ARTICLES

Effect of Surfactant-Perturbed Nanocaging on the Ground and Excited State Proton Transfer Reaction

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The effect of mixed cyclodextrin−surfactant systems on the ground and excited state proton transfer reactions of 4-methyl-2,6-diformylphenol (MFOH) in aqueous solution has been investigated by steady state and time-resolved fluorescence spectroscopy. It has been found that micellar media perturbs the solvation of MFOH and facilitates nanocaging. In the presence of micelle, MFOH preferentially resides in the interfacial region. Depending on the local pH due to compartmentalization of reaction media, normal or anionic form of MFOH dominates. Encapsulation of the probe within the cyclodextrin nanocavity enhances the shorter lifetime component of MFOH unexpectedly, which has been explained on the basis of reduced solvation and reduced dipolar effect due to confinement.

1. Introduction

Of late, the study of reactions in nanocavities and at various interfaces has been drawing the attention of the scientific community due to their vital role in many biological and natural processes.[1−3] One such reaction, namely excited state proton transfer (ESPT), is well-known and one of the most fundamental phenomenon consists of a reversible adiabatic transfer of a proton. In the excited state, the acidity constant of the species is significantly different from that of the parent ground state species.[2−4]

Aqueous solutions of cetyltrimethylammonium bromide (CTAB), polyoxyethylene(10)isooctylphenylether (Triton-X100), and sodium dodecyl sulfate (SDS) form micelles when their concentration exceeds their respective critical micellar concentration (CMC) (0.2 mM for Triton-X100; 0.9 mM for CTAB; 8 mM for SDS).[5] Such charged interfaces can drastically modify both the kinetics and the energetics of PT reactions with respect to their normal characteristics in aqueous solution[6] as the probe faces three different environments, namely, the highly polar bulk aqueous phase, the hydrocarbon core, and the Stern layer. The most obvious perturbation is the introduction of heterogeneities in the distribution of ionic reactants in the solution due to electrostatic interactions with the charged interface. Reaction rates and equilibria in micellar media are affected by solubilization of reactants, changes in local concentrations due to compartmentalization of reaction media, and changes in physicochemical properties of the medium.[7] Thus, the concentration of protons at a negatively charged micellar surface is higher than that in the bulk aqueous phase and the reverse is true for positively charged surfaces.[8−10] Besides modifying the effective local concentration of protons, the interface can also exert an even greater intrinsic effect on the rates due to differential stabilization and destabilization of the species involved in the PT process. Also, confinement in such self-organized assemblies imposes various constraints on the free movement of the reactants, thereby slowing down the rate of reactions that involve large-amplitude motions, an example being isomerization.

Cyclodextrins (CDs) have been recognized as effective nanosystems to encapsulate various molecules. They are basically oligosaccharides comprised of six, seven, or eight glucopyranose units, designated as α, β, and γ, respectively. CDs are water soluble containing a hydrophobic cavity, which can bind apolar molecules of suitable size to form host−guest-like complexes.[11] Much interest has been directed on the nature of hydrophobic force responsible for the binding since such interactions may provide a model for the active sites of enzymes.[12] The caging ability of CDs modifies the degrees of freedom of the reaction coordinates of the guest molecules leading to changes in the dynamics of elemental processes in chemistry like bond-breaking and making, proton and charge transfer, etc.[13−16] Douhal et al.[1] employed the well-known ESIPT probe, 3-hydroxyflavone (3-HF), as a means to study PT reaction in β- and γ-CDs and established the formation of 1:1 anionic inclusion complexes between 3-HF and CDs. The equilibrium constants obtained indicated a larger stabilization within the γ-CD cavity with respect to the β-CD cavity, the stabilization being due to hydrophobic effect and H-bonding interactions with the CD pockets.

Studies on mixed cyclodextrin−surfactant systems have aroused great interest owing to their wide-scale commercial applicability[17] and the ability of cyclodextrins to influence the physicochemical properties of micellar solutions. Inclusion complexes have been characterized by various techniques such as conductance,[18] NMR,[19] fluorescence,[20] surface tension,[21]

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kinetic methods,[22] diffusion coefficient,[23] etc. It has been established that once the micellization process starts, no interactions will occur between the CD and the micellar system.[24] It has also been found that the critical micelle concentration (CMC) shifts to higher values in the presence of CD, while the concentration of free monomers remains basically the same,[25] slightly increases,[26] or slightly decreases[27]depending on the surfactant. Cabaleiro-Lago et al.[28] studied the chemical behavior of β-CD/nonionic surfactant mixed systems and showed that the complexation equilibrium of the surfactant with the CD and the autoassociation of the surfactant occur simultaneously. Hence, free/uncomplexed CD exists in equilibrium with the micellar system.

