

# **Dilute Surfactant Methods for Carbonate Formations**

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## 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 fractured). 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, interfacial tension (IFT) and wettability studies. Addition of  $\text{Na}_2\text{CO}_3$  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-wet for many surfactants and water-wet for one surfactant. Addition of  $\text{Na}_2\text{CO}_3$  decreases anionic surfactant adsorption on calcite surface. Plans for the next quarter include conducting core adsorption, phase behavior, wettability and mobilization 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 fractured). 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, interfacial tension (IFT) and wettability studies. Addition of  $\text{Na}_2\text{CO}_3$  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-wet for many surfactants and water-wet for one surfactant. Addition of  $\text{Na}_2\text{CO}_3$  decreases anionic surfactant adsorption on calcite surface. Plans for the next quarter include conducting core adsorption, phase behavior, wettability and mobilization 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 fractured). 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 April 2003 through June 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.

## Experimental

### Phase Behavior and IFT

A fourth surfactant (Oil Chem Technology alkyl aryl Surfactant 6566) was added to the three surfactants already used in this study so far: an alkyl aryl sulfonate (Oil Chem Technology Surfactant 5166), a Gemini surfactant (Oil Chem Technology Surfactant 422) and an ethoxy sulfonate (Stepan Polystep B-27). All studies (phase behavior, wettability and adsorption) are not complete for all the 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  $\text{Na}_2\text{CO}_3$  concentration in the range of 0.1 M to 0.5 M. The surfactant used for the phase behavior experiments shown in Fig. 1 is the alkyl aryl sulfonate (Surfactant 6566). The concentration of the surfactant is kept fixed at 0.05 wt% active. 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  $\text{Na}_2\text{CO}_3$  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.

### **Wettability**

Wettability alteration to a 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. 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 have been 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<sup>0</sup>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 govern 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%  $\text{CaCO}_3$  (metals basis), consisting of 5- $\mu\text{m}$  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  $1.68 \text{ m}^2/\text{g}$ . Titration and UV spectrometry were used to measure the concentration of surfactant in the solution. A new titrator was installed. Coreflood experiments have started to measure adsorption in cores.

## Results and Discussion

### Phase Behavior

Fig. 1 shows the phase behavior of crude oil/brine ( $\text{Na}_2\text{CO}_3$ )/surfactant 6566 system. The concentration of the surfactant is kept constant at 0.5 wt% and the  $\text{Na}_2\text{CO}_3$  concentration is increased from 0 to 0.7 M. As the caustic concentration increases the turbidity of the solution increases, reaches a maximum and then decreases. In this case, the aqueous phase is observed to be the most turbid at a  $\text{Na}_2\text{CO}_3$  concentration of 0.3 M. The system may be close to the optimal at this point.

