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Review

Ecofriendly Natural Surfactants in the Oil and Gas Industry: A Comprehensive Review

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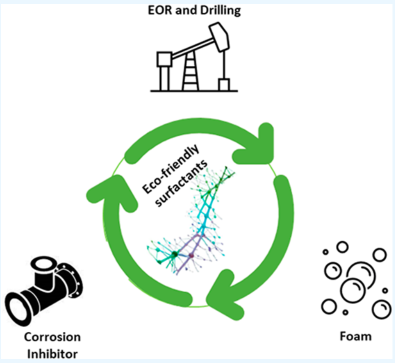
ABSTRACT: The use of different types of chemicals in upstream oilfield operations is critical for optimizing the different operations involved in hydrocarbon exploration and production. Surfactants are a type chemical that are applied in various upstream operations, such as drilling, fracturing, and enhanced oil recovery. However, due to their nonbiodegradability and toxicity, the use of synthetic surfactants has raised environmental concerns. Natural surfactants have emerged because of the hunt for sustainable and environmentally suitable substitutes. This Review discusses the role of natural surfactants in upstream operations as well as their benefits and drawbacks. The Review discusses the basic characteristics of surfactants, their classification, and the variables that affect their performance. Finally, the Review examines the possible applications of natural surfactants in the upstream oil sector and identifies areas that require further research.



1. INTRODUCTION

Oil serves as the primary source of the global energy supply. However, the extraction of crude oil is a complex process that involves various intricate operations. These operations are collectively referred to as upstream operations, which comprise drilling, completion, stimulation, and enhanced oil recovery, among others.[1−3] The choice of the appropriate upstream operation depends on several factors, including but not limited to the type of reservoir, the nature of the rock, the properties of the oil, and, most importantly, the geographical location of the field.[4−8]

As the oil and gas industry faces increasing pressure to adopt environmentally friendly practices, the utilization of natural surfactants aligns with the broader global goals of reducing carbon footprints and minimizing ecological disruptions.[9,10] Furthermore, the development of novel extraction and purification techniques has facilitated the large-scale production of natural surfactants, making them commercially viable and economically competitive options for various applications within the oil and gas sector.[11−13]

Enhanced oil recovery has become a critical technique for maximizing hydrocarbon production, particularly in mature oil fields where natural pressure declines. In this context, natural surfactants serve as indispensable agents in enhanced oil recovery (EOR) processes.[14−18] Surfactants injected into the reservoir act as emulsifiers, breaking down the oil−water interface and facilitating the mobilization and extraction of trapped oil.[19,20] This results in improved sweep efficiency and a more comprehensive recovery of oil reserves, making natural surfactants a valuable tool in extending the life of oil fields and increasing overall production.[21,22]

Furthermore, drilling operations face challenges such as wellbore instability and formation damage, necessitating stable drilling fluids. Natural surfactants play a crucial role in drilling and wellbore stabilization by reducing the surface tension between the drilling fluid and rock formations.[11,23] This stabilizes the wellbore, preventing fluid invasion and minimizing formation damage, leading to safer and more efficient drilling. Incorporating natural surfactants in drilling fluids not only enhances well productivity but also reduces operational costs and ensures sustainable oil extraction practices.[24−26]

Emulsion separation and transportation pose additional hurdles in the oil and gas industry, as extracted hydrocarbons are often contaminated with water and impurities in the form of emulsions.[17] To address this challenge, natural surfactants are employed in the process of emulsion breaking. By promoting the coalescence of water droplets, natural surfactants facilitate their separation from the oil phase, ensuring a higher quality of crude oil for further processing and preventing pipeline fouling or blockage.[27−29] This

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application of natural surfactants is critical in refining and transportation processes, optimizing resource utilization, and minimizing environmental impacts.

Apart from their practical applications, natural surfactants offer environmental benefits over their synthetic counterparts. Natural surfactants tend to be biodegradable, reducing their impact on the environment. This characteristic is particularly important in sensitive ecosystems or in cases of accidental spills, where the use of biodegradable surfactants can mitigate environmental harm. As sustainable practices gain prominence in the oil and gas industry, the incorporation of natural surfactants becomes increasingly valuable in demonstrating a commitment to environmental stewardship.

Natural surfactants hold immense importance in the oil and gas industry, playing a significant role in EOR, drilling, and wellbore stabilization, as well as emulsion separation and transportation processes. Their unique properties to reduce the interfacial tension (IFT) between different fluids make them invaluable tools in optimizing hydrocarbon extraction and production, improving overall efficiency, and reducing environmental impacts.[27] This paper will delve deeper into the applications and advantages of natural surfactants, shedding light on their role in advancing the oil and gas sector toward a sustainable and resource-efficient future.[17,28−30]

In recent years, there has been a growing emphasis on research and development initiatives focused on enhancing the properties and performance of natural surfactants in the oil and gas industry. Scientists and engineers are exploring innovative ways to tailor the molecular structures of these surfactants to optimize their efficiency in specific applications. The Review discusses a few natural surfactants and their applications in the upstream oil and gas industry. This Review is divided into different sections. The first section highlights the basics of natural surfactants, where different properties of natural surfactants are discussed in addition to the main sources of natural surfactants. The next section highlights the different applications of natural surfactants in oilfield operations such as in drilling, fracturing, enhanced recovery, and corrosion. Finally, prospects and research gaps are presented in the last sections.

2. BASICS OF NATURAL SURFACTANTS

2.1. Classification and Definition. Surfactants that are considered natural are derived from renewable sources such as plants or animals. They can be obtained through direct extraction without chemical synthesis or through chemical synthesis. Natural sources of surfactants include a variety of organisms such as animals, microorganisms, and bacteria, as well as different plant parts like leaves, flowers, roots, seeds, and extracted plant oils.[31]

The term "natural surfactant" is frequently employed in a broader sense than the one described earlier. Surfactants produced from natural raw materials are also categorized as natural surfactants. These comprise fatty acid esters of sugars as well as fatty acid esters or amides of amino acids. However, the term "natural surfactant" can have an even more generous usage. A surfactant that derives its polar headgroup or hydrophobic tail from a natural source is often considered a natural surfactant. For example, although alkyl glucosides are made from a "natural" sugar unit and a "non-natural" fatty alcohol, they are frequently deemed natural surfactants.[27]

Natural surfactants can be categorized based on their chemical composition, the ions present in the headgroup, and their source of origin. Chemical composition-based categorization of natural surfactants includes glycolipids, lipopeptides, phospholipids, and saponins. Classification based on the charge on the headgroup includes cationic, anionic, zwitterionic, or nonionic surfactants. Another classification could be the surfactants based on the natural headgroup and natural tail group. Another classification of natural surfactant was proposed as low molecular weight and high molecular weight biosurfactants.[32]

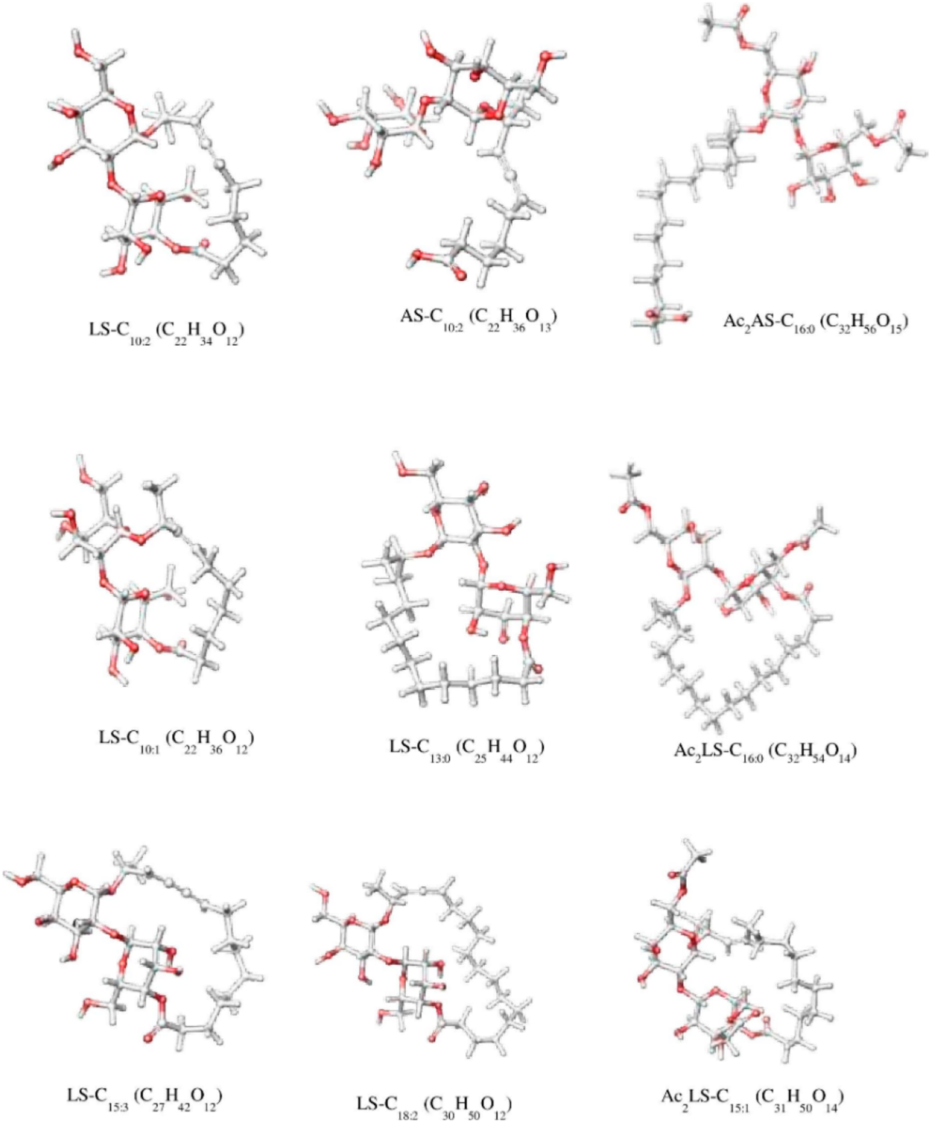
2.2. Properties of Natural Surfactants. Natural surfactants possess distinctive characteristics and have attracted attention for several reasons. Given the diverse functional properties exhibited by natural surfactants, including but not limited to emulsification, foaming, wetting, cleansing, surface activity, phase separation, and reduction of crude oil viscosity, they are highly versatile chemicals suitable for deployment across a wide spectrum of industrial processes.

