Unified Treatment of Luminescence Quenching Kinetics in Micelles with Quencher Migration on the Basis of a Generalized Smoluchowski Approach

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The problem of luminescence quenching in micelles assisted by quencher interphase migration is addressed by using a Smoluchowski approach without invoking any assumption neither on the statistical distribution of quenchers among the micelles nor on the independence of quenching and migration processes. The obtained decay function coincides to a good degree of accuracy with the prediction of the originally developed stochastic model of quenching. This illustrates the applicability of the Smoluchowski type of a general approach to reaction kinetics in microdisperse systems, such as micelles, and reveals several tacit assumptions of the original model. The effect of micelle size polydispersity on luminescence quenching kinetics is also discussed.

Introduction

Luminescence quenching in micelles and related self-organized molecular assemblies has been extensively studied for over 3 decades and has proven to be a relatively simple but very informative tool for probing the dynamics and structure of such systems.[1−6] Two limits of quenching are normally distinguished, depending on the reaction mechanism as well as on the excited state lifetime. In the case of short-lived excited states their deactivation is sensitive to the detailed mechanism of quenching, whereas the diffusive motion of reactants can normally be neglected. Long-range electronic energy transfer between singlet states is a typical example. On the other hand, the quenching kinetics of long-lived excited states is generally controlled by diffusion and is only weakly influenced by the details of reaction itself.

The basic idea in analyzing reaction kinetics in micelles is to separately consider the process within a finite volume and then to take the occupation statistics and the dynamics of reactant exchange between micelles into account.[6] When reaction is fast, each micelle acts as a cage, and the overall kinetics can be obtained by averaging the microscopic intramicellar kinetics with a given number of reactants over the equilibrium statistical distribution of reactants among the micelles. If reaction and exchange occur on comparable time scales, one has to use a stochastic approach to properly treat the migration-induced fluctuations.

The original model for migration-assisted luminescence quenching in micelles has been proposed in the middle 1970s, and having proved adequate in describing the experimental data, it is still the most widely used.[7,8] The model rests on the following assumptions: (1) monodisperse micelles; (2) Poisson occupation statistics for quenchers; (3) no more than one excited probe per micelle; (4) first-order diffusion-controlled intramicellar quenching; (5) first-order exchange of quenchers with the bulk phase. The analysis of the corresponding set of kinetic equations for each occupancy number leads to the expression for the experimentally observable ensemble-averaged survival probability $\Omega(t)$ of the probes following δ-pulse excitation

$$-\ln \Omega(t) = A_1 t + A_2[1 - \exp(-A_3 t)] \qquad (1)$$

with $A_1 = \bar{n}k_- k_q/(k_- + k_q)$, $A_2 = \bar{n}k_q^2/(k_- + k_q)^2$, and $A_3 = k_- + k_q$, where $\bar{n}$ is the average number of quenchers per micelle and k_q and k_- are the rate constants for quenching and for quencher exit from a micelle, respectively. In this instance and in further analysis the excitation self-decay term is factored out.

The original model has been elaborated upon by several authors to account for the micelle size polydispersity, various migration mechanisms of both probe and quencher, limited solubilization, high excitation efficiency, etc.[6] However, the way the theoretical analysis was carried out remained basically the same; that is, the problem was reduced to a set of coupled first-order rate equations for each occupancy number.

In this paper, we will start from a more general equation for the ensemble-averaged survival probability in the binary approximation,[9] i.e.,

$$-\ln \Omega(t) = c\int [1 - W(r_0,t)]\, d^3 r_0 \qquad (2)$$

where c is the quencher concentration and $W(r_0,t)$ is the survival probability at time t of the pair initially separated by r_0. Equation 2 is obtained in the thermodynamic limit for noninteracting species with quenchers being in excess, which applies well for luminescence quenching where the excitation efficiency is normally low and thus the concentration of excited probes is sufficiently small to neglect their mutual interference. This approach is exact when the probes diffuse much slower than the quenchers (the so-called target problem),[10] otherwise it provides the leading term in the density expansion.[11] In fact, the probes, typically large chromophore molecules, are less mobile than the quenchers in many cases of experimental interest.

