Fluorescence Quenching by Neutral Molecules in Sodium Dodecyl Sulfate Micelles

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Abstract: The quenching of pyrene, diethylindoloindole, and diethylindolocarbazole in methanol is studied as a function of the free-energy change involved in the quenching process. From the dependence of the rate constant of quenching on the free-energy change an outer-sphere electron transfer is proposed as the mechanism of the quenching. A study of the same quenching processes in SDS micelles indicates that the formal kinetics formulated previously remain valid for neutral quenchers. The individual rate constants were determined for three different quenchers. The influence of the free-energy change and the solubilization site on the intramicellar quenching rate constant is studied in the framework of a theoretical model for this process. An attempt is made to deduce from the quenching rate constant the resistance of the Stern layer and outer core to the translational movement of neutral molecules.

Introduction

Quenching of arene fluorescence in micellar medium by metal ions[1,2] or anions[3] is extensively studied. The formal kinetics of this process have been developed in a detailed way.[4-6] Recently Infelta, Kozak,[7] the authors,[8a] and Tachiya[8b] developed mathematical models for the intramicellar quenching rate constant. This model is applied to the quenching of pyrene by metal ions in sodium dodecyl sulfate (SDS) micelles.[9] The kinetics in Scheme I give an account of the fluorescence decay in a micelle and the dependence of the decay parameters on the concentration of quencher as surfactant.[9]

The fluorescence decay function is given by[1-3]

$$I(t) = A_1 \exp[-A_2t - A_3(1 - \exp(-A_4t))] \qquad (1)$$

The meanings of the terms A_1, A_2, A_3, and A_4 have been previously defined.[6]

Fluorescence quenching by organic quenchers has been studied by stationary methods,[10,11] flash spectroscopy,[11,12] and single photon counting.[13] However, a detailed quantitative analysis based on time correlated single photon counting observations has not yet been published.

Scheme I

$$D_m \xrightarrow{h\nu} D^*_m$$

$$D^*_0 \xrightarrow{k_7} D_0$$

$$D^*_m \xrightarrow{mk_{\text{qm}} + k_7} D_m$$

$$D^*_m + Q \xrightarrow{mk_{\text{m}}^-} D^*_{m-1} + Q_{\text{W}}$$

$$D^*_m + Q_{\text{W}} \xrightarrow{[Q]_{\text{W}}k_{\text{m}}^+} D^*_m + 1$$

$$D^*_m + M_n \xrightarrow{nk_{\text{hm}}[M]_{n+1}} D^*_{m+1} + M_{n-1}$$

$$D^*_m + M_{n-1} \xrightarrow{mk_{\text{hm}}[M]_{n-1}} D^*_{m-1} + M_n$$

M_n	micelle with *n* quenchers
D_m	micelle with a donor and *m* quenchers
$[Q]_{\text{m}}$	concentration of quenchers in the micellar phase
$[Q]_{\text{W}}$	concentration of quenchers in the water phase
$[M]_m$	concentration of micelles with *m* quenchers
$[Q]$	total quencher concentration
$[M]$	total micellar concentration
k_7	decay of the excited probe in absence of quencher
k_{qm}	rate constant for intramicellar quenching when only one quencher is present in the micelle
k_{m}^-	rate constant for a quencher to leave the micelle
k_{m}^+	rate constant for a quencher to enter the micelle from the water phase
k_{hm}	rate constant for a quencher to hop between two micelles

In this article, the quenching of pyrene, diethylindoloindole[14] (DEII), and dibutylindolocarbazole[14,15] (DBIC) by *m*-dicyanobenzene (mDCB), α-cyanonaphthalene (αNCN), and *p*-cyanotoluene (pCNT) is investigated.

Experimental Section

DEII and DBIC were prepared as described by Hünig.[14] The compounds were purified by column chromatography on silica gel using hexane–benzene (3:1) as eluent. Pyrene (Eastman) was purified by recrystallization from ethanol followed by column chromatography on silica gel with hexane as eluent. Prior to use all probes were purified by thin layer chromatography.

The quenchers mDCB (Aldrich), αNCN, and *p*-dicyanobenzene (pDCB) were purified by recrystallization from ethanol followed by twofold sublimation. *p*-Cyanotoluene (Suchardt) was purified by recrystallization from isopentane followed by twofold sublimation.

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[1] (a, M. A. J. Rodgers and M. F. da Silva e Wheeler, *Chem. Phys. Lett.*, **53**, 165 (1978); (b) N. J. Turro and A. Yekta, *J. Am. Chem. Soc.*, **100**, 5951 (1978); (c) M. Kalyanasundaram, M. Grätzel, and J. K. Thomas, *ibid.*; **97**, 3915 (1975).

