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Validity and Limitations of Some Methods and Models Commonly Used in Photophysical Studies of Micellar Systems

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Para avaliar suas validades e limitações, foram analisados dois formalismos usados para interpretar os equilíbrios e a dinâmica em sistemas micelares: 1) o método de Encinas e Lissi (*Chem. Phys. Lett.* **91**, 55 (1982)), usado para obter constantes para o equilíbrio de partição de supressores entre a fase aquosa e a pseudo-fase micelar, e 2) os modelos de Tachiya (*Chem. Phys. Lett.* **33**, 289 (1975) and *J. Chem. Phys.* **76**, 340 (1982)), para obter parâmetros cinéticos e analisar os mecanismos de supressão. É demonstrado que o método de Encinas e Lissi pode ser aplicado desde que: i) a sonda fluorescente esteja contida exclusivamente na fase micelar e sua concentração seja muito menor que a das micelas, e ii) para as micelas sem sonda, o número de agregação e a função de distribuição do surfactante sejam constantes em todo o intervalo no qual são variadas as concentrações de surfactante e supressor. Também é demonstrado que o método da função geradora de Tachiya só oferece soluções analíticas quando todas as constantes de velocidade que envolvem sonda e supressor em uma micela são independentes de, ou estão relacionadas linearmente com, o número de moléculas de supressor na micela. Através da comparação das velocidades de intercâmbio com as velocidades de supressão, são estabelecidas as condições para as quais os sistemas micro-heterogêneos podem apresentar um comportamento *quase*-homogêneo. Isto é deduzido para uma função de distribuição geral de moléculas de supressor. Os resultados são aplicados aos sistemas ftalocianina de zinco-oxigênio-quinonas em água.

Two formalisms commonly used to interpret equilibrium and dynamics in micellar systems are analyzed regarding their validity and limitations. 1) The method of Encinas and Lissi (*Chem. Phys. Lett.* **91**, 55 (1982)) to obtain partition equilibrium constants for quencher molecules between the aqueous phase and the micellar pseudophase. 2) The models of Tachiya (*Chem. Phys. Lett.* **33**, 289 (1975) and *J. Chem. Phys.* **76**, 340 (1982)) to obtain kinetic parameters and analyze quenching mechanisms. On the basis of detailed balance it is demonstrated that the method of Encinas and Lissi can be applied without any assumption on the quenching mechanism, as long as: i) the fluorescent probe is exclusively contained in the micellar phase and the probe concentration is much lower than that of the micelles, and ii) for micelles free of probe molecules, the micellar aggregation number and surfactant distribution function are constant over the whole range where the concentrations of both surfactant and quencher are varied. It is also demonstrated that the generating function method used by Tachiya will only render analytical solutions for cases where all the rate constants involving probe and quencher in a micelle are either independent or linearly related to the number of quencher molecules in a micelle. Through comparison of the exchange rates with the quenching rates, conditions are established for a microheterogeneous system to behave as *quasi*-homogeneous. This is deduced for a general distribution function of quencher molecules. The results are applied to the system zinc phthalocyanine-CTAB-oxygen-diphenylisobenzofurane in water.

Keywords: *micelles, photophysics, singlet molecular oxygen*

Introduction

Photochemical reactions in compartmentalized systems have been extensively studied as they serve as models for reactions in biological environments[1] or microheterogeneous polymerization[2]. Various reactions mechanisms have been investigated and a large number of models have been developed for excited state quenching[3-6]. Different situations can be found as excited state and quencher can be partitioned between the continuous phase and the microheterogeneous pseudophase[5,7], and the increase in local concentration can induce complex formation[8] and simultaneous quenching of excited states of very different intrinsic lifetimes[9].

Excited state deactivation can be used also to study location of molecules in microenvironments[10] and partition of a substance between the two phases[11]. All these subjects have been extensively studied and reviewed[12].

