



# The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review

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## Abstract

Enhanced oil recovery (EOR) processes have a great potential to maximize oil recovery factor of the existing reservoirs, where a significant volume of the unrecovered oil after conventional methods is targeted. Application of chemical EOR techniques includes the process of injecting different types of chemicals into a reservoir to improve the overall sweep efficiency. Surfactant flooding is one of the chemical EOR used to reduce the oil–water interfacial tension and to mobilize residual oil toward producing wells. Throughout the process of surfactant flooding, selecting a suitable surfactant for the reservoir conditions is quite challenging. Surfactants tend to be the major factor associated with the cost of an EOR process, and losing surfactants leads to substantial economic losses. This process could encounter a significant loss of surfactant due to adsorption into the porous media. Surfactant concentration, salinity, temperature, and pH were found to be as the main factors that influence the surfactant adsorption on reservoir rocks. Most of the research has been conducted in low-temperature and low-salinity conditions. Only limited studies were conducted in high-temperature and high-salinity (HT/HS) conditions due to the challenging for implementation of surfactant flooding in these conditions. This paper, therefore, focuses on the reviews of the studies conducted on surfactant adsorption for different surfactant types on different reservoir rocks under different reservoir conditions, and the influence of surfactant concentration, salinity, temperature, and pH on surfactant adsorption.

**Keywords** Surfactant flooding · Adsorption · Surfactant concentration · Salinity · Temperature · pH

## Introduction

Rising demand for oil has been noticed due to the fact that it remains the world's most powerful source of energy. This was observed by the increases in exploration and production of oil reservoirs. There was a huge development on the fields of maximizing the oil recovery and production enhancement in progress by oil and service companies. In conventional resources, the recovered volumes from the original oil in place are around 30%. Therefore, the development of more advanced techniques to recover additional oil is required in

order to meet energy demands. Also, conventional methods are not sufficient to increase the amount of recoverable volumes more than the existing reserves (Curbelo et al. 2007).

The applications of enhanced oil recovery (EOR) techniques include the process of injecting extra fluids represented in injecting chemicals or gases and/or thermal energy into a reservoir. The injected fluids will enhance the existing reservoir natural energy by the displacement of oil to a producing well. The mechanism of recovery enhancement involves the formed conditions caused by the interactions between injected fluids and oil resulting in lowering the interfacial tension, oil swelling, oil viscosity reduction, and wettability alteration. The selection of the suitable EOR method for implementation depends on the screening and the evaluation of reservoir properties and conditions as well as the economic feasibility (Green and Willhite 1998). Throughout the past 60 years, a major development has been made on chemical flooding that increased the potentiality of making it the most important EOR method (Demirbas et al. 2015). It was reported

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that chemical EOR has been successfully applied in many countries such as in the USA, China, Germany, France, Austria, and Canada. However, chemical flooding is an expensive recovery method because of the high cost of chemicals.

Chemical EOR application is divided into polymer flooding, surfactant flooding, and alkaline flooding and their combinations. The process of each chemical type is different, and the enhancement achieved by each type will influence the oil recovery by different mechanisms (Buchgraber et al. 2006; Dang et al. 2011). Surfactant flooding is known as the most promising methods among all chemical EOR processes. The mechanism of using surfactants during the surfactant flooding is mainly to reduce the interfacial tension, and for wettability alteration in order to increase the capillary number and to mobilize more oil toward the producing wells (Hirasaki and Zhang 2004). Several studies determined that most surfactants cannot be used in harsh reservoir conditions. Therefore, their poor performance at high-temperature and salinity conditions has led to developing new technologies, chemicals, and formulations in order to overcome these harsh conditions (Azam et al. 2013; Karnanda et al. 2013; Sheng 2015).

Surfactant flooding process encounters a significant loss of surfactant due to retention in the porous media (Amirianshoja et al. 2013). Surfactant retention is divided into precipitation, phase trapping, and adsorption. Surfactant retention due to precipitation and phase trapping can be avoided by choosing surfactants that are tolerant for temperature and salt. However, surfactant adsorption can be only minimized (Kamal et al. 2017; Liu et al. 2004). During the surfactant flooding process, the adsorption of surfactants from the injected slug may impact the effectiveness and the cost of the process (Amirianshoja et al. 2013). Usually, the cost of surfactants can reach half or more of the total project cost (Sheng 2011). Therefore, for an economic perspective, minimizing the amount of surfactant adsorption is a key point in designing surfactant flooding (Barati-Harooni et al. 2016). Surfactant adsorption can lead the surfactant flooding process to fail by affecting the performance of the surfactants which can influence the function of surfactants to lower the oil–water interfacial tension (Curbelo et al. 2007; Zargartalebi et al. 2015). Alkali is used in the alkaline–surfactant (AS) flooding to generate in situ surfactants which are formed from the chemical reaction between the alkali and acidic components in crude oil which can contribute in lowering the interfacial tension. In addition to that, alkali can increase the pH of the aqueous phase and minimize the surfactant used, and thus, it minimizes the surfactant adsorption which contributes to reducing the cost (Sheng 2011). This review will provide information on surfactant adsorption from recent studies to gain an in-depth understanding

of all the factors affecting surfactant adsorption process as well as their mechanisms.

