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# A spectral approach to determine location and orientation of azo dyes within surfactant aggregates

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ABSTRACT

The UV–vis absorption properties of azo dyes are known to exhibit a variation with the polarity and acidity of the dye environment. The spectral properties of a series of anionic azo dyes were characterized to further probe the interaction of these dyes with two types of surfactant aggregates: (1) the spherical micelles formed in aqueous solution by alkyltrimethylammonium bromide ($C_n$TAB) surfactants with $n$ = 10–16 and (2) the unilamellar vesicles spontaneously formed in water from binary mixtures of the oppositely-charged double-tailed surfactants cationic didodecyldimethylammonium bromide (DDAB) and anionic sodium dioctylsulfosuccinate (Aerosol OT or AOT). The observed dye spectra reflect the solvatochromic behavior of the dyes and suggest the location and orientation of the dye within the surfactant aggregates. Deconvolution of the overall spectra into sums of Gaussian curves more readily displays any contributions of tautomeric forms of the azo dyes resulting from intramolecular hydrogen bonding. The rich variation in UV/vis absorption properties of these anionic azo dyes supports their use as sensitive tools to explore the nanostructures of surfactant aggregates.



## 1. Introduction

The binding and solubilization of organic dye molecules with supramolecular species and with macromolecules have been extensively studied by spectral techniques. Electrostatic interactions, hydrophobic interactions, hydrogen bonds, pi-stacking, cation–pi interactions, and van der Waals forces are typical examples of the intermolecular forces that dominate the interaction of dye molecules with surfactant aggregates. The resulting self-assembled supramolecular structure often exhibits enhanced functionality, leading to applications of the supramolecular species as nanoscale catalysts and reaction vessels, agents for drug delivery, chemical sensors, media for transport processes, and tools for selective binding and solubilization.

An azo dye is a particular class of synthetic organic dye that possesses a number of chemical features that make the molecule a sensitive probe of its environment. Azo dyes contain the azo functionality, –N=N–, with attached aryl groups. These dyes may be further characterized by the size and substitution pattern of the aromatic rings. In particular, the dye absorption wavelength is observed to be sensitive to both the polarity and acidity of the dye's environment. When the excited state of an azo dye is more polar than its ground state, the dye exhibits positive solvatochromism with a bathochromic (red) shift in the UV–vis spectrum reflecting stabilization of the excited state in the polar solvent environment. Hypsochromic or blue shifts reflect stabilization of more non-polar excited states in more non-polar surroundings. For phenylazonaphthol dyes (i.e., those possessing a phenyl ring and an *ortho*-hydroxyl-substituted naphthalene ring), the propensity for formation of the tautomeric form (the "hydrazone") occurs in polar environments where the azo moiety participates in significant intramolecular hydrogen bonding (see Fig. 1) [1–5]. Azo dyes with substituents that behave as weak acids or weak bases in aqueous solution also exhibit a spectral dependence on the pH of the medium as substituents are protonated or deprotonated. Thus, the polarity and the acidity of the medium affect both the preferred structural form of the dye and the observed absorption $\lambda_{max}$.

Interactions of azo dyes with macromolecules and surfactant assemblies often lead to marked changes in the spectral properties of these dyes that provide insight into the dye's immediate environment. Previous spectroscopic investigations [6–8] of the interaction of azo dyes with micelles composed of cationic, anionic, zwitterionic, and non-ionic surfactants suggested that both the dye substitution pattern and the charge on the surfactant head group played major roles in locating the dye within the micellar environment. A charged moiety on the dye further controls the dye position. The dye may be confined to hydrophilic surroundings on the micellar surface or penetrate the core of the micelle.

