

PYRENE EXCIMER KINETICS IN MICELLES OF NON-IONIC SURFACTANTS

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Summary

The kinetics of excimer formation of pyrene solubilized in three nonylphenoxyethanols were studied using a technique developed recently. The values obtained for the kinetic parameters are similar to those obtained for other micellar systems, but the micellar solutions studied here show some unexpected changes with changing pyrene:micelle ratio. Results for pyrene excimer kinetics in nonane solution are also presented.

1. Introduction

A method of analysing reactions occurring in micelles has recently been developed and has been applied to the kinetics of pyrene excimer formation in micelles of the non-ionic surfactant Triton X-100 [1]. Following this [2], a study was made of this reaction in micelles of cetyltrimethylammonium bromide (CTAB); as in the former investigation, it was possible to study the effect on the kinetic parameters of varying the ratio μ of the number of pyrene molecules to the number of micelles. In this paper we report an extension of this work to the case of three surfactants belonging to a homologous series: *p*-nonylphenoxyethanols with 10, 40 and 100 ethylene oxide residues, abbreviated as N10, N40 and N100 respectively.

2. Experimental procedure

The experimental procedures used and the method of kinetic analysis have been described in detail elsewhere [1, 2]. As in the previous studies, μ was varied keeping the surfactant concentration constant. The surfactants, which were obtained from I.C.I. (Australia), were used as received. The ag-

gregation numbers, which were determined by membrane osmometry [3, 4], were as follows: N10, 155; N40, 7.0; N100, 2.0.

3. Results and discussion

The kinetic data for the three surfactant systems are summarized in Tables 1 - 3. Representative values for the three surfactants used here are given in Table 4 together with values for the other micellar and homogeneous systems. Table 4 also includes the values of the kinetic parameters for nonane obtained in this investigation. The significance of k_1 , k_2 , τ and τ' is as in the preceding papers [1, 2].

As for Triton X-100 and CTAB [1, 2], the pyrene monomer lifetime τ decreases in each surfactant system with increasing μ owing either to energy transfer to unexcited pyrene molecules as suggested previously or possibly to adventitious quenchers contained in the pyrene (which is unlikely in view of the high purity of the pyrene used).

TABLE 1

Kinetic parameters for the pyrene excimer reaction in aqueous *p*-nonylphenoxydecaoxyethanol (N10) micelles ($[N10] = 0.1176 \text{ M}$)

μ	k_1 ($\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)	k_2 ($\times 10^6 \text{ s}^{-1}$)	τ (ns)	τ' (ns)
6.830	4.15	5.83	143.8	50.9
5.464	3.98	5.76	152.5	50.4
4.553	3.98	5.89	162.4	50.2
3.903	1.42	5.68	175.4	51.3
3.415	0.976	5.49	159.0	48.9
2.732	0.255	5.79	161.5	49.1
2.276	0.395	5.87	182.3	52.7

TABLE 2

Kinetic parameters for the pyrene excimer reaction in aqueous N40 micelles ($[N40] = 0.02564 \text{ M}$)

μ	k_1 ($\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)	k_2 ($\times 10^6 \text{ s}^{-1}$)	τ (ns)	τ' (ns)
0.2620	2.547	19.66	54.9	22.7
0.2096	0.807	19.58	52.0	24.9
0.1747	0.267	19.56	56.7	26.3
0.1497	$< 10^{-4}$	19.58	55.5	26.4
0.1310	0.0118	19.58	55.5	27.7
0.1048	0.199	19.61	58.6	28.7
0.08733	0.892	19.58	60.3	29.8

TABLE 3

Kinetic parameters for the pyrene excimer reaction in aqueous N100 micelles ($[N100] = 0.01102 \text{ M}$)

μ	k_1 ($\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)	k_2 ($\times 10^6 \text{ s}^{-1}$)	τ (ns)	τ' (ns)
0.07285	6.01	2.98	195.7	33.2
0.05828	5.91	2.99	196.3	35.4
0.04857	5.91	2.98	209.5	35.8
0.04163	5.53	2.99	206.3	36.5
0.03238	5.37	2.98	218.7	38.9
0.02649	5.09	2.98	209.8	38.9
0.01821	5.06	2.98	217.1	41.4

TABLE 4

Summary of measured kinetic parameters for the pyrene excimer reaction in micellar and homogeneous solvents

Medium	μ	k_1 ($\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)	k_2 ($\times 10^6 \text{ s}^{-1}$)	τ (ns)	τ' (ns)
<i>Micellar solution</i>					
CTAB ^a	4.96	7.87	10.94	66.6	39.3
Triton X-100 ^b	5.54	6.96	2.25	219.6	41.1
N10 ^c	6.83	4.15	5.83	143.8	50.9
N40 ^c	0.262	2.55	19.7	54.9	22.7
N100 ^c	0.0729	6.01	2.98	195.7	33.2
<i>Homogeneous solution</i>					
Triethylene glycol ^a	—	64	19.2	411	186
Nonane ^c	—	1410	6.1	439	51
<i>n</i> -hexadecane ^b	—	86	3.8	331	54

^aRef. 1.

