



## Review Paper

# A review of fluid displacement mechanisms in surfactant-based chemical enhanced oil recovery processes: Analyses of key influencing factors



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## ARTICLE INFO

## Article history:

Received 9 May 2021

Accepted 28 October 2021

Available online 27 November 2021

Edited by Yan-Hua Sun

## Keywords:

Alkaline surfactant (AS) flooding

Alkaline-surfactant-polymer (ASP) flooding

Enhanced oil recovery (EOR)

Interfacial tension (IFT)

Nanoparticle-surfactant (NS) flooding

Surfactant adsorption

Surfactant-polymer (SP) flooding

Wettability alteration

## ABSTRACT

Surfactant-based oil recovery processes are employed to lower the interfacial tension in immiscible displacement processes, change the wettability of rock to a more water-wet system and emulsify the oil to displace it in subsurface porous media. Furthermore, these phenomena can reduce the capillary pressure and enhance spontaneous imbibition. The key factors affecting such immiscible displacement process are temperature, salinity and pH of the fluids, surfactant concentration and adsorption. Therefore, before any surfactant flooding process is applied, extensive studies of fluid-fluid and rock-fluid interactions are needed. The use of other chemicals along with surfactants in chemical enhanced oil recovery (cEOR) processes have been widely considered to exploit the synergy of individual chemicals and complement the weakness arises from each of them during immiscible displacement of fluids in porous media. Therefore, such combinations of chemicals lead to alkaline-surfactant (AS), surfactant-polymer (SP), alkaline-surfactant-polymer (ASP), and nanoparticle-surfactant (NS) flooding processes, among others. In this review study, we categorised the role and displacement mechanisms of surfactants and discussed the key factors to be considered for analysing the fluid displacement in porous media.

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## 1. Introduction

Due to its status as the world's primary energy source, the demand for oil and gas has been steadily increasing (Lakatos, 2005). However, on average, only 30% of the global oil production is achieved through the use of primary and secondary recovery methods. This amount of production is not sufficient to meet the world's energy consumption requirements. Such high energy demand has accordingly motivated many oil companies to develop advanced methods of recovery from oil and gas reservoirs (Morvan et al., 2009; Siggel et al., 2012). The production of the remaining oil after the primary stage, can be attributed to enhanced oil recovery (EOR) processes.

The application of enhanced oil recovery (EOR) or tertiary processes involves the injection external sources of energy (i.e., chemicals or gases and/or thermal energy) into reservoirs. The injected fluids enhance the overall oil displacement efficiency by modifying the forces on fluids, and hence mobilizing and producing

the trapped oil (Gbadamosi et al., 2018; Kamal et al., 2017). The mechanisms of recovery enhancement in tertiary processes involve a combination of conditions such as the interaction between injected fluids and oil resulting in lowering the interfacial tension, oil swelling, oil viscosity reduction, and wettability alteration among others. The selection of the suitable EOR method for implementation into a reservoir depends on the screening criteria which can be the evaluation of reservoir properties and conditions, and the economic feasibility (Green and Willhite, 1998).

Amongst all the EOR techniques, chemical EOR (cEOR) processes have been successfully applied in different types of reservoirs and they have been adjudged as the most promising because of their higher efficiency, technical and economic feasibilities (reasonable capital and operational costs) (Levitt and Pope, 2008). In cEOR processes, each type of chemical flooding relies on different mechanisms to enhance the oil recovery (Buchgraber et al., 2011). Surfactant flooding is known as the most promising methods among all cEOR processes. The main oil displacement mechanisms involved in surfactant injection are lowering the interfacial tension (IFT) between the displacing fluid and the residual oil and altering the reservoir wettability to more favourable conditions (Hirasaki

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and Zhang, 2003). Several studies determined that most surfactants cannot be used in harsh reservoir conditions. Therefore, their poor performance at high-temperature and high-salinity conditions has led to developing new technologies, chemicals, and formulations in order to overcome these harsh conditions (Azam et al., 2013; Sheng, 2015).

The present work aims to highlight the underlying mechanisms of surfactant flooding for cEOR and review the literature on the factors affecting the surfactant flooding process. The review covers the fundamentals and mechanisms of surfactant flooding with different additives in conventional and heavy oil reservoirs. We also summarised the advancements related to the use of surfactants, along with the current challenges that will require further investigation in future.

## 2. Surfactant flooding processes and underlying mechanisms

Surfactant is a surface-active substance which consists of a polar (hydrophilic) head and a nonpolar (hydrophobic) tail, which has an affinity to aqueous and non-aqueous phase due to the amphiphilic nature. Researchers have shown that all surfactant types can potentially reduce the IFT between the aqueous and oil phase and alter the reservoir wettability to promote more water-wet conditions. However, selecting the suitable type of surfactant is very crucial in terms of solubility, thermal and chemical stability, and adsorption of the surfactant under harsh reservoir conditions (Borchardt et al., 1985; Eftekhari et al., 2015).

Generally, surfactants are classified into main four groups: anionic, cationic, and non-ionic and zwitterionic (also known as amphoteric) (Gupta et al., 2020; Jia et al., 2017; Lu and Pope, 2017; Mejia et al., 2019; Pei et al., 2018; Saxena et al., 2019a). Anionic surfactants ionize in an aqueous solution with a negative charge, which is normally used in many products, such as detergents (alkyl benzene sulfonates), soaps (fatty acids), a foaming agent (lauryl sulfate) and wetting agent (di-alkyl sulfosuccinate) (Wu et al., 2017). In cEOR, they are commonly used in sandstone reservoirs, as they have low adsorption rates and high stability under high-temperature conditions (Kamal et al., 2017). Anionic surfactants, particularly sulfonate, sulfate and carboxylate types with high molecular weight, can efficiently reduce the IFT to ultra-low values and create a more stable solution at both alkaline and acidic pH (Yang et al., 2010). Sulfonate surfactants are highly suitable for crude oils with a high viscosity, high wax and high asphaltene contents. Additionally, they have high performance and stability at high temperature conditions; however, the precipitation at high salinity environments in the presence of divalent cations limits their performance. Alternatively, sulfate surfactants have a high tolerance to divalent cations and less chemical stability at a temperature higher than 60 °C. Carboxylate groups have the ability to reduce the IFT to ultra-low values with tolerances to high salinity and temperature (up to 120 °C) conditions (Kamal et al., 2017).

Cationic surfactants are ionised in aqueous solution to a positively charged long-chain group; therefore, they have a high adsorption rate in sandstone reservoirs and a great potential in carbonate reservoirs (Ma et al., 2013). Cationic surfactants can also be utilised as co-surfactants to enhance the performance of surfactants. This type of surfactants includes alcohols, phenols, ethers, esters, and amides and are used in cleaning skin wounds and removing the oil waxes from contaminated tools, etc. Cationic surfactants are not suitable EOR agent in sandstone reservoirs due to their high adsorption rate, while they can be used in carbonate formations for cEOR applications (Ma et al., 2013).

Non-ionic surfactants have a polar head group that has a strong affinity to water, and it does not ionize in the solution. Non-ionic surfactants are affected by the hydrogen bonding and van der

Waals interactions (Kamal et al., 2017). When the temperature increases, the hydrogen bonding weakens, leading to a poor dissolution of surfactant in the aqueous solution (Zhao et al., 2005). Moreover, the IFT reduction by non-ionic surfactants is lower compared to ionic surfactants, but some non-ionic surfactants (alkyl polyglycosides) can achieve ultra-low IFT by using co-solvents (e.g., alcohol) (Iglauer et al., 2009). The amphoteric (zwitterionic) surfactants can show either a negative or positive charge based on the pH level of the solution (Lv et al., 2011). The positive charge occurs due to the presence of cationic moieties (e.g., amines or quaternary ammonium groups), while the negative charge results from anionic moieties (e.g., sulfonic acid, carboxylic acid) (Zhang et al., 2019). There are different types of zwitterionic surfactants that have shown promising results for cEOR application such as carboxyl betaine type surfactants, hydroxyl sulfonate betaine type surfactants, didodecylmethylcarboxyl betaine, and alkyl dimethylpropane (Kamal et al., 2017; Massarweh and Abushaikh, 2020). Moreover, amphoteric surfactants with very low Critical Micelle Concentration (CMC) are used under high-temperature and high-salinity conditions, although these are considerably more expensive when compared to other surfactants (Lv et al., 2011).

Furthermore, biosurfactants from bio-based sources have also been used to reduce the IFT between injected fluids and the oil phase, reduce the capillary force and enhance the displacement process (Halim et al., 2017). Biosurfactants are synthesized by microorganisms and classified by their chemical composition, modular weight, physicochemical properties and mode of action and microbial origin (Pacwa-Płociniczak et al., 2011). Ke et al. (2018) tested the possibility of using lipopeptide biosurfactant produced by indigenous strain HB-2 (a novel species of the genus *Luteimonas*) to reduce the IFT. The results showed that the strain biosurfactant significantly reduced the IFT to a lower value and improved the emulsification of crude oil due to the increase in bacterial density, which contributed to the enhanced activities of both bioproduction and biodegradation. Surface and interfacial tension reduction and solubility improvement of hydrophobic organic compounds are a result of the formation of biosurfactant micelles. Moreover, the presence of micelles enhances the formation of microemulsions; thus, improves oil recovery.

The advantages of using biosurfactant over other chemical surfactants are due to the lower toxicity, high biodegradability, sustainability at extreme environmental conditions, and can be produced from renewable resources (Pereira et al., 2013; Gudiña et al., 2015). However, the application of biosurfactants for EOR processes has not been extensively investigated.

On the other hands, compared to conventional surfactants that have a tail group (hydrophobic) and a head group (hydrophilic), gemini surfactants are amphiphiles made up of two hydrophilic heads and two hydrophobic tails with a flexible or rigid spacer chain between them (Hou et al., 2019; Zana, 2003). The hydrophilic head group can be cationic, anionic, non-ionic, or zwitterionic. The hydrophobic tail can be short or long molecules and the spacer group can be polar (polyether) or non-polar (aliphatic or aromatic); and rigid (e.g., benzene) or flexible (e.g., methylene) (Kamal, 2016). The spacer group, which maintains and regulates the spacing between the two head groups, can range from C<sub>2</sub> to C<sub>12</sub>. Many experimental studies have proved that gemini surfactants have better performance compared to the conventional surfactants, as they have better surface and interfacial activities, lower critical micelle concentrations, lower Krafft points and better wetting properties, although the drawback is their cost (Kamal, 2016; Zana, 2003; Ye et al., 2008).

Based on previous studies, it was found that surfactants have a great potential in cEOR applications, and they are used to improve

the process of oil recovery by decreasing the interfacial tension, microemulsion generation and wettability alteration. In the rest of this study, the underlying mechanisms of surfactants are discussed in detail.

### 2.1. Interfacial tension reduction and microemulsions

In cEOR processes, one indicator or improved displacement efficiency is to achieve a high capillary number, which is the ratio of viscous forces to interfacial forces. Accordingly, to increase the capillary number value, it is necessary to either increase the viscosity of the displacing fluid (water) or reduce the interfacial tension between the oil and water (Donaldson et al., 1989; Guo et al., 2015; Khosravi, 2010). Increasing the viscosity of water demands high pumping pressure at facilities and may cause fracturing. Therefore, reducing the interfacial tension between the oil and water phases by using surfactants decreases capillary pressures and allows water to displace the trapped oil from the pores (Azodi and Nazar, 2013; Caenn et al., 1989; Shah, 2012; Xu et al., 2019). This can also enhance the oil recovery from shale and tight oil reservoirs, as the surfactants are capable of reducing the IFT to ultra-low values in very small pore spaces, which significantly lowers the capillary pressure and assists the oil displacement process (Gupta et al., 2020).

The main factors determining the IFT values are surfactant concentration in aqueous solutions, molecular structure, salinity, and temperature. A high surfactant concentration is more desirable than a low concentration in terms of ultralow IFT (generally, this should be at least the CMC, beyond which the IFT remains unchanged). In the presence of high surfactant concentrations, more oil will be solubilised; moreover, the solution is expected to form a type III Winsor solution, which leads to an increase in oil recovery (Hirasaki et al., 2011). However, new types of surfactants have been developed that can produce ultralow IFT at low concentrations, which reduces both the amount of surfactant required and the cost associated with the EOR process. One representative example of these surfactants was presented by Berger et al. (Berger and Lee, 2002), who developed a new series of alkyl aryl sulfonic acids (AASAs) that create ultralow IFT at very low surfactant concentration for sandstone and limestone formations. The required concentration of these surfactant solutions is low compared to that of conventional AASAs used in the oil and gas industry; this is because the solubility of this new series in water is greater than that of the conventional series. The properties of these two surfactants differ in terms of the position of the attached sulfonate group. However, there are also some similarities between these two surfactants, such as surface tension and CMC. The molecular structure of surfactants has a massive effect on the value of the IFT; with increasing the number of CH group in the surfactant, the interfacial energy decreases, which results in a low interfacial tension (Zhao and Zhu, 2003). Additionally, surfactant with longer hydrocarbon chain length leads to lower the IFT, due to the increase in the lipophilic group in the surfactant and possibility to increase their movement from the bulk aqueous phase to the oil/solution interface (Qiao et al., 2012).

Mixed surfactants exhibit strong synergism in terms of improving both the IFT and CMC values, which are more noticeable than those of the individual surfactants. This is because mixed surfactants lead to an increase in the length of the hydrophobic chain (via electrostatic interactions), which is both oriented and soluble in the oil phase (El-Batanoney et al., 1999; Li et al., 2017). Consequently, this synergism is used to reduce the IFT and CMC values between the oil and aqueous solution to ultralow values under harsh reservoir conditions (Jia et al., 2019; Li et al., 2016; Wang et al., 2001). Moreover, mixed surfactants have a greater

spontaneous emulsification ability through the formation of a film around the dispersed droplets and maintenance of droplet stability by strengthening the interfacial film (Izquierdo et al., 2005). Additionally, the presence of mixed surfactants (e.g., cationic/non-ionic) enhance the desorption capacity of the ion-pair mechanism and the solubilisation ability of the mixed micelles, meaning that they have a strong potential to alter the wettability of the reservoir (Hou et al., 2018). Further research conducted by Li et al. (2016) led to the development of a lipophilic surfactant by mixing hydrophilic anionic and cationic surfactants, which could be used for high-temperature and low-salinity sandstone reservoirs. Their results demonstrated that the IFT was reduced to an ultralow value while an improved thermal stability at temperatures as high as 76.5 °C was achieved over 120 days. Additionally, the adsorption of cationic surfactant on the negatively charged surface was reduced due to the cationic surfactant being hidden in the anionic-rich mixtures.

