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Photoisomerisation of diethyloxadicarbocyanine iodide in micelles

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Abstract

Photoisomerisation of 3,3'-diethyloxadicarbocyanine iodide (DODCI) is studied in cationic (cetyl trimethyl ammonium bromide, CTAB), anionic (sodium dodecyl sulfate, SDS) and neutral (triton X-100, TX) micelles using picosecond emission spectroscopy. On addition of the surfactants to an aqueous solution of DODCI, above the critical micellar concentration, the emission quantum yield and lifetime of DODCI increase due to a marked decrease in the photoisomerisation rate. The retardation of the photoisomerisation process, is attributed to the high microviscosity at the micellar interface, compared to bulk water. Assuming that the Smoluchowski limit and the same 'slip'/'stick' boundary condition hold for all three micelles, the effective microviscosities of the CTAB, SDS and TX micelles are estimated to be 70.0 ± 20 , 24.5 ± 2 and 26.0 ± 2 cP, respectively. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Photoisomerisation of organic molecules containing conjugated double bonds has attracted attention due to its crucial role in the process of vision [1–22]. Photoisomerisation processes near a hydrophobic surface are particularly important because they mimic the isomerisation of retinyl polyenes attached to proteins. The drastically altered local microviscosity at an interface, compared to bulk water, dramatically modifies the dynamics of twisting about the double bonds. The micellar aggregates serve as a simple model for the bio-membranes or an oil–water interface, provided one can ensure the presence of the probe molecule, selectively at the periphery of the

micelles. As a result, there has been an active interest in estimating the microviscosity of the micellar interfaces, using mainly the steady-state and time-resolved optical anisotropy and the kinetics of the formation of intramolecular excimers [23–29]. For the micelles, the reported microviscosities span a wide range, from a few cP to as high as 150 cP, with the average being between 15 and 35 cP [23–26]. The microviscosity of any micelle is higher than that of a linear alkane of comparable chain length and sometimes, higher than even that of the corresponding linear alcohols. This indicates a compact packing of the surfactant molecules in the micellar aggregates, in aqueous solution. Recent small angle X-ray and neutron scattering studies have provided quite detailed information on the structure of these micelles [30,31]. The discrepancy in the value of microviscosities, reported by the various photophysical

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techniques, is attributed to the different parts of the micellar aggregates probed by the different probe molecules. It may be noted that the recent time-resolved surface second harmonic generation (SSHG) experiments have demonstrated that for the air–water interface, the friction against the photoisomerisation dynamics is also different for the different probes [3,13,14]. While, for 3,3'-diethyloxadicarbocyanine iodide (DODCI), the isomerisation dynamics at the air–water interface has been found to be faster compared to that in the bulk water, for malachite green the dynamics has been found to be slower at the air–water interface. This is ascribed to the different shapes of the two probe molecules, as a result of which they probe different regions of the air–water interface [3,13,14]. In an earlier work, we showed that the isomerisation dynamics of DODCI inside the water pool of a microemulsion, is nearly three times slower compared to that in ordinary water [32]. Though photoisomerisation of many organic molecules is well studied in fluid solutions [1–12,16–21], there are few reports on the isomerisation dynamics at the micellar interface [22]. In the present study, we wish to report on the effect of three micelles, cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and triton X-100 (TX), on the isomerisation dynamics of DODCI. DODCI is highly soluble in water and its photoisomerisation in many different environments is studied in great detail [3,13,16–21,32]. The main advantage of using DODCI as a micellar probe is the fact that because of its positive charge it stays exclusively at the micelle–water interface and thus, scans a rather small region of uniform viscosity. Neutral molecules, e.g. stilbene, bi-naphthyl, become distributed over the entire region of the micellar aggregates and hence, probe a large region of varied viscosity.

2. Experimental

Laser grade DODCI (Exciton) was used as received. The surfactants, SDS (Aldrich), CTAB (Aldrich) and TX (Nacalai Tesque, Japan) were also used without purification. Quantum yields are measured using the reported quantum yield of DODCI in methanol [16,17] and that of Rhodamine 6G (R6G)

in ethanol [33]. For fluorescence lifetime measurements, the sample was excited at 570 nm, by the fundamental of a synchronously pumped Rhodamine 6G dye laser (Coherent 702-1) pumped by a cw mode locked Nd:YAG laser (Coherent Antares 76 s). The fluorescence decays were recorded using a Hamamatsu MCP PM tube (2809U). The response time of the apparatus for excitation at the fundamental laser wavelength 570 nm is ~ 100 ps. The fluorescence decays were analysed using the global lifetime analysis software (Photon Technology International). All the steady-state and time-resolved measurements were carried out at 20°C.

