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. Alfoterra-38 (0.05 wt%), Alfoterra-35 (0.05 wt%), SS-6656 (0.05 wt%), and DTAB (1 wt%) altered the wettability of the initially oil-wet calcite plate to an intermediate / water-wet state. Low IFT (~10^{-3} dynes/cm) is obtained with surfactants 5-166, Alfoterra-33 and Alfoterra-38. Plans for the next quarter include conducting wettability and mobilization studies.

TABLE OF CONTENTS

List of Graphical Materials

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. Alfoterra-38 (0.05 wt%), Alfoterra-35 (0.05 wt%), SS-6656 (0.05 wt%), and DTAB (1 wt%) altered the wettability of the initially oil-wet calcite plate to an intermediate / water-wet state. Low IFT (~10^{-3} dynes/cm) is obtained with surfactants 5-166, Alfoterra-33 and Alfoterra-38. Plans for the next quarter include conducting 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 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 July 2003 through September 2003. The five tasks for the project are: (1) Adsorption, (2) Wettability alteration, (3) Gravity and viscous mobilization, (4) Imbibition, and (5) Simulation. The second 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

Three alkyl propoxy sulfate surfactants: Alfoterra 33, Alfoterra 35 and Alfoterra 38 (from Sasol) were studied and compared to the three alkyl aryl sulfonate surfactants (Oil Chem Technology) already used in this study so far. 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. 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. A cationic surfactant, DTAB (Dodecyl trimethyl ammonium bromide) was also tested for comparison. In this case, field brine was used, because Sodium Carbonate is unnecessary for reduced adsorption (Austad and Standnes, 2003).

The synthetic brine was prepared by varying the Na_2CO_3 concentration in the range of 0.1 M to 0.5 M. 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 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.

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 80^0C 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. In some cases, there was very little oil left on the plate to observe the contact angle. The field brine was used in case of the cationic surfactant.

In cases where the drops were too small, it was difficult to measure the accurate contact angle and a post-wettability test was performed wherein the calcite plate was washed with brine to remove oil. This plate was then placed in the brine solution and an oil drop was deposited on the bottom of the surface with the help of an inverted needle. The contact angle measured on this drop gives the final wettability state of the plate.

Capillary Pressure & Mobilization

The centrifuge method is being used to measure the capillary pressure. The core is being aged with the field oil. Capillary pressure will be measured before any surfactant adsorption. Oil and surfactant solution are being equilibrated. The core will be saturated with the surfactant solution. And capillary pressure will be measured between the equilibrated oil and brine. Capillary number dependence of residual oil saturation in a carbonate core will be measured by the flooding method. Bond number dependence of a carbonate core will be measured by the centrifuge method. These experiments have been initiated in this quarter.

Results and Discussion

Phase Behavior

The phase behavior of crude oil / brine (Na_2CO_3) / Alfoterra surfactant system is studied at room temperature. The concentration of the surfactant is kept constant at 0.5 wt% and the Na_2CO_3 concentration is increased from 0 to 0.6 M. As the caustic concentration increases the turbidity of the solution increases, reaches a maximum and then decreases. The aqueous phase is observed to be the most turbid at a Na_2CO_3 concentration of ~0.2M for Alfoterra 38 and ~0.3 M for Alfoterra 35 and 33. 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 near-optimal regime, but the amount is very small (a thin layer). The aqueous phase becomes clear at the Na_2CO_3 concentration of 0.5 M indicating Windsor type II+ microemulsion.

