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ELSEVIER

22 October 1999

Chemical Physics Letters 312 (1999) 178–184

**CHEMICAL
PHYSICS
LETTERS**

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Solvation dynamics of 4-(dicyanomethylene)- 2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) in a microemulsion

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Received 20 May 1999; in final form 17 August 1999

Abstract

The photophysical process of the laser dye 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) is studied in aerosol-OT (AOT) microemulsions in *n*-heptane using picosecond spectroscopy. When AOT and water are added to a solution of DCM in *n*-heptane, some of the DCM molecules migrate from bulk *n*-heptane to the water pool. The absorption and emission peaks of the DCM molecules in the polar water pool are markedly red shifted from those in the bulk *n*-heptane and the emission intensity in the water pool is nearly 40 times higher. Dual emission is not observed in the microemulsions. DCM exhibits slow solvation dynamics in the water pool with an average solvation time of 1.23 ns. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The photophysical process of the laser dye, 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) has been the subject of several studies [1–10]. DCM contains a freely rotating electron donor group (dimethylamino, $-\text{N}(\text{CH}_3)_2$) and a strong acceptor group ($-\text{C}(\text{CN})_2$) separated by a stilbene-type moiety. In the electronically excited state of DCM, an electron is transferred intramolecularly. As a result, the excited-state dipole moment (26.3 D) of DCM is much higher than that in the ground state (5.6 D) which is manifested in the red shift in the absorption and emission spectra of DCM in polar solvents. Apart from intramolecular charge

transfer, DCM can also undergo a twist about the ethylenic double bond or about the bond joining the dimethylamino group and the aromatic ring resulting in a twisted intramolecular charge-transfer (TICT) state [7–12]. On the top of it, the instantaneously created highly polar excited state can undergo solvation in polar solvents resulting in a dynamic Stokes shift. Due to the involvement of a number of ultrafast processes there have been several attempts to delineate the primary photophysical processes of DCM. Unlike other TICT probes, DCM does not exhibit dual emission in any solvent. In polar solvents, DCM exhibits ultrafast solvation dynamics [1–4]. The intramolecular charge transfer process of DCM is extremely fast and could not be detected even in a femtosecond arrangement [1]. In methanol, DCM exhibits solvation dynamics with two components of 175 fs (36%) and 3.2 ps (64%) so that the

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overall solvation time is 2.1 ps [1–3]. In summary, in polar solvents, DCM exhibits bimodal solvation dynamics with one component in the 100 fs timescale and another of a few picoseconds [1–3].

In the present work, we have examined the photo-physics of DCM under a condition where both the TICT and the solvation dynamics occur in the much slower timescale of nanoseconds. For this purpose, we have employed aerosol-OT (AOT) microemulsions in *n*-heptane. The microemulsions refer to microdroplets of water with a radius of a few nanometers, in a hydrocarbon (e.g. *n*-heptane) surrounded by a layer of surfactant (AOT) molecules [13–17]. In a microemulsion, the polar end of the surfactants point inward and a considerable amount of water is encapsulated in the form of a water pool. The radius of the water pool is r_w (in Å) $\approx 2 w_0$, where w_0 is the ratio of the number of water molecules and the number of surfactants [15]. The static and dynamic behaviour of the water molecules in such a water pool is drastically different from that of bulk water. Several groups have reported a dramatic retardation of the rates of charge transfer [16,17] and solvation dynamics [18–23] in such a water pool. The solvation dynamics of water molecules or other fast solvents which occurs in a subpicosecond timescale in an ordinary liquid is slowed down by several orders of magnitude in microemulsions and occurs in the nanosecond timescale [18–24]. The intramolecular charge transfer also occurs in the nanosecond timescale in microemulsions [16,17]. A similar dramatic retardation of the solvation dynamics has been reported in several other self-organized molecular assemblies such as cyclodextrin [24,25] and lipid vesicles [26].

