SURFACTANT SOLUBILIZATION OF POLYCYCLIC AROMATIC HYDROCARBON COMPOUNDS IN SOIL–WATER SUSPENSIONS

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are hydrophobic compounds readily sorbed onto soil; the addition of surfactants to soil-water systems may solubilize PAH compounds by incorporation of the PAH in surfactant micelles. The solubilization of anthracene, phenanthrene and pyrene was evaluated in soil-water suspensions with several nonionic and anionic surfactants. The most effective surfactants were nonionic octyl- and nonyl- phenylethoxylates with 9 to 12 ethoxylate units. At soil-water mass ratios of about 1:7 to 1:2, greater than 0.1% by volume surfactant dose was required in order to initiate solubilization, with doses of 1% by volume resulting in 70 - 90% solubilization. The soil-water partition coefficient for anthracene was reduced by two orders of magnitude with 1% by volume phenylethoxylate surfactant. The solubilization of anthracene, phenanthrene and pyrene in soil-water systems occurs at surfactant doses, $[C_{surf}]$, much greater than the clean water surfactant critical micelle concentration. A surfactant-soil solubilization coefficient is derived as $C_{aq(s)} / S$, where $C_{aq(s)}$ is the observed aqueous solubility of PAH in the presence of surfactant, and $S$ is the specific sorption of PAH onto soil. $C_{aq(s)} / S$ is shown to be proportional to $C_{surf} - C_{CMC_{eff}}$, where $C_{CMC_{eff}}$ is the effective critical micelle concentration in the presence of soil. Additional information is needed on the sorption characteristics of surfactant on soil in order to describe more fully the PAH-surfactant solubilization process.

KEYWORDS

Anthracene, phenanthrene, pyrene, surfactant, soil, soil washing, soil decontamination, solubilization, PAH, dispersant.

INTRODUCTION

There is considerable concern regarding the contamination of natural soil-water systems by hydrophobic organic compounds. These types of compounds tend to sorb onto soil and are not readily amenable to remediation by soil washing or microbial degradation. The addition of surfactants to such systems may assist remediation by aiding desorption of the hydrophobic organic contaminant from soil. Surfactants possess both polar and non-polar regions on the same molecule, and at solution strength greater than the critical micelle concentration (CMC) surfactant molecules aggregate to form micelles. A micelle is an assembly of surfactant molecules having a nonpolar hydrocarbon-like core surrounded by the polar entities of the surfactant molecules. Surfactant solutions may solubilize hydrophobic contaminants from soil by reducing the work of adhesion between the contaminant and soil, resulting in desorption and incorporation of the organic compound within the aqueous phase surfactant micelle.
Several investigations in the last few years have assessed the potential for surfactants to treat contaminated soils (Ellis et al., 1984; McDermott et al., 1988; Rickabaugh et al., 1988; Rajput et al., 1989; Vigon and Rubin, 1989). Most of this work has consisted of laboratory screening studies using soil-water suspensions or small column apparatus. Tests with various surfactants and surfactant blends have been described. Generally, surfactant solutions in the range of 1 to 4% have been suggested as promising for scrubbing fuel components, PCBs and other chlorinated hydrocarbons from soil. The EPA has conducted a field test of in-situ soil washing with surfactant to evaluate removal of petroleum hydrocarbons (Nash and Traver, 1986). Potential difficulties for deployment of surfactants in soil clean-up included problems of soil clogging for in-situ use, separation and treatment of surfactant solutions, and recovery of surfactants for reuse. Rittmann and Johnson (1989) evaluated the use of dispersant to assist microbial degradation of lubricating oil in soil; the dispersant assisted the rate of microbial degradation when used in combination with slurry mixing and acclimated inoculum. The current literature contains essentially no information on the mechanism of surfactant-aided solubilization of hydrophobic organic compounds in soil-water systems.

The purpose of this investigation was to evaluate the solubilization of polynuclear aromatic hydrocarbons (PAH) using aqueous solutions of several surfactants in batch equilibrium extraction tests. The results are discussed in terms of an outline of a methodology which may be useful for interpreting solubilization data among different solutes and soils.

