

Effects of dimensionality on diffusion-controlled deactivation of excited species

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Abstract. The kinetics of diffusion-controlled deactivation processes is strongly affected by confinement of the reacting species in a space kept at molecular dimensions in at least one direction. In globular micelles the confinement is in all three dimensions, and the well-known kinetics is determined by a first-order rate constant representing the frequency of encounters of a pair of reactant molecules in the micelle, and the statistics of distribution of the reactants over the micelles. If the confinement is allowed to grow in one dimension into rods, or two dimensions into monolayers or bilayers, or in all three dimensions to a homogeneous solution, the deactivation kinetics is determined by one-, two-, or three-dimensional diffusion. Experimental examples of these cases are presented. Further complications occur on timescales where migration of the reactants between the dimensionally restricted structures must be considered. Of particular interest are systems which comprise clusters of small micelles, where the exchange between the micelles in a cluster is rapid. Experimental results for such a system composed of reversed AOT micelles is presented.

Keywords. Quenching; diffusion-control; micelle; confinement; reduced dimensionality.

1. Introduction

Light-induced processes in microheterogeneous media have come to play an important role in research around photochemical solar energy conversion and storage. Various photophenomena in such systems have been explored with respect to their ability to promote electron and energy transfer processes, and prevent backtransfer. Increasingly elaborate ordered systems are being built up towards this end (Balzani and Scandola 1991; Grätzel 1988; Kalyanasundaram 1987; Thomas 1984; Fendler 1982). The most simple systems utilize the binding – by hydrophobic or electrostatic effects – of small reactant molecules to micelles or membranes. The small molecules are mobile at the surface of or within the structures, and interact typically on each encounter, i.e. in a diffusion-controlled way. Even in these confined environments the diffusion-controlled kinetics is too, slow and unspecific to give an efficient photoconversion, and the initial electron transfer steps of the natural photosynthesis as well as most recent attempts to mimic it make use of components held rigidly in a prearranged structure. The kinetics of diffusion-controlled reactions in the structures is still important, however, both for the understanding of the subsequent steps in the process, and for the variety

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of loss processes that may occur due to the inescapable presence of electron and energy acceptors in the system.

The kinetics have been studied mainly for micellar systems (Infelta *et al* 1974; Tachiya 1975, 1982, 1983; Infelta and Grätzel 1983; van der Auweraer and De Schryver 1990; Almgren 1991), and particularly well for fluorescence quenching in such systems. A useful method to determine the micelle size has evolved from these studies (Atik and Singer 1978; Turro and Yekta 1978; Zana 1987), based on the fact that the statistical distribution of quenchers among the micelles is decisive for the observed fluorescence decay. Quenching will occur rapidly in micelles which contain quenchers at the moment of excitation, but only slowly or not at all in micelles originally without quenchers. The quenching process is described by a first-order quenching constant, k_q , which gives the frequency of reactive encounters between the excited probe and a quencher in the micelle. Since it can not be measured separately, the exponentiality of the basic quenching process is largely an assumption, supported by some model calculations and simulations of diffusive encounters in small spheres (Gösele *et al* 1979; Hatlee *et al* 1980; Tachiya 1980; Sano and Tachiya 1981; Van der Auweraer *et al* 1981).

If the small globules are allowed to grow the statistical distribution of the reactants among the individual micelles will ultimately become unimportant. This happens when the observation time, determined either by the quenching or by the natural lifetime of the excited species, is short compared to the time required for a diffusive displacement of the probe relative to the quencher over a distance comparable to the size of the micelle. The system is then effectively infinite, and the quenching rate is determined by one-, two-, or three-dimensional diffusion, depending on if the expansion has occurred in one, two, or three dimensions.

Small globular micelles of cetyltrimethylammonium chloride can be made to grow into very long flexible rods, or even thread-like micelles (Brown *et al* 1989), by the addition of various organic or highly polarizable counterions. The fluorescence quenching dynamics in micelles at various stages of this transition has been studied (Almgren *et al* 1988) and will be discussed first.

