

Toward a Hydrodynamic Description of Bimolecular Collisions in Micelles. An Experimental Test of the Effect of the Nature of the Quencher on the Fluorescence Quenching of Pyrene in SDS Micelles and in Bulk Liquids

Radha Ranganathan,* Carolina Vautier-Giongo, and Barney L. Bales

Department of Physics and Astronomy and The Center for Supramolecular Studies,
California State University at Northridge, Northridge, California 91330

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The simple hydrodynamic description of bimolecular collision rate constants afforded by the Stokes–Einstein–Smoluchowski (SES) equation is tested in a bulk liquid as well as in sodium dodecyl sulfate micelles. Fluorescence quenching of pyrene by three different quenchers is used as a model to study collision rate constants. One quencher is itself a cationic surfactant, one an uncharged long alkyl chain labeled with a nitroxide, and the third an uncharged aromatic compound. The SES equation is found to give a remarkably good description of the fluorescence quenching rate constant not only in bulk but also in micellar media. The fluorescence quenching rate constant is independent of the type of quencher and varies with temperature, viscosity (microviscosity in the case of micelles), and quencher concentration in accordance with the SES equation. A zero-order model of diffusion in micelles is introduced in which pyrene and quencher diffuse through the polar shell. The microviscosity of the shell is deduced from electron spin resonance measurements of one of the quenchers, which is also a nitroxide spin probe. The probability of quenching upon collision between reacting pairs is on the order of order unity in both bulk and micellar media. The observed slight departure of this probability from unity in the case of micelles is discussed and arguments show it to be accommodated by minor adjustments to the zero-order model.

Introduction

In recent papers, we have begun to test a hydrodynamic theory of bimolecular collisions in micelles using the quenching of pyrene fluorescence as the experimental model.^{1–3} The basis for the test of the theory is the Stokes–Einstein–Smolulchowski (SES) equation,^{4,5} which gives the rate constant for diffusion-controlled collisions (k_D) between two types of molecules, A and B in solution, as follows:

$$k_D = \frac{8RT}{3000\eta} \quad (1)$$

where $R = 8.31 \times 10^7$ erg/K is the gas constant, T the absolute temperature, and η the shear viscosity of the solution. The rate constant k_D is given in units of L/mol s when η is in units of poise. The rate constant of quenching is given by

$$k_q = Pk_D C_Q \quad (2)$$

where C_Q is the effective concentration of the quenchers in mol/L and P is the probability of quenching upon collision.

In view of some rather radical assumptions,⁴ eq 1 is already remarkable when applied to collisions in normal, homogeneous liquids, being independent of any property of either A or B. In particular, the size of the diffusing molecules does not enter, leading Debye⁶ to refer to eq 1 as “a peculiar but well-known result in colloid chemistry”. Thus, according to eq 1, all molecular pairs would collide with the same rate constant. If eq 1 is remarkable in normal liquids, then its application to

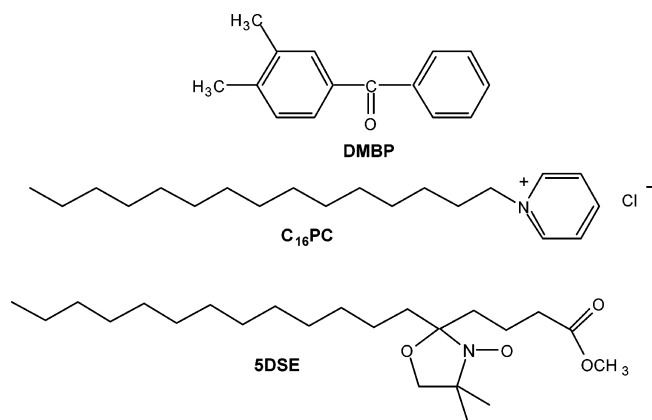
severely restricted geometric constraints of a micelle is suspicious at best. Nevertheless, preliminary work shows^{1–3} that eq 1 describes fluorescence quenching of pyrene in micelles rather well. The dependence of the linearity of the fluorescence quenching rate constant on T/η in micelles has been studied with varying the viscosity by (1) mixing a nonionic surfactant with sodium dodecyl sulfate (SDS)¹ and (2) varying the temperature.^{1,3} The proper dependence of the rate constant on the concentration of the quencher, C_Q , has been verified by varying the size of SDS, dodecyl trimethylammonium bromide (DTAB), and chloride (DTAC) micelles.³ Reekmans et al.⁷ studied the effect on k_q of changing micelle size by adding alkanes and alcohols. Croonen et al.⁸ studied the influence of NaCl. The size of the micelle enters indirectly because the rate constant of collisions depends on the quencher concentration, which is determined by the volume through which they diffuse. It is important to bear in mind that the effective concentration of the quencher in a micelle, C_Q , is very different from the concentration of the quencher $[Q]$ computed using the entire sample volume.

