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The Theoretical Background of Photophysical and Photochemical Processes in Micellar Aggregates – An Overview

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Abstract

Photophysical and photochemical processes of substrate molecules in micellar aggregates have been discussed by probability distribution of the molecules and also by thermodynamic equilibrium between the micellar aggregates and the substrates. Therefore at the beginning the distribution of solubilized molecules has been discussed in the micellar aggregation systems. Available cases of probability distributions have been considered for substrates among the micellar and water phases in the systems. Then, general expression including the probability distribution functions P_n has been derived for the luminescence quenching of substrates. This manuscript gives an overview of the theoretical treatment of photophysical and photochemical processes in micellar aggregates

1. Introduction

Chemical reaction mechanisms takes place in micelle solutions are very specific compared with those in fluid solutions. Micellar aggregation systems are mainly composed of two phases that is water phase and oil phase i. e. micellar phase, therefore it is essential to take into consideration the probability distribution of solutes in two phases. The reactions in micellar aggregates are important in understanding biological processes such as the reactions in cells of a living body. Recently micellar aggregation systems are studied and applied for the field of enhanced oil recovery[1)], controlling drug delivery, the digestion of fats and cholesterol[2)], and cleaning of surface.

It is interesting that the researches combined with photochemical processes and micellar aggregate systems give many information about the subject of the following two fields. The first one is to obtain the knowledge of precise structures of micellar aggregates through the observation of photophysical and photochemical processes of solubilized molecules as probes. Second one is that we are able to obtained the information of the chemical reactions taking place between heterogeneous phases or restricted space by spectroscopic observation.

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As luminescent probes in micellar aggregates systems, organic molecules or inorganic metal ions are dissolved directly in the systems or functional micelle with chromophores' groups are used. These luminescent probes have recently become widely used because photoluminescence techniques allow study of dynamic phenomena in the range of 10^{1} to 10^{-12} s, luminescence spectroscopy is a sensitive analytical tool, and luminescence spectra provide a means of identifying transients and inferring the nature of their environments (see **Fig. 1–1**).

In this article it was discussed in the beginning that the probability distribution of substrates among the micelle aggregation systems. These knowledge were required for the quantitative treatment of spectral and dynamic data. It is shown that probable statistics provide a natural extension of the simplest thermodynamic model and that the model is valid the probe is only partially micellized.

Time, sec	Units	Reactions in micellar aggregate systems
10^{-14}		Photoionization
10^{-13}		
10^{-12}	Pico sec.	
10^{-11}		Electron transfer of exciplex system
10^{-10}		
		Luminescence polarization of substrates
10^{-9}	Nano sec.	Fast reactions on the surface of micelle
		Reactions of substrates in micellar aggregates
10^{-8}		Excimer formation in micellar aggregates
10^{-7}		Cage effects of radical recombination
		Electron transfer from micellar phase to
10^{-6}	Micro sec.	aqueous phase
10^{-5}		Exit and entrance rates of substrates
10^{-4}		
		Separation of detergent molecules from
10^{-3}	Milli sec.	micelle
10^{-2}		Decomposition and reformation of micellar
		aggregates into/from detergent molecules
10^{-1}		
1	Second	

Luminescence

Quenching of fluorescence

Quenching of phosphorescence

Figure 1–1. Quenching of luminescence and reactions in micellar aggregate systems.

Combination of those statistic model and photoluminescence methods, we could determine the specific numbers for micellar aggregates, that is, partition coefficients, mean aggregation numbers, entrance and exit rates, and mean occupancy numbers of substrates. To analyze the experimental data, the statistic model has been used throughout this article.

2. The Number Distribution of Solubilized Molecules in Micellar Aggregates

By the distribution function P_n we mean the probability that a given micellar aggregate has n solubilized molecules associated with it. This function is useful in the analysis of photophysical and photochemical experimental results obtained from detergent solutions. To obtain P_n two general approaches to the problem can be made, a purely statistical approach or one that considers the thermodynamics of solubilization by considering the law of mass action. Different results can be obtained depending on the set of assumptions that are made and we shall see that in experiments such as luminescence quenching the possibility exists for verification of the nature of P_n. An apriori consideration of two approaches leads to a preference for the thermodynamic treatment of the problem, yet the several approaches in the literature have been purely statistical and the final test lies in results of different experiments.

2–1. Statistical Solubilization with Lack of Dynamic Equilibrium between Micellar Aggregates

The result of this approach, a Poisson distribution, is most often used in literature. Essentially, we consider that after an initial random solubilization the state of the system does not change with time, implying a lack of dynamic equilibrium between the micellar aggregates.

Let's place the following assumptions :

A) The probability of association with micelles of different size is the same so that it would be equivalent to consider the micelles monodisperse, that is, all of one size or aggregation number.

B) Probability of solubilization in a given aggregate is independent of the number of solubilized molecules already associated. Since the probability of solubilization is inversely proportional to total number of micellar aggregates, this assumption implies that solubilization does not disturb the micellar thermodynamics. It is clear that if the average number of solubilized molecules, $< n >$, becomes much more than unity this assumption cannot hold and experiments must be run such that $< n >$ is less than a few.

C) Once the initial random solubilization takes place the state of the system does not change with time implying lack of thermodynamic equilibrium between the micellar aggregates. This assumption, of course, cannot be true. But it is possible that after solubilization the time taken to reach

thermodynamic equilibrium is much longer than the time during which the experiments are performed. This time might be measurable, for example, in an experiments following the excimer emission of pyrene on sudden dilution the same free detergent solution.

The problem is now reduced to the case of having a set of fixed boxes [micellar aggregates, total number M] into which a number of marbles [solubilized molecules, total number N] are randomly placed. P_n is clearly given by a Binominal distribution

$$P_n = \frac{N!}{n!(N-n)!}\left(\frac{1}{M}\right)^n (1-\frac{1}{M})^{N-n}, \tag{2–1}$$

since $M \gg 1$, $N \gg 1$, $N \gg n$ above eq. (2–1) reduced to a Poisson distribution.

$$P_n = \frac{< n >}{n!} e^{-< n >}, \tag{2–2}$$

where the average number of solubilized molecules, $< n >$, is expressed as follows.

$$< n > = \frac{N}{M} = \frac{[S_m]}{[M]} .$$

Table 2–1. Nomenclature and abbreviations in section 2

Nomenclature	Abbreviations
Substrate and Solute	In biochemistry, the substrate is an intercellular material upon which an enzyme acts. However, it is discussed here the reaction of solutes with micellar aggregates, so that the solute dissolved in the micellar system called as the substrate in this article.
Micelle or micellar aggregate	When detergent or surfactant molecules are dissolved in water, those molecules coagulate together to make micelles. This aggregates is called as micelle or micellar aggregates and is formed by a predetermined number of detergent molecules (mean aggregation number).
P_n	The distribution function for the probability of finding n solubilized molecules in a given micellar aggregate.
n	The number of solubilized molecules in a micellar aggregate.
$< n >$	The mean number of substrates bound per micelle (or mean occupancy number of substrates).
M	The total number of micellar aggregates in the system.
$[M]$	The total micelle concentration.
N	The total number of substrates added in the system.
$[S]$	The total concentration of the substrates in the micellar system (or bulk concentration of the substrate in the system).
$[S_m]$	The concentration of the solute in the micellar aggregates.
$[S_w]$	The concentrations of the solute in water.
$[Det]$	The concentration of detergent.
CMC	Critical micelle concentration.
N_{agg}	Mean micelle aggregation numbers of detergents.
$[M]$, $[Det]$ and CMC	$[M] = ([Det] - CMC)/N_{agg}$.

