MINIMIZING SURFACTANT LOSSES USING TWIN-HEAD ANIONIC SURFACTANTS IN SUBSURFACE REMEDIATION
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Abstract

The economics of surfactant enhanced subsurface remediation are affected by losses of surfactants due to such phenomena as precipitation, sorption, etc. It is hypothesized that surfactants with twin head groups will exhibit lower losses in the subsurface as compared to single head group surfactants while maintaining high solubilization. The contaminant addressed in this research was naphthalene and the surfactants evaluated were mono- and di-sulfonated anionics (sodium dodecylbenzenesulfonate and alkyl diphenyloxide disulfonates). The results of this research demonstrated that disulfonates were significantly less susceptible to precipitation than monosulfonates and that disulfonates were less susceptible to sorption than monosulfonates, and also less prone to sorption than nonionic surfactants evaluated in other research. Disulfonates also exhibited greater solubilization of naphthalene than monosulfonates and slightly lower solubilization than nonionics. Solubility ratios were evaluated on both a molar (MSR) and weight (WSR) basis and corresponding micelle-phase/aqueous-phase partition coefficients (Km and Kw) were reported. This research demonstrated that disulfonate surfactants are less susceptible to losses than other surfactants evaluated, and thus are strong candidates for use in surfactant enhanced subsurface remediation.

Introduction

The use of surfactants to enhance subsurface remediation efforts has been of considerable interest in recent years (1 - 10). Micelle forming surface active agents can reduce interfacial tensions and assist in the solubilization of hydrocarbon contaminants in groundwater systems and, as such, show potential for greatly reducing the number of pore volumes to be pumped in a cleanup effort. Various chemical interactions in the subsurface, however, such as precipitation and sorption, can render the surfactant ineffective and significantly affect dosage requirements and the economics of the operation.

Anionic surfactants show potential for being more resistant to sorption in sandy and clay containing soils due to charge repulsion from the negatively charged soil surfaces. Furthermore, twin head group ionic surfactants would be expected to be less susceptible to precipitating in

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solution than single head group surfactants due to increased solubility and steric constraints. Thus, the hypothesis of this research is that surfactants with twin head groups will exhibit lower losses in the subsurface as compared to single head group surfactants while maintaining comparable solubilization. The objective of this research is to compare mono- and di-sulfonated surfactants with respect to precipitation and sorption losses and solubilization potential of hydrocarbon contaminants (HCs). These objectives are met by investigating the formation of precipitate with a cation as described by the solubility product, K_{sp} (11); the sorption of the surfactant on soil as defined by a distribution coefficient, K_d (9) and the maximum (plateau) sorption value, q_{max}; and the solubilization potential (the ability to enhance the total hydrocarbon concentration in solution due to the presence of the surfactant's micellar pseudo-phase) as commonly described by the micellar-water partioning coefficient, K_m (which defines partitioning of hydrocarbons between the aqueous phase and the micellar pseudo-phase (12)). The well known anionic surfactant sodium dodecylbenzenesulfonate (SDBS) is used for comparison with straight chain alkyl diphenyloxide disulfonates (DPDSs). A comparison between two dodecyl (C12) surfactants (SDBS and C12-DPDS) will yield insights as to the influence of the surfactant head groups. Also, characterization of other alkyl DPDSs of varying chain lengths provides a matrix of valuable information which contributes to our understanding of this class of surfactants.

Background

The extended periods of time required for pump and treat remediation of contaminated aquifers have made technologies that potentially improve the efficiency of remedial efforts important topics of research. Chemical enhancements, including surfactant usage, are among the technologies being evaluated (13). Interest in using surfactants for flushing contaminated soils is, in part, an outgrowth of the enhanced oil recovery research of the petroleum industry. It has been extensively documented that dilute solutions of aqueous surfactants can lower the interfacial tension between hydrocarbon phases and water, thereby enhancing the extraction of oil from porous media. The logical extension of this work is to use surfactants to remove trapped oils (residual saturation) from contaminated soils (2). The transfer of surfactant enhanced oil recovery technology to aquifer

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remediation, however, is not direct. The surfactant properties best suited for mobilizing a hydrocarbon free phase can differ significantly from those applicable to the successful solubilization of organic contaminants by a micellar surfactant solution (13). Surfactant enhanced subsurface remediation may also function by partitioning of hydrophobic contaminants into surfactant micelles. Micelles are aggregates of surfactants with a hydrophilic exterior (which makes the aggregate highly stable in water) and a hydrophobic interior (often referred to as a pseudo-oil phase). Partitioning of hydrophobic compounds into micelles increases the total aqueous concentration of the compound (referred to as solubilization) and has been demonstrated to be a function of the contaminant hydrophobicity (7, 12, 14, 15). Partitioning into the micelle is solely dependent on the concentration of the contaminant outside the micelle, and is independent of the source of the contaminant (sorbed, residual saturation, etc.). Thus, while interfacial tension reduction is only applicable to separate oil phases, solubilization into micelles is independent of the form of the contaminant.

