

Salinity Effect on the Surfactant Critical Micelle Concentration through Surface Tension Measurement

Naser Akhlaghi¹ and Siavash Riahi^{2*}

¹ Ph.D. Candidate, Department of Petroleum Engineering, Kish International Campus, University of Tehran, Kish, Iran

² Associate Professor, Institute of Petroleum Engineering, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

Received: April 10, 2019; *revised:* April 27, 2019; *accepted:* May 12, 2019

Abstract

One of the tertiary methods for enhanced oil recovery (EOR) is the injection of chemicals into oil reservoirs, and surface active agents (surfactants) are among the most used chemicals. Surfactants lead to increased oil production by decreasing interfacial tension (IFT) between oil and the injected water and to the wettability alteration of the oil reservoir rock. Since surfactants are predominantly expensive materials, it is required to consider an appropriate and high-performance plan for project economics when they are injected into oil reservoirs. One of the operational issues in surfactant flooding is the critical micelle concentration (CMC), which is usually achieved by the injection of surfactant at concentrations higher than CMC. Therefore, the lower the CMC is, the lower the amount of the material needed to be injected into the reservoir becomes, so it will help to economize the project. The salinity of the aqueous phase is a factor affecting the CMC, and with its optimal design, it can reduce the CMC. In this study, the variations of Triton X-100 CMC's as a nonionic surfactant were measured by altering the concentration of three salts with divalent ions (CaCl₂, MgCl₂, and Na₂SO₄) and a single-capacity ion salt (NaCl), as the predominant salts in the porous medium of oil reservoirs, using surface tension (ST) method at ambient temperature and pressure. Each of these salts was dissolved at three concentrations of 0.1, 0.5, and 1 wt.% in distilled water containing specific concentrations of surfactant, and the surfactant CMC in the presence of these salt concentrations was measured. The results showed that increasing the concentration of each salt resulted in a decrease in the CMC, and, in the studied salts, NaCl produced the lowest CMC.

Keywords: CMC, Triton X-100, Salinity, Surface Tension, Micelle, EOR

1. Introduction

One of the most promising chemical flooding methods is surfactant flooding, which is categorized as a subset of the chemical EOR processes. Enhanced oil recovery using surfactants relies on the ability of surfactant molecules to lower the interfacial tension (IFT) between the oil and the brine in the reservoir. For a sufficient IFT reduction, and hence incremental oil recovery, an appreciable number of surfactant molecules should be available on the brine-oil interface. To meet such a condition, the surfactant is

* Corresponding author:
Email: Riahi@ut.ac.ir

usually injected above the critical micelle concentration, which is the concentration at which surfactant molecules start to aggregate to form units called micelles. The hydrophobic ends of the surfactant molecules form the inner core, while the hydrophilic heads stick out into the aqueous medium. Depending on the surrounding conditions, the micelles, which has a colloidal size, form variant structural shapes, including spherical, cylindrical, or even layered. The formation of micelles is a dynamic process whereby they are continuously formed and destroyed by kinetic processes in the solution. Increasing the surfactant concentration above CMC will not have any effect on the surface or interfacial tension (Ahmadi et al., 2017; Freer et al., 2003; Hassenkam et al., 2011; Fuseni et al., 2017; Kamal et al., 2016; Abbas et al., 2018).

CMC is a property of a surfactant, which can be altered by changing some of the parameters such as temperature, salinity, etc. Also, it can affect its efficiency in industries, and, from the EOR perspective, and it helps economize the project. Some researchers have been working on measuring the CMC of different surfactants. Chen et al. investigated the temperature effect on the CMC of n-dodecyl polyoxyethylene monoether by Wilhelmy plate technique in the range of 10-80 °C. They also evaluated the effects of enthalpy and entropy on micelle formation. Their results indicated that the temperature of 321 K was excellent for their experiments (Chen et al., 1997).

Adding salt to a surfactant solution leads to a reduction in the CMC, which is much lower for nonionic surfactants than for ionic surfactants (Miyagishi et al., 2001).

Noll et al. studied the effect of temperature, salinity, and alcohol on the CMC of a series of surfactants and showed that the CMC of the studied surfactants increased with a rise in temperature, and the presence of electrolyte at a fixed temperature lowered the CMC but increased the sharpness of the onset of micellization (Noll et al., 1991).

Maeda et al. determined the CMC of dodecyl dimethyl amine oxide (DDAO) at 25 °C as a function of NaCl concentration for both nonionic and cationic species by measuring the surface tension. Their research showed that the CMC of the cationic species was lower than that of the nonionic species in the range of NaCl concentration higher than about 0.2 M, which strongly suggested an attractive interaction between the head groups of two cationic species in micelles, most probably the hydrogen bonding (Maeda et al., 1997).

Parak et al. evaluated the synergistic effect in micelle formation of surfactant mixtures at different mass ratios of various surfactants by the surface tension measurement method; a mixture consisted of anionic (alpha olefin sulfonate [AOS]) and nonionic (Triton X-100) surfactants at ratios of 1:2, 1:1, and 2:1. They concluded that the CMC of the mixed surfactants decreased by raising the mole fraction of TX100 in the system, which reduces the electrostatic repulsion of the charged head group of the anionic surfactant, thereby causing the mixture to reach CMC more easily. However, the CMC of the mixed surfactants was not intimately linked to the mole fraction of Triton X-100 in the mixture after equilibrium (Parak et al., 2015).

