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Effect of pH in the photophysics of 2-hydroxy 1-naphthaldehyde in micellar systems

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Abstract

The effect of variation of pH of different (non-ionic, anionic and cationic) micellar media on the photophysics of 2-hydroxy 1-naphthaldehyde (HNL) as monitored through its anionic band variation has been deliberated. Cationic micelle facilitated anion emission of HNL gets enhanced with increase of pH but the neutral emission remains the same. Addition of acid in cationic micelle causes a decrease in anion band intensity along with a blue shift while no such effect was observed in anionic or non-ionic micelles. Guest HNL is found deeper in non-ionic micelle and also the barrier for formation of anion conformer is increased. A possible drifting of guests from bulk water to micellar interior in anionic and non-ionic micelle is indicated through decreased anion band intensity. Addition of salt in the medium has the same effect on emission as with addition of base. In anionic micelle addition of salt causes to decrease the neutral band vastly and the anion band decreases due to combined effect of increased non-radiative decay rate and greater accessibility of HNL to hydroxyl ions in the interfacial region. Increase in temperature lowers the anion emission band intensity due to decrease in aggregation number, which is substantiated by change of entropy in the temperature range. With addition of base the lifetime of anion band is decreased in anionic and non-ionic micelles due to lower polarity in micelle while a marginal increase is observed in cationic micelle as the micelle itself promotes anion formation.

Keywords: Anionic emission; Micelles; pH variation; Deprotonation

1. Introduction

Photophysical and photochemical study in confined organized environments and at various interfaces play a vital role in many natural and biological processes [1]. Micelles are one of such organized environments. The most important property of such compartmentalized micellar media is that they have the ability to concentrate guest molecules into relatively small effective volumes and then to promote the re-encounter of such molecules [2–4]. This property also makes them a good device for inducing efficient electrostatic interactions between the micelle head groups and the guest molecules as well as strong hydrophobic interactions [5,6] of these molecules with the micelle chains. Many ultrafast processes become significantly affected in different micellar media. Much attention has been given to the mechanism of micelle-catalyzed reactions [2,4] but there are only a limited number of studies of micellar effects on the proton transfer reactions of hydroxy substituted guest molecules in the ground and excited state [7–10].

In general aromatic amines, phenols and aldehydes become more acidic in the excited state [11], while in the ground state the molecule remains in the neutral form. When it is excited it readily deprotonates to produce the anion in the excited state from which the large Stokes-shifted emission originates [12]. Various environmental studies and pH dependent ground and excited state study of 1-naphthol, 2-naphthol and their derivative 2-hydroxy 1-naphthaldehyde (HNL) and benzimidazoles have attracted considerable attention from spectroscopic point of view [13–17]. In a previous study [17], we analyzed the prototropic behavior of HNL in different solvents and found that protic polar solvent greatly accelerates the production of ground state ion through strong

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hydrogen-bonding solvation of this ion. It was also found that the emission properties of HNL are sensitive to the solvents in the form of appearance of a long wavelength band with a concomitant decrease in neutral band as we move from hydrocarbon to hydroxylic solvents. In polar and non-polar hydrocarbon solvents zwitterionic formation of the probe HNL occurs in the excited state due to intramolecular proton transfer but in polar protic and hydroxylic solvents formation of anion occurs more faster than the neutral and zwitterions form of the molecule. The effect is more prominent in presence of water. We observed the effects on the excited state proton transfer process (inter- and intramolecular) of HNL in different ionic and non-ionic micelles [18]. In aqueous solutions when a micellar aggregate is formed and the probe HNL binds to the micellar aggregate, it is partially shielded from bulk water and the absorption and emission properties of the molecule change. The emission bands of HNL get modulated when it binds to the different types of micelles and it is characterized by the properties of micelles.

It was found [17,18] that depending on both the solvent and micellar polarity, acidity and basicity HNL exists in the form of anion or in neutral form. In cationic micelle cetytrimethyl ammonium bromide (CTAB) the anion band intensity increases with the increase of micellar concentration both in ground state and excited state. Thus, we predicted that cationic (CTAB) micelle promotes the formation of anion through an electrostatic interaction while the fast deprotonation of the probe molecule (HNL) is significantly retarded inside anionic (Sodium dodecyl sulfate, SDS) and non-ionic (Tween-20, TW-20) micelles. In SDS, the intensity of anion emission decreases than the neutral emission, whereas in TW-20, both the band intensity uniformly increases. Since the polarity of micelles bring about dramatic effects on UV absorption and fluorescence behavior of anionic form of probe HNL so this anion must be an excellent probe for inspecting the interaction with micelles of inhomogeneous environments. There are many studies on excited state charge transfer process in different organized media [19–21] and also many charge transfer phenomenon have been studied in presence of different kind of additives (acid, base salt, etc.) [5,6], but there have been very little study on the effect of micelles and additives on the ultrafast deprotonation [7,18] of molecules like HNL. In the present paper, we would explore the binding of probe HNL to micelles (cationic, anionic and non-ionic) and the dramatically affected dynamics of anionic species (excited state intermolecular proton transfer) and spectral properties due to the presence of different additives with the help of time resolved and steady state emission and absorption spectroscopy.

2. Experimental details

2-Hydroxy 1-naphthaldehyde purchased from Fluka was purified by recrystallization followed by vacuum sublimation. Sodium dodecyl sulfate, cetyltrimethyl ammonium bromide and Tween 20 were used as received from Fluka or Aldrich Chemicals, USA. The inorganic salt KNO_2 was purchased locally and was of analytical grade. Triethylamine (TEA) and sulfuric acid (H_2SO_4) (E Merck, spectroscopic grade) were used as supplied but only after checking the purity fluorimetrically in the wavelength range of interest. The concentration of HNL used in all experiments was about 10^{-5} M and the emission was corrected for all the optical components. For measuring absorption and emission spectra deionized water (Millipore) was used. For all molecular solutions we took the miceller concentration very much above the 'critical micellar concentration' (CMC) values for all micelles. Before the spectral measurement generally we kept the miceller solution for 5–6 h for better equilibration, even for overnight in some cases. The absorption spectra at 300 K were recorded with a Shimadzu spectrophotometer (Model UV-2401 PC) and the emission spectra were obtained with a Hitachi F-4500 spectrophotometer. The quantum yields were determined by using a secondary standard method with recrystallized β-naphthol in MCH ($\varphi_f = 0.23$) as reference. The following relation was used for calculating the quantum yield,

$$\varphi_2 = \varphi_1 \left[\frac{\alpha_1 A_2 E_1 {n_2}^2}{\alpha_2 A_1 E_2 {n_1}^2}\right]$$

where subscripts 1 and 2 refer to the standard and the unknown molecule, respectively, φ's the fluorescence quantum yields, α's the optical densities at the same excitation wavelength, A's the spectral energy distribution of the emission monochromator and n's are the refractive indices of the respective solvents. For corrected emission spectra, E_1/E_2 is reduced to unity. For lifetime measurement the sample was excited with picosecond diode (IBH Nanoled-07). The emission was detected by a magic angle polarization using Hamamatsu MCP photomultipher (2809U). The time correlated single photon counting (TCSPC) set up consists of an ortec 935 QUAD CFD and a Tennelec TC 863 TAC. The data is collected with a PCA3 card (Oxford) as a multichannel analyzer. The typical FWHM of the system response is about 80 ps.

