Excited-State Proton Transfer Behavior of 7-Hydroxy-4-methylcoumarin in AOT Reverse Micelles

Sharmistha Dutta Choudhury,* Sukhendu Nath, and Haridas Pal*

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received: January 16, 2008; Revised Manuscript Received: April 16, 2008

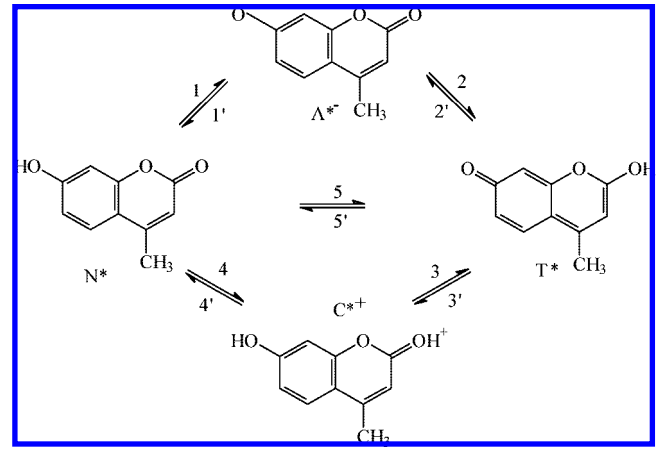
The excited-state proton transfer and phototautomerization of 7-hydroxy-4-methylcoumarin (7H4MC) dye has been studied in the confined water pools of AOT reverse micelles using steady-state and time-resolved fluorescence measurements. In the "dry" reverse micelles ([water]/[AOT], $w_0 = 0$), only the neutral form of the dye is present both in the ground and the excited states. At higher w_0 values, three prototropic forms, namely, neutral, anionic, and tautomeric, can be identified in the excited state, although only the neutral form of the dye is present in the ground state. From steady-state fluorescence results and time-resolved area-normalized emission spectra (TRANES), it is indicated that the anionic and tautomeric forms of the dye are the excited-state reaction products and that they arise apparently independently from the excited neutral form of the dye. In bulk water, however, there is no evidence of the tautomeric species and only the anionic form is observed in the excited state. The fluorescence quenching results of the three forms of 7H4MC by the different quenchers, potassium iodide, aniline, and *N*,*N*-dimethylaniline, suggest that the distribution of 7H4MC molecules in the reverse micelles is not diverse but that the different prototropic forms arise from the same population of the excited dye in the interfacial region.

1. Introduction

Proton and hydrogen atom transfer reactions play an important role in photochemistry and photobiology.[1–7] The acid−base characteristics of many molecules are significantly modulated upon electronic excitation, and different pathways of excited-state proton transfer reactions have been encountered in the literature.[6–13] A few to mention are intramolecular proton transfer via H-bonded vicinal groups, distal proton transfer by proton relay involving solvent H-bonded bridges, concerted biprotonic transfer within a doubly H-bonded dimer, coupled proton and electron transfer, or intermolecular double proton transfer with solvent molecules.[6–13]

The coumarin derivative, 7-hydroxy-4-methylcoumarin (7H4MC), has attracted considerable attention in relation to its excited-state proton transfer behavior because of its complex pH dependent fluorescence properties.[14–31] In the ground state, 7H4MC is mildly acidic ($pK_a \sim 7.7$), but on photoexcitation, 7H4MC renders strongly acidic ($pK_a^* \sim 0.45$) behavior.[14–17] Because of its remarkable photophysical properties and its utility in areas like fluorescent indicators for enzyme catalysis[18] and construction of acidity tunable dye lasers,[19–21] 7H4MC has been widely investigated experimentally[14–21,24–31] and theoretically.[22,23] Depending on the solvent and pH, multiple fluorescence spectra can be observed for 7H4MC corresponding to the excited neutral (N*, ∼380 nm), anionic (A*, ∼450 nm), cationic (C*, ∼412 nm), and tautomeric (T*, ∼480 nm) forms.[14,15,24] In the ground state, however, only the neutral, cationic, and the anionic forms can be identified at suitable pH conditions. The tautomeric form is an excited-state reaction product and arises because of proton transfer between the spatially separated acidic (OH) and basic (C═O) groups of 7H4MC. The prototropic transformations of 7H4MC have been quite extensively studied in aqueous and aqueous ethanolic solutions[14,15,25–30] and in the presence of

SCHEME 1: General Reaction Scheme for the Photoexcited States of 7H4MC[a]



[a] N*, A*−, C*+, and T* represent the excited states of the neutral, anionic, cationic, and tautomeric forms. Paths 1 and 5 are indicated to be predominant in AOT reverse micelles.

β-cyclodextrin hosts[31] by means of steady-state and time-resolved fluorescence measurements. The phototautomerization process in the excited 7H4MC dye has been suggested to take place either through "dissociative" two-step pathways[27,30] involving the anionic or cationic species as the intermediates or through a "nondissociative" one-step concerted proton transfer[14,15] from the hydroxyl to the carbonyl site via hydrogen-bonded solvent molecules. The different prototropic transformations that may be possible in 7H4MC dye are generally presented by a unified Scheme 1. Although much effort has been devoted to unravel the structural and mechanistic details of the excited-state species in different media, no investigations have been carried out on the excited-state proton transfer and phototautomerization behavior of 7H4MC in the confined water pools of reverse micelles.

