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Journal of Photochemistry and Photobiology A: Chemistry 109 (1997) 259–265

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Dual emission of 2-(2′-hydroxyphenyl)-benzimidazole in reverse micelle

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Received 13 December 1996; revised 7 April 1997; accepted 6 May 1997

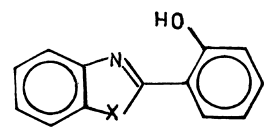
Abstract

Picosecond time resolved and steady state emission spectroscopy were employed to study the dual emission phenomenon of 2-(2′-hydroxyphenyl)-benzimidazole (HPBI) in aerosol OT (AOT) reverse micelle in *n*-heptane. It is observed that the microenvironment inside the water pool markedly affects the dual emission (normal and tautomer) of HPBI. While the normal emission is negligible in *n*-heptane, on addition of AOT and water its intensity increases gradually and reaches a moderate value ($\phi_f = 0.04$) at a water-to-surfactant ratio, $w_0 \approx 40$. The decay of the normal emission becomes faster with addition of water. The intensity and lifetime of the tautomer emission increase on addition of AOT. The increase in the intensity of the normal emission with w_0 is ascribed to the formation of the polyhydrates in which excited state intramolecular proton transfer is blocked. The increase in the intensity of the tautomer emission in reverse micelles, compared with *n*-heptane, is attributed to the reduction in the non-radiative rates. The polarity of the water pool inferred from both the emission parameters of the normal, and the tautomer emission is less than that of ordinary bulk water. © 1997 Elsevier Science S.A.

Keywords: Dual emission; Intramolecular proton transfer; Reverse micelle

1. Introduction

Water molecules in organized and restricted environments play a crucial role in many natural and biological processes. Recently, several groups have studied the solvation dynamics of the water molecules bound to cyclodextrins [1], reverse micelles [2] and micelles [3]. The effect of water molecules bound to organized assemblies on the intramolecular and intermolecular proton transfer processes has also been the subject of several recent studies [4–11]. Fleming et al. showed that in aqueous medium the rate of intermolecular proton transfer of protonated 1-aminopyrene increases considerably on binding with β-cyclodextrin [4]. Warner et al. studied the excited state intramolecular proton transfer (ESIPT) phenomenon with 10-hydroxybenzoquinoline (HBQ) in cyclodextrins and micelles using steady state spectroscopy and found that the steady state yield of the tautomer emission increases slightly on binding to cyclodextrins and micelles [5]. Sarkar et al. reported that compared with simple aqueous solutions, in micelles the intensity and lifetime of the tautomer emission of 2-(2′-hydroxyphenyl)-benzimidazole (HPBI) increase by a factor of nearly two while the normal emission is suppressed, and that the emission parameters of HPBI are good monitors of the micellization process [11]. In the present study we wish to examine how the reverse micelles affect the ESIPT process and the dual emission of HPBI.



Scheme 1.

The excited state intramolecular proton transfer (ESIPT) phenomenon has generated considerable interest recently because of its widespread implications [12–20]. The ESIPT phenomenon of HPBI and related molecules (Scheme 1) has, in particular, been studied in great detail [17]. HPBI exhibits dual emission, with a short wavelength (normal) emission around 360 nm and an anomalous Stokes shifted emission at around 460 nm originating from a tautomer (II) formed in the excited electronic state. The marked differences in the temporal characteristics, excitation spectra and temperature dependence of the two kinds of emission indicate that they originate from two different ground state species [17]. The tautomer emission originates from an intramolecularly hydrogen-bonded rotamer I which on excitation undergoes ultrafast ESIPT to form the phototautomer II, from which the tautomer emission results (Scheme 2). Since the ESIPT process is very fast (< 200 fs at ambient temperature) [13] the geometric requirement for the ESIPT process is very stringent. The

