

# Excited state intramolecular proton transfer in 2-(2'-aminophenyl) benzimidazole in micelles

Swadeshmukul Santra, Sneh K. Dogra \*

*Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India*

Received 24 November 1997; received in revised form 9 March 1998; accepted 7 April 1998

## Abstract

The excited state intramolecular proton transfer in 2-(2'-aminophenyl) benzimidazole (2-APBI) has been studied using absorption, fluorescence excitation spectra, steady state, and time resolved emission spectroscopy in anionic (sodium dodecyl sulphate, SDS), cationic (cetyltrimethylammonium bromide, CTAB) and non-ionic (Triton X-100, TX-100 and Tween-80) micelles. The spectral characteristics of the parent compound in these micelles are compared with those observed in different solvents to see the effect of these heterogeneous environments on the ground and excited singlet state spectral characteristics of 2-APBI. Observation of the tautomer emission has suggested that 2-APBI has been solubilized in these micelles. Double exponential decay of the normal emission in ionic micelles suggests the presence of rotamers I and IV, whereas the single exponential decay of the normal emission in TX-100 and Tween-80 suggests the existence of rotamer I and IV', respectively in these micelles. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* 2-APBI; Micelles; Normal emission

## 1. Introduction

It is well known that the compounds showing the excited state intramolecular proton transfer (ESIPT) have been the subject of active research [1–6] due to its widespread applications as sources of tunable dye laser [7–13], as materials for protecting against UV radiation damage [14,15] and as photochromic materials [16]. Recently [17–25], molecules undergoing intra- and intermolecular proton transfer reactions have been used as probe molecules to study the characteristics of the organized assemblies [26,27] like micelles, reverse micelles, cyclodextrins, etc. The reason being that molecules undergoing ESIPT exhibits dual fluorescence, one a normal Stokes shifted fluorescence band bearing a mirror image symmetry to the absorption spectrum and second a large Stokes shifted fluorescence band which originates from a tautomer formed in the excited state. The results further showed that the characteristics of both the fluorescence bands are function of polarity and hydrogen bond forming capacity of the solvents, temperature and the concentration of different conformers present in the ground state.

Recently we [28,29] and Sarkar et. al. [23] have employed 2-(2'-hydroxyphenyl)benzimidazole (2-HPBI), showing ESIPT behaviour, as a probe molecule to study the

characteristics of SDS, CTAB, TX-100, Tweens and Brij's under neutral, acidic and basic conditions. The fluorescence quantum yield ( $\phi_f$ ) of the normal band decreases, whereas that of the tautomer band increases when the concentration of the surfactant is increased. The lifetime of the normal emission nearly remains same below and above the critical micelle concentration (cmc) of the micelles, but the lifetime of the tautomer band increases sharply after cmc. The band maxima of the tautomer band, ground state equilibrium constants of the monocation–neutral and the neutral–monoanion equilibria have been used to determine the effective dielectric constants at the site of the micelles where these processes are occurring.

In the present study, we have used 2-(2'-aminophenyl)benzimidazole (2-APBI) as a probe molecule, also undergoing ESIPT reactions leading to amino-imine phototautomerism and showing dual fluorescence [30,31], to study the properties of SDS, CTAB, TX-100 and Tween-80, as well as, to see whether this molecule can act as a probe or not. The structures of different rotamers and tautomer of 2-APBI are given in Fig. 1. One advantage of 2-APBI is that the tautomer fluorescence is very sensitive to the solvent environment and is nearly absent in water. Further, because of the high  $pK_a$  value of the deprotonation of  $-NH_2$  group and increased basicity of  $-N=$  atom, formation of zwitterion

\* Corresponding author.

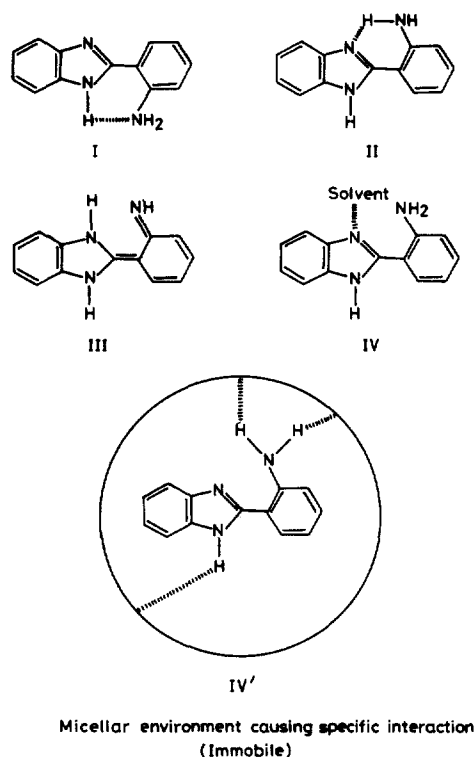


Fig. 1. Different rotamers and tautomer of 2-APBI.

will be inhibited in 2-APBI as observed in 2-HPBI [26–29] under the similar environments. Thus it seems that 2-APBI may prove to be a better probe molecule than 2-HPBI to study the characteristics of the organized assemblies.

