduction. Other studies also reported that the adsorption of a cationic surfactant on carbonate can be lessened by adding multivalent cations [34,165]. The adsorption value was reduced to 0.08 mg/g-rock and 0.01 mg/g-rock in the case of Lidam Sample 1 by

adding 1M CaCl_2 (146,900 ppm) and 1M MgCl_2 (203,200 ppm) in 1000 ppm GS12 surfactant solution, respectively.

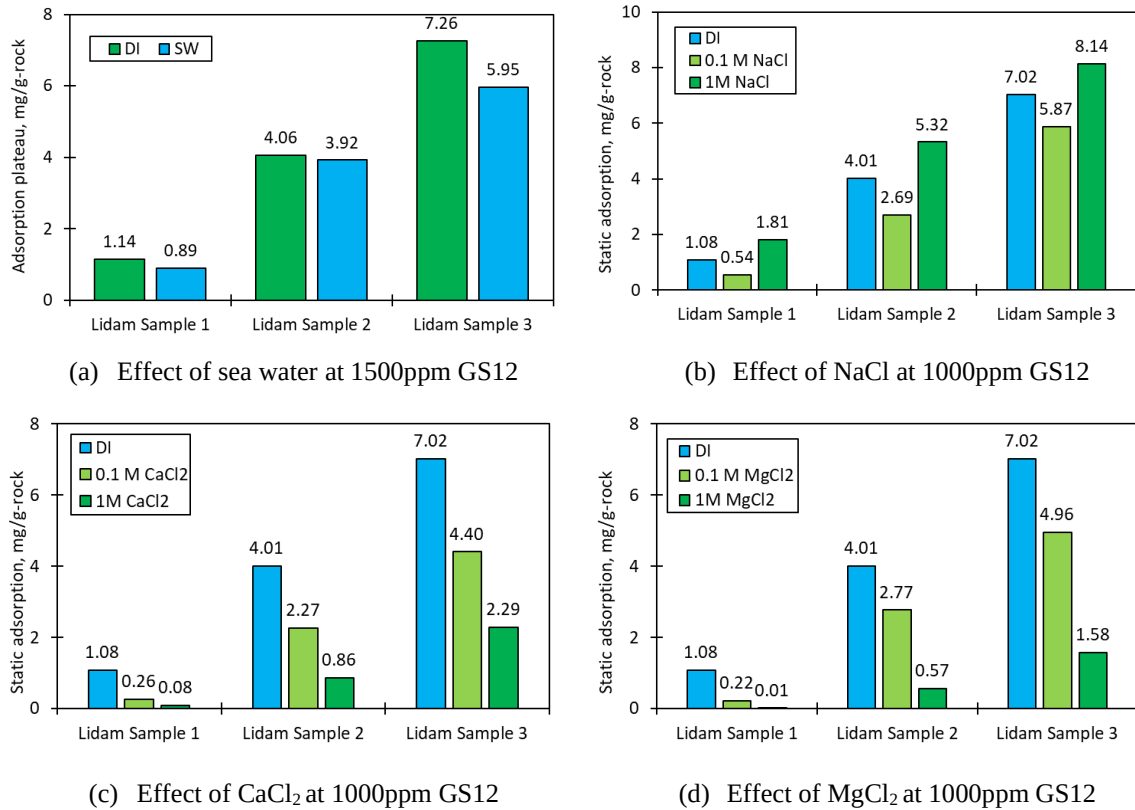


Figure 37: Effect of salinity on adsorption on GS12 on all adsorbents

4.3.6 Effect of Temperature

The effect of temperature has been analyzed on the static adsorption of GS12 on Lidam Sample 1 and Lidam Sample 2 as shown in Figure 38. Figure 38 displays adsorption of 1.14 mg/g-rock at 25 °C on Lidam Sample 1 at 1500ppm GS12 concentration which was reduced to 0.25 mg/g-rock at 80 °C. A similar trend was observed on Lidam Sample 2 in which the GS12 adsorption was decreased from 4.06 mg/g-rock to 2.83 mg/g-rock at 1500ppm by increasing the temperature from 25 °C to 80 °C, respectively. The decline in

adsorption with a temperature increase was seen to be around 78.07% and 30.29% for Lidam Sample 1 and Lidam Sample 2, respectively. The reduction of adsorption at elevated temperatures may be attributed due to the exothermic nature of the adsorption process. Other studies also show that the surfactant adsorption decreases with the increase in temperature [79,101,197]. The higher temperature causes higher translational kinetic energy. The force of interaction between GS12 and adsorbents becomes weaker at elevated temperatures, leading to the decrease of surfactant adsorption.

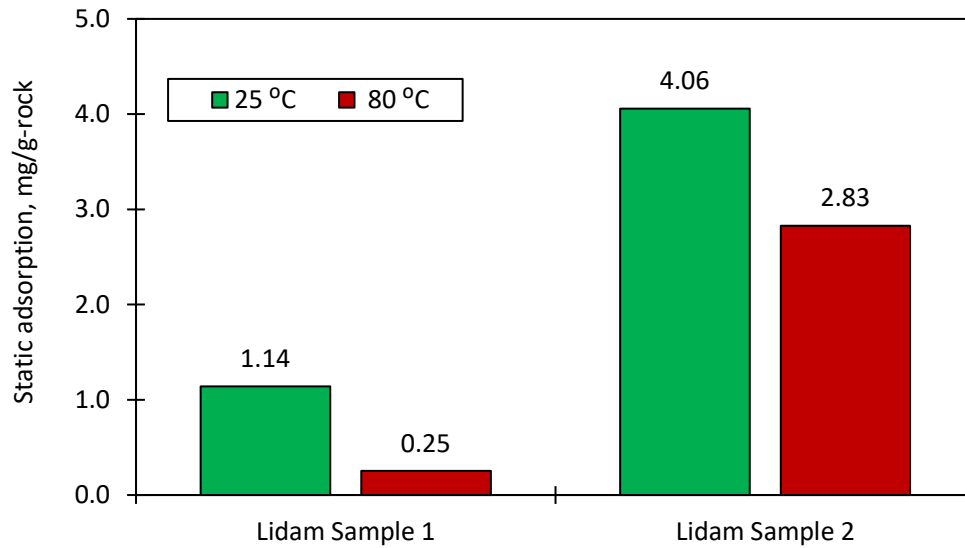


Figure 38: Effect of temperature on static adsorption on adsorbents at 1500ppm surfactant concentration prepared in DI water

The change in Gibbs free energy of adsorption (ΔG) was also calculated using Eq. (15) [198].

$$\Delta G = -RT \ln(55.5 \times 10^3 M_{adsorbate} K_L) \quad (15)$$

where, R is the universal gas constant (8.314 J/mol/K), T is the temperature in K, $M_{adsorbate}$ is the molecular weight of the adsorbate, and K_L is the Langmuir constant in L/mg.

The Langmuir adsorption constant (K_L) was used to evaluate the spontaneity of the adsorption process using ΔG . The ΔG at 25 °C was found to be -33.76 kJ/mol, -32.47 kJ/mol, and -31.96 kJ/mol for Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3, respectively. The negative value of the change in Gibbs free energy of adsorption shows that the adsorption process was spontaneous for all adsorbents.

4.3.7 Adsorption Reduction using Methylene Blue

A novel adsorption inhibition – methylene blue (MB) has been revealed in this study. MB is a cationic dye that is very cheap and can be easily available in the textile industry. Firstly, Lidam Sample 3 which contains a large amount of impurities was tested with 100ppm of MB (without surfactant) keeping the solid to liquid ratio of 1:15. Figure 39 shows Fourier-transform infrared spectroscopy (FTIR) of pure MB and Lidam Sample 3 before and after treatment. The FTIR spectra of pure MB shows a deep valley in the region of 3125 cm^{-1} – 3500 cm^{-1} . FTIR spectra of Lidam Sample 3 after treatment with 100ppm of MB also showed a similar deep valley in the region of 3125 cm^{-1} – 3500 cm^{-1} , indicating the adsorption of MB on the surface of the outcrop sample. This suggests that the addition of MB in the surfactant solution may help in reducing the GS12 adsorption on the studied dolomite rocks. Therefore, a series of adsorption experiments were conducted at 1500ppm GS12 concentration with the addition of MB on all adsorbents. The concentration of MB was varied from 100ppm to 500ppm.

Figure 40 presents the results of adsorption reduction on all adsorbents using methylene blue. The adsorption was reduced significantly by the small addition of MB. GS12 adsorption on Lidam Sample 1, Lidam Sample 2, and Lidam Sample 3 was reduced to 0.32 mg/g-rock, 0.77 mg/g-rock, and 4.06 mg/g-rock by the addition of only 100ppm MB in the surfactant solution. It is proposed that MB molecules are forming a bridge between the cationic GS12 and the negative binding sites of the adsorbents, resulting in electrostatic repulsion, therefore, decreasing the surfactant adsorption as shown in Figure 41. Adsorption of GS12 was further reduced by adding 300ppm and 500ppm of MB. The adsorption was reduced to 2.31 mg/g-rock on Lidam Sample 3 by using 500ppm MB. This suggests that more quantity of MB may be required if a carbonate rock contains a very high percentage of silicate and clay minerals. The maximum surfactant adsorption reduction using 500ppm MB was 8 times for the case of Lidam Sample 1 and Lidam Sample 2, and 3 times for Lidam Sample 3 as illustrated in Figure 40. Figure 42 shows the images of adsorbents obtained after the surfactant adsorption tests along with methylene blue. The color intensity was increased from left to right in the order Lidam Sample 1 < Lidam Sample 2 < Lidam Sample 3. Lidam Sample 3 showed an intense blue color depicting a higher percentage of MB adsorption.

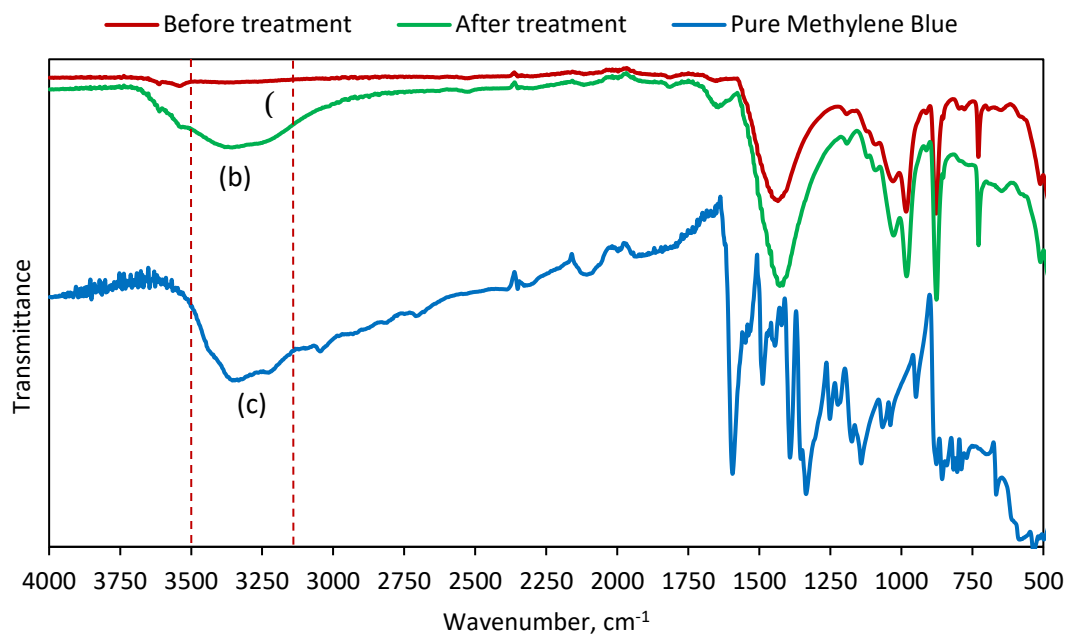


Figure 39: FTIR spectra: (a) Lidam Sample 3 before treatment, (b) Lidam Sample 3 after treatment, and (c) Pure methylene blue

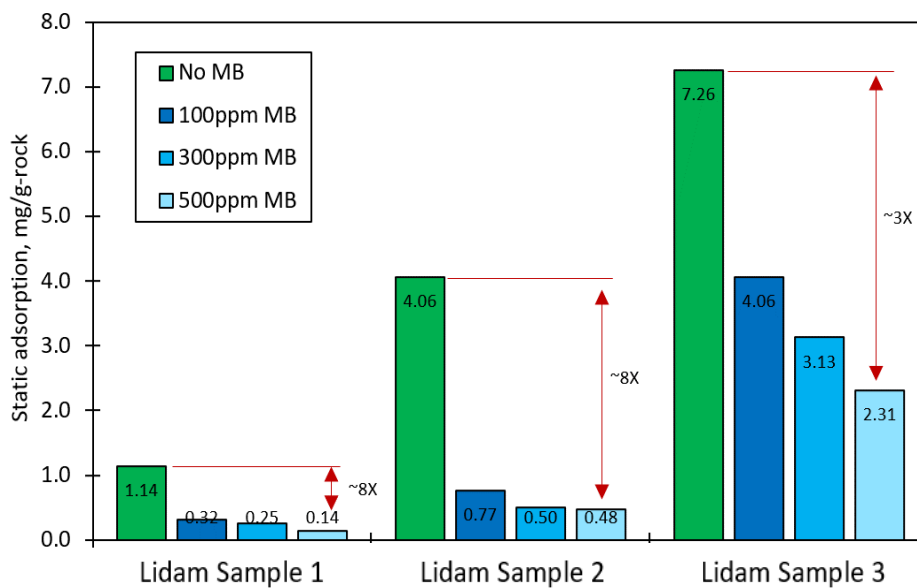
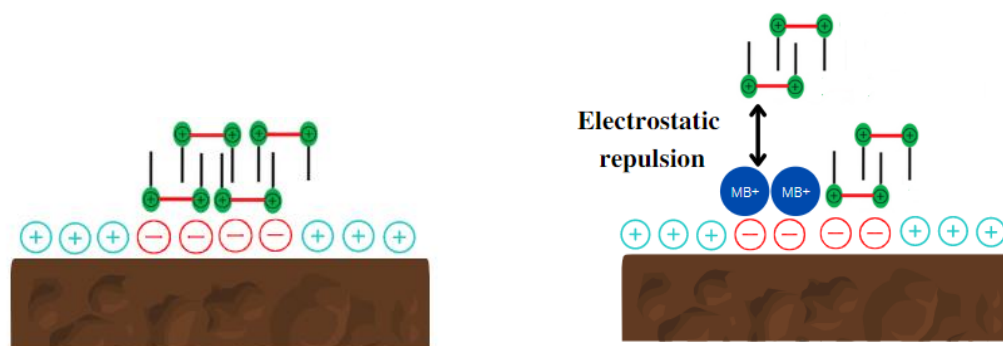


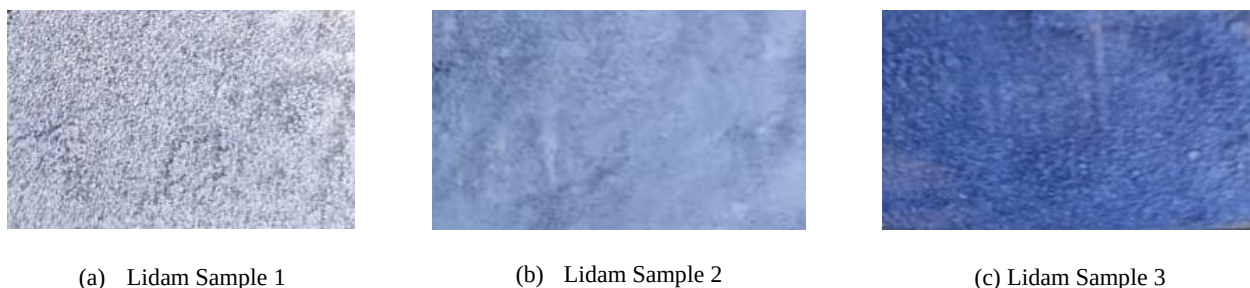
Figure 40: Adsorption reduction on all adsorbents using methylene blue at 1500ppm initial surfactant concentration.



(a) Interdigitated bilayer adsorption mechanism in carbonate [164]

(b) Adsorption reduction mechanism in carbonate using MB

Figure 41: Proposed adsorption reduction mechanism using methylene blue in carbonates (Saudi dolomite)



(a) Lidam Sample 1

(b) Lidam Sample 2

(c) Lidam Sample 3

Figure 42: Adsorbents after adsorption experiments with the addition of MB.

4.4 Conclusions

A detailed study regarding the adsorption of a cationic Gemini surfactant (GS12) on Saudi dolomite samples was carefully performed. The laboratory investigations were commenced to identify the adsorption equilibrium and kinetics behaviors of GS12. Following conclusions can be drawn from this study.

1. Static adsorption tests were conducted to generate the adsorption isotherms and the data for adsorption kinetics. Curve fitting was performed to analyze the data. Redlich-Peterson and Pseudo-second order models were found best to explain the adsorption isotherm and kinetics, respectively.
2. GS12 adsorption increases on Saudi dolomite as the surfactant concentration increases until reaching a saturation point.
3. Adsorption of cationic GS12 on Saudi dolomite samples increases with the increase of the percentage of impurities, such as quartz and montmorillonite.
4. GS12 adsorption was found reduced significantly at high temperatures and high concentrations of divalent salts (CaCl_2 and MgCl_2).
5. In terms of NaCl, a low salinity condition is suitable for reducing surfactant adsorption because of the expansion of the electric double-layer.
6. A novel adsorption inhibition – methylene blue (MB) has been discovered in this study. The addition of little quantity of MB in the surfactant solution will decrease the surfactant adsorption significantly. Eight times adsorption reduction was noticed by using 500ppm MB on the Saudi dolomite samples with little or no impurities.

