Development of Biosurfactant-mediated oil recovery in Model Porous Systems and Computer Simulations of Biosurfactant-Mediated Oil Recovery

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Disclaimer

Executive summary

Current technology recovers only one-third to one-half of the oil that is originally present in an oil reservoir. Entrapment of petroleum hydrocarbons by capillary forces is a major factor that limits oil recovery (1, 3, 4). Hydrocarbon displacement can occur if interfacial tension (IFT) between the hydrocarbon and aqueous phases is reduced by several orders of magnitude. Microbially-produced biosurfactants may be an economical method to recover residual hydrocarbons since they are effective at low concentrations.

Previously, we showed that substantial mobilization of residual hydrocarbon from a model porous system occurs at biosurfactant concentrations made naturally by *B. mojavensis* strain JF-1 if a polymer and 2,3-butanediol were present (2). In this report, we include data on oil recovery from Berea sandstone experiments along with our previous data from sand pack columns in order to relate biosurfactant concentration to the fraction of oil recovered. We also investigate the effect that the JF-2 biosurfactant has on interfacial tension (IFT). The presence of a co-surfactant, 2,3-butanediol, was shown to improve oil recoveries possibly by changing the optimal salinity concentration of the formulation.

The JF-2 biosurfactant lowered IFT by nearly 2 orders of magnitude compared to typical values of 28-29 mN/m. Increasing the salinity increased the IFT with or without 2,3-butanediol present. The lowest interfacial tension observed was 0.1 mN/m. Tertiary oil recovery experiments showed that biosurfactant solutions with concentrations ranging from 10 to 60 mg/l in the presence of 0.1 mM 2,3-butanediol and 1 g/l of partially hydrolyzed polyacrylamide (PHPA) recovered 10-40% of the residual oil present in Berea sandstone cores. When PHPA was used alone, about 10% of the residual oil was recovered. Thus, about 10% of the residual oil recovered in these experiments was due to the increase in viscosity of the displacing fluid. Little or no oil was recovered at biosurfactant concentrations below the critical micelle concentration (about 10 mg/l). Below this concentration, the IFT values were high. At biosurfactant concentrations from 10 to 40 mg/l, the IFT was 1 mN/m. As the biosurfactant concentration increased beyond 40 mg/l, IFT decreased to about 0.1 mN/m. At biosurfactant concentrations in excess of 10 mg/l, residual oil recovery was linearly related to biosurfactant concentration. A modified mathematical model that relates oil recovery to biosurfactant concentration

adequately predicted the experimentally observed changes in IFT as a function of biosurfactant concentration.

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Table of Contents

List of Figures

List of Tables

Relationship between biosurfactant concentration, interfacial tension, and oil recovery

ABSTRACT

Interfacial tension (IFT) between crude oil and water in the presence of varying concentrations of the biosurfactant produced by *Bacillus mojavensis* JF-2 bio-surfactant was determined. The effects of salinity and co-surfactant 2,3-butanediol were also studied. The biosurfactant lowered IFT by nearly 2 orders of magnitude compared to typical values of 28-29 mN/m. Increasing the salinity increased the IFT with or without 2,3-butanediol present. The lowest interfacial tension observed was 0.1 mN/m. Efficacy of the JF-2 biosurfactant was tested by using Berea sandstone cores and sand-packed columns flooded to residual oil saturation. Tertiary oil recovery experiments showed that biosurfactant solutions with concentrations ranging from 10 to 60 mg/l in the presence of 0.1 mM 2,3-butanediol and 1 g/l of partially hydrolyzed polyacrylamide (PHPA) recovered 10-40% of the residual oil present in Berea sandstone cores. When PHPA was used alone, about 10% of the residual oil was recovered. Thus, about 10% of the residual oil recovered in these experiments was due to the increase in viscosity of the displacing fluid. The remainder of the recovered oil was due to the effect of the JF-2 biosurfactant on interfacial tension between oil and the displacing aqueous phase. The relationship between interfacial tension (IFT) reduction and biosurfactant concentration was defined. Little or no oil was recovered at biosurfactant concentrations below the critical micelle concentration (about 10 mg/l). Below this concentration, the IFT values were high. At biosurfactant concentrations from 10 to 40 mg/l, the IFT was 1 mN/m. As the biosurfactant concentration increased beyond 40 mg/l, IFT decreased to around 0.1 mN/m. At biosurfactant concentrations in excess of 10 mg/l, residual oil recovery was linearly related to biosurfactant concentration. A mathematical model that relates oil recovery to biosurfactant concentration was modified to include the stepwise changes in IFT as biosurfactant concentrations changes. This model adequately predicted the experimentally observed changes in IFT as a function of biosurfactant concentration.

INTRODUCTION

The widespread use of petroleum hydrocarbons has resulted in the contamination of valuable groundwater resources. Petroleum hydrocarbons may exist in the vadose and saturated zones as a free liquid or ganglia of residual hydrocarbon (3, 7). Even if the free liquid hydrocarbon can be removed, substantial amounts of residual hydrocarbon remain entrapped by capillary forces and represent a long-term source of contamination (7). Entrapment of petroleum hydrocarbons by capillary forces is also a major factor that limits oil recovery (1, 19, 21). Current technology recovers only one-third to one-half of the oil that is originally present in an oil reservoir. Since almost all regions of the world have been intensively explored for oil, the discovery of large new oil resources is unlikely and the exploitation of oil resources in existing reservoirs will be essential in the future.

Surfactants of synthetic or biological origin enhance hydrocarbon biodegradation by increasing the apparent aqueous solubility of the hydrocarbon or by enhancing the interaction of the microbial cell with the hydrocarbon. Alternately, bulk hydrocarbon displacement can occur if the capillary forces that entrap the hydrocarbon are reduced. Interfacial tension (IFT) between the hydrocarbon and aqueous phases is largely responsible for trapping the hydrocarbon in the porous matrix. Ultra-low values (several orders of magnitude reduction) of IFT are needed for hydrocarbon mobilization. To achieve these ultra-low IFT values, very high concentrations ($> g\ l^{-1}$) of synthetic surfactants must be used, which makes chemical surfactant flooding expensive. Microbially-produced biosurfactants may be an economical method to recover residual hydrocarbons since they are effective at low concentrations (as indicated by their low critical micelle concentrations). However, the recovery of residual hydrocarbon by biosurfactants from model porous systems is inconsistent and often low.

