

**SURFACTANT MOBILITY IN UNSATURATED  
SOIL AND THE IMPACT ON SATURATED  
HYDRAULIC CONDUCTIVITY AND  
UNSATURATED DIFFUSIVITY**

**By**

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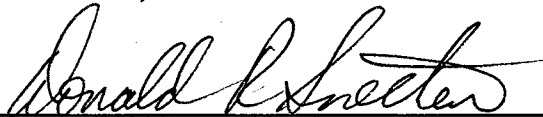
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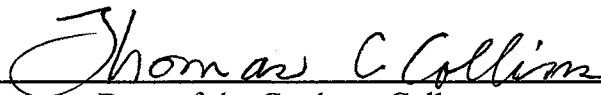


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## **Chapter I**

### **BACKGROUND, REVIEW, AND OBJECTIVES**

#### **Problem Statement**

Nonaqueous phase liquids (NAPLs) pose a serious problem with respect to environmental cleanup of soils and aquifers. NAPLs are liquid contaminants that are immiscible in water. Some of the more common NAPLs include hydrocarbon fuels, solvents, and pesticides. Some possible sources for release of these contaminants into the environment include leakage from pipelines and surface/subsurface storage tanks. NAPLs most often exist as residual saturation and can be found in both the saturated and unsaturated zones below the surface. Because of their low aqueous solubility and high interfacial tension with respect to water, NAPLs are not effectively removed from soils and aquifers by simple flush and treat methods. However, the petroleum industry has successfully tested surfactants for enhanced oil recovery. Consequently it has been reasoned that surfactants could also be applied for in situ environmental remediation. The effectiveness and efficiency of using surfactants for this purpose will depend on their contaminant emulsification/solubilization capability, subsurface mobility, and effects on porous media hydraulic properties.

The two overall objectives of this study are;

- to quantify the impact of surfactants on the hydraulic properties of saturated hydraulic conductivity and unsaturated diffusivity, and
- to determine surfactant transport characteristics in unsaturated soil along with delineation of the boundary conditions and soil attributes which have the greatest influence on mobility.

As detailed in the Research Focus, the first objective is addressed in Chapters II and III, while the second objective is addressed in Chapters III and IV. It will be shown in the following chapters that these objectives have not been adequately studied in any previous research.

### **Description of Surfactant Properties**

The word surfactant is a contraction for the term surface-active agent. These chemicals are described as being surface-active because of their tendency to concentrate at the aqueous interface with another phase, whether it be gas, solid, or liquid. As a consequence, various physical and chemical properties of the interface are affected. The surfactant tendency to concentrate at an aqueous interface is a result of an amphipathic molecular structure. Surfactants on the molecular level are comprised of both hydrophobic and hydrophilic components. The affinity of the hydrophilic component for water along with the tendency of the hydrophobic component to be expelled from this solvent causes surfactant molecules to concentrate at aqueous interfacial boundaries. Chemical structures commonly found in the hydrophobic portion of the molecule include

branched or linear hydrocarbon chains along with aromatic rings. The hydrophilic component contains either a polar or an ionic structural element. The physical and chemical behavior of surfactants show greater dependence on the nature of the hydrophilic part of the molecule.

Surfactants can be classified into one of the four groups listed below based on the charge of the hydrophilic component.

- 1) Nonionic (no charge)
- 2) Anionic (negative charge)
- 3) Cationic (positive charge)
- 4) Amphoteric (both positive and/or negative charges)

Anionic surfactants have the greatest commercial availability and are therefore the most likely candidates for utilization in environmental remediation. However, nonionics have also been tested.

Figure 1-1 shows the possible states of a surfactant in an aqueous solution. Within aqueous solutions at low concentration, surfactants exist only as individual monomers. As the concentration increases, the surface tension (solution/air interfacial tension) decreases. Interfacial tension can be defined as the amount of energy needed to increase the boundary area between two phases by a unit amount. When the surfactant concentration reaches a specific level, called the critical micelle concentration (CMC), molecular aggregates called micelles begin to form.

Micelles commonly contain 50 to 100 molecules and can assume various geometric shapes such as spheres, cylinders, and disks. In aqueous solutions, the

molecular hydrophobic parts point towards the center of the micelle while the hydrophilic parts are located on the outside. Structurally, a micelle can be conceptualized as having a water free hydrocarbon inner core, an outer core containing both water and hydrocarbons (palisade layer), and a hydrophilic shell (Hiemenz, 1986). For ionic surfactants, the outer shell is surrounded by counterions having an opposite charge.

At concentrations beyond the CMC, the monomer concentration remains constant and all excess surfactant is utilized in forming more micelles. Also, surface tension remains relatively stable once the CMC is reached. At substantially higher concentrations, the micelles themselves form structural arrangements called lyotropic liquid crystals. The laminar phase shown in Figure 1-1 is one example of a lyotropic liquid crystal. Within any surfactant solution, regardless of micelle formation, an equilibrium is established between concentration of the monomers in the bulk solution and those adsorbed at interfaces.

As previously stated, amphipathic molecular structure causes surfactants in an aqueous solution to concentrate at the phase boundaries present within a system. This is commonly referred to as hydrophobic adsorption. For surfactant solutions in contact with solid material, partitioning of the surfactant molecules at the liquid/solid interface is also facilitated by the mechanisms of precipitation and electrostatic attraction. Only ionic surfactants form precipitates. Precipitation and micelle formation are for the most part mutually exclusive. When the solubility limit is less than the CMC, surfactant precipitates can form but not micelles. The reverse is true if the CMC is less. The

temperature at which the solubility limit equals the CMC is called the Krafft point. Only micelles can form above the Krafft point, while precipitates can exist only at temperatures which are below. For anionic surfactants, the presence of positively charged multivalent counterions will increase the Krafft point and thereby enhance the potential for precipitation. The mechanisms of electrostatic attraction between a surfactant molecule and a solid surface include ion exchange, coadsorption, and hydrogen bonding. A more detailed discussion of surfactant sorption mechanisms at solid surfaces will be provided in following chapters of this manuscript.

### **Mechanisms of Surfactant Enhanced Environmental Remediation**

Emulsification and solubilization are the two mechanisms by which surfactants can enhance in situ removal of NAPLs from soils and aquifers. Figure 1-2 depicts a saturated system in which a NAPL droplet is attempting to move through a pore constriction. In order for the NAPL droplet to move through the constriction, it must be broken up into smaller droplets. This increase in interfacial area requires an energy input. The energy to be transferred results from pressure gradients in the adjacent water which is flowing around the droplet and through the pore. If these pressure gradients are not great enough, the droplet cannot be broken up (emulsified) to the extent necessary for it to be transported through the pore constriction. The needed energy requirements can be reduced by minimizing interfacial tension between the aqueous and NAPL phases. The addition of surfactants to the aqueous phase are ideal for this task. This is a concept which has been successfully tested in the petroleum industry for enhanced oil recovery.



However, for emulsification to work, ultralow interfacial tensions ( $< 1 \times 10^{-3}$  dynes/cm) need to be maintained within the subsurface porous media environment. For in situ environmental remediation, this can be very difficult to accomplish due to problems such as surfactant loss caused by adsorption/precipitation along with chemical changes in the flushing solution which occur with flow through soil and aquifer materials.

Solubilization is the second mechanism by which surfactants can enhance the removal of NAPL contaminants from the subsurface environment. Organic liquids, such as some petroleum products, are soluble in the aqueous phase to a limited extent. If the aqueous solution contains surfactants at concentrations above the CMC, dissolved organic molecules will have a tendency to become incorporated into micelle cores. This entrapment within micelles effectively reduces the concentration of the dissolved organics to a level below their solubility limit. Consequently, more organics are then dissolved into the aqueous phase. The increased amount of organic material which can be solubilized through this mechanism is dramatic. Vigon and Rubin (1989) found three nonionic surfactants at concentrations above 0.1% w/w to increase anthracene solubility by factors of 20 to 40.

Several factors such as surfactant CMC, octanol/water partition coefficient ( $K_{ow}$ ), surfactant structure, and solution electrolytes affect the degree of solubilization. Since enhanced solubilization requires micelle formation, surfactants with low CMC values are more efficient. Contaminants with a high  $K_{ow}$  have a greater tendency for solubilization by surfactants (West and Harwell, 1992). An increase in the size of the hydrophobic component of a surfactant molecule increases the radius of the hydrophobic

inner core of the micelle. This increases the capacity of organic material which can be incorporated into the micelle. The addition of solution electrolytes is found to increase the solubilization capacity of ionic surfactants

Enhanced solubilization by addition of surfactants to the water used in a pump and treat system can reduce remediation times significantly. This increased efficiency must be weighed against the increased operational costs involved in using surfactant chemicals.

### **Research Focus**

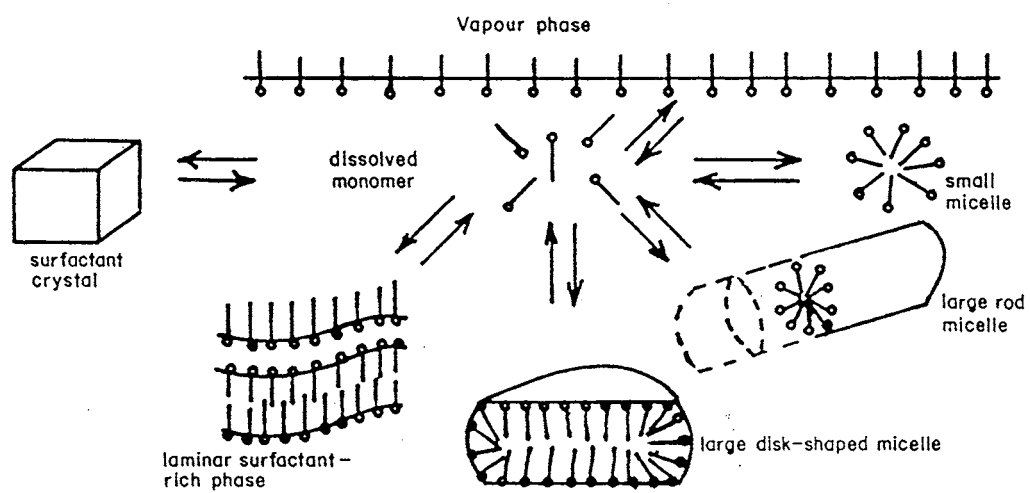
Figure 1-3 illustrates a hypothetical example of how surfactants would be utilized to remove contaminants present both above and below the water table. As shown, surfactants are introduced into the saturated zone with an injection well. Contaminants found in the unsaturated zone would be flushed using surfactant solution applied with a surface sprinkler system or even shallow subsurface drains. The contaminated ground water and surfactant are then extracted with a recovery well. At the surface, recovered surfactant is separated out and then reused. The surfactant may have to cycle through the system as many as 50 to 100 times to remove the contaminants present in the subsurface. Consequently, the effectiveness and efficiency of this type of environmental remediation will require the surfactant mass flux through the subsurface to be managed at an acceptable level.

Surfactant mass flux through the saturated and unsaturated zones will depend on the volumetric flow rate that the media is capable of maintaining along with the mobility

of surfactant molecules in the subsurface. The flow rate which can be maintained in a porous material depends on hydraulic properties such as saturated hydraulic conductivity or unsaturated diffusivity. If the presence of a surfactant reduces the hydraulic conductivity or unsaturated diffusivity, then the flow rate will be reduced and so to the effectiveness and efficiency of the cleanup program. Remediation practicality will also be determined by factors which impact surfactant mobility. These concerns are addressed in the following three papers which have been submitted for publication. The first paper (Chapter II) quantifies the effect that various surfactants have on the saturated hydraulic conductivity of two soils. The second and third papers (Chapters III and IV) focus on anionic surfactant mobility in unsaturated soil. Here, the factors which influence mobility along with the impact that anionic surfactants have on unsaturated diffusivity are discussed. Overall, these three papers provide a body of knowledge which can be used in applying surfactants for in situ environmental remediation.

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**Fig. 1-1.** Possible states of a surfactant in solution (Couper, 1984).

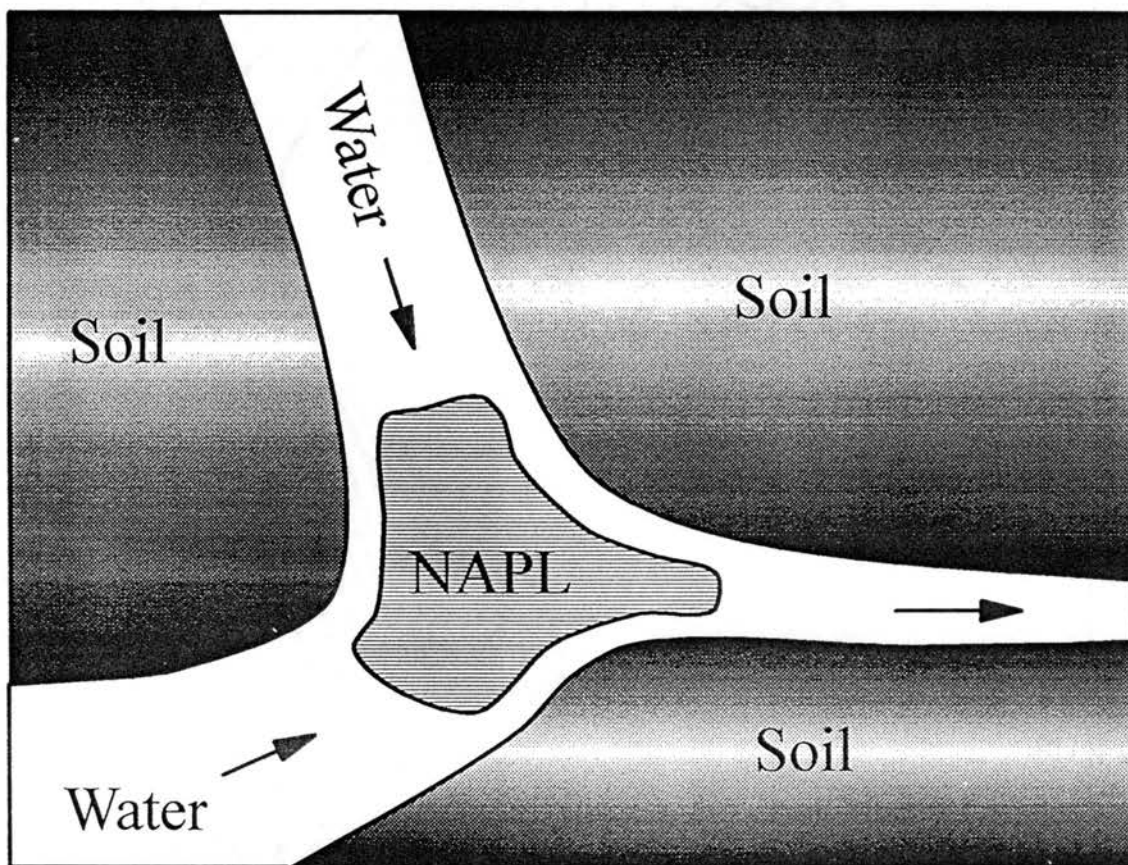
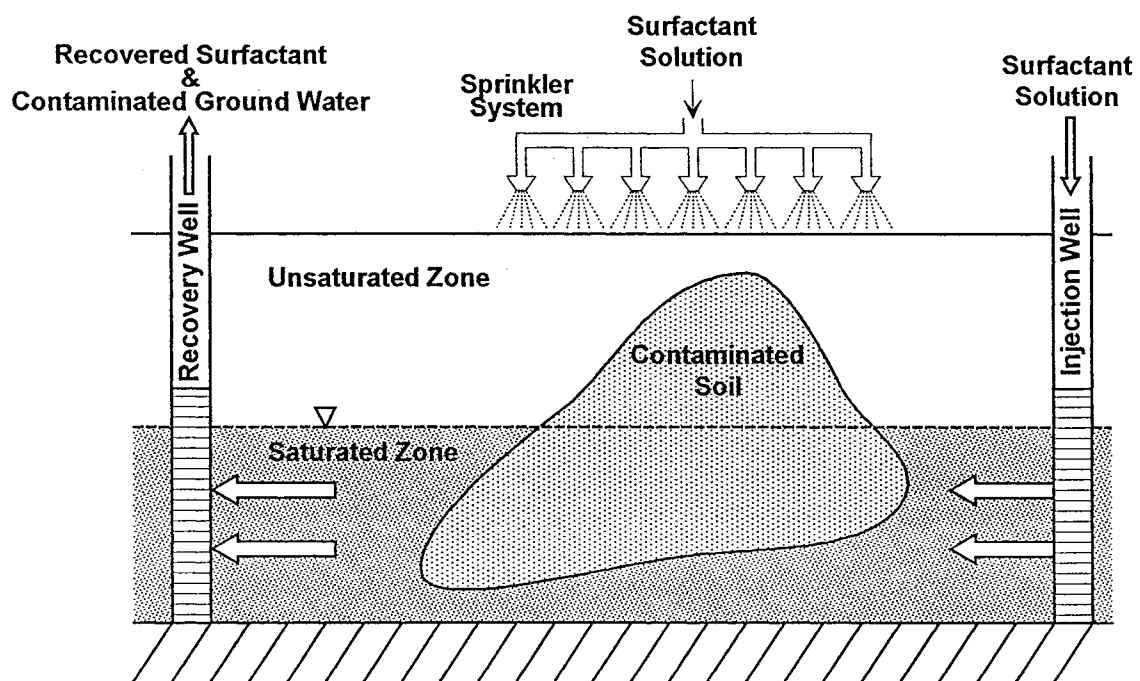


Fig. 1-2. Soil pore containing a NAPL droplet.



**Fig 1-3.** Example of surfactant enhanced environmental remediation.

## **Chapter II**

### **SURFACTANT INDUCED REDUCTIONS IN SOIL HYDRAULIC CONDUCTIVITY**

#### **Abstract**

Surfactant solutions are being proposed for in situ flushing of organic contaminants from soils and aquifers. The feasibility of surfactant additives in remediation may depend in large part on how these chemicals affect the hydraulic conductivity of the porous media. While there is evidence in the literature of conductivity loss during surfactant flushing (Miller et al., 1975; Nash et al., 1987), there has been little research on quantifying the process for unconsolidated sediments. Surfactant affected hydraulic conductivity reductions were measured in two soils (Teller loam and Dougherty sand). Testing was done with eight different surfacants at a variety of concentrations ( $10^{-5}$  to  $10^{-1}$  mole/kg), surfactant mixtures, and added solution electrolytes. The Teller was also tested with its organic matter removed. Maximum hydraulic conductivity decreases were 47% for the sand and over 2 orders of magnitude for the loam. Surfactant concentrations, surfactant mixtures, soil organic content, and added solution electrolytes all affected the degree of conductivity reduction. Results

indicate that surfactant affected hydraulic conductivity losses should be considered prior to in situ remediation and may preclude surfactant use in some fine grain soils.

## **Introduction**

The concept of using surfactant solutions for environmental soil flushing originated from their successful testing in the petroleum industry for enhanced oil recovery. Surfactants were employed to minimize interfacial tension between the oil and water phases. This results in the formation of a mobile oil/water emulsified phase which can then be extracted from the subsurface. Since numerous pore volumes of the flushing solution may be required for surfactant enhanced in situ remediation, the feasibility of this method may depend on soil hydraulic conductivity. If soil-surfactant interactions result in significant hydraulic conductivity reduction, this type of remediation may be impractical.

Surfactants are organic compounds comprised of both hydrophobic and hydrophilic components. This amphipathic structure causes surfactant molecules to concentrate in a specific orientation at interfaces within multiphase systems. The result is a reduction in interfacial tension. Above a certain concentration, called the critical micelle concentration (CMC), surfactant molecules in solution form aggregates called micelles. As a result of micelle formation, surface tension is usually minimum at or above the CMC. Surfactants are classified as being anionic, cationic, amphoteric (positive and/or negative molecular charge), or nonionic. Commercially, anionics are most common.



In environmental soil flushing, surfactants can be used for both emulsification and solubilization. Solubilization is the partitioning of organic contaminant molecules into the core of surfactant micelles. Micelles then act as mobile carriers within the aqueous phase for the organic contaminants. Laboratory studies by the American Petroleum Institute (1979 and 1985), Ducreux et al. (1990), Abdul et al. (1990), and Ang and Abdul (1991) indicate the feasibility of using surfactant solutions for porous media flushing. In a large scale model aquifer study conducted for the American Petroleum Institute (1985), a 4% solution containing equal amounts of both an anionic and nonionic surfactant was effective in removing up to 83% of the gasoline present in a sandy soil. The nonionic surfactant was added to increase the flow rate without decreasing the effectiveness of the anionic surfactant to extract gasoline. Ducreux et al., (1990) found that a 10 g/L NaCl preflush enhanced the effectiveness of an anionic surfactant in mobilizing non-soluble residual hydrocarbons.

Results of field studies have been mixed with respect to surfactant effectiveness. Nash et al. (1987) found little evidence that surfactants removed residual petroleum or organic solvents from a sandy soil. In that study, it was noted that the surfactant solutions dramatically decreased percolation rates. Abdul et al. (1992) field tested a 0.75% nonionic surfactant solution and found it removed 10% of oil and polychlorinated biphenyls from a sandy soil after a six pore volume flush. Sale et al. (1989) describe a field test where surfactant flushing solutions reduced residual oil saturation by 67%. Both the anionic and nonionic surfactant solutions used in their field study contained alkalis to reduce adsorption and polymers to control viscosity.

In this research, both a loam and a sand were tested to determine their suitability for soil flushing. The saturated hydraulic conductivity of the sand ( $3 \times 10^{-2}$  cm/s) would seem to make it an ideal candidate for soil flushing remediation while the lower conductivity ( $6 \times 10^{-5}$  cm/s) of the loam would place it at the perceived lower limit of practicality.

To make this research as extensive as possible, eight surfactants were examined. Likewise, two surfactants were tested over a concentration range of four orders of magnitude. Anionic surfactants may precipitate with ground water cations and cause reductions in soil hydraulic conductivity. West and Harwell (1992) note that any factor which lowers the CMC of a surfactant system will decrease the susceptibility of the surfactant to precipitation. Mixing an anionic surfactant with a nonionic surfactant commonly reduces the CMC. For this reason, anionic and nonionic surfactant mixtures were tested. The addition of an electrolyte such as NaCl to an anionic surfactant solution can both increase the micelle aggregation number and decrease the CMC (Hiemenz, 1986). Additional monovalent  $\text{Na}^+$  ions can also affect the soil cation exchange behavior of divalent ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  which coadsorb and/or form low solubility salts with some anionic surfactants. Consequently, anionic surfactant solutions containing high levels of NaCl were tested to determine if hydraulic conductivity reductions could be controlled.

Finally, Muecke (1979) has suggested that permeability can be affected by mutual solvents or surfactants which mobilize colloid-size material held in place by wetting or

interfacial forces. Thus, a simple test was developed to measure mobilization of colloid-sized material for the Dougherty sand using different surfactant solutions.

## **Materials**

### ***Surfactants***

Table 2-1 lists the surfactants used in this study. Symbols provided in the table will be used to designate specific surfactants. All of the surfactants were supplied by the Organics Division of the Witco Corporation. Of the eight surfactants tested, five were anionic or nonionic. These would be the most likely utilized for surfactant flushing remediation. One amphoteric and two cationic surfactants were also tested. Table 2-2 provides information on their aqueous solution properties. Surface tensions were measured with a Fisher Scientific Model 21 Tensiomat tensiometer, while viscosities were obtained with a Cannon Instrument Co. size 50 viscometer. From Table 2-2, it is evident that the nonionic surfactants have significantly lower CMC's than either of the anionic surfactants. The addition of NaCl at a concentration of 0.1 mole/kg causes a reduction in the CMC for the two anionic surfactants. It was also noted that the half-and-half anionic-nonionic surfactant mixtures showed lower CMC values than the individual anionic surfactants. Specific gravity for the surfactant solutions were all equal to 1.000 ( $\pm 0.003$ ), as calculated from data given by the manufacturer.

## ***Soil Types***

Teller loam (Thermic Udic Argiustoll) and Dougherty sand (Thermic Arenic Haplustalf) were the soils used. They were obtained from field locations near Perkins, Oklahoma. Characteristics of both soils are provided in Table 2-3. Properties were determined using the procedures described in *Methods of Soil Analysis, Part 1 & 2* (ASA and SSSA, 1982 and 1986). Specific surface area was calculated from water vapor sorption isotherms by use of the B.E.T. equation (Quirk, 1955). An indication of the clay minerals present in the two soils is found through comparison of the specific surface area and the percent clay content (Jury et al., 1991). With a specific surface area of 38 m<sup>2</sup>/g, a 17% clay content, 1.22% organic matter, and no observable swelling tendencies, illite should be the most common clay mineral present in the Teller Loam. For the Dougherty sand, a relatively high specific surface area (22 m<sup>2</sup>/g) compared with a low clay content (<2%) indicates that montmorillonite is the dominant clay mineral. Calcium is the dominant exchangeable cation present in both soils.

## **Experimental Procedures**

Falling-head permeability tests were used to monitor changes in saturated hydraulic conductivity (McWhorter and Sunada, 1977). The basic testing apparatus is shown in Figure 2-1. Saturated hydraulic conductivity values, K (L/T), were calculated using the following equation:

$$K = \frac{al}{At} \ln \left( \frac{h_0}{h_1} \right) \quad (2-1)$$

where  $a$  is the cross-sectional area of the buret ( $L^2$ ),  $A$  is the cross-sectional area of the soil column ( $L^2$ ),  $l$  is the length of the soil column ( $L$ ), and  $t$  is the time ( $T$ ) required for the hydraulic head,  $h$  ( $L$ ), to fall from  $h_0$  to  $h_1$ . The ratio of total head loss versus column length, or hydraulic gradient, ranged from three to six. This value is consistent with conservative lab practices but higher than common field conditions. All flows were well in the range of Darcy's law and matrix compression was trivial at the packing densities used. It is possible the relatively high gradients could help mobilized fines and speed up changes in the pore structure when compared to field conditions.