A key benefit of natural surfactants is their synthesis from naturally occurring materials, rendering them both cost-effective and sustainable. Furthermore, the biodegradability of natural surfactants represents a significant advantage compared to synthetic surfactants, which are often non-biodegradable. The surface-active properties of natural surfactants closely resemble those of their synthetic counterparts. Specifically, they are capable of reducing water surface tension to a similar extent as synthetic surfactants.[26]

Microbial biosurfactants have been noted to be superior to plant-based surfactants due to their ability to be easily scaled up, quick production time, and diverse range of properties. While plant-based biosurfactants have great emulsification properties, their production at an industrial level can be costly, and they also have certain issues such as solubility and hydrophobicity.[33]

Natural surfactants have numerous advantages, but also have some disadvantages that need to be addressed. One of the issues is their potential toxicity to the environment, which has been demonstrated in certain experiments. Although natural surfactants are less toxic than synthetic surfactants, they can still rupture erythrocytes, and their use must be carefully controlled. Large-scale production of natural surfactants can also be expensive, although waste substrates can be used to reduce costs. Getting pure substances is challenging because of the numerous stages involved in the processing of weak solutions. It is uncommon to come across microbial strains that produce excessive amounts, and the ones found usually have extremely limited output. The presence of excessive foam can hinder how much is produced, and elevated productivity is achievable only through immobilized systems. Despite these challenges, natural surfactants remain an interesting alternative to synthetic surfactants in a variety of applications, and their use can help in the enhanced cleanup of toxic environmental pollutants.

2.3. Important Natural Surfactants. Glycolipids are a type of surfactants composed of a lipid group and a carbohydrate group. The carbohydrate component may be mono- or oligosaccharide, and the lipid portion may be a fatty acid or hydrocarbon chain. Many microorganisms produce glycolipids, including bacteria, fungi, and algae. Rhamnolipids, sophorolipids, trehalolipids, and cellobiolipids are common classes under glycolipids. Microbial fermentation and chemical or enzymatic synthesis using renewable resources are all viable methods for producing glycolipids. In their Review, Grüninger et al. analyzed the pros and cons of each method and



$\text{LS-C}_{10:2}$ ($C_{22}H_{34}O_{12}$)

$\text{AS-C}_{10:2}$ ($C_{22}H_{36}O_{13}$)

$\text{Ac}_2\text{AS-C}_{16:0}$ ($C_{32}H_{56}O_{15}$)

$\text{LS-C}_{10:1}$ ($C_{22}H_{36}O_{12}$)

$\text{LS-C}_{13:0}$ ($C_{25}H_{44}O_{12}$)

$\text{Ac}_2\text{LS-C}_{16:0}$ ($C_{32}H_{54}O_{14}$)

$\text{LS-C}_{15:3}$ ($C_{27}H_{42}O_{12}$)

$\text{LS-C}_{18:2}$ ($C_{30}H_{50}O_{12}$)

$\text{Ac}_2\text{LS-C}_{15:1}$ ($C_{31}H_{50}O_{14}$)

Figure 1. Least-energy structures of the sophorolipid homologues. Adapted with permission from ref 35. Copyright 2021 Frontier.

concluded that enzymatic synthesis is the optimal approach for creating a diverse array of customized glycolipids.[34]

Rhamnolipids are crystalline acids consisting of a rhamnose sugar molecule attached to a β-hydroxy fatty acid through its carboxyl end. These surfactants are mainly made by Gram-negative bacterium *Pseudomonas aeruginosa*. These molecules consist of a rhamnose sugar headgroup and a long chain fatty acid tail. The number of rhamnose units in the headgroup and the length of the fatty acid tail can vary depending on the producing organism and growth conditions.

In recent times, rhamnolipids have garnered considerable interest because of their possible uses across different sectors, such as bioremediation, agriculture, and pharmaceuticals. They are primarily produced through microbial fermentation using renewable resources such as vegetable oils and waste materials, making them sustainable alternatives to chemical surfactants. Rhamnolipids have also been found to exhibit antimicrobial properties, making them potential candidates for use as natural antimicrobial agents.

The unique structure of rhamnolipids allows them to disrupt bacterial cell membranes, leading to cell lysis and death. Rhamnolipids are useful in the bioremediation of heavy metals and hydrocarbons, as well as in the production of cosmetics and pharmaceuticals. With a market value projected to reach $2.8 billion in 2023, rhamnolipids have the potential to serve as substitutes for synthetic surfactants and act as a significant platform chemical cluster.[33] Overall, rhamnolipids have demonstrated great potential as sustainable and versatile biosurfactants with a wide range of potential applications in various industries.

Sophorolipids, produced by the yeast *Candida bombicola*, are surfactants with a glucose sugar group and a long-chain fatty acid.[35] Figure 1 shows the structures of sophorolipid homologues. Sophorolipids have various applications, including the production of personal care products, detergents, and pharmaceuticals. Sophorolipids are a type of glycolipid biosurfactants produced by yeast. They consist of a hydrophilic sophorose sugar head and a hydrophobic fatty acid tail, which makes them ideal for reducing surface tension and for forming micelles.

The basic structure of sophorolipids is similar to that of other glycolipids, such as rhamnolipids, but they have different

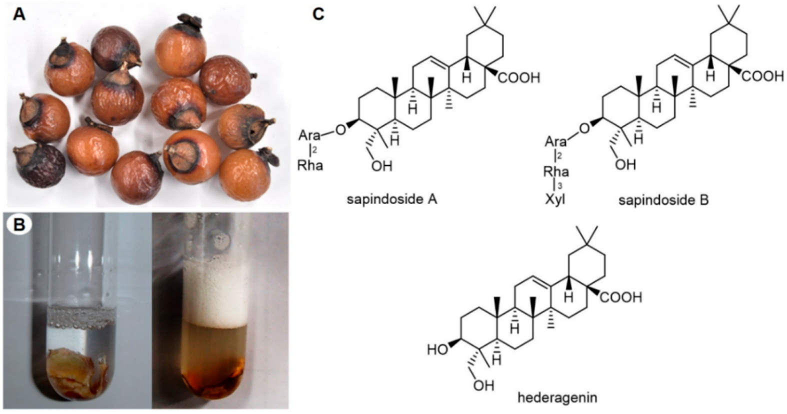


Figure 2. Image of (A) *Sapindus mukorossi* fruits and (B) the foam generated. (C) Chemical structures of saponins. Reprinted with permission from ref 39. Photograph courtesy of Rai et al. Copyright 2021 MDPI.

sugar moiety. Sophorolipids are produced through the fermentation of renewable resources, such as vegetable oils, and are considered sustainable alternatives to synthetic surfactants.[36] They have a wide range of applications in various industries, including bioremediation, food processing, and cosmetics. Sophorolipids are biodegradable, nontoxic, and exhibit low toxicity toward mammalian cells, making them an environmentally friendly alternative to traditional surfactants. The production of sophorolipids involves the optimization of fermentation conditions, including the pH, temperature, and nutrient composition, to achieve high yields. Sophorolipids exhibit broader commercialization potential due to their comparatively higher production yields compared with other glycolipid biosurfactants.

Lipopeptides are a prominent group of natural surfactants and are considered to be the second-largest group among such compounds. Lipopeptides generally composed of a short peptide chain and a hydroxy acid and are frequently cyclic in nature.[37] These compounds are predominantly isolated from bacterial strains, with *Bacillus* and *Pseudomonas* being the most commonly studied genera. Lipopeptides display a diverse array of biological effects, encompassing antibacterial, antifungal, and antiviral characteristics. They are seen as encouraging contenders for utilization in a variety of biomedical and industrial contexts.

Saponins represent a category of natural surfactant molecules that are found extensively throughout the plant realm. They are glycosides, meaning that they are composed of a sugar molecule (such as glucose or galactose) linked to a hydrophobic aglycone (nonsugar) moiety.[38] Saponins are classified based on the number of sugar units, such as monodesmosidic saponins, bidesmosidic saponins, and tridesmosidic saponins. The aglycone can be a triterpenoid or steroid and is responsible for the surfactant properties of saponins.

Saponins are named after their ability to form soaplike foams when mixed with water. Figure 2 shows images of *Sapindus mukorossi* fruits and the foam generated.[39] Figure 3 shows another structure of saponin. These compounds possess a variety of biological functions, such as anti-inflammatory, anticancer, and antiviral attributes. In addition, saponins are known to have emulsifying, dispersing, and wetting properties, which make them useful in a variety of industrial applications, including food, pharmaceuticals, and personal care products. Some common sources of saponins include legumes (such as beans and lentils), oats, quinoa, and yucca. Saponins are also found in some medicinal plants, such as ginseng, licorice, and soapwort.

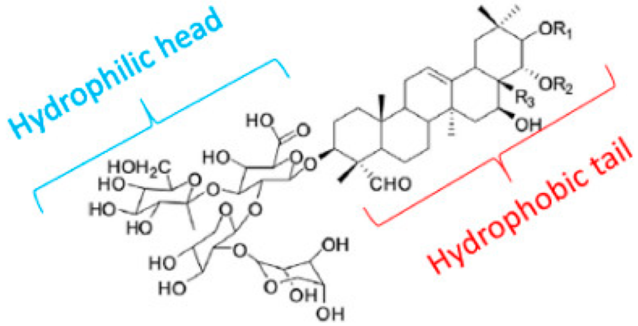


Figure 3. Molecular structure of saponin. Reprinted with permission from ref 40. Copyright 2020 Elsevier.

Tea saponin is a natural surfactant found in tea seeds, tea leaves, and other plant parts of *Camellia* plants.[41] Compared to other natural surfactants, it represents a more sustainable and economically feasible source as an agricultural and sideline product.[42,43] It belongs to the triterpenoid saponin family and has a complex structure consisting of a hydrophilic sugar moiety (glucose, galactose, and rhamnose) attached to a lipophilic aglycone of oleanolic or hederagenin (Figure 4).

