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Biosurfactants Produced From Agriculture Process Waste Streams To Improve Oil Recovery in Fractured Carbonate Reservoirs

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Abstract

We examined the ability of surfactin, an anionic lipopeptide surfactant produced by *Bacillus subtilis*, to mediate wettability changes that positively affect oil recovery in fractured carbonate rock. On both a weight for weight and a molar basis, surfactin has a greater ability to alter a carbonate rock to a more water-wet state than does sodium laureth sulfate (SLS). Surfactin, was produced by growing *Bacillus subtilis* on high-starch medium to represent agricultural effluent, and a suitable benchmark chemical surfactant was selected for comparative study. Cores and crushed samples of Lansing-Kansas City (LKC) carbonate reservoir material were cleaned and characterized. Crushed rock was aged in crude oil to ensure that it was strongly oil-wet and rapid wettability tests were performed to assess the wettability change mediated by low concentrations of surfactin and SLS. Static adsorption of surfactants on LKC rock was assessed and dynamic adsorption in intact cores was measured. Surfactin exhibits higher specific adsorption onto crushed LKC.

Introduction

Conventional surfactant flooding relies on the ability of the injected high-concentration surfactants to create ultra-low interfacial tension (IFT) between oil and water, thereby mobilizing the stranded oil.^{1,2} Due to the cost of injecting high-concentration chemical surfactants, the economics of surfactant injection have rarely been favorable in actual field applications. To improve process economics, injection of dilute surfactant solutions has been considered.³⁻⁵ The intent in this case is to not achieve ultra-low IFT and thus to recover only part of the stranded oil. Several studies have revealed that the injection of dilute surfactants into oil reservoirs can modify the wettability of the reservoir rock.⁶⁻¹³ This phenomenon may be useful in fractured carbonate reservoirs

where the wettability change can improve oil recovery by accelerating the spontaneous imbibition process.^{14,15}

The overall objective of this project is to evaluate the use of low-cost biosurfactants produced from agriculture process waste streams to improve oil recovery in fractured carbonate reservoirs. Specifically, we examine the ability of surfactin, an anionic lipopeptide surfactant (Figure 1) produced by *Bacillus subtilis*, to mediate wettability changes that positively affect oil recovery in fractured carbonate rock by accelerating the spontaneous imbibition process during water flooding. Experimental materials are representative of the Lansing-Kansas City (LKC) formation in central Kansas, a fractured carbonate reservoir exhibiting intermediate wettability.

The economic feasibility of this process, like many other enhanced oil recovery (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 are assessed for their effectiveness in mediating the wettability change of LKC carbonate rocks, and compared to similar concentrations of a benchmark chemical surfactant.

Adsorption of surfactants considered for EOR applications has been studied extensively.¹⁶⁻²¹ Surfactant retention is evaluated by comparing the adsorption isotherm of surfactin with that of the benchmark chemical surfactant.

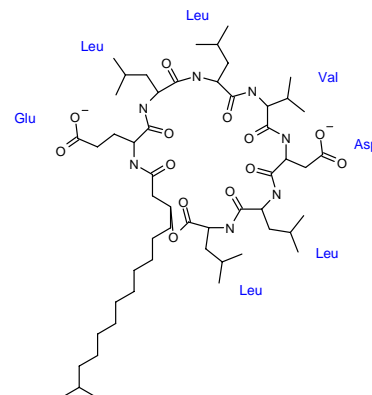


Figure 1 Structure of surfactin molecule

The use of surfactants in enhanced oil recovery has generally relied on the reduction in interfacial-tension between the oil and the flooding phase to improve microscopic sweep efficiency. This work investigates the ability of surfactants to alter wettability of carbonate reservoir rock to increase the rate and extent of spontaneous imbibition at low concentrations.

Wettability of core samples is expressed as Amott Wettability Index:²²

$$I_w = \frac{\Delta S_{ws}}{(\Delta S_{ws} + \Delta S_{wf})}, \quad (1)$$

where ΔS_{ws} = change in water saturation due to spontaneous imbibition, and ΔS_{wf} = change in water saturation due to forced imbibition. Amott wettability tests are in progress but results are not yet available and so in this paper we present data from rapid wettability tests performed on crushed LKC material.^{23;24}

Adsorption is often described in terms of models.^{25;26} Two common models are the Langmuir model:

$$n^* = \frac{k_H n_m C_{eq}}{1 + k_H C_{eq}}, \quad (2)$$

where

n^* = adsorption

k_H = Henry's law coefficient

n_m = monolayer loading

C_{eq} = equilibrium solution concentration,

and the Freundlich model:

$$n^* = A \times C_{eq}^B, \quad (3)$$

where A and B are constants. Both the Langmuir and Freundlich models are descriptive of the formation of a monolayer as seen in a Type I adsorption isotherm.²⁵

