

Novel Surfactants for Enhanced Oil Recovery



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Abstract After the primary and secondary methods of hydrocarbon production, the reservoir depletes and often relies on enhanced oil recovery techniques (EOR, a tertiary method) to reduce the residual oil saturation (S_{or}) to a minimum value. Amongst many methods, the chemical EOR (cEOR) technique of oil recovery is widely implemented. The cEOR technique aims to optimize mobility ratio and reduce interfacial tension (IFT) and the viscosity of in situ oil. A subclass of cEOR is surfactant flooding which uses the principle of IFT reduction to facilitate additional oil gain. This process incorporates the use of surfactants which promotes favorable wettability and forms in situ oil–water (o/w) emulsions driving the oil towards the producing well. This chapter provides insight into different classes and types of surfactants used in cEOR methods. The discussions on different surfactants are carried out broadly in terms of its effect on IFT, temperature stability, adsorption on rock matrix and effectiveness in saline environments.

Keywords Chemical enhanced oil recovery · Recovery mechanism · Surfactant types

1 Introduction

The primary mechanism to recover oil from a reservoir is dependent on the intrinsic pressure of a reservoir. After a certain production limit, the reservoir flow declines and further aid is necessary to maintain a prescribed level of flow rate. Hereafter,

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a secondary mechanism is adopted where the immiscible displacement of oil is achieved by waterflooding or the reservoir pressure is maintained by injecting gas [9]. Re-energizing the reservoir by external pressure maintenance mechanism helps to regain better production rates. However, after these efforts turn inadequate a tertiary method is implemented to recover the residual oil, mostly after a water-flood. Enhanced oil recovery (EOR) or tertiary techniques aim to reduce the residual oil saturation (trapped oil) and offer an additional incremental oil gain. A broader classification of different EOR techniques is listed in Fig. 1.

Chemical EOR (cEOR) is one of the most efficient tertiary recovery techniques which increases the recovery factor by improving both macroscopic (volumetric) as well as microscopic displacements. Yielding a favorable mobility ratio contributes to improving volumetric displacement. The objective of polymer EOR is to decrease the viscous fingering (Fig. 2) effect by reducing the mobility ratio between displacing and displaced fluid [38].

Pore-scale displacement is associated with micro displacement. Dominant capillary forces do not allow entire oil in contact with the injected fluid to be produced. Hence, a fraction of oil is inherently trapped by capillary forces. A dimensionless number known as capillary number (ratio of inertial by capillary force) is often used to characterize the efficiency of oil recovery from a pore volume. Capillary number (Ca) is expressed as:

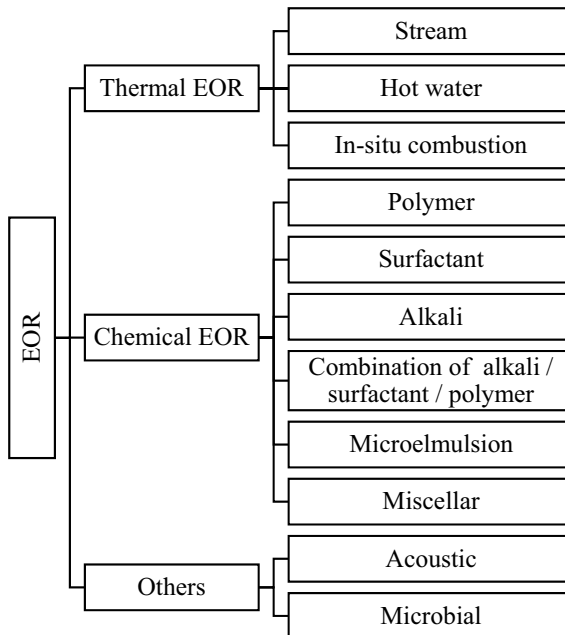


Fig. 1 Broad classification of EOR methods

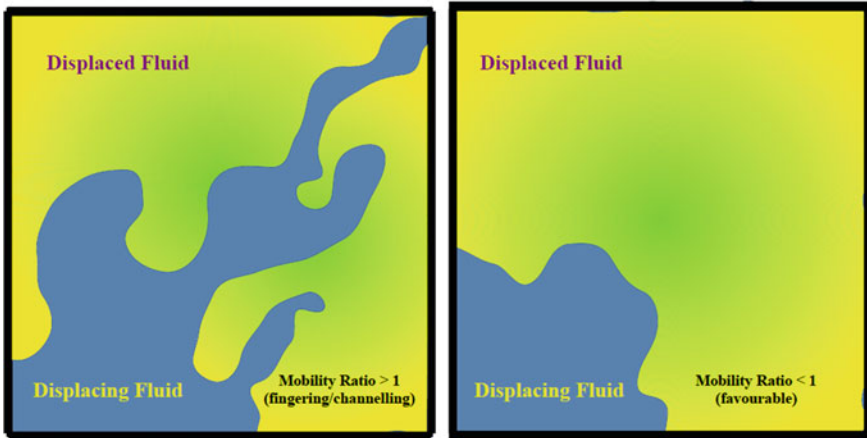


Fig. 2 Viscous fingering effect due to varied mobility ratio

$$Ca = \frac{\text{Viscous forces}}{\text{Surface or interfacial forces}} = \frac{\mu V}{\gamma \cos \theta} \tag{1}$$

