3nd Quarterly Report
Evaluation of Sub-micellar Synthetic Surfactants versus Biosurfactants for Enhanced LNAPL Recovery

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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
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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 and studied mixtures of biosurfactant and synthetic surfactants. We found that mixtures of biosurfactant and synthetic surfactants produced lower interfacial tension (IFT) than biosurfactant individually for all four oils – toluene, hexane, decane, and hexadecane. The biosurfactant used was rhamnolipid and the synthetic surfactants used were Alfoterra® 63 (less hydrophobic) and Alfoterra® 68 (more hydrophobic). Since Alfoterra® 68 was found to generate significantly lower IFT for all four oils than Alfoterra® 68, subsequent research focused on Alfoterra® 68. Also, in this reporting period we started studying the synthetic surfactant Alfoterra® 48 which has the same composition as Alfoterra® 68 but is 100 % branched and C12/C13 while Alfoterra® 68 is 50 % branched and 50 % linear. We studied the impact of surfactant structure on interactions between surfactant and oil.

Figure 1 shows the dynamic IFT of the mixture of 0.05 wt% rhamnolipid and 0.05 wt% Alfoterra® 68 with four oils as a function of salinity. The IFT of this mixture with toluene is observed to be much lower than those with hexane, decane, and hexadecane, indicating that Alfoterra® 68 is quite hydrophilic. The IFT results for toluene are a minimum at 3 wt% NaCl. At this salt concentration, the IFT is 0.013 mN/m. On the other hand, the IFT results for the other three oils decrease as the salinity increases. While it would be interesting to study the IFT behavior for these three oils at higher salt concentration, for salt concentration higher than 6 wt% the surfactant solutions became cloudy, which made it impossible to make IFT measurements.

The IFTs of mixtures of rhamnolipid and Alfoterra® 68 for toluene are significantly lower than those for hexane, decane, and hexadecane. Therefore, mixtures of rhamnolipid and Alfoterra® 68 were studied further (see Figure 2). Both surfactant systems with Alfoterra® 68 show minimum IFTs at 3 and 4 wt% NaCl. These minimum IFTs are 0.008 and 0.004 mN/m, which are about two orders of magnitude lower than the system that contains rhamnolipid only (IFT of 0.355 mN/m). When rhamnolipid is the only surfactant present in the system, the IFT decreases as the salinity increases; however, at salt concentrations higher than 4 wt%, the surfactant solution phase separates, which once again prevents IFT measurements. This also indicates that without Alfoterra® 68, the surfactant system is more hydrophilic and thus requires higher salt concentration to achieve the minimum IFT.

The results from Figures 1 and 2 show synergism for mixtures of rhamnolipid and Alfoterra® 68 in the IFT reduction for toluene, but not for hexane, decane, and hexadecane. Therefore, an alternative synthetic surfactant – Alfoterra® 48 – was studied. Alfoterra® 48 has the same number of PO groups and C12 and C13 hydrocarbons in the structure but Alfoterra® 48 has 100% branching of C12 and C13 in the structure while Alfoterra® 68 is 50% branched and 50% linear. It was hypothesized that with 100% branching the surfactant would form micelles with a larger inner core volume, which would help solubilize and lower the IFT for more of the long chain hydrocarbons.

Figure 3 shows the dynamic IFT of the mixture of rhamnolipid biosurfactant and Alfoterra® 48 with 3% NaCl for four oils. There is a pronounced reduction in IFT for toluene of the surfactant mixtures, especially at 0.07 wt% rhamnolipid and 0.03 wt% Alfoterra® 48 mixture, as compared with individual surfactant systems. However, the IFTs for hexane, decane, and hexadecane are lowest in the surfactant system that contains only Alfoterra® 48. This means that Alfoterra® 48 is more hydrophobic.

Figure 4 shows similar results as shown in Figure 1, but for the surfactant mixture of rhamnolipid and Alfoterra® 48. Compared with the results in Figure 1, the addition of Alfoterra® 48 helps to reduce the IFTs for all four oils better than that of Alfoterra® 68, even though the values for each oil are not one order of magnitude different. This proves the hypothesis that was stated earlier. Alfoterra® 48 produces IFT reduction for toluene, and hexane. Therefore, surfactant mixtures of rhamnolipid and Alfoterra® 48 with different ratios were evaluated for their ability to lower IFT for toluene and hexane, as shown in Figures 5 and 6, respectively.

