SOLVENT EFFECTS ON INTRAMOLECULAR EXCIMER FORMATION OF DIPYRENYLALKANES

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Summary

Measurements of excimer:monomer fluorescence intensity ratios for two pyrene derivatives, 1,3-dipyrenylpropane and 1,10-dipyrenyldecane, in two different types of mixed solvent are reported. In addition, the monomer: excimer fluorescence intensity ratios for both compounds in aqueous sodium dodecyl sulphate, cetyltrimethylammonium bromide and Triton X-100 have been determined. A discussion of the results in terms of the kinetics of excimer formation is given.

1. Introduction

The increasing interest in the use of fluorescent probe molecules to investigate the properties of surfactant micelles and biological membranes has led to the development of a number of methods for measuring such properties as the microviscosity of the medium. One technique for measuring microviscosities has relied on the postulated dependence of excimer:monomer emission ratios on viscosity for such excimer-forming systems as pyrene dissolved in surfactant micelles [1]. The procedure generally adopted is to set up "calibration curves" by measuring excimer:monomer fluorescence ratios as a function of viscosity for a solvent or a series of solvent mixtures. This can be done for excimer-forming molecules which are free or which are held together by an alkane or other inert type of chain. The excimer:monomer ratio is then measured for the same compound in the chosen environment, in this case the micelle interior, and subsequently used in conjunction with the calibration curve to obtain a value of the viscosity of the micelle interior. This procedure, when used with unlinked molecules, has already been criticized for its neglect of distributional effects [2]. It is the purpose of this
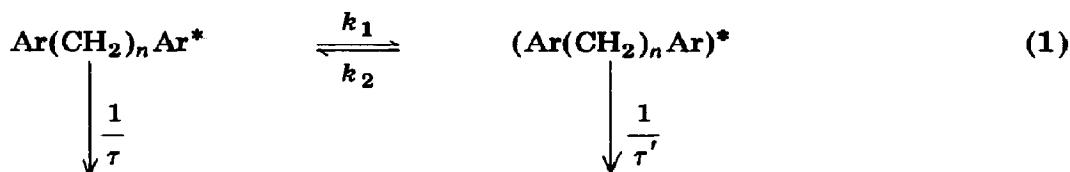
paper to show that there are other reasons for doubting whether this method is a reliable guide to micellar microviscosities.

2. Experimental procedure

The compounds used here consisted of two pyrene molecules linked by an alkane chain, 1,3-dipyrenylpropane and 1,10-dipyrenyldecane, both of which are known to undergo very efficient intramolecular excimer formation [3]. They were synthesized using the method of Zachariasse and Kuehnle [3]. Fluorescence data were obtained by dissolving the appropriate compound in the chosen solvent and determining the monomer and excimer fluorescence intensities with a fluorimeter which has been described elsewhere [4]. Complete dissolution of the probe molecules in aqueous surfactants was checked by examining the solutions for crystallites of the solute, which are readily detectable by their fluorescence under a UV lamp. All experiments were carried out at 25 °C.

3. Results and discussion

Intramolecular excimer formation in the compounds studied here can be represented by the following reaction scheme:

$$Ar(CH_2)_n Ar^* \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad (Ar(CH_2)_n Ar)^* \tag{1}$$

$$\Big\downarrow \frac{1}{\tau} \qquad\qquad\qquad\qquad \Big\downarrow \frac{1}{\tau'}$$

for which the fluorescence intensities in the steady state are given by

$$\frac{I'}{I} = \frac{I_0'}{I_0} \frac{k_1 \tau}{1 + k_2 \tau'} \tag{2}$$

Here I and I' are the measured fluorescence intensities of the excited monomer and of the intramolecular excimer respectively; I_0 and I_0' are these fluorescence intensities in the limiting cases of no excimer formation and complete excimer formation respectively.

In the procedure for viscosity measurements outlined in Section 1 it is necessarily assumed that the measured intensity ratio I'/I varies with the viscosity of the medium and is unaffected by a change in any other property of the medium. Although the assumptions on which this depends have never been stated in full, there are, in the light of eqn. (2), two conceivable ways in which such an intensity ratio dependence might occur.