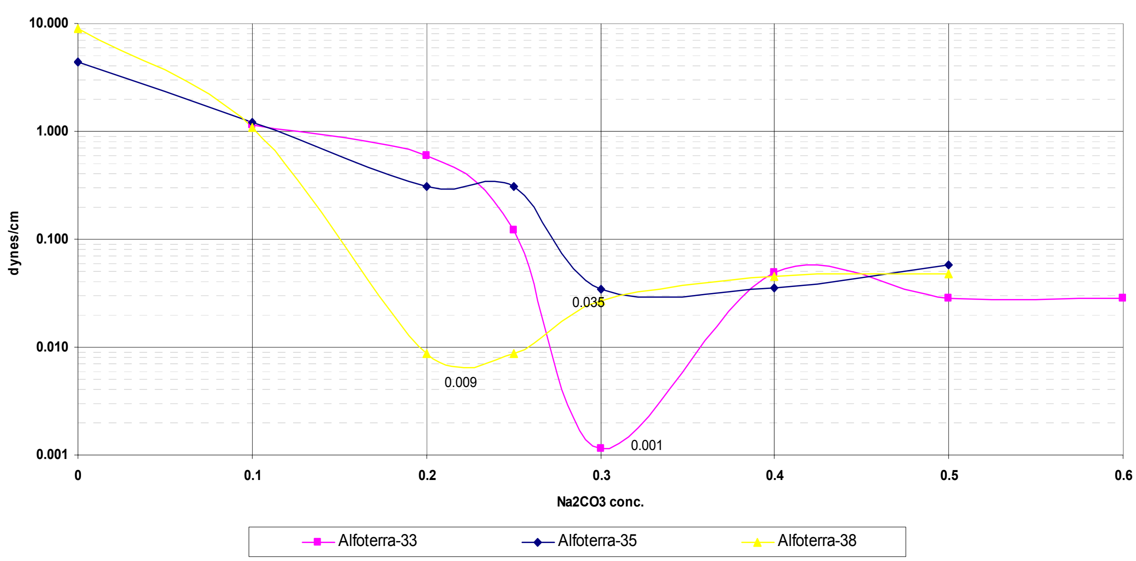

Fig. 1 – Interfacial tension of crude oil/brine (Na_2CO_3)/Alfoterra surfactants; surfactant concentration is kept fixed at 0.05 wt% while Na_2CO_3 concentration is varied. WOR =1.

Fig. 1 shows the IFT measurements for the Alfoterra surfactants studied. These IFTs are between the equilibrated oil and water phases. Surfactant Alfoterra 33 gives the lowest IFT (~10^{-3} mN/m and lower) and the IFT stays low for a large range of alkaline concentration. Surfactant Alfoterra 35 gives IFT of ~$4x10^{-2}$ mN/m for alkaline concentration of 0.3 M. Surfactant Alfoterra 38 gives IFT of ~$8x10^{-3}$ mN/m for alkaline concentration of 0.2 M. The lowest interfacial tension achieved with these propoxy sulfate surfactants are about an order of magnitude lower than those observed for the sulfonate surfactants.

Fig. 2 shows the IFT measurements for the cationic surfactant DTAB. The field brine is used in these experiments. IFT decreases with the increase of surfactant concentration, but reaches a plateau of ~0.04 mN/m. IFT at surfactant concentration of 1 wt% is about 0.5 mN/m. All of these tests (Figs 1 and 2) were conducted at the oil/water ratio of 1. It can be concluded that very low tensions can be generated with the anionic surfactants, but not with the cationic surfactant studied at concentrations below 1 wt%.

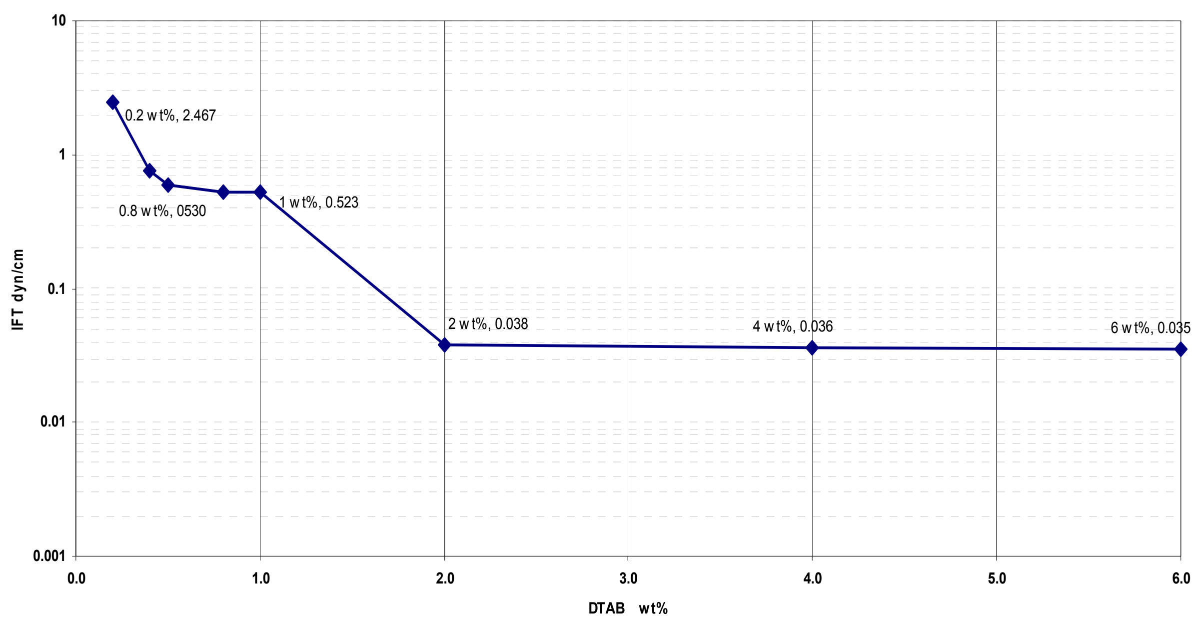

Fig. 2 – IFT of crude oil/field brine/surfactant DTAB system.

