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Studies on the molecular interaction of Neutral Red with surfactants

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ABSTRACT

The spectrophotometric studies of neutral red (NR) dye in an aqueous solution containing three different types of surfactants such as CTAB (cationic), SLS (anionic) and Triton X-100 (TX-100), Tween-20, 40,60 and 80 (nonionic) show that NR forms a 1:1 molecular complex with TX-100, Tweens and SLS. Such a type of interaction is absent in NR and CTAB. The thermodynamic and spectrophotometric properties of these complexes suggest that NR forms a strong charge transfer (CT) complex with TX-100 and Tweens whereas the interaction of NR with SLS is columbic in nature. Photogalvanic and photoconductometric studies also support the above interactions. In addition to this, the electron donating ability among the nonionic surfactants i.e., TX -100 and Tweens towards dye, role of surface in CT interaction between NR and nonionic surfactants have been pointed out.

Keywords: Neutral Red, CT interaction, cac, Photogalvanic, Isosbestic point

ARTICLE INFO

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1. Introduction

The most outstanding properties of surfactants are their ability to solubilize a variety of molecules which are

partially soluble or insoluble in water and their substantial catalytic effect on many chemical reactions [1, 2]. This is

possible because surfactants are long-chain molecules which can form organized structure [3] like micelles and reverse micelles in aqueous and non aqueous media. Malik et al. [4] 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. [5] 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 [6] 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 [7] studied the influence of a simple electrolyte KCl on the interaction between the anionic dyes C.I. Acid Orange (AO7) and the cationic surfactant, N-cetyl pyridinium chloride (CPC) in aqueous media and reported that the addition of KCl reduces the tendency of association between the dye and surfactant. Ghoreishi et al. [8] 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 (DRI6) using surfactant-selective electrode and spectrophotometry techniques. They found that DO26 forms strong CT complex with HTAB compared to DRI6. In the present paper, spectrophotometry was used to investigate the nature of interaction of a cationic dye, neutral red with different surfactants (ionic and nonionic) in aqueous micellar solutions at 298K. These studies have been supported by photogalvanic and photoconductivity effect of dye- surfactant systems.

2. Experimental

Neutral Red(3-amino-6-dimethylamino-2-methyl-phenazine hydrochloride) supplied by Sigma Chemicals was recrystallized from ethanol-water mixtures. The surfactants (a) nonionic: Triton X-100 (p-tert-octylphenoxypoly oxyehanol), Tween-20 (polyoxyethylene sorbitan monolaurate), Tween-40 (polyoxyethylene sorbitan monopalmitate), Tween-60 (polyoxyethylene sorbitan monostearate) and Tween-80 (polyoxyethylene sorbitan mono oleate), (b) cationic: CTAB (cetyl trimethyl ammonium bromide) and anionic: SLS (sodium lauryl sulphate) were obtained either from BDH (England) or Sigma Chemicals (USA) and used as received. 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 NR in the presence of surfactant solutions was studied in an H- shaped photoelectrochemical (PEC) cell. The detail of experimental setup for the measurement of photovoltage was mentioned earlier [9]. An aqueous solution containing surfactant ($\sim \times 10^{-2}$ M) and NR ($\sim \times 10^{-4}$ 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 pure dye, neutral red absorbs maximally at 456.6 nm in aqueous media. With the addition of surfactant, Tween-20 of varied concentrations (above CMC) to dye of fixed concentration, spectrum shifts to 532.4nm with an isosbestic point at 487 nm and also intensity increased with increasing concentration of surfactant(Fig .1). The visible absorption spectrums of dye, NR with other nonionic surfactants i.e., Tween-40, Tween-60, Tween-80 and TX-100 in aqueous media are similar to NR-Tween-20 system with shifts in their spectrums to 532.5nm 534nm 535.5nm and 460 nm, respectively. The absorption maxima of NR shift to 534nm in anionic surfactant, SLS (Fig.2) whereas ϵ_{\max} of pure dye remains unaltered in cationic surfactant environment. The thermodynamic and spectrophotometric parameters of dye - surfactant interactions are calculated based on spectrophotometric data. 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 [11]:

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

where [D] and [S] are the initial concentrations of dye and surfactant, respectively; ℓ is the optical pathlength of the solution; d and d_0 are the absorbances 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 NR with anionic and nonionic surfactants in aqueous media at 298K 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 [12]:

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

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

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

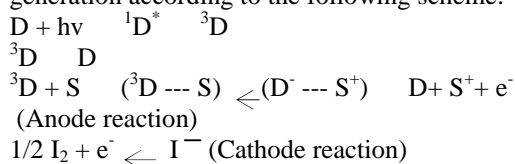
number of the maximum absorption in cm^{-1} . All the thermodynamic and spectrophotometric parameters of the complexes in aqueous media are presented in Table 1.

On illumination of the anode compartment of the PEC cell consisting of dye, NR and nonionic surfactants, 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 nonionic surfactants at 298K are shown in Fig. 3 and values are inserted in Table 2. The PEC cell with dye and ionic surfactants i.e., CTAB and SLS did not respond to irradiation and no photovoltage develop under the same condition.

A photoconductance is observed on illumination the solution of NR with nonionic surfactants which is reversible and reproducible with respect to dark conductivities of them. The growth and decay of photoconductivities of NR – nonionic surfactants 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 dark conductivity of dye with CTAB or SLS was high compared to dye- nonionic surfactant systems i.e., $2.5872 \times 10^{-3} \text{ mho cm}^{-1}$ due to the presence of excess ions of CTAB or SLS in the solution. The conductivity of NR-SLS and NR- CATB systems did not change in presence of light. The experimental data presented above are direct spectrophotometric evidence of molecular interaction between NR and surfactants. Since NR is a cationic dye, it is expected that the dye should form a strong complex with the anionic surfactant, SLS, favored by oppositely charged species. But the results presented in Tables 1 and 2 show that NR forms strong complexes with all nonionic surfactants, whereas a weak complex is formed with SLS.

From these observations, it can be concluded that the nature of interaction of NR with nonionic surfactants is different from that with SLS. This is further confirmed from the thermodynamic and spectrophotometric parameters. Both the equilibrium constant (K_c) and band shift ($\Delta\nu$) are high in the case of NR-nonionic surfactant systems. In the neutral surfactant micelle, the cationic 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 high electron density. This was also verified from the absorption spectra of NR in solvents of diverse nature. The molecular interaction between NR and nonionic surfactants in aqueous medium is considered to be a CT interaction. On the other hand, with negatively charged micelles of SLS, the cationic dye will be held in the stern region due to columbic interaction and with positively charged micelles of CTAB, the dye will be repelled. The generation of photo voltages with NR and surfactants can be explained if we assume that the interaction of NR with nonionic surfactants is of CT or electron – donor – acceptor type where

surfactants act as electron donor and the dye acts 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 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 [13], the CT complex is mostly nonionic in nature in the ground state but is predominantly ionic in the excited state. In the case of NR - SLS 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 same for both dark and illuminated conditions. On the other hand, the interaction of NR with nonionic surfactants is of the CT type, so a slight increase in conductivity during illumination can be explained; 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 NR in an aqueous media follow the order: Tween-80 > Tween-60 > Tween-40 > Tween-20 > TX-100 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 presence of an aryl group in TX - 100 results in opposite effect. It is an implication of the CT model that a 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 [14]. As the extent of CT increases, the intensity of transition which is measured by f or D should increase. At the same time, the strength of the interaction as measured by G^0 or K_c is expected to increase. So, a good correlation is expected between the intensity of the CT absorption band and the stability of the complex. The correlation between the intensity and stability of CT interaction of NR with nonionic surfactants is shown in Fig. 5. Thus, the experimental results from the spectrophotometric and thermodynamic parameters of the CT complexes agree well with the theoretical point of view. From the present study, it is found that prominent interaction between dye, NR and surfactants take place not only when the concentration of the surfactant is above the CMC value but also at below CMC to form CT complex. It is possible only if surfactant associate in lower concentration compared to CMC which is consider as a cac of surfactant [15]. Now this flexibility of micelle formation

of surfactants is a necessary criterion for complex formation.