Microorganisms produce a variety of biosurfactants (4), several of which generate the low interfacial tensions between the hydrocarbon and the aqueous phases required to mobilize residual hydrocarbon (4, 5, 12). In particular, the lipopeptide biosurfactant produced by *Bacillus mojavensis* strain JF-2 reduces the interfacial tension between oleic and aqueous phases to very low levels (<0.016 mN/m) (12, 17). The critical micelle concentration is 20 mg/l, indicating that the biosurfactant is effective even at very low concentrations (12). Residual oil is recovered when a biosurfactant-producing bacterium

and the nutrients needed to support growth are introduced into sandstone cores (14, 24, 27), but residual hydrocarbon recoveries were often low (5 to 20%) and required multiple pore volumes of recovery fluid (14, 24).

Previously, we showed that substantial mobilization of residual hydrocarbon from a model porous system occurs at biosurfactant concentrations made naturally by *B. mojavensis* strain JF-1 if a polymer and 2,3-butanediol were present (15, 18). The recovery of residual oil depends on the generation of low interfacial tensions in other to release oil that is entrapped in small pores. In this report, we include data on oil recovery from Berea sandstone experiments along with our previous data from sand pack columns (15, 18) in order to relate biosurfactant concentration to the fraction of oil recovered. A capillary desaturation curve was obtained between waterflood phase capillary numbers and residual oil saturation in Berea sandstone cores. This curve indicates the change in the magnitude of the capillary number required to lower residual oil saturation in a core. We also investigate the effect that the JF-2 biosurfactant has on interfacial tension (IFT). The presence of a cosurfactant, 2,3-butanediol was shown to improve oil recoveries (15, 18) possibly by changing the optimal salinity concentration of the formulation. For this reason, we also tested the effect of 2,3-butanediol on interfacial tension.

METHODS

Cultivation

Procedures for the growth of *Bacillus mojavensis* strain JF-2, preparation of cell-free culture fluids, and quantification of the JF-2 biosurfactant have been previously described (18). *Bacillus mojavensis* strain JF-2 was grown aerobically in medium E in 300-ml cultures. The medium were inoculated with *B. mojavensis* strain JF-2 (1% by volume) and incubated at 37°C without shaking for 24 hours. The culture was centrifuged to remove cells (10,000 x *g*; 10 min; 4 °C) and the concentration of the JF-2 biosurfactant in the cell-free culture fluid was determined by high-pressure liquid chromatography (10). The cell-free culture fluid was used immediately for analysis. When more dilute biosurfactant concentrations were required, the cell-free culture fluid was diluted with sterile medium E. The sufficient partially hydrolyzed polyacrylamide (PHPA) and 2,3-butanediol were added to give final concentrations of 1 g/l and 10 mM, respectively, prior to injection in the cores.

The Effect of Interfacial Tension

The effect of the biosurfactant concentration, salinity and the presence of 2,3-butanediol, a co-surfactant, on interfacial tension was determined. Cell-free culture fluid containing of the JF-2 biosurfactant was diluted two-fold and five-fold to give three aliquots of the original culture that contained 11, 28 or 57 mg/l of the JF-2 biosurfactant. The dilutions were preformed with uninoculated, sterile medium E in order to maintain the same salinity and chemical composition as the original culture. Each aliquot representing a different biosurfactant concentration was then split into three portions. Enough solid NaCl was added to one of the portions to give a final NaCl concentration of 75 g/l; another portion received enough NaCl to give a final NaCl concentration of 100 g/l. The remaining portion did not receive additional NaCl and had a NaCl concentration of 50 g/l, which is the NaCl concentration of medium E.

In another experiment, the effect of the presence of a co-solvent, 2,3-butanediol, was studied along with studying the effects of biosurfactant concentration and salinity. The experiment was conducted in a similar fashion as described above using two different cultures of *B. mojavensis* strain JF-2 that contained 54.0 and 58.0 mg/l of the biosurfactant. Each culture was split into equal volumes and to one portion enough solid 2,3-butanediol was added to give a final concentration of 10 mM. Each portion (e. g., with and without 2,3-butanediol) was then two- and five-fold diluted as described above. After dilution, the concentration of the JF-2 biosurfactant from one culture was 54, 27 and 11 mg/l while that of the other culture was 58, 29 and 12 mg/l.

Additional experiments were done at low biosurfactant concentrations. For these experiments, the biosurfactant was prepared aerobically in separate batches and had different biosurfactant concentrations. Some batches were diluted by one-half or one-quarter of the original biosurfactant concentration by diluting the cell-free culture fluid with sterile medium E.

Interfacial Tension Measurements (IFT)

Interfacial tension was measured by using a spinning drop tensiometer. For experiments where the effect of salinity and 2,3-butanediol were determined, duplicate measurements were made for each of the above treatments and a crude oil with 32^0 API

oil and a viscosity of 6.0 cp was used. Otherwise, each sample was measured three times and in some cases four times for greater accuracy and a 44° API crude oil was used. The tensiometer readings were taken at room temperature (26^0 C). The capillary tube of the tensiometer was filled with the biosurfactant solution or the sterile medium E. A drop of was then introduced into the aqueous phase by using a syringe and needle. IFT were measured as the tube rotated at high speeds.

Core Flooding

Berea sandstone cores were dried in an oven at 60^o C for 4 days. The dried cores were weighed and their length and diameter measured. The core was inserted into a Hassler holder and placed under vacuum for 24 hours to remove air. The core was placed at 2000 psig and then flooded with at least multiple pore volumes of deareated 5% NaCl brine. After brine saturation, the core was flooded to connate water saturation (until no more brine exited the core) with crude oil (32^o API gravity). The core was then flooded with 5% NaCl brine until near residual oil saturation, where only a trace of oil was detected in the effluent of the core.

After the core reached near residual oil saturation, cell-free culture fluid containing the indicated biosurfactant concentration and 1 g/l PHPA and 10 mM 2,3-butanediol was injected into core. Table 7 gives the pore volumes and flow rates used for biosurfactant injection. In most cases, the core was then treated with 5% NaCl brine after biosurfactant sludge was injected as indicated in Table 7. The flow rates used for post-flush brine injection are also given in Table 7.

Effluent samples were collected in flasks and the amounts of oil and brine collected were determined volumetrically.

