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ALTERNATIVE SURFACTANT FORMULATION FOR NON-AQUEOUS PHASE
LIQUID (NAPL) REMOVAL

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ALTERNATIVE SURFACTANT FORMULATION FOR NON-AQUEOUS PHASE
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This thesis is dedicated to my amazing parents. Thank you for believing in me,
encouraging me and helping me get this far.

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Abstract

Due to the inefficiency of the pump and treat method in removing hydrocarbon contamination from ground water, a new method called surfactant Enhanced Aquifer remediation (SEAR) has been developed. SEAR is just a chemical enhancement to the pump and treat method that consists of using surfactants to increase the solubility of the oil phase in the water and thus increase the removal of contaminants. A surfactant solution composed of 0.75 wt.% AOT and 0.19 wt.% Calfax 16L-35 was developed as a formulation for SEAR application. However, the limited biodegradability of the Calfax 16L-35 has led to the need for an alternative surfactant system. An alternative formulation composed of .75 wt.% AOT and 0.19 wt.% SDBS was developed and showed promising results. In this work, a new surfactant is introduced, called the Taiwan surfactant, and is tested to determine whether it can be used by itself in a SEAR application. The results of this work show that a 0.94 wt.% Taiwan surfactant formula meets all the criteria set for a SEAR application; it can form a middle phase microemulsion near 1 g NaCl/100 ml at room temperature with octane, it has a low adsorption on sand, a good oil mobilization capability and is stable. Furthermore, the performance of this system is comparable to the performance of the AOT/SDBS system meaning that either one of these two formulations can be use in place of the AOT/Calfax 16L-35 system.

The second part of this work focused on finding the HLD parameters of the surfactants of interest and on determining the accuracy of the HLD equation in predicting the optimum salinity of the three systems. An updated method was used in place of the Acosta's method to find the parameters, and the two methods were compared. It is shown in this work that both methods have limitations, but they both give good approximations

for the HLD of our three systems. Lastly, it is shown that the HLD method is a good correlation for describing microemulsion systems.

Chapter 1: Introduction

The presence of hydrocarbons in the subsurface is mainly due to the widespread use of hydrocarbons and chlorinated solvents [1]. If released near or at the surface, these non-aqueous phase liquids (NAPLs) can migrate and contaminate the water table. NAPLs that are lighter than water are called LNAPLs and those that are denser and thus sink below the water table are called DNAPLs; with the latter being the most difficult to remediate [2]. As the NAPLs migrate through porous media, a portion is trapped within the pores due to capillary forces and forms what's called the trapped oil or residual saturation and may occupy anywhere between 5 and 40% of the pore volume [1, 3, 4]. The standard remediation technique for NAPL removal is the pump-and-treat method. This technique consists of pumping the contaminated ground water to the surface. However, since the solubility of NAPLs is low, and they can be trapped underground by capillary forces, mass removal of the groundwater cannot efficiently remove the NAPL leading to subsequent contamination of fresh ground water. This method requires several years of treatment to reach treatment goals [5].

The inefficiency of the conventional pump-and-treat method has led to the consideration of chemical enhancements to pump-and-treat; more precisely the use of surfactants to enhance the aquifer remediation (SEAR). Surfactants are chemical agents that can be used to increase the solubility of the NAPL (solubilization) and/or increase the mobility of the organic phase by decreasing the interfacial tension between the NAPL and the groundwater (mobilization) [6]. Solubilization is based on the ability of surfactants to form micelles whereas mobilization occurs when the surfactant solution decreases the NAPL-groundwater interfacial tension (IFT) to an ultralow value, between 10^{-2} and 10^{-3}

dyne/cm [7] which means that the surfactant needs to form a type III microemulsion with the NAPL-Water system. Mobilization is the focus of this paper because previous work has shown that mobilization was significantly more effective than solubilization [1].

The current system of surfactants being used is composed of two anionic surfactants, Calfax 16L-35 and AOT at 0.19 wt.% and 0.75 wt.% respectively. Calfax 16L-35 is an alkyl diphenyloxide disulfonate with 16 carbons linear alkyl group mainly composed of monoalkyl and dialkyl sulfosuccinates (MADS and DADS) and AOT is a dioctyl sodium sulfosuccinate.

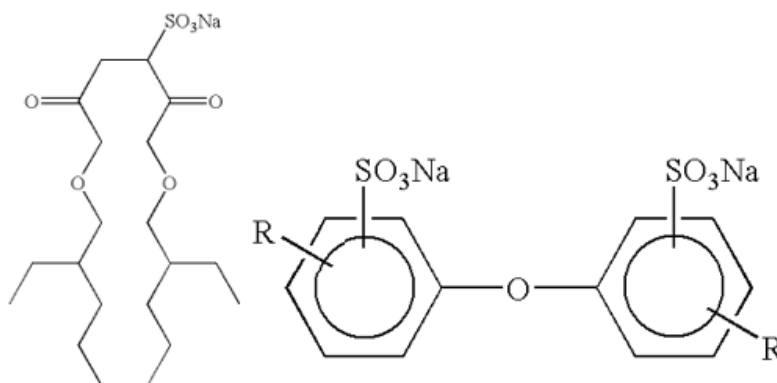


Figure 1: Approximate structures of AOT (left) and Calfax 16L-35 (right) [8]

The main issue with this system is the slow biodegradability of Calfax 16L-35. The purpose of SEAR is to remove ground water contamination; it would thus be counter intuitive to introduce a non-degradable or a slow degrading agent that may contaminate even more. A new formulation was developed that replaced the Calfax 16L-35 in the previous system with Sodium dodecyl benzenesulfonate (SDBS) which is a surfactant from the EPA safer chemical list [8]. The weight percentage of SDBS in the new formulation is 0.19 wt.% and the AOT concentration stays the same as the previous

formulation. This system showed satisfying results and can potentially be used to replace the previous AOT and Calfax 16l-35 system.

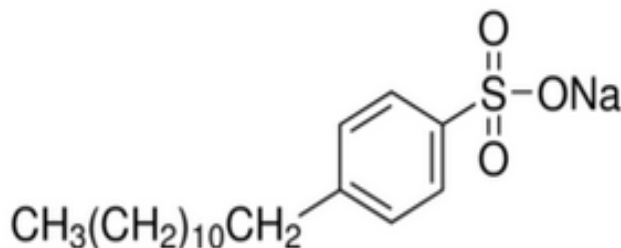


Figure 2: Structure of SDBS

The objective of this work is to compare the performance of a new surfactant system, called the Taiwan surfactant, with the performance of the previous two systems. The main goal being to determine if the Taiwan surfactant can be used in place of the last two systems in environmental remediation applications. The Taiwan surfactant is a blend of three anionic surfactants: AOT, a surfactant with a phosphate head group and an extended surfactant containing sulfate, ammonia and 2-4 polyethylene oxide groups; however, the structures of the last two surfactants are unknown. All three systems need to meet the following criteria: form type III microemulsions at or near 1g NaCl/100 ml with octane at room temperature with a total surfactant concentration less than 1 wt.%, have an IFT on the order of 10^{-2} mN/m or lower, be stable and have low adsorption on sand. The three systems are evaluated based on phase behavior studies, IFT measurements, stability and column studies. We are not working on a specific site for this work, so octane is used as the LNAPL and tap water is used as the aqueous phase.

For this project, the optimum salinities for the first two systems with octane were already determined in previous work and an approximation for the Taiwan surfactant was provided by the manufacturer. However, the behavior of a surfactant system depends on

many factors including the salinity of the aqueous phase, the temperature, nature of the oil phase... It is thus important to have a correlation that can predict how the surfactant behavior changes when any of those conditions change. In this work, the HLD parameters of the surfactants of interest will be determined. The HLD correlation is used because it is the one that takes into account most of the factors that affect the surfactant behavior. The HLD parameters for AOT, Calfax 16L-35, and SDBS were already found using Acosta's method [9] but that method was found to have limitations; so an updated method will be used in this work and the results will be compared to the values found using Acosta's method. The HLD of the three systems will also be calculated to determine how accurate the correlation is in predicting optimum conditions.

Chapter 2: Literature Review

Surfactant-Enhanced Aquifer Remediation (SEAR)

SEAR was developed as a way to improve NAPL removal using surfactants to increase the solubility and mobility of the NAPL. Surfactants are amphiphilic molecules and thus can be soluble in both water and oil and help improve the solubility of the NAPL in water. SEAR is just an improvement to the pump-and-treat method in which a surfactant solution is injected at an injection point and removed at an extraction point; several injection and extraction wells can be used to cover the contaminated site. When SEAR is used, a water flood is first applied to remove the easily recoverable NAPL. The surfactant solution is then injected to recover the NAPL trapped by capillary forces. A post water flood is later applied to remove the surfactant solution and the solubilized or mobilized NAPL remaining. The surfactant solution recovered can be used for reinjection [10].

SEAR works either by increasing the solubility of NAPL in the water by enhancing solubilization or by reducing the IFT between the NAPL and water for removal by mobilization. Mobilization has proven to remove more NAPL in less time, but it has a greater risk of uncontrolled NAPL movement as its being displaced by the surfactant solution. Using a mobilization flood thus requires the presence of an aquitard that can prevent a vertical NAPL migration. If this barrier is thin or inexistent, the surfactant solution should be designed to solubilize the contaminant. It is important to determine which one of the two methods is appropriate for a particular site. The solubilization properties of the surfactant can be increased by adding a cosolvent. However, cosolvents are avoided because they may complicate wastewater treatment, and cosurfactants are used as substitutes for cosolvents [10].

Before SEAR can be applied to a specific site, it is required to conduct a feasibility control to determine if SEAR can be applied. The feasibility analysis includes effectiveness, aquifer heterogeneity, permeability and capillary barrier considerations, contaminant viscosity, implementability, technology maturity and prior applications, regulatory/permitting issues, health and safety issues, and cost [10].

In the case of DNAPL, if SEAR is found applicable to a site after the feasibility analysis, the first step is to conduct a DNAPL source zone characterization. This step is important because it provides an understanding of the in situ conditions necessary for SEAR system design. The two purposes of the characterization are to determine how the DNAPL is distributed in the subsurface and to quantify the properties that will affect the application and design of SEAR fluids in the subsurface. The aquifer also needs to be characterized in order to test the sustainable injection and extraction rates for the aquifer and the wells [10].

The next step, and the focus of this work, is the selection of the appropriate surfactant system for the remediation. At locations where no capillary forces exist, solubilization is the preferred mode SEAR application. The surfactant solution enhances solubilization by forming micelles (Type I microemulsions) and thus increasing the solubility of the organic solvents in water; surfactants used in this case need to be hydrophilic. When capillary forces exist, the IFT of the NAPL and water needs to be reduced, and mobilization becomes the preferred SEAR application mode. For mobilization of the NAPL to be possible, the surfactant system selected needs to be equally soluble in the water and NAPL phase to form a Type III microemulsion.