Sammalkorpi et al. studied the properties of sodium dodecyl sulfate (SDS) aggregates in saline solutions of excess sodium chloride (NaCl) or calcium chloride (CaCl₂) ions through extensive molecular dynamics simulations with an explicit solvent. They observed that significantly more stable salt bridges between the charged SDS head groups were mediated by Ca²⁺ than Na⁺. The presence of these salt bridges helps stabilize the more densely packed micelles (Sammalkorpi et al., 2009).

Karnanda et al. investigated the effects of surfactant type, salt type, temperature, and pressure on the CMC of Triton X-405 and Zonyl FSE. They reported that temperature and pressure had no effect on the CMC of Triton X-405; however, the CMC of Zonyl FSE solutions decreased by increasing pressure

but leveled out by raising temperature except at temperatures higher than 80 °C, where CMC increased (Karnanda et al., 2013).

Khanamiri et al. studied the effect of brine composition on the rock and injected fluid properties. They observed that the CMC of their surfactant (SDBS) in the pure sodium chloride solution and $\text{Ca}^{2+}/\text{Na}^+$ ratio of 0.022 were nearly 105 mg/L and 65 mg/L respectively. The CMC of the surfactant without any salt was 500 mg/L. Their experiments showed that increased ionic strength in the presence of sodium chloride and the combination of sodium chloride and calcium chloride led to a reduction in CMC (Khanamiri et al., 2016).

Javadian et al. evaluated the micellization characteristics of mixtures of CTAB and TritonX-100 in aqueous media containing different concentrations of NaBr by surface tension (ST) method. They showed that decreasing the electrostatic interactions by raising the ionic strength of the solution had a better influence on the planar air/solution interface than on the convex micellar surface in the solution (Javadian et al., 2008).

Miyagishi et al. investigated the effect of a series of salts on the CMC of nonionic surfactants (N-acyl-N-methylglucamides). Their experiments illustrated that salt can lower the CMC value, and a decline in CMC was observed in the order of $\text{Ca} > \text{Na} > \text{K} > \text{Cs} > \text{Li}$ for cations and in the order of $\text{SO}_4 > \text{CO}_3 > \text{SO}_3 > \text{HPO}_4 > \text{F} > \text{Cl} > \text{Br} > \text{NO}_3 > \text{I} > \text{SCN}$ for anions (Miyagishi et al., 2001).

Since the injection of surfactant is mainly carried out at a concentration above the CMC, reducing CMC can help reduce the cost of EOR; hence, in this work, we investigated the effect of salts, predominantly in oil reservoirs, on the CMC of Triton X-100 as a nonionic surfactant, which is mainly used in surfactant flooding and has a low IFT and adsorption on reservoir rocks. Also, changes in CMC with ionic strength in the presence of monovalent and divalent ions were studied at ambient pressure and temperature in order to optimize the solution of surfactants injected to the oil reservoir. Surface tension (ST) method was used to measure CMC.

2. Experimental

2.1. Materials

a. Surfactant

The surfactant used in this study was Triton-X100, a nonionic surfactant with a density of 1.07 g/cm³ at a temperature of 20 °C as a liquid, and was prepared by Merck Company.

b. Salts

The salts used to prepare surfactant solutions included NaCl, MgCl₂, CaCl₂, and Na₂SO₄ and were all supplied by Merck Company.

2.2. Methodology

The effects of the salts on CMC were studied at ambient temperature and pressure, and all the experiments were carried out using a surface tension method with a pendant drop, as described below.

a. Solution preparation

Surfactant solutions were prepared on a mass basis. A 1000 mL standard beaker filled with distilled water, with the desired concentration of surfactant, and with the desired concentration of the different salts was used to obtain the desired concentrations using a stirrer and magnet. After achieving the

desired concentrations and diluting the solutions, all the solutions were held constant for 24 hours to insure that the solutions have reached an equilibrium (Maeda et al., 1997).

b. Surface tension measurement

In order to measure CMC, a pendant drop method was used to measure surface tension. Therefore, the surface tension of the surfactant solutions at different concentrations with specific concentrations of the salts in the air was measured by plotting the surface tension versus the surfactant concentration and selecting the surfactant concentration at which the trend of the graph changes as the CMC of each test.

In the current work, the pendant drop method was used to measure surface tension between the aqueous phase and air (Figures 1-3). In this method, the surface tension is easily calculated from the dimensions of a suspended drop photographed by a camera (Manshad et al., 2016). The assumptions used in this method are as follows:

1. The drop is symmetric and is suspended from a central vertical axis.
2. The drop is static, which means that the interfacial tension and gravity are the only forces available (Andreas et al., 1938).

