

# **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. Imbibition in an originally oil-wet 2D capillary is the fastest in the case of Alf-38 and slowest in the case of DTAB (among the surfactants studied). Force of adhesion studies and contact angle measurements show that greater wettability alteration is possible with these anionic surfactants than the cationic surfactant studied. The water imbibition rate does not increase monotonically with an increase in the surfactant concentration. A numerical model has been developed that fits the rate of imbibition. Plans for the next quarter include conducting simulation and imbibition 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. Imbibition in an originally oil-wet 2D capillary is the fastest in the case of Alf-38 and slowest in the case of DTAB (among the surfactants studied). Force of adhesion studies and contact angle measurements show that greater wettability alteration is possible with these anionic surfactants than the cationic surfactant studied. The water imbibition rate does not increase monotonically with an increase in the surfactant concentration. A numerical model has been developed that fits the rate of imbibition. Plans for the next quarter include conducting simulation and imbibition 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, 2004 through June, 2004. The five tasks for the project are: (1) Adsorption, (2) Wettability alteration, (3) Gravity and viscous mobilization, (4) Imbibition, and (5) Simulation. The fourth and fifth tasks were worked on this quarter. The results of imbibition and modeling are highlighted in this report.

## Experimental

Distilled, de-ionized water was passed through Milli Q cartridge filters to obtain water of resistivity 18.2 MΩ/cm and pH 7. This ultra pure water was used to prepare synthetic brine (brine with sodium chloride) and field brine. The composition of field brine is listed in Table 1. Toluene, methanol, APTES, trifluoroacetic acid and acetone were supplied by Sigma-Aldrich, Isopropyl alcohol and nitric acid from EM Science, hydrochloric acid from EMD, nitric acid, acetone and hydrogen peroxide were obtained from Mallinckrodt. All these chemicals were used as received.

Trade Name	Source	Structural Name	Active %	Molecular Weight	CMC (g/l)	Type
Alf-38	Sasol	Propoxylated sulfates-8PO	26.0%	715	0.005	Anionic
Alf-68	Sasol	Propoxylated sulfates-8PO	30.6%	667	0.014	Anionic
DTAB	Sigma	Dodecyl trimethyl ammonium bromide		308.3	4.625	Cationic

Table 1 - Surfactant Properties

Salt	g/l
CaCl <sub>2</sub> .2H <sub>2</sub> O	2.942
MgCl <sub>2</sub> .6H <sub>2</sub> O	2.032
NaCl	5.815
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O	0.007
Na <sub>2</sub> SO <sub>4</sub>	0.237

Table 2 - Composition of Field Brine

The properties of surfactants evaluated are listed in Table 2. Alf-38 and Alf-68 were supplied by Sasol. Alf-38 had a carbon chain length of 14 whereas Alf-68 had a carbon chain length of 12-13. Both the above surfactants had 8 propoxy groups present and were anionic. Dodecyl trimethyl ammonium bromide (DTAB) was also used as a reference. The solutions of Alf-38 (0.05, 0.26 and 1 wt%) were prepared in 0.2 M Na<sub>2</sub>CO<sub>3</sub> and the solution of Alf-68 (0.05 wt%) was prepared in 0.3 M Na<sub>2</sub>CO<sub>3</sub>. The surfactants were made in Na<sub>2</sub>CO<sub>3</sub> solution and the salinities were chosen to give the lowest interfacial tension for water-oil ratio equal to 1 (Seethepalli et al., 2004). The DTAB solution (1 wt%) was prepared in field brine. The crude oil has a density of 28.2 ° API, 19.1 cp viscosity, 0.2 acid number and 1.17 base number.

