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Most common surfactants employed in chemical enhanced oil recovery

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ABSTRACT

Chemical enhanced oil recovery (EOR) and particularly surfactant injection has recently received a great deal of attention. The suggested recovery mechanisms after injecting surfactants include wettability alteration and IFT reduction. If a surfactant is properly selected according to the environmental variables-such as pressure, temperature, salinity, it can lead to more efficient enhanced recovery from an oil reservoir. On the other hand, poor selection of the surfactant can result in a low recovery and can even become detrimental to the reservoir due to undesirable wettability alteration and possible rock dissolution resulting in a chemical reaction with displacing fluid and blockage of the pore space. Also, choosing the wrong surfactant without considering the rock mineralogy may result in high adsorption on the pore surface of the rock and unnecessary waste of resources. It is also worthy to note that surfactants are some of the most expensive chemicals used during EOR. Extensive literature review suggests that anionic surfactant are the preferred surfactant category for EOR especially when it comes to sandstone reservoirs. Occasionally, in specific situations a better performance have been reported after injecting cationic, non-ionic or mixtures of both surfactants, particularly when dealing with carbonate reservoirs. This paper presents in detail a review of the most commonly applied surfactants in EOR studies and the optimum application criteria for of each type. To the best of the authors' knowledge, such detailed and comprehensive review is not available in the literature, presently.

1. Introduction

Mechanisms of surfactant EOR mainly include decreasing interfacial tension (IFT) and shifting reservoir wettability towards strongly water-wets. The remaining oil saturation can be divided into two categories, firstly residual oil to water flooding, which usually is attached at pore wall, and secondly oil bypassed by the water flooding. Typically, the residual oil saturation will be in a range of 20–30% OOIP within contacting 100% of given oil zone by water flooding. The oil is immobile at this saturation range due to the surface tension between oil and water. Also, the differential pressure alone cannot overcome the high capillary pressure to move oil out from pores. However, the surfactants can reduce the interfacial tension, thereby decrease capillary pressure and allow water to remove the trapped oil as a result of water bypass. Furthermore, surfactant can also drive the reservoir wettability towards more water-wet and lifting off the attached oil film from the pore wall, thus decreasing residual oil saturation and enhancing oil recovery.

The concept of applying surfactants in enhanced oil recovery was introduced in the early 1900's. The initial unsuccessful efforts led to the creation of a new revolutionary theory related to the possibility of producing in-situ surfactants. This idea was initiated from the fact that naphthenic acids exist in the reservoir, naturally. The main question to be answered about this technique was whether the soap or, in other words, the surfactant would be produced once an alkali is injected into the pore

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space of the rock. Although this method had the potential to reduce the cost of injecting synthetic surfactants, the results achieved were not convincing in order for the method to be announced successful. Finally in the 1960s, yet again the research in this area focused on the use of synthetic surfactants, however, this time mainly on designing surfactants tailored for each specific circumstance using the less expensive raw material. In the 1980's, combining the benefits of alkali and surfactants resulted in the invention of one of the most important methods of chemical EOR called alkaline-surfactant-polymer, (ASP). Since then, tremendous amount of research work has been carried on designing different surfactants according to the situations at hand, however unfortunately there is no single body of text available in the literature to provide researchers with an overview of the various research work conducted to date and their outcomes. This paper is an attempt to bridge this gap in the literature and provide an overview of the history of surfactants and their use in EOR. In addition, since variation in the formation water salinity, oil composition and temperature can affect the performance of the surfactants by impacting on the interfacial tension (IFT) and wettability, the optimum conditions for the application of each reviewed surfactant are also discussed.

2. Significance of operational conditions

Decreasing interfacial tension and shifting reservoir wettability towards more water-wet are the main mechanisms of surfactant flooding in the reservoirs. To remove the alcohol and increase the solubilisation of oil and water in microemulsions, surfactants with branched hydrocarbon chains, adding ethylene oxide (EO), decreasing the hydrophilic propylene oxide (PO) groups to the surfactant are used [1]. Based on the survey results, decreasing interfacial tension has long been the goal of chemists to enhance oil recovery by developing economical surfactant for sandstone reservoirs [2]. However, for carbonated reservoirs, reservoir engineers have been focusing on using cationic surfactants to drive the reservoir wettability from oil-wet to water-wet, thus accelerating the oil production rate by decreasing the residual oil saturation.

2.1. Temperature

Karnanda et al. [3] explained that most of the surfactant solutions have a cloud point temperature beyond which the solution becomes cloudy and measuring the IFT or other parameters become almost impossible. However, the anionic surfactants solution have a Krafft point temperature, suggesting that the surfactants would precipitate as the temperature is lower that the Krafft point temperature. At this point, a surfactant becomes ineffective and drops out of the aqueous solution. Depending on the surfactant structure the cloud point temperature can be between 30 °C and 160 °C. Temperature can affect the IFT and critical micelle concentration (CMC) of surfactant systems and this effect is greater for anionic surfactants. Surfactants' phase separation (cloud point) at high temperatures could likely lead to the decrease of surfactant's concentration, thus exhibiting poor performance to decrease IFT [1]. Also, increasing temperature can shorten the time of an interfacial tension to reach equilibrium for Gemini surfactant solutions. However, the temperature plays a minor role for a mixing surfactant system because of synergism [4]. Hiemenz and Rajagopalan [5] in their book define CMC as a concentration level, at and above which the micelles which are the aggregation of surfactant molecules starts to form. CMC is an important factor in studying surfactants. After this threshold, the surfactant behaviour, especially its surface tension, stabilizes and stays constant regardless of any increase in its concentration. Most of the experiments in the literature indicate that temperatures above 120 °C results in either degradation or precipitation of most of the surfactant.

2.2. Interfacial tension (IFT)

Udeagbara [6] defines IFT as the force that exists between the molecules of the interface between two fluids. Subsequently, IFT holds these molecules together. A surfactant can reduce this force by getting adsorbed at the interface between two liquids or a liquid and a gas. Troy et al. in their book [7] explain that this force is often measured in dynes/cm and it can be affected by pressure, temperature, and the composition of each phase. Karnanda et al. [3] explained that lowering this force to low enough values can increase the oil recovery significantly. This is because the IFT gives rise to capillary forces in the porous media which are mainly responsible for the hydrocarbon trapped in the form of residual saturation.

2.3. Optimal salinity

In general, salinity has a significant effect on a surfactants' performance. In most of the cases, high salinity has an adverse impact on the efficiency of the surfactant, therefore in a high salinity situation the use of specifically developed surfactants with reasonable resistance towards this harsh environment is recommended. In an ideal situation, the goal should be to have an optimum salinity level for any particular surfactant. Hirasaki et al. [8] define the optimum salinity as a salinity at which equal quantities of oil and water can be mutually solubilized into a microemulsion which results in equal IFTs between microemulsion phase and excess oil or excess water phase [9]. Also, the water solubilisation capacity of a particular microemulsion is closely related to the partition of cosurfactants among water, oil and interfaces, chain length and nature of oil [9–11]. Further research indicated that the IFT measured at the optimum salinity is the minimum achievable IFT during lab experiments for IFT measurements. S.I.Chou & Shah [12] observed in their experimental research that maximum oil recovery is obtained if the salinity of connate water or chemical slug is maintained at the optimal salinity of the selected surfactant.

2.4. Surfactant concentration

Researchers all agree that concentration of the surfactant in a chemical slug always must be considerably above the critical micelle concentration so that micellization can be initiated. Hirasaki et al. [8], describe the reason as: at higher concentration more of the excess oil and water become solubilized and forms the middle phase or type III Winsor solution which leads to higher recovery. Therefore, low surfactant concentration is not desirable. Hirasaki et al. [8] reported that even if the concentration is higher than critical micelle concentrations but still close to it, the middle phase was instantaneous or not detected. On the other hand, it must be kept in mind that at a high concentration of surfactant end effect behaviour deviates from its normal. Apaydin & Kovscek [13] with their experiments showed that if the surfactant concentration is too high, it may cause the building of pressure gradient by end effect. This gradient will be from the outlet toward the inlet, against the direction of flow.

2.5. Co-solvent or Co-surfactant

Hirasaki et al. [8] explains that alcohol as a co-solvent softens up the surfactant film at oil/water interface and increases the equilibration rate and formation of low viscosity microemulsions. However, a disadvantage of using alcohol is to decrease solubilisation of oil and water in microemulsions, thus increasing the value of IFT with a certain surfactant [14]. This disadvantage might be compensated by using mixtures of cosolvents. For example, Reed and Healy used mixtures of an alcohol cosolvent with synthetic alkyl/ary1 sulfonates to run core flooding tests, showing the highest recovery of water flood residual oil by continuously injecting surfactant [15]. This co-surfactant can change the optimal salinity required to achieve an ultra-low IFT. Despite all the advantages, this popular agent must be selected cautiously. Hirasaki et al. [8] explained that if surfactant selected improperly it can decrease the solubilisation of oil and water in the microemulsion which, therefore, increases the minimum achievable IFT. In addition, if creating foam is desirable, alcohol destabilises the foam and results in reduced mobility control. Until recently, the use of the co-solvent or co-surfactant in most of the cases seemed inevitable. However, many studies recently have demonstrated the possibility of avoiding these additives by selecting a proper surfactant formulation and even sometimes mixing dissimilar surfactants.

2.6. Branched surfactants

Abe et al. [16] studied the microemulsion formation by mainly using branched tail polyoxyethylene sulfonate surfactants. The study suggested that if in a situation using co-solvent is not practical as a stabilising agent, alternatively using branched hydrocarbon surfactants at a temperature lower than 40 °C and sometimes room temperature is able to form a well stabilised microemulsion. Wormuth & Zushma in Ref. [17] found the reason of using branched surfactant at low temperature in phase behaviour of these surfactants in oil and water. They realised that adding salt or increasing the temperature shifts the phase diagram of the oil-rich, water-rich and surfactant rich (microemulsion) system from three-phase coexistence towards the unstable emulsion zone or two-phase coexistence. However for linear surfactants the three phase coexistence on the phase diagram shifts more towards the higher temperatures. Also, they also concluded that the branched surfactants are more lipophilic than linear surfactants and their lipophilicity is influenced by the amount and type of branching. In majority of the cases, branched surfactants are less capable of mixing equivalent amounts of oil and water, which clearly specifies that branched surfactant/oil/water mixtures are more distant from the tricritical point than linear surfactant/oil/water mixtures.

2.7. Added chemical group

2.7.1. Ethylene oxide (EO)- C_2H_4O/propylene Oxide(PO)- C_3H_6O

EPA [18] explains that Ethylene oxide with a formula of C_2H_4O and propylene oxide with the formula of C_3H_6 have been used as intermediate chemicals in the industry for different applications such as a fumigant and sterility for food and hospital equipment. Wu et al. [19] demonstrated that different locations of the ethylene oxide (EO) and propylene oxide (PO) in molecule structure result in different scales of hydrophile–lipophile (HLB) in surfactants. Furthermore, Hirasaki et al. [8] mentioned that adding EO/PO units to the chemical structure of a surfactant eliminates the need for the use of alcohol as a co-solvent to achieve low viscosity microemulsion and ultra-low IFT. Levitt et al. [20] claim that achieving a minimum IFT value in harsh environments is possible through adding ethylene oxide unit to the chemical formulation of the surfactant. The hydrogen bonding of ethylene oxide and water increases the interaction energy between the brine and oil plus it helps the surfactant to be adsorbed easier at the interface of water-oil and overcome the salting out effect which results in lower IFT.