In previous works we studied the singlet oxygen sensitization by carboxylated zinc phthalocyanine (ZnTCPc)[13] as well as the singlet and triplet quenching by electron transfer to quinones[14], both in hexadecyl trimethylammonium chloride (CTAC) and bromide (CTAB) micelles. Widely accepted formalisms were used in these studies for the quantification of the observed results: i) the method of Encinas and Lissi[11] for the evaluation of equilibrium data, and ii) the model developed by Tachiya for the case of Poisson distribution statistics of quencher molecules in the micelles[4], to interpret the dynamic aspects.

This work deals with the conditions under which a microheterogeneous system can be analyzed using the above cited methods and models, their validity and limitations, and the limits under which such systems can be treated as *quasi*-homogeneous.

Distribution Functions

The general validity of the method of Encinas and Lissi[11] to determine partition equilibrium constants of a quencher between micellar and aqueous phases, K_p, and its limitations are analyzed in this section. It will be demonstrated that its validity rests only on the following assumptions:

I. the fluorescent probe is exclusively contained in the micellar phase and the probe concentration is much lower than that of the micelles, and

II. for micelles free of probe molecules, the micellar aggregation number and surfactant distribution function among micelles remain constant over the whole range of surfactant and quencher concentrations used.

Conditions under which assumption (I) holds are easily attainable in practice. They imply normally that no micelles will contain more that one probe molecule. Thus the only real limitation of the method is the validity of assumption (II). So far as assumption (II) holds, the method is valid irrespective of the equilibrium and dynamic properties of the micelles containing probe molecules, that is of the probe nature and its interaction with both surfactant and quencher, and of the dynamics through which the quencher equilibrium is attained in micelles not containing a probe.

In what follows, subscripts *m* and *w* stand for concentrations in the micellar pseudophase and water, respectively. Square brackets represent concentrations referred to the total volume of the sample.

The quencher mass balance leads to the key equation of the method,

$$[Q]_t = \langle n \mid 0 \rangle .[Mic] + \langle n \mid 0 \rangle / K_p \quad (1)$$

where $[Q]_t$ is the overall quencher concentration, [Mic] the concentration of micelles, $\langle n \mid 0 \rangle$ the mean number of quencher molecules in probe-free micelles, *i.e.*, most of the micelles according to assumption (I), and

$$K_p = \frac{[Q]_m}{[Q]_w[Mic]} = \frac{\langle n \mid 0 \rangle}{[Q_w]} \quad (2)$$

We will analyze the conditions under which $[Q]_t$ and [Mic] are linearly related.

A set of, in principle, unknown exchange rate constants $k_+^{n|0}$ and $k_-^{n+1|0}$ can be assigned to the processes:

$$M^{n|0} + Q_w \xrightarrow{k_+^{n|0}.[Q]_w} M^{n+1|0}$$

$$M^{n+1|0} \xrightarrow{k_+^{n+1|0}} M^{n|0} + Q_w$$

where $M^{n|0}$ is a micelle containing *n* quencher molecules and no probe. If $P_{n|0}$ is the conditional probability that a micelle will contain *n* quencher molecules and no probe, $\langle n \mid 0 \rangle$ will be a function of $[Q]_w$ depending parametrically on all $K_j = k_+^{j-1|0} / k_-^{j|0}$, ($K_0 = 1$) as:

$$\langle n \mid 0 \rangle = \sum_{n=0}^{\infty} n.P_{n|0} = g([Q]_w) \quad (3)$$

Equation 3 allows to identify those systems having the same $\langle n \mid 0 \rangle$ values as those having the same quencher concentration in the aqueous phase. Note that in the general case K_p may depend on $\langle n \mid 0 \rangle$. A plot of $[Q]_t$ *vs.* [Mic] will be linear for those systems having the same $[Q]_w$. Here lays the potentiality of the method to infer the actual distribution function of Q. This conclusion is independent of whether the exchange equilibrium is attained by Q migration through the aqueous phase, as assumed before, or through direct micellar exchange of Q. In the latter case, the exchange rate constants are a function of the K_j's already used.