* To whom correspondence should be addressed. Fax: 91-22-25505151/25519613; e-mail: sharmidc@barc.gov.in (S.D.C.) and hpal@barc.gov.in (H.P.).

10.1021/jp8004019 CCC: $40.75
Published on Web 06/05/2008

Reverse micelles are spherical aggregates of surfactants dispersed in a nonpolar medium and consist of an inner water pool surrounded by a layer of surfactant molecules with their polar head groups oriented toward the inner water pool and the hydrocarbon chains oriented toward the bulk nonpolar medium outside. The average size of the reverse micelles is dependent on the amount of solubilized water and is expressed semiqualitatively by the water-to-surfactant molar ratio, $w_0 = [H_2O]/[\text{surfactant}]$.[32–35]The properties of the water encapsulated inside the reverse micelles differ markedly from those of bulk water. At least two types of water populations are expected inside the water pool: a shell of "bound" water molecules, which are strongly associated (by hydrogen bonding) with the polar head groups of the surfactants, and the "free" water molecules, which develop deep inside the core of the water pool on increasing w_0 as the hydration of the surfactant polar head groups becomes saturated.[35] On increasing w_0, the extent of free water in a reverse micelle increases over the bound water. Moreover, in reverse micelles, the bound and free water not only coexist but also exchange quite rapidly. Recent ultrafast infrared experiments by Moilanen and co-workers in the water nanopools of reverse micelles have revealed that the shell of water in the interfacial region has a different structure from that of bulk water.[36,37] The hydrogen bond network couples the water in the shell to the water in the core of the reverse micelles, and this coupled network has distinctly slower dynamics compared to that of bulk water. They have also demonstrated that confinement by an interface to form a nanoscopic water pool is the primary factor governing the dynamics of nanoscopic water rather than the presence of charged groups at the interface.[37] Hence, it is very interesting to understand how the modified hydrogen bond network of the confined water molecules inside reverse micelles can influence or modulate the proton transfer processes of a solubilized molecule. A variety of studies have been reported in the literature on this aspect.[38–46] Douhal et al. have observed three regions in the behavior of the confined water molecules within reverse micelles using a proton transfer probe.[46] The first region is observed at w_0 values less than 2, where the shell of water bound to the surfactant head groups is mainly formed and the confinement effects dominate the relaxation dynamics of the water molecules. The second region is observed at w_0 values from 2 to 5 where the core (water pool) of the reverse micelle is formed and its water content gradually increases changing the relaxation dynamics. The third region is found to lie beyond $w_0 = 5$ where the water pool is fully grown and where there is no further change in the observed relaxation dynamics. These studies are very significant because water pools inside reverse micelles are considered to mimic the biological water, and it is of current interest to elucidate the role of water in many biological functions and to understand small and fast structural changes in the water network which are decisive events in proton or H-atom transfer reactions. In this paper, we report the excited-state proton transfer and phototautomerizaton behavior of 7H4MC in sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles at various water pool sizes (w_0) using steady-state and time-resolved fluorescence measurements in an effort to shed some light on how the complex photophysical processes of this prototropic molecule is modified in a confined water environment.

2. Materials and Methods

The coumarin dye, 7H4MC, was obtained from Schuchardt München and was purified by recrystallization from acetonitrile. Aniline (AN) and *N*,*N*-dimethylaniline (DMAN) were obtained from Spectrochem (India) and were purified by vacuum distillation just before use. Potassium iodide (KI) from E-Merck was used as received. AOT was obtained from John Baker and was dried in vacuum prior to use. Spectroscopic grade heptane from Spectrochem (India) was used without further purification. Nanopure water with conductivity less than 0.1 μS cm^{-1} was obtained from a Millipore Elix3/A10 water purification system and was systematically added to prepare reverse micelle solutions with desired w_0 values. Since the ground state pK_a of 7H4MC is reported to be around 7.7, the pH of water was maintained at 5 to ensure that there is no preexistence of the anionic form of 7H4MC in the micellar solution. The AOT concentration was kept at 0.2 mol dm^{-3} throughout. The concentration of 7H4MC was kept much lower ($\sim 10-20 \times 10^{-6}$ mol dm^{-3}) than the reverse micelle concentrations ($\sim 0.1-1.7 \times 10^{-3}$ mol dm^{-3}) at all w_0 so that no more than one dye molecule could occupy an individual micelle. Freshly prepared solutions were used throughout.

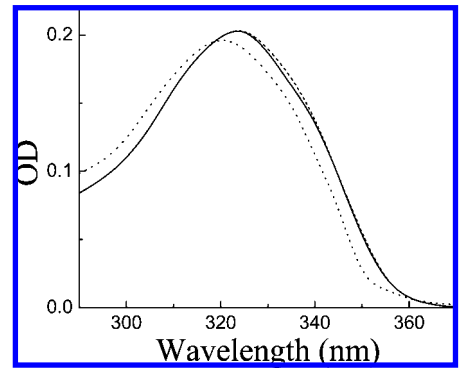


Figure 1. Absorption spectra of 7H4MC in water at pH 5 (•••) and in AOT reverse micelles with $w_0 = 0$ (—) and $w_0 = 40$ (---).

