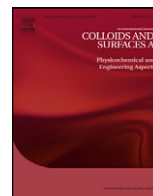




Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

An ^1H NMR investigation into the loci of solubilization of 4-nitrotoluene, 2,6-dinitrotoluene, and 2,4,6-trinitrotoluene in nonionic surfactant micelles

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ARTICLE INFO

Article history:

Received 30 August 2010

Received in revised form 4 November 2010

Accepted 9 November 2010

Available online 18 November 2010

Keywords:

Aggregation number

Tritons

Tergitols

Brij

Nitroaromatics

NMR

ABSTRACT

In this study, the enhancement in solubility of 4-nitrotoluene (4-NT), 2,6-dinitrotoluene (2,6-DNT), and 2,4,6-trinitrotoluene (TNT) and their loci of solubilization were determined in nonionic surfactant solutions containing linear alcohol ethoxylates (Brij-35, Brij-58, Brij-78, Brij-97 and Brij-98), alkylphenol ethoxylates (Tergitol NP-8 to NP-40), and octylphenol ethoxylates (Triton X-100, X-165, and X-305). In all surfactant solutions, 4-NT had the highest molar solubilization ratio (MSR) and TNT the lowest. For all surfactants, increasing the number of ethoxylate groups (EO) while keeping the hydrocarbon chain length constant decreased or did not significantly change the MSR. To determine the locus of solubilization, ^1H NMR spectroscopy was used to determine how the presence of a nitroaromatic solute changed the chemical shifts of the various hydrogen atoms on the surfactant molecule. For the linear alcohol ethoxylates, the greatest change in chemical shift for all three nitroarenes occurred at hydrogens in the hydrocarbon core of the micelle. At higher solute concentration, the nitroarenes spread to the first EO group near the core/shell interface. For both the Tritons and Tergitols, the chemical shift for a hydrogen on the phenyl ring changed the most upon the addition of the nitroarenes. As the nitroarene concentration increased, the chemical shifts for the hydrogens on the first EO group changed for all Triton and Tergitol surfactants. For all surfactants with shorter EO chains, the shifts for all ethoxylate hydrogens changed at higher nitroarene concentration. These results suggest that the solutes are preferentially solubilized at the core/shell interface but spread further into the shell and the core as solute concentration increases.

Published by Elsevier B.V.

1. Introduction

Nitroaromatic compounds are used in the production of explosives, urethanes, and dyes, and exposure to these compounds can cause health problems due to their toxicity and carcinogenicity (e.g. [1]). These compounds can become pollutants when they enter natural systems from corroded unexploded munitions casing, leaking storage tanks, or poorly managed disposal facilities. The treatment of industrial wastes from nitroaromatic production and the removal and/or treatment of nitroaromatic pollutants can involve dissolution, precipitation, biodegradation, photolysis, or other oxidative processes [2,3]. Some of these processes may involve using surfactants at concentrations high enough to form micelles. For example, surfactants have been found to enhance biological transformation, chemical photolysis, and aqueous solubility of nitroarenes [4–9]. Factors that influence the success of surfactants in these applications are the location of the solute in the

surfactant micelle and the amount that solubility is enhanced by the surfactant micelle.

Researchers have used X-ray diffraction, ultraviolet spectroscopy, fluorescence spectroscopy, and NMR spectroscopy to determine the location of an organic compound in a micelle (see [10] for summary). Proton NMR spectroscopy can be used to infer the location of a solute in a micelle by comparing the spectrum of the micellar solution containing the solute with that of a micellar solution with no solute. Shifts in the location of specific peaks in the spectra suggest that the local environment surrounding the corresponding hydrogen atom has changed, presumably due to the presence of the solute near that hydrogen. For low concentrations of certain compounds, no change in the proton chemical shift may be observed [11]. Proton NMR spectroscopy was used as early as the 1960s to study the structure and hydration of micelles in the presence and absence of solutes [12–15]. More recent applications can be found in the fields of biochemistry, where NMR spectroscopy has been used to investigate the interaction of cellular materials and micelles formed from biosurfactants or synthetic surfactants that are used as “membrane mimics” (such as sodium dodecyl sulfate) [16–20], and environmental engineering, where NMR spectroscopy can be used to determine where a pollutant is located in surfactant micelles that can be used

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with pump and treat operations to enhance pollutant removal [11,21,22].

Studies using ^1H NMR spectroscopy have shown that saturated hydrocarbons are located in the nonpolar interior or core of ionic and nonionic micelles, while the location of unsaturated hydrocarbons such as benzene and polycyclic aromatic hydrocarbons (PAHs) vary with surfactant type [10,13,22–24]. Wasylshen et al. [23] reported that benzene and naphthalene resided near the head group of cationic surfactants but were evenly distributed throughout a sodium dodecyl sulfate micelle. These results agree with work by Eriksson and Gillberg [13], who reported NMR studies that showed that benzene, *N,N*-dimethylaniline and nitrobenzene were located at the micelle–water interface of cationic cetyltrimethylammonium bromide. For nonionic surfactants, Bernardez [22] found that PAHs were solubilized in both the nonpolar core and the polar exterior or shell region of the micelle. This conclusion supports work by Stilbs [24] who reported based on his NMR data that it is reasonable to expect aromatics such as benzene to be solubilized in the polar and nonpolar region of the micelle. Very few studies have investigated the locus of solubilization of nitroaromatic compounds [13].

