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The Neutral Oil in Commercial Linear Alkylbenzenesulfonate and Its Effect on Organic Solute Solubility in Water

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■ Apparent water solubilities of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT), 2,4,5,2',5'-pentachlorobiphenyl (PCB), and 1,2,3-trichlorobenzene (TCB) were determined at room temperature in aqueous solutions of commercial linear alkylbenzenesulfonate (LAS), oil-free (solvent-extracted) LAS, and single-molecular 4-dodecylbenzenesulfonate. The extent of solute solubility enhancement by commercial LAS is markedly greater than that by other ionic surfactants below the measured critical micelle concentration (CMC); above the CMC, the enhancement data with LAS are comparable with other surfactants as micelles. The small amount of neutral oils in commercial LAS (1.7%), comprising linear alkylbenzenes (LABs) and bis(alkylphenyl) sulfones, contributes significantly to the enhanced solubility of DDT and PCB below the CMC; the effect is ascribed to formation of oil-surfactant emulsions. The oil-surfactant emulsion formed corresponds to ~9-10% of the commercial LAS below the CMC. The data suggest that discharge of wastewater containing a significant level of oils and surface-active agents could lead to potential mobilization of organic pollutants and LABs in aquatic environments.

Introduction

Linear alkylbenzenesulfonate (LAS) is currently the most widely used of the anionic surfactants in the detergent market that is formulated to replace the relatively persistent branched alkylbenzenesulfonates (ABS). LAS is prepared commercially as a heterogeneous surfactant by sulfonation of a (heterogeneous) linear alkylbenzene (LAB) feedstock. The product comprises a series of surface-active sulfonated hydrocarbons (having an average alkyl chain length of 12-13 carbons linked to the phenyl ring at the second to sixth chain carbon, with the alkyl substituent para to the sulfonate group) and a trace amount of unsulfonated neutral oils. The neutral oil consists of various linear alkylbenzenes (LABs) resulting from the incomplete sulfonation of the stock material and bis(alkylphenyl) sulfonates produced by the sulfonation process (1). A trace amount of tetralins has also been identified in the LAB mixture (2). In the sulfonation process, it is normal practice to maintain a certain level of free oils in the final product in order to control the quality; this oil content comprises between 1.0 and 2.2% of the active ingredient in commercial LAS (1). Although the sulfonated LAS components are relatively biodegradable (3) and are effectively removed from the wastewater into the sewage sludge under normal conditions of sewage treatment (4-6), the use of LAS or similar products by nations with inadequate sewage treatment facilities (or when the sewage load exceeds the design capacity) could conceivably result in discharge of relatively high levels of such surfactants into the environment. Moreover, sewage sludge has often been used for soil amendment, and this use has raised concern over the possible environmental impact of organic contaminants derived from the sludge (5, 7). In light of the molecular heterogeneity of commercial LAS, assessments of the behavior and effect of LAS would therefore call for investigations of the properties and activities of both the sulfonated components and

the neutral oil, since as a mixture the LAS behavior at different conditions may be influenced by either or both constituents.

In earlier studies, Hand and Williams (8) investigated the sorption characteristics of a number of single-component sodium alkylbenzenesulfonates as well as their mixtures that make up the major sulfonated constituents of the LAS; no data were given on the effect of neutral oils. The more stable LABs have been found to distribute widely in municipal wastes of southern California and nearby coastal sediments (9), in western Mediterranean sediments and fish tissues (10), and in wastewater, river water, and sediments of the Tokyo area (11). In their study of LAB pollution, Takada and Ishiwatari (11) concluded that the amount of LABs in detergents is sufficient to account for their levels in wastewater. In light of the relative persistence of LABs and the source from which they are derived, it is important to investigate the environmental effect of neutral oils in detergents as well as the process leading to the spread of LABs.

