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Studies on the molecular interaction of Azure dyes with sodium lauryl sulphate

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ABSTRACT

The absorption spectra of Azure dyes such as Azure A, Azure B and Azure C in aqueous solution of sodium lauryl sulphate (SLS) show that Azure dyes form 1:1 charge-transfer (CT) or electron-donor-acceptor (EDA) complex with SLS. The photogalvanic and photoconductometric studies also support the above interactions. From the thermodynamic, spectrophotometric and photophysical parameters of these complexes, the abilities of dyes to accept electron are found to be in the order: Azure C > Azure A > Azure B. There is a good correlation among the spectral and thermodynamic properties of these complexes.

Keywords: Azure dyes, CT interaction, Dye- surfactant, Photogalvanic

ARTICLE INFO

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1. Introduction

Surface active compounds are frequently use to solubilize molecules which otherwise would not be soluble in water. Solubilization in surfactant micelle has been studied extensively [1-3]. Corrin et al. and others [4-6] observed the

change in the colour of ionic dyes in the presence of oppositely charged ionic surfactant micelle. Matibinkov and coworkers [7] studied the effect of sodium lauryl sulphate (SLS) on Xanthene dyes and observed shifts in their λ_{max} at

lower surfactant concentration.

Malik et al. [8] reported the spectral changes of several dyes due to electrostatic interaction between the anionic surfactant and basic dye or cationic surfactant and acidic dye giving a stoichiometric dye – surfactant complex. Guha et al. [9] attributed the changes in absorption spectra and the decrease in fluorescence intensity of thionine dye due to formation of dye-surfactant complex with sodium lauryl sulphate (below CMC). The absorption spectra of some acid dyes with surfactants like Hyoxid X-100, X-200 and X-400 showed that the absorption peaks were influenced considerably [10] i.e., the spectra of acid red 88 in the presence of Hyoxid X-100 show a shift from 480 nm to 520 nm, thereby indicating dye- surfactant interaction.

Forte- Tavcer [11] studied the interactions of anionic dyes C.I Acid Red 88 (AR88) with cationic surfactant: N-Cetyl pyridinium chloride (CPC), N-dodecyl pyridinium chloride (DPC) and Octadecyl trimethyl ammonium bromide (OTMAB) in aqueous submicellar solution. Using continuous variation method, it was found that with increasing alkyl chain length of surfactants and number of benzene rings of dyes, the interaction becomes stronger. Ghoreishi et al. [12] studied the interaction between a cationic surfactant, hexadecyl trimethyl ammonium bromide (HTAB) and two anionic azo dyes, C.I. Direct Orange 26 (DO26) and Direct Red 16 (DR16) using surfactant-selective electrode and spectrophotometry techniques. They found that DO26 forms strong CT complex with HTAB compared to DR16. To know the behavior of Azure dyes towards the surfactants, we have studied the interaction between Azure dyes and SLS, an anionic surfactant in aqueous media. For this purpose, the thermodynamics and spectrophotometric properties of the Azure dyes - SLS systems have been reported in this paper. The photogalvanic effect of dye- surfactant system in a photoelectrochemical (PEC) cell and conductometric effect of the above systems have been also reported to substantiate their interaction.

2. Experimental

The azure dyes used in this study were obtained from Sigma Chemical, USA. These were Azure A (3-amino-7-dimethyl amino phenothiazinium chloride), Azure B (3-dimethyl amino-7-methyl amino phenothiazinium chloride) and Azure C (3-amino-7-methyl amino phenothiazinium chloride). These were doubly recrystallized from ethanol-water. The anionic surfactant, SLS (sodium lauryl sulphate) and other chemicals were of AR grade, supplied by BDH (England) and were used without further purification. Absorption spectra were recorded on a Shimadzu UV -Vis Spectrophotometer (model UV -160) with a matched pair of stoppered quartz cells of 1 cm optical pathlength.