Tea saponin is widely used in the agricultural industry as a natural pesticide, herbicide, and fungicide due to its ability to disrupt the cell membranes of pests and weeds, leading to their death. Tea saponin can be obtained from tea seeds or leaves through different techniques such as hot water extraction, ultrasonic-assisted extraction, and microwave-assisted extraction. The prevalent method for large-scale tea saponin production is hot water extraction, involving boiling tea seeds or leaves in water for several hours followed by filtration and refinement. Ultrasonic and microwave-assisted extractions are newer methods that use high-frequency sound waves or microwaves to break down the plant material and release the saponin. Tea saponin has shown promise as a sustainable alternative to synthetic pesticides due to its low toxicity, biodegradability, and environmental safety.

In addition to the above-mentioned surfactants, the literature has reported several other natural surfactants. Some

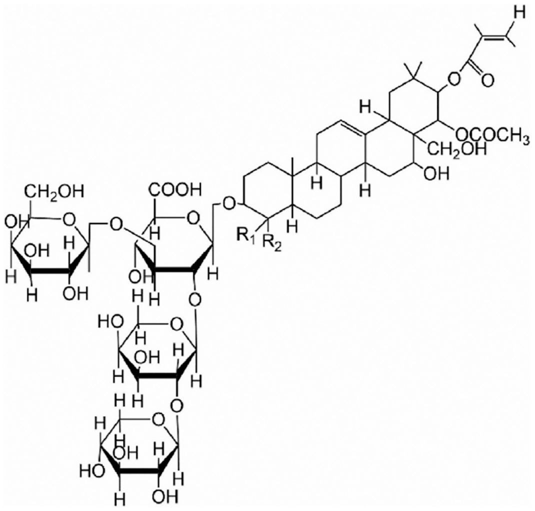


Figure 4. Structure of tea saponin. Reprinted with permission from ref 41. Copyright 2018 Elsevier.

other important classes of natural surfactants are fatty acids, neutral lipids, emulsan, and liposan, among others.[42,44−49]

There are various methods for preparing natural surfactants, and the method used depends on the type of surfactant being produced. One method involves extracting natural surfactants from sources, such as plants, animals, and microorganisms. For example, saponins can be extracted from the bark of the quillaja tree or from soap nuts, while phospholipids can be extracted from soybeans or egg yolks.

Another method involves microbial fermentation, which is used to produce natural surfactants, such as rhamnolipids. Bacteria are grown in a nutrient-rich medium, and the surfactant is extracted from the fermentation broth. Natural molecules can also be chemically modified to create surfactants with the desired properties. For instance, fatty acids can be chemically modified to produce surfactants with varying levels of hydrophobicity. Additionally, different natural surfactants can be combined to create surfactant blends with specific properties. After preparation, the natural surfactant is often purified and concentrated before use in various applications.

3. APPLICATIONS OF NATURAL SURFACTANTS IN THE OIL AND GAS INDUSTRY

3.1. Chemical-Enhanced Oil Recovery. Primary recovery involves extracting oil using natural reservoir pressure or simple pumps, while secondary recovery involves the injection of water or gas into the reservoir to move more oil toward the wells.[50−52] EOR, also known as tertiary oil recovery, is applied when the primary and secondary methods have already extracted most of the recoverable oil from the reservoir. EOR is critical in meeting the world's increasing energy needs by prolonging the life of current oil reservoirs and enhancing oil recovery.

Various EOR methods exist, including thermal, gas, and chemical EOR. Thermal enhanced oil recovery (EOR) techniques encompass the injection of heated water or steam into the reservoir to decrease the viscosity of the oil and enhance its recovery process. Gas EOR methods entail the injection of gases like nitrogen or carbon dioxide into the reservoir to elevate the pressure and move more oil toward the wells. Chemical enhanced oil recovery (EOR) techniques involve injecting substances, such as surfactants, alkalis, and polymers, into the reservoir. These adjustments target the properties of both the reservoir rock and the fluid, ultimately enhancing the movement of the remaining oil.[53] The database compiled by Aladasani et al. contains reservoir parameters for chemical enhanced oil recovery (EOR) that have been widely implemented across various regions. These parameters include an average oil characteristic of 32.6° API, an average porosity of 26.6%, an average oil saturation of 73.7% pore volume (PV), permeability ranging from 596 to 1520 millidarcies (ms), an average well depth of 2984.5 feet, and an average temperature of 121.6 °F.[54]

The selection of a chemical EOR method depends on factors like reservoir characteristics, chemical cost and availability, and the method's environmental impact. Every chemical has a specific function in the EOR process; polymers, for instance, are utilized to boost the viscosity of injected water and enhance sweep efficiency,[55,56] while surfactants are employed to decrease the IFT between oil and water and alter rock wettability.[57−59] Surfactant flooding plays various roles within the enhanced oil recovery (EOR) procedures. Its key role involves diminishing the interfacial tension between water and oil, which in turn amplifies the movement and displacement of oil from the reservoir rock. By lowering the interfacial tension, surfactants increase the capillary forces that trap oil in the rock pores, allowing for improved oil recovery. Another important function of surfactant flooding is the alteration of wettability. Surfactants have the ability to alter the wettability of the reservoir rock, inducing a greater affinity for oil and thereby enhancing the displacement of oil through injected water or gas. This alteration of wettability helps to overcome the capillary forces that hold the oil in the rock pores, facilitating its flow toward the production wells. Surfactant flooding is particularly effective in reservoirs with high oil viscosity or where the oil is trapped in small pores or as residual oil saturation. The use of surfactants can help reduce the capillary forces that hold the oil under these challenging reservoir conditions, allowing for a more efficient recovery of the trapped oil. Furthermore, surfactant flooding can also improve the sweep efficiency of injected water or gas. Through the reduction of interfacial tension and modification of wettability, surfactants assist in displacing oil from the reservoir rock, thereby enhancing its flow and ensuring a more comprehensive coverage of the reservoir area.[60]

Several researchers have reported the mechanism of wettability alteration in different types of rocks.[61] Additionally, a good candidate surfactant should have lower retention on the rock surface. The surfactant loss could occur due to several reasons, such as adsorption and phase trapping. The adsorption could be due to electrostatic or hydrophobic interactions. A schematic showing the mechanism of a gemini surfactant on carbonate and sandstone rock is shown in Figure 5, where a non-interdigitated bilayer mechanism was proposed for sandstone and interdigitated bilayer mechanism was proposed for carbonate rock.

Figure 5 explains the adsorption mechanism of a gemini surfactant on sandstone and carbonate rocks. Anionic surfactants have a negatively charged hydrophilic headgroup. They are effective at reducing the interfacial tension between oil and water, making them suitable for use in sandstone reservoirs. Sandstone reservoirs typically have negatively charged surfaces, and anionic surfactants can adsorb onto these surfaces, facilitating the release of oil trapped in the

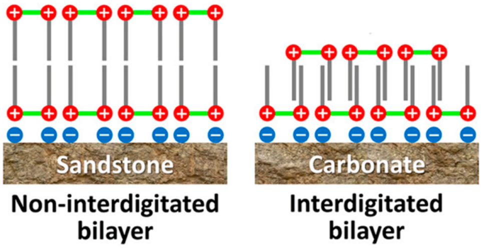


Figure 5. Adsorption mechanism of the Gemini surfactant on carbonate and sandstone rock. Reprinted with permission from ref 66. Copyright 2022 American Chemical Society.

porous rock.[62] The capacity of surfactants to modify wettability and decrease interfacial tension (IFT) has been extensively examined within the realm of enhanced oil recovery (EOR) and the formulation of stimulation fluids for unconventional liquid reservoirs (ULRs).[63,64] The success of modifying wettability greatly hinges on the surfactant's ionic characteristics. In chalk cores with an oil-wet nature, both cationic and anionic surfactants have been noted to shift the rock's wettability toward becoming more water-wet. However, cationic surfactants tend to exhibit greater efficacy in comparison to that of anionic surfactants during this transformation. This phenomenon can be explained by the creation of ion pairs between the positively charged ends of the surfactant molecules and the acidic constituents of crude oil that have adhered to the surface of carbonate rock.[63]

The process driving the wettability change through anionic surfactants entails the formation of ion pairs between the charged head groups of surfactant molecules and the crude oil components that have attached to the surface of the rock. This mechanism proves more efficient in shifting the rock's wettability toward greater water-wettability compared to the scenario where surfactant molecules are absorbed as a monolayer onto the rock's surface through hydrophobic interactions with the attached crude oil components. Dimeric surfactants, featuring a pair of charged head groups and two hydrophobic tails, have been suggested as enhancers of the wettability modification procedure.[63] Gemini surfactants, characterized by their linked head ends, are anticipated to be efficacious when ion-pair formation drives wettability alteration. Conversely, bolaform surfactants, where molecules are connected by their hydrophobic tails, are expected to exhibit greater efficacy in scenarios involving surfactant monolayer adsorption.[63]

The application of anionic surfactants in stimulation fluids for unconventional liquid reservoirs has demonstrated the ability to modify wettability. This leads to reduced contact angles, improved spontaneous imbibition, and enhanced oil recovery in comparison to nonionic surfactants.[64] The alterations in wettability caused by the inclusion of anionic surfactants in fracturing fluids can enhance the penetration of the matrix through spontaneous imbibition. This holds significance for the potential of enhanced oil recovery (EOR) in shale formations. Additionally, anionic surfactants have been found to reduce IFT, with slightly better capability than nonionic surfactants.[64]

The degree of wettability change and the optimal concentration of surfactants needed for the most pronounced alteration are contingent upon factors like salinity and the ethoxylation level within anionic surfactants.[65] With an increase in salinity, the magnitude of the maximum wettability change diminishes and the requisite surfactant concentration for achieving the maximum alteration also declines. Moreover, elevating the ethoxylation level in anionic surfactants augments the extent of wettability modification on calcite surfaces.[65] In summary, anionic surfactants have been shown to alter wettability toward a more water-wet state and reduce IFT, although cationic surfactants are generally more effective in wettability alteration.[63,64] The process of modifying wettability through anionic surfactants involves the formation of ion pairs with the crude oil components that have attached to the surface of the rock.[63] Factors such as salinity and ethoxylation can influence the extent of wettability alteration by anionic surfactants.[65] These findings have implications for the design and optimization of surfactant based EOR and stimulation fluids in oil reservoirs.

