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ORIGINAL PAPER

Confinement of 4,4-Diaminodiphenyl Sulfone by γ –CD in Micellar Environment: A Spectroscopic Investigation

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Abstract This paper reports the double confinement of 4,4-diaminodiphenyl sulfone (Dapsone) inside γ–cyclodextrin (CD) in presence of surfactants (cationic, anionic and nonionic) using steady-state and time-resolved fluorescence spectroscopy. Interpretation of fluorescence spectra, fluorescence anisotropy and time resolved fluorescence decay of the γ-CD•Dapsone•micellar system hints at lesser microviscosity and the partial release of the probe molecule from the supramolecular host–guest complex in ionic micelles, of which greater in cationic micelles, but due to greater restriction and rigidity in presence of non-ionic micelle makes the probe more rigidly inside CD. Changes in computed rotational decay also corroborate the above findings.

Keywords Cyclodextrins · Inclusion · Dapsone · Anisotropy · Mixed micelle

Introduction

Cyclodextrins (CDs), family member of macrocyclic receptors, are of great interest due to their ability to form inclusion complexes (host–guest complexes) with a variety of guest organic molecules [1]. CDs are basically water soluble cyclic oligosaccharides having six, seven or eight glucopyranose units containing a hydrophobic cavity which can bind guest molecule of suitable size [2]. The interactions mainly responsible for the inclusion complexes formed between CDs and the organic molecules are geometrical steric factors, hydrophobic interactions, hydrogen bonding, and London dispersion forces [3]. The experimental techniques like UV/visible spectroscopy, NMR spectroscopy, calorimetry, circular dichroism, X-ray crystallography, and fluorescence spectroscopy have been employed to study the Cyclodextrin inclusion complexes [4–6]. Theoretical studies on cyclodextrin inclusion complexes [7] show the confinement of a probe by the CD nano-cavity modifies the degrees of freedom of the reaction coordinates of the guest molecule leading to the change in molecular relaxation in the excited state [8] and this has got myriads of applications as drug and medicine storage and delivery [9,10].

Micelles are being extensively studied as elementary models for biological systems [11] and lots of interest has been engendered in the micellar activities on the nature and characteristics of different photophysical and photochemical processes [12,13]. The interactions of charged hydrophobic and hydrophilic groups can modify the kinetics and energetic of the charge transfer process with respect to their characteristics in aqueous solvent [14]. In micelles the probe may experiences a dry hydrophobic core, a wet spherical Stern layer, a defused Gouy Chapmann (GC) layer and the bulk water [15]. Depending on the chemical structure of the probe molecule, the reaction rates and equilibriums in the micellar media are affected due to the changes in physicochemical properties of the medium [16]. Differential stabilization and destabilization of the probe involved in the charge transfer process exert an intrinsic effect on the rates and local concentration of charges. So depending on the charge and structure the probe molecule can be incorporated inside the micelle, where the probe faces various constraints on the free movement.

The study on mixed assembly of cyclodextrin-surfactant has been drawing great interest due to their, commercial applicability and of vital role in biological and natural process

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[17–19]. The conductance, fluorescence, Nuclear Magnetic Resonance (NMR), surface tension, diffusion coefficient etc. methods shows the influence of cyclodextrin on the physicochemical properties of micellar solutions [20–24]. It also has been shown that after micelization process cyclodextrin does not interact at all with the micellar system [25] but the critical micellar concentration (CMC) value increases in presence of CD [26].

Dapsone (Chart 1) is a well-studied charge transfer molecule and the solvent effect has been extensively studied [27,28]. In earlier reports the photophysical changes of the probe inside CD-nano cavity, micellar- interface, reverse micellar- interface and polymer micelle composite have been investigated [29–31]. Intrigued by the possibilities of double confinement, we envisage constructing unique self assembled structures covered with surfactants using environment sensitive Dapsone as probe to monitor the charge transfer reaction in γ-CD covered with cationic, anionic and nonionic micelle. The modifications of functional moieties, such as γ-CD, inside the self assembled structure have been extremely important in the design of targeted drug carriers and molecule recognizers which have been proved to be extremely helpful in their applications of biomedical field. In this article we will try to address the molecular interactions in those complexes self-assembly of γ-CD and micelles by electronic absorption, fluorescence and time-resolved spectroscopy.

