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SPECTRAL STUDIES OF TOLUIDINE BLUE O IN THE PRESENCE OF SODIUM DODECYL SULFATE

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In the present investigation the absorption and emission spectral studies of toluidine blue O with SDS to understand the formation of photoactive monomer dyes and photoactive dimmer dyes were carried out. Like many organic dyes the optical properties of TBO changes in the presence of surfactant and due to the formation of ion associates and a micellar environment. The TBO is known to form dimmer in the presence of γ – cyclodextrin and metachromic TBO with charged synthesis biological polymers. In the present study new absorption band due to metachromic TBO was observed at 590 nm in the presence of SDS micelle and it shows the formation of a small fraction of meta chromic TBO and dimmer TBO.

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1. Introduction

The photochemistry of dyes has contributed to the understanding of the mechanism of electron transfer reactions in photo electrochemical devices [1-6]. Photo induced electron transfer processes in surfactant solutions are potentially important for efficient energy conversion and storage because surfactant micelles help to achieve the separation of the photoproducts by hydrophilic-hydrophobic interactions of the products with the micellar interface [7-10]. Dye-surfactant interactions are generally complex [11]. Molecular complexes having specific and characteristic physicochemical features may be formed. The dyes aggregation phenomena have attracted attention in the past and are nowadays receiving novel consideration [12-14] in view of possible new technical applications such as opto-electronic devices, optical logical elements, sensitizing agents in color photography, photoconductors, electroluminescent devices and electro optically active centers in photovoltaic systems, solar energy conversion, semiconductor photo catalysis, pollutant control, photodynamic therapy, Pharmaceutical preparation, besides the more traditional ones. Moreover, toluidine blue O (TBO) shows a pronounced ability to permeate the cellular membrane and to perform a photo-bacterial activity [14,15]. More traditionally, it is widely employed in the quantitative determination of an important anticoagulant molecule such as heparin [16-18]. Such a dye molecule is indeed one of the most widely employed in the staining applications. The most evident effect shown by TBO, among many other dyes examples is so-called metachromasia, i.e. the pronounced variation of the visible spectrum due to the aggregation phenomenon and the electrostatic interaction with the charged synthetic and biological polymers [9,20]. Recently, TBO molecules combined with gold chloride used as a stains to investigate chick

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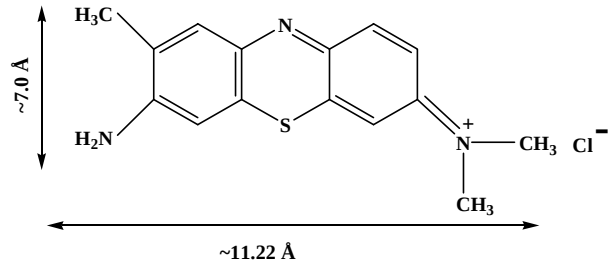
embryo neural tissue and poly (toluidine blue) film electrode are reported as a nitrite amperometric sensors [21,22].

Phenothiazine dye derivatives are most extensively studied and widely used in solar energy conversion. However, these dyes form photoinactive dimers in concentrated aqueous solution [23-25]. In order to prevent the formation of photoinactive dimers, the organized assemblies such as micelles, vesicles, bilayers, etc. are used. In the present investigation, we have carried out the absorption and emission spectral studies of Toluidine blue O with SDS to understand the formation of photoactive monomer dyes from photoinactive dimer dyes.

2. Experimental methods

Toluidine blue O, 3-Amino-7(dimethyl amino)-2-methyl phenothiazin-5-ium, (TBO) (Fig.1) was obtained from S.d. fine chemicals.



Toluidine Blue O (TBO)

Fig .1. Structure of TBO.

