

FAST KINETICS OF PYRENE EXCIMER FORMATION IN MICELLES OF CETYLTRIMETHYLAMMONIUM BROMIDE

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Summary

In this paper we report the results of a study of the time-resolved kinetics of the pyrene excimer in *n*-hexadecane and in aqueous micelles of cetyltrimethylammonium bromide (CTAB). The experiments in aqueous CTAB show that the kinetic parameters for the excimer formation and dissociation process resemble those obtained in other surfactant studies; the formation process occurs much more slowly in micellar environments than in homogeneous solvents. The complex variation of kinetic parameters and fluorescence lifetimes with changing pyrene:surfactant ratios appears to reflect the changing structure of the CTAB micelle with added solute. The rate constant for the bimolecular excimer formation step does not provide a reliable guide to the viscosity of the medium.

1. Introduction

Recently, in a study of the kinetics of pyrene excimer formation in aqueous Triton X-100, it was shown that it is possible to derive all the kinetic parameters involved by analysing the time dependence of the fluorescence emission of the excimer [1]. In extending these studies to cetyltrimethylammonium bromide (CTAB), a prime aim was to investigate a micelle with well-defined properties and with an inner structure consisting of only one region (the hydrocarbon core) apart from the periphery formed by the head groups. As in the previous study, a hydrocarbon solvent (in this case *n*-hexadecane) was chosen to provide a medium analogous to that of the C-16 chains of the CTAB micelle core,

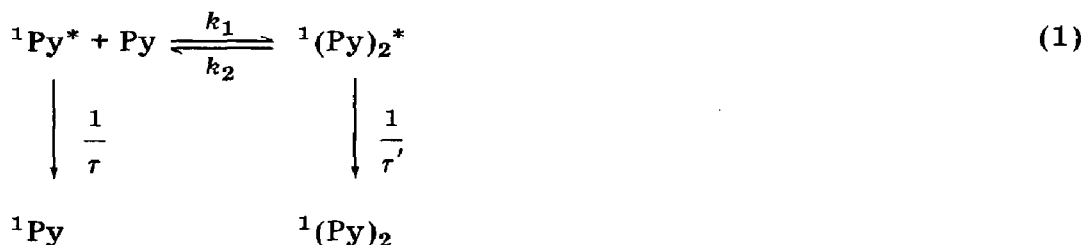
2. Experimental details

The nanosecond single-photon counting apparatus and the experimental techniques used here have been described previously [1]. The experiments

with pyrene solubilized in aqueous CTAB and in *n*-hexadecane were carried out at room temperature, oxygen being removed by nitrogen purging. Pyrene concentrations in aqueous CTAB were calculated from the absorption spectra of the solutions, using appropriate extinction coefficients.

3. Discussion

Excimer formation occurring as the result of exciting a pyrene molecule may be described by the following reaction scheme:



where τ and τ' are the lifetimes of the excited species and k_1 and k_2 are rate constants. The excimer fluorescence as a function of time is given by the following expression:

$$I(t) = C\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \quad (2)$$

Here C , λ_1 and λ_2 are constants [2]. Equation (2) will apply to each individual micelle if we regard micelles as separate containers in which reaction (1) takes place. Thus, if the probability of finding a micelle with x solute molecules is $P(x)$, the observed (bulk) excimer fluorescence intensity as a function of time will be given by

$$I'(t) = C' \sum_{x=2}^{\infty} I(t)P(x)x \quad (3)$$

where C' is a constant and the factor x in the summation weights each term for the number of light-absorbing solute molecules in the micelle. An example of the experimentally observed variation of $I'(t)$ with time can be found in Fig. 1. The rate constants of reaction (1) are contained in the parameters λ_1 and λ_2 in eqn. (2):

$$\lambda_{1,2} = \frac{1}{2} \left[k_1 c_{\text{Py}} + k_2 + \frac{1}{\tau} + \frac{1}{\tau'} \mp \left\{ \left(k_1 c_{\text{Py}} + \frac{1}{\tau} - k_2 - \frac{1}{\tau'} \right)^2 + 4k_1 k_2 c_{\text{Py}} \right\}^{1/2} \right] \quad (4)$$

By varying these rate parameters and the constant C' until the best fit of eqn. (3) to the experimental data is achieved, values of all five parameters (C' , k_1 , k_2 , λ and λ') can be obtained solely from measurements on the