[2] (a) S. S. Atik, M. Nam, and L. Singer, *Chem. Phys. Lett.*, **67**, 75 (1979); (b) N. J. Turro, M. Aikawa, and A. Yekta, *ibid.*, **14**, 473 (1974); (c) M. Grätzel, K. Kalyanasundaram, and J. K. Thomas, *J. Am. Chem. Soc.*, **96**, 7877 (1974); (d) F. Grieser and R. Tausch-Treml, *ibid.*, **102**, 7258 (1980).

[3] (a) R. R. Hautala, N. E. Schore, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 5508 (1973); (b) H. D. Burrows, S. J. Formoshino, F. J. Kaiwa, and E. J. Basburn, *J. Chem. Soc., Faraday Trans. 2*, **76**, 685 (1980); (c) M. F. A. Quina and V. G. Toscano, *J. Phys. Chem.*, **81**, 1750 (1977); (d) M. Van Bockstaele, J. Gelan, H. Martens, J. Put, J. C. Dederen, N. Boens, and F. C. De Schryver, *Chem. Phys. Lett.*, **58**, 211 (1978); (e) H. R. Eftink and C. A. Ghiron, *J. Phys. Chem.*, **80**, 486 (1976).

[4] A. M. Tachiya, *Chem. Phys. Lett.*, **33**, 289 (1975).

[5] P. P. Infelta, M. Grätzel, and J. K. Thomas, *J. Phys. Chem.*, **78**, 190 (1974).

[6] J. C. Dederen, M. Van der Auweraer, and F. C. De Schryver, *Chem. Phys. Lett.*, **68**, 451 (1979).

[7] M. D. Hatlee, J. J. Kozak, G. Rothenberger, P. P. Infelta, and M. Grätzel, *J. Phys. Chem.* **84**, 1503 (1980).

[8] (a) M. Van der Auweraer, J. C. Dederen, E. Geladé, and F. C. De Schryver, *J. Chem. Phys.*, **74**, 1140 (1980); (b) H. Sano and M. Tachiya, *J. Phys. Chem.*, in press.

[9] J. C. Dederen, M. Van der Auweraer, and F. C. De Schryver, *J. Phys. Chem.*, **85**, 1198 (1981). Similar results were reported by Cherry et al., *J. Am. Chem. Soc.*, **103**, 4479 (1981).

[10] A. Henglein and M. Scheerer, *Ber. Bunsenges. Phys. Chem.*, **82**, 1107 (1978).

[11] (a) Y. Waka, K. Yamamoto, and N. Mataga, *Chem. Phys. Lett.*, **53**, 542 (1978); (b) *ibid.*, **62**, 2 (1979); (c) N. Mataga in "Water and Metal Cations in Biological Systems", 5th ed., B. Rullman and K. Yugi, Eds., Japan Scientific Society Press, Tokyo, 1980.

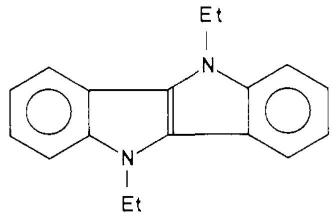
[12] (a) H. Schmehl and D. G. Whitten, *J. Am. Chem. Soc.*, **102**, 1438 (1980); (b) J. K. Thomas, *Acc. Chem. Res.*, **10**, 338 (1977).

[13] (a) M. Aikawa, A. Yekta, and N. J. Turro, *Chem. Phys. Lett.*, **68**, 283 (1979); (b) M. Aikawa, A. Yekta, J. M. Lin, and N. J. Turro, *Photochem. Photobiol.*, **32**, 297 (1980).

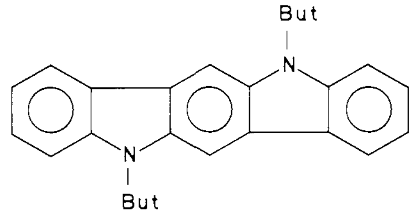
[14] (a) S. Hünig and H. C. Steinmetzer, *Tetrahedron Lett.*, **8**, 645 (1981); (b) *Justus Liebigs Ann. Chem.* **6**, 1096 (1976).

[15] Y. Moroi, M. A. Braun, and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 567 (1979).

0002-7863/82/1504-1800$01.25/0



DEII



DBIC

Fluorescence spectra were recorded on a Fica fluorimeter. Excitation always was at 337 nm, except for the quenching of αNCN where the excitation occurs at 370 and 410 nm for respectively DEII and DBIC.

The fluorescence decays were measured with time-correlated single-photon counting. The observed decay was fitted to the convolution of eq 1 with the lamp curve.

Results and Discussion

1. Quenching in Methanol. Upon quenching of pyrene, DEIC,[16] DEII with mDCB, pDCB, αNCN, and pCNT, no exciplex emission is observed. The fluorescence decreases exponentially and the inverse of the decay time is proportional to the quencher concentration.

The absence of exciplex emission indicates that the quenching occurs by immediate formation of an external ion pair or that the rate constant of exciplex dissociation toward the external ion pair is much larger than the rate constant for exciplex fluorescence.