CHAPTER 5

Adsorption Reduction of a Gemini Surfactant on Carbonate

Rocks: Static and Dynamic Conditions

Abstract

Surfactant flooding improves oil recovery by lowering the interfacial tension and/or altering the reservoir rock's wettability. However, surfactant losses caused by adsorption on the surface of the rock weaken the efficiency of this chemical enhanced oil recovery process. This study focuses on reducing adsorption of a cationic Gemini surfactant on carbonate rocks using formic acid. High-performance liquid chromatography integrated with an evaporative light scattering detector were employed to quantify both static and dynamic surfactant adsorptions. The results showed that the surfactant's adsorption on carbonate rocks was reduced dramatically by adding 1% formic acid to the surfactant solution. Static adsorption was reduced from 2.44, 1.62, and 1.51 mg/g-rock to 0.16, 0.14, 0.13 mg/g-rock on Guelph dolomite, Guff dolomite, and Indiana limestone, respectively. The dynamic adsorption of the surfactant on Indiana limestone was reduced from 0.269 to 0.041 mg/g-rock. It is believed that the carboxyl group released by the formic acid-rock reaction shields the surfactant from the rock surface resulting in lower adsorption. This is evidenced by the surfactant solution's pH dropping below the point of zero charge of the

rock, causing repulsion of the cationic surfactant molecules off the surface. This study provides a low-cost option that provides remarkable reduction in cationic surfactant adsorption on carbonate rocks.

5.1 Introduction

Carbonate reservoirs contain about 60% of the remaining oil reserves worldwide [185,186]. However, carbonate rocks are very heterogeneous, naturally fractured, and are categorized as either oil-wet or mixed wet [199]. Moreover, many of the carbonate rocks are tight (<50 mD permeability) [200,201]. Because of these complexities, incremental oil recovery by water flooding carbonate reservoirs is usually low [202]. Around 60% of the original oil in place (OOIP) remains trapped in oil reservoirs [203]. Therefore, enhanced oil recovery (EOR) methods have been considered to unlock the residual oil [204,205].

As a chemical EOR technique, surfactant flooding improves oil recovery by lowering oil/water interfacial tension (IFT) and/or changing wettability. A monomeric unit of a surfactant consists of a hydrophilic head and a hydrophobic tail [206]. Based on such molecular structure, surfactants are generally categorized into four types: anionic, cationic, zwitterionic, and non-ionic. A Gemini surfactant is an unusual type, which contains more than one hydrophilic head group and a hydrophobic tail group linked via a spacer at or near the head groups [207]. Gemini surfactants behave like two in one and show interesting properties the most special of which is the formation of aggregates at a significantly lower concentration in comparison with the monomeric types, resulting in very low critical micelle concentration (CMC). The lower CMC value aids in lowering IFT efficiently.

Recently, several studies have been published on Gemini surfactants that focus on their foaming characteristics [19], wettability alteration [208], reduction of interfacial tension [209,210], and surfactant-polymer solution rheology [7], adsorption [73,142,164,167]. Although surfactants are beneficial as EOR agents, they pose several challenges such as compatibility with high temperature and high salinity (HTHS) environments, adsorption on rocks, and cost.

There are several studies conducted on surfactant adsorption [211–217]. Surfactant adsorption is the most critical issue during surfactant flooding that can make or break the success of the EOR process. It is the transferring of surfactant molecules from the bulk phase to the liquid-solid interface [218,219]. The prime mechanism of ionic surfactants' adsorption on rocks is their electrostatic attraction towards the oppositely charged rock surface [151,220]. Surfactant adsorption causes loss of chemicals from an aqueous solution leading to the reduction of surfactant concentration. Consequently, IFT reduction is greatly impaired and would require a larger quantity of surfactant to achieve the goal. Therefore, the economics and efficiency of surfactant flooding are greatly based on its adsorption characteristics on the rock surface. In this regard, anionic surfactants are desirable for sandstone reservoirs, and cationic surfactants are preferred for carbonate rocks [151]. However, surfactant adsorption still occurs due to the rock impurities such as clay and/or silicate minerals [151,164,221,222]. Several research studies have been conducted to lower surfactant adsorption on rocks [151,223,224]. Since the most important factor affecting the adsorption process is the rock's surface charge density, which changes with the solution pH, the point of zero charge (PZC) is the pH at which there is no net charge on the rock

surface. For pH values lower than PZC, the adsorbents' surface charge will be positive and vice versa. Sandstone rocks exhibit a negative surface charge at higher pH values. Hence, the addition of alkali to the surfactant solution will reduce the adsorption of anionic surfactants on sandstone. Examples of such alkalis are sodium hydroxide, sodium carbonate, sodium polyacrylate, sodium tetraborate, ammonia [9,27,41,67,151,225]. However, this is not the case with cationic surfactants in carbonates since turning rock surface charge negative will increase cationic surfactant adsorption. Therefore, other techniques should be employed that will render rock surface more positively charged. Ahmadali and co-authors demonstrated that the presence of divalent cations (Ca^{2+} and Mg^{2+}) considerably lessens the adsorption of cationic surfactants on carbonates [34]. Ma et. al suggested that cetylpyridinium chloride's adsorption on natural carbonates can be decreased in the presence of 1 atm CO_2 in contrast with 1 atm of air [221]. The inclusion of CO_2 acidifies the surfactant solution making the carbonate surface more positive. Consequently, cetylpyridinium chloride's adsorption was reduced due to electrostatic repulsion.

In this study, formic acid was employed in reducing both the static and dynamic adsorptions of an in-house-synthesized, cationic, Gemini surfactant on three types of carbonate rock. To the best of our knowledge, such research work has not been conducted so far. The rocks were characterized using XRD and XRF techniques. PZC of adsorbents was determined using the pH drift method. Static adsorption tests were conducted using the linear shake method while dynamic adsorption was estimated by core flooding tests. Solutions were analyzed after the adsorption tests using HPLC (high-performance liquid

chromatography) integrated with an evaporative light scattering detector (ELSD) sensor.

The adsorption mechanism was investigated using standard adsorption isotherms.

5.2 Methodology

5.2.1 Adsorbents

Samples of Guelph dolomite, Guff dolomite, and Indiana limestone were used as adsorbents. The rock samples were crushed to powder and sieved to obtain a uniform particle size (90 – 180 μm).

5.2.2 Gemini Surfactant

The in-house-synthesized Gemini surfactant used in this study, code-named GS12, is cationic in nature as depicted in Figure 43. It is quaternary ammonium with bromide counter ions. Its spacer length is C12 and the hydrophobic tail is also C12; hence it is a 12-12 Gemini surfactant. This surfactant is tolerant of high temperature and high salinity (HTHS) environments because of the appropriate positioning of ethoxy units between the hydrophilic head and hydrophobic tail units [129]. One of the most interesting features of GS12 is its extremely low CMC value of about $8.26 \times 10^{-6} \text{ mol/L}$ (15.5 ppm).

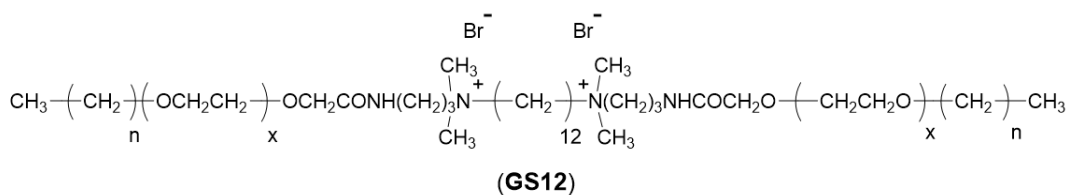


Figure 43: Chemical structure of quaternary ammonium Gemini surfactant (GS12) [129]

5.2.3 Rock Characterization: XRD and XRF

X-ray diffraction (XRD) and X-ray fluorescence (XRF) were employed on the rock powders to determine the rock mineralogical and elemental compositions, respectively.

5.2.4 Determination of Point of Zero Charge (PZC)

The rock surface charge is an important property in adsorption studies. PZC is the value of pH at which the rock surface charge is neutral. If the pH value is decreased below PZC, the rock surface carries a net positive charge and vice versa. PZC of each adsorbent was determined by the pH drift method using a 0.01 M NaCl solution as the background electrolyte. 30 mL samples of the background solution were prepared with pH values ranging between 4 and 11. The pH was adjusted using 0.1M HCl and 0.1M NaOH aqueous solutions. The adsorbent (0.2 g) was added to each sample and the final pH was noted after 24 hr. A plot of the difference between the initial and final pH values revealed the PZC at which such difference was zero [226].

5.2.5 High-Performance Liquid Chromatography

The concentration of the surfactant after adsorption tests was determined using high-performance liquid chromatography (HPLC) coupled with an evaporative light scattering detector (ELSD). The mobile phases were 0.1 M ammonium formate altered to pH 4.50 using formic acid and acetonitrile. A reversed-phase column - Acclaim™ surfactant plus having 3µm average particle size of the packing, 4.6mm in diameter and 150mm in length, was employed for detecting GS12. The gradient method used in the reversed-phase HPLC for the current study is shown in Table 19.

Table 19: Gradient methodology of HPLC

Time, min	Acetonitrile	Ammonium formate (pH = 4.5)	Flow rate (ml/min)
0	0	100	1
10	100	0	1
11	0	100	2

The calibration curve was constructed using surfactant solutions with known concentrations. The ELSD area of the investigated fluid was then used to find the concentration

5.2.6 Static Adsorption Experiments

Static adsorption tests were carried out using 1g of powdered adsorbents in 15ml of GS12 at several concentrations. The mixture was shaken for 24hr and then centrifuged for 30 minutes at 3000 rpm. Static adsorption can be determined using Eq. (16).

$$\Gamma_{\text{static}} = \left(\frac{\Delta C}{1000m_R} \right) V_s \quad (16)$$

where Γ_{static} (mg/g-rock) is the amount of surfactant adsorbed on the adsorbent's surface, $\Delta C = C^o - C$ where C^o (ppm) and C (ppm) are the surfactant's initial and final concentrations, respectively, V_s (ml) is the volume of the surfactant solution, and m_R (g) is the mass of the powdered adsorbent [227].

5.2.7 Dynamic Adsorption Experiments

In order to estimate the dynamic adsorption of GS12 on carbonate rock, flooding experiments were conducted on Indiana limestone core samples. Figure 44 shows a

schematic diagram of the core-flood setup. The core flood proceeded as follows: (a) the core sample was flooded with several pore volumes of deionized water (base fluid) to ensure complete saturation, (b) the sample was then flooded with about 20 pore volumes of the surfactant solution until the core effluent showed approximately the same concentration as the injected solution, and (c) the sample was flooded with base fluid to capture the desorption behavior. Waterflooding was continued until no surfactant peaks were observed in the HPLC system. All tests were performed at 0.25 mL/min injection rate, 2500 psi confining pressure, 1500 psi back pressure, and ambient temperature conditions. Dynamic adsorption was computed by Eq. (17).

$$\Gamma_{dynamic} = \frac{C^0V - \sum_{i=1}^N C_i V_i}{m} \quad (17)$$

where $\Gamma_{dynamic}$ (mg/g-rock) is the adsorption of the surfactant on Indiana limestone, C_0 (ppm) is the injection surfactant concentration, V is the total volume of injected surfactant solution (L), C_i (ppm) and V_i are the surfactant concentration and volume of the effluents collected at time period i , m (g) is the total mass of the dry core sample, and N is the total number of collected effluent samples.

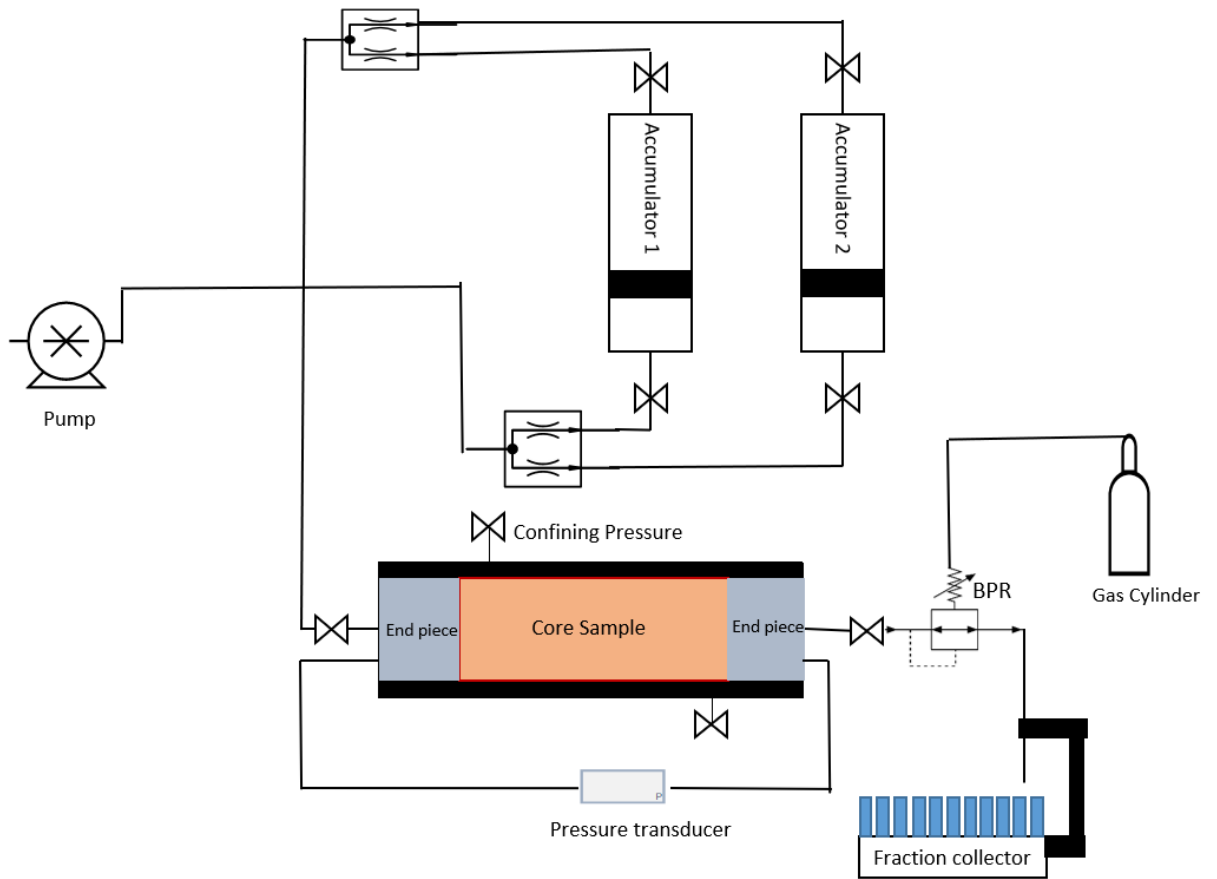


Figure 44: Schematic of the core flood setup.

5.2.8 Medical CT scanner

CT scans of the whole rock cores were conducted using a medical CT scanner with a resolution larger than 1 mm.

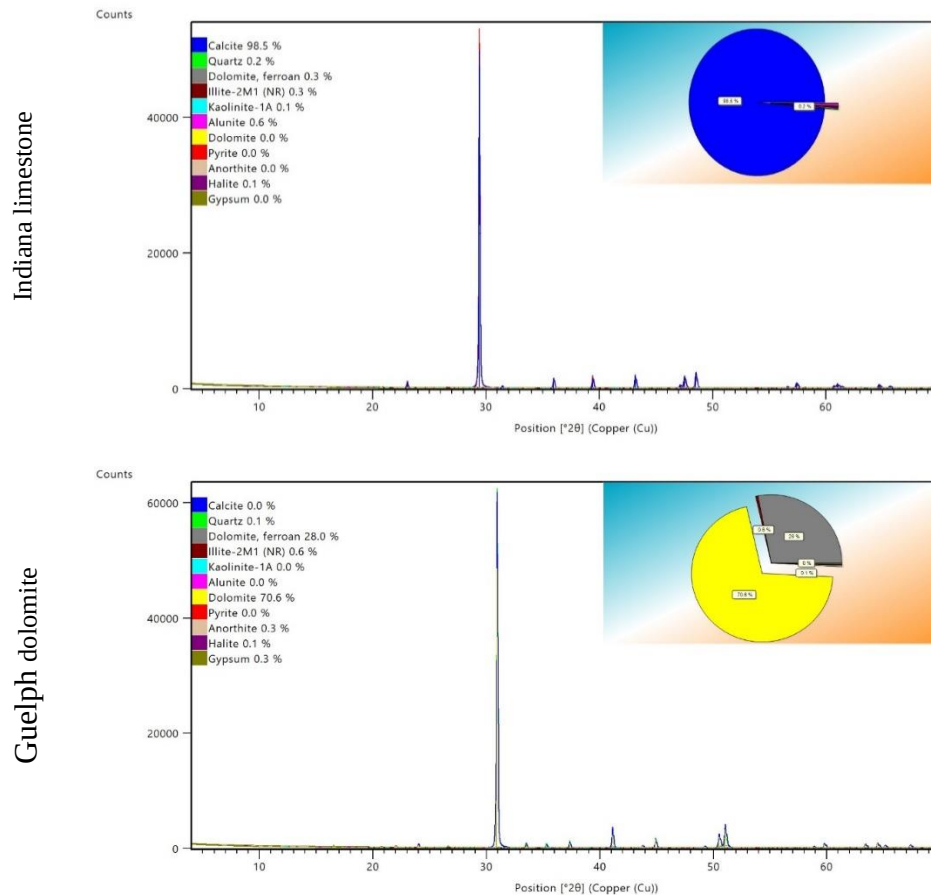
5.2.9 Adsorption Isotherm Models

Please see section 1.3 for the description of adsorption isotherm models.