**METHODS**

Phenanthrene, anthracene and pyrene were used in batch tests with 50 ml centrifuge tubes filled to zero headspace, sealed with Teflon-lined septa and secured with open-port screw caps. Test samples generally contained 6.25 g soil spiked with a measured volume of PAH stock solution in methanol; the methanol was allowed to evaporate over a period of 2-3 hours before use. The surfactant solution was prepared in BOD dilution water (APHA, 1985) having 0.02 M Ca(NO₃)₂ to assist centrifugation and solid phase separation at the completion of a test. The concentration for the liquid surfactants is reported as volume/volume, and for the solid surfactants as mass/mass. The sealed centrifuge tubes were mounted on a tube rotator and rotated for 15 minutes every half an hour to maintain the soil in suspension for an equilibration period of 24 hours or more.

The principal soil used in this study was an undisturbed, A horizon, subhumid, grassland soil of the Barnes-Hamerly Association (Mihelec and Luthy, 1988). The soil was air-dried and screened to pass a US standard No. 10 mesh (2 mm) sieve. The fraction of organic carbon in the soil was determined to be 0.96% by the Walkley-Black method (ASA, 1965). Some tests were performed also with a Hagerstown silt loam collected from the A horizon of the Agriculture Experimental Station, Pennsylvania State University. This soil was similarly air-dried and sieved, and its fraction organic carbon was determined to be 1.5%. The surfactants were obtained either directly from the manufacturer or chemical distributor and were used without further purification. Unlabeled PAH compounds were obtained from Aldrich Chemical Co., Wis. (purity > 98%), and ¹⁴C-labeled PAH were obtained from Amersham Corporation. The activity of ¹⁴C-labeled PAH used in individual tests was about 0.2 µCi per 50 ml sample.

The PAH doses for the various tests with 6.25 g soil were designed to attain an initial equilibrium concentration of the PAH near aqueous phase saturation. In the absence of surfactant and PAH supersaturation, the total amount of PAH that may exist in a soil-water system is given by the PAH sorbed on the soil in equilibrium with PAH at or below aqueous solubility. This may be estimated as:

\[
\text{Total PAH} = 0.63 \cdot K_{ow} \cdot f_{oc} \cdot C_{aq} \cdot m_s + C_{aq} \cdot v_l
\]

where \(f_{oc}\) is the fraction organic carbon in the soil, \(m_s\) is the mass of soil used, \(v_l\) is the volume of the aqueous phase, \(K_{ow}\) is the octanol-water partition coefficient, \(C_{aq}\) is the aqueous concentration of the PAH, and 0.63 is the proportionality between \(K_{ow}\) and the organic carbon normalized sorption coefficient \(K_{OC}\) for PAH as determined by Karickhoff et al. (1979). Considering the case of anthracene at aqueous solubility, \(C_{aq} = 73 \mu g/L\), and with \(K_{ow} = 35000\), 6.25g soil of \(f_{oc} = 0.0096\), and 45 ml of aqueous phase, the maximum loading of anthracene that may exist without exceeding saturation in the soil-water suspension is approximately 0.1 mg. Similarly, the organic loadings for pyrene and phenanthrene are estimated as 0.8 mg and 5 mg respectively.
Prior to analysis samples were centrifuged for 30 minutes, and aliquots withdrawn with a syringe and expressed through a pre-conditioned 0.22 μm PTFE membrane filter. 0.5 ml aliquots were injected into 20 ml polyethylene counting vials with 10 ml of liquid scintillation cocktail (Scintiverse II, Fisher Scientific). Samples were taken in triplicate and counted for ^14C on a Beckman LS 5000 TD Liquid Scintillation Counter to at least the 95% confidence level, using the H# quench monitoring technique with automatic quench compensation. The counts were obtained in DPM (disintegrations per minute) which could be related to the proportion of the total mass of PAH in the sample. The results were expressed as percent solubilization of the PAH, i.e. the fraction of the total PAH in the aqueous phase:

\[
\text{Solubilization (\%)} = \frac{(\text{measured sample DPM} - \text{sample blank DPM}) \times v_l \times 100}{\text{total DPM} \times \text{sample volume}} \tag{2}
\]

where sample volume is the volume of the aqueous surfactant phase counted; \(v_l\) is the total volume of the aqueous surfactant phase which was generally 45 ml (for the case of 6.25 g soil), and total DPM refers to the total radioactivity applied to the sealed tube system. The amount of PAH adsorbed on the soil was the difference between total added PAH and the solubilized PAH; losses through volatilization and sampling were negligible as verified in separate tests.

RESULTS AND DISCUSSION

Surfactant Selection and PAH Equilibration

Surface-active agents are characterized by the possession of both polar and non-polar regions on the same molecule. The polar or hydrophilic region may carry a positive or negative charge, giving rise to cationic or anionic surfactants respectively, or it may be composed of a polyoxyethylene chain as in most nonionic surfactants. The surfactants that were used in this study are listed in Table I along with known properties. They were selected on the basis of a literature survey of surfactant-aided soil washing and biodegradation studies in order to provide a range of surfactant types for the solubilization tests.

The solubilization tests involved the addition of aqueous surfactant solution to freshly-prepared PAR-dosed soil followed by an equilibration period of 24 hours during which time the samples were kept in suspension by a tube rotator. Tests were performed to evaluate the effects of PAH contact time with soil by dosing with PAH and equilibrating the PAH in soil-water suspension for 48 hours prior to addition of surfactant. The results for the two procedures with phenanthrene indicated that the longer PAH pre-equilibration time prior to the addition of surfactant had no significant effect on the solubilization of PAH.

PAH Partitioning in Soil Water Systems

Table II shows the measured aqueous concentrations for the three PAH compounds in soil-water suspension in the absence of surfactant. Observed values of 1.89, 0.114 and 0.047 mg/l for the aqueous concentrations of phenanthrene, pyrene and anthracene respectively are close to their reported aqueous solubilities (viz. 1.29, 0.135, and 0.073 mg/l respectively, Walters and Luthy, 1984). These data show that centrifugation and filtration with pre-conditioned filters effectively removed suspended phase material, and that the experimental design based on Equation (1) was appropriate for use in subsequent tests.

