

## **Influence of Surfactant Type, Surfactant Concentration, and Salinity on Interfacial Tension of a Brine/Live Oil/Surfactant Fluid System: A Case Study of Iranian Asmari Oil Reservoir**

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### **Abstract**

The chemical surfactant flooding can mobilize the trapped oil by lowering the interfacial tension between oil and brine and in some cases altering the reservoir rock wettability. In this work, the effect of surfactants on oil/brine interfacial tension was experimentally investigated. First, the effect of surfactants concentration was surveyed. Afterwards, the effect of salinity on surfactant behavior was studied. The experiments were carried out at ambient and reservoir temperatures (all at reservoir pressure) to clarify that we cannot generalize the ambient experimental results to reservoir ones and the experiments must be done in reservoir conditions to attain more certainty. Sodium dodecyl sulfonate, cetyl trimethyl ammonium bromide and Triton X-100 were used as the surfactants. The oil and brine samples of the Iranian Asmari reservoir were used. Pendant drop method was used to measure oil/brine interfacial tension. Based on the results, it is concluded that the anionic surfactant (SDS) has a better performance at reservoir and ambient temperatures. The superiority of SDS is more emphatic at reservoir temperature than ambient temperature. At reservoir temperature, the SDS solution lowers the interfacial tension significantly (0.4 mN/m) even when a very low concentration of SDS (0.04 wt.%) is added to brine.

**Keywords:** Surfactant, CTAB, SDS, Optimum Salinity, IFT

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### **1. Introduction**

It is estimated that two-thirds of crude oil remains in the oil reservoirs after primary and secondary (water flooding) recovery stages (Zeinolabedini Hezave et al., 2013). In order to satisfy the increasing global energy demand and the consumption forecast during the next decades, a more realistic solution to meet this need lies in sustaining the production from existing fields for several reasons (Sheng, 2011). The industry cannot guarantee new discoveries; new discoveries are most likely to lie in offshore, deep offshore, or problematic areas and will not be sufficient to meet our needs; producing

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unconventional resources like oil sands and oil shales would be more expensive than producing from existing depleted fields by enhanced oil recovery (EOR) methods.

One method that has received much attention and intensive study over recent years is the use of surfactant based chemical flooding.

In order to producing remaining oil, a detail understanding of the interaction among oil, water, and rock surface is necessary; Surface chemistry has a very important role in enhancing oil recovery; The interplay of capillary, viscous, and gravity forces is a determining factor.

The capillary number  $N_c$  is a dimensionless ratio of viscous to local capillary forces, often defined as in Equation 1. The viscous force will help oil mobilization, while the capillary forces favor oil trapping (Lake, 1989).

$$N_c = \frac{\mu v}{\sigma c \theta} \quad (1)$$

Capillary number must be on the order of  $10^{-3}$  in order to reduce the residual oil saturation to near zero. Since it is difficult to increase the fluid viscosity or flow rate by several magnitudes, the most logical way to increase the capillary number is to reduce the interfacial tension (IFT) or modify the wettability to intermediate states.

Surfactant addition has become very attractive because of its ability to reduce surface/interfacial tension between immiscible fluids, thereby increasing the capillary number necessary for mobilizing residual hydrocarbons in the reservoir.

A surfactant molecule has at least one hydrophilic group and at least one hydrophobic group. The surfactant molecule is usually presented by a “tadpole” symbol. While the hydrophilic portion is usually called head, the hydrophobic portion (usually hydrocarbon chain) is named tail. The hydrophilicity of a surfactant is determined by the structure of the head and the tail, e.g. the hydrocarbon chain length, the number of branches in the chain, and the functional groups, including ethoxylated group or propoxylated group. Surfactant molecules prefer to aggregate in solutions to form phases such as micellar solutions, microemulsions, and lyotropic liquid crystals. According to the charge of the head group, surfactants are categorized into five groups: anionic, cationic, nonionic, amphoteric, and polymeric surfactants (Holmberg et al., 2003, Tadors, 2005).

The use of surfactants in enhanced oil recovery has been studied extensively in the past. Seethepalli et.al investigated the interactions of dilute alkaline anionic surfactant solutions with crude oil on carbonate mineral surfaces. Anionic surfactants have been identified, which can change the wettability of the calcite surface to intermediate/water-wet condition as well as (or better than) the cationic surfactant DTAB when used with a West Texas crude oil in the presence of  $\text{Na}_2\text{CO}_3$ , which reduces the interfacial to very low values ( $<10^{-2}$  mN/m) (Seethepalli et al., 2004).

