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24 October 1997

**CHEMICAL  
PHYSICS  
LETTERS**

Chemical Physics Letters 278 (1997) 77–82

## Photoisomerisation near a hydrophobic surface. Diethyloxadicarbocyanine iodide in a reverse micelle

Anindya Datta, Debabrata Mandal, Samir Kumar Pal, Kankan Bhattacharyya

*Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India*

Received 13 May 1997; in final form 29 August 1997

### Abstract

A picosecond study indicates that inside the water pool of the aerosol-OT (AOT) microemulsion in *n*-heptane the photoisomerisation of 3,3'-diethyloxadicarbocyanine iodide (DODCI) is nearly three times slower compared to that in ordinary water. The slower isomerisation at the AOT–water interface implies greater friction experienced by DODCI compared to bulk water and is attributed to the electrostatic attraction between the DODC cation and AOT anion. This is in sharp contrast to the threefold faster photoisomerisation of DODCI at the air–water interface compared to bulk water.  
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### 1. Introduction

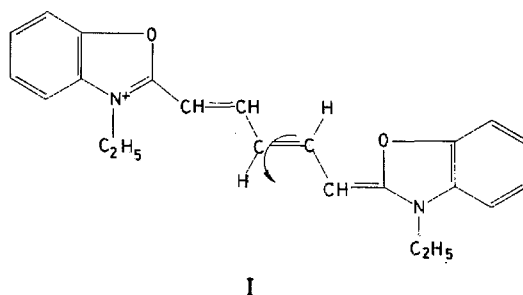
The behaviour of organic molecules near a hydrophobic surface (e.g. biological membranes, micellar interface, air–water interface) plays a crucial role in a wide variety of natural processes. The severely altered local density, composition, polarity and viscosity at the interface compared to bulk, profoundly affect many chemical and biological processes. As a result there has been vigorous interest in studying such interfaces using various techniques [1–9]. Several groups have used surface second harmonic and sum frequency generation to study a wide variety of interfaces [1] while others have used the evanescent wave or picosecond, total internal reflection technique [2]. These studies are mainly restricted to air–liquid, liquid–liquid and liquid–solid interfaces and have revealed marked differences in many properties of the organic molecules at such interfaces, compared to bulk liquids.

Many groups have used picosecond emission

spectroscopy to study a number of biologically relevant interfaces such as reverse micelles [3,5,6], cyclodextrins or dextrans [4,8,9], and micellar interfaces [7]. It is observed that in such confined systems the dynamics of many ultrafast processes is retarded significantly. For instance, the twisted intramolecular charge transfer process of toluidine naphthalene-sulphonate slows down nearly 50 times in cyclodextrin or dextrans, compared to bulk water [8]. The most prominent retardation is observed in the case of solvation dynamics. It is reported that while water solvation dynamics occurs in the sub-picosecond time-scale, inside cyclodextrin [4] or reverse micelles [5,6] or micelles [7] the solvation dynamics occurs in the nanosecond time-scale. The dielectric relaxation of such organised media also reveals a component 1000 times slower compared to bulk water [10,11].

In the present work we focus our attention on how the photoisomerisation dynamics of a polyene is affected in such an organized medium. The dynamics of photoisomerisation apart from its inherent theoret-