Figure 1 shows the partitioning of anthracene between soil and aqueous phase with varying concentrations of the surfactant Brij 30. The total mass of anthracene was 0.1 mg with soil mass varying from 3 to 15 g per 50 ml. The partition coefficient is defined as the ratio of the concentration of solute associated with the solid phase to its concentration in the liquid phase. In the absence of surfactant, the partition coefficient \(K_D\) is 650 ml/g, or log \(K_D = 2.8\). This agrees with a value of log \(K_D = 2.6\) as estimated from Equation (1). At a surfactant concentration of 0.1% by volume, the partition coefficient does not change appreciably (\(K_D = 320\) ml/g, log \(K_D = 2.5\)), and anthracene remains predominantly in the sorbed phase. As the surfactant dose increases to 0.5% and 1%, there is marked decrease in the partition coefficient (\(K_D = 12.5\) and 5.5 ml/g respectively for 0.5% and 1% v/v Brij 30). That the surfactant has little effect at concentrations up to 0.1% is in agreement with earlier studies which report < 10% solubilization for hydrophobic solutes in soil-water systems at surfactant doses of 0.1% and less.
Table I. Structures and Properties of Selected Surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Structure</th>
<th>Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brij 30</td>
<td>C_{12}H_{25}(OCH_{2}CH_{2})_{2}OH</td>
<td>Nonionic</td>
<td>Rubin and Vigon (1989)</td>
</tr>
<tr>
<td>(liquid, d = 0.95)</td>
<td>dodecylethoxylate with 4 ethoxylate units</td>
<td>(362.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[6.5 x 10^{-3}]</td>
<td></td>
</tr>
<tr>
<td>Igepal CA-720</td>
<td>C_{8}H_{17}-C_{6}H_{4}-O(CH_{2}CH_{2}O)_{12}H</td>
<td>Nonionic</td>
<td></td>
</tr>
<tr>
<td>(liquid, d = 1.04)</td>
<td>octylphenylethoxylate with 12 ethoxylate units</td>
<td>(735)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[-6 x 10^{-4}]</td>
<td></td>
</tr>
<tr>
<td>Triton X-100</td>
<td>C_{8}H_{17}-C_{6}H_{4}-O(CH_{2}CH_{2}O)_{x}H</td>
<td>Nonionic</td>
<td>McDermott et al. (1988)</td>
</tr>
<tr>
<td>(liquid, d = 1.08)</td>
<td>octylphenylethoxylate with average x = 9.5</td>
<td>(628)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[2 x 10^{-4}]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[3 - 3.3] x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Hyonic NP-90</td>
<td>C_{8}H_{19}-C_{6}H_{4}-O(CH_{2}CH_{2}O)_{x}H</td>
<td>Nonionic</td>
<td>Ellis et al. (1984)</td>
</tr>
<tr>
<td>(liquid, d = 1.06)</td>
<td>nonylphenylethoxylate with 9 ethoxylate units</td>
<td>(616)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[-7 x 10^{-5}]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[-5 x 10^{-5}]</td>
<td></td>
</tr>
<tr>
<td>Adsee 799</td>
<td>blend of polyoxyalkylated fatty acid esters</td>
<td>Nonionic</td>
<td>Ellis et al. (1984)</td>
</tr>
<tr>
<td>(liquid, d = 1.04)</td>
<td></td>
<td></td>
<td>Rajput et al. (1989)</td>
</tr>
<tr>
<td>Corexit 7664</td>
<td>blend of surfactant esters</td>
<td>Nonionic</td>
<td>Rittmann &amp; Johnson (1989)</td>
</tr>
<tr>
<td>(liquid, d = 1.02)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium lignin</td>
<td>sulfonated polymers of complex structure containing free phenolic, primary &amp; secondary alcoholic, and carboxylate groupings.</td>
<td>Anionic (1000-20,000)</td>
<td>Liu (1980)</td>
</tr>
<tr>
<td>sulfonate</td>
<td>(solid)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl</td>
<td>C_{12}H_{25}-C_{6}H_{4}-SO_{3}Na</td>
<td>Anionic</td>
<td>McDermott et al. (1986)</td>
</tr>
<tr>
<td>benzenesulfonate</td>
<td>(solid)</td>
<td>(348)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[-1.5 x 10^{-3}]</td>
<td></td>
</tr>
</tbody>
</table>

(1) CMC from Rosen (1989)
(2) CMC either direct or extrapolated from Mukerjee and Mysels (1971)
(3) CMC from Kile and Chiou (1989)
(4) CMC data from Attwood and Florence (1983)

Table II. Solubilization of PAH in Soil-Water Suspension in the Absence of Surfactant

<table>
<thead>
<tr>
<th>PAH Compound</th>
<th>Solubilization$^{(1,2)}$ (%)</th>
<th>Aqueous Conc. (mg/l)</th>
<th>Reported Solubility (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenanthrene</td>
<td>1.7</td>
<td>1.89</td>
<td>1.29</td>
</tr>
<tr>
<td>anthracene</td>
<td>2.1</td>
<td>0.047</td>
<td>0.073</td>
</tr>
<tr>
<td>pyrene</td>
<td>0.6</td>
<td>0.114</td>
<td>0.135</td>
</tr>
</tbody>
</table>

(1) mass PAH in aqueous solution / total mass PAH added
(2) 6.25 g soil per 50 ml total volume
Solubilization of PAH