Experimental Section

4,4-diaminodiphenyl sulfone (Dapsone) supplied by Aldrich Chemical Company, U.S.A. was recrystallized in ethyl acetate/petroleum ether before use. Spectroscopic grade γ-CD purchased from Aldrich Chemical Company, U.S.A. was used as received. Sodium Dodecyl Sulfate (SDS, purity ≥98.5), Cetyltrimethyl Ammonium Bromide (CTAB, purity ≥ 99), and Tween 20 (TW-20) are from Aldrich Chemical, U.S.A. Millipore Milli-Q system purified water was used for measuring the absorption and emission spectra. Concentration of primary stock solution of Dapsone in ethanol was 5 mM. The absorption spectra were recorded with a UV-2401 PC Shimadzu absorption spectrophotometer and fluorescence measurements were performed with a Hitachi F-4500 or Horiba Jobin Yvon Fluromax 4 spectrofluorimeter at 300 K using 1 cm path length quartz cuvette.

Fluorescence anisotropy or polarization measurements were performed as described elsewhere [28]. The time resolved emission spectra (with excitation at 295 nm) were recorded using time correlated single photon counting (TCSPC) technique in a Horiba Jobin Yvon instrument [30]. Time-resolved anisotropy data were taken in the usual way [32]. Fitting of lifetime decay was made so that χ^2 value is ~1 and Durbin Watson (DW) parameter is ~ 1–2

Results and Discussions

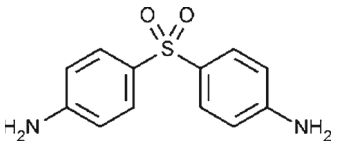
Steady State Absorption and Emission

The absorption spectra of Dapsone in water, aqueous solution of γ-CD and in presence of SDS surfactants are shown in Fig. 1a. Addition of 15 mM γ-CD shows 4 nm red shift, but with progressive addition of surfactants a decrease in absorbance along with a blue shift of 2 nm could be observed for SDS and TW-20 surfactants, though in pure SDS and TW-20 micellar solution the absorbance peak was at 294 nm and 290 nm, respectively (Table 1). On the other hand, addition of CTAB surfactant to the aqueous CD solution the absorbance decreases without any appreciable shift. This observation indicates that the environment of the mixed CD/probe/micellar system is neither like CD environment (γ-CD•Dapsone) nor like pure micellar environment. The decrease in absorbance could be due to the exclusion of the probe molecule from the γ-CD cavity in addition of surfactants.

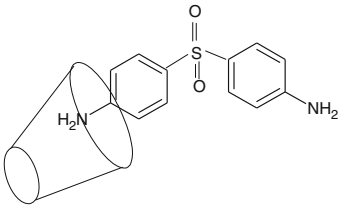
At room temperature (300 K) Dapsone shows a broad unstructured charge transfer band at 459 nm in water. Addition of γ-CD increases the emission intensity largely (~11 times at 15 mM) along with 28 nm blue shift. It was observed in our previous communication that γ-CD cavity encapsulates Dapsone, though major part of the molecule remains outside the cavity [28]. Upon addition of SDS surfactant to the aqueous solution of Dapsone the fluorescence intensity increases very little and the fluorescence peak position shifts 15 nm towards blue. But addition of CTAB and TW-20 surfactants to the aqueous solution of Dapsone huge increase in emission intensity along with a blue shift of 48 nm and 55 nm, respectively could be observed. Depending on the nature and characteristics of the probe molecule it can reside in the non polar core of a micelle or in the Stern layer or in the water-micelle interface. Considering electrostatic and hydrophobic force as main driving force we found that the probe molecule enters very little into the SDS micelle, whereas in CTAB and TW-20 micelle probe molecule resides at various positions of the water micelle interfacial region [31].

