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Excited State Proton Transfer of 1-Naphthol in a Hydroxypropylcellulose/Sodium Dodecyl Sulfate System

Partha Dutta, Arnab Halder, Saptarshi Mukherjee, Pratik Sen, Sobhan Sen, and Kankan Bhattacharyya*

Physical Chemistry Department, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

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Excited state proton transfer (ESPT) of 1-naphthol has been studied in a polymer (hydroxypropylcellulose, HPC)–surfactant (sodium dodecyl sulfate, SDS) aggregate. The ESPT process of 1-naphthol is drastically retarded in the HPC–SDS aggregate above the critical association concentration (cac). The cac of SDS for HPC is found to be 2 mM, which is much smaller than its cmc (8 mM). The time-resolved emission data indicate that at a low SDS concentration (<8 mM) the decay of the neutral emission and the rise and decay of the anion emission are very different from those in SDS micelles. Above the cmc of SDS, 1-naphthol molecules are distributed between the HPC–SDS aggregate and free SDS micelles.

1. Introduction

Dynamics of polar reactions in a liquid is governed by solvation. One of the simplest examples of a polar reaction is dissociation of an acid, $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$. In a nonpolar medium, this process is endothermic and is unfavorable because of a high energy barrier. However, in a polar solvent, dissociation of an acid becomes favorable because of the solvation of the products (proton and the anion) and the transition state. Recently, it has been demonstrated that the solvation dynamics of the water molecules becomes dramatically slow in many organized assemblies.¹ It is obviously of interest to find out how the slow solvation dynamics affects the proton-transfer process in an organized assembly.

Acidity and basicity of many molecules change on electronic excitation.² For instance, 1-naphthol is a weak base in the ground state ($\text{p}K_{\text{a}} = 9.5$). But in the first excited electronic state, the $\text{p}K_{\text{a}}^*$ of 1-naphthol in aqueous solution is about 0.5, that is, smaller than that in the ground state by 9 units. Hence, 1-naphthol is a strong acid in the excited state.^{3–6} Such a molecule which becomes an acid on excitation by a photon is called a photoacid. The acid–base behavior of 1-naphthol has been studied in liquid solutions^{2,3} and in supersonic jets.^{4–8} It has been demonstrated that the excited-state proton transfer (ESPT) of 1-naphthol requires adequate solvation of the polar transition state and the products (H^+ and A^-). It is

observed that, in a polar cluster of 1-naphthol with water in a supersonic jet, at least 30 water molecules are necessary for the ESPT process to occur.⁵ Methanol is a better proton acceptor than water. Thus, the ESPT process of 1-naphthol should be more facile in methanol. However, the ESPT process of 1-naphthol does not occur either in a cluster with methanol in a supersonic jet or in a solution in liquid methanol.⁶ It is proposed that methanol cannot solvate 1-naphthol sufficiently because of steric hindrance, that is, because of the difficulty in approaching the 1-naphthol molecule.⁶

In an organized assembly, for example, in the nanocavity of cyclodextrin and the surfactant aggregates (micelles and lipids), the steric hindrance for the water molecules to solvate a neutral molecule or ion is much more than that in bulk water. As a result of the steric hindrance and other local interactions, the movement of the water molecule in these organized assemblies is highly restricted.¹ The inadequate solvation of the 1-naphthol molecule and the ions (H^+ and A^-) markedly slows down the ESPT process in cyclodextrin,⁹ micelle,^{10a,11} and lipids¹⁰ by 1–2 orders of magnitude compared to that in bulk water. Il'ichev et al.^{10a} used nanosecond flash lamps to study micelles and vesicles using 1-naphthol as a probe. They detected two sites of solubilization of the probe with widely different ESPT reactivity. In a micelle, the rise time of the anion and the fastest component of the decay of the neutral form are in the sub-nanosecond scale.¹¹ Thus, compared to a nanosecond study, a picosecond study yields more reliable time constants.¹¹ In this work, we have used a picosecond setup to study the ESPT process in a polymer–surfactant aggregate.