The photogalvanic effect of Azure dyes in the presence of surfactant solutions was studied in an H- shaped photoelectrochemical cell. The detail of experimental setup for the measurement of photovoltage was mentioned earlier International Journal of Chemistry and Pharmaceutical Sciences

[13]. An aqueous solution containing surfactant ($\sim \times 10^{-2}$ M) and Azure dye ($\sim \times 10^{-5}$ M) were taken in the illuminated chamber and a saturated solution of I_2 in iodide was taken in the dark chamber. The solutions were deoxygenated by bubbling N_2 gas into the cell through side tubes for at least 30 min. The photovoltage was measured by connecting the electrodes to a digital electrometer (model 4022) and conductance was measured with a conductivity bridge (model 201).

3. Results and Discussion

The visible absorption spectra of mixed solution of a fixed concentration of Azure A and varying concentration of SLS above the CMC i.e., $0.4-1.5 \times 10^{-2} \text{ mol dm}^{-3}$ in aqueous media at 298 K are given in Fig.1. The dye absorbs maximally at 632nm. The spectrum shifts to 635nm in the presence of SLS. The visible absorption spectra of other azure dyes in aqueous solution of SLS behave similarly but spectrum of Azure B and Azure C shift from 646 to 643.5 and 615 to 620nm, respectively. The spectrophotometric data were employed to calculate the thermodynamic as well as spectrophotometric properties of dye-surfactant interaction. For a 1:1 complex, the equilibrium constant (K_c) and molar extinction coefficient (ϵ_c) can be determined by using modified Scott's equation [14]:

$$\frac{[D][S]l}{d-d_0} = \frac{[S]}{\epsilon_c - \epsilon_0} + \frac{1}{K_c(\epsilon_c - \epsilon_0)} \quad (1)$$

where [D] and [S] are the initial concentrations of dye and surfactant SLS, respectively; l is the optical pathlength of the solution; d and d_0 are the absorbance of dye at the absorption maximum of the complex with and without surfactant, respectively, and ϵ_c and ϵ_0 are the respective molar extinction coefficient of the complex and dye molecule at the absorption maximum of the complex. However, it is a prerequisite for the equation in the present form that the condition $[S] \gg [D]$ should hold and that the complex absorbs at a wavelength where the surfactant is completely transparent. $[D][S] / d - d_0$ vs. $[S]$ were plotted for Azure dyes with surfactant, SLS in aqueous media at 298K (Fig.2) which were found to be linear in all cases confirming 1: 1 complex formation.

From the slope and intercept of each plot, K_c and ϵ_c of the dye - surfactant interaction were calculated. The thermodynamic quantity ($-G^0$) of these complexes were obtained from the equilibrium constants at room temperature by the usual method. The experimental oscillator strength (f) and transition dipole moment (D) were calculated from the spectra of complexes using Eqs.2 and 3, respectively [15]

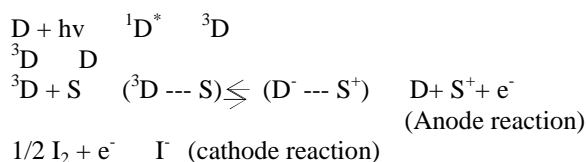
$$f = 4.319 \times 10^{-9} \epsilon_{\max} \overline{\nu}_{1/2} n^{-2} \quad \text{-----} \quad (2)$$

$$D = 0.09582 \left[\frac{\epsilon_{\max} \overline{\nu}_{1/2}}{\nu_{\max} n} \right]^{1/2} \quad \text{-----} \quad (3)$$

where n is the refractive index of the medium, ϵ_{\max} is maximum molar extinction coefficient, $\overline{\nu}_{1/2}$ is the width in