A completely different picture is observed if we add surfactants to the solution containing γ-CD (γ-CD•Dapsone). The fluorescence intensity decreases with down-shift of emission peak (2 nm) if we add SDS surfactant above 1 mM, and above 10 mM concentration of SDS no major spectral change was observed (Table 1). Comparatively greater decrease in fluorescence intensity could be observed on addition of CTAB surfactant (10 mM) with 3 nm blue-shifted peak position (Fig. 1b). Surprisingly, if we add TW-20 surfactant to γ-CD•Dapsone complex increased fluorescence intensity and remarkable hypsochromic shift (8 nm) is observed. So the environment experienced by the fluorophore is quite different than that was observed in pure CD-solution or in pure micellar solution.

Chart 1 Chemical structure of dapsone. 1:1 γ–cyclodextrin inclusion complex



Chemical structure of Dapsone



1:1 γ–cyclodextrin Inclusion complex

We know that to form inclusion or association complex the main driving force is hydrophobic and electrostatic force [28]. In the case of SDS surfactant the head groups are negatively charged and the main charge responsible for electrostatic attraction or repulsion in Dapsone is negative around the oxygen atom [29]. If SDS micelle encapsulates the γ-CD•Dapsone system then the probe experiences competitively less hydrophobic force due to nonpolar environment which will try to pull the probe outside the CD cavity. As a result fluorescence intensity should decrease but on the other hand negative head groups will try to increase the fluorescence intensity by pushing the probe molecule towards the CD cavity and nonaqueous environment. The observed fact indicates that the reduction in hydrophobic force effect is more prominent than the electrostatic repulsion and nonpolar environment effect.

In the case of CTAB surfactant the polar head groups are positive which will help the probe to be outside the γ-CD cavity, as a result more decrease in fluorescence intensity could be observed. The environment polarity affects a little which results 3 nm blue shift. But in the case of TW-20, the only driving force is hydrophobic which makes the γ-CD•Dapsone-micelle system more compact and more rigid. As a result a decrease in non-radiative channel [29] causes an increase of fluorescence intensity with greater blue shift. It is pertinent to mention here that no change in spectral signature of the probe molecule could be observed if the probe encapsulated in surfactants is allowed to interact with γ-CD. So it may be surmised that the emission signature of the probe uniquely changes when the probe encapsulated in γ-CD interacts with surfactants.

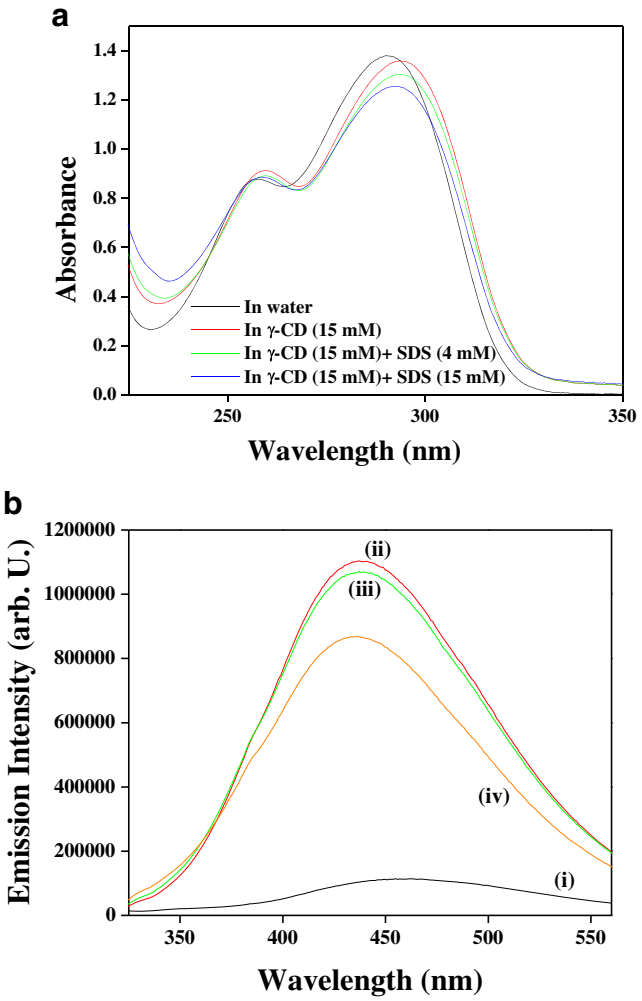


Fig. 1 **a** UV-visible absorption spectra of Dapsone in water, only γ -CD (15 mM), and in presence of SDS surfactant. Concentration of the Dapsone molecule was 0.05 mM. **b** Emission spectra of Dapsone in (i) water, (ii) γ -CD (15 mM), and inside γ -CD in presence of (iii) 2 mM and (iv) 5 mM CTAB surfactant