Our goal is to derive eq 1 starting from eq 2 invoking no assumptions on the statistical distribution of quenchers among the micelles. The purpose of this practice is 2-fold: first, to illustrate the applicability of the general approach to reaction kinetics in microheterogeneous systems and, second, to reveal several tacit assumptions of the original stochastic model. Strictly speaking, we use eq 2 for noninteracting species, which immediately implies Poissonian occupation statistics in a finite

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volume. However, we do not consider this distribution explicitly, as it is done in the original stochastic model, since eq 2 is already ensemble-averaged.

We begin by considering a simple example of static quenching by the energy transfer mechanism. Then we discuss the problem of diffusion-controlled luminescence quenching assisted by quencher interphase migration. A detailed model based on the Smoluchowski equation is developed and compared against a more simple model where one assumes quenching and migration to be two independent first-order processes. Finally, we comment on the effect of micelle size polydispersity on luminescence quenching kinetics and, in particular, discuss how to extract information of the micelle size distribution from the quenching data.

Energy Transfer

We first consider a simple case of the so-called static quenching by long-range radiationless energy transfer due to multipole coupling. We neglect for simplicity any donor−donor interactions and focus only on direct transfer from energy donor (excited probe) to an acceptor (quencher) which is assumed irreversible. No diffusion occurs on the time scale of the reaction.

The energy transfer rate between two chromophore molecules depends on the distance between the molecules and on their relative orientation, $\omega(r_0,\kappa^2)$, where κ^2 is the orientation factor. For example, in the case of dipole−dipole coupling, which is responsible for the singlet−singlet energy transfer between a variety of organic molecules, we have $\omega(r_0,\kappa^2) = {}^3/_2\kappa^2(R_F/r_0)^6\tau_0^{-1}$, where R_F is the Förster critical transfer distance and τ_0 is the radiative fluorescence lifetime of the donor. The survival probability of an excited donor in the presence of an acceptor at a distance r_0 is given by

$$W(r_0,t) = \langle \exp[-t\omega(r_0,\kappa^2)] \rangle \tag{3}$$

where angular brackets denote averaging over the orientation distribution, which is in general time-dependent.

Now we need to define the concentration c in terms of the average number of quenchers (acceptors) per micelle, $\bar{n}$. Clearly, $c = \bar{n}/V_1$, where V_1 is the volume of the micelle. Here we assume that quenchers are completely solubilized. Generalization to the case where quenchers are partitioned between micelles and the aqueous phase is straightforward. Integration over r_0 reduces to averaging over the distance distribution, and we finally obtain

$$-\ln \Omega(t) = \bar{n}[1 - \int W(r_0,t)\, f(r_0)\, \mathrm{d}r_0] \tag{4}$$

where $f(r_0)$ is the distance distribution function. As expected, eq 4 exactly coincides with that derived in a standard way considering the occupation statistics.[12]

Diffusion-Controlled Luminescence Quenching

We now consider diffusion-controlled quenching assisted by interphase migration of quenchers where we assume for simplicity that excited state deactivation occurs at the first diffusive encounter (Smoluchowski condition). First, we discuss a simple model, in the spirit of the original stochastic approach, where quenching and migration are treated as two independent first-order processes.

The rate constant for quenching, k_q, is obtained as the lowest eigenvalue of the diffusion-controlled reaction problem within a finite volume or, if the exponential kinetics is preassumed, as the inverse of the mean reaction time.[1] For example, in the case where the probe is fixed at the center and the quencher is allowed to diffuse freely within a sphere of radius R, we have approximately $k_q \approx [3\alpha/(1 - {}^9/_5\alpha)]D_1/R^2$, where D_1 is the quencher diffusion coefficient inside the micelle, $\alpha = a/R$, and a is the encounter distance.

