

Equilibrium Constant, Concentrations Study of *p*-Aminobenzoic Acid in Anionic, Cationic and Non-ionic Surfactants

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Abstract: *p*-aminobenzoic acid (*p*ABA) was used as a probe to study the equilibrium constant in ground and excited state and concentrations of anionic surfactant, cationic surfactant and non-ionic surfactant. The absorption and fluorescence spectral characteristics of *p*ABA were reported in aqueous micellar environments (SDS, CTAB and TW 80) at different pHs. The neutral and monoanion form of *p*ABA is present at both pHs 3 and 7 respectively. The blue shifted fluorescence maximum was accompanied by a great raise in intensity at pH 3 whereas at pH 7 the emission intensity a little increase with increasing micelles concentration. In the acidic medium, the CMC value is increased when compared to neutral solution. The strength of interaction between *p*ABA-micelles at both pHs was estimated using Hirose - Sepulveda equation and these calculated values was further used to estimate the free energy change of the interaction from the fluorescence data. These results from the absorption and fluorescence spectra of *p*ABA well explained that the nature of force and location of probe in ionic micelles and non-ionic micelles at different pHs.

Keywords: *p*-Aminobenzoic Acid, Ionic and Non-ionic Micelles, Binding Site

1. Introduction

The interaction of surfactants with various charges such as anionic, cationic, non-ionic and many organic neutral molecules has been investigated by the changes in the absorption and fluorescence spectrum [1-3]. These spectral changes after addition of organic molecules were moving into the core or surface of the micelles in the aqueous medium to change the various parameters. Surfactant-induced changes in absorption and fluorescence spectrum have been used to highlight various factors that contribute towards the growth of surfactant-organic molecules aggregates [4-7]. The binding behaviour of these aggregates provides the key to manufacturing of nanostructure materials [8, 9].

The acid-base equilibria for many organic molecules having functional groups such as -OH, -NH₂, -COOH, -N=N etc could be altered in micellar medium. This alteration could

be explained the perturbation of the acid-base equilibria by the electrostatic field effect of the charged interface. Santos et al [10] has been studied the binding of chloroquine species to ionic micelles of opposite charges in different pH. Then the interaction of 6-methoxyquinoline with sodium dodecylsulfate micelles was investigated using the spectral techniques at different pH [11]. Benzophenanthridine alkaloids [12, 13] namely Chelerythrine and Sanguinarine were structurally modified in sodium dodecylsulfate micelles with fluorescence modification at low and high pH.

Crystallographic, spectral and computational study of *p*-aminobenzoic acid was investigated with α -cyclodextrin [14], β -cyclodextrin [15, 16] and hydroxypropyl- β -cyclodextrin [17, 18] to form stable inclusion complex in aqueous solution and solid phase. Volumetric and calorimetric studies were also reported the inclusion complex formation of cyclodextrins with aminobenzoic acids [19]. Further the

supramolecular recognition behaviour of sulfonatocalix [6] arene with amino benzoic acid isomers were studied by fluorescence and nuclear magnetic resonance spectroscopy [20]. The influence of biologically active monovalent cations such as Na^+ and K^+ on α -cyclodextrin with pABA was studied at different pH and temperature of 298.15 K by ^1H NMR and calorimetry methods [21].

In the last few years, large number of organic molecules has been investigated in different solvents with various polarity, varying hydrogen ion concentration and β -cyclodextrin, 2-hydroxypropyl- β -cyclodextrin on the spectral characteristics of different fluorophores and computational methods [22-24]. The existence of various species such as dication, monocation, neutral, monoanion and dianion in many organic molecules at different pHs were involved in the ground and excited states to study the prototropic reaction in aqueous and β -cyclodextrin medium [25, 26]. This prototropic study of organic molecules has been further extended to non-aqueous environment in anionic sodium dodecylsulfate (SDS), cationic cetyltrimethylammonium bromide (CTAB) and neutral polyoxyethylene sorbitan-monooleate (Tween 80) with addition of *p*-aminobenzoic acid. The presence of functional groups ($-\text{NH}_2$, $-\text{COOH}$) in pABA makes them pH sensitive and better fluorescent probe.

2. Experimental

p-Aminobenzoic acid (pABA), Sodium dodecylsulphate (SDS), Cetyltrimethylammonium bromide (CTAB) and Polyoxyethylene sorbitan-monooleate (Tween 80) were obtained from Sigma-Aldrich. Analytical grade H_2SO_4 , NaOH and Triply distilled water were used to prepared acidic and basic solutions.