Notice that, $[S_m]=[S]-[S_w]$, so that if there is extensive solubility in water, $[S_m]$ is unknown. However in such cases probably there is fast equilibration and above assumption C) does not hold. Furthermore, if experiment shows that distribution is of the Poisson type assumption C) is not proven as a Poisson distribution can be obtained by certain restriction on the thermodynamics of the system and this will be discussed next section.

2–2. Solubilization Constrained by Thermodynamic Equilibrium

In this approach it is assumed that following solubilization the system has reached its thermodynamic equilibrium state. Law of mass action is applied to the individual association steps replacing activities with concentrations so that the validity of this approach to charged solubilized particles becomes questionable. However, if the solubilized molecules are neutral then the law of mass action will apply even if the individual micellar aggregates are ionic.

Let M_n be the concentration of micellar aggregates with n associated substrate molecules. Let $[S]$ and $[S_w]$ be the concentrations of added substrate (bulk concentration) and that remaining in water, respectively. A stepwise association model can be written as following scheme.

$$\begin{array}{lll} & M_0 + S_w \underset{K_1}{\rightleftharpoons} M_1 & \\ & \vdots & \\ \text{aqueous phase} & M_1 + S_w \underset{K_2}{\rightleftharpoons} M_2 & \text{micellar phase} \\ & \vdots & \\ & M_{n-1} + S_w \underset{K_n}{\rightleftharpoons} M_n & \end{array} \qquad (2\text{–}3)$$

The above relations show that a micellar aggregates are of one size or aggregation number, but as discussed in previous section 2–1, this need not be if M_n for each of the above reactions is independent of the micelle size and again this becomes valid if $< n >$ is not too large so that the process of micelle formation and dissociation is not heavily disturbed.

Applying the low of mass action, we have,

$$M_n = [M_n]/[M_{n-1}][S_w], \qquad (2\text{–}4)$$

and next relations are obtained.

$$[M_n]=[M_0][S_w]^n K_1 \cdot K_2 \cdot K_3 \cdots K_n, \qquad (2\text{–}5)$$

$$\sum_{n=0}^{\infty}[M_n]=[M], \qquad (2\text{–}6)$$

$$\sum_{n=0}^{\infty} n\,[M_n]=[S_m]=[S]-[S_w], \tag{2–7}$$

$$< n >\equiv [S_m]/[M]=\sum_{n=0}^{\infty} n\,[M_n]/\sum_{n=0}^{\infty}[M], \tag{2–8}$$

where the distribution function is given by

$$P_n=[M_n]/[M]. \tag{2–9}$$

The solution of the above set of equations (eq. (2–4)–(2–9)) would yield P_n but it is clear that the distribution function obtained depends on the thermodynamics of the individual steps of association, that is, K_1, K_2, $K_3 \cdots K_n$. We shall only consider here the most probable cases of the association steps.

Case1 : Simple equilibrium statistics

The thermodynamics of the association step is independent of the number of molecules already associated. That is, $K_1 = K_2 = \cdots = K_n = K$. This is a reasonable assumption if n is not large but we have already discussed that experiments must be such that $< n >$ is not large so that this will apply. The probability function based on this assumption was adopted for the first time to the analysis of excimer formations in micellar systems by Dorrance and Hunter[3]. This assumption, however, was not accepted by Selinger and Watkins, and other groups[4], for such conditions that a set of substrates and micellar aggregates may leads to the probability function of *case 1*.

Under the equilibrium condition of eq. (2–3), with the aid of eqs. (2–4) – (2–7), we have

$$[M_n]=[M_0]K^n[S_w]^n, \tag{2–10}$$

$$[M]=[M_0]/(1-K[S_w]), \tag{2–11}$$

$$[S_m]=[M_0]K[S_w]/(1-K[S_w])^2. \tag{2–12}$$

The summation in eqs. (2–6) and (2–7) must converge so that

$$K[S_w]<1, \text{ or } [S_w]<1/K \tag{2–13}$$

Equation (2–13) is interesting because it states that the quantity of the solute in the water phase increases as the added solute increases but it reaches a maximum limit of $1/K$ if crystallization does not occur.

In order to eliminate $K[S_w]$ from the above equations we divide eq. (2–12) by eq. (2–11) to ob-

tain $< n >$

$$< n > \equiv [S_m]/[M] = K[S_w]/(1-K[S_w]), \tag{2–14}$$

$$K[S_w] = \frac{< n >}{1+< n >}. \tag{2–15}$$

Dividing eq. (2–10) by (2–11) and using eq. (2–15) we have the following distribution function

$$P_n = K^n [S_w]^n / (1-K[S_w]), \tag{2–16}$$

or using the only parameter n

$$P_n = \frac{< n >^n}{(1+< n >)^{n+1}}. \tag{2–17}$$

This statistics function is very similar to the geometric distribution function but slightly different from it. Thus, we call this function as *simple equilibrium statistics*.

Another important parameter in the solubilization problem is the ratio of the fractionation of the solute between the water phase and micellar phase, or using the partition coefficient X, that is,

$$\mathrm{X} \equiv [S_m]/[S_w].$$

Again using eqs. (2–11) and (2–12) we have the following equation,

$$\mathrm{X} = \frac{K[M]}{1-K[S_w]}. \tag{2–18}$$

As the amount of solute decreases, $[S_w] \rightarrow 0$, and we have

$$X_{min} = K[M] \tag{2–19}$$

that is, when the substrate is very small, the fractionation toward the water phase is at its maximum. As the amount of solute increases, fractionation toward the micellar phase is favored. All of this could have been predicted from Lechatelier's Principle.

Experimental evidence has been proposed that cationic solutes exchanges quickly between anionic micelles. Because the substrates are counter ions and are interacted strongly on the surface of micellar aggregates, the following process must be also important in addition to scheme (2–3).

$$M_{n-1}^x + M_n^y \rightleftharpoons M_n^x + M_{n-1}^y.$$

Where x and y is used to distinguish each micellar aggregate. These experimental results can be categorized *case1* (*simple equilibrium statistics*).

Case2 : Poisson statistics

The thermodynamics of the association step is dependent upon the number of molecule already associated such that $K_n = K_1/n = K/n$. Here K is the binding constant of the first association step. This assumption cannot be justified other than the fact it results in a Poisson distribution which is also obtained in section 2−1 in the absence of thermodynamic equilibrium.