The surfactant system for a SEAR application needs to have minimal propensity to form liquid crystals, gels, or macroemulsions, have a rapid coalescence, a high contaminant solubilization or mobilization, be environmentally acceptable and biodegradable, have a low adsorption on soils, have a low critical micelle concentration (CMC), a low Krafft temperature and be recyclable. Liquid crystals, gels, and macroemulsions can plug pores, reduce aquifer permeability and prevent transport through the aquifer; they can be avoided by using a mixture of surfactants or a surfactant with a branched hydrophobic tail. Also, the purpose of SEAR being to remove contaminants from groundwater, it would be counterintuitive to use a surfactant system that will in turn constitute a new source of contamination. That's why it is important to select surfactants that biodegrade quickly but not too rapidly. It is also important to take into account the adsorption of the surfactant system. Sorption can cause substantial losses of surfactant and reduce its performance. Anionic surfactants are preferred for SEAR applications because the negative charge of the surfactant head repels the negative charges of the soil surfaces to minimize surfactant loss due to sorption [7, 10]. It is requiring to have a low CMC for the surfactant system because it decreases the amount of surfactant that needs to be used and hence decreasing the overall cost of the project. Finally, a low krafft temperature increases the ground water temperature range over which the surfactant system can be used. The focus of this work is to make sure that the surfactant systems meet all the criteria above.

Phase Behavior Correlations

As mentioned in the introduction, the surfactant system used for mobilization in SEAR applications needs to be able to form Type III microemulsions with the NAPL-groundwater system. A microemulsion is a thermodynamically stable dispersion made of water, oil, and surfactant with particles of 10-100 nm [11]. Microemulsions can either be oil-in water (Winsor Type I), water in oil (Winsor Type II) or both (Winsor Type III). In a Type III microemulsion, the surfactant is equally soluble in the water and oil phases and a separate middle phase is formed; the middle phase contains the surfactant and equal volumes of solubilized oil and water. Initially, the correlation between microemulsions and related system was based on phase behavior studies. However, this method being tedious and time consuming, researchers have developed empirical correlations to predict microemulsion types and properties [12]. These correlations include the Winsor R-ratio, the hydrophilic-lipophilic balance (HLB), the phase inversion temperature (PIT), and the hydrophilic-lipophilic deviation (HLD).

Winsor introduced the R-ratio:

$$R = \frac{A_{CO}}{A_{CW}} \quad \text{(Equation 1)}$$

Where A_{CO} represents the interactions between the surfactant adsorbed at the interface and the oil phase per unit area of interface and A_{CW} indicates the interactions between the surfactant adsorbed at the interface and the water phase per unit area (see Figure 3). When $R < 1$, an oil in water microemulsion is formed, when $R > 1$ a water in oil microemulsion is formed. When $R = 1$, the surfactant system interacts equally with the oil and water phases and a Type III microemulsion is formed; the interfacial tension reaches a minimum and the solubilization reaches a maximum [13].

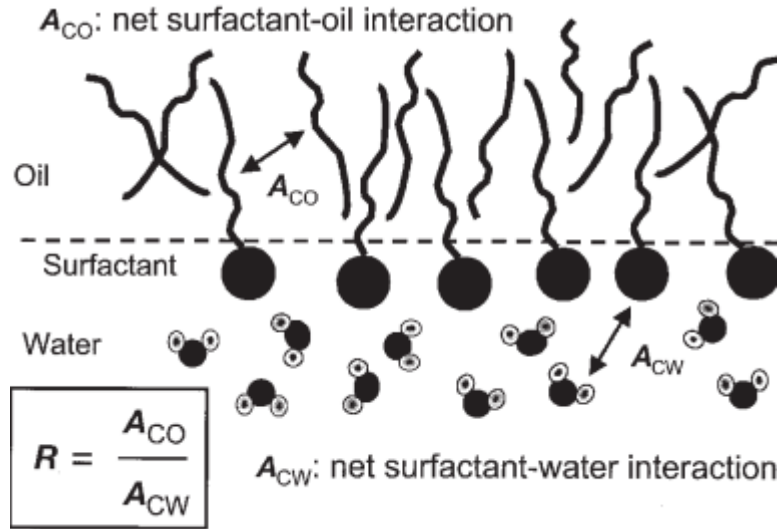


Figure 3: Illustration of Adsorbed Surfactant Interactions [13]

An example of a way to observe the transition from $R < 1$ to $R > 1$, is by doing a salinity scan. A salinity scan is a phase behavior scan where all the parameters (composition, temperature...) are kept constant except for salinity. When the salinity is increased from $R < 1$ to $R > 1$, it changes the phase behavior from a Winsor Type I to a Winsor Type II with an intermediate Type III phase behavior at $R = 1$ [14].

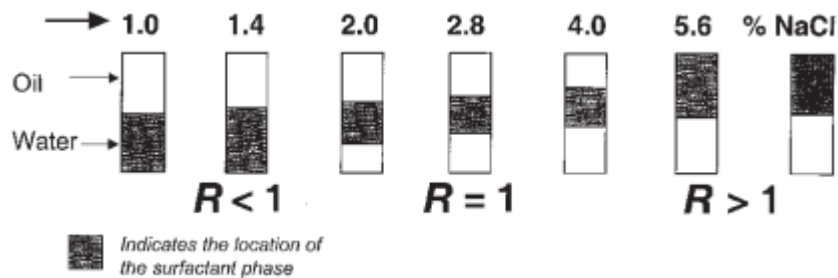


Figure 4: Phase behavior along a salinity scan [13]

However, forming a middle phase microemulsion is not as easy as forming micelles. It requires that the surfactant be equally soluble in the oil and water phases. This requirement is usually not met with a one surfactant system and requires the use of a

mixture of surfactants, a cosurfactant (e.g., alcohol), a hydrophilic and/or lipophilic linker.

Another method used to characterize microemulsions is the HLB method. It is a number between 0-40 that indicates the emulsifying behavior and is related to the balance between the hydrophilic and lipophilic portions of the surfactant. The HLB number is either calculated based on the structure of the molecule or experimental emulsification data; similar numbers are also assigned to substances frequently emulsified based on their emulsification experience. An emulsifying agent is thus chosen so that its HLB number matches the number of the substances to be emulsified. Materials with high HLB numbers are oil in water emulsifiers and those with low HLB numbers are water in oil emulsifier [11].

The phase inversion temperature (PIT) is another model developed for non-ionic surfactants. The PIT is the temperature at which an emulsion of non-ionic surfactant (or surfactant-cosurfactant mixture), oil and water switches from one Type to another. This method applies only to emulsions that show inversion at a particular temperature [11].

The methods described above are all practically limited. The Winsor R ratio is very difficult to estimate because there are many different variables that can alter the R value [13]. And the HLB method does not take into account the change of the HLB number with changes in the emulsification conditions (temperature, nature of the oil and water phases, presence of additives...) [11]. The HLD method, developed by Salager et al.[15], overcomes the limitations of these methods by taking into account the oil type, the aqueous phase salinity, the surfactant characteristics, the temperature of the system and the presence of additives. There are two forms of the HLD equation, one for ionic and

another one for non-ionic surfactants. Since the surfactants used in this work are anionic, the form of the HLD equation used is:

$$HLD = C_c + \ln(S) - k(EACN) - f(A) - \alpha(\Delta T) \quad (\text{Equation 2})$$

Where C_c is the characteristic curvature of the surfactant (surfactant hydrophobicity), S is the salinity of the aqueous phase in grams of NaCl per 100 ml, k is specific to the surfactant head group, $EACN$ is the equivalent alkane carbon number of the oil, $f(A)$ is a function of the alcohol type and concentration, α is a temperature constant and ΔT is the difference between the formulation temperature and the reference temperature (25°C). The signs indicate the way in which each variable alters the formulation and the values of the coefficients provide a way to evaluate the quantitative effect of those variables [13]. The HLD method can be related to the Winsor R ratio; a negative HLD value is equivalent to $R < 1$ and corresponds to an oil in water type microemulsion (Type I), a positive HLD value corresponds to $R > 1$ and indicates a water in oil (Type II) microemulsion. When the HLD value is Zero, a middle phase (Type III) microemulsion is formed equivalent to $R = 1$. The salinity at which a Type III microemulsion is formed is called the optimum salinity, S^* . The characteristic curvature reflects the tendency of the surfactant to form micelles (negative values of C_c) or reverse micelles (positive values of C_c) [9].

The C_c and k values of a surfactant are determined using a salinity scan like the one depicted in Figure. 4. To do so, the scan is usually done at the reference temperature, $T = T_{ref} = 25^\circ\text{C}$, when no alcohol is used ($f(A) = 0$) and for the optimum conditions HLD is zero and the salinity is S^* . The HLD equation, for a single surfactant system, can be rewritten as:

$$\ln(S^*) = K(EACN) - Cc \quad \text{Equation 3}$$

When a surfactant can form a middle phase microemulsion with a wide range of oils, its k and Cc values can be determined using Equation 3. By plotting $\ln(S^*)$ vs. $EACN$, the k and Cc values can be determined from the slope and the intercept of the resulting graph, respectively. However, some surfactants with long alkyl chains may form gels or liquid crystals with various oil phases which makes it difficult, and sometimes impossible, to observe the middle phase microemulsion and thus difficult to estimate the HLD parameters (k and Cc). Acosta et al.[9] proposed a linear surfactant mixing rule to be applied when situations like that arise. The linear mixing rule consists of mixing the surfactant of interest with a reference surfactant (k and Cc values are known) in which case a clear middle phase can form and the HLD parameters of the surfactant of interest can be easily estimated [16]. Equation 3 can be rewritten in the form of the linear mixing rule:

$$\ln(S_{mix}^*) = K_{mix}(EACN) - C_{c_{mix}} \quad \text{(Equation 4)}$$

Where:

$$\ln(S_{mix}^*) = \sum x_i \ln S_i^* \quad \text{(Equation 5)}$$

$$K_{mix} = \sum x_i K_i \quad \text{(Equation 6)}$$

$$C_{c_{mix}} = \sum x_i C_{c_i} \quad \text{(Equation 7)}$$

x_i is the mole fraction of surfactant i .

The k and Cc of the surfactant of interest can then be obtained from a plot of $\ln(S_{mix}^*)$ vs. $EACN$, knowing the k and Cc of the reference surfactant. The method used for finding the HLD parameters in this work is different from Acosta's method because the latter was found to have some limitations. Amongst those limitations, the Acosta method assumes a constant k value for surfactants with the same head group; however subsequent research

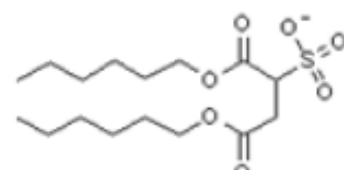
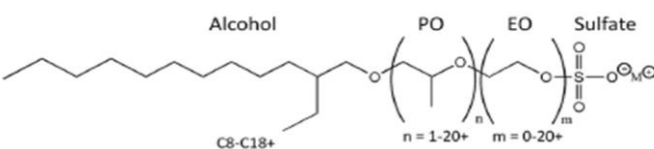
refuted that assumption. The HLD parameters determined in this work will be compared to the values previously obtained using Acosta's method. They will also be used to calculate the HLD of the three system formulations as way to determine the accuracy of the HLD method to predict middle phase microemulsion systems.

Chapter 3: Experimental Section

Materials

The surfactants used in this work are AOT, SDBS, Calfax 16L-35, Taiwan, Sodium dihexyl sulfosuccinate (AMA), and Alfoterra 8-41s. Alfoterra 8-41s is an extended surfactant with 8 carbon alkyl chain, 4 PO groups and 1 EO group. The general structure of Alfoterra surfactants and the structure of AMA can be found in Table 1.

Table 1: Molecular structure of AMA and Alfoterra surfactants

| Surfactant | Structure |
|-----------------------|--|
| AMA |  |
| Alfoterra Surfactants |  <p style="text-align: center;">General structure of ALFOTERRA® Surfactant</p> |

Detailed information of the surfactants used in this study can be found in Table 2.