A petri dish was first washed in a “piranha solution” (3.5% H<sub>2</sub>O<sub>2</sub> in 18 M H<sub>2</sub>SO<sub>4</sub>), followed by rinsing in water and acetone (Karrasch et al., 1993). Glass slides (1”x 3”) were first washed with HCL/HNO<sub>3</sub> (3:1) once and then cleaned with distilled water in an ultrasonic bath for 10 minutes. The glass slides were then aged with trifluoroacetic acid for 90 minutes and then stored in vacuum for 10 hours over solid KOH for 15 hours. These slides were then silanized using APTES (2% in 99% acetone) for 5 minutes and then washed with acetone. The silane linkages on the glass slides (AP glass) were then cured in an oven at 110 °C and stored under vacuum if not used instantaneously. Silanized AP glass slides have positive surface charge and in that sense good substitutes for calcite plates.

Two AP glass were brought together with a gap of 30 µm between them, the gap was filled with oil B, and the parallel plate assembly was then immersed in a surfactant solution such that the top edge of the AP glass was approximately 2 mm above the surfactant solution. Fig. 1 shows a schematic of the side view of the set up. AP glass slides are transparent and allow visualization of the imbibition process. The height of the surfactant solution is then monitored for 48 hours using a digital camera. The glass slides are then taken apart and the excess oil is

washed with water. A contact angle goniometer was used to measure the advancing and receding water/oil contact angles by the sessile drop method as described in the section below. All the contact angles were measured through the water phase.

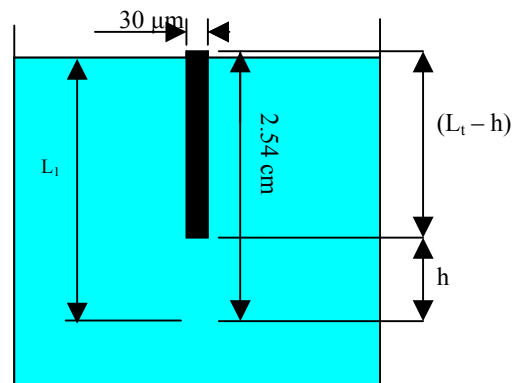


Fig. 1 - A schematic for parallel plate experiments (side view)

An optical glass cell, filled with the aqueous phase, was placed between a light source and a microscope. A horizontal mica/silicon plate was placed inside the aqueous phase. A U-shaped stainless steel needle attached to a motor driven syringe was used to introduce an oil droplet at the bottom surface of the plate. Decane was used as the probe oil. The volume of oil droplet was increased until the contact line moved outwards. A video frame grabber captured the image of the drop and contact angles were measured by fitting the drop shape to a solution of the Young-Laplace equation. The contact angle measured was the receding angle. The volume of the oil droplet was later decreased using the motor driven syringe until a neck forms. The angle formed by the droplet just before the detachment from the tip of the syringe is known as the advancing angle. On further reducing the volume of the oil droplet, the neck got thinner and finally broke. The oil volume was increased or decreased slowly in order to reduce the effect of viscous forces.

## Results and Discussion

### Imbibition

Alf-38 & 68 solutions were able to produce about 55% of the oil in core imbibition experiments. The following experiments were conducted to understand the mechanisms of imbibition. The parallel plate assembly (as described in methodology section) was immersed in the surfactant solution and the height of the surfactant solution imbibed between the parallel plates was recorded as a function of time. Fig. 2 shows a plot of height of the surfactant solution imbibed vs. time. It was observed that Alf-38 reaches the equilibrium height first followed by Alf-68, DTAB and  $\text{Na}_2\text{CO}_3$  solution. The equilibrium height was approximately the same for all the anionic surfactants and  $\text{Na}_2\text{CO}_3$  solution implying that the final capillary pressure is approximately equal. For DTAB, the aqueous phase-oil interface was wavy. Fig. 3 shows the images of the parallel plates dipped in Alf-68, DTAB and  $\text{Na}_2\text{CO}_3$  solution. The error bars in Fig. 2 show the minimum and maximum heights of the DTAB aqueous phase observed between the parallel plates.