Earlier studies showed that surfactant aggregation to form micelles or surfactant-oil emulsions leads to marked solubility enhancement of relatively water insoluble organic solutes (12-14). Such an enhancement effect would increase the dispersion of organic contaminants and alter their distribution patterns in aquatic systems. In this context, we are interested in the individual and combined effects on solubility enhancement of the neutral oils and heterogeneous surface-active components in LAS as it provides a model to study the impact of a mixed oil-surfactant system (emulsion) relative to its component species on the contaminant behavior in aquatic environments. In this study, data have thus been presented for (i) the apparent solubility of solutes (*p,p'*-DDT, 2,4,5,2',5'-PCB, and 1,2,3-trichlorobenzene) in aqueous solution of commercial LAS below and above the nominal CMC, (ii) the apparent solute solubility below and above the CMC of oil-free LAS (following solvent extraction), and (iii) the apparent solute solubility in aqueous solution of single-molecular sodium 4-dodecylbenzenesulfonate. Comparison of solubility enhancements by LAS and oil-free LAS gives an explicit account of the effect of neutral oils on the solubility of these solutes in the oil-surfactant solution. The effect of the molecular heterogeneity of sulfonated components in LAS on solute solubility is then accounted for by comparing the data obtained with oil-free LAS and 4-dodecylbenzenesulfonate.

Experimental Section

LAS in sodium salt form was obtained from Aldrich Chemical Co., Inc., and Fluka Chemical Corp. These surfactants are supplied as a technical-grade powder with a purity (i.e., the active ingredient) of 80-85%; the balance of the material is composed primarily of nonsurface-active sodium sulfate. The surface-active sulfonated alkylbenzenes of the LAS contain alkyl chain lengths ranging from 10 to 14 carbons and have an average molecular weight of ~348. The approximate alkyl chain distribution in LAS according to the supplier is 5% C₁₀, 45-50% C₁₁, 35% C₁₂, 10-15% C₁₃, and <0.05% C₁₄. The residual

neutral oil, as part of the active ingredient, is composed of unsulfonated LABs and bis(alkylphenyl) sulfones. Sodium 4-dodecylbenzenesulfonate (4-DBS) was purchased as a custom-synthesized compound from Aldrich with a purity of 98+%.

Test solutes were *p,p'*-DDT (DDT), 1,2,3-trichlorobenzene (TCB), and 2,4,5,2',5'-PCB (PCB). DDT and TCB were obtained from Aldrich as reagent-grade chemicals with a purity of 99+%, and PCB (99+%) was obtained as an analytical standard from the Foxboro Co. They were used as received. *n*-Hexane (UV grade) and petroleum ether (high purity), used for extractions, were obtained from American Burdick and Jackson. Ethanol, used for neutral oil extraction from LAS, was obtained from USI Chemical Co. Deionized water used for preparing solutions was obtained from a Sybron/Barnstead Nanopure II water treatment system.

The weight percent of neutral (free) oil in LAS was determined by using the American Oil Chemists' Society (AOCS) official method Dd 4-60 (15, 16). This gravimetric analysis is based on a sequential petroleum ether extraction of an ethanol-water solution of LAS, followed by evaporation of the residual petroleum ether at 60–70 °C and a final short drying step near 100 °C. Because of the possibility of loss of volatile low molecular weight LAB components during the drying step, the AOCS procedure was modified so that a temperature of ≤ 40 °C was maintained during drying. The neutral oil in LAS obtained by this method was 1.7% (on a weight basis, corrected for purity of the LAS). The LAB components in the neutral oil were identified by gas chromatography/mass spectrometry and bis(alkylphenyl) sulfones were confirmed by infrared spectroscopy using diphenyl sulfone as the standard. The extracted neutral oil was a highly viscous and distinctly yellow liquid, which was only sparingly soluble in water. The oil-free LAS was recovered as a white powder from the extracted water-ethanol solution of the LAS by drying the solution under low (~ 50 °C) heat over a period of 3–4 days.

Surface tension was determined by the DuNouy method. A Fisher Model 20 surface tensiometer was used to measure the force (in dynes per centimeter) required to pull a platinum-iridium ring free from the surfaces of a series of surfactant solutions of known concentrations. Plotted values were taken from the average values of a series of stable readings in consecutive measurements, and the critical micelle concentration (CMC) was determined from the inflection point of a plot of the surface tension (in dynes per centimeter) vs the logarithm of the surfactant concentration.

