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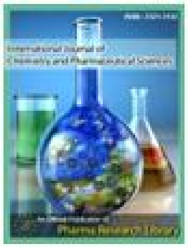

RESEARCH ARTICLE

Studies on the molecular interaction of Azure dyes with Triton X-100

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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 photo conductometric 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

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CONTENTS

1. Introduction

Surfactants possess a unique character of forming micelles and reverse micelles due to the presence of both hydrophobic and hydrophilic groups within the same molecule. They play an important role in solubilizing a variety of molecules insoluble in aqueous solution and their substantial catalytic effect on many chemical reactions [1-7]. 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 photo electrochemical (PEC) cell and conductometric effect of the above systems have been also reported to substantiate their interaction.

2. Materials and Methods

The azure dyes used in this study were obtained from Sigma Chemical, USA. These were Azure A (3-amino-7-dimethyl amino phenothiazainium chloride), Azure B (3-dimethyl amino-7-methyl amino phenothiazainium chloride) and Azure C (3-amino-7-methyl amino phenothiazainium chloride). These were doubly recrystallized from ethanol-water. The nonionic surfactant, Triton X- 100 (p-tert-octylphenoxy polyoxyethanol) 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 path length. The photogalvanic effect of Azure dyes in the presence of surfactant solutions was studied in an H- shaped photo electrochemical (PEC) cell. The detail of experimental setup for the measurement of photovoltage was mentioned earlier [13]. An aqueous solution containing surfactant (~ × 10^{-2} M) and Azure dye (~ × 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 Discussions

The visible absorption spectra of mixed solution of a fixed concentration of Azure A and varying concentration of TX-100 above the CMC i.e., 0.966 -3.5 x 10^{-2} mol dm^{-3} in aqueous media at 298 K are given in Fig.1. The dye absorbs maximally at 630nm. The spectrum shifts to 636nm in the presence of TX-100. The visible absorption spectra of other azure dyes in aqueous solution of TX-100 behave similarly but spectrum of Azure B and Azure C shift from 645.5 to 647 and 616 to 621nm, respectively.

The spectrophotometric data were employed to calculate the thermodynamic as well as spectrophotometreic 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]:

$$\frac{[D][S]\ell}{d-d_0} = \frac{[S]}{\varepsilon_c-\varepsilon_0} + \frac{1}{K_c(\varepsilon_c-\varepsilon_0)} \qquad (1)$$

where [D] and [S] are the initial concentrations of dye and surfactant TX-100, respectively; ℓ is the optical path length 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] >> [D] should hold and that the complex absorbs at a wavelength where the surfactant is completely transparent. [D] [S] ℓ/d- d_o vs. [S] were plotted for Azure dyes with surfactant, TX-100 in aqueous media at 298K which were found to be linear in all cases confirming 1: 1 complex formation(Fig.2). From the slope and intercept of each plot, K_c and ε_c of the dye - surfactant interaction were calculated. The thermodynamic quantity (-ΔG^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]:

$$f = 4.319 \times 10^{-9}\ \varepsilon_{max}\ \Delta\upsilon_{1/2}\ n^{-2} \qquad (2)$$

$$D = 0.09582 \left[\frac{\varepsilon_{max}\,\overline{\Delta\upsilon}_{1/2}}{\upsilon_{max}\, n}\right]^{1/2} \qquad (3)$$

where n is the refractive index of the medium, ε_{max} is maximum molar extinction coefficient, $-\Delta\upsilon_{1/2}$ is the width in cm^{-1} of the band at half intensity, and $-\upsilon_{max}$ 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, TX-100 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 inserted in Table 2. A photoconductance is observed on illumination the solution of Azure dyes with surfactant, TX-100 which is reversible and reproducible with respect to dark conductivities of them. The growth and decay of photoconductivites of Azure dyes – surfactant, TX-100 systems induced by illumination at 298K are shown in Fig. 4 and dark and photoconductivity of these systems are present in the Table 2.

The experimental data presented above are direct spectrophotometric evidence of molecular interaction between Azure dyes and TX-100 (Tables 1 and 2). Both the equilibrium constant and band shift are high in case of Azure C – TX-100 system and decreases from Azure A – TX-100 to Azure B – TX-100 system, respectively. In the nonionic surfactant micelle, the cationic dye can penetrate into the 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 TX-100 surfactant in aqueous medium is considered to be a CT interaction.