Chen et.al measured the interfacial tensions between oil and the solution of cationic Gemini surfactants by the spinning drop method. They found that Gemini surfactants are more effective and efficient than corresponding conventional surfactants in reducing the interfacial tension and can lower the tension of kerosene–water interface to ultra-low at a very low concentration without other additives. The addition of salt results in more effectiveness of surfactant in reducing the tension of kerosene–water interface. This indicates that salt has a positive effect on lowering the tension of kerosene–water interface. They reported that the more effectiveness of surfactant by the addition of salt is presumably because of the modification of the kerosene–water interface hydrophilic lipophilic

balance by the added salt. Another reason may be the compression of the electrical double layer of interface by the added salt, which can reduce the thickness and rigidity of interface film and lead to the reduction of interfacial tension (Chen et al., 2004).

Zhao et al. studied the dynamic interfacial tension behavior of the novel surfactant solutions and Daqing crude oil using the spinning drop method. Hexyl methyl naphthalene sulfonate (Hex-MNS), octyl methyl naphthalene sulfonate (Oct-MNS), decyl methyl naphthalene sulfonate (Dec-MNS), dodecyl methyl naphthalene sulfonate (Dodec-MNS), and tetradecyl methyl naphthalene sulfonate (Tetradec-MNS) were used as surfactants. It was found that the alkyl methyl naphthalene sulfonate surfactants, except for Hex-MNS, exhibit good dynamic interfacial tension behaviors. They observed that with increasing salinity, the required optimum surfactant concentration increases (Zhao et al., 2007).

Surfactant adsorption on rock surfaces has severely crippled this means of improving oil recovery due to the high cost associated with the large quantities of the surfactant needed. Therefore, the cost and precipitation of surfactants on rock surface must be studied in details since these factors weaken operations from the economic point of view. Therefore, the cheaper and more efficient surfactants must be found and used. Such surfactants must reduce the IFT significantly and change the surface wettability toward mixed wet states.

In this paper, the effects of surfactants on brine/live oil IFT was experimentally investigated by the pendant drop method. All tests were performed at reservoir pressure and ambient and reservoir temperatures. Three kinds of surfactants were used: sodium dodecyl sulfonate (SDS) as an anionic surfactant, cetyl trimethyl ammonium bromide (CTAB) as a cationic surfactant, and Triton X-100 as a nonionic surfactant. Brine and crude samples were from the Iranian Asmari reservoir.

The effect of salinity (total dissolved solids) on surfactant behavior was also investigated. The experiments were carried out at ambient and reservoir temperatures (all at reservoir pressure) to demonstrate that we cannot generalize the ambient experimental results to reservoir conditions and the experiments must be done in reservoir conditions to attain more certainty. Finally, the effect of various surfactants on IFT was surveyed, and, based on the results, the best surfactant was selected for the Asmari oil.

## 2. Materials and methods

Three kinds of surfactants were used: sodium dodecyl sulfonate (SDS) as an anionic surfactant, cetyl trimethyl ammonium bromide (CTAB) as a cationic surfactant and Triton X-100 as a nonionic surfactant. The surfactants were provided by Merck Company. The purity grade was more than 99% for all the surfactants.

The crude oil used in this investigation was an Asmari crude oil obtained from the Ahwaz oil field in Iran. Table 1 shows the crude specifications and its sampling conditions.

**Table 1**

The crude specifications and its sampling conditions (reported by the PVT Laboratory of NISOC).

<b>Sampling depth (m)</b>	2680
<b>Reservoir pressure (psi)</b>	3741
<b>Reservoir temperature (°F)</b>	191
<b>Bubble pressure (psi)</b>	3400
<b>GOR (SCF/STB)</b>	763

<b>Oil density at reservoir conditions ( gr/cc)</b>	0.7054
<b>Oil density at reservoir pressure, ambient temperature (gr/cc)</b>	0.7567
<b>Dead oil density (gr/cc)</b>	0.8754

The brine was also from the Asmari reservoir and obtained from the Ahwaz oil field in Iran. Table 2 shows the results of brine analysis; the brine salinity is 160050 ppm.

**Table 2**

The brine composition and specifications (reported by the Analytical Chemistry Laboratory of NISOC).

<b>Cl<sup>-</sup> (ppm)</b>	104725
<b>SO<sub>4</sub><sup>2-</sup> (ppm)</b>	700
<b>NO<sub>3</sub><sup>2-</sup> (ppm)</b>	105
<b>Ca<sup>2+</sup> (ppm)</b>	12400
<b>Mg<sup>2+</sup> (ppm)</b>	1093
<b>Fe<sup>2+</sup> (ppm)</b>	27
<b>Na<sup>+</sup> (ppm)</b>	41000
<b>Conductivity (ms)</b>	188.8
<b>Density (g/cc)</b>	1.1187
<b>pH</b>	4.44

Oil–water interfacial tensions were measured using the pendant drop method (Torsaeter and Abtahi). The experiments were performed using the Vinci pendant drop interfacial tension apparatus.

A series of surfactant solutions, including a certain amount of the surfactant and inorganic salt was confected. We combined various proportions of reservoir brine and distilled water to obtain the required salinity. Thereafter, a certain amount of surfactant was added to reach the desired concentration.