Application of eqs. (2−5) to (2−9) yields

$$[M_n]=[M_0][S_w]^n \frac{K^n}{n!}, \tag{2−20}$$

$$[\mathrm{M}]=[M_0]e^{K[S_w]}, \tag{2−21}$$

$$[S_w]=[M_0]K[S_w]e^{K[S_w]}, \tag{2−22}$$

$$<n>\equiv\frac{[S_m]}{[M]}=K[S_w], \tag{2−23}$$

$$P_n=\frac{[M_n]}{[M]}=\frac{<n>^n}{n!}e^{-<n>}. \tag{2−24}$$

Concerning the behavior of solubility we combine eqs. (2−21) and (2−22) to have the following equation.

$$\mathrm{X}=\frac{[S_m]}{[S_w]}=K[M]. \tag{2−25}$$

This shows that fractionation between the two phases is independent of the total added solute. Furthermore, eq. (2−25) leads to

$$\frac{[S]-[S_w]}{[S_w]}=K[M]. \tag{2−26}$$

Eq. (26) shows that there is no limit to the amount of solute in the water phase until crystallization occurs.

Case3 : Binomial distribution : Limited Poisson statistics

Let consider the case which is the *limited Poisson statistics*, that is, the solubilization of substrates in a micellar aggregate are restricted in number. Only j molecules are upper limit of soluble molecules. In this case, for the *nth* association step of substrates, k_e, the forward (or entrance) rate constant of micellization in eq. (2−3) is restricted as follows.

$$k_e = \left[1 - \frac{(n-1)}{j}\right] k_f \quad . \tag{2–27}$$

Here, k_f is the forward rate constant of the first association step and the exit (dissociation) rate constant of one substrate from M_n is nk_b that is same as *Poisson statistics of case2*. In this situation we have the following relations.

$$\frac{[M_1]}{[M_0]} = \frac{k_f [S_w]}{k_b} \quad , \tag{2–28}$$

$$[M_n]/[M_{n-1}] = [1-(n-1)/j]\, k_f [S_w]/jk_b \, . \tag{2–29}$$

Combination of eq. (2–4) and eqs. (2–28), (2–29) leads to

$$[M_n] = \frac{j!}{j^n n!(j-n)!} \cdot K^n [S_w]^n [M_0], \tag{2–30}$$

where K is the binding constant of the first association step, $K = k_f/k_b$.

From eqs. (2–26), (2–27) and (2–28), we have

$$K[S_w] = \frac{< n >}{\left(1 - \frac{< n >}{j}\right)} \quad . \tag{2–31}$$

The equilibrium constant shown by eq. (2–31) is entirely new and had not discussed yet. Equation item of summation (see eqs. (2–6) and (2–7)) shows binomial distribution, therefor the limited Poisson statistics of this case gives the binomial distribution function. Then we have the following equation for the probability distribution P_n that a given micelle is associated with n substrate molecules.

$$P_n = \frac{[< n > /(1 - < n > /j)]^n j!}{j^n n!(j-n)![j/(j - < n >)]^j} \quad . \tag{2–32}$$

Case 4 : Not be Simplified Distribution

We consider the case that association rate constant is controlled by eq. (2–27) but dissociation rate constant is independent of the number of molecules already associated as is the *case1*. This situation may be applicable when the size of the solute molecules is relatively large compared with the micelle aggregates, then the substrates exit from the micelle together with one or some fractions of the detergent molecules.

The following equations are obtained for this case.

$$[M_1]/[M_0] = k_f [S_w]/k_b \, , \tag{2–33}$$

$$\frac{[M_n]}{[M_{n-1}]} = [1-(n-1)/j]k_f[S_w]/k_b. \tag{2–34}$$

Using eqs. (2–33), (2–34) and (2–5), we have

$$[M_n] = \frac{j!}{j^n(j-n)!}K^n[S_w]^n[M_0]. \tag{2–35}$$

When we try to get the value of $< n >$ and P_n from eq. (2–34), equation items of summations come into the total equations and is not simplified. The most concise expression of the relation between $< n >$ and $K[S_w]$ we have the following simplest equation at the most for the parameters

$$< n > = \frac{n+\left[n^2(K[S_w])^n - n(K[S_w])^{n-1}\right]\{\exp(1/K[S_w])\}\,\Gamma(j,\ 1/K[S_w])}{1+n(K[S_w])^n(expK[S_w])\,\Gamma(j,\ 1/K[S_w])}\ . \tag{2–36}$$

Where, $\Gamma(\mathrm{j},\ 1/K[S_w])$ is incomplete gamma function and expressed as

$$\Gamma(\mathrm{j},\ 1/K[S_w]) = \int_{1/K[S_w]}^{\infty} e^t t^{(j-1)}dt. \tag{2–37}$$

We considered four representative cases of probability distributions of substrates among the micellar and water phases in the micelle solution systems. There may be many cases showing the corresponding probability distribution functions in the micellar aggregate systems and only consideration of these four cases are not sufficient to describe the phenomena of probability distribution in micelle systems. However, these four cases, especially the former two cases have sufficient bases to predict actual phenomena. Notice here that an extreme situation of $\mathrm{j} \to \infty$, *case 4* and *case 3* change into *case 1* and *case 2*, respectively.

Now, adding detergent molecules slowly into the water and at a definite concentration of detergent it begins to form micellar aggregates. This definite concentration is called by "critical micelle concentration" (*CMC*). Substrates were solubilized in the micelle solution, then stepwise association takes place according to eq. (2–3). If the micellization cause to change the photochemical and spectroscopic properties of probes (such as luminescence quantum yield, emission lifetime, spectral maxima of absorption and emission, and quenching rate constant etc.), the critical micelle concentration are given by the observation of these properties as a function of the detergent concentration.[5] The change of these spectroscopic properties are well known and are given the value for *CMC* of various detergent molecules.

Combination of eqs. (2–7) and (2–26) leads to

$$[S_w] = [S]/(1+K[M]), \tag{2–38}$$

$$[S_m] = K[M][S]/(1+K[M]). \tag{2-39}$$

The quantitative treatment of the photochemical properties are analyzed according to eqs. (2–38) and (2–39), and it may propose the equilibrium quantities between substrates and micellar aggregates.

Combination of partition coefficient or equilibrium constant with the information of rate constants may give the knowledge of the residence time and entrance rete of substrates in the micellar aggregates. These analyses are useful expect the case that the change of spectroscopic properties takes place the low detergent concentration under *CMC* . The properties are discussed precisely in section 3 –5 in order to explain the experimental data. In the next section, the dynamics is discussed including probability distribution of substrates in micellar aggregates.