2.7.2. Ethoxy unit- (C_2 H_5 O^-)

Kathel & Mohanty [21] showed that adding these anionic units increases the tolerance of surfactant in existence of divalent ions as well as the surfactant solubility in high salinity environments. They concluded that the higher the number of the ethoxy group, the higher the aqueous stability.

2.7.3. Functionalized polymeric surfactant (FPS)

Functionalized polymeric surfactant (FPS) can exhibit 5% of OOIP compared to the HPAM-EOR alone [22]. Surfactant-like monomers linked to the FPS backbone can pull them towards the oil/water interface and create an oil/water emulsion, thus improving the microscopic displacement efficiency, although the reduction of oil/water interfacial tension is in a range of 0.01–0.1 dyne/cm [22].

2.8. Zeta potential & pH

Zeta potential is the fundamental property in determining the stability for colloidal dispersions and emulsions. This potential is a measure of the magnitude of electrostatic repulsion/attraction between suspended particles. Higher magnitude of the electrostatic repulsion/attraction results in higher stability for an emulsion. Behrens [23] explains that adding acid to the emulsion causes reduction in the magnitude of zeta potential until finally it becomes neutralized or even positive. The effect is opposite for adding alkali that causes the magnitude of the negative zeta potential to rise. The pH is the most important factor in affecting the zeta potential in an emulsion. Reservoir pH is normally slightly acidic. As of Auttors' knowledge today to the majority of the research in literature, for long term surfactant stability at reservoir condition, it is always suggested to keep the emulsion pH at slightly alkaline levels. However, the reason behind it was unclear until in Ref. [24] Choi et al. evaluated the particle size distribution and surface property of a surfactant emulsion by changing the pH. They realised that increasing the pH up to 12 significantly reduced the mean particle diameters ($p < 0.05$). They interpreted the observations as: in an acidic environment, protonation of surfactant occurs which, subsequently, results in inadequate interfacial adsorption of the surfactant at the oil and water interface. Consequently, the aggregation of particles occurs as a result of a reduction in surfactant molecule's surface active properties. Later measuring the zeta potential of different emulsions with different pH supported the accuracy of interpretations by Choi et al. [24].

2.9. Divalent ions

The existence of divalent cations mainly Mg^{2+} and Ca^{2+}, is not desirable and should be kept at low levels. These cations have the potential of causing surfactant precipitation which can result in blocking the pores. Anionic surfactant systems are more sensitive to the divalent ions than monovalent ions, particularly at low surfactant concentrations [25]. Due to the ion exchange in the system of crude oil/brine/rock, phase behaviour becomes over optimum, leading to large surfactant retention [26,27]. Sodium metaborate has recently been introduced to sequester divalent ions as an alkali [28,29]. If this situation is inevitable then using more resistant surfactant such as surfactant with ethoxy, sulfonate or carboxylate units in their structure are recommended. Details related to each surfactant are disclosed further in this article.

2.10. Pressure

There is only limited information available on the effects of pressure on surfactant emulsion systems. Hara et al. [30], showed that pressure can affect the critical micelle concentration (CMC), however, the relationship was found not to be linear. Their measurements showed indicated that increasing the pressure first increased and then decreased the CMC. This area requires more research. The studies conducted to date have not been able to discover any significant impacts on the surfactant system due to pressure changes.

2.11. Sulfonate/Carboxylate

Hirasaki [8] explains that existence of sulfonate or carboxylate unit increases the surfactants' long–term stability at higher reservoir temperatures. In addition, Shupe [31] explains that sulfonate can help in the case of high salinity formation brine with a considerable amount of divalent ions. However, he recommends the sulfonate application for a temperature around 50 °C. Sharma and Gao [32] and Lu [33] reported that carboxylate surfactants displayed excellent performance and stability at high temperature and high salinity in the existence of divalent cations. These surfactants resulted in high oil recovery with low absorption in reservoir formation for both carbonate and sandstone reservoirs.

2.12. Sulfate

Shupe [31] in his patent explained that sulfate linkage in the molecular structure of a surfactant causes the molecules to be highly sensitive to temperature. This results in hydrolysis or other permanent degradation of the molecules to a non-reactive form. Therefore, surfactants with sulfate units are not suitable for formations with temperatures higher than surfactant critical temperature on pahse envelop. This temperature is a unique characteristic of each surfactant.

3. Surfactants and the optimum operating conditions

3.1. Anionic surfactants

3.1.1. Alkyl aryl sulfonates

Showell [34] in his book explains that alkyl aryl sulfonates had been introduced to the market for the first time in the 1930's and shortly after in 1945 they had become the main industrial surfactant component. The process for producing this surfactant involves a reaction between benzene and propylene tetramer which forms alkyl aryl. Following this, the sulfonation of alkyl aryl creates alkyl aryl sulfonates. The biggest downside of these surfactants is their non-biodegradability. The longer chain members of this family with C14 – C30 alkyl aryl compounds are used as hydrophobes that interact well with crude oil. Hirasaki et al., [8] investigated the effects of salinity in EOR process, using C9, C12 and C15 ortho-xylene sulfonates from this family of surfactants. The surfactants used in this research were made from oligomers of propylene. Injecting at different salinity, they concluded that continuous injecting of each surfactant at its optimal salinity can lead to the highest recovery. The biggest advantage of alkyl aryl sulfonate surfactants is their ability to be tailored based on the reservoir conditions. In addition comparing to other commercially available surfactants, the raw material are accessible at low cost in the market. Shupe [31] further explains that alkyl aryl sulfonate family are reasonably stable for a variety of crude oils at temperatures encountered in underground reservoirs, however, not very stable and effective in presence of high salinity or divalent ions. He suggests adding co-solvent/co-surfactant if applied in high salinity environments. The molecular structure of an Alkyl Aryl Sulfonate (Courtesy of OilChemTechnologies) is shown in Fig. 1.

3.1.2. Alkyl benzene sulfonate (linear)

Oya et al. [36] explain that alkyl benzene sulfonate (linear) is an anionic surfactant family and sub-category of alkyl aryl sulfonates with a negatively charged hydrophilic group. Furthermore, these researchers add that the length of the alkyl side chain varies between 10 and 14 carbon atoms. Currently, based on the new environment protection laws, this side should be branchless since branches on alkyl side slow down the biodegradation of the surfactant in nature. The existence of the sulfonate group increases the resistance of the surfactant towards temperature. This surfactant is aquatic toxic and toxicity increases with increasing the water salinity or hardness. Pena [37] evaluated the benefits of this surfactant family in EOR process. He observed that increasing the number of carbons in the alkyl chain reduces the CMC value. In addition, this surfactant family is able to reduce the IFT between water and crude oil. However, they performed better with crudes with carbon number from 7 to 10. The molecular structure of an Alkyl Benzene Sulfonate Courtesy of Procter&Gambl is shown in Fig. 2.

3.1.3. Alkyl sulfate (AS)

Alkyl sulfate is another family of anionic surfactants. According to Sigma Aldrich database [39] common examples of this family are sodium lauryl sulfate, sodium dodecyl sulfate and sodium octyl sulfate, however “R’ (Fig. 3) could be any

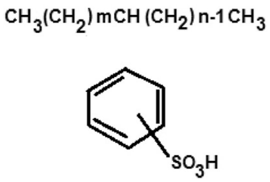


Fig. 1. Molecular structure of an alkyl aryl sulfonate, courtesy of OilChemTechnologies [35].

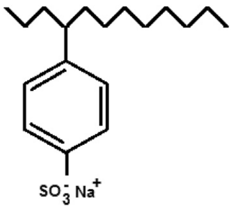


Fig. 2. Molecular structure of an alkyl benzene sulfonate courtesy of Procter&Gambl [38].

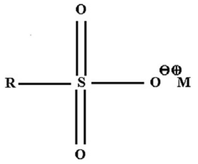


Fig. 3. Molecular structure of an alkyl sulfate [41].

hydrophobic hydrocarbon chain. Procter and Gamble [40] explain that this group of surfactants biodegrade really easily. The existence of the sulfate group makes the surfactant hydrophilic and soluble in water, however since the sulfate group is sensitive to temperature, the surfactant becomes insoluble in water at elevated temperatures.

3.1.4. *N-ethoxy sulfonate*

According to Sharma et al. [42], n-ethoxy sulfonate is an anionic surfactant family with cloud point over 100 °C. Sharma designed AV-70 or 7-ethoxy sulfonate and AV-150 or 15-ethoxy sulfonate to study n-ethoxy sulfonate, family. This unique design took the both advantage of EO and sulfonate group at the same time. The existence of sulfonate increases the surfactant long –term stability at higher reservoir temperatures. Ethoxylation of sulfonates improves their salt tolerance as well. Sharma et al. indicated that unlike other anionic surfactants these surfactants are stable and soluble with the injection of high salinity brine at high temperatures. Also, n-ethoxy sulfonate does not precipitate in the presence of divalent ions like Ca^{2+} and Mg^{2+}.

$$\mathrm{H}(OCH_2CH_2)_n - O - SO_2 - R$$

R = An alkyl radical, branched or linear, or an alkyl
n = Integer;

3.1.5. *Sodium dodecyl sulfate (SDS)*

This anionic surfactant is one of the most popular surfactants which belongs to the alkyl sulfate group. The research shows this surfactant to be a good partner for nanoparticles when injected as part of an EOR process [43]. IFT is reduced by nanoparticles enhancing the surface activity of anionic surfactant below its critical micelle concentration [43]. The cloud point of this surfactant is over 100 °C [44]. However, according to Shupe [31] presence of the sulfate group makes the surfactant sensitive to the temperature and its performance decreases at high reservoir temperatures. Using a mixture of nanoparticle and surfactant requires further investigation to overcome the challenge of nanoparticle adsorption on the reservoir rock. Pre-coating the rocks with nanoparticles is one of suggested ways today's by researchers. However, the feasibility of the idea is still unclear. The molecular structure of a Sodium Dodecyl Sulfate Courtesy of CIEC is shown in Fig. 4.

Fig. 4. -Molecular structure of a sodium dodecyl sulfate courtesy of CIEC [45].

3.1.6. *Alcohol Propoxy Sulfate (APS)*

Szlendak et al. [46] indicated that this surfactant is one of the main surfactants used in laboratory core floods. The structure of this anionic surfactant consists of a hydrophobe head which is C16-17 branched alcohol and seven propylene oxide group. Szlendak et al. [46] discovered that this surfactant performs well when used in combination with internal olefin sulfonate (IOS) and they achieved 30% additional recovery after injecting this surfactant in tertiary recovery. The aqueous and foam stability of APS is high especially in the presence of light oil at low temperatures [47]. In general, this surfactant is stable at salinities up to 6000 ppm with the optimum salinity being 4500 ppm [48]. The only downside to this surfactant is the existence of sulfate groups which makes it sensitive to temperature [31,40]. The molecular structure of an Alcohol Propoxy Sulfate (APS) courtesy is shown in Fig. 5.