### 3. Results and discussions

In this work, the effect of surfactants on brine/live oil IFT was experimentally investigated using the pendant drop method. All the tests were performed at reservoir pressure and ambient and reservoir temperatures. Three kinds of surfactants were used: SDS, CTAB, and triton X-100. The effect of salinity on surfactants behavior was also investigated.

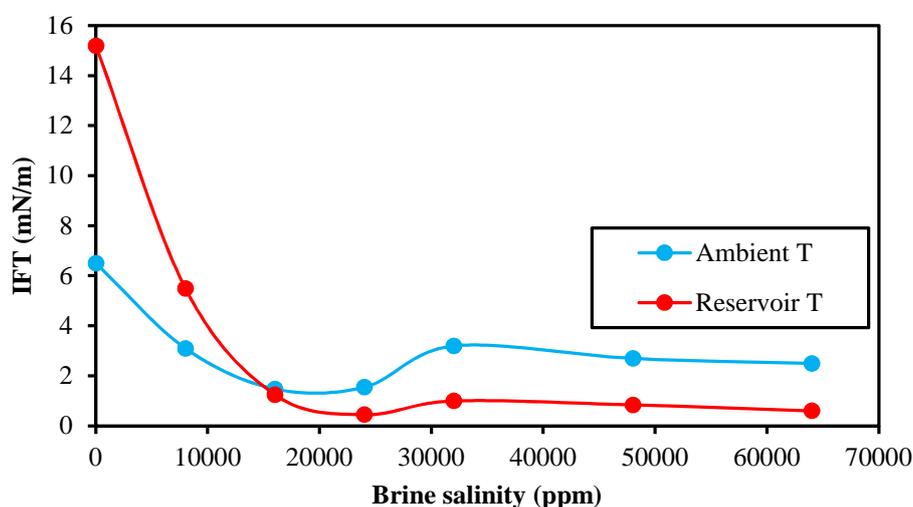
In addition, we surveyed the effect of various surfactants on IFT. Afterwards, based on the results, the best surfactant was selected for the Asmari oil.

Before performing the experiments, the accuracy of the apparatus was checked by measuring the interfacial tensions of distilled water/air and methanol/air fluid systems as the standard samples. The interfacial tensions of the distilled water/air and methanol/air fluid systems are 72.86 (Pallas and Harrison 1990) and 22.5 mN/m (Jasper 1972) at 20 °C respectively. The measured interfacial tensions were 72.5 and 25.35 mN/m for water/air and methanol/air respectively. Thus, the accuracy of the apparatus to measure interfacial tension is acceptable. In order to perform quality control check, every measurement was repeated at least twice.

The effect of salinity on the performance of 0.05 wt.% SDS solution is shown in Figure 1. The SDS precipitated in the brine with salinity of more than 65000 ppm. Therefore, measurements were conducted up to a salinity of 65000 ppm.

As shown in Figure 1, with increasing salinity up to 16000 ppm the IFT decreases from 6.5 mN/m to 1.48 mN/m at ambient temperature. Afterwards, a further increase in salinity causes a slight increase in IFT. This behavior is in agreement with previous researches. With increasing salinity, the repulsion between the charged head groups of surfactant decreases. When a high amount of ions are present in the solution, the repulsion forces are replaced by the attraction between the positive ions of brine and SDS negative surface charges at the molecular level, which causes a slight decrease in the repulsion effect between anionic charges of the SDS head groups. In other words, the positively charged ions neutralize the negative surface charges of the anionic surfactant (SDS). This leads to the easier accumulation of SDS molecules at the oil-brine interface, which reduces IFT. This is true up to a specific salinity called optimum salinity. When the salinity goes beyond the optimum salinity, increasing salinity causes inverse effects, which means the IFT increases with a further increase in salinity. The optimum salinity occurs at 16000 ppm for ambient temperature.

At reservoir temperature, an increase in salinity up to 24000 ppm causes a decrease in IFT from 15.2 mN/m to 0.45 mN/m; however, a further increase in salinity does not change the IFT considerably. Both temperatures have the same curve trends. Figure 1 surprisingly shows that the SDS solution decreases the IFT significantly up to the brine salinity of 65000 ppm. The 0.05 wt.% SDS in brine revealed the low IFT value of 0.6 mN/m at the salinity of 65000 ppm. This proves the high capability of SDS surfactant to lower the interfacial tension of the Asmari oil.