Procedures for sample equilibration are essentially the same as earlier reported (12, 13). A series of aqueous solutions were prepared for each surfactant with concentrations ranging from far below the CMC to ~ 3 times the CMC; concentrations of LAS were corrected for purity as indicated by the supplier. Solutions were placed in 25-mL Corex centrifuge tubes with Teflon cap liners, and either DDT, TCB, or PCB was added to each tube in an amount slightly more than required to saturate the solution. Triplicate samples were prepared for each surfactant concentration; they were then equilibrated on a reciprocating shaker for ~ 48 h at 24 ± 1 °C. The samples were subsequently centrifuged at 5000 rpm (2987g) for 40 min to separate the undissolved solute. Solute particles adhering to the glass walls above the liquid level were carefully removed with a cotton swab; the meniscus was aspirated to remove any particles on the surface. This centrifugation/cleaning procedure was repeated twice

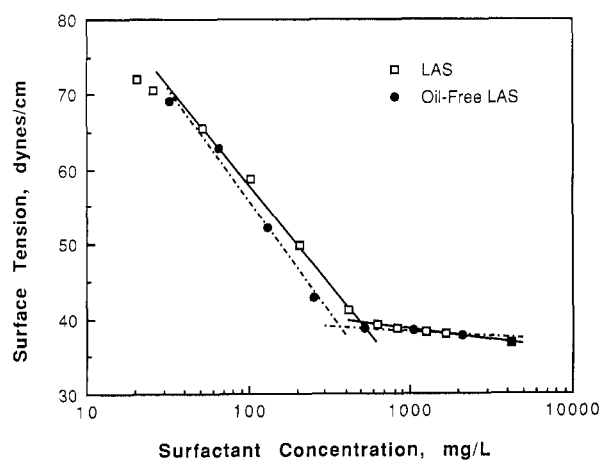


Figure 1. Plot of the surface tension vs the logarithm of surfactant concentration for LAS and oil-free LAS.

more. A measured sample of the supernatant was withdrawn and extracted in *n*-hexane and further dilutions were done in hexane as needed to bring the solute into a suitable concentration range. A pure water blank containing only the test solute was run (in triplicate) with each sample set as a check on analytical accuracy and to assure adequate equilibration.

Analysis of DDT and PCB was carried out by gas chromatography using a cross-linked methyl silicone (0.88- μ m film thickness) megabore capillary column (30 m \times 0.53 mm) with a 63 Ni electron capture detector. Analysis of TCB was done by gas chromatography using a cross-linked 5% phenyl methyl silicone (0.52- μ m film thickness) capillary column (25 m \times 0.32 mm) and a flame ionization detector.

Results and Discussion

To study the effect of a conventional surfactant on solute solubility, it is important to determine the nominal CMC of the surfactant since aggregation of surfactant molecules (i.e., formation of micelles) beyond the CMC causes a sharp change in the solvency of the surfactant (12–14, 17–20). The CMC is identified empirically as the concentration at which the plot of the surface tension of aqueous surfactant vs log surfactant concentration exhibits a pronounced break. While many commercial surfactants are highly surface active, they are often multicomponent mixtures, LAS being an example. When the surfactant contains a large amount of neutral oil, the “solution” may be emulsified over the entire concentration range and no visible CMC (i.e., monomer-micelle transition) will occur (13). Commercial LAS contains a small amount of neutral oil, and its solution exhibits a nominal CMC of ~ 500 mg/L as determined by the method described and shown in Figure 1. After removal of the neutral oil from LAS, the CMC for the resulting oil-free LAS is ~ 390 mg/L. This reduction suggests that a small quantity of oil-surfactant emulsion is formed in the original LAS solution, the amount being insufficient to fully suppress the monomer-micelle transition.

The apparent solubilities of DDT and PCB at room temperature (24 ± 1 °C) as a function of LAS concentration of the Aldrich sample in water are presented in Figures 2 and 3, respectively. The solubility data of DDT with Fluka LAS (data not shown) were found to be nearly identical with those with the Aldrich sample, and consequently all other studies were made with the Aldrich sample. Similar solubility enhancement data for TCB with LAS are shown in Figure 4. The apparent solubilities of

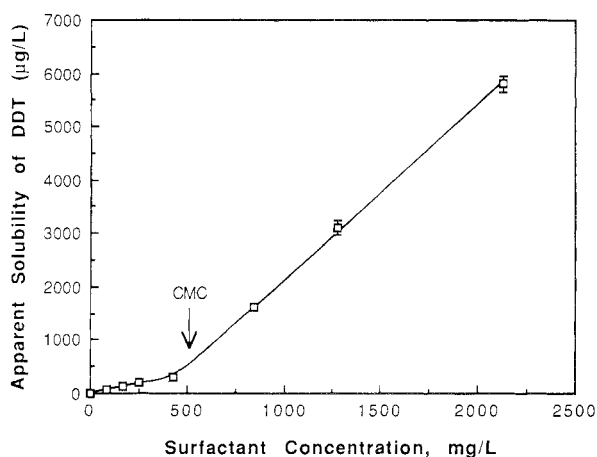


Figure 2. Apparent DDT solubility in aqueous solutions of LAS.