## 2. Materials and methods

2-APBI was procured from Aldrich Chemical (UK) and was purified by recrystallization from ethanol [30]. The purity of 2-APBI was checked by getting single spot on TLC, by IR, by NMR and the production of similar fluorescence spectra when excited with different wavelengths of radiation. All the solvents used were of AnalR grade and were further purified as suggested in the literature [32]. SDS was obtained

from Thomas Baker Chemicals and was crystallized twice from 95% ethanol. CTAB was procured from BDH Chemicals. High purity grade of Tween-80 and TX-100 were obtained from Aldrich Chemical and were used as received. AnalR grade HCl, H<sub>2</sub>SO<sub>4</sub> and NaOH (BDH) were used as received. Triply distilled water was used for making aqueous solutions.

Instruments used to measure absorption, fluorescence excitation spectra, fluorescence emission spectra and lifetimes of the excited singlet state, preparations of the solutions, adjustments of their pH and procedure to correct the fluorescence spectra and calculation of the fluorescence quantum yield ( $\phi_f$ ) were the same as described in our recent papers [28,33–35]. Wherever the normal and tautomer fluorescence bands were overlapped, the two were separated by drawing a bell shaped curve to each band and the  $\phi_f$  were determined for each band. pH less than and greater than 7 was adjusted by the addition of small amount of concentrated H<sub>2</sub>SO<sub>4</sub> and NaOH, respectively.

## 3. Results

### 3.1. Absorption spectra

The absorption band maxima ( $\lambda_{\max}^{\text{abs}}$ , nm) and log  $\epsilon_{\max}$  of 2-APBI in SDS (0.05 M, pH 9.0), CTAB (0.01 M, pH 7.0), Tween-80 (0.01 M, pH 5.7), TX-100 (0.01 M, pH 7.0), cyclohexane, acetonitrile and water (pH 7.0) are compiled in Table 1. The absorption spectra are depicted in Fig. 2. pH values in the respective micelles are so selected to ensure the presence of neutral 2-APBI. The long wavelength band maximum of 2-APBI is red shifted by 8 nm in SDS and by 25 nm in Tween-80, whereas the molar extinction coefficient at the band maximum is increased by 35 to 70% when compared with the band maximum in water. The shape of the long wavelength absorption band in all the micelles resemble with each other and in water except that it is broader than that in water. Its shape is different from that noticed in cyclohexane as a solvent in the sense that the shoulder (360 nm) observed in cyclohexane is not observed in micelles.

Table 1

Absorption band maxima ( $\lambda_{\max}^{\text{ab}}$ , nm), log  $\epsilon_{\max}$ , fluorescence band maxima ( $\lambda_{\max}^{\text{f}}$ , nm) and fluorescence quantum yield ( $\phi_f^{\text{N}}$ ,  $\phi_f^{\text{T}}$ ) when excited at 310 and 390 nm

| Solvent                        | $\lambda_{\max}^{\text{ab}}$ | $\lambda = 310 \text{ nm}$  |              | $\lambda = 390 \text{ nm}$  |             |
|--------------------------------|------------------------------|-----------------------------|--------------|-----------------------------|-------------|
|                                |                              | $\lambda_{\max}^{\text{f}}$ | $\phi_f$     | $\lambda_{\max}^{\text{f}}$ | $\phi_f$    |
| Cyclohexane                    | 360 (sh), 346 (3.99)         | 384, 525                    | 0.015, 0.005 |                             |             |
| Acetonitrile                   | 345 (4.15)                   | 400, 520                    | 0.06, 0.008  |                             |             |
| Water (pH 7.0)                 | 325 (3.90)                   | 415, –                      | 0.28, –      | 416, –                      | 0.30, –     |
| SDS (0.05 M) (pH 9.0)          | 333 (4.09)                   | 410, 490                    | 0.14, 0.01   | 412, 495                    | 0.13, 0.01  |
| CTAB (0.01 M) (pH 6.5)         | 345 (4.13)                   | 408, 516                    | 0.20, 0.025  | 408, 520                    | 0.18, 0.022 |
| Tween-80 (0.01 M) (pH 5.70)    | 350 (4.03)                   | 414, 505                    | 0.60, 0.03   | 414, –                      | 0.60, –     |
| Triton X-100 (0.01 M) (pH 7.0) | 345 (4.05)                   | 407, 512                    | 0.33, 0.012  | 408, 512                    | 0.22, 0.014 |

[2-APBI] =  $2 \times 10^{-5}$  M.