2. Experimental

DCM (laser grade, Exciton) and aerosol-OT (AOT, dioctylsulfosuccinate, sodium salt, Aldrich) were used as received. Preparation of the AOT microemulsion is described elsewhere [16–20]. The steady state absorption and emission spectra were recorded using a JASCO 7850 spectrophotometer and Perkin Elmer 44B spectrofluorimeter, respectively. For the lifetime measurement, the sample was excited at 300 nm with the second harmonic of a cavity

dumped rhodamine 6G (R6G) dye laser (Coherent 702-1) pumped by a cw mode locked Nd:YAG laser (Coherent Antares 76 s). The emission was detected at magic angle polarization using a Hamamatsu MCP 2809U photomultiplier. The full width at half maximum of the instrument response at 300 nm is about 50 ps. The fluorescence decays were deconvoluted using a global lifetime analysis software (PTI). Emission quantum yields were obtained using the reported quantum yield (0.44) of DCM in methanol [4].

3. Results

3.1. Steady state spectra

In *n*-heptane, DCM exhibits two absorption peaks at around 430 and 450 nm. On addition of 0.09 (M) AOT and subsequently water to *n*-heptane, the absorbance at the peak near 430 nm decreases with a concomitant increase in absorbance at wavelengths greater than 480 nm. The difference (Fig. 1) of the absorption spectra of DCM in *n*-heptane with AOT and water and that of DCM in *n*-heptane without AOT and water exhibits a negative absorption or depletion at 430 nm and a distinct peak at ~ 500 nm. The negative absorption at 430 nm clearly indicates that on addition of AOT and water, the population of DCM molecules in the bulk *n*-heptane decreases. On the other hand, the emergence of the positive absorption peak at 500 nm indicates that in the presence of AOT and water, the DCM molecules migrate to a highly polar region which is presumably the water pool of the microemulsion. Since DCM is insoluble in water, the positions of the absorption and emission maximum of DCM in water could not be ascertained. The position of the absorption maximum of DCM in the water pool (500 nm) is red shifted from that in methanol (470 nm) which suggests that the microenvironment of DCM in the water pool is more polar than methanol. It may be recalled that for another solvatochromic dye, Nile red, we had demonstrated earlier that one can easily follow the migration of the dye molecules from bulk *n*-heptane to the water pool, using the difference spectra such as Fig. 1 [17].

In *n*-heptane, DCM exhibits very weak emission with emission maxima at 500 and 535 nm (Fig. 2).

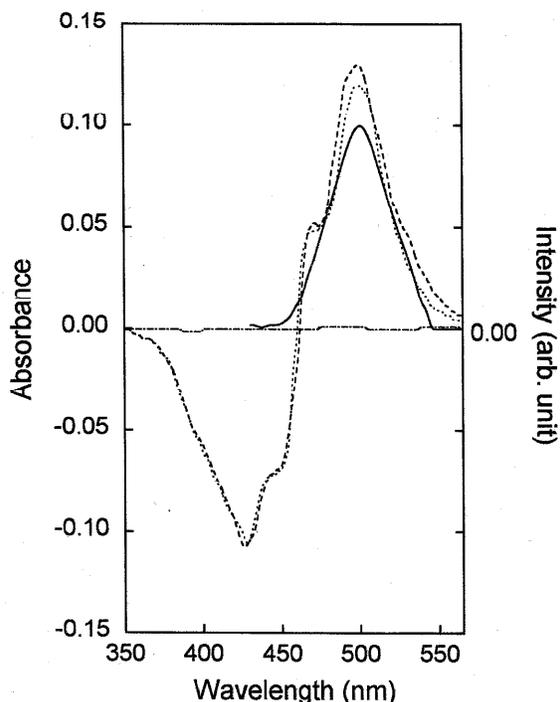


Fig. 1. Difference spectra between DCM in *n*-heptane with that of (i) DCM in *n*-heptane without AOT (.....), (ii) DCM in 0.09 M AOT, $w_0 = 0$ (---), (iii) DCM in 0.09 M AOT, $w_0 = 20$ (-·-·-), (iv) excitation spectrum of DCM in 0.09 M AOT in *n*-heptane, $w_0 = 20$ ($\lambda_{\text{em}} = 625$ nm) (—).

