Research Article
The Role of Salinity and Brine Ions in Interfacial Tension Reduction While Using Surfactant for Enhanced Oil Recovery

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Abstract: The reduction of IFT through application of surfactant is one of the widely known Enhanced Oil Recovery (EOR) methods in the petroleum industry. However, not much is known about the role of brine ions during this process. Thus, this study focuses on the capability of reducing IFT through salt ions in aqueous phase while using cationic surfactant. To determine the conditions required to reduce IFT between Brine Surfactant Solution (BSS) and oil. Experiments were carried out on a given sample of crude oil and carbonate rock slices. Dodecyl Trimethyl Ammonium Bromide (DTAB) was used as Cationic surfactant and effect of different concentrations of Ca^{+2}, Mg^{+2} were investigated. Concentrations of Ca^{+2}, Mg^{+2} were changed in range of (0.015-0.07 Wt %) while concentrations of other ions were kept constant. All experiments were carried out at 35°C. Results show that these divalent ions and their concentrations have significant influence on IFT. The IFT is in direct proportion to the salinity, that is, with rise in salinity, IFT increases significantly. An increase in concentration of divalent cations Ca^{+2} and Mg^{+2} causes a decrease in IFT between crude oil and BSS. However, strong effects on IFT are observed for Ca^{2+} relatively to Mg^{+2} under constant concentration of DTAB and same temperature.

Keywords: Cations, crude oil, divalent ions, dodecyl trimethyl ammonium bromide, salt ions

INTRODUCTION

Surfactants can be Non-ionic (no charge groups in its head), Anionic (with negative charge in its head), Cationic (with positive charge in its head) and Zwitterionic (a head with two oppositely charged groups).

Surfactant flooding is renowned as a method to produce trapped residual oil after water flooding (Hosseini *et al*., 2013). The micro-emulsions used to lower the IFT contain surfactant, hydrocarbon and water. Co-surfactant or an electrolyte may be added (Jamaloei and Rafiee, 2008). Surface-active agents are chemical substances that adsorb onto a surface or fluid-fluid interface when exist at low concentration in a system (Golabi *et al*., 2012). They contain both hydrophilic groups (tail) and hydrophobic groups (head) which makes them soluble in both organic solvents (e.g., oil) and water. The ability of surfactants to influence and interact with the properties of surfaces, allow them to be widely used in the industry as well as in the daily life. Surfactants can act in several ways to enhance oil production, by:

- Reducing the IFT between oil trapped in small capillary pores and the surrounding water

- Altering the wettability of the porous media towards water-wet
- Forming oil and water emulsions
- Improving the oil mobility

Surfactants are very sensitivity to the reservoir environment, fact which poses limitations in the surfactant flooding. However, their salt tolerance and their sensitivity to the presence of divalent and monovalent ions are also of great concern as investigated by Bansal and Shah (1978). These authors reported that an increase in IFT was observed with increase in $CaCl_2$ or $MgCl_2$ concentrations in connate water. Glover *et al*. (1979) asserted that divalent ions form sulfonate species that can strongly influence the micro-emulsion phase behavior, whereby, the effects were studied in detail by Celik *et al*. (1983). Experimental results by Kumar *et al*. (1984) have shown that the IFT of diluted petroleum sulfonate solutions against oil increased significantly upon additions of calcium or magnesium salts. In the present work, Spinning Drop IFT has been used to probe into the effects of brine divalent ions on the IFT between oil sample and surfactant solution.

Recently, special attention is turned to brine salinity impact and ion composition on EOR

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(Yousef *et al*., 2011a; Shabib-Asl *et al*., 2014). Extensive research on oil/brine/rock systems showed that injection of low salinity brines has a significant impact on the amount of recovered hydrocarbon (Yousef *et al*., 2011b). During water/oil displacements, IFT between crude oil and brine plays a crucial role, for it influences capillary number, capillary pressure, adhesion tension and the dimensionless time for imbibition (Buckley and Fan, 2007). The complex Crude oil systems, connate water and Interfacial phenomena in porous media, owe to fluid complexity of the reservoirs added to a lack of understanding of physical and chemical interactions between the fluids and porous surface. Furthermore, as asserted by Mungan (1966), understanding the role of interfacial forces in entrapment of residual oil, enables an effective and efficient oil recovery by water flooding.

