

Excited state intermolecular proton transfer and caging of salicylidine-3,4,7-methyl amine in cyclodextrins

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Abstract

The excited state intermolecular proton transfer (EIMPT) of salicylidine-3,4,7-methyl amine (SMA) has been studied using absorbance, steady state and time resolved emission spectroscopy in aqueous and polar aprotic media both in presence and absence of cyclodextrins (CDs). In the ground state, both the closed *cis* enol form and zwitterionic species coexist in all the solvents used. After encapsulation by β - and γ -CD, only intramolecularly H-bonded *cis* enol form exists in all the solvent media, while in α -CD both the species coexist. In the excited state, intermolecular proton transfer to water efficiently leads to the formation of anion in absence of CDs. Caging by CDs provokes a 15 (in β -CD) and 10 (in γ -CD) nm blue shift of the emission along with a decrease in intensity of the band, whereas no change is observed in presence of α -CD and glucose. The emission lifetime of anion decreases from 11.8 to 3.4 ns due to the formation of H-bonded complex. Analysis of the spectroscopic data by Benesi–Hildebrand plot shows that SMA forms 1:1 complex in the ground state with β - and γ -CD. Stern–Volmer plot reveals that β -CD is the stronger quencher of SMA anion compared to γ -CD.

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1. Introduction

The study of confinement effects on the behavior of molecules provides valuable information on the nature of the environment and dynamical properties of the system. Indeed the inclusion of guest molecules into the cavities of supramolecular hosts with molecular container properties has the potential to allow the novel chemical transformation to isolate reactive species, to mimic enzymatic activity and to promote uncommon spectroscopic effects [1–4]. Among the simplest systems for these studies are the inclusion complexes of the dyes with cyclodextrins (CDs) [1–5]. The reduced polarity and restricted space provided by the CD cavity markedly influence a number of photophysical and

photochemical pathways [6,7] and also can perturb the physical and chemical properties of different types of hydrophobic guest molecules. CDs can sufficiently shield the excited single state of molecules from nonradiative processes and thereby enhance their fluorescence intensity. The aqueous solubility of complexed molecules has also been observed to increase upon formation of inclusion complex with CDs [8,9]. In an earlier work, Verner et al. reported the influence of CDs upon the spectral properties of 2-(2'-hydroxy phenyl) benzazoles. These studies seem to indicate the differences in the extent of inter- and intramolecular proton transfer for the molecules in the aqueous solutions of cyclodextrins [10,11]. In the case of 2-(2'-hydroxy phenyl) benzimidazole (HBI) in aqueous solution of CD, they observed intermolecular interaction of HBI with CDs. Moreover, various solvents appear to weaken the intramolecular hydrogen bonding in HBI and facilitate the formation of strong intermolecular

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hydrogen bonds with CDs and solvent molecules. The study of inclusion complex in fundamental research furnishes information about nanocovalent intermolecular forces. The most important properties of an inclusion complex are that a host component can admit a guest component into its cavity without any covalent bonds being formed. This offers a means of studying intermolecular excited state proton transfer reactions in inclusion complexes of CDs [12,13]. These compounds are utilized in laboratories, industry, in home as ion exchangers, as catalyst in chemical reactions and for the micro-encapsulation of aromatic substances [14].

In this paper we address the issue of excited state intermolecular proton transfer reaction (EIMPT) of

salicylidine-3,4,7-methyl amine (SMA) both in presence and absence of cyclodextrins (CDs: α -, β -, and γ -CD) in aqueous and highly polar aprotic media like DMSO and DMF. The focus of this work is to characterize and compare the effect of micro-heterogeneous environments on the EIMPT process. Here we report the effect of reduction in polarity, as imposed by the β - and γ -CD microenvironment on the steady state and time resolved emission of SMA. The spectral data have been analyzed by Benesi–Hildebrand (B–H) and Stern–Volmer (S–V) plot. We have used the solvents methyl cyclohexane and dioxane for comparison. The molecular formula of SMA and the possible configuration of SMA are shown in Fig. 1.