5.3 Results and Discussions

5.3.1 Characterization of Adsorbents: XRD and XRF

XRD (Figure 45) and XRF (Table 20) tests on the 3 rock samples show that Indiana limestone contains 98.5% calcite along with 0.2% quartz, 0.3% Illite, and 0.1% Kaolinite. On the other hand, Guelph and Guff dolomites contain significant impurities such as illite (0.6% and 0.3%, respectively) and quartz (0.1% in Guelph), but no Kaolinite. The total clay content in Guelph dolomite is higher than that in Guff dolomite.



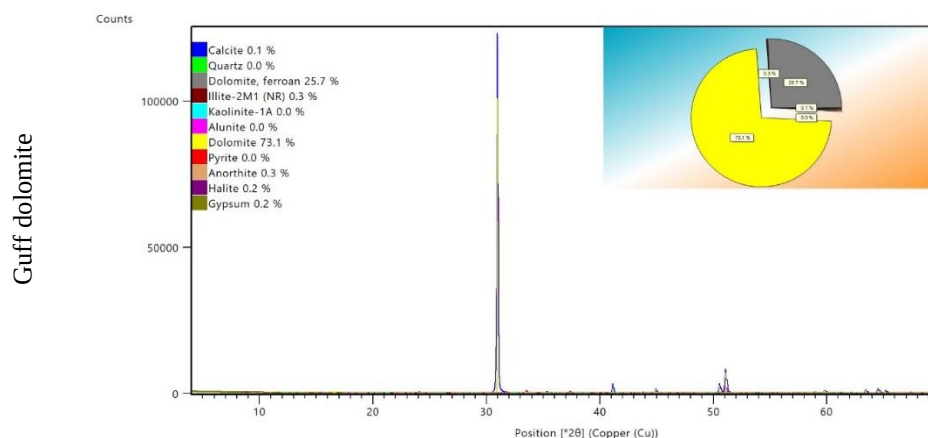


Figure 45: XRD of adsorbents

Table 20: XRF of adsorbents

Elements	Indiana Limestone	Guelph Dolomite	Guff Dolomite
Na	0.22	0	0
Mg	0.41	26.01	25.82
Al	0.31	0.47	0.5
Si	0.44	1.16	1.57
K	2.99	0.37	0.5
Ca	94.68	71.08	70.95
Ti	0.01	0.05	0.05
V	0	0.02	0.02
Cr	0	0.01	0.01
Mn	0.05	0.03	0.03
Fe	0.73	0.69	0.46
Cu	0	0.01	0.01
Sr	0.14	0.07	0.07
Nb	0.01	0.02	0.02

5.3.2 Determination of PZC

The results of the pH drift method are shown in Figure 46. As listed in Table 21, the PZC values of Indiana limestone, Guelph dolomite, and Guff dolomite are 9.98, 9.98, and 9.57, respectively. These suggest that if the solution pH is lowered below the corresponding PZC

of the adsorbent, the net positive surface charge on the adsorbent will help repel the cationic GS12 leading to adsorption reduction.

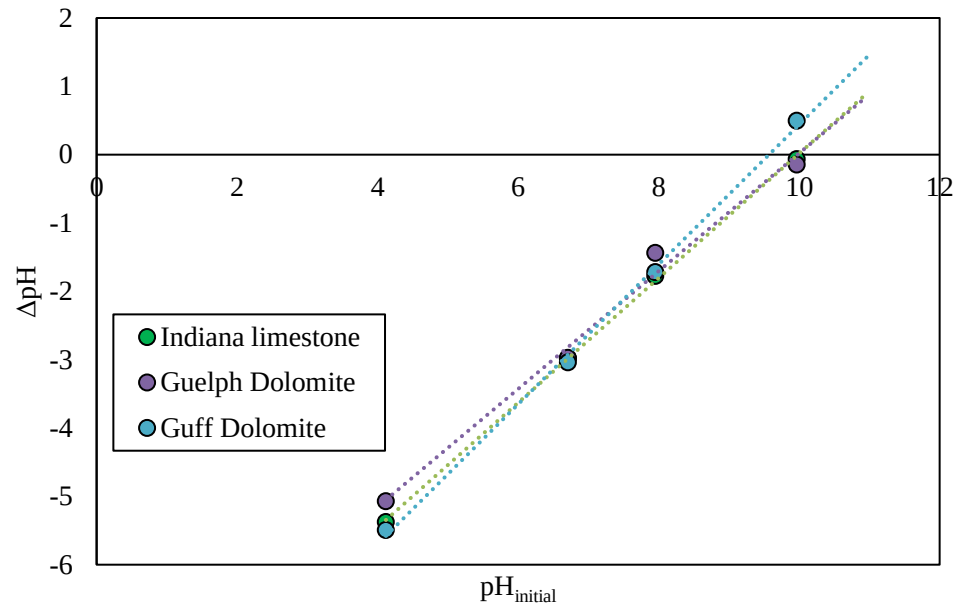


Figure 46: PZC determination of all adsorbents using pH drift method

Table 21: PZC values of all adsorbents

Rock type	PZC
Indiana limestone	9.98
Guelph Dolomite	9.98
Guff Dolomite	9.57

5.3.3 Static Adsorption of GS12 on all Adsorbents

Figure 47 presents the results obtained from static adsorption tests of GS12 on the rock samples. It is evident that surfactant adsorption on all rocks rises with the increase of concentration. The adsorption plateau was obtained at around 600ppm surfactant concentration. The average adsorption values in the plateau region for Indiana limestone,

Guelph dolomite, and Guff dolomite was about 1.51 mg/g-rock, 2.44 mg/g-rock, and 1.62 mg-g-rock, respectively. Adsorption on all adsorbents took place due to the presence of negative binding sites of silicate and/or clay minerals. Guelph dolomite contains the largest fraction of clay minerals, which caused the highest degree of adsorption as compared to the two other adsorbents. This is consistent with the previous studies [16,164,165].

To investigate further, the constructed adsorption isotherms were analyzed using standard adsorption isotherm models. The Levenberg-Marquardt algorithm was employed to perform nonlinear, least-squares curve fitting of the experimental data with the standard models. The objective was to determine the model parameters along with error metrics such as the mean absolute error (MAE), the mean squared error (MSE), and the coefficient of determination (R^2) for each adsorbent. Figure 48 presents a comparison of these models while the model parameters and error metrics are listed in Tables 22 and 23, respectively. Table 23 shows that the Redlich-Peterson model performed better than the others with the lowest error and highest R^2 . Redlich-Peterson model contains three parameters, integrates the features of both Freundlich and Langmuir, and does not assume an ideal monolayer adsorption behavior. However, the Langmuir model assumes monolayer adsorption behavior and showed comparable results to those of the Redlich-Peterson model. This is consistent with our previous findings that an interdigitated bilayer (equivalent to a monolayer) of cationic GS12 is formed on carbonate rocks [164].

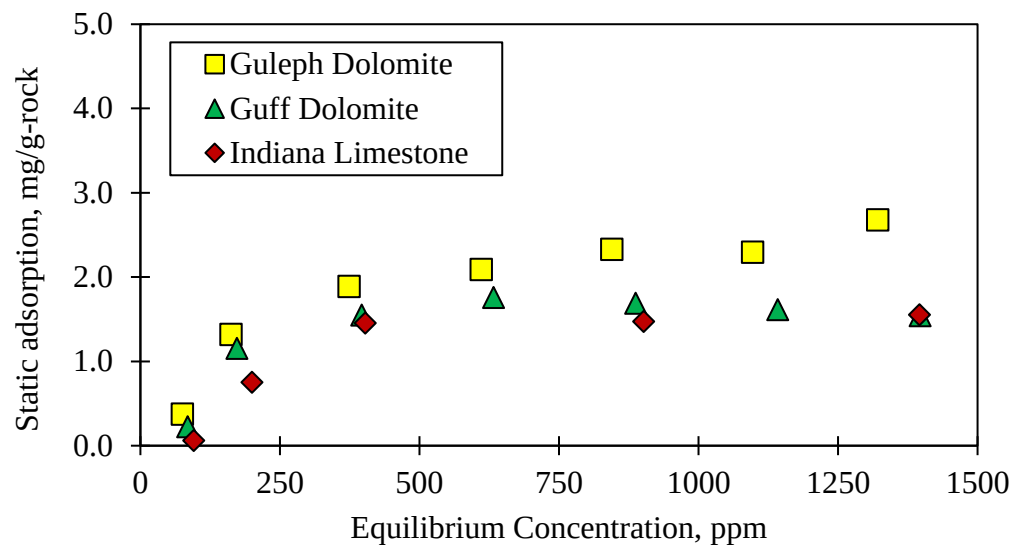


Figure 47: Static adsorption tests of all adsorbents

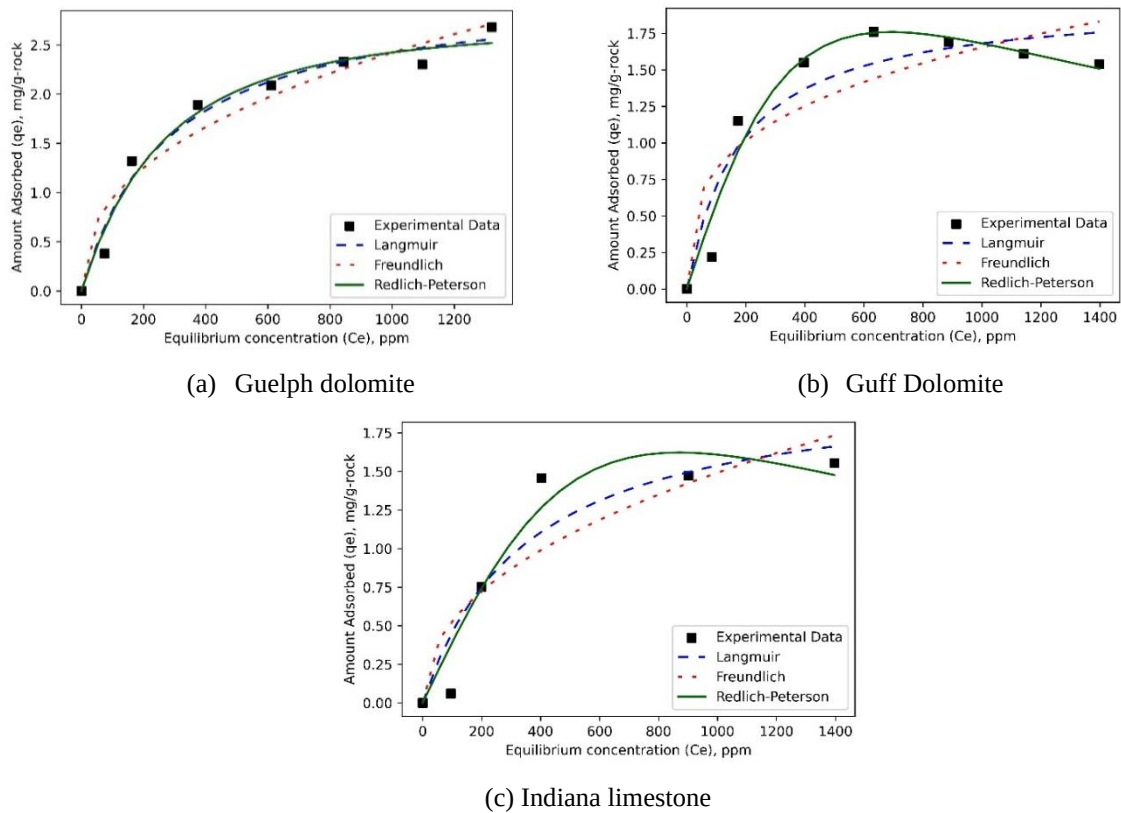


Figure 48: Adsorption isotherm modeling for all adsorbents

Table 22: Model parameters obtained after the curve fitting of the experimental data with adsorption isotherm models.

Rock Type	Langmuir	Freundlich	Redlich-Peterson
Guelph dolomite	$K_L = 0.003644$	$K_F = 0.1436$	$K_R = 0.00997$
	$q_m = 3.0895$	$n = 2.4454$	$\alpha_r = 0.001574$
			$\beta_r = 1.09876$
Guff dolomite	$K_L = 0.00562$	$K_F = 0.20316$	$K_R = 0.00618$
	$q_m = 1.9789$	$n = 3.2947$	$\alpha_r = 2.12675 \times 10^{-5}$
			$\beta_r = 1.7001$
Indiana limestone	$K_L = 0.002822$	$K_F = 0.06710$	$K_R = 0.003984$
	$q_m = 2.08363$	$n = 2.2273$	$\alpha_r = 3.37428 \times 10^{-6}$
			$\beta_r = 1.8804$

Table 23: Error metrics of the fitted adsorption isotherms

Rock type	Error metrics	Langmuir	Freundlich	Redlich-Peterson
Guelph dolomite	MAE	0.1125	0.1661	0.1158
	MSE	0.0209	0.0472	0.0201
	R^2	0.9748	0.9432	0.9758
Guff dolomite	MAE	0.1692	0.2327	0.075
	MSE	0.0433	0.081	0.016
	R^2	0.8971	0.8071	0.9619
Indiana limestone	MAE	0.1438	0.1963	0.1232
	MSE	0.0466	0.077	0.0272
	R^2	0.8924	0.8222	0.9372

5.3.3.1 Reduction of Static Adsorption

5.3.3.1.1 Effect of formic acid

Different acids were tried to lower the static adsorption of GS12 on all adsorbents. By adding 1% HCL acid to the surfactant solution, static adsorption on Guelph dolomite and Guff dolomite were lowered by about 73% and 79%, respectively. A similar test could not be conducted on Indiana limestone because of the fast mineral dissolution. However, the weaker formic acid caused a dramatic reduction in GS12 adsorption. Adding 1% formic

acid to the GS12 solution resulted in about 93.4%, 91.4%, and 91.4% adsorption reduction on Guelph dolomite, Guff dolomite, and Indiana limestone, respectively.

Adding HCL and formic acid reduced the surfactant solution's pH below the PZC of the adsorbents as shown in Figure 49. A previous study also shows that acidifying the surfactant solution results in a more positively charged surface [221]. However, at the same concentration, formic acid produced a pH lower than that with HCL acid, resulting in larger reduction in GS12 adsorption (Figure 50). The authors believe that the carboxyl group released by the formic acid-rock reaction shields the surfactant from the rock surface resulting in lower adsorption.

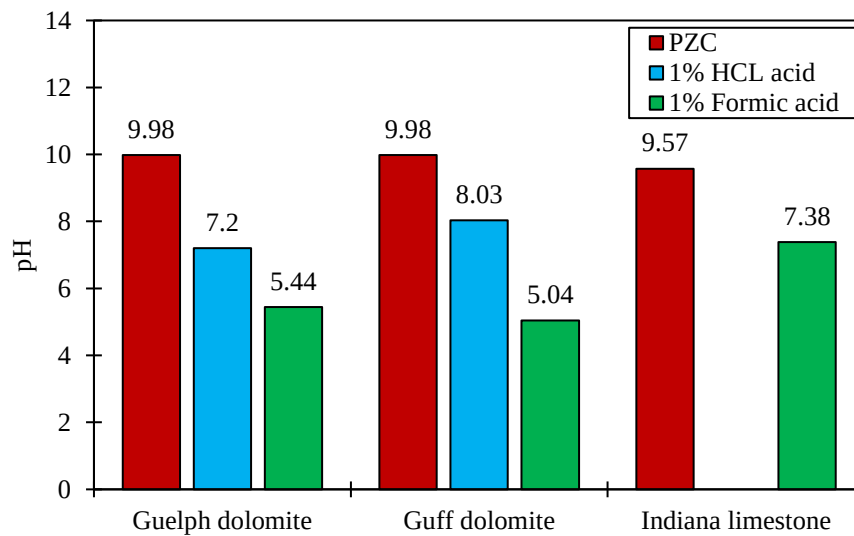


Figure 49: Comparison of PZC and pH decrement by adding HCL and formic acid in GS12

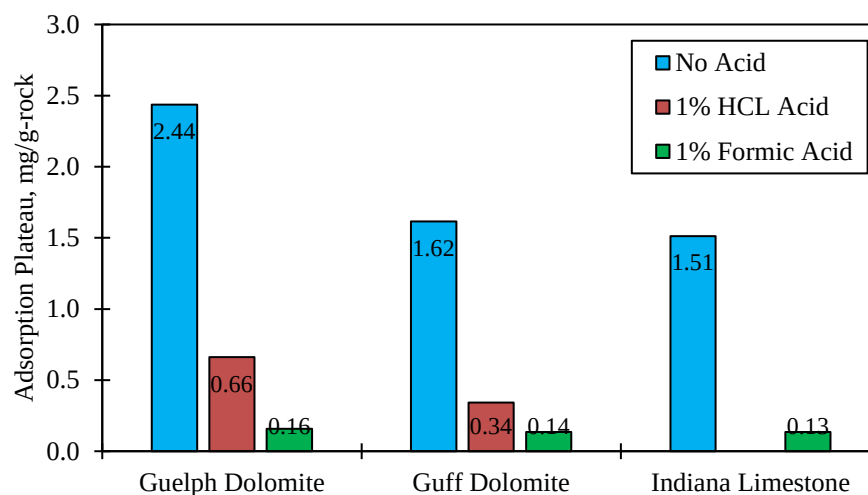


Figure 50: Adsorption reduction on all rocks using different acids at 1500ppm surfactant concentration

5.3.3.1.2 Effect of Low Salinity Water

The effect of low salinity water (LSW) was investigated on the adsorption of GS12 on Indiana limestone. Results were compared with the GS12 solution made in deionized water (DI) and high saline water (HSW) as shown in Figure 51. It was found that adsorption values were reduced in both HSW and LSW conditions. However, the percentage reduction of the surfactant adsorption was found higher in the case of the LSW condition as compared to the HSW condition. Static adsorption of GS12 on Indiana Limestone was reduced from 1.51 mg/g-rock to 0.18 mg/g-rock using LSW condition. This may be due to the expansion of the electric double layer at the solid-liquid interface.