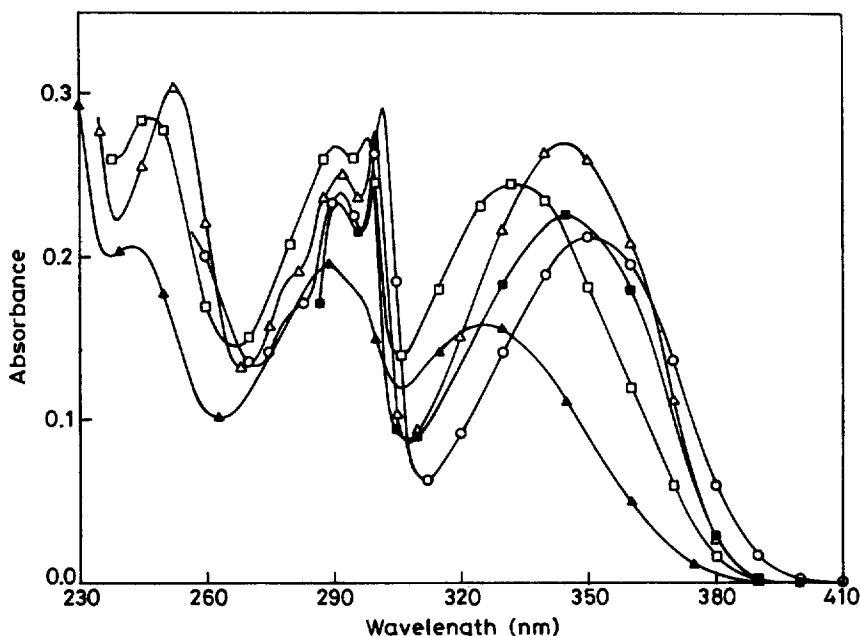


Fig. 2. Absorption spectra of 2-APBI in different environments.  $[2\text{-APBI}] = 2 \times 10^{-5}$  M,  $\square$ - $\square$ - $\square$ , SDS;  $\triangle$ - $\triangle$ - $\triangle$ , CTAB;  $\blacksquare$ - $\blacksquare$ - $\blacksquare$ , Triton X-100;  $\circ$ - $\circ$ - $\circ$ , Tween-80;  $\blacktriangle$ - $\blacktriangle$ - $\blacktriangle$ , Water.

### 3.2. Fluorescence spectra

The fluorescence spectra of 2-APBI have also been recorded under the above conditions and at different excitation wavelengths. The relevant data for only two excitation wavelengths are compiled in Table 1 and the fluorescence spectra are shown in Fig. 3. Unlike the absorption spectra, the emission results are different for different micelles. In Tween-80, the normal fluorescence band is blue shifted by

2–3 nm, whereas its fluorescence quantum yield ( $\phi_f^N$ ) is increased by a factor of two in comparison to that in water. The tautomer band appears at  $\sim 505$  nm with  $\phi_f^T \approx 0.03$ . In SDS, the normal band is blue shifted by 5 nm with decrease in the  $\phi_f^N$  by a factor of two, whereas the tautomer band is observed with  $\phi_f^T$  as 0.01. Lastly in CTAB and TX-100 the normal band is blue shifted by 8–9 nm and the tautomer band maxima are observed at 518 nm and 512 nm, respectively. The  $\phi_f^N$  in both CTAB and Triton X-100 are 0.20 and 0.33,

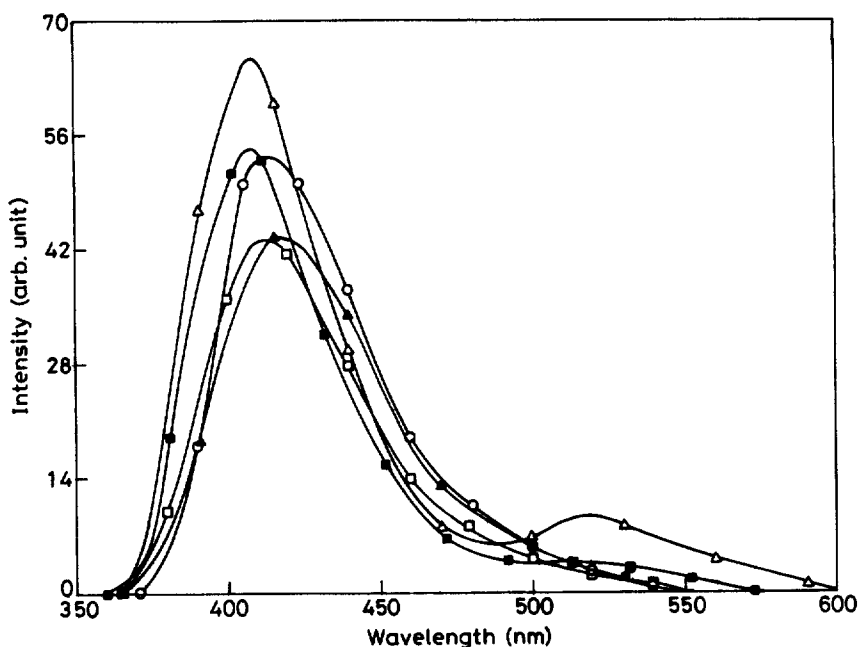


Fig. 3. Fluorescence spectra of 2-APBI in different environments.  $[2\text{-APBI}] = 2 \times 10^{-5}$  M,  $\square$ - $\square$ - $\square$ , SDS;  $\triangle$ - $\triangle$ - $\triangle$ , CTAB;  $\blacksquare$ - $\blacksquare$ - $\blacksquare$ , Triton X-100;  $\circ$ - $\circ$ - $\circ$ , Tween-80;  $\blacktriangle$ - $\blacktriangle$ - $\blacktriangle$ , Water;  $\lambda_{exc} = 310$  nm.

respectively, greater than that in SDS but smaller than that in Tween-80. On the other hand,  $\phi_f^T$  in CTAB is nearly twice as large as observed in SDS and much large in comparison to that in water, whereas  $\phi_f^T$  in TX-100 is nearly similar to that in SDS. Similar to that in water, fluorescence band maxima of both the bands are unaffected when excited with different wavelengths. It may also be pointed out here that the enhancement in  $\phi_f^T$  in these micelles is much larger than it is observed in case of other molecules showing ESIPT behaviour, e.g., 2-HPBI [28] and 10-hydroxybenzo[*h*]quinoline (HBQ) [20].

