

Evaluation of Sub-micellar Synthetic Surfactants versus Biosurfactants for Enhanced LNAPL Recovery

Period Covered by Report: February 1, 2004 through April 30, 2005

EPA Agreement Number: R83-0633-010

Title: Evaluation of Sub-micellar Synthetic Surfactants versus Biosurfactants for Enhanced LNAPL Recovery

Investigators: D. A. Sabatini, R. C. Knox, and M. J. McInerney

Institution: The University of Oklahoma

EPA Project Officer: Bala Krishnan

Project Period: November 1, 2004 through October 31, 2005

Project Amount: \$94,518

Research Category: Petroleum Environmental Technology – Recovery of free-phase LNAPL

Keywords: Biosurfactant, surfactant-enhanced subsurface remediation, LNAPL, interfacial tension, phase behavior, lipopeptide, rhamnolipid.

Objective: Surfactant-enhanced subsurface remediation (SESR) significantly reduces the time required to remove light non-aqueous phase liquids (LNAPLs) from contaminated aquifers by improving LNAPL solubility and/or mobility. The overall objectives of this research is to assess the relative technical and economic efficiency of using biosurfactants and their mixtures to recover free-phase LNAPL as compared to synthetic surfactants. Specific objectives of the research are: (1) to determine the optimum phase behavior of the lipopeptide biosurfactants made by *Bacillus* species and the rhamnolipid biosurfactant made by *Pseudomonas* species; (2) to determine the efficacy of mixtures of biosurfactants relative to single biosurfactants in producing low interfacial tension; and (3) to compare the efficacy of optimized biosurfactant formulations to that of synthetic surfactant formulations.

Progress Report/Accomplishments:

Biosurfactant / Oil Interactions: In the previous reporting period, we studied the interactions between biosurfactants and toluene. The concentration of biosurfactant was fixed at 0.1 wt%. During this reporting period, we varied the biosurfactant concentration and focused mostly on rhamnolipid biosurfactant, which was purchased from Jeneil Biosurfactant Company, Inc. The rhamnolipid came as a 15 w/v % solution and was used without any further purification. Besides toluene, decane was also studied as the oil phase.

We found that the rhamnolipid biosurfactant in salt solutions higher than 5 wt% were not soluble. Due to this, the interactions between biosurfactant and oil were studied using solutions with salt concentrations less than 5 wt%.

The dynamic IFT between each biosurfactant solution and oil was measured for 30 minutes. The dynamic IFT was found to decrease with increasing time. Figure 1 shows the dynamic IFT of the rhamnolipid biosurfactant with toluene as salinity was varied. It

can be seen that as the concentration of salt increases, the IFT decreases. This is because rhamnolipid is an anionic surfactant. As more salt is added to the solution, the repulsion between ionic head groups is reduced, causing the surfactant to become more hydrophobic. Therefore, it can be also expected that higher salt concentrations will help to reduce the IFT. However, due to the solubility problem as mentioned above, the salt concentration was limited to 4 wt%. The lowest IFT for toluene was 0.14 mN/m at 0.01 wt% rhamnolipid and 4 wt% salt. It also can be concluded that further reduction in the IFT between rhamnolipid solution and toluene will require the addition of a cosurfactant that is more hydrophobic than the rhamnolipid.

Figure 2 shows the results for decane. The IFT for decane was not as sensitive to salt concentration as was the toluene. In addition, low IFT between rhamnolipid and decane required a higher rhamnolipid concentration than with toluene. The lowest IFT found for decane was 0.45 mN/m at 0.1 wt% rhamnolipid and 2 wt% salt. Since decane is much more hydrophobic than toluene, the minimum IFT can be achieved at lower salt concentrations. For the same reason, the IFT of rhamnolipid is higher for decane than for toluene since rhamnolipid is a hydrophilic surfactant. The results for decane indicate that an additional component must be added to rhamnolipid solutions to help achieve lower IFT.

The results presented in Figures 1 and 2 will be repeated to ensure the accuracy of measurements.

Mixture of Surfactants:

Based on the results of interfacial interactions between rhamnolipid and toluene and decane, surfactants mixtures were studied. The rhamnolipid biosurfactant was mixed with two synthetic surfactants (Alfoterra® 63 and Alfoterra® 68) in two different ratios. These two surfactants are hydrophobic surfactants consisting of 50% branched and 50% linear C12 and C13 hydrocarbons in their structures. Alfoterra® 63 has only 3 PO groups while Alfoterra® 68 has 8 PO groups, which makes Alfoterra® 68 more hydrophobic.

Since the study of surfactant mixtures is still in the screening process, the dynamic IFT between each mixture and oils was measured for 15 minutes. Also the ratio of concentration between rhamnolipid and a synthetic surfactant was limited to 1:1.

Figure 3 shows the dynamic IFT of the mixture of rhamnolipid biosurfactant and Alfoterra® 63 with 3% NaCl for four oils. There is no pronounced difference in IFTs of the different surfactant mixtures with any of the oils. The minimum IFT found is 0.35 mN/m of the mixture of 0.05 wt% rhamnolipid and 0.05 wt% Alfoterra® 63 for toluene.