Table 2: Surfactant properties

| Name | Supplier | MW (g/mol) | Activity (%) |
|---|------------------------|------------|--------------|
| AOT (Dioctyl sulfosuccinate) | Lewis Chemical Company | 444.56 | 75 |
| Calfax 16L-35 | Brainerd Chemical Co | 408 | 35 |
| SDBS (Sodium dodecyl benzene sulfonate) | Stephan Co | 348 | 35 |
| Taiwan surfactant | Taiwan Surfactant | 475.3 | 54.4 |
| AMA (Dihexyl sulfosuccinate) | Sigma Aldrich | 388 | 80 |
| Alfoterra 8-41s | Sasol | 507 | 32.2 |

Hexane (95%), Octane (>99%), Decane (>99%) are used as the oil phases in this work and were purchased from Sigma Aldrich. Sodium Chloride (>99%) was purchased from Sigma Aldrich. Methanol (>99.0%) was purchased from Alfa Aesar. Calcium chloride dehydrate (>99.9 %) was also used and was provided by JT Baker.

The F-95 grade Ottawa sand used as an ideal sand in the column studies was provided by US Silica, Mill Creek, OK and the Canadian River Alluvium, used as non-ideal sand, was obtained from the Canadian River at a depth of three feet. The site was accessed through the Haskell Lemon Asphalt plant in Norman, Ok.

Methods

Microemulsion Phase Study

Microemulsion phase studies were conducted for the octane and tap water system that were used in place of site specific NAPL and aqueous phases. The aqueous phase contains water, surfactant/s and salt. A salinity scan, a phase behavior scan in which all components (surfactant concentration, surfactant/cosurfactant ratio, temperature) except the salinity are held constant, is conducted to find the optimum salinity for each system. 5 ml of aqueous phase, and 5 ml of oil phase are added to a 15 ml flat bottom test tube, hand shaken once a day for three days and left to equilibrium at least three days at room temperature. The aqueous phase is prepared first, and the meniscus is marked before the oil phase is added; the oil phase is then added using Eppendorf pipettes. After equilibrium, the results are visually interpreted as Type I, II, or III. The salinity of the sample with equal amounts of oil and water solubilized is determined as the “optimum salinity”, S^* , for that water/oil system. For all the three surfactant systems used, the total surfactant concentration was kept at 0.94 wt. %.

Similar salinity scans were conducted to find the k and C_c of the surfactants of interest. The procedure is the same as above except that in this case deionized water was used as the aqueous phase and three oil phases were used: hexane, octane and decane. Once the optimum salinities for each oil phase were determined, they were plotted against EACN to find the k and C_c of the surfactant of interest. For the Taiwan surfactant, a single surfactant system was used because it is capable of forming a middle phase microemulsion by itself and Equation 3 was used to find the HLD parameters. A linear mixing rule was used to find the parameters for AOT, Calfax 16L-35, and SDBS through Equation 4 with Alfoterra 8-41s as the reference surfactant. The total surfactant concentration for all the studies were kept at 0.07M.

Coalescence rates

To determine coalescence rates, Type III microemulsion systems were agitated and observed. The coalescence time is defined as the point where the three phases, water, oil and middle phase, are clearly visible even if the oil and/or water is still opaque.

Equilibrium IFT measurements

The IFT of the equilibrated samples was measured using a spinning drop tensiometer (M6500 Grace Instrument, Houston, Texas). A capillary tube was prefilled with the aqueous phase and 1-3 μL of oil phase was injected into the center of tube positioned horizontally in the designed compartment of the tensiometer. The tensiometer was set at 4000 RPM and the first measurement was taken 10-15 min after spinning. Measurements are then taken every 5 min until the readings were within $\pm 3\%$. The temperature of the sample compartment was maintained at 70°C using an ice pack.

Stability Studies

Stability studies of the surfactant systems were conducted to determine possible phase separation or precipitation at different calcium concentrations. Stability was studied by creating 5 ml of aqueous phase solutions in 15 ml flat bottom test tubes with calcium chloride concentrations from 50 to 500 ppm. The samples were kept at room temperature and observed daily for 7 days.

One-dimensional Sand pack tests

One-dimensional sand pack tests were used to conduct dynamic adsorption and oil recovery studies. Figure 5 shows the configuration of the system used for both studies. The glass chromatography column, 6 inches long and 1 inch in diameter, was packed with sand. F-95 grade Ottawa sand and Canadian River Alluvium (CRA) were used in this study. The dimensions of the sand pack were 1-inch-long and 1 inch in diameter. The peristaltic pump was used to inject liquids into the column using an injection line connected to a pressure gauge that measures the pressure drop across the column. The sample collector was used to collect the effluent liquid from the column. The fluid injection rate was kept at 0.3 ml/min for all the studies.

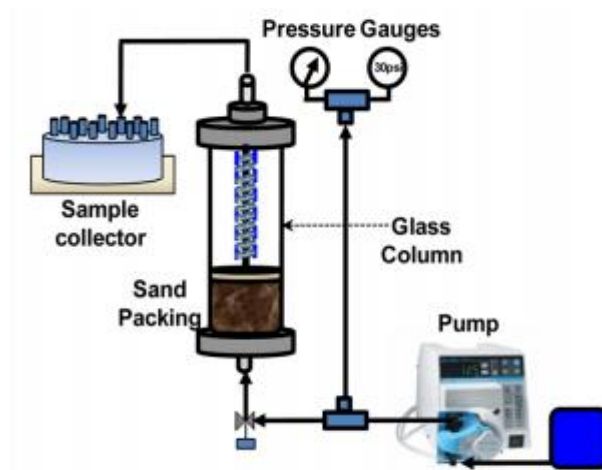


Figure 5: Configuration used for Sand Pack Tests

After the column is packed, tap water containing NaCl at the same salinity as the surfactant solution is pumped through the column until the soil is saturated. Two to three pore volumes of water were collected in a graduated cylinder before the sample collector is turned on. For the dynamic adsorption studies, one pore volume of surfactant solution was injected after the sample collector was turned on followed by 8-10 pore volumes of post water flush. The sample collector was set to collect half a pore volume per test tube. The samples were then analyzed using high performance liquid chromatography (HPLC). For the oil recovery studies, one pore volume of tap water was collected after the sample collector was turned on and before the oil injection. Then, about one milliliter (20% saturation) of oil is injected in the column followed by two pore volumes of tap water containing NaCl. One pore volume of the surfactant solution was then injected followed by a post-water flush until the exiting liquid is free of oil. The sample collector was set to collect one pore volume per test tube. At the end of the experiment, ten grams of soil was collected and mixed with ten millimeter of methanol. The sample was mixed for about 24 h, and the methanol was recovered and analyzed using an HP 5890 series II GC.

Chapter 4: Results and Discussion

Phase Behavior, IFT measurements and Coalescence rates

Table 3 summarized the three systems used in this paper and their compositions:

Table 3: Surfactant systems compositions

| | System 1 | | System 2 | | System 3 |
|--------------------|----------|---------------|----------|------|-------------------|
| Surfactants | AOT | Calfax 16L-35 | AOT | SDBS | Taiwan surfactant |
| Composition (wt.%) | 0.75 | 0.19 | 0.75 | 0.19 | 0.94 |

Phase behavior studies were conducted to determine the optimum salinity of the three systems with tap water and octane at room temperature. Figure 6 shows the salinity scans for all three systems. The small lines visible on the samples were drawn to indicate the level of surfactant aqueous phase before adding the octane. These lines appear to be in the center of the middle phase when Type III microemulsions are formed; they make it easier to visually determine the optimum salinity. As can be observed, the optimum salinity for Systems 1 and 3 are not easily determined visually because these two systems appear to form Type III microemulsions at more than one salinity. System 2 however, forms a Type III microemulsion at 0.7 wt.% salt, which is therefore the optimum salinity of the system. It is observed on Figure 6 that increasing the NaCl concentration shifts the microemulsion from Type I-III-II. This behavior can be explained using the Winsor R ratio (Equation 1); at the low salt concentration the A_{cw} , surfactant-water interactions are stronger than the A_{co} , surfactant-oil interactions, and a Type I microemulsion is formed because the surfactant is more soluble in water. As the salt concentration is increased, the A_{cw} is decreased; when a certain salinity is reached, the surfactant has an equal affinity to

the oil and water phases and a Type III microemulsion is formed. Eventually, the A_{co} become stronger than the A_{cw} and a Type II microemulsion is formed.

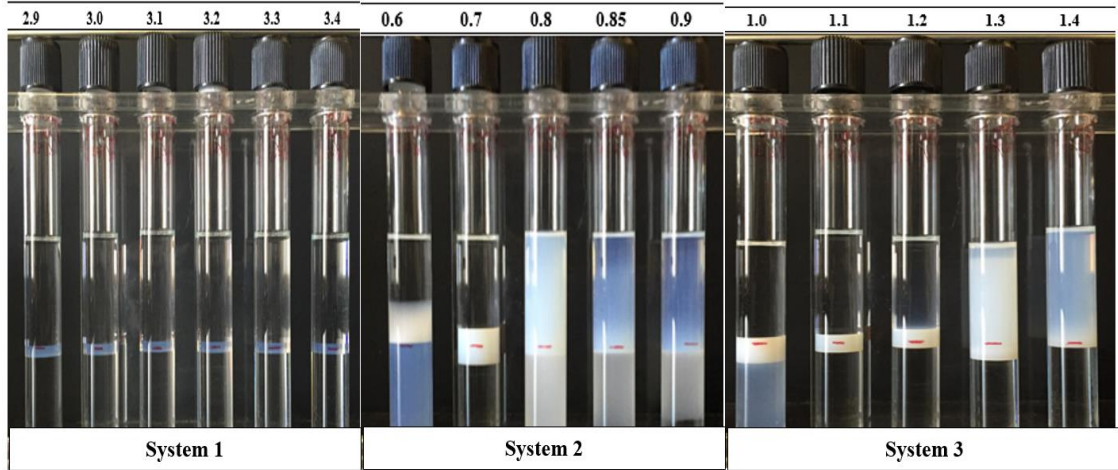


Figure 6: Phase behavior scans for Systems 1, 2, and 3

In order to find the optimum salinities for Systems 1 and 3, the interfacial tensions of some of the samples were measured. At the optimal salinity, the surfactant solubilizes an equal amount of water and oil and migrates in the middle because it is denser than oil but lighter than water. At those conditions, the IFT is minimized at the interface between the oil and water phase [16]. The IFT measurement data for Systems 1 and 3 as a function of salinity are shown in Table 4; notice that only two IFT measurements are taken for system 3, at 1.1 and 1.2 wt.% salinity because only these two samples show a middle phase microemulsion on Figure 6.

Table 4: IFT measurements for selected Systems 1 and 3 samples

| | NaCl (wt.%) | IFT (NM/m) |
|----------|-------------|-----------------|
| System 3 | 1.1 | 2.10E-03 |
| | 1.2 | 6.47E-03 |
| System 1 | 3 | 1.40E-02 |
| | 3.1 | 4.46E-03 |
| | 3.2 | 3.18E-02 |

Table 5 summarizes the optimum salinities along with the optimum coalescence times and optimum IFT values for the three systems.