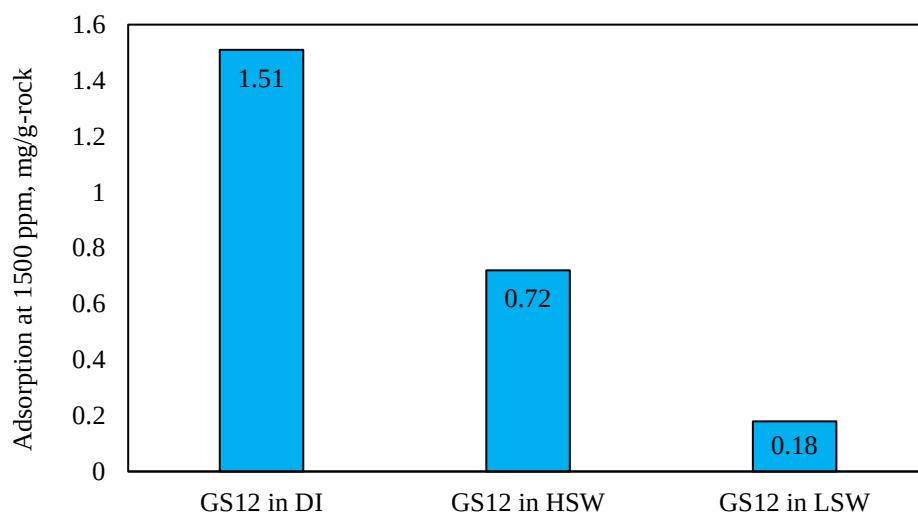


Figure 51: Adsorption reduction of GS12 on Indiana Limestone using low salinity water

5.3.4 Dynamic Adsorption

Dynamic adsorption of GS12 on Indiana limestone was investigated at 25 °C by the following three core floods:

1. Core flood with a GS12 solution at 1500 ppm concentration made in deionized water.
2. Core flood with a GS12 solution at 1500 ppm concentration with the addition of 1% formic acid.
3. Core flood with a GS12 solution at 1500 ppm concentration made in low salinity water (LSW).

The injection rate was kept at 0.25 mL/min for the three core floods. This rate corresponds to a superficial velocity of about ~0.3 m/day. The properties of the core samples are listed

in Table 24. In the first two tests, the core samples were saturated with deionized water, whereas the core sample was saturated with the low salinity water in the third core flood. After saturating the core sample, each test was conducted in two phases: (1) flooding with GS12 solution to capture the adsorption process followed by (2) flooding with the base fluid (deionized water in the first two core floods and low salinity water in the third core flood) to capture the desorption process. The effect of using formic acid and low salinity water (LSW) in the GS12 solution has been discussed in the following sections.

Table 24: Core sample characteristics

Condition	Diameter (mm)	Length (mm)	Dry Weight (g)	Bulk Vol. (ml)	Grain Vol. (ml)	Pore Vol. (ml)	Grain density (g/ml)	Porosity (%)	Permeability (mD)	
									Before flooding	After flooding
GS12 in DI	38.14	74.98	182.39	85.66	69.4	16.26	2.628	18.98	129	190
GS12 in formic acid	38.18	76.78	200.9	87.9	75.966	11.934	2.645	13.58	64	513
GS12 in LSW	38.15	74.13	189.88	84.74	71.74	13	2.647	15.34	155	156

5.3.4.1 Effect of Formic Acid

In this section, the first two core floods are compared. The surfactant concentration profiles in the core effluent of both floods are shown in Figure 52. Surfactant concentration in the effluent increased sharply in both cases till about 2 PVs injected then increased gradually till 5 PVs. In the no-acid test, the effluent's surfactant concentration became nearly equal to that of the injectant after 15 PVs. Surfactant flooding was continued till about 19 PVs followed by waterflooding for the desorption process for another 5 PV till the effluent did

not show any surfactant peak in the HPLC system. However, in the case with formic acid, the injected concentration of surfactant was nearly reached in the effluent at about 6 PVs. This flood was continued till about 21 PVs followed by about 7 to 8 PVs of waterflooding for the desorption phase.

Figure 53 presents the dynamic adsorption profile of the two core floods. It can be seen that the surfactant's adsorption was dramatically reduced by the addition of formic acid. This behavior verifies our static adsorption tests with and without formic acid. Adding formic acid acidified the GS12 solution making the rock surface charge more positive. Thus, the cationic surfactant was repelled and, consequently, its adsorption reduced. The dynamic adsorption of GS12 on Indiana limestone with and without formic acid was 0.041 and 0.269 mg/g-rock, respectively, which corresponds to an 84.76% reduction in adsorption (Figure 54). These findings are consistent with those of static adsorption tests shown in Figure 50. These differences are due to the higher surface area of the powdered adsorbents in the static tests.

Figure 55 shows the medical CT-scan images of the core samples after dynamic adsorption tests with and without formic acid in the surfactant solution. Formic acid created wormholes (dark spots in Figure 55(b)), which improved the core sample's permeability to 513 mD as listed in Table 24.

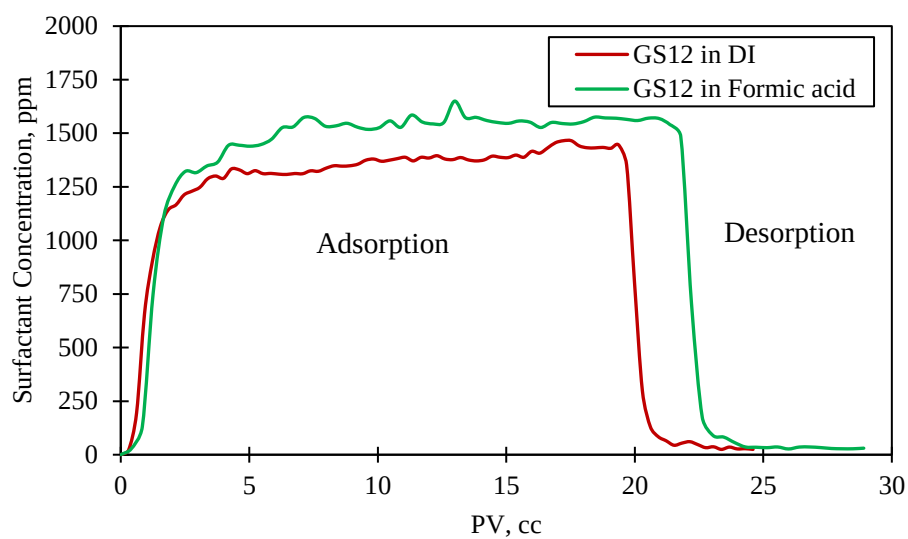


Figure 52: Surfactant concentration profiles obtained from the two core floods

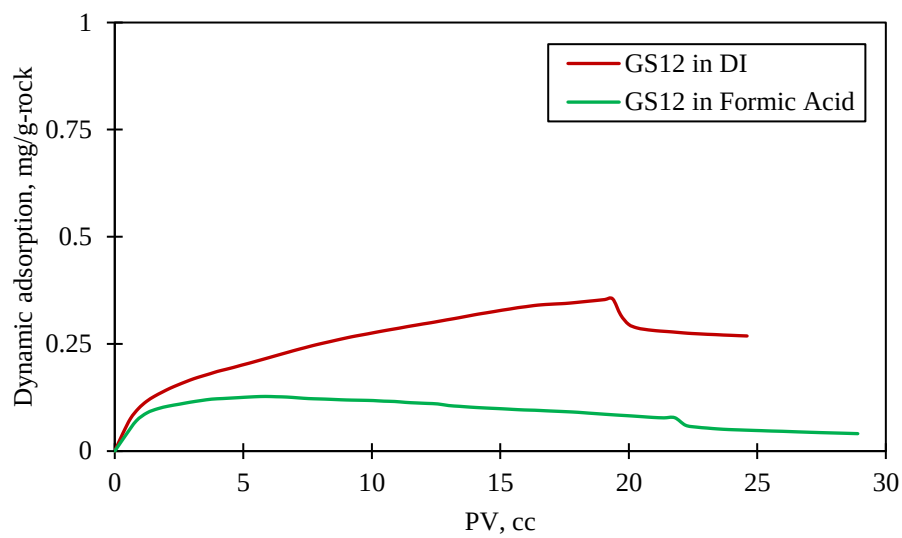


Figure 53: Dynamic adsorption profiles for the the two corefloods

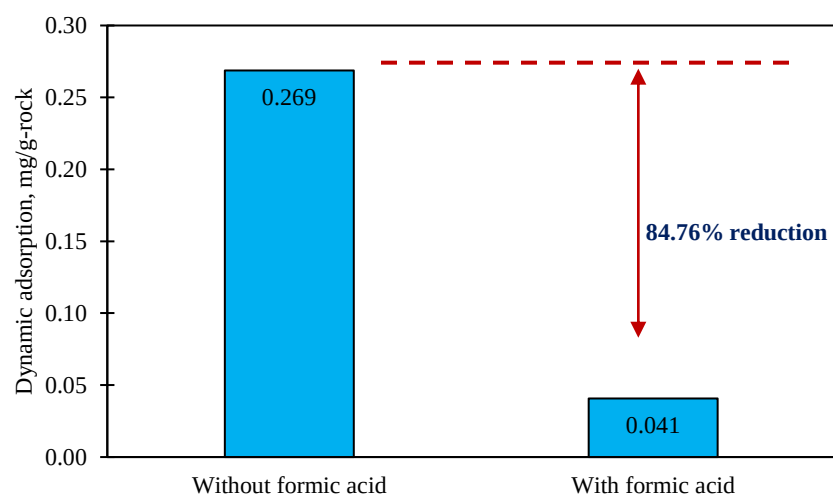
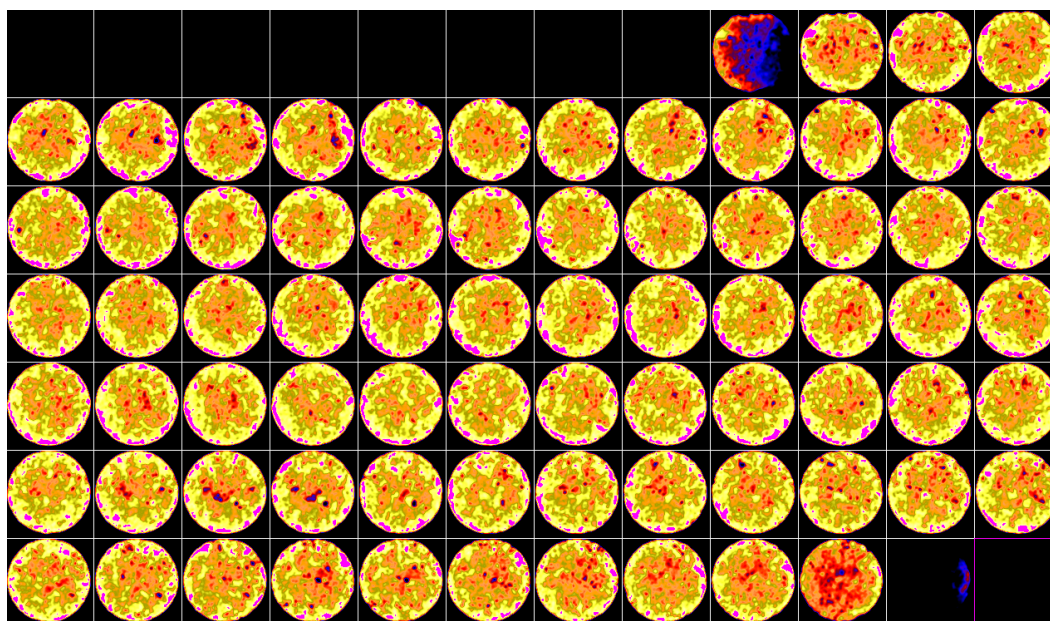
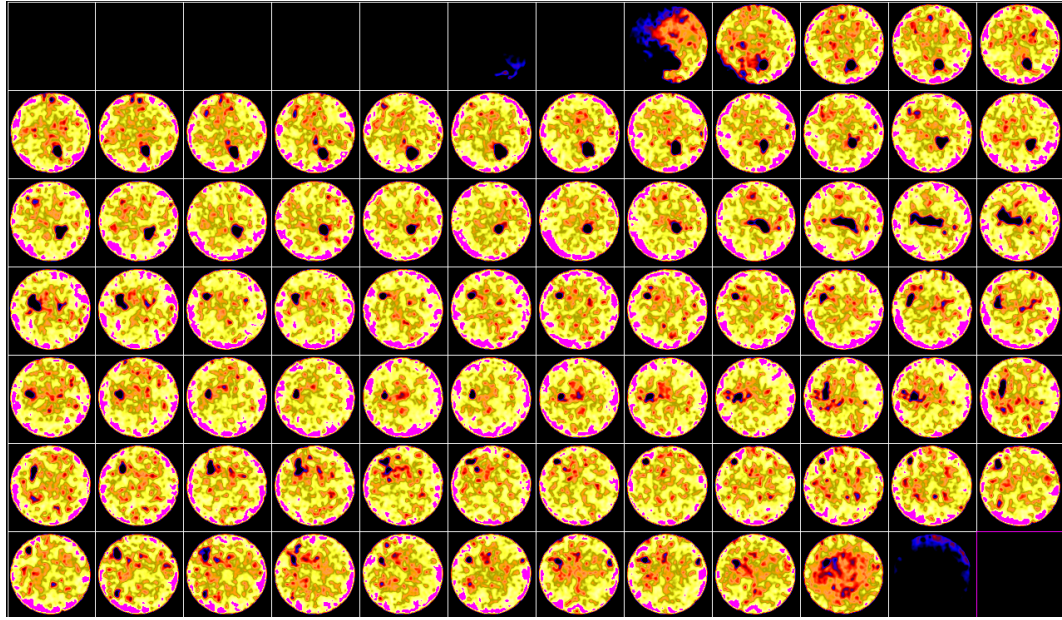


Figure 54: Comparison of dynamic adsorption values



(a)



(b)

Figure 55: Medical CT-scan images of the core sample after flooding with GS12 solution:

(a) without formic acid (b) with formic acid.

5.3.4.2 Effect of Low Salinity Water

The effect of low salinity water (LSW) was also investigated on the dynamic adsorption of GS12 on Indiana limestone. The first and third core floods were compared. LSW was made by diluting sea water ten times. The salinity of LSW was 6771 ppm. Figure 56 and

Figure 57 show surfactant concentration and dynamic adsorption profiles with and without LSW, respectively as a function of PV. The surfactant adsorption was reduced for the core flood of GS12 in LSW. The electric double layer at the solid-liquid interface expands under low salinity conditions [194]. This expansion resulted in the reduction of GS12 adsorption

on Indiana limestone. Nourani et al. also found that the surfactant adsorption was decreased under low salinity conditions [228]. Figure 58 shows that the dynamic adsorption was reduced from 0.269 to 0.11 mg/g-rock (59.11% reduction) using GS12 in LSW. The static adsorption results show that surfactant adsorption using LSW was reduced from 1.51 to 0.18 mg/g-rock at 1500 ppm surfactant concentration. These findings show that the use of the Gemini surfactant along with LSW will decrease the surfactant adsorption considerably.