## Surfactants

The term surfactant comes from surface-active agent, and surfactants are chemical compounds utilized to reduce the IFT between two different phases by adsorbing on a surface or a fluid–fluid interface. Surfactants are extensively used chemicals having various EOR applications due to their significance in IFTs reduction and their capability in changing wetting properties (Green and Willhite 1998). Surfactants are known as amphiphilic or amphipathic molecules which contain a polar (hydrophilic) portion and a nonpolar (hydrophobic or hydrocarbon loving) portion. The origin of the term amphiphilic comes from the Greek word “amphi,” meaning “both,” and this describes the fact that all surfactant molecules have at least two parts, the hydrophilic one which is soluble in a specific fluid, e.g., water, and the hydrophobic part which is insoluble in water (Tadros 2014).

According to the nature of the hydrophilic head group, surfactants are classified into different types, and this classification of surfactants is made based on the charges of the polar head group of the surfactant molecule. Surfactants are divided into the classes: anionics (negative charge), cationics (positive charge), nonionics (no charge), and zwitterionics (negative and positive charge) (Bera and Belhaj 2016; Tadros 2014).

### Anionic surfactants

Anionic surfactants are known by having a negative charge on their head group when they are in aqueous solution. These surfactants are widely used in EOR processes, and this is due to (1) their relatively low cost of manufacture, (2) they exhibit relatively low adsorption on sandstone rocks whose surface charge is negative, (3) their efficiency to reduce IFT, (4) their stability at high temperatures (Tadros 2014). Anionic surfactants based on their head polar groups can be classified into carboxylate, sulfate, sulfonate, and phosphate (Kronberg et al. 2014).

### Nonionic surfactants

Nonionic surfactants in aqueous solution do not have any charge on their head group, and they are mainly used as co-surfactant to improve the phase behavior of the surfactant. Nonionic surfactants are much more tolerant of high salinity. Nevertheless, their function of IFT reduction is less as compared to anionic surfactants which restrict them to be used as a primary surfactant in EOR applications. Therefore, a combination of anionic and nonionic is useful to increase

the tolerance to salinity (Sheng 2011). The most widely used nonionic surfactants are those based on ethylene oxide (EO) known as ethoxylated surfactants (Holmberg et al. 2002).

### Cationic surfactants

Cationic surfactants have positive charges on their head groups when they are in the aqueous phase, where they depend mainly on the atom of nitrogen to carry the charge (Kronberg et al. 2014). Cationic surfactants show high adsorption in sandstone reservoir and hence cannot be used for EOR application. However, these surfactants can be used for wettability alteration from oil wet to water wet in carbonate reservoir (Sheng 2011).

### Zwitterionic surfactants

These surfactants consist of two opposite charge active groups. The zwitterionic surfactant can be anionic, nonionic, anionic–cationic, or nonionic–cationic. The positive charge group is always ammonium, and the most common negative charge group is carboxylate. They are also called amphoteric surfactants (Holmberg et al. 2002). These surfactants are tolerant of temperature and salinity. However, their high cost has quit a restriction (Bera and Belhaj 2016; Sheng 2011).

## Surfactant flooding

Surfactants have a great potential in EOR applications, and they are used to enhance the recovery process efficiently by increasing the quantity of the residual oil extracted after secondary recovery process, which can possibly be around 60% of the original oil in place (Thomas and Ali 1999). Surfactant flooding is a chemical EOR method used for enhancing the oil recovery mechanism by recovering the capillary-trapped residual oil after waterflooding (Barati-Harooni et al. 2016). Surfactant flooding process depends on injecting surfactants to the reservoir along with injecting other chemicals. During surfactant flooding process, favorable phase behavior is targeted to achieve ultralow IFT between oil and water in order to mobilize the trapped oil (Sandersen 2012). The crude oil may contain organic acids, salts, alcohols, and other natural surface-active agents. Once crude oil is brought in contact with brine, these natural surfactants accumulate at the crude oil–brine interface and form an adsorbed film which lowers the interfacial tension of the crude oil–water interface (Olajire 2014). The main constraint influencing the surfactant flooding process is surfactant stability at reservoir conditions especially in high-temperature and high-salinity conditions. Other constraints include losses of the surfactants due to surfactant adsorption in the reservoir rock and trapping of the fluid in the pore structure

(Sandersen 2012). These losses should be minimized where the successful implementation of surfactant flooding process depends mainly on the cost of surfactants (Hirasaki et al. 2008).