A Shimadzu UV−vis spectrophotometer (model UV-160A) was used for recording the absorption spectra, and a Hitachi spectrofluorimeter (F-4010) was used for measuring the steady-state fluorescence spectra. The time-resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer (Edinburgh Instruments, Model 199). A hydrogen-filled coaxial flash lamp having pulse duration around 1 ns (fwhm) was used as the excitation source. The fluorescence decay curves were analyzed by a reconvolution procedure using a proper instrument response function obtained by substituting the sample cell with a light scatterer. The decay curves were fitted by considering either single exponential or multiexponential decay functions. The quality of the fits was judged from the reduced chi-square (χ_r^2) values and from the distribution of the weighted residuals among the data channels. For all the accepted fits, the χ_r^2 values were close to unity and the distribution of the weighted residuals was quite random among the data channels.[47] For the construction of time-resolved area-normalized emission spectra (TRANES), fluorescence decays were recorded for 7H4MC in AOT reverse micelles over the entire emission spectrum of the dye at 10 nm intervals. These fluorescence decays were fitted to a three-exponential decay function, and the fitted decays were scaled with the steady-state fluorescence intensities following the usual procedure.[48] The time-resolved emission spectra thus generated were fitted to cubic spline functions[49] and were normalized to unit area to generate the TRANES.[50,51]

3. Results and Discussion

Figure 1 shows the absorption spectra of 7H4MC in water at pH 5 and in AOT reverse micelles at different w_0 values. In all the cases, only the neutral form of the dye is observed with

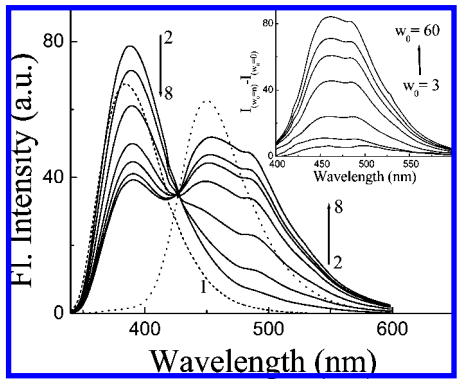


Figure 2. Fluorescence emission spectra of 7H4MC in water (•••) and AOT reverse micelles at (1) $w_0 = 0$ (---), (2) $w_0 = 3$, (3) $w_0 = 5$, (4) $w_0 = 10$, (5) $w_0 = 20$, (6) $w_0 = 30$, (7) $w_0 = 40$, and (8) $w_0 = 60$ on excitation at 320 nm. The inset shows the difference spectra of the emission from reverse micelles at higher w_0 values ($w_0 = 3-60$) with respect to the emission from the reverse micelles with $w_0 = 0$ after normalization.

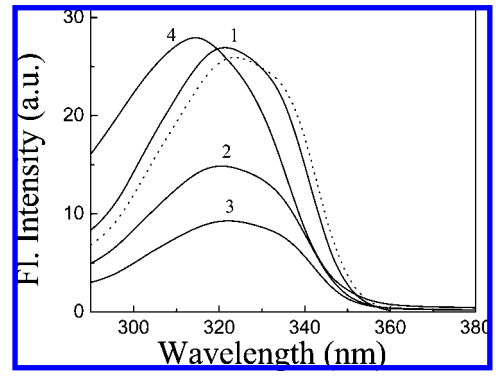


Figure 3. Excitation spectra of 7H4MC in AOT reverse micelles at $w_0 = 0$ monitored for 380 nm emission (•••) and at $w_0 = 10$ monitored for (1) 380, (2) 450, and (3) 490 nm emission and (4) in bulk water monitored for the 450 nm emission.