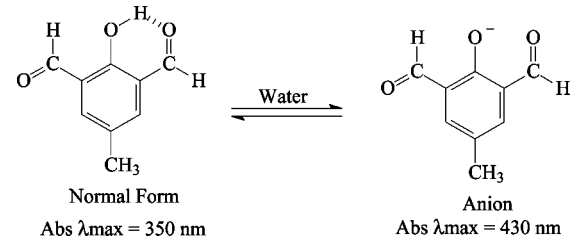
In view of such drastic effects of mixed CD−micellar systems on chemical reactions, in the present work we have used methyl-2,6-diformylphenol (MFOH) as a probe to monitor the PT reaction in three such systems, employing different micellar environments, viz. cationic, anionic, and neutral. MFOH is a well-studied PT probe[4,29] and effects of different solvent environments on it have extensively been investigated.[30] In an earlier study, we explored the PT reaction within CD nanocavities employing MFOH as a probe.[4] Three different solvents, water, DMF, and DMSO, were chosen for this purpose. It was established that although DMSO and DMF exhibit similar interactions with MFOH individually, the interactions change significantly in the presence of CDs. The CD pockets, on the other hand, do not produce any substantial effect on PT on their own. In an aqueous solution of MFOH, no spectral changes are observed on addition of CDs indicating that the probe is stabilized by the solvation of the dynamic water cage and hence refuses to enter into the CD nanocavity.[4] In this article, we have addressed the issue of how different micellizations perturb the water solvation facilitating nanocaging of MFOH.

2. Experimental Section

2.1. Materials and Solutions. MFOH was prepared in the inorganic chemistry department of this institute in a similar way to that reported earlier.[4,30] The compound was recrystallized from methanol and dried before use. Triply distilled water was used throughout and was checked for residual fluorescence before use. AR grades SDS, CTAB, Triton-X100, and α-CD from Aldrich have been used. The concentration of MFOH was maintained at $\sim 5 \times 10^{-6}$ mol dm^{-3} and the concentration of micelles was varied as required, while the concentration of α-CD was maintained at 14 mM. The solutions were all freshly prepared. Since the fluorescence quenching by dissolved oxygen was unimportant, the fluorescence measurements were made with nondegassed solution. All the experiments were performed at ambient temperature (23 °C).

2.2. Instruments. The room temperature absorption and emission spectra were recorded on a Shimadzu UV−vis recording spectrophotometer, UV-2401 (PC) S220V and Fluoro Max 3 (Jobin Yvon Horiba) fluorimeter, respectively. For lifetime measurements, the sample was excited either at 375 or 440 nm light with a picosecond diode laser (IBH Nanoled-07). The emission was collected at a magic angle polarization, using a Hamamatsu MCP photomultiplier (R3809) based on time a correlated single photon counting (TCSPC) technique. The TCSPC setup consists of an Ortec 9327 discriminator and Fluoro Hub Single Photon Counting controller. The data were collected with a DAQ card as a multichannel analyzer. The typical fwhm of the system response using a liquid scatterer was about 86 ps. The fluorescence decays were deconvoluted using data station v2.3 IBH DAS6 software. The quality of fit was judged in terms of χ^2 values and weighted residuals.

SCHEME 1



3. Results

3.1. Steady State Measurements. The absorption spectra of MFOH in aqueous medium show two bands at 350 and 430 nm, as mentioned earlier (Scheme 1).[30] These bands have been attributed to the intramolecularly H-bonded normal (primary) form and the solvated molecular anionic species, respectively. The relative absorbance of the two bands is highly dependent on the concentration of MFOH used due to the equilibrium between the two species being pH dependent. We have, therefore, maintained the concentration of MFOH at $\sim 5 \times 10^{-6}$ M (optical density within 0.2−0.4; pH 6.7). On gradual addition of the anionic micelle SDS, the absorbance of the primary form increases with a concomitant decrease of the anionic absorbance. The observations completely reverse on adding CTAB to the aqueous solution of MFOH. In fact, the normal form disappears at a [CTAB] ≈ 9 mM. Similar types of observations are obtained when the neutral micelle Triton-X100 is added instead, although the changes obtained in this case are not that prominent (Figure 1). It is worth mentioning here that in the presence of the three different micellar environments, namely anionic (SDS), cationic (CTAB), and neutral (Triton-X100), isosbestic points are observed at 382 nm in all three cases (Figure 1), reflecting the effect of environmental inhomogeneity on the equilibrium between the normal form and the anion in each case. When α-CD is added to the three micellar solutions, the absorbance of the primary form of MFOH is enhanced at the expense of the anionic form. In fact, the normal form reappears in the case of the MFOH solution containing CTAB. No change is observed when glucose is added in place of α-CD in all three solutions.

The emission spectra of MFOH in pure water (Figure 2) shows a peak at 525 nm when excited at 350 nm, which shifts to 530 nm when excited at 430 nm. On gradual addition of the anionic surfactant SDS, the emission spectra is slightly enhanced in intensity (around CMC). A drastic quenching along with a blue shift from 525 to 516 nm (when $\lambda_{exc} = 350$ nm) is observed beyond CMC (at least 10 times CMC, i.e. 80 mM) with an isoemissive point at 486 nm whereas, for the 430 nm excitation, the peak at 530 nm remains unchanged in position but undergoes substantial quenching ($\lambda_{exc} = 430$ nm) (Figure 2). Now, on addition of α-CD to this solution, the emission peak at 516 nm (corresponding to $\lambda_{exc} = 350$ nm) remains unchanged in position with no significant change in intensity. On the other hand, concomitant quenching is observed with subsequent addition of α-CD when the excitation wavelength is 430 nm. In both cases, no significant change is observed when glucose is added in lieu of α-CD.