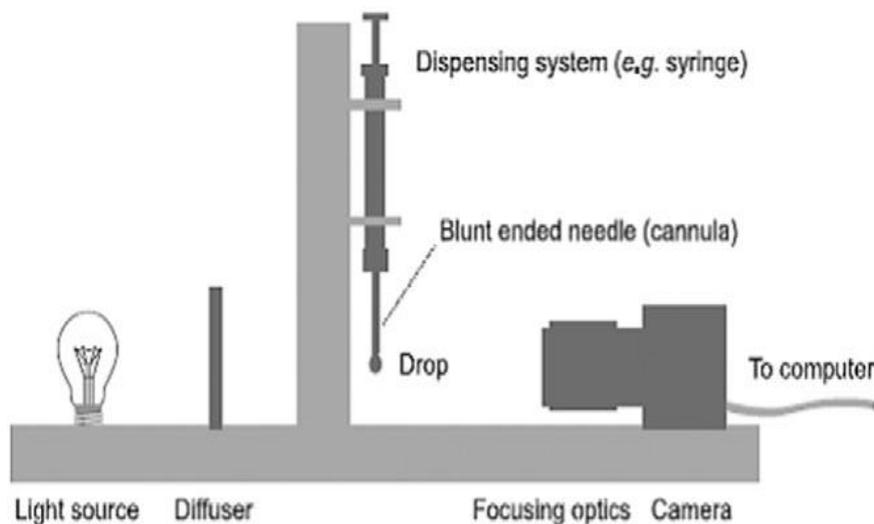


Figure 1

A typical setup of pendant drop method (Berry et al., 2015).

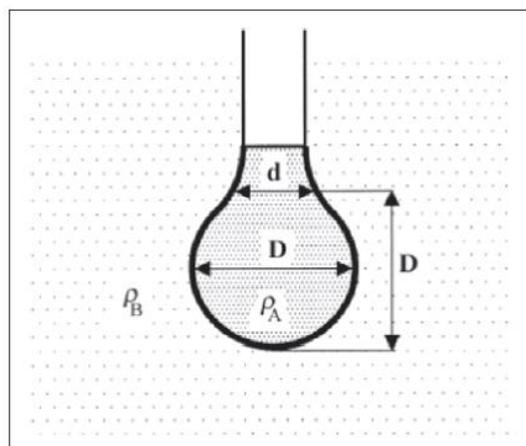


Figure 2

Associated parameters of pendant drop method (Drelich et al., 2002).



Figure 3
IFT-PDSA-02 apparatus from APEX Co. analyzing drop shape.

The device used herein to calculate the CMC of the surfactant is an IFT-PDSA-02 apparatus from APEX Co. analyzing drop shape.

In this apparatus, a drop of a fluid in the other fluid is formed, and the interfacial tension is calculated by measuring the drop shape and solving a form of the Laplace equation (Chen et al., 2000). The following equation is used to calculate interfacial tension:

$$\Delta P = \gamma + \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{1}$$

where, ΔP is the pressure difference between the inside and the outside of the droplet, and γ represents the surface tension (ST); R_1 and R_2 are the main radii of the curvature. By setting the camera in front of the cell, the drop formed can be seen on the monitor screen. By using the apparatus software, the drop form is analyzed, and finally the output of the software is surface tension.

3. Results and discussion

3.1. Salinity effects on the CMC

In this section, the effects of calcium, magnesium, sodium, sulfate, and chloride ions, which are commonly found in the reservoir rock porous media and considered as the dominant ions in this environment, on the change of CMC are discussed.

To understand the effects of these parameters on the CMC, four types of brine with different weight percentages of 0, 0.1, 0.5, and 1 wt.% were designed to dissolve the studied surfactant at different concentrations. Then, changes in the CMC were measured using the surface tension method. In order to evaluate the effects of ionic strength on the CMC variations, ion strength was calculated for each solution. The ionic strength equation is defined by:

$$I = \frac{1}{2} * \sum_{i=1}^n (C_i * Z_i^2) \tag{2}$$

where, $\frac{1}{2}$ coefficient is due to including both cations and anions, and C_i is the molar concentration of ion i (M, mol/L); Z_i represents the charge number of ion i , and n stands for the number of ions available in the solution.

a. Ca^{2+} effect

Ca^{2+} as a divalent ion is one of the most important ions in the reservoir chemical processes, so its effect on CMC should be investigated. For this purpose, CaCl_2 salt was dissolved in distilled water at specific concentrations, and nonionic Triton X-100 surfactant was then dissolved in the desired brine at concentrations of 25, 50, 75, 100, 110, 120, 130, 135, 140, 150, 175, 200, and 250 ppm; finally, the surface tension between the solution and air was obtained.

For example, the curve of surface tension (ST) is drawn as a function of surfactant concentration at 0.5 wt.% of CaCl_2 in order to determine the CMC, as depicted in Figure 4.