The purpose of this work is 3-fold: (1) to further test eqs 1 and 2 in micelles, with particular emphasis on varying the nature of the colliding pair, (2) to test eqs 1 and 2 in bulk liquid and determine the quenching probability P (a quenching probability P emerges from eqs 1 and 2 when applied to micelles that are dependent on the model of diffusion employed), and (3) to lend support for a simple model^{1,3} in which all quenchers and pyrene diffuse through the polar shell as detailed below. Three very different quenchers with structures as in Scheme 1 are employed.

DMBP and 5DSE are sparingly soluble in water, as is pyrene. Thus to a good approximation the quenchers encounter pyrene

* To whom correspondence should be addressed. E-mail: radha.ranganatha@csun.edu.

SCHEME 1



in the micelle environment. C₁₆PC is itself a surfactant. We take advantage of the fact that nitroxide spin probes are excellent quenchers of pyrene⁹ and employ 5DSE as a quencher. None of the three quenchers show appreciable migration from one micelle to another during the lifetime of pyrene as discussed below. The viscosity in eq 1 is estimated from the rotational correlation time of 5DSE, incorporated into the micelles, measured by EPR.¹⁰ The quenching rate constant, k_q , is measured by time-resolved fluorescence quenching (TRFQ).

Theory

Time-Resolved Fluorescence Quenching (TRFQ). The quenching rate constant, k_q , has been of interest in theoretical investigations because it can be measured experimentally and models the reaction rate constant between solubilized reactants in micelles. Fluorescence quenching in globular micelles has been observed to be a first-order kinetic process, that is, the fluorescence decay due to a single quencher is described very well by an exponential decay, $\exp(-k_q t)$, thus defining a first-order quenching rate constant, k_q .^{11,12} Assuming that the quenching rate constant due to n quenchers in a micelle is nk_q and that the quenchers are distributed randomly among the micelles (Poisson distribution) leads to the Infelta–Tachiya equation for the time-dependent fluorescence decay, $F(t)$.^{13–15} Under the conditions that probes and quenchers do not migrate between micelles during of the lifetime of the excited probe,¹⁵ the Infelta–Tachiya equation becomes

$$F(t) = F(0) \exp\{-k_0 t + \langle N_q \rangle [\exp(-k_q t) - 1]\} \quad (3)$$

The quantity $F(0)$ denotes the initial fluorescence intensity, k_0 is the decay rate constant of excited probe in a micelle when no quenchers are present, and $\langle N_q \rangle$ is the average number of quenchers per micelle given by

$$\langle N_q \rangle = \frac{[Q]}{[M]} \quad (4)$$

where $[Q]$ is the total molar quencher concentration in solution and $[M]$ is the micelle molar concentration. Equation 4 tacitly assumes that a negligible concentration of quenchers partition into the aqueous phase. A fit of eq 3 to the fluorescence decay data yields k_q and $\langle N_q \rangle$.

The Smoluchowski Equation. If quenching occurs only upon a collision encounter (contact) between the probe and quencher, then the Smoluchowski or absorption boundary condition prevails.^{16–18} In the Smoluchowski derivation, a particle is assumed fixed in space at the center of a sphere of influence

and the collision rate is the arrival rate of particles on this sphere.^{16,19} The result for the probe–quencher collision rate constant is

$$k_D = 4\pi R_{pq} D \quad (5)$$

where D is the mutual diffusion coefficient of the probe and quencher and R_{pq} is the radius of the sphere of influence around the probe. The Stokes–Einstein equation for the diffusion coefficient, D_q , of a quencher molecule of radius R_q in a medium of viscosity η is¹⁹

$$D_q = \frac{RT}{6\pi\eta N_0 R_q} \quad (6)$$

where N_0 is the Avogadro number. A similar expression holds for the diffusion coefficient D_p for a probe molecule. The mutual diffusion coefficient D is the sum of D_p and D_q . Taking R_{pq} to be the sum of the radii of probe and quencher, assumed to be of the same radius, yields eq 1 for the bimolecular collision rate constant, k_D . The assumption of equal radii for the two diffusing particles is not very restrictive. For example, a factor of 4 difference in their radii results in less than a 50% error in the prediction of eq 1.⁵ The quenching rate constant, k_q , is then given by the product of the bimolecular collision rate constant and the concentration of the quencher (eq 2). The quenching rate constant in a bulk solvent is given by

$$k_q = P k_D [Q] \quad (7)$$

Application of the SES Equation to Micelles. In a bulk liquid, the computation of the quencher concentration, $[Q]$, is straightforward, the viscosity is uniform throughout the sample, and both the quencher and pyrene diffuse through the entire volume of the sample. Thus, the only remaining parameter in eq 2 is the probability of quenching, P . In a micelle, the situation is far more interesting. First, the quencher concentration, C_Q , depends on the volume through which the quencher diffuses which is very likely different from the micelle volume. Second, the viscosity is very unlikely to be uniform throughout the micelle. Third, the volume through which the quencher and pyrene diffuse could be different. This last possibility would decrease the deduced value of P in eq 2 because quenching can occur only within the overlap of the two volumes. Similar ideas were discussed by Dederen et al.²⁰ and Van der Auweraer et al.²¹