Figure 4 shows similar results for mixtures of rhamnolipid biosurfactant and Alfoterra® 68. The surfactant ratio in the mixtures significantly affects only the IFT for toluene even though the addition of Alfoterra® 68 to the rhamnolipid solution also decreases the IFT for the other three oils. The IFT for toluene is markedly reduced to 0.0099 ± 0.0012 mN/m.

From both Figures 3 and 4, it can be seen that Alfoterra® 68 can produce lower IFT for all four oils than Alfoterra® 63. Therefore, our hypothesis that the rhamnolipid biosurfactant solution needs to be amended to achieve lower IFT is corroborated.

Future work: In the future, the following work will be done:

- Surfactant mixtures will be further studied.
- The solid-surfactant interactions will be evaluated by conducting adsorption studies.
- Surfactant-water interactions, such as foaming, precipitation, and phase separation properties, will be evaluated.
- Column studies will be performed using the optimum formulations of single and mixed – surfactant systems to find the oil removal efficiency.

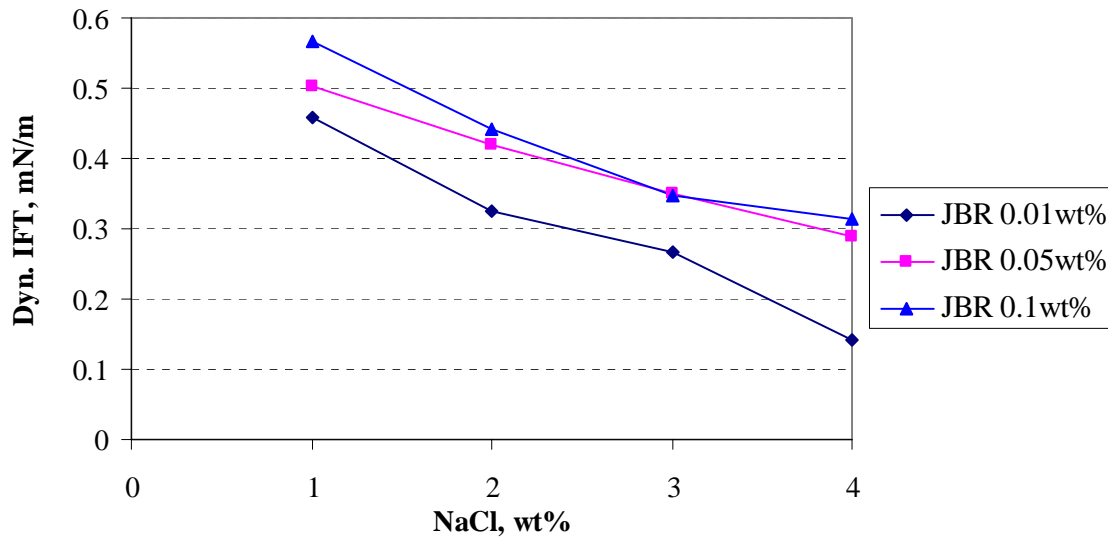


Figure 1. Dynamic IFT of Rhamnolipid Biosurfactant (JBR) versus Salinity (Toluene)

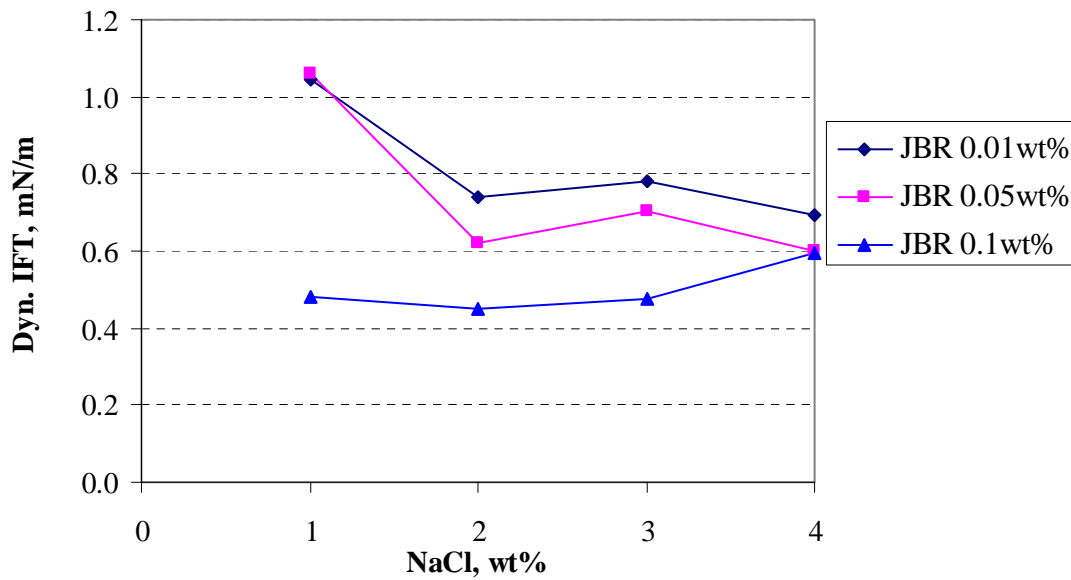


Figure 2. Dynamic IFT of Rhamnolipid Biosurfactant (JBR) versus Salinity (Decane)