Surfactant flooding in EOR is divided into three types. The first type is micelle/polymer flooding where it can assist in achieving high displacement efficiency. The procedure involves injecting a slug containing surfactant, co-surfactant, alcohol, brine, and oil. The second type is microemulsion flooding, and it can be beneficial in high-temperature and high-salinity conditions. It is also useful for low-permeable zones where the polymer and/or alkali cannot operate. The main mechanism of this type is to reduce the IFT to an ultralow value by generating microemulsions in the reservoir. The injection slug in this process mainly consists of surfactants, co-surfactants, alcohol, and brine. The third type is the alkaline–surfactant–polymer (ASP) flooding. In this type, low IFT value is achieved by adding alkaline at low surfactant concentration, and this will contribute in cost reduction as lower surfactant concentration is used (Rosen et al. 2005; Sandersen 2012; Schramm 2000).

## Surfactant losses

The success of surfactant flooding is subjected to the reduction in surfactant loss in the reservoir. The injected slug may witness a reduction in the surfactant concentration as it transports through the reservoir. Surfactant losses take place in the reservoir due to different mechanisms, i.e., surfactant adsorption, surfactant precipitation, surfactant degradation, surfactant polymer mixing, and surfactant partitioning in the residual oil phase (Donaldson et al. 1989). When surfactant slug comes in contact with the reservoir rock, adsorption of surfactant takes place on the rock surface. Due to adsorption, the surfactant concentration in the injected slug decreases and the amount remaining behind is insufficient to achieve ultralow IFT and to mobilize the trapped residual oil (Trushenski et al. 1974).

## Surfactant adsorption

Surfactants adsorb onto solid surfaces as monomers rather than as micelles. Surface-active molecules can be adsorbed onto reservoir rocks from aqueous solutions by a number of mechanisms, i.e., ion exchange, ion association, hydrophobic bonding, adsorption by the polarization of  $\pi$  electrons, and adsorption by dispersion forces (Dang et al. 2011; Paria and Khilar 2004; Somasundaran and Huang 2000; Zhang and Somasundaran 2006). Surfactant adsorption during the surfactant flooding process is the most critical problem that can influence the success or failure of this process (Azam et al.

2014). Surfactant adsorption may occur on the rock surface due to the electrostatic interaction and van der Waals interactions that arise between the surfactant and solid surface (Kamal et al. 2017).

Generally, surfactant adsorption depends on many factors such as surfactant type, surfactant concentration, surfactant equivalent weight, ionic strength, pH, salinity, and temperature (Azam et al. 2014; Baviere et al. 1988; Paria and Khilar 2004; Siracusa and Somasundaran 1987). These factors can also influence the dissolution behavior of minerals, and therefore, it will cause significant changes in the adsorption of surfactants into the rock surface (Siracusa and Somasundaran 1987). In this review, we will discuss the effect of the main factors affecting surfactant adsorption which are: surfactant concentration, surfactant, salinity, temperature, and pH. Practically, surfactant adsorption can only be reduced to a certain limit due to the fact that it cannot be fully eliminated. The performance of the surfactant flooding process will be improved, and good recovery efficiency can be achieved only if the process is economically optimized by reducing surfactant adsorption (Park et al. 2015).

### Surfactant concentration

Surfactant adsorption is a major factor that strongly affects the surfactant flooding process. Therefore, any reduction in surfactant concentration from the injected slug may decrease the surfactant efficiency to reduce oil–water IFT. This may lead the whole process to economic failure. Several studies discussed the effect of surfactant concentration on the adsorption of ionic and nonionic surfactants onto reservoir rocks. Based on the rock type, the rock surface charge is either negatively charged such as sandstone or positively charged such as carbonates. At low surfactant concentrations, surfactant adsorption is determined according to the charge on the electrical double layer of the solid surface. The adsorption of surfactant molecules at low concentrations on the rock surface occurs as a single monomer. When surfactant concentration increases, these monomers start to aggregate and associate among themselves to form micelles. Micelles are accumulated molecules where they usually contain 50 or more surfactant molecules (Bera et al. 2013a; Liu 2008; Li et al. 2011; Miura et al. 2013; Torn et al. 2003; Xu et al. 2008).

Anionic surfactants adsorption increases with increasing surfactant concentration. At low surfactant concentration below critical micelle concentration (CMC), the charge in the electrical double layer controls the extent of adsorption. This is described by the electrostatic interactions that arise between the surfactant head group and the net charge present on the solid surface. As surfactant concentration increases, lateral interactions will appear between the adsorbed surfactant molecules; it drives surfactant to aggregate the rock

surface showing an increase in the adsorption density. When reaching CMC, any addition of surfactant will not have any effect on adsorption and it displays a plateau behavior. In this case, adsorption remains constant (Adak et al. 2005; Budhathoki et al. 2016; Kamal et al. 2017).

Boomgaard et al. (1987) explained the adsorption of non-ionic surfactants. At low surfactant concentration, hydrogen bonding between the nonionic surfactant chain and the hydroxyl groups on the rock surface is the main mechanism of adsorption. Nonionic surfactants through hydrogen bonding adsorb as monomers. As surfactant concentration increases, micelles are formed due to the hydrophobic interactions which occur between the adsorbed monomers gathering at the liquid–rock interface (Curbelo et al. 2007).

