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INTERACTION OF p- AMINO BENZOIC ACID (PABA) WITH IONIC AND NONIONIC MICELLES BY FLUORESCENCE

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ABSTRACT

Micellar solubilization is a powerful alternative for dissolving hydrophobic compounds in aqueous environment. Fluorescence and absorption spectroscopy are the two techniques used to monitor the micellar solubilization studies of p-amino benzoic acid (PABA). PABA is an aromatic compound with acidic functional group, is non essential nutrient, used as a sunscreen. Externally, it prevents sunburn and skin cancer from UV light. The emission intensity of PABA is significantly enhanced in nonionic and anionic micellar media and decreased in cationic micellar media of different surfactants. The solubilizing action of the surfactant has also been determined by theoretical calculated spectral parameters like empirical fluorescence coefficient, quantum yield, molar absorption coefficient and stokes' shift value. The fluorescence as well as the theoretically calculated spectral data have been used to characterize the heteroenvironment of the micelles in terms of their polarity, probe solubilization site and critical micellar concentration (CMC). This article briefly discusses the importance of surfactants in biological system model as well as the use of micelles in pharmacy as an important tool that finds numerous applications.

Keywords: PABA, fluorescence, absorbance, micelles.

INTRODUCTION

By spectroscopic studies, it has been explained that different solubilized molecules are found in different regions of micelles[1,2]. Surfactants are known to play a vital role in many processes of interest in both fundamental and applied science. The formation of colloid sized clusters in solutions known as micelle, have particular significance in pharmacy because of their ability to increase the solubility of sparingly soluble substances in water[3]. The most striking feature of micelles is the ability to solubilize a variety of compounds in its different regions[4]. Nadine Arnand et al. studied the influence of pH, surfactant and synergic agent on the luminescent properties of terbium chelated with PABA and other benzoic acid derivatives in aqueous solution[5]. Milton studied the absorption spectra of the azo derivatives of PABA and also analyzed the effect of pH and salt added to it[6]. S.I. Akberova studied PABA as an inducer of endogenous interferon and regulator and displays a virucidal, synergistic antiviral effect when combined with chemical drug and of a direct anticoagulant[7]. S Thiele-Bruhn et al. analyzed the PABA by soil absorption which is found in environment as an antibiotic[8]. Hanafi Tanojo et al. investigated the interdependence of the fluorescence intensity and pH of PABA solution in various acid-base mixtures[9]. M. Carlson and R.D. Thomson determined PABA in pharmaceuticals by HPLC[10]. Shaw et al. studied photoreactions of PABA in presence and absence of oxygen using light at 254nm and greater than 290 nm[11]. ES Lianidou and PC Toannou explained the spectroscopic determination of PABA in biological fluids by use of Tb-sensitized luminescence[12]. J.H. Turnbull et al. studied the effect of β-cyclodextrin on the luminescence of PABA[13].

EXPERIMENTAL

The fluorescence studies were made with Perkin-Elmer Fluorescence Spectrophotometer model 204A with a silica cell of 1 cm path length. All experiments were carried out at room temperature. Absorption spectra of PABA were taken on double beam specord UV-Vis spectrophotometer.

The stock solution of analytically pure PABA was prepared in double distilled water keeping the final concentration of compound at 2 x 10^{-5} M and 1 x 10^{-4} M for fluorescence and absorption spectra respectively. All the surfactants used were either of Sigma (USA) or BDH (UK) products.

The following surfactants were employed-

(A) Nonionic surfactants

(i) Polyoxyethylene tert-octyl phenol (TX - 100)
(ii) Polyoxyethylene sorbitain monolaurate (Tween – 20)
(iii) Polyoxyethylene sorbitain monooleate (Tween - 80)

(B) Anionic surfactants

(i) Dodecylbenzene sodium sulphonate (DBSS)
(ii) Dioctyl sodium sulphosuccinate (DSSS)
(iii) Sodium lauryl sulphate (SLS)

(C) Cationic surfactants

(i) Cetylpyridinium chloride (CPC).
(ii) Cetytrimethyl ammonium bromide (CTAB)
(iii) Myristyltrimethyl ammonium bromide (MTAB)

