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SITE OF DYE SOLUBILIZATION IN SURFACTANT MICELLES

ABSTRACT

Comparisons of visible spectra of fluorinated analogs of the dye Orange OT and two of its isomers in dodecane, in a pyridine/water mixture, in micelles of dodecylpyridinium bromide, and in micelles of cetylpyridinium chloride suggest that the solubilized dye molecules prefer an environment which is more polar than that of the micelle's hydrocarbon core. Comparisons of nuclear magnetic resonance spectra of the dyes in deuterated pentane, in a pyridine/D₂O mixture, and in micelles of dodecylpyridinium bromide lead to the same conclusion.

Key words: dyes, surfactants, micelles, visible spectra, NMR spectra.

INTRODUCTION

The ability of a surfactant to greatly increase the water solubility of a variety of substances is undoubtedly associated with its tendency to form micelles. In fact, this phenomenon is the basis for the employment of dyes in determining critical micelle concentrations (Mukerjee and Mysels 1971). At concentrations below its critical micelle concentration (CMC), a surfactant is present in solution primarily in the form of monomeric surfactant ions and counterions and has little influence on the solubilities of other solutes. Above the CMC, most of the surfactant added to a solution aggregates to form micelles which readily solubilize dyes. Micelles occur in various sizes and shapes. Those involved in the present study are spherical and have aggregation numbers between 70 and 140.

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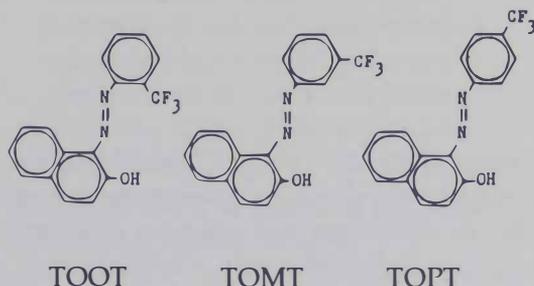
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The primary goal of our research was to augment our knowledge of dye solubilization sites in micelles. According to Fendler and Fendler (1975), "Although no quantitative description of the mechanism of solubilization is available, a knowledge of the location of the solubilize in the micelle is necessary for an understanding of micellar catalysis...The use of micelles in synthetic organic chemistry to alter the yields and reaction pathways has great potential." The possibility that micelles could serve as models for enzymes has stimulated considerable research (Hiemenz, 1986). Fendler and Fendler (1975) have warned, however, that "...ample evidence is accumulating which renders aqueous micelles to be relatively poor models for complex bioorganic interactions."

A number of investigators have used nuclear magnetic resonance (NMR) spectroscopy to investigate solubilization sites in micellar systems. Fendler and Fendler (1975) discussed and provided references for the initial research in this area. Lindman, Olsson and Söderman (1995) reviewed recent NMR studies of surfactant solutions. We

decided to employ the technique in an attempt to learn something about the orientation in micelles of solubilized fluorinated analogs of Orange-OT isomers. The dyes have the following structures:



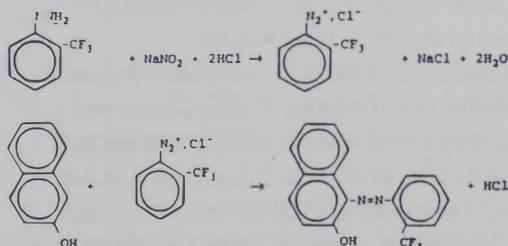
We also wanted to see what could be learned from visible spectrophotometry, a tool successfully employed by Jacobs, Geer and Anacker (1972) to gain information about the environment of the dyes Orange OT and dimethyl-aminoazobenzene in solutions containing micelles of tetradecylpyridinium chloride. Fendler and Fendler (1975) and Hiemenz (1986) provided references to some of the other investigations that used this technique to learn something about solubilization sites in micelles.