Cationic surfactants have a positively charged hydrophilic headgroup. They are preferred for carbonate reservoirs. Carbonate reservoirs are often composed of rocks, such as limestone or dolomite, that have positively charged surfaces. Cationic surfactants can interact with these positively charged surfaces and improve oil recovery by displacing oil from the porous structure of the carbonate rock.[62]

The capacity of natural surfactants to lower the interfacial tension (IFT) between the oil and water phases has been thoroughly examined. Although the reduction of the IFT to ultralow values is difficult to achieve with natural surfactants, they can still effectively reduce the IFT at concentrations near their critical micelle concentration (CMC). For instance, saponins extracted from plants have been reported to reduce the IFT between oil and water phases by up to 76% at room temperature and 93.2% at high temperature when used at a concentration of 0.2 wt %. Other natural surfactants, such as rhamnolipids and sophorolipids, have also shown promising results in reducing IFT%.[67]

One of the early studies on the application of natural surfactants for EOR was conducted by Chhetri et al. in 2009.[68] Soapnut fruit pericarp shells from Nepal were employed to extract the saponin compound, which exhibited effectiveness in diminishing interfacial tension (IFT) and enhancing oil recovery. The research findings suggested that employing natural surfactants could offer a potentially viable substitute for synthetic surfactants. This is because they are not only proven to be effective but also have the advantages of being economical and environmentally benign.

Kumar et al. synthesized a polymeric surfactant, known as PMES, using nonedible vegetable oil (*Jatropha*) to aid in EOR.[69] The method entails blending acrylamide monomer with methyl ester sulfonate (MES), sourced from *Jatropha* oil, utilizing a free radical polymerization mechanism. The resultant polymeric surfactant possesses characteristics of both a surfactant and a polymer, offering the potential to control the mobility ratio and reduce interfacial tension (IFT). The CMC of the aqueous PMES solution was found to be 2.74 mN/m when tested against crude oil (Figure 6). However, this value was decreased to 0.37 mN/m when 2.5 wt % NaCl was added. To assess the efficiency of the polymeric surfactant in enhanced oil recovery (EOR), experiments involving core flooding were conducted within a sandpack setup. The experiments resulted in over 26% additional recovery compared to that of conventional water flooding. Recoveries were greater at higher temperatures, which is attributed to the swelling of the crude oil and a decrease in the IFT.

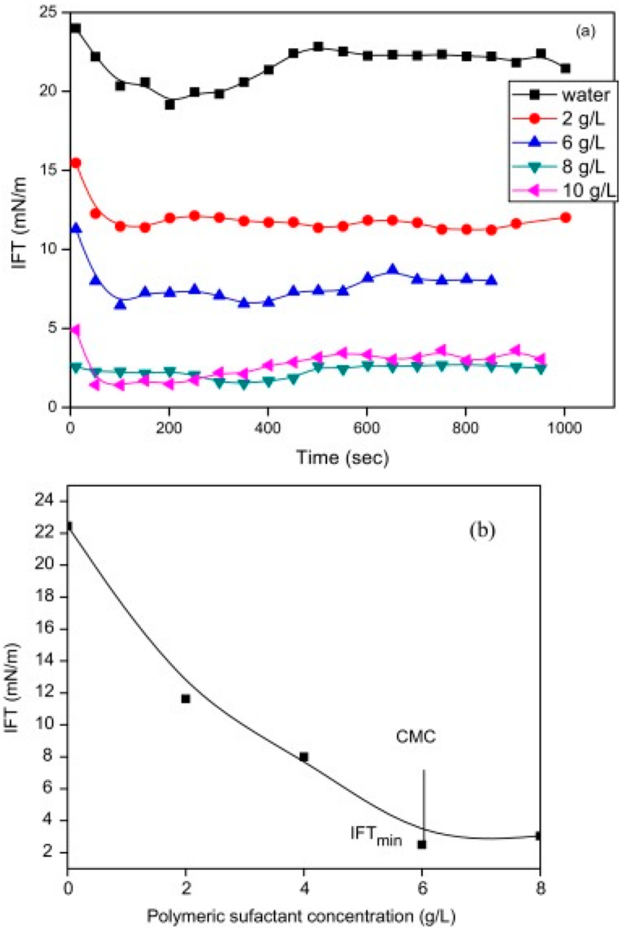


Figure 6. (a) Dynamic IFT and (b) equilibrium IFT of PMES solutions. Reprinted with permission from ref 69. Copyright 2016 Elsevier.

Another study explored the use of the extract of powdered *Myrtus communis* leaves as a natural surfactant.[70] The effectiveness of the surfactant was assessed through a range of experiments, encompassing measurements of interfacial tension (IFT) and the injection of both chemical slugs and surfactant into carbonate plugs. The study also investigated the adsorption of a surfactant onto carbonate rock. Results showed that the natural surfactant was capable of reducing the IFT to 0.861 mN/m at a CMC of 5000 ppm, and this value was further decreased at optimal salinity and alkali conditions. Ultimately, the study observed increases in oil recovery of 14.3% and 16.4% through the use of surfactant flooding.

Deymeh et al. (2012) conducted a study on the extraction of a natural cationic surfactant from *Seidlitzia rosmarinus* and its potential use in EOR.[71] The research findings indicated that the natural surfactant demonstrated significant efficacy in decreasing the interfacial tension (IFT) between oil and water. In their experiments, the IFT values decreased from 32 to 9 mN/m at the CMC point of 8 wt %.

Scientists have altered cashew nutshell liquid (CNSL) extracted from discarded shells of the *Anacardium occidentale* plant, investigating its potential as a natural substitute for traditional surfactants.[72] The research encompassed phase behavior analysis, interfacial tension (IFT) assessments, critical micelle concentration (CMC) measurements, and core flooding analysis. These evaluations aimed to ascertain the suitability and recovery potential of the modified cashew nutshell liquid derivatives on sandstone reservoirs.[73] The IFT was significantly reduced from 10.46 to 1.66 mN/m when the CMC was 1 g/L. At laboratory temperature, the CNSL derivatives were found to have increased the additional recovery factor and displacement efficiency by 12% OOIP and 32.5%, respectively.[72] In a study by Moradi et al. (2019), it was discovered that a naturally sourced surfactant derived from *Tribulus terrestris* could considerably improve oil recovery through smart water flooding.[73] The surfactant was found to be highly compatible with synthetic seawater, resulting in a reduced IFT and increased oil recovery in carbonate reservoirs.

Eslahati et al. (2020) investigated the effect of using a natural surfactant from afalfa in conjunction with smart water for EOR in carbonate reservoirs.[74] The study found that the combination of natural surfactant and smart water significantly reduced the IFT and contact angle. Another study evaluated the effectiveness of a nonionic biosurfactant derived from *Acanthophyllum* plant root extract (APRE) in enhancing oil recovery.[75] The scientists performed multiple experiments to evaluate the enhanced oil recovery (EOR) capabilities of this surfactant. They conducted measurements of interfacial tension (IFT) within the oil−water system and carried out a contact angle examination to appraise changes in the wettability of carbonate rock. Additionally, they executed tests to assess the emulsion stability, compatibility, and effectiveness of surfactant flooding. The influence of diverse ions from various salts on IFT, carbonate rock wettability, and chemical interactions was also investigated. Moreover, the researchers evaluated the stability of emulsions formed by the surfactant through observational analyses. The compatibility test conducted at 25 °C showed that negligible sediment was formed below the salinity of 50 000 ppm. The IFT at CMC in formation water (optimum concentration of 12,000 ppm) was reduced from an initial value of 2.16 to 1.06 mN/m.

The optimum IFT value at different salinities was also determined. Furthermore, with a concentration of 10 000 ppm of the surfactant and formation water (FW), the researchers managed to change the wettability of the carbonate rock from a highly oil-wet condition (168°) to a water-wet state (60.3°). Finally, in the core flood test, the researchers determined the effects of different slug sizes and soaking time. Overall, the results of the study indicate that APRE-derived biosurfactants have the potential to be an effective alternative to traditional surfactants in enhancing oil recovery. Nafisifar et al. (2021) investigated the efficiency of an anionic surfactant extracted from linseed oil in a sandstone reservoir.[76] Interfacial tension (IFT), contact angle, and core flooding experiments were carried out. The outcomes indicated that the natural surfactant effectively lowered both the IFT and the contact angle.

Choosing an appropriate surfactant for surfactant flooding plays a vital role in ensuring the success of the enhanced oil recovery (EOR) process. However, it can be challenging to choose the right surfactant for reservoir conditions. Variables such as surfactant concentration, salinity, temperature, and pH can impact the adsorption of surfactants onto reservoir rocks. Taking these factors into account is crucial in order to avoid substantial surfactant losses caused by adsorption into the porous media.[77]

The hydrophilic−lipophilic balance (HLB) value is a semiempirical scale that is widely used for the selection of surfactants in EOR applications. The HLB value signifies the equilibrium between the hydrophilic and lipophilic characteristics of a surfactant. Surfactants with high lipophilicity are not easily soluble in water, while surfactants with high hydrophilicity may not effectively adsorb at the oil−water interface. Therefore, surfactants with appropriate HLB values are preferred for EOR applications.[78] For example, sodium lignosulfonate synthesized from bagasse has an HLB value of 11.6, which classifies it as an oil-in-water (O/W) emulsion. The HLB value of a surfactant can affect its performance in surfactant flooding.[79]

In the context of methanol-in-diesel emulsions, the suitable surfactant HLB value for stability is not well understood. However, it has been observed that a surfactant HLB value of 5 is suitable for water-in-diesel emulsions and a surfactant HLB value of 12.9 is suitable for oil-in-ethanol emulsions. Further research is needed to determine the appropriate surfactant HLB value for stable methanol-in-diesel emulsions.[80]

To conclude, surfactant flooding stands as an efficient approach for enhancing oil recovery in EOR operations. Choosing an appropriate surfactant is of utmost importance, taking into account elements such as surfactant concentration, salinity, temperature, and pH. The HLB value of a surfactant plays a significant role in its performance and stability in surfactant flooding. Further research is needed to better understand the relationship between the surfactant HLB value and the stability of methanol-in-diesel emulsions.

