PHOTOLUMINESCENCE PROBES OF MICELLE SYSTEMS.
CYCLIC AZOALKANES AS QUENCHERS OF 1,5-DIMETHYLNAPHTHALENE FLUORESCENCE

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Quenching of the fluorescence of detergent solutions of 1,5-dimethylnaphthalene by a series of bicyclic azoalkanes has been investigated. A model is employed which postulates that the azo quenchers are partitioned between the aqueous phase and micelles.

1. Introduction

During the past several years a number of reports have appeared which describe the utilization of photoluminescence probes for the investigation of the composition, structure and dynamics of micellar systems [*]. Both fluorescence [5–11] and phosphorescence [12–14] probes have been effective in the evaluation of micellar parameters.

Knowledge of solute binding constants K is important for the development of a quantitative theory of the solubilizing action of micelles. Knowledge of solute rate constants for entrance (k_f) into and exit (k_b) from micelles is essential for development of a quantitative understanding of the dynamics of solubilization. In most cases studied, the photoluminescent probe, or a quencher or both have been completely micellized. The use of Poisson statistics has proven to be generally applicable and effective in interpreting the results of such investigations [5,15–17].

We report here a study of the quenching of a completely micellized fluorescent probe (1,5-dimethylnaphthalene, 1) by a series of cyclic azoalkanes (2. 3, 4 and 5) that exist to a significant extent in both aqueous and micellar environments.
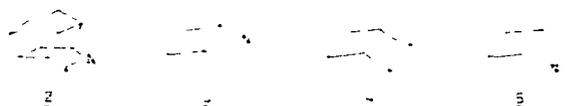
2. Experimental

Hexadecyltrimethylammonium bromide (HDTBr)

and sodium dodecyl sulfate (SDS) were washed several times with ether and recrystallized from 95% EtOH two times. Compound 1 (Chemical Samples Co.) was purified by sublimation in vacuo.

The structures of the azoalkanes used as quenchers in this work are given in scheme I.

Scheme I

Sample 3 was obtained from Professor P.S. Engel, Department of Chemistry, Rice University, Houston, Texas. The other azoalkanes were prepared as previously described [18].

The emission spectra were recorded with a Hitachi Perkin–Elmer MPF-2A spectrofluorimeter. The fluorescence quantum yields were determined by comparing the corrected fluorescence spectra with the corrected fluorescence spectrum of quinine sulfate after the method reported in a previous paper [18]. Lifetimes were measured using the time-correlated single-photon counting technique. The design and performance of the instrument have been described in a previous paper [9].

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* For a general discussion of the properties peculiar to micellar solutions, see refs. [1–4].

3. Results

3.1 Spectroscopic properties

Compound 1 possesses a low solubility in water so that its fluorescence is detected only from the micellar phase. The higher fluorescence quantum yield of 1 in water ($\phi_F \approx 0.5$) allows for a high sensitivity and signal/noise value.

The absorption spectra of the series of bicyclic azoalkanes 2 through 5 display low transition probabilities in the region from 280 to 320 nm, thereby providing "optical windows" [18] for selective excitation of donor 1 which possesses strong absorption in this region.

Compounds 2 through 4 exhibit relatively strong fluorescence in micellar solution ($\phi_F \approx 0.3-0.5$), while 5 shows a very weak emission. The absorption and emission parameters of 2–5 are summarized in table 1. As was shown in a previous paper [18], the lowest $n-\pi^*$ absorption band of these azo compounds shows vibration in structure in nonpolar organic solvent but is broad and poorly resolved in aqueous solution. A comparison of the spectral characteristics in micellar solution with that observed in water and hydrocarbon solvent indicates that, on the average, the "organic" bicyclic azoalkanes in micellar solution are in a water-like environment rather than a hydrocarbon-like environment.