The observations are markedly different when CTAB, which forms cationic micelle, is added to the aqueous solution of MFOH. In this case, on exciting the solution at 350 or 430 nm, the emission peak at 525 nm rises initially followed by a decrease (at CTAB concentration around CMC) (Figure 3 inset) and ultimately undergoes a substantial enhancement accompanied by a blue shift to 521 nm on complete micellization (at ∼10 times CMC, i.e. 9 mM). On addition of glucose, no further

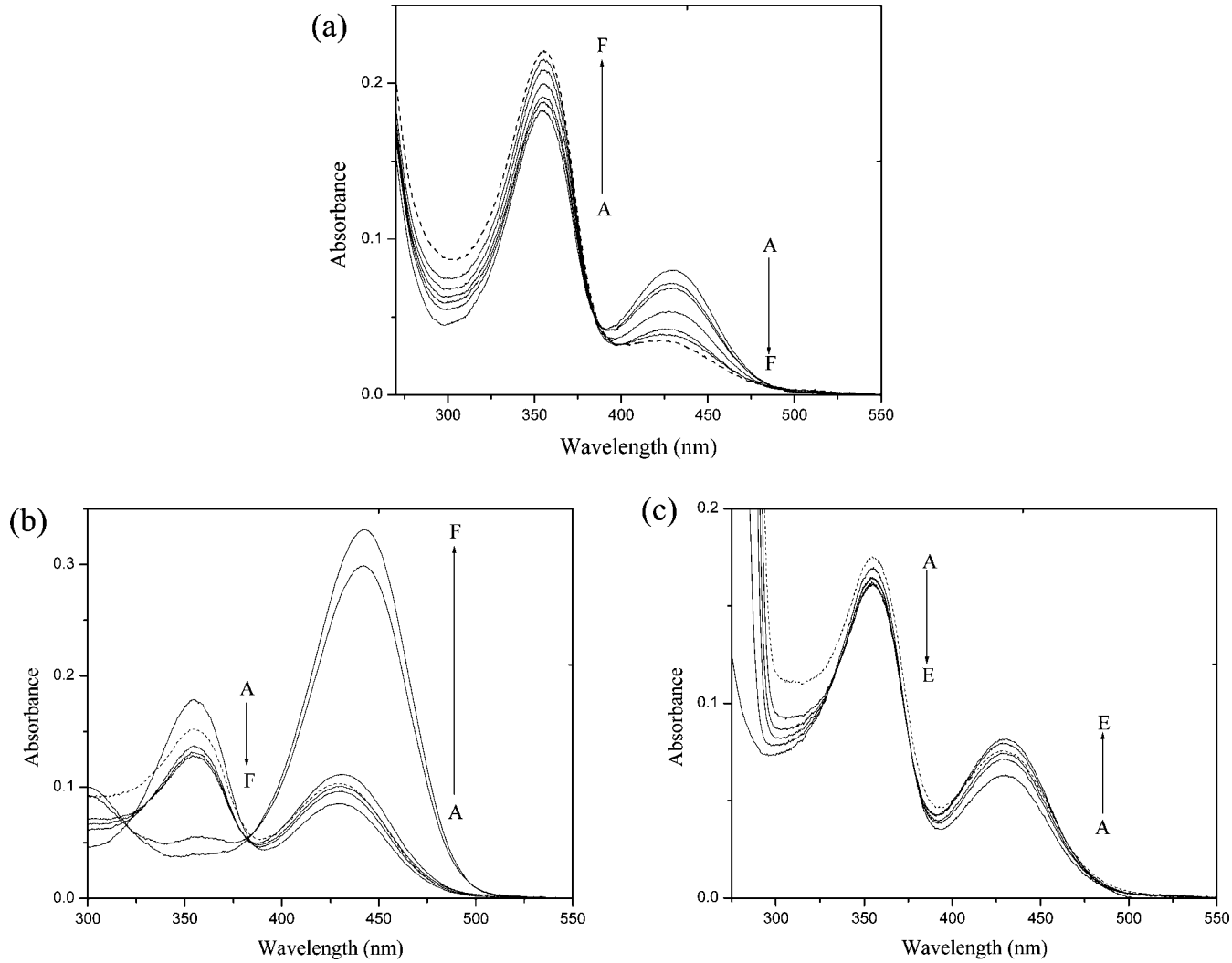


Figure 1. Absorption spectra of MFOH in water in the presence of (a) SDS, (b) CTAB, and (c) Triton-X100. A dotted line indicates the spectra in the presence of α-CD ([α-CD] = 14 mM). [SDS] in mM = A (0), B (11.86), C (18.27), D (31.04), E (46.09), F (63.15). [CTAB] in mM= A (0), B (1.38), C (1.79), D (2.42), E (4.07), F (5.69). [Triton-X100] in mM = A (0), B (0.1), C (0.2), D (0.5), E (1.0).

change occurs. On the other hand, addition of α-CD leads to severe quenching of the emission spectra along with a red shift by about 4 nm thereby bringing the peak back to 525 nm (Figure 3).