ical interest [12–15] is important for understanding the vision process because of the retinyl polyenes [19,20]. In the present work we report on the dynamics of this process inside a reverse micelle. The reverse micelle refers to an aggregate of a surfactant (in the present case negatively charged AOT molecules) in a nonpolar medium (e.g. *n*-heptane) with their ionic groups pointing inwards [34,35]. Each aggregate contains about 20 surfactant molecules and has a radius  $\approx 15$  Å. Such aggregates are formed at AOT concentrations above  $\approx 1$  mM and can encapsulate a considerable amount of water to form a so-called water pool. Such microemulsions are good models of biological membranes and water molecules confined in biological assemblies. In *n*-heptane, the radius ( $r_w$ ) of such a water pool is approximately  $2 w_0$  (in Å) where  $w_0$  is the ratio of the number of water molecules to that of the surfactant molecules [35]. Thus by varying  $w_0$  one can go from a small water pool of radius 8 Å ( $w_0 = 4$ ) to a large one with radius 24 Å ( $w_0 = 12$ ). Since neutral molecules, e.g. stilbene, bi-naphthyl, etc., reside predominantly in the bulk *n*-heptane they are unsuitable for studying photoisomerisation at such an interface. For the present study we have chosen the well known laser dye and saturable absorber, 3,3'-diethyl-oxadicarbocyanine iodide (DODCI, I) because, firstly, as DODC carries a positive charge it stays exclusively in the water pool near the negatively charged head group of the surfactant, AOT. Secondly, the photophysics of DODCI and other carbocyanine dyes in many solvents has been studied in great detail [21–33]. In the ground state DODCI assumes an all-trans configuration [24]. Following electronic excitation DODCI undergoes ultrafast twisting about its conjugated double bonds (Scheme 1). In the twisted geometry the excited state becomes close in energy to the ground state so that a rapid nonradiative transition occurs from the twisted excited state to the twisted ground state. From the twisted ground state the molecule can either revert back to the initial all-trans configuration or to the cis-photoisomer. Eisenthal et al. studied the photoisomerisation of DODCI at the water surface and observed that the photoisomerisation of DODCI at the air–water interface is 3 times slower compared to that in the bulk water [1,22]. This indicates that the air–water interface offers less friction to the photois-



Scheme 1. Structure of the DODCI cation.

somerisation of DODCI than bulk water. In the present Letter we wish to study how much friction the water–AOT interface offers to this process.

## 2. Experimental

Laser grade DODCI (Exciton) was used as received. Purification of the AOT (dioctyl sulphosuccinate, sodium salt, Aldrich), preparation of the microemulsion and the laser system are described elsewhere [6]. Quantum yields were measured using reported quantum yields of DODCI in methanol [28,29]. The fluorescence decays were analysed using the global lifetime analysis software (Photon Technology International).

## 3. Results and discussion

In aqueous solution the absorption spectrum of DODCI exhibits a peak at 580 nm with a shoulder at 550 nm, while the emission spectrum with a peak at 600 nm bears mirror-image relation to the absorption spectrum (Fig. 1). DODCI is insoluble in *n*-heptane or in 0.06 M AOT in *n*-heptane in the absence of water. However, it dissolves in 0.06 M AOT in *n*-heptane in the presence of water. In 0.06 M AOT in *n*-heptane at  $w_0 > 0$ , DODCI exhibits absorption and emission spectra very similar to those in water except with a red shift of nearly 20 nm (Fig. 2).

The fluorescence decay of DODCI in water is a single exponential with a lifetime ( $\tau_f$ ) of  $620 \pm 10$  ps (Fig. 3a). This value is similar to the lifetime of DODCI in water measured by Streak camera by Sitzman and Eisenthal ( $520 \pm 60$  ps) [22] and Magde

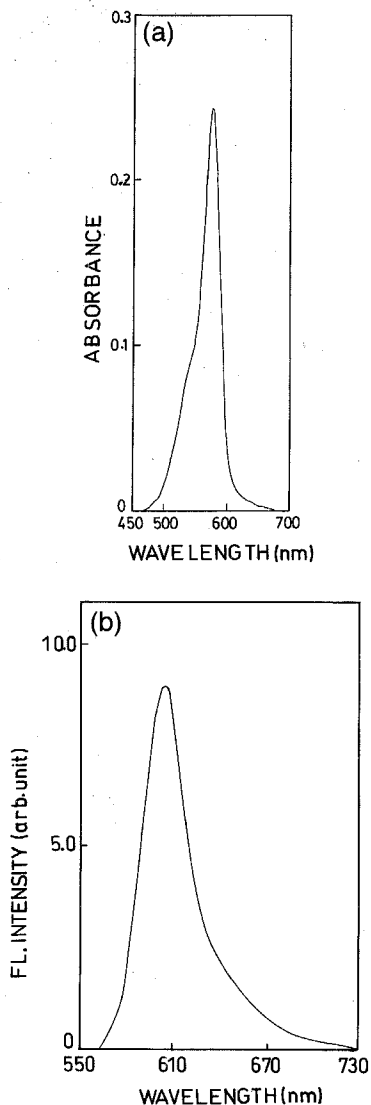


Fig. 1. (a) Absorption spectrum of  $1 \times 10^{-6}$  M DODCI in water. (b) Emission spectrum of  $1 \times 10^{-6}$  M DODCI in water ( $\lambda_{\text{ex}} = 540$  nm).