Gemini surfactants have the ability to reduce the IFT to ultra-low values at low surfactant concentrations. Gao and Sharma (2013a) experimentally studied sulfate-based gemini surfactants and reported that such surfactants had an excellent salinity tolerance, as no precipitation or separation was observed. They reported these surfactants are more desirable in high-temperature and high-salinity conditions. The performance of gemini surfactant can be improved by interaction with another gemini surfactant. This is due to the formation of mixed micellar aggregates in the mixture. This means that the molecules of the mixed surfactants adsorbed at the oil-solution interface may have a compact arrangement and a better condition to modify the properties of the oil and water interface, which favours the reduction of IFT and weakens the effect of temperature on it. Ye et al. (2008) demonstrated that a combination of synthesized gemini surfactants (surfactant one:  $m-s-m = 14-4-14$  and surfactant two:  $m-s-m = 16-4-16$ , where  $m$  and  $s$  stand for the carbon atom number in the alkyl chain and the spacer, respectively) appeared to be more effective in decreasing the IFT compared to the individual gemini surfactants. Moreover because of the synergism, the IFT was no longer affected by temperature, and it remained constant as the temperature rose from 30 to 80 °C. Hou et al. (2019) investigated the efficiency of synthesising an anionic-non-ionic gemini surfactant in high-temperature and high-salinity reservoirs. These investigators reported the gemini surfactant enhanced the surface activity and interfacial activity better than sodium dodecyl benzene sulfonate surfactant at 120 °C. Moreover, the synthesized mixed surfactant created stable microemulsions that were stronger than those created by TX-10 surfactant. Ultralow IFT and wettability alteration were achieved at high salinity conditions; thus, oil recovery was improved.

The presence of micelles in the aqueous and oil phases is the main mechanism by which microemulsions are created and depend strongly on the temperature and salinity conditions. The microemulsions created in this way can improve the recovery of oil from sandstone and carbonate reservoirs by reducing the IFT and promoting a miscible displacement (Healy et al., 1976). Microemulsion phase behaviour is a critical concept that impacts the success of surfactant flooding. The most common classification of microemulsion phase behaviour was first proposed by Winsor in 1948, who defined four types of microemulsions (Winsor, 1948). The microemulsion phase behaviour can be moved from Type I to Type III and then Type II by increasing the salinity under constant temperature and pressure conditions (Chai et al., 2007; Nordiyana et al., 2016). While, type four (IV) is an extension of type III, formed by increasing the concentration of the surfactant until the whole liquid transforms into a single-phase (Salleh et al., 2019; Ahmed and Elraies, 2018). Type III is preferred for EOR applications, as it provides the lowest IFT. Moreover, the presence of Type I and type II are unfavourable for achieving ultralow IFT with surfactant and

unfavourable for an EOR process, respectively (Barnes et al., 2008). This is because; in the presence of type I, the surfactant is concentrated in the aqueous phase, which leads to an increase in the IFT of oil and microemulsions (Green and Willhite, 1998; Sahni et al., 2010). While in type II, surfactant forms water in oil microemulsions which reduces the oil-microemulsion IFT that traps the surfactant in residual oil and increases the IFT of water-microemulsions, this leads to surfactant retention in the oil phase (Massarweh and Abushaikha, 2020; Healy et al., 1976).

A summary of research conducted over the last two decades into improving oil recovery efficiency by means of surfactant flooding through IFT reduction and microemulsion stability formed via surfactant is presented in Table 1.

## 2.2. Wettability alteration

The mechanism of alteration of the reservoir wettability from oil-wet to intermediate-wet or more water-wet conditions is among the key factors that significantly improve the oil recovery in surfactant flooding processes (Nowrouzi et al., 2020; Zargar et al., 2020). This helps to mobilise residual oil and produce it through the spontaneous imbibition process. Generally, carbonate reservoirs and fractured reservoirs are characterised as oil-wet or mixed-wet; thus, the imbibition process of water is either poor or cannot occur due to the negative capillary pressure (Andersen et al., 2014). Accordingly, to increase the oil recovery from these types of reservoirs, the wettability of the reservoir matrix must be made more favourable in order to allow water to imbibe into the rock matrix and push the oil out of the matrix into the fracture (Standnes and Austad, 2000a; Zhang et al., 2006a).

Surfactants can change carbonate reservoir wettability to more favourable water-wet conditions by means of either ion-pairing or surfactant adsorption mechanisms. The ion-pairing mechanism that changes the wettability of carbonate rock using cationic surfactants occurs by the reaction of anionic components (mainly of the carboxylic group) adsorbed on the rock surfaces from the crude oil and the positive head of the cationic surfactants. Therefore, ion-pairs that are soluble in the oleic phase will be formed along with the surfactant monomers as a result of these electrostatic attractions. Accordingly, the oil will be desorbed, and the rock surface will become more water-wet (Salehi et al., 2008; Wang et al., 2011). Seethepalli et al. (2004a) analysed the wettability alteration in oil-wet/mixed-wet carbonate reservoirs through the use of anionic and cationic surfactants. Their research confirmed that both the anionic and cationic surfactants altered the wettability of carbonate surfaces (limestone, marble, dolomite, and calcite) to intermediate/water-wet conditions. Gupta et al. (2009) conducted similar experiments, in which they observed changes in the contact angle of limestone core samples under four reservoir conditions (low to high temperatures and salinities). Propoxy sulfate and ethoxy sulfate surfactants altered the rock wettability to water-wet conditions, and the contact angle was decreased with increasing reservoir temperature. Oil recovery was increased between 35% and 70% original oil in place (OOIP) for the four reservoir rock types, and the rate of oil recovery increased with wettability alteration toward water-wet, at higher temperatures and fracture density.

Standnes and Austad (2000b) have verified that cationic surfactant alters the wettability of carbonate rock via the mechanism of ion-pair formation between the cationic surfactant and negatively charged carboxylates adsorbed from the crude oil, as shown in Fig. 1a. In the absence of electrostatic interaction, the surfactant adsorption mechanism alters the carbonate wettability via replacement of the hydrophobic substances from the crude oil adsorbed on the solid surface with hydrophobic groups of non-ionic or anionic surfactant molecules (Standnes and Austad,

2000b; Hou et al., 2016; Jarrahan et al., 2012). As shown in Fig. 1b, the anionic surfactant is able to change the wettability of carbonate surface to water-wet by forming a small water film between the organic coated surface and the oil. Hence, weak capillary forces are created during the imbibition process as a result of hydrophobic interaction between the tail of the surfactant and the adsorbed organic material from the oil.

Furthermore, zwitterionic surfactants effectively alter the wettability of both sandstone and carbonate rocks to more water-wet surfaces. Kumar and Mandal (2019b) showed that zwitterionic surfactants effectively change the wettability of sandstone and carbonate surfaces through ion-pairing between the zwitterionic hydrophilic head and the adsorbed basic components of the crude oil on sandstone rock; and the ammonium ions form ion-pairs with the adsorbed acidic components of the crude oil on carbonate surfaces. Therefore, with an increase in the surfactant concentration, the desorption of crude oil components will increase, resulting in more water-wet rock surfaces.

Non-ionic surfactants have the ability to change the wettability of carbonate toward a less oil-wet condition or becoming an intermediate-wet condition. Ayirala et al. (2006) experimentally investigated the wettability altering capability of non-ionic surfactant on dolomite rock. Their results revealed that, with a high concentration of non-ionic (ethoxy alcohol) surfactant, the dolomite surface wettability changed from strongly oil-wet to less oil-wet. This is because more non-ionic surfactant molecules were available in the bulk solution to attach to the rock surface and change the wettability status of the rock.

Moreover, other studies revealed that non-ionic surfactant could change the wettability from oil-wet to water-wet conditions (Golabi et al., 2012; Jarrahan et al., 2012; Souayeh et al., 2018; Wu et al., 2006). Souayeh et al. (2018) studied the effect of using a non-ionic surfactant with low-salinity brine on wettability alteration of oil-wet calcite surfaces. Their results revealed that the non-ionic surfactant was able to alter the calcite wettability from a strong oil-wet condition to a water-wet condition. The presence of low-salinity brine had no significant effect on the surface wettability alteration; thus, the wettability alteration of the calcite surfaces was attributed to the non-ionic surfactant only. They concluded that the dominant mechanisms of wettability alteration by the non-ionic surfactant were: (1) The formation of a surfactant double layer and adsorption of the hydrophobic component of the non-ionic surfactant on the hydrophobic calcite surface might be a reasonable explanation of the wettability change process. (2) Hydrogen bonds might formed on the solid surface between the surfactant's ethoxy groups and the hydroxyl or carboxylic groups of the crude oil, which can lead to the detachment of organic compounds from the calcite surface.

Similarly, surfactant flooding can increase the recovery of hydrocarbon from shale oil reservoirs by altering the wettability from mixed-wet/oil-wet to water-wet conditions. Additionally, shale reservoirs undergo high capillary pressure due to the small pore sizes; therefore, surfactant flooding can lower the capillary pressure by reducing the IFT (Curtis, 2010). By contrast, the relationship between reservoir wettability and gas recovery in shale gas reservoirs differs from that in shale oil reservoirs. To achieve high gas recovery from shale reservoirs, reservoir wettability should be closer to oil-wet conditions to avoid water imbibition (Dehghanpour et al., 2013; Kantzas et al., 1997). This is because water imbibition in tight reservoirs can block gas flow passages and cause high residual gas saturation. Sun et al. (2015) used a commercial non-ionic surfactant to alter shale gas wettability from water-wet to intermediate-wet in order to improve the gas recovery. Zhou et al. (2016) investigated the effect of mixed anionic (ammonium dodecyl sulfate) and cationic (*n*-octadecyl trimethyl



**Table 1**

Summary of the recent studies demonstrating the effect of different types of surfactants on the IFT reduction, microemulsion stability and oil recovery under different reservoir conditions.

Authors	Type and name of surfactant	Experimental conditions	Oil recovery factor	Key remarks
Zaitoun et al. (2003)	Anionic: SS-6066, S-6066 A and ANTISORB	Temperature: 55 °C Salinity: 108,333 TDS formation brine, 66,013 TDS injection brine.	36% OOIP after water flooding	High surfactant solubility at high salinities with low IFT. Surfactant adsorption was reduced.
Seethepalli et al. (2004a)	Anionic: SS-6656, Alfoterra-33, 35, 38, 63, 65 & 68	Temperature: 70 °C, Salinity: CaCl <sub>2</sub> ·2H <sub>2</sub> O 2.9 kg/m <sup>3</sup> , MgCl <sub>2</sub> ·6H <sub>2</sub> O 2.032 kg/m <sup>3</sup> , NaCl 5.815 kg/m <sup>3</sup> , Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.007 kg/m <sup>3</sup> , Na <sub>2</sub> SO <sub>4</sub> 0.237 kg/m <sup>3</sup>	>50% OOIP	IFT reduction and wettability alteration were achieved on carbonate surfaces. Surfactant adsorption into the carbonate was diminished.
Liu et al. (2004)	Anionic: Alkyl-aryl sulfonic acid	Room temperature (22 °C).	13% OOIP after the alkaline-surfactant injection	Reduction of oil-water interfacial tension. Improving chemical flooding during extended waterflooding process.
Iglauer et al. (2009)	Non-ionic: Alkyl polyglycosides (APG)	Temperature: 70 °C Salinity: NaCl 20–100 kg/m <sup>3</sup> , CaCl <sub>2</sub> 10 kg/m <sup>3</sup>	85% OOIP	IFT reduction independent of both salinity and temperature. Low IFT achieved at optimum alcohol chain length, co-surfactant, and surfactant molar ratio.
Ahmadi and Shadizadeh (2013)	Non-ionic: <i>Ziziphus spina christi</i>	Temperature: 100 °C Pressure: 10342 kPa Salinity: 15 kg/m <sup>3</sup>	81.08% OOIP	Low IFT and high aqueous phase viscosity achieved in carbonate reservoirs. Low-cost surfactant with low environmental impact.
Ko et al. (2014)	Anionic: Polyoxyalkylene glycol Anionic co-surfactant: Dodecyl alkyl sulfate	Temperature: 60 °C Salinity: 0–50 kg/m <sup>3</sup>	26.6% OOIP after water flooding	The branched surfactant generates effective microemulsion systems at high concentration. Optimal and detrimental salinity values for microemulsion stability were identified. Microemulsion stability increases in the presence of a co-surfactant.
Lu et al. (2014c)	Anionic: Internal olefin sulfonate	Temperature: 38 °C Salinity: 28 kg/m <sup>3</sup>		Displacement stability, microemulsion phase behaviour and viscosity evaluated in terms of critical velocity. High oil recovery achieved as a result of improving microemulsion viscosity leads.
Lu et al. (2014a)	Anionic: Guerbet alkoxy carboxylates	Temperature: 120 °C Salinity: 69 kg/m <sup>3</sup>	90.5% OOIP	High surfactant performance and stability in the presence and absence of alkali. Low IFT to an ultra-low value under high temperature, salinity, and hardness conditions.
Lu et al. (2014b)	Anionic: Guerbetalkoxy carboxylate surfactant with internal olefin sulfonates	Temperature: 100 °C with high Salinity: 117 kg/m <sup>3</sup>	65.9% of the remaining oil after water flooding	IFT reduction, wettability alternation and good aqueous stability achieved under harsh reservoir conditions. High oil recovery obtained from fractured carbonate rocks with no mobility control agent.
Parra et al. (2016)	Anionic: Combination of carboxylate and internal olefin sulfonate.	Temperature: 78 °C Salinity: 100 kg/m <sup>3</sup>	40% OOIP	High viscous forces achieved during low IFT surfactant flooding. Microemulsion viscosity increased by changing the salinity of the aqueous surfactant. Microemulsions increased the oil recovery from fractured oil-wet carbonate reservoirs.
Li et al. (2016)	Anionic: Nonylphenyl ethoxylate carboxylate (60 mol%) with Cationic: Quaternary ammonium salt (40 mol%)	Temperature: 75.5 °C Salinity: NaCl 350 kg/m <sup>3</sup> .	16.4–23.5% OOIP after water flooding	Mixed surfactants exhibited high thermal stability with ultra-low IFT and high oil solubilisation. Presence of mixed surfactant hindered the adsorption of cationic surfactant.
Jia et al. (2017)	Anionic: Sodium dodecyl sulfate with Cation: <i>N</i> -dodecyl- <i>N</i> -methylpyrrolidinium bromide	Temperature: 30–70 °C.	25% after water flooding	Mixed surfactants effectively reduced the IFT to an ultralow value. The optimal molar ratio for the mixed surfactants should be determined to achieve the ultralow IFT.
Lu and Pope (2017)	Anionic: Propylene oxide, internal olefin sulfonate Cosolvents: Isobutyl alcohol, triethylene glycol mono butyl ether	Temperature: 38 °C and 58 °C Salinity: 0.0303 kg/m <sup>3</sup> TDS (5 kg/m <sup>3</sup> Na <sub>2</sub> CO <sub>3</sub> and 0.0254 kg/m <sup>3</sup> NaCl)	95% OOIP	The viscosity of the generated microemulsions is sensitive to the amount and type of the co-solvent added to the surfactant solution. Microemulsion viscosity was successfully controlled at optimum salinity. Oil recovery increased due to increases in surfactant flood rate.
Pei et al. (2018)	Cationic: Hexadecyltrimethylammoniumbromide with SiO <sub>2</sub> NPs	Temperature: 50 °C	40% OOIP	Emulsions stability was improved due to the presence of nanoparticles and surfactant.

