# Dilute Surfactant Methods for Carbonate Formations

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# Disclaimer

# Abstract

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally factured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope, yet it was developed for sandstone reservoirs in the past. The goal of this research is to evaluate dilute (hence relatively inexpensive) surfactant methods for carbonate formations and identify conditions under which they can be effective. We have conducted adsorption, phase behavior and wettability studies. Addition of $Na_2CO_3$ decreases IFT with a minimum at about 0.2 M. Addition of surfactant decreases IFT further. In the absence of surfactant the minerals are oil wet after aging with crude oil. Addition of surfactant solution decreases the contact angle to intermediate wettability. Addition of $Na_2CO_3$ decreases anionic surfactant adsorption on calcite surface. Plans for the next quarter include conducting adsorption, phase behavior and wettability studies.

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# Executive Summary

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally factured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope, yet it was developed for sandstone reservoirs in the past. The goal of this research is to evaluate dilute (hence relatively inexpensive) surfactant methods for carbonate formations and identify conditions under which they can be effective. We have conducted adsorption, phase behavior and wettability studies. Addition of $Na_2CO_3$ decreases IFT with a minimum at about 0.2 M. Addition of surfactant decreases IFT further. In the absence of surfactant the minerals are oil wet after aging with crude oil. Addition of surfactant solution decreases the contact angle to intermediate wettability. Addition of $Na_2CO_3$ decreases anionic surfactant adsorption on calcite surface. Plans for the next quarter include conducting adsorption, phase behavior and wettability studies.

## Introduction

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally factured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope (Spinler et al., 2000), yet it was developed for sandstone reservoirs in the past (Bragg et al., 1982).

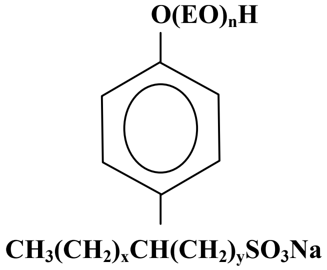
The goal of this research is to evaluate dilute surfactant methods for carbonate formations and identify conditions under which they can be effective. Adsorption, phase behavior, wettability alteration, IFT gradient driven imbibition, blob mobilization at high capillary and Bond numbers will be quantified. An existing laboratory simulator will be modified to incorporate the mechanisms of surfactant transport and effective parameters will be developed to model this process in a dual porosity reservoir simulator. Field-scale simulations will be conducted to identify criteria under which dilute surfactant methods are feasible without active mobility control.

This report summarizes our results for the period of January 2003 through March 2003. The five tasks for the project are: (1) Adsorption, (2) Wettability alteration, (3) Gravity and viscous mobilization, (4) Imbibition, and (5) Simulation. Only the first two tasks were worked on in this quarter. The results of phase behavior and wettability will be highlighted in this report; adsorption results were highlighted in the last report.

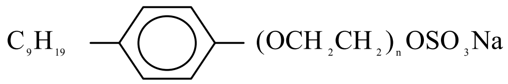
## Experimental

### Phase Behavior

Three surfactants have been used in this study so far: an alkyl aryl sulfonate (Oil Chem Technology Surfactant 5-166), a Gemini surfactant (Oil Chem Technology Surfactant 4-22) and an ethoxy sulfonate (Stepan Polystep B-27). The molecular structure of Surfactant 4-22 is shown below,



where n = 6 and x + y = 14-16. The chemical formulae surfactant B-27 is,



where n = 4. All studies (phase behavior, wettability and adsorption) are not complete for all three surfactants. These surfactants are all anionic; therefore Sodium Carbonate is used to reduce adsorption. The phase behavior of the crude oil/brine/surfactant system was characterized by the bottle tests. Two systems were studied: one without synthetic surfactant and one with. In the first case, the optimum salinity for the in-situ surfactants formed by the reaction between the naphthenic acids present in the crude with alkali present in the brine was determined. In the second case, the optimum salinity / alkali concentration in the presence of synthetic surfactant was found. Sodium carbonate acts both as an alkali and a salinity-altering agent.

The synthetic brine was prepared by varying the $Na_2CO_3$ concentration in the range of 0.05 M to 0.25 M in the first case and between 0.1 M to 0.5 M for the second case. The surfactant used for the phase behavior experiments shown below is the alkyl aryl sulfonate (Surfactant 5-166). The concentration of the surfactant is kept fixed at 0.05 wt% active in the second case. For each of the two cases, six glass vials were thoroughly cleaned, labeled and kept in contact with the brine solutions prepared above for a period of 24 hours. This brine solution was then discarded and replaced by 3-ml. fresh brine of the same concentration. Same volume of crude oil was then added to each of these vials. The crude oil and brine were left to equilibrate for a period of two days or more. The water-oil ratio was kept fixed at 1. The pH of the equilibrated brine in all cases was found to be greater than 10. The dual-role played by $Na_2CO_3$ both as salinity and a pH-altering agent should be kept in mind. The IFT between the upper phase crude oil and the lower aqueous phase was measured in every case by using a spinning drop tensiometer. Care was taken to avoid sucking in the middle phase microemulsion for the purpose of IFT determination.