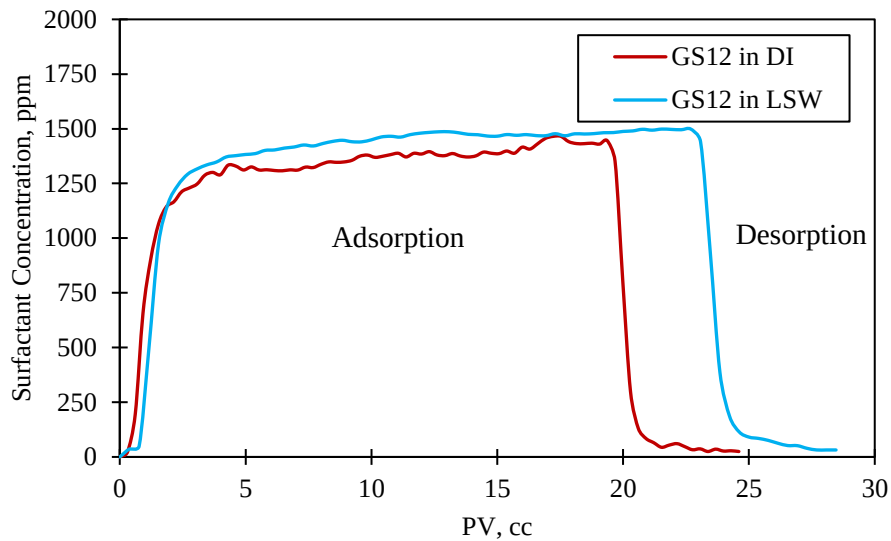


Figure 56: Surfactant concentration profiles obtained from the two core floods with and without LSW

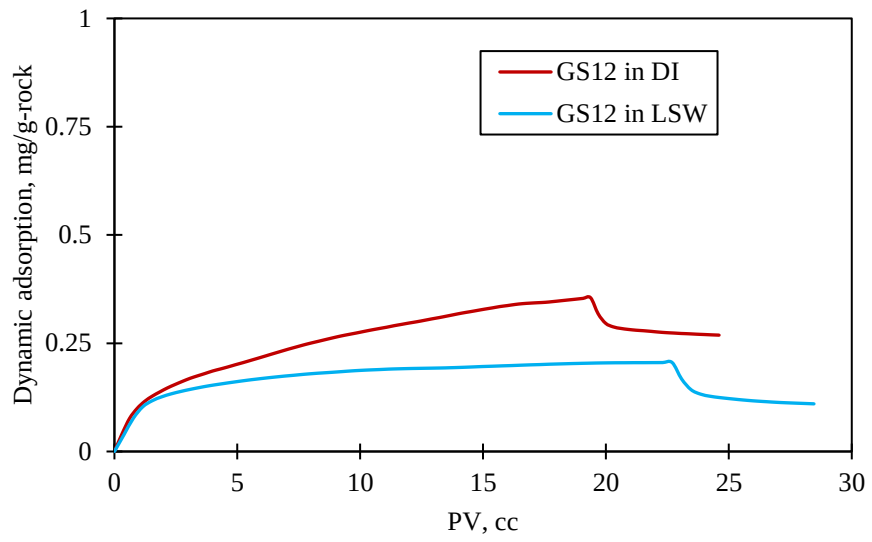


Figure 57: Dynamic adsorption profiles for the two core floods with and without LSW

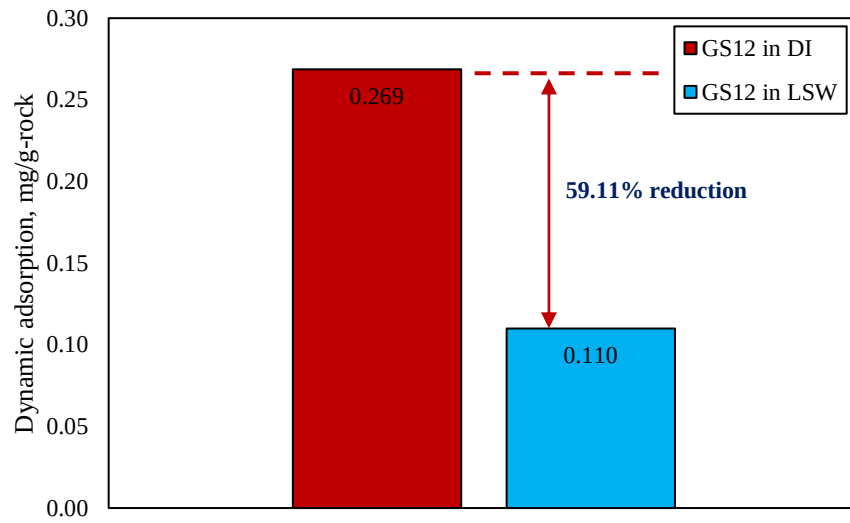


Figure 58: Comparison of dynamic adsorption values

5.4 Conclusions

The static and dynamic adsorption of a synthesized, cationic, Gemini surfactant (GS12) on carbonate rocks have been investigated in this study. The following conclusions can be drawn:

1. GS12 adsorption on Guelph dolomite, Guff dolomite, and Indiana limestone is promoted by the presence of impurities, such as quartz, montmorillonite, kaolinite, and Illite in the rock fabric.
2. By the pH drift method, the point of zero charge (PZC) of each carbonate rock was found around a pH of 10.
3. Adding 1% formic acid lowered the surfactant solution's pH below PZC, resulting in reduced static adsorption.
4. Adding 1% formic acid to 1500 ppm GS12 solution reduced the surfactant's static adsorption on Guelph dolomite, Guff dolomite, and Indiana limestone from 2.44, 1.62, and 1.51 to 0.16, 0.14, and 0.13 mg/g-rock, respectively.
5. With 1% formic acid, the dynamic adsorption of GS12 on Indiana limestone was reduced from 0.269 to 0.041 mg/g-rock. To the best of our knowledge, such a lower amount of adsorption of Gemini surfactants on carbonates has never been seen before.
6. The adsorption of GS12 was reduced from 1.51 mg/g-rock to 0.18 mg/g-rock under static conditions and from 0.269 mg/g-rock to 0.11 mg/g-rock under dynamic conditions using ten times diluted LSW.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Adsorption studies of an in-house synthesized cationic Gemini surfactant have been conducted on different types of carbonate rocks including local Saudi carbonate outcrop. Following conclusions can be drawn from this study.

1. Firstly, the adsorption mechanism of cationic GS12 was investigated. It is proposed that an interdigitated bilayer is formed on carbonate rocks, whereas a non-interdigitated bilayer in sandstone rock samples.
2. A mineralogical study was conducted to analyze the influence of individual minerals. It was found that the mineral type considerably affects GS12 adsorption. Clay minerals showed more negative effects as compared to silicate minerals (quartz and K-feldspar). Carbonate minerals (calcite and dolomite) showed very little amount of adsorption.
3. The maximum amount of surfactant adsorbed at 1500ppm was in the order of montmorillonite > kaolinite > Illite > K-feldspar > quartz > dolomite > calcite.

4. The reduction of surfactant adsorption on the mineral surface using divalent ions (Ca^{2+} and Mg^{2+}) was found higher than that of monovalent ions (Na^{+}) because of higher ionic strength.
5. Local Saudi carbonate outcrops were also studied. Redlich-Peterson and Pseudo-second order models were found best to explain the adsorption isotherm and kinetics, respectively.
6. GS12 adsorption was found reduced significantly at high temperatures and high concentrations of divalent salts (CaCl_2 and MgCl_2) on Saudi carbonate.
7. A novel adsorption inhibitor – methylene blue (MB) has been discovered in this study.
 - a. Eight times adsorption reduction was noticed by using 500ppm MB on the Saudi dolomite samples.
 - b. A mineralogical study showed that only 100ppm of MB reduced GS12 adsorption on quartz surface to 0.67 mg/g-rock.
 - c. The percentage of adsorption reduction in Illite and kaolinite was 59.05% and 80.26%, respectively by using 500ppm MB in 1500ppm GS12 aqueous solution.
 - d. Therefore, a little addition of MB in the surfactant solution will help in the reduction of surfactant adsorption on carbonate reservoirs containing quartz and clay minerals as impurities.

8. The effect of the point of zero charge (PZC) was also analyzed. The addition of 1% formic acid lowers the surfactant solution pH below PZC, resulting in the GS12 adsorption reduction due to electrostatic repulsion.
 - a. The reduced static adsorption values on Guelph dolomite, Guff dolomite, and Indiana limestone were 0.16, 0.14, and 0.13 mg/g-rock, respectively.
 - b. The dynamic adsorption of GS12 on Indiana limestone was reduced from 0.269 to 0.041 mg/g-rock by adding 1% of formic acid in the surfactant solution.
9. The effect of low salinity water (LSW) was investigated. LSW expands the electric double layer, resulting in lowering the surfactant adsorption. The static and dynamic adsorption of GS12 was reduced to 0.18 and 0.11 mg/g-rock, respectively using ten times diluted LSW.

6.2 Recommendations

This study can be extended further. Following are the recommendations for future work.

1. Investigate the proposed technique to analyze the individual effect of using methylene blue, formic acid, and low salinity water on oil/water interfacial tension and wettability alteration.
2. Test the oil recovery experiments along with methylene blue, formic acid, and low salinity water.

REFERENCES

- [1] Babadagli T. Philosophy of EOR. J Pet Sci Eng 2020;188:106930.
<https://doi.org/10.1016/j.petrol.2020.106930>.
- [2] Deng X, Kamal MS, Patil S, Hussain SMS, Zhou X. A Review on Wettability Alteration in Carbonate Rocks: Wettability Modifiers. Energy & Fuels 2020;34:31–54. <https://doi.org/10.1021/acs.energyfuels.9b03409>.
- [3] Schlumberger. Resource Library. Market Analysis 2007.
<https://www.slb.com/resource-library>.
- [4] Masalmeh SK, Wei L, Blom C, Jing X. EOR Options for Heterogeneous Carbonate Reservoirs Currently Under Waterflooding. Abu Dhabi International Petroleum Exhibition and Conference, Society of Petroleum Engineers; 2014.
<https://doi.org/10.2118/171900-MS>.
- [5] Demirbas A, Alsulami HE, Hassanein WS. Utilization of Surfactant Flooding Processes for Enhanced Oil Recovery (EOR). Pet Sci Technol 2015;33:1331–9.
<https://doi.org/10.1080/10916466.2015.1060503>.
- [6] Kamal MS, Hussein IA, Sultan AS. Review on Surfactant Flooding: Phase Behavior, Retention, IFT, and Field Applications. Energy & Fuels 2017;31:7701–20. <https://doi.org/10.1021/acs.energyfuels.7b00353>.

- [7] Kalam S, Kamal MS, Patil S, Hussain SMS. Impact of Spacer Nature and Counter Ions on Rheological Behavior of Novel Polymer-Cationic Gemini Surfactant Systems at High Temperature. *Polymers (Basel)* 2020;12:1027. <https://doi.org/10.3390/polym12051027>.
- [8] Fogang LT, Kamal MS, Hussain SMS, Kalam S, Patil S. Oil/Water Interfacial Tension in the Presence of Novel Polyoxyethylene Cationic Gemini Surfactants: Impact of Spacer Length, Unsaturation, and Aromaticity. *Energy & Fuels* 2020;acs.energyfuels.0c00044. <https://doi.org/10.1021/acs.energyfuels.0c00044>.
- [9] Belhaj AF, Elraies KA, Mahmood SM, Zulkifli NN, Akbari S, Hussien OS. The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review. *J Pet Explor Prod Technol* 2020;10:125–37. <https://doi.org/10.1007/s13202-019-0685-y>.
- [10] Olajire AA. Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: Prospects and challenges. *Energy* 2014;77:963–82. <https://doi.org/10.1016/j.energy.2014.09.005>.
- [11] Stosur GJ. EOR: Past, Present and What the Next 25 Years May Bring. SPE International Improved Oil Recovery Conference in Asia Pacific, Society of Petroleum Engineers; 2003. <https://doi.org/10.2118/84864-MS>.

- [12] Ghosh P, Mohanty KK. Novel Application of Cationic Surfactants for Foams With Wettability Alteration in Oil-Wet Low-Permeability Carbonate Rocks. *SPE Journal* 2018;23:2218–31. <https://doi.org/10.2118/179598-PA>.
- [13] Hill HJ, Reisberg J, Stegemeier GL. Aqueous Surfactant Systems For Oil Recovery. *Journal of Petroleum Technology* 1973;25:186–94. <https://doi.org/10.2118/3798-PA>.
- [14] Olajire AA. Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: Prospects and challenges. *Energy* 2014;77:963–82. <https://doi.org/10.1016/j.energy.2014.09.005>.
- [15] Santvoort J van, Golombok M. Viscoelastic surfactants for diversion control in oil recovery. *J Pet Sci Eng* 2015;135:671–7. <https://doi.org/10.1016/j.petrol.2015.10.030>.
- [16] Ma K, Cui L, Dong Y, Wang T, Da C, Hirasaki GJ, et al. Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. *J Colloid Interface Sci* 2013;408:164–72. <https://doi.org/10.1016/j.jcis.2013.07.006>.
- [17] Simjoo M, Dong Y, Andrianov A, Talanana M, Zitha PLJ. CT Scan Study of Immiscible Foam Flow in Porous Media for Enhancing Oil Recovery. *Ind Eng Chem Res* 2013;52:6221–33. <https://doi.org/10.1021/ie300603v>.

- [18] Andrianov A, Farajzadeh R, Mahmoodi Nick M, Talanana M, Zitha PLJ. Immiscible Foam for Enhancing Oil Recovery: Bulk and Porous Media Experiments. *Ind Eng Chem Res* 2012;51:2214–26. <https://doi.org/10.1021/ie201872v>.
- [19] Kalam S, Kamal MS, Patil S, Hussain SMS. Role of Counterions and Nature of Spacer on Foaming Properties of Novel Polyoxyethylene Cationic Gemini Surfactants. *Processes* 2019;7:502. <https://doi.org/10.3390/pr7080502>.
- [20] Alarifi SA, Mahmoud MA, Kamal MS. Interactions of DTPA chelating agent with sandstone rocks during EOR: Rock surface charge study. *Fuel* 2018;232:684–92. <https://doi.org/10.1016/j.fuel.2018.06.003>.
- [21] Pal S, Mushtaq M, Banat F, Al Sumaiti AM. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. *Pet Sci* 2018;15:77–102. <https://doi.org/10.1007/s12182-017-0198-6>.
- [22] Hirasaki G, Miller CA, Puerto M. Recent Advances in Surfactant EOR. *SPE Journal* 2011;16:889–907. <https://doi.org/10.2118/115386-PA>.
- [23] Lawson JB. The Adsorption Of Non-Ionic And Anionic Surfactants On Sandstone And Carbonate. *SPE Symposium on Improved Methods of Oil Recovery*, Society of Petroleum Engineers; 1978. <https://doi.org/10.2118/7052-MS>.

- [24] Wang D, Maubert M, Pope GA, Liyanage PJ, Jang SH, Upamali KAN, et al. Reduction of Surfactant Retention in Limestones Using Sodium Hydroxide. SPE Journal 2019;24:092–115. <https://doi.org/10.2118/194009-PA>.
- [25] Zhou X, Han M, Fuseni AB, Yousef AA. Adsorption of an Amphoteric Surfactant onto Permeable Carbonate Rocks. SPE Improved Oil Recovery Symposium, Society of Petroleum Engineers; 2012. <https://doi.org/10.2118/153988-MS>.
- [26] Alvarado V, Manrique E. Enhanced Oil Recovery: An Update Review. Energies (Basel) 2010;3:1529–75. <https://doi.org/10.3390/en3091529>.
- [27] Koparal G. Surfactant Retention Analysis in Berea Sandstones. MS Thesis, UT Austin: 2019.
- [28] Thibaut A, Misselyn-Bauduin AM, Grandjean J, Broze G, Jérôme R. Adsorption of an Aqueous Mixture of Surfactants on Silica. Langmuir 2000;16:9192–8. <https://doi.org/10.1021/la000302e>.
- [29] Kosmulski M. Chemical Properties of Material Surfaces. Marcel Dekker, New York: CRC Press; 2001.
- [30] Chilingar G V., Yen TF. Some Notes on Wettability and Relative Permeabilities of Carbonate Reservoir Rocks, II. Energy Sources 1983;7:67–75. <https://doi.org/10.1080/00908318308908076>.

- [31] Roehl P, Choquette P. Carbonate petroleum reservoirs. Berlin: Springer Science & Business Media; 1985.
- [32] Lippman F. Sedimentary Carbonate Minerals, Springer-Verlag. New York City 1973.
- [33] Hartshorne NH, Stuart A. Crystals and the Polarizing Microscope. Edward Arnold & Co London 1950.
- [34] Ahmadall T, Gonzalez M V., Harwell JH, Scamehorn JF. Reducing Surfactant Adsorption in Carbonate Reservoirs. SPE Reservoir Engineering 1993;8:117–22. <https://doi.org/10.2118/24105-PA>.
- [35] Yang HT, Britton C, Liyanage PJ, Solairaj S, Kim DH, Nguyen QP, et al. Low-Cost, High-Performance Chemicals for Enhanced Oil Recovery. SPE Improved Oil Recovery Symposium, Society of Petroleum Engineers; 2010. <https://doi.org/10.2118/129978-MS>.
- [36] Chang Q. Surface of Solution. Colloid and Interface Chemistry for Water Quality Control, Elsevier; 2016, p. 161–74. <https://doi.org/10.1016/B978-0-12-809315-3.00009-8>.
- [37] Zana R, Talmon Y. Dependence of aggregate morphology on structure of dimeric surfactants. Nature 1993;362:228–30. <https://doi.org/10.1038/362228a0>.

- [38] Janjua AN, Sultan AS, Kamal MS. Ultra-Low Interfacial Tension, Thermal Stability and Static Adsorption of Novel Viscoelastic Surfactant With Heavy Reservoir Oil. SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, Society of Petroleum Engineers; 2018. <https://doi.org/10.2118/192322-MS>.
- [39] Li K, Jing X, He S, Wei B. Static Adsorption and Retention of Viscoelastic Surfactant in Porous Media: EOR Implication. *Energy & Fuels* 2016;30:9089–96. <https://doi.org/10.1021/acs.energyfuels.6b01732>.
- [40] Tadros TF. *An Introduction to Surfactants*. Walter de Gruyter GmbH, Berlin/Boston. 2014.
- [41] Wang D. Surfactant retention in limestones. MS Thesis, UT Austin: 2018.
- [42] Mejia M. Experimental investigation of surfactant flooding in fractured limestones. MS Thesis, UT Austin: 2018.
- [43] Solairaj S. New Method of Predicting Optimum Surfactant Structure for EOR. MS Thesis, UT Austin: 2011.
- [44] Yasari E, Pishvaie MR, Khorasheh F, Salahshoor K, Kharrat R. Application of multi-criterion robust optimization in water-flooding of oil reservoir. *J Pet Sci Eng* 2013;109:1–11. <https://doi.org/10.1016/j.petrol.2013.07.008>.
- [45] Kalam S, Abu-Khamsin SA, Al-Yousef HY, Gajbhiye R. A novel empirical correlation for waterflooding performance prediction in stratified reservoirs using

artificial intelligence. *Neural Comput Appl* 2020. <https://doi.org/10.1007/s00521-020-05158-1>.

- [46] Lake L, Schmidt R, Review PV-O, 1992 U. A niche for enhanced oil recovery in the 1990s. Schlumberger Ltd 1992.
- [47] Solairaj S, Britton C, Kim DH, Weerasooriya U, Pope GA. Measurement and Analysis of Surfactant Retention. SPE Improved Oil Recovery Symposium, Society of Petroleum Engineers; 2012. <https://doi.org/10.2118/154247-MS>.
- [48] Novosad J. Laboratory evaluation of lignosulfonates as sacrificial adsorbates in surfactant flooding. *Journal of Canadian Petroleum Technology* 1984;23:24–8. <https://doi.org/10.2118/84-03-01>.
- [49] Dang CTQ, Chen ZJ, Nguyen NTB, Bae W, Phung TH. Development of Isotherm Polymer/Surfactant Adsorption Models in Chemical Flooding. SPE Asia Pacific Oil and Gas Conference and Exhibition, Society of Petroleum Engineers; 2011. <https://doi.org/10.2118/147872-MS>.
- [50] Paria S, Khilar KC. A review on experimental studies of surfactant adsorption at the hydrophilic solid–water interface. *Adv Colloid Interface Sci* 2004;110:75–95. <https://doi.org/10.1016/j.cis.2004.03.001>.