3.1.7. *Alkyl (or alcohol) Ethoxy Sulfate (AES)*

This anionic surfactant is stable in high pH and salinity in the presence of alkali, and at temperatures up to 83 °C for long periods of time even in the presence of divalent ions [50]. Procter and Gamble [40] (Fig. 6) reported that injection of diluted AES solution of 0.2 wt% in Berea sandstone had resulted in additional recoveries of 35–50% of the residual oil in place.

3.1.8. *Alpha-Olefin Sulfonate (AOS)*

In Ref. [51], this family of surfactants with a general chemical formula of $R\text{-}CH{=}CH{-}\ (CH_2)_n\text{-}SO_3\ Na$, R = C10~20 commercially recognized as sodium linear alpha olefin sulfonate was studied by researchers. Their research outcome showed that this family of surfactant performs particularly well in the presence of divalent ions and has a high biodegradation rate. Rieger and Rhein [52] in their book wrote that the number of carbon atoms in the structure of these surfactants varies between 10 and 20. The most common formula from this family is the one with 14–16 carbons and it is commonly known as sodium C14-16 olefin sulfonate; C14-16-alkane hydroxy and C14-16-alkene, sodium salts; sodium alpha-olefin (C14-16) sulfonate or AOS. In regards to advantages of AOS, they are stable over the wide range of pH, and exhibit good foaming and detergent ability even in the existence of hard water. In numerous research work conducted to date, this surfactant has been used as an alternative foaming agent. In addition, it provides a reasonable acid resistance and can be consumed in emulsion polymerisation. The Molecular

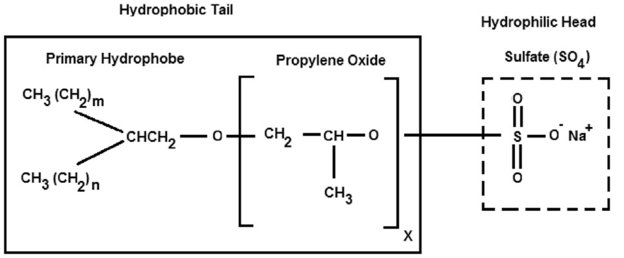


Fig. 5. Molecular structure of an Alcohol Propoxy Sulfate (APS) courtesy of [49].

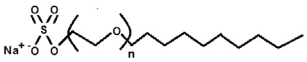


Fig. 6. Molecular structure of an Alkyl (or Alcohol) Ethoxy Sulfate (AES) Courtesy of Procter&Gamble [40].

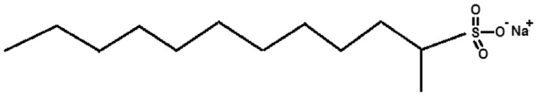


Fig. 7. Molecular structure of an Alpha-Olefin Sulfonate(AOS) Courtesy of Wei & Navarrete [53].

structure of an Alpha-Olefin Sulfonate (AOS) Courtesy of Wei & Navarrete is shown in Fig. 7.

3.1.9. *Alpha olefin sulfate*

This surfactant is very similar to AOS and IOS when used in EOR processes [8]. However, as it was explained in the beginning of this article, the existence of sulfate group restricts its application in the reservoir because of its thermal sensitivity. This instability happens because of the weakness of the C-O-S bond.

3.1.10. *Alkyl polyalkoxy alkyl sulfonate or alkyl aryl polyalkoxy alkyl sulfonate*

In another of Shupe's Patents [31] it is indicated that this surfactant is stable at high salinities between 70,000 ppm and 220,000 ppm, even if divalent ions are present. The sulfonate group increases the resistance of surfactants to high-temperature environments of up to 150 °C and enables the surfactant to form stable foams at higher temperatures. Shupe's Patents [31] realised this surfactant performs well on its own as well as in combination with other anionic surfactants such as petroleum sulfonate, an alkyl sulfonate, or an alkyl aryl sulfonate. The number of alkoxy group determines the solubility of the surfactant in a solution. Heating the emulsion can increase the solubility of surfactants, however at the same time it has a negative impact on the stability of the surfactant.

$$RO(R'O)_n R''SO_3^- M^+$$

R = An alkyl radical, branched or linear, or an alkyl aryl having from 8 to 24 carbon atom in the alkyl chain;
R' = Ethyl or a mixture of ethyl and propyl with relatively more ethyl than propyl;
R" = Ethyl, propyl, hydroxypropyl or butyl;
N= Integer from 1 to 20 and preferably from 2 to 8;
M+ = A monovalent cation such as ammonium, sodium, lithium or potassium [31].

3.1.11. *Branched alkyl benzene sulfonate*

C15-18 BABS/C16-18 BABS are the most common surfactants from this family that has been used in EOR studies. This family is classified as anionic surfactants with a similar behaviour to linear alkyl benzene sulfonate as explained earlier. The existence of sulfonate groups increases the surfactant's long–term stability at high reservoir temperatures. Comparing to linear alkyl benzene sulfonate, it is more expensive and it biodegrades slower. Therefore, its application is declining around the world. The molecular structure of a Branched Benzene Sulfonate Courtesy is shown in Fig. 8.

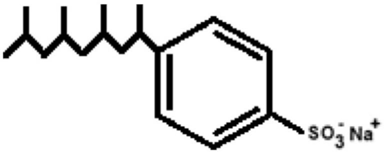


Fig. 8. Molecular structure of a branched benzene sulfonate courtesy of Kott, Scheibel, Severson, Cripe, & Burckett-St [54].

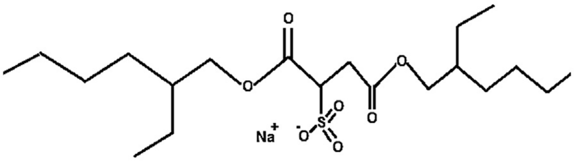


Fig. 9. Molecular structure of a Docusate Sodium Courtesy of Kott et al. [54].

3.1.12. *Docusate sodium*

Dang et al. [55], explain that this is a double tail anionic surfactant with a chemical formula of $C_{20}H_{37}NaO_7S$ .The results of the investigation conducted by these researchers on applying docusate sodium in ASP flooding indicated that it is a well-suited candidate for ASP flooding especially for conventional reservoirs. Furthermore, as an outcome of this study, the phase behaviour of docusate sodium in combination with the polymer (alcoflood 254S) showed that increasing the concentration of this surfactant in solution increases the viscosity of the mixture. This surfactant when mixed with a commercial surfactant called Synperonic® PE/F68 made a stable mixture even at temperatures above 100 °C and has a considerable positive effect on EOR in small and thin reservoirs. However, numerical simulation studies claim that this mixture is not a good candidate for fractured or low permeability reservoirs. The molecular structure of a Docusate Sodium Courtesy is shown in Fig. 9.

3.1.13. *Ethoxy or propoxy glycidyl sulfonates*

Hirasaki et al. [8] reported that this anionic surfactant has a high solubility over an extensive range of optimal salinities. It can form a stable microemulsion with n-octane as the oil at temperatures up to 120 °C. However, higher temperatures and salinities may lead to phase separation or reaching cloud points. Hirasaki et al. [8] claim this sensitivity can be reduced by mixing the surfactant with more thermal stable surfactants such as internal olefin sulfonate (IOS). The molecular structure of Ethoxy Glycidyl Sulfonate Courtesy is shown in Fig. 10.

3.1.14. *Alkyl ether sulfates*

Alkyl ether sulfates display a better aqueous stability compared to internal olefin sulphonates [21]. The existence of sulfate in their structure makes them very sensitive to high-temperature. Also, they are not very stable at high salinities [31]. Adding more ethoxy group to their structure increases the stability of the surfactants at high salinity and high-temperature environments. However, using these surfactants in harsh conditions (temperature higher than 120 °C and salinity greater than 180,000 ppm) is not recommended [21]. The molecular structure of an Ether Sulfate Courtesy is shown in Fig. 11.

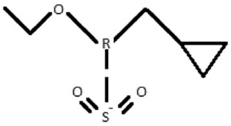


Fig. 10. Molecular structure of ethoxy Glycidyl sulfonate courtesy of Masaki, Furukawa, & Takenaka [56].

Fig. 11. Molecular structure of an Ether Sulfate Courtesy of Andjelic et al. [41].

3.1.15. *Guerbet alkoxy sulfate*

Levitt et al. [20] reported that the ester linkage in sulfate structure of this anionic surfactant might become hydrolyzed at temperatures above 60 °C or in low or neutral pH environments. Using alkali that effectively propagated the formation assists the surfactant to become more stable at higher temperatures and this only happens over a specific range of alkalinity. Adkins et al. [50], conducted the pH stability experiments for Guerbet alkoxy sulfate which indicated that at elevated pH, this surfactant is reasonably stable and it is not significantly degraded even after about 1.6–2.2 years at 100 °C or 4–6 years at 83 °C.

$$C_nH_{2n+1}O - PO_x - EO_y - SO_3^{o-}$$

Wherein.

n = is an integer between 12 and 44, inclusive,
x = is an integer between 0 and 50, inclusive, and
y = is an integer between 0 and 100, inclusive [57].

3.1.16. *Gemini Anionic Surfactants*

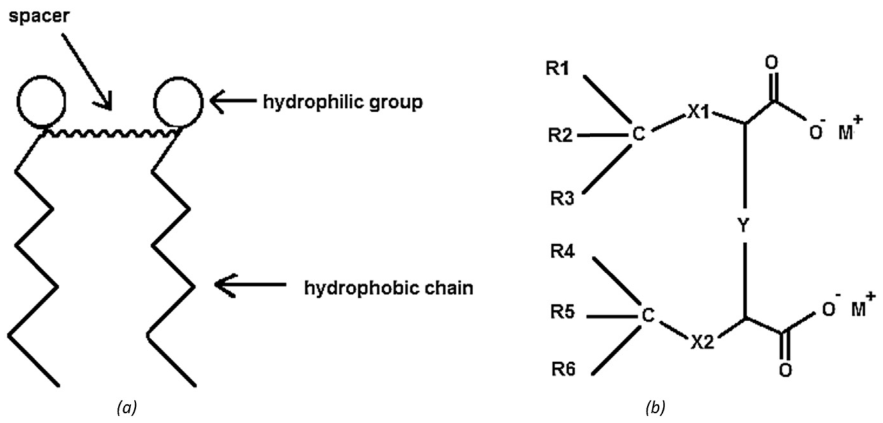
When it comes to the application of Gemini surfactants in EOR, work of Gao et al. (2013) is one of the highlights in this area. These researchers investigated the effect of Gemini surfactants on IFT as well as their stability. These compounds are named according to the length of hydrophobic tail and linking spacer group, for example in formula 14-2-14, 14 relates to the length of the hydrophobic tail and 2 is the length of the spacer. There are many varieties of Gemini surfactants around. However, Gao et al. (2013) research mainly focused on 18-2-18, 20-2-20, 14-4-14, 16-4-16, 18-4-18, 20-4-20, etc. Varying these numbers affects the IFT and static adsorption of surfactants. CMC values in Geminis are two to three orders of magnitude lower than conventional surfactants. Gao et al. (2013) suggested in general Geminis are very stable in aqueous solutions even in high temperatures (up to 85 °C), high salinity and hard brines (up to 20 wt % NaCl and 5 wt % $CaCl_{12}$) without any phase separation or precipitation. In addition achieving ultra-low IFT with these surfactants is possible and their adsorption is less than conventional surfactants. Gao et al., after their vast investigation on Gemini surfactants, it was recommended that this particular surfactant could be used in harsh conditions. The molecular structure of a Gemini Anionic Surfactant and Anionic Gemini Surfactant Courtesy is shown in Fig. 12.