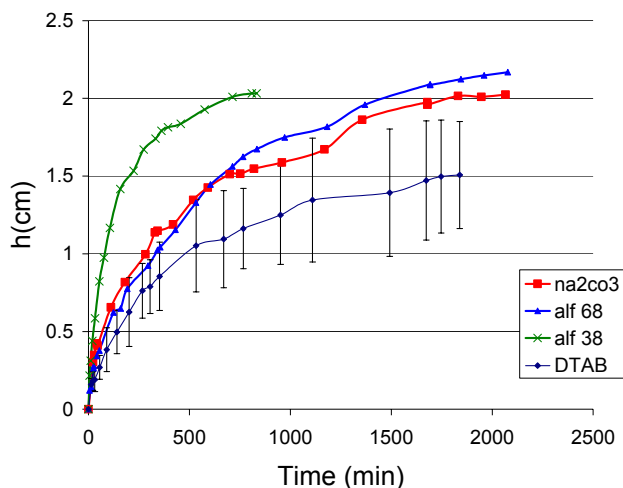


Fig. 2 - Height of surfactant solution vs. time

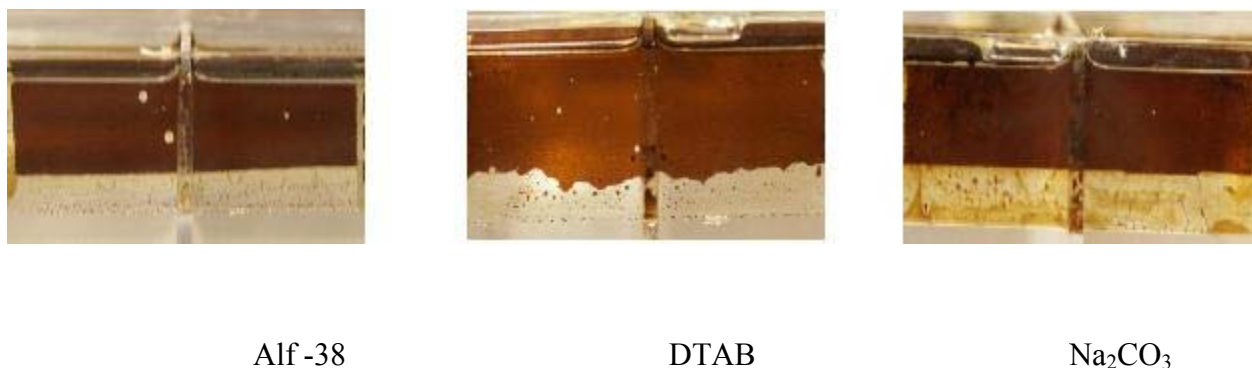


Fig. 3 - Parallel plates dipped in Alf-68, DTAB and Na<sub>2</sub>CO<sub>3</sub> solution after 150 minutes

Fig. 4 shows a snapshot of the experiment with Alf-38 (0.05 %) at some intermediate time. Three distinct regions were observed: region 1- oil, region 2- transition region, and region 3- aqueous phase. The transition region represents the region with an oil film sticking to the AP glass surface. This transition region is very distinct in the case of Alf-38. Alf-68 shows a thin transition region, whereas DTAB does not show any. Alf-38 readily adsorbs at the oil-water interface and lowers the interfacial tension thus displacing the bulk oil out of the parallel plates. But the process to remove the adsorbed oil molecules on the AP glass surface may be slower than the lowering of the interfacial tension. Also, because the IFT is low, adhering oil film does not increase the free energy of the system significantly. So an oil film adheres to AP glass when the bulk oil is displaced from that region. This is also seen for Alf-68 and Na<sub>2</sub>CO<sub>3</sub> solutions. The region 2 is absent for the DTAB solution clearly indicating a difference in mechanism of oil displacement by cationic and anionic surfactant solutions. The AFM scans and force measurements after this imbibition experiment show that DTAB leaves behind a lot of oil on AP mica surface.