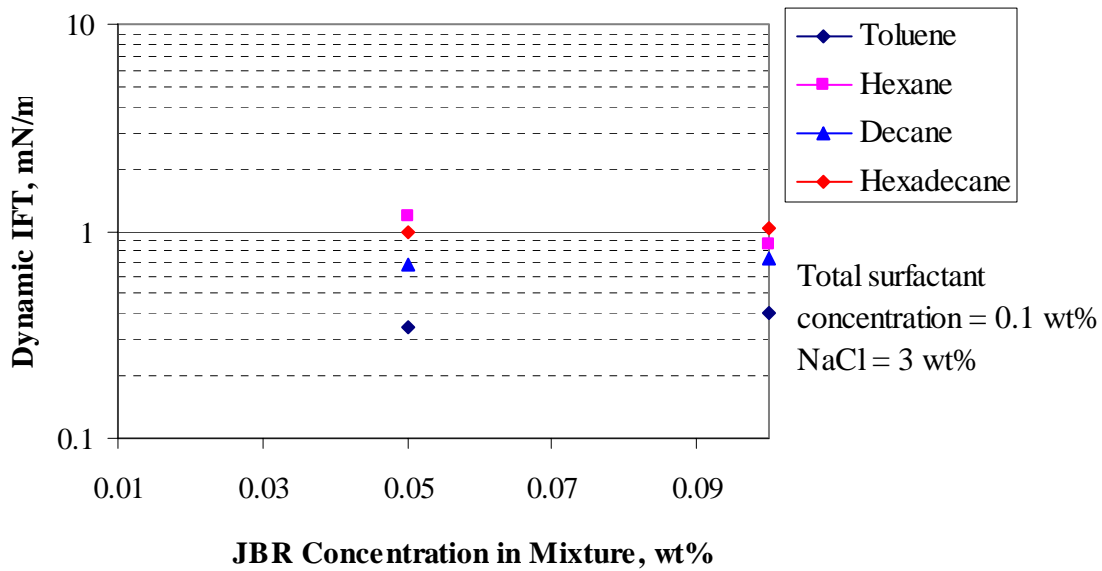


Figure 3. The IFT of Rhamnolipid Biosurfactant (JBR)/Alfoterra® 63 (AF 63) mixture versus JBR Concentration in Mixture for Four Oils

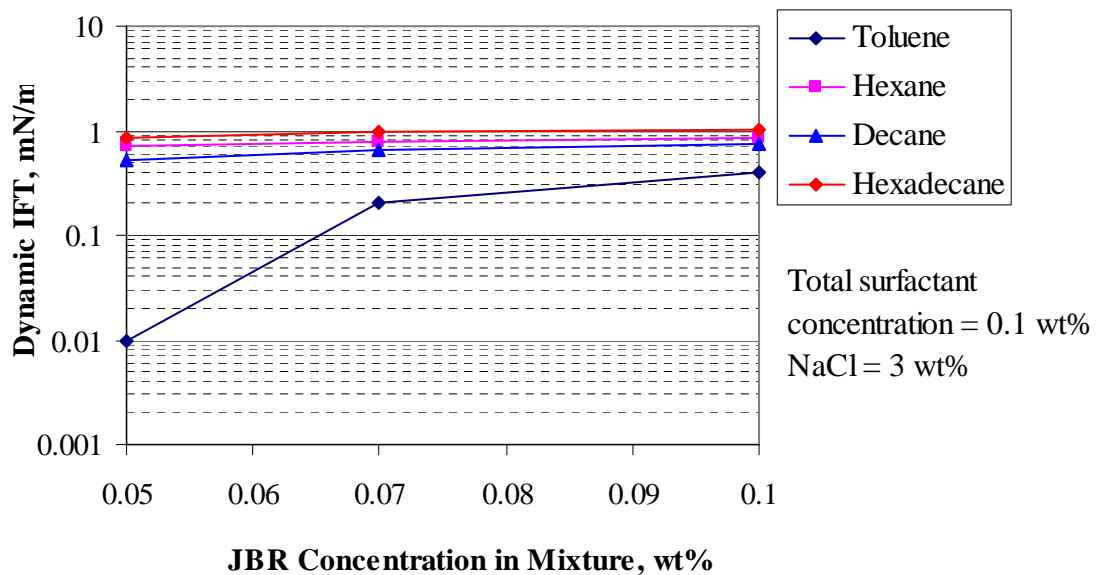


Figure 4. The IFT of Rhamnolipid Biosurfactant (JBR)/Alfoterra® 68 (AF 68) mixture versus JBR Concentration in Mixture for Four Oils