where, μ is the viscosity of the injected aqueous phase, V is the velocity and γ is the oil/water interfacial tension (IFT). Ca can be increased by reducing the magnitude of interfacial tension between oil and water. Higher Ca minimizes the residual oil saturation trapped inside the pore volume. During water flooding operation Ca is typically in a range of 10^{-7} to 10^{-6} which results to a significant amount of residual oil saturation. An increase in Ca to 10^{-4} to 10^{-3} reduces the trapped oil by 90% [13]. Residual oil saturation ideally reaches a value of zero if Ca is increased to 10^{-2} which can be achieved by lowering of IFT between oil and aqueous phases, alteration of wettability and interfacial rheological properties [21, 42]. Both of these phenomena can be accomplished by the use of surfactants along with the displacing fluid (brine). Surface-active-agents or surfactants are fundamentally organic compounds that have a solvent loving and solvent fearing group known as hydrophilic and hydrophobic groups respectively in case the solvent is water [33]. The addition of surfactants brings down the IFT to lower values and weakens the capillary forces within the pore network [10]. Surfactant on mixing with aqueous solution tends to adsorb between the interface of oil and water and reduces the free energy of the given solution (Fig. 3). With the eventual increase in the concentration of surfactant, micelles are formed which are highly dynamic. Critical micelle concentration (CMC is the minimum concentration of surfactant required to initiate the formation of micelles; which is one of the most vital properties of a surfactant.

The solubility of a surfactant is a function of temperature. The minimum temperature beyond which micelles are formed is called a Krafft point which is usually dictated by the melting point of the hydrocarbon tail [29]. It is important to note that due to the immobile hydrocarbon tail below the Krafft point, the solubility of the surfactant is significantly less and bears no CMC. In that case, the solution

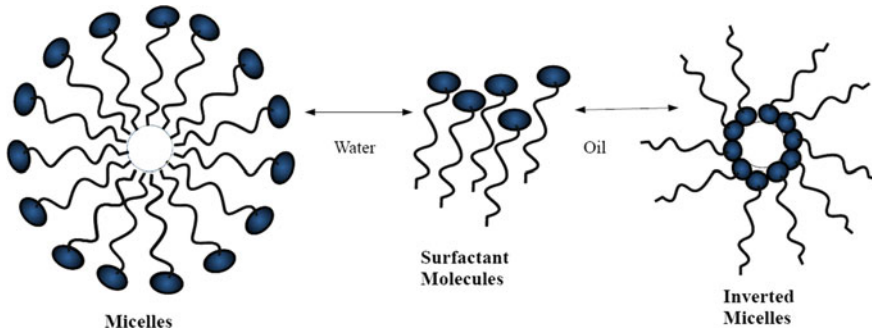


Fig. 3 Oil in water (o/w) emulsion (micelles) and water in oil (w/o) emulsion (inverted micelles)

appears cloudy and phase separation becomes unavoidable [22]. The mark of CMC also affects the physical properties of an oil–water solution with a surfactant, e.g.: trend of conductance of a surfactant solution turns non-linear beyond CMC [44]. Furthermore, surface tension decreases with an increase in surfactant concentration till CMC, past which its value remains constant [5]. Hydrophile-lipophile balance (HLB) is another parameter to profile surfactants. It specifies the inclination of a surfactant to form oil in water (o/w) or water in oil (w/o) emulsion. The value of HLB varies from 0 to 20, where 0 corresponds to absolute hydrophobic behavior, and 20 to complete hydrophilic molecule of surfactant. Furthermore, lipophilic surfactants are characterized by a low HLB value typically less than 9 whereas, a value greater than 11 signifies that the surfactant is hydrophilic [35].

1.1 General Overview on the Effect of Surfactant on IFT and Wettability Alteration

The natural existing oil reservoirs can be classified as oil-wet, water wet and mixed wet based on the contact angle measurements (typically measure for water droplet). On oil-wet conditions, this contact angle (of water) is greater than 90° , while a contact angle less than 90° exhibits water-wet conditions. In oil-wet reservoirs, the matrix retains the oil in micropores due to the presence of capillarity resulting in the trapping of oil. The water-wet reservoirs, on the other hand, get easily filled with water in microchannels which leaves the oil phase to occupy more permeable channels with larger pore throat size. Hence, the water wet reservoirs support spontaneous imbibition allowing easy flow of oil towards the producing well. Production is difficult to achieve from a reservoir bearing oil-wet conditions owing to which there lies a constant attempt to change its wettability to water-wet conditions. This process is known as wettability alteration.

The interfacial tension of the formed droplet during the liquid–liquid interaction at the time of surfactant injection serves as an important factor for the stability

of the emulsion. The value of the interfacial tension declines faster in the case of droplets in the size of microscale as compared to milliscale droplets. Smaller droplet sizes lead to a smaller diffusion boundary layer thickness, which reduces the time required for the surfactant molecule to diffuse into the depletion region away from the aggregated bulk. The surfactant in the outer phase catalyzes the reduction of the interfacial tension, but the decaying rate of the interfacial tension is independent of the phase to which surfactant is added for milliscale droplets. The stability of the emulsion is also deeply affected by the surface gradient of the fluid–fluid interface which infers the response of the interface deformation. It can also be linked to the probability of the droplet coalescence. Surfactants, when used in EOR techniques, lower the IFT between oil–water systems and mobilizes the oil to form oil pools or banks. It primarily helps to reduce the capillary forces and allows the oil to gain mobility and avoid retrapping. Mechanism of emulsion formation and its associated behavior with pore throat size are described in Figs. 4, 5 and 6.

