Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138 (2015) 818–826

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Effect of nanosize micelles of ionic and neutral surfactants on the photophysics of protonated 6-methoxyquinoline: Time-resolved fluorescence study

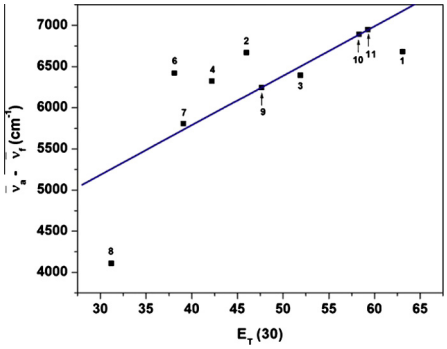
Tej Varma Y., Sunita Joshi, Debi D. Pant *

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

HIGHLIGHTS

- Photophysical properties of protonated 6-methoxyquinoline have been monitored in micellar medium.
- Polarity, viscosity, refractive index and E_T (30) of the local environment estimated.
- Location of protonated 6-methoxyquinoline in the micellar media has been probed.
- Modulated photophysics of protonated 6-methoxyquinoline in micelles have been reported.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form 24 October 2014
Accepted 26 October 2014
Available online 13 November 2014

Keywords:
6-Methoxyquinoline monocation
Edge excitation red shift
Water–micelle interface
Life-time
Anisotropy
Photophysics

ABSTRACT

The excited state dynamic studies have been carried out to investigate the effects of micellar surface charge on the photophysics of protonated 6-methoxyquinoline ($6MQ^+$) in anionic, sodium dodecylsulphate (SDS), cationic, cetyltrimethylammonium bromide (CTAB) and neutral, triton X-100 (TX100) surfactant at premicellar, micellar and postmicellar concentrations in aqueous phase at room temperature. At premicellar concentrations of SDS, there is a slight decrease in emission intensity and at micellar and postmicellar concentrations, increase in emission intensity and blue shift of spectrum has been observed. The blue shift in fluorescence spectrum and slight increase in quantum yield are attributed to incorporation of solute molecule to the micelles. Edge excitation red shift (EERS) in fluorescence maximum of $6MQ^+$ has been observed in all the surfactant solutions studied. The EERS has been ascribed in terms of solvent relaxation process. In SDS surfactant system, due to heterogeneous restricted motion of solvent molecules, the solvent viscosity increases which results in an increase in net magnitude of EERS. The fluorescence decay components of $6MQ^+$ fit with multi exponential functions in all the micellar systems studied. The location of the probe molecule in micellar systems is justified by a variety of spectral parameters such as refractive index, dielectric constant, E_T (30), EERS, average fluorescence decay time, radiative and non radiative rate constants, and rotational relaxation time.

Introduction

The photophysics and photochemistry of dyes in general are of considerable interest in the appreciations of various phenomena in pico to micro-second range, viz, fluorescence, phosphorescence,

* Corresponding author. Tel.: +91 1596515288.
E-mail address: ddpant@pilani.bits-pilani.ac.in (D.D. Pant).

http://dx.doi.org/10.1016/j.saa.2014.10.118
1386-1425/

long- and short-range excitation energy transfer, electron transfer and various modes of quenching. Interaction of a dye with a solvent at the molecular level is reflected in its visible and fluorescence spectra [1–8]. Interesting features of such phenomena may occur in surfactant and micellar solutions which are of general and particular interest in view of the special role of surfaces in guiding and modifying physicochemical processes [9,10]. Micelles are well-known aggregates of surfactants, formed in aqueous solutions above a critical micellar concentration [11,12]. They consist of a hydrocarbon core sequestered within a polar surface, thus resembling an oil droplet with a polar coating, suspended in a bulk aqueous phase. The apolar core is essentially dry [13,14]. Micelles are not rigid ensembles. The local concentration of H^+ and OH^- ions in the vicinity of the Stern layer is greater for anionic and cationic micelles, respectively, due to electrostatic attraction. Aqueous micellar environments modify a number of photophysical processes because of a change in the micro-polarity and microviscosity inside the micellar core and/or the micelle–water interface compared to those in the bulk aqueous phase. A fluorescent molecular probe plays an important role in demonstrating the micro-polarity as well as the microviscosity around the probe in such micro-heterogeneous environments. Surfactant solutions comprising of normal or reverse micelles are a topic of recent investigations due to their unusual physicochemical properties and immense technological applications [15–19]. The basic intention of such studies is twofold: first, to see the modification of the photophysical processes due to the change in the microenvironment from the bulk medium to the micellar medium around the probe and second, to study the microenvironments following a well-known photoreaction.