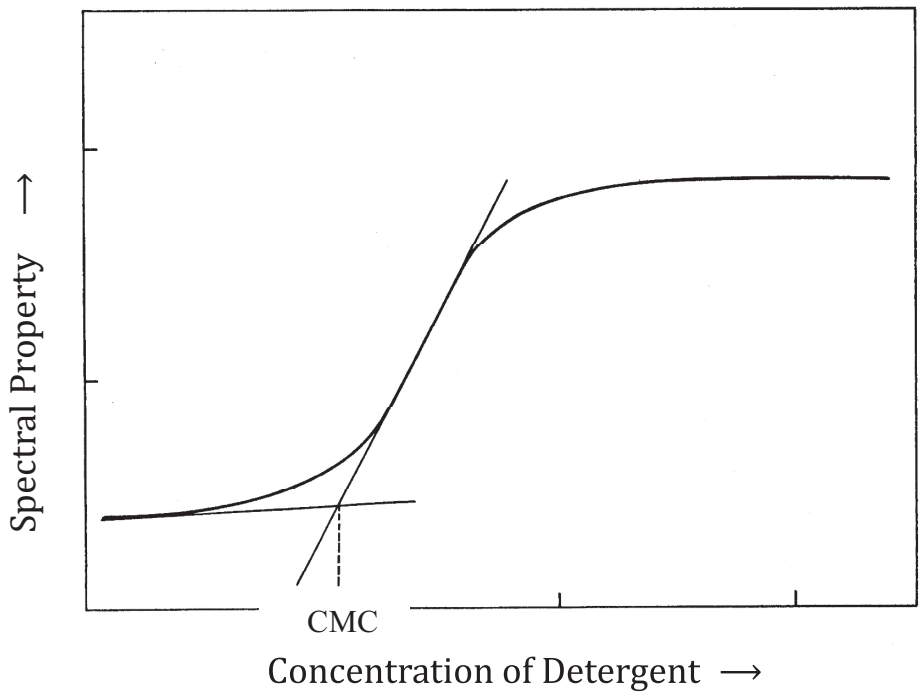


Figure 2–1. Schematic representation of the commonly observed dependence of an observed spectroscopic property (photoluminescence quantum yield, luminescence lifetime, luminescence maximum, luminescence quenching constant, degree of luminescence polarization, etc.) on concentration of detergent. The "break" in the spectral property usually is related to the onset of formation of micellar aggregates at the "critical micelle concentration" or *CMC* .

3. Dynamics of Luminescence Quenching in Micellar Aggregates

3–1. General Expression of Luminescence Quenching Including the Probability Distribution Functions

In this section we consider the quantum yield and the time dependence of luminescence intensity

after pulse excitation of energy donor (D) as a function of quenchers (Q) in the system of micellar aggregates including the association of donor and acceptor.

Consider the association of light absorbing molecules D and quencher molecules Q with micellar aggregates. It can be seen that those sites where D is excited in the absence of Q emit light as if there were no quencher added micelle solution, while sites have one or more Q associated with them will be partially or totally quenched. Therefore, the luminescence intensity and decay shape depend on the joint distribution of donor–quencher molecules.

To make the analysis simple we make the assumption on the probability of association of Q with the micelle is not related to the number of D molecules already associated so that the joint probability, $P(n_D, n_Q)$, that a given micellar aggregate has n_Q of Q molecules and n_D of D molecules associated with it is given by

$$P(n_D, n_Q) = P(n_D)P(n_Q). \tag{3–1}$$

We can describe the kinetics of the system by **scheme I**. And here notation, definition and description in this section 3 are summarized in **table 3–1**. Notice that since we focus on the quenching of substrates (D) we do not consider any self–quenching by D or excimer formation, and these experiments are best run at $< n >= [D]/[M] \ll 1$. Furthermore and as usual, excitation wavelength must be selected such that Q does not absorb any light.

The objective is then to find ϕ_D^0/ϕ_D through I_D (emission intensity of D^*). From the **scheme I**, we have the following relations.

$$d[M^*(n_D, n_Q)]/dt = I^a(n_D, n_Q) - \left(\tau_D^{-1} + n_Q k_q\right)[M^*(n_D, n_Q)]. \tag{3–2}$$

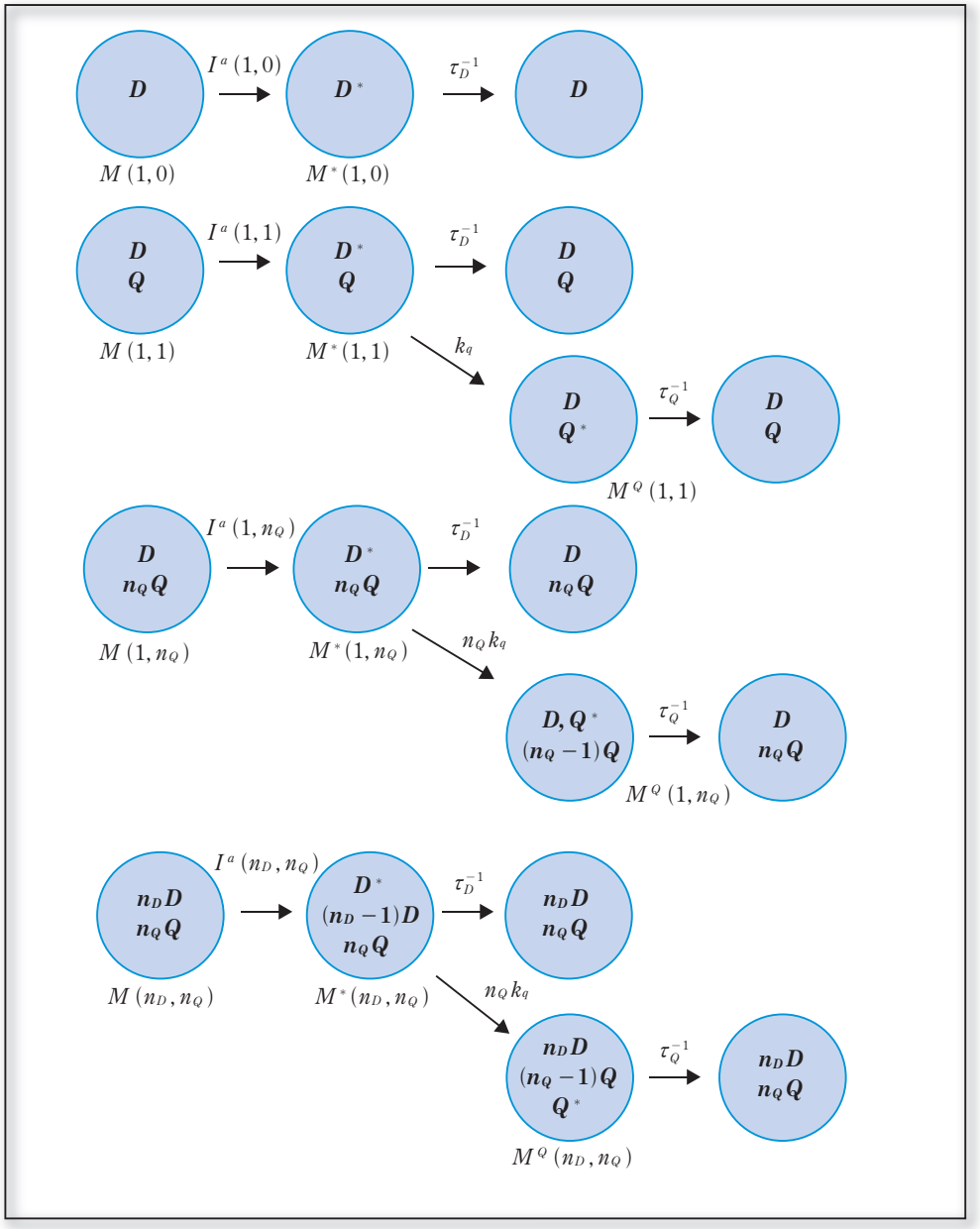
From definition we have

$$I_D = k_r \sum_{n_D=1}^{\infty} \sum_{n_Q=0}^{\infty} [M^*(n_D, n_Q)]. \tag{3–3}$$

We shall consider the both cases of steady state illumination and pulsed excitation. For photostationary conditions we set eq. (3–2) equal to zero and obtain the following equation.

$$I_D = \phi_D^0 \sum_{n_D=1}^{\infty} \sum_{n_Q=0}^{\infty} \frac{I^a(n_D, n_Q)}{1 + (k_q \tau_D) n_Q} \ . \tag{3–4}$$

$I^a(n_D, n_Q)$ is defined as the quantity of light absorbed by micelles of $M(n_D, n_Q)$ and is proportional to the number of D molecules, n_D, the extinction coefficient of one D molecule, ε, and the concentration of $M(n_D, n_Q)$ so that the following relation is obtained.