3. Results and discussions

3.1. Absorption

In an earlier paper [17], it was observed that the protic solvent, water or alcohol containing base (TEA) promotes the formation of FTNL anion in the ground state which shows a band at ~395 nm through the strong intermolecular hydrogen bonding between solute and solvent as evinced by the band at ~410 nm. Similar to hydroxylic solvent, in cationic micellar environment (CTAB) the molecule shows same type of effects. But in anionic (SDS) and non-ionic (TW-20) micellar media the higher wavelength absorption band at ~410 nm totally disappears [18]. In the ground state, the acid and base

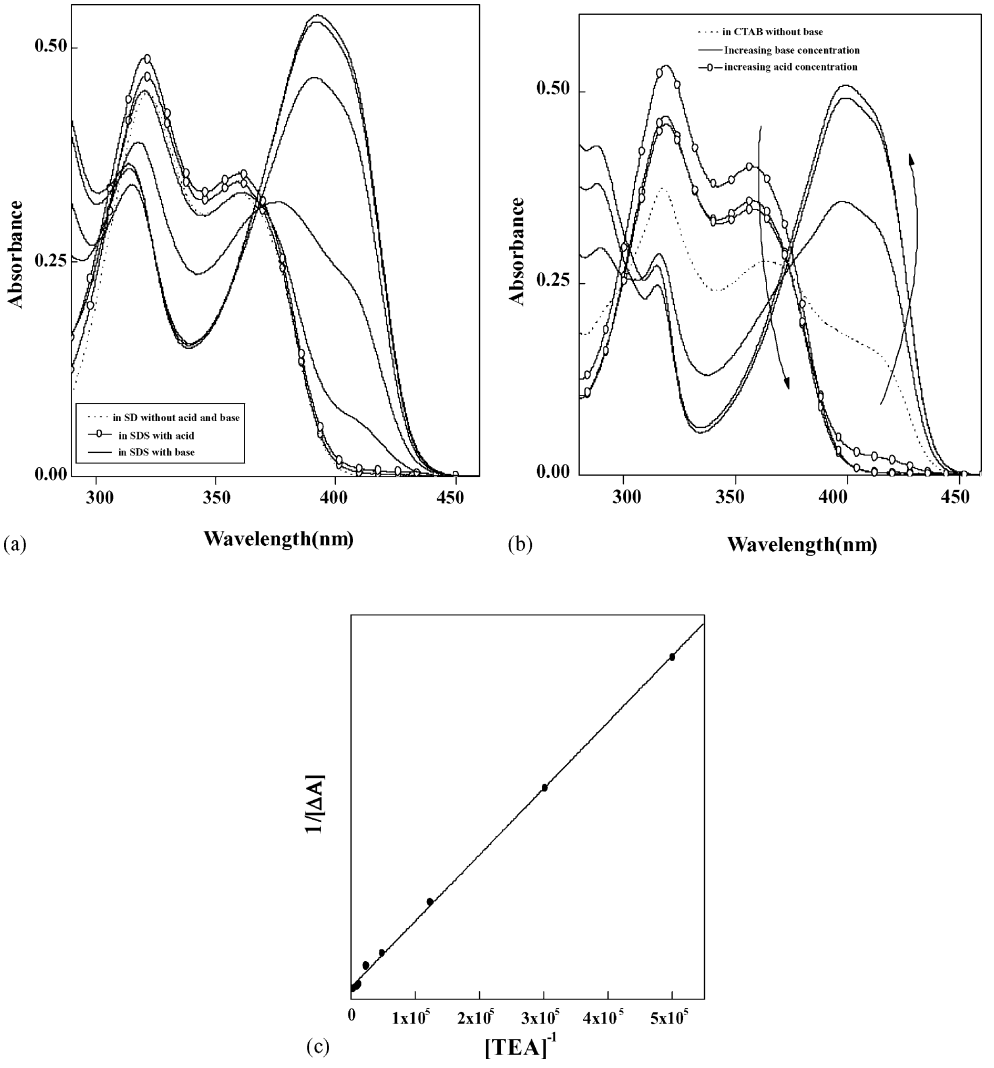


Fig. 1. Electronic absorption spectra of HNL in (a) SDS and in the presence of base (TEA, range of TEA = $0 - 4 \times 10^{-4}$ mol dm^{-3}), in presence of acid (H_2SO_4, range of acid = $0 - 4 \times 10^{-5}$ mol dm^{-3}); (b) in CTAB and in the presence of base (TEA, range of TEA = $0 - 4 \times 10^{-4}$ mol dm^{-3}), in presence of acid (H_2SO_4, range of acid = $0 - 4 \times 10^{-5}$ mol dm^{-3}); (c) Benesi–Hildebrand plot for the formation of HNL (2×10^{-5} mol dm^{-3}) derived anion in aqueous SDS solution in presence of base TEA.

effect in the micellar media of the molecule shows some interesting results. The absorption spectra of UNL at different acid and base concentration have been studied in different micelles. Fig. 1a and b depicts the effect of base and acid concentration on the absorption spectra of HNL in 30 mM SDS and in 8 mM CTAB as a representative plot. All the experimental data are shown in Table 1. In fully micellized state of SDS, the band due to intermolecular hydrogen bonding at

Table 1
Absorption and emission maxima and binding constants (K) in different micelles

Media	Absorption band maxima (nm)			Emission band maxima (nm)		Binding constant
				Normal band	Anionic band	(10^2 M^{-1})
Water	407	360	318	345	455	
CTAB	407	364	318	348	467	230
CTAB + TEA	398	–	315	348	468	
CTAB + H_2SO_4	–	360	319	348	436	
SDS	–	362	321	337	435	255
SDS + TEA	391	–	315	338	451	
SDS + H_2SO_4	–	361	320	338	435	
TW-20	–	358	318	335	447	375