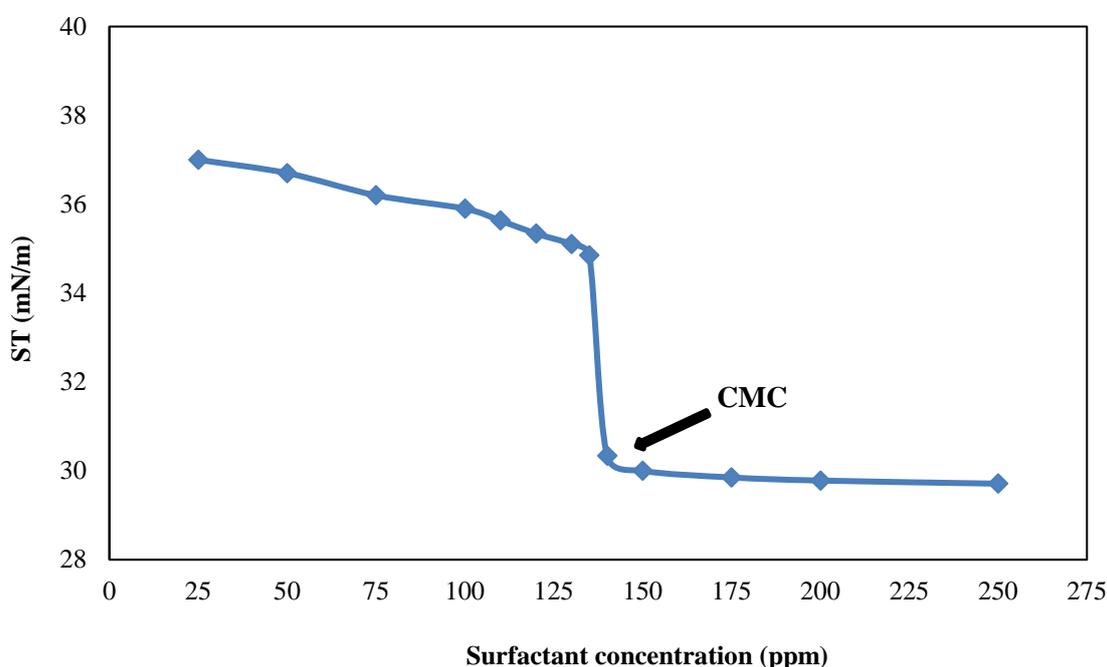


Figure 4

Determination of the CMC amount of surfactant at 0.5 wt.% of CaCl_2 .

Figure 5 also shows CMC changes and ionic strength against increasing the concentration of calcium ion.

As shown in Figure 5, increasing the concentration of this ion leads to a decrease in the CMC. Reduction in the CMC was relatively low by raising the concentration of calcium ion from 0 to 0.5 wt.%, but at high concentrations of calcium ion (0.5 to 1 wt.%), the drop in the CMC was significant. The results confirmed the effect of calcium ion on CMC.

Moreover, it is obvious that raising the concentration of calcium ion leads to an increase in ionic strength and a decrease in the CMC. Therefore, the CMC of this surfactant is reduced in the presence of calcium ions in a concentration range of 0.5 to 1 wt.% due to increased ionic strength.

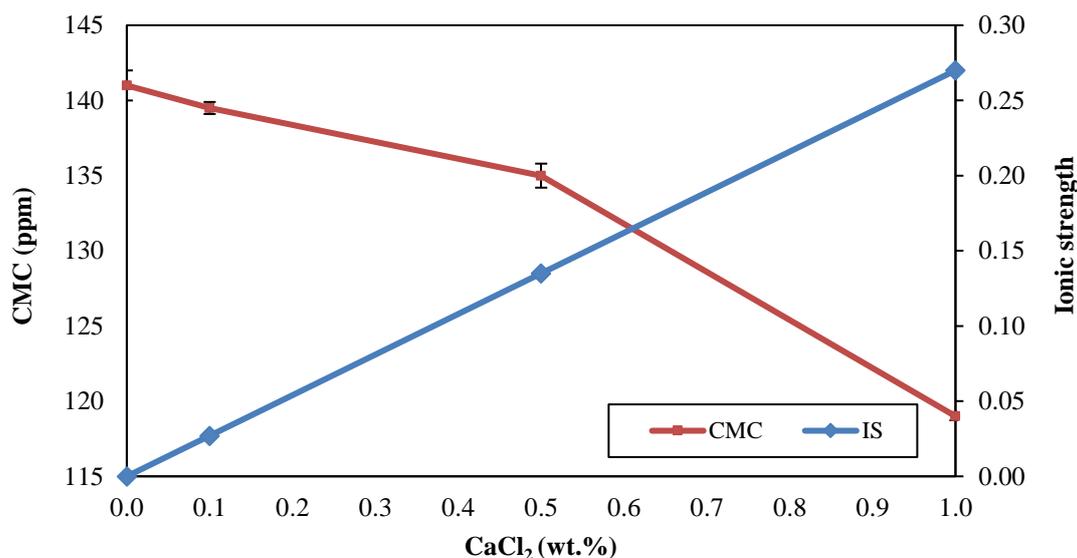


Figure 5

CMC and ionic strength versus CaCl₂ wt.%.

b. Mg²⁺ effect

Another divalent ion, the effect of which on CMC was studied in this study, was Mg²⁺ ion. Mg²⁺, like calcium ion, is one of the most effective cations in the porous medium influencing the chemical mechanisms of the reservoir. Similar to the previous section, the effect of this ion on CMC was investigated at four concentrations of 0, 0.1, 0.5, and 1 wt.%, and the CMC was determined using the ST method.