Fluorescence spectroscopy is a sensitive technique where one can study the effects of local solvent environment around a molecular probe situated in the micelle which can be characterized from the wavelength, shape and the intensity of the spectrum. The surrounding solvent effects of a probe molecule can be quantified by the Stokes shift, which is measured by the difference of emission and absorption maxima, emission wavelength dependence of excitation spectrum and excitation wavelength dependence of the fluorescence spectrum. So it is interesting to study the photophysical properties of molecular probes sensitive to solvent environment in molecularly organized assemblies.

6-Methoxyquinoline (6MQ) is a parent molecule of spectroscopically well known molecules such as quinine sulphate, quinidine and cinchonine. Recently we have studied the effect of micellar charge on the photophysics of quinine sulphate [20]. It is well known that the fluorophore in 6MQ is a quinoline ring with the methoxy group at the sixth position and the vinyl group causes minor changes in the photophysics. The photophysics of 6MQ has been explored in detail in the past [21–24], in order to understand the excited state dynamics and found to be sensitive to the surrounding solvent environments. The photophysical processes in 6MQ and related molecules have been explored for designing fluorescence optical sensors for halides [25,26]. The spectroscopy of 6MQ was earlier reported by Schulman [27]. In case of 6MQ at pH < 4 the emission of the mono-cation is observed and in basic medium only neutral 6MQ species are observed. The solvent relaxation process in quinine sulphate and related compounds in different solvents and at various temperatures has been reported in the past [21–23,28,29]. 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 around 160 K a rapid charge transfer from methoxy group to the quinoline ring take place, followed by solvent relaxation at ambient temperature in the polar fluid medium. Using solvatochromic shift method, recently we have calculated dipole moment of 6MQ, $6MQ^+$ and found higher dipole moment in the excited state compared to the ground state [30].

In this paper we report the spectral and fluorescence lifetime and fluorescence anisotropy properties of protonated 6-methoxyquinoline ($6MQ^+$) in different ionic and neutral surfactants using steady state absorption and fluorescence techniques and time resolved lifetime and fluorescence anisotropy techniques. $6MQ^+$ has been studied in sodium dodecylsulphate (SDS), cetyltrimethylammonium bromide (CTAB), and Triton X-100 (TX100) surfactants in aqueous phase, as examples of anionic, cationic and neutral surfactants, respectively. Measurement of fluorescence anisotropy plays an important role, owing to the fact that any factor affecting size, shape, or segmental flexibility of a molecule will affect the parameter [31]. It directly reflects any motional restriction imposed on the fluorophore by the environment. Keeping these in mind we have investigated steady-state fluorescence anisotropy of $6MQ^+$ in different micellar systems. This study provides a detailed picture of dynamics and location of $6MQ^+$ in micelles by a variety of spectral parameters like fluorescence peak position as a function of excitation wavelength, fluorescence decay times, rate constants for radiative and non-radiative relaxation and temporal anisotropy decay of fluorescence.

Experimental

6-Methoxyquinoline (6MQ) obtained from Aldrich was used as such. All the samples of protonated 6-methoxyquinoline ($6MQ^+$) were prepared by dissolving the appropriate concentration of 6MQ in 1 N H_2SO_4 containing Milli Q water. The final concentration of $6MQ^+$ in all the systems studied was 10^{-5} M. The surfactant, cetyltrimethylammonium bromide (CTAB) was purchased from Merck, sodium dodecylsulphate (SDS) and triton X-100 (TX100) surfactants were purchased from SISCO. All surfactants were used as received. The concentrations of surfactants in the solutions prepared were well above, at and below the critical micellar concentration (c.m.c.). The c.m.c. of CTAB. SDS and TX100 surfactants are 1.0 mM, 8 mM, and 0.2 mM, respectively.

Absorption spectra were taken using thermo scientific evolution 201 UV–Vis. spectrophotometer and fluorescence spectra were recorded with 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 ±1.0 nm.

For anisotropy decay measurements, the samples were excited at 372 nm using a picoseconds diode laser (Horiba Jobin Yvon). The emission intensities at parallel (I_{II}) and perpendicular ($I_{\perp}$) polarizations were collected alternatively until a perfect peak difference was reached. The analysis of the data was done using IBH DAS 6 decay analysis software. The quality of the fits was determined from the reduced x^2 values and the randomness of the residuals of the fitted function to the data. The time-resolved anisotropy $r(t)$ was calculated using the following relation:

$$r(t) = [I_{II}(t) - GI_{\perp}(t)]/[I_{II}(t) + 2GI_{\perp}(t)] \quad (1)$$

where G is the grating factor of the emission monochromator of the TCSPC system.

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 at 375 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 data acquisition and IBH DAS6 for data analysis. The signals were collected at the magic angle (54.7°). The decay times were determined