

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Soil Clean Up by in-situ Surfactant Flushing. III. Laboratory Results

O. Keith Gannon^a; Peter Bibring^a; Kevin Raney^a; J. Anthony Ward^a; David J. Wilson^a; Julie L. Underwood^b; Kenneth A. Debelak^b

^a DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY NASHVILLE, TENNESSEE ^b

DEPARTMENT OF CHEMICAL ENGINEERING, VANDERBILT UNIVERSITY NASHVILLE, TENNESSEE

To cite this Article Gannon, O. Keith , Bibring, Peter , Raney, Kevin , Ward, J. Anthony , Wilson, David J. , Underwood, Julie L. and Debelak, Kenneth A.(1989) 'Soil Clean Up by in-situ Surfactant Flushing. III. Laboratory Results', Separation Science and Technology, 24: 14, 1073 – 1094

To link to this Article: DOI: 10.1080/01496398908049891

URL: <http://dx.doi.org/10.1080/01496398908049891>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Soil Clean Up by *in-situ* Surfactant Flushing. III. Laboratory Results

**O. KEITH GANNON, PETER BIBRING, KEVIN RANEY,
J. ANTHONY WARD, and DAVID J. WILSON***

DEPARTMENT OF CHEMISTRY

JULIE L. UNDERWOOD and KENNETH A. DEBELAK

DEPARTMENT OF CHEMICAL ENGINEERING

VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Data on the solubilization of *p*-dichlorobenzene (DCB), naphthalene, and biphenyl in aqueous solutions of sodium dodecylsulfate (SDS) (0-100 mM concentration) indicate increases in effective solubilities of these hydrophobic compounds by factors of roughly 20 to 100. DCB is effectively removed from spiked clay-sand mixtures by leaching with SDS solutions in laboratory columns. Surfactant solutions loaded with DCB are satisfactorily treated by gentle extraction with hexane, and the recovered surfactant solution satisfactorily solubilizes biphenyl. A simple model for predicting the solubilization behavior of surfactants is developed and tested experimentally.

INTRODUCTION

A major problem in the remediation of hazardous waste sites is the removal of hydrophobic organics from the vadose zone and the zone of

*To whom correspondence should be addressed. Senior research associate, AWARE, Inc.

saturation. If these contaminants are volatile and are present in the vadose zone, *in-situ* soil vapor stripping provides an efficient, cost-effective method; this technique cannot be used, however, for nonvolatile materials such as PCBs, nor can it be used for dense nonaqueous phase liquids (DNAPLs) such as trichloroethylene in the zone of saturation. For such situations, *in-situ* surfactant flushing may provide an effective approach. *In-situ* techniques have been reviewed by Clarke and Mutch (1) and by Ghassemi (2).

Ellis, Payne, and McNabb (3) described the use of aqueous solutions of nonionic surfactants for flushing PCBs, petroleum hydrocarbons, and chlorinated phenols from soils. These workers found removal efficiencies of over 90% with 1.5% surfactant solutions; these efficiencies were orders of magnitude greater than those which could be obtained by flushing with water alone.

These workers also carried out treatability studies of the aqueous surfactant-contaminant solutions resulting from surfactant flushing, and noted that a serious problem arose here. It was possible to remove the surfactant and the contaminant from the water, but they were unable to find a process which would allow recovery of the surfactant for reuse. Reuse of the surfactant is essential for cost-effective application of the technique, and they suggested that future work be directed toward the problem of developing a surfactant flushing scheme that permitted recovery of the surfactant. They found that hydrolysis of the surfactant is effective as a treatment technique for removing both surfactant and hydrophobic organics from the leachate waters, but this destroys the surfactant, making recycling out of the question. Foam fractionation of these relatively concentrated surfactant solutions was not feasible, in that the bulk of the water being treated was removed in the foam. Adsorption techniques (activated carbon, clays, etc.) were also not feasible, again because of the high concentrations of surfactant present in the leachates. Ellis and his coworkers suggested that their limited testing indicated that ultrafiltration was a possibility. They regarded the development of a scheme in which the surfactant solution could be separated from the contaminants and recycled as a crucial next step in the development of the surfactant flushing technique.

Nash (4) carried out a small-scale field test of surfactant flushing at Volk Air National Guard Base, Wisconsin. Soil which was heavily contaminated with oil and other hydrocarbons at a fire pit used for training purposes was treated both in lab columns and *in situ* in the fire pit. Nash's laboratory studies were very encouraging, with extensive removal after the passage of 12 pore volumes of surfactant solution through the contaminated soil. The results of the *in-situ* study were not

encouraging, however; several of the holes clogged during the course of the work, and the results were complicated by a heavy rain which may have washed material into the holes. We feel that Nash's field test demonstrates that surfactant flushing will not work if the surfactant solution cannot penetrate the soil to be treated, and note that the soils in the field test contained in the range of 1,000 to 13,500 mg/kg of oil and grease.

The effectiveness of surfactant flushing in removing contaminants from soil and aquifers is closely related to the ability of these substances to solubilize water-insoluble compounds. Surfactant molecules or ions have a hydrophobic portion (often a long hydrocarbon chain) and a hydrophilic portion (an ionic or polar head, or a polyethoxyethylene chain). These species therefore tend to concentrate at polar-nonpolar interfaces (such as air-water), and, at sufficiently high concentrations, form aggregates (micelles) in aqueous solutions such that the polar or ionic portions of the molecules are presented to the aqueous phase, while the nonpolar hydrocarbon tails of the molecules are clustered together away from contact with the water molecules. The interior of a micelle, consisting of the hydrocarbon tails of the surfactant species, is a nonpolar phase, and may therefore dissolve substantial quantities of nonpolar solutes which are virtually insoluble in normal aqueous solutions. This phenomenon is known as solubilization; by means of solubilization the amount of a hydrophobic solute which can be "dissolved" in water can be increased manyfold. The amount of solubilizate which is solubilized is approximately a linear function of the surfactant concentration, provided that this is above the critical micelle concentration (cmc, the surfactant concentration at which micelles first start to form). Below the cmc, solubilization does not occur, although the presence of a hydrophobic solute may reduce the cmc of a surfactant in solution substantially.

