FLUORESCENCE AND ENERGY TRANSFER OF DYE–DETERGENT SYSTEMS IN THE PREMICELLAR REGION*

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Summary

The fluorescence lifetimes of dyes and also the energy transfer between dyes with closely located S_1 levels were studied in the presence of detergents. These dye–detergent systems can be considered as one of the model membrane systems of chloroplasts and show some peculiar features when the detergent has the opposite charge to that of the dye. The energy transfer efficiency between rhodamine 6G (Rh-6G) and pinacyanol (PC) in the presence of sodium lauryl sulphate (SLS) showed a distinct peak in the premicellar region, *i.e.* for [SLS] a little less than the critical micelle concentration. A long dimer-like lifetime was observed in the acridine orange (AO)–SLS system in the premicellar region. These findings and the absorption and fluorescence spectra revealed that the dye molecules are associated with dye-rich induced micelles which reduce the average distance (AO–AO or Rh-6G–PC) between dye molecules in the premicellar region.

1. Introduction

The importance of dye–detergent aggregate formation and its potential significance to photochemical problems have been explored recently by several researchers including ourselves [1 - 6]. The investigation of such a problem deserves more attention, in our opinion, despite its rather complex chemical nature.

2. Energy transfer between rhodamine 6G and pinacyanol enhanced with sodium lauryl sulphate in the premicellar region by the formation of dye-rich induced micelles

The efficiency of energy transfer between dyes is enhanced by the presence of an appropriate detergent. This effect has been the subject of recent intense research [1, 3, 7 - 9]. Whereas the earlier studies [7 - 9] were limited to detergent concentrations above the critical micelle concentration (CMC), estimations

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of the energy transfer (ET) efficiency were made both above and below the CMC for the rhodamine 6G–3,3′-diethylthiacarbocyanine iodide (Rh-6G–DTC) system with sodium lauryl sulphate (SLS) as a detergent. (It is quoted in ref. 1 that A.K. Ghosh has found evidence of enhanced energy transfer below the CMC. However, his data were not included in the article.) The maximum efficiency was observed for an [SLS] a little less than the CMC, *i.e.* in the premicellar region [1].

In the present paper the mechanism of enhancement of the ET efficiency with SLS, especially in the premicellar region, is described for the system Rh-6G (donor) and pinacyanol (acceptor). This system seems to be especially suited to such a study because the nature of the dye–detergent interaction can be determined as a function of [SLS] from the spectral characteristics of pinacyanol with SLS [10].

3. Results and discussion

3.1. Critical micelle concentrations of sodium lauryl sulphate solutions

The CMC determined for an SLS solution in the absence of dye was 7.4 ± 0.1 mM, in good agreement with the most reliable published value (8.1 mM) [11]. In the presence of both dyes (Rh-6G, 1.43×10^{-5} M; pinacyanol, 1.57×10^{-4} M), the equivalent conductivity plotted against $[SLS]^{1/2}$ showed a deviation from linearity for [SLS] $\gtrsim$ 6.1 mM. This deviation is quite similar to that found by Mukerjee and Mysels [10] for the pinacyanol–SLS system. If we estimate the CMC of the system as the point of intersection of two lines extrapolated from above and below the CMC, we obtain the value 7.0 ± 0.1 mM. The presence of dyes caused only a small shift in the CMC.

3.2. Spectra of pinacyanol in aqueous and sodium lauryl sulphate solutions

Absorption spectra of pinacyanol–SLS solutions showed a very striking [SLS]-dependent change, which was essentially the same as that reported by Mukerjee and Mysels [10]. For [SLS] above and just below the CMC (hereafter called region A) the solution was blue. Two bands, mentioned in ref. 10 but slightly shifted to longer wavelengths (the α band at 610 nm and the β band at 565 nm), were observed. A fluorescence band appeared at 656 nm. Both the α band and the β band disappeared in the low [SLS] region and an absorption band (γ band) appeared at 480 nm. The solution was red in this region, which is hereafter called region B.