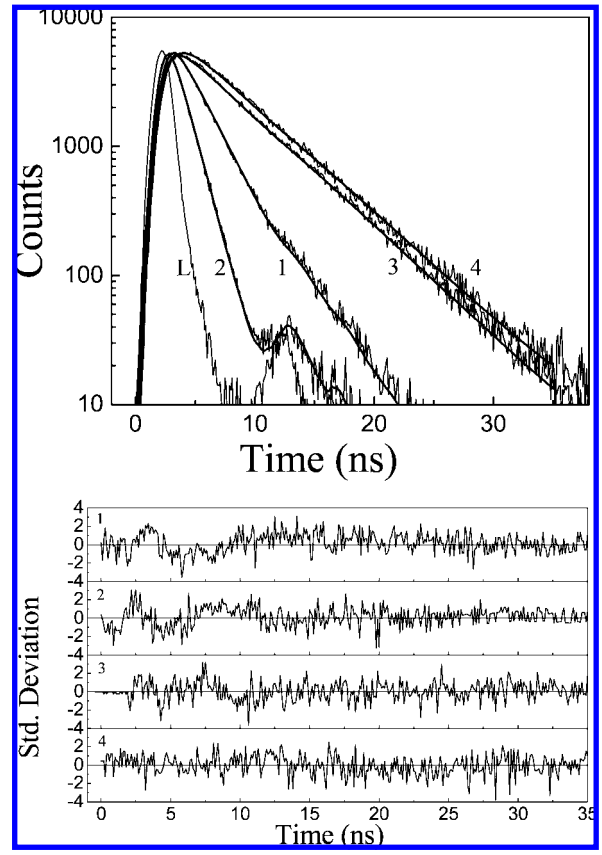


Figure 4. Time-resolved fluorescence decays of 7H4MC in AOT reverse micelles monitored at (1) 380 nm, $w_0 = 0$, (2) 370 nm, $w_0 = 20$, (3) 450 nm, $w_0 = 20$, and (4) 530 nm, $w_0 = 20$. *L* is the instrument response function. The excitation wavelength was 320 nm in all cases. Lower panel shows the distribution of the weighted residuals among the data channels for the respective fits, 1–4.

maximum around 320 nm in water[14] and around 324 nm in AOT reverse micelles. The slight red shift in AOT reverse micelles is similar to that reported in alcohols as compared to that in water and has been attributed to greater stabilization of the π-electron system of 7H4MC in the ground state than in the excited state by specific H-bonding interactions.[14] No spectral changes were observed on addition of water at pH 5 to the dry ($w_0 = 0$) reverse micelles. Hence, only the neutral form of the dye exists in the ground state. Since the solubility of 7H4MC in heptane is negligible but is enhanced significantly in the presence of AOT, it may be expected that 7H4MC resides at the interfacial region of the reverse micelles toward the water pool.

The fluorescence spectrum of 7H4MC in dry AOT reverse micelles shows a single emission peak with maximum around 383 nm, which corresponds to the emission from the excited neutral form (N*) of the dye.[14,15,24] With the first addition of water ($w_0 = 3$) to the reverse micelles, there is an enhancement and a small red shift (~5 nm) of the emission from the neutral form at around 388 nm with the appearance of a hump in the higher wavelength region around 480 nm. With subsequent increase in the w_0 values, two humps are clearly observed in addition to the emission from the neutral form: one around 458 nm which corresponds to the emission from the anionic form (A*) and another around 487 nm which corresponds to the emission from the tautomeric form (T*) of the dye.[14,15,24] The intensity of emission from these two species increases at the cost of emission from the neutral form of the dye, and an isoemissive point is observed at 426 nm. In pure water at this pH condition (pH 5), however, only the anionic form with emission around 450 nm is observed and there is no evidence of emission from the neutral or the tautomeric form. The formation of the anionic species in water is consistent with the excited-state $pK_a^* \sim 0.45$ for 7H4MC. The emission spectra of 7H4MC in water and AOT reverse micelles at different w_0 values are shown in Figure 2. The inset of Figure 2 shows the difference emission spectra of 7H4MC in AOT reverse micelles with higher w_0 with respect to the normalized emission in dry reverse micelles, and it is quite clear that both the anionic and the tautomeric forms appear simultaneously at all the w_0 values. The ratio of the two species also remains almost constant at all w_0 values. It is obvious that both these species are excited-state reaction products since there is no evidence of these forms in the absorption spectra of 7H4MC in AOT reverse micelles. The excitation spectra of the dye in water and in AOT at different w_0 values collected at emission wavelengths of 380, 450, and 480 nm (Figure 3) show only one peak around 320 nm corresponding to the neutral form of 7H4MC, which confirms that the neutral form is exclusively present in the ground state. The question remains as to whether both the anionic and the tautomeric forms arise concurrently from the excited neutral form or whether the tautomeric form arises subsequent to the formation of the anionic form, which is a result of the fast excited-state proton transfer from 7H4MC to the solvent water. The appearance of an isoemissive point in the emission spectra suggests that the simultaneous formation of the anionic and the

TABLE 1: Decay Parameters[a] for the Different Prototropic Forms of 7H4MC in AOT Reverse Micelles[b]

	neutral[c] (370/380 nm)			anion[c] (450 nm)					tautomer[c] (530 nm)				
w_0	a_1	τ_1 (ns)	χ_r^2	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ_r^2	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ_r^2
0	0.097	2.34	1.03										
20	0.128	1.20	1.11	−0.013	1.00	0.06	4.89	1.07	−0.091	1.01	0.102	5.00	1.10

[a] The intensity decays were fitted according to $I(t) = \sum_i a_i \exp(-t/\tau_i)$ for single and biexponential decays. [b] The neutral form decay was monitored on the blue side and the tautomer decay was monitored on the red side to minimize contribution from the anionic form. [c] The error limit in the lifetime values are ±0.1 ns.

tautomeric forms at constant proportions from the excited neutral form could be more likely. As mentioned earlier, since the proton-donating group (OH) and the proton-accepting group (C═O) of 7H4MC are separated from each other, a direct transfer of the proton is not possible and the transfer has to take place through a solvent bridge. Very recently, Georgieva et al. have studied the excited-state proton transfer in 7H4MC along a H-bonded water wire of three water molecules bridging the proton donor and acceptor groups using theoretical calculations.[23] Considering that the number of water molecules in an AOT reverse micelle with a w_0 value of 3 is about 100,[52] it is obvious that sufficient water molecules would be available for bridging the OH and C═O groups of 7H4MC even at low w_0 values.

