

**EXPERIMENTAL EVALUATION OF OIL RECOVERY
FROM CARBONATE ROCKS BY GEMINI SURFACTANTS**

BY

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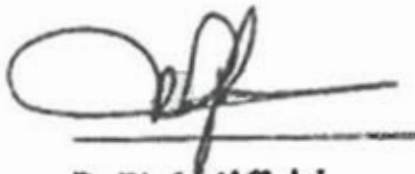
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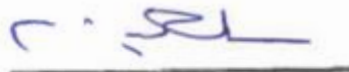
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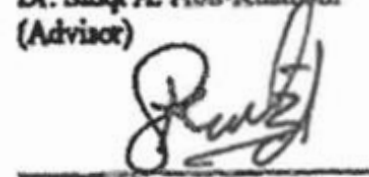
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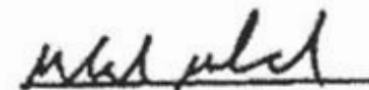
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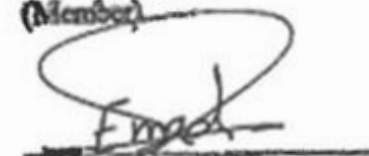
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2024

Dedication

With heartfelt affection, I dedicate this dissertation to my father, praying that Allah bestows upon him good health, well-being, and a long life filled with His satisfaction and obedience. I also dedicate this work to the one who eagerly awaited to celebrate this achievement, someone I deeply wish was alive to share this moment with me: my mother. May Allah bless her, have mercy upon her, forgive her sins, and grant her the highest ranks in Jannatul Firdaus. Finally, I dedicate this work to my wife and my beloved daughters, whose patience and heartfelt prayers provided me with the strength to persevere in this endeavor.

"اللهم ارحم أمي واغفر لها وأسكنها فسيح جناتك وأجزها عني خير الجزاء"

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ABSTRACT

Full Name : Khaled Hussein Mohammed Al-Azani
Thesis Title : Experimental Evaluation of Oil Recovery from Carbonate Rocks by Gemini Surfactants
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Surfactant injection into hydrocarbon reservoirs is a proven method for enhanced oil recovery, leveraging its ability to reduce interfacial tension between oil and water and potentially alter rock wettability. However, challenging conditions in carbonate reservoirs, like high temperature and salinity, present stability issues for surfactants. To tackle this, a series of ethoxylated quaternary ammonium cationic Gemini surfactants has been developed in-house, tailored for high salinity and temperature. Despite extensive evaluation demonstrating their superior performance, their oil recovery efficacy remains unexplored. This research fills this gap by investigating the oil recovery performance of one of these surfactants (GS8), a critical step in enhanced oil recovery advancement.

This research work evaluates the oil recovery efficacy of an internally synthesized surfactant through coreflooding experiments across five phases. These experiments simulate harsh conditions typical of carbonate reservoirs, with temperatures of 100°C, pressures exceeding 3000 psi, and salinity levels representative of formation water and seawater in the Middle East (i.e., seawater and formation water salinities of more than 57,000 and 213,000 ppm, respectively). Rock samples, aged in crude oil at their irreducible water saturation for nearly three weeks at 100°C, were used. The surfactant concentration was consistently maintained at 2500 ppm in all experiments. High-performance liquid

chromatography was employed to assess surfactant concentration in the produced effluent, providing insight into dynamic retention.

In the initial phase, the study compared the performance of internally synthesized single-component ethoxylated quaternary ammonium cationic Gemini surfactants (GS) and betaine-type zwitterionic surfactants (ZIS), where five coreflooding experiments were conducted using Indiana limestone samples. When injected post-seawater flooding, both surfactants achieved approximately 11–12% recovery of initial oil in the core (OOIP) without the need for additional cosolvents or cosurfactants, a departure from previous formulations. This enhancement primarily resulted from wettability alteration from oil-wet to intermediate-wet conditions, supported by contact angle and oil/water interfacial tension measurements. Introducing a one-pore-volume slug of standard acrylamide copolymer at 2000 ppm between seawater and surfactant floods increased oil recovery to around 16–17% OOIP for both surfactants. Effluent analysis showed surfactant dynamic retention values of 0.44 and 0.61 mg/g-rock for GS and ZIS, respectively, indicating their high efficiency for enhanced oil recovery in carbonate reservoirs.

In the subsequent phase, four coreflooding experiments were conducted on Indiana limestone cores at specific injection rates (0.10, 0.25, 0.50, and 1.00 cc/min). Each experiment involved continuous seawater flooding followed by continuous flooding with solution of the Gemini surfactant in seawater. The recovery factor by surfactant flooding was higher at lower injection rates (0.10 and 0.25 cc/min), indicating sufficient time for surfactant-mediated wettability alteration and oil mobilization, with 0.25 cc/min being the optimum rate tested. However, slower injection rates correlated with higher dynamic

retention, implying a trade-off between high oil recovery, and minimizing dynamic retention when injecting the Gemini surfactant.

The third phase presents findings from three coreflooding experiments on heterogeneous Indian limestone core samples with varying permeabilities. Results showed the highest recovery factor in low-permeability rocks and the lowest in high-permeability rocks for both seawater and surfactant floods. Surfactant floods led to additional recoveries of 31%, 23%, and 19% for low (10 mD), medium (100 mD), and high-permeability (>1,000 mD) samples, respectively. Nuclear magnetic resonance (NMR) analysis confirmed these results, with effluent analysis indicating dynamic retention highest in the lowest permeability and lowest in the highest permeability rock. NMR analysis suggested that surfactant performance and dynamic retention were influenced by the larger surface area of low-permeability rocks, facilitating increased surfactant contact. The fourth phase showcases one coreflooding experiment on carbonate plug obtained from a Saudi Arabian outcrop. Continuous seawater flooding, followed by continuous flooding a solution of an in-house-designed cationic Gemini surfactant dissolved in seawater, resulted in additional oil recovery attributed to wettability alteration by the surfactant. The calculated dynamic retention fell within an acceptable range for surfactant dynamic retention. Static adsorption tests demonstrated increased adsorption with higher surfactant concentration, showcasing the applicability and effectiveness of the surfactant on local carbonate rocks.

Lastly, in the fifth phase, four coreflooding experiments tested various solutions, including a Gemini surfactant in seawater, a Gemini surfactant in ten-times diluted seawater, a Gemini surfactant in seawater with 1 wt% DTPA, and a Gemini surfactant in seawater with 300 ppm methylene blue. Continuous injection of GS surfactant in seawater resulted in an

additional oil recovery of around 23% OOIP, with a dynamic retention of 0.37 mg/g-rock. Chemical flooding with GS/LowSal water yielded 26.3% OOIP extra oil recovery, with a dynamic retention of 0.35 mg/g-rock. Incorporating DTPA into the recovery process led to the largest additional oil recovery among all tested solutions, approximately 37% OOIP, with a dynamic retention of 0.41 mg/g-rock. However, adding methylene blue with the GS slowed down the recovery process, requiring a larger volume of chemical solution. This phase underscores the synergistic effects of combining the cationic Gemini surfactant with other additives or methods to optimize oil recovery while balancing surfactant retention.

ملخص الرسالة

الاسم الكامل: خالد حسين محمد العرّاني

عنوان الرسالة: التقييم التجريبي لاستخلاص النفط من الصخور الكربونية بواسطة عناصر السطح الفعالة الثنائية

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2024م

يُعد حقن المواد الخافضة للتوتر السطحي في مكامن الهيدروكربون طريقة مجربة لتعزيز استخلاص النفط، بسبب قدرتها على تقليل التوتر السطحي بين النفط والماء وربما تغيير قابلية بلل الصخور. ومع ذلك، فإن الظروف الصعبة في خزانات الكربونات، مثل ارتفاع درجة الحرارة والملوحة، تمثل مشكلات تتعلق باستقرار المواد الخافضة للتوتر السطحي. ولمعالجة هذه المشكلة، تم تطوير سلسلة من المواد الخافضة للتوتر السطحي كاتيونية الأمونيوم الرباعية الإيثوكسيلية محلياً، وهي مصممة خصيصاً للملوحة العالية ودرجة الحرارة العالية. على الرغم من التقييم الشامل الذي يوضح أدائها المتفوق، إلا أن فعاليتها في استخلاص الزيت لا تزال غير مستكشفة. يسد هذا البحث هذه الفجوة من خلال دراسة أداء استخلاص الزيت عبر إحدى هذه المواد (GS8)، والتي خطوة حاسمة في تقدم عملية استخلاص النفط المعزز. يقوم هذا العمل البحثي بتقييم فعالية استخلاص الزيت من مادة خافضة للتوتر السطحي مُصنَّعة داخلياً من خلال تجارب حقن عينات الصخور خلال خمس مراحل. تحاكي هذه التجارب الظروف القاسية النموذجية لمكامن الكربونات، مع درجات حرارة تصل إلى 100 درجة مئوية، وضغوط تتجاوز 3000 رطل لكل بوصة مربعة (psi)، ومستويات ملوحة تمثل مياه التكوين ومياه البحر في الشرق الأوسط. تم استخدام عينات الصخور، المعتقدة في النفط الخام عند تشبع الماء غير القابل للاختزال لمدة ثلاثة أسابيع تقريباً عند 100 درجة مئوية. تم الحفاظ على تركيز الفاعل بالسطح باستمرار عند 2500 جزء في المليون (ppm) في جميع التجارب. تم استخدام التحليل اللوني السائل عالي الأداء لتقييم تركيز الفاعل بالسطح في السوائل المنتجة خلال التجارب، مما يعطي انطباع عن الإحتفاظ الديناميكي.

تضمنت المرحلة الأولى من هذا البحث عمل مقارنة بين أداء خافض للتوتر السطحي الجوزائي الكاتينيوني رباعي الأمونيوم أحادي العنصر (GS8) أو خافض للتوتر السطحي زويتيريوني من نوع البيتين (ZIS)، وكلاهما تم

تصنيعهما محلياً. تم حقن أي من المادتين بعد تدوييهما في عينة من ماء البحر إلى عينات الصخور بعد حقن ماء البحر. أثبتت نتائج هذه المرحلة مدى فعالية أي من هاتين المادتين في تعزيز وزيادة الإنتاج بدون الحاجة إلى أي عناصر مساعدة. أظهرت النتائج أيضاً مستوى متدني من الاحتجاز الديناميكي لأي من هاتين المادتين. في المرحلة الثانية تم اختبار الوقت اللازم لخفض التوتر السطحي الجوزائي الكاتيوني رباعي الأمونيوم أحادي العنصر (GS) في تغيير خاصية البلل عند حقنه بعد ماء البحر عن طريق اختبار معدلات حقن مختلفة. أظهرت النتائج تزايد في نسبة الإنتاج مع زيادة معدلات الحقن 0.10، 0.25، و 0.50 سم³/دقيقة والتي انخفضت عند معدل حقن 1.00 سم³/دقيقة. على العكس من ذلك، كانت نسبة الإنتاج باستخدام GS أعلى عند اختبار أقل معدلات الحقن (0.10 و 0.25 سم³/دقيقة)، مما يشير إلى توفر الوقت الكافي لتغيير قابلية التبلل بواسطة الـ GS. ومع ذلك، فإن معدلات الحقن الأبطأ ترتبط بارتفاع الاحتجاز الديناميكي، مما يعني وجود مفاضلة بين الاستخلاص العالي للنقط وتقليل الاحتجاز الديناميكي عند استخدام الـ GS. تعرض المرحلة الثالثة نتائج ثلاث تجارب أساسية على عينات أساسية من الحجر الجيري غير المتجانسة ذات نفاذية متفاوتة. وأظهرت النتائج أن أعلى نسبة إنتاج كانت في الصخور ذات النفاذية المنخفضة سواءً باستخدام ماء البحر أو محلول الـ GS. أكد تحليل الرنين المغناطيسي النووي (NMR) هذه النتائج، حيث يشير تحليل النفايات السائلة إلى الاحتفاظ الديناميكي الأعلى في أدنى نفاذية وأدنى في الصخور الأعلى نفاذية. يشير استخدام NMR إلى أن أداء الـ GS واحتجازه الديناميكي يتأثران بمقدار المساحة السطحية لحبيبات الصخر، بحيث كلما زادت هذه المساحة زادت قدرة الـ GS على تغيير خاصية البلل للصخرة، والتي تتناسب عكسياً مع نفاذية الصخور.

تعرض المرحلة الرابعة تجارب على عينات الصخور الكربونية من تنوءات في المملكة العربية السعودية. أدى الحقن المستمر بمياه البحر، الذي أعقبه حقن مستمر بمحلول الـ GS المذاب في مياه البحر، إلى زيادة في إنتاج الزيت والذي يعزى إلى تغير قابلية البلل بواسطة الـ GS. أكدت اختبارات NMR وتحليل السوائل المنتجة هذه النتائج، مع وقوع الاحتجاز الديناميكي ضمن نطاق مقبول. وأخيراً، تضمنت المرحلة الخامسة أربع تجارب أساسية، تتضمن كل منها حقن العينات بمياه البحر متبوعة بالحقن المستمر لمحلول كيميائي. تم اختبار محاليل مختلفة، بما في ذلك الـ GS المذاب في مياه البحر، الـ GS المذاب في مياه البحر المخففة، والـ GS المذاب في مياه البحر مع 1% بالوزن DTPA، والـ GS المذاب في مياه البحر مع 300 جزء في المليون من الميثيلين الأزرق. أدى الحقن المستمر للـ GS المذاب

في مياه البحر إلى زيادة الإنتاج بمعدل 23% من الزيت المتبقي في الصخر، مع اختزال ديناميكي بحوالي 0.37 ملجم/جم من الصخر. بينما أدى الغمر الكيميائي بـ الـ GS المذاب في ماء البحر المخفف إلى استخلاص إضافي للنفط بنسبة 26.3%، مع اختزال ديناميكي بحوالي 0.35 ملجم/جم من الصخر. نتج عن أدى دمج DTPA مع الـ GS إلى أكبر نسبة إنتاج بين جميع المحاليل المختبرة؛ حيث نتج عن ذلك نسبة إنتاج بحوالي 37%، مع اختزال ديناميكي بحوالي 0.41 ملجم/جم من الصخر. في المقابل، ادت إضافة الميثيلين الأزرق مع الـ GS إلى إبطاء عملية الانتاج، والذي تطلب كمية أكبر من المحلول الكيميائي. تؤكد هذه المرحلة على التأثيرات التآزرية للجمع بين الـ GS مع إضافات أو طرق أخرى لتحسين استخلاص الزيت مع موازنة الاحتجاز الديناميكي للـ GS.

CHAPTER 1

INTRODUCTION

1.1 Research Motivation

Approximately 60% of the world's oil reserves are found in carbonate reservoirs [1]. The oil production from mature carbonate reservoirs in the Middle East accounts for more than 40% of the world daily oil production [2]. Most of these reservoirs are naturally fractured with a complex pore system and high degree of heterogeneity. Their wettability varies from mixed-wet to oil-wet. These reservoirs are also known to be under harsh reservoir conditions, i.e. high reservoir temperature and the high salinity of formation water (HTHS) [3,4]. These conditions pose a great challenge to chemical EOR (cEOR) processes due to their effect on the stability, water solubility, and the rheological properties of the chemicals (e.g., surfactants) used. Therefore, the need for screening the candidate chemicals that can withstand these conditions in addition to improving the oil recovery is inevitable and is an important aspect of cEOR design for these reservoirs.

1.2 Research Objectives

The objectives of this research work are as follows:

1. Evaluate surfactants synthesized in-house as agents for EOR in carbonate reservoirs including Middle East reservoirs through coreflooding experiments.

2. Establish trends between oil recovery and the different influential parameters including injection rate and permeability. Those trends can be quantitatively established through the different experiments.
3. Investigate the synergistic effect of different methods/additive with the in-house synthesized Gemini surfactant.

1.3 Summary of Research Work

The dissertation was divided into five main phases to cover a wide range of experimental parameters. The phases are as follows:

Phase I: Evaluation of various surfactants, both with and without polymers, in order to establish a comparison with our in-house synthesized surfactant. The aim is to demonstrate their efficacy in enhancing oil recovery as standalone components, without requiring a cosolvent or cosurfactant.

Phase II: Investigate the effect of injection rate on the recovery performance of the in-house synthesized Gemini surfactant. The aim is to investigate the residence time required for the surfactant to modify the rock wettability and, hence, boost oil recovery.

Phase III: Study the oil recovery performance of an in-house Gemini surfactant on rocks with varying permeability. This research aims to establish a platform for examining the influence of the rocks' surface area on the effectiveness of oil recovery.

Phase IV: Study the in-house developed surfactants by using local rock samples collected from outcrop location in Saudi Arabia.

Phase V: Study the synergistic effect of the in-house modified surfactant in the presence of low-salinity water, a chelating agent, or methylene blue.

1.4 Dissertation Structure

This dissertation consists of eight chapters. The initial chapter, Chapter 1, serves as an introduction to the dissertation work, elucidating its motivation and research objectives. It also offers a comprehensive overview of the dissertation's content. Chapter 2, the second chapter, provides background information on the topic, including a literature review and an identification of research gaps. Chapters 3 through 7 outline the work undertaken in different phases of the research. Specifically, Chapter 3 covers Phase I, Chapter 4 discusses Phase II, Chapter 5 addresses Phase III, Chapter 6 delves into Phase IV, and Chapter 7 explores Phase V. Finally, Chapter 8 presents the conclusions drawn from the research findings and offers recommendations for future studies.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Background

Crude oil is mostly recovered from hydrocarbon reservoir through several stages [5]. The primary recovery stage involves the production of oil by the natural drive mechanisms caused by the natural energy of the reservoir rocks and fluids. This energy is stored in the reservoir rocks and fluids in the form of pressure, and it can be sourced from the gas-cap drive, solution-gas drive, water drive, the effect of gravity, expansion of rocks and fluids, or combinations of these mechanisms. However, the continuous production of oil causes the reservoir pressure to drop and some of the stored fluid energy to be lost. This decline makes it necessary for the operator to boost or maintain the reservoir pressure in a process referred to as the secondary recovery stage. In this stage, the additional oil recovery is a result of the augmentation of the natural energy of the reservoir through the injection of water (or gas). However, despite the additional oil recovered by the waterflooding, the combined oil recovery from the primary and secondary stages is usually low. This is because large amount of oil droplets remains as isolated and trapped in the pores or as films around the rock material resulting in a high residual oil saturation which ranges from 20% to 35% in the water-flooded regions. Therefore, typically 10% to 25% of the oil originally in place (OOIP) is recovered from the reservoir after primary stage and around 25% to 40% of the OOIP is recovered at the end of the waterflooding mode [6–9]. These recovery

factors, however, might be different from one reservoir to another depending on the characteristics of the reservoir rocks and fluids [10]. To prevent the deterioration of the oil production rates from the mature fields and to achieve the target global oil production rates, the development of tertiary or enhanced oil recovery (EOR) methods and the selection of the best EOR techniques becomes highly important to the oil producers [11].

Enhanced oil recovery, mostly known as EOR, refers to as the process of injecting materials that are not usually present in the hydrocarbon reservoir. These materials can be gas, heat or chemicals [12]. Numerous methods can be applied in EOR such as chemical flooding, microbial recovery, gas injection and thermal recovery (**Figure 2-1**) [13–16]. The ultimate aim of EOR is to improve overall oil recovery by improving the microscopic and macroscopic displacement efficiencies. These improvements can be achieved by influencing the rock and fluids' properties such as oil/water viscosity, rock wettability, interfacial tension (IFT), capillary pressure, and the mobility ratio of between the displacing and displaced fluids [6,7,14–18]. **Figure 2-2** presents the global count of EOR projects in the period from 1971 until 2017 based on the data published by the International Energy Agency (IEA) ¹.

¹ <https://www.iea.org/>

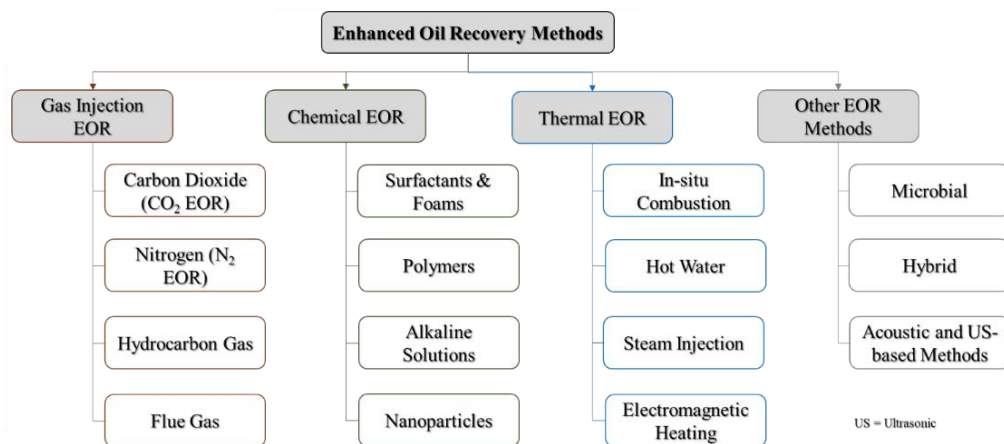


Figure 2-1. Different EOR methods (modified after [19])

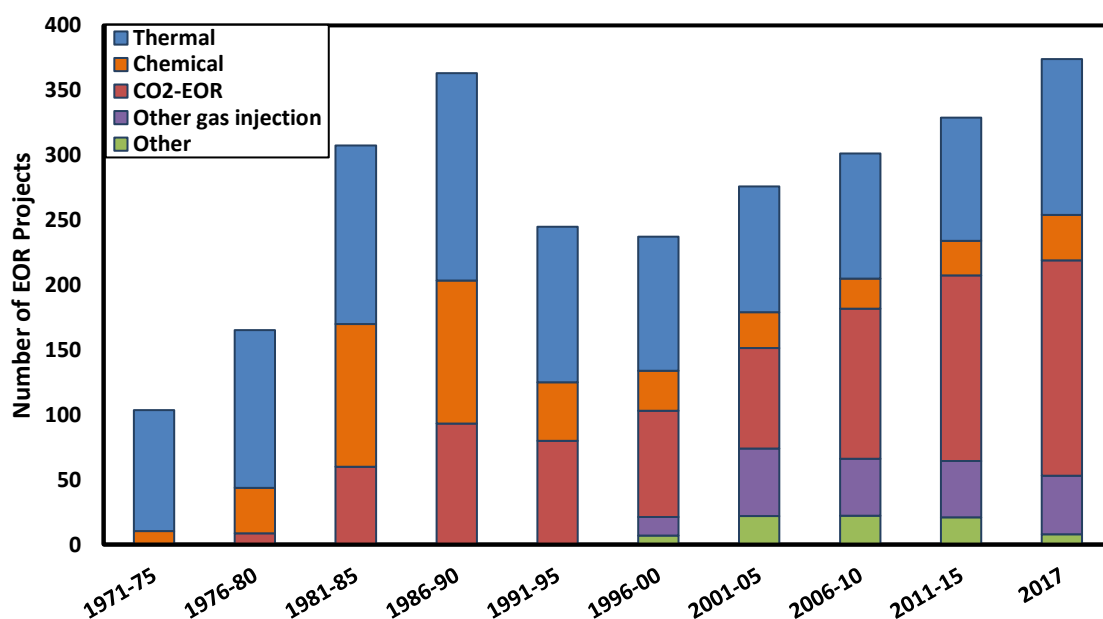


Figure 2-2. The global number of EOR projects in the period of 1971-2017²

Chemical enhanced oil recovery (cEOR) is considered as one of the important EOR methods and a lot of research has been conducted in the area of cEOR [20]. cEOR involves the use of different chemicals such as alkalis, surfactants, polymers, and/or their different combinations (i.e., Surfactants/Polymers (SP) flooding, Alkali/Polymer (AP) flooding, and Alkalis/Surfactants/Polymers (ASP) flooding) [21]. These chemicals are used for different

² Data source: <https://www.iea.org/commentaries/whatever-happened-to-enhanced-oil-recovery>

purposes; polymers are used as viscofying agents to increase the viscosity of the displacing phase (i.e., water) and, hence, controlling the mobility of the flowing phases. They also act as agent to reduce the adsorption of surfactants due to the competition of adsorption sites between surfactants and polymers [22]. The alkali and surfactants, on the other hand, are used to reduce the IFT between the displacing and displaced fluids (i.e., water and oil). Alkali also help in reducing the adsorption of some types of surfactants and polymers by modifying the surface electrical charge of the reservoir rock [23,24]. The following sections will provide more details of some of these processes.

2.2 Surfactant Flooding

Residual oil saturation is generally controlled by the ratio of the viscous forces (F_v) to the capillary forces (F_c). This ratio is defined in terms of the dimensionless capillary number (N_c) given by the following equation [25]:

$$N_c = \frac{F_v}{F_c} = \frac{v\mu}{\sigma \cos(\theta)} \quad (2-1)$$

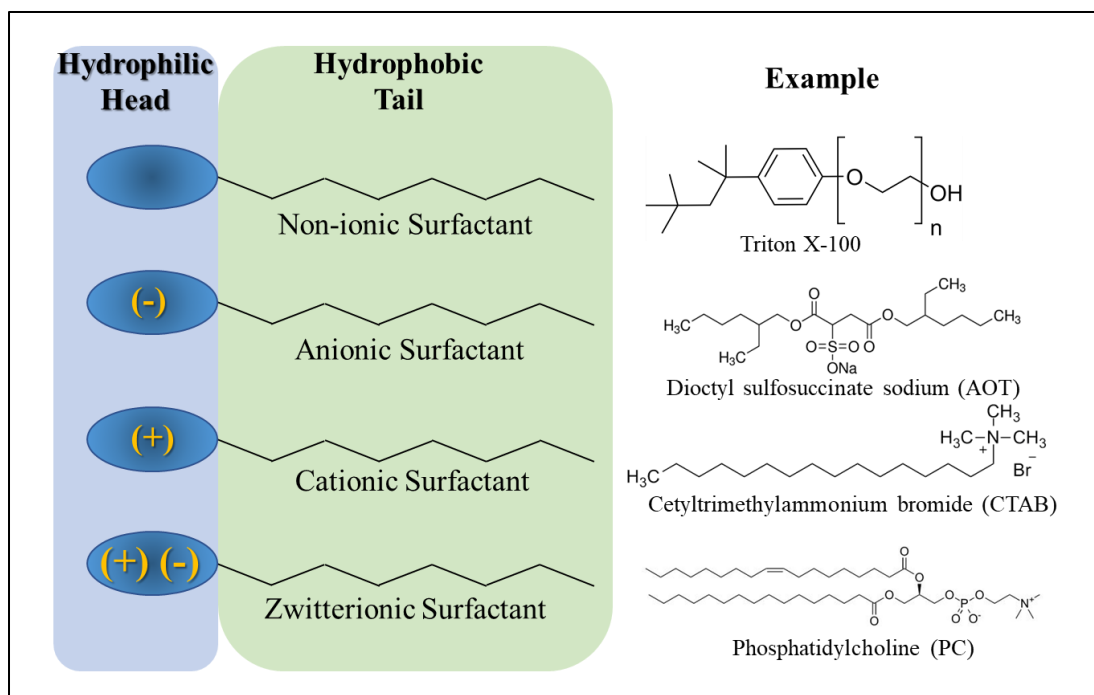
where v is the interstitial velocity of the displacing fluid, μ is the viscosity of the displacing fluid, σ is the IFT between the displacing and displaced fluid, and θ is the contact angle. Other forms of the capillary number are also available at [26].

Typical waterflooding projects correspond to capillary number of around 10^{-7} to 10^{-6} . To produce an additional oil from the water flood, the capillary number needs to increase to around 10^{-5} [27–29]. This can be achieved by different means. First, the viscous forces can be increased by allowing high pressure drop which can be achieved by increasing either the injection rate or the viscosity of the injected fluid. However, this approach is not

effective because increasing the pressure drop by many orders of magnitude is not feasible as it may exceed the formation fracture pressure. Alternatively, the most practical way to increase the capillary number is by reducing the capillary forces via decreasing the IFT. To illustrate, the IFT can be decreased from about 30 dyne/cm in typical oil/water system to ultra-low values of less than 10^{-3} dyne/cm. This ultra-low value of IFT can be achieved using surfactants and/or their different formulations [5,30]. The idea of using surfactants with the injected water to lower the water/oil IFT and/or modify rock wettability and, hence, improving the oil recovery dates back to the early 1900s [31]. Surfactant flooding process is well-established cEOR method and the process has been well-developed over the past 90 years [32]. Many publications have been presented to describe the use of surfactants as EOR agents and the advances in the process [19,20,33,34]..

2.2.1 Definition of Surfactants

Surface active agents (commonly known as surfactants) are generally organic compounds with their molecules of amphiphilic nature. Their molecules consist of two distinguishing parts, namely a water-soluble (hydrophilic) head and an oil-soluble (hydrophobic) tail. The hydrophobic tail can be either a long-chain hydrocarbon, fluorocarbon, a siloxane chain, or a short polymer chain [21]. The hydrophilic head, in contrast, may be negatively charged (anionic), positively charged (cationic), non-ionic (possesses no charge), or zwitterionic (having both negative and positive charges) [35]. Accordingly, surfactants are classified into four categories depending on the charges of the hydrophilic group as illustrated by **Figure 2-3**.



2.2.2 Types of Surfactants

Improper selection of the surfactant for EOR may not be effective in increasing the oil recovery. This can also result in adverse effects such as undesirable wettability alteration and dissolution of the rocks which may lead to blocking the pore space. The rock mineralogy needs also to be considered when selecting the surfactants to avoid the high retention rates of the surfactants and the unnecessary waste of resources [37]. This subsection will provide some details of the most common classes of surfactants used in EOR applications.

Anionic Surfactants

Anionic surfactants are mostly applied in sandstone reservoirs because the negatively charged sandstone surface makes them the desirable option for such option. Because of that and, since most of the cEOR work has been conducted in sandstone reservoirs, anionic

surfactants are the most commonly used class of surfactants in the oil industry [33]. The most important classes of anionic surfactants for cEOR purposes are sulfates, sulfonates, and carboxylates. **Table 2-1** presents the subcategories of anionic surfactants as presented by Negin et al. [37].

Sulfate surfactants. It was shown that a surfactant with sulfate added to its molecular structure becomes very sensitive to high temperatures. These surfactants hydrolyze and degrade at high temperatures. Therefore, sulfate-based surfactants are not of good choice for applications in high temperature reservoirs [38].

Sulfonate/Carboxylate surfactants. According to Hirasaki et al. [39], the presence of carboxylate or sulfonate units improves the long-term thermal stability of surfactants. The sulfonate also improves the tolerance of the surfactants to high salinity water with high amounts of divalent ions [38]. Finally, studies have shown that carboxylate surfactants exhibited remarkable performance under HTHS conditions [40].

Cationic Surfactants

Cationic surfactants have been shown to be more effective wettability modifier in carbonate rocks than anionic surfactants due to the strong ion-pair interactions caused by the cationic heads [41,42]. **Table 2-2** presents the most used cationic surfactants for EOR applications.

Table 2-1: Classes of anionic surfactants (adopted from [37])

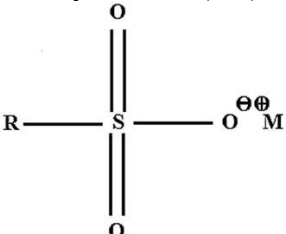
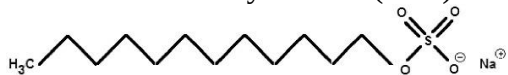
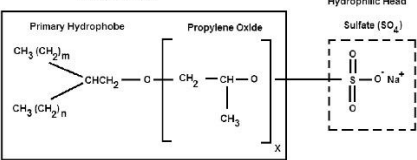
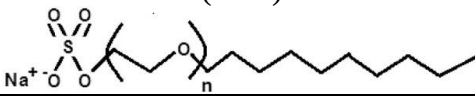
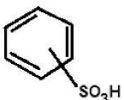
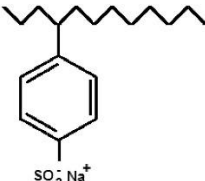
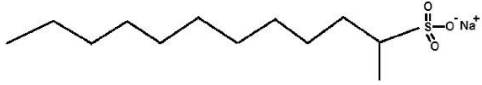
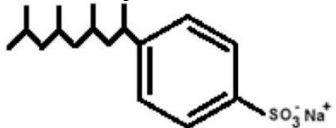
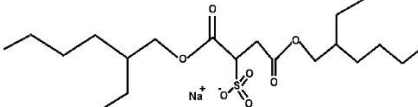
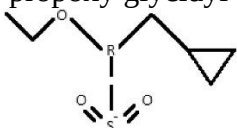
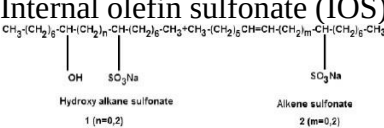
Class	Name/structure	Remarks
Sulfate	Alkyl sulfate (AS) 	- E.g., sodium dodecyl sulfate, sodium lauryl sulfate, and sodium octyl sulfate - Biodegradable - Low solubility in water at high temperature
	Sodium dodecyl sulfate (SDS) 	- Better be applied with nanoparticles - Sensitive to high temperatures
	Alcohol Propoxy Sulfate (APS) 	- Better performance when used with IOS - Stable at salinity up to 6,000 ppm - Temperature-sensitive
	Alkyl (or alcohol) Ethoxy Sulfate (AES) 	- Alkali makes it stable in high pH and HTHS environments up to 83 °C
	Alpha olefin sulfate 	- Similar to IOS and AOS - Thermally instable
	Alkyl ether sulfates	- Better aqueous stability than IOS - Temperature-sensitive - Low tolerance to salinity
	Guerbet alkoxy sulfate	- Hydrolyzes at temperatures above 60 °C - Low tolerance to low or neutral pH environments
	TDA-9PO-sulfate	- Salt-tolerant - High hydrophobicity → high adsorption - Temperature-limited up to 60 °C only
	Alkyl alcohol propoxylated sulfate	- Effective in IFT reduction at low concentrations - Salt-tolerant - Temperature-sensitive above 60 °C

Table 2-1: (Cont)

Class	Name/structure	Remarks
Sulfonate/ Carboxylate	Alkyl aryl sulfonates $\text{CH}_3(\text{CH}_2)_m\text{CH}(\text{CH}_2)_{n-1}\text{CH}_3$ 	- First time in the market in 1930s - Low-cost raw material - Stable at high temperature - Cannot withstand high salinity
	Alkyl benzene sulfonate (linear) 	- Sub category of alkyl aryl sulfonates - Chain length of alkyl from 10 to 14 carbon atoms - Toxicity increases with salinity - Lower CMC with higher carbon number
	N-ethoxy sulfonate	- High stability in HTHS environments - No precipitation when divalent ions are present
	Alpha-Olefin Sulfonate (AOS) 	- Perform well with divalent ions - Highly biodegradable - Stable over wide range of pH - High foamability in hard water - E.g., sodium C14-16 olefin sulfonate; C14-16-alkane hydroxy
	Alkyl polyalkoxy alkyl sulfonate or alkyl aryl polyalkoxy alkyl	- High salt-tolerance (70,000-220,000 ppm) - Thermally-stable (up to 150 °C)
	Branched alkyl benzene sulfonate 	- Similar behavior to linear alkyl benzene sulfonate - More expensive and less biodegradability
	Docusate sodium 	- Double-tail surfactant - Good candidate for ASP flooding - Higher thermal stability when mixed with Synperonic® PE/F68
	Ethoxy or propoxy glycidyl sulfonates 	- High water-solubility at different salinities - Weak thermal stability
	Internal olefin sulfonate (IOS) $\text{CH}_3-(\text{CH}_2)_5-\text{CH}(\text{CH}_2)_n-\text{CH}(\text{CH}_2)_5-\text{CH}_3$  Hydroxy alkane sulfonate 1 (n=0,2) Alkene sulfonate 2 (n=0,2)	- Stable in aqueous solutions - Tolerant to salinity less than 6,000 ppm - Not tolerant to divalent ions
	Sulfonated, ethoxylated alcohol or alkyl phenol $\text{RO}(\text{CH}_2)(\text{CH}_2)_x\text{CH}_2\text{CH}_2\text{SO}_3^-\text{M}^+$	- Stable at temperatures above 50 °C - Tolerant to high salinity and divalent ions

	Sodium petroleum sulfonate $\text{R}-\text{N} \begin{cases} (\text{CH}_2-\text{CH}_2-\text{O})_x\text{H} \\ (\text{CH}_2-\text{CH}_2-\text{O}_y)\text{H} \end{cases}$	- Not stable in hard water - Stable at high reservoir temperatures
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Table 2-2: Most common cationic surfactants for EOR applications (adopted from [37])

Name	Structure	Remarks
Cetyl Trimethyl Ammonium Bromide (CTAB)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}(\text{H}_2\text{C})_{15}-\text{N}^+-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \text{Br}^-$	- Good candidate for EOR process in carbonate reservoirs - Mainly wettability-altering agent - Stable up to 100 °C and 60,000 ppm salinity
Coco Alkyl Trimethyl Ammonium Chloride	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{R}-\text{N}^+-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right] \text{Cl}^-$	- Commercial name is Arquad C-50 - More effective in sandstone reservoir
Stearyl Trimethyl Ammonium Chloride	$\begin{array}{c} \text{Cl}^- \\ \\ \text{H}_3\text{C}-\text{N}^+-\text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}_{17}\text{H}_{35} \end{array}$	- Commercial name is Arquad T-50 - Not recommended for carbonate reservoirs
Dodecyl Trimethyl Ammonium bromide (DTAB)	$\begin{array}{c} \text{Br}^- \\ \\ \text{Me}-\text{N}^+-\text{Me} \\ \\ \text{Me}-\text{C}_{12}\text{H}_{25} \end{array}$	- Stable at 60,000 salinity and 100 °C - Wettability modifier in carbonates - Unable to achieve ultra-low IFT values - Better used with nonionic surfactants
Ethoxylated alkyl amine	$\text{R}-\text{N} \begin{cases} (\text{CH}_2-\text{CH}_2-\text{O})_x\text{H} \\ (\text{CH}_2-\text{CH}_2-\text{O}_y)\text{H} \end{cases}$	- Applicable to HTHS carbonates (CO₂ foaming agent)

Non-ionic Surfactants

Because they lack the charge in their hydrophilic heads, non-ionic surfactants do not ionize in water. Therefore, the solubility of these surfactants on water is governed by the hydrogen bonding between water and the hydrophilic head group such as ethylene oxide chain [43]. The increase of the temperature results in weak hydrogen bonding due to the increase in thermal energy. This results in less solubility of these surfactants in water and, hence, turbid solutions form Kamal et al. [33]. The head groups of non-ionic surfactants are typically

polar like glucose in alkyl polyglucosides while their tails are typically linear or branched [19]. **Figure 2-4** shows the most common classes of non-ionic surfactants. Non-salt tolerant are shown to be high salt-tolerant. Their capability to reduce the IFT is minimal compared with other ionic surfactants [44]. **Table 2-3** presents some of the tested nonionic surfactants for EOR applications reviewed by Negin et al. [37].

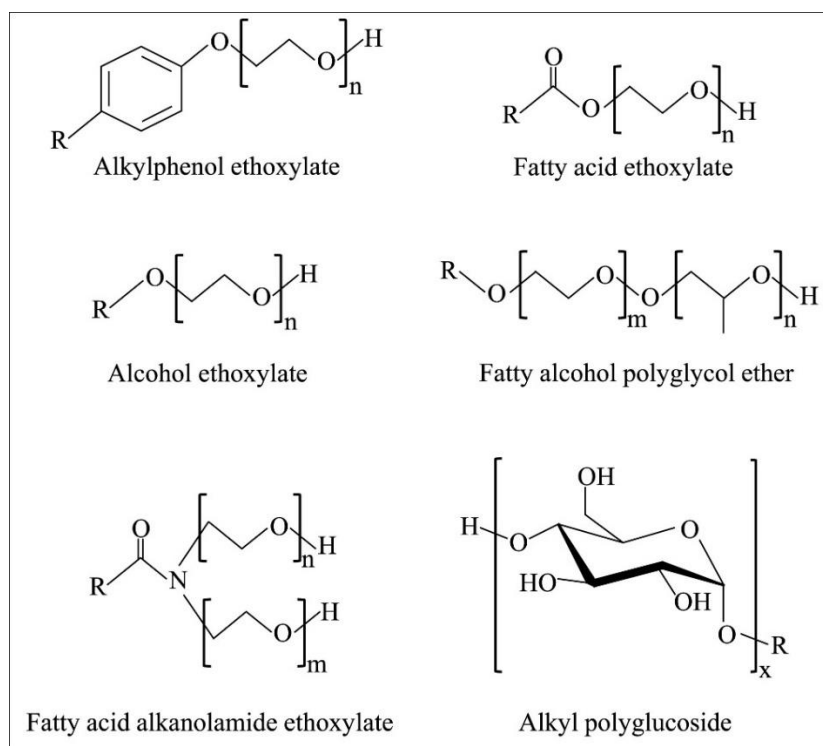


Figure 2-4. Structure of common nonionic surfactant [45]

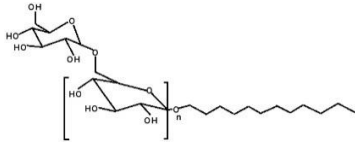
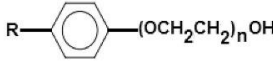
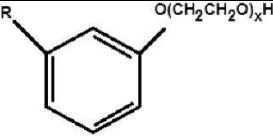
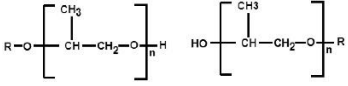
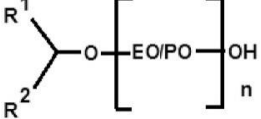
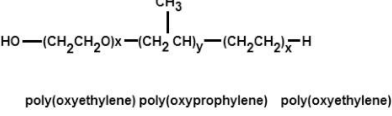
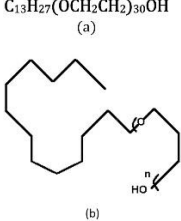
Zwitterionic Surfactants

The head groups of zwitterionic (amphoteric) surfactants consist of both positive and negative charges in which a short methylene segment separates these charges [46]. A lot of attention has been paid to the use of surfactants in the oilfield [47]. These surfactants have distinguishable properties that make them of great interest to the oil industry [48]. These properties include their salt tolerance, excellent biodegradability, high solubility in water, and high thermal stability [46,49–51]. Zwitterionic surfactants can be good

candidates for EOR purposes due to their compatibility with surfactants from other classes.

They are relatively insensitive to hard water and stable in acids and bases [23].

Table 2-3: Most common nonionic surfactants for EOR applications (adopted from [37])

Name	Structure	Remarks
Alkyl ethoxy Carboxylated	$RO(CH_2CH_2O)_xCH_2COO^-M^+$	- Nonionic at neutral pH; and anionic at high pH - Compatible with HTHS when ethoxy and carboxylate group are combined
Alkyl Polyglycoside (APG)		- Good at HTHS (180,000 ppm and 80 °C) - Requires co-solvent to form microemulsion
NEODOL ethoxylate 91-8	$RO - (CH_2CH_2O)_n - H$	- Thermally stable up to 60 °C only
NEODOL 67 propoxylated sulfate (N67-7POS)	$RO - (OHCH_2CH_2CH_2)_n - O - SO_3^-M^+$	- Performs well with divalent ions - Not compatible with high salinity
Nonylphenol “N” ethoxylate	 Nonylphenol ethoxylate where n varies by product	- Compatible with HTHS (200,000 ppm salinity and 100 °C) when used with cationic surfactants - Acts as a wettability modifier
Polyethoxylated alkyl phenols		- Compatible with high salinity and divalent ions - Low water solubility at 37-51 °C
Poly (Ethylene/Propylene) glycol ether		- Applicable to HTHS environments - Biodegradable
Secondary Alcohol “N” ethoxylate/propoxylate		- HTHS application (up to 200,000 ppm salinity and 100 °C) when mixed with cationic surfactants
Synperonic® PE/F68	 poly(oxyethylene) poly(oxypropylene) poly(oxyethylene)	- Good for ASP flooding - Not effective for fractured or low-permeability reservoir - High thermal stability (above 100 °C)
Tridecyl Alcohol 30 Ethoxylate(TDA 30 EO)		- Similar to alkylphenol ethoxylate - HTHS application (up to 200,000 ppm salinity and 100 °C) - Wettability modifier

Triphenylmethane (TPM)		- Insoluble in water - Adaptive to HTHS (up to 186,000 ppm salinity and above 70 °C)
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Gemini Surfactants

Gemini surfactants are novel surfactants which have recently been used for EOR and many other applications due to their distinctive properties [52–54]. They were first recognized by [55] and then got their names by (Menger & Littau, 1991). Gemini surfactants have shown unique properties such as the low critical micelle concentration (CMC) and aggregate behavior, high efficiency in lower the oil/water IFT, rheological properties, wetting and foaming properties, and high-water solubility which make them of great interest for academic and industrial communities [57–60]. The structure of Gemini surfactants is different from that of conventional surfactants in that there are more than one hydrophobic tail group and hydrophilic head group in the Gemini surfactants connected by a spacer at or near the hydrophilic heads as illustrated by **Figure 2-5** [61,62]. The hydrophilic head of Gemini surfactants can be cationic, anionic, nonionic, or zwitterionic just in a similar manner as the conventional surfactants (Muhammad Shahzad Kamal, 2016). The addition of the spacer results in increasing the hydrophobicity of these surfactants compared to that of the conventional surfactants [64]. The spacer can be polar or non-polar and flexible or rigid and its length controls the gap between the two heads and ranges from C₂ to C₁₂ [65]. The common spacers of Gemini surfactants include azobenzene, ethylene oxide, Perylene tetracarboxylic diimide, stilbene, Polyoxyethylene,

Tetracarboxylic diimide, 2-butyryl, methylene, and polyether [65–71]. Finally, Gemini surfactants are named based on the length of the spacer group and the hydrophobic tail. To illustrate, a surfactant named as t - s - t where t denotes the number of carbon atoms in the hydrophobic tail and s represents the number of carbon atoms in the spacer group [37,63].

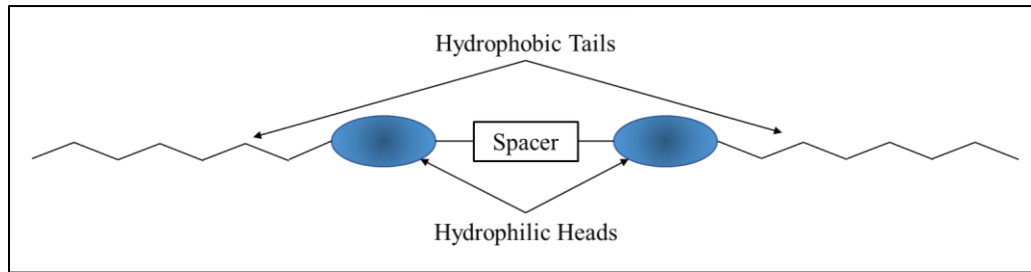


Figure 2-5. Structure of Gemini surfactant

2.2.3 Mechanisms of Oil Recovery by Surfactants

Additional oil can be recovered using surfactants through different mechanisms including lowering the oil/water IFT and altering the rock wettability [2,33]. These mechanisms are briefly described in the following subsections.

Interfacial Tension Reduction

Interfacial tension (mostly known as IFT) is defined as the attraction force between the molecules present at the interface of two fluids. When one of the fluids is air and the other is liquid, this force is termed surface tension. The SI unit of IFT is mN/m which is also equivalent to dynes per centimeter (dyne/cm) [72]. In water/hydrocarbon system, the IFT causes the capillary force to increase, which has a significant role in the trapping of hydrocarbon in the porous media [19].

As stated earlier, large capillary numbers can be achieved by reducing the IFT between the oil and water using surfactants. Studies have shown that low concentrations of surfactants could reduce the IFT to values below 0.01 dyne/cm. The process by which surfactants

reduce the oil/water IFT is called surfactant adsorption. In this process, some of the water and oil molecules at the water/oil interface are replaced by surfactant molecules. This arrangement of molecules causes a strong interaction between the hydrophilic heads of the surfactants and water on one side, and the hydrophobic tails of the surfactants and oil on the other side [73,74]. The type and concentration of the ions present in water determine the ability of surfactants to reduce the oil/water IFT. Therefore, there is an optimal salinity (expressed in terms of NaCl content) at which the oil/water IFT is reduced to its ultralow values [75]. This optimum salinity, however, is reduced due to the presence of divalent/multivalent cations along in a surfactant solution with a given NaCl concentration. This makes the surfactant less tolerant to NaCl salinity and, hence, the ability of the surfactant to reduce the IFT is adversely affected [76,77]. The factors influencing the IFT reduction by surfactants include temperature, pressure, salinity, pH, concentration of surfactant, type of surfactant, and the composition of oil [78].

Wettability Alteration

Wettability is defined as the tendency of a fluid to spread on, or adhere to, a solid surface when it coexists with other immiscible fluids [79]. This adhesion is a result of stable distribution of fluids in the porous media caused by the presence of different forces such as van der Waals forces, electrostatic forces, and structural forces [80]. When two fluids coexist, the fluid with the highest affinity to adhere to the solid surface is called the wetting phase [81]. In petroleum systems, different rock types have different wettability characteristics and rock can be classified as water-wet, oil-wet, and neutral-wet (or intermediate-wet). **Figure 2-6** shows the classification of the wettability of rock systems based on contact angle measurements. Sandstone generally has been shown to have water-

wet to intermediate-wet properties. Carbonates, however, usually exhibit intermediate-wet to oil-wet properties [82].

Oil recovery from carbonate reservoirs is significantly affected by the rock wettability. Due to the retention of oil in oil-wet carbonate reservoirs by the capillary forces and since adequate pressure gradients cannot be applied across these reservoirs, high oil saturations remain in such formations after water-flooding, considerable oil recovery can be achieved by the alteration of the wetting conditions of these reservoirs. A lot of research have shown that oil recovery can be increased significantly in these reservoirs by altering the rock wettability from oil-wet or intermediate-wet conditions to water-wet conditions [83,84]. Surfactants can, therefore, be good agents to attain this wettability alteration [85].

Coating and cleaning are the two main mechanisms by which wettability in carbonate reservoirs are altered by surfactants [19]. The coating mechanism is related to anionic surfactants where a monolayer is created on the surface of the carbonate rock by the interaction of the hydrophobic tail with the adsorbed oil. The result is that the initially oil-wet rock becomes covered with the surfactants' hydrophilic head groups which alters the wettability of the rock to become more water wet. The later mechanism is related to cationic surfactants, and it is based on the formation of ion pairs between the acidic portion of the adsorbed crude oil and the cationic heads of the surfactants. The originally water-wet surface then becomes exposed because the formed ion pairs remove the adsorbed layer of oil off the rock surface.

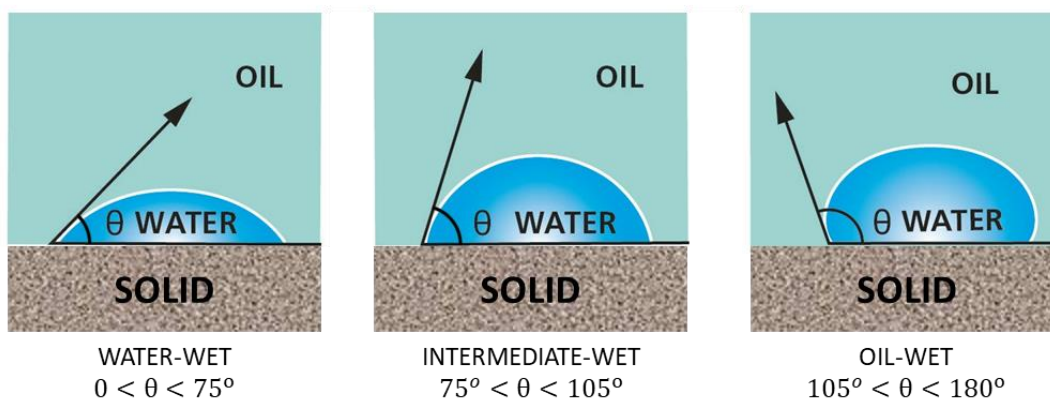


Figure 2-6. Wettability of reservoir rock based on contact-angle measurements³

2.2.4 Parameters Involved in Studying Surfactants

It is important to understand the parameters involved when it comes to surfactant characterization. Several authors summarized the most important parameters used in characterizing surfactants [19,37]. Some of those parameters are briefly described in the following subsections.

Critical Micelle Concentration

One of the important parameters in studying surfactants is the critical micelle concentration (CMC). CMC is defined as the surfactants' concentration at and above which the aggregation of surfactant molecules, called micelles, start to form (**Figure 2-7.a**) [86]. At the CMC, there is an abrupt variation in different physiochemical properties such as the surface tension, viscosity, and thermal and electrical conductivities as shown in **Figure 2-7.b**. at concentrations greater than the CMC, there is a stabilization in the behavior of surfactant regardless of any further increase in the concentration [37]. Different methods are used for measuring the CMC of surfactants. Those methods can be direct or indirect.

³ Photo modified from: <https://www.biolinscientific.com/blog/why-is-wettability-important-in-enhanced-oil-recovery>

In the direct methods, a specific property such as the surface tension, electrical conductivity, viscosity, osmotic pressure, or the refractive index (RI) is measured at different surfactant concentration. The CMC is then selected as the point of discontinuity or point of change in the slope of the plot of the measured property versus concentration. The indirect methods, on the other hand, the CMC is determined by monitoring the change of a given property of a substance added to the surfactant (i.e. probe) as reflected by the change in surfactant concentration [87]. In EOR applications, however, CMC are mostly determined from IFT measurements [88]. The factors influencing the CMC of the surfactant include the surfactant's molecular structure like the length of the hydrophobic chain, pressure, aqueous salinity, ionic composition, temperature, and pH [89,90].

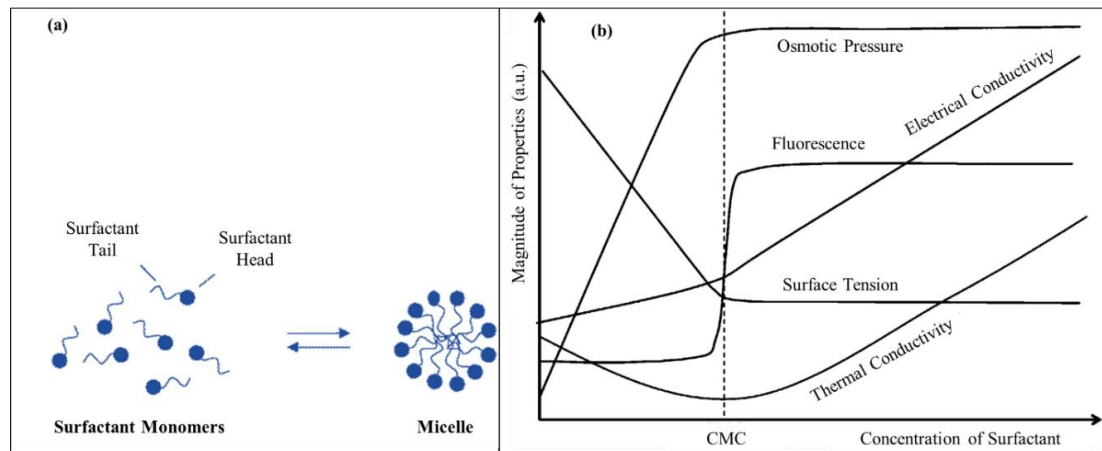


Figure 2-7. Formation of micelle (a) and the effect of the effect of concentration of surfactant on surfactant properties (modified after Sabahi et al. [91])

Krafft Temperature

The temperature at which the CMC of a surfactant is determined is referred to as the Krafft temperature (T_K) or the critical micelle temperature (CMT). Below this temperature, the micelles of surfactants cannot be formed and the surfactant becomes insoluble. A sharp increase in the solubility of surfactant is then noticed at the Krafft temperature (N. A. Malik

& Ali, 2016). The methods of determination of the Krafft temperature include the measurement of a specific property of the surfactant solution such as the electrical conductivity at elevated temperatures. The measured property is then plotted against the measurement temperature. The Krafft temperature, hence, corresponds to the temperature of the break in the property-temperature plot [93,94].

Microemulsion Phase Behavior

Microemulsion is defined as thermodynamically stable and homogeneous dispersion of two immiscible fluids such as hydrocarbon and water with surfactant molecules as the stabilizing agents [95]. At equilibrium conditions, microemulsions can be classified based on Winsor [96] into three types as shown in **Figure 2-8**. In Winsor's type I systems (No. 2 and 3), an excess oil phase coexists with an oil-in-water (O/W) microemulsion. This system is also referred to as lower phase. Winsor's type II systems (No. 6 and 7), however, are designated by the coexistence of an excess water phase with water-in-oil (W/O) microemulsion. This system is also referred to as upper phase. Changing from type I to type II, the microemulsion goes through Winsor's type III system (middle phase) where three distinctive phases coexist including oil, water, and microemulsion (No. 4 and 5). An entire single-phase microemulsion phase where the whole oil and water transform into single phase can also be formed at high surfactant concentration [2,97,98]. The factors which determine the transformation between different microemulsion systems include salinity, surfactant molecular weight and concentration, concentration of co-surfactant used, temperature change, oil/brine ratio, and oil characteristics [99].