In Figure 5, it can be seen that the addition of Alfoterra® 48 helps to lower the IFT. However, the surfactant mixture with more rhamnolipid (0.07 wt%) than that of Alfoterra® 48 (0.03 wt%) produces lower IFT for toluene while the opposite is observed for hexane in Figure 6. This is because Alfoterra® 48 is much more hydrophobic than rhamnolipid, resulting in better ability of Alfoterra® 48 to solubilze hexane (more hydrophobic oil).

In short, we have demonstrated that several rhamnolipid biosurfactant and synthetic surfactant mixtures (Alfoterra® 68 and Alfoterra® 48) have the potential to lower IFTs for toluene and hexane. These surfactant systems and their IFTs are summarized in Table 1. Some out of these surfactant systems will be evaluated in for adsorption and column studies below.

Surfactant / Water Interactions: The interactions of interest between surfactant and water include foaming, precipitation, and phase separation properties. In this reporting period, precipitation and phase separation studies were conducted.

Precipitation studies were done by using the method described by Zhao et. al.[1] to determine the Krafft temperature of the surfactant solutions. The Krafft temperature is the lowest temperature at which no precipitate exists. In this study, Krafft temperature was determined from the lowest temperature at which a 1 wt% surfactant in deionized water solution is still clear. The Krafft temperatures for selected surfactant solutions shown in Table 1 were all determined to be 0^oC.

Phase separation studies were conducted with selected surfactant solutions listed in Table 1. These solutions were prepared and mixed, then centrifuged for 10 minutes. After centrifugation, all the solutions remained in one homogeneous phase, indicating that no phase separation was experienced for these surfactant solutions.

Surfactant / Solid Interactions: In order to study surfactant – solid interaction, we studied the adsorption of surfactant on solid surfaces in column tests. Ottawa sand was used as the solid media. The average grain size diameter is 0.212 mm.

The adsorption of Rhamnolipid biosurfactant was evaluated using 0.1 wt% solution in a column test. Column studies were conducted in glass chromatography columns purchased from Kontes Company (diameter of 2.5 cm and a length of 15 cm).

The column was first packed with sand and saturated with deionized water for about 12 hours. A tracer test was done using NaCl 1 wt% solution followed by deionized water to determine the value of one pore volume and the hydrodynamics of the flow system. The rhamnolipid biosurfactant was then flushed through the column. The column effluent was connected to a variable wavelength detector. At the wavelength of 212 nm, the variable

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[1] Zhao, F., Rosen, M. J. "Relationship of Structure to Properties of Surfactants. 12. Synthesis and Surface Properties of Long-Chain 2-Pyridinium Alkanoates." J. Phys. Chem. (1984) 88, 6041-6043.

wavelength detector can detect the concentration of rhamnolipid in the solution as it comes out of the column. The adsorption test showed minimal adsorption of rhamnolipid on the solid surfaces, as can be seen in Figure 7. The number of moles rhamnolipid adsorbed per gram solid was found to be 2.34 x 10^{-9} mol surfactant/gram solid; this corresponds to approximately 0.20 % of the surfactant being adsorbed.

Column Study: Column studies were performed to evaluate the oil (toluene) removal efficiency using surfactant mixture of rhamnolipid (0.07 wt%) and Alfoterra® 68 (0.03 wt%) at 3 wt% NaCl. Figure 8 shows the fraction of toluene removed by surfactant flushing through the sand packed column. A removal efficiency of 90 % was obtained.

Future work: In future work, the following studies will be conducted:

- Surfactant mixtures will be further studied, specifically looking at higher rhamnolipid ratios in rhamnolipid/synthetic surfactant mixtures.
- The solid-surfactant interactions will be further evaluated by conducting adsorption studies.
- Foaming properties of the surfactant solutions will be studied.
- More column studies will be performed using the optimum formulations of single and mixed – surfactant systems to find the oil removal efficiency.

