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Role of Surfactant and Salinity on Crude Oil-Water Interfacial Tension in a part of an Oilfield of Upper Assam Basin

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Abstract:

The petroleum crisis led to a significant research effort in the development of new Enhanced Oil Recovery (EOR) methods for oil recovery from depleted oil fields. Different studies have led to the development of different EOR methods based on the brine phase. The earlier studies have shown that altering the chemistry of the brine phase affects the oil recovery efficiency.

Among the various EOR methods, Chemical Enhanced Oil Recovery (CEOR) has been used worldwide for many decades and the fundamental CEOR is the Surfactant Flooding which reduces the oil-water Interfacial Tension (IFT) and in turn improves the oil recovery efficiency. Another emerging EOR method is the injection of low saline water into the oil reservoir. Lager et al. (2006) observed an increase in pH of the bulk fluid during the laboratory experiment on the injection of low saline water. According to Morrow et al. (1998) and Tang and Morrow (1997), high pH generates in-situ surfactants in the reservoir which reduces the interfacial tension between the reservoir oil and water that in turn increases the oil recovery efficiency. Earlier studies have shown that the combination of low saline water with surfactant can be more beneficial than low salinity brine injection or Surfactant Flooding alone and therefore can be more attractive economically. Also, it is observed that IFT of a hydrocarbon versus water decreases with decreasing the concentration of salt in the aqueous phase (Kumar, 2012).

Keeping this view in mind, the present study has been undertaken to study the role of surfactant and salinity of brine on the Crude Oil-Water IFT in a part of an oilfield of Upper Assam Basin. Two types of surfactants (Sodium Dodecyl Sulphate & Cetyl Trimethyl Ammonium Bromide) have been used in the present study in various concentrations. Based on the reservoir brine salinity, salt solutions of various concentrations have been used both with and without the surfactant to study the effects of brine salinity and surfactant on Crude Oil-Water IFT. The study shows that, IFT between the Crude Oil-Water decreases with increasing the concentration of surfactant and decreasing the salinity of the brine.
Keywords: EOR, CEOR, IFT, Surfactant Flooding, basin.

Introduction:

Currently the daily oil production comes from the mature or maturing oil fields and reserves replacement is not keeping pace with the growing energy demand. With the increasing energy demands over the years, it has become a necessity to find new ways of improving the extraction of Original Oil In Place (Armentano, 1985). Enhanced Oil Recovery (EOR) is one of such processes wherein 'foreign' fluids are introduced into the reservoir with the help of various processes to improve the oil recovery efficiency (Tunio et al., 2011).

Around 40% of residual oil is still left behind after the action of primary and secondary recovery methods (Zitha et al., 2011). According to Hirasaki et al., (2011), EOR methods can be applied along with the primary and secondary recovery methods as well. Chemical Flooding, one of the EOR methods are now getting importance to recover the trapped oil after primary and secondary recovery methods. Surfactant Flooding, a Chemical Enhanced Oil Recovery (CEOR) method has garnered some attention in the recent years for its effectiveness where surfactants are used to significantly reduce the Interfacial Tension (IFT) between the crude oil and water/brine in the reservoir (Chierici, 1995; Yuan et al., 2015). The main target of Surfactant Flooding is to decrease the capillary trapped Residual Oil Saturation (ROS) after a waterflood which will increase the Microscopic Displacement Efficiency that in turn increases the oil recovery efficiency (Riisoen, 2012). Another effect of the Surfactant Flooding is that it may alter the wettability of the rock (Lake, 1984), which can lead to higher oil recovery. The efficiency of the surfactant depends on several factors, such as the character of the surfactant, temperature and the salinity of the brine (Riisoen, 2012).

The efficiency of the process could be reduced due to the surfactant loss by adsorption on rock surface and in turn reduction of IFT between water and oil, which ultimately renders the process technically unviable. According to Friedman (1986), Alagic & Skauge (2010) and Alagic et al. (2011); surfactant retention increases with increasing the salinity of the aqueous phase. Studies carried out by Hirasaki et al. (1983), Stournas (1984) and Mannhardt & Jha (1994) also have shown that combining surfactant with low salinity water containing low concentration of divalent ions improves the performance of Surfactant Flooding.