The rate constant for the exit of a quencher from the micelle, k_-, can be determined by considering the radial diffusion problem in a square-well potential.[13,14] At long enough times ($t > R^2/D_1$), the decay of the probability for a quencher to be found inside the micelle is well-approximated by a single exponential with $k_- \approx [3/(1/\kappa_1 + \gamma^2 K + {}^1/_5)]D_1/R^2$, where κ_1 is the interface permeability, K is the equilibrium partition constant equal to the ratio of equilibrium concentrations outside and inside micelles, and $\gamma^2 = D_1/D_2$, where D_2 is the quencher diffusion coefficient in the bulk phase. Normally K is rather large (the potential well is very deep) for micelles and we can neglect the permeability term (which would be important for vesicles), and, hence, $k_- \approx 4\pi D_2 R/KV_1$, where V_1 is the micelle volume. The migration rate is thus determined by diffusion of free quencher molecules away from the micelle.[15] The exponential stage of the escape kinetics lasts for a very long time, provided the well is sufficiently deep. However, asymptotically it falls into the inverse square-root stage typical of free diffusion. This indicates that quencher reentries back into the micelle come into play. We will discuss these effects later in some more detail, but for the time being we simply assume that migration obeys first-order kinetics, in accord with the original stochastic model.

For a two-phase system eq 2 can be transformed into

$$-\ln \Omega(t) = -\ln \Omega_1(t) - \ln \Omega_2(t) \tag{5}$$

the indices corresponding to the inner ($i = 1$) and the outer ($i = 2$) phase, respectively. (N.B.: Since ln Ω is given by the space integral, according to eq 2, the two phases contribute multiplicatively to the overall survival probability.) The Ω_i are given by

$$-\ln \Omega_i(t) = c_i V_i[1 - \bar{W}_i(t)] \tag{6}$$

where $\bar{W}_i(t)$ denote pair survival probabilities averaged over initial uniform distribution. Each $\bar{W}_i(t)$ can be thought of having two components, $\bar{W}_{ji}(t)$, each corresponding to a quencher which does not react with the excited probe by time t and is found inside or outside the micelle, respectively. The pair survival probabilities satisfy the following rate equation

$$\dot{\bar{\mathbf{W}}}_i = \begin{pmatrix} -(k_q + k_-) & k_+/V_2 \\ k_- & -k_+/V_2 \end{pmatrix} \bar{\mathbf{W}}_i \tag{7}$$

where we have introduced the rate constant for entry, k_+, in the same way it was done in the original stochastic model.[8] Clearly, $\bar{W}_i(t) = \bar{W}_{1i}(t) + \bar{W}_{2i}(t)$. The concentrations, c_i, can be expressed in terms of the average number of quenchers per micelle, $\bar{n}$, as follows: $c_1 = \bar{n}/V_1$ and $c_2 = \bar{n}/KV_2$, where we have used the relation for the equilibrium partition constant, i.e., $K = k_+/k_-V_2$.[6]

Solving eq 7 and taking the limit of $V_2 \to \infty$, we finally arrive at

$$-\ln \Omega_1(t) = \frac{\bar{n}k_q}{k_q + k_-}\{1 - \exp[-(k_q + k_-)t]\} \tag{8}$$

$$-\ln \Omega_2(t) = \frac{\bar{n}k_q k_-}{k_q + k_-}t - \frac{\bar{n}k_q k_-}{(k_q + k_-)^2}\{1 - \exp[-(k_q + k_-)t]\} \tag{9}$$

which immediately brings us to eq 1. In principle, one can recover $\Omega_2(t)$ directly from experiment, if a micellar solution is prepared in which quenchers are initially partitioned only in the outer phase.