A zero-order model of the application of eq 2 to micelles assumes the following:

1. A simple approximately spherical core–shell model describes the SDS micelle. This model, advanced by Hartley,^{22,23} has stood the test of countless experiments; in fact, the claim was already made 20 years ago²⁴ that “the overwhelming majority of experimental and theoretical studies have confirmed the classical picture”, thus we consider the basic model to be sound. In addition to a wealth of other support,²⁴ the agreement between theoretical and experimental results on the hydration of micelle surfaces supports the model.^{25–27}

2. Pyrene and all quenchers diffuse throughout the volume of the polar shell and nowhere else. Almgren et al.²⁸ showed that aromatic probes and aromatic or ionic quenchers reside preferentially in the polar shell. This assumption is a reasonable zero-order approximation for the quenchers considered here and is supported by the results themselves. Since one of the quenchers is itself a spin probe used to measure the microviscosity, assumption 2 leads immediately to assumption 3.

3. The spin probe diffuses throughout the volume of the polar shell and nowhere else and thus reports a viscosity which is the average of the zone through which pyrene and the quenchers diffuse.

In the zero-order model the volume in which the reactants diffuse is

$$V_{\text{shell}} = \frac{4}{3}\pi\{R_m^3 - R_c^3\} \quad (8)$$

for a micelle of radius R_m and a core radius R_c . The hydrocarbon core volume of a micelle of aggregation number N is NV_{tail} , where V_{tail} is the volume of the alkyl chain embedded in the core, so that R_c is

$$R_c = \left\{ \frac{3}{4\pi} NV_{\text{tail}} \right\}^{(1/3)} \quad (9)$$

R_m and R_c differ by the thickness of the polar shell, which includes headgroups, counterions, and hydration water. We take $R_m - R_c = 5 \text{ \AA}$ as determined by high-resolution small-angle neutron scattering.²⁹ Recalling that k_q is the quenching rate constant due to a single quencher, the quencher concentration, C_Q , is thus due to one molecule in volume V_{shell} , so that

$$C_Q = \frac{10^{27}}{N_0 V_{\text{shell}}} \quad (10)$$

where V_{shell} is in \AA^3 and the factor 10^{27} converts V_{shell} from \AA^3 to liters. To determine C_Q , it is necessary to measure N .

Materials and Methods

The quenching rate constants of pyrene fluorescence due to the quenchers (see Scheme 1) 3,4-dimethylbenzophenone (DMBP), cetylpyridinium chloride ($C_{16}PC$), and 5-doxysearic acid methyl ester (5DSE) were determined by TRFQ methods. Pyrene, DMBP, $C_{16}PC$, and 5DSE were obtained from Sigma-Aldrich. Pyrene was purified by recrystallization from ethanol. A 25 mM stock solution of the pyrene was prepared and stored in the freezer. An aliquot of the pyrene solution sufficient to provide about 0.01 molecules of pyrene per micelle was added to a vial and the solvent evaporated by a slow stream of dry N_2 gas. A 50 or 100 mM solution of SDS was added to the vial and gently stirred for 24 h. Methanol (Fluka Chemicals) was the medium for measurements of k_q in bulk. A fourth quencher 16DSE (Sigma-Aldrich), consisting of the nitroxide label at the 16th carbon of the alkyl chain, was also employed in the case of methanol. Micellar k_q was determined for SDS micelles in water. The detergent SDS (purity >99%) was from Lancaster Synthesis, Inc. Nanopure water from Sybron/Barnstead Nanopure II was used as the solvent. The two detergent concentrations, $[SDS] = 50$ and 100 mM , in the absence of added sodium chloride yield two different aggregation numbers. Further micelle size variation was obtained by adding sodium chloride (analytical reagent grade from Fisher) to the SDS solution. All materials other than pyrene were used as received. The quencher concentration was varied in the range of 0.3–1.0 molecules per micelle.

TRFQ experiments were carried out with a nanosecond flashlamp pumped FL900 lifetime spectrometer (Edinburgh Analytical Instruments). Pyrene was excited at $\lambda = 334 \text{ nm}$ and the fluorescence decay was monitored at $\lambda = 390 \text{ nm}$ with a photomultiplier tube by the time-correlated single photon counting technique at 1-ns time resolution for a total decay time of $1 \mu\text{s}$. The decay curves were corrected for instrument response

TABLE 1: Lifetimes of Pyrene Fluorescence in Methanol

| temp, K | $1/k_0$, ns | $1/k_0$, ns |
|---------|------------------|----------------|
| 288 | 395 ^a | |
| 293 | 385 ^a | |
| 298 | 372 ± 10^a | 387 ± 17^b |
| 303 | 349 ^a | |

