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. V. Micellar Solubilization of Some Aromatic Contaminants

Julie L. Underwood[a]; Kenneth A. Debelak[a]; David J. Wilson[b]; Jennifer M. Means[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE [b] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Underwood, Julie L. , Debelak, Kenneth A. , Wilson, David J. and Means, Jennifer M.(1993) 'Soil Clean up by *in-situ* Surfactant Flushing. V. Micellar Solubilization of Some Aromatic Contaminants', Separation Science and Technology, 28: 8, 1527 — 1537

To link to this Article: DOI: 10.1080/01496399308018056

URL: http://dx.doi.org/10.1080/01496399308018056

SEPARATION SCIENCE AND TECHNOLOGY, 28(8), pp. 1527–1537, 1993

Soil Clean Up by *in-situ* Surfactant Flushing. V. Micellar Solubilization of Some Aromatic Contaminants

JULIE L. UNDERWOOD and KENNETH A. DEBELAK
DEPARTMENT OF CHEMICAL ENGINEERING

DAVID J. WILSON and JENNIFER M. MEANS
DEPARTMENT OF CHEMISTRY

VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

ABSTRACT

The solubilities of mixtures of naphthalene, biphenyl, and phenanthrene in 50 and 100 mM aqueous sodium dodecylsulfate solutions at room temperature were determined. There does not appear to be any appreciable tendency for these compounds to form solid solutions with each other, and the solubilities of the mixture components in the micellar surfactant solutions are to a fairly good approximation equal to the solubilities of the individual pure components.

INTRODUCTION

The remediation of hazardous waste sites in which soil and groundwater have become contaminated with volatile and/or nonvolatile organics is a major problem in the United States. The removal of organics (either sorbed or present as dense nonaqueous phase liquid—DNAPL) from contaminated aquifers by simple water flushing is turning out to be a very slow process, so there is great interest in the development of alternative technologies. Surfactant flushing appears to have some potential in this regard. In 1985 Ellis, Payne, and McNabb published the results of a lab-scale study of surfactant flushing (1), which was followed 2 years later by Nash's report of a small-scale field study (2). Vigon and Rubin examined the questions of surfactant selection and dosage optimization (3). Our group has published on several experimental and theoretical aspects of surfactant flushing (4–9).

A crucial element in surfactant flushing is the ability of solutions having surfactant concentrations above the critical micelle concentration to drastically increase the solubilities of hydrophobic solutes (The critical micelle concentration, or cmc, is the minimum concentration of surfactant at which surfactant molecules/ions start to form aggregates or micelles.) The phenomenon has been known for many years, and it was discussed in detail by McBain and Hutchinson (10). Solubilization can be described as the dissolving of a hydrophobic solute in the nonpolar phase present within the interiors of the surfactant micelles. In previous papers (5–7) we examined some aspects of the solubilization of single components into surfactant micelles; this included solubilization data on *p*-dichlorobenzene, naphthalene, and biphenyl, and confirmation of a relationship between micellar/water partition coefficients (K_{sw}) and octanol/water partition coefficients reported earlier by Valsaraj et al. (11).

Studies of micellar solubilization equilibria have focused on the location of solubilized organic compounds in micelles (12–18), the effect of salt addition on micelles (13, 15, 17), the effect of increased surfactant concentrations (13–15, 17, 19), and the sizes of micelles under various conditions (12, 13, 15, 17). Both single (14–16, 19) and multicomponent (12–14, 16–18) equilibrium studies have been conducted with organic compounds such as alcohols, alkanes, and aromatics. The multicomponent studies have investigated the influence of one compound on another in a micelle: synergistic, antagonistic, or no effect on solubilization.

In most hazardous waste sites, mixtures of compounds must be removed, rather than a single constituent. We therefore examine here the micellar solubilization of mixtures of hydrophobic organic compounds; the polynuclear aromatic hydrocarbons naphthalene, biphenyl, and phenanthrene were selected.