We felt that the results obtained by Ellis et al. (3) made a very strong case for pursuing the surfactant flushing technique further, to see if the critical problem of treatability of the leachate and recycling of the surfactant could be overcome. These workers used nonionic surfactants because of their quite low cmc values, but this essentially rules out one potentially promising treatment technique, solvent extraction. Those solvents which would be effective in extracting the hydrophobic contaminants would also almost certainly be at least fairly effective in extracting the nonionic surfactants. We believed that the comparatively low cmc's of nonionic surfactants as compared to ionic surfactants was an advantage which might well be outweighed by the extremely low solubilities of many ionic surfactants in nonpolar solvents, which would make treatment by solvent extraction a possibility. In earlier papers we

developed mathematical models for surfactant flushing in laboratory columns and in the field by means of injection and recovery wells (5), and we also investigated a model for the solubilization process which is so crucial to surfactant flushing (6).

In the following sections we describe the results of some laboratory studies we have made on the feasibility of using an anionic surfactant, sodium dodecylsulfate (SDS), for surfactant flushing. First we report solubilization data on *p*-dichlorobenzene (DCB), naphthalene, and biphenyl in SDS solutions ranging in concentration from 0 to 100 mM. We then describe the results of some surfactant flushing experiments on clay-sand mixtures spiked with DCB. Third, we examine data on the gentle solvent extraction into hexane of DCB solubilized in SDS solutions. The paper closes with a discussion of a simple theory for predicting the effectiveness of a given surfactant in solubilizing any particular hydrophobic contaminant; this theory is checked against our data on the solubilization of DCB, naphthalene, and biphenyl in SDS solutions.

EXPERIMENTAL WORK

Our experimental work has been carried out with three hydrophobic organic compounds as models for contaminants such as benzene, toluene, PCBs, and chlorinated solvents; the model compounds used are DCB, naphthalene, and biphenyl. The surfactant used, SDS, was selected because it is cheap, nontoxic, and anionic. (One expects that anionic surfactants would tend to sorb much less on clays, etc. than cationic surfactants, since the sorption sites on clay minerals are generally themselves anionic.) We used SDS from Fluka; its purity was reported to be 99+. High purity material is necessary if one is to avoid interferences with the UV spectrophotometric methods of analysis for the aromatic contaminants which we used.

Solubilization Experiments

The first experiments were designed to ascertain the ability of SDS to solubilize the model compounds. Surfactant solutions having concentrations in the range 0 to 100 mM (2.8%) were prepared, and excess solid DCB, naphthalene, or biphenyl was added to 500 mL of the surfactant solution. The solution was then magnetically stirred overnight to permit

the model compound to equilibrate with the surfactant solution, and then allowed to settle for several hours. Portions of the resulting solutions were then taken for analysis by ultraviolet spectrophotometry. (All of the model compounds show strong absorption in the 200–300 nm range; SDS and water do not absorb in this range.) Solutions containing surfactant concentrations above about 8 mM required dilution with SDS solution before they could be analyzed. It was found that increases in effective solubility (true solubility plus solubilization in micelles) by factors of 20–100 were achieved at the higher surfactant concentrations, and that the effective solubility was in all cases essentially a linear function of the surfactant concentration above the cmc. These results indicate that micelles of ionic surfactants can greatly increase the solubilities of these hydrophobic organic compounds. Data for DCB, naphthalene, and biphenyl at room temperature (25°C) are shown in Figs. 1, 2, and 3, respectively. The data points designated by squares in Fig. 2 pertain to solutions which were 0.1 M in NaCl; the presence of inert salts is well known to decrease the cmcs of ionic surfactants, and this effect results in a shift of the solubilization curve to the left.

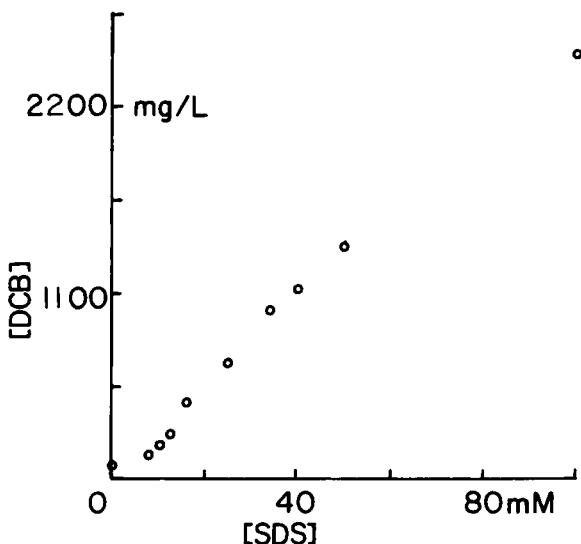


FIG. 1. DCB concentration (mg/L) as a function of SDS concentration (mM).

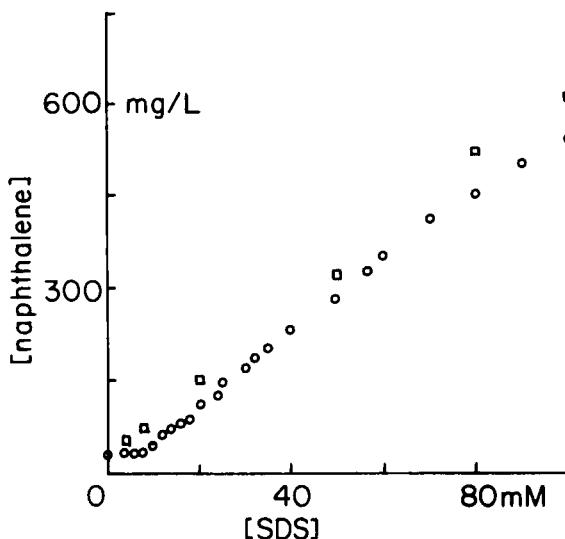


FIG. 2. Naphthalene concentration (mg/L) as a function of SDS concentration (mM) (circles). Squares represent runs in which 0.1 M NaCl was present.

