

# Interface of AOT/Igepal CO720/cyclohexane/water mixed reverse micelle by spectroscopic approach

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## Abstract

Visible spectra of Safranin T (ST) in anionic reverse micelle (AOT/cyclohexane/water), non-ionic reverse micelle (Igepal CO720/cyclohexane/water) and mixed reverse micelles of AOT/Igepal CO720/cyclohexane/water at different compositions and different  $\omega$  ( $=[\text{water}]/[\text{surfactant}]$ ) have been studied. Charge transfer band of Safranin T in reverse micellar and mixed reverse micellar medium has been isolated both in ground and excited state. Iodide ion induced dynamic quenching at low quencher concentration becomes a combination of both the dynamic and static quenching at high quencher concentration. Iodide ion induced quenching study has been used as a tool to identify the altered interface of AOT/Igepal CO720/cyclohexane/water mixed reverse micelle compared to AOT/cyclohexane/water reverse micelle. Absorption and fluorescence spectra of ST in polyethylene glycol coated interface of AOT reverse micelle has been observed to identify the role of poly(oxyethylene) group of Igepal CO720 on spectral behavior of ST in mixed reverse micelle.

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**Keywords:** Mixed reverse micelle; Charge transfer interaction; Dynamic quenching; Static quenching; Poly(oxyethylene) group

## 1. Introduction

The cationic dye (Safranin T) forms 1:1 charge transfer complexes with ionic micelles SDS and non-ionic micelles Triton X100, Tweens, Brijes and Igepals [1–4]. Charge transfer interaction of ST in micellar medium has been extended to the reverse micelles of Triton X100, Tweens [5] and Igepals [6]. Charge transfer interaction of ST with polyethylene glycols [7] of varying degree of polymerization was performed to elucidate the role of poly(oxyethylene) group of non-ionic surfactant in ST-non-ionic surfactant interactions. Reverse micelles (RM) formed by ionic surfactants in a mixture of water and hydrocarbon as the oil have been extensively studied in recent years [8,9] because they provide easily controlled model compounds for the behavior of biomembranes and could improve our understanding of reactivity and interactions in confined media. Bis(2-ethyl-1-hexyl) sulfosuccinate (AOT) is the best known representative of this class of compounds and has been studied by spectroscopic technique [10].

It is well known that certain mixtures of surfactants can provide better performance than pure surfactants for stability and activity of enzyme [11], extraction of protein [12], synthesis of nanoparticles [13] etc. and thus it is expected that altered interface and enhanced solubilisation of water in water-in-oil (w/o) microemulsions will be achieved with certain surfactant mixtures. Shah et al. [14–16] had modeled the mechanism of water solubilisation and phase separation due to the coalescence of droplets in reverse micelle and mixed reverse micelle and verified by Zana et al. [17,18], Tondre et al. [19], Paul et al. [20] for both single and mixed surfactant systems. As proposed by Nazario et al. [21], there are two possibilities for the exact solubilisation site of non-ionic co-surfactant in the reverse micelles: (1) immersed in micellar water pool and (2) solubilise in the AOT surfactant head group region. Liu et al. [22] have studied the properties associated with the microenvironment near the surfactant-water interface and core of the waterpool of the mixed reverse micelle by fluorimetric technique using cationic dye tris(2,2'-bipyridine) ruthenium dichloride hexahydrate and anionic dye 1,8-anilinonaphthalenesulfonic acid, respectively.

In the present study charge transfer band has been identified in reverse micelle of AOT, Igepal and mixed reverse

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micelle of AOT and Igepal with cationic dye ST. Composition and  $\omega$  dependent variation of charge transfer interactions and fluorescence quenching of ST have been observed in AOT/Igepal/cyclohexane. Fluorescence quenching of ST by copper sulfate and potassium iodide has been performed in reverse and mixed reverse micellar medium. Meier [23] reported the alteration of interface of AOT reverse micelle in presence of polyethylene glycol (PEG) and hence the interaction of ST with PEG in AOT reverse micelle has been included in this work. Variation of spectroscopic properties of ST in mixed reverse micelle and polyethylene glycol covered AOT reverse micelle has been used as comparative study.

## 2. Experimental

The surfactant polydisperse poly(oxyethylene) nonyl phenol (Igepal CO720) is commercially available having structure  $(4-(C_9H_{19})C_6H_4(OCH_2CH_2)_nOH, n \sim 12)$  and it is an Aldrich product used without further purification. PEG 400 and 600 were of BDH products. The numbers correspond to their average molar masses [24]. Safranin T (ST) (E. Merck) was recrystallised twice from ethanol–water mixture before use. Spectroscopic grade cyclohexane (E. Merck) was used. The solvent used for the measurement was rigorously purified following standard procedure [25], because even a trace of moisture in solvent can affect the absorption and fluorescence properties of the experimental solutions. Absorption spectra were recorded using a Shimadzu (Japan) UV–vis 1700 model spectrophotometer with a matched pair of silica cuvettes. Fluorescence spectra were taken in a F-II A spectrofluorimeter (Spex, INC, NJ, USA) with a slit width of 1.25 nm. All the measurements were done thrice. Doubly distilled water was used for solution preparation. Phosphate buffer was used for solution preparation of Safranin T and the analytical concentration of the buffer was  $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ . pH of the solutions were found 7 ( $\pm 0.2$ ). Potassium iodide and copper sulfate, used for fluorescence quenching study, were obtained from E. Merck (Germany).