### Wettability

Wettability alteration to a more water wet state of the minerals can also be a potent recovery mechanism in fractured carbonate formations. Hence one of the objectives of this study is to determine whether the surfactants can alter the wettability of oil-contacted regions of the porous rocks. Gemini surfactant 4-22 was used. It is 50% active in the results shown below. Advancing contact angle measured through the water phase is used as the measure to characterize rock mineral wettability. Four types of carbonate rock minerals, namely, Iceland spar calcite, dolomite, marble and lithographic limestone were used.

Synthetic reservoir brine was equilibrated with the crude at a water-oil ratio of one and these pre-equilibrated fluids were then used for all the subsequent experiments. The mineral plates were ground on a diamond lap with a 600# mesh size. The plates were then rinsed with synthetic reservoir brine. The mineral plate was placed in a glass cuvette containing brine and the advancing contact angle for a sessile oil drop was measured using a goniometer to characterize the mineral wettability before aging. The wet mineral plate was then immersed in a vial containing crude oil. The mineral plate was aged in the crude oil for a period of 44 hrs at an elevated temperature of $80^0$C to compensate for the geological times for which the reservoir rock was exposed to the crude at near room temperature. The mineral plate was then immersed in an optical glass cuvette containing brine. Some of the oil sticking to the plate immediately left the mineral surface. Advancing contact angle was measured to quantify the mineral wettability after aging with the crude. The mineral plate was kept in contact with the brine for around one hour after which the brine was replaced with the surfactant + brine solution. Care was exercised not to expose the mineral surface to air-water interface where some crude forms a thin oil slick. The evolution of the advancing contact angle was then studied using the goniometer over a period of 48 hours or more.

**Adsorption**

Surfactant loss due to adsorption is one of the important criteria that governs the economics of the dilute surfactant flooding methods for carbonate formations. The carbonate mineral chosen for the preliminary experimental trials was calcite. The synthetic calcite powder, 99.5% $CaCO_3$ (metals basis), consisting of 5-μm particles, was supplied by AESAR. The surface area of calcite powder was measured using Coulter SA 3100 surface area and pore size analyzer by BET method. For calcite powder the surface area was found to be 1.68 $m^2/g$. UV spectrometry was used to measure the concentration of surfactant in the solution.

## Results and Discussion

### Phase Behavior

Fig. 1 shows the phase behavior of crude oil/brine ($Na_2CO_3$) system without any synthetic surfactant. The aqueous phase is observed to be the most turbid at a $Na_2CO_3$ concentration of 0.15 M. This could be due to the micellar solubilization of the crude in the aqueous phase microemulsion formed by the in situ surfactant made by the reaction of alkali and the crude oil. At this salinity, the system is close to optimum. On further increasing the $Na_2CO_3$ concentration, the aqueous phase becomes progressively clearer. At a concentration of 0.25 M $Na_2CO_3$, the aqueous phase becomes clear indicating Windsor type II+ microemulsion. At this point the system is called over-optimum.

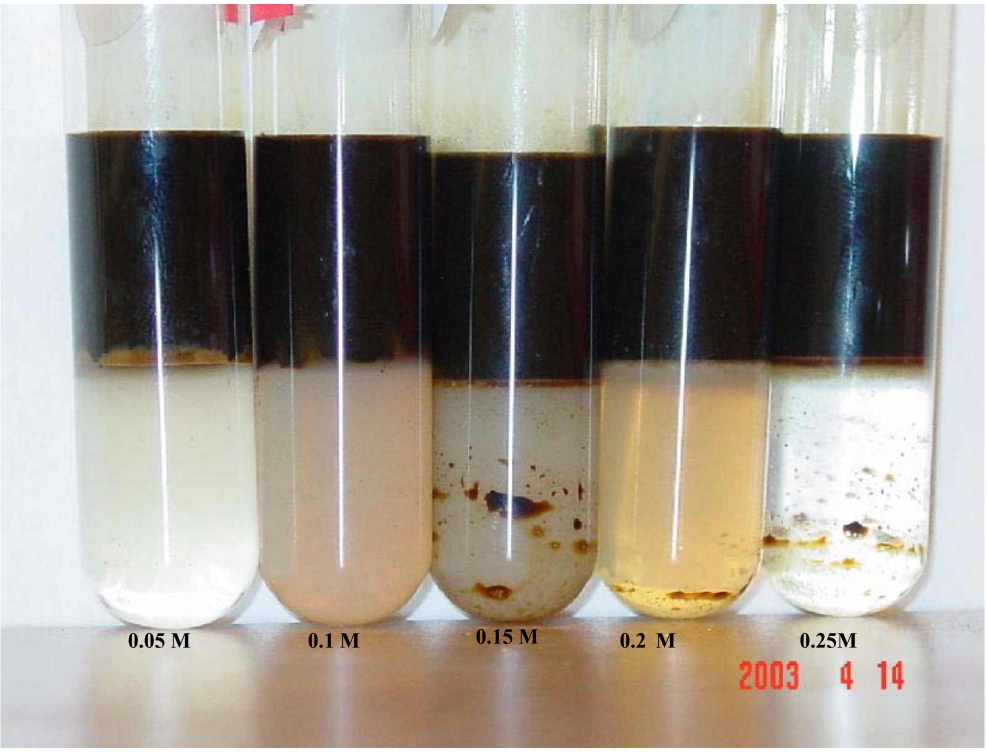


Fig. 1 – Phase behavior of crude oil/brine ($Na_2CO_3$) system, WOR =1.

