Exploratory Study of the Effect of Polyelectrolyte–Surfactant Aggregates on Photochemical Behavior[1]

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Abstract: Various photochemical processes have been examined in aggregates of poly(styrenesulfonate) and dodecyltrimethylammonium bromide. Laser flash and luminescence studies provide information on the nature of these aggregates; at the same time, it is of interest to examine the way in which the aggregates can control the photochemical behavior of various substrates. It is concluded that up to 50% coverage the detergent is almost quantitatively associated with the polymer; the aggregate formed should be regarded as an aggregate of aggregates, with a large number of small (7–10 units) surfactant clusters. These local aggregates behave as "minimicelles", but form at concentrations well below the critical micellar concentration for this surfactant. The formation of these relatively nonpolar aggregates occurs with concurrent coiling of the polyelectrolyte chain and leads to extensive probe protection from negatively charged quenchers. By contrast, micelles of the same surfactant only protect from positively charged quenchers. Rather unusual phenomena were observed in the case of triplet xanthone, which following excitation has been shown to relocate from the PSS/DTB aggregates to a highly polar environment, presumably the aqueous phase.

Organized systems of various types have been the subject of intensive research during the last decade.[3–5] Photochemical techniques have played an important role in the examination of the nature of the various types of aggregates (e.g., micelles). For example, luminescence techniques have been employed to determine micellar parameters such as aggregation number, critical micellar concentration (cmc), and the partition of solutes between the micellar and aqueous pseudophases.[6–8] On the other hand, organized systems have provided new environments where photoreactions frequently proceed with consequences different from those observed in homogeneous solution.[9]

Aggregates formed by interaction of surfactants with polyelectrolytes have been the subject of only limited study, although the importance of polymer–surfactant interactions has been recognized in fields as varied as enhanced oil recovery, isolation of membrane bound proteins, polymer solubilization, conformational changes in biopolymers, and mineral flotation and flocculation.[11]

In particular, photochemical techniques have received virtually no attention in the case of polyelectrolyte–surfactant systems. A few recent studies have examined intramolecular photoprocesses (such as excimer formation) in polyelectrolytes,[14,15] as well as their interaction with several photoactive probes,[16–19] some of which can be regarded as amphiphilic substrates.

Another recent approach in the study of polyelectrolyte–surfactant aggregates is the use of surfactant-selective electrodes.[12,13,20] This approach has already been used for the poly(styrenesulfonate)–dodecyltrimethylammonium system[13] discussed in this report. The work by Hayakawa and Kwak[13] unequivocally demonstrates the importance of cooperative effects in these aggregates.

In this report we explore the use of photochemical probes in order to characterize polyelectrolyte–surfactant aggregates. We also examine the way in which these aggregates affect the behavior of excited states, their mobility, and their quenching by ionic and neutral substrates. We have also examined briefly the behavior of free radicals in these systems and the effect of external magnetic fields. Most experiments were carried out by using either fluorescence or laser flash photolysis techniques.

Experimental Section

Materials. Dodecyltrimethylammonium bromide, DTB (Sigma Chemical Co.), was purified by repeated recrystallizations from acetone. Sodium poly(styrenesulfonate), PSS, was a commercial sample from Aldrich. The polymer was purified by reprecipitation from water by 2-propanol addition 3 times and 1 time by methanol addition. Several fractions were collected in each one of the dissolution–reprecipitation cycles. The lowest molecular weight fractions were strongly yellow and were discarded. The first fractions which account for a few percent of the starting material gave a white solid. These fractions were used after drying under vacuum for 2 days; they were found to have a molecular weight of ~130 000 as determined from the intrinsic viscosity in aqueous 0.5 M NaCl solution and the known Mark-Houwink parameters.[22] 8-Anilino-1-naphthalenesulfonic acid, ammonium salt, ANS (Aldrich), was used without treatment. Benzophenone (Aldrich) and xanthone (Fluka, puriss) were recrystallized twice from ethanol. Tetramethylammonium bromide (Aldrich) was used as received. Cetyltrimethylammonium chloride (CTAC) from K & K was purified as indicated in an earlier report.[23] Sodium dodecyl sulfate, SDS (BDH, specially pure), was used as received. 1,4-Cyclohexadiene (Aldrich), 1,3-cyclohexadiene,

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Effect of Polyelectrolyte–Surfactant Aggregates

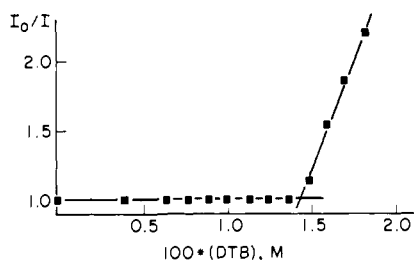*J. Am. Chem. Soc., Vol. 106, No. 21, 1984* 6275

Figure 1. Dependence of the fluorescence intensity from biphenyl on the concentration of the surfactant DTB.

(Aldrich), and 1-methylnaphthalene (Aldrich) were distilled under vacuum before use. Pyrene and phenanthrene (Aldrich) were purified by recrystallization from ethanol. All inorganic salts were analytical grade. Water (HPLC grade from Fisher) was employed to prepare the solutions.

Steady-State Spectroscopy and Photolysis. Absorption and fluorescence spectra were measured on Varian 219 and Perkin-Elmer LS-5 computerized spectrophotometers, respectively. A Hanovia 150-W Xe/Hg lamp installed in a Bausch & Lomb housing was used for the steady-state photolysis experiments. Irradiations were carried out under oxygen-free conditions, unless otherwise stated, in sample cells made of rectangular (7 × 7 mm²) Suprasil tubing.

Laser Photolysis Experiments. A Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ/pulse) or a Lumonics TE 860 excimer laser (at 308 nm with Xe–HCl mixtures, ~4 ns, up to 80 mJ/pulse) was used for sample excitation. Transient absorptions were monitored by using a detection system with nanosecond response. The signals, initially acquired by an R-7912 Tektronix transient digitizer, were processed by a PDP-11/23 computer, which also provided suitable facilities for experiment control, data storage, and hard-copy output. Further details have been reported elsewhere.[24] The samples (usually 1 or 2 mL) were contained in Suprasil cells made of rectangular (3 × 7 mm²) or square (7 × 7 mm²) tubing.

