

# Wettability Alteration Mechanism for Oil Recovery from Fractured Carbonate Rocks

R. Gupta · K. K. Mohanty

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**Abstract** Oil can be recovered from fractured, initially oil-wet carbonate reservoirs by wettability alteration with dilute surfactant and electrolyte solutions. The aim of this work is to study the effect of salinity, surfactant concentration, electrolyte concentration, and temperature on the wettability alteration and identify underlying mechanisms. Contact angles, phase behavior, and interfacial tensions were measured with two oils (a model oil and a field oil) at temperatures up to 90°C. There exists an optimal surfactant concentration for varying salinity and an optimal salinity for varying surfactant concentration at which the wettability alteration on an oil-aged calcite plate is the maximum for anionic surfactants studied. As the salinity increases, the extent of maximum wettability alteration decreases; also the surfactant concentration needed for the maximum wettability alteration decreases. IFT and contact angle were found to have the same optimal salinity for a given concentration of anionic surfactants studied. As the ethoxylation increases in anionic surfactants, the extent of wettability alteration on calcite plates increases. Wettability of oil-aged calcite plates can be altered by divalent ions at a high temperature (90°C and above). Sulfate ions alter wettability to a greater extent in the presence of magnesium and calcium ions than in the absence. A high concentration of calcium ions can alter wettability alone. Magnesium ions alone do not change calcite plate wettability. Wettability alteration increases the oil recovery rate from initially oil-wet Texas Cordova Cream limestone cores by imbibition.

**Keywords** Wettability alteration · Fractured carbonates · Optimal salinity · Divalent ions · Imbibition · Anionic surfactants

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## 1 Introduction

Many of carbonate reservoirs are fractured and oil-wet in nature (Roehl and Choquette 1985; Chillenger and Yen 1983). Oil recovery field experience in carbonate reservoirs has been reviewed by Manrique et al. (2006). Very few processes work for fractured oil-wet carbonates and many of them have to rely on gravity drainage if the formation is highly fractured. Miscible gas injection, steam injection, and chemical treatment have been considered to recover oil from highly fractured oil-wet carbonates reservoirs. For example, Christiansen (1990) discuss gravity drainage with CO<sub>2</sub> gas flooding in Yates field. Reduction in oil-gas interfacial tension (IFT) decreases capillary pressure and gravity pushes the oil down. Oil-phase swelling and viscosity reduction also help in improving oil recovery. Shahin et al. (2006) have studied thermal-assisted gas oil gravity drainage for Qurn Alam fractured carbonate reservoir in Oman. Al-Hadhrami and Blunt (2001) have discussed steam injection in fractured carbonates. High temperature can induce wettability alteration, steam can vaporize the light ends, and gravity can drain the oil down. In both the above methods, oil remains the wetting phase with respect to the draining vapor phase which slows the drainage rate. This work looks into the chemical treatment for fractured oil-wet carbonates reservoirs.

Chemical treatment for wettability alteration is one of the techniques to recover oil from such reservoir. Cationic (Austad and Milner 1997; Standnes and Austad 2000a,b), anionic (Seethepalli et al. 2004; Adibhatla and Mohanty 2008; Hirasaki and Zhang 2004; Gupta and Mohanty 2010), and nonionic (Xie et al. 2004; Gupta and Mohanty 2010) surfactants and just electrolytes (Tweheyo et al. 2006) have been used to alter the wettability of originally oil-wet carbonate rocks. Austad and co-workers (Austad and Milner 1997; Standnes and Austad 2000a,b) have shown that cationic surfactants can recover oil from chalk cores by spontaneous counter-current imbibition due to wettability alteration. Tweheyo et al. (2006) have studied the effect of divalent ions on wettability alteration of carbonates. They found that SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> ions can change the wettability at 100°C and above without any surfactants in the system. The extent of wettability alteration increases with the increase in temperature. Adibhatla and Mohanty (2008) and Gupta and Mohanty (2010) have shown that dilute anionic and non-ionic surfactant (concentration < 0.1 wt%) solutions can give oil recovery as high as 60% OOIP from oil-wet carbonate cores. This process is a gravity driven process. The surfactant molecules diffuse/flow from fractures into the matrix and change wettability and IFT. The reduction in IFT decreases the entry capillary pressure. Gravitational forces overcome the entry capillary pressure, and water invades the matrix and pushes the oil from the top. The key to recovering oil is the wettability alteration to preferentially water-wet intermediate-wet conditions.

Oil is formed in source rocks and migrates to originally water-wet reservoirs. The polar components of oil collect at the oil–water interface (Freer et al. 2003) and adsorb on the solid surface if the water film becomes unstable. Hirasaki (1991), Mohanty et al. (1981), and Menezee et al. (1989) studied the effect of surface forces on thickness and stability of wetting films and thus on the contact angles. The film thickness depends on the applied capillary pressure and the disjoining pressure, which in turn depends in brine, oil, and mineral compositions. Buckle et al. (1998) showed that interactions between polar oil components and solid, surface precipitation of asphaltene type molecules from oil, acid/base, and ion binding between ion sites on solid/brine and oil/brine or a combination of them could be responsible for wetting of mineral surfaces by a crude oil. Hamouda and Gomari (2006) worked with a system of *n*-decane/fatty acid/water on calcite plates at elevated temperature. He showed that the wettability (contact angle) follows the same trend as partition coefficient of fatty acid and IFT which in turn depends on pH and thus on zeta potential of calcite.

The mechanism of wettability alteration by surfactants on carbonates has not been understood completely. It has been hypothesized (Austad and Milner 1997) that cationic surfactants use ion pairing to desorb polar organic components from originally oil-wet surfaces. Kumar et al. (2008) propose micellar solubilization of adsorbed organic components by anionic surfactants. This work studies the change in wettability on an initially oil-wet calcite plate by anionic surfactants. We explore possible mechanisms of wettability alteration. We analyze the effect of surfactant concentration, aqueous phase salinity, and surfactant type (chain length and number of EO/PO groups) on wettability alteration.

## 2 Methodology

### 2.1 Material

Two oils were used in this study. Most of the experiments were done with a model oil which was prepared by adding 1.5 wt% of cyclohexanepentanoic acid to *n*-decane. This was inspired by the study of Wu et al. (2008) who had studied adsorption of several naphthenic acids on calcite powders. The acid (98% active) and *n*-decane were supplied by Sigma-Aldrich. It is called the “model oil” in this article. The other oil used was from a West Texas fractured carbonate reservoir. It is called the “field oil” in this article. It had 28.2° API, 23.8 cp viscosity (at 27°C), 0.2 acid number, and 1.17 base number. Na<sub>2</sub>CO<sub>3</sub> and NaCl were used to change salinity of the aqueous phase. Na<sub>2</sub>CO<sub>3</sub> was supplied by EMD with 99.5% purity. NaCl was supplied by VWR International. Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> · 2H<sub>2</sub>O, and MgCl<sub>2</sub> · 6H<sub>2</sub>O used to vary divalent ion concentration in brine were supplied by Sigma-Aldrich. Calcite (Iceland spar) plates used for wettability experiments were supplied by Scientific Ward. In this study, we worked with the anionic surfactants listed in Table 1. Texas Cordova cream limestone core samples listed in Tables 2 and 3 were used for imbibition experiments.