It should be noted that the solvents affect the ESPT of 1-naphthol (R^*OH) in a number of ways. Apart from solvating the transition state and the products, solvent affects the diffusional separation and geminate recombination of the anion (R^*O^-) and the proton.^{2c–d} Because of this, the fluorescence decays of the neutral form (R^*OH)

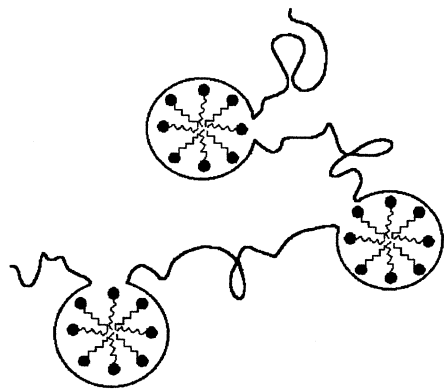
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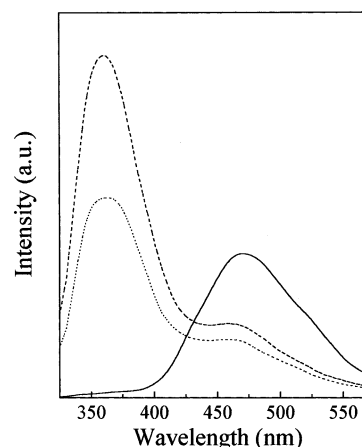
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Chart 1. Schematic Representation of the "Necklace" Model of Polymer–Micelle Aggregation

and the anion (R^*O^-) are nonexponential even in pure water and the asymptotic behavior is described by a power law ($t^{-3/2}$).^{2c-e} Huppert and Pines carried out a detailed analysis of the decays of R^*OH and R^*O^- in water.^{2c}

In the present work, we report on the ESPT process of 1-naphthol in a polymer–surfactant aggregate consisting of a polymer, hydroxypropylcellulose (HPC), and a surfactant, sodium dodecyl sulfate (SDS). Interaction of water-soluble polymers with surfactants is a subject of several recent studies.^{12–28} The interaction between a polymer and a surfactant leads to the formation of a "necklace" (Chart 1). According to this model, the polymer–surfactant aggregates consist of a series of spherical micelles surrounded by the polymer segments and connected by the polymer strands. The polymer chain shields the peripheral region of the micelles from bulk water and displaces an appreciable amount of water. Thus, the polymer chain makes the Stern layer of an ionic micelle more hydrophobic and restricted. Such an aggregate is formed above a particular concentration of the surfactant called the critical association concentration (cac). The cac of a surfactant for a polymer is often much lower than its critical micellar concentration (cmc). In the presence of a polymer at a surfactant concentration above the cmc, the system consists of both polymer–surfactant aggregates and free micelles. In the present work, we have studied the ESPT process of 1-naphthol in an aggregate of HPC and SDS. We have also studied the partitioning of the probe between the polymer–surfactant aggregate and the SDS micelles

**Figure 1.** Emission spectra of 1-naphthol with (i) (—) no HPC and SDS, (ii) (---) 0.25 wt % HPC and 12 mM SDS, and (iii) (···) 0.25 wt % HPC and 50 mM SDS.

above the cmc. We will show that the ESPT process in the aggregate is very different from that in the SDS micelle.

2. Experimental Section

1-Naphthol (Merck, 99.9+%) was purified by vacuum sublimation followed by recrystallization from 1:1 aqueous methanol. SDS (Aldrich) and HPC ($M = 1 \times 10^5$ Da, Aldrich) were used as received. An aqueous solution of HPC is made by allowing the polymer to soak in water for 24 h. The steady-state absorption and emission spectra were recorded in a JASCO 7850 spectrophotometer and a Perkin-Elmer 44B spectrofluorimeter, respectively.

For the measurement of fluorescence lifetime, we used a time correlated single photon counting setup.²⁹ Briefly, the sample was excited at 300 nm by the second harmonic of a rhodamine 6G dual jet dye laser with DODCI as saturable absorber (Coherent 702-1) synchronously pumped by a CW mode locked Nd:YAG laser (Coherent Antares 76s). The emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (2809U). Our time correlated single photon counting (TCSPC) setup consists of Ortec 935 QUAD CFD and Tennelec TC 863 TAC. The data are collected with a PCA3 card (Oxford) as a multichannel analyzer. The typical fwhm of the system response is about 50 ps.