### Salinity

Salinity is one of the factors that influence surfactant adsorption. The most commonly used surfactants in chemical EOR are anionic surfactants. Usually, these surfactants are strongly influenced by adsorption on rock surfaces due to the presence of salt and divalent cations. Thus, it is a challenge to design surfactant formulations that are salinity and hardness resistant (Tabary 2013).

High-salinity water is not desirable for anionic surfactants due to the fact that it can precipitate resulting from the interaction between salt ions and the surfactant. On the other hand, increasing the salinity will reduce the repulsive forces arising between the anionic surfactant molecules and the rock surface (Azam et al. 2013; Kamal et al. 2017). This agrees with the experimental investigation done by Baviere et al. (1988) and Mannhardt et al. (1993).

The effect of salinity on the anionic surfactant adsorption at the solid–liquid interface was discussed by many researchers (Behrends and Herrmann 1998; Koopal et al. 1996; Nevskiaia et al. 1998; Paria and Khilar 2004). The presence of salt improves the adsorption of anionic surfactants on a negatively charged solid surface. Koopal et al. (1996) explained the influence of ionic strength on the adsorption of anionic and cationic surfactants onto an oppositely charged solid surface. At low surfactant concentration, the initial adsorption occurs at low-salinity conditions. Attractions between the head group and the surface arise due to an increase in the ionic strength that causes adsorption to be reduced. As surfactant concentration increases, ionic strength rises which shows a decrease in mutual head group repulsion, and thus, adsorption is increased.

Salinity has also an impact on nonionic surfactants which it can change its solubility, surface activity, and adsorption at the solid–liquid interface (Paria and Khilar 2004; Rosen and Kunjappu 2012). Table 1 summarizes several studies that highlighted the effect of salinity on surfactant adsorption.

**Table 1** Summary of several studies highlighting the effect of salinity on surfactant adsorption

Author(s)	Name of the surfactant and type	Salinity (ppm)	Effect of salinity
Baviere et al. (1988)	Alpha-olefin sulfonate (AOS) (anionic)	600–80,000 NaCl	AOS was found to be a good candidate for chemical EOR at intermediate and high salinities over a wide range of temperatures
Denoyel and Rouquerol (1991)	TX-100 (nonionic)	10,000	The effect of salinity on the adsorption of TX-100 on quartz shows that the presence of NaCl shifts the plateau concentration level of the surfactant toward lower equilibrium concentrations. This will reduce the CMC of TX-100 due to an increase in lateral interactions between polar chains as salinity increases. Thereby, a rise in adsorption is noticed at the plateau
Partyka, Lindheimer, and Faucompre (1993)	Monoalkyl trimethyl ammonium bromide (DDTAB) (cationic)	100,000	Adsorption isotherms on silica in the presence of NaBr show that adsorption decreases when salt concentration increases. This was attributed to competitive adsorption between the surfactant and $\text{Na}^+$ ions on the silica surface
Mannhardt et al. (1993)	Diphenyletherdisulfonate/alpholinsulfonate (DPES/AOS) blend (anionic) Alkyl amido betaine (BT) (amphoteric)	21,000–147,000	The adsorption of the anionic surfactant (DPES/AOS) on sandstone is very low in low-salinity brine. However, adding divalent ions increase adsorption significantly. This was illustrated by the ionic strength effect. The adsorption of the amphoteric surfactant is extremely high on sandstone mainly in the presence of divalent ions. Meanwhile, its adsorption on limestone are lower than on the sandstone and are also increased in the presence of divalent ions
Nevskaia et al. (1998)	TX-100 (nonionic) (NP4S, NP10S, and NP25S) (anionic)	20,000 NaCl	For the nonionic surfactant (TX-100), the NaCl effect described different adsorption behaviors on different rock types which are associated with the interaction of salt cations with different surface hydroxyl groups. In contrast, the anionic surfactants demonstrated the same adsorption behavior on different rock types in the presence of NaCl. The increase in the adsorbed amount was attributed to the negative surface charge compensation by $\text{Na}^+$ ions
Puerto et al. (2010)	Alkoxy/ated glycidyl sulfonates (AGS) (anionic) Internal olefin sulfonates (IOS) (anionic)	120,000	AGS/IOS has the potential to overcome high-temperature (85–120 °C) and high-salinity limitation and still provide an ultralow IFT
Dang et al. (2011)	The (anionic) hydrolyzed polyacrylamide	10,000–30,000 NaCl 20,000 $\text{CaCl}_2$	This is a simulation study of surfactant/polymer adsorption. The outcomes of this study showed that surfactant adsorption increases with the increase in NaCl concentration and the increase in divalent ion content. The increase in adsorption is attributed to that when salt concentration increases it drives the surfactant to the interface. Therefore, Repulsion forces decrease in the adsorbed layer