Some nonionic surfactants, notably $\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_6\text{OH}$, C_{12}E_6 , are good solvents in neat fluid form for hydrophobic probes and quenchers, and with water form liquid crystalline phases which are all accessible at room temperature and have lamellar, cubic, and hexagonal structure. In addition, isotropic phases with normal and reversed micelles are also formed. By just adding water a transition from a three-dimensional homogeneous solution to two-, one-, and zero-dimensional systems (the latter represented by small micelles) can be achieved. Fluorescence quenching in such a system is presented in § 3 (Almgren and Alsins 1990).

The results from the studies of one- and two-dimensional systems show nonexponential decay curves without distinct features which would allow a qualitative statement about the dimensionality. There is little hope, therefore, that fluorescence quenching could be used to identify fractal systems, with fractal dimensions between 1 and 3. Clusters of small micelles are systems which in a sense are intermediate between the zero-dimensional case of the small micelles and systems of higher dimensions. The anionic surfactant AOT (Aerosol OT) solubilizes water in the form of small droplets in hydrocarbons. These water-in-oil microemulsions or reversed micelles have been very intensely studied (Day and Robinson 1979; Kotlarchyk and Chen 1982; Robinson *et al* 1985; Eicke *et al* 1986, 1989; Howe *et al* 1987; Lang *et al* 1988), and there is

some indication on the formation of clusters of micelles under certain conditions. By utilization of excited states with widely varying lifetimes it was possible to distinguish between intramicellar deactivation and deactivation by migration or exchange between the individual micelles in a cluster (Jóhannsson *et al* 1991). This study is reported briefly in §4.

2. From spheres to rods

CTAC at a concentration of 40 mM forms small micelles which are supposed to be globular. Addition of sodium chloride give little change of the micelle size, whereas the addition of a variety of more strongly bound counterions gives rise to an excessive growth of the aggregates, as seen clearly from a strong increase of the viscosity of the solution, and often also viscoelastic effects. With sodium chlorate the viscosity starts to increase when 40 mM has been added, and continues to grow to very high values – at 100 mM it has grown by about a factor of 100 (Almgren *et al* 1988). Long thread-like micelles are known to exist in these solutions (Brown *et al* 1989).

Fluorescence decay curves were determined for pyrene, solubilized at a low concentration (1×10^{-5} M) in micelles of CTAC (40 mM) with sodium chlorate added to concentrations between 0 and 100 mM, both with and without the quencher, benzophenone, at a fixed concentration of 4.50×10^{-4} M. The family of decay curves in figure 1 show first the purely exponential decay of pyrene in the small micelles without salt and quencher. Curve 1 was obtained with quencher present, and is a

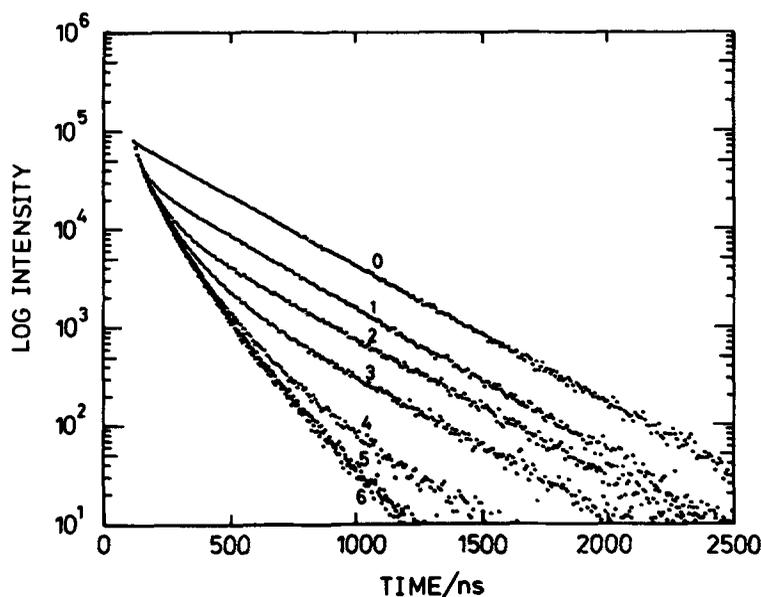


Figure 1. Fluorescence decay curves for pyrene (1×10^{-5} M) quenched by benzophenone (4.50×10^{-4} M) in CTAC micelles. Curve 0: CTAC without salt and quencher. Curve 1: quencher but not salt. In 2–6 increasing amounts of NaClO_3 were present = 32.7, 41.4, 49, 70.6 and 101 mM, respectively. Reproduced with permission from Almgren *et al* (1988b).

