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Studies on Molecular Interaction of Rose Bengal with Surfactants

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Abstract

The spectroscopic investigation on anionic dye, Rose Bengal with three different types of surfactants such as CTAB(cationic), SLS(anionic) and Triton X-100(TX-100), Tween-20, 40, 60, 80(nonionic) in aqueous media show that Rose Bengal forms a 1:1 molecular complex with TX-100,Tweens and CTAB. No interaction is observed between Rose Bengal and SLS. The thermodynamic and spectrophotometric properties of these complexes suggest that Rose Bengal forms a strong charge transfer complex with TX-100 and Tweens whereas the interaction of Rose Bengal with CTAB is columbic in nature. Photogalvanic and photoconductometric studies also support the above interactions.

Keywords: Rose Bengal, CT interaction, CMC, Photoconductivity

Contents

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1. Introduction

Surfactants are surface active agents which can form organized structures like micelles and reverse micelles in aqueous and non-aqueous media due to the presence of both hydrophobic and hydrophilic groups within the same molecule. The most outstanding properties of surfactants are their ability to solubilize a variety of molecules which are insoluble in aqueous solution and their substantial catalytic effect on many chemical reactions [1]. Akbaş et al. [2] studied the interaction of anionic dye-cationic surfactant in mixtures of cationic and nonionic surfactants and concluded that the alkyl chain length and the number of polyethylene in nonionic surfactants do not have an enormous effect on the values of absorbance. Matibinkov et al. studied the effect of sodium lauryl sulfate (SLS) on xanthene dyes and observed shifts in their λ_{max} at lower surfactant concentrations. Corrin et al. and others [3-5] observed the change in the colour of ionic dyes in the presence of oppositely charged ionic surfactant micelle. Ghoreishi et al. studied the interaction between a cationic surfactant, hexa trimethyl ammonium bromide (HTAB) and two anionic Azo dyes i.e., C.I. Direct Orange 26 (DO26) and Direct Red 16 (DR16) using surfactant – selective electrode and spectrophotometry techniques. The result indicates that DO26 forms strong CT complex with HTAB compared to DR16. In the present paper, spectrophotometry was used to investigate the nature of interaction of an anionic dye, Rose Bengal with different surfactants (ionic and nonionic) in aqueous micellar solution at 298K. These studies have been substantiated by photogalvanic and photoconductivity effects of dye-surfactant systems.

2. Materials and Methods

Rose Bengal, supplied by Sigma Chemicals was recrystallized from ethanol-water. The surfactants, cationic: CTAB (cetyltrimethyl ammonium bromide), anionic: SLS (sodium lauryl sulphate) and nonionic: TX-100 (p-tert-octylphenoxypolyoxyethanol), Tween-20 (polyoxyethylene sorbitan monolaurate), Tween-40 (polyoxyethylene sorbitan monopalmitate), Tween-60 (polyoxyethylene sorbitan monostearate), Tween-80 (polyoxyethylene sorbitan monooleate) were obtained either from BDH (England) or Sigma Chemicals (USA). They were of AR grade and used as received. The absorption spectra were recorded on a Shimadzu UV- Visible spectrophotometer (model UV-160) with a matched pair of quartz cells of 1 cm optical path length. The photogalvanic effect of Rose Bengal in the presence of surfactant solution was studied in an H-shaped photoelectrochemical (PEC) cell. Details of the experimental setup for the measurement of photovoltage have been described earlier [6]. The photovoltage was measured by connecting the electrodes to a digital electrometer (model 4022) and conductance was measured with a digital conductivity bridge (model 201).

3. Result and Discussion

The visible absorption spectrum of aqueous solution of dye, Rose Bengal (RB) shows its maxima at 549 nm. With varying concentration of surfactant, Tween-40 above its CMC (~ 10^{-3} M) in fixed concentration of dye (~ 10^{-5} M) in aqueous media, the wavelength shifts to 563.2 nm, also intensity rises with increase in concentration of surfactant at 298K as shown in Fig.1.