Table 1 (continued)

Author(s)	Name of the surfactant and type	Salinity (ppm)	Effect of salinity
Zhou et al. (2013)	NPSO (anionic) TTSS-12 (anionic)	112,228.8	The stability of this surfactant flooding system was evaluated at 110 °C and all experiments showed that it's stable at high-temperature and high-salinity conditions and still has the potential to maintain ultralow IFT
Ingrid Hov (2014)	SDBS (anionic)	1169–11,688 NaCl	Adsorption of surfactants decreases in the low- and medium-salinity conditions onto illite clay more than high-salinity conditions. That is due to the expansion of the electrical double layer when salinity decreases which causes adsorption to decrease
ShamsiJazeyi, Verduzco, and Hirasaki (2014)	NI-blend Neodol-67 (N) and IOS15-18 (I) (anionic)	35,000	The influence of sodium polyacrylate as a sacrificial agent was evaluated in different minerals/rocks for NI-blend. It was found that sodium polyacrylate has the ability to reduce adsorption of anionic surfactant on carbonates, clay minerals, and Berea sandstone. From the adsorption experiments, it was highlighted that the increase in salinity or $\text{Ca}^{2+}$ ions in the brine leads to higher adsorption of anionic surfactants
Bera and Mandal (2015)	Sodium dodecyl sulfate (SDS) (anionic)	–	The amount of adsorption of SDS on sand surface increased with the increase in salinity due to low electrostatic repulsion
Li et al. (2016)	Polyoxyethylene carboxylate and quaternary ammonium salt mixture (anionic–cationic)	5000	They explained that the adsorption of cationic surfactants on the negatively charged surface (sandstone rock) is reduced when it's present in anionic-rich surfactants above the CMC. They also noticed that the adsorption amount was further reduced in the use of the alkaline–surfactant–polymer system
Budhathoki et al. (2016)	A mixture of sodium alkyl ethoxylate propoxylate sulfate (extended surfactant) and sodium alkyl ethoxy sulfates (SAES) (anionic)	301,710 TDS Total hardness ( $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ) of 12,973	Adsorption was found severe on Berea sandstone under high saline environment. This is mainly due to the adsorption of cations $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ present in high TDS brine onto the negatively charged sand surface. This causes the anionic surfactant to be positively charged and that increases adsorption dramatically. However, after adding polystyrene sulfonate (PSS), the surfactant adsorption is decreased by more than half. Therefore, polystyrene sulfonates (PSS) can be used as a sacrificial agent in minimizing adsorption of anionic surfactants in sandstone reservoirs

**Table 1** (continued)

Author(s)	Name of the surfactant and type	Salinity (ppm)	Effect of salinity
Yekeen et al. (2016)	Sodium dodecyl sulfate (SDS) (anionic)	10,000–50,000 NaCl 1000–10,000 CaCl <sub>2</sub> 250–10,000 AlCl <sub>3</sub>	Adsorption of SDS was high on kaolinite because of the strong electrostatic attractions that present between the negative charges of the surfactant head groups and the positive charges that present on the kaolinite surface. A significant effect of salinity on adsorption was found. Consequently, with the increase in salinity concentrations for NaCl and CaCl <sub>2</sub> salts, adsorption was found to be increasing, while in the presence of AlCl <sub>3</sub> and CaCl <sub>2</sub> surfactant adsorption was found to be higher compared to NaCl salt
Yuan et al. (2018)	Trimethyl tetradecyl ammonium chloride (cationic) Sodium lauryl sulfate (anionic)	60,000 NaCl	A static adsorption comparison study shows that the cationic surfactant trimethyl tetradecyl ammonium chloride overtakes that of anionic surfactant sodium lauryl sulfate in the presence of salt

## Temperature

Researchers initially explained the effect of temperature on surfactant adsorption where adsorption is generally an exothermic process. They indicated that the increase in temperature leads to a considerable decrease in the adsorption of surfactants due to an increase in the kinetic energy of the species (Fava and Eyrin 1955; Hartman et al. 1946; Somasundaran and Fuerstenau 1972; Ziegler and Handy 1981). Kulkarni and Somasundaran (1976) addressed the effect of ionic strength and temperature on the adsorption of surfactants. Adsorption increases with the increase in temperature at low ionic strength while it decreases at high ionic strength with the temperature decrease (Ziegler and Handy 1981). The effect of temperature on surfactant adsorption depends on the adsorption density. The process of surfactant adsorption can be either enthalpy driven or entropy driven (Hirasaki and Zhang 2003). For surfactants with low adsorption density (enthalpy-driven adsorption), when the temperature increases, it causes the adsorption density to increase. Meanwhile, adsorption density is reduced with temperature increase for surfactants with high adsorption density (entropy-driven adsorption) (Kamal et al. 2017).

Surfactant flooding is commonly operated under low-temperature and low-salinity conditions. Anionic and nonionic surfactants are the most favorable surfactants to be used in these conditions. On the other hand, at high-temperature and high-salinity conditions, anionic surfactants show low slat resistance (Kamal et al. 2018).