On addition of AOT when a reverse micelle is formed, the emission maximum of DCM exhibits a marked red shift to 570 nm (Fig. 2). On addition of water when a microemulsion is formed, the emission maximum shifts further to the red at 625 nm (Fig. 2). The excitation spectrum of the red-shifted emission (at 625 nm) in the microemulsion exhibits a peak at 500 nm (Fig. 1) which is similar to the absorption peak of DCM molecules in the water pool. This demonstrates that the emission peak at 625 nm in AOT microemulsions is due to the DCM molecules in the water pool and is not due to the DCM molecules in the bulk *n*-heptane. The position of the emission maximum of DCM in the water pool is very similar to that in highly polar and protic solvents (e.g. methanol, dimethylsulfoxide or formamide) [2,3,5,6]. In summary, the steady state absorption and emission spectra of DCM in the water pool of AOT microemulsions indicate that the mi-

croenvironment of DCM in the water pool is highly polar.

For the measurement of the emission quantum yield (ϕ_f) of DCM in *n*-heptane, the sample and the standard (DCM in methanol, $\phi_f = 0.44$ [4]) were excited at 450 nm. The ϕ_f of DCM in *n*-heptane is 0.01. For the measurement of ϕ_f of DCM in the water pool where the absorption maximum is at 500 nm, the sample and standard (DCM in methanol) were excited at 500 nm. The results indicate that ϕ_f of DCM in the AOT microemulsion is 0.4, 0.4, and 0.35 at $w_0 = 0, 4$ and 20, respectively. Thus the emission intensity of DCM in 0.09 (M) AOT at $w_0 = 0$ and $w_0 = 20$ is nearly 40 and 35 times higher, respectively, than that in *n*-heptane. Rettig and Majenz reported [7] that the non-radiative decay rate of DCM decreases with an increase in the polarity of the solvent. Thus the increase in the emission intensity of DCM in going from non-polar *n*-heptane to the polar water pool is due to the decrease in the non-radiative rate of DCM in the polar water pool.

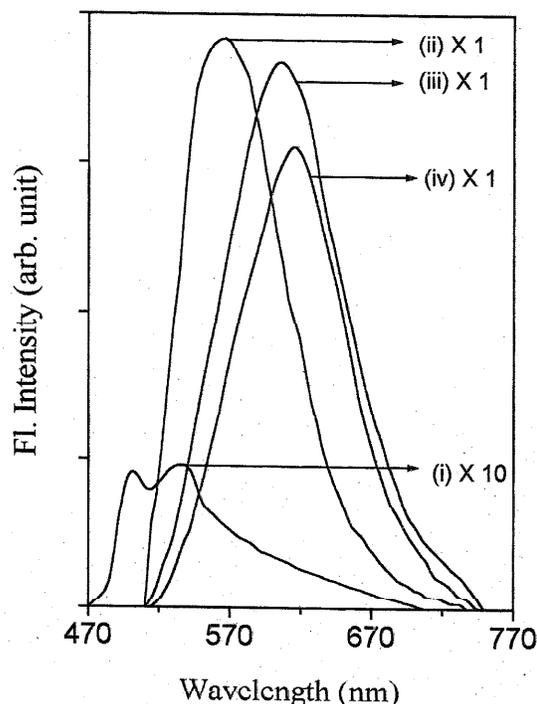


Fig. 2. Emission spectra of DCM in (i) *n*-heptane without AOT ($\lambda_{\text{ex}} = 450$ nm), (ii) 0.09 M AOT, $w_0 = 0$ ($\lambda_{\text{ex}} = 500$ nm), (iii) 0.09 M AOT, $w_0 = 4$ ($\lambda_{\text{ex}} = 500$ nm), (iv) 0.09 M AOT, $w_0 = 20$ ($\lambda_{\text{ex}} = 500$ nm).