Solubility enhancement can be quantified by determining the increase in solute concentration at one surfactant concentration or at several surfactant concentrations. In the latter case, the enhancement in solubility as a function of surfactant concentration has been represented as the molar solubilization ratio (MSR) in which both the surfactant and solute concentrations are given in units of molarity, or less commonly as the weight solubilization ratio (WSR) in which both the surfactant and solute concentrations are given in mass per volume. Both ratios are determined from the slope of the plot of solute concentration versus surfactant concentration. Variations in surfactant structure change the value of MSR. In general, as a nonionic surfactant becomes more polar by decreasing the length of the nonpolar chain, the MSR of some solutes such as aliphatic hydrocarbons tends to decrease [10,25]. For several nitroaromatic compounds, the MSR values were higher for Brij-58 with a nonpolar chain of 16 carbons than for Brij-35 with a nonpolar chain of 12 carbons [8]. When the nonionic surfactant becomes more polar by lengthening the ethoxylate chain, which increases the number of ethoxylate (EO) groups $\text{C}_2\text{H}_4\text{O}$, the MSR has been shown to increase, decrease, or remain the same depending on the solute [10,25]. For nitroaromatic compounds, the MSR values did not systematically vary when the nonpolar ethoxylate chain on Tergitol (nonylphenol ethoxylate) surfactants was increased from 10 to 40 EO units [8].

While some solubility enhancement has been quantified for several nitroaromatic compounds, very little work has examined the locus of solubilization. The objective of this study, therefore, was to investigate how nonionic surfactant structure influences the locus of solubilization of 4-nitrotoluene, 2,6-dinitrotoluene, and 2,4,6-trinitrotoluene in micellar solutions of nonionic surfactants. Surfactant structures that vary in both the nonpolar chain and ethoxylate chain were examined.

2. Materials and methods

2.1. Materials

Three solid nitroaromatic compounds, 4-nitrotoluene (4-NT, $\text{C}_6\text{H}_4(\text{CH}_3)\text{NO}_2$, 137.1 g mol^{-1} ; 99% pure, Aldrich), 2,6-dinitrotoluene (2,6-DNT, $\text{C}_6\text{H}_3(\text{CH}_3)(\text{NO}_2)_2$, 182.14 g mol^{-1} ; 98% pure, Aldrich), and 2,4,6-trinitrotoluene (TNT, $\text{C}_6\text{H}_2(\text{CH}_3)(\text{NO}_2)_3$, 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. Stock solutions were prepared in acetone (Fisher Scientific) and

aliquots of the stock were placed in vials and allowed to evaporate forming a solid mass of each nitroarene.

To systematically examine surfactant structure, nonionic surfactants were selected that varied in both the length of the nonpolar portion and the polar portion of the molecule. The surfactants included polyoxyethylenated straight-chain alcohols (Brij-35, Brij-58, Brij-78, Brij-97, Brij-98; Aldrich Chemical, standard grade), nonylphenol ethoxylates [Tergitol NP-8 (<0.3% water), Tergitol NP-10 (<0.3% water), Tergitol NP-15 (<0.5% water), and Tergitol NP-40 (<1.0% water) from Dow Chemical] and octylphenol ethoxylates [Triton X-100, Triton X-165 (70% solution), and Triton X-305 (70% solution) from Sigma Aldrich]. Relevant properties are listed in Table 1 including the empty total and core volumes, which were calculated using methods from Elworthy and Patel [26] and Tanford [27] or from values reported in the literature. The core volumes provided for the Tergitol surfactants were based on nonylphenols that may be structural isomers of the ones used in the current study. To examine the locus of solubilization of the nitroarenes, solutions of all the surfactants were prepared in D_2O (Aldrich) at concentrations of approximately 9 g L^{-1} . Experiments were not run with 4-NT and Tergitol NP-8 because 4-NT lowers the cloud point of Tergitol NP-8 to at or below room temperature [8]. To examine solubility enhancement, solutions of some of these surfactants (Triton X-100, Triton X-165, Triton X-305, Brij-78, Brij-97, and Brij-98) ranging in concentration from 1.0 to 10.0 g L^{-1} were made in 18 M Ω MilliQ water (de-ionized water purified by a Millipore MilliQ Plus water system). For the other surfactants, the solubility enhancement as a function of surfactant concentration has been reported previously (all four Tergitol surfactants, Brij-35 and Brij-58 [8]).

2.2. Methods

To determine the solubility of the nitroaromatic compounds in surfactant solutions, batch mixing experiments were conducted following the procedure in Luning Prak [8]. After mixing the solids with the surfactant, the solids were allowed to settle before an aqueous sample was taken. Previous work has shown that sorption is not a problem in these systems [8], and comparison of the settling procedure with those of centrifugation and filtration through 0.45 micron PTFE syringe filter (Millipore Corporation) showed the same results. Aqueous samples were analyzed using a high performance liquid chromatograph (Agilent 1100 Series HPLC) equipped with a C-18 column (Platinum, 100A, $5\ \mu\text{m}$, 150 mm by 4.6 mm, Alltech) and a variable wavelength detector set to 254 nm. Samples (10 μL) 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 nitroaromatic components [9].

Samples containing nitroaromatic compounds dissolved in surfactant solutions made using D_2O were also analyzed by ^1H NMR spectroscopy using a JEOL ECX 400-MHz Nuclear Magnetic Resonance Spectrometer to determine proton chemical shifts. Proton measurements for each surfactant were taken sequentially at 20°C with the surfactant solution with no nitroaromatic solute taken at the beginning and end of the run to determine the precision. As an external reference, a D_2O solution containing 0.75 wt% 3-(trimethylsilyl) propionic acid-2,2,3,3,- d_4 acid sodium salt (TSP) was used in a coaxial tube and assigned to 0 ppm. The presence of the surfactant shifted the HDO peak from that of pure deuterated water, but the addition of the nitroaromatic to the surfactant solution did not change the HDO peak relative to the surfactant only solution within the precision of the instrument. The NMR was equipped with a T10 pulse-field gradient probe that was tuned to ^1H . For these experiments, 8 scans were acquired using a 45%

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