Furthermore, the application of natural surfactants derived from sources like plant saponins, rhamnolipids, sophorolipids, and natural cationic surfactants has exhibited encouraging outcomes in diminishing the interfacial tension (IFT) between oil and water phases. The polymeric surfactant, known as PMES, synthesized using nonedible vegetable oil was found to aid in EOR by decreasing the IFT and regulating the mobility ratio. Studies have shown that natural surfactants and polymeric surfactants could be promising alternatives to synthetic surfactants for EOR, as they are cost-effective, environmentally friendly, and effective.

Employing natural surfactants has the potential to shift the wettability of rocks toward increased hydrophilicity. Figure 7 illustrates the gradual reduction of the contact angle of oil droplets on the rock surface within an aqueous solution that includes the surfactant at its critical micelle concentration (CMC). Figure 8 demonstrates that different salts at specific concentrations also have a significant impact on the contact angle. The adsorption of surfactant molecules to the rock surface results in the formation of a thin film between the surface and the oil droplets, thereby decreasing the contact angle. Soluble ions within the system can also modify the rock's wettability through processes like ion exchange and the salt-in effect. In situations of low salinity, reactions may occur that trigger additional dissolution of carbonate rock and cause a change in its wettability toward greater hydrophilicity.

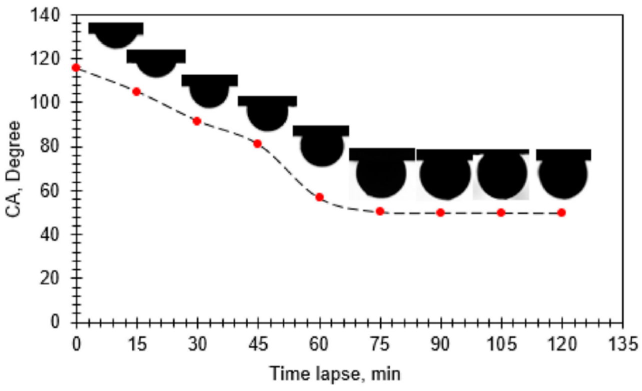


Figure 7. Contact angle of an oil droplet on a carbonate cross-section over time in the presence of a surfactant solution of CMC at 75 °C. Reprinted with permission from ref 40. Copyright 2020 Elsevier.

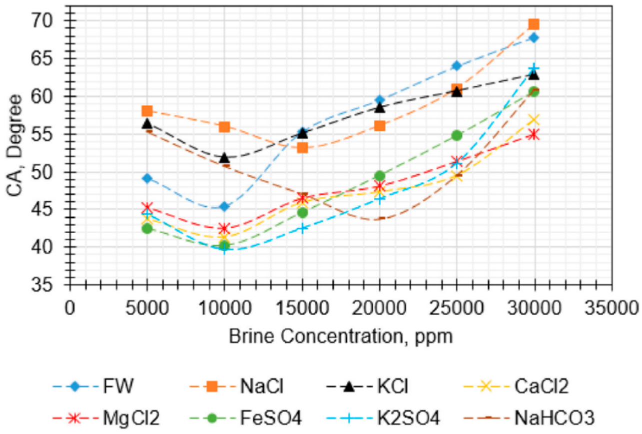


Figure 8. Effect of various salinity concentrations on the contact angle at surfactant CMC and 75 °C. Reprinted with permission from ref 40. Copyright 2020 Elsevier.

Ahmadi et al. conducted research concerning the utilization of a natural surfactant extracted from leaves of the mulberry tree in the context of enhanced oil recovery (EOR).[81] Within this investigation, microsized particles from mulberry leaves were employed to create a microfluid formulation, which was subsequently evaluated for its surfactant characteristics. The findings indicated that a minor concentration of only 1 wt % of microsized mulberry leaf particles within the microfluid had the capability to lower the interfacial tension (IFT) of a system containing distilled water and kerosene by as much as 60%. This reduction was evident from the decrease in drop area (Figure 9). The researchers also evaluated the impact of the extracted surfactant on sweep efficiency during brine flooding, a common technique used in EOR. They utilized a core displacement apparatus to assess how the surfactant impacted the effectiveness of fluid displacement within porous media. The outcomes revealed that the natural surfactant led to a

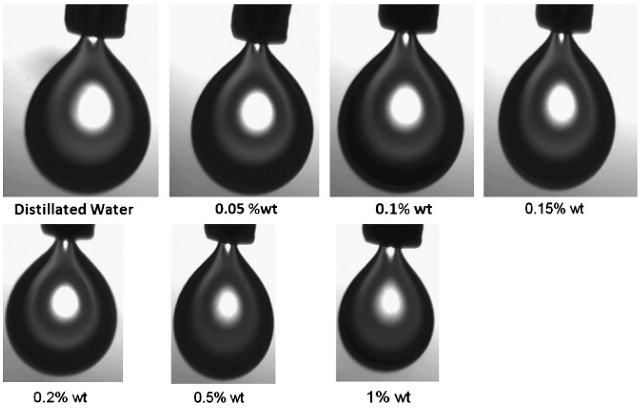


Figure 9. Drop's surface area at various concentrations of natural surfactant. Reprinted with permission from ref 81. Copyright 2014 Elsevier.

Table 1. Details and Summary of the Use of Natural Surfactants in EOR

surfactant	class	extraction method	sources	concentration	temperature (°C)	IFT reduction (%)	increase in RF (%)
Gemini surfactant[66]	ionic nonionic	chemical synthesizing	plant seeds	0.1−5.0 wt %	40−70	92.86	15−19
saponins[67,68]	anionic	hot water extraction alcohol extraction steam distillation	soapnut shells	0.01−1.0 wt %	80−150	76−93.2	
MES[69]	anionic	solvent extraction hydrodistillation	vegetable oils	0.0−4.0 wt %	30	68.75	
PMES[69]	anionic	solvent extraction hydrodistillation	vegetable oils	0.0−4.0 wt %	25−500	86.5	26
Myrtus communis[70]	anionic	steam distillation solvent extraction	*Myrtus communis*	500−7000 ppm	25−130	93.11	14.3−16.4
Seidlitzia rosmarinus[71]	cationic	solvent extraction	rosemary saltbush	0.0−10.0 wt %		71.88	
CNSL[73]	anionic	solvent extraction	*Anacardium occidentale*	0.1−1.0 wt %	80	84.13	12−32.5
alfalfa[74]	ionic	steam distillation solvent extraction	alfalfa	0.0−4.0 wt %	70	63.39	19.2
APRE[75]	nonionic	solvent extraction	plant roots	400−40 000 ppm	25	50.93	7.49−23.78

substantial enhancement in sweep efficiency, increasing it from 49% to 66.8% of the original oil in place (OOIP).

Table 1 summarizes the details of natural surfactant for EOR applications, from the type of the surfactants, its concentration, testing temperature, IFT reduction, and oil recovery increase from the surfactant tested with core flooding. Gemini surfactants with 0.1−5.0 wt % concentrations reduce the IFT of the oil as much as 92.86% while increasing the recovery to 15−19% of the OOIP. Saponins and MES with 0.01−1.0 and 0.0−4.0 wt % concentrations lower the IFT to 76−93.2% and 68.75%, respectively. PMES, the same concentration used for MES shows a better result to reduce the IFT to 86.5% and enhance the recovery to 26%. Surfactants from *Myrtus communis* with a concentration of 500−7000 ppm reduce the IFT to 93.11% with recovery enhancement range from 14.3−16.4% of the OOIP.

Seidlitzia rosmarinus tested from 0.0−10.0 wt % reduce the IFT to 71.88%. CNSL also raises the incremental of oil recovery from 12−32.5% by lowering the IFT to 84.13% with 0.1−1.0 wt % concentration. A 0.0−4.0 wt % alfalfa surfactant concentration can reduce the IFT to 63.39% and increase the oil recovery to 19.2. The same trend result is shown in APRE surfactant 400−40 000 ppm with 50.93% IFT reduction and an oil recovery increase of 7.49−23.78%.

Surfactant−crude oil compatibility is a pivotal consideration in enhanced oil recovery and other oilfield applications.[82] For optimal performance, surfactants need to be soluble within the crude oil phase, enabling them to significantly reduce the interfacial tension. This compatibility ensures their effective migration into the oil phase, enabling the formation of micelles that mitigate the capillary forces responsible for entrapping oil within the rock pores. Additionally, surfactants might induce the emulsification of the crude oil, resulting in the formation of stable oil-in-water or water-in-oil emulsions. The type and stability of these emulsions play crucial roles in influencing oil mobility and the efficiency of the separation process.

Achieving compatibility with reservoir rock is another essential factor in successful oil recovery operations. This entails understanding how surfactants interact with the surfaces of the reservoir rocks. The interaction can lead to wettability alterations, influencing the flow and displacement of oil. Moreover, surfactants' potential adsorption onto rock surfaces must be gauged, as excessive adsorption might hinder their effectiveness and even lead to potential formation damage. Furthermore, compatibility with the reservoir's formation water is vital to prevent any detrimental impact on rock surfaces.[83] Ensuring harmonious compatibility between surfactants and both the reservoir rock and the fluid within the reservoir is a multifaceted endeavor that directly affects the efficacy of enhanced oil recovery strategies.

One of the considerations in the utilization of surfactants for enhanced oil recovery (EOR) is their potential to alter wettability. The interaction between surfactants and the surfaces of reservoir rocks can lead to significant changes in wettability. This phenomenon directly influences the flow behavior of oil within the rock matrix. Depending on the extent and nature of the alteration, surfactants can either enhance or impede the flow of oil, impacting the overall recovery efficiency. The ability of surfactants to modify wettability is a critical factor that requires meticulous evaluation and optimization to achieve the desired outcomes in EOR operations.