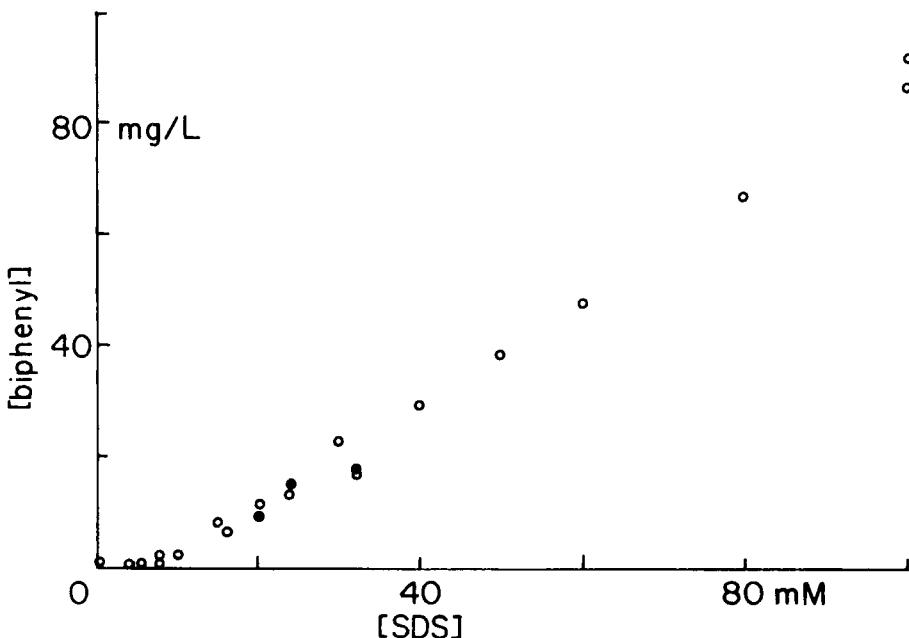


FIG. 3. Biphenyl concentration (mg/L) as a function of SDS concentration (mM). Solid circles represent runs with recycled SDS solution.

Surfactant Flushing Experiments

The ability of these surfactant solutions to extract the model compounds from aquifer material was next investigated. Soil samples for soil extraction runs were prepared by thoroughly mixing finely ground soil (mostly clay) with an appropriate amount of washed sea sand. Soil extraction runs were made using 250 g samples of soil, sand (washed fine sea sand), or soil/sand mixtures which had been spiked with the contaminant. Spiking was done by dissolving 1 g DCB, naphthalene, or biphenyl in approximately 20 mL hexane. This solution was then added slowly, with vigorous shaking, to the soil sample. The mixture was then vigorously shaken for an additional couple of minutes; then it was placed in a hood and the hexane allowed to evaporate. The mixture was agitated several times during this process, which usually required about 30 min. A few preliminary experiments were made in which the spiked sample was flushed in a Buchner funnel; this did not permit control of the flow rate of surfactant solution solution, so the following procedure was used for most of this work. The spiked sample was placed in a Pyrex laboratory leaching column (see Fig. 4) which already contained approximately 250 g sand (a thickness of about 10 cm). The underlying sand layer served to

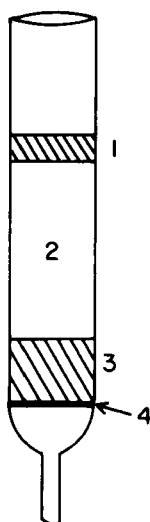


FIG. 4. Diagram of a laboratory soil surfactant flushing column. 1: 50 g sand layer. 2: Spiked soil or soil/sand sample. 3: 250 g sand filter layer. 4: Coarse fritted glass filter.

filter particulates from the effluent SDS solution. After the spiked soil sample was placed in the column, another 50 g portion of sand was added to prevent soil from the soil/sand samples from becoming suspended in the overlying surfactant solution. SDS solution (100 mM) was then added to the column until the level of the liquid was about 1 cm above the top of the sand, and the column was allowed to stand for 24 h to permit trapped bubbles to escape. SDS solution (1.5 L) was then added to the column and allowed to flow through the soil sample at the desired rate. Samples of effluent (20 mL) were collected at 100 mL intervals and analyzed by UV absorption. Centrifugation was required with some effluent samples in order to remove suspended particulates which interfered with spectrophotometric analysis.

Preliminary extraction runs were made with DCB, naphthalene, or biphenyl in which these compounds were removed from sand. The results are shown in Figs. 5 and 6, and indicate that the model compounds are readily solubilized from sand.

In the course of this work it was found that only a fraction of the spike was recovered in the surfactant eluate. We suspected that significant amounts of the contaminant compounds were being volatilized during the evaporation of the hexane solvent used in the spiking process, as the

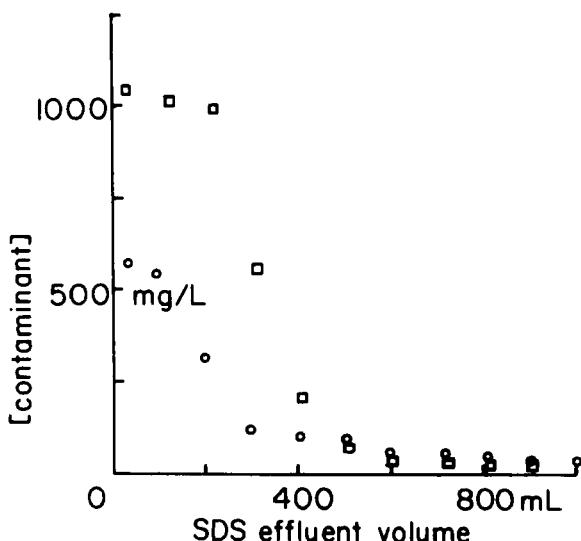


FIG. 5. Effluent naphthalene (circles) and DCB (squares) concentrations as functions of the volume of SDS (100 mM) passed through spiked sea sand in extraction columns.

