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Solvation dynamics of DCM in micelles

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Abstract

The solvation dynamics of 4-(dicyanomethylene)-2-methyl-6(*p*-dimethylaminostyryl) 4H-pyran (DCM) have been studied in neutral (Triton X-100, TX), cationic (cetyl trimethyl ammonium bromide, CTAB) and anionic (sodium dodecyl sulfate, SDS) micelles using picosecond time-resolved Stokes shift. Above the critical micellar concentration for all three micelles, DCM exhibits wavelength-dependent fluorescence decays. At short wavelengths, a fast decay is observed while, at long wavelengths, a distinct growth precedes the decay. The time-dependent Stokes shift indicates that the water molecules in the Stern layer of the micelles relax on a timescale which is markedly slower than the sub-picosecond relaxation dynamics in pure water.

1. Introduction

Relaxation behavior of the water molecules, bound to various organized media and perturbed by the local electrostatic and hydrogen-bond interactions, is of fundamental importance to understanding many natural and biological processes [1–14]. Fleming et al. [2] first reported that while solvation dynamics of Coumarin dyes in ordinary bulk water occurs on a sub-picosecond timescale (310 fs), in γ-cyclodextrin (γ-CD) the solvation dynamics exhibits a component on the nanosecond timescale. Nandi and Bagchi [3] attributed the observed retardation of the solvation process to the freezing of the solvent translational modes inside the cyclodextrin cavity. Subsequently, solvation dynamics has been studied in many organized media such as the water surface [4], protein [5], micro-emulsions [6–9], sol–gel glass [10], polymer hydrogel [11], lipid [12] and micelles [13,14]. Recently we have reported that the laser dye 4-(dicyanomethylene)-2-methyl-6(*p*-dimethylamino-styryl) 4H-pyran (DCM, I) exhibits slow solvation dynamics on the nanosecond timescale in a microemulsion [9]. In the excited state DCM undergoes several ultrafast processes, such as intramolecular charge transfer, (ICT), twisting about the double bond and solvation dynamics [15–18]. Due to the ICT process, the excited state dipole moment (26.3 D) of DCM is much higher than that in the ground state (5.6 D). Solvation dynamics of DCM in methanol has been found to be bi-exponential, with one component on the 100 fs timescale and another in that of a few picoseconds [15–18]. In the present work, we report on the time-dependent Stokes shift of DCM in three micelles: neutral Triton X-100 (TX), anionic sodium dodecyl sulfate (SDS) and cationic cetyl trimethyl ammonium bromide (CTAB). We have previously

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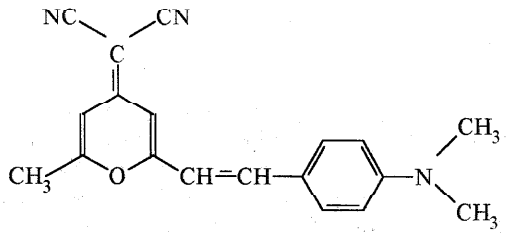
observed dramatic retardation of solvation dynamics in these three micelles using Coumarin 480 (C-480) [13] and 4-aminophthalimide (4-AP) [14] as probes. However, since the probes used in earlier studies are highly soluble in water, it is not possible to rule out the presence of the probes at least partially in the bulk water. Since DCM is insoluble in water, it stays exclusively inside the micellar aggregates and hence reports most faithfully the dynamics of the micelles.

2. Experimental

DCM (laser grade, Exciton) and Triton X-100 (Aldrich) were used as received.



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Other surfactants (Aldrich) were purified by recrystallisation. Steady-state absorption and emission were recorded on JASCO 7850 and Perkin Elmer 44B instruments, respectively. For lifetime measurement, the sample was excited at 300 nm with the second harmonic of a cavity dumped rhodamine 6G dual jet dye laser with DODCI as saturable absorber (Coherent 702-1) pumped by a cw mode locked Nd:YAG laser (Coherent Antares 76s). The emission was detected at magic angle polarization using a Hamamatsu MCP 2809U photomultiplier. The full width at half maximum (FWHM) of the instrument response at 300 nm is ca. 80 ps. The fluorescence decays were deconvoluted using a global lifetime analysis software (PTI). Reconstruction of the time-resolved spectra was done following the procedure described by Maroncelli and Fleming [23]. For determination of the emission quantum yield (ϕ_f), DCM in methanol, ($\phi_f = 0.44$) [18] was used as standard.