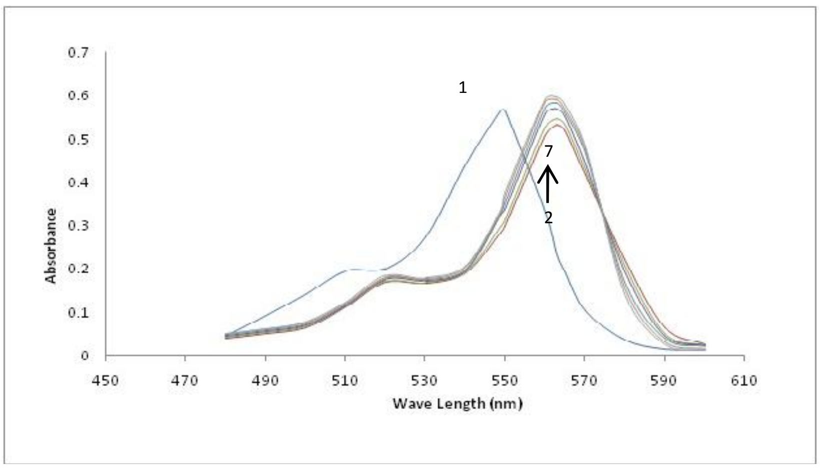

Figure 1: The visible absorption spectra of Rose Bengal and Tween-40 in water at 298K. Concentration of Rose Bengal: 6.18 x 10^{-5} mol dm^{-3} and concentration of Tween-40 (10^{-3} mol dm^{-3}): (1) 0.0, (2) 3.52, (3) 5.28, (4) 7.04, (5) 10.56, (6) 12.32, (7) 17.60.

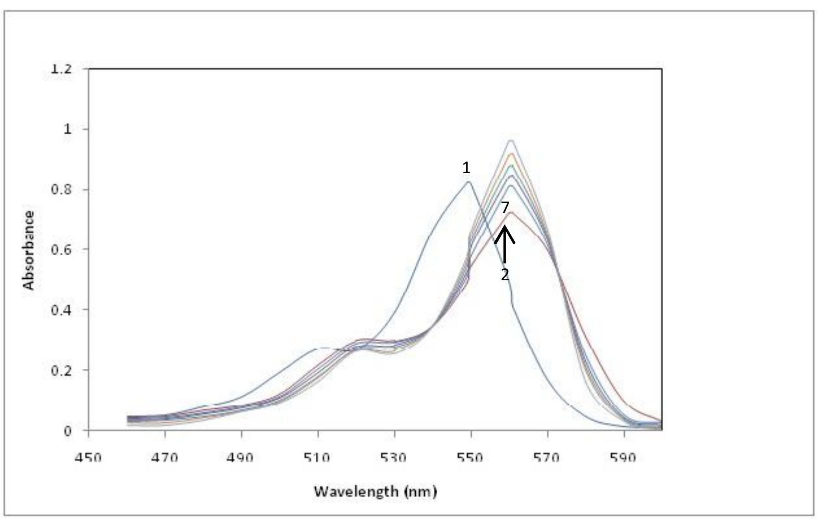

Figure 2: The visible absorption spectra of Rose Bengal and CTAB in water at 298K.

Concentration of Rose Bengal: 1.0 x 10^{-5} mol dm^{-3} and concentration of CTAB (10^{-3} mol dm^{-3}): (1) 0.0, (2) 1.50, (3) 2.50, (4) 3.50, (5) 4.50, (6) 10.00, (7)12.50.

The absorption spectra of dye, Rose Bengal with other nonionic surfactants i.e., TX-100, Tween-20, Tween-60 and Tween-80 in aqueous media are similar to RB -Tween-40 systems with shifts in their spectra to 562.4, 565.3, 564.45 and 562.2 nm, respectively. According to the literature available [7], CMC of the nonionic surfactants e.g., TX-100, Tween-20, Tween-40, Tween-60 and Tween-80 in aqueous media are 2.5, 0.5, 0.23, 0.21 and 0.10 (x 10^{-4}) mol dm^{-3}, respectively. The absorption maxima of RB shifts to 560.8 nm in cationic surfactant, CTAB (CMC, 1.0x10^{-3} mol dm^{-3}) which is shown in Fig.2 whereas λ_{max} of pure dye remains unaltered in anionic surfactant, SLS environment.