Materials and methods

Biosurfactant

Surfactin was produced as previously described.^{27;28} *Bacillus subtilis* strain 21332 from the American Type Culture Collection was maintained and stored as recommended by Gherna & Pienta²⁹. 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 (5.0 g pancreatic digest of

peptone and 3.0 g beef extract per liter, pH 6.0) and incubating for 18-24 h at 30 °C with agitation at 150 min⁻¹. Typical seed cultures contained $4.0 \pm 0.6 \times 10^8$ cells/ml at the end of the incubation period. *Bacillus subtilis* strain 21332 has been shown to grow on high-starch agricultural waste streams, with no difference in the production of surfactin, but to minimize variability a defined medium is used in this work. Surfactin was produced in 2 liter Erlenmeyer flasks containing 1 liter of nutrient medium (0.5 % (w/v) purified potato starch, 0.396 g/l (NH₄)₂HPO₄, 0.015 g/l FeSO₄·7H₂O, 0.00196 g/l MnSO₄·H₂O, 0.197 g/l MgSO₄·7H₂O, 0.0010 g/l CaCl₂·2H₂O, 5.678 g/l Na₂HPO₄, 4.08 g/l KH₂PO₄.) The culture was incubated at 30 °C for 72-96 h. Cells were removed by centrifugation and surfactin was isolated from the supernatant by precipitation as described by Cooper *et al.*³⁰ 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. Surfactin was checked for stability in brine and found to be sensitive to salt concentration, especially that of divalent cations. In order to avoid precipitation of surfactants, all aqueous tests were performed using reverse-osmosis (RO) water (18 MΩ).

Benchmark surfactant

Candidate benchmark surfactants: Sodium laureth sulfate (SLS, STEOL CS-330), sodium dodecyl sulfate, (SDS, STEPANOL WA-EXTRA) and sodium dodecylbenzene sulfonate (BIO-SOFT D-40) were obtained from Stepan Chemical Company, Northfield, IL and diluted as required using RO water. A ring tensiometer (Fisher Model 20, Fisher Scientific) was used to measure interfacial tension between various concentrations of surfactants and Soltrol 130 (ChevronPhillips Chemical Company, Borger, TX).

Surfactant concentration determination

Surfactant concentration was determined by potentiometric titration with a cationic surfactant, Hyamine 1622, using a surfactant-ion specific electrode (Model SUR1502, pHoenix Electrode Company, Houston, TX).

Rock cores

Lansing-Kansas City core material from T15S R12W Sec 28, Hall-Gurney Field, Gore Oil Company Luerman #7 was obtained from the Kansas Geological Survey where it was cleaned by Soxhlet extraction using a toluene/methanol azeotrope and dried to constant weight. However, on flooding with oil, all cores produced effluent that was yellowish in color and supported somewhat stable foam on shaking. The effluent oil also absorbed strongly in the ultraviolet. The colored material was filtered through an Al₂O₃ column but the UV-absorbing component was only retained very weakly, suggesting that it represents non-polar organic compounds that had been trapped in the core. The presence of UV-absorbing, oil-soluble material is problematic because it (a) is likely to be

active in determining the wettability of the carbonate surface, (b) leads to inaccuracies in porosity measurements, and (c) interferes with the detection of *n*-stilbene tracer. To ameliorate these problems, an additional, more aggressive cleaning regime was adopted.³¹ Cleaning was carried out in a Hassler-Type coreholder by flooding the core with tetrahydrofuran (THF, T425-4, Fisher Scientific) and allowing to soak for up to three days at 45 °C. This was repeated until the effluent was colorless. The THF was displaced with chloroform (C298-1, Fisher Scientific), followed by methanol (A433-F, Fisher Scientific) and finally RO water. To protect the core sleeve from the THF, the cores and distribution plugs were shrink-wrapped at 190 °C using 1.6:1 FEP Teflon® heat-shrinkable tubing (Zeus Industrial Products Inc, Orangeburg, SC) before placing them in the core holder. The shrink wrap was removed after cleaning. LKC rock was also crushed for use in rapid wettability and static adsorption studied. The crushed rock was cleaned in the same sequence of solvents as the cores.

Adsorption

Adsorption of surfactants onto rock material was measured in static and dynamic systems. To measure static adsorption, 2.0 g of crushed rock (53-300 μm) was added to 30 ml of surfactant solution and shaken for 24 h. The mixture was centrifuged and the difference in concentration between the starting solution and the supernatant was used to calculate a specific adsorption in mg surfactant/g rock.