Proton transfer is dramatically affected by the ability of the solvent molecules to reorganize and solvate the ion pair formed. Hence, in bulk water, although the phototautomerization process should be possible for 7H4MC, because of the greater stabilization of the hydrated proton and the corresponding anionic form by solvation, the equilibrium probably shifts in favor of the anionic form rather than the tautomeric form. Consequently, only the anionic form can be observed in bulk water under similar pH conditions. In the confined environment of the reverse micellar interface, this preferential stabilization of the anionic form over the tautomeric form would be less because of a reduction in the number of available water molecules or the partially broken hydrogen-bonded network structure of water encapsulated within the reverse micelle. Hence, both the prototropic forms can be formed in reasonable proportions and can be detected in the fluorescence emission spectra in reverse micelles. The fact that both the forms persist even at very high w_0 values further supports that 7H4MC molecules are actually present at the surfactant−water interfacial region of the reverse micelles rather than deep inside the water pool where the properties of the water molecules are more like that of bulk water especially at high w_0 values. In contrast to AOT reverse micelles, where both the anionic and the tautomeric forms can be observed at all w_0 values, in ethanol−water mixed solvent, only the tautomer emission is observed at lower water concentrations and the anionic form appears only when the water concentration is made significantly high, about 4.5 mol dm^{-3}.[27] Another aspect that needs to be considered in the present case is the high negative charge density of the AOT reverse micellar interface and the effect of the Na^+ counterions. It has been proposed that at lower w_0 values the counterions have lower mobility and are distributed between the fixed head group charges with the probability of finding a free ion increasing with w_0.[53] Cohen et al. have also observed that most of the Na^+ counterions are confined to a small layer adjacent to the negatively charged sulfonate groups of AOT.[45] For 7H4MC dye, however, formation of the anionic species is observed at all w_o values irrespective of the presence of the negatively charged interface and the screening effect of the counterions. Thus, the observed prototropic features are related more to the modified water structure within the reverse micelle water pool than to the nature of the interface or the counterions.

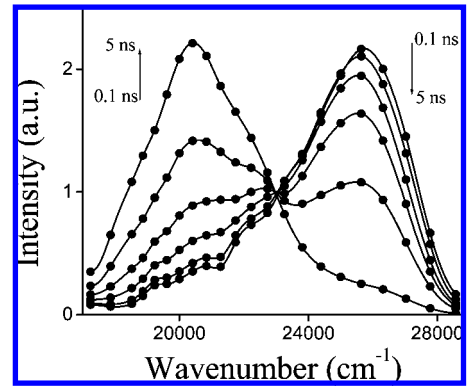


Figure 5. TRANES for 7H4MC in AOT reverse micelle with w_0 = 20 at 0.1, 0.2, 0.5, 1, 2, and 5 ns showing an isoemissive point at 23 000 cm^{-1}.

Fluorescence lifetimes for the different prototropic forms were monitored at 380 nm for the dry reverse micelle and at 370 (to avoid overlap), 450, and 510 nm in AOT reverse micelles with w_0 = 20. The decay traces along with the residuals are presented in Figure 4, and the corresponding data are presented in Table 1. It is clearly seen that on addition of water, the lifetime of the neutral species (~380 nm) decreases because of the participation of the processes leading to the formation of the anionic and the tautomeric species in the excited state. Accordingly, a growth component is clearly observed in the fluorescence transients at 450 and 510 nm, which effectively corresponds to the decay time of the neutral species at 380 nm. The single exponential decay of the neutral form at 370 nm also indicates that the back reactions from the excited anionic and tautomeric forms to the excited neutral form are either negligible or not occurring at all within the time resolution (1 ns) of the present instrument. Because of strong overlap of the emission spectra, the actual lifetimes of the anionic and the tautomeric forms of the dye could not be characterized very definitely though the results indicate that they could be almost in the similar range of about 5.00 ± 0.1 ns (cf. Table 1). In dioxane−water mixed solvents, de Melo and Macanita have made an estimation for the fluorescence lifetimes of the neutral, anionic, and tautomeric forms of 7H4MC as 2.60, 5.20, and 5.45 ns, respectively,[25] which are almost in the similar range as measured in the present systems.