Early laboratory studies of surfactant enhanced removal of different organic solutions using both batch extraction and column studies were deemed successful, but a proposed larger scale study was abandoned due to concerns regarding the cost effectiveness of using surfactants at large sites (16). Cost effectiveness can be addressed by considering less expensive surfactants; by designing the surfactant system to minimize surfactant losses due to precipitation, sorption, and partitioning into residual phases; by looking at surfactant recovery and recycling techniques (17, 18, 19); and by focusing the surfactant flood on the region of residual saturation.

Stellner, et al, (11) evaluated precipitation phase boundaries of mixtures of anionic and cationic surfactants over a wide range of concentrations by considering regular solution theory and solubility relationships and developed a model to predict their results. Stellner and Scamehorn (20) considered the effects of sodium chloride (NaCl) concentration and counterion binding on charged micelles in an effort to predict precipitation of the anionic surfactant sodium dodecyl sulfate (SDS) by calcium. A series of mechanistic and semiempirical mass action equations were developed by Jafvert and Heath (21) to calculate precipitation phase boundaries and aqueous micelle and monomer surfactant concentrations for the anionic surfactant dodecyl sulfate (DS) in conjunction

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with soil and sediment components. Jafvert (22) also determined the distribution of various polycyclic aromatic hydrocarbons (PAHs) in several media containing DS micellar solutions in varying concentrations and demonstrated that the sorption potential for various PAHs are about the same for DS micelles and natural media on an organic carbon normalized basis.

Liu et al. (23) investigated the sorption of micelle-forming and lamellae-forming nonionic surfactants onto soil. Sorption of both types of surfactants were found to fit a Freundlich isotherm at concentrations below critical micelle or aggregate concentrations. Above these critical concentrations, though, micelle-forming surfactants demonstrated constant levels of sorbed mass while lamellae-forming surfactants appeared to continue sorbing with an increase in surfactant dosage.

Palmer et al. (9) compared the sorption of nonionic surfactants (NISs) with neutral organic contaminants (NOCs) on two subsurface media. Hydrophobic partitioning appeared adequate for predicting the sorption behavior of the NOCs but not the NISs indicating that mineral surfaces were also affecting sorption of the amphiphilic NISs. The nature of the soil's organic matter also seemed to influence the sorption of NISs but not NOCs. Interaction of the NISs with the more "recent" soil was described by nonlinear isotherms while NIS sorption on oxidized "recent" soil resulted in linear sorption isotherms similar to those with the more "mature" soil; this observation was attributed to a wide distribution of polar functional groups within its organic fraction.

Nash (1) conducted laboratory studies for removing hydrocarbons and chlorinated hydrocarbons from soils using surfactants. The initial laboratory results showed promise; however, a subsequent field demonstration demonstrated no removal. It should be noted that field tests must account for losses of surfactants through adsorption, precipitation and phase trapping at field conditions as well as the effect of chromatographic separation of the surfactant components into individually ineffective components. For solubilization to occur, concentrations must be maintained above the CMC during remediation.

Vignon and Rubin (24) systematically evaluated surfactant selection and dosage optimization for solubilization of sorbed anthracene and biphenyl using alkylphenolethoxylated and alkylethoxylated surfactants. The researchers observed that surfactant dosages greater than 0.1

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percent by weight (surfactant added) were required to obtain significant improvement in chemical desorption. Abdul et al. (3) evaluated four groups of surfactants for the solubilization of automatic transmission fluid (ATF) from shallow sandy aquifer material. The percent recovery of ATF from the sand increased from 23 percent by washing with water alone to 80 percent by washing with ethoxylated alcohol surfactants.

Edwards et al. (12) investigated the use of alkyl and alkyl-phenol polyoxyethylenes to enhance the solubilization of polycyclic aromatic hydrocarbons (PAHs). The resulting values of log Km appeared to be a linear function of log Kow for a given surfactant solution in keeping with prior observations by Valsaraj and Thibodeaux (14). West (7) utilized the same surfactants and evaluated the solubilization of chlorinated organic compounds and established that the Km partition coefficients were a function of contaminant hydrophobicity (Kow), with the resulting log Km versus log Kow results being consistent with Edwards et al. (12) and Valsaraj and Thibodeaux (14). These researchers have thus demonstrated that solubilization results obtained for one contaminant can provide valuable information on the solubilization of other contaminants by analysis of their relative hydrophobicities (as indicated by Kow).