Figure 6 shows variations in CMC as a function of the weight percentage of this ion. By increasing the concentration of magnesium ion, the CMC begins to decrease. Of course, the rate of reduction in the CMC is lower at low magnesium ion concentrations (up to 0.5 wt.%) compared to high concentrations of magnesium ions (0.5 to 1 wt.%), which behaves quite similar to calcium ion; moreover, the CMC values in the presence of each ion, i.e. calcium and magnesium, are almost similar at the four selected concentrations of ions, with a difference of less than 1 to 2 ppm.

Furthermore, according to Figure 6, ionic strength linearly rises with increasing the concentration of magnesium ion. As can be seen, increasing the concentration of magnesium ion leads to an increase in ionic strength but a reduction in the CMC. In this section, the behavior of magnesium ion is quite similar to that of calcium ion, with the difference that the ionic strength at certain concentrations is slightly smaller in the presence of calcium ion than magnesium ion, which can be attributed to the higher atomic mass of magnesium ion compared to calcium ion.

According to Figures 5 and 6, the ionic strength of the solutions was increased by increasing the concentrations of magnesium and calcium ions. The CMC of the surfactant was decreased by increasing the ionic strength.

c. SO₄²⁻ effect

The SO₄²⁻ ion is one of the anions that is commonly found in the formation water of oil reservoirs and mainly affects the chemical interactions of the reservoir. Thus, the effect of the concentration of this

ion on the CMC was evaluated herein.

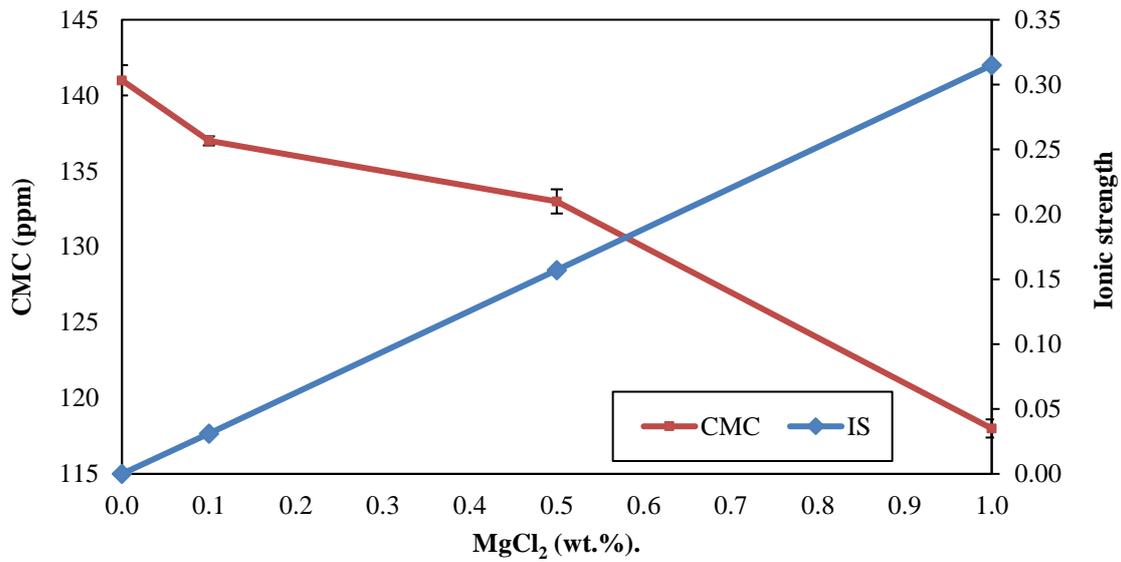


Figure 6

CMC and ionic strength versus MgCl₂ wt.%.

Figure 7 shows the variations of the CMC and ionic strength as a function of the sulfate ion concentration. It delineates the variations in the CMC in the presence of sulfate ion at four concentrations of 0, 0.1, 0.5, and 1 wt.%. Increasing the concentration of sulfate ion leads to a fall in the CMC. In fact, increasing the concentration of sulfate ion by 0.1 wt.% decreases the CMC to 2 ppm, while raising the ion concentration from 0.1 to 0.5 wt.% significantly reduces the CMC to 31 ppm; a further rise in the concentration of this ion from 0.5 to 1 wt.% decreased the rate of CMC reduction. Therefore, it can be concluded that an increase in sulfate ion leads to a decrease in the CMC, but above a certain concentration, the rate of reduction drops.