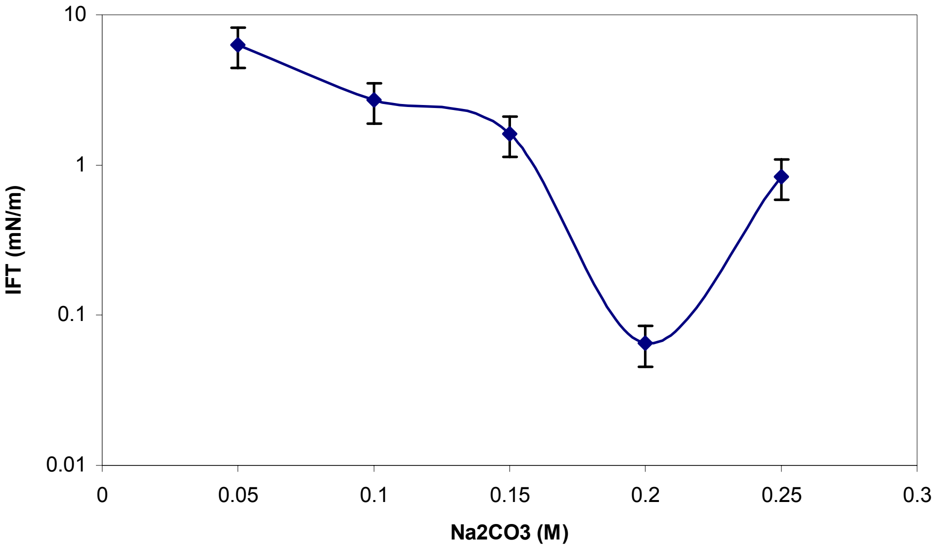


Fig. 2 – IFT of crude oil/brine system as a function of $Na_2CO_3$ concentration

Fig. 2 shows the IFT measurements for this system. The minimum IFT is obtained at a $Na_2CO_3$ concentration of 0.15 M as expected from the visual observations of the bottle tests. It should be noted that the minimum IFT is of the order of $10^{-2}$ M $Na_2CO_3$. Fig. 3 shows the phase behavior of crude oil/brine ($Na_2CO_3$)/surfactant system. In this case, the aqueous phase is observed to be the most turbid at a $Na_2CO_3$ concentration of 0.2 M. The system may be close to the optimal at this point. The aqueous phase becomes progressively clearer on further increase of $Na_2CO_3$ concentration indicating over optimal system. A middle phase microemulsion is also observed in the nearly optimal regime. The aqueous phase becomes clear at the $Na_2CO_3$ concentration of 0.5 M. Fig. 4 shows the IFT measurements for this system. Interestingly, two local minima are observed for this system at the $Na_2CO_3$ concentrations of 0.2 M and 0.4 M respectively. However, the absolute minimum IFT occurs at a $Na_2CO_3$ concentration of 0.2 M, which is in line with the prediction based on the visual observations. A plausible hypothesis could be that the two kinds of surfactant molecules present in this system, i.e., natural surfactants and the synthetic surfactant, have different optimal salinities. In that case, the first minimum at 0.2 M $Na_2CO_3$ may correspond to the near optimal salinity for the natural surfactants. The IFT of the system is the lowest at this point due to the synergistic effect of the synthetic surfactant for which the system in under optimal. The second minimum may correspond approximately to the optimal salinity of the synthetic surfactant. However the IFT of the system may not be as low as in the first minimum because the system is strongly over-optimal with respect to the natural surfactants and thus the synergistic effect is not present.