Solubilization may be envisioned as the dissolution of a substance by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution (Rosen, 1989). The amount of material solubilized is small until a critical concentration of the surfactant is reached, after which the solubilized concentration may increase approximately linearly with surfactant concentration. The critical surfactant concentration is nominally the surfactant concentration at which micelles or surfactant aggregates start to form in the aqueous phase. In the soil-water systems considered, the surfactant dose required to achieve PAH solubility is considerably in excess of the reported value of the surfactant-water CMC. Figure 2 shows the solubilization of anthracene by the surfactant Brij 30. Brij 30 has a CMC = 6.4 x 10⁻⁵ M, which is equivalent to a surfactant dose of 2.5 x 10⁻³ % v/v; solubilization is observed only at surfactant doses > 0.1% which is 40 times greater than the CMC. The presence of soil results in a change in the solubilization pattern, presumably because the surfactant sorbs onto the soil, resulting in aqueous phase surfactant being considerably less than the total added. Figure 2 shows also that the solubilization of anthracene for both soils was similar, probably because of similar morphology and because the values for the fraction organic carbon for the soils were not very different (~1% and 1.5%).

Additional tests were conducted with individual surfactant concentrations at doses < 0.1% and confirmed that at low surfactant doses solubilization was not substantial, e.g. for phenanthrene at surfactant doses of 0.01, 0.05 and 0.10%, solubilization was between 2 and 3% which was not significantly different from 1.7% solubilization in the absence of surfactant. The sorption of surfactant on soil has been demonstrated by Vigon and Rubin (1989) for Sterox NJ (a nonylphenolethoxylate with 8 to 9 ethoxylate groups), Sterox DF and Sterox DJ (dodecylphenolethoxylates with 5, and 8 to 9, ethoxylate units respectively), with prepared soil having 4% organic carbon at a soil-water ratio of about 1 g per 100 ml. At 0.1% surfactant dose, 65 - 95% of the surfactants were sorbed to soil, and sorption decreased to 4 - 80% at 1% dose. Sterox DF was most strongly sorbed to soil, while Sterox NJ showed the least sorption. Surfactant sorption was less as the hydrophobic portion of the surfactant was diminished (e.g. nonyl- vs dodecyl-) and the number of ethoxylate groups was increased (e.g. from 5 to 8 - 9).

Data for surfactant solubilization of pyrene and anthracene are presented in Figure 3. The solubilization curves for phenanthrene showed similar behaviour. The nonionic surfactants Brij 30, Triton X-100, Igepal CA-720 and Hyonic NP-90 are seen to be the most effective in producing solubilization. The anionic surfactants sodium ligninsulfonate and
and sodium dodecylbenzenesulfonate (SDBS) have the least solubilizing ability at the doses considered. The presence of inorganic salts in the mineral medium used in the solubilization tests may have affected solubilization by the anionic surfactants by assisting surfactant sorption and precipitation from solution (Rosen, 1989). Corexit 7664 and Adsee 799, both surfactant esters, do not produce substantial solubilization until the surfactant dose applied is 1%.

Table III. Effect of Solids Loading on the Solubilization of Phenanthrene

<table>
<thead>
<tr>
<th>Solubilization, %</th>
<th>Mass of Soil used, g per 50 ml total volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.25</td>
</tr>
<tr>
<td>No surfactant</td>
<td>1.7</td>
</tr>
<tr>
<td>1% sodium ligninsulfonate</td>
<td>5.5</td>
</tr>
<tr>
<td>1% SDBS</td>
<td>1.3</td>
</tr>
<tr>
<td>1% Corexit 7664</td>
<td>19</td>
</tr>
<tr>
<td>1% Adsee 799</td>
<td>21</td>
</tr>
<tr>
<td>1% Brij 30</td>
<td>56</td>
</tr>
<tr>
<td>1% Hyonic NP-90</td>
<td>68</td>
</tr>
<tr>
<td>1% Triton X-100</td>
<td>68</td>
</tr>
<tr>
<td>1% Igepal CA-720</td>
<td>73</td>
</tr>
</tbody>
</table>
Surfactant solubilization

Figure 3. Solubilization of Pyrene and Anthracene by Various Surfactants with 6.25 g soil/50 ml. The Total Mass of Pyrene and Anthracene was 0.8 and 0.1 mg Respectively.