Petrophysical properties of the Berea sandstone cores are given in Table 1. Brine viscosity ranged from 1.03 to 1.1 cp and crude oil viscosity ranged from 2.0 to 6.0 cp.

Establishment of a capillary desaturation curve for Berea sandstone cores

Capillary number is defined as the ratio of inertial to capillary forces. Capillary number increases with increases in the inertial forces or decreases in the interfacial forces. Increases in capillary number lower the residual oil saturation in the core and increase residual oil recovery(20).

Table 1. Petrophysical properties of the Berea sandstone cores.

Core	Porosity (%)	Pore volume (ml)	Absolute permeability (md)	$K_{O, Eff}$ (md)	$K_{W, Eff}$ (md)	Oil saturation (%)	Residual oil (ml)
1	13.9	23.9	35	27.2	13.7	20.9	5
2	23.1	39	26.5	14.3	8.3	15.1	5.9
3	13.9	18.9	31.3	21.3	1.2	20.9	4.8
4	13.4	27	31	14.3	4.2	24.8	6.7
5	14.9	25	34.8	21.1	5.2	40.8	10.2
6	18	30	22.8	19.2	2.8	36	10.8
7	16.7	29		21.6	6.7	51.4	14.9
8	15.7	26.5	29.7	21.6	5.4	39.6	10.5
9	18.4	31	103	36.3	20.2	36.8	11.4
10	17.9	31.5	108	39.5	13.8	39	12.3
11	18.2	32	72	39.5	15.9	35.3	11.3
12	18.2	32	72.2	39.5	4.5	35.6	11.4
13	17.4	30	68.7	37.7	4.3	40	12
14	18.2	31.8	60.9	38	5	39.6	12.6
15	18.4	32.5	122.2	48	6	39.4	12.8
16	18.7	33	240.1	47.8	8.8	36.1	11.9

Capillary number is mathematically defined as:

$$N_{CP} = \frac{v\mu}{\sigma}$$

where, v: velocity through porous media (cm/sec), $Q/ A\Phi$

μ: viscosity of displacing fluid (brine), cp

σ: Interfacial tension between oil and water, dynes/cm

and Q: the waterflooding rate, A is the core's cross-sectional area and Φ is the porosity of the core.

Berea sandstone cores were dried in an oven at 60^0 C for four days, then weighed and its length and diameter were measured. The core was placed under vacuum for 24 h to remove trapped air inside the core, saturated with deareated 5.0 % NaCl brine, and flooded to connate water saturation using crude oil. In the water flooding phase, 5.0% NaCl brine was injected at a flow rate of 2.5 ml/h until the core reached residual oil saturation (e. g., until no more oil was recovered from the core). The rate of brine

injection was doubled (5.1 ml/h) and the core was again water flooded to residual oil saturation. The doubling of the flow rate continued until the brine flow rate reached a maximum of 576.0 ml/h. The amount of oil recovered at each flow rate was measured and the residual oil saturation determined.

RESULTS

The Effect of Salinity, 2,3-Butanediol and Biosurfactant Concentration on Interfacial Tension

The biosurfactant concentration of three replicate cultures of *B. mojavensis* strain JF-2 grown at different times with different inocula was of 57, 54 and 58 mg/l to give a mean and standard deviation of 56.3 ± 2.1. The coefficient of variation was 3.7%, indicating a high degree of reproducibility in biosurfactant concentration among cultures grown at different times and with different inocula.

Table 2 summarizes the effects of biosurfactant concentration, salinity and the presence of 2,3-butanediol on the interfacial tension between culture medium and crude oil.

Table 2. Summary of interfacial tension measurements at different biosurfactant concentrations, salinities with and without 2,3-butanediol. Duplicate measurements were made for each treatment and a crude oil with 32^0 API oil and a viscosity of 6.0 cp was used.

Biosurfactant concentration (mg/l)	Additions	Interfacial tension (mN/M) at different NaCl concentrations.		
		50 g/l	75 g/l	100 g/l
57	none	0.2 (0.15)	0.7 (0.7)	3.5 (0.8)
	butanediol	0.2 (0.08)	1.5 (0.2)	2.0 (0.8)
28	none	0.8 (0.7)	1.1 (0.2)	2.6 (1.9)
	butanediol	0.4 (0.2)	2.4 (0.4)	2.2 (0.7)
11	none	1.6 (1.0)	3.2 (0.8)	3.8 (0.7)
	butanediol	2.0 (1.2)	2.0 (0.4)	3.6 (1.0)

The lowest interfacial tension was 0.1 mN/m. This is two orders of magnitude lower than the typical IFT between crude oil and water of 29 to 32 mN/m as reported by Green and Willhite (1998) (6). The interfacial tensions were lower at 50 g/l NaCl than at the higher salinities regardless of the biosurfactant concentration.

Two-factor analysis of variance was used to determine whether the biosurfactant concentration and salinity significantly effected interfacial tension. Table 3 shows the mean interfacial tensions of each treatment and Table 4 shows the results of the analysis of variance.

Table 3. Effect of salinity and biosurfactant concentration on interfacial tension between culture medium and crude oil without 2,3-butanediol. . Duplicate measurements were made for each treatment and a crude oil with 320 API oil and a viscosity of 6.0 cp was used.

Biosurfactant concentration (mg/l)	Mean interfacial tensions at different salinities		
	50 g/l	75 g/l	100 g/l
57	0.1	0.8	3.5
28	1.0	1.2	2.8
11	1.4	3.4	4.1

Table 4. Two-factor analysis of variance summary table on the effects of salinity and biosurfactant concentration on interfacial tension between culture medium and crude oil.

Source of variance	Sums of squares	Degrees of freedom	Mean squared deviation from the mean	F value	P value	F critical
Concentration	16.3	2	8.1	7.953	0.00192	3.354
Salinity	43.1	2	21.6	21.05	3.1E-06	3.354
Interaction	6.6	4	1.7	1.622	0.19753	2.728
Within cells	27.7	27	1.0			
Total	93.7	35				

The analysis of variance shows that there were significant differences among all of the treatments ($P<0.05$). Both the biosurfactant concentration and the NaCl concentration affected the interfacial tension. Increasing the NaCl concentration significantly increased the interfacial tension as did decreasing the biosurfactant concentration. There was no significant interaction between these two factors.

