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Deuterium Isotope Effect on 4-Aminophthalimide in Neat Water and Reverse Micelles[†]

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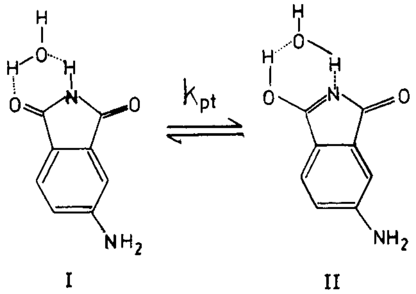
Picosecond time-resolved emission of 4-aminophthalimide (4-AP) in neat water and D_2O and in the water pool of aerosol OT reverse micelles in *n*-heptane is reported. It is proposed that in protic solvents 4-AP undergoes ultrafast solvent-mediated proton transfer and the emission originates from the proton-transferred species. The abrupt decrease in the emission quantum yield and lifetime of 4-AP in protic solvents is attributed to the reduction in the S_1-S_0 energy gap in the proton-transferred species. Nearly 4-fold increase in the emission quantum yield (ϕ_f) and lifetime (τ_f) of 4-AP is observed in neat D_2O compared to water. This is ascribed to the retardation of the nonradiative $S_1 \rightarrow S_0$ internal conversion processes on deuteration of the imide proton. In neat water or D_2O the solvation dynamics is too fast to be detected using our picosecond setup. However, in the water pool of reverse micelles the relaxation of the water (or D_2O) slows down appreciably. The initial component of the solvation dynamics in reverse micelles, in the case of D_2O, is observed to be 1.5 times slower than that in the case of H_2O.

1. Introduction

One of the long-standing goals of chemistry and biology is to understand the behavior of the water molecules bound to different organized and biological systems.[1,2,4] The interplay between the solvation of biomolecules by water and the very strong water−water attraction plays a major role in the structure, dynamics, and reactivity of organic and biological molecules in aqueous media. The relaxation times of water molecules present in biological molecules can be directly determined using the time dependent Stokes shift of suitable probe molecules.[2−12,14,15] Recently several groups have applied this method to study relaxation times of water molecules in cyclodextrin,[4d] reverse micelles,[14a,15a] and micelles.[15b] In neat water the solvation dynamics of coumarin dyes occurs on the femtosecond time scale.[4] However the solvation dynamics of water molecules slows down by several orders of magnitude in cyclodextrin cavities,[4d] in the water pool of reverse micelles,[14,15a] and in the Stern layer of the micelles.[15b] The nanosecond dynamics of water molecules in cyclodextrin cavities has been attributed to the freezing of the translational modes.[2c,d] The nanosecond dynamics of bound water molecules in such organized media is consistent with the recent dielectric relaxation and pulsed NMR studies of water molecules bound to biological systems.[23]

In an earlier publication we have reported that coumarin 480 exhibits nanosecond dynamics in the water pool of reverse micelles.[15a] In the present study we report on the solvation dynamics of 4-aminophthalimide (4-AP) in reverse micelles. The emission intensity and lifetime of 4-AP are extremely sensitive to hydrogen-bonding solvents.[12,24] The fluorescence quantum yield of 4-AP decreases 70 times from 0.7 in dioxane to 0.01 in water.[24] However, there have been few attempts to explain this remarkable change. Ware et al. proposed that the very fast component of solvation of 4-AP in alcoholic solvents at low temperature is due to the specific interactions between 4-AP and alcohol molecules.[16] Harju et al. proposed that 4-AP undergoes solvent mediated proton transfer (Scheme 1).[12] In the present work we have attempted to shed further light on the specific interaction of 4-AP and water by studying the deuterium isotope effect on the emission properties of 4-AP. Recently several groups have reported the deuterium isotope effect on ultrafast processes.[2e,6−9,13] Eisenthal et al. and Gaudel et al. reported a nearly 20−40% reduction in the rate of localization and hydration of electron in D_2O compared to H_2O.[6] Yoshihara et al. observed a 10% reduction in the solvation dynamics of coumarin 480 in deuterated methanol compared to the undeuterated one.[8] Barbara et al. found that the back electron transfer in mixed valence compounds shows 40% reduction in D_2O while the same for a betaine dye exhibits a 15% retardation in deuterated alcohol relative to the protonated ones.[7] Bagchi et al. carried out a detailed theoretical study of the deuterium isotope effect on the ultrafast solvation dynamics in aqueous medium and reported excellent agreement with the experimental results.[2e] Dynamics of another ultrafast process, excited state intramolecular proton transfer remains more or less unaffected on deuteration.[13] However, for azaindole, which undergoes excited state double proton transfer, Petrich et al. reported a 3-fold increase of the emission lifetime and quantum yield in D_2O compared to H_2O.[9] In the present study, we report on the deuterium isotope effect on the emission properties of 4-AP in neat water and on the solvation dynamics of 4-AP in the water pool of aerosol OT (AOT) reverse micelles in *n*-heptane.