In our derivation we have assumed that all micelles are independent, each quencher is involved with only one micelle during reaction, and other micelles cause no obstruction to its free diffusion in the bulk phase. This is also a tacit assumption of the original stochastic model. It works well at low micelle concentrations, high quencher concentrations, and slow migration rates. Many-body effects cannot be neglected when luminescence quenching in a cluster of micelles is considered.

Our next step is a more elaborate model where we will not decouple quenching and migration processes. We assume that the probe is immobile at the center of a spherical micelle and the quencher diffuses around, both inside the micelle and in the outer bulk phase, being able to quench the excitation at the first encounter. The problem can be formulated in terms of the diffusion equation for the probability density, $\rho(r,t)$, satisfying the following standard boundary conditions

$$-D_1 \frac{\partial \rho_1}{\partial r}|_{r=R} = -D_2 \frac{\partial \rho_2}{\partial r}|_{r=R} = k_1\rho_1 - k_2\rho_2|_{r=R} \tag{10}$$

$$\rho_1(a,t) = 0 \tag{11}$$

where k_i ($i = 1, 2$) are the rate constants of crossing the interface, R is the micelle radius, and a is the contact distance.

First, we will seek for the Green's function, $g(r_0|r,t)$, for a quencher which, having started from inside the micelle ($r_0 < R$), does not quench the excitation by time t. Following the standard procedure,[16] we obtain for the Laplace transform, $\hat{g}(\epsilon) = \int_0^\infty g(t)\, e^{\epsilon t}\, dt$, of the components

$$\hat{g}_1(r_0|r,\epsilon) = \frac{\sinh[q_1(r_< - a)]}{4\pi q_1 r_0 r D_1}\frac{\psi(r_>)}{\psi(a)}, \quad \text{for } r < R \tag{12}$$

$$\hat{g}_2(r_0|r,\epsilon) = \frac{\kappa_1 R \exp[-q_2(r - R)]}{4\pi r_0 r D_2}\frac{\sinh[q_1(r_0 - a)]}{\psi(a)}, \quad \text{for } r > R \tag{13}$$

where

$$\psi(x) = \lambda p_1 \cosh(\lambda - q_1 x) - p_2 \sinh(\lambda - q_1 x) \tag{14}$$

$q_i = [\epsilon/D_i]^{1/2}$, $\lambda = q_1 R$, $p_1 = 1 + q_2 R + \kappa_2$, $p_2 = p_1 - \kappa_1(1 + q_2 R)$, $\kappa_i = k_i R/D_i$, $r_< = \min(r_0,r)$, and $r_> = \max(r_0,r)$.

Integrating over r we get the pair survival probability

$$\hat{W}_1(r_0,\epsilon) \equiv \int_0^\infty 4\pi r^2 \hat{g}(r_0|r,\epsilon)\, dr = \frac{1}{\epsilon}\left[1 - \frac{a\psi(r_0)}{r_0\psi(a)}\right], \quad \text{for } r_0 < R \tag{15}$$

In order to calculate $\Omega_1(t)$, we have only to integrate the reaction probability, $1 - W(r_0,t)$, over the starting position and multiply the result by the quencher number density, which is given by the average number of quenchers per micelle, $\bar{n}$, divided by the volume of the micelle available for quenchers, i.e., $^4/_3\pi(R^3 - a^3)$. We finally obtain

$$-\ln \hat{\Omega}_1(\epsilon) = \frac{3\bar{n}\alpha D_1}{\epsilon^2 R^2(1 - \alpha^3)}\left[1 + \frac{\alpha\phi(\alpha\lambda) - p_1 + p_2}{\psi(\alpha\lambda)}\lambda\right] \tag{16}$$

where $\phi(x) = \lambda p_1 \sinh(\lambda - q_1 x) - p_2 \cosh(\lambda - q_1 x)$.