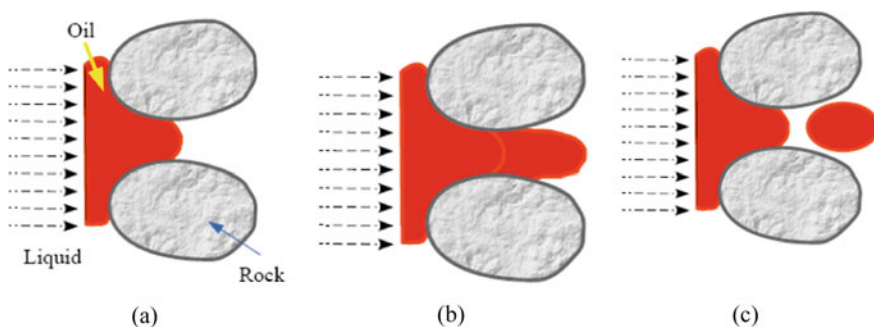


Fig. 4 Snapping off mechanism of emulsion formation: **a** residual oil trapped inside rock grains, **b** trapped oil elongates as it comes in contact with the surfactants present in the displacing fluid or injected fluid, **c** oil gets snapped off and forms emulsion. Adapted with permission from [46] as per open access policy. Copyright 2019 Society of Chemical Industry and John Wiley & Sons Ltd.

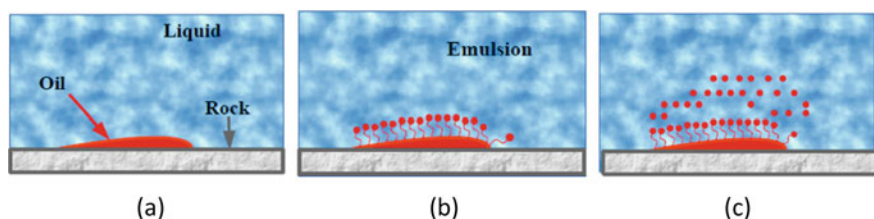


Fig. 5 Shear based emulsion formation: **a** oil film trapped as residual, **b** emulsion droplet formation by shearing action of liquid (displacing fluid) which has emulsifying properties due to the presence of surfactants, **c** oil–water emulsion formed due to shearing mechanism, gets dispersed in the liquid phase and additional emulsions being formed reducing the oil film. Adapted with permission from [46] as per open access policy. Copyright 2019 Society of Chemical Industry and John Wiley & Sons Ltd.

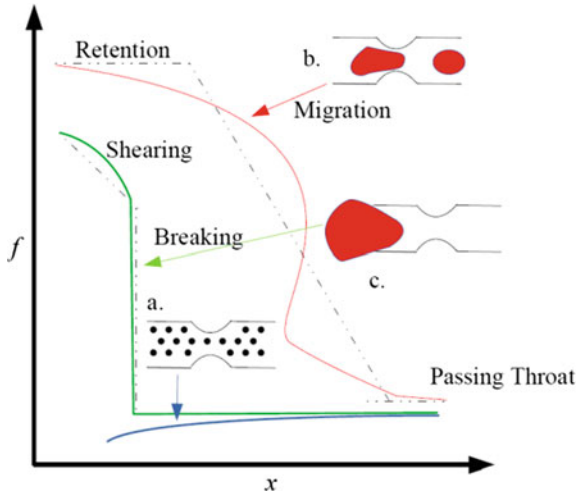


Fig. 6 The resistance factor 'f' for different droplet size emulsions: **a** the emulsion droplet size is far smaller than the throat diameter, **b** the emulsion droplet size is slightly larger than the throat diameter but smaller than the pore diameter, **c** the emulsion droplet size is significantly larger than the pore throat diameter. 'f' is the resistance factor and is defined as the ratio of the pressure difference between the inlet and outlet of a throat, and x is the length of pore throat. Adapted with permission from [46] as per open access policy. Copyright 2019 Society of Chemical Industry and John Wiley & Sons Ltd.

Crude oil having long hydrocarbon chains typically possess a negative charge which gets adsorbed on the surface of minerals bearing a positive charge. The interaction between the cationic monomer and the anionic groups leads to the formation of ion pairs which are non-soluble in aqueous and soluble in the oleic phase. This ion pair causes desorption at the oil, water and rock interface which facilitate easy entry of water eventually changing the surface to water-wet. Anionic surfactant cannot desorb the negatively charged groups from the reservoir rock surface. But they form water-wet bilayer between the surface of the rock and oil, which generate weak capillary forces through hydrophobic interaction and facilitate easy incursion of water and expulsion of oil.

2 Types of Surfactants and Their Role in EOR

The nature of the surfactant is characterized by the hydrophilic group which can be cationic, anionic, non-ionic, or amphoteric. These hydrophilic groups are positively and negatively charged in the case of cationic and anionic surfactants, respectively. Non-ionic surfactants do not ionize and are rather soluble in water through hydrogen bonding [45]. Amphoteric surfactants have a hydrophilic group that bears both negative and positive charges.