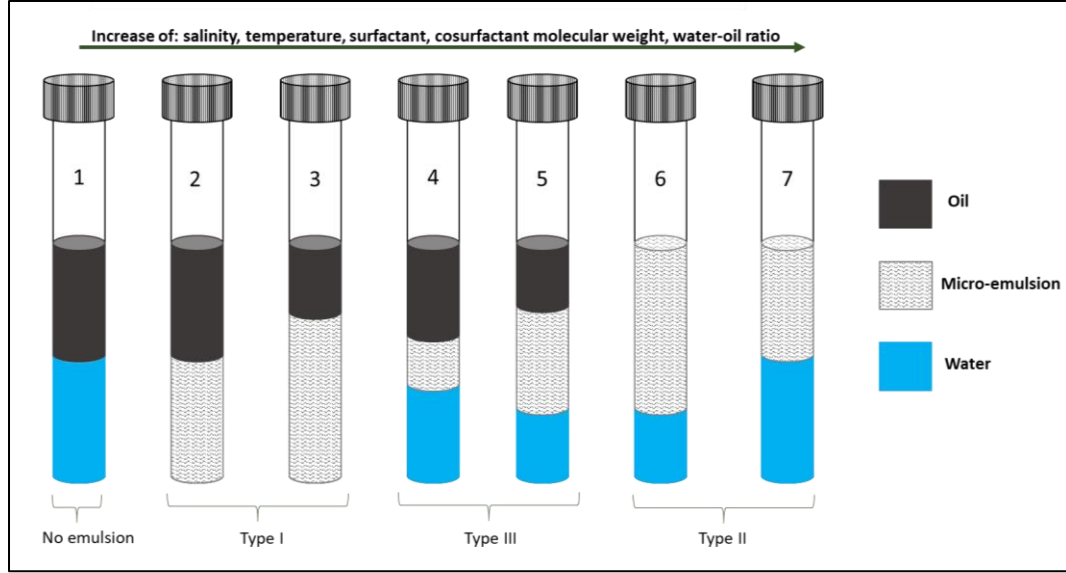


Figure 2-8. Winsor-based classification of microemulsion (modified after Pal et al. [2])

Solubilization Parameters

The solubilization parameters of oil and water (P_o and P_w) are defined as the ratio of the amount of oil (or water) that could be solubilized by surfactant to the volume of the surfactant in the microemulsion phase [100,101]. Mathematically, these ratios are expressed as follows [5]:

$$P_o = \frac{\text{volume of oil in microemulsion } (V_{ome})}{\text{volume of surfactant in microemulsion } (V_{sur})} \quad (2-2)$$

$$P_w = \frac{\text{volume of water in microemulsion } (V_{wme})}{\text{volume of surfactant in microemulsion } (V_{sur})} \quad (2-3)$$

It was reported that ideal microemulsion for oil recovery is produced at the optimum solubilization which occurs when P_o and P_w are equal. This is determined by plotting the solubilization parameters for a given surfactant system versus salinity. The point of intersection of the two parameters corresponds to the optimum salinity (**Figure 2-9**).

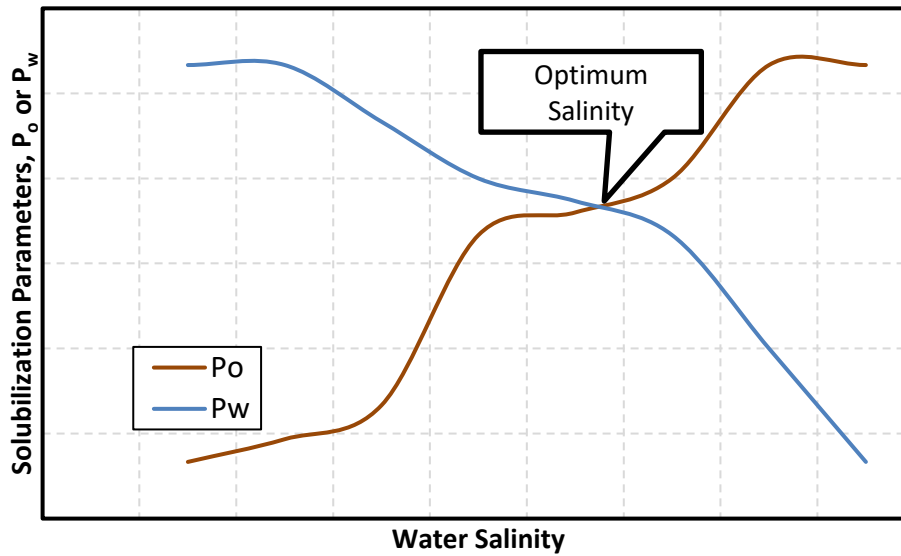


Figure 2-9. Solubilization parameters versus salinity for optimal salinity determination

Optimum Salinity

Generally, salinity significantly affects the performance of surfactants and higher salinity has an opposing effect on the surfactant efficiency. We have seen previously that the optimum salinity corresponds to the salinity at which the oil and water solubilization parameters are equal. This indicates that, at the optimum salinity, the amounts of oil and water solubilized in the microemulsion are equal [39]. The resulting IFTs between microemulsion phase and excess water or excess oil will then be equal at optimum salinity [102]. Research has also shown that the measured IFT at the optimum salinity is the minimum possible IFT value among all the IFT measurements. It was also shown that the maximum oil recovery is achieved at connate water or chemical slug salinity equal to the optimum salinity for the surfactant used [37,103].

2.3 Mobility Control

Polymers are used as enhanced-oil recovery agents in order to decrease the mobility contrast between the displacing and displaced fluids. To illustrate, to avoid the bypass of the displaced fluid and to reduce the fingering effects, the mobility of the displacing fluid needs to be less than or equal to that of the displaced phase [104,105]. The effectiveness of the polymer flooding is quantified by the mobility ratio (M) which is defined as the ratio of the mobility of the injected fluid (usually water) to that of the displaced fluid (mostly oil) [106]. Mathematically,

$$M = \frac{\lambda_{displacing}}{\lambda_{displaced}} = \frac{k_w/\mu_w}{k_o/\mu_o} \quad (2-4)$$

where k_w is the effective permeability to water, μ_w is the viscosity of water, k_o is the effective permeability to oil, and μ_o is the viscosity of oil. For quantitative interpretation of the mobility ratio, a water/oil mobility ratio that greater than unity indicates that the water phase is more mobile than the oil phase and that it will finger through the oil resulting in an early water breakthrough and poor recovery. By contrast, water/oil mobility ratio of less than or equal to unity will indicate a more effective and piston-like displacement of oil by water [107].

Varity of polymers have been investigated for their use in cEOR applications [108–112]. Kamal et al. [113] presented a review of the most commonly used water-soluble polymers for low-temperature and low-salinity (LTLS) EOR applications. His review focused on the rheology, thermal stability, adsorption behavior of different polymers in sandstone and carbonate reservoirs. The list of polymers in the review includes partially hydrolyzed

polyacrylamide (HPAM), hydrophobically modified associating polyacrylamides, novel copolymers of polyacrylamide, cationic polymers, thermo-viscosifying polymers, and different biopolymers. Amongst those, HPAM exhibits good viscofying capability at LTLS conditions. Other copolymers such as acrylamide (AM), Acrylamide and 2-Acrylamido-2-Methylpropane Sulfonic Acid (AM-AMPS), and a cationic polymer of AM-VP are also used as copolymers for HTHS conditions. Thermo-viscofying polymers also exhibit good performance in HTHS conditions. Due to its high water-solubility, HPAM is still the most commonly used polymer in the field although the focus has been shifted towards the application of novel copolymers. The chemical structure of HPAM is illustrated in **Figure 2-10**.

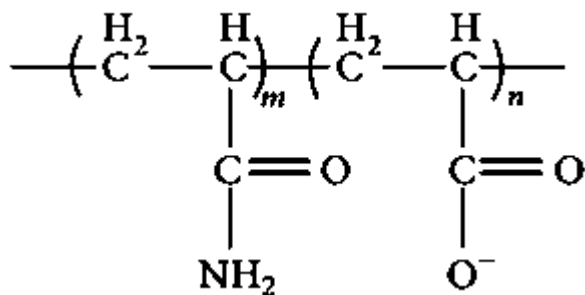


Figure 2-10. Chemical structure of HPAM [114]

2.4 Literature Review

The literature review presented here mostly focuses on surfactant applications for carbonate reservoir. It begins by summarizing the different synthesis of surfactants that can be applied for harsh reservoir conditions. The most recent available studies conducted to evaluate the oil recovery using surfactant flooding in carbonate rocks will then be discussed. Further studies presented to improve the oil recovery by surfactants through the

addition of different other agents like polymers, alkalis, and nanoparticles will also be summarized. Finally, the effect of solution gas on the behavior and performance of surfactant as EOR agent will be presented from previous studies.

2.4.1 Synthesis of Surfactants for Harsh Reservoir Conditions

Harsh reservoir conditions (i.e., high temperature and high salinity) pose many challenges in the design of surfactant due to poor thermal stability and solubility in formation and injection brine. The commercially available surfactants such as alkyl benzyl sulfonate, petroleum sulfonate, and polyoxyethylene ether cannot withstand those conditions. These surfactants are subjected to hydrolysis at elevated temperatures. The presence of reservoir ions at high concentrations also causes the precipitations of these surfactants. Due to their low thermal stability, low solubility in water, and adsorption on reservoir rocks, the selection of surfactants for high-temperature and high-salinity reservoir is a challenging task Kamal et al. [115]. This, therefore, necessitates the need to develop high-performance surfactants that can withstand harsh reservoir conditions. Many attempts have been done to synthesize and tune different kinds of surfactants for their application in such reservoir conditions. The section presents summaries of the available studies attempting to synthesize and/or modify different surfactants for this purpose.

Shakil Hussain et al. [116] synthesized and evaluated two amido-amine-based cationic Gemini surfactants named dodecanoic acid [3-({4-[(3-dodecanoylamino)propyl]-dimethyl-amino]-butyl}-dimethyl-amino)-propyl]-amide dibromide (12-4-12) and dodecanoic acid [3-({6-[(3-dodecanoylamino)-propyl]-dimethyl-amino]-hexyl}-dimethyl-amino)-propyl]-amide dibromide (12-6-12) (**Figure 2-11**). The synthesized surfactants showed high thermal stability with no structural decomposition at elevated temperatures up to 250 °C as

indicated by the thermogravimetric analysis (TGA). NMR and Fourier transform infrared (FTIR) spectroscopy analysis were used to evaluate the long-term thermal stability of the surfactants. Their results showed that the surfactants are thermally stable at 90 °C for 10 days. Measurements of the IFT of the surfactants at varying temperatures up to 80 °C showed that the IFT decreases with increasing the temperature and the length of the spacer.

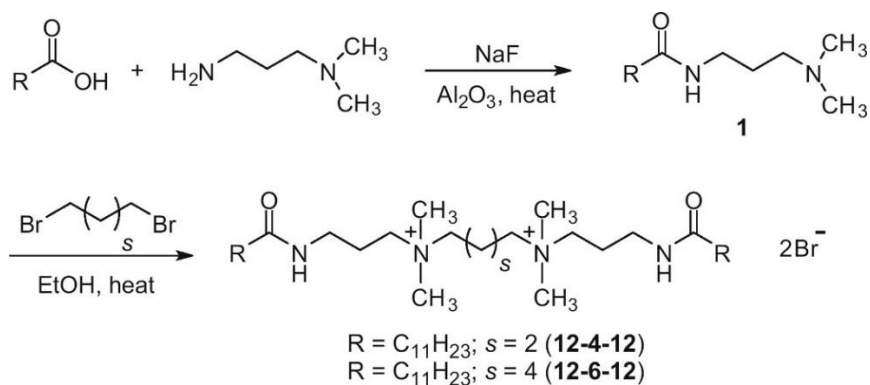


Figure 2-11. Synthesis route of surfactants developed by Shakil Hussain et al. [116]

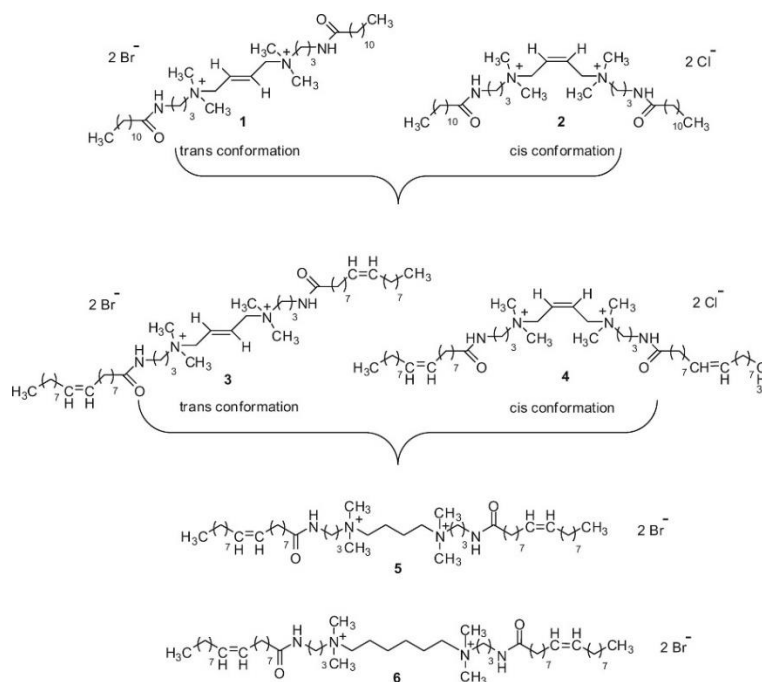


Figure 2-12. Chemical structure of surfactants synthesized by Hussain et al. [117]

Six amido-amine-based cationic Gemini surfactants (**Figure 2-12**) with different hydrophobic tails were synthesized by Hussain et al. [117] from commercially available

carboxylic acids. The newly synthesized surfactants showed short- and long-term thermal stability with no structure degradation and decomposition at temperatures below 200 °C and 90 °C, respectively. It was concluded that this high thermal stability makes these surfactants as attractive candidates for oilfield application.

In order to improve their solubility in water, Hussain et al. [118] modified the chemical structure of sulfobetaine-based zwitterionic surfactants, namely Ethoxylated alkyl amidosulfobetaine, with varying degree of ethoxylation (**Figure 2-13**). They incorporated ethoxy units within the framework of the surfactant. Solubility test using 1 wt% solutions of the surfactants showed good solubility of the modified surfactants in deionized water, formation brine (213,734 ppm), and seawater (57,643 ppm). The surfactants also exhibited excellent heat stability at temperatures up to 280 °C as indicated by thermogravimetric analysis. Their IFT, thermal stability, and rheological behavior were also investigated by Kamal et al. [115]. Both surfactants also showed superior foamability and high-water solubility. These surfactants were also shown to be compatible with the commercial copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid. It was concluded that the varying degree of ethoxylation of the zwitterionic surfactants of betaine type can show distinguishable properties such as tolerance to salinity, high thermal stability, and the remarkable surface properties which make them as good candidate for harsh reservoir conditions.

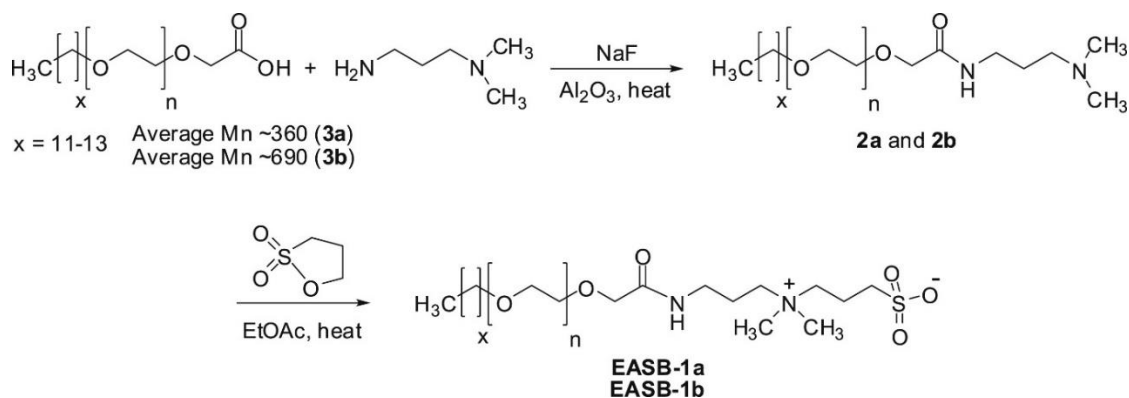


Figure 2-13. Synthesis route of surfactants developed by Hussain et al. [118]

Kamal et al. [51] synthesized two zwitterionic surfactants named 3-(N -stearamidopropyl- N,N -dimethyl ammonium) propanesulfonate and 3-(N -oleamidopropyl- N,N -dimethyl ammonium) propanesulfonate with a saturated and unsaturated tail, respectively (**Figure 2-14**). The evaluation results showed that only the surfactant with the unsaturated tail demonstrated superior solubility in synthetic formation brine and seawater (57,643 ppm and 213,734, respectively) while the one with saturated tail was discarded due to its poor solubility. The unsaturated surfactant was tested for its thermal stability in seawater solution by aging it for 2 weeks at 90 °C. The thermal stability was confirmed by the Fourier-transform infrared spectroscopy (FTIR) and NMR analysis. IFT measurements showed that the unsaturated surfactant could reduce the oil/water IFT to 0.1 mN/m at varying conditions. The addition of the unsaturated surfactant to the acrylamide and 2-acrylamido-2-methylpropane sulfonic acid (AM-AMPS) as copolymer showed an improvement in the oil recovery from 8 to 21% OOIP by the use of the SP mixture. It was concluded that the use of the synthesized unsaturated surfactant with the polymer can be greatly applied in harsh reservoir conditions.

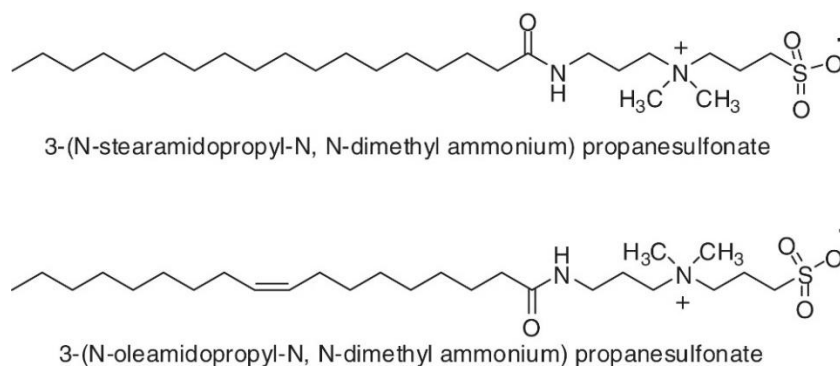


Figure 2-14. Chemical structure of surfactants synthesized by Kamal et al., [51]

Hussain et al. [119] synthesized three betaine-based polyoxyethylene zwitterionic surfactants (**Figure 2-15**). These surfactants have an unsaturated tail with different ionic headgroups, namely: sulfobetaine, carboxybetaine, and hydroxy sulfobetaine. The synthesized surfactants are oleyl polyoxyethylene amidopropyl sulfobetaine (OPAS), oleyl polyoxyethylene amidopropyl hydroxy sulfobetaine (OPAH), and oleyl polyoxyethylene amidopropyl carboxybetaine (OPAC). Solubility tests showed that the synthesized surfactants have good solubility in formation and sea water. Thermogravimetric analysis showed that the surfactants are thermally stable with degradation temperature above 290 °C. These properties make the synthesized surfactants of great interest for their application in challenging reservoir conditions.

Another three betaine-based polyoxyethylene amphoteric surfactants (**Figure 2-16**) were also synthesized by Kamal et al. [120] having three different hydrophilic group (i.e., carboxybetaine, sulfobetaine, and hydroxysulfobetaine) and unsaturated hydrophobic groups. The synthesized surfactants showed high long-term thermal stability for a period

of 3 months as indicated by NMR and Fourier transform infrared (FTIR) spectroscopy analysis with no observed structural changes regardless of the hydrophilic group.

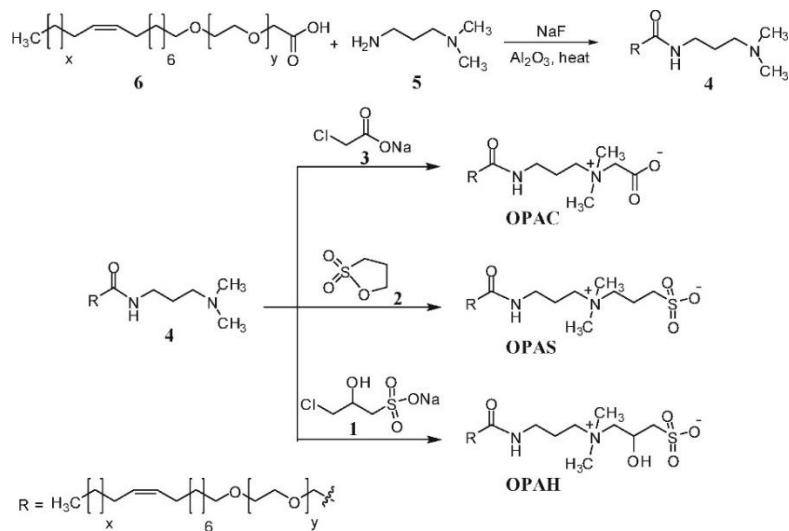


Figure 2-15. Synthesis of betaine-based polyoxyethylene zwitterionic surfactants with different ionic headgroups [119]

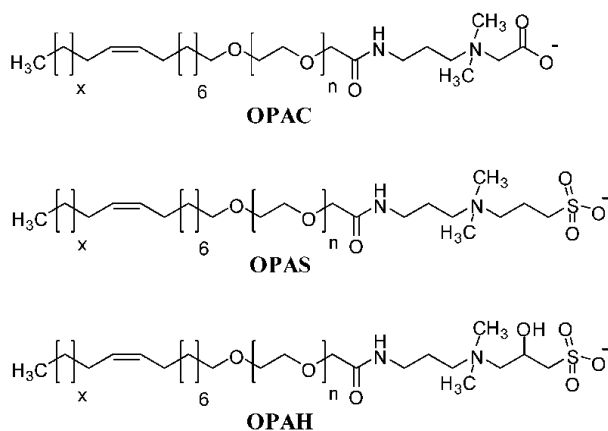


Figure 2-16. Chemical structure of surfactants synthesized by Kamal et al. [120]

Hussain et al. [121] synthesized different quaternary ammonium Gemini surfactants with changed length of spacer group (**Figure 2-17**). These surfactants showed superior solubility in deionized water, seawater, and formation water without precipitation for a period of three months at 90 °C. Thermal gravimetric analysis showed decomposition

temperature of the surfactants high than 227 °C. These surfactants can be of a good choice to be applied in reservoirs of high temperature and high salinity.

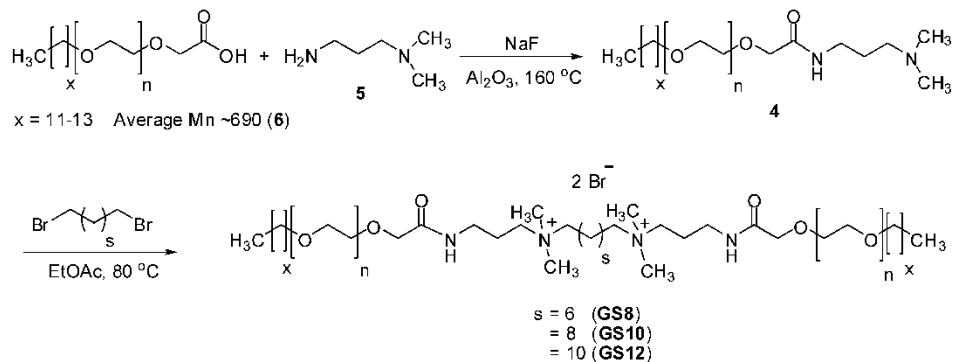


Figure 2-17. Synthesis route of surfactants developed by [121]

Two other zwitterionic surfactants which are sulfobetaine-based polyoxyethylene were also synthesized by Kamal et al. [115] by introducing the ethylene oxide (EO) units into the tail group in order to improve their solubility in formation and seawater. The IFT, thermal stability, and rheological properties of the synthesized surfactants were then investigated at varying temperatures, concentration, and ethoxylation degree. The surfactants showed good solubility in water with varying salinity (i.e., distilled water, seawater, and formation water). The surfactants also showed excellent thermal stability with no structure change by aging at 90 °C. Lower IFT was observed with surfactant with EASB-1a surfactant (surfactant with lesser EO unit) than EASB-1b (with higher EO units). Rheological experiments also showed that the viscosity of acrylamide copolymer was reduced when the surfactants were added with the higher prominent effect with EASB-1a. **Figure 2-18** shows the chemical structure of the studied surfactants and copolymer.

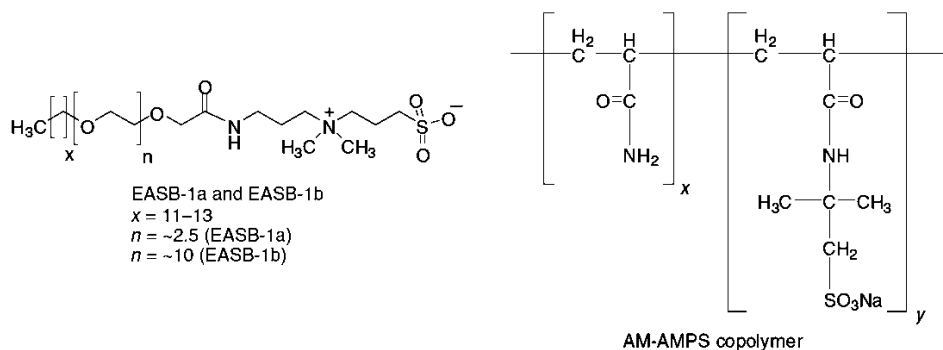


Figure 2-18. Chemical structure of surfactants and copolymer Kamal et al. [115]

Hussain et al. [122] also synthesized six poly(ethylene oxide) zwitterionic surfactants with different hydrophobic tail and ionic headgroups for oilfield applications (**Figure 2-19**). These surfactants showed how solubility in both high- and low-salinity brines caused by the presence of ethoxy units between the amide group and aromatic ring. Aging the surfactant samples for 10 days demonstrated their good long-term thermal stability. Thermogravimetric analysis also revealed no structure decomposition of the surfactants at temperatures below 300 °C. The hydrophilic headgroup was also shown not to significantly influence the CMC and other surface properties compared with the hydrophobic tail with benzene ring.

Deljooei et al. [123] synthesized and tested a surfactant named (S)-2-Dodecanamido-Aminobutanedioic acid from L-Aspartic acid (an amino acid) for its applications in EOR process. The surfactant was tested for its ability in oil/water IFT reduction at different water salinities, wettability alteration, and increasing the oil recovery. Iranian-filed formation water, 40,000-ppm seawater, 31 °API crude oil from Gachsaran oilfield, and sandstone core plugs from Aghajari outcrop formation in southern Iranian oilfields were used in the evaluation experiments. The results showed that there was a reduction in the oil/water IFT to a minimum of around 10 mN/m and there was a shift in the wetting conditions towards

more water-wet state at the CMC (1983 ppm) of the surfactant. The results also showed additional oil recovery of around 11% and 6% OOIP using the new surfactant in the presence of 20,000 and 40,000 ppm salinities, respectively.

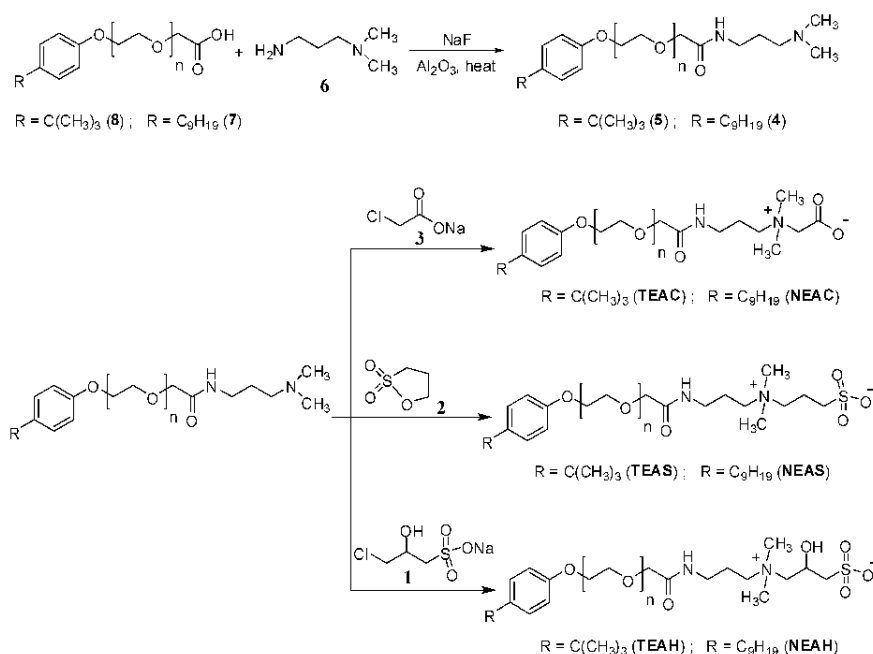


Figure 2-19. Synthesis route of surfactants developed by Hussain et al. [122]

Finally, Abdelhamid et al. [43] prepared five organometallic surfactants (OMS) based on the complexes of Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , and Mn^{2+} ions from which the surfactant were named after (i.e., MOS- Ni^{2+} , MOS- Co^{2+} , MOS- Cu^{2+} , MOS- Fe^{3+} , and MOS- Mn^{2+}). The surface tension of these surfactants was measured in formation water with 18,090 ppm salinity at 25 °C. These measurements showed that the CMCs of these surfactants were in the range from 18.4 to 37 mol/L. The IFT between the surfactant at their CMC and heavy asphaltenic crude oil was also measured at different temperatures (20-70 °C). The results showed that increasing the temperature resulted in a decrease in the oil/surfactant IFT to a range from 0.1 to 0.01 mN/m which makes them of great interest to EOR applications.

2.4.2 Evaluation of Surfactants Oil Recovery in Carbonates

Lu et al. [4] developed a surfactant formulation that can be applied for EOR in challenging carbonate reservoir conditions. The developed formulation consisted of new carboxylate surfactant. The formulation was evaluated through IFT measurements, contact angle measurements, and oil recovery experiments. The material used in the experimental work include high salinity seawater (38,393 ppm), high salinity formation brine (116,969 ppm), extremely vuggy and synthetically-fractured composite carbonate core sample, dead crude oil, and surrogate oil (i.e., 70 wt% dead crude oil and 30 wt% cyclohexane). The formulation showed good aqueous stability and resulted in ultra-low IFT and in hard brine at 100 °C. The surfactant also exhibited low retention at 0.086 mg/g of rock. Static imbibition and dynamic core-flood experiments were conducted under HTHS conditions. These experiments showed oil recovery of around 66% and 33%, respectively. The chemical flood was applied using the favorable salinity gradient [124]. The increased oil recovery was attributed to the reduction in IFT and alteration of rock wettability. However, the flooding experiment was conducted at a high flow rate of 6 ft/D and low injection pressure.

Three commercial surfactants (AN-120, NX-1510, and TR-880) were experimentally evaluated by Najimi et al. [125] for their potential in EOR applications in carbonate rocks. 29-°API crude oil and formation water (TDS: 132,224 ppm) from Sarvestan Iranian oilfield, and synthetic brine of varying salinity were used. The oil/water IFT was measured at different concentrations of these surfactants using distilled water, formation water, and the synthetic brine at 78 °C and atmospheric pressure. The effect of the surfactants on contact angle of carbonate thin sections was also evaluated. The results show that TR-880

is the best in reducing the IFT (**Figure 2-20**) while NX-1510 at 1,000 ppm was the best in altering the rock wettability towards water-wet state. Oil recovery core-flooding experiments were also conducted using carbonate rock samples from Asmari carbonate outcrop resulted demonstrated that 5.5% OOIP could be recovery by injecting of TR-880 at 1,000 ppm at 78 °C.

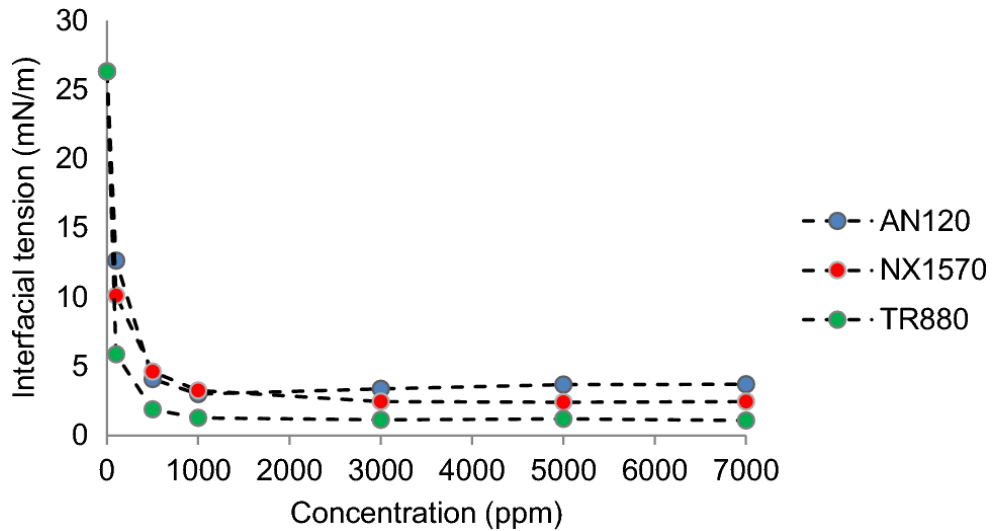


Figure 2-20. Oil/water IFT results obtained by Najimi et al. [125] using formation water and crude oil

Eslahati et al. [126] introduced the alfalfa natural surfactant for EOR applications. The hydrophobic part of the alfalfa saponin consists of triterpenoid or steroid backbone attached to its hydrophilic part, which is composed of numerous saccharide residues, through glycoside bonds. A series of experiments were conducted to evaluate the newly developed surfactant. Materials used include formation water (7,240.4 mmol/L) and seawater (966 mmol/L) respectively from an Iranian oil field and Arabian Gulf, kerosene for IFT and contact angle measurements, crude oil from carbonate Iranian reservoir, and two outcrop carbonate rock samples for imbibition tests. IFT measurements showed that the tested surfactant could result in IFT reduction of around 29 mN/m at its CMC concentration of 4 wt%. This non-ionic natural surfactant could also alter the wettability towards more-water-

wet conditions as indicated by the contact angle measurements. The imbibition testes showed that the used surfactant could advance the oil recovery by around 19% OOIP.

Figure 2-21 shows the molecular structure of saponins of the Alfalfa plant.

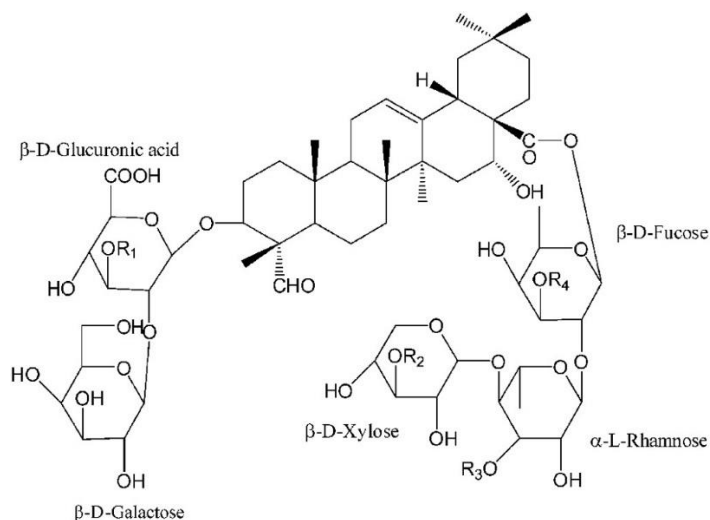


Figure 2-21. Molecular structure of saponins of the Alfalfa plant investigated by Eslahati et al. [126]

Dashtaki et al. [127] experimentally evaluated the extract of Vitagnus (**Figure 2-22**) as a natural surfactant for its use in EOR applications. The materials used include 29 °API crude oil from Sarvestan oilfield in Iran, Arabian Gulf brine, and carbonate rock samples from the Asmari outcrop Formation. IFT measurements at different conditions (i.e., from atmospheric to reservoir conditions of 3,000 psi and 180 °C) showed that the surfactant solution (3000 ppm) resulted in around 82% reduction in the IFT. Measurements of the contact angle of an oil droplet showed a significant alteration of the wetting behavior the rocks towards more water-wet conditions. Oil recovery experiments at 70 °C and 2000 psi showed an incremental oil recovery of around 12% OOIP by using the tested natural surfactant. The also mentioned that this additional oil recovery can also be attributed to other mechanisms including the improved water/oil emulsion and the wettability alteration.

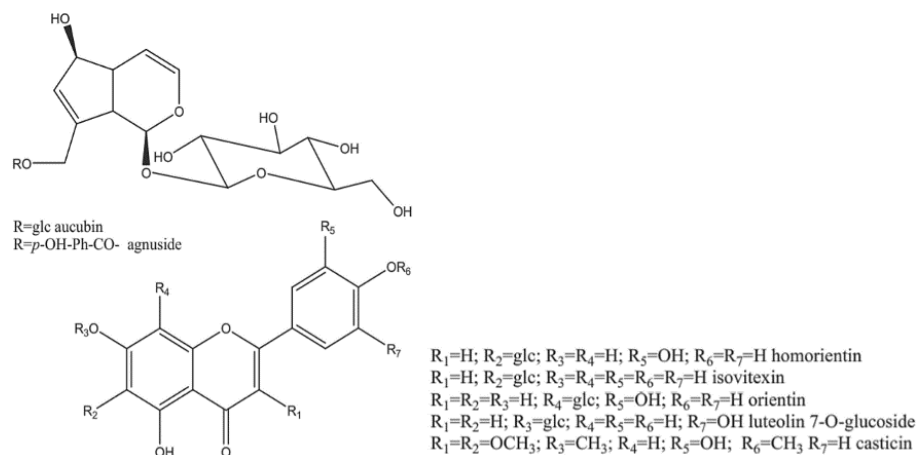


Figure 2-22. Chemical structure of Vitagnus investigated by Dashtaki et al. [127]

The performance of saponin as a non-ionic surfactant was studied by Khayati et al. [128] through IFT measurement, wettability alteration, and core-flooding experiments. The measurements were conducted with a wide range of NaCl salinity (i.e., from 0 ppm to 100,000 ppm). The IFT measurements showed a CMC of the surfactant of 5,000 ppm and the reduction in oil/water IFT was around 67% in salt-free system and around 77.3% in solution with 100,000 ppm NaCl (**Figure 2-23**). The surfactant was also shown to be salt-tolerant at high salt concentration of NaCl. The surfactant also showed a reduction of contact angle in carbonate rock by around 6° to 17° for the tested range of salinity (**Figure 2-24**). Oil recovery coreflooding experiments from carbonate rock sample with surfactant solution containing 30,000 ppm NaCl at the CMC of the surfactant was improved by 6.23% OOIP. The carbonate rock sample used was obtained from the outcrops in south Iran and crude oil was collected from one of the oilfields in southwest Iran.

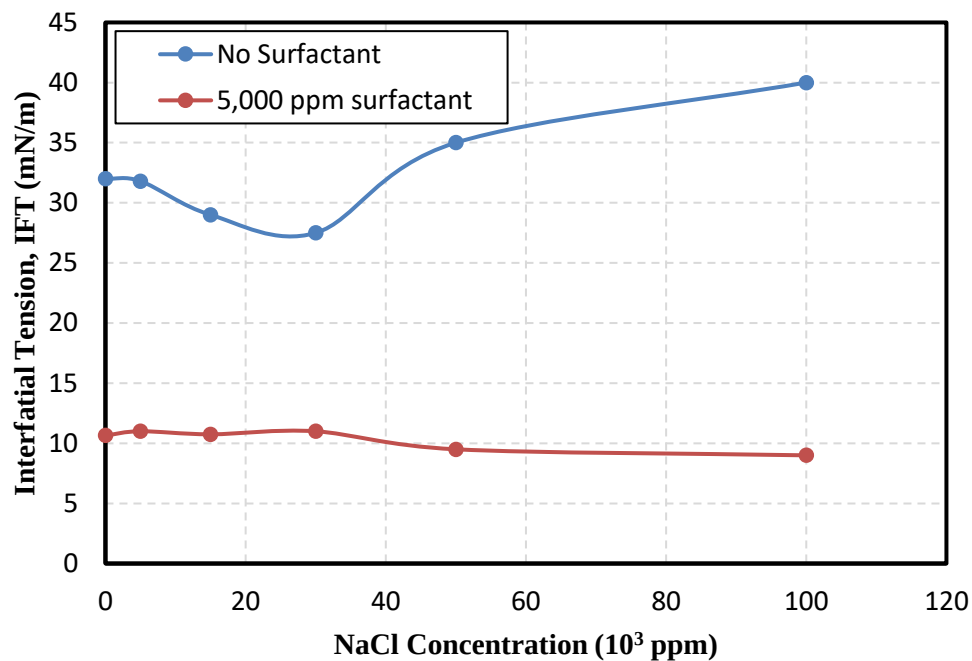


Figure 2-23. IFT versus salt concentration obtained by Khayati et al. [128]

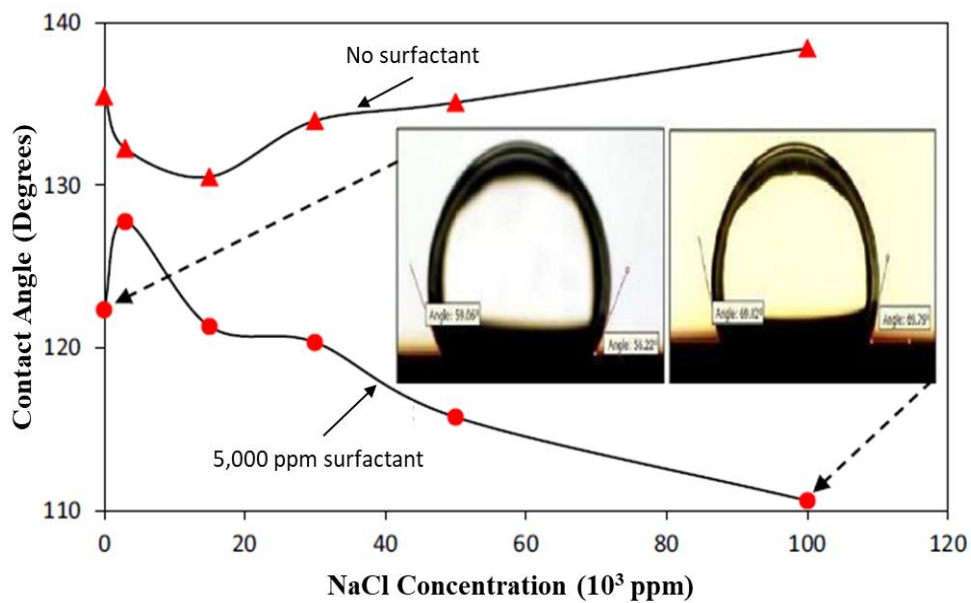


Figure 2-24. Contact angle versus salt concentration on carbonate rock obtained by Khayati et al. [128]

2.4.3 Evaluation of Surfactants/Polymer Oil Recovery

Polymers are added to surfactants to improve their mobility and to avoid the bypass of the fluids towards the production wells. Many studies have been presented to evaluate the effectiveness of SP flooding schemes on the oil recovery.

Malik et al. [129] evaluated two SP systems for their application in EOR through thermal stability, rheology, IFT, and core-flooding experiments at varying salinity, temperatures, and surfactant concentrations. Both SP systems consisted of partially HPAM as the polymer while the surfactants used are the non-ionic polyethylene glycol ether-based surfactant in one system and the anionic alcohol propoxylate sulfate-based surfactant in the other. **Figure 2-25** shows the chemical structures of the used surfactants. Synthetic seawater (57,643 ppm) and formation water (213,700 ppm) were used. Thermal stability test revealed that the non-ionic surfactant was thermally stable at 80 °C while the anionic surfactant showed structural changes after aging. The system with the anionic surfactant was not recommended for HT conditions due to its thermal instability. The core-flooding experiments with SP system containing the non-ionic surfactant showed that this formulation can withstand HTHS conditions as it could result in additional 26% OOIP oil recovery at concentrations of 0.0025 g/g polymer and 0.002 g/g surfactant at 90 °C. The flooding experiments were conducted using Indiana limestone core sample with 3.81 cm diameter and 30.48 cm length.

Al-Amodi et al. [130] also evaluated different SP systems consisting of fluorinated amphoteric (zwitterionic) and fluorinated anionic surfactants (**Figure 2-26**) with partially HPAM for their applications in oil recovery from carbonate reservoirs. The thermal stability, IFT, and adsorption on rock surface were examined. The rheological properties

of the SP were also evaluated at varying surfactant type and concentration, salinity, and temperature. The tested surfactants showed high thermal stability at 90 °C. Anionic-based surfactant resulted in decreasing the viscosity and the storage modulus of the HPAM while the zwitterionic-based surfactant did not show any effect on the rheology of the HPAM. The zwitterionic-based only showed high water-solubility in seawater (57,643 ppm) at 90 °C while the anionic-based surfactant did not. Oil recovery core-flooding experiment at 90 °C using an SP solution with 2,500 ppm HPAM and 0.001 g/g zwitterionic-based surfactant resulted in additional 42% OOIP oil recovery from Indiana limestone core sample with 3.81 cm diameter and 30.48 cm length.

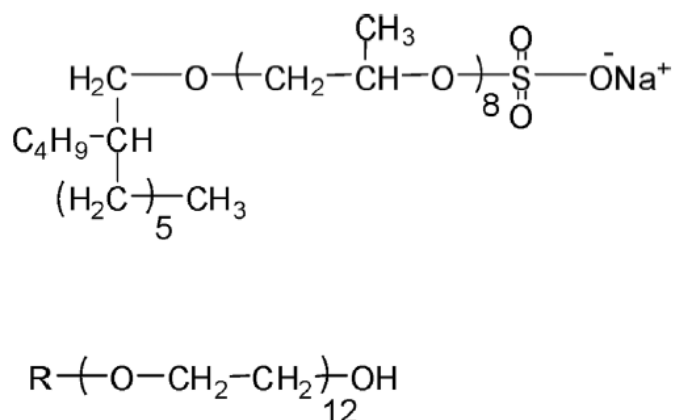


Figure 2-25. Chemical structure of the surfactants investigated by Malik et al. [129]

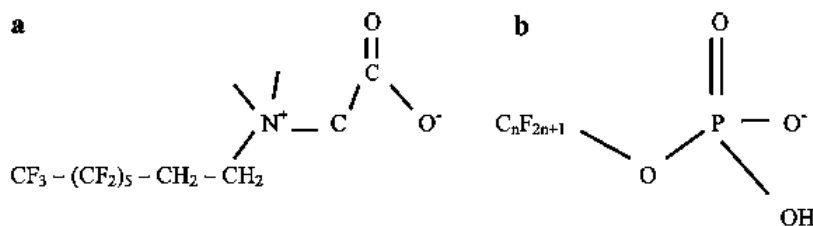


Figure 2-26. Chemical structure of (a) zwitterionic-based and (b) anionic-based surfactants investigated by Al-Amodi et al. [130]

Kurnia et al. [23] investigated the performance of different formulations of binary mixtures of zwitterionic and anionic surfactants for the purpose of developing alkali-free cEOR flood. The screened surfactants are DAO, CHS, AES, AAS, ABS, APS, and TAE. The material used in their study include different selected surfactants, 40 °API crude oil from shale formation in North Dakota, 1% NaCl brine, and HPAM (i.e., 12–18 million Daltons) as polymer. IFT measurements and phase behavior studies respectively showed that the designed formulations could achieve ultralow IFT and that middle-phase (i.e., Winsor Type III) microemulsion could also be formed. Two recovery experiments at 45 °C using Bentheimer sandstone core plugs showed an average of around 34 % OOIP of incremental oil recovery by surfactant floods with different ratios of CHS and APS. To demonstrate the limitations of the screened surfactant formulations, the authors recommended the extension of their investigation to cover higher temperatures, wider range of salinity, and different types of crude oil.

Han et al. [131] developed a surfactant-polymer formulation using commercially available surfactants (i.e., AES, CAS, ABS, and AOS) and HPAM. A series of experiments were conducted to evaluate different surfactant-polymer formulations including IFT measurements, phase behavior, and core-flooding at 45 °C. In addition to the used surfactants and polymer, the material used include Daqing dead crude, synthesized Daqing formation and injection brine, and Berea sandstone cores. The results showed that a formulation of AES/ABS with a mixing ratio of 6/4 demonstrated a remarkable aqueous stability and could result in ultralow IFT between the crude oil and the brine at a brine concentration of 1.25 wt% NaCl. Recovery tests showed that around 30% OOIP of

incremental oil was recovered by surfactant flood using AES/ABS formulation along with HPAM.

Ge et al. [132] conducted a series of laboratory tests to develop a novel alkali-free and salt-tolerant surfactant/polymer flooding system including rheological analysis, IFT measurements, and recovery experiments all at 45 °C. N-phenyloctadecanoidamidopropyl-N, N-dimethylcarboxylbetaine (POAPMB) was used as the surfactant and a biopolymer produced by *Kosakonia oryzae* was used. The materials used include Daqing oil sand, formation brine, and crude oil. The formulated binary surfactant/polymer mixture could reduce the IFT to ultralow values below 0.01 mN/m at surfactant concentration of 500 ppm. Oil recovery experiments showed an incremental oil recovery of around 15% and 16% OOIP with two parallel samples using the designed SP formulation resulted in the improvement of the displacement and sweep efficiency.

2.4.4 Evaluation of Additives with Surfactants for Oil Recovery in Carbonates

Proper formulations of different surfactant mixtures with other additives also can improve the recovery even at harsh environments which cannot be achieved using only one kind of surfactant. Also, effective chemical EOR requires careful formulation of the utilized surfactant slug [23].

Al-Hashim et al. [133] presented a study evaluating the applicability of ASP EOR method in Saudi carbonate reservoirs. The tested surfactants were Triton X-102 and Ethoxylated sulfonate (Dodi flood B1083) and FLOCON 4800C was used as the polymer. Dead Arab-D crude oil, synthetic seawater (57,670 ppm), and synthetic softened brine (66,971 ppm)

were used in all the experiments. Screening tests of the slugs showed that B1083 surfactant was of good choice for harsh conditions in Saudi Arabian reservoirs. The addition of NaHCO_3 and Na_2CO_3 alkalis resulted in reducing the adsorption of B1083 on carbonate rock to less than 1 wt%. The conducted core-flooding experiments on Arab-D carbonate rock samples demonstrated the effectiveness of the designed ASP formulation in enhancing the oil recovery from carbonate Saudi reservoirs. The flooding experiments were carried out at 99 °C with ASP consisting of 0.5% B1083 surfactant, 500 ppm polymer, and 1% NaHCO_3 and Na_2CO_3 (1:1 ratio) prepared using the softened brine.

Omidi et al. [134] investigated the use of synthetic Fe_3O_4 /eggshell nanocomposite (NC) in improving the performance of cetyltrimethylammonium bromide (CTAB) and TR-880 surfactants (**Figure 27**) in EOR applications. Their work also used crude oil from Iranian oilfield, 3% brine, carbonate core samples from Asmari outcrop. The experimental results showed that the IFT and the contact angle were decreased from 29.1 mN/m and 136° to 0.18 mN/m and 60.7°, respectively, by the use of a hybrid chemical solution of NC and surfactants. Oil recovery improvement by around 8% OOIP was also achieved by using the hybrid solution with 500 ppm and 1,000 ppm NC and CTAB, respectively, at 65 °C.

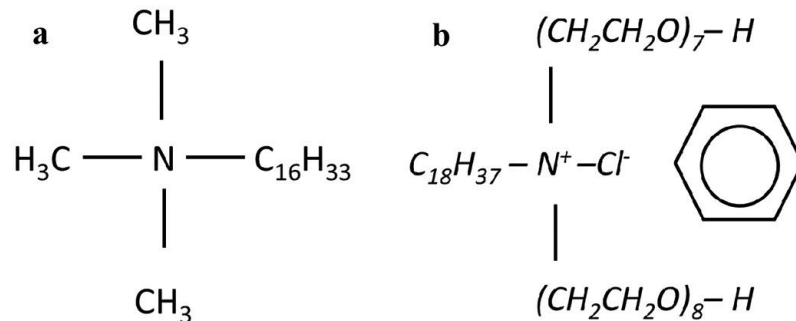


Figure 2-27. Chemical structure (a) CTAB and (b) TR-880 investigated by Omidi et al. [134]

Rezaei et al. [135] investigated the use of integrated solutions of surfactants, alkali, and nano-fluid flooding for EOR applications. The investigated surfactants include two anionic commercial surfactants, namely sodium dodecylbenzene sulfonate (SDBS) and linear alkylbenzene sulfonic acid (LASA), and two amphoteric coconut di-ethanol amide (CDEA) and cocamido propyl betaine (CAPB) surfactants. The tested alkalis are the sodium carbonate (Na_2CO_3) and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) while silica (SiO_2), zinc oxide (ZnO), and nanoclay cloisite 30B were used as nanoparticles. Synthetic formation water (SFW) (198,000 ppm NaCl), synthetic seawater (SSW) (5,000 ppm NaCl), crude oil, and outcrop carbonate rocks from Iranian fields were used in the displacement experiments. Their experiments showed that blends of CAPB and Na_2CO_3 and CAPB and silica SiO_2 are of good choice for core-flooding experiments at their optimum concentrations under ambient conditions. Adsorption tests also showed that using Na_2CO_3 or SiO_2 could reduce the adsorption of CAPB on dolomite rocks by around 60% and 36%, respectively. Imbibition tests of blends of CAPB (0.025 wt%) with Na_2CO_3 (0.1 wt%) or SiO_2 (0.1 wt%) resulted in additional 18% and 15% oil recovery for both solutions, respectively. Core-flooding experiments with both blends also showed around 20% and 12% additional oil recovery compared with SFW flood.

2.4.5 Influence of Design Parameters on Oil Recovery

To achieve its best recovery, the design of surfactant flooding process needs to consider several parameters including the type chemicals used alongside, the concentration of the chemicals, slug size, and others. This section provides a summary of some of the available studies conducted to experimentally evaluate some of those parameters.

Khan et al. [136] conducted different core-flooding experiments to evaluate the additional oil recovery obtained from the use of an ASP slug followed by polymer and chase water. The ASP slug composed of 0.1 wt% sodium dodecyl sulfate (SDS), 0.075 wt% sodium dodecylbenzene sulfonate (SDBS), 2,000 ppm polyacrylamide, and 0.7 wt% sodium hydroxide (NaOH). The slug was designed based on the analyses of viscosity and surface tension data obtained by the authors on different formulations of the slug constituents. Different core samples collected from Sanand oil field-Mesana block of Cambay basin in India were used and diesel oil and brine were used for the oil and displacing fluid, respectively. The results showed an additional oil recovery of more than 20% of the original oil in place compared with conventional waterflooding. However, the flooding experiments were conducted at room temperature.

Samanta et al. [137] carried out a series of core-flooding experiments to evaluate the effectiveness of surfactant and surfactant-polymer slugs in increasing oil recovery. The flooding runs were conducted using laboratory sand packs that was packed in a core holder with a length and diameter of 35 cm and 7 cm, respectively. Sodium Dodecyl Sulfate (SDS) was used as surfactant and partially HPAM was used as polymer. 1.0 wt% brine and crude oil were used in their work. It was concluded from their experimental results that polymer-surfactant slug resulted in higher recoveries than in the case of injecting the same pore volume of surfactant slug alone. This was attributed to the reduction in the mobility ratio caused by the augmentation of surfactant by polymer. However, the flooding experiments were conducted at room temperature.

Felix et al. [138] carried out a comparative study through core-flooding experiments to investigate different flooding schemes that can be implemented in polymer-surfactant

flooding. The first scheme involved injecting a slug of Sodium Dodecyl Sulfate followed by a slug of gum Arabic slug. The second scheme, involved injecting a mixture of Dodecyl Sulfate and gum Arabic slug and the last scheme involved soaking the core with Sodium Dodecyl Sulfate followed by a slug of gum Arabic slug. All the schemes were applied after water-flood. The results showed that the first scheme resulted in the least oil recovery while the highest recovery was obtained with the second scheme. They concluded that implementing SP flooding require a special care in selecting the scheme of injection due to the great influence of the injection scheme on the oil recovery. The experiments however were conducted using packed glass beads at room temperature.

Ahmed [139] in his MS thesis evaluated the effectiveness of using Thermo-viscosifying Polymer (TVP) and the copolymer Acrylamido Tertiary Butyl Sulfonate (ATBS)/acrylamide (AM) with different grades of amphoteric carboxybetain surfactants (SS-880 and SS-885) as EOR agents in carbonate rocks. Synthetic FW (229,870 ppm), synthetic SW (57,612 ppm), medium crude oil (24.6 °API), outcrop carbonate rock samples from Riyadh, and Indiana core samples were used. Several core-flooding experiments were conducted at 90 °C to investigate the effect of chemical formulations, slug size, and injection sequence on oil recovery. The results showed that injecting 3.5PV of slug consisting of 0.25 wt% ATBS/AM and 0.05 wt% SS-880 resulted in the highest oil recovery of around 12% OOIP. Using this formulation, the results also showed that the highest oil recovery was attained using the SW-SP-SW flooding scheme compared to other schemes like SW-P-S-SW, SW-S-SW-P-SW, or SW-P-SW-S-SW. This recovery was attributed to the advantageous synergies between the chemicals.