3.1.17. *Internal olefin sulfonate (IOS)*

This anionic surfactant starts from C15-C18 to C24-C28 with twin tailed hydrophobe [46]. The presence of branches in this surfactant structure makes using alcohol as co-solvent under 60 °C unnecessary [8]. Levitt et al. [47] demonstrated that the presence of sulfonate unit in this compound increases the surfactant long –term stability at higher reservoir temperature and makes the IOS to be stable at high temperature up to 200 °C. Levitt et al. [47] in their article report this surfactant as one of the main common surfactants used in core floods by researchers. It is stable in aqueous solutions and forms a stable foam even at low concentration. The results of Levitt et al. (2006) investigation predicts better performance for this surfactant in low temperatures and with light oils. Tertiary flooding in tight oil sandstone using this surfactant was successful and could recover up to 30% of the remaining oil in place [47]. The surfactant is stable in salinity up to 6000 ppm with the optimum salinity at 4500 ppm [48]. Among all the surfactant in this group C15-C18 has higher resistance towards salinity. However the stability of these groups in presence of divalent ions is limited [59]. The molecular structure of an Internal Olefin Sulfonate Courtesy is shown in Fig. 13.

3.1.18. *Sulfonated, ethoxylated alcohol or alkyl phenol*

Shupe [31] in his patent explains that sulfonated, ethoxylated alcohol or alkyl phenol, has been designed as surfactant specifically suitable for reservoirs with temperatures higher than 50 °C and formation water having considerable amount of salt or divalent ions such as calcium or magnesium. The sulfonate group increases the surfactant's resistivity towards temperature and salinity without hydrolysing or becoming insoluble. The general chemical formula of this surfactant family is shown in Fig. 14. In addition Shupe (1978) claims that some anionic surfactants such as petroleum sulfonate, alkyl sulfonate or alkyl aryl sulfonate perform well in combination with this surfactant family, however, injecting this surfactant by itself in EOR processes also carries satisfactory results.



(a) (b)

Fig. 12. (a)- Molecular Structure of a Gemini Anionic Surfactant, (b) -Molecular Structure one Anionic Gemini Surfactant Courtesy of Mahanthappa, Sorenson, & Coppage [58].

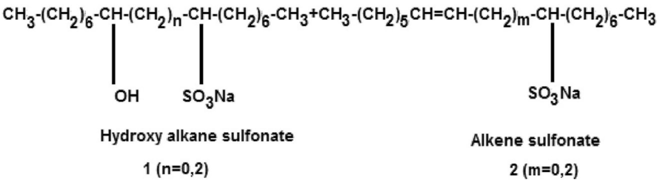


Fig. 13. Molecular structure of an internal olefin sulfonate courtesy of Shi, Liao, & Liu [60].

$$RO(CH_2)(CH_2)_xCH_2\ CH_2SO_3^-M^+$$

Fig. 14. Molecular formula of sulfonated, ethoxylated alcohol.

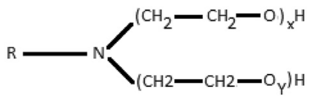


Fig. 15. Molecular structure of a sodium petroleum sulfonate courtesy of Shupe (1978). R = is an alkyl or alkyl aryl radical wherein the number of carbon atoms in alkyl chains varies from 8 to 20, x = is an integer from 1 to 20. M^+ = is a metallic cation or ammonium ion.

3.1.19. *Sodium petroleum sulfonate*

Loza et al. [61], report that this family of anionic surfactants are not very stable in hard water environments and tend to precipitate from solutions even in the presence of relatively low concentrations (about 50–100 ppm) of divalent ions such as calcium and magnesium. Shupe [31] demonstrated that the presence of sulfonate groups make sodium petroleum sulfonate reasonably stable at temperatures encountered at a majority of the reservoirs however their stability and affectivity in presence of high salinity or divalent ions is not satisfying. The molecular structure of a Sodium Petroleum Sulfonate Courtesy is shown in Fig. 15.

3.1.20. *TDA-9PO-sulfate*

Sharma and Gao et al. [32] demonstrated that Tridecyl- 9 propylene oxide-sulfate, with the commercial name of “Petrostep S13-C”, is a salt-tolerant anionic surfactant. Comparing with Gemini surfactants and sodium hexadecyl sulfate, this surfactant is more hydrophobic which results to more adsorption at the solid-water interface. These researchers also confirmed that sulfate groups reduce the thermal stability of the molecule and only can be used up to 60 °C [32]. The molecular formula of TDA-9PO-Sulfate is shown in Fig. 16.

3.1.21. *Alkyl alcohol propoxylated sulfate*

Wu et al. in Ref. [62] reported that this anionic surfactant is an efficient candidate for EOR. It is able to reduce IFT even at low concentrations without any assistance from co-surfactants or alkalis. Some formulation from this family performs well in lowering IFT even in high salinity reservoirs and could recover up to 50% of the residual oil in place in tertiary recovery only with dilute 0.2 wt% surfactant concentration. Wu et al. studies indicated the disadvantage of alkyl alcohol propoxylated sulfate as its high-level adsorption on sandstone comparing to other anionic surfactants. In addition existence of sulfate group in this formula makes the surfactant sensitive to temperature and hence it's not suitable for temperature above 60 °C. The molecular formula of an Alkyl Alcohol Propoxylated Sulfate is shown in Fig. 17.

$$CH_3 - 12(CH_2) - (OCH_2 - CHOH) - 9(OCH_2CHCH_3) - O - SO_3^-$$

Fig. 16. Molecular formula of TDA-9PO-sulfate.

$$R - OHCH_2CH_2CH_2)_nOSO_3^-M^+$$

Fig. 17. Molecular formula of an alkyl alcohol propoxylated sulfate. R = An alkyl radical, branched or linear, or an alkyl aryl; n = Integer. M+ = A monovalent cation such as ammonium, sodium, lithium or potassium.

3.2. *Nonionic surfactants*

3.2.1. *Alkyl ethoxy Carboxylated*

Friedli [63] in his book wrote that alkyl ethoxy carboxylated also known as carboxylated nonionic performs as nonionic at neutral pH and anionic at alkaline pH. Furthermore, the book explains that the common way of processing alkyl ethoxy carboxylated is adding sodium chloroacetate to and ethoxylated alcohol. Levitt et al. [20] reported that the combination of ethoxy and carboxylate group increases this surfactant's resistivity to high temperature and high salinity. The existence of ethoxy group itself in the structure of this surfactant makes the surfactant stable in high salinity environments as well as the presence of divalent ions. Furthermore, Levitt et al. (2012) added that ethoxy unit forms a hydrogen bond with water which increases the interaction energy of water/oil surface and, subsequently, reduces the IFT. Simultaneously, the presence of carboxylate group raises the surfactant long–term stability at higher reservoir temperatures. The molecular formula for alkyl ethoxy carboxylated is shown in Fig. 18.

3.2.2. *Alkyl Polyglycoside (APG)*

Santa et al. [65] investigations on emulsion behaviour of APG in harsh conditions indicated that this surfactants performs well under elevated temperatures and high salinity conditions and if co-solvent is added it forms microemulsion with chain length up to 14 carbons. This stability is due to the high interaction energy between water and APG molecules. Chemical structures of the glucose, leads to high solubility of APG even in the harsh environments of 180,000 ppm, and 80 °C in the existence of divalent ions. This rare behaviour of APG results in low IFT under various conditions. The molecular structure of an Alkyl Polyglycoside (APG) Courtesy is shown in Fig. 19.

3.2.3. *NEODOL*

Researchers from Shell [67] have designed NEODOLs surfactant for EOR purposes. NEODOL alcohols are entitled based on the number of carbon atoms present in the chemical formula of the product. For example, NEODOL 91 is a blend of C9, C10 and C11 alcohols. For NEODOL ethoxylated or propoxylated the description of the parent alcohol is written as well as the EO or

$$RO(CH_2\ CH_2\ O)_x\ CH_2\ COO^-\ M^+$$

Fig. 18. Molecular formula for alkyl ethoxy carboxylated [64]. R = a C_8 to C_{18} alkyl group. X = a number averaging about 1–15. M = an alkali metal or an alkaline earth metal cation.

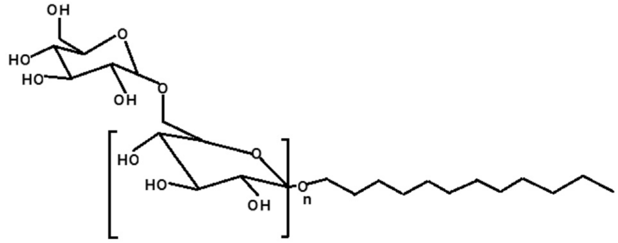


Fig. 19. Molecular structure of an alkyl polyglycoside (APG) courtesy of Leray [66].

Table 1
Current available NEODOL products in market provided by Shell company [67].

Alcohol	Ethoxylate/Propoxylate	
NEODOL 9	NEODOL 1-5- EO	NEODOL 25-12- EO
NEODOL 91	NEODOL 23-1- EO	NEODOL 45–2.25- EO
NEODOL 91-5	NEODOL 23-2- EO	NEODOL 45-7- EO
NEODOL 1	NEODOL 23-3- EO	NEODOL 45-13- EO
NEODOL 23	NEODOL 25-3- EO	NEODOL 91-2.5- EO
NEODOL 25	NEODOL 25-5- EO	NEODOL 91-6- EO
NEODOL 45	NEODOL 25-6.5- EO	NEODOL 91-8- EO
NEODOL 67	NEODOL 25-7- EO	NEODOL 375 -POS
NEODOL 135	NEODOL 25-9- EO	NEODOL 67-7 POS

PO unit mole number, e.g. NEODOL 91 is subsequently followed by a number indicating the average moles of ethylene oxide (EO) added. The recent Neodol products from the Shell Company are listed in Table 1. These surfactants are all nonionic and hydrophobic surfactants. Researchers from Shell recently discovered that adding other surfactants such as IOS to NEODOLs forms a blend which is more hydrophilic. These surfactants have been used successfully up to 57 °C.