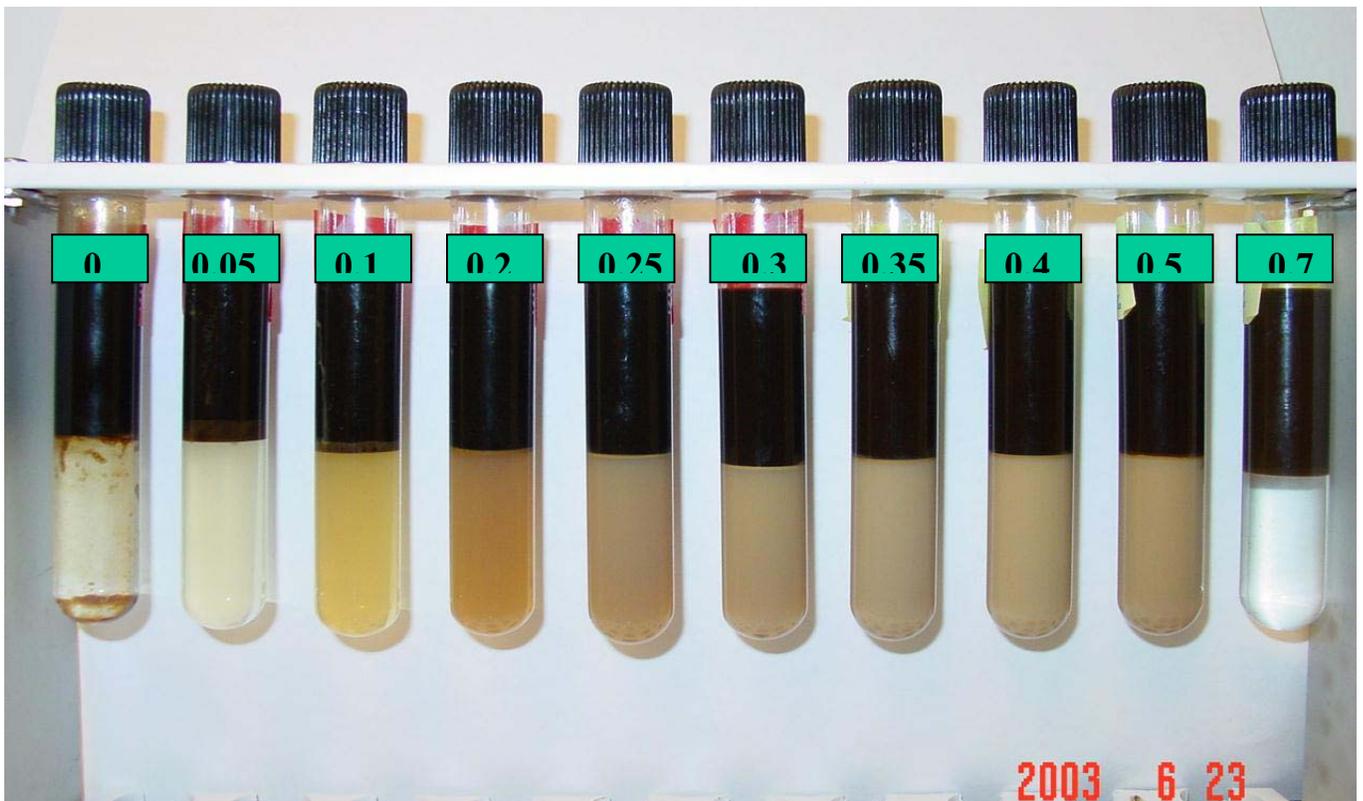


Fig. 1 - Phase behavior of crude oil/brine ( $\text{Na}_2\text{CO}_3$ )/surfactant 6566 system; surfactant concentration is kept fixed at 0.05 wt% while  $\text{Na}_2\text{CO}_3$  concentration is varied. WOR =1.

The aqueous phase becomes progressively clearer on further increase of  $\text{Na}_2\text{CO}_3$  concentration indicating over optimal system. A middle phase microemulsion is also observed in the nearly

optimal regime. The aqueous phase becomes clear at the  $\text{Na}_2\text{CO}_3$  concentration of 0.7 M indicating Winsor type II+ microemulsion. At this point the system is called over-optimum.

Fig. 2 shows the IFT measurements for this system along with those of the other surfactants already studied. These IFTs are for the equilibrated phases. Surfactant 5166 gives the lowest IFT ( $\sim 10^{-2}$  mN/m and lower) and the IFT stays low for a large range of alkaline concentration. Surfactant 6566 gives IFT of  $10^{-1}$  mN/m and lower for alkaline concentration of 0.3-0.5 M. Surfactant 4-22 gives IFT mostly greater than  $10^{-1}$  mN/m. The surfactant-free system shows a minimum IFT at  $\text{Na}_2\text{CO}_3$  concentrations of 0.25 M. Interestingly, two local minima are observed for the surfactant systems. 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 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 is under optimal. The second minimum may correspond approximately to the optimal salinity of the synthetic surfactant.