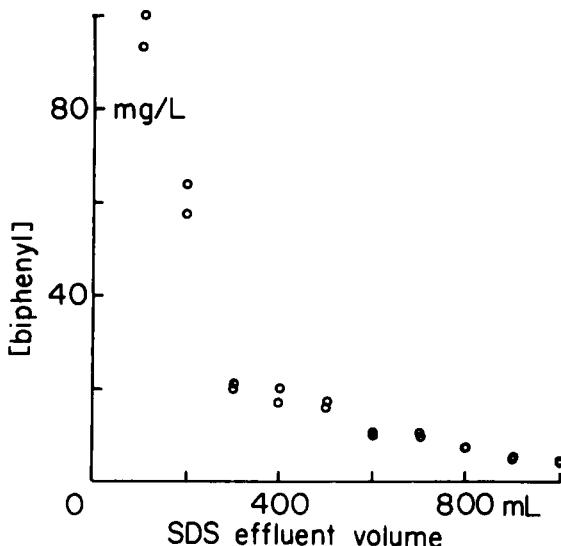


FIG. 6. Effluent biphenyl concentration as a function of the volume of SDS (100 mM) passed through spiked sea sand in an extraction column.

characteristic odors of DCB, naphthalene, and biphenyl were very marked during this step. This point was investigated as follows. Soil samples of 250 g (sand, 1:5 grey clay:sand, and 1:3 red clay:sand) were spiked with DCB in the usual way. These were then flushed in columns, as described above, with 1 L of 100 mM SDS, and samples were collected for UV analysis. The thoroughly drained soil samples were then extracted in a Soxhlet extractor for 6-12 h with hexane or methanol, and the solvent extract was analyzed for DCB. The results of these experiments are shown in Table 1, and they indicate that approximately two-thirds of

TABLE 1
Soil Column Mass Balance of DCB^a

Column composition	DCB removed by SDS flush (g)	DCB removed by extraction (g)	Total DCB removed (g)
Sand	0.356	0.005	0.361
Grey clay/sand, 1:5	0.195	0.100	0.295
Red clay/sand, 1:3	0.321	0.005 ^b	0.326

^a1 g DCB was added to each soil sample initially.

^bThis column was flushed with methanol rather than hexane.

the initial 1 g DCB spike is lost during the evaporation of the hexane solvent. In the flushing experiments reported below, we have therefore assumed that 70% of the initial DCB spikes have been lost due to volatilization and have taken 0.3 g as the initial DCB sample size in all calculations.

Two separate series of column flushing runs were made, one with a red (ferruginous) clay and the other with a grey clay, both common in the Nashville, Tennessee, area. We found that flow rates through clay:sand mixtures having a clay:sand ratio larger than 1:3 were too slow to permit convenient measurement. Data are presented for the elution of DCB from 1:5 and 1:4 red clay:sand mixtures with 100 mM SDS in Fig. 7; similar plots for 1:5 and 1:4 grey clay:sand mixtures are shown in Fig. 8. The fraction of DCB removed is plotted against the volume of SDS solution which has passed through the column. The results of these and other runs did not show any significant difference between the behaviors of the two clays.

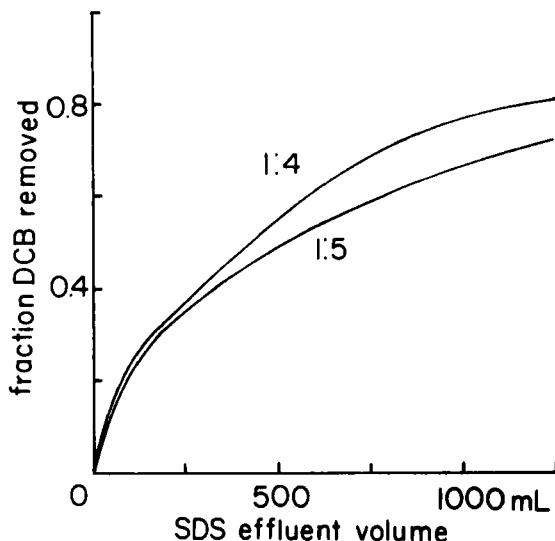


FIG. 7. Removal efficiencies of 0.3 g samples of DCB versus the volume of 100 mM SDS passed through the column. Soil samples were red clay:sand in the proportions 1:4 and 1:5.

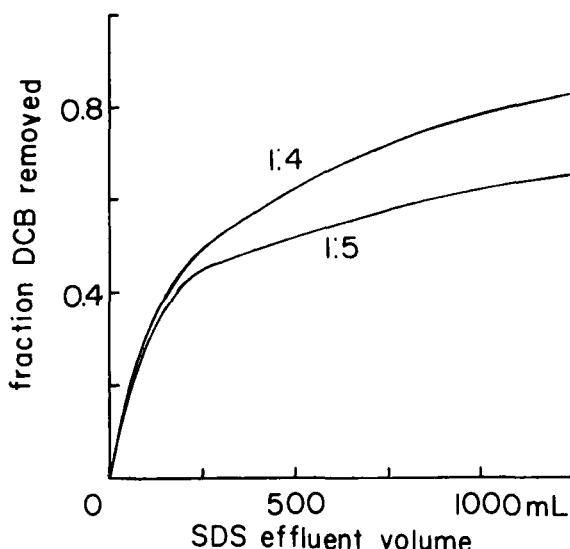


FIG. 8. Removal efficiencies of 0.3 g samples of DCB versus the volume of 100 mM SDS passed through the column. Soil samples were grey clay:sand in the proportions 1:4 and 1:5.

We did observe that, contrary to our expectations, removal was more efficient from the soil samples containing the larger proportions of clay. The flow rates through these samples were substantially slower than those through soil samples containing smaller concentrations of clay, which suggested that this apparently anomalous removal efficiency might be associated with a slow rate of equilibration of DCB between the surfactant solution and the adsorbed state. We therefore carried out a number of runs on matched columns (identical soil sample compositions, identical SDS solution concentrations) in which different surfactant solution flow rates were used. A typical pair of results is shown in Fig. 9, in which 1:5 grey clay:sand spiked with DCB is flushed with 100 mM SDS at the maximum flow rate possible (gravity controlled, Curve 1) and at a flow rate of 100 mL/h (Curve 2). At the rapid flow rate, only about 65% of the DCB is removed by 1.2 L SDS; at the slow flow rate, slightly over 90% is removed, indicating that the rate of equilibration of the contaminant between the surfactant solution and the adsorbed state is an important limiting factor.