3.2 Dependence of spectral and dynamic properties on quencher concentration

In the first series of quenching experiments, the concentration of azoalkanes 2–5 was varied from 0 to 4×10^{-3} M, while that of 1 was fixed at 1.5×10^{-4} M. For the quenching systems of 2, 3 and 4, fluorescence of 1 decreases with increasing concentration of
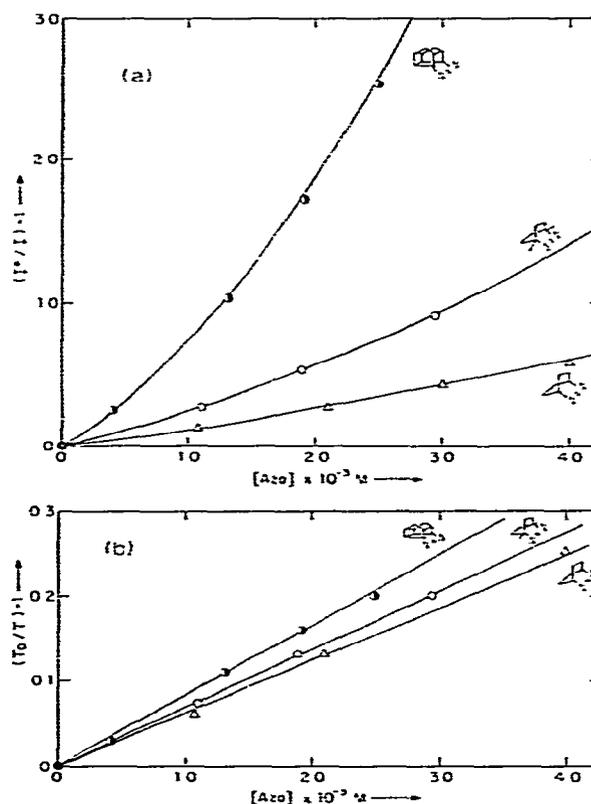

Fig. 1. (a) The plots of I^0/I against the concentration of azoalkanes in 0.01 M HDTBr solution at 22°C. (b) The plots of τ^0/τ against [Azo] in 0.01 M HDTBr solution at 22°C.

quenchers, while the emission of the azo compounds exhibits a corresponding increase. Since the fluorescence of quencher 5 is too weak to be detected, in this case only the donor fluorescence is observed. The spectral changes show an isosbestic point. Reabsorption of the fluorescence of 1 by azo compounds is negligible in the concentration region used due to the

Table 1

Compound	$\dfrac{K}{1+K[M]}$ a)	K (M^{-1})	$\dfrac{k_f}{1+K[M]}$ b)	k_f (M^{-1}s^{-1})	Exit rate k_b (s^{-1})
2	444	473	4.6×10^9	4.9×10^9	1.0×10^7
3	160	164	3.8×10^9	3.9×10^9	2.4×10^7
4	62.5	63	3.4×10^9	3.4×10^9	5.4×10^7

a) The values are obtained from the slope in fig. 2.
b) The values are obtained from the slope in fig. 1b. $\bar{n} = 72$ was used. [M] = 1.4×10^{-4} M. Temperature 22–24°C.

low absorbance of the azo quenchers.

Stern—Volmer (SV) plots for the quenching of the fluorescence of 1 are shown in fig. 1a. The plots of the ratio of fluorescence intensity in the absence and presence of quencher (I^0/I) against the concentration of azoalkanes [Azo], do not yield straight lines but deviate upwards for each quencher studied. The fluorescence decay of 1 fits single exponential decay and the derived fluorescence lifetime was found to decrease slightly with increasing the concentrations of the quenchers. The plots for the ratio of the lifetime in the absence and presence of quenchers (τ_0/τ) versus [Azo] is also shown in fig. 1b. Although the change of the lifetime is very small compared with the change of fluorescence intensity, the plots give straight lines.

In order to determine whether the deviation from linearity in the SV plot for fluorescence intensity ratio is general for fluid solutions or is peculiar only to micellar solutions, quenching studies were investigated in isooctane solution. The plots of I^0/I and τ_0/τ as a function of [Azo] in isooctane solution give the same slopes within the experimental error. From the slope and the lifetime of 1 without quencher, a quenching rate constant of 1.0×10^{10} M^{-1} s^{-1} is derived. This value is close to that expected for the diffusion rate constant in isooctane solution. Therefore, in ordinary fluid solution, the quenching mechanism is understood to be conventional SV-type dynamic quenching.

We conclude that the deviation from the SV plots for the system 1—(2, 3, 4 and 5) is peculiar to the micellar solutions. We show below that the extent of the curvature of the plot may be related to the solubility of the azoalkanes in micelles.