EXPERIMENTAL

The sodium dodecylsulfate used was obtained from Fluka and reported to be 98% pure. Other chemicals employed were hexane (Fisher, certified and spectranalyzed), phenanthrene (Eastman and Fluka), naphthalene (Fisher), and biphenyl (Aldrich).

Analyses of the mixtures of aromatic compounds were carried out by ultraviolet absorbance measurements made on a Hitachi Model 100-40 UV-VIS spectrophotometer. To determine the concentration in a solution containing a single component, calibration curves were made at 251.3 nm (phenanthrene), 311.4 nm (naphthalene), and 247.0 nm (biphenyl). The slopes of the absorbance versus concentration curves were 0.3918 ± 0.0031 absorbance units per mg/L phenanthrene, 0.001678 ± 7.3×10^{-6} absorbance units per mg/L naphthalene, and 0.1115 ± 0.0026 absorbance units per mg/L biphenyl.

The spectra of phenanthrene, naphthalene, and biphenyl overlap sufficiently that a somewhat more elaborate procedure was needed to determine the concentrations of these compounds in mixtures by spectrophotometry. The extinction coefficients ϵ_{ij} of compound j at wavelength i were measured for the three compounds at 13 wavelengths in the 247–311.5 nm region. Beer's law was assumed to apply to the individual compounds in the mixtures, so that the absorbance at wavelength i is given by

$$A_i = \sum_{j=1}^{3} \epsilon_{ij} L C_j, \qquad i = 1, 2, \ldots, 13 \tag{1}$$

where A_i = absorbance at wavelength i
ϵ_{ij} = extinction coefficient of component j at wavelength i
L = optical path length = 1.00 cm
C_j = concentration of compound j

One then uses the method of least squares to obtain the best set of values of the C_j's for solving the overdetermined set, Eq. (1) (20).

Thus, generally,

$$\text{Error} = \sum_{i=1}^{n} \left(A_i - \sum_{j=1}^{m} \epsilon_{ij} C_j \right)^2 \tag{2}$$

where n = number of wavelengths used (13 here)
m = number of compounds present (3 here)

The conditions that must be satisfied if the error is to be minimized are

$$\frac{\partial \text{ Error}}{\partial C_k} = 0 = \sum_{i=1}^{n} 2\left(A_i - \sum_{j=1}^{m} \epsilon_{ij} C_j \right)(-\epsilon_{ik}), \qquad k = 1, \ldots, m \tag{3}$$

This can be rearranged in the form

$$\sum_{j=1}^{m} \left(\sum_{i=1}^{n} \epsilon_{ij}\epsilon_{ik} \right) C_j = \sum_{i=1}^{n} \epsilon_{ik} A_i \tag{4}$$

or equivalently as

$$\sum_{j=1}^{m} F_{kj} C_j = B_k, \qquad k = 1, 2, \ldots, m \tag{5}$$

where

$$F_{kj} = \sum_{i=1}^{n} \epsilon_{ij}\epsilon_{ik} \tag{6}$$

and

$$B_k = \sum_{i=1}^{n} \epsilon_{ik} A_i \tag{7}$$

In matrix notation, Eq. (5) can be written as

$$FC = B \tag{8}$$

so that the concentrations (the elements of the vector C in Eq. 8) are given by

$$C = F^{-1}B \tag{9}$$

A computer program was written to solve Eqs. (9); the program also permitted the calculation of the standard deviations of the concentrations.

Studies were performed to determine the solubilities of mixtures of phenanthrene/naphthalene, phenanthrene/biphenyl, naphthalene/biphenyl, and phenanthrene/naphthalene/biphenyl in 50 and 100 mM aqueous sodium dodecylsulfate (SDS) solutions. SDS and the organic compounds were added to 500 mL water to make the solutions. The mole fractions of the aromatics in the solid phase ranged from 0.05 to 0.95. All solids were added in excess so that the mole fractions of the solids would remain essentially constant during the equilibration. Duplicates of some of the solutions were made to check the reproducibility of the technique. In a few cases the solids were melted together over boiling water before adding them to the SDS solutions to try to form a solid solution. The solutions were stirred constantly until equilibrium was reached, usually about a week at ambient temperature, very nearly 20°C. The equilibrium concentrations of the aromatics in the solutions were then determined by UV spectrophotometry and the computer program described above.