Table 5: Salinity, IFT measurements, and coalescence rates at optimum conditions for each surfactant system

| Systems | Optimum Salinities, wt% NaCl | Optimal IFT | Coalescence time, minutes |
|---------|------------------------------|-------------|---------------------------|
| 1 | 3.1 | 4.46E-03 | <1 |
| 2 | 0.7 | 7.14E-03 | <5 |
| 3 | 1.1 | 2.10E-03 | <6 |

Table 5 shows that all three systems have ultralow IFTs ($<10^{-2}$ mN/m) at the optimal points and coalescence rates less than 30 min. This behavior shows that all three systems satisfy the requirement of high solubilization required for a SEAR application. However, the optimum salinity for System 1 exceeds the 1 g NaCl/100 ml requirement for this project; this system appears to be too hydrophilic. There are several reasons why high salinity is not desired for this project. First, it contaminates the groundwater since high salinity means high concentration of sodium and chloride ions that may remain in the water table after treatment. The second reason is that it increases the adsorption of the surfactant on the soil. The presence of sodium ions decreases the repulsion between the surfactant head groups and the soil surface thus increasing the adsorption of the surfactant [11]. The last reason is that a high salt concentration increases the density of the surfactant solution which can cause it to sink at the bottom of the aquifer. However, for the purposes of this project it is imperative for the surfactant to float above the water table reason why the maximum salt concentration used cannot exceed 2 g NaCl/100 ml.

According to Salager et al. [13], high solubilization means a more solubilized phase per solubilizing surfactant which increases the opacity of the middle phase. Thus, contrary to the early definitions, a good microemulsion is not transparent at all. Looking at Figure 6,

System 1 produces a very translucent middle phase whereas Systems 2 and 3 produce very opaque middle phases. Based on the definition provided above for a good microemulsion, System 2 and 3 have higher solubilization capacity than System 1. It can thus be hypothesized that these two systems will provide better oil recoveries than System 1. The sand pack experiments results will be used to confirm this hypothesis.

Surfactant Stability

The stability of the three surfactant systems was studied at room temperature (~ 23°C) with calcium chloride concentrations ranging from 50 to 500 ppm. Sodium chloride was also added to the samples in the concentration determined previously at the optimum salinity. The results are summarized in Table 6:

Table 6: Days for separation at room temperature for the three systems with different calcium chloride concentrations

| Days for separation at room temperature | | | |
|--|-----------------|-----------------|-----------------|
| PPM Calcium | System 1 | System 2 | System 3 |
| 50 | 3 | 7+ | 7+ |
| 100 | 3 | 7+ | 7+ |
| 200 | 3 | 4 | 7+ |
| 300 | 3 | 3 | 3 |
| 400 | 3 | 1 | 3 |
| 500 | - | 1 | 3 |

The conclusion that can be drawn from these results is that System 3 is the most stable of the three systems. Under 200 ppm calcium, this system can stay stable over seven days and three days when the calcium concentration is between 300 and 500 ppm. System 2 is slightly more sensitive to calcium than System 3. It is stable over seven days when the calcium concentration is under 100 ppm but above 400 ppm it is stable for about a day. Lastly, System 1 appears to be the more sensitive to calcium than the other two systems

under 200 ppm. However, between 300 and 400 ppm it has the same stability as System 3. Furthermore, for System 1 it was impossible to form a clear/single phase at 500 ppm calcium; the solution formed a coacervate immediately after it was made. Precipitation was observed for Systems 2 and 3 and phase separation for System 1.

Sand Pack Experiments

Oil Mobilization in Sand Packs

The column studies are used to evaluate the oil mobilization capacity of the three systems at the optimized formulations. The experiments were conducted at room temperature on two different types of sand; Ottawa and Canadian River Alluvium (CRA). Ottawa sand is considered to be a more ideal sand and thus should provide higher oil recoveries than CRA. The results below will discuss the accuracy of that prediction.

For the column studies with Ottawa sand, one pore volume (1 PV) was about 4.18 ml. 1 PV of surfactant solution, 0.94 wt.% total surfactant concentration, was used to displace 0.84 ml (20% saturation) of oil phase. The aqueous phase is tap water and the oil phase used is octane. Table 7 shows the cumulative oil recoveries obtained for the three surfactant systems.

Table 7: Description of oil mobilization tests for the three systems on Ottawa sand

| System | NaCl (wt%) | Mass of sand used (g) | Initial oil concentration (mg/kg of sand) | Final oil concentration (mg/kg of sand) | Cumulative oil recovery (%) |
|---------------|-------------------|------------------------------|--|--|------------------------------------|
| 1 | 3.1 | 23.2 | 36183 | 1554 | 95.7 |
| 2 | 0.7 | 22.6 | 37189 | 121 | 99.7 |
| 3 | 1.1 | 22.8 | 36824 | 579 | 98.4 |

Overall, all three systems provide very good oil recovery. System 2 gave the highest oil recovery followed by system 3. As hypothesized, System 1 gave the lowest recovery most likely due to the lower solubilization capacity of this system. The total surfactant

concentration used is the same for all three systems, however, System 1 appears to solubilize less oil than the other two systems. The reason may be related to the CMC of these systems; if System 1 has a higher CMC than the other two systems then at the same surfactant concentration it will solubilize less oil. The CMC of the systems need to be determined to confirm that statement.

The results for the oil recovery studies with CRA sand are provided in Table 8. The total surfactant concentration is also 0.94 wt.% but one pore volume was about 4.7 ml. The 20% oil saturation corresponds to 0.94 ml of oil.

Table 8: Description of oil mobilization tests for the three systems on CRA sand

| System | NaCl (wt.%) | Mass of sand used (g) | Initial oil concentration (mg/kg of sand) | Final oil concentration (mg/kg of sand) | Cumulative oil recovery (%) |
|--------|-------------|-----------------------|---|---|-----------------------------|
| 1 | 3.1 | 20.6 | 45109 | 1763 | 96.1 |
| 2 | 0.7 | 21.5 | 43232 | 543 | 98.7 |
| 3 | 1.1 | 20.9 | 44410 | 338 | 99.2 |

The cumulative oil recovery for systems 1 and 3 on CRA sand are higher than on Ottawa sand which is opposite to the expected results. Only System 2 gave a lower oil recovery on CRA than on the Ottawa sand. The results of this study thus show that these surfactant systems can mobilize as much oil on a realistic sand like CRA as on an ideal sand like the Ottawa sand. The only difference observed was that in the case of CRA fine particles were coming out in the effluent from the column. This is due to the fact that CRA contains clays and fines particles that when in contact with the surfactant get washed out. Ottawa sand, on the other hand, is an ideal sand. It is composed of 99.8% silica and does not contain any clays or fine particles.

Dynamic Adsorption of Surfactant

Dynamic adsorption tests are conducted for all three systems on Ottawa and CRA sand. All the experiments were conducted using 0.94 wt.% total surfactant concentration under NaCl concentration corresponding to the optimum salinities in Table 5. One pore volume of surfactant solution was used corresponding to about 40 mg of total surfactant injection.

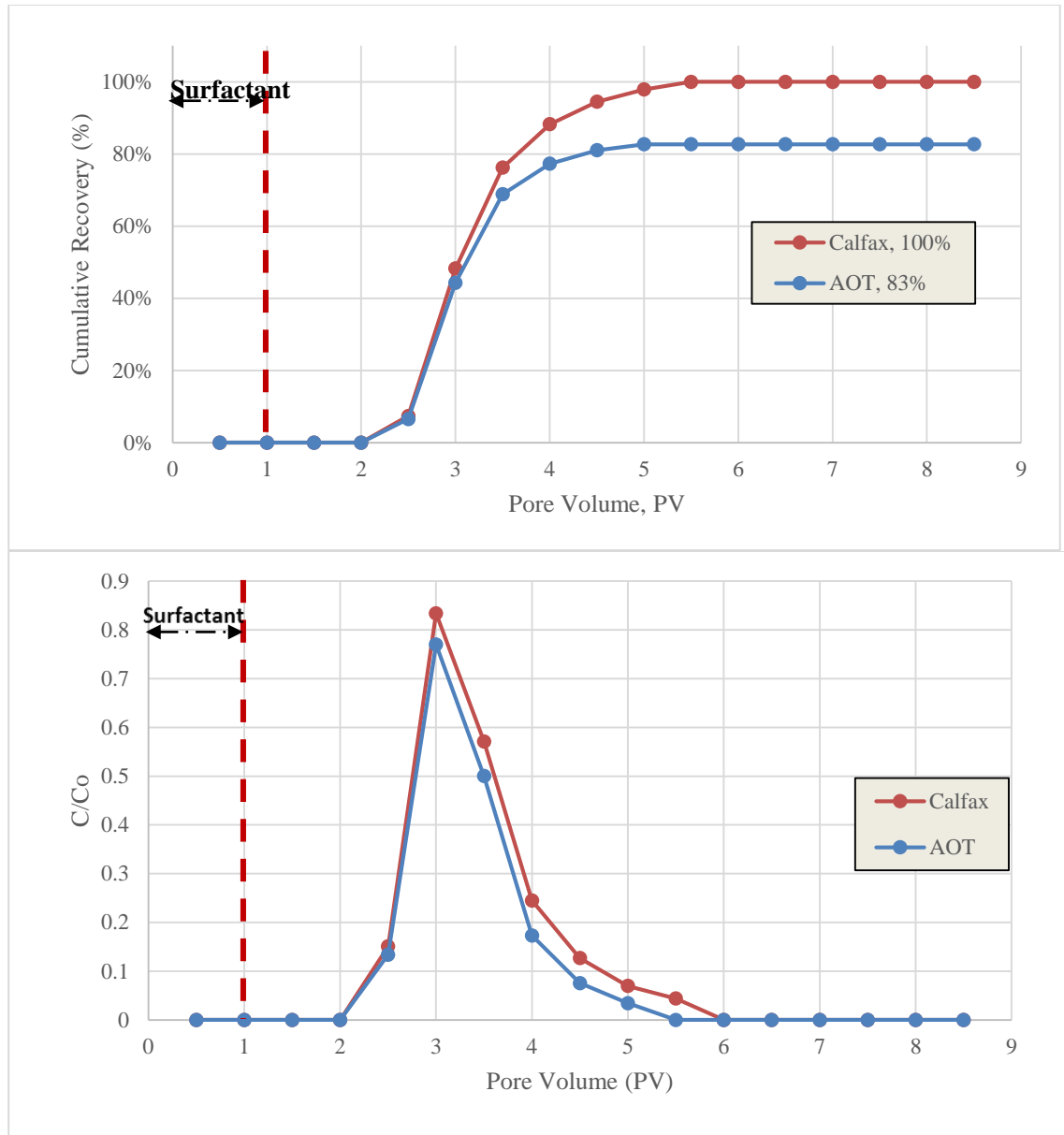


Figure 7: Analysis of adsorption tests samples for System 1 on Ottawa sand

Figure 7 shows the cumulative recovery and normalized concentration of System 1 on Ottawa sand. It can be observed that only AOT adsorbs on the sand, all of the Calfax 16L-35 is recovered. 17% of the total amount of AOT injected was lost on the sand which corresponds to 0.23 mg/g of sand of total surfactant loss for System 1. The results of the dynamic adsorption test for Systems 2 and 3 are illustrated on Figures 8 and 9.