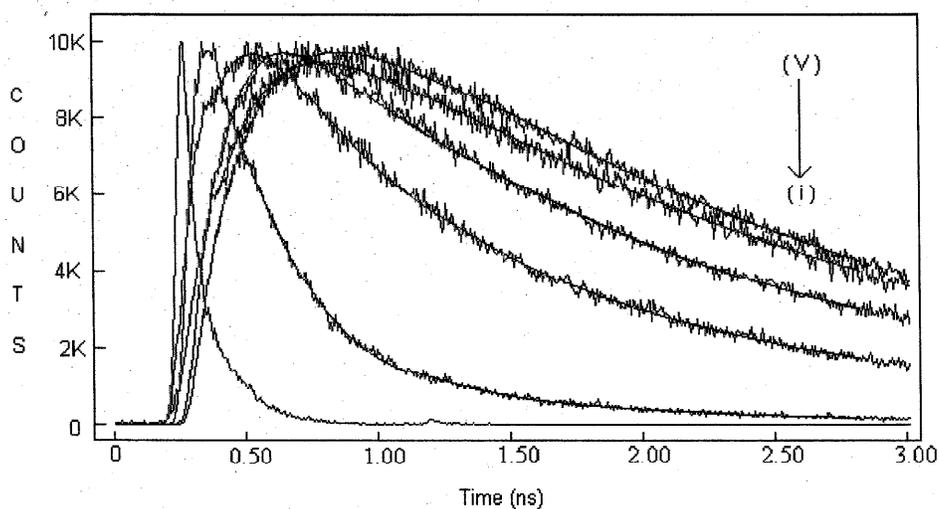


Fig. 3. Fluorescence decays of DCM in 0.09 M AOT in *n*-heptane, $w_0 = 20$, at (i) 530, (ii) 585, (iii) 615, (iv) 645 and (v) 680 nm.

Dual emission is not observed either in the reverse micelles ($w_0 = 0$) or in the microemulsions ($w_0 > 0$).

3.2. Time-dependent Stokes shift

In the AOT microemulsions, the DCM molecules reside both in bulk *n*-heptane and inside the water pool. However, it is evident that one can selectively excite the DCM molecules in the water pool by exciting at 500–520 nm. Unfortunately, this wavelength of excitation was not available within the fundamental wavelength range (590–630 nm) of our dye laser (R6G/DODCI). For time-resolved studies, we excited the samples with the second harmonic of our dye laser at 300 nm where both the DCM molecules in bulk *n*-heptane and in the water pool absorb. The emission lifetime of DCM in *n*-heptane is found to be very short (≈ 50 ps). In AOT microemulsions, the overall contribution of the DCM molecules in bulk *n*-heptane to the total emission is extremely small in the 550–700 nm region because of the inherent weakness of the emission of DCM in bulk *n*-heptane and also because the emission maximum of DCM in *n*-heptane is very much blue shifted to 530 nm. Further, as DCM does not exhibit dynamic Stokes shift in *n*-heptane, the contribution due to the DCM molecules in bulk *n*-heptane to the observed dynamic Stokes shift in the microemulsion is negligible. In the present work, we have studied

the dynamic property of DCM in a large water pool ($w_0 = 20$, $r_w = 40$ Å) because in the small water pools ($w_0 < 10$) the solvation of the surfactants does not become complete and the water pools do not