410 nm totally disappears but due to addition of base a new band arises at 412 nm. Increasing base concentration further this band intensifies with a blue shift at ~392 nm and there is a parallel decrease of lower wavelength band at 362 nm with increase of base concentration (Fig. 1a). An isosbestic point could be observed at 369 nm between the bands. Large value of molar extinction co-efficient at higher wavelength side in all the micelles clearly establish that the lowest energy transition in HNL is of $\pi \rightarrow \pi^*$ nature. Blue shift observed in the absorption spectrum establish the formation of anion by deprotonating the –OH (Fig. 1a). In the base (TEA) induced absorption, the spectral changes of the molecule accompanied by the appearance of isosbestic points and the formation of 392 nm band confirm the exclusive formation of the corresponding anion. The changes in the absorbance (ΔA at 410 nm) as a function of TEA concentration ([TEA] $\gg$ 1), where [TEA] refer to the initial concentration of TEA, can be related to Eq. (1) which is frequently utilized as the Benesi–Hildebrand expression [22,23]

$$\Delta A = \frac{K\Delta\varepsilon[\mathrm{HNL}][\mathrm{TEA}]}{1 + K[\mathrm{TEA}]} \quad (1)$$

$$\frac{1}{\Delta A} = \frac{1}{\Delta\varepsilon[\mathrm{HNL}]} + \frac{1}{K\Delta\varepsilon[\mathrm{HNL}][\mathrm{TEA}]}$$

where $\Delta\varepsilon$ is the difference in molar absorption coefficient between the anion and [HNL] at a given wavelength and K is the equilibrium constant of the reaction. A good linear fitting of double reciprocal plot (Fig. 1c) between ΔA^{-1} versus $[\mathrm{TEA}]^{-1}$ confirms that there is equilibrium between normal form and anionic form of the molecule [23]. From the intercept and slope of the plot K is evaluated to be $145.2 \times 10^2\ \mathrm{M}^{-1}$. It is observed that by adding acid in the fully micellized solution no such change occurs but only a slight increase in absorbance occurs in the higher energy bands. Same type of result occurs in the other micellar medium TW-20. Previously we observed that CTAB itself promotes the anion formation [18] in HNL and the 415 nm band intensifies with a blue shift to 399 nm by adding base in CTAB, whereas there is a decrease in intensity of 363 nm band. Addition of acid causes the band at 410 nm to totally disappear while the other two higher energy bands become intensified (Fig. 1b).

No temperature effect could be observed in micellized condition for HNL in the ground state, but addition of inorganic salt such as KNO_2 at a fixed pH affects in the same way as base in both the ionic and non-ionic micelles.

3.2. Emission

It has been found that water molecules are greatly involved in the rate-limiting step for the prototropism of HNL in the excited singlet state and greatly accelerates the photodynamics through the hydrogen-bonding solvation of both the starting HNL and its anion [17]. Earlier [18] we described the solubilization of HNL in different anionic, cationic and non-ionic micelles. In the absence of additives more than 90% of HNL guests are present in undissociated forms within the micellar phase and we may be allowed to expect that the location and orientation of this bichromorphic guest molecule in the micellar host be reflected in the dependence of their fluorescence intensities on the CTAB, SDS and TW-20 concentration [18]. HNL guest has the carbonyl and hydroxyl substitutions and exhibits two bands at 345 and 448 nm when micelles are absent [17]. In the presence of cationic micelle CTAB the fluorescence intensity of anion derived from HNL intensifies with red shift around 20 nm along with an increase in intensity in the normal 345 nm emission band. Above CMC of CTAB the neutral (345 nm) and red shifted anion (470 nm) conformer exhibit 4- and 23-fold increase in emission intensity, respectively. Totally opposite effect is observed in anionic micelle SDS. Above CMC of SDS the intensity of neutral emission increases by nearly 30 times with a blue shift compared to the emission band without SDS and the anion emission intensity falls from 3.7 to 0.37 times compared to that of neutral emission intensity [18]. The ratio of neutral and anionic emission changes from 0.33 to 2.5, from normal condition to fully micellized condition in SDS, whereas in TW-20 above CMC there is a very significant increase in the intensity of the neutral emission, nearly 14 times and along with this the anion emission exhibits 10 times enhancement [18]. Measured CMC values (for SDS, Fig. 2a) in all micelles establish that the fluorophore (HNL) could be employed as a new fluorescent probe for micellar onset in aqueous solution (Table 1). To have an idea of how strongly the emitting species is bound to the non-polar micelles, a quantitative estimate of the binding constants (K) of the emitting species have been calculated from the fluorescence intensity dependent data on surfactant concentration following relation (2) derived by Almgren et al. [24]

$$\frac{I_\alpha + I_0}{I_C - I_0} = 1 + \{K[M]\}^{-1} \quad (2)$$

where I_α, I_0 and I_C are the corresponding emission intensity of HNL under complete micellization, absence of surfactants and in presence of intermediate concentration of surfactants, respectively. [M] is related to the surfactants concentration (S) and aggregation number (N) following the relation (3):

$$[M] = \frac{S - \mathrm{CMC}}{N} \quad (3)$$

The value of N is taken as 60, 62 and 83 for SDS, CTAB and TW-20, respectively [19,25]. Fig. 2b shows a typical plot of $(I_\alpha - I_C)$ versus $(I_C - I_0)/[M]$ for the neutral band of HNL in SDS and from the slope of the fitted straight line we can calculate the binding constants (K) of the state. It has been noted that binding constant is very high in non-ionic micelle ($375 \times 10^2\ \mathrm{M}^{-1}$) compared to the one calculated in the ionic micelles ($230 \times 10^2\ \mathrm{M}^{-1}$ in CTAB, $255 \times 10^2\ \mathrm{M}^{-1}$ in SDS) (Table 1). Various shifts and enhancement or abatement of emission and absorption bands in three micelles surely indicate that the location of the emitting fluorophore may not