^a Bubbling argon gas. ^b Freeze–pump–thaw.

by deconvolution with the instrument scattering profile obtained with a scattering solution. Decay curves in methanol were measured at a few selected temperatures between 10 and 40 °C and for various quencher concentrations at each temperature. Experiments in SDS solutions were conducted at 25 °C. The sample temperature was maintained with circulating water. In the case of methanol, dry argon gas was bubbled through a fixed volume of sample (2 mL) for 10 min to deoxygenate the samples. See Table 1 for the lifetimes of pyrene fluorescence in methanol in the absence of quencher after this treatment, together with the lifetime after a rigorous treatment of repeated freeze–pump–thaw cycles. Table 1 shows that bubbling with argon gas is effective in deoxygenating methanol. The quencher concentrations were determined by monitoring the absorption with a Varian Cary 2400 spectrophotometer at (i) $\lambda = 260 \text{ nm}$ and an extinction coefficient, ϵ , in methanol of $4200 \text{ M}^{-1} \text{ L cm}^{-1}$ for $C_{16}PC$,^{30,31} (ii) $\lambda = 270 \text{ nm}$ and ϵ of $15262 \text{ M}^{-1} \text{ L cm}^{-1}$ for DMBP in water,³² and (iii) $\lambda = 424 \text{ nm}$ and ϵ of $11 \text{ M}^{-1} \text{ L cm}^{-1}$ for 5DSE in methanol determined through a methanolic solution of a known amount of 5DSE. The corrected decay curves were fitted to a single-exponential decay in the case of methanol and to the Infelta model, eq 3, for SDS solutions.

Microviscosity values previously determined by ESR for SDS micelles using 5DSE in water with and without NaCl were used.² For SDS micelles, the microviscosity depends only on the values of N and not on the particular surfactant and salt concentrations. For those values of N for which the microviscosity values were not available by measurement, interpolated values were used.

Results

The decay curves of fluorescence quenching of pyrene in methanol are shown in Figure 1. A single-exponential decay fit yields k_q . Micellar quenching was observed in SDS micelles and the decay curves, Figure 2, show that the long-time behavior in the presence of quencher parallels that in the absence of quencher. This means that the intermicellar migration rate is not significant for the quencher/micelle systems of the present studies¹⁵ and eq 3 applies. Fits to the Infelta equation (eq 3) return k_q and $\langle N_q \rangle$. The aggregation number, N , is then obtained from $\langle N_q \rangle$ using eq 4 with the micelle concentration

$$[M] = \frac{[SDS] - [SDS_{\text{free}}]}{N} \quad (11)$$

calculated from the known total detergent concentration $[SDS]$ and the computed values of the aqueous monomer concentrations $[SDS_{\text{free}}]$.^{33,34} The volume of the hydrocarbon portion of the SDS molecule is close to 350 \AA^3 .^{32,35} The value of V_{tail} forming the core depends on the percentage of the hydrocarbon units of the alkyl chain that is embedded within the core. The literature often reports that about two methylene groups are fully exposed to water^{2,36,37} leading to a value of $0.83 \times 350 \text{ \AA}^3$ for V_{tail} . With this value for V_{tail} , and the N derived from TRFQ, V_{shell} is calculated according to eqs 8 and 9. Table 2 gives the

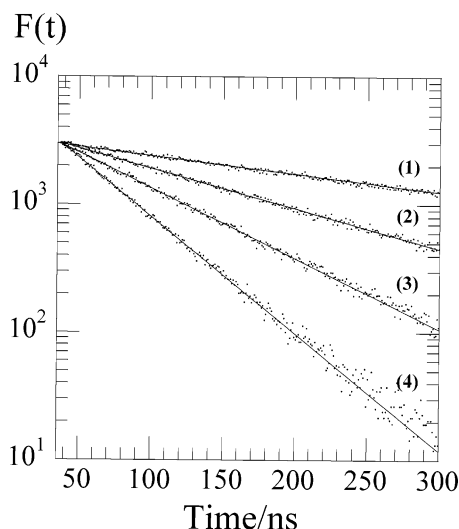


Figure 1. Fluorescence decay of pyrene in methanol for various concentrations of the quencher hexadecylpyridinium chloride, C₁₆PC, at 15 °C. The values of the C₁₆PC concentrations are (1) 0, (2) 0.59, (3) 1.17, and (4) 2.19 mmol L⁻¹. The four curves are the data together with their least-squares fits to a single-exponential decay.

