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Solubilization of Nitroaromatic Compounds from Multi-Component Mixtures into Nonionic Surfactant Micellar Solutions

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This study investigated the solubilization of 2-component and 3-component mixtures of 4-nitrotoluene (4-NT), 2,6-dinitrotoluene (2,6-DNT), and 2,4,6-trinitrotoluene (TNT) in solutions of Brij-35, Brij-58, and alkyl phenol ethoxylates (Tergitol NP-10 to NP-40). 4-NT had the highest molar solubilization ratio (MSR) and TNT the lowest. For all 2-component systems with 4-NT, the MSR of 2,6-DNT and TNT increased. When either 2,6-DNT or TNT was present, the MSR values increased slightly for Tergitol NP-10 (NP10) and Tergitol NP-13 (NP13). For 3-component systems, TNT's MSR increased for all the surfactants, while significant increases in the MSR of 4-NT and 2,6-DNT were found for NP10 and NP13.

Keywords dinitrotoluene; MSR; solubility; trinitrotoluene

INTRODUCTION

Contamination of soil, groundwater, and surface water by nitroaromatic compounds can occur when chemical production (explosives, urethane, dyes) supplies are improperly handled or when unexploded ordnance casings rust at military training or battlefield sites (1). Some of these compounds pose a potential threat to human health, due to their carcinogenic nature (2). The ultimate health risk of these pollutants depends on how rapidly they can be removed through engineering technologies or on how quickly they can be transformed in situ by biological or chemical agents into less harmful products. Removal technologies such as pump and treat operations and transformation processes such as photolysis are often limited by the solubility of the organic compound in the aqueous phase. One way of enhancing the solubility is to add surfactants at concentrations to form micelles and solubilize the organic compound. Studies have examined the impact of micellar surfactants on the single-component solubility, biological transformation, and chemical photolysis of nitroaromatic compounds (3–7). Pilot-scale studies have demonstrated that using surfactants in conjunction with pump-and-treat operations can effectively remove low solubility compounds (8,9). No study, however, has examined the solubility of mixtures of nitroaromatic compounds in surfactant solutions. Since these compounds are commonly found in mixtures, understanding the behavior of such mixtures in surfactant solution can be used to screen surfactants for use in chemical photolysis, biological degradation, or pump and treat systems.

The concentration of individual components when solubilized from mixtures is not related in a simple manner to single solute solubilities (10–20). In the presence of a co-solute, the concentration of organic compounds in micellar solutions has been found to decrease, remain the same, or increase over single-component systems depending on the co-solute and the surfactant. For example, studies have found that naphthalene enhanced the solubility of phenanthrene in Triton X-100 (14), but decreased phenanthrene's solubility in Brij-35 (16). It is difficult, therefore, to predict the solubility behavior of nitroaromatic mixtures in the absence of experimental data.

Solubility enhancements have been previously quantified using the molar solubilization ratio (MSR) and the micelle-water partition coefficient (K_{mic}). The MSR, which is the ratio of the mols of solute solubilized to the mols of surfactant present as micelles, can be obtained from the slope of the solubility curve above the critical micelle concentration (CMC). The CMC is the concentration of surfactant at which micelles are formed. The K_{mic}, which represents the distribution of solute between surfactant micelles and the aqueous phase, is given as

$$K_{mic} = \frac{X_{m,j}}{X_{a,j}} \tag{1}$$

Here $X_{m,j}$ is the mol fraction of the *j*th solute in the micellar phase and $X_{a,j}$ is the mol fraction of the *j*th solute in the micelle-free aqueous phase. The value of $X_{m,j}$ can be calculated from the MSR (14):

$$X_{m,j} = \frac{MSR_j}{1 + \sum_{j=1}^{n} MSR_j} \tag{2}$$

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and $X_{a,j}$ may be estimated as

$$X_{a,j} = C_{a,j,cmc} V_w. \quad (3)$$

Here $C_{a,j,cmc}$ is the solute concentration at the CMC, and V_w is the molar volume of water ($0.01805\,M^{-1}$ at 25°C). Often times, $C_{a,j,cmc}$ is estimated as the solubility in water. For single-component systems with the surfactants and nitroaromatic compounds used herein, this estimate was appropriate (7).

The objective of this work was to quantify the solubilization of mixtures of nitroaromatic compounds and to develop an understanding of the solubilization process. Since the surfactant structure and co-solute play an important role in this process, the goals of this work were to determine the extent of solubilization of nitroaromatic mixtures containing up to three nitroaromatic compounds and to determine the influence of nonionic surfactant structure on the solubilization behavior.

EXPERIMENTAL

Materials

Three solid nitroaromatic compounds, 4-nitrotoluene (4-NT, $C_6H_4(CH_3)NO_2$, $137.1\,g\,mol^{-1}$; 99% pure, Aldrich), 2,6-dinitrotoluene (2,6-DNT, $C_6H_3(CH_3)(NO_2)_2$, $182.14\,g\,mol^{-1}$; 98% pure, Aldrich), and 2,4,6-trinitrotoluene (TNT, $C_6H_3(CH_3)(NO_2)_3$, $227.15\,g\,mol^{-1}$; >95% pure, Eastman Chemical) were used in these studies as representatives of explosives or intermediates in the production of explosives, polyurethanes, and toluene diisocyanate. Mixtures of two or three compounds were prepared by dissolving the compounds in acetone (Fisher Scientific) to form a solution of known concentration. Concentrations were selected to insure that undissolved components remained at the end of each experiment and that the solid nitroarenes did not form a liquid upon mixing.