Husein et al. [140] carried out several core-flooding experiments to determine the best injection scheme for the ASP flooding. In their work three injection patterns were investigated: continuous ASP, flooding, alternating ASP with water-flooding, and tapering water to ASP ratio. The material used include a 120-cm long sandstone core sample, paraffin oil, 15,000-ppm brine representing the Central Malay Basin, Hydrolysed Polyacrylamide as the polymer, Sodium Hydroxide as the alkali, and Sodium Dodecyl Sulphate as the surfactant. The effectiveness of these flooding schemes was evaluated by the ultimate oil recovery at the end of the cycle. Their results showed that the higher recovery was achieved with the ASP alternating with water, followed by tapered water to ASP ratio while the least recovery was with the continuous ASP flooding. They suggested that the ASP alternating with water-flooding should be followed for field applications due to its best performance and high oil recovery. However, their study did not consider the flooding under reservoir conditions such as the pressure, temperature, and initial water saturations.

Haghighi and Firozjahi [141] investigated the use of combined surfactant-smart water-flooding in oil recovery from carbonate rock. The non-ionic surfactant dodecanoylglucosamine and smart water with concentration of 43,091 ppm were combined and applied for the recovery experiments. The flooding experiments were conducted using carbonate rock plugs obtained from Asmari formation and the crude oil was collected from Ahwaz oilfield in Iran. The oil recovery experiments using water, surfactant, and combined surfactant-smart water were 36, 52, and 66% OOIP, respectively. These results demonstrate the effectiveness of the combination of surfactant with smart water in improving the oil recovery in carbonate reservoirs.

2.4.6 Effect of Solution Gas on Surfactant Flooding

Most of the research performed to evaluate surfactant flooding has been conducted using dead (degassed) crude oil due to the simplicity of the experimental procedures. However, in the real hydrocarbon reservoirs, substantial amounts of natural gas mixtures are dissolved in the crude oil making it what is so-called live oil. The chemical compositions of dead crude oil are different from reservoir oil which contains naturally occurring gases like methane, ethane, and other similar gases. Many studies have shown that the presence of dissolved gas and its composition significantly affect the phase behavior of surfactant/brine/oil system. A recent study by Marliere and Creton [24] showed that increasing the GOR of recombined crude oil reduced the optimal salinity. It also showed that the optimal salinity of a recombined crude oil with dissolved gas containing methane, ethane, and propane is much less than that containing methane alone. However, although Nelson [142] stated that there is no significant difference in the oil recovery efficiency when using dead or live crude oil, he still recommends conducting core-flooding experiments using live crude oil when designing for surfactant flooding. The literature review conducted by Southwick et al. [143] revealed that all crude oils do not behave similarly when tested with methane with respect to surfactant solubility. Therefore, they recommended conducting separate experiments on the target crude oil before making any decision. Core-flooding experiments conducted by Southwick et al. [143] using both dead and crude oil showed that the difference between the recovery when using live and dead crude oil make it of great consideration in designing chemical floods. This is because applying chemical flood that is designed based on dead oil to the field conditions would be over optimum and underperforming.

To account for the effect of gas in surfactant flooding, and due to the difficulties encountered when working and handling the live crude oil, surrogate oil having an equivalent alkane carbon number (EACN) approximately equal to that of the live crude oil can be used. The concept of EACN was proposed by Cayias et al. [144] and it is the weighted-average of the alkane carbon number (CAN_i) of the each pure component i in the oil based on its mole fraction (x_i). Mathematically,

$$EACN_{oil} = \sum_i ACN_i x_i \quad (2-5)$$

Knowing the EACN of the live oil, the surrogate oil can be prepared by mixing the dead crude oil with low-EACN hydrocarbons such as toluene, cyclohexane, or decalin to match live oil and account for the effect of dissolved gas. EACN for live oil can be estimated from the dead oil EACN, solution gas-oil-ratio (GOR), and the composition of the solution gas. For dead oil, the EACN can be determined experimentally through salinity scans of surfactant formulation using different mixtures of the dead crude oil and lighter hydrocarbon with known EACN [145]. Based on the concept of the EACN, the phase behavior (e.g., minimum IFT and optimum salinity) of a system consisting of surrogate oil, brine, and surfactant should be similar to that of a system with live crude oil, brine, and surfactants. However, due to the complexity accurately identifying the composition of crude oil, Equation (2.5) is not applicable for crude oil systems [26].

Several authors used surrogate oil in their experiments based on the concept of EACN. For example, Fortenberry [146] in his thesis used surrogate oil consisting of almost 87 wt% crude oil and 13 wt% decalin for recovery and phase behavior experiments. Lu et al. [4] also used surrogate oil consisting of 70 wt% dead crude oil and 30 wt% cyclohexane to

match the live oil EACN for their recovery experiments. In their IFT and phase behavior tests, Han et al. [131] also used surrogate oil prepared by mixing 73 wt% dead crude oil from Daqing oilfield with 27 wt% jet fuel. However, the investigation of Jang et al. [147] found the optimum salinity of surrogate oil samples was different from that of the dead crude oil or the live crude oil although the solubilization ratios of surrogate oil were close to that of live oil.

2.5 Research Gap

It can be concluded from the previous literature review that, although there are many studies that have addressed the recovery performance of different surfactants, no studies have addressed the oil displacement efficiency by Gemini surfactants, specifically in carbonate reservoirs. Consequently, significant efforts have been devoted to synthesize or develop surfactants tailored for application in such harsh conditions. One successful endeavor has been the in-house development of a series of ethoxylated quaternary ammonium cationic Gemini surfactants, specifically engineered for use in high salinity and high-temperature carbonate reservoirs. These surfactants have undergone extensive evaluation, which has consistently demonstrated their superior performance under the tested conditions. However, despite their promising characteristics, the oil recovery performance of these surfactants has not been evaluated. This research aims to address this gap by investigating the oil recovery performance of a member of these surfactants (GS8), thereby fulfilling a critical objective in the field of enhanced oil recovery.

CHAPTER 3

ENHANCED OIL RECOVERY IN CARBONATE RESERVOIRS USING SINGLE COMPONENT SYNTHESIZED SURFACTANTS UNDER HARSH RESERVOIR CONDITIONS

Abstract

Surfactants are commonly used for enhanced oil recovery (EOR) applications in carbonate hydrocarbon reservoirs due to their ability to reduce oil/water interfacial tension and/or alter rock wettability towards more water-wet conditions. They are usually used as formulations consisting of more than two surfactants to achieve optimum performance. Although this approach may result in extra recovery in coreflooding experiments, there is a risk of chromatographic separation and potential phase separation when these surfactants are injected into the reservoir. The current study, however, focuses on injecting a single component ethoxylated quaternary ammonium cationic Gemini surfactant (GS) or a betaine-type zwitterionic surfactant (ZIS), both synthesized in-house, to mitigate these potential issues. Several coreflooding experiments were conducted using Indiana limestone samples at 100 °C, pressures greater than 3,000 psi, and seawater and formation water salinities of 57,745 ppm and 213,768, respectively. Continuous injection of either

surfactant solution (at 2,500 ppm in seawater), after seawater flooding recovered almost 11-12% of the initial oil in the core (OOIP). The results demonstrate that the GS or the ZIS alone can achieve this relatively high oil recovery without the need for additional cosolvent(s) or cosurfactant(s), unlike most of the previously developed surfactant formulations. Injecting a one-pore-volume slug of a standard acrylamide copolymer at 2,000 ppm between the seawater and the surfactant floods increased the oil recovery by either surfactant to around 16-17% OOIP. This improvement in oil recovery was mainly due to wettability alteration from oil-wet to intermediate-wet conditions, as revealed by the contact angle and oil/water IFT measurements. Effluent analysis of the produced aqueous phase showed surfactant dynamic retention values of 0.44 and 0.61 mg/g-rock of both the GS and the ZIS, respectively. Such high oil recovery and low dynamic retention reflect the high efficiency of the GS and the ZIS for EOR applications in carbonate reservoirs.

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3.1 Introduction

Enhanced oil recovery (EOR) methods are mostly applied as a tertiary process after the primary and secondary recovery processes. They are primarily applied to extract the trapped oil from the depleted mature fields by altering the interactions of the rock/fluid or fluid/fluid in the subsurface hydrocarbon reservoirs [148–150]. The end goal of EOR is to increase oil recovery which is achieved by boosting oil displacement efficiencies on both the micro and macro scales. Chemical flooding (cEOR) is one of the EOR methods and involves injecting different chemicals into the reservoir. The injection of surfactants, alkali, polymers, or any combination of them are all examples of cEOR process [151]. Surfactant

flooding is among the effective cEOR techniques that are widely applied to modify the wettability of the rocks by shifting it from oil-wet state to water-wet conditions and/or lower the oil/water interfacial tension (IFT), which are very crucial for the oil recovery [152–154]. The IFT, for example, is the capillary number's controlling factor, which is directly related to oil saturation. To illustrate, reducing the oil/water IFT to values around 10^{-3} or 10^{-2} mN/m can result in capillary number values of around to values of around 10^{-6} or 10^{-4} which correspond to residual oil saturations of less than 10% [155,156]. Shifting the rock wettability to water wet from initially oil-wetting state is another important mechanism in improving oil recovery [157]. Alteration of rock wettability from oil-wet or intermediate-wet states towards water-wet conditions results in substantial improvement in oil recovery [153,158,159]. However, the performance of surfactants is highly affected by many factors including salinity, pH, surfactant structure, temperature, and rock lithology [160]. Therefore, careful screening of surfactants for EOR applications is very important for successful utilization [161].

EOR application in carbonate reservoirs has been given considerable attention since they hold more than 50% world's proven reserves [162–164]. Oil output from carbonate formations in the Middle East account for nearly half of the world's daily production [165]. However, compared with sandstone reservoirs, the oil recovery from carbonate ones is relatively low due to the nature of these reservoirs. To illustrate, carbonate reservoirs mostly operating under challenging conditions of high temperature and high salinity (HTHS) (i.e., temperature > 85 °C and water salinity $> 100,000$ ppm) [166,167]. In addition, carbonate reservoirs are very heterogeneous due to the presence of natural fractures, vugs, and faults which affect the sweep efficiency [168–170]. Furthermore, the wettability of

these reservoirs varies from oil-wet to mixed-wet conditions [166,171,172]. As a result, the applications of EOR in these reservoirs is of great challenge.

In the literature, numerous studies have been carried out to investigate the applicability and effectiveness of various surfactant/chemical formulations in carbonate reservoirs [155,170,173–178]. However, limited studies focus on using single component surfactants for oil recovery applications. Additionally, a few works are available on the applications of cationic Gemini and zwitterionic surfactants for oil recovery [179–181]. These two classes of surfactants are of great interest to the oil industry due to their superior characteristics including their high thermal stability, high solubility in saline brines, low critical micelle concentrations (CMC), rheological properties, and ability to lower the oil/water IFT [182–188]. Several attempts have been conducted to synthesize and evaluate different cationic Gemini and zwitterionic surfactants to withstand the HTHS conditions of hydrocarbon reservoirs [189–192].

This work evaluates the oil recovery performance of a single component in-house synthesized ethoxylated quaternary ammonium cationic Gemini (GS) and an in-house synthesized betaine-type zwitterionic surfactants (ZIS) from carbonate rock samples under HTHS conditions. Coreflooding experiments were conducted by injecting either surfactant solution at 2,500 ppm following a seawater flood. In other experiments, one PV of polymer solution at 2,000 ppm was injected after the seawater flood followed by continuous injection of the GS or the ZIS solutions. The workflow also involved contact angle (CA) and oil/water IFT measurement along with effluent analysis. The results reflect the efficiency of the evaluated GS and ZIS for EOR applications in HTHS carbonate reservoirs as single components, without the need of an alkaline or a cosurfactant.

3.2 Experimental Work

3.2.1 Materials

Rock Samples. A total of five coreflooding experiments were carried out using five individual Indiana limestone rock samples. X-ray diffraction (XRD) analysis on a powder sample from this rock indicated that it is mostly calcite. Since this is a comparative study, a limited variation in rocks' porosity and permeability is required. Hence, Indiana limestone is selected owing to its relative homogeneity on the core scale. The properties of these samples are listed in **Table 1-3**.

Table 3-1: Properties of rock samples used in this work

Sample	Length (cm)	Diameter (cm)	He-gas Porosity (%)	Brine permeability (mD)
IL-16	30.48	3.792	18.34	117.5
IL-21	30.48	3.752	15.61	116.9
IL-23	30.48	3.785	16.36	118.0
IL-03	30.48	3.752	18.05	113.8
IL-18	30.48	3.785	17.74	110.3

Salts and Brines. High-salinity brine (SW) was prepared for waterflooding and chemical injection experiments. It mimics Arabian Gulf water whose salinity is around 57,745 ppm [193]. Another brine (FW) was also synthesized with a composition similar to typical formation water found in the Jurassic Arab formation of the Middle East, which has a salinity of about 214,000 ppm. The compositions of the simulated SW and FW brines are shown in **Table 3-2**. The prepared brines were filtered using filter paper to remove any undissolved solids. The synthesized SW and FW were prepared by dissolving different laboratory-grade salts provided by Sigma Aldrich in DIW. **Table 3-3** presents the

viscosities and densities of the FW, SW, and prepared surfactant solutions at room conditions.

Table 3-2: Compositions of prepared formation and seawater brines used in this work

Salts	Concentration (ppm)	
	SW	FW
NaHCO ₃	165	487
Na ₂ SO ₄	6,339	517
NaCl	41,172	150,419
CaCl ₂	1,802	52,788
MgCl ₂	8,266	9,555
TDS →	57,745	213,768

Table 3-3: Physical properties of fluids in this study

Fluid	Density (g/cc) @ 21.5 °C	Viscosity (cP) @ 21.5 °C
Seawater	1.0406	1.1243
Formation Water	1.0412	2.0028
GS (2,500 ppm)	1.0417	1.1745
ZIS (2,500 ppm)	1.0410	1.1450
SF (2,500)	1.0409	1.1941
Crude Oil	0.8743	17.3

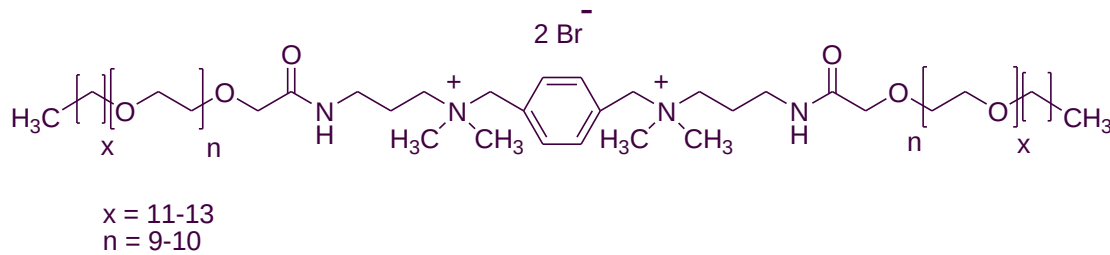
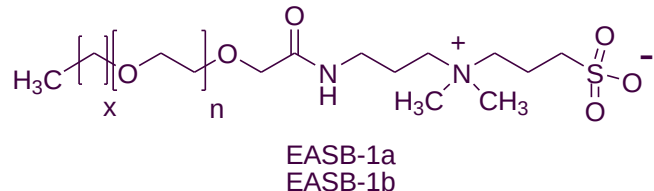
Crude Oil. Stock tank crude oil (i.e., degassed crude oil) collected from a carbonate reservoir in the Middle East was used to saturate the rock samples as well as for contact angle (CA) measurements. The oil was filtered using a 5- μ m, in-line filter to remove any fine particles or residues that could result in flow blockage. The density and viscosity of crude oil at room temperature are also listed in **Table 3-2**, with crude oil viscosity of 2.482 cP at 100 °C and 3000 psi.

Chemicals. The in-house-synthesized surfactants used in this work were an ethoxylated, quaternary ammonium, cationic Gemini surfactant (GS)[194] and a betaine-type zwitterionic surfactant (ZIS)[183]. The synthesis and physiochemical evaluation of these surfactants are described elsewhere. The structures of these surfactants are shown in **Table 3-4**. The results obtained from the applications of these surfactants was compared with a surfactant formulation (SF) similar to that reported by Abalkhail et al. [173]. This formulation consists of C₂₈ Guerbet alcohol (C₂₈-35PO-65EO-COONa) carboxylated at the University of Texas at Austin, C₁₅-C₁₈ internal olefin sulfonates (IOS) provided by Shell Chemical Company, and carboxyl betaine provided by Oil Chem Technologies. AM-ATBS as a standard copolymer of acrylamide, commercially known as Flopaam AN132SH, was also used as a mobility buffer in this work and was supplied by SNF FLOERGER in a powder form. All the chemical solutions were prepared in the synthesized SW.

Surfactants Screening & Selection. It is worth mentioning that the Gemini and zwitterionic surfactants used in this work have undergone a thorough and extensive evaluation and screening process following the criteria presented by Kamal et al. [161]. The screening process included testing their thermal stability under harsh reservoir conditions, compatibility with high-salinity water, phase behavior, wettability alteration, IFT measurements, and static and dynamic adsorption experiments. These surfactants showed strong compatibility with both FW and SW with no precipitations after aging for long period at elevated temperatures. The interested reader may refer to the previously published articles for more details [183,194–203]. Although these surfactants have shown low CMC values of less than 100 ppm, low concentrations in the flooding process may

lead to ineffective performance while high concentrations may result in higher costs. The concentration of 2500 ppm was selected based on the initial screening experiments. Compared to literature-reported surfactant concentrations, this concentration is still moderate and cost effective since no other cosolvent nor other cosurfactant is required to aid the performance the surfactants used in this work.

Table 3-4: Chemical structure of in-house synthesized surfactants evaluated in this study

Surfactant	Structure
GS	 $x = 11-13$ $n = 9-10$
ZIS	 EASB-1a EASB-1b

3.2.2 Rock/Fluid Parameters

To explore the effect of the targeted surfactants on rock wettability, oil-brine static CA measurements were conducted on substrates of Indiana rock samples before and after treatment in each surfactant solution. The substrates were cut from Indiana rock samples having the same composition as that of the rocks used in the coreflooding test, but with lesser porosity and permeability for better and more accurate measurements. They were oil-aged at 100 °C for almost three weeks. CA measurements were repeated after soaking the rock samples in a 2,500-ppm-solution of each surfactant for four days at laboratory conditions. All CA measurements were conducted at ambient conditions using Attension

Theta Optical Tensiometer provided by Biolin Scientific. Following the modified method described by Deng et al. [204], the J-shaped method was used where the surrounding phase is the denser phase (water in this case) and the droplet formed by injecting the lighter phase (oil in this case). The contact angle is then measured relative to the lighter phase. Hence, the resulting droplet is for oil and the CA values are related to the oil phase, not for water phase. The IFT measurements were also conducted between the crude oil and each surfactant solution utilizing a spinning drop tensiometer made by Krüss of Germany. A thorough evaluation of the wettability alteration capability and the IFT measurements of the in-house-synthesized cationic Gemini and zwitterionic surfactants have been presented in the literature [195–197].

3.2.3 Coreflooding Experiments

Apparatus. A schematic of the core-flooding system is shown in **Figure 3-1**. It consists of a Hastelloy core holder, a dual injection pump, confining and back-pressure pumps, a back-pressure regulator, a heating bath, and fluids' accumulators. More details on the flooding setup can be found elsewhere [205].

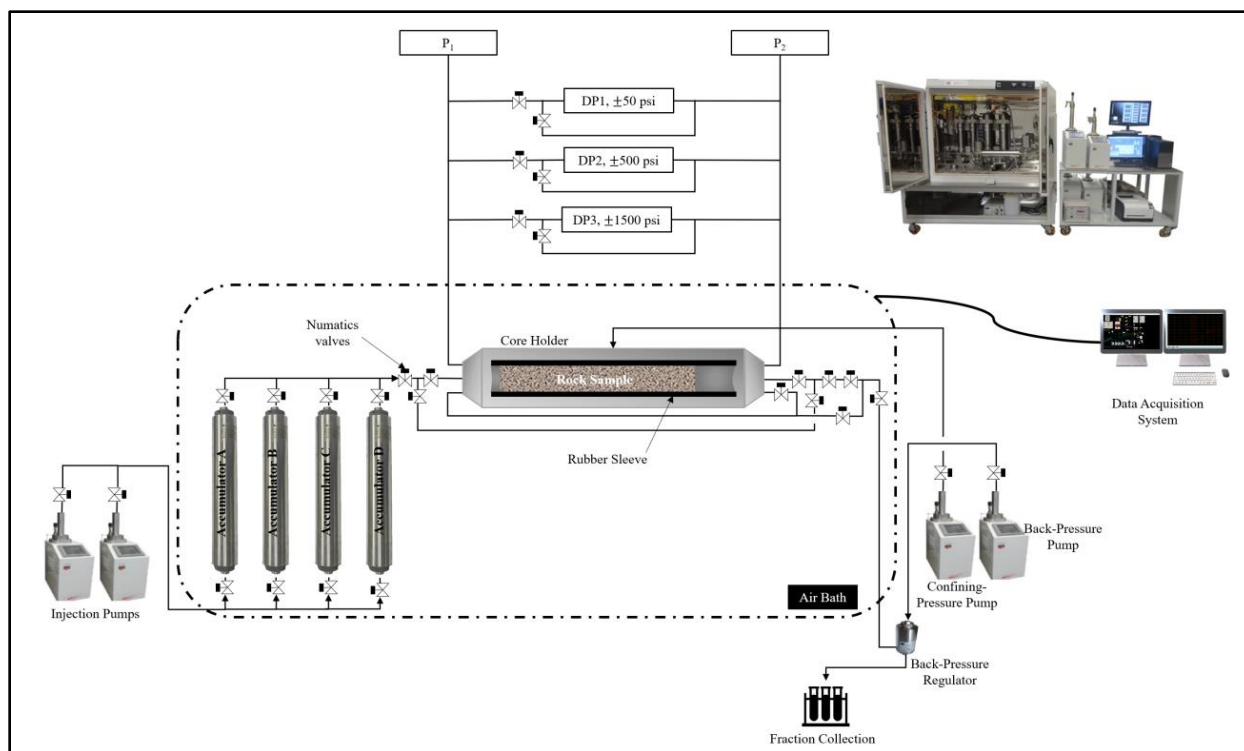


Figure 3-1. Schematic of the coreflooding system

Preparation of rock samples. Each rock sample was vacuum-saturated with the prepared formation brine after which their liquid permeabilities were measured. To establish the irreducible water saturation (S_{wi}), several pore volumes (PVs) of crude oil were injected continuously into each core sample in a drainage process at variable flow rates. This drainage process resulted in initial water saturations ranging from 32 to 35% in all rock samples confirming their homogeneous nature. Such relatively high initial saturations can be attributed to microporosity in the cores that is characteristic of many carbonate rocks [206,207]. The samples were then aged for three weeks (~21 days) under static conditions by immersion in the crude oil and kept at 100 °C. The aging enhances adsorption of the crude's polar components onto the rock surface, which is responsible for shifting the rock wettability towards more oil-wet conditions [207].

Oil recovery tests. Each oil-aged sample was heated to 100 °C and flooded under confining and pore pressures of 4,000 and 3,000 psi, respectively. A flooding test started by injecting one to two PVs of the crude oil at 1 cc/min followed by SW injection until oil production virtually ceased (oil cut < 2%), which took four to five PVs of SW. Thereafter, chemical flooding ensued, which involved five to six PVs of a surfactant solution until oil production ceased. In two chemical floods one PV of the polymer solution preceded the surfactant solution. Both the SW flooding and the subsequent chemical floods were injected 0.25 cc/min, which is corresponding to field injection flux of 1 ft/day. It should be mentioned that the total pore volumes of injected fluids were a compromise between experimental time and sufficient oil recovery. The effluent was collected in 15-ml glass vials every 20 minutes. Some oil was produced as an emulsion, which was broken by either adding a known volume of toluene or by heating it to 70-90 °C [208]. A summary of the flooding experiments conducted is presented in **Table 3-5**.

Table 3-5. Summary of coreflooding experiments conducted in this study

Experiment No.	Rock Sample	Flooding Steps	Injection rate (cc/min)
1	IL-21	1. SW 2. GS at 2,500 ppm	0.25
2	IL-23	1. SW 2. ZIS at 2,500 ppm	0.25
3	IL-16	1. SW 2. SF at 2,500 ppm	0.25
4	IL-03	1. SW 2. One PV of AN132SH at 2,000 ppm 3. GS at 2,500 ppm	0.25
5	IL-18	1. SW 2. One PV of AN132SH at 2,000 ppm 3. ZIS at 2,500 ppm	0.25

Relative permeability. Using the relative permeability (rel-perm) curves can also provide a qualitative indication of the modification of rock's wettability during the surfactant flooding process [152]. In the literature, several methods have been employed to calculate the rel-perm curves from unsteady-state flooding experiments, including the simple Corey model [208,209], Toth et al. method [174,210], or the industry standard Johnson–Bossler–Neumann (JBN) method [175,211,212], which is used in this work. The JBN method requires the pressure drop across the sample (ΔP), the cumulative oil production (N_p), the cumulative injected water volume (W_i) expressed in terms of injected pore volumes (Q_i) given by:

$$Q_i = \frac{W_i}{V_p} \quad (3-1)$$

The average water saturation (S_{wa}) in the core during the flooding experiment is calculated from the cumulative oil production:

$$S_{wa} = S_w + \frac{N_p}{V_p} \quad (3-2)$$

The oil fractional flow (f_{o2}) and the water saturation (S_{w2}) at the outlet of the core sample are given by Eq. 3-3 and Eq. 3-4, respectively.

$$f_{o2} = \frac{dS_{wa}}{dQ_i} \quad (3-3)$$

$$S_{w2} = S_{wa} - f_{o2}Q_i \quad (3-4)$$

The relative injectivity, I_r , is used to calculate the individual relative permeabilities and can be obtained according to Eq. 3-5.

$$I_r = \frac{\left(\frac{q}{\Delta P}\right)}{\left(\frac{q}{\Delta P}\right)_i} \quad (3-5)$$

where the subscript i denotes the initial condition used to calculate the relative permeability.

The relative permeability to oil (k_{ro}) and the relative permeability to water (k_{rw}) are then calculated by Eqs. 3-6 and 3-7, respectively.

$$k_{ro} = f_{o2} \frac{d\left(\frac{1}{Q_i}\right)}{d\left(\frac{1}{Q_{ir}}\right)} \quad (3-6)$$

$$k_{rw} = \frac{1-f_{o2}}{f_{o2}} \frac{\mu_w}{\mu_o} k_{ro} \quad (3-7)$$

As the above equations indicate, the JBN method is based on graphical analysis and involves some non-linear regression, which could cause considerable inaccuracy.

3.2.4 Effluent Analysis

Surfactant retention by the core sample was also evaluated by analyzing the coreflood effluent. Several evaluation methods are available in the literature, including potentiometric high-performance liquid chromatography (HPLC) [173,201,213–215], Hyamine titration [216], and UV–visible spectroscopy [217] among others. In this work, an Agilent 1200 series HPLC was used with acetonitrile (C_2H_3N) as the mobile phase A. A solution consisting of 15.8 g of ammonium formate (NH_4COOH) dissolved in 2500 ml of deionized water with its pH adjusted to 4.3 by the addition of 2 ml of formic acid (CH_2O_2) into the solution was used as mobile phase B. The HPLC uses an acclaim surfactant plus column (3 μm , 4.6 $\times$ 150 mm). The concentrations of the surfactants in collection vials were determined from the calibration curves, which were constructed for each surfactant solution by plotting the chromatographic integral area and the surfactant concentration [215]. It should be noted that experiments involving a polymer flood were

not analyzed to avoid any damage to the HPLC column due to high polymer's viscosity. The dynamic retention of surfactants was then calculated using Eq. 3-8, which is based on simple material balance [199]:

$$\Gamma_{dynamic} = \frac{C^0 V - \sum_{i=1}^N C_i V_i}{m_r} \quad (3-8)$$

where $\Gamma_{dynamic}$ is the surfactant dynamic retention (mg/g-rock), C^0 (ppm) is the concentration of injected surfactant, V (L) is the total volume of injected surfactant solution, C_i (ppm) is the concentration of the surfactant solution collected at time period i , V_i (L) is the volume of the collected effluent at time i , N is the number of collection vials, and m_r (g) is the mass of the dry core sample.

3.3 Results & Discussions

3.3.1 Contact Angle Measurements

Figure 3-2 presents the CA measurements, where the images to the left show the initial CA after aging the samples in crude oil for three weeks. Measured within the oil phase, the average CAs of the three aged samples ranged between 26° and 33°, indicating strong oil-wet conditions. Fig 2.b shows the CA of the rock after soaking it in the GS solution. The average angle was around 65° indicating nearly 40° increase in the CA from the initial state. Although the rock was still oil wet, the change in CA is significant and a longer soaking period could have resulted in more wettability alteration. This can be attributed to the large surfactant molecule, which may require a longer time to diffuse into the oil phase. Fig 2.d shows the effect of the ZIS solution. The average angle was around 75° indicating some 41° change in the CA from the initial state, thus shifting the rock surface to

intermediate-wet. The average contact angle with the SF surfactant was around 45° (SF Fig 2.f) indicating a shift of 12° only. Such a low change in the CA reveals the weak effect of this surfactant on rock wettability.

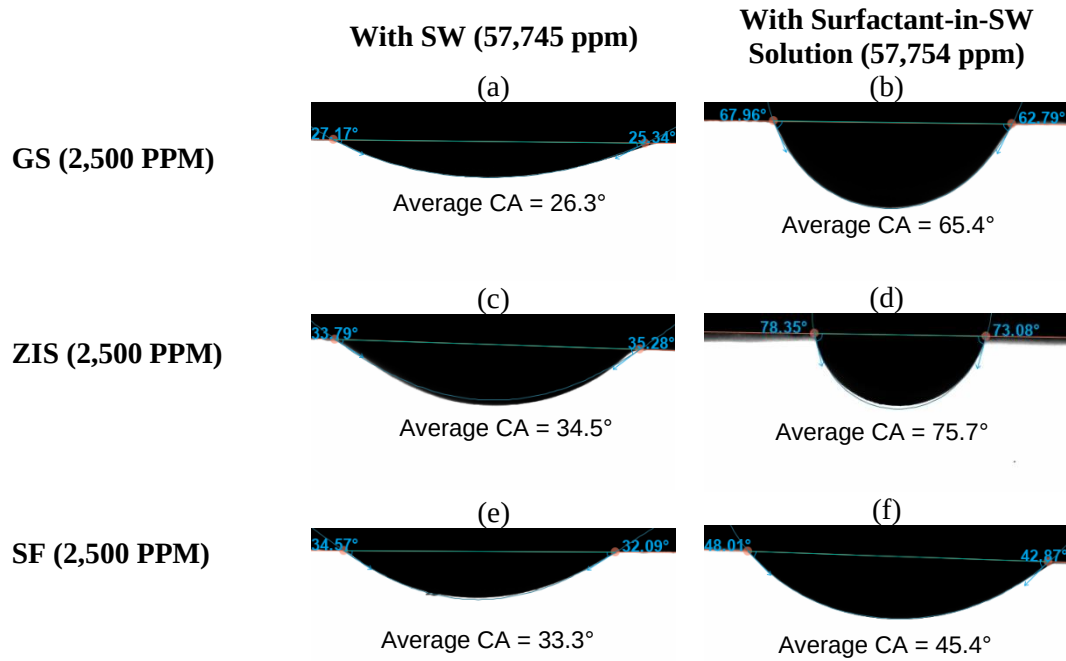


Figure 3-2. Contact angle of oil droplet on the surface of oil-aged Indiana limestone rock disk against brine (left) and against surfactant solutions with indicated concentrations (right)

3.3.2 IFT Measurements

Figure 3-3 shows the oil/surfactant IFT vs temperature measured in three different surfactant solutions: GS, ZIS, and SF, all at 2,500 ppm. The results show that the GS and the ZIS solutions reduced the oil/water IFT to less than 1.0 mN/m with SF reducing it below 0.1 mN/m. This shows that the efficiency of the SF is apparently due to its IFT reduction power more than its wettability alteration.

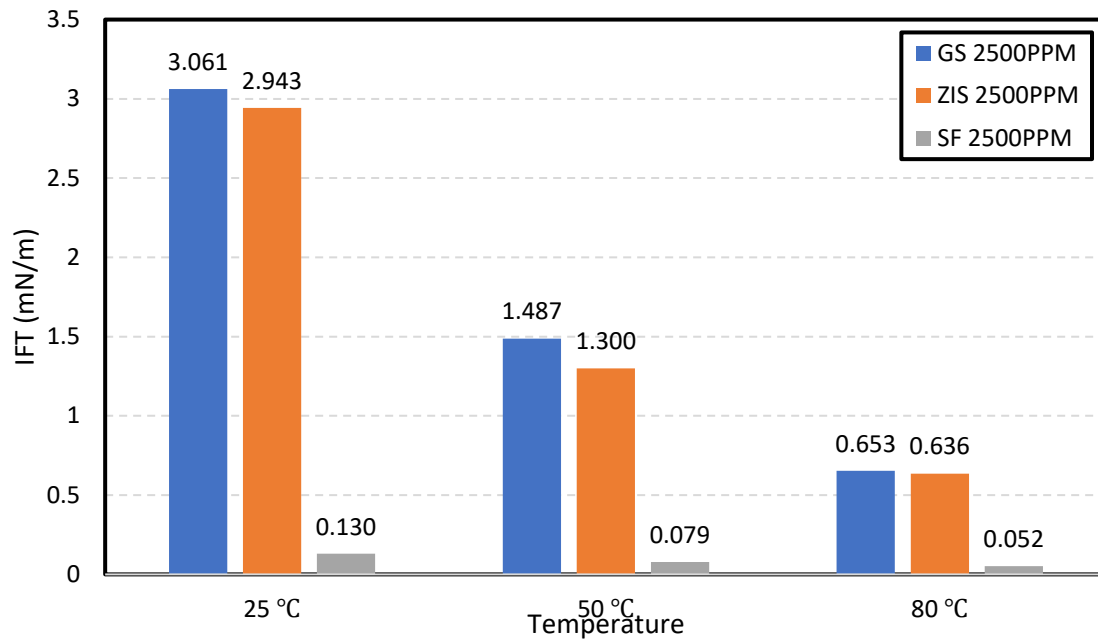


Figure 3-3. Results of oil/surfactant IFT measurements at different temperatures

3.3.3 Oil Recovery Results

Seawater flooding. Figures 3-4 through 3-8 show the oil recovery plots vs PVs injected for the five flooding experiments. The ultimate oil recovery from the SW floods ranged between 54.3 and 56.9% OOIP. Such a narrow range indicates the homogeneity of the rock samples in terms of pore structure, porosity, permeability, and initial water saturations. Water breakthrough in all experiments occurred at between 0.15 and 0.19 PVs injected.

Chemical performance. Figure 3-4 shows the performance of the GS along with the average oil saturation vs the number of PVs injected. It can be observed that it took around 1.5 PV of surfactant injection before oil production resumed (i.e., the plateau from 4 to 5.5 PV). This is attributed to the time it took the oil bank to form and break through, which in turn depends on the time needed for the GS to alter the rock wettability. Moreover, this could be explained by examining the large and complicated molecular structure of the GS, which requires longer time for the GS to diffuse into and interact with the residual crude

oil in place, and hence a delayed oil recovery. The injected GS solution (about 6 PVs) resulted in an additional oil recovery of around 12% OOIP, raising the ultimate oil recovery to around 67.9% at the end of the flooding process. The chemical flood reduced the residual oil saturation to 20%.

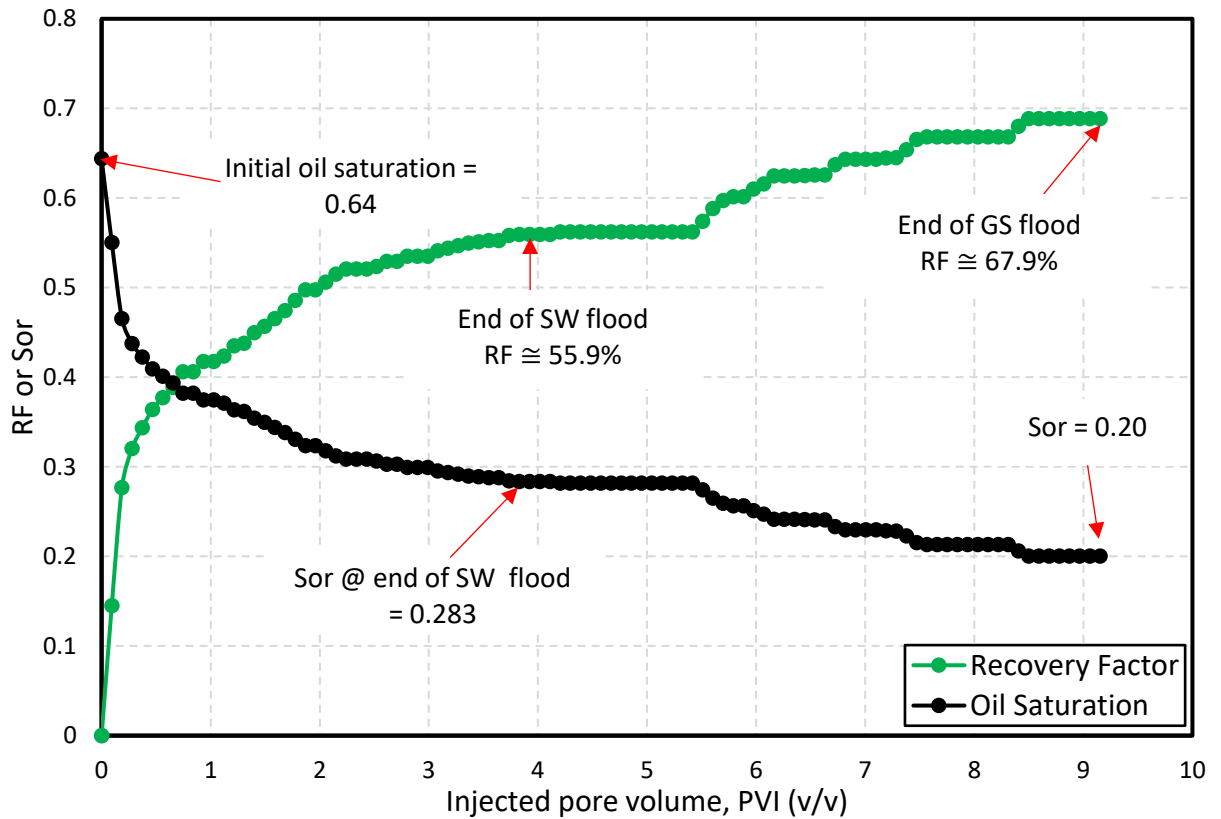


Figure 3-4. Oil recovery results for GS coreflood (Exp. 1)

The ZIS surfactant produced nearly identical results (**Figure 3-5**) except for the oil production response, which took one third of the time. This can be attributed to the larger increase in the contact angle, which caused the oil bank to form faster. As for the SF, even though the CA increase with this surfactant was much smaller, the larger IF reduction resulted in a similar oil production response as the ZIS surfactant (**Figure 3-6**). The results of those three experiments demonstrate the effectiveness and efficiency of the in-house synthesized GS and ZIS surfactants in comparison to the SF, which was developed for the

same purpose and gave almost the same oil recovery. Both GS and ZIS outperform SF in that they do not require cosolvent, alkaline, or cosurfactant to effect incremental oil recoveries as SF does.

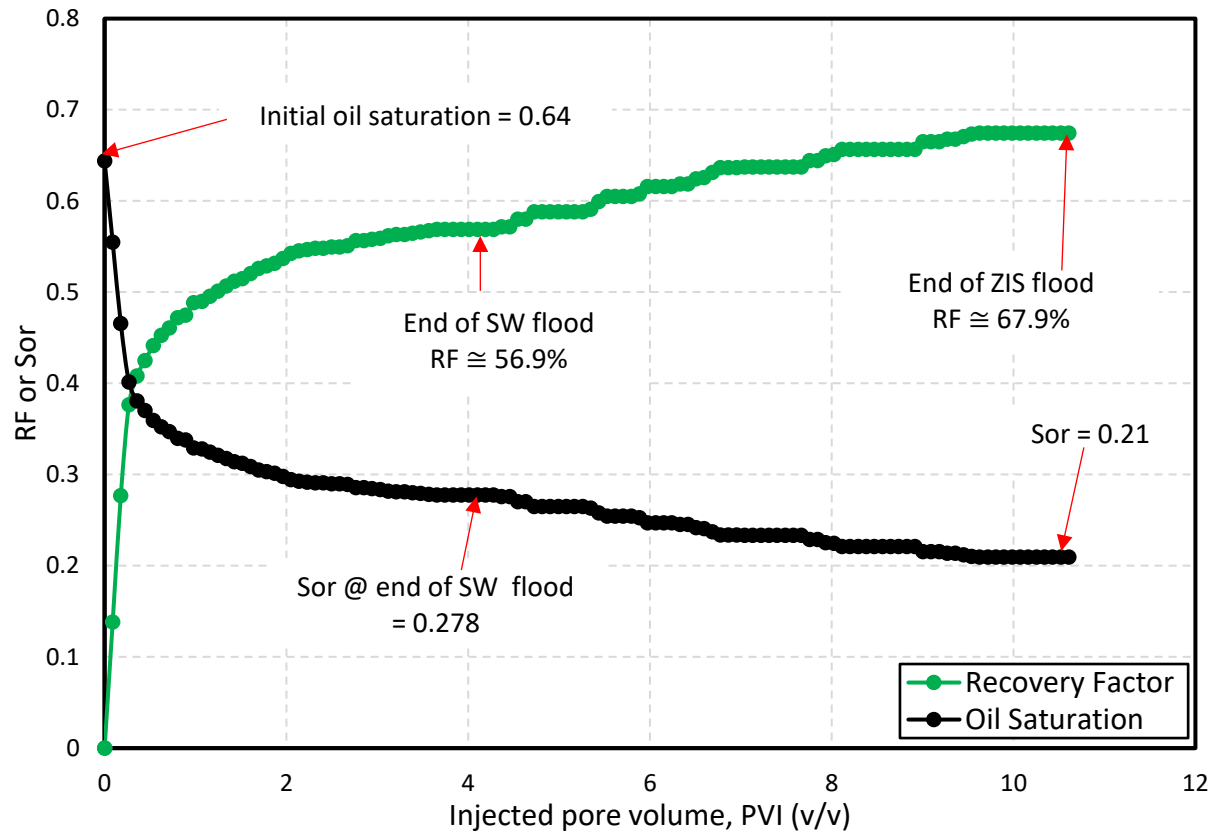


Figure 3-5. Oil recovery results for ZIS coreflood (Exp. 2)

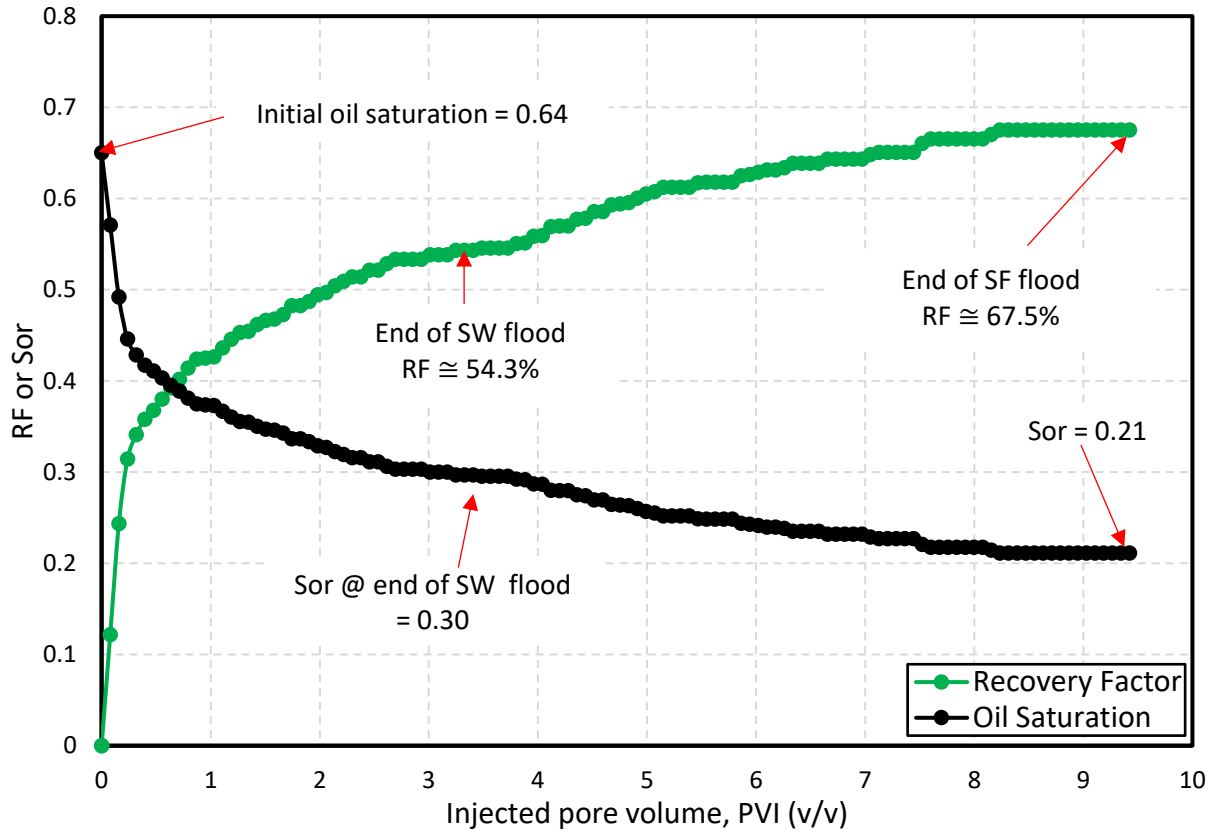


Figure 3-6. Oil recovery results for SF coreflood (Exp. 3)

Figures 3-7 and 3-8 show the oil recovery performance by the polymer/surfactant flooding scheme along with the average oil saturation for Experiments 4 and 5, respectively. It can be observed that injecting around one PV of the polymer solution resulted in an incremental oil recovery of around 5-6% OOIP for both experiments. The GS and ZIS flooding phases clearly demonstrate the improvement in the displacement efficiency of both surfactant solutions. The post-polymer oil recovery by GS and ZIS was around 16.7 and 15.1% OOIP, respectively, raising the ultimate oil recovery factors to around 77.3 and 77.9% OOIP. The increased surfactant efficiency and oil production can be attributed to improved flood conformance promoted by the polymer, which enabled the surfactant to contact the microscopic and macroscopic residual oil. The increase in oil recovery by the injected

polymer slug is caused by the shift in the fractional-flow curve (**Figure 3-9**) given by Eq. 9 for linear flow in horizontal systems [218]:

$$f_w = \frac{1}{1 + \frac{k_{ro}}{k_{rw}} \frac{\mu_w}{\mu_o}} \quad (3-9)$$

where f_w is the water fractional flow, k_{ro} and k_{rw} are the oil and water relative permeabilities, respectively, and μ_w and μ_o are the viscosities of water and oil, respectively. This shift translates into an increase in the average water saturation in the polymer-flooded part of the rock.

The same behavior described in Exp. 1 regarding the contact time it took the GS solution to mobilize the remaining oil is observed in the polymer flood too. That is, it required around one PV of surfactant solution to effect additional oil recovery (the plateau from 4.5 to 5.5 PV in Figure 7). The residual oil saturations at the end of the chemical flooding in Exps. 4 and 5 were around 14% and 15%, respectively.

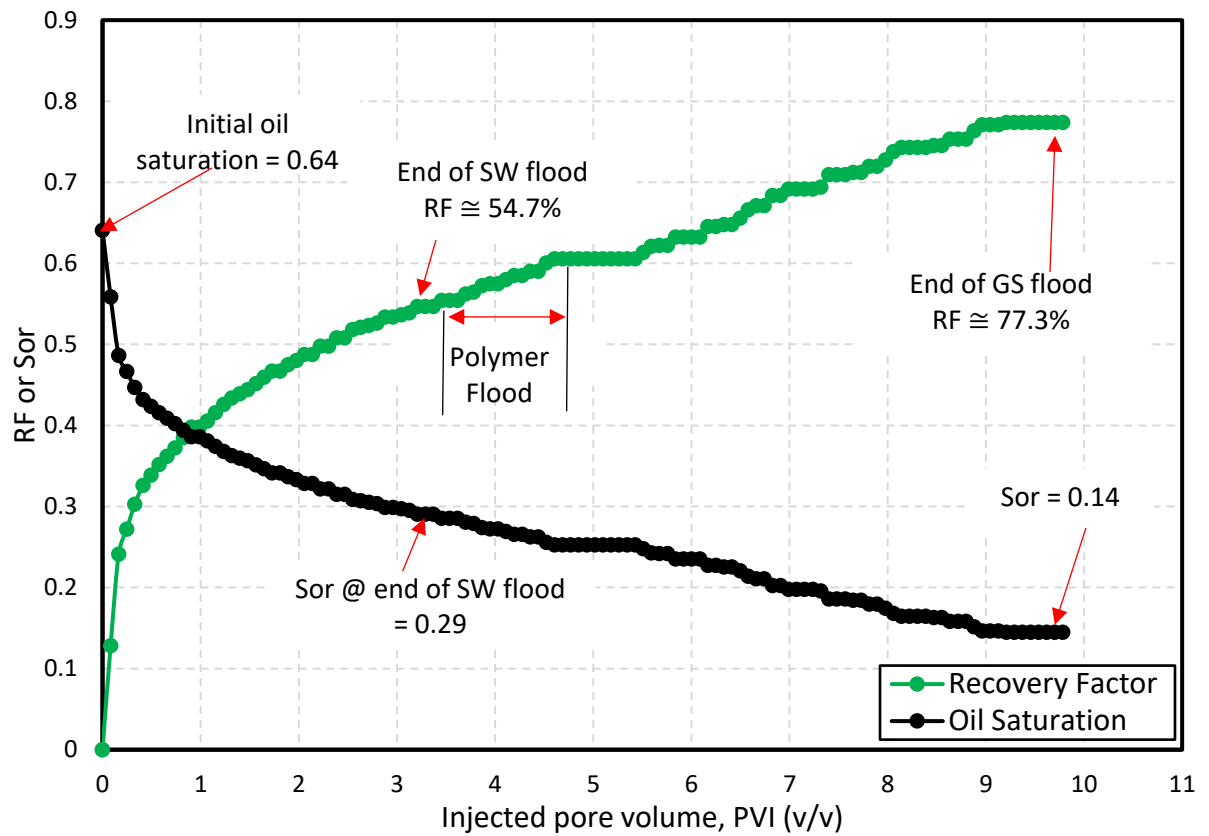


Figure 3-7. Oil recovery results of coreflooding experiment # 4

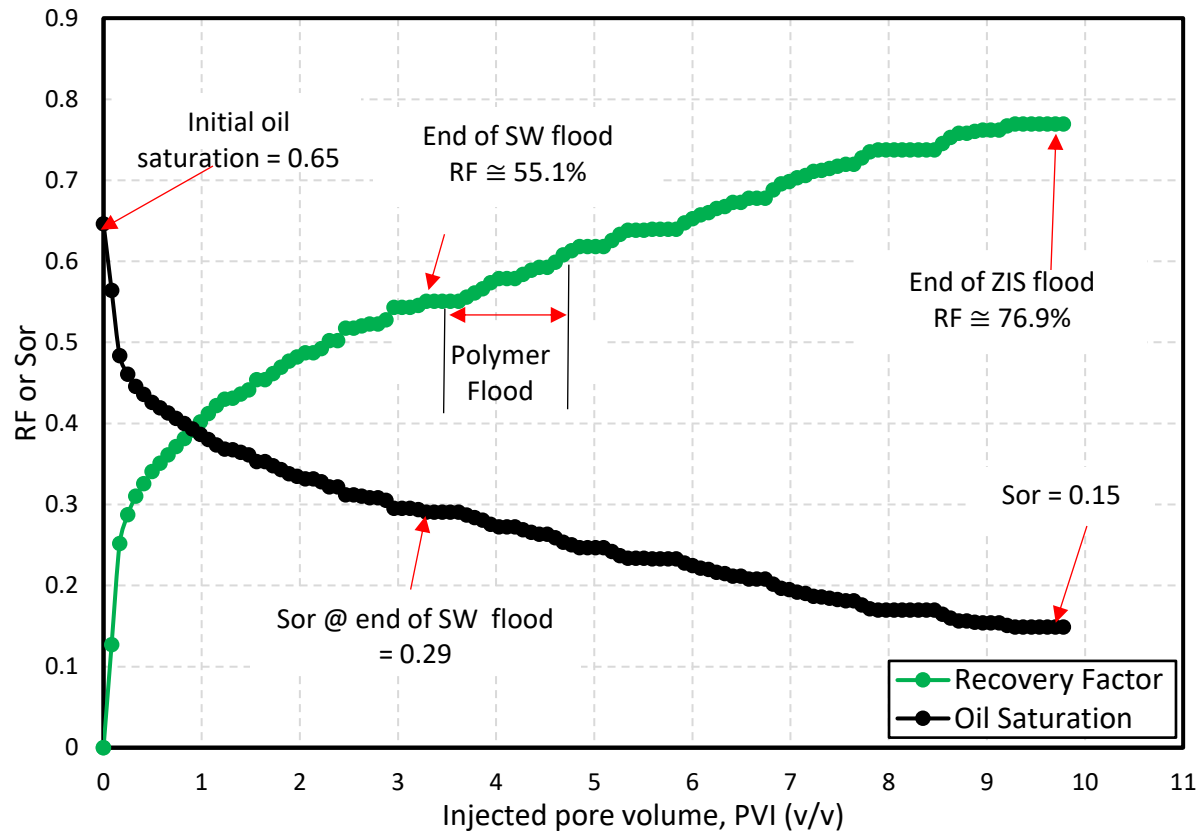


Figure 3-8. Oil recovery results of coreflooding experiment # 5

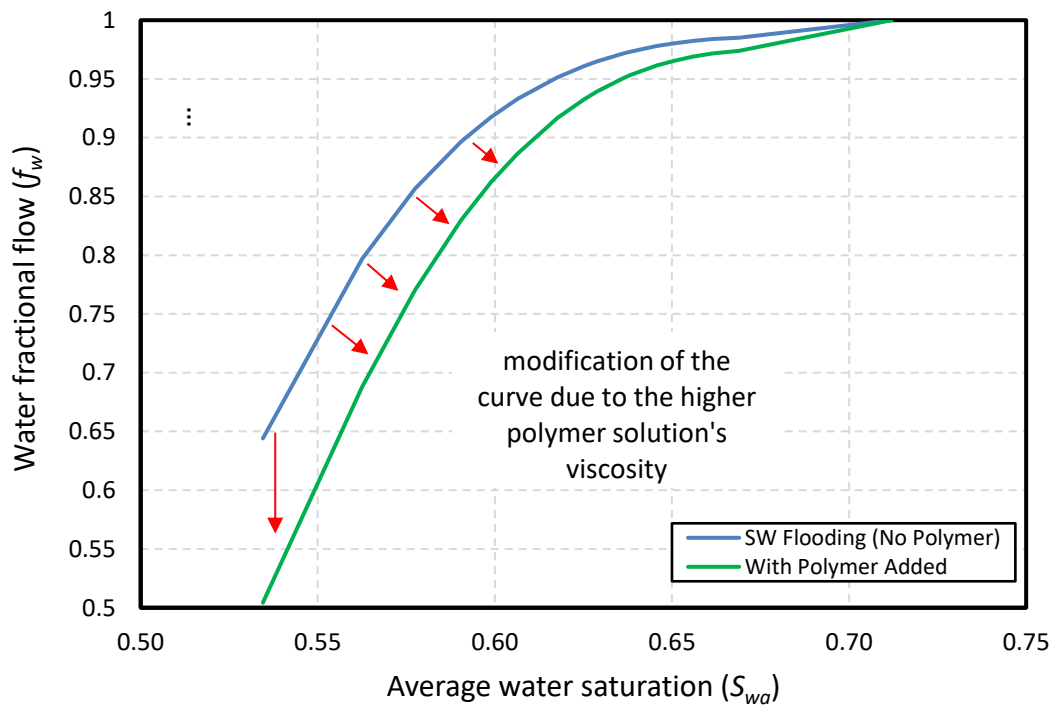


Figure 3-9. Fractional flow curves for low and high viscosity solutions

Pressure Drop. Figure 3-10 shows the differential pressure throughout the core samples during the flooding process. The ΔP ranged between 7.6 and 8.8 psi at the end of the SW flood. This very narrow range is another indication of the homogeneity of the selected rock samples. At the end of the GS and ZIS floods (Exps. 1 & 2), the average ΔP was around 5 psi, which is due to the reduction of oil saturation in the core samples. It is noticed that there was no increase in the pressure drop during the surfactant injection. Since the formed O/W microemulsion is stable, its droplet size is relatively small, and has low viscosity, the Jamin effect responsible for the additional flow resistance in the porous media is minimum [219–221]. Therefore, the pressure drop is assumed to be caused by the flow of oil and water only and any additional pressure drop due to the formed O/W microemulsion can be neglected. On the other hand, the ΔP during the SF flood (Exp. 3) increased initially to about 11 psi then decreased to an average of 6 psi. Besides the development and displacement of an oil bank, the initial pressure increase can also be attributed to the formation of a microemulsion promoted by the large reduction in IFT as well as precipitation of the surfactant within the pore space. A similar trend of pressure increase was also observed by Li et al. [222] who attributed it to surfactant adsorption.