Absorption spectral measurements were carried out with a Shimadzu UV 1601 PC model UV-Visible spectrophotometer and fluorescence measurements were made by using a Shimadzu spectrofluorimeter model RF-5301PC. The pH of solutions was adjusted in the range of 1-12 by adding appropriate amount of H_2SO_4 or NaOH. In SDS and CTAB, the pH was maintained by adding NaOH and H_2SO_4 , and no buffers were used in this case. The concentration of pABA used was 1×10^{-5} M. The stock solutions were prepared in methanol but the final solutions did not contain more than 1% methanol. The surfactant concentration was varied within the range 5×10^{-2} to 10×10^{-5} M depending on the nature of the used surfactant. Before the spectral measurements we kept the micellar solution for 5-6h generally for better equilibration, even for overnight in some cases.

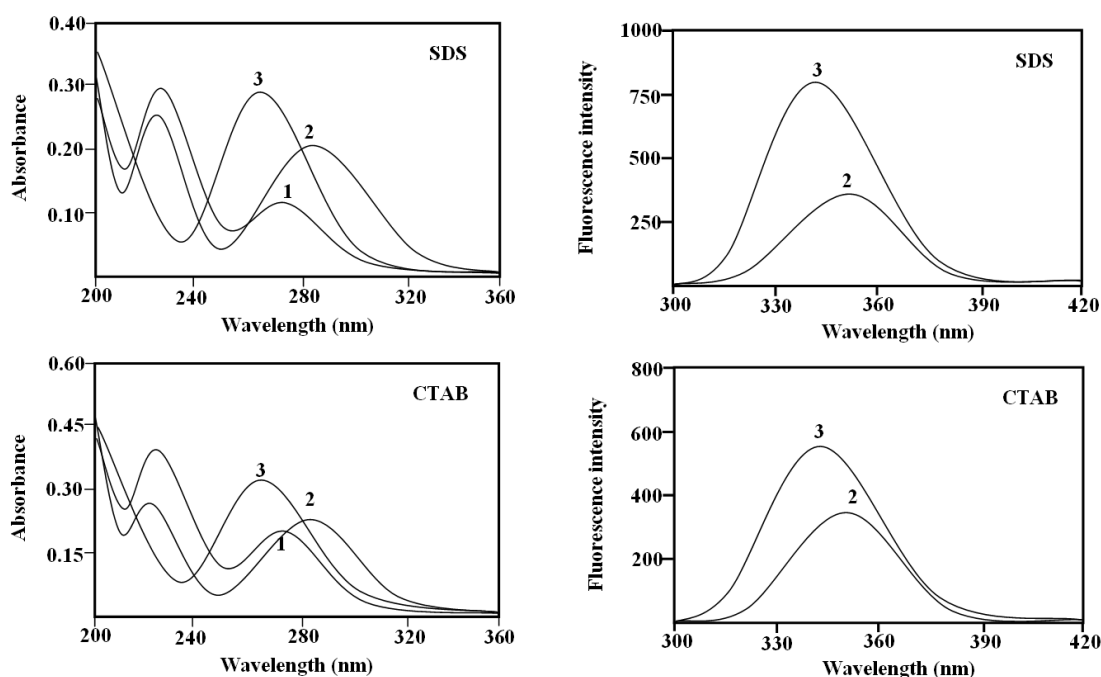


Figure 1. Absorption and fluorescence spectra of prototropic species of pABA in SDS and CTAB. 1. Monocation, 2. Neutral and 3. Monoanion.

Table 1. Absorption and fluorescence maxima of various prototropic species of pABA in aqueous, SDS and CTAB medium.

Species	Aqueous		SDS		CTAB	
	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}
Monocation	271.2	nf	271.2	nf	271.2	nf
	226.0		226.0		226.0	
Neutral	280.0	350	283.0	346	285.2	343
	218.4		220.0		221.0	
Monoanion	265.4	338	265.4	338	265.4	337