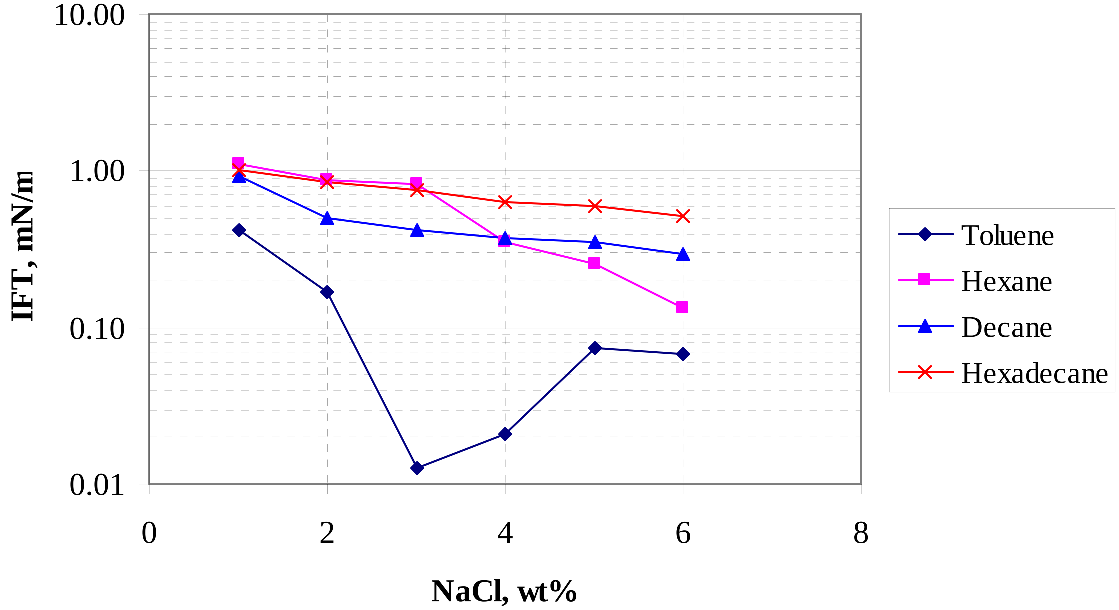

Figure 1. Dynamic IFTs of Mixtures of Rhamnolipid/Alfoterra® 68 = 0.05/0.05 (wt%) versus Salt Concentration for Four Oils