Table-1: Fluorescence intensity of p-amino benzoic acid (PABA) in presence and absence of surfactants.
λ_{ex} = 280nm P.M. Gain = 2
λ_{em} = 345 mn Sensitivity Range = 1

S.No.	Nature of surfactant	Range of conc. used (%)	Fluorescence intensity in absence of surfactants	Maximum fluorescence intensity
1.	TX-100	0.03	30	Out of scale
2.	Tween – 20	0.5	30	37
3.	Tween – 80	0.5	30	38
4.	DBSS	0.5	30	44
5.	DSSS	0.5	30	40
6.	SLS	0.5	30	49
7.	CPC	0.5	30	30
8.	CTAB	0.5	30	33
9.	MTAB	0.5	30	36

Table -2: Absorbance Maxima (λ_{max}) , Molar Extinction Coefficient (log ε),Fluorescence Emission (λ_{em}) and Quantum yield (ϕ_f) values of PABAat different concentrations of TX- 100

S.N.	% of TX-100 (w/v)	λ_{max} (nm)	logε (dm^3 mol^{-1} cm^{-1}))	λ_{em} (nm)	ϕ_f
1.	0.000	275	4.7412	345	0.07109
2.	0.003	275	4.7853	340	0.10091
3.	0.005	275	4.7983	335-340	0.10091
4.	0.007	270	4.8286	330-335	0.13531
5.	0.01	265	4.8564	305-310	0.13740
6.	0.03	265	4.9156	305-310	0.13740
7.	0.05	265	4.9597	305-310	0.13740

The purity of the surfactants was checked by determining their CMC values with help of surface tension measurements, employing drop weight method. The values thus obtained coincided with the reported values. The absolute fluorescence quantum yield of the compound was calculated relative to anthracene

solution as standard. Fluorescence emission obtained is in the same range as that of the compound. Approximate corrections were made to compensate for the different absorptions of the compounds and the 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.

RESULTS AND DISCUSSION

p-Amino benzoic acid (PABA) in its aqueous solution showed a maximum emission wavelength at 345 nm. The maximum excitation peak intensity appeared at 280 nm.

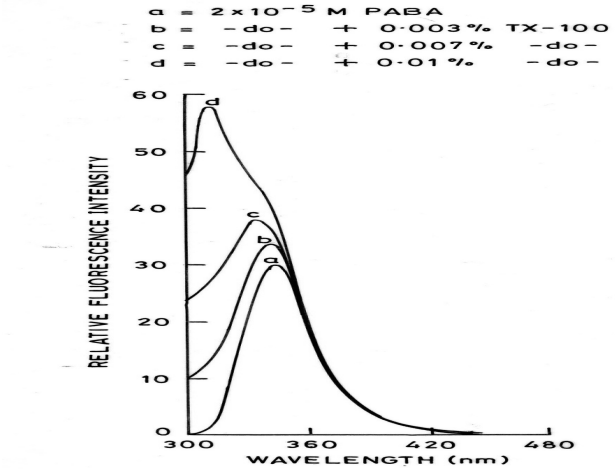

Fig.-1: Influence of addition of TX-100 on fluorescence intensity of $2x10^{-5}$ M PABA solution

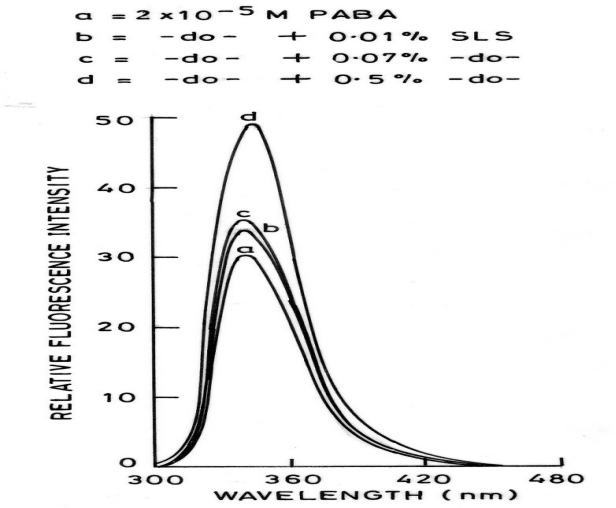

Fig.-2: Influence of addition of SLS on fluorescence intensity of $2x10^{-5}$ M PABA solution