Viscosity Measurements. The intrinsic viscosity of the PSS fraction used was measured at 298 K in an capillary viscometer of Ubbelohde type. Five PSS concentrations (1.36 g/dL and lower) in 0.5 M NaCl were measured. The plot of the reduced viscosity against PSS concentration was linear under these conditions, thus enabling the usual extrapolation to obtain the intrinsic viscosity (a value of 0.35 dL/g was obtained). Other viscosity measurements were carried out by employing the same viscometer at 298 K.

Xanthone Solubility Measurements. The solubilities were determined from the UV absorbance of saturated solutions at 338 nm. Cells of different optical paths were used in order to cover the range of solubilities from water to the more concentrated polyelectrolyte–surfactant mixtures. Calibration of the signals was carried out in each one of the solutions by adding small aliquots (up to 10 μL) of a concentrated xanthone solution in acetonitrile to a known volume of the solution under study. Saturation was achieved by sonication of the solid (in excess) for several 15-min intervals. After each sonication, more solid was added in order to ensure the nucleation of small particles formed during sonication (which can have higher solubility). The solutions were then centrifuged, and the absorbance was recorded; typically, 45–60 min of sonication was sufficient to achieve the equilibrium. The solubility in pure water was (0.5 ± 0.1) × 10⁻⁴ M; addition of 28 mM PSS did not have any significant effect. The solubility in 28 mM PSS–14 mM DTB was (2.7 ± 0.2) × 10⁻⁴ M. All measurements were carried out at 298 K.

Determination of the Critical Micellar Concentration for DTB. The critical micellar concentration, cmc, was measured by monitoring the fluorescence from biphenyl at 290 nm as a function of DTB concentration. As a consequence of the difference in the biphenyl fluorescence quantum yields in the two media,[25] the fluorescence intensity reflects the partitioning between the two pseudophases. A plot of I°/I (ratio of the fluorescence intensities in the absence (I°) and present (I) of DTB) vs. the DTB concentration shows a sharp break (Figure 1) at the cmc as is usual in these types of plots. The value obtained was 14.4 mM in pure water at 295 K and is in good agreement with previous data from other methods.[26]

Fluorescence Lifetimes. A PRA-Nitromite LN-100 nitrogen laser, providing a pulse of ca. 0.3 ns at 337.1 nm, was used for excitation. The time evolution of the luminescence signal was monitored by using an
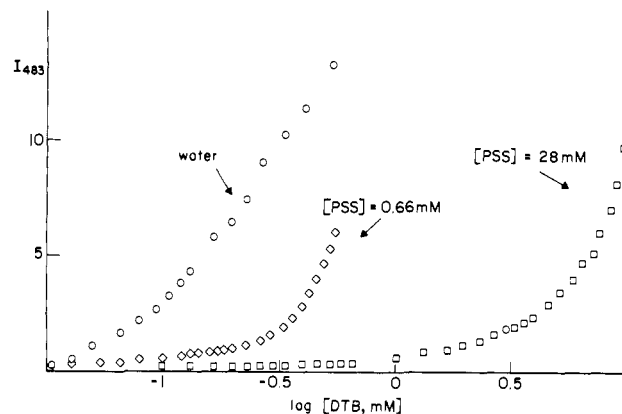

Figure 2. Dependence of the fluorescence intensity of ANS ($\lambda_{emission}$ = 483 nm) on the surfactant concentration for pure water (O), for [PSS] = 0.66 mM and [NaCl] = 0.04 M (◊), and [PSS] = 28 mM (□).

RCA-4840 photomultiplier tube and a Tektronix 7633 storage oscilloscope.

Results and Discussion

The first part of our experiments concentrated on the characterization of the aggregates. We have examined the possibilities of photochemical probes as a way of determining properties such as the degree of surfactant binding to the polyelectrolyte, or the type of environment they provide to guest molecules. Preliminary work was carried out with neutral polymers and positively or negatively charged polyelectrolytes; the work reported herein refers to PSS and its interaction with DTB which seemed amenable to study by techniques such as fluorescence and laser photolysis. When the composition of the mixture is not specifically mentioned, the experiments were carried out in 28 mM PSS, with 14 mM DTB.

A. Nature of the Aggregates. The interaction between PSS and DTB has recently been examined by Kwak et al.[13] who established that the detergent interacts strongly with the polyelectrolyte, in a process that involves a strong cooperative effect. Typically, binding takes place about 2 orders of magnitude below the cmc for the surfactant in pure water and is almost quantitative until the fraction covered reaches or somewhat exceeds 0.5. Unfortunately, Kwak's studies have all been carried out in submillimolar solutions, which do not match the conditions under which photochemical experiments, particularly laser photolysis, can be conveniently carried out. This is mostly due to three problems: (i) limited probe solubility in very dilute systems, (ii) partition between pseudo-phases favoring the aqueous media, and (iii) possibly high occupancy levels if one tries to overcome (i) and (ii) by using high probe/aggregate ratios. Basically, one would like to increase the concentration of polyelectrolyte by at least an order of magnitude. These aggregates have not been characterized well enough that we could confidently assume that such a change in concentration would have little or no effect on their characteristics; the following experiments examine this question. All experiments in this section were carried out in aerated solutions.

A1. 8-Anilino-1-naphthalenesulfonic Acid (ANS) as a Probe. ANS has been widely used as a probe to examine the microenvironment of molecular aggregates and biological systems.[27–29]
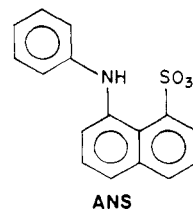
ANS

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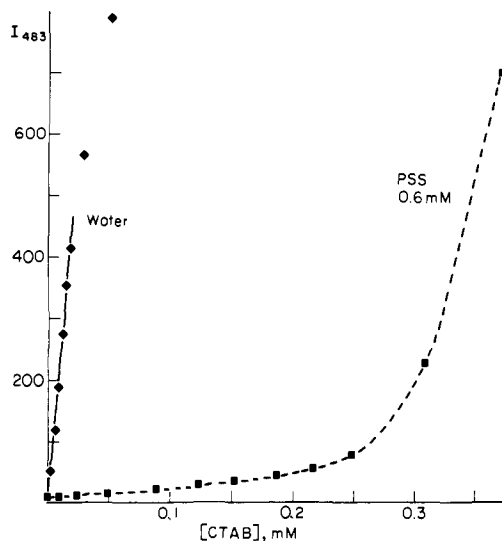(28) Andley, V. P.; Chakrabarti, B. *Biochemistry* **1981**, *20*, 1687–1693.