A second two-factor analysis of variance was conducted to assess the effect of 2,3-butanediol on interfacial tension. For this analysis, only data at a biosurfactant concentration of 28 mg/l was used since it was not possible to obtain interfacial tension

measurements at all salt concentrations at the other two biosurfactant concentrations. The mean values obtained from this analysis are shown in Table 5 and the summary statistics are shown in Table 6.

Table 5. Effect of the presence of 2,3-butanediol on interfacial tension between culture medium and crude oil at a biosurfactant concentration of 28 mg/l. . Duplicate measurements were made for each treatment and a crude oil with 32^0 API oil and a viscosity of 6.0 cp was used.

Additions	Mean interfacial tensions at salinities (g/l) of		
	50	75	100
None	0.4	0.75	1.2
2,3-Butanediol	0.4	2.5	2.2

Table 6. Two factor analysis of variance summary table on the effect of the presence of 2,3-butanediol on interfacial tension between culture medium and crude oil.

Source of variance	Sums of squares	Degrees of freedom	Mean squared deviation from the mean	F value	P value	F critical
Butanediol	5.0	1	5.0	24.9	9E-5	4.41
Salinity	8.3	2	4.1	20.6	2E-5	3.35
Interaction	2.9	2	1.4	7.24	0.005	3.35
Within cells	3.6	8	0.2			
Total	19.9	23				

Again, increasing salinity negatively impacted the interfacial tension with the lowest values once again obtained at 50 g/l salt. Interestingly, interfacial tensions were significantly lower in the presence of 2,3-butanediol compared to replicate treatments without 2,3-butanediol. The interaction between these two factors was also significant.

Table 7. Summary of oil recovery data at biosurfactant concentrations above and below the critical micelle concentration. Corrected percent residual oil recovery is corrected for the amount of residual oil recovered by polymer alone.

Core	Biosurfactant concentration (mg/l)	Volume of recovery sludge (PV)	Biosurfactant injection rate (ml/h)	Volume of brine post flush (PV)	Post-flush rate (ml/h)	Residual oil recovered (ml)	Percent residual oil recovery	Corrected percent residual oil recovery (%)
1	11	2	3.14	0	3.14	0	0	0
2	39	2	3.14	3	3.14	2.3	39	29.3
3	38	1	2.54	1	5.14	2	47	37.3
4	38	1	5.14	1	10	3	45	35.3
5	21	1	5.4	1	30.9	2.7	26.5	16.8
6	21	1	6.4	1	30.9	3	27.8	18.1
7	10.5	1	6.4	1	30.9	2	13.4	3.7
8	10.5	1	6.4	1	30.9	1.7	16.2	6.5
9	11	2	5.14	1	20.53	2.3	20.2	10.5
10	11	1	5.14	1	20.53	1.7	13.8	4.1
11	11	1	5.14	1	20.53	1.8	15.9	6.2
12	5.5	1	5.14	1	20.53	1	8.8	0
13	5.5	1	5.14	1	20.53	1.2	9.6	0
14	2.75	1	5.14	1	20.53	1.3	10.3	0.6
15	2.75	1	5.14	1	20.53	1.7	13.3	3.6
16	0	1	6.43	1		1.2	9.7	0

Core flood experiments

Table 7 summarizes the results of a series of core flood experiments with different biosurfactant concentrations and flow regimes. Little or no oil was recovered at biosurfactant concentrations less than 21 mg/l. At biosurfactant concentrations ranging from 2.75 to 11 mg/l, the amount of residual oil recovered was similar to that of the control that lacked biosurfactant (Core 16, Table 7). Oil recovery at these low biosurfactant concentrations are most likely the result of increase in viscous forces due to polymer injection. When the biosurfactant concentration was 21 mg/l (Cores 5 and 6; Table 7), additional residual oil was recovered. At a biosurfactant concentration of 39 mg/l (Core 2-5; Table 7), the percent of residual oil that was recovered, corrected for residual oil recovered by the polymer alone, was twice that when the biosurfactant concentration was 21 mg/l (Table 7). These data indicate that once a threshold value of biosurfactant is reached, residual oil recovery becomes linearly proportional to the biosurfactant concentration. This linear dependence of residual oil recovery on biosurfactant concentration was observed previously in sand pack columns at higher biosurfactant concentrations (16). The threshold value is between 10 to 20 mg/l, which is the critical micelle concentration of the JF-2 biosurfacant (5).

Capillary desaturation

To determine if the residual oil recoveries by biosurfactant injection were an artifact of the core flooding process (e. g., unusually high residual oil saturations or flow rates that may not be reflective of actual field conditions), a capillary desaturation curve was generated by measuring the oil saturations at different flow rates. The residual saturations and the capillary numbers obtained with different flow rates are shown in Table 8 and this relationship is plotted in Figure 1.

Table 8. Residual oil saturation and capillary Number with increase flow rates

Qw (cc/hr)	$S_{or,WF}$ (%)	N_{CP}
2.5	.3667	1.51 E-5
5.0	.3458	3.02 E-5
10.5	.3396	6.34 E-5
20.53	.3292	1.24 E-4
30.86	.3104	1.86 E-4
61.0	.3021	3.68 E-4
123.4	.2688	7.45 E-4
246.9	.2479	1.49 E-3
493.1	.2250	2.98 E-3
576.0	.2250	3.48 E-3

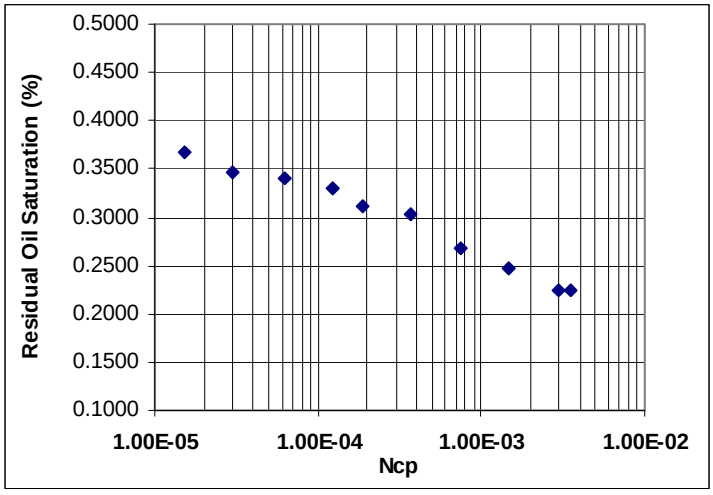

Figure 1. Berea sandstone capillary desaturation curve.