3.2.4. NEODOL ethoxylate 91-8

Barzegar et al. [68], explained that this nonionic surfactant is made of high-purity C9-C11 NEODOL alcohol with an average of 8 mol of ethylene oxide per mole of alcohol. The primary alcohol of NEODOL 91-8 contains C9, C10 and C11 with a molecular weight of 160, while Ethoxylated NEODOL 91-8 has a molecular weight of 524. Barzegar et al. [68] reported that this surfactant was more effective in enhancing oil recovery for tight fractured reservoirs. As mentioned above by researchers from Shell [67], these surfactants alone are not good candidates for temperature more than 60 °C. However, they added that EO units increase the stability of surfactants in high salinity environments with the presence of divalent ions. The molecular formula for NEODOL Ethoxylate 91-8 is shown in Fig. 20.

3.2.5. NEODOL 67 propoxylated sulfate (N67-7POS)

Hirasaki et al. [8] reported that this hydrophobe surfactant is a NEODOL alkoxylated that contain 7 propylene oxide units. This product has been developed and manufactured by Shell using C16-C17 high purity primary alcohols. Flaten et al. in Ref. [69] found out a solution to improve the thermal sensitivity of this compound, which is due to existence of sulfate group in using IOS in combination with this surfactant at high temperatures. In Ref. [59] researchers from Shell showed that the surfactant blend with IOS didn't indicate any phase separation from cloudy solutions or liquid crystalline dispersions. In addition, its performance was excellent in the presence of divalent ions however it did not perform well in high salinity environments. The molecular formula of NEODOL 67 Propoxylated Sulfate (N67-7POS) is shown in Fig. 21.

$$\mathbf{RO-(CH_2CH_2O)_n-H}$$

Fig. 20. Molecular formula for NEODOL Ethoxylate 91-8. R = Blend of C9, C10 and C11 alcohols; n = Integer from 1 to 20 an average number of 8.

$$\mathbf{RO-(OHCH_2CH_2CH_2)_n-O-SO_3^-M^+}$$

Fig. 21. Molecular formula of NEODOL 67 propoxylated sulfate (N67-7POS). R = Blend of C16 and C17 alcohols; N= Integer from 1 to 20 with an average of 7; M+ = A monovalent cation such as ammonium, sodium, lithium or potassium.

3.2.6. Nonylphenol "N" ethoxylate

According to Dow chemical company [70], this nonionic family is the sub-category of alkylphenol ethoxylate. Sharma et al. (2013), who studied EOR application of NP-10 EO, NP-30 EO, NP-50 EO and NP-70 EO summarising that these compounds all have cloud points over 100 °C. They recommended that in harsh conditions of carbonate reservoir such as high temperatures up to 100 °C and high salinity up to 200,000, mixture of this surfactant with a cationic surfactant increases the recovery since this mixture has higher aqueous stability compared with the nonionic surfactant on its own. Furthermore, these researchers suggested that the main mechanism for oil recovery by this surfactant is wettability alteration and increasing the number of EO units in Nonylphenol "N" Ethoxylate structure, adversely affects the surfactant performance by reducing its wettability alteration capability and increasing the IFT of the surfactant. The study showed Nonylphenol "N" Ethoxylate is able to recover up to 80% of OOIP during spontaneous imbibition. The molecular structure of a Nonyl Phenol "N" Ethoxylate is shown in Fig. 22.

3.2.7. Polyethoxylated alkyl phenols

Shupe [31] wrote that this nonionic surfactant is effective for surfactant flooding in formations containing high salinity water or hard water. However Shupe believed, one of the disadvantages of this family of surfactant is their low cloud point which make them insoluble at temperatures in the range of 37 °C–51 °C. The molecular structure of a Poly Ethoxylated Alkyl Phenol is shown in Fig. 23.

3.2.8. Poly (Ethylene/Propylene) gylcol ether

Glycol ethers, depending on whether they are made from ethylene oxide or propylene oxide, are labelled as either "e-series" or "p-series" glycol ethers. De and Bernhard [73] explained that this nonionic surfactant family are surface active agents to increase the capillary displacement efficiency of an aqueous flooding medium. Levitt et al. [20] claimed these surfactants to be thermally stable because of having high cloud points and majority of them are stable in aqueous solutions as well. Furthermore, this research showed the hydrophilic structure of this group makes them stable even at high salinity environments. This group is biodegradable and only a few of them are

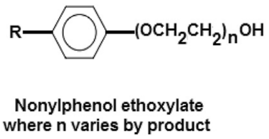


Fig. 22. Molecular structure of a Nonyl phenol "N" Ethoxylate, R = $C_9H_{19}C_6H_4$, 1 <n < 100, courtesy of Bathe & Montgomery [71].

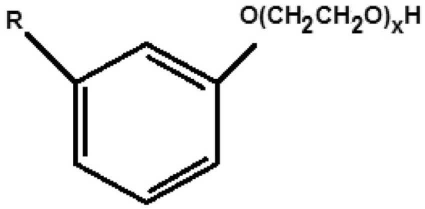


Fig. 23. Molecular structure of a poly ethoxylated alkyl phenol, courtesy of Cristobal, Tan, Metivier, Lu, & Lambert, [72].

considered toxic. Ethylene glycol butyl ether (EGBE), which is the most popular co-solvent in EOR studies, is a member of this group and has been used in a great deal of researches to increase surfactant solubility under high salinity conditions to overcome the salting out effect. The molecular structure of Propylene Glycol Ether is shown in Fig. 24.

3.2.9. *Secondary Alcohol "N" ethoxylate/propoxylate*

According to Sharma et al. [42], these nonionic surfactants with high solubility are good candidates for oil recovery. Their research showed that mixture of this surfactant and a cationic surfactant had a high aqueous stability in harsh conditions such as high temperature up to 100 °C and high salinity up to 200,000 ppm. Therefore, this blend is suitable for carbonate reservoirs. Mohan [75] also reported that having cloud points over 100 °C, these surfactants' performance is stable even in high salinity formations above 35000 ppm and in the presence of divalent ions. Furthermore, various studies indicated that the secondary flooding with this group of surfactant could recover around 80% of OOIP which is normally 60% for water flooding. The outcome of Mohan's study claimed wettability alteration as the main mechanism of recovery while using Secondary Alcohol "N" Ethoxylate/Propoxylate [75]. There is not much data available regarding the temperature boundaries for this group of surfactant. However, one study on the thermal degradation of alcohol ethoxylate found that these surfactants are stable up to 300 °C in an inert nitrogen atmosphere [76]. The molecular structure of a Secondary Alcohol "N" Ethoxylate is shown in Fig. 25.

3.2.10. *Synperonic® PE/F68*

Dang et al. [55] used this nonionic surfactant successfully in ASP flooding with the polymer (alcoflood 254S) in conventional reservoirs. The results demonstrated that this surfactant can reduce the viscosity with the higher the concentration of the surfactant the higher the reduction in viscosity. Consequently, Dang et al. (2012) reported that this surfactant is usually used in combination with Docusate Sodium ($C_{20}H_{37}NaO_7$ S) which is very effective for EOR in small and thin reservoirs. However, the simulation conducted in this study indicated that this mixture is not effective for fractured or low permeability reservoirs. The optimum salinity for this mixture is 3% salt concentration and the mixture is thermally stable even at the high temperature above 100 °C. The molecular formula of Synperonic® PE/F68 is shown in Figs. 26 and 27.

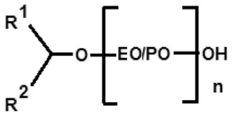


Fig. 25. Molecular structure of a secondary alcohol "N" Ethoxylate, modified after [77].

$$HO\text{-}(C_2H_4O)m\text{-}(C_3H_6O)n\text{-}H$$

Fig. 26. Molecular formula of Synperonic® PE/F68. N= Integer from 1 to 20 and preferably from 2 to 8; M+ = A monovalent cation such as ammonium, sodium, lithium or potassium.

3.2.11. *Tridecyl Alcohol 30 Ethoxylate(TDA 30 EO)*

According to Sharma et al. [42], this nonionic surfactant performs very similar to alkylphenol ethoxylate family. Therefore, the results of the application of this surfactant in EOR was almost identical with alkylphenol ethoxylate. These researchers reported that its application in carbonate reservoir in high temperatures up to 100 °C and high salinity up to 200,000 ppm resulted in good recovery and once gain wettability alteration was detected as the main mechanism for oil recovery. Injection of TDA 30 EO was able to recover up to 80% of OOIP during spontaneous imbibition. According to a chemical database written by Arokor [79], increasing the number of EO units increases the hydrophilicity of the surfactant molecules and makes it more soluble in water. The chemical formula of Tridecyl Alcohol 30 Ethoxylate and Tridecyl Alcohol "N" Ethoxylate is shown in Fig. 28.

3.2.12. *Triphenylmethane (TPM)*

Siggel et al. [80], suggested that this nonionic surfactant with a chemical formula of $C_{19}H_{16}$ to be classified as a viscoelastic/pseudo plastic surfactant especially at low concentration (<0.5 w/w). This study showed that the surfactant has acceptable sandstone and clay injectivity and adsorption values. Although TPM (Fig. 29) is insoluble in water, it has good stability in harsh conditions of high salinity (up to 18.6% TDS), in coexistence of divalent ions and in high temperatures (>70 °C [80].

3.2.13. *Tergitol surfactants*

Nanoemulsions have been in a central theme of surfactant EOR in recent years due to its unique characteristics. The physicochemical properties of nonoemulstions shows great potential to decrease residual oil saturation after water flooding. Ajay Mandal, etc., characterized the physicochemical properties of nanoemulsions deployed by using Tergitol 15-S-5, Tergitol 15-S-9, and Tergitol 15-S-12. Their experimental results showed that 30% of OOIP was recovered after water flooding by injecting the nanoemulsions [82].

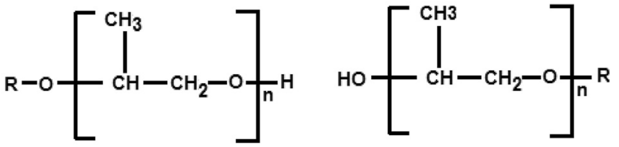
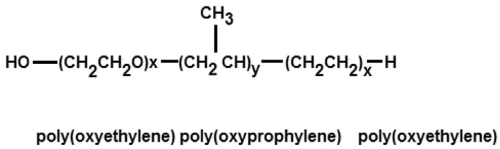


Fig. 24. Molecular structure of Propylene Glycol Ether, n = 1, 2, 3 modified after [74].



$$HO—(CH_2CH_2O)x—(CH_2\overset{CH_3}{CH})_y—(CH_2CH_2)_x—H$$

Fig. 27. Molecular structure of a Synperonic® PE/F68, modified after Berrill, Davies, Lewis, & Meakin [78].