The Green's function for a quencher which starts from outside the micelle and does not quench the excitation by time t can be derived in a similar fashion. We obtain the following result for the pair survival probability

$$\hat{W}_1(r_0,\epsilon) = \frac{1}{\epsilon}\left\{1 - \frac{a}{r_0}\frac{\kappa_2\lambda \exp[-q_2(r_0 - R)]}{\psi(a)}\right\}, \quad \text{for } r_0 > R \tag{17}$$

Integrating further over r_0, we obtain

$$-\ln \hat{\Omega}_2(\epsilon) = \frac{3\bar{n}\alpha\lambda\kappa_1(1 + \gamma\lambda)D_1}{\epsilon^2(1 - \alpha^3)\psi(\alpha\lambda)R^2} \tag{18}$$

A reasonable approximation that allows us to simplify eqs 16 and 18 so that the inversion of the Laplace transform, $f(t) = (1/2\pi i)\int_{\sigma-i\infty}^{\sigma+i\infty} \hat{f}(\epsilon)\, e^{\epsilon t}\, d\epsilon$, could be performed analytically is to consider the solution at relatively long times, $\tau = R^2/D_1 \gg 1$, i.e., after "relaxation" within the potential well. In this limit we have approximately

$$-\ln \hat{\Omega}_1(\epsilon) \cong \frac{\bar{n}w_0}{\epsilon(w_1 + (\epsilon w_2)^{1/2} + \epsilon)} \tag{19}$$

$$-\ln \hat{\Omega}_2(\epsilon) \cong \frac{\bar{n}\nu_0}{\epsilon^2(\nu_1 - (\epsilon\nu_2)^{1/2} + \epsilon)} \tag{20}$$

where

$$w_0 \cong k_q, \quad w_1 \cong k_q + k_-, \quad w_2^{1/2} \cong k_- R/D_2^{1/2} \tag{21}$$

$$\nu_0 \cong k_q k_-, \quad \nu_1 \cong k_q + k_-, \quad \nu_2^{1/2} \cong k_q R/D_2^{1/2} \tag{22}$$

These expansions, although rigorously valid only for $\tau \gg 1$, work well even for $\tau \sim 1$. The rate constants k_q and k_- in eqs 21 and 22 are actually not exactly equal to those defined previously within the framework of the original stochastic model. We have, approximately, $k_q \approx [3\alpha/(1 - {}^1/_2\alpha)]D_1/R^2$ and $k_- \approx [3/(1/\kappa_1 + \gamma^2 K + {}^1/_2)]D_1/R^2$. However, typically for micelles $\alpha \ll 1$ and $\gamma^2 K \gg 1$, so the corrections are negligible.

The inverse Laplace transforms of eqs 19 and 20 are

$$-\ln \Omega_1(t) = \frac{\bar{n}w_0}{w_1}\left[1 - \frac{z_1\Phi(z_2) - z_2\Phi(z_1)}{z_1 - z_2}\right] \tag{23}$$

$$-\ln \Omega_2(t) = \frac{\bar{n}\nu_0}{\nu_1}\left\{t - \frac{1}{\nu_1}\left[1 - \frac{2[\nu_2 t]^{1/2}}{\pi^{1/2}} - \frac{\nu_2}{\nu_1} + \frac{x_1^3\Phi(-x_2) - x_2^3\Phi(-x_1)}{\nu_1 t(x_1 - x_2)}\right]\right\} \tag{24}$$

where

$$z_{1,2} = (1 \pm [1 - 4w_1/w_2]^{1/2})[w_2 t/4]^{1/2}, \quad x_{1,2} = (1 \pm [1 - 4\nu_1/\nu_2]^{1/2})[\nu_2 t/4]^{1/2} \tag{25}$$

and $\Phi(z) = \exp(z^2)\,\mathrm{erfc}(z)$. The kinetics essentially depend on the values of dimensionless parameters $b = [w_2/w_1]^{1/2}$ and $h = [\nu_2/\nu_1]^{1/2}$. For micelles, both b and h are normally smaller than