### 2.2 Oil–Brine Surfactant-Phase Behavior and IFT

5 ml of surfactant solution was mixed with 5 ml of the field oil or the model oil. Na<sub>2</sub>CO<sub>3</sub> was used to change salinity in the case of field oil experiments. NaCl (with 0.025 wt% Na<sub>2</sub>CO<sub>3</sub> fixed) or Na<sub>2</sub>CO<sub>3</sub> (no NaCl) was used to vary salinity in the case of model oil experiments. The tubes were equilibrated on a tube rotator for 3 days and then left to settle on the shelf for 5 days. These experiments were conducted at room temperature. The number and volumes of phases were observed.

Interfacial tension was measured using a spinning drop tensiometer supplied by Temco. Because the surfactant concentration was low, the amount of middle phase microemulsion (if present) was small. It was difficult to measure IFT for oil–microemulsion phases and brine–microemulsion phases separately. Oil and brine samples were taken close to the interface or the middle phase (if present) with the intention of including the middle phase in the IFT sample and the IFT between oil and microemulsion phase was measured.

### 2.3 Wettability Test

Wettability was evaluated by measuring water–oil contact angles on calcite plates using a Kruss goniometer. Calcite plates were immersed in a cuvette filled with brine, and an oil drop was placed either on the top or bottom of the plate (Seethapalli et al. 2004). The contact angle is defined as the angle formed by the oil–water interface and the solid surface through the

**Table 1** Surfactants studied

Code	Surfactant type	Active wt%	MW/CMC
Alf-33	Sulfate, 3PO	28.1	485 10 ppm
Alf-35	Sulfate, 5PO	28	588 6 ppm
Alf-38	Sulfate, 8PO	26.0	715 5 ppm
Alf-68	Sulfate, 8PO	30.6	667 14 ppm
CS130	Sulfate, 1EO	25.3	346 167 ppm
CS230	Sulfate, 2EO	25.5	382 119 ppm
B330	Sulfate, 3EO	27.7	422 91 ppm
B27	Sulfate, 4EO	29.9	– 175 ppm
I-1518	Sulfonate (C15–C18)	25.4	– –
I-1720	Sulfonate (C17–C20)	27.7	– –
I-2024	Sulfonate (C20–C24)	23.8	– –
DF	Disulfonate	45.6	542 –

MW molecular weight, CMC  
critical micellar concentration

**Table 2** Cores used in imbibition experiments using field oil

Core #	Surf.	$L$ (mm)	Swi	$K$ (md)	$\phi$ (%)	$T$ ( $^{\circ}\text{C}$ )
2B	Alf-68	67	0.2505	11.44	25.24	90
15A	DF	74	0.3052	17.43	28.28	90

$\phi$  porosity,  $L$  length,  $T$  Temperature, *Surf.* Surfactant

**Table 3** Cores used in imbibition experiments using model oil

Core #	Surf.	$L$ (mm)	Swi	$K$ (md)	$\phi$ (%)	$T$ ( $^{\circ}\text{C}$ )
5 M	0.25 wt% Alf-38 0.1 M NaCl + 0.25 wt% $\text{Na}_2\text{CO}_3$	152.2	0.303	76.56	22.2	25
9 M	0.5 wt% Alf-38 0.5 M NaCl + 0.25 wt% $\text{Na}_2\text{CO}_3$	143.3	0.266	71.33	20.1	25

$\phi$  porosity,  $L$  length,  $T$  Temperature, *Surf.* Surfactant

brine phase. Calcite plates were polished on a 600 mesh diamond plate. Polished plates were aged first in a brine and then in the model oil for 1 day at room temperature to render them oil-wet. Second set of plates were aged for 2 days at 90°C in the field oil. Water–oil contact angle on calcite plates was 26° before aging and about 170° after aging. The cyclohexanepentanoic acid adsorbs on the positively charged calcite surface rendering it oil-wet. When an oil-aged calcite plate is contacted with a surfactant solution, some of the oil float up leaving behind many drops on the plate. The contact angle of the drop usually changes with time, but the change in contact angle becomes negligible after 4 h. Thus, we monitored the evolution of contact angles for about 24 h following surfactant treatments. These contact angles were advancing angles, and we measured them for 4 drops per each experiment. In cases where the oil drop size was less than 0.1 mm, it was difficult to measure an accurate contact angle and a post-wettability test was conducted (Seethepalli et al. 2004; Adibhatla and Mohanty 2008; Gupta and Mohanty 2007). In such cases, the plate was washed with brine, and fresh drops of oil were placed at the bottom using an inverted needle. The post-wettability test gives a measure of the receding contact angle, which would be lower than the advancing contact angles.

## 2.4 ATR-IR Spectroscopy

To investigate the mechanism of wettability alteration by surfactants, we conducted attenuated total reflection infrared (ATR-IR) spectroscopy on calcite plates. The calcite infrared (IR) signal was taken as the background, and adsorbed molecules on the surface were monitored after treatment with oil and surfactant solutions. A modified model oil was used in these experiments to make a calcite plate oil-wet. This oil had 20 wt% cyclohexanepentanoic acid in *n*-decane to obtain a strong IR absorption signal for the adsorbed acid on the calcite surface. Alf-38 in NaCl brine with 0.25 wt% Na<sub>2</sub>CO<sub>3</sub> was used to alter the wettability.

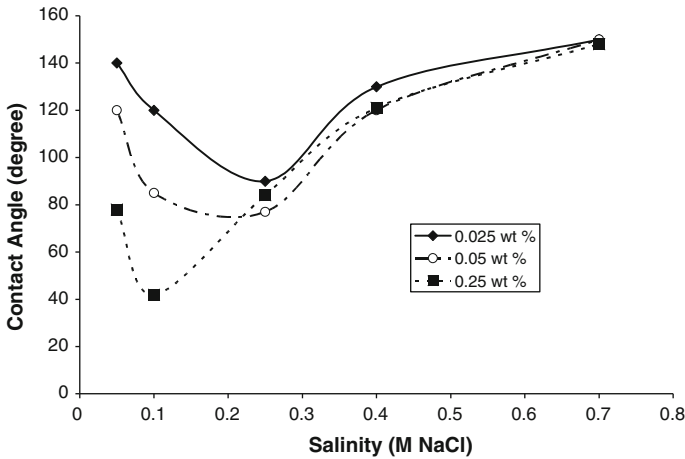
## 2.5 Spontaneous Imbibition

Cores listed in Tables 2 and 3 were used for imbibition experiments using field oil and model oil, respectively. Brine saturated cores were injected with 5 pore volumes (Pvs) of oil to reach residual water saturation. The oil saturated cores in Table 2 were aged in field oil for 60 days at 80°C to make them oil-wet, while cores in Table 3 were aged in model oil for 20 days at 25°C. The aged cores were immersed in a surfactant solution in an imbibition cell; the core represented the matrix and the gap between the core and the imbibitions cell represented the fracture. Oil drained from the core floated up and collected at the top of the imbibition cell. The oil recovery was monitored as a function of time. This study was done at 90°C for cores in Table 2; for cores in Table 3, the temperature was 25°C.