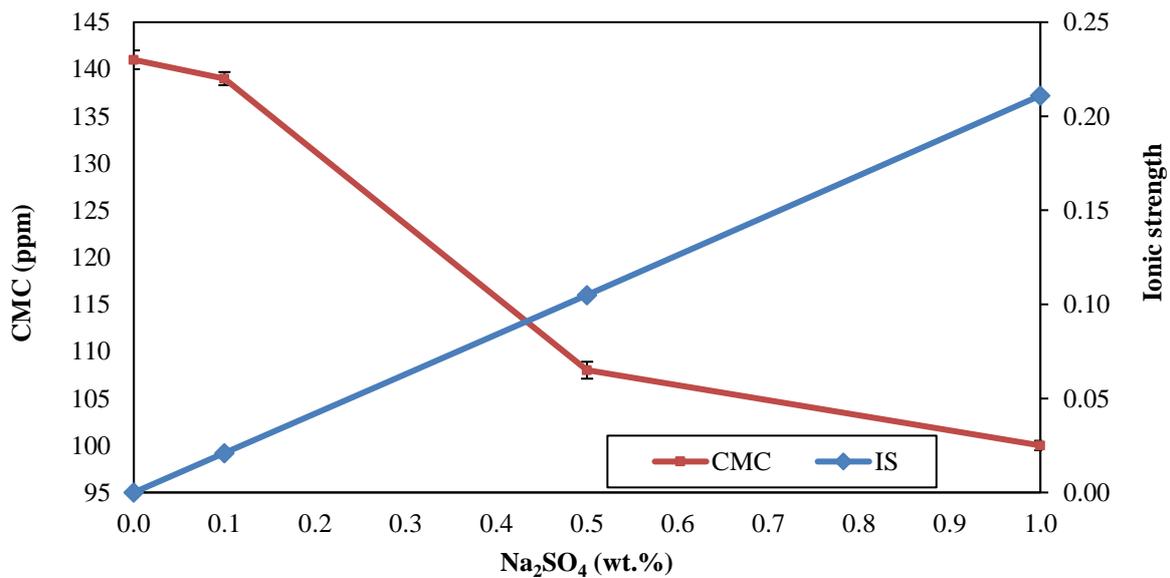


Figure 7

CMC and ionic strength versus Na₂SO₄ wt.%.

It is clear that increasing sulfate ion concentration and the TDS of the solution raise ion strength but reduce the CMC. The difference in ionic strength at concentrations of 0.5 to 1 wt.% is greater than that at concentrations of 0.1 to 0.5 wt.% and 0 to 0.1 wt.%.

Furthermore, at concentrations of 0.1, 0.5, and 1 wt.% of this divalent anion, ionic strength is lower compared to divalent cations, and similarly, the CMC in the presence of divalent anions is lower than in the presence of divalent cations.

So far, it can be concluded that at equal concentrations of various ions, when the ionic strength level is lower, the CMC is also reduced and optimized.

d. Na⁺ effect

The Na⁺ ion, as a mono-valent ion commonly found in most oil reservoirs, usually results from the reduction of CMC levels, as indicated in the literature (Thongngam et al., 2005). Figure 8 shows CMC and ionic strength alterations against increasing sodium ion concentration. As can be seen, an increase in sodium ion concentration results in a decrease in the CMC. The rate of decrease in CMC at low sodium ion concentrations is low (at sodium concentrations from 0 to 0.5 wt.%), while it is very high at high concentrations of sodium ion (from 0.5 to 1 wt.%); thus, the curve slope at high sodium ion concentrations is much higher than that at low sodium concentrations.

Comparing Figure 7 with Figures 4, 5, and 6 confirms that sodium ion has the greatest effect on reducing CMC at a concentration of 1 wt.%. The lowest CMC's were found in the presence of sulfate ion at a concentration of 0.5 wt.% and in the presence of magnesium ion at a concentration of 0.1 wt.%. This comparison shows that increasing the concentration of monovalent ions such as sodium in the brine leads to a significant reduction in the CMC. These days, the injection of low salinity water (the injection of water with a TDS of less than 8,000 to 10,000 ppm) into the oil-wet reservoirs is very much considered as an enhanced oil recovery (EOR) technique; hence, it can be concluded that the most effective ion for the simultaneous injection of Triton X-100 non-ionic surfactant and low salinity water into the reservoir is sodium ion, and subsequently, sulfate, magnesium, and calcium ions are the most effective contributing ions in this scenario, which produce the lowest CMC and greatly reduce the operational cost of the injection of this surfactant.

As can be inferred from this figure, similar to the other ions discussed earlier, at an increased sodium ion concentration, ion strength increases, while the CMC is reduced. It indicates again that by increasing the ionic strength of a specific ion, the CMC level is reduced, so there is an inverse relationship between the ionic strength and the CMC in the presence of an ion.

Moreover, at 1 wt.% concentration, sodium ion has the lowest ionic strength as well as CMC compared to the other divalent ions. Since the reduction in the CMC at a concentration of 1 wt.% of sodium ion is very significant, it can be understood that, with a smaller ionic strength of an ion at a certain concentration compared to the other ions, it can produce a lower CMC for non-ionic Triton X-100 surfactant. Therefore, the sodium ion is the most effective ion for reducing the CMC and for injection along with the Triton X-100 surfactant. Since the concentration of this ion in sea water and formation water is much higher than that of the other ions, especially the divalent ions, the flooding of this surfactant into the reservoir can be very practical. Furthermore, the reduction in the CMC in the presence of sulfate divalent anion in comparison with magnesium and calcium divalent cations can be attributed to the presence of two sodium ions in Na₂SO₄ salt.