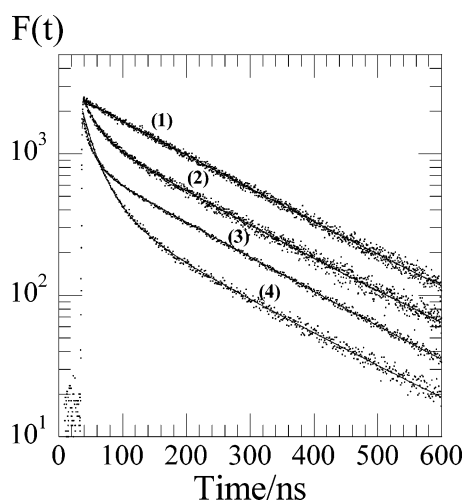


Figure 2. Fluorescence decay of pyrene in SDS micelles, [SDS] = 50 mmol L⁻¹, in the absence (1) and in the presence of the quenchers (2) 5DSE, (3) DMBP, and (4) C₁₆PC at 25 °C. Curve 1 shows the data and the fit to a single-exponential decay. The three quenched decay data (dots) together with their least-squares fits (solid lines) to the Infelta–Tachiya model (eq 3) are purposely chosen to be at different quencher concentrations, 0.37, 0.50, and 0.7 mM, respectively, to separate the curves for clarity.

values of V_{shell} for the various samples studied in this work. The respective values of the microviscosity obtained from ESR using 5DSE are also given. Published values of viscosity are available for methanol.³⁸ The SES prediction for k_q is tested for bulk liquid in Figure 3 and for micelles in Figure 4. The abscissas are given as $8RT[Q]/3000\eta$ for bulk and $8RTC_Q/3000\eta$ for micelles. Thus the slope yields the quenching probability P . The solid lines in Figures 3 and 4 are fits to the data yielding $P = 0.9$ in methanol and $P = 0.7$ in SDS micelles. Two main remarkable points about the observed behavior of k_q are that the data points for the different quenchers fall on the same line and that the slope is of the order of unity as expected of the SES equation (eq 2) for diffusion-controlled reactions.

Discussion

The linearity of the curve in Figure 3 shows that the SES describes the quenching rate constant rather well in bulk liquid

TABLE 2: Quenching Rate Constants (k_q), Microviscosities (η), Core Radii (R_c), and Shell Volumes (V_{shell}) for SDS Micelles

| quencher | [SDS], mol L ⁻¹ | [NaCl], mol L ⁻¹ | k_q , 10 ⁷ s ⁻¹ | η , ^a cP | R_c , Å | V_{shell} , ^b 10 ⁴ Å ³ |
|----------------------|-------------------------------|--------------------------------|--|-----------------------------|--------------|---|
| C ₁₆ PC | 0.05 | 0 | 4.18 | 7.2 | 16.7 | 2.33 |
| C ₁₆ PC | 0.05 | 0.029 | 3.57 | 8.1 | 17.5 | 2.52 |
| C ₁₆ PC | 0.05 | 0.093 | 3.13 | 9.3 | 18.5 | 2.79 |
| C ₁₆ PC 1 | 0.05 | 0.2 | 2.78 | 10.3 | 19.4 | 3.02 |
| C ₁₆ PC 1 | 0.05 | 0.4 | 2.25 | 11.6 | 21.2 | 3.51 |
| DMBP | 0.10 | 0.025 | 3.94 | 8.0 | 17.3 | 2.49 |
| DMBP | 0.10 | 0.05 | 3.56 | 8.7 | 18.1 | 2.67 |
| DMBP | 0.10 | 0.10 | 3.30 | 9.3 | 18.5 | 2.78 |
| DMBP | 0.10 | 0.15 | 3.02 | 10.0 | 19.1 | 2.94 |
| DMBP | 0.10 | 0.21 | 2.77 | 10.5 | 19.6 | 3.07 |
| DMBP | 0.10 | 0.25 | 2.63 | 11.0 | 20.0 | 3.20 |
| DMBP | 0.10 | 0.28 | 2.43 | 11.2 | 20.4 | 3.32 |
| DMBP | 0.10 | 0.31 | 2.39 | 11.4 | 20.6 | 3.37 |
| DMBP | 0.10 | 0.025 | 2.23 | 11.5 | 21.0 | 3.47 |
| 5DSE | 0.05 | 0.1 | 3.01 | 9.5 | 18.6 | 2.82 |
| 5DSE | 0.05 | 0.2 | 2.44 | 10.6 | 19.7 | 3.11 |
| 5DSE | 0.05 | 0.4 | 2.17 | 11.5 | 21.0 | 3.49 |
| 5DSE | 0.10 | 0.063 | 3.01 | 9.3 | 18.5 | 2.77 |
| 5DSE | 0.10 | 0.125 | 2.74 | 10.2 | 19.3 | 2.99 |
| 5DSE | 0.10 | 0.25 | 2.55 | 11.1 | 20.3 | 3.27 |

^a From previously determined values of microviscosity of the polar shell of SDS micelles as a function of the aggregation number.²

^b Calculated according to eqs 8 and 9 and using a shell thickness $R_m - R_c = 5$ Å.