# 3 Results and Discussion

## 3.1 Wettability Alteration by Surfactants

Wettability alteration of an oil-aged calcite plate can depend on parameters like brine salinity, oil composition, type of surfactant, concentration of surfactant, and temperature. Figure 1 shows the dependence of the final contact angle on salinity at a fixed Alf-38 concentration. Sodium Chloride (NaCl) was used to change the brine salinity keeping sodium carbonate concentration fixed at 0.25 wt%. Na<sub>2</sub>CO<sub>3</sub> was added to keep the brine pH (at about 9.5)



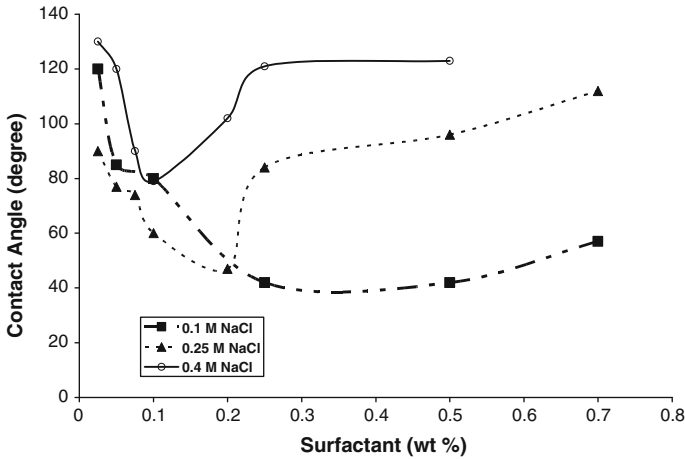
**Fig. 1** Effect of salinity on contact angle at a fixed 0.25 wt%  $\text{Na}_2\text{CO}_3$  for varying Alf-38 concentration (using model oil)

above the point of zero charge (PZC) of calcite. As pH increases, the calcite surface charge changes from positive to negative as it crosses its PZC. Crossing PZC reduces the adsorption of anionic surfactants on carbonate rocks. The PZC for limestone is around 9.2, and the PZC for dolomite is about 7.4 (Gonzalez 1989). Figure 1 shows that for a given Alf-38 concentration, the contact angle decreases and then increases with the increase in salinity. The salinity at which the contact angle is the minimum is termed as the optimal salinity for wettability.

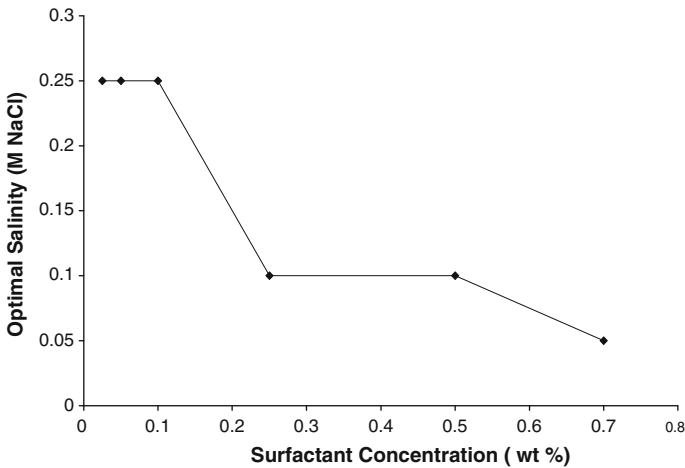
The occurrence of a minimum contact angle with varying salinity (keeping the surfactant concentration fixed) can be explained in term of partitioning of surfactants. Surfactants tend to stay in the aqueous phase at low salinity and move to the oil phase at high salinity, due to the electrostatic interaction between electrolytes and surfactants. However, at an intermediate salinity the surfactant has equal affinity for both aqueous and oleic phases. The amount of surfactant is the highest at the interface in this condition. It is possible that surfactants at the oil–brine interface solubilize the adsorbed cyclohexanepentanoic acid on calcite and thus change the contact angle, which could explain the occurrence of the minimum contact angle. It is also possible that the micelle head–head spacing is smaller at high salt concentration and its capacity to solubilize the adsorbed acid decreases as salt concentration increases.

Figure 2 shows the dependence of the final contact angle on Alf-38 concentration at fixed NaCl and  $\text{Na}_2\text{CO}_3$  (0.25 wt%) concentrations. The contact angle was found to decrease and then increase with increasing surfactant concentration. The surfactant concentration at the minimum contact angle is termed as the optimal surfactant concentration at a given salinity. As surfactant concentration increases, the number of micelles should increase, which should increase the solubilization of adsorbed acids. That argument does not support the existence of a minimum contact angle. Further investigation is needed.

The optimal salinity (excluding the constant  $\text{Na}_2\text{CO}_3$  concentration) for the minimum contact angle for different surfactant concentrations is shown in Fig. 3. This data is derived from Fig. 1. As the surfactant concentration increases, the optimal salinity decreases. At low surfactant concentration, more salt is needed to drive the surfactant to the interface and then to the oil phase. Apparently, at a higher surfactant concentration, less amount of salt is needed to do the same. As the surfactant concentration increases, the minimum contact angle decreases, as shown in Fig. 1. Higher the bulk surfactant concentration, higher is the

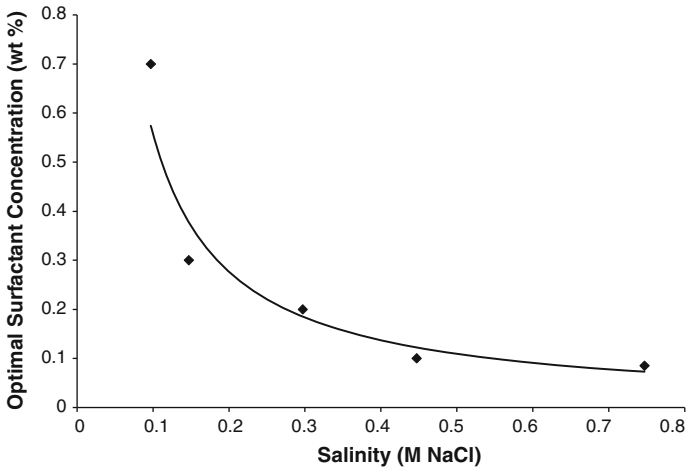


**Fig. 2** Effect of Alf-38 concentration on contact angle at a fixed 0.25 wt% Na<sub>2</sub>CO<sub>3</sub> and varying NaCl concentration (using model oil)