The spectrophotometric data were employed to calculate the thermodynamic as well as spectrphotometric properties of dye-surfactant interaction. For a 1:1 complex, the binding constant, K_c and molar extinction co-efficient (ε_c) can be determined by using Scott's equation in the following modified form:

$$[D][S]\,\ell/d\text{-}d_o = [S]\,/\varepsilon_c\text{-}\varepsilon_o + 1\,/K_c(\varepsilon_c\text{-}\varepsilon_o) \qquad (1)$$

Where [D] and [S] are the initial concentrations of dye and surfactant, respectively. ℓ is the optical path length of the solution; d and d_o are the absorbance of the dye at the absorption maximum of the complex with and without surfactant, respectively. ε_c and ε_o are the respective molar extinction co-efficient of the complex and dye at the absorption maximum of the complex. [D][S] ℓ/d-d_o vs. [S] were plotted for Rose Bengal with cationic and nonionic surfactants in aqueous media at 298K which were found to be linear in all cases, confirming the formation of 1:1 complex (Fig. 3). From the slope and intercept of each plot and with the value of ε_o which is 4,748 m^2mol^{-1} of RB at λ_{max} of the complex, K_c and ε_c of the dye-surfactant interaction were calculated. The thermodynamic quantity (-ΔG^0) of these complexes was obtained from the equilibrium constants at room temperature by the usual method.

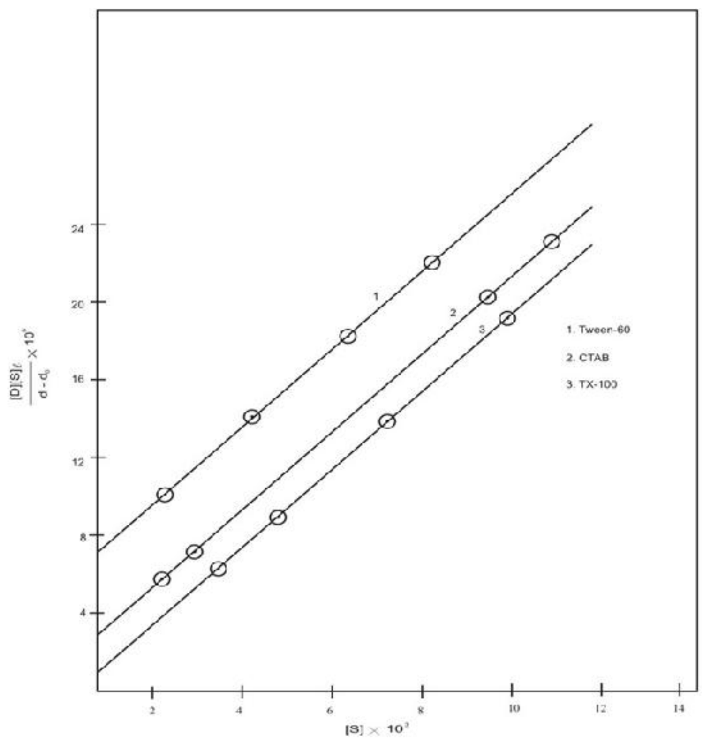

Figure 3: Plots of [D][S] ℓ/d-d_o vs. [S] for Rose Bengal complexes with different nonionic and cationic surfactants: (1) Tween-60, (2) CTAB and (3) TX-100

The experimental oscillator strength (f) and transition dipole moment (D) were calculated from the spectra of complexes using Eqs. 2 and 3, respectively [8]:

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

$$D = 0.09582\, [\varepsilon_{max}.\ \Delta\bar{\upsilon}_{1/2} / \bar{\upsilon}_{max}\, n]^{1/2} \qquad (3)$$

where n is the refractive index of the medium, ε_{max} is the maximum molar extinction coefficient, $\Delta\bar{\upsilon}_{1/2}$ is the width in $cm^{-1}$of the band at half intensity, and $\bar{\upsilon}_{max}$ is the 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.