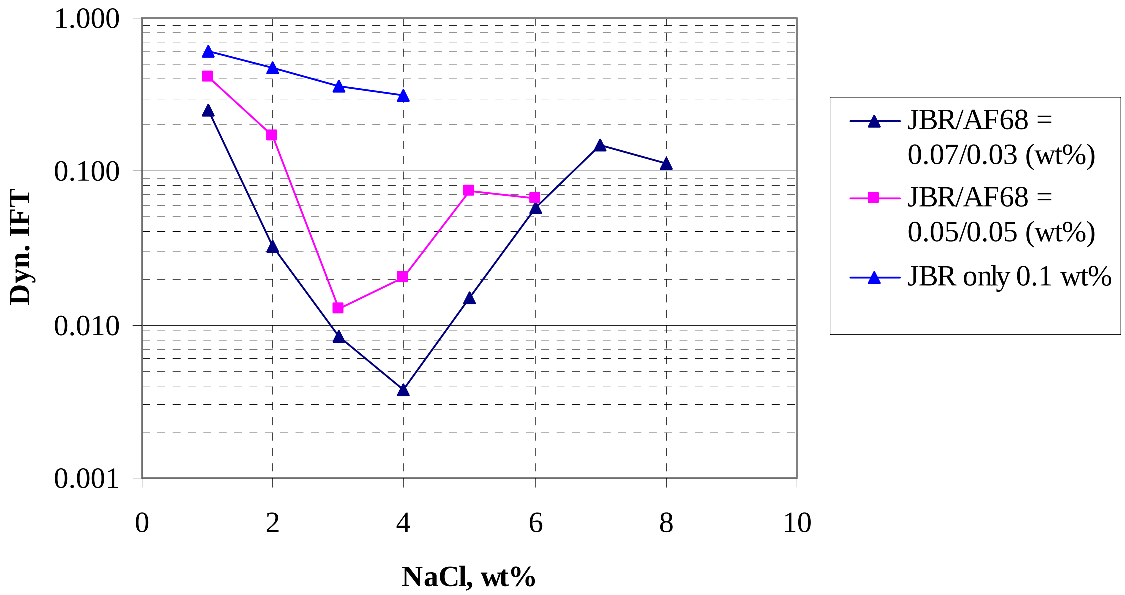

Figure 2. Dynamic IFTs of Mixtures of Rhamnolipid and Alfoterra® 68 versus Salt Concentration for Toluene

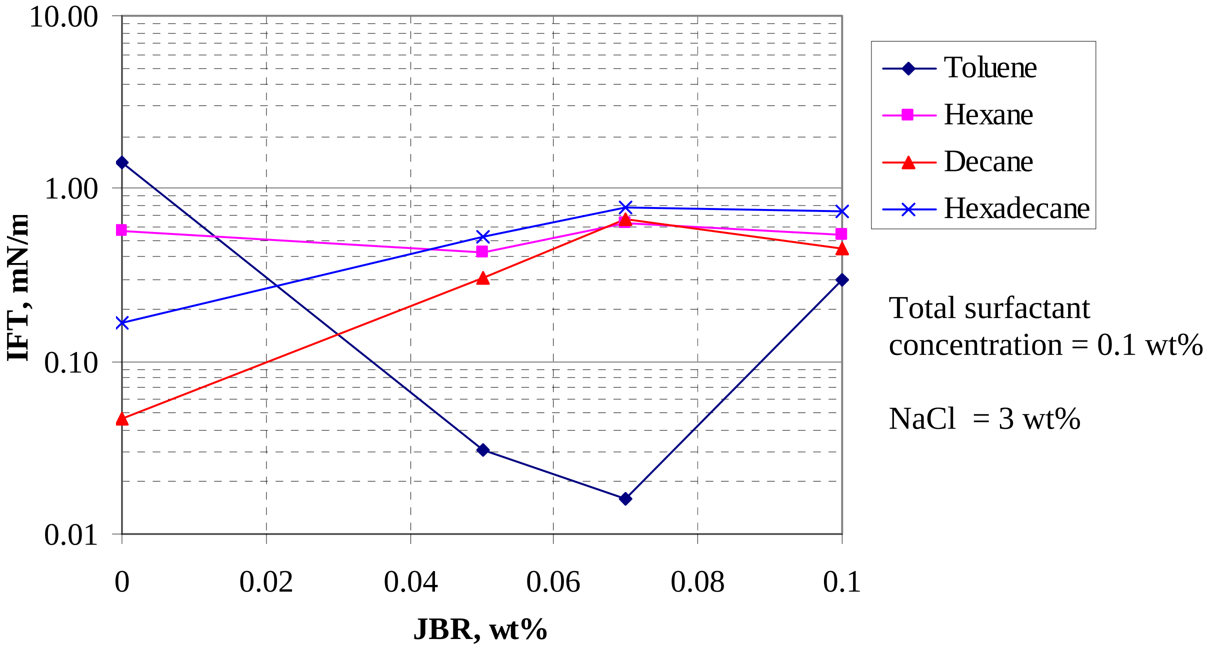

Figure 3. The IFTs of Mixture of Rhamnolipid and Alfoterra® 48 versus Rhamnolipid Concentration in Mixture for Four Oils