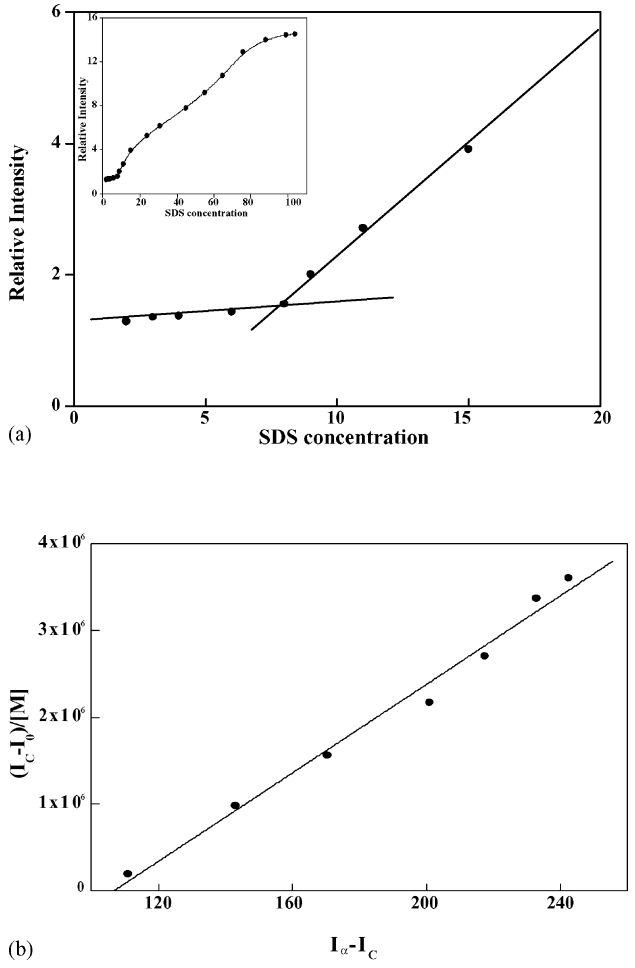
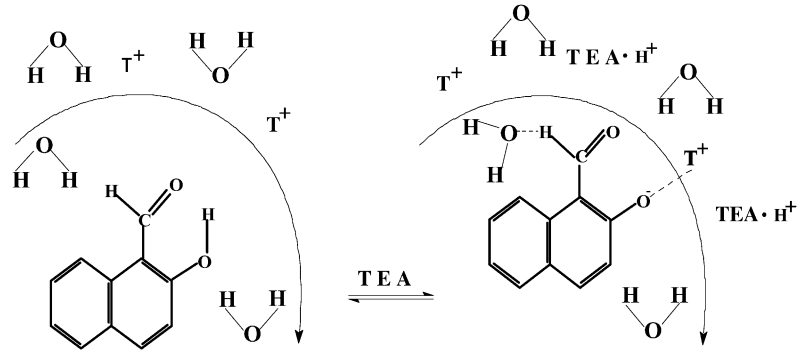


Fig. 2. (a) Variation of relative intensity of emission of HNL in aqueous solution with SDS concentration, inset shows the full range of variation of relative intensity with concentration; (b) plot of $(I_\alpha - I_C)$ vs. $(I_C - I_0)/[M]$ in SDS medium.

be same in all the three micelles. From the ratio of neutral and anionic emission bands in micelle (CTAB) compared to free water we observe 10 times enhancement of the anion emission than the neutral emission. Such enhancement of the anion emission is possibly due to the combined effect of increased non-radiative conversion to anionic form from the neutral one and also the reduction in the non-radiative rates of the anionic conformer to ground state inside the cationic micelle. Compared to CTAB and SDS the Stern layer is very much thin in non-ionic micelle (TW-20). Due to this thinness of the Stern layer the probe HNL remains partially in the GC layer while in TW-20 the probe is almost entirely confined to the much thicker Stern layer. The inherent positive charge of CTAB is expected to cause the lowest proton concentration and highest hydroxyl ion concentration in its immediate vicinity, which is in GC layer, and due to this effect the deprotonation rate, is facilitated in CTAB micelle. In SDS micelle, the local hydroxyl ion concentration around HNL in GC layer is lower than CTAB. This leads to slower rate of deprotonation and consequently the higher intensity of neutral emission. In fully micellized state of SDS the neutral emission band increases roughly 10 times than anionic emission. The relative enhancement and blue shift of neutral band compared to anionic band in TW 20 is due to reduced rate of transition from neutral state to anionic state as energy barrier for formation of anion increases with decrease of solvent polarity. The effective diffusion coefficients of the probe HNL in the micellar media have been calculated from the equation

$$R = \frac{200A}{V}\sqrt{\frac{Dt}{\pi}} \tag{4}$$

where R is the percentage of probe released, A the cross sectional area of the cell, V the volume of mixture, t the time and D is the diffusion coefficient. From the values of the different diffusion coefficients in different micellar media (Table 2), we may conclude that diffusion to anionic state in CTAB is greater than SDS. In all three micelles, the excitation spectra monitored at both the neutral and anion emission are identical to the absorption spectra, which discards the possibility of involvement of any impurity. The above findings establish that the fluorophore (HNL) could be employed as a new fluorescent probe for micellar onset in aqueous solution.



$T^{\pm}C_{19}H_{42}BrN$ (CTAB)

Scheme 1.

Table 2
Fluorescence lifetime, quantum yield, radiative and non-radiative constants and diffusion constants in different media

Media	Lifetime τ_f (ps)	Quantum yield (φ_f)	Radiative constant, K_r (10^8 s^{-1})	Non-radiative constant, K_{nr} (10^9 s^{-1})	Diffusion constant, D (10^{-5} cm^2 s^{-1})
CTAB	174	0.028	1.6	5.58	4.36
CTAB + TEA	182	0.036	1.97	5.29	
SDS	156	0.026	1.66	6.24	1.09
SDS + TEA	95	0.020	2.1	10.3	
TW-20	27×10^2	0.027	0.11	0.35	2.85
TW-20 + TEA	205.4	0.018	0.87	4.78	

In fully micellized state of cationic micelle CTAB, HNL shows two red shifted fluorescence bands. On addition of base we observed a further increase in the anionic emission band intensity/quantum yield with a ∼5 nm red shift (Fig. 3a, change of pH 7 to 12), Table 2. The increase in anion band intensity of HNL with addition of base is due to hydrogen abstraction. Pure CTAB also brings about an increase in anion emission of HNL. Thus, the reason for much increase in HNL derived anion emission intensity in base added fully micellized CTAB is two-fold. The repulsive electrostatic interaction of cationic head group of CTAB and $TEA{\cdot}H^+$ after hydrogen abstraction would effectively decrease the concentration of amine (Scheme 1) in micellar cage. So in Gouy–Chapman layer the –OH ion concentration increases to facilitate the anion band intensity [6] (Fig. 3a). The excitation at isosbestic point (369 nm) in absorption spectra of base added HNL produces same type of emission characteristics in respect of anion band as that with 280 nm excitation. In Fig. 3 we have only presented the emission spectra with excitation at 280 nm only to get the whole region