For electron transfer in a polar solvent,[17] ΔG_2, the free energy change of quenching, is given by

$$\Delta G_2 = E^\circ_{D^+/D} - E^\circ_{A/A^-} - h\nu_{00} - e^2/4\pi\epsilon\epsilon_0\alpha \qquad (2)$$

where $E^\circ_{D^+/D}$ is the reduction potential of the oxidized form of the donor, E°_{A/A^-} the reduction potential of the oxidized form of the acceptor, a the distance between A^- and D^+ in meters, ν_{00} the excitation energy of the probe in eV, ϵ the dielectric constant of the solvent, and ϵ_0 the permittivity in the vacuum ($C^2\ V^{-1}\ m^{-1}$).

In Table I the influence of ΔG_2 on k_q, the observed rate contant for quenching, is shown. The experimentally observed single exponential decay over a broad range of ΔG_2 values indicates the absence of back-reactions from the exciplex or from the external ion pair to the locally excited state. For the most negative ΔG_2 values k_q approaches k_d, the diffusion rate constant, obtained by the Debeye equation.[18] This indicates that the primary step for these systems is electron transfer at 5 to 8 Å, the sum of the radii of donor and quencher, without restrictions for their mutual orientation.

For less negative ΔG_2 values, the electron-transfer process becomes slower than diffusion controlled.

$$D^* + A \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} AD^* \xrightarrow{k_r} A^-/D^+ \qquad (3)$$

and

$$k_q = k_r k_d/(k_{-d} + k_r)$$

From this expression k_r can be formulated from

$$k_r = (k_{-d}/k_d)(1/k_q - 1/k_d) \qquad (4)$$

with

$$(k_d/k_{-d}) = 4000\pi N_A a^3/3 \qquad (5)$$

where N_A stands for the Avogadro number. The numerical value of k_r can be calculated assuming 5.5 Å for a and a value of 2.4×10^{10} L mol^{-1} s^{-1} for k_d.

As indicated in Table I, upon decreasing ΔG_2, k_r increases asymptotically to a value of $(3 \pm 1) \times 10^{11}$ s^{-1}. If quenching proceeds by electron transfer k_r should be given[19] by

$$k_r = k_0 \exp[-(1 + \Delta G_2/\lambda)^2(\lambda/4RT)] \qquad (6)$$

or

$$RT \ln k_r + \Delta G_2/2 = RT \ln k_0 - \lambda/4 - \Delta G_2^2/4\lambda \qquad (7)$$

In Figure 1 a plot of $RT \ln k_r + \Delta G_2/2$ vs. ΔG_2^2 is shown. Except for the most negative ΔG_2 values the linear relationship of eq 7 is followed. The linear regression yields a value of 0.34 eV for λ and 1.5×10^{11} s^{-1} for k_0. These results agree with those obtained by Weller[17] for quenching in acetonitrile. For the most negative ΔG_2 values (DEII quenched by mDCB, pDCB, and αNCN), the extrapolated values of k_r using eq 7 and our experimental value of λ and k_0 are much smaller than those obtained from eq 4. The calculated values of k_r are 1.1×10^{10} and 1.4×10^9 s^{-1} for mDCB and pDCB, respectively, while the observed diffusion-controlled value of k_q requires that k_r should be at least three to four times k_{-d} or 1.5×10^{11} s^{-1}. This discrepancy is due to nuclear tunnelling[20] which populates an excited state of a C=C or of a C≡N vibration, reducing ΔG_2 by 0.2 or 0.28 eV for each vibrational quantum.

2. Quenching in Micellar Medium. (a) Quenching of Pyrene by mDCB. The observed fluorescence decay can be analyzed according to eq 1 where

$$A_2 = k_7 + S_2[Q] \qquad (8)$$

$$S_2^{-1} = \frac{(1 + K[M])A_4}{(k_m^+ + k_{hm} + K[M])k_{qm}} \qquad (9)$$

$$A_3 = S_3[Q] \qquad (10)$$

$$S_3^{-1} = \frac{1}{K} + [M]\frac{A_4^2}{k_{qm}^2} \qquad (11)$$

$$A_4 = k_{qm} + k_m^- + k_{hm}[M] \qquad (12)$$

Plotting A_3 as a function of the quencher concentration yields a linear relationship from which the slope S_3 can be determined.

From a plot of S_3^{-1} as a function of the total SDS concentration minus the critical micelle concentration (cmc) (Figure 2), assuming $k_{qm} >> k_m^- + k_{hm}[M]$, a value of the aggregation number, N_{agg}, is obtained (50 ± 12) as well as the value of binding constant K (1000 ± 300 L mol^{-1}). The variation of A_2 as a function of the quencher concentration yields a slope S_2 and an intercept which within experimental error is equal to k_7.