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Table 1 (continued)

Authors	Type and name of surfactant	Experimental conditions	Oil recovery factor	Key remarks
Ke et al. (2018)	Lipopeptide biosurfactant produced by indigenous strain HB-2	Temperature: 25 °C	11% OOIP after water flooding	High sweep efficiency was achieved by blocking the highly permeable water channels and increasing the displacement efficiency. Low IFT achieved by the metabolism process. The ability to degrade the crude oil long-chain hydrocarbons (emulsification of crude oil by).
Seo et al. (2018)	Non-ionic: Synthetic biosurfactant	Temperature: 25 °C	90% OOIP	The degree of IFT reduction by biosurfactant is superior to that of conventional surfactants. The efficiency biosurfactant for IFT reduction is decreased as oil viscosity increases. High sweep efficiency by biosurfactant flooding compared to SDS flooding.
Saxena et al. (2019a)	Anionic: Synthesized surfactant from soap-nut oil	Temperature: 25–75 °C Salinity: NaCl 0–60 kg/m <sup>3</sup>	30% OOIP after water flooding	IFT reduction and wettability alternation were achieved in sandstone rock at an optimum salinity. Winsor III microemulsions were generated, which improved the oil displacement.
Jia et al. (2019)	Anionic: Sodium dodecyl sulfate Cationic: 1-Dodecyl-3-methylimidazolium chloride	Temperature: 85 °C Salinity: NaCl 50 kg/m <sup>3</sup>	16.1% after waterflooding	The mixture of surfactants successfully reduced the IFT and altered wettability. Mixed surfactants stabilised microemulsions under high-salinity and high-temperature conditions.
Hou et al. (2019)	Anionic: Synthesized Gemini surfactant Nonanoic: TX-100	Temperature: 120 °C Salinity: 200 kg/m <sup>3</sup>	17.3% OOIP after waterflooding	Surface activity and ultralow IFT were achieved under high-salinity conditions. The synthesized surfactant showed strong emulsification and wettability alteration characteristics.
Mejia et al. (2019)	Anionic: Tridecyl alcohol propoxy sulfate, internal olefin sulfonate	Temperature: 24 °C Pressure: 710 kPa.	40% OOIP	High oil recovery was achieved in high-permeability fractured carbonate reservoirs. Surfactant flooding mechanisms have different timescales in fractured carbonate reservoirs.
Mohammadi et al. (2019)	Anionic: Sodium dodecyl sulfate (SDS)	Temperature: 85 °C Pressure: 17237 kPa Salinity: In total 198 kg/m <sup>3</sup>	55% OOIP	Brine ions help anionic surfactant to reduce IFT and create favourable wettability. High spontaneous imbibition and high capillary numbers were achieved. Surfactant and low-salinity seawater improved the microscopic sweep efficiency.
Tay et al. (2019)	Anionic: Internal ketone sulfonates	Temperature: 60 °C Salinity: TDS 31 kg/m <sup>3</sup>	99% after water flooding	Good surfactant solubility, suitable for EOR in seawater conditions. More future work needed for this surfactant.
Gupta et al. (2020)	Anionic: Proprietary (S1) Amphoteric: Lauramidopropyl hydroxysultaine (S2), Non-ionic: 9-Octadecenamide (S3)	Temperature: 100–650 °C Pressure: Up to 37921 kPa Salinity: (KCl & CaCl <sub>2</sub> ) 35–150 kg/m <sup>3</sup>	29–34% OOIP	Asphaltene precipitation was significantly decreased. The amphoteric surfactant achieved superior performance in shale and sandstone core samples.
Kurnia et al. (2020)	Anionic: Alcohol propoxy sulfate (C <sub>6-10</sub> , C <sub>10-13</sub> , C <sub>10-16</sub> , C <sub>16-17</sub> ) Zwitterionic: Cocamidopropyl hydroxysultaine	Temperature: 45 °C, Pressure: 3447 kPa, Salinity: NaCl 10–40 kg/m <sup>3</sup>	63–75% OOIP	Ultralow IFT achieved via mixed surfactant. Mixed surfactants achieved excellent oil recovery without alkali.
Wang et al. (2001)	Non-ionic: Ether caxhoxylated, Anionic: Ampholytic surfactants, novel structure surfactant (LF)	Temperature: 86.9 °C Salinity: 55–195 kg/m <sup>3</sup>		The synergistic effect of the two surfactants has a strong salt tolerance, leading to ultralow IFT. The mixture of surfactants achieved good performance in oil displacement and huff and puff processes in high-salinity formations.
Berger and Lee (2002)	Anionic: Synthesized alkylaryl sulfonic acids (AASA)	Temperature: 55 °C Salinity: 130 kg/m <sup>3</sup>		High ultra-low IFT achieved with tolerance to high total dissolved solid brines and divalent salts. Low surfactant concentration helps to prevent scale formation and corrosion.
Zhao et al. (2006)	Anionic: Different length chain of (hexyl, octyl, decyl, dodecyl and tetradecyl) methylnaphthalene sulfonate	Temperature: 70 °C Salinity: NaCl 0–50 kg/m <sup>3</sup>		Ultralow IFT was achieved over a wide range of salinities. The presence of inorganic salt with the surfactant decreased the IFT.

Table 1 (continued)

Authors	Type and name of surfactant	Experimental conditions	Oil recovery factor	Key remarks
Gao and Sharma (2013a)	Anionic: Synthesized Gemini surfactant (14-2-14, 18-2-18, C <sub>12</sub> -SO <sub>4</sub> -Na <sup>+</sup> , C <sub>14</sub> -SO <sub>4</sub> -Na <sup>+</sup> , C <sub>16</sub> -SO <sub>4</sub> -Na <sup>+</sup> )	Temperature: 45, 55, 85 °C Salinity: NaCl 200 kg/m <sup>3</sup> , CaCl <sub>2</sub> 500 kg/m <sup>3</sup>		High tolerance to extreme salinity and hardness conditions. This surfactant can potentially be used as a co-solvent and co-surfactant. Lowest surfactant adsorption into Berea cores.
Kumar and Mandal (2019a)	Zwitterionic: N-Tetradecyl-N	Temperature: 30, 80 °C for IFT 40–560 °C for stability Salinity: NaCl 0–20 kg/m <sup>3</sup>		High thermal stability with salt tolerance of 20% salinity. IFT reduced in the presence of salt. Surfactant adsorption found to be within the acceptable adsorption range.
Ye et al. (2008)	Cationic: Mixture of synthesized gemini types: 14-4-14 and 16-4-16	Temperature: 30–80 °C		IFT is very sensitive to the temperature. Temperature has an influence on dynamic interfacial tension. IFT of mixed gemini surfactants has weakened the sensitivity to the temperature.

ammonium) surfactants in changing the wettability of two types of shale gas rocks. Their results indicated that low concentrations of mixed surfactants altered the wettability from intermediate water-wet to more oil-wet, as well as decreasing the capillary pressure and IFT between gas and liquid phases. Although some research has been conducted in this area, further research is needed if the relationship between reservoir wettability and gas recovery in shale reservoirs is to be fully understood.

A summary of the recent investigations into reservoir wettability alteration via surfactant flooding to improve the displacement efficiency in porous media is presented in Table 2.

### 3. Factors affecting surfactant flooding

There are other parameters that affect the performance of a surfactant flooding process. These are linked to the displacement mechanisms through their impact on IFT, wettability and micro-emulsion phase behaviour. The most critical parameters-temperature, salinity, pH, adsorption, and concentration-are discussed in this section.

#### 3.1. Effect of temperature

The reservoir temperature influences the chemical flooding process in many ways: specifically, it affects the surfactant adsorption, the Critical Micelle Concentration (CMC) of the solution and the IFT. Generally, the increase in the temperature leads to a decrease in the solubility of the hydrophobic tail in the water and move the surfactant to the oil-solution interface; thus, decreasing the IFT (Gao and Sharma, 2013b). Moreover, surfactant adsorption on the rock surface presents a challenge in the context of surfactant flooding. However, temperature has a significant effect on the rate of surfactant adsorption, increasing temperature results in a significant decrease in the rate of surfactant adsorption; this is due to the increase of the kinetic energy of the species (Fava and Eyring, 1956). Azam et al. (2014) conducted laboratory experiments to investigate the effect of temperature on the adsorption of anionic surfactant into Berea sandstone samples. They concluded that the adsorption of anionic surfactant reduced slightly from 0.9604 to 0.491 mg/g under an increase in temperature from 25 to 75 °C. Ziegler and Handy (1981) also conducted laboratory experiments to demonstrate the effect of temperature on the adsorption of a non-

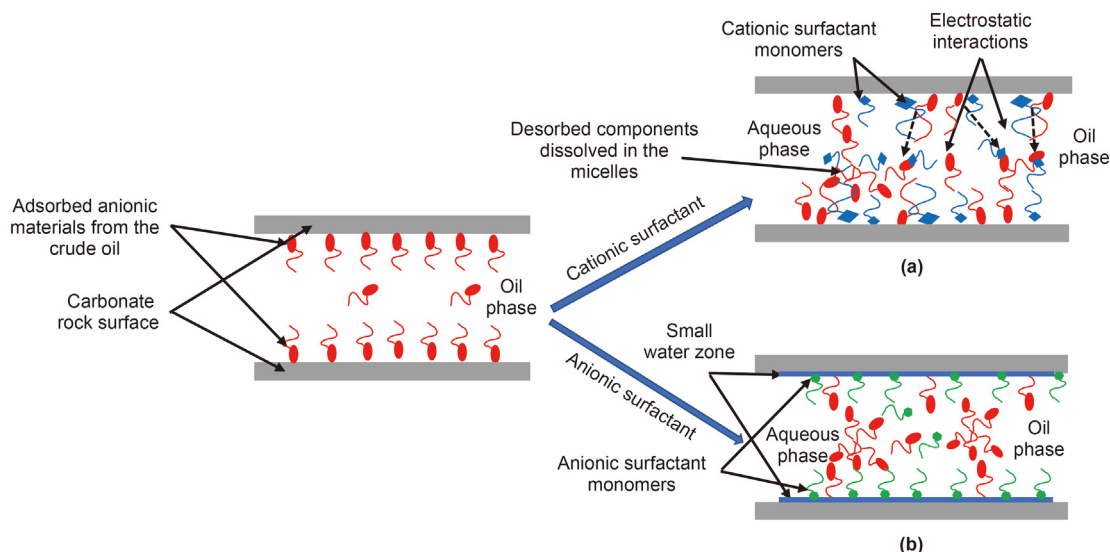


Fig. 1. Schematic of wettability alteration of carbonate rock caused by (a) cationic surfactant (ion-pairing mechanism) and (b) anionic surfactant (surfactant adsorption mechanism) (adopted from Standnes and Austad (2000b)).

**Table 2**  
Summary of the recent studies demonstrating the effect of different surfactant types on wettability alteration under different reservoir conditions.

Reference	Type and name of surfactants	Experimental condition	Oil recovery factor	Key remarks
Standnes and Austad (2000b)	Cationic: C8TAB, C10TAB, C12TAB, C16TAB, Hymine, ADMBACI Anionic: S-150, B1317, S-74, APES, Gafac, SDS	Temperature: 40, 70 °C.	70% OOIP	Cationic surfactant altered the wettability of low-permeability chalk. Imbibition mechanism initiated by mixed surfactants. Mixed surfactants generated weak capillary forces.
Ayirala and Rao (2004)	Non-ionic: Ethoxy alcohol Anionic: Ethoxy sulfate	Ambient temperature Salinity: 0.05, 1.5, 3.5, 5.0 kg/m <sup>3</sup>	75% OOIP	Oil recovery enhanced by altering the wettability to mixed-wet conditions. The hypothesised mechanism of mixed-wettability development involves the rupture of thin wetting water film followed by surfactant adsorption on the rock surface.
Gupta et al. (2009)	Anionic: Propoxy sulfate Non-ionic: Ethoxy sulfates, 15-S, NP	Temperature: 0–90 °C Salinity: 0–80 kg/m <sup>3</sup>	35–70% OOIP	Surfactants altered the fractured carbonate's wettability. Water-wet conditions increased oil recovery at high temperatures and fracture density.
Jia et al. (2019)	Anionic: Sodium dodecyl sulfate Cationic: 1-Dodecyl-3-methylimidazolium chloride	Temperature: 85 °C Salinity: NaCl 50 kg/m <sup>3</sup>	16.1% after waterflooding	IFT reduction and stabilised microemulsions created by mixed surfactants. Wettability of quartz surface altered by removing the adsorbed composition of crude oil.
Hou et al. (2019)	Anionic-non-ionic: ANG (synthesized Gemini surfactant)	Temperature: 120 °C Salinity: 200 kg/m <sup>3</sup>	17.3% OOIP after waterflooding	IFT reduction and wettability alteration achieved in a high-salinity environment.
Madani et al. (2019)	Anionic: Synthesized amino-acid-based	Temperature: 25 °C Pressure: 18615 kPa Salinity: 50 kg/m <sup>3</sup>	60.23% OOIP	Wettability alteration of sandstone and carbonate reservoirs affected by surfactant concentration. High oil recovery achieved in the sandstone reservoir.
Rabbani et al. (2019)	Anionic: Platinum foam plus	Ambient temperature Salinity: 20 kg/m <sup>3</sup>	4.23% after waterflooding	High surfactant flooding efficiency achieved in strong oil-wet tight carbonate rocks.
Mofrad and Dehaghani (2020)	Cationic: Cetyltrimethylammonium bromide Anionic: Sodium dodecyl sulfate	Salinity: Seawater with changing the concentrations of KCl (0.849, 1.0, 2.6 kg/m <sup>3</sup> )	51–55% OOIP	Wettability altered toward water-wet conditions at optimum surfactant concentration. High oil recovery achieved by smart combination flooding.
Seethapalli et al. (2004b)	Anionic: Sulphonates (4–22, 5–166, SS-6566), Alforterra (33, 35, 38, 63, 65, 68). Cationic: Dodecyl trimethyl ammonium bromide (DTAB)	Temperature: 30 °C Salinity: different brine composition		Anionic surfactant altered the carbonate surface wettability. The presence of alkali can suppress adsorption of the anionic surfactant.
Jarrhian et al. (2012)	Cation: C12TAB Non-ionic: Triton X-100 Anionic: SDS	Ambient temperature		Wettability alteration is controlled by the surfactant structure. The cationic surfactant is more effective in altering the wettability of dolomite rocks.
Ayirala et al. (2019)	Non-ionic: Ethoxylated alcohol	Temperature: 25, 95 °C Pressure: 1379, 20684 kPa Low and high salinity		Carbonate wettability was improved at low- and high-salinity brines. Capillary and adhesion forces improved by wettability alteration and IFT reduction.
Kumar and Mandal (2019b)	Zwitterionic: N-Hexadecyl-N, N-dimethyl-2-ammonio-1-ethanecarbonate (C16DmCB)	Salinity: NaCl 0–4 kg/m <sup>3</sup>	3.0% & 18.95% OOIP	Surfactant effectively altered the wettability of oil-wet sandstone and carbonate rock surfaces. Wettability alteration by zwitterionic due to the io-pairing mechanism. The adsorption of surfactant increased with increasing salinity.
Souayeh et al. (2018)	Non-ionic: Two series of polyethoxylated	Temperature: 75 °C Salinity: Different synthetic formation brine composition		Two non-ionic surfactants were able to alter the wettability of the calcite surface from strongly oil-wet to water-wet. Wettability of the calcite surface can be altered over a wide range of salinity.