Steady State Fluorescence Anisotropy

The steady-state fluorescence anisotropy reveals the rotational diffusion of the entrapped molecules [33], which is a measure of the rigidity of the environment. The fluorescence anisotropy variation of Dapsone in γ-CD•Dapsone-micelle (anionic) system at different concentrations has been represented in Fig. 2. In the presence of SDS and CTAB surfactant after an initial increase in steady-state anisotropy a decrease in anisotropy could be observed but in presence of CTAB surfactant decrease in anisotropy is more. In γ-CD•Dapsone-TW-20 micellar system the fluorescence anisotropy increases with TW-20 concentration (Table 2). This observation indicates that the probe molecules face less restriction in presence of SDS micellar system and even lesser restriction in CTAB micellar system but the probe molecules face greater restrictions in γ-CD•Dapsone-TW-20 system. So this observation possibly points to the fact that the probe molecules are getting released partially from γ–CD cavity with addition of SDS

Table 1 Absorption, emission maxima, the emission lifetimes (τ_f) data, normalized pre-exponential factors (a_i) from the multi-exponential fit to the fluorescence decay of Dapsone (0.005 mM), average lifetimes in water, different mixed CD-micelles system. The excitation and observation wavelength were 295 nm and 431–459 nm, respectively

System	λ_{max}^{abs} (nm)	λ_{max}^{ems} (nm)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)	$\langle\tau\rangle$ (ns)	χ^2
Dye + water	290	459	0.20	0.19	0.80	0.92			0.77	0.988
Dye + γ-CD (15 mM)	294	439	0.32	0.69	0.68	0.98			0.89	0.992
Dye + SDS (15 mM)	294	444	0.37	0.21	0.49	0.98	0.16	3.03	1.04	1.109
Dye + CTAB (5 mM)	292	437	0.25	0.19	0.28	0.97	0.48	4.26	2.36	0.967
Dye + TW-20 (2 mM)	297	411	0.28	0.21	0.60	0.95	0.12	4.08	1.12	1.031
Dye + γ-CD + SDS (15 mM)	294	436	0.21	0.59	0.63	1.01	0.16	1.23	0.96	1.008
Dye + γ-CD + CTAB (5 mM)	290	404	0.22	0.57	0.56	0.99	0.22	1.48	1.01	0.992
Dye + γ-CD + TW-20 (2 mM)	290	431	0.24	0.53	0.48	1.15	0.28	2.58	1.40	0.985

surfactant and the release of the probe molecules from the cavity is more in presence of CTAB surfactant.

Micropolarity and Microviscosity

Comparison of the fluorescence properties of the probe in the mixed CD-micellar environment with those of the probe in pure or mixed solvents of known polarity helps us to estimate the micropolarity of the said environment [34]. But it should be kept in mind that the polarity of the heterogeneous medium is not exactly same as that of the homogeneous media. Dapsone has been used to get an estimate of the polarity of the micro-heterogeneous environment as the charge transfer emission of Dapsone is polarity sensitive. The local polarity around the fluorophore in the mixed CD-micellar system has been determined using the calibration curve of the emission maxima of Dapsone in different polar solvents with known values of E_T (30) [35]. The calibration curve thus generated may not reflect the actual polarity of mixed micelle-CD system but, it may help in estimation of polarity around the probe. From the calibration curve it is observed that the environment of the probe inside mixed CD-micellar system is different and less polar than that of the bulk aqueous solution (Fig. 3a). In the presence of TW-20 micelle the environment is more nonpolar than that in presence of SDS and CTAB micelle (Table 2).