Fluorescence quenching may be used to identify the systems with constant $[Q]_w$. However, it may be seen that any procedure leading to the same result, say a chemical or electrochemical method, would be equally valid.

The fluorescence intensity is:

$$I_f = \sum I_n.\Phi_f^n \quad (4)$$

where I_n is the photonic flux absorbed by a probe molecule in a micelle containing n quencher molecules and ϕ_f^n is the fluorescence quantum yield under the same conditions. The first quantity can be expressed as:

$$I_n = I_a \; P_{n|1} \tag{5}$$

where I_a is the overall absorbed photonic flux, and $P_{n|1}$ is the conditional probability that a micelle occupied by n quencher molecules contains a fluorescent probe. Equation 5 holds as long as the absorption coefficient of the probe does not depend on n. However, this assumption can be easily removed.

The conditional probability $P_{n|1}$ depends on all the equilibrium constants $k_+^{j-1|1} / k_-^{j|1}$, $j = 1,2,...$, while ϕ_f^n depends on $k_f^{n|1}$, $k_{nr}^{n|1}$, $k_q^{n|1}$, $k_+^{n|1}$, $k_-^{n|1}$, where subindexes *f*, *nr* and *q* refer to fluorescence, non-radiative and quenching rate constants respectively. Accordingly, the ratio I_f / I_a depends only on $[Q]_w$:

$$I_f/I_a = f([Q]_w) \tag{6}$$

and rate constants characteristic of micelles containing one probe molecule. Any interaction existing between probe and quencher is taken into account. The equilibrium in probe free micelles determines $[Q]_w$, which in turn determines the mean occupation of Q in micelles containing one probe. For this to be true, either $P_{n|0}$ and $P_{n|1}$ are the same or assumption (I) assures that the perturbation is negligible. Assumption (II) is used implicitly as it assures constancy of all the quencher exchange rate constants, irrespective of surfactant and quencher concentrations. This demonstrates that within assumptions (I) and (II), and no other, samples showing constant I_f / I_a satisfy Eq. 1 with constant $\langle n \mid 0 \rangle$ and K_p. A curvature on the plot $[Q]_t$ *vs.* [Mic] may be a sign of breakdown of assumption (II).

It should be noted that the method can be applied as well if the fluorescent probe is confined to the aqueous phase. In this case Eq. 6 also holds and assumption (I) is no longer necessary.

If the probe is contained in the micellar phase, the method may be of no use at high occupation numbers, even if the surfactant statistics are not influenced by the quencher. For example, a system in which the quencher enters the micellar phase up to a saturation limit will show Stern-Volmer plots converging to an upper constant, which does not depend on the micellar concentration, as the quencher concentration increases. The method cannot be used near to the limit where a further increase in quencher concentration does not result in an increase in I_{f0}/I_f. Of course, this situation does not appear if the quencher is contained in the aqueous phase.

Basic mechanism and models

The following mechanism will be considered:

$$S_n + h\upsilon \xrightarrow{I_{an}.\phi_n} {}^*S_n$$

$${}^*S_n \xrightarrow{k_0^n} S_n \; (+h\upsilon)$$

$${}^*S_n \xrightarrow{k_q^n} S_n \text{ or products}$$

$${}^*S_n + Q_w \xrightarrow{k_+^n.[Q]_w} {}^*S_{n+1}$$

$${}^*S_n \xrightarrow{k_-^n} {}^*S_{n-1} + Q_w$$

In this scheme, S_n and ${}^*S_n$ (replacing the notation $M^{n|1}$, ${}^*M^{n|1}$) represent a sensitizer, either in the ground state or in an excited state, respectively, in a micelle containing n quencher molecules; ϕ_n is 1 for singlet state and ϕ_{isc} for triplet excited state, respectively. k_0^n includes radiative and non radiative deactivation. k_q^n is the total quenching rate constant for the excited state, associated with product formation, which may include energy transfer.