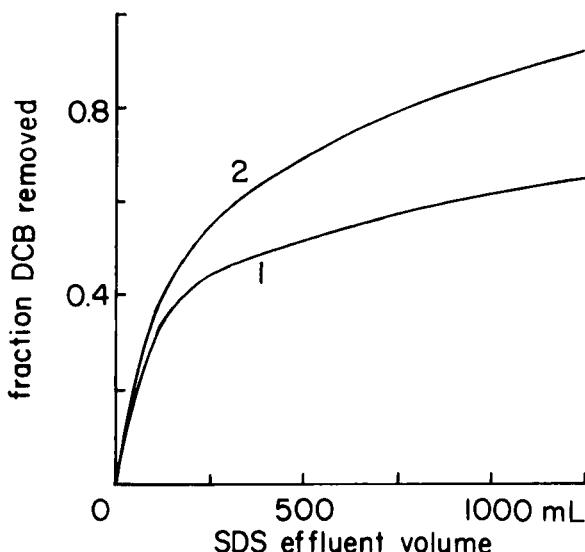


FIG. 9. Removal efficiencies of 0.3 g samples of DCB from grey clay:sand (1:5) mixtures versus volume of 100 mM SDS passed through the columns. Curve 1 represents a column through which the SDS solution was gravity fed continuously as rapidly as possible. Curve 2 represents a column through which the SDS solution moved at a rate of 100 mL/h.

Treatment of Contaminant-Laden Surfactant Solution

As noted earlier, a major problem with the surfactant flushing technique has been the development of a method for recovering the used surfactant solution for recycle. In this section we report on the use of gentle solvent extraction techniques for the removal of DCB, biphenyl, and naphthalene from SDS solutions into hexane.

The use of a standard laboratory extraction technique (vigorous shaking in a separatory funnel) results in the formation of extremely persistent emulsions; this approach was therefore quickly discarded.

Preliminary experiments were carried out in which 350 mL portions of SDS solution were saturated with the model compound and then filtered to remove any solid crystals. The solution was placed in an Erlenmeyer flask and 100 mL hexane was added. The flask was stoppered and stirred magnetically at a low rate of speed. At suitable intervals the aqueous layer

was sampled for analysis by UV spectrophotometry. The stirring rate was maintained at a speed which did not result in disruption of the water-hexane interface.

In Fig. 10 we see results on the kinetics of naphthalene removal from deionized water by gentle extraction with hexane. Figure 11 shows the kinetics of naphthalene removal from 100 mM SDS solution by this gentle extraction procedure. The removal of DCB from 50 mM SDS solution is shown in Fig. 12. In all these runs we see that roughly 90–95% removal of the contaminant has taken place in a period of the order of a day. The percent removal figures are acceptable, but the rate of the process is too slow. Excellent removal of biphenyl was also obtained by this method, but the kinetics were not followed. The solid points in Fig. 3 were obtained with used SDS solution from which the biphenyl had been removed by gentle solvent extraction with hexane; it is apparent that this recycled solution is just as effective as fresh solution in solubilizing biphenyl.

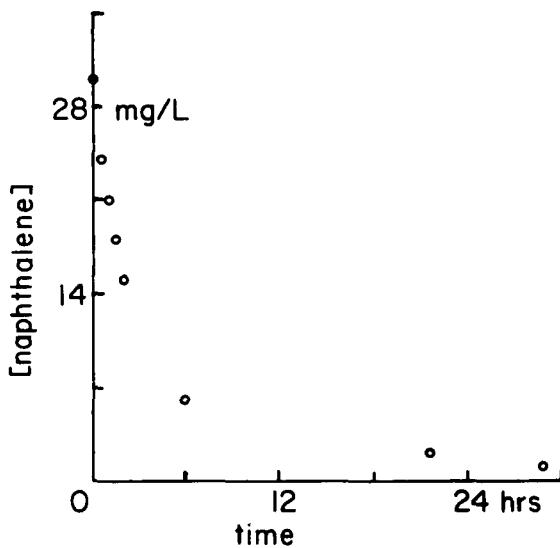


FIG. 10. Naphthalene concentration (mg/L) in the aqueous phase as a function of time during a gentle extraction run. Here naphthalene was being extracted from naphthalene-saturated deionized water.

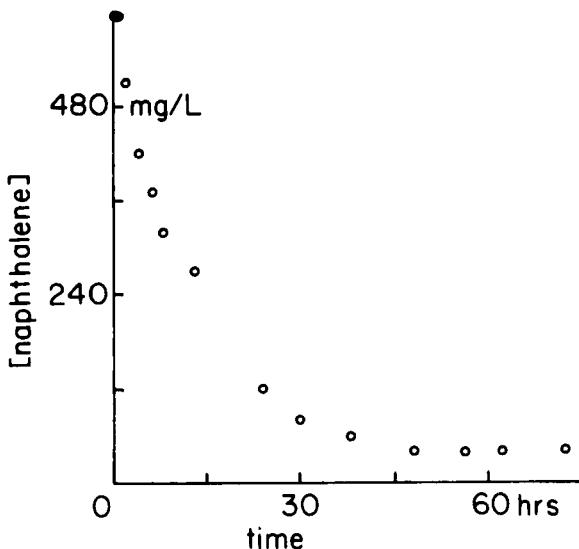


FIG. 11. Naphthalene concentration (mg/L) as a function of time during a gentle extraction run. The naphthalene was being extracted from naphthalene-saturated 100 mM SDS solution.

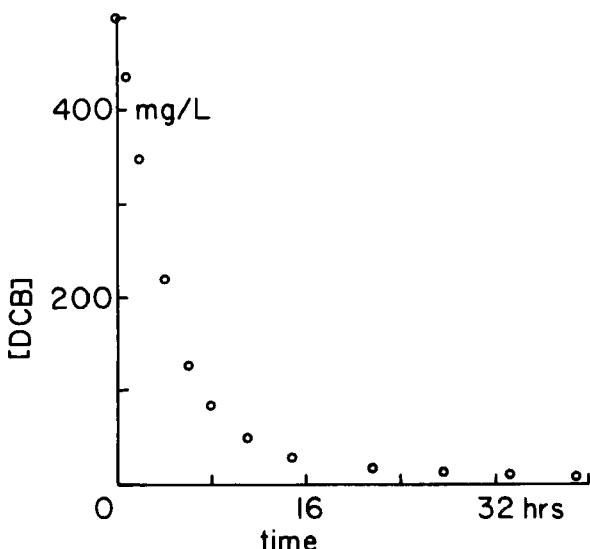


FIG. 12. DCB concentration (mg/L) as a function of time during a gentle extraction run. DCB extraction was from DCB-saturated 100 mM SDS solution.