Solubilization and Solids Concentration

Table III illustrates the effect of solids loading on the solubilization of phenanthrene in the presence of 1% aqueous surfactant solution. The total amount of phenanthrene in the individual systems was held constant at 5 mg. The data show that the effect of soil content is not uniform for all the surfactants studied. For the surfactants Corexit 7664 and Adsee 799, the solubilization decreases markedly with increasing soil content, as at 1% surfactant dose these surfactants are on that part of the solubilization curve where a small change in the amount of surfactant produces a significant change in the PAH solubilized. The other surfactants show a small decrease in solubilization because the 1% surfactant dose is on the flat part of the solubilization curve and, therefore, not particularly sensitive to the changes
in aqueous-phase micelle concentration that may result from varying soil content. The effect of solid-water ratio on solubilization is believed to be dependent on whether the 1% surfactant dose is near that required to produce micelles in the soil-water suspensions.

Surfactant Solubilization and Effective CMC

A soil-water partition coefficient for surfactant systems may be defined as:

$$K_{D(s)} = S / C_{aq(s)}$$  \hspace{1cm} (3)

where $S$ is the PAH sorbed onto the soil ($\mu g/g_s$) and $C_{aq(s)}$ refers to the PAH concentration in the liquid phase in the presence of surfactant. $K_{D(s)}$ decreases with increasing surfactant concentration (refer to Figure 1) as the PAH is solubilized and favors the aqueous phase. The reciprocal of $K_{D(s)}$ (i.e., a surfactant-soil solubilization coefficient) is plotted in Figure 4 as $C_{aq(s)} / S$ for pyrene and anthracene with the four nonionic ethoxylate surfactants, as a function of surfactant dose. Solubilization is minimal until the surfactant dose is about 0.1%, a value considerably above the CMC, which is presumably due to sorption of surfactant on soil. The elevated surfactant concentration at which solubilization initiates in the presence of soil may be thought of as an "effective CMC", [CMC$_{eff}$]. If one considers

Figure 4. The Soil-Surfactant Solubilization Relationship for Pyrene and Anthracene with Nonionic Ethoxylate Surfactants.
that portion of the $C_{aq(S)} / S$ relationship at $C_{\text{surf}}$ greater than the "effective CMC", the $C_{aq(S)} / S$ relationship appears linear, i.e. the $C_{aq(S)} / S$ relationship may be described as:

$$C_{aq(S)} / S = k_1 (C_{\text{surf}} - C_{MC_{\text{eff}}}) + k_2 \quad (4)$$

$k_1$ being the slope of the solubilization relationship with an intercept $k_2$ at $C_{\text{surf}} = C_{MC_{\text{eff}}}$. Solubilization is approximately constant for surfactant concentrations $< C_{MC_{\text{eff}}}$ and this portion of the $C_{aq(S)} / S$ plot suggests that the intercept $k_2$ may be interpreted as the inverse of a partition coefficient in the presence of surfactant monomers.

The general features of the solubilization of PAH by surfactants in soil-water suspensions may be described by considering the partitioning of PAH between two compartments: the surfactant micelles in solution and the solid phase. At surfactant concentrations less than that necessary to produce micelles in the presence of soil, the PAH is predominantly sorbed onto soil; at surfactant concentrations greater than that necessary to produce micelles in the presence of soil, the PAH is partitioned between micelle and soil. Equation (4) may be re-arranged to express PAH solubilization:

$$\text{Solubilization (\%)} = 100 \left[ k_1 v_1 (C_{\text{surf}} - C_{MC_{\text{eff}}}) + k_2 v_1 \right] / \left[ m_s + k_1 v_1 (C_{\text{surf}} - C_{MC_{\text{eff}}}) + k_2 v_1 \right] \quad (5)$$

This expression agrees very well with the solubilization data presented earlier.