RESULTS

Figures 1 through 6 show the results of the experiments on binary mixtures; in these the solubilities are plotted as functions of mole fraction of one of the components in the solid phase. Each point on the graphs represents one experiment. The relative errors in each calculated solubility value were determined in the computer analysis of the data; these are shown on the graphs as error bars.

The solubilities of mixtures of phenanthrene and naphthalene in 50 and 100 mM SDS are depicted in Figs. 1 and 2. The solubilities of both of the compounds do not seem to depend significantly on the mole fraction of phenanthrene in the solid phase. The solubilities of the compounds in the mixture are approximately the same as their individual solubilities. These latter are shown in Table 1. As expected, the solubilities of the compounds

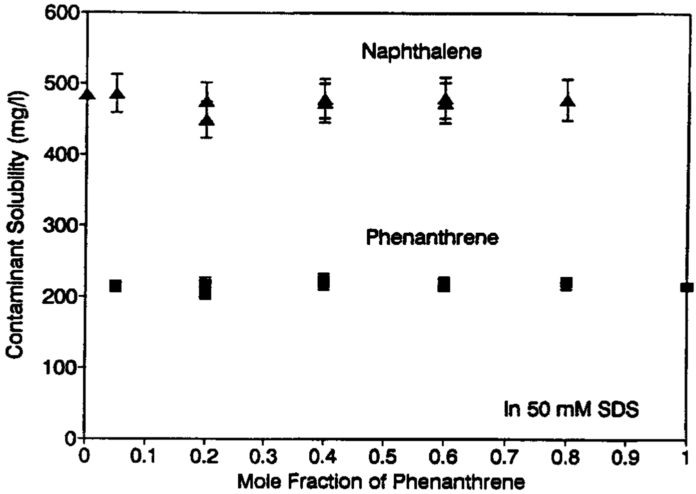

FIG. 1 The solubilities of mixtures of phenanthrene and naphthalene in 50 mM aqueous SDS at 20°C.

are approximately proportional to the SDS concentration since this is well above the cmc of SDS (8 mM).

Figures 3 and 4 show the solubilities of phenanthrene and biphenyl in 50 and 100 mM SDS as functions of the mole fraction of phenanthrene in the solid phase. These solubility values have greater errors associated with

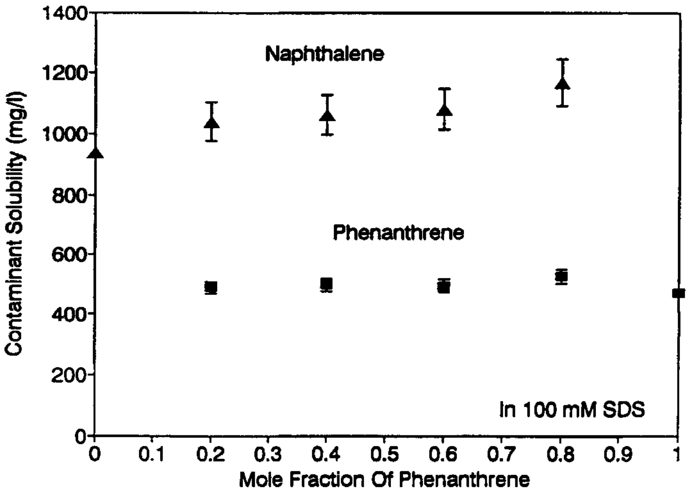

FIG. 2 The solubilities of mixtures of phenanthrene and naphthalene in 100 mM aqueous SDS at 20°C.