To have a better idea about the different emissive species present in the reverse micellar systems and to understand the correlation between them, we also performed the TRANES analysis. TRANES is suggested to be an elegant model free method to identify the formation of intermediates in the excited-state processes like electron or proton transfer, excimer/exciplex formation, and solvent relaxation.[50,51] The occurrence of N number of isoemissive points in TRANES generally indicates the presence of $N + 1$ emissive species in the system, which

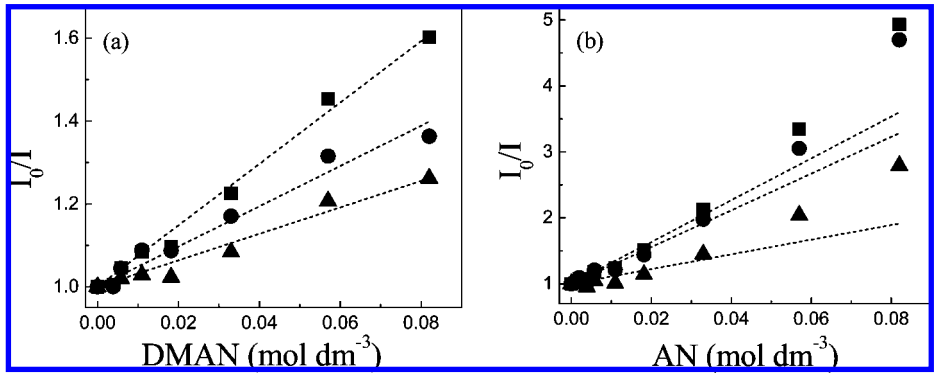


Figure 6. Stern-Volmer plots for the fluorescence quenching of 7H4MC by (a) DMAN and (b) AN monitored at 390 nm (●) for the neutral form, at 450 nm (▲) for the anionic form, and at 490 nm (■) for the tautomeric form in AOT reverse micelles at $w_0 = 20$.

TABLE 2: Stern-Volmer Quenching Constants, K_{SV}, for the Different Forms of 7H4MC in AOT Reverse Micelles at $w_0 = 20$

	K_{SV}, dm^3 mol^{-1}		
quencher	neutral	anion	tautomer
AN	27	11	31
DMAN	5	3	7

may or may not be kinetically coupled. However, for three independent species, two clear isoemissive points can be observed in different time intervals only if their fluorescence lifetimes and spectral peaks are significantly different from each other.[51] The TRANES for 7H4MC in AOT reverse micelles at $w_0 = 20$ are presented in Figure 5. Only one isoemissive point is observed in the present case, although the presence of three emissive excited-state species is clearly indicated for the present systems from the steady-state and time-resolved emission studies. Such an observation in TRANES could be due to the similar fluorescence lifetimes and strong overlapping of the emission spectra of the anionic and tautomeric forms. Further, if both the anionic and the tautomeric forms are considered to arise simultaneously from the same excited neutral species, following two parallel channels, then only one isoemissive point may be expected as observed in the TRANES: the emission from the short-lived neutral form dominating at the shorter times and the emission from both the anionic and the tautomeric forms dominating at the longer times. However, considering the limited time resolution of the instrument, it is difficult to comment further on the exact dynamics of formation of the different prototropic forms.

Another question that arises in the present context is whether there is some distribution of 7H4MC within the different regions of the reverse micelle and if so whether both the anionic and the tautomeric forms arise from the same population of excited neutral dyes or from those present in different locations. Bardez et al. investigated the localization of different excited-state proton donors such as 2-naphthol and sulfonated 2-naphthol derivatives in various regions of reverse micelles and the corresponding ability of the microenvironment to accept a proton.[43] It was found that charged photoacids like 2-naphthol sulfonato derivatives were localized within the water pool of reverse micelles in the ground state and showed proton transfer activity, whereas no deprotonation could be observed for 2-naphthol which is located in the hydrophobic interface irrespective of the w_0 value. In the present study, since 7H4MC is a hydrophilic neutral molecule, it will be solubilized in the interfacial region of the reverse micelle toward the water pool. In case of a distribution in the dye localization sites, it may be possible that the tautomeric species arise from the 7H4MC molecules located in the interfacial region of the AOT reverse micelles and that the anionic species arise from the 7H4MC molecules which are located deep inside the water pool where the anion could be better stabilized by solvation. To resolve this issue, we studied the fluorescence quenching of 7H4MC in AOT reverse micelles at $w_0 = 20$ by three different quenchers: DMAN, AN, and KI. The quenching of different coumarin derivatives with aromatic amines has been studied previously and is explained because of electron transfer from the amines to the excited coumarin dyes.[54,55] The heptane:water partition coefficients of DMAN and AN are 251 and 1, respectively, so DMAN is expected to preferentially quench those 7H4MC molecules that are present in the heptane-like phase and AN is expected to quench the dye molecules present in both the heptane-like and the waterlike phases.[56] The quencher KI, on the other hand, should quench the 7H4MC molecules present deep inside the water pool of the reverse micelles. Figure 6a and b shows the Stern-Volmer plots according to eq 1 for the quenching of 7H4MC emission by DMAN and AN monitored at 380, 450, and 480 nm corresponding to the three prototropic forms of the dye.