**Fig. 3** Effect of Alf-38 surfactant concentration on optimal salinity (at a fixed 0.25 wt% Na<sub>2</sub>CO<sub>3</sub>, using model oil)

concentration of surfactant at the interface, higher is the dissolution of acid molecules on the calcite surface and hence more would be the wettability alteration (that gives lower value of contact angle). The optimal surfactant (Alf-38) concentration for different values of NaCl concentration (and fixed 0.25 wt% Na<sub>2</sub>CO<sub>3</sub>) is shown in Fig. 4. As the salt concentration increases, the optimal surfactant concentration decreases. This trend is consistent with that in Fig. 3 and can be explained similarly. It can be seen in Fig. 2 that as the brine salinity increases, the optimum contact angle increases. Wettability alteration from oil-wet to water-wet condition (contact angle < 90°) cannot be obtained above 0.6 M NaCl for this surfactant and oil. These figures imply that as the salinity of the reservoir goes up the amount of the surfactant needed to get the highest wettability alteration would decrease, but the extent of wettability alteration would also decrease.



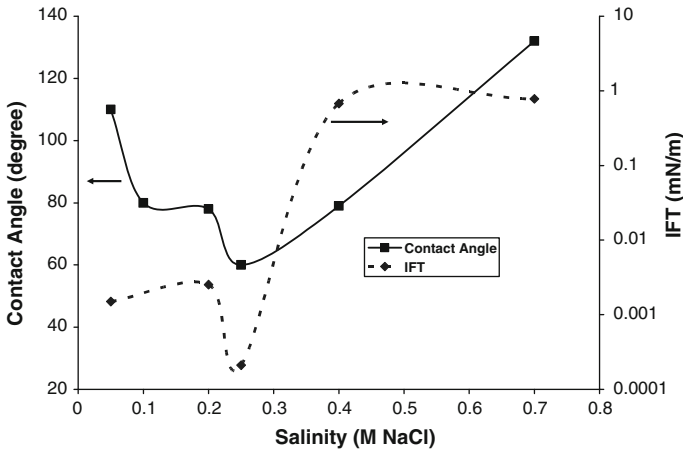
**Fig. 4** Effect of NaCl salinity (at a fixed 0.25 wt%  $\text{Na}_2\text{CO}_3$ ) on optimal Alf-38 surfactant concentration (using model oil)

Earlier studies (Healy et al. 1976 and Lake 1989) have shown that for a given surfactant concentration there exists an optimal salinity which gives a minimum IFT. To understand the relation between optimal salinity for a given surfactant concentration for wettability and optimal salinity for IFT, we measured both contact angles and IFT with the model oil for 0.1 wt% Alf-38 at a fixed 0.25 wt%  $\text{Na}_2\text{CO}_3$  and variable NaCl concentrations, as shown in Fig. 5. The water to oil ratio (WOR) ratio was one in IFT experiments and very large ( $>100$ ) in contact angle experiments. The results show that the optimal salinity for wettability and IFT coincides at about 0.25 M NaCl. This result also supports the argument that optimal values for IFT and wettability occur at a salinity where surfactant has equal affinity for oil and aqueous phase. Figure 6 shows that IFT decreases with an increase in surfactant concentration for a fixed salinity for the model oil Alf-38 system and it does not go through a minimum IFT like the wettability experiments. Interfacial surfactant concentration increases, third phase amount increases, and IFT decreases with an increase in surfactant concentration. IFT was measured between the middle phase (if exists) and the oil phase. Vijapurapu and Rao (2003) found a similar trend and showed that IFT becomes constant at high surfactant concentrations.

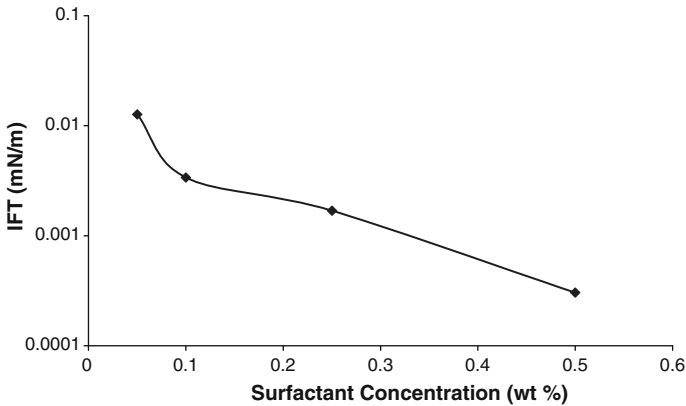
This study was extended from the two-component oil to a field oil. Figure 7 shows the contact angle as a function of surfactant concentration at a fixed  $\text{Na}_2\text{CO}_3$  concentration (no NaCl) for two different surfactants, B27 and Alf-38. In each case, there was a minimum contact angle. The optimum surfactant concentrations were found to be 0.05 and 0.1 wt%, respectively for B27 and Alf-38. At the optimal condition, B27 was found to give an intermediate-wet condition, while Alf-38 showed a water-wet condition. This trend for the field oil is similar to that seen for the model oil in Fig. 2.

Figure 8 shows contact angle and IFT as a function of salinity ( $\text{Na}_2\text{CO}_3$ ) for 0.05 wt% Alf-38. Both IFT and contact angle values have a minimum at the same salinity. This trend for the field oil is similar to that seen for the model oil in Fig. 5. Figure 9 shows the IFT between microemulsion phase and oil as a function of surfactant concentration at a fixed salt concentration (0.25 M  $\text{Na}_2\text{CO}_3$ ). IFT decreases with the increase in surfactant concentration; similar trend was seen for the model oil in Fig. 6.