2.1 Cationic Surfactants

Cationic surfactants are those which comprise a positive hydrophilic head in combination with a halide group. Due to its positive charge, it is habitually attracted to negative charges. Hence, its application is limited. Clays being one of the most abundant and dominant compositions of reservoir rocks are negatively charged. Upon interaction with a cationic surfactant, it adsorbs these surfactants into its matrix exposing the hydrophobic part to the hydrocarbon fluid. Additionally, by the means of these cationic surfactants, a water-wet reservoir can turn into an oil-wet. Hence, cationic surfactants are very effective to alter reservoir rock wettability. However, the cationic surfactant has found wide applications in carbonate formation as they have relatively small adsorption in calcite minerals. Studies have found that oil recovery from limestone (a carbonate rock) is higher subjected to spontaneous imbibition (Fig. 7). It is generally observed that oil recovery is significantly less for anionic surfactants such as sodium dodecyl sulfate (SDS) from calcite rich cores. As compared to the family of C_n TABs (Fig. 4a), heavy-headed phosphonium surfactants (C_{10} TPPB, C_{12} TPPB) contribute to higher oil recovery. For C_n TAB, as the number of carbon atom increases, CMC and IFT decreases [19].

The wettability alteration due to surfactant is due to the interaction between rock type, a cationic surfactant, salinity, and crude oil composition. The presence of salt with a cationic surfactant like C_n TAB also largely affects the competence of wettability alteration after sometime when it reaches its limiting value of concentration, consequently increasing repulsive forces which accounts for higher contact angle of the droplet. On the contrary, the diffusion of surfactants into the aqueous phase is inhibited at higher salt concentrations owing to which it displays adverse effects on wettability [14, 17]. Furthermore, from a rheological standpoint, low-frequency oscillations show viscoelastic liquids behavior and viscoelastic solid behavior is displayed at higher frequencies [20]. Higher elastic properties imply extensional flow which is useful to sweep oil from trapped pores [2]. Some cationic surfactants like hexadecyl pyridinium chloride monohydrate [$C_{21}H_{38}ClN.H_2O$] (CPC) shows higher adsorption in carbonate formation (Fig. 8) especially those rich in silica and aluminum [24]. Nonetheless, due to the high capital expenditure during the synthesis process of cationic surfactants owing to the high-pressure hydrogenation process, their use is limited.

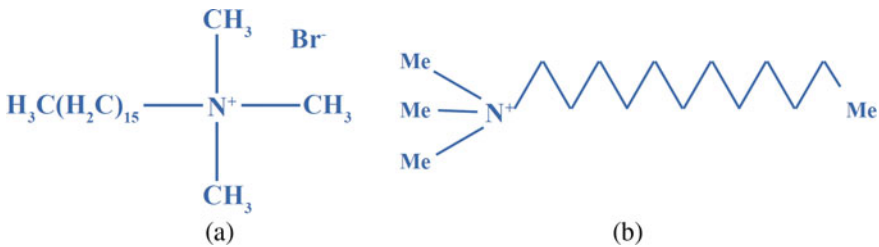


Fig. 7 **a** Structure of cetyl trimethyl ammonium bromide (CTAB), **b** structure of dodecyl trimethyl ammonium (DTAB)

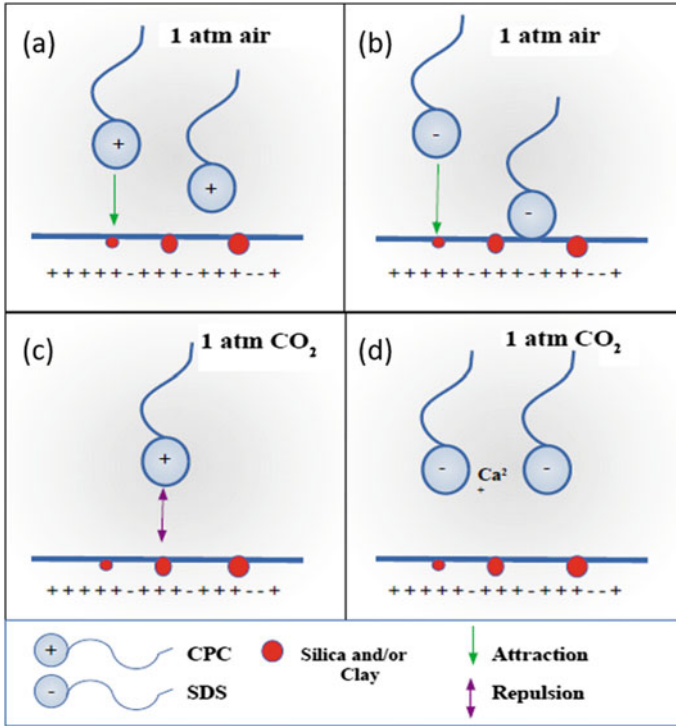


Fig. 8 Mechanisms for CPC/SDS adsorption on natural carbonates in the presence/absence of CO₂: **a** CPC adsorption on natural carbonates in DI water equilibrated with 1 atm air, **b** SDS adsorption on natural carbonates in DI water equilibrated with 1 atm air, **c** CPC adsorption on natural carbonates in DI water equilibrated with 1 atm CO₂, **d** SDS adsorption on natural carbonates in DI water equilibrated with 1 atm CO₂. (CPC: Hexadecylpyridinium chloride monohydrate [C₂₁H₃₈CINH₂₀]). Adapted with permission from [24]. Copyright 2013 Elsevier

2.2 Anionic Surfactant

Anionic surfactants are those which comprise of a negative charge on their hydrophilic end. The functional group end contains phosphate, carboxylate, sulfonate, etc. Anionic surfactants are widely used as they are easily available and undergo very low adsorption especially when implemented in sandstone reservoirs (negatively charged sandstone). They are efficiently used to reduce IFT and bears stability under high-temperature conditions [18]. Anionic surfactant dominates the market owing to its low cost of manufacture and highly potent detergency.