3. Results and Discussion

3.1. Effect of PH

The selected amphoteric molecule pABA in this manuscript having $-\text{COOH}$ and $-\text{NH}_2$ groups at 4th position in the aromatic ring. The absorption and emission spectra of pABA at different acid and base concentrations have been

studied in the aqueous solutions of SDS and CTAB. Figure 1 illustrates the effect of acid and base concentration on the absorption and emission spectra of pABA in 0.05 M SDS and 0.01 M CTAB. The absorption and emission maximum in different pHs were shown in Table 1. Five prototropic species of pABA such as dication (DC), monocation (MC), neutral (N), monoanion (MA) and dianion (DA) were observed in the aqueous solution. The absorption and emission maximum of all prototropic species for pABA in aqueous solution were reported in the earlier literature [27]. But in the case of micellar environment, these species whether or not formed in the ground and excited states, but earlier references reported these types of ionic species were formed in SDS, CTAB and TW 80 micelles. From the comparison of absorption and emission maximum in aqueous solution, the monocation, neutral, monoanion of pABA was appeared at 271 nm & non-fluorescence, 280 & 350 nm and 265 & 338 nm in the micellar environment. At a small hydrogen ion concentrations (pH 1), the monocation of pABA was formed in SDS and CTAB medium from the protonation takes place at 4-position of amino group without changing in absorption and emission maximum compared aqueous solution. Then the hydrogen ion concentrations at pH range of 2.0 to 3.5 in micellar environment the absorption maximum was moving

to the red shift and blue shift in emission maximum for neutral pABA. At neutral pH, the monoanion of pABA was formed without change in the absorption and emission maximum in the micellar environment, it is due to deprotonation from the carboxyl group.

The ground state pKa of monocation - neutral and neutral - monoanion equilibria have been calculated using Henderson equation [28] in aqueous, SDS, CTAB solution according to equation (1) and the equilibria was shown in Figure 2.

$$pK_a = pH + \log \frac{C_1}{C_2} \quad (1)$$

The excited state acidity constant of this neutral - monoanion equilibrium, pK_a^* has been calculated using Förster cycle [29] according to equation (2):

$$pK_a - pK_a^* = \frac{E_{HX} - E_X}{2.303RT} \quad (2)$$

where E_{HX} and E_X are the energies of electronic transitions for the conjugate acid and base, respectively.

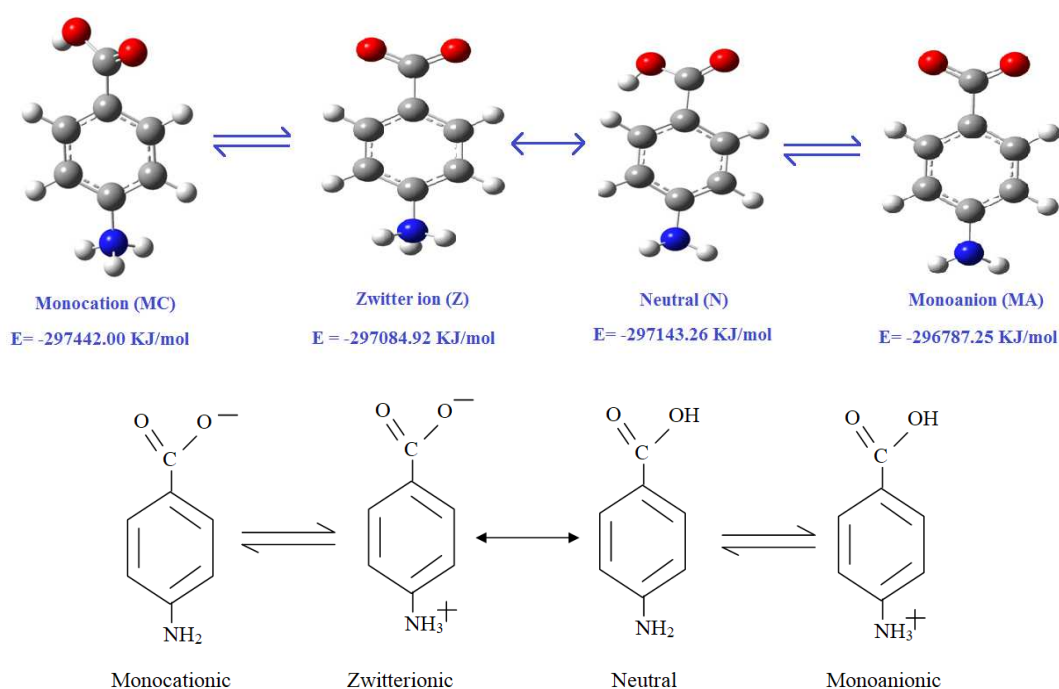


Figure 2. The conversion of three species of PABA in different pH.

The ground and excited state acidity constant (pK_a and pK_a^*) values for the equilibrium between monocation - neutral and neutral - monoanion of pABA in aqueous, SDS, CTAB media were determined spectrophotometrically and fluorometrically methods. The ground state acidity constant for monocation - neutral equilibrium (pK_{a1}) and neutral - monoanion equilibrium (pK_{a2}) in aqueous solution were calculated as 2.42 and 4.80, in agreement with the literature ($pK_{a1} = 2.39$ and $pK_{a2} = 4.91$) [30].