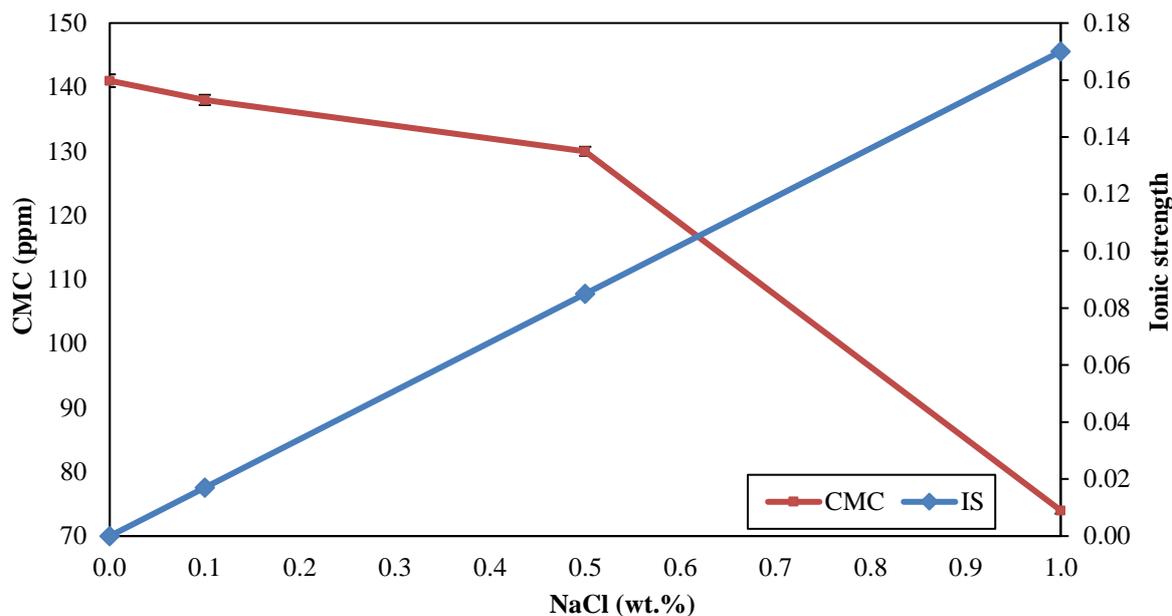


Figure 8

CMC and ionic strength versus NaCl wt.%.

As can be seen in Figures 5, 6, 7, and 8, the intersection points of the CMC and ionic strength curves are respectively at salt concentrations of 0.62, 0.59, 0.56, and 0.62 wt.%. For all the four salts, the numbers are very close, and these intersection points are much closer in the case of the cations.

The formation of the micelle is the result of three main forces:

1. Repulsive forces between the hydrophobic tail groups of surfactant molecules and solvent;
2. Electrostatic repulsion forces between the hydrophilic head groups of the surfactant molecules due to the bonding of water molecules to the polar head and increasing the volume of that part (hydration of water).
3. Van der Waals attractive forces between the groups of the surfactant tail.

Salts have been shown to greatly reduce CMC because they decrease the repulsion between charged head groups and thus lead to the formation of micelles at lower concentrations of surfactant monomer. This is usually explained as hydrocarbon and electrostatic contributions to the Gibbs free energy change of micelle formation (Kresheck et al., 1975; Palladino et al., 2011). By adding salts to surfactant solutions, electrostatic repulsion between polar head groups decreases and micelles are formed at lower concentrations. Salts also reduce electrical charges at the micelle surface, which indicates an increase in the degree of opposite ions bonding due to the neutralization of the surface. As can be seen in Figures 5-8, after the intersection points expressing this fact, the slope of CMC trend line was steeper for cations, but it was gentler for divalent anion, which is attributed to the ability of these ions and their ionic strength to form micelles and to their surface charges. This can be caused by the behavior of the salt altering micelle formation. Moreover, increasing ionic strength raises the tendency of water molecules to react with the ions, which results in a more pronounced hydrophobic interaction between the surfactant tail groups. This is in good agreement with the results obtained by Miyagishi et al. who used a series of salts for other types of nonionic surfactants (Miyagishi et al., 2001). Although CMC's were very close at four concentrations of surfactant for the divalent ions of calcium and magnesium, magnesium ions were more efficient than calcium ions in reducing the CMC. In addition, in the case of

divalent ions, sulfate anion had a lower CMC at high salt concentrations than calcium and magnesium cations and showed better performance. Although sulfate ion highly reduced the CMC at low concentrations (0 to 0.5 wt.%), the other ions with an opposite electrical charge led to the highest reduction in the CMC at high concentrations (0.5 to 1 wt.%). Adding the salts to the surfactant solution resulted in an increased soluble ion strength and showed that by increasing the ionic strength of each salt, the CMC was decreased. Also, it was found out that ionic strength has an opposite relationship with the CMC. However, by examining the ionic strength of the four studied salts at a concentration of 1 wt.%, we discovered that when the ionic strength of an ion at a certain concentration is lower than that of the other ions at the same concentration, the CMC is lowered. For example, the ionic strength of the solutions made in this study at a concentration of 1 wt.% was the lowest for NaCl, Na₂SO₄, MgCl₂, and CaCl₂ salts respectively, and the CMC followed the same trend.

Considering that all the CMC's obtained in this study were calculated by surface tension method, to investigate the effect of the studied surfactant on reducing the interfacial tension between the surfactant solutions and crude oil (oil sample from Karanj oil field), as a sample, IFT values were measured at surfactant concentrations higher than the CMC (150 ppm) and in the presence of the mentioned salts at a concentration of 0.5 wt.%. All the experiments of this stage were carried out at ambient temperature and atmospheric pressure.