### 3.3. Fluorescence excitation spectra

The fluorescence excitation spectra recorded at different emission wavelengths in SDS and CTAB resemble with each other and with those recorded in non-polar or less polar solvents, i.e., fluorescence excitation spectra recorded at emission wavelengths less than 440 nm has a maximum at 334 nm with a shoulder at 345 nm, whereas the fluorescence excitation spectra recorded at emission wavelengths greater than 500 nm possess a maximum at 355 nm with a shoulder at 365 nm. The difference between the fluorescence excitation

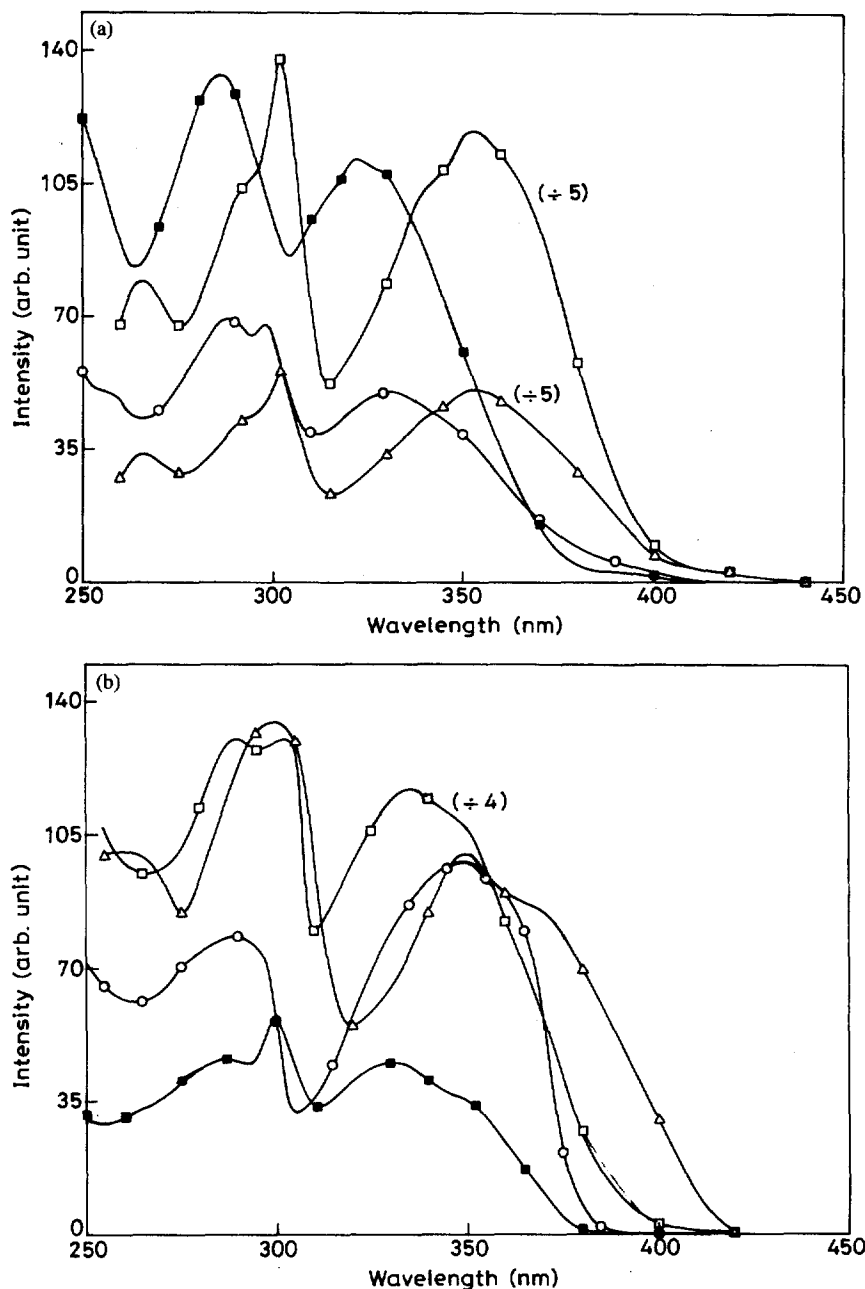


Fig. 4. (a) Fluorescence excitation spectra of 2-APBI in different environments. [2-APBI] =  $2 \times 10^{-5}$  M,  $\square$ - $\square$ - $\square$ , Tween-80 ( $\lambda_{em}$  = 413 nm);  $\triangle$ - $\triangle$ - $\triangle$ , Tween-80 ( $\lambda_{em}$  = 470 nm);  $\blacksquare$ - $\blacksquare$ - $\blacksquare$ , Water ( $\lambda_{em}$  = 390 nm);  $\circ$ - $\circ$ - $\circ$ , Water ( $\lambda_{em}$  = 480 nm). (b) Fluorescence excitation spectra of 2-APBI in different environments. [2-APBI] =  $2 \times 10^{-5}$  M,  $\square$ - $\square$ - $\square$ , SDS ( $\lambda_{em}$  = 400 nm);  $\triangle$ - $\triangle$ - $\triangle$ , SDS ( $\lambda_{em}$  = 520 nm);  $\blacksquare$ - $\blacksquare$ - $\blacksquare$ , Cyclohexane ( $\lambda_{em}$  = 410 nm);  $\circ$ - $\circ$ - $\circ$ , Cyclohexane ( $\lambda_{em}$  = 525 nm).