Another critical aspect is the adsorption of surfactants on the surfaces of reservoir rocks. While some degree of adsorption is expected, excessive accumulation of surfactants can result in altered rock properties. This excess adsorption might lead to diminished surfactant effectiveness and, in severe cases, contribute to potential formation damage. The intricate balance between ensuring sufficient adsorption for improved oil recovery and preventing adverse consequences underscores the need for comprehensive testing and understanding of surfactant behavior within the reservoir environment.[53]

The harmonious compatibility of surfactants with the formation water within reservoirs is of paramount importance. Any introduction of surfactants should not negatively impact the interaction between reservoir rock surfaces and native formation water. A lack of compatibility could lead to formation damage or even the precipitation of minerals, adversely affecting reservoir permeability and the overall reservoir.[56] Ensuring that surfactants coexist favorably with the existing formation water chemistry requires a deep understanding of the interplay between these components.

Achieving this balance is integral to maximizing the benefits of surfactant based EOR strategies while minimizing potential drawbacks.

3.2. Foam Related Applications. The potential applications of natural surfactants, such as saponins, in various industries are strengthened by the fact that they provide foam stability as a desirable feature. Saponin-stabilized foam, in particular, has been observed to possess remarkable stability even under harsh conditions such as high temperatures, indicating that it is resistant to common destabilizing factors like liquid drainage, bubble coalescence, and coarsening. This exceptional stability can be credited to the unique structure of natural surfactants, which allows them to create a more rigid and compact adsorption layer at the air–liquid interface in comparison to synthetic surfactants. As a result, the usage of natural surfactants in foam-based applications can yield several benefits, including better stability and sustainability than traditional surfactants.[67]

The development and stability of emulsions during natural surfactant flooding are subject to a range of factors, including the existence of natural surfactants, the viscosity of the crude oil, and the interfacial tension between oil and water. Crude oil contains inherent surfactants such as asphaltene and resin, which have the capacity to initiate and stabilize emulsions. These surfactants can engage with both the oil and water phases, leading to a reduction in interfacial tension and fostering the creation of emulsions. The existence of dense particles like asphaltenes and resins can exert a substantial influence on the oil's viscosity, subsequently impacting the stability of emulsions.

The stability of the emulsions is crucial for their effectiveness in enhanced oil recovery. Emulsion stability refers to the ability of the emulsion to resist phase separation and maintain its dispersed state. Aspects such as fluctuations in droplet size, properties of the fluid, attributes of the physical model, and operating conditions can all have an impact on the stability and rheological attributes of emulsions. Understanding these factors is important for designing efficient emulsion treatments and optimizing the operation of equipment.

Emulsions have a pivotal role in enhanced oil recovery (EOR), as they enhance the efficiency of fluid displacement and the coverage volume of the displacing fluid. The creation and stability of emulsions during natural surfactant flooding hold significance as essential considerations in EOR endeavors. The emulsification process involves the interaction between surfactants and crude oil, which leads to the formation of emulsions. The type of emulsion formed (oil-in-water or water-in-oil) depends on the hydrophilicity of the surfactants, salinity, and water–oil ratio. Hydrophilic surfactants tend to form oil-in-water emulsions, while hydrophobic surfactants can be reverted to water-in-oil emulsions. The rheological properties of emulsions, such as viscosity and flow behavior, also affect their stability and performance in EOR. It has been observed that emulsions can enhance oil recovery by up to 5% compared to systems without emulsions.

The foamability of the foam stabilized by saponin was observed to be favorable at both ambient temperature and 60 °C. Additionally, the saponin-stabilized foam exhibited a higher duration for almost 100% liquid drainage in comparison to SDS-stabilized foam. The optimal concentration required to achieve maximum foam stability was found to decrease from 0.4 wt % at room temperature to 0.1 wt % at 60 °C.[67]

In a recent study by Emadi et al., the use of natural surfactants for EOR was investigated. Specifically, the researchers examined the impact of Cedr extract (CE), derived from the plant *Ziziphus spina-christi*, as a surfactant in controlling the mobility during the EOR process. The study focused on analyzing the effectiveness of the foam generated by CE in controlling the mobility, a critical factor that affects the displacement efficiency of oil in reservoirs.

The use of CE as a natural surfactant is particularly appealing due to its low cost, making it a viable option for practical implementation in the oil and gas industry. Overall, the findings of this study suggest that CE has significant potential as a natural surfactant for EOR applications. By generating foam to control mobility, CE offers a promising solution for improving the efficiency of oil recovery processes. Furthermore, the utilization of natural surfactants such as CE could provide an environmentally friendly alternative to traditional surfactants, which may have harmful impacts on the ecosystem.

As a result of its potential to enhance the efficiency of oil displacement and boost oil recovery from reservoirs, the surfactant-based foam has important uses in enhanced oil recovery (EOR). The injection of surfactant-stabilized foams into the reservoir to displace and mobilize trapped oil is a well-established EOR technology.[83]

Surfactants are necessary for foam formation because they stabilize gas bubbles in the aqueous phase. Surfactants reduce surface tension at the gas–water interface, allowing stable foams to develop. The capacity of the foam to move through the reservoir and displace the trapped oil is determined by foam stability, which is critical for effective EOR applications.[82]

When contrasted to the oil in the reservoir, foam works as a mobility control agent, lowering the mobility of the displacing fluid (gas–liquid foam). The restricted mobility of the foam improves the sweep efficiency by contacting a wider section of the reservoir and increasing the displacement of trapped oil. By directing injected fluid from high-permeability zones to low-permeability zones, surfactant-based foam can increase the sweep efficiency in heterogeneous reservoirs. This diversion lowers fingering and enhances the conformity of injected fluid to the reservoir structure.

To manage gas mobility in the reservoir, foam can be employed as an alternative to the typical gas flooding procedures (e.g., CO_2 flooding). The use of foam can help to alleviate the negative effects of gas override while also improving the volumetric sweep efficiency.

Surfactant-based foams may be customized to individual reservoir conditions such as temperature, salinity, and reservoir rock properties. Because of this versatility, foam flooding is a flexible EOR approach that can be used in a variety of reservoir types. Surfactant-based foams are a well-established and efficient EOR technology with multiple successful field applications. It is a potential technology for improving oil recovery and enhancing reservoir performance because of its combination of foam formation, stability, mobility control, and compliance with reservoir conditions.

3.3. Drilling. Natural surfactants have attracted significant attention, as they have shown potential in various industries, including drilling. Drilling operations involve several challenges, such as the presence of oil, gas, water, and rock formations that require specific techniques and chemicals for successful operations. Traditional surfactants used in drilling fluids are synthetic, and their environmental impact is a

Table 2. Details of Natural Surfactants Used in Drilling Applications

surfactant type	class	extraction method	sources	application
saponins[12]	anionic	alcohol extraction	yucca plants	shale inhibitor
		steam distillation	Korean red ginseng	
CO[86]	nonionic	hydro distillation	*Chromolaena odorata*	scale inhibitor
		solvent extraction		
SODS[84]	anionic	solvent extraction	soybean	emulsifier
phospholipids[85]	nonionic	solvent extraction	eggyolk	
Seidlitzia rosmarinus[85]	cationic	solvent extraction	rosemary saltbush	CGA-based drilling fluid
henna plant[85]	nonionic	solvent extraction	henna plant	
lignin[85]	nonionic	solvent extraction	wood	lubricant

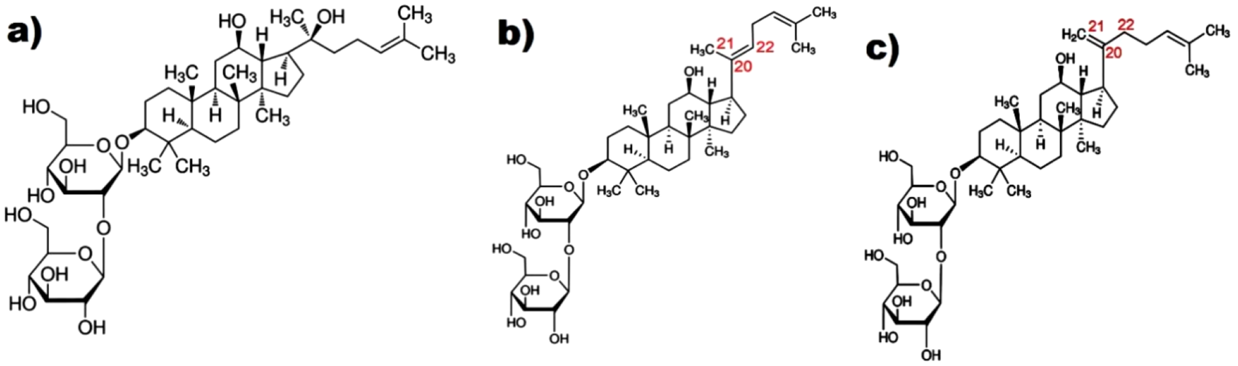


Figure 10. Molecular structures of ginsenosides: (a) Rg3, (b) Rg5, and (c) RK. Reprinted from with permission from ref 12 Copyright 2019 Elsevier.

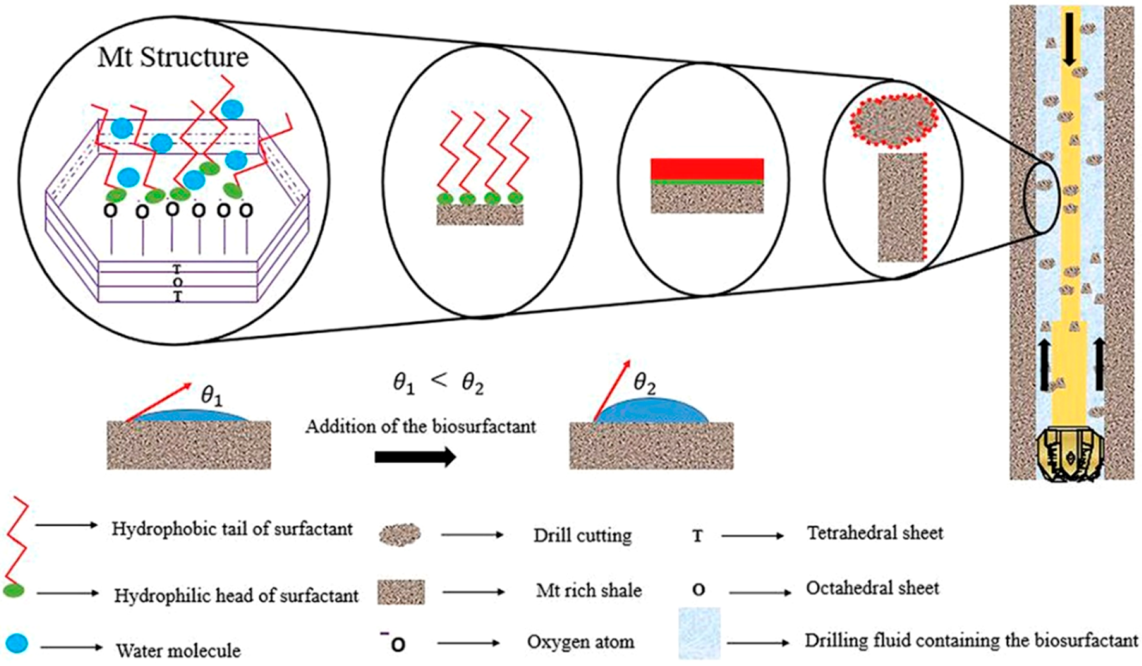


Figure 11. Mechanism of clay swelling inhibition using a biosurfactant. Reprinted with permission from ref 12. Copyright 2019 Elsevier.

concern. In contrast, natural surfactants have a reduced environmental impact, are biodegradable, and can function similarly to their synthetic counterparts. Table 2 discusses the application of natural surfactants in drilling fluids and their potential benefits.