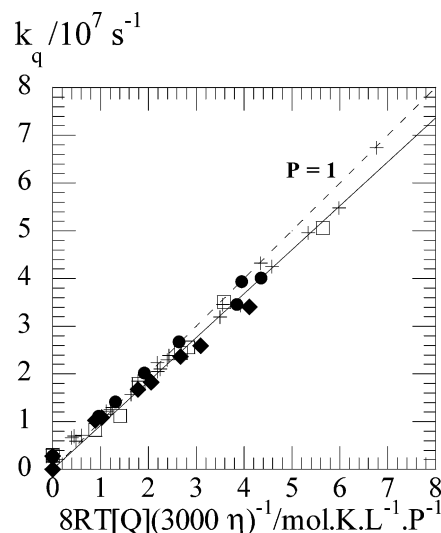


Figure 3. Fluorescence quenching rate constant, k_q , of pyrene due to (+) C₁₆PC, (●) DMBP, (◆) 5DSE, and (□) 16DSE in methanol at various temperatures (10–40 °C) versus $8RT[Q]/(3000\eta)^{-1}$. Linear least-squares fit of the combined C₁₆PC, DMBP, 5DSE, and 16DSE data obtained at the different temperatures to the Stokes–Einstein–Smoluchowski equation (eq 2) to a straight line yields a slope of 0.9. The dashed line is obtained when $P = 1$.

for the four different quenchers. The fact that the quenching probability is near unity shows that effective quenching occurs on each bimolecular encounter and that higher order corrections for nonspherical molecules, flexible molecules with the reaction center localized within the molecule, and even charged molecules are minor and can be neglected at the present level of precision.⁴ Quenching of pyrene by C₁₆PC in water at 25 °C was investigated by Almgren and co-workers.³⁹ Despite complications thought to be due to association of the fluorophore and quencher below the cmc of C₁₆PC, a second-order quenching rate constant of 6.3×10^9 L/mol s was deduced from the variation of the decay constants with quencher concentration.³⁹ Using $\eta = 0.0089$ P for water at 25 °C,³⁸ a quenching

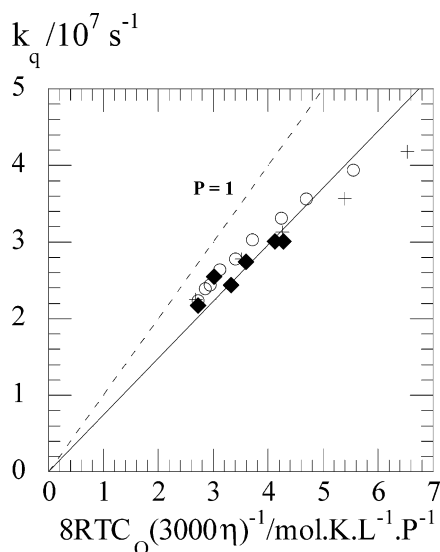


Figure 4. Fluorescence quenching rate constants, k_q , of pyrene due to (+) $C_{16}PC$, (○) DMBP, and (◆) 5DSE in SDS micelles at 25 °C versus $8RTC_Q(3000\eta)^{-1}$. Linear least-squares fits of the combined $C_{16}PC$, DMBP, and 5-DSE data to the Stokes–Einstein–Smoluchowski equation (eq 2) yield straight line of slope 0.74. The dashed line is the theoretical line for a quenching probability of unity.

probability of $P = 0.85$ may be computed from eqs 1 and 7, in good agreement with the results in Figure 3.

The data in Figure 4 show that indeed that the quenching rate constant of pyrene is almost independent of the nature of the quencher for the three quenchers studied in this work. This supports purpose 1 of the work, encouraging further work in which a wider variety of quenchers are chosen to test item 3 of the zero-order model. The data in Figure 4 are rather linear; however, for $C_{16}PC$, there is a slight curvature concave downward. Furthermore, the data do not extrapolate to the origin, although due to the micelle sizes encountered in this study, the data fall rather far from the origin. Fitting the three sets of data to a straight line without constraining the fit to pass through the origin yields slopes of 0.6, 0.5, and 0.5 for $C_{16}PC$, 5DSE, and DMBP, respectively. A straight line from the origin tangent to the lower data points for $C_{16}PC$ has a slope of 0.8. Therefore, despite the fact that the data do not seem to tend exactly to the origin, as the SES requires (in Figure 4, the fit is constrained to pass through the origin), shows that, even in micelles, the SES describes the quenching rate constant rather well. A nonzero intercept has long been a problem in describing rotational motion of molecules even in bulk liquid as is discussed by Dote et al. and references therein.⁴⁰ Given the limited systematic data that are presently available in micelles, it is premature to try to address whether a nonzero intercept can be understood by modest departures from the zero-order model. The slopes of the curves in Figure 4, if interpreted entirely as a quenching probability, yield $P = 0.7 \pm 0.2$, which already may be considered a success of the SES description. It is unlikely that the minor difference between $P = 0.7$ and $P = 1$, if it turns out to be significant in future work, may be attributed to a real decrease in the quenching probability upon collision. This is clear from the fact that the nitroxide group of 5DSE rotates rapidly (rotational correlation time < 1 ns) and almost isotropically,⁴¹ so there is no reason to suspect that the pyrene–5DSE colliding pair would behave any differently in the micelle than in a bulk liquid. The pyridinium group of the flexible molecule $C_{16}PC$ is also expected to rotate rapidly, while DMBP, being a rigid molecule, rotates more slowly. Nevertheless, all

three molecules quench pyrene at nearly the same rate. If there were to be some steric hindrance to the quenching or orientational effects, we would expect the differences in the three quenchers to emerge in the micelles.