As expected, the ΔP during the polymer floods (Exp. 4 and 5) increased to about 13 and 14 psi, respectively. At the end of the GS and ZIS flooding (Exps. 4 & 5), the ΔP fell to 5.5 and 4.5 psi, respectively. Due to the higher oil recovery from these experiments compared to Exp. 1 and 2, the terminal ΔP should have fell to lower values. However, the residual polymer solution's saturation overwhelmed the flow dynamics.

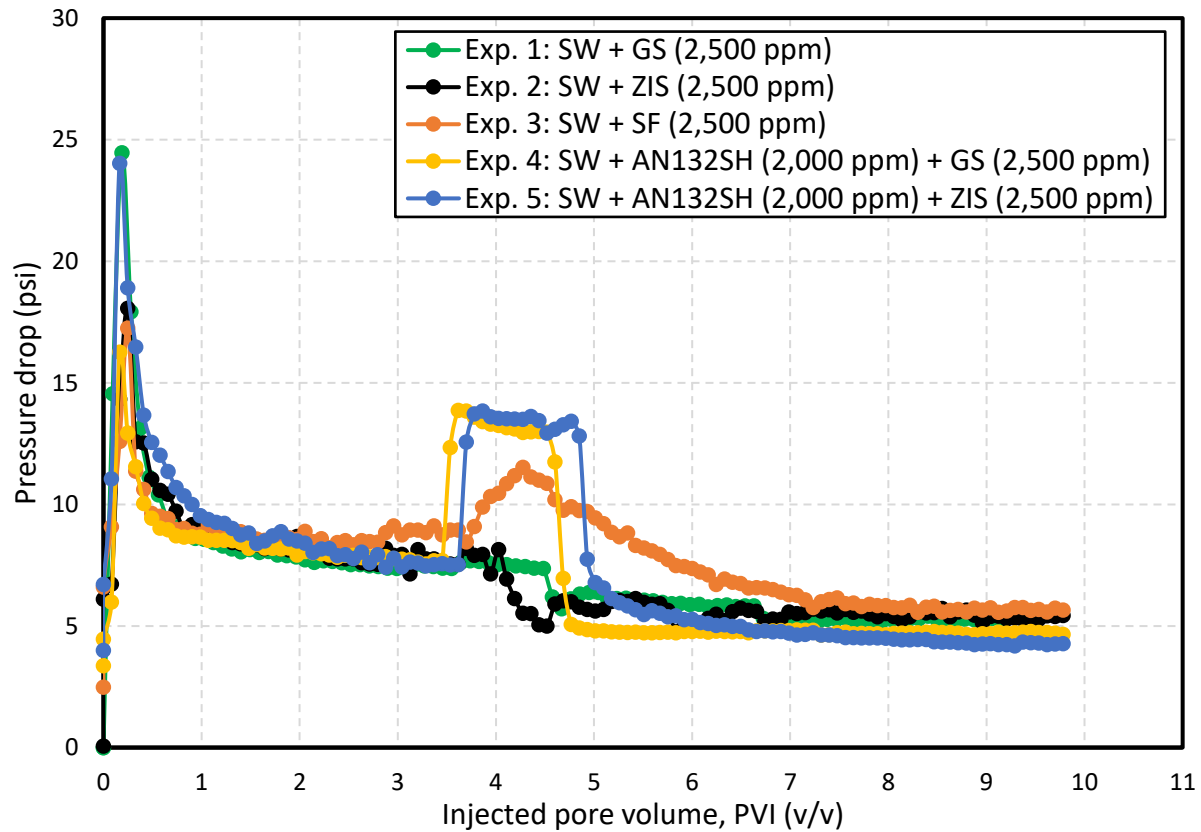


Figure 3-10. Pressure drop across the rock samples during the flooding experiments

Relative permeability. The JBN technique was applied to construct the relative permeability curves from the rock/fluid system. **Figures 3-11** and **3-12** show the oil/water rel-perm data and curve fits for Exps. 1 and 2, respectively. The crossover saturations for the SW floods in both experiments were almost identical at 0.52 and 0.55 indicating intermediate-wettability conditions of the rock samples, which explains the high oil recovery during the SW flood. During surfactant flooding, these points shifted to 0.65 and 0.66, respectively. These significant shifts in the cross-over saturations are the result of the change in rocks' wettability by the surfactants. This is also demonstrated by the increase in rel-perm to oil and the shift in the residual oil saturation from around 29% after SW flooding to around 20% at the end of the surfactant flood.

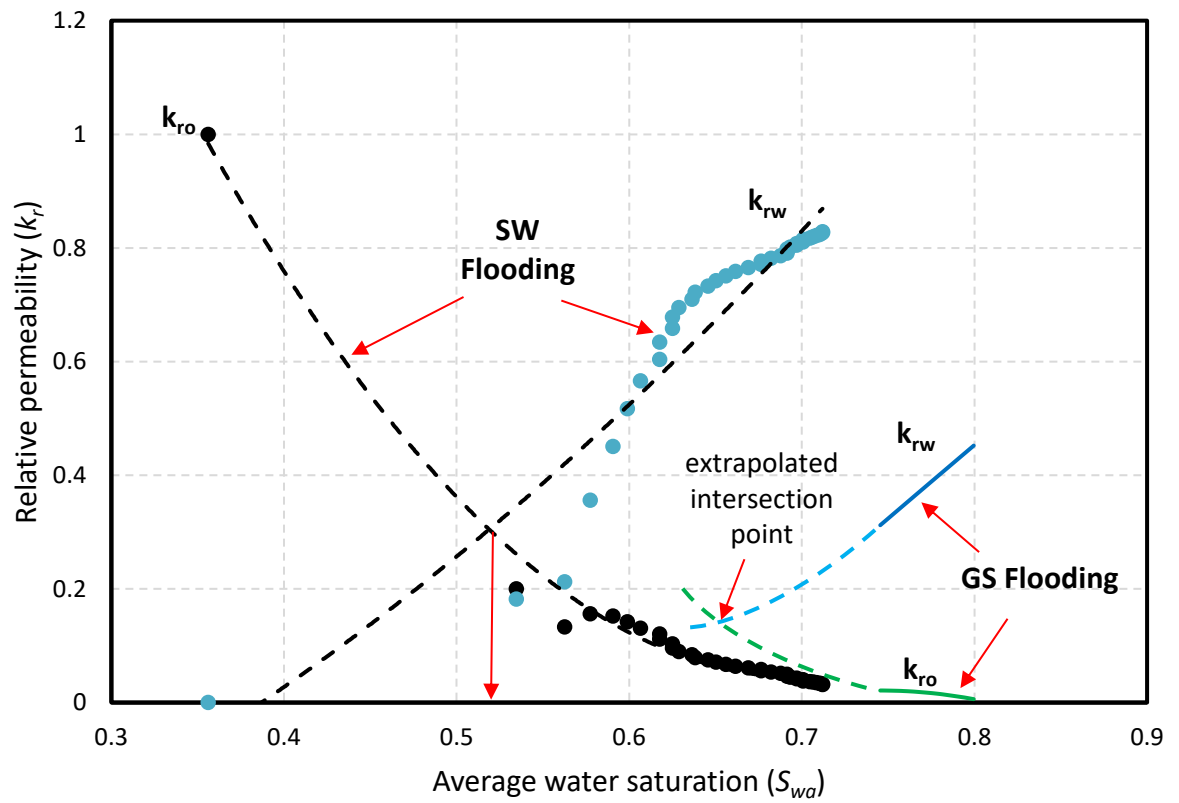


Figure 3-11. Relative permeability curves produced from the JBN method for Exp.1 (SW +GS)

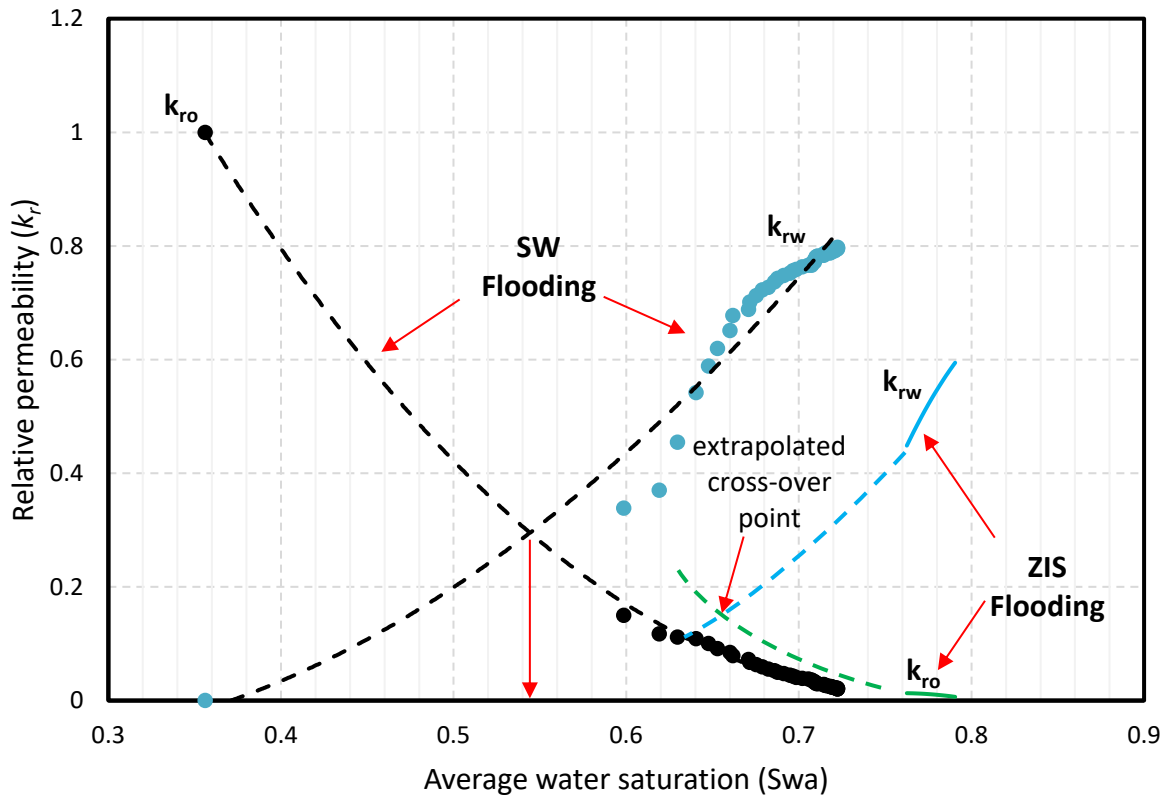


Figure 3-12. Relative permeability curves produced from the JBN method for Exp.2 (SW + ZIS)

3.3.4 Effluent Analysis

Figure 3-13 shows the surfactant concentration in the core-flood's effluent during Exp. 1. The maximum surfactant concentration was around 2,191 ppm at the end of the flood. Using Eq. 3-8, the dynamic retention value of the GS was about 0.44 mg/g-rock. **Figure 3-14** shows the same plot for ZIS surfactant (Exp. 2) with a similar maximum concentration but a larger retention value of about 0.62 mg/g-rock. These retention values are still below some of the reported values of field pilot tests, which were designed based on an average retention value of 0.7 mg/g rock [223]. The retention of both surfactants can be attributed to adsorption and/or partitioning into the oil phase, which requires further analysis. For SF surfactant (Exp. 3), **Figure 3-15** reveals a rather low effluent concentration (an average of 1,100 ppm). However, this surfactant's dynamic retention jumped to about 1.00 mg/g-rock,

which is attributed to the surfactant's instability as displayed by solution milkiness (photo insert in Figure 15). Such instability is caused by the addition of IOS to the formulation, which is not stable in SW. Therefore, precipitation of the surfactant could have happened in addition to its adsorption and/or partitioning into the oil phase, which supports the earlier conclusion about the ΔP increase during the SF flood. **Table 3-6** provides a summary of all the experimental results of the coreflooding experiments.

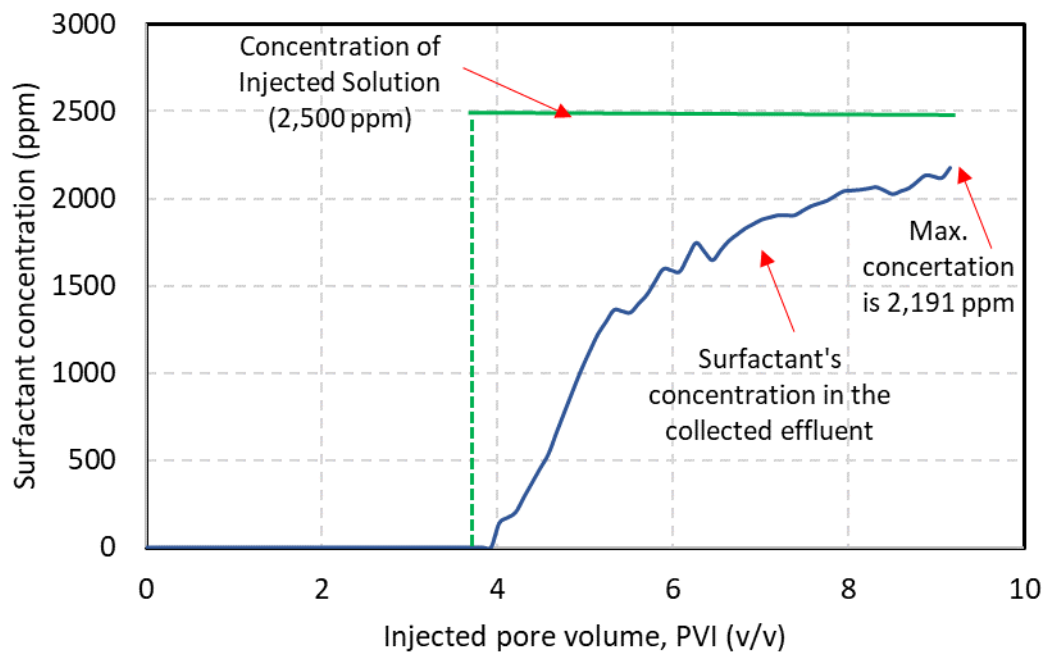


Figure 3-13. GS surfactant concentration in the coreflood effluent (Exp. 1)

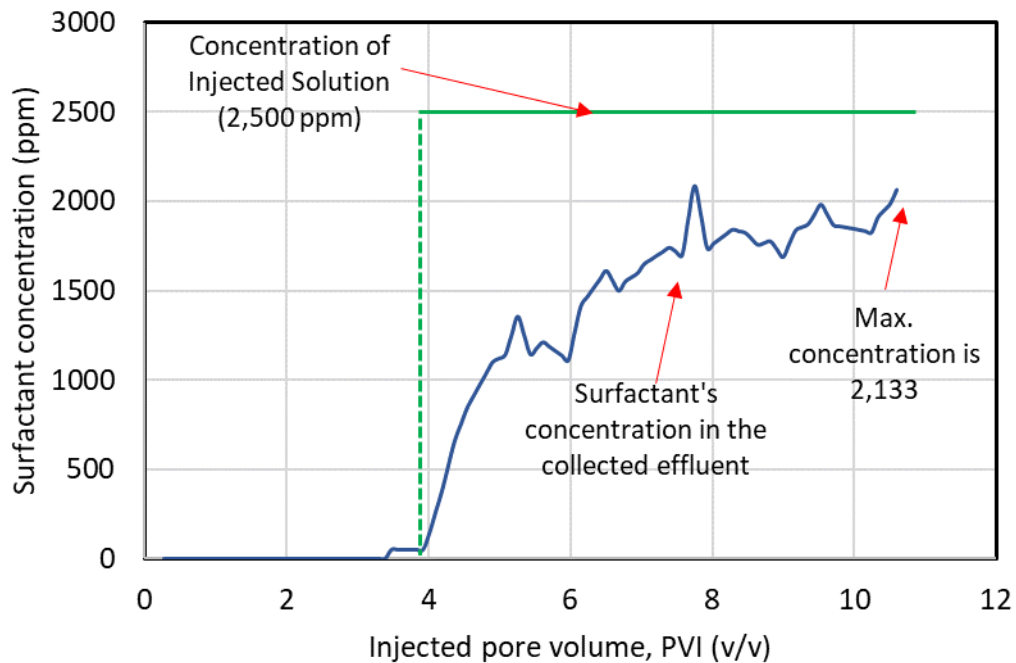


Figure 3-14. ZIS surfactant concentration in the coreflood effluent (Exp. 2)

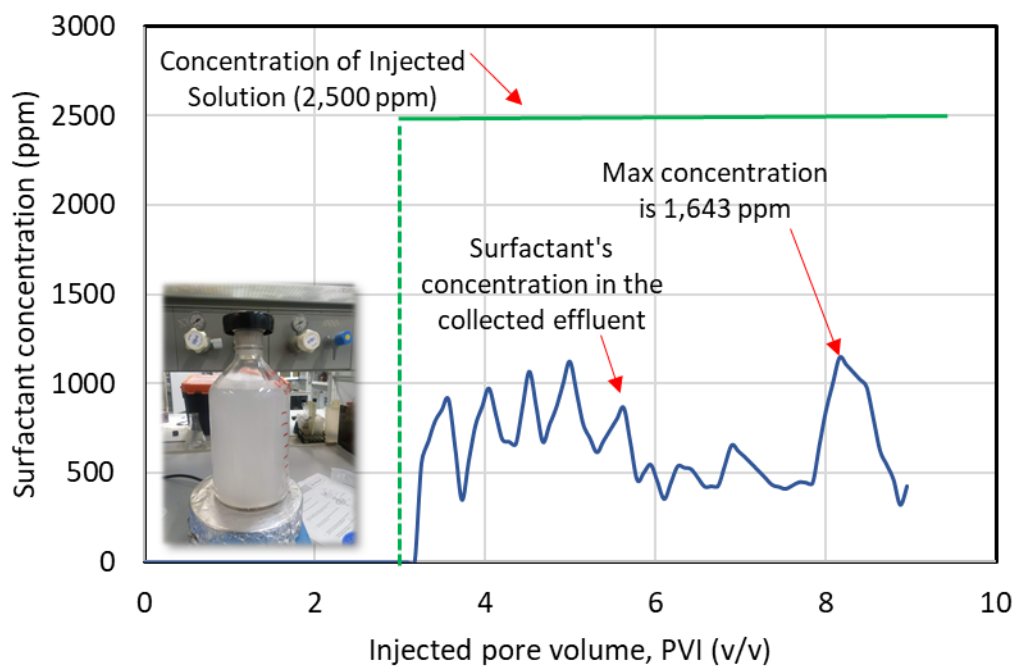


Figure 3-15. SF surfactant concentration in the coreflood effluent (Exp. 3)

Table 3-6. Summary of the results of coreflooding experiments conducted in this study

Experiment No.	Oil recovery after SW injection (% OOIP)	Additional oil recovery after chemcail injection (%OOIP)	Dynamic retention (mg/g-rock)
1	55.9	12.0	0.44
2	56.9	11.0	0.62
3	54.3	13.2	1.00
4	54.7	Polymer: 5.9 GS: 16.7	--
5	55.1	Polymer: 6.7 ZIS: 15.1	--

3.4 Conclusions

In this work, the oil recovery performances of two in-house-synthesized surfactants - a cationic Gemini (GS) and a zwitterionic (ZIS) - were evaluated and compared to that of a previously designed surfactant formulation (SF), all at 2,500 ppm concentrations. The evaluation was carried out on limestone rock samples under HTHS conditions. The following are the main conclusions:

1. After a flood with simulated seawater, both surfactants yielded similar incremental oil recoveries of about 12% of the initial oil in the core sample (OOIP) with residual oil saturations of about 21%. The SF surfactant yielded similar results.
2. Injecting a 1-PV slug of a 2000-ppm solution of an acrylamide polymer between seawater and surfactant resulted in about 5% additional oil recovery by polymer and an additional 16-17% each by the GS and ZIS solutions.
3. Both GS and ZIS surfactants increased the oil recovery by changing the rock wettability from strongly oil-wet to intermediate-wet state, while the SF surfactant improves oil recovery by reducing the oil/water IFT considerably.

4. The dynamic retention of the GS and ZIS surfactants is below the industry's allowed value of 1 mg/g-rock while that of the SF surfactant was at that value. The SF showed instability at the high salinity level of the flood.
5. The high oil recovery and low dynamic retention indicate the potential efficiency of the GS and ZIS for EOR applications in carbonate rock under harsh conditions, without the need of an alkaline or a cosurfactant.

CHAPTER 4

ROLE OF INJECTION RATE ON CHEMICAL ENHANCED OIL RECOVERY USING A GEMINI SURFACTANT UNDER HARSH CONDITIONS

Abstract

Introducing surfactants into a hydrocarbon reservoir is considered one of the most effective methods for enhanced oil recovery (EOR), mainly due to their ability to reduce interfacial tension and modify rock wettability. However, experimental parameters play a significant role in surfactant flooding. As an important design parameter, this work specifically investigates how the injection rate influences the oil recovery performance of a locally synthesized Gemini surfactant. Four coreflooding experiments on carbonate core samples were conducted, each at a specific injection rate (0.10, 0.25, 0.50, and 1.00 cc/min) under simulated reservoir conditions. The conditions include 100 °C temperature, pressures exceeding 3,000 psi, and formation water and seawater salinities of 213,768 ppm and 57,745 ppm, respectively. Each experiment involved initial continuous seawater flooding followed by continuous flooding with a 2,500-ppm surfactant solution. The results revealed an increasing trend in the recovery factor with injection rates by seawater flooding. Recovery factors at 0.10, 0.25, and 0.50 cc/min rates were 43.7%, 46.6%, and 49.1% of the oil initially in place (OOIP), respectively. However, at 1.00 cc/min, the factor decreased

to 48.1% OOIP after seawater flooding, possibly due to poor conformance control. In contrast, the recovery factor at the end of surfactant flooding was higher at lower injection rates (i.e., 0.10 and 0.25 cc/min), reflecting sufficient time for the surfactant to alter rock wettability and mobilize oil, with 0.25 cc/min as the optimum tested rate. However, effluent analysis revealed that slower injection rates correlated with higher dynamic retention (e.g., 0.383 mg/g-rock at 0.10 cc/min) compared to higher injection rates (e.g., 0.295 mg/g-rock at 1.00 cc/min). This implies a trade-off in choosing the injection rate when using the Gemini surfactant—balancing high oil recovery against minimizing dynamic retention. Consequently, this study emphasizes the need to carefully consider injection rates in surfactant flooding for optimal EOR outcomes.

This work is available at: <https://doi.org/10.1021/acs.energyfuels.3c04505>.

4.1 Introduction

Carbonate reservoirs, which hold more than 60% of the world's proven reserves [162–164], pose numerous difficulties for oil recovery processes. Operating conditions of carbonate reservoirs are typically challenging as the reservoir temperatures surpass 85°C and the salinity of connate water exceeds 100,000 ppm [166,167]. Carbonate reservoirs vary in wettability and can be strongly oil-wet or mixed wet [166,171,172]. Moreover, the rock permeability in these reservoirs ranges from very low to exceptionally high, mainly due to natural fractures, faults, and vugs, resulting in suboptimal waterflooding sweep efficiency [168–170].

The injection of water into hydrocarbon reservoirs is a commonly employed method to increase oil recovery and maintain reservoir pressure. Nonetheless, owing to the substantial

interfacial tension (IFT) between the injected water and the oil in place, a significant portion of the crude oil remains in place, leading to ineffective recovery [224]. Therefore, the need to reduce the oil/water IFT is inevitable for better oil displacement. The IFT can be reduced by the addition of surfactant to the injected water as a chemical EOR (cEOR) process [225]. Some surfactants not only reduce the oil/water IFT but can also change the rock wettability from an oil-wet state to a neutral or even a water-wet state, resulting in significant improvement in oil recovery [152,153,158,159]. Both the IFT and rock wettability (measured by contact angle) are controlling factors in the capillary number, N_c . Thus, surfactant flooding has been widely applied for increasing oil recovery from hydrocarbon reservoirs [169,226–228].

Surfactants, characterized by their amphiphilic nature, consist of a hydrophilic (water-soluble) head and a hydrophobic (water-insoluble) tail [161,229,230]. Commonly employed in cEOR applications are cationic, anionic, nonionic, and zwitterionic surfactants [231]. A distinctive class of surfactants, known as Gemini surfactants, has gained prominence in cEOR due to their unique properties and qualities [232–234]. These surfactants exhibit notable features, including a low critical micelle concentration (CMC) and a strong ability to reduce the IFT between oil and water. Their favorable wettability, foaming, and rheological characteristics, combined with high solubility in water, make them highly attractive for various applications in the oil and gas industry [182,184,187,188]. Distinguishing themselves from conventional surfactants, Gemini surfactants incorporate a spacer positioned at or near the hydrophilic heads. This spacer connects multiple hydrophobic tail groups and hydrophilic head groups [235,236]. Despite their exceptional attributes, there is a scarcity of studies that focused on discussing the

practical utilization of Gemini surfactants, particularly within the context of cEOR in carbonate rocks [181,185,186,237–241]. Pal et al. [242] investigated cationic Gemini surfactants through sandpack flooding with surfactant-polymer formulations. The tests achieved additional oil recoveries of 29.8–34.6%. Pal et al. [243] developed oil-in-water nanoemulsions using Gemini surfactant, polymer, and silica nanoparticles for EOR. Coreflooding experiments demonstrate a 26 % tertiary oil recovery. Ma et al. [244] introduced an anionic-nonionic Gemini surfactant for EOR. The characteristics of the surfactant include a critical surface tension of around 29 mN/m, and low CMC, and it could reduce IFT and alter the rock's wettability. Coreflooding experiments resulted in a 7% improvement in oil recovery. Pal and Mandal [245] investigated flooding a system of Gemini surfactant/polymer/nanoparticle for chemical EOR in sandstone rock systems. Using CMG-STARs simulations revealed ultra-low interfacial tension and altered wettability. Oil saturation was reduced to 29 % with {14-6-14 GS + PHPA + SiO₂ chase water}, achieving tertiary recoveries of 15–19%. Mpelwa et al. [246] synthesized and evaluated sulphonate Gemini surfactants which could reduce oil/water IFT to ultralow values ($<10^{-3}$ mN/m). The surfactant was characterized by surface activity and rheological behaviors. Pal and Mandal [247] evaluated the interfacial activity of Gemini surfactant/polymer/nanoparticle-stabilized Pickering nanoemulsions. Coreflooding tests demonstrated the efficiency of these nanoemulsions. Fattahi et al. [248] explored the synergies between silica nanoparticles and surfactants (cationic ionic liquid, anionic Gemini, nonionic emulsifier). While the silica could alter the rock wettability to strongly water-wet, surfactants exhibited varied effects on IFT and wettability. The nonionic

Gemini surfactant was identified for fractured reservoirs by reducing IFT and modifying wettability.

The imperative need for the development and evaluation of surfactants capable of withstanding high salinity and high-temperature (HTHS) reservoir conditions remains crucial. These conditions, coupled with other influential factors such as pH and rock lithology, significantly affect the efficacy of surfactant flooding techniques [160,161]. Design parameters like injection rate, surfactant concentration, slug size, and injection schemes are additional factors that impact the performance of surfactant flooding [249,250]. While various researchers have investigated the effects of injection rates in waterflooding [251–254], it is noteworthy that the influence of injection rates on oil recovery in surfactant flooding differs from its impact in traditional waterflooding. This distinction arises due to the critical role of flow velocity and the duration of injection in surfactant flooding [255].

The goal of this study is to assess how the injection rate influences the trend of oil recovery using a locally produced cationic Gemini surfactant (GS) as an EOR agent specifically designed for application in carbonate rocks under HTHS conditions. The investigation comprises four coreflooding experiments, wherein a 2,500 ppm GS solution is injected following a seawater flood. Additionally, effluent analysis is conducted at the end of each flooding test to evaluate the retention characteristics of the studied surfactant at the different injection rates. The outcomes of this study aim to provide valuable insights into the significance of the injection rate in the context of a surfactant-based cEOR process.

4.2 Experimental Work

4.2.1 Materials

Rock Samples. Four Indiana limestone rock samples with identical properties were used in the flooding experiments. Even though there are differences in the porosity and permeability of the samples, we believe that these variations fall within the acceptable range for conducting this comparative study. Calcite is the predominant mineral in these samples, as evidenced by X-ray diffraction (XRD) of a powdered sample. **Table 4-1** lists the rock samples' properties and the tested injection rates.

Table 4-1: Properties of Rocks and Corresponding Injection Rate

Experiment No.	Sample No.	Length (cm)	Diameter (cm)	Porosity (%)	Brine permeability (mD)	Tested injection rate (cc/min)	Darcy's velocity (ft/day)
1	IL-53	10.15	3.75	16.5	101.3	0.10	0.428
2	IL-22	10.16	3.75	16.2	99.9	0.25	1.069
3	IL-4	10.21	3.75	17.6	121.7	0.50	2.139
4	IL-17	10.17	3.75	17.8	123.8	1.00	4.277

Salts and Brines. Different laboratory-grade salts supplied by Sigma Aldrich were used to formulate the brines after dissolution in deionized water. An artificial formation brine (FW) with a salinity of around 214,000 ppm was prepared to fully saturate the rock samples. Synthetic seawater brine (SW) with salinity close to that of the Arabian Gulf water (around 57,745 ppm salinity) was also formulated for secondary and tertiary injections [193]. Additionally, these brines underwent filtration using filter paper to eliminate any remaining undissolved or undesirable solid particles; their compositions are shown in **Table 4-2**.

Table 4-2: Compositions of synthesized formation brine and seawater

Salts	Concentration (ppm)	
	SW	FW
NaHCO ₃	165	487
Na ₂ SO ₄	6,339	517
NaCl	41,172	150,419
CaCl ₂	1,802	52,788
MgCl ₂	8,266	9,555
TDS →	57,745	213,768

Crude Oil. For saturation and aging purposes, dead crude oil (i.e., stock tank /degassed) sourced from a carbonate reservoir production site in the Middle East was employed. To mitigate the risk of flow obstructions during oil flooding due to fine particles or residues, the crude oil underwent filtration using a 5- μ m, in-line filter. The viscosity of the crude oil at the flooding conditions of 100 °C and 3,000 psi was measured and found to be 2.48 cP. The SARA analysis of a crude oil sample using IATROSCAN MK-7s FID revealed the presence of 23.05% saturates, 44.22% aromatics, 22.97% resin, and 9.76% asphaltenes. The total base number (TBN) and total acid number (TAN) of the crude oil as obtained following the ASTM titration method are 0.76 mg KOH/g and 0.04 mg KOH/g, respectively.

Chemicals. An internally produced cationic Gemini surfactant with the structure shown in **Figure 4-1** was tested in this work. The surfactant was synthesized and physiochemically evaluated as presented by Shakil Hussain et al. [194]. The surfactant solution was prepared by dissolving the GS in the prepared SW to a tested concentration of 2,500. Despite the low CMC of the GS, typically below 100 ppm, employing such a minimal concentration is neither practical nor efficient because it could lead to suboptimal flood performance caused by surfactant retention. Conversely, high surfactant concentrations could result in increased

expenses. Therefore, we believe that the 2,500-ppm concentration remains a practical and economical choice in comparison to surfactant concentrations found in the literature, which frequently necessitate the use of cosurfactants and cosolvents to enhance surfactant efficacy. Additional information regarding the screening and preliminary assessment of the surfactant group, as well as the rationale behind choosing such concentration, can be found in previously published articles [191,194–196,198–203]. In those studies, the surfactant was initially synthesized and characterized with the aid of MALDI-TOF MS, FTIR, ^1H NMR, and ^{13}C NMR spectroscopy. Then it was assessed for its thermal stability and salt tolerance. To illustrate, the solubility of the surfactant was tested in deionized water (DW), synthetic SW, and synthetic FW. This revealed that this surfactant has excellent solubility and high resistance to high salinity levels with no signs of precipitation or cloudiness. It also exhibited excellent thermal stability at temperatures exceeding oilfield temperatures of higher than 90 °C. To illustrate, the short-term thermal stability tests showed that the decomposition temperature of the surfactant was close to 300 °C based on thermographic analysis. Additionally, the long-term thermal stability tests showed that the surfactant solution in either DW, SW, or FW was stable over a period of around three months at 90 °C [191,194]. What is more, a thorough investigation of the wettability alteration characteristics was then conducted[196]. Finally, static adsorption and retention characteristics have also been evaluated [202,203,256].

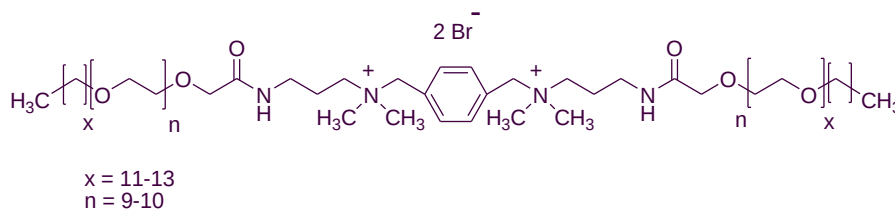


Figure 4-1. Molecular structure of the assessed cationic Gemini surfactant

4.2.2 Core-Flooding Experiments

Apparatus. Figure 4-2 presents an illustrative diagram of the coreflooding arrangement employed in this study. The primary components of the setup include a dual injection pump, a Hastelloy core holder, pumps for controlling the confining and back pressures, a heating bath, fluids' accumulators, and a back-pressure regulator. The flooding system (CFS700) was manufactured by VINCI technologies and the specific details of its components can be found in other publications [205,257,258].

Core sample preparation. Each core sample was initially saturated with FW following the vacuum saturation method. The liquid permeability of each rock was confirmed by continuous injection of FW through it. To establish the irreducible water saturation (S_{wi}) and estimate the OOIP, the variable-rate drainage process was applied by flooding each core sample with several pore volumes (PVs) of crude oil. The resulting initial water saturations for the samples ranged between 33 and 34%. The presence of micropores within Indiana limestone and most carbonate rocks could be the main reason for such relatively high irreducible water saturations [206,207]. To establish a strongly oil-wet state, the rock samples were aged for 21 days by immersing them in crude oil at 100 °C under static conditions [207]. This aging process facilitates the adsorption of the polar components of the oil onto the rock matrix.

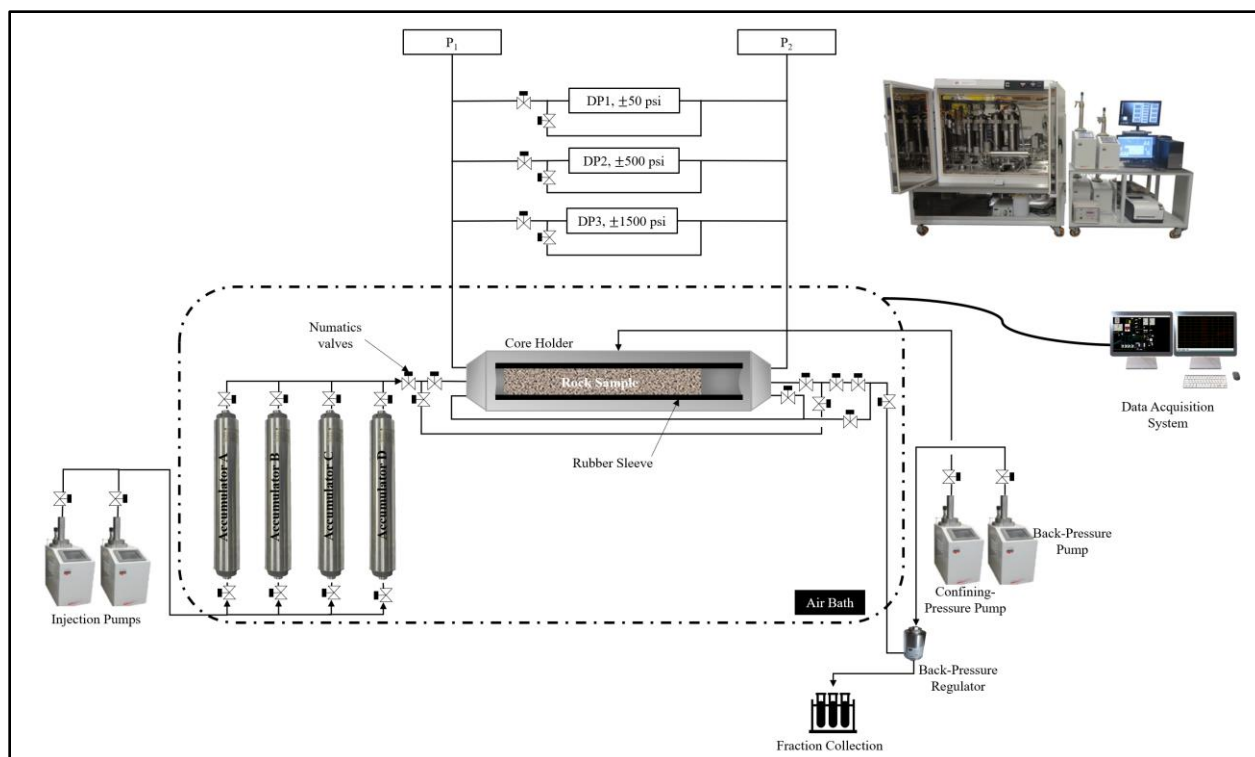


Figure 4-2. Illustration of the core-flooding setup

Oil recovery experiments. Every sample was placed into the core holder, heated to 100 °C, and subsequently flooded under pore and confining pressures of 3,000 and 4,000 psi, respectively. A small volume of the crude oil, measured in pore volumes (PVs), was initially injected at a rate of 1 cc/min. This step aimed to establish the flow conditions and replace the aged crude oil. Subsequently, continuous flooding with SW was initiated that continued until oil production nearly ceased (i.e., water cut exceeded 98%), which required about five to seven PVs of SW depending on the injection rate. Following this, chemical flooding ensued, which entailed the injection of 6 to 8 PVs of the GS solution until oil production ceased, after which the flood was terminated. Both the SW and surfactant floods were conducted on each sample at the corresponding flow rate as presented in **Table 4-1**, which also shows their respective Darcy's velocity. The produced effluent was gathered in 15-ml glass vials at different time intervals depending on the injection rate. To illustrate, 5

ml of the effluent was collected in each vial and the corresponding collection time for 0.1 cc/min was 50 minutes, for 0.25 cc/min was 20 minutes, for 0.5 cc/min was 10 minutes, and for 1 cc/min was 5 minutes. During surfactant flooding, and to ensure precise volume measurement, some vials required either heating up to 70-90 °C or adding a known amount of toluene to break the microemulsion as recommended by Sakthivel et al. [208]. Toluene is used because it is neither soluble in nor miscible with water. This makes it a good solvent to separate the oleic phase from the water phase by the mechanism of “like dissolve like”. To illustrate, toluene is a nonpolar compound, and it will attract the oil (a nonpolar component) during oil-water separation (a process of demulsification), and due to this attraction, it breaks the emulsion into its constituents. This results in a clear interface between both phases and the reading of the volumes is easier and more accurate.

4.2.3 Effluent Analysis

The surfactant concentration in the flood effluent was determined using the effective potentiometric HPLC (high-performance liquid chromatography) technique [173,202,213–215]. An Agilent 1200 series HPLC system was utilized, featuring an attached evaporative light scattering detector (ELSD). Acetonitrile (C_2H_3N) served as mobile phase A, while a 0.1 M ammonium formate (NH_4COOH) with a pH of 4.3 adjusted by formic acid (CH_2O_2) acted as the carrier phase B. The analysis utilized an Acclaim Surfactant Plus column (3 μm , 4.6 x 150 mm).

The concentration was evaluated for the aqueous phase. The aqueous phase produced during the flooding test was collected in vials, separated from the oil phase, and then subjected to this analysis. It should be noted that the separation of the aqueous phase was done before adding toluene for the purpose described in the oil recovery experiments

section. This is because the addition of toluene may alter the compositions of the fluids and may lead to inaccurate estimation of surfactant concentration. After that, the separated aqueous phase was transferred to the HPLC vials using a single syringe and a single 0.45- μm syringe filter. The vials are then placed on the rack of the HPLC autosampler. From the HPLC, the ELSD area is obtained for each vial, which was then used as input to the predeveloped equation to calculate the corresponding concentration. To establish an HPLC calibration equation for a given surfactant, surfactant solutions are prepared at a wide range of concentrations (e.g., 100, 250, 500, ..., 2,700 ppm). Using the HPLC, the corresponding ELSD area for each vial is obtained, which is plotted against the surfactant's concentration. The calibration equation is then a best-fit equation that correlates the chromatographic integral area with the surfactant concentration [215]. **Figure 4-3** presents a summary of the procedure for getting the dynamic retention using the HPLC for collected effluent for the coreflooding test. The surfactant's dynamic retention during the flooding process was then calculated from the surfactant's concentration based on a straightforward material balance approach as given by Eq. 4-1 [199]. In the equation, dynamic retention (mg/-g-rock) is denoted by $\Gamma_{dynamic}$, the initial surfactant concentration (2,500 ppm) is denoted by C^0 , cumulative volume of surfactant injected (mL) is denoted by V , the mass of the dry rock sample (g) is denoted by m_r , and the volume of surfactant solution collected in each vial (mL) and its concentration (ppm) are denoted by V_i and C_i , respectively. A thorough evaluation of dynamic retention is still a complex process due to its dependence on many factors including rock's surface area, permeability, and tortuosity. This necessitates the need for the investigation of these factors, which is beyond the objective of this work.

$$\Gamma_{dynamic} = \frac{C^0 V - \sum_{i=1}^N C_i V_i}{m_r} \quad (4-1)$$

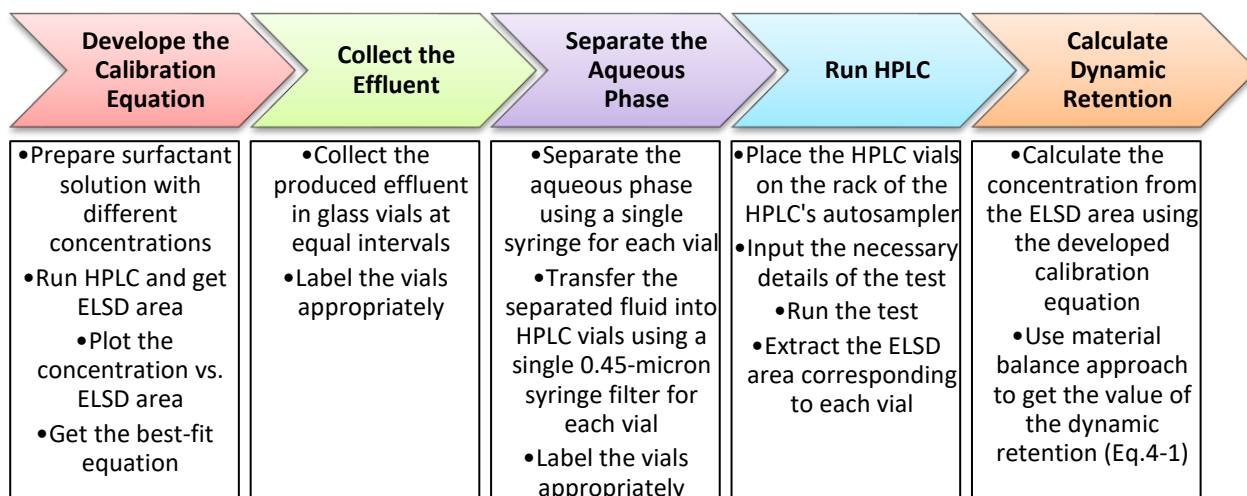


Figure 4-3. Procedure of effluent analysis to get the dynamic retention using the HPLC

4.3 Results & Discussions

4.3.1 Oil Recovery Results

Seawater flooding performance. Figures 4-4 to 4-7 illustrate the profiles of oil recovery and oil saturation versus the volume of seawater (SW) injected (expressed in pore volumes, PVs) for the four flooding tests. The oil recovery factors during the seawater floods were 43.7%, 46.6%, 49.1%, and 48.1% of the oil initially in place (OOIP) with injection rates of 0.10, 0.25, 0.50, and 1.00 cc/min, respectively. Correspondingly, the residual oil saturations were 37.3%, 35.2%, 34.0%, and 34.2%, respectively.

Given the consistent rock properties and initial states of the rocks, the sole variable in these experiments was the injection rate. Consequently, the observed increase in oil recovery with higher injection rates can be attributed to elevated viscous forces and larger capillary numbers. However, it is noteworthy that the recovery factor at an injection rate of 1.00 cc/min did not follow this trend. This deviation could be attributed to poor conformance control resulting from the higher flood velocity at that injection rate.

Chemical performance. In **Figure 4-4**, the oil recovery behavior of the GS solution at an injection rate of 0.10 cc/min is presented along with the corresponding residual oil saturation. The injection of the GS solution (approximately 6 pore volumes) led to an extra oil recovery of nearly 20% of the OOIP, bringing the total recovery factor to approximately 63.8% at the end of the flood. The residual oil saturation was reduced to nearly 24% by the end of the chemical flood. Similarly, **Figure 4-5** illustrates the outcomes of the flood at 0.25 cc/min. It required the injection of nearly 5 pore volumes of the GS solution to recover an additional 23% OOIP from the sample. The corresponding residual oil saturation was 20% at the end of the chemical flood. The results of the 0.50 and 1.00 cc/min floods are depicted in **Figures 4-6** and **4-7**, respectively. The GS solution at these injection rates yielded additional oil recoveries of 16.2% and 17.8% OOIP, respectively, with corresponding residual oil saturations of approximately 23.2% and 25.1%. **Figure 4-8** combines the oil recovery profiles for the four tested injection rates and shows the variations in the recovery speed during the four flooding experiments.

The variation in the recovery factors and production trends during surfactant flooding can be attributed to the available time for the GS to achieve wettability alteration. To illustrate, contact angle and IFT measurements presented in the previous publications [196,258] revealed that the Gemini surfactant is more efficient in altering rocks' wettability than reducing the oil/water IFT. For example, the Gemini surfactant could alter the rock's wettability from a strongly oil-wet state to an intermediate or water-wet state. This was determined through contact angle measurements and by a shift in the oil/water relative permeability curves calculated from coreflooding experiments using the JBN method. However, the oil/water IFT was only reduced to around 3 mN/m in surfactant solution with

a concentration of 2,500 ppm under laboratory conditions. Since no ultralow IFT was achieved by this surfactant, it was inferred that wettability alteration is the primary mechanism driving any enhanced recovery from this Gemini surfactant. What is more, wettability alteration by the GS is a time-dependent process. Therefore, we could see that, at lower injection rates (i.e., 0.10 and 0.25 cc/min) the incremental recovery by the GS solution is higher than that achieved at higher injection rates (i.e., 0.50 and 1.00 cc/min). On the contrary, it can be noticed that at the highest tested injection rate, it took a very long time for the surfactant to start mobilizing the oil; that is, the oil production at the injection rate of 1.00 cc/min commenced after injecting around 3 PVs of the surfactant solution. This is because high flow velocities cause shorter interaction times between the GS and the rock matrix for complete wettability alteration. Therefore, higher injection rates during the surfactant flood produce less oil recovery. Although the injection rate of 0.10 cc/min provides more residence time for the surfactant, the pressure drop (see **Figure 4-9**) and the viscous forces corresponding to this rate were not sufficient to displace the mobilized oil by the GS solution, as explained previously in the SW recovery performance. Hence, the injection rate of 0.25 cc/min produced optimum conditions of viscous displacement and wettability alteration to cause the largest oil recovery by the SW/GS flood since it provided sufficient time for the surfactant to mobilize the oil and the necessary viscous forces to displace that mobilized oil.

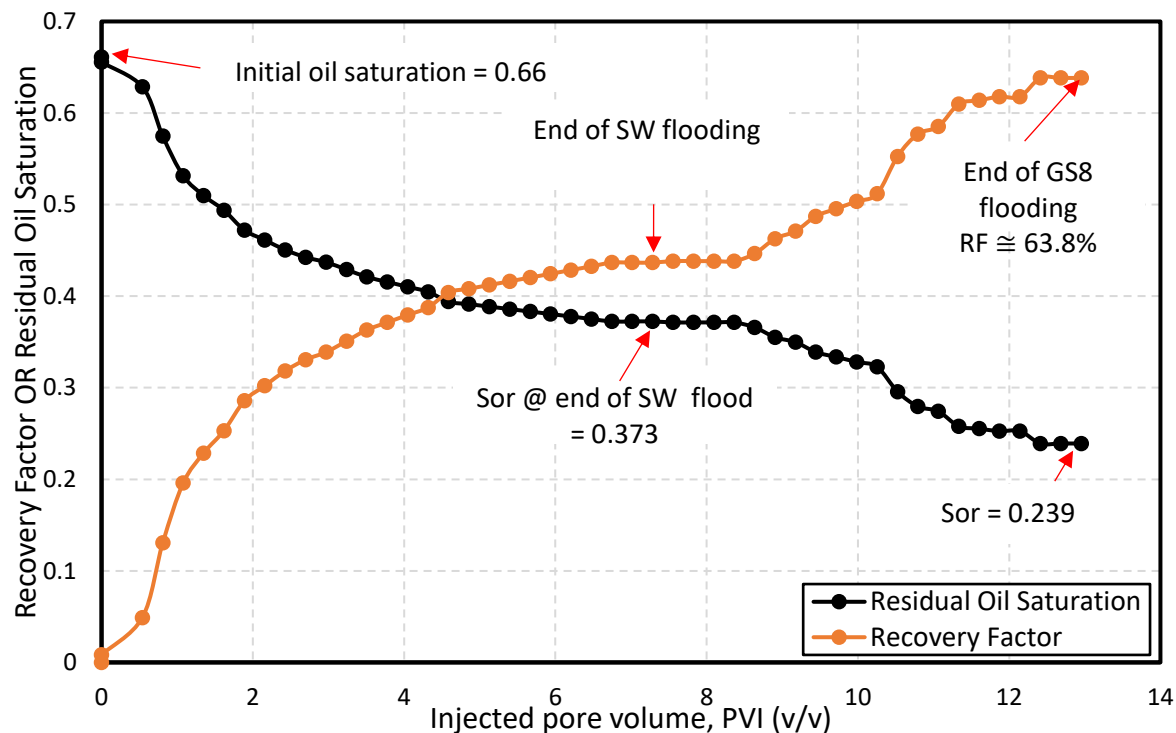


Figure 4-4. Oil recovery results for injection rate at 0.10 cc/min

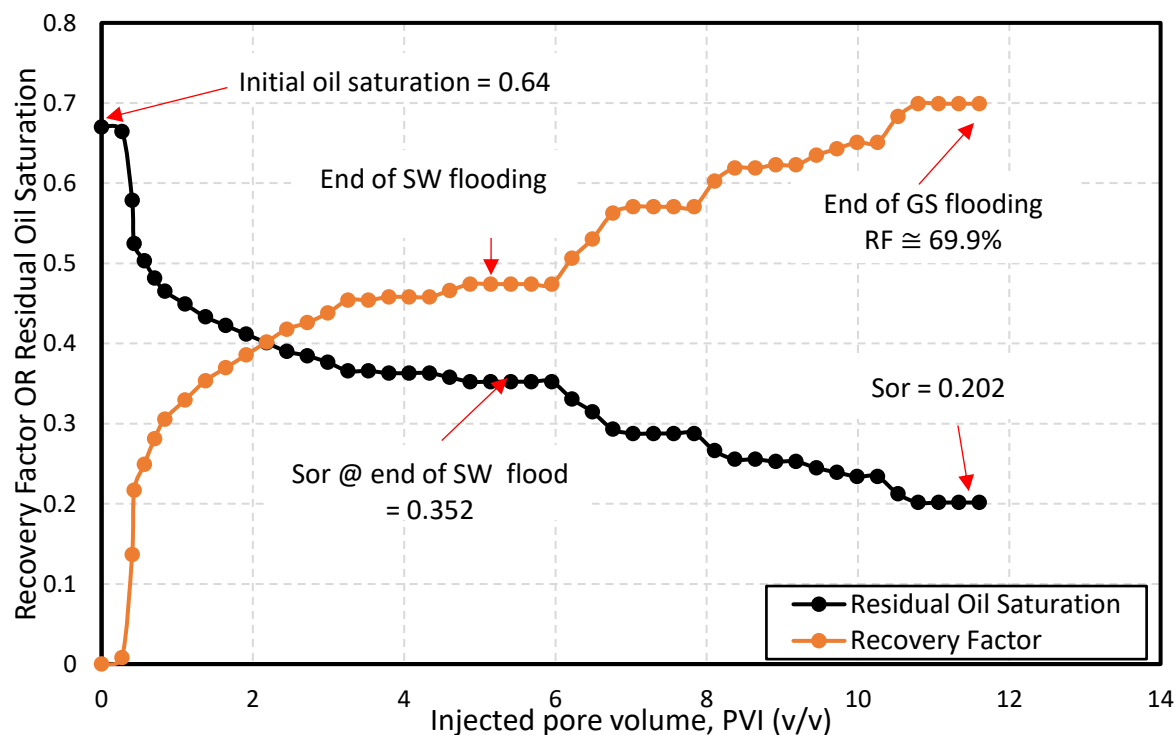


Figure 4-5. Oil recovery results for injection rate at 0.25 cc/min

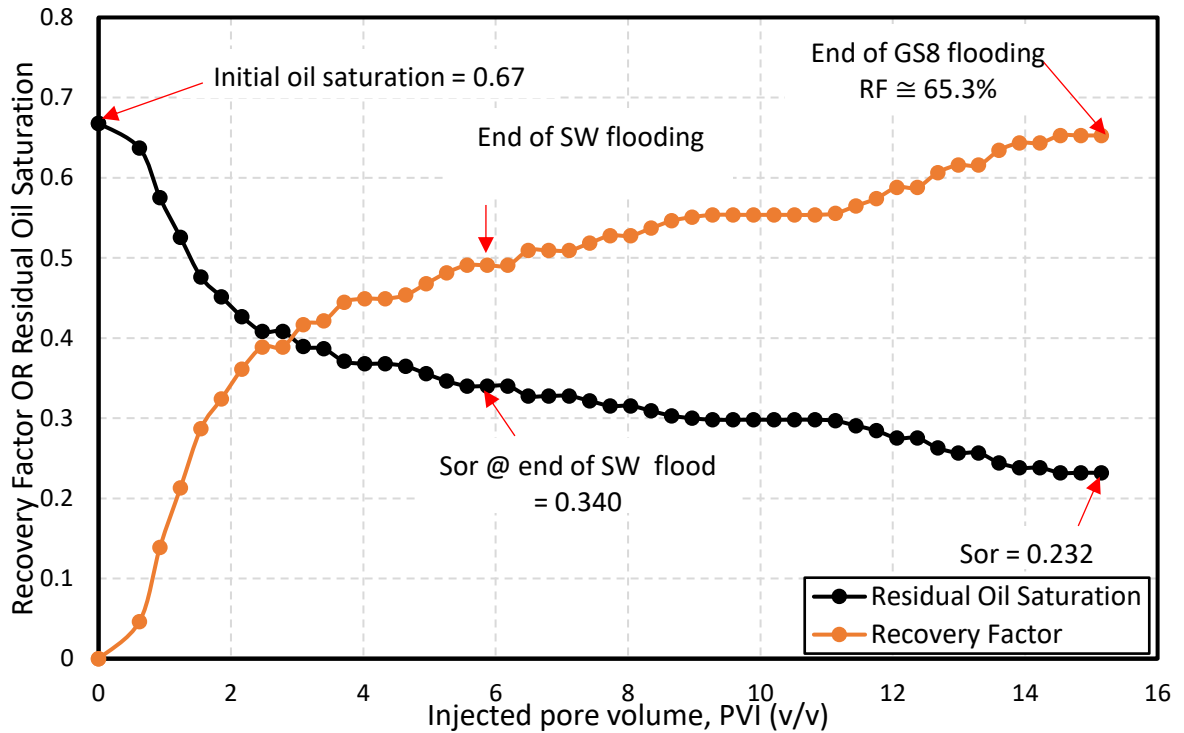


Figure 4-6. Oil recovery results for injection rate at 0.50 cc/min

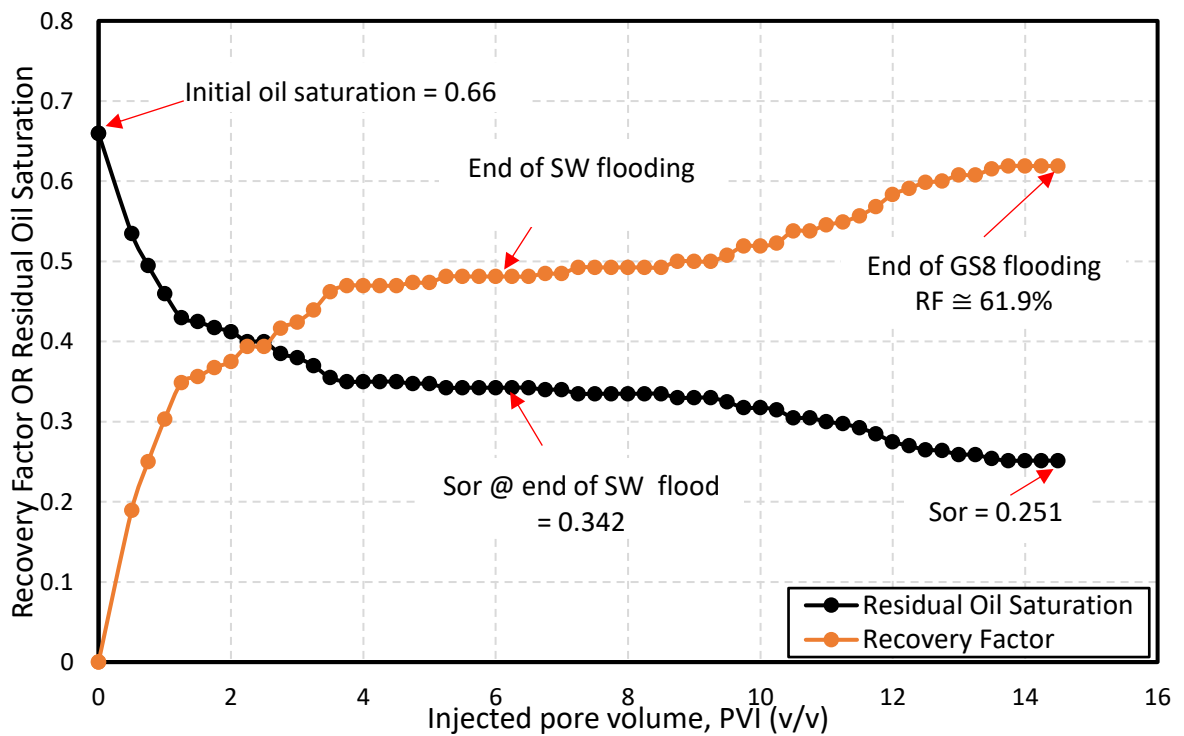


Figure 4-7. Oil recovery results for injection rate at 1.00 cc/min

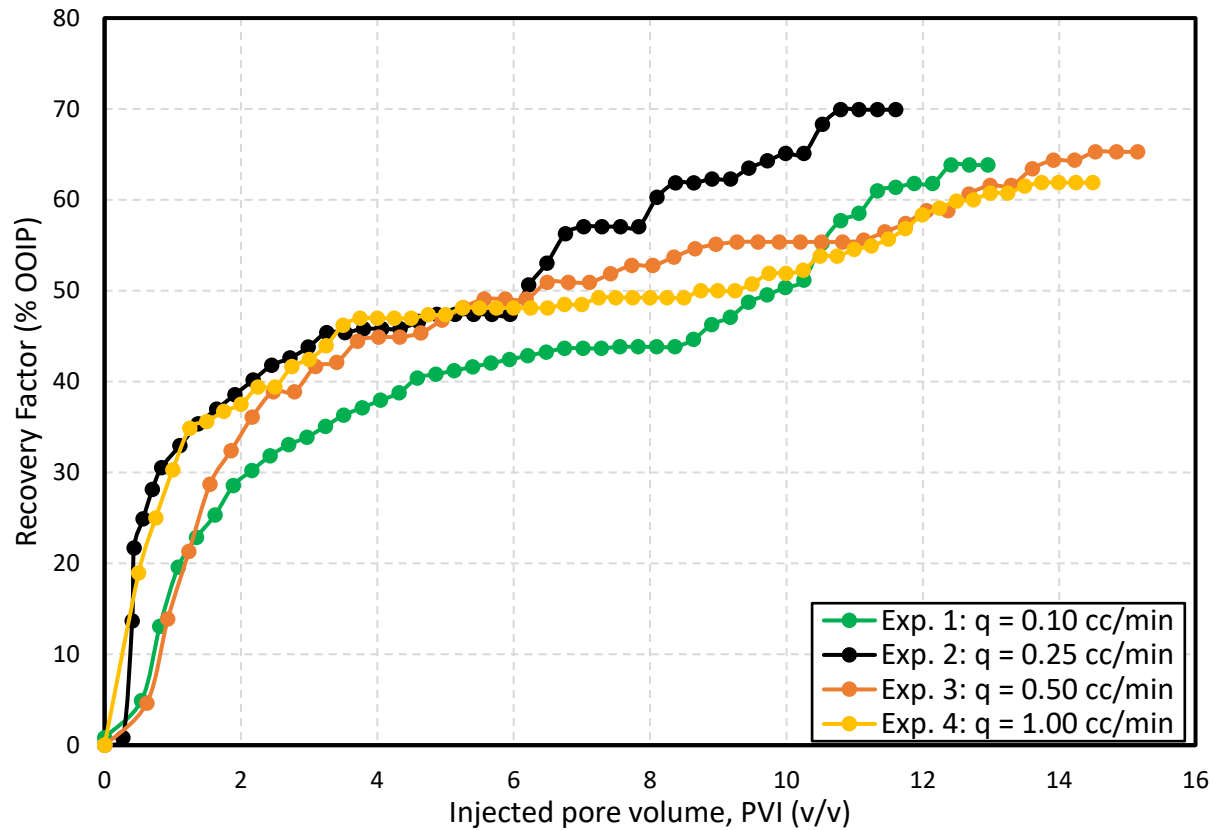


Figure 4-8. Oil recovery profiles for the four tested injection rates

Pressure drop behavior. Figure 4-9 depicts the differential pressure across the flooded samples throughout the flooding tests, with the lower ΔP curve corresponding to a lower injection rate and vice versa. Observations revealed that there was no rise in the pressure drop during the injection of surfactants. Instead, the pressure drop decreased during surfactant flooding, attributable to the reduction in oil saturation following oil mobilization by surfactant flooding. The pressure drop data also indicated the amount of pore volume of SW injected to achieve the breakthrough. To illustrate, the maximum pressure drop during SW flooding corresponds to the breakthrough time. The four samples required nearly the same amount of SW to achieve the breakthrough which was from 0.75 PV.

