Kinetics of quenching of luminescent probes in micellar systems. II

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In a previous paper [Chem. Phys. Lett. **33**, 289 (1975)] we treated the kinetics of quenching of luminescent probes in micellar systems, assuming that the distribution of solubilized molecules among the micelles obeys Poisson statistics. In this paper we extend our treatment to a more general case where there is a limit to the number of solubilized molecules in any one micelle. Mechanisms for migration of solubilized molecules between micelles are also discussed.

I. INTRODUCTION

Since the pioneering work of Förster and Selinger,[1] there has been a great volume of work on fluorescence quenching and energy transfer in micellar systems. It was pointed out by Dorrance and Hunter[2] that the statistics of a probe distribution among the micelles was an important parameter in these measurements.

In a previous paper[3] we presented a theoretical treatment of the kinetics of quenching of luminescent probes in such systems. We proposed the following kinetic model, which is hereafter referred to as the Tachiya model:

$$
\begin{aligned}
&P_n^* \xrightarrow{k_0} P_n\,, \quad n=0,1,\ldots\,,\\
&P_n^* + A \underset{(n+1)k_-}{\overset{k_+}{\rightleftharpoons}} P_{n+1}^*\,, \quad n=0,1,\ldots\,, \qquad (1)\\
&P_n^* \xrightarrow{nk_q} P_n\,, \quad n=1,2,\ldots\,.
\end{aligned}
$$

Here P_n^* stands for a micelle containing an excited probe and n quencher molecules, while P_n stands for a micelle which contains n quencher molecules but no excited probe. A stands for a quencher molecule in the aqueous phase. k_0 is the total decay constant of the excited state in the absence of a quencher. k_+ is the rate constant for entry of a quencher molecule into a micelle, while k_- is the rate constant for exit of a quencher molecule from a micelle containing *one* quencher molecule. k_q is the rate constant for quenching of an excited probe in a micelle containing *one* quencher molecule. Throughout this paper we use the symbols k_0, k_+, and k_- instead of k_f, k, and k' in Ref. 3. Based upon the above model, we derived[3] the following equation for the total concentration $P^*(t)$ of excited probes at time t:

$$
P^*(t) = P^*(0)\exp\left[-\left(k_0 + \frac{k_q k_+[A]}{k_- + k_q}\right)t - \frac{k_q^2 k_+[A]}{k_-(k_- + k_q)^2}\{1-\exp[-(k_- + k_q)t]\}\right]\,, \qquad (2)
$$

where $P^*(0)$ is the initial total concentration of excited probes and [A] is the concentration of quencher molecules in the aqueous phase. In terms of the average number $\bar{n}$ of quencher molecules in a micelle, which is given by $k_+[A]/k_-$, $P^*(t)$ is expressed as

$$
P^*(t) = P^*(0)\exp\left[-\left(k_0 + \frac{k_- k_q \bar{n}}{k_- + k_q}\right)t - \frac{k_q^2 \bar{n}}{(k_- + k_q)^2}\{1-\exp[-(k_- + k_q)t]\}\right]\,. \qquad (2')
$$

Several years after our work quite a few papers[4-10] were almost simultaneously published on the same subject. However, these papers except Ref. 10 treated only simple cases which were all included in our general case. In other words, the results presented in these papers can be easily obtained by taking suitable limits in Eq. (2). For example, when $k_- \ll k_q$, Eq. (2) reduces to Eq. (4) in Ref. 7. On the other hand, when $k_- \ll k_q$ and $k_+[A] \ll k_0$, it reduces to Eq. (2) in Ref. 4, Eq. (3) in Ref. 5, Eq. (11) in Ref. 6, and so on. In their earlier treatment Infelta *et al.*[11] obtained an equation which accidentally coincides with Eq. (2). However, their treatment is wrong, as first pointed out by Hentz.[12] In the Appendix we show how their treatment is wrong. In their later paper,[6] following closely the method developed by us, they treated a simple case which was included in the general case already solved by us. Turro *et al.*[8] reviewed our work.

In the Tachiya model the following assumptions are involved [see the second equation of Eq. (1)]:

(I) There is no limit to the number of solubilized molecules in any one micelle, and there is no variation in the entry rate constant (k_+) with the number of solubilized molecules already present.

(II) When a micelle contains n solubilized molecules, the rate constant for exit of a solubilized molecule from the micelle is n times as fast as when it contains one solubilized molecule.

As we first showed[3] in 1975, these assumptions lead to the conclusion that the distribution of solubilized molecules obeys Poisson statistics.

The assumption that there is no limit to the number of solubilized molecules in a micelle is not so bad when the average number of solubilized molecules in a micelle is relatively small. However, when the average number is large, use of this assumption is not justified, and one has to take into account that there is a limit to the number of solubilized molecules in a micelle.

In order to take into account this effect, Hunter[13] recently proposed the following expression for the rate constant of entry into a micelle which already contains n solubilized molecules:

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$$\text{entry rate constant} = \left(1 - \frac{n}{m}\right)k_+ ,\qquad n = 0, 1, \ldots, m , \tag{3}$$

where m is the limit to the number of solubilized molecules in a micelle. He studied the distribution of solubilized molecules among the micelles when the entry rate constant is given by Eq. (3).

In this paper we treat the kinetics of quenching of luminescent probes in micellar systems when the rate constant for entry of a quencher molecule into a micelle is given by Eq. (3) instead of k_+. The rate constant for exit of a quencher molecule from a micelle containing n quencher molecules is still assumed to be given by nk_-. We also assume, as in our previous treatment, that the luminescent probe is exclusively dissolved in the micellar phase. In Sec. II we treat the decay kinetics of excited probes in the presence of a quencher. In Sec. III we investigate the dependence of the total luminescence intensity on quencher concentration. In Sec. IV we discuss mechanisms for migration of solubilized molecules between micelles.

II. DECAY KINETICS OF EXCITED PROBES

A. General

Using the kinetic approach originally developed by us,[3] Hunter[13] studied the distribution of solubilized molecules among the micelles when the entry and the exit rate constants are given by $[1-(n/m)]k_+$ and nk_-, respectively. His result is recast into

$$Q_n = \binom{m}{n}\left(\frac{k_+[\mathrm{A}]}{mk_- + k_+[\mathrm{A}]}\right)^n \left(\frac{mk_-}{mk_- + k_+[\mathrm{A}]}\right)^{m-n} ,\qquad n = 0, 1, \ldots, m , \tag{4}$$

where Q_n is the probability of finding a micelle which contains n solubilized molecules, and [A] is the concentration of solubilized molecules in the aqueous phase. Equation (4) shows that the distribution of solubilized molecules among the micelles is described by a binomial distribution. Using a combinatorial approach, Miller *et al.*[14] also reached the same conclusion. In the limit of $m \to \infty$, Eq. (4) reduces to the Poisson distribution.