Surfactants are chemical substances that adsorb on or concentrate at a surface or fluid-fluid interface and alter the interfacial properties significantly; in particular, they decrease the Interfacial Tension (Green and Willhite, 1998). This surface/interface adsorption leads to pronounced physical changes, reduces the surface/interfacial tensions and alters the wettability of a surface (Zheng, 2012). The surface can be between solid and liquid, between air and liquid or between two immiscible liquids (Porter, 1994). Surfactant can be classified as anionic, cationic, nonionic and amphoteric according to the presence of formally charged hydrophilic groups in its head (Xavier, 2011).

Earlier studies have shown that, salts can have a pronounced effect on the IFT of crude oil-brine system. The effect of salts on the IFT of crude oil-brine system depends on the type and amount of surface active material present in it. The presence of salt in the aqueous phase can alter the distribution of surface active component of crude oil to aqueous phase by Salting-out Effect. Also, salts can accelerate the diffusion of surface active components from bulk solution to the interface (Bai et al., 2010). Thus, the IFT of crude oil-brine system is a complex function of the concentration of salt and surface active components.

Several authors have shown that the concentration of the surface active components in the oil phase increases with increasing the concentration of monovalent salts in the water phase (Bennett & Larter, 1997; Standal et al., 1999). It is found that, IFT of a hydrocarbon versus water decreases with decreasing the concentration of salt in the aqueous phase (Kumar, 2012). Also, according to Price (1976), the aqueous solubility of petroleum hydrocarbon species decreases with increasing the salinity due to Salting-out Effect. Based on the studies on the effect of formation brine salinity level on the crude oil-water IFT, Okasha and Al-Shiwaish (2009) found that the IFT between crude oil and brine decreases with decreasing the volume percent of formation brine in the water phase.

The present work aims to study the role of surfactant and salinity on crude oil-water IFT in a part of an Oilfield of Upper Assam Basin which is a category-I basin in India. The individual effects of surfactant and salinity on crude oil-water IFT has been studied in the present work. The effect of brine salinity on the crude oil-water IFT has been studied under constant surfactant concentration. Also, a work has been done on the effect of surfactant on crude oil-water IFT under constant brine salinity in the study area. Although, the usage of proper concentration of surfactant and salinity is yet to be applied on a large scale in this basin, the suitability of the method and the proper selection of surfactant and salt are definitely to be considered in future.

Experimental Works:

As discussed above, the salinity and surfactant concentration plays a very important role on crude oil-water IFT which in turn affects the oil recovery efficiency. For this study, we have collected analytical data on formation brine and crude oil sample from the study area. Two surfactants namely Sodium Dodecyl Sulphate (SDS) and Cetyl Trimethyl Ammonium Bromide (CTAB) have been used to see their effects on crude oil-brine IFT. The effects of the surfactants (SDS & CTAB) and different water (600 ppm, 1000 ppm, 1404 ppm, 2000 ppm as NaCl and distilled water) on the crude oil-water IFT have been studied in the present work based on a series of laboratory experiments.

Sodium Dodecyl Sulphate ($NaC_{12}H_{25}SO_4$) is an anionic surfactant used widely as a detergent and fat emulsifier. The hydrophobic part has a C12 hydrocarbon chain attached to a sulphate group and the hydrophilic part has a sodium ion (Paroor, 2012). Cetyl Trimethyl Ammonium Bromide ($C_{19}H_{42}BrN$) is another surfactant which is best known for its antiseptic qualities and its role in the extraction of DNA (Wilkie, 1996). It is a quaternary ammonium surfactant. The hydrophobic part is the C16 hydrocarbon chain and the hydrophilic head is the ammonium.