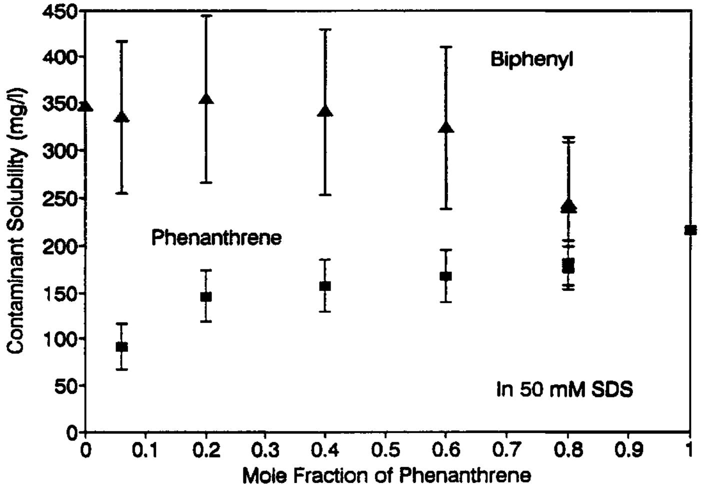

FIG. 3 The solubilities of mixtures of phenanthrene and biphenyl in 50 mM aqueous SDS at 20°C.

them than the solubilities shown in Figs. 1 and 2 because both phenanthrene and biphenyl absorb fairly strongly at some of the same wavelengths in the ultraviolet region. In the case of phenanthrene and biphenyl in 50 mM SDS, the biphenyl solubility decreases slightly while phenanthrene solubility increases with the mole fraction of phenanthrene in the solid phase,

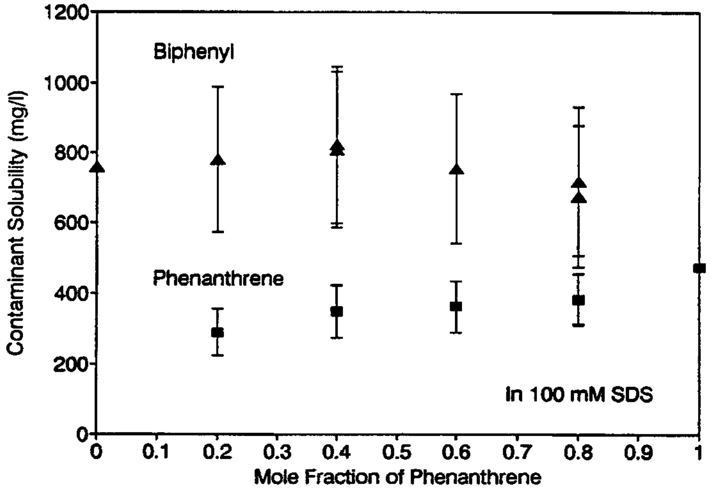

FIG. 4 The solubilities of mixtures of phenanthrene and biphenyl in 100 mM aqueous SDS at 20°C.

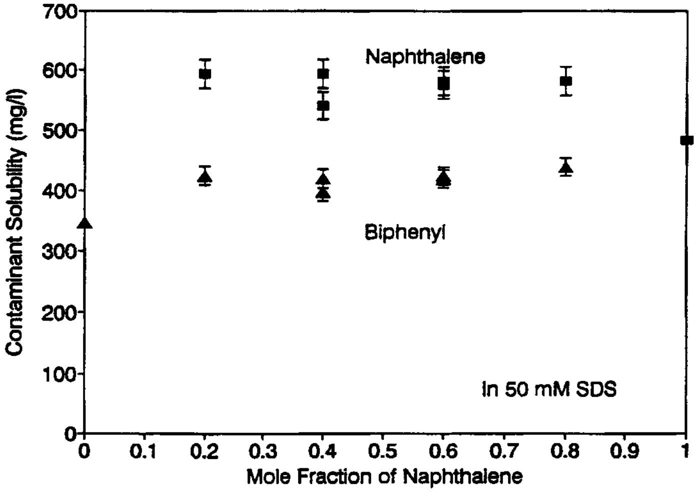

FIG. 5 The solubilities of mixtures of naphthalene and biphenyl in 50 mM aqueous SDS at 20°C.

but the effect is not large. This trend is not as apparent in the runs in 100 mM SDS, but the phenanthrene solubility does appear to increase slightly and the biphenyl solubility decreases slightly.