If the laser intensity is not so strong, the probability that two or more probes will be excited in a micelle is negligible, compared with the probability that one probe will be excited. Under this condition, one has only to consider micelles which contain only one excited probe. Let $P_n^*(t)$ denote the concentration of micelles which contain an excited probe and n quencher molecules. For a sufficiently rapid excitation pulse, it is a reasonable assumption that the efficiency of excitation of a probe is independent of the number of quencher molecules contained in the micelle. Using Eq. (4) together with this assumption, the initial condition is given by

$$P_n^*(0) = P^*(0)\binom{m}{n}\left(\frac{k_+[\mathrm{A}]}{mk_- + k_+[\mathrm{A}]}\right)^n \left(\frac{mk_-}{mk_- + k_+[\mathrm{A}]}\right)^{m-n} ,\qquad n = 0, 1, \ldots, m , \tag{5}$$

where $P^*(0)$ is the total concentration of excited probes at time zero and [A] is now the concentration of quencher molecules in the aqueous phase.

After excitation, the rate equations are given by

$$\frac{dP_0^*}{dt} = -(k_0 + k_+[\mathrm{A}])P_0^* + k_- P_1^* ,$$

$$\frac{dP_n^*}{dt} = \left(1 - \frac{n-1}{m}\right)k_+[\mathrm{A}]P_{n-1}^* - \left[k_0 + \left(1 - \frac{n}{m}\right)k_+[\mathrm{A}] + nk_- + nk_q\right]P_n^* + (n+1)k_- P_{n+1}^* ,\quad n = 1, 2, \ldots, m-1 , \tag{6}$$

$$\frac{dP_m^*}{dt} = \left(1 - \frac{m-1}{m}\right)k_+[\mathrm{A}]P_{m-1}^* - (k_0 + mk_- + mk_q)P_m^* .$$

By means of the generating function[15] of $P_n^*(t)$, viz.,

$$F(t, s) = \sum_{n=0}^{m} s^n P_n^*(t) , \tag{7}$$

Eq. (6) may be transformed into a partial differential equation

$$\frac{\partial F}{\partial t} = \left[k_- - \left(k_- + k_q - \frac{k_+[\mathrm{A}]}{m}\right)s - \frac{k_+[\mathrm{A}]}{m}s^2\right]\frac{\partial F}{\partial s} + [k_+[\mathrm{A}]s - (k_0 + k_+[\mathrm{A}])]F . \tag{8}$$

Equation (8) can be solved by a standard technique.[16] The solution is given by

$$F = (s - s_1)^{mu_1/k_+[\mathrm{A}]}(s - s_2)^{mu_2/k_+[\mathrm{A}]} \times G\left\{\frac{s - s_1}{s - s_2}\exp[(s_2 - s_1)(k_+[\mathrm{A}]/m)t]\right\} , \tag{9}$$

where s_1 and s_2 are the solutions of the following quadratic equation:

$$\frac{k_+[\mathrm{A}]}{m}s^2 + \left(k_- + k_q - \frac{k_+[\mathrm{A}]}{m}\right)s - k_- = 0 ,$$

and are given by

$$s_1 = \frac{-m(k_- + k_q) + k_+[\mathrm{A}] + \{[m(k_- + k_q) - k_+[\mathrm{A}]]^2 + 4mk_-k_+[\mathrm{A}]\}^{1/2}}{2k_+[\mathrm{A}]} ,$$
$$s_2 = \frac{-m(k_- + k_q) + k_+[\mathrm{A}] - \{[m(k_- + k_q) - k_+[\mathrm{A}]]^2 + 4mk_-k_+[\mathrm{A}]\}^{1/2}}{2k_+[\mathrm{A}]} . \tag{10}$$

It is easy to show that $s_2 < 0 < s_1 < 1$. u_1 and u_2 are given by

$$u_1 = \frac{(s_1 - 1)k_+[\mathrm{A}] - k_0}{s_1 - s_2} ,\qquad u_2 = \frac{(s_2 - 1)k_+[\mathrm{A}] - k_0}{s_2 - s_1} , \tag{11}$$

respectively. $G(y)$ is an arbitrary function and is determined by the initial condition imposed on the generating func tion.

Initially, viz., immediately after excitation, the concentration of micelles which contain an excited probe and n quencher molecules is given by Eq. (5). Accordingly, the initial condition on the generating function is given by

$$F(0, s)=P^*(0)\left(\frac{mk_- + k_+[\mathrm{A}]s}{mk_- + k_+[\mathrm{A}]}\right)^m . \tag{12}$$

From Eqs. (9) and (12) one obtains

$$G(y)=P^*(0)\left[\frac{(mk_- + k_+[\mathrm{A}]s_1)-(mk_- + k_+[\mathrm{A}]s_2)y}{(mk_- + k_+[\mathrm{A}])(s_1-s_2)}\right]^m y^{-(mu_1/k_+[\mathrm{A}])} . \tag{13}$$

Therefore, the generating function is given by

$$F=P^*(0)\,e^{-k_0t}\left[\frac{(s-s_2)(mk_- + k_+[\mathrm{A}]s_1)}{(mk_- + k_+[\mathrm{A}])(s_1-s_2)}\exp\{[(s_1-1)/m]k_+[\mathrm{A}]t\}-\frac{(s-s_1)(mk_- + k_+[\mathrm{A}]s_2)}{(mk_- + k_+[\mathrm{A}])(s_1-s_2)}\exp\{[(s_2-1)/m]k_+[\mathrm{A}]t\}\right]^m . \tag{14}$$

The total concentration $P^*(t)$ of excited probes is expressed as

$$P^*(t)=\sum_{n=0}^{m} P_n^*(t) . \tag{15}$$

Comparing Eq. (15) with Eq. (7), one obtains

$$\begin{aligned}P^*(t)&=F(t, 1)\\ &=P^*(0)\,e^{-k_0t}\left[\frac{(1-s_2)(mk_- + k_+[\mathrm{A}]s_1)}{(mk_- + k_+[\mathrm{A}])(s_1-s_2)}\exp\{-[(1-s_1)/m]k_+[\mathrm{A}]t\}-\frac{(1-s_1)(mk_- + k_+[\mathrm{A}]s_2)}{(mk_- + k_+[\mathrm{A}])(s_1-s_2)}\exp\{-[(1-s_2)/m]k_+[\mathrm{A}]t\}\right]^m .\end{aligned} \tag{16}$$

Equation (16) describes the kinetics of quenching of excited probes when there is a limit to the number of quencher molecules in a micelle. In the limit of $m\to\infty$, Eq. (16) reduces to Eq. (2).

