

## **WETTABILITY ALTERATION OF CARBONATE ROCK MEDIATED BY BIOSURFACTANT PRODUCED FROM HIGH-STARCH AGRICULTURAL EFFLUENTS**

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### **ABSTRACT**

Surfactants can be used to alter wettability of reservoir rock, increasing spontaneous imbibition and thus improving oil yields. Commercial synthetic surfactants are often prohibitively expensive and so a crude preparation of the anionic biosurfactant, surfactin, from *Bacillus subtilis*, able to be grown on high-starch industrial and agricultural effluents, has been proposed as an economical alternative. To assess the effectiveness of the surfactin, it is compared to a commercially available surfactant. The wettability change mediated by dilute solutions of commercial anionic surfactant (STEOL CS-330) and surfactin was assessed using two-phase separation, and water flotation techniques; and surfactant loss due to retention and adsorption the rock was determined. Qualitative tests indicate that on a molar basis, surfactin is more effective than STEOL CS-330 in altering wettability of crushed Lansing-Kansas City carbonates from oil-wet to water-wet state. Adsorption isotherms of STEOL CS-330 and surfactin on crushed Lansing-Kansas City outcrop and reservoir material showed that surfactin has higher specific adsorption on these oomoldic carbonates.

### **INTRODUCTION**

Enhanced oil recovery methods are used throughout the world as a means of increasing energy supply. The injection of surfactants into oil reservoirs can improve oil recovery by mobilizing the oil stranded by capillary forces (Gogarty 1977). The most commonly used method is to inject a high-concentration surfactant solution into the formation to create an ultra-low interfacial tension between the surfactant bank and the residual oil, hence mobilizing trapped oil. Another method uses a low-concentration surfactant solution to change the wettability of the reservoir rock to a more water-wet state, promoting the spontaneous imbibition during waterflooding. This method can be very useful in fractured carbonate reservoirs where the wettability change can improve oil recovery by accelerating the spontaneous imbibition process (Chillenger & Yen 1983; Roehl & Choquette 1985).

The economic feasibility of this process, like many other EOR applications, is determined by the improved oil recovery and the degree of retention of injected chemicals in the reservoir. In this work, dilute solutions of surfactin produced by bacteria grown on high-starch liquid media were assessed for their effectiveness in mediating the wettability

change of carbonate rocks, and compared to similar molar concentrations of a benchmark chemical surfactant. Adsorption of surfactants considered for EOR applications has been studied extensively (Celik 1979; Glover 1979; Trogus *et al.* 1979; Krumrine *et al.* 1980; Meyers & Salter 1981; Novosad 1981). Surfactant retention was evaluated by comparing the adsorption isotherm of surfactin with that of the benchmark chemical surfactant.

## EXPERIMENTAL DETAILS

### Materials

Benchmark surfactant: Sodium laureth sulfate, an anionic ethoxylated surfactant (STEOL CS-330) was obtained from Stepan Chemical Company, Northfield, IL and diluted as required using reverse-osmosis (RO) water (18 M $\Omega$ ).

Biosurfactant: *Bacillus subtilis* strain 21332 was obtained from the American Type Culture Collection and maintained and stored as recommended by Gherna & Pienta (1989). Cells were grown in maintenance broth and harvested in early stationary phase, and -80 °C freezer stocks were prepared. Seed inocula were prepared from the freezer stocks by adding one thawed tube of cells (1 mL) to 50 mL of Difco nutrient broth and incubating for 18-24 h at 30 °C with agitation at 150 min<sup>-1</sup>. The pH 6.0 nutrient broth contained (per liter) 5.0 g pancreatic digest of peptone and 3.0 g beef extract. Typical seed cultures contained  $4.0 \pm 0.6 \times 10^8$  cells/ml at the end of the incubation period. Production of surfactin was accomplished in 500 ml Erlenmeyer flasks containing 250 mL of nutrient media. Media contained 0.5% (w/v) purified potato starch, 0.396 g/l (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 0.015 g/l FeSO<sub>4</sub>·7H<sub>2</sub>O, 0.00196 g/l MnSO<sub>4</sub>·H<sub>2</sub>O, 0.197 g/l MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.0010 g/l CaCl<sub>2</sub>·2H<sub>2</sub>O, 5.678 g/l Na<sub>2</sub>HPO<sub>4</sub>, 4.08 g/l KH<sub>2</sub>PO<sub>4</sub>. The culture was incubated at 30 °C for 72 h, at which time cells were removed by centrifugation. Surfactin was isolated from the resulting supernatant by precipitation as described by Cooper *et al.* (1981) except that the crude powder was not washed with methylene chloride or filtered. Briefly, the pH of the cell-free supernatant was adjusted to 2.0 by addition of concentrated HCl, precipitating the surfactin. The precipitate was collected by centrifugation, resuspended in nanopure water, and its pH adjusted to 7.0. The suspension was then frozen at -80 °C and quantitatively lyophilized to dryness. This crude surfactin preparation was diluted in RO water as required for subsequent testing.