Table 2  
Excited state lifetimes (ns) recorded under different environments

| Solvent                        | $A_1'$ | $A_1''$ | $\tau_1'$ | $\tau_1''$ | $\tau_2$ |
|--------------------------------|--------|---------|-----------|------------|----------|
| Cyclohexane                    | 70.8   | 29.2    | 1.40      | 3.48       | 0.85     |
| Water (pH 7.0)                 | 78.6   | 21.4    | 0.89      | 5.95       | —        |
| SDS (0.05 M) (pH 9.0)          | 59.6   | 40.4    | 0.59      | 7.40       | —        |
| CTAB (0.01 M) (pH 6.5)         | 82.9   | 17.1    | 1.05      | 5.65       | 1.84     |
| Tween-80 (0.01) (pH 6.8)       | —      | —       | —         | 6.25       | —        |
| Triton X-100 (0.01 M) (pH 7.0) | —      | —       | 1.75      | —          | 2.00     |

[2-APBI] =  $2 \times 10^{-5}$  M,  $\lambda_{exc}$  = 354 nm,  $\lambda_{em}$  (normal) = 410 nm,  $\lambda_{em}$  (tautomer) = 520 nm.

Table 3  
Binding constant ( $K_s$ ) of 2-APBI with different micelles and the cmc of the micelles

| Micelles    | Neutral   |   |
|-------------|-----------|---|
|             | $K_s$     | cmc   |
| SDS         | 330       | $7.4 \times 10^{-3}$                          |
|             | —         | —   |
| CTAB        | 580 (900) | $9.0 \times 10^{-4}$ ( $8.7 \times 10^{-4}$ ) |
| Tween-80    | 1873      | $5.7 \times 10^{-5}$                          |
|             | —         | —   |
| TritonX-100 | 600       | $3.9 \times 10^{-4}$                          |
|             | —         | —   |

Data recorded in parentheses are obtained using fluorescence data.

spectra and the absorption spectra recorded in these micelles is that no shoulder is observed in the long wavelength absorption band of 2-APBI in these micelles. On the other hand the fluorescence excitation spectra in TX-100 and Tween-80 at all the emission wavelengths in the range of 380–520 nm are similar to each other and similar to the absorption spectra. The fluorescence excitation spectra recorded in Tween-80 and water are shown in Fig. 4a and those recorded in SDS and cyclohexane are shown in Fig. 4b.

### 3.4. Excited state lifetimes

The fluorescence decays of the tautomer band in 0.01 M CTAB and TX-100 follow a single exponential with a lifetime of 1.84 ns and 2.00 ns, respectively. In Tween-80 and SDS, the fluorescence intensities were too low to measure the tautomer emission decay. These lifetimes are nearly two times greater than that in cyclohexane. The rate of radiationless decay (obtained from  $k_{nr} = 1/\tau_1 - \tau_1/\phi_n^T$ , where  $\tau_1$  is the lifetime of the excited state of the tautomer,  $\phi_n^T$  is the fluorescence quantum yields of the tautomer band and  $k_{nr}$  is the radiationless decay) in cyclohexane ( $117 \times 10^7 \text{ s}^{-1}$ ) is nearly 2.2 times greater than that in CTAB ( $53 \times 10^7 \text{ s}^{-1}$ ) and 2.4 times greater than that in TX-100 ( $49.4 \times 10^7 \text{ s}^{-1}$ ). As observed for other fluorophore probe molecules [36–39], the solvent induced fluorescence quenching in these micelles is also small. On the other hand normal emission follows double exponential in SDS and CTAB, as observed in all the solvents, whereas in TX-100 and Tween-80, this emission

follows single exponential, depicting a long lived species in Tween-80 (6.25 ns) and short lived species in TX-100 (1.8 ns). The lifetimes of both the components are greater in micelles when compared to those in water, except for the short lived component in SDS. This can also be explained on the same lines as done for the tautomer band in these micelles. The relevant data are compiled in Table 2.

### 3.5. Binding constants and CMC

The binding constants ( $K_s$ ) of 2-APBI and the cmc of all the micelles have been determined using the method of Hirose and Sepulveda [40]. The data are compiled in Table 3. The agreement of the cmc values determined in the present work with the literature is very good [41,42]. The values of  $K_s$  is minimum for SDS and maximum for Tween-80.