3. Results

3.1. Steady-state spectra

As already mentioned, DCM is insoluble in water. However, in the presence of the surfactants above their respective critical miceller concentration (cmc), DCM is solubilized in water and shows intense emission with a quantum yield (ϕ_f) of 0.55, 0.40 and 0.35, respectively, in 10 mM TX (cmc = 0.26 mM), 100 mM CTAB (cmc = 0.9 mM) and 100 mM SDS (cmc = 8 mM) (Fig. 1). For all the three micelles the emission maximum of DCM is at 620 nm. The position of the emission maxima of DCM in micelles are similar to that of DCM in highly polar solvents, e.g. methanol, formamide, etc, [19,20]. It may be recalled that in pure hydrocarbon (e.g. *n*-heptane) DCM exhibits very weak emission with $\phi_f = 0.01$ and maximum at 530 nm [9]. It has been reported that the emission quantum yield of DCM increases with an increase in solvent polarity and is 0.44 in methanol [15–18,21,22]. The emission maximum (620 nm) and quantum yields (0.35–0.55) of DCM in TX, SDS and CTAB suggest that, in the presence of the micelles, DCM molecules do not stay

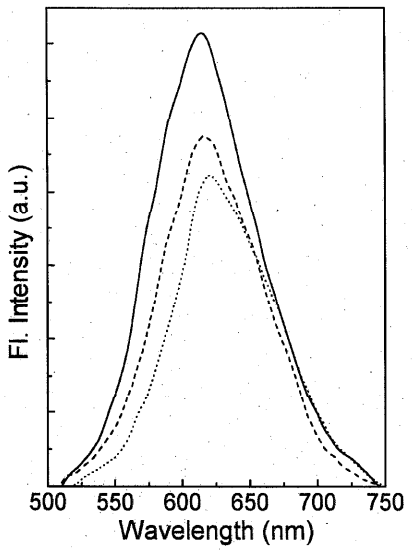

Fig. 1. Emission spectra of DCM in 10 mM TX (—), 100 mM CTAB (- - -) and 100 mM SDS (· · ·).

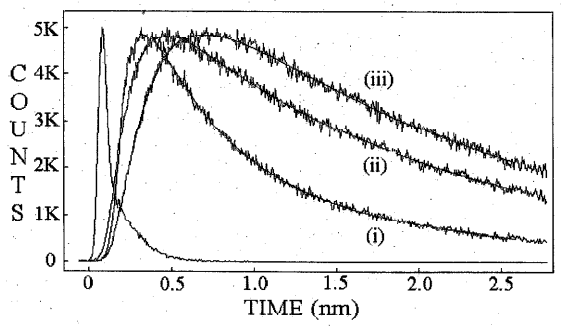

Fig. 2. Fluorescence decays of DCM in 10 mM TX at (i) 540 nm, (ii) 620 nm, (iii) 720 nm.

in the 'dry' hydrocarbon core of the micelles and stay in the highly polar peripheral Stern layer of the micelles.

3.2. Time-resolved spectra

It is observed that, in the three micelles, the fluorescence decays of DCM at the red end differ significantly from those at the blue end (Fig. 2 and Fig. 3). In all the micelles, at the red end of the emission spectra, a distinct rise precedes the decay while, at the blue end only, a decay is observed. For instance, in 10 mM TX, at the red end (720 nm), the time-resolved emission data for DCM is fitted to a bi-exponential decay with a rise time of 220 ps and a decay component of 3 ns. For the same sample at the blue end (540 nm), one observes a bi-exponential decay with two decay components of 330 ps (65%) and 1.77 ns (35%). Such a wavelength-dependent emission decay indicates a time-dependent Stokes shift of the emission spectra. In this case, the energy of the probe dipole continuously decreases with time due to solvation causing a decay at the blue end and a growth at the red end of the emission spectra. In order to get detailed information on the solvation dynamics, the time-resolved emission spectra of DCM in the three miceller solutions are constructed at different times from the decays recorded at different wavelengths (Fig. 4) following the procedure described by Maroncelli and Fleming [23]. The reconstructed response function $C(t)$, defined as,

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

were calculated using the peak frequencies $\nu(\infty)$, $\nu(t)$ and $\nu(0)$ at times ∞, t and 0, respectively. The time constant of the solvation dynamics in the Stern layer of the micelles is obtained from the temporal dependence of $C(t)$. Fig. 5 shows the decay of $C(t)$ and Table 1 summarizes the decay characteristics of $C(t)$ for the three micelles. It is readily seen that for

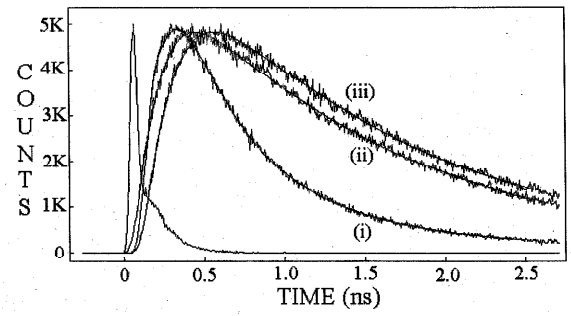

Fig. 3. Fluorescence decays of DCM in 100 mM SDS at (i) 540 nm, (ii) 620 nm, (iii) 720 nm.

