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FLUORESCENCE AND LIGHT SCATTERING STUDIES ON THE INTERACTIONS OF 2-HYDROXY-3-NAPHTHOIC ACID WITH IONIC AND NONIONIC SURFACTANTS

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ABSTRACT

The solublization of 2-hydroxy-3-naphthoic acid (2-H-3-NA) solubilizate into the micellar core of certain surfactants has been studied with the help of fluorescence spectroscopy. The various surfactants used for the study are nonionic as well as ionic ones. The nonionic surfactants are TX-100 and Brij-35 the anionics are DBSS and DSSS and two of the cationic surfactants are CPC and CTAB. The fluorescene peak height enhanced gradually on increasing the nonionic surfactant concentration, reaching to a limiting value with no shift in the peak position. A red shift occurred in the emission maxima in cationic surfactant media. The solubilization phenomenon was also confirmed by absorption spectral studies and light scattering measurements. Quantum yield measurements were made in these micellar media at different concentrations using anthracene as fluorescenece standard. Calculations were done for stokes' shift of 2-H-3-NA at different concentrations. The calculated results are in fair agreement with the experimental results. Environmental studies of the effect of nonaqueous solvent ethanol on the fluorescence spectra of the 2-H-3-NA compound were made. On increasing the ethanol concentration the fluorescence emission maxima showed enhancemant reaching a limiting value at its higher concentration. Thus, an understanding of the process of solubilization is expected to helps understanding the interplay of the different favourable and unfavourable forces guiding micellization.

Keywords: Solubilization, Micellar media, Fluorescence and 2-H-3-NA.

INTRODUCTION

Many characteristics of molecules, for example, absorption and fluorescence spectra, deportonation and protonation Equilibria etc., are changed drastically in micellar media. Recently polymersurfactant systems are under extensive investigation[1-3] due to their wide industrial applications. The most striking feature of micelles is the ability to solubilize variety of compounds in its different regions[4]. Most common surfactants form spherical micelles at low concentration, with aggregation no. of the order of 60 to 100 molecules per micelle[5]. It is well known that the formation of several favorable and unfavorable forces like hydrophobic and head group repulsion forces. Thus an understanding of the interplay of the different favorable and unfavorable forces guiding micellization. Nandi and co-workers[6(a-c)] have developed a model of micellization. V. Prop. and M. Haba[7]. studied the absorption and emission spectra of 2-H-3-NA in 70 solvents and 3 mixed solvents.

The present study is carried out to investigate the solubilization of 2-hydroxy-3-naphthoic acid in the presence of various surfactant micelles, employing fluorescence and absorption spectral studies and light scattering measurements. The results have been interpreted from the quantum yield and Stokes' shift measurements.

MATERIAL AND METHODS

Fluorescence studies were made with a Perkin-Elmer spectrophotomeer model 204A. For excitation and emission spectra the slit width was kept at 10nm. Absorption stectum of 2-H-3-NA were taken on a single beam, microprocesser controlled Hp-8452. A diode Array spectrophotometer. Light scattering studies were made with Brice-phoenix

universal light scattering photometer model no. 2000 at 90° angle in conjuction with multiflex galvanometer.

The stock solution of analytical pure grade 2-H-3-NA (Sigma Chemicals) was prepared in distilled ethanol. All the experiments were made at room temperature (23-25°C)and were performed in 1% ethanolic medium keeping the final conc. of 2-H-3-NA at 10^{-5} M. All the surfactants were "Sigma" (USA) or BDH products and used as such.

The surfactants employed were

(A) Nonionic
1. Polyxyethylene tert-octylphenol(eq-10)[TX-100]
2. Polyxyethylene (23)lauryl ether [Brij-35]

(B) Cationic
1. Centyltrimethylamminium bromide [CTAB]
2. Centylpyridinium chloridnium chloride [CPC]

(C) Anionic
1. Dodecylbenzyl sodium sulphonate [DBSS]
2. Diocyl sodium sulphosuccinate [DSSS]

The purity of the surfactants was checked by determining their cmc values with the help of surface tention measurements, employing drop weight method. The absolute flurescence fluorescence quantum yield of the compound was calculated relative to anthracene solution as standard. Each time the total intensity of flourencene emission was measured for the standard and the sample from the area of the corrected flourence spectrum recorded over thewhole range of emission under identical conditions.