SCHEME 1: Solvent-Mediated Proton Transfer in 4-AP



AOT forms micelles in hydrocarbon solvents (e.g. *n*-heptane) with aggregation number about 20 and radius 15 Å.[19−21] On addition of water to the AOT/heptane system, a microemulsion

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TABLE 1: Emission Properties of 4-AP in Water and D_2O

solvent	λ^{em}_{max} (nm)	ϕ_f	τ_f (ns)
neat water	550	0.010	1.2
neat D_2O	550	0.045	5.7
heptane + 0.09 M AOT	450	0.600	15.7
heptane + 0.09 M AOT + H_2O ($w_0 = 12$)	530	0.040	3.3[a]
heptane + 0.09 M AOT + D_2O ($w_0 = 12$)	530	0.120	10.0[a]

[a] Decay time at the longest wavelength (660 nm).

is formed that is basically a water droplet surrounded by the surfactant molecules (AOT) in *n*-heptane. The radius of the water droplet or the so-called water pool in *n*-heptane is roughly equal to $2w_0$, where w_0 is the ratio of the concentrations of the water and the AOT molecules.[19e] Thus the radius or size of the water pool can be systematically varied on addition of water. Recently Bright et al. and Sarkar et al. reported that the solvation dynamics of H_2O molecules is significantly slowed down inside the water pool of the reverse micelles.[14a,15a] More recently, Nandi and Bagchi proposed a multishell continuum model that quantitatively explains the nanosecond dynamics in the water pool of the reverse micelles.[2f] 4-AP forms a very strong hydrogen bond with water. Since in the confined region of the water pool, motion of water (or D_2O) molecules around the probe (4-AP) molecules involves the hydrogen bond between solute (4-AP) and the surrounding water (D_2O) molecules, the solvation dynamics is expected to be influenced by deuteration. We will show that the solvation dynamics of 4-AP, indeed, exhibits deuterium isotope effect.

2. Experimental Section

4-AP (Kodak) was purified by repeated recrystallization from a 1:1 water–ethanol mixture. Purification of sodium dioctyl sulfosuccinate (AOT, Aldrich) is described elsewhere.[15a,19c] 4-AP is nearly insoluble in *n*-heptane, but its solubility increases in the presence of 0.09 M AOT. To a 0.09 M solution of AOT in *n*-heptane, solid 4-AP was added, and the solution was allowed to stand for a few hours. The supernatant liquid was decanted and filtered, and to it water (or D_2O) was added using a microliter syringe. The laser system and the method of constructing the time-resolved emission spectra are described in detail in our earlier publications.[15] The wavelength of excitation for the steady state and time-resolved studies is 300 nm.

3. Results

3.1. Emission Properties of 4-AP in Neat Water and D_2O. As reported in the literature the emission intensity of 4-AP is extremely low (0.01) in water.[24] However, in neat D_2O, the emission quantum yield (ϕ_f) and lifetime (τ_f) of 4-AP are about four times larger than those in neat water (Table 1). Figures 1 and 2 describe respectively the emission spectra and fluorescence decays of 4-AP in water and D_2O. The absorption spectra of 4-AP in neat water and D_2O are identical. The fluorescence decays of 4-AP in neat water and D_2O exhibit no wavelength dependence, indicating that the solvation dynamics in neat water or D_2O is too fast to be detected in our picosecond setup (resolution ~40 ps).