Adsorbents: Miami oolitic outcrop (MI), Bethany Falls oomoldic outcrop (BF), and oomoldic Lansing-Kansas City reservoir material (L7) from the Hall-Gurney Field in Russell County, KS (Gore Oil Company, Leurman #7 lease, T15S R12W Sec 28) were obtained from Alan Byrnes at Kansas Geological Survey (KGS). Samples were crushed using a ball mill, sieved to remove particles <53 and >300  $\mu$ m and then cleaned by immersion in a series of solvents (tetrahydrofuran, chloroform, methanol, water). Solvents were replaced periodically until no coloration was seen. Specific surface area was obtained using a Gemini II 2370 surface area analyzer. Specific surface area of crushed Miami was of 2.7 m<sup>2</sup>/g and that of BF was 0.76 m<sup>2</sup>/g. All the rocks originally were oil- or mixed-wet. After cleaning they all became water-wet.

A surfactant-selective combination electrode (Model SUR1502 from pPhoenix Electrode Company, Houston, TX,) was used to determine concentration of anionic surfactants in aqueous solution by titration with Hyamine 1622. Soltrol 130 (Chevron Phillips Chemical Company, Borger, TX) was used for wettability tests.

### Experimental Procedure

Static adsorption isotherms were obtained by measuring surfactant concentration before and after equilibrating with crushed rock. Thirty ml of the each surfactant solution was added to a 50 ml centrifuge tube containing a known mass of crushed rock. The tubes were capped and shaken horizontally at 50 min<sup>-1</sup> for 24 or 48 h to establish adsorption equilibrium. The samples were then centrifuged for 30 min at 3000 min<sup>-1</sup>. Supernatants were separated and analyzed for residual surfactant concentrations. The difference in concentration between the stock solutions and the samples was used to evaluate the adsorption. All adsorption experiments were carried out at room temperature.

To evaluate the effectiveness of surfactants in mediating wettability, samples of crushed BF rock were aged in crude oil (from the Lansing - Kansas City Field C Zone at ~880 m (~2900 ft)) at 90 °C for 7 d, rinsed with Soltrol 130 and immersed in 420 ppm surfactant solutions for 24 h as described for the adsorption tests above. The samples were centrifuged and the rocks were separated and dried. Following drying, two qualitative tests were performed: a two-phase separation (adapted from Somasundaran & Zhang 1997) and a flotation test (Wu *et al.* 2006). In the two-phase separation test 0.2 g of dried rock following treatment with surfactant was mixed with 20 ml of RO-water in a 40 ml glass scintillation vial and 20 ml Soltrol 130 was added. The samples were shaken gently and allowed to settle for 1 h. A visual inspection of the distribution of rock between the aqueous and oil phases gives a qualitative indication of wettability. Similarly, in the flotation test, 0.2 g rock was added to a test tube containing 10 ml of RO water and the mass of rock sinking to the bottom of the water column indicated the wettability change mediated by the surfactant.

## **RESULTS AND DISCUSSIONS**

Static adsorption experiments were performed with different surfactant solution mass/rock mass ratios to identify whether this affected the degree of adsorption observed. Different masses of cleaned crushed rock were placed in 30 ml of surfactant solutions of known concentration. Figure 1 shows that for a 1.44 mmol/l solution of STEOL CS-330 adsorption on both Miami and BF rocks, specific adsorption declines with increasing rock mass. More work will have to be done to investigate this phenomenon. The same trend was observed for a 0.37 mmol/l solution of surfactin on BF rock (Figure 2), but adsorption of surfactin was higher than that of STEOL CS-330. The greater adsorption on Miami compared to BF is consistent with Miami's higher specific surface area.

Figure 3 shows STEOL CS-330 adsorption isotherms obtained using different masses of rock. The results are consistent with the earlier observations that higher masses of

adsorbent exhibit lower specific adsorption. Good linear correlations were obtained between residual concentrations and rock masses for the selected initial concentrations (Figure 4). Multiple tests confirmed that this effect was repeatable, and that for a given mass of rock, consistent results were obtained.