RESULTS AND DISCUSSION

Fluorescence studies

The maximum excitation wavelength was 355 nm. The emission spectrum of 2-H-3-NA in 1% ethanolic medium showed a peak at 503 nm; and a shoulder was formed at 410-415 nm. All the nonionic surfactants caused an enhancement in fluorescence intensity The shoulder got more prominent with increase in surfactant concentration but did not convert into a peak even at higher concentration. The changes in the fluorescence intensity of 2-H-3-NA on varing concentration of TX-100 are illustrated in Fig. -1. The effect of anionic surfactants was least as compared to nonionic and cationic surfactants, with DBSS the shoulder got more prominent with increase in surfactant concentration and at higher concentration it converted into main peak and main peak became the shoulder with cationic surfactant enhancement in fluorescence intensity was observed with CTAB and a red shift of 5 nm was observed. The effect of CPC was different from all other surfactants. It produced a pronounced decreasing effect on the fluorescence intensity of the compound, fluorescence intensity decreased with increase in CPC concentration and reached to a zero value and the shape of peak became broad at the higher concentration of the surfactant.

The fluorescence intensity at minimum and maximum concentration of the surfactants of the surfactants are given in Table -1.

Absorption studies

There appeared an absorption peak at 352 nm, which increased on increasing the concentration of almost all surfactants with a red

Table - 1: Fluorescence Intensity of 2-H-3-NA ($1x10^{-5}$M) in absence and presence of surfactants [lex 355 nm, lem 503nm, P.M. Gain 2, Sensitivity Range 3]

S.No.	Name of Surfactant	Relative fluorescence Intensity in Absence of Surfactant	Relative fluorescence intensity at maximum concentration of surfactant	Range of concentration used (in%)
1.	TX-100	44	82	0.10
2.	Brij-35	44	55	0.90
3.	DBSS	45	55	0.30
4	DSSS	43	44	0.05
5.	CTAB	44	80	0.10
6.	CPC	44	00	0.07

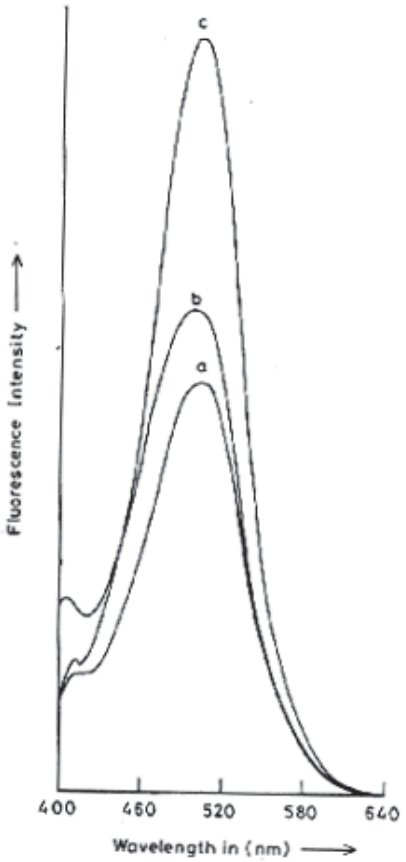

Fig. - 1 : Influence of addition of TX-100 on fluorescence intensity of $1x10^{-5}$M, 2-H-3-NA solution

(a) 0.00 %
(b) 0.01 %
(c) 0.05 %
(d) 0.10 %

shift. With TX-100 there was a red shift 6 of nm. With anionic surfactants there was a gradual small increase in absorbance with no shift. With cationic surfactants O.D. first increased then decreased with a red shift of 2 nm.

Light scattering studies

It was observed that all the three types of surfactants caused progressive drop in the scattering flux leading to almost zero value on increasing their concentration. The concentration required to reach the minimum value of scattering flux was different for each surfactant. The results are illustrated in Fig.- 2.