and Windsor ( $560 \pm 70$  ps) [26]. In 0.06 M AOT in *n*-heptane at  $w_o = 4$  the lifetime of DODCI increases to 1410 ps. With an increase in  $w_o$ , the lifetime ( $\tau_f$ ) and quantum yield ( $\phi_f$ ) of emission of DODCI decrease slightly. The emission properties of DODCI in AOT microemulsions and water are tabulated in Table 1. Radiative ( $k_r$ ) and nonradiative rates ( $k_{nr}$ ) are calculated using the equations,  $\phi_f = k_r \tau_f$  and  $(\tau_f)^{-1} = k_r + k_{nr}$ .

The nonradiative rate ( $k_{nr}$ ) of DODCI has been identified as the rate of isomerisation about the double bond [21–33]. The observation that the rate of the nonradiative process, i.e. isomerisation rate, at the AOT–water interface is nearly 3 times slower compared to that in ordinary bulk water which indicates that the AOT–water interface offers more friction to the photoisomerisation of DODCI than ordi-

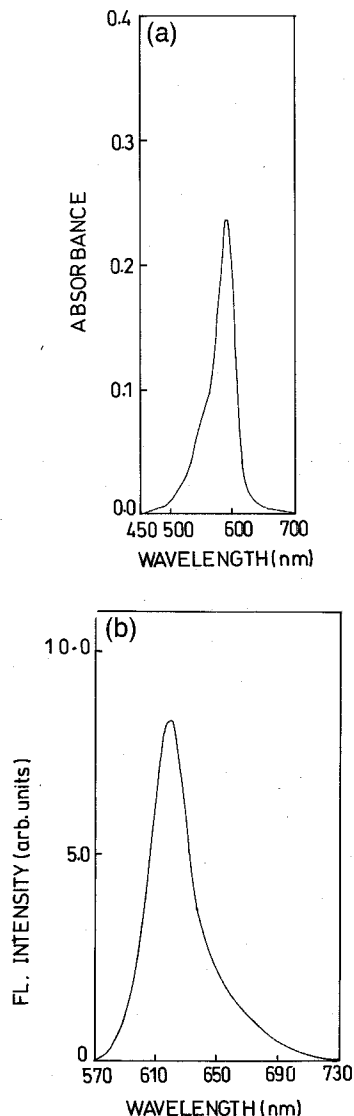


Fig. 2. (a) Absorption spectrum of  $1 \times 10^{-6}$  M DODCI in 0.06 M AOT in *n*-heptane ( $w_o = 12$ ). (b) Emission spectrum of  $1 \times 10^{-6}$  M DODCI in 0.06 M AOT in *n*-heptane ( $w_o = 12$ ,  $\lambda_{\text{ex}} = 560$  nm).

