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ELECTRONIC SPECTRAL STUDIES OF 2–AMINOPYRIDINE IN SURFACTANT MICELLES

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ABSTRACT

The electronic spectral studies include the effect of different micellar media on the fluorescence and absorption spectral behaviour of 2–aminopyridine. It is a medicinally and analytically important molecule. The solubilizing action of the surfactant has been supplemented by the theoretically calculated spectral parameters, like quantum yield, molar extinction coefficient, and Stokes' shift. The red shift in λem appears to be due to the hydrogen–bonding capability of amino group of the compound to the surfactant micelles. The results have been attributed to micellization of surfactants.

Key words : 2–Aminopyridine, Fluorescence, Micelles, Solubilization

INTRODUCTION

Micelles have been the subject of numerous investigations because of their importance as model system for mimicking biomembranes[1,2]. The capacity of water insoluble solutes to get dissolved in micelles is called solubilization. Nandi and coworkers[3] have done extensive investigations on micellar effects of the surfactants. Acharya *et al.*[4,5] have worked on the solubilization of various polyaromatic organic compounds by nonionic and ionic surfactants. As the aminopyridine nucleus often occurs in the drug or in their metabolic transformation products, 2–aminopyridine has been used as a fluorescent label[6]. Wilson *et al.*[7] correlated the fluorescence and phosphorescence excitation and emission spectra of four antihistamines having 2–aminopyridine and 2–aminopyrimidine. Comparative studies of the fluorescence behaviour of some mono– and di–aminopyridine were presented by Baeyens and De Moerloose[8]. Deng *et al.*[9] have studied the deuterium isotope effects on the fluorescence of phenyl pyridine. Recently, fluorescence quenching by pyridine and its derivatives induced by intermolecular H–bonding to pyrrole containing hetero–aromatics have been investigated by Herbich *et al.*[10]. The picosecond dynamics of stepwise double proton transfer reaction in the excited state of aminopyridine/acetic acid system have been studied by Ishikawa *et al.*[11]. We

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report here, the investigations carried out on solubilization of 2–aminopyridine occurring in the surfactant micelles, employing fluorescence and absorption spectral techniques. Some spectral parameters, like, ϕ_F, logϵ, and Stoke's shift calculated theoretically help in understanding the solubilization process and explaining the forces guiding micellization.

EXPERIMENTAL

All the fluorometric and absorption experiments were carried out with Perkin– Elmer Fluorescence Spectrophotometer Model No. 204 A with a synchronized Model No. 0.56 strip chart recorder and Hewlet Packard (HP) 8452 A diode array spectrophotometer, respectively. The stock solution of analytically pure 2–aminopyridine (BDH, UK) was prepared in distilled ethanol. All the experiments were made at room temperature (23–25°C) and in 3% ethanolic medium keeping the final concentration of 2–aminopyridine at 3.0×10^{-3} M and 10^{-4} M for fluorescence and absorption spectra, respectively. All the surfactants used were either of Sigma (USA) or BDH (UK) products.

(1) Nonionic surfactants

(i) TX–100 (Polyoxyethylene tertoctyl phenol)

(ii) Tween–20 (Polyoxyethylene sorbitain monolaurate)

(iii) Tween–40 (Polyoxyethylene sorbitain palmitate)

(2) Anionic surfactants

(i) DBSS (Dodecylbenzyl sodium sulphonate)

(ii) DSSS (Dioctylsodium sulphosuccinate)

(iii) SLS (Sodium lauryl sulphate)

(3) Cationic surfactants

(i) CTAB (Cetyltrimethyl ammonium bromide)

(ii) CDBAC (Cetyldimethyl benzyl ammonium chloride)

(iii) CPC (Cetylpyridinium chloride)

The purity of surfactant was checked by determining their CMC values with the help of surface tension measurement, employing drop weight method. The absolute fluorescence quantum yield (ϕ_F) of the compound was calculated relative to anthracene solution as standard. Each time, the total intensity of fluorescence emission was measured for the standard and the sample from the area of the fluorescence spectrum recorded over the whole range of emission under identical conditions. Molar extinction coefficient (ϵ) data have been reported in terms of its logarithm log ϵ, The Stokes' shift data have also been calculated in different micellar media and are expressed in terms of nanometers.

RESULTS AND DISCUSSION

2–Aminopyridine in its 3% ethanolic solution showed a maximum emission wavelength at range 360–365 nm. The maximum excitation peak intensity appeared at 300 nm. All the nonionic surfactants caused an enhancement in fluorescence intensity of 2–aminopyridine. A small red shift of 2–3 nm was observed with the nonionics. Among these surfactants TX–100 exerted maximum effect. The changes in the fluorescence intensity of 2–aminopyridine on adding TX–100 are given in Fig. 1. The anionic surfactants caused a gradual decrease in peak position and emission intensity with a blue shift of 5 nm, whereas the emission intensity with all the cationic surfactants initially showed an enhancement and at their higher concentration, a small lowering occurred. The minimum and maximum fluorescence intensity in absence and presence of all the three classes of surfactants is given in Table 1. The fluorescence spectral changes on addition of CTAB are shown in Fig. 2. The absorption spectra gave a peak at 290 nm. All the nonionic surfactants caused an enhancement in absorbance on increasing their concentration. The absorbance of 2–aminopyrdine decreased gradually on increasing the concentration of anionic surfactants. On addition of the cationic surfactants, absorbance decreased initially and further increased to a small extent at higher concentration of the surfactants. A gradual decrease in the fluorescence emission intensity of 2–aminopyridine was observed on increasing the concentration of ethanol accompanied by a blue shift of 10–15 nm.