To systematically examine the surfactant structure, nonionic surfactants were selected whose hydrophile-lipophile balance (HLB) ranged from 13.2 to 17.8. These surfactants were used as supplied from Dow Chemical [Tergitol NP-10 (NP10, <0.3% water), Tergitol NP-13(NP13, <0.3% water), Tergitol NP-15 (NP15, <0.5% water), and Tergitol NP-40 (NP40, <1.0% water)] and Aldrich Chemical [Brij-35, Brij-58, both standard grade)]. Lower HLB surfactants were not used because a previous study found that 4-NT lowers the cloud point of Tergitol NP-8, with an HLB of 12.6, to at or below room temperature (7). Solutions of these surfactants ranging in concentration from 1.0 to $15.0\,g\,L^{-1}$ were made in 18 MΩ MilliQ water (de-ionized water purified by a Millipore MilliQ Plus water system). Relevant properties are listed in Table 1 along with core and micellar volumes of the empty micelles, which are based on literature values (21–24).

Methods

Batch mixing experiments were conducted following the procedure in Luning Prak (7). An acetone solution containing the nitroaromatic compounds was added to 14-mL borosilicate glass vials (Pierce, Rockford, IL), and the acetone evaporated. For the 3-component system, equilimolar concentrations of the components could not be used because a liquid organic phase formed. To avoid this phase change and insure enough of each component to reach equilibrium, the mole fractions used were 0.103, 0.180, and 0.717 for TNT, 2,6-DNT, and 4-NT, respectively. Five milliliters of surfactant solution or Milli-Q water were added to each vial, and duplicates were made for each surfactant concentration. The vials were capped with Teflon

TABLE 1
Selected properties of nonionic surfactants

Trade name	Average molecular formula	Molar mass ($g\,mol^{-1}$)	HLB[a]	CMC[b] (mM)	Na[c]	Volume of 1 empty micelle (nm^3) Core	Total
Tergitol NP-10	$C_9H_{19}(C_6H_4)O(CH_2CH_2O)_{10}H$	683	13.2	0.083	276	100[d]	250[d]
Tergitol NP-13	$C_9H_{19}(C_6H_4)O(CH_2CH_2O)_{13}H$	793	13.9	NA	95	57[d]	210[d]
Tergitol NP-15	$C_9H_{19}(C_6H_4)O(CH_2CH_2O)_{15}H$	881	15.0	0.11	80	28[d]	191[d]
Tergitol NP-40	$C_9H_{19}(C_6H_4)O(CH_2CH_2O)_{40}H$	1983	17.8	0.23	30	11[d]	100[d]
Brij-35	$C_{12}H_{25}(CH_2CH_2O)_{23}OH$	1198	16.9	0.062	40	13[e]	261[e]
Brij-58	$C_{16}H_{33}(CH_2CH_2O)_{20}OH$	1124	15.7	0.0037	~70	30[e]	347[e]

[a] Hydrophile-lipophile balance, Dow Chemical for Tergitols, Aldrich for others.

[b] Critical micelle concentration, for Tergitols (35), others (15).

[c] Aggregation numbers for Tergitols are based on data given in Schick et al. (22); Brij-35 value is from Rosen (25); $C_{16}H_{33}(CH_2CH_2O)_{21}OH$ (aggregation number of 70) is similar to Brij-58.

[d] Calculated from data and analysis (21–24).

[e] Ref. (24).

screw caps and shaken on a Labquake tube shaker (Barnstead International) at room temperature for at least 48 hours to reach equilibrium. After shaking, the solids were allowed to settle before an aqueous sample was taken. All 3-component experiments were run twice, on separate dates, to verify that the settling behavior produced consistent results, and previous work has shown that sorption is not a problem in these systems (7). A comparison of the settling procedure with those of centrifugation and filtration through 0.45 micron PTFE syringe filter (Millipore Corporation) showed the same results. To determine if evaporating the components from the acetone influenced the solubilization behavior, an experiment was run in which 4-NT and 2,6-DNT were weighed as solids separately into vials and equilibrated with NP40. The MSR values obtained in this manner were the same as when both components were evaporated from acetone together.

Aqueous samples were analyzed using a high performance liquid chromatograph (Agilent 1100 Series HPLC) equipped with a C-18 column (Platinum, 100A, $5\,\mu m$, 150 mm by 4.6 mm, Alltech) and a variable wavelength detector set to 254 nm. Samples ($10\,\mu L$) were injected into an eluent of 50% methanol in water for an isocratic separation with a flow rate of 0.75 mL min^{-1}. Retention times were 6 min for TNT, 8 min for 2,6-DNT, and 10 min for 4-NT. This analytical method is a small modification of a technique that has been used successfully for quantifying concentrations of individual nitroaromatic components (7,26).