3. Results

3.1. Steady-State Spectra. In bulk water,³ 1-naphthol exhibits a very weak emission from the neutral form at ~ 360 nm (emission quantum yield, $\phi_f = 0.002$) and relatively strong emission ($\phi_f = 0.11$) from the anion at ~ 460 nm. Addition of 0.25 wt % HPC to a 4×10^{-5} M aqueous solution of 1-naphthol does not affect the intensity of the neutral (R^*OH) and the anion (R^*O^-) emission (Figure 1). On gradual addition of SDS to this solution, the emission intensity of R^*OH and R^*O^- remain unchanged up to about 2 mM SDS. On further increase in SDS concentration, the intensity of the neutral emission increases rapidly, reaching a maximum enhancement of ~ 100 times at 12 mM SDS, as shown in Figure 1. It may be noted that SDS alone causes enhancement of the neutral emission of 1-naphthol by a much lower magnitude.¹¹ In the absence of HPC, at 12 mM SDS, the neutral emission of SDS exhibits a fluorescence enhancement of only about 20 times, and a nearly 90-fold enhancement occurs at a much higher SDS concentration (140 mM).¹¹

The enhancement of the neutral emission is obviously due to the drastic inhibition of the ESPT process, which

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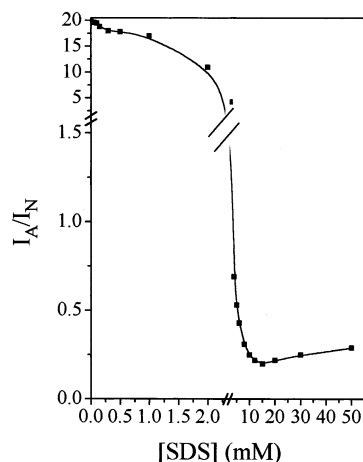


Figure 2. Plot of the ratio of the intensity of the anion emission (I_A) and the intensity of the neutral emission (I_N) for an aqueous solution of 1-naphthol containing 0.25 wt % HPC and various concentrations of SDS against concentration of SDS.

is the main nonradiative process in the excited state of 1-naphthol (R^*OH). In the presence of HPC and of SDS below the cmc, the neutral emission originates predominantly from the 1-naphthol molecules inside the HPC–SDS aggregate. The marked difference in the enhancement of the emission of R^*OH at 360 nm in the HPC–SDS aggregate compared to that in a SDS micelle indicates that the microenvironment in a HPC–SDS aggregate is very much different from that in a SDS micelle.

In 0.25 wt % HPC, the intensity of the neutral emission increases with SDS concentration up to 12 mM. For a SDS concentration greater than 12 mM, the intensity of the neutral emission gradually decreases with an increase in SDS concentration.

The variation of the intensity of the anion emission (at 460 nm) with SDS concentration is very different from that of the neutral emission (Figure 1). In the presence of 0.25 wt % HPC, the intensity of the anion emission decreases monotonically with the increase in SDS concentration. Compared to the cases of 0.25 wt % HPC and 0 mM SDS, the intensity of the anion emission decreases by a factor of 1.7 at a SDS concentration of 12 mM and by a factor of 2 at 50 mM.

The absorption and the excitation spectra of the neutral (360 nm) and the anion emission (460 nm) of 1-naphthol in a solution containing 0.25 wt % HPC and 12 mM SDS are shown in Figure 3. It is readily seen that the absorption and the excitation spectra of 1-naphthol in the HPC–SDS aggregate are identical. This rules out the presence of any impurity.

The break in the plot of the ratio of the intensity of the anion emission (I_A) and the intensity of the neutral emission (I_N) (Figure 2) is a good monitor to indicate formation of HPC–SDS aggregate or SDS micelles. In the absence of HPC, the intensity of the neutral emission of 1-naphthol shows a break at 8 mM (i.e. cmc of SDS).¹¹ In the presence of 0.25 wt % HPC, a similar break is observed at the SDS concentration 2 mM, which is at least 4 times smaller than the cmc of SDS (8 mM). Thus, the critical association concentration (cac) of SDS for HPC reported by 1-naphthol is about 2 mM. The cac of SDS is found to be independent of the concentration of HPC in the range 0.25–1 wt %.

3.2. Time-Resolved Studies. **3.2.1. Effect of HPC on the Decay of Neutral and Anion Emission of 1-Naphthol.** In an aqueous solution of 1-naphthol, the fluorescence decay at 360 nm (i.e. of R^*OH) shows a decay of 35 ps and