Scheme I. Kinetic scheme for the analysis of photoluminescence quenching of substrates in micelle aggregation systems. Circles, D and Q indicate micelles, energy donor and quencher molecules, respectively.

$$\frac{I^a(n_D,\,n_Q)}{I^a_{total}(n_D,\,n_Q)} = \frac{\varepsilon \cdot n_D \cdot [M(n_D,\,n_Q)]}{\sum_{n_D=1}^{\infty}\sum_{n_Q=0}^{\infty}\varepsilon \cdot n_D \cdot [M(n_D,\,n_Q)]}\,. \tag{3–5}$$

Dividing the numerator and denominator of eq. (3–5) by the total micelle concentration we get

Table 3–1. Nomenclature and abbreviations in section 3

Nomenclature	Abbreviations
$M^*(n_D, n_Q)$	Micelles with one D^*, (n_D-1) of D and n_Q of Q in them.
$M(n_D, n_Q)$	Micelles with n_D of D and n_Q of Q in them.
$I^a(n_D, n_Q)$	Quantity of light absorbed by above micelle, i.e., $M(n_D, n_Q)$.
$I^a_{total}(n_D, n_Q)$	Total quantity of light absorbed by all micelles including n_D.
I_D	Emission intensity from D^*.
τ_D^{-1}	Total decay rate constant in the absence of Q.
k_q	Unimolecular rate constant of quenching by one Q. Unit, (s^{-1}). Notice that we assume that the total rate constant of quenching in $M(n_D, n_Q)$ is $n_Q \cdot k_q$.
k_r	Radiative rate constant of D^*.
$\phi_D^0 = k_r\tau_D$	Luminescence yield of D in the absence of Q.
$\phi_D = I_D/I^a_{total}$	Total light intensity absorbed by micellar solutions.
$P_n(n_Q, n_D)$	The joint probability, $P_n(n_Q, n_D)$, that a given micellar aggregate has n_Q of Q molecules and n_D of D molecules associated with it. $M^*(n_D, n_Q)/[M]$.

$$\frac{I^a(n_D, n_Q)}{I^a_{total}(n_D, n_Q)} = \frac{n_D \cdot P(n_D, n_Q)}{\sum_{n_D=1}^{\infty}\sum_{n_Q=0}^{\infty} n_D \cdot P(n_D, n_Q)} \ . \tag{3–6}$$

Using eq. (3–1), eq. (3–6) becomes

$$\frac{I^a(n_D, n_Q)}{I^a_{total}(n_D, n_Q)} = \frac{n_D \cdot P(n_D)\cdot P(n_Q)}{\sum_{n_D=1}^{\infty} n_D P(n_D) \sum_{n_Q=0}^{\infty} P(n_Q)} \ . \tag{3–7}$$

Considering the relations

$$\sum_{n_D=0}^{\infty} n_D P(n_D) = < n_D > = \frac{[D]}{[M]}, \quad \text{and} \quad \sum_{n_Q=0}^{\infty} P(n_Q) = 1,$$

the following relation is obtained.

$$\frac{I^a(n_D, n_Q)}{I^a_{total}(n_D, n_Q)} = \frac{n_D}{< n_D >} P(n_D)\cdot P(n_Q). \tag{3–8}$$

Substitution eq. (3–8) into eq. (3–4) gives for the quantum yield of donor luminescence.

$$\phi_D = \frac{I_D}{I^a_{total}} = \phi_D^0 \frac{1}{< n >} \sum_{n_D=1}^{\infty} n_D P(n_D) \sum_{n_Q=0}^{\infty} \frac{P(n_Q)}{1+(k_q\tau_D)n_Q} \ . \tag{3–9}$$

And the final form of intensity quenching is obtained

$$\frac{\phi_D}{\phi_D^0} = \sum_{n_Q=0}^{\infty} \frac{P(n_Q)}{1+(k_q\tau_D)n_Q} \ . \tag{3–10}$$

Notice that eq. (3–10) shows that quenching is independent of the concentration of D as expected. Also when quenching becomes very fast, i.e., $k_q\tau_D \to \infty$, then only the first term in the above sum is important and we have

$$\frac{\phi_D}{\phi_D^0} = P(n_Q = 0) = P_0 . \tag{3–11}$$

Equation (3–11) has a very simple physical picture. It states that light emission is only from micelles including no quenchers, i.e., P_0. Such measurements then yield the fraction of empty micelles. We shall apply eq. (3–10) to several statistical cases in later section.

Now we consider the time dependent behavior of luminescence decay after short pulse excitation. Solving eq. (3–2) we have

$$[M^*(n_D, n_Q, t)] = [M^*(n_D, n_Q, t=0)] exp(-t/\tau_D) \cdot exp(-k_q n_Q t). \tag{3–12}$$

Using eq. (3–12) and eq. (3–3), it can be shown that the luminescence decay function is given by

$$I_D(t) = k_{rad} \exp(-t/\tau_D) \sum_{n_D=1}^{\infty} \sum_{n_Q=0}^{\infty} [M^*(n_D, n_Q, t=0)] exp\{-(k_q t) n_Q\}. \tag{3–13}$$

Right after excitation we have, using eq. (3–8)

$$\frac{[M^*(n_D, n_Q, t=0)]}{\sum_{n_D=1}^{\infty} \sum_{n_Q=0}^{\infty} [M^*(n_D, n_Q, t=0)]} = \frac{I^a(n_D, n_Q)}{I^a_{total}(n_D, n_Q)} = \frac{n_D}{< n_D >} P(n_D) \cdot P(n_Q). \tag{3–14}$$

Substitution eq. (3–14) for eq. (3–13) gives

$$I_D(t) = k_{rad} \left\{ \sum_{n_D=1}^{\infty} \sum_{n_Q=0}^{\infty} [M^*(n_D, n_Q, t=0)] \right\} \sum_{n_D=1}^{\infty} n_D P(n_D) \sum_{n_Q=0}^{\infty} exp(-k_q n_Q t) P(n_Q).$$

So that the final equation is obtained as

$$I_D(t) = I_D(0) exp\left(-\frac{t}{\tau_D}\right) \sum_{n_Q=0}^{\infty} exp(-k_q n_Q t) \cdot P(n_Q). \tag{3–15}$$

Notice that the steady state quenching eq. (3–10) could also be derived by integration of eq. (3–15) over all time. Again if $k_q \to \infty$, that is quenching being very fast in the time scale of decay, then only the first term in the summation is important and we have

$$I_D(t) = I_D(0) exp\left(-\frac{t}{\tau_D}\right) \cdot P(n_Q = 0). \tag{3–16}$$

That is by adding quencher the shape of decay does not change and only the initial intensity drops by the factor $P(n_Q = 0)$ that is the fraction of micelles including no quenchers.