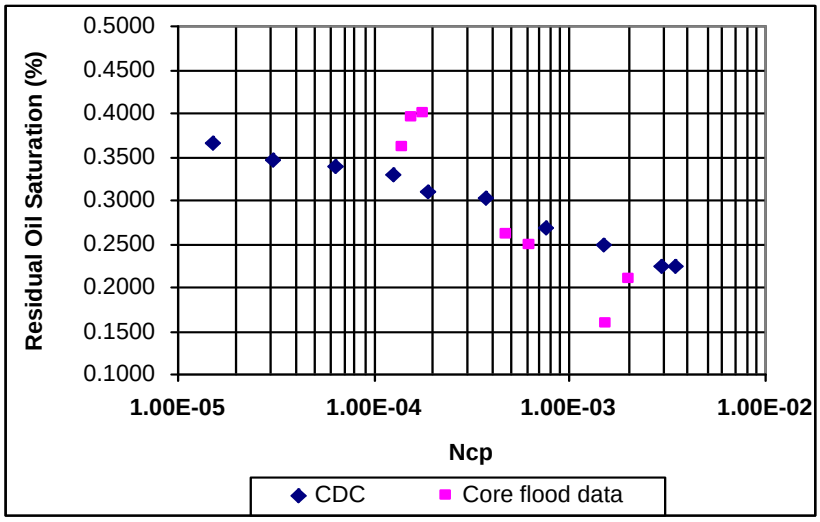

Figure 2. Comparison of core data with the capillary desaturation curve.

Figure 2 shows this same curve as in given in Figure 1, with the residual oil saturations obtained for some of the Berea sandstone cores used in the biosurfactant flooding experiments included.

Hysteresis of the oil trapping process results in larger inertial force being required to displace oil from a pore for discontinuous systems, where capillary number is increased in a stepwise manner, compared to a system that is continuous (capillary number does not

change) or where capillary number changes continually(20). Because it is expected that the biosurfactant process will be used in fields that have undergone water-flooding to near residual oil saturations, the discontinuous process is more representative of he capillary number requirements to displace residual oil be biosurfactants. Comparison of the residual oil saturations of cores used for biosurfactant injection to the capillary desaturation curve shows that in some case higher and in other cases lower residual oil saturations were obtained. Thus, our experimental model is representative of the expected field conditions. When the capillary number at a given residual oil saturation for an individual core water flood is lower than that for the same residual oil saturation on the capillary desaturation curve, this would be advantageous from a tertiary recovery point of view since displacement will be a discontinuous process and the capillary number required to mobilize oil would be higher than that required for continuous process.

Analysis of relationship between fractional oil recovery and surfactant concentration

Table 9 summarizes the data that relate biosurfactant concentration to residual oil recovery for Berea sandstone and sand-packed column experiments. The data on residual oil recovery from Berea sandstone are corrected for the amount of oil produced by the polymer alone are included. Injection of the polymer alone in sand-packed columns did not recovery residual oil. These data can be used to relate interfacial tension, biosurfactant concentration, and oil recovery.

Figure 3 shows that the fraction of oil recovered by the viscous-biosurfactant solution, either corrected or not corrected for the contribution of the polymer, is linearly dependent on biosurfactant concentration when the concentration is greater than about 10 mg/l. When bio-surfactant concentration was close to 10-11 ppm, the fraction of oil recovered was close to zero. The data from sand-packed experimental systems also show a linear relationship between the fraction of oil recovered and biosurfactant concentration (15). However, the slope of this line differs from that obtained with Berea sandstone cores. This may reflect the differences in the petrophysical properties of the two porous systems or differences in the treatment protocols for biosurfactant injection. With sand packs, a viscous pre-flush ahead of the biosurfactant solution and post flush with different viscosities were used.

Table 9. Residual oil recoveries from sandstone and sand-packed model systems with different biosurfactant concentrations.

Surfactant concentration (ppm)	Oil recovery (Frac.)	Oil recovery after removing polymer contribution (Frac.)
41	0.39	0.29
38	0.48	0.38
38	0.45	0.35
21	0.27	0.17
21	0.28	0.18
10.5	0.13	0.04
10.5	0.16	0.07
11.0	0.14	0.04
11.0	0.16	0.06
5.5	0.09	0.0
5.5	0.10	0.0
2.75	0.10	0.06
2.75	0.13	0.04
920	0.64	-
920	0.63	-
283	0.53	-
283	0.48	-
43	0.22	-
43	0.22	-