It was evident that a more efficient method of mass transfer between the aqueous and organic phases was needed if the gentle extraction technique were to be viable. A simple countercurrent extraction apparatus, sketched in Fig. 13, was therefore constructed; this, to date, has been run in the batch mode. The Pyrex glass column is 85 cm long and of 3.4 cm internal diameter. It is closed with rubber stoppers at both ends. The bottom stopper is fitted with a glass sampling port and a glass "T"-shaped tube (8 mm o.d.) to produce relatively large droplets of hexane. A Cole-Parmer Masterflex peristaltic pump is used to pump the hexane from the top of the column to the bottom. A layer of woven knitted plastic (from a simple pot-cleaner) is placed in the column at the organic-aqueous interface to facilitate coalescence of the droplets of hexane.

Contaminated surfactant solution is created by preparing an SDS solution of the desired concentration and then allowing it to equilibrate with excess solid DCB. This solution is then filtered to remove any DCB crystals which may be suspended in it. The column is then charged with approximately 700 mL of this solution, and a 20-mL sample of solution is taken at this time for analysis. Hexane (30 mL) is then added on top of

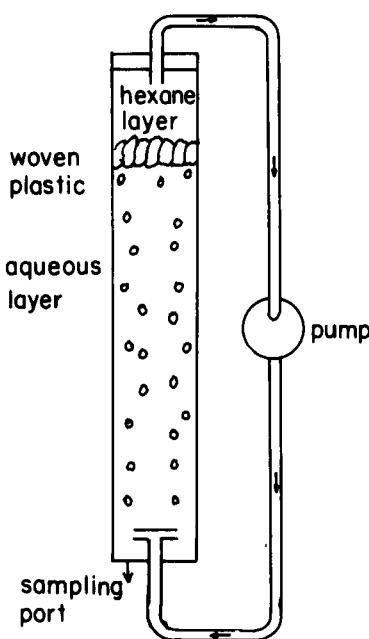


FIG. 13. The column used for carrying out gentle extraction.

the SDS solution, and the woven plastic is placed at the aqueous-organic interface. The pump is then started, and hexane is added at the top of the column as needed to prevent the pump from sucking air. Samples (20 mL) of the SDS solution are taken via the sample port at the bottom of the column, and are analyzed by UV absorption.

The results of several runs are shown in Figs. 14-18. The hexane flow rate in the runs plotted in Figs. 14-16 was 19 mL/min, and the SDS concentrations were 25, 50, and 100 mM. DCB removals of the order of 95% or better were obtained in every case; the times required for this were 3, 3, and 9.5 h. We see that the percent removal rate is decreased with increasing SDS concentration.

The effect of the hexane flow rate is seen by a comparison of Figs. 14, 17, and 18. The SDS concentration was 25 mM in these three runs; the hexane flow rates were 19, 49, and 90 mL/min. The times required for 95% removal of the DCB were 3, 2, and about 0.75 h, respectively. As expected, increasing the rate at which the hexane-aqueous phase interface is

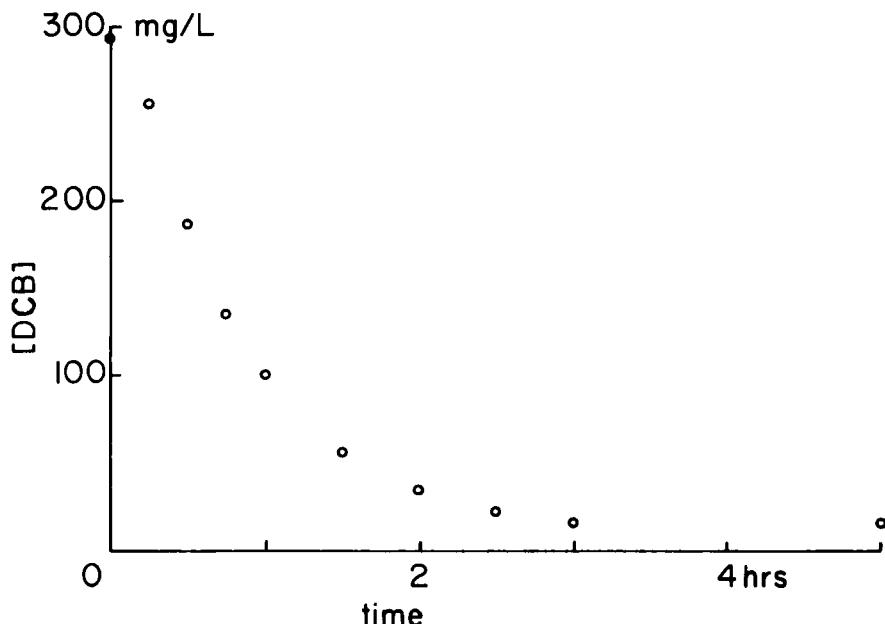


FIG. 14. DCB concentration in the aqueous phase versus time for a run in the column apparatus. The hexane flow rate was 19 mL/min, and the SDS concentration in the aqueous phase was 25 mM.

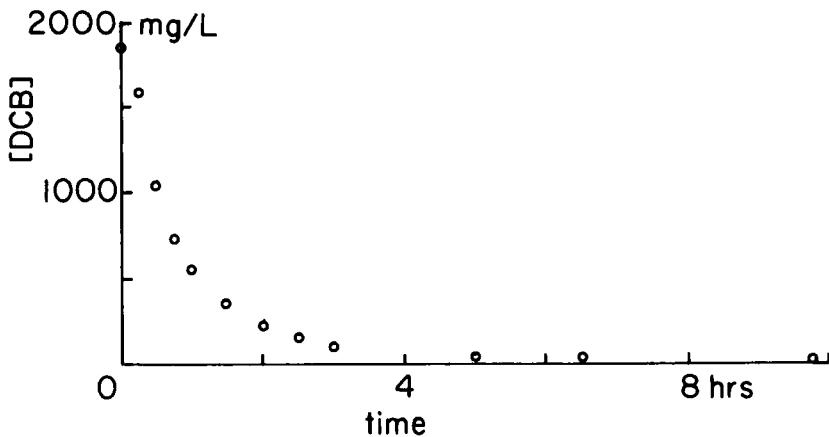


FIG. 15. DCB concentration in the aqueous phase versus time for a run in the column apparatus. The hexane flow rate was 19 mL/min, and the SDS concentration in the aqueous phase was 50 mM.