**Fig. 5** Contact angle and IFT values for 0.1 wt% Alf-38 at varying salinity with 0.25 wt%  $\text{Na}_2\text{CO}_3$  (using model oil)

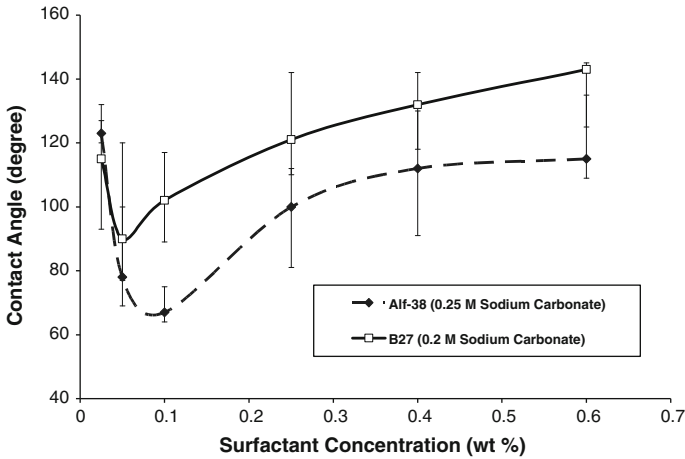


**Fig. 6** IFT values with varying Alf-38 concentration at a fixed salinity of 0.25 M NaCl and 0.25 wt%  $\text{Na}_2\text{CO}_3$  (using model oil)

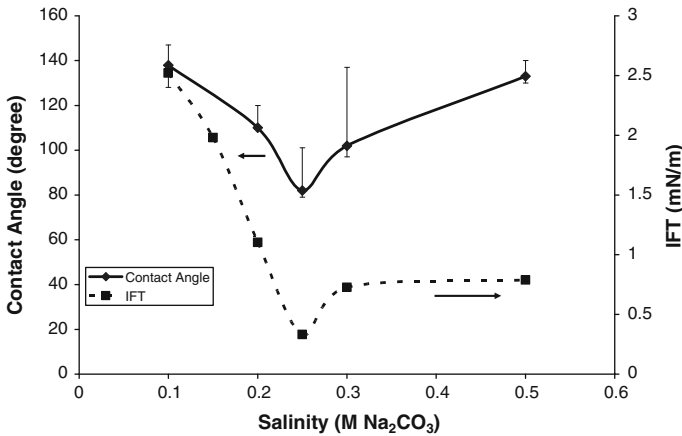
### 3.2 Mechanism of Wettability Alteration

The type of interaction between adsorbed organic acid and anionic surfactants during wettability alteration is not yet understood. [Standnes and Austad \(2000b\)](#) hypothesized that anionic molecules co-adsorb with acid molecules where surfactants have strong hydrophobic–hydrophobic interaction with acid molecules. The negatively charged head groups face the bulk solution, thus rendering the solid water-wet. High pH offered by sodium carbonate can change the surface charge to negative causing minimal adsorption of surfactant at the calcite surface. [Kumar et al. \(2008\)](#) had inspected solid surfaces by AFM after such a surfactant treatment and noticed removal of adsorbed material, not further adsorption of surfactants. To further investigate, we conducted ATR-IR spectroscopy on calcite plates treated with a model oil.

Figure 10 shows IR spectrum for various cases. The calcite plate treated with the model oil (called “Wet Oil” in the figure caption) shows significant absorption for methyl and methylene C–H bond stretching ( $3000\text{--}2800\text{ cm}^{-1}$ ) and bending ( $1500\text{--}1300\text{ cm}^{-1}$ ). There is also

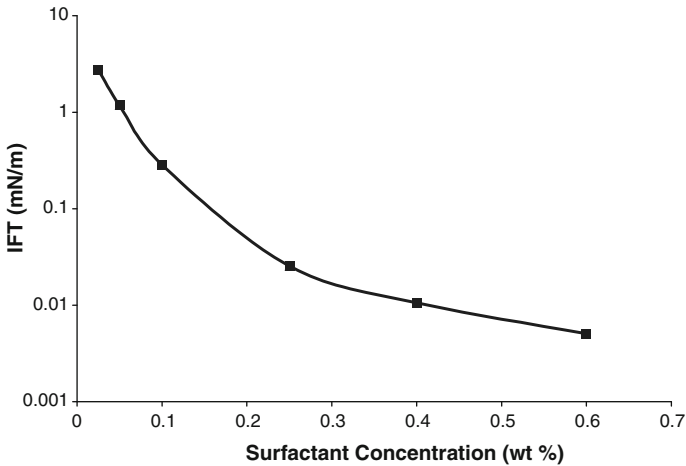


**Fig. 7** Contact Angle with varying surfactant concentration (using field oil)

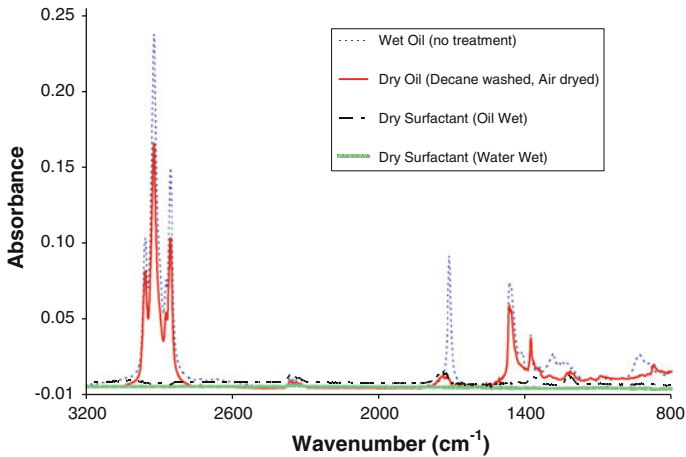


**Fig. 8** Contact angle and IFT values for 0.05 wt% Alf-38 at varying Na<sub>2</sub>CO<sub>3</sub> concentration (using field oil)

a strong carbonyl (C = O) stretch at  $1710\text{ cm}^{-1}$ . When an oil-aged calcite plate is washed in *n*-decane and air dried (called “Dry Oil” in the figure caption), the peak due to *n*-decane remains the same but the amplitude of carbonyl absorption peak (due to acid) decreases. Decane washes all the acid molecules near the surface except the acid molecules adsorbed on the surface. The peak at  $1760\text{--}1710\text{ cm}^{-1}$  shows the infrared spectrum for the adsorbed acid molecules. Figure 10 also shows IR spectra for oil-wet calcite plate treated with 0.3 wt% Alf-38 surfactant (called “Dry Surfactant” in the figure caption). These plates were washed in water and dried in air before obtaining their IR spectrum. After surfactant treatment, one of the plates was oil-wet and other was water-wet (according to the contact angle measurement). Since, all the decane is washed away, both the plates show no C–H absorption bands. The carbonyl peak is present in the case of the oil-wet plate, but not for the water-wet plate. Figure 11 shows IR spectra for  $2000\text{--}1600\text{ cm}^{-1}$  capturing the carbonyl absorption stretching by adsorbed cyclohexanepentanoic acid. IR spectra of *n*-decane washed and air dried oil-aged calcite plate show adsorption band at  $1760\text{--}1710\text{ cm}^{-1}$  depicting the presence of adsorbed