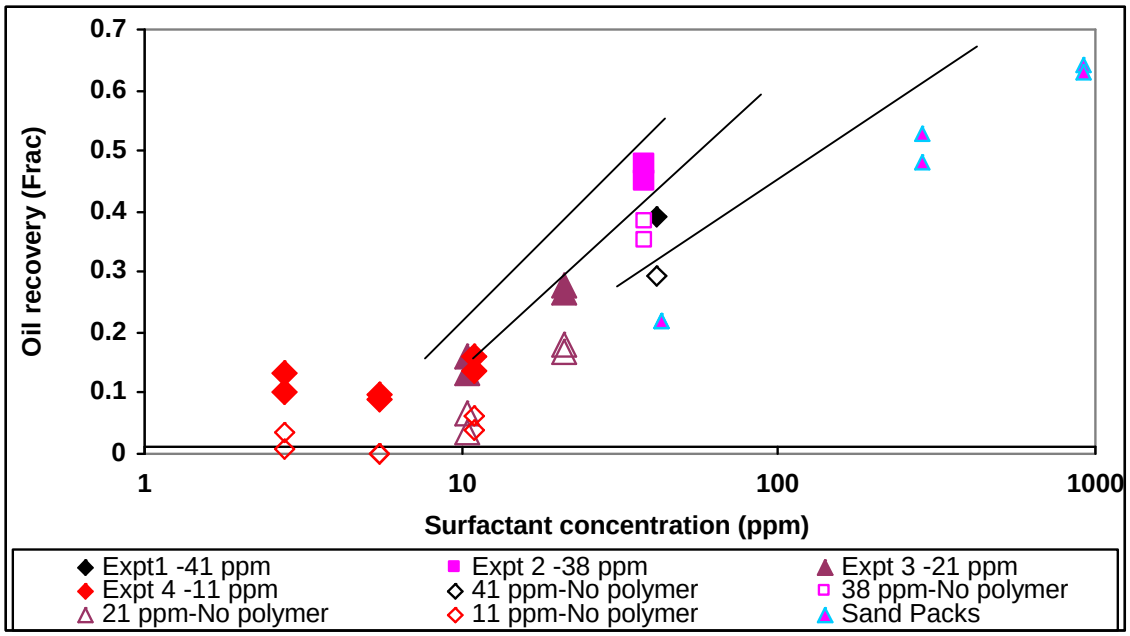

Figure 3. Plot of tertiary oil recovery from cores (before and after removing the polymer contribution) and sand-packed columns as a function of biosurfactant concentration.
The closed symbols represent tertiary oil recoveries using the viscous-surfactant solution from sandstone cores before correcting for the polymer contribution. The open symbols are the recoveries after the 10% residual oil recovered by the polymer solution alone was subtracted from the oil recovery data. Measurements from surfactant treatment of horizontal sand packs were also included in the plot (small closed triangles). In the sand pack experiments, each pack was flooded with a pore volume of viscous surfactant solution. These points are included to provide a greater range of surfactant concentrations over which oil recovery could be analyzed. The single solid diamond represents the oil recovery fraction after two pore volumes of biosurfactant (11 mg/l) was flooded through a core.

After correcting for the contribution of the polymer contribution, a single pore volume treatment at 11 mg/l of the biosurfactant did not recover any oil, but the two pore volume treatment at 11 mg/l of the biosurfactant recovered 0.1 of the residual oil. The adsorption of the biosurfactant to the porous matrix or trapping of the micelles in the pores may have lowered the effective biosurfactant concentration and prevented oil recovery when only one pore volume of the biosurfactant solution was used (6). Adsorption of biosurfactant in the second pore volume would have been reduced, allowing for some residual oil recovery oil. As found with synthetic surfactants, these data indicate that adsorption and trapping of biosurfactants occur. This probably lowers the biosurfactant concentration below that needed for oil recovery. Biosurfactant-mediated water floods would require large volumes of recovery fluid or a high concentration of biosurfactant.

Mathematical model relating oil-water interfacial tension to JF-2 biosurfactant concentration

The construction and analysis of a mathematical relationship between oil-water interfacial tension (IFT) and biosurfactant concentration, salinity and co-surfactant 2,3-butenediol is presented here. Last year, we reported on the dependence of IFT and bio-surfactant concentration, salinity, and co-surfactant alcohol using a two-way analysis of variance method (18). We found that, at biosurfactant concentrations made naturally by *B. mojavensis* strain JF-2, IFT between the aqueous and oil phases was lowered by two orders of magnitude in some cases. Increasing salinity from 5% NaCl to 7.5 and 10%, with or without 2,3-butanediol present, increase the interfacial tension. The lowest IFT observed was 0.1 mN/m at 5% NaCl in the presence of 2,3-butanediol.

Here the effect of all three variables on IFT between oil and water is studied and a mathematical relationship between oil-water IFT and bio-surfactant concentration is presented.

Interfacial tension values at different biosurfactant concentrations are shown below in Table 10. These data were obtained using biosurfactant samples from different batches of aerobically grown cultures. The method of preparation and composition was the same for each batch. A spinning drop tensiometer was used to measure the data used to calculate IFT. Each measurement was repeated three times for greater accuracy.

Figure 4 shows a stepwise decrease in IFT with increasing biosurfactant concentration. The IFT between crude oil and 5% NaCl brine was measured first and its value was repeatedly found to be 29.0 mN/m. Interfacial tension first decreased from 29 mN/m to 1.0 mN/m as biosurfactant concentration increased from 0.0 to 11.0 mg/l. From 11.0 mg/l to 41.0 mg/l, the IFT stayed steady in a region close to 1.0 dyne/cm. When the bio-surfactant concentration increased beyond 41.0 ppm, IFT declined again with increasing concentration until it reached a region between 54-58 ppm. At this point, IFT was close to 0.1 dyne/cm. On the basis of conservative error at concentrations close to 58 ppm, IFT appeared to remain unchanged at concentrations beyond 58.0 ppm. But this has not been confirmed because 58.0 ppm was the highest concentration obtained in the laboratory.

Table 10. Interfacial tension values at different bisurfactant concentrations.

Concentration of surfactant (ppm)	IFT (Dynes/cm)
58.0	0.35
29.0	0.38
11.6	1.88
54.0	0.168
27.0	0.42
10.8	0.37
57.0	0.10
28.5	1.50
11.4	2.50
11.0	2.54
41.0	1.21
38.0	1.48
21.0	1.50
10.5	2.00
11.0	0.93
5.5	3.00
2.75	4.20

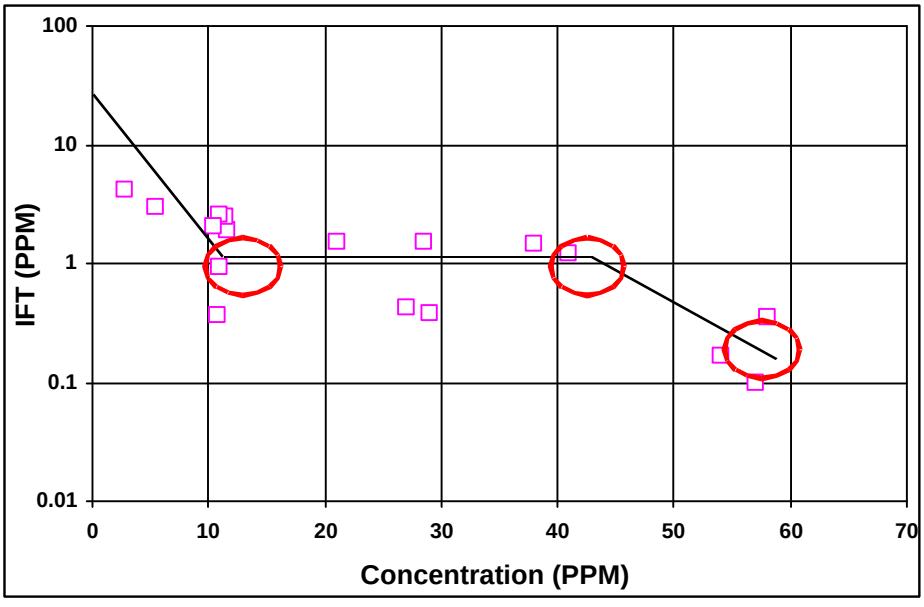

Figure 4. The relationship between interfacial tension and biosurfactant concentration.