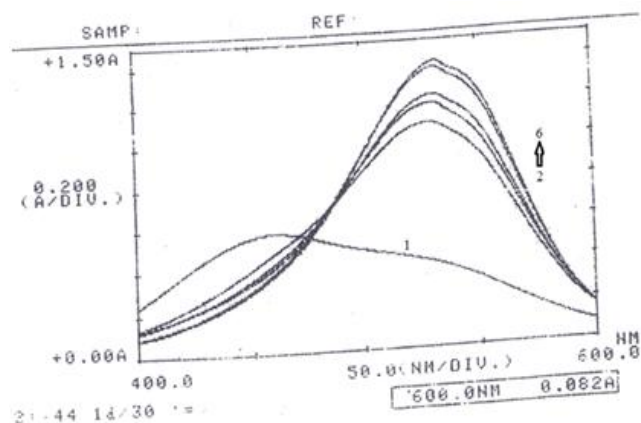


Figure 1: The visible absorption spectra of NR and Tween-20 in water at 298K. Concentration of NR: 1.245×10^{-4} mol dm^{-3} and concentrations of Tween-20 (10^{-3} mol dm^{-3}): (1) 0.0, (2) 1.284, (3) 2.167, (4) 4.307, (5) 6.474 and (6) 8.614.

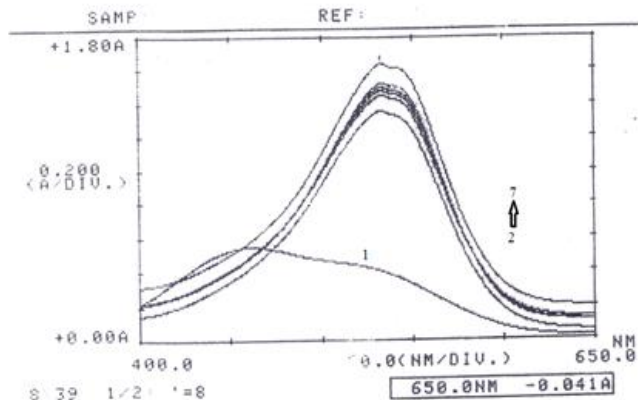


Figure 2: The visible absorption spectra of NR and SLS in water at 298K. Concentration of NR: 1.245×10^{-4} mol dm^{-3} and concentrations of SLS (10^{-3} mol dm^{-3}): (1) 0.0, (2) 4.4, (3) 6.0, (4) 7.6, (5) 9.2 (6) 10.8 and (7) 12.4.

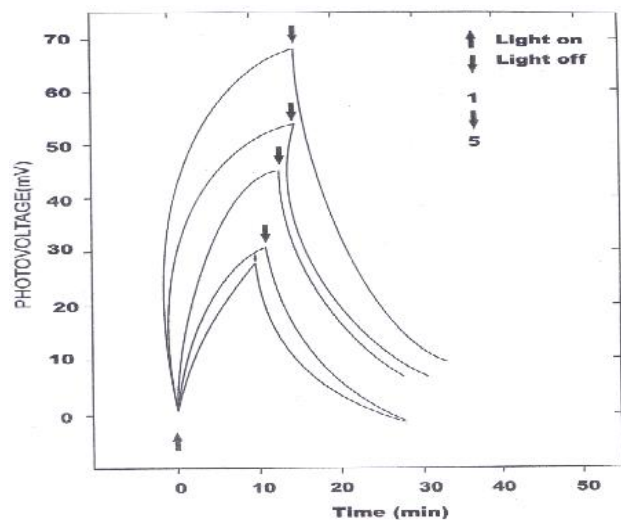


Figure 3: Growth and decay photovoltage of Neutral Red - nonionic surfactant systems at 298K. The nonionic

surfactants are: (1) Tween-80, (2) Tween-60, (3) Tween-40, (4) Tween-20 and (5) Triton X-100.