The solubilities of naphthalene and biphenyl in 50 and 100 mM SDS are illustrated in Figs. 5 and 6. The solubilities of the compounds do not seem

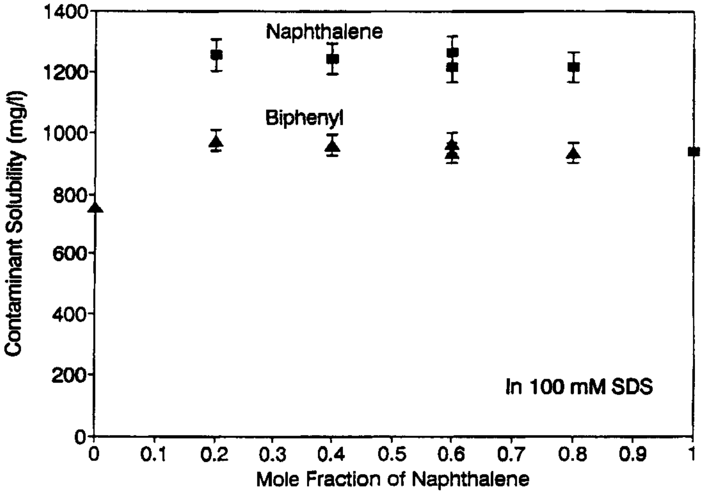

FIG. 6 The solubilities of mixtures of naphthalene and biphenyl in 100 mM aqueous SDS at 20°C.

TABLE 1
Comparison of Individual and Average Mixture Solubilities in 50 and 100 mM SDS[a]

Compound mixture and SDS concentration (#1/#2)	Compound 1 (mg/L)		Compound 2 (mg/L)	
	Ind. sol.	Mix. sol.	Ind. sol.	Mix. sol.
Naph/Biph: 50 mM	484	578	347	420
100 mM	938	1238	759	954
Phen/Naph: 50 mM	215	217	484	476
100 mM	471	500	938	1088
Phen/Biph: 50 mM	215	165	347	301
100 mM	471	352	759	759

[a] Ind. sol. = individual solubility. Mix. sol. = solubility as a component in the mixture.

TABLE 2
Solubilities of Mixtures of Phenanthrene (P), Naphthalene (N), and Biphenyl (B) in 50 mM SDS[a]

MF P, N, B	P concentration (mg/L)	N concentration (mg/L)	B concentration (mg/L)
0.2, 0.6, 0.2	175.93 ± 19.08	634.92 ± 32.62	418.38 ± 54.35
0.2, 0.6, 0.2	179.15 ± 18.52	634.29 ± 32.07	429.87 ± 52.75
0.6, 0.2, 0.2	185.95 ± 16.04	538.39 ± 28.10	370.23 ± 45.44
0.6, 0.2, 0.2	181.73 ± 16.39	543.32 ± 28.61	373.87 ± 46.40
0.2, 0.2, 0.6	146.98 ± 17.33	549.80 ± 29.40	423.33 ± 50.03
0.33, 0.33, 0.33	170.61 ± 17.48	595.85 ± 30.71	391.95 ± 49.93
0.33, 0.33, 0.33[b]	163.75 ± 17.76	614.69 ± 30.95	411.09 ± 50.89

[a] MF = mole fraction in solid phase.

[b] Solids melted together before adding to SDS solution.

TABLE 3
Solubilities of Mixtures of Phenanthrene (P), Naphthalene (N), and Biphenyl (B) in 100 mM SDS[a]

MF P, N, B	P concentration (mg/L)	N concentration (mg/L)	B concentration (mg/L)
0.2, 0.2, 0.6	321.07 ± 63.24	1571.59 ± 79.62	1067.08 ± 175.72
0.2, 0.6, 0.2	357.43 ± 67.95	1579.99 ± 78.33	988.55 ± 188.28
0.6, 0.2, 0.2	363.42 ± 72.90	1632.64 ± 81.63	992.52 ± 201.96
0.33, 0.33, 0.33	347.72 ± 62.63	1534.34 ± 76.48	980.76 ± 173.74

[a] MF = mole fraction in solid phase.

to be functions of the mole fraction of naphthalene in 50 or 100 mM SDS. The average solubilities of both compounds in the mixtures are perhaps slightly higher than their individual solubilities given in Table 1.