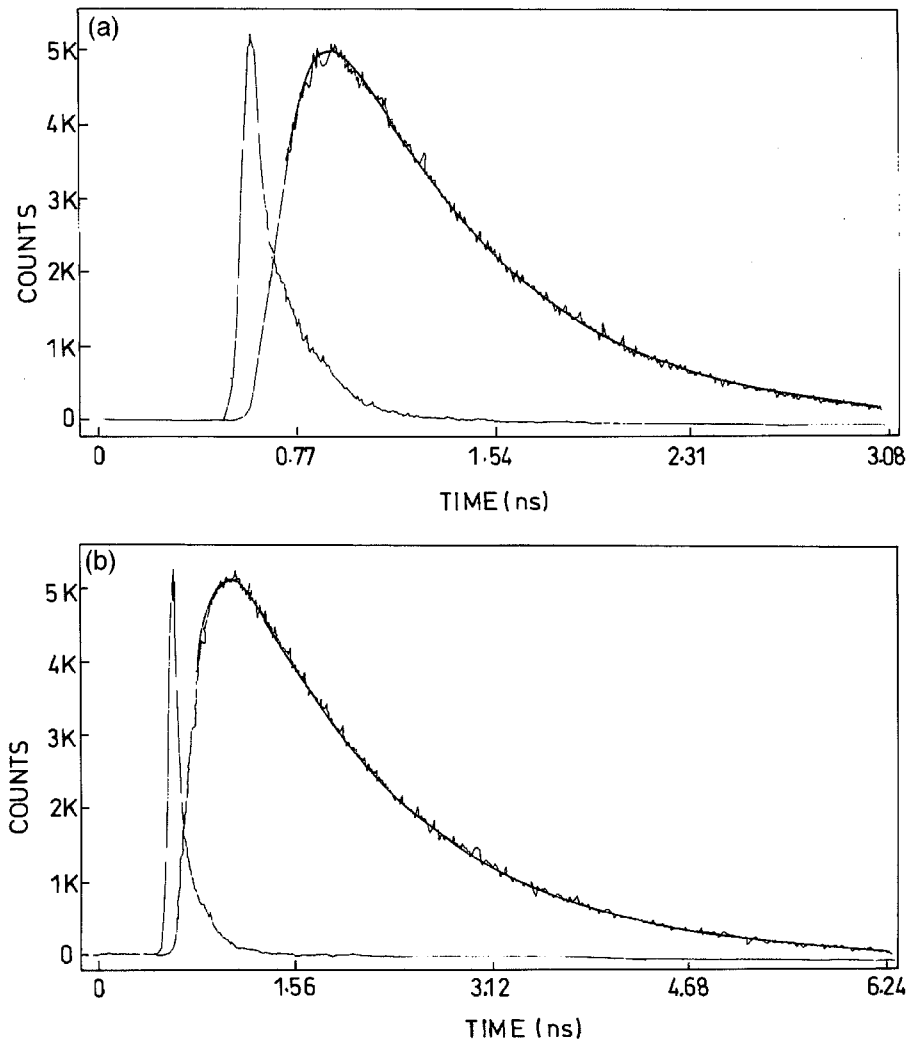


Fig. 3. (a) Decay of  $1 \times 10^{-6}$  M DODCI in water ( $\lambda_{ex} = 570$  nm,  $\lambda_{em} = 660$  nm) (1 K = 1000 counts). (b) Decay of  $1 \times 10^{-6}$  M DODCI in 0.06 M AOT in *n*-heptane ( $w_o = 12$ ;  $\lambda_{ex} = 570$  nm,  $\lambda_{em} = 660$  nm; 1 K = 1000 counts).

nary bulk water. It may be recalled that Eisenthal et al. showed that at the air–water interface isomerisation of DODCI is 3 times faster compared to bulk water [22]. This clearly indicates that the microenvi-

ronment of the water pool 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 negatively charged AOT anion. The main differences between the air–water and the AOT–water interface are as follows. Firstly, as revealed in solvation dynamics experiments [5,6], the water molecules in the water pool of the reverse micelle are several thousand times slower than ordinary water. Secondly, since in its all-trans configuration DODCI is a rod-like molecule with the positive charge at one end, at a water–nonpolar interface it is expected to point its positive charge into the water

Table 1  
Emission properties of  $1 \times 10^{-6}$  M DODCI

Medium	$\phi_f$	$\lambda_{max}^{em}$ (nm)	$\tau_f$ (ns)	$k_r \times 10^{-9}$ ( $s^{-1}$ )	$k_{nr} \times 10^{-9}$ ( $s^{-1}$ )
water	0.31	600	0.62	0.50	1.11
0.06 M AOT/ <i>n</i> -heptane					
$w_o = 4$	0.59	620	1.41	0.42	0.29
$w_o = 12$	0.45	620	1.34	0.34	0.41