^bRef. 2.

^cThis work.

The variation in the rate constant k_1 for the excimer formation step, however, is rather unexpected: with increasing μ k_1 rises rapidly in N10 after going through a minimum, follows the same behaviour but in a much more extreme form for N40 and shows only a very slight rise for N100. The origins of this variation are probably complex since there are at least four factors dependent on μ which might influence k_1 .

(i) The first factor is the relative orientation of pyrene molecules. Pyrene molecules can be thought of as being planar with a thickness small compared with their extent. This raises the possibility of anisotropic motion playing an important part in this reaction. Thus at low values of μ each solubilized pyrene molecule has a relatively large volume available to it, and two

pyrene molecules might with relative ease take up an edge-on mutual configuration so that they can react following a relatively efficient sideways motion. With increasing μ the more crowded environment will mean that the mutual side-on configuration will be harder to attain and the reaction will be more likely to occur via the less efficient full face motion of the pyrene molecules. At still higher values of μ the close proximity of the reacting molecules will make mutual diffusion less important, and the reaction will proceed much more quickly. This reasoning will only apply when rotational diffusion of the pyrene molecules is not appreciably faster than translational diffusion. We have not been able to find any published data on the rotational diffusion of pyrene in micelles, but anisotropic motion occurs for rhodamine 6G which is an approximately planar molecule [5]. The relaxation times for the two types of rotation are of the order of 2 ns and 500 ps. This motion is clearly much faster than the excimer formation reaction. However, rhodamine 6G is solubilized predominantly in the aqueous phase at the micelle interface, whereas pyrene is most probably solubilized further into the micelle if not in the micelle interior itself (see below). In addition, theoretical studies [6] indicate that translational diffusion becomes four times faster in relation to rotational diffusion on going from an isotropic medium to a membrane which has many structural similarities to micelles. Further evidence bearing on this comes from a study of the strongly anisotropic motion of perylene (a planar molecule similar to pyrene) in solution using pulsed fluorimetry [7]; the ratio of the rotational diffusion constants about axes perpendicular and parallel to the plane of the molecule was found to be 10. Thus we cannot rule out anisotropic diffusion as an explanation of the variation of k_1 with μ . This would explain the data for N40 and N10, and the values of μ for N100 would, on this model, all lie above that corresponding to the minimum in k_1 .

(ii) Secondly, there are changes in the solubilization sites of pyrene molecules. Here we suppose that, as μ increases, the pyrene molecules, having filled all the available sites of one type, now start to occupy sites of another type at which the reaction proceeds at a different rate. Nuclear magnetic resonance (NMR) studies [8, 9] indicate that benzene is solubilized in the aqueous phase at the surface of CTAB micelles, although at high values of μ solubilization deeper into the core becomes significant. These results have been borne out by polarity studies [10] where the solubilized molecules are assumed to be distributed between the peripheral and core regions of the micelles. The extent to which these findings apply here is open to question since the distribution of pyrene between these two regions may differ from that of the benzene derivatives used in this work [10]. It therefore seems plausible that pyrene molecules are initially solubilized in the hydrocarbon region near the interface between it and the ethylene oxide region, and with successive additions they are likely to penetrate more deeply into the micelle core. Such a mechanism would be expected to give a monotonic variation of k_1 with μ ; to explain the minima observed with N10 and N40 another mechanism must be invoked. The extent to which the two regions are actually distinguishable can also be questioned in view of the large

size of the pyrene molecule in comparison with the extent of the nonylphenyl region of the surfactant micelle.

(iii) There may be changes in micelle structure. However, data on changes in the nature of micelles with added solute are lacking, most reported work being concerned with changes in micellar structure brought about by increases in surfactant concentration. We therefore have no reliable guide as to whether such changes might occur in the systems studied here, and whether they would affect k_1 .

(iv) For specific interactions between pyrene molecules and between pyrene and surfactant molecules once again data which might provide some indication of the importance of these effects are lacking. Such effects, however, may become important if high micellar pyrene concentrations arise because not all of the micelle (*e.g.* only the nonylphenol region) is available to the solubilized pyrene, particularly at high μ values.