cm^{-1} of the band at half intensity, and $\bar{\nu}_{\text{max}}$ is wave number of the maximum absorption in cm^{-1} . All the thermodynamic and spectrophotometric parameters of the complexes in aqueous media are presented in Table 1. On illumination of the anode compartment of the PEC cell consisting of Azure dyes and surfactant, SLS a photovoltage develops and attains maximum value (V_{oc}) within a few minutes. When illumination is stopped, the photovoltage decays very slowly to original dark value establishing the reversibility of the photoinduced effect. The growth and decay curves for photovoltage generation in cells with different Azure dyes at 298K are shown in Fig. 3 and values are also inserted in Table 1. The dark conductivity as well as photoconductivity of Azure dyes in presence of surfactant SLS were merely remain same i.e., $3.0 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The experimental data presented above are direct spectrophotometric evidence of molecular interaction between Azure dyes and SLS (Table-1). Both the equilibrium constant and band shift are high in case of Azure C–SLS system and decreases from Azure A –SLS to Azure B–SLS system, respectively. In the anionic surfactant micelle, the cationic dye can reach to the stern layer of micelle to form a strong CT complex. This was also verified from the absorption spectra of Azure C in solvents of diverse nature. The molecular interaction between Azure dyes and SLS surfactants in aqueous medium is considered to be a CT interaction.

The generation of photovoltages with Azure dyes and surfactant, SLS can be explained if we assume that the interaction of Azure dyes with SLS is of CT or electron – donor – acceptor type where surfactant acts as electron donor and the dyes act as electron acceptor. During the photovoltage generation, the colour of the solution does not change appreciably. In the presence of oxygen, photovoltage is not generated which supports the participation of triplet dye in photovoltage generation according to the following scheme:



where D, S represent the dye and surfactant, respectively.

Photovoltage is not produced in the absence of surfactants which indicates that the interaction of triplet dye and surfactant is mainly responsible for generation of photovoltage through the formation of CT complex. According to Mulliken's CT theory [16], the CT complex is mostly nonionic in nature in the ground state but is predominantly ionic in the excited state. In the case of Azure dye - SLS systems, the interaction is ionic in nature, so no new ionic species are generated when the system is illuminated. Due to this, in conductometric measurement, conductivity remains same for both dark and illuminated conditions. From the experimental results presented in Table 1, it is revealed that the electron accepting ability of

Azure dyes from SLS in an aqueous media follow the order: Azure C > Azure A > Azure B. The structural consideration of the dyes also supports the above order. As the number of methyl group attached in amine function of thiamine ring increases, the electron acceptability of dye decreases. Considering the positive inductive effect of methyl group, more number of its delocalized the positive charge of sulphur in thiamine ring as a result electron acceptability from SLS decreases. So, there is a good agreement between experimental and theoretical based on structural view. From the present study, it is found that prominent interaction between Azure dyes and surfactant, SLS take place not only when the concentration of the surfactant is above the CMC value. Thus, the surface formation in the form of micelle is a necessary criterion for complex formation. The interfaces (micelle/water) favour the complex formation, a phenomenon related to surface catalysis.

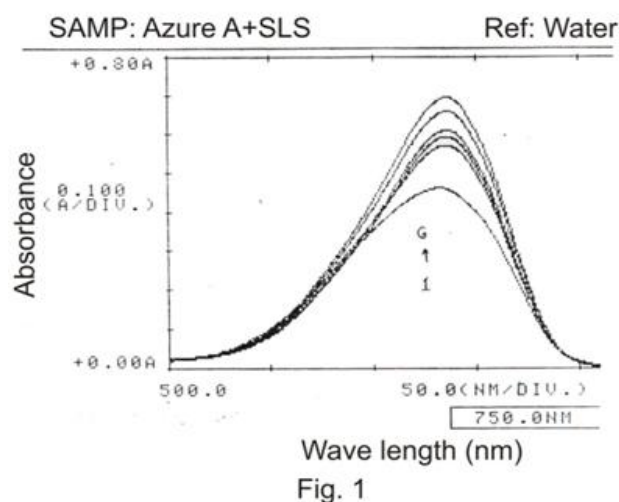


Figure 1: The visible absorption spectra of Azure A and SLS in water at 298K..Concentration of Azure A: $1.2 \times 10^{-5} \text{ mol dm}^{-3}$ and concentration of SLS ($10^{-2} \text{ mol dm}^{-3}$): (1) 0.0, (2) 0.40, (3) 1.0, (4) 1.4, (5) 1.45 (6)1.52.