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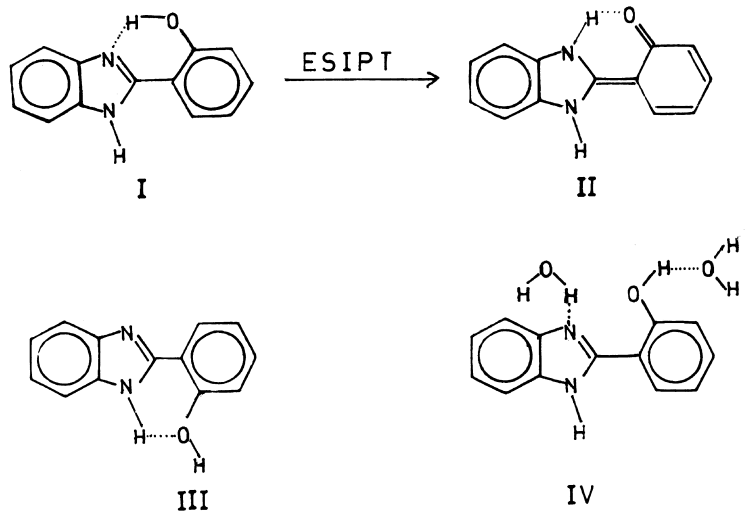
PII S1010-6030(97)00152-4



Scheme 2.

ESIPT process is markedly inhibited if the migrating hydroxyl-proton is not hydrogen bonded to the terminus, i.e. the N-atom of the imidazole ring (e.g. in rotamer III or the intermolecularly hydrogen-bonded polyhydrate, IV). In protic solvents or on addition of a very small amount of water to an aprotic solvent, the intramolecular hydrogen bond between the migrating proton and the terminus is disrupted and IV is formed. Recently several groups have studied how the disruption of the intramolecular hydrogen bond affects the ESIPT and a closely related process, excited state double proton transfer (ESDPT) phenomena [8,14,15,17]. Chou et al. reported that in the case of 7-azaindole (7-AI) on gradual addition of water to an aprotic solvent (ether or dioxane), the intensity of the tautomer emission initially increases and then decreases at very high water concentrations while the intensity of the normal emission decreases monotonically on addition of water [14]. They attributed the increase in the tautomer emission at low water concentration to the solvent mediated proton transfer in a cyclically hydrogen bonded 1:1 monohydrate. The decrease in the intensity of the tautomer emission at high water concentration is ascribed to the formation of polyhydrates. In the case of HPBI we have earlier demonstrated that on addition of water to dioxane the quantum yield of the normal emission increases from a negligible value in dioxane to a moderately high value of 0.14 at 50% water (v/v) and decreases at higher concentration of water, and that the intensity of the tautomer emission increases slightly and then decreases at high water concentration [17]. The increase in the intensity of normal emission is ascribed to the disruption of intramolecular hydrogen bonds and consequently ESIPT. We have now decided to extend our earlier work on the effect of microaddition of water to reverse micelles where a considerable amount of water can be solubilized inside a hydrocarbon solvent (e.g. *n*-heptane) using surfactants.

Aerosol OT (AOT) forms reverse micelles in *n*-heptane of aggregation number about 20 and radius 15 Å [21–27]. On addition of water to these reverse micelles a water-in-oil microemulsion is produced which refers to the nanometre sized water droplets, called water pool, surrounded by a layer of surfactant molecules (AOT, in the present case), dispersed in the non-polar organic solvent [21]. In *n*-heptane the radius of the water pool is roughly $2w_0$ (Å) where w_0 is the ratio of the number of water molecules to the number of surfactant (AOT) molecules [22]. Thus with rise in w_0 from 8 to 40 the radius of the water pool r_w increases from 16 Å to 80 Å. Recent studies on the structure and dynamics of the reverse micelles indicate that for small water pools ($w_0 < 10$) the water molecules are held very tightly by the polar head groups of the surfactant while for large pools ($w_0 > 30$) the water molecules, particularly those at the centre, are relatively free [2,7–9,21–27]. The water molecules in the water pool are highly structured, less mobile and have a polarity less than that of ordinary bulk water and are thus quite similar to those bound to biological systems. Though many photophysical processes have been studied in reverse micelles using time resolved emission spectroscopy [2,8,23–25], there is almost no study on ESIPT in reverse micelles. Only recently, a closely related process ESDPT in 7-AI in reverse micelles has been reported [8]. In the present work we have investigated how the highly structured water molecules of the reverse micelles affect the ESIPT phenomenon.