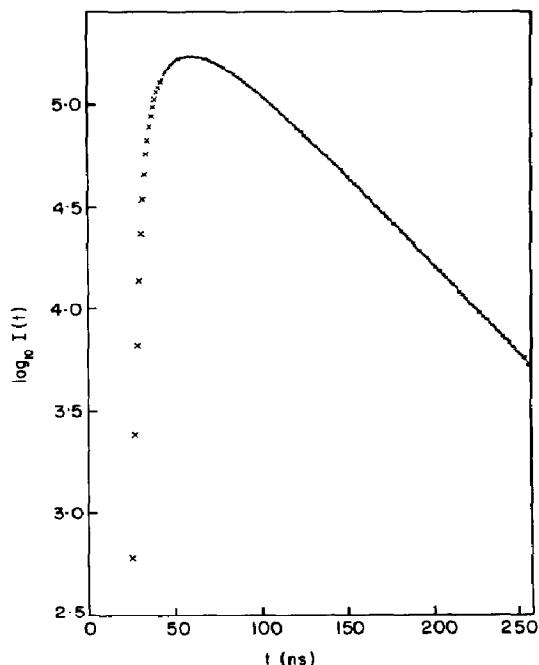


Fig. 1. The fluorescence intensity of the pyrene excimer as a function of time in micellar CTAB: x, experimental points (to avoid congestion in the diagram only alternate points are shown); —, the best fit of eqn. (3) (see text) to the experimental data. One channel corresponds to 1.0214 ns. $[\text{pyrene}] = 5.192 \times 10^{-3} \text{ M}$; $[\text{CTAB}] = 5.626 \times 10^{-2} \text{ M}$.

excimer. Such a line of best fit is shown in Fig. 1, passing through the experimentally observed points. In this procedure the aggregation number of CTAB was taken to be 75 [3].

In treating the data for pyrene in *n*-hexadecane, two relations (derivable from eqn. (4)) from Hauser and Klein [4] were used:

$$\lambda_1 + \lambda_2 = \frac{1}{\tau} + \frac{1}{\tau'} + k_2 + k_1 c_{\text{Py}} \quad (5)$$

$$\lambda_1 \lambda_2 = \frac{1}{\tau} \left(\frac{1}{\tau} + k_2 \right) + \frac{k_1}{\tau'} c_{\text{Py}} \quad (6)$$

The plots of $\lambda_1 + \lambda_2$ and $\lambda_1 \lambda_2$ against c_{Py} , from which the rate parameters for pyrene in *n*-hexadecane were derived with the aid of eqns. (5) and (6), are shown for one pyrene concentration in Fig. 2. The parameters k_1 , k_2 , τ and τ' for pyrene in aqueous CTAB at seven different values of the pyrene: micelle ratio μ are listed in Table 1. In Table 2 values of k_1 , k_2 and τ at the extremes of high μ and low μ are given; an average value has been taken for τ' . Values of these parameters for pyrene excimer formation in other media, including Triton X-100, are provided for comparison. Table 2 also includes the rate parameters derived here for pyrene in *n*-hexadecane.