3.2. Steady State Emission Properties of 4-AP in Reverse Micelles. In 0.09 M AOT in *n*-heptane, 4-AP exhibits strong fluorescence ($\phi_f = 0.6$) with emission maximum at 450 nm. On addition of water or D_2O the absorption spectra exhibits very slight change (Figure 4). However, in reverse micelles on addition of water or D_2O the emission intensity of 4-AP decreases markedly and the spectra exhibit a significant red shift (Figure 3 and Table 1) compared to $w_0 = 0$. At $w_0 = 12$, the emission intensity of 4-AP decreases nearly 15 times in the case of water and 5 times for D_2O. Above $w_0 = 12$ the emission intensity of 4-AP remains more or less unchanged for both H_2O and D_2O.

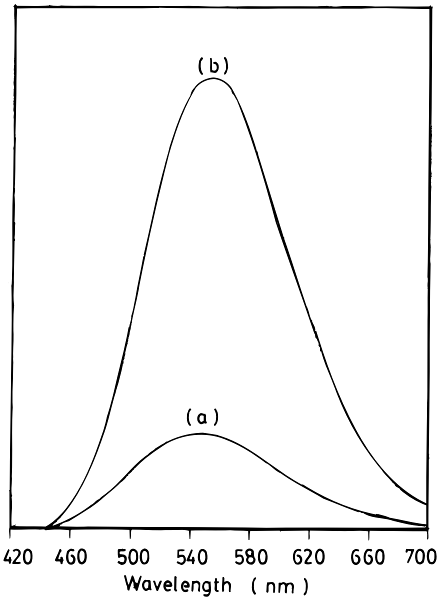

Figure 1. Emission spectra of 1.2×10^{-4} M 4-AP in (a) water and (b) D_2O.

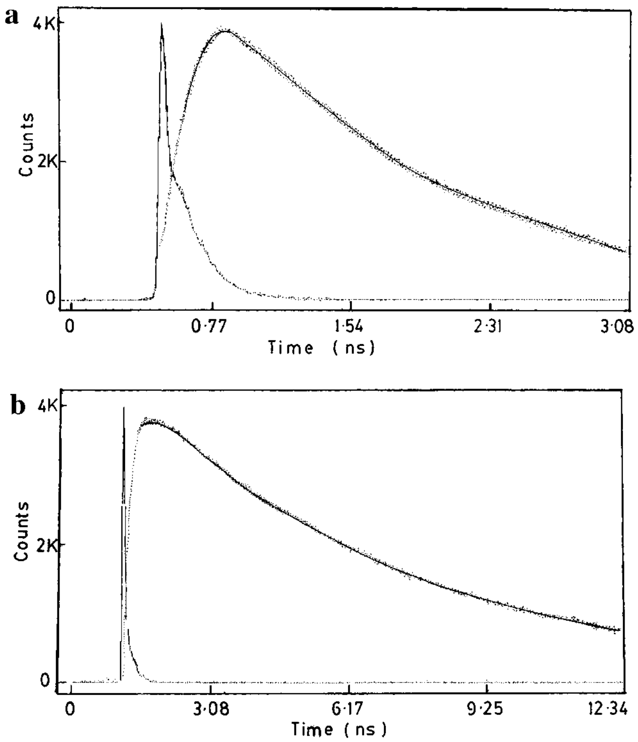

Figure 2. Fluorescence decays of 1.2×10^{-4} M 4-AP in (a) water (at 550 nm) and (b) D_2O (at 550 nm).