Rigid columns 4.15 cm in diameter and 15 cm long were used. They were packed in uniform lifts at dry bulk densities of  $1.65 \text{ g/cm}^3$  for the Teller loam and  $1.70 \text{ g/cm}^3$  for the Dougherty sand. Those densities correspond to porosities of 38% and 36%, respectively. Studies have shown many surfactants to be actively biodegraded by microorganisms commonly found in the environment (Huddleston and Allred, 1967). Microbial growth may cause pore clogging which is beyond the scope of this study. Thus, the soil was sieved and heated to  $105^\circ \text{C}$  for 24 h before packing in order to destroy most resident soil microorganisms. The columns were vacuum saturated with deaired, surfactant free, nominal soil water solution ( $0.001 \text{ mole/kg NaCl}$  and  $0.001 \text{ mole/kg CaSO}_4$ ). Natural pore waters were not available for these surface soils, thus the test solution, which contained low concentrations of monovalent and divalent ions common to soils, was used in an attempt to maintain an equilibrium soil chemistry.

### *Teller Loam Tests*

Changes in the loamy soil hydraulic conductivity were measured with respect to a variety of surfactants, different concentrations of the same surfactant, mixtures of anionic and nonionic surfactants, presence or absence of soil organic matter, and inclusion of additional electrolyte in the surfactant solution. After saturation, the Teller loam columns were flushed with approximately one pore volume of soil water solution. (A pore volume is equal to the total volume occupied by the voids within the soil column.) Initial soil hydraulic conductivities were then obtained. Next, the surfactant solution was substituted into the supply reservoir and hydraulic conductivity was monitored with respect to the number of pore volumes of influent.

Five series of tests were completed using the Teller loam. Tests were normally conducted for a period of four days. The first series compared eight different surfactants at 0.1 mole/kg concentrations. This corresponds to a 3-8% by weight surfactant solution, which brackets the upper limit of what would be required for soil flushing.

The second series determined the surfactant concentration at which hydraulic conductivity reduction first becomes significant. Two different surfactants, A1 and N3, were tested at  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$  and  $10^{-1}$  mole/kg concentrations. Based on results of this series, all later tests on the Teller were conducted at a 0.01 mole/kg concentration. This level corresponds to the lower limit (0.3-0.8%) at which surfactants would be applied for soil flushing. Abdul et al. (1990) tested a variety of surfactants and found that solution concentrations of 0.5% and above were effective in removing automatic

transmission fluid from a sandy material. A surfactant system concentration as high as 4% was tested by the American Petroleum Institute (1985) with encouraging results.

The third test series compared anionic-nonionic mixtures to single surfactant solutions. Two mixed surfactant solutions containing equal molar amounts of A1 and N3 or A2 and N1, with an overall concentration of 0.01 mole/kg, were compared with solutions of individual surfactants. At the completion of this series, the soil was extruded from the columns, sectioned into quarters, and the samples analyzed to determine the distribution of surfactants. Anionic surfactants in the soil samples were extracted with acetone and then analyzed using the Methylene Blue Method (APHA et al., 1985). Nonionic surfactants were extracted with acetone and analyzed using the Ammonium Cobalthiocyanate Method (Longman, 1975). The test using the A1 and N3 solution mixture was run through two cycles, where the surfactant was followed by a soil water solution flush to determine if the lost hydraulic conductivity could be recovered. Since the conditions of this test differed from the others within the series, surfactant distribution in the soil column was not determined.

The fourth series explored the influence of residual organic matter in the loam. Testing done on three columns with soil organic matter (1.22%) were compared with tests on three columns where the soil organic matter had been removed by hydrogen peroxide oxidation (ASA and SSSA, 1986). These three pairs of tests were conducted with the 0.01 mole/kg A1 and N3 surfactant solutions along with the soil water solution as a control.

The fifth and final test series was conducted to investigate whether high levels (0.1 mole/kg) of NaCl in either the surfactant solution, or both the surfactant solution and a preflush, could moderate the hydraulic conductivity reduction caused by anionic surfactants. Two columns were run with solutions containing 0.1 mole/kg of NaCl and 0.01 mole/kg of A1 or A2. A third test utilized a 7.5 pore volume 0.1 mole/kg NaCl preflush, followed by an A1-NaCl solution.

### ***Dougherty Sand Tests***

Changes in the sand's conductivity were measured with eight different surfactants and four mixtures. Procedures for determining saturated hydraulic conductivity losses for the sand were somewhat different from those used for the loam. After saturation, the columns were flushed with approximately four pore volumes of soil water solution. Following the preflushing, initial saturated hydraulic conductivities were determined. Columns were then flushed with four pore volumes of 0.05 mole/kg surfactant solution and allowed to equilibrate for 12 h. A surfactant affected hydraulic conductivity was then determined. The equilibration period was necessary to maintain a realistic duration of soil-surfactant contact and was chosen based on the calculated water travel time along a 15 cm (column length) flow path under a hypothetical hydraulic gradient of 0.005. A single series of tests were conducted with the Dougherty sand using the eight different surfactants, two anionic-nonionic mixtures, and two mixtures containing NaCl and an anionic surfactant. All tests were run with 0.05 mole/kg solution concentrations, with the exception of the control.



During the Dougherty tests, some column effluent contained significant amounts of soil colloids which were not observed during the Teller tests. A simple testing procedure was devised to determine the relationship between effluent colloids and conductivity reduction. Figure 2-2 illustrates the apparatus. A 300 ml flask was filled with approximately 200 cm<sup>3</sup> of sand between two washed gravel layers. A brass tube open to the bottom gravel layer allowed effluent collection. The sand was preflushed by pouring four pore volumes of soil water solution into the top of the flask while applying suction to the brass tube. Then it was leached with an additional 4 pore volumes of 0.05 mole/kg surfactant solution and allowed to equilibrate for 12 h. At the end of the equilibration, one pore volume of effluent was collected. The effluent solution was analyzed for nonvolatile solids which is a measure of suspended inorganic solids (APHA et al., 1985).

## **Experimental Results**

### ***Teller Loam***

Figure 2-3 presents results of the first test series which compared different surfactants at 0.1 mole/kg concentrations. Figure 2-3a displays the test results for the nonionic surfactants while the ionic surfactants are represented by Figure 2-3b. It is apparent that the ionic surfactants caused a greater hydraulic conductivity decrease than the nonionic surfactants. Maximum hydraulic conductivity reduction for the ionic surfactants was over 2 orders of magnitude within 0.6 pore volumes. For the nonionic surfactants, maximum hydraulic conductivity reduction was 0.5 to 1.5 orders of

magnitude over a 1.5 to 4.0 pore volume range. Results from a test run with soil water solution are also provided in Figures 2-3a and 2-3b for comparison. Figure 2-3c shows that partial recovery of hydraulic conductivity losses caused by the N3 surfactant was achieved by purging the column with the soil water solution. On this plot, the two declining limbs on the curve reflect hydraulic conductivity loss due to surfactant injection, while the two rising limbs represent hydraulic conductivity recovery from soil water solution flushing. It should be noted however, that other tests in this study (N3 at 0.01 mole/kg, A1 at 0.01 and 0.1 mole/kg, and A1 & N3 at 0.01 mole/kg) showed no significant recovery of hydraulic conductivity after a water solution flush.

Figure 2-4 presents the results of the second series, which compared surfactant concentration effects. For both surfactants tested, A1 (Figure 2-4a) and N3 (Figure 2-4c), significant hydraulic conductivity reduction did not occur until a concentration level of 0.01 mole/kg was reached. The maximum rate of decrease occurred with the highest solution concentration (0.1 mole/kg). From Figures 2-4b (surfactant A1) and 2-4d (surfactant N3), it appears that for solution concentrations of 0.01 mole/kg and above, the total injected surfactant mass at which hydraulic conductivity reduction begins to occur is  $10^{-4}$  to  $10^{-3}$  moles injected across an inlet area of 9.6 cm. Hydraulic conductivities in Figures 2-4b and 2-4d have been corrected for the small linear decrease which occurs due to flushing with soil water. This decrease is probably the result of chemical adjustments of the soil to the soil water used. A moderate reduction with the  $10^{-4}$  mole/kg N3 solution may be due to other factors such as bubble formation within the column caused by gases escaping from solution. On whole, Figure 2-4 suggests that

hydraulic conductivity reduction may be related more closely to concentration of the surfactant solution injected rather than the actual mass of surfactant injected. For both surfactants, the concentration where significant hydraulic conductivity reduction begins is above the CMC. At present, the basis for any possible relationship is uncertain.

Figure 2-5 presents the results of the third series, which compared mixed, anionic-nonionic surfactant systems to single surfactant solutions. Figure 2-5a shows that the mixed system containing A1 and N3 behaved closer to its nonionic component, N3. The other mixed system, which contained surfactants A2 and N1, initially mimicked the behavior of the nonionic component, N1, for the first 1.4 pore volumes but subsequently showed dramatic hydraulic conductivity reductions more representative of the anionic component, A2.

Upon completion of the third test series, the soil columns were extruded, quartered, and analyzed for surfactant distribution. Figures 2-5b and 2-5c represent those results. The values within the parentheses represent the total pore volumes of injected surfactant solution. Figure 2-5b shows soil column surfactant distributions from the tests where single component surfactant solutions were used. Most of the surfactant recovered was at the column inlet, which indicates a high degree of sorption. The soil column surfactant distribution from the test run with the A2 and N1 mixed solution is shown in Figure 2-5c. Again, the greatest amount of total surfactant recovered was at the inlet. However, relative distributions of the two surfactants indicates preferential sorption of the nonionic surfactant over the anionic surfactant. This is apparent because the A2 anionic surfactant increases in concentration from the inlet to the center of the

column while the N1 nonionic surfactant shows a decrease with distance from the inlet. Similar preferential adsorption of a nonionic surfactant over an anionic surfactant on activated carbon was demonstrated by Schwuger and Smolka (1975). For the five columns analyzed for surfactant distribution, the anionic surfactant recovery was approximately 50% while the nonionic surfactant recovery averaged 80% of total mass injected. Differences in extraction efficiency may be the result of adsorption mechanisms being more complex for ionic surfactants than for nonionic surfactants. This is due to electrostatic interactions with charged solid surfaces, which play a significant role in the adsorption of ionic surfactants but not nonionic surfactants (Rosen, 1989). Therefore, anionic surfactant extraction efficiency is less because acetone has a limited effect in countering the electrostatic component of ionic surfactant adsorption.

Figure 2-6 presents the results of the fourth series which examined the effects of soil organic content. The absence of soil organic matter tends to magnify the hydraulic conductivity reduction. All columns run with the nonorganic Teller showed greater hydraulic conductivity decreases compared to corresponding columns with soil organic matter. Organic matter tends to aggregate soil particles thereby adding stability to the soil structure. Consequently, the removal of the organic matter may accelerate alteration of soil structure with a resulting decrease in hydraulic conductivity.

Figure 2-7 presents the results of the final Teller series which tested the effects of adding NaCl to anionic surfactant solutions. In Figure 2-7a results of columns run with solutions containing both 0.1 mole/kg NaCl and 0.01 mole/kg anionic surfactant (A1 or A2) are compared against solutions containing only the surfactants. Although the

hydraulic conductivity loss was still significant, its was less for the combined NaCl electrolyte and surfactant solutions. Results of tests run with soil water solution and 0.1 mole/kg NaCl alone are also provided in Figure 2-7a for comparison purposes. Figure 2-7b shows that using a 7.5 pore volume preflush of 0.1 mole/kg NaCl prior to injection of the A1-NaCl solution added no further improvement over what was obtained with the A1-NaCl solution by itself. In Figures 2-7a and 2-7b, normalized conductivity ( $K/K_{\text{initial}}$ ) was used to make comparison of results between tests easier.

### ***Dougherty Sand***

Table 2-4 presents the results of the testing on the Dougherty sand with eight surfactants, two anionic-nonionic mixtures, and two solutions containing NaCl and anionic surfactants. All tests in this series utilized 0.05 mole/kg solutions. The largest decrease in conductivity was 47% for the A1 surfactant and the smallest was 14% for N1. Anionic-nonionic mixtures showed conductivity decreases slightly more than that obtained for the straight nonionic solutions. Anionic surfactant solutions containing NaCl affected hydraulic conductivity reductions less than those of the anionic surfactant solutions alone. The mixture of A1 & NaCl produced the smallest conductivity loss (9%) of all of the tests where surfactants were used. Table 2-4 also presents the results of the soil dispersion tests. Generally nonionic and cationic solutions caused minimal dispersion, while anionic solutions and mixtures containing anionic surfactants produced effluent solids up to 7680 mg/l. Clearly, anionic surfactant solutions have the greatest potential for dispersion and mobilization of solids in the Dougherty sand.

## Discussion

### *Teller Loam*

Figures 2-5b and 2-5c show that for falling-head tests, surfactants tended to be sorbed closest to the inlet of the column. Undoubtedly that is the column region where reduction in hydraulic conductivity occurred. Consequently, surfactant affected hydraulic conductivity measurements for the loam should be considered as effective values. A model with flow perpendicular to two soil layers provides the simplest relationship for the effective hydraulic conductivity which was measured. This relation can be expressed as:

$$K = l / \left( \frac{l_s}{K_s} + \frac{(l-l_s)}{K_u} \right) \quad , \quad (2-2)$$

where  $K$  is the measured hydraulic conductivity,  $l$  is the total length of the soil column,  $l_s$  is the surfactant affected length within the column,  $K_s$  is the actual surfactant affected hydraulic conductivity, and  $K_u$  is the unaffected soil hydraulic conductivity. From equation (2-2), it is apparent that  $K_s < K$ . Thus, the actual hydraulic conductivity in the portion of the column most affected by the surfactant is less than the effective values measured.

Calculations based on specific surface area and porosity indicate an average pore radius of  $1 \times 10^{-6}$  cm for the Teller. Surfactant adsorption on soil surfaces can form nonionic monolayers and ionic bilayers which may be several nanometers ( $10^{-7}$  cm) in thickness (Ottewill, 1984). Consequently, it would initially appear that adsorption alone could be a mechanism for hydraulic conductivity reduction in the loam. However, most

flow occurs in larger pores. From Poiseuille's formula for flow in a porous media comprised of "bunched" capillary tubes, an effective pore radius for the loam can be estimated from:

$$K = \frac{\phi r^2 \rho g_c}{8\mu}, \quad (2-3)$$

where  $\phi$  is porosity,  $r$  is effective pore radius (L),  $\rho$  is fluid density (M/L<sup>3</sup>),  $g_c$  the is gravitational constant (L/T<sup>2</sup>), and  $\mu$  is absolute viscosity (M/LT). Using equation (2-3) and a hydraulic conductivity of  $6 \times 10^{-5}$  cm/s, the effective pore radius for the Teller was calculated as  $1 \times 10^{-4}$  cm. This suggests that surfactant adsorption onto soil surfaces may clog the smaller pores, but would not be expected to greatly constrict the larger pores which carry the bulk of the total porous media flow. Therefore, different mechanisms need to be investigated in order to explain the hydraulic conductivity losses observed in the Teller.

Changes in soil pH could alter the chemical equilibrium of the soil and result in the formation of inorganic precipitates which would affect hydraulic conductivity. For our study, this was probably not the case because both the surfactant solutions and the two soils were compatible with respect to pH (Tables 2-2 and 2-3).

The viscosities of the 0.1 mole/kg surfactant solutions listed in Table 2-2 are greater than that of water. Equation (2-3) indicates that increasing the fluid viscosity will result in reduced hydraulic conductivity. However, hydraulic conductivity reductions in the Teller were measured in orders of magnitude losses and not the tens of percent which can be accounted for by differences in viscosity.

Anionic surfactants may cause hydraulic conductivity reductions through precipitation as calcium salts. The presence of calcium as the dominant cation in both

soils makes this mechanism a strong possibility. As shown in Table 2-2, the addition of NaCl electrolyte to the anionic surfactant solutions, causes the CMC to decrease significantly. Lowering the CMC can in turn reduce calcic surfactant salt precipitation and therefore moderate hydraulic conductivity losses. Test results presented in Figure 2-7 and Table 2-4 seem to confirm calcic surfactant salt precipitation as a mechanism by which anionic surfactants can effect hydraulic conductivity reductions. Although the addition of NaCl did moderate the effect significantly, measurable hydraulic conductivity losses still occurred and therefore must be accounted for by other processes. Precipitation may also account for some of the conductivity reductions caused by the cationic and amphoteric surfactants.

Precipitation would not be a dominant mechanism of conductivity reduction in the loam when leached with nonionic surfactants. Here, the possibilities may include soil structure alteration caused by dispersion or even the formation of pore clogging surfactant lyotropic liquid crystals, which may form in response to a soil solution environment containing high levels of both inorganic electrolytes and residual organic matter. Mustafa and Letey (1969) showed that two nonionic surfactants decreased aggregate stability in hydrophobic soils. Miller et al. (1975) suggested that the nonionic surfactant affected flow rate decreases in hydrophobic soils could be related to aggregate destabilization, micelle formation, or particle migration.



### ***Dougherty Sand***

Differences in viscosity between the 0.05 mole/kg surfactant solutions and water can account for much of the hydraulic conductivity reductions observed in the sand. In Table 2-4, the calculated viscosity effects on conductivity are presented along with the observed reductions. Viscosity increases can explain most of the nonionic, and anionic-nonionic mixture losses. With straight anionic or cationic solutions, viscosity can account for 1/3 to 1/2 of the observations, but for the amphoteric solution it will only produce 1/4 of the conductivity reductions. Viscosity effects may be negated by surfactant sorption on to soil particles. With the removal of surfactant from the soil solution, the solution viscosity would return to that of water. Thus, the causes of the losses may be due in part to the other processes described previously. Mixing anionic surfactants with either nonionic surfactants or NaCl appears to be a viable means to maintain conductivity in this soil.

When all surfactants are included, the correlation between soil colloid dispersion and hydraulic conductivity reduction is negligible ( $r^2 = 0.02$ ). However, if the viscosity effect is subtracted from the conductivity change to obtain a residual conductivity change, clear trends develop. Figure 2-8 shows the residual change versus nonvolatile solids for each test. Highlighted areas show that the different types of surfactant solutions occupy different regions on the residual change versus nonvolatile solid graph. Thus, in the anionic and amphoteric solutions, the residual conductivity change is probably affected by colloid dispersion and pore blocking. For the cationic solutions, other processes must be at work.

## Conclusions

Hydraulic conductivity reductions observed in this study vary significantly with respect to the different surfactants and the two soils tested. Factors influencing reductions include surfactant type, surfactant solution concentration, combined surfactant systems, soil organic content, and added electrolytes. Teller loam would be a marginal candidate for soil flushing remediation. For this soil, hydraulic conductivity reductions over two orders of magnitude would make most surfactant flushing remediation impracticable. Consequently, for fine soils with moderate initial hydraulic conductivities, careful consideration of the proper surfactant solution system will be required.

Hydraulic conductivity losses in the sand were modest. Viscosity effects, if not negated by sorption processes, could account for much of the decrease. The Dougherty sand is representative of an ideal candidate for surfactant flushing remediation. The measured hydraulic conductivity reduction, should not in most cases significantly reduce the practicality of flushing remediation.

It appears that a number of processes contributed to the conductivity losses observed here. While several processes are probably at work in each case, a significant process with anionic surfactants in the loam was probably surfactant precipitation, while viscosity increases appear to be an important factor for all surfactants in the sand. It is not apparent if there is a single dominant process in the loam when leached with the nonionic surfactants. Our results are specific to the soils and surfactants tested. However, other conditions can be quantified using the procedures outlined in this paper.

Such measurements should significantly contribute to the feasibility analysis and efficient design of field remediation procedures.

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**Table 2-1****Surfactant List**

Surfactant Type	Abbreviation	Chemical Name	Trade Name <sup>1</sup>
Nonionic	N1	Alkyl Polyoxyethylene Glycol Ether	Witconol SN-90
	N2	Alkylphenol Ethoxylate	Witconol NP-100
	N3	Alkyl Polyoxyalkylene Glycol Ether	Witconol 1206
Anionic	A1	Sodium Lauryl Sulfate	Witcolate A Power
	A2	Sodium Alpha Olefin Sulfonate	Witconate AOS
Cationic	C1	Tallowamine Ethoxylate	Witcamine 6606
	C2	Methyl Quaternary of Propoxylated Diethylethanolamine	Emcol CC-9
Amphoteric	AM1	Amido Cocobetaine	Emcol 5430

<sup>1</sup> Witco Corporation trade names.

**Table 2-2**  
**Surfactant Solution Properties**

Surfactant	Molecular Weight	Critical Micelle Conc. moles/kg	Surface Tension <sup>1</sup> at C>CMC dynes/cm	Solution Viscosity <sup>1</sup>			pH
				C=10 <sup>-2</sup> mole/kg gm/(cm-sec)	C=5X10 <sup>-2</sup> mole/kg gm/(cm-sec)	C=10 <sup>-1</sup> mole/kg gm/(cm-sec)	
N1	490	1.7E-4	33	0.0103	0.0119	0.0138	5.8
N2	640	1E-5<>1E-4	36	0.0105	0.0152	0.0284	5.8
N3	825	1E-5<>1E-4	36	0.0105	0.0131	0.0176	6.7
A1	288	9.0E-3	39	0.0102	0.0104	0.0117	7.5
A2	324	1.3E-3	39	0.0102	0.0114	0.0123	7.3
C1	590	1E-5<>1E-4	44	0.0104	0.0117	0.0136	8.8
C2	550	6.0E-3	40	0.0104	0.0111	0.0121	5.5
AM1	415	1.6E-4	34	0.0102	0.0102	0.0114	5.4
A1 & N3	-	1E-5<>1E-4	39	-	0.0127	0.0147	7.7
A2 & N1	-	6.0E-4	36	-	0.0115	0.0132	6.7
A1 & NaCl	-	1.9E-4	35	0.0098	0.0105	-	-
A2 & NaCl	-	2.8E-4	35	0.0099	0.0105	-	-

<sup>1</sup> Temperature = 22 C. For water at T = 22 C, surface tension equals 72.4 dynes/cm and viscosity is 0.0096 g/(cm-s). Surface tension precision =  $\pm 0.5$  dynes/cm. Viscosity precision =  $\pm 0.00005$  g/(cm-s).

Table 2-3

Soil Characteristics

<i>Soil</i>	<i>USDA Classification</i>	<i>Extractable Bases</i>	<i>Cation Exchange Capacity<sup>1</sup></i>	<i>pH</i>	<i>Specific Surface Area</i>	<i>Organic Carbon Content</i>
		<i>meq/100g</i>	<i>meq/100g</i>		<i>m<sup>2</sup>/g</i>	<i>weight %</i>
Teller	"Loam" 52% Sand 31% Silt 17% Clay	Na <sup>+</sup> = 0.84 K <sup>+</sup> = 0.99 Ca <sup>+2</sup> = 6.28 Mg <sup>+2</sup> = 2.39	~14	6.0	37.8	1.2
Dougherty	"Sand" 98% Sand 2% Silt and Clay	Na <sup>+</sup> = 1.40 K <sup>+</sup> = 0.14 Ca <sup>+2</sup> = 2.40 Mg <sup>+2</sup> ~ 0.00	~5	5.9	21.8	0.1

<sup>1</sup> Cation exchange capacity was calculated assuming a base saturation of 75 percent, which is average for the Payne County, Oklahoma, area from which these soils were obtained.



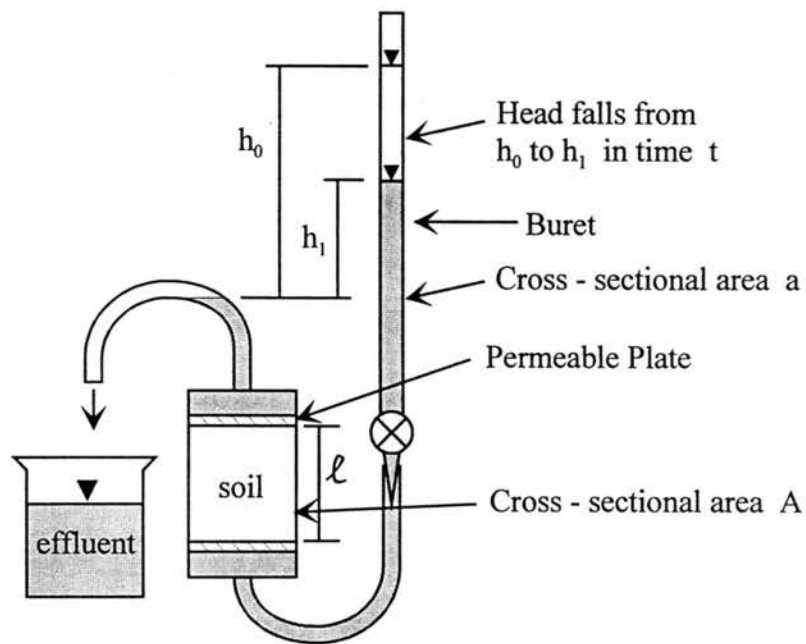
Table 2-4

## Dougherty Sand Test Results

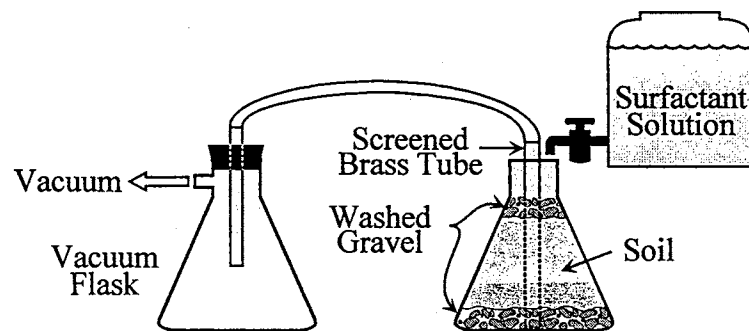
Injection Solution <sup>1</sup>	Percent Change in Hydraulic Conductivity	Maximum Possible Change in Hydraulic Conductivity Due to Viscosity Effects	Effluent Nonvolatile Solids (mg/kg)
Water	+4.7	0.0	176
N1	-14.1	-19.6	194
N2	-44.0	-37.0	125
N3	-21.9	-26.9	139
A1	-46.5	-16.0	6752
A2	-34.7	-16.0	7677
C1	-40.5	-18.2	147
C2	-42.8	-13.0	289
AM1	-27.9	-6.2	6002
A1 & N3	-27.3	-24.6	2360
A2 & N1	-23.6	-16.7	5850
A1 & .1 mole/kg NaCl	-9.4	-8.8	4019 <sup>2</sup>
A2 & .1 mole/kg NaCl	-20.3	-8.8	5439 <sup>2</sup>

<sup>1</sup> Surfactant solution concentrations are 0.05 mole/kg.