Since specific adsorption was seen to decline with increasing rock mass, all subsequent experiments were done using a fixed mass of rock (2.0 g) and surfactant solution (30 ml) to ensure that results were comparable. To compare the adsorption levels of surfactin with STEOL CS-330, adsorption isotherms for both were obtained using crushed BF and L7 rocks (Figure 5). In both cases, surfactin had a higher specific adsorption, and the maximum adsorption density was reached at a lower concentration. This reflects the lower critical micelle concentration (CMC) of surfactin at 25°C, variously reported as 7.5 µmol/l (Heerklotz & Seelig 2001), 9.4 µmol/l (Ishigami *et al.* 1995) and 24.1 µmol/l (Cooper *et al.* 1981), compared to 100 µmol/l for sodium laureth sulfate (Mukerjee & Mysels 1971).

The isotherms for surfactin and STEOL CS-330 on both L7 and BF rocks exhibit the four regions seen in a typical adsorption isotherm (Tabatabai *et al.* 1993; Figure 6). Region I, which is also known as the Henry's law region, corresponds to adsorption of surfactant monomers and there is a linear relationship between the concentration and adsorption density. The main mechanism of adsorption is electrostatic attraction between the charged head group of the surfactant molecule and surface of the rock. Region II is characterized by a sharp increase in the adsorption, corresponding to the formation of bilayers and aggregates on the solid surface. Surfactant tail groups can form aggregates by hydrophobic bonding in this region. In Region III the same forces are responsible for adsorption. However, there is a decrease in the slope of the adsorption isotherm. In this region aggregate-aggregate interactions and formation of hemimicelles (monolayer aggregates) and admicelles (bilayer aggregates) become more important. Region IV shows the attainment of the critical micelle concentration (CMC) and adsorption density reaches a plateau as micelle formation competes with surfactant adsorption. Physical bases for these adsorption regimes were proposed by Sharma (1995) and are shown schematically in Figure 7.

The effectiveness of surfactants in mediating wettability changes was observed through two qualitative tests: a two-phase separation test and a flotation test. It was concluded from both tests that surfactin is more effective on a molar basis in reversing the wettability of oil-wet crushed carbonate rocks. Figure 8 shows the results of a two-phase separation test and demonstrates the effectiveness of surfactin in changing the wettability. These results were confirmed by performing a flotation test on the oil-wet rock samples in contact with both surfactants (Figure 9).

## CONCLUSIONS

1. Qualitative tests indicate that on a molar basis, surfactin is more effective than STEOL CS-330 in altering wettability of crushed Lansing-Kansas City carbonates from oil-wet to water-wet state.
2. Both STEOL CS-330 and surfactin exhibit typical adsorption isotherms with four distinct regions.
3. Adsorption isotherms of STEOL CS-330 and surfactin on crushed Lansing-Kansas City outcrop and reservoir material showed that surfactin has higher specific adsorption on these oomoldic carbonates.
4. It is important to standardize and report the mass of rock, and concentration and volume of surfactant solution used to develop adsorption isotherms.

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## FIGURES

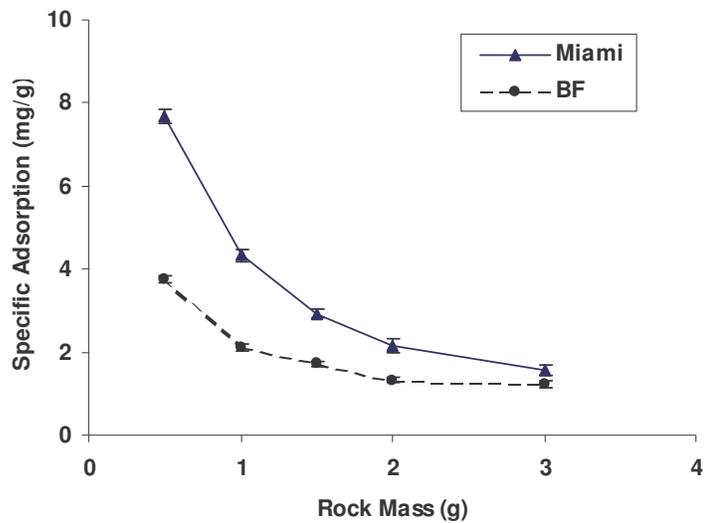


Figure 1 Adsorption of 1.44 mmol/l STEOL CS-330 vs. mass of crushed BF and Miami rocks.  
Error bars = 1 Std. Dev., n = 3