Materials and Methods

The alkyl DPDS surfactants used in this research were from the DOWFAX series as supplied by Dow Chemical Company (Midland, MI) and consisted of: [R] 8390 hexadecyl (C16-DPDS), XDS 8174 dodecyl (C12-DPDS), and [R] 3B2 decyl (C10-DPDS). The chemical structure of the DPDS series is shown in Fig. 1 and molecular weights and formulas of these surfactants along with SDBS are listed in Table I. A comparison of the average molecular weights for the DPDSs with their chemical structure indicates that in each case about 20 percent of the surfactant by weight is double tailed. SDBS was purchased from Aldrich Chemical Company (Milwaukee, WI) in dry flake form (ca. 96% active) and was used without further purification.

The DOWFAX products were received in liquid form as aqueous solutions at concentrations of about one molar. C10- and C16-DPDSs were high purity products (i.e., low salts, 0.1 to 0.3 percent NaCl, and no methylene chloride) and as such were used without further purification.

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C12-DPDS, however, required boiling under vacuum to remove methylene chloride and purification via micellar enhanced ultrafiltration (25) to lower NaCl from about one percent to 0.12 percent.

The DOWFAX C10- and C16-DPDSs meet the requirements of FDA Food Additive Regulation 21 CFR 178.3400 (Emulsifiers and/or surface-active agents), meaning they may be used in all *indirect* food additive applications such as adhesives, paper coatings, and other items that may come in contact with food (26). C10- and C16-DPDSs also meet the requirements of EPA Pesticide Regulation 40 CFR 180.1001 (c) as an inert ingredient in pesticides (26). Furthermore, C10- and C16-DPDSs are classified as biodegradable by test criteria of the Soap and Detergent Association's semi-continuous activated sludge procedure (26). The C12-DPDS, though being of the same structure as the C10- and C16-DPDSs, is still experimental in status and not yet classified under the previous regulations/standards.

Critical micelle concentrations (CMCs) were estimated by the capillary rise method which consisted of measuring meniscus rise in small volume pipettes (Fisher Scientific Company, Pittsburgh, PA; 1/10 ml capacity with markings at 1/1000 ml). For each surfactant, a series of dilutions were made and samples placed in 30 ml beakers. The pipette was then taken from weaker to stronger solutions measuring rise from a reference mark (0.09 ml mark), being careful to rinse the pipette thoroughly in each subsequent solution. Prior to use, the pipette had been cleaned with concentrated sulfuric acid and rinsed in hydrochloric acid and deionized water.

Reagent grade calcium chloride was used for precipitation assays and as an additive in some sorption experiments. Precipitation assays were conducted with 100 ml of solution in 120 ml glass jars and results were determined by visual observation supplemented with a dye assay. The solutions consisted of varying concentrations of surfactants and calcium (Ca) and were mixed at room temperature and chilled at 4°C before incubating at 15°C for at least seven days with daily shaking by hand. The dye assay was conducted by adding a small amount (ca. 1 mg) of pinacyanol chloride (Aldrich Chemical Company) to the surfactant/calcium solution. In the absence of micelles, pinacyanol chloride yields a violet color in aqueous solution; however, when sorbed to micelles, a blue color appears (27).

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For sorption experiments, Canadian River alluvium (CRA) was used; it consists of 91% sand, 2% silt, and 7% clay and has an organic carbon content (foc) of 0.0024 (9). Sorption experiments were conducted with 5 grams of soil (CRA) and 25 ml of surfactant solution in 34 ml glass vials. Experiments were conducted with SDBS and C12-DPDS -- both with and without a 0.010 N Ca addition (i.e., 0.005 M CaCl$_2$). Samples were shaken mechanically for at least 24 hours at room temperature (ca. 22°C) after which they were centrifuged to remove colloidal soil interference prior to high performance liquid chromatography (HPLC) analysis. Samples without Ca addition were not adequately separated by centrifugation and thus were passed through a 0.2 um syringe filter prior to injection (a 0.45 um filter was not able to remove this colloidal interference which was evidenced by a brown color in the solution); soil-water blanks allowed correction for background interference.

Naphthalene (Aldrich Chemical Company, 99% purity) was used as the contaminant of interest for solubilization determinations. It is reported as having a solubility limit at 25°C commonly ranging between 30 and 34 mg/l (28). To ensure an excess of hydrocarbon product was present in the test samples, 20 ml of surfactant solution were added to about 0.02 g of naphthalene in solid form (an equivalent of 1,000 mg/l). The strongest sample in the C12-DPDS series, however, required a naphthalene addition of 0.35 g to insure an excess and, in all cases, an excess of naphthalene was confirmed after each experiment by visual inspection. Samples were agitated on a mechanical wrist action shaker for at least 24 hours prior to analyses. All solubilization assays were conducted with a one percent methanol addition under the assumption that it was needed to enhance the rate of solubilization. However, subsequent analyses with naphthalene-water blanks without surfactant or methanol, showed that five hours on the mechanical shaker were adequate to achieve complete solubility. To confirm that the methanol addition did not affect the total amount of naphthalene solubilized, a series of samples were run using SDBS with methanol (as described above) and without methanol. The solubilization results (not shown) were nearly identical for both methods, as was also demonstrated by Edwards et al. (12).