In the presence of SDS micelles, pK_{a1} was shifted from 2.42 (aqueous solution) to 2.52, whereas in the presence of CTAB, the pK_{a1} was very slightly reduced to 2.40 from 2.42 when compared to the aqueous medium. Another equilibrium neutral - monoanion value was reduced in SDS and that was increased in CTAB micelles. The equilibrium shift was consistent with pABA being located in the charged micelles and electrostatic effects on the surface of micelles may be related to the observed differences in pK_a values. The charge

distribution in the surface of micelles originates an electric potential that spreads onto the environment, affecting the proton distribution around the micelles.

The positive charge of monocation of pABA and negative charge of SDS in interfacial layer and the negative charge of monoanion of pABA and positive charge of CTAB are strongly attracted due to electrostatic attraction between opposite charges. However, pK_a^* value calculated for neutral – monoanion equilibrium was not accurate as the fluorescence band maximum of the monoanion species could not be calculated precisely. The acidity constant for this equilibrium at the excited state pK_a^* has also been calculated using Förster cycle as mentioned above.

3.2. Effect of Micelles

In order to demonstrate the effect of acidic and neutral micellar environments on the photophysics of pABA in the

presence of anionic surfactant SDS, cationic surfactant CTAB and non-ionic surfactant TW80 with respect to bulk water have been done at two pHs (3 and 7) of the solution. Absorption and fluorescence spectra of pABA in an aqueous solution with varying concentrations of SDS surfactants at two pHs have been recorded keeping the concentration of pABA fixed in each case. The concentrations of SDS, CTAB and TW80 taken into account are pre-micellar, micellar and post-micellar concentrations. The absorption and fluorescence spectra of fixed concentrations of pABA (2×10^{-5} M) in SDS (2×10^{-3} M to 5×10^{-2} M), CTAB (4×10^{-4} M to 1×10^{-2} M) and TW80 (2×10^{-5} M to 5×10^{-4} M) surfactants of different concentrations in aqueous media at two pHs were shown in figures 3 and 4. Table 2 describes the absorption and fluorescence maxima and other calculated parameters of pABA in SDS, CTAB and TW 80.

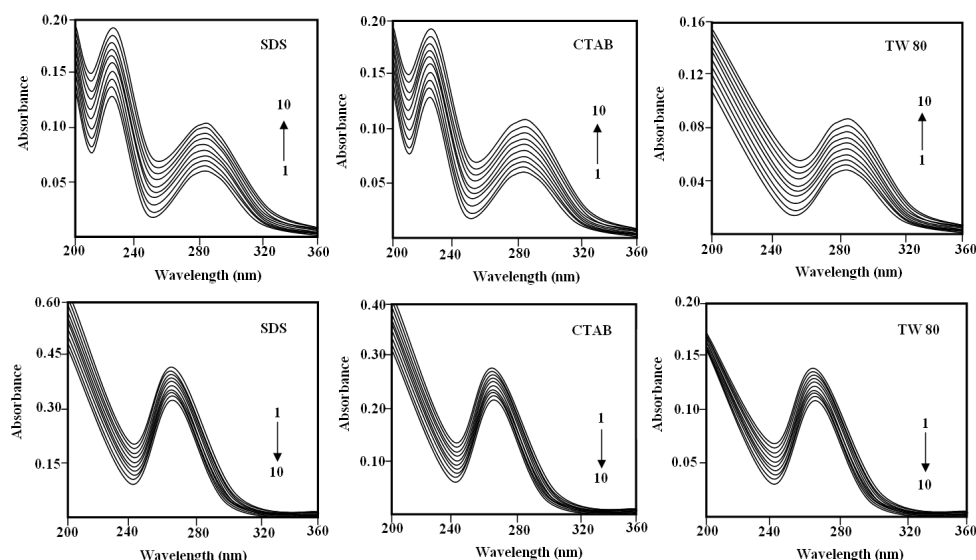


Figure 3. Absorption spectra of pABA in different SDS, CTAB and TW 80 concentrations (mol dm^{-3}) at pH 3.0 and pH 7.0.