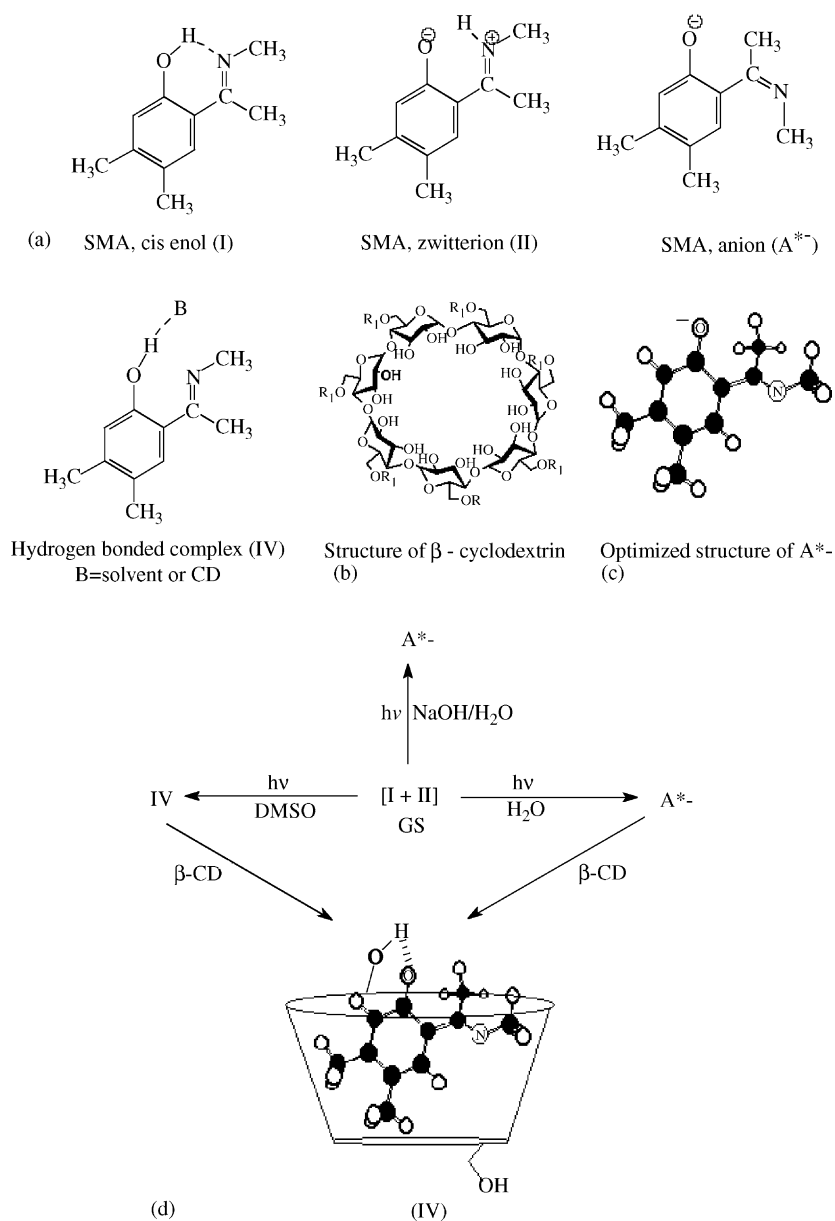


Fig. 1. (a) Structural formula of SMA and possible configuration of SMA; (b) structural formula of β -cyclodextrin; (c) optimized geometry of SMA anion in the excited state and (d) Scheme I.