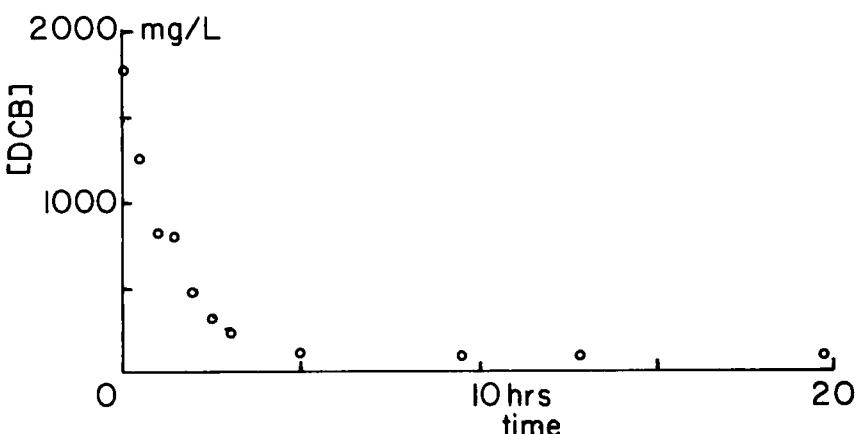


FIG. 16. DCB concentration in the aqueous phase versus time for a run in the column apparatus. The hexane flow rate was 19 mL/min, and the SDS concentration in the aqueous phase was 100 mM.

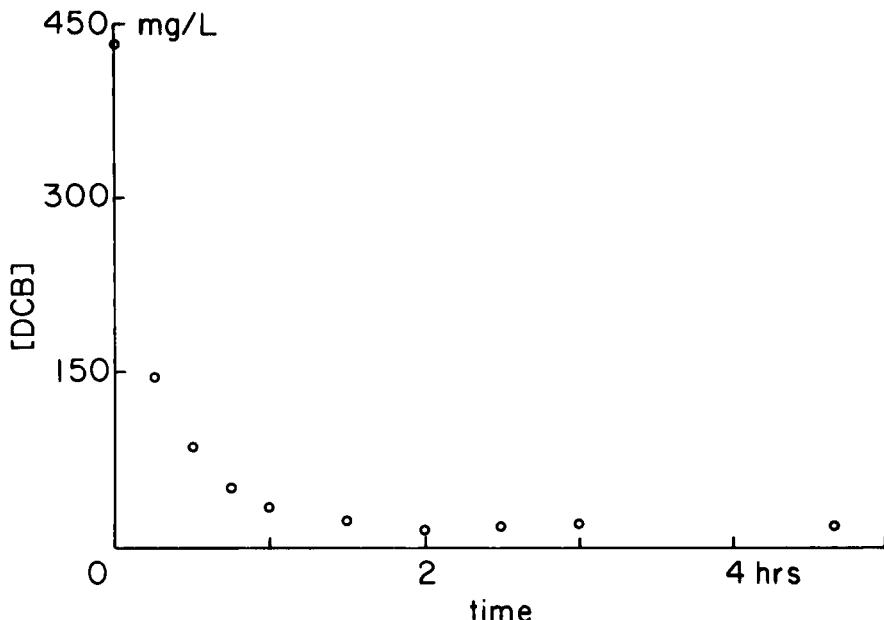


FIG. 17. DCB concentration in the aqueous phase versus time for a run in the column apparatus. The hexane flow rate was 49 mL/min, and the SDS concentration in the aqueous phase was 25 mM.

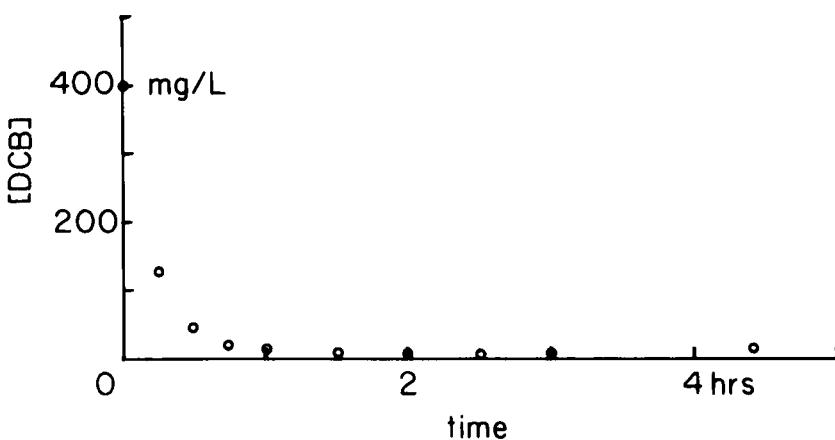


FIG. 18. DCB concentration in the aqueous phase versus time for a run in the column apparatus. The hexane flow rate was 90 mL/min, and the SDS concentration in the aqueous phase was 25 mM.

supplied to the system very markedly increases the rate of mass transfer.

THEORETICAL MODEL FOR SOLUBILIZATION

Solubilization is crucial to the surfactant flushing technique. A simple theory which would permit calculation of the solubilizing power of a given surfactant for a particular hydrophobic compound would therefore be extremely useful in making a preliminary assessment of the feasibility of surfactant flushing in any particular situation. We present here an approach which is substantially simpler than our previous effort (6). For a brief introduction to solubilization which includes a presentation of the two-phase distribution approach used here, see Vold and Vold (7).

Let us assume that the concentrations of the contaminant in the interiors of the micelles and in the aqueous phase outside the micelles are related by the simple distribution law

$$K = \frac{C_{\text{micelle}}}{C_{\text{aqueous}}} \quad (1)$$

where C_{micelle} = concentration of contaminant in the hydrophobic phase inside the micelles, mol/L

C_{aqueous} = concentration of contaminant in the aqueous phase outside the micelles, mol/L

This formula is a very good approximation for the distribution of solutes between water and solvents immiscible in water. Since the interiors of the micelles are rather like micro-droplets of hexane or other hydrocarbon solvent, this would appear to be a reasonable approximation to use for calculating solubilizate concentrations in the micellar interiors.