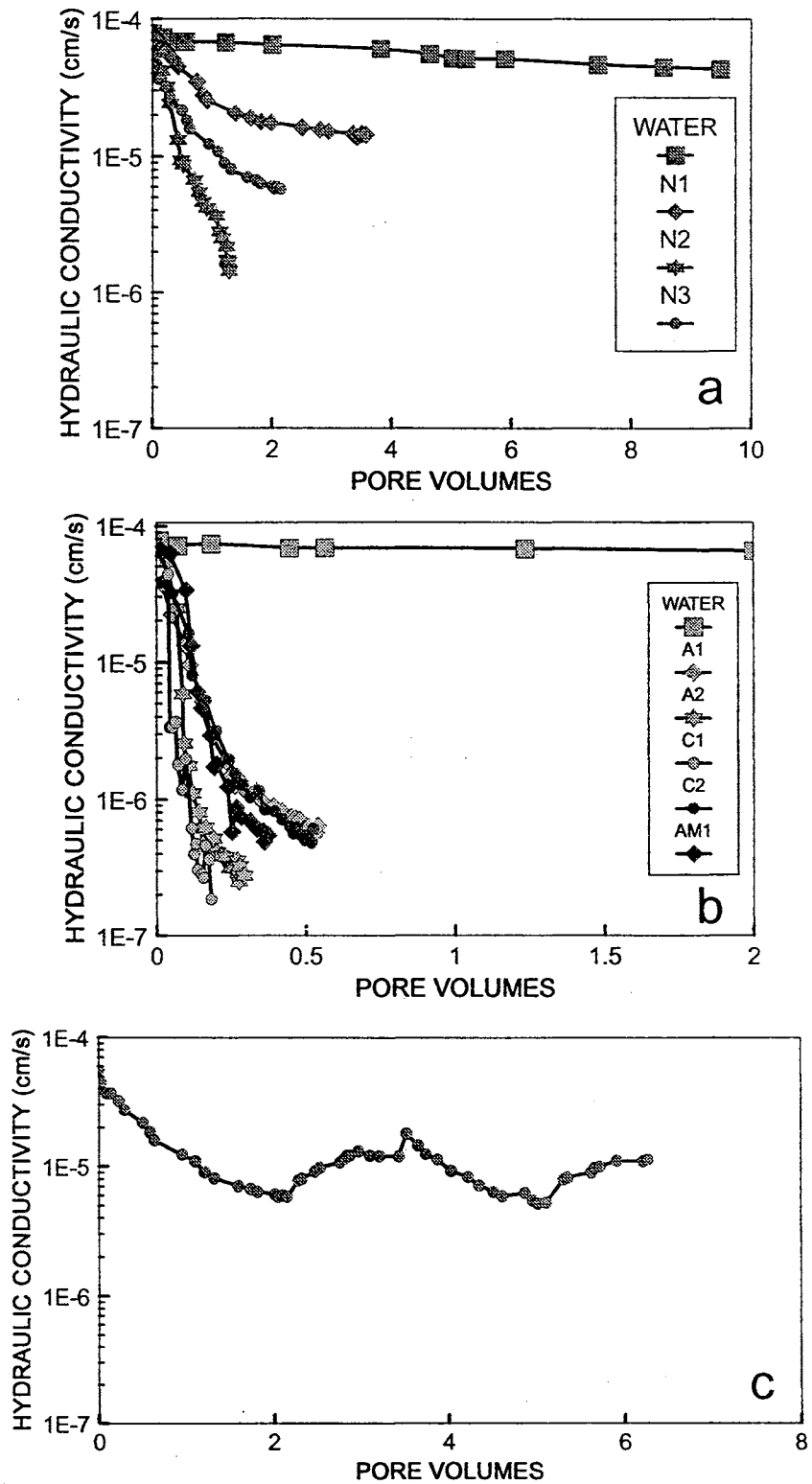
<sup>2</sup> Value corrected for NaCl content.



**Fig. 2-1.** Falling-head permeability test apparatus.



**Fig. 2-2.** Dispersion test apparatus.



**Fig. 2-3.** Teller loam test series #1. Soil hydraulic conductivity versus pore volume - 0.1 mole/kg solution concentrations. (a) Nonionic surfactants. (b) Ionic surfactants. (c) N3 surfactant and water flush reduction-recovery cycles.

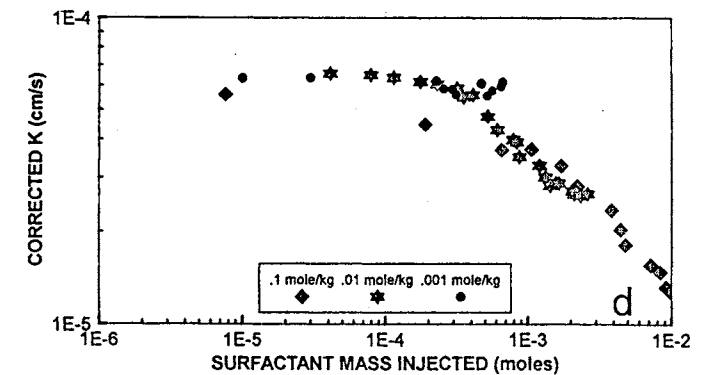
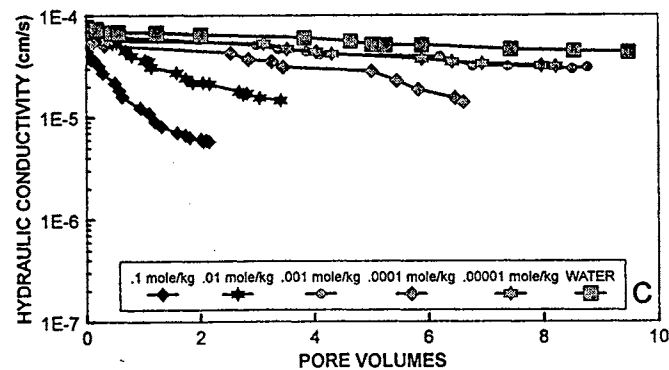
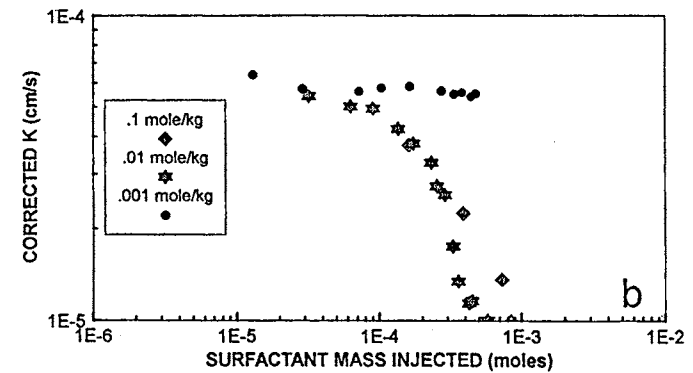
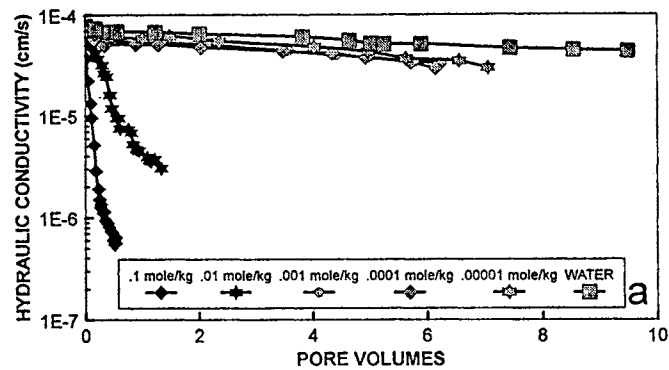
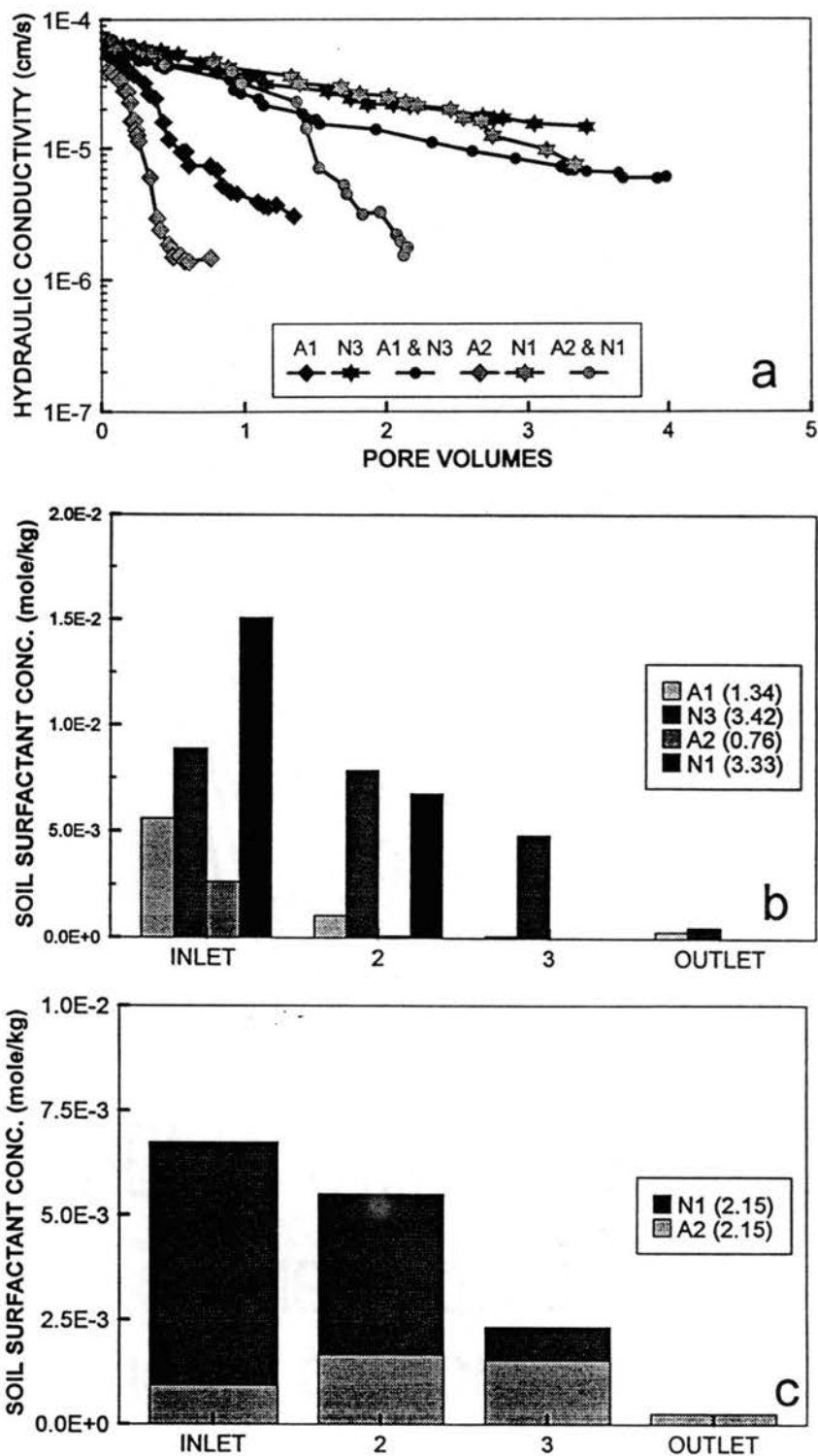
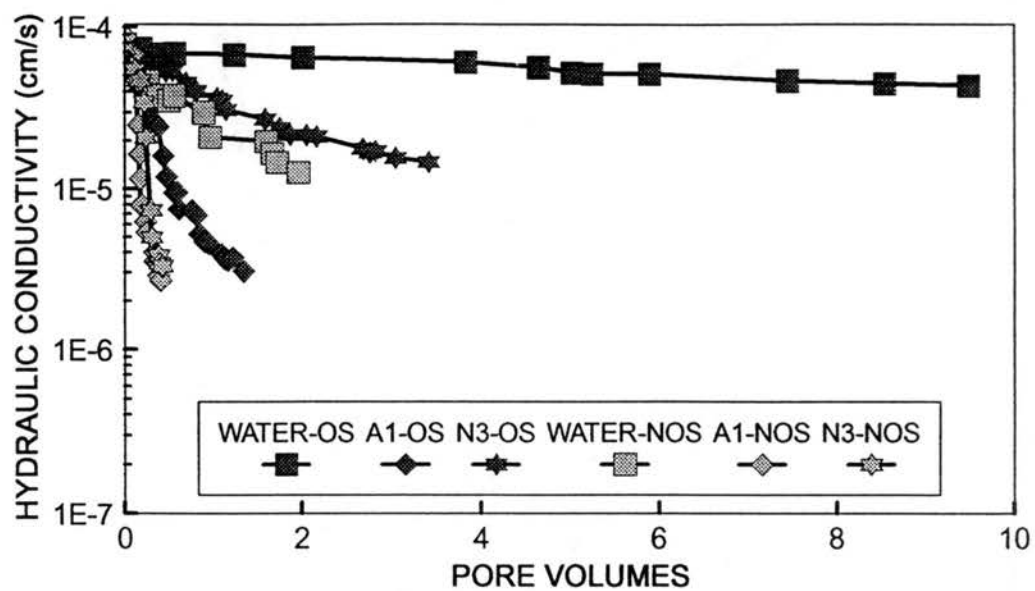


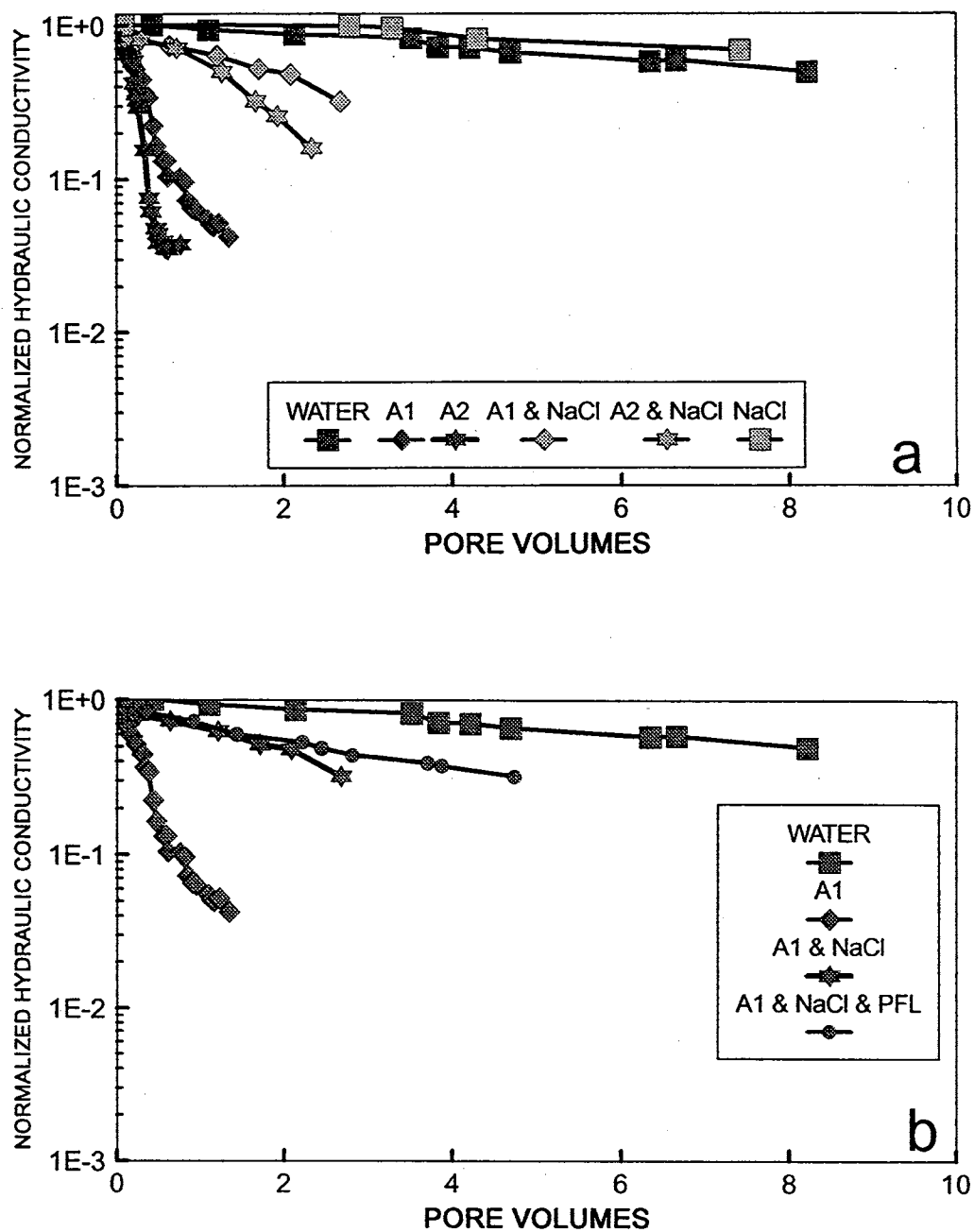
Fig. 2-4. Teller loam test series #2. (a & c) Soil hydraulic conductivity versus pore volume as a function of surfactant solution concentration (mole/kg). (b & d) Corrected soil hydraulic conductivity versus mass of surfactant injected as a function of surfactant solution concentration. (a & b) Surfactant A1. (c & d) Surfactant N3.



**Fig. 2-5.** Teller loam test series #3. (a) Hydraulic conductivity versus pore volume for mixed anionic-nonionic surfactant solutions (0.01 mole/kg) as compared to single component surfactant solutions (0.01 mole/kg). Soil column surfactant distributions from single component surfactant solution tests (b) and A2-N1 mixed solution test (c). Injected pore volumes are given in parentheses.

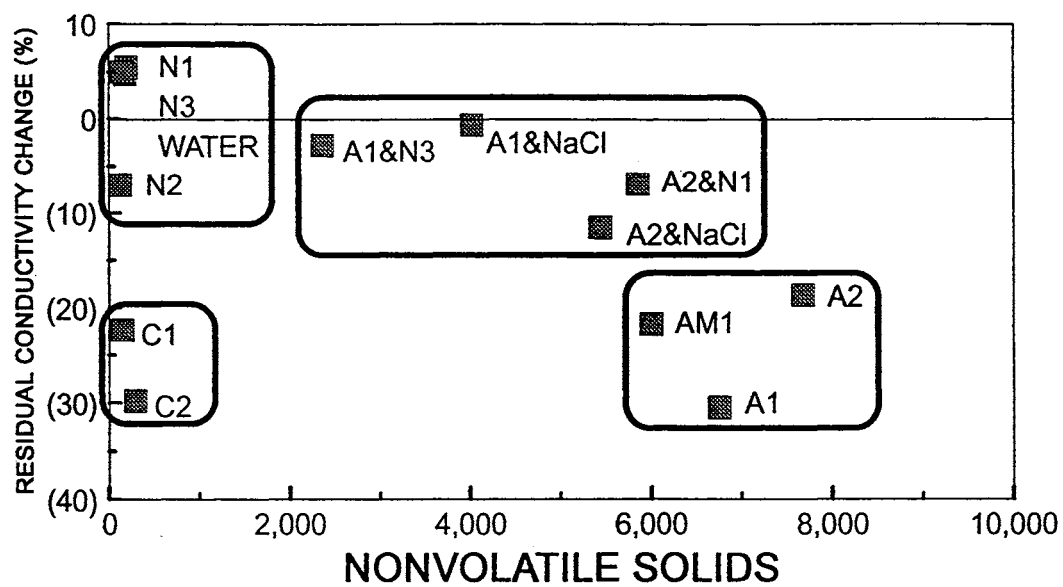


**Fig. 2-6.** Teller loam test series #4. Soil organic matter content as a factor in hydraulic conductivity reduction of surfactant (0.01 mole/kg) affected soil. OS - soil contains organic matter. NOS - soil does not contain soil organic matter.



**Fig. 2-7.** Teller loam test series #5. (A&B) Normalized hydraulic conductivity versus pore volume. (a) Effects of adding 0.1 mole/kg NaCl electrolyte to 0.01 mole/kg anionic surfactant solutions. (b) Effect of using a 0.1 mole/kg NaCl preflush (PFL).





**Fig. 2-8.** Dougherty sand test series. Residual hydraulic conductivity change versus nonvolatile solids.

## **Chapter III**

### **ANIONIC SURFACTANT MOBILITY IN UNSATURATED SOIL 1: TRANSPORT CHARACTERISTICS**

#### **Abstract**

Surfactants are being increasingly considered for in situ environmental remediation of soils. The efficiency and effectiveness of using surfactants for this purpose may depend on their mobility under unsaturated flow conditions. For this reason, transient horizontal unsaturated column tests were used to study anionic surfactant transport characteristics in Teller loam. Two commercial anionic surfactants, an alkyl ether sulfate (AES) and a linear alkylbenzene sulfonate (LAS), were tested. For both surfactants, the concentration and moisture content profiles plotted versus the Boltzmann transform ( $\text{distance}/\text{time}^{0.5}$ ) exhibited similarity between tests, which differed only in time duration. Similarity of the concentration profiles is an indication that surfactant chemical equilibrium conditions prevailed during testing. Penetration of the AES and LAS concentration fronts were respectively one-half and one-fifth the advance of the wetting front, indicating a high degree of sorption. Both surfactants significantly reduced soil moisture diffusivities at volumetric moisture contents above 0.23.

## **Introduction**

The successful testing of surfactants for enhanced oil recovery by the petroleum industry has led to their consideration for contaminant flushing from soils. The efficiency and effectiveness of using surfactants for in situ environmental remediation of soils located above the water table will in part be determined by their mobility under unsaturated flow conditions. If the surfactants utilized become immobilized through precipitation and/or adsorption, then cleanup procedures may be impractical.

A considerable amount of research has been conducted on surfactant mobility in saturated porous media. However, for unsaturated soils, the investigation of surfactant transport characteristics has been limited. Mustafa and Letey (1971) found two nonionic surfactants to increase unsaturated diffusivity values in a water-repellent soil, while having little or no effect on the diffusivities in a wettable soil. Miller and Letey (1975) determined through a series of unsaturated vertical column experiments that nonionic surfactant mobility during leaching was far greater in a wettable soil than one which was water-repellent. Remediation effectiveness under unsaturated flow conditions was demonstrated by a field pilot test in which a nonionic surfactant was successfully employed to remove oils and polychlorinated biphenyls from the vadose zone (Abdul et al., 1992; Abdul and Ang, 1994). Because of the modest amount of previous work, more study is required regarding anionic surfactant transport in unsaturated soils. Anionics are the most common surfactant type commercially available and in all likelihood the most economical for utilization in soil flushing remediation. For these reasons, this study focused strictly on anionic surfactants.

## Flow Theory

The investigation of surfactant transport characteristics was conducted using testing procedures described by Brown and Allred (1992). In these tests, an anionic surfactant solution was injected into the inlet of a horizontally mounted soil column. Transient horizontal flow in unsaturated porous media can be expressed as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( K(\theta) \frac{\partial h}{\partial x} \right) = \frac{\partial}{\partial x} \left( K(\theta) \frac{\partial \Psi}{\partial x} \right) = \frac{\partial}{\partial x} \left( K(\theta) \frac{\partial \Psi}{\partial \theta} \frac{\partial \theta}{\partial x} \right) = \frac{\partial}{\partial x} \left( D(\theta) \frac{\partial \theta}{\partial x} \right) \quad (3-1)$$

where  $t$  is time (T),  $x$  is distance (L),  $\Psi$  is the pressure head (L), and the unsaturated hydraulic conductivity,  $K(\theta)$ , is a function of the volumetric moisture content,  $\theta$ . The unsaturated diffusivity,  $D(\theta)$  ( $L^2/T$ ), is defined as:

$$D(\theta) = \frac{k(\theta) \rho g_c}{\mu} \frac{\partial \Psi}{\partial \theta} \quad (3-2)$$

Equation (3-2) implies that surfactant solutions introduced into unsaturated porous media can affect diffusivity values by altering the moisture content dependent intrinsic permeability,  $k(\theta)$  ( $L^2$ ), the pressure head versus moisture content relationship,  $\frac{\partial \Psi}{\partial \theta}$  (L), or the fluid properties of density,  $\rho$  ( $M/L^3$ ), and viscosity,  $\mu$  ( $M/LT$ ). The gravitational acceleration constant,  $g_c$  ( $L/T^2$ ), is of course constant.

Bruce and Klute (1956) showed that equation (3-1) can be solved as an ordinary differential equation using a method devised by Boltzmann in 1894. A substitution of  $\lambda = x/\sqrt{t}$  is used to transform equation (3-1) into the following form:

$$-\frac{\lambda}{2} \frac{d\theta}{d\lambda} = \frac{d}{d\lambda} \left( D(\theta) \frac{d\theta}{d\lambda} \right) \quad (3-3)$$

Using laboratory tests in which a solution is injected into the inlet of a horizontally mounted soil column, the diffusivity versus moisture content relationship can be

determined by rearranging equation (3-3) and integrating with respect to  $\lambda$  over the boundary conditions:

$$\begin{aligned}\theta &= \theta_i, \text{ for } \lambda \rightarrow \infty \text{ (} x \rightarrow \infty \text{ or } t = 0\text{)} \\ \theta &= \theta_0 \text{ for } \lambda = 0 \text{ (} x = 0 \text{ and } t > 0\text{)}\end{aligned}\quad (3-4)$$

where  $\theta_i$  is the initial moisture content, and  $\theta_0$  is the inlet moisture content. The diffusivity relationship can then be defined as:

$$D(\theta_*) = -\frac{1}{2} \left( \frac{d\lambda}{d\theta} \right)_{\theta_*} \int_{\theta_i}^{\theta_*} \lambda d\theta \quad (3-5)$$

where  $\theta_*$  is an arbitrary moisture content between  $\theta_i$  and  $\theta_0$ . The term,  $\left( \frac{d\lambda}{d\theta} \right)_{\theta_*}$ , represents the derivative at  $\theta = \theta_*$ . Given the testing conditions previously stated, equation (3-5) can be easily evaluated after determining the moisture content profile along the soil column.