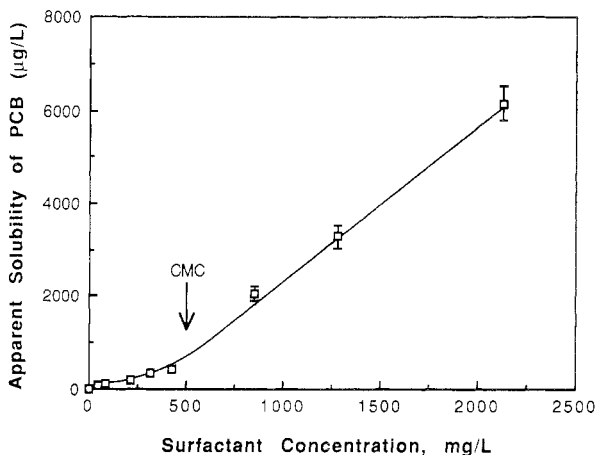


Figure 3. Apparent 2,4,5,2',5'-PCB solubility in aqueous solutions of LAS.

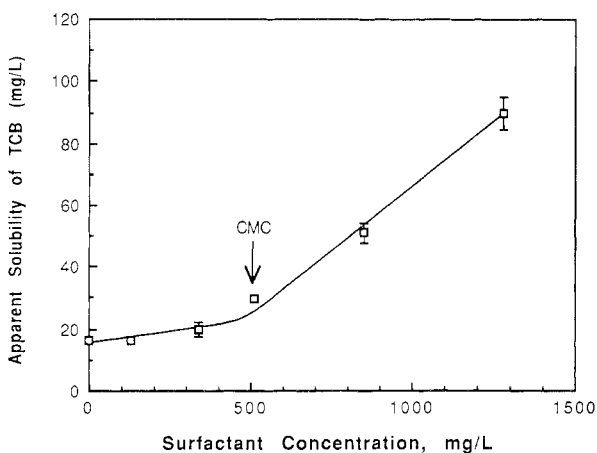


Figure 4. Apparent 1,2,3-trichlorobenzene solubility in aqueous solutions of LAS.

DDT and PCB in aqueous solution of oil-free LAS are shown in Figure 5. Lastly, the solubility of DDT in aqueous solution of sodium 4-dodecylbenzenesulfonate (4-DBS) and that of DDT and PCB in the solutions of LAS and oil-free LAS at below-CMC concentrations are shown in expanded scale in Figure 6. The intrinsic water solubilities of DDT, PCB, and TCB at 25 °C are 5.5 µg/L, 11 µg/L, and 18 mg/L, respectively; they are used for subsequent data analyses. The effect of a trace quantity of sodium sulfate in the LAS solution on organic solute solubility is ignored, as its influence on ionic strength would be practically insignificant.

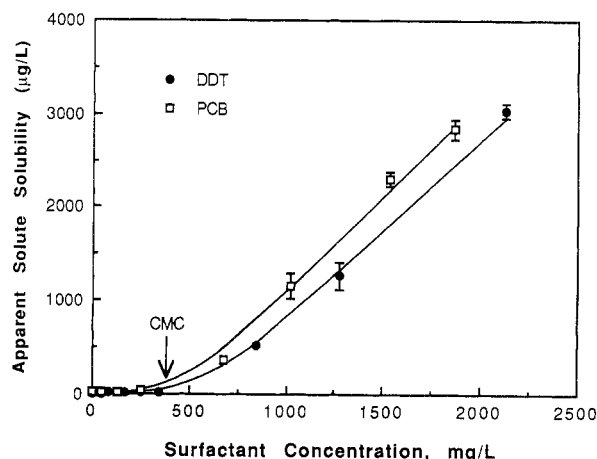


Figure 5. Apparent DDT and 2,4,5,2',5'-PCB solubilities in aqueous solutions of oil-free LAS.