6276 *J. Am. Chem. Soc., Vol. 106, No. 21, 1984*

Abuin and Scaiano

Figure 3. Dependence of the fluorescence intensity of ANS on the concentration of the surfactant CTAB.

Figure 4. Effect of the addition of tetramethylammonium bromide (O) and DTB ($\Diamond$) on the reduced viscosity of an aqueous solution of PSS (20 mM) at 298 K. Note that the viscosity for [DTB] = 5.7 mM is essentially the same as for water.

Table I. Spectral Data for Pyrene Fluorescence in Several Systems

system	I_1/I_3	λ_1	λ_3
water	1.54	374	384.4
	1.59[a]		
	1.87[b]		
PSS (28 mM)	1.55	375	386
PSS/DTB[c]	1.15[d]	375	386
DTB micelles	1.20	375	386
toluene	1.04	375.5	386.3
	1.04[b]		
	1.11[a]		
2-propanol	1.07	374	384.6
	1.08[b]		

[a] From ref 33. [b] From ref 34. [c] Concentrations: 28 mM PSS and 14 mM DTB. [d] When DTB is added to a PSS solution, the value of I_1/I_3 is reduced and at 7 mM DTB reaches 1.15; further addition does not modify significantly this ratio. (see also: Bloor, D. M.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 657–669.)

It is well-known that in polar media ANS shows a weak fluorescence that peaks at 520 nm. By contrast, in nonpolar solvents or when it is incorporated in nonpolar aggregates the fluorescence shifts to 480 nm and shows an increase in quantum yield of several orders of magnitude.[27-29]

When DTB is added in concentrations below its cmc to a solution of ANS in water, the fluorescence of the probe increases and shifts in the way characteristic of a decrease in environmental polarity. The effect is illustrated in Figure 2 for the addition of DTB up to 0.45 mM to a 0.6 mM solution of ANS in water (more concentrated DTB solutions caused precipitation to occur). Addition of PSS up to 28 mM to a 0.6 mM aqueous solution of ANS did not lead to any significant change in the fluorescence intensity and spectrum. Some degree of ANS binding to the polyelectrolyte could have been expected owing to the hydrophobic characteristics of the polymer;[18] however, this was not observed in the range of concentrations used in this work in the case of solutions in pure water. Addition of 0.04 M sodium chloride to PSS concentrations over 20 mM seems to favor binding, since ca. 30% increase in ANS fluorescence intensity was observed upon addition of the salt. No significant effect was observed at PSS concentrations below 10 mM.

The addition of DTB to solutions of ANS and PSS in water led to almost no change in the fluorescence until a threshold concentration was reached. By comparison with the results in pure water, one has to conclude that almost no free DTB is present in the system. The data for [PSS] = 0.66 mM in the presence of [NaCl] = 0.04 M are also illustrated in Figure 2 and agree well with the values reported by Kwak,[13,30] thus indicating that the use of ANS as a probe is reasonably reliable. The results for the higher concentrations of PSS (see also Figure 2) follow the same pattern mentioned above. Analysis of these data indicate that for concentrations of DTB of up to 50% (i.e., coverage = 0.5) of the concentration of PSS, over 90%, and possibly as much as 95%, of the detergent is bound to the polyelectrolyte. We note that the use of a log scale in Figure 2, while convenient in order to cover several orders of magnitude in concentration, also tends to mask the threshold concentration, which in a linear scale is sharper than suggested by Figure 2. Similar effects have been observed with other surfactants, such as cetyltrimethylammonium chloride (CTAC) and bromide (CTAB); the results for the latter are illustrated in Figure 3, now using a linear concentration scale.

A note of caution on the use of ANS seems appropriate. Since ANS interacts strongly with DTB, and may even form small
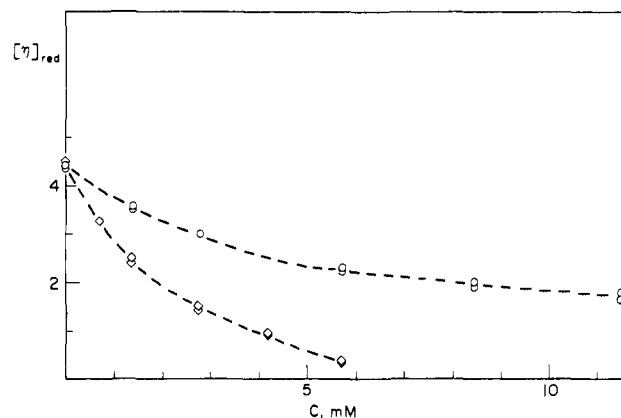
aggregates, it may promote the release of DTB from PSS–DTB aggregates, by simply displacing the association equilibrium. In this sense, the concentration of DTB detected by the probe in the aqueous pseudo-phase may be slightly higher than that present in the absence of the fluorescent probe.

A2. Viscosity Effects. The viscosity of aqueous solutions of polyelectrolytes is strongly dependent upon the conformation of the polymeric chain. This conformation is in turn dependent on the environment (e.g., ionic strength) sensed by the macromolecule.[22,31]

Addition of DTB to PSS solutions causes a sharp decrease in viscosity. Figure 4 shows this effect, where the values have been expressed as reduced viscosities [$\eta_r = (\eta - \eta_o)/\eta_o[\text{PSS}]$] in dL/g units.

Control experiments show that these concentrations on DTB, when added to pure water, do not have a significant effect on the viscosity. The addition of equivalent amounts of tetramethylammonium bromide to the PSS solution causes a decrease in the viscosity compatible with the effect of salts on polyelectrolyte conformation[22] but is less pronounced than that observed when DTB is added. The sharp decrease in viscosity upon addition of DTB is attributed to a coiling of the initially more extended polyelectrolyte chain. Comparison of the data in Figure 4 with the results using ANS as a probe and with literature reports[22,31,32] indicates that the effects on the viscosity should be interpreted in terms of coiling of the chain that accompanies the cooperative binding of the surfactant.

A3. Pyrene as a Polarity Sensor. The vibrational structure of the fluorescence bands from pyrene is widely recognized as a good sensor for environmental polarity.[33,34] Winnik et al.[34] have

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(30) Here the concentrations are comparable with those used in earlier work.[13]

(31) Kowblansky, M.; Zema, P. *Macromolecules* **1981**, *14*, 1451.