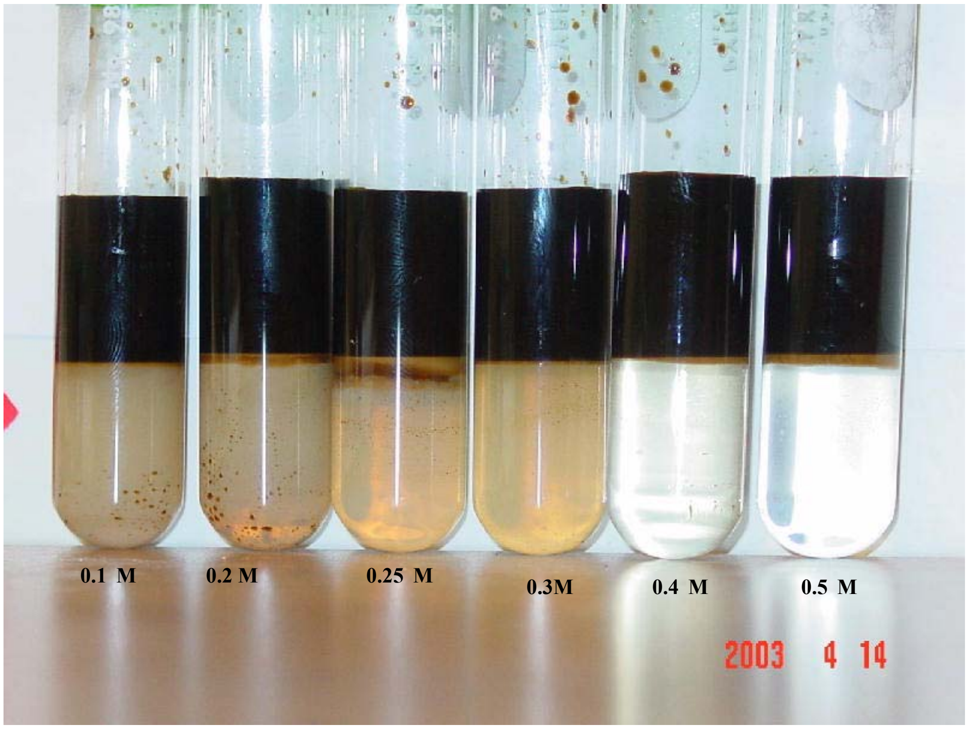


Fig. 3 - Phase behavior of crude oil/brine ($Na_2CO_3$)/surfactant system; surfactant concentration is kept fixed at 0.05 wt% while $Na_2CO_3$ concentration is varied. WOR =1.

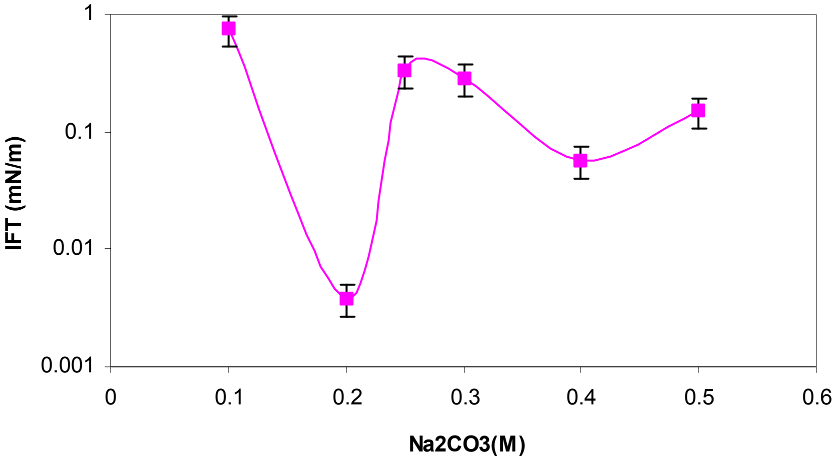


Fig. 4 – IFT of crude oil/brine/surfactant system. Surfactant concentration is fixed at 0.05 wt%.

## Wettability

Fig. 5 – Advancing angle of the sessile oil droplet in contact with the calcite plate.

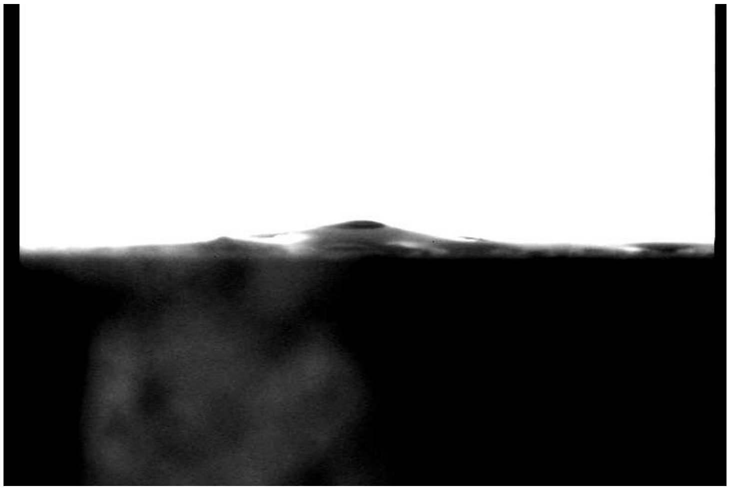


Fig. 6 – Advancing angle of the oil drop on calcite after aging it with the crude.