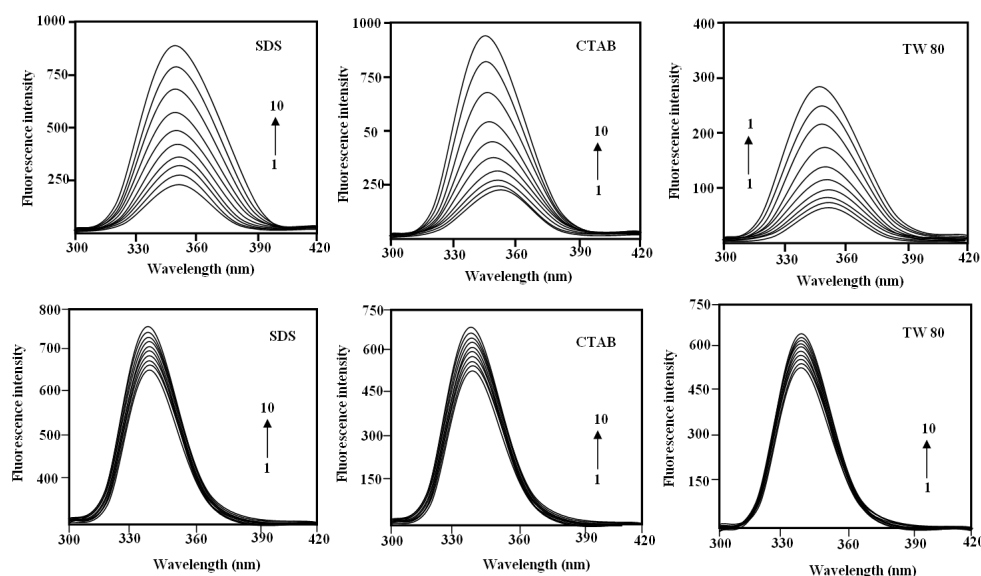
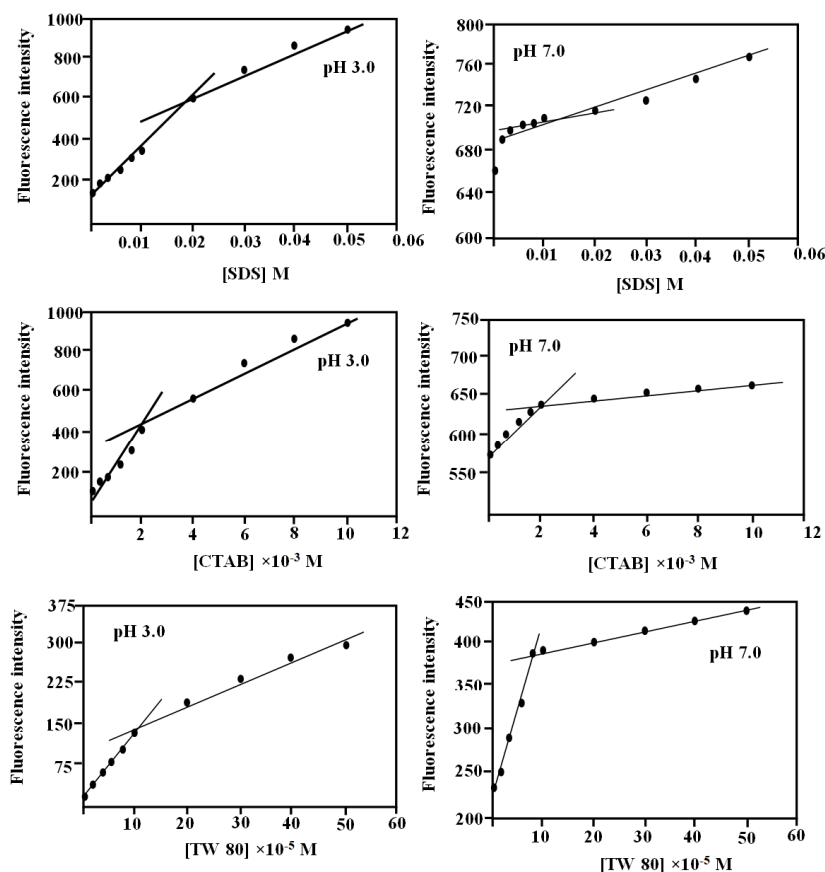


Figure 4. Fluorescence spectra of 4ABA in different SDS, CTAB and TW 80 concentrations (mol dm^{-3}) at pH 3.0 and pH 7.0.

Table 2. Absorption, fluorescence maxima, CMC, binding constant and free energy of pABA in SDS, CTAB and TW 80 at two pHs.