$C_{13}H_{27}(OCH_2CH_2)_{30}OH$

(a)

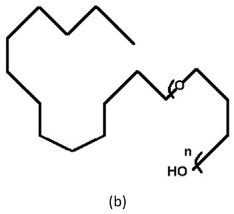


Fig. 28. (a)- Chemical formula of Tridecyl Alcohol 30 Ethoxylate, (b)- Molecular Structure of a Tridecyl Alcohol "N" Ethoxylate, n = 30, Courtesy of AroKorHoldings [79].

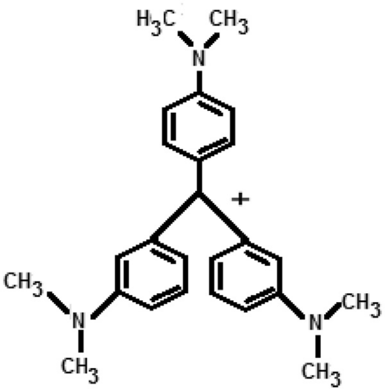
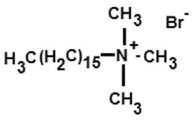


Fig. 29. Molecular structure of a Triphenylmethane, Modified after Bhasikuttan & Mohanty [81].

3.3. Cationic surfactants

3.3.1. Cetyl Trimethyl Ammonium Bromide (CTAB)

The other names of this compound are cetrimonium bromide, palmityl trimethyl ammonium bromide, Hexadecyl trimethyl ammonium bromide. Vatanparast et al. [83], conducted an investigation on phase behaviour of CTAB which showed this amine-based cationic surfactant to be suitable for EOR process in carbonate reservoir and performs well in combination with nano silica particles. Studying the relationship between temperature and IFT revealed, increasing the temperature leads to a reduction in IFT, however when the minimum IFT point is reached, increasing the temperature further results in increasing the IFT. Observing constant high oil recovery despite high IFT value indicated that wettability alteration is the main mechanism of recovery. Sharma and Mohanty (2013) managed to synthesise this compound. Their studies indicated the CTAB solution in brine to be stable and clear up to 100 °Cand 60,000 ppm salinity. However, the solution was not aqueous stable at temperatures above 100 °C. These researchers also confirmed that despite its stability, CTAB (Fig. 30) was not able to reduce the IFT to ultra-low values or alter the wettability of the carbonate rock.



$\mathrm{H_3C(H_2C)_{15}{-}\overset{CH_3}{\underset{CH_3}{N^{+}}}{-}CH_3\quad Br^{-}}$

Fig. 30. Molecular structure of Cetyl Trimethyl Ammonium Bromide, Modified After Milne [84].

3.3.2. Coco Alkyl Trimethyl Ammonium Chloride

For the first time, Sharma et al. [42] patented this compound. This liquid cationic surfactant with a commercial name of Arquad C-50 is made of fatty acids of coconut oil and has a cloud point of over 100 °C. Mixing this surfactant with Nonyl Phenol 10 Ethoxylate increased the cloud point to even higher than 130 °C. The experiments conducted by Sharma et al. (2013) showed that Coco Alkyl Trimethyl Ammonium Chloride was more successful in sandstone reservoir compared to carbonate reservoir in reducing the IFT and altering the wettability. The molecular structure of Alkyl Trimethyl Ammonium Chloride is shown in Fig. 31.

3.3.3. Stearyl Trimethyl Ammonium Chloride

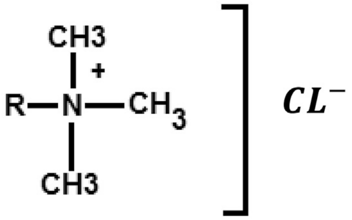
Stearyl Trimethyl Ammonium Chloride with the commercial name of "Arquad T-50" is also a cationic surfactant with cloud point over 100 °C. This compound also was patented by Sharma et al. [42] and has almost identical characteristics similar to Coco Alkyl Trimethyl Ammonium Chloride. Application of this surfactant in carbonate reservoirs is not recommended since it couldn't alter the wettability of carbonate rocks efficiently. The molecular structure of a Stearyl Trimethyl Ammonium Chloride Cortesy is shown in Fig. 32.

3.3.4. Dodecyl Trimethyl Ammonium bromide (DTAB)

DTAB also was investigated by Sharma and Mohanty [42]. Similar to CTAB this cationic surfactant has a cloud point of over 100 °C which can be increased to 130 °C when mixed with a nonionic surfactant. DTAB forms a clear and stable aqueous solution with injection brine of 60,000 ppm TDS at temperatures under 100 °C The study conducted by Sharma and Mohanty (2013) suggested DTAB is able to alter the wettability from oil-wet to intermediate water-wet in carbonate rock samples. However, it could not reduce the IFT to ultra-low values. The mixture of these nonionic and DTAB in dilute concentrations can recover up to 80% of the OOIP even in harsh conditions of carbonate reservoir. This value is 70% for injecting only DTAB (Fig. 33) on its own in low concentration (see Fig. 34).

3.3.5. Ethoxylated alkyl amine

According to Chen et al. [88], ethoxylated alkyl amine performs as a cationic surfactant when carrying low numbers of the EO group in its molecular structure. Adding a higher number of EO units to the surfactant makes it perform more like a nonionic surfactant. The existence of the EO and R units in this compound increases its cloud point to higher temperatures. The higher resistance of surfactants by increasing the number of the EO group happens as a result of making the surfactant more hydrophilic. However, for achieving the unusual temperatures over 120 °C, requires an additional hydrophilic group. One of the most common protonated groups is an amine. Chen et al. (2012)



$\left[\mathrm{R{-}\overset{CH3}{\underset{CH3}{N^{+}}}{-}CH_3}\right]\ CL^{-}$

Fig. 31. Molecular structure of Alkyl Trimethyl Ammonium Chloride, Modified after Kuper & Kuzma [85].

Fig. 32. Molecular structure of a Stearyl Trimethyl Ammonium Chloride Cortesy of Ash & Ash [86].

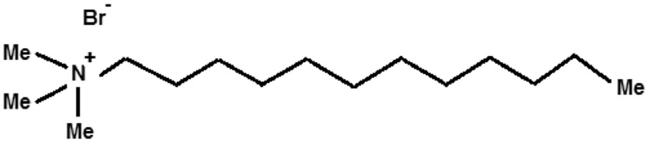


Fig. 33. Molecular structure of a dodecyl trimethyl ammonium, courtesy of ChemNet [87].

investigation on carbonate reservoir indicated that this surfactant can even be a good candidate for forming a stable CO_2/water foam at high temperatures and salinities (up to 180,000 ppm). The molecular structure of an Ethoxylated Alkyl Amine is shown in Fig. 34.

3.4. Surfactant mixtures

3.4.1. Combination "A"- mixture of alkyl ether sulfate and alkyl propoxy Ethoxy Sulfate

Mohan [75] reported that the mixture of these two surfactants is successful in lowering the IFT (as low as 10^{-3} dynes/cm) and altering the wettability from oil-wet to intermediate or slightly water-wet in harsh conditions of low permeability (2–5 md) reservoir. Mohan [75] explained that it has performed well in high salinity solutions of up to 45,000 ppm TDS in the presence of divalent ions. 36,000 ppm TDS is estimated as an optimum operating condition. The presence of sulfate groups increases the sensitivity of the surfactant to high temperatures. Mohan [75] indicated that this mixture is successful at temperatures up to 52 °C and is able to result in the additional recovery of 28% of the residual oil in place. Furthermore, Mohan tested another mixture which he referred to as combination "B". Further details about this mixture are presented below.

3.4.2. Combination "B"- mixture of alkyl propoxy sulfate and alkyl ethoxy sulfonates

The second mixture, "B", which is slightly different from mixture "A" has also been tested by Mohan [75] on samples representing a low permeability (2–5 md) carbonate reservoir. The results have shown that combination "B" emulsion is effective even in high salinities of up to 45,000 ppm TDS and in the presence of high divalent ions. The surfactant performance in lowering the IFT (down to 10^{-3} dynes/cm) and changing the wettability of carbonate rocks from oil-wet to intermediate or to slightly water-wet, is quite similar to mixture "A". Similar to mixture "A" the optimum salinity for this surfactant is also 36,000 ppm TDS, however the tertiary recovery using this blend has resulted in extra 14% oil recovery which is almost half of the recovery using mixture "A". The study suggested further investigation on the types of rocks as the lower recovery with mixture B could be related to the mineralogy of the specific type of rock samples used for the test and results could be different for other types of rocks.

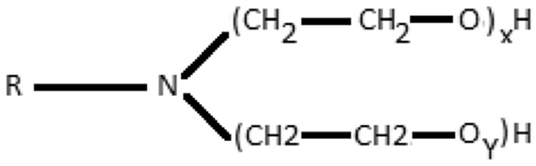


Fig. 34. Molecular structure of an ethoxylated alkyl amine, modified after Welton, Todd, & McMechan [89].

3.5. Bio surfactant

Bio-based surfactants have fascinated scientists due to their renewable resources and outstanding surface properties [90]. Sen [91] stated that microbial enhanced oil recovery was initiated in 1947. Sen [91] explained that the Biotechnological recovery process consists of injecting carefully chosen groups of natural bacteria into the reservoir to improve oil recovery through specific metabolic events. Sen in his article specifies that bacteria such as Bacillus sp, RLichenysinhamnolipid Acinetobacter, Emulsan, Alasan, Pseudomonas, Rhamnolipid, Rhodococcus, Viscosin and Trehaloselipids are among the most applied bio surfactants in the EOR process. Sen classified the reasons for slow employment of bio surfactants in EOR process as unpredictability in situ performance, low ultimate oil recovery factor, uncertainty about meeting the engineering design standards by microbial processes and a general hesitation about processes involving live bacteria.

Torres et al. [92], investigated the difference in performance of natural surfactants (one produced by a bacteria and two of vegetal origin) to synthetics surfactants (cationic, anionic, nonionic and zwitterionic) for its potential use in enhanced oil recovery EOR application. Torres eat al [92], concluded natural surfactant rhamnolipid which is created by Pseudomonas and guar gum exhibited similar and sometimes better, surface tensions, foaming capabilities, resistance to high salinity up to 46,800 mg/L, and resistance to high temperatures up to 70 °C compared to the synthetic surfactants normally used in EOR processes. An investigation by Daoshan et al. [93] on using biosurfactant-rhamnolipid-fermentation liquor (RH) as a sacrificial agent showed that loss of ORS due to static adsorption can be reduced by 25–30% when RH is mixed with ORS or pre-adsorbed on sandstone. The core-flooding experiments showed that enhanced oil recovery with the formulation of ASP of 0.2 wt% RH and 0.15 wt% ORS is 7% more than that with the formulation of ASP of only 0.15 wt% ORS, and is equal to that with the formulation of ASP of 0.3 wt% ORS. Result of Daoshan et al. [93] research revealed that using RH is able to reduce the cost of ASP flooding. Injecting formulation of ASP of 0.2 wt% RH and 0.15 wt% ORS in a pilot scale resulted in 16.6%(OOIP) enhanced oil recovery in the entire area of the experiment.