The addition of Triton-X100 to the aqueous solution of MFOH leads to an enhancement in the emission spectra, both before and after CMC, whether the excitation wavelength is maintained at 350 nm or at 430 nm (Figure 4). Addition of α-CD leads to quenching, an observation not obtained in the case of glucose.

3.2. Time-Resolved Measurements. Table 1 depicts the lifetime values of MFOH obtained on excitation of the solutions at either 375 nm (λ_{mon} = 525 nm) or at 440 nm (λ_{mon} = 530 nm). A biexponential decay nature is observed in all the cases studied here (Figures 5 and 6). The lifetime values obtained reflect that the contribution of the shorter component changes significantly for λ_{exc} = 375 nm, whereas when the anionic species is excited (λ_{exc} = 440 nm), this change is not so prominent. As seen from the table, the shorter component increases in amplitude in the presence of SDS, while the reverse is observed in the case of CTAB as well as Triton-X100. It is interesting to note that on addition of α-CD, the shorter component again increases for all three micellar solutions, a feature evident from Figure 6 also.

4. Discussion

The absorption spectra of MFOH show a single peak at 350 nm in nonpolar solvents and hence this peak can be proposed to be due to the normal form. In aqueous media, another peak is observed at 430 nm, which increases at the expense of the 350 nm peak on addition of a base like NaOH and hence the 430 nm peak can be attributed to the anionic species of MFOH.[30] The enhancement of the normal form in the presence of SDS micelle can be explained on the basis of reprotonation of the anionic species in the lower pH region (Stern layer) of the negatively charged micelle.[31] On the other hand, in the case of the cationic micelle CTAB, a higher pH in the micelle-bulk water interface facilitates anion formation. The ether groups at the Stern layer of the neutral micelle, Triton-X100, also favor the enrichment of the anion over the normal form by accepting the proton from MFOH. These effects are clearly reflected from the positive and negative slopes of the plots of absorbance vs surfactant concentration (Figure 7). Further, the increase in the normal form of the probe at the expense of the anionic form on addition of α-CD can be attributed to the probe entering the CD cavity for all three cases.

At this juncture, it is worth mentioning that in our earlier study[4] we have shown that both the normal form and the anion

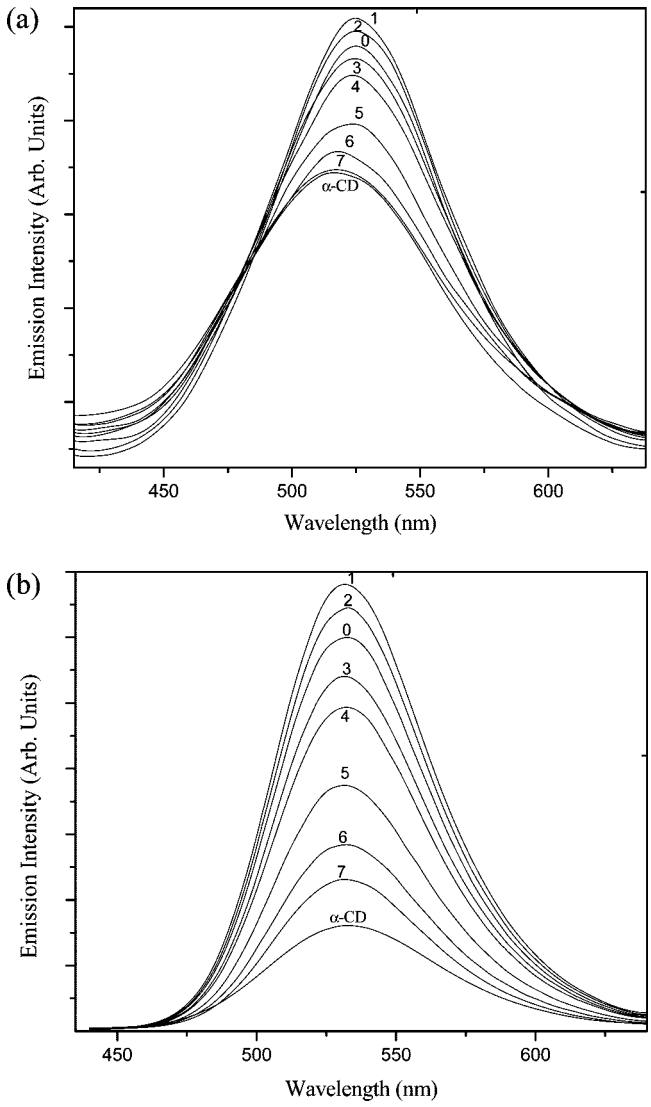


Figure 2. Emission spectra of MFOH in water in the presence of SDS at (a) $\lambda_{exc} = 350$ nm and (b) $\lambda_{exc} = 430$ nm. The spectra on addition of α-CD have also been shown. [SDS] in mM = 0 (0), 1 (1.39), 2 (6.73), 3 (11.86), 4 (18.27), 5 (31.04), 6 (46.09), 7 (63.15).