## 3. Results and discussion

### 3.1. Absorption study

The absorption spectra of ST in the reverse micelle of AOT/cyclohexane at different water content have been given in Fig. 1. In aqueous solution of ST, the absorption maximum is at 522 nm and it is shifted to 532.5 nm in reverse micelle of AOT (0.2 M). On gradual addition of water in the reverse micelle, i.e. with increasing  $\omega$  ( $=[\text{water}]/[\text{AOT}]$ ), absorbance decreases without any shift in the spectral maxima (Fig. 1). There has an isosbestic point at 540 nm and from the isosbestic point and bathochromic shift in spectral maxima, it may be assumed that there is a probability of formation of ST–reverse micelle charge transfer complex. ST may be localized at the interface of AOT reverse micelle by electron donor–acceptor complexation between the negatively charged sulfonate group and the positively charged dye ST similar to the complexes between dye Auramine O and AOT reverse micelle [26].

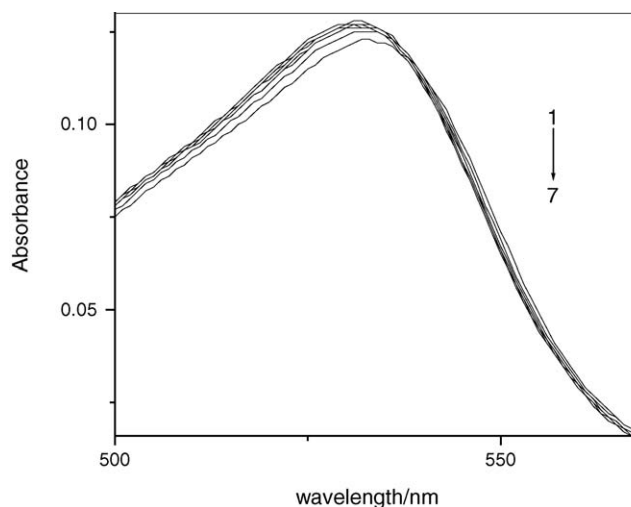


Fig. 1. Absorption spectra of Safranin T in AOT/cyclohexane reverse micelle at (1)  $\omega = 2.5$ , (2)  $\omega = 5$ , (3)  $\omega = 7.5$ , (4)  $\omega = 10$ , (5)  $\omega = 12.5$ , (6)  $\omega = 15$  and (7)  $\omega = 17.5$  where  $[\text{AOT}] = 0.2 \text{ M}$ .

In the second phase of study, the change in absorption behavior of ST has been observed in Igepal CO720 reverse micelle solubilised in the solvent cyclohexane. At low  $\omega$  ( $\leq 5$ ), the absorption maximum of ST has been observed at 540 nm and the absorption band has been designated as the charge transfer band. With increasing  $\omega$ , the absorbance of ST decreases with concomitant blue shift in absorption maxima and level up at 532.5 nm at  $\omega = 11$ .

On gradual increase in mole fraction of non-ionic surfactant Igepal CO720 ( $3 \leq \omega \leq 11$ ) in the reverse micelle of AOT, absorbance has been enhanced with red shift in absorption maxima. For the reverse micelle of AOT the absorption maxima of ST is at 532.5 nm which is shifted to 540 nm at mole fraction of Igepal = 0.05. On further increasing the mole fraction of Igepal CO720 the absorption maxima remains unaltered but the absorbance of the charge transfer band has been enhanced (Fig. 2a). Simultaneously, the change in absorbance and absorption maxima has been studied at different water content of the mixed reverse micelles for each composition. With increasing  $\omega$ , absorbance of ST decreases with a hypsochromic shift in the spectral maxima. At higher  $\omega$  the absorption maxima were at 532.5 nm which is identical to the absorption maxima of ST in AOT reverse micelle as well as the absorption maxima of ST in Igepal reverse micelle at  $\omega = 11$ . On further addition of water to the mixed reverse micelle the absorption maxima remains unaltered. All the spectra at different  $\omega$  have been given in Fig. 2b and from the figure it is evident that all the spectral lines passes through an isosbestic point at 522 nm. So, there is a possibility of charge transfer complexation of ST–mixed reverse micelle.

### 3.2. Determination of vertical ionization potential of non-ionic reverse micelles and anionic/non-ionic mixed reverse micelles

From the variation of absorption maxima in the reverse micellar medium, the vertical ionization potential of the reverse micelles and mixed reverse micelles has been calculated using

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