When the entry and the exit rate constants are given by $[1-(n/m)]k_+$ and nk_-, respectively, the average number $\bar{n}$ of solubilized molecules in a micelle is given by

$$\bar{n}=\frac{mk_+[\mathrm{A}]}{mk_- + k_+[\mathrm{A}]} . \tag{17}$$

Therefore, the total concentration of excited probes is expressed in terms of the average number $\bar{n}$ as

$$\begin{aligned}P^*(t)=P^*(0)\,e^{-k_0t}&\left[\frac{(1-s_2)(m-\bar{n}+\bar{n}s_1)}{m(s_1-s_2)}\exp\{-[\bar{n}(1-s_1)/(m-\bar{n})]k_-t\}\right.\\ &\left.-\frac{(1-s_1)(m-\bar{n}+\bar{n}s_2)}{m(s_1-s_2)}\exp\{-[\bar{n}(1-s_2)/(m-\bar{n})]k_-t\}\right]^m ,\end{aligned} \tag{16'}$$

where

$$\begin{aligned}s_1&=\frac{-(m-\bar{n})(k_-+k_q)+\bar{n}k_-+\{[(m-\bar{n})(k_-+k_q)-\bar{n}k_-]^2+4\bar{n}(m-\bar{n})k_-^2\}^{1/2}}{2\bar{n}k_-} ,\\ s_2&=\frac{-(m-\bar{n})(k_-+k_q)+\bar{n}k_--\{[(m-\bar{n})(k_-+k_q)-\bar{n}k_-]^2+4\bar{n}(m-\bar{n})k_-^2\}^{1/2}}{2\bar{n}k_-} .\end{aligned} \tag{10'}$$

Let us consider the short time and the long time behaviors of $P^*(t)$. When t is sufficiently small, $\exp[-\bar{n}(1-s_i)k_-t/(m-\bar{n})]$ $(i=1, 2)$ in Eq. (16′) can be expanded, and one obtains

$$\begin{aligned}\frac{P^*(t)}{P^*(0)}e^{k_0t}&=\left(1-\frac{\bar{n}k_qt}{m}\right)^m\\ &=1-\bar{n}k_qt .\end{aligned} \tag{18}$$

It is interesting to note that the short time behavior of $P^*(t)$ does not explicitly depend on m, being determined only by k_0 and $\bar{n}k_q$.

On the other hand, when t is sufficiently large, the second term in the brackets [ ] in Eq. (16′) can be neglected compared with the first term, since in such cases $\exp[-\bar{n}(1-s_2)k_-t/(m-\bar{n})]\ll\exp[-\bar{n}(1-s_1)k_-t/(m-\bar{n})]<1$. Therefore, one obtains

$$\begin{aligned}\frac{P^*(t)}{P^*(0)}e^{k_0t}&=\left[\frac{(1-s_2)(m-\bar{n}+\bar{n}s_1)}{m(s_1-s_2)}\right]^m\\ &\times\exp\{-[m\,\bar{n}(1-s_1)/(m-\bar{n})]k_-t\} .\end{aligned} \tag{19}$$

For large t, $P^*(t)$ decays exponentially, and the decay constant and the amplitude are given by $k_0+m\bar{n}(1-s_1)k_-/(m-\bar{n})$ and $P^*(0)[(1-s_2)(m-\bar{n}+\bar{n}s_1)/m(s_1-s_2)]^m$, respectively.

B. Numerical results

If the total concentration of quencher molecules is [Q], one obtains

$$\bar{n}[\mathrm{M}]+[\mathrm{A}]=[\mathrm{Q}]\ , \tag{20}$$

where [M] is the concentration of micelles. Elimination of [A] from Eqs. (17) and (20) yields the following quadratic equation for $\bar{n}$:

$$\bar{n}^2-\left(\frac{[\mathrm{Q}]}{[\mathrm{M}]}+m+\frac{mk_-}{k_+[\mathrm{M}]}\right)\bar{n}+\frac{m[\mathrm{Q}]}{[\mathrm{M}]}=0\ . \tag{21}$$

One solution of Eq. (21) is larger than m, and is physically unacceptable. The physically acceptable solution of Eq. (21) is given by

$$\bar{n}=\frac{1}{2}\left\{\frac{[\mathrm{Q}]}{[\mathrm{M}]}+m+\frac{mk_-}{k_+[\mathrm{M}]}-\left[\left(\frac{[\mathrm{Q}]}{[\mathrm{M}]}+m+\frac{mk_-}{k_+[\mathrm{M}]}\right)^2-\frac{4m[\mathrm{Q}]}{[\mathrm{M}]}\right]^{1/2}\right\}\ . \tag{22}$$

Equation (16′) together with Eq. (22) describe the kinetics of quenching of excited probes for given values of [Q] and [M].

Using Eq. (16′), we have numerically calculated the decay kinetics of excited probes for several sets of values of parameters. We have considered cases where $k_-/k_+[\mathrm{M}]\ll 1$, which physically means that quencher molecules are much more stable in the micellar interior than in the aqueous phase. In these cases the average number $\bar{n}$ is approximated by

$$\begin{aligned}\bar{n}&=\frac{[\mathrm{Q}]}{[\mathrm{M}]}\ , &&\text{for } \frac{[\mathrm{Q}]}{[\mathrm{M}]}\le m\ ,\\ &=m\ , &&\text{for } \frac{[\mathrm{Q}]}{[\mathrm{M}]}> m\ .\end{aligned} \tag{23}$$

Typical results are shown in Figs. 1–3, where $[P^*(t)/P^*(0)]e^{k_0 t}$ is plotted against $k_q t$. In all these figures $k_-=0.1k_q$ is arbitrarily assumed.