The stability of the formed oil/water microemulsion, characterized by relatively small droplet size and low viscosity, minimizes the Jamin effect. The Jamin effect, known for

contributing to additional resistance to flow in porous media, is thereby diminished [219–221]. Consequently, the primary factor influencing the pressure drop is the flow of oil and water, and any further pressure drop arising from the formed oil/water microemulsion can be disregarded.

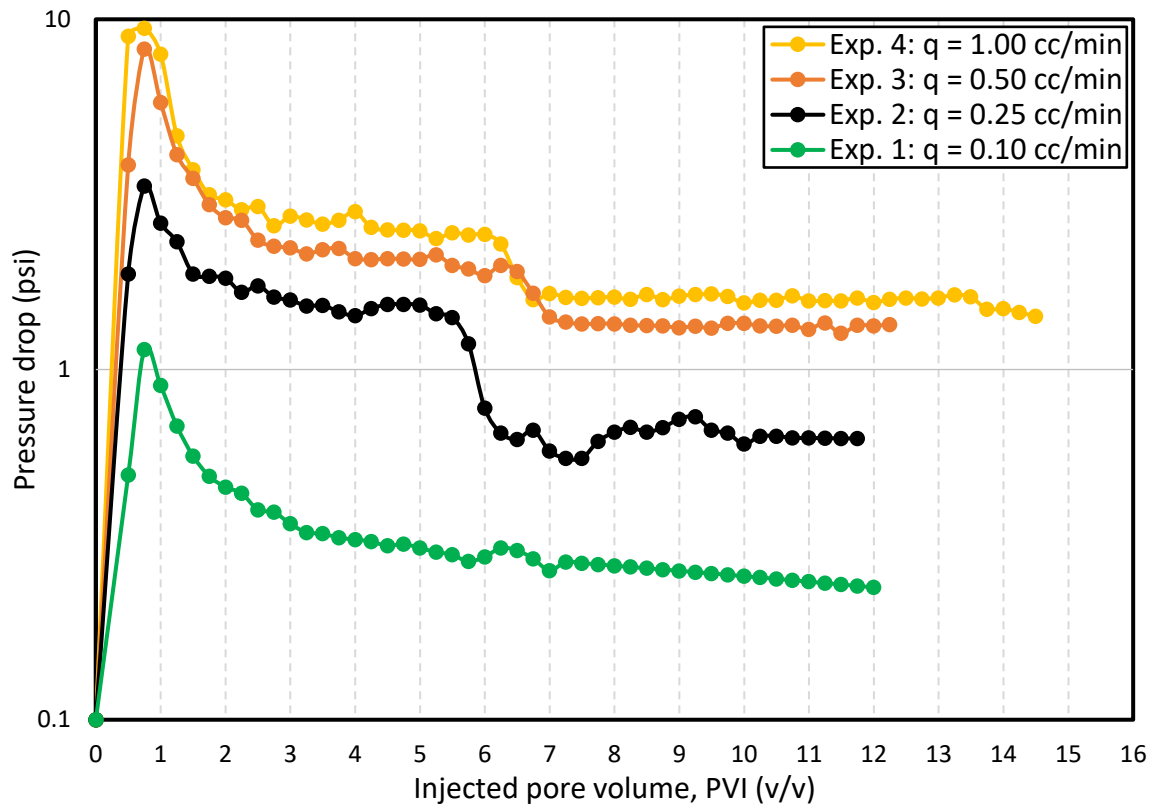


Figure 4-9. Profiles of the pressure drop across the cores during SW and GS flooding

4.3.2 Effluent Analysis

Before the calculation of the concentration of surfactant in the produced effluent, the calibration equation had to be constructed. This was done by plotting surfactant concentration versus the corresponding ELSD area (**Figure 4-10**). From the figure, the surfactant concentration is calculated from the ELSD area using the following best-fit equation. The corresponding coefficient of determination (R^2) is 0.9978.

$$C_{GS}(ppm) = -3 \times 10^{-7} \times A_{ELSD}^2 + 0.0602 \times A_{ELSD} + 171.9 \quad (4-2)$$

where C_{GS} is the concentration of surfactant in ppm and A_{ELSD} is the ELSD area obtained from the HPLC.

Using Eq. 4-2, the concentration of the GS in the produced effluent is then calculated from the obtained ELSD area from the HPLC for each vial. The green line of **Figure 4-11** shows the concentration of the GS in the effluent during the GS floods at the injection rate of 0.10 cc/min. The highest concentration of surfactant was around 2,147 ppm throughout the surfactant flooding. The corresponding GS's dynamic retention was around 0.383 mg/g-rock. The black line of **Figure 4-11** shows a similar plot for the injection rate of 0.25 cc/min. The maximum concentration and the calculated dynamic retention are 2,294 ppm and 0.372 mg/g-rock, respectively. For the injection rate of 0.50 cc/min, the orange line of **Figure 4-11** shows the highest concentration of around 2,401 ppm, and the calculated dynamic retention (0.178 mg/g-rock) was the lowest among the tested injection rates. Finally, the concentration of the effluent during the injection rate of 1.00 cc/min is shown by the yellow line in **Figure 4-11**. The corresponding dynamic retention for this experiment was 0.295 mg/g-rock. It is worth noting that some of the surfactant could have partitioned into crude oil which is not accounted for as retention. This needs to be further investigated and it is beyond the goal of this work.

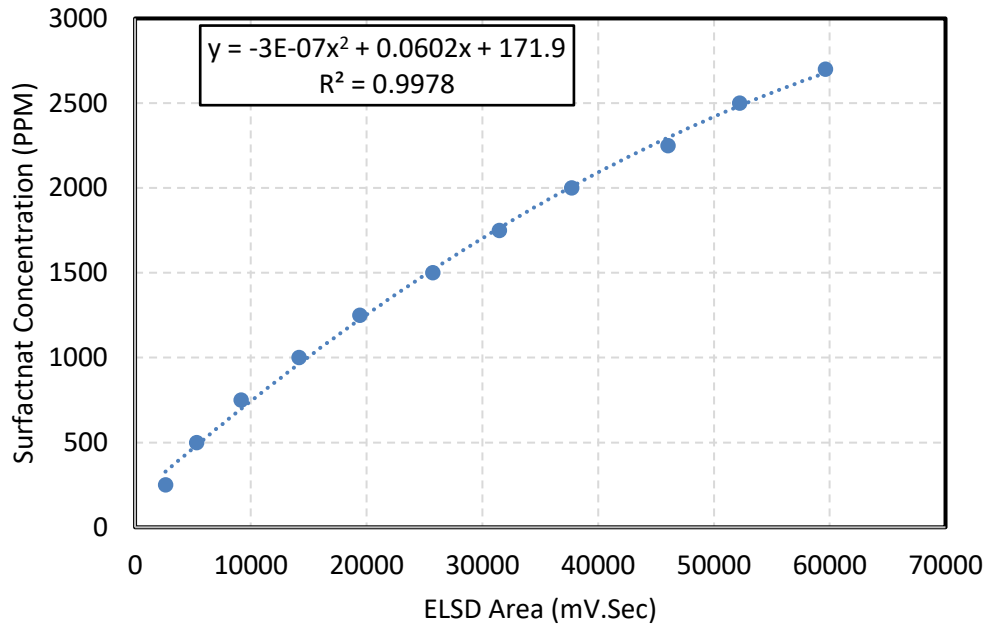


Figure 4-10. Calibration curve for obtaining the relationship between surfactant concentration and ELSD area

As explained earlier, lower injection rates provide more residence time for the surfactant solution. This explains the large dynamic retention with the low injection rates. Additionally, the surfactant could be trapped within the pores, which requires high viscous forces to dislodge it. **Figure 4-12** provides a summary of the results presented in this work. The figure shows that the oil recovery by surfactant flooding at an injection rate of 0.25 cc/min is slightly higher than that obtained at 0.10 cc/min by 3% OOIP. However, the oil recovery by these injection rates is still much higher than those obtained by 0.50 and 1.00 cc/min injection rates by more than 7 and 9 % OOIP, respectively. Therefore, it can be concluded that the oil recovery at low injection rates is higher than that obtained by high injection rates, with an optimum rate of 0.25 cc/min.

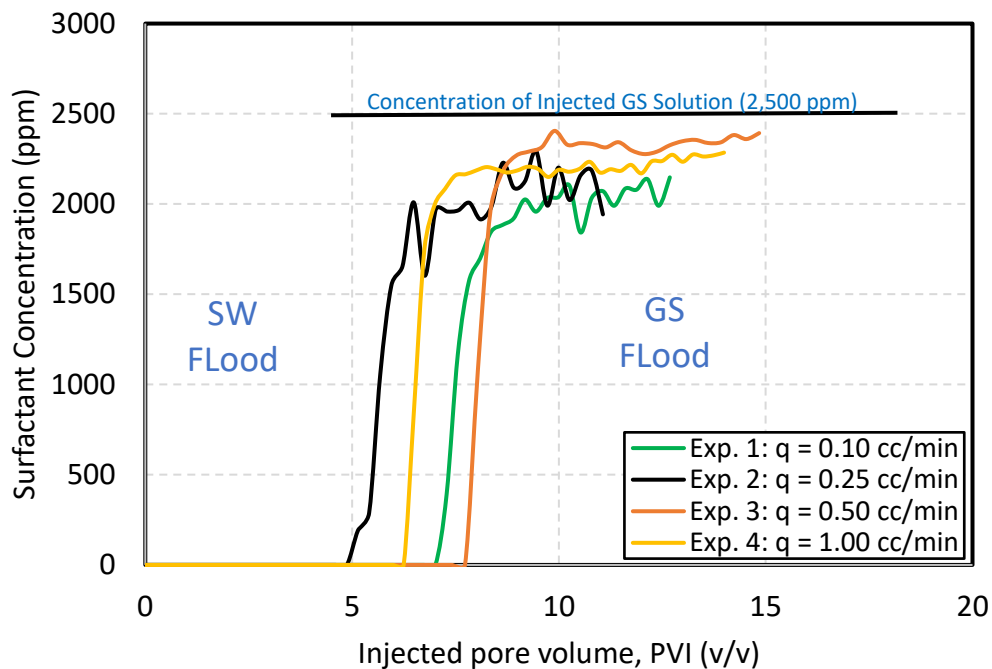


Figure 4-11. The concentration of the GS in the coreflood effluent for all the experiments

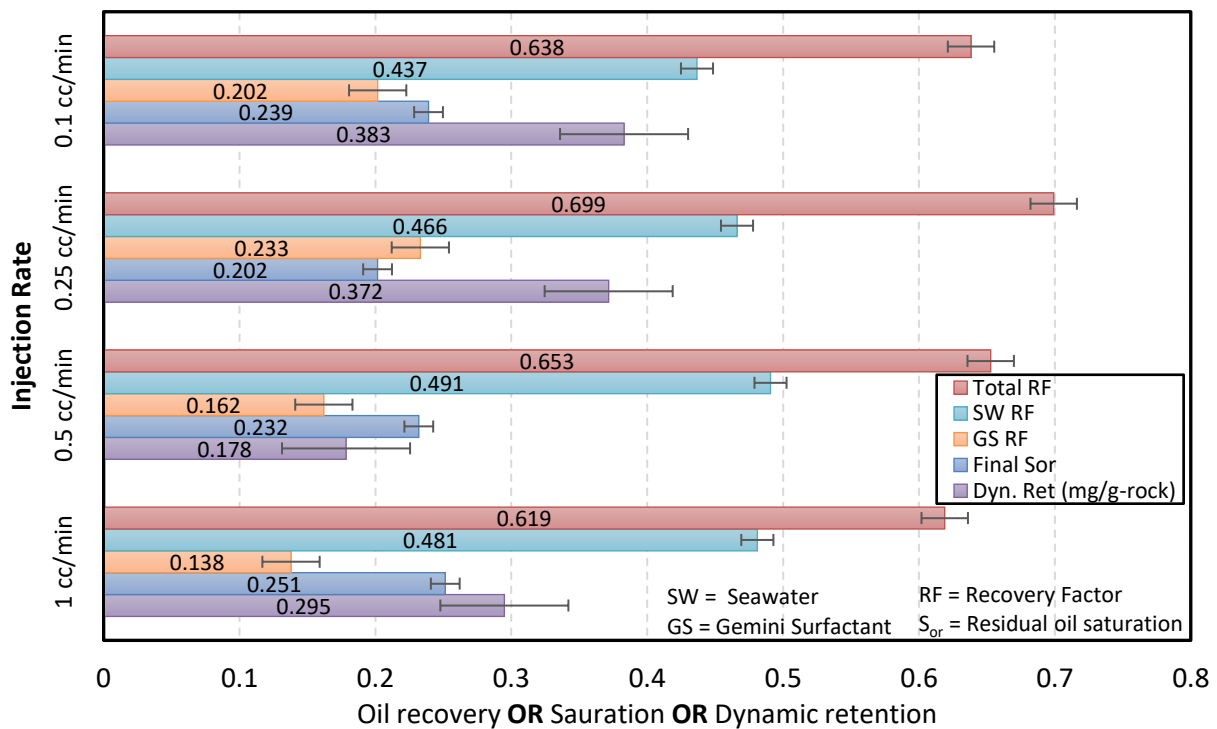


Figure 4-12. Summary of all core-flooding tests

4.4 Conclusions

In this work, the role of the injection rate on the cEOR performance of an in-house designed, cationic Gemini surfactant was evaluated with Indiana limestone rocks. The tests were conducted with a 2,500-ppm surfactant solution under HTHS conditions. The key findings/conclusions of this work are as follows:

1. The oil recovery factor after a seawater flood increased with increasing injection rate due to the larger viscous forces that improve oil displacement. However, at the highest injection rate tested (1.00 cc/min), the recovery factor showed a decrease, which is attributed to poorer flood conformance.
2. Low injection rates provided longer residence time for the surfactant to interact with the rock matrix and, hence, better oil mobilization by surfactant flooding. It was shown that the surfactant flooding at the injection rates of 0.10 and 0.25 cc/min resulted in higher oil recovery (respectively 20% and 23% OOIP) than flooding at injection rates of 0.50 and 1.00 cc/min (respectively 16% and 13.6% OOIP), with 0.25 cc/min as the optimum injection rate.
3. A longer surfactant residence time caused higher surfactant retention. The dynamic retention of surfactant during injection rates of 0.10 and 0.25 cc/min was higher than that resulted during high injection rates of 0.50 and 1.00 cc/min.
4. This study emphasizes the need to carefully consider injection rates in surfactant flooding strategies for optimal EOR outcomes. To illustrate, when deciding the injection rate for surfactant flooding, it is important to strike a balance between achieving higher incremental oil recovery and minimizing the surfactant's dynamic retention.

CHAPTER 5

CHEMICAL ENHANCED OIL RECOVERY UNDER HARSH CONDITIONS: INVESTIGATION OF ROCK PERMEABILITY AND INSIGHTS FROM NMR MEASUREMENTS

Abstract

Injecting surfactant into a hydrocarbon reservoir stands out as a highly effective method for EOR due to its ability to reduce water/oil IFT and alter rock wettability in certain cases. However, the efficiency of this process is compromised in heterogeneous reservoirs, especially carbonates, characterized by significant permeability variations. This study presents findings from three coreflooding experiments on heterogeneous carbonate core samples with different permeabilities. The experiments were conducted under representative reservoir conditions of 100 °C, pressures higher than 3,000 psi, and seawater salinities and formation water of 57,745 ppm and 213,768 ppm, respectively. In each experiment, seawater was continuously injected followed by continuously injecting a 2,500-ppm solution of in-house synthesized Gemini surfactant. Results revealed that the recovery factor was highest in low-permeability rocks and lowest in high-permeability rocks for both seawater and surfactant floods. Surfactant floods yielded additional

recoveries of 31%, 23%, and 19% for low, medium, and high-permeability samples, respectively. Nuclear magnetic resonance (NMR) analysis on short analogous core plugs at different flooding stages confirmed these results. Effluent analysis on the produced aqueous phase indicated that dynamic retention was highest (0.467 mg/gm-rock) in the lowest permeability and lowest (0.146 mg/gm-rock) in the highest permeability rock. NMR analysis suggested that the surfactant's recovery performance and dynamic retention were influenced by the larger surface area of low-permeability rocks, facilitating increased contact with the surfactant. Utilizing NMR monitoring in this work enhances EOR insights through integrated studies and coreflooding experiments and establishes a novel framework for complex reservoir conditions.

This work is available at: <https://doi.org/10.1016/j.geoen.2024.212764>.

5.1 Introduction

Water injection into hydrocarbon reservoirs is a widely used method to enhance oil recovery and sustain reservoir pressure. However, the substantial interfacial tension (IFT) between the injected water and the existing oil leads to a significant portion of crude oil being left unrecovered, resulting in suboptimal recovery rates [224]. Consequently, it becomes imperative to minimize the IFT between oil and water for more effective oil displacement. One approach to achieve this is by incorporating surfactants into the injected water as part of a chemical enhanced oil recovery (cEOR) process [225]. Certain surfactants not only decrease the IFT between oil and water but also can transform the rock's condition from oil-wet to either neutral or weakly water-wet, thereby contributing significantly to improved oil recovery [152,153,158,159]. The reduction in IFT and the

alteration of rock wettability, as indicated by the contact angle, are both pivotal factors influencing the capillary number, N_c , defined by Eq. 5-1:

$$N_c = \frac{\mu \times v}{\sigma \cos \theta} \quad (5-1)$$

where μ is the viscosity, v is the flow velocity, σ is the interfacial tension, and θ is the contact angle. Surfactant flooding has, thus, been widely applied for boosting the oil recovery from hydrocarbon reservoirs [169,226–228].

Surfactants are amphiphilic compounds having a water-soluble (hydrophilic) head and a water-insoluble (hydrophobic) tail [161,229,230]. Cationic, anionic, nonionic, and zwitterionic surfactants are the commonly employed classes of surfactants in EOR applications [231]. Significantly, several studies on surfactant flooding have noted favorable production responses from carbonate rocks when cationic surfactants are introduced [259]. The favorable result is ascribed to the formation of ion pairs between the cationic head groups of surfactants and the carboxylate components of the oil [260–265]. The formation of these ion pairs is considered a crucial factor in anchoring the oil phase on carbonate rock surfaces [266,267]. Through the formation of ion pairs, cationic surfactants aid in detaching adsorbed carboxylates, leading to the restoration of the hydrophilic nature of the mineral surface.

As a novel class of surfactants, Gemini surfactants have also been used for EOR applications owing to their superior characteristics [232–234]. They show exceptional properties such as a low critical micelle concentration (CMC) and a satisfactory ability to lower oil/water IFT. Their wetting, foaming, and rheological properties as well as high solubility in water make them of great interest for applications in the oil and gas sector

[182,184,187,188]. They differ from conventional surfactants in that their structures possess a spacer at or near the hydrophilic heads which connects more than one hydrophobic tail group and hydrophilic head group [235,236]. However, limited work is reported in the literature about the applicability of Gemini surfactants, specifically in EOR [181,237–241,244]. Additionally, most of the reported studies on oil recovery by Gemini surfactants are applied on sandstone rocks [181,243,245,246,248,268–270].

Carbonate reservoirs, encompassing over 60% of the world's proven oil reserves [162–164], pose several challenges for EOR applications. Operating conditions of these reservoirs are usually difficult where reservoir temperatures exceed 85 °C and connate water's salinity is higher than 100,000 ppm [166,167]. Wettability in carbonate reservoirs is diverse, ranging from strong oil-wet conditions to mixed-wet states [166,171,172]. Moreover, rock permeability varies from very low to extremely high due to the existence of natural fractures, faults, and vugs, which result in poor water sweep efficiency [168–170]. The need for the development and screening of surfactants that are tolerant to high salinity and high temperature (HTHS) conditions is still crucial. This is because these conditions along with other affecting factors, such as the pH and rock lithology, significantly affect the performance of surfactant flooding [160,161].

The latter challenge, along with the others, makes it of great importance to evaluate the performance of surfactant flooding over a wide range of rock permeability. Several authors have investigated the injection of varying EOR agents through rocks of different permeabilities. Z. Liu et al. [271] studied the influence of the pore network on the performance of surfactant/polymer flooding through conglomerate rocks of different permeability. Mejia et al. [272] used micromodels having high-permeability fractures to

study the oil recovery by the injection of tridecyl alcohol propoxy sulfate surfactant. Through spontaneous imbibition experiments, Deng et al. [198] examined the effect of permeability on the oil recovery performance of a Gemini surfactant when wettability is the dominant oil recovery mechanism using spontaneous imbibition tests. Other scholars studied the surfactant EOR process through either tight or fractured/high-permeability rocks [170,217,273–277]. Among all, however, no available work has investigated the EOR performance of a cationic Gemini surfactant through coreflooding experiments in heterogeneous carbonate rocks. Also, only a few works have been published on the utilization of nuclear magnetic resonance (NMR) as a supportive technique for the evaluation of surfactant and chemical flooding [224,271].

This work aims to evaluate the internally synthesized, quaternary ammonium, cationic Gemini surfactant (GS) as an EOR agent for applications in heterogeneous Indiana carbonate rocks of different permeabilities under HTHS experimental conditions. The investigational work involved carrying out several coreflooding experiments by injecting a 2,500 ppm GS solution following a seawater flood. Nuclear magnetic resonance (NMR) was applied as an auxiliary technique at the end of different flooding stages to help explain the results attained. Additionally, effluent analysis using high-performance liquid chromatography (HPLC) was conducted at the end of each flood to evaluate the dynamic retention characteristics of the used surfactant at different permeability scales. The results demonstrate the efficacy of the examined GS as an EOR agent and its applications in different permeability carbonate rocks under HTHS conditions. In this study, employing NMR monitoring for EOR is a groundbreaking method, offering insights at the pore level beyond static measurements. Innovatively correlating NMR findings with EOR

performance, especially in grasping surfactant effectiveness amid rock heterogeneity, enhances our understanding. NMR assessments of pore size distribution, fluid distribution, and saturation provide a comprehensive perspective on EOR efficiency. The integration of NMR and adsorption studies in this research also yields practical insights for optimizing EOR strategies in challenging carbonate reservoirs, potentially leading to more effective and economically feasible practices. Integrating coreflooding experiments with NMR and dynamic retention analysis establishes a novel framework for EOR studies, particularly in addressing complex reservoir conditions and varying rock properties.

5.2 Experimental Work

5.2.1 Materials

Rock Samples. In this work, three individual Indiana limestone core samples were used to perform three different coreflooding experiments. Calcite is the most dominant mineral of these rocks, as shown by the X-ray diffraction (XRD) testing of a powder sample from these rocks. The samples were labeled as IMP-M2, IL-22, and IHP-HP1 representing rocks with low, medium, and high permeability, respectively. Shorter plugs from the same cores were also prepared for NMR studies where the same flooding tests were repeated on these plugs (explained later). Each plug is believed to be representative of its parent core sample as confirmed by the data presented in **Table 5-1**. As will be shown under the NMR results, the samples exhibited diverse pore size distributions, which are frequently identified in Indiana limestone [278]. This indicates the samples' heterogeneity and aligns with the objective of the study. This characteristic makes them effective representatives of the carbonate rocks.

Salts and Brines. For water and chemical injection, high-salinity brine (SW) was prepared with a salinity of around 57,745, which simulates the Arabian Gulf water [193]. Formation brine, simulating formation water (FW) salinity of about 214,000 ppm, was also synthesized for saturating the rock samples to mimic reservoir conditions. Provided by Sigma Aldrich, different laboratory-grade salts were dissolved in deionized water (DIW) for the preparation of the FW and SW. The prepared SW and FW brines have the compositions presented in **Table 5-2**. Filter paper was also utilized to filter the FW and SW for the removal of any suspending particles or undissolved solids. Room conditions viscosity and density of the SW, FW, and the surfactant solution are listed in **Table 5-3**.

Table 5-1: Rock Samples' Properties

Sample ID	Length (cm)	Diameter (cm)	Porosity (%)	Liquid permeability (mD)	Remark
IMP-M2	10.16	3.752	13.39	9.74	Low permeability
IMP9	5.311	3.752	14.55	12.3	
IL-22	10.16	3.752	16.16	99.9	Medium permeability
IL-22S	5.311	3.752	16.12	101.3	
IHP-HP1	10.16	3.752	15.3	1689.4	High permeability
IHP5	5.311	3.752	13.92	1697.7	

Table 5-2: Compositions of prepared formation brine and seawater

Salts	Concentration (ppm)	
	SW	FW
NaHCO ₃	165	487
Na ₂ SO ₄	6,339	517
NaCl	41,172	150,419
CaCl ₂	1,802	52,788
MgCl ₂	8,266	9,555
TDS →	57,745	213,768

Table 5-3: Physical properties of fluids used

Fluid	Density (g/cc) @ 21.5 °C	Viscosity (cP) @ 21.5 °C
Synthesized SW	1.0406	1.1243
Synthesized FW	1.0412	2.0028
GS solution (2,500 ppm in SW)	1.0417	1.1745
Crude Oil	0.8743	17.3

Crude Oil. To saturate and age the rock samples, degassed (i.e., stock tank) crude oil collected from the production facility of a carbonate reservoir located in the Middle East was used. To avoid any flow blockage during oil floods which could be caused by the presence of fine particles or residues, an in-line filter (5- μ m) was used to filter the crude oil. The viscosity and density of crude oil at lab conditions are also shown in **Table 5-3**. At flooding conditions of 100 °C and 3,000 psi the crude's viscosity was 2.482 cP. The saturates, aromatics, resin, and asphaltenes content of the crude oil is 23.05%, 44.22%, 22.97%, and 9.76%, respectively, as revealed by IATROSCAN MK-7s FID. Acquired using the ASTM Titration technique, the total acid number (TAN) and total base number (TBN) of the crude oil are 0.04 mg KOH/g and 0.76 mg KOH/g, respectively.

Chemicals. Ethoxylated, quaternary ammonium, cationic, Gemini surfactant (GS) synthesized in-house was used in this work whose structure is shown in **Figure 5-1**. The synthesis and preliminary evaluation of the GS were presented by Shakil Hussain et al. [194]. The surfactant solution was prepared at a concentration of 2,500 ppm by dissolving the GS in the simulated SW. More details about the screening and prior evaluation of the surfactant as well as the selection of such concentration are presented in the previously published articles [194–196,198–203]. However, it is worth mentioning that this surfactant

Coreflooding Experiments

Apparatus. A schematic diagram of the core flooding setup used in this work is illustrated

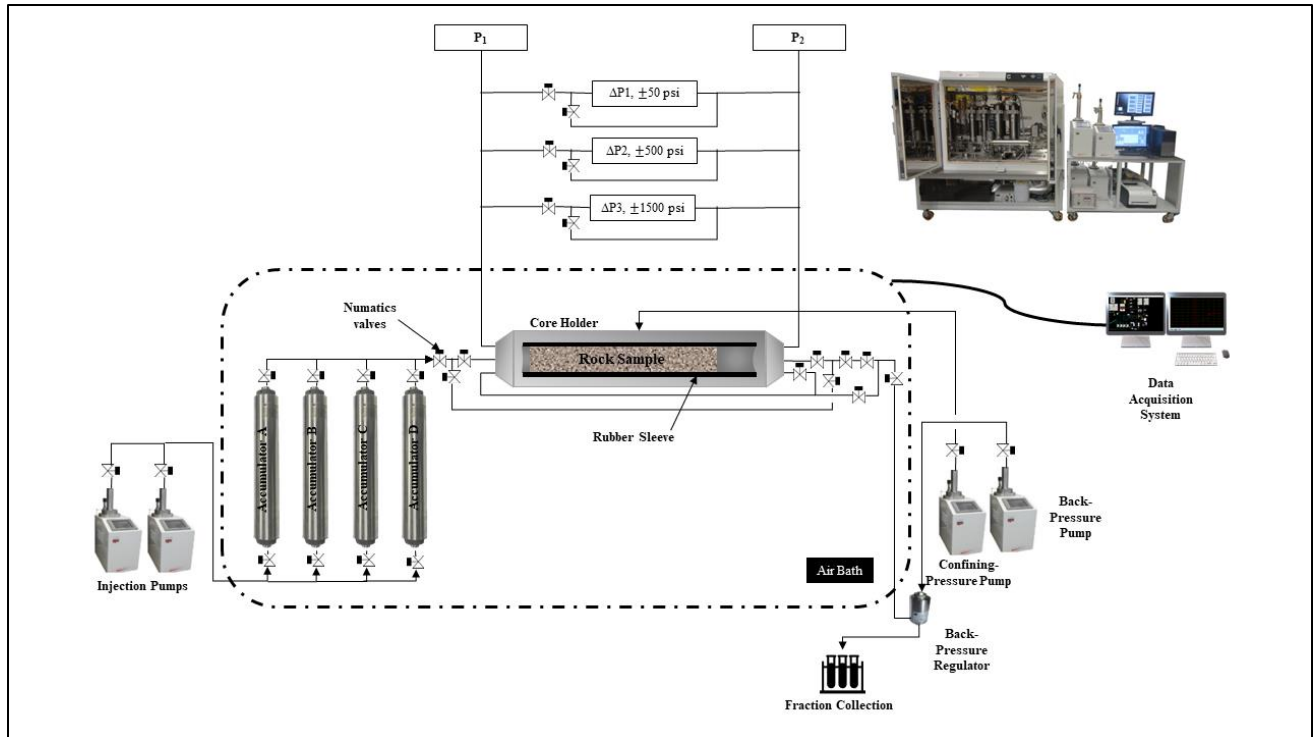


Figure 5-2. Illustration of the coreflooding setup

Preparation of core samples. The vacuum saturation method was used to saturate each core sample with the prepared formation brine which was then injected through each sample to measure its liquid permeability. To determine the initial water saturation (S_{wi}), a variable-rate drainage process was employed by flooding each core sample with multiple pore volumes (PVs) of crude oil. The resultant initial water saturations fell within the range of 33% to 36%. The relatively elevated irreducible water saturations can be attributed primarily to the presence of microporosity in the rocks, a characteristic feature of most carbonate rocks [206,207]. The rocks then underwent a 21-day aging period immersed in crude oil at 100 °C under static conditions. This approach aimed to enhance the adsorption of the polar components of the oil onto the rock surface. The aging process was also important to ensure that the samples exist at extreme oil-wet conditions [207].

Oil recovery experiments. Each sample was loaded into the core holder and heated to 100 °C and then flooded under pore and confining pressures set at 3,000 and 4,000 psi, respectively. A few PVs of the crude oil were initially injected at 1 cc/min to establish the flow conditions and replace the aging crude oil. This was followed by a continuous flood with SW until oil production virtually ended (i.e., water cut reached 98% and above) in which nearly 4 – 5 PVs of SW were injected. Thereafter, chemical flooding ensued, and this involved flooding with 5 – 6 PVs of the GS solution. This flood was also terminated when oil production ceased. Both the SW and surfactant floods were conducted at a flow rate of 0.25 cc/min, which corresponded to a Darcy velocity of 1 ft/day. 15-ml glass vials were used to collect the produced effluent at 20-minutes interval (5 ml in each vial). Some vials required heating up to 70-90 °C or adding a pre-determined amount of toluene to break the microemulsion for accurate reading of the volumes [208]. **Table 5-4** summarizes the flooding tests conducted in this work. Despite the low CMC of the GS, which is mostly less than 100 ppm, it is not reasonable and effective to use such a low concentration since it may result in poor flood performance due to surfactant retention. On the other hand, high surfactant concentrations may lead to higher costs. Therefore, we believe that the 2,500-ppm concentration is still reasonable and cost effective compared to surfactant concentrations reported in the literature, which often require cosurfactants and cosolvents to aid the surfactant's performance.

Table 5-4: Summary of coreflooding experiments

Experiment No.	Permeability	Core sample	Flooding Steps	Injection rate (cc/min)
1	Low	IMP-M2	4. SW 5. GS solution at 2,500 ppm	0.25
		IMP9		
2	Medium	IL-22		
		IL-22S		
3	High	IHP-HP1		
		IHP5		

5.2.3 NMR Measurements

Motivation and physics. The following equation describes the governing phenomena of NMR T_2 relaxation in porous media [279]

$$\frac{1}{T_2} = \frac{1}{T_{2,bulk}} + \frac{1}{T_{2,surface}} + \frac{1}{T_{2,diffusion}} = \frac{1}{T_{2,bulk}} + \rho_2 \frac{S}{V} + \frac{1}{12} D (\gamma g t_e)^2 \quad (5-2)$$

where $T_{2, bulk}$ is relaxation due to the bulk fluid dipolar interaction (ms), $T_{2, surface}$ is relaxation due to the surface interaction (ms), $T_{2, diffusion}$ is relaxation due to the fluid diffusion (ms), ρ_2 is the transverse surface relaxivity ($\mu\text{m/s}$), S/V is the specific surface area to the pore volume ratio ($1/\mu\text{m}$), D is the diffusion coefficient of the bulk fluid (m^2/s), γ is the ^1H proton nuclei gyromagnetic ratio (MHz/T), g is the internal magnetic field gradient (T/m), and t_e is the inter-echo time (ms).

It is well-known that NMR-derived permeability is directly proportional to the T_2 logarithmic mean value (T_{2LM}) for single-fluid saturated rock cores based on the Schlumberger Doll research model [280]. This can be verified by investigating Eq. 5-2. For cases where NMR relaxation is due to the surface properties and the pore volume alone, Eq. 5-2 can be reduced to [281]:

$$\frac{1}{T_2} = \frac{1}{T_{2,surface}} = \frac{1}{T_{2LM}} = \rho_2 \frac{S}{V} \quad (5-3)$$

The ratio of the specific area of the pore to the pore volume, which is correlated to the pore size, is as follows:

$$\frac{S}{V} = F_s/r \quad (5-4)$$

where F_s is the shape factor, which depends on the pore model, and r is pore-throat radius, which is related to the permeability of the rock.

A comparison of Eqs. 5-3 and 5-4 yields:

$$T_{2LM} = \frac{1}{\rho_2 F_s} r = C \times r \quad (5-5)$$

where C is a constant. Eq. 5-4 suggests that the NMR T_{2LM} is inversely proportional to the surface area of the rock sample. Also, Eq. 5-5 reveals that the larger the pore throat radius (or permeability), the larger the T_{2LM} is. Knowing these relations will, therefore, help in explaining the results of the oil recovery and the dynamic retention values obtained from samples with different permeabilities.

Apparatus. NMR measurements in this work were obtained with the NMR Geospec2 Oxford instrument operating at a magnetic field strength of 0.05 Tesla (equivalent to a Larmor frequency of 2.23 MHz for ^1H) at ambient conditions.

Procedure. The NMR measurements were performed on each plug sample. The measurements were conducted at the end of each stage of the plug's preparation and flooding such as FW saturation (i.e., 100% S_{wi}), after establishing the irreducible water saturation (i.e., before and after aging of the rock), after SW flooding, and at the end of the

GS flooding. Although removal of the plug sample from the core holder at the end of each flooding stage to conduct NMR measurements may result in the disturbance of the capillary forces [282], this procedure was believed effective and did aid in proving the concept the current study was aimed at.

Before loading the plug sample into the NMR sample holder, the fluid sticking to the outer surface of the plug was removed by rolling the plug on a blank paper. This procedure obviated the appearance of such fluid in the T_2 relaxation as bulk fluid. The plug was then wrapped with plastic wrap (i.e., NMR-silent material) to prevent loss of fluid saturation during the measurements. The Carr-Purcell-Meiboom-Gill CPMG pulse sequence was applied to acquire the T_2 relaxation time data by adjusting the number of echoes to capture the full signal decay at a fixed echo time of 0.1 ms [283,284]. A signal-to-noise ratio minimum of 100 was set as a constraint rather than fixing the number of scans. The CPMG signal decay was inverted to T_2 relaxation time distribution using Tikhonov regularization methods [285].

5.2.4 Effluent Analysis

The surfactant's dynamic retention was also monitored during the flooding process by analyzing the produced effluent. It was calculated using Eq. 6, which applies simple material balance [199]:

$$\Gamma_{dynamic} = \frac{C^0 V - \sum_{i=1}^N C_i V_i}{m_r} \quad (5-6)$$

where $\Gamma_{dynamic}$ is the dynamic retention of surfactant (mg/g-rock), C^0 (ppm) is the initial surfactant concentration, V (L) is the cumulative volume of pumped surfactant solution, C_i

(ppm) is the surfactant concentration collected at time step i , V_i (L) is the effluent's volume at time step i , N is the number of vials, and m_r (g) is the weight of the core plug prior saturation.

The concentration of the surfactant in the produced effluent was obtained using the potentiometric HPLC, which had been proven an effective technique [173,202,213–215]. The Agilent 1200 series HPLC was employed with an attached evaporative light scattering detector (ELSD). Acetonitrile (C_2H_3N) was the mobile phase A and a 0.1 M ammonium formate (NH_4COOH) with pH of 4.3 adjusted by formic acid (CH_2O_2) as the mobile phase B. The HPLC utilizes an acclaim surfactant plus column ($3\ \mu m$, $4.6 \times 150\ mm$). The produced aqueous phase collected in the vials during the flooding test was separated from the oil phase and subjected to this analysis. The concentration of the surfactant in each vial was then calculated from the calibration curve constructed for the surfactant solution before running the HPLC analysis. The chromatographic integral area is then plotted with surfactant concentration to construct the calibration curve [215].

5.3 Results & Discussions

5.3.1 Oil Recovery Results

Seawater flooding. Figures 5-3 through 5-5 present oil recovery and oil saturation profiles versus PVs injected for the three flooding experiments. The eventual oil recovery factors at the end of SW floods were 55.1%, 47.4%, and 40.6% OOIP for the low-, medium-, and high-permeability samples, respectively, which required around 6, 5, and 3.5 PVs of injected SW to achieve those recoveries. The corresponding residual oil saturations were

30.1%, 35.2%, and 38.7%, respectively. It is worth noting that the oil recovery factor after injecting about one PV through each sample was around 40%, 33%, and 34% OOIP, respectively, indicating that a smaller amount of injected SW could recover more oil from the low-permeability sample than the higher-permeability ones. This can be attributed to the high-permeability sample's large and continuous flow paths, which allowed SW to pass through the rock without sweeping much of the resident oil. On the other hand, the relative lack of such flow paths in the low-permeability sample forced SW to invade a larger portion of the pore space resulting in the highest oil recovery [286].

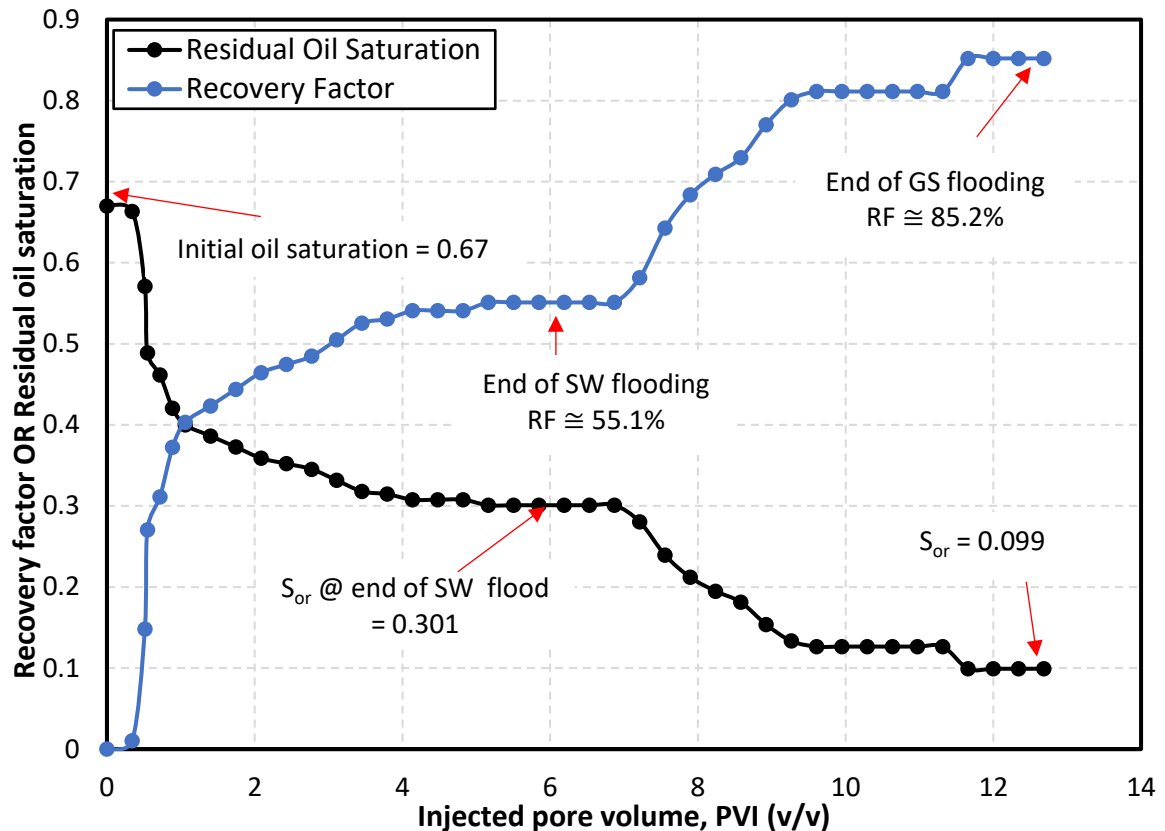


Figure 5-3. Results of the oil recovery from the low-permeability flood

Performance of chemical flooding. Figure 5-3 also shows the oil recovery performance of the GS solution with the low-permeability sample along with the corresponding residual

oil saturation. The pumped GS solution (nearly 6 PVs) resulted in a further oil recovery of approximately 30% OOIP, increasing the overall oil recovery factor to around 85.2% at the end of the flooding process. The residual oil saturation was reduced to nearly 10% at the end of the chemical flood. Similarly, **Figure 5-4** and **Figure 5-5** show the recovery factor along with the residual oil saturation for the medium- and high-permeability samples, respectively. It required injecting nearly 6 PVs of the GS solution to recover an additional 23% and 20% OOIP from the medium- and high-permeability samples, respectively. The corresponding residual oil saturations are 20% and 28% post chemical injection. As justified during the SW flooding, the highest oil recovery from the low-permeability rock could be due to the better conformance control within that sample and the smaller pore sizes compared to the higher-permeability rocks. Moreover, the three figures reveal that the largest portion of oil could be recovered continuously from the low-permeability sample after injecting almost 3.5 PVs of the GS solution without any intermittent. On the other hand, the oil recovery profile for the higher-permeability sample appeared as a step-like profile. This indicates that the rate of oil recovery is faster with the low-permeability sample than that with the higher permeability ones. Finally, comparing the rate of oil recovery between the three samples tested in this work supports the conclusion made by Deng et al. [198], who showed that oil recovery by wettability alteration is faster in low-permeability rocks. Wettability alteration has also been proven to be the GS's main oil recovery improvement mechanism [258]. To illustrate, the measurements of contact angle and IFT discussed in earlier publications indicate that the tested Gemini surfactant is more effective in changing the wettability of rocks than in reducing the IFT between oil and water. Specifically, the Gemini surfactant exhibited the ability to transition the rock's

wettability from a pronouncedly oil-wet condition to an intermediate or water-wet state. This shift was identified through contact angle measurements and a noticeable alteration in the oil/water relative permeability curves, as discerned from coreflooding experiments utilizing the JBN method. However, it is important to note that, under laboratory conditions, the oil/water IFT was only reduced to approximately 3 mN/m in a surfactant solution with a concentration of 2,500 ppm. Given the absence of achieving an ultralow IFT with this surfactant, it can be inferred that the primary mechanism contributing to enhanced recovery is the alteration of wettability. This could be achieved by forming ion-pair between the cationic surfactant molecules and the negatively charged carboxylic groups on organic molecules, leading to the desorption of these molecules from the rock surface [287]. As will be demonstrated under the NMR section, low-permeability rock samples feature small pore throats and large surface areas relative to those of the higher permeability ones. The larger surface area would enhance surfactant interaction with the rock surface, which resulted in favorable wettability alteration of the rock and, hence, better oil recovery.

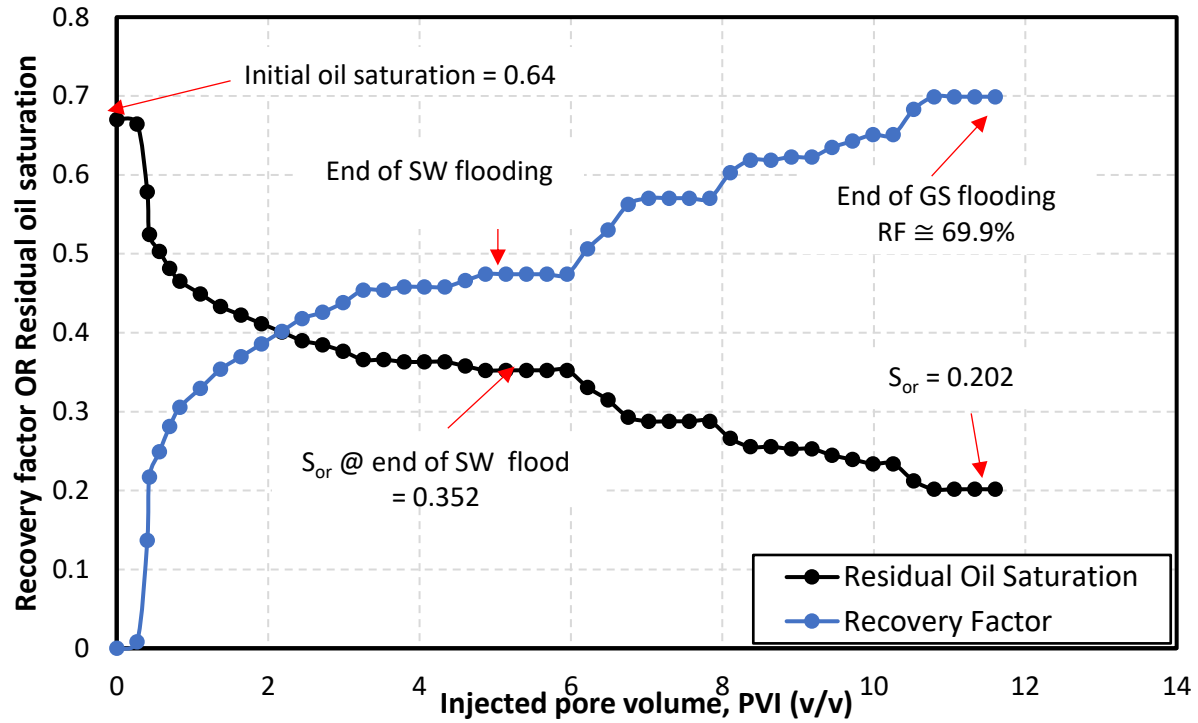


Figure 5-4. Results of the oil recovery from the medium-permeability flood

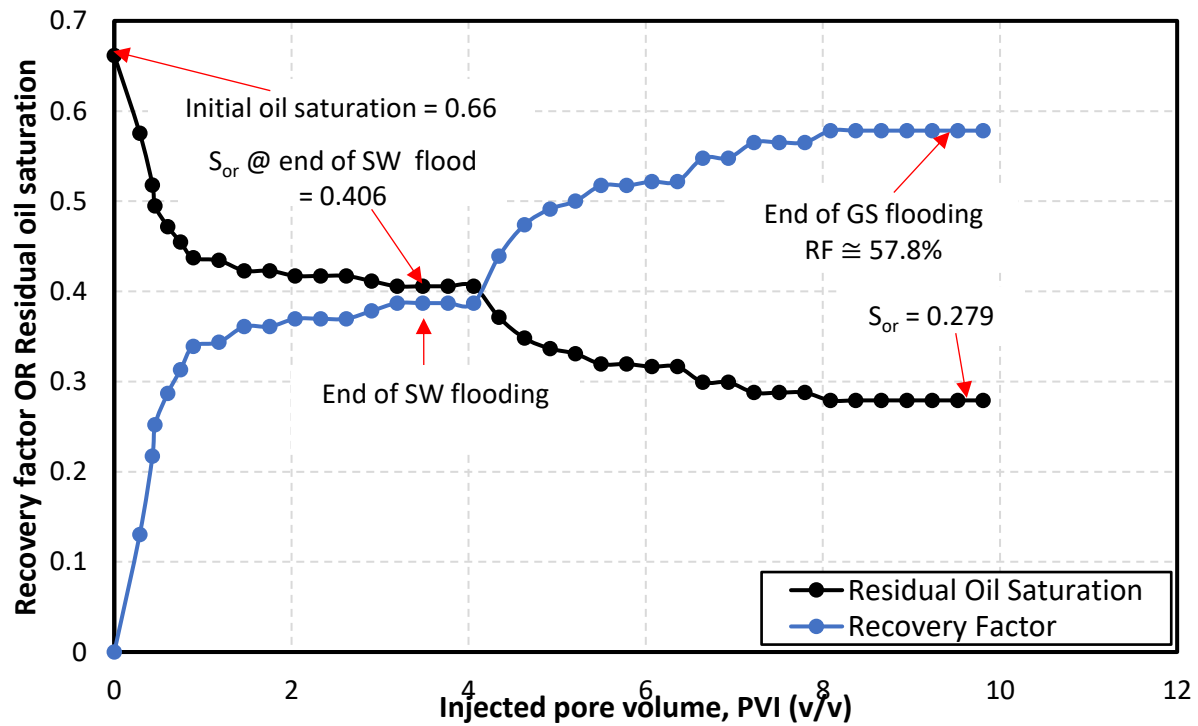


Figure 5-5. Results of the oil recovery from the high-permeability flood

Pressure drop profiles. Figure 5-6 presents the differential pressure across the cores throughout the floods. The ΔP curves for the low and medium permeability plugs were almost identical except that the former was about 10 times larger than the latter. This ratio is nearly equal to the ratio of the two plugs' permeabilities. The step drop in ΔP at about 5 PVs coincided with the start of the GS flood, which further reduced the oil saturation. Finally, the reading of the pressure drop for the highest-permeability sample (Exp. 3) was very low and we could notice that it increased from around 0.1 psi at the beginning of the flooding to around 0.4 psi at the end of the GS injection. Although some investigators have attributed the increase in the pressure drop during surfactant flooding to surfactant adsorption [222], it cannot be the case for this flooding test as the effluent analysis (discussed later) showed a minimum surfactant dynamic retention after flowing through this high-permeability rock. Others could have attributed it to the formation of the high viscosity microemulsion, which results in the Jamin effect that is responsible for the increase in the pressure drop within the pore network [219–221]. This, however, is still not the case since the increase in the pressure drop was already noticed even during the SW flooding, at which there is no possibility for the formation of microemulsion. If another reason comes into play, this could be due to the high residual oil saturation in the sample where an oil bank is formed but could not be displaced by the injected fluids. This is because the oil bank is bypassed due to the flow of the injected SW or GS through the larger flow paths in the high-permeability sample.

