PHOTOINDUCED ELECTRON TRANSFER BETWEEN AROMATIC HYDROCARBONS AND ARENE DIAZONIUM SALTS IN MICELLAR SOLUTIONS

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In micellar sodium dodecylsulfate (SDS) solution ground-state charge-transfer complexes between aromatic hydrocarbons and diazonium salts can be detected by UV absorption. The hydrocarbon fluorescence quenching occurs by both static and dynamic mechanisms and can be described by an established kinetic scheme.

1. Introduction

Micellar aggregates of ionic surfactant molecules consist of an inner hydrophobic core and an outer multiple layer of charged end groups, oppositely charged counter ions and solvating water molecules [1]. Thus, photoinduced electron-transfer reactions between a hydrophobic donor solubilized within an anionic micelle and a cationic acceptor may proceed efficiently due to the high local concentration of the reacting species. According to the theory of electron-transfer reactions, the donor and acceptor are required to be separated by a distance of no more than 4–6 Å for efficient reaction to occur [2,3]. However, the radius of a sodium dodecylsulfate (SDS) ($CH_3(CH_2)_{11}OSO_3^{\ominus}Na^{\oplus}$) micelle is estimated to be ≈18 Å [4]. Thus, we expect that for electron transfer to occur within this system, diffusion of the micellized donor to the micellar boundary must occur. With this assumption, the limiting rate for micellar electron-transfer reactions can be calculated to be $k_{et} \leqslant 5 \times 10^8\ M^{-1}\ s^{-1}$, since the microviscosity within an SDS micelle has been determined to be $\eta \geqslant 10$ cP [5]. However, experimentally it is found that micellar photoelectron transfer reactions can occur with rate constants of 10^9–$10^{11}\ M^{-1}\ s^{-1}$ [6–8]. Additionally, static quenching of donor fluorescence has been observed [9,10] which indicates that under certain conditions, a diffusion step is not required.

In order to explain these results a modified model of the detailed micellar structure has been proposed in which "channels" of water may penetrate the hydrophobic micellar core [7,10,11]. Static quenching in this case can be explained in terms of a tunneling mechanism [6]. Alternatively, it has been suggested that ground-state charge-transfer complexes which penetrate the micellar Stern layer [10] are responsible for the static quenching. In either case we expect that diffusional processes may also contribute to the overall quenching event, since diffusion of either a hydrophobic donor to the micellar boundary, or a cationic acceptor within the water channels, may occur within the excited state lifetime. Thus, the total quenching of fluorescence which is observed should consist of both static and dynamic quenching processes.

It is the aim of the present work to completely describe the micellar photoinduced electron-transfer quenching of aromatic hydrocarbons in terms of a kinetic scheme which allows for both static and dynamic quenching. The aromatic hydrocarbons anthracene (Ac) and 1,4-dimethylnaphthalene (DMN) were chosen as electron donors, and aromatic diazonium salts as electron acceptors. Experiments have been per-

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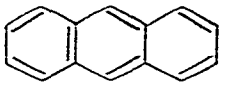
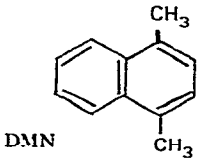
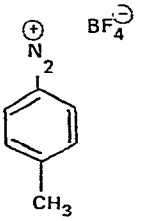


Ac



DMN



MeDS

formed using the anionic detergent SDS, for which it has been shown that aromatic hydrocarbons are located entirely within the hydrophobic core of the micelle [12]. It is assumed that the cationic water soluble diazonium salts, like methyl viologen [7], are located in the water phase. Quenching of the fluorescence of the aromatic hydrocarbon donors by diazonium salts in homogeneous solution is well established [13]. Additionally, it has been shown that in homogeneous solution, ground-state complexes of these donor/acceptor pairs may be observed by means of their charge-transfer absorptions [13].

2. Experimental

Arene diazonium salts were prepared by diazotization of the corresponding anilines in 40% HBF_4 [13]. Anthracene (VEB Laborchemis Apolda) and 1,4-dimethylnaphthalene (Aldrich Chemical Co.) were sublimed and distilled respectively. The lumophors were solubilized in 0.1 M SDS (Bio-Rad) by ultrasonic mixing and, as for solutions of the diazonium salts, used immediately after preparation.