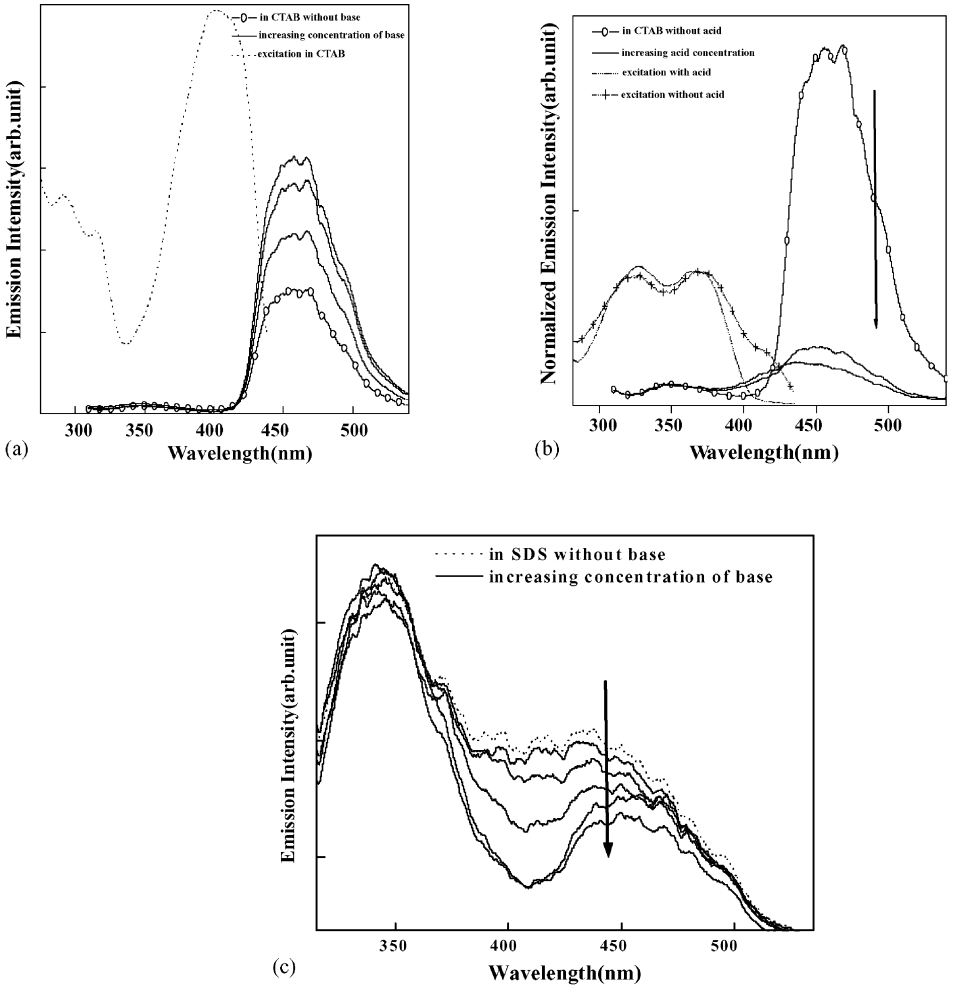


Fig. 3. Fluorescence emission spectra (λ_{exc} = 280 nm) and fluorescence excitation spectra monitoring at 450 nm of HNL (a) in aqueous CTAB solution with presence of base (TEA, pH 7–12); (b) in aqueous CTAB solution with absence of acid and with presence of acid (H_2SO_4, pH 6.5–2); (c) fluorescence emission spectra in aqueous SDS solution with presence of base (TEA) (λ_{exc} = 280 nm).

of spectrum. The calculated non-radiative decay rate for the anionic band tends to decrease in presence of base (Table 2). Now with addition of acid (H_2SO_4) in fully micellized state of CTAB completely opposite picture is found. The anionic band intensity at 455 nm decreases with a blue shift in presence of acid but in the whole process the neutral band position and intensity almost remains the same (Fig. 3b, change of pH 6.5 to 2). The excitation spectrum in Fig. 3a and b corresponding to anionic band in micellized state and in presence of base and acid clearly reflects the absorption spectrum which confirms that the fluorescence band at 455 nm is due to main absorbing species in the ground state, which is intermolecularly hydrogen bonded species. This points that the role of acid is somehow to oppose the anion formation (Fig. 3b). This may be due to the presence of positive ion of acid, the proton concentration is increased and as a result the hydroxyl ion concentration in the immediate vicinity of HNL decreases and that consequently hinders the deprotonation process.

In the case of anionic micelle SDS, opposite picture is observed with base addition. HNL shows that the intensity of neutral band remains almost same while the anion band intensity decreases a little with a 10 nm red shift (Fig. 3c, pH upto 12) on addition of base in fully micellized condition. Quantum yield also decreases in the basic medium compared to the neutral medium. In ground state SDS does not promote the intermolecular hydrogen bonding (band at 410 nm disappears in SDS) but in the presence of base a new band arises at 412 nm due to anion formation. From this type of experimental result we can infer that in SDS the decrease of anion emission is presumably due to the drifting of HNL from the bulk water to the interior of micelle. The decrement of anion emission in the interior of micelle is due to the fact that hydroxyl concentration faces most significant high rate of deprotonation process in presence of TEA in SDS. This effect is clearly explained in later section. Almost same type of result was observed in TW-20 when base is added as observed in the case of SDS. However, we could not observe much spectral change in SDS and TW-20 solution with addition of acid. As the acid does not have any effect in the interior of the micellar media, the unchanged spectral change in SDS and TW-20 points that the guest HNL stays interior part of micelles.

3.2.1. Effect of inorganic salt

With a view to study the effect of modulated electric field in micelle on the proton transfer photophysics and also to get an idea about the position of HNL inside different micelles inorganic salt was added in fully micellized condition. Addition of inorganic salt such as KNO_2 was found to affect same way as the base in earlier section in both the ionic and non-ionic micelles in the ground state. To observe the location of HNL inside the micellar media we have studied the variation of the emission properties of HNL with addition of salt in fully micellized state. We made it sure in control experiment that KNO_2 did not quench the higher wavelength band of HNL in water solution. Addition of salt does not show much effect in