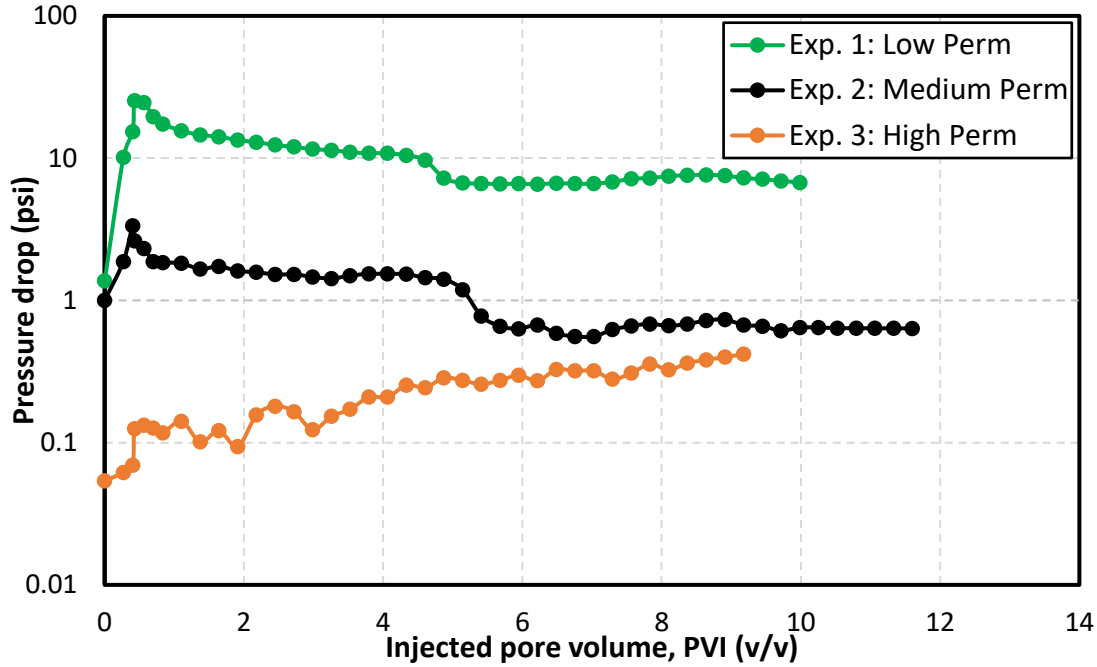


Figure 5-6. Profiles of the pressure drop across the cores during SW and GS injection

5.3.2 NMR Results

Figure 5-7 presents the T_2 relaxation time distribution of the formation brine and crude oil used in this study. The T_2 peak value of the bulk brine is at 1412.5 msec while the crude oil at 141.25 msec, which is due to the higher crude oil viscosity. The T_2 distribution of crude oil also exhibits a broad range of T_2 components, which is due to the different hydrocarbon chemistries that exist in the crude oil [288].

The T_2 relaxation time distributions for the three different Indiana limestone samples (IMP9, IL-22S, and IHP5) at $S_w = 100\%$ are shown in **Figure 5-8**. The NMR porosity and T_2 logarithmic mean ($T_{2,LM}$) values are also listed in **Table 5-5**. These values support the relation presented in Eq. 5-5 in which higher $T_{2,LM}$ values correspond to higher liquid permeability. Furthermore, the NMR porosity also matches the measured helium porosity. The T_2 distributions for the fully brine-saturated samples indicate the rock core samples

have bimodal pore size distribution. To provide more insights into rock heterogeneity, the $T_{2,peak}$ (i.e., the T_2 corresponding to the peak value at $S_w = 100\%$) for each sample is divided by its corresponding $T_{2,LM}$ as shown in **Table 5-5**. The deviation of the ratio from unity indicates the samples' heterogeneity. The higher the ratio, the higher the heterogeneity of the rock [289]. The values indicate that IMP5 exhibits the least pore size heterogeneity, whose T_2 components span in a narrower range as compared to samples IL-22S and IHP9. **Figure 5-9** illustrates the difference between $T_{2,peak}$ and $T_{2,LM}$.

Table 5-5: Summary of coreflooding experiments

Sample ID	ϕ_{NMR} (p.u.)	$T_{2,LM}$ (ms)	$T_{2,peak}$ (ms)	$T_{2,peak}/T_{2,LM}$	Recovery Factor from NMR (%)
IMP9	15.0	90.0	193.1	2.15	54.4
IL-22S	15.9	111.1	372.8	3.36	43.4
IHP5	14.2	193.6	578.0	2.99	40.2

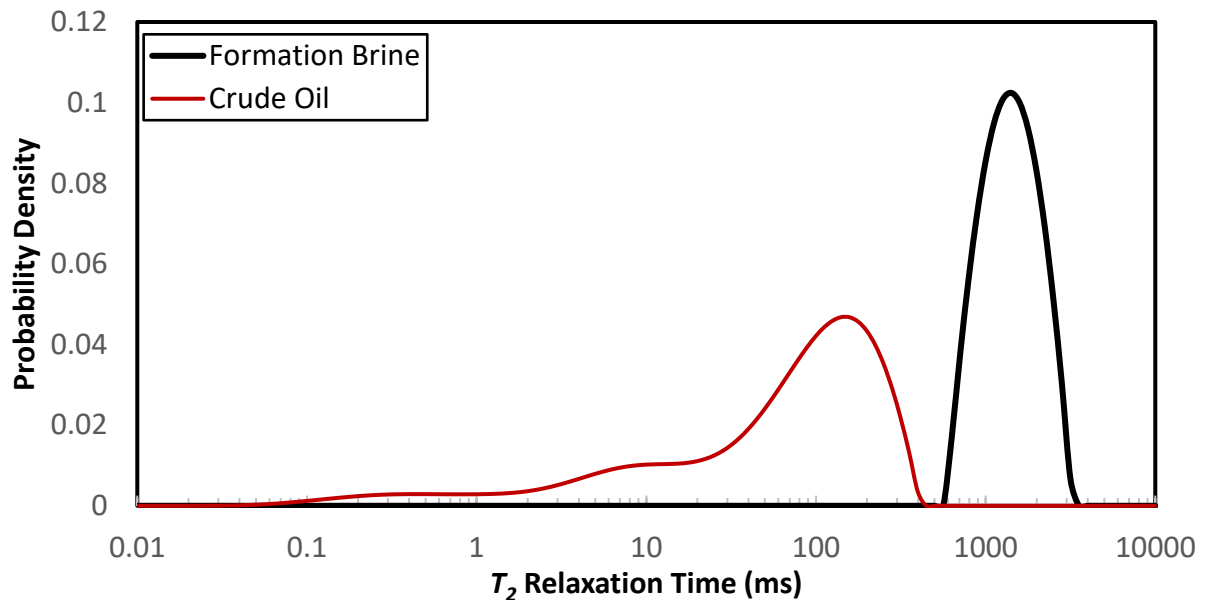


Figure 5-7. Distribution of the T_2 relaxation time for the formation brine and crude oil used in this study

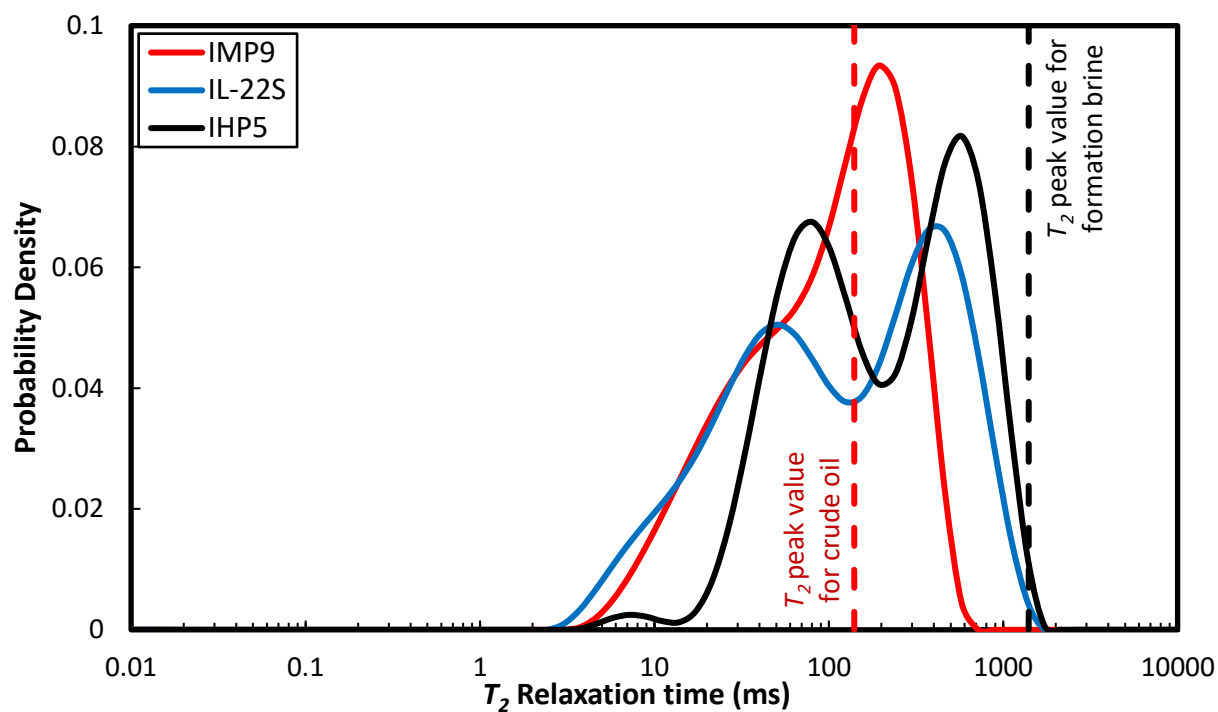


Figure 5-8. Distribution of the T_2 relaxation time at full brine saturation ($S_w = 1$)

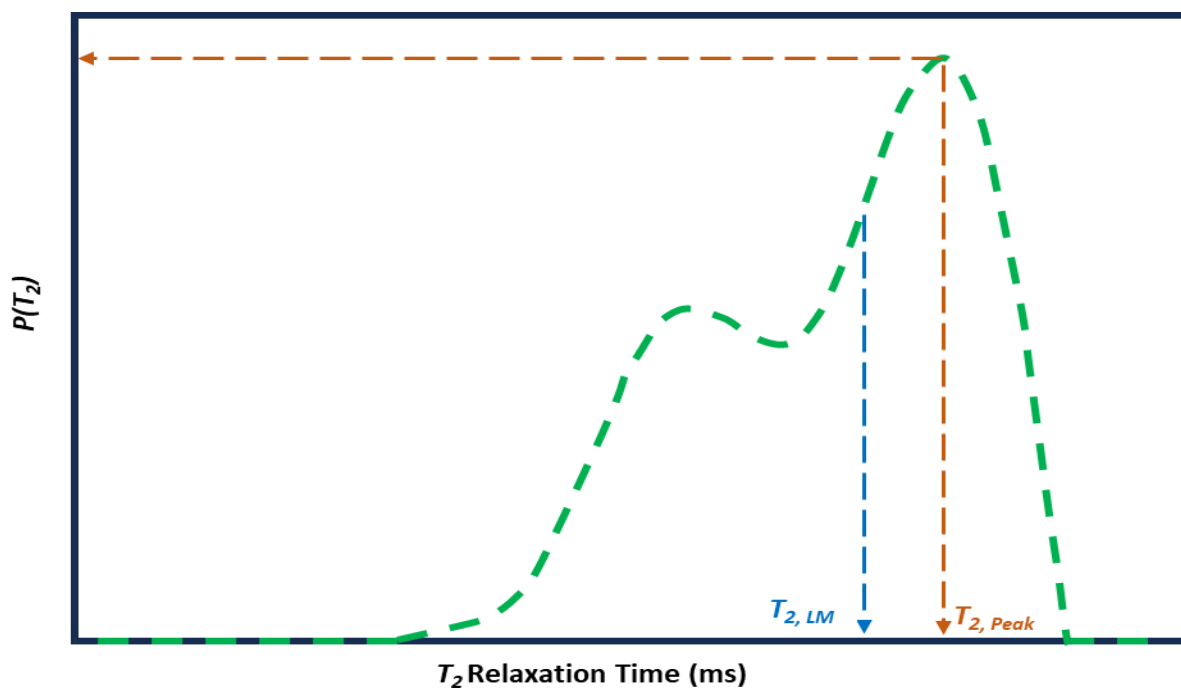


Figure 5-9. Illustration of the difference between $T_{2, LM}$ and $T_{2, peak}$

When the three core plugs were flooded with oil down to irreducible water saturation their T_2 peak values were shifted to 64.49 msec, indicating similar wettability status for all samples as shown in **Figure 5-10**. The shift of the T_2 from the vertical, red-dashed line indicates surface relaxation effects (oil starts to stick to the pore walls) shifting the rock samples into less water-wet condition. However, the bulk relaxation component dominates the T_2 relaxation time distribution because the formation brine is covering most of the pore walls causing the NMR to detect the crude oil as a bulk mobile phase.

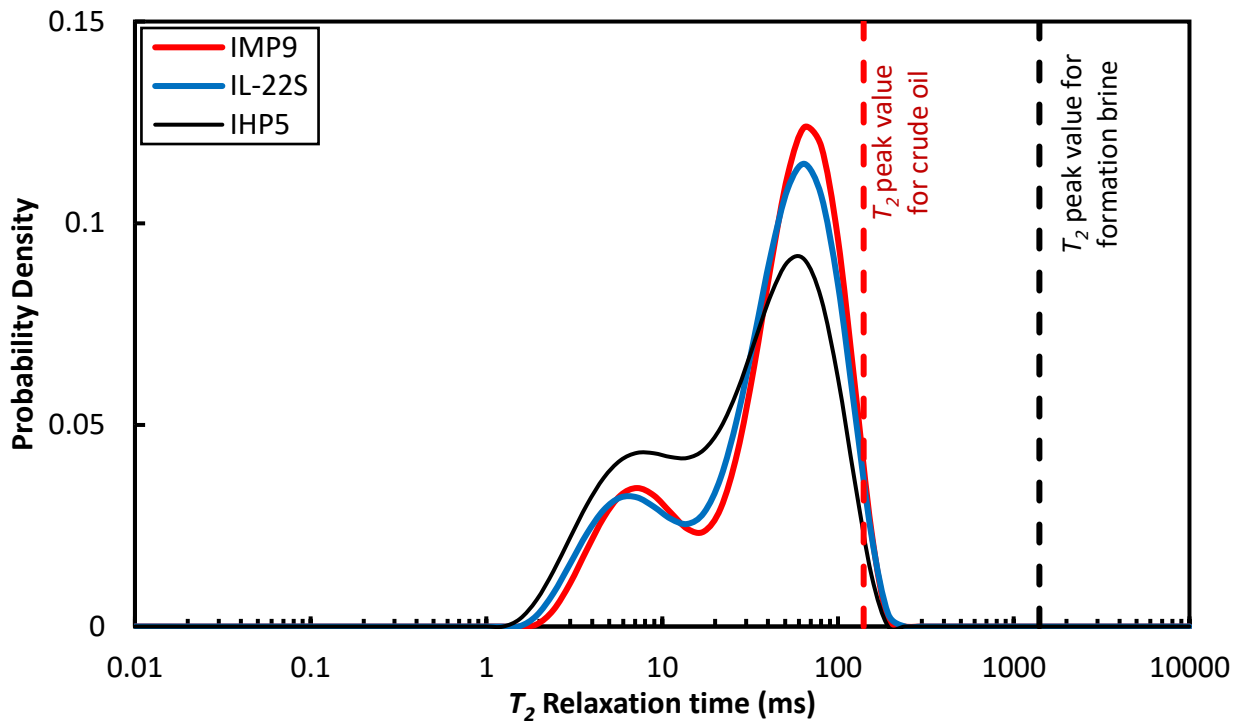


Figure 5-10. Distribution of the T_2 relaxation time after crude oil flooding and aging (Swi)

Seawater was then injected into each sample. The T_2 relaxation time distributions for each sample after SW flooding are plotted in **Figure 5-11**. The appearance of T_2 components that are larger than the bulk crude oil's T_2 relaxation components is due to seawater invasion into the macropores. The amplitude of the larger T_2 components differs from one sample to the other, which indicates different fluids' saturations (different displaced oil

volumes). Generally, a higher oil volume displacement causes a higher T_2 amplitude. From these results, it can be concluded that the displacement of crude oil from sample IMP9 using seawater was the strongest among the different samples due to its largest T_2 magnitude.

The incremental oil recovery following the GS flood is reflected in the increase in the amplitude of the large T_2 components. IMP9 showed the highest recovery of oil (more water in the macropores) as compared to IL-22S and IHP5, which is a similar trend to the SW flood case as demonstrated in **Figure 5-12**. The oil recovery factor was calculated from the T_2 relaxation time distribution using Eq. 5-7:

$$\text{Recovery Facotr from NMR} = \left(\frac{1 - P(T_{2,S_o}) - P(T_{2,S_{wi}})}{1 - P(T_{2,S_{wi}})} \right) \times 100\% \quad (5-7)$$

Based on the schematic diagram shown in **Figure 13** different oil and water saturations are extracted from the T_2 relaxation time distribution after the GS flood. Recovery factors from NMR are an approximate approach to qualitatively evaluate the efficiency of the cEOR. The calculated values in this study (see **Table 5-5**) are in direct correlation with the values obtained from the coreflood tests. The sample with the lowest $T_{2,LM}$ value (IMP9) showed the highest recovery factor from NMR, confirming the coreflood results, whereas sample IHP5 showed the highest recovery factor. A plausible explanation is that the pore structure is relatively less heterogonous in sample IMP9 as confirmed by **Figure 5-8**.

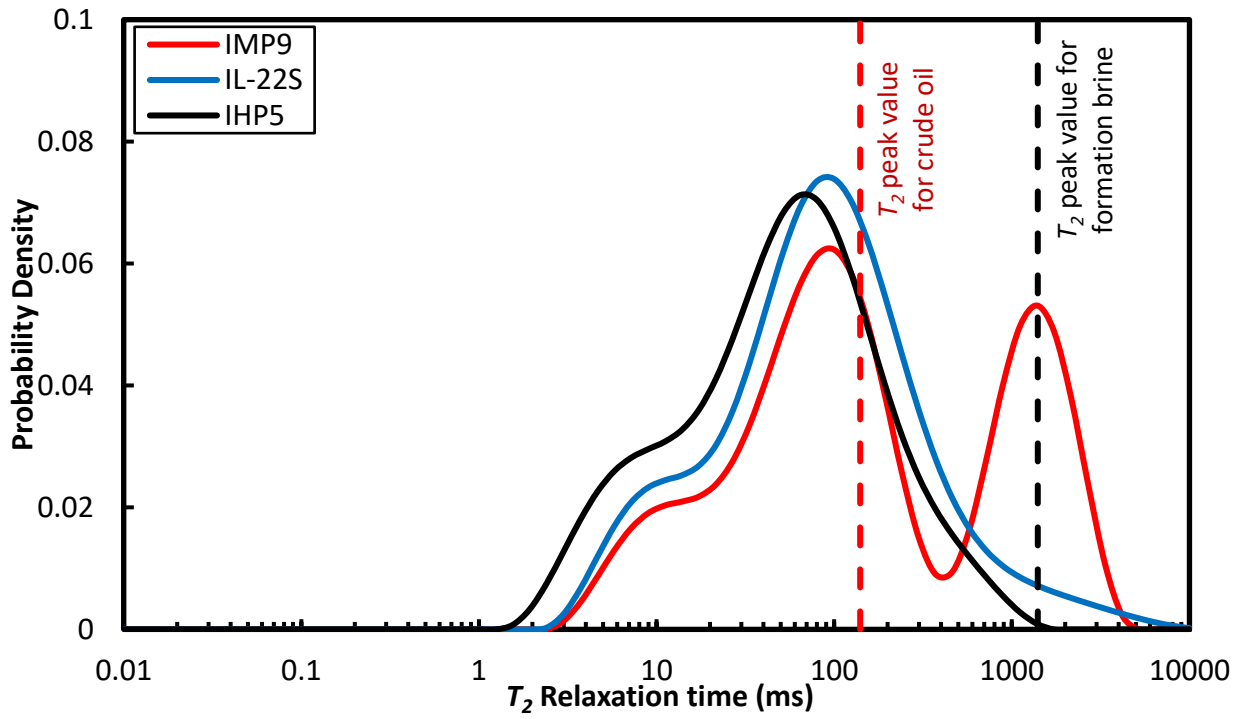


Figure 5-11. Distribution of the T_2 relaxation time after seawater flooding

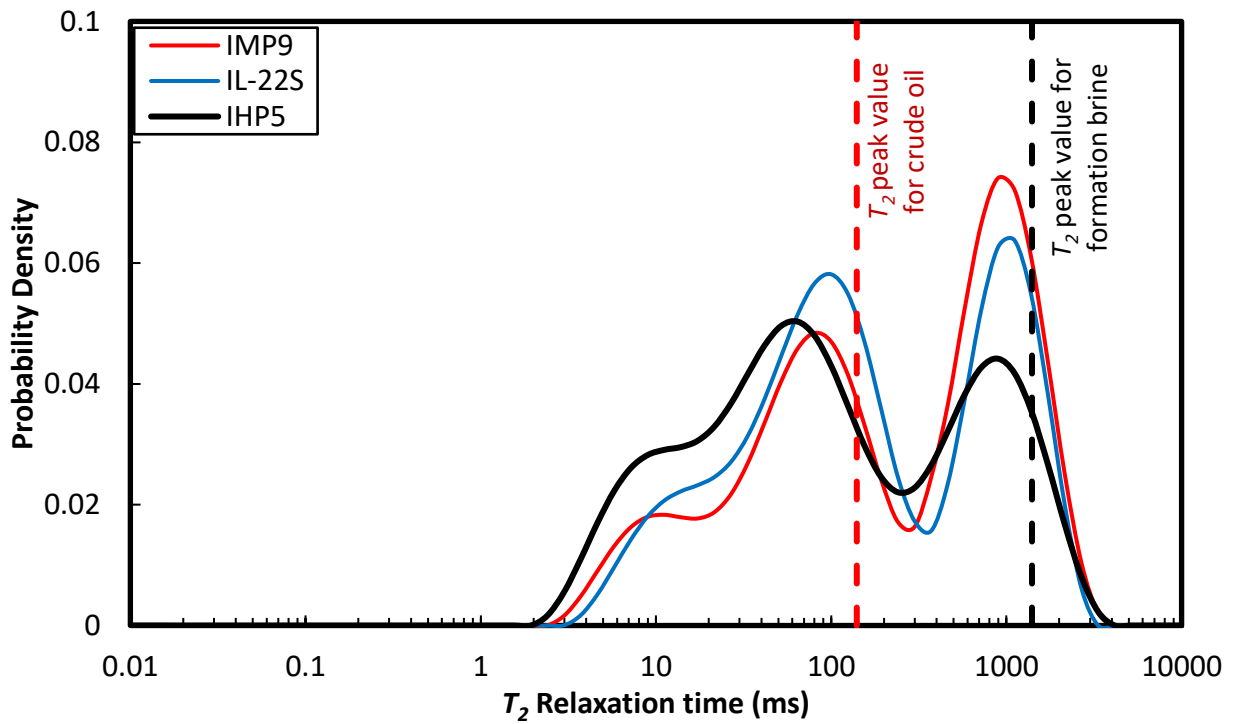


Figure 5-12. Distribution of the T_2 relaxation time after surfactant flooding

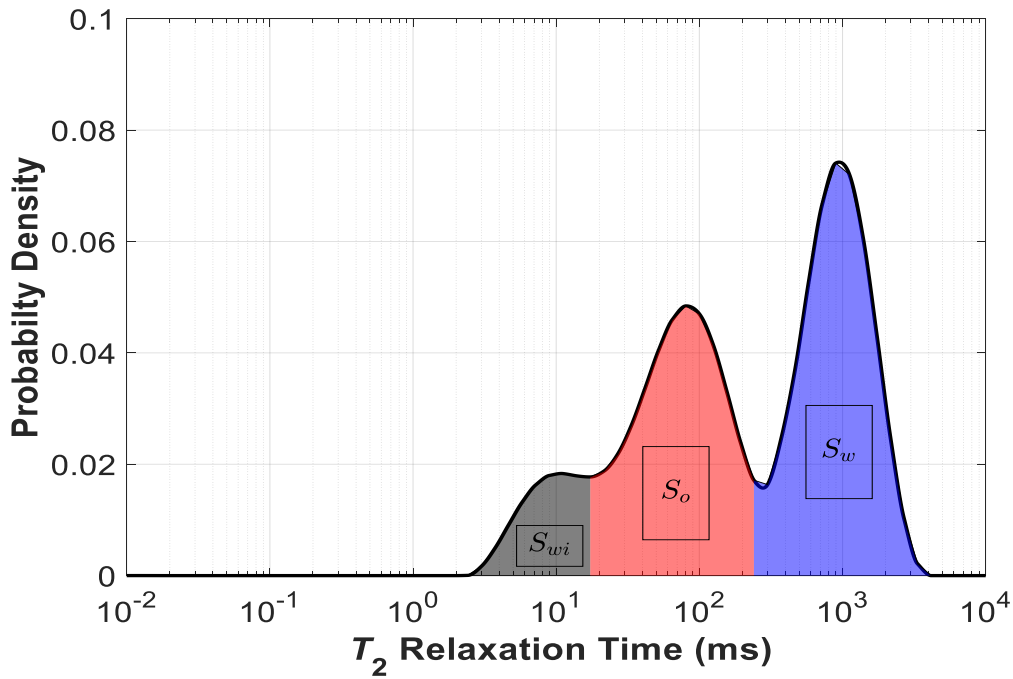


Figure 5-13. Schematic diagram showing the different T_2 peaks and what they correspond to

5.3.3 Effluent Analysis

The red line of **Figure 5-14** presents the concentration of the GS in the effluent during GS-flood's through the low-permeability rock. The maximum concentration of the surfactant was nearly 1,896 ppm throughout the flooding process. There was a gradual increase in the concentration of the GS in the effluent with rock's surface, reflecting good conformance and better contact of the injected surfactant solution before it broke through. Using Eq. 6, the GS's dynamic retention was about 0.467 mg/g-rock. The blue line of **Figure 5-14** shows a similar plot for the medium-permeability rock. The highest concentration reached, and the corresponding calculated dynamic retention are 2,294 ppm and 0.372 mg/g-rock, respectively. For the high-permeability rock, the green line of **Figure 5-14** shows a low dynamic retention value of 0.202 mg/g-rock. More GS adsorption caused by a larger surface area coupled with more GS trapping by smaller pores explain the larger retention

values of low-permeability rock (IMP9/IMP-M2 pair). On the other hand, effluent concentration plots for the medium and high permeability samples show a dramatic and immediate increase in the GS concentration immediately after the injection commenced. These cases also demonstrate the low conformance and limited contact of the injected GS solution with the rock surfaces, resulting in earlier breakthrough of the GS solution. Finally, the partitioning of the GS into the oil phase can also be an attributing reason for its retention and this requires further analysis. **Figure 5-15** offers a comprehensive overview of the results presented in this study.

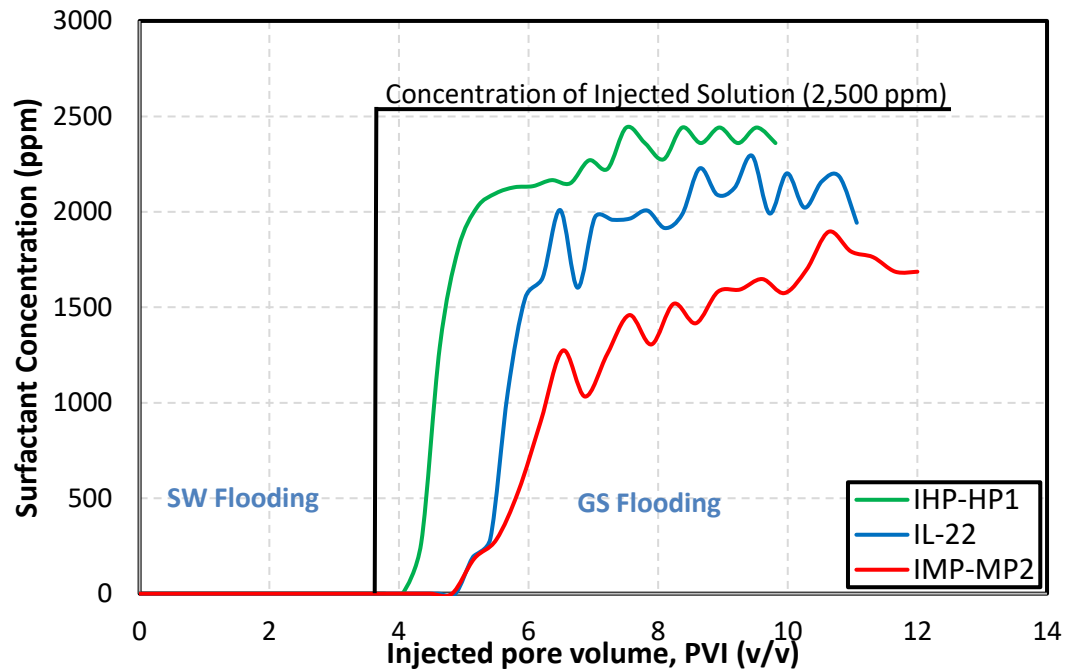


Figure 5-14. Concentration of the GS in the coreflood effluent for all the conducted experiments

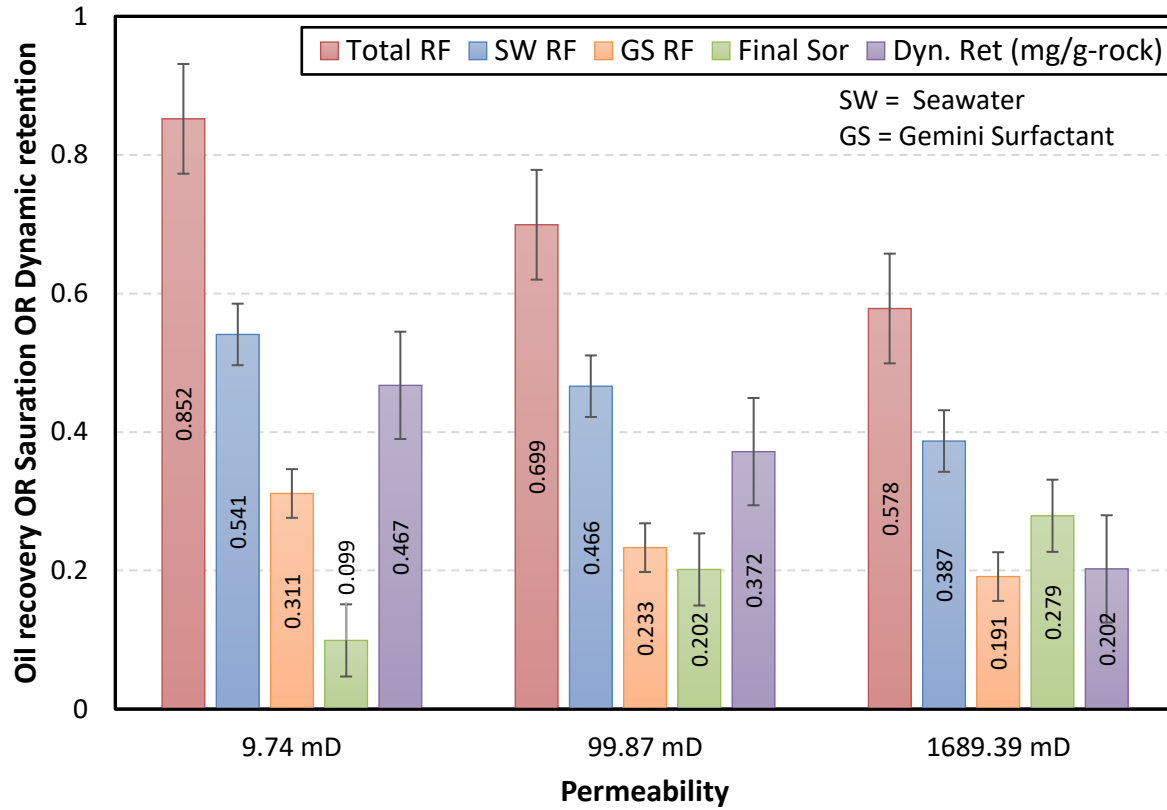


Figure 5-15. Summary of all coreflooding tests

5.4 Conclusions

In this study, the EOR performances of an in-house developed, cationic, Gemini surfactant was evaluated using three limestone rock samples of different orders of permeability. The experiments were carried out using a surfactant solution with a concentration of 2,500 ppm under HTHS experimental conditions. The following are the main conclusions:

1. The oil recovery factor following a sea-water flood was the highest (around 54% OOIP) in the lowest-permeability sample and the lowest (around 38% OOIP) in the highest-permeability sample. This is attributed to better flood conformance in the low-permeability rock owing to its more homogeneous pore network.

2. At the end of the surfactant flood, the maximum oil recovery factor (31% OOIP) was achieved with the low-permeability rock as opposed to the minimum oil recovery factor (19% OOIP) achieved with the high-permeability rock.
3. NMR measurements conducted on shorter samples of the same rocks confirmed this trend of recovery performance.
4. NMR measurements revealed that the highest oil recovery at the end of the GS flood in the the low-permeability rock was attributed to its relatively large surface area, which facilitated more contact by the GS molecules leading to a shift to a more favorable wetting state.
5. Dynamic retention of the GS was the highest (0.467 mg/g-rock) in the low-permeability sample and the least (0.202 mg/g-rock) in the high-permeability sample, which is attributed to the larger contact of the GS with the rock surface in the lower-permeability rocks.
6. The results demonstrate the efficacy of the evaluated GS across a wide range of rock permeability. They also proved that the NMR technique is a supportive auxiliary technique that can be applied during the surfactant or chemical flooding process.

CHAPTER 6

EVALUATION OF A GEMINI SURFACTANT FOR ENHANCED OIL RECOVERY ON LOCAL HETEROGENEOUS CARBONATE ROCKS UNDER HARSH CONDITIONS

Abstract

Carbonate reservoirs in the Middle East account for more than 50% of the world's daily oil production. Despite their significant contribution, these reservoirs pose considerable challenges to the oil recovery process due to adverse characteristics such as high heterogeneity, oil-wet nature, and the presence of natural fractures. Surfactant flooding has emerged as an effective technique to enhance oil recovery in such reservoirs, primarily because of the capability of surfactants to reduce water/oil interfacial tension and positively modify rocks' wettability. This study showcases the outcomes of coreflooding tests conducted on outcrop rock samples from a local area in Saudi Arabia. The experiments were conducted in conditions mimicking those of a reservoir, with a temperature held at 100 °C, pressures surpassing 3,000 psi, and water salinities resembling those of connate water and seawater, exceeding 213,000 ppm and 57,000 ppm respectively. The experiment involved first continuously flooding with seawater, then switching to continuous flooding

with a solution containing a specially designed cationic Gemini surfactant dissolved in seawater, at a concentration of 2,500 ppm. After seawater flooding, the results revealed a marked incremental oil recovery by the surfactant flood. This extra oil recovery by surfactant was attributed to the wettability alteration of the rock by the tested surfactant. Nuclear magnetic resonance examinations on a shorter identical core plug at the end of the different injection stages confirmed the results. The produced aqueous phase was subjected to effluent analysis, which indicated dynamic retention of around 0.51 mg/gm-rock, falling within an acceptable range for surfactant dynamic retention. Furthermore, static adsorption tests demonstrated an increase in adsorption for an increase in surfactant concentration. The presented results demonstrate the applicability and effectiveness of the surfactant on local carbonate rocks. This integrated work establishes an innovative framework for conducting EOR studies under challenging reservoir conditions.

6.1 Introduction

Oil stored within carbonate reservoirs accounts for more than 50% of the world's hydrocarbon reserves [290], and addressing their gradual depletion necessitates more efficient methods for enhancing oil recovery [291]. Carbonate reservoirs frequently pose operational difficulties, especially when the temperatures surpass 85 °C and water's salinity exceeds 100,000 ppm [167,173,292]. The wettability of these reservoirs can vary, with some being mixed-wet while others exhibit strong oil-wet characteristics [171,172,293]. The presence of faults, natural fractures, and vugs in carbonate rock leads to a wide range of permeabilities, which contributes to suboptimal waterflooding efficiency [168,169,294,295].

One of the most successful strategies for boosting oil production from carbonate reservoirs is surfactant flooding [226–228,296]. Its effectiveness is largely attributed to the modification of carbonate rock wettability and/or the reduction of interfacial tension (IFT) between water and oil [176,297–301]. These two parameters are fundamental factors influencing the capillary number [230]. Surfactants are molecules with an amphiphilic nature, featuring a water-loving (hydrophilic) head and a water-hating (hydrophobic) tail [152,158,159,217,302]. Surfactants utilized in EOR are generally classified into four commonly used groups: anionic, cationic, nonionic, and zwitterionic surfactants. [231]. Notably, various researches on surfactant injection have observed positive production trends in carbonate rocks with the introduction of cationic surfactants [259]. Flooding with cationic surfactants is appealing because they share the same electrical charge as carbonate mineral surfaces. The positive result is credited to the development of ion pairs between the positively charged surfactants' head groups and the carboxylate components present in the oil [260–263,266]. The creation of the ion pairs is regarded as a critical factor in effectively securing the oil phase adsorbed onto the surfaces of carbonate rocks [266,267]. By forming ion pairs, the cationic surfactants assist in removing adsorbed carboxylates, thereby restoring the hydrophilic nature of the mineral surface. Nevertheless, some reports suggest that anionic surfactants may exert a more pronounced effect on modifying the wettability of carbonate rock. To illustrate, certain types of anionic surfactants like sulphonates and propoxylated sulfates have been found to modify the wettability of calcite surfaces at low concentrations more effectively towards intermediate or water-wet states compared to the cationic surfactant DTAB [303]. While anionic surfactants are typically not favored for applications in carbonate rocks due to their tendency for high adsorption,

this issue could be alleviated by raising the pH of the surfactant solution by the addition of alkali [213,304].

Gemini surfactants, recognized as an innovative class of surfactants, have been utilized in EOR applications because of their outstanding features [232–234,305]. They demonstrate special properties, including a modest critical micelle concentration (CMC) and a high ability to reduce the oil/water IFT at low concentrations. Their remarkable wetting, rheological, and foaming properties, along with high water solubility, deem them appealing for use in the oil and gas industry [182,184,187,188]. Setting themselves apart from conventional surfactants, the structure of Gemini surfactants contains a spacer located at or near their water-loving heads. This spacer connects multiple water-hating tail groups and water-loving head groups within their structures [235,236]. However, there is a limited number of studies reported in the literature concerning the suitability and application of Gemini surfactants, especially in the context of EOR [181,237–241,244,305]. Furthermore, most of the documented studies on oil recovery using Gemini surfactants focus on their application in sandstone samples [181,243,245,246,248,268–270]. To demonstrate, the primary emphasis in many of these studies was to investigate various Gemini surfactants on sandstone rocks and/or to employ Gemini surfactants alongside other materials such as nanoparticles or additional surfactants. The necessity to develop and assess surfactants that are capable of enduring high-temperature and high-salinity (HTHS) conditions remains paramount. These conditions, combined with other factors like the pH and rock lithology, significantly influence the effectiveness of the surfactant [160,161]. Previous publications by the authors presented the results of oil recovery performance of a member of in-house developed cationic Gemini surfactants through coreflooding. We proved that it can

improve oil recovery as a single-component [306], investigated the role of injection rate on the displacement efficiency [307], and evaluated the performance on heterogeneous rock samples with different permeability [308]. While those studies were conducted using Indiana rock samples, this work aims to provide some insights into the oil recovery performance of the Gemini surfactant when injected through oil-saturated local rock samples collected from an outcrop formation.

Considering that nearly the majority of the world's daily oil production originates from carbonate reservoirs located in the Middle East [165], this research work focuses on assessing the efficiency of the surfactant flooding process when applied to carbonate rocks that are similar to those oil-bearing formations. An internally developed cationic ammonium-based Gemini surfactant (GS) by Shakil Hussain et al. [194] was employed as an EOR agent, primarily through coreflooding experiments conducted under HTHS conditions. The GS was continuously injected in a tertiary recovery mode as a solution at a concentration of 2,500 ppm in synthetically prepared seawater following seawater flooding. Nuclear magnetic resonance (NMR) was utilized as a supplementary technique after the end of the injection stages. Surfactant concentration in the collected effluent was also evaluated using high-performance liquid chromatography (HPLC). The findings suggest that due to the effective nature of the GS, it is suited as a standalone component for EOR applications in the Middle East under HTHS conditions. This integrated work establishes an innovative framework for conducting EOR studies in challenging reservoir conditions.

6.2 Experimental Work

6.2.1 Materials

Rock Samples. Rock samples were collected from outcrops of the Miocene age Dam formation found in the Lidam area west of Dhahran (**Figure 6-1**). The Dam features a rock texture with fabric-preserved dolomite with dolomitized ooids and skeletal grains and has interparticle porosity similar to the one found in the Arab-D reservoir. Although of a much younger age, the Dam has been deemed an excellent analog to the Jurassic Arab formation in the Middle East [309]. The Lidam area provides an excellent opportunity for studying outcrops, boasting over 40 well-exposed outcrops of the Dam Formation. In Iraq and Iran, the intervals that produce hydrocarbons contain stratigraphic equivalents of the Dam Formation. In specific fields, these formations act as sealing rocks for the reservoirs located beneath them [310]. Further details can be found in the work published by Bashri et al. [311] and the thesis of Salih [312].

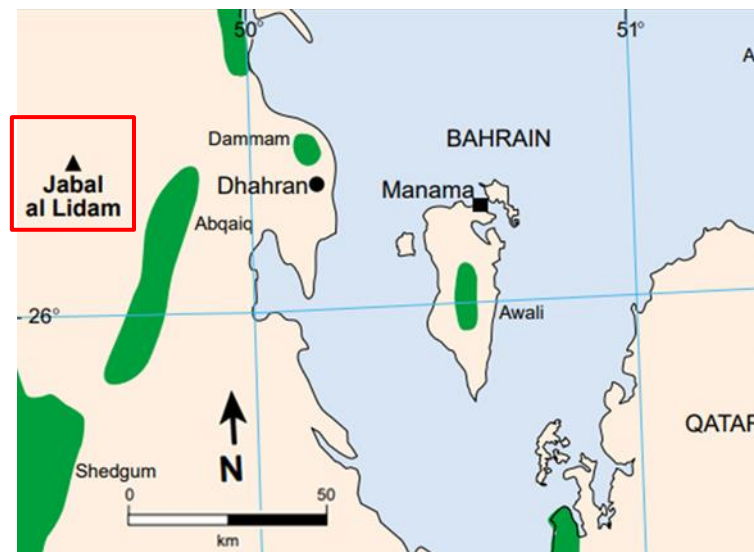


Figure 6-1. A map showing Jabal al Lidam (the Dam Formation) in eastern Saudi Arabia [309]. The green areas represent oilfields in the respective areas

Multiple core samples were cored from the collected rock using a 1.5-inch coring bit. X-ray diffraction (XRD) on powders of these rocks and quantitative evaluation of minerals scanning (QEMSCAN) were employed to inspect the mineralogical composition of the rocks. Visual inspection of the prepared core samples revealed high heterogeneity with varying pore structures. The image taken for a slice (i.e., 1.5” x 2 mm) from one of the cored samples (**Figure 6-2(a)**) shows the abundance of skeletal molds/grains. This necessitates the visualization of the samples through micro-computed chromatography (μ CT) and medical CT scanning. The porosity of the samples was measured using a helium porosimeter while their permeability was measured after brine saturation using a coreflooding setup (discussed later). For the flooding tests, two samples, short and long, were used. The long sample (LID-9) was employed as the primary sample for the main flooding test, whereas the shorter sample (LID-3) was utilized for NMR measurements conducted at the end of various flooding stages. **Figure 6-2(b)** shows images of other slices from the cored samples (i.e., 1.5” x 2 mm) where the presence of cross-bedded skeletal grains. This results in the appearance of a channel-like pore system along the flow direction. **Table 6-1** summarizes the properties of the two rock samples tested in this work.

Table 6-1: Properties of investigated rock samples

Sample ID	Length (cm)	Diameter (cm)	Connected Porosity (%)	Pore Volume (mL)	Approximate Liquid permeability (mD)
LID-9	10.2	3.8	34.1	39.94	2,500
LID-3	7.6	3.8	32.9	23.66	2,500

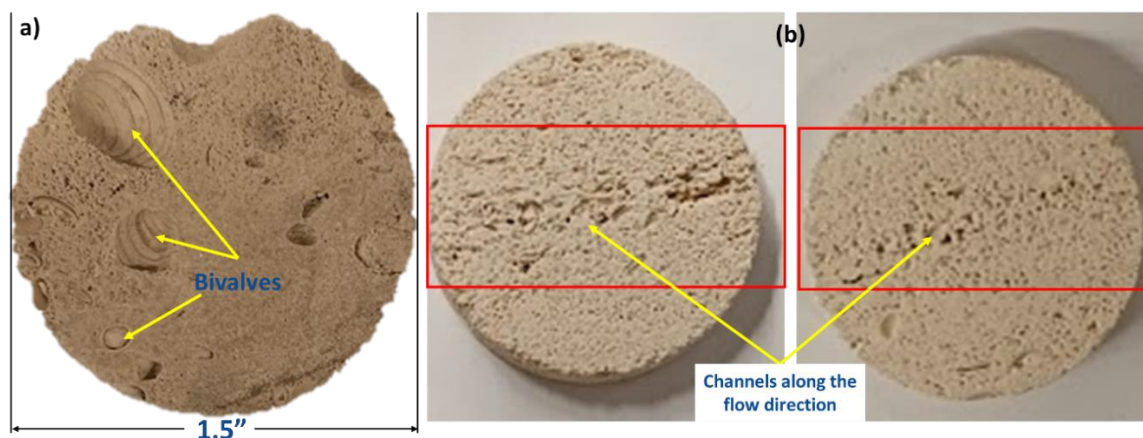


Figure 6-2. Images showing the cross-sections of Lidam core samples

Salts and Brines. High-salinity seawater brine (SW) having a salinity of more than 57,000 ppm, mirroring the characteristics of Arabian Gulf water [193], was prepared for secondary and chemical injections. Another brine representing reservoir formation water (FW) whose salinity is higher than 213,000 ppm was also prepared to saturate the rocks. Various laboratory-based salts from Sigma Aldrich were mixed in deionized water to prepare both brines. **Table 6-2** presents the compositions of these brines.

Table 6-2: Compositions of prepared formation brine and seawater

Salts	Concentration (ppm)	
	Seawater	Formation water
NaHCO ₃	165	487
Na ₂ SO ₄	6,339	517
NaCl	41,172	150,419
CaCl ₂	1,802	52,788
MgCl ₂	8,266	9,555
TDS →	57,745	213,768

Crude Oil. Degassed (i.e., dead) oil collected from a Middle East reservoir was used to set initial oil saturation and age the rock samples. To eliminate the risk of flow blockages during oil floods, which may arise from the fine particles or residues in the oil, a 5- μ m in-line filter was employed to purify the oil. At the experimental conditions comprising a temperature of 100 °C and

pressure of 3,000 psi, the oil's viscosity was nearly 2.5 cP. A SARA analysis on an oil sample using ATROSCAN® MK7s FID showed that the oil contains 23.1% saturates, 44.1% aromatics, 23.0% resin, and 9.8% asphaltenes.

Chemicals. In this study, an in-house synthesized, cationic, ammonium-based Gemini surfactant (GS) was utilized, and its structure is illustrated in **Figure 6-3**. The surfactant is not commercially available, and has not been explored for oil recovery performance by researchers other than our research group. Details of the synthesis and initial assessment of the GS have been previously presented by Shakil Hussain et al. [194]. To prepare the surfactant solution, the GS was dissolved in simulated SW at a concentration of 2,500 ppm. Although the designed GS generally exhibits a CMC, which has been previously assessed and reported by our research group, typically falling below 100 ppm, using such a low surfactant concentration is neither efficient nor practical. This is because it could result in poor displacement efficiency induced by surfactant retention. However, employing high surfactant concentrations may result in an undesired increase in expenses, so a concentration of 2,500 ppm was chosen, which should be practical and cost-effective compared to the concentrations available in the literature, which usually require the use of co-surfactants and co-solvents to enhance surfactant efficiency [173]. Further details related to screening and initial evaluation of the surfactant group, in addition to the reasoning behind choosing this concentration, can be referenced in previously published work by the research group [191,194–196,198–203]. In these studies, the surfactant was initially created and characterized using ^{13}C NMR spectroscopy, MALDI-TOF MS, FTIR, and ^1H NMR. Subsequently, the surfactant underwent assessments for salt tolerance and thermal stability. For instance, the solubility

of the GS group was examined in deionized water (DW), simulated FW, and simulated SW. The results indicated great solubility and extreme resistance to elevated salinity, without any observed precipitation or cloudiness. Furthermore, the surfactant exhibited remarkable thermal stability, even at temperatures surpassing typical oilfield conditions of over 90 °C. In short-period thermal stability tests, the surfactant decomposes at high temperatures as high as 300 °C, according to thermographic analysis. Moreover, long-period thermal stability tests indicated that the surfactant solution persisted stable in either DW, FW, or SW for approximately three months at 90 °C [191,194]. Additionally, a comprehensive examination of the characteristics related to wettability alteration was subsequently carried out [196]. Lastly, the static adsorption and retention characteristics were also assessed [202,203,256].

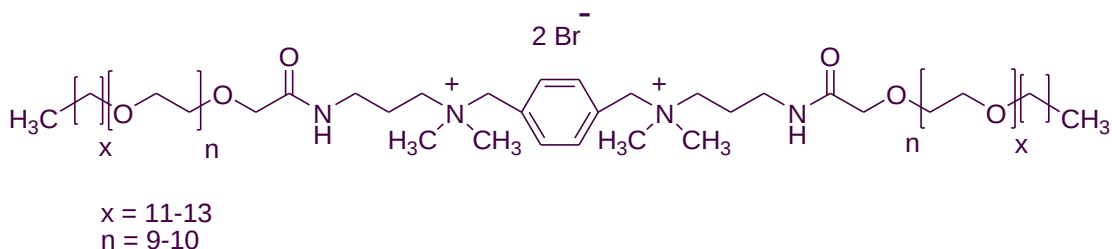


Figure 6-3. The structural composition of the cationic Gemini surfactant examined in this research

6.2.2 Contact-angle Measurements

To examine the impact of GS solutions on rock wettability, static contact angle (CA) measurements between oil and brine were conducted on Indiana rock substrates before and after treatment with various concentrations of the GS. These substrates, approximately 2 mm x 1 inch in size, were derived from collected rock samples. The measurements were relatively difficult due to the high permeability of the samples that the added water droplet was soaking into the samples. The measurements were then conducted between air and

water, where the substrate was placed on the holder of the instrument, and a water droplet was added to its surface from which the CA is automatically measured. Before testing, the substrates underwent oil aging at 100°C for nearly three weeks. The CA of each substrate was measured after aging, representing the pre-treatment value. Subsequently, different substrates were immersed in 30 ml of each surfactant solution for approximately 4 days under ambient conditions, and the CA was measured again to determine the post-treatment value. The change in CA reflects the alteration in wettability, with a higher change indicating a more effective alteration. Contact angle measurements were conducted using specialized equipment, specifically the Attension Theta Optical Tensiometer manufactured by Biolin Scientific.

6.2.3 Coreflooding Experiments

Apparatus. The coreflooding setup (CFS700) illustrated in **Figure 6-4** was used for carrying out the oil recovery experiments. It is manufactured by VINCI technologies. It can be employed for conducting chemical and gas EOR experiments. It can be operated at extremely high pressures and high temperatures and can accommodate corrosive and saline fluids. It has been thoroughly described in our previous publications [205,306,308].

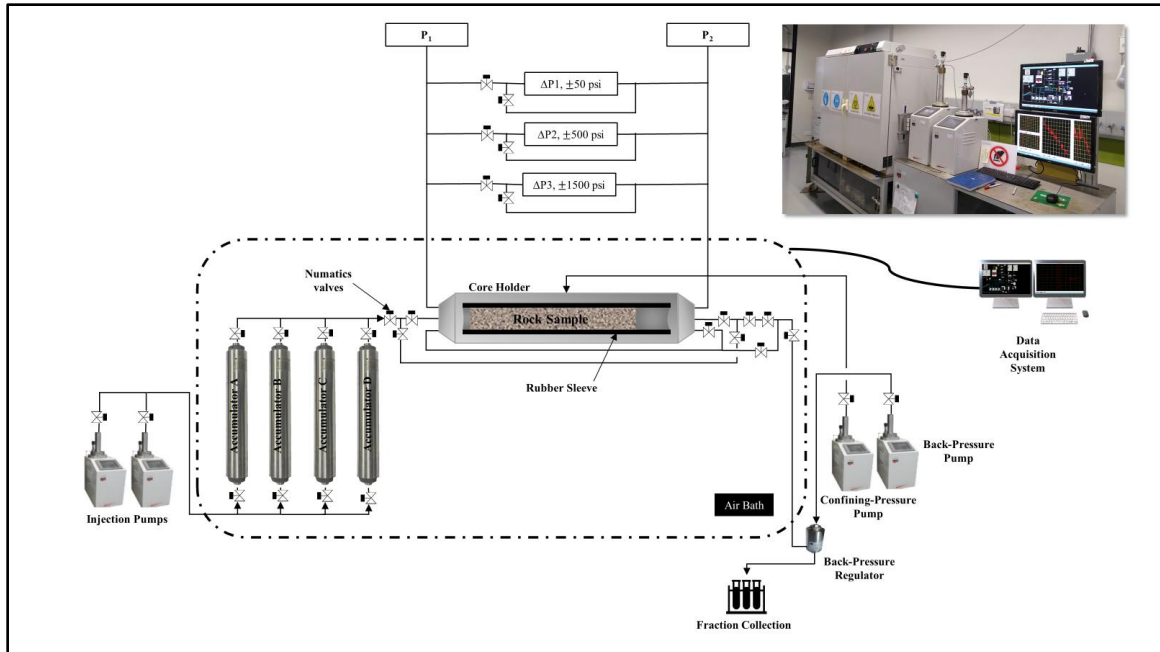


Figure 6-4. Diagram of the coreflooding setup

Preparation of core samples. The core plugs were saturated with the prepared formation water using the vacuum saturation procedure. Following this saturation, the brine was pumped through each sample to obtain its absolute permeability. After the absolute permeability of the rock was measured through FW injection, the injection was shifted to the variable-rate drainage process to set the irreducible water saturation (S_{wi}), where oil was injected into each sample. This was commenced by displacing the remaining FW in the inlet and outlet line (through the bypass) to eliminate (or reduce) the dead volume. Then, oil injection was diverted into the rock sample initially at a rate of 0.05 cc/min. The injection rate was continuously changed, and the other injection rates were 0.1, 0.2, 0.5, 1, 2, and 5 cc/min. The injection rate was successively changed after the oil cut by the injection rate increased above 98%. This required injecting around 1.5-2 pore volumes (PVs) of the oil, especially at the low injection rates. Only 1-1.5 PVs of crude oil were injected at higher oil rates since most of the water was already displaced at lower injection

rates. The subsequent initial water saturations achieved for LID-9 and LID-3 rock samples were 33% and 32.5%, respectively. Subsequently, the samples were removed from the core holder and placed in the aging cell after which they were immersed in crude oil. The samples were aged for 21 days at a temperature of 100 °C at static conditions. This aging process played a significant role in enhancing the adhesion of the polar constituents of the oil onto the surface of the rock, ensuring that the samples remained in the extreme oil-wet state [207].

Oil Recovery Experiments. A single sample was mounted in the core holder and the system was heated to 100 °C before being flooded under injection and overburden pressures of 3,000 and 4,000 psi, respectively. Initially, a few PVs of oil were pumped through the sample at a rate of 1 cc/min to initiate flooding conditions and saturate the rock with fresher oil than the aging oil. This was succeeded by a continuous displacement of oil with seawater until oil production ceased (i.e., confirmed by water cut exceeding 98%), in which nearly 3–4 PVs of SW were required. Subsequently, chemical injection commenced, involving the injection of several PVs of the chemical solution. The SW and the GS solution were injected at a flow rate of 0.25 cc/min, corresponding to 1 ft/day of Darcy velocity. This injection rate has been deemed the best injection rate based on our previous investigation [307]. The effluent was collected in 15-ml pyrex vials at 20-minute intervals (5 ml in each vial).

6.2.4 NMR Measurements

Apparatus. NMR measurements were performed using the NMR Geospec2 Oxford instrument which operates at a strength of magnetic field of 0.05 Tesla at ambient conditions. This corresponds to a Larmor frequency of 2.23 MHz for ^1H .

Procedure. NMR measurements were conducted on the short core plug. The measurements were carried out at various stages of flooding, including after saturation with formation water (i.e., 100% S_{wi}), following setting the initial water saturation (prior to and after oil-aging the rock), at the end of SW flooding, and upon completion of GS injection. Despite potential disruptions to capillary forces that may occur when the rock is unmounted from the core holder for NMR measurements after each flooding stage [282], the approach was deemed effective and contributed to the continuous monitoring of oil recovery throughout the flooding test.

Before placing the plug sample in the holder of the NMR instrument, any fluid adhering to the plug's surface was wiped by gentle rolling of the sample on a clean sheet of paper. This prevents the presence of this fluid in the T_2 relaxation data as part of the bulk fluid. Plastic wrap, specifically designed to be NMR-silent, was then used to securely wrap the core sample to ensure the preservation of fluid saturation at the measurement time. The T_2 relaxation time data was acquired utilizing the pulse sequence of Carr-Purcell-Meiboom-Gill (CPMG). Echoes' number was tailored to get the full signal decay with a constant echo time of 0.1 ms [283,284]. Rather than fixing the number of scans, a minimum signal-to-noise ratio (SNR) of 100 was established as a limit. The CPMG signal decay was then transformed into a distribution of T_2 relaxation time following Tikhonov methods [313]. More details of the NMR principles and measurement method are presented elsewhere [308,314].