Two critical concentrations were identified from inspection of Figure 4. The first critical biosurfactant concentration is around 11 mg/l. At this concentration, IFT decreases to 1.0 mN/m. IFT value remains unchanged until the biosurfactant concentration reaches 41.0 mg/l. The biosurfactant concentration of 11.0 mg/l may represent the critical micellar concentration (CMC) for the bio-surfactant. At the CMC, the concentration of surfactant molecules is sufficient to form micelles. The CMC of the purified JF-2 biosurfactant has been reported to be 10 mg/l (11), consistent with our findings. The second critical biosurfactant concentration is between 40 and 60 mg/l and this is where another decrease in IFT is observed. This region may the critical microemulsion concentration (CMEC). When surfactant concentrations reach the CMEC, a third phase called a microemulsion (in addition to the oil and aqueous phases) forms. The microemulsion phase is generally associated with ultra-low IFT values. The microemulsion phase region contains oil, water, and a microemulsion that may have oil and/or water molecules surrounded the surfactant molecules (6, 13). The two critical biosurfactant concentration regions are indicated with circles in Figure 4 below.

Mathematical model

The mathematical model used to represent the change in IFT with changing biosurfactant concentration had been previously derived from laboratory experiments on synthetic surfactants (2, 23). It has also been used in an earlier model for biosurfactant-based microbial enhanced oil recovery (26). Approximating IFT through this relationship is straightforward. Studies have shown that other equations may be required where IFT is a function of the equivalent alkane number of the crude oil, salinity, or temperature. The exponent, ES, is an exponent factor that decides the dependency of interfacial tension on biosurfactant concentration. The concentration exponent is reported to be less than unity at low concentrations. The equation is shown below as Equation (a).

$$\mathrm{Log}_{10}(IFT_{C,\,Surf}) = \mathrm{Log}_{10}(IFT_{Min}) + (\mathrm{Log}_{10}(IFT_{Max}/IFT_{Min}))*((C_{Surf,Max} - C_{Surf})/Delsuf)^{ES} \quad \ldots. (a)$$

Based on our analyses, we will use a different system of nomenclature from Equation (a) to identify parameters used to predict IFT as a function of biosurfactant concentration as illustrated in Figure 5.

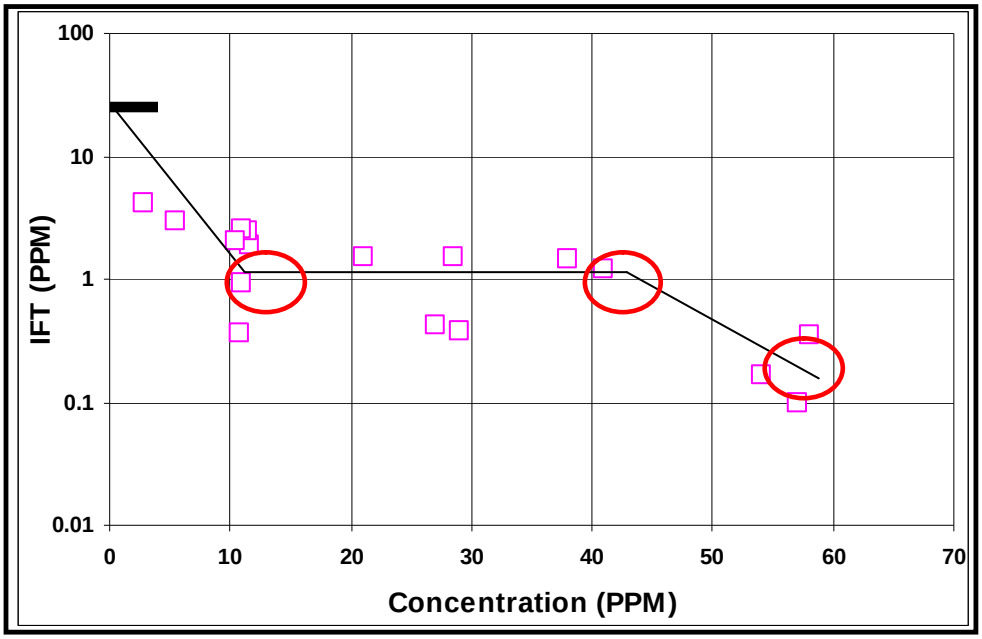

Figure 5. The relationship between interfacial tension and biosurfactant concentration.

To model the stepwise profile that we obtained, the two concentration ranges were identified. One range was between 0.0 mg/l and 41.0 mg/l. In this range, IFT reaches a minimum of 1.0 mN/m once the CMC of 11.0 mg/l is reached and appears to remain constant until 41 mg/l. The value 41.0 mg/l is called the higher critical micellar concentration (CMCH) and 11.0 mg/l is called the lower critical micellar concentration (CMCL). This region is is defined by Equation (b). When concentrations exceed 41 mg/l, Equation (c) is used to define the relationship between IFT and higher biosurfactant concentrations. The minimum concentration for this region is called the higher critical micellar concentration and the maximum concentration (CMAX) has been assumed to equal a biosurfactant concentration greater than 58.0 mg/l. The IFT reaches a minimum of 0.1 mN/m at a critical microemulsion concentration (CMEC) of 58.0 mg/l and from then IFT is assumed to remain constant with further increases in biosurfactant concentrations.

For bio-surfactant concentrations between 0.0 and 41.0 mg/l, the model is defined by Equation (b).

$$Log_{10}(IFT_{C,\,Surf}) = Log_{10}(IFT_{Min1}) + (Log_{10}(IFT_{Max}/IFT_{Min,1}))*((C_{Surf.,CMCH} - C_{Surf})/Delsuf1)^{ES1} \ldots. (b)$$

For bio-surfactant concentrations between 41.0 to 58.0 mg/l and for larger biosurfactant concentrations, the model is defined by Equation (c).

$$Log_{10}(IFT_{C,\,Surf}) = Log_{10}(IFT_{Min2}) + (Log_{10}(IFT_{Min2}/IFT_{Min1}))*((C_{Surf.,Max} - C_{Surf})/Delsuf2)^{ES2} \ldots\ldots (c)$$

Model prediction

When the biosurfactant concentration is between 0 and 41 mg/l, the model has a specific set of values (Table 11). These parameters differ when the concentration exceeds 41 mg/l (Table 12). This way, the stepwise behavior of the IFT is modeled by using the same mathematical equation, but with different parametric values. The model prediction is shown in Figure 6 below. The values for the parameters were obtained from the laboratory measurements.