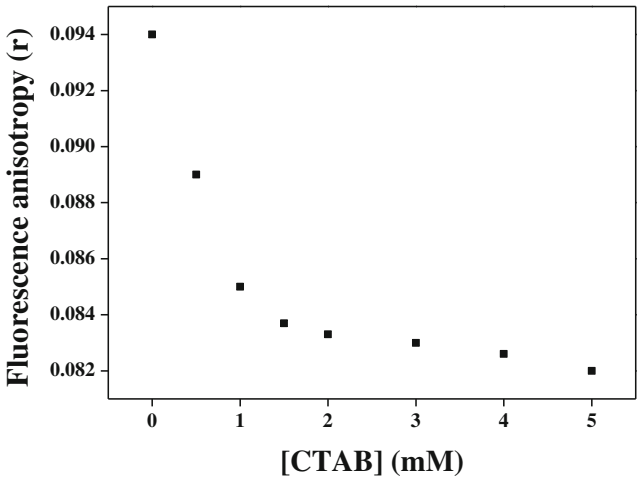


Fig. 2 Plot of fluorescence anisotropy against CTAB surfactant concentration

On the other hand, by comparing the steady-state fluorescence anisotropy of the probe in the mixed CD-micellar environment with those in the solvents of known viscosity the microviscosity of the local environment around the fluorophore can be estimated [35,36]. The calculated values of viscosity of the glycerol-water mixture have been used to measure the anisotropy values [37]. By changing the gradual proportion of water-glycerol mixture the variation of fluorescence anisotropy with viscosity, a calibration curve (Fig. 3b) has been generated and the computed values of the viscosity from the calibration curve have been given in Table 2. It is observed that the viscosity decreases in presence of SDS and CTAB micellar environment though the rate of decrease in CTAB micellar system is greater. The above observational facts corroborate our previous explanation.

Time-Resolved Studies

The fluorescence decay (excited at 295 nm and monitored at respective fluorescence maxima) of the probe molecule was measured at different micellar systems. In aqueous solution Dapsone shows bi-exponential decay [29], of which the lifetime component sensitive to the environment has been assigned to be originated from the charge transfer state and the other one is attributed to the locally excited state [32,38]. Addition of γ –CD to the aqueous solution of Dapsone bi-exponential decay was observed. In this situation the probe is not fully encapsulated inside the CD-cavity, rather a major part of the molecule including one aniline group is outside the CD cavity [28]. Thus in the presence of γ–CD, the fast component of lifetime is due to average lifetime of the free probe molecule and the slow component is due to the γ-CD•Dapsone complex. Interesting situation could be found when surfactants were added to the γ-CD•Dapsone complex.

Table 2 Values of Fluorescence maximum, $E_T(30)$, steady state anisotropy and viscosity in γ-CD and in three different mixed cyclodextrin-micelle systems

Environment	Emission maximum (nm)	$E_T(30)$	Anisotropy r	Viscosity η (cP)
Dye + γ-CD (15 mM)	439	59.22	0.094	1.53
Dye + γ-CD + SDS (15 mM)	437	58.84	0.086	1.37
Dye + γ-CD + CTAB (5 mM)	436	58.59	0.082	1.18
Dye + γ-CD + TW-20 (2 mM)	431	57.47	0.124	1.98

Addition of SDS surfactant to the aqueous γ-CD•Dapsone solution results in a sharp decrease in faster component with a lesser amplitude and slight decrease in the slower component with greater amplitude (Table 1). On the other hand, addition of cationic surfactant results an extra slowest third component along with a decrement of slower component. The third component may be due to the γ-CD•Dapsone•micelle complex, whereas the decrease of slower component may be due to the greater release of the probe molecule from the γ–CD cavity in the presence of CTAB micelle (Fig. 4a). But addition of TW-20 surfactant increases the slower component along with a new probe-micelle third component (Table 1).

