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Steady state and time-resolved fluorescence spectroscopy of quinine sulfate dication bound to sodium dodecylsulfate micelles: Fluorescent complex formation

Sunita Joshi, Debi D. Pant*

Department of Physics, Birla Institute of Technology and Science (BITS) Pilani, Pilani 333031, Rajasthan, India

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ABSTRACT

Interaction of quinine sulfate dication (QSD) with anionic, sodium dodecylsulphate (SDS) surfactant has been studied at different premicellar, micellar and postmicellar concentrations in aqueous phase using steady state, time-resolved fluorescence and fluorescence anisotropy techniques. At premicellar concentrations of SDS, the decrease in absorbance, appearance of an extra fluorescence band at lower wavelengths and tri-exponential decay behavior of fluorescence, are attributed to complex formation between QSD molecules and surfactant monomers. At postmicellar concentrations the red shift in fluorescence spectrum, increase in quantum yield and increase in fluorescence lifetimes are attributed to incorporation of solute molecules to micelles. At lower concentrations of SDS, a large shift in fluorescence is observed on excitation at the red edge of absorption spectrum and this is explained in terms of distribution of ion pairs of different energies in the ground state and the observed fluorescence lifetime behavior corroborates with this model. The temporal fluorescence anisotropy decay of QSD in SDS micelles allowed determination of restriction on the motion of the fluorophore. All the different techniques used in this study reveal that the photophysics of QSD is very sensitive to the microenvironments of SDS micelles and QSD molecules reside at the water-micelle interface.

1. Introduction

Understanding the structure of micelles under various physico-chemical conditions has found immense research interest due to the applications of such systems in industries to modify the mechanism and dynamics of chemical reactions [1–3] and designing drug carrier and delivery systems [4]. Micelles are known to exist in varying sizes, shapes and compositions depending upon salt conditions, temperature, pH, and composition of solution. Micelles are found as an approximate model for drug and DNA delivery vehicles, and also to mimic many characteristics of biological bilayer membranes [5]. Apart from the micellar structure and properties, other important constituent that plays crucial role in influencing micro-reactions happening inside the micellar environment is its confined water. The properties of confined water, such as viscosity, polarity, mobility, etc. are very different from that of bulk water due to their confinement, specific interactions and presence of microenvironment containing ions or salts [6]. The study of photophysical properties, such as fluorescence excitation and emission spectra and their shifts, the relative intensity of vibrational bands, anisotropy, quantum yields, and excited-state lifetimes, of probes has provided significant information on the micellar structure at the molecular level [2,7].

The photophysical behavior of Quinine sulfate dication (QSD) (Quinine sulfate in 1 N H_2SO_4 solution of water) has been studied extensively in homogeneous medium [8–28] and in some restricted environments [29,30]. Generally in bulk non-viscous solvents, dipolar solvent relaxation around the fluorophore in the excited state occurs on a time scale much faster than the fluorescence lifetime of the fluorophore. Thus, the peak of the fluorescence spectrum does not depend on the excitation wavelength. However, QSD is a rare emitter in which the solvent relaxation around the probe molecule occurs in nanosecond time scale and comparable to fluorescence lifetime of the probe and consequently the fluorescence spectrum shifts toward lower energy as the excitation wavelength increases. This effect is known as edge excitation red shift (EERS). EERS directly monitors the microenvironment and dynamics around a fluorophore. The EERS observed in QSD and related compounds has been very sensitive to polarity, viscosity and the temperature [22]. The solvent relaxation process in quinine sulfate and related compounds in different solvents and at various temperatures has been reported in the past [23–26]. It was shown that the methoxy group plays an important role in the photophysics of these molecules. From the temperature dependence of fluorescence characteristics, it was suggested that

* Corresponding author. Tel.: +91 1596515651.
E-mail address: ddpant@pilani.bits-pilani.ac.in (D.D. Pant).

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around 160 K a rapid charge transfer from methoxy group to the quinoline ring takes place, followed by solvent relaxation at ambient temperature in the polar fluid medium.

There are many reports in the literature about the interaction between oppositely charged dye and surfactant forming an ion-pair complex, which are generally non-fluorescent [31–35]. In this paper, our goal has been to study the effect of micro-heterogeneous environment of micelles on to the photophysics of QSD molecule and we report an interesting behavior of fluorescence of QSD at different concentrations of SDS. This study demonstrates that QSD molecule has the potential to serve as a sensitive probe for studying the microenvironments in chemical, micellar and biological systems.

2. Experimental

Quinine sulfate (QS) was purchased from Alfa Aesar and used as received. All the solvents were either of spectroscopic grad or were checked for their purity. All the samples of quinine sulfate dication (QSD) were prepared by dissolving the appropriate concentration of QS in 1 N H_2SO_4 containing Milli Q water. The final concentration of QSD in all the systems studied was 10^{-4} M. The surfactant, sodium dodecylsulphate (SDS) was purchased from SISCO and was used as received. Absorption spectra were taken with the help of dual beam JASCO V-570 UV/Vis/NIR spectrophotometer and fluorescence and excitation spectra were recorded with the help of Shimadzu, RF-5301PC Spectrofluorometer. The data were analyzed using related software. The spectral shifts obtained with different sets of samples were identical in most of the cases and values were within $\pm$ 1.0 nm.

