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Spectroscopic Investigation of ß-Naphthol in Micellar Media

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Abstract: ß-Naphthol is a fluorescent aromatic compound and has pharmaceutical and analytical importance. The present study is carried out to investigate the solubilization of ß-Naphthol in presence of various surfactants at their critical micellar concentration, employing fluorescence technique. The enhanced fluorescence emission intensity as well as quantum yield values in micro heterogeneous micellar environment prove that the suspending hydrophobic molecules ß-Naphthol is solubilized. The solubilization phenomenon has also been confirmed by absorption spectral studies and light scattering measurements. Theoretical parameters were also determined; the calculated results are in fair agreement with the experimental results.

Keywords**:** ***Absorption Spectral Studies, Fluorescence, Light Scattering Measurements, Solubilization***

I. INTRODUCTION

ß-Naphthol is popular due to its wide applications in biomedical and forensic sciences as a good fluorescent acid –base indicator for 8-9 pH range [1]. The acid base properties of **ß**-Naphthol serve as an excellent example of excited state acid base chemistry. N.Mataga et al. [2] have studied the absorption and emission spectra of ß-Naphthol in presence of ethers and esters and they observed that both absorption and emission bands of naphthols shift to red. Solubilization is one important surfactant property that is directly related to micelle formation. It is the spontaneous dissolution of a substance (solid, liquid or gas) by irreversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically isotropic solution with reduced thermodynamic activity [3]. Surfactant micelles have received much attention because micelles are able to solubilize hydrophobic organic compounds which have low water solubility through incorporation of them into the hydrocarbon like core of the micelle and partitioning of hydrophobic organic compound between micelle cores of surfactant and surrounding water.

Micelles can be of any desired charge type and can adopt different shapes and internal packing, depending on the chemical structures of the constituent monomers and the ionic strength of the medium [4-7]. It has been reported that the solubility of PAH increases linearly with surfactant concentration above the critical micelle concentration (CMC) [8-10]. There have been many published studies in the literature on the solubilization behaviours of surfactants [11–13]. However, most of the previous studies related to solubilizing of PAHs on the use of conventional surfactants having single monomers with a single hydrophobic tail and a single hydrophilic head group [14,15].

The present paper includes a study on the influence of various nonionic, anionic and cationic surfactants on the fluorescence and absorption spectra of ß-naphthol. The results have been interpreted from the calculation of molar extinction coefficient and quantum yields of ß-naphthol fluorescence in various micellar media, and Stokes' shift calculation at various concentrations of ß-naphthol.

II. MATERIAL AND METHODS

All fluorometric, absorption and light scattering experiments were carried out with the following three instruments:

Perkin- Elmer Fluorescence Spectrophotometer Model No. 204 A with a synchronized model no. 056 Strip Chart Recorder. Hewlett Packard (HP) 8452 A diode array spectrophotometer.

Brice- Phoenix Universal Light Scattering Photometer Model No. 2000.

The stock solution of analytically pure ß-naphthol (Sigma Chemicals) was prepared in distilled ethanol due to its low solubility in water. A 10^{-3} M solution was diluted upto 10^{-5} M by adding water, ethanol or surfactant solution.

All the surfactants used were either of sigma (USA) or BDH product. The following surfactants were employed.

A. Nonionic

Polyoxyethylene Tertoctyl Phenol (TX-100), Polyoxyethylene Sorbitan Monolauriate (Tween-80) and Polyoxyethylene Sorbitan Monopalmitate (Tween-40).

B. Cationic

Cetyltrimethyl Ammonium Bromide (CTAB), Cetylpyridinium Chloride (CPC) and Cetylpyridinium Bromide (CPB).

C. Anionic

Dodecylbenzene sodium sulphonate (DBSS), Dioctylsodium Sulphosuccinate (DSSS) and Sodiumlauryl Sulphate (SLS). The purity of surfactant was checked by determining their CMC values with the help of surface tension measurement, employing drop weight method. By using appropriate equations, various spectral parameters like quantum yield and molar extinction coefficient were calculated in micellar media at different concentrations and stokes shift were calculated at different concentrations of the compound. 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.

III.RESULT AND DISCUSSION

The Stock solution of ß-naphthol was prepared in pure ethanol. The concentration of the compound was kept at 1x10-5 M in 1% ethanolic medium throughout the experiment.