RESULTS AND DISCUSSION

Solubility behavior was determined for systems containing one, two, or three nitroaromatic compounds. For all combinations of surfactant and nitroaromatic compound(s), the nitroaromatic compound concentration increased linearly with increasing surfactant concentration as demonstrated in Fig. 1 for TNT dissolved into NP13. The slopes of these lines, which represent the MSR, were calculated using least-squares linear regression of at least ten data points and are summarized in Table 2 along with their 99% confidence intervals. The aqueous solubility values and the $\log K_{mic}$ values as calculated from Eqs. 1–3 are also given in Table 2. The error for solubility is the standard deviation of replicate vials and for $\log K_{mic}$ is the propagated error of the MSR and aqueous solubility.

Dissolution from Single-Component Mixtures into Surfactant Solution

Of the 18 MSR values for the single component systems, the confidence intervals of fourteen overlap those reported in the literature (7). For values that did not overlap, the values in Table 2 are all higher than those reported by at most 0.033 for 4-NT, 0.011 for 2,6-DNT, and 0.005 for TNT as are listed in the notes below Table 2. As was found previously, this current study found no trend in MSR with increasing ethoxylate chain length on the Tergitols, and the MSR values for Brij-58 solutions were higher than those of Brij-35 (7). The lack of change in MSR with an increase in ethoxylate chain length was also reported by Tokiwa (27) for the solute Yellow OB. The constant MSR value was reported for the dissolution of the dye in dodecyl polyoxyethylene ethers with oxyethylene chain lengths varying from 7 to 20. He explained this trend by showing that as the surfactant became more nonpolar (shorter EO chain length), more monomers joined to form a micelle (larger aggregation number) and each micelle contained a larger amount of dye. For a given number of monomers (surfactant concentration), fewer micelles were formed, but their larger capacity enabled the MSR to remain constant.

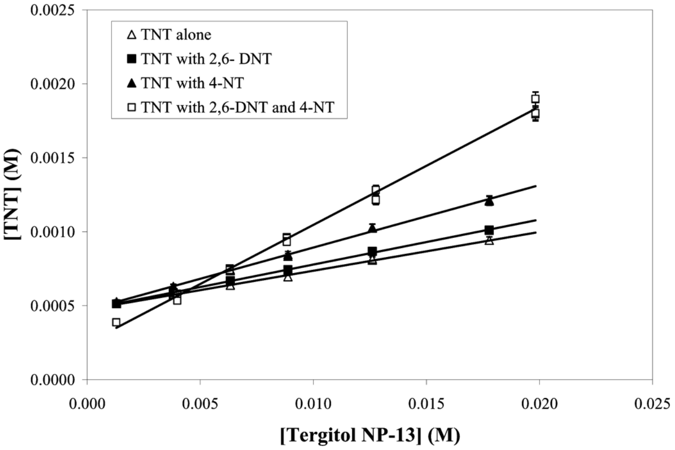

FIG. 1. Solubility of TNT in Tergitol NP-13 solutions when dissolved from single-component and multi-component nitroaromatic compound solids.

Dissolution from Two-Component Mixtures into Surfactant Solution

For all the two-component systems tested, the aqueous solubility values did not vary significantly from the single-component systems values of 305 ± 3, 160 ± 3, 111 ± 2 mg L^{-1} as shown in Table 2 for 21°C. These single-component values are slightly higher than values reported of 295 ± 3 and 151 ± 4 mg L^{-1} for 4-NT and 2,6-DNT at 19 °C, respectively, and 97 ± 3 mg L^{-1} at 20°C, which is expected because solubility increases with temperature (7,26).

The change in the solubility behavior for the two-component system depended on the co-solute and the surfactant. In all but one outlier, the presence of a co-solute either increased the MSR or did not change the MSR of a solute as determined by the 99% confidence intervals. The presence of 4-NT increased the MSR values for 2,6-DNT and TNT in all surfactants (between 13 and 100%) as shown in Fig. 1 for TNT in NP13. The presence

TABLE 2
Molar solubilization ratios (MSR) and micelle-water partition coefficients (K_{mic}) of nitroaromatic compounds dissolved from single-component and multi-component systems (errors are the 99% confidence intervals for slopes and standard deviations for aqueous solubilities)