Table 1: Thermodynamic and spectrophotometric properties of Rose Bengal - surfactant complexes in aqueous media at 298 K

Surfactant [a]	**K_cx10^{-3} (dm^3 mol^{-1})** [b]	**-ΔG° (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)
CTAB	0.522	15.646	560.8	370	14,759	3.181	7.102
Triton X -100	2.155	19.020	562.4	434	14,525	2.951	2.166
Tween-20	0.075	10.698	565.3	526	9,391	0.033	0.729
Tween-40	0.091	11.194	563.2	459	9,598	0.326	0.774
Tween-60	0.238	13.560	564.5	498	14,101	0.493	0.783
Tween-80	0.366	14.630	562.2	428	9,270	0.524	0.798

[a] Concentrations range of surfactants is 0.15 -7.8 x 10^{-2} mol dm^{-3} and conc. of RB dye is 1.0 x 10^{-5} mol dm^{-3}.
[b] K_c values are the average of four to five measurements with an average deviation of 5%.

On illumination of the anode chamber of the PEC cell consisting of dye, RB and nonionic surfactants, a photovoltage develops and attains its maximum value (V_{oc}) within a few minutes. When illumination is stopped, the photovoltage decays very slowly to the original dark value, establishing the reversibility of the photoinduced effect. The growth and decay curves for photovoltage generation in cells with different nonionic surfactants at 298K are shown in Fig.4 and values are enlisted in the Table 2.

The PEC cell with dye and ionic surfactants i.e., CTAB and SLS did not respond to irradiation and no photovoltage develops under the same condition.

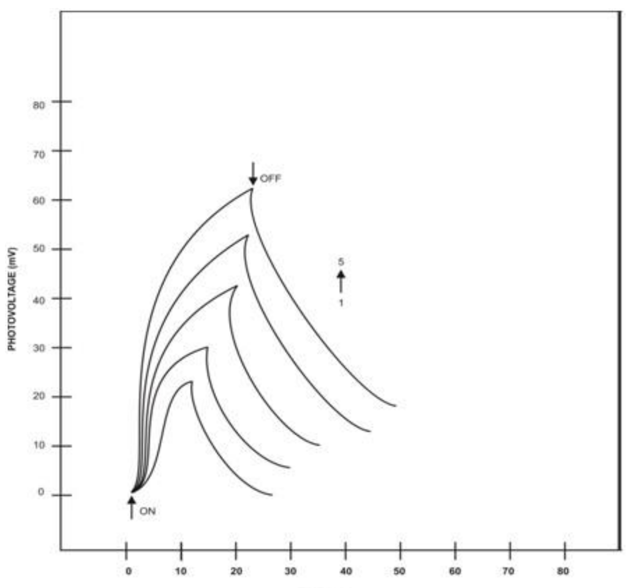

Figure 4: Growth and decay photovoltage of Rose Bengal-nonionic surfactant systems at 298K. The surfactants are: (1) TX-100, (2) Tween-20, (3) Tween-40, (4) Tween-60 and (5) Tween-80.

Table 2: Open-circuit photovoltage (V_{oc}) and conductivities of Rose Bengal - surfactant systems in aqueous media at 298K

Surfactant [a]	**Photovoltage (V_{oc}) (mV)**	**Dark Conductivity x 10^5 (mho cm^{-1})**	**Photo Conductivity x 10^5 (mho cm^{-1})**
CTAB	-	-	-
Triton X-100	24	3.0	4.1
Tween -20	30	3.3	5.6
Tween-40	42	3.5	6.5
Tween-60	53	3.8	7.6
Tween-80	63	4.0	8.7

[a] Concentration range of surfactants is 0.938 -8.7x 10^{-3} mol dm^{-3} and conc. of RB dye is 1.0 x 10^{-5} mol dm^{-3}.

The measured dark conductivities of Rose Bengal in the presence of nonionic surfactants changed on illumination and these changes were almost reversible and reproducible. The growth and decay of photoconductivity induced by illumination at 298K are shown in Fig. 5.The dark and photo conductivities of Rose Bengal-nonionic surfactant systems are presented in Table 2. In the case of CTAB, the dark conductivity is 3.15 x 10^{-4} mho cm^{-1} which is very high compared to the value in the presence of nonionic surfactants. This is apparently due to the presence of excess ions of CTAB in the solution. The conductivity of Rose Bengal with CTAB did not change on illumination.