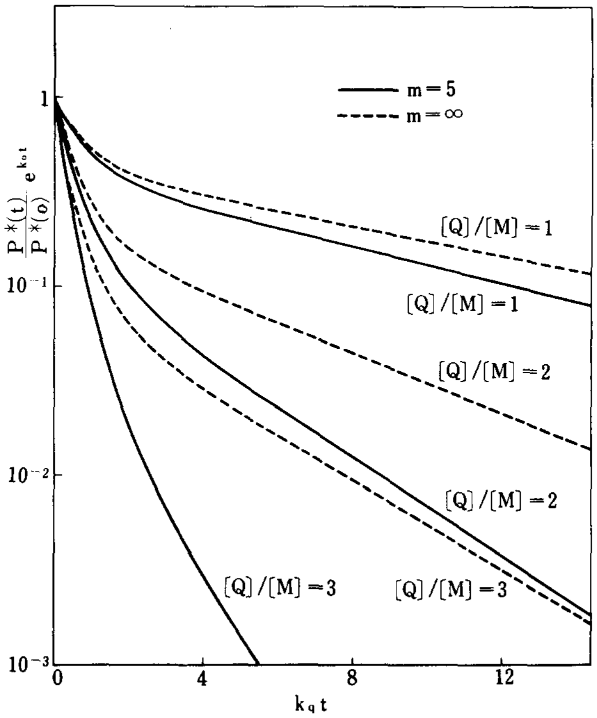

FIG. 2. Variation in the decay curve of excited probes with [Q]/[M] when m is assumed to be 5. The decay curves for the Poisson distribution ($m=\infty$) are also included for comparison.

Figure 1 shows the variation in the decay curve with m for a fixed value of [Q]/[M]. In this figure the value

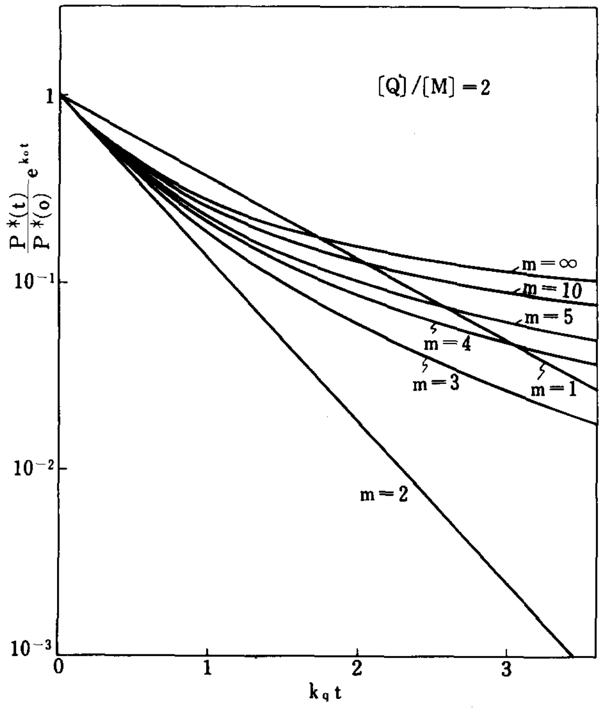

FIG. 1. Variation in the decay curve of excited probes with the assumed value of m when [Q]/[M] is fixed at 2. $k_-/k_+[\mathrm{M}]\ll 1$ and $k_-=0.1k_q$ are assumed throughout Figs. 1–5. $m=\infty$ corresponds to the Poisson distribution.

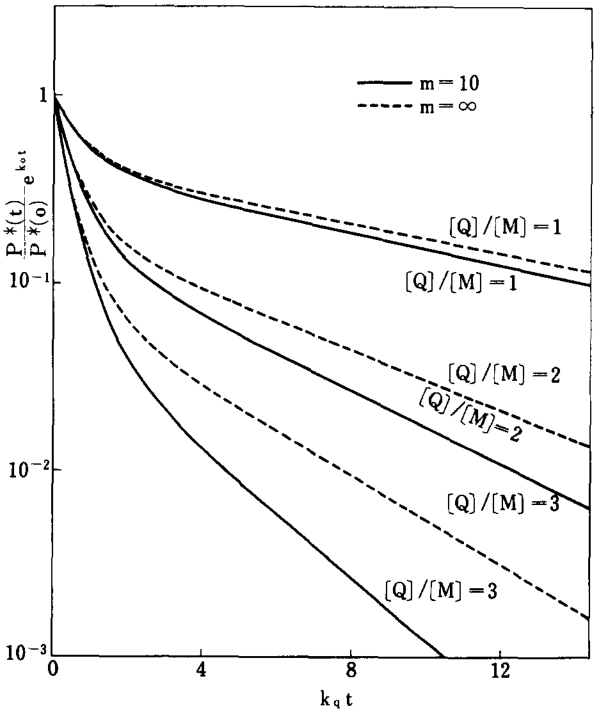

FIG. 3. Variation in the decay curve of excited probes with [Q]/[M] when m is assumed to be 10. The decay curves for the Poisson distribution ($m=\infty$) are also included for comparison.

of [Q]/[M] is fixed at 2. For $m \le [\mathrm{Q}]/[\mathrm{M}]$ the decay curves are linear in the semilog plot over the entire time range. The reason for this linearity comes from the fact that we are considering cases where $k_-/k_+[\mathrm{M}] \ll 1$. In these cases quencher molecules have a strong tendency to remain in the micellar phase, and for $m \le [\mathrm{Q}]/[\mathrm{M}]$ all the micelles accommodate as many quencher molecules as they can. In other words, they contain an equal number (m) of quencher molecules, so that the linear decay curves are obtained. When the value of m exceeds [Q]/[M], the decay curves become nonlinear, and flatter with increasing m. For large t, however, the decay curves become linear even for $m > [\mathrm{Q}]/[\mathrm{M}]$, as expected from Eq. (19), and the slopes are given by $m\bar{n}(1-s_1)k_-/2.303(m-\bar{n})$. On the other hand, in the short time limit, the decay curves for $m \ge [\mathrm{Q}]/[\mathrm{M}]$ are seen to converge into a single line. This is to be expected, since the short time behavior of $[P^*(t)/P^*(0)]e^{k_0 t}$ does not explicitly depend on m [see Eq. (18)] and in the present cases $\bar{n}$ is given by [Q]/[M] for $m \ge [\mathrm{Q}]/[\mathrm{M}]$ [see Eq. (23)].