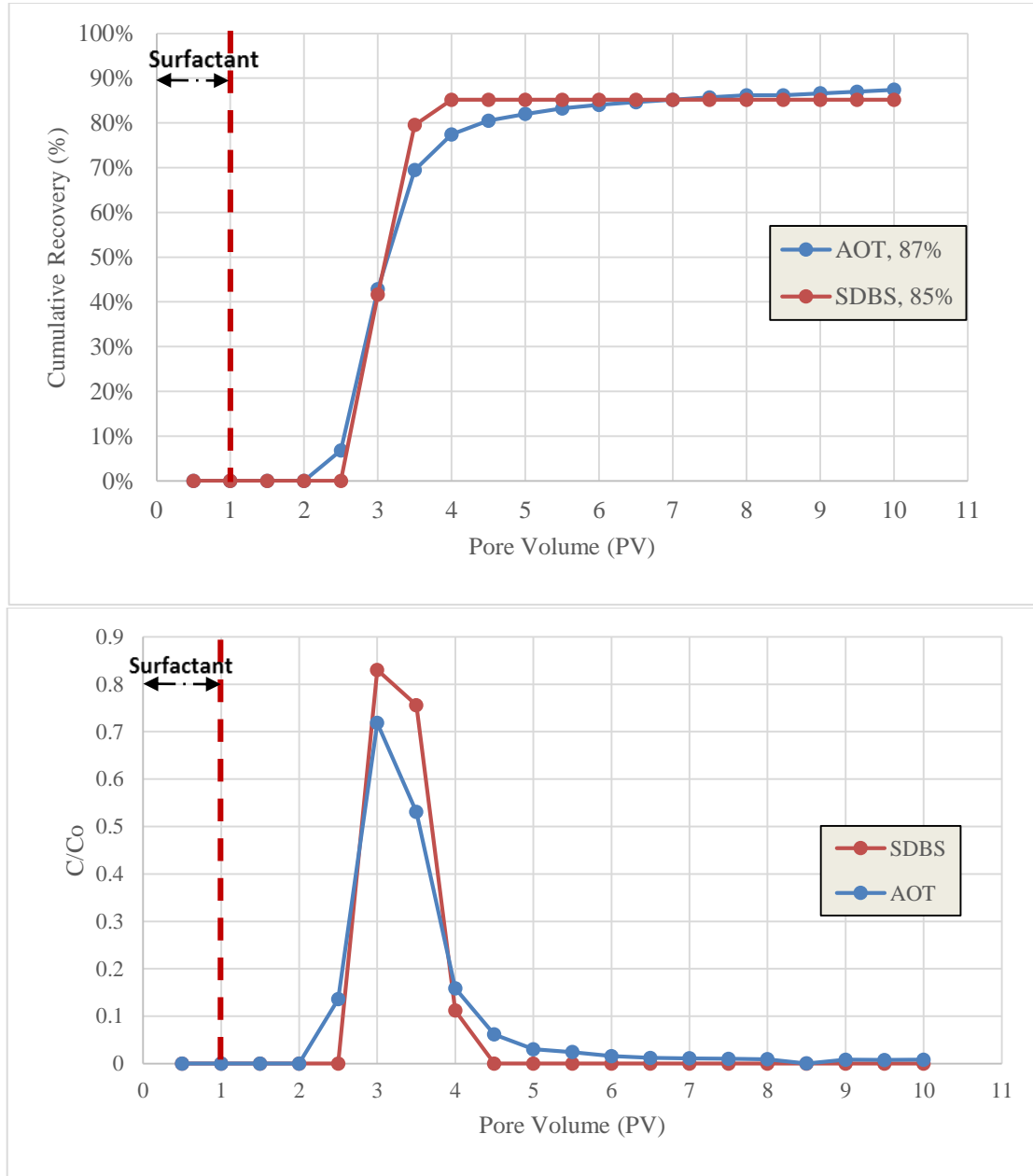


Figure 8: Analysis of adsorption tests samples for System 2 on Ottawa sand

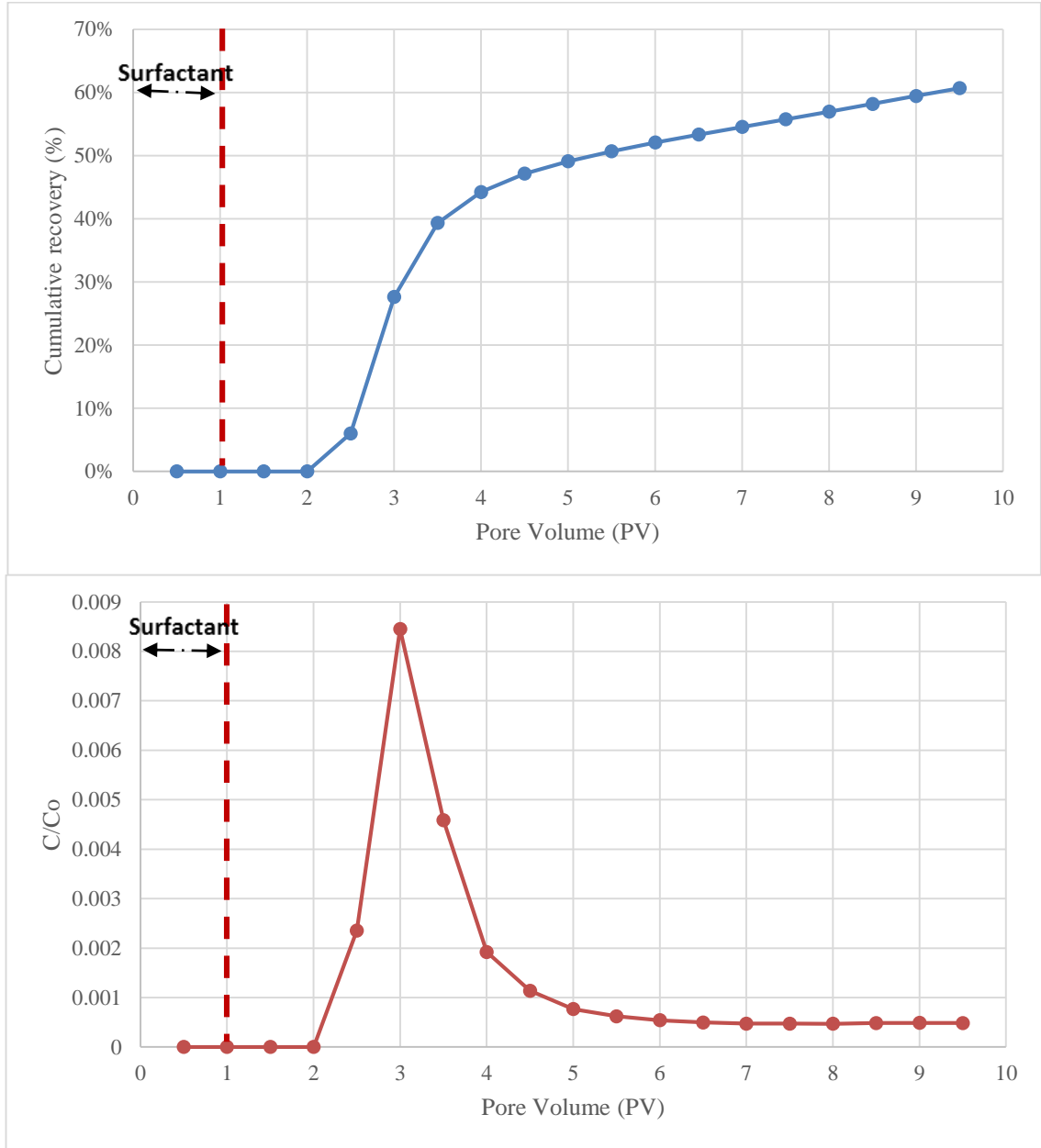


Figure 9: Analysis of adsorption tests samples for System 3 on Ottawa sand

Contrarily to System 1, in System 2 both surfactants were adsorbed at approximately the same percentage; 15% and 13% of the injected SDBS and AOT were lost on the sand respectively. The total amount of surfactant loss in System 2 was 0.23 mg/g of sand and is the same as the surfactant loss in System 1. System 3, on the other hand, had a much

higher surfactant adsorption than Systems 1 and 2. As can be observed of Figure 9 only 61% of the injected surfactant was recovered which corresponds to a surfactant loss of 0.67 mg/g of sand; about three times the amount loss for the other two systems. Taiwan surfactant contains AOT which has a low adsorption on sand, as can be seen from the results of System 1 and 2, so the high adsorption observed for System 3 may be due to the other two surfactants present in the Taiwan surfactant. Looking at Figure 9, it can be observed that the Taiwan surfactant may still be desorbing after the experiment was stopped. So, the amount of surfactant adsorbed may be slightly lower than calculated in this work.

Despite the relatively high adsorption of the Taiwan surfactant, all three surfactant systems have low adsorption on the Ottawa sand. These results show one of the advantages of using a low surfactant concentration (<1 wt.%); the total amount of surfactant used is already small which results in small surfactant losses even when most of the surfactant injected is adsorbed. Another possible explanation for these results is the amount of time the surfactant solution is in contact with the sand. The dynamic adsorption tests take about 2 to 3 hours to complete after the surfactant solution is injected, but previous research has shown that surfactants should be in contact with the soil for about 1 day for adsorption to reach completion [17, 18].

When the adsorption tests were performed on CRA sand, some of the sand was coming out with the surfactant solution similar to what was observed for the oil mobilization experiments. In order to analyze the samples, syringe filters with 0.45 micrometer pores were used to separate the solution from the sand. After analyzing the samples, two observations were made. First, not all the samples were able to be analyzed with the

HPLC probably due to the presence of some impurities. And second, the samples that were able to be analyzed had relatively low concentrations of surfactants in them. Those results were the same for all three surfactant systems.

The data obtained for the dynamic adsorption tests on CRA cannot be reported because they are incomplete and will most likely not reflect the actual amount of surfactant recovered in the samples. The concentration of surfactant in the samples analyzed were low because most of the surfactant coming out of the column is adsorbed on the soil that is also coming out. And when the samples are filtered some of the surfactant in the effluent liquid may also stay on the filters which increases the amount of error in the data. So, for the CRA sand, HPLC is not an accurate method to determine the amount of surfactant adsorbed. An alternative method that can analyze both the effluent liquid and soil from the column needs to be used. However, looking at the oil mobilization results we can speculate that the amount of surfactant lost on CRA sand is about the same or just slightly higher than on Ottawa sand since the oil recovery was about the same for both type of sands.

Determining the K and Cc parameters

The optimum salinities determined in this work were for a specific set of conditions (NAPL, temperature...). These conditions were just assumed for the purposes of this research. However, the NAPL, water phase electrolyte concentration, ground water temperature... will change from one site to the other; and the optimum salinity for each of those systems will change when the conditions change. It is thus important to have a correlation that will estimate the optimum salinity and decrease the time spent on phase behavior studies.

The HLD concept is considered to be the most practically applicable correlation to describe microemulsion systems [16] because it takes into account most of the parameters that affect the behavior of the surfactant system. The k and C_c are the key parameters that describe the hydrophilic-lipophilic nature of surfactants [12]. The k parameter depends on the hydrophilicity of the head group while the C_c corresponds to the hydrophobicity of the surfactant tail. In this work, the k and C_c parameters will be determined for the surfactants of interests using both a single anionic surfactant system and the linear mixing rule for two surfactant systems.