HPLC analyses for anionic surfactants were conducted using a UV wave length of 225 nm, flow rate of 1.0 ml/minute, and a mobile phase of 85% methanol with .006 M tetrabutyl

ammonium hydroxide (Fisher Scientific Company, HPLC grade) as an ion paring agent. Naphthalene determination by HPLC was as above except that a mobile phase of 70% methanol was utilized. All HPLC analyses were performed on a Beckman System Gold chromatograph (Beckman Instruments, Inc., San Ramon, CA) with a 150 X 4.6 mm Nucleosil C18 reverse phase column (Alltech Assoc., Inc., Deerfield, IL).

Results and Discussion

Critical Micelle Concentration. Results of capillary rise assays conducted at room temperature (ca. 22°C) are shown in Fig. 2. As evidenced, with increasing surfactant concentration and thus decreasing surface tension, the height of capillary rise in the pipette decreased until the critical micelle concentration (CMC) was surpassed. Beyond the CMC, no further decrease in surface tension was realized and thus a constant level of capillary rise per further increase in surfactant concentration was observed. Estimations of CMCs from the plots on Fig. 2 are based on the intersections of extentions of straight line graph portions as occurring in the declining surface tension region and in the constant level region associated with higher surfactant concentrations and are reported in Table II (A) along with CMC values from other sources (B) where available. Since a decrease in surface tension results in a decrease in capillary rise, the plots shown in Fig. 2 reveal the relative order of the surface tensions for micellar solutions of the different surfactants investigated. SDBS with its single polar head group is less attracted to the polar solvent (water) and thus more surface active. The DPDSs collectively, with their larger polar moiety have a greater polar solvent attraction than SDBS and thus display a higher surface tension beyond the CMC. Within the DPDS series, however, an increase in hydrocarbon chain length, and thus an increase in hydrophobicity, displays an increase in surface tension which is unexpected. This same trend, though, has been observed by others (29). This observation might be explained by considering that a larger hydrophobic tail could exert more energy into micelle formation above the CMC and thus have less influence on surrounding surfaces or interfaces. Estimates of the surface tensions corresponding to the capillary rise isotherms are possible with a method described by Adamson (30) based on a development by Bashforth and Adams (31) as

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extended by Sugden (32) and are shown by the secondary Y-axis in Fig. 2. Minimum surface tension values determined by this procedure for fully developed micellar solutions are also included in Table II (C). Changes in solution density were not considered and accurate temperature controls were not employed during the experiments; however, the deionized water blanks were calculated to have a surface tension of 72.0 mN/m by this procedure which is a reasonable value.

Precipitation. Results of precipitation assays conducted at 15° are shown in Fig. 3. For the SDBS assays, the presence of precipitate as a heavy white flock was in all cases easy to confirm by visual inspection. The SDBS experiments were extended to 22°, 30°, and 45°C, over which range the amount of floc diminished with increase in temperature but the estimated boundary of precipitation remained unchanged for the degree of accuracy used. From Fig. 3, log Ksp for SDBS is estimated to be 8.6 and the location of the break point between the negative and positive slopes on the precipitation boundary is indicative of a CMC value of about 1 mM.

For C10-, C12-, and C16-DPDS no precipitate was observed for calcium concentrations up to 0.1 M (log Ca(uM) = 5). The entire matrix of C16-DPDS and selected samples of C10- and C12-DPDS were checked with pinacyanol chloride and only those samples that were obviously well below the CMC tested negative for micelles. This indicated that micelles were present for the alkyl DPDSs throughout the region where precipitation occurred for SDBS, thus confirming the absence of precipitate for the alkyl DPDSs.

Sorption. Fig. 4 shows the results of soil sorption experiments. It is common to conduct this assay with a 0.010 N (0.005 M) Ca addition to provide a uniform background matrix and promote the separation of solid and liquid phases during centrifugation. As shown in Fig. 4, the SDBS assay with Ca yielded a higher slope than the SDBS assay without Ca addition which is indicative of greater surfactant losses. In this case, however, the difference in slope is due to precipitation rather than sorption, as confirmed by inspection of Fig. 3. For the Ca concentration used here, the precipitation boundary shown in Fig. 3 would correspond with an SDBS concentration of about 0.00026 M or 0.090 g/L. Thus, minimal precipitation would be realized

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between the no calcium and calcium isotherms at low SDBS concentrations as shown in Fig. 4. However, with an increase in the SDBS concentration, the experiments with calcium move further into the region of precipitation, and thus exhibit greater losses due to precipitation and a corresponding increase in deviation from the assays conducted without calcium. The SDBS assay without calcium, which yielded a lower slope, is used herein to determine Kd (at lower concentrations) and q_{max} (over the entire concentration range). These results illustrate both the possibility of confusing precipitation with sorption and the danger precipitation poses to the success of a surfactant enhanced soil remediation project.