The inverse of S_2 as a function of the total SDS concentration vs. the cmc is plotted in Figure 3. If in a first analysis the above-mentioned assumption is maintained, S_2/S_3 equals $k_m^- + k_{hm}[M]$. This ratio is found to be independent of the SDS concentration (Table II) and hence equal to k_m^- (0.95×10^7 s^{-1}). Since $k_m^- >> k_{hm}[M]$, eq 9 can be simplified to

$$S_2^{-1} = \frac{1}{k_m^+} + \frac{[SDS]_{tot} - cmc}{k_m^- N_{agg}} \qquad (13)$$

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[16] In micellar medium DEIC was replaced by the more soluble DBIC. Both compounds have identical emission spectra and singlet lifetimes.

[17] H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 258 (1968).

[18] J. B. Birks, "Organic Molecular Photophysics", Vol. I, J. B. Birks, Ed., Wiley, London, 1973, pp 403 ff.

[19] (a) R. D. Marcus, *J. Chem. Phys.*, **24**, 966, 979 (1956); (b) *Annu. Rev. Phys. Chem.*, **15**, 155 (1966).

[20] (a) S. Efrima and M. Bixon, *Chem. Phys.*, **13**, 447 (1976); (b) N. F. Kestner, J. Jogan, and J. Jortner, *J. Phys. Chem.*, **78**, 2148 (1979).

Table I. Quenching in Methanol

D	A	k_q, L mol^{-1} s^{-1}	k_r, s^{-1}	ΔG_2, eV	$RT \ln k_r + \Delta G_2/2$	$\Delta G_2{}^2$
DEII	pDCB	2.2×10^{10}	$(1.4 \times 10^{9})^a$	−0.86		0.742
DEII	mDCB	2.3×10^{10}	$(1.1 \times 10^{10})^a$	−0.76		0.578
DEII	αNCN	1.7×10^{10}	1.7×10^{11}	−0.66	0.31	0.43
DEIC	pDCB	1.8×10^{10}	2.3×10^{11}	−0.36	0.47	0.128
DEII	pCNT	1.3×10^{10}	7.6×10^{10}	−0.32	0.466	0.102
DEIC	mDCB	1.3×10^{10}	7.6×10^{10}	−0.26	0.496	0.067
pyrene	mDCB	7.4×10^{9}	2.5×10^{10}	−0.18	0.508	0.032
DEIC	αNCN	1.15×10^{10}	5.7×10^{10}	−0.16	0.539	0.0250
pyrene	αNCN	5.1×10^{10}	1.5×10^{10}	−0.08	0.545	0.006

[a] Calculated by eq 6.

Table II. Quenching of Pyrene by mDCB: Influence of the SDS Concentration on S_2/S_3

[SDS]	S_2/S_3, s^{-1}
0.1164	9.1×10^{6}
0.0912	1.1×10^{7}
0.0696	8.9×10^{6}
0.0466	1.01×10^{7}
0.0228	9.1×10^{6}

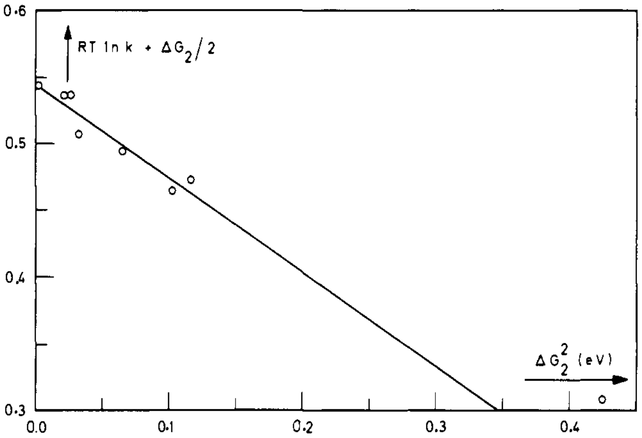

Figure 1. Quenching in methanol: $RT \ln k_r + \Delta G_2/2$ vs. $\Delta G_2{}^2$.

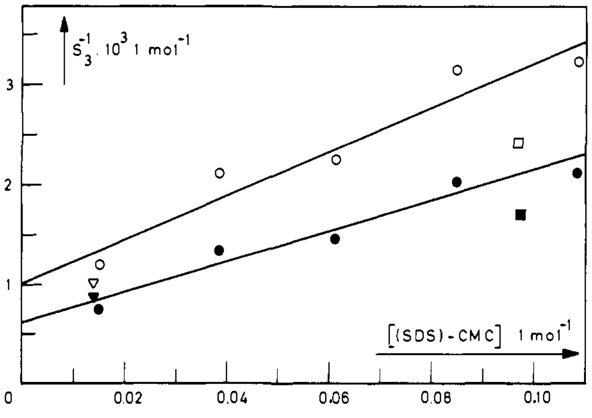

Figure 2. Quenching by mDCB in SDS: ▽ ▼, DEII; ○ ●, pyrene; □ ■, DBIC; ▽ ○ □ $S_3{}^{-1}$ vs. (SDS) − cmc; ▼ ■ ●, $k_{qm}{}^2/(A_4{}^2S_3)$ vs. (SDS) − cmc.