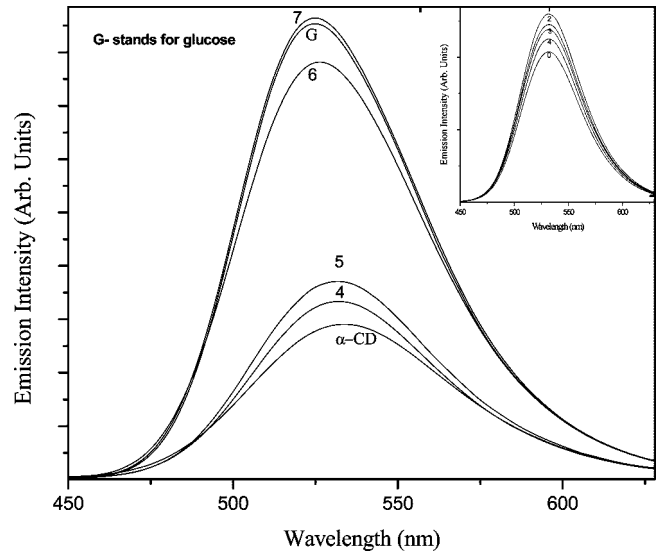


Figure 3. Emission spectra of MFOH in the presence of CTAB and also on addition of α-CD and glucose at $\lambda_{exc} = 430$ nm. [CTAB] in mM = 0 (0), 1 (0.08), 2 (0.41), 3 (0.86), 4 (1.38), 5 (2.42), 6 (4.07), 7 (5.69). The inset shows the spectra when the concentration of CTAB is varying between 0 and 1.38 mM.

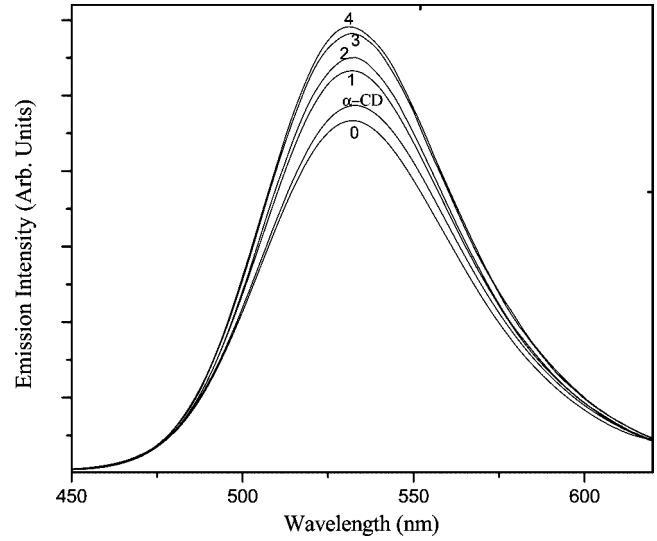


Figure 4. Emission spectra of MFOH in the presence of Triton-X100 and Triton-X100 + α-CD at $\lambda_{exc} = 430$ nm. [Triton-X100] in mM = 0 (0), 1 (0.1), 2 (0.2), 3 (1.5), 4 (2.0).

of MFOH remain effectively solvated in dynamic water cages. We did not find any significant spectral change in both the ground and excited state in the presence of CDs. In the present work, the prominent spectral changes can be inferred to be due to various possibilities, such as hydrogen bonding[32,33] or assembling.[34] Now, on addition of α-CD, it is likely that MFOH undergoes H-bonding with the −OH groups available at the rim of the CD cavities.[9] However, CDs being oligosaccharides composed of glucose moieties, a similar type of H-bonding would also be expected when glucose is added to the MFOH−surfactant solution. Therefore, if the spectral shift was due to H-bonding only, this shift would also have been observed when glucose was added instead of α-CD, which was not the case. It is pertinent to mention at this point that the cavity size of α-CD is compatible with the dimension of MFOH. In fact, it has been observed by semiempirical studies that the end-to-end distance from the methyl group side of MFOH is 4.34 Å while the diameter of α-CD is 4.5 Å.[4] So, MFOH can enter within the α-CD cavity. Indeed, the increase of the normal form on addition of α-CD indicates that the normal form is favored in the hydrophobic interior of the CD cavity. Hence, as observed in this present work, it can be proposed that the different electrostatic environments produced by micellization perturb the dynamical water cage around MFOH facilitating the phenomenon of nanocaging.[35,36] Thus, a drastic spectral change is observed in all three types of micellar solutions of MFOH on addition of α-CD. Hence, it can be inferred that the probe, in this case, does enter into the α-CD cavity.