- [51] Somasundaran P, Huang L. Adsorption/aggregation of surfactants and their mixtures at solid–liquid interfaces. *Adv Colloid Interface Sci* 2000;88:179–208. [https://doi.org/10.1016/S0001-8686\(00\)00044-0](https://doi.org/10.1016/S0001-8686(00)00044-0).
- [52] Zhang R, Somasundaran P. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Adv Colloid Interface Sci* 2006;123–126:213–29. <https://doi.org/10.1016/j.cis.2006.07.004>.
- [53] Maubert M, Jith Liyanage P, Pope G, Upamali N, Chang L, Ren G, et al. ASP Experiments in Indiana Limestone using NaOH to Reduce Surfactant Retention. SPE Improved Oil Recovery Conference, Society of Petroleum Engineers; 2018. <https://doi.org/10.2118/190187-MS>.
- [54] Rosen MJ, Li F. The Adsorption of Gemini and Conventional Surfactants onto Some Soil Solids and the Removal of 2-Naphthol by the Soil Surfaces. *J Colloid Interface Sci* 2001;234:418–24. <https://doi.org/10.1006/jcis.2000.7293>.
- [55] Trogus FJ, Sophany T, Schechter RS, Wade WH. Static and Dynamic Adsorption of Anionic and Nonionic Surfactants. *Society of Petroleum Engineers Journal* 1977;17:337–44. <https://doi.org/10.2118/6004-PA>.
- [56] Li F, Rosen MJ. Adsorption of Gemini and Conventional Cationic Surfactants onto Montmorillonite and the Removal of Some Pollutants by the Clay. *J Colloid Interface Sci* 2000;224:265–71. <https://doi.org/10.1006/jcis.2000.6721>.

- [57] Lv W, Bazin B, Ma D, Liu Q, Han D, Wu K. Static and dynamic adsorption of anionic and amphoteric surfactants with and without the presence of alkali. *J Pet Sci Eng* 2011;77:209–18. <https://doi.org/10.1016/j.petrol.2011.03.006>.
- [58] Grigg RB, Bai B. Sorption of Surfactant Used in CO₂ Flooding onto Five Minerals and Three Porous Media. *SPE International Symposium on Oilfield Chemistry*, Society of Petroleum Engineers; 2005. <https://doi.org/10.2118/93100-MS>.
- [59] Zhang D, Liu S, Yan W, Puerto M, Hirasaki GJ, Miller CA. Favorable Attributes of Alkali-Surfactant-Polymer Flooding. *SPE/DOE Symposium on Improved Oil Recovery*, Society of Petroleum Engineers; 2006. <https://doi.org/10.2118/99744-MS>.
- [60] Levitt D, Bourrel M. Adsorption of EOR Chemicals Under Laboratory and Reservoir Conditions, Part III: Chemical Treatment Methods. *SPE Improved Oil Recovery Conference*, Society of Petroleum Engineers; 2016. <https://doi.org/10.2118/179636-MS>.
- [61] Cottin C, Morel DC, Levitt D, Cordelier PR, Pope GA. (Alkali) Surfactant Gas injection : Attractive Laboratory Results under the Harsh Salinity and Temperature Conditions of Middle East Carbonates. *Abu Dhabi International Petroleum Conference and Exhibition*, Society of Petroleum Engineers; 2012. <https://doi.org/10.2118/161727-MS>.

- [62] Levitt D, Klimenko A, Jouenne S, Chamerois M, Bourrel M. Overcoming Design Challenges of Chemical EOR in High-Temperature, High Salinity Carbonates. SPE Middle East Oil and Gas Show and Conference, Society of Petroleum Engineers; 2013. <https://doi.org/10.2118/164241-MS>.
- [63] Chevallier E, Moreau P, Renard S, Tabary R, Bazin B, Douarche F, et al. Recent Progress in Surfactant Flooding in Carbonate Reservoirs, 2013. <https://doi.org/10.3997/2214-4609.20142634>.
- [64] Abalkhail N. Chemical enhanced oil recovery application in a high-temperature, high-salinity carbonate reservoir. MS Thesis, UT Austin: 2018.
- [65] Southwick JG, van den Pol E, van Rijn CHT, van Batenburg DW, Boersma D, Svec Y, et al. Ammonia as Alkali for Alkaline/Surfactant/Polymer Floods. SPE Journal 2016;21:010–21. <https://doi.org/10.2118/169057-PA>.
- [66] Sharma H, Weerasooriya U, Pope GA, Mohanty KK. Ammonia-Based ASP Processes for Gypsum-Containing Reservoirs. SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers; 2014. <https://doi.org/10.2118/170825-MS>.
- [67] Sharma H, Lu J, Weerasooriya UP, Pope GA, Mohanty KK. Adsorption in Chemical Floods with Ammonia as the Alkali. SPE Improved Oil Recovery Conference, Society of Petroleum Engineers; 2016. <https://doi.org/10.2118/179682-MS>.

- [68] Shamsijazeyi H, Hirasaki G, Verduzco R. Sacrificial Agent for Reducing Adsorption of Anionic Surfactants. SPE International Symposium on Oilfield Chemistry, Society of Petroleum Engineers; 2013. <https://doi.org/10.2118/164061-MS>.
- [69] ShamsiJazeyi H, Verduzco R, Hirasaki GJ. Reducing adsorption of anionic surfactant for enhanced oil recovery: Part I. Competitive adsorption mechanism. *Colloids Surf A Physicochem Eng Asp* 2014;453:162–7. <https://doi.org/10.1016/j.colsurfa.2013.10.042>.
- [70] ShamsiJazeyi H, Verduzco R, Hirasaki GJ. Reducing adsorption of anionic surfactant for enhanced oil recovery: Part II. Applied aspects. *Colloids Surf A Physicochem Eng Asp* 2014;453:168–75. <https://doi.org/10.1016/j.colsurfa.2014.02.021>.
- [71] Wang J, Han M, Fuseni AB, Cao D. Surfactant Adsorption in Surfactant-Polymer Flooding for Carbonate Reservoirs. SPE Middle East Oil & Gas Show and Conference, Society of Petroleum Engineers; 2015. <https://doi.org/10.2118/172700-MS>.
- [72] Esmaeilzadeh P, Bahramian A, Fakhroueian Z. Adsorption of Anionic, Cationic and Nonionic Surfactants on Carbonate Rock in Presence of ZrO₂ Nanoparticles. *Phys Procedia* 2011;22:63–7. <https://doi.org/10.1016/j.phpro.2011.11.009>.

- [73] Atkin R, Craig VSJ, Wanless EJ, Biggs S. Adsorption of 12- s -12 Gemini Surfactants at the Silica–Aqueous Solution Interface. *J Phys Chem B* 2003;107:2978–85. <https://doi.org/10.1021/jp026626o>.
- [74] Nasir Janjua A, Sultan AS, Shahzad Kamal M. Ultra-low interfacial tension, thermal stability and static adsorption of novel viscoelastic surfactant with heavy reservoir oil. Society of Petroleum Engineers - SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition 2018, SATS 2018, Society of Petroleum Engineers; 2018. <https://doi.org/10.2118/192322-ms>.
- [75] Ruthven D. Principles of adsorption and adsorption processes. John Wiley and Sons, New Jersey, NJ, USA: 1984.
- [76] Elmorsi TM. Equilibrium Isotherms and Kinetic Studies of Removal of Methylene Blue Dye by Adsorption onto Miswak Leaves as a Natural Adsorbent. *J Environ Prot (Irvine, Calif)* 2011;02:817–27. <https://doi.org/10.4236/jep.2011.26093>.
- [77] Langmuir I. THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. PART I. SOLIDS. *J Am Chem Soc* 1916;38:2221–95. <https://doi.org/10.1021/ja02268a002>.
- [78] H. M. F. Freundlich. Over the adsorption in solution. *Journal of Physical Chemistry* 1906;57:1100–7.

- [79] Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 2010;156:2–10. <https://doi.org/10.1016/j.cej.2009.09.013>.
- [80] Al-Ghouti MA, Da'ana DA. Guidelines for the use and interpretation of adsorption isotherm models: A review. J Hazard Mater 2020;393:122383. <https://doi.org/10.1016/j.jhazmat.2020.122383>.
- [81] Temkin M, Pyzhev V. Recent modifications to Langmuir isotherms. Acta Physiochim URSS 1940:217–25.
- [82] Liu Q-S, Zheng T, Wang P, Jiang J-P, Li N. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chemical Engineering Journal 2010;157:348–56. <https://doi.org/10.1016/j.cej.2009.11.013>.
- [83] Saadi R, Saadi Z, Fazaeli R, Fard NE. Monolayer and multilayer adsorption isotherm models for sorption from aqueous media. Korean Journal of Chemical Engineering 2015;32:787–99. <https://doi.org/10.1007/s11814-015-0053-7>.
- [84] Pérez-Marín AB, Zapata VM, Ortuño JF, Aguilar M, Sáez J, Lloréns M. Removal of cadmium from aqueous solutions by adsorption onto orange waste. J Hazard Mater 2007;139:122–31. <https://doi.org/10.1016/j.jhazmat.2006.06.008>.

- [85] Koopal LK, van Riemsdijk WH, de Wit JCM, Benedetti MF. Analytical Isotherm Equations for Multicomponent Adsorption to Heterogeneous Surfaces. *J Colloid Interface Sci* 1994;166:51–60. <https://doi.org/10.1006/jcis.1994.1270>.
- [86] S. Lagergren. Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens, Handlingar* 1898;1.
- [87] Liu Z, Zhao G, Brewer M, Lv Q, Sudhölter EJR. Comprehensive review on surfactant adsorption on mineral surfaces in chemical enhanced oil recovery. *Adv Colloid Interface Sci* 2021;294:102467. <https://doi.org/10.1016/j.cis.2021.102467>.
- [88] Wang H, Zhou A, Peng F, Yu H, Yang J. Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II). *J Colloid Interface Sci* 2007;316:277–83. <https://doi.org/10.1016/j.jcis.2007.07.075>.
- [89] Weber WJ, Morris JC. Kinetics of Adsorption on Carbon from Solution. *Journal of the Sanitary Engineering Division* 1963;89:31–59. <https://doi.org/10.1061/JSEDAI.0000430>.
- [90] Kamal MS. A Review of Gemini Surfactants: Potential Application in Enhanced Oil Recovery. *J Surfactants Deterg* 2016;19:223–36. <https://doi.org/10.1007/s11743-015-1776-5>.

- [91] Massarweh O, Abushaikha AS. The use of surfactants in enhanced oil recovery: A review of recent advances. *Energy Reports* 2020;6:3150–78. <https://doi.org/10.1016/j.egyr.2020.11.009>.
- [92] Kalam S, Abu-Khamsin SA, Kamal MS, Patil S. A review on surfactant retention on rocks: mechanisms, measurements, and influencing factors. *Fuel* 2021;293:120459. <https://doi.org/10.1016/j.fuel.2021.120459>.
- [93] Liu Z, Ghatkesar MK, Sudhölter EJR, Singh B, Kumar N. Understanding the Cation-Dependent Surfactant Adsorption on Clay Minerals in Oil Recovery. *Energy & Fuels* 2019;33:12319–29. <https://doi.org/10.1021/acs.energyfuels.9b03109>.
- [94] Zeng T, Kim KT, Werth CJ, Katz LE, Mohanty KK. Surfactant Adsorption on Shale Samples: Experiments and an Additive Model. *Energy & Fuels* 2020;34:5436–43. <https://doi.org/10.1021/acs.energyfuels.9b04016>.
- [95] Li N, Zhang G, Ge J, Luchao J, Jianqiang Z, Baodong D, et al. Adsorption Behavior of Betaine-Type Surfactant on Quartz Sand. *Energy & Fuels* 2011;25:4430–7. <https://doi.org/10.1021/ef200616b>.
- [96] Peng M, Nguyen A V. Adsorption of ionic surfactants at the air-water interface: The gap between theory and experiment. *Adv Colloid Interface Sci* 2020;275:102052. <https://doi.org/10.1016/j.cis.2019.102052>.

- [97] Fainerman VB, Aksenenko EV, Kovalchuk VI, Mucic N, Javadi A, Liggieri L, et al. New view of the adsorption of surfactants at water/alkane interfaces – Competitive and cooperative effects of surfactant and alkane molecules. *Adv Colloid Interface Sci* 2020;279:102143. <https://doi.org/10.1016/j.cis.2020.102143>.
- [98] Liu Z, Hedayati P, Ghatkesar MK, Sun W, Onay H, Groenendijk D, et al. Reducing anionic surfactant adsorption using polyacrylate as sacrificial agent investigated by QCM-D. *J Colloid Interface Sci* 2021;585:1–11. <https://doi.org/10.1016/j.jcis.2020.11.090>.
- [99] Zdziennicka A, Jańczuk B. Modification of adsorption, aggregation and wetting properties of surfactants by short chain alcohols. *Adv Colloid Interface Sci* 2020;284:102249. <https://doi.org/10.1016/j.cis.2020.102249>.
- [100] Zhao F, Wang S, Guo J. Experimental and Molecular Dynamics Simulation Study on the Effects of the Carbon Chain Length of Gemini Surfactants on the Inhibition of the Acid-Rock Reaction Rate. *Langmuir* 2021;37:5232–41. <https://doi.org/10.1021/acs.langmuir.1c00171>.
- [101] Belhaj AF, Elraies KA, Alnarabiji MS, Abdul Kareem FA, Shuhli JA, Mahmood SM, et al. Experimental investigation, binary modelling and artificial neural network prediction of surfactant adsorption for enhanced oil recovery application. *Chemical Engineering Journal* 2021;406:127081. <https://doi.org/10.1016/j.cej.2020.127081>.

- [102] Madani M, Zargar G, Takassi MA, Daryasafar A, Wood DA, Zhang Z. Fundamental investigation of an environmentally-friendly surfactant agent for chemical enhanced oil recovery. *Fuel* 2019;238:186–97. <https://doi.org/10.1016/j.fuel.2018.10.105>.
- [103] Nourafkan E, Hu Z, Wen D. Controlled delivery and release of surfactant for enhanced oil recovery by nanodroplets. *Fuel* 2018;218:396–405. <https://doi.org/10.1016/j.fuel.2018.01.013>.
- [104] Jia H, Lian P, Leng X, Han Y, Wang Q, Jia K, et al. Mechanism studies on the application of the mixed cationic/anionic surfactant systems to enhance oil recovery. *Fuel* 2019;258:116156. <https://doi.org/10.1016/j.fuel.2019.116156>.
- [105] Yuan M, Nie W, Zhou W, Yan J, Bao Q, Guo C, et al. Determining the effect of the non-ionic surfactant AEO9 on lignite adsorption and wetting via molecular dynamics (MD) simulation and experiment comparisons. *Fuel* 2020;278:118339. <https://doi.org/10.1016/j.fuel.2020.118339>.
- [106] Chen C, Wang S, Kadhum MJ, Harwell JH, Shiao B-J. Using carbonaceous nanoparticles as surfactant carrier in enhanced oil recovery: A laboratory study. *Fuel* 2018;222:561–8. <https://doi.org/10.1016/j.fuel.2018.03.002>.
- [107] Tombácz E, Szekeres M. Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. *Appl Clay Sci* 2006;34:105–24. <https://doi.org/10.1016/j.clay.2006.05.009>.

- [108] Nandwani SK, Chakraborty M, Gupta S. Adsorption of Surface Active Ionic Liquids on Different Rock Types under High Salinity Conditions. *Sci Rep* 2019;9:14760. <https://doi.org/10.1038/s41598-019-51318-2>.
- [109] Sekhon BS. Gemini (dimeric) surfactants. *Resonance* 2004;9:42–9. <https://doi.org/10.1007/BF02834987>.
- [110] Brycki BE, Kowalczyk IH, Szulc A, Kaczerewska O, Pakiet M. Multifunctional Gemini Surfactants: Structure, Synthesis, Properties and Applications. *Application and Characterization of Surfactants, InTech*; 2017. <https://doi.org/10.5772/intechopen.68755>.
- [111] Pal N, Saxena N, Mandal A. Equilibrium and dynamic adsorption of gemini surfactants with different spacer lengths at oil/aqueous interfaces. *Colloids Surf A Physicochem Eng Asp* 2017;533:20–32. <https://doi.org/10.1016/j.colsurfa.2017.08.020>.
- [112] Pal N, Saxena N, Mandal A. Studies on the physicochemical properties of synthesized tailor-made gemini surfactants for application in enhanced oil recovery. *J Mol Liq* 2018;258:211–24. <https://doi.org/10.1016/j.molliq.2018.03.037>.
- [113] Pal N, Verma A, Ojha K, Mandal A. Nanoparticle-modified gemini surfactant foams as efficient displacing fluids for enhanced oil recovery. *J Mol Liq* 2020;310:113193. <https://doi.org/10.1016/j.molliq.2020.113193>.