2. Experimental details

HPBI was synthesized and purified as described previously [28]. AOT (dioctyl sulphosuccinate, sodium salt, Fluka) was purified following standard procedures [22]. *n*-Heptane was freshly distilled. Absorption and emission spectra were recorded in JASCO 7850 and Perkin–Elmer MPF 44B spectrophotometers respectively. All the excitation spectra were taken in ratio mode which corrects for lamp intensity variation. The quantum yields were determined with respect to that of quinine sulphate in 1 N H_2SO_4 as 0.55. The fluorescence decays were recorded in a picosecond set-up described

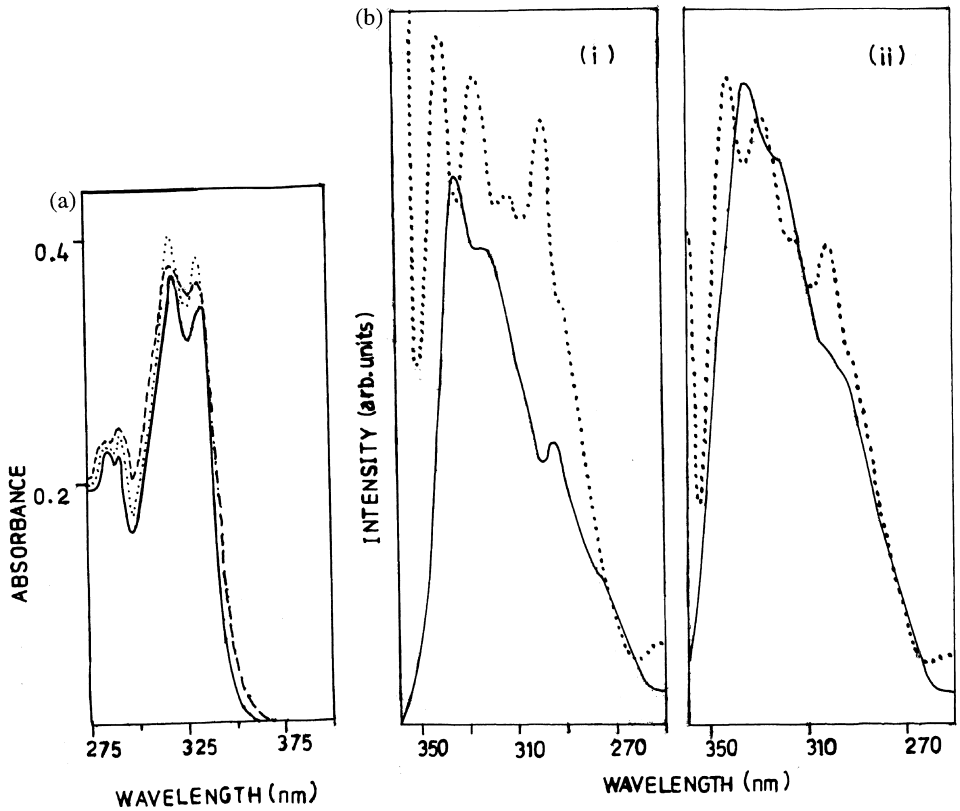


Fig. 1. (a) Absorption spectra of 3.3×10^{-5} M HPBI in *n*-heptane (———), 0.09 M AOT reverse micelle, $w_0=0$ (· · ·) and $w_0=40$ (- - -). (b) Excitation spectra of 3.3×10^{-5} M HPBI in AOT reverse micelle at 360 nm (· · ·) and 460 nm (———); (i) $w_0=0$, (ii) $w_0=40$.

elsewhere [17]. The fluorescence lifetime data were deconvoluted using a global lifetime analysis software (PTI) [29] and the goodness of the fit was tested using χ^2 and Durbin–Watson parameters.