				Two nitroaromatics			
Surfactant	Temp (°C)	Nitroaromatic	Single nitroaromatic	With 4-NT	With 2,6-DNT	With 2,4,6-TNT	Three nitroaromatics
Brij-35	19	4-NT					
		MSR	0.28 ± 0.03		0.32 ± 0.01	0.32 ± 0.01	0.34 ± 0.01
		log K_{mic}	3.77 ± 0.04		3.74 ± 0.04	3.79 ± 0.01	3.75 ± 0.01
		2,6-DNT					
		MSR	0.12 ± 0.01	0.14 ± 0.004		0.12 ± 0.004	0.12 ± 0.002
		log K_{mic}	3.87 ± 0.02	3.82 ± 0.02		3.82 ± 0.02	3.79 ± 0.01
		TNT					
		MSR	0.020 ± 0.001	0.025 ± 0.001	0.020 ± 0.002		0.028 ± 0.001
		log K_{mic}	3.38 ± 0.02	3.35 ± 0.03	3.33 ± 0.04		3.47 ± 0.01
Brij-58	19.5	4-NT					
		MSR	0.38 ± 0.01		0.40 ± 0.01	0.39 ± 0.01	0.42 ± 0.003
		log K_{mic}	3.86 ± 0.02		3.81 ± 0.02	3.85 ± 0.01	3.81 ± 0.01
		2,6-DNT					
		MSR	0.16 ± 0.01	0.18 ± 0.01		0.16 ± 0.004	0.14 ± 0.01
		log K_{mic}	3.96 ± 0.02	3.86 ± 0.02		3.94 ± 0.01	3.85 ± 0.01
		TNT					
		MSR	0.025 ± 0.003	0.032 ± 0.001	0.029 ± 0.001		0.036 ± 0.002
		log K_{mic}	3.51 ± 0.02	3.44 ± 0.01	3.47 ± 0.02		3.55 ± 0.01
Tergitol NP-10	21	4-NT					
		MSR	0.37 ± 0.02		0.60 ± 0.10	0.41 ± 0.01	0.56 ± 0.04
		log K_{mic}	3.80 ± 0.02		3.92 ± 0.03	3.84 ± 0.01	3.89 ± 0.01
		2,6-DNT					
		MSR	0.12 ± 0.002	0.28 ± 0.05		0.14 ± 0.01	0.18 ± 0.01
		log K_{mic}	3.84 ± 0.01	3.98 ± 0.05		3.85 ± 0.01	3.88 ± 0.03
		TNT					
		MSR	0.023 ± 0.001	0.044 ± 0.003	0.031 ± 0.002		0.068 ± 0.005
		log K_{mic}	3.43 ± 0.01	3.54 ± 0.03	3.48 ± 0.03		3.77 ± 0.02
Tergitol NP-13	21	4-NT					
		MSR	0.35 ± 0.01		0.53 ± 0.04	0.39 ± 0.01	0.61 ± 0.02
		log K_{mic}	3.81 ± 0.01		3.87 ± 0.02	3.82 ± 0.02	3.91 ± 0.01
		2,6- DNT					
		MSR	0.12 ± 0.01	0.24 ± 0.02		0.13 ± 0.004	0.19 ± 0.01
		log K_{mic}	3.83 ± 0.02	3.93 ± 0.03		3.83 ± 0.01	3.88 ± 0.01
		TNT					
		MSR	0.026 ± 0.001	0.042 ± 0.002	0.030 ± 0.001		0.079 ± 0.003
		log K_{mic}	3.45 ± 0.02	3.53 ± 0.02	3.47 ± 0.01		3.81 ± 0.01
Tergitol NP-15	21	4-NT					
		MSR	0.41 ± 0.03		0.45 ± 0.02	0.33 ± 0.02	0.42 ± 0.004
		log K_{mic}	3.83 ± 0.01		3.83 ± 0.01	3.77 ± 0.01	3.81 ± 0.01
		2,6-DNT					
		MSR	0.12 ± 0.004	0.20 ± 0.01		0.12 ± 0.01	0.13 ± 0.003
		log K_{mic}	3.84 ± 0.01	3.98 ± 0.01		3.79 ± 0.03	3.82 ± 0.01

(*Continued*)

TABLE 2
Continued

Surfactant	Temp (°C)	Nitroaromatic	Single nitroaromatic	Two nitroaromatics With 4-NT	Two nitroaromatics With 2,6-DNT	Two nitroaromatics With 2,4,6-TNT	Three nitroaromatics
		TNT					
		MSR	0.025 ± 0.002	0.032 ± 0.003	0.024 ± 0.003		0.050 ± 0.002
		log K_{mic}	3.46 ± 0.03	3.44 ± 0.03	3.38 ± 0.05		3.69 ± 0.01
Tergitol NP-40	21	4-NT					
		MSR	0.28 ± 0.01		0.33 ± 0.01 0.34 ± 0.01	0.30 ± 0.01	0.33 ± 0.01
		log K_{mic}	3.74 ± 0.01		3.74 ± 0.01 3.73 ± 0.01	3.75 ± 0.01	3.74 ± 0.01
		2,6-DNT					
		MSR	0.12 ± 0.01	0.16 ± 0.01 0.16 ± 0.003		0.13 ± 0.01	0.12 ± 0.01
		log K_{mic}	3.83 ± 0.03	3.83 ± 0.01 3.81 ± 0.01		3.84 ± 0.01	3.80 ± 0.01
		TNT					
		MSR	0.023 ± 0.004	0.032 ± 0.004	0.029 ± 0.003		0.031 ± 0.001
		log K_{mic}	3.41 ± 0.06	3.45 ± 0.05	3.45 ± 0.04		3.51 ± 0.01
None	21	4-NT					
		Caq (mg L^{-1})	305 ± 3		312 ± 5	307 ± 3	309 ± 3
		2,6- DNT					
		Caq (mg L^{-1})	160 ± 3	162 ± 3		163 ± 4	133 ± 6
		TNT					
		Caq (mg L^{-1})	111 ± 2	108 ± 2	111 ± 2		83 ± 3

Notes: All values fall within the range of the literature values except for the following which are higher: TNT/Brij-35 $0.020 \pm 0.001 > 0.016 \pm 0.001$; NT/Brij-58 $0.38 \pm 0.01 > 0.359 \pm 0.009$ TNT/NP13 $0.026 \pm 0.001 > 0.021 \pm 0.001$; NT/NP13 $0.35 \pm 0.01 > 0.315 \pm 0.013$ (7).

of 2,6-DNT increased the MSR of TNT and 4-NT by a small amount (8 and 35%) in only the more nonpolar surfactants, NP10 and NP13. An outlier is a small increase in MSR (18%) for 4-NT in NP40. The presence of TNT slightly increased the MSR of 4-NT in NP10 and NP13 (~11%) and the MSR of 2,6-DNT in only NP10 (~17%). For the surfactants where the MSR did not increase much, the K_{mic} values remained the same or declined slightly due to the presence of a co-solute in the micelle. In systems where the solubility was enhanced to a greater extent, the K_{mic} values for all solutes remained the same or rose slightly in those surfactants.