According to the dependence of the exchange rate constants on the number of quencher molecules, different models can be worked out to account for the system equilibrium distribution function and dynamics. Tachiya developed analytical expressions for two simple models: 1) non-interacting quenchers, leading to a Poisson equilibrium distribution[4], and 2) non-interacting quenchers with a saturation limit, leading to a binomial distribution[6]. Daraio *et al.* extended model (1) to the simultaneous quenching of singlets and triplets. The relevant variables to obtain the excited state decay are P_n, the probability that a micelle with an excited probe will contain n quencher molecules. A common feature is the change of the initial quencher equilibrium distribution, $P_n(t = 0)$ (equal to $P_{n|1}$) into a non-equilibrium distribution, $P_n(t)$, depending on the value of the quenching constants.

The response of the system to a light pulse can be quite generally obtained by solving the set of coupled rate equations:

$$\frac{d[{}^*S_n]}{dt} = k_+^{n-1}.[Q]_w.[{}^*S_{n-1}] + k_-^{n+1}.[{}^*S_{n+1}] - \\ -(k_0^n + k_+^n.[Q]_w + k_-^n + k_q^n).[{}^*S_n] \tag{7}$$

where it should be taken into account that some constants are excluded from the balance for $n = 0$ and, in the case of quencher saturation, for $n = n_{max}$.

On solving the preceding system of equations, a generating function[4] may be defined:

$$F(t,R) = \sum_n R^n \cdot [{}^*S_n](t) \tag{8}$$

where the summation extends over all possible values of the occupation number n. $\partial F/\partial t$ is expressed as a function of F and $\partial F/\partial R$. It may be shown that for a first order partial differential equation to be obtained, the rate constants k_0^n, k_+^n, k_-^n, and k_q^n should be linear functions of n as it occurs

in the models already described (see above). As soon as higher powers of n appear, higher derivatives $\partial^k F/\partial R^k$ arise and the solution of the problem becomes more involved. The Poisson and the binomial models are the only realistic ones that satisfy the condition of linearity, so no other model is expected to yield a simple analytical solution by this method.

The time dependent solution of the mechanism in the Poisson limit is:

$$[^*S] = [^*S]_0.\exp[-(k_0 + \alpha.k_-<n>)t - \\ - <n>\alpha^2(1 - e^{-\gamma.t})] \quad (9)$$

$$\alpha = k_q/\gamma; \quad \gamma = k_q + k_-$$

where <n> coincides with <n | 0> and k_0 is taken as a constant.

For the binomial distribution the corresponding expressions can be found elsewhere[6]. At low occupation numbers, $n << n_{max}$, the two models are indistinguishable.

It may be readily demonstrated that the mechanism will yield linear Stern-Volmer plots if Eq. 9 approaches monoexponential behavior[15]. This requires, in turn, that the second term in the exponential vanishes. In this case [*S] decays with a pseudo-first order rate constant:

$$k_{uni} = k_0 + \alpha.k_-.<n> \quad (10)$$

This situation can be reached even at short times when $k_- >> k_q$, which means that quenchers exchange repeatedly between micelles before any quenching process occurs. In this case, the product $\alpha.k_-$ becomes equal to k_q. This means also that the quencher distribution within micelles containing a probe molecule does not change with time, remaining always equal to the initial distribution, which is also equal to the equilibrium distribution in probe-free micelles.

In the opposite case, when $k_- << k_q$ (closed micelles) or $k_- \approx k_q$, the quencher distribution in micelles containing an excited probe varies with time, as excited states with greater n are preferentially removed, and curved Stern-Volmer plots are obtained.