All the nonionic surfactants caused an enhancement in peak value of fluorescence intensity. There is a blue shift of 30-35 nm in case of TX-100 and 2-3 nm in case of Tween-20 and Tween -80. Influence of addition of TX-100 on fluorescence intensity of 2 x 10^{-5} M PABA solution is shown in Fig. 1. The fluorescence intensity of PABA increased on adding anionic surfactants to it. Out of all, the three anionics employed only higher concentration of SLS and DBSS showed 2-3 nm red shift in peak position. Influence of addition of SLS on fluorescence intensity of 2 x 10-^{5} M, PABA solution is shown in Fig.2. Cationic surfactants caused no shift in peak position. CPC sharply decreased emission intensity whereas CTAB and MTAB at lower concentration slightly increased emission intensity and at their higher concentration it decreased. The enhancement in emission intensity was found to be minimum in cationic micellar media. The minimum and maximum fluorescence intensity in absence and presence of all three classes of surfactants is given Table-1.

The absorption spectra gave a peak at 275 nm. The absorbance increased on increasing the concentration of nonionic and anionic surfactants. For nonionic surfactants absorbance increased in TX-100 with a blue shift of 5-10 nm. Cationics showed parallelism with the fluorescence intensity. The calculated fluorescence quantum yield data of surfactant added PABA solution show parallelism with change in fluorescence intensity of the compound. With nonionic surfactants, the value of fluorescence quantum yield increased continuously. Similarly anionic surfactants also increased the value of fluorescence quantum yield (ϕ_f) of PABA. The Molar Extinction Coefficient ($\log \varepsilon$) calculation data also show gradual increase with increase in concentration enhanced, was obtained for TX- 100, which has been supported by absorbance, $\log \varepsilon$ and ϕ_f values. The changes in the theoretical spectral data are shown in Table 2.

The results indicate that nonionic surfactants had a stronger enhancement on fluorescence and absorption behaviour of PABA. The maximum fluorescence enhancement was obtained for TX- 100 which has been supported by absorbance, $\log \varepsilon$ and ϕ_f Values. The results so obtained can be explained in a better manner by considering oblate ellipsoidal model for TX-100. The octaphenyl group and the polyoxyethylene group of TX-100 can separate 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[14]. Both the anionic and cationic surfactants increased the emission intensity slowly. The ionic micelles have higher polarity which may be asserted to the loose fluctuating and disordered structure of these micelles. Here in ionic micellar media, the hydrophilic solubilizate must leave its aggregate and exclude water molecule inside the ionic micelle. These processes cause slow solubilization. The blue shift observed may be attributed to the protic nature solvent, as hydrogen-donor solvent-interaction takes place between solubilizate and solvent. This may also be because of the difference in solvation energy of the solute in the ground and excited state. The shift here may be explained as resulting from greater contribution of the mesomeric forms of lower energy to the excited state. The absorption spectra are less affected on adding surfactants as absorption is less sensitive to its environment as compared to fluorescence. Sufficiently large value of $\log \varepsilon$ is assigned to π-π^* transitions. The enhancement of fluorescence of PABA in TX–100 can be attributed to the increase in quantum efficiency of fluorescence. Furthermore, the quantum yield is higher in nonpolar medium because of the lesser effect of the other deactivation processes which compete with fluorescence.[15] Thus the increased ϕ_f values showed that the micelles have been possibly adsorbed on to the dispersed microcrystal of PABA. The molecules of PABA have been subsequently solubilized by incorporation into the interior nonpolar core of the micelles. The presence of a nucleophillic pyridine ring in CPC causes a continuous decreasing effect in emission intensity and behaves differently from other cationics which have linear alkyl and aryl groups.

As PABA is a pharmaceutically important, the present kind of study of micellar solubilization of PABA molecules is of great important. It signifies faster transport of PABA molecules requisite to the site of action by the processes of micellization followed by solubilization, the process which otherwise would have been a slow one.

Thus, one can generalize the present physical understanding to the study the phenomenon of micellar solubilization. It has pharmacological application as the solubilizate PABA is analytically and pharmacologically important for medical research.

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