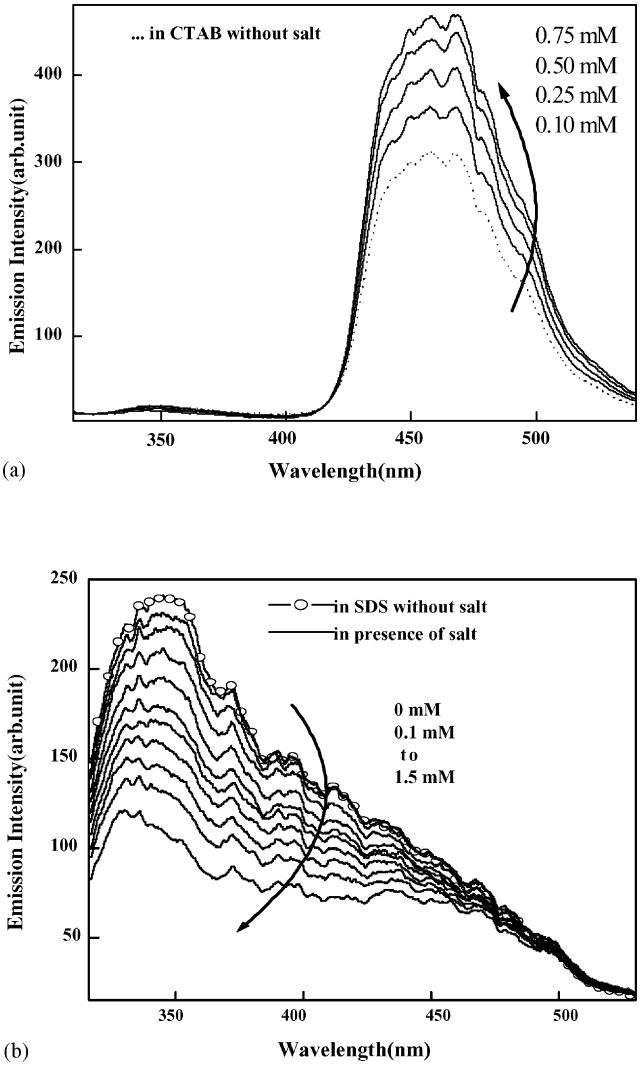


Fig. 4. Variation of emission of HNL in addition of inorganic salt (KNO_2) at a fixed pH ~6.5 (a) in CTAB solution and (b) in SDS solution (λ_{exc} = 280 nm).

TW-20 but distinct change could be observed in ionic micelles [5]. Fig. 4a and b shows the KNO_2 concentration dependent emission spectra of HNL at fully micellized condition in CTAB and SDS. The anion band intensity increases with increase of KNO_2 concentration along with a slight decrease in neutral band intensity at fully micellized condition of HNL in CTAB (Fig. 4a). In SDS again a different effect could be observed. With addition of salt both the neutral and anionic band intensity could be observed to decrease but the rate of decrease of neutral band is larger than anion band (Fig. 4b).

Addition of inorganic salt, which acts mainly in the interfacial region, shows that in TW-20 the emission (neutral and anion) remains unaffected. This suggests that the emitting species is not available in the water–micellar interfacial region.

In cationic micelle the neutral band intensity decreases whereas anion band intensity increases with the addition of inorganic salt (Fig. 4a). Addition of inorganic salt causes a reduction in the thickness of the ionic atmosphere

surrounding the polar head group and as a consequence of this a decreased repulsion between them would ensue [26,27]. This effect is manifested in increase of aggregation number. And thus by addition of salt the electric field around the hydroxyl group gets modified by the counterion binding, thereby facilitate the production of hydroxyl ion concentration. This in turn causes an increase in anion emission and decrease in neutral emission.

The change of emission band intensity due to the addition of inorganic salt in ionic micelle implies that molecule resides near the Gouy–Chapman layer [18]. In SDS due to addition of salt the molecule cannot go to the inside of the core region of micelle and consequently the local hydroxyl concentration around the anionic SDS surfactants increases and does not cause suppression of the deprotonation process, leading to lowering of intensity of neutral emission band (Fig. 4b). The deprotonation effect should lead to corresponding increase in anion band intensity. But possibly due to the increase in non-radiative rate (similar to addition of base in Table 2) with addition of salt the corresponding increase in anion band intensity is not observed.

3.2.2. Temperature effect

The spectral characteristics of HNL for the both bands neutral and anion (formed by deprotonation of hydroxyl group) in fully micellized state for both ionic and non-ionic micelles were recorded at different temperatures and are described in Fig. 5a and b. Two different types of effects were observed in ionic and non-ionic micelles. In cationic and anionic micelles with the increase of temperature from 20 to 60 °C it is observed that the anionic band intensity decreases a lot but the neutral band intensity almost remains the same [26] (Fig. 5a). A slightly different behavior was observed in the case of non-ionic micelle TW-20. In TW-20, the anionic band intensity also decreases with similar increase of temperature but the rate of decrease in anion band intensity is lower than that in the case of ionic micelle (Fig. 5b). From thermodynamics, we know the Gibb's equation as $G = H - TS$, where H is the enthalpy, S the entropy and T is the absolute temperature. Using the above relation in micellar state we get [27]:

$$\Delta G = RT \ln \mathrm{CMC} \tag{5}$$

and

$$S = \left(\frac{\delta G}{\delta T}\right)_V \tag{6}$$

Again we know

$$\Delta H = R\{\delta/\delta(1/T) \ln \mathrm{CMC}\}_P \tag{7}$$

So from Gibb's equation, the entropy change

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

Using Eqs. (5)–(8) we calculated the change in entropy values in the three micelles for two different temperatures. With

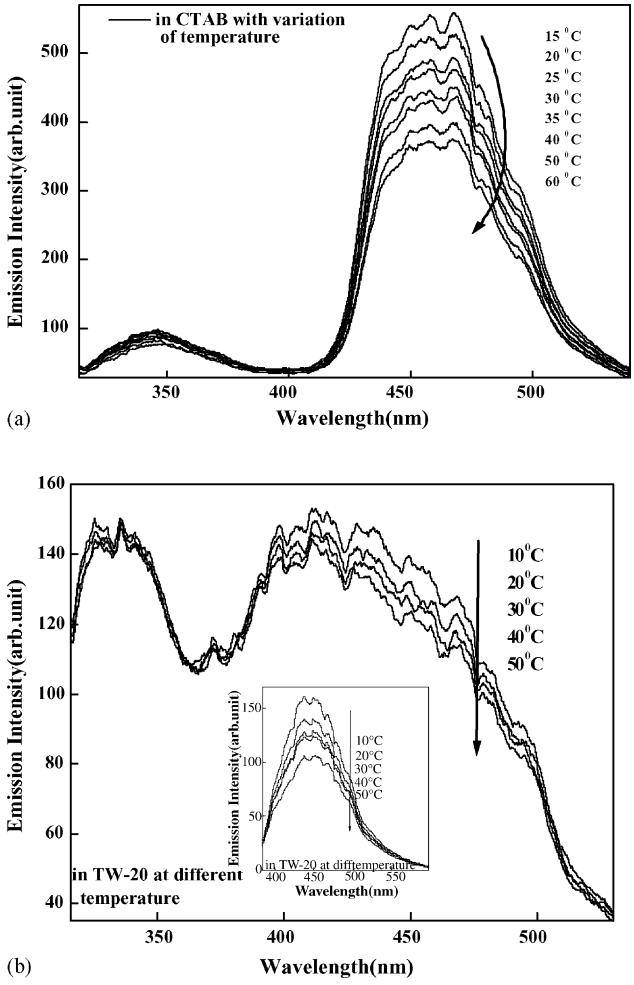


Fig. 5. Fluorescence emission of HNL with variation of temperature (10–60 °C) at a fixed pH ~ 6.5 in (a) CTAB solution and (b) SDS solution (λ_{exc} = 280 nm), inset shows the fluorescence emission of anionic band (λ_{exc} = 380 nm).

increasing the temperatures from 15 to 50 °C we observed that the change in entropy (ΔS) for ionic micelles is larger than change in ΔS for non-ionic micelle.