Alkyl aryl sulfonates (Fig. 9) were first introduced around the 1930s and soon captured the market. It is produced by the reaction between propylene tetramer and benzene. The higher member of this family of surfactants are hydrophobic and interact well with crude oil. Higher recovery can be attained when used with optimum salinity. On the contrary, these are non-biodegradable. One of the prime benefits

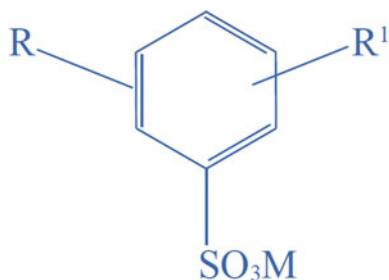


Fig. 9 Structure of alkyl aryl sulfonates

of alkyl aryl sulfonate surfactant is its ability to adapt as per reservoir conditions. Additionally, they are stable for a range of crude oils at different temperatures. However, at higher salt concentrations especially in the presence of divalent salts, this class of anionic surfactants is not stable [12].

Linear alkyl benzene sulfonate (Fig. 10) is a subclass of anionic alkyl aryl sulfonates. Alkyl chains with higher carbon number are not synthesized or used, as increasing the number of carbon atoms slows the biodegradability of the surfactant. The sulfonate group is essential for temperature resistance. Linear alkyl benzene sulfonate is toxic and becomes more poisonous with increasing salinity and hardness of water [30]. On the other hand, increasing the value of the carbon in the alkyl chain reduces the value of CMC [32].

This linear variant of surfactant significantly reduces the value of IFT especially with crudes with a carbon number from 7 to 10. Alcohol propoxy sulfate (APS) is the structure of anionic surfactant consisting of a hydrophobe tail that is a higher carbon branched alcohol along with 7 propylene oxide groups.

The alcohol propoxy sulfate (APS) (Fig. 11) is used alongside internal olefin sulfonate (IOS) to increase the hydrocarbon sweep up to 30% [43]. It is widely used in reservoirs with light oil and low temperature due to the high stability of foam

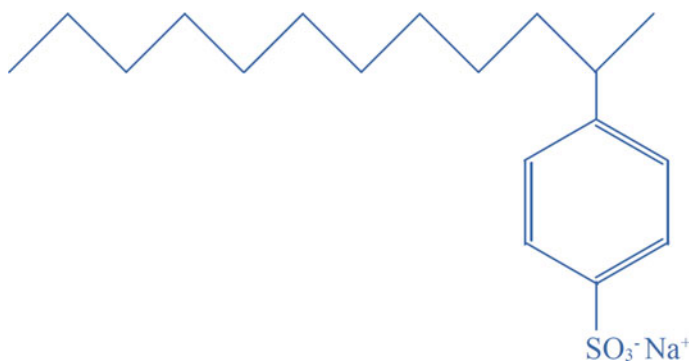


Fig. 10 Molecular structure of alkylbenzene sulfonate

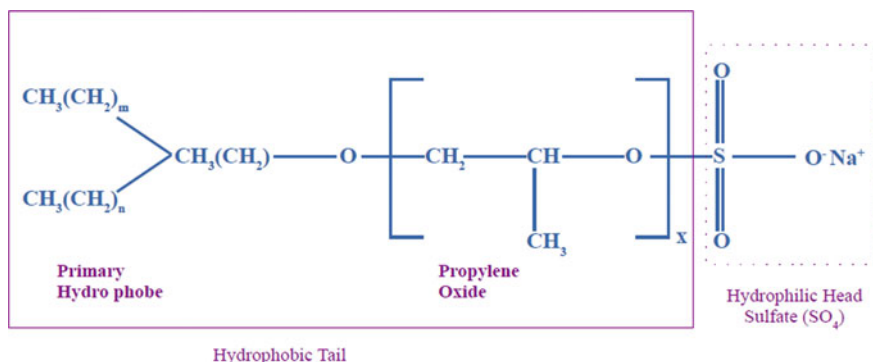


Fig. 11 Structure of alcohol propoxy sulfate

in an aqueous medium [23]. The surfactant is stable at high saline formations and its optimum salinity is at 4500 ppm, but the presence of a sulfate group makes it vulnerable to drastic temperature changes and high-temperature conditions. Alkyl ether sulfates are anionic surfactants that show high aqueous stability. However, the sulfate group makes it vulnerable to drastic temperature changes or high formation temperature and gets easily precipitated in high saline conditions. The addition of the ethoxy group to the initial structure increases the stability of the surfactant in high temperature and saline environment, still, its effectiveness declines at a temperature higher than 120 °C and salinity greater than 180,000 ppm [31]. N-ethoxy sulfonate gives an upper hand in terms of stability at higher reservoir temperatures due to its improvised design and does not precipitate in the presence of divalent ions like Ca^{2+} and Mg^{2+} [36]. Sodium Dodecyl Sulfate (SDS) (Fig. 12) is the most popular surfactant from the sulfate family group. This surfactant improves the EOR process alongside nanoparticles (NPs). The cloud point of SDS is over 100 °C [8]. Mixing NPs with SDS prevents the problem of NP adsorption on the reservoir rock.