The generation of photovoltages with Azure dyes and surfactant, TX-100 can be explained if we assume that the interaction of Azure dyes with TX-100 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:

$D + h\nu \rightarrow {}^1D^* \rightarrow {}^3D$
${}^3D \rightarrow D$
${}^3D + S \rightarrow ({}^3D \text{ --- } S) \rightarrow (D^- \text{ --- } S^+) \rightarrow D + S^+ + e^-$
(anode ← reaction)

Where D and S represent the dye and surfactant, respectively. Photovoltage is not produced in the absence of nonionic surfactants which indicates that the interaction of triplet dye and nonionic 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 represented by a resonance hybrid of a nonionic ground state structure, (${}^3D$ --- S) and an ionic excited state structure, (D^- --- S^+). The excited or CT state is formed by the transfer of an electron from the nonionic surfactant, an electron donor to the dye, an acceptor on light absorption of suitable energy. So, upon light excitation of dye- nonionic surfactant systems, the primary charge separation takes place, forming a negatively charged dye and positively charged surfactant and this charge separation causes photovoltage in PEC cell. From conductivity study, it is observed that conductivities of Azure dyes- TX-100 systems increase slightly during illumination and it is reversible. So, it can be concluded that the nature of interaction between dyes and TX-100 is CT type due to generation of new ionic species in the excited state of the complex (Table 2). From the experimental results presented in Tables 1 and 2, it is revealed that the electron accepting ability of Azure dyes from TX-100 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 TX-100 decreases. So, there is a good agreement between experimental and theoretical based on structural view.

Form the present study, it is found that prominent interaction between Azure dyes and surfactant, TX-100 takes place 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.

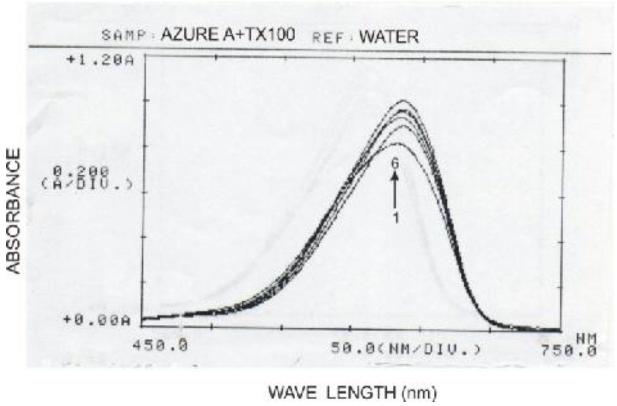

Fig.1 The visible absorption spectra of Azure A and TX-100 in water at 298K. Concentration of Azure A: $2.0\text{x}10^{-5}$ mol dm^{-3} and concentrations of TX-100 (10^{-2} mol dm^{-3}): (1) 0.0, (2) 0.966, (3) 1.891, (4) 2.454, (5) 2.816 and (6) 3.500.

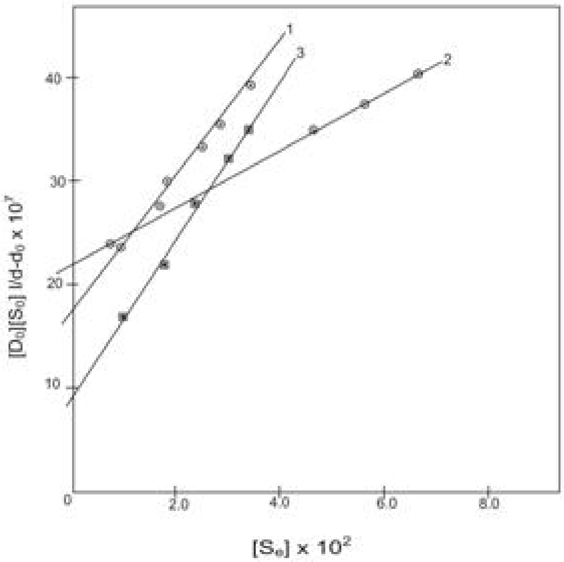

Fig.2 Plots of [D][S] ℓ/d-d_o vs. [S] for Azure dyes complexes with surfactant ,TX- 100 :(1) Azure A, (2) Azure B and (3) Azure C.