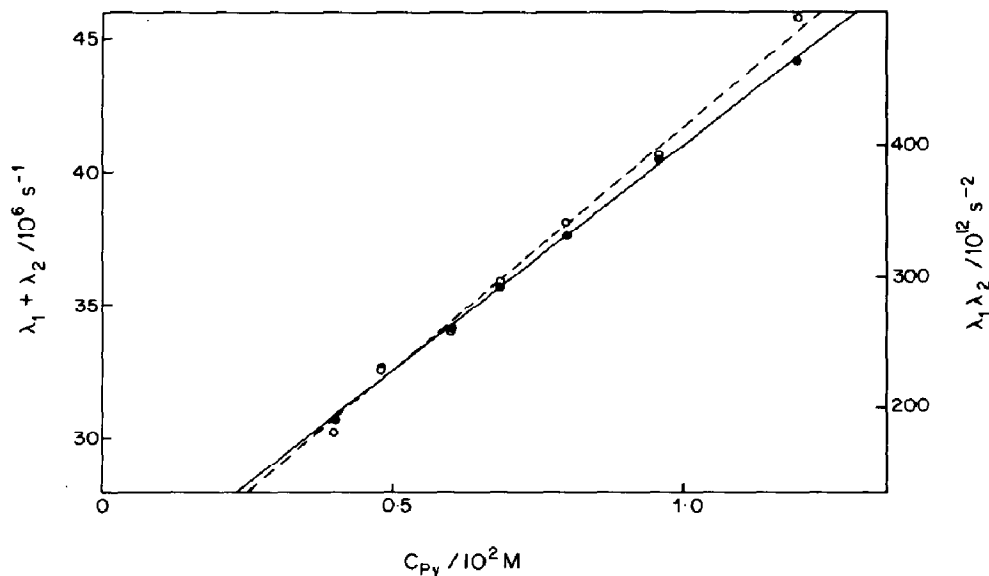


Fig. 2. Plots of eqns. (5) and (6) (see text) for pyrene in *n*-hexadecane: \circ , $\lambda_1 + \lambda_2$; \bullet , $\lambda_1 \lambda_2$.

TABLE 1

Kinetic parameters for pyrene excimer formation in aqueous cetyltrimethylammonium bromide as a function of the pyrene:micelle ratio μ

μ	$k_1 (\times 10^7 \text{ M}^{-1} \text{ s}^{-1})$	$k_2 (\times 10^6 \text{ s}^{-1})$	τ (ns)	τ' (ns)
4.955	7.87	10.94	66.6	39.3
3.964	6.59	10.67	67.1	34.2
3.304	6.12	8.64	68.4	32.7
2.830	5.52	8.33	69.4	32.4
2.478	5.20	7.58	71.7	32.6
1.982	5.40	5.33	78.1	34.1
1.652	5.26	4.99	81.3	36.3

These values have been calculated by taking the aggregation number of CTAB to be 75 [3]; $[\text{CTAB}] = 5.626 \times 10^{-2} \text{ M}$.

All three values of k_1 for micellar systems (for high μ and low μ in CTAB and for Triton X-100) are clustered about a value of $6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; this is very much lower than the values for homogeneous solvents, which can be up to two orders of magnitude larger. If k_1 is used to calculate the viscosity η [1, 13], the values shown in Table 2 (together with those obtained from fluorescence depolarization measurements and from bulk viscosity measurements) are obtained. It is clear, even at a casual glance, that viscosities determined by different methods both for homogeneous solvents and for micellar systems are widely divergent. This is not due to any systematic difference. For example, bulk viscosity measurements give higher values than do measurements based on excimer formation for Trigol; in *n*-hexadecane and

TABLE 2

Kinetic and other parameters for pyrene excimer formation in various media

Solvent system	k_1 ($\times 10^7 M^{-1} s^{-1}$)	k_2 ($\times 10^6 s^{-1}$)	τ (ns)	τ' (ns)	Reference	η (cP)	K^a (M^{-1})	K^b (M^{-1})
Aqueous CTAB ($\mu = 4.955$)	7.87	10.94	66.6	34.5 ^c	This work	127 ^d 190 ^d	3.81	38.5
Aqueous CTAB ($\mu = 1.652$)	5.26	4.99	81.3					
Aqueous Triton X-100	6.9	2.4	236	42	1	145 ^d [1]	14.8	96.8
Aqueous sodium dodecyl sulphate	—	6	500 ^f	63 ^f	4	—	—	—
<i>n</i> -Hexadecane	86	3.8	331	54	This work	11.6 ^d , 3.454 ^g (at 20 °C [6]), 3.44 ^g (at 20 °C [7]), 3.07 ^g (at 25 °C [7]), 3.98 ^g (at 25 °C [8])	—	—
Cyclohexane	670	6.5	450	65	2	1.49 ^d , 0.960 ^g (at 20 °C [9]), 0.93 ^g (at 22 °C [9]), 0.801 ^g (at 30 °C [10])	—	—
Trigol (triethylene glycol)	64	19.2	411	186	1	15.6 ^d [1], 38 ^g (at 20 °C [11]), 37 ^g (at 25 °C [12])	—	—

^a Stern-Volmer constant for excimer formation, calculated from kinetic parameters.^b Stern-Volmer constant for excimer formation from steady state measurements.^c Average of the values in Table 1, fifth column.^d From excimer formation kinetics.^e From fluorescence depolarization measurements.^f Values assumed in calculating k_2 .^g From bulk viscosity measurements.