The first way is the situation where all six parameters I_0', I_0, k_1, k_2, τ and τ' on the right-hand side of eqn. (2) depend solely on the viscosity of the medium and on no other property of the medium. However, there is some
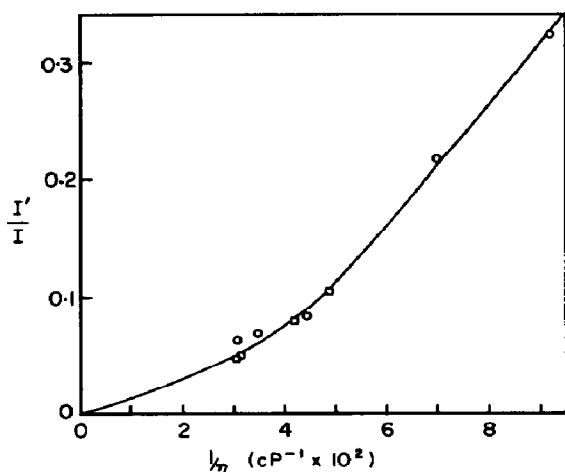
Fig. 1. Excimer:monomer fluorescence intensity ratios I'/I as a function of the reciprocal viscosity $1/\eta$ for ethylene glycol–(triethylene glycol) solvent mixtures: O, 1,3-dipyrenyl-propane; □, 1,10-dipyrenyldecane.
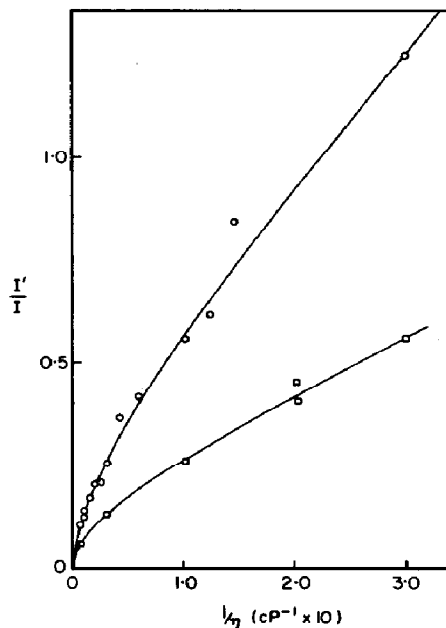
Fig. 2. Excimer:monomer fluorescence intensity ratios I'/I as a function of the reciprocal viscosity $1/\eta$ for n-hexadecane–(liquid paraffin) solvent mixtures: O, 1,3-dipyrenyl-propane; □, 1,10-dipyrenyldecane.

doubt whether this is in fact so, at least for the linked pyrene molecules studied here. Figures 1 and 2, when compared, show that the same compound gives different values of I'/I for different solvent systems having the same measured viscosity. Furthermore, direct measurements of the rate constant k_2 for unlinked pyrene molecules in three solvents (in order of decreasing viscosity) triethylene glycol [5], n-hexadecane [6] and cyclohexane [7] give the values 19.2×10^6 s^{-1}, 3.8×10^6 s^{-1} and 6.5×10^6 s^{-1} respectively, showing that at least one of the parameters in eqn. (2) does not necessarily have any clear dependence on solvent viscosity.

The second, and rather more likely, justification which could be adduced in support of the procedure for measuring viscosities is to assume that we are dealing exclusively with systems where $k_2\tau \ll 1$ (β conditions [8]). Equation (2) then becomes

$$\frac{I'}{I} = \frac{I_0'}{I_0} k_1 \tau \tag{3}$$

and the observed fluorescence intensity ratio no longer depends on k_2 or τ'. On this assumption the same values of I'/I will be obtained for different solvents of the same viscosity when the four parameters I_0', I_0, k_1 and τ depend solely on the viscosity of the medium; the behaviour of k_2 and τ' with changing medium is no longer important.