S.No.	Medium	λ_{max}	$\log \epsilon$	λ_{flu}	CMC	Binding Constant	ΔG (-ve) KJ/mol
1	Water (pH 3.0)	280	3.81	349			
2	Water (pH 7.0)	224	3.97	338			
3	SDS (pH 3.0)	282	3.48	348	16×10^{-3}	80	-11.03
4	SDS (pH 7.0)	226	4.00	339	10×10^{-3}	37	-9.09
5	CTAB (pH 3.0)	287	4.00	343	1.8×10^{-3}	485	-15.57
6	CTAB (pH 7.0)	226	3.96	337	1.1×10^{-3}	320	-14.54
7	TW 80 (pH 3.0)	267	4.04	337	13×10^{-5}	7820	-22.57
8	TW 80 (pH 7.0)	289	3.71	346	9×10^{-5}	5630	-21.77

**Figure 5.** Plot of fluorescence intensity versus concentration of SDS, CTAB and TW 80.

On addition of the surfactants to the aqueous solution of pABA at pH 3 leads to a red shift (λ_{abs} – 280 nm to 289 nm with respect to micelles) in the absorption maximum whereas the absorption maximum has no significant shift at pH 7 in all the micelles. The molar extinction coefficient of the longer wavelength absorption band was increased with increasing concentration of all micelles. At pH 7, the molar extinction coefficient was decreased with increasing concentration of all micelles. These results in absorption spectrum and absorbance reveal to change the microenvironment of neutral and monoanion species of pABA.

Figure 4 depict the fluorescence spectra of pABA in aqueous solution of SDS, CTAB and TW 80 as a function of surfactant concentrations. Addition of surfactants to an

aqueous solution of pABA at both pHs resulted in the variety of fluorescence signals. At pH 3 gradual additions of surfactants (SDS, CTAB and TW 80) is associated with a slight blue shift of the emission maximum along with an enhancement of the emission intensity. The monoanion fluorescence maximum of pABA not much affected with the addition of the surfactants. It was clear that the fluorescence enhancement in acidic media was stronger than that in neutral media. The above observations reflect the micro environments around the fluorophore in the micellar solutions being quite different from those in the bulk aqueous phase at two pHs. A blue shift and enhanced emission intensity in the neutral emission spectrum within the micellar solutions further suggests that the polarity of the micellar environments is less than the polarity of the bulk water [31, 32].

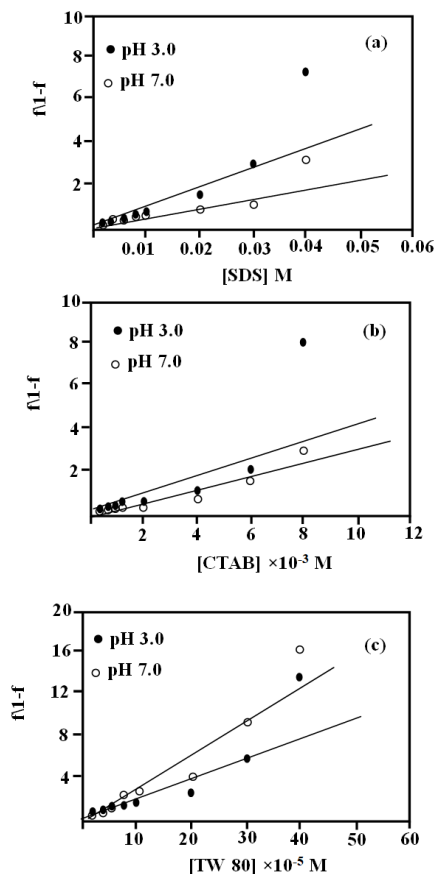


Figure 6. Plot of $f/(1-f)$ against surfactant concentration (a) SDS, (b) CTAB and (c) TW 80.

3.3. Critical Micelle Concentration

The changes in fluorescence maximum and intensity with the addition of surfactants can be attributed to the passage of pABA molecule from a highly polar aqueous medium to a relatively nonpolar micellar environment. At lower surfactant concentrations the change in fluorescence response was not high. However, after a certain micellar concentration, fluorescence intensity shows a marked change. These sharp break points are conventionally assigned to critical micelle concentration. Typical plots of fluorescence intensity variation with surfactant concentration are shown in Figure 5 and the critical micellar concentrations obtained from the inflexion points for the micelles are compiled in Table 2. Generally, the CMC value was decreased with increase in pH. In the acidic medium, the CMC value was higher in all the micelles when compared to the neutral solution.