**Fig. 9** IFT values with varying Alf-38 concentration at a fixed salinity of 0.25 M Na<sub>2</sub>CO<sub>3</sub> (using field oil)

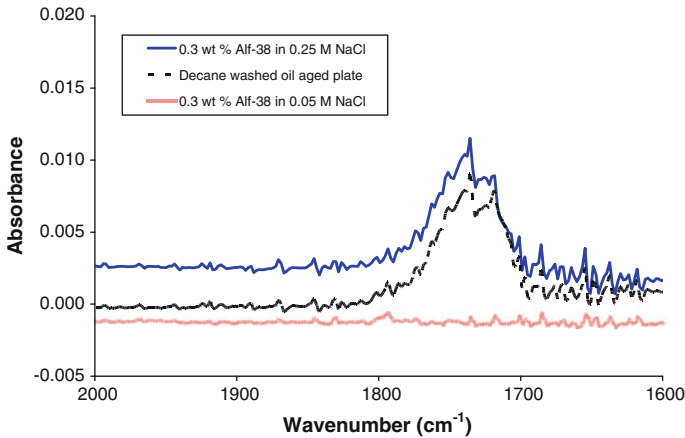


**Fig. 10** Infrared absorption Spectrum on calcite plate (using modified model oil and Alf-38)

acid on surface. This plate was not treated with surfactant and thus was oil-wet with a final contact angle of 158°. When an oil-aged plate is treated with 0.3 wt% Alf-38 in 0.25 M NaCl with 0.25 wt% Na<sub>2</sub>CO<sub>3</sub> brine and air-dried, the carbonyl adsorption band was still present. The salinity in this case was above optimal, and the plate was oil-wet. When 0.3 wt% Alf-38 in 0.05 M NaCl with 0.25 wt% Na<sub>2</sub>CO<sub>3</sub> brine is used to treat the oil-aged plate, the wettability is altered to water-wet condition. This air-dried plate shows no carbonyl absorption peak in its IR spectrum. Thus, it shows that anionic surfactant removes the adsorbed acid molecules from the surface to alter the wettability.

### 3.3 Effect of Surfactant Structure

The effect of anionic surfactant structure on wettability alterations investigated below. Figure 12 shows the effect of the degree of propoxylation (PO) on the final contact angle at

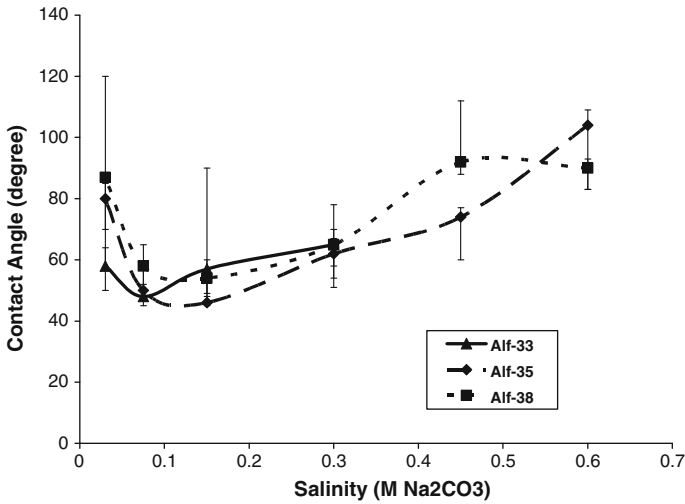


**Fig. 11** Infrared spectrum for carbonyl stretching absorption

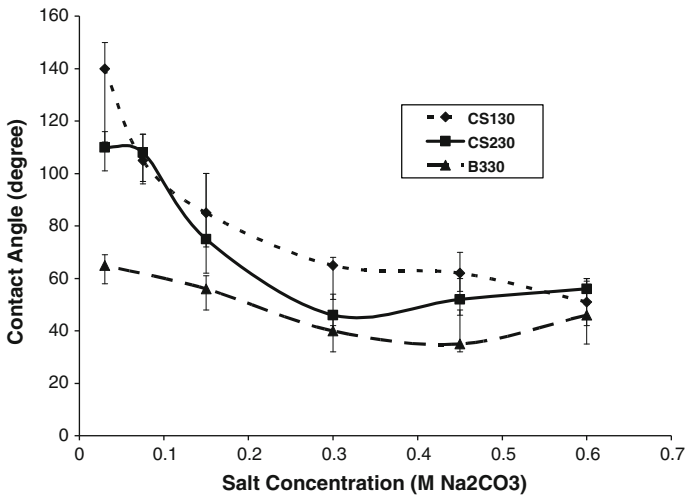
0.2 wt% of surfactant concentration with the model oil.  $\text{Na}_2\text{CO}_3$  is used to change the salinity. Alf-33, Alf-35, and Alf-38 have 3, 5, and 8 PO groups, respectively, but the same hydrocarbon chain. The optimal salinity and contact angles are found to be similar. The effect of the degree of ethoxylation (EO) is studied in a similar system. CS130, CS230, and B330 have 1, 2, and 3 EO groups, respectively. The contact angles generally decrease with the degree of EO, but the optimal salinity is found to decrease and then increase with the increase in EO groups, as shown in Fig. 13. Seethepalli et al. (2004) also saw the non-monotonic trend in optimal salinity for IFT for this system. A set of sulfonates are used to study effect of hydrocarbon chain length. I-1518, I-1720, and I-2024 have 15–18, 17–20, and 20–24 carbons in the tail group, respectively. Figure 14 shows that the contact angle does not follow a monotonic trend with the hydrocarbon chain length. Also, these sulfonates do not alter the wettability of calcite plates and have advancing contact angles of  $130^\circ$  and greater under the conditions studied.

### 3.4 Wettability Alteration with Divalent Ions

Tweheyo et al. (2006) conducted imbibition experiments and found that wettability of chalks can be altered at high temperatures by divalent ions like  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  without any surfactant. We investigate the effect of these ions on the wettability of a calcite plate aged with the model oil, with an initial contact angle of about  $150^\circ$ – $170^\circ$ . The brines used to study the effect of divalent ions are reported in Table 4 along with their nomenclature. The equivalent monovalent ion concentration is kept constant at 0.576 mol/l in all the brines. The base case magnesium, calcium, and sulfate concentrations were taken as 0.045, 0.013, and 0.025 M, respectively. Figure 15 shows the effect of sulfate ions in the presence of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions on wettability of calcite with temperature. At the room temperature, brines MgCa2S (base case concentration of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and twice the base case  $\text{SO}_4^{2-}$  concentration) and MgCa4S could not alter the wettability with advancing contact angle  $\sim 150^\circ$ . At  $70^\circ\text{C}$ , these brines alter the wettability of the plates to intermediate-wet condition with contact angle values  $\sim 86^\circ$ . At  $92^\circ\text{C}$ , MgCa4S was found to have advancing contact angle of  $35^\circ$ , and MgCa2S had  $54^\circ$ , thus rendering the calcite surface water-wet. The  $\text{SO}_4^{2-}$  ions at the