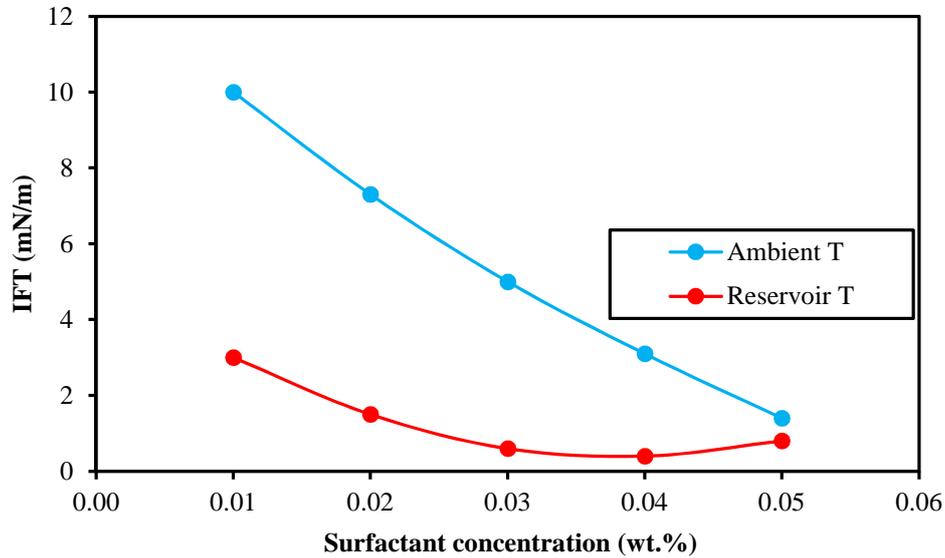


**Figure 1**

The effect of salinity on the performance of 0.05 wt.% SDS solution at ambient temperature (20 °C) and reservoir temperature (88.3 °C) and all at reservoir pressure (3741 psi).

Figure 2 presents the effect of the SDS concentration on the IFT of brine/oil/surfactant system. The brine salinity is 65000 ppm. At ambient temperature, with increasing the SDS concentration from 0.01 wt.% to 0.05 wt.%, the IFT decreases from 10 mN/m to 1.4 mN/m. At reservoir temperature, with increasing the SDS concentration from 0.01 wt.% to 0.04 wt.%, the IFT decreases from 3 mN/m to 0.4 mN/m. Afterwards, a further increase in concentration causes a little increase in IFT. At reservoir

temperature, the SDS solution lowers the interfacial tension significantly (0.4 mN/m) although a very low concentration of SDS (0.04 wt.%) was utilized into brine. Unlike the anionic surfactant, the cationic surfactant did not precipitate in brine salinity up to reservoir brine salinity (160050 ppm).

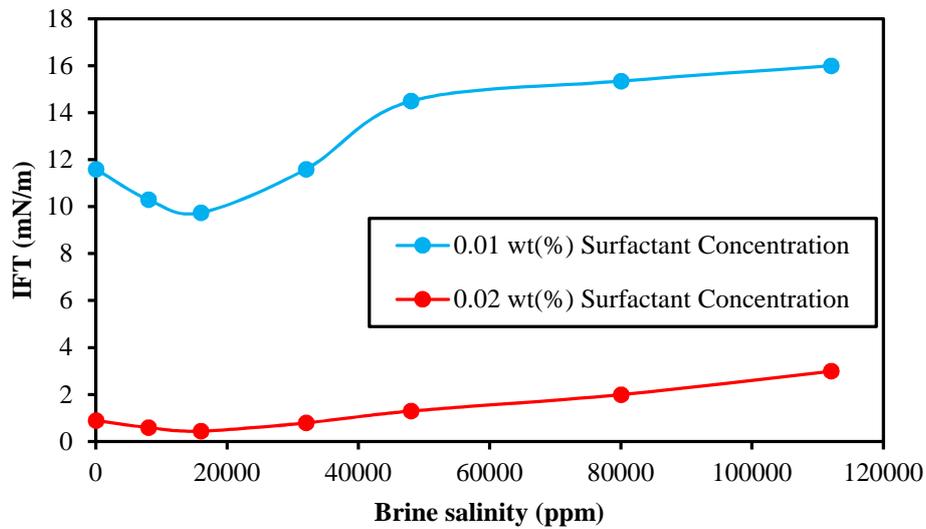


**Figure 2**

The effect of the SDS concentration on the IFT of brine/oil/surfactant system for ambient temperature (20 °C) and reservoir temperature (88.3 °C) and all at reservoir pressure (3741 psi); The brine salinity is 65000 ppm.

Figure 3 shows the effect of salinity on the performance of 0.01 wt.% and 0.02 wt.% CTAB solution at ambient temperature. For 0.01 wt.%, an increase in salinity up to 16000 ppm causes a decrease in IFT, but with a further increase in salinity, the IFT increases. Therefore, the optimum salinity occurs at 16000 ppm for 0.01 wt.%.

For a 0.02 wt.% solution, an increase in salinity up to 16000 ppm causes a decrease in IFT; a more increase in salinity raises the IFT but not as much as what happened when 0.01 wt.% solution was used. Therefore, the optimum salinity occurs at 16000 ppm for a 0.02 wt.% solution. SDS is more efficient than CTAB in saline water.