unity, and we can further simplify the solution by expansion in terms of these small parameters

$$-\ln \Omega_1(\tau) \cong \frac{\bar{n}w_0}{w_1}\{1 - \exp(-\zeta) - (b/\pi^{1/2})[F(\zeta^{1/2})(2\zeta + 1) - \zeta^{1/2}]\} \quad (26)$$

$$-\ln \Omega_2(\tau) \cong \frac{\bar{n}\nu_0}{\nu_1^2}\left\{\zeta - 1 + \exp(-\zeta) - \frac{h}{\pi^{1/2}}[F(\zeta^{1/2})(2\zeta + 3) - 3\zeta^{1/2}]\right\} \quad (27)$$

where $F(z) = -i(\pi^{1/2}/2)\exp(-z^2)\,\mathrm{erf}(iz)$ and $\zeta = w_1 t = \nu_1 t$. Thus, we can see that the leading terms in expansions 26 and 27 coincide with eqs 8 and 9, that is, with the original model. We now analyze the corrections.

At short times ($\zeta < 1$) we have

$$-\ln \Omega_1(t) \approx \bar{n}k_q t \quad (28)$$

$$-\ln \Omega_2(t) \approx \frac{1}{2}\bar{n}k_- k_q t^2 \quad (29)$$

while at very long times

$$-\ln \Omega_1(t) \approx \frac{\bar{n}k_q}{k_q + k_-}\left[1 - \frac{b}{(\pi\zeta)^{1/2}}\right] \quad (30)$$

$$-\ln \Omega_2(t) \approx \frac{\bar{n}k_q k_-}{k_q + k_-}(1 + 2h/(\pi\zeta)^{1/2}) \quad (31)$$

Note that eq 28 is valid at short times but after the diffusion transient, typical of the early stage of kinetics in a small closed volume,[1] has passed away, i.e., after relaxation within the well has already taken place. The square-root type of corrections are characteristic of free diffusion.[17] If we assume that migration is very fast, that there is no concentration difference between the micellar phase and the bulk phase, and that the quencher diffusion coefficients are equal for the two phases, we should be able to derive the Smoluchowski expression for the time-dependent rate constant from eq 31 (it governs the asymptotic behavior of the overall survival probability). Indeed, if we take $k_- \approx 4\pi DR/V_1$ and $k_q \approx 4\pi Da/V_1$, assume that $k_- \gg k_q$, extract the concentration from the right-hand side of eq 31, and take the first derivative with respect to time, we finally obtain, for the time-dependent rate constant, $k(t) = 4\pi aD(1 + a/[\pi Dt]^{1/2})$, which is exactly the Smoluchowski result. Note that eq 2 is equivalent to $-\ln \Omega = c\int_0^t k(t')\,dt'$.[17]

For micelles, it is rarely the case that migration is faster than quenching. In most cases it is vice versa, $k_- \ll k_q$, that is, $k_q/k_- \approx \alpha\gamma^2 K \gg 1$. This is because K is normally very large. Thus, $b \approx [3/K]^{1/2} \ll 1$, and the expansion in eq 26 is justified. Moreover, b is typically so small that the corresponding correction to Ω_1 can be neglected. However, the value of $h \approx \alpha\gamma^2[3K]^{1/2}$ is uncertain. While $K \gg 1$ and we have also assumed (on the basis of experimental evidence) that $k_q/k_- \approx h(K/3)^{1/2} \gg 1$, α and γ are small. If K is so large that $h > 1$, the expansion in eq 27 is not justified but the contribution of the outer component Ω_2 to the overall ensemble-averaged survival probability becomes negligibly small, since it is proportional to k_-/k_q. If $h < 0$, as assumed in eq 27, the expansion is justified, but h may not be much less than unity, and in this case the correction may be important.