3.3. Time-Resolved Emission Properties of 4-AP in Reverse Micelles. In the absence of water or D_2O in 0.09 M AOT in *n*-heptane the fluorescence decay of 4-AP exhibits no wavelength dependence, the lifetime being 15.7 ns (Table 1). However, in the presence of water or D_2O, fluorescence decays of 4-AP exhibit significant wavelength dependence in reverse micelles (Figure 5). As mentioned already, the radius of the water pool of AOT reverse micelles in *n*-heptane is roughly equal to $2w_0$ (in angstroms).[19e] The dependence of solvation dynamics on the size of water pool is discussed in earlier works.[14a,15a] In the case of 4-AP in small water pools ($w_0 < 5$), the decays are very long and the time-resolved Stokes shift show very poor convergence. Therefore, in the present work, we focus our attention only on rather big water pools of $w_0 = 12$, which correspond to water pools of diameter about 48 Å.[19e] As shown in Figure 5 in the reverse micelles the fluorescence decays at the red end exhibit distinct growth while those at the blue end exhibit fast decays. At $w_0 = 12$ at the longest wavelength the decay in the case of D_2O (10 ns) is nearly three times slower than that in the case of water (3.3 ns) (Table 1). The wavelength dependence of the decays in the reverse micelles indicates that the solvation dynamics is slowed down inside the reverse micelles and hence is detected in our picosecond setup. From the best fits to the decays the time-resolved emission spectra were constructed by fitting the time-resolved spectra to a log-normal function as described by Fleming and Maroncelli.[4c] Finally the correlation function $C(t)$ defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

was calculated. $\nu(t)$, $\nu(\infty)$, and $\nu(0)$ respectively denote the frequencies corresponding to the emission maxima at times t, ∞, and zero. Figure 6 describes the time-resolved emission spectra in the case of water and D_2O. Figure 7 describes the decay of $C(t)$. Table 2 summarizes the decay characteristics of $C(t)$ of 4-AP in reverse micelles. It is readily seen that for both water and D_2O the decay of $C(t)$ is biexponential with a major component of 340 ps for H_2O (500 ps for D_2O) and a minor component of several nanoseconds.

4. Discussions

Before discussing the deuterium isotope effect on 4-AP, it is necessary to assign the species responsible for emission of 4-AP in protic solvents. In aprotic solvents with increase in the polarity the fluorescence quantum yield (ϕ_f) and lifetime (τ_f) decreases slightly while the emission spectrum exhibits a red shift.[24] ϕ_f of 4-AP decreases from 0.73 in dioxane ($E_T(30) = 36$) to 0.63 in acetonitrile ($E_T(30) = 45.3$), and the τ_f decreases from 15 to 14 ns while the emission maximum shifts from 435 nm in dioxane to 458 nm in acetonitrile.[24] In protic solvent, however, the emission quantum yield, lifetime, and emission energy decrease markedly. For instance, in *tert*-butanol ($E_T(30) = 43.5$), which is less polar than acetonitrile, the ϕ_f is only 0.18, which is 3.5 times smaller compared to that in acetonitrile, while the emission maximum exhibits a huge red shift of 43 nm compared to acetonitrile to 501 nm.[24] The 70-times reduction in ϕ_f of 4-AP in going from dioxane to water is also accompanied by a 12-fold reduction in the lifetime from 15 ns in dioxane to 1.2 ns in water. These facts indicate that the nature of the emitting state of 4-AP in the protic solvents is distinctly different from that in the aprotic solvents. Following Harju et al.[12] and Ware et al.,[16] we assign the emitting state of 4-AP in protic solvents to the proton-transferred species **II** (Scheme 1). The main reason for not observing a rise time of the emission band of the proton-transferred species **II** of 4-AP at long wavelengths in neat water in a picosecond setup by Harju et al.[12] and in the present study is the fact that such a proton transfer process among hydrogen-bonded systems occurs on the time scale of 100 fs[13] and hence is too fast to be detected in a picosecond setup. In the solvation dynamics study in reverse micelles, we are, thus, studying solvation of the proton-transferred species **II**. The marked decrease of the emission quantum yield of 4-AP in neat water compared to that in dioxane may be attributed to the reduction of the S_1-S_0 gap by about 5000 cm^{-1} in water relative to dioxane and the consequent enhancement of the nonradiative rates.[18]