Figures 2 and 3 show the variation in the decay curve with [Q]/[M] for fixed values of m. In Figs. 2 and 3 the value of m is fixed at 5 and 10, respectively. In these figures the decay curves for the Poisson distribution ($m=\infty$) are also included for comparison. When [Q]/[M] is much smaller than the value of m, the decay curves for the truncated distribution differ little from those for the Poisson distribution. See, for example, two curves corresponding to $[\mathrm{Q}]/[\mathrm{M}]=1$ in Fig. 3. The upper curve corresponds to the Poisson distribution and the lower one to $m=10$. The difference between the two curves seems negligible compared with the experimenta accuracy which is presently attainable. When [Q]/[M] increases and approaches the value of m, however, the difference between the decay curves for the truncated distribution and those for the Poisson distribution becomes significant. Compare, for example, two curves corresponding to $[\mathrm{Q}]/[\mathrm{M}]=3$ in Fig. 2. The upper curve corresponds to the Poisson distribution and the lower one to $m=5$. The great difference between the two curves demonstrates that the assumption of Poisson statistics for the distribution of quencher molecules among the micelles is not justified when the magnitudes of m and [Q]/[M] are comparable.

III. DEPENDENCE OF LUMINESCENCE INTENSITY ON QUENCHER CONCENTRATION

A. General

The total luminescence intensity I is given by

$$I = k_r \int_0^\infty P^*(t)\,dt\,, \tag{24}$$

where k_r is the radiative decay rate constant. From Eqs. (16′) and (24) one obtains the following equation for the ratio of total luminescence intensities in the presence and absence of a quencher:

$$\frac{I}{I_0} = m!\,(m-\bar{n})k_0\left[\frac{(1-s_1)(\bar{n}-m-\bar{n}s_2)}{m(s_1-s_2)}\right]^m \sum_{l=0}^{m} \frac{1}{l!\,(m-l)!}\left[\frac{(1-s_2)(m-\bar{n}+\bar{n}s_1)}{(1-s_1)(\bar{n}-m-\bar{n}s_2)}\right]^l \frac{1}{(m-\bar{n})k_0+[m(1-s_2)-l(s_1-s_2)]\bar{n}k_-}\,, \tag{25}$$

where I_0 is the total luminescence intensity in the absence of a quencher and the average number $\bar{n}$ is given by Eq. (17).

The corresponding equation for the Poisson distribution is obtained from Eqs. (2′) and (24):

$$\frac{I}{I_0} = \frac{k_0}{k_-+k_q}\exp\left[-\frac{k_q^2\bar{n}}{(k_-+k_q)^2}\right]\int_0^1 x^{\{[k_0(k_-+k_q)+k_-k_q\bar{n}]/(k_-+k_q)^2\}-1}\exp\{[k_q^2\bar{n}/(k_-+k_q)^2]x\}\,dx\,, \tag{26}$$

where the average number $\bar{n}$ is now given by $k_+[\mathrm{A}]/k_-$. By expanding the exponential function in the integral, Eq. (26) can alternatively be written as

$$\frac{I}{I_0} = k_0(k_-+k_q)\exp\left[-\frac{k_q^2\bar{n}}{(k_-+k_q)^2}\right]\sum_{l=0}^{\infty}\frac{1}{l!}\left[\frac{k_q^2\bar{n}}{(k_-+k_q)^2}\right]^l \frac{1}{k_0(k_-+k_q)+k_-k_q\bar{n}+l(k_-+k_q)^2}\,. \tag{26′}$$

Equation (26) or (26′) is the reduced form of Eq. (25) in the limit of $m\to\infty$. Equation (26′) was derived by Turro *et al.*,[8] although there was a minor error in their original equation. When $k_- \ll k_q$, Eq. (26′) reduces to Eq. (3) in Ref. 7. On the other hand, when $k_- \ll k_q$ and $k_+[\mathrm{A}] \ll k_0$, it reduces to Eq. (5) in Ref. 17.

Let us consider the small $\bar{n}$ and the large $\bar{n}$ behaviors of I/I_0 to be given by Eq. (25). When $\bar{n}$ is sufficiently small compared with m, s_1 and $\bar{n}s_2$ are expanded into

$$\begin{aligned} s_1 &= \frac{k_-}{k_-+k_q} + \frac{2k_-^2k_q}{m(k_-+k_q)^3}\bar{n}\,,\\ \bar{n}s_2 &= -\frac{m(k_-+k_q)}{k_-} + \frac{k_-^2+3k_-k_q+k_q^2}{k_-(k_-+k_q)}\bar{n}\,. \end{aligned} \tag{27}$$

Substituting Eq. (27) into Eq. (25), one obtains, for sufficiently small $\bar{n}$,

$$\begin{aligned} \frac{I}{I_0} &= (m-\bar{n})k_0\left[1-\frac{k_q^2}{m(k_-+k_q)^2}\bar{n}\right]^m \\ &\quad\times \frac{1}{(m-\bar{n})k_0+\dfrac{mk_-k_q}{k_-+k_q}\bar{n}} + k_0\bar{n}\frac{k_q^2}{(k_-+k_q)^2}\frac{1}{k_0+k_-+k_q} \\ &= 1-\frac{k_q(k_0+k_-)}{k_0(k_0+k_-+k_q)}\bar{n}\,. \end{aligned} \tag{28}$$

Note that the small $\bar{n}$ behavior of I/I_0 does not explicitly depend on m. However, $\bar{n}$ itself is generally dependent on m, as seen from Eq. (22).

On the other hand, when $\bar{n}$ is very close to m, s_1 and s_2 are expanded into

$$s_1 = 1 - \frac{k_q}{m k_-}(m - \bar{n}) \, , \qquad (29)$$
$$s_2 = -\frac{1}{m}(m - \bar{n}) \, .$$

Substituting Eq. (29) in Eq. (25), one obtains

$$\lim_{\bar{n} \to m} \frac{I}{I_0} = \frac{k_0}{k_0 + m k_q} \, . \qquad (30)$$

The physical meaning of Eq. (30) is transparent. In the limit of $\bar{n} \to m$, all the micelles contain an equal number of quencher molecules and this number is m, so that I/I_0 is given by Eq. (30).

B. Numerical results

Using Eq. (25), we have numerically calculated the dependence of the luminescence intensity on quencher concentration for several sets of values of parameters. We have again considered cases where $k_-/k_+[\mathrm{M}] \ll 1$. Typical results are shown in Figs. 4 and 5, where I_0/I is plotted against [Q]/[M]. In Fig. 4, cases where $k_0 = 0.1 k_q$ are considered, while in Fig. 5, $k_0 = k_q$ is assumed. In both figures, $k_- = 0.1 k_q$ is assumed, as in Figs. 1–3.