3. Results

In aqueous solution, DODCI exhibits moderately strong fluorescence with the emission maximum (λ_{em}^{max}) at 580 nm, quantum yield $\phi_f = 0.3$ and lifetime $\tau_f = 700$ ps. On the addition of the surfactants, below the critical micellar concentration (CMC), the ϕ_f of DODCI decreases slightly (by 10–15%) for CTAB and TX, while the wavelengths of absorption and emission maxima remain unchanged. For SDS, however, below the CMC, the absorption spectrum of DODCI changes completely, indicating the formation of complexes involving the oppositely charged DODC cation and the dodecyl sulfate (DS) anion and the solution becomes almost nonfluorescent. Above the CMC, for SDS the absorption and the emission spectra typical of DODCI are restored, which indicates that DODCI is solubilised at an SDS concentration higher than the CMC. For all the micelles, the emission quantum yield of DODCI increases 2–3 times above the CMC, with a red shift of the absorption and emission spectra by ~ 20 nm. Figs. 1 and 2 describe the absorption and the emission spectra, respectively, of DODCI at different surfactant concentrations, while Fig. 3 describes the variation of the quantum yield of its emission with the surfactant concentrations. It is evident that the change in ϕ_f of DODCI is sharp around the reported CMC of SDS at 8 mM. For CTAB and TX, though the ϕ_f increases above the CMC, the change is not sharp at the reported CMC of CTAB (~ 1 mM) and TX (~ 0.26 mM). In all the three cases, the emission quantum yield saturates at a surfactant concentration

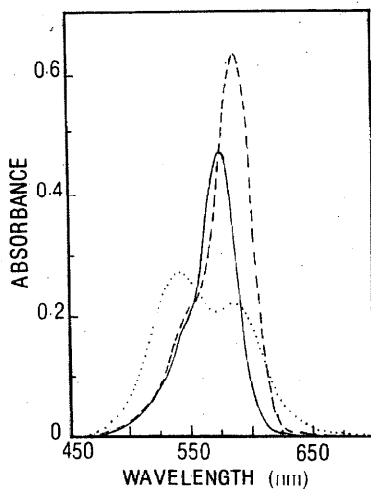


Fig. 1. Absorption spectrum of 2×10^{-6} M DODCI in (a) water (—), (b) 4 mM SDS (···) and (c) 100 mM SDS (---).

of < 100 mM. Due to the saturation of ϕ_f below 100 mM and since, at a surfactant concentration of 100 mM, the λ_{em}^{max} and ϕ_f of DODCI are quite different from those in the bulk water, one may assume that, at 100 mM, almost all the DODCI molecules remain bound to the micelles and experience an environment different from the bulk water

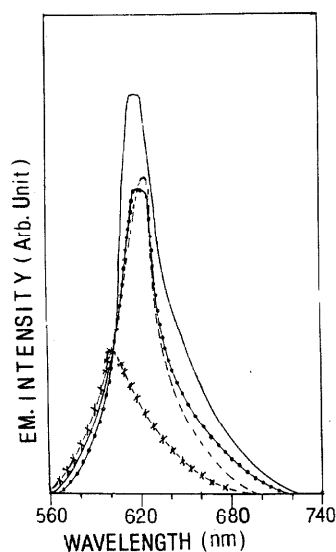


Fig. 2. Emission spectrum of 2×10^{-6} M DODCI in (a) water ($\times \times$), (b) 100 mM SDS (---), (c) 100 mM CTAB (—) and (d) 100 mM TX (···). $\lambda_{ex} = 530$ nm.

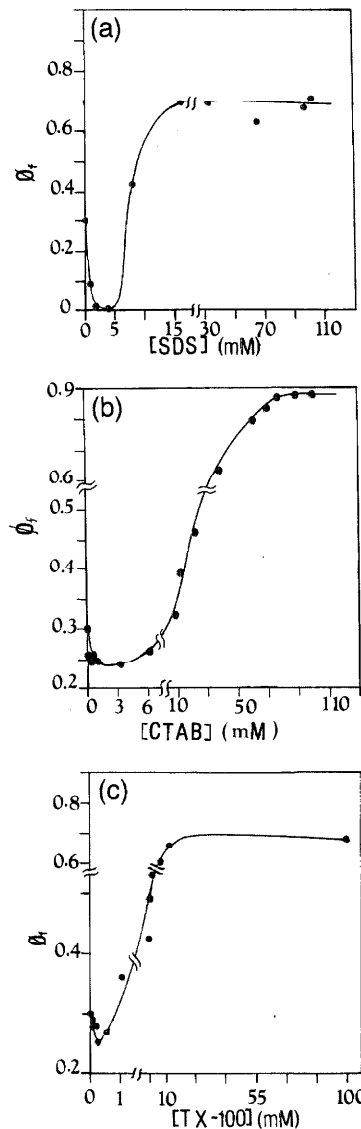


Fig. 3. Variation of quantum yield of 2×10^{-6} M DODCI with concentration of (a) SDS, (b) CTAB and (c) TX. $\lambda_{ex} = 530$ nm.

and that the contribution of free DODCI in bulk water is negligible.