$$\frac{I_0}{I} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \qquad (1)$$

The quenching by DMAN is seen to be very poor whereas an upward curvature is observed in the Stern-Volmer (SV) plots for quenching by AN (Figure 6b). No quenching could be observed with KI within the concentration range that could be used in AOT reverse micelles (up to 8 mM). Quenching of the emission from the anionic form was, however, observed in the same concentration range of KI in bulk water. These results thus clearly suggest that 7H4MC is neither present in the heptane phase nor deep inside the water pool but is preferentially solubilized at the surfactant−water interfacial region of the reverse micelles where it can easily be accessed by the quencher-like AN. Moreover, because of the greater solubility of AN in the interfacial region, the preferential accumulation of AN in this region can cause significant static quenching at higher quencher concentrations leading to a positive deviation in the SV plots.[54,55] The SV constants, K_{SV}, determined from the linear portions of the SV plots for AN and DMAN are listed in Table 2. As mentioned earlier, the lifetimes of the anionic and tautomeric species could not be characterized definitely in the present case, and accordingly, the quenching constants, k_q, could also not be determined and ascribed unambiguously for either of the forms. Apparently, the quenching constants for the neutral and the tautomeric forms are more or less similar and seem to

be somewhat higher than the anionic form. The lower quenching rate for the anionic form as indicated from the present results could be either because of its less favorable redox potential for quenching by electron transfer or because of the migration of the anionic form somewhat deeper inside the water pool, following its formation, so that the quenching by AN/DMAN becomes less efficient. The present results, however, indicate that the anionic and the tautomeric forms arise from the same population of excited neutral 7H4MC dyes situated mainly in the interfacial region of the reverse micelles.

Conclusion

Prototropic properties of 7H4MC dye have been investigated in AOT reverse micelles using steady-state and time-resolved fluorescence studies. Observed results indicate that three prototropic forms of 7H4MC exist in the excited state and that all of them arise from the same neutral form of the excited dye solubilized at the interfacial region of the reverse micelles. The anionic species is formed by excited-state proton transfer from 7H4MC to water and the tautomeric species arises because of proton relay across a H-bonded water bridge between the C═O and OH groups of 7H4MC. This proposition is also supported by the observation of a single isoemissive point in the TRANES of the present system. The fact that both the anionic and the tautomeric forms persist even at high w_0 values, whereas only the anionic form is observed in bulk water, is an indication that the 7H4MC molecules mainly reside in the interfacial region of the reverse micelles where the properties of the water molecules are quite different than in bulk water. Formation of different prototropic species by the excited dye molecules localized in the interfacial region is also supported by the differential quenching rates observed with different quenchers having selective solubilization in the nonpolar heptane-like phase, in the interfacial region, and inside the water pool. Though our measurements are limited to nanosecond time scales, the results tentatively indicate that the tautomeric and anionic forms of 7H4MC evolve apparently independently from the excited neutral form of the dye in the confined environment of the reverse micelle. To the best of our knowledge, ours is the only report to demonstrate the multiple prototropic processes of excited 7H4MC dye in a reverse micelle.

Acknowledgment. We would like to acknowledge Dr. M. Kumbhakar for many fruitful discussions. We are also thankful to Dr. S. K. Sarkar, Head, RPCD and Dr. T. Mukherjee, Director, Chemistry Group, BARC, for their constant encouragement and support.