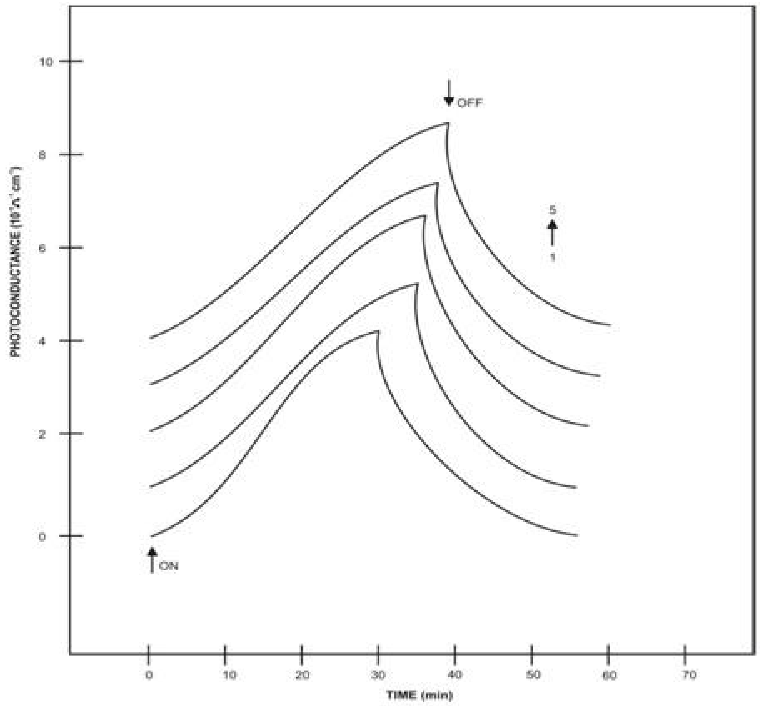

Figure 5: Growth and decay photoconductivity of Rose Bengal-nonionic surfactant systems at 298K.The surfactants are: (1) TX-100, (2) Tween-20, (3) Tween- 40, (4) Tween-60 and (5) Tween-80.

The spectrophotometric data are the direct evidence of molecular interaction between Rose Bengal and surfactants. Since Rose Bengal is an anionic dye, it is expected that the dye should form a strong complex with the cationic surfactant, CTAB, favoured by oppositely charged species. But the results presented in Tables 1 and 2 show that Rose Bengal forms strong complexes with all nonionic surfactants similar to CTAB.

In the neutral surfactant micelle, the anionic dye can penetrate the micelle to form a strong CT complex at a polar site, on the oxygen of the hydroxyl group for having comparatively higher electron density. This was also verified from the absorption spectra of RB in solvents of diverse nature. The molecular interaction between RB and nonionic surfactants in aqueous medium is considered to be a CT interaction. On the other hand, with the positively charged micelles of CTAB, the anionic dye will be held in the Stern region due to columbic interaction and the dye will be repelled by the negatively charged micelles of SLS.

The photovoltage generated by Rose Bengal – nonionic surfactant systems can be explained if we assume that the interaction of RB with nonionic surfactants is of CT (or) electron – donor- acceptor type where surfactants act as electron donor and the dye acts as electron acceptor. The various steps that take place in the photoredox reaction leading to the generation of photovoltage in the PEC cell, consisting of RB- nonionic surfactant in the anode compartment and I^-/I_2 in the cathode compartment, can be described as follows:

$$D + h\nu \rightarrow {}^1D^* \rightarrow {}^3D$$
$${}^3D \rightarrow D$$
$${}^3D + S \rightarrow ({}^3D \text{-----} S) \rightleftharpoons (D^- \ldots\ldots S^+) \rightarrow D + S^+ + e^- \quad \text{(anode reaction)}$$
$$\tfrac{1}{2} I_2 + e^- \rightarrow I^- \quad \text{(cathode reaction)}$$

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 [9], the CT complex is mostly nonionic in nature in the ground state but is predominantly ionic in the excited state. In the case of Rose Bengal – CTAB system, 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 the same for both in dark and illuminated conditions. On the other hand, the interaction of Rose Bengal with nonionic surfactants is of the CT type, so a slight increase in conductivity during illumination is observed. This change is reversible i.e., new ionic species are generated only in the excited state of the complex. From the experimental results presented in Tables 1 and 2, it is revealed that the strength of nonionic surfactants as electron donor towards Rose Bengal in aqueous media follow the order: TX-100> Tween-80> Tween-60> Tween-40> Tween-20 and this is in accordance with the increasing alkyl hydrocarbon chain length which in turn, increases the electron density at the electron donating centre of the molecule due to inductive effect.