typical decay for a situation where the simple Infelta model applies (Infelta 1979):

$$\ln[F(t)/F(0)] = -k_0t + n(\exp(-k_qt) - 1), \quad (1)$$

where $F(t)$ and $F(0)$ are the fluorescence intensities (number of counts) recorded at time t and time 0, respectively, k_0 the decay constant of pyrene without quencher, and n the mean number of quenchers per micelle. Knowing the concentrations of quencher and surfactant in micelles, the mean aggregation number, $\langle a \rangle$, is obtained from n .

Curves 2 and 3, with 32.7 and 41.4 mM sodium chlorate, respectively, also fit well to the simple Infelta model, but with much larger values of n . The aggregation numbers obtained for curves 1, 2, and 3, were 90, 175, and 290, respectively. The micelles grew quite substantially before the viscosity was much affected. With further addition of chlorate the exponential tail of the decay was not well developed over the time-window of the measurements, as in curve 4 at 49 mM. Curves 5 and 6, with 70.6 and 101 mM chlorate, are identical within the noise levels, and represent the limiting decay curve for long aggregates. The extreme growth of the flexible cylinders in this range of chlorate concentrations, which is so evident from the viscosity data, have no effect on the deactivation kinetics; the cylinders are already effectively infinite.

The treatment of the quenching in long cylinders as a process limited by diffusion in one-dimension requires some comment. When the excited probe and the closest quencher are initially far apart, an encounter requires a diffusion over the separation distance in the direction of the axis of the cylinder. This is the one-dimensional diffusion. When quencher and probe are close, however, all three dimensions are important, which means that they may escape an encounter and reaction, even if they are at the same coordinate along the cylinder axis. To handle this, the excited probe is assumed to be surrounded by a reaction zone, a segment of the cylinder having the same volume as a sphere with the cylinder radius, R , i.e. with the length $l = 2/3 R$, in which the encounter frequency between the probe and a quencher is k_q , comparable in magnitude to the quenching constant in a micelle with approximately the same volume. Using this concept a boundary condition can be set up, and the diffusion problem solved, resulting in an equation for the fluorescence decay (Almgren *et al* 1988):

$$\ln\left(\frac{F(t)}{F(0)}\right) = -k_0t - \frac{2c_0}{h} \left(\exp(Bt) \operatorname{erfc}(Bt)^{1/2} - 1 + \frac{2(Bt)^{1/2}}{\pi^{1/2}} \right), \quad (2)$$

where c_0 is the number of quenchers per unit length of the cylindrical micelle, and can be calculated from the quencher concentration if the radius of the micelles is given. The parameter $h = 2k_qR/(3D_m)$ measures the importance of reaction versus diffusion. $B = h^2D_m$ where D_m is the sum of the diffusion coefficients for probe and quencher.

Curve 5 and several similar decay curves obtained at other quencher concentrations gave good fits to (2). Assuming the cylinder radius to be 21 Å, the length of an all-*trans* C₁₆-chain, D_m was obtained as $9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, and k_q as $2.4 \times 10^7 \text{ s}^{-1}$. The latter value agrees well with $k_q = 1.9 \times 10^7 \text{ s}^{-1}$ for the quenching in the spherical micelles without added sodium chlorate.

Equation (2) was used to interpret deactivation data for several systems in CTAC/CIO₃ with consistent and reasonable results. The determined D_m values for a

Table 1. Diffusion coefficients in long cylindrical CTAC/CIO₃ micelles from parameters determined by fitting decay curves to (2).