Ionic azo dyes may also adopt an intermediate configuration within surfactant aggregates when one of the aryl rings attached to the azo moiety contains only neutral hydrophobic substituents. For such dyes, the aryl ring with the charged moiety may be positioned

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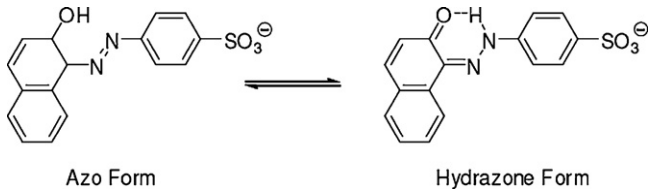


**Fig. 1.** Intramolecular hydrogen bonding dictates the equilibrium between the azo and hydrazone tautomers.

in the hydrated layer of a micelle with the second neutral aromatic ring penetrating the core of a micelle; this is especially true in non-ionic and cationic micelles [6,7].

Azo dyes with hydroxyl groups oriented ortho to the azo moiety have been observed to generally favor the azo form in non-ionic micelles [9], consistent with the presence of the less polar micellar microenvironment and the typical direction of the shift in the azo–hydrazone equilibrium with the polarity of the environment [9]. However, particular substitution patterns on the aromatic rings of the dye are hypothesized to stabilize the hydrazone tautomer in non-ionic micelles; in particular, when a sulfonate group is oriented ortho to a hydroxyl group on a naphthalene ring, the more polar hydrazone tautomer dominates in the presence of non-ionic micelles [9].

In this investigation we have used UV–vis spectroscopy to characterize the interaction of an extensive range of anionic azo dyes with two major systems of host surfactant aggregates in aqueous solution. These aggregates were selected to examine the role of both surfactant alkyl chain length and aggregate structure on dye localization. The first system is comprised of the cationic micelles formed by alkyltrimethylammonium bromide ($C_n$TAB) surfactants with $n$ = 10–16. These single-chain surfactants form spherical micelles in aqueous solution at their critical micelle concentration [10–18]. The range of alkyl chain lengths investigated permits the influence of micellar size on dye localization to be explored. The second major class of host systems are the unilamellar vesicles constructed in water from binary mixtures of the oppositely-charged double-tailed surfactants of different molecular structure, cationic didodecyldimethylammonium bromide (DDAB) and anionic sodium dioctylsulfosuccinate (Aerosol OT or AOT). These "catanionic" vesicles possess interfacial regions comprised of hydrophilic surfactant head groups that define the inner and outer surfaces of the bilayer shell. Our previous investigations [19] reveal that a significant positive net charge exists on the outer surface for DDAB-rich vesicles (i.e., those with surfactant composition of ≥50% by weight DDAB) due to an asymmetry of surfactant distribution across the inner and outer surfaces. We selected a 95%/5% DDAB/AOT vesicle composition to parallel the high net positive surface charge that exists on $C_n$TAB micelles but with a larger aggregate radius of about 110 nm (compared with micellar radii of about 3 nm [20]). Thus, the DDAB/AOT vesicles allow an investigation of the influence of aggregate size on azo dye position.

The results of the current investigation demonstrate that the sensitive spectral properties of azo dyes can be a powerful means of characterizing the interaction of dye molecules with host systems. Our analysis for deciphering the complex spectral behavior of azo dyes in surfactant assemblies enables a straightforward delineation of both dye location within a surfactant aggregate as well as preferred structural form (azo vs. hydrazone).