Wettability

Figs. 3 – 7 show the advancing contact angles measured at different stages of the experiment for the calcite mineral with surfactant Alfoterra 33. 0.3 M Na_2CO_3 solution brine was used. 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. 3. Fig. 4 shows that 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 180^0. When exposed to the surfactant - brine solution, the advancing contact angle decreases with time and stabilizes at a value of about 40^0-90^0 depending on the drop size. Fig. 5 shows the plate upper surface after one hour. Oil leaves the surface, but does not look water-wet. Fig. 6 shows the calcite plate after 48 hours. Most of the oil has left the plate due to low interfacial tension. The wettability was found to be in the intermediate to oil-wet state.

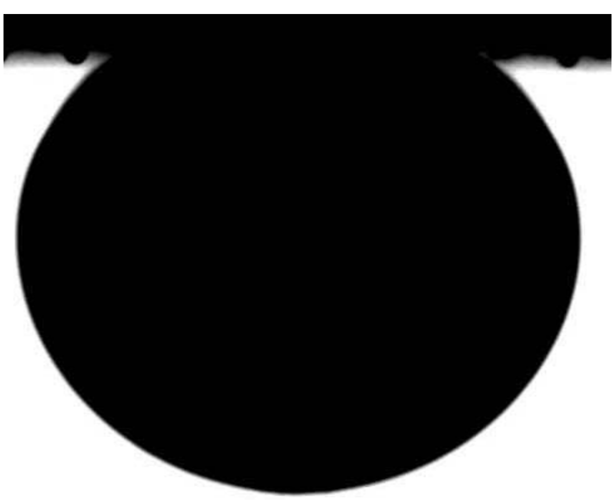

Fig. 3 – Receding and advancing angles of the sessile oil droplet in contact with the calcite plate before aging with crude oil.

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 1 hour after Alfoterra 33 solution addition.

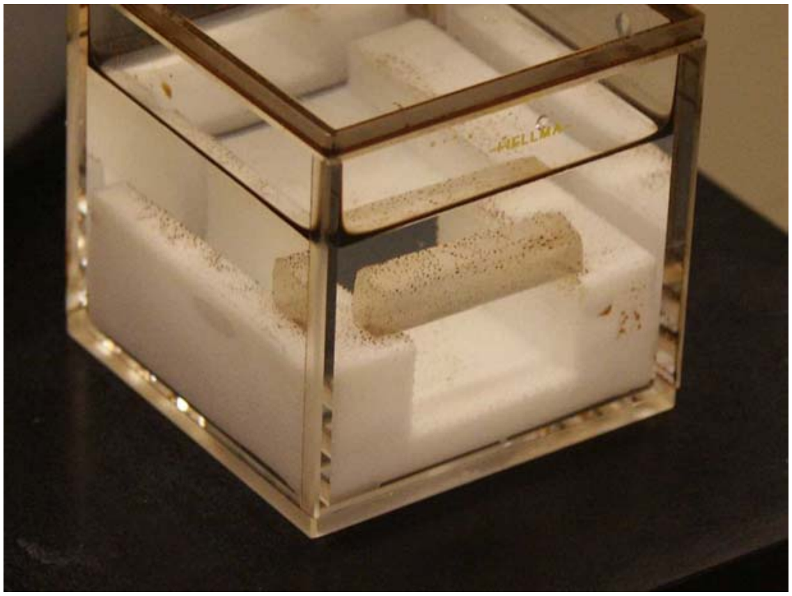

Fig. 6 – Image of the calcite plate 48 hours after Alfoterra 33 solution addition.