Solute	$10^{11}D$ (m ² s ⁻¹)	Solute	$10^{11}D$ (m ² s ⁻¹)
Py	4.6 ± 1.3	BP	3.4 ± 1.8
MeA	3.6 ± 0.8	BPC ₆	1.4 ± 1.8
Az	3.8 ± 1.2	CPC	0.9 ± 1.8
GAz	2.6 ± 0.8	A18	0.5 ± 1.2

Abbreviations: Py = pyrene, MeA = 9-methylanthracene, Az = azulene, GAz = guaiazulene (1,4-dimethyl-7-isopropylazulene), BP = benzophenone, BPC₆ = 1-(4-benzoylphenyl)hexane, CPC = cetylpyridinium chloride, A18 = octadecyl anthracene-9-carboxylate.

number of probe-quencher pairs could be split into individual diffusion coefficients (Alsins and Almgren 1990) with results as collected in table 1. Values around $7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ were quoted for the diffusion coefficients of some simple aromatic compounds in hexadecane (Alwatter *et al* 1973), larger by a factor of about 20 than in the micelles. The diffusion rate is thus reduced substantially as compared to that in the homogeneous solution. The compounds with long substituent chains have diffusion coefficients reduced even further. As discussed by Alsins and Almgren (1990) these results do not totally agree with results obtained by NMR methods for the surfactant diffusion in similar systems (Söderman *et al* 1985, 1987).

3. Three to zero dimensions: the C₁₂E₆-water system

The nonionic surfactant hexa-ethyleneglycol-mono-*n*-dodecylether in neat fluid form is a good solvent for hydrophobic substances like the probe-quencher pair pyrene and BPC₆, (1-(4-benzoylphenyl)hexane). When water is added a number of liquid crystalline phases are formed successively, figure 2 (Mitchell *et al* 1983). The surfactant solubilizes some water in the form of reversed micelles before the separation of the lamellar phase, which is built by very thin bilayers. The thickness of the hydrophobic domain is only 13.6 Å according to X-ray results (Clunie *et al* 1969). At higher water content a cubic phase is found, followed by a hexagonal phase with long cylinders. In the isotropic micellar phase the most dilute solutions contain small globular micelles, whereas the solution just outside the hexagonal phase contains long rod-like micelles.

The reactants used in this study were completely confined to the hydrophobic domains of the surfactant aggregates even at the highest water content (97% w/w). The local concentrations of probe and quencher remained constant, therefore, when water was added, and the changes in the decay curves are due only to changes in the mobility of the reactants and the geometry of the hydrophobic domains.

The decay curves in figure 3 are corrected by multiplication with the factor $\exp(k_0 t)$ for the unquenched decay of the probe, so that the uppermost pair of curves, which represent small micelles at 3% w/w, have constant tails in the region where all excited

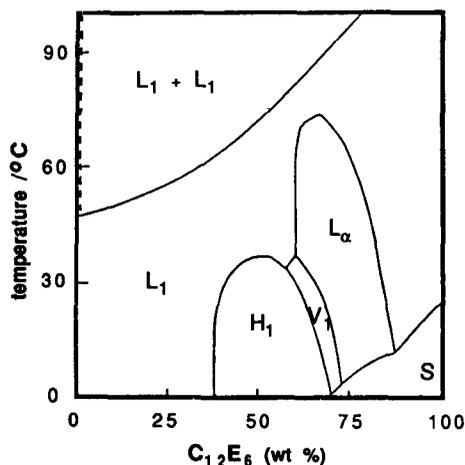


Figure 2. The phase diagram of C₁₂E₆-water showing the regions of existence of the isotropic solution phase, L₁, surrounding three liquid crystalline phases, H₁ = hexagonal, V₁ = cubic, and L_α = lamellar. Reproduced with permission from Mitchell *et al* (1983).