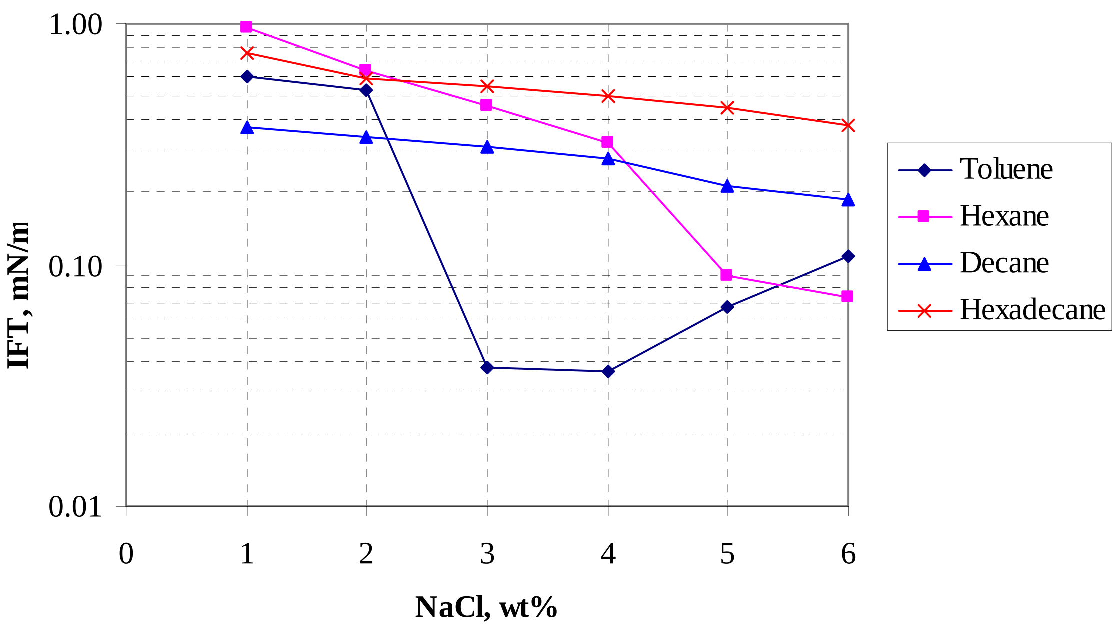

Figure 4. Dynamic IFTs of Mixtures of Rhamnolipid/Alfoterra® 48 = 0.05/0.05 (wt%) versus Salt Concentration for Four Oils

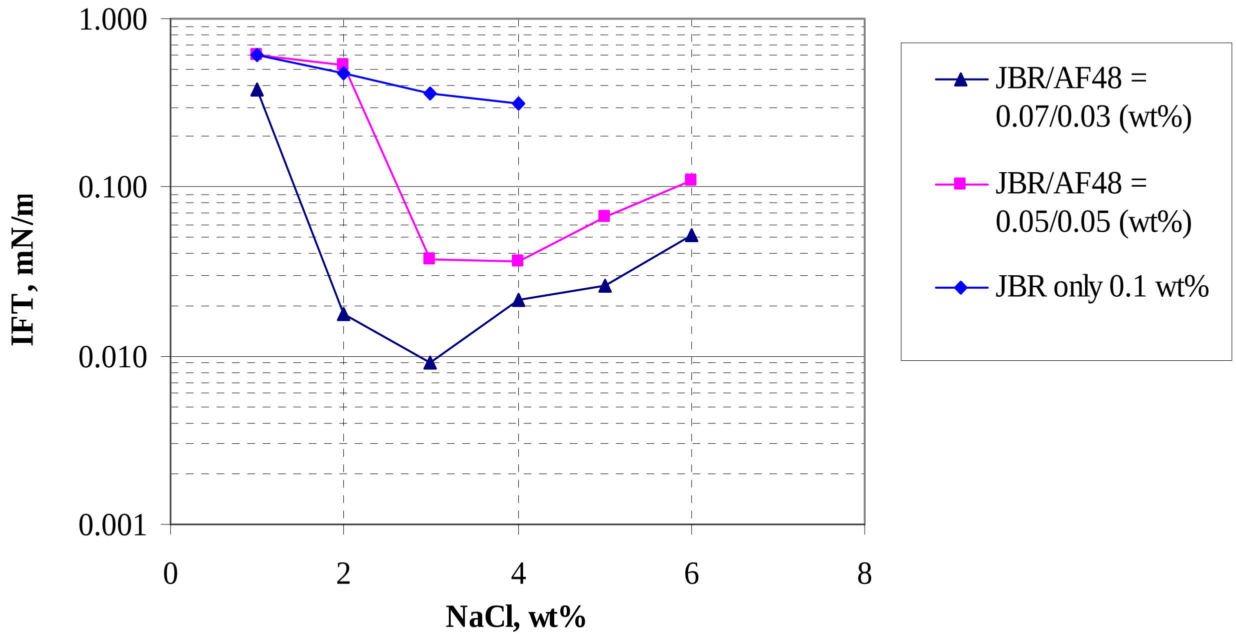

Figure 5. Dynamic IFTs of Mixture of Rhamnolipid and Alfoterra® 48 versus Salinity for Toluene