In the presence of the surfactants, the fluorescence decays of DODCI remain similar to that in water for CTAB and TX, at concentrations below the CMC. Above the CMC, the lifetime of DODCI become longer than that in water for all the three micelles. Fig. 4 depicts the fluorescence decays of DODCI in water without the surfactants and at a

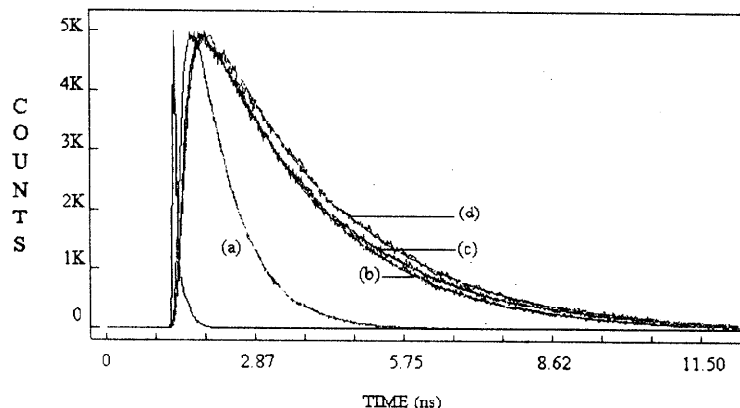


Fig. 4. Decay of 2×10^{-6} M DODCI in (a) water, (b) 100 mM SDS, (c) 100 mM CTAB and (d) 100 mM TX. $\lambda_{\text{ex}} = 570$ nm, $\lambda_{\text{em}} = 625$ nm. (1 K = 1000 counts.)

surfactant concentration of 100 mM, where almost all the DODCI molecules remain bound to the micellar aggregates with a negligible amount in the bulk water. Compared to bulk water, in the presence of the micelles at 100 mM surfactant concentration, the lifetime of DODCI increases about three times to 2.25, 2.36 and 2.55 ns in the SDS, CTAB and TX micelles, respectively. Table 1 summarises the emission quantum yield (ϕ_f), lifetime (τ_f) and emission maxima ($\lambda_{\text{em}}^{\text{max}}$) of DODCI in different micelles. From the observed ϕ_f and τ_f , the radiative (k_r) and the nonradiative rates (k_{nr}) in the micelles are calculated using the relations, $\phi_f = k_r \tau_f$ and $(\tau_f)^{-1} = k_r + k_{\text{nr}}$. It is readily seen that in comparison to water, the nonradiative rates of DODCI decreases by about 20, 7 and 8 times in the CTAB, SDS and TX, micelles, respectively. It is also evident that the slight errors in quantum yield measurement lead to a moderate uncertainty ($\pm 10\%$) in the value of the nonradiative rates for TX and SDS, while for CTAB where the

value of k_{nr} is rather low, the uncertainty is much higher ($\pm 30\%$).

4. Discussion

The nonradiative rate (k_{nr}) of DODCI has been identified as the rate of isomerisation about the double bond [6,11–21]. The observation that the rate of the nonradiative process, i.e. the isomerisation rate at the micellar interface, is significantly slower compared to that in ordinary bulk water, suggests that the micellar environment offers more friction to the photoisomerisation of DODCI than that in ordinary bulk water. Evidently, the magnitude of reduction in the isomerisation rate of DODCI in the three micelles is much greater than the nearly three-fold reduction in the rate of isomerisation of dihexyl tetramethyl indocyanine dye in SDS [22]. As mentioned earlier, the rate of isomerisation of DODCI at the air–water interface is three times faster compared to bulk water [22]. This clearly indicates that the microenvironment of the micellar interface is different from the air–water interface. It is obvious that, because of its positive charge, the DODC cation is constrained to stay near the periphery of the micelle, with the positive charge on DODCI pointing towards the bulk water and the rod-like hydrocarbon portion sticking into the nonpolar interior of the micellar aggregates. At the air–water interface, the polyene part of DODC remains projected in the vapour phase.

Table 1
Emission properties of 1×10^{-6} M DODCI

Medium	ϕ_f^a	$\lambda_{\text{em}}^{\text{max}}$ (nm)	τ_f^b (ns)	k_r (10^{-9} s^{-1})	k_{nr} (10^{-9} s^{-1})
Water	0.28	600	0.70	0.40	1.00 ± 0.03
100 mM SDS	0.70	615	2.25	0.31	0.133 ± 0.013
100 mM CTAB	0.89	625	2.36	0.38	0.047 ± 0.014
100 mM TX	0.68	620	2.55	0.27	0.125 ± 0.012

^a $\pm 3\%$.