As already pointed out, different values of I'/I are obtained for different solvent systems having the same viscosity. In view of the foregoing arguments, this could be due to two causes.

(1) β conditions may not apply even though the method of viscosity determination based on eqn. (3) is valid.

(2) Alternatively, this method of viscosity determination is not valid and eqn. (3) does not provide a reliable guide to the viscosity of the medium (regardless of whether β conditions are or are not present) if one or more of the parameters k_1, τ, I_0 or I_0' varies with properties of the medium other than the viscosity. In the following discussion we attempt to choose between these two possibilities.

The condition which must be satisfied if β conditions are to hold is that $k_2\tau' \ll 1$. With regard to the compounds studied here the only relevant data available are for 1,3-dipyrenylpropane in methylcyclohexane [9] for which $k_2\tau' = 0.24$. Unfortunately, instead of adopting one of the more reliable procedures available [10, 11] for the analysis of the kinetics, Zachariasse *et al.* [9] chose a method which depends on the doubtful assumption that τ' does not change with temperature (*e.g.* see ref. 12, where τ' for an exciplex system is shown to drop significantly as the temperature falls from 20 to -80 °C). In addition, there is an apparent lack of a linear low temperature region [9], which makes it difficult to reach any conclusion about the existence of β conditions at these temperatures. The existing data for un-linked pyrene molecules in triethylene glycol [5], *n*-hexadecane [6], cyclo-hexane [7] and nonane [13] give values for $k_2\tau'$ of 3.57, 0.202, 0.423 and 0.311 respectively. Thus β conditions may apply in alkane solvents but they do not appear to hold for triethylene glycol. Although these results are inconclusive in relation to the linked pyrene molecules studied here, the data for the unlinked pyrene systems suggest that it is less likely that β conditions hold in the ethylene glycol–(triethylene glycol) solvent system than in the *n*-hexadecane–(liquid paraffin) solvent mixtures.

Even if, in spite of what has been said in the preceding paragraph, we could conclude that β conditions hold for the systems of interest, the derivation of values of the viscosity of micellar systems using the calibration curve procedure outlined in Section 1 still relies on the dependence of the four parameters I_0, I_0', k_1 and τ of eqn. (3) being solely on the viscosity of the medium. Nothing appears to be known about the variation in I_0 and I_0' with solvent but some data on k_1 and τ for unlinked pyrene molecules exist: these show a rise in k_1 with falling viscosity [5, 6, 7, 13] for homogeneous solvents while τ remains roughly constant. However, the viscosities obtained from these experimental values of k_1 using the Stokes–Einstein equation do not agree with the bulk viscosity measurements [6]; this type of discrepancy has been found for other systems [14].

The only measurements on linked excimer-forming compounds of this type are those of Johnson [10] on linked carbazoles. The experimental data and the conclusions drawn from these measurements are important for the present discussion, since both k_1 and k_2 (which were measured directly

in a homologous series of solvents) varied with viscosity η in the following manners:

$$k_1 = C\eta^a \tag{4}$$

and

$$k_2 = C'\eta^a \tag{5}$$

Here $a = -0.34$ for alkane solvents and $a = -0.51$ for alcohol solvents. The dicarbazolylalkanes thus show a definite dependence on viscosity, and the question arises whether the dipyrenylalkanes are characterized by a similar dependence.

To test this the data of Figs. 1 and 2 are plotted in Fig. 3 on a logarithmic basis; straight lines are obtained with non-zero slopes γ. If the relations (4) and (5) hold, then eqn. (2) becomes

$$\frac{I'}{I} = \frac{I_0'}{I_0} \frac{C\tau}{\eta^{-a} + C'\tau'} \tag{6}$$

and eqn. (3) (β conditions) becomes

$$\frac{I'}{I} = \frac{I_0'}{I_0} \eta^a C\tau \tag{7}$$

The linear plots of Fig. 3 might suggest that eqn. (7) (β conditions) is appropriate. Such a conclusion, however, should be treated with caution for the following reasons.