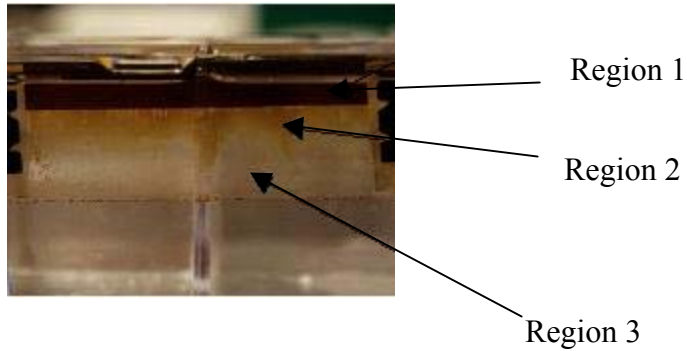


Fig. 4 - Parallel plates in Alf-38 (0.05 %)

Apart from changing wettability, surfactants also play an important role in changing the interfacial tension. It was seen that when the parallel plates were immersed in distilled water, there was no water imbibition. This meant that the capillary pressure was higher than the gravitational force, which is the driving force for surfactant imbibition. So both processes (reduction in interfacial tension and wettability alteration) can be achieved by surfactant-aided gravity drainage.

The parallel plate imbibition experiment was conducted with three different surfactant concentrations of Alf-38: 0.05, 0.26 and 1 wt %. The parallel plate experiments show that the time taken to displace oil did not vary linearly with concentration. Fig. 5 shows the height of oil-water interface vs. time. It was seen that 0.26 wt% Alf-38 displaced oil between the parallel plates the quickest, followed by 0.05 wt% and finally 1 wt%. Also the equilibrium height for 0.05 wt% and 0.26 wt% solutions were approximately same, implying that the equilibrium interfacial tensions for both concentrations are equal. But for the case of 1 wt %, the equilibrium position was the lowest among the Alf-38 solutions. This means that interfacial tension depends on surfactant concentration nonmonotonically. The optimal salinity depends on the surfactant concentration; these experiments were conducted at a fixed salinity. Another interesting thing observed was that the transition region (region 2) for 1 wt % Alf-38 solution was very thin.

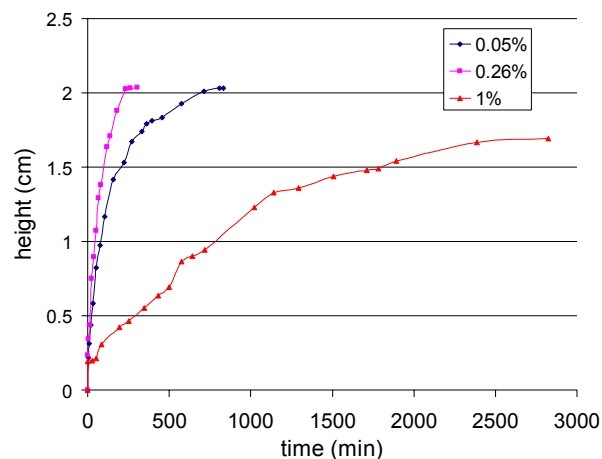


Fig. 5 - Height of surfactant vs. time for different concentration of Alf-38 solution.

After treating the parallel plates with surfactant for two days, decane-water contact angles were measured. Fig. 6 summarizes the advancing and receding contact angles. It was again observed that oil-aged AP glass treated with Alf-38 and Alf-68 are more water wet as compared to those treated with DTAB and  $\text{Na}_2\text{CO}_3$ . This observation confirms the result from the AFM scans and force measurements.