EXPERIMENTAL

Since 1-(α,α,α -trifluoro-2-tolylazo)-2-naphthol,

1-(α,α,α -trifluoro-3-tolylazo)-2-naphthol, and

1-(α,α,α -trifluoro-4-tolylazo)-2-naphthol, i.e., TOOT, TOMT, and TOPT, respectively, were prepared by similar procedures, we provide details for the preparation of only the first dye. The pertinent reactions are:



A solution containing 0.10 mole of 2-aminobenzotrifluoride (Aldrich), 25 ml of concentrated hydrochloric acid, and 40 ml of H_2O was prepared. To it were added 100 g of ice. Then 70 g more of ice and a solution containing 0.10 mole of $NaNO_2$ in 50 g H_2O were added with stirring. The resulting mixture was then added with vigorous stirring to a mixture of 100 g of ice and a solution containing 0.10 mole of β -naphthol (MCB), 40 g KOH and 100 ml H_2O . A yellow precipitate formed immediately. After about 45 minutes of continuous stirring, the reaction mixture was filtered. The solid obtained (crude TOOT) was washed with water and dried overnight at $\sim 70^\circ C$. The TOOT was then recrystallized twice from ethanol and vacuum dried at $70^\circ C$. The TOOT, TOMT, and TOPT crystals prepared had melting points of 161-162, 172-173, and 143-143.8 $^\circ C$, respectively.

The dodecylpyridinium bromide monohydrate (DPB) was part of a batch prepared for earlier work (Jacobs, Geer and Anacker 1972). The cetylpyridinium chloride monohydrate (CPC) was purchased from Acros Organics, the pyridine and n-dodecane from Lancaster, the deuterium oxide and the deuterated n-pentane from Cambridge Isotope Laboratories, and the acetone from Fisher Scientific. Reagent grade sodium bromide and sodium chloride were obtained from Malinckrodt and Baker, respectively. Water used in solution preparation was distilled from alkaline permanganate. Pyridine/water mixtures were prepared by mixing equal volumes of pyridine and water. Solutions containing CPC were examined while several degrees above room temperature to prevent crystallization of the surfactant. In the NMR work, solutions of the dyes in deuterated n-pentane and in pyridine/ D_2O mixtures were saturated.

A Cary 219 spectrophotometer was employed to obtain visible spectra and a Bruker DRX500 MHz spectrometer

tuned to ^{19}F was used in the NMR work. The NMR experiments were run at 300 K. Freon-113 was used as an external reference.

RESULTS AND DISCUSSION

We used dye concentrations such that the likelihood that any micelle would contain more than one solubilized dye molecule was small. According to an earlier study (Anacker 1958), the CMC of CPC in 0.500 M NaCl is 4.7×10^{-5} M and the micelles in this medium have an aggregation number close to 136. This means that the micelle concentration in the CPC solutions (0.0600 M CPC, 0.500 M NaCl and $\sim 1.03 \times 10^{-4}$ M dye) used in our studies was (0.0600 - 0.000047)/136 M, i.e., 4.4×10^{-4} M. The ratio of dye molecules to micelles was therefore $1.03 \times 10^{-4}/4.4 \times 10^{-4} = 0.23$. Using the CMC and aggregation number of DPB in 0.500 M NaBr from another study (Jacobs, Geer, and Anacker 1972), one calculates a ratio of 0.13 for the number of dye molecules to DPB micelles in the present work. Dye molecules experienced no overcrowding!

Visible spectra obtained in this research are displayed in Figures 1-3. Since a switch from DPB with twelve carbons in the hydrocarbon chain to CPC with sixteen carbons in the hydrocarbon chain had little effect on any spectrum, we can conclude that a dye molecule had considerable freedom in making a site selection within the micelle. Spherical CPC micelles have diameters of about 55 Å (Anacker 1958). This is substantially greater than the maximum dimension possessed by any of the dyes.

Dye spectra obtained in the presence of surfactants have features (wavelength at which the absorption maximum occurs and its height relative to that of the adjacent and shorter wavelength shoulder) which resemble more closely those obtained in the pyridine/water mixture than those obtained with