ionic surfactant into sandstone rock samples. The results obtained from the static adsorption experiments indicated that, at low surfactant concentrations, the rate of adsorption decreased as the temperature increased over a range from 25 to 95 °C. This is due to the increase of kinetic energy at higher temperatures, at which point the force of interaction becomes weaker. While at high concentrations, the rate of adsorption increased with increasing temperature. Additionally, the process of surfactant adsorption is generally an exothermic process which can be either enthalpy driven, or entropy driven, and the temperature has a different influence on surfactant adsorption depending on the adsorption density (Belhaj et al., 2020; Hirasaki and Zhang, 2003). Therefore, in the presence of surfactants with low adsorption density, when the temperature increases, it causes the adsorption density to be higher (enthalpy driven adsorption). On the other hand, adsorption

density becomes lower for surfactants with high adsorption density (entropy-driven adsorption) when the temperature increases (Kamal et al., 2017). Moreover, a study by Bera et al. (2013) confirmed that with an increase in temperature, the adsorption capacity decreases (in case of entropy-driven adsorption) due to two main reasons: (1) The solution viscosity decreases with increasing temperature; therefore, the rate of diffusion of the adsorbate between the exterior boundary layer and inner pores of reservoir rocks decreases. (2) Temperature affects the equilibrium adsorption capacity of the sand particles depending on whether the adsorption process is exothermic or endothermic. On the other hand, for non-ionic surfactant the adsorption increases with increasing temperature. As the temperature increases, the head groups of surfactants dehydrate, becoming less hydrophilic and more compact, resulting in increased surface activity and



adsorption quantities. Adsorption of the non-ionic surfactant onto crushed Berea sandstone reduced with increasing temperature at low concentrations, but it increased with increasing temperature at high concentrations (Ziegler and Handy, 1981). Also, at high temperatures, phase separation (cloud point) of non-ionic surfactants may result in a reduction in surfactant concentration (Zhao et al., 2005; Hirasaki et al., 2011). At high temperatures of 95 °C, a zwitterionic surfactant was synthesized with exceptionally low CMC values to reduce the adsorption rates by decreasing free monomers of the surfactant in the solution (Bataweel and Nasr-El-Din, 2012). However, at temperatures exceeding 120 °C, the majority of the surfactants will either degrade or precipitate (Negin et al., 2017).

It should be noted that each surfactant has a different CMC value, which may change with the temperature (Emrani and Nasr-El-Din, 2015; Islam et al., 2015). For ionic surfactants, the Krafft point (Krafft temperature) is defined as the minimum temperature at which micelles can be formed in a solution (Dicharry et al., 2016). Therefore, at temperatures below the Krafft point, surfactant crystals will separate from the solution as the solubility decreases. The solubility of ionic surfactant accordingly increases as the temperature increases to the Krafft point, where the CMC is achieved (Inada et al., 2017; Miyake and Oyama, 2009).

On the other hand, for non-ionic surfactants, the solubility is characterised by the cloud point: depending on the structure of the surfactant, the cloud point varies from 60 to 120 °C. When this temperature is exceeded, the surfactant begins to degrade or precipitate (Aktar et al., 2020; Negin et al., 2017). The precipitation and separation of non-ionic surfactants at the cloud point leads to a decrease in the surfactant concentration, which therefore increases the IFT and decreases the surfactant performance (Hirasaki et al., 2011).

When the temperature of a non-ionic surfactant solution reaches the cloud point, the solution becomes turbid, and species begin to separate. This is due to the polyoxyethylene groups of the surfactants hydrating as the temperature increases beyond the cloud point (Mukhopadhyay et al., 2019). Experiments performed by Ye et al. (2008) demonstrated that temperature is the main factor that influences the interfacial tension of a surfactant solution; with increasing temperature, the IFT between the crude oil and surfactant solution decreases. Moreover, the temperature affects the dynamic interfacial tension, in that increasing the temperature decreases the time required for the IFT to reach the solution equilibrium. However, when mixing surfactants, the effect of temperature is neglected due to the effect of synergism. This is attributed to the aggregation of surfactant molecules at the interface between the oil and solution; thus, the compact arrangement and better ability to modify the interface properties of oil and water is the dominant mechanism to reduce the IFT, and the temperature has a lesser effect on IFT reduction. Karnanda et al. (2013) found that temperature and pressure have no effect on the CMC of Triton X-405, a non-ionic surfactant; however, the CMC of Zonyl FSE anionic surfactant decreases with increasing pressure and levels out with increasing temperature until 80 °C, beyond which point the CMC increases. Puerto et al. (2012) demonstrated that, at high reservoir temperatures, the cloud point of non-ionic surfactants (such as alkoxylatedglycidyl ether sulfonate, or AGES) negatively affects the surfactant performance during the EOR process. This adverse effect of AGES occurs because the aqueous saline solutions of AGES separate into two liquid phases at the cloud point temperatures. Accordingly, the Krafft and cloud points for ionic and non-ionic surfactants, respectively, should be tested before surfactants are used under reservoir conditions (Schramm, 2000; Schott, 2005). The effect of temperature on surfactant stability and EOR efficiency is summarised in Table 3.

Furthermore, temperature has a significant impact on the

wettability alteration process. As the temperature rises in carbonate reservoirs, the water-wetting behaviour seems to dominate. In studies conducted by Zhang et al. (2006)c and Austad et al. (2005) spontaneous imbibition from chalk resulted in an increase in oil recovery with a rise in temperature. This improvement was attributed to the higher affinity of  $\text{SO}_4^{2-}$  ions for the carbonate surface at higher temperatures, which causes the negatively charged carboxylate groups ( $\text{R-COO}^-$ ) of the sulfate ions to be attracted onto the positively charged carbonate surface, releasing the oil from the rock surface, and changing the wettability of the rock to a more water-wet state. Moreover, the non-ionic surfactants have beneficial effects on decreasing the contact angle between the non-ionic surfactant and carbonate surface at high-temperature condition (Gupta and Mohanty, 2010), while temperature increase has a mixed effect on wettability alteration by zwitterionic surfactants (Adejare et al., 2012).

### 3.2. Effect of salinity

The presence of a saline environment has a significant influence on surfactant performance, as high-salinity conditions have an adverse impact on the solubility of surfactants, because surfactants tend to stay in the oleic phase which hinders achieving lower IFT (El-Batanoney et al., 1999). Therefore, an optimum salinity should be attained at which equal quantities of oil and water can be solubilised to form microemulsions (Hirasaki et al., 2011; Gao and Sharma, 2013b). An experimental investigation conducted by Chou and Shah (1981) proved that maximum oil recovery was achieved when the salinity of connate water and polymer solution were at the optimum surfactant formulation salinity.

Anionic surfactants are sensitive to high-salinity aqueous solutions, as the surfactants begin to precipitate due to interaction between the salt ions and surfactant molecules (Al-Hashim et al., 1988). Additionally, the increase in salinity increases the adsorption of anionic surfactants on Berea sandstone due to the increase in the surface acidity and the composition of the electric double layer, which reduces the electrostatic repulsive between the surfactant monomers and the surface of the clay minerals (Kwok et al., 1993). Furthermore, as anionic surfactants are commonly used in chemical EOR processes, their adsorption on limestone and sandstone increases with the increase in divalent cations. This is due to the presence of cations and their adsorptions on the rock surface, which reduces the repulsion forces between the anionic surfactant molecules and the negative charges on the rock surface; this, in turn, allows surfactant molecules to be adsorbed on the rock surface (Azam et al., 2013). Moreover, the presence of a high  $\text{Ca}^{2+}$  concentration in limestone rocks increases the surfactant precipitation (Al-Hashim et al., 1988). On the other hand, the presence of divalent cations can reduce the adsorption of cationic surfactants into carbonate rocks, as cations with stronger positive charges will be adsorbed on the carbonate surface (Ma et al., 2013). Moreover, anionic surfactants have the ability to change carbonate wettability to more water-wet only when the brine salinity is low, particularly when divalent ions like  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are present. Multivalent cations can interact with anionic surfactants, causing precipitation and decreasing the wettability altering effect in carbonate rocks (Deng et al., 2019). Gupta and Mohanty (2011) experimentally showed that with increasing the salinity, the optimum concentration of surfactant decreased, and it resulted in an increase of the optimal contact angle.

Baviere et al. (1988) experimentally investigated the potential of alpha-olefin sulfonate (AOS), an anionic surfactant, for EOR processes under conditions of high temperature, salinity, and hardness. The results show that the AOS surfactant has high salt tolerance even in the presence of calcium ions. The solubility of the AOS

**Table 3**  
Summary of several studies highlighting the surfactant stability under high-temperature conditions.

Reference	Type and name of surfactants	Experimental conditions	Type of formation	Summary of results
Karnanda et al. (2013)	Anionic: Zonyl FSE fluorosurfactant Non-ionic: Triton X-100, Triton X-405	Temperature: 20–90 °C Pressure: 13790 kPa Salinity: Brine 1 NaCl 100 kg/m <sup>3</sup> , Brine 2 NaCl 95 kg/m <sup>3</sup> and CaCl <sub>2</sub> 5 kg/m <sup>3</sup> , Brine 3 NaCl 83 kg/m <sup>3</sup> and CaCl <sub>2</sub> 17 kg/m <sup>3</sup>	Sandstone	Temperature significantly affects the IFT of oil and the brine solution in the presence of non-ionic surfactant. The CMC value for the anionic surfactant increased gradually with increasing temperature.
Azam et al. (2014)	Anionic: Synthesized surfactant contained C18 carbon chain and a sulfonate headgroup	Temperature: 25–70 °C pH: Sodium meta borate (9.5) & sodium tetra borate (10.5)	Sandstone	Anionic surfactants performed better at higher pH and temperature values. Surfactant adsorption reduction occurs due to the translational kinetic energy.
Adkins et al. (2010)	Anionic: Two types of Guerbet ethoxylates, C13–7PO, C16–17–7PO, C20–24 IOS, C12–15–3EO	Temperature: 85, 100, 120 °C Pressure: 3447 kPa	Sandstone	Hydrolysis of surfactant enhanced the stability and controlled decomposition of the ether sulfate surfactants. A wide range of surfactant structures can be used for high-temperature conditions.
Ghosh and Obasi (2013)	Non-ionic: Different chain length of alkyl-polyglucoside (APG)	Temperature: 104 °C Salinity: 263,000 TDS	Carbonate	Eco-friendly surfactant is suitable for high-temperature and high-salinity conditions. Optimum oil recovery was achieved from a carbonate reservoir under high-temperature and high-salinity conditions.
Wei et al. (2020)	Non-ionic: APG	Temperature: 20–115 °C Salinity: NaCl, MgCl <sub>2</sub> , CaCl <sub>2</sub> 10–160 kg/m <sup>3</sup>	Sandstone	Surfactant adsorption decreased slightly at elevated temperature. Surfactant adsorption proven to be a spontaneous entropy-driven process.
Abbas et al. (2020)	Anionic: Aerosol-OT	Temperature: 25–85 °C Salinity: NaCl 0, 20, 35, 60 kg/m <sup>3</sup>	Quartz sand Kaolinite illite Montmorillonite	Temperature increased the surfactant CMC. High temperature led to reduction in surfactant adsorption.
Hocine et al. (2018)	Anionic: Alkyl ether sulfates, alkyl glyceryl ether sulfonates, alkyl benzene sulfonates and internal olefin sulfonates	Temperature: 100 °C Salinity: 2 kg/m <sup>3</sup> , containing 0.3 kg/m <sup>3</sup> of (Ca <sup>2+</sup> & Mg <sup>2+</sup> )		Anionic surfactants sustain high-temperature conditions and outstanding stability over year-long storage. Sulfonate-based surfactants exhibit remarkable stability at high-temperature conditions.
Puerto et al. (2012)	Anionic: Alkyl glyceryl ether sulfonates (AGES), internal olefin sulfonate (IOS)	Temperature: 85–120 °C Salinity: NaCl 10–230 kg/m <sup>3</sup>		An excellent solubility of mixed surfactants at different temperature ranges. Surfactant formed single-phase micellar solutions at low temperature. Surfactant separated into rich and lean liquid phases above the cold point temperature.
Austad et al. (2005)	Cationic: C8TAB	Temperature: 30, 90, 130 °C	Carbonate	Water-wet condition increased with increasing the temperature for carbonate reservoirs. The adsorption of cationic surfactant into chalk increased with increasing the temperature. Spontaneous imbibition from chalk resulted in an increase in oil recovery with a rise in temperature.

surfactant in high-salinity brines can be achieved through the addition of an alcohol or increasing the temperature. Thus, AOS has high solubility and low IFT at high temperatures across a high range of salinities. The surfactant adsorption on kaolinite increased slightly as salinity increased even at high surfactant concentrations.

The solubility, surface activity and adsorption of non-ionic surfactants are affected by salinity. Nevskaia et al. (1998) found that Triton X-100 (a non-ionic surfactant) exhibits three different types of adsorption behaviour in the presence of NaCl when different types of quartz rocks (QA, QB and QC) are used. The adsorption of Triton X-100 was decreased when NaCl was added to the solution on the QA sample and increased when testing on the QB rock; moreover, no changes were observed during testing on the QC rock. These different behaviour is associated with the interactions between salt cations and different surface hydroxyl groups, as well as

the presence of surface impurities rather than salt-TX-100 interactions. The effect of aqueous phase salinity on the surfactant flooding process is summarised in Table 4.