**Effective CMC and the Solubilization Relationship**

The data presented here demonstrate that nonionic surfactants at doses of 0.1 to 1% by volume may solubilize PAH from soils at solids-to-liquid mass ratios ranging from about 1:7 to 1:2. Among the nonionic surfactants considered here, the octyl- and nonyl- phenylethoxylate surfactants with 9 to 12 ethoxylate units demonstrated the best solubilizing characteristics.

The ability of a surfactant to solubilize a PAH, or other hydrophobic organic compound, from soil is dependent on various factors:

(i) The interaction of PAH with surfactant monomers,
(ii) The sorption of PAH on soil,
(iii) The sorption of surfactant on soil and its effect on increasing the wetability of soil, and
(iv) The partitioning of aqueous-phase PAH with the surfactant micelle.

The PAH considered here interact weakly with surfactant monomers, i.e. in the absence of soil there may be a factor of 2 to 3 solubility enhancement in PAH-saturated solution at $C_{\text{surf}} < C_{MC}$, with solubility increasing substantially in a linear fashion with surfactant concentration at $C_{\text{surf}} > C_{MC}$ (Edwards and Luthy, 1989; Kile and Chiou, 1989). The presence of soil results in sorption of surfactant with the result that $C_{MC_{\text{eff}}} >> C_{MC}$. It appears, based on the limited results shown here, that in the presence of soil the aqueous phase partitioning of PAR increases in a linear fashion with surfactant micelle concentration, i.e., surfactant-soil solubilization is proportional to $C_{\text{surf}} - C_{MC_{\text{eff}}}$. This relationship may be true provided that further surfactant sorption on soil is not significant as surfactant concentration is increased above $C_{MC_{\text{eff}}}$. Clearly, information is required on the sorption characteristics of surfactant on soil in order to more fully describe the surfactant solubilization process.

The slope of the solubilization relationship, $k_1$, is dependent in part on the partition coefficient, $K_M$, between aqueous-phase PAH and micelle:

$$K_M = \frac{[C_M]}{[M]} \frac{[C_{aq}]}{[C_{aq}]} \quad (6)$$

where $C_M$ is the concentration of PAH compound in the micellar phase, mol/l micelle; $C_{aq}$ is the concentration of PAH compound in the aqueous phase, mol/l water; and $[M]$ is the micelle concentration, mol/l water. The moles surfactant in the micellar phase per unit volume of liquid is:

$$N \frac{[M]}{[C_{aq}]} = C_{\text{surf}} - C_{MC_{eff}} \quad (7)$$

where $N$ is the aggregation number, i.e. the average number of surfactant molecules per micelle, and $C_{\text{surf}}$ and $C_{MC_{eff}}$ are expressed in mol/l water. Thus

$$K_M / N = C_M / ((C_{\text{surf}} - C_{MC_{eff}}) C_{aq}) \quad (8)$$

Almgren et al. (1979) have shown for clean water systems and two surfactants that $K_M / N$ is directly proportional to the boiling point of a PAH solute. Using their data, Jafvert (1989) has shown $K_M / N$ is directly proportional to PAH.
octanol-water partition coefficient, $K_{OW}$. Since the partitioning of PAH onto soil may be expressed by $K_{OC}$ which is also proportional to $K_{OW}$, the partitioning of PAH between surfactant micelle and soil may be formulated as (Jafvert, 1989):

$$\frac{S}{(C_{aq}f_{OC})} \propto K_{OW} \propto \frac{C_{M}}{[(C_{surf} - C_{MC eff}) C_{aq}]} \tag{9}$$

This indicates a linear relationship between $C_{M}/S$ and $C_{surf} - C_{MC eff}$. The relationship between $C_{aq}(s)$ and $C_{M}$ requires knowledge of the mass of surfactant in the micelle phase in the presence of soil. The approaches indicated by Equations (4) and (9) suggest a framework whereby additional information on the nature of the surfactant-soil interaction, and the sensitivity of the solubilization relationship to $f_{OC}$, may be incorporated in surfactant-specific correlations for various PAH solutes and soils.

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