2. Experimental

2.1. Materials and solutions

Salicylidine-3,4,7-methyl amine (SMA) (Fig. 1a) was synthesized from a stoichiometric mixture of a particular salicylaldehyde and methyl amine in methanol by standard procedure [15] in the Department of Chemistry, University of Wrocław, Poland. The solid products were recrystallised from methanol and dried before use. All the solvents used, water (triply distilled), dimethylsulphoxide (DMSO), and dimethyl formamide (DMF) were of spectroscopic grade (Aldrich or Merck), and were checked for residual fluorescence before use. All the CDs used were commercial products (Aldrich) of best quality ($\geq 98\%$) and were used without further purification. The concentration of SMA was maintained at $(3\text{--}6) \times 10^{-5} \text{ mol dm}^{-3}$, and the concentration of CDs are varied as required. The solutions were all freshly prepared. Since the fluorescence quenching by dissolved oxygen was unimportant, the fluorescence measurements were made with non-degassed solution. All the experiments were performed at ambient temperature (23°C). The relative quantum yields (ϕ_f) of SMA were determined by comparing the fluorescence intensity integrated over the range of emission wavelength of 4-methyl-2,6-diformylphenol (MFOH) ($\phi_f = 0.48$) in solution phase [16].

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. In all cases, 1 cm path length quartz cell was used. The pH of the solution was measured using a standard pH meter. The transient fluorescence lifetimes at room temperature were recorded with a SP-70 nanosecond spectrometer (Applied Photo Physics, UK) using a pulsed nitrogen lamp based on the time correlated single photon counting technique. The quality of fits over the fluorescence decay curves was assessed by reduced $\chi^2 = 0.9 \pm 0.3$.

3. Results and discussion

3.1. Steady state spectra in absence of cyclodextrins

The molecule, SMA shows two bands at 335 and 390 nm region in aqueous and polar aprotic media like DMSO and DMF (Fig. 2). On the gradual addition of NaOH ($\sim 2\text{--}3 \text{ mM}$), a strong band appeared at 365 nm at the expense of both 335 and 390 nm bands. SMA shows a single absorption band at 335 nm in non-polar solvent like methyl cyclohexane. The 335 and 365 nm bands can be assigned to the intramolecularly H-bonded *cis* enol form and the anion of SMA, respectively. Salicylidine aniline and its derivatives usually show a broad

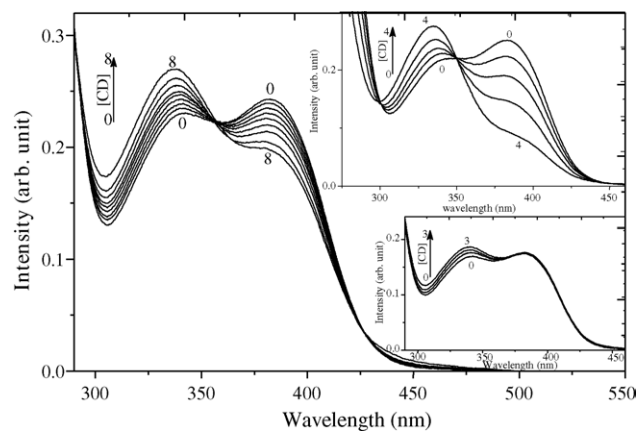


Fig. 2. Absorption spectra of SMA in water at room temperature, with varying concentration of γ -CD. Range of [CD] $\sim 0\text{--}7.6 \text{ mM}$. Inset up and down shows the varying concentration of β - and α -CD, respectively; range of [CD] $\sim 0\text{--}4 \text{ mM}$ for both β - and α -CD.

absorption band peaking around 400–440 nm. Different explanations were proposed to explain the origin of the band, such as zwitterionic species or intermolecular H-bonded complex [17–22]. In the case of Schiff bases, it has been shown that the zwitterionic species can be formed in any solvent if the hydroxyl group is present in the molecule [23,24]. Accordingly, the 390 nm absorption band can be assigned to the zwitterionic species of SMA. It is observed that the intensity of 390 nm absorption band decreases gradually on increasing and decreasing the pH of the medium. This band is the most stable and remain unaffected at pH 7.1. This confirms that the 390 nm species is a zwitterionic species.