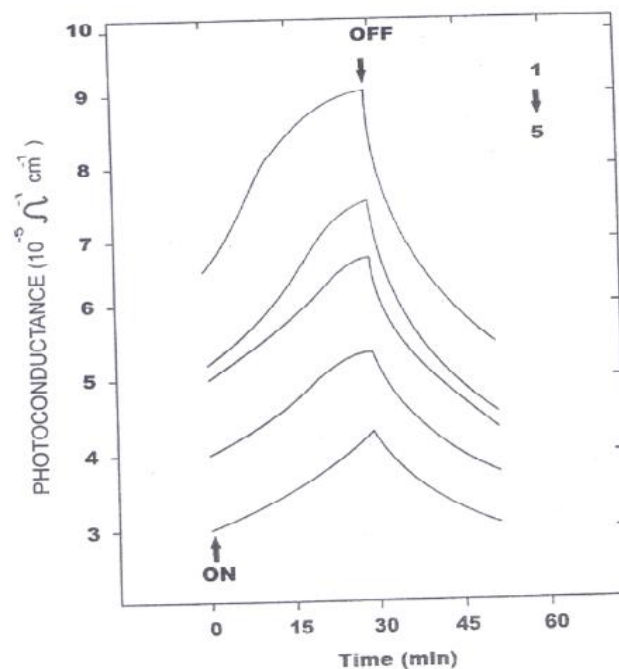


Figure 4: Growth and decay photoconductivity of Neutral Red -nonionic surfactant systems at 298K. The nonionic surfactants are: (1) Tween-80, (2) Tween-60, (3) Tween-40, (4) Tween-20 and (5) Triton X-100.

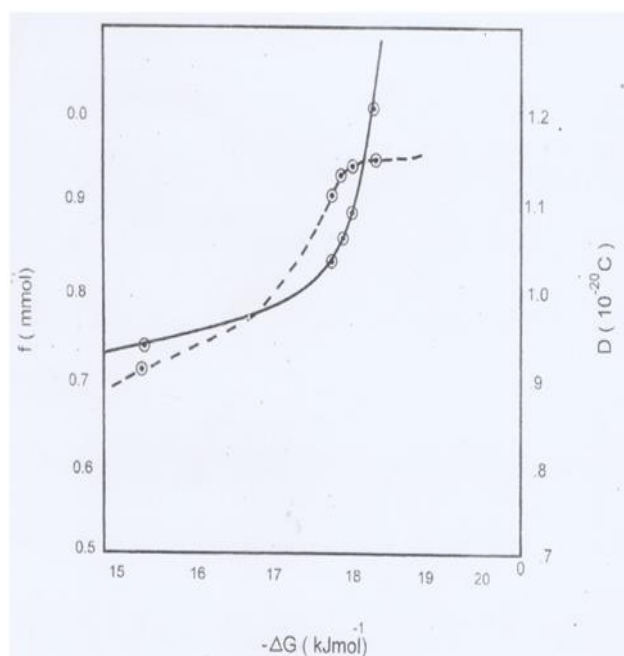


Figure 5: Correlation between the intensity of the CT absorption band (oscillator strength, f and transition dipole moment, D) and the stability of the complex (free energy, $-G^0$) for the CT complexes of NR with Triton X-100, Tween-20 to Tween-80 (with increase in number of Twens).

Table 1: Thermodynamic and spectrophotometric properties of NR – Surfactants complexes in aqueous media at 298 K

Surfactant ^a (CMC, mM) ^[10]	$K_c \times 10^{-2}$ (dm ³ mol ⁻¹) ^b	- G^0 (kJ mol ⁻¹)	Complexed band				
			λ_{max} (nm)	Band shift U^- (cm ⁻¹)	ν_c (m ² mol ⁻¹)	f(m mol ⁻¹)	D(10 ⁻²⁰ C)
SLS (8.0)	6.614	16.09	534.0	3175	1514	0.669	0.901
Triton X-100 (0.25)	7.816	16.504	460	162	640	0.737	0.909
Tween-20 (0.05)	14.50	18.035	532.4	3119	1315	0.832	1.119
Tween-40 (0.023)	15.333	18.173	532.5	3122	879	0.857	1.136
Tween-60 (0.021)	15.625	18.220	534	3175	1206	0.989	1.138
Tween-80 (0.01)	18.00	18.571	535.5	3227	1174	1.007	1.146