The value of $P = 0.7$ results from using the microviscosity derived for the rotational motion of 5DSE to the translational motion of pyrene and the quenchers. Using 5DSE as one of the quenchers has the obvious advantage of eliminating the uncertainty whether the microviscosity of the quencher and the spin probe are different. The fact that the microviscosity derived from rotational motion may be applied to translational motion was well established, even for complex fluids, by Buchachenko and co-workers.⁴² Thus, a nonunity slope in Figure 4 is not likely to be due to the use of incorrect values of the microviscosity. The importance of including the microviscosity in the SES was firmly established in studies of mixed micelles of SDS and a sugar-based nonionic surfactant.¹ Good agreement was achieved by including the microviscosity and very poor agreement without it.

First-Order Correction to the Zero-Order Model. In what follows we show that the observed small departure of P from unity can be rationalized by requiring just small departures from the zero-order model that are encompassed within the quantity C_Q . At least two types of refinements are obvious. The first involves leaving intact the assumption that the quencher and pyrene diffuse through the same volume, but this volume is different from V_{shell} . In order for P to increase from 0.7 to 1.0, the diffusion volume would have to be 30% larger than that of V_{shell} . Studies of the hydration of the polar shell of SDS micelles²⁵ and SDS micelles mixed with a nonionic sugar-based surfactant¹ support the zero-order model. The experimentally observed volume percentage occupied by water is in excellent agreement with a simple theory based on the zero-order model.^{1,25} Only one parameter enters into the theory (either the shell thickness or the volume inaccessible to water due to the headgroup). Leaving this parameter fixed, the variation in micelle hydration is in excellent agreement with theory as the micelles grow under the influence of added salt or surfactant.²⁵ Furthermore, upon insertion of a bulky sugar headgroup, the expected amount of expelled water is very nearly equal to the volume of the headgroup computed from molecular models. A detailed discussion and critical evaluation of the agreement between theory and experiment may be found in the published work of Bales et al.^{1,3,26} One criticism was that small excursions by 5DSE from the polar shell into the core and out into the water, were they to be of similar probability, would be difficult to detect since averaging 0% water in the core and 100% water outside the shell would result in about 50% water. Weighting the results²⁵ with 50% water would change them very little. Thus, to maintain agreement between experimental and theoretical values of the micelle hydration, this volume increase must involve excursions of the two molecules more or less equally into the core and into the aqueous phase. We find that excursions of approximately 0.8 Å into the core and 0.8 Å out into the aqueous phase are sufficient to increase P from 0.7 to 1.0.

Alternatively, we could suppose that the volumes through which pyrene and the quenchers diffuse are slightly different. Figure 5 shows a schematic of the core–shell model of a micelle of radius R_m having core radius R_c . A portion of the region of diffusive motion of two molecules is shown as two zones. Each zone extends symmetrically about the center of the micelle between a distance $R_{min,i}$ and $R_{max,i}$ ($i = 1, 2$ identifies the molecule) from the center; only a portion of each zone is shown for clarity. We simplify the discussion by assuming that each

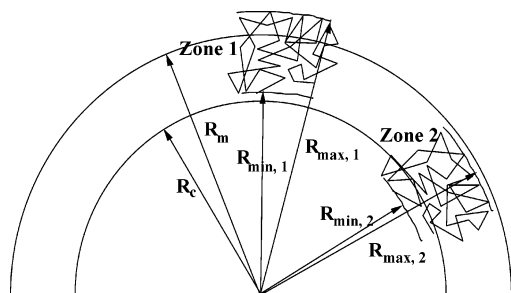


Figure 5. Schematic of the core-shell model of a micelle of radius R_m having core radius R_c , showing the region of diffusive motion of two molecules as two zones. Each zone extends symmetrically about the center of the micelle between a distance $R_{\min,i}$ and $R_{\max,i}$ ($i = 1, 2$ identifies the molecule) from the center; only a portion of each zone is shown for clarity.

molecule, i , may be found with equal probability at any point within its zone of volume $V_{\text{zone},i}$ and is not found outside that zone. Thus the probability that both molecules will be found in the volume of overlap and thus collide is just $V_{\text{overlap}}^2 / V_{\text{zone},1} V_{\text{zone},2}$ and may be interpreted as the slope of the line in Figure 4. For the most general case, the probability is a somewhat complicated expression involving $R_{\min,i}$ and $R_{\max,i}$ ($i = 1, 2$). To illustrate, we consider two simple cases.