For nonionic surfactants generally, adsorption increases with increasing temperature. This was proposed by Corkill et al. (1966), and they found that adsorption of surfactant molecules at different temperatures increases as temperature increases. The increase in temperature affects the surfactant's head group making it compact and less hydrophilic, therefore increasing the surface activity and adsorption values. Non-ionic surfactants behavior was deeply investigated at various temperatures where it was also suggested that at low surfactant concentrations, adsorption of nonionic surfactants is reduced as temperature increases. Meanwhile, at high surfactant concentrations, the opposite is correct (Ziegler and Handy 1981).

Puerto et al. (2010) explained that reservoirs with temperatures varying from 70 to 120 °C are suitable candidates for surfactant flooding. However, high-temperature reservoir conditions can affect the stability of surfactants to operate for the period of the project which could be for years. Sheng (2015) discussed that most researchers consider 93.3 °C as reservoir temperature limit even though specific surfactants can be applied at high-temperature reservoirs up to 150 °C. These surfactants could be stable under such conditions. However, they must be also applicable corresponding to other conditions as well such as low adsorption which can contribute to minimizing the cost. Table 2 summarizes

**Table 2** Summary of several studies highlighting the effect of temperature on surfactant adsorption

Author(s)	Name of the surfactant and type	Temperature (°C)	Salinity (ppm)	Main findings
Baviere et al. (1988)	Alpha Olefin Sulfonate (AOS) (anionic)	30–50	600–80,000	They concluded that AOS is a very good candidate for surfactant flooding at low, intermediate, and high salinities over a wide range of temperatures
Zaitoun, Fonseca, and Berger (2003)	SS-6066 A ANTISORB™	55	110,000	This study showed a good stability of the selected surfactants at bottom-hole temperature. Adsorption of the primary surfactant (SS-6066 A) onto the formation rock was reasonable and (ANTISORB™) surfactant helped to lower the adsorption of the primary surfactant
Bataweel and Nasr-El-Din (2012)	GreenSurf-687 or Amph-GS (amphoteric) Amph-SS (amphoteric)	95	172,000	In this study, amphoteric surfactants maintained lower IFT level but did not show high recovery values. They also used amphoteric surfactants to help in reducing adsorption by operating in extremely low CMC values. This method enhanced chemical propagation through the core sample
Tabary (2013)	Olefin sulfonates (OS) (anionic) Alkyl aryl sulfonates (AAS) (anionic) Alkyl ether sulfates (AES) (anionic) Alkyl glyceryl ether sulfonates (AGES) (anionic)	120	220,000	It was found that in high-temperature conditions (up to 120 °C) good oil recovery can be achieved. It was also found that low adsorption values can be obtained using properly designed formulations as well as adsorption inhibitors
Han et al. (2013)	OCT-1, OCT-4 and C2405 (amphoteric)	95	–	It was found that amphoteric surfactants are good candidates to be used for carbonate reservoirs with low adsorption level, due to the positive surface charge that exists in the carbonate rocks. OCT-1 and C2405 achieved lower adsorption amount than 1.0 mg/g rock
Zhang et al. (2013)	Hydroxyl sulfobetaine (zwitterionic)	95	84,000	They found that dynamic adsorption of the sulfobetaine in the three chemical formulations attained less than 1.0 mg/g rock, which meets the criteria of field application
Lu et al. (2014)	Guerbet alkoxy carboxylates (anionic) IOS (anionic)	100	116,969	Ultralow IFT and good aqueous stability were achieved for the nominated surfactants for a carbonate reservoir
Yuan et al. (2015)	Formulation 1 (AOS + AEC) and formulation 2 (AES + AI)	90–120	200,000	They discovered that dynamic adsorption is lower than the static adsorption of each surfactant formulation. They discussed possible explanations of low adsorption of the two surfactant formulations: 1—Reduction in adsorption due to the electrostatic repulsion between the negatively anionic charge in the surfactant solutions and negatively charged crushed rock surface 2—Reduction in adsorption occurs when a surfactant with large head absorbed on the rock surface which leads to strong steric hindrance that causes inhibition of adsorption 3—Reduction in adsorption due to that the process is exothermic, and the high temperature of 100 °C is unfavorable to adsorption
Li et al. (2016)	Mono carbon chain Polyoxyethylene Carboxylate (anionic) Petroleum Sulfonate (PS) (anionic) Quaternary ammonium salt (cationic)	76.5	5000	Surfactants showed very good thermal stability for over 120 days. Sodium carbonate was tested to reduce surfactant adsorption in these conditions, and it showed very good results