3.4. pABA–Micelle Binding

The binding constant (K_s) to all the micelles have been determined using the Hirose – Sepulveda equation [33].

$$\frac{f}{1-f} = K_s [D]_t - K_s CMC \quad (3)$$

where $[D]_t$ is the total surfactant concentration and 'f' is the fraction of the pABA bound to micelle.

$$f = \frac{I - I_w}{I_m - I_w} \quad (4)$$

where I , I_m , and I_w are the absorption or fluorescence intensities at intermediate micellar concentration, at complete micellization and in the absence of micelles, respectively. K is being the binding constant. The values of 'f' used vary between 0.2 to 0.8 in order to have the minimized error. A plot of $f/(1-f)$ versus $[D]_t$ is a straight line (Figure 6). The binding constant values have been determined from the slopes of the individual plots.

The thermodynamic parameter ΔG which is an indicator of a tendency of the binding of pABA to micelles, was calculated using the following equation:

$$\Delta G = -RT \ln K \quad (5)$$

The interactions of pABA with micelles are exothermic. As seen in Table 2, the standard free energy change values for pABA in TW 80 are bigger than in CTAB and SDS. Therefore, pABA interacts with non-ionic micelles more easily and stronger than with cationic and anionic micelles in both pHs.

The photophysical characteristics of *p*-aminobenzoic acid have been well studied in various solvents and buffer solutions [27]. The solvent study revealed that ICT emission is not present in pABA. The absorption and emission spectrum in the aqueous solution at pH 7 is largely blue shifted than the other solvents. Acidic pH did not affect the appearance of the spectrum except for a red shift. This effect of the pH on the absorption and emission spectrum indicates that the carboxyl group was ionized at pH 7.

The effect of SDS, CTAB and TW 80 on the fluorescence spectra of pABA more sensitive to the corresponding effect of the absorption spectra. With an increasing the micelles concentration, the fluorescence intensities of pABAs increased in all the micelles at both pHs. Therefore, pABA tend to move towards micellar environment. In the absence and presence of micelles, a single emission was observed at both pHs. In pH 3, blue shift emission maximum was observed in all the micelles, while in pH 7 there is no significant shift noticed with an increasing the micelle concentration. The molecular species of pABA showing the remarkable rise in fluorescence intensity with all the surfactants. Figure 7 shows the probable location of neutral and monoanion species of pABA in SDS and CTAB. In micelles, the blue shifted emission at pH 3 suggests that the amino group is present in the non-polar environment of micelles. These observations indicate that all the micelles provide pABA with less polar environments than water. Thus, the blue shifted emission should be the normal emission originated from the initially excited state of the neutral species. At pH 7 there is no significant shift emission maxima along with a small enhancement in the micellar medium clearly established that the anionic species of pABA may be present in the aqueous medium.

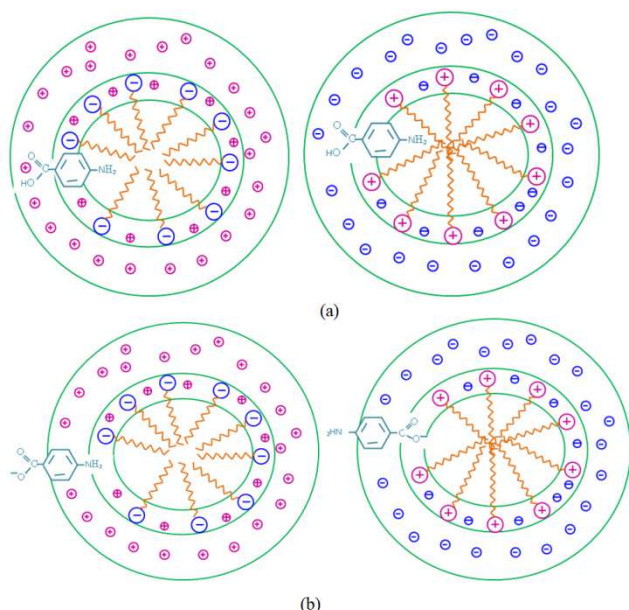


Figure 7. The probable location of neutral and monoanion of pABA (a) neutral and (b) monoanion in SDS and CTAB.

The trend observed in the spectral characteristics of the monoanion was varied to that for the neutral pABA. This is expected because the monoanion will be present in the interfacial region and enough water molecules will be present at the interface to solvate them. From the above discussion and the data of Table 2, it can be qualitatively concluded that pABA is transferred from a highly polar and protic phase to a less polar and protic site in the micellar phase. The strength of binding interaction favourable for neutral species in all the micelles indicates that the micelles provide a hydrophobic environment to the probe. This result about binding strength and hydrophobic environment gives more interaction for neutral comparing to anionic species. In case of SDS, the binding constant of monoanion species is lower than its neutral molecule because electrostatic repulsion between the anionic sulphate groups and the anionic species of carboxylic acid unfavorable the binding process. Electrostatic interactions cause generally a red shift of absorption and emission as the polarity of the solvent increases [34].