Since we wish to determine the maximum contaminant concentration in the surfactant solution, we assume that the aqueous phase is in equilibrium with solid (liquid) contaminant, and that the contaminant concentration in the aqueous phase is therefore the saturation concentration, C_s . The contaminant concentration in the micelle is then given by $C_{\text{micelle}} = KC_s$. The total effective concentration of contaminant in the solution is then given by

$$C_{\text{total}} = [\text{moles solute in aqueous phase} + \text{moles solute in micelle interiors}]/\text{total volume of solution} \quad (2)$$

If the surfactant solution is relatively dilute (<5%, say), then we can approximate that the number of moles of solute in 1 liter of the solution is given by $C_s \cdot 1$ liter.

The volume of micelle interior phase in 1 liter of solution is given by 1 liter $\cdot (C_{\text{surf}} - \text{cmc}) \cdot V_{\text{tail}}$, where C_{surf} is the total molar surfactant concentration, cmc is the critical micelle concentration of the surfactant (about 0.008 M for SDS), and V_{tail} is the molar volume of the surfactant hydrocarbon tail. For SDS, the molar volume of dodecane, $\text{C}_{12}\text{H}_{26}$, should be a good approximation to V_{tail} . This molar volume must be in liters. If one divides the molecular weight of dodecane, 170.33 g/mol, by its density, 0.766 g/mL, one obtains a molar volume of 0.222 L.

The number of moles of contaminant dissolved in this volume of micellar phase is given by

$$1 \text{ liter} \cdot (C_{\text{surf}} - \text{cmc}) \cdot V_{\text{tail}} \cdot C_{\text{micelle}}$$

Use of Eq. (1) then yields

$$C_{\text{total}} = C_s \cdot [1 + KV_{\text{tail}} \cdot (C_{\text{surf}} - \text{cmc})] \quad (3)$$

if $C_{\text{surf}} > \text{cmc}$, and

$$C_{\text{total}} = C_s$$

if $C_{\text{surf}} < \text{cmc}$.

A plot of C_{total} versus C_{surf} is therefore predicted to be flat at surfactant concentrations below the cmc, and to be linearly increasing with surfactant concentration above the cmc with a slope of $C_s KV_{\text{tail}}$. Values for K should be rather similar to the distribution coefficients for the contaminants between a hydrocarbon such as hexane or octane, and water. The slope of the plot, which is a measure of the surfactant's solubilizing power for the solute under consideration, can then be calculated independently of any measurements of solubilization.

We measured the distribution coefficients for DCB, naphthalene, and biphenyl between water and hexane; preliminary values of these and the aqueous solubilities of these compounds are listed in Table 2. The distribution coefficients were determined by extracting 1 L of saturated aqueous solution with 1 mL of hexane and substituting the results into Eq. (4):

$$K = \frac{V_w}{V_h} \left(\frac{C_w^0}{C_w} - 1 \right) \quad (4)$$

TABLE 2
Aqueous Solubilities and Hexane/Water Distribution
Coefficients for DCB Naphthalene, and Biphenyl

Compound	Aqueous solubility (mol/L)	Distribution coefficient
DCB	5.4×10^{-4}	950
Naphthalene	2.3×10^{-4}	1490
Biphenyl	5.3×10^{-6}	3870

where V_w = volume of aqueous phase

V_h = volume of organic (hexane) phase

C_w^0 = initial solute concentration in aqueous phase

C_w = final solute concentration in aqueous phase

These distribution coefficients and the value of V_{tail} calculated above, 0.222 L, were used to calculate theoretical values for the slopes of plots of C_{total} versus C_{surf} for these three model compounds; these were then converted to (mg/L)/mM. Experimental values of the slopes were obtained from the data plotted in Figs. 1-3. The experimental and theoretical values are compared in Table 3; the data suggest that this very simple approach permits one to get a fairly good qualitative estimate of the solubilizing power of a surfactant for any particular hydrophobic contaminant. This should be useful in preliminary screening to assess the feasibility of surfactant flushing.

CONCLUSIONS

Solubilization results in solubility enhancement factors of the order of 20-100 in 100 mM SDS solutions. Like the nonionic surfactants used in

TABLE 3
Solubilizing Power of SDS for DCB, Naphthalene, and
Biphenyl [(mg/L)/mM]

Compound	Observed slope	Calculated slope
DCB	26 ± 1 mg/mmol	17 mg/mmol
Naphthalene	5.7 ± 0.1	9.7
Biphenyl	0.94 ± 0.02	0.70

previous studies, SDS, an ionic surfactant, is able to mobilize hydrophobic organics sorbed on soils. Gentle solvent extraction with a nonpolar organic solvent appears to be a promising technique for the treatment of contaminant-laden surfactant solutions so that these can be reused. It appears that the solubilizing power of a surfactant for a given hydrophobic contaminant can be predicted qualitatively by a simple theory which requires as input the distribution coefficient of the contaminant between water and a hydrocarbon solvent such as hexane, the solubility of the contaminant in water, and the molar volume of the hydrophobic group of the surfactant species.

Acknowledgments

We are indebted to the Water Resources Research Center of the University of Tennessee and to AWARE, Inc., for support of this work.

REFERENCES

1. J. H. Clarke and R. D. Mutch Jr., "An Overview of In Situ Management Technologies Including Innovative Approaches," in *Proceedings of the Second Annual Hazardous Materials Conference West*, Long Beach, California, December 3-5, 1986, pp. 110-123.
2. M. Ghassemi, "In Situ Technologies for Site Remediation," in *DOE Model Conference Abstracts*, Oak Ridge, Tennessee, October 3-7, 1988, p. 59.
3. W. E. Ellis, J. R. Payne, and G. D. McNabb, *Treatment of Contaminated Soils with Aqueous Surfactants*, U.S. EPA Report No. EPA/600/2-85/129, PB 86-122561, 1985.
4. J. H. Nash, *Field Studies of In Situ Soil Washing*, U.S. EPA Report No. EPA/600/2-87/110, PB 88-146808, 1987.
5. D. J. Wilson, "Soil Clean Up by *in-situ* Surfactant Flushing. I. Mathematical Modeling," *Sep. Sci. Technol.*, 24, 863 (1989).
6. H. J. Wayt and D. J. Wilson, "Soil Clean Up by *in-situ* Surfactant Flushing. II. Theory of Micellar Solubilization," *Ibid.*, 24, 905 (1989).
7. R. D. Vold and M. J. Vold, *Colloid and Interface Science*, Addison-Wesley, Reading, Massachusetts, 1983.

Received by editor February 9, 1989