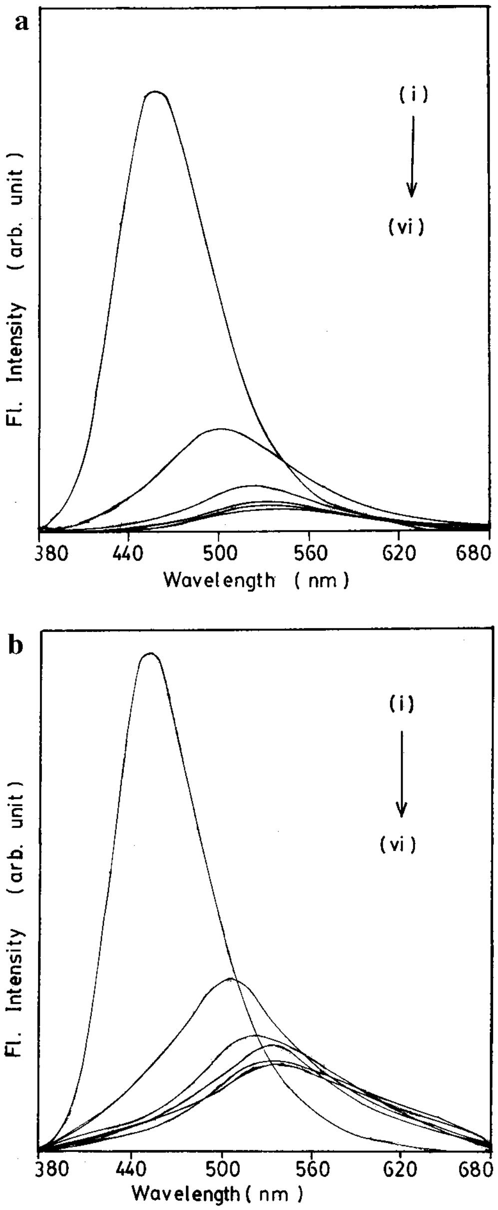

Figure 3. Emission spectra of 4 × 10^{-5} M 4-AP in AOT reverse micelles using (a) water, (i) $w_0 = 0$, (ii) $w_0 = 2$, (iii) $w_0 = 4$, (iv) $w_0 = 8$, (v) $w_0 = 12$, and (vi) $w_0 = 32$; (b) D_2O, (i) $w_0 = 0$, (ii) $w_0 = 2$, (iii) $w_0 = 4$, (iv) $w_0 = 8$, (v) $w_0 = 12$, and (vi) $w_0 = 32$.

The most significant finding of the present work is the nearly 4-fold increase in the lifetime and quantum yield of 4-AP in neat D_2O compared to water in neat solvents as well as in reverse micelles and the deceleration of the solvation dynamics of 4-AP in reverse micelles in the presence of D_2O by a factor of 1.5 compared to that in water. The deuterium isotope effect on the emission quantum yield and lifetime in neat water and in reverse micelles can be explained in terms of the model proposed in the case of 7-azaindole by Petrich et al.[9] 4-AP undergoes rapid exchange of the acidic imide proton with deuterium in deuterated solvents.[12] Among the different vibrational modes of 4-AP, the N−H stretching mode of the imide group has the highest frequency. It is well-known that in the $S_1 \rightarrow S_0$ nonradiative internal conversion (IC) processes the highest frequency mode (i.e. the N−H stretch in this case) acts as the acceptor mode.[18] On deuteration of the imide proton, the frequency of the N−D stretch becomes much less, and this causes considerable retardation in the nonradiative $S_1 \rightarrow S_0$

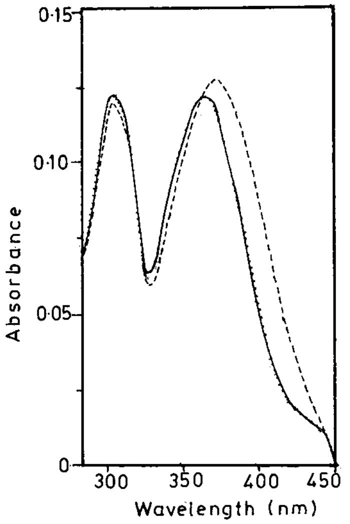

Figure 4. Absorption spectra of 4 × 10^{-5} M 4-AP in AOT reverse micelles using water: (i) $w_0 = 0$ (—); (ii) $w_0 = 12$ (- - -).