The enhancement in solubility of one component in the presence of another component has been found for other systems. The presence of naphthalene was shown to enhance the solubility of phenanthrene in Triton X-100 solutions (14), and the presence of propyl paraben was found to increase the solubility of methyl paraben in solutions of the nonionic surfactant cetomacrogol (20). These enhancements have been attributed to a change in the micellar structure, which allowed for more solute to be solubilized (14,20)

Dissolution from Three-Component Mixtures into Surfactant Solution

For the three-component system, the aqueous solubility of 2,6-DNT and TNT was less than that of the single-component system. The lowering of aqueous solubility when dissolving from 3-component solids has also been found in polycyclic aromatic hydrocarbon (PAH) systems where the solubility of fluoranthene when dissolved from a solid mixture containing fluoranthene, phenanthrene, and pyrene was lower than the solubility when dissolved from single-component or two-component systems containing these compounds (15). Such behavior can be attributed to the formation of nonaqueous phase liquids (NAPLs) or the formation of solid solutions (28). The 3-component nitroaromatic compound mixture took the form of solid crystals prior to mixing with the aqueous phase but became semisolid after mixing with the solution.

This semi-solid was not a NAPL, because NAPL formation would result in the solubility of all components to decline to a value proportional to their mole fraction in the liquid phase, which was not the case here.

The MSR values in the three component system equaled or were greater than those in the single-component systems. For TNT, the MSR was enhanced over the single component values for every surfactant (24 to 180%) as demonstrated in Fig. 1 for NP13 and to levels higher than the two-component systems, except for NP40 where the levels were the same as when 4-NT was a co-solute. For 2,6-DNT, the MSR values were only enhanced over single-component values for NP10 and NP13 (>50% increase), and these increases were similar to those found for the 2-component systems. For 4-NT, increases were found for all surfactants except for the outlier NP15, but only NP10 and NP13 were greater than 50%. NP15 and NP40 enhancements were similar to those found for 2-component systems. As in the two-component system, the K_{mic} values remained the same or declined slightly due to the presence of a co-solutes in the micelle for surfactants with small changes in MSR, but K_{mic} values for all solutes remained the same or rose slightly in systems where the MSR increased to a greater extent.

Unlike the single component system that showed no variation of MSR with surfactant structure, the general trend in MSR for the 3-component system is that the MSR values decreased as the surfactant HLB increased, except that below an HLB of 13.9, the MSR decreased again. The presence of a "maximum point" in MSR when ethoxylate chain length is varied has been seen by other researchers. Diallo et al. (29) reported maximum MSR values for benzene at an HLB of 15, for toluene at 14, and for o-xylene at 13.5 when solubilized in dodecyl alcohol ethoxylates. Direct comparison between the two systems, however, is complicated by the fact that they were solubilizing liquid organic compounds, whose partitioning behavior may be different. As in the two component systems, the increase in MSR may be attributable to a change in micelle structure, as will be discussed below.

Locus of Solubilization

Solubilization behavior is often explained in terms of the location of the solute within the micelle. Mukerjee proposed a two-state model, which divides the micelle into a hydrophobic core consisting of the nonpolar chain of the surfactant and an "interfacial" region outside the core (shell) consisting of the polar portion of the surfactant chain [(summary in (25)]. More detailed versions subdivide the interfacial region into the micelle-solvent interface, between the hydrophobic head groups on the nonionic surfactants, between the hydrophilic head groups and the first few carbons of the core (palisade layer), and more deeply in the palisade layer (25). No research has established the location of nitroaromatic compounds within micelles, but work has been conducted on aromatic compounds such as benzene and PAHs (e.g 19,30). Based on the behavior of other aromatic compounds and the MSR data presented herein, the behavior of nitroaromatic compounds within the micelle can be speculated.

One way to assess if these nitroaromatic compounds are located in the micellar core is to compare the volume of the micellar core with the amount of solute in each micelle, which can be calculated by multiplying MSR by aggregation number of the surfactant. The decline in micellar core volume and amount of solute per micelle in the three-component system as a function of surfactant HLB are shown in Figs. 2a and 2b along with power-law correlations of the parameters in the form

$$\text{Parameter} = \text{a HLB}^{\text{b}} \tag{4}$$

Diallo et al. (29) used this functional form when speculating on the location of linear alkanes in dodecyl alcohol