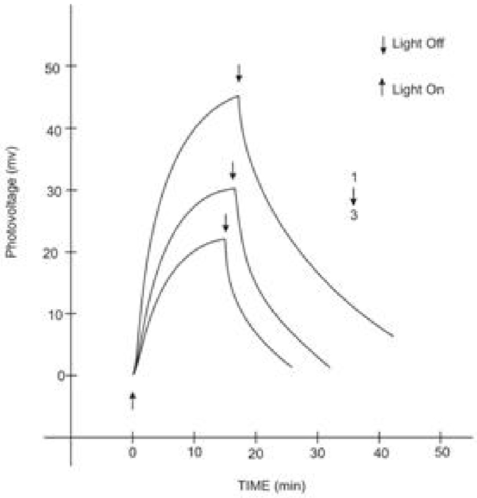

Fig.3 Growth and decay photo voltage of Azure dyes – TX-100 systems at 298K. The Azure dyes are: (1) Azure C, (2) Azure A and (3) Azure B.

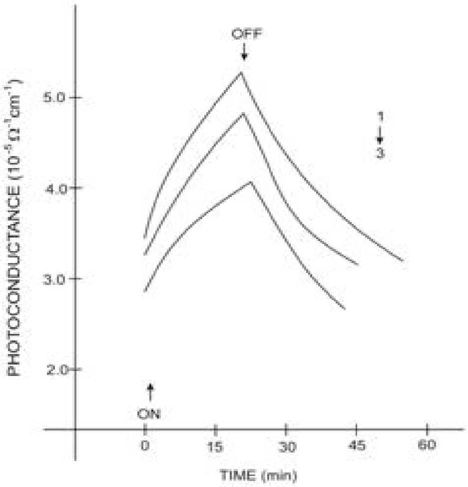

Fig.4 Growth and decay photoconductivity of Azure dyes – TX- 100 systems at 298K. The Azure dyes are: (1) Azure C, (2) Azure A and (3) Azure B.

Table 1. Thermodynamic and spectrophotometric properties of Azure dyes- TX-100 complexes in aqueous media at 298 K

Azure [a] dyes	K_c (dm^3 mol^{-1})[b]	- ΔG^o (kJ mol^{-1})	*Complexed band*				
			λ_{max}(nm)	Band Shift $\Delta\bar{\upsilon}$(cm^{-1})	ε_c (m^2 mol^{-1})	f (m mol^{-1})	D (10^{-20}C)
Azure A	38.44	2.153	636.0	149.74	4150.01	2.292	2.029
Azure B	12.91	1.509	647.0	35.92	6739.33	3.091	2.378
Azure C	83.64	2.612	621.0	130.71	4203.06	2.031	1.888

[a] Concentrations range of surfactant,TX-100 is 0.747 -6.688 x 10^{-2} mol dm^{-3} and conc. of Azure dyes are 2.0 x 10^{-5} mol dm^{-3}.
[b] K_c values are the average of four to five measurements with an average deviation of 5%.

Table 2. Open-circuit photo voltage (V_{oc}) and conductivities of Azure dyes-TX- 100 systems in aqueous media at 298K

Azure dyes[a]	Photovoltage (V_{oc}) (mV)	Dark conductivity × 10^5 (ohm^{-1} cm^{-1})	Photoconductivity × 10^5 (ohm^{-1} cm^{-1})
Azure A	30	3.265	4.823
Azure B	22	2.872	4.108
Azure C	45	3.436	5.276

[a] Concentration Azure dyes and surfactant,TX-100 are 2.0 × 10^{-5} mol dm^{-3} and 1.035 × 10^{-3} mol dm^{-3}, respectively.

4. Conclusion

Finally, it can be concluded that the nature of interaction of Azure dyes belongs to thianine class with nonionic surfactant, TX-100 is CT by the donation of a lone pair of electrons of the oxygen atom of the terminal –OH group of hydrophilic part of TX-100 to the lowest vacant molecular orbital of Azure dyes.

5. Acknowledgement

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