Although the emission spectra of MFOH in water show a single band for the anionic species, the existence of the normal form cannot be ruled out. It is quite apparent that the anion is the primary fluorescing species thus rendering the normal form undetectable. This interpretation is further supported by the time-resolved study at the picosecond level of resolution that shows a biexponential nature of the decay obtained (Table 1) in water. The shorter component obtained in water agrees well with the fast component obtained in a nonpolar solvent, *n*-heptane, and hence can be ascribed to the normal form.[37] The longer component, on the other hand, can safely be assigned to the anionic species of MFOH in conformity with the observation

TABLE 1: Lifetime Components of MFOH in Water, in the Absence and Presence of Different Surfactants and α-CD[a]

	λ_{mon} = 525 nm; λ_{exc}= 375 nm		λ_{mon} = 530 nm; λ_{exc} = 440 nm	
medium	τ_1 (ps)	τ_2 (ps)	τ_1 (ps)	τ_2 (ps)
water	400 (5)	4750 (95)	800 (2)	4800 (98)
water + SDS	150 (23)	4600 (77)	750 (2)	4850 (98)
water + SDS + α-CD	150 (25)	4700 (75)	800 (3)	4860 (97)
water + CTAB	600 (2)	5300 (98)	600 (4)	5200 (96)
water + CTAB + α-CD	200 (5)	4750 (95)	1200 (2)	5300 (98)
water + Triton-X100	200 (5)	4750 (95)	550 (2)	4800 (98)
water + Triton-X100 + α-CD	100 (6)	4800 (94)	850 (3)	4900 (97)

[a] The percentage contributions of the corresponding lifetimes are indicated in parenthesis. The χ^2 values range from 0.99 to 1.20.

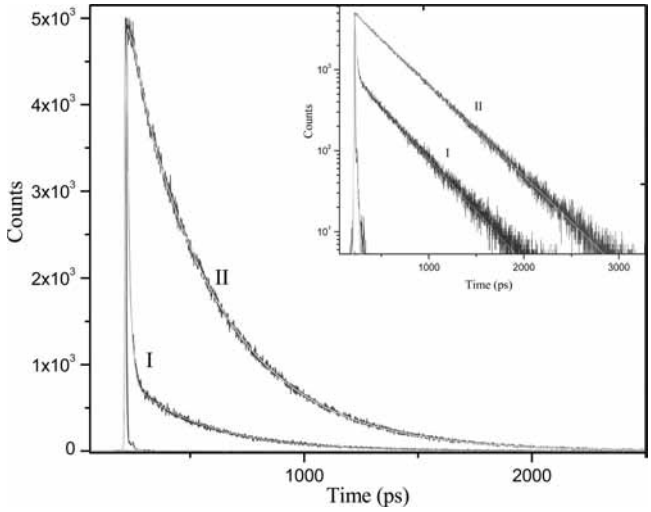


Figure 5. Typical decay profile of MFOH in water, in the presence of (I) SDS and (II) CTAB (λ_{exc} = 375 nm, λ_{mon} = 525 nm). Global analysis of the decay and the lamp profile is also shown. The inset shows the decay profile in log scale.

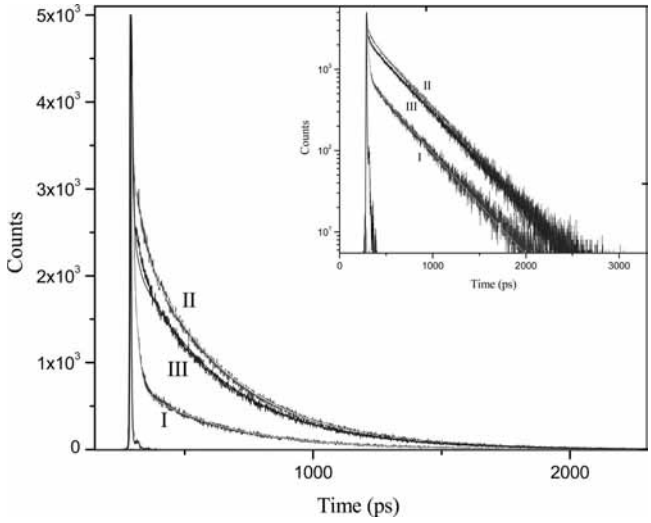


Figure 6. Typical decay profile of MFOH in water, in the presence of (I) SDS + α-CD, (II) CTAB + α-CD, and (III) Triton-X100 + α-CD (λ_{exc} = 375 nm, λ_{mon} = 525 nm). Global analysis of the decay and the lamp profile is also shown. The inset shows the decay profile in log scale.

obtained earlier in the nanosecond regime.[30] The fast decaying character of MFOH is primarily due to lesser solvation of the normal form in comparison to the anion in water. It can also be proposed that the nonradiative pathways are more dominant in the emission of the normal form thus reducing its lifetime (in comparison to the anion) due to the possibility of rotation of the formyl group, while the rotations may be hindered in the case of the anion due to the dipolar effect (Scheme 2). The existence of the normal form in the excited state is reflected in the emission band being blue-shifted by 5 nm when excited at 350 nm in comparison to the peak at 530 nm when the excitation wavelength is maintained at 430 nm. At this juncture, it is appropriate to mention that the time-resolved measurements also denote that larger amplitudes are obtained for the shorter component and vice versa when λ_{exc} = 375 nm in comparison to the situation when λ_{exc} = 440 nm thereby lending further support to our proposition that the normal form does exist along with the anion in the excited state (Table 1).