**Figure 3**

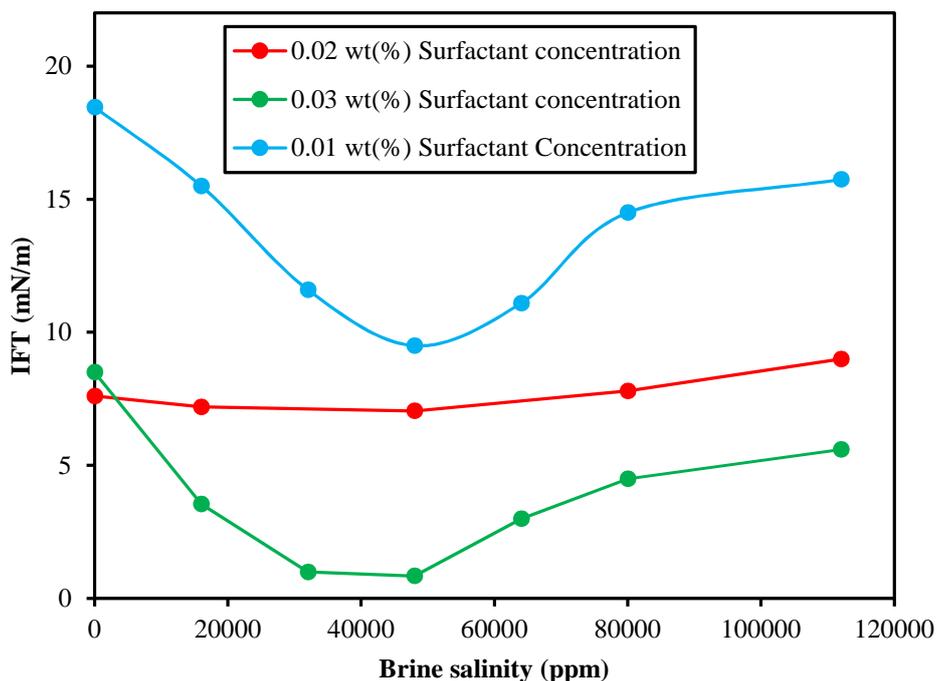
The effect of salinity on the performance of 0.01 wt.% and 0.02 wt.% CTAB solutions at ambient temperature (20 °C) and reservoir pressure (3741 psi).

Figure 4 shows the effect of salinity on the performance of the CTAB solution at reservoir temperature. The concentrations of 0.01 wt.%, 0.02 wt.%, and 0.03 wt.% were used. For 0.01 wt.%, an increase in salinity up to 48000 ppm first causes a decrease in IFT; however, a further rise in salinity raises the IFT. Therefore, the optimum salinity occurs at 48000 ppm. The optimum salinity for the concentration of 0.02 wt.% is also 48000 ppm; however, salinity has a negligible effect on the behavior of the 0.02 wt.% solution.

The trend for the 0.03 wt.% solution is the same as that of the 0.01 wt.% solution although the optimum salinity for the 0.03 wt.% solution occurs at 32000 ppm. The IFT at the optimum salinity is 0.85 mN/m.

The curves for the 0.01 wt.% and 0.03 wt.% solutions show that the net effect of salinity up to 112000 ppm is positive, i.e. the IFT at a salinity of 112000 ppm is still lower than that of the distilled water.

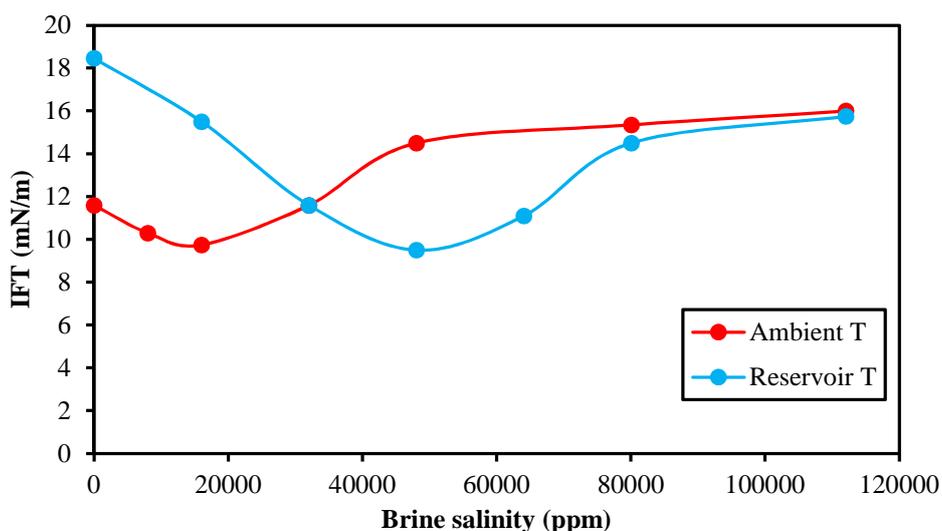
It is revealed from Figure 4 that the 0.03 wt.% CTAB solution can be an appropriate candidate for the Asmari oil because it shows a minimum value of IFT (0.85 mN/m).