The quantity I_0/I increases with the quencher concentration [Q]/[M], when the value of [Q]/[M] is lower than m. In the low concentration limit, the curves in Fig. 4 and those in Fig. 5 are seen to converge into a single line. This is to be expected, since the low concentration (small $\bar{n}$) behavior of I_0/I does not explicitly depend on m [see Eq. (28)] and in the present cases $\bar{n}$ is given by [Q]/[M] for [Q]/[M] < m [see Eq. (23)]. When the value of [Q]/[M] exceeds m, I_0/I becomes constant. The reason for this constancy is as follows: For [Q]/[M] $\geq m$ the average number $\bar{n}$ is equal to m [see Eq. (23)], so that I_0/I is given by Eq. (30), viz., being independent of [Q]/[M].

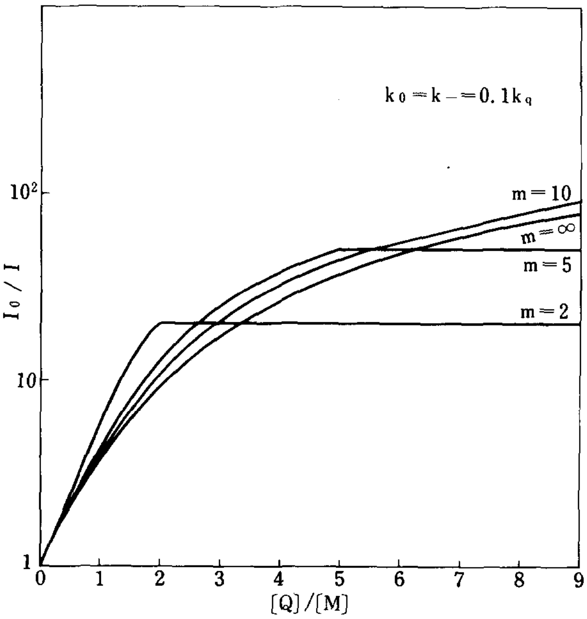

FIG. 4. Dependence of luminescence intensity on quencher concentration. $k_0 = 0.1 k_q$ is assumed. $m = \infty$ corresponds to the Poisson distribution.

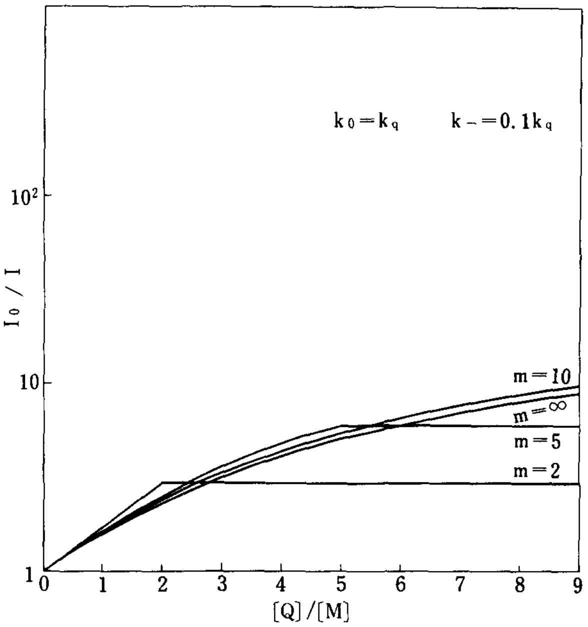

FIG. 5. Dependence of luminescence intensity on quencher concentration. $k_0 = k_q$ is assumed. $m = \infty$ corresponds to the Poisson distribution.

IV. MECHANISMS FOR MIGRATION OF SOLUBILIZED MOLECULES BETWEEN MICELLES

In the original Tachiya model the migration of solubilized molecules between micelles is assumed to occur via the aqueous phase. As stated in Sec. I, in his model the solubilization dynamics is described by

$$\mathrm{M}_n + \mathrm{A} \underset{(n+1)k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{M}_{n+1} \qquad (31)$$

if there is no limit to the number of solubilized molecules in any one micelle. Here M_n stands for a micelle containing n solubilized molecules and A stands for a solubilized molecule in the aqueous phase. When there is a limit to the number of solubilized molecules in a micelle, Eq. (31) is modified as

$$\mathrm{M}_n + \mathrm{A} \underset{(n+1)k_-}{\overset{k_+[1-(n/m)]}{\rightleftharpoons}} \mathrm{M}_{n+1} \, . \qquad (32)$$

In Secs. II and III we have extended our previous treatment to the case where the solubilization dynamics is described by Eq. (32).

In Eq. (31) the rate constant for exit of a solubilized molecule from a micelle is proportional to the number of solubilized molecules the micelle contains. Instead of Eq. (31) some workers[13,18] have proposed the following kinetic model:

$$\mathrm{M}_n + \mathrm{A} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{M}_{n+1} \, . \qquad (33)$$

In this model the exit rate constant is independent of the number of solubilized molecules the micelle contains.

It has been suggested[13] that if a solubilized molecule leaves a micelle not as an isolated molecule but as a cluster consisting of a solubilized molecule and several surfactant molecules, the solubilization dynamics might very well be described by Eq. (33). In our opinion, however, even if a solubilized molecule leaves a micelle as such a cluster, the solubilization dynamics is still described by Eq. (31), not by Eq. (33). The reason is as follows: The rate at which a surfactant cluster leaves a micelle is, as Hunter noticed, independent of the number of solubilized molecules the micelle contains. However, the probability that the surfactant cluster will contain a solubilized molecule is proportional to the number of solubilized molecules the micelle contains. Therefore, the rate at which a surfactant cluster containing a solubilized molecule leaves a micelle should be proportional to the number of solubilized molecules the micelle contains.

Henglein and Proske[19] have suggested another mechanism in which the migration of solubilized molecules occurs during micelle collisions. For this mechanism the solubilization dynamics may be described by[20]

$$\mathrm{M}_n + \mathrm{M}_j \underset{(j+1)k}{\overset{nk}{\rightleftharpoons}} \mathrm{M}_{n-1} + \mathrm{M}_{j+1} \,. \tag{34}$$

In Eq. (34) it is assumed that when two micelles, one containing n solubilized molecules, the other containing j solubilized molecules, collide, the probability that a solubilized molecule will migrate from the former micelle to the latter is proportional to n, while the probability that a solubilized molecule will migrate from the latter to the former is proportional to j. We have shown[20] that when the solubilization dynamics is described by Eq. (34), the distribution of solubilized molecules among the micelles still obeys Poisson statistics.