(a) If the dicarbazolylalkane excimers observed by Johnson have lifetimes of the order of 50 ns (typical for excimers [5, 6, 7, 13] and exciplexes [15]) then, from his data, we obtain $k_2\tau' \gg 1$ for all but the lowest
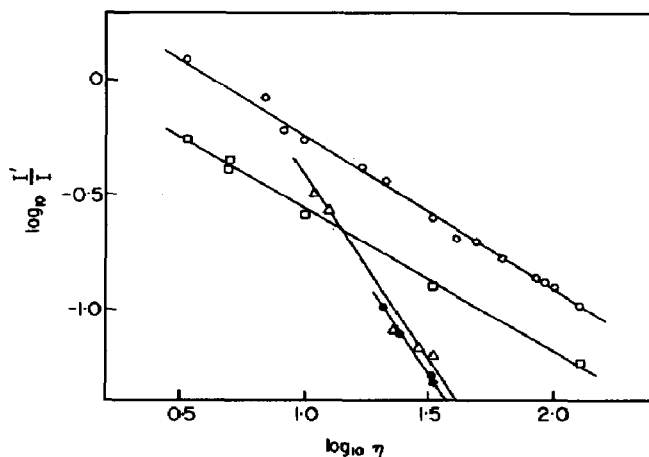

Fig. 3. A logarithmic plot of I'/I vs. η for the following systems: $\bigcirc$, 1,3-dipyrenylpropane in n-hexadecane–(liquid paraffin) mixtures; $\square$, 1,10-dipyrenyldecane in n-hexadecane–(liquid paraffin) mixtures; $\triangle$, 1,3-dipyrenylpropane in ethylene glycol–(triethylene glycol) mixtures; $\bullet$, 1,10-dipyrenyldecane in ethylene glycol–(triethylene glycol) mixtures.

viscosity alcohols. Thus for these compounds β conditions may not hold and this may also be the case for the dipyrenylalkanes studied here. The fact that linear plots are nevertheless obtained is explained by the circumstance that eqn. (6) can be approximated by eqn. (7) over a limited viscosity region. If we expand these two equations in a power series of $\delta = \eta_1 - \eta$, where η_1 is the viscosity at which the right-hand sides of eqns. (6) and (7) are exactly equal, and then take the series to first order and equate coefficients of δ, we obtain

$$\gamma = \frac{a}{1 + C'\tau'\eta_1{}^a} \tag{8}$$

where γ is the slope of the linear plots of the type obtained in Fig. 3. The exponents obtained from Fig. 3 are thus smaller than the exponent a of eqn. (7) by a factor $1/(1 + C'\tau'\eta_1{}^a)$.

(b) The rate constant data of El-Bayoumi et al. [16] for 1,3-dinaphthyl-propane in ethanol—glycerol mixtures do not give linear logarithmic plots of the type found for 1,3-dicarbazolylpropane [10] in a homologous series of pure solvents, indicating that the dipyrenylalkanes studied here (in solvent mixtures as opposed to pure solvents) may not conform to eqns. (4) and (5).

In these arguments, (a) suggests that the linear plots of Fig. 3 may not necessarily be evidence of β conditions, even assuming that the rate constants for the systems studied here depend on viscosity in the way found by Johnson [10]; whereas (b) suggests that this type of viscosity dependence may not even occur for linked compounds in solvent mixtures. If the systems investigated here were to show such a viscosity dependence and if β conditions were applicable in these cases (both contrary to the preceding discussion), we would still be confronted with different values of C and C' for different solvent systems, which raises the problem (already apparent in Figs. 1 and 2) of which calibration system to choose in carrying out the experiments described in the introduction.