3–2. Statistics of substrates and quenching phenomena

We consider the two most prevalent form of statistics to the steady state illumination case of eq. (3–10) and pulsed excitation case of eq. (3–15).

(1) *Poisson Statistics* ; $P_n = \frac{[M_n]}{[M]} = \frac{< n >^n}{n!} e^{-< n >}$

The general expression is obtained as

$$\frac{\phi_D}{\phi_D^0} = e^{-<n_Q>} \sum_{n_Q=0}^{\infty} \frac{<n_Q>^{n_Q}}{\{1+(k_q\tau_D)n_Q\}n_Q!} . \tag{3–17}$$

The above sum cannot be solved easily unless we consider integer values of $k_q\tau_D$. For the interesting case of fast quenching

$$\left(\phi_D/\phi_D^0\right)_{fast\ quenching} = e^{-<n_Q>} = \exp(-[Q]/[Micelle]),$$

or we obtain a relationship similar to Perrin's model for static quenching[6],

$$ln\left(\phi_D/\phi_D^0\right) = \frac{[Q]}{[Micelle]} \qquad for\ fast\ quenching, \tag{3–19}$$

which can be used to obtain the total micelle concentration and, hence , the aggregation number.

For time dependent decay we obtain,

$$I_D(t) = I_D(0)\,exp\left(-\frac{t}{\tau_D}\right)exp<n_Q> \sum_{n=0}^{\infty} \frac{\{<n_Q> exp\,(-k_q t)\}^{n_Q}}{n_Q!} ,$$

reducing to

$$I_D(t) = I_D(0)\,exp\left(-\frac{t}{\tau_D}\right)exp\,[-<n_Q>\{1-exp\,(-k_q t)\}]. \tag{3–20}$$

Equation (3–20) was derived on similar arguments by M. A. J. Rodgers and M. F. DaSilva Wheeler[7].

Notice that for finite values of $k_q t$ the analysis of steady state quenching is not simple (see eq. (3–17)). However, time dependent decay can be extrapolated to time zero yield $\{I_D(0)\,exp\,(-<n_Q>)\}$ which can be analyzed. Care must be taken to ensure that Q does not absorb the exciting light.

(2) Simple Equilibrium Statistics ; $P_n = \frac{<n>^n}{(1+<n>)^{n+1}}$

Application of eq. (3–10) gives

$$\frac{\phi_D}{\phi_D^0} = \frac{1}{1+<n_Q>} \sum_{n_Q=0}^{\infty} \frac{1}{1+(k_q\tau_D)n_Q} \left(\frac{<n_Q>}{1+<n_Q>}\right)^{n_Q} . \tag{3–21}$$

Again the above sum is only easily solved for integer values of $k_q\tau_D$. For the interesting case of fast quenching $(k_q\tau_D \to \infty)$ where only the first term in the summation of eq. (3–21) is important and we have

$$\frac{\phi_D^0}{\phi_D} = 1+<n_Q> = 1+\frac{[Q]}{[M]} . \tag{3–22}$$

This is just like the Stern–Volmer equation except for the fact that the interpretation of slope is different.

For time dependent decay we used eq. (3–15) to obtain

$$I_D(t) = I_D(0)\,exp\left(-\frac{t}{\tau_D}\right)\frac{1}{1+n_Q}\sum_{n_Q=0}^{\infty}\frac{<n_Q>}{1+<n_Q>}exp\,(-k_q n_Q t).$$

Reducing to

$$I_D(t) = I_D(0)\,exp\left(-\frac{t}{\tau_D}\right)\cdot\frac{1}{1+<n_Q>\{1-exp\,(-k_q t)\}}\ . \tag{3–23}$$

Again, as in the case of the Poisson distribution, the analysis of steady state quenching for finite values of $k_q\tau_D$ is difficult (eq. (3 – 21)) but the extrapolation of the decay tail would yield $I_D(0)\cdot\frac{1}{1+<n_Q>}$ and, hence, the total micelle concentration. Again, care must be taken so that the quencher does not absorb part of the exciting light.

3–3. Application to Quenching of Luminescent Probes. Categorized Cases of Static and Dynamic Quenching

We wish to find, in terms of the known or measurable quantities of the total substrate concentration $[S]$ and the total micelle concentration $[M]$, the concentrations of the substrate in water $[S_w]$, micelle bound $[S_m]$ and the probability distribution P_s that a given micelle is associated with s substrate molecules. A stepwise association model was able to written as eq. (2–3). Thermodynamics of the simplest solubilization model led to eqs. (2–20) – (2–26) and the following results.

$$[S_w] = [S]/(1+K[M]), \tag{3–24}$$

$$[S_m] = K[M][Q]/(1+K[M]), \tag{3–25}$$

$$P_s = \frac{<s>^s}{s!}e^{-<s>}\ , \tag{3–26}$$

$$<s> = K[S]/(1+K[M]). \tag{3–27}$$

Combination of eq. (3–24) and (3–25) lead to

$$K = [S_m]/[S_w][M]\ , \tag{3–28}$$

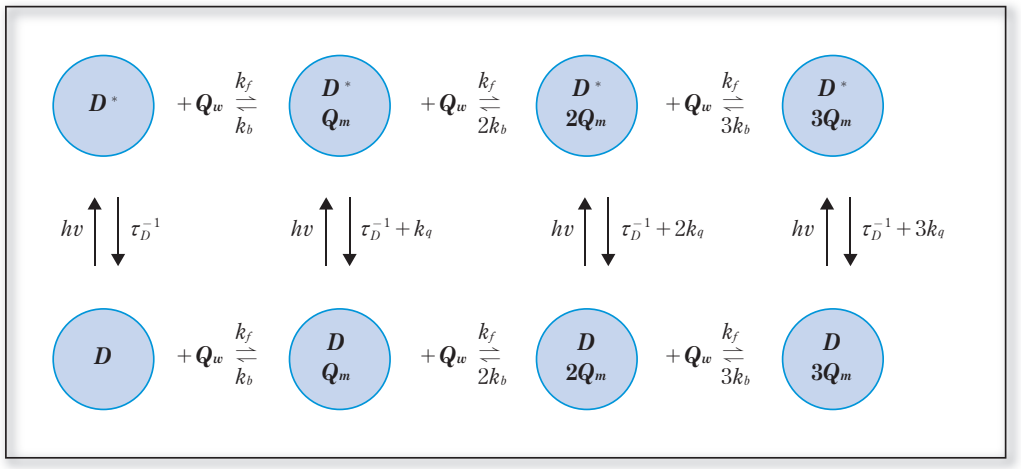
so that the stepwise solubilization model that leads to Poisson statistics of eq. (3–26) can, "symbolically", be represented by the following equilibrium.

$$\text{aqueous phase}\quad S_w + M \overset{K}{\rightleftarrows} S_m \quad \text{micellar phase} \tag{3–29}$$

With the aid of eqs. (3−24) − (3−27) one can predict the behavior of the general system where both donor and quencher species are partitioned between the water and micelle phases. However, as in practice, it will be more revealing to consider the simplified case where donor species, D, are almost exclusively micellized and at sufficiently low concentration such that $[D]/[M] \ll 1$ to ensure no self−interaction as already mentioned.