TABLE 3

Measured lifetimes of aromatic hydrocarbons in cetyltrimethylammonium bromide micelles

<i>Solute</i>	τ (ns)	μ^a	$P(\geq 2)/P(1)^b$	<i>Reference</i>
Pyrene	66.6	4.955	27.44	This work
Pyrene	81.3	1.652	1.605	This work
Pyrene	117	0.188	0.100	18
Pyrene	140	0.15	0.0788	19
Pyrene	165	0.014	0.0065	20
Pyrene	188	—	—	21
Naphthalene	10 - 16	0.25 - 7.5	0.36 - 240	22, 23

^a The ratio of the number of solute molecules to the number of surfactant micelles (see ref. 3).

^b The ratio of the number of micelles with occupancies greater than or equal to 2 to those with an occupancy of 1.

cyclohexane the situation is reversed. The drawbacks of using rate constant measurements to derive viscosities have been fully discussed elsewhere [13]. The micellar interior, being spatially limited and probably anisotropic [14], imposes additional limitations, and there are indications that there is no well-defined link between fluorescence depolarization and micellar microviscosity [15].

The values (shorter than 100 ns) of the pyrene monomer lifetime τ obtained in these experiments are unusually small compared with the fluorescence lifetime (about 400 ns [16]) of pyrene in homogeneous solvents. The values in CTAB obtained here probably result from quenching by the bromide counterions, which presumably have access to the excited pyrene molecules during their lifetimes. Bromide ions are known to quench pyrene fluorescence efficiently [17]. An additional factor contributing to the lifetime-shortening effect may be Förster-type energy transfer between excited and ground state molecules; this appears to have been observed for pyrene in Triton X-100 [1].

It is of interest to compare the pyrene lifetimes obtained here with those determined by other groups of researchers. These lifetimes are summarized in Table 3. With the exception of the values in CTAB reported here, lifetime values have been determined by fitting the observed monomer curve to a simple exponential decay. However, the data in Table 3, third and fourth columns, show that the values of μ at which these determinations were made are in many cases sufficiently high to bring about significant excimer formation. For this reason the published values of τ included in Table 3 are of doubtful accuracy. In spite of this, a general trend can be observed for the pyrene lifetime data in Table 3: as μ decreases, τ increases (as would be expected if the lifetime shortening observed in CTAB micelles were due to Br^- ion quenching and if, as μ decreases, the probability of pyrene

molecules colliding with Br^- ions in the vicinity of the micelle becomes smaller).

Table 3 also includes lifetime data for naphthalene in CTAB; although the small values of τ (naphthalene in homogeneous organic solvents has a lifetime, in the absence of oxygen, of about 100 ns [2]) substantiate the hypothesis of quenching by Br^- ions, the small lifetimes could equally well be due to the monomer decay curves (from which the lifetimes were measured) being affected significantly by excimer formation. Other aromatic molecules show a shortening in fluorescence lifetime on being solubilized in aqueous CTAB; this effect has been found to occur for anthracene but not for perylene [24], in agreement with the known tendency for anthracene (and pyrene and naphthalene) to be quenched more efficiently by Br^- ions than perylene is [17].

The precise mechanism of quenching by Br^- ions under these conditions has been the subject of a continuing controversy [18, 19, 21, 25]. Quite apart from the changes caused by Br^- -ion-quenching effects, fluorescence lifetimes can, with a change in medium, also undergo seemingly arbitrary changes, the nature of which is far from clear. For example, changes in fluorescence lifetime have been observed which cannot originate in a simple quenching process. Thus, pyrene solubilized in phospholipid dispersions can have its lifetime reduced to 40 ns [25]; the quaternary ammonium groups that are present will have little or no quenching action on the excited pyrene molecules [17]. In contrast with its fluorescence lifetime in organic solvents (see earlier), naphthalene has a lifetime of 45 ns in water and 23 ns in cetyltrimethylammonium chloride micelles [22] (quenching of excited naphthalene by Cl^- ions is known to be inefficient [17]); pyrene as well has lifetimes which change unpredictably in water and surfactants from the values in organic solvents [23]. We are forced to conclude that the change in a micellar environment brings about marked changes in the intrinsic properties of the excited molecule. Some recent measurements [26] serve to emphasize this point: the radiative rate constant for pyrene in a series of micelles is not constant but depends on the surfactant; changes by as much as a factor of 2 are possible. It is clear that much more needs to be known not only about the precise mechanism by which quenching of molecules in micelles by ions occurs but also about the properties of excited molecules in micelles.

