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Fluorescence Study of p-Nitroacetophenone in Different Micellar Media

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ABSTRACT

Fluorescence technique is an important tool for investigation of interaction between micelles and molecules. By spectroscopic studies, it has been explained that different solubilized molecule are found in different regions of micelles. The most striking feature of micelles is their ability to solubilize variety of compound in different regions. This process is expected to be most pronounced in the region of critical micellar concentration (CMC) of particular surfactant. P-Nitroacetophenone is a fluorescence aromatic compound and has pharmaceutical and analytical importance. The present study is carried out to investigate the solubilization of p-Nitroacetophenone in presence of various surfactants at their critical micellar concentration or marginally above the critical micellar concentration, employing fluorescence technique. The solublization phenomenon has also been confirmed by absorption spectral studies. Spectral parameters like, quantum yield, Stokes' shift were also calculated in micellar media at different concentration.

Keywords: Fluorescence, micellization, solubilization, p-Nitroacetophenone, critical micellar concentration.

INTRODUCTION

In a system formed by a solvent, an association colloid and at least one other component (the solubilizate), the incorporation of this other component into or on the micelles is called micellar solubilization, or, briefly, solubilization. The most striking feature of micelles is their ability to stabilize variety of compound in different region. By spectroscopic studies[1,2] it has been explained that different solubilized molecule are found in different regions of micelles. Surfactants have been extensively used in areas related to detergency, emulsification, pharmaceuticals, agriculture, enhanced petroleum recovery, etc. as the surfactants exhibit pronounced interfacial properties[3-6]. Recently, polymer surfactant systems are under extensive investigation[7]. P-Nitroacetoacetophenone (p-NAP) is a fluorescent aromatic compound and has analytical and pharmaceutical importance. Resonance Raman spectroscopic and density functional theory of p- Nitroacetophenene were studied to illustrate protective nature of $–NO_2$ and $–COCH_3$ group in it[8]. Triple state properties of P-Nitroacetophenone were investigated by using laser flash photolysis and phosphorescence technique. It is found that it produced phosphorescence on excitation at 278nm with a

decay time of 15ns[9].Tatiana V. bukharking et al[10] developed a process of p- Nitroacetophenone and benzoic acid manufacture by the liquid phase oxidation of aromatic compound.
The electron affinity of eight well known nitroaromatic and nitroheterocyclic radiosensitizatizers were studied by quantum mechanical approach by Y.G. Smeyer and coworkers[11]. A charge transfer reaction between p-NAP during the irradiation of DNA with X-rays was also studied[12]. The effects of p-Nitroacetophenone on the radiation chemistry of thymine and uracil in the deaerated aqueous solution have also been studied[13]. Studies were also made on p-NAP sensitized liquid peroxidation by C.M. Krisma and A.K. Ray[14]. Yin Gang Wong et al[15] described the photochemistry of p-Nitroacetophenone in 2-propanol.
The present study is carried out to investigate the solubilization of p-Nitroacetophenone in presence of various surfactants at their critical micellar concentration or marginally above the critical micellar concentration, employing fluorescence and absorption spectral studies.

MATERIALS AND METHODS

Analytically pure p-NAP was a sigma sample. The surfactants used to made the studies are (a) nonionic surfactants (i) Tx-100 polyoxyethylenetertoctyl phenyl ether (ii) Tween-40 polyoxy ethylene sorbitan monopalmitate (iii) Tween-20; polyoxyethylenesorbitanmonolaurate (b) Cationic surfactants (i) CTAB: cetyltrimethylammonoum bromide (ii) CPB: cetylpyridinium bromide (iii) CPC: cetylpyridinium chloride and (c) Anionic surfactants (i) DBSS: Dodecylbenzyl sodium sulphonate (ii) DSSS: Dioctyl sodium sulphosuccinate (iii) SLS: Sodium lauryl sulphate. All the surfactants were either of sigma(USA) or BDH (UK) products.
The stock solution of p-NAP was prepared in methanol. The concentration of compound was kept at $1x10^{-6}$M for fluorescent study and $1x10^{-5}$M for absorption study. The concentration of the compound was kept constant throughout the experiment. The fluorescence spectrum was taken with Perkin Elmer Fluorescence Spectrophotometer model number 204A with a synchronized model number 056 strip chart recorder and absorption spectra were taken on Hewlett Packard (HP) 8452A diode array spectrophotometer. The purity of surfactants was checked by determining their CMC value with the help of surface tension measurement, employing drop weight method. The absolute fluorescence quantum yield of the compound relative to anthracene solution is taken as standard and sample from the area of the fluorescence spectrum were recorded over the whole range of emission under identical conditions.