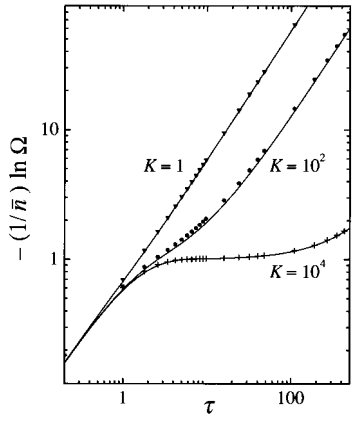

Figure 1. Luminescence quenching kinetics in monodisperse micelles, $-(1/\bar{n})\ln\Omega$ versus $\tau = D_1 t/R^2$, for $\alpha = 0.2$, $D_1/D_2 = 0.2$, $\kappa_1 = 1$, and several values of $K = 1$, 10^2, and 10^4. Symbols correspond to the numerical inverse Laplace transform of the exact solution (eqs 16 and 18); full lines are calculated within the approximate model (eq 1) with $k_- = [3/(1/\kappa_1 + \gamma^2 K + {}^1/_2)]D_1/R^2$ and $k_q = [3\alpha/(1 - {}^3/_2\alpha)]D_1/R^2$. Self-decay is not included. Note the log−log scale of the plot.

We have compared the "exact" solution of the problem at hand (eqs 16 and 18) obtained by numerical inversion of the Laplace transform with the approximate solution of eq 1 for several parameter values typical of micellar systems. Selected results are shown in Figure 1. The conclusion is that the approximate model works fairly well and the deviations between the two models would fall within experimental error. However, both models have a significant drawback, because they consider an isolated micelle and neglect any many-body effects, such as the possibility for a quencher to visit more than one micelle during the excitation lifetime and obstruction during quencher diffusion in the bulk phase. These effects are not so important at low micelle concentrations, while at high concentrations, and particularly for clusters of micelles, one has to advance a more elaborate approach.[18]

Polydispersity

Since the theory considers isolated micelles, it can be easily generalized to account for the micelle size polydispersity, provided the size distribution does not change on the time scale of the reaction (which is not necessarily the case, especially at high surfactant concentrations). In this simple situation we have only to average eq 1 over the weight distribution of the micelle aggregation numbers, $sM(s)$. The only problem is how the rate constants k_q and k_- depend on the aggregation number s. However, once we know the way the reactants are located within the micelle, we also know the dependence of the rate constants on the radius of the micelle and, hence, on the aggregation number. Here we consider only rather small spherical micelles to which the above quenching model applies. Simple arguments[19] predict $s \propto R^3$. Rodlike micelles require special treatment. For instance, the rate constant for quenching in such structures is time-dependent.[20]

The most convenient situation where one can readily extract information on the micelle size distribution from luminescence quenching data is the situation where there is no migration during the excited state lifetime. Then one simply measures the amplitude of the final exponential stage of the excitation decay as a function of quencher concentration and by a polynomial fit obtains the weight-average aggregation number, the variance, and possibly higher cumulants of the weight distribution, $sM(s)$.[21] A well-developed exponential tail is

observed only if the distribution $M(s)$ does not extend to very large s.

In the presence of slow migration, the final stage of kinetics will also be approximately exponential but with a different decay constant than that of the unquenched decay (that would indicate the presence of migration). For $k_- \ll k_q$ the long-time limit of eq 1 is $\Omega \cong \exp[-\bar{n}(1 + k_- t)]$. This is what we have to average over $sM(s)$. It is reasonable to assume that $\bar{n} = \eta s$, where $\eta = [Q]_{mic}/([S] - cmc)$ with $[Q]_{mic}$ denoting the concentration of solubilized quenchers and [S] the surfactant concentration. Note that since k_- is inversely proportional to R^2, the dependence of $\bar{n}k_-$ on s is only weak ($\sim s^{1/3}$). This ensures the exponential tail of the luminescence decay in polydisperse micelles with slow migration of quenchers. Performing cumulant expansion, we can calculate in a standard fashion for the final stage of decay with the amplitude B_0 and the decay constant B_1:

$$-\frac{1}{\eta}\ln B_0 = \langle s\rangle_w - \frac{1}{2}\sigma_w{}^2\eta + ... \qquad (32)$$

as previously, and

$$\frac{B_1}{\eta} = \langle k_-\rangle\left(\langle s\rangle_w - \frac{1}{3}\sigma_w{}^2\eta + ...\right) \qquad (33)$$

where $\langle s\rangle_w$ is the weight-average aggregation number, $\sigma_w{}^2$ is the variance of the weight distribution, and $\langle k_-\rangle$ is the average migration rate constant. Actually, B_1 also contains a self-decay contribution, but it can be easily factored out.

Another approach to analyzing luminescence decays in polydisperse micellar systems is based on an exponential series fit to experimental curves in order to recover an underlying distribution of lifetimes.[22] The method is particularly useful if $k_q(s) \gg 1/\tau_0$, and the lifetime distribution pattern has two well-separated regions corresponding to "quenched" and "unquenched" amplitudes, and the ratio of their integrated contributions, $r(\eta)$, can be directly determined from experimental data. Another measurable quantity is $1/(1 + r(\eta))$, which happens to be the Laplace transform of the weight distribution. To recover the distribution, one has to perform the inverse Laplace transformation (the maximum entropy method is used). This method is very efficient if there is no migration. Slow migration would also cause no major problem as the decay constant $\bar{n}k_- \ll k_q$ is only weakly s-dependent and falls into the region of "unquenched" amplitudes. One should be very delicate here, however. If the "unquenched" region shows a distribution of lifetimes, it may not necessarily be only due to the inhomogeneous environment sensed by the probe[23] but also due to migration. If this effect is not properly taken care of, the inverse Laplace transformation (a well-known ill-posed problem) may yield erroneous results for the micelle size distribution.

Concluding Remarks

We have addressed the problem of luminescence quenching in micelles without invoking any assumption on the occupation statistics. Instead, we have employed a Smoluchowski approach which reduces, at low concentration of excited probes, to the problem of an isolated pair of reactants. The model in its present formulation describes the reaction between neutral molecules. Generalization to ionic species would require use of the Debye−Smoluchowski approach. We have solved a simple but detailed model of diffusion-controlled reaction, where the probe is fixed at the center of the spherical micelle while the quencher is allowed to diffuse freely within the micelle and in the outer bulk phase. In contrast to the original stochastic model, we have made no assumption on the independence of the quenching and migration processes. We have found that although certain corrections are introduced, the two approaches are, in fact, equivalent, as far as micellar systems are concerned. On one hand, this illustrates the applicability of the Smoluchowski type of a general approach to microdisperse systems, such as micelles. On the other hand, we can now clearly see that although the original stochastic model deals with the time-dependent fluctuations of the occupancy distribution in the whole ensemble of micelles, it is actually restricted to considering an isolated micelle subjected to a noise (fluctuating number of reactants). It is very interesting to notice in this respect that eq principally coincides with the result of the Kubo random frequency modulation theory for Gaussian noise with exponential correlation function.[24]

The model of intramicellar quenching where the probe remains immobile at the center of the micelle while the quencher moves freely is certainly not the most realistic. However, the analysis of this simple model shows that quenching and migration can be decoupled. A more realistic model should consider solubilization of reactants on the micelle surface. A detailed analysis of the diffusion-controlled reaction on a spherical surface has been performed with a conclusion that it is well-approximated by the pseudo-first-order kinetic law.[25] Now, if we assume that quenching and migration can be decoupled, we can still use eqs 5−9 to describe the migration-assisted quenching kinetics; the rate constants should only be redefined. Note that eqs 5−9 do not explicitly consider the occupancy statistics.

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