Fig. 4 also shows the results of the C12-DPDS assay with Ca addition for comparison to the SDBS results discussed above. C12-DPDS was also tested without Ca addition (data not shown) yielding essentially the same results as in the case with Ca, thus corroborating the prior conclusion that C12-DPDS precipitation did not occur. For comparison to other research, estimates of Kd were made based on the slopes of nearly straight line graph portions in the region of Ce values at and below about 0.5 g/l (Table III). These sub-CMC range coefficients provide valuable information about monomer surfactant sorption activity when low concentrations are considered (for example, residual surfactant concentrations after a remedial effort has ceased, migration of dilute surfactant releases, etc.). The Kd values for SDBS and C12-DPDS are significantly different (95% confidence interval) and the much lower slope of the C12-DPDS (factor of ca. 3) indicates that considerably less loss due to sorption would be expected if C12-DPDS were used in a soil remediation process. For comparison, Table III shows Kd values for four nonionic surfactants with the same media (9). The Kd value of C12-DPDS, used in this research, is well below (ca. 3 to 13 times) the nonionics indicating significantly less loss due to sorption. This result is due to ethoxylated nonionics sorbing readily on silica surfaces while anionics are repelled by the negative charge that occurs on silica under natural conditions.

A Langmuirian analysis of the data shown in Fig. 4 was conducted to determine maximum sorption coefficients (q_{max} – the value where q plateaus in a fully developed micellar solution) and comparisons are made with results of other research with nonionic surfactants using a different media, as shown in Table III. As shown, the maximum sorption (q_{max}) of SDBS is comparable

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to the nonionic surfactants; however, the maximum sorption of C12-DPDS is about five to seven times lower which is indicative of the potential for significantly lower levels of surfactant losses in the subsurface. It should be noted that this comparison is between two different media and in this respect the above comparison of Kd values is stronger since it is for the same media.

These results corroborate the hypothesis that twin-head (dual ionic groups) anionic surfactants evidence increased charge and steric hindrances to sorption. While only one media was evaluated in this research, it is anticipated that these same fundamental mechanisms will be active in other media (except in the case where a significant number of positively charged sites occur in the media which is highly unlikely for typical subsurface media). Further research can address this supposition.

Solubilization. Solubilization assays were conducted for SDBS, C10-DPDS, C12-DPDS, and C16-DPDS using naphthalene as the solubilizate. In all cases, linear functions of solubilized naphthalene versus surfactant dosage were evidenced well beyond the CMCs with maximum surfactant concentrations in the range of 55 to 100 mM as shown in Fig. 5. These results indicate not only the hydrocarbon solubilization capability but also the higher solubility limits of the anionic surfactants themselves. Naphthalene concentrations at the origin (in deionized water blanks with one percent methanol) were in the range of 0.23 to 0.27 mM (29 to 34 mg/l) which are in keeping with reported water solubility values for naphthalene (28).

Table IV summarizes the solubilization results where the molar solubility ratio (MSR) is the slope of the solubilization isotherm beyond the CMC and log Km (a function of MSR) is the coefficient for partitioning between aqueous and micellar phases on a molar basis (12). In all cases in this research, MSR determinations were based on straight line functions with "r squared" regression coefficients greater than 0.97. A linear relationship between log Km and log Kow for various HCs as solubilized by SDBS has been demonstrated elsewhere (14); by this relation, naphthalene's Kow yields a log Km of approximately 4.0 which is corroborative of the 4.04 value obtained in this work. This reinforces the fact that these equilibrium results are applicable for any contaminant with a similar hydrophobicity, irrespective of whether the contaminant exists as

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residual saturation, in sorbed form, etc. (as discussed in the *Background* section). Also using the log Km versus log Kow relationships, it is possible to estimate the Km values for other contaminants with these surfactants by virtue of the relative hydrophobicity of the contaminants (Kow).

For comparison, results of other research on naphthalene solubilization by nonionics (12) are included in Table IV. Also shown are weight solubility ratios (WSRs) obtained by plotting the data shown in Fig. 5 with both coordinates in mg/l (not shown). An analysis of the results on a weight basis is deemed beneficial when practical issues such as purchasing materials and field application are considered. Analogous to Km, the partition coefficient on a weight basis (Kw) is calculated as:

$$Kw = X'm/X'a \tag{1}$$

Where X'm is the weight (or mass) fraction of the HC (naphthalene) in the micellar pseudo phase and X'a is the weight fraction of the HC in the aqueous phase at solubility equilibrium. They are determined as:

$$X'm = WSR/(1 + WSR) \tag{2}$$

and,

$$X'a = (HC \text{ concentration in mg/l at the CMC) (weight volume of water,}$$
$$\text{i.e., } 0.000001 \text{ l/mg)} \tag{3}$$