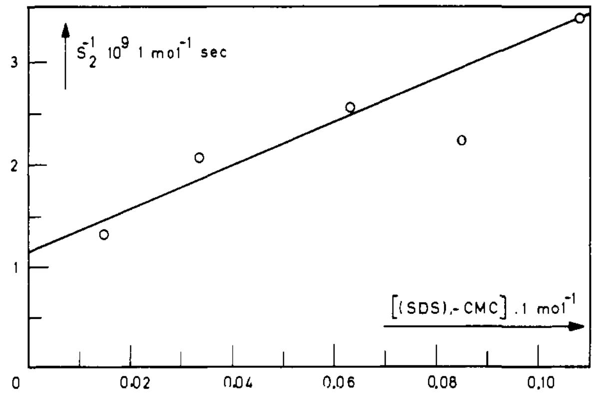

Figure 3. Quenching of pyrene by mDCB in SDS: $S_2{}^{-1}$ vs. (SDS) − cmc.

Table III. Averaged k_{qm} Values

probe	quencher	A_4,[a] s^{-1}	k_{qm}, s^{-1}	ΔG_2,[b] eV	k_q, L mol^{-1} s^{-1}
pyrene	mDCB	3.5×10^{7}	2.7×10^{7}	−0.29	7.4×10^{9}
DBIC	mDCB	4.2×10^{7}	3.5×10^{7}	−0.26	1.3×10^{10}
DEII	mDCB	5.8×10^{7}	5.1×10^{7}	−0.76	2.3×10^{10}
DBIC	αNCN	8.0×10^{7}		−0.16	1.15×10^{10}
DEII	αNCN	1.0×10^{8}		−0.66	1.7×10^{10}
DEII	pCNT	8.1×10^{7}	7.5×10^{7}	−0.32	1.3×10^{10}

[a] Bimolecular k_q in methanol. [b] In methanol.

Table IV. Quenching of Pyrene with mDCB

	$k_m{}^+$, L mol^{-1} s^{-1}	$k_m{}^-$, s^{-1}	N_{agg}	K, L mol^{-1}	k_{qm}, s^{-1}
uncorrected	9×10^{9}	9×10^{6}	50	1000	3.5×10^{7}
corrected	1.15×10^{10}	7.6×10^{6}	77	1500	2.7×10^{7}

Table V. Quenching of DBIC and DEII by mDCB[a]

	[SDS], L^{-1} mol	[mDCB], L^{-1} mol	A_3	$A_4 \times 10^{-7}$ s	$A_2{}^{-1} \times 10^{9}$ s^{-1}
DBIC	0.11	0.00269	0.92 ± 0.6	4.1 ± 2.5	12.6 ± 1.3
DBIC	0.11	0.00413	1 ± 0.25	6.8 ± 1.9	11.1 ± 0.5
DBIC	0.11	0.00854	3.4 ± 0.9	3.25 ± 0.7	19.3 ± 4.5
DEII	0.025	0.00125	0.78 ± 0.5	6.2 ± 3	10.7 ± 1
DEII	0.025	0.00266	1.91 ± 0.4	9 ± 2	9.4 ± 0.9
DEII	0.025	0.00348	4.7 ± 2.7	4 ± 1.8	15.9 ± 10
DEII	0.025	0.00348	4.32 ± 2	4.3 ± 1.5	13.6 ± 5
DEII	0.025	0.00266	3.37 ± 1.5	4.7 ± 1.5	13.4 ± 4
DEII	0.025	0.00209	1.44 ± 0.45	6.5 ± 1.7	10.5 ± 0.8

[a] The decay parameters are given with their 99% confidence intervals calculated with the assumption that the decay parameters are uncorrelated. These intervals are 2.6 times larger than the corresponding standard deviations.

From the slope and intercept of Figure 3 a value of (0.9 ± 0.2) × 10^{10} L mol^{-1} s^{-1} and (4.5 ± 0.4) × 10^{8} s^{-1} is obtained for respectively $k_m{}^+$ and $k_m{}^-N_{agg}$. If $k_{qm} >> k_m{}^-$ parameter A_4 equals k_{qm} (Table III).

For the system pyrene–mDCB the above-made assumption is not valid, and corrected values of $k_m{}^-$, $k_m{}^+$, N_{agg}, and K are obtained by an itterative approach. Since $k_{hm}[M]$ is neglibible, this correction does affect the above-mentioned linear relationship of $S_3{}^{-1}$ and $S_2{}^{-1}$. The corrected values are reported in Table IV.