**Figure 4**

The effect of salinity on the performance of 0.01 wt.%, 0.02 wt.%, and 0.03 wt.% CTAB solutions at reservoir temperature (88.3 °C) and reservoir pressure (3741 psi).

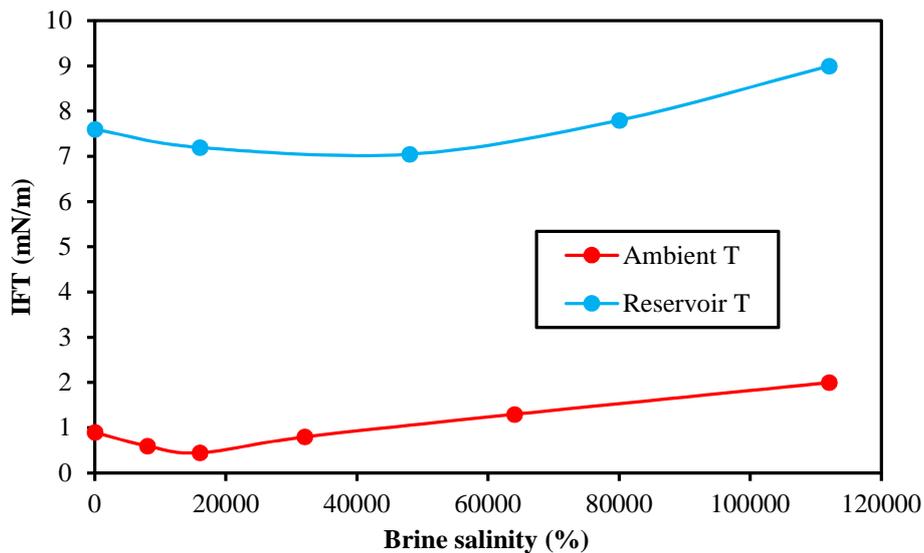
Figure 5 shows the effect of salinity on the behavior of 0.01 wt.% CTAB solution at ambient and reservoir temperatures. The optimum salinities for ambient and reservoir temperatures are 16000 ppm and 48000 ppm respectively. The IFT curve for ambient temperature lies under the reservoir one up to a salinity of 32000 ppm; thereafter, the trend is the opposite up to a salinity of 112000 ppm, where two curves approach each other. Hence, the 0.01 wt.% CTAB solution is not a good candidate for the Asmari oil.



**Figure 5**

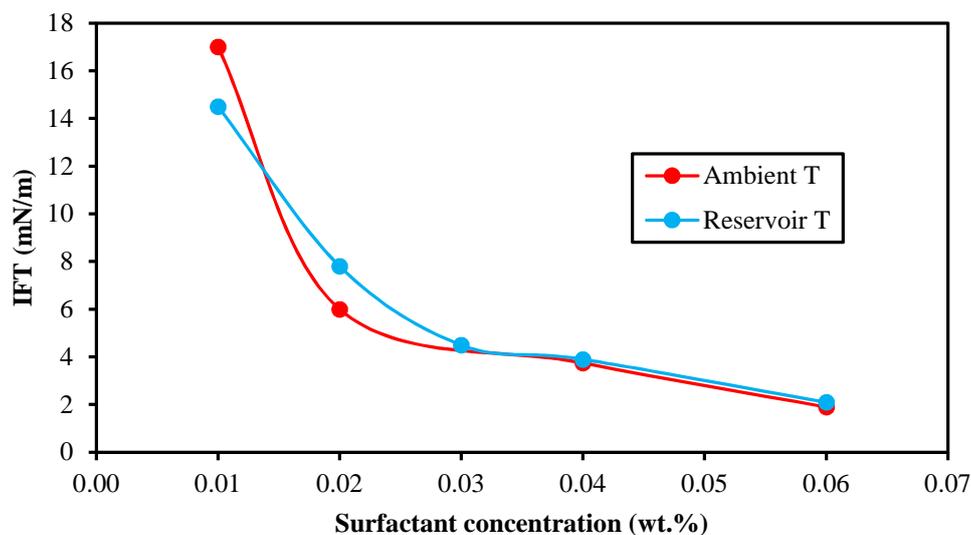
The effect of salinity on the behavior of 0.01 wt.% CTAB solution at ambient temperature (20 °C) and reservoir temperature (88.3 °C), and all at reservoir pressure (3741 psi).