## 4. Discussion

The anionic SDS micelles consists of  $C_{12}$  hydrocarbon chain with  $-\text{SO}_4^-$  as a polar head group and in cationic micelles CTAB,  $C_{16}$  is a hydrocarbon chain with trimethylammonium ion as a polar head group. On the other hand, in non-ionic Tween-80 micelles, the hydrocarbon chain is of  $C_{17}$  atoms with highly substituted polyethylene oxide furan ring as a polar part and in TX-100, the hydrocarbon chain is a substituted alkyl group as *p*-(1,1,3,3-tetrabutyl)phenoxy group. In other words, if the core of ionic micelles is polar, it will be due to the seepage of water molecules, which has been substantiated by various studies [43–46]. Though conflicting views are available about the structure of TX-100 [47–49], spherical nature of TX-100 is preferred over the oblate one. If the spherical shape is assumed for TX-100, it is necessary that some of the oxyethylene groups ought to be present in the core of the hydrophobic region of the micelles. This view will allow the outer portion to be offering more channels for the seepage of water. Nothing much is known about the structure of Tween-80, except that hydrocarbon core consists of carbon chain longer than that of TX-100 and will be more hydrophobic [25] than TX-100.

Our earlier study on 2-APBI [30,31] has shown that although rotamer I is slightly more stable (by 0.27 kJ mol<sup>-1</sup>) than rotamer II, both the rotamers can exist in the ground

state in non-polar medium (based on the Maxwell–Boltzmann distribution population ratio of rotamer II to rotamer I being 0.9) and the proportion of rotamer II decreases further with the increase of polarity and hydrogen bonding nature of the solvents. This will lead to the open solvated structure IV. The rotamer I gives rise to double exponential decay. The amplitude of the short lived emission decreases and that of the long lived emission increases with the increase in the polarity and protic nature of the solvents. The rotamer II gives rise to the tautomer emission with a single exponential decay. The  $\phi_n^T / \phi_n^N$  is much smaller even in non-polar solvents, the ratio decreases further with increase in the polarity and hydrogen bonding capacity of the solvents. The decrease in the fluorescence intensity of the tautomer band is due to the competition between the inter- and intramolecular hydrogen bonding (i.e., formation of rotamer IV at the expense of rotamer II) and increase in the rate of non-radiative process. The above results indicate that there are more than one conformers for the normal emission and only one for the tautomer emission. Further shoulder towards the red of the long wavelength absorption band maximum corresponds to the rotamer II.

#### 4.1. Ionic Micelles

All the results observed in the present study do indicate that 2-APBI is transferred from the polar and protic aqueous medium to the less polar and protic micellar environments. The red shifts observed in the long wavelength absorption spectra of 2-APBI in these micelles clearly indicate that the proportion of rotamer II increases in the order of SDS and CTAB. The results are consistent with the earlier findings that the core of CTAB is more hydrophobic than SDS [28,37]. These results are substantiated by: (i) the fluorescence excitation spectra (Fig. 4a and b), (ii) by the appearance of tautomer emission in SDS and CTAB, with  $\phi_n^T$  (CTAB) greater than  $\phi_n^T$  (SDS) and (iii) the tautomer emission following a single exponential decay. The enhancement in the tautomer emission in SDS and CTAB is due to the decrease in the non-radiative rates in the excited state of the tautomer and the increase in the relative proportion of the rotamer II, responsible for tautomer emission over the rotamer I. The former is substantiated by the increase in the lifetime of 2-APBI in CTAB. The relative increase in the amount of II over I in less polar and protic medium is due to: (i) the smaller dipole moment (1.74 D) of II in comparison to I (2.95 D) [31] and, (ii) smaller intermolecular hydrogen bonding interactions towards the core of the micelles. The above explanation means that the relative proportion of rotamer I (responsible for normal emission) will decrease. This will lead to the relative decrease in the emission intensity of the normal band in the non-polar medium when compared to that in aqueous medium. The decrease in the fluorescence quantum yield of normal emission of 2-APBI in SDS and CTAB, in comparison to that in aqueous medium seems to be in line with the above explanation. The larger decrease in

the normal emission in SDS in comparison to that in CTAB may be explained as follows. Lifetime data (Table 2) confirm the presence of at least two rotamers (I and IV) which give rise to normal fluorescence. The similar data in CTAB show that there is a slight decrease in the amplitude as well as the lifetime of the long lived rotamer and the increase in the amplitude as well as the lifetime of the short lived rotamer when compared to the data in water. On the other hand, the amplitude and lifetime of the short lived rotamer in SDS is lowered when compared to CTAB or water. It thus appears that the main reason for the smaller  $\phi_n^N$  in SDS is due to the decrease in the lifetime of the short lived rotamer even though its amplitude is also decreased slightly. This could be because 2-APBI in SDS may be present close to Stern layer and thus ion–dipole interaction may lead to fluorescence quenching, whereas in case of CTAB, 2-APBI seems to be present away from the Stern layer.