When the solubilization dynamics of quencher molecules is described by Eq. (34) instead of Eq. (31), the rate equations corresponding to Eq. (9) in Ref. 3 are written as

$$\frac{dP_0^*}{dt} = -\left(k_0 + \sum_{j=1}^{\infty} jkM_j\right)P_0^* + \sum_{j=0}^{\infty} kM_j P_1^* \,,$$

$$\frac{dP_n^*}{dt} = \sum_{j=1}^{\infty} jkM_j P_{n-1}^* - \left(k_0 + \sum_{j=1}^{\infty} jkM_j + \sum_{j=0}^{\infty} nkM_j + nk_q\right)P_n^* + \sum_{j=0}^{\infty}(n+1)kM_j P_{n+1}^* \,, \quad n = 1, 2, \ldots \,, \tag{35}$$

where M_j is the concentration of micelles containing j quencher molecules, and following the notations in this paper we have used the symbol k_0 instead of k_f in Ref. 3. By utilizing the following relations:

$$\sum_{j=0}^{\infty} M_j = [\mathrm{M}] \,, \quad \sum_{j=0}^{\infty} jM_j = \bar{n}[\mathrm{M}] \,, \tag{36}$$

where [M] is the total concentration of micelles and $\bar{n}$ is the average number of quencher molecules in a micelle, Eq. (35) is rewritten as

$$\frac{dP_0^*}{dt} = -(k_0 + \bar{n}k[\mathrm{M}])P_0^* + k[\mathrm{M}]P_1^* \,,$$

$$\frac{dP_n^*}{dt} = \bar{n}k[\mathrm{M}]P_{n-1}^* - (k_0 + \bar{n}k[\mathrm{M}] + nk[\mathrm{M}] + nk_q)P_n^* + (n+1)k[\mathrm{M}]P_{n+1}^* \,, \quad n = 1, 2, \ldots \,. \tag{37}$$

Equation (37) has the same mathematical form as Eq. (9) in Ref. 3, with k[A] and k' replaced by $\bar{n}k$[M] and k[M], respectively. Therefore, $P^*(t)$ is obtained by simply replacing k_+[A] and k_- in Eq. (2) of this paper by $\bar{n}k$[M] and k[M], respectively:

$$P^*(t) = P^*(0) \exp\left[-\left(k_0 + \frac{k[\mathrm{M}]k_q\bar{n}}{k[\mathrm{M}] + k_q}\right)t - \frac{k_q^2\bar{n}}{(k[\mathrm{M}] + k_q)^2}\{1 - \exp[-(k[\mathrm{M}] + k_q)t]\}\right] \,. \tag{38}$$

Note that in contrast to Eq. (2′) the decay kinetics described by Eq. (38) explicitly depends on the concentration of micelles. I/I_0 is similarly obtained by replacing k_- in Eq. (26) or (26′) by k[M]:

$$\frac{I}{I_0} = \frac{k_0}{k[\mathrm{M}] + k_q} \exp\left[-\frac{k_q^2\bar{n}}{(k[\mathrm{M}] + k_q)^2}\right] \int_0^1 x^{\{[k_0(k[\mathrm{M}]+k_q)+k[\mathrm{M}]k_q\bar{n}]/(k[\mathrm{M}]+k_q)^2\}-1} \exp\{[k_q^2\bar{n}/(k[\mathrm{M}] + k_q)^2]x\}\, dx$$

$$= k_0(k[\mathrm{M}] + k_q) \exp\left[-\frac{k_q^2\bar{n}}{(k[\mathrm{M}] + k_q)^2}\right] \sum_{l=0}^{\infty} \frac{1}{l!}\left[\frac{k_q^2\bar{n}}{(k[\mathrm{M}] + k_q)^2}\right]^l \frac{1}{k_0(k[\mathrm{M}] + k_q) + k[\mathrm{M}]k_q\bar{n} + l(k[\mathrm{M}] + k_q)^2} \,. \tag{39}$$

De Schryver *et al.*[10] considered a case where the migration of solubilized molecules between micelles occurs partly via the aqueous phase and partly during micelle collisions.

When there is a limit to the number of quencher molecules in a micelle, Eq. (34) may be modified as

$$\mathrm{M}_n + \mathrm{M}_j \underset{(j+1)[1-(n-1/m)]k}{\overset{n[1-(j/m)]k}{\rightleftharpoons}} \mathrm{M}_{n-1} + \mathrm{M}_{j+1} \,, \tag{40}$$

where m is the limit to the number of quencher molecules in a micelle. Correspondingly, Eq. (35) is modified as

TABLE I. Decay kinetics of excited probes and dependence of luminescence intensity on quencher concentration.

Migration mechanism	Solubilization dynamics	Decay kinetics	Quencher concentration dependence
Via the aqueous phase	Eq. (31)	Eq. (2) or (2′)	Eq. (26) or (26′)
	Eq. (32)	Eq. (16) or (16′)	Eq. (25)
During micelle collisions	Eq. (34)	Eq. (38)	Eq. (39)
	Eq. (40)	Eq. (43)	Eq. (45)

$$
\begin{aligned}
\frac{dP_0^*}{dt} &= -\Big(k_0+\sum_{j=1}^{m} jkM_j\Big)P_0^* + \sum_{j=0}^{m}\Big(1-\frac{j}{m}\Big)kM_jP_1^* ,\\
\frac{dP_n^*}{dt} &= \sum_{j=1}^{m} j\Big(1-\frac{n-1}{m}\Big)kM_jP_{n-1}^* - \Big[k_0+\sum_{j=1}^{m} j\Big(1-\frac{n}{m}\Big)kM_j\\
&\quad +\sum_{j=0}^{m} n\Big(1-\frac{j}{m}\Big)M_j+nk_q\Big]P_n^* + \sum_{j=0}^{m}(n+1)\Big(1-\frac{j}{m}\Big)kM_jP_{n+1}^* , \quad n=1,2,\ldots,m-1 ,\\
\frac{dP_m^*}{dt} &= \sum_{j=1}^{m} j\Big(1-\frac{m-1}{m}\Big)kM_jP_{m-1}^* - \Big[k_0+\sum_{j=0}^{m} m\Big(1-\frac{j}{m}\Big)M_j+mk_q\Big]P_m^* .
\end{aligned}
\tag{41}
$$