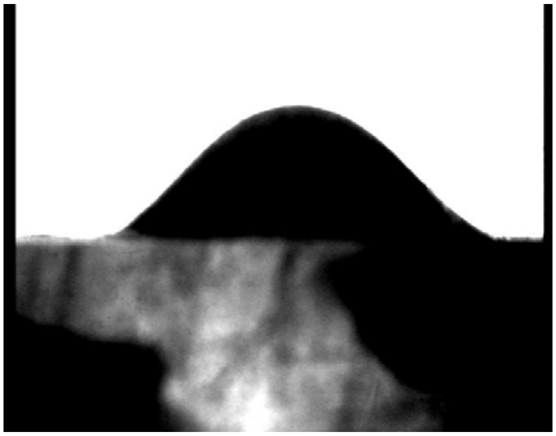


Fig. 7 – Image of oil drop on calcite 1h after surfactant solution addition

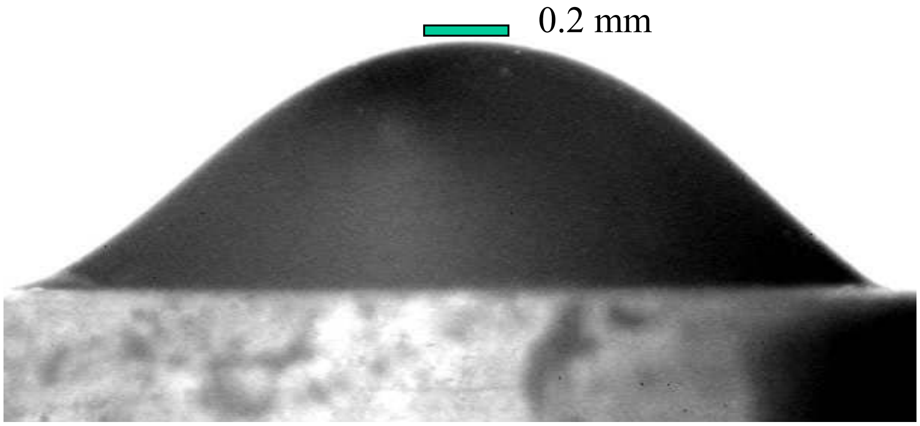


Fig. 8 – Image of one of the larger oil droplet sticking to calcite plate after 24 hours.

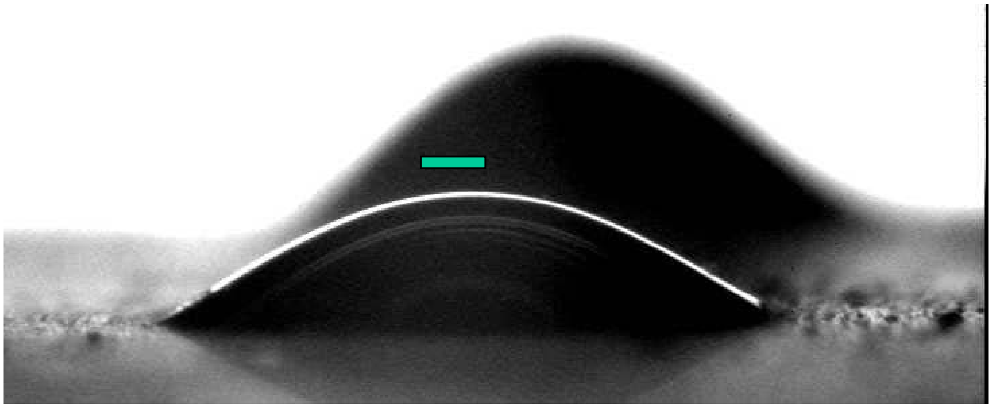


Fig. 9 – Image of one of the larger oil droplet sticking to calcite plate after 48 hours.

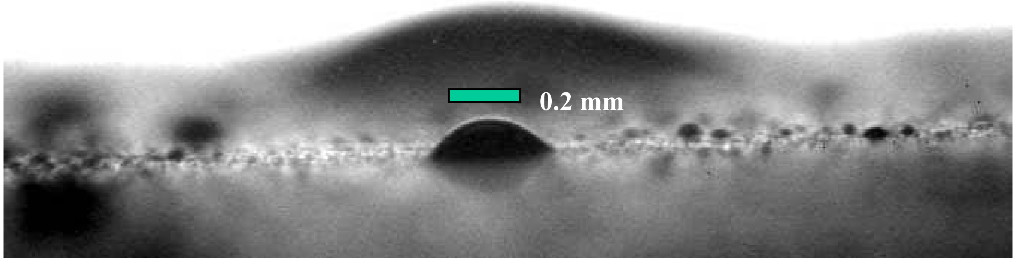


Fig. 10 – Image of one of the smaller oil droplet sticking to calcite plate after 48 hours.

Figs. 5 – 10 show the advancing contact angle measured at different stages of the experiment for the calcite mineral. Fig. 5 is shown inverted. Before aging with oil, the mineral plate is intermediate wet with advancing contact angle greater than $90^0$ and receding contact angle less than $90^0$ as shown in Fig. 5. Fig. 6 shows after aging calcite with crude at elevated temperature for 44 hrs, the mineral plate becomes completely oil wet with an advancing contact angle close to $180^0$. When exposed to the surfactant + brine solution, the advancing contact angle decreases with time and stabilizes at a value of about $140^0$. Fig. 7- Fig. 10 show the evolution of the advancing contact angle with time. The wettability, in this case, can be said to alter from an oil-wet state to an intermediate-wet state by the application of this surfactant.

Figs. 11 – 15 show the advancing contact angles as measured at different stages of the experiment using marble. Marble too, like calcite, is intermediate wet before aging with oil as shown in Fig.11. After aging with crude for 44 hrs at $80^0$C, the mineral becomes almost completely oil wet as shown in Fig. 12. After the mineral plate is exposed to the surfactant (0.05 wt%) + brine, significant amount of oil was observed to have left the mineral plate. Fig. 13 - Fig. 15 show the evolution of contact angles for the droplets of varying sizes sticking to the mineral plate. Interestingly, while the smaller droplets were observed to exhibit advancing contact angles less than $90^0$, the larger droplets had an advancing contact angle of about $140^0$. This indicates the presence of significant wettability heterogeneity on the surface of the mineral plate.