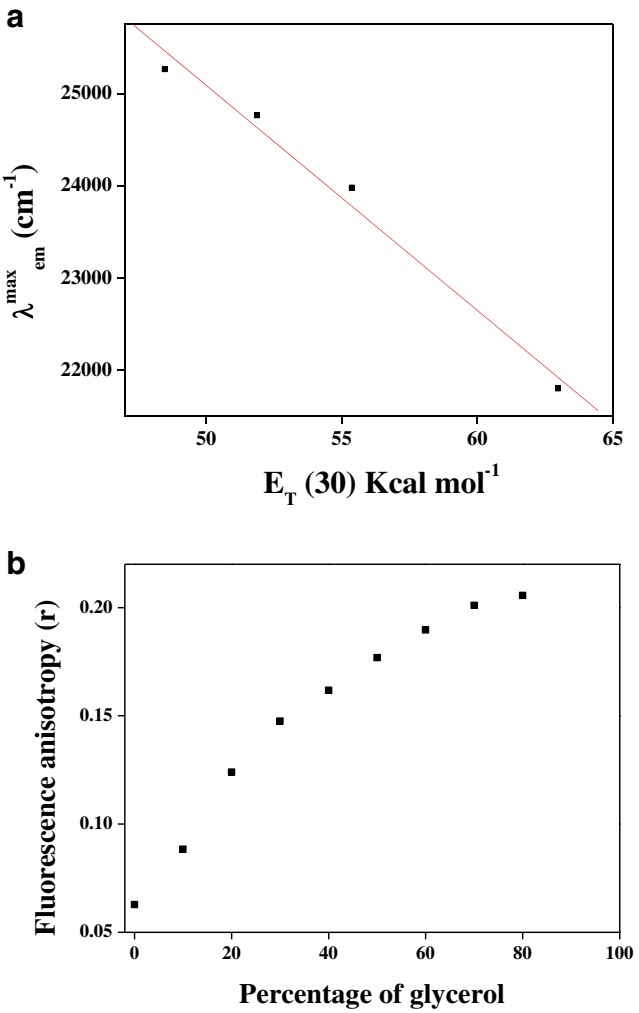


Fig. 3 **a** Variation of fluorescence maximum of Dapsone in different solvents as a function of E_T (30). **b** Plot of fluorescence anisotropy against different proportion of glycerol-water mixture

So, these observations leads us to the fact that in presence of SDS micelle the probe molecules face less restriction (may be due to the little protrusion of the probe molecule) and in presence of CTAB-micelle Dapsone experiences lesser restriction (may be due to greater protrusion of the probe molecule) and as a result the slow component decreases in both the cases. But the observation is opposite in presence of TW-20 micelle. Here the probe molecule experiences greater restriction on the rotational freedom which may arise due to rigid encapsulation of the γ-CD•Dapsone complex.

To get additional information about the rotational relaxation of the probe molecule inside the γ-CD•Dapsone-micelle inclusion complex the time-resolved emission anisotropy data were taken in aqueous solvent, in γ–CD and in different CD-probe-surfactant environment by exciting the probe at 295 nm. The rotational decay time in water as well in different complexes system fitted to single exponential function. In aqueous solvent the rotational decay time is about 890 ps and in γ–CD it is about 980 ps. This small change in rotational decay indicates major part of the probe molecule is in water. In pure SDS, CTAB and TW-20 micellar environment the rotational decay times are 1,440 ps, 1,830 ps and 1,940 ps, respectively [31]. This observation points towards the molecular incorporation inside the micelle. But addition of SDS surfactant to the CD-probe solution the rotational decay time increases to 1,150 ps though it is less than that in neat SDS micelle (Table 3). Addition of CTAB surfactant increases the rotational decay time but it is less (Fig. 4b) than in CTAB. Upon addition of TW-20 surfactant the rotational decay time increases in comparison to that in γ–CD.

The increase in rotational decay time possibly means the molecule does not experience water-like situation, rather it feels little restricted environment. In the steady state observation the sample is continuously illuminated with a beam of light and fluorescence spectrum is observed. During this exposure molecules get excited and the charge separation occurs then electrostatic effect comes into play. Steady state observation is actually the average of the time resolved phenomena [32]. On the other hand in anisotropy decay measurement the sample is exposed to the pulse of light and decay occurs very fast and in this time-frame all the molecules may not be in equilibrium. As a result the molecule takes some time to experience all the effective forces which we observe in the