Dynamic adsorption was measured in a one-inch diameter L7 core plug saturated with RO-water in a Hassler type core holder. A known mass and concentration of surfactant solution was circulated through the core for 24 h at 2 ml/min. Equilibrium concentration of the solution was determined by potentiometric titration for replicate samples. This was repeated for several concentrations and the relation between adsorption and equilibrium concentration was plotted. The pump and tubing were drained between concentration and the coreholder and pore volume were considered in calculating the dilution factor of the next solution.

Wettability

Tests of wettability using two-phase separation and flotation methods were done at room temperature on crushed rock samples.³² Samples of crushed LKC 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 (w/v) surfactant solutions for 24 h. 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)²³ and a flotation test²⁴. 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 Discussion

Commercial preparations of several synthetic anionic surfactants were investigated for use as a benchmark. The candidates were selected on the basis of physical similarity to surfactin. All are anionic surfactants with a hydrophobic tail of carbon number ~12, though they have only a single charge and a much smaller hydrophilic head than surfactin. They are readily available, and are well studied. Interfacial tensions between Soltrol 130 oil and surfactants at varying concentrations are shown in Figure 2. The IFT between RO water and Soltrol 130 is 35.8 mN/m.

At low concentrations, the IFT of sodium laureth sulfate (SLS) was closest to that of surfactin and SLS was chosen for comparison in this work. The difference in IFT between the benchmark surfactants and surfactin in terms of molarity is greater than is apparent in Figure 2 since there is a marked difference in molecular weight (SDS, 265 g/mol; SLS, 397 g/mol; sodium dodecylbenzene sulfonate, 325 g/mol; surfactin 1047 g/mol).

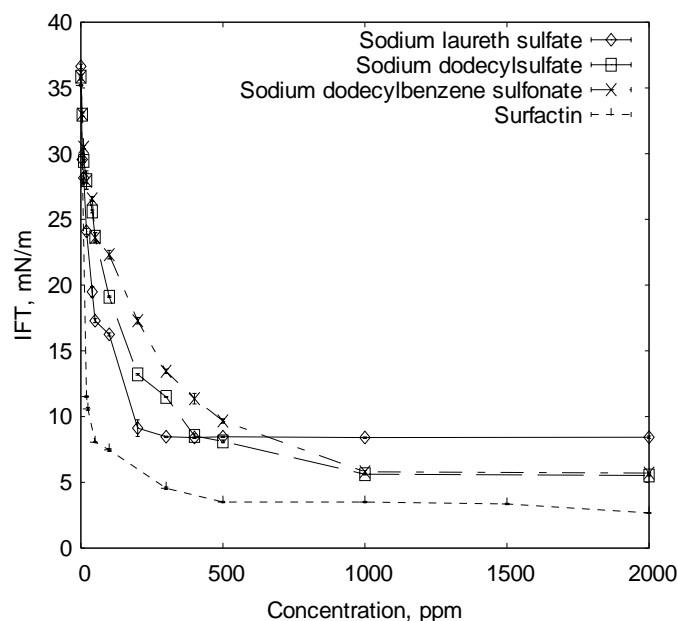


Figure 2 Interfacial tension between surfactants and Soltrol 130 at room temperature. Error bars = 1 standard deviation, n = 3

Static adsorption of SLS and surfactin onto cleaned, crushed LKC reservoir material is shown in Figure 3. The magnitude of the adsorption is different for the two surfactants, but both show a typical Type I adsorption isotherm with four distinct regions.³³

Data reported elsewhere³² indicate that the specific adsorption declines with mass of rock and this was explained by sedimentation of the crushed rock even under moderate shaking with a concomitant reduction in free surface area.

This underlines the importance of reporting quantities to allow comparison of data between workers.

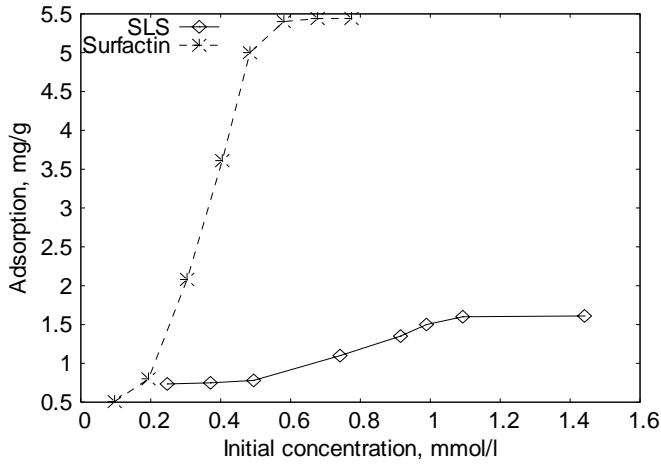


Figure 3 Adsorption of SLS and surfactin onto clean crushed LKC reservoir material