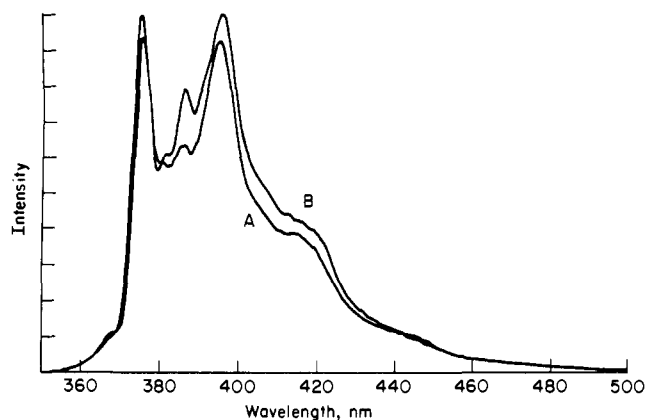(32) Fishman, M. L.; Eirich, F. R. *J. Phys. Chem.* **1975**, *79*, 2740–2744.

Figure 5. Pyrene fluorescence spectra in water (A) and in PSS/DTB aggregates (B).

carried out extensive studies which illustrate the possibilities of pyrene fluorescence for this purpose.

We have examined the 1/3 intensity ratio for the vibrational bands in pyrene fluorescence in several systems in order to examine the type of microenvironment in the case of PSS/DTB aggregates. Table I summarizes our observations, while Figure 5 shows the fluorescence spectra in water and in PSS (28 mM)/DTB (14 mM) solution. PSS itself has very little effect on the fluorescence from pyrene (see Table I). The results in Table I show that the environment sensed by singlet pyrene in PSS/DTB aggregates is less polar than that in DTB micelles.

The data presented to this point indicate that DTB binds strongly to PSS, that this binding is almost quantitative for DTB–PSS ratios of up to ~0.5, and that this interaction is accompanied by coiling of the polymer chain. Further, the microenvironment in the organic pseudo-phase is less polar than that of conventional micelles of the same surfactant.

B. Excited-State Dynamics. In this section we present a series of experiments in attempts to examine the mobility of probes and quenchers in PSS/DTB aggregates, the competition between static and dynamic quenching processes, and the size of the aggregates. Some of the systems examined lead to the formation of radical pairs whose behavior will be discussed in another section.

Our experiments have been frequently carried out in a mixture containing 28 mM PSS and 14 mM DTB. The latter is quite close to the cmc for this detergent; however, it should be noted that the concentration of *free* DTB is in fact much lower (probably below 1 mM) than that required for the formation of conventional micelles. Experiments in this section have been carried out in deaerated solutions.

B1. Quenching of Phenanthrene Triplets. Phenanthrene is essentially insoluble in water but incorporates well into aggregates such as micelles, where its mobility is expected to be even lower than that of the surfactant.[35] Its triplet state has a characteristic T–T absorption spectrum with λ_{max} = 483 nm,[36] which can be easily monitored in laser flash experiments. The triplet lifetimes observed in PSS/DTB aggregates were usually around or in excess of 50 μs and are probably controlled by low levels of impurities.

We have used three types of quenchers in order to cover the different kinds of electrostatic interactions, i.e., negative (NO_2^-), positive (Cu^{2+}), and neutral (1,3-cyclohexadiene). All of these are excellent quenchers of phenanthrene triplets in homogeneous solutions.

Dynamic quenching was examined by monitoring the effect of quencher addition on the decay of phenanthrene triplets, i.e.,

$$k_{exptl} = k_o + k_q[Q] \qquad (1)$$

(33) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1976**, *99*, 2039–2044.
(34) Doug, D. C.; Winnik, M. A. *Photochem. Photobiol.* **1982**, *35*, 17–21.
(35) Burkey, T. J.; Griller, D.; Lindsay, D. A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1983–1985.
(36) Scaiano, J. C. *J. Photochem.* **1982**, *18*, 395–396.

Table II. Quenching of Phenanthrene Triplets

solvent system	$k_q/(M^{-1} s^{-1})^a$	quencher
acetonitrile/water (1:1)	$(1.87 \pm 0.07) \times 10^9$	NO_2^-
PSS/DTB[b]	$(1.17 \pm 0.12) \times 10^7$	NO_2^-
acetonitrile/water (1:1)	$(6.0 \pm 1.2) \times 10^8$	Cu^{2+}
PSS/DTB	$(2.1 \pm 0.4) \times 10^8$	Cu^{2+}
acetonitrile/water (1:1)	$\sim 6 \times 10^{9\,c}$	1,3-cyclohexadiene
PSS/DTB	$(2.5 \pm 0.5) \times 10^9$	1,3-cyclohexadiene

^{a} Errors as $\pm 2\sigma$. ^{b} Concentrations: 28 mM PSS and 14 mM DTB. ^{c} Reference 42.

Table III. Lifetime of Singlet Pyrene in Various Systems

solvent system	τ/ns^a	
	nitrogen	air
water	205	136
PSS (28 mM)	250	180
PSS/DTB[b]	385	300
SDS micelles (0.06 M)	400	200
DTB micelles (0.04 M)	180^c	120

^{a} Typical error $\pm 10\%$. ^{b} Concentrations: 28 mM PSS and 14 mM DTB. ^{c} Probably controlled by bromide quenching.
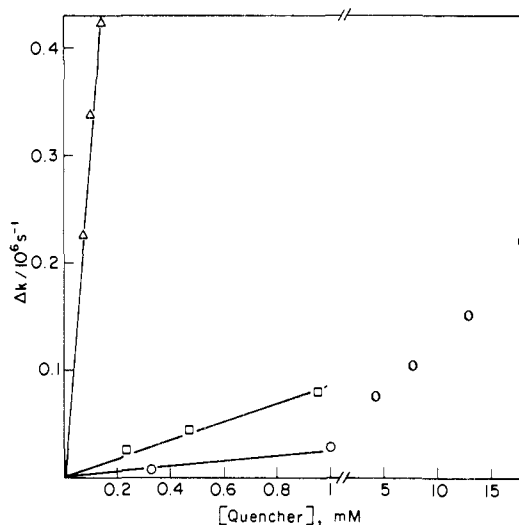

Figure 6. Quenching of phenanthrene triplets by various substrates in PSS/DTB according to eq 1 (corrected for k_o): by nitrite ions (O), by 1,3-cyclohexadiene (△), and by Cu^{2+} (as $CuSO_4$) (□).

where k_{exptl} is the pseudo-first-order rate constant for triplet decay, k_o has the same meaning but in the absence of quencher ($k_o = \tau_o^{-1}$), k_q is the bimolecular rate constant for triplet quenching, and [Q] is the bulk quencher concentration. All the plots were reasonably linear (suggesting that eq 1 is a good approximation), and the corresponding results have been summarized in Table II. A typical set of plots is shown in Figure 6.