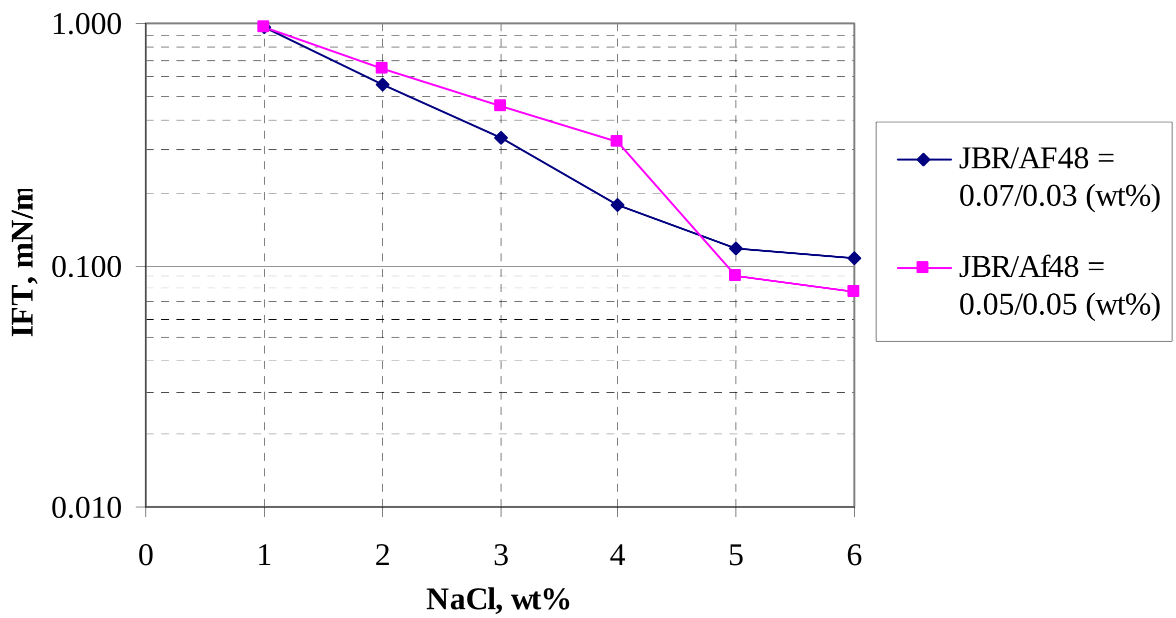

Figure 6. Dynamic IFTs of Mixture of Rhamnolipid and Alfoterra® 48 versus Salinity for Hexane