Taiwan Surfactant

The Taiwan surfactant is capable of forming a middle phase microemulsion with hexane, octane, and decane at room temperature and without the addition of alcohol or cosurfactant. A salinity scan was performed with a total surfactant concentration of 0.07M with the three oil phases mentioned above. The typical microemulsion phase transition is the same as the one observed on Figure 6. The optimum salinities (S^*) were determined by visual observation of the samples and using the coalescence rates. At the optimum formulation, the middle phase appears to have the same amount of solubilized oil and water and it has the fastest coalescence rate. Table 9 shows the S^* of the Taiwan-oil systems used. Using Equation 3, $\ln(S^*)$ versus EACN is plotted in Figure 10

Table 9: Optimal salinity of Taiwan surfactant with hexane, octane, and decane

| Oil | EACN | S^* (g/100 ml) |
|--------|------|------------------|
| Hexane | 6 | 1 |
| Octane | 8 | 1.6 |
| Decane | 10 | 2.1 |

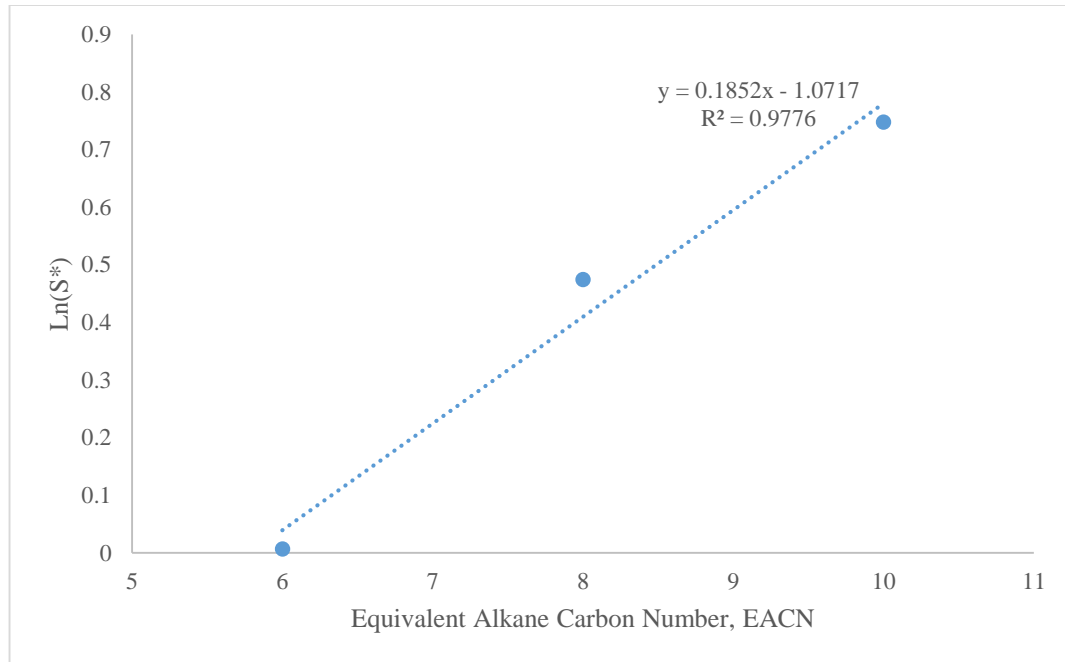


Figure 10: Plot of $\ln(S^*)$ Vs. EACN for the Taiwan surfactant

It is observed from Table 9 and Figure 10 that the optimum salinity increases with increasing oil EACN. This trend can be explained using the Winsor R ratio. When the EACN increases, the oil-oil interaction increases which decreases the interactions between the oil and surfactant molecules (A_{co}). To balance this effect, the A_{cw} is decreased by increasing the salt concentration.

Applying a linear regression model to the data plotted in Figure 10 gives the following equation:

$$\ln(S^*) = 0.1852 * EACN - 1.0717 \quad \text{(Equation 8)}$$

Comparing this equation to Equation 3, the slope and intercept correspond to the k and C_c values of the Taiwan surfactant respectively; 0.19 ± 0.03 and 1.07 ± 0.23 . The k value is higher than 0.17, which is the value assumed using Acosta's method. The C_c value is positive which means that the surfactant is hydrophobic and has a tendency to

form Type II microemulsions. To our knowledge, this is the first time the k and C_c of the Taiwan surfactant are reported in the literature.

Sodium Dodecyl Benzene Sulfonate (SDBS)

SDBS is not capable of forming a middle phase microemulsion by itself with the oils used in this study, so the linear mixing has to be used to find the HLD parameters for this surfactant. In this study, Alfoterra 8-41s is used as the reference surfactant. Alfoterra 8-41s is capable of forming a translucent middle phase microemulsion by itself with various oils, and when mixed with SDBS, a middle phase microemulsion is formed which makes it easier to determine the HLD parameters of SDBS. The k and C_c of Alfoterra 8-41s where previously determined to be 0.053 and -2.47 respectively [16].

Salinity scans were performed with a total surfactant concentration of 0.07M with hexane, octane, and decane as the oil phases. While the total surfactant concentration remained the same, three different salinity scans were performed with SDBS molar ratios of 30, 50, and 70 %. The reason for varying the molar ratios is to have more accurate values of k and C_c . The optimal salinities obtained for the different molar ratios of SDBS with the different oils are summarized in Table 10. Here also the optimum salinities are determine based on visual observation of the sample.

Table 10: Optimum salinity of the SDBS/Alfoterra 8-41s system with hexane, octane, and decane for different molar ratios of SDBS

| SDBS molar ratio, % | Hexane, S^*_{mix} | Octane, S^*_{mix} | Decane, S^*_{mix} |
|---------------------|---------------------|---------------------|---------------------|
| 30 | 15.1 | 17.8 | 19.5 |
| 50 | 14.3 | 16.8 | 18.5 |
| 70 | 13.7 | 16.3 | 18.0 |

In Table 10, it can be observed that the optimal salinities of the SDBS/Alfoterra 8-41s system decreases as the molar ratio of SDBS increases. This phenomenon can be explained by the fact that SDBS is less hydrophilic than Alfoterra 8-41s, thus increasing the ratio of SDBS decreases the overall hydrophilicity of the surfactant system which in turn decreases the amount of salt required for achieving a middle phase microemulsion. Even though the optimum salinities change when the molar ratios of the surfactants are changed, the k and C_c values are found based on linear regressions and thus should be the same regardless of the molar ratio of SDBS used. Figure 11 shows the plots of $\ln(S^*_{mix})$ versus EACN.

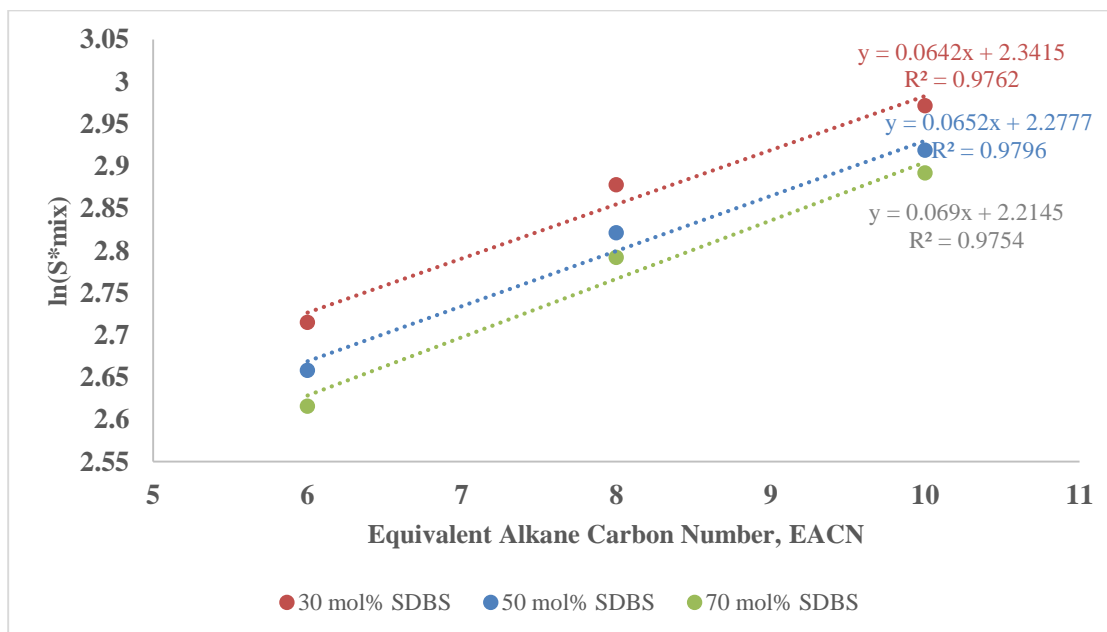


Figure 11: Plots of $\ln(S^*_{mix})$ Vs. EACN for the SDBS/Alfoterra 8-41s system

Applying Equation 4, the slope and intercept of the graphs correspond to the k_{mix} and $C_{c_{mix}}$ respectively. The k and C_c of SDBS can be calculated using Equations 7 and 8. Table 11 summarized the k_{mix} , $C_{c_{mix}}$ along with the k and C_c of SDBS calculated:

Table 11: Calculated k and Cc values of SDBS from experimentally determined values k_{mix} and C_{cmix}

| SDBS molar ratio, % | k_{mix} | C_{cmix} | k, SDBS | C_c , SDBS |
|---------------------|-----------|------------|---------|--------------|
| 30 | 0.064 | -2.34 | 0.09 | -2.04 |
| 50 | 0.065 | -2.28 | 0.08 | -2.09 |
| 70 | 0.069 | -2.21 | 0.08 | -2.11 |

Averaging the values in Table 11, the k and C_c of SDBS are found to be 0.08 ± 0.006 and -2.08 ± 0.03 respectively. The k value obtained in this case is significantly ($\sim 53\%$ lower) different from the 0.17 value assumed in Acosta's method. The C_c found in this case is also lower than the value found using Acosta's method; Steven Abbott [19] has a value of -0.9 for the C_c of SDBS.

AOT

AOT is also a surfactant that cannot form a middle phase microemulsion by itself. The same procedure used for SDBS is used to find the k and C_c of AOT in this work. Table 12 and Fig 12 show the salinities obtained for the different molar ratios of AOT with the different oils and the plots of $\ln(S^*_{mix})$ vs. EACN respectively.