#### 4.2. Non-ionic micelles

Although the absorption spectrum of 2-APBI in non-ionic micelles is nearly similar to that in CTAB, the emission characteristics are different in TX-100 and Tween-80. For example, the normal emission follows a single exponential decay. This is substantiated by the fact that  $\chi^2$  observed for a single exponential and a double exponential analysis were similar and the major amplitude in the double exponential analysis is the same as found with only one exponential. Further the fluorescence excitation spectra recorded at different emission wavelengths give rise to only one band, resembling with the absorption spectrum. These results clearly suggest that in non-ionic micelles, the main population of 2-APBI is due to the rotamers (I and IV) which give rise to the normal fluorescence and the rotamer II will be present in small amount. The results of the previous sections have shown that two kinds of rotamers are responsible for the normal emission, i.e., rotamer I and solvated rotamer IV. Further the amplitude of short lived rotamer decreases with the increase in the polarity and hydrogen bonding nature of the solvents. Since in non-polar solvents (cyclohexane) due to poor solvating nature, the proportion of rotamer I will be larger than that of rotamer IV, we propose that short lived species is rotamer I and long lived species is rotamer IV. Qualitatively the proportions of short lived and long lived rotamers in SDS and CTAB are consistent with the above assignment. Based on the above discussion and our results, we propose that rotamer I is the main species in TX-100 and rotamer IV is the main species in Tween-80. This can be explained as follows. Even though there may not be enough seepage of water molecules in the non-ionic micelles, the presence of hydrophilic oxyethylene chains are polar enough to remove the intramolecular hydrogen bonding in the rotamer II and leads to the intermolecular hydrogen bonding between the amino proton and the oxyethylene oxygen. Since the number of oxyethylene groups in Tweens (20) on the average are larger than those present in TX-100 (10), the

proportion of rotamer IV will be larger in Tween-80 than in TX-100. In other words, 2-APBI in Tween-80 is present in the polar region of the micelles and in TX-100, it may be towards the core of the micelles, consistent with the fluorescence band maxima and the lifetime data.

Lastly, the large red shift observed in the absorption spectrum and the fluorescence excitation spectra of 2-APBI in Tween-80 suggests some kind of interaction between the oxyethylene oxygen and the proton of the amino group. This will lead to the formation of solvated 2-APBI rotamer (IV') presumably different from the normal solvated rotamer IV, in the sense that IV' will be immobile as compared to IV. This is supported by the presence of an isosbestic point in the absorption spectrum of 2-APBI in Tween-80, whereas similar kind of isosbestic point is not present in other micelles, very high value of the binding constant and the smallest rate of non-radiative process. Similar kind of observation is also observed when 2-APBI is solubilized in  $\beta$ -cyclodextrin [34]. The long lived species is formed by the intermolecular hydrogen bonding between the secondary hydroxyl oxygen of the upper rim of the  $\beta$ -cyclodextrin and the amino hydrogen atom.

## 5. Conclusions

Following conclusions can be drawn from the above studies. Different kinds of rotamers are present in the ionic micelles. The proportion of rotamer II leading to the tautomer emission is maximum in the most hydrophobic micelle, CTAB. The short lived emission is assigned to rotamer I and long lived emission to the rotamer IV or IV'. In the ionic micelles, the normal emission is mainly due to the rotamer I, whereas in non-ionic micelles rotamer I is the main emitting species in TX-100 and rotamer IV' is the species responsible for the normal emission in Tween-80. The presence of rotamer IV' is substantiated by the isosbestic point in the absorption spectrum of 2-APBI in Tween-80, very high value of binding constant and the presence of long lived species. Thus it can be concluded that 2-APBI can be a better probe than 2-HPBI to explore the characteristics of micelles, specially for non-ionic micelles, because the tautomer emission is completely absent in aqueous medium and the normal emission intensity increases by a factor of two in non-ionic micelles.

## Acknowledgements

The authors are thankful to the Department of Science and Technology, New Delhi for the financial support to the project no. SP/S1/H-39/96.

## References

- [1] M. Kasha, *J. Chem. Soc. Faraday Trans. II* 82 (1986) 2379.
- [2] L.G. Arnaut, S.J. Formosinho, *J. Photochem. Photobiol. A: Chem.* 75 (1993) 1.