To date, most of the researchers have examined different aspects of the problem wherein most of the concerns were on the effect of changes in the oil/water IFT (Mungan, 1964), the oil-water-rock contact angle (Leach *et al*., 1962) and the adsorption of the surface-active agent on the rock surfaces (Taber, 1958), the effect of flooding rate along with variations in the IFT (Wagner and Leach, 1966). To evaluate an EOR technique, vital parameters such as wettability alteration and IFT in terms of its efficiency are required. Current interests in brine injection as a potential EOR method and the role of these parameters need a better understanding (Abdallah and Stukan, 2012). Under the assumption that the oil is distributed in droplets whose movement is restricted only by the pore throats, effects of viscosity are negligible due to negligible static/near static condition, the following equation may be applied: $\Delta p = 2\sigma(1/r_1 - l/r_2)$, wherein Δp is the pressure drop necessary to displace an oil droplet through a pore throat, σ is the oil brine IFT, r_1 is the radius of curvature at the forward and smaller end of the deformed droplet and r_2 is the larger radius. This relation shows that a decrease in IFT enables the oil droplets to be more easily displaced (Kennedy and Guerrero, 1953).

Many literatures show that low salinity brines have a significant impact on the amount of oil displaced but uncertainties are in the mechanisms of the displacement (Alotaibi and Nasr-El-Din, 2009). To date, the contribution of interfacial rheology in relevant technologies has been practically neglected, although the effect of IFT and wettability on efficiency of oil recovery has been identified long ago (Lakatos and Lakatos-Szabo, 2001).

In this study, the focus is on the role of divalent ions in reducing IFT between oil sample and aqueous phase while using cationic surfactant (DTAB). For this purpose, Spinning Drop method (Spinning Drop Tensiometer SVT20N) was used.

Table 1: Brine composition SB$_1$

Composition	Concentration (mg/L)
Na$^+$ and K$^+$	1552.5
Cl$^-$	939.4
HCO$_3^-$	2263.5
SO$_4^{2-}$	13.5
Total dissolved solid	4768.9

Table 2: Brine composition SB$_2$

Composition	Concentration (mg/L)
Na$^+$ and K$^+$	3105
Cl$^-$	1878.8
HCO$_3^-$	4527
SO$_4^{2-}$	27
TDS	9537.8

Table 3: Crude oil properties

Total acid number MgKOH/g	Total base number MgKOH/g	Density g/cc
0.173	0.749	0.812

Fig. 1: Spinning drop tensiometer SVT20N for measuring IFT

MATERIALS

Cationic surfactants: In this research Cationic surfactants Dodecyl Trimethyl Ammonium Bromide (DTAB) with the formula of $C_{12}N(CH_3)_3$ Br, molecular weight 308.34 g/mol, CMC of 0.418 wt% at 25°C was used. This cationic surfactant was supplied by sigma Aldrich. The grade of this cationic surfactant is equal or rather than 98%.

Synthetic Brine (SB): Two deferent Synthetic Brines termed SB$_1$ (4768.9 mg/L) and SB$_2$ (9537.8 mg/L) were used as the brine whose compositions are shown in Table 1 and 2.

Oil sample: In this research, crude oil filtered from surface active material was used. Table 3 shows the crude oil properties.

Experimental set-up and procedures: Different concentrations of salts CaCl$_2$ and MgCl$_2$ were first added to SB$_1$ and followed by 0.75 wt% DTAB which makes the aqueous phase. The process is repeated for SB$_2$ using the same salts and the same amount of DTAB. The spinning drop (Fig. 1) technique has been used to evaluate the IFT between oil and the solution by measuring the shape of the oil drop in the chemical

solution contained in a capillary tube. The capillary spins around its axis at a constant speed, deforming the drop under the effect of centrifugal acceleration. This deformation results from the IFT between the fluids, which is related to the density of the liquids present, temperature and rotation of the system. In order to eliminate human errors and a great time-loss, an automatic measuring system has been newly developed by combining a video image analysis, an automatic recording system and a computer for determination of the IFT by the spinning drop technique.

RESULTS AND DISCUSSION

In the reservoir, when brine and oil come in contact, they create a particular angle with the rock surface, if the brine concentration changes, the corresponding contact angle changes (Ligthelm *et al.*, 2009). For such a change, there are two crucial mechanisms. The first one is the change in brine/oil interfacial tension and the second impact comes from the change of brine/rock surface wettability (Okasha and Alshiwaish, 2009). As per aforementioned, Dodecyl Trimethyl Ammonium Bromide (DTAB) was used as Cationic surfactant and effect of different concentrations of brine divalent components (Ca^{+2}, Mg^{+2}) on reduction of IFT between oil and aqueous phase was studied. Two different Brine salinities SB_1 and SB_2 were used in this experiment.

Salinity effect on IFT reduction: Figure 2 illustrates salinity effect on IFT reduction while using cationic surfactant DTAB and shows that total brine salinity has significant influence on IFT reduction.

The comparison between A and B curves indicates that IFT is in direct proportion to the salinity; i.e., with rise of salinity, IFT increases significantly. Comparison of C and D in Fig. 3 also confirms this fact. It can be due to precipitation of cationic surfactant in high salinity.