3. Results

Fig. 1(a) describes the absorption spectra of HPBI in *n*-heptane with and without AOT and water. On addition of AOT and subsequently water the absorption spectrum of HPBI in *n*-heptane remains more or less unaffected except for a very slight increase in the absorbance (Fig. 1(a)). The excitation spectra (Fig. 1(b)) of the normal (at 360 nm) and the tautomer emission (460 nm) in AOT in the presence and in the absence of water exhibit significant differences indicating that they originate from different species, as observed earlier in homogeneous solutions [17].

Unlike the absorption spectra, the emission spectrum of HPBI changes considerably on addition of AOT and water (Fig. 2 and Table 1). In pure *n*-heptane, in the absence of AOT and water, the emission spectrum of HPBI exhibits a single peak at 465 nm corresponding to the tautomer emission with negligible normal emission at 360 nm (Fig. 2). On addition of 0.09 M AOT the normal emission becomes perceptible with a peak at 360 nm with quantum yield $\phi_f^N=0.005$. On addition of water the quantum yield of the normal emission increases to 0.012 at $w_0=8$ ($r_w\approx16$ Å) and finally to 0.04 at $w_0=40$ ($r_w\approx80$ Å). Thereafter no further increase in ϕ_f^N is noted with a rise in w_0 (Figs. 2 and 3).

The quantum yield of the tautomer emission ϕ_f^T of HPBI increases from 0.4 in *n*-heptane to 0.53 in 0.09 M AOT and increases slightly further on addition of water, to 0.55 at $w_0=8$ attaining a maximum value of 0.6 at $w_0\approx40$ (Figs. 2 and 3). Table 1 summarizes the emission characteristics of HPBI in *n*-heptane–AOT–water solution, correcting the quantum yields for the slight changes in the absorbance on addition of AOT. Fig. 3 depicts the variation of the quantum yield of the normal and the tautomer emission of HPBI with w_0. It should, however, be reiterated that at each wavelength of excitation, several species (I, III and IV) absorb and it is difficult, if not impossible to ascertain the fraction of light absorbed by the different species. Thus the quantum yield mentioned in the present work merely describes the relative intensities of the normal and the tautomer emission bands and their intensity variation on addition of AOT and water to *n*-heptane.

The time resolved studies indicate (Fig. 4(a) and Table 1) that for the normal emission at $w_0=0$ the decay is biexponential with components 1.6 and 3.2 ns and the decay becomes faster with a rise in w_0. From Table 1 it is readily seen that at $w_0=40$ the average lifetime ($a_1\tau_1+a_2\tau_2=940$ ps) of the normal emission of HPBI is slower than that in neat water (420 ps) and is close to that in 75% dioxane in water [17]. The decay of the tautomer emission is single exponential both in *n*-heptane and reverse micelles. The life-