## **Materials**

### ***Surfactants***

Surfactants are organic compounds that on the molecular level are comprised of both hydrophobic and hydrophilic groups. This amphipathic structure causes surfactant molecules to concentrate at boundaries between phases, thereby altering interfacial properties such as surface tension. Above a certain solution concentration, called the critical micelle concentration (CMC), surfactant molecules form aggregates called micelles. Surface tension usually reaches a minimum value at or above the CMC. Surfactants are classified according to charge of the hydrophilic group as being anionic, cationic, amphoteric (positive and/or negative molecular charge), or nonionic. For this investigation anionics were used exclusively.

The two commercial surfactants utilized were a sodium alkyl ether sulfate (AES) and a sodium linear alkyl benzene sulfonate (LAS). These surfactants were chosen based on their properties and widespread commercial availability. Table 3-1 lists some of the characteristics of the two surfactants. Both surfactants are comprised of a series of homologs, and the active ingredient weight percent of the AES and LAS surfactant products was 39% and 91%, respectively.

Surface tension and CMC values were measured with a Fisher Scientific Model 21 Tensiomat tensiometer. Viscosities were obtained with a Cannon Instrument Co. size 50 viscometer. The specific gravity was essentially equal to 1 for the 0.025 mole/kg surfactant solutions tested.

### *Soil*

Teller loam (Thermic Udic Argiustoll) was the soil tested throughout the study. It was obtained from a field location near Perkins, Oklahoma and is typical of top soils from the southern plains region. Its characteristics are presented in Table 3-2. Properties were determined using the procedures described in *Methods of Soil Analysis, Part 1 & 2* (ASA and SSSA, 1982 and 1986). Specific surface area was calculated from water vapor sorption isotherms by use of the B.E.T. equation (Quirk, 1955). The Teller was chosen for testing because its anionic surfactant sorption potential made it a good candidate for studying transport characteristics. The sorption potential of the soil was expected to be significant due to a high level of exchangeable  $\text{Ca}^{+2}$  (6.28 meq/100g) and a relatively large specific surface area (37.8  $\text{m}^2/\text{g}$ ).

## Experimental Procedures

Column tests were carried out following procedures described by Brown and Allred (1992). Figure 3-1 shows the apparatus used to conduct the transient unsaturated tests. A computer controlled syringe pump was used to inject a 0.025 mole/kg surfactant solution into the inlet of a dry soil column. The 0.025 mole/kg injection concentration is above the CMC for both surfactants. In terms of weight percent, the surfactant solution concentrations were approximately 0.9%, which is approximately the level required for environmental remediation.

The volumetric moisture content and hence the soil moisture potential at the column inlet were maintained at constant values throughout the timed duration of the test. This was accomplished by using the computer controlled syringe pump to regulate the instantaneous injected flow at a rate inversely proportional to the square root of elapsed time. The proportionality constant used for determining the injection rate was based on total test duration time and the volume of solution to be injected. Along with the injection rate function, soil and solution properties will also affect the inlet moisture content.

The column itself was comprised of individual acrylic rings and packed with Teller loam to an average dry bulk density of  $1.60 \text{ g/cm}^3$ , which corresponds to a porosity of 0.40. Prior to packing, the loam was placed in an oven at 105 C for 24 h to obtain initial soil moisture contents of 0.01 or less and to reduce microorganisms which may interact with the surfactants during testing. The individual rings had a diameter of 3.5 cm and a length of 0.5, 1.0, or 2.0 cm. The shorter rings were placed adjacent to the

column inlet to provide better resolution of the surfactant concentration and moisture content profiles within this region. Overall column length ranged from 16 to 27 cm. Upon test completion, the soil column was broken apart and the soil from within each ring divided into two parts, one for analysis of volumetric moisture content and the other for determination of anionic surfactant concentration.

Volumetric moisture content along the column was determined by oven drying the soil sample at 105 C for 24 h. The mean of the injected moisture percent accounted for by oven drying was 98%. Prior to chemical analysis, an extraction process was required to separate the anionic surfactant from the moist soil. The extraction process found to be the most successful required multiple steps. First, 10 ml of a 0.1 mole/kg NaCl solution was added to an Erlenmeyer flask containing a 5 g sample of moist soil. The flask was then hand-shaken and allowed to equilibrate 30 m. After this, 90 ml of reagent grade acetone was added, and the flask placed in a shaker bath for 1 h at 300 rpm. Next, a 1 ml quantity of the extraction solution was taken from the flask and diluted to 100 ml with deionized water. The 100 ml sample was chemically analyzed for anionic surfactant concentration using the standard methylene blue method (APHA et al., 1985). The analyzed concentration value was in turn used to determine the amount of surfactant present in the soil from within each ring of the column. The mean of the percent surfactant recovered from each test was 95%.

The NaCl solution enhances surfactant extraction efficiency by reducing electrostatic attractions and/or precipitation. Multivalent cations can coadsorb anionic surfactants onto soil particles (Gaudin and Chang, 1952). Sodium ions will prevent this



by competing with divalent calcium ( $\text{Ca}^{+2}$ ) and magnesium ( $\text{Mg}^{+2}$ ) ions for soil cation exchange sites. The presence of an electrolyte such as NaCl will also reduce the anionic surfactant CMC (Rosen, 1989). Surfactant precipitates should dissolve if the CMC is reduced to a level below the solubility limit for a Ca-surfactant or Mg-surfactant salt. The addition of acetone enhances extraction by reducing hydrophobic adsorption of anionic surfactants to soil particles. Surfactant molecules can dissolve in some polar solvents without distorting the liquid structure to a significant extent. As a result, surfactants present in such solvents will have little tendency to concentrate at interfaces (Rosen, 1989).

Tests were conducted with both AES and LAS to investigate anionic surfactant transport characteristics. The use of the previously discussed procedure for calculating unsaturated diffusivities is valid only if the moisture content profiles ( $\theta$  versus  $\lambda = x/\sqrt{t}$ ) show similarity for tests of different time duration but equivalent boundary conditions. Consequently, a series of three tests were conducted for each surfactant in order to test similarity. Within each test series, the boundary conditions given in equation (3-4) were kept constant while the time duration of the tests varied from 12 to 24 to 72 h. The total injection volumes for the 12, 24, and 72 h tests were 14.1, 20.0, and 34.6 ml, respectively. The distributions of the resident divalent cations ( $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) present in the soil columns from both the AES and LAS 72 h tests were also determined. This was accomplished by extracting the  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  from soil samples with 1 N ammonium acetate followed by analysis with an inductively coupled plasma instrument (ICP).

Several other tests were also conducted. A representative soil water solution (0.001 mole/kg  $\text{CaSO}_4$  and 0.001 mole/kg NaCl) was injected in three tests of different

time duration (24, 48, and 72 h). The average moisture content profile from these tests was then used for comparison with surfactant affected profiles. In another test, a 0.025 mole/kg sodium iodide (NaI) solution was injected over a period of 72 h to compare AES and LAS concentration profiles with those of a common cation ( $\text{Na}^+$ ) and anion ( $\text{I}^-$ ).  $\text{Na}^+$  was analyzed using an ICP after extraction from soil with 1 N ammonium acetate.  $\text{I}^-$  was extracted from soil samples using deionized water and then chemically analyzed with an ion chromatograph. The percent injected mass accounted for by the extraction and chemical analysis techniques were 83% for  $\text{Na}^+$  and 88% for  $\text{I}^-$ .

## Experimental Results

Test results from the AES and LAS surfactants are shown in Figures 3-2 and 3-3, respectively. Figures 3-2a and 3-3a show the surfactant concentration profiles. Concentration values are given in mole/kg of total porous media which includes both the soil and the soil water solution. The values were reported in this manner because the analysis techniques do not distinguish between surfactant in the solution phase and that adsorbed onto soil particles. Moisture content profiles are provided in Figures 3-2b and 3-3b, while diffusivity values are plotted in Figures 3-2c and 3-3c. To check for similarity, the surfactant concentration and moisture content profiles were plotted with respect to the Boltzmann transform,  $\lambda = x/\sqrt{t}$ , where  $x$  is the distance in cm from the column inlet and  $t$  is the time duration of the test in seconds.

As shown in Figures 3-2a and 3-3a, the 12, 24, and 72 h concentration profiles all show similarity. The profiles exhibited by both surfactants are somewhat unique in that

peak values are found at a location between the column inlet and the wetting front edge as shown in Figures 3-2b and 3-3b.

Figures 3-2b and 3-3b also show similarity in the volumetric moisture content profiles from the 12, 24, and 72 h tests. For comparison purposes, the averaged moisture content profile from the three water tests is also included. The moisture content profiles for both surfactants contain two steeply declining limbs. One is the wetting front edge, while the other begins at the column inlet and ends at a Boltzmann transform (or distance) value which coincides with the surfactant concentration front shown in Figures 3-2a and 3-3a. Of special interest regarding the LAS surfactant, is a notch at the base of this steeply declining limb adjacent to the inlet. Here, moisture contents show a small but significant reversal in the usual trend of continuous decrease from inlet to wetting front edge. The averaged moisture content profile from the water tests shows no steeply declining limb adjacent to the inlet. The inlet moisture contents of the AES and LAS surfactant tests averaged 0.33 and 0.35, respectively. The inlet moisture content from the water tests was 0.29. Consequently, the inlet moisture contents are maintained at higher levels when surfactants are injected.

Because of the similarity achieved in the moisture content profiles from the surfactant tests, equation (3-5) can be applied to calculate diffusivity values. Representative moisture content curves were used in determining these values. The representative curves were generated by averaging data from the 12, 24, and 72 h surfactant tests. For comparison, diffusivity values were also calculated from the moisture content profile produced from the water tests. AES and LAS affected

diffusivity values along with those from the water tests are plotted as a function of moisture content in Figures 3-2c and 3-3c. For AES, the surfactant affected diffusivities are greater than those from the water tests in a moisture content range of 0.18 to 0.23. The AES peak value is  $0.002 \text{ cm}^2/\text{s}$  at a moisture content of 0.21. Above 0.23, the AES surfactant affected diffusivities become significantly less than those from the water tests. LAS affected diffusivities are greater than those calculated from the water tests at a moisture content range of 0.20 to 0.23. The LAS peak value is  $0.0016 \text{ cm}^2/\text{s}$  at a moisture content of 0.23. Above 0.23, LAS affected diffusivities are less than the calculated water test values. A unique aspect to the LAS affected diffusivities plotted in Figure 3-3c is the presence of negative values. The lowest value of  $-0.0019 \text{ cm}^2/\text{s}$  is found at a moisture content around 0.23. The significance of these negative diffusivities are discussed in the next section.

For comparison, Figure 3-4 shows concentration profiles from the AES, LAS, and NaI 72 h tests. The wetting front edge for all three tests was found at a  $\lambda = x/\sqrt{t}$  value of  $0.032 \text{ cm}/\text{s}^{0.5}$ . A common cation such as sodium ( $\text{Na}^+$ ) is adsorbed close to the inlet while exclusion causes an anion such as iodide ( $\text{I}^-$ ) to be concentrated at the wetting front edge. The AES and LAS anionic surfactants exhibit behavior which is between these two extremes. The AES concentration front advanced one-half the distance of the wetting front while the distance penetrated by the LAS was one-fifth. This is evidence of significant surfactant sorption during testing. Figure 3-5 depicts the distribution of the resident divalent cations present in the soil columns after the 72 h AES and LAS tests were conducted. As shown,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  were displaced from the inlet and

concentrated at the wetting front edge. With LAS, there was a second peak in both the  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  profiles which coincides with the maximum surfactant concentration.

## **Discussion**

Both the AES and LAS surfactant concentration profiles in Figures 3-2a and 3-3a show similarity between the 12, 24, and 72 h tests. This suggests that equilibrium conditions existed with respect to chemical interactions involving the AES and LAS surfactants. Or more precisely, all AES and LAS chemical interactions occurred in a relatively instantaneous manner during testing. If surfactant chemical interactions were not instantaneous, it would be impossible obtain similarity in concentration profiles plotted against the Boltzmann transform for tests having the same boundary conditions but different time duration.

Due to varying degrees of surfactant sorption, concentration fronts did not penetrate as far into the column as did wetting fronts. Here, sorption refers to the solute mobility reducing mechanisms of adsorption and/or precipitation. Adsorption of anionic surfactants within unsaturated soils can be either electrostatic or hydrophobic in nature. Organic matter and clay minerals dominate adsorption processes at soil particle surfaces. With the exception of very low pH conditions, these soil colloids tend to have a net negative charge. Tables 3-1 and 3-2 show that the soil and anionic surfactant solutions used in this study were only slightly acidic. Consequently, simple anion exchange between negatively charged surfactant molecules and positively charged sites on soil surfaces was not expected to be significant. However, it is well known that anionic

surfactants can be coadsorbed at negatively charged sites (Gaudin and Chang, 1952; Rea and Parks, 1990). Essentially, coadsorption involves multivalent cations such as  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  which bridge surfactant anions and negatively charged soil particles. A relatively high  $\text{Ca}^{+2}$  level of 6.28 meq/100g in the Teller loam makes coadsorption a likely factor in reducing anionic surfactant mobility.

Hydrophobic adsorption also affects surfactant mobility. It results from the surfactant tendency to attempt escape from the aqueous environment by concentrating at phase boundaries. Under unsaturated flow conditions, these boundaries include solid/liquid and gas/liquid interfaces. A second form of hydrophobic adsorption occurs where there is strong interaction between the hydrophobic groups of oncoming surfactant molecules and those already adsorbed at soil particle surfaces. The interaction is enhanced by increasing the length of the hydrophobic portion of the surfactant molecule (Rosen, 1989).

Precipitation as a calcium or magnesium salt is another sorption mechanism which can immobilize anionic surfactants. This is an important factor to consider due to the high levels of  $\text{Ca}^{+2}$  present in the Teller loam (Table 3-2). Schwuger (1984) noted that surfactants similar to AES, which contain oxyethylene structural groups, exhibit resistance to precipitation. Consequently, AES mobility is probably governed by other factors. Due to coadsorption and precipitation, soils containing a significant amount of exchangeable  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  may cause problems with surfactant enhanced environmental remediation. In laboratory testing, Ducreux et al. (1990) overcame this by preflushing a soil with a NaCl solution to displace the exchangeable  $\text{Ca}^{+2}$ .

The dominant sorption mechanism affecting the two surfactants tested in this study is unclear. It is likely that more than one factor is involved in reducing the mobility of a particular anionic surfactant. Also, the importance of the various sorption mechanisms may change from one surfactant to the next. The factors affecting mobility become even more complicated when one considers that most commercial surfactants are comprised of a series of homologs. This can lead to chromatographic separation by the soil of the homolog components which make up the commercial surfactant. Mannhardt and Novosad (1991) used a binary surfactant mixture in a saturated core flood test and found that an 18 carbon alkyl chain homolog appeared in the column effluent prior to a 12 carbon alkyl chain homolog. This result appears contrary to intuition but was explained as being caused by the preferential incorporation of the more hydrophobic (longer chain length) homolog into micelles, which in turn prevents sorption. Implications with respect to the AES and LAS tests are that the shorter alkyl chain length homologs are present at the column inlet while the longer chain length homologs are found at the surfactant concentration front. Because of this chromatographic effect, surfactant solution properties in the soil may vary with location, and in severe cases impact surfactant enhanced remediation.

The inlet surfactant concentration was less than the peak profile concentration for the tests which were conducted in this study. There are two possible explanations. First, chromatographic separation as described in the preceding paragraph could be a factor. The shorter alkyl chain length homologs, which are most likely to be present at the inlet, are less efficient in terms of hydrophobic adsorption (Rosen, 1989). Second, the inlet

capacity for surfactant coadsorption may be reduced due to displacement of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  by  $\text{Na}^{+}$ . Evidence for such displacement is shown in Figure 3-5. In the commercial products tested,  $\text{Na}^{+}$  is provided as the counterion and therefore injected along with both anionic surfactants.

As implied by equation (3-2), diffusivity values are a function of the intrinsic permeability,  $k(\theta)$ , the fluid density,  $\rho$ , the fluid viscosity,  $\mu$ , and the pressure head versus moisture content relationship,  $\frac{\partial \Psi}{\partial \theta}$ . The  $\rho$  and  $\mu$  of the surfactant solutions used in this study are not significantly different from those of water. Hence, these fluid properties are not responsible for diffusivity differences observed between the AES/LAS surfactant and water tests. With respect to water, Allred and Brown (1994) found high concentration surfactant solutions (0.01 to 0.1 mole/kg) to significantly reduce the permeability of the Teller loam during saturated tests. Also with comparison to water, surfactant solutions have lower surface tensions which can lead to a reduction in  $\frac{\partial \Psi}{\partial \theta}$ .

Insight into the shape of surfactant affected moisture content profiles along with their corresponding diffusivity values are provided in Figure 3-6 for AES and Figure 3-7 for LAS. From equation (3-5), the diffusivities calculated with respect to moisture content are large where the profile is flat and small where the profile is steep.

In Figures 3-6a and 3-7a, the profile is steep from I to II. This segment of the moisture content profile corresponds to the part of the column where high surfactant concentrations reside. This is confirmed by the surfactant concentration profiles which are also plotted in Figures 3-6a and 3-7a. Diffusivity values calculated between I and II are lower than diffusivities from the water tests at corresponding moisture contents because the high surfactant concentrations probably affect reductions in both  $k(\theta)$  and



$\frac{\partial \Psi}{\partial \theta}$ . Large surfactant affected diffusivity reductions may need to be considered prior to initiation of in situ soil flushing remediation.

Steep profile segments are also found from III to IV in Figure 3-6a and from III<sub>B</sub> to IV in Figure 3-7a. These segments represent a region of the soil column located directly behind the wetting front. Due to sorption, the AES and LAS surfactant penetration did not extend to this distance. The ranges of moisture content represented by these profile segments are 0.01 to 0.18 for the AES tests and 0.01 to 0.20 for the LAS tests. Because of the steep slopes, diffusivity values are relatively small. For the moisture contents specified, the calculated diffusivities are equivalent to those determined from the water tests (Figures 3-2c and 3-3c). This indicates that surfactant injection had no impact on the region of the column directly behind the wetting front. Here, soil conditions were the same as those for the water tests.

The segments between II and III in Figure 3-6a and II and III<sub>B</sub> in Figure 3-7a correspond to a transition zone in the column where surfactant concentrations are low and various soil chemical components initially adjacent to the inlet may have been displaced. The slopes between II and III in Figure 3-6a and III<sub>A</sub> and III<sub>B</sub> in Figure 3-7a are nearly flat. Diffusivity values calculated along these segments are significantly higher than water test diffusivities calculated at similar moisture contents. For the LAS moisture content profile, the segment between II and III<sub>A</sub> exhibits a slope reversal which leads to the calculation of negative diffusivity values. Abrupt changes in  $\frac{\partial \Psi}{\partial \theta}$  can account for the transition zone diffusivity values. Insight into how these abrupt changes occur is given in Figures 3-6b and 3-7b. In these figures, hypothetical soil wetting curves have been drawn for both water and surfactant solution. The transition zone  $\frac{\partial \Psi}{\partial \theta}$  shown in the

figures represents a jump from the surfactant solution curve to the water curve. The large diffusivities calculated for the moisture content slope segments between II and III for AES and III<sub>A</sub> and III<sub>B</sub> for LAS represent a large decrease in  $\Psi$  relative to  $\theta$  as is indicated by equation (2) and shown in Figures 3-6b and 3-7b. This assumes that  $k(\theta)$  remains essentially unchanged. The reversal in the LAS moisture content slope between II and III<sub>A</sub> represents a decrease in  $\Psi$  relative to an increase in  $\theta$ . When  $\frac{\partial \Psi}{\partial \theta}$  is negative, so is diffusivity. It should be noted that transition zone moisture contents and corresponding diffusivity values are artifacts of the test boundary conditions. If inlet and initial moisture content values for the AES and LAS tests were changed then so would the moisture content range representing the transition zone.

## Summary and Conclusions

Test results from this study are summarized as follows.

- 1) AES and LAS surfactant concentration profiles plotted versus the Boltzmann transform show similarity between tests which differed only in time duration. This indicates that chemical interactions involving the surfactants quickly reached equilibrium conditions.
- 2) Sorption mechanisms substantially reduced the mobility of both anionic surfactants under the unsaturated flow conditions which were tested. The LAS surfactant was affected to a greater extent than AES.
- 3) Anionic surfactants can modify the moisture content distribution in soils.
- 4) Unsaturated soil diffusivities are reduced where anionic surfactants such as AES and LAS are present in high concentrations. This is especially true when moisture

contents are high. At a moisture content of 0.30, both surfactants decreased unsaturated diffusivity values by 25%.

The listed results suggest two important implications with respect to surfactant enhanced environmental remediation. First, the molecular structure of an anionic surfactant plays an important role in determining its subsurface mobility under unsaturated flow conditions. This is indicated by the widely different concentration front advances within soil columns by the AES and LAS surfactants. Therefore, the type of anionic surfactant must be chosen carefully. Second, anionic surfactant affected reductions in diffusivity will cause a decrease in the capability of a soil to transmit unsaturated flow. This will reduce remediation effectiveness and/or efficiency and consequently must be taken into account before cleanup procedures begin.

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Table 3-1

## Surfactant Characteristics

Chemical Name	Trade Name <sup>1</sup>	Abbreviation	Chemical Formula	pH <sup>2</sup>	Viscosity <sup>2</sup> gm/(cm-s)	Critical Micelle Conc. mole/kg	Surface Tension <sup>2</sup> dynes/cm
Sodium Alkyl Ether Sulfate	Witcolate 7093	AES	$C_{6-10}H_{13-21}(OCH_2CH_2)_3OSO_3Na$ C <sub>6</sub> = 18% C <sub>8</sub> = 35% C <sub>10</sub> = 47%	6.9	0.0104	0.005	34.4
Sodium Linear Alkylbenzene Sulfonate	Witconate 90F	LAS	$C_{10-13}H_{21-27}C_6H_4SO_3Na$ <C <sub>10</sub> = <2% C <sub>10</sub> = <25% C <sub>11</sub> = 25% to 50% C <sub>12</sub> = >25% C <sub>13</sub> = <15%	6.6	0.0104	0.001	33.8

<sup>1</sup> Both surfactants were obtained from the Witco Corp.

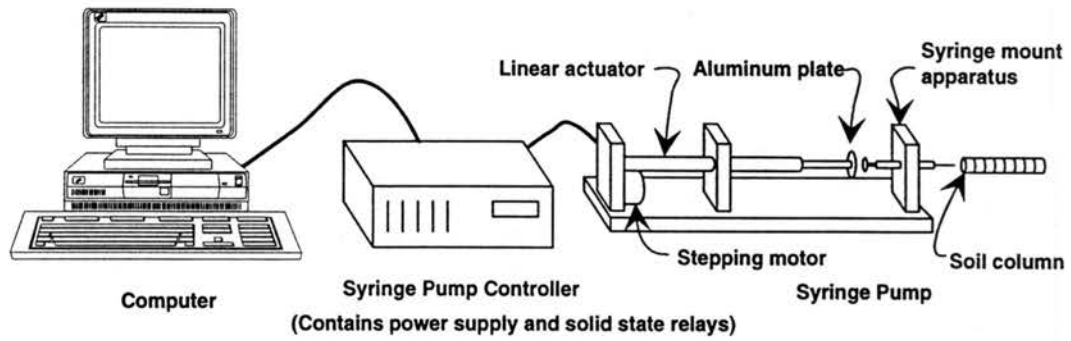
<sup>2</sup> Properties were obtained for 0.025 mole/kg surfactant solutions. Temperature = 22 C. For water at T = 22 C, surface tension is 72.4 dynes/cm and viscosity is 0.00956 gm/(cm-s).