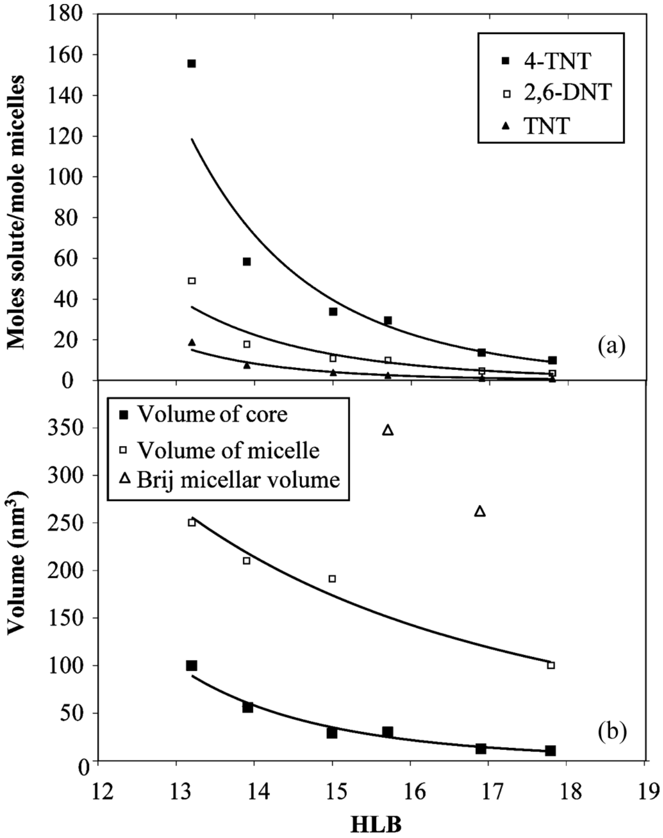

FIG. 2. (a) Mols of solute per mol of surfactant micelles for the three-component system. Lines shown are power-law fits: mols 4-NT/mole micelle = 5.0×10^{11} HLB$^{-8.6}$; moles 2,6-DNT/mole micelle = 4.2×10^{10} HLB$^{-8.1}$; and moles TNT/mole micelle = 2.6×10^{12} HLB^{-10}. (b) The volume of the whole micelle and the core of the micelle. Lines are exponential fits of all the core data, V_{core} (nm^3) = 1.3×10^{10} HLB$^{-7.3}$ and only the micelle volume of the Tergitol surfactants, $V_{micelle}$ (Tergitols, nm^3) = 6.2×10^5 HLB$^{-3.0}$.

ethoxylates. A similar value of the exponent, b, in both their experiment results and the core volume led them to hypothesize that the linear alkanes were located in the core of the micelle, which was consistent with other researchers (29). Values of *a* and *b* are given in Table 3 for the core volume of an empty micelle, the micellar volume of an empty micelle, and the amount of solute per micelle for the single-component and three-component nitroarene systems. For the surfactants used herein, the exponent on HLB for the core volume is −7.3. When examining the dependence of the mols of solute per mol micelles on HLB, it can be seen that the dependence on HLB for the nitroaromatic compounds in the single-component systems is similar with exponents of −6.4 to −7.5, which may be caused by the solutes partitioning into the core at these low solute concentrations. For the 3-component system, however, the values are more negative, ranging from −8.1 to −10. These results suggest that either the micelle core is growing at different amounts for different surfactants to accommodate more solute or that the location of the solute may be changing, thereby altering the functional dependence on HLB (19,30).

If the nitroaromatic compounds spread throughout the micelle, then the amount solubilized should depend on the micellar volume, resulting in a similar functional dependence of both on HLB. As can be seen in Fig. 2b, the micellar volume does not follow a pattern with HLB with the micellar volume of Brij-35 and Brij-58, at HLB values of 15.7 and 16.9, being much higher than those of the Tergitols. Also, the power-law fit of the Tergitol micellar volumes produces an exponent of −3.0 for HLB, which is much smaller than those of the nitroaromatic compounds. This suggests that the nitroaromatic compounds are not spread throughout the micellar volume.

Researchers have found that solutes can reside in several locations, and the distribution of the solute has been found to depend on the solute concentration and the surfactant. In the nonionic surfactant Triton X-100, benzene was found to populate the micellar shell at low benzene concentrations and spread to the core at higher benzene concentrations (summary by (30)). For PAHs, the surfactant ethoxylate chain length has been found to influence the distribution of solute between the locations in a nonionic surfactant micelle. In a study of the dissolution of naphthalene and phenanthrene from a hexane solution into surfactant solutions, it was found that in the more nonpolar Brij-30 ($C_{12}H_{25}(CH_2CH_2O)_4OH$) and Tergitol NP-10, the PAHs distributed themselves in both the micellar core and micellar shell at all PAH concentrations tested. In contrast, in the less nonpolar Brij-35, the PAHs preferentially occupied the micelle shell at low concentration and the shell and core at higher concentrations (17,19). In their case, the MSR values of the PAHs were higher in Tergitol NP10 system than in the Brij-35 system. It is likely that the concentration of nitroaromatic compounds studied here represents a "high" concentration for all surfactants tested. If the nitroaromatic compounds behave similarly to benzene and PAHs, they are likely to be located in the shell and the core.