RESULTS AND DISCUSSION

The maximum excitation peak for methanolic solution of p-NAP was recorded at 280nm. The emission wavelength of p-NAP was found at 325nm (Fig. 1).

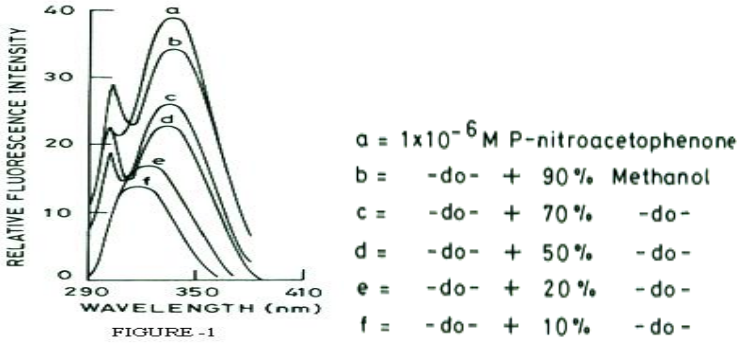

FIGURE -1

FLUORESCENCE EMISSION SPECTRA

Out of three categories the maximum effects on solubilization of compound is shown by nonionic surfactants. All the nonionic surfactants caused an enhancement in fluorescence intensity of p-NAP with blue shift of 5-15nm, out of all the nonionic surfactants rate of increase in fluorescence intensity is maximum for Tx-100 added solution, which reaches out of scale at higher concentration of surfactant(Fig.2). On addition of any anionic surfactant, a gradual increase in fluorescence intensity was observed. All the cationic surfactants caused a small increase in fluorescence intensity with no shift in peak position. The minimum and maximum fluorescence intensity in the absence and presence of all the three classes of surfactants is given in table 1.

Table 1. Minimum and maximum fluorescence intensity of p-Nitroacetophenone in absence and presence of surfactant

s.no.	Name of surfactant	Concentration of surfactant (%)	Fluorescence intensity in absence of surfactants	Maximum fluorescence intensity
1.	Tween-20	0.1	39	61
2.	Tween-40	0.07	39	78
3.	Tx-100	0.005	39	80
4.	CTAB	0.1	39	48
5.	CPC	0.1	40	44
6.	CPB	0.1	39	49
7.	SLS	0.1	40	48
8.	DSSS	0.1	39	51

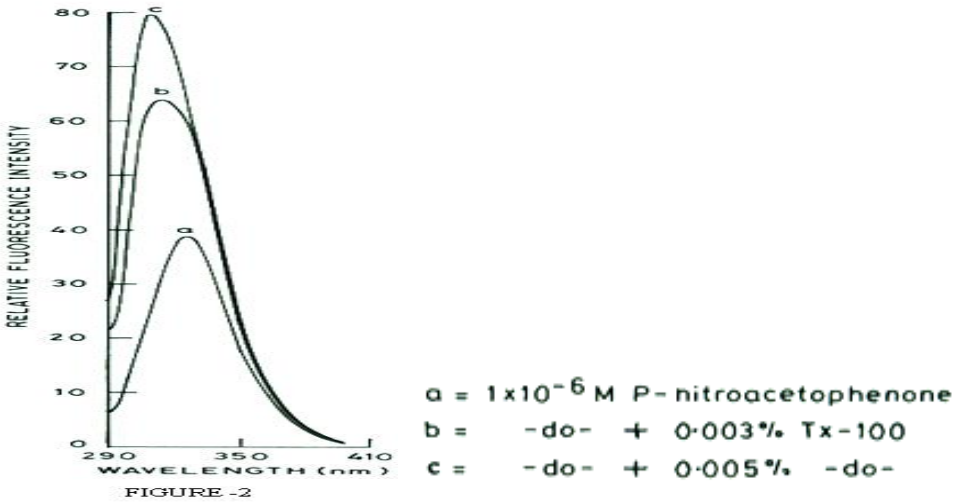

FIGURE -2

FLUORESCENCE EMISSION SPECTRA

The absorption spectra gave a peak at 280nm. On addition of any of the nonionic surfactants, continuous increase in absorbance was observed with 5nm blue shift in absorption spectra. The absorbance value increased gradually on increasing the concentration of all the anionic and cationic surfactants. The molar extinction coefficient data also showed gradual increase with increase in concentration of all the nonionic, anionic and cationic surfactants. The quantum yield values and molar extinction coefficient values for Tx-100 added solution is shown in table 2.