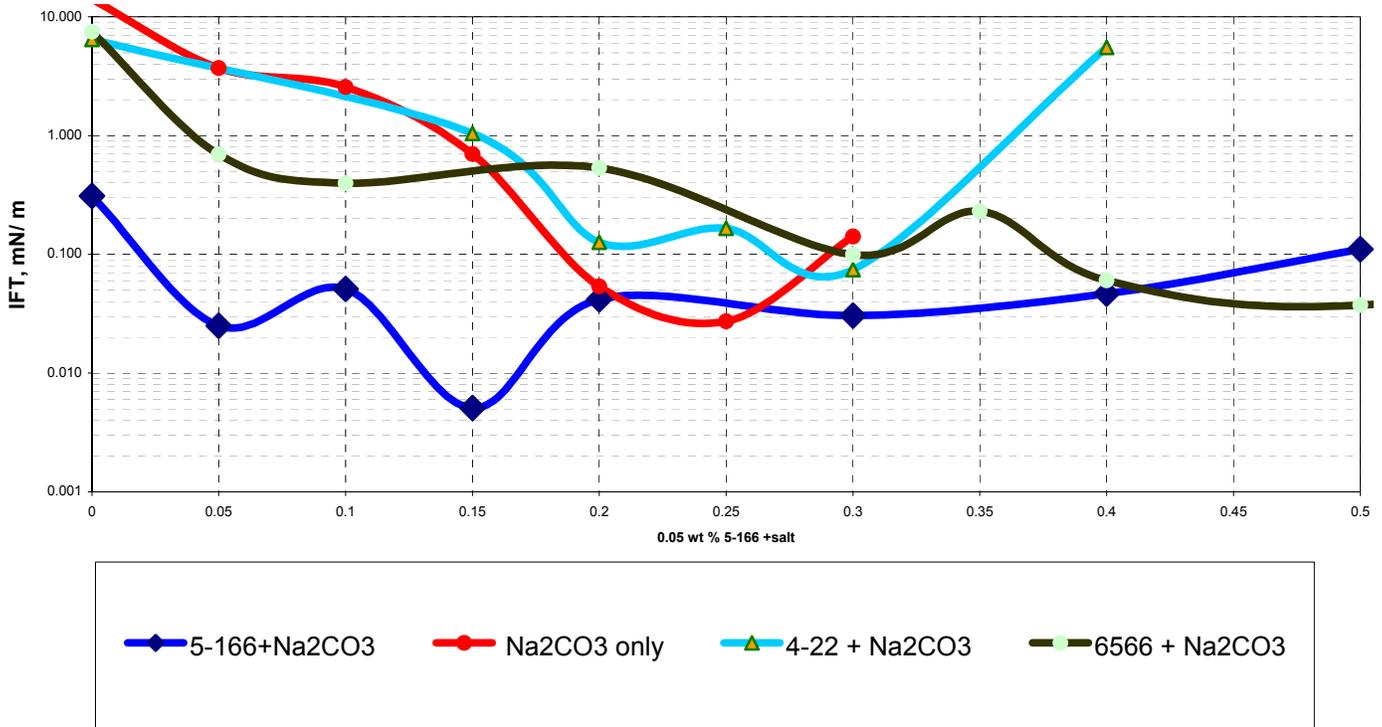


Fig. 2 – IFT of crude oil/brine/surfactant system. Surfactant concentration is fixed at 0.05 wt%. The x-axis shows the Na<sub>2</sub>CO<sub>3</sub> concentration in M.

### Wettability

Figs. 3 – 7 show the advancing contact angles measured at different stages of the experiment for the calcite mineral with surfactant 6566. Before aging with oil, the mineral plate is intermediate wet with advancing contact angle greater than 90° and receding contact angle less than 90° as shown in Fig. 3. Fig. 4 shows after aging calcite with crude oil at elevated temperature for 44 hrs, the mineral plate becomes completely oil wet with an advancing contact angle close to 180°. When exposed to the surfactant + brine solution, the advancing contact angle decreases with time and stabilizes at a value of about 40°-90° depending on the drop size. Fig. 5 shows the plate upper surface after 48 hours. Fig. 6 and Fig. 7 show two representative drops of different sizes.

The wettability, in this case, can be said to alter from an oil-wet state to slightly water-wet state by the application of this surfactant 6566.



Fig. 3 – Receding and advancing angles of the sessile oil droplet in contact with the calcite plate before aging with crude oil.



Fig. 4 – Advancing angle of the oil drop on calcite after aging it with the crude oil.



Fig. 5 – Image of oil drops on calcite 48h after surfactant solution addition (entire plate).

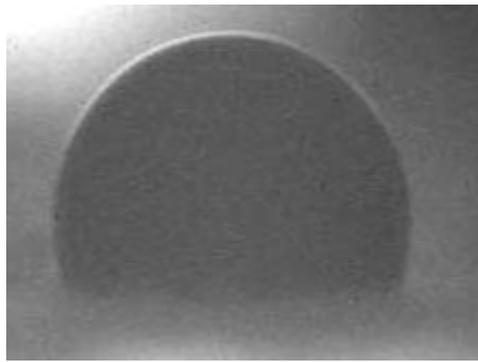


Fig. 6 – Image of one of the larger oil droplets (~0.7 mm) sticking to calcite plate after 48 hours.

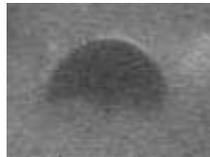


Fig. 7 – Image of one of the smaller oil droplets (0.15 mm) sticking to calcite plate after 48 hours.