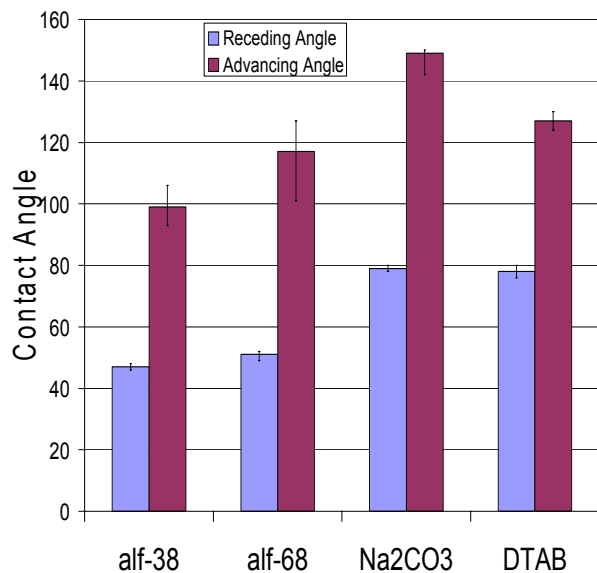


Fig. 6 – Post-wettability contact angles for different surfactant solutions.

## Simulation

The equations of motion of a liquid flowing into a capillary under the influence of surface tension and hydrostatic pressure were examined by Washburn (1921). The Lucas-Washburn equation (Zhud et al., 2000) assumes a quasi-steady process where gravity and viscous forces are balanced by the capillary force. But this treatment neglects the inertial effects due to changes in momentum of the liquid column. These inertial effects were analyzed in detail by Zhud et al. (2000) and Starov (2004). The above treatments were for a liquid imbibing into a capillary at a constant interfacial tension.

In this work, we present a very simple model for a surfactant solution imbibing into parallel plates where the capillary pressure changes with time. The parallel plates are initially oil-wet and so the capillary pressure ( $P_c \equiv P_o - P_w$ ) is negative, thus opposing the imbibition of surfactant solution into the parallel plates. The system is modeled as a pseudo-steady state process (Poiseuille flow) driven by gravitational forces and opposed by capillary and viscous forces (in both oil and water phases). The equation of motion is represented by,

$$\begin{aligned} \rho_2 g(L_1 - h) - \rho_1 g(L_t - h) + P_c = \frac{dh}{dt} (\mu_2 h + \mu_1 (L_t - h)) / c \\ + \frac{d \left( \left( \frac{dh}{dt} \right) (\rho_2 h + \rho_1 (L_t - h)) \right)}{dt} \end{aligned} \quad (1)$$

with boundary conditions:

$$h = 0 @ t = 0, \quad (2)$$

$$\frac{dh}{dt} = c \frac{\rho_2 g L_1 - \rho_1 g L_t + P_c}{\mu_1 L_t} @ t = 0, \quad (3)$$

where  $\mu$ ,  $\rho$ ,  $P_c$ , and  $c$  are viscosity, density, capillary pressure and a constant based on the plate geometry, respectively. The subscript 2 and 1 represent water and oil, respectively. The other

variables are as shown in Fig. 1. In deriving equation 1, the capillary pressure at the top oil-air interface is neglected. The oil-water capillary pressure is given by

$$P_c = \frac{\gamma \cos \theta}{r} = \frac{\gamma'}{r}, \quad (4)$$

where  $\theta$  and  $\gamma$  are dynamic contact angle and dynamic interfacial tension, respectively. Note,  $\gamma' \equiv \gamma \cos \theta$ . For the parameters of our experiment, the inertial term is negligible. Then equation 1 simplifies to a first order differential equation given by

$$\frac{dh}{dt} (\mu_2 h + \mu_1 (L_t - h)) = c(\rho_2 g(L_1 - h) - \rho_1 g(L_t - h) + P_c). \quad (5)$$

The above equation has an analytical solution for constant capillary pressure, given by

$$t = \frac{(\mu_2 - \mu_1)}{(\rho_2 - \rho_1)gc} \left( h + \left( \frac{\mu_1 L_t}{(\mu_2 - \mu_1)} + \frac{\rho_2 g L_1 - \rho_1 g L_t + P_c}{(\rho_2 - \rho_1)g} \right) \right) \ln \frac{(\rho_2 g L_1 - \rho_1 g L_t - P_c - (\rho_2 - \rho_1)gh)}{(\rho_2 g L_1 - \rho_1 g L_t - P_c)} \quad (6)$$