On photoexcitation, SMA shows a single emission band peaking around 440 nm in aqueous media, which is found to be independent of any excitation wavelength. The excitation spectra of 440 nm emission band occurred around 340 nm region and agrees reasonably well with the absorption spectra (335 nm). On addition of NaOH, the intensity of the emission band increases gradually without any change in the position of the band. Thus, the 440 nm band can safely be assigned to the anion of SMA both in presence and absence of NaOH. The emission spectra of SMA show a single band at 420 nm in DMSO, DMF, and dioxane. On addition of a strong base like triethylamine (TEA), the intensity of the band increases without any change in the position of the band. Accordingly, the 420 nm band can be assigned to the intermolecularly H-bonded complex of SMA.

3.2. Spectroscopic studies in presence of cyclodextrins

On the addition of β - or γ -CD to the aqueous solution of SMA, the 390 nm band gradually decreases with an increase in the intensity of the 335 nm band. An isosbestic point is observed at 350 and 356 nm in each case of β - and γ -CD (Fig. 2). Similar observations are found when β - or γ -CD is added to a solution of SMA in DMSO and DMF. On the other hand, 390 nm band does not show any significant change by

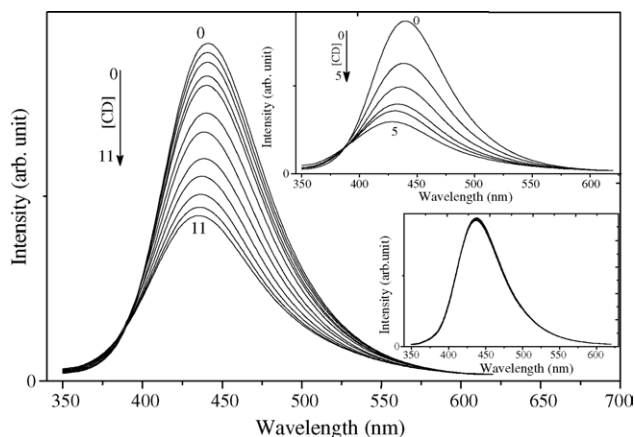


Fig. 3. Fluorescence emission spectra of SMA ($\sim 10^{-5}$ M) in water on the addition of γ -CD ([CD] mM: 0.0 (0), 0.1 (1), 0.2 (2), 0.4 (3), 0.6 (4), 1.0 (5), 1.9 (6), 2.8 (7), 4.2 (8), 5.7 (9), 7.3 (10), 8.8 (11)). Inset shows for β -CD (up) and α -CD (down), range of [CD] ~ 0 –4 mM.

the added α -CD. On gradual addition of β - or γ -CD, the 440 nm emission intensity is found to decrease with a concomitant shift of the band to 425 and 430 nm, respectively, as shown in Fig. 3. An isoemissive point is observed at 398 and 390 nm in each case of β - and γ -CD, respectively, reflecting an equilibrium between the two species in both cases. No such changes are found in the emission spectra by the added α -CD (Fig. 3, inset [down]). On the other hand, on the addition of CD (β - or γ -CD) to the DMF and DMSO solution of SMA, the intensity of the 425 nm band is enhanced without any change in the position of the band as shown in Fig. 4.

In the ground state, disappearance of the 390 nm band and enhancement of the 335 nm band by the added CDs indicates that the probe SMA (guest) experiences less polarity in the CD environment [14]. Hence, the disappearance of zwitterionic absorption shows that the movement of proton