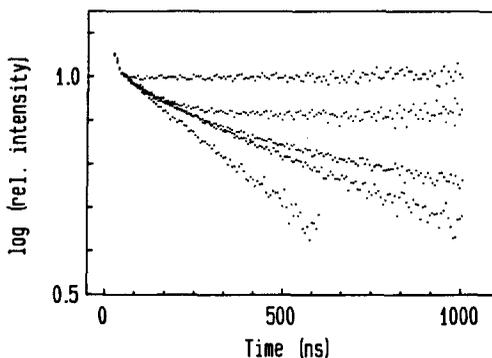


Figure 3. Quenched fluorescence decay curves for pyrene with 1-(4-benzoylphenyl)hexane as quencher, solubilized in various phases of the system C₁₂E₆-water. The decays were multiplied by the factor $\exp(k_0 t)$ to remove the natural decay. The curves represent from above: small micelles without quencher, and with quencher (0-dim), long cylindrical micelles (1-dim), lamellar phase (2-dim), and last, neat surfactant as solvent (3-dim). Reproduced with permission from Almgren and Alsins (1990).

probes are found in micelles without quenchers. Apart from the initial rapid decay, due to a fluorescent impurity in the surfactant preparation, this pair of curves forms another example of the applicability of the simple Infelta model. The third curve was obtained at 33% w/w, which is still in the isotropic micelle region, but indistinguishable results were obtained also for a composition in the hexagonal phase. This must certainly represent the quenching course in long cylindrical micelles, and the similarity of the results for compositions within and just outside the hexagonal phase show that the same type of structures is present in both. The decay fits (2) well.

A decay from the lamellar phase is shown next, representing a two-dimensional case. The main features are similar to the one-dimensional case, and the decay fits

(2) reasonably well, but results then in very high values of the diffusion coefficient. When a one-dimensional model is used in a two-dimensional case, many more quenchers are in reality present within a certain distance from the excited probe than assumed in the model, which is compensated for by very high values of the diffusion coefficients. Before discussing the two-dimensional model, let us note that the three-dimensional case with the neat surfactant as solvent produces a pure exponential decay from which a second-order rate constant, k_2 , can be determined and, using the Debye-Smoluchowski relation

$$k_2 = 4\pi a D_m L, \quad (3)$$

also, the relative diffusion coefficient a is the encounter radius and L Avogadro's constant.

The two-dimensional case is by far the most difficult to handle mathematically. Exact solutions for the fluorescence decays are available for both the radiation and Smoluchowski boundary conditions (see Almgren 1991 and Almgren and Alsins 1990 and references cited therein), but these contain integrals over complicated expressions involving Bessel functions and are not easily handled by fitting programs. Owen (1975) gave a practical approximate solution (unfortunately not quite correct, Almgren and Alsins 1990) for the Smoluchowski boundary condition, i.e. the purely diffusion-controlled case, which we used in the evaluations.

$$\ln(F(t)/F(0)) = -k_0 t - R^3 n_0 Q_2, \quad (4)$$

$$Q_2 = 14.180(t/\tau_q)^{1/2} + 3.17t/\tau_q, \quad (5)$$

where n_0 is the number density of quenchers in the layer, R is the half thickness of the layer, assumed equal to the encounter radius, and $\tau_q = R^2/D_m$. The most problematic feature of this equation is that it requires the process to be purely diffusion-controlled.

Measurements of the fluorescence quenching decays were made at several compositions and temperatures in this system and are fully reported elsewhere (Almgren and Alsins 1990). Values of the diffusion coefficients at various compositions, interpolated or extrapolated to a common temperature, 20°C, are collected in table 2.

The values of the diffusion coefficients are directly comparable – there are no factors due to the different dimensionalities involved. The reported value for the neat phase is uncertain due to severe impurity problems, but the diffusion was certainly not faster

Table 2. The relative diffusion coefficient at 20°C, or extrapolated to 20°C, for pyrene and 1-(4-benzoylphenyl) hexane in several phases of the system $C_{12}E_6$.

Weight% surfactant	Phase	Model	$D_m \times 10^{11}$ ($m^2 s^{-1}$)
33	L_1	1 dim	9.3
50	H	1 dim	10.1
62	$V_1; L_\alpha$	2 dim	5.3
68	$V_1; L_\alpha$	2 dim	5.5
75	L_α	2 dim	6.5
100	Neat	3 dim	2.7

in the neat phase than in the aggregated systems. All values are sensitive to the values chosen for R , and the only valid conclusion is, perhaps, that the mobilities of the reactants are comparable in all the structures; there may be an increase with increasing curvature of the structure (which increases the available headgroup area for the surfactant). The value obtained for D_m in the CTAC/ ClO_3 cylinders was $6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for this pair (Almgren *et al* 1988b).