^b ± 0.02 ns.

with the positively charged head group dipped in water and the lower density of molecules at the vapour side decreases the friction against the twisting motion. In contrast, the high microviscosity of the micelles seriously inhibits the twisting motion about the conjugated double bonds of DODCI. It is readily seen that the lifetime and isomerisation rate of DODCI in the micelles, reported in this work, is slower than that in *n*-decanol [17]. Assuming, that at the high-viscosity region beyond *n*-decanol ($\eta = 14$ cP), the Smoluchowski limit holds for all the three micelles and decanol and also that the same 'stick'/'slip' boundary condition is applicable, the isomerisation rate is inversely proportional to the bulk viscosity and comparing the isomerisation rate in Table 1 with that ($0.233 \times 10^9 \text{ s}^{-1}$) reported for *n*-decanol [17], the microviscosities of the CTAB, SDS and TX micelles are estimated to be 70.0 ± 20 , 24.5 ± 2 and 26.0 ± 2 cP, respectively. The microviscosities are summarised in Table 2.

The observed retardation of the isomerisation process could also be due to the reduced polarity of the micellar interface compared to ordinary bulk water since, even for trans-stilbene, the rate of photoisomerisation has been reported to depend on the polarity of the medium [6,11]. Hicks et al. [11] observed that the slope of the isoviscous plots of $\ln(k_{\text{iso}})$ against $1/T$ decreases with an increase in the viscosity. They attributed this to the reduction of the barrier, at higher viscosity and lower polarity, due to the polarity effect [11]. Waldeck and co-workers examined this problem, in considerable detail, and concluded that a barrier for the isomerisation process can be extracted for solvents, such as nitriles, where the solvent relaxation time is much faster than the excited state lifetime [6,10]. In the slower alcoholic solvents, incomplete solvation obscures the observation of a well-defined barrier [6]. Since the solvent relaxation in the micelles is quite slow (200–1500

ps) [34], it is doubtful whether one can extract any activation barrier for DODCI in the micelles. Further, Velsko and Fleming [17] have demonstrated that for DODCI in alcoholic solvents the isoviscous plots of $\ln(k_{\text{iso}})$ against $1/T$ do not show much variation of the slope with an increase in viscosity, which indicates that the effect of polarity on the barrier height is relatively unimportant in the case of DODCI [17]. Another argument against the polarity factor is that the isomerisation dynamics of DODCI is found to be slower in a charged micelle CTAB compared to that in the uncharged and less polar TX micelle, while according to the polarity effect one would expect the opposite trend. Though clearly more experiments are needed to conclusively establish the exact mechanism of the increased friction at the micellar interface, it seems that the changes in the barrier height, due to the reduced local polarity of the micellar interface, play a minor role in this case.

It may also be pointed out that the magnitudes of the reduction in the isomerisation rate, in the micellar environments, do not follow the trend of the reduction in solvation dynamics in the micellar media [34]. The solvation dynamics, which are governed by the longitudinal relaxation time, are retarded by nearly a factor of 1000 compared to bulk water, due to the reduction in the dielectric relaxation time in the micellar media [34]. Nandi and Bagchi proposed a theoretical model for the slower dielectric relaxation of water molecules in such organized environments [35]. The solvation times, in the micelles, are of the order TX > SDS > CTAB [34]. While solvation dynamics is fastest in SDS and slowest in TX, the photoisomerisation of DODCI is found to be slowest in CTAB and fastest in SDS. This may be ascribed to the fact that while the solvation dynamics are governed by the longitudinal dielectric relaxation times, isomerisation is controlled by the local viscosity.

Table 2
Microviscosities of the micelles

Surfactant	Microviscosity (cP)
SDS	24.5 ± 2
CTAB	70.0 ± 20
TX	26.0 ± 2

5. Conclusion

In summary, the photoisomerisation dynamics of the positively charged dye DODCI are observed to be markedly slower at the micellar interface compared to that in bulk water. Due to its rod like shape,

the dye DODCI dips its positively charged end in the water and sticks its polyene part inside the alkyl chains of the micellar aggregate. The increased microviscosity of the micelles offers more friction to the isomerisation process than does ordinary bulk water. The possibility of change in the barrier height, in the relatively less polar micellar interface, seems to be relatively unimportant in this case. Finally, assuming that the Smoluchowski limit and the same 'stick'/'slip' boundary condition hold in the case of the micelles and *n*-decanol, the microviscosities of CTAB, SDS and TX are estimated to be 70.0 ± 20 , 24.5 ± 2 and 26.0 ± 2 cP, respectively.

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