(b) Quenching of DEII and DBIC by mDCB. The observed fluorescence decay can be analyzed according to eq 1, but parameter A_2 is, contrary to the above-described system, for these shorter living probes determined by the first term k_7 (Table V). Since $k_m{}^-$ is a rate constant characteristic of the quencher–micelle system and independent of the nature of the donor (if no specific

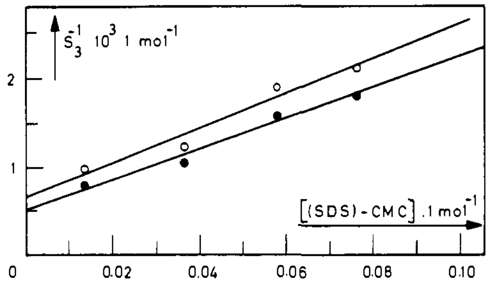

Figure 4. Quenching of DEII by pCNT in SDS: ○, S_3^{-1} vs. (SDS) − cmc; ●, $k_{qm}^2/(A_4^2S_3)$ vs. (SDS) − cmc.

Table VI. Quenching with pCNT

	k_m^-, s^{-1}	K, L mol^{-1}	N_{agg}	k_{qm}, s^{-1}
uncorrected	7.2×10^6	1600 ± 300	51 ± 7	8.1×10^7
corrected	6.1×10^6	1900 ± 300	60 ± 7	7.5×10^7

interactions occur), k_{qm} can be calculated from parameter A_4 (Table V). Multiplying S_3^{-1} by k_{qm}^2/A_4^2 should yield $1/K + [M]$. The obtained values are plotted in Figure 2 and found to correspond, within experimental error, with those of the previously mentioned pyrene–mDCB system. This indicates that for small numbers of quencher and probe per micelle the aggregation number of the micelle and the binding constant of the quencher is unaffected by the solubilized probe.

(c) Quenching of DEII by pCNT. This system can be compared to the probe–quencher system mentioned under section b. The dependence of S_3^{-1} upon [SDS] − cmc is the total SDS vs. cmc concentration is given in Figure 4. Assuming k_m^+ to be diffusion controlled (vide infra) k_m^- can be calculated from the uncorrected data. From parameter A_4 the rate constant k_{qm} is obtained and is found to be nine times larger than k_m^-. Application of the correction procedure mentioned above yields corrected values for the parameters of this system (Table VI).

(d) Quenching of DEII and DBIC by αNCN. The obtained fluorescence decay curves can be fitted to eq 1; no dependence of A_2 on the quencher concentration is observed. The plot of S_3^{-1} vs. [SDS] − cmc is given in Figure 5. The value fo K, obtained from the intercept should be larger than 5000, while the aggregation number equals 66 ± 10. The values of k_m^- obtained in section 2a–c are identical with those obtained for respectively benzene[21] or toluene.[21] If we assume the same to be true for αNCN in comparison with naphthalene, a value between 10^6 and 1.5×10^5 s^{-1} can be estimated for k_m^-. This is not in contradiction with the above-estimated value for K. Parameter A_4 equals 10^8 s^{-1} for DEII and 8×10^7 s^{-1} for DBIC, and is two orders of magnitude larger than k_m^-; hence A_4 equals k_{qm} and no correction of N_{agg} is necessary.

Discussion

1. Parameters Describing the Binding of the Quencher. k_m^+ corresponds to the value calculated by Almgren[21] for a neutral quencher assuming the process to be diffusion controlled. It is larger than the values experimentally obtained for arenes.[21] A possible explanation for this difference can be related to an hypothesis formulated by Hunter.[22] In the water phase the nonpolar arenes could be associated with some surfactant monomers leading to a decrease of their diffusion coefficient. For the more polar nitriles this association should not occur. It must be remarked here that for these neutral quenches k_m^+ is larger than for metal cations where it decreases upon increasing the charge of the cation.[9]

In contrast to the situation encountered with metal ions, hopping of the quencher between the micelles is not an important process for mDCB. Although k_{hm} increases upon decreasing the charge of the metal ion,[9] it becomes again rather small for a neutral quenching. An explanation could be given on the basis of the fact that ionic quenchers are mostly bound by electrostatic interactions and "bound quenchers" are not only present in the Stern layer but also in the "inner part" of the Gouy–Chapman layer[23] as some kind of Bjerrum pairs.[24] Interactions between the Gouy–Chapman layers of two micelles, a phenomenon occuring already at relatively large intermicellar distances, will decrease the binding of the quencher. Neutral quenchers are present in the outer core of the Stern layer and are mostly bound by "hydrophobic" interactions. These interactions remain until close contact exists between the hydrocarbon parts of two micelles. The values of K obtained for mDCB (1500 L mol^{-1}), pCNT (1900 L mol^{-1}) correspond fairly well to those[21] obtained for the arenes without a nitrile group (benzene, 1000 L mol^{-1}; toluene, 5300 L mol^{-1}).