Sodium dodecyl sulfate (SDS) was purchased from S.d. fine chemicals and was used as received. Water was doubly distilled, the second distillation over alkaline potassium permanganate, using an all-glass apparatus (Borosil) and used in all experiments. All the experiments were carried out at room temperature (25°C). Analytical grade methanol, acetonitrile and ether (S.d. fine) were purchased and used as received unless otherwise mentioned. Commercially available ethanol was distilled over calcium oxide and was used. Purification of solvents was carried out according to the reported procedures [26].TBO was purified by column chromatography on neutral alumina using ethanol: benzene (7:3 v/v) containing 0.4 ml glacial acetic acid per 100 ml [27,28]. Spectrally pure fractions were crystallized by concentrating the eluate under vacuum and the crystals were dried in a vacuum desiccators at room temperature to give spectrally pure dyes . λ_{max} = 630 nm and $\varepsilon_{63\tilde{3}}$ = 51441 $dm^3\ mol^{-1}\ cm^{-1}$). Absorption spectral studies were carried out by using a CARY 500 scan UV-Vis-NIR-spectrophotometer. Fluorescence studies were performed on a JASCO 6300 spectrofluorometer. The TBO molecules were excited at 595 nm, and the emission spectra were recorded with a slit width of 10 and 5 nm excitation and emission slits, respectively. All the measurements were carried out at room temperature (25^0C). A 10^{-6} mol dm^{-3} solutions of TBO were prepared daily for experiments. For the study of the influence of SDS, the SDS solutions were prepared daily from the stock solution. The various concentrations of SDS solutions were prepared by pipetting an aliquot of the stock solution into a 10ml SMF and then the solutions were made up to the mark with distilled water. The mixture of dye and SDS solutions were stirred uniformly for 30 minutes and allowed to equilibrate for 15 minutes before recording the absorption and emission spectra. The molecular dimensions of TBO molecules were measured by simulating the molecular model using Biosym-Insight II molecular modeling software on a silicon graphics computer system.

3. Results and discussion

3.1 Absorption spectral studies

The absorption spectra of TBO in the presence of different concentrations of SDS are shown in Fig. 2. In the absence of SDS, TBO shows an absorption band at 630 nm (Fig. 2 (a)), which corresponds to the monomer TBO [29,30]. Addition of increasing concentration of SDS led to a continuous decrease in absorbance (630 nm) (without significant change in the λ_{max}) to reach a minimum with the addition of SDS at [SDS]< CMC ($\approx 0.25 \times 10^{-3}$ mol dm^{-3}). In addition to that new peaks were appeared at 590 and 490 nm, respectively, are shown in Fig. 2. (e) (0.25×10^{-3}). The monomer peak at 630 nm and the new peaks were increased simultaneously upon increasing the concentration of SDS (Fig. 2. (f)). The absorption intensity at 490 nm was decreased upon further increasing the concentrations of SDS (Fig. 2. (f-h) and disappeared, whereas absorption intensities at 630 nm and 590 nm are increased simultaneously with increasing the concentrations of SDS (Fig. 2. (f-i). On further increasing the concentrations of SDS the absorption band at 630 nm increased and attained saturation, at the same time the absorption peak at 590 nm was decreased with red shift and merged to the 630 nm monomer peak. Recently, the researchers have reported the electrostatic interactions of polyanionic quantum dots and charged synthetic biological polymers with positively charged TBO [31,32]. The TBO dye forms a metachromic state and the absorption band appears around 510 nm and at 490 nm, respectively. In the present study, we expect that the new absorption band appeared at 490 nm is due to the formation of metachromic state TBO interacting with the anionic SDS (Fig .3).