The calculated fluorescence quantum yield data (ϕ_F) of surfactants added 2–aminopyridine solutions showed parallelism with changes in fluorescence intensity of the compound. With nonionic surfactants, the ϕ_F values continuously increased. With anionic surfactants, the ϕ_F data obtained are in decreasing order, whereas with cationic surfactants, the ϕ_F values first increased and then showed a small lowering further. The ϕ_F values obtained were highest for TX–100 added 2–aminopyridine, which are given Table 2. The Molar extinction coefficient ($\log \in$) value calculation showed a gradual increase as the concentration of the nonionic surfactant was increased. With all anionic and cationic surfactants, the $\log \in$ values first decreased and then increased on further addition of surfactant. The data are given in Table 2. The calculated Stokes' shift values obtained are higher for very dilute solutions of 2–aminopyridine. The calculated theoretical data are given in Table 3.

Table 1. Fluorescence intensity of 2–aminopyridine in absence and presence of surfactant λem = 360–365 nm, λex = 300 nm, P.M. Gain = 1, Sensitivity range = 0.3

Name of surfactant	Fluorescence intensity in absence of surfactant (nm)	Concentration of surfactant used (%)	Maximum fluorescence intensity (nm)
TX–100	45	0.5	95
Tween–20	47	0.9	87
SLS	47	0.03	45
DBSS	48	0.001	50
CPC	48	0.03	71
CTAB	48	0.01	53

The result indicated that nonionic surfactants had a stronger enhancement effect on the fluorescence and absorption behaviour of 2–aminopyridine. The maximum fluorescence enhancement was obtained for TX–100, which has been also supported by absorbance, and log ϵ and ϕ_F values. The results so obtained can be explained in a better manner by considering the

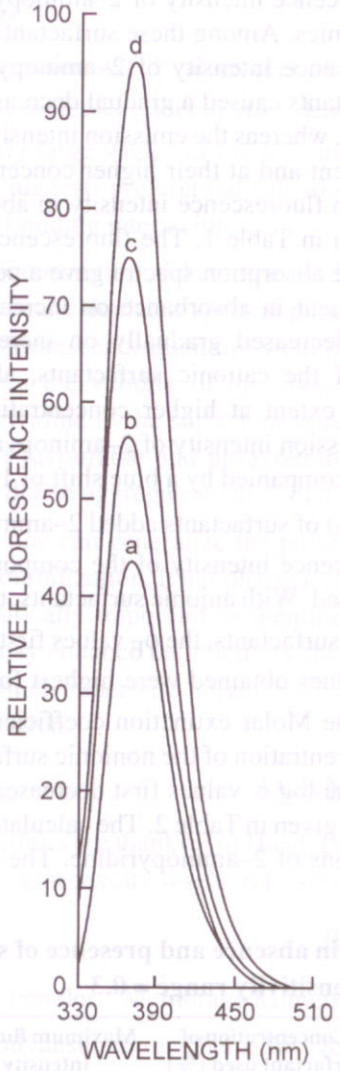

Fig. 1 The changes in the fluorescence intensity of 2–aminopyridine on adding TX–100 are given
(a) 3 x 10^{-5} M 2–Aminopyridine
(b) 3 x 10^{-5} M 2–Aminopyridine + 0.005 % TX–100
(c) 3 x 10^{-5} M 2–Aminopyridine + 0.3 % TX–100
(d) 3 x 10^{-5} M 2–Aminopyridine + 0.5 % TX–100