Table 3-2

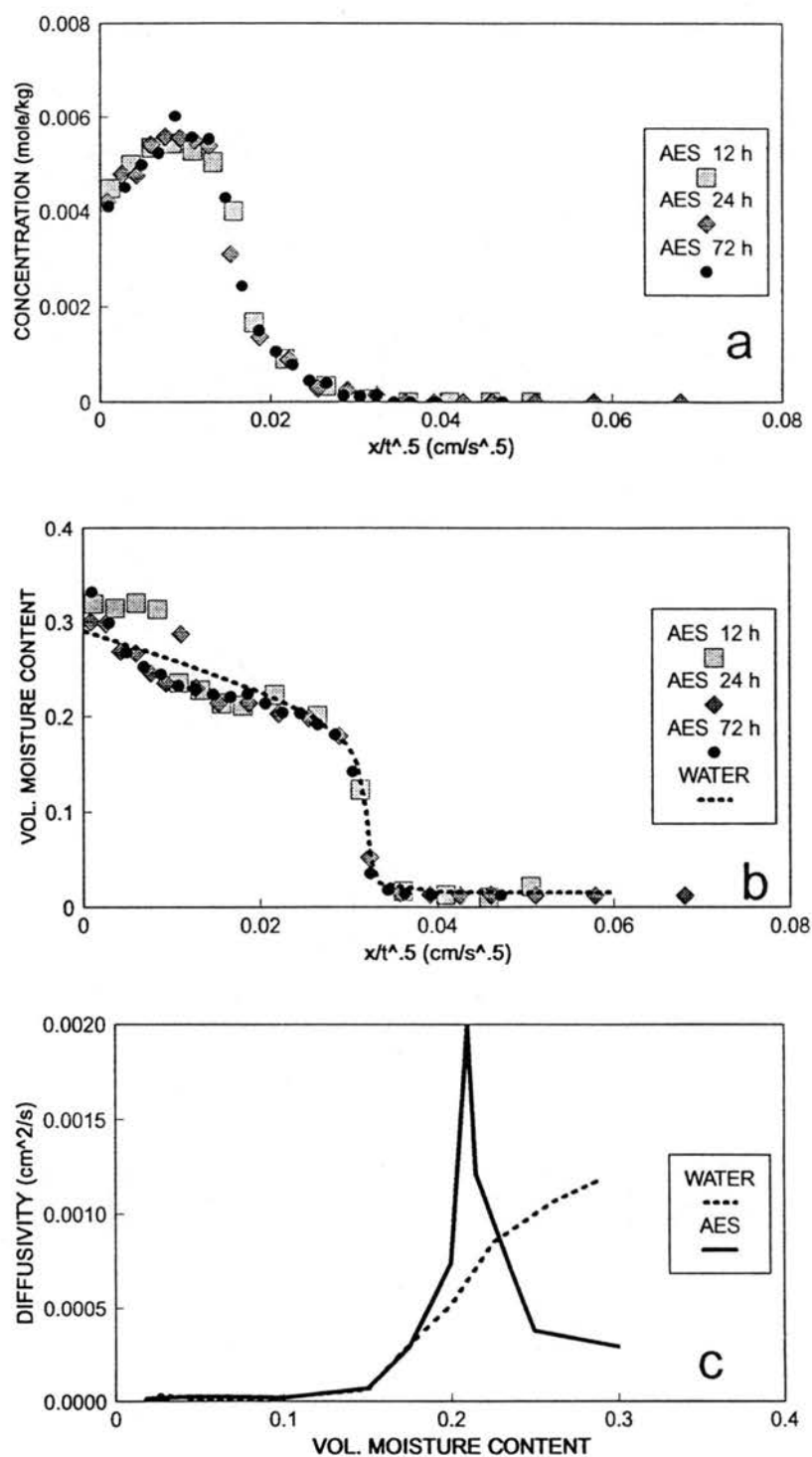
## Soil Characteristics

<i>Soil</i>	<i>USDA Classification</i>	<i>Extractable Bases</i>	<i>Cation Exchange Capacity<sup>1</sup></i>	<i>pH</i>	<i>Specific Surface Area</i>	<i>Organic Carbon Content</i>
		<i>meq/100g</i>	<i>meq/100g</i>		<i>m<sup>2</sup>/g</i>	<i>weight %</i>
Teller	"Loam" 52% Sand 31% Silt 17% Clay	Na <sup>+</sup> = 0.84 K <sup>+</sup> = 0.99 Ca <sup>+2</sup> = 6.28 Mg <sup>+2</sup> = 2.39	~14	6.0	37.8	1.2

<sup>1</sup> Cation exchange capacity was calculated assuming a base saturation of 75 percent, which is average for the Payne County, Oklahoma, area from which these soils were obtained.

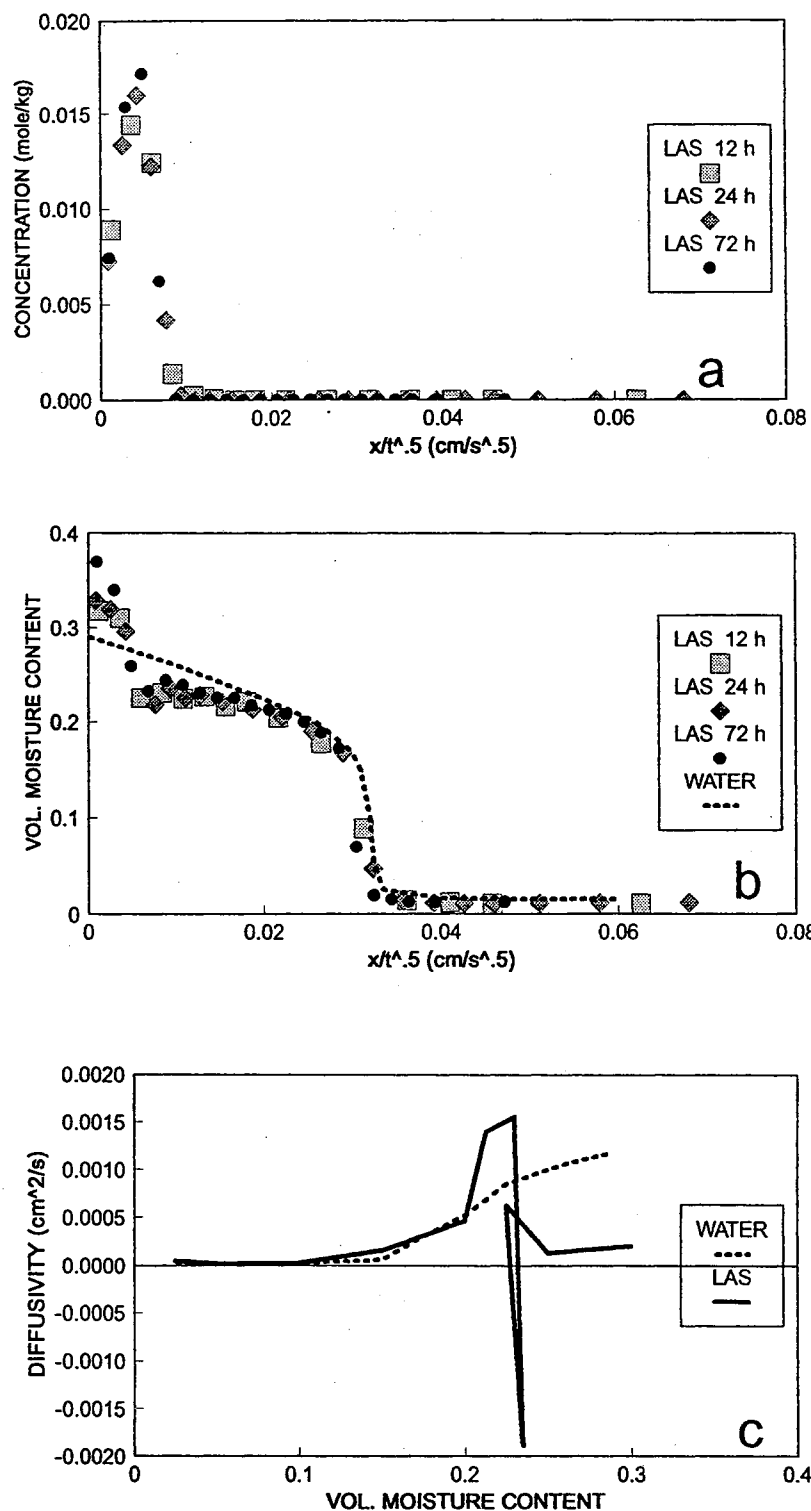


**Fig. 3-1.** Testing apparatus.



**Fig. 3-2.** AES test results. (a) Surfactant concentration profiles. (b) Volumetric moisture content profiles. (c) Calculated diffusivity values plotted versus moisture content.





**Fig. 3-3.** LAS test results. (a) Surfactant concentration profiles. (b) Volumetric moisture content profiles. (c) Calculated diffusivity values plotted versus moisture content.

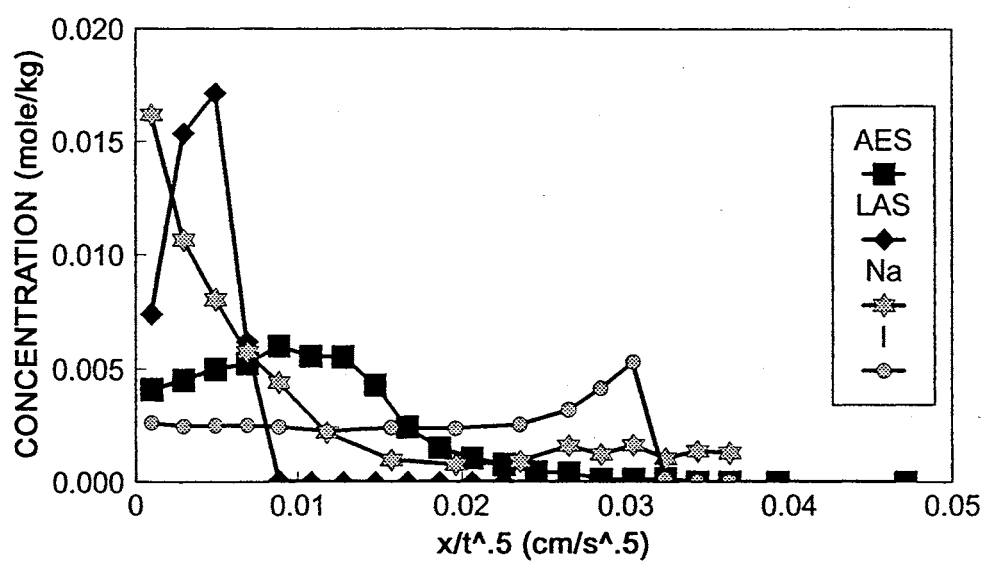
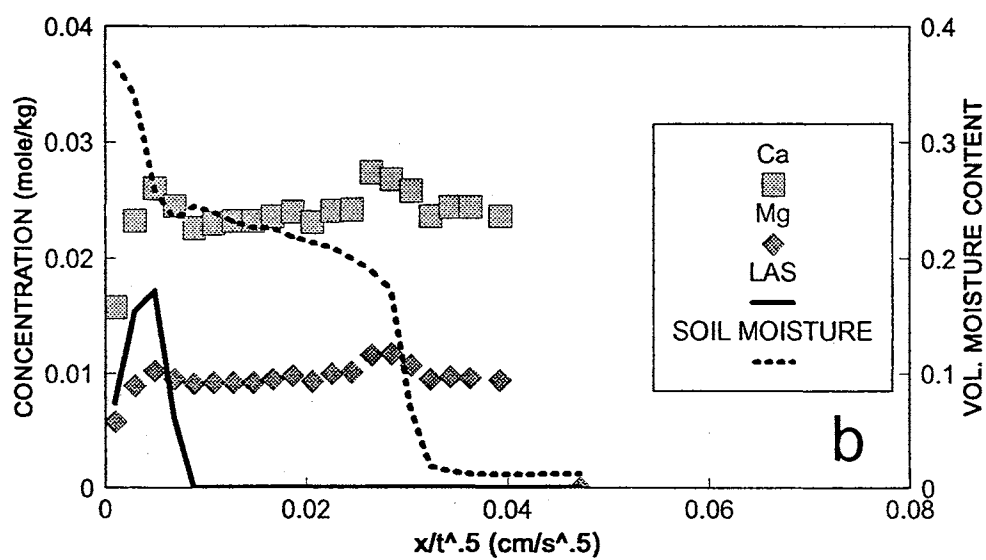
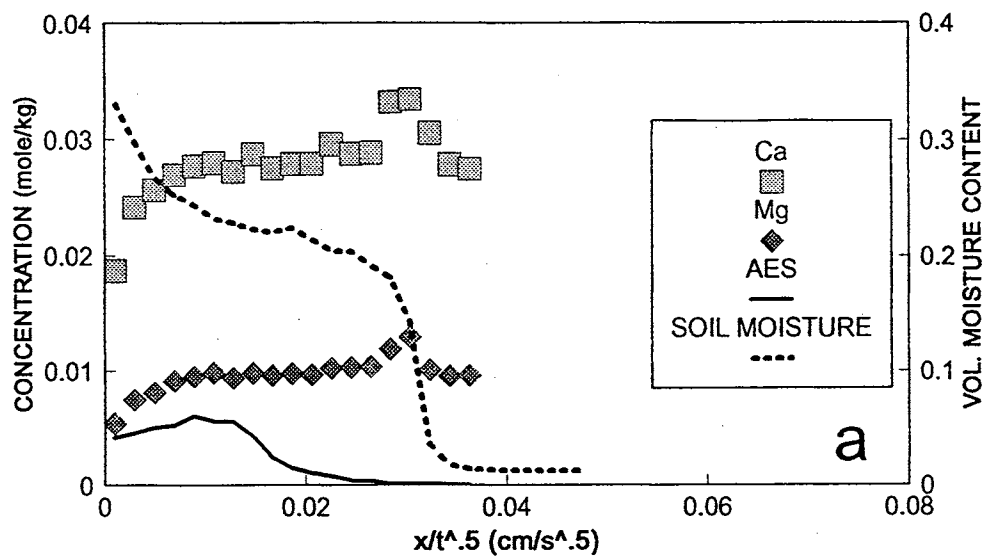
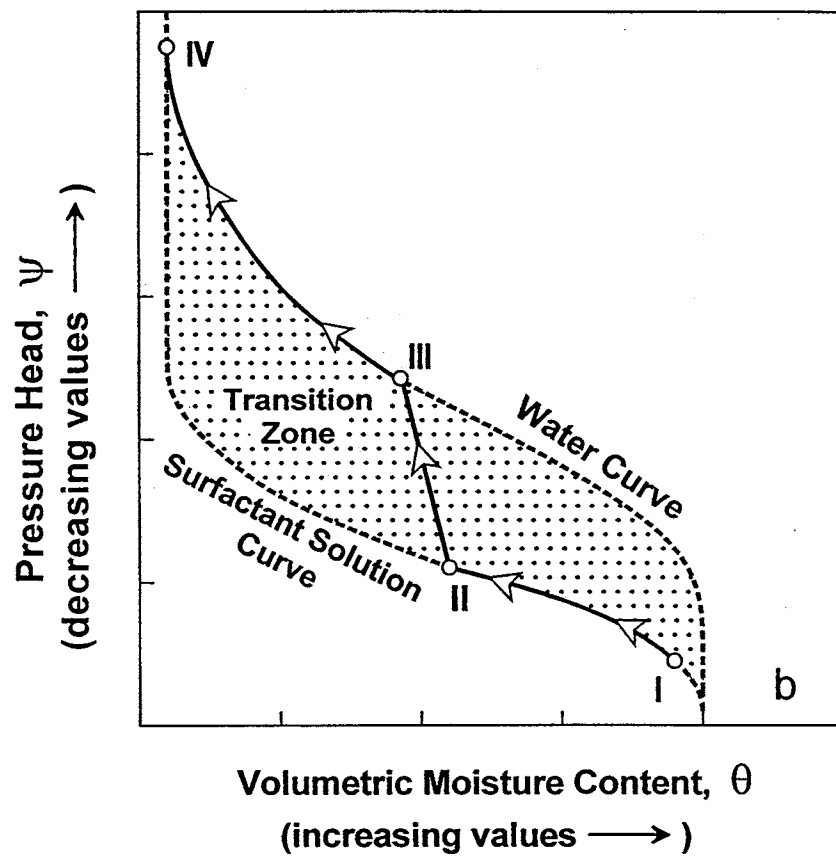
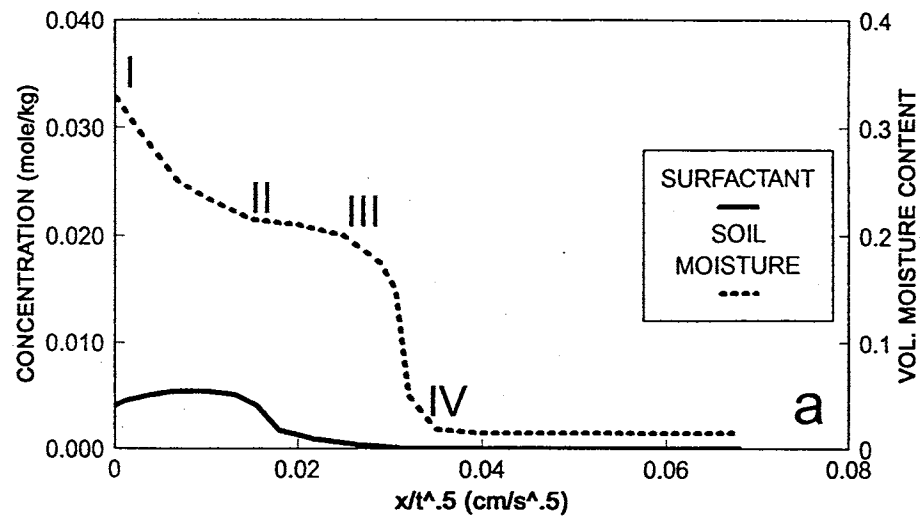


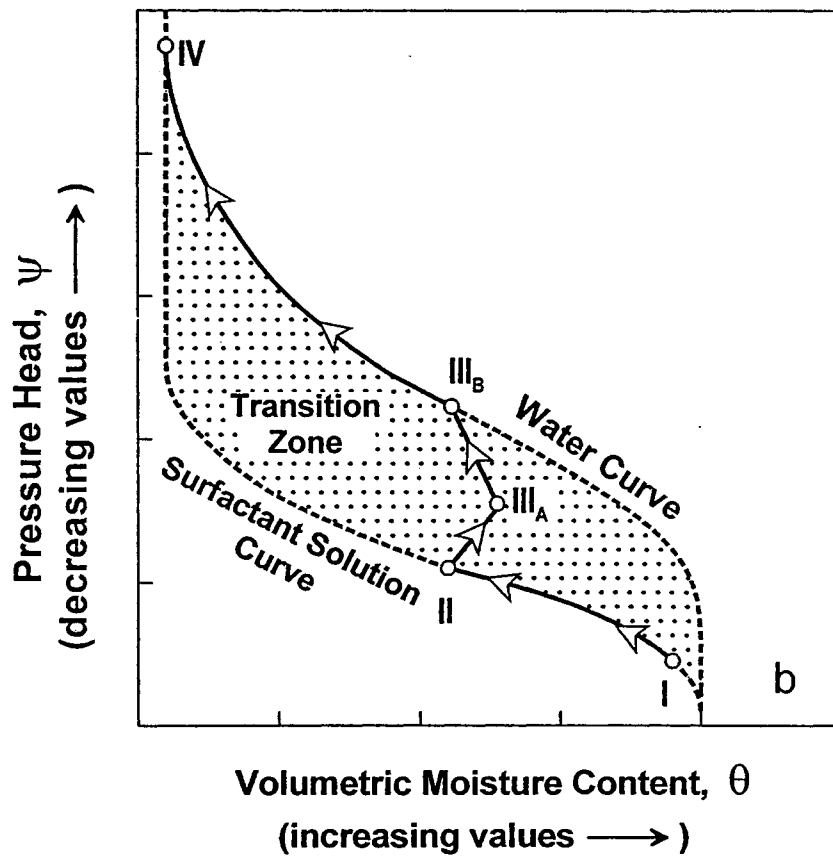
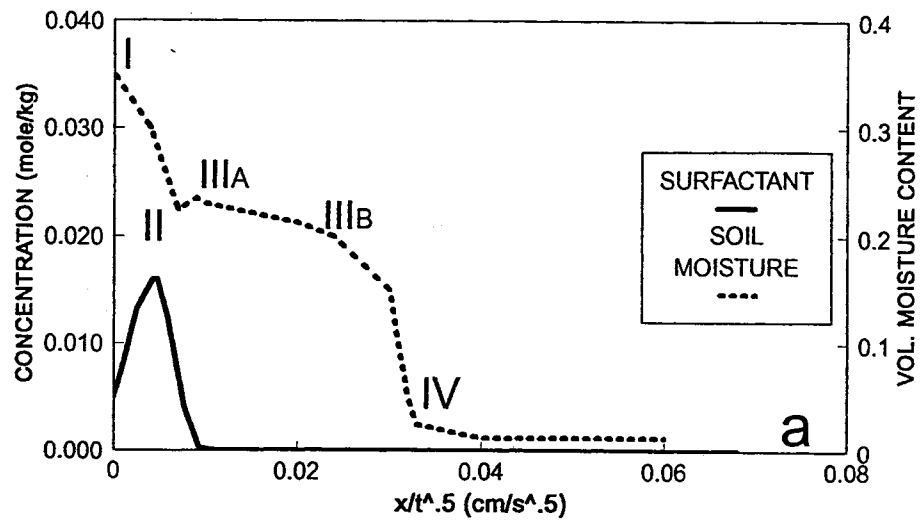
Fig. 3-4. AES, LAS, Na<sup>+</sup>, and I<sup>-</sup> concentration profiles.



**Fig. 3-5.** Divalent cation ( $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) distribution. (a) 72 h AES test. (b) 72 h LAS test.



**Fig. 3-6.** (a) AES moisture content and surfactant concentration profiles.  
 (b) Hypothetical wetting curves showing the  $\Psi$  versus  $\theta$  relationship for the AES tests.



**Fig. 3-7.** (a) LAS moisture content and surfactant concentration profiles.  
 (b) Hypothetical wetting curves showing the  $\Psi$  versus  $\theta$  relationship for the LAS tests.

## **Chapter IV**

### **ANIONIC SURFACTANT MOBILITY IN UNSATURATED SOIL 2: BOUNDARY CONDITION AND SOIL ATTRIBUTE EFFECTS**

#### **Abstract**

The effectiveness and efficiency of using surfactants for in situ environmental remediation may depend on their mobility in unsaturated soil. For this reason, transient unsaturated column tests were used to study the influence of boundary conditions and soil attributes on anionic surfactant transport. In these tests, aqueous surfactant solutions were injected into the inlet of horizontally mounted soil columns. Two commercial anionic surfactants were used, an alkyl ether sulfate (AES) and a linear alkylbenzene sulfonate (LAS).

The overall study was divided into two parts. First, boundary condition effects including injected surfactant solution concentration, initial moisture content, and inlet moisture content were investigated. Increasing the injection solution concentration increased anionic surfactant mobility in the column while changing the initial and inlet moisture contents had no significant impact. Second, the influence of soil attributes such as texture, dominant exchangeable cation, and resident organic matter were observed. With respect to texture, mobility was greatest in a sandy soil as compared to two loamy

soils. Both surfactants, especially LAS, were found to be more mobile in a  $\text{Na}^+$  dominated soil rather than one dominated by  $\text{Ca}^{+2}$ . The absence of soil organic matter increased LAS mobility.

## **Introduction**

Surfactant flushing may be a viable remediation technique for the removal of contaminants located in soils above the water table. The effectiveness and efficiency of using surfactants for this purpose will largely depend on mobility under unsaturated flow conditions. To date, laboratory work (Mustafa and Letey, 1971; Miller and Letey, 1975) and field pilot studies (Abdul et al., 1992; Abdul and Ang, 1994) have focused on nonionic surfactants with respect to use in unsaturated soil. More study is needed on anionic surfactants. Anionic surfactants are the most widespread type of surfactant in terms of commercial availability and would in all likelihood be the most economical for utilization in environmental remediation. For these reasons, two common anionic surfactants were chosen for testing.

Anionic surfactant mobility under unsaturated flow conditions was tested using experimental procedures described by Allred and Brown (in review). These tests were maintained under strict boundary conditions and involved the injection of an aqueous surfactant solution into the inlet of a horizontally mounted soil column. This study addressed the influence of boundary conditions and soil attributes on anionic surfactant mobility. The boundary conditions tested include injected surfactant solution concentration, initial soil moisture content, and inlet moisture content. For soil

attributes, the effects of texture, dominant exchangeable cation, and the presence of organic matter were investigated.

## **Materials**

### ***Surfactants***

The two commercial surfactants utilized were a sodium alkyl ether sulfate (AES) and a sodium linear alkyl benzene sulfonate (LAS). These two surfactants were chosen based on their properties along with also having widespread commercial availability. Table 4-1 lists some of the characteristics of the two surfactants. Both surfactants are comprised of a series of homologs, and the active ingredient weight percent of the AES and LAS surfactant products was 39% and 91%, respectively. Surface tension and CMC values were measured with a Fisher Scientific Model 21 Tensiomat tensiometer. Viscosities were obtained with a Cannon Instrument Co. size 50 viscometer. The specific gravity was essentially equal to 1 for the 0.025 mole/kg solutions listed in Table 4-1.

### ***Soils***

Teller loam (Thermic Udic Argiustoll), Slaughterville loam (Thermic Udic Haplustoll), and Dougherty sand (Thermic Arenic Haplustalf) were obtained from field locations in Payne County, Oklahoma. The Teller and Dougherty are soils formed from the weathering of alluvial sediments while the Slaughterville is a weathered eolian deposit. Soil characteristics are presented in Table 4-2. These characteristics were



determined using the procedures described in *Methods of Soil Analysis, Part 1 & 2* (ASA and SSSA, 1982 and 1986). Specific surface area was calculated from water vapor sorption isotherms by use of the B.E.T. equation (Quirk, 1955). Teller loam was used for the majority of the tests. This particular soil was chosen because its sorption potential made it a good candidate for studying anionic surfactant transport. The sorption potential of the soil was expected to be significant due to a high level of exchangeable  $\text{Ca}^{+2}$  (6.28 meq/100g) and a relatively large specific surface area (37.8  $\text{m}^2/\text{g}$ ).

### **Experimental Procedures**

A computer controlled syringe pump apparatus, as described by Brown and Allred (1992), was used to conduct transient unsaturated experiments on anionic surfactant transport. In these experiments, 20 ml of surfactant solution were injected into the inlet of a horizontally mounted soil column. The majority of the tests conducted used 0.025 mole/kg injected surfactant solution concentrations, which in weight percent is approximately 0.9% for both surfactants. Test duration was 24 h except for two boundary condition tests run at 96 h.

The inlet moisture content, and hence inlet soil moisture potential, were held constant during testing. The computer controlled syringe pump accomplished this by regulating the injected flow at a rate inversely proportional to the square root of elapsed time. Along with injection rate, the inlet moisture content value also depends on properties of the soil and the injection solution.

The column itself was comprised of individual acrylic rings and packed with soil to an average dry bulk density of  $1.60 \text{ g/cm}^3$ , which corresponds to a porosity of 0.40. The individual rings had a diameter of 3.5 cm and a length of 0.5, 1.0, or 2.0 cm. The shorter rings were placed adjacent to the column inlet to provide better resolution of the surfactant concentration and moisture content profiles within this region. Overall column length ranged from 18 to 35 cm. Upon test completion, the soil column was broken apart and the soil from within each ring divided into two parts for analysis of volumetric moisture content and anionic surfactant concentration.