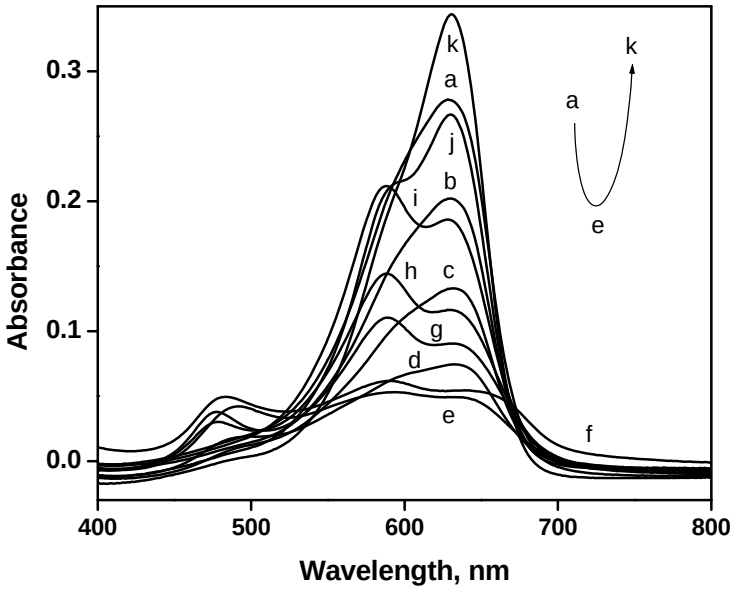


Fig . 2. Absorption spectra of TBO (5.54×10-6 mol dm-3) at various SDS concentrations. [SDS]: (a) 0, (b) 0.02×10^{-3}, (c) 0.05×10^{-3}, (d) 0.1×10^{-3}, (e) 0.25×10^{-3}, (f) 0.9 x 10^{-3}, (g) 1.8×10^{-3}, (h) 2.0×10^{-3} (i) 2.5×10^{-3}, (j) 3.0×10^{-3} and (k) 4.0×10^{-3} mol dm^{-3}.

The peak observed at 590 nm (Fig. 2 (0.9×10^{-3}) is very similar to the dimer absorption band noticed in the absorption spectra of higher concentrations of TBO in the absence of SDS. Similar type of absorption band has been reported for TBO with γ–cyclodextrin inclusion complexes [30]. This clearly indicates that the absorption band, which appeared at 590 nm in the presence of SDS, is due to the formation of dimer TBO [30].

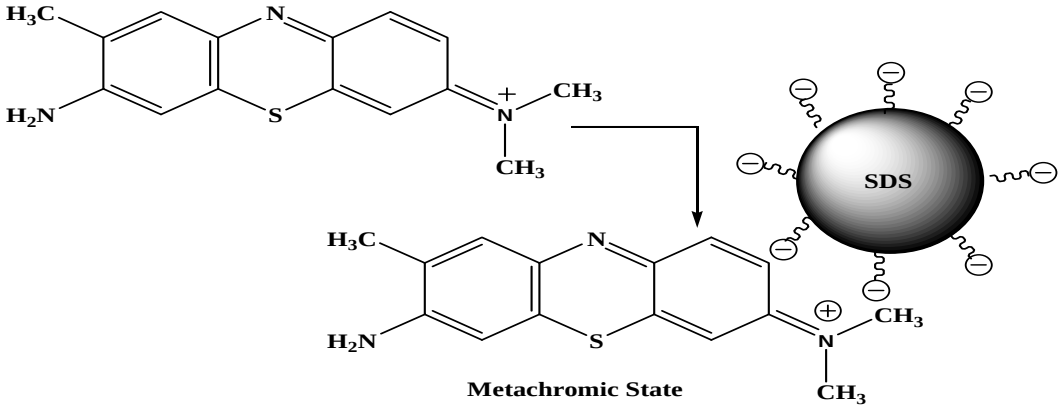


Fig .3. Metachromic interaction between Toluidine blue O and SDS.

The graph plotted against concentrations of SDS vs absorbance of TBO are shown in Fig. 4. The Fig. 4 shows that the addition of increasing concentration of SDS led to a continuous decrease in absorbance (630 nm) (without significant change in the λ_{max}) to reach a minimum with the addition of SDS at [SDS] < CMC ($\approx 0.25 \times 10^{-3}$ mol dm^{-3}), then began to increase again when the [SDS] was increased. Previously, the researcher has reported a smooth curve for organic dye molecule with surfactant. The organic dye molecules interact with surfactant to form monomer dimer equilibrium between below and above the CMC. In the present study, we observed a broad curve above CMC of SDS. It clearly indicates that there is an existence of metachromatic TBO in between the formation of monomer and dimer equilibrium, above CMC (Fig. 2 (e-h)).

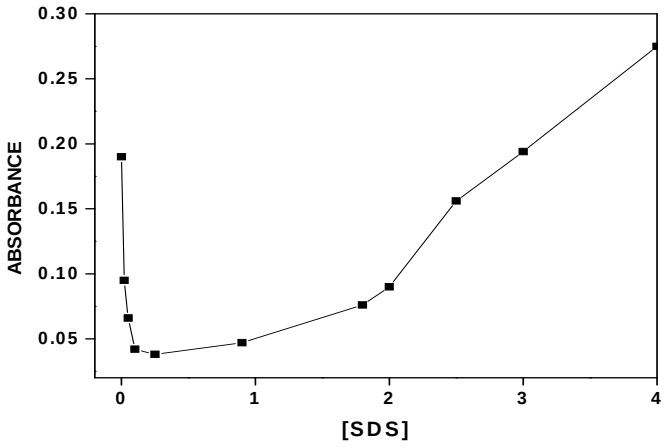


Fig. 4. Plot of absorbance of TBO vs [SDS].