For the present study, the density of the crude oil and the prepared brines were determined using Mud Balance in the laboratory of Department of Petroleum Engineering, Dibrugarh University, Dibrugarh, Assam as the density difference between crude oil and brine is essential for determining the crude oil-brine IFT using a Tensiometer. The Interfacial Tension between the crude oil and the prepared brine was then determined using M6500 Spinning Drop Tensiometer in the laboratory of Department of Petroleum Engineering, Dibrugarh University, Dibrugarh, Assam. The instrument works on the 'Spinning Drop Method' and is capable of measuring ultralow IFT down to 10^{-6} mN/m up to a maximum value of 2 mN/m.

Effects of surfactant on crude oil-water IFT:

As mentioned above, Sodium Dodecyl Sulfate (SDS) and Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant have been used in the present study to see their effects on crude oil-water IFT. The water used in this study is the distilled water. The results of the experiment are given in Table 1 & 2.

Table 1: The results of the crude oil-water IFT for different concentrations of SDS

Concentration of SDS in brine (%)	**Crude Oil-Water Interfacial Tension (mN/m)**
0.3	5.57×10^{-3}
0.5	4.12×10^{-3}
1	3.7×10^{-3}
2	2.7×10^{-3}
3	2.55×10^{-3}
4	2.35×10^{-3}

Table 2: The results of the crude oil-water IFT for different concentrations of CTAB

Concentration of CTAB in brine (%)	**Crude Oil-Water Interfacial Tension (mN/m)**
0.2	1.63×10^{-3}
0.3	1.47×10^{-3}
0.35	1.44×10^{-3}
0.5	1.36×10^{-3}
0.7	1.01×10^{-3}
1	0.96×10^{-3}
1.2	0.95×10^{-3}
1.5	0.90×10^{-3}
1.7	0.87×10^{-3}

A comparative study have been made between the effects of SDS and CTAB on crude oil-water IFT and shown in the Figure 1.

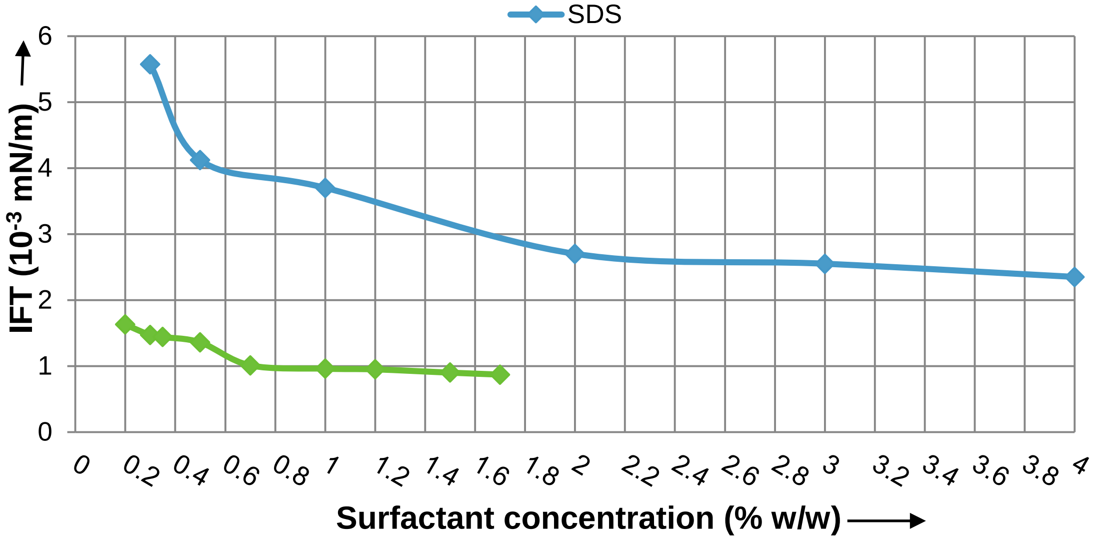

Figure 1: Effect of surfactant on crude oil-water IFT

Effects of brine salinity on crude oil- brine IFT without using surfactant:

As discussed above, salinity of the brine phase has a vital role on the oil-brine IFT which in turn affects the oil recovery efficiency. In the present study, four different brines were prepared to see their effects on the crude oil-brine IFT. Out of the four different saline water, two are low saline water (600 ppm and 1000 ppm as NaCl), one is high saline water (2000 ppm as NaCl) and the other is the water having the same salinity (1404 ppm as NaCl) as in the formation brine of the study area. No surfactant was used during this experiment. The result of the experiment is given in Table 3.