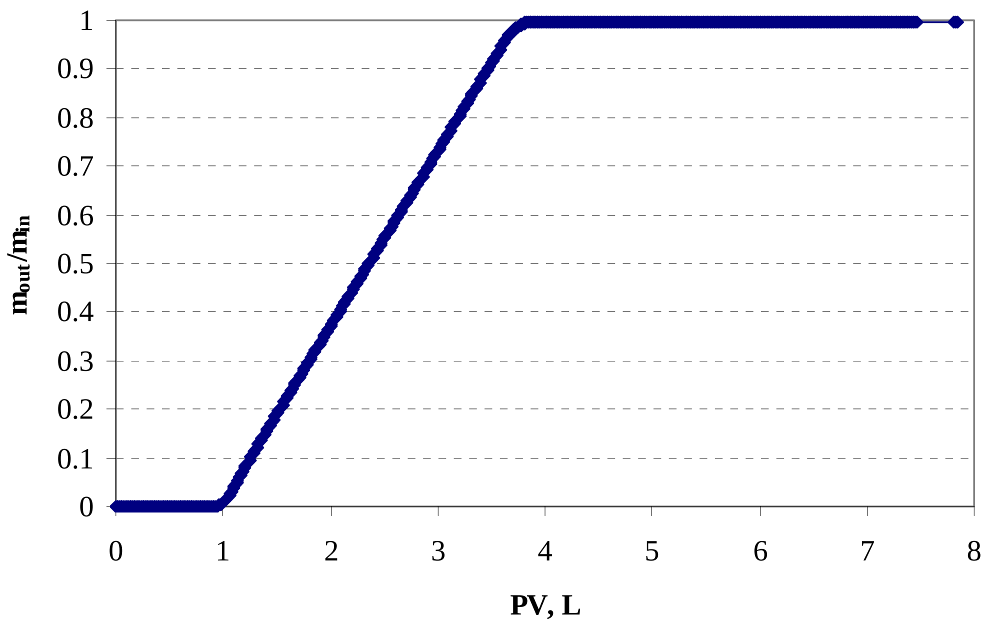

Figure 7. Adsorption Test in Column for Rhamnolipid Biosurfactant Solution

m_{out} = amount of surfactant coming out of column
m_{in} = amount of initial flushing surfactant solution

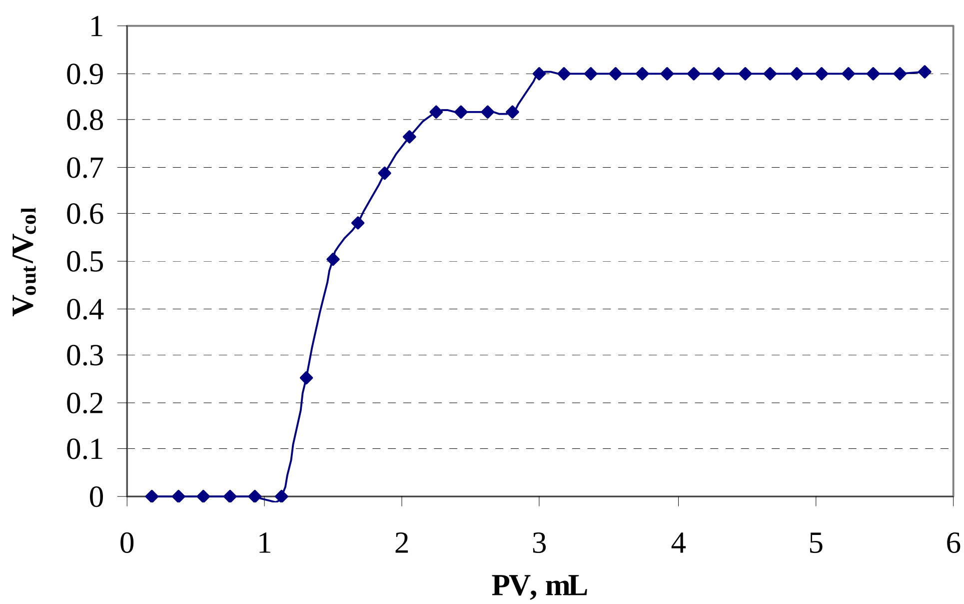

Figure 8. Toluene Removal Efficiency of Rhamnolipid and Alfoterra® 68 mixture

V_{out} = volumn of toluene removed from column
V_{col} = volume of toluene in left in column before surfactant flushing

Table 1. Potential Surfactant Mixture Systems and Their IFTs

Rhamnolipid, wt%	**Alfoterra®68, wt%**	**Alfoterra®48, wt%**	**NaCl, wt%**	**Oil**	**IFT, mN/m**
0.05	0.05		3	Toluene	0.013
			4		0.021
			5		0.074
			6		0.067
0.07	0.03		2	Toluene	0.033
			3		0.008
			4		0.004
			5		0.015
			6		0.059
0.05		0.05	3	Toluene	0.037
			4		0.036
			5		0.067
0.07		0.03	2	Toluene	0.018
			3		0.009
			4		0.022
			5		0.026
			6		0.051
0.05		0.05	5	Hexane	0.091
			6		0.078