Table 12: Optimum salinity of the AOT/Alfoterra 8-41s system with hexane, octane, and decane for different molar ratios of AOT

| AOT molar ratio, % | Hexane, S^*_{mix} | Octane, S^*_{mix} | Decane, S^*_{mix} |
|--------------------|---------------------|---------------------|---------------------|
| 30 | 9.2 | 11.2 | 13.1 |
| 50 | 4.8 | 6.3 | 7.65 |
| 70 | 1.7 | 2.4 | 3.4 |

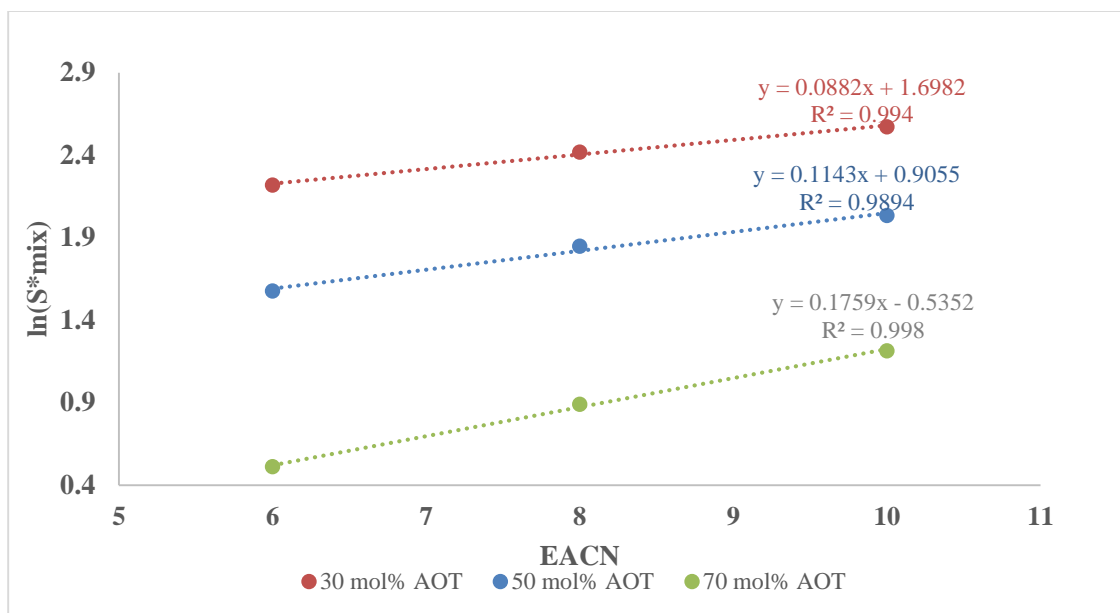


Figure 12: Plots of $\ln(S^*_{mix})$ Vs. EACN for the AOT/Alfoterra 8-41s system

Two observations can be made based on Table 12 and Figure 12. First the optimum salinities are much lower for the AOT/ Alfoterra 8-41s system than for the SDBS/Alfoterra 8-41s, and second the optimum salinities decrease is much more significant when the molar ratio of AOT increases than it did in the case of SDBS. These two results are due to the fact that AOT is a hydrophobic surfactant contrarily to SDBS which is hydrophilic; thus a surfactant system containing AOT will require less salt to reach the optimum than a system with SDBS would.

However as can be observed in Table 13, the k and C_c parameters for AOT change when the molar ratio of AOT/Alfoterra 8-41s changes.

Table 13: Calculated k and Cc values of AOT from experimentally determined values k_{mix} and C_{cmix}

| AOT molar ratio, % | k_{mix} | C_{cmix} | k, AOT | C_c , AOT |
|--------------------|-----------|------------|--------|-------------|
| 30 | 0.089 | -1.70 | 0.17 | 0.1 |
| 50 | 0.11 | -0.91 | 0.18 | 0.66 |
| 70 | 0.18 | 0.54 | 0.23 | 1.82 |

These results clearly show a limitation of the linear mixing rule because as mentioned above, the HLD parameters are constants and should not change, like observed in Table 13, when the molar ratios of the cosurfactants are changed.

In order to obtain the actual HLD parameters of AOT, the data in Table 13 are extrapolated to zero. Figure 13 shows the graph of C_c , AOT plotted against the molar ratio of Alfoterra 8-41s:

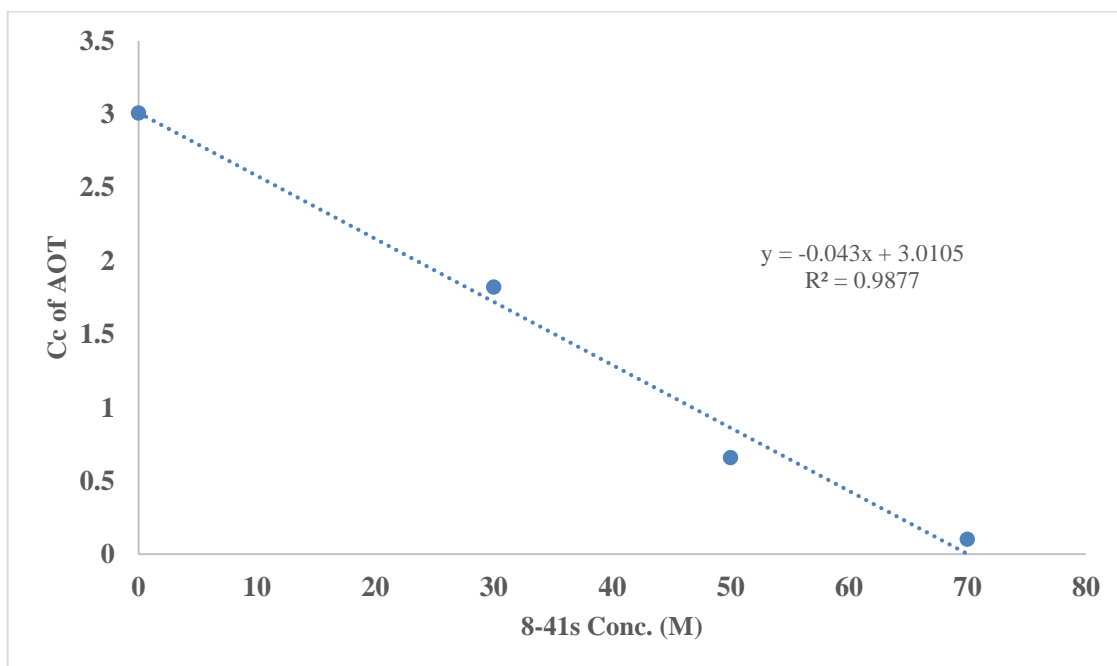


Figure 13: Plot of C_c (AOT) Vs. Conc. 8-41s

A linear regression applied to data plotted in Fig 13 gives the equation:

$$Cc(AOT) = -0.043 * (mol \% Alforterra\ 8 - 41s) + 3.0105 \quad (\text{Equation 9})$$

So when the molar ratio of Alforterra 8-41s is zero, the Cc of AOT is equal to 3.01.

Applying the same extrapolation to the k values in Table 13 gives a k of 0.27 for AOT.

The values obtained were double checked by using AMA as a reference with AOT. The experimental procedure was the same except only a molar ratio of 50 % AOT and 50% AMA was used. The k and Cc obtained in this case were 0.32 and 3.07 respectively; which are very close to values obtained with the Alforterra surfactant. Steven Abbott has a value of 2.55 for the Cc of AOT [19] using AMA as the reference surfactant and assuming a k of 0.17. Here again the experimentally determined k value differs significantly ($\sim 60\%$ *higher*) from the value assumed in Acosta's method.

The observation that can be made in this case is that the linear mixing rule is respected when AMA is used as the reference surfactant but not Alforterra 8-41s. A possible explanation is that the structures of the surfactants are the reason for this behavior. Looking back at the structures of AOT and AMA, it can be observed that both are dialkyls which means that the two surfactants mix relatively well together. However, Alforterra 8-41s has a long alkyl chain group so when it's combined with AOT, the two surfactants may not mix well at the oil/water interface. This observation may lead to a more general hypothesis that the linear mixing rule does not apply to mixtures of dialkyl and long chain alkyl surfactants.

Calfax 16L-35

The HLD parameters of Calfax 16L-35 also have to be determined using a reference surfactant. However, Calfax 16L-35 is a very hydrophilic surfactant, so using Alforterra 8-41s in this case will require a very high salinity to reach the optimum formulation

conditions. It is therefore not practical to use a hydrophilic surfactant to find the HLD parameters of Calfax 16L-35. The only hydrophobic surfactant, used in this study that can form a middle phase microemulsion by itself is the Taiwan surfactant. So, it will be used as the reference surfactant to find the k and C_c of Calfax 16L-35.

Salinity scans were conducted with a total surfactant concentration of 0.07M and a 30% molar ratio of Calfax 16L-35. For the Calfax 16L-35/Taiwan system, the optimum salinities were determined based on visual observation first then using IFT measurements. That's because the range of middle phases for this system were very broad and the coalescence rates were almost the same making it hard to accurately determine the optimum salinities visually. In Figure 14, the $\ln(S^*_{mix})$ was plotted against EACN for the values determined visually and those determined using IFT measurement. As can be observed, the values are slightly different in the two cases. The HLD parameters of Calfax 16L-35 are calculated based on the k_{mix} and $C_{c_{mix}}$ values obtained using the optimum salinities determined from IFT measurements because they are more accurate.

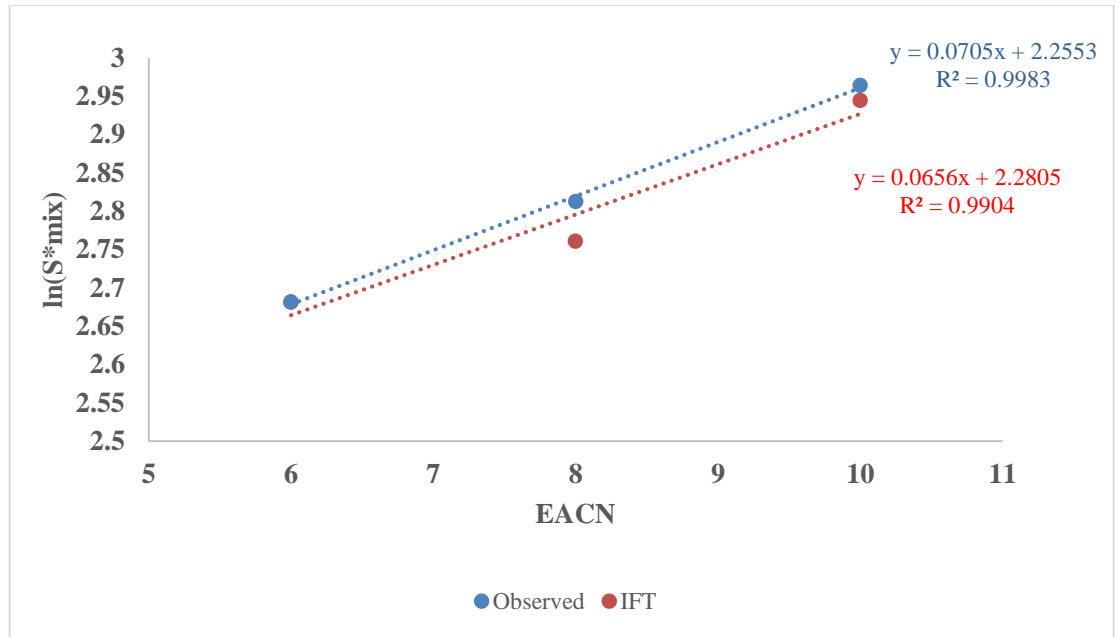


Figure 14: Plots of $\ln(S^*_{mix})$ Vs. EACN for the Calfax 16L-35/Taiwan system

Using the K and C_c previously determined for the Taiwan surfactant and the values of k_{mix} and $C_{c_{mix}}$ obtained from Figure 14, the k and C_c of Calfax 16L-35 calculated are -0.21 and -10.07 respectively. The C_c values is lower than the value of -6.9 determined by Donna Stacy [8] using Acosta's method. The k value found, however, does not make sense. Looking back at the HLD equation, a negative k value suggests that the optimum salinity decreases as the EACN of the oil increases. Such a trend would be impossible because increasing the EACN decreases the A_{c_o} which in turn calls for an increase in salinity to decrease the A_{c_w} .

We can speculate that these results may be due to the fact that the Taiwan surfactant is already a mixture of three different surfactants. Thus, a mixture of the Taiwan surfactant with Calfax 16L-35 may not follow the linear mixing rule.