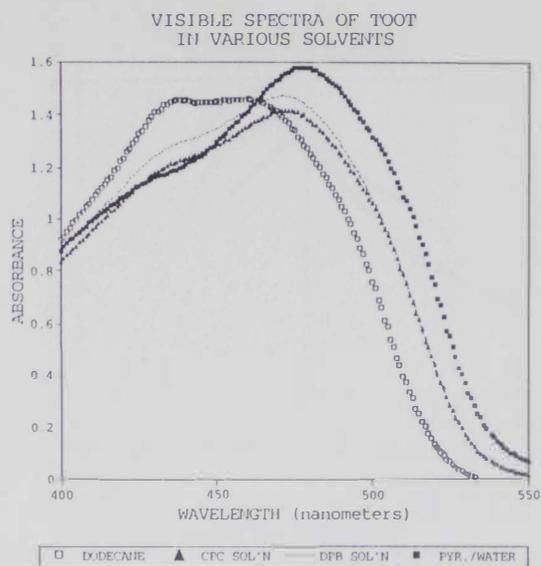


Figure 1. Visible spectra of TOOT in dodecane, pyridine/water (50% each by volume), aqueous cetylpyridinium chloride solution (0.0600 M CPC, 0.500 M NaCl), and aqueous dodecylpyridinium bromide solution (0.0606 M DPB, 0.500 M NaBr). TOOT concentration = 1.024×10^{-4} M.

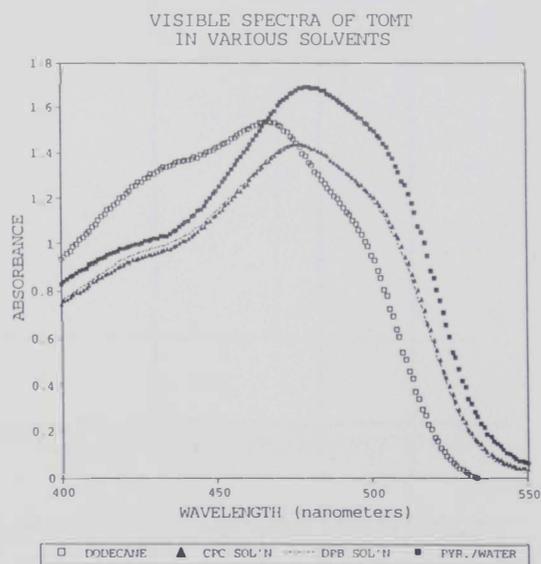


Figure 2. Visible spectra of TOMT in dodecane, pyridine/water (50% each by volume), aqueous cetylpyridinium chloride solution (0.0600 M CPC, 0.500 M NaCl), and aqueous dodecylpyridinium bromide solution (0.0606 M DPB, 0.500 M NaBr). TOMT concentration = 1.037×10^{-4} M.

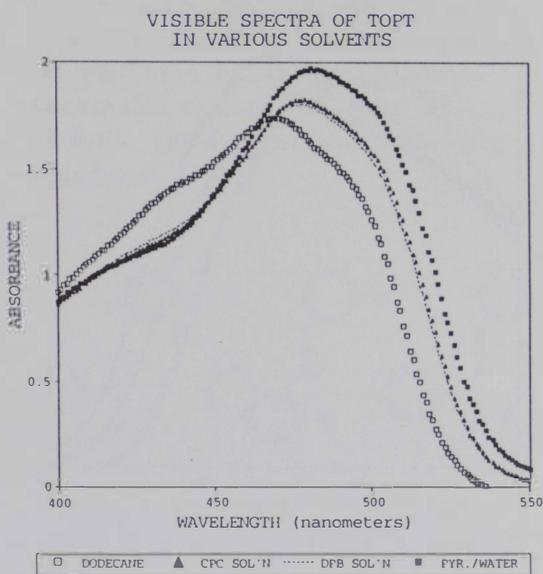


Figure 3. Visible spectra of TOPT in dodecane, pyridine/water (50% each by volume), aqueous cetylpyridinium chloride solution (0.0600 M CPC, 0.500 M NaCl), and aqueous dodecylpyridinium bromide solution (0.0606 M DPB, 0.500 M NaBr). TOPT concentration = 1.036×10^{-4} M.

dodecane. This was also the case in the earlier study (Jacobs, Geer, and Anacker 1972). If pyridine/water and dodecane can serve as crude models of the micelle's surface and interior, respectively, the spectra suggest that the dyes, or parts of them, reside in relatively polar environments. Since the dyes themselves are virtually water insoluble, their environments must also have some non-polar character.

NMR spectra obtained in this study make up Figures 4-6. Since the spectrum of a dye in a DPB/NaBr/D₂O solution more closely resembles that of the dye in a pyridine/D₂O solution than that of the dye in deuterated pentane, we again may conclude that when solubilized by a micelle, a dye's -CF₃ group experiences an environment that more closely resembles the micelle's surface than the micelle's interior.