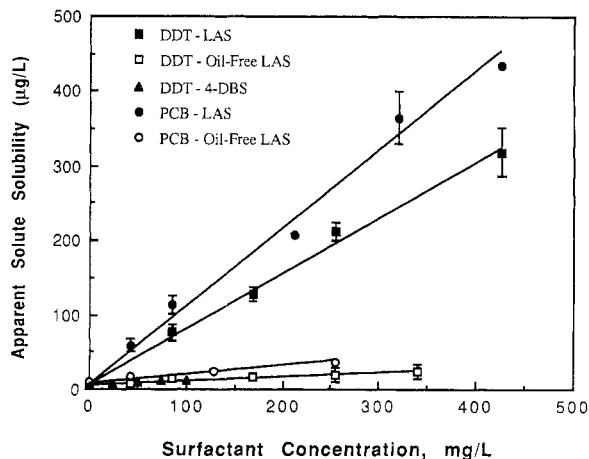


Figure 6. Apparent DDT and 2,4,5,2',5'-PCB solubilities in dilute aqueous solutions of LAS, oil-free LAS, and 4-DBS.

The results indicate that the apparent solubilities of highly insoluble DDT and PCB are extremely sensitive to LAS concentration, especially above the (nominal) CMC of the surfactant (i.e., where micelles are formed). The TCB data show only a small solubility enhancement below the CMC of LAS, which is attributed to the much greater water solubility of the solute that makes it less sensitive to dilute surfactant concentrations, as noted previously (12, 13). Whereas the strong enhancement effect by surfactants above the CMC is not surprising, the effect of LAS below the CMC on DDT and PCB solubilities (Figure 6), which shows solubility increments of ~0.75 µg/L for DDT and 1.1 µg/L for PCB per mg/L LAS, is much more pronounced than noted for other ionic surfactants (discussed later). The below-CMC LAS effect is ~2–15 times greater than that exhibited by some aquatic humic and fulvic acids (21, 22).

For surfactants consisting of molecularly homogeneous species, the solute solubility enhancements can be accounted for by partition interactions of solute with monomers and micelles of the surfactant. Below the CMC surfactants exist as monomeric species and above the CMC the concentration of monomers stays essentially constant at its CMC value, with the micelle concentration being the difference between the total concentration and the CMC. The respective partition coefficients of a solute with a mixture of surfactant monomers and micelles may be calculated from a plot of the apparent solubility vs surfactant concentration (12), which should yield two distinct slopes according to eq 1, where S_w^* is the apparent solu-

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc} \quad (1)$$

bility of the solute at the total stoichiometric surfactant concentration of X , S_w is the water solubility in "pure water", X_{mn} is the concentration of the surfactant as monomers, and X_{mc} is the concentration of the surfactant in micelle form with $X_{mc} = X - \text{CMC}$. The K_{mn} term refers to the solute partition coefficient between monomers and water and the K_{mc} term to the corresponding partition coefficient between micelles and water. For such micelle-forming surfactants, the K_{mc} is found to be much greater in magnitude than K_{mn} because of the much larger micellar environment relative to the monomer for solute partition interactions.

The data in Figures 2–5 are consistent with the idea that micelles are formed above the CMC in the solution of LAS; two relatively distinct slopes are noted for the test solutes far above and below the nominal CMCs of these surfactants. However, the magnitude of DDT solubility enhancement below the nominal CMC of untreated LAS (Figure 6) is more than 100 times that of DDT with relatively (molecularly) homogeneous anionic sodium dodecyl sulfate (SDS) and ~30 times that with cationic cetyltrimethylammonium bromide (CTAB) (12). On the other hand, the enhancement data of DDT and TCB above the CMC of untreated LAS are comparable to the above-CMC results with SDS and CTAB. The difference in below-CMC enhancement between LAS and SDS and CTAB is striking. It suggests that some components other than sulfonated hydrocarbons in LAS contribute to the observed effect. Since LAS is heterogeneous in its surface-active components and contains neutral oils, it is of interest to investigate which factor is primarily responsible for the observed solute solubility enhancement below the CMC. A logical approach for evaluating the effect of neutral oils in LAS is to compare the solubility enhancement of untreated LAS and of oil-free LAS. The effect of molecular heterogeneity can then be assessed by comparing the solute solubilities in solutions of the oil-free LAS and of single-molecular 4-DBS. The requisite data are in Figures 5 and 6.