One application of natural surfactants in drilling is their use as shale inhibitors. Shale formation is a common occurrence during drilling operations, leading to wellbore instability, reduced drilling efficiency, and equipment failure. Synthetic surfactants such as polyglycols are effective at inhibiting shale swelling. However, their toxicity and nonbiodegradability pose significant environmental concerns. Natural surfactants such as saponin extracted from the yucca plant have shown potential as shale inhibitors in drilling fluids.

A synthesized compound derived from leaf extracts of the *Chromolaena odorata* (CO) leaf, a herbaceous perennial known

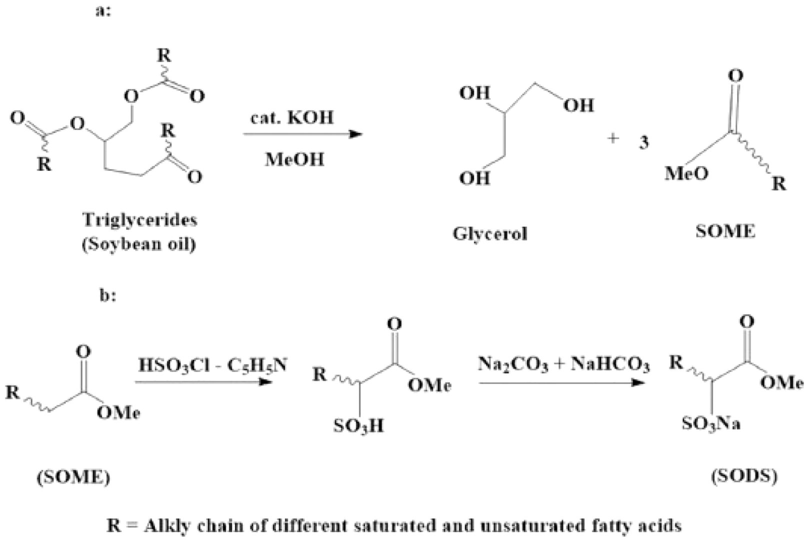


Figure 12. Synthetic scheme of synthesis of SODS. Reprinted with permission from ref 84. Copyright 2022 Elsevier.

for its high saponin content, was studied for its potential to inhibit shale during drilling operations. CO is abundant in many parts of the world, and its leaf extracts are readily available and easily synthesized. Moreover, they are biodegradable and have been traditionally used in many countries for the treatment of fresh cuts.

The potential application of this compound in inhibiting shale during drilling operations could offer a promising solution to mitigate the challenges associated with shale formation and improve the efficiency of the drilling processes. Saponin has been shown to reduce the swelling index of shale samples similar to KCl, indicating its effectiveness as a shale inhibitor. Ghasemi et al. explored the potential of employing Korean red Ginseng root extract as an inhibitor of clay swelling.[12] This extract contains abundant nonionic surfactants, specifically ginsenosides Rg3, Rg5, and RK1.

The structure is shown in Figure 10. For purposes of comparison, a cationic surfactant (CTAB) and an inorganic salt (potassium chloride), recognized as effective clay swelling inhibitors, were also employed. The fluid samples prepared with the biosurfactant solution displayed unique properties compared to the baseline fluid. The montmorillonite (Mt) particles exhibited an impressive loading capacity that led to reduced rheological effects, limited control over fluid loss, and the creation of stable Mt pellets. Furthermore, the dispersion of these particles displayed complete instability, causing effective sedimentation over time. The Mt particles also displayed a greater contact angle, indicating less hydrophilicity, and were larger in size and more aggregated compared to the baseline. The fluid samples also showed less mass loss and improved shale cuttings recovery. A schematic of the recovery mechanism and surfactant-clay interactions is given in Figure 11.

Another application of natural surfactants in drilling is as emulsifiers. Emulsions occur during drilling operations when oil and water mix, leading to difficulties in separating the two phases. Synthetic surfactants such as nonionic surfactants are commonly used as emulsifiers in drilling fluids. However, their high cost and environmental impact have led to the exploration of natural surfactants as alternative emulsifiers.

Natural surfactants such as lecithin extracted from soybeans and phospholipids from egg yolk have shown potential as emulsifiers in drilling fluids. Lecithin has been shown to effectively emulsify oil and water, leading to a reduction in the IFT between the two phases. Paswan et al. investigated the potential use of a soybean oil-derived organic surfactant (SODS), which was formulated within the laboratory and utilized as an emulsifier to create an environmentally friendly oil-in-water (O/W) emulsion mud system.[84] The synthesis scheme is given in Figure 12. This study aimed to explore the practical application of SODS as a potential alternative to conventional surfactants in the petroleum industry.

One of the major advantages of SODS is its cost-effectiveness, as soybean oil is readily available and relatively inexpensive compared to traditional surfactants. Moreover, it does not require any preprocessing before utilization, which further reduces the overall production cost. Therefore, SODS could potentially offer a more economical and sustainable solution for emulsion mud systems in the petroleum industry. Furthermore, SODS has the potential for large-scale production and could be easily scaled up for commercial use. This makes it a promising candidate for future applications in the petroleum industry, where the demand for ecofriendly and cost-effective solutions continues to rise. In summary, the findings of Paswan et al. suggest that SODS could be a viable alternative to conventional surfactants for the formulation of environmentally friendly O/W emulsion mud systems. Its cost-effectiveness and potential for large-scale production make it a promising solution for the petroleum industry.

Ahmadi et al. investigated the potential of two newly discovered natural surfactants derived from the roots of *Seidlitzia rosmarinus* and leaves of the henna plant to prepare colloidal gas aphron (CGA) fluids (Figure 13). Based on the experimental outcomes in this research, the investigators deduced that the two natural surfactants are well-suited for formulating drilling fluids based on CGA. In addition, these surfactants have no negative environmental impact, and they are much cheaper than the commercial and industrial surfactants currently in use. Overall, the findings of this study suggest that the newly discovered natural surfactants have great potential for use in the petroleum industry as an environmentally friendly alternative to conventional surfactants. Table 2 summarizes the use of natural surfactants in drilling processes in the oil and gas industry.

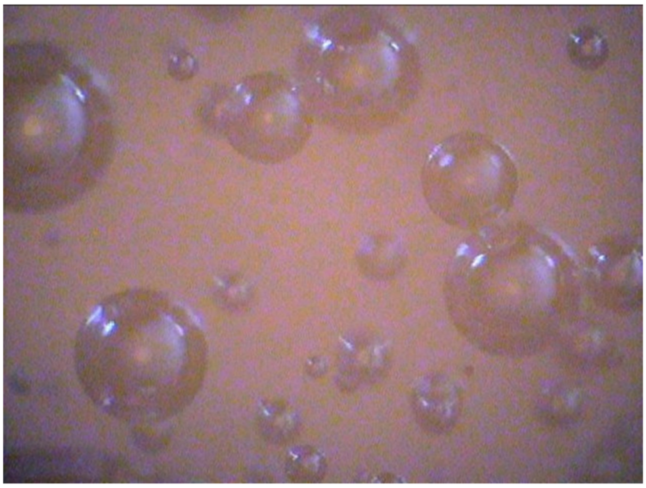


Figure 13. Aphronized fluid prepared from henna extract.[85] Copyright 2015 Elsevier.

Natural surfactants can also act as lubricants in drilling operations. The high friction generated during drilling can lead to equipment failure and a reduced drilling efficiency. Synthetic surfactants such as fatty-acid-based lubricants are commonly used to reduce friction during drilling. However, their environmental impact has led to the exploration of natural surfactants as alternative lubricants. Natural surfactants such as lignin, extracted from wood, have shown potential as lubricants in drilling fluids. Lignin has been shown to reduce friction during drilling operations, leading to an improved drilling efficiency.

Saponifiable fatty acid esters, derived from sources such as vegetable oils and animal fats, are notable for their potential in surfactant synthesis. Triglycerides found in these resources can be hydrolyzed into glycerol and fatty acid molecules.[87,88] The obtained fatty acids, such as oleic, stearic, and palmitic acids, serve as essential building blocks for anionic and nonionic surfactants. By chemically modifying these fatty acids, researchers can create an array of surfactant structures with varying hydrophilic−lipophilic balances (HLB) to cater to specific applications, from emulsification to detergent formulations.[88]

Nonsaponifiable fatty acid esters, predominantly derived from plant sources, encompass a spectrum of compounds with distinct functional attributes. Phytosterol esters, for instance, exhibit surface-active properties and are classified as nonionic surfactants.[87] These can be synthesized through esterification reactions, enabling the tailoring of their amphiphilic characteristics.[89] Carotenoid esters, on the other hand, are potential candidates for cationic surfactant synthesis due to their positively charged moieties. These unique esters open avenues for the development of surfactants suited for various applications, from cosmetics to pharmaceuticals.[90]

Terpene esters, sourced from essential oils and plant extracts, present intriguing possibilities for surfactant synthesis. Limonene and its derivatives, for instance, can be functionalized to produce nonionic surfactants. The hydrophobic terpene backbone and the hydrophilic ester group combine to create amphiphilic structures, enabling applications in cleaning products and personal care formulations.[91]

The synthesis of surfactants from major fatty acid esters found in natural resources holds promise for sustainable and environmentally friendly formulations.[90] By harnessing the inherent diversity of these esters and tailoring their properties through chemical modification, researchers can design surfactants that cater to the specific demands of various industries.[89,91] As the need for greener and biodegradable alternatives gains prominence, the exploration of fatty acid esters from natural sources as surfactant precursors is set to play a pivotal role in shaping the future of surfactant chemistry.