Figure 6 depicts the effect of salinity on the behavior of 0.02 wt.% CTAB solution at ambient and reservoir temperatures. The optimum salinities for ambient and reservoir temperatures are 16000 ppm and 48000 ppm respectively. The IFT curve for ambient temperature lie under the reservoir temperature curve. The difference between two curves is about 6 units. The tests at ambient temperature were carried out for comparison only.. Since the results in reservoir conditions are more important, the 0.02 wt.% CTAB solution is not also a good candidate for the Asmari oil.



**Figure 6**  
The effect of salinity on the behavior of 0.02 wt.% CTAB solution at ambient temperature (20 °C) and reservoir temperature (88.3 °C), and all at reservoir pressure (3741 psi).

Figure 7 presents the effect of the CTAB concentration on the IFT of brine/oil/surfactant system at ambient and reservoir temperatures; the brine salinity is 65000 ppm. At ambient temperature, with increasing CTAB concentration from 0.01 wt.% to 0.02 wt.%, the IFT decreases from 17 mN/m to 6 mN/m. Thereafter, the reduction rate of IFT slows down.

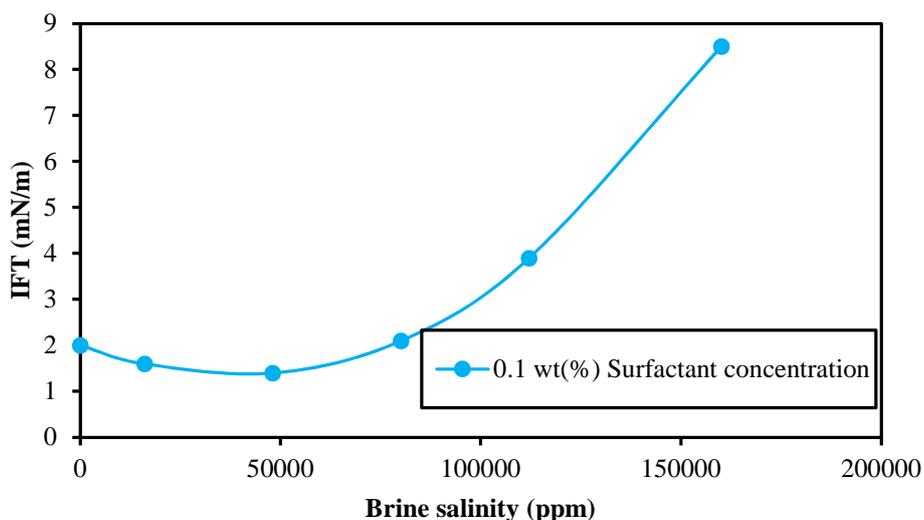


**Figure 7**

The effect of the CTAB concentration on the IFT of brine/oil/surfactant system for ambient temperature (20 °C) and reservoir temperature (88.3 °C), and all at reservoir pressure (3741 psi); The brine salinity is 65000 ppm.

The curves for both temperatures are nearly the same and lie on each other from a concentration of 0.03 wt.% to 0.06 wt.%. The nonionic surfactant solution became turbid at reservoir temperature, so the measurements were conducted for ambient temperature only. The nonionic surfactant did not precipitate in brine salinity up to the reservoir brine salinity (160050 ppm).

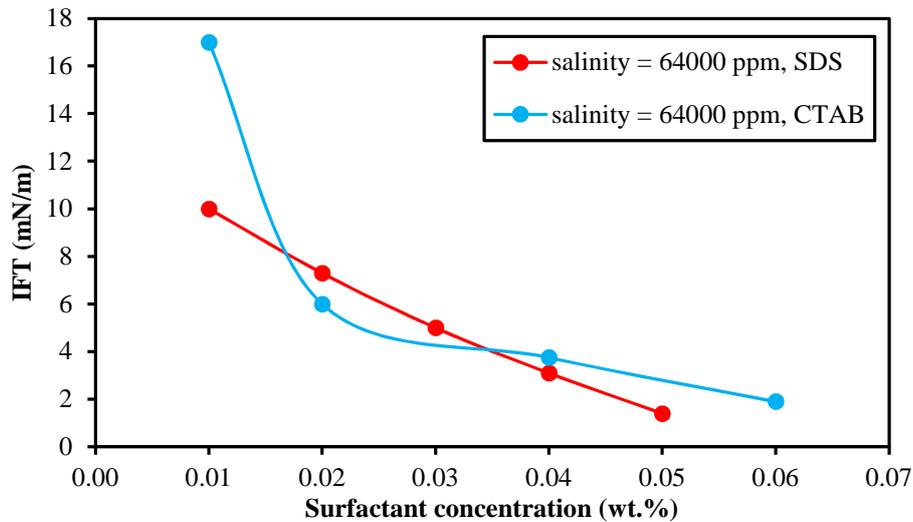
Figure 8 shows the effect of salinity on the behavior of 0.1 wt.% Triton X-100 solution at ambient temperature. The IFT is 1.4 mN/m at the optimum salinity (48000 ppm).