Suppose in case 1, zone 1 lies entirely within the polar shell displaced symmetrically from the two surfaces of the polar shell. Thus, $R_{\min,1} = R_c + \delta$ and $R_{\max,1} = R_m - \delta$. Suppose that zone 2 extends beyond these two surfaces symmetrically by the same amount; i.e., $R_{\min,2} = R_c - \delta$ and $R_{\max,2} = R_m + \delta$. It is straightforward to show that the probability is given by the following:

$$P(\text{case 1}) = \frac{((R_m - \delta)^3 - (R_c + \delta)^3)}{((R_m + \delta)^3 - (R_c - \delta)^3)} \quad (12)$$

For $\delta = 0$, we have the zero-order approximation and eq 12 properly yields unity. The probability given in eq 12 decreases with δ , reaching $P(\text{case 1}) = 0.7$ at $\delta = 0.44$ Å. Any core radius in the range $R_c = 16$ –22 Å, appropriate for an SDS micelle of aggregation number in the range $N = 50$ –120, taken together with a shell thickness of 5 Å yields the same result within 1 part in 700. Thus, the probability computed for case 1 does not change appreciably with N .

For case 2, suppose that both zones have thickness equal to that of the shell, 5 Å, and that one is displaced outward by δ and the other displaced inward by the same amount. Thus, $R_{\min,1} = R_c + \delta$, $R_{\max,1} = R_m + \delta$, $R_{\min,2} = R_c - \delta$, and $R_{\max,2} = R_m - \delta$. This yields

$$P(\text{case 2}) = \frac{((R_m - \delta)^3 - (R_c + \delta)^3)^2}{((R_m + \delta)^3 - (R_c + \delta)^3)((R_m - \delta)^3 - (R_c - \delta)^3)} \quad (13)$$

Equation 13 yields a probability of 0.7 when $\delta = 0.40$ Å.

The purpose of introducing cases 1 and 2 is to get an idea of how much displacement of the two zones is needed in order to reduce the probability from unity for the zero-order model to about 70%, which is observed experimentally. In both cases, and in others, including asymmetric displacements, a displacement of about 8–10% of the shell thickness is sufficient to reduce the probability by 30%. We are not yet able to propose a particular arrangement of the zones to account for the experimental results in SDS at 25 °C, but we do note that the

zone for the spin probes must be consistent with the observed values of the polarity expressed as a percent of volume occupied by water.^{1,3,26,27}

The problem of diffusion-controlled reactions in micelles has been addressed theoretically^{17,18,43–46} and experimentally in spherical and cylindrical micelles.^{12,47,48} These studies have concentrated on the roles of dimensionality and finite restricted media and the effect of the quenching mechanisms on reaction rates in model systems. The treatment in these microscopic models is basically along the lines of the Smoluchowski approach; that is, they rely on a hydrodynamic description of the reaction medium and solve the diffusion equation for the pair survival probability for several model situations as follows: (a) probe and quencher restricted to motion on the surface of a sphere, (b) probe fixed at the center of a sphere while the quencher moves freely in the volume, and (c) quencher fixed at the surface of a sphere while the probe moves freely in the volume. These are idealized conditions, not entirely physical. For particles diffusing on the surface of a sphere of radius R_s , model a, the results of the calculations for the first-order quenching rate constant in micelles may be summarized as^{11,15,18,46}

$$k_q = \frac{\gamma D}{R_s^2} \quad (14)$$

where γ is of the order of unity and depends on the sizes of the micelle and the diffusing particle. The functional similarity of eq 14 to the 3-D expression of eq 2, namely, the direct proportionality to the diffusion constant and inverse proportionality to the size of the reaction domain, results in numerically similar values for k_q calculated from eqs 2 and 14. Using typical values for γ between 0.3 and 0.5^{17,18} and eq 6 employing probe and quencher radii of 3 Å, one may calculate values of k_D that are 25–45% of those computed from eq 1. Hence not only the features of eq 14 but also the numerical values are close to the predictions of the SES. Therefore from the values of k_q alone we cannot distinguish between the two equations. The main point here is that the use of the Stokes–Einstein expression for D in eq 5 eliminates the dependence on the type of quencher quite clearly and explains this essential feature of the experimental observations.

Conclusions

Using fluorescence quenching, a prototype of diffusion-controlled reactions, in bulk liquid and micelles, we have shown that the reaction rate constant is independent of the nature of the colliding pair. The results as displayed by Figures 3 and 4 support a hydrodynamic description of collisions in bulk solvents as well as within the restricted region of the micelle. Use of the Stokes–Einstein equation for the mutual diffusion coefficient reveals the role of temperature and microviscosity in reaction rates in micelles explicitly. The quenching probability is near unity in bulk liquids and about 70% in SDS micelles.

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