The monoexponential behavior in the fast exchange limit holds independently of the functionality of k_q^n on n. This can be easily demonstrated taking into account the rate expressions of Eq. 7 and summing over all possible values of n. In this way, the overall rate of excited state decay is obtained as:

$$k_{uni} = \frac{1}{[^*S]}\frac{d[^*S]}{dt} = \frac{1}{[^*S]}\cdot\sum_{n=0}^{\infty}\frac{d[^*S_n]}{dt} = \\ = -(k_0 + <k_q>(t)) \quad (11)$$

$$<k_q>(t) = \sum_{n=0}^{\infty} k_q^n \cdot \frac{[^*S_n](t)}{[^*S](t)} \quad (12)$$

Equation 11 is a generalization of Eq. 10. If $<k_q>(t)$ is time independent, then the decay will be monoexponential. For this to be true, the fraction $[^*S_n]/[^*S]$ should not depend on time, as we stated above. This last statement means that the mean occupation number of Q in excited state containing micelles, is equal to the initial value. The microheterogeneity nature of the system is still present in the mean value $<k_q>$ of Eq. 12.

Singlet oxygen sensitization by phthalocyanines in CTAB micelles

For singlet oxygen sensitization by ZnTCPc (S) using 1,3-diphenylisobenzofuran (DF) as singlet oxygen scavenger, we found that the kinetic data could be interpreted by the standard *quasi*-homogeneous mechanism[13,16], which yields for the singlet oxygen generation quantum yield, ϕ_Δ, and the rate of DF consumption:

$$\Phi_\Delta = \frac{\Phi_{isc}.S_\Delta.k_{O2}.[^3O_2]_t}{k_3 + k_{O2}.[^3O_2]_t} \quad (13)$$

$$(-\frac{d[DF]}{dt})^{-1} = \frac{1}{I_a.\Phi_\Delta}.(1 + \frac{\beta}{[DF]}) \quad (14)$$

$$\beta = k_d/k_r \quad (15)$$

where k_3 represents the triplet state decay rate constant. The rate constants: k_{O2} (for reaction of ^3S and $^3O_2$), and k_r (for reaction of DF with singlet oxygen) are dependent on the surfactant concentration. Both S and DF are fully incorporated into the micellar pseudophase.

Microheterogeneity is included in the mechanism in two ways: first, the sensitizer is quenched in micelles by ground state molecular oxygen, which is partitioned between the micelles and water; second, singlet molecular oxygen, which is also partitioned between the two phases, reacts with DF in the micelles. Because of the mean occupation number of S and DF, the probability that a single micelle contains the two substances is negligible[13], of the order of 1/1000. So singlet oxygen has to migrate from its production site to its reaction site[17-19].

Occupation of the micelles by ground state molecular oxygen

Lee and Rodgers[16] found that the partition equilibrium constant for singlet molecular oxygen between aqueous and CTAB phases is:

$$K_\Delta^{'} = \{^1O_2\}_m / \{^1O_2\}_w = 4 \quad (16)$$

In Eq. 16 the keys represent concentrations referred to true phase volumes, either micelles or water. If we define f as the ratio between the micellar and the total volume, then $f = \langle m \rangle . V_m . [Mic]$, where V_m is the surfactant molar volume. For CTAB 0.1 M, considering $\langle m \rangle = 90$ [20] and $V_m = 0.365$ L/mol [21], we calculate $f = 0.0365$. For $f << 1$ the value in Eq. 16 can be converted into an equilibrium constant expressed as a function of concentrations referred to total volume:

$$K_\Delta = \frac{[^1O_2]_m}{[^1O_2]_w[Mic]} = \frac{1}{[Mic]} \cdot \frac{\{^1O_2\}_m}{\{^1O_2\}_w} \cdot \frac{f}{1-f} \cong$$

$$\cong K'_\Delta \cdot \langle m \rangle \cdot V_m \cong 130\ M^{-1} \quad (17)$$

If we consider the oxygen concentration in 0.1 M CTAB, 3.15×10^{-4} M [22], and the value for the partition constant for ground state oxygen, $K'_G = 2.8$ [22], the mean occupation number of oxygen in the micelles is $\langle n \rangle_{O2} = K'_G . \langle m \rangle . V_m . [^1O_2]_w = 0.026$. With this later value in mind, we can safely neglect multiple occupation of a micelle by oxygen.