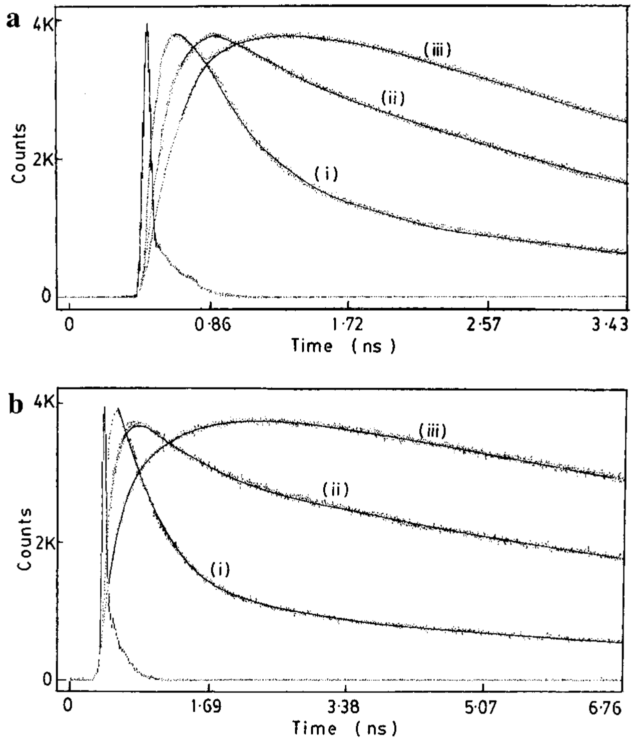

Figure 5. Fluorescence decays of 4 × 10^{-5} M 4-AP in AOT reverse micelles in the case of (a) water, $w_0 = 12$, at (i) 460, (ii) 500, and (iii) 645 nm; (b) D_2O, $w_0 = 12$, at (i) 460, (ii) 500, and (iii) 660 nm.

transitions.[18] Thus the enhancement of the emission quantum yield and lifetime of 4-AP in D_2O, compared to water, both in neat solvents as well as in reverse micelles may be ascribed to the slower $S_1 \rightarrow S_0$ nonradiative IC processes in the presence of D_2O. It may be mentioned that the nearly 4-fold deuterium isotope effect on emission intensity and lifetime in neat water and the 3-fold isotope effect in reverse micelles are similar in magnitude to the 3−20-fold deuterium isotope effects on nonradiative processes reported in the literature.[9,18]

The retardation of the solvation dynamics of 4-AP inside the water pool of the reverse micelles compared to the femtosecond relaxation in ordinary bulk water reiterates the fact that the highly structured water molecules present inside the pool are much slower than bulk water.[2f,4d,14,15,19] It may be noted that the emission energy, quantum yield, and lifetime of 4-AP also indicate that the water pool is distinctly less polar than ordinary water. From Table 2 it is evident that the solvation dynamics of 4-AP in reverse micelles at $w_0 = 12$ is dominated by a component of 340 ps in the case of H_2O and 500 ps for D_2O. The observation that the solvation dynamics inside the water pool is 1.5 times slower in the presence of D_2O (500 ps) compared to that in the presence of water (340 ps) can be explained in terms of the reported deuterium isotope effect on the solvation dynamics and electron transfer rates of organic molecules[2e,6−8] and the properties of D_2O.[22] Because of its higher mass and consequently, lower frequency of vibrations, D_2O is a more compact, denser, and slower liquid compared to water.[22] The dielectric relaxation time of D_2O (10.4 ps) is 25% slower than that of H_2O (8.3 ps).[22b] In the case of the strongly