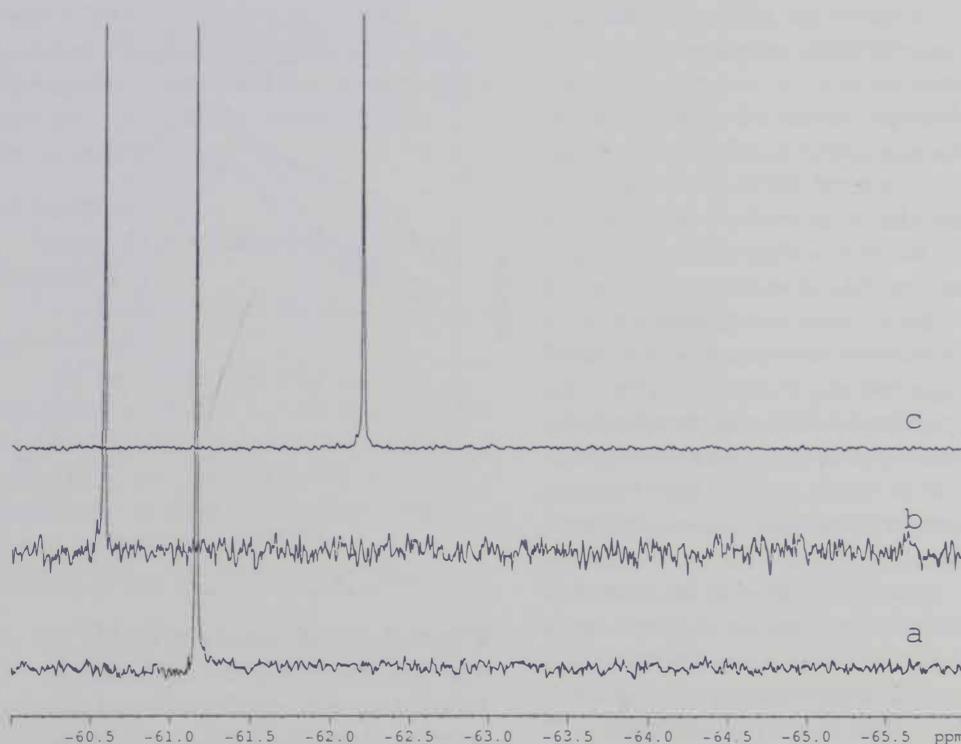


Figure 4. NMR spectrum of TOOT in a) pyridine/D₂O (50% each by volume), b) aqueous dodecylpyridinium bromide solution (0.0573 M DPB, 0.478 M NaBr, 9.80×10^{-5} M TOOT), and c) pentane-d₁₂.