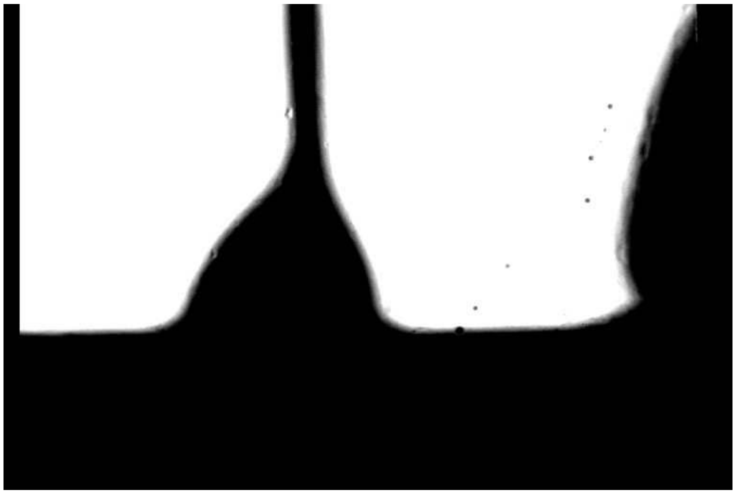


Fig. 11 – Advancing angle of the sessile oil droplet in contact with the marble plate.

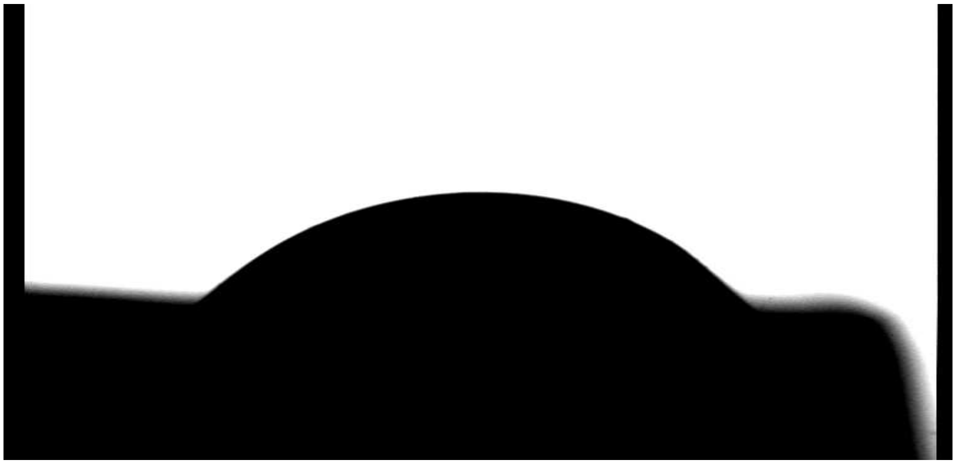


Fig. 12 – Image of the oil drop on marble plate after aging it with crude at $80^0$C.

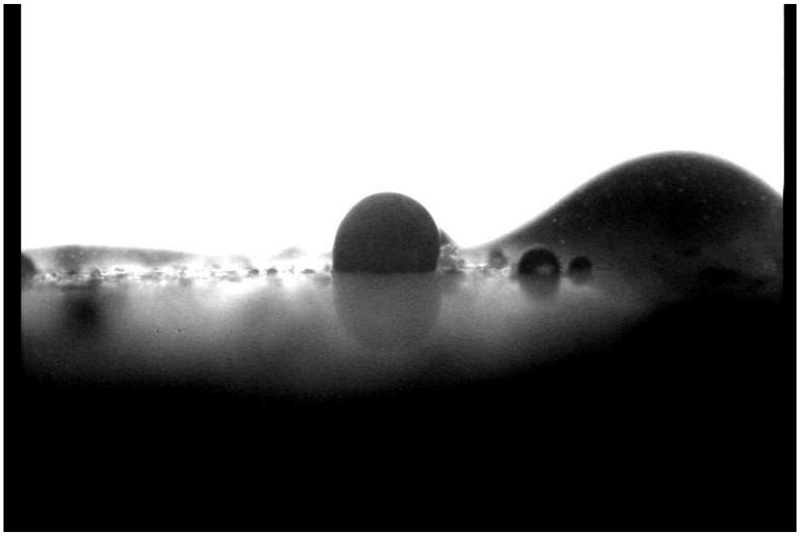


Fig. 13 – Images of the oil droplets of varying sizes sticking to marble plate 24 hours after being exposed to surfactant + brine.