Table 11. Parameter values for biosurfactant concentrations between 0.0 and 41.0 mg/l

Variable	Value
$C_{Surf.,Min}$ (mg/L)	0.0
$C_{Surf.,CMCH}$ (Higher critical micellar concentration) (mg/L)	0.041
$C_{Surf.,CMCL}$ (Lower critical micellar concentration) (mg/L)	0.011
IFT_{Min1} (dynes/cm)	1.0
IFT_{Max} (dynes/cm)	29
ES1	7.0
Delsuf1 (mg/L)	$C_{Surf.,CMCH} - C_{Surf.,Min}$

Table 12. Parameter values for concentrations between 41.0 and 58.0 ppm

Variable	Value
$C_{Surf.,CMCH}$ (mg/L)	0.041
$C_{Surf.,Max}$ (mg/L)	0.080
$C_{Surf.,CMEC}$ (Critical microemulsion concentration)	0.058

(mg/L)	
IFT_{Min2} (dynes/cm)	0.1
IFT_{Min1} (dynes/cm)	1.0
ES2	3.0
Delsuf2 (mg/L)	$C_{Surf.'Max} - C_{Surf.'CMCH}$

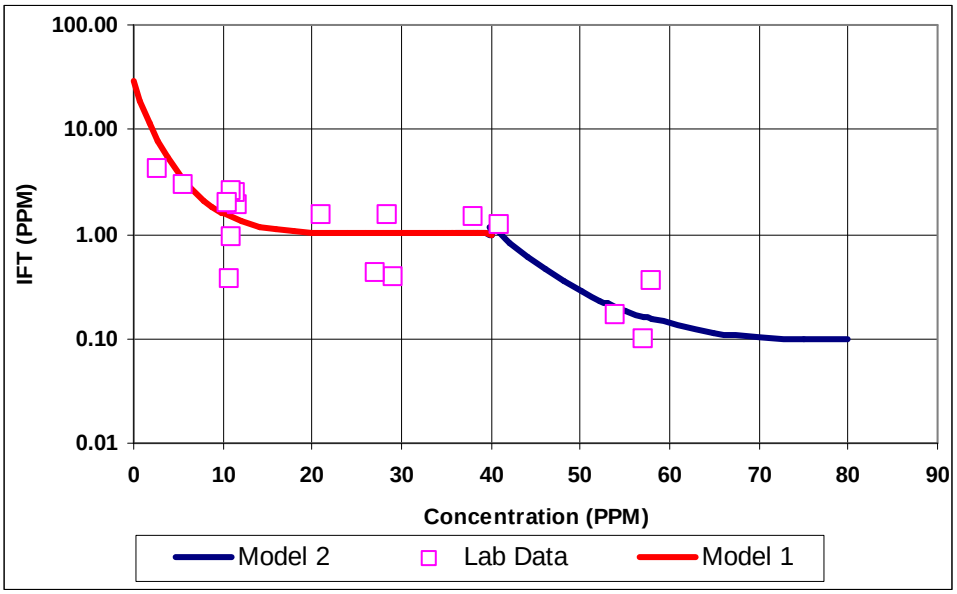

Figure 6. Comparison between model prediction (line) and laboratory measurements (squares)

DISCUSSION

The interfacial tension increases as biosurfactant concentration decreases because less biosurfactant is present at the interface between oil and water. Consequently, work that is done to bring the immiscible phases together results in higher interfacial tension. This is explained in detail by Rosen (1978) (22). Healy et al. (1976) (8) showed that salt ions repel biosurfactant molecules from the aqueous phase into the hydrocarbon phase as salinity increases. This results in an increase the IFT between the hydrocarbon and aqueous phases and explains the rise in IFT with increasing salinity

The increase in IFT in the presence of a co-surfactant such as 2,3-butanediol may be because alcohols alter biosurfactant behavior and raise the optimal salinity of the biosurfacant. Optimal salinity is the salinity where the lowest IFT can be found. Hsieh

and Shah (1977) (9) and Wade et al. (1978) (25) have shown that addition of water soluble alcohols raises the optimal salinity of a surfactant system and consequently, the IFT. It is to be noted that at high alcohol concentrations, the addition of more alcohol does not affect the optimal salinities or IFT of a formulation. An interesting observation was that the salinity effects were more pronounced at lower concentrations and the co-surfactant did not alter this sensitiveness to salinity.

We have modified our previous model that related biosurfactant concentration to IFT (26) by incorporating the stepwise behavior of IFT as a function of biosurfactant concentration. By using the same relationship with different input parameter values for different concentration ranges of the biosurfactant, we are able to model the changes in IFT behavior more accurately. A single set of parameter values did not model the observations accurately. A maximum biosurfactant concentration of 80.0 mg/l was used. This is an assumed value equal to the critical microemulsion concentration. The model has also been further improved by estimating the model parameters from laboratory data. The concentration exponent, 'ES' has a value greater than one for both critical biosurfactant concentrations. Though one expects that the value of ES should be less than unity for low biosurfactant concentrations (6), no specific surfactant concentration has been defined in the literature where ES would become less than unity. Since a value for ES of 7.0 for the first concentration range and 3.0 in the second concentration range provided a good fit, they were used in the model to simulate biosurfactant-based oil recovery.

CONCLUSIONS

The bacteria *Bacillus mojavensis JF- 2* produced a bio-surfactant that lowered interfacial tension between crude oil and water by two or more orders of magnitude.

Increasing salinity of the aqueous phase from 50 g/l to 10o g/l increased IFT with larger increases at lower bio-surfactant concentrations.

Addition of 2,3-butanediol caused an increase in IFT.

Two critical biosurfactant concentrations exit where marked changes in interfacial tension occur. Thus, interfacial tension changes in a stepwise manner as biosurfactant concentration increases.

At biosurfactant concentrations above the critical micelle concentration, residual oil recovery is a linear function of biosurfactant concentration.

A mathematical model that relates oil recovery to biosurfactant concentration was modified to include the stepwise changes in IFT as biosurfactant concentrations changes. This model adequately predicted the experimentally observed changes in IFT as a function of biosurfactant concentration.

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