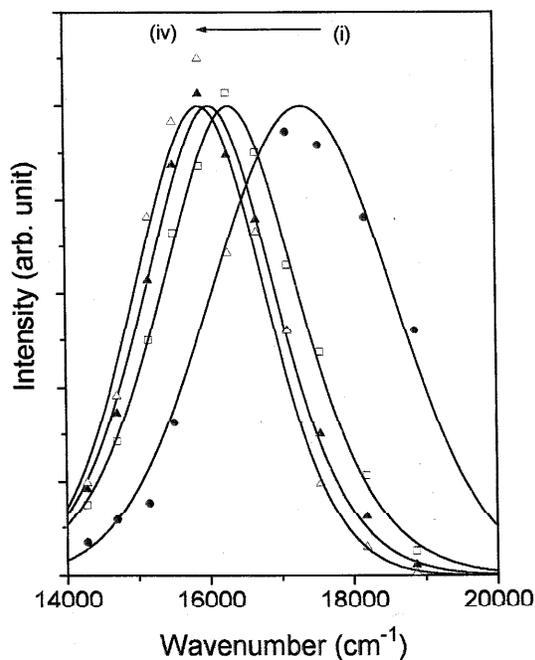


Fig. 4. Time-resolved emission spectra of DCM in 0.09 M AOT in *n*-heptane, $w_0 = 20$, at (i) 0 (•), (ii) 1000 (□), (iii) 3000 (▲) and (iv) 7000 ps (△).

develop fully [14]. It should, however, be remembered that several groups have studied the effect of the variation of the size of the water pool on the solvation dynamics in microemulsions and observed that the solvation dynamics become faster as the size of the water pool increases [18–22]. In the large water pools of the microemulsions, the emission decays of DCM are much slower than in *n*-heptane and are very strongly dependent on the wavelength of detection. The decays at the blue end exhibit fast decay while those at the red end show a distinct growth preceding the decay (Fig. 3). The wavelength dependence of the emission decays suggests that DCM exhibits solvation dynamics in the water pools of the microemulsion. From the observed decays, we reconstructed the time-resolved emission spectra (TRES, Fig. 4) following the method discussed by Maroncelli and Fleming [27]. The emission maxima were obtained by fitting the TRES to a log-normal function. The solvation dynamics is described by the decay of the response function $C(t)$ which is defined as

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

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are respectively the emission frequencies at time zero, t and infinity. The

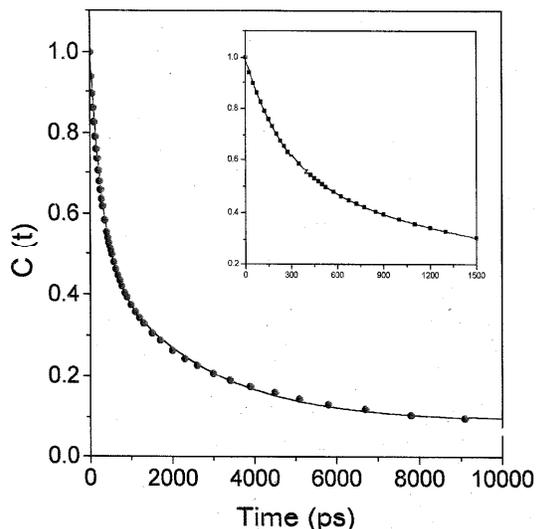


Fig. 5. Decay of response function, $C(t)$ of DCM in 0.09 M AOT in *n*-heptane, $w_0 = 20$. The points denote the actual values of $C(t)$ and the solid line denotes the best fit to a bi-exponential decay. The decay of the initial portion is given in the inset.

Table 1
Decay parameters of $C(t)$ of DCM in AOT microemulsions, $w_0 = 20$

$\Delta\nu$ (cm^{-1})	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau_s\rangle$ (ps)
1600	0.55	280	0.45	2400	1230

decay of $C(t)$ is shown in Fig. 5. The results show that DCM exhibits bimodal solvation dynamics with an average solvation time of 1.23 ns (Table 1).

4. Discussion

For molecules undergoing TICT, one often observes dual emission peaks in polar solvents, one corresponding to the ‘non-polar’ or locally excited (LE) state and the other due to the charge transfer (CT) state [28,29]. The absence of dual emission peaks in the steady state emission spectrum of DCM in a microemulsion indicates that the TICT process is inherently extremely fast and remains so in the AOT microemulsions. It may be noted that dual emission of DCM has not been reported in any solvent. Thus the absence of dual emission of DCM in a microemulsion is consistent with earlier observations [1–4]. The observed emission peak of DCM in an AOT microemulsion at 620 nm at $w_0 = 20$ (570 nm at $w_0 = 0$) is assigned to the polar TICT state due to the marked red shift of the emission maximum, higher ϕ_f and longer emission life time compared to those of DCM in the non-polar solvent *n*-heptane. The wavelength-dependent decay of DCM in microemulsions and the dynamic Stokes shift in the nanosecond timescale is obviously due to solvation and not due to vibrational relaxation because the vibrational relaxation, being a property of the probe itself, is unlikely to slow down inside the microemulsion, and should occur in a 10 ps timescale as reported earlier [1].