Generation of singlet molecular oxygen by ZnTCPc

As oxygen does not quench the ZnTCPc singlets, the triplet quenching by oxygen can be also described by Eq. 9. The fraction of triplets which produce singlet oxygen, F, is:

$$F = \int_0^\infty S_\Delta \cdot \frac{[^3S](t)}{[^3S]_0} \cdot \sum_{n=0}^{\infty} k_q^n \frac{[^3S_n](t)}{[^3S](t)} \cdot dt \quad (18)$$

from which, under the assumption of rapid equilibration and $k_q^n = n.k_q$:

$$\Phi_\Delta = \frac{\Phi_{isc} \cdot S_\Delta \cdot k_q \cdot \langle n \rangle_{O2}}{k_3 + k_q \cdot \langle n \rangle_{O2}} \quad (19)$$

By comparing Eqs. 13 and 19 and taking into account Eq. 17 and the discussion about its applicability to ground state oxygen, we obtain an interpretation of the *quasi*-homogeneous rate constant for the reaction of ground state oxygen with a triplet sensitizer:

$$k_{O2} = \frac{k_q \cdot \langle n \rangle_{O2}}{[^3O_2]_t} = \frac{k_q \cdot K_G}{1 + K_G \cdot [Mic]} \quad (20)$$

If we take the value of $2 \times 10^9\ M^{-1}\ s^{-1}$ for k_{O2} in CTAB 0.1 M [23,24], considering K_G to be 92 M^{-1}, obtained from K'_G as in Eq. 17, a value of *ca.* $2 \times 10^7\ s^{-1}$ is calculated for the first order intramicellar rate constant k_q. This value can be compared with $k_- = 2 \times 10^8\ s^{-1}$ [25], which assures that partition equilibrium is attained.

Reaction of singlet oxygen with DF

The following mechanism can account for singlet oxygen decay in the presence of DF in micelles:

$$^1O_2)_w \xrightarrow{k_+.[^1O_2]_w} {}^1O_2)_m$$

$$^1O_2)_m \xrightarrow{k_m} {}^1O_2)_w$$

$$^1O_2)_w \xrightarrow{k_{ext}} {}^3O_2)_w$$

$$^1O_2)_m \xrightarrow{k_{int}} {}^3O_2)_m$$

$$^1O_2)_m \xrightarrow{k_r^m.n_{DF}} \text{Products}$$

where k_r^m is the unimolecular rate constant for reaction of singlet oxygen with one DF molecule in a micelle.

The first order rate constant of $[^1O_2]_t$ decay can be calculated in the *quasi*-homogeneous approximation as:

$$k_d = \frac{1}{[^1O_2]_t} \cdot \frac{d[^1O_2]_t}{dt} = \frac{1}{[^1O_2]_t} \cdot \left[\frac{d[^1O_2]_m}{dt} + \frac{d[^1O_2]_w}{dt}\right] =$$

$$= (k_{int} + k_r^m \langle n \rangle_{DF}) \cdot \frac{[^1O_2]_m}{[^1O_2]_t} + k_{ext} \cdot \frac{[^1O_2]_w}{[^1O_2]_t} \quad (21)$$

If we replace the two concentration ratios in Eq. 21 as a function of K'_Δ using Eqs. 16 and 17 it follows:

$$k_d = \frac{K'_\Delta \cdot f \cdot (k_{int} + k_r^m \langle n \rangle_{DF}) + (1-f) \cdot k_{ext}}{(1-f) + K'_\Delta \cdot f} =$$

$$= \frac{K_\Delta [Mic] \cdot (k_{int} + k_r^m \langle n \rangle_{DF}) + k_{ext}}{1 + K_\Delta [Mic]} \quad (22)$$

This equation has been already obtained [16,26]. It is interesting to note that it holds as long as equilibrium is maintained for the distribution of $^1O_2$. This is evidenced by the presence of K'_Δ.