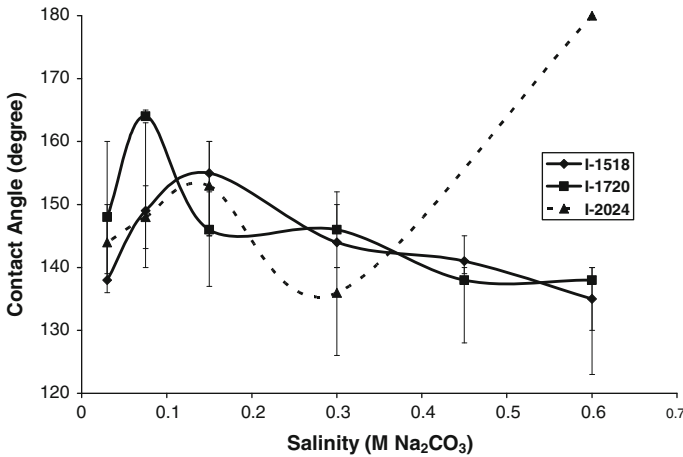
**Fig. 12** Effect of PO group on wettability of calcite plates using model oil and 0.2 wt% surfactant concentration



**Fig. 13** Effect of EO group on wettability of calcite plates using model oil and 0.2 wt% surfactant concentration

higher temperature can desorb cyclohexanepentanoic acid from the solid surface and occupy the sites freed, thus decreasing the affinity of the solid to oil.

Figure 16 shows the final contact angles for several brines at 90°C. The sulfate ions and calcium ions are found to change the contact angle to water-wet conditions. Higher sulfate concentration with constant  $Mg^{2+}$  and  $Ca^{2+}$  concentration causes a higher degree of wettability alteration, though  $SO_4^{2-}$  ions alone do not alter the contact angle to a similar extent (as in the case of brine 0Mg0Ca4S). Brine 4Mg0Ca0S was not able to alter wettability of the calcite plate, which shows that  $Mg^{2+}$  ions by themselves cannot change wettability. However, in the presence of  $SO_4^{2-}$  ions they are found to alter the wettability (e.g., 4Mg0CaS).



**Fig. 14** Effect of chain length on wettability of calcite plates using model oil and 0.07 wt% surfactant concentration

**Table 4** Brines used for wettability experiment with model oil at high temperature

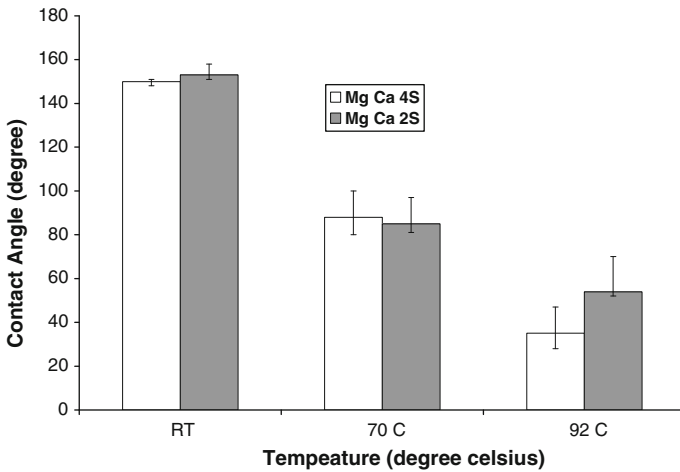
Brine code	NaCl	Mg.Cl.	Ca.Cl.	Na <sub>2</sub> SO <sub>4</sub>
MgCa0S	26.884	9.150	1.911	0.000
MgCa4S	15.195	9.150	1.911	14.204
0Mg0Ca4S	21.975	0.000	0.000	14.204
MgCa2S	21.039	9.150	1.911	7.102
4Mg0Ca0S	12.624	36.599	0.000	0.000
4Mg0CaS	9.702	36.599	0.000	3.551
5Ca0Mg0S	26.066	0.000	9.557	0.000
5Ca0MgS	23.143	0.000	9.557	3.551

*Mg.Cl.* = MgCl<sub>2</sub> · 6H<sub>2</sub>O, *Cal.Cl.* = CaCl<sub>2</sub> · 2H<sub>2</sub>O, values are in g/l

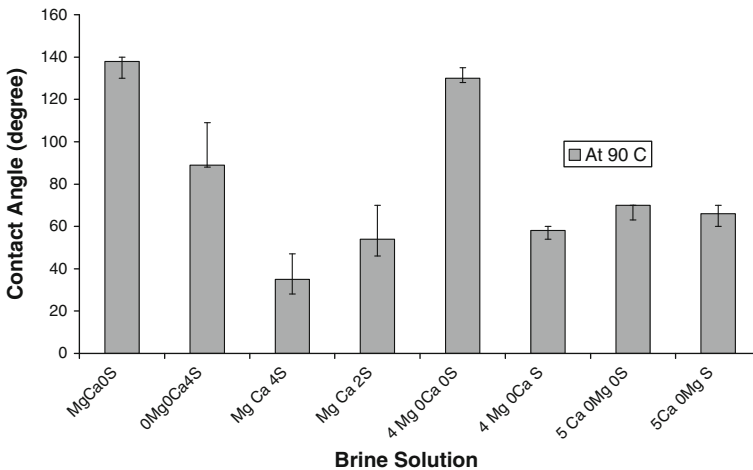
Tweheyo et al. (2006) made similar observations with chalk. At five times the base value (as in 5Ca0Mg0S), the calcium ions alone can alter the contact angle to 70°, though it could not alter the wettability at the base case concentration in the presence of magnesium ions (brine MgCa0S). In the presence of sulfate (as in 5Ca0MgS) the contact angle is altered to 66°. It shows that calcium ions alone can alter the wettability, but the extent of wettability alteration is slightly higher in the presence of sulfate ions. The advancing contact angles with these brines at room temperature ranges from 145–180°. High temperature is needed for the ion exchange which brings about wettability alteration.

### 3.5 Oil Recovery by Imbibition

The effect of wettability on oil recovery was investigated. Imbibition experiments were conducted at 90°C for initially oil-wet carbonate rocks shown in Table 2. 0.05 wt% of Alf-68 and DF surfactants was used. Both are anionic surfactants, and the field oil was used in these experiments. The sodium carbonate optimal salinity (for minimum IFT) for this concentration of surfactant was found to be 0.125 and 0.066 M for DF and Alf-38, respectively.