The interaction between crude oil and aqueous phase is taken into account by the capillary pressure term which depends on  $\gamma'$ . In our experiments,  $\gamma'$  changes with time at the beginning as the surfactant and oil molecules diffuse and try to get to a thermodynamic equilibrium. We have not captured this mixing mechanistically in this simplistic model. Instead we have introduced a mixing time parameter,  $\beta$ , for the lowering of  $\gamma'$ , given by

$$\gamma' = \gamma'_\infty + (\gamma'_0 - \gamma'_\infty) \exp(-t / \beta) \quad (7)$$

where  $\gamma'_0$  and  $\gamma'_\infty$  are the initial and the equilibrium values of  $\gamma'$ . Since the dynamic contact angle could not be measured, the interfacial tension,  $\gamma$  and  $\cos \theta$  are combined together as  $\gamma'$ . Higher the value of  $\beta$ , slower  $\gamma'$  approaches its equilibrium value.  $\gamma'_\infty$  can be calculated from the final height reached by the surfactant solutions.  $\gamma'_0$  can be calculated from equation 4 by

measuring the initial velocity of the aqueous phase imbibing into the gap between the parallel plates.  $\beta$  can then be obtained by fitting the solution to equation 5 to the experimental data (Fig. 7). The values of the mixing time,  $\beta$ , and  $\gamma_0$  for Alf-38, Alf-68 and 0.2 M  $\text{Na}_2\text{CO}_3$  solution were found to be 12, 20, 24 hours and 0.21, 0.3, 0.31 dynes/cm, respectively. This shows that mixing of the surfactants with oil is slow, of the order of a day.

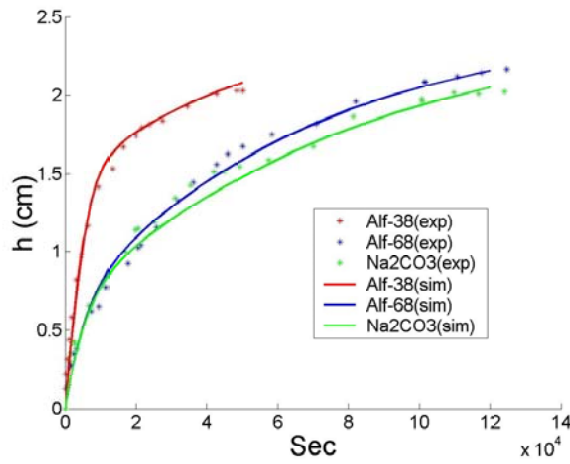


Fig. 7 - Experimental and theoretical curves for height of surfactant vs. time.

### **Technology Transfer**

We have written a paper, SPE 93009, for presentation at the 2005 SPE international symposium on Oilfield Chemistry. We had an annual project review for our industrial consortium, Institute for Improved Oil Recovery in Fall, 2004. The attendees included BP, Exxon, Marathon, Conoco-Phillips, Halliburton, Schlumberger, Core Lab, Oil Chem Technology, and Sasol.

## **Conclusions**

Anionic surfactants (Alfoterra 35, 38) recover about 55% of the oil in about 200 days by imbibition driven by wettability alteration and gravity in the core-scale (Task 4). To understand the mechanisms, imbibition experiments were conducted in initially oil-wet 2D capillaries. Both anionic and cationic surfactants can help imbibe water into initially oil-wet capillaries. The imbibition is the fastest in the case of Alf-38 and slowest in the case of DTAB (among the surfactants studied). Force of adhesion studies and contact angle measurements show that greater wettability alteration is possible with these anionic surfactants than the cationic surfactant studied. The water imbibition rate does not increase monotonically with an increase in the surfactant concentration (Task 4). A numerical model has been developed that fits the rate of imbibition. (Task 5) The anionic surfactants look promising but core-scale and field-scale experiments need to be conducted to better evaluate the surfactant methods for fractured media.

## **Plans for Next Reporting Period**

- Imbibition experiments (Task 4)
- Simulation (Task 5)

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