Static quenching effects, detectable by a decrease in the transient optical density before significant triplet decay takes place, were quite evident in the case of Cu^{2+}. The effect is a clear indication of an association of the quencher with the aggregate and results from excitation of phenanthrene having a quencher as a nearby neighbor. Detailed analysis of static effects is difficult for phenanthrene because of the possibility of singlet and triplet quenching (the former lives ca. 60 ns);[37] other examples (vide infra) are better suited for this analysis.

The dynamic quenching data (Table II) show good protection from negative quenchers, probably reflecting the excess charge in the polyelectrolyte, and a small effect in the case of 1,3-cyclohexadiene, which in micellar solutions has been recognized as a very mobile molecule which partitions well between the two pseudo-phases.[8]

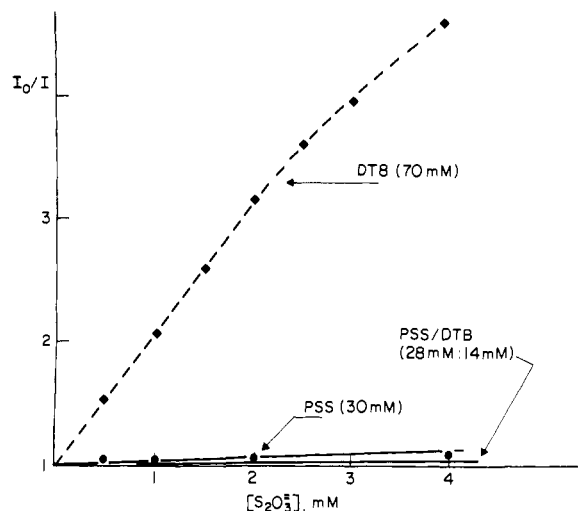(37) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker, New York, 1973; Section 1.

Figure 7. Quenching of pyrene fluorescence by $S_2O_3^{2-}$ in the presence of various combinations of PSS and DTB.

Table IV. Apparent Rate Constants for the Quenching of Pyrene Fluorescence

solvent system	$k_q/(M^{-1} s^{-1})$	quencher
water	$5 \times 10^{8\,a}$	Eu^{3+}
PSS (28 mM)	$3.5 \times 10^{9\,b}$	Eu^{3+}
PSS/DTB	$1.5 \times 10^{9\,b}$	Eu^{3+}
water	6×10^7	$S_2O_3^{2-}$
PSS/DTB	(no quenching)	$S_2O_3^{2-}$

[a] From: Ziemicki, H.; Cherry, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 4479–4483. [b] Based on initial slopes (i.e., $c \rightarrow 0$).

PSS/DTB aggregates offer little protection from positively charged quenchers and in fact induce static quenching processes.

B2. Quenching of Pyrene Singlets. The results in section A3 clearly show that pyrene singlets reside in the nonpolar environment provided by the polyelectrolyte–surfactant aggregates. The singlet lifetimes measured by monitoring the fluorescence signals at various wavelengths (frequently 400 nm) following laser (337.1 nm) excitation are shown in Table III and are reasonable for systems of this type. While the lifetime of 385 ns reported here for PSS/DTB corresponds to 50% coverage, the value was the same at 30% or higher coverages. Within the limitations of the technique used (see Experimental Section) all the decay profiles appeared to follow single exponential behavior.

The fluorescence from pyrene was readily quenched by Eu^{3+} ions; by contrast no quenching by $S_2O_3^{2-}$ could be detected under conditions (up to 50 mM) where efficient quenching was observed in micellized DTB. Figures 7 and 8 illustrate the quenching data, while Table IV summarizes the results.

In the concentration range used ($\leq 10^{-6}$ M pyrene) no excimer fluorescence was detected. It should however be noted that when the pyrene concentration was $\sim 10^{-6}$ M only monomeric fluorescence was detected in 28 mM PSS in water. Addition of 3 mM DTB leads to efficient excimer formation. The excimer emission decreases and eventually disappears at higher surfactant concentrations, suggesting that the number of pyrene-solubilizing DTB clusters had increased to the point where double occupancy was not significant.

B3. Xanthone T–T Spectroscopy and Lifetimes. Xanthone is particularly well suited for studies of the type carried out here. It has a very strong absorption band at about the nitrogen laser excitation wavelength (337.1 nm), its triplet state has an intense and easily monitored T–T absorption band, and its lifetime has been shown to be strongly dependent upon the polarity and hydrogen bonding characteristics of the media.[24]

Since xanthone is a relatively polar molecule and the aggregates examined here are present in low concentration, we carried out some preliminary measurements of the solubility of xanthone in these systems. The details of these experiments are provided in the Experimental Section, but the main conclusion is that under
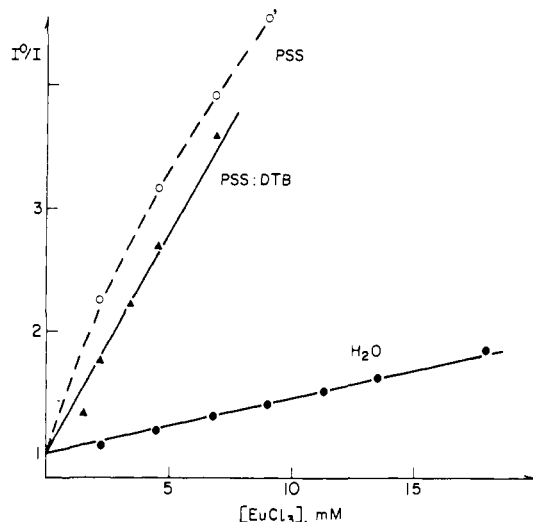