On the other hand, the rate of DF consumption is:

$$-\frac{d[DF]}{dt} = k_r^m \cdot [^1O_2]_m \cdot \langle n \rangle_{DF} =$$

$$= k_r \cdot [^1O_2]_t \cdot [DF] \quad (23)$$

Under steady state conditions, $[^1O_2]_t$ is given by:

$$[^1O_2]_t = \frac{I_a \Phi_\Delta}{k_d} \quad (24)$$

with k_d given by Eq. 22. If we replace Eq. 24 in Eq. 23, we obtain an expression for the rate of consumption of DF which is of the same form as Eq. 14:

$$\left(-\frac{d[DF]}{dt}\right)^{-1} = \frac{1}{I_a \cdot \Phi_\Delta} \cdot \left(1 + \frac{\beta'}{[DF]}\right) \quad (25)$$

$$\beta' = \frac{(K'_\Delta \cdot f \cdot k_{int} + (1-f) \cdot k_{ext}) \cdot [Mic]}{K'_\Delta \cdot f \cdot k_r^m} \quad (26)$$

Finally, by working with the last equality of Eq. 23, we obtain the relationship between k_r and k_r^m, taking into account Eq. 17:

$$k_r = k_r^m \cdot K_\Delta / (1 + K_\Delta \cdot [Mic]) \quad (27)$$

In 0.1 M CTAB, $k_{ext} = 2.5 \times 10^5\ s^{-1}$ and $k_{int} = 4.0 \times 10^4\ s^{-1}$ [16], and the first term in the numerator of Eq. 26 is negligible. If we consider the experimental value range for $\beta' = 1$ to $3 \times 10^{-4}\ M$[13], we obtain $k_r^m = 0.6$ to $1.8 \times 10^7\ s^{-1}$. This can be compared with a value of $5.7 \times 10^6\ s^{-1}$ calculated from Eq. 27 considering $k_r = 6.5 \times 10^8\ M^{-1}\ s^{-1}$ [23].

Discussion

The validity of the *quasi*-homogeneous mechanism can now be tested. For it to be applicable, $k_q << k_-$ is needed (see Section 3). For the quenching of the sensitizer triplet state by oxygen, it should be noted that as $\langle n \rangle_{O2} << 1$ (see *Basic mechanism and models* Section), no assumptions on the oxygen distribution statistics and on the dependence of k_q on *n* are needed. Thus, Eq. 20 may be applied regardless of the statistics followed. The exit rate constant of ground state oxygen from a CTAB micelle is $2 \times 10^8\ s^{-1}$ [25]. This has to be compared with our estimation of $2 \times 10^7\ s^{-1}$ for the reactive rate constant. The difference should be large enough to assure an equilibrium distribution for ground state oxygen. So far as we worked at a single micellar concentration and at only one oxygen concentration (air saturated solutions), the difference between a microheterogeneous system and a homogeneous one is impossible to appreciate: this is equivalent to obtaining a Stern-Volmer constant with only one quencher concentration. Of course, the second order rate constants obtained depend on the micellar concentration. The results obtained cannot be extended to other oxygen concentrations before a thorough study of the dependence of ϕ_Δ on $[O_2]_t$ is made.

For the reaction between DF and singlet oxygen the fast equilibration limit for singlet oxygen must be valid for a *quasi*-homogeneous formalism to apply, as the discussion following Eq. 22 demonstrates. The exit of singlet oxygen from a micelle takes place with a rate constant of the order of $k_- = 5 \times 10^7\ s^{-1}$ [27] and the intramicellar decay occurs mainly by the reaction with DF with a rate constant of the order of $5 \times 10^6\ s^{-1}$, ($k_{int} = 4.0 \times 10^4\ s^{-1}$ provides a minor deactivation channel). Therefore, the exit rate is greater than the overall internal decay rate. At the same time, the pseudo-unimolecular singlet oxygen entrance rate constant is $k_+ [Mic] = k_- K [Mic]^* \approx 6 \times 10^6\ s^{-1}$, greater than $k_{ext} = 2.5 \times 10^5\ s^{-1}$. Under these conditions the singlet oxygen equilibrium distribution is clearly preserved.

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