Absorption spectra were recorded on a Specord UV–VIS spectrometer (VEB Carl Zeiss Jena), fluorescence spectra on a Hitachi-PE MPF-2A fluorimeter. Fluorescence lifetimes were measured using single-photon counting [8] or pulsed laser fluorimeter (LIF 200, ZWG AdW Berlin, N_2 laser, $E_{1/2} = 0.5$ ns) [14] techniques, and were analyzed using a computer deconvolution method. All measurements were carried out in air saturated solutions at 20°C.

3. Results and discussion

3.1. Ground-state complexes

The absorption spectra of Ac (1.8×10^{-4} M) or DMN (7.5×10^{-4} M) in SDS (0.1 M; [micelle] = 1.6×10^{-3} M) are identical to those observed in non-polar *n*-hexane. In the presence of *p*-methylbenzenediazonium tetrafluoroborate (MeDS) however, new shoulders on the long wavelength tail of the hydrocarbon absorptions are observed at wavelengths up to 550 nm. Additionally, in the case of Ac, an enhancement in the region of its own absorption is observed. These new absorptions are attributed to charge-transfer (CT) complexes between the hydrocarbon donor and diazonium salt acceptor, by analogy to those observed previously in homogeneous solution [13]. Analysis of the complex absorptions according to the method of Hildebrand and Benesi [13] (fig. 1) allows determination of the following complex formation constants K_c and extinction coefficients E_c:

Ac: $K_c = 210\ M^{-1}$, $E_c^{380} = 2380\ M^{-1}\ cm^{-1}$;

DMN: $K_c = 27\ M^{-1}$, $E_c^{380} = 280\ M^{-1}\ cm^{-1}$.

The formation constants are larger than the corre-

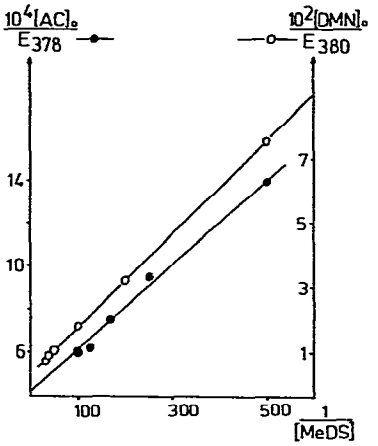


Fig. 1. Benesi–Hildebrand treatment of the CT absorptions of 1,4-dimethylnaphthalene (DMN) ([DMN] = 7.5×10^{-4} M), and anthracene (Ac) ([Ac] = 1.8×10^{-4} M), respectively; *p*-methylbenzene diazonium tetrafluoroborate (MeDS) in 0.1 M Na-dodecylsulfate solutions; E_λ = extinction of the complex at the wavelength, λ.

sponding constants in homogeneous solution [‡]. Evidently, micellization of the substrates significantly enhances complex formation, a phenomenon which has been observed previously for CT complexation of pyrene and methylviologen in 0.1 M SDS and methanol (K_c = 704 M^{-1} in SDS; K_c = 3.4 M^{-1} in methanol) [10]. This effect is obviously related to the high concentration of the positive counter ions at the micelle Stern layer. In effect, the concentration of the acceptor associated with the micelles is larger than its analytical concentration; hence, the calculated complex formation constants are too high.

It is possible that the enhancement in complexation efficiency is caused by solvation effects on the surface or Stern layer of the micelle. However, only a small solvent effect on K_c is observed in homogeneous solution [‡]. The formation of CT complexes between a micellized hydrocarbon donor and hydrophilic acceptor can be explained in terms of the "channel" micelle model structure. In the water filled channels, a diazonium cation can approach a donor localized within the micelle core, up to the distance of 3–4 Å necessary for CT complexation [15]. Alternatively, assuming a spherical micelle with a closed Stern layer, then complex formation is only possible if the donor is localized near the polar surface of the micelle. However, the results of UV, NMR and fluorescence measurements on micellized aromatic hydrocarbons [12] do not support this interpretation.