Alpha-olefin sulfonate family of anionic surfactants are very efficient in reservoirs with high divalent ion concentration and has a high biodegradation rate. The most common of these surfactants are sodium C14-16 olefin sulfonate; C14-16 alkane hydroxy and C14-16 alkene sodium salts; sodium alpha-olefin sulfonate. Other advantages of alpha-olefin sulfonate include stability over a wide range of

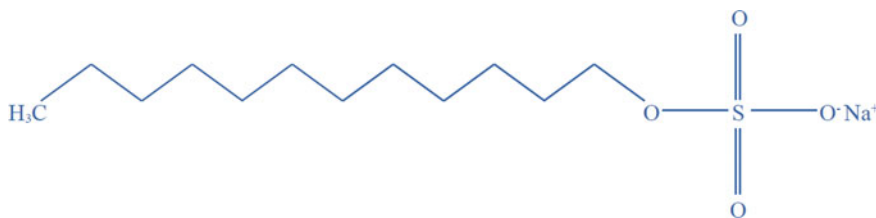


Fig. 12 Structure of sodium dodecyl sulfate (SDS)

pH, good foaming ability even in the case of hard water, and acid resistance, hence it is used often with polymeric fluids. Branched alkyl benzene sulfonate is another anionic surfactant in which the existence of the benzene group makes it long term stable against high reservoir temperature conditions but turns it non-biodegradable in nature. Alpha olefin sulfate is very similar to alpha-olefin sulfonate however it has thermal sensitivity due to the C–O–S bond [12].

Docusate sodium is a double tail anionic surfactant. It is used worldwide in ASP flooding of conventional reservoirs. Increasing the concentration of docusate sodium drastically increases the viscosity of the displacing fluid which makes it favorable to deploy for recovery in case of thin small laminated reservoirs [6]. Ethoxy or propoxy glycidyl sulfonates is an upgraded member from the family of sulfonates surfactant that is resistant to a high range of salinity variations. It is also used to form highly stable macroemulsion with high-temperature tolerance [12]. Alkyl ether sulfates, on the other hand, show excellent aqueous stability but the sulfate group present in it makes it sensitive to drastic temperatures. Moreover, it is not stable in high salinities. Internal olefin sulfonates (IOS) has two hydrophobic tails. The presence of sulfonate unit in this surfactant makes it stable for a long term in high-temperature reservoir conditions (up to 200 °C) [31]. The characteristic of aqueous stability and stable foaming at low concentration makes it widely used by researchers for core flooding operations. IOS has optimum salinity at 4500 ppm and enhances the recovery up to 30% on being introduced to sandstone for tertiary recovery operations. The only drawback is its instability in regions of high divalent ion concentration. Sulfonated, ethoxylated alcohol also known as alkyl phenol is designed for reservoirs with high salinity or divalent ion concentration [40]. Sodium petroleum sulfonate is a family of anionic surfactant and precipitates even in low salt concentration in water [7]. TDA-9PO-Sulfate (Tridecyl-9 propylene oxide sulfate) has a commercial name 'Petrostep S13-C', which is an anionic surfactant with a high tolerance level of salt [37]. Alkyl alcohol propoxylated sulfate is a very strong anionic surfactant that can reduce the interfacial tension even when employed at low concentrations. Carboxybetaine based anionic surfactant and amphoteric surfactant show the potential to replace all the existing surfactants as they are highly compatible with drastic reservoir conditions [16].

2.3 Nonionic Surfactants

Nonionic surfactants do not undergo ionization, rather hydrogen bonding and van der Waals forces primarily influence its solubility. The inferior dissolution of nonionic surfactant transpires due to elevated thermal energy and poor hydrogen bonding at higher temperatures, which consequently forms a turbid solution. The temperature where this type of surfactant develops turbidity is marked as a cloud point [45]. Fundamentally, the cloud point depends on factors like the number of ethylene oxide units, the concentration of the surfactant used and branched chains. Although nonionic surfactants bear high salinity tolerance, yet the magnitude of IFT reduction achieved

by its use is lower as compared to cationic and anionic surfactants [1]. Alkyl ethoxy carboxylates are the most common nonionic surfactants at normal pH, although they behave as anionic surfactant at alkaline pH conditions. The character of resistivity to high temperature and high salinity condition is due to the ethoxy group along with the carboxylate compound. The ethoxy unit present in the surfactant increases interaction energy (as a result of the hydrogen bond formation with water molecule) while the carboxylate group increases long term stability in the high-temperature conditions. Alkyl polyglycoside is a non-ionic surfactant used under high-temperature reservoirs even at a high concentration of divalent ions. Due to the structure of the glucose, it can work in high temperatures and be stable at a maximum salinity of 180,000 ppm [34]. Nonylphenol ethoxylate belongs to the family of alkyl phenol ethoxylate. The cloud point for this class of nonionic surfactants is over 100 °C. The surfactant is generally used as a co-surfactant along with the cationic surfactant in carbonate reservoirs that bears high temperature (up to 100 °C) and salinity conditions. The nonylphenol ethoxylate mainly acts on the wettability of reservoirs and can recover 80% of oil in place under the spontaneous imbibition process. Secondary alcohol ethoxylate/propxylate, another non-ionic surfactant is characterized by high solubility. It is used as a co-surfactant alongside cationic surfactant in carbonate reservoirs having extreme conditions. Moreover, in an inert atmosphere, the surfactant is stable up to temperatures as high as 300 °C [27]. Tridecyl alcohol ethoxylate known by the trade name TDA-30-EO is used as a co-surfactant in high temperature (approximately 100 °C) and salinity of 200,000 ppm [36]. The hydrophilicity of the reservoir can be increased by just adding more numbers of ethoxylate units which increases its solubility in water. Poly ethoxylated alkylphenols are used for EOR in high salinity reservoirs but its low cloud point makes it insoluble even at a moderate temperature range of 35–50 °C [40]. Poly glycol ether, a nonionic surfactant is classified as 'r series' and 'p series' based on the constituent chemical at the time of preparation, namely, ethylene oxide and propylene oxide respectively. They work in extremely high temperatures and have elevated cloud points. This surfactant family consists of completely biodegradable members.