3.6. Zwitterionic surfactant

This particular type of surfactant usually refers to the amphiphilic organic compounds that holds both hydrophobic groups in their tail and hydrophilic groups in their heads. Only recently this type of surfactant gained attention in the oil and gas industry. To the knowledge of writers there has not been significant research on the application of zwitterionic surfactants in EOR. One of the highlighted studies in this area took place by

Zhang et al., [90]. These researchers created a novel zwitterionic surfactant derived from castor oil. When dispersed in water the surfactant could reduce the interfacial tension between crude oil and water to ultra-low value as 5.4 × 10−3 mN/m at low concentration of 0.010 g/L in the absence of any alkali. Zhang et al. [90], showed that this bio-based surfactant has strong electrolyte tolerance, temperature resistance and thermo stability, better wetting and foaming performance which makes it a potential oil recovery enhancer.

4. Conclusions

A comprehensive review of the existing surfactants and surfactant mixtures and their application for EOR processes has been presented. Below are the main conclusion which can be drawn from this review:

(1) Surfactants are classified as anionic, cationic, nonionic, bio surfactant and zwitterionic surfactants.
(2) Majority of cationic surfactants form stable solutions in brine.
(3) Nonionic surfactants are effective for surfactant flooding in formations containing high salinity water or hard water.
(4) For carbonate reservoirs, cationic surfactants or mixtures of them with nonionic surfactants are the most effective EOR agent. They increase the production mainly through wettability alteration.
(5) In contrast, anionic surfactants are not good EOR agents for carbonate reservoirs and their combination with the cationic type surfactant reduces the production.
(6) Anionic surfactants are the most effective candidate for sandstone reservoir either on their own or in the mixture with other anionic surfactants.
(7) A problem with stability and effectiveness of surfactant solutions rises when they are used in specific temperature conditions in the range of 70 °C to 120 C and above, high pressures (e.g. 4000 psi), and high concentrations of divalent metals such as calcium, magnesium, etc. (e.g. up to 3000 ppm or more) and high salt content (e.g. 180,000 ppm or more).
(8) Solving the problem of emulsion stability and viscosity in reservoir is possible through choosing suitable chemical units and their numbers plus tuning the pH level. Stability is assessed by measuring zeta potential. The higher this magnitude shows higher stability for the emulsion. For EOR process slightly alkali pH is recommended.
(9) The type and number of the chemical units in a surfactant formula affects the ability of the surfactant in reducing the IFT, altering the wettability, decreasing/increasing the viscosity, thermal stability and its resistance in high salinity and hardness conditions.
(10) Using ethylene oxide propylene oxide units or branched surfactants eliminate the need to use co-solvent to reach low IFT and viscosity.
(11) Using of Ethoxy unit increases the tolerance of the surfactant in the existence of divalent ions as well as the surfactant solubility in high salinity environments.
(12) Sulfonate group increases the thermal stability of surfactant and sulfate on the other hand decreases its thermal stability.
(13) Carboxylate surfactants displayed good performance and stability at high temperatures, high salinity with existence of divalent cations.

Type of surfactant	Cationic	Anionic	Nonionic	Zeitterionic
Advantages	- Form stable solutions in brine - Cationic surfactants or mixtures of them with nonionic surfactants are the most effective EOR agent for carbonate reservoirs	- Effective candidate for sandstone reservoir	- Effective for surfactant flooding in formations containing high salinity water or hard water.	New generation of surfactants, has strong electrolyte tolerance, temperature resistance and thermo stability, better wetting and foaming performance
Dominant Mechanism	Reducing IFT and Wettability Alteration	Reducing IFT	Reducing IFT	Reducing IFT and Wettability Alteration

References

[1] G. Hirasaki, C.A. Miller, M. Puerto, Recent Advances in Surfactant EOR, 2011.

[2] J.J. Sheng, Status of surfactant EOR technology, Petroleum 1 (2) (2015) 97–105.

[3] W. Karnanda, M.S. Benzagouta, A. AlQuraishi, M.M. Amro, Effect of temperature, pressure, salinity, and surfactant concentration on IFT for surfactant flooding optimization, Arab. J. Geosci. 6 (9) (2013) 3535–3544.

[4] Z. Ye, F. Zhang, L. Han, P. Luo, J. Yang, H. Chen, The effect of temperature on the interfacial tension between crude oil and gemini surfactant solution, Colloids Surfaces A Physicochem. Eng. Aspects 322 (1) (2008) 138–141.

[5] P.C. Hiemenz, R. Rajagopalan, Principles of Colloid and Surface Chemistry, third ed., Taylor & Francis, New York, 1997. Revised and Expanded.

[6] S.G. Udeagbara, Effect of Temperature and Impurities on Surface Tension of Crude Oil, reprint), Universal Publishers, USA, 2010.

[7] D.B. Troy, J.P. Remington, P. Beringer, Remington: the Science and Practice of Pharmacy, illustrated, Lippincott Williams & Wilkins, USA, 2006.

[8] G. Hirasaki, C.A. Miller, M. Puerto, Recent advances in surfactant EOR, SPE J. 16 (04) (2011).

[9] A. Bera, K. Ojha, T. Kumar, A. Mandal, Water solubilization capacity, interfacial compositions and thermodynamic parameters of anionic and cationic microemulsions, Colloids Surfaces A Physicochem. Eng. Aspects 404 (2012) 70–77.

[10] A. Bera, T. Kumar, K. Ojha, A. Mandal, Screening of microemulsion properties for application in enhanced oil recovery, Fuel 121 (2014) 198–207.

[11] A. Bera, K. Ojha, A. Mandal, T. Kumar, Interfacial tension and phase behavior of surfactant-brine–oil system, Colloids Surfaces A Physicochem. Eng. Aspects 383 (1–3) (2011) 114–119.

[12] S.I. Chou, D.O. Shah, The optimal salinity concept for oil displacement by oil-external microemulsions and graded salinity slugs, J. Can. Petr. Technol. 20 (03) (1981).

[13] O.G. Apaydin, A.R. Kovscek, O.G. Apaydin, A.R. Kovscek, Surfactant concentration and end effects on foam flow in porous media, Transp. Porous Media 43 (3) (2001) 511–536.

[14] S.J. Salter, The influence of type and amount of alcohol on surfactant-oil-brine phase behavior and properties, in: SPE Annual Fall Technical Conference and Exhibition., Colorado Society of Petroleum Engineers, Denver, 1977. SPE-6843-MS.

[15] R.L. Reed, R.N. Healy, Some physicochemical aspects of microemulsion flooding: a review, Improv. Oil Recovery by Surfactant Polym. Flooding (1977) 383–437.

[16] M. Abe, D. Schechter, R.S. Schechter, W.H. Wade, U. Weerasooriya, S. Yiv, Microemulsion formation with branched tail polyoxyethylene sulfonate surfactants, J. Colloid Interface Sci. 114 (2) (1986) 342–356.

[17] K.R. Wormuth, S. Zushma, Phase behavior of branched surfactants in oil and water, Langmuir 7 (10) (1991) 2048–2053.

[18] EPA, Ethylene Oxide. Ethylene Oxide, United States Environmental Agency, USA, 2013.

[19] J. Wu, Y. Xu, T. Dabros, H. Hamza, Effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance, Colloids Surfaces A Physicochem. Eng. Aspects 252 (1) (2005) 79–85.

[20] D. Levitt, S. Dufour, G.A. Pope, D.C. Morel, P.R. Gauer, Design of an ASP flood in a high-temperature, high-salinity, low-permeability carbonate, in: International Petroleum Technology Bangkok, Thailand: International Petroleum Technology Conference, 2012.

[21] P. Kathel, K.K. Mohanty, EOR in Tight Oil Reservoirs through Wettability Alteration. SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers, New Orleans, Louisiana, USA, 2013.

[22] L. Co, Z. Zhang, Q. Ma, G. Watts, L. Zhao, P.J. Shuler, et al., Evaluation of functionalized polymeric surfactants for EOR applications in the Illinois Basin, J. Petroleum Sci. Eng. 134 (2015) 167–175.

[23] E.J. Behrens, Investigation of Loss of Surfactants during Enhanced Oil Recovery Applications - Adsorption of Surfactants onto Clay Materials [Department of Chemical Engineering], Norwegian University of Technology and Science: Norwegian University of Technology and Science, 2013.

[24] K.-O. Choi, N.P. Aditya, S. Ko, Effect of aqueous pH and electrolyte concentration on structure, stability and flow behavior of non-ionic surfactant based solid lipid nanoparticles, Food Chem. 147 (2014) 239–244.

[25] R.C. Nelson, Further Studies on Phase Relations in Chemical Flooding, 1981, pp. 73–104.

[26] S.P. Gupta, Dispersive mixing effects on the Sloss field micellar system, Soc. Petroleum Eng. J. 22 (04) (1982) 481–492.

[27] C. Glover, M. Puerto, J. Maerker, E. Sandvik, Surfactant phase behavior and retention in porous media, Soc. Petroleum Eng. J. 19 (03) (1979) 183–193.

[28] J. Zhang, Q.P. Nguyen, A. Flaaten, G.A. Pope, Mechanisms of enhanced natural imbibition with novel chemicals, SPE Reserv. Eval. Eng. 12 (06) (2009) 912–920.

[29] Flaaten A, Nguyen QP, Pope GA, Zhang J. A systematic laboratory approach to low-cost, high-performance chemical flooding. Conference a Systematic Laboratory Approach to Low-cost, High-performance Chemical Flooding. Society of Petroleum Engineers.

[30] K. Hara, H. Kuwabara, O. Kajimoto, K. Bhattacharyya, Effect of pressure on the critical micelle concentration of neutral surfactant using fluorescence probe method, J. Photochem. Photobiol. A Chem. 124 (3) (1999) 159–162.

[31] Shupe RD. Surfactant oil recovery process usable in high temperature formations containing high salinity water. Google Patents; 1978.

[32] Sharma MM, Gao B. Salt-tolerant anionic surfactant compositions for enhanced oil recovery (eor) applications. USA: Google Patents; 2014.

[33] J. Lu, Development of Novel Surfactants and Surfactant Methods for Chemical Enhanced Oil Recovery, Doctor of Philosophy, The University of Texas at Austin, Austin, Texas, USA, 2014.

[34] M. Showell (Ed.), Powdered Detergents. Illustrated, Taylor & Francis, New York, USA, 1997.

[35] OilChemTechnologies, ANIONIC SURFACTANTS. Oil Chem Technology, 2010. Texas, USA.

[36] M. Oya, Y. Takemoto, Y. Ishikawa, Large decrease in acute aquatic toxicity of linear alkylbenzene sulfonate in hard water and seawater by adding adsorbent, J. Oleo Sci. 57 (1) (2008) 15–21.

[37] A.L.M.L. Pena, Experimental Evaluation of Linear Alkylbenzene Sulphonates for Enhanced Oil Recovery, Instituto Superior Técnico, 2015.

[38] Procter&Gamble. PG, Linear Alkybenzene Sulfonate (LAS), Glossary of Procter & Gamble. USA: P&G, 2014.