Dynamic adsorption of SLS onto LKC core material demonstrates a Type I isotherm, (Figure 4). Data for surfactin are not yet available. Fitting the SLS data to the Langmuir model (Equation 2), yielded $n_m = 1.676 \text{ mg/cm}^3$ and $k_H = 3.383$ ($R^2 = 0.934$). Using the Freundlich model (Equation 3), excluding point (0,0), the fit was $A = 1.270$, $B = 0.327$ ($R^2 = 0.833$). Neither model fits the data well but the Langmuir model is a slightly better fit and is probably more descriptive of the process, though it might be more appropriate to model each region separately.

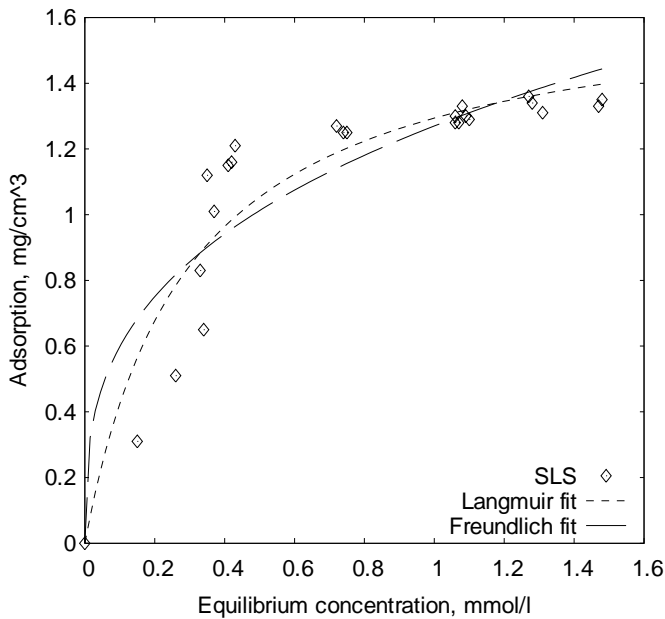


Figure 4 Dynamic adsorption of SLS on LKC reservoir core showing fits to Langmuir and Freundlich models

Rapid wettability tests of crushed, crude oil-aged LKC material indicate that surfactin had a greater effect on wettability than did SLS. Surfactin was effective in

transferring the rock into the aqueous phase in both two-phase (Plate 1) and flotation tests (Plate 2). Amott wettability tests on intact cores are under way and will be reported in a later paper.



Plate 1 Two-phase separation tests of crude oil-aged carbonate rocks in water and surfactant solution (l-r: water, SLS, surfactin)

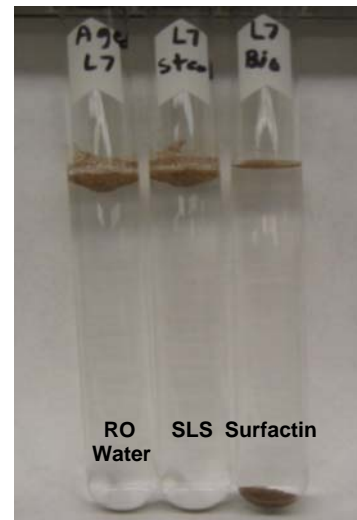


Plate 2 Water flotation tests of crude oil-aged carbonate rocks in water and surfactant solution (l-r: water, SLS, surfactin)

Conclusions

- Surfactin is more effective than sodium laureth sulfate at changing wettability of crushed LKC material to a more water-wet state on both molar and weight bases.
- Sodium laureth sulfate and surfactin exhibit typical adsorption isotherms with four distinct regions.
- Surfactin exhibits higher specific adsorption onto crushed LKC than does SLS.

Acknowledgements

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Nomenclature

ΔS_{ws}	Change in water saturation due to spontaneous imbibition
ΔS_{wf}	Change in water saturation due to forced imbibition
Ad	Adsorption, mg/cm ³ or mg/g
C_{eq}	Equilibrium concentration, mmol/l
EOR	Enhanced oil recovery
IFT	Interfacial tension
k_H	Henry's law coefficient
I_w	Amott wettability to water
$L7$	Luermann #7 LKC reservoir rock
LKC	Lansing-Kansas City
n^*	Adsorption, mg/cm ³
n_m	Monolayer loading, mg/cm ³
RO	Reverse osmosis
SDS	Sodium dodecyl sulfate
SLS	Sodium laureth sulfate

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