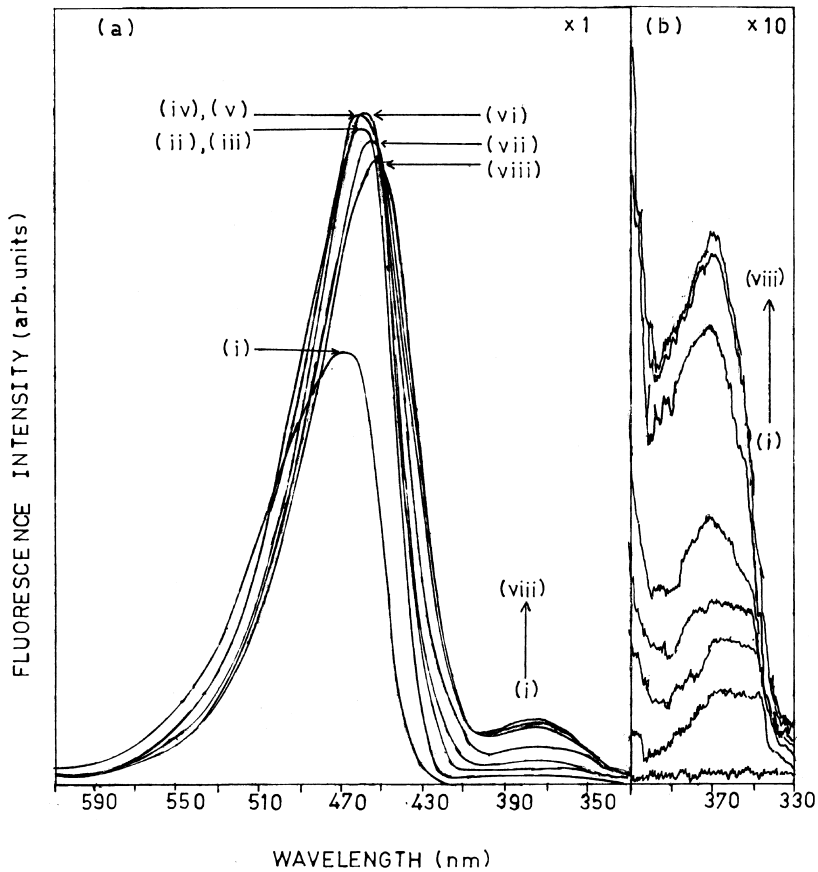


Fig. 2. Emission spectra of 3.3×10^{-5} M HPBI: (a) normal and tautomer emission, (i) in *n*-heptane, (ii)–(viii) in 0.09 M AOT, $w_0=0$, 4, 8, 16, 32, 40 and 50; (b) normal emission 10 times magnified.

Table 1
Emission characteristics of HPBI in AOT/*n*-heptane reverse micelles [a]

[AOT] (M)	w_0	Normal					Tautomer		
		λ_N^{max} (nm)	ϕ_f^N	τ_1 (ns)	τ_2 (ns)	a_1	λ_T^{max} (nm)	ϕ_f^T	τ_f^T (ns)
0	0	–	–	–	–	–	465	0.40	3.6
0.09	0	360	0.005	1.60	3.2	0.60	460	0.53	5.0
0.09	8	360	0.012	1.20	2.5	0.70	458	0.55	5.0
0.09	40	360	0.040	0.46	1.2	0.35	455	0.60	4.6

[a] λ_T^{max}, ϕ_f^T and τ_f^T are the emission maxima, quantum yield and lifetime of the tautomer, and λ_N^{max}, ϕ_f^N and τ_f^N denote those of the normal emissions.

time of the tautomer emission increases from 3.6 ns in *n*-heptane to 5 ns in 0.09 M AOT at $w_0=0$ and up to $w_0=8$. On further increase in w_0, the tautomer lifetime decreases slightly to 4.6 ns (Table 1 and Fig. 4(b)). For the tautomer emission, at the highest water content ($w_0=40$), the quantum yield ($\phi_f^T=0.6$) and lifetime ($\tau_f^T=4.6$ ns) are nearly twice as large as the quantum yield and lifetime of the tautomer emission of HPBI in water (0.3 and 1.8 ns respectively) [17] which clearly indicates that the polarity of the water pool is very different from that of ordinary bulk water.

4. Discussion

The significant increase in the intensity and lifetime of the normal and the tautomer emission of HPBI on addition of AOT and water to *n*-heptane indicates that the majority of the HPBI molecules are located inside the reverse micelles and very few reside in bulk *n*-heptane. The intensity and lifetime of the tautomer and the normal emission depend on two factors, relative ground state populations of the species giving rise to the tautomer (rotamer I) and the normal emission (III and IV) and the non-radiative rates in the corresponding excited states. Before explaining the present results obtained for HPBI in reverse micelles it is important to notice the basic differences between the ESIPT process in HPBI and the ESDPT processes in 7-AI in reverse micelles reported earlier [8]. In the case of 7-AI while in homogeneous solutions, microaddition of water causes an increase in the intensity of the tautomer emission [14], in AOT reverse micelles addition of water instead of enhancing the tautomer emission com-

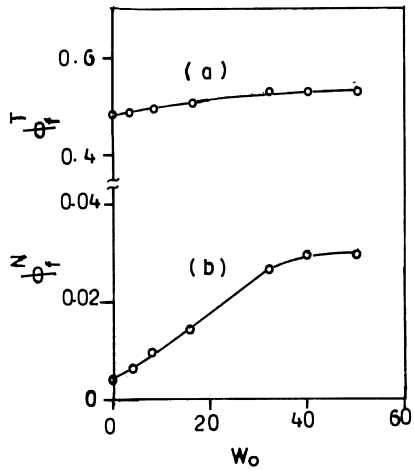


Fig. 3. Variation of the quantum yield of the tautomer (a) and the normal (b) emission of HPBI with w_0.