Accuracy of the HLD Equation

The HLD parameters found in this work along with the values found in the literature, using Acosta’s method, are summarized in Table 14:

Table 14: Summary of experimental and literature values of k and Cc for the surfactants studied

| Surfactants | Experimental values | | Literature values | |
|---------------|---------------------|--------|-------------------|------|
| | k | Cc | k | Cc |
| AOT | 0.27 | 3.01 | 0.17 | 2.55 |
| Calfax 16L-35 | -0.21 | -10.07 | 0.17 | -6.9 |
| SDBS | 0.08 | -2.08 | 0.17 | -0.9 |
| Taiwan | 0.19 | 1.07 | - | |

We are not using alcohol in our three systems, so $f(A) = 0$; we are assuming that we are at room temperature, $T = 23^{\circ}\text{C}$ so $\Delta T = 2$. From the literature, α for anionic surfactant has been reported as 0.01°C [15, 20]. So Equation 2 can be simplified to:

$$HLD = C_{c_{mix}} + \ln(S_{mix}^*) - K_{mix}(EACN) - \alpha(\Delta T) \quad \text{(Equation 10)}$$

The K and Cc’s are given in Table 14, the composition and optimum salinities of the three systems are provided in Tables 3 and 5. The oil phase used is octane so the EACN = 8.

Table 15: Calculated HLD values for Systems 1, 2, 3 based on experimental and literature k and Cc values

| | HLD values based on experimental parameter values | HLD values based on Literature parameters values |
|----------|---|--|
| System 1 | 0.0046 | 0.30 |
| System 2 | -0.36 | 0.011 |
| System 3 | -0.33 | - |

The HLD values calculated with the parameters found in this work are negative for Systems 2 and 3 and positive for System 1. So, the optimum salinities for Systems 2 and

3 are lower than predicted whereas the optimum salinity for System 2 is higher than predicted by the HLD equation. To explain this, we can compare the optimum salinity of System 3 to the one found using octane when determining the HLD parameters for the Taiwan surfactant. These results can be explained by the fact that DI water as the aqueous phase when the HLD parameters were determined but Tap water is used as the aqueous phase in our study. Previous research has shown that the presence of counterions in water like potassium, calcium, cesium... decrease or increase the optimum salinity depending on the type of surfactant used and the oil phase. In this case, the optimum salinity differs from the predicted values when we switch from DI water to tap water because the later contains other counterions in addition to the sodium and chloride that's being added. These results confirm that one the limitations of the HLD equation is its failure to take into account the effect of other ions besides Cl^- on the optimum salinity.

For System 1, the values calculated in this work gave an HLD value closer to zero than the literature values found by Acosta's method but the inverse is true for system 2. Based on these results for Systems 1 and 2, it is hard to conclude which of the two methods gives a better approximation of optimum salinities. Both methods give HLD values close enough to zero to conclude that either one can be used to determine the HLD parameters for a given surfactant.

Chapter 4: Conclusion

The objective of this work was to determine whether the Taiwan surfactant could be used in place of the AOT/Calfax 16L-35 and AOT/SDBS systems in environmental remediation applications. The results of this work showed that the Taiwan surfactant can indeed be used for SEAR application and that it can be used to replace the AOT/Calfax system. The Taiwan and AOT/SDBS systems have comparable performances, both can form Type III microemulsions near 1 g NaCl/100 ml with a total surfactant concentration less than 1 wt.%, they have fast coalescence rates (<6 min), and ultralow IFT ($<10^{-3}$). Both systems also have similar stabilities with calcium chloride, have very high oil mobilization on both Ottawa and CRA sand, and finally have relatively low adsorption on Ottawa sand. These systems outperform the AOT/Calfax 16L-35 system that exhibit high salinity requirements, is more sensitive to calcium than the other two systems, and has slightly lower oil mobilization capacity than the other two systems.

It can be concluded that either the Taiwan or the AOT/SDBS systems can be used to replace the AOT/Calfax 16L-35 system. However, since there are no correlations that exist for predicting the aqueous phase stability of a surfactant system, it would be recommended to conduct stability tests for each specific site groundwater. In this work, the sensitivity to calcium alone was tested at room temperature, because surfactants are most sensitive to calcium ions, but in reality the presence of other ions in the aqueous phase and the temperature of the site may also affect the surfactant stability. Another method for measuring surfactant adsorption also needs to be used/developed for sands like CRA with fine particles. For our surfactant systems, the amount of surfactant adsorbs does not really affect the cost of the project because the amount of surfactants used is so

small that there may not be a need for recycling them. But, it is important to know how much surfactant is left after treatment to make sure the concentration is below the maximum toxicity level for aquatic life.

In order to decide which one of the two systems, Taiwan or AOT/SDBS, is more appropriate for SEAR application it is necessary to determine the system that best fits the rest of the criteria. Therefore, future work needs to determine the cost of using Taiwan surfactant versus AOT/SDBS, the biodegradability of the two systems but also the toxicity and the Krafft temperature.

The second part of this work consisted on finding the HLD parameters for the four surfactants of interested using an experimental procedure different from Acosta's method. The HLD method is used as a method to estimate the optimum salinity of a surfactant system when the conditions aqueous phase and/or oil phase conditions change. The results of this work show that the HLD correlation gives close approximation of the optimum salinity and that either the Acosta's method or the updated method used in this work can be used to estimate HLD parameters. However, both methods have their own limitations; Acosta's method fails to calculate a specific k values for each surfactant and the method used in this work showed that not all surfactants mixtures are linear.

An important limitation of the HLD equation found in this work is its failure to take into account the effect of other ions besides Cl^- on the optimum salinity. It is thus recommended to use the HLD method as a tool to estimate the optimum salinity; it does not eliminate the need to perform phase behavior studies when the conditions of the oil/water/surfactant system change. For future work, it is recommended to mix AOT and Calfax with different reference surfactants in order to determine the limitations of the

linear mixing rule. Finally, in this work the α of the surfactants were not determined. In the literature, the value of this parameter is reported as 0.01°C for anionic surfactants; however, as with the k parameters, this parameter may differ from one surfactant to another. It is thus important to experimentally determine the α values of the surfactants of interest to have a more accurate estimation of the optimum salinities when temperature changes.

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Appendix A: Pictures from Column Studies

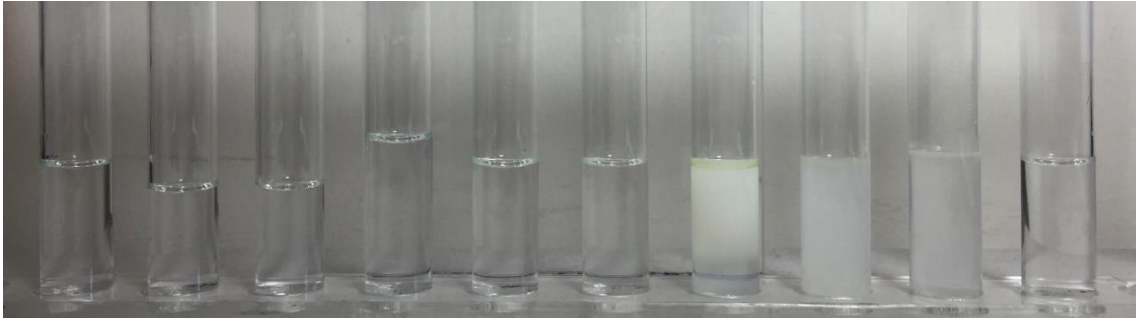


Figure 15: Pore Volumes collected from Column Study on Ottawa Sand with System 1 (0.75 wt.% AOT, 0.19 wt.% Calfax 16L-35, and 3.1 wt.% NaCl)

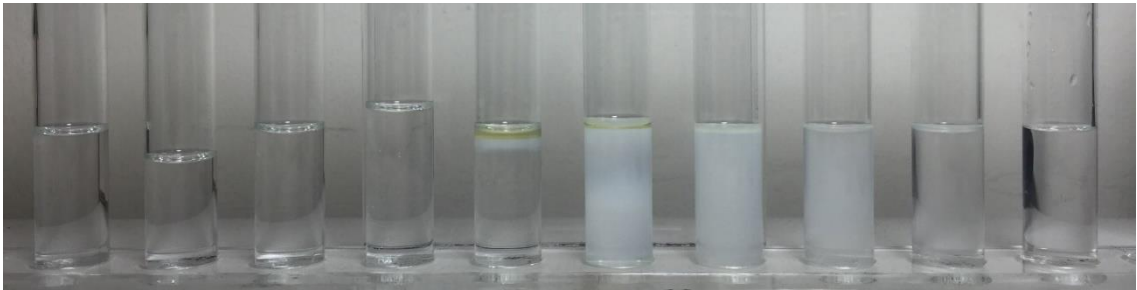


Figure 16: Pore Volumes collected from Column Study on Ottawa Sand with System 2 (0.75 wt.% AOT, 0.19 wt.% SDBS, and 0.7 wt.% NaCl)

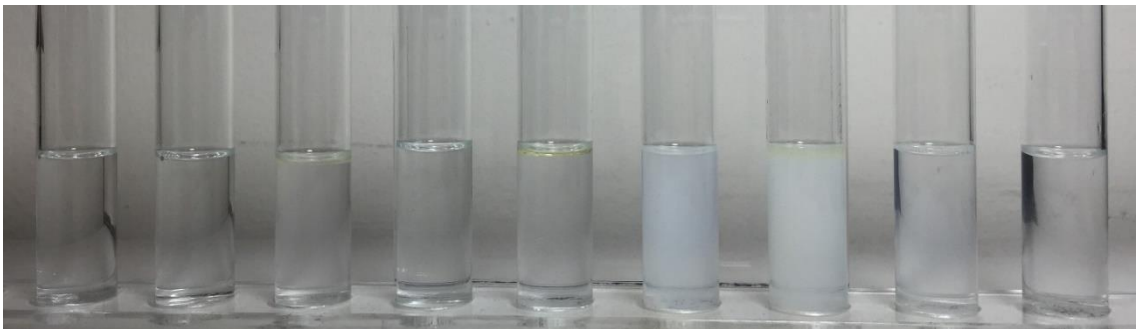


Figure 17: Pore Volumes collected from Column Study on Ottawa Sand with System 3 (0.94 wt.% Taiwan, and 1.1 wt.% NaCl)

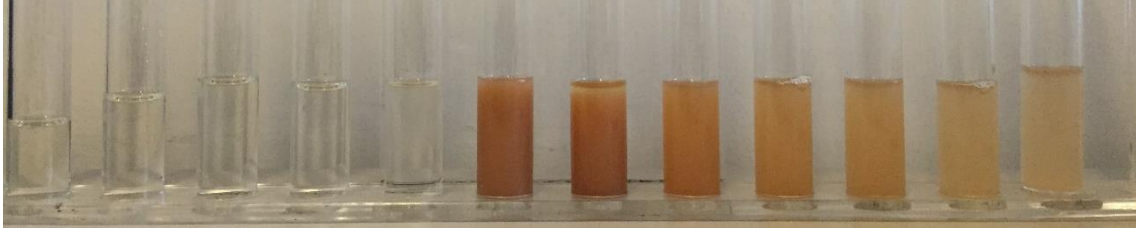


Figure 18: Pore Volumes collected from Column Study on CRA Sand with System 1 (0.75 wt.% AOT, 0.19 wt.% Calfax 16L-35, and 3.1 wt.% NaCl)



Figure 19: Pore Volumes collected from Column Study on CRA Sand with System 2 (0.75 wt.% AOT, 0.19 wt.% SDBS, and 0.7 wt.% NaCl)



Figure 20: Pore Volumes collected from Column Study on CRA Sand with System 3 (0.94 wt.% Taiwan, and 1.1 wt.% NaCl)