There exist a large number of general situations which will be a function of probe residence time (exit rate), probe entrance rate, quenching rate within the micellar aggregate, decay rate of the donor, etc. We consider here only situations for which the decay of the micellized donor is fast relative to its exit rate from the micelle. This restriction ensures that the excited donor will remain within the micelle during its lifetime. In practice aromatic compounds appear to possess exit rates of the order of $10^6\ s^{-1}$ or less[8]; thus, our discussion will refer most usefully to *fluorescent probes*. The recent discovery of a wide range of *phosphorescent probes*[9] or micellar aggregates requires consideration of an extended kinetic scheme which allows for escape of the excited donor into aqueous phase.

The kinetic scheme for which D and D^* are completely micellized is given in **Scheme II** where the circles symbolize micelles, τ_D is the luminescence lifetime of a luminescent probe molecule D in the absence of quenchers, Q_w is the water solubilized quencher, k_f and k_b are respective forward and backward rate constant of quenching in the micelle. The above scheme assumes that for a given micelle the quencher escape or reaction probability is proportional to the number of quenchers present, the former assumption being one that leads to Poisson statistics as discussed in former section. It is expected, and it will be shown, that the above scheme leads to a complicated function for the description of donor luminescence intensity reducing the reliability in the fit of data to theory. We can, however, break the above kinetic scheme into theoretically distinct and experimentally realizable cases by introducing the concept of *static quenching*. By "static" or "active" quenching we mean the condition where the micelles containing D^* and Q are completely quenched. In terms of the above kinetic scheme this means $k_r \ll \left(\tau_D^{-1} + k_b\right)$. Static quenching is expected when the mode of quenching is very fast such as in energy transfer processes. It will be shown that static quenching implies observation of single exponential decay of luminescence and that such measurements are crucial to an understanding of the system under study. $I_D(t)$ is measured following pulse excitation and when in steady state irradiation the ratio of luminescence intensity in the presence and absence of quencher, I_D/I_D^0 is measured.



Scheme II. A generalized scheme for analysis of photoluminescence quenching data obtained from micelle solutions. D, Q_w and Q_m represent donor molecule, water and micelle solubilized quenchers, respectively.

Category 1 : Static quenching, quencher is totally micellized

This is the simplest case and one that leads only to information about the mean micelle aggregation number. Here emission occurs *only from that fraction of* D^* *containing micelles that are free of quencher molecules,* that is, $P_0 = \exp - < n_Q >$ where $< n_Q >= [Q]/[M]$. Though the overall luminescence intensity is reduced, *the measured lifetime of* D^* *remains constant upon addition of* Q (see fig. 3–1(a)).

For continuous irradiation we have

$$\ln\left(I_D^0/I_D\right) = [Q]/[M]. \tag{3–30}$$

This equation has the same functional form as the Perrin's model but the *constant* of "active sphere volume" has been replaced by the total micelle concentration, an experimental *variable*.[6)] A knowledge of the total micelle concentration would, of course, lead to the mean micelle aggregation number. In contrast to other methods of aggregation number measurement, the above method offers the possibility of simple experimentation and is not limited to detergent concentrations near the critical micelle concentration, *CMC*. Analysis of the above type has been used to evaluate the mean aggregation number of sodium dodecyl sulfate successfully.[5a)] The reported quenching of pyrene fluorescence by amines probably can also be categorized as this case. [10)]

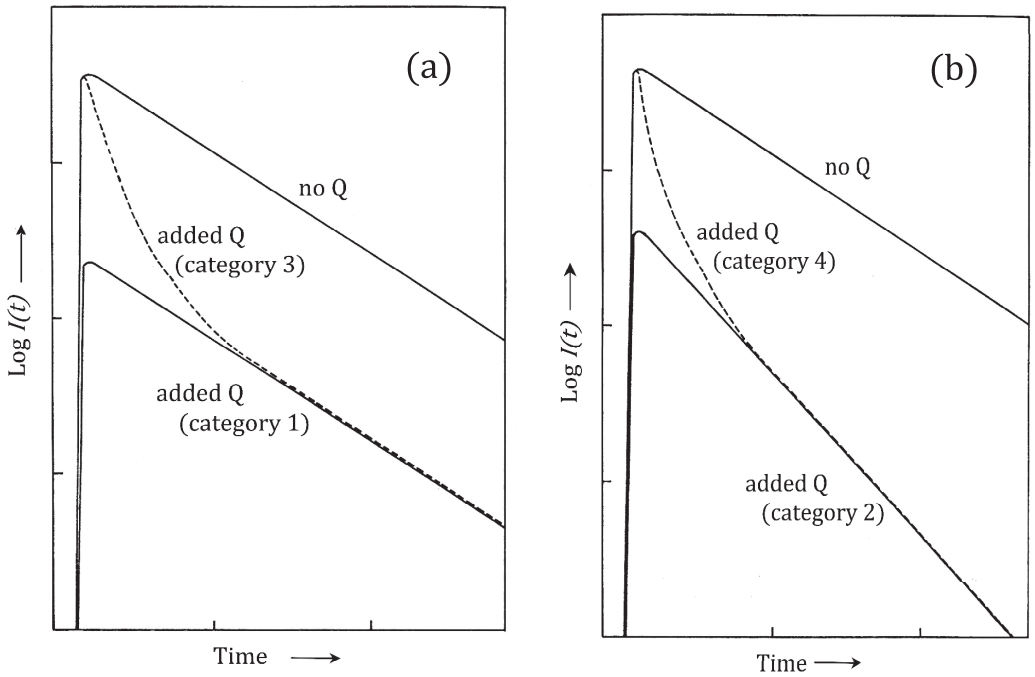


Figure 3–1. Schematic representation of (a) category 1 (limit of complete static quenching of D^* when a micelle contains at least one Q and no quenching of D^* when a micelle contains no Q), and category 3 (limit of nonstatic quenching). Decay of D* is strictly exponential for category 1 and nonexponential for category 3. In both categorized cases Q is completely micellized. (b) Category 2 (limit of static quenching with partially micellized quencher) and category 4 (limit of nonstatic quenching with quencher partially micellized).