The above results in both the ionic micelles may be explained as the increase of temperature causing a disruption of the structure of water around the hydrophobic groups that in turn opposes the micellization and consequently the anion emission intensity is diminished [28] (Fig. 5a). In TW-20 with increasing temperature there is an increase of amount of water trapped by the micelle, and thus a decrease in aggregation number. So due to the decrease in rate of disruption of water in TW-20 than ionic micelles the rate of decrease of intensity of anionic band is lower in non-ionic micelle than that in ionic one (Fig. 5b).

3.3. Time resolved studies

As we know that the lower accessibility of probe molecule towards bulk water automatically implies slower deprotonation rate but the actual situation depends on the probe used

in the medium. Many groups described the ESIPT process of different probe molecules in different media [29,30]. Robinson et al. [31] showed that the deprotonation rate monotonically decreases as the alcohol content increases in aqueous solution of the probe 1-naphthol. The reduction of ESIPT in these cases may be due to a less polar and less protic microenvironment than bulk water. Dramatic increase in anion band lifetime (more than 10 times) of HNL in TW-20 compared to that aqueous solution was observed while there is a marginal increase in lifetime of anion band in ionic micelles (Table 2). Time resolved data confirm the steady state emission results in micelles [18].

Lifetime of HNL was measured at different concentrations of each micelle monitoring at 450 nm band and excited at 405 nm. It is very difficult to extract meaningful decay time data in inhomogeneous micellar systems, as the probe molecule HNL may exist in different locations that is, bulk water, micelle–water interface or hydrocarbon core of the micelles [32]. Obviously, the decay of the emission is expected to be multiexponential. To minimize the contribution of free HNL in bulk water all the decays were recorded at a concentration much higher than the 'CMC' of the surfactants when whole probe molecule HNL remains bound to the micelles. Fluorescence decay curves of HNL in 100 mM SDS, 64 mM CTAB and 24 mM TW-20 in aqueous solutions are shown in Fig. 6a–c by exciting the solutions at 405 nm and monitoring the decay at the fluorescence maxima. The decay curves followed a single exponential decay in anionic micelles and biexponential in non-ionic micelle, Table 2. Probably in non-ionic micelle not all the HNL molecules are inside the hydrocarbon core and some contribution of HNL in micelle–water interface makes the decay bi-exponential.

It is seen that in CTAB the lifetime of the decay of the anion emission is 175 ± 10 ps, which is nearly two times than that in alcohol (Fig. 6a). In SDS, it is observed that anionic part decays with lifetime 156 ± 20 ps (Fig. 6b). In neutral TW-20, the lifetime of the decay of HNL anion emission is found to be 2 ± 1 ns (Fig. 6c).

Single exponential decay indicates that the probe fluorophore is present at one site of the micelle and that is completely solubilized. The values of the radiative (K_r) and non-radiative (K_{nr}) decay constants can be calculated from the following relations:

$$K_r = \frac{\varphi_f}{\tau_f}, \quad K_{nr} = \frac{1}{\tau_f} - K_r$$

Values of φ_f, τ_f and decay constants are complied in the Table 2. The increase in the fluorescence quantum yield and lifetime clearly indicates that the rates for the non-radiative processes diminish in the micelles. Addition of base in CTAB makes nearly no change in anionic band lifetime but in SDS and TW-20 the lifetime reduces drastically in presence of base (Table 2; Fig. 6a–c).

For non-ionic micelle very long lifetime is observed whereas, for ionic micelle the lifetime increase is not much

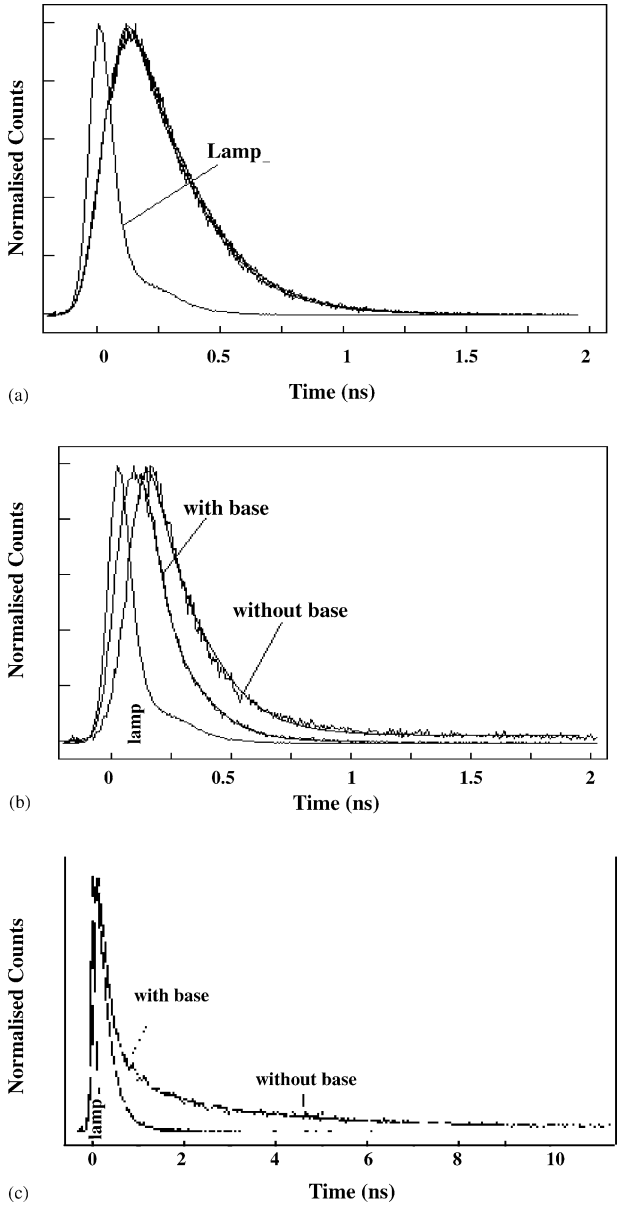


Fig. 6. Fluorescence decay of 2×10^{-5} mol dm^{-3} HNL in (a) 20 M CTAB; (b) 70 M SDS; (c) 10 M TW-20; with $\lambda_{em} = 450$ nm and $\lambda_{ex} = 405$ nm.

compared to that of free molecule HNL [17]. Compared to water the excited state deprotonation rate is intensified generally in all micelles but that is pronounced only in ionic micelles. In presence of base a substantial decrease in the intensity and lifetime of the anion emission is observed in TW-20 (Fig. 6c). This reduction in the deprotonation rate may be ascribed to the lower polarity of the micellar media and the lower accessibility of the HNL molecule encaged in the micelle to the water molecules. Similar dramatic reduction in the rates of other ultrafast processes was observed earlier in many organized media [33,34]. Opposite to this is observed in CTAB, the lifetime of anionic emission band increases marginally in case of fully micellized state of HNL with addition of base (Fig. 6a; Table 2). This is because cationic micelle

CTAB itself promotes the deprotonation process and the presence of base facilitates this promotion also a reduction in the non-radiative rate of the anion inside the micelle in general compared to solution helps to increase the lifetime in CTAB.

