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 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 acquired field oil and core samples and field brine compositions from Marathon. We have conducted preliminary adsorption and wettability studies. Addition of Na_2CO_3 decreases anionic surfactant adsorption on calcite surface. Receding contact angles increase with surfactant adsorption. 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 acquired field oil and core samples and field brine compositions from Marathon. We have conducted preliminary adsorption and wettability studies. Addition of Na_2CO_3 decreases anionic surfactant adsorption on calcite surface. Receding contact angles increase with surfactant adsorption. 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, yet it was developed for sandstone reservoirs in the past.

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.

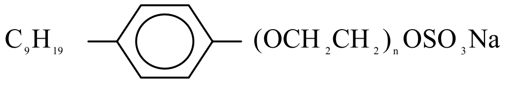
This report summarizes our results for the period of October 2002 through December 2002. The five tasks for the project are: (1) Adsorption, (2) Wettability alteration, (3) Gravity and viscous mobilization, (4) Imbibition, and (5) Simulation. Only the first two tasks were worked on in this quarter; the activities are described in the next section.

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 adsorption of surfactants on minerals more typical of sandstone reservoirs has been studied extensively. However there is little published literature on the adsorption of surfactants on the carbonate minerals (Hanna 1983; Lawson 1978; Tabatabai 1989; Gonzalez 1989). The objective of this study is to determine the mechanism of adsorption of cationic, non-ionic and anionic surfactants on carbonate minerals.

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.

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 (Johnson Mathey Inc., Catalog No. 11403). Anionic surfactant Polystep B-27 supplied by Stepan was used. The chemical formulae of this surfactant is,



where n = 4. 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.

Procedure

A stock solution of high concentration of surfactant was prepared and diluted to obtain the solutions of lower concentrations. The pH of all the solutions was measured using an Acumet pH/mV Benchtop meter. The pH electrode was left in the magnetically stirred solution till an equilibrium value was reached which required approximately 10 minutes. Ten sample solutions covering the concentration range between 10^{-5} M to 10^{-2} M were prepared by diluting the 10^{-2} M surfactant solution with deionised water. UV absorption index was obtained for these solutions at a wavelength of 277 nm and these values were used to construct the calibration curve for our system. The calibration test was then repeated and a good match was observed. For the experiments on adsorption, another batch of solutions each weighing 10 g was prepared in the concentration range of 10^{-4} M to 10^{-2}M. These solutions were then contacted with carefully measured 10 g of calcite powder in 50 ml vials. The vials were corked and gently shaken so that the calcite powder comes into contact with the surfactant solution thoroughly. The solutions were allowed to equilibrate with the calcite powder for 48 hours subject to gentle periodic shakings. The slurry was then centrifuged at 1200 rpm for 20 minutes to separate the solid particles from the liquid solution. The supernatant was carefully pipetted out to avoid the solid particles. The supernatant was then centrifuged again for 20 minutes to obtain particle free supernatant. The pH of all the supernatant solutions was measured again. UV spectrometry was used to determine the residual surfactant concentration in the supernatant liquid. The above procedure was then repeated with 0.05 M solution of Na_2CO_3 containg surfactant to study the effect of Na_2CO_3 on the surfactant adsorption.