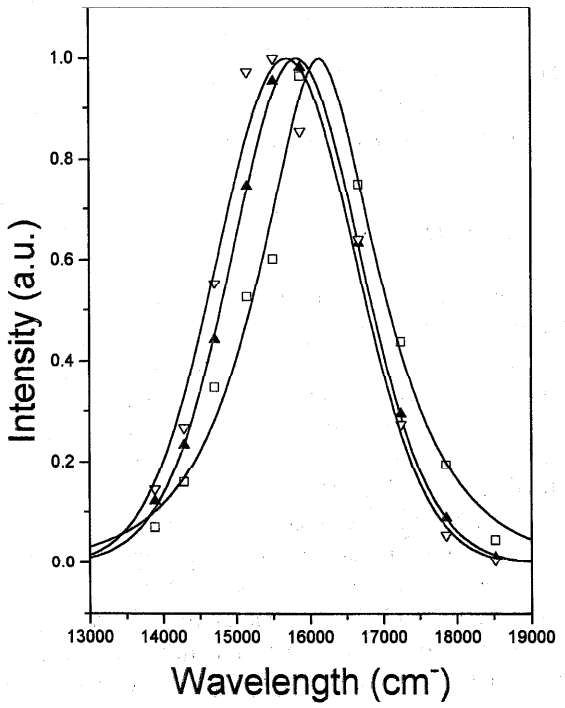

Fig. 4. Time-resolved emission spectra of DCM in 100 mM SDS at 0 ps (□), 1000 ps (▲), and 10000 ps (▽).

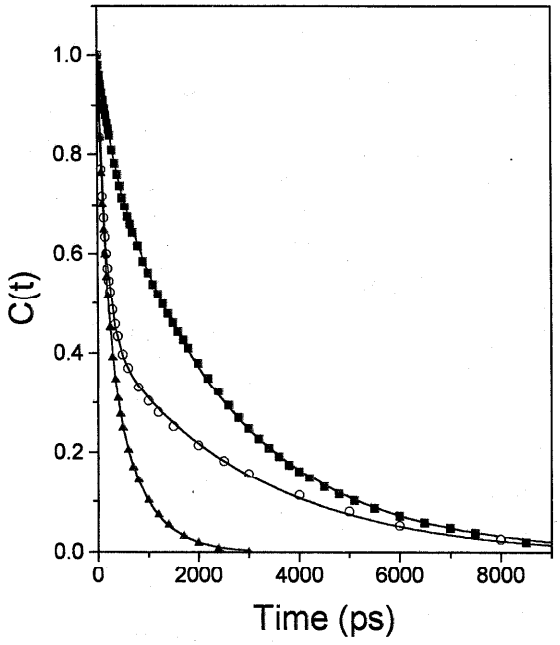

Fig. 5. Decay of response function, $C(t)$ of DCM in (i) 10 mM TX (■), (ii) 100 mM SDS (∘) and (iii) 100 mM CTAB (▲). The points denote the actual values of $C(t)$ and the solid line denotes the best fit to a bi-exponential decay.

the three micelles the average solvation times $\langle\tau_s\rangle$ defined as $\sum a_i\tau_i$ are 2.10, 1.40 and 0.40 ns, respectively, for TX, SDS, and CTAB.

4. Discussions

The steady-state emission spectra indicate that DCM does not exhibit dual emission in the three micelles. This suggests that the ICT process of DCM remains ultrafast in the three micelles. From the similarity of the observed emission maximum and quantum yield of DCM in the micelles to that of DCM in methanol [15–20] we assign the 620 nm emission band to the polar TICT state.

In a micellar solution, there are three possible locations of the probe, bulk water, the inner hydrocarbon core and the peripheral Stern layer. Since DCM is insoluble in water the first possibility is ruled out. In a hydrocarbon the emission quantum yield of DCM is extremely low (0.01) and lifetime is very short (< 50 ps) [9]. Further, in *n*-heptane the emission maximum of DCM is very much blue shifted to 530 nm and the decay does not exhibit wavelength dependence [9]. Thus the DCM molecules staying in the 'dry' hydrocarbon core of the micelles is not expected to contribute to the observed solvation dynamics. Thus the solvation dynamics is appeared to be exclusively due to the DCM molecules in the peripheral Stern layer.