In SDS and CTAB micelles both the hydrophobic and electrostatic interaction comes into play on the pABA whereas in TW 80 only the hydrophobic force was present due to the absence of columbic interaction. At pH 3 the blue shifted emission maximum is responsible for hydrophobic interaction between pABA and micelles. Therefore the hydrophobic interaction is predominant over the electrostatic interaction. The enhancement of the neutral emission intensity in SDS and CTAB is much higher than those observed in TW 80. In the absence of electrostatic interaction, pABA would go to the core of the micelles. At pH 7 the anion emission intensity of pABA is slightly increased with increasing concentration of micelles. Therefore the anion species of pABA will be located in the aqueous medium. The electrostatic field in the ionic micelles would restrict pABA to go to the micellar region. The neutral

species of pABA is greater binding than anionic species of pABA. The interaction of organic molecules in micelles was involved by the nature of the force and location of the probe. This one clearly explains with the support from the calculation of binding constant for all micelles in the presence of probe. This parameter in this medium is an important parameter based on the fluorescence data.

The amino group of neutral form of pABA is located in the interior of micellar and the carboxylic acid group is present at the micelle-water interface in both the micelles. The anion form is present in the micelle-water interface. The red shifted absorption in SDS and CTAB can be due to the H-bonding effect of the pABA in micellar environments. The hydrogen bonding can occur between the lone pair electrons on the oxygen atom of the solvent molecule with the hydrogen atom of the carboxylic acid group of pABA. The penetration of the pABA and its location in micelles depends on the nature of the force and polarity variation with different layers in SDS and CTAB micelles. Another factor for the interaction between pABA and micelles, the flexibility of aliphatic chain determines the movement of pABA easier towards into the inside of micellar environment. This is more easily to make in CTAB micelles compared to SDS micelles.

3.5. Polarity of the Micellar Environments

Quantitatively, the observation of a high value of binding constant for neutral pABA was completely micellized upto a high concentration of micelles. The spectral characteristics of pABA in surfactants are useful for understanding the nature and polarity of the binding sites. In order to estimate the nature of the average binding site in the cationic, anionic and non-ionic micelles, correlation of spectral shifts with different polarity parameters in homogeneous environments was carried. The polarity scales, i.e. Stokes shift versus $E_T(30)$ polarity parameters [35] have been used to determine the polarity at the binding site of the micelles. It is shown in Figure 8 that the plot of stokes shift versus $E_T(30)$ shows excellent linear variation. Substitution of corresponding values for SDS, CTAB and TW 80 allowed us to determine polarity values corresponding to solvent polarity parameter $E_T(30)$ of 58.5, 47.5 and 48.5 respectively. These values are well within the range of some literature [36].

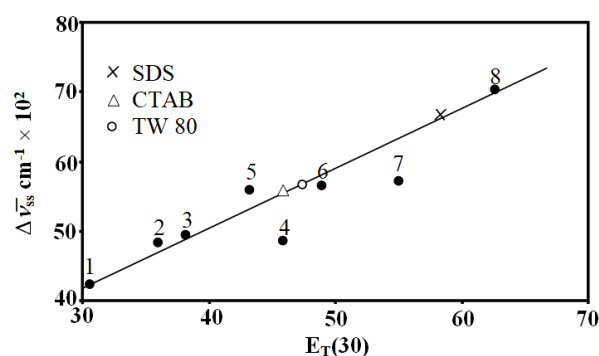


Figure 8. Plot of Stokes shifts (cm^{-1}) of pABA versus $E_T(30)$: 1. cyclohexane, 2. dioxane, 3. ethyl acetate, 4. acetonitrile, 5. *t*-butyl alcohol, 6. 2-propanol, 7. methanol, 8. water.

4. Conclusion

The prototropic reactions of pABA was studied in micellar environments – 0.05 M SDS and 0.01 M CTAB with pH range from 1 to 14. The monocation – neutral and neutral – monoanion equilibrium constant values were shifted in micellar environments compared to aqueous medium. With increasing of SDS, CTAB and TW 80, the absorption and emission data was considerably changed at two pHs due to the changing microenvironment of neutral and monoanion species of pABA. Binding constant and solvent polarity parameter ET(30) was calculated from the emission data. Finally the nature of the force and the probable location of neutral and monoanion species of pABA was predicted in SDS, CTAB and TW 80 micellar environments.

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