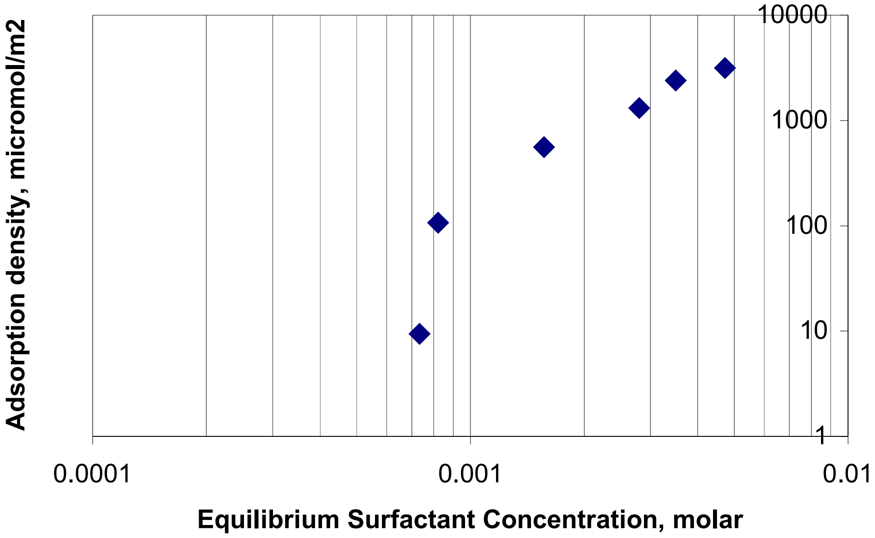


Fig. 1 – Adsorption of surfactant B-27 on calcite powder

Results

The pHs of all the surfactant solutions used for the adsorption experiment were found to be between 6 and 7 before contacting calcite powder. However after adsorption the pH values of the supernatant were found to be in the range of 8-9. Some amount of $CaCO_3$ from the mineral possibly dissolves in water and the presence of CO_3^{-2} ions raises the pH of the supernatant. Fig. 1 shows the variation of the adsorption density of the surfactant with its equilibrium molar concentration. Although Region 1 and Region 4 appear to be missing, Region 2 and Region 3 are conspicuous. There is a need to broaden the concentration range and go to the lower and higher concentrations so as to observe the missing regions. Fig. 2 shows the adsorption isotherm of the surfactant in 0.05 M Na_2CO_3 solution. In this case, the concentration of the surfactant in the supernatant after adsorption was found to be higher than the initial concentration before adsorption and hence a negative adsorption density. This kind of behavior was also observed by Tabatabai et al.(1993) for some electrolyte concentrations. The presence of Na_2CO_3 raises the pH of the solution beyond the point of zero charge for the calcite which was found to be about 8.2 by Somasundaran et al. (1967). This causes the surface to acquire negative charge and repel the like charged anionic polar head group of the surfactant. Tabatabai et al.(1993) reasoned that the surfactant molecules were repelled from the interfacial region of the calcite particles and got concentrated in the upper part of the vial, from which supernatant was removed, causing an apparent 'negative adsorption'. More experiments are planned to determine the experimental reproducibility, the effect of field brine, and the effect of surfactant structure.

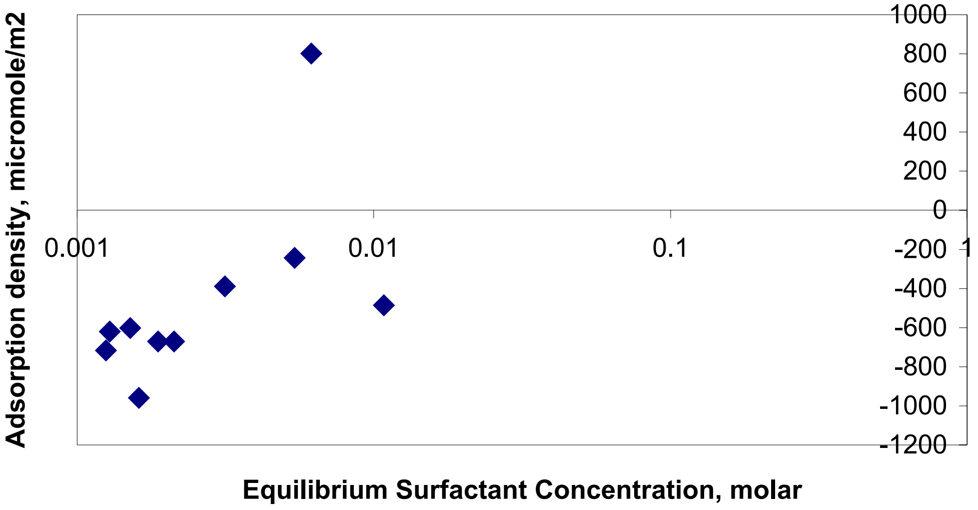


Fig. 2 – Adsorption of surfactant on calcite in the presence of 0.05 M Na_2CO_3 solution

Wettability Alteration

Many researchers have shown that the wettability is changed from more oil-wet to less oil-wet due to treatment with cationic (Austad & Milter, 1997) and anionic surfactants (Chen et al., 2000). This would involve removal of adsorbed oil components from mineral surface. The mechanism of wettability alteration is, however, not clear. Austad & Milter (1997) hypothesize that the cationic surfactant forms reverse micelles in the oil phase. These reverse micelles complex with the adsorbed oil components on the solid surface and remove them. It is not clear, however, how the hydrocarbon tails (these are the groups exposed in reverse micelles) take part in complexation. These groups are not very different in cationic surfactants from those in anionic surfactants. The cationic surfactant, however, changes wettability more strongly than anionic surfactants. The role of hydrophilic-lipophilic balance (HLB) on the wettability alteration needs to be studied.

Surfactant-brine-oil phase behavior will be quantified. Crude oil-treated mineral surfaces will be exposed to surfactant solutions. The morphology of the surface molecules will be probed by the AFM. This would be studied as a function of the type and HLB of surfactants. Dynamics of wettability alteration will be studied by dynamic contact angle measurement (Buckley et al., 1998). Core wettability will be measured by measuring capillary pressure curves with brine and surfactant solutions. Mixed-wet porous media have both positive and negative parts in their capillary pressure curves which can be probed by the Semi-Dynamic Method (Lenormand et al., 1993). The extent and the rate of wettability change will be needed for the reservoir simulation of this process.