phase and insert its nonpolar polyene part in the nonpolar phase. Thus at the air–water interface the polyene part of DODC is projected in the vapour phase while at the AOT–water interface the polyene part resides among the alkyl chains of the surfactant (AOT). Obviously, because of the electrostatic attractions between the DODC cation and AOT anion, the polyene part may get entangled inside the alkyl chains of the AOT. This may cause considerable hindrance to the isomerisation process. It may be noted that the surface second harmonic generation experiment demonstrates that, while for DODCI the isomerisation is faster at the air–water interface in comparison to bulk water, for malachite green the isomerisation at the air–water interface is slower than that in the bulk water [1,22,23]. To explain this Eisenthal and his colleagues proposed that DODCI and malachite green probe different parts of the air–water interface [1,22,23]. At the air–water interface the polyene part of DODC stays in the vapour phase where the density of molecules is much less compared to bulk water. Thus the reduced friction experienced by DODC at the air–water interface may be due to the lower density at the vapour side, while the greater friction experienced at the AOT–water interface may be due to the alkyl chains which remain in close proximity to the polyene part due to the electrostatic attraction between the DODCI and AOT ions. It should also be pointed out that the isomerisation rate in the water pool of the reverse micelle reported in this work is intermediate between those in *n*-butanol and *n*-pentanol [29]. Thus the friction experienced by DODC at the AOT–water interface is in between that of *n*-butanol and *n*-pentanol.

The observed retardation of the isomerisation process inside the water pool of the reverse micelle may also be due to the reduced polarity of the water pool compared to ordinary bulk water. Several groups have reported that even for trans-stilbene the rate of photoisomerisation depends on the polarity of the medium which affects height of the barrier for the isomerisation process [16–18]. Hicks et al. observed that the slope of the isoviscous plots of  $\ln(k_{\text{iso}})$  against  $1/T$  decreases with increase in the viscosity which they attributed to the reduction of the barrier at higher viscosity due to polarity effect. Waldeck and coworkers examined this problem in consider-

able detail and showed that a barrier can be extracted for solvents such as nitriles where the solvent relaxation time is very much faster than the excited state lifetime [16,17]. In the slower alcoholic solvents incomplete solvation obscures the observation of a well defined barrier [16]. Since we have already shown that solvent relaxation in the water pool of the microemulsions is slow [6,7] it is doubtful whether one can extract any activation barrier for DODCI in the microemulsions. Again for DODCI the isoviscous plots of  $\ln(k_{\text{r},\text{o}})$  against  $1/T$  in alcoholic solvents do not show much variation of the slope with increase in viscosity indicating that the effect of polarity on the barrier height may be unimportant [29]. Further experiments are needed to conclusively establish the relative importance of the increased friction at the AOT–water interface and the possible changes in the barrier height due to the reduced local polarity.

With increase in  $w_0$ , as the water pool swells in size the solvation dynamics [5,6] and intramolecular charge transfer processes [3] in the microemulsion become faster. In the present case the rate of photoisomerisation increases from  $0.29 \times 10^9 \text{ s}^{-1}$  in the small water pool of  $r_w = 8 \text{ \AA}$  ( $w_0 = 4$ ) to  $0.41 \times 10^9 \text{ s}^{-1}$  in the big pool of  $r_w = 24 \text{ \AA}$  ( $w_0 = 12$ ). Obviously the magnitude of change in the rate of photoisomerisation with increase in  $w_0$  is much smaller than the change in the rate of solvation dynamics [5,6] or intramolecular charge transfer [3] process with increase in  $w_0$ . In the small water pools the probe molecules remain very close to the charged head group of the surfactant and hence are strongly held while in the big pools those probes near the centre of the pool becomes relatively free [5,6,34,35]. However, since DODCI is itself positively charged, it always stays close to the negatively charged AOT headgroups due to strong electrostatic attraction. Thus even with increase in  $w_0$  as the size of the pool increases the microenvironment of DODCI remains more or less same. This is responsible for the small change in magnitude in the photoisomerisation rate of DODCI.

#### 4. Conclusion

In summary, the photoisomerisation dynamics of the positively charged dye DODC is observed to be

nearly 3 times slower in the water pool of AOT/*n*-heptane microemulsions than in bulk the water. This is attributed to the rod-like shape of the dye which sticks its positively charged end in the water pool close to the negatively charged head group of the AOT and its polyene part inside the alkyl chains of the oppositely charged surfactant. The alkyl chains of the oppositely charged surfactant offer more friction to the isomerisation process than does ordinary bulk water. However, the possibility of change of the barrier height in the relatively less polar water pool cannot be ruled out.

### Acknowledgements

Thanks are due to Council of Scientific and Industrial Research (CSIR) and Department of Science and Technology, Government of India for generous research grants. CSIR is also thanked for providing fellowships to AD, DM and SKP.

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