3.2. Emission spectral studies

More generally, any change in absorbance depending on the addition of surfactants was systematically associated with a similar variation in the emission intensity [31-38]. The emission spectrum of TBO in the absence of SDS shows an emission maximum at 660 nm, when TBO was excited at 595 nm (30). The emission spectra recorded for TBO with different concentrations of SDS are shown in Fig. 5. The TBO fluorescence was strongly altered by SDS surfactant. Very similar behavior is observed as we observe in the absorption spectral studies. The emission intensity reached a maximum value at [SDS]≥ CMC ($\approx 4.0 \times 10^{-3}$ mol dm^{-3}) without further change (Fig. 6).

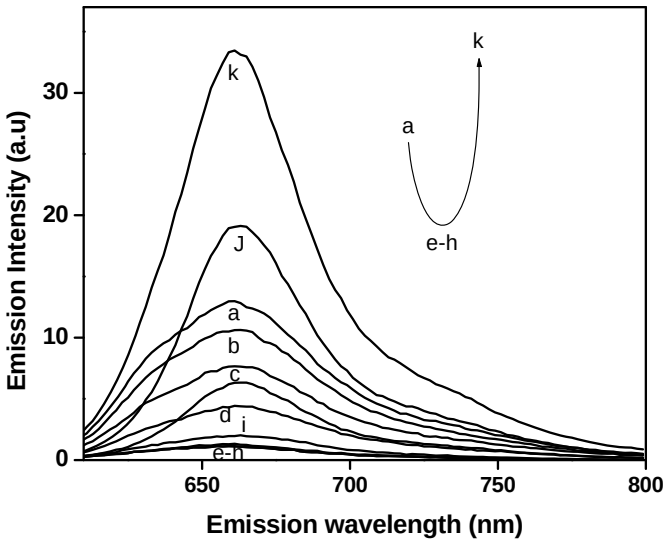


Fig. 5. Emission spectra of TBO (5.54×10^{-6} mol dm^{-3}) at various SDS concentrations. [SDS]: (a) 0, (b) 0.02 × 10^{-3}, (c) 0.05 × 10^{-3}, (d) 0.1 × 10^{-3}, (e) 0.25 × 10^{-3}, (f) 0.9 x 10^{-3}, (g) 1.8 × 10^{-3}, (h) 2.0 × 10^{-3}, (i) 2.5 ×10^{-3}, (j) 3.0 × 10^{-3} and (k) 4.0× 10^{-3} mol dm^{-3}.

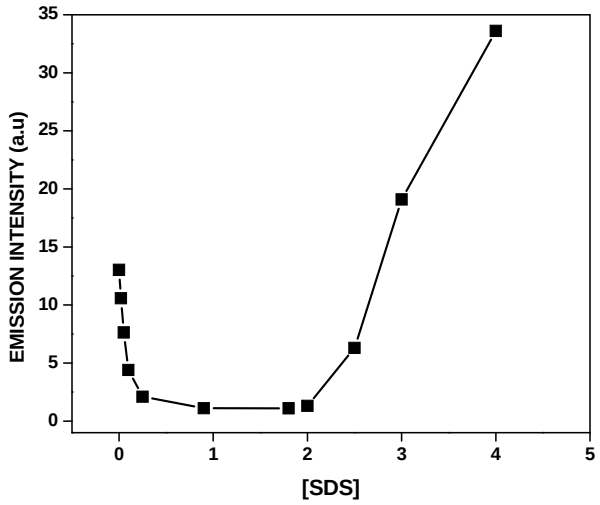


Fig. 6. Plot of emission intensity of TBO vs [SDS]. λ_{em} = 630 nm.