Effect of ethanol

Enhancement in the fluorescence intensity was also observed on adding ethanol to the

Table - 2 : Stokers' shift data for 2-H-3-NA at room temperature.

S.No.	Concentration of compound	Relative Fluorescence	λex (nm) Intensity	Iem (nm)	P.M. Gain	μ	Stokes' shift (cm^{-1})
1.	$7x10^{-6}$M	28	355	503	2	3	8288
2.	$1x10^{-5}$ M	44	355	503	2	3	8288
3.	$7x10^{-5}$ M	46	355	506	1	3	8406
4.	$1x10^{-4}$ M	66	355	507	1	3	8445
5.	$1x10^{-3}$M	70	330	500	1	3	10303

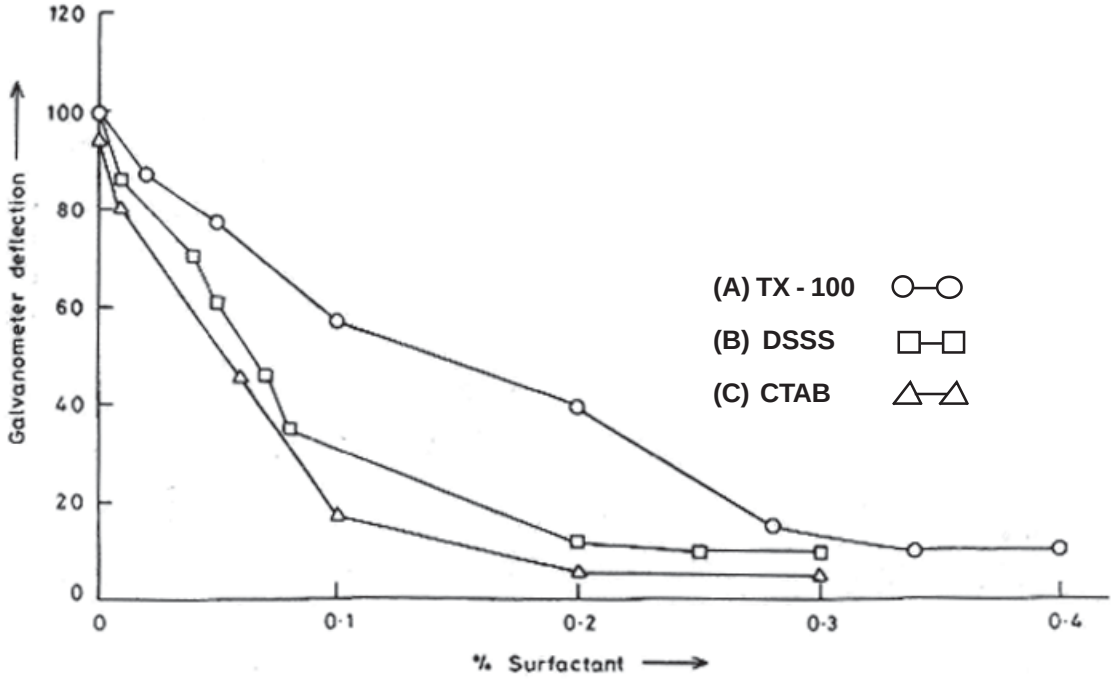

Fig. - 2: Influence of surfactants on light scattering of 1x10^{-5} M 2-H-3-NA solution

solution of 2-H-3-NA. The enhancement in the fluorescence intensity was accompanied by blue shift of 3 nm in the emission wavelength in 60% and above ethanolic medium.

Stokes' shift measurements

An increase in Stokes' shift was observed and this was due to the intramolecule proton transfer in the excited state as shown in Fig.-3. The absorption spectrum corresponds to form (A) but the fluorescence spectrum corresponds to form (B). Such abnormally large stokes' shift due to process (i) occurring in the excited state are to be expected in compounds that contain two groups situated ortho to one another , one of which becomes strongly acidic in the exited state, and other strongly basic. The results are given in Table - 2. The variation in Stokes' shift (from8288

Table - 3 : Absorption Maxima (la), Molar Absorptivity (e), Florescence Maxima (I_F) and Quantum yield (f_F) values of 2H-3-NA at different concentrations of TX-100.