The relation between the intensity of the CT absorption band and the stability of the complex should exist if CT resonance is the dominant factor in stabilizing the complex [10]. As the extent of CT increases, the intensity of the transition which is measured by f or D should increase. At the same time, the strength of the interaction as measured by – ΔG^0 or K_c is expected to increase. So, a good correlation is expected between the intensity and stability of CT interaction of RB with nonionic surfactants as shown in Fig.6. Thus, the spectrophotometric and thermodynamic parameters of the CT complexes obtained from the experiments agree with the theoretical point of view.

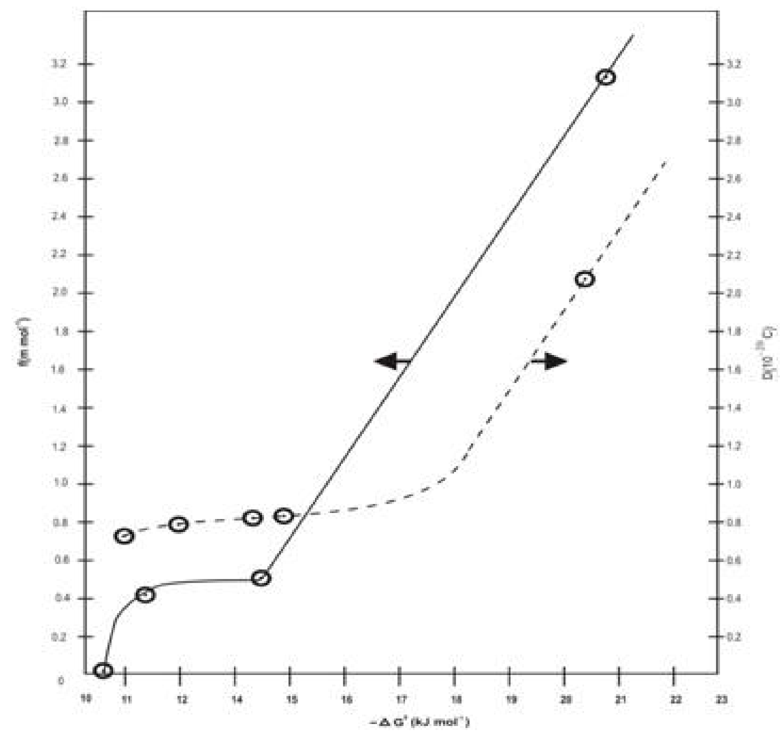

Figure 6: Correlation between the intensity of the CT absorption band (oscillator strength, f and transition dipole moment, D) and the stability of the Complex (free energy, - ΔG^o) for the CT complexes of RB with Tweens and Triton X- 100 in aqueous media. The dotted and solid curves represent the variation of D and f from Tween-20 to Tween-80 followed by Triton X- 100.

It has been found in the present study that prominent interaction takes place only when the concentration of the surfactant is above the CMC value indicating that surface formation in the form of a micelle is a necessary criterion for complex formation. The interfaces (micelles/water) favour the complex formation due to adsorption of RB from solution and thus increase the concentration of the complex, a phenomenon related to surface catalysis.

4. Conclusion

Finally, it can be concluded that the nature of interaction of Rose Bengal, an anionic dye with the three types of surfactants is as follows: 1) CT interaction with nonionic surfactants by the donation of a lone pair of electrons of the oxygen atom of the –OH group of TX-100 and Tweens to the lowest vacant molecular orbital of Rose Bengal, 2) Ionic interaction with positively charged CTAB, and 3) No interaction with negatively charged SLS.

5. Acknowledgement

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