Volumetric moisture content was determined by oven drying the soil sample at 105 C for 24 h. The mean of the injected moisture percent accounted for by oven drying was 95%. The anionic surfactants were extracted from soil samples using a combination of acetone and a 0.1 mole/kg NaCl solution. The methylene blue method (APHA et al., 1985) was then used for chemical analysis. The mean of the percent injected surfactant accounted for by extraction and analysis was 90%. A more detailed discussion of procedures is provided by Brown and Allred (1992) and Allred and Brown (in review).

### ***Boundary Condition Tests***

All tests conducted during this part of the study used Teller loam soil. The three boundary conditions investigated were injected surfactant solution concentration, initial moisture content, and inlet moisture content. For each boundary condition, two sets of tests were conducted. One set was with the AES surfactant and the other with LAS. Injected surfactant concentration effects were tested with 0.01, 0.025, and 0.1 mole/kg

solutions at an initial soil column moisture content of 0.01. Although the injection rate was held constant for the concentration effect experiments, variability in surfactant solution properties caused differences in inlet moisture content between tests within a given set. Initial moisture contents were varied from 0.01 to 0.08 to 0.16 while the injected surfactant solution concentration was 0.025 mole/kg and the inlet moisture contents averaged 0.32 for AES and 0.36 for LAS. To test the effects of only the inlet moisture content on mobility of both surfactants, two tests differing with respect to injection rate were conducted while keeping injection concentration (0.025 mole/kg) and initial soil moisture content (0.01) constant. Injection rate was varied between the two tests by using the same injection solution volume (20 ml) but different test duration times (24 h and 96 h).

### ***Soil Attribute Tests***

The attributes tested with respect to both AES and LAS were texture, dominant exchangeable cation, and resident organic matter. Soil texture effects on surfactant mobility were studied using the Teller loam, Slaughterville loam, and Dougherty sand. Surfactant mobility as affected by the dominant soil cation was investigated by replacing the resident soil cations in the Teller loam with either  $\text{Na}^+$  or  $\text{Ca}^{+2}$ . Replacement was accomplished through two equilibration and drainage cycles for 1 kg of Teller loam with 2 kg of 0.2 mole/kg NaCl or  $\text{CaCl}_2$  solution. Results of the AES and LAS tests conducted with the Na-Teller and Ca-Teller were then compared with those from tests run on the unaltered soil. The effects of resident soil organic matter on AES and LAS

mobility were studied by testing these surfactants on nonorganic Teller loam and then comparing the results with those obtained using unaltered Teller loam which contained 1.2% organic carbon. The nonorganic Teller was prepared using a hydrogen peroxide oxidation procedure (ASA and SSSA, 1986). All tests conducted during this part of the study had 0.025 mole/kg injection solution concentrations, 24 h time durations, and initial moisture contents of 0.01.

## **Experimental Results**

Test results are presented in plots of surfactant concentration versus distance. The concentration values are given in mole/kg of the total porous media. Here, total porous media is meant to include both soil solids and soil solution. Distance refers to the length in cm from the column inlet. The evaluation of surfactant mobility was based on the distance the concentration front advanced within the soil column. Moisture content profiles from the boundary condition tests are also provided.

### ***Boundary Condition Tests***

Figure 4-1 depicts the results of the test series in which surfactant injection concentrations were varied. The AES data are shown in Figures 4-1a (surfactant concentration) and 4-1c (moisture content). LAS surfactant concentration and moisture content profiles are presented in Figures 4-1b and 4-1d, respectively. For both surfactants, the column distance penetrated by the concentration front increased with an increase in the injection solution concentration. The AES surfactant had roughly twice

the mobility of LAS in tests having similar conditions. The ratio of peak concentration to inlet concentration for the 0.01, 0.025, and 0.1 mole/kg tests was 1.11, 1.33, and 1.33 for AES and 1.24, 2.21, and 3.58 for LAS. Allred and Brown (in review) provide two explanations for the inlet surfactant concentrations being significantly less than peak profile values. Inlet moisture contents and inlet surfactant concentrations were also observed to increase with increasing AES or LAS injection concentrations. For LAS, the moisture content profiles from the 0.01 and 0.025 mole/kg tests exhibit notches which coincide with the surfactant concentration fronts. The notch from the 0.01 mole/kg test is readily apparent while the one from the 0.025 mole/kg test is more subtle. These notches represent a reversal in the usual trend of a continuous decrease in moisture content from inlet to wetting front edge. The significance of a moisture content profile slope reversal has been discussed by Allred and Brown (in review). Although there is no notch present in the moisture content profile from the 0.1 mole/kg LAS test, a steep drop-off corresponding to the surfactant concentration front does occur.

Results from the test series in which initial moisture contents were varied are provided in Figures 4-2a and 4-2c for AES and 4-2b and 4-2d for LAS. As shown, increasing the initial moisture content causes an increase in the distance penetrated by the wetting front. However, this has no significant impact on surfactant mobility.

Figure 4-3 illustrates the effects of inlet moisture content only on AES and LAS transport. A decrease in the injection rate, which is reflected by a reduction in the inlet moisture content and a slight increase in the wetting front penetration, affected at best a

very small increase in AES and LAS surfactant mobility. Again, note the large notch in the moisture content profile from the LAS test having the lower injection rate.

### *Soil Attribute Tests*

AES and LAS surfactant mobility in three different soils are shown in Figures 4-4a and 4-4b, respectively. When compared to the two loamy soils, surfactant mobility was greater in the Dougherty sand by a factor of two for AES and by a factor of four for LAS. Concentration profiles for the Teller and Slaughterville soils were similar for both surfactants tested. Dougherty concentration profiles had a rather flat distribution from inlet to front while the profile configurations of the Teller and Slaughterville resemble a left-truncated bell shape.

Figure 4-5 shows the effect on surfactant mobility due the dominant exchangeable cation present in the soil. AES results are given in Figure 4-5a while those for LAS are provided in Figure 4-5b. As determined from concentration front positions, both surfactants exhibited the greatest mobility in the  $\text{Na}^+$  dominated Teller. The least mobility was found in the  $\text{Ca}^{+2}$  dominated soil. The difference in surfactant mobility between the  $\text{Na}^+$  and  $\text{Ca}^{+2}$  dominated Teller was greatest with LAS.

As depicted in Figure 4-6, only the LAS mobility seems to be affected by resident soil organic matter. Figure 4-6b shows that LAS mobility increased when organic matter is removed from the Teller loam.

## Discussion

Surfactant mobility will depend on the amount of sorption which takes place. Here, sorption refers to the mechanisms of adsorption and/or precipitation. There are a number of different sorption mechanisms which can reduce anionic surfactant mobility in unsaturated soils. These include anion exchange, coadsorption, hydrophobic adsorption, and precipitation. At low pH, surface sites on soil particles and resident organic matter become protonated and assume positive charge (Bohn et al., 1985). This in turn gives rise to an anion exchange capacity which allows negatively charged surfactant molecules to become electrostatically adsorbed. Testing by Clementz and Robbins (1976), indicated that small amounts of dodecylbenzene sulfonate were adsorbed at positively charged crystal edge sites on montmorillonite. Because injection solution and soil pH values were at most only slightly acidic (Tables 4-1 and 4-2), it is unlikely that anion exchange played a major role in governing surfactant mobility during the tests conducted in this study. However, electrostatic attraction between soil and anionic surfactants may be possible due to coadsorption (Gaudin and Chang, 1952). Essentially, coadsorption involves multivalent cations such as  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  which bridge surfactant anions to the clay minerals or resident soil organic matter which usually have negative charge. Hydrophobic adsorption also affects surfactant mobility. It results from the surfactant tendency to attempt escape from the aqueous environment by concentrating at phase boundaries or by interacting with surfactant which has been previously adsorbed at an interface (Rosen, 1989). Additionally, precipitation can immobilize anionic surfactants (West and Harwell, 1992). The most likely precipitates in soils are Ca-surfactant and

Mg-surfactant salts. Therefore, as with coadsorption, soils having high levels of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions pose a threat with respect to anionic surfactant precipitation.

AES and LAS test results can be explained in part by the various sorption mechanisms previously described. Surfactant mobility was noticed to increase with an increase in injection concentration (Figure 4-1). At the highest injection level (0.1 mole/kg), the AES surfactant concentration profile is relative flat with a front position coinciding with the leading edge of the moisture content curve. These are indications that AES overwhelms the sorption capacity of the Teller loam when injected at this concentration (4% by weight). For LAS on the other hand, the soil sorption capacity is not met with the 0.1 mole/kg injected solution. This is evident from the concentration profile which penetrates only half the distance of the wetting front edge. Consequently, even with a soil having high sorption capacity, application of a moderately high solution concentration may in some cases increase anionic surfactant mobility to a level practical for environmental remediation.

The initial and inlet moisture content boundary conditions did not greatly impact anionic surfactant mobility (Figures 4-2 and 4-3). At least for the Teller loam, this suggests that mobility depends much less on flow conditions and more on the sorption capacity of the soil with respect to a particular surfactant.

From the results presented in Figure 4-4, it is evident that soils such as the Dougherty sand are good candidates for surfactant enhanced remediation while those such as the Teller loam and Slaughterville loam are only marginal. Two explanations can account for the increased surfactant mobility in the Dougherty as compared to the Teller



and Slaughterville soils. First, the lower specific surface area of the sand reduces the amount of solid/liquid interface available for surfactant adsorption. Second, the Dougherty has lower amounts of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  than the loamy soils (Table 4-2). Because of this, anionic surfactant mobility in the sand was less likely to be reduced due to coadsorption and/or precipitation.

Both surfactants had greater mobility in the  $\text{Na}^+$  saturated Teller and less where the soil was  $\text{Ca}^{+2}$  dominated (Figure 4-5). Mobility in the unaltered Teller, which contained a mixture of monovalent and divalent cations, was between these two extremes. These results indicate the influence of coadsorption and/or precipitation processes which in turn depend on the amount of multivalent cations which are present. One implication from this set of tests and those conducted by Ducreux et al. (1990) is that NaCl preflushing prior to environmental remediation can enhance anionic surfactant mobility. Saturated core flood tests done by Lau and O'Brien (1988) show that anionic surfactant mobility can also be increased through addition of large amounts of NaCl (4% by weight) to the injection solution.

LAS mobility was observed to increase when the resident soil organic matter was removed from the Teller loam (Figure 4-6). Removal of the organic matter reduces the cation exchange capacity along with making the soil less hydrophobic. This could have the effect of limiting both coadsorption and hydrophobic adsorption, thereby increasing LAS mobility. It is unclear why AES mobility is not affected by the resident organic matter.

AES was significantly more mobile than LAS under all conditions tested. Schwuger (1984) noted that surfactants similar to AES, which contain oxyethylene structural groups, exhibit resistance to precipitation. AES may be more resistant than LAS with respect to other sorption mechanisms as well. Therefore, surfactant molecular structure becomes an important criteria where mobility is concerned.

## **Summary and Conclusions**

The following is a list of the results obtained from the tests conducted in this study on anionic surfactant mobility in unsaturated soil.

### ***Boundary Condition Effects***

- 1) Increasing the concentration of the applied surfactant solution can substantially increase anionic surfactant mobility.
- 2) Mobility is not affected by the initial moisture content of the soil.
- 3) The application rate of a surfactant solution, which is reflected by the moisture content at the point of introduction, has only a slight impact on mobility.

### ***Soil Attribute Effects***

- 4) Anionic surfactants show good mobility in course grained soils having low  $\text{Ca}^{+2}/\text{Mg}^{+2}$  concentrations and specific surface area.
- 5) Anionic surfactants are significantly more mobile in a soil dominated by exchangeable  $\text{Na}^{+}$  rather than  $\text{Ca}^{+2}$ .

- 6) Depending on the anionic surfactant utilized, resident soil organic matter may or may not effect mobility .

The most important implication from the test results is that sorption processes govern the mobility of anionic surfactants in unsaturated soil while hydraulic boundary conditions have little or no affect. Consequently, the effectiveness and/or efficiency of in situ surfactant enhanced environmental remediation above the water table will depend in large part on soil attributes and the applied concentration of the anionic surfactant.

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Table 4-1

## Surfactant Characteristics

Chemical Name	Trade Name <sup>1</sup>	Abbreviation	Chemical Formula	pH <sup>2</sup>	Viscosity <sup>2</sup> gm/(cm-s)	Critical Micelle Conc. mole/kg	Surface Tension <sup>2</sup> dynes/cm
Sodium Alkyl Ether Sulfate	Witcolate 7093	AES	$C_{6-10}H_{13-21}(OCH_2CH_2)_3OSO_3Na$ $C_6 = 18\%$ $C_8 = 35\%$ $C_{10} = 47\%$	6.9	0.0104	0.005	34.4
Sodium Linear Alkylbenzene Sulfonate	Witconate 90F	LAS	$C_{10-13}H_{21-27}C_6H_4SO_3Na$ $<C_{10} = <2\%$ $C_{10} = <25\%$ $C_{11} = 25\% \text{ to } 50\%$ $C_{12} = >25\%$ $C_{13} = <15\%$	6.6	0.0104	0.001	33.8

<sup>1</sup> Both surfactants were obtained from the Witco Corp.

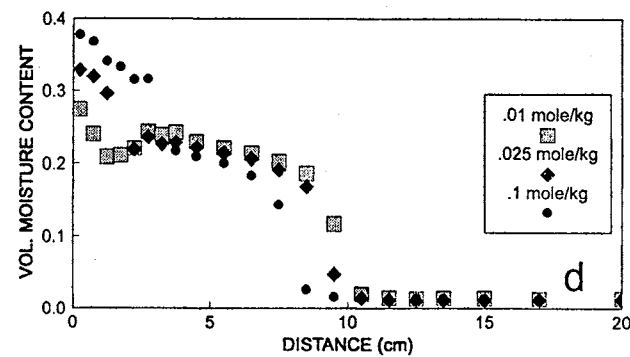
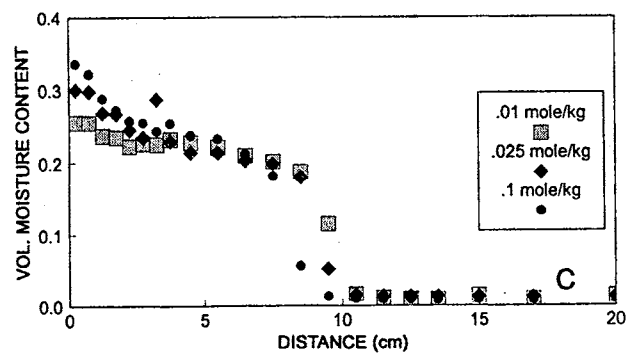
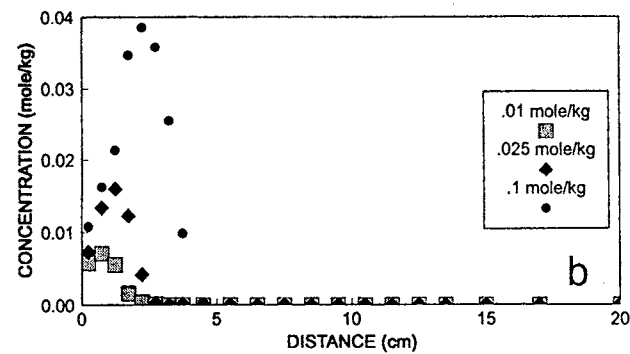
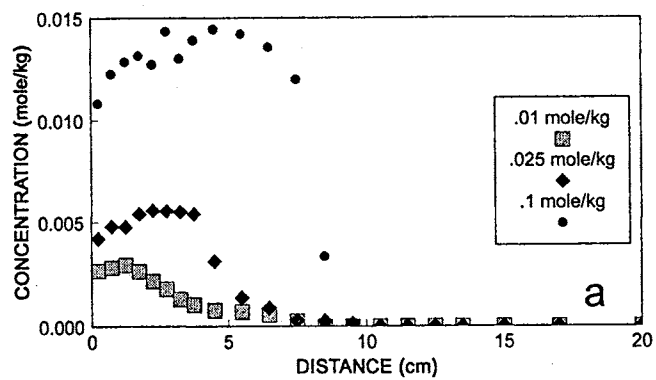
<sup>2</sup> Properties were obtained for 0.025 mole/kg surfactant solutions. Temperature = 22 C. For water at T = 22 C, surface tension is 72.4 dynes/cm and viscosity is 0.00956 gm/(cm-s).

Table 4-2

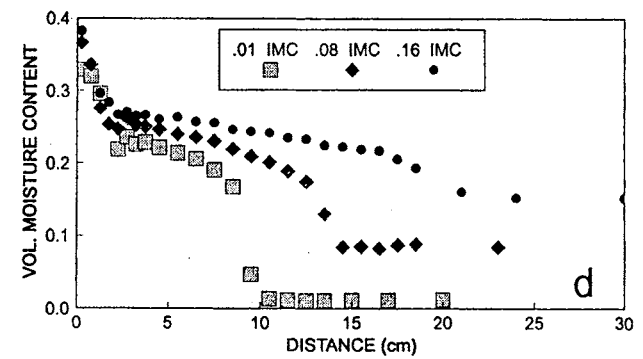
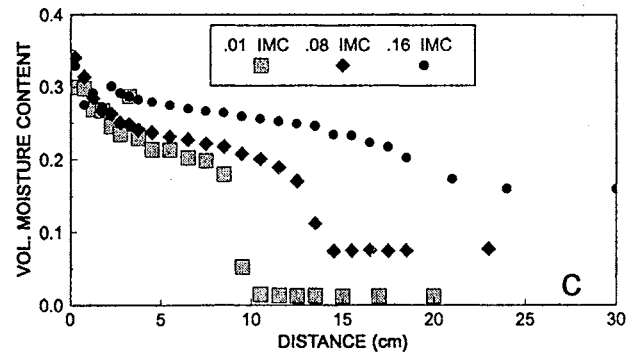
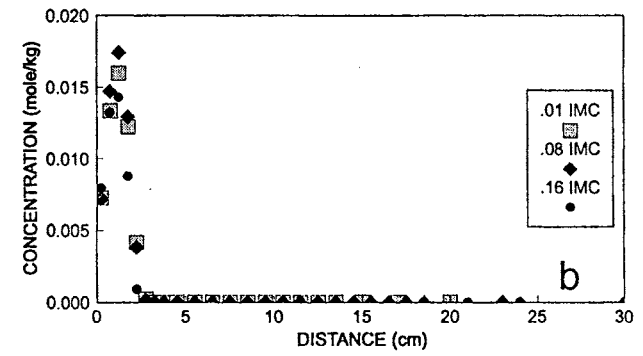
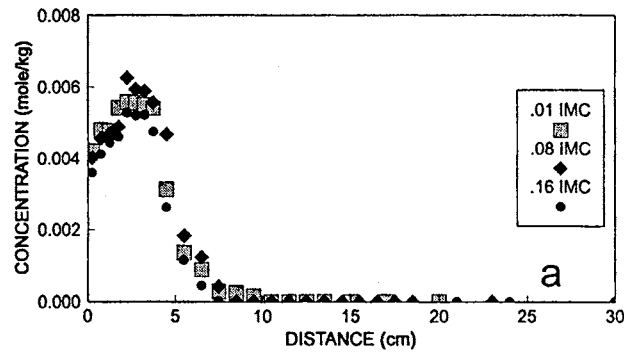
## Soil Characteristics

<i>Soil</i>	<i>USDA Classification</i>	<i>Extractable Bases</i>	<i>Cation Exchange Capacity<sup>1</sup></i>	<i>pH</i>	<i>Specific Surface Area</i>	<i>Organic Carbon Content</i>
		<i>meq/100g</i>	<i>meq/100g</i>		<i>m<sup>2</sup>/g</i>	<i>weight %</i>
Teller	"Loam" 52% Sand 31% Silt 17% Clay	Na <sup>+</sup> = 0.84 K <sup>+</sup> = 0.99 Ca <sup>+2</sup> = 6.28 Mg <sup>+2</sup> = 2.39	~14	6.0	37.8	1.2
Dougherty	"Sand" 98% Sand 2% Silt and Clay	Na <sup>+</sup> = 1.40 K <sup>+</sup> = 0.14 Ca <sup>+2</sup> = 2.40 Mg <sup>+2</sup> ~ 0.00	~5	5.9	21.8	0.1
Slaughterville	"Loam" 47% Sand 35% Silt 18% Clay	Na <sup>+</sup> = 0.22 K <sup>+</sup> = 0.26 Ca <sup>+2</sup> = 8.05 Mg <sup>+2</sup> = 1.62	~14	8.0	----	0.5

<sup>1</sup> Cation exchange capacity was calculated assuming a base saturation of 75 percent, which is average for the Payne County, Oklahoma, area from which these soils were obtained.

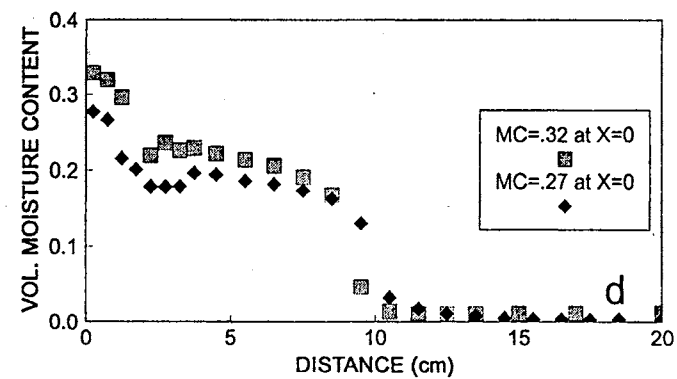
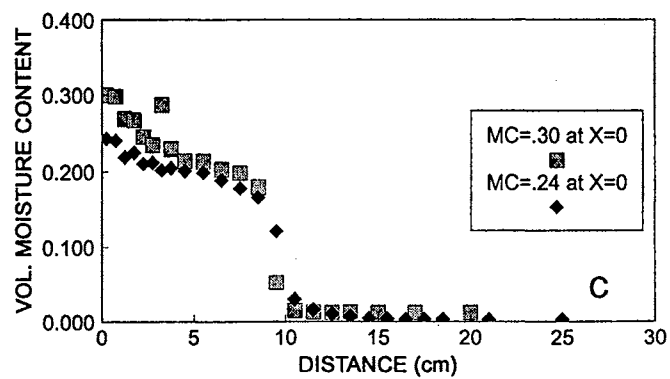
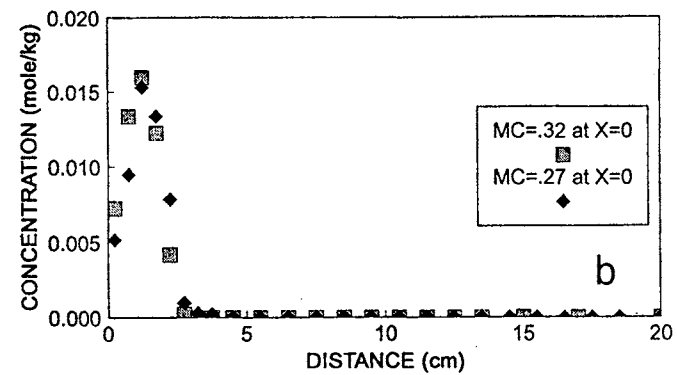
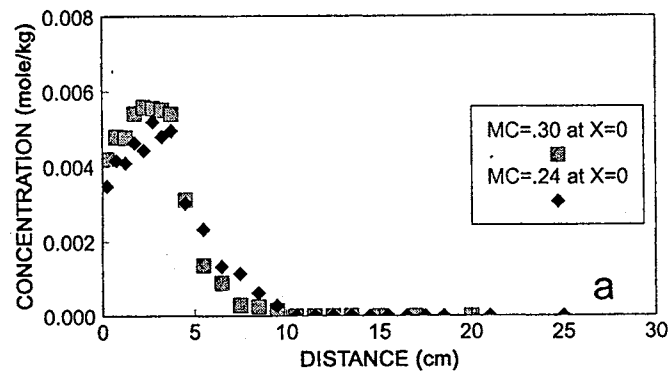


**Fig. 4-1.** Results of tests in which surfactant injection concentration varied. (a) AES concentration profiles. (b) LAS concentration profiles. (c) AES moisture content profiles. (d) LAS moisture content profiles.