S. No.	Concentration TX-100 used	λa (nm)	log e (dm^3 mol^{-1} cm^{-1})	λem (nm)	ϕ_F 2-H-3-NA
1.	0.00	352	4.33	503	0.756
2.	0.01	352	4.34	503	0.764
3.	0.05	354	4.34	504-505	0.795
4	0.10	356	4.37	505	0.827

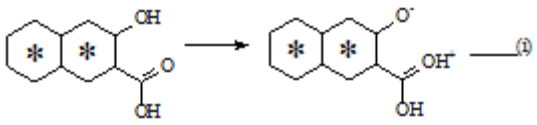

Fig. - 3: Intramolecular proton transfer in the excited state of 2-H-3-NA molecule

for 7x 10^{-6}M 2-H-3-NA to 0303 for 1x 10^{-3}M 2H-3-NA)) indicate that large energy changes occur on varying the concentration of the comound.

The results indicate that nonionic and cationic surfactants had a stronger enhancement effect than the system in which here was no surfactant presen the maximum fluorescence enhancemet was obtained by adding TX-100. An oblate ellipsoidal model has been postualted for TX-100[8]. A spherical model requires, mixing of the hydrophobic part and the hydrophobic part. However, in oblate polyxyethylene group of TX-100 can separate each other and each layer packs well. This model therefore predicts the hydrophobic and less fluid interior of the TX-100 micelle. Indeed Kano *et al* [9] have found that the ionic micelle. The non polar environment of the TX-100 micellar interior may be preferable to incorporatehydrophobic 2-H-3-NA molecules. Also it seems that the conformational chance of 2-H-3-NA after excitation is restricted by the rigidly of the micellar interiour of TX-100. The higher polarity of ionic micelles may be ascribed to the loose, fluctuating and disorders structures of these micelles[10,11]. 2-H-3-NA must leave its aggregate and exclude water molecules inside of the ionic micelle. These processes should cause low solublization. It is assumed that the ionic micelles are too hydrophilic too solubilization. It is assumes that tha ionic micelles are too hydrophilic to solubilize the hydrophobic 2-H-3-NA molecules to larger extent. Among cationic surfactants CPC behaves anomalously by decreasing the fluorescence of the compound which is probably caused by its nucleophilic pyridine nucleus. Other cationic surfactants have linear alkyl and aryl groups.

The absorption spectra of the compound are very less affected on adding surfactants as compared to the fluroscence spectra. This may be, because absorptionis less sensitive to its environment as compared to fluorescence, No major change in the nature of absorption spectrum indicates no structural changes due to complex formation or dissociation or hydrogen bonding between the compound in the ground state and the surfactant. The blue shift in the emission wavelength may be due to the change of the medium.

The calculated quantum yield values (f_F) are in good agreement with the flurescence intensity. The quantum yield values increased on increasing the surfactant concentration (except CPC) and was found to be highest for TX-100 added solubilizate solution, which are given in Table -3. These high quantum yield values in micellar medium may be attributed to[12-13]

i) lesser effects of other deactivation processes which compete with fluorescence.
ii) That the rate of non-radiative processes are less in micellar medium in comparison to those in aqueous medium.
iii) Due to the absorption of the fluorophore at the micellar surface, which decreases the rate of collision of the fluorophore by water molecules.

Conclusion

It is apparent that 2-H-3-NA is not fully solubilized in 1% ethanolic medium. The suspended particles of 2-H-3-NA solubilized on addition of surfactants or on increasing the ethaol concentration. This is also supported by light scattering studies, since the scattering of incident light by the suspended particles decreased on addition of surfactants. Thus, there appears to be straightforward correlation between solubilizing action and enhancement in fluorescence emission.

Thus, the present analysis indicates that diring solubilization of a solubilizate into the surfactant system, the incorparationof the solubilizate influences the balance of the favourable ad unfavourable conditions guiding micellization.

The solubilization process finds extensive application in the industrial, pharmaceutical and biochemical fields. The present kind of analysis is expected to be useful in these fields.

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