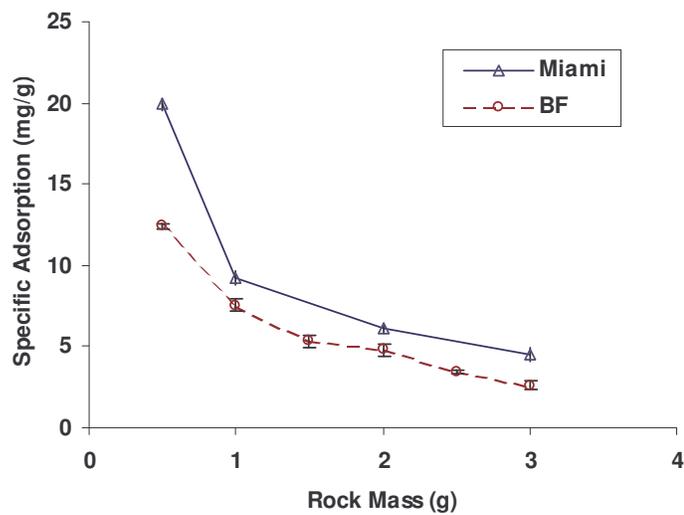


Figure 2 Adsorption of 0.37 mmol/l surfactin vs. mass of crushed BF and Miami rocks.  
Error bars = 1 Std. Dev., n = 3

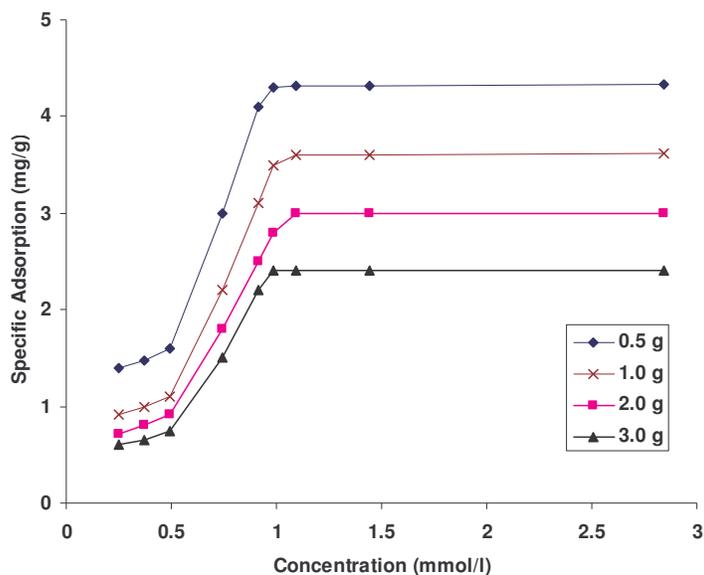


Figure 3 STEOL adsorption isotherms on different masses of crushed BF rock to show decline in adsorption with increasing rock mass

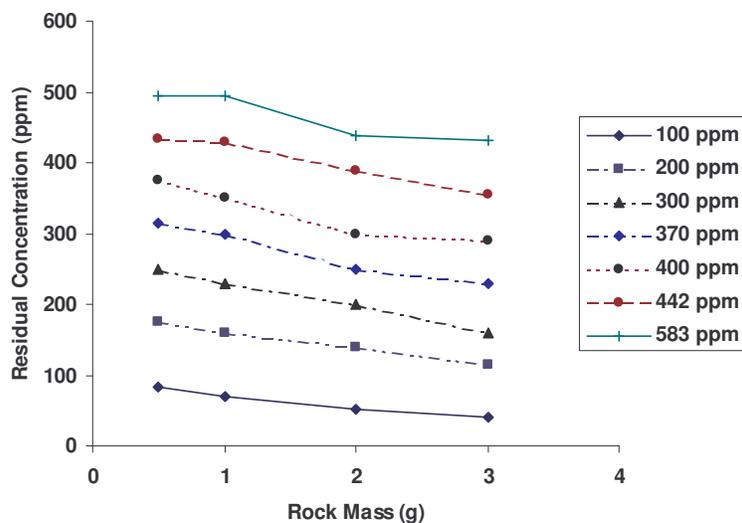


Figure 4 Residual concentrations versus rock mass for various initial concentrations of STEOL CS-330 on crushed BF rock