**Figure 8**

The effect of salinity on the behavior of 0.1 wt.% Triton X-100 solution at ambient temperature (20 °C) and reservoir pressure (3741 psi).

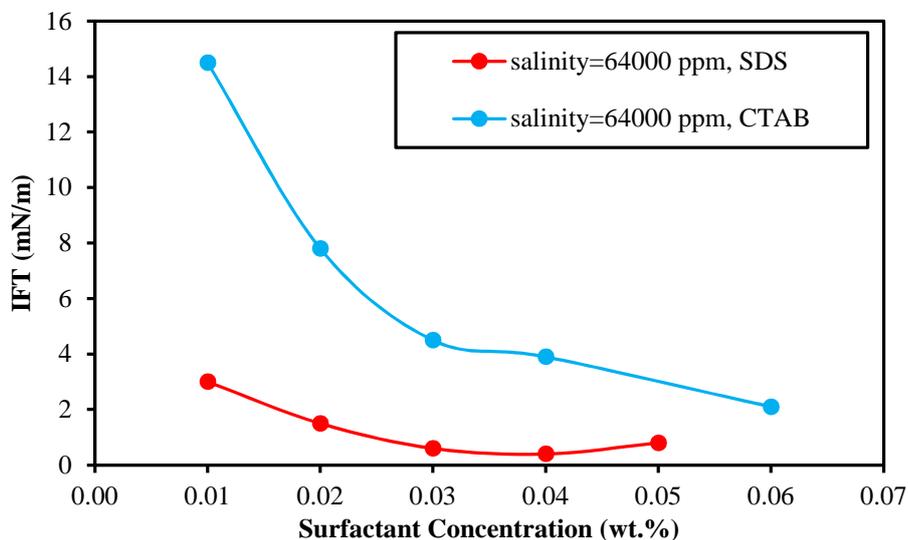
Figure 9 compares the performance of the SDS and CTAB surfactants at ambient temperature. The brine salinity is 64000 ppm. For the SDS surfactant, increasing concentration of the solution from 0.01 wt.% to 0.05 wt.% reduces the IFT from 10 mN/m to 1.4 mN/m. For the CTAB solution, increasing concentration from 0.01 wt.% to 0.06 wt.% decreases the IFT from 17 mN/m to 1.9 mN/m. Thus, it is concluded that the anionic surfactant has a better performance in brine at ambient temperature, but this superiority is not considerable.



**Figure 9**

The interfacial tension versus surfactant concentration in brine solution (64000 ppm) for the SDS and CTAB surfactants at ambient temperature (20 °C) and reservoir pressure (3741 psi).

Figure 10 illustrates the interfacial tension versus surfactant concentration in brine solution (64000 ppm) for the SDS and CTAB surfactants at reservoir temperature. For the SDS solution, with increasing concentration from 0.01 wt.% to 0.05 wt.%, the IFT drops from 3 mN/m to 0.8 mN/m. For CTAB solution, raising the concentration from 0.01 wt.% to 0.06 wt.% reduces the IFT from 14.5 mN/m to 2.1 mN/m. Therefore, it is concluded that the anionic surfactant shows a better performance in brine also at the reservoir temperature.



**Figure 10**

The interfacial tension versus surfactant concentration in brine solution (64000 ppm) for the SDS and CTAB surfactants at reservoir temperature (88.3 °C) and reservoir pressure (3741 psi).

#### 4. Conclusions

In the present study, the effect of surfactants on the interfacial tension of surfactant/brine/oil was studied. The brine and oil samples were from the Iranian Asmari reservoir. All the tests were carried

out at reservoir pressure, and at ambient and reservoir temperatures. Three kinds of surfactants were used: SDS, CTAB, and triton X-100. The effect of salinity on surfactants behavior was also investigated. The IFT measurements were conducted by the pendant drop method. Very low interfacial tensions were observed in reservoir conditions as follows:

- ) The fluid system of 0.05 wt.% SDS in brine with a salinity of 24000 ppm and live oil shows the interfacial tension of 0.45 mN/m.
- ) The fluid system of the 0.03 wt.% CTAB in brine with a salinity of 32000 ppm and live oil shows the interfacial tension of 0.85 mN/m.
- ) The fluid system of the 0.04 wt.% SDS in brine with a salinity of 65000 ppm and live oil shows the IFT of 0.4 mN/m.

Based on the results, it is concluded that the anionic surfactant (SDS) has a better performance at reservoir and ambient temperatures. The superiority of SDS is more emphatic at reservoir temperature than ambient temperature.

### Nomenclature

CTAB	: Cetyl trimethyl ammonium bromide
IFT	: Interfacial tension
SDS	: Sodium dodecyl sulfonate,
V	: Fluid velocity (cm/s)
Greek	
	: Contact angle (degree)
$\mu$	: Fluid viscosity (poise)
	: Interfacial tension (dyne/cm)

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