In the presence of SDS micelle, before CMC is reached, the anionic head groups abstract the H^+ ion from the probe thereby resulting in a slight augmentation of the anionic emission whether the solution is excited at 350 or 430 nm. When micelle formation is complete, a drastic quenching accompanied by a blue shift from 525 to 516 nm (λ_{exc} = 350 nm) is observed. Now, the phenomenon of fluorescence quenching may arise due to hydrogen bonding dynamics in the electronic excited state or due to the ultrafast internal conversion (IC) process or due to a photoinduced electron transfer (PET) reaction.[32,38] MFOH is a well-studied probe,[4,29,30] and in aqueous media it undergoes proton loss by electronic excitation. Now, IC mainly results in red shifts in the spectra but here quenching occurs along with a 9 nm blue shift, which can be inferred to be due to the formation of a new species, probably the H-bonded complex of the normal form with the solvent by virtue of the probe experiencing a lower pH in the Stern layer of the anionic micelle.[31] The increase in the contribution of the H-bonded normal form of the probe at the expense of the anion is supported further by an increase in the amplitude of the shorter lifetime component (Table 1). The quenching of the emission peak at 530 nm after micellization is due to reprotonation of the MFOH anion at the low pH Stern layer. Now, on addition of α-CD/glucose, the emission spectra remain unchanged (when λ_{exc} = 350 nm) implying that the peak at 516 nm is due to a H-bonded complex with the solvent and hence the system as a whole is unable to penetrate the CD cavity owing to its large size. The anionic peak at 530 nm is quenched further in the presence of α-CD. Now, it is generally expected that the anion would remain in a solvated condition and hence would have a larger dimension. In this situation, it is unlikely that it would enter the CD cavity. In fact, we had observed in our earlier study[4] that the anion in a solvated state in pure aqueous media is indeed unable to enter into the CD cavity. However, in the present study, the quenching of the anion in α-CD (but not in glucose) denotes that the solvation is perturbed in micellar media and the repulsion faced from the negatively charged head groups of the SDS micelle compels the anionic species of MFOH to enter into the CD cavity on reprotonation by the hydrogen at the rim of the α-CD cavity (Scheme 3).