- [114] Shakil Hussain SM, Kamal MS. Effect of large spacer on surface activity, thermal, and rheological properties of novel amido-amine cationic gemini surfactants. *J Mol Liq* 2017;242:1131–7. <https://doi.org/10.1016/j.molliq.2017.07.128>.
- [115] Deng X, Shahzad Kamal M, Patil S, Muhammad Shakil Hussain S, Zhou X, Mahmoud M. Wettability alteration of locally synthesized cationic gemini surfactants on carbonate rock. *J Mol Liq* 2021;344:117817. <https://doi.org/10.1016/j.molliq.2021.117817>.
- [116] Ahmad HM, Murtaza M, Kamal MS, Hussain SMS, Mahmoud M. Cationic gemini surfactants containing biphenyl spacer as shale swelling inhibitor. *J Mol Liq* 2021;325:115164. <https://doi.org/10.1016/j.molliq.2020.115164>.
- [117] Kamal MS, Hussain SMS, Fogang LT, Sultan AS. Impact of Spacer and Hydrophobic Tail on Interfacial and Rheological Properties of Cationic Amido-Amine Gemini Surfactants for EOR Application. *Tenside Surfactants Detergents* 2018;55:491–7. <https://doi.org/10.3139/113.110591>.
- [118] Murtaza M, Kamal MS, Hussain SM, Mahmoud M. Experimental Investigation of Newly Synthesized Gemini Surfactants as Shale Inhibitors in Drilling Fluids. SPE/PAPG Pakistan Section Annual Technical Symposium and Exhibition, Islamabad, Pakistan: SPE; 2019. <https://doi.org/10.2118/201181-MS>.
- [119] Murtaza M, Kamal MS, Hussain SMS, Mahmoud M, Syed NA. Quaternary ammonium gemini surfactants having different spacer length as clay swelling

- inhibitors: Mechanism and performance evaluation. *J Mol Liq* 2020;308:113054.
<https://doi.org/10.1016/j.molliq.2020.113054>.
- [120] Gao M, Wang X-G, Lv W-F, Zhou Z-H, Zhang Q, Ma D-S, et al. Adsorption behaviors of branched cationic gemini surfactants and wettability in quartz–solution–air systems. *Soft Matter* 2020;16:5450–7.
<https://doi.org/10.1039/D0SM00689K>.
- [121] Cao M, Song X, Wang J, Wang Y. Adsorption of hexyl--bis(dodecyldimethylammonium bromide) gemini surfactant on silica and its effect on wettability. *J Colloid Interface Sci* 2006;300:519–25.
<https://doi.org/10.1016/j.jcis.2006.03.080>.
- [122] Ao M, Xu G, Pang J, Zhao T. Comparison of Aggregation Behaviors between Ionic Liquid-Type Imidazolium Gemini Surfactant [C₁₂-4-C₁₂im]Br₂ and Its Monomer [C₁₂mim]Br on Silicon Wafer. *Langmuir* 2009;25:9721–7.
<https://doi.org/10.1021/la901005v>.
- [123] Zhou Q, Somasundaran P. Synergistic adsorption of mixtures of cationic gemini and nonionic sugar-based surfactant on silica. *J Colloid Interface Sci* 2009;331:288–94.
<https://doi.org/10.1016/j.jcis.2008.11.062>.
- [124] Aliabadian E, Sadeghi S, Rezvani Moghaddam A, Maini B, Chen Z, Sundararaj U. Application of graphene oxide nanosheets and HPAM aqueous dispersion for

- improving heavy oil recovery: Effect of localized functionalization. *Fuel* 2020;265:116918. <https://doi.org/10.1016/j.fuel.2019.116918>.
- [125] Lashari N, Ganat T. Emerging applications of nanomaterials in chemical enhanced oil recovery: Progress and perspective. *Chin J Chem Eng* 2020;28:1995–2009. <https://doi.org/10.1016/j.cjche.2020.05.019>.
- [126] Lashari N, Ganat T, Otchere D, Kalam S, Ali I. Navigating viscosity of GO-SiO₂/HPAM composite using response surface methodology and supervised machine learning models. *J Pet Sci Eng* 2021;205:108800. <https://doi.org/10.1016/j.petrol.2021.108800>.
- [127] Lyu Y, Gu C, Tao J, Yao X, Zhao G, Dai C. Thermal-resistant, shear-stable and salt-tolerant polyacrylamide/surface-modified graphene oxide composite. *J Mater Sci* 2019;54:14752–62. <https://doi.org/10.1007/s10853-019-03967-x>.
- [128] Lashari N, Ganat T. Synthesized graphene oxide and fumed aerosil 380 dispersion stability and characterization with partially hydrolyzed polyacrylamide. *Chin J Chem Eng* 2021;34:307–22. <https://doi.org/10.1016/j.cjche.2020.09.035>.
- [129] Hussain SMS, Kamal MS, Murtaza M. Synthesis of Novel Ethoxylated Quaternary Ammonium Gemini Surfactants for Enhanced Oil Recovery Application. *Energies (Basel)* 2019;12:1731. <https://doi.org/10.3390/en12091731>.

- [130] Chorro M, Chorro C, Dolladille O, Partyka S, Zana R. Adsorption Mechanism of Conventional and Dimeric Cationic Surfactants on Silica Surface: Effect of the State of the Surface. *J Colloid Interface Sci* 1999;210:134–43. <https://doi.org/10.1006/jcis.1998.5936>.
- [131] Hocine S, Pousset B, Courtaud T, Degré G. Long Term Thermal Stability of Chemical EOR Surfactants. Day 2 Tue, March 27, 2018, SPE; 2018. <https://doi.org/10.2118/190361-MS>.
- [132] Bear GR. Universal detection and Quantitation of surfactants by high-performance liquid chromatography by means of the evaporative light-scattering detector. *J Chromatogr A* 1988;459:91–107. [https://doi.org/10.1016/S0021-9673\(01\)82019-7](https://doi.org/10.1016/S0021-9673(01)82019-7).
- [133] Farooq U, Tweheyo MT, Sjöblom J, Øye G. Surface Characterization of Model, Outcrop, and Reservoir Samples in Low Salinity Aqueous Solutions. *J Dispers Sci Technol* 2011;32:519–31. <https://doi.org/10.1080/01932691003756936>.
- [134] Jaafar MZ, Nasir AM, Hamid MF. Measurement of Isoelectric Point of Sandstone and Carbonate Rock for Monitoring Water Encroachment. *Journal of Applied Sciences* 2014;14:3349–53. <https://doi.org/10.3923/jas.2014.3349.3353>.
- [135] Kasha A, Al-Hashim H, Abdallah W, Taherian R, Sauerer B. Effect of Ca^{2+} , Mg^{2+} and SO_4^{2-} ions on the zeta potential of calcite and dolomite particles aged with stearic acid. *Colloids Surf A Physicochem Eng Asp* 2015;482:290–9. <https://doi.org/10.1016/j.colsurfa.2015.05.043>.

- [136] Sadeed A, Al-Hashim H, Sauerer B, Abdallah W. Influence of Halide Anions Cl⁻, Br⁻, and I⁻ on the Zeta Potential of Oil-Wet Carbonate Surfaces. *Energy & Fuels* 2019;33:7094–109. <https://doi.org/10.1021/acs.energyfuels.9b01139>.
- [137] Alotaibi MB, Nasr-El-Din HA, Fletcher JJ. Electrokinetics of Limestone and Dolomite Rock Particles. *SPE Reservoir Evaluation & Engineering* 2011;14:594–603. <https://doi.org/10.2118/148701-PA>.
- [138] Hiorth A, Cathles LM, Madland M v. The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability. *Transp Porous Media* 2010;85:1–21. <https://doi.org/10.1007/s11242-010-9543-6>.
- [139] Ruiz-Agudo E, Kowacz M, Putnis CV, Putnis A. The role of background electrolytes on the kinetics and mechanism of calcite dissolution. *Geochim Cosmochim Acta* 2010;74:1256–67. <https://doi.org/10.1016/j.gca.2009.11.004>.
- [140] Mannhardt K, Schramm LL, Novosad JJ. Effect of Rock Type and Brine Composition on Adsorption of Two Foam-Forming Surfactants. *SPE Advanced Technology Series* 1993;1:212–8. <https://doi.org/10.2118/20463-PA>.
- [141] Buckley JS, Liu Y. Some mechanisms of crude oil/brine/solid interactions. *J Pet Sci Eng* 1998;20:155–60. [https://doi.org/10.1016/S0920-4105\(98\)00015-1](https://doi.org/10.1016/S0920-4105(98)00015-1).

- [142] Mivehi L, Bordes R, Holmberg K. Adsorption of Cationic Gemini Surfactants at Solid Surfaces Studied by QCM-D and SPR: Effect of the Rigidity of the Spacer. *Langmuir* 2011;27:7549–57. <https://doi.org/10.1021/la200539a>.
- [143] Caracciolo G, Pozzi D, Mancini G, Caminiti R. Role of the Spacer Stereochemistry on the Structure of Solid-Supported Gemini Surfactants Aggregates. *Langmuir* 2007;23:10040–3. <https://doi.org/10.1021/la7014995>.
- [144] McIntosh TJ, McDaniel RV, Simon SA. Induction of an interdigitated gel phase in fully hydrated phosphatidylcholine bilayers. *Biochimica et Biophysica Acta (BBA) - Biomembranes* 1983;731:109–14. [https://doi.org/10.1016/0005-2736\(83\)90403-0](https://doi.org/10.1016/0005-2736(83)90403-0).
- [145] Mou J, Yang J, Huang C, Shao Z. Alcohol Induces Interdigitated Domains in Unilamellar Phosphatidylcholine Bilayers. *Biochemistry* 1994;33:9981–5. <https://doi.org/10.1021/bi00199a022>.
- [146] Li D, Fang W, Feng Y, Geng Q, Song M. Stability properties of water-based gold and silver nanofluids stabilized by cationic gemini surfactants. *J Taiwan Inst Chem Eng* 2019;97:458–65. <https://doi.org/10.1016/j.jtice.2019.02.017>.
- [147] Zhao F, Wang S, Shen X, Guo J, Liu Y. Study on mechanism of Gemini surfactant inhibiting acid rock reaction rate. *Colloids Surf A Physicochem Eng Asp* 2019;578:123629. <https://doi.org/10.1016/j.colsurfa.2019.123629>.

- [148] Le Guenic S, Chaveriat L, Lequart V, Joly N, Martin P. Renewable Surfactants for Biochemical Applications and Nanotechnology. *J Surfactants Deterg* 2019;22:5–21. <https://doi.org/10.1002/jsde.12216>.
- [149] Kralova I, Sjöblom J. Surfactants Used in Food Industry: A Review. *J Dispers Sci Technol* 2009;30:1363–83. <https://doi.org/10.1080/01932690902735561>.
- [150] Farias CBB, Almeida FCG, Silva IA, Souza TC, Meira HM, Soares da Silva R de CF, et al. Production of green surfactants: Market prospects. *Electronic Journal of Biotechnology* 2021;51:28–39. <https://doi.org/10.1016/j.ejbt.2021.02.002>.
- [151] Kalam S, Abu-Khamsin SA, Kamal MS, Patil S. A review on surfactant retention on rocks: mechanisms, measurements, and influencing factors. *Fuel* 2021;293:120459. <https://doi.org/10.1016/j.fuel.2021.120459>.
- [152] Kalam S, Abu-Khamsin SA, Kamal MS, Patil S. Surfactant Adsorption Isotherms: A Review. *ACS Omega* 2021;6:32342–8. <https://doi.org/10.1021/acsomega.1c04661>.
- [153] Amirianshoja T, Junin R, Kamal Idris A, Rahmani O. A comparative study of surfactant adsorption by clay minerals. *J Pet Sci Eng* 2013;101:21–7. <https://doi.org/10.1016/j.petrol.2012.10.002>.

- [154] Liu Q, Dong M, Zhou W, Ayub M, Zhang YP, Huang S. Improved oil recovery by adsorption–desorption in chemical flooding. *J Pet Sci Eng* 2004;43:75–86. <https://doi.org/10.1016/j.petrol.2003.12.017>.
- [155] Shehata AM, Nasr-El-Din HA. Zeta Potential Measurements: Impact of Salinity on Sandstone Minerals. Day 1 Mon, April 13, 2015, SPE; 2015. <https://doi.org/10.2118/173763-MS>.
- [156] Somasundaran P, Agar GE. The zero point of charge of calcite. *J Colloid Interface Sci* 1967;24:433–40. [https://doi.org/10.1016/0021-9797\(67\)90241-X](https://doi.org/10.1016/0021-9797(67)90241-X).
- [157] Prédali J-J, Cases J-M. Zeta potential of magnesian carbonates in inorganic electrolytes. *J Colloid Interface Sci* 1973;45:449–58. [https://doi.org/10.1016/0021-9797\(73\)90160-4](https://doi.org/10.1016/0021-9797(73)90160-4).
- [158] Jiang T, Hirasaki GJ, Miller CA. Characterization of Kaolinite ζ Potential for Interpretation of Wettability Alteration in Diluted Bitumen Emulsion Separation. *Energy & Fuels* 2010;24:2350–60. <https://doi.org/10.1021/ef900999h>.
- [159] Chen L, Zhao Y, Bai H, Ai Z, Chen P, Hu Y, et al. Role of Montmorillonite, Kaolinite, or Illite in Pyrite Flotation: Differences in Clay Behavior Based on Their Structures. *Langmuir* 2020;36:10860–7. <https://doi.org/10.1021/acs.langmuir.0c02073>.

- [160] Pecini EM, Avena MJ. Measuring the Isoelectric Point of the Edges of Clay Mineral Particles: The Case of Montmorillonite. *Langmuir* 2013;29:14926–34. <https://doi.org/10.1021/la403384g>.
- [161] Du Y, Zhang Q, Zhu Y, Zhou Z, Zhang F, Zhang L, et al. Adsorption of extended surfactants at the water-PTFE interface: The effect of PO number. *J Mol Liq* 2022;348:118465. <https://doi.org/10.1016/j.molliq.2021.118465>.
- [162] Guo J, Xia Y, Liu Y, Liu S, Zhang L, Li B. Microscopic adsorption behaviors of ionic surfactants on lignite surface and its effect on the wettability of lignite: A simulation and experimental study. *J Mol Liq* 2022;345:117851. <https://doi.org/10.1016/j.molliq.2021.117851>.
- [163] Tiwari S, Namsani S, Singh JK. Effect of salt on the adsorption of ionic surfactants at the air-water interface. *J Mol Liq* 2022;360:119498. <https://doi.org/10.1016/j.molliq.2022.119498>.
- [164] Kalam S, Abu-Khamsin SA, Kamal MS, Hussain SMS, Norrman K, Mahmoud M, et al. Adsorption Mechanisms of a Novel Cationic Gemini Surfactant onto Different Rocks. *Energy & Fuels* 2022;36:5737–48. <https://doi.org/10.1021/acs.energyfuels.2c00684>.
- [165] Cui L, Ma K, Abdala AA, Lu LJ, Tanakov I, Biswal SL, et al. Adsorption of a Switchable Cationic Surfactant on Natural Carbonate Minerals. *SPE Journal* 2015;20:70–8. <https://doi.org/10.2118/169040-PA>.

- [166] Saha R, Uppaluri RVS, Tiwari P. Effect of mineralogy on the adsorption characteristics of surfactant—Reservoir rock system. *Colloids Surf A Physicochem Eng Asp* 2017;531:121–32. <https://doi.org/10.1016/j.colsurfa.2017.07.039>.
- [167] Khan S, Gbadamosi A, Norrman K, Zhou X, Hussain SMS, Patil S, et al. Adsorption Study of Novel Gemini Cationic Surfactant in Carbonate Reservoir Cores—Influence of Critical Parameters. *Materials* 2022;15:2527. <https://doi.org/10.3390/ma15072527>.
- [168] Parakala S, Moulik S, Sridhar S. Effective separation of methylene blue dye from aqueous solutions by integration of micellar enhanced ultrafiltration with vacuum membrane distillation. *Chemical Engineering Journal* 2019;375:122015. <https://doi.org/10.1016/j.cej.2019.122015>.
- [169] Balarak D, Bazzi M, Shehu Z, Chandrika K. Application of Surfactant-Modified Bentonite for Methylene Blue Adsorption from Aqueous Solution. *Oriental Journal of Chemistry* 2020;36:293–9. <https://doi.org/10.13005/ojc/360212>.
- [170] Mijinyawa AH, Durga G, Mishra A. A sustainable process for adsorptive removal of methylene blue onto a food grade mucilage: kinetics, thermodynamics, and equilibrium evaluation. *Int J Phytoremediation* 2019;21:1122–9. <https://doi.org/10.1080/15226514.2019.1606785>.

- [171] Koyuncu H, Kul AR. Removal of methylene blue dye from aqueous solution by nonliving lichen (*Pseudevernia furfuracea* (L.) Zopf.), as a novel biosorbent. *Appl Water Sci* 2020;10:72. <https://doi.org/10.1007/s13201-020-1156-9>.
- [172] Dao HM, Whang C-H, Shankar VK, Wang Y-H, Khan IA, Walker LA, et al. Methylene blue as a far-red light-mediated photocleavable multifunctional ligand. *Chemical Communications* 2020;56:1673–6. <https://doi.org/10.1039/C9CC08916K>.
- [173] Zaghibani N, Hafiane A, Dhahbi M. Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration. *Sep Purif Technol* 2007;55:117–24. <https://doi.org/10.1016/j.seppur.2006.11.008>.
- [174] Giannakopoulou PP, Petrounias P, Rogkala A, Lampropoulou P, Gianni E, Papoulis D, et al. Does the Methylene Blue Test Give Equally Satisfactory Results in All Studied Igneous Rocks Relative to the Identification of Swelling Clay Minerals? *Minerals* 2020;10:283. <https://doi.org/10.3390/min10030283>.
- [175] Miller C, Bageri BS, Zeng T, Patil S, Mohanty KK. Modified Two-Phase Titration Methods to Quantify Surfactant Concentrations in Chemical-Enhanced Oil Recovery Applications. *J Surfactants Deterg* 2020;23:1159–67. <https://doi.org/10.1002/jsde.12442>.
- [176] Saxena N, Kumar A, Mandal A. Adsorption analysis of natural anionic surfactant for enhanced oil recovery: The role of mineralogy, salinity, alkalinity and

- nanoparticles. *J Pet Sci Eng* 2019;173:1264–83.
<https://doi.org/10.1016/j.petrol.2018.11.002>.
- [177] Pokrovsky OS, Schott J, Thomas F. Dolomite surface speciation and reactivity in aquatic systems. *Geochim Cosmochim Acta* 1999;63:3133–43.
[https://doi.org/10.1016/S0016-7037\(99\)00240-9](https://doi.org/10.1016/S0016-7037(99)00240-9).
- [178] Heberling F, Trainor TP, Lützenkirchen J, Eng P, Denecke MA, Bosbach D. Structure and reactivity of the calcite–water interface. *J Colloid Interface Sci* 2011;354:843–57. <https://doi.org/10.1016/j.jcis.2010.10.047>.
- [179] Foxall T, Peterson GC, Rendall HM, Smith AL. Charge determination at calcium salt/aqueous solution interface. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 1979;75:1034.
<https://doi.org/10.1039/f19797501034>.
- [180] Iler R. The chemistry of silica. Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica 1979.
- [181] Mucha M, Maršálek R, Bukáčková M, Zelenková G. Interaction among clays and bovine serum albumin. *RSC Adv* 2020;10:43927–39.
<https://doi.org/10.1039/D0RA01430C>.
- [182] Ghosh D, Bhattacharyya KG. Adsorption of methylene blue on kaolinite. *Appl Clay Sci* 2002;20:295–300. [https://doi.org/10.1016/S0169-1317\(01\)00081-3](https://doi.org/10.1016/S0169-1317(01)00081-3).