[39] SigmaAldrich, Alkyl Sulfates, 2015 ed., Sigma-Aldrich Co. LLC, USA, 2015.

[40] Procter&Gamble, PG. Alkyl(or Alcohol) Ethoxy Sulphate (AES), Glossory of P&G. USA: Procter & Gamble, 2014.

[41] Andjelic S, Erneta M, Fevola MJ, Sun FC. Polyglyceryl compounds and compositions. USA: Google Patents; 2012.

[42] G. Sharma, K. Mohanty, Wettability Alteration in High-temperature and High-salinity Carbonate Reservoirs, 2013.

[43] P. Esmaeilzadeh, N. Hosseinpour, A. Bahramian, Z. Fakhroueian, S. Arya, Effect of ZrO2 nanoparticles on the interfacial behavior of surfactant solutions at air–water and n-heptane–water interfaces, Fluid Phase Equilibria 361 (0) (2014) 289–295.

[44] gbiosciences. Sodium Dodecyl Sulfate. G-Biosciences Research Product. USA2014.

[45] P.S. CIEC, Surfactants. The Essential Chemical Industry, UK: University of York, 2013.

[46] Szlendak SM, Nguyen NM, Nguyen QP., Szlendak SM, Nguyen NM, Nguyen QP. Laboratory investigation of low-tension-gas flooding for improved oil recovery in tight formations. SPE vol. 159841; 2013.

[47] D. Levitt, A. Jackson, C. Heinson, L.N. Britton, T. Malik, V. Dwarakanath, et al., Identification and evaluation of high-performance EOR surfactants, in: SPE/DOE Symposium on Improved Oil Recovey, Society of Petroleum Engineers, Tulsa, Oklahoma, USA, 2006.

[48] M. Srivastava, J. Zhang, Q.P. Nguyen, G.A. Pope, A systematic study of alkali surfactant gas injection as an enhanced oil recovery technique, in: SPE Annual Technical Conference and Exhibition, USA Society of Petroleum Engineers, New Orleans, Louisiana, 2009.

[49] D. Levitt, A. Jackson, C. Heinson, L.N. Britton, T. Malik, V. Dwarakanath, et al., Identification and evaluation of high-performance EOR surfactants, SPE Reserv. Eval. Eng. 12 (02) (2009).

[50] S. Adkins, P.J. Liyanage, G.W.P. Pinnawala Arachchilage, T. Mudiyanselage, U. Weerasooriya, G.A. Pope, A New Process for Manufacturing and Stabilizing High-performance EOR Surfactants at Low Cost for High-temperature, High-salinity Oil Reservoirs. SPE Improved Oil Recovery, Society of Petroleum Engineers, Tulsa, Oklahoma, USA, 2010.

[51] ArokorHolding, Sodium Alpha-olefin Sulfonate. Chemicalland21, Arokor Holding Inc., Seoul, South Korea, 2013.

[52] M. Rieger, L.D. Rhein, Surfactants in Cosmetics, second ed., Taylor & Francis, New York, USA, 1997, 2, illustrated, revised.

[53] Wei Z, Navarrete RC. High temperature gellant for viscosity modification of low and high density brines. Google Patents; 2007.

[54] Kott KL, Scheibel JJ, Severson RG, Cripe TA, Burckett-St LJCT. Laundry detergents comprising modified alkylbenzene sulfonates. USA: Google Patents; 2006.

[55] C.T.Q. Dang, N.T.B. Nguyen, Z. Chen, H.X. Nguyen, W. Bae, T.H. Phung, A Comprehensive Evaluation of the Performances of Alkaline/Surfactant/Polymer Flooding in Conventional and Unconventional Reservoirs. SPE Asia Pacific Oil and Gas, Australia Society of Petroleum Engineers, Perth, 2012.

[56] Masaki M, Furukawa Y, Takenaka K. Process for preparation of glycidyl sulfonate derivative. USA: Google Patents; 1999.

[57] Weerasooriya UP, Pope GA, Nguyen QP. Method of manufacture and use of large hydrophobe ether sulfate surfactants in enhanced oil recovery (eor) applications. Google Patents; 2011.

[58] Mahanthappa MK, Sorenson GP, Coppage KLN. Dicarboxylate gemini surfactant that forms a lyotropic liquid crystal. USA: Google Patents; 2014.

[59] Shell, Enordet Surfactants for Enhanced oil Recovery, Shell Chemicals: Shell Company, 2015.

[60] C. Shi, G. Liao, W. Liu, Synthesis of internal olefin sulfonate and its application in oil recovery, Arab. J. Sci. Eng. 39 (1) (2014) 37–41.

[61] Loza R, Cooper AJ, Coffey GP. Enhanced oil recovery, anionic surfactants. USA: Google Patents; 1990.

[62] Y. Wu, S. Lglauer, Y. Tang, W.A. Goddard, Branched alkyl alcohol propoxylated sulfate surfactants for improved oil recovery, Tenside Surf. Det. 47 (3) (2010) 152–161.

[63] F. Friedli, Detergency of Specialty Surfactants, illustrated, Taylor & Francis, New York, 2001.

[64] Cripe TA. Process for making alkyl ethoxy carboxylates. Google Patents; 1993.

[65] M. Santa, G. Alvarez-Jürgenson, S. Busch, P. Birnbrich, C. Spindler, G. Brodt, Sustainable Surfactants in Enhanced Oil Recovery, in: SPE Enhanched Oil Recovery Conference, Malaysia Society of Petroleum Engineers, Kuala Lumpur, 2011.

[66] C. Leray, Glycosides of Fatty Alcohols, Cyberlipid Center, USA, 2014.

[67] Shell, NEODOL. Product Data, Shell Oil Company, 2015.

[68] B. Barzegar Alamdari, M. Kiani, H. Kazemi, Experimental and numerical simulation of surfactant-assisted oil recovery, in: Tight Fractured Carbonate Reservoir Cores. Eighteenth Oil Recovery Symposium, Society of Petroleum Engineers, Tulsa, Oklahoma, USA, 2012.

[69] A. Flaaten, Q.P. Nguyen, G.A. Pope, J. Zhang, A systematic laboratory approach to low-cost, high-performance chemical flooding, SPE Reserv. Eval. Eng. 12 (05) (2009).

[70] Company TDC, DOW™ Nonylphenol Ethoxylate Surfactants, The Dow Chemical Company, Midland, MI, United States of America, 2010.

[71] Bathe DP, Montgomery FJ. Compositions, methods and articles concerning pharmaceutical nitric oxide and controlled patient delivery systems thereof. USA: Google Patents; 2012.

[72] Cristobal G, Tan WE, Metivier P, Lu R, Lambert F. Combination of polymer and surfactant for improved laundry. USA: Google Patents; 2012.

[73] De GM, Bernhard K. Flooding process for recovering oil from subterranean oil-bearing strata. USA: Google Patents; 1941.

[74] S.A. Lewis, Propylene Glycol Ethers. OECD SIDS, American Chemistry Council, Italy, 2003.

[75] K. Mohan, Alkaline surfactant flooding for tight carbonate reservoirs, in: SPE Annual Technical Conference and Exhibition, Louisiana Society of Petroleum Engineers, New Orleans, 2009.

[76] S.K.C. Evetts, M. Levin, M. Stafford, High-temperature stability of alcohol ethoxylates, J. Am. Oil Chemists' Soc. 72 (no 7) (1995) 811–816, 106 p.

[77] Souter PF, Meek M, Tarbit DJ, Boutique JP. Enzyme stabilized liquid detergent composition. USA: Google Patents; 2013.

[78] Berrill SA, Davies RJ, Lewis DA, Meakin BJ. Solubilisation of drugs in HFA propellant by means of emulsions. USA: Google Patents; 2003.

[79] AroKorHoldings I, Tridecyl Alcohol Ethoxylate Chemicalland2013. http://www.chemicalland21.com/specialtychem/perchem/SODIUM%20ALPHA%20OLEFIN%20SULFONATE.htm.

[80] L. Siggel, M. Santa, M. Hansch, M. Nowak, M. Ranft, H. Weiss, et al., A new class of viscoelastic surfactants for enhanced oil recovery, in: SPE Imroved Oil Recovery Symposium, Society of Petroleum Engineers, Tulsa, Oklahoma, USA, 2012.

[81] A.C. Bhasikuttan, J. Mohanty, Targeting G-quadruplex structures with extrinsic fluorogenic dyes: promising fluorescence sensors, Chem. Commun. 51 (36) (2015) 7581–7597.

[82] A. Mandal, A. Bera, K. Ojha, T. Kumar, Characterization of Surfactant Stabilized Nanoemulsion and its Use in Enhanced Oil Recovery, Society of Petroleum Engineers, 2012.

[83] H. Vatanparast, A.H. Alizadeh, A. Bahramian, H. Bazdar, Wettability alteration of low-permeable carbonate reservoir rocks in presence of mixed ionic surfactants, Petroleum Sci. Technol. 29 (18) (2011) 1873–1884.

[84] G.W.A. Milne, Gardner's Commercially Important Chemicals: Synonyms, Trade Names, and Properties, Wiley, 2005.

[85] Kuper C, Kuzma M. Compositions of suspended carbon nanotubes, methods of making the same, and uses thereof. USA: Google Patents; 2003.

[86] M. Ash, I. Ash, Handbook of Green Chemicals: Synapse Information Resources, 2004.

[87] ChemNet. Dodecyl trimethyl ammonium bromide (DTAB), Global Chemical Market China, NetSun Co., Ltd., Zhejiang, 2013.

[88] Y. Chen, A.S. Elhag, B.M. Poon, L. Cui, K. Ma, S.Y. Liao, et al., Ethoxylated cationic surfactants for CO2 EOR, in: High Temperature, High Salinity Reservoirs. Eighteenth SPE Improved Oil Recovery Symposium Tulsa, Society of Petroleum Engineers, Oklahoma, USA, 2012.

[89] Welton T, Todd B, McMechan D. Methods for effecting controlled break in pH dependent foamed fracturing fluid. USA: Google Patents; 2007.

[90] Q.-Q. Zhang, B.-X. Cai, W.-J. Xu, H.-Z. Gang, J.-F. Liu, S.-Z. Yang, et al., Novel zwitterionic surfactant derived from castor oil and its performance evaluation for oil recovery, Colloids Surfaces A Physicochem. Eng. Aspects 483 (2015) 87–95.

[91] R. Sen, Biotechnology in petroleum recovery: the microbial EOR, Prog. Energy Combust. Sci. 34 (6) (2008) 714–724.

[92] L. Torres, A. Moctezuma, J.R. Avendaño, A. Muñoz, J. Gracida, Comparison of bio- and synthetic surfactants for EOR, J. Petroleum Sci. Eng. 76 (1–2) (2011) 6–11.

[93] L. Daoshan, L. Shouliang, L. Yi, W. Demin, The effect of biosurfactant on the interfacial tension and adsorption loss of surfactant in ASP flooding, Colloids Surfaces A Physicochem. Eng. Aspects 244 (1–3) (2004) 53–60.