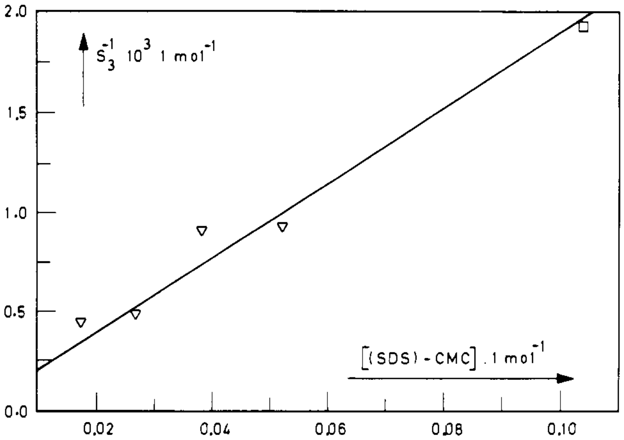

Figure 5. Quenching by αNCN in SDS: □, the probe is DBIC; ▽, the probe is DEII.

Introduction of the polar cyano group seems to have a rather small influence on K, which seems mostly determined by the surface of the apolar part of the quencher. This observation also suggests the predominance of hydrophobic effects on the binding of neutral quenchers. The small influence of the cyano group on K can furthermore indicate that even in the micelle the environment of the quencher remains, at least locally, rather polar. This corresponds[21,25] to a solubilization site near to the surface.

2. Discussion of k_{qm}. (a) Theoretical Model for k_{qm}. Almgren and Grieser[21] observed that in a micelle where there is no preferential solubilizing site for the probe and the quencher, more than 50% of the probes and the quenchers are less than 5 Å from the surface. For aromatic molecules where there exists a preferential adsorption[25] at the surface, this will be even more so. As a consequence one can, when the number of quenchers is not too large,[7,8] consider an intramicellar quenching as a diffusion process on a spherical surface to form an encounter complex followed by the quenching itself. As long as the number of quenchers is not too large, tangential diffusion will on the average be necessary over much larger distances than radial diffusion (to make the distance between D* and A in both dimensions less than the encounter distance R_{AD}). On a globe one needs only three coordinates to represent the relative positions of A and D*: R_A and R_D (their respective distances) from the center of the sphere and θ, and the angle between R_A and R_D. On a spherical surface with radius R_M, only the angle θ changes during the diffusion process.

It was shown[8] that after long times k_θ is given by

$$k_\theta = 4\pi s_1(s_1 + 1)(D/R_M^2) \qquad (14)$$

where D is the mutual tangential diffusion coefficient of A and D, R_M the radius of the surface on which the diffusion occurs, s_1 the constant depending on R_{AD}/R_M, and k_θ the rate constant

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[21] M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **101**, 279 (1979).

[22] T. F. Hunter, *Chem. Phys. Lett.*, **75**, 122 (1980).

[23] J. Frahm and S. Dieckman, *J. Colloid Interface Sci.*, **75**, 440 (1979).

[24] J. Bockris and A. Reddy, "Modern Electrochemistry", Plenum Press, New York, 1973, pp 253–267.

[25] P. Mukerjee and J. R. Cardinal, *J. Phys. Chem.*, **82**, 1614 (1978).

Table VII. Comparison of k_{qm} for αNCN and mDCB

	κ	σ^a	$s_1(s_1 + 1)$	$\kappa k_\theta \times s$	$k_\theta/k_{-\theta}$
mDCB	0.694	0.0443	0.33	8×10^{-4}D	0.046
αNCN	0.698	0.0492	0.39	1.2×10^{-3}D	0.051

[a] For an encounter distance of 6 Å.

for a diffusion-controlled process on a spherical surface.

For a diffusion-controlled quenching k_{qm} is given by

$$k_{\mathrm{qm}} = k_{\mathrm{dm}} = 4\pi D\kappa s_1(s_1 + 1)R_{\mathrm{M}}^2 \qquad (15)$$

where κ represents the fraction of probe quencher pairs in the micelle for which the radial distances from the center of the micelle differ less than R_{AD}. Furthermore

$$k_\theta/k_{-\theta} = R_{\mathrm{AD}}^2(4R_{\mathrm{M}}^2 - R_{\mathrm{AD}}^2) \simeq R_{\mathrm{AD}}^2/4R_{\mathrm{M}}^2 \qquad (16)$$

hence

$$k_{-\theta} = \pi D s_1(s_1 + 1)/R_{\mathrm{AD}}^2 \qquad (17)$$

where $k_{-\theta}$ is rate constant for rotational back-diffusion.

The transient effects on k_{qm} can be discarded.[7] For the quenching of DEII by αNCN k_{qm} may be put equal to κk_θ. Assuming DEII and αNCN are present in the core and the Stern layer, κ is about 0.7 for an encounter distance of 6 Å. Therefore, k_θ for DEII and αNCN equals 1.5×10^8 s^{-1}. After 0.5 ns k_θ differs less than 25% from its stationary value. This is in agreement with our experimental observations that it was always possible to fit the observed fluorescence decay to eq 1. Transient effects on k_{qm} are thus rather unimportant.