In the transient region between regions A and B, the α and β bands increased in intensity and the γ band decreased in intensity with [SLS]. The 656 nm fluorescence was observed in this region. The lower boundary of this region with region B shifted to a higher [SLS] with the concentration of pinacyanol. The upper boundary with region A was in the premicellar region when the dye concentration was low. However, it shifted to a higher [SLS] with the concentration and ultimately reached the CMC.

On the basis of their conductivity and spectral experiments, Mukerjee and Mysels [10] concluded that there was formation of dye-rich induced micelles below the CMC where SLS, when alone, does not micellize or micellizes to a

lesser extent. The formation of micelles is induced by the presence of the dye which has the opposite charge to that of SLS. Their concentration is very small and dyes are highly concentrated on them. The presence of dye-rich induced micelles plays a very important role in the energy transfer presently studied, as shown below.

3.3. Energy transfer efficiency

In the estimation of ET efficiency as a function of [SLS], we studied only the region where the 656 nm fluorescence of pinacyanol was observed, *i.e.* region A and the transient region. We measured fluorescence spectra of mixed solutions of Rh-6G and pinacyanol in the presence of SLS. ET was revealed by the quenching of the donor fluorescence and by the appearance of sensitized fluorescence of the acceptor. The fluorescence intensities of the donor and acceptor observed for the mixed solution are denoted I_1 and I_2 respectively. The fluorescence intensity of the blank solution (acceptor–SLS) is denoted I_3. The excitation wavelength was 480 nm. The experimentally determined e value

$$e = \frac{I_2 - I_3}{I_1 + (I_2 - I_3)} \tag{1}$$

was used in the estimation of the ET efficiency. The e values are plotted as a function of [SLS] in Fig. 1 for two concentrations 1 and 2 of the dyes.

When we compare the variation of e with [SLS] with the change in the absorption spectra, a close correspondence is found between them. For dye concentration 2 the maximum value of e is in the premicellar region near the point where the dye–detergent salt (with the γ band) disappears and the dye molecules are associated with the dye-rich induced micelles (as shown by the β band). For the larger dye concentration (concentration 1), the maximum is close to the CMC. When we add more SLS the dyes are successively diluted, as is apparent by the increase in the α band intensity. The aggregation number of dye-rich induced micelles must be smaller than that of the normal micelles since the former undergo the dilution process and change themselves continuously into normal micelles at the CMC. It should be remarked that even below the CMC some of the dye-rich induced micelles are diluted by SLS and carry only one dye molecule

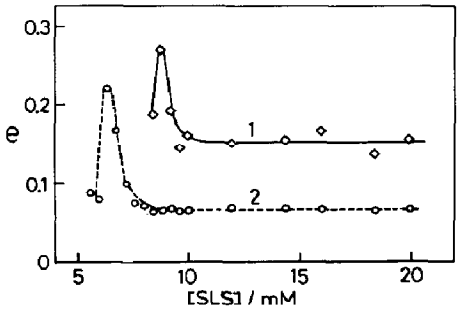

Fig. 1. e *vs.* [SLS] for fixed dye concentrations: curve 1, [Rh-6G] = 1.4×10^{-5} M, [pinacyanol] = 1.6×10^{-4} M; curve 2, [Rh-6G] = 1.1×10^{-6} M, [pinacyanol] = 1.1×10^{-5} M.

when the dye concentration is low. This explains the decrease in e after it had attained a peak.

If N is the number of excited donor monomers, e_{ET} is the ET efficiency and q_D (or q_A) is the quantum yield of the donor monomer (or the acceptor monomer) in the mixed solution we have

$$\frac{Ne_{ET}q_A}{N(1-e_{ET})q_D} = \frac{I_2 - I_3}{I_1} \tag{2}$$

or

$$e_{ET} = \frac{(I_2 - I_3)/q_A}{I_1/q_D + (I_2 - I_3)/q_A} \tag{3}$$

For well above the CMC the value of e is essentially constant. In such a region both the donor and the acceptor dyes are present as monomers associated with micelles and the ET is intermicellar. Both q_D and q_A are constant. The ratio q_D/q_A can be estimated as nearly equal to 300. Putting this value and the observed value of e in eqn. (3), we obtain an ET efficiency very close to unity.