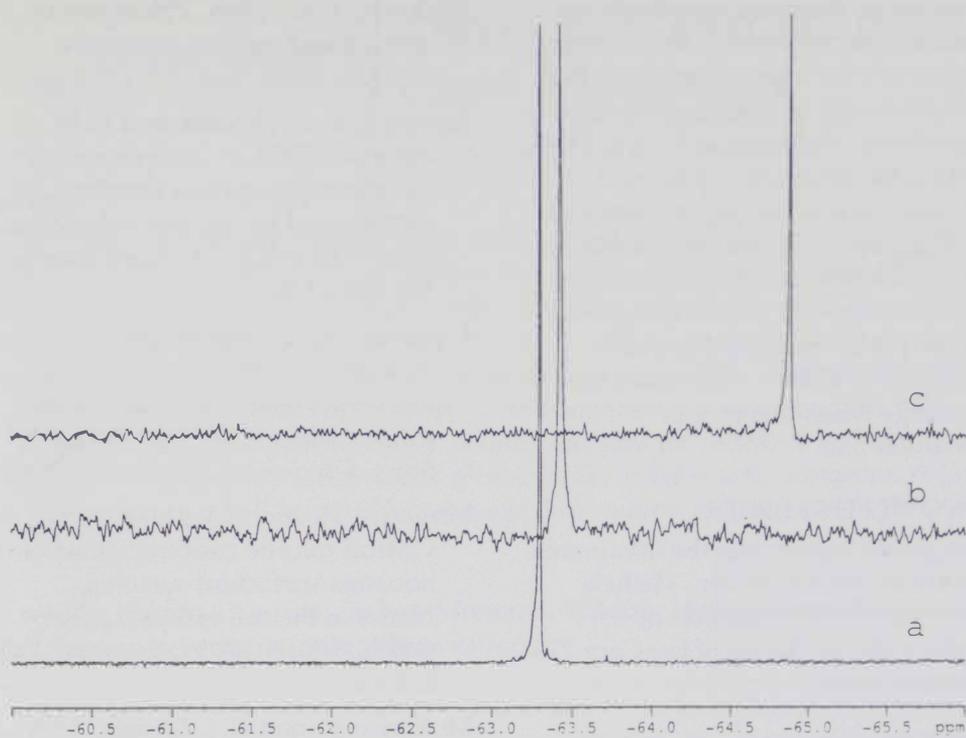


Figure 5. NMR spectrum of TOMT in a) pyridine/D₂O (50% each by volume), b) aqueous dodecylpyridinium bromide solution (0.0631 M DPB, 0.486 M NaBr, 1.00 x 10⁻⁴ M TOMT), and c) pentane-d₁₂.

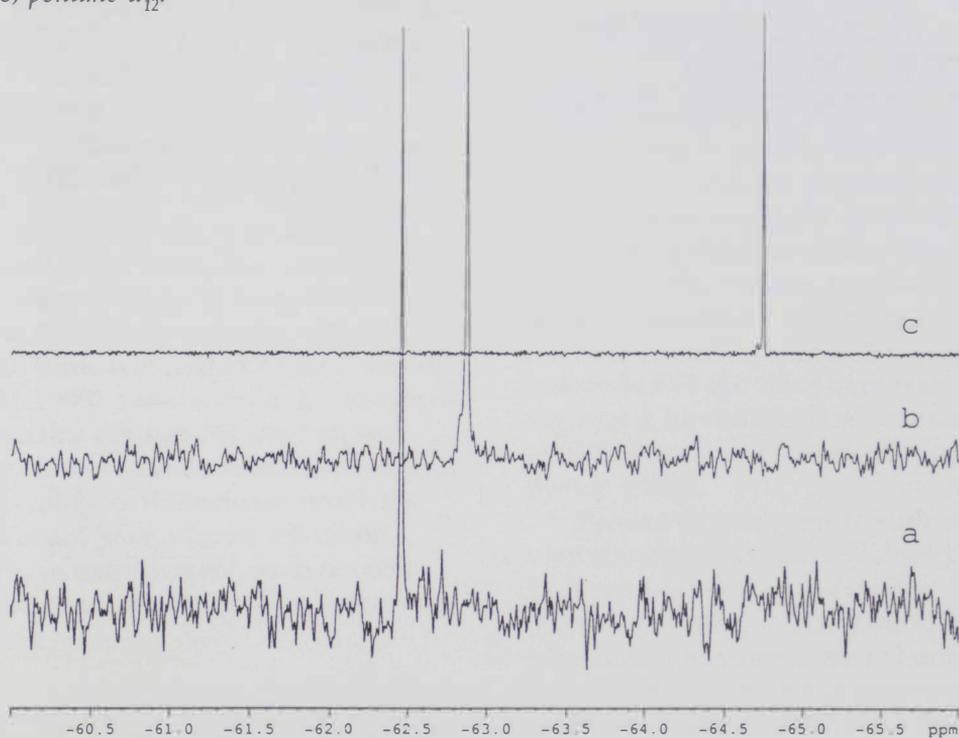


Figure 6. NMR spectrum of TOPT in a) pyridine/D₂O (50% each by volume), b) aqueous dodecylpyridinium bromide solution (0.0635 M DPB, 0.500 M NaBr, 1.11 x 10⁻⁴ M TOPT), and c) pentane-d₁₂.

One factor that may contribute to the tendency of the dyes to show some preference for the micelle surface is the mutual phobicity of hydrocarbons and fluorocarbons (Mukerjee and Yang 1976). According to Mukerjee and Mysels (1975), resistance to mixing of these two kinds of groups "reduces their tendency to micellize when attached to the same chain and causes the W-trifluoro group to sample predominantly the water-micellar core interface rather than the core average when this core is hydrocarbon-like."

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