Before entering into an analysis of the data, we point out that no evidence for formation of a CT complex or an exciplex in those D—Q systems was observed in the emission decay, absorption or fluorescence spectra.

3.3. Analysis of the quenching data

The quenching data can be analyzed by a quenching equation based on a model which assumes only static quenching occurs and of that the quencher is only partially micellized. In such a case, a kinetic scheme of luminescence will be represented as shown in scheme II.
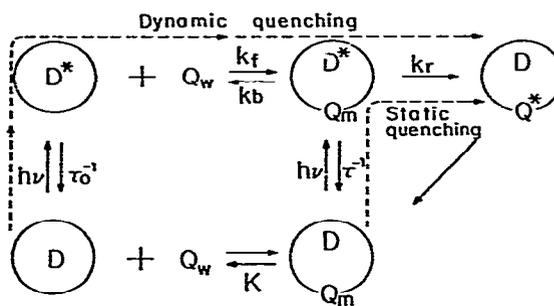
Scheme II.

In scheme II the circles symbolize micelles and D. Q_W and Q_M represent donor molecule, water and micelle solubilized quenchers, respectively. The forward and backward rate constants of micellization are k_f and k_b, respectively, and k_r is the unimolecular reactive rate constant of quenching in the micelle. The following relations have been obtained for the above kinetic scheme based on the postulate of stepwise solubilization and Poisson statistics [15—17].

From this model the ratio of luminescence intensity in steady state irradiation and the decay constant are given by the equations

$$I^0/I = (\tau_0/\tau)\exp\{K[Q]/(1 + K[M])\}\ ,\qquad (1)$$

$$\tau^{-1} = \tau_0^{-1} + k_f[Q_W]\ ,\qquad (2)$$

where

$$[Q_W] = [Q]/(1 + K[M])\ ,\quad [M] = ([Det] - [CMC])/\bar{n}\ .\qquad (3)$$

Here [Q], $[Q_W]$ and [M] denote the total, micelle bound quencher concentrations and total micelle concentration, respectively and [Det], [CMC] and $\bar{n}$ represent the detergent, critical micelle concentrations and average aggregation number, respectively. The equilibrium constant $K = [Q_M]/[Q_W][M]$ is also derived from the stepwise solubilization model based on Poisson statistics.

Fig. 2 shows that plots of $\ln[(I^0/I)\tau/\tau_0]$ against [Azo] yields straight lines. The variation of fluorescence intensity of donor obeys the quenching equation (1) (fig. 2); however, the fluorescence lifetime changes slightly. The quenching behavior suggests that the micelle bounded fluorescence of 1 is quenched predominantly by micelle bounded quencher (static quenching), a small amount of dynamic quenching caused
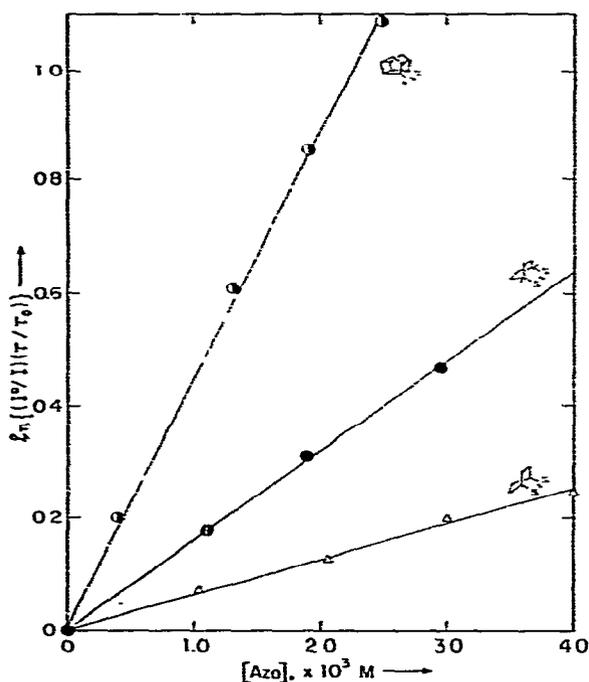
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Fig. 2. The plots of ln $[(I^0/I)\tau/\tau_0]$ against [Azo] in 0.01 M HDTBr solution at 22°C.

by the water solubilized quencher could still be occurring.