Near to and below the CMC we can assume that the ET efficiency is essentially determined by the statistical distribution of the donor and acceptor dyes among the dye-rich induced micelles (in the premicellar region) or the normal micelles (above the CMC) and that q_A and q_D are constant in these micelles. Enhancement of the ET efficiency is thus observed in the premicellar region and it is due to the inclusion of the donor and acceptor dyes in the dye-rich induced micelles.

4. Fluorescence decay in the acridine orange–sodium lauryl sulphate system: formation of dye-rich induced micelles below the critical micelle concentration

The presence of dye-rich induced micelles in the acridine orange–sodium lauryl sulphate (SO–SLS) system can be shown most directly by a fluorescence lifetime study, as described below.

The observed lifetimes are shown in Table 1. The lifetime of 3 - 4 ns observed for dilute aqueous solutions is in good accord with the monomer lifetime in aqueous solution reported by Knof *et al.* [12]. For higher [AO] a long lifetime decay component with $\tau \approx 11$ - 13 ns appeared, which is close to the lifetime of the dimer (14 ns) reported by these researchers.

For AO–SLS systems the lifetime varied as a function of [SLS] in a pattern (a short lifetime of about 4.5 ns changed to a longer lifetime of 6 - 8 ns which then changed to a lifetime of 3 - 4 ns). The boundary [SLS] of these regions moved to a higher [SLS] with the increase in [AO]. The lifetime of about 4.5 ns found for small [SLS] was related to the fluorescence band at 640 nm attributable to the dye molecule in the dye–detergent complex. The lifetime of 3 - 4 ns found for large [SLS] corresponds to the appearance of monomer-type absorption spectra. This is undoubtedly related to the monomer dye associated with the micelle.

TABLE 1

Fluorescence lifetimes of AO–SLS systems

[SLS] (M)	[AO] (M)						
	2×10^{-6}	5×10^{-6}	5×10^{-5}	2×10^{-4}	5×10^{-4}	2×10^{-3}	5×10^{-3}
0	3.2[a]	3.0[a]	3.1[a]	9.5 4.1[a]	11.2 4.1[a]	11.3	12.8
2×10^{-3}	6.2	5.5	4.6	4.5	4.5	4.5	
4×10^{-3}	6.0	6.2	5.2	5.9	6.2	5.5	
5×10^{-3}	6.2	7.2	5.4				
6×10^{-3}	3.3[a]	5.6	7.6 3.5[a]	6.6	6.6	5.6	
7×10^{-3}	3.4[a]	3.2[a]	7.0 3.3[a]				
8×10^{-3}	3.7[a]	3.3[a]	3.6[a]	8.4 4.2[a]	7.3	6.4	
1×10^{-2}	3.4[a]	3.3[a]	3.7[a]	6.8 3.9[a]	7.1 4.0[a]	6.5	
2×10^{-2}	3.3[a]	3.4[a]	3.5[a]	3.8[a]	3.8[a]	7.6 4.3[a]	

[a] Monomer lifetime (see text).

A longer lifetime (6 - 8 ns) was observed between these two regions. It was found in the intermediate [SLS] region where the 640 nm fluorescence (mentioned above) decreased in intensity and the 545 nm (monomer) fluorescence increased in intensity with [SLS], and where the change in absorption spectra (from aggregate type to monomer type) occurred. It should be noted that the lifetime observed in this intermediate region is not between 4.5 ns (dye–detergent complex) and 3 - 4 ns (monomer dye) but is *longer* than both. This shows the presence of dye molecules in the dimer-like state. The presence of such an entity in the premicellar region clearly shows that the dye molecules are locally concentrated in the dye-rich induced micelles.

The boundary [SLS] region where we observed both the aggregate fluorescence and the monomer fluorescence was found above the CMC for large [AO]. This was explicable on the basis of the P_2/P_1 ratio in the Poisson distribution of the dye among micelles. We noticed, however, that the boundary crossed the CMC and entered the premicellar region for a very small dye concentration (*e.g.* 2×10^{-6} M). These findings show that the dilution of dye-rich induced micelles occurs below the CMC and some of the micelles carry only one dye molecule below the CMC when the dye concentration is low. We can explain these observations by treating the distribution of dye molecules among the dye-rich induced micelles statistically.

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