### 3.3. Effect of pH

The pH is one of the factors affecting surfactant flooding efficiency, as the rate of surfactant adsorption is influenced by the rock surface charges, which vary with changes in pH. The point of zero charge (PZC) is the pH value at which the net charge on the surface (surface charge density) is zero. It is an essential rock characteristic because at pH levels greater than their PZC, the surfaces develop a negative charge (Grigg et al., 2004). Therefore, to determine the causes of adsorption, the PZC of the adsorbents (crushed calcite and crushed sandstone rock samples) should be measured. An

**Table 4**  
Summary of several studies highlighting the influence of salinity conditions on surfactant flooding for the EOR process.

Reference	Type and name of surfactants	Salinity	Type of formation	Summary of results
Baviere et al. (1988)	Anionic: Alpha olefin sulfonates (AOS)	Injected brine: NaCl 0.6–80 kg/m <sup>3</sup>	Charentes kaolinite	Low IFT and high solubility were achieved under high-salinity conditions. The adsorbed amount of sulfonate on kaolinite moderately increased with increasing salinity.
Aoudia et al. (2010)	Anionic: Ethoxylated sulfonates	Injected brine: NaCl 30 kg/m <sup>3</sup>	Carbonate	Ultralow IFT and high oil recovery were achieved at high-salinity and high-temperature conditions.
Ghosh and Obasi (2013)	Zwitterionic: Amphoteric surfactants Non-ionic: Different chain length of alkyl-polyglucoside (APG)	Injected brine: 263 (TDS)	Carbonate	Low surfactant concentration showed excellent salinity tolerance. IFT values are not affected at high salinity and temperature conditions.
Lu et al. (2014b)	Anionic: Novel Guerbet alkoxy carboxylate, with IOS co-surfactant	Initial salinity 117 kg/m <sup>3</sup> Surfactant salinity 57 kg/m <sup>3</sup> Injected brine 10 kg/m <sup>3</sup>	Carbonate	Novel surfactant was able to reduce the IFT to ultralow values. The wettability of carbonate rock changed in high-salinity and -hardness environments.
Nevskaia et al. (1998)	Non-ionic: Triton X-100 Anionic: NP4S, NP10S, NP25S	Surfactant solution salinity: NaCl 1–20 kg/m <sup>3</sup> , CaCl <sub>2</sub> 1–10 kg/m <sup>3</sup>	Sandstone	Three different types of adsorption behaviour observed when using different quartz rocks. Interaction of salt ions with rock surface minerals increases the surfactant adsorption rate. Adsorption of an anionic surfactant on quartz and kaolin rocks increased in the presence of NaCl.
Saxena et al. (2019b)	Anionic: Soap-nut surfactant	Surfactant solution salinity: NaCl 0–30 kg/m <sup>3</sup>	Carbonate Sandstone Bentonite	High salinity increased surfactant adsorption. Adsorption process affected by rock mineralogy and morphology.
Gupta and Mohanty (2010)	Anionic: Sodium dodecyl sulfate	Surfactant solution salinity: NaCl 10 kg/m <sup>3</sup> , CaCl <sub>2</sub> 1 kg/m <sup>3</sup>	Kaolinite	Surfactant adsorption varied with formation type. Surfactant adsorption in the presence and absence of salts follows the Langmuir isotherm models. Trivalent and divalent ions salts increase surfactant adsorption, while mono-ions decrease adsorption. The surfactant adsorption is controlled by the effect of an electrostatic double layer in the presence of salts.
Gupta and Mohanty (2011)	Anionic: Different types of sulfate surfactant (3PO to 8PO) m, (1EO to 4EO), (C <sub>15</sub> –C <sub>18</sub> ), (C <sub>17</sub> –C <sub>20</sub> ), (C <sub>20</sub> –C <sub>24</sub> )	Salinity: NaCl 1–7 kg/m <sup>3</sup> , Na <sub>2</sub> CO <sub>3</sub> 2.5 kg/m <sup>3</sup>	Carbonate	Surfactant concentration required for maximal wettability alteration on a calcite plate decreases as salinity increases. For each surfactant, IFT and contact angle have their optimum values at the same salinity.

opportunity arises where anionic surfactants, when used in cEOR processes, do not suffer from substantial adsorption losses due to the negative surface charge on sandstone at high pH levels (Azam et al., 2013). In an environment with pH lower than PZC, the hydroxyl minerals of the rock will acquire a positive charge, which leads to an increase in anionic surfactant adsorption due to the negative charges of the surfactant's group being attracted to the rock surface (Reaction 1). While, at a pH greater than PZC, the number of hydroxyl groups on the rock surface will be reduced due to the reaction of rock minerals with the hydroxyl groups in the solution; thus, negatively charged hydrated mineral oxides on the solid surface adsorb cationic surfactant (Reaction 2) (Azam et al., 2013; Belhaj et al., 2020; Liu, 2008; Hanamertani et al., 2018). The following reactions describe the mechanism of Berea sandstone acquiring positive and negative charges at low and high pH, respectively:



Therefore, to reduce the adsorption on Berea sandstone in the presence of anionic surfactant, alkalis such as sodium hydroxide or sodium carbonate is used to increase the pH and decrease the density of positive charges on the rock surfaces (Azam et al., 2013; Hirasaki et al., 2011). This was confirmed by Azam et al. (2013), who experimentally investigated the effect of pH on static adsorption onto Berea sandstone using synthesized anionic surfactant. The results revealed that the silica fraction in Berea sandstone acquired a positive charge at low pH and negative charge at high pH.

Therefore, at high pH (above 9.0), the adsorption of anionic surfactants on the rock surface will be reduced due to the repulsive forces between the surfactant head group and the negative charges on the rock surface. Mushtaq et al. (2014) addressed the effect of changing pH in the vicinity of PZC (pH of 7.98), on the adsorption of an anionic surfactant on Malaysian sandstone. In the absence of alkali, the static adsorption of surfactant was higher (3.66 and 4.49 mg/g) at pH values lower than 7.98, while in the presence of alkali at pH greater than 7.98 the surfactant adsorption significantly decreased (0.43 and 0.86 mg/g). Similarly, Bera et al. (2013) studied the adsorption behaviour of cationic surfactant (cetyltrimethylammonium bromide) on the clean sand particles. They demonstrated that adsorption of cationic surfactant increases with increasing the pH of the solution, because the cationic surfactant (with positively charged head groups) is strongly attracted to negatively charged sand surfaces rock at high pH values.

#### 3.4. Effect of surfactant adsorption

The adsorption of surfactant on rock surfaces in porous media is an essential parameter when assessing surfactant flooding in EOR processes and is considered to be the main mechanism of surfactant retention. The process of surfactant adsorption into the reservoir rocks leads to a decrease in surfactant concentration, which in turn deteriorates the favourable properties for the displacement process and reduces the efficiency of the surfactant flooding (Liu et al., 2020). On the other hand, surfactant adsorption is one of the factors that govern the economics of the surfactant flooding process. The adsorption process depends on a number of

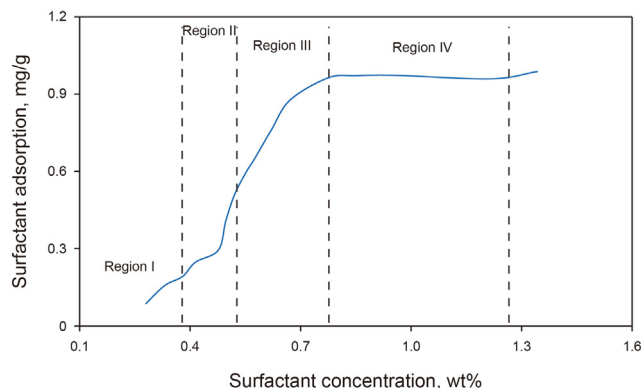


Fig. 2. Surfactant adsorption isotherm on Berea sandstone at 25 °C (adopted from Azam et al. (2013)).

parameters, including the surfactant type, rock morphology and mineralogy characteristics, charges on the rock surface, the type of electrolytes present in the solution, and the presence of a co-surfactant and alcohols (Liu et al., 2004).

Anionic surfactants are recommended for use in sandstone reservoirs, as their adsorptions are relatively low compared to other surfactant types. Sandstone rocks contain a large fraction of silica and small fractions of carbonate and silicate minerals. The silica has a negative charge; therefore, the forces of electrostatic repulsion between the sandstone formation and the anionic surfactant are high, which prevent surfactant adsorption into the sandstone (Ma et al., 2013; Lawson, 1978).

However, adsorption could occur when clay minerals (mainly kaolinite and illite) are present in a sandstone due to the surface charges of clay which are originated from isomorphous substitution, lattice defects, and broken bond. Therefore, the adsorption of an anionic surfactant on the clay minerals is controlled by electrostatic and van der Waals forces (Iglauer et al., 2010; Kwok et al., 1993; Tombácz and Szekeres, 2006).

Adsorption of an anionic surfactant on sandstone is divided into four regions, as shown in Fig. 2. In region I, with increasing surfactant concentration, the adsorption increases linearly as a result of electrostatic interactions between the head group charge and net charge present on the sandstone surface, and the adsorption follows Henry's law. While in region II, the adsorption increases sharply because of the presence of surface aggregates (surface colloids, monolayer, and bilayers) due to lateral interaction between hydrocarbon chains and surface monomers. In region III, the adsorption slightly increases as a result of the electrical neutralization of the sandstone surface by the adsorbed surfactant. Finally, in region IV, the adsorption is constant with an increase in surfactant concentration, as in this region CMC is achieved; thus, any increase in surfactant concentration contributes to the micellization in solution; consequently, adsorption is constant (Azam et al., 2013).

Selecting the correct surfactant type is an essential criterion in EOR designs. Therefore, it is necessary to carry out experimental work in order to characterise the performance of a surfactant that provides favourable interactions with the oil than the rock surface. Curbelo et al. (2007) investigated the adsorption mechanisms of non-ionic surfactants on sandstone rocks, with a focus on the effect of the surfactant ethoxylation degree. ENP95 and ENP150 (prepared from non-ionic surfactants, namely nonyl phenol oxyethylene) with different degrees of ethoxylation were used as non-ionic surfactants. Based on the core flood experiments, the

ethoxylation degrees were found to influence the adsorption of ENP95 and ENP150 into the rock samples. The adsorption rate for ENP95 was higher than that of ENP150, as the ethoxylation degree of the former (9.5) is lower than that of the latter (15.0). This shows that the adsorption of non-ionic surfactant increases with the decrease of the ethoxylation degree due to the surface area of the polar part of ENP90 (low degree of ethoxylation) being lower than that of ENP150 (higher degree of ethoxylation). Therefore, with increasing the degree of ethoxylation, the amount of surfactant required to cover the internal surface of the rock decreases, leading to lower adsorption. In another study, Amiriashoja et al. (2013) investigated the effect of the mineralogical composition of clay on surfactant adsorptions. Sodium dodecyl (anionic) and Triton X-100 (non-ionic) surfactants were used with different types of minerals (quartz, montmorillonite, billite, and kaolinite), which were mixed with clay. They found that the amount of non-ionic surfactant adsorption varied with various adsorbents, while adsorption rates were also higher compared to the anionic surfactant. The amount of clay mineral in the adsorbents was found to be directly related with the adsorption of non-ionic surfactants, as the amount of adsorbed surfactants increased at the higher percentage of clay minerals (clay content varied from 5% wt to 20 wt% of the mixture).

Furthermore, the adsorption of zwitterionic surfactants on carbonate rock surface increased with increasing surfactant concentration as a result of electrostatic and hydrophobic interactions, as well as micellar systems. However, the adsorption is considered low as temperature or salinity increased (Niето-Alvarez et al., 2014).

On the other hand, cationic surfactants show very low adsorption into carbonate rocks, as calcite and dolomite minerals have a positive surface charge; therefore, cationic surfactants are suitable chemicals for use in carbonate reservoirs (Lippmann, 2012). However, some studies indicated that hydrogen ions act as potential determining ions for carbonates, which means that the surface charge on the mineral depends on the equilibrium pH of the solution. The complication of surface charge on carbonates, therefore, makes it difficult to determine whether cationic or anionic surfactants should be used to reduce the electrostatic attraction forces between the surfactant molecules and the formation surfaces (Ma et al., 2013; Ahmadall et al., 1993). Ahmadall et al. (1993) experimentally evaluated the adsorption of cationic surfactants on carbonate minerals. Two cationic surfactants (cetylpyridinium chloride, or CPC, and dodecylpyridinium chloride, or DPC) were used with synthetic calcite and natural dolomite. Their results showed that the cationic surfactants demonstrated significantly lower adsorptions compared to the anionic surfactant with a similar hydrophobic chain length. The addition of salts with multivalent cations decreased the adsorption of the cationic surfactants while increased the adsorption of the anionic surfactant. This is because the addition of cations and lattice ions of the carbonate rocks significantly affected the minerals' surface charge and increased the anionic surfactant adsorption. Moreover, the study concluded that there is a possibility of decreasing the surfactant loss due to the adsorption into carbonate reservoir rocks through the use of cationic surfactants with a proper concentration of multivalent electrolyte as an additive.

Other studies have also reported the successful application of polyelectrolytes as a sacrificial agent to minimise the adsorption of ionic surfactants on oppositely charged surfaces (Budhathoki et al., 2016; Shamsijazeyi et al., 2014; Weston et al., 2014). The presence of polyelectrolytes eliminates electrostatic attractions when they are adsorbed on the rock surface and cover the positive charges. Budhathoki et al. (2016) demonstrated that a polyelectrolyte can reduce surfactant adsorption into a Berea sandstone and Ottawa sand in environments with extremely high salinity. Polystyrene



sulfonate (PSS) with four different molecular weights was used as a sacrificial agent. The results showed that in the absence of PSS, high surfactant adsorption occurred, while in the presence of PSS, adsorption was significantly reduced to less than half of the former case. This is due to the adsorption of PSS on the rock surface, which results in a lower surfactant adsorption into sandstone rocks; subsequently, the presence of PSS improved the oil recovery through surfactant flooding. Also, similar results were reported in studies conducted by [Shamsijazeyi et al. \(2014\)](#) and [Weston et al. \(2014\)](#), in which they demonstrated that an enough amount of polyacrylate significantly minimises the adsorption of the anionic and cationic surfactants.