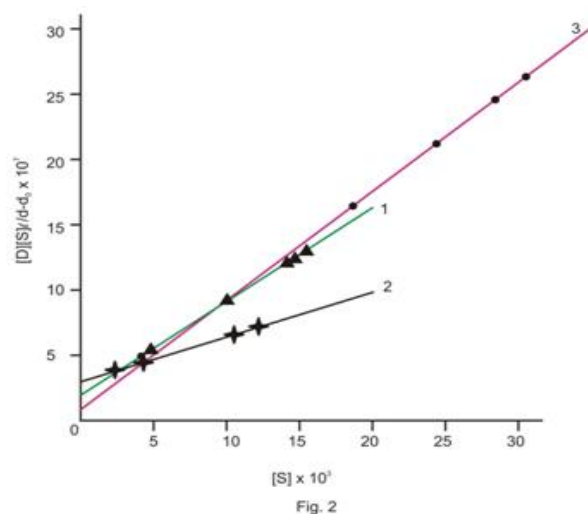


Figure 2: Plots of $[D][S] / d-d_0$ vs. $[S]$ for Azure dyes complexes with SLS surfactant: (1) Azure A, (2) Azure B and (3) Azure C.

Table 1: Thermodynamic, spectrophotometric properties and open-circuit photovoltage (V_{oc}) of Azure dyes- SLS complexes in aqueous media at 298K

Azure dyes ^a	$K_c \times 10^{-2}$ ($\text{dm}^3 \text{mol}^{-1}$) ^b	$-G^\circ$ (kJ mol^{-1})	Photovoltage (V_{oc}) (mV)	Complexed band				
				λ_{max} (nm)	Band Shift (cm^{-1})	f^c ($\text{m}^2 \text{mol}^{-1}$)	f (mol^{-1})	D (10^{-20}C)
Azure A	4.296	15.022	25	635.5	86.3	5271.2	2.533	2.134
Azure B	3.056	11.455	18	643.5	60.1	9146.2	3.588	2.555
Azure C	8.500	16.712	30	620.0	131.2	5268.1	2.350	2.029

^a Concentrations range of surfactant, SLS is $0.28 - 3.10 \times 10^{-2} \text{ mol dm}^{-3}$ and conc. of Azure dyes are $1.2 \times 10^{-5} \text{ mol dm}^{-3}$.

^b K_c values are the average of four to five measurements with an average deviation of 5%.

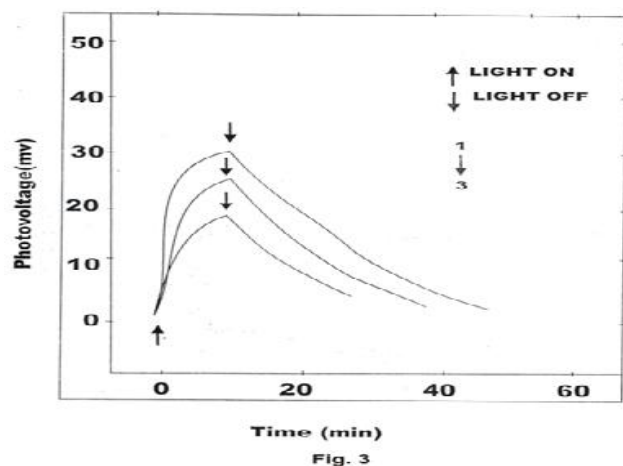


Figure 3: Growth and decay photovoltage of Azure dyes-SLS systems at 298K. The Azure dyes are: (1) Azure C, (2) Azure A and (3) Azure B.

4. Conclusion

Finally, it can be concluded that the nature of interaction of Azure dyes belongs to thianine class with anionic surfactant, SLS is CT by the donation of a lone pair of electrons of the oxygen atom of the $-\text{SO}_4$ group of SLS to the lowest vacant molecular orbital of Azure dyes.

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