To develop our procedure to measure contact angle on mineral surfaces, we have studied contact angle of a field oil with a 1 wt% NaCl brine on a calcite surface, 25 °C, at different concentrations of Na_2CO_3 and an anionic surfactant. The calcite was immersed in the brine solution. An oil drop was injected into the brine solution at the bottom of the calcite plate. The oil drop rises and contacts the calcite plate. Oil can be injected or withdrawn from the drop. The advancing and receding contact angles can be obtained by capturing the images of the drops adjacent to the plate. Figure 3 shows the receding contact angles at different surfactant and Na_2CO_3 concentrations. The contact angle between the oil and the 1 wt% NaCl brine is about 40. As the Na_2CO_3 is added, the contact angle increases, i.e., oil wettability increases. As the surfactant concentration increases, the contact angle also increases. The contact angle cell is being modified to do the advancing contact angles measurement. The increase of oil-wettability may be associated with surfactant adsorption and exposure of the hydrophobic tails. These experiments were conducted to develop the contact angle measuring procedure. Careful experiments of wettability alteration will be measured with the field oil and brine obtained from Marathon.

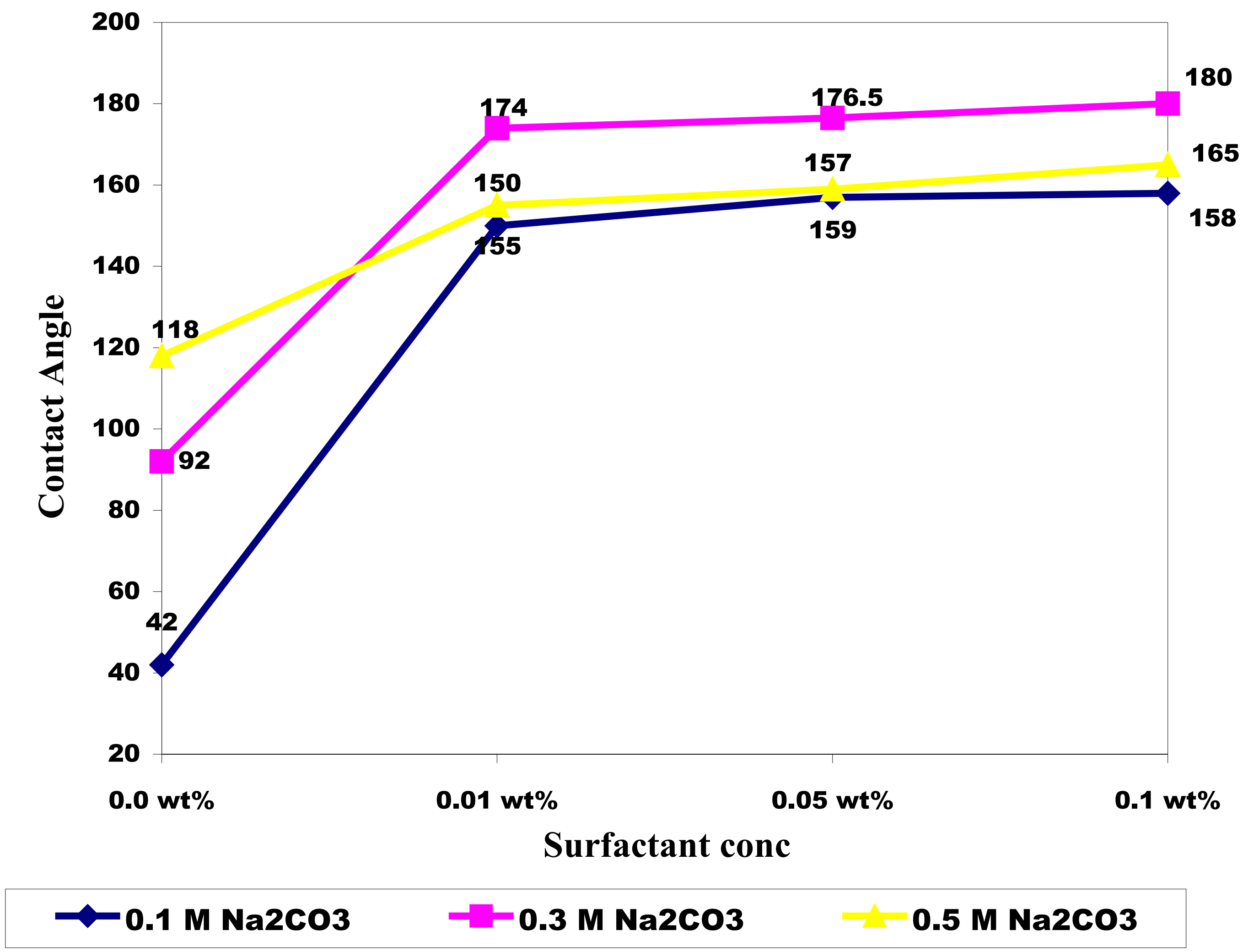


Figure 3. Effect of surfactant and Na_2CO_3 concentration on contact angle on calcite

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.

Summary

- Preliminary experiments show that adsorption of anionic surfactants on calcite can be decreased by addition of Na_2CO_3. (Task 1)
- Receding contact angles increased on a calcite surface as the surfactant and Na_2CO_3 concentration increased. (Task 2)

Plans for Next Reporting Period

- Adsorption measurements (Task 1)
- Wettability and phase behavior measurements (Task 2)

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