3.2. *Fluorescence quenching*

MeDS is an efficient electron acceptor and hence quenches the fluorescence of Ac via an electron transfer mechanism [2,13,16]. We have studied the reaction in acetonitrile using both steady-state (fluorescence intensity) and time-resolved (fluorescence lifetime) techniques. Plots of I_0/I and τ_0/τ are linear (fig. 2) and yield quenching rate constants of 6.8 × 10^{10} M^{-1} s^{-1} and 6.9 × 10^{10} M^{-1} s^{-1}, respectively. These values are identical within experimental error, and thus we conclude that in acetonitrile the electron-transfer reaction

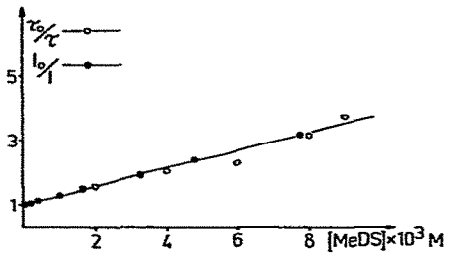


Fig. 2. Stern–Volmer plot of the fluorescence lifetime, λ, and fluorescence intensity, I, respectively, of anthracene Ac ([Ac] = 5 × 10^{-5} M) with *p*-methylbenzene diazonium tetrafluoroborate (MeDS) as quencher in acetonitrile; λ_{ex} = 356 nm; λ_{em} = 400 nm.

occurs by a dynamic mechanism, and that no static quenching occurs at the concentration of quencher used.

In 0.1 M SDS the fluorescence intensity of Ac is quenched by solubilized MeDS more efficiently than in homogeneous solution. In this case, however, the data cannot be analyzed by a simple Stern–Volmer relationship (fig. 3). A plot of the fluorescence lifetime versus [MeDS] is linear and yields values of k_{et} and τ_0 of 8.4 × 10^{10} M^{-1} s^{-1} and 3.2 ns, respectively. The steady-state fluorescence behaviour is characteristic of static quenching phenomena. Indeed, a plot of the ex-

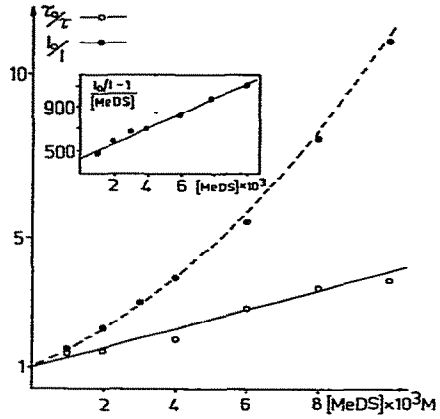


Fig. 3. Stern–Volmer plot of the fluorescence intensity, I, and fluorescence lifetime, τ, respectively, of anthracene Ac ([Ac] = 5 × 10^{-5} M) with *p*-methylbenzene diazonium tetrafluoroborate (MeDS) as quencher in 0.1 M sodium dodecylsulfate solutions. Dashed line is data calculated according to eq. (1a) (see text). Insert is plot according to eq. (1b) (see text).

[‡] For example, K_c = 0.6 M^{-1} for the complex between *p*-chlorobenzene diazonium tetrafluoroborate and Ac in acetonitrile [14].

[‡] For example, K_c for the 2-nitro-4-decyloxybenzene diazonium tetrafluorobenzene/pyrene CT complex increases only twice on going from 1,2-dichloroethane to acetonitrile.