Table 3: The results of the crude oil-brine IFT for different brine salinity

Brine Salinity (ppm as NaCl)	**Crude Oil-Brine Interfacial Tension (mN/m)**
2000	3.8×10^{-3}
1404	3.5×10^{-3}
1000	3.2×10^{-3}
600	2.9×10^{-3}

Effect of surfactant on crude oil-brine IFT at constant brine salinity:

A study has been made to see the effects of different concentration of surfactants (SDS & CTAB) on crude oil-brine IFT using a constant brine salinity of 1404 ppm (as NaCl) which is the formation brine salinity of the study area as mentioned above. The results of the experiment are given below in Table 4 & 5 and Figure 2.

Table 4: The results of the effects of SDS on crude oil-brine IFT at 1404 ppm (as NaCl) brine salinity

Concentration of SDS (% w/w)	**Crude Oil-Brine Interfacial Tension (mN/m)**
0.5	4.3×10^{-3}
1	3.7×10^{-3}
2	2.9×10^{-3}
3	2.8×10^{-3}

Table 5: The results of the effects of CTAB on crude oil-brine IFT at 1404 ppm (as NaCl) brine salinity

Concentration of CTAB (% w/w)	**Crude Oil-Brine Interfacial Tension (mN/m)**
0.5	1.47×10^{-3}
0.7	1.13×10^{-3}
1	1.1×10^{-3}
1.2	1.03×10^{-3}

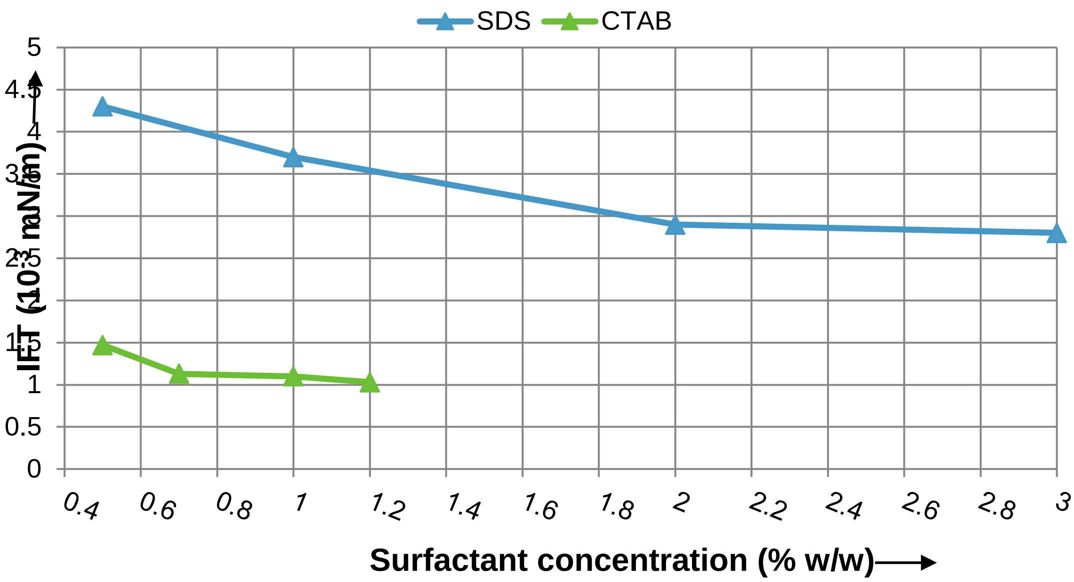

Figure 2: Effect of surfactant on crude oil-formation brine IFT

Effect of brine salinity on crude oil-brine IFT at constant surfactant concentration:

From the earlier studies, it is observed that the combined effect of surfactant and salinity is more on oil-water IFT than the effect of surfactant and salinity alone. The aqueous solubility of petroleum hydrocarbon species increases with decreasing the salinity of brine (Price, 1976) as mentioned above. In the present study, the effect of different salinity brine (600 ppm, 1000 ppm, 1404 ppm and 2000 ppm as NaCl) on crude oil-brine IFT has been studied in the presence of 2 % (w/w) and 0.7 % (w/w) SDS and CTAB respectively. The concentration of SDS and CTAB in the brine phase are taken 2 % (w/w) and 0.7 % (w/w) respectively as, above these concentration, the value of IFT between crude oil-water are almost constant (Figure 1 & 2). The results of the experiment are given in Table 6 & 7.