Removal of neutral oils from LAS results in ~10-fold reduction in the apparent solubility of DDT and PCB below the nominal CMC of the surfactant (Figure 6), but has relatively minor effect above the CMC (Figures 2, 3, and 5). That the oil content has minor effect above the CMC can be explained on the basis that the micelles themselves behave as a separate microscopic phase for solute partitioning. Consequently, the incorporation of a small amount of neutral oils to the micelles (or the coexistence of oil-surfactant emulsions with micelles) would not be expected to have a major impact on the solvency of the micelle (12, 13). The small difference in solubility enhancement of DDT between 4-DBS and oil-free LAS systems (Figure 6) shows that the effect of the molecular heterogeneity in LAS is relatively small and therefore that it is the neutral oil that is responsible for the large differences in solubility enhancement below the CMC. Note here that the DDT solubility enhancement with pure 4-DBS is measured over a very low concentration range because 4-DBS has a low solubility and does not exhibit a monomer-micelle transition due to its high Krafft point (4-DBS is therefore not a good practical surfactant). The small heterogeneity effect with LAS is consistent with the relatively linear solubility enhancement below the CMC; for a highly molecular heterogeneous surfactant, such as Triton X-405 (an octylphenol polyethoxylate), the successive micellization of monomers of widely different solubilities results in an exponential rise of the solubility

data below the nominal CMC (12).

We now consider whether the effect of neutral oil on solubility enhancement below the CMC can be effectively accounted for by solute partition into the oil. The neutral oil content extracted from LAS is ~1.7% by weight according to the analytical method described. If one were to assume that this neutral oil, as a mixture of LASs and bis(alkylphenyl) sulfones, possesses the same solvency as a good solvent such as octanol, one would find this amount of neutral oil to be inadequate by itself to account for the observed solute solubility enhancement. In such an oil-surfactant system, the enhancement effect may be more logically related to and explained by solute solubility in an oil-surfactant emulsion that is formed below the CMC and that corresponds to a much greater LAS aggregation mass (and thus greater solubility enhancement) than the neutral oil alone. A good example of the oil-surfactant emulsion formation giving rise to a bulklike solvency may be found in the commercial petroleum sulfonates, which consist of sulfonated hydrocarbons and free mineral oils, with the oil content ranging from 20 to 35% by weight (13). In the case of LAS, however, the small amount of neutral oils would not be sufficient to emulsify all the sulfonated hydrocarbons; consequently, the solution of LAS below the CMC should be a mixture of sulfonated hydrocarbon monomers and oil-surfactant emulsions, with the latter being the minor component. This assumed composition is in keeping with the fact that a nominal CMC exists in LAS solution, the CMC of the oil-containing LAS (500 mg/L) is slightly greater than that of the oil-free LAS (390 mg/L), and the plot of surface tension vs log surfactant concentration gives a somewhat sharper break at the CMC after the neutral oil is removed from the LAS.

The amount of the oil-surfactant emulsion below the CMC of LAS may be estimated by relating the observed apparent solubility of DDT to the concentration of emulsion and the concentration of the sulfonated monomers below the CMC as

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{em}K_{em} \quad (2)$$

with

$$X = X_{mn} + X_{em} \quad (3)$$

where X_{em} is the concentration of oil-surfactant emulsion and K_{em} is the solute partition coefficient between the emulsion phase and water. In this analysis, the K_{mn} value is taken as that of the oil-free LAS below the CMC; the corresponding K_{em} value is assumed to approximate that of the solute with the emulsion formed in the solution of Pyronate 40, a surfactant comprising ~20% aliphatic oil in alkyl-aryl sulfonated hydrocarbons (13) and giving about the same average molecular weight as the LAS. Table I gives a list of calculated K_{mn} , K_{mc} , and K_{em} values for the selected solutes with LAS, oil-free LAS, and other surfactants from this and earlier studies.

By use of $\log K_{mn} = 4.08$ for DDT with the oil-free LAS and $\log K_{em} = 6.14$ for DDT with the emulsion formed by Pyronate 40 (13), the calculated X_{em} is ~9–10% of the LAS concentration below the CMC. According to this calculation, the enhancement effect below the CMC of LAS is controlled predominantly by the $X_{em}K_{em}$ term in eq 2. The increased mass of oil-surfactant emulsions over the oil content and the much greater solute partition efficiency with emulsions than with monomers indicate that association of sulfonated components with neutral oil in forming emulsions reinforces the solvency of the sulfonated components below the CMC. The PCB solubility data with LAS and oil-free LAS may be similarly explained, although a quantitative account of the data requires an