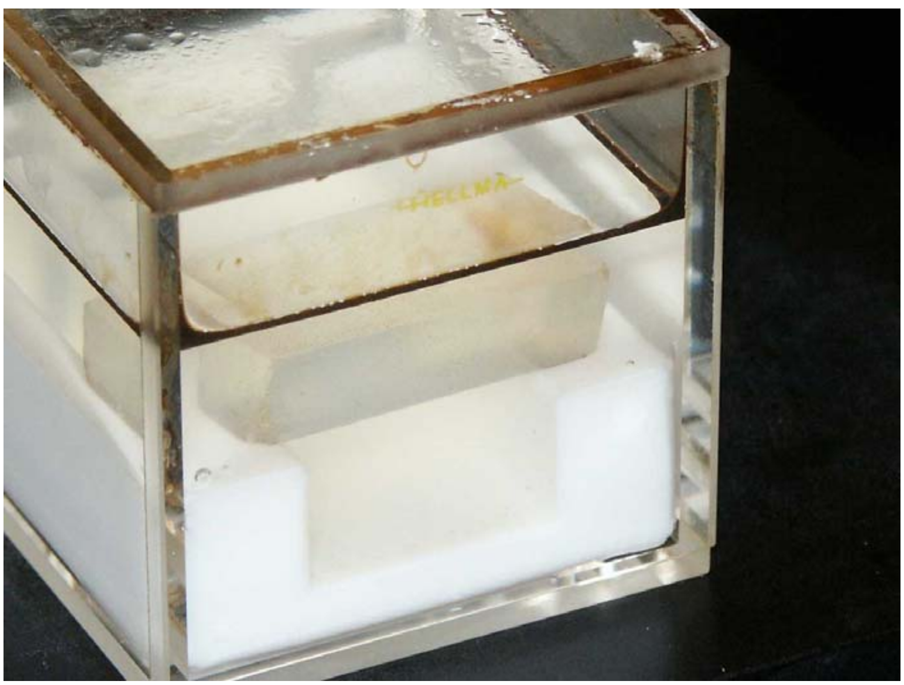

Fig. 7 – Image of the calcite plate 48 hours after Alfoterra 35 solution addition.

Fig. 7 shows the calcite plate after 48 hours in the Alfoterra 35 solution. 0.3 M Na_2CO_3 solution brine was used. Most of the oil has left the plate in Fig. 7. The post-wettability test indicated that the contact angle is about 75, i.e., the intermediate to water-wet state. Surfactant Alfoterra 38 also showed a similar behavior (photos not shown).

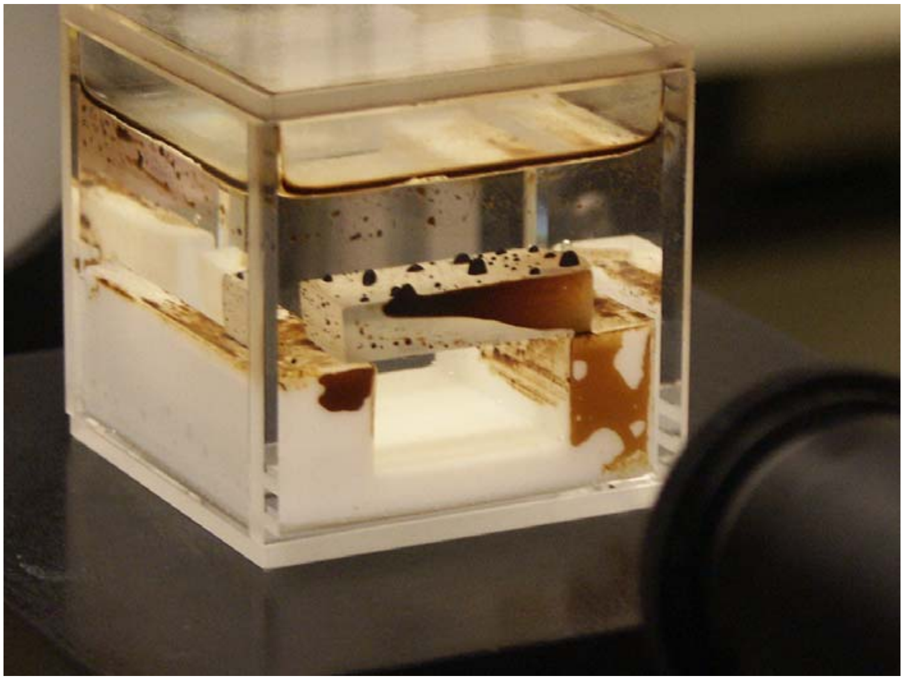

Fig. 8. Image of the calcite plate 48 hours after 1 wt% DTAB solution addition.

Wettability tests for the DTAB were conducted with the field brine at 1 and 0.5 wt%. Fig. 8 shows the calcite plate after 48 hours of contact with 1 wt% surfactant. Oil drops attached are bigger than those seen with the Alfoterra surfactants; this is a result of higher IFT. The contact angles of these oil drops are between 70-100. For the 0.5 wt% surfactant solution, the contact angles were about 140 (photos not shown). Thus DTAB does not change the wettability, if the concentration is small. At about 1 wt%, wettability changes to intermediate to water-wet.

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

Conclusions

- Alfoterra-38 (0.05 wt%), Alfoterra-35 (0.05 wt%), SS-6656 (0.05 wt%), and DTAB (1 wt%) altered the wettability of the initially oil-wet calcite plate to an intermediate / water-wet state. Low IFT (~10^{-3} dynes/cm) is obtained with surfactants 5-166, Alfoterra-33 and Alfoterra-38. (Task 2)

Plans for Next Reporting Period

- Wettability and interfacial tension measurements (Task 2)
- Mobilization experiments (Task 3)

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