^aConcentration range of surfactants is $0.04 - 3.6 \times 10^{-2}$ mol dm⁻³ with a fixed concentration of NR, 1.245×10^{-4} 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 photovoltage (V_{oc}) and conductivities of NR-Surfactant systems in aqueous media at 298 K

Surfactant ^a	Photovoltage (V_{oc}) (mV)	Dark conductivity $\times 10^5$ (ohm ⁻¹ cm ⁻¹)	Photoconductivity $\times 10^5$ (ohm ⁻¹ cm ⁻¹)
CTAB	-	-	-
SLS	-	-	-
Triton X-100	28	3.053	4.291
Tween-20	34	3.825	5.410
Tween-40	45	4.423	6.655
Tween-60	53	4.631	7.512
Tween-80	67	5.462	8.954

^a Concentration NR and surfactants are 2.075×10^{-5} mol dm⁻³ and 2.849×10^{-3} mol dm⁻³, respectively.

4. Conclusion

Finally, it can be concluded that the nature of interaction of NR, a cationic phenazine dye with three types of surfactant varies: CT interaction with nonionic surfactants by the donation of a lone pair of electrons of the oxygen atom of the -OH group of Triton X-100 and Tweens to the lowest vacant molecular orbital of NR, ionic interaction with negatively charged SLS and no interaction with positively charged CTAB.

5. Acknowledgement

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6. References

1. K.L. Mittal, Micellization, solubilization and microemulsions, vols 1 and 2, Plenum, New York, 1977.
2. E.J.R. Sudholter, G.B. Van de Langkruis, J.B.F.N. Engberts, Micelles Structure and Catalysis. Rec.Trav.Chim.Pays-Bas. **1980**, 99: 73-82.
3. J.H. Fendler, E.J. Fendler, Catalysis in micellar and macromolecular systems, Academic Press, London, **1975**.
4. W.U. Malik, O.P. Jhamb, Spectrophotometric studies on the interaction of surface active agents with dyes. J. Electroanal. Chem. **1970**, 27: 151-157.
5. S.N. Guha, P.N. Moorthy, K.N. Rao, Spectral and fluorimetric studies on the effect of surfactants on thionine. Proc. Indian Acad. Sci. **1982**, 91: 73-85.
6. S.R. Karmaker, P.P. Kulkarni, M.P. Savsani, Ind. J. Textile Research. **1988**, 13: 45.

7. P. Forte-Tavcer, The influence of a simple electrolyte KCl on Surfactant-Dye interactions in water solution. *Int. J. Polym. Mats.* **2000**, 47: 727-733.
8. S. M. Ghoreishi, M. Bech-Pour, AG. Farsani, J. Hazard. *Mats.* **2006**, 138: 133-141.
9. A.K. Jana, S. Rajavenii, Studies on the molecular interaction of Phenazine dyes with Triton X-100. *Spectrochim. Acta Part A.* **2004**, 60: 2093-2097.
10. S.P. Moulik, Micelles:Self-organized surfactant assemblies. *Current Sci.* **1996**, 71(5): 368- 376.
11. R.L. Scott, Some Comments on the Benesi-Hilderbrand equation. *Rec. Trav. Chem.* **1956**, 75: 787-789.
12. A.K. Jana, Sushil K. Mukhopadhyay, Benoy B. Bhowmik. Absorption Spectra of nitroanilines in micellar solution-II. *Spectrochim. Acta A.* **2002**, 58(8): 1697-1702.
13. R.S. Mulliken, W.B. Person, *Molecular Complexes.* Wiley-Inter science, New York and London, **1969**.
14. Robert S. Mulliken. *Molecular Compounds and their Spectra. II.* *J. Am. Chem. Soc.* **1952**, 74(3): 811- 824.
15. P. Jana-Sur, A.K. Chakraborty, Studies on the interaction of bacterial capsular Polysaccharide-Klebsiella K16 with cationic and mixed surfactants. *Colloid Polym. Sci.* **2006**, 284: 596-603.