perimental data according to eq. (1b) [17], assuming both static and dynamic quenching, yields a straight line. The static part

$$I_0/I = (1 + K_c[Q])(1 + k_{et}\tau_0[Q]) . \quad (1a)$$

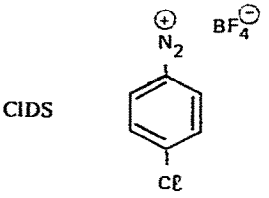
$$\frac{I_0/I - 1}{[Q]} = K_c + k_{et}\tau_0 + K_c k_{et}\tau_0[Q] . \quad (1b)$$

of the overall fluorescence quenching can be determined using the equation

$$(I_0/I)\tau/\tau_0 = 1 + K_c[Q] . \quad (2)$$

The formation constant, $K_c = 184 \pm 21$ M^{-1}, thus obtained agrees well with that calculated from the UV analysis of CT complex formation between Ac and MeDS in SDS (fig. 1). Thus, we conclude that the static quenching occurs as a result of ground-state CT complex formation between the reactants. Calculation of the dependence of I_0/I upon [MeDS], using eq. (1a), and values of K_c and $k_{et}\tau_0$ of 210 M^{-1} (from the UV experiment) and 268 M^{-1} (from the lifetime measurements), agrees well with the experimental data (dashed line in fig. 3). This demonstrates that the fluorescence quenching of Ac by MeDS in micellar solutions can be described well by a combination of static and dynamic quenching mechanisms.

Quenching of the fluorescence of DMN by *p*-chlorobenzenediazonium tetrafluoroborate (ClDS) exhibits similar behavior. In acetonitrile a plot of I_0/I versus [ClDS] is linear and yields a quenching constant, k_{et} of 8.1×10^{10} M^{-1} s^{-1} (table 1). In 0.1 M SDS the DMN fluorescence is quenched by ClDS more efficiently than in acetonitrile; however, in this case, the micellar effect is smaller than that observed for the Ac/MeDs donor/acceptor pair. A plot of I_0/I is linear to a concentration of ClDS $\approx 3 \times 10^{-4}$ M, above which curvature is observed. The Stern—Volmer constants determined from the linear part of the plots are larger than for homogeneous solution quenching. Again the deviations from linearity can be explained by static quenching due to the formation of CT complexes between DMN and ClDS. Analysis of the data according to equation 1b yields a straight line (inset, fig. 4). The extent of complexation, and thus static quenching of DMN is smaller than that of Ac, since the former has and $E^{ox}_{1/2} \approx 1.35$ V † compared to $E^{ox}_{1/2} = 1.09$ V for Ac. The effect of para chloro substitution ($\sigma_p = 0.23$) of the diazonium salt on K_c can be calculated using the Hammett constant ($\rho = 0.4$) for K_c as determined in homogeneous solution [13]. In this manner, the formation constant for the CT complex between DMN and ClDS, $K_c = 39$ M^{-1} can be evaluated, using K_c



† The polarographic half wave oxidation potential $E^{ox}_{1/2}$ for 2,3-dimethylnaphthalene. The position of the substituents has only a small effect on $E^{ox}_{1/2}$. For example, for 2,6-dimethylnaphthalene $E^{ox}_{1/2} = 1.36$ V [18].

Table 1
Rate constants for quenching of hydrocarbon fluorescence by *p*-chlorobenzenediazonium tetrafluoroborate ([ClDS] = (0.3–3) × 10^{-4} M)

Solvent	10^4 [fluorophor] (M)	[DMN]/[Micelle] a)	τ_0(ns)	10^{-10} k_{et} (M^{-1} s^{-1})
13 M SDS	14.7 DMN b)	0.66	44	5.0
11 M SDS	15.4 DMN	0.85	45	5.3
23 M SDS	55.6 DMN	1.47	44	5.0
12 M SDS	30.3 DMN	1.59	43	4.2
CH_3CN	44.2 DMN	–	10.8	8.1
CH_3CN	0.5 Ac c)	–	4.1	6.8
CH_3CN	0.5 Ac d,e)	–	4.5	6.6

a) [Micelle] calculated assuming an aggregation number of 60.
b) $\lambda_{ex} = 320$ nm, $\lambda_{em} = 339$ nm. c) $\lambda_{ex} = 356$ nm; $\lambda_{em} = 400$ nm.
d) experiments performed in deaerated solution.
e) quencher MeDS [1–10] × 10^{-3} M].