References and Notes

(1) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127.
(2) Formosinho, S. J.; Arnaut, L. G. *J. Photochem. Photobiol., A: Chem.* **1993**, *75*, 21.
(3) Chen, Y; Gai, F.; Petrich, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 10158.
(4) Lin, G. C.; Awad, E. S.; El-Sayed, M. A. *J. Phys. Chem.* **1991**, *95*, 10442.
(5) English, D. S.; Das, K.; Zenner, J. M.; Zhang, W.; Kraus, G. A.; Larock, R. C.; Petrich, J. W. *J. Phys. Chem. A* **1997**, *101*, 3235.
(6) Agmon, N. *J. Phys. Chem. A* **2005**, *109*, 13.
(7) Mohammed, O. F.; Pines, D.; Dryer, J.; Pines, E.; Nibbering, E. T. J. *Science* **2005**, *310*, 83.
(8) Balamurali, M. M.; Dogra, S. K. *Chem. Phys.* **2004**, *305*, 95.
(9) Ingham, K. C.; Abu-Elgheit, M.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1971**, *93*, 5023.
(10) Bardez, E.; Chatelain, A.; Larrey, B.; Valeur, B. *J. Phys. Chem.* **1994**, *98*, 237.
(11) Kim, T. G.; Lee, S. I.; Jang, D.; Kim, Y. *J. Phys. Chem.* **1995**, *99*, 12698.
(12) Nakagawa, T.; Kohtani, S.; Itoh, M. *J. Am. Chem. Soc.* **1995**, *117*, 7952.
(13) Tanner, C.; Manca, C.; Leutwyler, S. *Science* **2003**, *302*, 1736.
(14) Moriya, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 6.
(15) Moriya, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1873.
(16) Cohen, B.; Huppert, D. *J. Phys. Chem. A* **2001**, *105*, 7157.
(17) Cohen, B.; Huppert, D. *J. Phys. Chem. A* **2002**, *106*, 1946.
(18) Chen, R. F. *Anal. Lett.* **1968**, *1*, 423.
(19) Trozzolo, A. M.; Dienes, A.; Shank, C. V. *J. Am. Chem. Soc.* **1974**, *96*, 4699.
(20) Shank, C. V.; Dienes, A.; Trozzolo, A. M.; Myer, J. A. *Appl. Phys. Lett.* **1970**, *16*, 405.
(21) Dienes, A.; Shank, C. V.; Trozzolo, A. M. *Appl. Phys. Lett.* **1970**, *17*, 189.
(22) Georgieva, I.; Trendafilova, N.; Aquino, A.; Lischka, H. *J. Phys. Chem. A* **2005**, *109*, 11860.
(23) Georgieva, I.; Trendafilova, N.; Aquino, A.; Lischka, H. *J. Phys. Chem. A* **2007**, *111*, 127.
(24) Kobayashi, T. *J. Phys. Chem.* **1978**, *82*, 2277.
(25) Seixas de Melo, J.; Macanita, A. L. *Chem. Phys. Lett.* **1993**, *204*, 556.
(26) Abdel-Mottaleb, M. S. A.; El-Sayed, B. A.; Abo-Aly, M. M.; El-Kady, M. Y. *J. Photochem. Photobiol., A: Chem.* **1989**, *46*, 379.
(27) Bardez, E.; Boutin, P.; Valeur, B. *Chem. Phys. Lett.* **1992**, *191*, 142.
(28) Seixas de Melo, J.; Fernandes, P. F. *J. Mol. Struct.* **2001**, *565*, 69.
(29) Yakatan, G. J.; Juneau, R. J.; Schulman, S. G. *Anal. Chem.* **1972**, *44*, 1044.
(30) Schulman, S. G.; Rosenberg, L. S. *J. Phys. Chem.* **1979**, *83*, 447.
(31) Hoshiyama, M.; Kubo, K.; Igarashi, T.; Sakurai, T. *J. Photochem. Photobiol., A: Chem.* **2001**, *138*, 227.
(32) *Reverse Micelles*; Luisi, P. L., Straub, B., Eds.; Plenum Press: New York, 1984.
(33) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: London, 1987.
(34) Luisi, P. L.; Giomini, M.; Pileni, M. P.; Robinson, B. H. *Biochim. Biophys. Acta* **1988**, *947*, 209.
(35) Jain, T. K.; Varshney, T. K.; Maitra, A. *J. Phys. Chem.* **1989**, *93*, 7409.
(36) Piletic, I. R.; Moilanen, D. E.; Spry, D. B.; Levinger, N. E.; Fayer, M. D. *J. Phys. Chem. A* **2006**, *110*, 4985–4999.
(37) Moilanen, D. E.; Levinger, N. E.; Spry, D. B.; Fayer, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 14311–14318.
(38) Escabi-Perez, J. R.; Fendler, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 2234.
(39) Sarkar, M.; Guha Ray, J.; Sengupta, P. K. *J. Photochem. Photobiol., A: Chem.* **1996**, *95*, 157.
(40) Andrade, S. M.; Costa, S. M. B.; Pansu, R. *Photochem. Photobiol.* **2000**, *71*, 405.
(41) Mukherjee, T. K.; Panda, D.; Datta, A. *J. Phys. Chem. B* **2005**, *109*, 18895.
(42) Angulo, G.; Organero, J. A.; Carranza, M. A.; Douhal, A. *J. Phys. Chem. B* **2006**, *110*, 24231.
(43) Bardez, E.; Monnier, E.; Valeur, B. *J. Phys. Chem.* **1985**, *89*, 5031.
(44) Bardez, E.; Goguillon, B-T.; Keh, E.; Valeur, B. *J. Phys. Chem.* **1984**, *88*, 1909.
(45) Cohen, B.; Huppert, D.; Solnstev, K. M.; Tsfadia, Y.; Nachliel, E.; Gutman, M. *J. Am. Chem. Soc.* **2002**, *124*, 7539.
(46) Douhal, A.; Angulo, G.; Gil, M.; Organero, J. A.; Sanz, M.; Tormo, L. *J. Phys. Chem. B* **2007**, *111*, 5487.
(47) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum Publishers: New York, 1999.
(48) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221.
(49) Somoza, M. M.; Andreatta, D.; Murphy, C. J.; Coleman, R. S.; Berg, M. A. *Nucleic Acids Res.* **2004**, *32*, 2494.
(50) Koti, A. S. R.; Krishna, M. M. G.; Periasamy, N. *J. Phys. Chem. A* **2001**, *105*, 1767.
(51) Koti, A. S. R.; Periasamy, N. *J. Chem. Phys.* **2001**, *115*, 7094.
(52) Cho, C. H.; Chung, M.; Lee, J.; Nguyen, T.; Singh, S.; Vedamuthu, M.; Yao, S.; Zhu, J.-B.; Robinson, G. W. *J. Phys. Chem.* **1995**, *99*, 7806.
(53) Faeder, J.; Ladanyi, B. M. *J. Phys. Chem. B* **2000**, *104*, 1033.
(54) Kumbhakar, M.; Nath, S.; Mukherjee, T.; Pal, H. *J. Chem. Phys.* **2005**, *123*, 034705.
(55) Kumbhakar, M.; Nath, S.; Pal, H.; Sapre, A. V.; Mukherjee, T. *J. Chem. Phys.* **2003**, *119*, 388.
(56) Dutta Choudhury, S.; Kumbhakar, M.; Nath, S.; Sarkar, S. K.; Mukherjee, T.; Pal, H. *J. Phys. Chem. B* **2007**, *111*, 8842.

JP8004019