It is readily seen that the solvent relaxation time in the neutral micelle TX (2100 ps) is much slower than those in CTAB (400 ps) and SDS (1400 ps) (Table 1 and Fig. 5). This result is similar to those obtained earlier in the case of C-480 and 4-AP [13,14] and can be explained in terms of the structures of the three micelles. Recent small angle neutron scattering studies [24–26] have revealed detailed information on the structure of these micelles. These studies indicate that the core of any micelle is essentially dry and contain the alkyl chains. The 'dry' core is surrounded by a spherical shell which contains the polar (for neutral TX) or the ionic head groups (for ionic CTAB and SDS) and water molecules. The spherical shell is called Stern layer for an ionic micelle and palisade layer for a neutral one. For TX the palisade layer is about 25 Å thick while the Stern layers of CTAB and SDS are quite thin (6–9 Å) [24–26]. Evidently, in the case of TX, the probe DCM molecule is totally enclosed inside the palisade layer and is unexposed to the fast-moving bulk water molecules. For the thin Stern layer of CTAB and SDS, the major portion of the probe molecule (DCM) sticks out to bulk water and experiences fast solvation dynamics.

Very recently, Telgmann and Kaatze [27] reported that aqueous micellar solutions exhibit three different dielectric relaxation times in a slow (μs), intermedi-

Table 1
Decay characteristics of the solvent response function, $C(t)$, of DCM in micelles

	$\Delta\nu$ (cm^{-1})	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau_s\rangle$ [a] (ps)
TX-100	950	0.15	300	0.85	2440	2100
SDS	450	0.55	160	0.45	2900	1400
CTAB	550	0.50	170	0.50	630	400

[a] $\langle\tau_s\rangle = a_1\tau_1 + a_2\tau_2$.

ate (10 ns) and fast (0.1 ns) timescale. They attributed the slow relaxation time to the exchange of monomers between micellar aggregates and free monomers and the fastest component to the rotation of the polar head groups. The intermediate relaxation time on a 10 ns timescale is similar to the relaxation dynamics in the Stern layer. According to the continuum theory [28], the solvation time (τ_s) is given by $\tau_s = (\varepsilon_\infty/\varepsilon_0)\tau_D$, where ε_∞ and ε_0 denote infinite frequency and static dielectric constant and τ_D, is the dielectric relaxation time. One may assume that ε_∞ in the Stern layer of the micelles is same as that of water i.e. ≈ 5 [28]. Since the micellar interface resembles alcohol [13,14], one may use $\varepsilon_0 = 30$. Then using the dielectric relaxation time of 10 ns, one immediately calculates a solvation time of $(5/30) \times 10$, i.e. 1.67 ns which is similar to the observed solvation time for the three micelles.

It may be noted that the total Stokes shift, $\nu(0)$–$\nu(\infty)$ detected for DCM in the three micelles are 950, 550 and 450 cm^{-1} for TX, CTAB and SDS, respectively. The spectral shift is considerably less than that observed in methanol (3800 cm^{-1}) or glycol (2400 cm^{-1}) [15] and that reported in our recent work in micro-emulsion (1600 cm^{-1}) [9]. It may be recalled that earlier studies also indicate that the spectral shift for the probes, C-480 and 4-AP in micelles are much less than those observed in homogeneous solvents [13,14]. It seems that the picosecond setup used in this study is unable to detect the ultrafast component of solvation which occurs on the < 80 ps timescale. However, the present study clearly reveals a component of solvation on the 400–2100 ps timescale which is substantially slower than the sub-picosecond dynamics observed in bulk water [2].

Recently, it has been demonstrated that the relaxation of ions about an instantaneously created dipole occurs on the nanosecond timescale [29,30]. Since the solvation dynamics observed in the ionic micelles (CTAB and SDS) is slower than that in neutral TX, the role of the ionic solvation appears to be minor. Further, we have recently demonstrated that slow, nanosecond dynamics is also observed in neutral micro-emulsions which are free from ions [31]. Thus the slow relaxation observed in this case appears to be due to the restricted motion of the water molecules in the Stern layer of the micelles and not to ionic relaxation. ESR studies indicate that the chain dynamics of surfactants occurs on the 100 ns timescale [32]. This is much slower compared to the timescale of solvation dynamics (0.4–2.1 ns) reported in the present work. Since the polar or charged head groups of the surfactants in the micellar aggregates are tethered to the surfactant chains, their motion is expected to be very slow. However, one cannot totally rule out the contribution of the local motion of the head groups to the solvation dynamics in the micelles.

5. Conclusion

The present work demonstrates that DCM can be solubilized in water in the presence of neutral, cationic and anionic micelles and that the ICT process of DCM remains ultrafast in micelles so that dual emission is not observed. The solvation dynamics of DCM in the three micelles is considerably slower than that of DCM in a polar solvent like methanol [15] or other probes in bulk water [2,28]. It is observed that the solvation dynamics in the neutral micelle TX is slower than those in ionic micelles and this is attributed to the thick palisade layer in TX which completely shields the probe DCM from bulk water. The observed timescale of solvation dynamics (0.4–2.1 ns) in micelles is consistent with the recent dielectric relaxation study in micelles [27] and is ascribed to the constrained water molecules in the stern (palisade) layer of the micelles.

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