- [183] Han M, AlSofi A, Fuseni A, Zhou X, Hassan S. Development of Chemical EOR Formulations for a High Temperature and High Salinity Carbonate Reservoir. Conference Proceedings, IPTC 2013: International Petroleum Technology Conference, European Association of Geoscientists & Engineers; 2013.
- [184] Zhong X, Pu H, Zhou Y, Zhao JX. Static Adsorption of Surfactants on Bakken Rock Surfaces in High Temperature, High Salinity Conditions. Day 2 Tue, April 09, 2019, SPE; 2019. <https://doi.org/10.2118/193589-MS>.
- [185] Ahmadi MA, Shadizadeh SR. Adsorption of Novel Nonionic Surfactant and Particles Mixture in Carbonates: Enhanced Oil Recovery Implication. Energy & Fuels 2012;26:4655–63. <https://doi.org/10.1021/ef300154h>.
- [186] Ghosh P, Sharma H, Mohanty KK. ASP flooding in tight carbonate rocks. Fuel 2019;241:653–68. <https://doi.org/10.1016/j.fuel.2018.12.041>.
- [187] Gao B, Sharma MM. A New Family of Anionic Surfactants for Enhanced-Oil-Recovery Applications. SPE Journal 2013;18:829–40. <https://doi.org/10.2118/159700-PA>.
- [188] Páhi AB, Király Z, Mastalir Á, Dudás J, Puskás S, Vágó Á. Thermodynamics of Micelle Formation of the Counterion Coupled Gemini Surfactant Bis(4-(2-dodecyl)benzenesulfonate)-Jeffamine Salt and Its Dynamic Adsorption on Sandstone. J Phys Chem B 2008;112:15320–6. <https://doi.org/10.1021/jp806522h>.

- [189] Yang W, Cao Y, Wang Y, Ju H, Jiang Y, Geng T. Effects of unsaturated double bonds on adsorption and aggregation behaviors of amide-based cationic Gemini surfactants. *Colloids Surf A Physicochem Eng Asp* 2021;611:125778. <https://doi.org/10.1016/j.colsurfa.2020.125778>.
- [190] Chan SA, Kaminski MA, Al-Ramadan K, Babalola LO. Foraminiferal biofacies and depositional environments of the Burdigalian mixed carbonate and siliciclastic Dam Formation, Al-Lidam area, Eastern Province of Saudi Arabia. *Palaeogeogr Palaeoclimatol Palaeoecol* 2017;469:122–37. <https://doi.org/10.1016/j.palaeo.2016.12.041>.
- [191] Bashri M, Abdullatif O, Salih M. Sedimentology and facies analysis of Miocene mixed siliciclastic–carbonate deposits of the Dam Formation in Al Lidam area, eastern Saudi Arabia. *Arabian Journal of Geosciences* 2017;10:472. <https://doi.org/10.1007/s12517-017-3244-1>.
- [192] Ziegler MA. Late Permian to Holocene Paleofacies Evolution of the Arabian Plate and its Hydrocarbon Occurrences. *GeoArabia* 2001;6:445–504. <https://doi.org/10.2113/geoarabia0603445>.
- [193] Pethkar AV, Paknikar KM. Recovery of gold from solutions using *Cladosporium cladosporioides* biomass beads. *J Biotechnol* 1998;63:121–36. [https://doi.org/10.1016/S0168-1656\(98\)00078-9](https://doi.org/10.1016/S0168-1656(98)00078-9).

- [194] Tang G-Q, Morrow NR. Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery. *J Pet Sci Eng* 1999;24:99–111. [https://doi.org/10.1016/S0920-4105\(99\)00034-0](https://doi.org/10.1016/S0920-4105(99)00034-0).
- [195] Saikia BD, Mahadevan J, Rao DN. Exploring mechanisms for wettability alteration in low-salinity waterfloods in carbonate rocks. *J Pet Sci Eng* 2018;164:595–602. <https://doi.org/10.1016/j.petrol.2017.12.056>.
- [196] Derkani MH, Fletcher AJ, Fedorov M, Abdallah W, Sauerer B, Anderson J, et al. Mechanisms of Surface Charge Modification of Carbonates in Aqueous Electrolyte Solutions. *Colloids and Interfaces* 2019;3:62. <https://doi.org/10.3390/colloids3040062>.
- [197] Zhong X, Pu H, Zhou Y, Zhao JX. Comparative Study on the Static Adsorption Behavior of Zwitterionic Surfactants on Minerals in Middle Bakken Formation. *Energy & Fuels* 2019;33:1007–15. <https://doi.org/10.1021/acs.energyfuels.8b04013>.
- [198] Zhou X, Zhou X. THE unit problem in the thermodynamic calculation of adsorption using the Langmuir equation. *Chem Eng Commun* 2014;201:1459–67. <https://doi.org/10.1080/00986445.2013.818541>.
- [199] Ding L, Jouenne S, Gharbi O, Pal M, Bertin H, Rahman MA, et al. An experimental investigation of the foam enhanced oil recovery process for a dual porosity and

- heterogeneous carbonate reservoir under strongly oil-wet condition. *Fuel* 2022;313:122684. <https://doi.org/10.1016/j.fuel.2021.122684>.
- [200] Ghosh P, Mohanty KK. Laboratory treatment of HPAM polymers for injection in low permeability carbonate reservoirs. *J Pet Sci Eng* 2020;185:106574. <https://doi.org/10.1016/j.petrol.2019.106574>.
- [201] Song H, Ghosh P, Mejia M, Mohanty K. Polymer Transport in Low-Permeability Carbonate Rocks. *SPE Reservoir Evaluation & Engineering* 2022;1–14. <https://doi.org/10.2118/206024-PA>.
- [202] Sharma G, Mohanty KK. Wettability Alteration in High-Temperature and High-Salinity Carbonate Reservoirs. *SPE Journal* 2013;18:646–55. <https://doi.org/10.2118/147306-PA>.
- [203] Jeon PR, Lee C-H. Effect of surfactants on CO₂ solubility and reaction in CO₂-brine-clay mineral systems during CO₂-enhanced fossil fuel recovery. *Chemical Engineering Journal* 2020;382:123014. <https://doi.org/10.1016/j.cej.2019.123014>.
- [204] Wei B, Zhang X, Liu J, Xu X, Pu W, Bai M. Adsorptive behaviors of supercritical CO₂ in tight porous media and triggered chemical reactions with rock minerals during CO₂-EOR and -sequestration. *Chemical Engineering Journal* 2020;381:122577. <https://doi.org/10.1016/j.cej.2019.122577>.

- [205] Belhaj AF, Elraies KA, Janjuhah HT, Tasfy SFH, Yahya N, Abdullah B, et al. Electromagnetic waves-induced hydrophobic multiwalled carbon nanotubes for enhanced oil recovery. *J Pet Explor Prod Technol* 2019;9:2667–70. <https://doi.org/10.1007/s13202-019-0653-6>.
- [206] Shen T, Gao M. Gemini surfactant modified organo-clays for removal of organic pollutants from water: A review. *Chemical Engineering Journal* 2019;375:121910. <https://doi.org/10.1016/j.cej.2019.121910>.
- [207] Kamal MS. A Review of Gemini Surfactants: Potential Application in Enhanced Oil Recovery. *J Surfactants Deterg* 2016;19:223–36. <https://doi.org/10.1007/s11743-015-1776-5>.
- [208] Deng X, Shahzad Kamal M, Patil S, Muhammad Shakil Hussain S, Zhou X, Mahmoud M. Wettability alteration of locally synthesized cationic gemini surfactants on carbonate rock. *J Mol Liq* 2021;344:117817. <https://doi.org/10.1016/j.molliq.2021.117817>.
- [209] Fogang LT, Kamal MS, Hussain SMS, Kalam S, Patil S. Oil/Water Interfacial Tension in the Presence of Novel Polyoxyethylene Cationic Gemini Surfactants: Impact of Spacer Length, Unsaturation, and Aromaticity. *Energy & Fuels* 2020;34:5545–52. <https://doi.org/10.1021/acs.energyfuels.0c00044>.

- [210] Gao B, Sharma MM. A New Family of Anionic Surfactants for Enhanced-Oil-Recovery Applications. SPE Journal 2013;18:829–40. <https://doi.org/10.2118/159700-PA>.
- [211] Özdemir U, Özbay B, Veli S, Zor S. Modeling adsorption of sodium dodecyl benzene sulfonate (SDBS) onto polyaniline (PANI) by using multi linear regression and artificial neural networks. Chemical Engineering Journal 2011;178:183–90. <https://doi.org/10.1016/j.cej.2011.10.046>.
- [212] Ahn CK, Woo SH, Park JM. Selective adsorption of phenanthrene in nonionic–anionic surfactant mixtures using activated carbon. Chemical Engineering Journal 2010;158:115–9. <https://doi.org/10.1016/j.cej.2009.12.014>.
- [213] Belhaj AF, Elraies KA, Alnarabiji MS, Abdul Kareem FA, Shuhli JA, Mahmood SM, et al. Experimental investigation, binary modelling and artificial neural network prediction of surfactant adsorption for enhanced oil recovery application. Chemical Engineering Journal 2021;406:127081. <https://doi.org/10.1016/j.cej.2020.127081>.
- [214] Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 2010;156:2–10. <https://doi.org/10.1016/j.cej.2009.09.013>.
- [215] Tran T, Gonzalez Perdomo ME, Haghighi M, Amrouch K. Study of the synergistic effects between different surfactant types and silica nanoparticles on the stability of

- liquid foams at elevated temperature. *Fuel* 2022;315:122818.
<https://doi.org/10.1016/j.fuel.2021.122818>.
- [216] Asl FO, Zargar G, Manshad AK, Iglauer S, Keshavarz A. Experimental investigation and simulation for hybrid of nanocomposite and surfactant as EOR process in carbonate oil reservoirs. *Fuel* 2022;319:123591.
<https://doi.org/10.1016/j.fuel.2022.123591>.
- [217] Tavakkoli O, Kamyab H, Shariati M, Mustafa Mohamed A, Junin R. Effect of nanoparticles on the performance of polymer/surfactant flooding for enhanced oil recovery: A review. *Fuel* 2022;312:122867.
<https://doi.org/10.1016/j.fuel.2021.122867>.
- [218] Ahmadi MA, Shadizadeh SR. Adsorption of Novel Nonionic Surfactant and Particles Mixture in Carbonates: Enhanced Oil Recovery Implication. *Energy & Fuels* 2012;26:4655–63. <https://doi.org/10.1021/ef300154h>.
- [219] Najafabadi NF, Delshad M, Sepehrnoori K, Nguyen QP, Zhang J. Chemical Flooding of Fractured Carbonates Using Wettability Modifiers. *All Days, SPE*; 2008. <https://doi.org/10.2118/113369-MS>.
- [220] Arabloo M, Ghazanfari MH, Rashtchian D. Spotlight on kinetic and equilibrium adsorption of a new surfactant onto sandstone minerals: A comparative study. *J Taiwan Inst Chem Eng* 2015;50:12–23. <https://doi.org/10.1016/j.jtice.2014.12.012>.

- [221] Ma K, Cui L, Dong Y, Wang T, Da C, Hirasaki GJ, et al. Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. *J Colloid Interface Sci* 2013;408:164–72. <https://doi.org/10.1016/j.jcis.2013.07.006>.
- [222] Nandwani SK, Chakraborty M, Gupta S. Adsorption of Surface Active Ionic Liquids on Different Rock Types under High Salinity Conditions. *Sci Rep* 2019;9:14760. <https://doi.org/10.1038/s41598-019-51318-2>.
- [223] Belhaj AF, Elraies KA, Mahmood SM, Zulkifli NN, Akbari S, Hussien OS. The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review. *J Pet Explor Prod Technol* 2019. <https://doi.org/10.1007/s13202-019-0685-y>.
- [224] Liu Z, Zhao G, Brewer M, Lv Q, Sudhölter EJR. Comprehensive review on surfactant adsorption on mineral surfaces in chemical enhanced oil recovery. *Adv Colloid Interface Sci* 2021;294:102467. <https://doi.org/10.1016/j.cis.2021.102467>.
- [225] Lv W, Bazin B, Ma D, Liu Q, Han D, Wu K. Static and dynamic adsorption of anionic and amphoteric surfactants with and without the presence of alkali. *J Pet Sci Eng* 2011;77:209–18. <https://doi.org/10.1016/j.petrol.2011.03.006>.
- [226] Mustafa S, Dilara B, Nargis K, Naeem A, Shahida P. Surface properties of the mixed oxides of iron and silica. *Colloids Surf A Physicochem Eng Asp* 2002;205:273–82. [https://doi.org/10.1016/S0927-7757\(02\)00025-0](https://doi.org/10.1016/S0927-7757(02)00025-0).

- [227] Li Y, Hu X, Liu X, Zhang Y, Zhao Q, Ning P, et al. Adsorption behavior of phenol by reversible surfactant-modified montmorillonite: Mechanism, thermodynamics, and regeneration. *Chemical Engineering Journal* 2018;334:1214–21. <https://doi.org/10.1016/j.cej.2017.09.140>.
- [228] Nourani M, Tichelkamp T, Gawel B, Øye G. Method for Determining the Amount of Crude Oil Desorbed from Silica and Aluminosilica Surfaces upon Exposure to Combined Low-Salinity Water and Surfactant Solutions. *Energy & Fuels* 2014;28:1884–9. <https://doi.org/10.1021/ef402494c>.

Selected Publications

1. **Kalam, S.**, Abu-Khamsin, S. A., Kamal, M. S., Hussain, S. S., Norrman, K., Mahmoud, M., & Patil, S. (2022). Adsorption Mechanisms of a Novel Cationic Gemini Surfactant onto Different Rocks. Energy & Fuels. <https://doi.org/10.1021/acs.energyfuels.2c00684>
2. **Kalam, S.**, Abu-Khamsin, S. A., Kamal, M. S., & Patil, S. (2021). A review on surfactant retention on rocks: mechanisms, measurements, and influencing factors. Fuel, 293, 120459. <https://doi.org/10.1016/j.fuel.2021.120459>
3. **Kalam, S.**, Abu-Khamsin, S. A., Kamal, M. S., & Patil, S. (2021). Surfactant Adsorption Isotherms: A Review. ACS omega, 6(48), 32342-32348. <https://doi.org/10.1021/acsomega.1c04661>
4. **Kalam, S.**, Kamal, M. S., Patil, S., & Hussain, S. M. S. (2020). Impact of Spacer Nature and Counter Ions on Rheological Behavior of Novel Polymer Cationic Gemini Surfactant Systems at High Temperature. Polymers, 12(5), 1027. <https://doi.org/10.3390/polym12051027>
5. **Kalam, S.**, Kamal, M. S., Patil, S., & Hussain, S. M. (2019). Role of counterions and nature of spacer on foaming properties of novel polyoxyethylene cationic gemini surfactants. Processes, 7(8), 502. <https://doi.org/10.3390/pr7080502>

6. Fogang, L. T., Kamal, M. S., Hussain, S. S., **Kalam, S.**, & Patil, S. (2020). Oil/Water Interfacial Tension in the Presence of Novel Polyoxyethylene Cationic Gemini Surfactants: Impact of Spacer Length, Unsaturation, and Aromaticity. *Energy & Fuels*, 34(5), 5545-5552. <https://doi.org/10.1021/acs.energyfuels.0c00044>
7. Mahboob, A., **Kalam, S.**, Kamal, M. S., Hussain, S. S., & Solling, T. (2022). EOR Perspective of microemulsions: A review. *Journal of Petroleum Science and Engineering*, 208, 109312. <https://doi.org/10.1016/j.petrol.2021.109312>
8. **Kalam, S.**, Yousuf, U., Abu-Khamsin, S. A., Waheed, U. B., & Khan, R. A. (2022). An ANN model to predict oil recovery from a 5-spot waterflood of a heterogeneous reservoir. *Journal of Petroleum Science and Engineering*, 210, 110012. <https://doi.org/10.1016/j.petrol.2021.110012>
9. **Kalam, S.**, Abu-Khamsin, S. A., Al-Yousef, H. Y., & Gajbhiye, R. (2020). A novel empirical correlation for waterflooding performance prediction in stratified reservoirs using artificial intelligence. *Neural Computing and Applications*, 1-18. <https://doi.org/10.1007/s00521-020-05158-1>
10. **Kalam, S.**, Khan, R. A., Khan, S., Faizan, M., Amin, M., Ajaib, R., & Abu-Khamsin, S. A. (2021). Data-Driven Modeling Approach to Predict the Recovery Performance of Low-Salinity Water- floods. *Natural Resources Research*, 1-21. <https://doi.org/10.1007/s11053-020-09803-3>

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