Figure 8. Quenching of pyrene fluorescence by Eu^{3+} in the presence of PSS (28 mM) and PSS (28 mM)/DTB (14 mM) and in water.
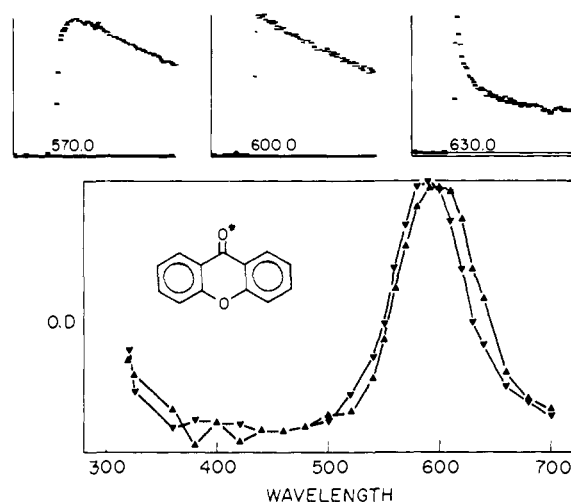

Figure 9. Top: OD traces obtained at 570, 600, and 630 nm; the total time scale is 1.6 μs for all traces. Bottom: Spectra averaged during the first 40 ns following laser excitation (▲) and after the fast decay is complete (▼) (about 1 μs).

our experimental conditions xanthone is predominantly but not completely solubilized in the PSS/DTB aggregates. Typically, 20% or less should be present in the aqueous pseudo-phase in the PSS/DTB aggregate most frequently used (28 mM PSS, 14 mM DTB).

The spectroscopy of this system turns out to be relatively complex (vide infra); however, when the triplet is monitored at 600 nm, one observes first-order decays with typical lifetimes of ~ 2.4 μs. For comparison, in micellized DTB (e.g., 20 mM) we have measured a lifetime of ~ 15 ns. The latter is consistent with earlier studies of benzophenone in cetyltrimethylammonium bromide micelles which showed efficient triplet quenching by the bromide counterions.[23] We take this result to mean that the bromide ions have been essentially quantitatively replaced by the polymer as counterions for the detergent.

As pointed out above the triplet decay traces at 600 nm follow clean first-order kinetics; however, this is essentially the only wavelength at which they do so. Figure 9 (top) shows traces obtained at 570, 600, and 630 nm. At 630 nm we observe two decay processes, with approximate lifetimes of 90 and 2300 ns, respectively. Two simple interpretations can be given to the fast decay: (i) that this decay simply leads to the deactivation of a fraction of the triplets or (ii) that this decay reflects the interconversion of the fast decaying triplet to the long-lived transient, also characterized (vide infra) as a triplet state. These two possibilities can be easily distinguished by examining the traces

Effect of Polyelectrolyte–Surfactant Aggregates

J. Am. Chem. Soc., Vol. 106, No. 21, 1984 6279

at λ < 600 nm, such as the one at 570 nm shown in Figure 9; this trace shows a buildup of the transient that then decays with the long lifetime mentioned before. The buildup seems to be concurrent with the decay at 630 nm, although accurate lifetime measurements are difficult in traces of this type. Further evidence for the interconversion mechanism can be obtained by examining the time evolution of the transient spectra. This is also shown in Figure 9, for spectra recorded during the first 40 ns following the laser pulse and about 1 μs after excitation. The most interesting feature of these spectra is that the transients observed in the short and long time scales agree well with the spectra for xanthone triplets in relatively nonpolar and polar solvents,[24] respectively. Thus, we propose that xanthone undergoes a relocation following laser excitation, and that this relocation reflects the motion of the triplet from the nonpolar environment provided by the PSS/DTB aggregates to a polar hydrophilic media. It is not clear whether this polar media is actually the aqueous phase or segments of the polyelectrolyte which are mostly free from detergent (note that these experiments were carried out at 50% coverage).

The arguments presented above mean that the triplet and ground states of xanthone partition differently between water and the PSS/DTB aggregates; in other words the two states have very different solubility properties. Interestingly, recently reported values of the dipole moments for these two states lead to 3.0 and 3.27 D for the ground and triplet states, respectively.[38] However, these experiments were carried out in carbon tetrachloride as solvent, where xanthone has a low-lying n,π^* triplet state.[24] Xanthone is unusually sensitive to solvent effects, and about 0.03 M 2-propanol added to carbon tetrachloride is enough to lead to an inversion of states and a low-lying π,π^* triplet.[24] It is quite possible that the dipole moment change relevant in the PSS/DTB system is that corresponding to the π,π^* state. Unfortunately, this value has not been determined in the case of xanthone, although for other carbonyl compounds having low-lying π,π^* states the change can easily exceed 1.5-D units. We propose that the relocation of xanthone upon excitation is triggered by a relatively large change in dipole moment that leads to large solubility differences between the ground and triplet states.

Following these observations in the PSS/DTB system, we carried out similar experiments in cetyltrimethylammonium chloride micelles. Similar relocation processes seem apparent, though they are not as large, or as easily detectable, as in the case of PSS/DTB aggregates. It seems likely that in the comparatively polar environment of the micellar systems the preference of the triplet for the aqueous phase would not be as pronounced.

B4. Quenching of Xanthone Triplets. The presence of two distinct triplet states (vide supra) as well as their efficient interconversion makes the interpretation of triplet quenching processes relatively complex. One way to simplify to some extent this problem is to monitor the total triplet concentration at 600 nm, where the two species show an isobestic point (see Figure 9). While for all practical purposes the traces at this wavelength follow good single exponential behavior, it is also clear that there is a trade-off of information as a result of the gain in simplicity.

Nitrite ions that are very inefficient quenchers of phenanthrene triplets in PSS/DTB aggregates (vide supra) readily quench xanthone triplets. Figure 10 shows the quenching plot obtained; the time scale of these measurements was long enough to ensure that the "fast" decay had been completed. Although at the exploratory level of this work we do not intend to propose a detailed quenching mechanism, the initial slope leads to an apparent rate constant of ca. 4 × 10^9 M^{-1} s^{-1}, reflecting easy access of the quencher to the xanthone triplets. We believe that the reason for the marked difference between phenanthrene and xanthone triplets is due to the fact that while the latter undergoes a relocation, phenanthrene does not. Quite clearly, the relocation of xanthone exposes it to a negative quencher, thus supporting the idea that the long decay process takes place from the aqueous phase.
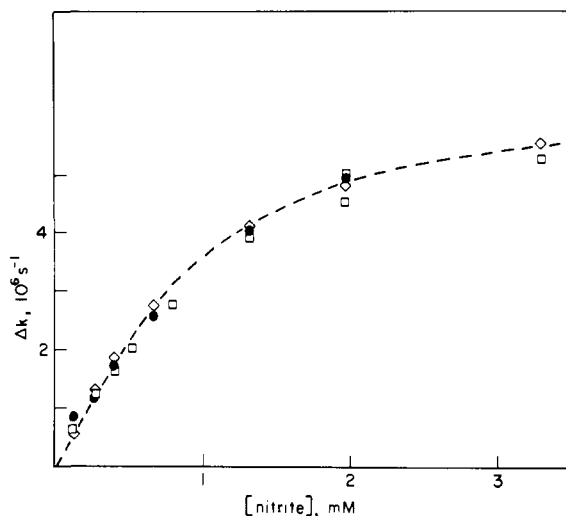