The solubilities of mixtures of phenanthrene, naphthalene, and biphenyl in 50 and 100 mM SDS are given in Tables 2 and 3. The naphthalene and biphenyl solubilities appear to be greater than their individual solubilities, in some cases by a factor of about 1.5 (in 100 mM SDS). Phenanthrene solubility is decreased in both 50 and 100 mM SDS when in the presence of naphthalene and biphenyl, also in some cases by about a factor of 1.5.

DISCUSSION

The solubilization experiments with phenanthrene and naphthalene indicate that the two compounds do not form a solid solution but act independently of each other. The solubilities of these compounds present in the solid phase as mixtures are not very different from their individual solubilities in SDS solutions. Solute interactions do not seem to be occur-

TABLE 4

Example Calculation of the Concentration of Phenanthrene (P) and Naphthalene (N) in 100 mM SDS[a]

$$\rho_{\text{dodecane}} = 0.7487\ \text{g/cm}^3\ (21)$$

$$\text{MW}_{\text{dodecane}} = 170.34\ \text{g/mol}\ (21)$$

$$C_{\text{phen}} = 500\ \text{mg/L}$$

$$C_{\text{naph}} = 1100\ \text{mg/L}$$

$$\begin{matrix}\text{Molar volume}\\ \text{of dodecane}\end{matrix} = \left(170.34\,\frac{\text{g}}{\text{mol}}\right)\left(\frac{\text{cm}^3}{0.7487\ \text{g}}\right)\left(\frac{10^3\ \text{L}}{10^6\ \text{cm}^3}\right) = 0.2275\,\frac{\text{L}}{\text{mol}}$$

$$\text{SDS critical micelle concentration} = 8\text{mM}$$

$$\begin{matrix}\text{Number of mols of micellar}\\ \text{phase per L in 100 mM SDS}\end{matrix} = 100\ \text{mM} - 8\ \text{mM} = 92\ \text{mM}$$

$$\left(0.2275\,\frac{\text{L dodecane}}{\text{mol}}\right)(92\ \text{mM})\left(\frac{10^{-3}\ \text{mols/L}}{1\ \text{mM}}\right) = 0.02093\,\frac{\text{L mic. ph.}}{\text{L solution}}$$

$$\left(1100\,\frac{\text{mg N}}{\text{L}}\right)\left(\frac{10^{-3}\ \text{g}}{\text{mg}}\right)\left(\frac{\text{L solution}}{0.02093\ \text{L mic. ph.}}\right)\left(\frac{\text{mol}}{128.16\ \text{g N}}\right) = 0.410\,\frac{\text{mols N}}{\text{L mic. ph.}}$$

$$\left(500\,\frac{\text{mg P}}{\text{L}}\right)\left(\frac{10^{-3}\ \text{g}}{\text{mg}}\right)\left(\frac{\text{L solution}}{0.02093\ \text{L mic. ph.}}\right)\left(\frac{\text{mol}}{178.24\ \text{g P}}\right) = 0.134\,\frac{\text{mols P}}{\text{L mic. ph.}}$$

[a] mic. ph. = micellar phase.

TABLE 5
Estimated Concentration of Contaminants in SDS Micellar Phase

	Contaminant concentration in micellar phase		
SDS concentration (mM)	P concentration (M)	N concentration (M)	B concentration (M)
50	0.127	0.387	—
100	0.134	0.410	—
50	0.102	—	0.210
100	0.099	—	0.235
50	—	0.461	0.278
100	—	0.462	0.296

ring between naphthalene and phenanthrene even when they are melted together before being added to the SDS solution.