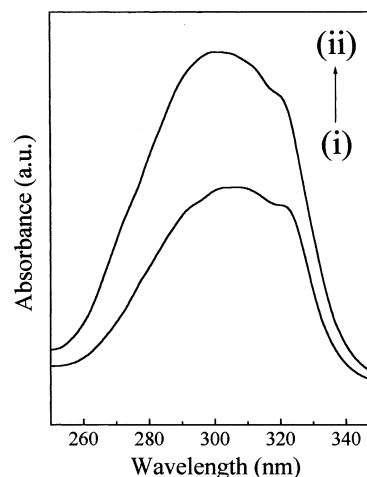
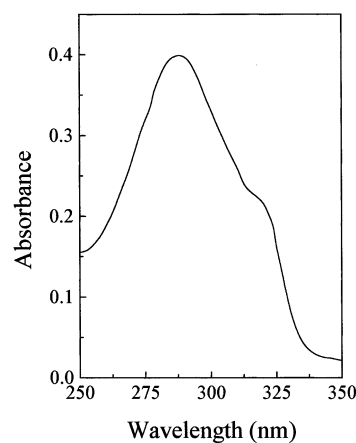


Figure 3. (a) Absorption spectrum of an aqueous solution of 1-naphthol containing 0.25 wt % HPC and 12 mM SDS. (b) (i) Excitation spectrum at 360 nm and (ii) excitation spectrum at 460 nm for an aqueous solution of 1-naphthol containing 0.25 wt % HPC and 12 mM SDS.

the anion emission at 460 nm exhibits a rise of 35 ps and a decay of 8 ns.³ In our setup of response function 50 ps, the 35 ps rise and decay component could not be detected. In the presence of 0.25 wt % HPC (without SDS) of an aqueous solution of 1-naphthol, the decay at 360 nm is observed to be faster than the response time (50 ps) of our setup while at 470 nm we observed a very fast rise (<50 ps) followed by a decay of lifetime \sim 8 ns. This and the steady-state results indicate that, in the absence of SDS, in 0.25 wt % HPC alone the ESPT process of 1-naphthol remains very similar to that in bulk water. In other words, HPC alone does not cause inhibition of ESPT of 1-naphthol.

On addition of SDS to a 1-naphthol solution containing 0.25 wt % HPC, the fluorescence decays remain unchanged up to about 2 mM (i.e. cac) SDS. Above 2 mM SDS, both the decays at 360 nm (R^*OH) and at 460 nm (R^*O^-) are found to be very different from those in pure water or in SDS micelles. In the following section, we will discuss the effect of SDS on the temporal characteristics of the decays at 360 and 460 nm in the presence of 0.25 wt % HPC. As a representative, parts a and b of Figure 4 show respectively the decays of the neutral and the anion emission of 1-naphthol in the presence of 0.25 wt % HPC and 12 mM SDS. Tables 1 and 2 summarize respectively the decay parameters of the neutral and the anion emission at various SDS concentrations.

3.2.2. Effect of SDS on the Decay of Neutral Emission in 0.25 wt % HPC. In a SDS micelle the neutral emission of 1-naphthol decays with the lifetime 1.6 ns.¹¹ In the

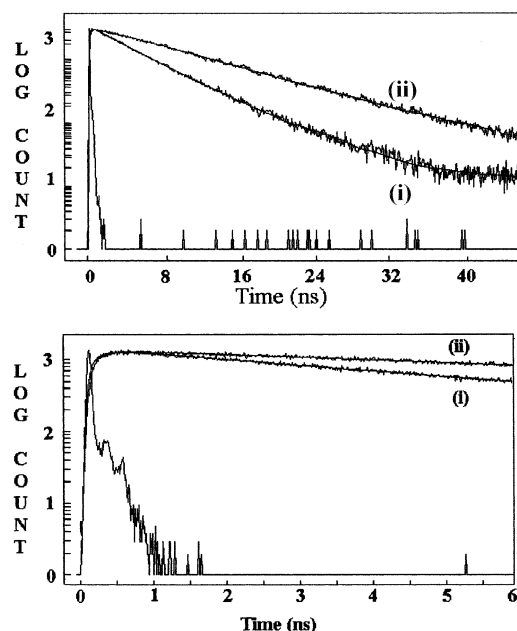


Figure 4. (a) Fluorescence decays of an aqueous solution of 1-naphthol containing 0.25 wt % HPC and 12 mM SDS: (i) $\lambda_{em} = 360$ nm; (ii) $\lambda_{em} = 460$ nm; resolution = 96 ps/ch. (b) Fluorescence decays of an aqueous solution of 1-naphthol containing 0.25 wt % HPC and 12 mM SDS: (i) $\lambda_{em} = 360$ nm; (ii) $\lambda_{em} = 460$ nm; resolution = 12 ps/ch.