Triphenylmethane also known as TMP Fig. 13, is a nonionic surfactant. Being insoluble in water, TPM shows excellent stability in high salinity (up to 18.6%) and high temperature (>70 °C) [41]. A secondary linear ethoxylated alcohol, known as Tergitol surfactant has foamability characteristics. Tergitol 15-S-12 shows the maximum stability in distilled water as well as in saline water. The surface excess value for the nonionic surfactant increases with the decrease of molecular cross-section of the polar head group. At a particular CMC, the micelle sizes of this surfactant increase with an increase in ethylene oxide number (EON). A higher EON value yields greater HLB value. As compared to water flooding, additional recovery of 26% is observed for Tergitol 15-S-12 [25].

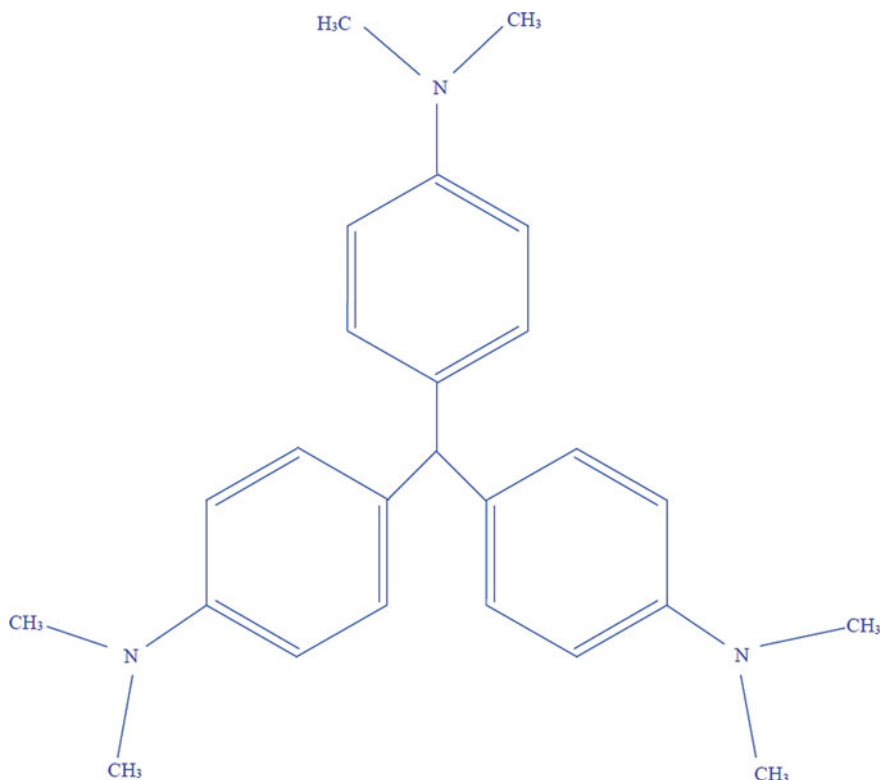


Fig. 13 Structure of triphenylmethane (TPM), a nonionic surfactant

2.4 Zwitterionic Surfactant

Zwitterionic or amphoteric surfactant (Fig. 14) is amphiphilic organic compounds that have both negative and positive charges in its hydrophilic head. The presence of dual charge engages its application in both sandstone and carbonate reservoirs. Moreover, due to its net neutral nature, it has a superior tolerance level in high saline environments. The most common surfactant in this family is made from castor oil that can achieve ultra-low interfacial tension value of 5.4×10^{-3} mN/m at very low concentrations in the absence of alkaline mediator. Zwitterionic surfactants have strong thermal stability, electrolytic tolerance, foam capability, and wetting performance which makes it an important chemical for EOR development in the future. It undergoes interaction with anionic surfactants like SDS as well as cationic ones like DTAB [26]. Like any other surfactant, increasing the concentration of the zwitterionic surfactant decreases the value of the surface tension until the point of CMC. For a solution having 5000 ppm concentration, the value of surface tension observed is 33.25 mN/m. Reduced adsorption after the point of CMC will not allow further lowering in the value of the surface tension. The value of the IFT decreases with