### 3.5. Effect of surfactant concentration

Surfactant concentration is among the critical factors that should be carefully designed in order to achieve effective and economical surfactant flooding in EOR processes. The surfactant concentration determines the IFT reduction and the surfactant adsorption rate. The ability of surfactant to reduce IFT differs from one surfactant type to another. Accordingly, to achieve a low IFT, the first step is to find the CMC for each surfactant. [Santos et al. \(2009\)](#) experimentally evaluated the effect of electrolytes on the micellization process for non-ionic and anionic surfactants. These results showed that the CMC values for non-ionic surfactants decreased as the number of ethene oxide (EO) groups in the molecular structure increased. Moreover, for the anionic surfactants, the CMC values were higher compared to the non-ionic surfactants due to the presence of electrostatic repulsion between the head groups. Moreover, higher cationic surfactant concentrations result in more water-wet on treated rock samples. Therefore, higher surfactant concentrations promoted higher recovery through imbibition. Cationic surfactants with higher hydrophobicity forms ion pairs with adsorbed organic molecules ([Standnes and Austad, 2000b](#)). Higher hydrophobicity, on the other hand, lowers the surfactant's CMC value, resulting in a lesser number of surfactant monomers, which affects desorption efficiency. Alternatively, increasing surfactant concentration leads to reduced contact angle between the anionic surfactant system and carbonate rock surface ([Alvarez et al., 2014](#)). Similar behaviour is expected for non-ionic and zwitterionic surfactants in regard to carbonate rocks, as increasing surfactant concentration leads to reduce the contact angle ([Souraki et al., 2019](#); [Amirpour et al., 2015](#)). Moreover, because of the amphoteric charges on the heads of zwitterionic surfactants, the wettability modification process in carbonate rocks is considered fast ([Kumar and Mandal, 2017](#)).

Any reduction in the surfactant concentration caused by surfactant adsorption decreases the efficiency of surfactant to reduce the IFT. The adsorption of anionic surfactant increases at higher surfactant concentrations. At surfactant concentrations lower than the CMC value, the rate of adsorption is controlled by the charge on the electrical double layer. Moreover, at higher concentrations, the rate of the adsorption is controlled by the surfactant aggregation in the forms of monomers and micelles on the surface of the formation rock. The addition of surfactants will have no effect on the adsorption rate when the concentration reaches the CMC value, meaning that it will remain constant ([Budhathoki et al., 2016](#)). In the presence of non-ionic surfactants, at low surfactant concentrations, the surfactant is adsorbed on the rock surface in a monomer form through the hydrogen bonding between the surfactant chain and the hydroxy groups. By contrast, at high surfactant concentrations, surfactant adsorption occurs due to the hydrophobic interactions of micelles with the adsorbed monomers at the liquid/rock interface ([Curbelo et al., 2007](#)).

## 4. Synergetic impact of surfactant and other additives for EOR applications

In order to enhance the displacement process in reservoirs, different displacement mechanisms can be applied in a single process simultaneously. This can be achieved through the use of chemical additives such as alkalis, polymer, and nanoparticles along with surfactant flooding to improve the recovery efficiency.

Furthermore, processes of this kind can be adapted to improve the recovery of oil from heavy oil reservoirs. There are heavy oil reserves in which oil viscosity can be as high as 10,000,000 mPa s, in which thermal methods (cyclic steam stimulation, steam flooding, in-situ combustion and steam-assisted gravity drainage, etc.) are utilised ([Gates and Larter, 2014](#); [Kapadia et al., 2015](#); [Sharifi Haddad and Gates, 2017](#); [Sherratt et al., 2018](#)). However, these methods may not be economically or practically viable in thin and deep reservoir zones due to the excessive heat loss and the high energy input requirements for continuous steam generation ([Sherratt et al., 2018](#)). Additionally, the high viscosity of heavy oil rules out the use of certain immiscible displacement processes in conventional reservoirs for mobility control purposes. Therefore, surfactant-based processes have been considered to improve the recovery from heavy oil reservoirs by enhancing emulsion generation ([Bryan and Kantzas, 2008](#); [Yuan et al., 2015](#)).

A large number of studies have been conducted to investigate the fundamentals and mechanisms of surfactant flooding with different additives in conventional and heavy oil reservoirs; these are discussed in the following sections.

### 4.1. Alkaline-surfactant (AS) flooding

Alkaline flooding is an EOR process in which an alkali such as sodium carbonate, sodium orthosilicate, or ammonium carbonate is added to generate soap *in situ*. The soap is generated through interaction between the injected alkali and the fatty acid components of the oil, which creates an emulsified crude oil in displaced water with ultralow IFT. However, the sweep efficiency from the field for alkaline projects is relatively low due to problems associated with precipitation and scaling, which cause formation damage ([Sheng, 2013a](#)). Additionally, the IFT may not remain low under these circumstances, as it is challenging to maintain the optimum salinity for the microemulsions.

To achieve high-efficiency alkaline flooding without increasing the IFT value or causing any formation damage, a low concentration of surfactant will be added to the mixture to ensure that the optimal salinity range is reached, and the flooding efficiency is enhanced. The synergetic effect of adding an alkali to surfactant flooding results in a reduction of the oil/water IFT and in surfactant adsorption on the rock due to the increased pH level, which occurs as a consequence of decreasing the positive charge on the surface ([Hazarika and Gogoi, 2020](#); [Liu, 2008](#); [Thomas et al., 2001](#)). Moreover, the presence of alkali and surfactant generates a stable microemulsions owing to the reduced IFT, which improves the oil sweep efficiency.

Many researchers have shown that the synergy between the surfactant and alkali in reducing the oil/water IFT ([Hunky et al., 2010](#); [Peru and Lorenz, 1990](#); [Thomas et al., 2001](#)). [Chen et al. \(2013\)](#) conducted experiments to investigate the mechanisms of alkali surfactant flooding for enhancing heavy oil recovery and noticed that the oil/water IFT reduction is one of the mechanisms helping to enhance the heavy oil recovery. Additionally, they investigated the IFT reduction in the presence of different concentrations of Na<sub>2</sub>CO<sub>3</sub> solution. They concluded that the presence of the optimum concentration of Na<sub>2</sub>CO<sub>3</sub> solution with the optimum concentration of APG1214 (type of environmental-friendly alkyl

polyglycoside surfactant) surfactant led to a decrease in the IFT to the lowest value of 0.03 mN/m. This is because of the presence of the optimum concentration of alkali leads to providing an appropriate level of  $\text{OH}^-$  at the oil/water interface, which reacts with fatty acid components of the oil and produce *in situ* surfactants to decrease the IFT. Furthermore, surfactant adsorption on silicate mineral (kaolinite) was found to be reduced in the presence of sodium bicarbonate. The presence of alkalis helps alter the reservoir wettability towards a more water-wet condition. Hunky et al. (2010) conducted laboratory tests to demonstrate the effect of alkaline surfactant flooding for heavy oil recovery in oil-wet sandpicks. The results indicated that adding NaOH alkali to a non-ionic surfactant (Igepal) reduced the IFT and significantly increased the heavy oil recovery; this is due to the ionisation of organic acids in the oil which react with the alkali and generate surfactants *in situ*. Moreover, the injected mixture altered the wettability from a strongly oil-wet to a water-wet condition.

Emulsification is one of the AS flooding mechanisms that can increase oil recovery in the tertiary recovery phase. Alkali and surfactant together generate stable microemulsions, under the condition of low/ultra-low IFT, which can enhance sweep efficiency, resulting in increased oil recovery using an AS system. The emulsification process enhances oil recovery in most cases through two mechanisms: (1) emulsification and entrainment; and (2) emulsification and entrapment. In the case of emulsification and entrainment, the IFT is considerably decreased, allowing the droplets of crude oil to be emulsified into the water phase. Then, the droplets are then transported in conjunction with the aqueous phase (Massarweh and Abushaikh, 2020). As a result of this process, oil bulks are gradually produced in the form of fine particles. While emulsification-entrapment mechanism involves the formation of emulsion droplets that plug pore throats and water channels. As a consequence, the water-to-oil mobility ratio decreases, and surfactant solution will be directed to upswept regions, leading to improving both areal and vertical sweep efficiencies (Massarweh and Abushaikh, 2020; Mehranfar and Ghazanfari, 2014). The laboratory core flood experiments conducted by Bryan et al. (Bryan and Kantzas, 2007) revealed that an alkaline/surfactant solution reduced the IFT and formed microemulsions and further showed that the sweep efficiency was improved by plugging the larger rock pores. The results demonstrated that, in addition to the IFT reduction, the emulsification and entrapment of oil droplets are also responsible for oil recovery improvement. Similarly, Liu et al. (2007) experimentally assessed the effect of alkaline ( $\text{Na}_2\text{CO}_3$ , NaOH)/surfactant flooding in a sandpack saturated with heavy oil (with a viscosity of 1800 mPa s) at ambient temperature and atmospheric pressure conditions. Their results indicated that the oil recovery was improved by 24% relative to the initial oil in place. The synergetic effect of  $\text{Na}_2\text{CO}_3$  and surfactant reduced the IFT, which helps with generating oil in water microemulsions and an oil bank and thus improving the oil recovery. Liu et al. (2006) conducted alkaline surfactant flood experiments using heavy oil of 14° API in a high-salinity condition. The results showed that the emulsification of oil in brine will not occur if the alkali or surfactant are used alone; however, the combination of  $\text{Na}_2\text{CO}_3$  with a very diluted surfactant reduces the IFT to ultralow values.

Additionally, increasing pH through the use of an alkali leads to improved surfactant consistency and reduced water hardness, thus increasing the sweep efficiency (Khosravi, 2010). Moreover, the presence of the alkali facilitates the reaction of naphthenic acids in oils with the base and produces a surfactant *in situ*. A surfactant will therefore be generated in a system with higher fatty acid content; accordingly, the optimum salinity depends on the concentration of the generated surfactant, injected surfactant, and water/oil ratio (Sheng, 2013b).

Surfactant adsorption into the reservoir rocks should be minimised to ensure economic feasibility and enhance the efficiency of the flooding process. If an anionic surfactant with a negatively charged head group is added to carbonate rocks with positively charged surfaces, this will increase the surfactant adsorption into the rock (Krumrine et al., 1982). Thus, the presence of an alkali can both increase the pH and change the positive charge of the calcite surface to a negative charge, thereby decreasing the surfactant adsorption (Mohan, 2009). Zhang et al. (2006b) conducted laboratory experiments to investigate the surfactant adsorption on dolomite sand formations using anionic surfactant with and without sodium carbonate. The results indicated that the presence of sodium carbonate resulted in a ten-fold reduction in surfactant adsorption compared to the adsorption in the absence of sodium carbonate. A summary of recent experimental studies on AS flooding for EOR, where different types of alkalis, and surfactants were used under different experimental conditions, is presented in Table 5.

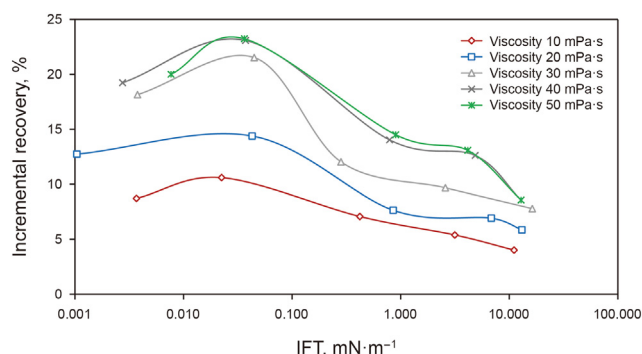
#### 4.2. Surfactant-polymer (SP) flooding

Surfactant flooding has the ability to reduce the IFT between the oil and water to an ultralow value, change the wettability toward water-wet, and emulsify the crude oil; by contrast, polymer flooding works by increasing the displacing fluid viscosity to improve the sweep efficiency (Sheng, 2013c). By combining the positive effect of both the surfactant and polymer into one flooding process, particularly in heavy oil, depleted and water-flooded reservoirs, the challenges of surfactant flooding alone for reservoirs of this kind can be eliminated.

The surfactant in the surfactant/polymer flooding improves the microscopic displacement efficiency, while polymer increases the oil sweep efficiency. In some cases, surfactant/polymer flooding is considered more efficient when compared to alkaline surfactant polymer (ASP) flooding, owing to the former's strong emulsification capacity and low interfacial tension. The presence of alkali may also cause pipeline corrosion and a reduced emulsification process due to the precipitation caused by the reaction between alkali and clay minerals in the reservoir (Yin and Zhao, 2017). Liu et al. (2017) investigated the mechanisms of surfactant/polymer flooding-based oil recovery by means of sandpack, natural core and micro-model experiments. The results showed that oil recovery was significantly increased through enhancing the displacing fluid viscosity when a polymer was used; this is due to the reduced mobility ratio between the displacing fluid and the oil phase. Moreover, in the presence of surfactant, in the case of SP flooding, decreased IFT reduces the adhesion forces, meaning that residual oil will easily move out of the pores as the capillary displacement ratio increases, which in turn improves the oil efficiency. Yin and Zhao (2017) investigated the influence of viscosity and IFT on improving the oil recovery during surfactant/polymer flooding using a 2D vertical heterogeneous model. The results revealed that salinity negatively impacts both polymer viscosity and oil recovery while increasing the polymer concentration helps to minimise this effect. The surfactant-polymer mixture significantly improves the oil recovery, as the polymer pushes surfactant into more pore spaces and displaces the oil from the pores with a reduced IFT. They concluded that mobility control is the main factor affecting the SP flooding in heterogeneous reservoirs, as well as that reducing the IFT to an ultralow value is another factor that helps with forming emulsions and thus improves mobility. However, in some cases IFT reduction to ultra-low values in SP flooding is not required to improve the oil recovery. Yu et al. (2010) experimentally proved that there is an optimum IFT provided higher oil recovery better than the stated ultra-low IFT as shown in Fig. 3. It shows the relationship between

**Table 5**  
Summary of the recent studies of the effect and mechanism of AS flooding on the EOR process.

Author	Type of alkali	Type of surfactant	Type of formation	Experimental conditions	Summary of results
Chen et al. (2013)	Sodium carbonate	Non-ionic: APG1214	Sandstone	Temperature: 50 °C Salinity: 0.5 wt% NaCl	Ultra-low IFT was achieved in the presence of alkali. Oil recovery was increased as flooding formed water in oil microemulsions with heavy oil at the displacement front and oil in water emulsion on the swept region. Tertiary oil recovery was improved by 19.4%.
Krumrine et al. (1982)	Sodium silicates, sodium hydroxide	Anionic: Petroleum sulfonate surfactants	Sandstone	Ambient conditions Salinity: 0.1–1.0 wt% NaCl	AS solution combinations with a high pH significantly reduced the IFT. Surfactant retention is greatly reduced by the presence of alkaline. AS flooding (with small volume of surfactant), oil recovery was increased from 40% to 70%.
Hunky et al. (2010)	Sodium hydroxide	30 commercial surfactants of anionic, cationic, and non-ionic	Sandstone	Temperature: 20–40 °C Salinity: TDS 0.65 wt%	Heavy oil viscosity was reduced, and mobility improved in the presence of alkali with non-ionic surfactant. The use of AS flooding results in higher heavy oil recovery. Alkali with non-ionic surfactant altered the wettability from oil-wet sand to water-wet sand.
Bryan and Kantzas (2007)	Sodium carbonate	Anionic: Sodium alkane sulfonate	Sandstone Carbonate	Ambient temperature Pressure: 2070 kPa Salinity: 20 kg/m <sup>3</sup> NaCl	AS flooding reduced the IFT to levels that allow microemulsions to form under normal reservoir flow rates. The microemulsion generated by AS flooding blocked rock pores, resulting in increased sweep efficiency. AS flooding has considerable potential for heavy oil recovery after primary production.
Hirasaki and Zhang (2003)	Sodium bicarbonate, sodium carbonate	Anionic: Sodium dodecyl 3EO sulfate, sodium tetradecyl (Guerbet) 4PO sulfate	Carbonate	Temperature: 80 °C Salinity: 2.5 wt% NaCl, 0.55w t% KCl, 0.06 wt% Na <sub>2</sub> SO <sub>4</sub>	The presence of sodium carbonate changed the charge of the calcite which is generally positively charged to negative charge. The wettability alternating is a function of the aging time and temperature and the surfactant formulation. Adsorption of anionic surfactants is reduced by the presence of an alkali, particularly sodium carbonate.
Liu et al. (2013)	Sodium hydroxide, sodium carbonate	Anionic: Alkyl sulfates, AOS	Sandstone	Ambient conditions Salinity: 1.1–3.8 wt%	Ultra-low IFT was achieved, leading to an easy dispersion of heavy oil in formation brine. Tertiary oil recovery in sandpack was between 20% and 30%. For thin heavy oil reservoirs, AS is an excellent EOR process.