Table 2. Absorption maxima, molar extinction coefficient, fluorescence maxima and quantum yield of p-Nitroacetophenone at different concentration of Tx-100

S. No.	Concentration of Tx-100 used (%)	Absorption Maxima(nm)	Molar extinction coefficient(dm3/mol cm)	Fluorescence maxima(nm)	Quantum Yield
1.	0.00	280	5.4099	325	0.7841
2.	0.003	280	5.6074	310	0.9212
3.	0.005	280	5.6919	310	0.9828
4.	0.009	280	5.7774		

The Stocks' shift values were continuously increased with increase in concentration of p-NAP. The calculated Stokes' shift data of p-NAP at room temperature are given in table 3.

Table 3. Stocks' Shift data of p-Nitroacetophenone at room temperature

S. No.	Concentration of compound(M)	λ_{ex}(nm)	Fluorescence Intensity(nm)	λ_{em}(nm)	Fluorescence intensity	Stokes' Shift (cm-1)
1.	1x10-6	285	21	325	39	4318
2.	1x10-5	285	17	325	27	4318
3	5x10-5	280	13	320	24	4464
4.	1x10-4	275	10-11	320	22	5113

The results indicated that nonionic surfactants had a stronger enhancement effect on fluorescence and absorption behavior of p-NAP. The maximum enhancement was obtained for Tx-100, which has been supported by absorbance, log ε and Φ_f values.

In miceller media many characteristics of organic compound changes remarkably. Thus above observations can be explained by the solubilizing action of surfactant micelles. This process is expected to be most pronounced in the region of critic micelle concentration (CMC) of particular surfactant. The maximum enhancement was observed with Tx-100 which can be attributed to the increase in quantum efficiency. According to the observed results, the nonpolar environment of Tx-100 micelle interior and similarly of other nonionic micelle may be preferable to incorporate the hydrophobic solublized molecule then the ionic surfactant micelle[16]. Tx-100 solubilize the solute molecule very efficiently because of oblate ellipsoidal model of Tx-100. Kano et al[17] have found that interior of Tx-100 is more hydrophobic than those of ionic micelles. The highest solubilizing effect of Tx-100 may also be due to presence of ether linkage in it, while other nonionic surfactants employed were esters. On adding the nonionic surfactants, an enhancement in fluorescence intensity was observed. In anionic micelle, the solubilized molecules are transferred from more polar and protic water phase to less protic micellar phase.

The increased solubility of p-NAP in anionic surfactants is due to resonance which made the molecule cationic in nature which is highly solubilized with anionic surfactant and cause increased in fluorescence intensity as well as quantum yield. The solubilized molecules are dispersed as microcrystal in water which would colloid with anionic micelle to penetrate into the micelle to penetrate into the micellar interior, here the anionic surfactant have formed 1:1 complex with the protonated solubilized molecule. The complex is called ion association complex[18].

The increase in log ε and Φ_f values in anionic surfactants indicate that the rate of nonradiative process are less in micellar system in comparison to those in water. This may be due to decrease in intersystem

crossing rate as pointed out by Shizuka et al[19]. Another reason is micellar surface, which decrease the rate of collision deactivation of the fluorophore by water molecule.

A blue shift is due to the difference in solvation energy of the solute in the ground state[20]. The large Stokes' shift values for p-NAP are due to H-bond formation between the solute and solvent in the ground state. These bonds break following excitation, but reforms following proton transfer. The present analysis indicates that during solubilization of solubilizate into the surfactant system, the incorporation of the solubilizate influence the balance of favorable and unfavourable forces guiding micellization and the structural changes occurring due to aggregation, dissociation and hydrogen bonding. Micelle media provided by all types of surfactants enhance solubilization of the compound.

APPLICATIONS

The method has extensive applications in field of analytical chemistry, biochemistry, medicine, light and for determination of concentration and structure of compounds.

CONCLUSIONS

Experimental data showed that all the surfactants have increasing effect on solubilization of p-Nitroacetophenone, but the maximum enhancement in solubilization was observed in nonionic micellar media. After interpreting and comparing the results obtained for p-NAP, it is found that the theoretically calculated spectral parameter like molar extinction coefficient, Stokes' shift, quantum yield values and empirical fluorescence coefficient are in good agreement with experimental results. This proves the validity of the assumption made.

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