**Table 2** (continued)

Author(s)	Name of the surfactant and type	Temperature (°C)	Salinity (ppm)	Main findings
Lin et al. (2017)	Surfactant formulation MSD (amphoteric)	90–110	115,000 TDS + 8000 Ca <sup>+2</sup> Mg <sup>+2</sup>	They studied the adsorption of MSD on clean sand and oil sand. They found that the surfactant adsorption on oil sand is higher than on clean sand. They attributed that to the behavior of the lipophilic groups of the surfactant where they stretch into the oil sand surface, and thus hydrogen bonds are formed with hydroxyl groups of oil
Puerto et al. (2018)	Surfactant blend of an internal olefin sulfonate, a betaine, and an ethoxylated carboxylate (anionic)	90–94	–	They studied surfactant adsorption using static and dynamic adsorption methods. They found that the two methods were matching with each other using the selected blend. They also indicated that total adsorption on the dolomite rock was in 0.5 mg/g range

several studies that highlighted the effect of temperature on surfactant adsorption.

## pH

The pH has a major influence on surfactant adsorption where the charge of solid surfaces varies with the change of pH. Surfactant adsorption magnitude differs at different pHs depending on the surfactant charge which interacts with the charges available at the surface. As the pH of the surfactant solution increases, it reduces the number of hydroxyl groups in the surface affecting the formation of hydrogen bonding. This makes hydrated mineral oxides on the solid surface to be negatively charged. At lower pH, surfactant solution drives the mineral hydroxyl to acquire a positive charge which increases adsorption of surfactants by attracting the negatively charged surfactant molecules to the rock surface. Berea sandstone, e.g., contains mainly silica oxides, and by increasing pH from a low value (acid condition) to the medium pH (5–7) or higher pH (base condition), it imposes an increase in the negative charges of the rock surface (Azam et al. 2013; Hanamertani et al. 2017; Lv et al. 2011).

Surface charges that exist on surfactants as well as the rock surface have a direct effect on the surfactant adsorption. Anionic surfactants carry negative charge where cationic surfactants carry a positive charge and they are by default attracted to positively charged surfaces and negatively charged surfaces, respectively. Surface charges are intensely affected by salinity and pH of the formation brine. Generally, if brine chemistry effect is neglected and water is at neutral pH, anionic surfactants have a tendency for adsorption on carbonates due to the existence of positive charges (basic state) on the rock surface, while cationic surfactants have a tendency for adsorption on sandstone due to the existence of negative charges (acidic state) on the rock surface (Bera et al. 2013b; Harkot and Jańczuk 2009; Wei et al. 2012).

Another important factor that affects the surface charge of the rock is the solution pH. The rock surface charge density depends on the pH variation while in contact with the surfactant solution. The pH value at zero surface charge density on the surface is named the point of zero charges (PZC) (Grigg et al. 2004; Mushtaq et al. 2014).

Generally, the use of alkali in surfactant flooding is to generate in situ soap from its reaction with crude oil components so that the amount of the injected surfactant can be reduced. Therefore, it reduces the surfactant concentration to be used and that will decrease operating costs and significantly improves the profit of chemical flooding projects. Alkali is also used as a chemical agent to reduce surfactant adsorption on the rock surface by increasing the pH of the medium to enhance surfactant stability. In the case of anionic surfactants which their head group structure is negatively charged, when alkali is used it increases the pH of the environment and that will generate a strong electrostatic repulsive force between the surfactant and the reservoir rock surface, and thereby surfactant adsorption is significantly reduced (Dang et al. 2011). However, the influence of alkali in lowering adsorption of anionic surfactants is limited to reservoirs with low salinity/hardness, due to the fact that alkali is sensitive to divalent cations Ca<sup>2+</sup> and Mg<sup>2+</sup>, which reduces its effectiveness and drives it to precipitate. On the other hand, cationic surfactants which their head group is positively charged are usually used for positively charged carbonate reservoirs (ShamsiJazeyi et al. 2013).

The most common used alkali is sodium carbonate where it consumes the multivalent cations that cause surfactant to precipitate. Sodium metaborate is another alkali which is used in high-salinity conditions due to its ability to sustain under high-salinity conditions (Flaaten et al. 2010). Sodium polyacrylate is introduced as a sacrificial agent as it can be used to reduced surfactant adsorption on dolomite