One explanation of the results for phenanthrene and naphthalene is that 1) the compounds are present in dilute concentrations within the SDS micelles, and 2) the compounds are not mutually soluble. Under these circumstances, one would expect that the observed solubilities of the two compounds would be just the solubilities of the individual compounds in SDS. One can estimate the concentrations of the hydrocarbon solutes in the micellar phase as shown in the sample calculation of Table 4, in which we estimate the volume of the micellar phase present in 1 L of solution by assuming that the SDS dodecyl group has a molar volume equal to that of the dodecane molecule. Such calculations for the various solutes give the concentrations of hydrocarbons in the micellar phase given in Table 5. The maximum micellar hydrocarbon concentration appearing in Table 5 is less than 0.5 M, so we see that these micellar solutions of hydrocarbons are relatively dilute.

Given the sizes of the error bars on the data, prudence suggests that one not try to interpret relatively slight trends. One can certainly conclude that the components of these mixtures act, to a fairly good approximation, independently, and that there does not seem to be much evidence for the formation of solid solutions of the hydrocarbons. These results suggest that there are no unpleasant surprises awaiting the surfactant flushing practitioner when there are polynuclear aromatic hydrocarbon mixtures to be dealt with; that micellar solubilities for individual components are likely to be a reasonable guide as to what will happen with mixtures of hydrophobic organics of this type.

REFERENCES

1. W. E. Ellis, J. R. Payne, and G. D. McNabb, *Treatment of Contaminated Soils with Aqueous Surfactants*, U.S. EPA Report EPA/600/2-85/129, PB 86-122561, February 1985.
2. J. H. Nash, *Field Studies of In Situ Soil Washing*, U.S. EPA Report EPA/600/2-85/110, PB 88-146808, February 1987.
3. B. W. Vigon and A. J. Rubin, *J. Water Pollut. Control Fed.*, *61*, 1233 (1989).
4. D. J. Wilson, *Sep. Sci. Technol.*, *24*, 863 (1989).
5. H. J. Wayt and D. J. Wilson, *Ibid.*, *24*, 905 (1989).
6. O. K. Gannon, P. Bibring, K. Raney, J. A. Ward, D. J. Wilson, J. L. Underwood, and K. A. Debelak, *Ibid.*, *24*, 1073 (1989).
7. A. N. Clarke, P. D. Plumb, T. K. Subramanyan, and D. J. Wilson, *Ibid.*, *26*, 301 (1991).
8. D. J. Wilson and A. N. Clarke, *Ibid.*, *26*, 1177 (1991).
9. J. L. Underwood, K. A. Debelak, and D. J.Wilson, *Ibid.*, In Press.
10. M. E. L. McBain and E. Hutchinson, *Solubilization*, Academic Press, New York, 1955.
11. K. T. Valsaraj, A. Gupta, L. J. Thibodeaux, and D. P. Harrison, *Partition of Low Molecular Weight Aliphatic Halocarbons between Aqueous and Surfactant Micellar Phases*, Department of Chemical Engineering, Louisiana State University, 1987.
12. A. M. Jacobson andE. Z. Casassa, *J. Colloid Interface Sci.*, *142*, 480 (1991).
13. I. M. Kolthoff and W. F. Graydon, *J. Phys. Colloid Chem.*, *55*, 699 (1951).
14. M. A. Chaiko, R. Nagarajan, and E. Ruckenstein, *J. Colloid Interface Sci.*, *99*, 168 (1984).
15. H. W. Offen, D. R. Dawson, and D. F. Nicoli, *Ibid.*, *80*, 118 (1981).
16. M. Gonzales, J. Vera, E. B. Abuin, and E. A. Lissi, *Ibid.*, *98*, 152 (1984).
17. E. Valenzuela, E. B. Abuin, and E. A. Lissi, *Ibid.*, *102*, 46 (1984).
18. R. Nagarajan, M. A. Chaiko, and E. Ruckenstein, *J. Phys. Chem.*, *88*, 2916 (1984).
19. D. A. Edwards, R. G. Luthy, and Z. Liu, *Environ. Sci. Technol.*, *25*, 127 (1991).
20. D. J. Wilson, *Anal. Chem.*, *30*, 1578 (1958).
21. D. R. Lide (Ed.), *Handbook of Chemistry and Physics*, 71st ed., CRC Press, Boca Raton, Florida, 1990.

Received by editor September 28, 1992