Figure 10. Quenching of xanthone triplets (monitored at 600 nm) by nitrite ions in PSS/DTB ($\diamond$) and PSS 28 mM ($\bullet$) and in PSS/DTB ($\square$) monitored at 560 nm.
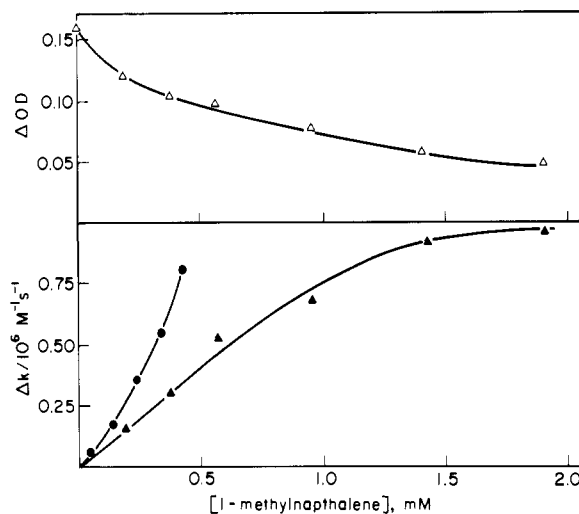

Figure 11. Effect of 1-methylnaphthalene on the behavior of xanthone triplets. Top: Decrease of the yield of triplet xanthone (as measured by the transient OD at 600 nm) upon addition of quencher for PSS/DTB aggregates. Bottom: Effect of the quencher on the kinetics of decay for xanthone triplets in PSS 28 nM ($\bullet$) and in PSS/DTB ($\blacktriangle$).

Consistently with this, when the kinetics were examined at 630 nm, we find that the effect of the quencher on the fast decay is minor in comparison with its effect on the slow process, suggesting that *before* relocation triplet xanthone is also well protected from negatively charged scavengers.

Another rather interesting quencher is 1-methylnaphthalene, which is essentially transparent at the excitation wavelength (337 nm) and leads to the sensitized formation of its easily detectable triplet state ($\lambda_{max} \sim$ 420 nm).[39] Examination of partition data for 1-methylnaphthalene in micellar systems[35,39,40] leads to the expectation that this quencher should be predominantly solubilized in the organic pseudo-phase. Addition of 1-methylnaphthalene to PSS/DTB solutions containing xanthone leads to a combination of static and dynamic triplet quenching. Static quenching leads to a decrease of the transient optical density due to triplet xanthone observed "immediately" after excitation (monitored at 600 nm) and is believed to reflect the presence of xanthone and quencher in the same aggregate (i.e., in close proximity) at the time of excitation. Figure 11 (top) shows the effect of 1-methyl-

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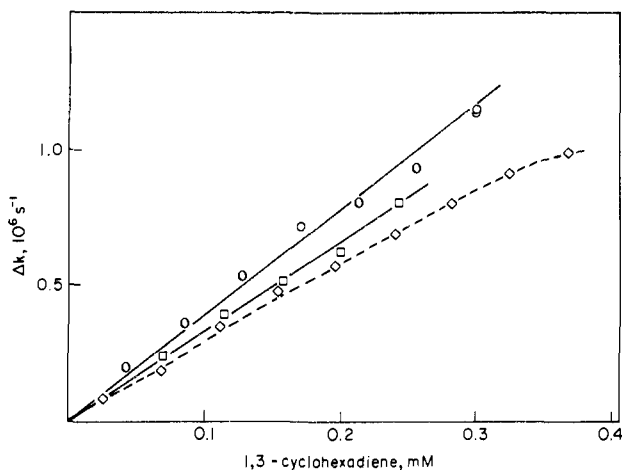
6280   *J. Am. Chem. Soc., Vol. 106, No. 21, 1984*

Abuin and Scaiano

Figure 12. Quenching of xanthone triplets by 1,3-cyclohexadiene in DTB micellar solution (O), PSS 28 mM (□), and PSS/DTB (◊).

naphthalene on the optical density at 600 nm immediately ($\leq$10 ns) following laser excitation. By contrast, in the case of PSS alone (no DTB) the changes were only ca. 15% of those in the PSS/DTB aggregate. A crude estimate of the size of the aggregates can be obtained by estimating the concentration of quencher necessary to reduce the initial transient optical density by a factor of 2.7. This condition is fulfilled for around or slightly less than 1 mM 1-methylnaphthalene, which given the concentration of DTB (14 mM) requires the aggregates sensed by xanthone to contain 7–10 detergent units. Since the polymer has a chain length of ca. 630 units, and the level of coverage is around 50%, the number of detergent molecules per polymer chain is about 300. Quite clearly, the PSS/DTB system should be regarded as an aggregate of aggregates.

The dynamic part of the quenching process, also included in Figure 11, reflects the combined mobility of probe and quencher, which allows pairs that were not neighbors at the time of excitation to approach sufficiently for energy transfer to occur. The plot is not completely linear, probably reflecting the simplification introduced by monitoring the absorption of xanthone triplets at the isosbestic point (vide supra). Most likely xanthone is largely responsible for the mobility (exit and entry processes) required for quenching to occur.

When the transient optical absorptions are monitored at 420 nm (were the signals are largely due to triplet 1-methylnaphthalene) we observe a "jump" followed by a buildup, the latter being approximately concurrent with the decay processes observed at 600 nm. The result is indicative of two different mechanisms leading to the same transient (the 1-methylnaphthalene triplet) and is entirely consistent with the mechanism proposed above involving a combination of static and dynamic quenching.