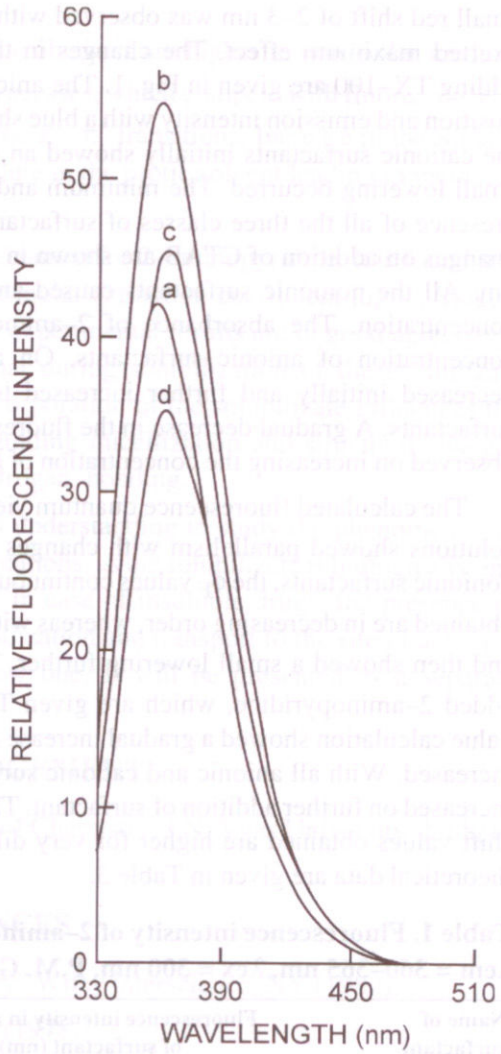

Fig. 2 Fluorescence spectral changes on addition of CTAB
(a) 3 x 10^{-5} M 2–Aminopyridine
(b) 3 x 10^{-5} M 2–Aminopyridine + 0.005 % CTAB
(c) 3 x 10^{-5} M 2–Aminopyridine + 0.07 % CTAB
(d) 3 x 10^{-5} M 2–Aminopyridine + 0.3 % CTAB

Table 2. Absorption maxima (λa), fluorescence maxima (λem), molar extinction coefficient (log ∈) and quantum yield (ϕ_F), of 2–aminopyridine at different concentration of TX–100

S.No.	TX–100 used (%)	λa (nm)	Log ∈ (dm^{-3} mol^{-1} cm^{-1})	λem (nm)	ϕ_F
1.	0.0	290	3.54	360–365	0.537
2.	0.001	290	3.73	360–365	–
3.	0.07	280	4.14	365	0.55
4.	0.3	270–280	–	365	0.608
5.	0.5	270	4.47	365	0.634

Table 3. Stokes' shift data of 2–aminopyridine at room temperature

S.No.	Concentration of the compound (M)	FI	λex (nm)	λem (nm)	PM–Gain	Sensitivity (μ)	Stokes' Shift (cm^{-1})
1.	1×10^{-5}	10	300	360–365	1	0.1	5785
2.	5×10^{-5}	26	300	360–365	1	0.1	5785
3.	7×10^{-5}	30	300	360	1	0.1	5555
4.	1×10^{-4}	35	300	360	1	0.1	5555
5.	3×10^{-4}	37	305	355–360	1	0.3	4775
6.	5×10^{-4}	58	310	355	1	0.3	4089
7.	1×10^{-3}	50	315	350	1	0.3	3174

oblate ellipsoidal model for TX–100[12]. The octaphenyl group and the polyoxyethylene group of TX–100 can separate each other and each layer packs well. This model predicts the hydrophobic and less fluid interior of the TX–100 micelle. This fact has also been supported by Kano *et al.*[13]. Hence, the nonpolar environment of the TX–100 micelle interior may be preferable to incorporate the hydrophobic 2–aminopyridine than the ionic surfactant micelle. The higher polarity of ionic micelles may be asserted to the loose, fluctuating and disordered structures of these micelles[14]. It is assumed that the ionic micelles are too hydrophilic 2–aminopyridine molecules to larger extent. In ionic micellar media, the 2–aminopyridine must leave its aggregate and exclude water molecules inside the ionic micelle. These processes cause slow solubilization. However, the decrease in fluorescence intensity observed on the addition of anionic and cationic surfactants indicates electrostatic preferential interaction between the polar substituent group of the solubilizate molecule and the ionic head group of the surfactant, which may result in change in the geometry of the solubilizate molecule wherein loses coplanarity. The red shift in the peak wavelength in micellar media is attributed to the hydrogen bonding capacity of the amino group of 2–aminopyridine. The continuous decrease in the emission

intensity on adding solvent to the solubilizate accompanied by a blue shift may be attributed to the protic nature of ethanol (solvent), here, hydrogen–donor solvent–interactions take place between the solute and solvent. Absorption is less sensitive to its environment as compared to fluorescence; thus, the absorption spectra of 2–aminopyridine were very less affected on adding surfactants.

The quantum yield values (ϕ_F) of fluorescence obtained are higher in non–polar medium because of the lesser effect of other deactivation processes, which compete with fluorescence[15]. Sufficiently large values of log $\in$ is assigned to the $\pi - \pi^*$ transitions. Increase in the Stokes' shift data suggests preferential solvation of the solute in the protic solvent leading to increased hydrogen bonding interaction.

After interpreting and comparing the results obtained for 2–aminopyridine, it is found that the theoretical calculated spectral parameters like molar extinction coefficient log $\in$, Stokes' shift and fluorescence quantum yield (ϕ_F) and the experimental results are in good agreement. This proves the validity of the investigations that during solubilization of the solubilizate 2–aminopyridine in the surfactant system, the incorporation of the solubilizate influences the balance of favourable and unfavourable forces guiding micellization and structural changes occurring due to aggregation, dissociation and hydrogen–bonding.

Thus, one can generalize the present physical understanding to study the phenomenon of micellar solubilization. It has pharmaceutical applications, as the solubilizate is biologically and pharmaceutically important as mentioned earlier. In case of insoluble drugs, the presence of micelles may enhance their activity through solubilization and transport to the site of action, a process which otherwise might have been a slow one. It will be presented as a separate communication.

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