**Fig. 3.** Relationship between interfacial tension and incremental oil recovery (adopted from Yu et al. (2010)).

incremental recovery and IFT at different polymer viscosities, as the IFT gradually increased from ultra-low values ( $10^{-3}$  mN), the incremental recovery increased and reached the maximum between  $10^{-2}$  and  $10^{-1}$  mN and then started to decrease, showing that the maximum recovery was achieved at low IFT not at ultra-low IFT.

Surfactant/polymer flooding refers to the addition of a surfactant solution that has a hydrophobic group to a water-soluble polymer chain in order to enhance the oil recovery. However, different properties of the surfactant–polymer mixture could lead to the separation of two phases in a flowing stream; therefore, this combination should be carefully investigated. The reservoir salinity, temperature and adsorption influence the polymer viscosity, while the reduction of IFT is influenced by the temperature, crude oil properties and the reduction of surfactant caused by the reservoir rock adsorption (Kang et al. 2000, 2008).

Several studies have looked at surfactant–polymer interactions in the bulk, and the results have been widely described in the

literature. These interactions are determined by electrostatic (polymers can bond with the oppositely charged surfactant) and/or hydrophobic forces (interactions between non-ionic polymers and ionic surfactants) (Bureiko et al., 2015; Kwak, 1998). These interaction forces can be impacted by a number of other factors such as ionic strength (type of salt added, concentration and valence), concentration of surfactant and/or polymer, chemical structures of molecules, degree of branching, charge density (Langevin, 2001). The bulk interactions can cause significant changes in the bulk concentrations of free surfactant and polymer.

Additionally, the relative charge and hydrophobicity of the polymer and surfactant have an impact on their interaction. In particular, strong interaction is remarked in mixtures of poly-electrolytes with oppositely charged surfactants e.g., SDS and polyvinylamine (PVAm), where both electrostatic attraction and cooperative hydrophobic effects play important roles (Claesson et al., 2010; Jiang et al., 2011; Kwak, 1998). Therefore, the strong interaction results in a significant increase in viscosity and even gel formation. On the other hand, weak interaction consists of a neutral polymer and a charged surfactants e.g., sodium dodecyl sulfate (SDS) and poly(*N*-vinylformamide) (PVFAM), in which the nature of the interactions mostly comprises weak electrostatic attractions and/or hydrophobic forces (Taylor et al., 2007).

Surfactant and polymer can be combined in one single chemical component to execute the same mechanisms of the surfactant and polymer, i.e., IFT reduction and mobility control (Tadros, 2009). Therefore, the polymeric surfactant has a high viscosity and high surface active which helps to work effectively in both mobility control and oil emulsification. Moreover, the separation of the two components in the system during the flooding is avoided as a result of using surfactant and polymer as a single component (Guo et al., 2016; Sarsenbekuly et al. 2017a, 2017b). Additionally, the polymeric surfactant has strong shear thinning behaviour compared to the

**Table 6**  
Summary of the recent studies on the effect and mechanism of SP flooding on the EOR process.

Author	Type of surfactant	Type of polymer	Experimental conditions	Summary of results
Zhu et al. (2013)	Sodium petroleum sulphonate, heavy alkyl benzene sulphonate	Partially hydrolyzed KYPAM polymer	Temperature: 40 °C Total salinity: 5.4 kg/m <sup>3</sup>	The viscosity ratio of the SP fluid to the crude oil is a critical factor in achieving maximum oil recovery. The lower the IFT, the higher the incremental oil recovery. Emulsification performance of SP flooding and surface wettability have a significant influence on the oil recovery.
Feng et al. (2012)	Zwitterionic: Betaine	Partially hydrolyzed polyacrylamide (HPAM)	Temperature: 60 °C, Total salinity: 1.4 kg/m <sup>3</sup>	The presence of polymer accelerated the reduction of the oil/water IFT. Ultralow IFT achieved via betaine surfactant. The sandpack flooding results showed high oil recovery with SP flooding compared to polymer flooding.
Samanta et al. (2011)	Anionic: Sodium dodecyl sulfate (SDS)	Partially hydrolyzed polyacrylamide (HPAM)	Ambient conditions	The presence of polymer increased the sweep efficiency by decreasing the mobility ratio. Synergies of the SP flooding increased the oil recovery more than surfactant flooding.
Yin and Zhao (2017)	Anionic: Sulfonate	Partially hydrolyzed polyacrylamide (HPAM)	Temperature: 45 °C Pressure: 1000–2000 kPa Salinity: 2.5–8.5 kg/m <sup>3</sup>	Salinity negatively impacts the polymer viscosity while increasing the concentration helps to minimise this effect. The surfactant–polymer mixture significantly improves the oil recovery. Mobility control is the main factor affecting the SP flooding in heterogeneous reservoirs.
Yu et al. (2010)	Anionic: Petroleum sulfonate	Partially hydrolyzed polyacrylamide (HPAM)	Salinity: 0.865 kg/m <sup>3</sup>	Maximum recovery was achieved at low IFT not at ultra-low IFT. Stable emulsion was formed in the presence of polymer and higher displacement was obtained.
Liu et al. (2017)	LAL, KPS-1 & KPS-2 surfactant	Partially hydrolyzed polyacrylamide (HPAM)	Salinity: 0.315 & 3.3 kg/m <sup>3</sup>	Oil recovery increased by the increase of the viscosity ratio between water and oil or the decrease of IFT. The generated emulsion with low IFT and high viscosity improved the oil displacement efficiency.

polymer solution; at high shear rates, polymeric surfactant and polymer solution have low viscosity (desirable during the injection process), while at higher shear rates, the polymeric surfactant has higher viscosity compared with the polymer solution. This allows the polymeric surfactant to have higher mobility control and sweep efficiency at the zone that was far away from the wellbore compared to the polymer solution (Li et al., 2018). However, IFT reduction by a polymeric surfactant is considered weak ( $\sim 10^{-1}$  mN/m) due to high molecular weight and associated macromolecular-weight surfactants when compared to surfactant flooding ( $< 10^{-3}$  mN/m) (Co et al., 2015). This reduction is still considered low enough to generate microemulsions between the oil and injected solution; moreover, higher viscosity improves the sweep efficiency while also improving the stability of the emulsions due to the adsorption of polymeric surfactant at the oil/water interface (Tadros, 2009). A summary of recent experimental studies of SP flooding for EOR, where different types of surfactants and polymers were used under different experimental conditions, is presented in Table 6.

#### 4.3. Alkaline-surfactant-polymer (ASP) flooding

Alkaline-surfactant-polymer (ASP) is a process involving the injection of a mixed slug of alkali, surfactant, and polymer. The synergies between these three components improve the sweep efficiency by means of three mechanisms. The first of these is lowering the IFT over a wider range of salinity due to the microemulsions created from the generated soap (a surfactant generated *in situ* from the reaction of alkaline solution and organic acids in the crude oil) and the injected surfactant. The generated soap has low optimum salinity, while the synthetic surfactant has high optimum salinity; therefore, the resultant IFT reduction leads to mobilizing the remaining oil and improving the macroscopic sweep efficiency (Nelson et al., 1984). The second mechanism is the presence of the alkali, which reduces surfactant adsorption into the rock surface. The polymer can also help to reduce the surfactant adsorption via the adsorption competition between the surfactant and polymer

(Sheng, 2013a). The third mechanism increases the slug viscosity by means of a polymer, which in turn reduces the mobility ratio. This helps to improve the sweep efficiency, stabilise microemulsions and prevent them from coalescence (Deng et al., 2002; Sheng, 2013a). Huang and Dong (2004) assessed the synergistic effects and potentials of ASP flooding in sandstone oil reservoirs. The IFT was reduced through the use of anionic surfactants and with a slight additional reduction in the presence of a low-concentration NaOH alkaline, while an ultra-low IFT was achieved at a high concentration of NaOH alkaline. Oil recovery from the coreflood experiments revealed that ASP flooding improved the sweep efficiency with more than 39.1% of the initial oil in place (IOIP), compared to IOIP recoveries of 19.9% and 31.1%, respectively in polymer flooding and surfactant/polymer slug experiments.

Hou et al. (2004) reported the balance between IFT reduction and viscosity increase on the oil recovery in different heterogeneous porous media. A critical displacement viscosity was proposed as a dominant oil recovery mechanism for ASP flooding, which can be used to optimise the ASP flooding chemical formula. If the viscosity of the ASP solution is lower than the critical displacement viscosity, the sweep efficiency of ASP flooding is dominated by the ASP viscosity, and the IFT reduction has a minimum effect on oil recovery. Both viscosity and IFT reduction contribute to oil recovery when the ASP viscosity exceeds the critical displacement viscosity. In addition, the study concluded that the contribution of ultra-low IFT to oil recovery decreased with an increasing degree of reservoir heterogeneity, while the contribution of apparent viscosity was found to increase when the degree of the reservoir heterogeneity increased.

Most surfactants in ASP flooding require a high concentration of alkali. However, alkali can react with rock minerals and cause many technical problems: these may include scale formations near wellbore and production systems, reduction of injectivity and a decrease in polymer viscoelasticity. The concentration of alkali should therefore be decreased without affecting the process efficiency. In a study conducted by Hou et al. (2001), they showed that decreasing the alkali concentration led to increasing IFT; however,



**Table 7**  
Summary of the recent studies of the effect and mechanism of ASP flooding on the EOR process.

Author	Type of alkali	Type of surfactant	Type of polymer	Experimental conditions	Summary of results
Huang and Dong (2004)	NaOH, Na <sub>2</sub> CO <sub>3</sub>	1298 soft acid, 1298 hard acid	Polyacrylamides.	Temperature: 49 °C Salinity: 4.1 kg/m <sup>3</sup>	The presence of alkali helped to slightly reduce IFT for oils with a low acid number. Synergies of the ASP system improved the oil recovery to a greater extent than polymer or surfactant/polymer slug floods.
Hou et al. (2005)	NaOH	Alkyl benzene sulfonate	Partially hydrolyzed polyacrylamide	Salinity: 6.8 kg/m <sup>3</sup>	The alkali has an adverse effect on the viscoelasticity of the ASP solution. Ultra-low IFT is responsible for the oil recovery from the homogenous reservoirs. ASP solution viscoelasticity contributes more to recovery from heterogeneous reservoirs. Using low alkali concentration reduced both the effect of the scaling problem and the cost of ASP flooding.
Hou et al. (2004)	NaOH	Sodium alkylbenzene sulfonate	Polyacrylamide	Temperature: 45 °C Salinity: 3.7 kg/m <sup>3</sup>	The sweep efficiency of ASP in the heterogeneity reservoir can be improved by reaching the appropriate viscosity of the displacing solution. The reduction of IFT to an ultralow value made a minimum contribution to the oil recovery. The viscosity of the ASP solution was the dominant parameter for the oil recovery efficiency of ASP flooding. ASP flooding is significantly affected by the wettability condition of the core. Water-wet and oil-wet are considered favourable conditions for enhanced oil recovery for ASP flooding.
Han et al. (2006)	NaOH	Sodium alkylbenzene sulfonate	Hydrolyzed polyacrylamide	Ambient conditions	Sodium carbonate in ASP flooding reduced the surfactant adsorption on carbonate surfaces at low salinity concentrations. Reduction of surfactant adsorption is affected primarily by the reservoir salinity. The optimal salinity for alkaline conditions mainly depends on the soap to surfactant ratio.
Zhang et al. (2006b)	Na <sub>2</sub> CO <sub>3</sub> , NaOH	Ammonium C16-17 7PO, sulfate (N67, 7POS), internal olefin sulfonate (IOS)	Hydrolyzed polyacrylamide, Flopaam 3330S	Ambient temperature Salinity: NaCl 0.002–90 kg/m <sup>3</sup>	Surface tension increases slightly with the increase of polymer concentration and decreases with increased alkali concentrations. Low anionic surfactant concentrations slightly reduced the alkali/polymer solution viscosity; however, significant viscosity improvement was achieved at higher surfactant concentration. Rock and reservoir fluid properties affected ASP slug selections.
Mandal and Ojha (2008)	NaOH	Sodium dodecyl sulfate, sodium dodecylbenzene sulfonate	Polyacrylamide	Temperature: 25–45 °C.	Surfactant adsorption was reduced in the presence of low-cost alkali. The presence of polymer and alkali had no significant effect on reducing the IFT.
Feng et al. (2012)	Lignin	Betaine	Partially hydrolyzed polyacrylamide	Temperature: 90 °C Salinity: 136.6 kg/m <sup>3</sup>	The combination of organic ASP resolved the problem of salt precipitation in an inorganic ASP system. The reaction between the organic alkali and the acidic components in the heavy oil generated in-situ soap, which helps with generating adequate W/O emulsions. Ultra-low IFT and low adsorption were achieved by using ASP flood for the carbonate reservoir. The coreflood results using limestone and carbonate rocks showed high oil recovery.
Fu et al. (2016)	Ethanolamine	Shengli petroleum sulfonate	Hydrolyzed polyacrylamide	Salinity: 136.6 kg/m <sup>3</sup>	Chemical formulations with ultra-low IFT for a high-permeability, non-fractured, high-temperature and salinity carbonate reservoir were achieved. Sodium carbonate and sodium hydroxide cannot be used as alkali in rocks containing anhydrite and dolomite, respectively. Low surfactant retention on carbonate surfaces was achieved for economic ASP flooding.
Abalkhail et al. (2019)	Na <sub>2</sub> CO <sub>3</sub> NaOH	Internal olefin sulfonates with varying ranges of carbon numbers	Hydrolyzed polyacrylamide, Flopaam 3330S	Temperature: 100 °C Salinity: 60 kg/m <sup>3</sup>	
Abalkhail et al. (2020)	Sodium chloride, potassium chloride, sodium sulfate & sodium hydroxide	Carboxylate and sulfonate surfactants, IOS with a varying range of carbon numbers	Hydrolyzed polyacrylamide, Flopaam 3330S	Temperature: 100 °C Salinity 60 kg/m <sup>3</sup>	

the viscoelasticity of the ASP solution was increased. High viscoelasticity is an advantage for the displacement in heterogeneous porous media, which helps with displacing residual oil from unswept areas. They concluded that the high viscoelasticity of the ASP solution is an important factor in achieving better displacement efficiency, while an ultra-low IFT value is not an important

factor in improving oil recovery. This is because, in the presence of an ASP solution with ultralow IFT and low viscosity, it is difficult for the solution to efficiently invade and displace the residual oil from the porous media, as the most displacing fluid flows through the flowing channel of water formed by water flooding. Therefore, the viscoelasticity of the ASP solution is a more important factor than

ultra-low IFT. A summary of recent experimental studies on ASP flooding for EOR, where different types of alkalis, surfactants and polymers were used under different experimental conditions, is presented in Table 7.