3.3. Self-aggregation of $(D^+ S^-)_n$ type between TBO and SDS

Like many organic dyes,[39-46] the optical properties of TBO changes in the presence of a surfactant and (below and above CMC) owing to the formation of ion associates and a micellar environment. Competitive columbic-hydrophobic interactions [39-47] governs the micellar binding of the cationic TBO dye. Earlier, spectral peculiarities were noticed in the behavior of dye-surfactant systems carrying opposite charges [38,47-49]. The typical changes observed in the fluorescence intensity of cationic TBO dye (D^+) species involved in a D^+-S^- interaction upon increasing the concentration of an anionic surfactant SDS (S^-) are summarized in (Fig. 6). (i). At very low [S^-] (below the CMC, part (1) in (Fig. 7) there is a formation of a dye-surfactant salt starting with the ion-pair D^+-S^- (Fig. 7 (a)) and continuing with dye-surfactant aggregates depicted as $(D^+$-$S^-)_n$ complexes(47) (Fig. 8 (b)). (ii) A dye monomeric-multimeric equilibrium is

progressively established at slightly higher [S^-] (lower premicellar region ([S^-] << CMC) and the emission intensity starts to decrease as dye-surfactant-rich aggregates $(D^+\text{-}S^-)_n$ are increasingly initiated. Both electrostatic and hydrophobic interactions may operate in the stabilization of these aggregates, but the electrostatic attractions must be predominant at this S^- concentration. Upon increasing [S^-], the dye emission decreases (part (2) in (Fig. 7) to a minimum for a given concentration of S^- which is lower than the CMC. This behavior is probably due to the presence of some premicelles with monomeric dye content, which provides the dye with a micellar-like environment in this SDS region; it also means that the $(D^+\text{-}S^-)_n$ aggregates begin to be progressively transformed into induced premicelles [50]. (iii). Near and just below the CMC (Fig. 8. (c)) the progress of the reorganization of $(D^+\text{-}S^-)_n$ aggregates into premicelles with

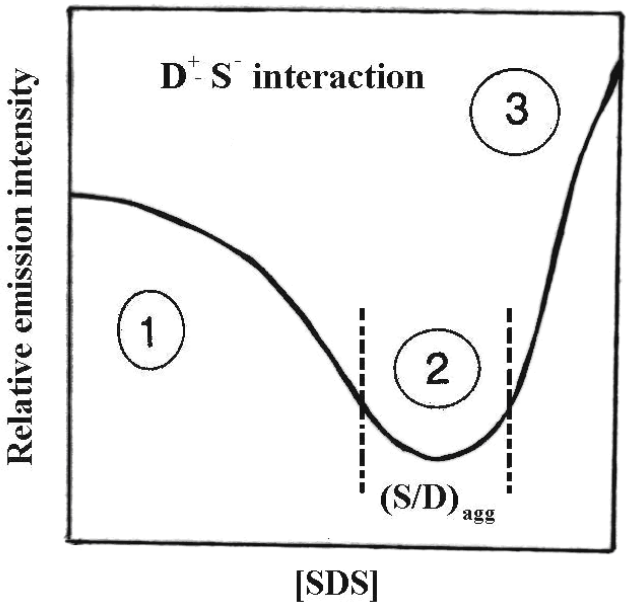


Fig. 7. Typical behavior of a $D^+\text{-}S^-$ interaction type between a cationic dye (D^+) and anionic surfactant (S^-) of opposite charges showing the variation in the relative emission intensity of the dye depending on increasing the concentration of SDS (S^-).

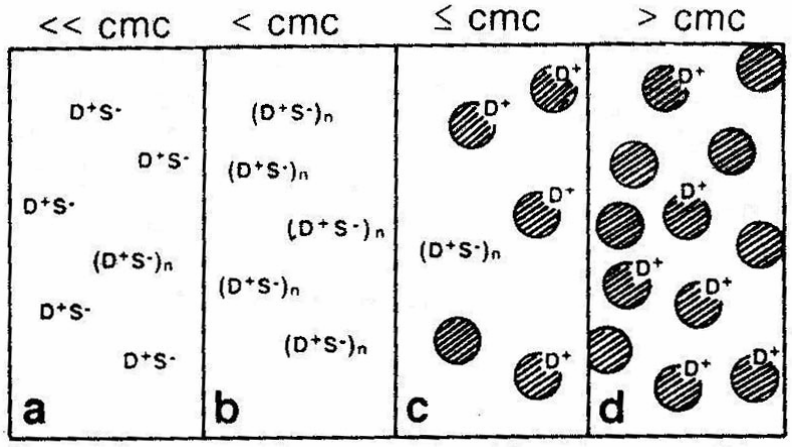


Fig.8. Interaction models of dye-surfactant systems ($D^+\text{-}S^-$) of opposite charges.