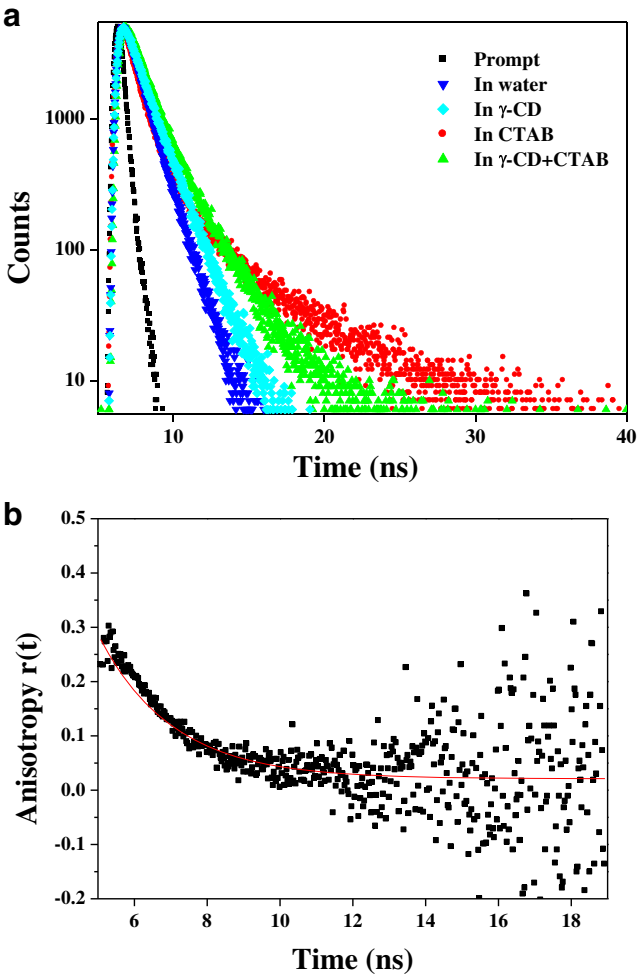


Fig. 4 **a** Time-resolved fluorescence intensity decay profile of Dapsone in water, γ -CD (15 mM), CTAB surfactant (5 mM) and in mixed CD-CTAB surfactant environment. **b** Fluorescence anisotropy (r(t)) decay of Dapsone in γ -CD (15 mM) - CTAB (5 mM) mixed CD-surfactant environment

steady state experiments. But time resolved anisotropy decay hints that the molecule takes time to release from the cyclodextrin cavity. So, the probe molecule inside γ-CD•Dapsone-SDS complex tries to get out from the CD cavity and feels lesser restriction. On the other hand, the probe experiences even lesser restriction in the presence of CTAB micellar system. But inside γ-CD•Dapsone–TW-20 complex probe experiences greater restriction.

Table 3 Values of fluorescence anisotropy decay and rotational time (τ_{rot}) of Dapsone in water and in different micellar systems. The excitation wavelength was 295 nm and monitored at their corresponding steady state emission wavelength maxima

Environments	τ_r (ns)	DW[a]	χ^2
Dye + water	0.89	1.91	1.01
Dye + γ-CD (15 mM)	0.98	1.83	0.94
Dye + SDS (15 mM)	1.44	1.94	0.96
Dye + CTAB (5 mM)	1.83	1.98	1.04
Dye + TW-20 (2 mM)	1.94	1.87	0.96
Dye + γ-CD + SDS (15 mM)	1.15	1.86	0.98
Dye + γ-CD + CTAB (5 mM)	1.03	1.89	1.03
Dye + γ-CD + TW-20 (2 mM)	1.54	1.76	1.09

[a] *DW* Durbin-Watson parameter

Conclusion

The perturbation of cationic, anionic and nonionic surfactants on the charge transfer properties of Dapsone inside γ–CD cavity has been demonstrated in this paper. The formation of inclusion complex of the γ-CD•Dapsone remarkably changes the spectral properties in presence of the micellar environment. It is found that upon induction of SDS surfactant into the γ-CD•Dapsone complex the mixed micellar system become less rigid. Upon addition of CTAB surfactant to the γ-CD•Dapsone similar spectroscopic signature could be observed, but with greater amplitude. But addition of TW-20 surfactant results the micellar environment more compact, more rigid and less mobile.

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