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# Spectroscopic studies of interaction of safranine T with ionic surfactants

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ABSTRACT

Dye–surfactant interaction has great importance in scientific fields. The dye–surfactant interactions are generally complex processes. Safranine T is a photosensitive cationic dye whose ground and excited state spectra are affected by the surfactant. Anionic surfactant at low concentration forms complex with dye molecule. In anionic surfactant media, dye also forms dimer. After cmc (critical micelle concentration), charge transfer complex is formed between the anionic surfactant micelle and safranine T molecule. SDBS and SDMA form isosbestic point. 212 does not form charge transfer complex but it acts as a quencher. In case of SDS, maximum decrease in the value of absorbance of dye is observed compared to other surfactants and in case of SDMA, minimum decrease of fluorescence intensity is noticed. Cationic surfactants have little interaction with this cationic dye. CTAB has no interaction.

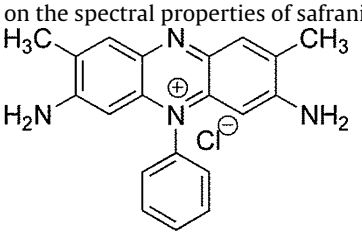


## 1. Introduction

Dye–surfactant interactions have broad applications in photographic, textile and paper industries, medicinal chemistry and environmental sciences [1]. In addition, such type of interaction also has importance in other scientific fields such as analytical chemistry, luminescence and laser chemistry [2]. Surfactants are long chain molecules having hydrophobic and hydrophilic groups in the same molecule [3]. They can form organized structure like micelle and reverse micelle. The most important property of surfactant is its ability to solubilize a variety of molecules which are insoluble in water. Surfactant molecules form micelle at a particular concentration which is known as critical micelle concentration or cmc. Cmc is detected by changing in physical properties such as surface tension, conductivity, viscosity, spectroscopic property, etc. [4–7]. Micelle is a self-organizing system which may provide microenvironment for processes involving macromolecules such as dye, protein, etc. Micelles are suitable media to study the electron transfer and energy transfer interactions [8].

Dye–surfactant interaction is generally complex process having specific and characteristic photochemical features. Various parameters such as the charge and the alkyl tail length of the surfactants and the type and the position of the substituents in the aromatic ring of the dye molecules can effect the interactions between surfactant and dye molecules [9,10]. Safranine T is a photosensitive dye whose ground and excited state spectra are affected by the surfactant. It is a reddish brown phenazine dye soluble in water. Safranine T is an aromatic cationic dye. In micellar media, ionic dye forms molecular complexes with oppositely charged micelle due to electrostatic interactions. Literature survey tells that there is no interaction between similarly charged dye–micelle systems [11]. The nonionic surfactants form charge transfer complex with cationic dye such as safranine T. Nonionic surfactant molecules act as an electron donor and the cationic dye molecule acts as an electron acceptor centres [8]. The oxygen containing group of nonionic surfactants acts as the electron donating centres. When surfactant solutions are added to the dye solutions, the spectral band of dye shifts due to change in microenvironment. When dye is incorporated into the micelle, its de-aggregation changes in chromophoric length, charge transfer interaction, etc. But this is very difficult to point out which force is responsible for dye–surfactant interactions.

Therefore, we have to carry out a systematic investigation here in order to understand the nature of the interaction and the cause of the spectral changes. The present manuscript deals with the effect of different types of ionic surfactants including gemini surfactant on the spectral properties of safranine T.

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## 2. Materials and methods

### 2.1. Materials

Safranine T is purchased from Fluka. The anionic surfactants, sodium dodecylbenzene sulfonate (SDBS), sodium N-dodecanoyl sarcosinate (SDDS) and sodium dodecyl sulfate (SDS) are obtained from Sigma and N-dodecanoyl-N-methyl alaninate (SDMA) is a gifted sample. The cationic surfactants, dodecyltrimethylammonium bromide (DTAB) and tetradecyltrimethylammonium bromide (TTAB) have been purchased from Sigma, and cetyltrimethylammonium bromide (CTAB) is received from Alfa Aesar (UK). The gemini surfactant, N, N′-ethylene (bis(sodium N-dodecanoyl-β-alaninate)) (212) is a gifted sample. All the surfactants have been desiccated before use. Double distilled deionized water is used for all sample preparations.

### 2.2. Preparation of safranine T solution

A stock solution of safranine T (1.049 mM) is prepared by adding a known weight of the compound in water. Then the mixture is sonicated to yield a clear solution. The experimental concentration of solution of safranine T is prepared from it by dilution. It shows a maximum absorption peak at 520 nm and emission maxima at 580 nm.

### 2.3. UV–visible absorption studies

Absorption spectra have been recorded using a UV 1601 Shimadzu (Japan) spectrophotometer with a 10 mm path length quartz cuvette. The spectra have been taken in 400–600 nm wave-length range. A small quantity of the safranine T stock solution (10 μl) is added to 2.5 ml of water to reach a final concentration of 4.179 μM for safranine T. The concentration of the surfactant solution is changed from the lower value to higher one than that of critical micelle concentration or cmc by progressive addition of a concentrated surfactant solution into water using a Hamilton microsyringe. The absorbance intensity is measured at 520 nm wavelength.