Table 1. Decay Parameters of the Neutral Emission (360 nm) of 1-naphthol in Aqueous Solution Containing 0.25 wt % HPC at Different Concentrations of SDS

[SDS],(mM)	a_1^*	τ_1^a (ns)	a_2^*	τ_2 (ns)
4	0.17	0.40	0.83	5.40
5	0.10	0.60	0.90	6.30
6	0.10	0.60	0.90	6.70
8	0.10	0.60	0.90	8.00
12	0.10	2.20	0.90	8.50
20	0.20	1.30	0.80	6.70
30	0.45	1.60	0.55	6.20
50	0.70	1.60	0.30	5.70

* ± 0.03 . $a \pm 5\%$.

Table 2. Decay Parameters of the Anion Emission (460 nm) of 1-naphthol in Aqueous Solution Containing 0.25 wt % HPC at Different Concentrations of SDS

[SDS], mM	a_1^a	τ_1 (ns) ^b	a_2^a	τ_2 (ns) ^b
4	0.13	0.30	0.87	9.65
5	0.05	0.30	0.95	10.20
8	-0.02	2.20	1.02	10.20
10	-0.02	2.40	1.02	10.30
12	-0.07	3.00	1.07	10.40
15	-0.07	2.40	1.07	10.10
20	-0.19	1.30	1.19	9.80
30	-0.25	0.80	1.25	9.00
50	-0.48	0.60	1.48	8.60

$a \pm 0.03$. $b \pm 5\%$.

presence of 0.25 wt % HPC, at a SDS concentration greater than the cac but less than the cmc, the decay at 360 nm shows a minor component of 0.4–0.6 ns and a major component of 5.4–8 ns (Table 1). The relative contribution of the short component decreases with increase in SDS concentration up to around the cmc. The variation of the decay components of R^*OH with SDS concentrations suggests that the microenvironment of 1-naphthol in the HPC–SDS aggregate changes with SDS concentration. As more and more SDS molecules gather around 1-naphthol and the polymer (HPC), there is a marked retardation in the ESPT process and other nonradiative pathways in the excited state of 1-naphthol. This leads to the increase

in intensity and lifetime of the neutral emission of 1-naphthol with an increase in SDS concentration up to 12 mM.

In the presence of 0.25 wt % HPC and above the cmc of SDS, 1-naphthol displays a micelle-like decay component of 1.6 ns whose contribution increases with SDS concentration. It is obvious that above the cmc of SDS the 1-naphthol molecules are distributed between the HPC–SDS aggregate and free SDS micelles. The 1.6 ns decay component obviously arises from the probes in the SDS micelles. But even at 50 mM SDS a substantial amount of 1-naphthol molecules remains confined in the HPC–SDS aggregate and exhibits a very long decay component (Table 1).

3.2.3. Effect of SDS on the Decay of Anion Emission in 0.25 wt % HPC. In SDS micelles, at a concentration much above the cmc at 460 nm, one observes a rise time of 600 ps and a water-like decay of 8 ns.¹¹ In the presence of 0.25 wt % HPC and at a SDS concentration above the cac, the lifetime of the decay of the anion is found to be around 10 ns, which is longer than that in bulk water (8 ns) (Table 2). This indicates that the anion in the HPC–SDS aggregate experiences an environment different from that in water. This is in sharp contrast to the case of 1-naphthol in SDS micelles, where the anion, once formed, is immediately expelled to bulk water and, hence, displays a bulk water-like decay.¹¹

For a SDS concentration up to 8 mM, the anion emission of 1-naphthol in the HPC–SDS aggregate displays a rise faster than our instrument response. This indicates that for the few 1-naphthol molecules in the HPC–SDS aggregate which undergo ESPT, the ESPT occurs in a very fast time scale. Above 8 mM a slow rise (τ_1) of 2–3 ns precedes the decay (Figure 4 and Table 2). The rise time is much longer than that in SDS micelles (0.6 ns).¹¹ At a concentration much above the cmc, as more and more 1-naphthol migrates from the HPC–SDS aggregate to SDS micelles, the rise time becomes shorter. At 50 mM SDS, the rise time becomes very close to that in SDS micelles (0.6 ns, Table 2).

4. Discussion

The most interesting finding of this work is obviously the sharp increase in the intensity and lifetime of the neutral (R^*OH) emission of 1-naphthol in 0.25 wt % HPC at a concentration of SDS above the cac. This clearly indicates marked suppression of the ESPT process inside the HPC–SDS aggregate. Before attempting a deeper analysis of the data, one should keep in mind the following difficulties.