According to eq. (1) the slopes of the plots in fig. 2 provide the value of $K/(1 + K[M])$. From knowledge of aggregation number $\bar{n}$, [M] can be evaluated and consequently values of K can be derived. The equilibrium constants obtained in this manner are summarized in table 1. With knowledge of the value of K, evaluation of the slope of the plot of τ^{-1} (see fig. 1b) permits derivation of the value of k_f via eq. (2). Finally, using the K and k_f values, one can derive the value of the exit rates (k_b) of the azoalkane from the micelle. The values of k_f and k_b are also shown in table 1.

3.4. Variation of the micelle concentration at fixed donor–quencher concentration

In a series of experiments, the micelle concentration was varied from 0.025 M to 0.25 M at fixed donor and quencher concentrations. When the concentration of detergent was increased, the fluorescence intensity of

1 increased and that of the azo compound decreased.

The experimental data were analyzed according to the following equations obtained from eq. (1):

$$\left[\ln\left(\frac{I^0}{I}\frac{\tau}{\tau_0}\right)\right]^{-1} = \frac{[M]}{[Q_M]} = \frac{1 + K[M]}{K[Q]} , \qquad (4a)$$

$$\left[\ln\left(\frac{I^0}{I}\frac{\tau}{\tau_0}\right)\right]^{-1}$$

$$= (1/K[Q])\{1 + (K/\bar{n})([Det] - [CMC])\} , \qquad (4b)$$

$$\left[\ln\left(\frac{I^0}{I}\frac{\tau}{\tau_0}\right)\right]^{-1} \approx (1/K[Q])\{1 + (K/\bar{n})[Det]\} . \qquad (4c)$$

The plots of $\{\ln[(I^0/I)\tau/\tau_0]\}^{-1}$ versus [Det] gave straight lines as is shown in fig. 3. According to eq. (4) from the slope and intercept of the plot at fixed [Q], magnitudes of K and $\bar{n}$ may be derived. The values for the equilibrium constants and aggregation numbers obtained for both HDTBr and SDS micellar solution in this manner are summarized in table 2.
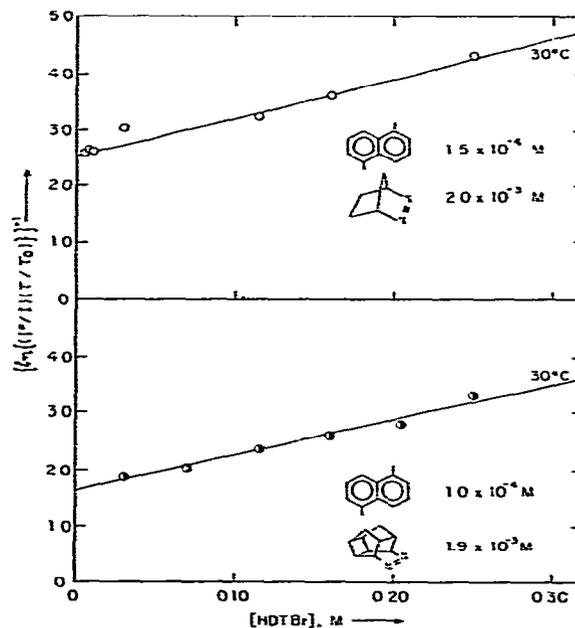

Fig. 3. The plots of $\{\ln[(I^0/I)\tau/\tau_0]\}^{-1}$ versus HDTBr concentration at fixed donor and quencher concentrations.

Table 2

Micelles	Quencher	$\bar{n}$ [a]	K (M^{-1}) [a]
HDTBr		80	339
		81	192
SDS		71	1900

[a] The values of $\bar{n}$ and K are obtained from the slope and intercept in fig. 3 at 30°C.

4. Discussion

4.1. Partition coefficients and micelle parameters

Poisson statistics of the solubilized molecules leads to the following relation [15–17]

$$[Q_M]/[Q_W] = K[M] . \tag{5}$$

Consider the limiting cases of $K[M]$ instead of the partition coefficient. $[Q_M]/[Q_W]$.