monomeric D^+ content results in an increase in the fluorescence intensity in this higher premicellar region. Similar data were reported [51] showing that the presence of premicelles provides the dye with a micellar-like environment in this [S^-] < CMC region. (iv). On further addition of S^- the

premicelles change gradually into ordinary micelles above the CMC. Obviously, with increasing [micelle], only unoccupied or singly occupied micelles are present in solution (Fig. 8 (d)) [39-46]. The fluorescence intensity is then enhanced (part (3) of Fig. 7) as the D^+ molecules are individually bounded to micelles, since the (short distance) dye-dye interactions involved in the $(D^+S^-)_n$ aggregates are reduced. The intensity reaches a limiting level at higher $[S^-]$ ($[SDS] \geq 4.0 \times 10^{-3}$ mol dm^{-3}) when all D^+ are compartmentalized in normal micelles. The schematic representation of a charged micelle with its ionic atmosphere (Gouy-Chapman layer) and the possible location of the TBO dye (D^+) in the Stern layer are shown in Fig. 9. In SDS micelle, the $-SO_4^-$ group is highly hydrophilic and water may easily penetrate into the interior of these micelles; the D^+-S^- columbic interaction is

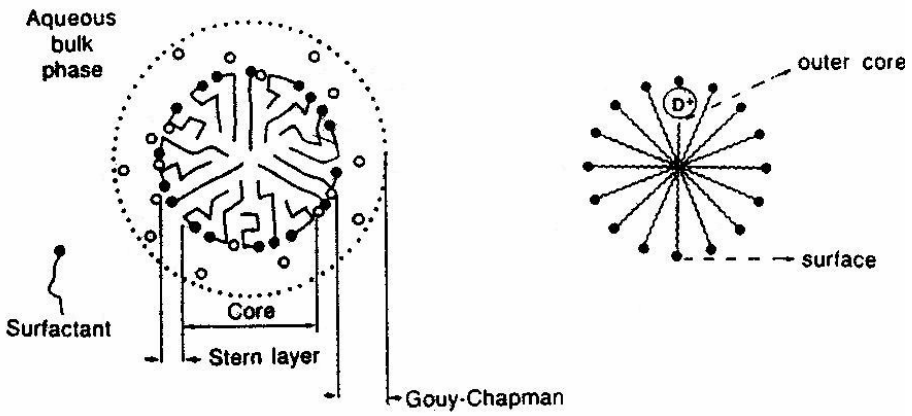


Fig. 9. Schematic representation of a charged micelle (SDS) with its ionic atmosphere (Gouy-Chapman) and possible location of the dye D^+ (TBO) in the Stern layer.

predominant and TBO (D^+) readily interacts electrostatically with the SDS anionic head groups of Stern layer. The TBO is known to form dimer in the presence of □-cyclodextrin (□-CD) and metachromic TBO with charged synthetic and biological polymers. In the present study, the new absorption band due to metachromic TBO was observed at 490 nm with low intensity and dimer TBO was observed at 590 nm in the presence of SDS micelle and it shows that the occupation of TBO at the Stern layer of the micelle leads to the formation of a small fraction of metachromic TBO and dimer TBO.

4. Conclusions

The absorption and emission spectral properties of TBO in the presence of surfactant (sodium dodecyl sulfate (SDS)) were studied. The changes in the absorbance and emission intensities of TBO at different concentrations of SDS were observed. It is found that at premicellar SDS concentration, the electrostatic interaction led to the formation of a dye (D^+)-surfactant (S^-) ion-pair (D^+-S^-). At increased SDS concentration, the formation of dye-surfactant rich aggregates $(D^+$-$S^-)_n$ are initiated and at the CMC of SDS, the TBO molecules (D^+) are bound to SDS micelle to form metachromatic TBO and dimer TBO. The absorbance and emission intensity of TBO reached a limiting level at higher [SDS] (above the CMC of SDS ($\approx 4.0 \times 10^{-3}$ mol dm^{-3})) when all D^+ are compartmentalized in normal micelles to form more amount of monomer TBO.

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