Category 2 : Static quenching, quencher is partially micellized

Experimental results that fall in this category can lead to information about the mean micelle aggregation number, the quencher binding constant and mean residence time in the micelle aggregate. Because quenching is static, as in *category 1*, emission still occurs only from that fraction of D^* containing micelles that are free of quencher molecules, that is, $P_0 = \exp - < n_Q >$, where now according to eq. (3–27) the average number of quencher per micelle is $< n_Q >= K[Q]/(1+K[M])$. The lifetime τ of the emitting states is, however, reduced by dynamic diffusional quenching by water solubilized quencher molecules Q_w. This is shown in the equation

$$\tau^{-1} = \tau_D^{-1} + k_f[Q_w], \tag{3–31}$$

where the rate constant of quenching equals the forward rate constant of binding k_f since every association results in complete quenching. It should be noticed that the observed rate constant of quenching need not be diffusion controlled since it is limited to the value of forward binding constant k_f.

Figure 3–1(b) shows the expected luminescence decay shape corresponding to *category 2*.

Substituting eq. (3–24) in (3–31) we have

$$\tau^{-1} = \tau_D^{-1} + k_f [Q]/(1 + K[M]), \tag{3–32}$$

which leads to the interesting prediction that *the observed luminescence lifetime increases as function of increasing detergent concentration*. This is simply a result of the fact that increased detergent concentration reduces the quantity of water solubililized quenchers. For continuous irradiation we have

$$I_D^0/I_D = (1 + k_f \tau_D [Q_w]) \exp\{K[Q]/(1 + K[M])\}, \tag{3–33}$$

where the first and second terms are contribution to intensity quenching from dynamic and static quenching, respectively. A series of author's investigations[8] of 1, 5–dimethylnaphthalene fluorescence by cyclic azo compounds has been shown to be of the *category 2* type and from the data mean micelle aggregation number, quencher binding constant and residence time ($k_b^{-1} = K/k_f$) have been derived. It should be notice that eq. (3–33) reduces to eq. (3–30) when the quencher becomes totally micellized, that is, $K[M] \gg 1$.

Category 3 : Nonstatic quenching, quencher is totally micellized

It was seen that static quenching (*category 1* and *2*) was distinguished by the fact that the luminescence decay is single exponential. Conversely, nonstatic quenching is distinguished by nonexponential decay of luminescence. This is because the lifetime of D^* in a given micelle depends on the number of cohabitant quencher molecules. With the assumption that for a given micelle the quenching probability is proportional to the number of cohabitant quencher molecules, it can be shown that the luminescence decay function is given by

$$I_D(t)/I_D(0) = \exp\{-[t/\tau_D + < n_Q > (1 - \exp(-k_q t))]\}, \tag{3–34}$$

and for continuous irradiation

$$\frac{I_D}{I_D^0} = e^{-<n_Q>} \sum_{n_Q=0}^{\infty} \frac{< n_Q >^{n_Q}}{\{1 + (k_q \tau_D) n_Q\} n_Q!}, \tag{3–35}$$

where for totally micellized quenchers $< n_Q > = [Q]/[M]$ (above equation is exactly same with eq. (3–17) which we obtained for **scheme I**). The dashed curve of fig. 3–1(a) shows typical decay pattern expected from eq. (3–34). The quenching of pyrene fluorescence by Cu^{2+} ions in SDS seems categorizable to this case 3 and data has yielded the mean interaction time, k_q^{-1}, of micelle bound substrates for this case.[7] It is to be noted that eq. (3–35) reduced to (3–30) of *category 1* when $k_q \tau_D \to 0$, that

is, when quenching becomes static.

Category 4 : Nonstatic quenching, quencher is partially micellized

This is the most general case and the total picture of **Scheme II** must be considered. If $[M_q^*]$ represents the concentration of D^* containing micelles bound to n_Q quencher molecules, then the general rate equations are

$$d[M_0^*]/dt = -(\tau_D^{-1} + k_f[Q_w])[M_0^*] + k_b[M_1^*], \tag{3–36}$$

$$\frac{d[M_q^*]}{dt} = k_f[Q_w][M_{q-1}^*] - \{\tau_D^{-1} + k_f[Q_w] + n_Q(k_q + k_b)\}[M_q^*] + (n_Q + 1)k_b[M_{q+1}^*]. \tag{3–37}$$

The general solution to this difference–differential equation has already been reported[11] and is reproduced here. For the luminescence decay function, one obtains

$$\frac{I_D(t)}{I_D(0)} = \exp\left\{-\left[\frac{t}{\tau} + < n_Q > \alpha_q^2 (1 - e^{-(k_q + k_b)t})\right]\right\}, \tag{3–38}$$

where

$$\tau^{-1} = \tau_D^{-1} + k_Q[Q_w], \tag{3–39}$$

and

$$k_Q = \alpha_q k_f, \ \alpha_q = k_q/(k_q + k_b), \tag{3–40}$$

where $[Q_w]$ and $< n_Q >$ are given by eqs. (3–24) and (3–27), respectively. For continuous irradiation the luminescence intensity can be found by integration of (3–38) over all time. The result is

$$\frac{I_D}{I_D^0} = \frac{\tau}{\tau_0} e^{-< n_Q > \alpha_q^2} \sum_{n_Q = 0}^{\infty} \frac{(< n_Q > \alpha_q^2)^{n_Q}}{\{1 + (k_q + k_b)\tau_D n_Q\} n_Q!}. \tag{3–41}$$

The dashed curve of fig. 3–1(b) shows typical decay of luminescence expected of eq. (3–38). Ideally, analysis of data on the basis of eq. (3–38) would yield all parameters obtainable in categories 1~3. In practice, the fit of data to so many parameters is complicated. Notice that eq. (3–38) is reduceable to those applicable to categories 1~3 when assumptions pertaining to those categories are imposed on it. Furthermore, the dynamic quenching rate constant k_Q can be much smaller than the forward association constant k_f if the residence time is much shorter than the interaction time constant (eq. (3–40)). The quenching of pyrene fluorescence[12] by methylene iodide and nitromethane was analyzed on the basis of an equation similar to (3–38) and seems to be *category 4*. Experiments with the quenching of

1, 5 – dimethyl naphthalene fluorescence in detergent by oxygen[13] under high pressure also appear to follow *category 4*.

3–4. Situations Involving Excited Donor Escape and Quenching in the Aqueous Phase

Situations other than those consider here have been encountered in the literature, particularly with triplet probes. For example, a study of the sensitization of rare earth ion luminescence by energy transfer from aromatic hydrocarbon triplet donors in SDS solution has been reported. The results are consistent with nearly complete micellization of probe but suggest a rapid exchange of the probe with aqueous phase relative to quenching. In this case, $k_q \ll k_b$ and eq. (3–38) becomes

$$I_D(t)/I_D(0) = \exp[-(t/\tau + k_q < n_q > t)]. \tag{3–42}$$

In such a situation, k_q the interaction constant for quenching, may be evaluated.

Another important situation is one for which all the important quenching of a strongly micellized probe occurs *in the aqueous phase*. In this case, the exit of the probe from the micelle may become the rate limiting process for donor decay, i.e., quenching occurs with unit efficiency at sufficiently high (aqueous) quencher concentration[12]. The quenching of triplet 1–bromonaphthalene by NO_2^- ions in SDS solution was found to conform to this case. The kinetics for this situation cannot be readily derived from standard steady state considerations. The resulting expression allows evaluation of k_b.

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