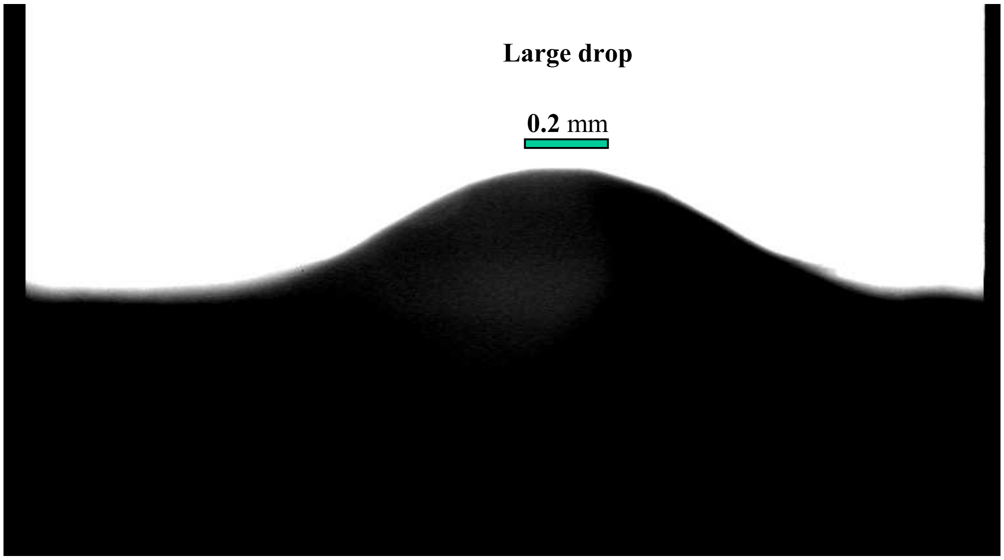


Fig. 14 – Image of one of the larger oil droplets sticking to the marble plate 48 hours after being exposed to surfactant + brine.

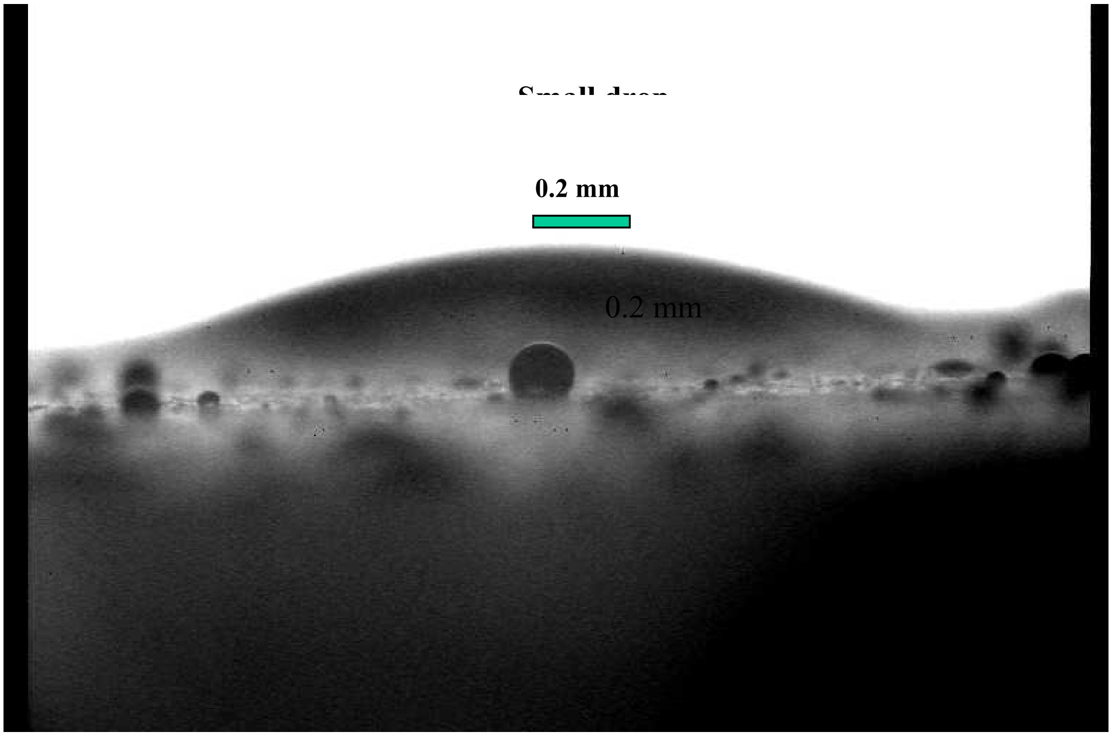


Fig. 15 – Image of one of the smaller oil droplets sticking to the marble plate 48 hours after being exposed to surfactant + brine.

The results of the experiments with the dolomite and lithographic limestone are similar. All the results have been summarized in Table 1.