Table I. Partition Coefficients of Solutes with Monomers (K_{mn}), Micelles (K_{mc}), and Emulsions (K_{em}) Formed by LAS and Other Ionic Surfactants

surfactant	1,2,3-TCB ^c	<i>p,p'</i> -DDT	2,4,5,2',5'-PCB ^c
	log K_{mn}		
SDS ^a	ND	2.68	NA
CTAB ^a	ND	3.54	NA
LAS (oil-free)	NA	4.08	3.98
4-DBS	NA	4.18	NA
	log K_{mc}		
SDS ^a	3.54	5.38	NA
CTAB ^a	3.80	5.88	NA
LAS	3.69	5.76	5.48
LAS (oil-free)	NA	5.54	5.32
	log K_{em}		
Petronate L ^b	3.94	6.32	NA
Petronate HL ^b	3.94	6.32	NA
Pyronate 40 ^b	3.77	6.14	NA

^aData from Kile and Chiou (12). ^bData from Kile et al. (13).
^cND, not detectable; NA, not available.

experimental K_{em} that is not available. When the same calculation is applied to the data of TCB (Figure 4), with log $K_{em} = 3.77$ as obtained with Pyronate 40 (13), the predicted S_w^*/S_w is ~ 1.3 at $X = \text{CMC}$ of the LAS, which is in reasonable agreement with the experimental $S_w^*/S_w = 1.4$. The estimated oil-surfactant content (9–10%) vs the neutral oil content (1.7%) of LAS is in reasonable agreement with the free-oil content in Pyronate 40 ($\sim 20\%$), which causes a complete emulsion of the product in water, i.e., the oil-surfactant emulsion is ~ 5 times the amount of free oils.

By reference to the observed solute solubility enhancement by oil-surfactant emulsions in LAS, one may expect formation of similar emulsions following the discharge of large quantities of various surfactant species and oil components in aquatic systems to play an important role in the mobility of highly insoluble organic contaminants. The formation of oil-surfactant emulsions could also become an important pathway for the transport of relatively water insoluble oil components (such as LABs) in aquatic environments, since without the stabilization through emulsion formation these oil components would be more readily attenuated by sorption to sediments. While the foregoing data illustrate the efficiency of low levels of oil-surfactant emulsions in enhancing the apparent solubility of relatively insoluble organic contaminants, the application of such surfactants as LAS may also be expected to improve the economic use of surfactants for in situ treatment of subsoils and aquifers contaminated with hazardous organic chemicals (23–25). The physical basis that leads to enhanced solubilization of organic contaminants is thus important in assessing both the contaminant mobility in water receiving such oil-containing surfactants and the engineering design for improving the in situ treatment of contaminated soils and aquifers.

From the standpoint of minimizing the environmental transport of organic contaminants, it is important that the level of both sulfonated agents and neutral oils in LAS and other surfactants in wastewater be reduced before discharge. Studies of Brunner et al. (5) and Rapaport and Eckhoff (6) indicated that the sewage treatment currently in operation in Switzerland, the United States, Canada, and Germany effectively reduces LAS to less than ppm levels. While no data are given on influent and effluent levels of neutral oils in the sewage, the oil content after the treatment process is likely low. At this time no sufficient data are available for the level of other surfactants

in sewage effluents. If one assumes that concentrations for all other surfactants are comparable in magnitude with that of LAS, it is then probably safe to assume that the effluent levels of surfactants and oil components after sewage treatment would not contribute significantly to the enhanced mobility of organic contaminants in aquatic environments, based on the enhancement data of oil-surfactant emulsions from this study. The circumstance of much concern is where large amounts of surfactants are being discharged and no adequate facilities are available for wastewater treatment, a case more likely to be found in some developing countries.

The benefit in the use of sewage sludge containing LAS and other surfactants as soil amendment may be subject to reevaluation of its potential impact on the mobility of organic pollutants under certain conditions. The amount of LAS in sludge has been reported to be as high as 5 g/kg (4, 5, 7) and the annual input of LAS from sludge to surface soils in Switzerland is estimated to be $\sim 1 \text{ g/m}^2$, the total loading for all surfactants being much greater (5). Currently no data are available to show whether sludge-amended soils could lead to formation of oil-surfactant emulsions. The enhancement data for oil-surfactant emulsions from this and previous studies (13) may be coupled with field emulsion concentrations, when such emulsions occur, for conducting a priori assessments of the enhanced transport of organic contaminants in surface and groundwater systems.