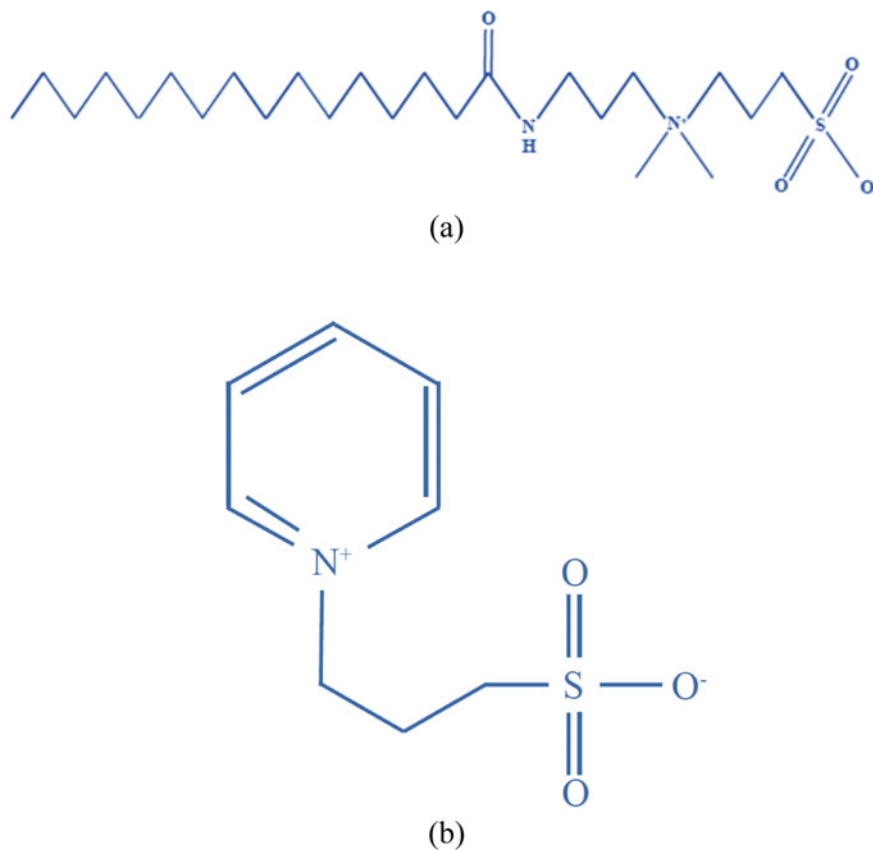


Fig. 14 **a** Molecular structure of amidosulfobetaine-16, **b** general chemical structure of the geminal zwitterionic surfactant 3-(1-pyridinio)-1-propanesulfonate

an increase in the concentration of the surfactant. Sample containing 500 ppm of the zwitterionic surfactant easily pulls down the IFT value to 0.0377 mN/m from 17 mN/m [28].

Zwitterionic surfactant shows no precipitation even at a temperature of 90 °C and a salt concentration of 20%. The solubility of surfactant and salt increase with an increase in temperature [4]. The thermo-gravimetric analysis shows excellent temperature stability up to a temperature of 160 °C. The flooding experiments using the zwitterionic surfactant show additional recovery of up to 30% [3]. A class of zwitterionic surfactants has positively charged ammonium and negatively charged carboxylate ions. The hydrocarbon lengths generally have a carbon chain of 12–14 carbons whose CMC is found to be 60 ppm. At this value of CMC this surfactant effectively sweeps residual oil as it achieves ultra-low interfacial tension profile between the oil–water interface. Moreover, it can alter wetting conditions from oil to water as observed from core flood experiments. The presence of both hydrophobic

and hydrophilic groups reduces the amount of surfactant loss due to adsorption during recovery operation and also induces characteristics of good thermal stability with excellent salt tolerance [15]. Carbonate reservoirs are excellent candidates for carboxybetaine based zwitterionic surfactants. Along with excellent salt tolerance capability and high thermal stability, it also shows a low degree of adsorption in a positively charged carbonate reservoir. However, few surfactants of this class show contrary results. Zwitterionic surfactants derived from sulfobetaine shows excellent pH tolerance. They are further divided into two classes based on the saturated or unsaturated nature of their tail. Amidosulfobetaine zwitterionic surfactant with a saturated tail shows poor solubility in saline and freshwater reservoirs, whereas, with an unsaturated tail it shows excellent solubility in both saline and freshwater reservoirs. The latter surfactant with unsaturated tail shows no sign of decomposition at high temperatures (up to 225 °C), thereby showing excellent thermal stability. The CMC of this amidosulfobetaine unsaturated surfactant is $1.02 \times 10^{-4} \text{ mol L}^{-1}$ in saltwater and $2.05 \times 10^{-4} \text{ mol L}^{-1}$ in freshwater. The value of the IFT for this surfactant lies close to $10^{-1} \text{ mN m}^{-1}$ and remains tolerant to changes in temperature and salinity. This surfactant shows the best result when deployed as a co-surfactant along with polymeric surfactant [15]. The novel alkyl-hydroxyl-sulfobetaine (C_{16}HSB and C_{18}HSB) shows high IFT reduction when used with HPAM. Additionally, it has significant stability and shows the potential for a new opportunity in high temperature and high salinity reservoirs [11]. Gubert amine-oxide is another zwitterionic surfactant that shows low IFT at low CMC value [39].

3 Conclusion

This chapter laid an overview of common, as well as novel surfactants that has emerged in surfactant eOR. Most of the recent research and findings have been generally on anionic surfactants as they are found to be more suitable for sandstone reservoirs; which are relatively more abundant and accessible. Anionic surfactants mostly work by reducing IFT at o/w interfaces. However, for carbonate reservoir, the cationic surfactants are preferred over anionic surfactants due to their ability to alter wettability. Nonionic surfactant emerges as an apt candidate for reservoirs that bear high salinity with extreme formation water hardness. Zwitterionic surfactants are fairly explored later and they yield low IFT values and also own the potential to alter the wettability of reservoir rock. They are also known to have high thermal stability and tolerate strong electrolytes due to their net charge neutrality.

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