The values measured here for the pyrene excimer lifetime τ' in CTAB micelles (around 35 ns) are lower than those observed in Triton X-100 micelles and in homogeneous solvents, suggesting that some quenching by Br^- ions takes place. The value of k_2 , however, is of the order of those measured in other homogeneous and micellar systems (Table 2), unlike the values of k_1 for which marked differences are apparent.

The parameters measured in this investigation show a complicated behaviour with changing μ ratios. As μ decreases, k_1 decreases, k_2 shows a remarkable decrease to less than half its original value, τ increases and τ' appears to go through a minimum. This is in contrast with the situation in

Triton X-100 [1], in which k_1 , k_2 and τ' were constant, the only changes being observed in τ . With regard to this last effect, the decrease in τ in CTAB on going from low values of μ to high values of μ (see Table 1) is very similar to the changes in τ found in Triton X-100 [1] and may, as for Triton X-100, be due to the increased probability of energy transfer at high values of μ .

A possible explanation of the changes in k_1 , k_2 and τ' (which receives some support from the earlier discussion of the pyrene monomer lifetime) is in the changes in the properties of the micelle as the number of pyrene molecules in the micelle increases. Eriksson and Gillberg [27] found that, in a nuclear magnetic resonance (NMR) study of aromatic molecules solubilized in CTAB micelles, the chemical shifts and linewidths of some of the surfactant protons changed as the solute:micelle ratio increased and were suggestive of a transition around $\mu = 1$. In particular, hydrocarbon chain mobilities (calculated from linewidth broadening) decreased until this transition point was reached and then increased again. In the region of increasing chain mobility ($\mu > 1$; the measurements recorded here were all taken in this region) solute molecules, by separating the head groups and generally "loosening" the structure of the micelle, apparently reduce the rigidity of the micelle [28]. Thus the excimer formation step k_1 , which is normally taken to be diffusion controlled [13], is slow at low μ values and then increases with increasing μ as added solute molecules reduce the rigidity of the micelle interior. The inner environment of the CTAB micelle, judging from the k_1 values, appears to be rather rigid and it is possible that such a loosening of structure affects the other parameters measured here.

In other NMR work [29] it has been found that the signal due to the $-\text{CH}_2-$ protons of the CTAB splits into two peaks at pyrene:micelle ratios greater than about 3.8. Above this value of μ there may be two types of micelle present, perhaps differing in shape or in the way that the pyrene molecules are accommodated. The variations in k_2 and τ' with decreasing μ are complex; k_2 shows a marked decrease whereas τ' goes through a minimum and returns to its initial value. Although it is not clear what specific effects are involved here, a change of micellar structure with changing μ is undoubtedly important in giving rise to this behaviour.

One difficulty not hitherto mentioned is connected with the solubilization site of the pyrene molecule in the micelle. If the pyrene molecules are localized in one part of the micelle by preferential solubilization (*e.g.* in the hydrocarbon core), then the volume available to them is smaller than the micellar volume (the total mass of the micelle divided by the surfactant density) on which the kinetic calculations are based. Only k_1 would be affected: the true value of k_1 would be smaller than the measured value by a factor given by the ratio of the two volumes. However, it is not clear from the available evidence whether we can say that the pyrene molecules occupy specific solubilization sites. Thus, NMR evidence has been interpreted as showing that unsubstituted aromatic hydrocarbons are preferentially solubilized in the interior of the micelle [18, 29], but Wennerström and Lindman [30], in reviewing the available evidence, conclude (a) that we

should not argue in terms of distinct solubilization sites but rather in terms of "different affinities to different parts of the micelle" which determine the distribution of solute molecules within the micelle and (b) that the distribution of aromatic molecules within micelles tends to favour the micelle-water interface. We feel that the variation of the kinetic parameters with μ which we have observed should be regarded as being caused by changes in the structure (shape, rigidity, alkyl chain conformation etc.) of the micelle rather than by changes in the particular sites in the micelle at which the pyrene molecules are localized. However, the exact nature of the structural changes occurring and their precise effects on k_1 , k_2 , τ and τ' are not clear. In this respect there is still a large gap in our knowledge of micellar behaviour.

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