**Table 3** Summary of several studies highlighting the effect of pH on surfactant adsorption

Author(s)	Name of the surfactant and type	Main Findings
Krumrine, Falcone, and Campbell (1982)	Petroleum sulfonate (anionic)	This study illustrated that the use of sodium silicate, sodium tripolyphosphate, and sodium carbonate reduced surfactant adsorption significantly on Berea core material
Mannhardt et al. (1993)	Diphenyletherdisulfonate/alphofinsulfonate (DPES/AOS) blend (anionic) Alkyl amido betaine (BT) (amphoteric)	This study was conducted on Berea sandstone/clay/limestone and concluded that Berea sandstone carries a negative surface charge at pH 7 in both brines, while Indiana limestone is negatively charged in the NaCl brine and positively charged in the reservoir brine The clay fraction in Berea sandstone carries a higher negative charge than the whole Berea rock or its quartz fraction
Dang et al. (2011)	The (anionic) hydrolyzed polyacrylamide (HPAM)	This simulation study of surfactant/polymer adsorption illustrated that the surface charges of minerals depend on pH. As pH increases, the rock surfaces become more negatively charged. Also, high pH condition induces the protons to become dissociated from the carboxyl groups on HPAM, which in turn becomes negatively charged. That results in an increase in the pH and the repulsive forces between surfactant molecules and rock surfaces; therefore, surfactant adsorption is reduced
Elraies (2012)	Synthesized polymeric surfactant (anionic)	The author reported that surfactant adsorption decreased significantly on Berea sandstone by adding alkali (sodium carbonate) to the surfactant solution. The main reason for that is when pH increases to a higher level, it increases the negative charges on the sand surface, also due to the fact that electrostatic repulsive forces attract additional surfactant to the solution when adding alkali to the system
Azam et al. (2013)	Synthesized sulfonate surfactant (anionic)	The PZC value was determined (8.0) which indicated that the Berea sandstone carries a negative charge at pH above 8.0. At pH value lower than the PZC, surfactant adsorption was somewhat high at 0.96 mg/g. The use of the alkalis (sodium tetraborate) and (sodium metaborate) decreased the positive charge of the Berea sandstone surface due to an increase in the pH. This led to reducing the surfactant adsorption significantly to (0.28 mg/g) and (0.36 mg/g), respectively. However, it was observed that Sodium tetraborate was more efficient than sodium metaborate in reducing surfactant adsorption. This effect may be due to the lowering of the ionic strength and high-salinity tolerance of sodium tetraborate as compared to sodium metaborate
Mushtaq et al. (2015)	Synthesized surfactants FS-1 and FS-2 (anionic)	The addition of alkali reduced the adsorption for both surfactants on sandstone. Adsorption for FS-1 was reduced from 4.32 mg/g at pH 6 to 0.51 mg/g at pH 10. Adsorption for FS-2 was reduced from 4.94 mg/g at pH 6 to 0.89 mg/g at pH 10. This is due to the shift of rock surface charges from positive to predominantly negative. The surface negative charges generate repulsive forces with the negative charges on the surfactants and significantly reduces adsorption
Li and Ishiguro (2016)	Sodium dodecyl sulfate (SDS) (anionic)	They studied the adsorption of SDS on porous silicon dioxide powder gels and they observed that silica adsorbs SDS because it has a hydrophobic surface on siloxane. The SDS adsorption decreases when pH increases on the silica due to the increase in electrostatic repulsion. They also observed when the repulsion becomes larger, SDS adsorption cannot be detected. The influence of pH through electric potential on SDS adsorption was confirmed with the measured zeta potential, the modified Langmuir equation, and the 1-pK basic Stern model
Tagavifar et al. (2018)	Tridecyl alcohol propoxy sulfate Internal olefin sulfonate IOS Guerbet alkoxyate carboxylate (anionic)	By using alkali ( $\text{Na}_2\text{CO}_3$ ) anionic surfactant adsorption was reduced almost linearly with pH on Indiana limestone above the pH value of 9. They stated that the dominant adsorption mode on calcite and clay is charge-regulated in low pH conditions, whereas the dominant adsorption mode at pH values of ~ 10 is hydrogen bonding

(ShamsiJazeyi et al. 2013). Table 3 summarizes several studies that highlighted the effect of pH on surfactant adsorption.

## Conclusion

Adsorption of surfactants on the rock surfaces may result in a reduction in their concentrations that may possibly reduce their efficiency and affect their performance in practical

EOR applications. Reduction in IFT of the oil–water–rock system to an ultralow value is the main function of surfactants. However, surfactant loss due to adsorption impairs their effectiveness and may turn the process to be economically unfeasible. Reducing the amount of surfactant adsorption is necessary to avoid the failure of the whole process. This review highlights the influence of surfactant concentration, salinity, temperature, and pH on surfactant adsorption. Adsorption increases with increasing surfactant

concentration. When a surfactant is at a concentration below the CMC, surface aggregation occurs and a large increase in the adsorption is noticed. However, at concentrations above the CMC, an increase in the concentration has no effect on the adsorption behavior. It was also found that salinity has an influence on surfactant adsorption due to the interactions that arise between salt ions and the surfactant molecules. Increasing reservoir brine salinity increases the adsorption of surfactants on rock surfaces due to the decrease in the repulsive forces between adsorbed molecules. The increase in temperature generally leads to a considerable decrease in the adsorption of surfactants due to an increase in the kinetic energy of the species. The pH effect on surfactant adsorption is significant where surfactant adsorption magnitude varies at different pHs depending on the surfactant charge which interacts with the charges available at the surface. Most of the research has been conducted in low-temperature and low-salinity conditions. Only limited studies were conducted in high-temperature and high-salinity (HT/HS) conditions due to the implementation challenges of surfactant flooding in these conditions.

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