Acknowledgments

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Registry No. DDT, 50-29-3; 2,4,5,2',5'-PCB, 37680-73-2; 1,2,3-TCB, 87-61-6; 4-DBS, 2211-98-5.

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Laboratory Studies of Surfactant-Enhanced Washing of Polychlorinated Biphenyl from Sandy Material

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■ To assess the suitability of an alcohol ethoxylate surfactant for washing contaminants from soils, the sorption of the surfactant by a sandy soil was studied and the extent of washing of polychlorinated biphenyls (PCBs) from the soil was evaluated. The surfactant adsorption is described by an S-shaped isotherm, consistent with a Langmuir-type monomolecular adsorption followed by adsorption of the surfactant micelles. After only 10 washings with water, the surfactant concentration in the effluent samples decreased from as high as 10 000 mg/L to less than 60 mg/L. PCBs could be effectively washed from the sand by using surfactant solutions. After 20 washings about 66, 86, and 56% of the PCBs were washed from the columns by 5000, 10 000, and 20 000 mg/L surfactant solutions, respectively. This is equivalent to a reduction in PCBs from 1728 mg/kg to about 614, 251, and 769 mg/kg, respectively. The mechanisms responsible for the PCB removal from the sand are presented and discussed.

Introduction

Great effort and expense are currently required for disposal of wastes containing polychlorinated biphenyls (PCBs); a primary source is PCB-laden oil used in transformers and capacitors because of its excellent dielectric and fire-resistant properties. This oil has in some cases contaminated soil and groundwater with PCBs. PCBs are found as mixtures of chlorinated biphenyls having varying degrees of chlorination and are suspect carcinogens. Their use in most industrial applications has been banned since 1979 (1). Because of the strongly hydrophobic nature of PCBs and their very low water solubility, PCBs migrate through soils very slowly; dissolved in water, their rate of migration could be less than a few centimeters per year (2, 3). However, these same properties that limit the spread of PCBs also limit the extent of water washing of PCBs from contaminated soil. Technologies being used to clean up PCB-contaminated soils are costly and include excavation and disposal in a hazardous waste facility or excavation and incineration. More cost-effective methods are needed to clean up sites that are contaminated with PCBs. The feasibility of enhanced washing of PCBs from soils by an aqueous surfactant solution was assessed in this laboratory study.

Previous laboratory studies have shown that aqueous solutions of commercially available surfactants washed

PCBs, petroleum products, and other organic compounds from sandy geologic material (4, 5). However, several potential problems were identified concerning the use of aqueous surfactant solutions to clean contaminated soil in situ. The surfactant itself should be environmentally safe, in that it should not be toxic or hazardous, and it should be easily removed from the subsurface by anthropogenic or natural processes. Further, because of the surface-active properties of surfactants, they could disperse soil-clay particles; this could lead to clogging of the soil pore space and to the diversion of the surfactant solution from the contaminated zone. Therefore, it is expected that in situ surfactant washing could present difficulties in applying, containing, and recovering the surfactant(s).

In a recent study, the effectiveness of each of 10 surfactants in washing an oil from a sandy aquifer material was evaluated (6). The surfactants included at least one example from each of four main groups of commercial surfactants: (1) ethoxylated alcohols (nonionic), (2) ethoxylated nonylphenols (nonionic), (3) sulfates (anionic), and (4) sulfonates (anionic). From that study, a group of alcohol ethoxylate surfactants was judged to be promising for the in situ washing of petroleum products from hydrogeologic systems, because among the 10 surfactants studied the ethoxylate surfactants caused minimum dispersion of soil colloids, they showed high solubilization and dispersion of the low water solubility oil, they have low critical micelle concentrations, and they washed more than 80% of the oil from sandy material in batch washing studies. This study was carried out to evaluate the effectiveness of one of the previously selected alcohol ethoxylate surfactants to enhance the washing of Aroclor 1248 from a sandy soil.

The specific objectives of this laboratory study were (1) to determine the adsorption of an alcohol ethoxylate surfactant on a sandy soil and the extent to which the adsorbed surfactant could be washed from the soil with water and (2) to evaluate the extent to which aqueous solutions of the surfactant could wash Aroclor 1248 (hereafter referred to as PCBs) from the soil.

Materials and Methods

Materials. The sandy material used in this study was from the water table region (~6.5 ft deep) of a shallow