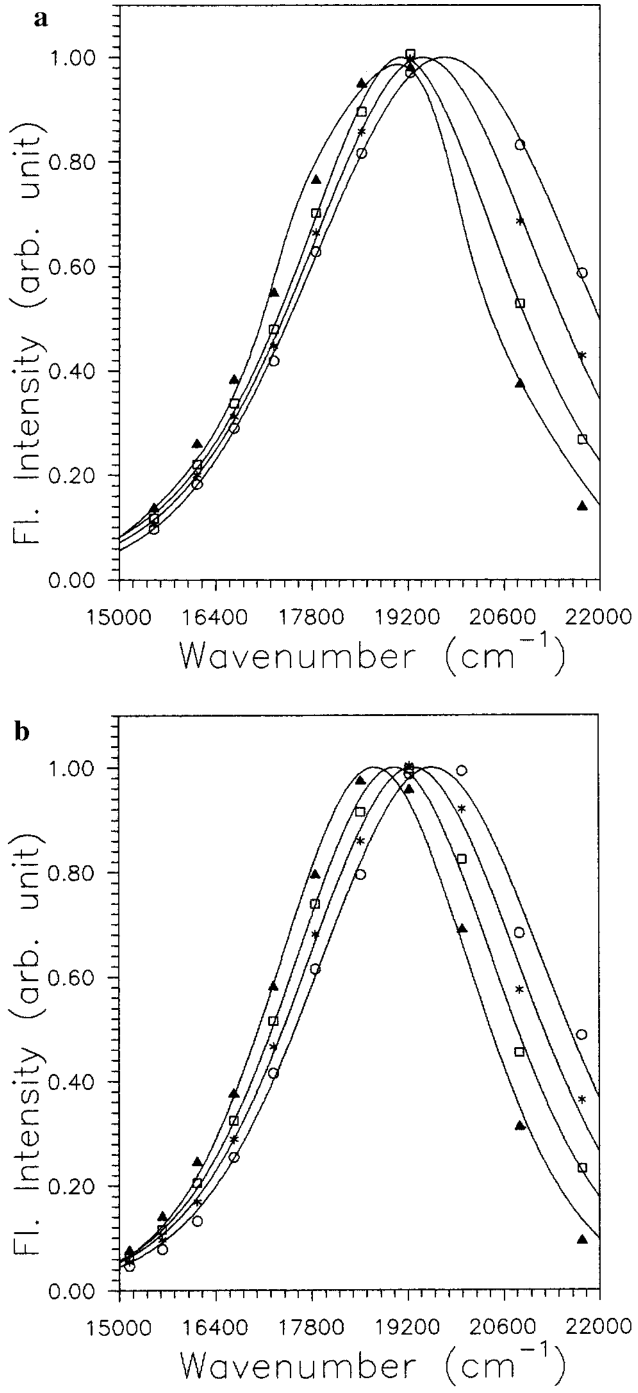

Figure 6. Time-resolved emission spectra of 4 × 10^{-5} M 4-AP in AOT reverse micelles ($w_0 = 12$) using (a) water at (i) 0 (○), (ii) 150 (*) (iii) 425 (□), and (iv) 1600 (▲) ps; (b) D_2O at (i) 0 (○), (ii) 200 (*), (iii) 525 (□), and (iv) 1800 (▲) ps.

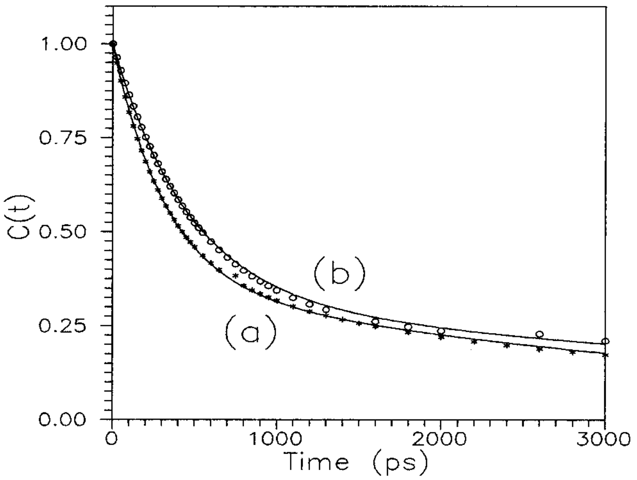

Figure 7. Decay of the solvent response function, *C*(*t*) of 4-AP in AOT reverse micelles using (a) water (*) and (b) D_2O (○).