The maximum excitation wavelength was 325 nm. The wavelength of maximum emission was obtained at 355-360 nm with a shoulder at 415-420 nm. The fluorescence studies were carried out in presence of nonionic, anionic and cationic surfactants. Detailed studies with various types of surfactants are given below:

All the non-ionic surfactants viz., TX-100, Brij-35, Tween-20, Tween-80 caused enhancement in the fluorescence intensity of ß-naphthol which was continuous with increase in concentration of the surfactant. The order of enhancement with surfactant was TX-100 >Tween-20 >Tween-80 >Brij-35.

A very slight enhancement in the fluorescence intensity was observed with all the three anionic surfactants employed. The cationic surfactants employed viz., CTAB, CDBAC, and CPC. The concentrations of all the cationic surfactants were varied from 0.001% to 0.45%. CTAB and CDBAC have very similar effect whereas CPC had pronounced decreasing. The results are given in Table 1. The Fluorescence Emission Spectra is shown in Fig.1.

TABLE 1: EFFECT OF SURFACTANTS ON THE FLUORESCENCE INTENSITY (F.I.) OF ß- NAPHTHOL
λex = 325nm, λem = 355-360 nm, P.M. Gain = 2, Sensitivity Range = 0.1

S. No.	% of TX-100 (w/ V)	F.I	λem (nm)	% of SLS (w/ V)	F.I	λem (nm)	% of CPC (w/v)	F.I	λem (nm)
1.	0.00	25	355-360	0.00	25	355-360	0.00	25	355-360
2.	0.007	28	355-360	0.05	28	355-360	0.07	21	355-360
3.	0.3	51	355-360	0.3	32	355-360	0.3	16	355-360
4.	0.5	58	355-360	0.5	32	355-360	0.5	15	355-360

The absorption spectrum of a solution of 1x10-4M β-naphthol gave two well defined peak at 274 nm and 328 nm, a shoulder at 266 nm and a small peak at 286 nm. The peak height at 274 was maximum. The nonionic and anionic surfactants caused small increase in the absorbance, while with cationic surfactants absorbance first increased and then decreased. The light scattering measurements on β-naphthol were made at a concentration of 1x10-4 M in 1% ethanol. Sharp decrease in galvanometer deflection was observed on addition of each surfactant. The anionic and cationic surfactants behaved in a way similar to that of nonionic surfactant.

The variations in Stokes' shift (from 2600.21 for 1x10^{-6} M compound to 3027 for 1x10^{-4} M compound) indicate that energy changes occur in the excited state of the molecule on varying the concentration of the compound at room temperature. The calculated values are given in Table II.

TABLE II : STOKE'S SHIFT DATA OF ß-NAPHTHOL AT ROOM TEMPERATURE

S.No.	Concentration of the compound	F. 1.	λex(nm)	λem (nm)	P.M. gain	Sensitivity(μ)	Stokes' shift (cm^{-1})
1.	1x10^{-6} M	20	325	355	3	0.1	2600
2.	3x10^{-6} M	30	325	356	3	0.1	2680
3.	7x10^{-6} M	62	324	356	3	0.1	2775
4.	1x10^{-5} M	24	325	355-358	1	0.1	2758
5.	3x10^{-5} M	44	324	356-358	1	0.1	2853
6.	5x10^{-5} M	71	324	358	1	0.1	2932
7.	7x10^{-5} M	94	324	359	1	0.1	3009
8.	9x10^{-5} M	40	324	358-359	1	0.1	3009
9.	1x10^{-4}M	42	323	358	1	0.1	3027

The fluorescence quantum yield of ß-naphthol has been calculated for its ethanolic solution, on adding different concentrations of nonionic, anionic and cationic surfactant solution. Amongst all the surfactant Φ_F values were highest for TX-100 added ß-naphthol solutions. The fluorescence quantum yield (Φ_F) values were calculated relative to anthracene in ethanol as standard. Data obtained from the calculation shows the enhancement in the Φ_F value for all the nonionic surfactants. With anionic surfactants enhancement in the ΦF was not as high as that with the nonionic surfactant and with all the cationic decrease in Φ_F value was observed and it was least for the CPC added solution. The molar extinction coefficient (log ε) values increased with increase in concentrations of all nonionic, anionic surfactants (except SLS) and CPC. While with rest of the cationic surfactants and SLS the logs values first increased and then decreased. The increase in the fluorescence intensity can be attributed to the increase in the quantum efficiency and quantum efficiency (Φ_F) values were highest for TX-100 added solutions. This increase in quantum yield (Φ_F) suggests that the surfactants have solubilized the suspended molecules of the solubilizate. Furthermore, the quantum yield of fluorescence is higher in nonionic nonpolar medium, because of the lesser effect of other deactivation processes which compete with fluorescence [16]. Thus, the increase in quantum yield suggests that the surfactants have solubilized the suspended molecules of the solubilizate. Among the nonionic surfactants TX-100 has been found to possess highest solubilizing effect. This anomaly may be due to ether linkage in TX-100 and Brij-35 while other nonionic surfactants employed are esters. The disappearance of shoulder at 415-420 nm at higher concentration of the surfactants as in case of β-naphthol, clearly confirms the occurrence of solubilization on adding surfactant and also suggests its presence to be due to the scattering by suspended particles. The magnitude of Stokes' shift depends on several factors. The large Stokes' shift values of ß-naphthol are due exclusively to hydrogen bond donated from its hydroxyl group to the solvent (protic) in the ground states. This bond breaks following excitation to S_1 but reforms following proton transfer [17]. Plot Of % Anionic Surfactant Vs. Scattering Intensity is shown in Fig.2.