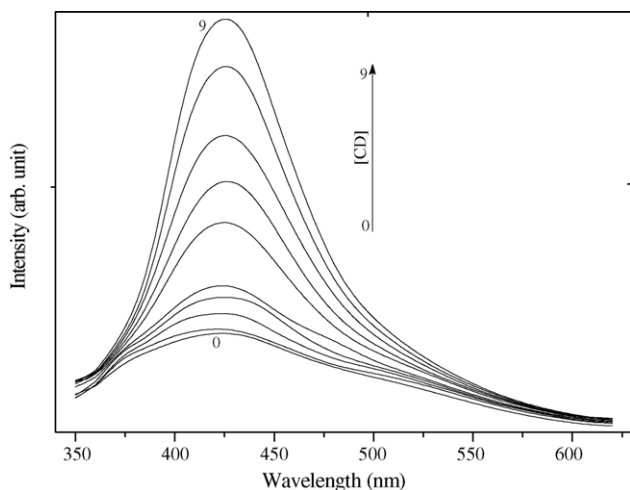


Fig. 4. Fluorescence emission spectra of SMA in DMSO in the presence of β -CD. ([CD] mM: 0 (0), 0.2 (1), 0.5 (2), 0.9 (3), 1.2 (4), 1.5 (5), 1.9 (6), 2.2 (7), 3.0 (8), 4.0 (9)).

is seriously affected due to caging of SMA molecule in CDs. The SMA shows a single absorption band at 335 nm in non-polar solvents like methyl cyclohexane and *n*-hexane. Hence, it can be said that the zwitterion is converted to the primary closed intramolecularly H-bonded SMA inside the CD cavity (Fig. 2). In other words, CDs perturb the zwitterion formation, which may be due to the restricted motion of hydrogen imposed by CD cavity.

We have used the Benesi–Hildebrand (B–H) linear regression analysis to obtain ground state association constant (K_g) for SMA-CD inclusion complex. The method provides a reliable information on the stoichiometry of the complex [25,26]. The B–H analysis for 1:1 stoichiometry gives the Eq. (1)

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K_g} \frac{1}{[\text{CD}]} \quad (1)$$

where I_0 is the initial fluorescence intensity of free guest, I_1 the intensity of guest–host complex, I the observed fluorescence intensity of guest and guest–host mixture and K_g is the ground state association constant for the 1:1 complex formation.

The observed data satisfy Eq. (1) giving rise to a linear fit as shown in Fig. 5A i.e. the linear B–H plot indicates that ground state inclusion complex has a 1:1 stoichiometry. The K_g values obtained from the slope and intercept of the plots are 681.7 M^{-1} for β -CD and 239.6 M^{-1} for γ -CD. We have also analyzed the fluorescence quenching of SMA emission by the Stern–Volmer (S–V) mechanism as described earlier [27]. Fig. 5B shows the S–V plots for the fluorescence quenching of the excited state SMA anion (A^{*-}) by β - and γ -CD. The concentration of the CDs is adjusted to $\sim 10^{-3}$ M so that all the (A^{*-}) species would be included in the CD cavity. The bimolecular quenching constant (k_q) of SMA obtained from the S–V plots by the added β - and γ -CD are 5.6×10^{10} and $0.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The observed isoemissive points respectively at 398 and 390 nm in case the of β - and γ -CD (Fig. 3) and also the linear S–V plot (Fig. 5B) reveals 1:1 association between β - or γ -CD and SMA in the excited state. The above k_q values reflects that SMA is bound to CDs strongly. At a glance, the k_q values and spectral changes (Fig. 3) simultaneously indicate that the quenching efficiency is highly dependent on the size of the CDs and also on the polarity imposed by the CD. The k_q values are higher and the required effective CD concentration is lower where CD provides the optimum space to the guest molecule. The observations also suggests that anion cannot be formed in this low polar media inside CD cavity. Both Shizuka et al. [13] and Eaton [28] suggested that the environment inside the CD cavity is less polar than the bulk aqueous phase. Hence, it is quite likely that H-bonded complex should form inside the CD cavity, due to the decrease of the polarity of the media. In aqueous solution, the observed bimolecular rate constants which are approximately similar to the diffusion controlled reaction rate for the H-bonded inclusion complex, reflect that the quenching occurs by collision. Again,

