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# Photophysical study of a charge transfer oxazole dye in micelles: Role of surfactant headgroups

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ABSTRACT

Photophysics of 5-(4′′-dimethylaminophenyl)-2-(4′-sulfophenyl)oxazole, sodium salt (DMO) which undergoes intramolecular charge transfer in the excited state was studied in micelles. In the cationic and the nonionic micelles, significantly higher fluorescence quantum yield is observed in comparison to the anionic micelles, due to much lower accessibility of DMO to the water molecules in the former micelles than the latter. Time-resolved fluorescence decays were characterized by a fast ($\tau_1$) and a slow ($\tau_2$) component of decay in all the micelles. The fast decay component ($\tau_1$) increases significantly in going from the anionic micelles to the cationic micelles, because of the poorly hydrated headgroup region of the latter micelles compared to the former. Furthermore, much higher value of the slow component of decay ($\tau_2$) is observed for the cationic and the neutral micelles than the anionic micelles. This is attributed to the increased penetration of water molecules into the micellar core of the anionic micelles compared to the cationic and the neutral micelles.



## 1. Introduction

Micelles are self-organized molecular assemblies of amphiphilic molecules possessing a hydrophobic core constituted of hydrocarbon chains (hydrophobic tail) and a hydrophilic shell which comprise charged and/or polar head groups (Scheme 1), a few counterions and water molecules associated with the ionic or polar head groups [1–3]. Photophysical studies of dyes in micellar media have drawn a particular interest because dye–surfactant interactions closely mimic many biological processes in biomembranes [4,5]. Aqueous micellar environments modify a number of photophysical processes [6–12] because of a change in the micropolarity and microviscosity inside the micellar core and/or the micelle–water interface compared to the bulk aqueous phase. Fluorescent probes based on intramolecular charge transfer (ICT) play an important role in demonstrating the effects of micropolarity as well as the microviscosity around the probe in such microheterogeneous media [7–11]. Among them, studies involving the well known anionic dye 2,6-ptoluidinonaphthalene sulfonate (TNS) have limitations [7] for use to probe the microenvironment of the cationic surfactants. Although another anionic dye, 8-anilino-1- naphthalene sulfonate (ANS) have been used to study the microenvironments of cationic micelles [8], the use of ANS or TNS as probes for the anionic micelles is lacking. Recently, Chattopadhyay et al. [9] have used a cationic charge transfer dye, phenosafranin to monitor the microenvironments of anionic micelles, but, its use in the cationic micelles is lacking till date. Moreover, two neutral fluorescent dyes trans-ethyl-p-(dimethylamino)-cinnamate (EDAC) [10,11] and 3-acetyl-4-oxo-6,7-dihydro-12H-indolo-[2,3-a]-quinolizine (AODIQ) [12] were used recently to study dye–micelle interactions. Although both EDAC and AODIQ displayed multiexponential fluorescence decays in the micellar aggregates, mean fluorescence lifetime was used to discuss the microenvironments of different micelles, instead of discussing the origin of two or more fluorescence decay components. A new environment-sensitive fluorescent probe 5-(4′′-dimethylaminophenyl)-2-(4′-sulfophenyl)oxazole, sodium salt (DMO, Scheme 1) has recently been developed, which undergoes twisted intramolecular charge transfer (TICT) in the excited state and showed remarkable solvent polarity sensitive fluorescence [13]. The study of the photophysics of DMO in the micellar environments may be used as a tool to understand the interaction, distribution, and localization of the dye in biological systems, since micelles are considered as simple model membrane systems. So, we have undertaken the study of the photophysics of the anionic dye DMO in differently charged micelles by means of steady state and time resolved fluorescence spectroscopy to assess the location of the dye, micropolarity of the dye