4. Conclusion

Based on the above results and discussion our present work demonstrates the probing of anionic (SDS), cationic (CTAB) and non-ionic (TW-20) micelles in presence of different additives with the help of HNL utilizing the environmental sensitivity of its normal and anionic bands. Computed values of binding constants reveal that in non-ionic micelle the binding is strong as probe HNL tries to enter in the core region and in ionic micelles lesser penetration is indicated. The non-radiative decay rate decreases in presence of base in fully micellized state of CTAB, as evinced from intensification and red shift of anionic band. Acid effect only opposes the deprotonation rate in cationic micelle. In anionic (SDS) and non-ionic (TW-20) micelles presence of base causes an increase in non-radiative rate from anionic state while the neutral emission remains almost the same. Addition of salt causes proliferation of hydroxyl ion concentration due to counterion binding in modified electric field around hydroxyl group in cationic micelle as reflected in enhanced anion emission. In SDS addition of salt makes local hydroxyl concentration around the anionic surfactants increase and does not cause any suppression of the deprotonation process, which leads to the lowering of intensity of neutral emission band. But the corresponding increase in anion band intensity in SDS is not observed due to the increase in non-radiative rate. For both the ionic micelles with increase of temperature the anion band intensity decreases with normal band remaining unchanged. The increase of temperature causes a disruption of the structure of water around the hydrophobic groups that in turn opposes the micellization. The rate of decrease of anionic band intensity is lower in non-ionic micelle than that in ionic one is in commensurate with the decrease in the rate of disruption of water in non-ionic micelle than that in ionic micelle. Compared to water in some micelles the rate of excited state deprotonation of HNL is retarded and in some micelles it is enhanced. For TW-20 and SDS in presence of base a large change in lifetime and change in anion intensity are observed. Presence of base augments the deprotonation of HNL already favored in CTAB and the lifetime increases a little due to combined effect of decreased non-radiative rate and increased deprotonation rate.

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References

[1] K.B. Eisenthal, Chem. Rev. 96 (1996) 343.
[2] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975, p. 19.
[3] N.J. Turro, A.L. Buchachenko, V.K. Tarasov, Acc. Chem. Res. 28 (1995) 69.
[4] S. Tascioglu, Tetrahedron 52 (1996) 11113.
[5] S. Panja, P. Chowdhury, S. Chakravorti, Chem. Phys. Lett. 368 (2002) 654.
[6] H. Umeto, K. Abe, C. Kawasaki, T. Igarashi, T. Sakurai, J. Photochem. Photobiol. A 156 (2003) 127.
[7] D. Mandal, S.K. Pal, K. Bhattacharya, J. Phys. Chem. A 102 (1998) 9710.
[8] S.K. Das, S.K. Dogra, J. Colloid Interface Sci. 205 (1998) 443.
[9] D. Zhong, A. Douhal, A.H. Zewail, Proc. Natl. Acad. Sci. U.S.A. 97 (2000) 14056.
[10] B. Cohen, D. Huppert, K.M. Solntsev, Y. Tsfadia, E. Nachliel, M. Gutman, J. Am. Chem. Soc. 124 (2002) 7539.
[11] H. Shizuka, Acc. Chem. Res. 18 (1985) 141.
[12] M. Kasha, J. Chem. Soc. Faraday Trans. II 82 (1986) 2379.
[13] E. Pines, G.R. Fleming, J. Phys. Chem. A 95 (1991) 10448.
[14] R. Krishnan, J. Lee, G.W. Robinshon, J. Phys. Chem. 94 (1990) 6365.
[15] G.W. Robinshon, J. Lee, P.S. Thistlewaite, J. Phys. Chem. 90 (1986) 4224.
[16] P. Chowdhury, S. Panja, A. Chatterjee, P. Bhattacharya, S. Chakravorti, J. Photochem. Photobiol. A 170 (2004) 131.
[17] P. Chowdhury, S. Panja, S. Chakravorti, J. Phys. Chem. A 107 (2003) 83.
[18] P. Chowdhury, S. Chakravorti, Chem. Phys. Lett. 395 (2004) 103.
[19] J. Saroja, Ramachandran, S. Saha, A. Samanta, J. Phys. Chem. A 103 (1999) 2906.
[20] K. Bhattacharya, M. Chowdhury, Chem. Rev. 93 (1993) 507.
[21] Y.B. Jiang, X.J. Wang, M.G. Jin, L.R. Lin, J. Photochem. Photobiol. A 139 (2001) 5.
[22] A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
[23] P. Chowdhury, S. Panja, S. Chakravorti, Spectrochim Acta A 60 (2004) 2295.
[24] M. Almgren, F. Griesser, J.K. Thomas, J. Am. Chem. Soc. 101 (1979) 279.
[25] M.E. Haque, A.R. Das, S.P. Moulick, J. Colloid Interface Sci. 217 (1999) 1, and references cited therein.
[26] D. Attwood, A.T. Florence, Surfactant Systems, Chapman & Hall, 1983, p. 92.
[27] D. Attwood, A.T. Florence, Surfactant Systems, Chapman & Hall, 1983, p. 101.
[28] K. Kumiyama, H. Inoue, T. Nakagawa, Kolloid-Z-U-Z Polymere 183 (1962) 68.
[29] E. Pines, G.R. Fleming, J. Phys. Chem. 95 (1991) 10448.
[30] G.W. Robinson, P.S. Thistlewaite, J. Lee, J. Phys. Chem. 90 (1986) 4224.
[31] J. Lee, G.W. Robinson, S.P. Webb, L.A. Philips, J.H. Clark, J. Am. Chem. Soc. 108 (1986) 6538.
[32] W.R. Ware, in: V. Ramamurthy (Ed.), Photochemistry in Organized and Constrained Media, VCH Publishers, New York, 1991, p. 563.
[33] R.E. Rites, D.M. Willard, N.J. Levinger, J. Phys. Chem. B 102 (1998) 2705.
[34] A. Douhal, T. Fiebig, M. Chachisvilis, A.H. Zewail, J. Phys. Chem. A 102 (1998) 1657.