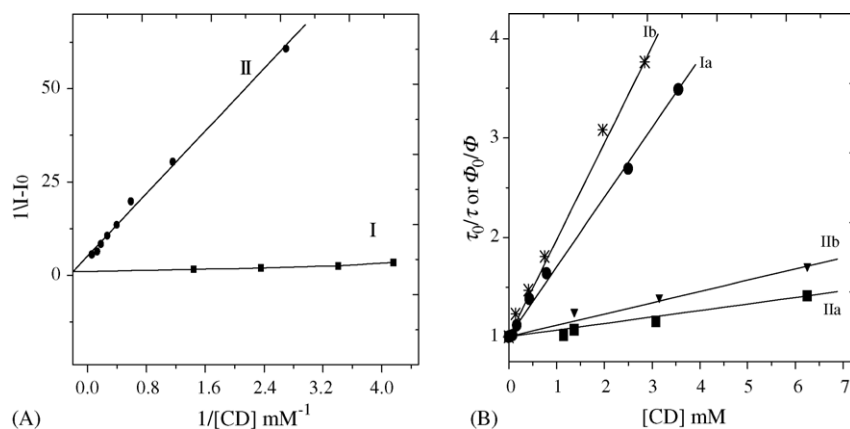


Fig. 5. (A) Benesi–Hildebrand plot for SMA complexed to β -CD (I) and γ -CD (II) assuming 1:1 SMA–CD complex; (B) Stern–Volmer plots for the quenching of SMA anion (A^{*-}) molecule by β -CD (Ia: τ_0/τ and Ib: Φ_0/Φ) and by γ -CD (IIa: τ_0/τ and IIb: Φ_0/Φ).

the enhancement of the intensity of intermolecular H-bonded species in DMSO (Fig. 4) and DMF by the added CD suggest that the hydroxyl group of CD (Fig. 1a) plays an important role in forming the H-bond with SMA molecules. Hence in non-aqueous media only enhancement in the formation of inclusion complex is observed. The increase in the intensity may be due to the formation of ternary complex between SMA, CD and non-aqueous electron donor solvent molecules [25]. This type of H-bonding interaction can significantly be responsible for the quenching of SMA anion (A^{*-}) in aqueous solution. The decrease in intensity and quantum yield (ϕ_f) due to H-bonded complex formation in β - and γ -CD solution is probably associated with the decrease in the micro-polarity, as previously observed with various aromatic molecules [29]. Shizuka et al. [13] made a similar type of observation in the case of 2-naphthol. The reaction equilibrium shifts towards the H-bonded complex on encapsulation in β - or γ -CD. They observed a decrease in the proton dissociation process due to the hydrophobic environment of the CD cavity.

Our steady state results corroborate the results of the time-resolved studies. The lifetime values (τ_f) of 440 nm emissive species and also quantum yields gradually decrease by the added CDs. The τ_f values of SMA in aqueous solution, in absence of CDs (11.8 ns) are significantly different compared to that obtained at higher concentration of CDs. At 4 mM concentration of β -CD, the τ_f value of SMA is 3.4 ns ($\lambda_{\text{mon}} = 440$ nm). This indicates that the species responsible for 440 nm emission is different from that of 425 nm emission species. An appreciable decrease in the τ_f value of SMA in CD environment indicates that the microenvironment of anion is different from that of H-bonded complex [30]. The decrease of τ_f can also be explained from the consideration that the H-bonded complex is formed within the β -CD. The decrease of τ_f values with varying concentration of in γ -CD is lower compared to that of β -CD. The formation of a host (CD)–guest (SMA) inclusion complex by CD is primarily determined by the tightness of fit i.e. matching between the guest and CD cavity. In the case of SMA, we observed a 10 nm blue shift (440–430 nm) in the case of γ -CD and

15 nm blue shift in the case of β -CD. Moreover the required CD concentration for effective fluorescence quenching is lower in the case of β -CD compared to γ -CD. As for example τ_f values at 4 mM concentration of β - and γ -CD are 3.4 and 8.2 ns, respectively. It is pertinent to mention two more points to explain these observations. Firstly, it is quite likely that due to less polar environment the anion gets less effectively solvated and thereby less stabilized (energetically high) in CD cavity than in the bulk water media. Secondly, it is also possible that due to less polar environment and the presence of hydroxyl group at the outer realm of CD in a circularly organized pattern (Fig. 1b), H-bonded complex formation occurs with SMA (Scheme I in Fig. 1d). The second explanation appears to be more justified when we see that at a very high concentration of β -CD, the lifetime value of anion drastically reduces to a value close to the lifetime value of the intermolecular H-bonded species as obtained in pure DMSO solvent (3.8 ns). Hence, lowering the polarity of the microenvironment across the probe (fluorophore) we can explain both the enhancement of 425 nm emission and decrease of 440 nm emission intensity.