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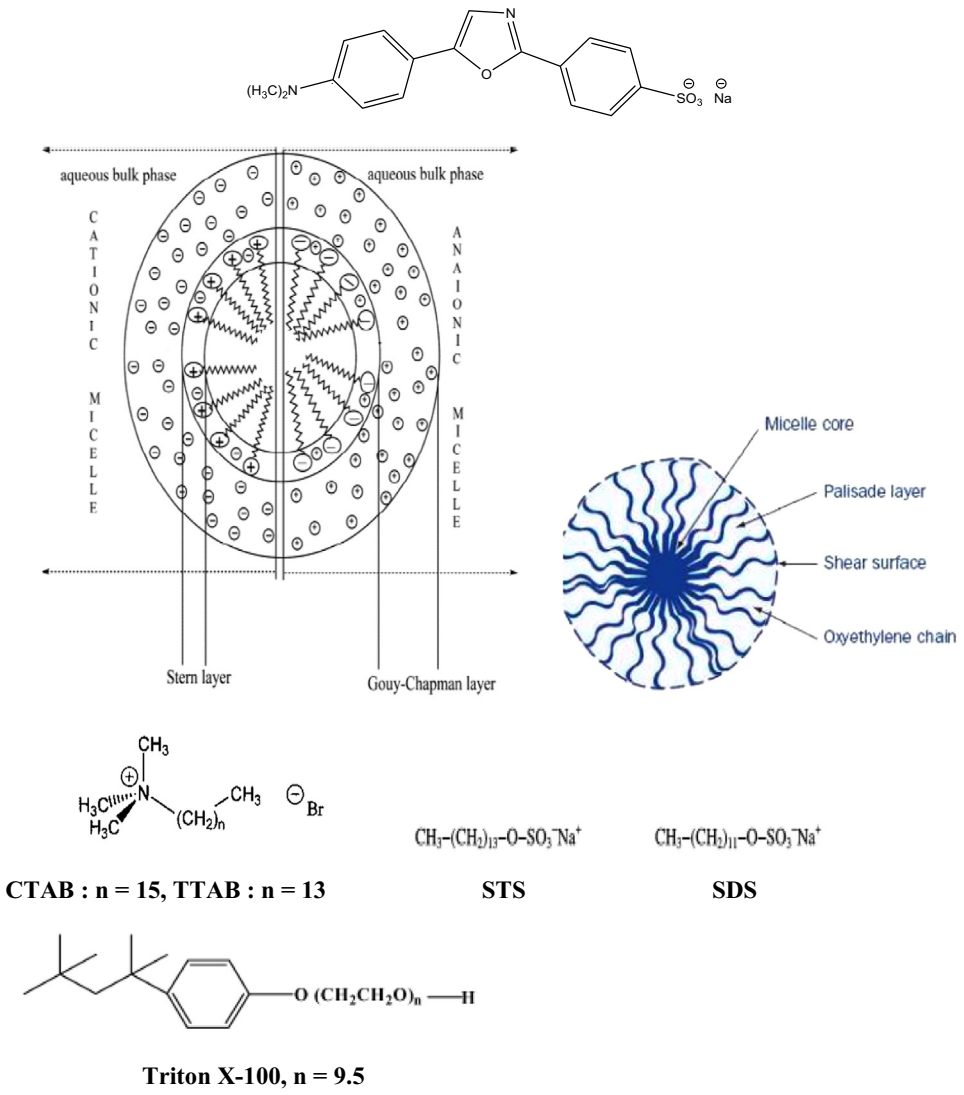


**Scheme 1.** Representation of 5-(4′′-dimethylaminophenyl)-2-(4′-sulfophenyl)oxazole, sodium salt (DMO) (top); ionic and non-ionic micelles and the surfactants used (bottom). CTAB: $n=15$, TTAB: $n=13$, STS, SDS, Triton X-100, $n=9.5$.

environment, and the role of the surfactant headgroup in the dye–surfactant interactions. In this report, we present results on the photophysical studies of the anionic dye DMO in the (i) cationic micelles of Cetyltrimethylammonium bromide (CTAB) and Tetradecyltrimethylammonium bromide (TTAB), (ii) anionic micelles of Sodium dodecyl sulfate (SDS) and Sodium tetradecyl sulfate (STS) and, (iii) the non-ionic micelles of Triton X-100 (TX-100). The results show distinctly different photophysics between the anionic and the cationic micelles highlighting the role of the charge of the surfactant headgroup and the micellar size.

## 2. Materials and methods

5-(4′′-dimethylaminophenyl)-2-(4′-sulfophenyl)oxazole, sodium salt (DMO) was purchased from Molecular Probes Inc. The surfactants Cetyltrimethylammonium bromide (CTAB), Sodium dodecyl sulfate (SDS), Tetradecyltrimethylammonium bromide (TTAB), Sodium tetradecyl sulfate (STS) and Triton X-100 (TX-100) were obtained from Sigma-Aldrich and used as received. The stock solutions of the surfactants were prepared in deionized water (from Millipore Milli-Q nanopure water system). The final concentration of DMO was 4 μM in aqueous micellar solutions for the measurements of UV–vis, steady state and time-resolved fluorescence decays. The micelle concentration, [M], was kept at least 90 times higher than the probe concentration to warrant a low probability of having two or more DMO molecules within a single micelle. The micelle concentration was determined from the surfactant concentration, [S], the aggregation number, $N_{agg}$, and the critical micelle concentration, cmc, as follows:

$$[M] = ([S] - cmc)/N_{agg} \quad (1)$$

Quantum yields ($\Phi$) of the dye were determined with respect to its solution in ethanol as a reference ($\Phi=0.72$) [13]. All of the spectroscopic measurements were performed at 25 °C in cuvettes of 1 cm optical path. Absorption and fluorescence spectra were recorded on a Cary 4 spectrophotometer (Varian) and a FluoroMax 3.0 (Jobin Yvon, Horiba) spectrofluorometer, respectively. Time-resolved fluorescence measurements were recorded with a commercial time-correlated single photon counting (TCSPC) set up from Edinburgh Instruments (instrument response function (IRF=80 ps), excitation at 375 nm and fitted using FAST software provided by Edinburgh Instruments the details of which could be found elsewhere [14,15].