The fluorescence decays are found to be multiexponential in the HPC–SDS aggregate. In the case of a micro-heterogeneous medium like a polymer–surfactant aggregate, the properties (diffusion coefficient, polarity, etc.) of the medium change drastically over a short distance. During its excited state lifetime, the probe undergoes diffusion over a distance and, hence, experiences widely different properties of the medium. Complete analysis of the problem involves a position dependent diffusion coefficient and a position dependent dielectric constant. These quantities are still unknown for a polymer–surfactant aggregate. Thus, at this stage, it is extremely difficult to extend the analysis made by Pines and Huppert^{2c} to a complex system, namely, the HPC–SDS aggregate. Nevertheless, we will attempt to draw some qualitative conclusions.

We have noted earlier that at a SDS concentration between 2 and 8 mM (i.e. above the cac but below the cmc)

the neutral (R^*OH) emission is mainly due to the 1-naphthol confined in the HPC–SDS aggregate. The biexponential decay of the R^*OH emission qualitatively indicates the presence of two sites. In one of them, 1-naphthol undergoes ESPT, giving rise to a component in the 0.4–0.6 ns time scale. About 10% of the 1-naphthol molecules reside in this site. In the other site, occupied by 90% of the 1-naphthol molecules, the ESPT process is totally prevented, giving rise to a very long lifetime of R^*OH (5.4–8 ns).

Since, in a HPC–SDS aggregate, very few 1-naphthol molecules undergo ESPT, the anion (R^*O^-) emission is observed to be quite weak. But the anion formed in the HPC–SDS aggregate does not leave the aggregate, and hence, its lifetime is longer than that in bulk water. However, one should note that the rise time of the anion does not match the short component of the neutral emission. Such a discrepancy between the rise at 460 nm and the decay of 360 nm is earlier noted in the case of micelles¹¹ and even in aqueous alcohol mixtures.^{3b} It is obvious that the ESPT process of 1-naphthol is quite complicated not only in a complex medium but also in a binary solvent mixture.

At an SDS concentration above 8 mM (i.e. the cmc), there are two kinds of aggregates, the HPC–SDS aggregate and the free SDS micelles. The probe 1-naphthol is distributed among these two environments. With an increase in SDS concentration, the concentration of the free micelles also increases and more 1-naphthol molecules migrate from the polymer–surfactant (HPC–SDS) aggregate to the SDS micelles. Since the SDS micelle causes smaller fluorescence enhancement compared to that of the HPC–SDS aggregate, the emission intensity of the neutral form of 1-naphthol decreases at a SDS concentration above the cmc. Above the cmc, as more and more 1-naphthol molecules bind to SDS micelles, the contribution of the micelle-like decay of 1.6 ns at 360 nm increases and a rise time of 0.6 ns at 460 nm, typical of 1-naphthol bound to SDS micelles, is observed.¹¹ At 50 mM SDS,

nearly 70% of the 1-naphthol molecules remain bound to the SDS micelle but 30% still reside inside the HPC–SDS aggregate (Table 1).

5. Conclusion

The present work indicates that 1-naphthol readily binds to the HPC–SDS aggregates and the ESPT process of 1-naphthol is seriously inhibited in the aggregate comprising the cellulose, HPC, and the surfactant, SDS. The plot of the ratio of the intensities of the anion and the neutral emission shows a break at 2 mM SDS, which is the cac of SDS for the HPC. The cac determined in this work is nearly 4 times smaller than the cmc of SDS. The steady-state spectra and the decay parameters of the neutral molecule (360 nm) and the anion (460 nm) indicate that a vast majority of the 1-naphthol molecules in the HPC–SDS aggregate do not undergo deprotonation at all. For them, the neutral emission exhibits a decay component of 5.4–8 ns. Thus, the HPC–SDS aggregate causes a much greater enhancement of the neutral emission than that caused by SDS micelles. The variation of the intensity and the decay components of neutral (R^*OH) HPC with SDS concentration suggest that the microenvironment of the probe 1-naphthol in HPC–SDS changes with SDS concentration. The anion of 1-naphthol bound to the HPC–SDS displays a lifetime (10.3 ns) different from that in bulk water (8 ns^{2,3}). Above the cmc, as free SDS micelles are formed, the 1-naphthol molecules are partitioned between the HPC–SDS aggregate and free micelles. With a rise in the SDS concentration, the contribution of 1-naphthol in SDS micelles increases.

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