The first limiting case is that the quencher is strongly solubilized in the micelle, that is $K[M] \gg 1$. For such a situation eq. (4) reduces to

$$\left[\ln\left(\frac{I^0}{I}\frac{\tau}{\tau_0}\right)\right]^{-1} = \frac{[M]}{[Q]}$$

$$= (1/\bar{n}[Q])([Det] - [CMC]) . \tag{6}$$

If a plot of $\{\ln[(I^0/I)\tau/\tau_0]\}^{-1}$ versus [Det] yields a straight line, the slope and the [Det] value at $\{\ln[(I^0/I)\tau/\tau_0]\}^{-1} = 0$ will allow derivation of aggregation numbers and critical micelle concentrations, respectively (see fig. 4, case 1). This is the case for Ru(bipy)$_3^{2+}$ quenched by 9-methylanthracene in SDS solution as reported previously [12]. Experimentally this condition corresponds to $K \gtrsim 5 \times 10^3$ M^{-1}, if [M] $\approx 10^{-3}$ M.

The second case is such that the quencher is not solubilized well in the micelle, that is $K[M] \ll 1$. Under this condition, eq. (4) reduces to
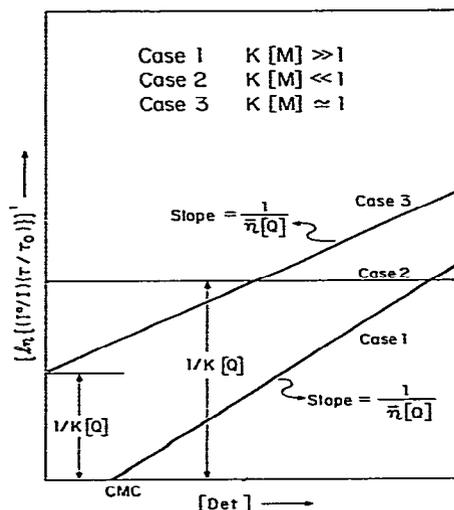

Fig. 4. Theoretical plot of $\{\ln[(I^0/I)\tau/\tau_0]\}^{-1}$ against [Det] expected from eq. (4) at fixed donor and quencher concentrations.

$$\left[\ln\left(\frac{I^0}{I}\frac{\tau}{\tau_0}\right)\right]^{-1} = \frac{1}{K[Q]} . \tag{7}$$

In the limiting case of eq. (7) a plot of $\{\ln[(I^0/I) \times \tau/\tau_0]\}^{-1}$ against [Det] is constant, and a plot of this function versus $[Q]^{-1}$ allows evaluation of K (case 2 in fig. 4). Experimentally the condition corresponds to $K < 2 \times 10^2$ M^{-1}, if [M] $\approx 10^{-3}$ M.

In a third situation, the solubility of the quencher in the micelle is somewhere between the two extremes of the above two cases, that is $K[M] \approx 1$.

The equilibrium constant for this case is expected to be 5×10^3 M$^{-1} \geqslant K \geqslant 2 \times 10^2$ M^{-1}. In this case, the condition $1 \gg (K/\bar{n})$[CMC] is readily achieved and eq. (4c) is appropriate for analysis of the data, i.e., if a plot of $\{\ln[(I_0/I)\tau/\tau_0]\}^{-1}$ versus [Det] gives a straight line, the slope is equal to $1/\bar{n}[Q]$ and intercept is equal to $1/K[Q]$ (case 3 in fig. 4). Experimental situations that fall in this intermediate case can lead to information about $\bar{n}$, K, k_f and k_b. Analysis of our data reveals that quenching of the fluorescence of 1 by cyclic azoalkanes falls into this intermediate case.

The dynamic character of solubilization provides an explanation for the fact that the spectroscopic properties of the "organic" bicyclic azoalkanes indicate

that they reside in a rather water-like environment in micellar solution.

4.2. Aggregation number

Mean aggregation numbers of 95 [19], 72 [10,11] (light scattering technique) and 75 [10,11] (pyrene excimer formation) for HDTBr, and of 63 [20] (osmometry), 62 [21] (light scattering technique), 74 [22] (Pyrene excimer formation) and 60 [12] (quenching of luminescence) for SDS micellar solution have been reported at 25°C. The values for aggregation numbers obtained in this work (80 for HDTBr and 71 for SDS at 30°C) are in agreement with previously reported values. The general agreement of results with other methods of measurement serves as support that the physical assumption made in the derivation of eq. (1) and the model given in scheme II are essentially correct.

Acknowledgement

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