The steady state fluorescence anisotropy was measured with Shimadzu, RF-5301PC Spectrofluorometer using a set of polarizer. Steady state anisotropy r is defined as

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (1)$$

where I_{VH} and I_{VV} are the intensities obtained from the excitation polarizer oriented vertically and emission polarizer oriented in horizontal and vertical directions, respectively. The factor G is defined as $G = I_{HV}/I_{HH}$. The data were analyzed using related software.

The fluorescence lifetimes were measured from time resolved intensity decays by the method of time correlated single photon counting technique (TCSPC). The light source used was picoseconds diode laser (Nano LED) at 372 nm and 300 nm (Horiba Jobin Yvon, USA). The typical response time of this laser system was 70 ps. The fluorescence decays were deconvoluted using the Datastation software for acquisition and IBH DAS-6 for data analysis. The signals were collected at the magic angle (54.7°). The decay times were determined using the non-linear least square method by time TCSPC technique. Goodness of the fits was evaluated by the x^2 criterion and the randomness of the residuals of the fitted function to data. Care was taken in data analysis to differentiate between the mono exponential, bi and tri-exponential fits by judging the x^2 values, standard deviation and weighted residuals. For all the lifetime measurements fluorescence decays were analyzed by multi-exponential iterative fitting program provided by DAS-6 decay analysis software.

$$F(t) = \sum_i \alpha_i \exp(t/\tau_i) \quad (2)$$

where α_i is a pre-exponential factor representing the fractional contribution to the time resolved decay of the component with a lifetime τ_i. Average lifetimes $\langle\tau\rangle$; for biexponential decays of fluorescence were calculated from the decay times and pre-exponential factors using the following equation:

$$\langle\tau\rangle = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2}{\alpha_1\tau_1 + \alpha_2\tau_2} \quad (3)$$

and for triple

$$\langle\tau\rangle = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2 + \alpha_3\tau_3^2}{\alpha_1\tau_1 + \alpha_2\tau_2 + \alpha_3\tau_3} \quad (4)$$

3. Results and discussion

3.1. Absorption and fluorescence spectral properties

The molecular structure of QSD is shown in Fig. 1. In dilute sulfuric acid solutions (1 N H_2SO_4), quinine sulfate is present as a dicationic species, which is quite stable [23]. The nitrogens are adequately bound as the ammonium salt by strong acid of the medium effectively preventing n, π^* and n, σ^* transitions from occurring. The quinoline ring is the main fluorophore responsible for the absorption; methoxy group is very sensitive to the surrounding environment and responsible for photophysical behavior of QSD [22–27]. The vinyl group which absorbs around 180 nm, is not considered an active chromophoric group in the near UV–vis region.

The visible absorption spectra of mixed solution of a fixed concentration of QSD at 10^{-4} M for different concentrations of SDS ranging from 4×10^{-4} M to 1×10^{-2} M in aqueous media at 298 K are illustrated in Fig. 2. The absorption spectrum in aqueous bulk water shows two bands L_a and L_b at 348 and 318 nm, respectively.

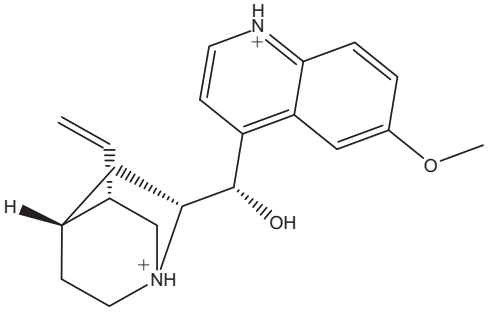

Fig. 1. Structures of QSD molecule.

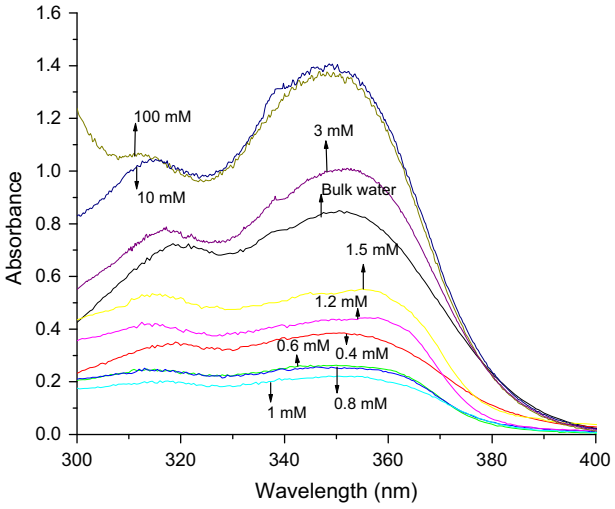

Fig. 2. Absorption spectra of QSD in bulk water and in different concentrations of SDS surfactant.