With these points in mind, it is of interest to examine the viscosity values for a number of micellar systems derived by comparing the excimer: monomer fluorescence intensity ratio for the micelle with a calibration curve. These systems are summarized in Table 1. The viscosity obtained obviously depends on which probe is used and on which solvent system is taken as a reference. Values of viscosity obtained by direct measurement of k_1 for excimer formation of unlinked pyrene molecules using the Stokes—Einstein equation [14] (Table 1), which involves fewer assumptions than in measuring I'/I ratios, also differ from the values obtained using diarylalkane molecules. Thus, this method of determining micellar viscosities is clearly unreliable, although it is not possible to conclude with any certainty whether this is because β conditions do not hold or because there is an intrinsic lack of any meaningful dependence of the parameters on the right-hand side of eqn. (3) on the viscosity of the medium. From the preceding discussion, both causes could well be operative in leading to the failure of this method for determining viscosities.

TABLE 1

Excimer:monomer fluorescence ratios and calculated viscosity data at 25 °C for 1,3-dipyrenylpropane and 1,10-dipyrenyldecane in aqueous sodium dodecyl sulphate (SDS), aqueous cetyltrimethylammonium bromide (CTAB), aqueous Triton X-100 and aqueous cetyltrimethylammonium chloride (CTAC)

Measurement	Surfactant			
	SDS	CTAB	Triton X-100	CTAC
1,3-Dipyrenylpropane				
I'/I	0.417[a]	0.120	0.0649	—
η^{b} (cP)	10.1	19.2	29.7	—
η^{c} (cP)	15.6	111	≈250	—
1,10-Dipyrenyldecane				
I'/I	0.0313	0.0629	0.0330	—
η^{b} (cP)	57.1	30.6	54.1	—
η^{c} (cP)	≈330	119	≈300	—
η^{d} (cP)	19	—	—	—
η^{e} (cP)	4	—	—	—
η^{f} (cP)	—	35.3	145	—
η^{g} (cP)	10	42	—	20.8
η^{h} (cP)	9	39	—	31

[a] Measured using freshly prepared solutions (see text).

[b] Calculated by comparison with I'/I values for ethylene glycol–(triethylene glycol) solvent mixtures (Fig. 1).

[c] Calculated by comparison with I'/I values for n-hexadecane–(liquid paraffin) solvent mixtures (Fig. 2).

[d] From measurements on 1,3-dipyrenylpropane in n-hexadecane–(liquid paraffin) mixtures [17].

[e] From measurements on 1,3-diphenylpropane in n-hexadecane–(liquid paraffin) mixtures [17].

[f] Calculated from directly measured values of k_1 for pyrene excimer formation from refs. 5 and 6.

[g] From measurements on bis(4-biphenylmethyl)ether in alcohols and alcohol mixtures [18]. Bis(1-naphthylmethyl) ammonium chloride gives a value that is 50% lower.

[h] From measurements on bis(1-naphthyl)propane in ethanol–glycerol mixtures [19].

Solutions of sodium dodecyl sulphate (SDS) show aging effects which are not well understood [20] and this could be the cause of the discrepancy between the two values for 1,3-dipyrenylpropane in SDS (using n-hexadecane–(liquid paraffin) mixtures as the reference solvents): the measurements in SDS reported here were carried out with solutions which were used within 1 h of preparation.

Apart from the disagreement between different determinations of the microviscosity of the same micelle, there are other reasons for regarding viscosity measurements using calibration curves with distrust. In one case where β conditions were postulated, a plot of I/I' against η, although linear for most of the solvents and solvent mixtures used, did not pass through the origin, as would have been expected for β conditions (see earlier) [18]. In

another case no indication is given of whether the calibration curves used are linear and conform to the assumed β conditions [19]. Other authors have found non-linear plots of $1/k_1$ *versus* η in various solvent mixtures for linked excimer-forming compounds [17].

A further complication, which has been pointed out in the earlier discussion and elsewhere [5, 6, 14], is that a simple relationship between k_1 and bulk viscosity may not exist even in homogeneous solvents. This is particularly apparent for 1,3-dicarbazolylpropane in solvents which are not members of a homologous series [10], where any meaningful dependence of rate constant on viscosity vanishes. This observation has particular relevance for measurements in micelles, which can hardly be regarded as members of the solvent series used as the reference system. It is clear that the use of methods for micellar microviscosity measurements based on excimer: monomer fluorescence intensity ratios should be avoided wherever possible.

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