From these results (Table IV) it can be seen that the solubilization potentials of alkyl DPDSs tested here are less than nonionics on a molar basis as commonly observed (12). As expected for the alkyl DPDS series, solubilization potential increased with increasing hydrocarbon chain length (15). SDBS had a lower partition coefficient than its C12-DPDS counterpart, but this difference is diminished when compared on a weight basis due to the larger molecular weight of the alkyl

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DPDS. The apparent increase in solubilization potential of the C12-DPDS over SDBS could be due to increased solubilization into its larger palisade layer where the benzene ring structures would constitute some affinity for the aromatic solubilizate or, perhaps, because of a larger micelle volume due to steric considerations associated with the larger DPDS polar head group. The arrangement or configuration of the occasional double tailed DPDSs (discussed in Materials and Methods) in the micellar structure are unknown; however, their presence could also contribute to the solubilization potential of the alkyl DPDSs. If these double tailed surfactants are flexible enough to allow both tails to enter the micelles interior, an increased core volume would be realized for a given aggregation number; however, if the surfactant structure is rigid, even the additional hydrocarbon chains along the exterior of the palisade layer might contribute to secondary solubilization potentials. It should be noted that a similar discussion concerning the effects of double hydrocarbon tails could also be offered for SDBS due to the positioning of the polar head group on the hydrophobic moiety occurring at differing locations.

Summary and Conclusions

This research evaluated the hypothesis that surfactants with twin head groups will exhibit lower losses in the subsurface as compared to single head group surfactants while maintaining high solubilization. A comparison was made between one mono-sulfonated and three di-sulfonated surfactants with respect to precipitation and sorption losses and solubilization potential of naphthalene. The surfactants utilized were characterized as to critical micelle concentration and minimum surface tension by the capillary rise method. Results of experiments showed that disulfonates were less susceptible to precipitation than monosulfonates and that disulfonates were less susceptible to sorption than monosulfonates evaluated in this research and less prone to sorption than nonionic surfactants evaluated by others. Disulfonates also exhibited a greater potential for solubilization of naphthalene than monosulfonates and a slightly lower solubilization potential than nonionics. Disulfonate surfactants thus demonstrated excellent characteristics for use in surfactant enhance subsurface remediation. Further research addressing the biodegradability and

fate of these surfactants and their metabolites in the subsurface will be a vital step in assessing the utility of these surfactants in field applications.

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Table I. Anionic surfactants used in this research.

Surfactant	Average MW	Design mol formula
SDBS (C12)	348.48	$C_{12}H_{25}C_6H_4SO_3Na$
C10-DPDS	542	$C_{10}H_{21}C_{12}H_7O(SO_3Na)_2$
C12-DPDS	575	$C_{12}H_{25}C_{12}H_7O(SO_3Na)_2$
C16-DPDS	642	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$

Table II. Critical micelle concentrations and surface tensions.

Surfactant	(A) CMC by intersection of straight lines	(B) CMCs from other sources	(C) Micellar surface tension* (mN/m)
SDBS	4.0 mM (1.4 g/l)	1.2 mM (0.4 g/l) **	31.8
C10-DPDS	6.3 mM (3.4 g/l)	6 mM (3 g/l) ***	37.0
C12-DPDS	5.0 mM (2.9 g/l)	- - - - -	38.8
C16-DPDS	6.3 mM (4.0 g/l)	3 mM (2 g/l) ***	49.2

* Calculated from capillary rise (30)

** Reference (33)

***Estimated from surface tension data developed by a maximum bubble pressure method as provided by Dow Chemical Co. (26)

Table III. Surfactant losses due to sorption on CRA.

Surfactant	Kd (cm3/g)	qmax (g/g)	K_L (g/l)	Soil : water (g : ml)
SDBS (C12)	8.3	0.0114	0.729	1 : 5
C12-DPDS	3.1	0.0016	0.703	1 : 5
CA 620 *	10.8	----	----	1 : 5
CO 660 *	19.7	----	----	1 : 5
CO 630 *	31.2	----	----	1 : 5
CO 620 *	41.1	----	----	1 : 5
CA-720 **	----	0.0103	----	1 : 7.2
NP-10 **	----	0.0077	----	1 : 7.2
X-100 **	----	0.0119	----	1 : 7.2

Kd   Linear distribution coefficient

qmax   Langmuirian sorption capacity

K_L Langmuirian sorption coefficient

*   Nonionic surfactants--alkylphenolpolyoxyethoxylates--same media (9)

**   Nonionic surfactants--alkylphenol ethoxylates--different media (23)

Table IV. Solubilization of Naphthalene.