The wettability of surfactant 6566 on calcite is contrasted with those of the other surfactants in Figs. 8. It shows the advancing contact angles measured at different stages of the experiments. Surfactant 6566 brings back the wettability of calcite to the water-wet region where as the other surfactants reduce the wettability to intermediate or less oil-wet state. It is interesting to note that surfactant 5166 showed the best IFT behavior, but surfactant 6566 shows the best wettability behavior among the systems studied.

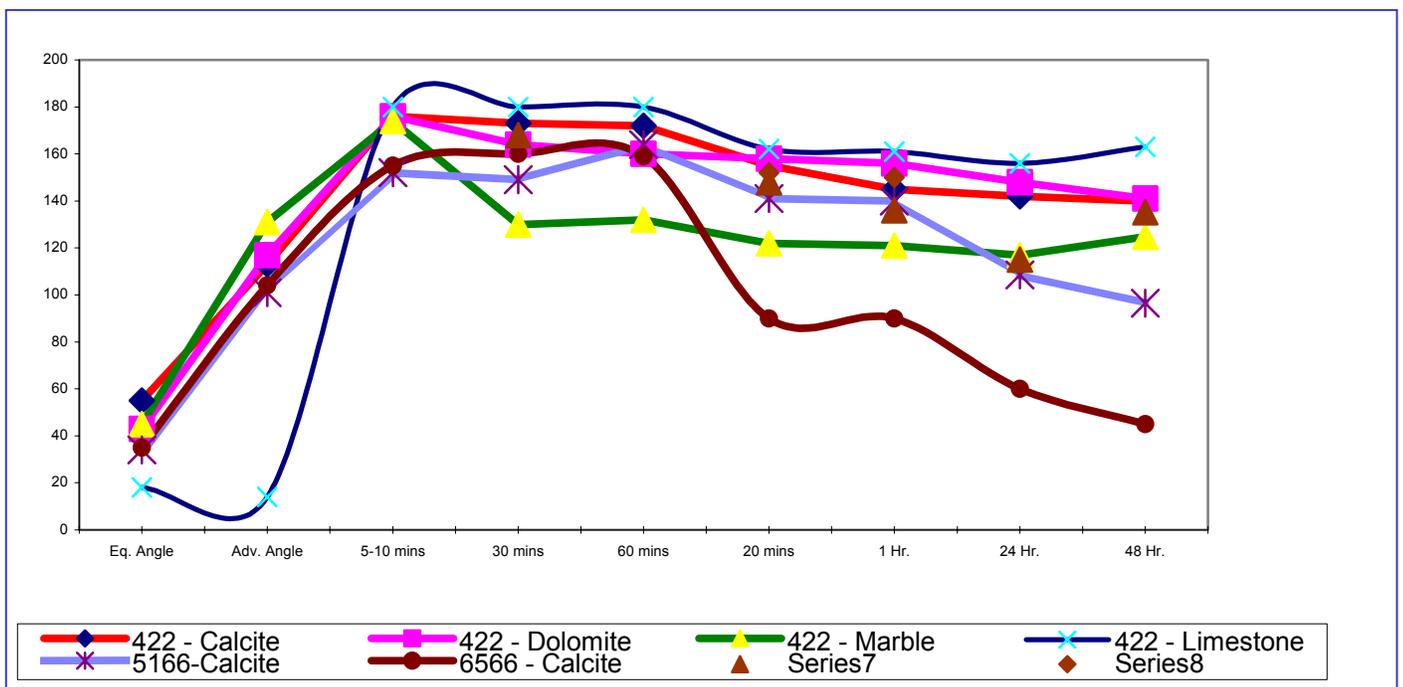


Fig. 8. Contact angle at different stages of the wettability experiments.

### 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. We are working with Oil Chem

Technology on surfactants. These collaborations are extremely important to the success of our project.

### **Conclusions**

- Surfactant 6566 can reduce the contact angle from oil-wet to water-wet; but the interfacial tension is reduced to only 0.1 mN/m. Surfactant 5166 can reduce the contact angle from oil-wet to intermediate-wet; but the interfacial tension is reduced to below 0.01 mN/m (Task 2)

### **Plans for Next Reporting Period**

- Finish core adsorption measurements (Task 1)
- Wettability, interfacial tension, and phase behavior measurements (Task 2)
- Initiate mobilization experiments (Task 3)

## References

Bragg, J. R. et al.: "Loudon Surfactant Flood Pilot Test," SPE/DOE 10862, SPE/DOE 3<sup>rd</sup> 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/DOE Improved Oil Recovery Symposium, Tulsa, April 3-5, 2000.