The use of natural surfactants in drilling fluids has several potential benefits. Natural surfactants are biodegradable, environmentally friendly, and nontoxic. They also have a lower cost compared to synthetic surfactants. The use of natural surfactants can lead to improved drilling efficiency, reduced wellbore instability, and an increased equipment lifespan. Additionally, the use of natural surfactants can improve the environmental impact of drilling operations.

In conclusion, natural surfactants have shown potential as alternatives to synthetic surfactants in drilling fluids. Their effectiveness as shale inhibitors, emulsifiers, and lubricants has been demonstrated. Natural surfactants have the potential to improve drilling efficiency, reduce wellbore instability, and improve the environmental impact of drilling operations. The use of natural surfactants in drilling fluids is an area of active research, and their potential benefits make them promising alternatives to synthetic surfactants.

3.4. Corrosion.

Corrosion is a major problem in the oil and gas industry because it leads to the degradation of equipment and infrastructure, resulting in downtime and increased maintenance costs. The industry has faced increasing costs for oil mining and transportation, partially as a result of equipment damage caused by corrosive substances such as media that contain dissolved H_2S, Cl^-, O_2, and CO_2. Corrosion in carbon steel pipelines is a common example in this industry, occurring in environments that contain water and CO_2.[92−95] Corrosion inhibitors are commonly used to prevent or mitigate corrosion, and natural surfactants have shown promise as effective corrosion inhibitors, as presented in Table 3. Natural surfactants such as saponins, glycolipids, and rhamnolipids have been investigated for their potential as corrosion inhibitors in the oil and gas industry. These surfactants have shown good performance in reducing

Table 3. Details of Natural Surfactants Used for Corrosion Inhibitor Applications

surfactant type	class	extraction method	sources	efficiency (%)
saponins[96,97]	anionic	alcohol extraction steam distillation	*Gongronema latifolium* *Bredelia ferruginea*	93.7−96.5
glycolipids[98]	nonionic	solvent extraction	*Pseudomonas mosselii*	80−87
rhamnolipds[100]	nonionic	solvent extraction	*Pseudomonas aeruginosa*	68.4
gemini[101]	ionic nonionic	chemical synthesizing	ethane dibromide	96.17

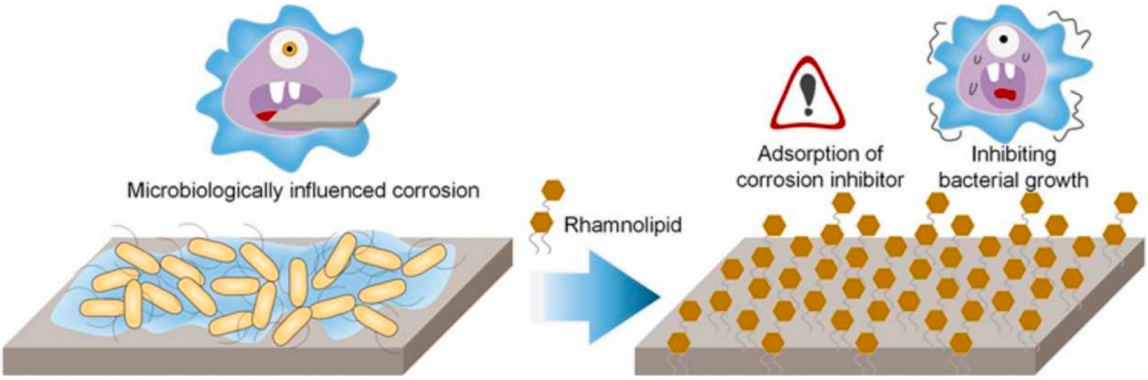


Figure 14. Schematic of corrosion inhibition using rhamnolipids. Reprinted with permission from ref 100. Copyright 2022 Elsevier.

corrosion rates by forming a protective film on metal surfaces, preventing the corrosion reaction from occurring.

Saponins, which are widely found in plants, have been found to be effective in reducing the corrosion rate of carbon steel in acidic environments. Studies have shown that saponins can adsorb onto metal surfaces and form a protective film, reducing the corrosive attack on the metal.[96] The natural extract-derived surfactants demonstrated strong inhibition properties in an acidic environment, exhibiting efficiency rates of up to 93.7% and 96.5%.[96]

Saponins extracted from other sources have also shown good potential as corrosion inhibitors.[97] Glycolipids, produced by microorganisms, have also been found to be effective in reducing the corrosion rate of metal.[98] In both abiotic and mixed consortia systems, the biosurfactant molecules demonstrated an inhibition efficiency for corrosion ranging from 80% to 87%. These surfactants can form a stable complex with metal ions, preventing them from participating in the corrosion reaction. Glycolipids extracted from different sources such as *Pseudomonas aeruginosa*, *Burkholderia cepacia*, and *Rhodococcus erythropolis* have been studied for their potential as corrosion inhibitors.[99]

Rhamnolipids, also produced by microorganisms, have shown potential as effective corrosion inhibitors due to their ability to form a stable film on metal surfaces. Rhamnolipids have been investigated for their use in mitigating corrosion and have shown good performance in reducing corrosion rates in X70 carbon steel.[100]

A schematic of corrosion inhibition using rhamnolipids is given in Figure 14. Rhamnolipids produced by *Pseudomonas aeruginosa* have been extensively studied for their potential as corrosion inhibitors in the presence of simulated seawater. In addition to their ability to reduce corrosion rates, natural surfactants also offer several other advantages in the oil and gas industry. They are biodegradable and nontoxic, making them environmentally friendly, and they can be easily produced on a large scale using microbial fermentation or plant extraction methods.

Another study reported that gemini surfactant increases the efficiency of the surfactant to prevent mild steel corrosion to 96.17% using ethane dibromide synergized with sodium tosylate (NaTos). The inhibition efficiencies exhibited variations with different organic salts. The highest inhibition efficiency reached 96.17% in the case of the gemini-additive system at a temperature of 60 °C.[101]

In conclusion, natural surfactants have shown great potential as effective corrosion inhibitors in the oil and gas industry. Saponins, glycolipids, rhamnolipids, and gemini surfactants have been studied extensively for their potential as corrosion inhibitors and have shown good performance in reducing corrosion rates. Additional investigations are required to fine-tune the application of these natural surfactants in anti-corrosion contexts and to delve into the potential of other natural surfactants for similar purposes.

4. PROSPECTS AND CHALLENGES

Natural or biobased surfactants offer a number of potential benefits for oilfield applications. These surfactants are derived from renewable sources such as plant extracts, bacteria, or fungi and have been shown to be biodegradable, nontoxic, and environmentally friendly. In addition, natural surfactants often exhibit unique properties, such as high stability and strong emulsification, which can make them particularly effective in oilfield applications. One promising source of natural surfactants is plant extracts, which contain a variety of compounds with surfactant properties. Saponins, which are found in multiple plant species, have strong surfactant properties and can effectively lower the surface tension of oil and water. Similarly, bacteria and fungi also serve as sources of natural surfactants, with rhamnolipids, sophorolipids, and glycolipids being notable examples. Rhamnolipids have been proven to be highly effective in reducing the surface tension of oil and water, which enhances the oil recovery efficiency.

Although they possess promise in oilfield applications, natural surfactants encounter specific challenges that must be tackled for their complete and effective utilization. The main challenge hindering the production of genuine natural surfactants is the expensive workup process. These surfactants are typically found in small amounts, making separation a laborious task. In many cases, the cost of isolating and separating natural surfactants outweighs the cost of producing synthetic surfactants with similar properties. However, as the demand for natural surfactants increases, it is likely that production costs will decrease, making them more competitive with synthetic alternatives. The cost-related challenges faced by genuine natural surfactants could be resolved by developing fermentation processes that generate biosurfactants in abundant quantities. Yeast and bacteria are capable of producing surface-active agents effectively, and there is a growing focus on leveraging biotechnological methods to manufacture amphiphilic compounds.

Another challenge is the variability of natural surfactants. Due to their origin from natural sources, the characteristics of natural surfactants can differ based on both the source and the extraction method employed. This can make it difficult to develop consistent and reliable formulations for use in oilfield applications. However, advances in technology and a better understanding of the properties of natural surfactants are helping to address this challenge. Despite these challenges, the prospects of natural/biosurfactants in oilfield applications are bright. With the increasing demand for sustainable and environmentally friendly technologies in the oil and gas industry, natural surfactants offer a promising solution for improving the efficiency of oil recovery.

5. SUMMARY AND CONCLUDING REMARKS

The operations in the oil and gas industry are complex and require various chemical agents to optimize the process. Surfactants are a critical class of chemicals used in several applications, such as drilling and EOR. They function by reducing the IFT between immiscible fluids, facilitating emulsification and dispersion, and improving oil recovery. Surfactants can be categorized according to their molecular structure, charge, and the composition of their hydrophilic and hydrophobic components. The effectiveness of surfactants is impacted by various factors such as temperature, salinity, concentration, and the presence of other chemical compounds.

Natural surfactants are an emerging area of research that offers promising prospects for the oil and gas industry. The use of natural surfactants can reduce the environmental impact of upstream operations, as they are biodegradable and have lower toxicity. Moreover, the increasing demand for sustainable and environmentally friendly technologies is driving the adoption of natural surfactants. However, the efficacy of natural surfactants is contingent upon multiple factors, encompassing their origin, molecular configuration, and compatibility with reservoir conditions. Consequently, additional research is necessary to fine-tune the utilization of natural surfactants within the oil and gas sector. In conclusion, the use of surfactants, both synthetic and natural, offers several benefits in the oil and gas industry and can play a vital role in enhancing oil recovery, reducing environmental impact, and ensuring sustainable practices.

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Notes

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