6.2.5 Static & Dynamic Adsorption Tests

Apparatus. The static and dynamic adsorption tests were performed on an HPLC system from Agilent Technologies (Agilent 1260 Infinity) with an attached evaporative light

scattering detector (ELSD, Agilent 1260 Infinity II). A gradient method utilizing two mobile phases was used, where one was acetonitrile (CH₃CN) and the other was 0.1 M ammonium formate (NH₄OOCH) with a pH of 4.3 modified using formic acid (HCOOH). The HPLC system employed a reversed-phase AcclaimTM Surfactant Plus column (3 μm packed particles, 4.6 mm diameter ×150 mm length).

Static Adsorption. To measure the quantity of surfactant adsorbed onto the surface of the rock, static adsorption tests were carried out. The rock sample was crushed into a powder and then added to different surfactant solutions at a mass ratio of 1:15. The mixture was extensively shaken on a linear shaker for 24 hours at ambient conditions. Afterward, the mixture underwent centrifugation at 3000 rpm for 5 minutes, and the supernatant was collected and filtered. The unknown surfactant concentration in the supernatant was then quantified using HPLC. The static adsorption was determined using Eq. 6-1.

$$\Gamma_{static} = \frac{C^0 - C}{m} \cdot V_s \quad (6-1)$$

where Γ_{static} denotes surfactant's static adsorption (mg/g-rock), C^0 is the before-treatment surfactant concentration (ppm), V_s (L) denotes the volume of the GS solution, C is the after-treatment surfactant concentration in ppm, m (g) is the mass of the rock powder.

Effluent Analysis (Dynamic Retention). The aqueous phase of the collected coreflooding effluent was separated, filtered, and transferred to special HPLC vials. The samples were then analyzed using the HPLC, which gave an ELSD area for each vial that was converted into surfactant concentration through an initially developed calibration equation. In the calibration process, the chromatographic integral areas are plotted against surfactant concentrations to generate the calibration plot [215]. The dynamic retention of the GS

during the flooding was then obtained through material balance, where surfactant concentration is used for the calculation. Several scholars have demonstrated the effectiveness of this method [173,202,213,214]. More details of the procedure can be found in recently published work from this laboratory [307].

6.2.6 Zeta Potential Measurements

To track the effect of the addition/injection of the GS on the charge of the rock surface, the zeta potential (ζ) was measured, which could facilitate the interpretation of the static adsorption results. The measurements were accomplished using the Anton Paar Litesizer 500, with a size range of approximately 3.8 nm to 100 μm . This determines the net surface charge of minerals in an aqueous solution. The measurements were conducted on the same samples prepared as described under the “Static Adsorption” subsection. Following agitation of the samples on a linear shaker, they underwent centrifugation using the Hermle Z326K at a speed of at least 3000 RPM for approximately 3 minutes to achieve a clear supernatant.

6.3 Results & Discussions

6.3.1 Rock Characterization Results

Based on XRD analysis of the rock powder, dolomite was found to be the most dominant mineral in these rocks (see **Table 6-3** for the composition). This was confirmed by the QEMSCAN results, which also revealed traces of other minerals like quartz, calcite, and others (**Figure 6-5**). A 3D image of the sample is also shown in **Figure 6-6**. The image to the left of the figure shows the distributions of the large pores on the surface and inlet of

the sample while the right image shows the distribution of the large pores inside the sample.

Figure 6-7 shows the density of the LID-9 sample obtained from medical CT scanning.

The slices show the high heterogeneity of the sample and the scattering of the large pores.

The heterogeneity of the samples makes them good representatives of carbonate rocks,

especially in the Middle East. **Figure 6-8** shows the pore-size distribution as obtained from

the micro CT imaging. In the figure, the sum of the pore volumes is plotted versus the

length of pores having that sum. The figures show various pore sizes where a large portion

of the pores are small with a scattered distribution of large pores.

Table 6-3: Compositions of rock samples based on XRD analysis

Mineral	Dolomite	Calcite	Quartz	Halite	Others
Composition (%)	99.5	0.1	0.1	0.05	0.25

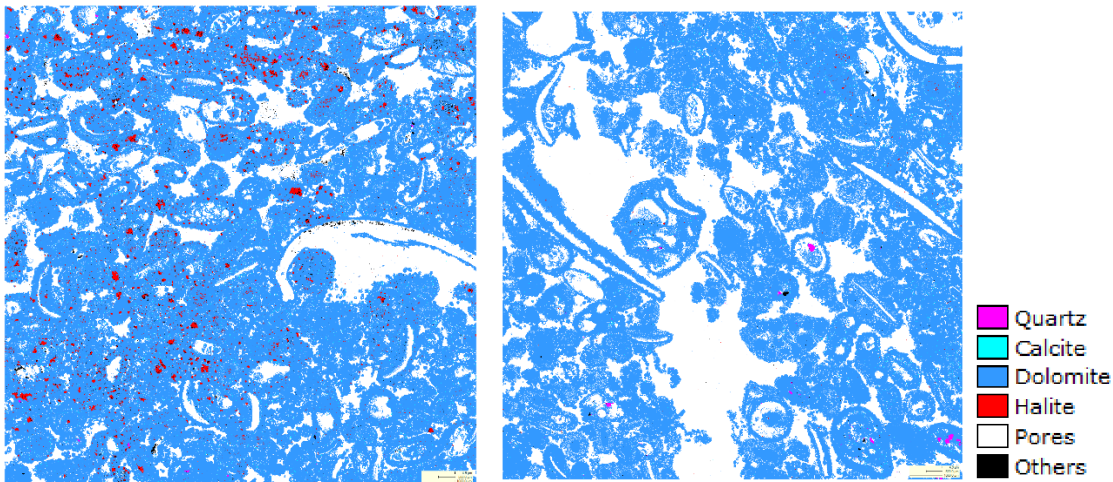


Figure 6-5. Distribution of minerals in Lidam samples based on QEMSCAN

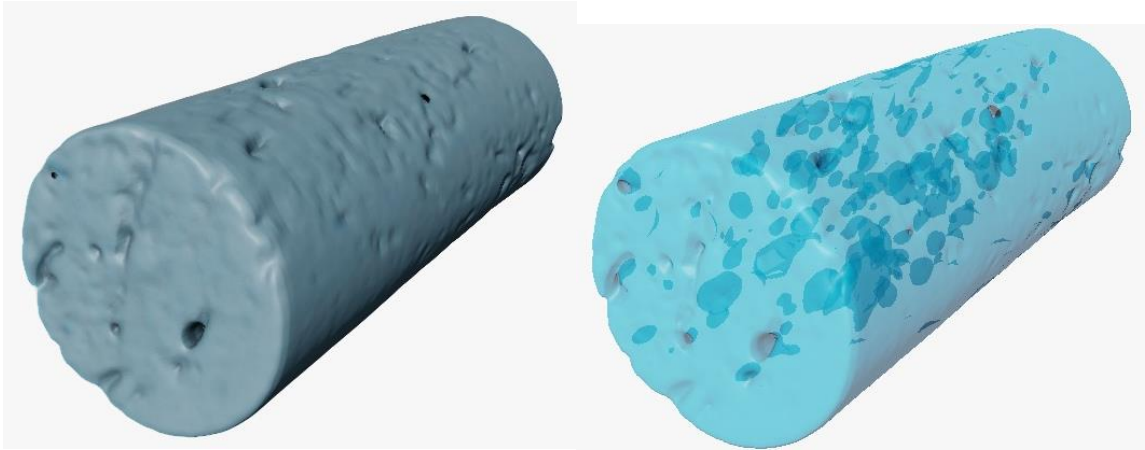


Figure 6-6. 3D images of LID-9 obtained from the medical CT scanning

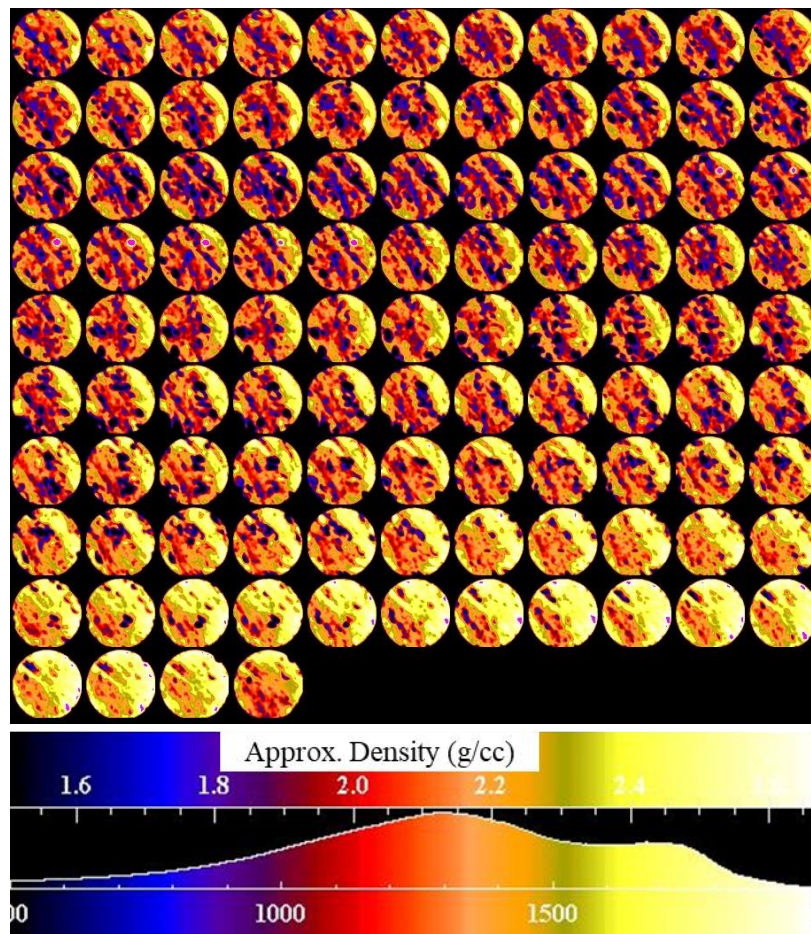


Figure 6-7. Slices of LID-9 based on medical CT scanning

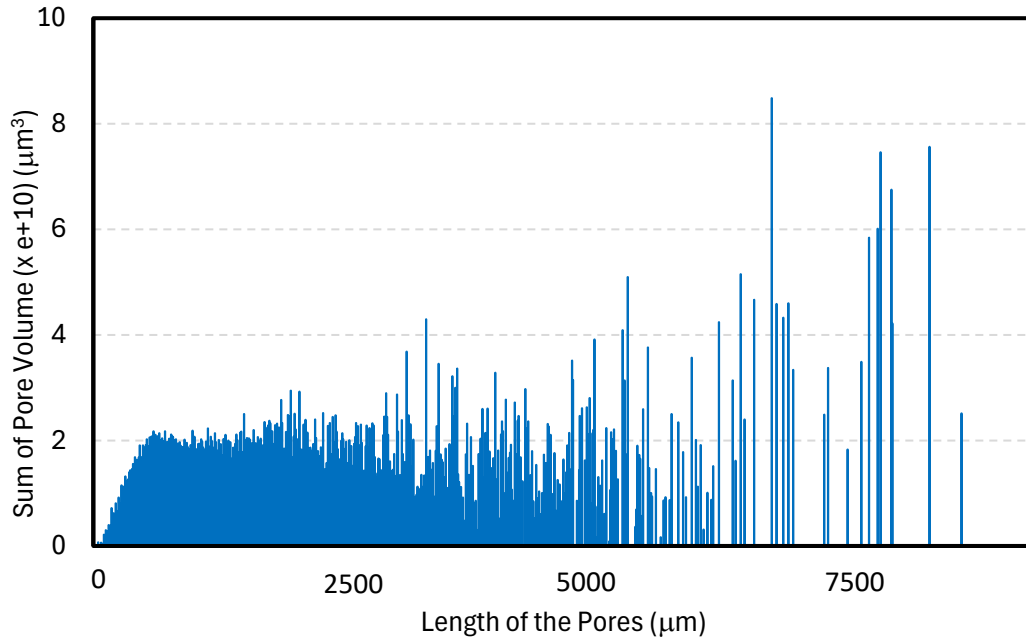


Figure 6-8. Pore-size distribution of LID-9 based on micro CT scanning

6.3.2 Results of Contact Angle Measurements

Figure 6-9 presents the results of air-water CA measurements both before treatment in GS solutions at different surfactant concentrations (i.e., after oil aging of the rock substrate) and after treatment with the surfactant solutions. Initially, all the samples were strongly oil-wet as indicated by the initial CA values. The results show that the contact angles after treatment in surfactant solution at different concentrations are almost identical, where the rock wettability changed to almost intermediate wet state. These findings demonstrated that the most significant improvement in rock wettability occurred when the rock samples were immersed in surfactant solutions containing concentrations of 1,500 ppm and 2,500 ppm, with a change in the CA of around 36° . It was previously mentioned that opting for a surfactant concentration of 2,500 ppm would be both practical and cost-effective compared to concentrations mentioned in existing literature, which often necessitate the use of additional agents like co-surfactants and co-solvents to enhance surfactant

efficiency. Despite the use of a high surfactant concentration, the dynamic retention remains low. Furthermore, employing lower concentrations would be impractical and inefficient due to potential surfactant retention, which could diminish the efficiency of the surfactant solution in the oil displacement process. For example, if a concentration of 1,500 ppm was used, the retention might reduce the surfactant concentration to levels below 1,500 ppm, which are not efficient for wettability alteration. However, injecting surfactant solution with a concentration of 2,500 ppm would not be significantly affected by the retention since the concentration would be reduced to values which are still efficient in wettability alteration.

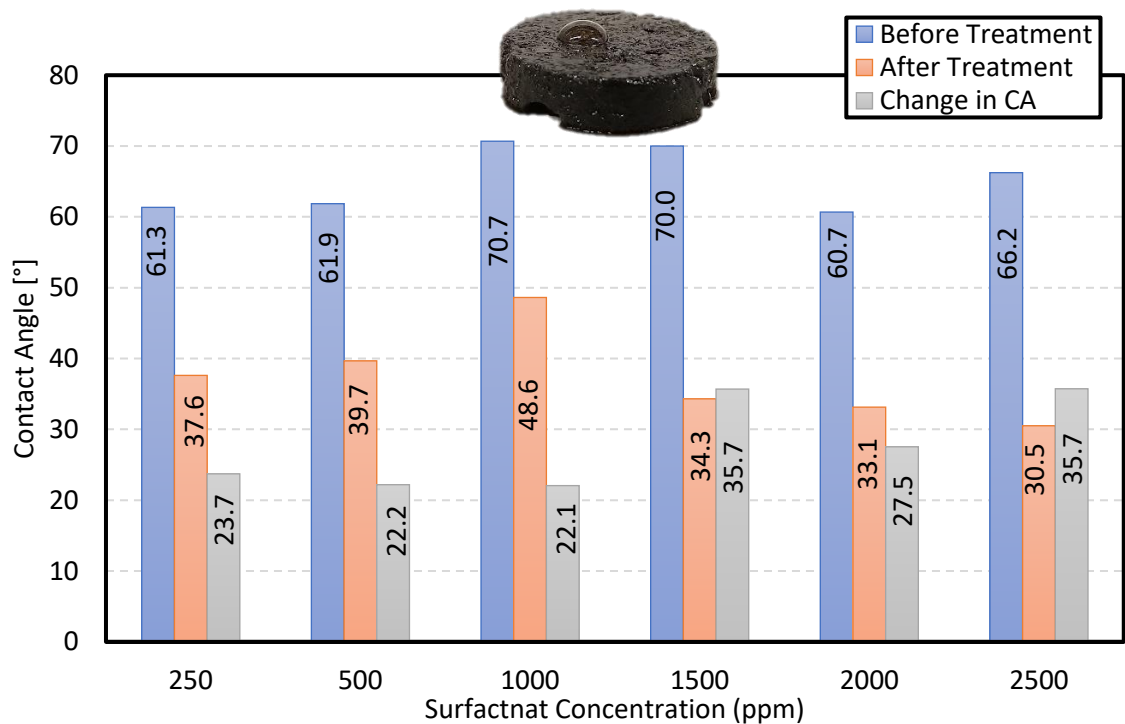


Figure 6-9. CA measurements before and after rock treatment with different surfactant concentrations

6.3.3 Oil Recovery Results

Figure 6-10 presents oil recovery factor and oil saturation curves versus the injected PVs for coreflooding LID-9. The oil recovery factor is seen to follow an almost linear relationship with the injected pore volumes both before and after the breakthrough. This can be attributed to the good connectivity of the channel-like pore system within the rock sample (see **Figure 6-2(b)**). The final oil recovery factor at the end of SW injection is 54.5% for sample LID-9, which required around 4 PVs of injected SW. The equivalent residual oil saturation was 29.6%. Due to the presence of large pores within the sample breakthrough occurred fast after injecting around 0.3 PV of SW. Despite this, the oil recovery showed a linear relationship with the injected pore volume even after the breakthrough. **Figure 6-10** also presents the oil recovery efficiency of the GS flooding. The injected GS solution, totaling nearly 4-5 PVs, resulted in an increasing the oil recovery by almost 17% OOIP, elevating the total oil recovery factor to almost 72% at the end of the GS injection process. The oil saturation was brought down to nearly 18%. It can be seen that oil production by surfactant flooding started after injecting more than one pore volume of the surfactant solution, reflecting a delay in the oil recovery. This delay has been attributed to the large molecular structure of the surfactant which requires more time for the surfactant to diffuse into the oil phase [306]. In addition, the common practice in surfactant flooding is to inject a slug of surfactant solution and chase it by SW. However, this was not the case in this work as the main mechanism of the oil recovery by the GS is wettability alteration, which is proven to be a time-dependent process that explains the required large amount of surfactant solution to achieve this oil recovery. To illustrate, in our previous works [306,308], it was shown that the GS is stronger in modifying rocks'

wettability than in decreasing the oil/water interfacial tension (IFT). For instance, it could shift the rock's wettability to either an intermediate or water-wet condition from the initial oil-wet state, as evidenced by the changes in the measured contact angle as well as the changes in water/oil relative permeability curves derived from the data of the coreflooding following the JBN technique. However, under ambient environment, the oil/water IFT was barely lowered to nearly 3 mN/m using a GS concentration of 2500 ppm. Since the surfactant did not achieve an ultralow IFT, it suggests that wettability change is the main mechanism contributing to any improved oil recovery from the surfactant. Finally, the heterogeneity of the sample and the large pore volume may also contribute to the need for such a large amount of injected surfactant solution.

The change in pressure (ΔP) across the sample was continuously monitored during the entire flooding test. However, due to the significantly high permeability of the rock, the pressure drop was not high enough to be recorded and presented herein. The maximum recorded pressure drop was around 0.07 psi, which was observed at breakthrough during SW flooding.

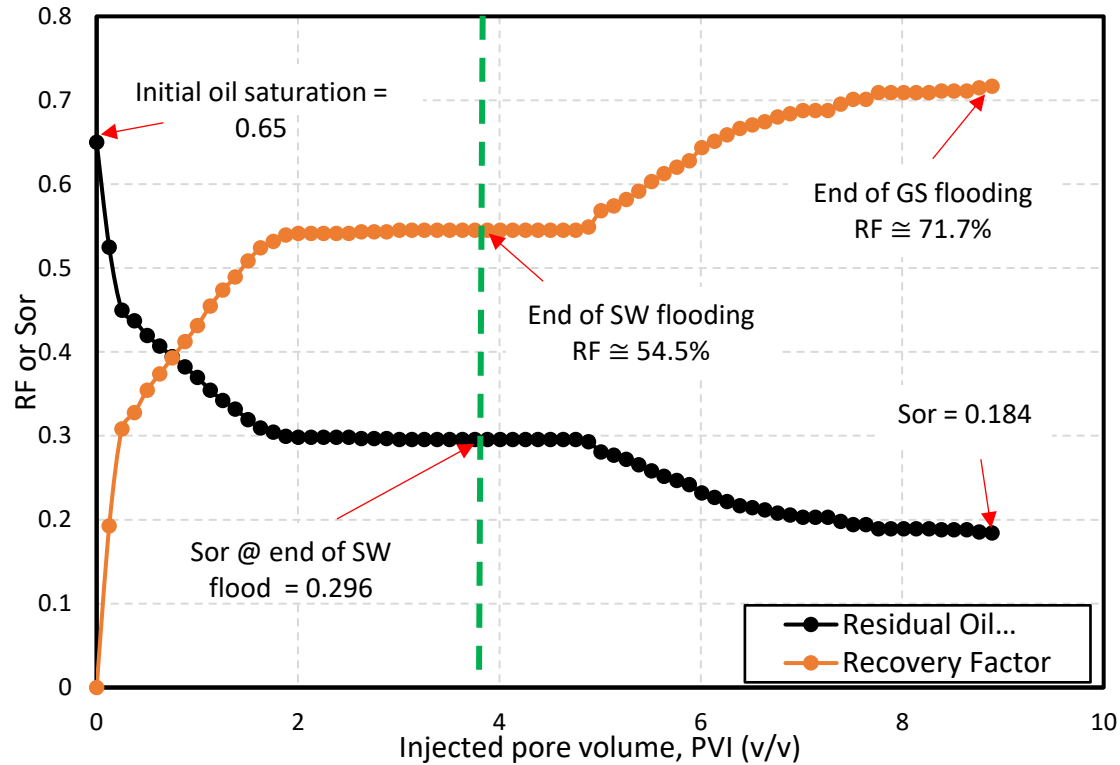


Figure 6-10. Oil recovery factor and residual oil saturation of the coreflooding test based on the long-core sample (LID-9)

6.3.4 NMR Results

Figure 6-11 illustrates the distribution of T_2 relaxation time of both formation water and oil. The T_2 peak value for the bulk formation brine is almost 1412.5 msec and that for the oil is 141.25 msec. this variation is attributed to the higher viscosity of the oil. T_2 distribution of crude oil displays a wide range of components because of the diverse hydrocarbon chemistries present in oil [288]. It should be noted that these peaks are obtained by conducting T_2 measurements of the bulk fluids of both FW and crude oil. The corresponding values of these peaks are then translated into the dashed vertical lines of Figure 6-12, which are set as references for indicating the location of the peak of the T_2 of the rocks after the different flooding stages.

In **Figure 6-12**, the T_2 relaxation time distributions for LID-3 at $S_w = 1$ are represented by the blue line. The distributions for 100%-brine-saturated samples suggest an unimodal pore size distribution in the rock, a common feature in carbonate rocks [278]. Upon flooding the core plug with oil to initial water saturation, the T_2 peak value shifts to 64.5 msec, as indicated by the black line in **Figure 6-12**. The deviation in the T_2 from the vertical, red-dashed line suggests that oil is adhering to the pore walls (i.e., surface relaxation effects), indicating a shift in rock's wettability into a less water-wet state. Despite this, the bulk relaxation component predominates the distribution of T_2 relaxation time, as formation water covers the majority of the pore walls, resulting in detecting oil as a bulk mobile phase. The T_2 relaxation time distributions after SW injection are shown in orange in **Figure 6-12**. The emergence of T_2 components greater than the bulk components of oil is because the macropores are invaded by seawater. The amplitude corresponding to the larger T_2 components corresponds to the volume of water displaced, with a higher displacement of oil volume leading to a higher T_2 amplitude. The additional oil recovery post-GS flooding is evident in the increased amplitude of the T_2 component, featuring a large peak corresponding to the peak value of formation water, indicating more water-wetting conditions.

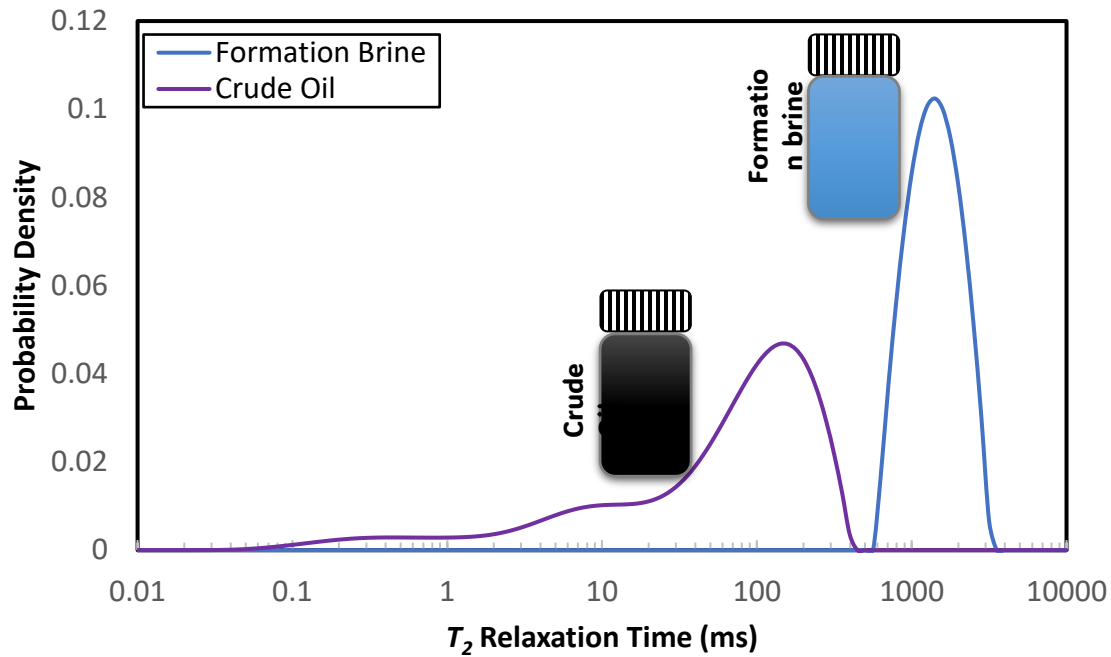


Figure 6-11. T_2 relaxation time distribution for the formation brine and crude oil used in this work

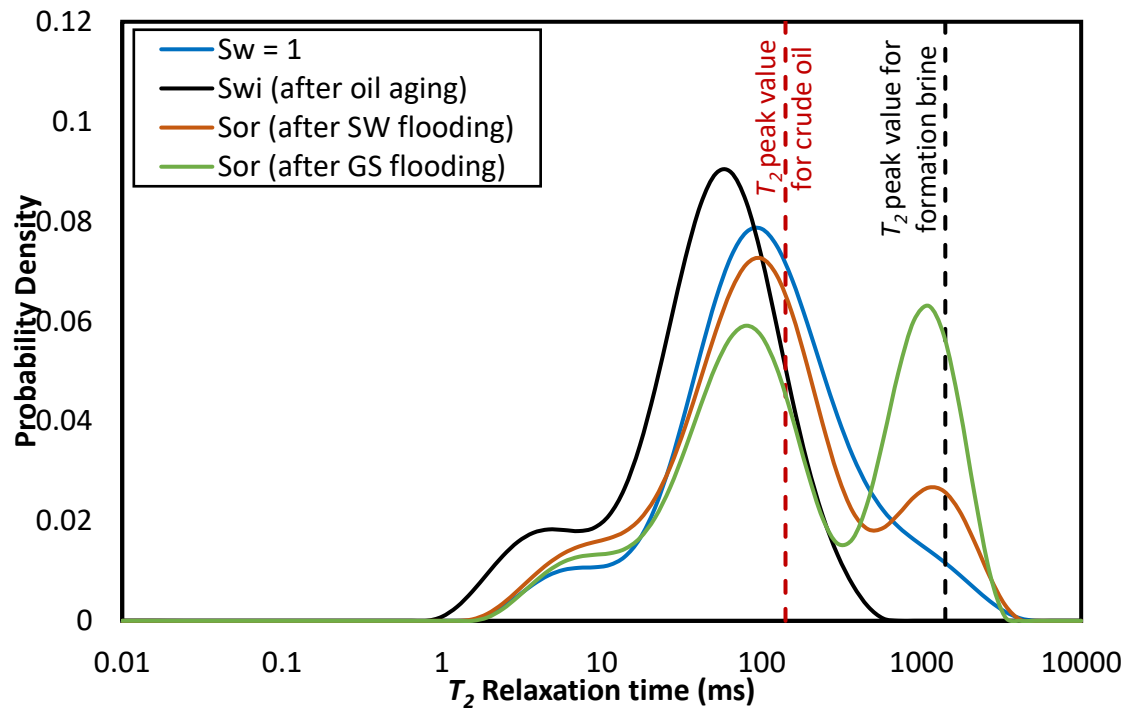


Figure 6-12. Distribution of the T_2 relaxation time throughout the flooding test on LID-3

6.3.5 Static Adsorption

The static adsorption of the GS was calculated using Eq. 1 after attaining the ELSD area from the HPLC peak, which was then converted into surfactant concentration via the calibration curve. The amounts of surfactant adsorbed along with the corresponding initial concentration are shown in **Figure 6-13(a)**. The adsorption of the cationic GS was linked to the creation of an interdigitated bilayer on the carbonate rock [202,214]. The high adsorption is primarily attributed to the robust electrostatic attraction resulting between the cationic surfactant and the negatively charged binding sites arising from quartz impurities present on the rock surface [202,203].

The zeta potential of the rock suspended in an aqueous solution of the GS at different concentrations is shown in **Figure 6-13(b)**. The zeta potential of the rock grains was 2.37 mV in the absence of the GS. The magnitude of the zeta potential, however, increased towards more positive values in the cases where the GS was present. This increase along with the relatively low magnitudes of the zeta potential (less than 10 mV) reflects the adsorption of the GS onto the rock surface. The increase in the zeta potential implies that the surface of the rock becomes more positive due to the adsorption of the surfactant into the surface of the rock. Moreover, the increase in the magnitude of the zeta potential can be indicative of the shift of the rock wettability towards a more water-wet state from a less water-wet state [315]. The error bars in Fig. 12-b are constructed based on the standard deviation of the measurements. The pH of the SW was 7.8, which changed to 7.4-7.5 after adding the GS. The pH of the GS solutions after mixing with the rock powder is also displayed in **Figure 6-13(b)**. These values indicate no significant changes in the pH after the GS interacts with the rock surface. This minor change in the pH indicates that the H^+

and OH^- ions are not contributing to the adsorption process. **Figure 6-14** shows the particle-size distribution of the rock powder used for static adsorption tests, which was obtained using HELOS particle size analyzer.

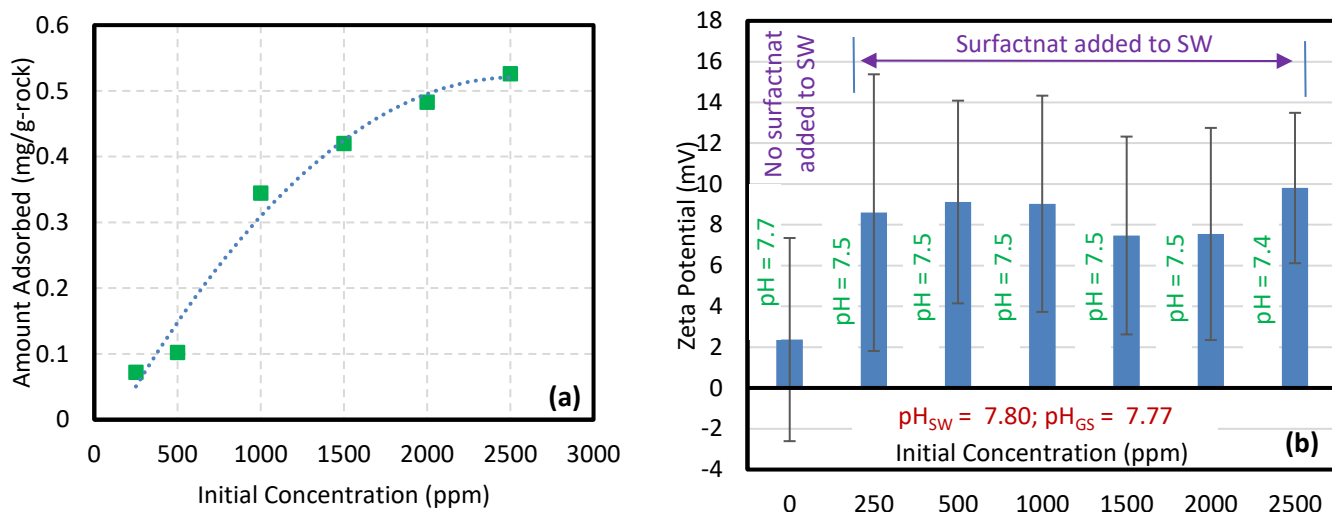


Figure 6-13. Static adsorption of the GS (a) and zeta potential of rock powder suspended on the solutions of the GS (b)

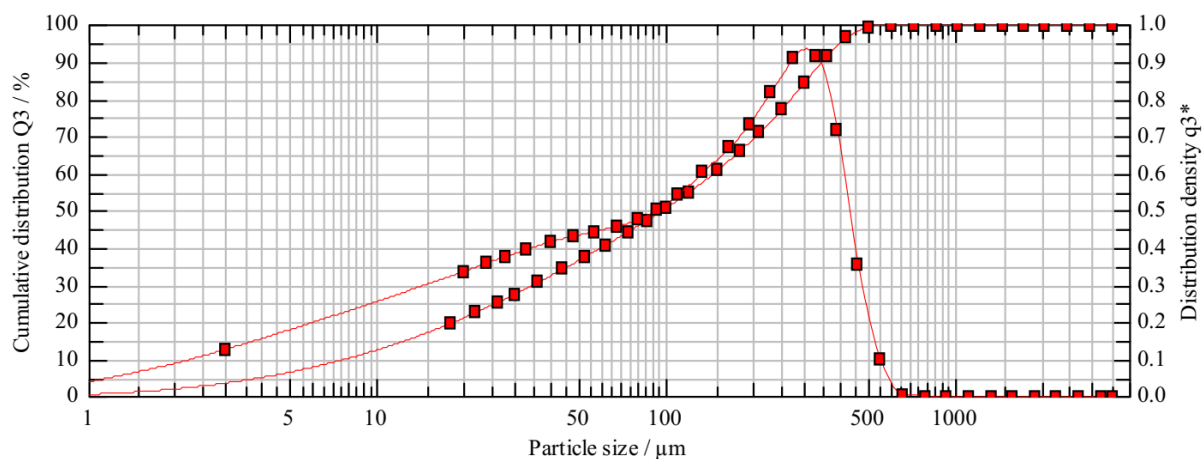


Figure 6-14. particle-size distribution of the rock powder used for static adsorption tests

6.3.6 Effluent Analysis

In **Figure 6-15**, the concentration of the Gemini surfactant in the aqueous phase in the effluent is depicted. The highest concentration of the GS reached nearly 2,200 ppm during the flooding process. A sudden rise in surfactant concentration is observed in the effluent,

indicating the rapid breakthrough of the surfactant solution. Utilizing a material balance approach, the GS's dynamic retention was determined to be around 0.510 mg/g-rock, falling within an acceptable range since some field pilot tests were designed based on an average retention value of 0.7 mg/g rock [223]. Moreover, retention values ranging from 0.5-0.9 mg/g rock have been reported based on laboratory coreflooding experiments. The relatively high dynamic retention can be attributed to the presence of the impurity in the rock composition. To illustrate, quartz and clay minerals, present in the rock sample, have been shown to cause high adsorption of the Gemini surfactant [203]. The heterogeneity of the sample could have contributed to the high retention of surfactant. Finally, it's worth noting that splitting the GS into the oil phase could also contribute to its retention, necessitating further analysis.

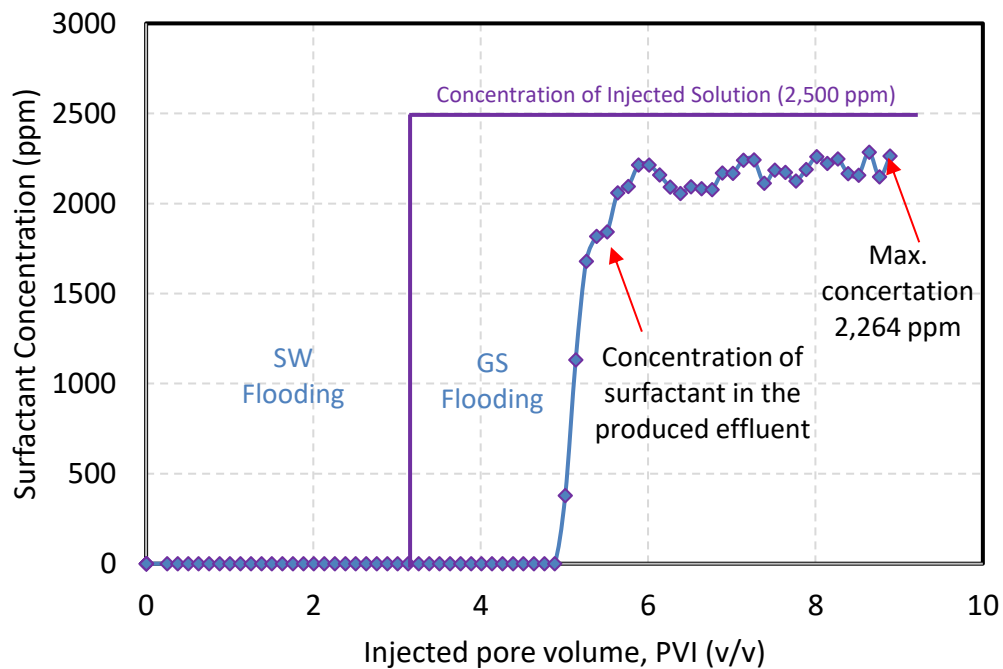


Figure 6-15. Concentration of the GS in the coreflood effluent

6.4 Summary & Conclusions

In this research work, the oil displacement efficiency of an in-house synthesized, ammonium-based, cationic Gemini surfactant was assessed for its use in carbonate rocks of the Middle East. Coreflooding tests were carried out with a 2,500-ppm surfactant solution under HTHS experimental conditions on rocks collected from a local carbonate outcrop in Saudi Arabia. The following points represent the main conclusions and observations of the work:

1. The collected rock samples showed significant heterogeneity, which makes them a good representation of carbonate reservoirs in the Middle East.
2. Static adsorption on rock powder was increased with increasing surfactant concentration.
3. Following a seawater flood, the surfactant flood resulted in a significant additional oil recovery of around 17% OOIP.
4. NMR measurements carried out on a shorter sample of the identical rock validated this pattern of recovery performance.
5. The surfactant showed dynamic retention of around 0.510 mg/g-rock, which is below the average value retention of some designed pilot field tests.
6. The findings highlight the effectiveness of the tested Gemini surfactant (GS) on the local rock samples, which show a high degree of heterogeneity.
7. The findings establish the NMR technique as a valuable supplementary method applicable in surfactant and other chemical flooding processes in complex rock systems.

CHAPTER 7

SYNERGISTIC PERFORMANCE OF A GEMINI SURFACTANT FOR ENHANCED OIL RECOVERY UNDER HARSH CONDITIONS

Abstract

Surfactant injection into hydrocarbon reservoirs is a proven method for enhanced oil recovery, leveraging its ability to reduce interfacial tension between oil and water and potentially alter rock wettability. This study investigates the effectiveness of integrating various additives/methods, including low-salinity water, DTPA, or methylene blue, into the oil recovery process using a modified cationic Gemini surfactant, particularly in challenging conditions. Four coreflooding experiments were carried out in Indiana limestone cores at 100 °C, each involving continuous injection of a chemical solution following continuous seawater flooding. The solutions were either the surfactant in seawater, the surfactant in 10 times diluted seawater, the surfactant in seawater with 1 wt% DTPA, or the surfactant in seawater with 300 ppm methylene blue, all at a constant surfactant concentration of 2,500 ppm. The seawater-flood phase yielded oil recovery ranging from 46% to 49% of the original oil in place and residual oil saturations between 33% and 35.5%. The GS8-in-seawater and the GS8-in-diluted-seawater floods produced incremental oil recoveries of 23% and 26.3% OOIP, respectively. The surfactant's dynamic

retentions were 0.37 and 0.35 mg/g-rock, respectively. Incorporating DTPA into the recovery process led to the largest additional oil recovery among all tested solutions at approximately 37% OOIP, resulting in an ultimate oil recovery of 84% OOIP with a dynamic retention of 0.41 mg/g-rock. However, adding methylene blue with the GS8 slowed down the recovery process, requiring a larger volume of chemical solution. Overall, the study highlights the synergistic effects of combining the surfactant with other additives or methods to optimize oil recovery while maintaining low surfactant retention.

7.1 Introduction

Surfactant flooding in oil reservoirs is a proven EOR technique due to the chemicals' ability to lower the oil/water interfacial tension (IFT) and, in some cases, to alter the rock wettability towards more water-wet conditions, both of which are favorable mechanisms in oil displacement [152,159,316–318]. Wettability alteration of rocks from oil-wet to water-wet is a favorable oil recovery mechanism since it results in better oil displacement by the injected water. This is also reflected in the reversal of capillary pressure from negative to positive values. Surfactants can also form oil/water microemulsions, which improves the oil's mobility and, hence, the microscale sweep efficiency [319,320].

Distinguished by their amphiphilic nature, surfactants consist of a hydrophilic (water-loving) head and a hydrophobic (water-repelling) tail [161,229,230]. Frequently utilized surfactants in chemical enhanced oil recovery (cEOR) applications are anionic, cationic, nonionic, and zwitterionic [231]. Gemini surfactants represent an innovative class characterized by two hydrophobic tail groups and two hydrophilic head groups [185]. The linkage between the two monomers can be established through a spacer, which may be a

chemical bond or a functional group [321], positioned either at the head groups or the tail groups. When both the head groups and the tail groups are identical, the Gemini surfactant is termed a symmetric dimeric surfactant [322]. Gemini surfactants offer a significant advantage due to their high efficiency in reducing interfacial tension (IFT) [323,324]. Compared to conventional surfactants, they demonstrate notably lower critical micelle concentration (CMC) and achieve ultralow IFT more rapidly. Moreover, Gemini surfactants exhibit enhanced rheological properties in comparison to their conventional counterparts [325].

Despite their exceptional attributes, there is a scarcity of studies focusing on their practical utilization, particularly within the context of cEOR in carbonate rocks [181,186,237,239–241]. The need for the development of surfactants that can withstand the harsh conditions of carbonate reservoirs arises from the fact these reservoirs hold over 60% of the globe's proven reserves [162–164]. The high salinity of these reservoirs, however, affect the behavior of the injected chemicals. To illustrate, the stability of surfactants, their solubility, and their CMC are all affected by the presence of salt in the formation and injected waters [326–328]. Therefore, scientists have been actively exploring surfactants and combinations of surfactants that exhibit effective performance in high-salinity environments.

Previous studies by our research group have led to the synthesis of a group of Gemini surfactants for applications in harsh conditions of carbonate reservoirs, specifically high temperatures and high salinity (HTHS). These surfactants have undergone thorough evaluation and screening [191,194–196,198–203]. Following chemical characterization by MALDI-TOF MS, FTIR, ^1H NMR, and ^{13}C NMR spectroscopy, a member of this group (GS8) underwent testing for both salt tolerance and thermal stability. Solubility tests

conducted in deionized water (DW), seawater (SW), and formation brine (FW) exhibited outstanding solubility, showing no signs of precipitation or cloudiness even under elevated salinity levels. Moreover, it demonstrated remarkable thermal stability, enduring temperatures exceeding typical oilfield conditions, surpassing 90 °C without degradation. Short-term thermal stability tests indicated that the surfactants decompose at a temperature as high as 300 °C based on thermographic analysis. Long-term tests conducted over approximately three months at 90 °C revealed the stability of the surfactant solution in either DW, SW, or FW [191,194]. Subsequently, an in-depth investigation into its wettability alteration characteristics was carried out [196]. Finally, the static adsorption and retention characteristics of GS12 were evaluated [202,203,256].

An approach to accommodate surfactants in high-salinity conditions involves combining them with materials that stabilize or enhance their performance [195]. Chelating agents are compounds characterized by possessing at least two groups, typically termed ligands, capable of donating electrons to form coordination bonds with a central metal atom [329]. Known for their ability to form complexes with metal ions, they prove an effectiveness in mitigating the adverse effects of high-salinity, high-hardness brines on surfactants [330]. By sequestering metal ions, chelating agents prevent them from interfering with surfactant functionality [331,332]. Beyond that, previous studies have shown that chelating agents alone exhibit a water-wettability alteration potential on various rock types [333–336]. Studies also showed that diethylenetriaminepentaacetic acid (DTPA) can reduce the oil/water IFT [337] and increase oil recovery as demonstrated by coreflooding experiments [334,338]. The effect of incorporating chelating agents with viscoelastic surfactants was also investigated through micromodels [339]. A combination of GS8 with DTPA resulted

in a better wettability alteration by either a Gemini surfactant solution or DTPA solution alone [195].

Injection of low-salinity (LowSal) water or modified seawater has also been proven to be an effective method to enhance the oil displacement efficiency from sandstone or carbonate reservoirs. The method is attractive due to its simplicity, low cost, and ease of implementation [340]. It involves injecting brine with a lower salinity level compared to the water naturally present in the formation or that of normal seawater. Reducing the salinity of the injected water can reduce oil/water IFT, oil/rock capillary pressure, and can alter the rock wettability [338,341,342]. Other proposed mechanisms include pH increase, mineral dissolution, fines migration, microemulsion formation, and multi-ion exchange [157,343,344]. The utilization of low salinity water was found to reduce both the static and dynamic adsorptions of a member of in-house synthesized surfactant (GS12) [256].

Methylene blue (MB) is a cationic thiazine dye with a distinctive blue color, commonly employed in various industries including textile, paper, cosmetics, and pharmaceuticals [345,346]. With a molecular formula of $C_{16}H_{18}N_3ClS$ and a molecular weight of 319.85 g/mol, MB exhibits high solubility in water and forms a reliably stable solution at typical room temperatures [347]. It has been tested for its capability for reducing adsorption of GS12 with favorable results [200]. However, no studies have tested its effectiveness in oil recovery with surfactant flooding.

Despite the previous investigation of the different chemicals with the GS8, there is no attempt to investigate the oil displacement efficiency by the surfactant when prepared in different makeup fluids. This study provides a comparative investigation of combining our GS8 with solutions of either DTPA, LowSal water, or Methylene blue for application under

the HTHS conditions of carbonate reservoirs. The investigation comprises four coreflooding experiments, each involving a solution of the tested chemical augmented by a 2,500-ppm concentration of the GS8. Additionally, effluent analysis was performed focusing on the determination of the concentration of the surfactant in the produced effluent through high-performance liquid chromatography (HPLC).

7.2 Experimental Work

7.2.1 Materials

Rock Samples. In this comparative study, four coreflooding experiments were carried out on four identical Indiana limestone rock samples whose properties are listed in **Table 7-1**. The XRD analysis on a powder sample of this rock showed the dominance of calcite. The objective of each flood is also listed in **Table 7-1**.

Table 7-1: Properties of rock samples and corresponding objective

Experiment No.	Sample ID.	Length (cm)	Diameter (cm)	Porosity (%)	Liquid permeability (mD)	Objective in Chemical Flooding
1	IL-22	10.16	3.75	16.2	99.9	Gemini surfactant in seawater
3	IL-31	10.20	3.75	16.3	101.2	Gemini surfactant in LowSal water
3	IL-35	10.21	3.75	16.6	107.1	Gemini surfactant in DTPA solution
4	IL-32	10.17	3.75	15.8	102.7	Gemini surfactant in seawater methylene blue solution

Salts and Brines. Synthetic Arabian Gulf water (SW) and formation brine (FW) with salinities exceeding 57,000 ppm and 213,000 ppm, respectively, were prepared for saturation and flooding purposes. They were prepared by dissolving different

laboratory-grade salts in deionized water to represent the flood and reservoir waters of oil fields in the Middle East. **Table 7-2** outlines their compositions.

Table 7-2: Compositions of synthesized brines

Salts	Concentration (mg/L)		
	Seawater	Formation water	Low Salinity Water
NaHCO ₃	165	487	16.5
Na ₂ SO ₄	6,339	517	633.9
NaCl	41,172	150,419	4,117.2
CaCl ₂	1,802	52,788	180.2
MgCl ₂	8,266	9,555	826.6
TDS →	57,745	213,768	5,774.5

Crude Oil. Crude oil obtained from an oil field in the Middle East was utilized to saturate and age the rock samples. The crude oil exhibits a viscosity of 2.48 cP under flooding conditions of 100 °C and 3,000 psi. Analysis of the crude oil's composition using IATROSCAN MK-7s FID showed the following SARA fractions: saturates content of 23.05%, aromatics content of 44.22%, resin content of 22.97%, and asphaltenes content of 9.76%. Moreover, the crude oil's total base number (TBN) and total acid number (TAN), determined via ASTM titration, were measured to be 0.76 mg KOH/g and 0.04 mg KOH/g, respectively.

Chemicals. The in-house tailored cationic Gemini surfactant, GS8, whose synthesis and evaluation are described elsewhere [194], was used in this study as a chemical flooding agent. The commonly used chelating agent DTPA (Diethylenetriamine pentaacetate) and methylene blue (MB) used in this work were provided by Nouryon

(Saudi Arabia) and Sigma Aldrich, respectively. The salts used in the preparation of the synthetic brines were also provided by Sigma Aldrich.

7.2.2 Preparation of Chemical Solutions

In this work, four 2500 ppm surfactant solutions were prepared in different base chemical solutions. The first was prepared by dissolving the GS8 in SW and this represents the reference case to which the other experiments are compared. The second was prepared by dissolving the GS8 in LowSal water, which was a ten-time diluted SW (see the composition of the LowSal water in **Table 7-1**). The third was prepared by dissolving the GS8 in 1% DTPA solution, also prepared in SW. To aid its solubility in SW, potassium hydroxide (KOH) was gradually added to the DTPA/SW solution until the solution became clear with no precipitated DTPA or KOH. The final pH of the DTPA/SW solution was around 7.28. The concentration of the DTPA was identified as a crucial concentration, where its effectiveness in altering wettability was influenced by the presence of salts without diminishing it [195]. Finally, the fourth solution was prepared by dissolving the GS8 in an MB/SW solution at an MB concentration of 300 ppm. To remove the undissolved traces of the MB, the MB/SW solution was filtered before adding the GS8 to it. The concentration of the surfactant remained at 2,500 ppm in all the prepared chemical solutions. This concentration of surfactant is believed to be practical and cost-effective for oil recovery experiments since it resulted in good oil recovery and low dynamic retention. Additionally, this surfactant can boost oil recovery without requiring a cosolvent or a cosurfactant compared with literature-reported formulations. Although the surfactant has a low CMC of around 100 ppm or less, the utilization of such concentration is not feasible as it may result in low oil recovery due to surfactant loss by retention.

7.2.3 Measurements of Contact Angle and IFT

To investigate how the specific chemical solutions influenced rock wettability, static contact angle (CA) measurements between oil and brine were carried out on Indiana rock samples both before and after treatment with each chemical solution. These substrates (~2 mm x 1 inch) were derived from Indiana rock samples with identical compositions to those used in the coreflooding experiments, with relatively low porosity and permeability to ensure precision in the measurements. Before testing, the substrates underwent oil aging at 100°C for nearly three weeks. The CA on each substrate was measured after aging and the measured CA represents the before-treatment value. Different substrates were then soaked in 30 ml of each chemical solution for around 4 days at ambient conditions. The CA was then measured to represent the after-treatment value. The change in CA is the difference between the before- and after-treatment values. The higher the change in the CA the better the wettability alteration is. Contact angle measurements and interfacial tension assessments were both conducted using specialized equipment. Specifically, an Attension Theta Optical Tensiometer provided by Biolin Scientific was utilized to perform all CA measurements, while the IFT between the crude oil and each prepared chemical solution was measured using a spinning drop tensiometer manufactured by Krüss, Germany. The IFT measurements were conducted at a spinning speed ranging from 3,500 to 4,500 RPM, depending on the chemical solution. After reaching the intended temperature, the droplet is allowed to stabilize after which the measurement is performed. For each temperature, the measurements are taken 100 times, each for 1 minute of spinning, and the average value of the measurements is then reported. This measurement method is considered dynamic because of the shear force resulting from the spinning.

7.2.4 Coreflooding Experiments

VINCI CFS700 coreflooding system (**Figure 7-1**) was employed in this study. The equipment has high pressure and high temperature ratings, and it can accommodate high salinity and corrosive fluids. Further details of the equipment are available in previous publications [205,258,307].

Core sample preparation. The rock samples were vacuum-saturated with synthetic FW. On the coreflooding system, the liquid permeability of each sample was measured by flooding FW through the sample. The irreducible water saturation (S_{wi}) was then established by pumping several pore volumes (PVs) of crude oil into each sample through a variable-rate drainage process. The resulting irreducible water saturations ranged from 33 to 34%. The existence of micropores in Indiana limestone and many carbonate rocks may contribute significantly to the relatively high irreducible water saturations observed [206,207]. In order to establish a predominantly oil-wet state, rock samples underwent a 21-day aging process by immersion in crude oil at 100 °C under static conditions [207]. This aging procedure facilitates the adsorption of polar components from the oil onto the rock matrix [308].

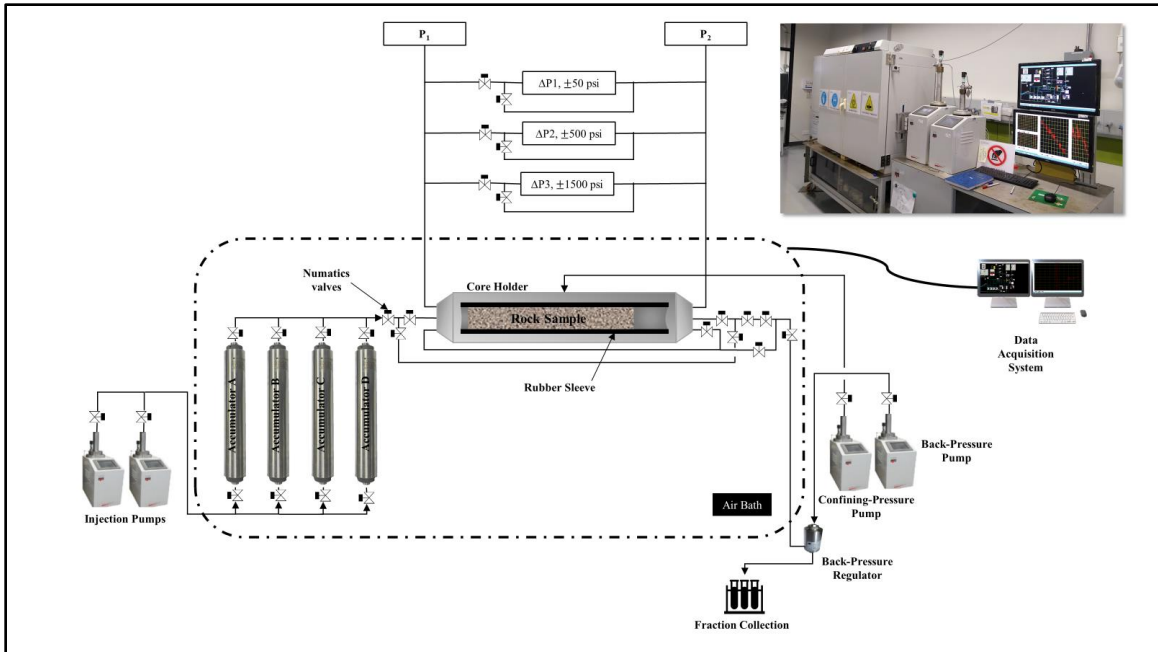


Figure 7-1. Schematic of the core-flooding setup

Oil recovery experiments. The oil recovery experiments (details in **Table 7-3**) were conducted on the aged core samples at 100 °C and under 3000 psi of pore pressure and 4000 psi confining pressure. The flooding was initiated by injecting between 1 and PVs of crude oil through each sample at a rate of 1 cc/min to establish the flow and saturate the samples with oil fresher than the aging oil. SW flooding followed until oil production ceased, as noticed by the increased water cut which exceeded 98%. The flooding was then switched to chemical injection, where each surfactant solution was continuously injected until no more oil was produced. The SW and chemical floods were carried out at an injection rate of 0.25 cc/min, corresponding to Darcy's velocity of around 1 ft/day. This injection rate was selected based a prior evaluation of different injection rates [307].

Table 7-3: Summary of coreflooding experiments

Experiment No.	Rock Sample	Flooding Steps	Experiment code
1	IL-22	1. SW 2. GS8 in SW at 2,500 ppm	Exp. 1
2	IL-31	1. SW 2. GS8 in 10x diluted LowSal at 2,500 ppm	Exp. 2
3	IL-35	1. SW 2. GS8 in 1 wt% DTPA/SW solution at 2,500 ppm	Exp. 3
4	IL-32	1. SW 2. GS8 in 300 ppm MB/SW solution at 2,500 ppm	Exp. 4

7.2.5 Effluent Analysis

The concentration of surfactant in the flood effluent was assessed through the effective potentiometric HPLC (high-performance liquid chromatography) technique. The detailed procedure of the method is presented in our published work [307]. A setup consisting of an Agilent 1200 series HPLC system equipped with an attached evaporative light scattering detector (ELSD) was utilized. Acetonitrile (C_2H_3N) was employed as mobile phase A, while a carrier phase B comprised of 0.1 M ammonium formate (NH_4COOH) with a pH of 4.3, adjusted by formic acid (CH_2O_2). The analysis was conducted using an Acclaim Surfactant Plus column (3 μm , 4.6 x 150 mm). It is worth mentioning that a calibration curve and equation were constructed for each tested chemical formulation through which the HPLC ELSD area was used to calculate the surfactant's concentration. Additionally, none of the tested chemicals except the GS8 had a peak on the HPLC signal and, hence, the concentration of the surfactant could be acquired precisely.