Figure 9 illustrates the IFT values at a concentration of non-ionic Triton X-100 surfactant equal to 150 ppm with four types of salts at a concentration of 0.5 wt.% in solution.

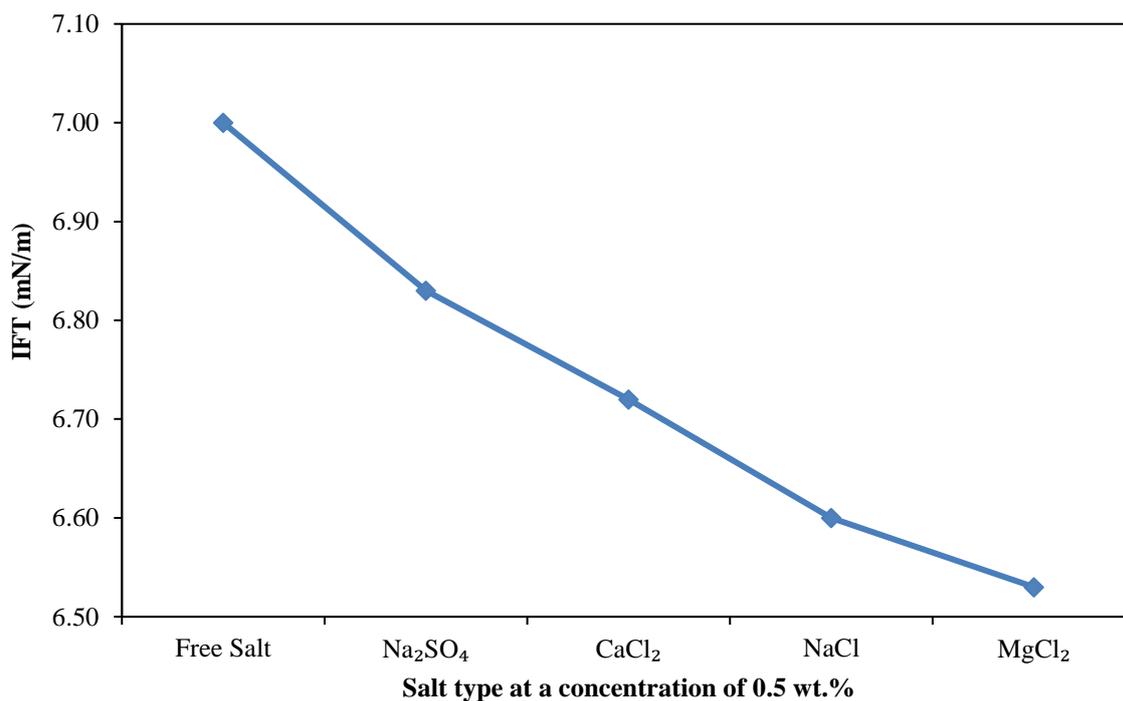


Figure 9

IFT values versus salt type, CaCl₂, MgCl₂, Na₂SO₄, and NaCl, all at a concentration of 0.5 wt.%.

According to this figure, cations had a lower IFT than anions at a specific concentration of salt (0.5 wt.%), which can be attributed to the type of crude oil and its compounds. Additionally, cations had a better interaction with the desired surfactant, which has also been approved by Zhou et al. (Zhou et al., 2017). Furthermore, in the case of divalent cations, magnesium produced a smaller IFT value due to a higher ionic strength, which, was not very tangible. In addition to magnesium, sodium had a lower IFT

value than calcium with this crude oil too, which was ascribed to the lower CMC of this ion compared to calcium divalent ion.

4. Conclusions

In summary, we assessed four predominant salts which play an important role in reducing the amount of the CMC and are mostly found in oil reservoirs. The effect of NaCl, CaCl₂, MgCl₂, and Na₂SO₄ salts on the CMC of Triton X-100 as a non-ionic surfactant was investigated at four concentrations of 0, 0.1, 0.5, and 1 wt.%. The results show that increasing the concentration of each of these salts leads to a reduction in the CMC although NaCl has a greater effect than the other salts; in fact, adding 1 wt.% of NaCl reduces the CMC by about 50%, i.e. decreasing the CMC from 141 ppm to 74 ppm by raising the concentration of NaCl from 0 to 1 wt.%. The order of the magnitude of the CMC reduction is NaCl, Na₂SO₄, MgCl₂, and CaCl₂ respectively; the CMC at a concentration of 1 wt.% of these salts was 74, 100, 118, and 120 ppm respectively. The addition of the salts to the surfactant solution results in an increased ion strength and indicates that by increasing the ionic strength of each salt, the CMC is decreased. It can be concluded that the best salt for surfactant flooding is NaCl, which significantly reduces the cost of flooding and improves the condition of the injection with a proper reduction in the CMC.

Nomenclature

AOS	Alpha olefin sulfonate
CMC	Critical micelle concentration
CTAB	Cetyl trimethylammonium bromide
DDAO	Dodecyl dimethyl amine oxide
EOR	Enhanced oil recovery
IFT	Interfacial tension
ppm	Part per million
SDBS	Sodium dodecyl benzene sulfates
SDS	Sodium dodecyl sulfate
ST	Surface tension
TDS	Total dissolved solids
wt.%	Weight percent

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