pletely quenches it [8]. The complete absence of the tautomer band of 7-azaindole in the presence of water in reverse micelles indicates that for 7-AI the behaviour in reverse micelles is different from that observed in the case of homogeneous solutions. However, in the case of HPBI the effect of microaddition of water in reverse micelles is similar to that obtained in homogeneous mixtures of water and dioxane. The emission quantum yield of the normal emission of HPBI increases from a negligible value in *n*-heptane to 0.04 in 0.09 M AOT at $w_0 = 40$ (corresponding to a water concentration of 3.6 M). This is very similar to the increase in the quantum yield of the normal emission of HPBI on addition of water to dioxane. In reverse micelles, with increase in w_0, the lifetime of the normal emission decreases indicating acceleration of the non-radiative rates. Obviously such an increase in the non-radiative rates is expected to reduce the emission intensity. Despite this the intensity of the normal emission is observed to increase with w_0. This indicates that on addition of water the population of the species giving rise to the normal emission increases considerably which offsets the effect of the increase in the non-radiative rates. Obviously addition of water causes the formation of more and more of the polyhydrated species IV in which ESIPT is blocked and this gives rise to increased normal emission. The gradual increase in the intensity of normal emission of HPBI on addition of water

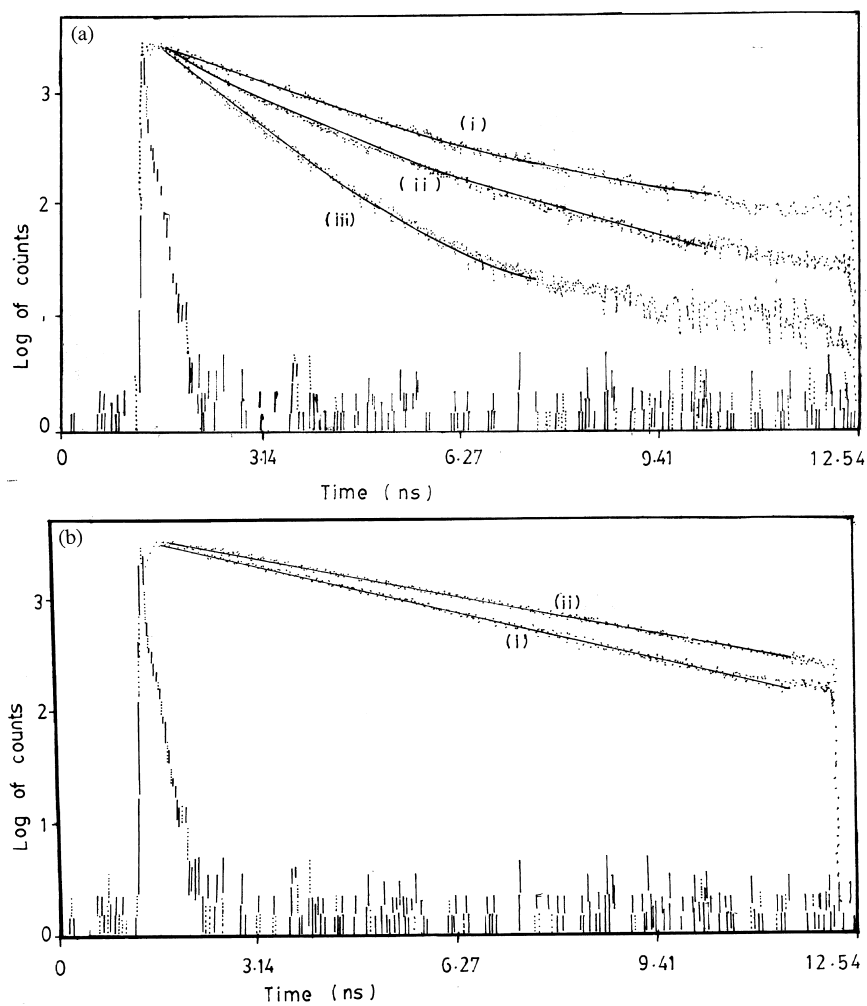


Fig. 4. (a) Fluorescence decay of 3.3×10^{-5} M HPBI in *n*-heptane + 0.09 M AOT at 360 nm, (i) $w_0 = 0$ (ii), $w_0 = 8$, (iii) $w_0 = 40$. (b) Fluorescence decay of 3.3×10^{-5} M HPBI at 460 nm; (i) in *n*-heptane, (ii) in *n*-heptane + 0.09 M AOT + water ($w_0 = 40$).

to reverse micelles is thus attributed to the formation of the polyhydrate IV. The quantum yield and lifetime of the normal emission of HPBI in AOT reverse micelles at $w_0 = 40$ are quite different than those in neat water and are actually close to those in 75% dioxane in water.

In reverse micelles the tautomer emission of HPBI exhibits 1.5 times enhancement in the emission quantum yield compared with *n*-heptane. This enhancement is accompanied by an increase in the lifetime by similar magnitude (Table 1). Thus the fluorescence enhancement of the tautomer emission of HPBI in reverse micelles may be due to the decrease in the non-radiative rates in the excited state of the tautomer. The quantum yield and lifetime values at $w_0 = 40$ in reverse micelles are actually close to those in 75% dioxane in water (v/v) ($E_T(30) = 50$) [17]. The emission properties of the tautomer emission of HPBI in AOT reverse micelles at $w_0 = 40$ is also similar to those in micellar media ($\phi_f^T = 0.6$ and $\tau_f^T = 4.8$ ns) [11]. Thus the emission properties of the tautomer emission of HPBI correspond to an effective $E_T(30)$ of around 50.