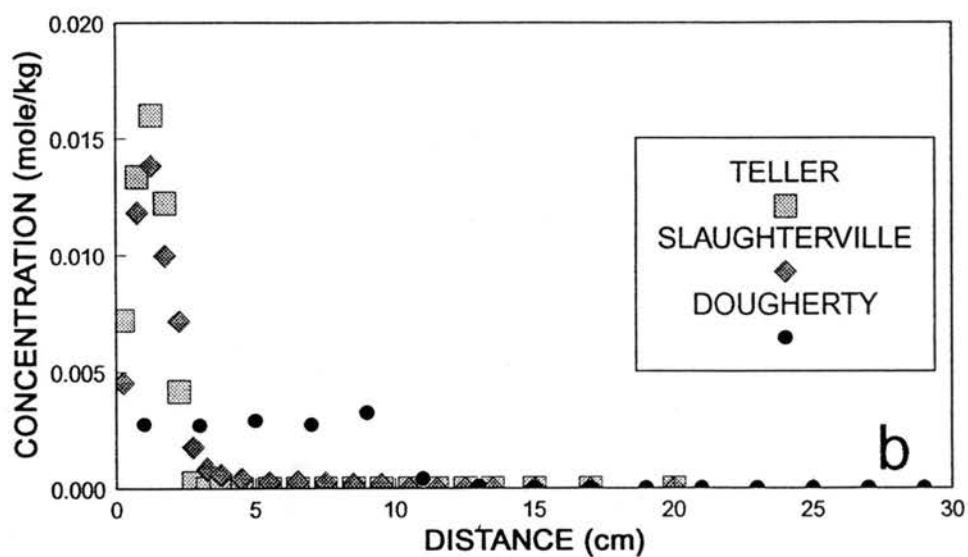
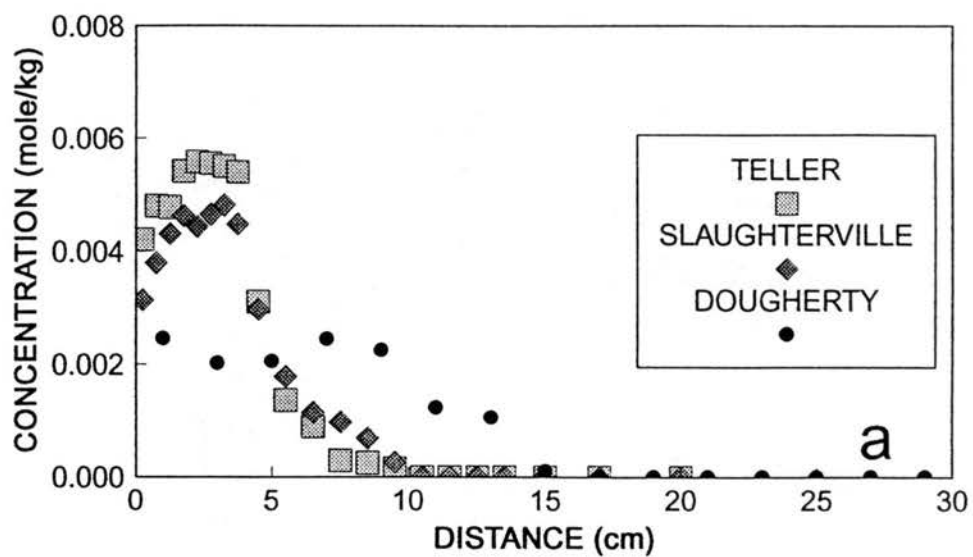


**Fig. 4-2.** Results of tests in which initial moisture content varied (IMC). (a) AES concentration profiles. (b) LAS concentration profiles. (c) AES moisture content profiles. (d) LAS moisture content profiles.

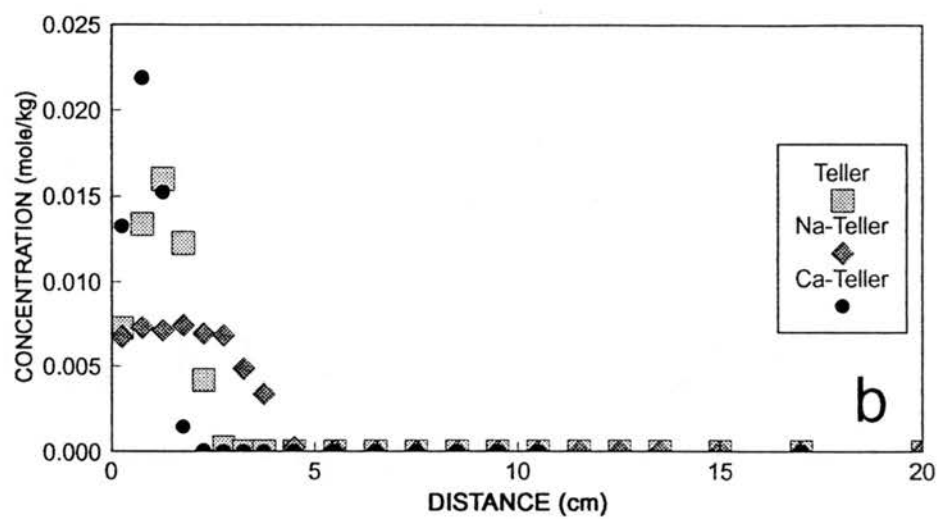
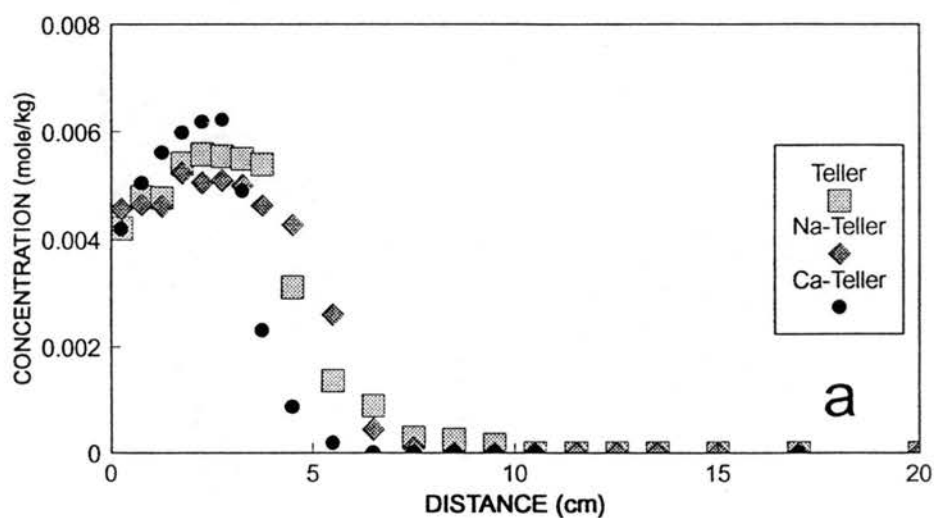




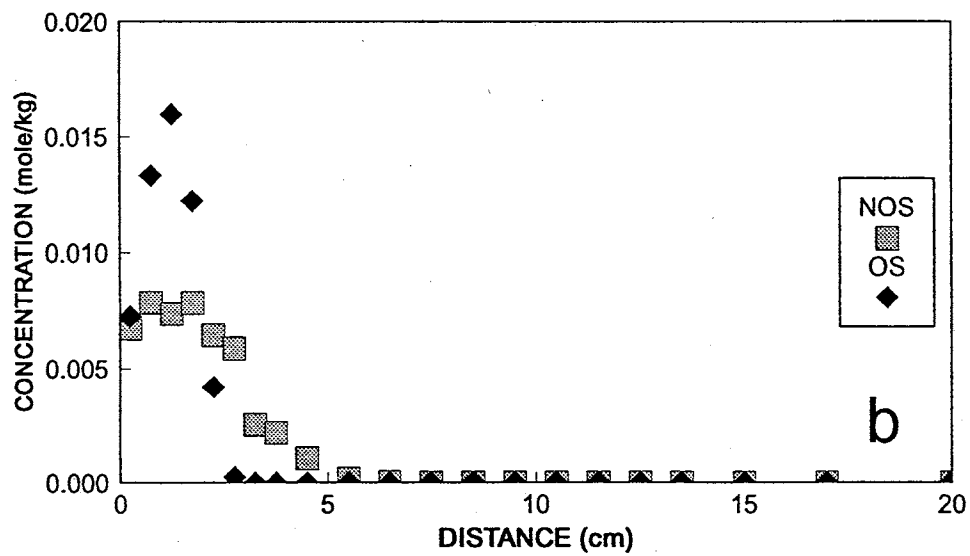
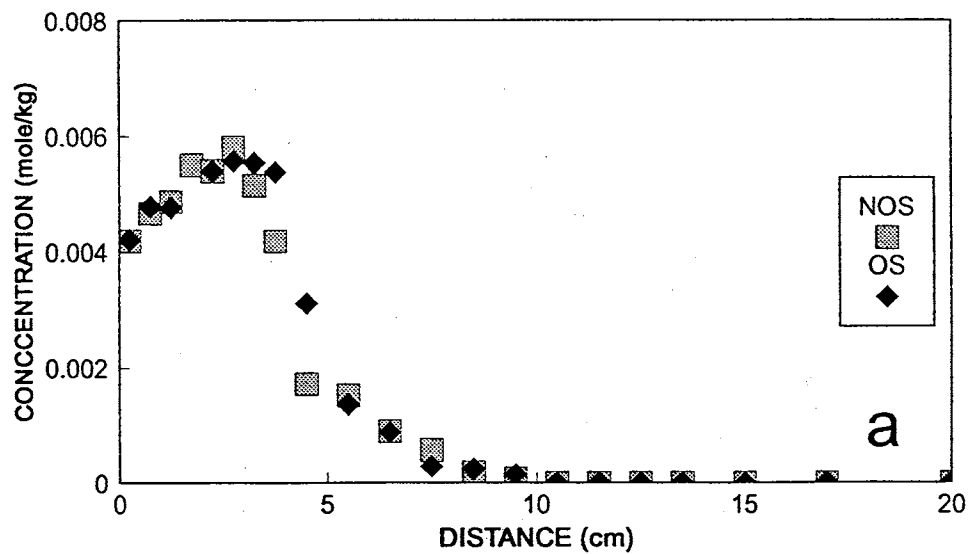
**Fig. 4-3.** Results of tests in which inlet moisture content varied (MC at  $X=0$ ). (a) AES concentration profiles. (b) LAS concentration profiles. (c) AES moisture content profiles. (d) LAS moisture content profiles.



**Fig. 4-4.** Results of surfactant testing on different soils. (a) AES concentration profiles. (b) LAS concentration profiles.



**Fig. 4-5.** Dominant exchangeable cation effects. (a) AES concentration profiles. (b) LAS concentration profiles.



**Fig. 4-6.** Soil organic matter effects. NOS - nonorganic soil. OS - organic soil.  
 (a) AES concentration profiles. (b) LAS concentration profiles.

## **Chapter V**

### **FUTURE RECOMMENDATIONS**

The overall objectives of this research included quantification of surfactant mobility in unsaturated soil along with the impact on saturated hydraulic conductivity and unsaturated diffusivity. These objectives have been accomplished and the results of this study should prove useful in designing in situ surfactant enhanced environmental remediation procedures.

Future research could be focused in three areas. First, a more detailed investigation needs to be conducted on the effects of anionic surfactant molecular structure. Chemical structural characteristics such as benzene ring presence, hydrocarbon chain length/branching, number of oxyethylene units, and the type of head group may all play an important part in how anionic surfactants behave in the subsurface. A variety of structurally different anionic surfactants would need to be tested with respect to mobility in unsaturated soil along with their influence on unsaturated diffusivity and saturated hydraulic conductivity. The goal of this research would be to provide guidance in choosing the proper surfactant to be used in an environmental remediation program.

The second research topic which needs to be addressed is the effect that surfactants have on geotechnical properties of soil. Different surfactants should to be

tested to determine how they affect a soil in terms of Atterberg limits, consolidation, shear strength, and moisture/density relationships. The surfactant impact on these properties may be an important consideration in terms of future construction activities at the remediation site.

Finally, permeability reducing surfactants could be incorporated into the design of clay liners for landfills and surface impoundments. Surfactants could be used to decrease the flow rate and make materials which were initially unsuitable for use as liners more practical. Unsuitable material would be those soils having hydraulic conductivities which are too high. Long term laboratory and field permeability tests would need to be conducted with a variety of different surfactants and soils in order to determine the feasibility of such an application.

## **APPENDICES**

## **Appendix A**

### **Data from Teller Loam Falling-Head Permeability Tests Used to Determine Saturated Hydraulic Conductivity**



**Table A-1**

**Data from Teller Loam Falling-Head Permeability Test #1**

Water Solution (0.001 mole/kg NaCl and 0.001 CaSO <sub>4</sub> )	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.01	7.81
0.07	7.12
0.18	7.37
0.45	6.81
0.57	6.84
1.24	6.74
2.01	6.48
3.83	6.07
4.64	5.61
5.03	5.20
5.25	5.12
5.89	5.13
7.45	4.65
8.54	4.47
9.49	4.33

**Table A-2****Data from Teller Loam Falling-Head Permeability Test #2**

N1 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.02	7.25
0.06	7.29
0.15	6.04
0.23	5.79
0.34	5.13
0.43	4.51
0.75	3.49
0.86	2.79
0.92	2.57
1.40	2.08
1.65	1.91
1.82	1.79
1.99	1.77
2.51	1.63
2.81	1.57
2.96	1.53
3.37	1.47
3.43	1.39
3.51	1.47
3.58	1.45

**Table A-3**

**Data from Teller Loam Falling-Head Permeability Test #3**

N2 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.03	5.10
0.09	4.27
0.15	4.18
0.24	3.22
0.30	2.43
0.43	1.32
0.48	0.94
0.51	0.88
0.70	0.67
0.78	0.55
0.85	0.46
0.91	0.42
1.07	0.37
1.13	0.28
1.17	0.25
1.24	0.22
1.26	0.18
1.28	0.17
1.29	0.14

**Table A-4**

**Data from Teller Loam Falling-Head Permeability Test #4**

N3 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.00	5.61
0.03	4.47
0.09	3.67
0.14	3.67
0.23	3.20
0.29	2.72
0.50	2.17
0.58	1.83
0.63	1.59
0.95	1.23
1.10	1.09
1.21	0.90
1.32	0.81
1.59	0.70
1.73	0.67
1.81	0.63
2.01	0.61
2.05	0.58
2.10	0.60
2.15	0.58

**Table A-5**

**Data from Teller Loam Falling-Head Permeability Test #5**

A1 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.02	3.73
0.05	2.22
0.10	1.33
0.11	0.96
0.16	0.52
0.19	0.29
0.23	0.19
0.25	0.15
0.26	0.13
0.28	0.14
0.31	0.11
0.33	0.12
0.36	0.09
0.39	0.09
0.42	0.08
0.45	0.07
0.47	0.07
0.48	0.07
0.50	0.06
0.51	0.06
0.51	0.05
0.53	0.06
0.54	0.06

**Table A-6**

**Data from Teller Loam Falling-Head Permeability Test #6**

A2 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.04	5.35
0.07	2.47
0.09	0.59
0.09	0.26
0.11	0.18
0.12	0.11
0.14	0.08
0.15	0.06
0.16	0.05
0.16	0.06
0.18	0.04
0.19	0.05
0.20	0.04
0.22	0.04
0.23	0.04
0.25	0.03
0.25	0.03
0.26	0.03
0.27	0.04
0.28	0.02
0.28	0.03
0.29	0.03
0.29	0.03

**Table A-7**

**Data from Teller Loam Falling-Head Permeability Test #7**

C1 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.01	6.36
0.04	4.38
0.05	0.34
0.05	0.34
0.07	0.37
0.07	0.18
0.09	0.12
0.10	0.20
0.12	0.06
0.13	0.04
0.13	0.05
0.14	0.03
0.15	0.03
0.16	0.03
0.16	0.05
0.18	0.04
0.18	0.02

**Table A-8**

**Data from Teller Loam Falling-Head Permeability Test #8**

C2 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.01	3.85
0.06	3.19
0.11	1.61
0.12	0.80
0.17	0.52
0.20	0.32
0.24	0.20
0.26	0.15
0.27	0.13
0.29	0.13
0.31	0.10
0.34	0.12
0.36	0.08
0.40	0.08
0.42	0.07
0.45	0.06
0.46	0.06
0.47	0.06
0.49	0.05
0.50	0.05
0.50	0.05
0.52	0.05
0.53	0.06



**Table A-9**

**Data from Teller Loam Falling-Head Permeability Test #9**

AM1 Surfactant Solution (0.1 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.01	6.66
0.05	6.24
0.10	3.37
0.12	1.32
0.14	0.61
0.15	0.46
0.18	0.29
0.19	0.17
0.20	0.18
0.24	0.12
0.25	0.06
0.27	0.09
0.28	0.07
0.31	0.07
0.33	0.06
0.34	0.06
0.36	0.06
0.36	0.05
0.37	0.06
0.38	0.05

**Table A-10**

**Data from Teller Loam Falling-Head Permeability Test #10**

N3 Surfactant Solution (0.1 mole/kg) and Water Flush - 2 Cycles			
Pore Volumes	Conductivity K x 10 <sup>5</sup> cm/s	Pore Volumes	Conductivity K x 10 <sup>5</sup> cm/s
0.00	5.61	2.87	1.21
0.03	4.47	2.97	1.31
0.09	3.67	3.10	1.21
0.14	3.67	3.21	1.20
0.23	3.20	3.43	1.19
0.29	2.72	3.52	1.79
0.50	2.17	3.65	1.45
0.58	1.83	3.74	1.24
0.63	1.59	3.87	1.13
0.95	1.23	4.03	0.92
1.10	1.09	4.22	0.83
1.21	0.90	4.35	0.71
1.32	0.81	4.51	0.63
1.59	0.70	4.61	0.58
1.73	0.67	4.87	0.62
1.81	0.63	4.96	0.55
2.01	0.61	5.02	0.51
2.05	0.58	5.11	0.52
2.10	0.60	5.31	0.79
2.15	0.58	5.36	0.82
2.28	0.78	5.62	0.89
2.32	0.80	5.66	0.97
2.47	0.91	5.72	0.99
2.53	0.97	5.91	1.10
2.76	1.07	6.21	1.09
2.81	1.14	6.26	1.13
2.84	1.21		

**Table A-11**

**Data from Teller Loam Falling-Head Permeability Test #11**

A1 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.00	7.16
0.04	5.39
0.08	4.98
0.12	4.89
0.18	4.17
0.23	3.71
0.30	3.18
0.33	2.63
0.38	2.44
0.43	1.60
0.47	1.18
0.56	0.95
0.59	0.95
0.61	0.75
0.76	0.74
0.81	0.69
0.84	0.52
0.90	0.47
0.94	0.46
1.09	0.39
1.13	0.37
1.16	0.36
1.22	0.37
1.34	0.31

**Table A-12**

**Data from Teller Loam Falling-Head Permeability Test #12**

A1 Surfactant Solution (0.001 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.17	6.29
0.38	5.58
0.95	5.28
1.36	5.29
2.14	5.08
3.59	4.38
4.41	3.96
5.00	3.81
5.79	3.38
6.26	3.32

**Table A-13**

**Data from Teller Loam Falling-Head Permeability Test #13**

A1 Surfactant Solution (0.0001 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.16	5.87
0.34	5.04
0.90	5.12
1.29	5.07
2.04	4.74
3.49	4.33
4.34	4.15
4.93	3.78
5.72	3.35
6.16	2.94

**Table A-14**

**Data from Teller Loam Falling-Head Permeability Test #14**

A1 Surfactant Solution (0.00001 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5$ cm/s
0.17	6.52
0.40	5.94
1.01	5.84
1.49	6.17
2.35	5.46
4.03	4.83
4.97	4.34
5.63	3.69
6.57	3.48
7.06	2.97

**Table A-15****Data from Teller Loam Falling-Head Permeability Test #15**

N3 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.00	7.47
0.05	6.55
0.10	6.46
0.15	6.32
0.23	6.10
0.30	5.96
0.42	5.72
0.46	5.33
0.54	5.39
0.69	4.52
0.80	4.02
1.04	3.63
1.11	3.54
1.14	3.11
1.59	2.73
1.75	2.41
1.87	2.18
2.05	2.17
2.16	2.12
2.68	1.77
2.76	1.68
2.82	1.71
3.05	1.55
3.42	1.46

**Table A-16**

**Data from Teller Loam Falling-Head Permeability Test #16**

N3 Surfactant Solution (0.001 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.13	6.28
0.40	6.21
3.00	5.15
3.38	4.67
3.87	4.47
4.11	4.16
6.21	3.92
6.79	3.18
7.40	3.18
8.51	2.98
8.78	3.08



**Table A-17**

**Data from Teller Loam Falling-Head Permeability Test #17**

N3 Surfactant Solution (0.0001 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.11	5.42
0.33	5.10
2.54	4.27
2.86	3.71
3.26	3.54
3.46	3.11
5.01	2.83
5.45	2.27
5.83	1.86
6.47	1.53
6.62	1.40

**Table A-18**

**Data from Teller Loam Falling-Head Permeability Test #18**

N3 Surfactant Solution (0.00001 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.13	6.45
0.37	5.65
3.20	5.33
3.53	4.69
4.04	4.42
4.32	4.18
5.90	3.73
6.42	3.50
6.95	3.36
7.97	3.19
8.22	3.13

**Table A-19****Data from Teller Loam Falling-Head Permeability Test #19**

A2 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.03	3.88
0.07	3.91
0.10	3.57
0.13	3.32
0.16	2.78
0.18	2.73
0.20	2.26
0.21	1.63
0.23	1.65
0.24	1.40
0.25	1.27
0.26	1.14
0.34	0.61
0.39	0.30
0.41	0.24
0.47	0.19
0.49	0.17
0.50	0.15
0.55	0.15
0.58	0.14
0.61	0.14
0.76	0.15

**Table A-20****Data from Teller Loam Falling-Head Permeability Test #20**

N1 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.00	7.19
0.10	6.21
0.29	5.78
0.38	5.36
0.78	4.81
0.88	4.25
1.32	3.60
1.38	3.16
1.68	2.97
1.81	2.62
2.02	2.51
2.14	2.27
2.22	2.13
2.45	1.99
2.54	1.71
2.67	1.63
2.75	1.25
3.13	0.98
3.33	0.76

**Table A-21**

**Data from Teller Loam Falling-Head Permeability Test #21**

A1 & N3 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.00	6.24
0.03	5.49
0.19	5.30
0.26	4.79
0.32	4.82
0.40	4.38
0.44	4.14
0.47	4.36
0.90	3.38
0.93	2.83
0.97	2.65
1.10	2.41
1.13	2.14
1.41	1.85
1.44	1.69
1.50	1.67
1.53	1.54
1.93	1.40
2.32	1.11
2.61	0.95
2.91	0.83
3.24	0.73
3.29	0.68
3.33	0.69
3.65	0.65
3.68	0.59
3.93	0.59

**Table A-22**

**Data from Teller Loam Falling-Head Permeability Test #22**

A2 & N1 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.07	7.01
0.21	6.39
0.36	5.57
0.44	4.49
0.91	3.98
0.98	3.17
1.36	2.27
1.43	1.43
1.52	0.71
1.70	0.52
1.72	0.45
1.83	0.31
1.96	0.33
2.07	0.22
2.10	0.20
2.12	0.15
2.15	0.18

**Table A-23**

**Data from Nonorganic Teller Loam Falling-Head Permeability Test #23**

Water Solution (0.001 mole/kg NaCl and 0.001 mole/kg CaSO <sub>4</sub> )	
Pore Volumes	Saturated Hydraulic Conductivity K x 10 <sup>5</sup> cm/s
0.26	4.64
0.38	3.78
0.50	3.54
0.56	3.77
0.89	2.98
0.96	2.10
1.60	1.98
1.67	1.66
1.72	1.46
1.96	1.26

**Table A-24**

**Data from Nonorganic Teller Loam Falling-Head Permeability Test #24**

A1 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.01	8.72
0.10	6.69
0.14	4.67
0.15	2.49
0.16	1.64
0.18	1.15
0.18	0.79
0.24	0.63
0.25	0.54
0.33	0.40
0.34	0.35
0.35	0.35
0.38	0.29
0.40	0.27



**Table A-25****Data from Nonorganic Teller Loam Falling-Head Permeability Test #25**

N3 Surfactant Solution (0.01 mole/kg)	
Pore Volumes	Saturated Hydraulic Conductivity $K \times 10^5 \text{ cm/s}$
0.00	7.32
0.08	5.71
0.12	5.46
0.15	4.67
0.18	4.71
0.22	3.46
0.24	2.08
0.30	0.74
0.31	0.50
0.38	0.37
0.39	0.38
0.39	0.34
0.43	0.33

**Table A-26**

**Data from Teller Loam Falling-Head Permeability Test #26**

NaCl Solution (0.1 mole/kg)	
$K_{\text{INITIAL}} = 8.3 \times 10^{-5} \text{ cm/s}$	
Pore Volumes	Normalized Hydraulic Conductivity ( $K/K_{\text{INITIAL}}$ )
0.01	1.00
0.09	1.01
2.79	0.99
3.30	0.96
4.30	0.81
7.42	0.69

**Table A-27**

**Data from Teller Loam Falling-Head Permeability Test #27**

A1 Surfactant (0.01 mole/kg) and NaCl (0.1 mole/kg) Solution	
$K_{\text{INITIAL}} = 3.5 \times 10^{-5} \text{ cm/s}$	
Pore Volumes	Normalized Hydraulic Conductivity ( $K/K_{\text{INITIAL}}$ )
0.00	1.00
0.01	0.85
0.03	0.83
0.11	0.82
0.25	0.79
0.64	0.73
1.21	0.63
1.71	0.52
2.09	0.48
2.68	0.32

**Table A-28**

**Data from Teller Loam Falling-Head Permeability Test #28**

A2 Surfactant (0.01 mole/kg) and NaCl (0.1 mole/kg) Solution	
$K_{\text{INITIAL}} = 4.2 \times 10^{-5} \text{ cm/s}$	
Pore Volumes	Normalized Hydraulic Conductivity ( $K/K_{\text{INITIAL}}$ )
0.00	1.00
0.03	0.89
0.05	0.91
0.15	0.84
0.30	0.80
0.72	0.71
1.26	0.50
1.67	0.32
1.93	0.26
2.34	0.16

**Table A-29**

**Data from Teller Loam Falling-Head Permeability Test #29**

A1 Surfactant (0.01 mole/kg) and NaCl (0.1 mole/kg) Solution plus NaCl Preflush	
$K_{\text{INITIAL}} = 5.2 \times 10^{-5} \text{ cm/s}$	
Pore Volumes	Normalized Hydraulic Conductivity ( $K/K_{\text{INITIAL}}$ )
0.03	1.00
0.12	0.98
0.20	0.81
0.27	0.92
0.35	0.83
0.91	0.72
1.43	0.60
2.22	0.53
2.45	0.49
2.81	0.44
3.70	0.39
3.87	0.38
4.73	0.32

## **Appendix B**

### **Data from Unsaturated Tests**

**Table A-30**

**Unsaturated Test #1**

Injected Solution: 0.025 mole/kg AES Injection Volume = 14.1 ml Time Duration of Test = 12 h Soil Type: Teller Loam Initial Soil Moisture Condition: Dry			
Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	1.20	0.32	4.49
0.75	3.61	0.31	4.99
1.25	6.01	0.32	5.35
1.75	8.42	0.31	5.44
2.25	10.83	0.23	5.29
2.75	13.23	0.23	5.05
3.25	15.64	0.21	4.01
3.75	18.04	0.21	1.68
4.50	21.65	0.22	0.91
5.50	26.46	0.20	0.34
6.50	31.27	0.12	0.06
7.50	36.08	0.02	0.00
8.50	40.90	0.01	0.00
9.50	45.71	0.01	0.00
10.50	50.52	0.02	0.00