Surfactant	MSR	log Km	WSR	log Kw
SDBS (C12)	0.0516	4.04	0.0190	2.76
C10-DPDS	0.0540	4.06	0.0128	2.60
C12-DPDS	0.1045	4.32	0.0233	2.85
C16-DPDS	0.1320	4.41	0.0263	2.90
- - - - - - - - - -	- - - - - -	- - - - - -	- - - - - -	- - - - - -
Brij 30 *	0.137	4.59		
Igepal CA-720 *	0.323	4.63		
Tergitol NP-10 *	0.368	4.57		
Triton X-100 *	0.338	4.64		

* Nonionic surfactants (12).

FIGURE CAPTIONS

Fig. 1. Straight chain diphenyloxide disulfonates (DPDSs) [Dow Chemical Co. (26)]

Fig. 2. Capillary rise and surface tension versus surfactant concentration (capillary diameter = 0.04461 cm)
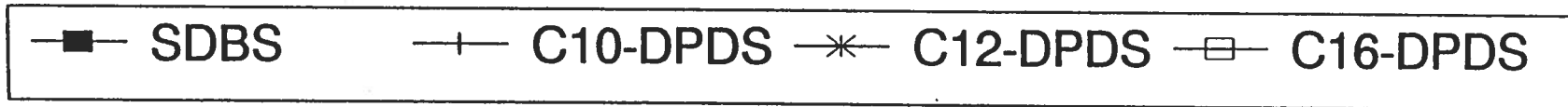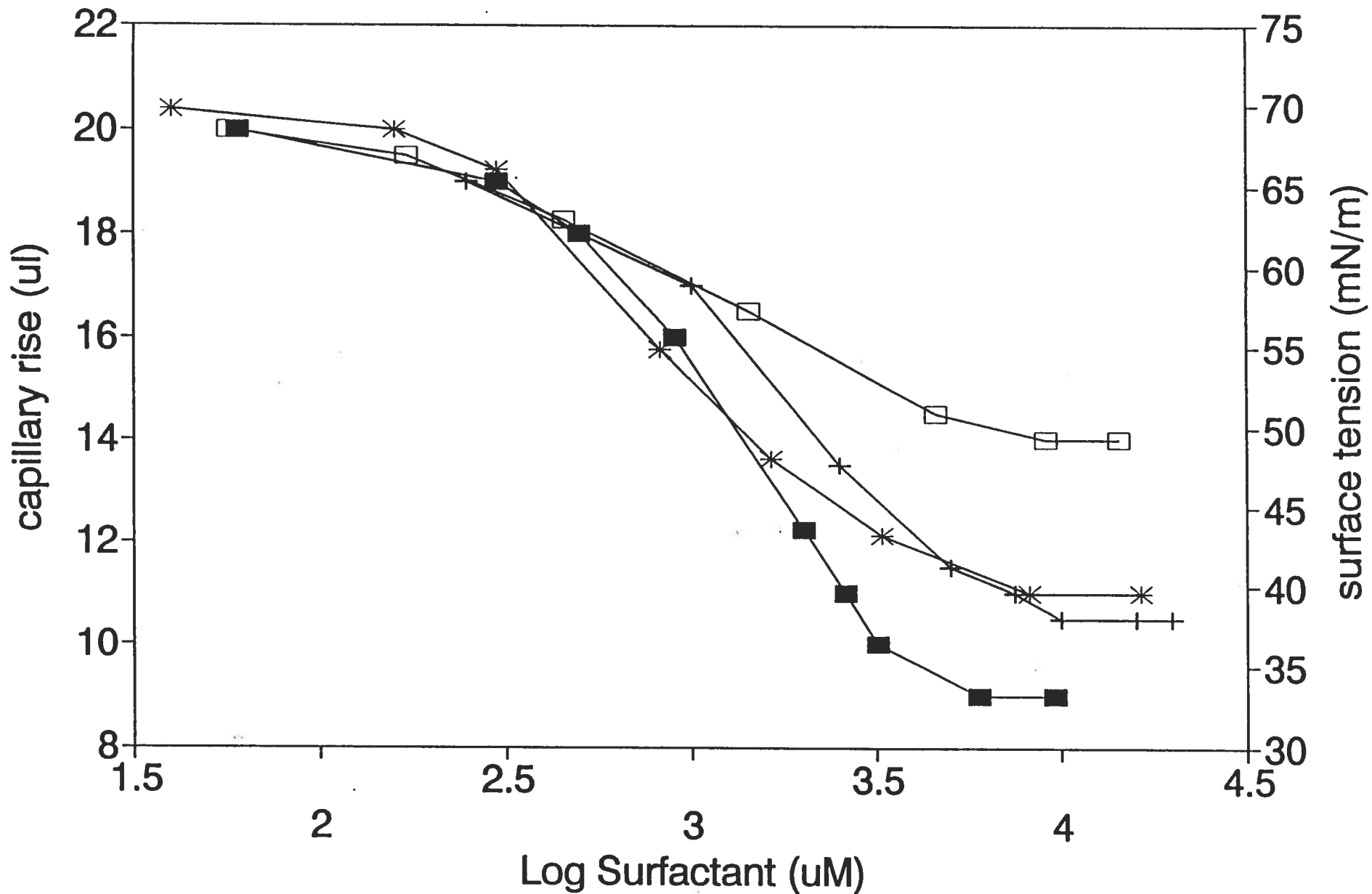
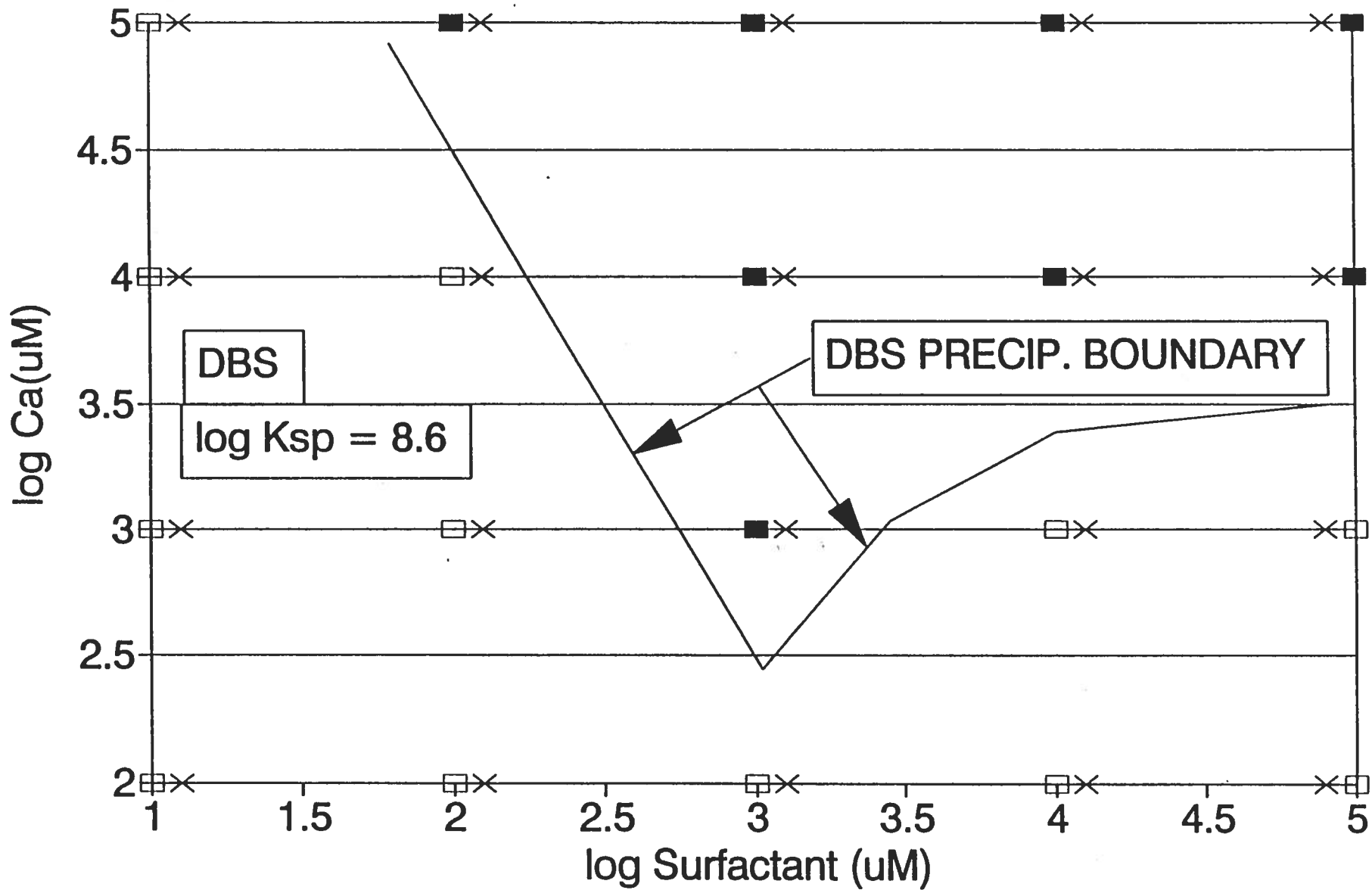Fig. 3. Precipitation of anionic surfactants with calcium at 15° C

Fig. 4. Adsorption of SDBS and C12-DPDS on soil (CRA) (calcium addition is 0.010 N where indicated). Mass of surfactant sorbed per mass of soil is plotted as a function of the equilibrium surfactant concentration in solution.

Fig. 5. Solubilization of naphthalene by anionic surfactants

$$C_nH_{2n+1}C_{12}H_7O(SO_3Na)_2$$

diphenyloxide disulfonates