It is evident that for the large water pool ($w_0 = 40$) the polarity of the reverse micelles reported by the normal and the tautomer emission of HPBI is much lower than that of ordinary water and is actually close to those in 75% dioxane in water (v/v). Thus the present study indicates that the interior of the water pool resembles 75% dioxane in water with an $E_T(30)$ value of around 50 at $w_0 = 40$. This conclusion is consistent with the polarity of the water pool reported by earlier studies [7–9]. It should also be noted that in a homogeneous mixture on addition of water to dioxane the intensity of the tautomer emission decreases after reaching a maximum at around 50% water–dioxane mixture [17]; in the case of reverse micelles one observes only a monotonic increase in ϕ_f^T with w_0. This is presumably because of the fact that even at $w_0 = 40$ the polarity of the water pool is much less than that of bulk water and never reaches the polarity of the 50% water–dioxane mixture.

5. Conclusion

This work demonstrates that the quantum yield ϕ_f and lifetime τ_f of the tautomer and normal emission of HPBI are markedly affected when the molecules are transferred from the bulk *n*-heptane to the water pool of the reverse micelles. The variation of the intensity and lifetime of the tautomer and the normal emission of HPBI in the reverse micellar environment is explained in terms of the variations observed in homogeneous solutions [17]. The results indicate that the highly polar and protic microenvironment of the water pool enhances both the tautomer and the normal emission for HPBI. The emission parameters corresponding to the normal and the tautomer emission indicate that inside the water pools the HPBI molecules experience a polarity much less than that of bulk water. The microenvironment of the water pool at $w_0 = 40$ resembles 75% dioxane in water [17] or aqueous micelles [11]. It would definitely be more interesting if one could selectively excite the different ground state species (I, III or IV) and study their emission properties separately. Unfortunately, the rather broad absorption and excitation spectra in fluid solutions and the reverse micelles prevent such studies. It seems that high resolution spectroscopy of HPBI–water clusters in a supersonic jet would reveal such information.

Acknowledgements

Thanks are due to SERC, Department of Science and Technology, Government of India and to Council of Scientific and Industrial Research (CSIR) for generous research grants. S.D., A.D., N.S. and K.D. thank CSIR for providing fellowships.

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