## Table 1

| **Contact Angle** | **Marble** | **Limestone** | **Dolomite** | **Calcite** |
|---|---|---|---|---|
| Equilibrium Angle | 45 | 160 | 43 | 55 |
| Advancing Angle | 130 | 168 | 115 | 113 |
| Receding Angle | 36 | 137 | 42 | 33 |
| After aging the mineral surface with oil at $80^0$ C for 44 hrs. Note that all angles reported are advancing contact angles measured through the water phase. | | | | |
| **1. In synthetic brine only** | | | | |
| - 5-10 mins | >170 | 180 | >170 | >170 |
| - 30 mins | 130 | 180 | 164 | >170 |
| - 60 mins | 132 | 180 | 160 | >170 |
| **2. In 0.05 wt % surfactant (active)** | | | | |
| - 20 mins | 122 | 162 | 158 | 155 |
| -1 hour | 121 | 161 | 156 | 145 |
| -24 hours | 90 (small drops), 158 (large drops) | 156 | 148 | 140 (small drops), 151 (large drops) |
| -48 hours | 146 (large drops), 85 (small drops) | 163 | 141 | 140 |

## Adsorption

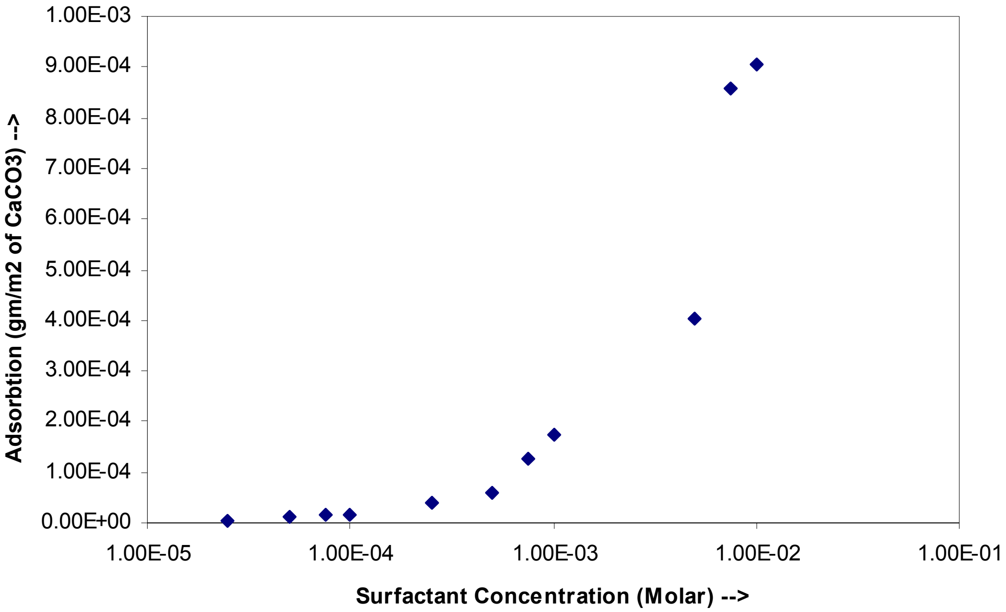


Fig. 16 - Adsorption isotherm of the surfactant 4-22 on calcite at 25$^0$C

In the last report, the adsorption of Polystep B-27 was studied. Addition of $Na_2CO_3$ suppresses most of the adsorption. The adsorption of Gemini surfactant 4-22 at 25 °C is shown in Figure 16. It shows the first three regions of adsorption. A typical adsorption isotherm is characterized by four regions, attributed to four different dominant mechanisms being operative in each region (Somasundaran & Krishnakumar 1997). Region 1 has a constant slope of unity under constant ionic conditions. The dominant operative mechanism in this very low concentration range is the electrostatic interaction between the polar head group of surfactant and oppositely charged mineral surface. The slope of the adsorption isotherm increases in the Region 2. This is attributed to the surfactant aggregation at the surface through lateral chain-chain interaction between the hydrocarbon chains. Region 3 exhibits a decrease in the slope of adsorption isotherm. This is primarily due to repulsive electrostatic forces produced by the charge reversal of the mineral surface by surfactant adsorption. Region 4 and the plateau correspond to the maximum surface coverage as determined by the micelle formation in the bulk. As reported in the last report, adsorption is lowered to less than $10^{-4}$ gm/m$^2$ in the presence of $Na_2CO_3$.

## Technology Transfer

Marathon oil company is one of the major producers in West Texas carbonates. We have briefed them about our project plans and have received field samples. This collaboration is extremely important to the success of our project.

## Conclusions

- Preliminary experiments show that adsorption of anionic surfactants on calcite can be decreased by addition of $Na_2CO_3$. (Task 1)
- Addition of surfactant reduces the contact angle from oil-wet to intermediate-wet. The interfacial tensions decrease to below 0.01 dynes/cm. (Task 2)

## Plans for Next Reporting Period

- Adsorption measurements in cores (Task 1)
- Wettability, interfacial tension, and phase behavior measurements (Task 2)

# References

Bragg, J. R. et al.: "Loudon Surfactnat Flood Pilot Test," SPE/DOE 10862, SPE/DOE 3rd Joint Symposium on EOR, Tulsa, April 4-7, 1982.

Spinler, E. A. et al.: "Enhancement of Oil Recovery Using Low Concentration Surfactant to Improve Spontaneous or Forced Imbibition in Chalk," SPE 59290, SPE/DOEImproved Oil Recovery Symposium, Tulsa, April 3-5, 2000.

Somasundaran, P., Krishnakumar, S.: "Adsorption of surfactants and polymers at the solid-liquid interface," Colloids and Surfaces, 123-124 (1997) 491-513.