## 2. Experimental methods

### 2.1. Materials

#### 2.1.1. Dye solutions

Aqueous stock solutions (each 4 mM) of the following azo dyes (obtained commercially and recrystallized as necessary) were prepared: α-naphthol orange (α-NO; 4-(4-hydroxy-1-naphthylazo)benzenesulfonic acid, sodium salt; TCI); acid orange 8 (AO-8; 4-[(2-hydroxy-1-naphthyl)azo]-3-methylbenzenesulfonic acid, sodium salt; ICN Biomedicals, Inc.); acid red 88 (AR-88; 4-(2-hydroxy-1-naphthylazo)-1-naphthalenesulfonic acid, sodium salt; Acros); chrome violet (CV; 4-hydroxy-3-(2-hydroxy-1-naphthylazo)benzenesulfonic acid, sodium salt; TCI); DAP (4-aminoazobenzene-4′-benzoic acid; Acros); DHPB (4-(2,6-dimethyl-4-hydroxyphenylazo)benzenesulfonic acid; Aldrich); ethyl orange (EO; 4-[4-(diethylamino)phenylazo]benzenesulfonic acid, sodium salt; Aldrich); HMB (4′-hydroxy-2′-methyl-1,1′-azobenzene-4-sulfonic acid, sodium salt, Aldrich); MHPB (4-(3-methyl-4-hydroxyphenylazo)benzenesulfonic acid, Aldrich); methyl red (MR, 2-(4-Dimethylaminophenylazo)benzoic acid, Aldrich); methyl orange (MO, 4-dimethylaminoazobenzene-4′-sulfonic acid, sodium salt; Allied Chemical and Dye Corporation); MOPB (4-(4-methoxyphenylazo)benzenesulfonic acid, sodium salt, Aldrich); naphthylamine brown (NB; 1-(4-Hydroxy-1-naphthylazo)-2-naphthyl-4-sulfonic acid, sodium salt; City Chemicals) orange II (O-II; 4-[(2-Hydroxy-1-naphthyl)azo]benzenesulfonic acid, sodium salt, sodium salt; Aldrich); orange IV (O-IV; 4-[(4-Anilinophenyl)azo]benzenesulfonic acid, sodium salt, MCB Reagents); PHAP (*p*-hydroxyazophenyl-*p*′-sulfonate or 4-hydroxyazobenzene-4′-sulfonic acid, sodium salt; TCI); tropaeolin O (TO; 4-[2,4-dihydroxyphenylazo]benzenesulfonic acid, sodium salt; Aldrich). A 5 mM stock solution in 200 proof ethanol of the dye PAP (4-aminoazobenzene-4′-sulfonic acid, TCI) was also prepared. Fig. 2 presents the chemical structures of these dyes.

Azo dyes may be characterized by the size and substitution pattern of the aromatic rings joined to the azo functionality. One of these aromatic rings is designed as the linking ring (i.e., the ring with the sulfonate substituent that electrostatically links to the surfactant head group), and the second aromatic ring is denoted the terminal ring. These dyes may vary in the positioning of the linking ring with respect to the sulfonate group, in the number and position of substituents on the aromatic rings, and in the relative position of the sulfonate and azo groups on the aromatic ring (e.g., para vs. ortho).

#### 2.1.2. Surfactant solutions

Aqueous stock solutions of the following surfactants (obtained from Aldrich) were prepared: decyltrimethylammonium bromide ($C_{10}$TAB, stock solution = 424.9 mM); dodecyltrimethylammonium bromide ($C_{12}$TAB, stock solution = 101.3 mM); myristyltrimethylammonium bromide ($C_{14}$TAB, stock solution = 22.56 mM); cetytrimethylammonium bromide ($C_{16}$TAB, stock solution = 5.789 mM); didodecyldimethylammonium bromide (DDAB, stock solution = 15.25 mM or 0.706 wt%); sodium dioctylsulfosuccinate (AOT, Sigma, 99%, stock solution = 22.45 mM or 0.998 wt%). All aqueous solutions were prepared with 18.2 MΩ ultrapure water at pH 5 obtained from a Milli-Q Plus Millipore water filtration system.

#### 2.1.3. Micellar and vesicle solutions

$C_n$TAB micellar samples were prepared by first adding surfactant stock solution to Millipore ultrapure water, followed by added dye stock solution to give final surfactant concentrations of 119 mM $C_{10}$TAB, 28.4 mM $C_{12}$TAB, 28.36 mM; 6.32 mM $C_{14}$TAB, and 1.62 mM $C_{16}$TAB with [dye] = 10–50 μM. Each of these final surfactant concentrations was selected to be at a level above the critical micelle concentrations (0.068, 0.016, 0.0036, and 0.00092 M for $n$ = 10, 12, 14, and 16) [21] to ensure the presence of spherical micelles with no more than one dye molecule per micelle for surfactants with $n$ = 10–14 and a maximum of an average of 2.5 dye molecules per $C_{16}$TAB micelle at 50 μM dye. Cationic-rich unilamel-