It is clear from the above that the distinction between (i), (ii), (iii) and (iv) is not entirely clear cut, and also that the magnitude of each of these four effects can vary between micelles. Without more data an unambiguous explanation of the variations observed in k_1 is not possible.

The lifetime of the pyrene excimer τ' is relatively insensitive to changes in μ , as has been found in the previous studies [1, 2]. Thus, τ' remains constant with increasing μ for N10 and shows a gradual fall for N40 and N100 (Tables 1 - 3). For all three surfactants k_2 remains constant with changing μ . As with k_2 , τ' depends more on the specific interactions of the pyrene excimer with surfactant molecules than on the physical characteristics of the micelle.

In Table 4 the experimental values obtained in this work are compared with those for other micellar systems and homogeneous solvents. The values characteristic of homogeneous solvents provide some guide to the nature of the environment in which the pyrene is located. Thus the values of k_2 and τ' change little on going from nonane to *n*-hexadecane, but these values differ appreciably from those for triethylene glycol. The corresponding values for the micellar systems are, with two exceptions (the k_2 values for N40 and perhaps for CTAB), much closer to the corresponding values in the homogeneous alkane solvents than to those in triethylene glycol, suggesting that the pyrene molecules are preferentially solubilized in the part of the micelle made up of the nonylphenol residues (this is remarkable in N100 where the ethylene oxide region is so much more extensive than the hydrocarbon region), presumably at least partly because the ethylene oxide chains in the aqueous environment are heavily solvated. This finding is consistent with the results obtained from NMR investigations [8, 9]. It should be noted that the absence of any significant variation of k_2 and τ' with μ suggests, on this interpretation, that changes in the solubilization site of pyrene ((iii) above) are relatively unimportant for the micellar systems studied here.

The micellar environment provided by these surfactants must differ considerably in many respects from that of nonane; the k_1 values in the micelles are very much lower than for liquid nonane. While no quantitative

significance should be attached to this [2], it is clear that the micellar environment must be very viscous in comparison with the hydrocarbon solvent.

An unexpected feature of the results obtained here is the variation between micelles shown by τ . In N10 and N100 τ has values (around 150 ns and 200 ns respectively) which, while low, are still reasonably close to the usually accepted values for homogeneous solvents [2]. The value in N40, however, lies between 50 and 60 ns. This observation cannot be explained by energy transfer (since μ for the N10 measurements was much higher than for N40) nor is it plausible that the surfactant molecules can efficiently quench excited singlet pyrene molecules (as for example in CTAB [2] where the bromide ion is known to be an efficient quencher of pyrene). We have no explanation for this phenomenon which seems to be part of the generally unusual behaviour of N40 compared with that of the other two surfactants.

Little comparable work has appeared in the literature, the only parallel study to have come to our notice being an investigation of excimer formation of pyrene and sodium 5-[1-pyrenyl]pentanoate in micelles of cetyltrimethylammonium chloride (CTAC) and sodium dodecyl sulphate [11]. However, these workers assumed (without providing any justification) that the reverse step k_2 of the excimer formation reaction could be neglected, *i.e.* that $k_1[\text{pyrene}]$ is very much greater than k_2 . For CTAB (which should behave in a very similar way to CTAC) k_1 is of the order of $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and k_2 varies from 5×10^6 to 10^7 s^{-1} [2]. At a pyrene concentration of $2.08 \times 10^{-4} \text{ M}$ (the highest used in this study [11]) and with the aggregation number of CTAC assumed to be 59 [11], the average pyrene concentration in the micelles will be 0.065 M at $[\text{CTAC}] = 0.010 \text{ M}$, assuming that the density of the micelles is unity and that all of the micellar volume is available to the solubilized pyrene. By no stretch of the imagination does the approximation $k_1[\text{pyrene}] \gg k_2$ hold, and the closeness of k_1 to k_2 for other micellar systems (ref. 2 and this work) suggests that this may be a general result except at very high values of μ . More reliable procedures [1, 12] for both transient and stationary state experiments are to be preferred.

It would thus seem that the constancy of k_2 and the large variations in k_1 for any one surfactant reflect on the one hand the fact that only excimers with a highly specific configuration are formed and on the other hand that profound changes occur in the micelle interior, *e.g.* in the way that the surfactant molecules are packed together, as a result of introducing successively more pyrene molecules. There is a need for more physicochemical measurements (in particular those using NMR, electron spin resonance and light scattering techniques) of micelle structure in the presence of solutes. Only when such data become available can the kinetics of the systems studied here be interpreted correctly.

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