### 2.4. Fluorescence emission studies

The spectra and intensity of fluorescence emission and anisotropy of safranine T have been measured using a Perkin Elmer LS 55 fluorescence spectrophotometer with a 10 mm path length quartz cuvette. A 10 μl volume of the stock safranine T solution is added to 2.5 ml of water to attain a concentration of 4.179 μM for safranine T. A concentrated surfactant solution is stepwise added continuously into aqueous safranine T solution using a Hamilton microsyringe and the emission spectra are recorded after excitation. Fluorescence spectra are measured from 540 to 690 nm with excitation and emission slit widths fixed at 9 nm and 4 nm, respectively. The scan time is fixed at 250 nm per minute and the fluorescence intensity is measured at 580 nm wavelength. For anisotropy measurement, the wavelengths of excitation and emission are 520 nm and 580 nm, respectively. The measured anisotropy value is the average of five consecutive values. The sample temperature is allowed to stabilize at 300 K before each measurement.

## 3. Results and discussion

### 3.1. Absorption in surfactant solution

#### 3.1.1. Effect of anionic surfactant

In an aqueous solution, the phenazine dye safranine T exists in cationic form. It shows a maximum absorption peak at 520 nm. The effect of an anionic surfactant of a range of lower to higher concentration than cmc is studied on the absorption spectra of safranine T presenting some new peaks. If SDS is added up to 3.14 mM concentration in aqueous solution, then a decrease in absorption at 520 nm is observed. After addition of higher concentration (up to 5.91 mM) of SDS, the peak is blue shifted to 505 nm with an additional shoulder peak at 530 nm and absorption increases shown in Fig. 1(a). When [SDS] is 7.68 mM, the shoulder peak appears as clear peak (much prominent). After that, peak at 505 nm disappears and absorbance value increases for the peak at 530 nm. The latter one becomes independent of concentration after 10 mM of SDS. Initially, when anionic SDS is added to the cationic safranine T solution, it forms complex with the dye molecules and so intensity decreases. After this, two peaks appear one at 505 nm and another at 530 nm due to the formation of the dimer of the dye [12]. Such type of dimer can be formed in case of many dyes particularly those having strong aggregating character, e.g., crystal violet, dimethyl methylene blue. This can be explained in terms of dye surfactant interaction. Here, sulphate anions of SDS bind with the dye cations forming dimers after minimizing the mutual repulsive forces. This dimer may induce the formation of premicellar surfactant aggregate with the solubilized dye content. Here, as the surfactant concentration is increased, more and more micelles are gradually formed with appearing of two absorption peaks of safranine T. In the formed micelle, the peak at 505 nm disappears gradually with the appearance of the main absorption peak of the dye at 530 nm. This indicates that dimers disappear in the micellar media where surfactant molecules tend to aggregate to form the micelles (cmc of SDS is 8 mM, Table 1). Such spectral changes of dye are observed due to electrostatic interaction between oppositely charged molecules and van der Waals interaction between adjacent surfactant chains and organic moiety of the dye following the changes of the chromophoric microenvironment. The higher wavelength peak at 530 nm is identified as charge transfer peak and appears between the surfactant micelle and acceptor safranine T molecule [13].

In Fig. 1(b), absorbance of the dye in SDDS solution decreases at 520 nm similar to that in SDS solution. At 3.95 mM SDDS concentration, the spectra appear as two peaks one as main peak at 510 nm and another as shoulder peak at 535 nm. At 10.63 mM concentration of SDDS, shoulder peak becomes main peak. After that absorption increases with increase in surfactant concentration and peak at 510 nm disappear. At very high concentration of SDDS, absorbance becomes independent of concentration. At low concentration of surfactant, SDDS molecule forms complex with dye molecule and hence absorbance decreases. The new spectra with two peaks appear due to the formation of dimer. Here, sarcosinate anions bind with the cationic portion of the dye. This dimer is stable in the SDDS concentration ranging from 3.95 to 10.63 mM. In the micellar media, dimer breaks due to the reduction of the polarity of the medium. The peak at 535 nm appears due to the formation of charge transfer complex between SDDS micelle and dye molecule. After cmc of SDDS, intensity is constant over a wide range of surfactant concentration indicating that all the dye molecules are incorporated into the hydrophobic micellar core.

In case of SDBS solution, absorbance at 520 nm decreases. Then, two peaks appear in the spectra at 506 and 532 nm indicating the formation of dimer. After 0.77 mM concentration of SDBS, the peak at 532 nm becomes prominent. After that, with increasing surfactant concentration, absorbance increases and peak gradually disappears at 506 nm. Here, sulphonate anion binds with this cationic dye. In the micellar media, only peak at 532 nm appears. This indicates that dimer is also unstable in SDBS micelle like other anionic micellar systems. The peak at 532 nm is also due to the formation of charge transfer complex between micelle and safranine T. After 0.2 mM SDBS concentration, it forms an isosbestic point at