TABLE 3

Power-law fits of the functional dependence of micellar volume, core volume, and mols of solute per mol micelles on surfactant HLB, parameter = a HLB^b, along with the coefficient of determination, R^2

Parameter	a	b	R^2
Core volume	1.3×10^{10}	−7.3	0.97
Micellar volume (Tergitols only)	6.2×10^{5}	−3.0	0.97
Single component system			
Mols 4-NT per mol micelles	2.0×10^{10}	−7.5	0.91
Mols 2,6-DNT per mol micelles	3×10^{8}	−6.4	0.87
Mols TNT per mol micelles	2×10^{8}	−6.7	0.93
Three component system			
Mols 4-NT per mol micelles	5.0×10^{11}	−8.6	0.96
Mols 2,6-DNT per mol micelles	4.2×10^{10}	−8.1	0.95
Mols TNT per mol micelles	2.6×10^{12}	−10	0.98

Further support for some of the nitroaromatic molecules being located near the "interfacial region" between the core and the shell of the micelle is that the MSR values in the multi-component system remained the same or increased over those of the single-component systems. While a constant MSR could suggest that the solutes are occupying different locations within the micelle or the co-solute is occupying space between the solute molecules, an increasing MSR requires that the micelle expand to accommodate a greater volume (12,14,31). Micellar expansion can occur when a solute lowers the interfacial tension at the surfactant hydrophilic tail-polar shell interface by positioning itself at interfacial region of the hydrophobic core of the micelle, which has been demonstrated for benzene (32,33). This can occur for single-ring aromatic compounds because they are slightly polar due to the resonance of the pi-electrons in the aromatic ring (34). If the expansion depends on the amount solubilized, it makes sense that the presence of 4-NT, which was solubilized to a greater extent than the others, increased the MSR values of 2,6-DNT and TNT for all surfactants in both the two-component and three-component systems. It would also make sense that TNT, which is solubilized the least, would see the most enhancement by the presence of the other compounds.

In conclusion, this study shows that the MSR values of 4-NT, 2,6-DNT, and TNT when solubilized from 2-component or 3-component mixtures into non-ionic surfactant solutions remain the same or increase over the single-component values. Increases in MSR are generally found for the more nonpolar surfactants, NP10 and

NP13. Power-law correlations generated for the micellar volume, the micellar core volume, and mols of solute per mol micelles as a function of surfactant HLB show that in single-component systems, the dependence on HLB is similar for the micellar core volume and the mols of solute per mol micelles. In the three-component system, however, neither the micellar volume nor the core volume are similar to the mols of the solute per mol of micelles. The result that MSR increases in the multi-component system requires that the micelle volume increase. This may be caused by the solutes locating themselves at the hydrophobic tail-polar shell interface, where they can lower the interfacial tension and allow for the expansion. Since no measurements were made to determine the location of these solutes in these surfactants, these conclusions are based on conjecture. Future work will involve using spectroscopic techniques to help determine the location.