The comparatively higher lifetime value and less blue shift in γ -CD than in β -CD solution may be attributed to greater cavity size of γ -CD, which results in a loosely bound complex with SMA, i.e. in the γ -CD cavity the anion and the H-bonded complex coexist in equilibrium. To get more corroborative evidences we have done some theoretical calculations at the AM1 level of approximation [31]. The optimized geometry of SMA in the ground state (GS) and excited state (ES) reflects that the effective diameter of different species of SMA are: *cis* enol 5.81 Å (GS), 5.64 Å (ES); anion 6.14 Å (GS) and 6.13 Å (ES). Again, the inner diameter of α -, β - and γ -CD are 4.5, 7.8 and 9.5 Å, respectively [32]. This shows that the excited SMA anion (A^{*-}) cannot enter the α -CD cavity whereas SMA effectively fits into the β -CD cavity and imperfectly binds to the γ -CD. This is also reflected by the lower k_q value [$5.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (β -CD) and $0.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (γ -CD)] in presence of γ -CD. Thus it can be assumed that the entry of water molecule

into the encapsulated center is completely forbidden in β -CD cavity, where in γ -CD, the entry of water molecule is not completely restricted. The water molecules inside the cavity may provide greater stability to the anion in γ -CD cavity compared to β -CD cavity. The question still remains as to whether there is any chance of intermolecular H-bond complex formation with the OH group in the outer surface of CDs. This can be ruled out as we have not observed any H-bonded complex formation in small core α -CD (4.5 Å) (Fig. 3), and in cavity-less glucose solution. The anion remains unaltered in presence of α -CD and in glucose solution. In the two cases, the lifetime values of 440 nm species (A^{*-}) are 11.8 and 11.8 ns, respectively, i.e. same as that of the anion in water (11.8 ns). Steady state fluorescence anisotropy measurements have also been done to add further support to the claim that inclusion complexes have been formed between SMA and CDs. The polarization ratio R ($R = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH})$; $G = I_{HV} / I_{HH}$) [33] is 0.0065 in aqueous solution of SMA ($\lambda_{ex} = 440$ nm) in the absence of CD. The values of R in presence of α -, β -, and γ -CD are 0.042 and 0.20 and 0.25, respectively. This reflects the fact that the rotational relaxation of the excited SMA anion is somewhat restricted in the CD cavity. From the increase of 425 nm emission intensity in DMSO and DMF, we propose that the restriction on the molecular motion imposed by CD is responsible for lowering the nonradiative decay rates and hence increase of fluorescence intensity [34]. It seems from our observation that the deactivation rate of anion ($0.8 \times 10^{10} \text{ s}^{-1}$) in pure water is slower compared to that of H-bonded complex ($3.0 \times 10^{10} \text{ s}^{-1}$) in presence of CDs.

4. Conclusion

Among the three CDs, only β - and γ -CD can form inclusion complex with SMA. α -CD cannot form inclusion complex due to small cavity diameter. The study of proton transfer reaction using SMA as the probe molecule in aqueous media shows that SMA forms 1:1 complexes with β - and γ -CD both in the ground and excited state. Our results show that SMA molecule particularly fits in β -CD whereas it is loosely bound in γ -CD due to different cavity size. The increase of higher energy emission and decrease of the lower energy emission is basically due to the lowering of the polarity of the medium. The CDs complexation gives rise to a much less polar microenvironment around SMA fluorophore, resulting in the destabilization of the anionic state. The anion cannot exist in this less polar environment. Interaction of SMA with CDs stabilizes the non-ionic form of SMA through intermolecular hydrogen bonding.

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