4. Clusters of reversed micelles

Small droplets of water are formed in hydrocarbon solvents by the action of surfactants like AOT (Day and Robinson 1979; Kotlarchyk and Chên 1982; Robinson *et al* 1985; Eicke *et al* 1986, 1989; Howe *et al* 1987; Lang *et al* 1988). Water soluble probes and quenchers interact very rapidly in the small droplets, and since they are confined in the droplets on a short timescale, the fluorescence decays conform well with the simple Infelta model. An example is shown in figure 4 where the fluorescence from pyrenetetrasulfonate was quenched by potassium iodide. The composition was 0.2 M AOT and 1.64 M water in dodecane. Two quencher concentrations 1.5 and 3.0 mM were used, and resulted in an estimated aggregation number of 92 (for the surfactant) and a quenching constant $k_q = 2.5 \times 10^8 \text{ s}^{-1}$. A slight increase of the decay constant

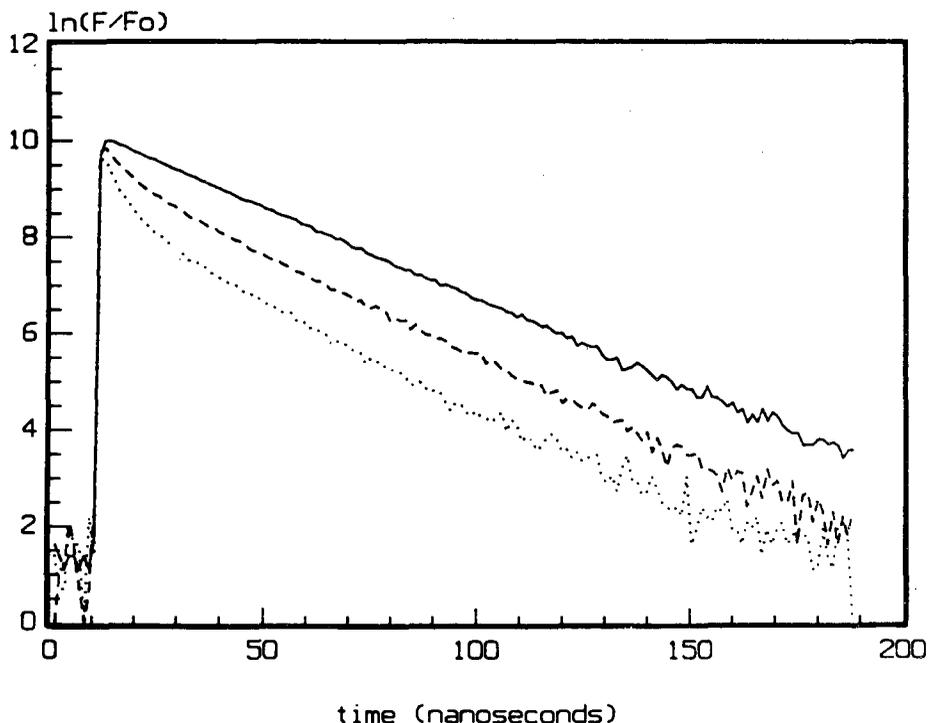


Figure 4. Fluorescence decay of pyrenetetrasulfonate quenched by KI in w/o microemulsion droplets, formed by AOT 0.194 M in dodecane, with a water to surfactant molar ratio of 8.3. Uppermost curve: no quencher, middle curve: 1.5 mM, and lowest curve: 3.0 mM. Reproduced with permission from Jóhannsson *et al* (1991).