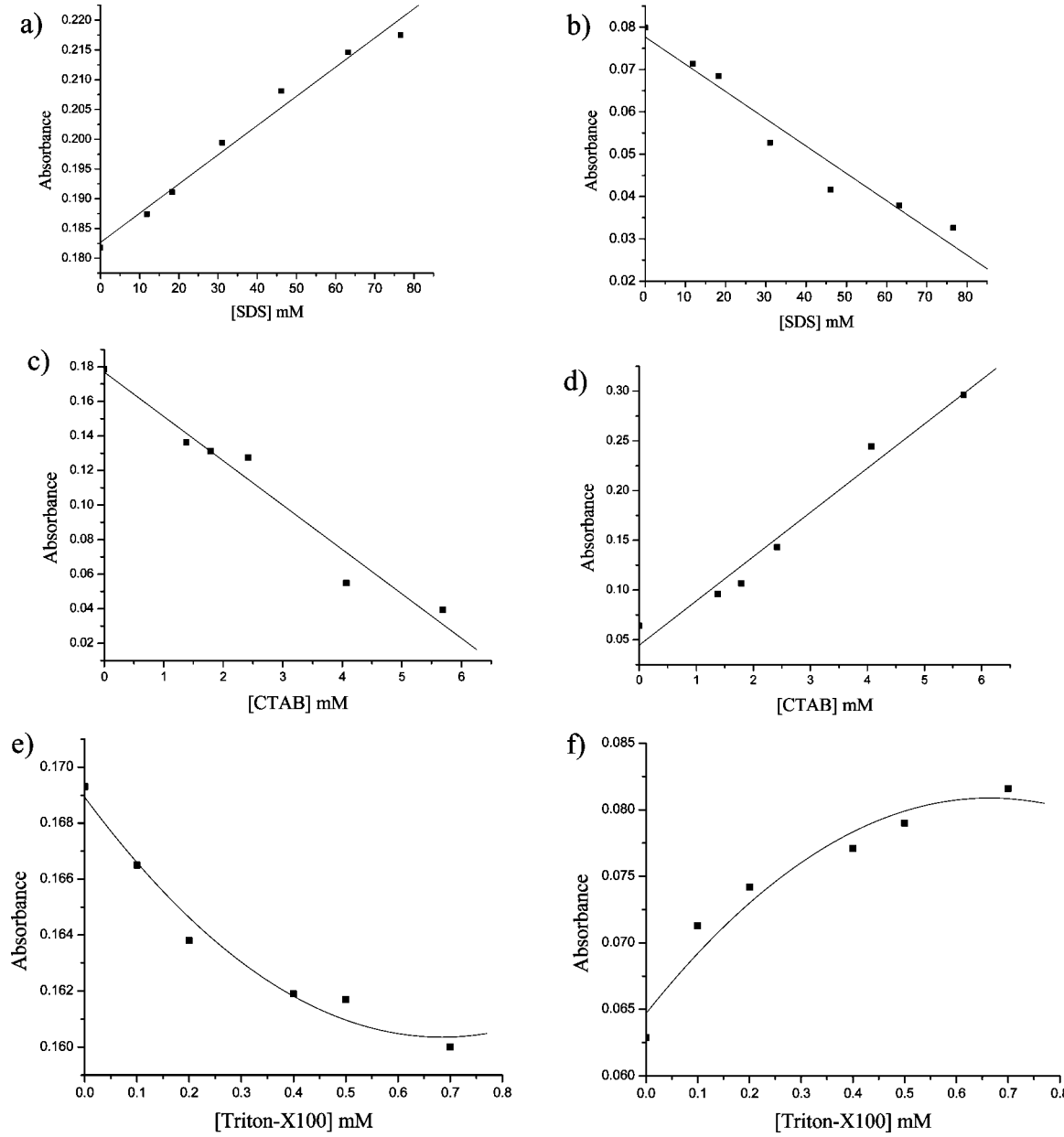
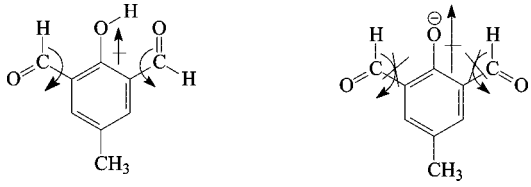
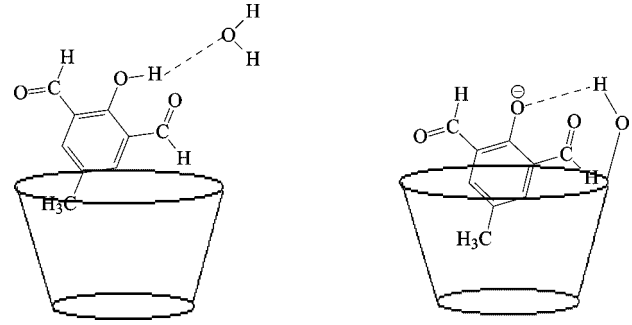


Figure 7. Plot of absorbance vs surfactant concentration at $\lambda_{max} = 355$ nm for (a) SDS, (c) CTAB, and (e) Triton-X100, and at $\lambda_{max} = 430$ nm for (b) SDS, (d) CTAB, and (f) Triton-X100}.

SCHEME 2



SCHEME 3



The initial increase in emission intensity of the probe on addition of CTAB ([CTAB] = 0.3 mM) can be argued on the basis of change in the dielectric constant of the medium. Before complete micellization, further extraction of H^+ ion from MFOH is hindered due to lack of solvation of the ion by the cationic micelle. Once micellization is achieved, the emission intensity rises sharply because of progressive anion formation at the Stern layer, which is enriched with OH^- ions compared to bulk water. The 4 nm blue shift, in this case, may be due to an energetically higher interaction of MFOH anion with the negatively charged OH^- ions on account of mutual repulsion. We can, therefore, argue that if MFOH had entered into the hydrocarbon core of the micelle, the shorter lifetime component would be expected to enhance in CTAB also, which is not observed here. Hence, it can safely be proposed that MFOH resides mainly in the Stern layer. On addition of α-CD, substantial quenching along

with the red shift back to the original position occurs because of the shift in equilibrium experienced by the probe due to its entrance into the α-CD cavity on reprotonation. It is worth mentioning here that although the shorter lifetime component is expected to reduce in amplitude within the CD nanocavities because of reduced degrees of freedom, it is seen that its contribution increases, implying that the dipolar effect (Scheme 2) dominates over the effect of restricted motion within the cavity.

5. Conclusion

The present study demonstrates the influence of surfactant/α-CD mixed systems on the proton transfer reaction of MFOH due to electrostatic interactions with the charged interfaces of the various micelles and confinement within the CD cavity. The perturbation produced by the micellar environment assists nanocaging of the probe and modifies the PT reaction significantly. The anionic interface favors reprotonation, while the cationic Stern layer promotes PT. It is observed that reprotonation plays a crucial role in the increase of the contribution of the shorter lifetime component to the decay profile. The reprotonation accompanied by nanocaging also enhances the shorter component, although the nonradiative pathways are expected to reduce on account of captivation in the CD cavities. This anomalous observation is explained on the basis of dominance of the dipolar effect over the reduced degrees of freedom within the CD cavity.

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