The total Stokes shift detected in this work (1600 cm^{-1}) is less than that in methanol ($\Delta\nu = 3800 \text{ cm}^{-1}$) or in ethylene glycol ($\Delta\nu = 2400 \text{ cm}^{-1}$) as reported in previous femtosecond studies [2,3]. It seems that in our picosecond arrangement (response time, 50 ps) we might have missed the ultrafast component of the solvation dynamics which occurs

in the femtosecond timescale [2,3]. As a result, in this case, we are observing only the behaviour in the long timescale. Nevertheless, the results clearly indicate that in the microemulsion DCM exhibits a slow component of solvation in the nanosecond timescale, which is consistent with the nanosecond solvation dynamics reported for other probes in microemulsions [18–23].

While the dielectric relaxation time (τ_D) of ordinary water is 10 ps, the dielectric relaxation of aqueous protein solutions [30], micelles [31] and microemulsions [32] exhibits a component in the 10 ns timescale. The nanosecond solvation dynamics in microemulsions and in other organized assemblies (micelles, cyclodextrins, lipids, etc.) have been attributed to their slower dielectric relaxation times [18–25]. It is difficult to quantify the result obtained for DCM in microemulsions because of the inherent inhomogeneity of the water pool where both the dielectric constant and relaxation time vary quite strongly as a function of distance from the ionic head groups and this inhomogeneity may be responsible for the multi-exponential decay of $C(t)$ [16,18–23]. A semi-quantitative analysis of the result may be as follows. According to the continuum theory, the solvation time (τ_s) is given by $\tau_s = (\epsilon_\infty / \epsilon_0) \tau_D$, where ϵ_∞ , ϵ_0 are, respectively, the high frequency and the static dielectric constant. Since the microemulsions resemble alcohols in polarity, $\epsilon_0 = 30$ –40 [17,19,20]. If one assumes that ϵ_∞ of the water pool is same as that of water (i.e. 5) and uses $\tau_D \approx 10$ ns for the water pool [32], one can immediately calculate the solvation time, τ_s to be $(5/30) \times 10$, i.e. 1.67 ns. This is remarkably close to the observed solvation times of 1.23 ns for DCM in a microemulsion. It may be recalled that similar values have been reported as the solvation times of several other probes in microemulsions [18–20].

5. Conclusion

The present work demonstrates that when AOT and water are added to a solution of DCM in *n*-heptane, some of the neutral DCM dye molecules migrate from the bulk *n*-heptane to the water pool of the microemulsions. This is evidenced by the decrease in the absorbance at 430 nm due to the DCM

molecules in the bulk *n*-heptane and the enhancement of the absorption peak at 500 nm of the DCM molecules in the water pool. No dual emission due to LE and TICT states of DCM is observed in the reverse micelles and microemulsions. The observed emission peak in reverse micelles at 570 (for $w_0 = 0$) and at 625 nm (for $w_0 = 20$) is assigned to the highly polar TICT state. This indicates that in the reverse micelles and microemulsions the TICT process of DCM remains ultrafast, as in other solvents. The emission quantum yield of DCM in the water pool of the microemulsion is about 40 times higher than that of DCM in *n*-heptane and the emission peak is markedly red shifted compared to that in *n*-heptane. In the water pool of the microemulsion, DCM exhibits solvation dynamics with an average solvation time of 1.23 ns, which is markedly slower than the ultrafast solvation dynamics of DCM in the polar solvents [1–3] but is similar to that of other probes in microemulsions [18–20] and that predicted from the simple continuum theory.

Acknowledgements

Thanks are due to Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), Government of India, for generous research grants. CSIR is also thanked for providing a fellowship to S.K.P., D.M. and D.S.

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