#### 4.4. Nanoparticle-surfactant (NS) flooding

Over recent years, nanotechnology has made substantial progress in improving oil recovery by enhancing the properties of chemicals and displacement mechanisms in pore spaces to increase the efficiency of commonly used methods, such as the use of nanoparticles (NPs) with surfactants for surfactant flooding foam injection processes, among others (Bashir et al., 2019; Rafati et al., 2016, 2018a). Adding nanoparticles to the surfactant can favourably modify its properties and accordingly improve the efficiency of the surfactant flooding in EOR processes (Cheraghian and Hendraningrat, 2016; Sun et al., 2017; Yousefvand and Jafari, 2018). The synergetic effects of nanoparticles and surfactants help with stabilising microemulsions or foam structures in porous media by modifying the interface of liquids (microemulsions) or gas and liquid (foam), which involves complex interface phenomena (Almahfood and Bai, 2018; Bashir et al., 2018b; Li et al., 2020; Rafati et al., 2018b; Singh and Mohanty, 2015). Almohsin et al. (2018) studied the effect of adding SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> NPs to three different types of surfactants (non-ionic, anionic, and cationic) on the stability of microemulsions at high-temperature conditions. Their results indicated that adding SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> NPs to anionic and cationic surfactants generate microemulsions that remain stable for a long time and will not be separated under higher temperatures. This is due to nanoparticles being stable over time and resistant to coalescence between droplets, which is one of the main mechanisms underpinning demulsification by breaking crude oil emulsion into oil and water phases (Kong and Ohadi, 2010). The generation of stabilised microemulsions accordingly helps to improve the sweep efficiency and oil recovery.

Furthermore, NPs can effectively reduce the IFT of the water/oil phase; as they are adsorbed on the interface, and through electrostatic repulsion forces between the surfactant molecules and NPs, surfactant diffusion into the interface can be enhanced (Almahfood and Bai, 2021; Bashir et al., 2019; Nourafkan et al., 2018; Ravera et al., 2006). Moreover, NPs can be adsorbed on the rock surface, which alters the wettability of the carbonate and sandstone reservoirs (Lim et al., 2015; Dehghan Monfared et al., 2016). Following their experimental studies, Giraldo et al. (2013) concluded that the presence of a low concentration of alumina NPs in an anionic surfactant could change the wettability from oil-wet to water-wet thereby improving the recovery. Additionally, Hammood et al. (2019) studied the effect of using SiO<sub>2</sub> nanoparticles in sodium dodecyl sulfate (SDS) surfactant on the IFT reduction and wettability alteration in carbonate reservoirs. The results showed that an increase of SiO<sub>2</sub> NPs concentration reduced the IFT between the oil and aqueous solution. This is because the SiO<sub>2</sub> NPs were adsorbed on the interface of the fluids and created a layer between the two phases, thereby reducing the friction forces between the phases and generating a lower IFT.

Additionally, SDS-SiO<sub>2</sub> NPs changed the wettability from oil-wet to water-wet, which helped to improve the oil recovery. Similarly, Alhuraishawy et al. (2019) confirmed that the use of the same nanoparticles and surfactant can improve the oil recovery from carbonate reservoirs. These authors highlighted that this improvement in oil recovery was due to the deposition of SiO<sub>2</sub> NPs on the pore walls of porous media, resulting in the wettability alteration. They further noted that blocking of pore throats may occur if higher SiO<sub>2</sub> NPs concentrations are used. Moreover, the addition of NPs to the surfactant solution improves the solution's

rheological properties, which can facilitate oil recovery by means of surfactant flooding (Ravera et al., 2006).

The huge amount of surfactants required to reduce the IFT to an ultralow value, along with the associated costs, both constitute drawbacks of chemical flooding. Recent studies have found that the presence of nanoparticles could result in reduced surfactant adsorption, which can be referred to less direct contact between the surfactant and rock surface. Nourafkan et al. (2018) experimentally evaluated the reduction in the adsorption of a mixture of anionic and non-ionic surfactants through the use of TiO<sub>2</sub> NPs at optimum salinity in a sandstone rock. The results revealed that TiO<sub>2</sub> NPs have potential applications in EOR processes, as this approach can successfully reduce the surfactant adsorption to half of the initial adsorption level. This occurs due to the NPs' ability to transport through the porous medium carrying the surfactant, thereby reducing direct contact between the surfactant and rock surface. Additionally, the oil recovery in the presence of TiO<sub>2</sub> NPs with the mixed surfactant was increased by 7.81% of OOIP when compared to surfactant alone.

Generally, for sandstone reservoirs with a negatively charged surface, using a positive charge surfactant (cationic surfactant) will lead to a huge amount of surfactant being adsorbed on sandstone rocks. Therefore, an anionic surfactant (which is a negatively charged type) would be the best option for this type of reservoir. However, the adsorption of anionic surfactant may still occur due to salinity, hardness, and the presence of clay. Agrawal et al. (2019) studied the influence of surface-modified silica with anionic surfactant on reducing surfactant adsorption into clay-containing reservoirs. Static and dynamic experiments were used with two types of injection: single-step injection, involving an injection of pre-mixed NPs and surfactant, and two-step injection, where porous media was pre-treated with the NPs, followed by surfactant injection. These results demonstrated that surfactant adsorption was much lower under the two-step injection than when SiO<sub>2</sub> NPs were used. Recovery was increased by 10% at 80 °C in the presence of NPs and surfactant. Another related study was carried out by Suresh et al. (2018); here, the dynamic adsorption experiments on a sandpack demonstrated that the surfactant adsorption was reduced threefold in the presence of negatively charged silica NPs. This is due to the charge and high surface area of the SiO<sub>2</sub> NPs in which they were adsorbed on the rock surface so that the surfactant effectively improved the oil recovery. Zargartalebi et al. (2015) studied the influence of adding silica NPs to anionic surfactant in an enhanced oil recovery process by measuring the IFT and surfactant adsorption. Their results revealed that the presence of SiO<sub>2</sub> NPs at low surfactant concentrations reduced the IFT, while the IFT increased at high surfactant concentrations. Surfactant adsorption was found to be significantly lower in the presence of nanoparticles at all surfactant concentrations, and remarkably low when hydrophobic NPs were used. The uses of nanoparticles on surfactant flooding for EOR processes are summarised in Table 8.

## 5. Summary of the key findings and challenges

This manuscript has presented a critical review of the most recent research into surfactant flooding for enhanced oil recovery. The reviewed studies show that surfactant flooding is used to mobilise and recover the residual oil from the pore spaces of the rock through reducing the IFT between oil-water phases, creating microemulsions and a shift in wettability towards more water-wet conditions. Different types of surfactants are used for EOR; thus, when designing an oil recovery process, the most appropriate surfactant should be selected. The selection process itself requires a series of tests to facilitate understanding of the most suitable type of surfactant and its concentration while also considering the

**Table 8**  
Summary of several studies highlighting the presence of nanoparticles in the surfactant flooding.

Author	Types and name of surfactants	Name of nanoparticles	Experimental conditions	Oil recovery factor	Summary of results
Nourafkan et al. (2018)	Anionic: Alkyl aryl sulfonic acid	Titanium (IV) oxide	Temperature: 40 °C	91.66% OOIP	Surfactant retention was reduced by 50% in the presence of NPs. The presence of NPs reduced the direct interaction between the surfactant groups and the rock surface. Compared to the surfactant alone, oil recovery was increased by 7.81% of OOIP.
Omidi et al. (2020)	Anionic: SDS Non-ionic: LAPE Zwitterionic: TR-880 Cationic: CTAB	Fe <sub>3</sub> O <sub>4</sub> /eggshell	Temperature: 65 °C Pressure: 17236 kPa Salinity: NaCl 0–90 kg/m <sup>3</sup>	55.15% OOIP	The presence of NPs had a favourable impact on surfactant's performance in terms of IFT reduction and wettability alteration. Oil recovery improved by 8.16% of OOIP. Mixed NPs and surfactant effectively shifted the relative permeability curves to the right, decreased the capillary number and improved the mobility ratio. Surfactant adsorption was reduced by 40% due to the presence of NPs. The presence of NPs helped in altering the porous media wettability. Oil recovery was increased by 18% compared to surfactant flooding.
Franco et al. (2020)	Anionic: Commercial surfactants (SA and SB)	Commercial nanoparticles (CAN and CNB)	Temperature: 50 °C Pressure: 9997 kPa Salinity: NaCl 57 kg/m <sup>3</sup> , CaCl <sub>2</sub> ·2H <sub>2</sub> O 135 kg/m <sup>3</sup> , MgCl <sub>2</sub> ·2H <sub>2</sub> O 380 kg/m <sup>3</sup> , BaCl <sub>2</sub> ·H <sub>2</sub> O 0.996 kg/m <sup>3</sup> , KCl 74 kg/m <sup>3</sup>	28% OOIP	The rheological properties of surfactant injected during the EOR process were improved in the presence of NPs. Oil recovery was improved by 4.85% compared to recovery with surfactant only. Surfactant adsorption in the sand was decreased by 50% in the presence of NPs. NPs significantly improved surfactant retention. The SDS surfactant improved silica NPs' stability and reduced the extent of salt-induced agglomeration. NPs/surfactant improved the oil recovery at high salinity and temperature conditions. Small size and low concentration of NPs are desirable for EOR applications.
Cheraghian (2016)	Anionic: SDS	Titanium dioxide	Salinity: NaCl 17.1 kg/m <sup>3</sup> , Na <sub>2</sub> SO <sub>3</sub> 0.1 kg/m <sup>3</sup> , CaCl <sub>2</sub> 3.2 kg/m <sup>3</sup> , MgCl <sub>2</sub> ·6H <sub>2</sub> O 0.9 kg/m <sup>3</sup> , Na <sub>2</sub> HCO <sub>3</sub> 0.02 kg/m <sup>3</sup>	51% OOIP	
Venancio et al. (2020)	Anionic: SDS	Silica	Salinity: NaCl, MgCl <sub>2</sub> ·6H <sub>2</sub> O		
Chaturvedi and Sharma (2021)	Anionic: SDS	Silica NPs	Temperature: 30–90 °C Pressure: 206 kPa Salinity: NaCl 0–80 kg/m <sup>3</sup> pH: 2–12		

reservoir temperature, the salinity of the formation and injected waters, the pH, and the surfactant adsorption into the rock.

A number of chemical additives, such as alkalis, polymers, and nanoparticles, have been used in surfactant flooding to both improve the surfactant flooding mechanism and enhance the oil

sweep efficiency. Each chemical additive used in surfactant flooding has different effects on oil recovery mechanisms, an understanding of which is key to designing a successful EOR process. Although many studies have been conducted on the application of surfactants for EOR processes, there are still challenges that need to

**Table 9**  
Flooding mechanisms and challenges of surfactants flooding application for EOR.

Type of flood	Flooding mechanisms	Example problems
Alkali-surfactant flooding	Reducing the IFT between the trapped oil and the injected fluid. Forming in-situ microemulsions, which lead to plugging waterflooded channels and improving process sweep efficiency. Improving mobility ratio by reducing the mobility of the water through plugging the water-swept pores using emulsified oil droplets. The presence of alkali increases the pH, which significantly reduces the electrostatic adsorption of the surfactant.	Scaling build-up and clay swelling due to the presence of inorganic alkaline agents. High salinity and high divalent cation concentration negatively affect the emulsification process. An excessive amount of alkalis results in salt concentration that increases beyond the optimum value, thus increasing IFT.
Surfactant-polymer flooding	Adequate reductions in IFT to an ultralow value and altering the surface wettability. Improving both microscopic and macroscopic sweep efficiency. Creating significantly high oil microemulsion at low IFT. Boosting microemulsion stability due to the adsorption at the oil/water interface.	Separation and loss of the two components during the process: either surfactant solubilisation and rock adsorption or polymer degradation. Reservoir heterogeneity affecting the success of the process. High costs associated with the process.
Alkali-surfactant-polymer flooding	Reducing the IFT between the trapped oil and the injected fluid. Reducing surfactant and polymer adsorption through the presence of alkali. Polymer improves the stability of the generated microemulsion by increasing its viscosity. A wide range of salinity conditions are presented for the mixed in situ-generated soap and injected surfactant in which the IFT is low.	Large amount of alkali required scaling problems and corrosion in production facilities. Surfactant precipitation due to the presence of divalent cations in a hard-brine environment. Polymer degradation, plugging and formation damage; associated difficulties in treating the microemulsions produced.
Nanoparticle-surfactant flooding	Reducing the IFT of the oil/water interface and altering the wettability of carbonate rocks to a more water-wet condition. Improving the effective viscosity of the surfactant solution. Reducing surfactant adsorption on the rock surface. Forming stabilised microemulsion and improving its stability.	Poor stability and dispersion problems of nanoparticles under harsh reservoir conditions. Reservoir heterogeneity that might reduce the performance of NPs within porous media. Limited pilot studies.

be addressed. Some of these are summarised in Table 9 for future investigation.

## Acknowledgements

The authors acknowledge the School of Engineering at the University of Aberdeen for providing the required facilities to complete this review study; also, Ahmed Bashir would like to thank the Faculty of Engineering University of Khartoum, Sudan, for the financial support of his studies at the University of Aberdeen.

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