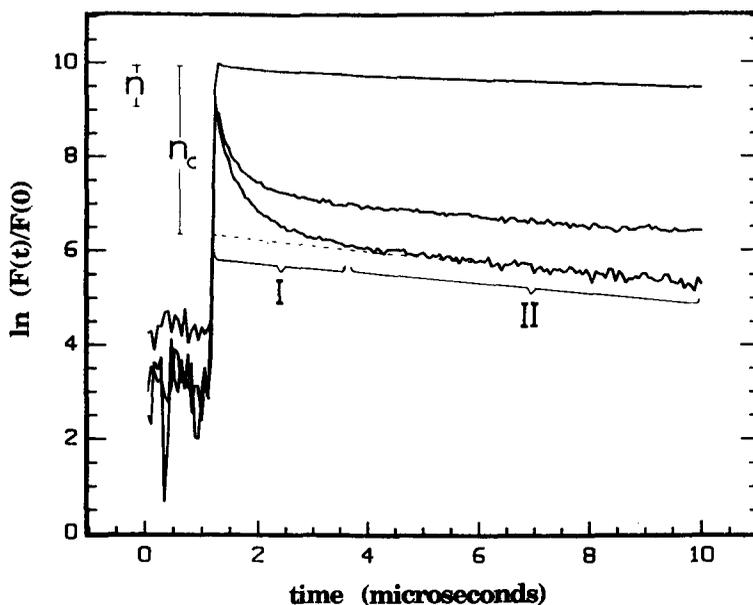


Figure 5. Phosphorescence decay of $\text{Cr}(\text{bpy})_3^{2+}$ with KI (2.0 mM) as quencher. AOT 0.194 M, water/AOT = 8:3. The solvent was *iso*-octane in the middle curve, otherwise dodecane. n marks the extent of prompt deactivation within the micelles, n_c the extent of intermicellar deactivation in the clusters, process I. Reprinted with permission from Jóhannsson *et al* (1991).

of the final exponential tail indicates that some migration of the reactants between the droplets occurred.

In order to study this exchange process in detail it is advantageous to select a long-lived probe (Jóhannsson *et al* 1991). Figure 5 shows the phosphorescence decay of $\text{Cr}(\text{bpy})_3^{3+}$ using the same quencher, KI, as in figure 4 and the same composition of the system. The time scale now extends over 10 microseconds. The first impression is again that an Infelta type of decay is obtained. There are some important differences, however: there is an initial, unresolved deactivation, marked out with n in the figure, and the initial fast deactivation I occurs on the microsecond timescale, two orders of magnitude slower than that in figure 4, indicating a much larger confinement with an average number of quenchers equal to n_c . These observations are all rationalized by the assumption that reversed micelles in this composition range form clusters containing about n_c/n micelles on average. The prompt deactivation is the intramicellar process studied in figure 4; it is of course not resolved on the long timescale, but n could nevertheless be determined and gave an aggregation number of about 80, in reasonable agreement with the value quoted above. The exponential tail, II, in figure 5 stems from excited probes in clusters without quenchers. The generalization of the simple Infelta model to include clusters of micelles results in the following equation (Jóhannsson *et al* 1991):

$$\ln(F(t)/F(0)) = -k_0t + n(\exp(-k_qt) - 1) + (n_c - n)(\exp(-k_{cq}t) - 1), \quad (6)$$

where the first-order rate constant k_{cq} represents quenching within the cluster, resulting from an exchange of excited probes and quenchers between the micelles in the cluster.

The results from the measurements indicate that there are about 8 micelles per cluster in the system discussed. The cluster size decreases on dilution with dodecane, and when *iso*-octane is used as the solvent (middle curve in figure 5). The exchange frequency between micelles in the cluster is about $3 \times 10^6 \text{ s}^{-1}$ (Johannsson *et al* 1991).

5. Conclusions

For reactants confined in small globular micelles the main determinant of the overall deactivation kinetics is the statistical distribution of the reactants over the small volumes. In sufficiently large volumes the statistical effects will disappear. The decay becomes exponential as in a homogeneous solution only if the growth occurs in all three dimensions. Strongly non-exponential decays are observed if the space remains restricted in one or two directions.

In systems with a hierarchy of structures, like clusters of small micelles, a study of deactivation on different timescales can distinguish between processes inside the smallest units, between the units that make up the cluster, and processes that involve an exchange between the clusters.

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