The effect of Mg^{2+} and Ca^{2+} on IFT reduction: According A, B, C and D curves in Fig. 2 and 3 increase in concentration of divalent cations (Ca^{2+} and Mg^{2+}) in brine has an important role and causes reduction in IFT at presence of cationic surfactant DTAB. This reduction is due to same electric charge of the divalent cations which increase the electric charge of the cationic surfactant to compress the interfacial double layer. Thus, by increasing the repulsion between surfactant molecules with the same charge in the micelle, more surfactant molecules could enter the micelle to enlarge the radius of the micelle particle, resulting in a decrease of IFT.

The effect of Mg^{2+} and Ca^{2+} in the presence of different salinities: Figure 2 shows that in SB_1, an increase in concentration of Ca^{2+} (0.015-0.07 Wt %)
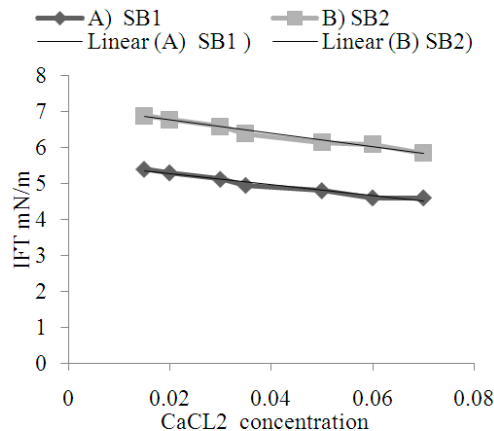
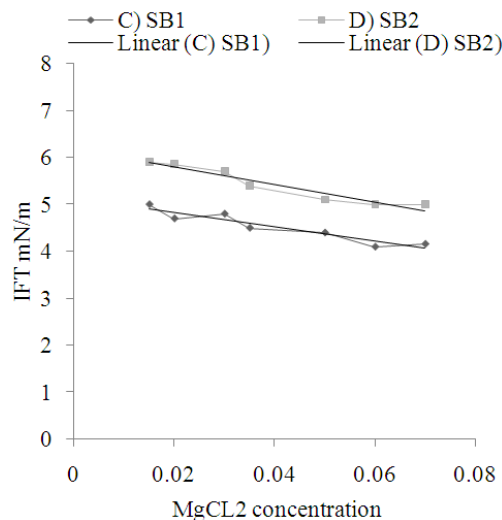Fig. 2: Effects of Ca Cl$_2$ concentrations on IFT

Fig. 3: Effects of MgCl$_2$ concentrations on IFT

lowered the IFT 0.8 mN/m (from 5.4 to 4.6 mN/m), whereas this reduction in SB_2 with the same condition was from 6.9 to 5.8 mN/m. It can be concluded that the increases in Ca^{2+} concentration in brine has stronger effects on IFT in higher salinity. The similar behavior was observed for Mg^{2+} under the same condition.

According to C and D curves in SB_1 the increase of concentration of Mg^{2+} from 0.015 to 0.07 Wt % causes a reduction in IFT from 5 to 4.16 mN/m. This change in SB_2 and same condition was 0.9 reductions in IFT from 5.9-5 mN/m. These results show that in higher salinities the increase of Mg^{2+} has stronger effect on IFT reduction.

Comparison of Ca^{2+} and Mg^{2+} effects on IFT reduction: At SB_2 the increase in Ca^{2+} concentration in comparison to Mg^{2+} in the same condition has stronger effect on IFT reduction. When concentration of Ca^{2+} changes from 0.015 to 0.07 Wt**%** there is a reduction in IFT from 6.09 to 5.85 mN/m, while Mg^{2+} decreases from 5.9 to 5 and this behavior is reverse in SB_1. It

seems this result refers to individual properties of Mg^{2+} and Ca^{+2}.

CONCLUSION

The present study shows the influence of divalent ions (Ca^{2+} and Mg^{2+}) on IFT between reservoir oil and brine surfactant solution. Based on the experimental results obtained from this study, the following conclusions were drawn:

- Under constant concentration of DTAB (0.75 wt%) and 25°C, an increase in concentration of divalent cations Ca^{2+} and Mg^{2+}, the IFT between crude oil and Brine Surfactant Solution decreases.
- At SB_2 an increase in Ca^{2+} concentration in comparison to Mg^{2+} under same condition has stronger effect on IFT reduction and an opposite behavior is observed in SB_1.
- When the Salinity is increased, the ability of Ca^{2+} and Mg^{2+} to reduce IFT is also increased.
- An increase in total brine salinity causes a significant increase in IFT between crude oil and Brine Surfactant Solution. This behavior might owe to precipitation of cationic surfactant in high salinity.

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