IV. CONCLUSIONS

The present analysis indicates that during solubilization of solubilizate into the surfactant system. the incorporation of the solubilizate influence the balance of favourable and unfavourable forces guiding micellization and the structural changes occurring due to aggregation, dissociation and hydrogen bonding. Thus we can generalize the present physical understanding to study the effects of different kinds of solubilizates. We hope to address this problem in future.

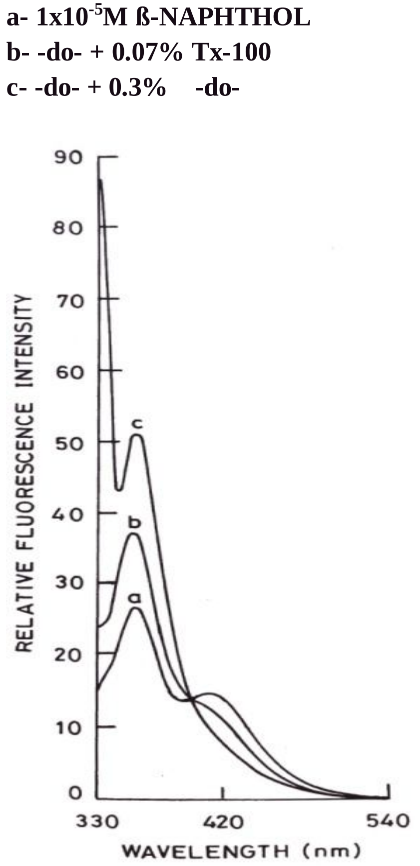

Fig.1. Fluorescence Emission Spectra

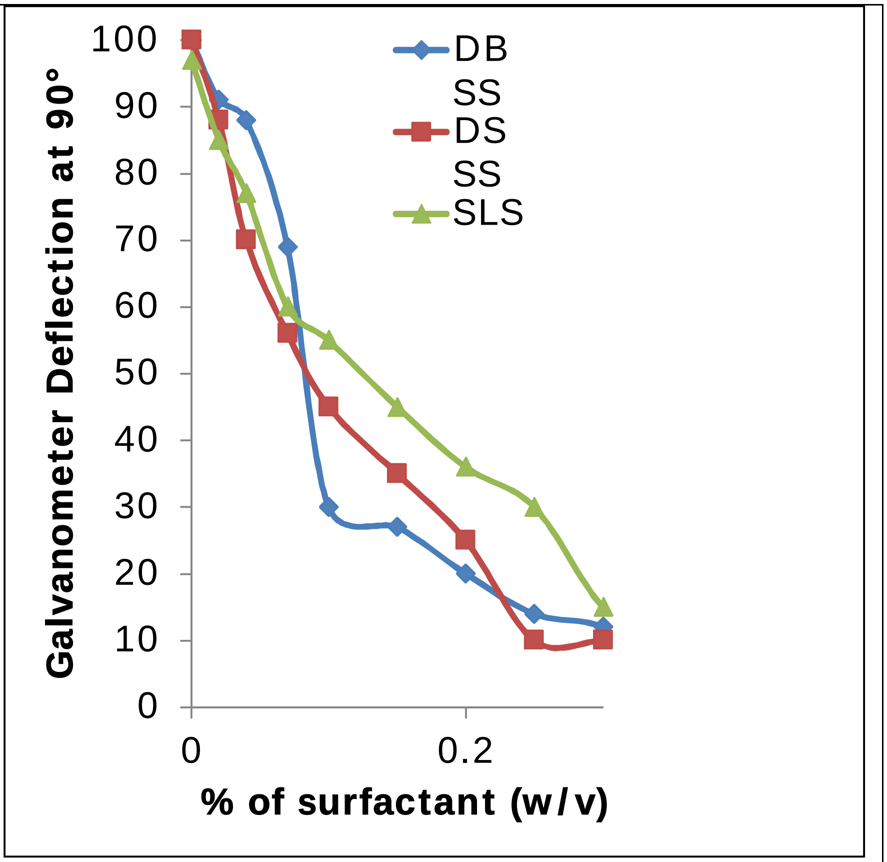

Fig.2. Plot Of % Anionic Surfactant Vs. Scattering Intensity

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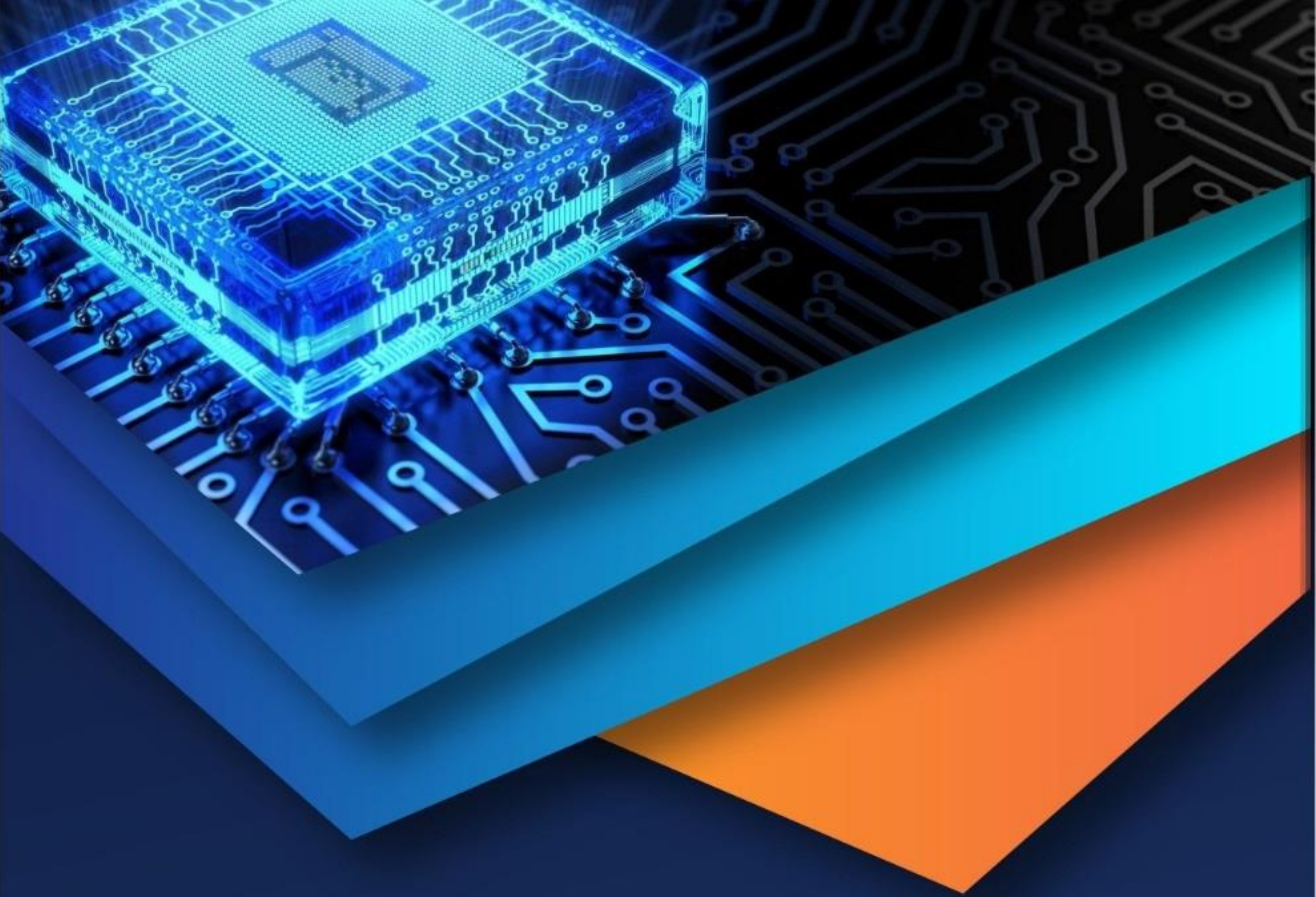

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