TABLE 2: Decay Characteristics of *C*(*t*) of 4-AP in 0.09 M AOT in *n*-Heptane at $w_0 = 12$

	$\Delta\nu$ (cm^{-1})	a_1	τ_1 (ps)[a]	a_2	τ_1 (ns)[b]	$\langle\tau\rangle$[c] (ns)
H_2O	1251	0.67	340	0.33	5	1.93
D_2O	1116	0.67	500	0.33	6	2.33

[a] ±20 ps. [b] ±0.5 ns. [c] $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$.

hydrogen-bonded solute−solvent systems, such as the 4-AP: water system, the motion of the solvent molecules in the first solvation shell around the solute involves the hydrogen bonds. The water (or D_2O) molecules inside the water pool are highly structured and involve extensive hydrogen bonds.[19] Replacement of the proton (of both the imide and the solvents) by deuterium in the case of D_2O is expected to slow down the solvation dynamics significantly. This is responsible for the slower solvent relaxation time in the case of D_2O inside the microemulsions at $w_0 = 12$. It may be mentioned that the 50% deuterium isotope effect on the solvation dynamics of 4-AP in reverse micelles observed in the present study is similar in magnitude to the 40% deuterium isotope effect on ultrafast back electron transfer in mixed valence compounds in D_2O reported by Barbara et al.[7a] and the 35% slowing down of the appearance time of solvated electron reported by Eisenthal in D_2O.[6a] However for alcoholic solvents a lower value of deuterium isotope effect was reported by Barbara et al.[7b] and Yoshihara et al.[8] It appears that quantitative analysis of the present result can be done using a proper combination of the multishell continuum model proposed for reverse micelles by Bagchi et al.[2f] and the theoretical model proposed by the same group[2e] taking into account the effect of the low-frequency vibration (or libration) on the ultrafast solvation dynamics in neat water. Unfortunately, information on several important parameters are missing. For instance, data on the dielectric relaxation times of the water molecules in microemulsions is available only up to a frequency of 10 MHz corresponding to 100 ns,[21] which is inadequate to describe the picosecond dynamics reported in the present work. Secondly, low-frequency intermolecular vibrations play a major role in ultrafast solvation dynamics as discussed by Bagchi et al.[2e] However, data on far IR frequencies in reverse micellar system as well as their isotope dependence are also unavailable. Evidently, when these data become available one could follow the models proposed by Bagchi et al. for neat water[2e] and reverse micelles[2f] to explain the present results.

Nevertheless, the results may be explained semiquantitatively as follows. The reverse micelles contain broadly two kinds of water.[2f,15a,19−22] The water molecules close to the surfactants are very strongly held by the ionic head groups of surfactants and hence are described as bound water, while those water molecules near the center of the pool are more or less free. Whenever there is a combination of free and bound water molecules (such as in the present case or in aqueous protein solutions, etc.), one usually observes two different time constants in the dielectric relaxation with one of the time constants in the picosecond time scale (about 10 ps) and the other in the nanosecond time domain (around 10 ns).[23] The effective dielectric constant of the water pool in reverse micelles as determined by the position of emission maxima of 4-AP in this work and also using different probes in earlier works[17] is close to that of alcohol i.e. around 30−40. If one makes a reasonable assumption that the infinite frequency dielectric constant of water in reverse micelles is same as that in water, i.e., 5, the longitudinal relaxation time ($\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$) would be approximately 10/6 ps = 1.67 ps corresponding to the fast component of the dielectric relaxation and 1.67 ns corresponding to the slower relaxation time. Obviously with our apparatus (resolution ~40 ps) we missed the fast component of 1.67 ps. However the average relaxation time $\langle\tau\rangle$, Table 2) observed by us is very close to the value of 1.67 ns predicted by this simple calculation.[25] However one should note that the average solvation times also exhibit a 20% deuterium isotope effect.

5. Conclusion

The marked decrease of quantum yield and lifetime of 4-AP in protic solvents appears to be due to ultrafast solvent-mediated proton transfer.[12,16] The present work demonstrates significant deuterium isotope effect on the emission properties of 4-AP in neat water and in reverse micelles and also on its solvation dynamics in reverse micelles. Compared to that in H_2O, the lifetime and quantum yield of 4-AP in D_2O increase nearly 4.5 times. In reverse micelles, the solvation dynamics is found to occur on the nanosecond time scale for both H_2O and D_2O. However, the solvation dynamics in the case of D_2O is observed to be slower than that for H_2O. The very strong interaction of 4-AP with protic solvents highlighted in the present work did not receive adequate attention in earlier works. Evidently, 4-AP provides new testing grounds for studying femtosecond hydrogen bond dynamics[10a] in neat liquids, in organized media, and in solvent clusters in jets.

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