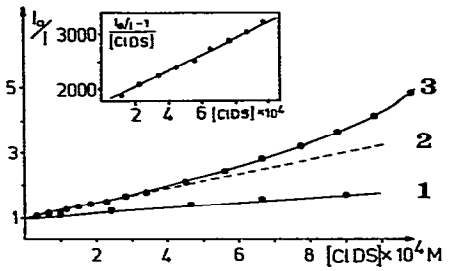


Fig. 4. Stern–Volmer plot of the fluorescence intensity, I, of 1,4-dimethylnaphthalene DMN ([DMN] = 4.4 × 10^{-3} M) with *p*-chlorobenzene diazonium tetrafluoroborate as quencher in acetonitrile (1), in 0.1 M sodium dodecylsulfate solutions by [CIDS] < 3 × 10^{-4} M (2), and [CIDS] > 3 × 10^{-4} M (3), respectively. Insert is plot of data according to eq. (1b) (see text).

= 27 M^{-1} for MeDS (σ_p = –0.17) ‡‡. This small value explains the smaller extent of static quenching of DMN by CIDS.

3.3. Lifetime measurements.

The above results allow two conclusions to be drawn concerning the time-resolved fluorescence measurements: (1) The dynamic quenching occurs with higher rate constants than expected for a diffusion-controlled reaction inside a micelle. Therefore, the micelle must be penetrable by hydrophilic molecules. (2) Both static and dynamic quenching is observed. Thus, the quencher must be located close to the micelles and interact with the donor at a separation of less than 18 Å.

Additionally, the following assumptions can be made: (3) Within the lifetime of the excited micellized donor, the distribution of quencher molecules with respect to the individual micelles is constant. (4) The quencher distribution can be described by a Poisson function.

With these assumptions a rate expression may be derived which explains the exponential nature of the time-resolved fluorescence decay [7], and allows a more informative interpretation of the data,

$$\ln(I_t/I_0) = \langle S\rangle[\exp(-k/\tau_1) - 1] = t/\tau_0 \,. \qquad (3)$$

‡‡ Because of the large bathochromic shift of the CIDS complex, a direct spectroscopic determination of K_c was not possible.

The average number of quencher molecules per micelle ([Q]/[micelles]) is given by $\langle S\rangle$, and τ_1 is the fluorescence lifetime for the case of one associated quencher molecule per micelle. For $\langle S\rangle \geqslant 1$ and $\tau/\tau_1 < 0.5$, then eq. (3) becomes [7]

$$\ln(I_\epsilon/I_0) = -(1/\tau_0 + \langle S\rangle/\tau_1)t = -t/\tau \,, \qquad (4)$$

where τ is the experimentally determined fluorescence lifetime. This linear relationship has been observed previously in several cases [1,7,19]. From eq. (4) it follows:

$$1/\tau = 1/\tau_0 + (1/[\text{micelle}]\,\tau_1)[Q] \,, \qquad (5)$$

$$\tau_0/\tau = 1 + (\tau_0/[\text{micelle}]\,\tau_1)[Q] \,. \qquad (6)$$

Eq. (6) is analogous to the Stern–Volmer relationship. Thus, the results of the time-resolved fluorescence quenching of Ac by MeDS can be interpreted in terms of eqs. (4) and (6). At high values of $\langle S\rangle$ the experimental data can be described by eq. (4). For the lowest quencher concentration ([MeDS] = 1 × 10^{-3} M; $\langle S\rangle$ = 0.6) deviations from linearity are observed at long times in agreement with the limitations of eq. (4). The value of k_{et} calculated in fig. 3 corresponds with the quotient $1/\tau_1$ [micelle] in eq. (6). For [micelle] of 1.6 × 10^{-3} M a unimolecular rate constant $k_1 = 1/\tau_1$ = 1.3 × 10^8 s^{-1} is determined for the quenching of one micellized anthracene singlet by one associated diazonium salt. This value is one order of magnitude greater than the rate constant determined for pyrene excimer formation within a micelle containing two pyrene molecules [20].

In the present case the larger value of k_1 can be explained if the water soluble MeDS quencher can diffuse through water channels within the micelle. Thus, the results of the present study are consistent with a model of an "open" micelle.

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