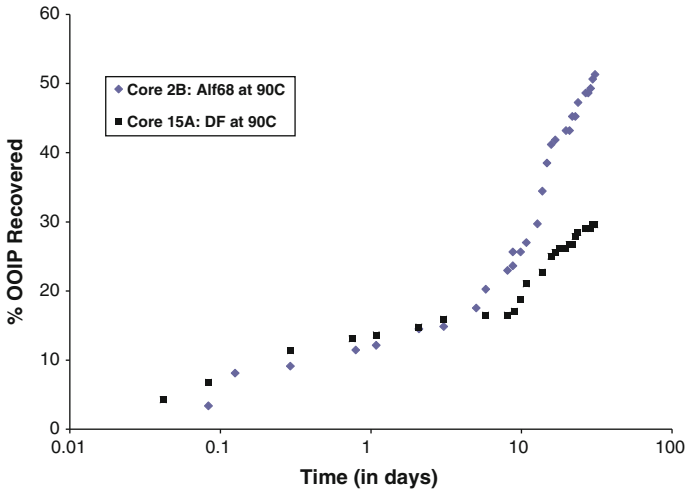


**Fig. 15** Effect of temperature on contact angle for brines MgCa4S and MgCa2S (using model oil; RT room temperature)

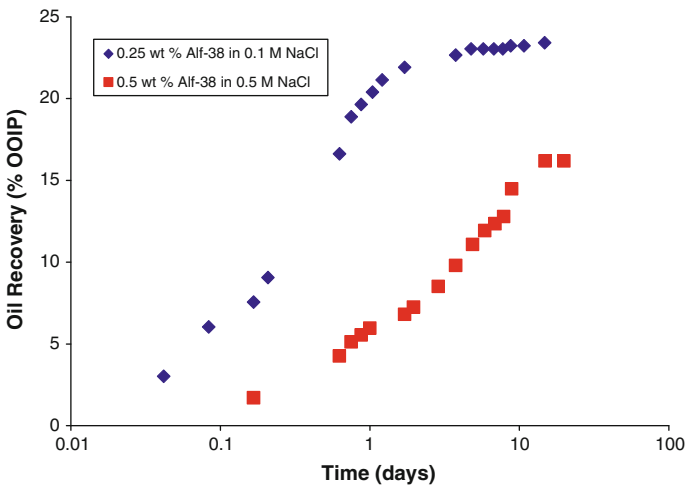


**Fig. 16** Contact angle for different brines at 90°C (using model oil)

The final contact angles were found to be 109° and 40° for DF and Alf-68, respectively. The imbibition experiment was conducted at optimal salinity of the surfactant solution. The oil recovery with time can be seen in Fig. 17. Alf-38 could recover about 53% of OOIP in 30 days, while the DF in the same time could get about 30%. It is interesting to observe that DF could recover a significant amount of oil from the core at 109° contact angle. Surfactants reduce the oil–brine IFT and thus reduce the capillary pressures to a low value. In case of DF, the capillary pressures are low but negative due to the oil-wet nature of the core. At such low IFT, gravitational forces can overcome negative capillary pressure and imbibe brine into the core and push oil out from the top of the core. When wettability is altered to water-wet condition; both capillary forces and gravity forces aid in oil recovery, thus explaining the higher recovery rate in case of Alf-68. This high rate of oil recovery with dilute surfactant treatments appears quite promising and cost effective.



**Fig. 17** Oil recovery during imbibition experiments for 0.05 wt% surfactants, DF and Alf-68, at optimal salinity (using field oil)



**Fig. 18** Oil recovery during imbibition experiments for 0.25 and 0.5 wt% Alf-28 at 0.1 and 0.5 M NaCl, respectively (using model oil)

Table 3 shows the details of the model oil-aged cores used to further investigate the effect of wettability on oil recovery rates. These experiments were conducted at 25°C. Core 5M was imbibed in 0.25 wt% Alf-38 with 0.1 M NaCl and 0.25 wt% Na<sub>2</sub>CO<sub>3</sub> brine. The final contact angle of oil–brine with calcite plate was 47°. This is also the optimal salinity at this surfactant concentration. Core 9M was imbibed in 0.5 wt% Alf-38 with 0.5 M NaCl and 0.25 wt% Na<sub>2</sub>CO<sub>3</sub> brine. The salinity is over-optimal with the final contact angle of 120°. In 5 days, Core 5M recovers 22% OOIP compared to 10% by Core 9M, as shown in Fig. 18. Though the surfactant concentration used for imbibition is higher for Core 9M, its recovery rate is slower compared to that for Core 5M. It shows that the oil recovery rate depends on the final wettability and not on the amount of surfactant used.



To apply this process in a highly fractured reservoir, surfactant solutions can be injected in a horizontal well drilled perpendicular to the fractures at the bottom of the reservoir and the fluids can be produced through a horizontal well placed on the top of the reservoir, again perpendicular to the fractures. The surfactant solution would fill the fractures first, then imbibe into the matrix in a manner similar to the imbibitions tests described above, oil would be produced into the top part of the fractures, and would be pumped out by the top production horizontal well. The produced surfactant solution can be recycled. The role of gravity, viscous, and capillary forces will be different in the field condition from those in our laboratory imbibitions experiments due to differences in the fracture spacing, reservoir thickness, and heterogeneity. We have addressed the scale-up issues in another publication [Adibhatla and Mohanty 2007](#). Reservoir rocks are heterogeneous. Such studies must be done for each rock type in the reservoir and the variations must be incorporated in the reservoir simulation.

#### 4 Conclusions

- For the oils and surfactants studied, there exists an optimal surfactant concentration for varying salinity and an optimal salinity for varying surfactant concentration at which the wettability alteration on an oil-aged calcite plate is the maximum for anionic surfactants. Concentration of surfactants in the interface region can explain the occurrence of optimal salinity for wettability alteration.
- As the salinity increases, the surfactant concentration needed for the maximum wettability alteration on a calcite plate decreases, but the extent of wettability alteration itself decreases.
- IFT and contact angle were found to have the same optimal salinity for a given concentration of anionic surfactants studied. Also, IFT was found to be decreasing (and in some cases reaching a plateau value) for increasing surfactant concentrations at a fixed salinity.
- Anionic surfactants desorb the naphthenic acid from the calcite surface to alter wettability.
- As the EO increases in anionic surfactants, the extent of wettability alteration on calcite plates increases.
- Wettability of oil-aged calcite plates can be altered by divalent ions at a high temperature (90°C and above). Sulfate ions alter wettability to a greater extent in the presence of magnesium and calcium ions than in the absence. A high concentration of calcium ions alone can alter wettability. Magnesium ions alone do not change the calcite plate wettability.
- Wettability alteration increases the oil recovery rate from initially oil-wet Texas Cordova Cream limestone cores by imbibition. When wettability is altered to a water-wet condition, both capillary forces and gravity forces aid in oil recovery for anionic surfactants.

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