By utilizing the total concentration of micelles [M] and the average number of quencher molecules in a micelle $\bar{n}$, Eq. (41) is rewritten as

$$
\begin{aligned}
\frac{dP_0^*}{dt} &= -(k_0+\bar{n}k[\mathrm{M}])P_0^* + \Big(1-\frac{\bar{n}}{m}\Big)k[\mathrm{M}]P_1^* ,\\
\frac{dP_n^*}{dt} &= \bar{n}\Big(1-\frac{n-1}{m}\Big)k[\mathrm{M}]P_{n-1}^* - \Big[k_0+\bar{n}\Big(1-\frac{n}{m}\Big)k[\mathrm{M}]\\
&\quad + n\Big(1-\frac{\bar{n}}{m}\Big)k[\mathrm{M}]+nk_q\Big]P_n^* + (n+1)\Big(1-\frac{\bar{n}}{m}\Big)k[\mathrm{M}]P_{n+1}^* , \quad n=1,2,\ldots,m-1 ,\\
\frac{dP_m^*}{dt} &= \bar{n}\Big(1-\frac{m-1}{m}\Big)k[\mathrm{M}]P_{m-1}^* - \Big[k_0+m\Big(1-\frac{\bar{n}}{m}\Big)k[\mathrm{M}]+mk_q\Big]P_m^* .
\end{aligned}
\tag{42}
$$

Equation (42) has the same mathematical form as Eq. (6), with $k_+[\mathrm{A}]$ and k_- replaced by $\bar{n}k[\mathrm{M}]$ and $[1-(\bar{n}/m)]k[\mathrm{M}]$, respectively. Therefore, $P^*(t)$ is obtained by simply replacing $k_+[\mathrm{A}]$ and k_- in Eq. (16) by $\bar{n}k[\mathrm{M}]$ and $[1-(\bar{n}/m)]k[\mathrm{M}]$, respectively:

$$
P^*(t)=P^*(0)\,e^{-k_0t}\left[\frac{(1-s_2)(m-\bar{n}+\bar{n}s_1)}{m(s_1-s_2)}\exp\{-[\bar{n}(1-s_1)/m]k[\mathrm{M}]t\}-\frac{(1-s_1)(m-\bar{n}+\bar{n}s_2)}{m(s_1-s_2)}\exp\{-[\bar{n}(1-s_2)/m]k[\mathrm{M}]t\}\right]^m ,
\tag{43}
$$

where

$$
\begin{aligned}
s_1 &= \frac{1}{2\bar{n}k[\mathrm{M}]}\left(-[(m-\bar{n})k[\mathrm{M}]+mk_q]+\bar{n}k[\mathrm{M}]+\{[(m-2\bar{n})k[\mathrm{M}]+mk_q]^2+4(m-\bar{n})\bar{n}k^2[\mathrm{M}]^2\}^{1/2}\right) ,\\
s_2 &= \frac{1}{2\bar{n}k[\mathrm{M}]}\left(-[(m-\bar{n})k[\mathrm{M}]+mk_q]+\bar{n}k[\mathrm{M}]-\{[(m-2\bar{n})k[\mathrm{M}]+mk_q]^2+4(m-\bar{n})\bar{n}k^2[\mathrm{M}]^2\}^{1/2}\right) .
\end{aligned}
\tag{44}
$$

I/I_0 is similarly obtained by replacing k_- in Eq. (25) by $[1-(\bar{n}/m)]k[\mathrm{M}]$:

$$
\frac{I}{I_0}=m!\,mk_0\left[\frac{(1-s_1)(\bar{n}-m-\bar{n}s_2)}{m(s_1-s_2)}\right]^m\sum_{l=0}^{m}\frac{1}{l!\,(m-l)!}\left[\frac{(1-s_2)(m-\bar{n}+\bar{n}s_1)}{(1-s_1)(\bar{n}-m-\bar{n}s_2)}\right]^l\frac{1}{mk_0+[m(1-s_2)-l(s_1-s_2)]\bar{n}k[\mathrm{M}]} ,
\tag{45}
$$

where s_1 and s_2 are given by Eq. (44).

Similar curves to those in Figs. 1–5 can be obtained by numerically calculating Eqs. (43) and (45).

In Table I we summarize the results on the decay kinetics of excited probes and on the dependence of luminescence intensity on quencher concentration for various migration mechanisms. These results will be useful for analyzing experimental data.

APPENDIX

Here we follow the notations in Infelta *et al.*'s paper.[11] Our criticism of their treatment is concerned with the calculation of $Q(t)dt$, which is the number of moles of P* that disappear during t and $t+dt$ as a result of the quenching action of A. They calculated $Q(t)dt$ in the following way:

The number of moles of A which enter the micelles between t_1 and $t_1 + dt_1$ is given by

$$n[\mathrm{A}]_w[\mathrm{M}]\, dt_1 \ . \tag{A1}$$

The number of moles of A which entered the micelles last between t_1 and $t_1 + dt_1$ and are in the micelles at time t is given by

$$n[\mathrm{A}]_w[\mathrm{M}]\, dt_1 \exp[-k'(t-t_1)] \ . \tag{A2}$$

Then they calculated the number of moles of A which entered the micelles last between t_1 and $t_1 + dt_1$ and are at time t in the micelles *containing* P*. They considered this quantity to be given by

$$n[\mathrm{A}]_w[\mathrm{M}]\, dt_1 \exp[-k'(t-t_1)] \frac{P^*(t)}{[\mathrm{M}]} \ . \tag{A3}$$

They considered the following way to derive Eq. (A3): The number of moles of micelles *containing* P*, which is equal to the number of moles of P* is $P^*(t)$, while the total number of moles of micelles is [M]. Therefore, the probability that A which is in a micelle will be found in a micelle *containing* P* is given by $P^*(t)/[\mathrm{M}]$. This probability is in general given by $R(t)/[\mathrm{AM}]$, where [AM] is the number of moles of A which are in the micelles and $R(t)$ is the number of moles of A which are in the micelles *containing* P*. If the average number of A in a micelle *containing* P* is equal to the average number of A in a micelle which does not contain P*, this probability is, as they considered, given by $P^*(t)/[\mathrm{M}]$. At $t = 0$ the two average numbers are, of course, equal. At $t > 0$ the average number of A in a micelle *containing* P* decreases, because the more A molecules a micelle contains, the faster P* in it decays. Correspondingly, the average number of A in a micelle which does not contain P* first increases. In other words, at $t > 0$ the average number of A in a micelle *containing* P* is smaller than the average number of A in a micelle which does not contain P*. Therefore, the probability that A which is in a micelle will be found in a micelle *containing* P* is not given by $P^*(t)/[\mathrm{M}]$. Accordingly, the number of moles of A which entered the micelles last between t_1 and $t_1 + dt_1$ and are in the micelles *containing* P* at time t is not given by Eq. (A3).

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