7.3 Experimental Work

7.3.1 Results of Contact Angle and IFT Measurements

Figure 7-2 illustrates the interfacial tension (IFT) between crude oil and various chemical solutions at different temperatures. The findings indicate that, at ambient temperature, incorporating either DTPA or MB with the GS8 led to a significant decrease in IFT compared to surfactant solutions in seawater or LowSal water. However, elevating the temperature to the maximum tested level of 80 °C resulted in a significant decrease in IFT between crude oil and the GS8 in both seawater and LowSal water. This reduction in IFT with temperature was not observed when either DTPA or MB were present. Despite this, the measured IFT values between the crude oil and the various solutions at the highest temperature remain comparable. However, the IFT achieved by all the solutions is almost the same for all the chemical solutions, that the additional oil recovery will not be attributed to IFT reduction.

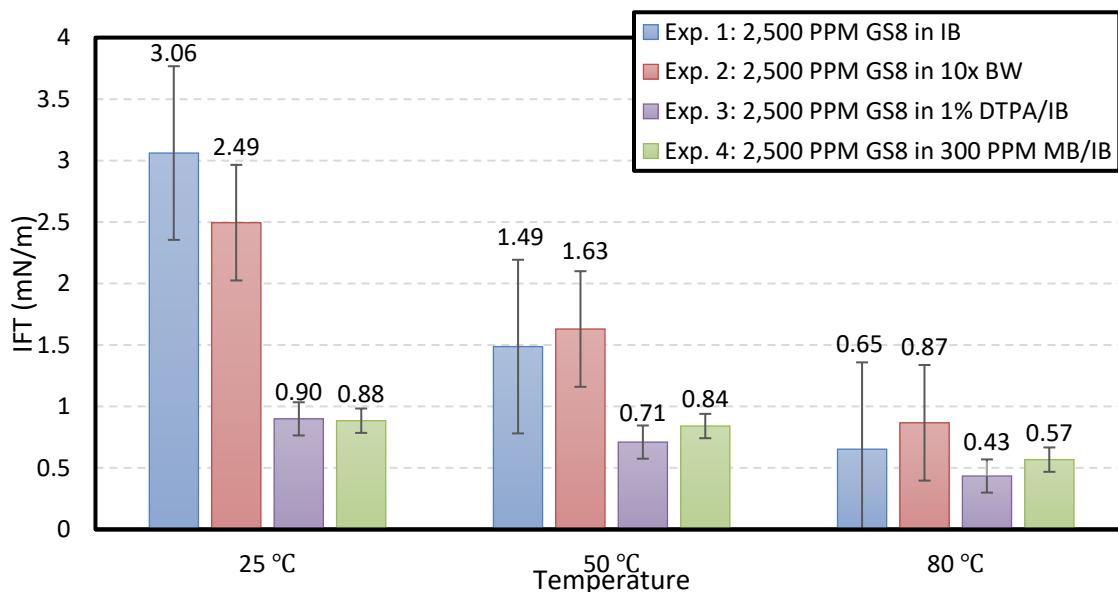


Figure 7-2. IFT values between oil and different chemical solutions

Figure 7-3 presents the results of CA measurements both before treatment in a chemical solution (i.e., after oil aging of the rock substrate) and after treatment with the chemical solutions. Initially, all the samples were strongly oil-wet as indicated by the initial CA values. The findings reveal that the changes in CA after treatment with surfactant solutions prepared in both seawater and LowSal water are nearly identical, with CA changes of approximately 39° and 41° respectively. Treatment with the GS8 dissolved in the DTPA solution resulted in the most significant change in CA among all prepared solutions with a CA change of around 52°. The better performance when DTPA was included can be attributed to the enhanced stability of the GS8 by DTPA. To illustrate, the inclusion of the chelating agent mitigated the adverse effects of metal ions found in SW, which can detrimentally impact the surfactant's performance [195]. Conversely, treatment with the solution containing the GS8 dissolved in 300 ppm MB had a detrimental effect on wettability alteration, exhibiting the smallest change in CA (approximately 35°) among all other solutions. This negative impact of the MB could be attributed to the competition between the cationic GS8 and the cationic MB for adsorption sites on the rock surfaces. For instance, it is believed that MB acts as a bridge between the rock sample and the cationic Gemini surfactant [200]. However, as discussed later, while this is advantageous in reducing surfactant adsorption, it adversely affects wettability alteration.

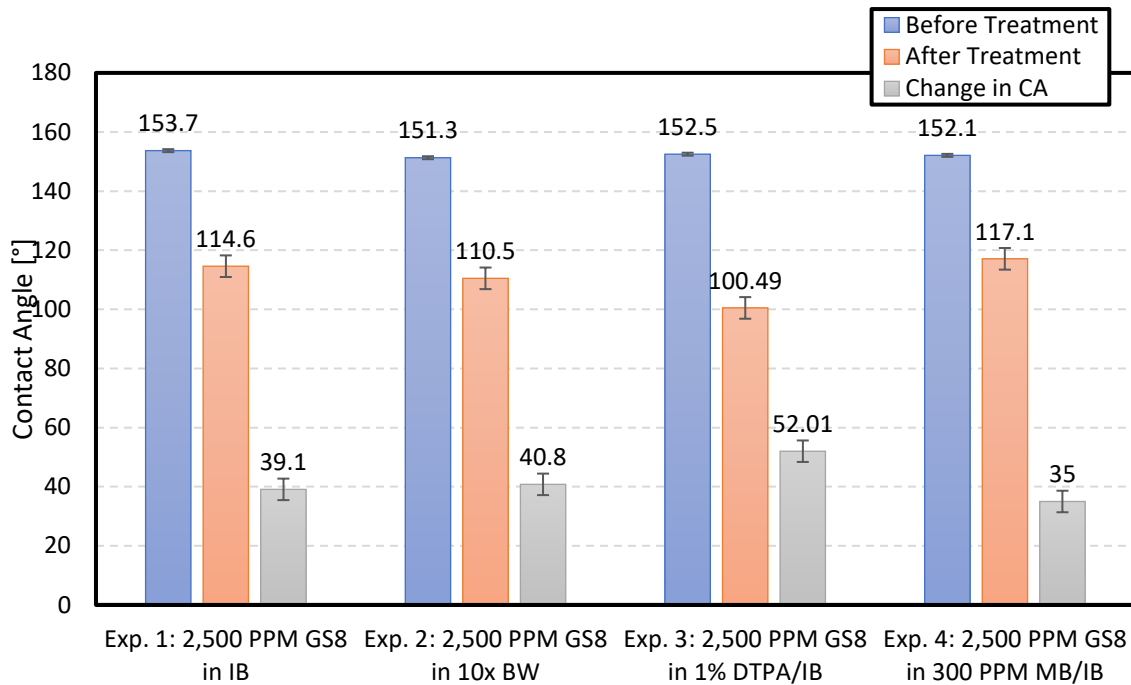


Figure 7-3. CA measurements before and after rock treatment with different chemical solutions

7.3.2 Results of Coreflooding Experiments

The results of the oil recovery floods are presented in **Figures 7-4 to 7-7** while **Figure 7-8** combines the results of the four experiments. The results show that the oil recovery factor for the four experiments ranges between 46% and 49% of the OOIP.

Seawater flooding. The residual oil saturation achieved by SW flooding ranges from 33% to 35.5%. The narrow range of oil recovery factors and residual oil saturation after SW flooding confirms the identity of the core samples used in this work. The SW flooding was halted when the oil production at the effluent reached zero.

Results of chemical flooding. The results of **Figure 7-4** show an additional oil recovery of around 23% OOIP after injecting around 5-6 pore volumes of the GS8 solution. The final oil recovery is around 70% OOIP and the corresponding residual oil saturation is nearly 20%. The primary mechanism driving this additional oil recovery is primarily

attributed to wettability alteration. This is exemplified by contact angle and IFT measurements presented both in this study and our previous publication [258], indicating that the GS8 is more effective in shifting the wettability of rocks than in lowering the oil/water IFT. For instance, the GS8 demonstrated the ability to shift the rock's wettability from a strongly oil-wet state to a predominantly intermediate-wet state. This assertion was also confirmed by observing a shift in the cross-over saturation points in the oil/water relative permeability curves, as calculated from coreflooding experiments using the JBN method. Since the GS8 did not achieve ultralow IFT, it was concluded that wettability alteration serves as the main mechanism behind enhanced recovery by the Gemini surfactant. The results of the GS8/LowSal water flood in tertiary mode are presented in **Figure 7-5**. The incremental oil recovery is around 26.3% OOIP, increasing the total oil recovery factor to around 73% OOIP and reducing the residual oil saturation to closely 18%. Since both chemical solutions in Exp. 1 and Exp. 2 resulted in a similar wettability alteration as demonstrated by the similar magnitude of the change in the CA, the higher oil recovery using LowSal water instead of SW can be attributed to fines migration or the formed microemulsion caused by salinity gradient, which are both mechanisms of LowSal waterflooding. However, there was no precipitated particles were detected in the effluents throughout this chemical flooding. There was also no abnormal increase in the pressure drop (presented later) which might be caused by the formation damage resulting from the fines migration [348]. Therefore, the fines migration is excluded leaving microemulsion as the possible cause. Microemulsion could have promoted better conformance control and, hence, a relatively higher oil recovery.

Formation of microemulsion during is confirmed by observing the collected effluent in some vials during Exp. 2. **Figure 7-9** presents some images of the collected effluents. **Figure 7-9(a)** shows the effluent collected during SW flood with no emulsion detected in the aqueous phase. **Figure 7-9(b)** shows the collected effluent in the early stages of chemical flooding, also revealing no microemulsion in the aqueous phase. However, as time progresses, there is a noticeable change in the color and texture of the aqueous phase in the effluent, as shown in **Figure 7-9(c)**. The image reveals an oil-in-water (O/W) microemulsion, which is also referred to as Winsor's type I or lower phase system [2,96]. This change in effluent behavior is not solely due to LowSal; rather, it is attributed to the presence of a negative salinity gradient resulting from the high salinity SW introduced during the SW flooding stage followed by the LowSal/surfactant solution. **Figure 7-9(d)** displays a mixture of crude oil and a surfactant solution prepared in LowSal water at laboratory conditions, where no microemulsion is formed solely by LowSal. This highlights the impact of the salinity gradient on the effluent behavior, and the oil recovery.

The results of incorporating DTPA in the recovery process, where the GS8 was dissolved in 1 wt% of DTPA prepared in seawater, are shown in **Figure 7-6**. The additional oil recovery by this chemical solution is the largest among all the tested solutions, which was approximately 37% OOIP. Consequently, the final oil recovery significantly rose to 84% OOIP, reducing the residual oil saturation to approximately 11%. What can be seen from the oil recovery profile is that oil was slowly produced during the chemical flooding before a large oil bank was produced and increased the oil recovery dramatically. This significantly higher oil recovery is mainly due to the better wettability alteration caused by the GS8/DTPA/SW mixture, as evidenced from the CA angle measurements. Additional

oil recovery by the incorporation of DTPA with the GS8 might also be due to the observed middle-phase emulsion, which was closer to what is shown in **Figure 7-9(b)**. Furthermore, the carboxylic groups present in the chelating agent would enhance oil solubility and facilitate the displacement of residual oil [331].

Finally, **Figure 7-7** shows the outcomes of using MB with the GS8. The results indicate a slow recovery process when MB is included as indicated by the larger volume of chemical solution required to increase the oil recovery. To illustrate, it required injecting around 11 pore volumes of the chemical solution to achieve an oil recovery increment of around 27% OOIP, compared with injecting around 6 pore volumes only to attain approximately 23% OOIP in the absence of MB (i.e., Exp. 1). Nonetheless, the ultimate oil recovery in this experiment rose to around 76% OOIP, with residual oil saturation decreasing to roughly 16%. This slow recovery process is hypothetically caused by the MB molecules serving as a bridge between the cationic GS8 and certain interactive sites on the rock. This bridging mechanism induces electrostatic repulsion, thereby reducing the interaction of the GS8 with the rock and consequently slowing down the wettability alteration process facilitated by the GS8.

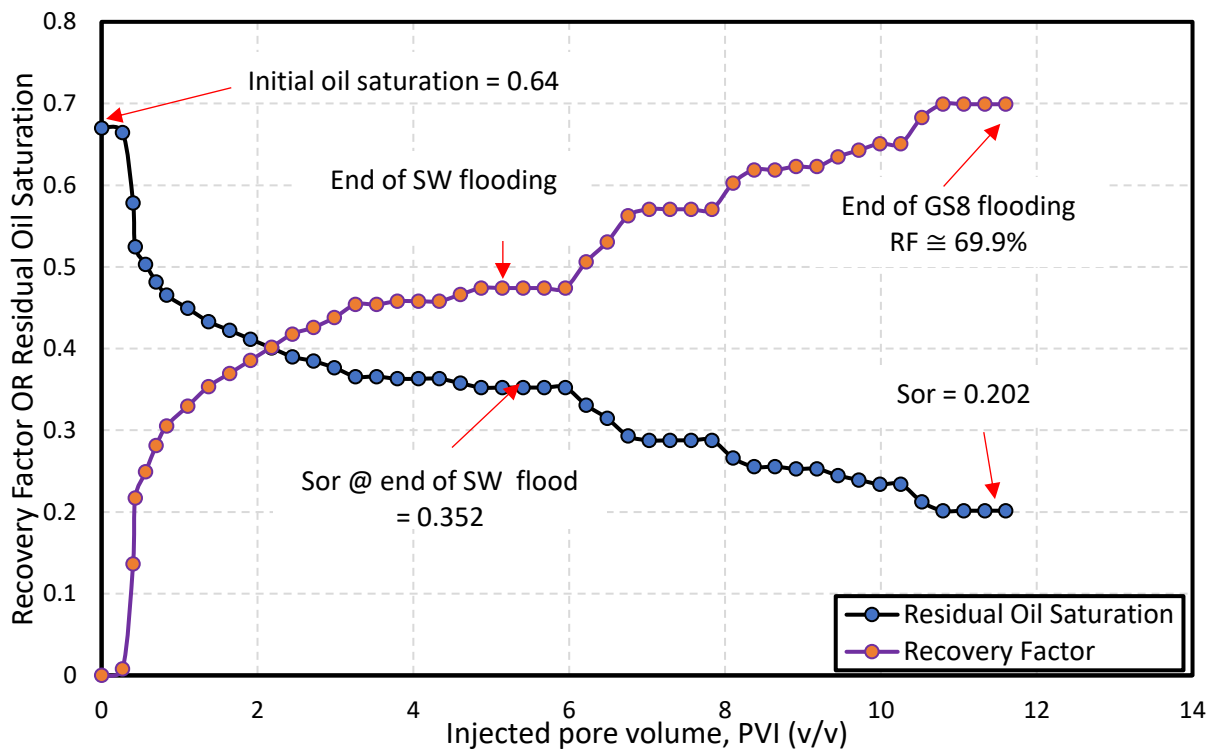


Figure 7-4. Results of oil recovery for Exp. 1 (GS8/SW)

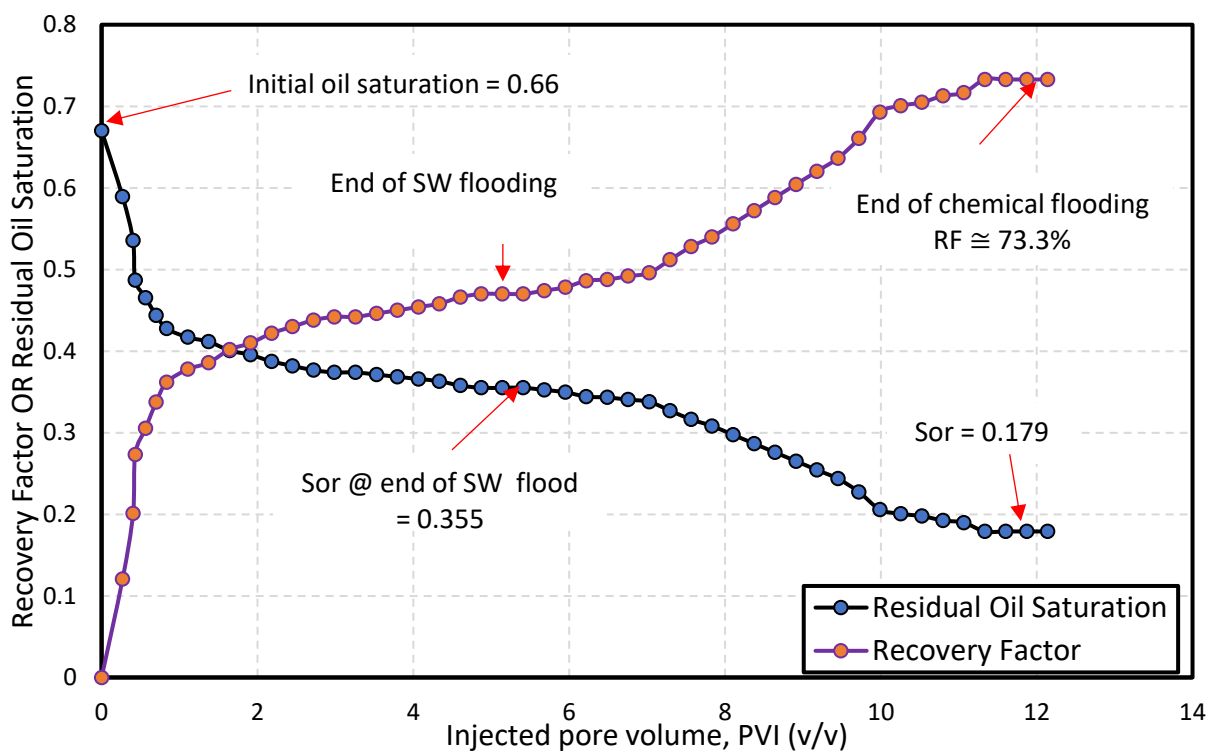


Figure 7-5. Results of oil recovery for Exp. 2 (GS8/LowSal)

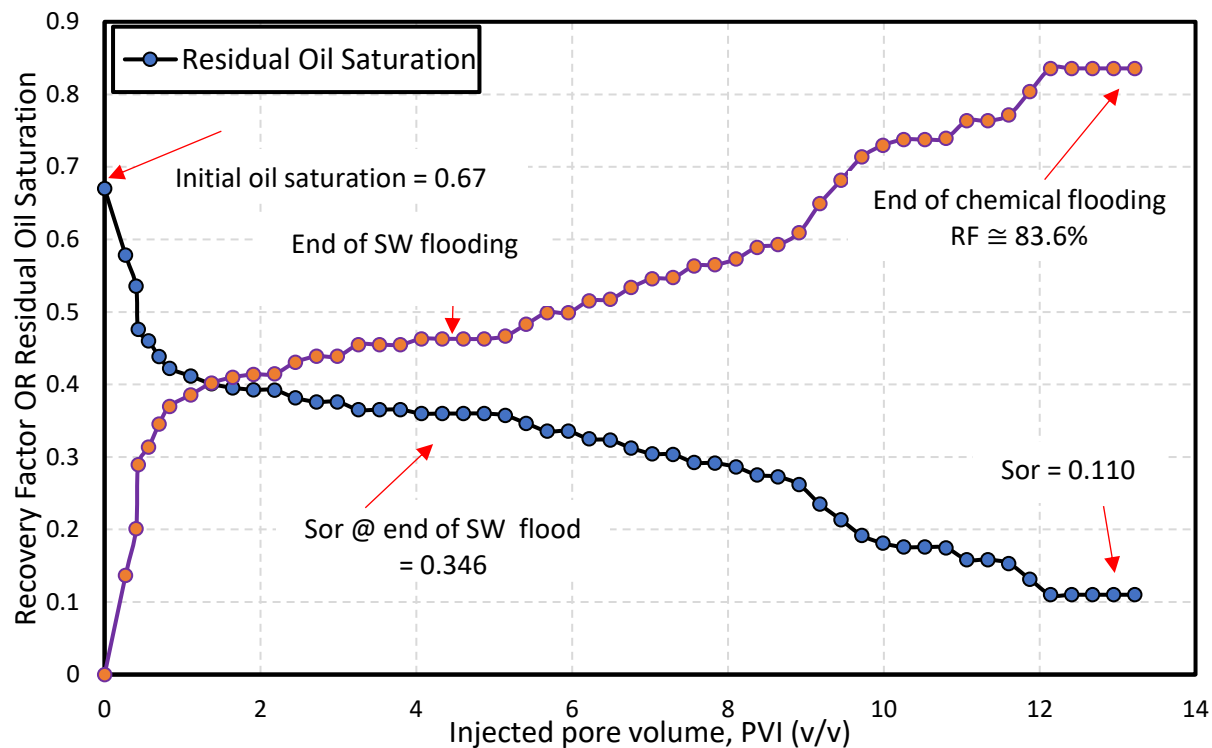


Figure 7-6. Results of oil recovery for Exp. 3 (GS8/DTPA/SW)

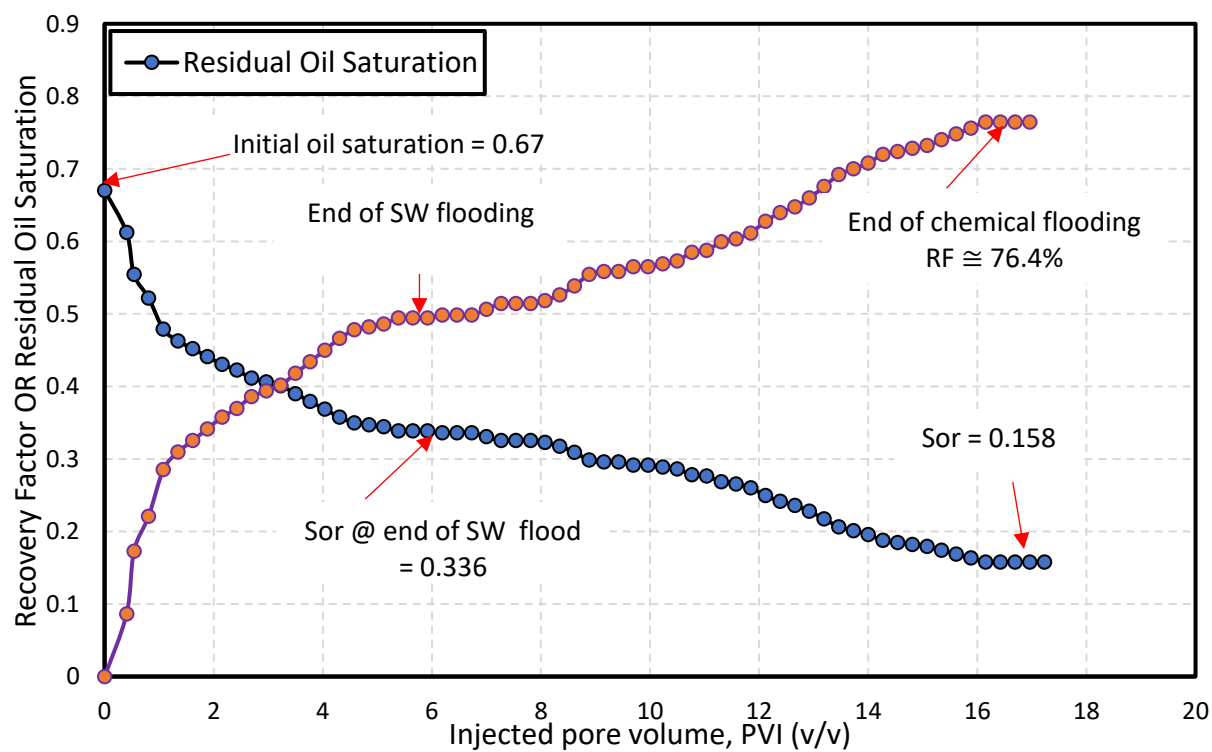


Figure 7-7. Results of oil recovery for Exp. 4 (GS8/MB/SW)

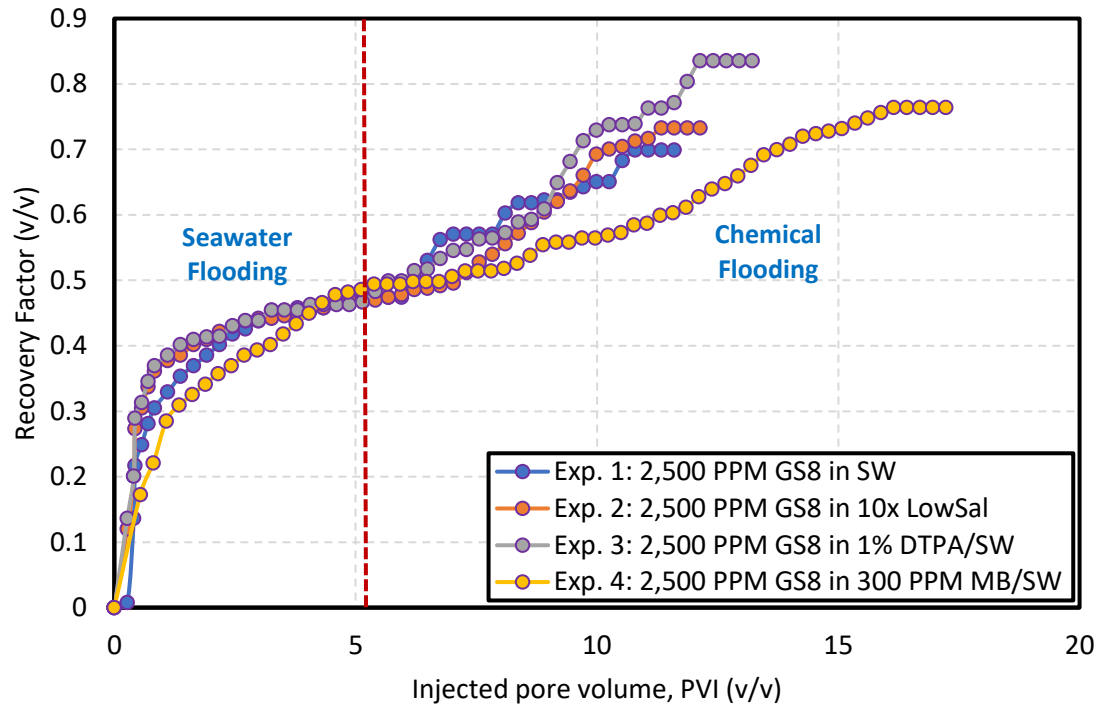


Figure 7-8. Results of oil recovery for the four experiments

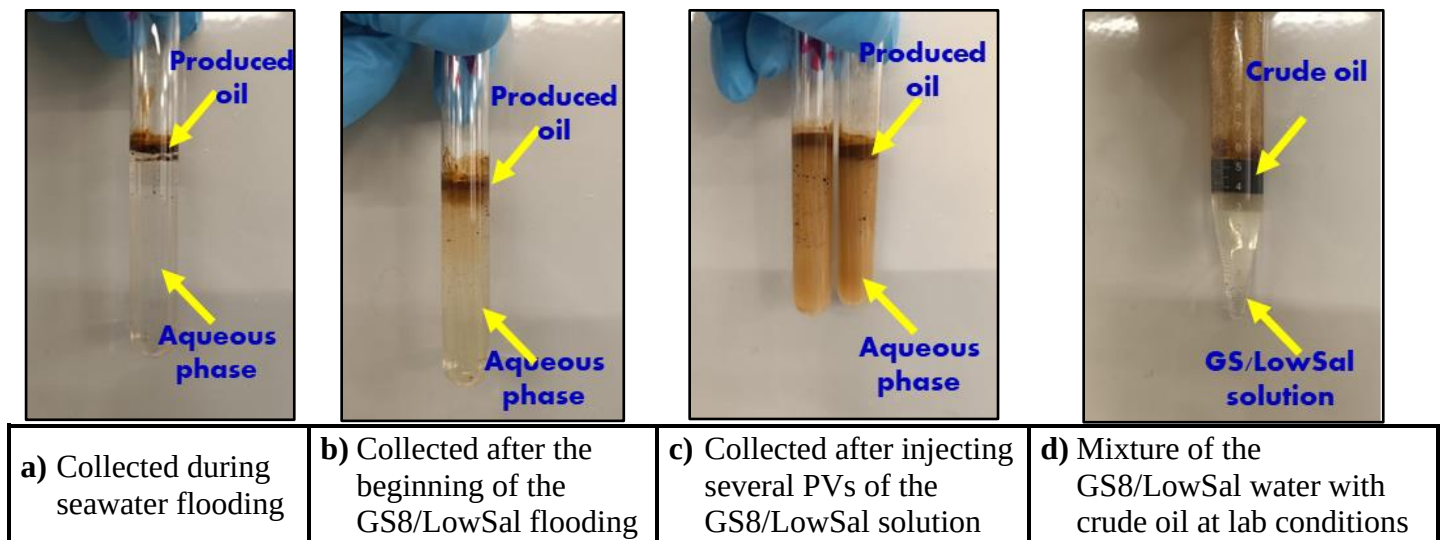


Figure 7-9 Evolution of the Effluent during GS8/LowSal flooding test (Exp. 2)

Pressure drop profiles. Figure 7-10 presents the differential pressure across the flooded samples during the SW and chemical injections. Initially, the pressure drop (ΔP) increased to a maximum of 3.5 to nearly 4 psi at breakthrough then dropped to a level of 1.1 to 1.5 psi towards the end of the SW flood. During the chemical floods, a further significant

decrease in the pressure is attributed to the reduction in the remaining oil saturation. Although we concluded that a microemulsion was formed during the chemical flood of Exp. 2, the pressure drop did not show any increase, reflecting the low viscosity and/or volume of the formed microemulsion. During chemical injection in Exp. 3, the pressure drop showed a slight increase during the period of injecting 8 to 10 PVs, which could be an indication of the formation of the microemulsion that could be another factor responsible for the significant oil recovery during this experiment.

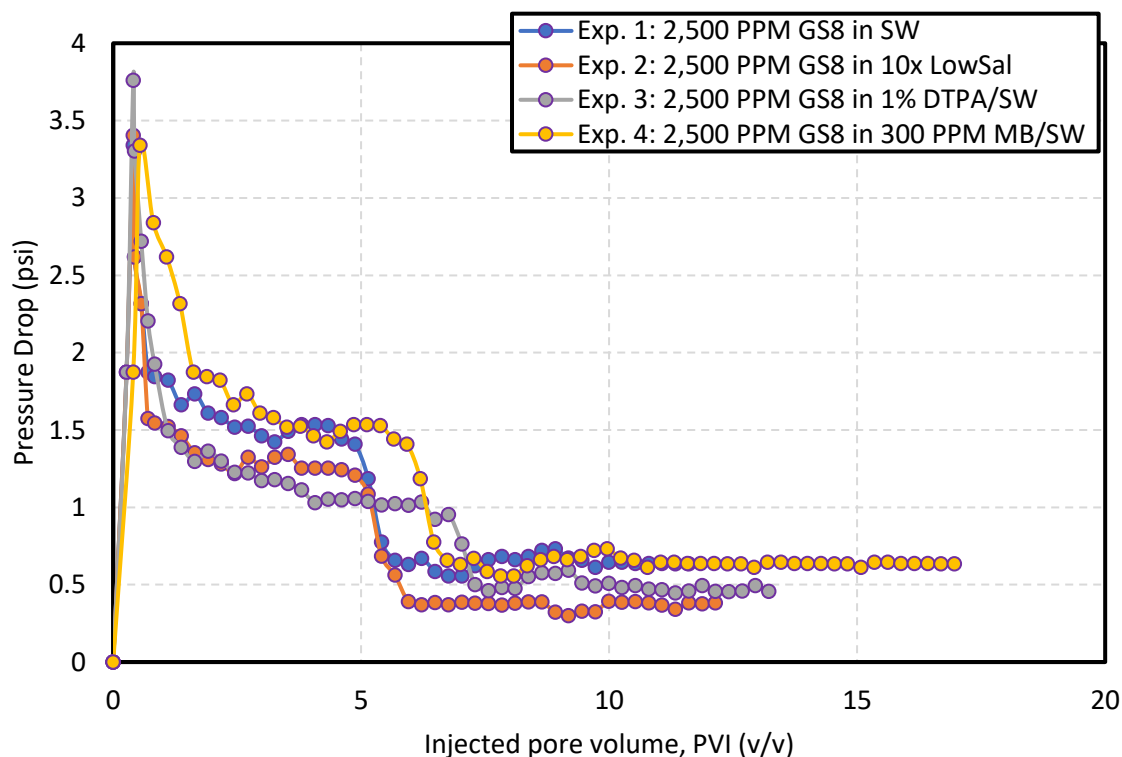


Figure 7-10. Differential pressure across the rock samples during SW and chemical injections

7.3.3 Results of Effluent Analysis

Before calculating the concentration of the surfactant in the produced effluent, it was necessary to develop a calibration equation for each chemical solution. This involved plotting the surfactant concentration against the ELSD area and extracting a best-fit

equation. This equation was then employed to calculate the surfactant concentration from the HPLC ELSD for each vial in all the experiments, which helped estimate the surfactant's dynamic retention.

Figure 7-11 shows the effluent's surfactant concentration versus the injected pore volume for each experiment. The plots show zero concentration during seawater flooding followed by a rapid increase at chemical breakthrough, which leveled off gradually towards the end of the flood.

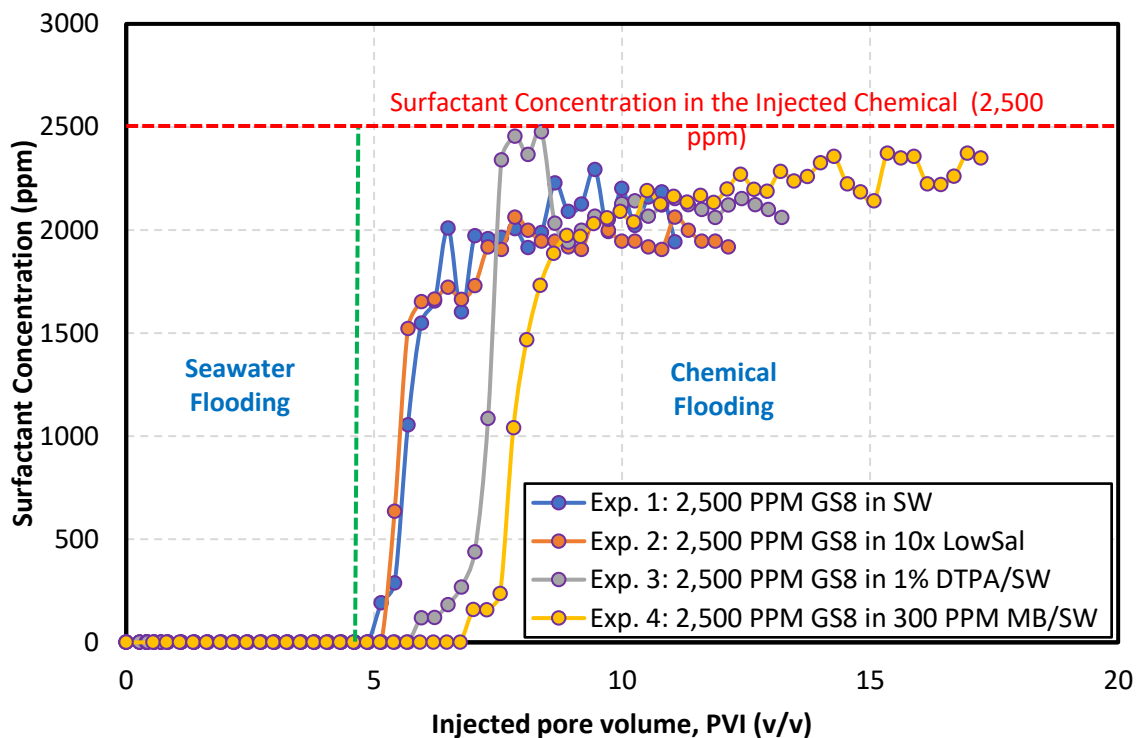


Figure 7-11. Surfactant concentration in the effluent for the four experiments

The blue curve of **Figure 7-11** corresponds to GS8 dissolved in seawater (Exp.1) and shows a highest surfactant concentration of around 2,300 ppm with a corresponding estimated dynamic retention is 0.372 mg/g-rock. The orange curve in the figure corresponds to GS8 dissolved in LowSal water (Exp.2) where the surfactant's maximum

concentration reached nearly 2,000 ppm with a corresponding estimated dynamic retention of 0.335 mg/g-rock, which is nearly 10% less than that observed in Exp. 1. This lower dynamic retention proves the effectiveness of LowSal water in minimizing the adsorption of Gemini surfactant onto carbonate rocks. Kalam et al. [256] attribute such reduction to the enlargement of the electric double layer occurring at the interface between the solid and liquid phases.

The grey curve of **Figure 7-11** shows the effect of dissolving the GS8 in 1wt% DTPA/SW solution (Exp.3). Following breakthrough, the surfactant concentration rose to almost its injected concentration before it decreased and leveled out at about 2,150 ppm. The initial high concentration of surfactant can be explained by either of two factors. Firstly, the presence of DTPA enhances the stability of the surfactant, allowing it to remain in solution until oil production begins, at which point the surfactant partitions into the oil phase. This is because the DTPA serves as a sequestering agent that can improve the stability of the surfactant in the solution. Secondly, during the early stages of chemical flooding, surfactant trapping and accumulation in the rock may have occurred due to the formed microemulsion which locked the surfactant in it. This is clearly indicated by the not-so-fast rise in concentration of the surfactant at the beginning. Subsequently, the surfactant trapped and accumulated within the rock is produced, leading to a sudden increase in surfactant concentration to a value close to that of the injected surfactant concentration. The subsequent calculated dynamic retention is 0.407 mg/g-rock. The relatively high dynamic retention coincides with the high oil recovery, indicating the partitioning of the surfactant into the oil phase.

The yellow curve of **Figure 7-11** shows the results of the flood that involved GS8 dissolved in a 300 ppm MB/SW solution (Exp.4). The highest concentration of surfactant reached around 2,400 ppm and the corresponding estimated dynamic retention is 0.397 mg/g-rock, which is slightly higher than that of Exp. 1. Involving MB in the flooding process is supposed to reduce the adsorption of the GS8 onto the rock. Given the large amount of injected chemical solution (i.e., GS8/MB/SW solution), which is two folds of that injected in Exp. 1, the calculated dynamic retention in Exp. 4 can be considered low and the MB still has a positive effect in reducing surfactant adsorption.

Figure 7-12 provides an overview of the outcomes of this study's coreflooding experiments. This includes data on oil recovery factors achieved through seawater and chemical flooding, as well as the overall recovery factor, residual oil saturation, and dynamic retention observed for each experiment.

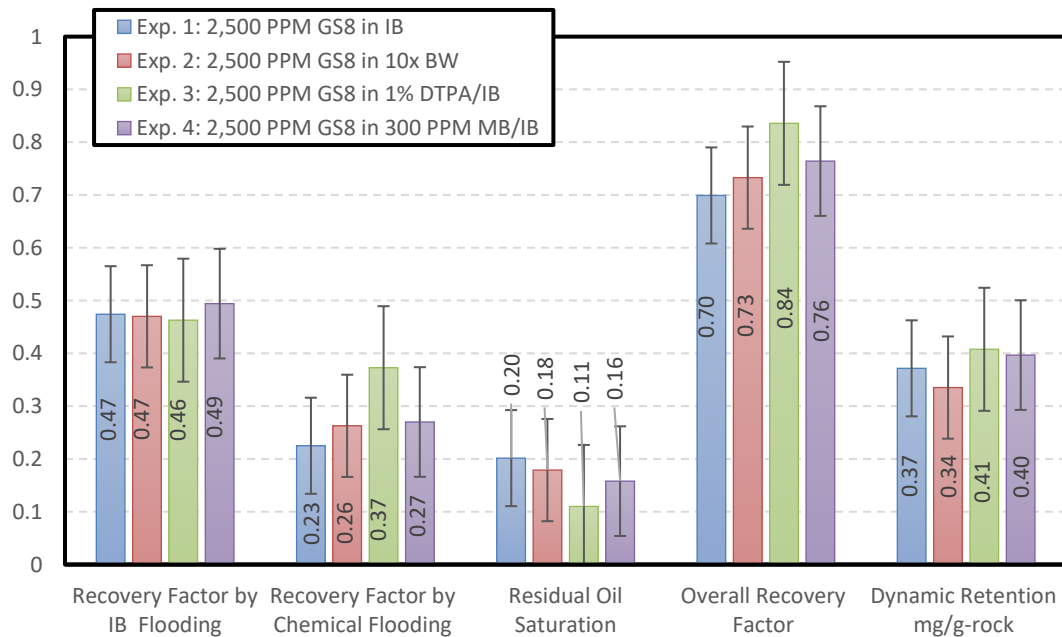


Figure 7-12. Summary of all coreflooding tests

7.4 Summary & Conclusions

This work provides insights into the effect of coupling low-salinity water, DTPA, or methylene blue with a cationic Gemini surfactant on oil recovery from Indiana limestone cores under harsh conditions. Four coreflooding experiments were executed where, in each experiment, seawater injection was followed by a continuous injection of a chemical solution. The injected chemical solutions consisted of either the surfactant dissolved in seawater (Exp.1), the surfactant dissolved in 10 times diluted seawater (LowSal) (Exp.2), the surfactant added to a 1 wt% DTPA in seawater solution (Exp.3), or the surfactant added to a 300 ppm MB in seawater solution (Exp.4). The surfactant concentration in all injected chemical solutions was 2,500 ppm. The main conclusions drawn from this study are as follows:

1. The oil recovery factor after the seawater flood phase in the four experiments ranged between 46% and 49% of the OOIP. The corresponding residual oil saturations ranged between 33% and 35.5%. These narrow ranges confirm the identity of the core samples used in this work.
2. Continuous injection of GS8 in seawater solution resulted in further oil recovery of about 23% OOIP, increasing the final oil recovery factor to around 70% OOIP. The residual oil saturation was lowered to about 20%. The resulting dynamic retention was estimated at 0.37 mg/g-rock.
3. Substituting seawater with LowSal as the GS8 solvent resulted in an increasing the oil recovery factor by about 26.3% OOIP, increasing the total oil recovery to about 73% OOIP and reducing the residual oil saturation roughly to 18%. The resulting dynamic

- retention was estimated at 0.35 mg/g-rock. The higher oil recovery and lower dynamic retention indicate the effectiveness of LowSal over seawater as a GS8 solvent.
4. Adding methylene blue to the GS8 solution slowed the recovery process as reflected by the larger volume of chemical solution required to increase the oil recovery. The dynamic retention was slightly higher at 0.40 mg/g-rock.
 5. Incorporating DTPA in the recovery process, where the GS8 was dissolved in 1 wt% of DTPA in seawater solution, showed the largest incremental oil recovery of just about 37% OOIP. The ultimate oil recovery rose to 84% OOIP, while the residual oil saturation dropped to nearly 11%. The resulting dynamic retention was calculated as 0.41 mg/g-rock. This performance reflects the synergetic effect between the GS8 and DTPA.
 6. This study demonstrates the synergistic effect of the GS8 when combined with other additives. While some chemicals enhanced the performance of the surfactant others showed the potential to reduce its retention, albeit at the expense of oil recovery as in the case of MB. Hence, there is a need for an optimization study to strike a balance between these effects.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This work aimed at evaluating the oil displacement efficiency of a member of in-house synthesized quaternary ammonium cationic Gemini surfactants in carbonate rocks, mainly through coreflooding experiments. The experiments were conducted under harsh conditions typical of carbonate reservoirs, with temperatures of 100°C, pressures exceeding 3000 psi, and salinity levels representative of formation water and seawater in the Middle East. The salinities of the tested fluids include seawater and formation water salinities of more than 57,000 and 213,000 ppm, respectively. The following are the main conclusions of the five experimental phases.

1. The in-house Gemini surfactant proved superior performance in increasing the oil recovery from carbonate rocks when used as a standalone surfactant without the need for a cosurfactant or a cosolvent.
2. This research underscores the importance of meticulously determining injection rates in surfactant flooding strategies to maximize enhanced oil recovery outcomes. It highlights the necessity of finding a delicate equilibrium between enhancing incremental oil recovery and reducing the dynamic retention of surfactants when determining the injection rate for surfactant flooding.

3. Experiments on rocks with different permeability showed the effect of rock permeability and the surface area on the performance of the GS. Low-permeability rocks correspond to high rocks' surface area which provides more contact of the surfactant to alter the rock's wettability and, hence, increase the oil recovery.
4. Utilizing NMR monitoring in this work enhances EOR insights through integrated studies and coreflooding experiments and establishes a novel framework for complex reservoir conditions.
5. The study confirms the effectiveness of the GS in enhancing oil recovery from local highly heterogeneous rock outcrops.
6. Replacing seawater with LowSal as the aqueous phase of the GS solution increased oil recovery and reduced dynamic retention, highlighting LowSal's superiority.
7. Injecting the GS dissolved in a 1 wt% DTPA/seawater solution, significantly boosted oil recovery compared to the GS alone, showing GS/DTPA synergistic effect.
8. The synergistic effect of the GS when combined with other additives was demonstrated. While some chemicals enhanced the performance of the surfactant others showed the potential to reduce its retention, albeit at the expense of oil recovery as in the case of MB. Hence, there is a need for an optimization study to strike a balance between these effects.

8.2 Recommendations

The following are the recommendations to be made to expand the scope of the findings of this research work.

1. Perform the static adsorption tests in the presence of crude oil at more realistic reservoir conditions.
2. Conduct a thorough investigation of the chemicals and methods investigated in Phase V to optimize the performance of the GS in the presence of those materials, specifically DTPA and Methylene blue.
3. Study the synergistic impact of polymers with the GS. To illustrate, surfactant/polymer (SP) formulations can be designed and tested for rheological properties as well as the oil displacement efficiency.
4. Perform flooding tests utilizing the state-of-the art facilities like dynamic micro-CT scanning, microfluidics, or magnetic resonance imaging (MRI) to visualize the flow behavior of fluids during the injection of the GS.
5. Study the performance of the Gemini surfactant with live crude oil.

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VITAE

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Google Scholar: <https://scholar.google.com/citations?user=YqsZue0AAAAJ&hl=en>

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EDUCATION

Ph.D., Petroleum Engineering, 2019 – 2024

King Fahd University of Petroleum & Minerals, Saudi Arabia

Dissertation Title: *Experimental Evaluation of Oil Recovery from Carbonate Rocks by Gemini Surfactants*

M.Sc., Petroleum Engineering, 2016 – 2019

King Fahd University of Petroleum & Minerals, Saudi Arabia

Thesis Title: *Mitigation of CO₂ Gravity Override by Solvent Blending*

B.Sc., Petroleum Engineering, 2011 – 2016

King Fahd University of Petroleum & Minerals, Saudi Arabia

Awarded with First Honor

Short courses

- | | |
|---|------|
| - Basic Safety Training for Labs Users | 2023 |
| - Applications of Machine Learning using Python | 2020 |
| - Chemical EOR for Carbonate Reservoirs (KFUPM) | 2019 |
| - First Aid (KFUPM) | 2016 |
| - Oil and Gas Industry (KFUPM) | 2016 |
| - Introduction to Marketing (KFUPM) | 2015 |
| - Introduction to MATLAB (KFUPM) | 2015 |
| - New Employee Safety Training (NEST) (Schlumberger) | 2015 |
| - Principles of Project Management (KFUPM) | 2015 |
| - Hydrogen Sulfide (H ₂ S) & Breathing Apparatus (BA) Training
(Rawabi United Safety Services Co. Ltd.) | 2013 |

RESEARCH INTERESTS

- Chemical Enhanced Oil Recovery
- CO₂ Enhanced Oil Recovery
- Pressure/Volume/Temperature (PVT) Relationships
- Phase Behavior
- Applications of Machine Learning in Oil & Gas

RESEARCH CAPABILITIES

- Proposing ideas
- Developing/designing methodologies
- Teamwork
- Writing & analysis skills

LABORATORY EXPERIENCE

- Skilled in working with laboratory instruments and setups including:
 - High pressure/temperature (HPHT) coreflooding system
 - HPHT PVT system
 - High-performance liquid chromatograph (HPLC)
 - HPHT rolling-ball viscometer
 - HPHT live-oil recombination cell
- Design of different setups (e.g., fluid saturating & rock aging setups)
- Safety regulations at workplace

COMPUTER SKILLS

- MATLAB
- Python
- MS Office Package
- CMG Simulation Package
- Surfer Geostatistical Software

WORK EXPERIENCE

King Fahd University of Petroleum & Minerals, Saudi Arabia

Teaching assistant for different courses

September 2019 – present

- Advanced Petrophysics
- Advanced Reservoir Engineering
- Computational Multiphysics Modeling
- Reservoir Simulation
- Mathematical Methods in Petroleum Engineering

September 2016 – May 2019

- Water Flooding
- Reservoir Fluid Properties
- Reservoir Rock Properties

Miscellaneous

- Serve as a reviewer for different journals **2023-present**
- Serve as the membership chairperson of the SPE-KFUPM Student Chapter **2023-2024**
- Intern at Schlumberger Dhahran Carbonate Research Center (SDCR) for two months **2015**
- Served as the secretary of the SPE-KFUPM Student Chapter **2015/2017**
- Worked at the KFUPM bookstore checkout point for two weeks **2016**
- Worked at KFUPM's Research Institute for two months as a lab assistant in sample preparation **2016**

LANGUAGE SKILLS

- Arabic – Native language
- English – Excellent oral and writing skills

PROFESSIONAL MEMBERSHIP

- | | |
|--|--------------|
| - American Rock Mechanics Association (ARMA) | 2022-present |
| - Society of Petrophysics and Well Logging Association (SPWLA) | 2019-present |
| - Society of Petroleum Engineers (SPE) | 2013-present |

ACTIVITIES

- | | |
|---|--------------|
| - Participation in KFUPM Annual Volunteering Day | 2011-present |
| - Attending meetings, seminars, and workshops hosted by various societies and student chapters | 2013-present |
| - Participated in KFUPM Major Selection Program | 2014-2016 |
| - Participated in the Petro Bowl Middle East Regional Qualifier Contest (Bahrain) - 3 rd place in the region | 2015 |

AWARDS & HONORS

- | | |
|---|-----------|
| - Certificate of Completion of Asphaltene Flow Assurance Short Course | Feb. 2024 |
| - Certificate from the Arabian Safety Training Center for completing Effective Laboratory Health and Safety Management training | 2023 |
| - Received different certificates from Elsevier in recognition of review contributions | 2023/2024 |
| - Certificate from CMG Ltd. for completing a training course of Introduction to Thermal EOR modeling | 2020 |
| - Fully funded Ph.D. scholarship from KFUPM | 2019 |
| - Certificate for participating in the 2019 CPG-Young Professional Technical symposium - KFUPM | 2019 |
| - Certificate for attending a workshop on Chemical EOR for Carbonate Reservoirs - KFUPM | 2019 |
| - Awarded for serving as the secretary of the SPE-KFUPM Student Chapter for the term 2017-2018 | 2018 |
| - Certificates for presenting two technical papers in the 2018 SPE-KSA Annual Technical Symposium & Exhibition (ATS&E) | 2018 |
| - Fully funded M.Sc. scholarship from KFUPM | 2016 |
| - Recipient of 1 st honor award from KFUPM at the end of the B.Sc. | 2016 |
| - Fully funded B.Sc. scholarship from the Ministry of Higher Education in Yemen | 2010 |
| - Awarded by the Ministry of Education and various authorities for ranking 8 th in Yemeni high school | 2009 |
| - Winner of multiple awards for securing 3 rd place in inter-governorate high school science competitions in Yemen | 2008 |

PUBLICATIONS (h-index: 7; No. of Citations: 209; scopus)

Journal Publications

Al-Azani, K.; Abu-Khamsin, S.; Kamal, M.S.; Patil, S.; Hussain, S.M.S.; Norrman, K.; Evaluation of a Gemini Surfactant for Enhanced Oil Recovery on Local Heterogeneous Carbonate Rocks Under Harsh Conditions. (**revised**).

Al-Azani, K., Abu-Khamsin, S., Elsayed, M., Patil, S., Shakil Hussain, S. M., Al Shalabi, E., Hassan, A. M., & Kamal, M. S.; Chemical enhanced oil recovery under harsh conditions: Investigation of rock permeability and insights from NMR

measurements. *Geoenergy Science and Engineering* **2024**: 212764. <https://doi.org/10.1016/j.geoen.2024.212764>.

Al-Azani, K.; Abu-Khamsin, S.; Kamal, M.S.; Patil, S.; Hussain, S.M.S.; Al-Shehri, D.; Mahmoud, M.; Role of Injection Rate on Chemical Enhanced Oil Recovery Using a Gemini Surfactant under Harsh Conditions. *Energy & Fuels* **2024**, 38(5): 3682–3692. <https://doi.org/10.1021/acs.energyfuels.3c04505>.

Al-Azani, K.; Abu-Khamsin, S.; Kamal, M.S.; Patil, S.; Zhou, X.; Hussain, S.M.S.; Mahmoud, M.; Enhanced Oil Recovery in Carbonate Reservoirs Using Single Component Synthesized Surfactants under Harsh Reservoir Conditions. *Energy & Fuels* **2023**, 37(15): 11004–11016. <https://doi.org/10.1021/acs.energyfuels.3c01909>.

Al-Azani, K.; Abu-Khamsin, S.; Al-Abdrabalnabi, R.; Kamal, M. S.; Patil, S.; Zhou, X.; Hussain, S. M. S.; Al Shalabi, E. Oil Recovery Performance by Surfactant Flooding: A Perspective on Multiscale Evaluation Methods. *Energy & Fuels* **2022**, 36 (22), 13451–13478. <https://doi.org/10.1021/acs.energyfuels.2c02544>.

Glatz, G.; Alafnan, S.; Gholami, R.; Raza, A.; Mahmoud, M.; Al-Azani, K.; Awotunde, A. Effect of Kerogen Maturity on the Adsorption Capacity of CO₂ and CH₄: A Molecular Investigation. *Fuel* **2022**, 327, 125188. <https://doi.org/10.1016/j.fuel.2022.125188>.

Isah, A.; Hiba, M.; Al-Azani, K.; Aljawad, M. S.; Mahmoud, M. A Comprehensive Review of Proppant Transport in Fractured Reservoirs: Experimental, Numerical, and Field Aspects. *J. Nat. Gas Sci. Eng.* **2021**, 88, 103832. <https://doi.org/10.1016/j.jngse.2021.103832>.

Al-Azani, K. H.; Abu-Khamsin, S. A.; Sultan, A. S. Experimental Study of Blending CO₂ with Triethyl Citrate for Mitigating Gravity Override During Reservoir Flooding. *Arab. J. Sci. Eng.* **2021**, 46 (7), 6787–6796. <https://doi.org/10.1007/s13369-020-04901-z>.

Al-Azani, K.; El-Husseiny, A.; Mahmoud, M.; Al-Yousef, H.; Elsayed, M. Numerical and Experimental Study to Determine the Permeability Anisotropy in Porous Rocks from Probe Permeameter Measurements. *Arab. J. Sci. Eng.* **2021**, 46 (7), 7019–7030. <https://doi.org/10.1007/s13369-021-05433-w>.

Al-AbdulJabbar, A.; Al-Azani, K.; Elkatatny, S. Estimation of Reservoir Porosity From Drilling Parameters Using Artificial Neural Networks. *Petrophysics - SPWLA J. Form. Eval. Reserv. Descr.* **2020**, 61 (03), 318–330. <https://doi.org/10.30632/PJV61N3-2020a5>.

Al-Azani, K. H.; Abu-Khamsin, S. A.; Sultan, A. S. Solubilities of Carbon Dioxide in Ethyl Benzoate and Triethyl Citrate at High Temperatures and Pressures. *J. Chem. Eng. Data* **2020**, 65 (4), 1857–1868. <https://doi.org/10.1021/acs.jced.9b01092>.

Al-Azani, K.; Elkatatny, S.; Ali, A.; Ramadan, E.; Abdurraheem, A. Cutting Concentration Prediction in Horizontal and Deviated Wells Using Artificial Intelligence Techniques. *J. Pet. Explor. Prod. Technol.* **2019**, 9 (4), 2769–2779. <https://doi.org/10.1007/s13202-019-0672-3>.

Conference Papers

Al-Azani, K.; Al-Yousef, H.; Mahmoud, M. Effect of Permeability Anisotropy on Probe Permeameter Measurements. *SPE Middle East Oil and Gas Show and Conference*. Society of Petroleum Engineers: Manama, Bahrain 2019. <https://doi.org/10.2118/194769-MS>.

Al-Azani, K.; Elkatatny, S.; Abdulraheem, A.; Mahmoud, M.; Al-Shehri, D. Real-Time Prediction of the Rheological Properties of Oil-Based Drilling Fluids Using Artificial Neural Networks. *SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition*. Society of Petroleum Engineers: Dammam, Saudi Arabia 2018. <https://doi.org/10.2118/192199-MS>.

Al-Azani, K.; Elkatatny, S.; Abdulraheem, A.; Mahmoud, M.; Ali, A. Prediction of Cutting Concentration in Horizontal and Deviated Wells Using Support Vector Machine. In *SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition*; Society of Petroleum Engineers: Dammam, Saudi Arabia, 2018. <https://doi.org/doi.org/10.2118/192193-MS>.

Al-Jaberi, J.; Al-Azani, K.; Fraim, M. Calculation of Sulfur Deposition in Gas Condensate Wells in Middle East. In *Society of Petroleum Engineers - SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition 2017*; Society of Petroleum Engineers: Dammam, Saudi Arabia, 2017. <https://doi.org/10.2118/188000-MS>

Patent

Abu-Khamsin, S. A.; Al-Azani, K. H. Method for Mitigating Gas Override in an Oil Reservoir. US20210032969A1, February 2021