**Table A-31**

**Unsaturated Test #2**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 14.1 ml

Time Duration of Test = 12 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3 \text{ (cm/s}^{0.5}\text{)}$	Moisture Content	Surfactant Conc. $C \times 10^3 \text{ (mole/kg)}$
0.25	1.20	0.32	8.91
0.75	3.61	0.31	14.41
1.25	6.01	0.23	12.44
1.75	8.42	0.23	1.38
2.25	10.83	0.23	0.24
2.75	13.23	0.23	0.08
3.25	15.64	0.22	0.00
3.75	18.04	0.22	0.00
4.50	21.65	0.20	0.00
5.50	26.46	0.18	0.00
6.50	31.27	0.09	0.00
7.50	36.08	0.01	0.00
8.50	40.90	0.01	0.00
9.50	45.71	0.01	0.00
13.00	62.55	0.01	0.00



**Table A-32**

**Unsaturated Test #3**

Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.30	4.21
0.75	2.55	0.30	4.80
1.25	4.25	0.27	4.78
1.75	5.95	0.27	5.41
2.25	7.65	0.25	5.58
2.75	9.36	0.23	5.55
3.25	11.06	0.29	5.50
3.75	12.76	0.23	5.40
4.50	15.31	0.21	3.12
5.50	18.71	0.21	1.37
6.50	22.11	0.20	0.89
7.50	25.52	0.20	0.29
8.50	28.92	0.18	0.25
9.50	32.32	0.05	0.15
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

**Table A-33****Unsaturated Test #4**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.33	7.25
0.75	2.55	0.32	13.35
1.25	4.25	0.30	15.99
1.75	5.95	0.44	12.23
2.25	7.65	0.22	4.18
2.75	9.36	0.24	0.25
3.25	11.06	0.23	0.00
3.75	12.76	0.23	0.00
4.50	15.31	0.22	0.00
5.50	18.71	0.21	0.00
6.50	22.11	0.21	0.00
7.50	25.52	0.19	0.00
8.50	28.92	0.17	0.00
9.50	32.32	0.05	0.00
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

**Table A-34**

**Unsaturated Test #5**

Injected Solution: 0.025 mole/kg AES Injection Volume = 34.6 ml Time Duration of Test = 72 h Soil Type: Teller Loam Initial Soil Moisture Condition: Dry			
Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.50	0.98	0.33	4.10
1.50	2.95	0.30	4.51
2.50	4.91	0.27	4.99
3.50	6.87	0.25	5.23
4.50	8.84	0.24	6.02
5.50	10.80	0.23	5.57
6.50	12.77	0.23	5.54
7.50	14.73	0.22	4.29
8.50	16.70	0.22	2.44
9.50	18.66	0.22	1.51
10.50	20.62	0.21	1.06
11.50	22.59	0.20	0.78
12.50	24.55	0.20	0.45
13.50	26.52	0.19	0.40
14.50	28.48	0.18	0.14
15.50	30.44	0.14	0.12
16.50	32.41	0.04	0.15
17.50	34.37	0.02	0.00
18.50	36.34	0.01	0.00
20.00	39.28	0.01	0.00
24.00	47.14	0.01	0.00

**Table A-35****Unsaturated Test #6**

Injected Solution: 0.025 mole/kg AES for Displacement of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$

Injection Volume = 34.6 ml

Time Duration of Test = 72 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3 \text{ (cm/s}^{0.5}\text{)}$	$\text{Ca}^{+2}$ Concentration $C \times 10^3 \text{ (mole/kg)}$	$\text{Mg}^{+2}$ Concentration $C \times 10^3 \text{ (mole/kg)}$
0.50	0.98	18.69	5.39
1.50	2.95	24.18	7.45
2.50	4.91	25.67	8.06
3.50	6.87	27.02	9.09
4.50	8.84	27.77	9.50
5.50	10.80	28.04	9.83
6.50	12.77	27.30	9.38
7.50	14.73	28.79	9.79
8.50	16.70	27.57	9.58
9.50	18.66	27.97	9.75
10.50	20.62	27.97	9.63
11.50	22.59	29.62	10.20
12.50	24.55	28.79	10.28
13.50	26.52	28.89	10.37
14.50	28.48	33.23	11.89
15.50	30.44	33.46	12.92
16.50	32.41	30.56	10.08
17.50	34.37	27.89	9.54
18.50	36.34	27.52	9.58
20.00	39.28		
24.00	47.14		

**Table A-36**

**Unsaturated Test #7**

Injected Solution: 0.025 mole/kg LAS  
Injection Volume = 34.6 ml  
Time Duration of Test = 72 h  
Soil Type: Teller Loam  
Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.50	0.98	0.37	7.42
1.50	2.95	0.34	15.35
2.50	4.91	0.26	17.14
3.50	6.87	0.23	6.20
4.50	8.84	0.24	0.06
5.50	10.80	0.24	0.00
6.50	12.77	0.23	0.00
7.50	14.73	0.23	0.00
8.50	16.70	0.23	0.00
9.50	18.66	0.22	0.00
10.50	20.62	0.21	0.00
11.50	22.59	0.21	0.00
12.50	24.55	0.20	0.00
13.50	26.52	0.19	0.00
14.50	28.48	0.17	0.00
15.50	30.44	0.07	0.00
16.50	32.41	0.02	0.00
17.50	34.37	0.02	0.00
18.50	36.34	0.01	0.00
20.00	39.28	0.01	0.00
24.00	47.14	0.01	0.00

**Table A-37**

**Unsaturated Test #8**

Injected Solution: 0.025 mole/kg LAS for Displacement of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$

Injection Volume = 34.6 ml

Time Duration of Test = 72 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3 \text{ (cm/s}^{0.5}\text{)}$	$\text{Ca}^{+2}$ Concentration $C \times 10^3 \text{ (mole/kg)}$	$\text{Mg}^{+2}$ Concentration $C \times 10^3 \text{ (mole/kg)}$
0.50	0.98	15.72	5.84
1.50	2.95	23.15	8.93
2.50	4.91	26.02	10.16
3.50	6.87	24.53	9.50
4.50	8.84	22.55	9.09
5.50	10.80	23.00	9.21
6.50	12.77	23.20	9.21
7.50	14.73	23.23	9.17
8.50	16.70	23.63	9.46
9.50	18.66	24.00	9.79
10.50	20.62	23.13	9.34
11.50	22.59	24.13	9.95
12.50	24.55	24.23	10.08
13.50	26.52	27.40	11.64
14.50	28.48	26.82	11.68
15.50	30.44	25.80	10.74
16.50	32.41	23.58	9.46
17.50	34.37	24.43	9.75
18.50	36.34	24.38	9.63
20.00	39.28	23.60	9.42
24.00	47.14		

**Table A-38****Unsaturated Test #9**

Injected Solution: 0.025 mole/kg NaI

Injection Volume = 34.6 ml

Time Duration of Test = 72 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Na <sup>+</sup> Concentration $C \times 10^3$ (mole/kg)	I <sup>-</sup> Concentration $C \times 10^3$ (mole/kg)
0.5	0.98	16.18	2.63
1.50	2.95	10.64	2.47
2.50	4.91	8.03	2.49
3.50	6.87	5.75	2.51
4.50	8.84	4.42	2.44
6.00	11.79	2.20	2.24
8.00	15.71	0.97	2.41
10.00	19.64	0.77	2.37
12.00	23.57	0.90	2.54
13.50	26.52	1.61	3.20
14.50	28.48	1.22	4.15
15.50	30.44	1.63	5.30
16.50	32.41	1.05	0.13
17.50	34.37	1.36	0.00
18.50	36.34	1.29	0.00
22.00	43.21		0.00

**Table A-39**

**Unsaturated Test #10**

Injected Solution: 0.1 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.34	10.84
0.75	2.55	0.32	12.28
1.25	4.25	0.29	12.89
1.75	5.95	0.27	13.18
2.25	7.65	0.26	12.75
2.75	9.36	0.25	14.35
3.25	11.06	0.24	13.03
3.75	12.76	0.25	13.93
4.50	15.31	0.24	14.44
5.50	18.71	0.23	14.21
6.50	22.11	0.21	13.59
7.50	25.52	0.18	12.01
8.50	28.92	0.06	3.35
9.50	32.32	0.01	0.00
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00



**Table A-40**

**Unsaturated Test #11**

Injected Solution: 0.1 mole/kg LAS Injection Volume = 20.0 ml Time Duration of Test = 24 h Soil Type: Teller Loam Initial Soil Moisture Condition: Dry			
Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.38	10.76
0.75	2.55	0.37	16.23
1.25	4.25	0.34	21.32
1.75	5.95	0.33	34.69
2.25	7.65	0.32	38.53
2.75	9.36	0.32	35.80
3.25	11.06	0.23	25.49
3.75	12.76	0.22	9.82
4.50	15.31	0.21	0.29
5.50	18.71	0.20	0.11
6.50	22.11	0.18	0.00
7.50	25.52	0.14	0.00
8.50	28.92	0.03	0.00
9.50	32.32	0.02	0.00
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

**Table A-41****Unsaturated Test #12**

Injected Solution: 0.01 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3 \text{ (cm/s}^{0.5}\text{)}$	Moisture Content	Surfactant Conc. $C \times 10^3 \text{ (mole/kg)}$
0.25	0.85	0.26	2.66
0.75	2.55	0.26	2.82
1.25	4.25	0.24	2.95
1.75	5.95	0.23	2.64
2.25	7.65	0.22	2.16
2.75	9.36	0.23	1.79
3.25	11.06	0.23	1.30
3.75	12.76	0.23	1.03
4.50	15.31	0.23	0.77
5.50	18.71	0.22	0.70
6.50	22.11	0.21	0.57
7.50	25.52	0.20	0.25
8.50	28.92	0.19	0.00
9.50	32.32	0.12	0.00
10.50	35.72	0.02	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
19.00	64.64	0.01	0.00

**Table A-42**

**Unsaturated Test #13**

Injected Solution: 0.01 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.27	5.72
0.75	2.55	0.24	7.08
1.25	4.25	0.21	5.53
1.75	5.95	0.21	1.62
2.25	7.65	0.22	0.43
2.75	9.36	0.24	0.15
3.25	11.06	0.24	0.00
3.75	12.76	0.24	0.00
4.50	15.31	0.23	0.00
5.50	18.71	0.22	0.00
6.50	22.11	0.21	0.00
7.50	25.52	0.20	0.00
8.50	28.92	0.19	0.00
9.50	32.32	0.12	0.00
10.50	35.72	0.02	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

**Table A-43****Unsaturated Test #14**

Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Content = 0.08

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.34	4.01
0.75	2.55	0.31	4.56
1.25	4.25	0.28	4.69
1.75	5.95	0.27	4.89
2.25	7.65	0.26	6.26
2.75	9.36	0.25	5.93
3.25	11.06	0.25	5.88
3.75	12.76	0.24	5.56
4.50	15.31	0.24	4.67
5.50	18.71	0.23	1.84
6.50	22.11	0.23	1.24
7.50	25.52	0.22	0.42
8.50	28.92	0.22	0.00
9.50	32.32	0.21	0.00
10.50	35.72	0.20	0.00
11.50	39.12	0.19	0.00
12.50	42.53	0.17	0.00
13.50	45.93	0.11	0.00
14.50	49.33	0.07	0.00
15.50	52.73	0.07	0.00
16.50	56.13	0.08	0.00
17.50	59.54	0.07	0.00
18.50	62.94	0.07	0.00
23.00	78.25	0.08	0.00

**Table A-44**

**Unsaturated Test #15**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Content = 0.08

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.37	7.19
0.75	2.55	0.34	14.70
1.25	4.25	0.28	17.41
1.75	5.95	0.25	12.93
2.25	7.65	0.25	3.82
2.75	9.36	0.26	0.15
3.25	11.06	0.25	0.00
3.75	12.76	0.25	0.00
4.50	15.31	0.25	0.00
5.50	18.71	0.24	0.00
6.50	22.11	0.24	0.00
7.50	25.52	0.23	0.00
8.50	28.92	0.22	0.00
9.50	32.32	0.21	0.00
10.50	35.72	0.20	0.00
11.50	39.12	0.19	0.00
12.50	42.53	0.17	0.00
13.50	45.93	0.13	0.00
14.50	49.33	0.08	0.00
15.50	52.73	0.09	0.00
16.50	56.13	0.08	0.00
17.50	59.54	0.09	0.00
18.50	62.94	0.09	0.00
23.00	78.25	0.08	0.00

Table A-45

**Unsaturated Test #16**

Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Content = 0.16

Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.33	3.59
0.75	2.55	0.27	4.11
1.25	4.25	0.29	4.43
1.75	5.95	0.27	4.61
2.25	7.65	0.30	5.27
2.75	9.36	0.29	5.19
3.25	11.06	0.29	5.21
3.75	12.76	0.28	4.75
4.50	15.31	0.28	2.62
5.50	18.71	0.27	1.16
6.50	22.11	0.27	0.44
7.50	25.52	0.27	0.00
8.50	28.92	0.26	0.00
9.50	32.32	0.26	0.00
10.50	35.72	0.26	0.00
11.50	39.12	0.25	0.00
12.50	42.53	0.25	0.00
13.50	45.93	0.25	0.00
14.50	49.33	0.23	0.00
15.50	52.73	0.23	0.00
16.50	56.13	0.22	0.00
17.50	59.54	0.22	0.00
18.50	62.94	0.20	0.00
21.00	71.44	0.17	0.00
24.00	81.65	0.16	0.00
30.00	102.06	0.16	0.00

**Table A-46**

**Unsaturated Test #17**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Teller Loam

Initial Soil Moisture Content = 0.16

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.38	7.96
0.75	2.55	0.34	13.23
1.25	4.25	0.30	14.29
1.75	5.95	0.28	8.77
2.25	7.65	0.27	0.90
2.75	9.36	0.27	0.00
3.25	11.06	0.27	0.00
3.75	12.76	0.27	0.00
4.50	15.31	0.26	0.00
5.50	18.71	0.26	0.00
6.50	22.11	0.26	0.00
7.50	25.52	0.26	0.00
8.50	28.92	0.25	0.00
9.50	32.32	0.24	0.00
10.50	35.72	0.24	0.00
11.50	39.12	0.23	0.00
12.50	42.53	0.23	0.00
13.50	45.93	0.22	0.00
14.50	49.33	0.22	0.00
15.50	52.73	0.22	0.00
16.50	56.13	0.22	0.00
17.50	59.54	0.21	0.00
18.50	62.94	0.19	0.00
21.00	71.44	0.16	0.00
24.00	81.65	0.15	0.00
30.00	102.06	0.15	0.00

Table A-47

**Unsaturated Test #18**

Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 96 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.43	0.24	3.48
0.75	1.28	0.24	4.16
1.25	2.13	0.22	4.10
1.75	2.98	0.22	4.64
2.25	3.83	0.21	4.44
2.75	4.68	0.21	5.19
3.25	5.53	0.20	4.80
3.75	6.38	0.20	4.95
4.50	7.65	0.20	3.03
5.50	9.36	0.20	2.33
6.50	11.06	0.19	1.33
7.50	12.76	0.18	1.14
8.50	14.46	0.17	0.62
9.50	16.16	0.12	0.28
10.50	17.86	0.03	0.00
11.50	19.56	0.02	0.00
12.50	21.26	0.01	0.00
13.50	22.96	0.01	0.00
14.50	24.67	0.00	0.00
15.50	26.37	0.00	0.00
16.50	28.07	0.00	0.00
17.50	29.77	0.00	0.00
18.50	31.47	0.00	0.00
21.00	35.72	0.00	0.00
25.00	42.53	0.00	0.00
31.00	52.73	0.00	0.00



Table A-48

**Unsaturated Test #19**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 96 h

Soil Type: Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.43	0.28	5.18
0.75	1.28	0.27	9.47
1.25	2.13	0.22	15.30
1.75	2.98	0.20	13.36
2.25	3.83	0.18	7.84
2.75	4.68	0.18	0.99
3.25	5.53	0.18	0.29
3.75	6.38	0.20	0.23
4.50	7.65	0.19	0.00
5.50	9.36	0.19	0.00
6.50	11.06	0.18	0.00
7.50	12.76	0.17	0.00
8.50	14.46	0.16	0.00
9.50	16.16	0.13	0.00
10.50	17.86	0.03	0.00
11.50	19.56	0.02	0.00
12.50	21.26	0.01	0.00
13.50	22.96	0.01	0.00
14.50	24.67	0.01	0.00
15.50	26.37	0.00	0.00
16.50	28.07	0.00	0.00
17.50	29.77	0.00	0.00
18.50	31.47	0.00	0.00
20.00	34.02	0.00	0.00
22.00	37.42	0.01	0.00

**Table A-49****Unsaturated Test #20**

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Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Dougherty Sand

Initial Soil Moisture Condition: Dry

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Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
1	3.40	0.18	2.46
3.00	10.21	0.15	2.03
5.00	17.01	0.17	2.06
7.00	23.81	0.16	2.45
9.00	30.62	0.16	2.25
11.00	37.42	0.10	1.23
13.00	44.23	0.07	1.06
15.00	51.03	0.01	0.10
17.00	57.84	0.00	0.00
19.00	64.64	0.00	0.00
21.00	71.44	0.00	0.00
23.00	78.25	0.00	0.00
25.00	85.05	0.00	0.00
27.00	91.86	0.00	0.00
29.00	98.66	0.00	0.00

**Table A-50**

**Unsaturated Test #21**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Dougherty Sand

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
1.00	3.40	0.19	2.76
3.00	10.21	0.22	2.71
5.00	17.01	0.17	2.90
7.00	23.81	0.15	2.73
9.00	30.62	0.16	3.26
11.00	37.42	0.08	0.41
13.00	44.23	0.04	0.07
15.00	51.03	0.00	0.01
17.00	57.84	0.00	0.00
19.00	64.64	0.00	0.00
21.00	71.44	0.00	0.00
23.00	78.25	0.00	0.00
25.00	85.05	0.00	0.00
27.00	91.86	0.00	0.00
29.00	98.66	0.00	0.00

Table A-51

Unsaturated Test #22

Injected Solution: 0.025 mole/kg AES Injection Volume = 20.0 ml Time Duration of Test = 24 h Soil Type: Slaughterville Loam Initial Soil Moisture Condition: Dry			
Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.24	3.14
0.75	2.55	0.23	3.80
1.25	4.25	0.22	4.31
1.75	5.95	0.22	4.62
2.25	7.65	0.21	4.43
2.75	9.36	0.21	4.65
3.25	11.06	0.21	4.81
3.75	12.76	0.21	4.48
4.50	15.31	0.21	2.98
5.50	18.71	0.20	1.79
6.50	22.11	0.19	1.15
7.50	25.52	0.18	0.98
8.50	28.92	0.17	0.69
9.50	32.32	0.09	0.26
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.00	0.00
13.50	45.93	0.00	0.00
15.00	51.03	0.00	0.00
17.00	57.84	0.00	0.00
20.00	68.04	0.00	0.00

**Table A-52**

**Unsaturated Test #23**

Injected Solution: 0.025 mole/kg LAS  
Injection Volume = 20.0 ml  
Time Duration of Test = 24 h  
Soil Type: Slaughterville Loam  
Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.29	4.53
0.75	2.55	0.23	11.82
1.25	4.25	0.20	13.82
1.75	5.95	0.19	9.96
2.25	7.65	0.18	7.20
2.75	9.36	0.19	1.76
3.25	11.06	0.18	0.82
3.75	12.76	0.18	0.58
4.50	15.31	0.18	0.39
5.50	18.71	0.18	0.25
6.50	22.11	0.17	0.27
7.50	25.52	0.17	0.21
8.50	28.92	0.16	0.16
9.50	32.32	0.16	0.16
10.50	35.72	0.11	0.00
11.50	39.12	0.02	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.00	0.00
15.00	51.03	0.00	0.00
17.00	57.84	0.00	0.00
20.00	68.04	0.00	0.00

**Table A-53**

**Unsaturated Test #24**

Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Calcium Dominated Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.30	4.19
0.75	2.55	0.27	5.05
1.25	4.25	0.29	5.61
1.75	5.95	0.28	5.99
2.25	7.65	0.26	6.26
2.75	9.36	0.25	6.19
3.25	11.06	0.25	6.23
3.75	12.76	0.24	4.91
4.50	15.31	0.24	2.31
5.50	18.71	0.24	0.86
6.50	22.11	0.23	0.19
7.50	25.52	0.21	0.00
8.50	28.92	0.07	0.00
9.50	32.32	0.01	0.00
10.50	35.72	0.01	0.00
17.00	57.84	0.01	0.00

**Table A-54**

**Unsaturated Test #25**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Calcium Dominated Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.39	13.20
0.75	2.55	0.31	21.87
1.25	4.25	0.25	15.22
1.75	5.95	0.27	1.44
2.25	7.65	0.27	0.05
2.75	9.36	0.26	0.00
3.25	11.06	0.26	0.00
3.75	12.76	0.25	0.00
4.50	15.31	0.26	0.00
5.50	18.71	0.26	0.00
6.50	22.11	0.22	0.00
7.50	25.52	0.16	0.00
8.50	28.92	0.03	0.00
9.50	32.32	0.01	0.00
10.50	35.72	0.01	0.00
17.00	57.84	0.01	0.00

**Table A-55**

**Unsaturated Test #26**

Injected Solution: 0.025 mole/kg AES

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Sodium Dominated Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.31	4.57
0.75	2.55	0.32	4.64
1.25	4.25	0.31	4.62
1.75	5.95	0.32	5.23
2.25	7.65	0.29	5.06
2.75	9.36	0.30	5.10
3.25	11.06	0.27	5.01
3.75	12.76	0.28	4.63
4.50	15.31	0.25	4.27
5.50	18.71	0.22	2.60
6.50	22.11	0.21	0.44
7.50	25.52	0.16	0.09
8.50	28.92	0.02	0.00
9.50	32.32	0.01	0.00
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00



**Table A-56**

**Unsaturated Test #27**

Injected Solution: 0.025 mole/kg LAS

Injection Volume = 20.0 ml

Time Duration of Test = 24 h

Soil Type: Sodium Dominated Teller Loam

Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.32	6.73
0.75	2.55	0.33	7.28
1.25	4.25	0.31	7.11
1.75	5.95	0.32	7.42
2.25	7.65	0.29	6.92
2.75	9.36	0.28	6.80
3.25	11.06	0.24	4.85
3.75	12.76	0.23	3.35
4.50	15.31	0.24	0.24
5.50	18.71	0.23	0.07
6.50	22.11	0.22	0.00
7.50	25.52	0.18	0.00
8.50	28.92	0.07	0.00
9.50	32.32	0.01	0.00
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

**Table A-57**

**Unsaturated Test #28**

Injected Solution: 0.025 mole/kg AES  
Injection Volume = 20.0 ml  
Time Duration of Test = 24 h  
Soil Type: Nonorganic Teller Loam  
Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.27	4.19
0.75	2.55	0.28	4.67
1.25	4.25	0.28	4.88
1.75	5.95	0.29	5.51
2.25	7.65	0.24	5.41
2.75	9.36	0.23	5.81
3.25	11.06	0.20	5.16
3.75	12.76	0.20	4.20
4.50	15.31	0.21	1.72
5.50	18.71	0.19	1.52
6.50	22.11	0.18	0.90
7.50	25.52	0.16	0.58
8.50	28.92	0.11	0.19
9.50	32.32	0.02	0.09
10.50	35.72	0.01	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

Table A-58

## Unsaturated Test #29

Injected Solution: 0.025 mole/kg LAS  
 Injection Volume = 20.0 ml  
 Time Duration of Test = 24 h  
 Soil Type: Nonorganic Teller Loam  
 Initial Soil Moisture Condition: Dry

Distance (cm)	Boltzmann Trans. $x/t^{0.5} \times 10^3$ (cm/s <sup>0.5</sup> )	Moisture Content	Surfactant Conc. $C \times 10^3$ (mole/kg)
0.25	0.85	0.33	6.73
0.75	2.55	0.32	7.83
1.25	4.25	0.31	7.35
1.75	5.95	0.31	7.82
2.25	7.65	0.27	6.44
2.75	9.36	0.26	5.87
3.25	11.06	0.21	2.53
3.75	12.76	0.22	2.17
4.50	15.31	0.22	1.06
5.50	18.71	0.21	0.18
6.50	22.11	0.19	0.03
7.50	25.52	0.17	0.00
8.50	28.92	0.09	0.00
9.50	32.32	0.02	0.00
10.50	35.72	0.02	0.00
11.50	39.12	0.01	0.00
12.50	42.53	0.01	0.00
13.50	45.93	0.01	0.00
15.00	51.03	0.01	0.00
17.00	57.84	0.01	0.00
20.00	68.04	0.01	0.00

## **VITA**

**Barry J. Allred**

**Candidate for the Degree of**

**Doctor of Philosophy**

**Dissertation: SURFACTANT MOBILITY IN UNSATURATED SOIL AND THE  
IMPACT ON SATURATED HYDRAULIC CONDUCTIVITY AND  
UNSATURATED DIFFUSIVITY**

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### **Biographical:**

**Education:** Graduated from Ponca City High School, Ponca City, Oklahoma in 1976; received Bachelor of Science degree in Geology from Oklahoma State University in December 1980; received Master of Science degree in Geology from Northern Illinois University in December of 1986; received Master of Science degree in Geology from Western Michigan University in December of 1987; Completed the requirements for the Doctor of Philosophy degree with a major in Biosystems Engineering at Oklahoma State University in May 1995.

**Experience:** Employed by Conoco Inc. in Houston, Texas as an exploration geophysicist, 1983-1986; employed by ERM Southwest Inc. in Houston, Texas as a hydrogeologist, 1988-1989; employed by the Biosystems and Agricultural Engineering Department at Oklahoma State University in Stillwater, Oklahoma as a research engineer, 1989-1995.

**Professional Memberships:** Association of Ground Water Scientists and Engineers, American Geophysical Union, Oklahoma Academy of Science.