Table 6: Results of the effect of brine salinity on crude oil-brine IFT at constant concentrations of SDS

Brine Salinity (ppm as NaCl)	**Concentration of SDS (% w/w)**	**Crude oil-Brine Interfacial Tension (mN/m)**
2000	2	3.3×10^{-3}
1404	2	2.9×10^{-3}
1000	2	2.7×10^{-3}
600	2	2.4×10^{-3}

Table 7: Results of the effect of brine salinity on crude oil-brine IFT at constant concentrations of CTAB

Brine Salinity (ppm as NaCl)	**Concentration of CTAB (% w/w)**	**Crude oil-Brine Interfacial Tension (mN/m)**
2000	0.7	1.17×10^{-3}
1404	0.7	1.13×10^{-3}
1000	0.7	1.10×10^{-3}
600	0.7	1.06×10^{-3}

Graphs have been plotted (Figure 3) comparing the effects of brine salinity on crude oil-brine IFT with and without the presence of surfactant (SDS & CTAB).

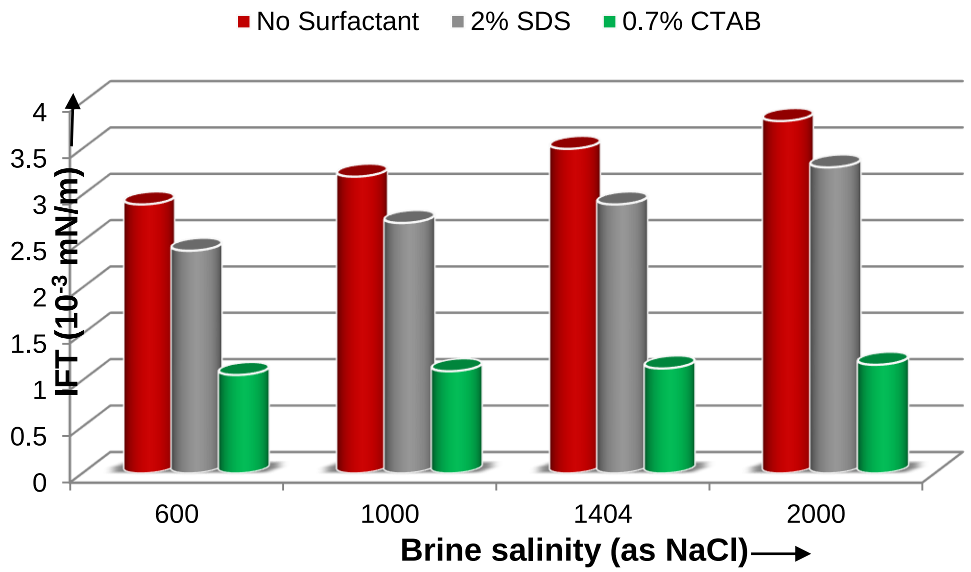

Figure 3: Effect of brine salinity on crude oil-brine IFT at different surfactant concentration

Discussion:

As mentioned above, surfactant and salinity have a vital role on the alteration of oil-water interfacial tension which in turn affects the oil recovery efficiency. From Figure 1, it is seen that the crude oil-water IFT decreases from 5.57×10^{-3} mN/m to 2.7×10^{-3} mN/m when the SDS concentration increases from 0.3 % to 2 % (w/w). Thereafter, the variation of IFT is almost negligible with the increase of SDS concentration up to 4 % (w/w). Also, there is a decrease in crude oil-water IFT from 1.63×10^{-3} mN/m to 1.01×10^{-3} mN/m when the CTAB concentration increases from 0.2 % to 0.7 % (w/w). Further increase of CTAB concentration upto 1.7 % (w/w) in the brine phase showing almost constant value of IFT as shown in Figure 1. It is therefore seen that, the crude oil-water (distilled water) IFT decreases with increasing the concentration of SDS and CTAB upto a value of 2 % and 0.7 % respectively which are the Critical Micelle Concentration (CMC) of SDS and CTAB. It is also observed that, a smaller concentration of CTAB can reduce the crude oil-water IFT significantly compared to a relatively higher concentration of SDS as shown in Figure 1.

From the study of the effect of brine salinity on crude oil-brine IFT, it is observed that the IFT value decreases from 3.8×10^{-3} mN/m to 2.9×10^{-3} mN/m when the salinity of the brine is reduced from 2000 ppm to 600 ppm (as NaCl) (Table 3). No surfactant was used during this experiment. Thus, in the absence of surfactant in the brine phase, the crude oil-brine IFT decreases with decreasing the brine salinity in the study area. Kumar (2012) also found that lowering the salinity of the aqueous phase reduces the IFT of a hydrocarbon versus water as mentioned above.

From the study of the effect of surfactant (SDS & CTAB) on crude oil-brine IFT at 1404 ppm (as NaCl) brine salinity which is the salinity of the formation brine of the study area, it is observed that the IFT of the crude oil-brine system decreases from 4.3×10^{-3} mN/m to 3.6×10^{-3} mN/m when the SDS concentration increases from 0.5 % to 3 % (w/w) (Table 4). Also, the IFT value of the said hydrocarbon verses water system is reduced from 1.47×10^{-3} mN/m to 1.03×10^{-3} mN/m when the CTAB concentration is increased from 0.5 % to 1.2 % (w/w) (Table 5). It is seen that the Critical Micelle Concentration of SDS and CTAB are 2 % (w/w) and 0.7 % (w/w) respectively for the crude oil-brine system of the study area (Figure 2).

As mentioned above, a study has been made on the effect of brine salinity on the crude oil-brine IFT at the Critical Micelle Concentration of SDS and CTAB. From the study it is observed that the crude oil-brine IFT of the study area decreases with decreasing the salinity of the brine (Table 6 & 7 and Figure 3). For both the SDS and CTAB, the IFT values are low (2.4×10^{-3} & 1.06×10^{-3} mN/m) for low salinity brine 600 ppm (as NaCl) compared to the values (3.3×10^{-3} & 1.17×10^{-3} mN/m) and values (2.3×10^{-3} & 1.13×10^{-3} mN/m) for high salinity brine of 2000 ppm (as NaCl) and formation brine of 1404 ppm (as NaCl) respectively. Also, it is observed that the effect of CTAB is more in lowering the crude oil-brine IFT in the study area compared to SDS.

Thus, it is seen that salinity of brine and surfactant play a significant role in changing the crude oil-brine Interfacial Tension in the study area. The IFT of the oil-brine system decreases with decreasing the brine salinity and increasing the surfactant concentration. The effect of CTAB is more on lowering the IFT compared to SDS.

Conclusion:

Based on the different studies on the effect of surfactant and salinity on crude oil-water/brine IFT, following conclusions are drawn-

1. For the crude oil-water/brine system of the study area, the Critical Micelle Concentration (CMC) of SDS and CTAB are 2 % (w/w) and 0.7 % (w/w) respectively.
2. In the absence of surfactant, the crude oil-brine IFT decreases with decreasing the brine salinity in the study area.
3. In the absence of salt in the water phase, the crude oil-brine IFT decreases with increasing the surfactant (SDS & CTAB) concentration upto the CMC.
4. The crude oil-formation brine (1404 ppm as NaCl) IFT of the study area decreases with increasing the surfactant (SDS & CTAB) concentration upto the CMC. The effect of CTAB on the IFT is more than SDS.
5. At the CMC of surfactant (SDS & CTAB) in the brine phase, the crude oil-brine IFT decreases with decreasing the brine salinity in the study area.

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