(b) Influence of ΔG_2 on k_{qm}. As shown in Table III k_{qm} increases when ΔG_2 decreases when $E°_{\mathrm{D^+/D^*}}$ becomes less positive. Comparing αNCN to mDCB for which $E°_{\mathrm{A/A^-}}$ is less negative, one should observe an increase in k_{qm} on going from αNCN to mDCB. But as shown in Table III one obtains a decrease of k_{qm} for the three probes. This effect shows that, for reactions which are nearly diffusion controlled in methanol, one can assume for the moment that the reaction is also diffusion controlled for these systems in the micelle (cf. below). It is furthermore not likely that D is much larger for αNCN than for mDCB. The difference of the product κk_θ must then be due to a change of κ, R_{M}, or $s_1(s_1 + 1)$, parameters which are influenced by the way the quencher is solubilized. When the probe and quencher are only present in the Stern layer, $R_{\mathrm{M}} = 20$ Å; when they are both present in core and Stern layer, $R_{\mathrm{M}} = 15$ Å. If the probe is present in the core and the Stern layer and the quencher only in the Stern layer, one can propose that

$$1/R_{\mathrm{M}}^2 = 0.5(1/R_{\mathrm{SC}}^2 + 1/R_{\mathrm{C}}^2) = 3.49 \times 10^{-3}\ \text{Å}^{-2}$$

This yields an average value of 16.9 Å for R_{M}. Assuming that αNCN and DEII are present in the core and the Stern layer and the more polar mDCB is present only in the Stern layer, one can calculate that $R_{\mathrm{M}} = 15$ Å for the system DEII and αNCN and 16.9 Å for the system DEII and mDCB. The values of κ, σ, κ_θ, and $k_\theta/k_{-\theta}$ for αNCN and mDCB are given in Table VII. This table indicates that for a diffusion-controlled reaction the different k_{qm} values for αNCN and mDCB can be rationalized by a difference in average solubilization. Using the values of k_{qm} obtained for αNCN and mDCB and the calculated κ and $\sigma(R_{\mathrm{AD}}^2/4R_{\mathrm{M}}^2)$ values,[7] one can calculate $k_{-\theta}$. For mDCB and αNCN $k_{-\theta}$ equals 2.7×10^9 and 2.2×10^9 s^{-1}. Comparing these $k_{-\theta}$ values to k_{r} in methanol, one finds that they are of the same order of magnitude for pyrene. For DEII $k_{-\theta}$ is, however, much smaller than k_{r}, justifying the above-made assumption.

(c) Determination of the Intramicellar Viscosity. For the system DEII–αNCN, the quenching is diffusion controlled. With $R_{\mathrm{AD}} = 6$ Å, $R_{\mathrm{M}} = 15$ Å, and $k_{\mathrm{qm}} = 1.0 \times 10^8$ s^{-1}, one can calculate that

$$k_{\mathrm{qm}} = 1.0 \times 10^8\ \mathrm{s}^{-1} = 1.8 \times 10^{-3}\ \mathrm{D}\ \text{Å}^{-2}$$

This yields for the diffusion coefficient D a value of 6.3×10^8 Å^{-2} s^{-1} or 6.3×10^{-6} cm^2 s^{-1}. If one can assume a Stokes–Einstein relationship and a value of 2.5 Å for the radius of αNCN and DEII, a value of 3.2 cP is obtained for the intramicellar viscosity. This value for the viscosity obtained from the translational diffusion coefficient is much smaller than that obtained by Weber et al.[26a] by fluorescence depolarization and equals that obtained for intramolecular excimer formation by Zachariasse.[26b] This difference could suggest that the intramicellar "viscosity" differs for rotational and transitional motions as suggested by Rodgers.[27]

Conclusions

Quenching by neutral quenchers can be described by the same overall kinetics assumed for the quenching by ionic quenchers. In contrast to ionic quenchers, binding of the quenchers to the micelle occurs by hydrophobic interactions. This is shown by the small k_{hm} values and the decrease of k_{m}^- upon increasing the surface of the apolar part of the quenchers. Transient effects on k_{qm} seem to be absent on the time scale of the experiment, and the experimental values obtained for k_{qm} are compatible with the proposed theoretical model. The difference in viscosity obtained for different types of motions inside a micelle requires caution in the use of concept of "viscosity" for a "micelle".

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Registry No. SDS, 142-87-0; DEII, 80243-03-4; DBIC, 80243-04-5; mDCB, 626-17-5; pDCB, 623-26-7; αNCN, 86-53-3; pCNT, 104-85-8; pyrene, 129-00-0.

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(26) (a) M. Shinytrsky, A. C. Dranot, and G. Weber, *Biochemistry*, **10**, 2106 (1977). (b) K. A. Zachariasse, *Chem. Phys. Lett.*, **57**, 429 (1978).

(27) M. D. J. Rodgers and R. B. Da Silva e Wheeler, *Chem. Phys. Lett.*, **42**, 584 (1976).