- [3] L.G. Arnaut, S.J. Formosinho, *J. Photochem. Photobiol. A: Chem.* 75 (1993) 21.
- [4] S.M. Ormson, R.G. Brown, *Prog. React. Kinet.* 19 (1994) 45.
- [5] D. LeGourrierec, S.M. Ormson, R.G. Brown, *Prog. React. Kinet.* 19 (1994) 211.
- [6] M. Mosquera, M.C.R. Rodriguez, F. Rodriguez-Prieto, *J. Phys. Chem.* 101 (1997) 2766 and references listed therein.
- [7] P.T. Chou, D. McMorrow, T.J. Aartsma, M. Kasha, *J. Phys. Chem.* 88 (1984) 5562.
- [8] A.U. Acuna, F. Amat-Guerri, J. Catalan, A. Costela, J.M. Figuera, J.M. Munoj, *Chem. Phys. Lett.* 132 (1986) 567.
- [9] A. Costela, J.M. Munoj, A. Douhal, J.M. Figuera, A.U. Acuna, *Appl. Phys. B* 49 (1989) 545.
- [10] A.U. Acuna, F. Amat-Guerri, A. Costela, A. Douhal, J.M. Figuera, F. Florido, R. Sastra, *Chem. Phys. Lett.* 187 (1991) 98.
- [11] J. Sepioi, H. Bulska, A. Grabowska, *Chem. Phys.* 104 (1987) 607.
- [12] P.T. Chou, M.L. Martinez, J.H. Clements, *Chem. Phys. Lett.* 204 (1993) 395.
- [13] P.T. Chou, M.L. Martinez, J.H. Clements, *J. Phys. Chem.* 97 (1993) 2618.
- [14] T. Werner, G. Wossner, H.E.A. Kramer, in: S.P. Pappas, F.H. Winslow (Eds.), *Photodegradation and Photostabilization of Coatings*, ACS Symposium Series 15, American Chemical Society, Washington, DC, 1981, p. 1.
- [15] D.B. O'Connor, G.W. Scott, D.R. Coulter, A. Yavroulan, *J. Phys. Chem.* 95 (1991) 10252.
- [16] H. Durr, H. Bouas Laurent (Eds.), *Photochromism, Molecules and Systems*, Elsevier, Amsterdam, 1990.
- [17] J.E. Hansen, E. Pines, G.R. Flemming, *J. Phys. Chem.* 96 (1992) 6904.
- [18] D.F. Eaton, *Tetrahedron* 43 (1987) 1551.
- [19] V. Ramamurthy, D.F. Eaton, *Acc. Chem. Res.* 21 (1988) 300.
- [20] E.L. Roberts, P.T. Chou, T.A. Alexander, R.A. Agbaria, I.M. Werner, *J. Phys. Chem.* 99 (1995) 5431.
- [21] M. Belletete, M. Lachapelle, G. Durocher, *J. Phys. Chem.* 94 (1990) 5337.
- [22] S. Kundu, N. Chattopadhyay, *Chem. Phys. Lett.* 228 (1994) 79.
- [23] N. Sarkar, K. Das, S. Das, A. Dutta, D. Nath, K. Bhattacharyya, *J. Phys. Chem.* 99 (1995) 17711.
- [24] S. Pandey, R.S. Sarpal, S.K. Dogra, *J. Colloid Int. Sci.* 172 (1995) 407.
- [25] S.K. Saha, S. Pandey, S.K. Dogra, *Indian J. Chem.* 34A (1995) 771.
- [26] E.L. Roberts, J.K. Dey, I.M. Werner, *J. Phys. Chem.* 100 (1996) 19681.
- [27] E.L. Roberts, J.K. Dey, I.M. Werner, *J. Phys. Chem. A* 101 (1997) 5296.
- [28] S.K. Das, A. Bansal, S.K. Dogra, *Bull. Chem. Soc. Jpn.* 70 (1997) 307.
- [29] S.K. Das, S.K. Dogra, *J. Chem. Soc. Faraday Trans. I* 94 (1998) 139.
- [30] A.K. Mishra, S.K. Dogra, *J. Photochem.* 31 (1985) 333.
- [31] S. Santra, S.K. Dogra, *Chem. Phys.* 226 (1998) 285.
- [32] J.A. Riddick, W.B. Bunger, in: A. Weisberger (Ed.), *Techniques of Chemistry*, Vol. 8, Organic Solvents, Wiley-Interscience, New York, 1970, pp. 522, 644, 695.
- [33] S. Santra, S.K. Dogra, *Chem. Phys.* 207 (1996) 103.
- [34] S. Santra, S.K. Dogra, *J. Photochem. Photobiol. A: Chem.* 101 (1996) 221.
- [35] J.K. Dey, S.K. Dogra, *J. Phys. Chem.* 98 (1994) 3638.
- [36] W. Weichmann, H. Port, W. Frey, F. Larmer, T. Elsasser, *J. Phys. Chem.* 95 (1991) 1918 and references listed therein.
- [37] R.S. Sarpal, M. Belletete, G. Durocher, *J. Phys. Chem.* 97 (1993) 5007.
- [38] R.S. Sarpal, S.K. Dogra, *Chem. J. Soc. Faraday Trans. I* 88 (1992) 2725.
- [39] R.S. Sarpal, S.K. Dogra, *J. Photochem. Photobiol. A: Chem.* 69 (1993) 329.
- [40] C. Hirose, L. Sepulveda, *J. Phys. Chem.* 85 (1982) 3689.

- [41] P. Mukherjee, K.J. Mysels, *Critical Micelle Concentration of Aqueous Surfactant Systems*, NSRDS-NBS, Washington, DC, 1971, p. 36.
- [42] S.C. Bhattacharyya, H.T. Das, S.P. Moulik, *J. Photochem. Photobiol. A: Chem.* 71 (1993) 257.
- [43] F.M. Menger, B.J. Boyer, *J. Am. Chem. Soc.* 106 (1984) 1109.
- [44] W.D. Turley, H.W. Offen, *J. Phys. Chem.* 88 (1984) 5549.
- [45] M.A. Rogers, M.E. Wheeler, *Chem. Phys. Lett.* 43 (1976) 587.
- [46] R.S. Sarpal, S.K. Dogra, *J. Photochem. Photobiol. A: Chem.* 88 (1995) 147.
- [47] A.A. Ribeiro, E.A. Dennis, *J. Phys. Chem.* 80 (1976) 1746.
- [48] R.P. Cooney, C.G. Barraclough, T.W. Healy, *J. Phys. Chem.* 87 (1983) 1868.
- [49] R.J. Robson, E.A. Dennis, *J. Phys. Chem.* 81 (1977) 1075.