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REFERENCES

1. Hashimoto, A.; Sakino, H.; Kojima, T.; Yamagami, E.; Tateishi, S.; Akiyama, T. (1982) Sources and Behavior of Dinitrotoluene Isomers in Sea-water. *Water Res.*, 16 (6): 891.
2. National Institute for Occupational Safety and Health. (1985) Current Intelligence Bulletin 44: Dinitrotoluenes; DHHS (NIOSH) Publication No. 85–109: Cincinnati, OH.
3. Hodgson, J.; Rho, D.; Guiot, S.R.; Ampleman, G.; Thiboutot, S.; Hawari, J. (2000) Tween 80 enhanced TNT mineralization by *Phanerochaete chrysosporium*. *Can. J. Microbiol.*, 46 (2): 110.
4. Larson, R.A.; Jafvert, C.T.; Bosca, F.; Marley, K.A.; Miller, P.L. (2000) Effects of surfactants on reduction and photolysis (>290 nm) of nitroaromatic compounds. *Environ. Sci. Technol.*, 34 (3): 505.
5. Diehl, C.A.; Jafvert, C.T.; Marely, K.A.; Larson, R.A. (2002) Surfactant-assisted UV-photolysis of nitroarenes. *Chemosphere*, 46 (4): 553.
6. Boopathy, R. (2002) Effect of food-grade surfactant on bioremediation of explosives-contaminated soil. *J. Hazard Mater.*, 92 (1): 103.
7. Luning Prak, D.J. (2007) Solubilization of nitrotoluenes in micellar nonionic surfactant solutions. *Chemosphere*, 68 (10): 1961.
8. Knox, R.C.; Sabatini, D.A.; Harwell, J.H.; Brown, R.E.; West, C.C.; Blaha, F.; Griffin, C. (1997) Surfactant remediation field demonstration using a vertical circulation well. *Ground Water*, 35 (6): 948.
9. Svab, M.; Kubal, M.; Muellerova, M.; Raschman, R. (2009) Soil flushing by surfactant solution: Pilot-scale demonstration of complete technology. *J. Hazard Mater.*, 163 (1): 410.
10. Lovgren, T.; Heikius, B.; Lundberg, B.; Sjoblom, L. (1978) Simultaneous solubilization of steroid hormones I: Estrogen and C21 steroids. *J. Pharm. Sci.*, 67 (10): 1419.
11. Schott, H.; Sayeed, F.A.A. (1986) Micellar solubilization of cholesterol and of mixtures of cholesterol with cholesterol esters of C18 fatty acids by a nonionic surfactant. *J. Colloid Interf. Sci.*, 112 (1): 144.
12. Jacobson, A.M.; Casassa, E.Z. (1991) Multicomponent solubilization in aqueous micelles of dodecyl-and tetradecyltrimethylammonium bromide: Solubilization equilibria. *J. Colloid Interf. Sci.*, 142 (2): 480.
13. Kumar, S.; Singh, H.N. (1992) Competitive solubilization of Sudan IV and anthracene in micellar systems. *Collid. Surface*, 69 (1): 1.
14. Guha, S.; Jaffe, P.R.; Peters, C.A. (1998) Solubilization of PAH mixtures by a nonionic surfactant. *Environ. Sci. Technol.*, 32 (7): 930.
15. Luning Prak, D.J.; Pritchard, P.H. (2002) Solubilization of polycyclic aromatic hydrocarbon mixtures in micellar nonionic surfactant solutions. *Water Res.*, 36 (14): 3463.
16. Hill, A.; Ghoshal, S. (2002) Micellar solubilization of naphthalene and phenanthrene from nonaqueous phase liquids. *Environ. Sci. Technol.*, 36 (18): 3901.
17. Bernardez, L.A.; Ghoshal, S. (2004) Selective solubilization of polycyclic aromatic hydrocarbon from multicomponent nonaqueous-phase liquids into nonionic surfactant micelles. *Environ. Sci. Technol.*, 38 (22): 5878.
18. Matsuoka, K.; Hirosawa, T.; Honda, C.; Endo, K.; Moroi, Y.; Shibata, O. (2007) Thermodynamic study on competitive solubilization of cholesterol and β-sitosterol in bile salt micelles. *Chem. Phys. Lipids*, 148 (1): 51.
19. Bernardez, L.A. (2008) Investigation on the locus of solubilization of polycyclic aromatic hydrocarbons in non-ionic surfactant micelles with 1H NMR spectroscopy. *Colloid. Surface. A*, 324 (1–3): 72.
20. Crooks, M.J.; Brown, K.F. (1973) A note on the solubilization of preservative mixtures by cetomacrogol. *J. Pharm. Pharmacol.*, 25 (4): 281.
21. Becher, P. (1961) Nonionic surface-active compounds IV. Micelle formation by polyoxyethylene alkanols and alkyl phenols in aqueous solutions. *J. Colloid Sci.*, 16 (1): 49.
22. Schick, M.J.; Atlas, S.M.; Eirich, F.R. (1962) Micellar structure of non-ionic detergents. *J. Phys. Chem.*, 66 (7): 1326.
23. Birdi, K.S. (1974) Determination of size and shape of micelles by gel filtration chromatography. *Polym. Sci.*, 252 (718): 551.
24. Saitoh, T.; Hoshino, H.; Yotsuyanagi, T. (1994) Volume constraint effect on solute partitioning to Triton X-100 micelles in water. *J. Chem. Soc. Faraday Trans.*, 90 (3): 479.
25. Rosen, M.J. (2004) *Surfactant and Interfacial Phenomena*, 3rd Ed.; John Wiley: New York.
26. Luning Prak, D.J.; O'Sullivan, D.O. (2007) Solubility of 4-nitrotoluene, 2,6-dinitrotoluene, 2,3-dinitroluene, and 1,3,5-trinitrobenzene in pure water and seawater. *J. Chem. Eng. Data*, 52 (6): 2446.
27. Tokiwa, F. (1968) Solubilization behavior of sodium dodecylpolyoxyethylene sulfates in relation to their polyoxyethylene chain lengths. *J. Phys. Chem.*, 72 (4): 1214–1217.
28. Peters, C.A.; Wammer, K.H.; Knightes, C.D. (2000) Multicomponent NAPL solidification thermodynamics. *Transp Porous Med.*, 38 (1–2): 57.
29. Diallo, M.S.; Abriola, L.M.; Weber, Jr. W.J. (1994) Solubilization of nonaqueous phase liquid hydrocarbons in micellar solutions of dodecyl alcohol ethoxylates. *Environ. Sci. Technol.*, 28 (11): 1829.
30. Atwood, D.; Florence, A.T. (1983) *Surfactant Systems: Their Chemistry and Biology*; Chapman and Hall: London, U.K.
31. Lundberg, B.; Lovgren, T.; Heikius, B. (1979) Simultaneous solubilization of steroid hormones II: androgen and estrogens. *J. Pharm. Sci.*, 68 (5): 542.
32. Mukerjee, P.; Cardinal, J.R. (1978) Benzene derivatives and naphthalene solubilized in micelles. Polarity of microenvironment, location and distribution in micelles, and correlation with surface activity in hydrocarbon-water systems. *J. Phys. Chem.*, 82 (14): 1620.
33. Nagarajan, R.; Chaiko, M.A.; Ruckenstein, E. (1984) Locus of solubilization of benzene in surfactant molecules. *J. Phys. Chem.*, 88 (13): 2916.
34. Hornback, J.M. (2006) *Organic Chemistry*, 2nd Ed.; Thomson Brooks/Cole: Belmont, CA.
35. Pennell, K.D.; Adinolfi, A.M.; Abriola, L.M.; Diallo, M.S. (1997) Solubilization of dodecane, tetrachloroethylene, and 1,2, dichlorobenzene in micellar solutions of ethoxylated nonionic surfactants. *Environ. Sci. Technol.*, 31 (5): 1382.