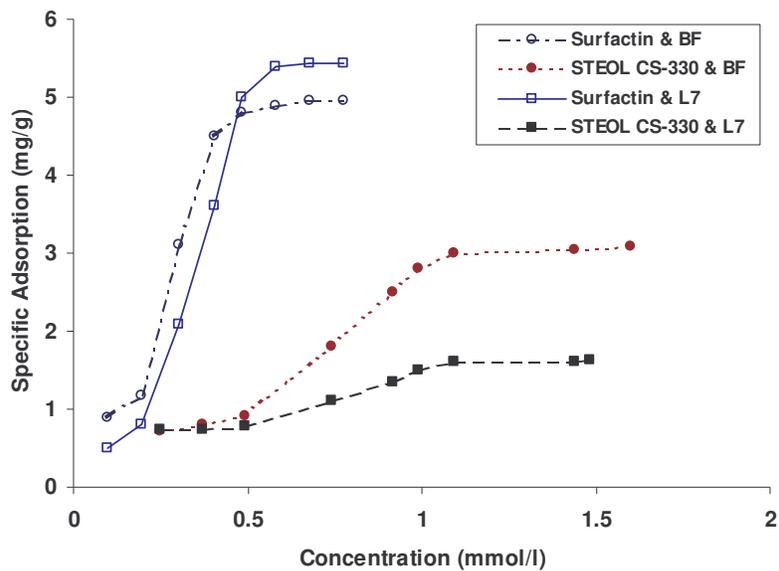


Figure 5 Adsorption isotherms of 30 ml of 420 ppm STEOL CS-330 and surfactin on 2.0 g of crushed BF and L7 rocks

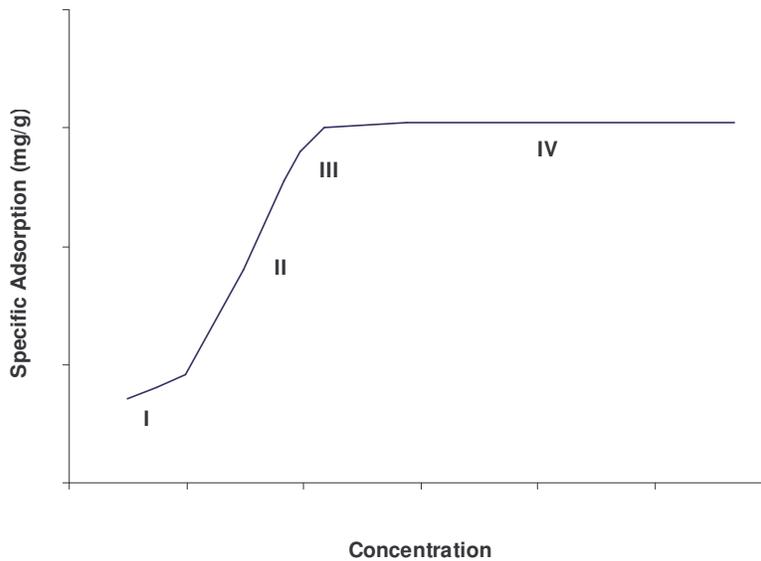


Figure 6 Typical adsorption isotherm of surfactant on rock indicating four regions (after Tabatabai *et al.* 1993)

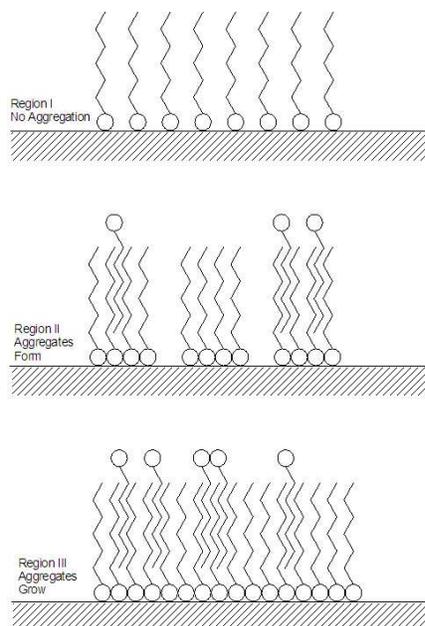


Figure 7 Suggested physical bases for the first three regions seen in a typical adsorption isotherm (after Sharma 1995)



Figure 8 Two-phase (Soltrol 130/water) separation tests showing the effectiveness of surfactants in altering the wettability of crude oil-aged BF rock exposed to surfactant solutions for 24 h (left: No surfactant; center: STEOL CS-330; right: surfactin).



Figure 9 Water flotation tests showing the effectiveness of surfactants in altering the wettability of crude oil-aged BF rock exposed to surfactant solutions for 24 h (left: No surfactant; center: STEOL CS-330; right: surfactin).