Another quencher examined in these experiments was 1,3-cyclohexadiene, which in homogeneous solution quenches xanthone at close to diffusion control (Figure 12).[41] In this case we observe efficient, but almost entirely, dynamic quenching. The plots of k_{decay} vs. [1,3-cyclohexadiene] are linear and for PSS/DTB lead to a second-order rate constant, $k_q \sim 3 \times 10^9$ M^{-1} s^{-1}, the value being about 4 times larger than the initial slope in the case of 1-methylnaphthalene (Figure 11, bottom). The absence of extensive static quenching (by comparison with 1-methylnaphthalene) is attributed to the higher solubility in water and overall mobility of 1,3-cyclohexadiene.[8] This, in turn, leads to faster overall dynamic quenching and the requirement of substantially lower quencher concentrations than in the case of 1-methylnaphthalene.

Quenching by cupric ions (sulfate salt) also led to curved quenching plots. The initial second-order rate constants extrap-

Table V. Lifetime of Benzophenone Triplets in Several Organized Systems under Oxygen-Free Conditions

system	τ_T/ns	ref
CTAC micelles	310	24
CTAB micelles	17	24
CTAC micelles (3% Br⁻)	170	24
SDS micelles	320	48
DTB micelles	15 ± 4	this work
PSS/DTB aggregates	320 ± 30	this work
PSS (no association?)	>1200	this work

olated to [Cu^{2+}] → 0 led to $k_q = 1.1 \times 10^9$ and 0.9×10^9 M^{-1} s^{-1} for PSS 28 mM and PSS/DTB aggregates, respectively.

B5. Behavior of Benzophenone Triplets. The photobehavior of benzophenone in micellar solution has been the subject of considerable attention in the last few years.[23,43-51] The decay of the benzophenone triplet usually leads to the formation of radical pairs whose behavior is quite different from that observed in homogeneous solution.[24,43,50,51] Earlier work from this laboratory[24,50] has demonstrated that in order to examine the behavior of the triplet state, it is necessary to monitor the signals at around 600 nm, where the ketyl radical, Ph$_2$ĊOH, is essentially transparent. Measurements of this type lead to a triplet lifetime of ca. 300 ns in deaerated PSS/DTB solutions and ca. 260 ns in air saturated systems. The small difference between these lifetimes is indicative of considerable protection from oxygen quenching; in this time scale the effect is, while interesting, not unlike the effect observed in micellar solutions. When the signals are monitored at 540 nm, where both the triplet state and the ketyl radical have strong absorptions, we systematically measure apparent lifetimes longer than those monitored at 600 nm. Earlier work from this laboratory[24] (mostly in sodium dodecyl sulfate micelles) has shown that this effect is due to the overlap both in wavelength and time of the signals from the triplet state and the ketyl radical. The behavior of the radical pairs will be discussed in a separate section. Table V summarizes the triplet lifetimes obtained in several relevant systems, including data from earlier work. As in other systems presented above, PSS/DTB aggregates offer remarkable protection from negative quenchers (i.e., the bromide counterions). By contrast with xanthone, benzophenone shows no evidence of relocation, consistently with the small change (in fact a decrease) of dipole moment upon excitation.[38]

Addition of 1,4-cyclohexadiene (a good precursor of radical pairs)[52] led to considerable shortening of the triplet lifetime. For 4.5 mM 1,4-cyclohexadiene we measured $\tau_T = 44$ ns and for 12 mM $\tau_T \sim 12$ ns, in both cases for the standard mixture, 28 mM PSS and 14 mM DTB. The transient spectrum observed after triplet decay was that characteristic of the diphenylhydroxymethyl radical.[52]

C. Behavior of Radical Pairs. Radical pairs in compartmentalized systems can provide considerable information on the nature of these compartments.[53,54] The experiments reported here concentrate on benzophenone as a radical-pair precursor, although a few experiments have also been carried out by using dibenzyl

(41) For example, quenching of xanthone triplets by 1,3-cyclohexadiene at 300 K in methanol solvent occurs with a rate constant, $k_q = 8.5 \times 10^9$ M^{-1} s^{-1}.[42]

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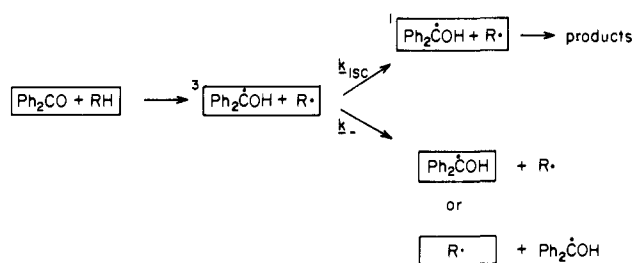(50) Thurnauer, M. C.; Meisel, D. *J. Am. Chem. Soc.* **1983**, *105*, 3729–3731.

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Effect of Polyelectrolyte–Surfactant Aggregates

J. Am. Chem. Soc., Vol. 106, No. 21, 1984 6281

Scheme I

$$Ph_2CO + RH \longrightarrow {}^3Ph_2\overset{.}{C}OH + R\cdot \overset{k_{ISC}}{\underset{k_-}{\rightleftharpoons}}$$

$$\boxed{Ph_2\overset{.}{C}OH + R\cdot} \longrightarrow products$$

$$\boxed{Ph_2\overset{.}{C}OH} + R\cdot$$

or

$$\boxed{R\cdot} + Ph_2\overset{.}{C}OH$$

ketone, which, in the case of micellar solution, has been extensively studied in Turro's laboratory.[53-56] All experiments were carried out in deaerated solutions.

C1. Photolysis of Benzophenone in PSS/DTB Aggregates. The behavior of the triplet state has already been discussed in section B5. As pointed out earlier, its decay leads to the formation of a triplet radical pair. In the absence of added hydrogen donor, the PSS/DTB aggregate is expected to behave as the hydrogen donor; indeed, the triplet lifetime measured is comparable with those obtained in micellar solution.[24,28] The decay traces obtained in this system strongly resemble those reported for micellar systems,[24] with clean exponential decay at $\lambda \geq 600$ nm but somewhat complex behavior where the ketyl radical and triplet-state signals overlap extensively (e.g., 540 nm). This has been shown[24] to result from the competition of radical-pair intersystem crossing (ISC) with exit from the aggregate, as outlined in Scheme I. Thus, while the triplet lifetime measured at 600 nm was ~300 ns, first-order fitting of the decay traces at 540 nm led to a lifetime of ~500 ns. The difference is attributed to the effect of underlying ketyl radical signals at this wavelength. Treatment of the data as in earlier work[24,48] suggests that $k_{ISC} \sim 2-5 \times 10^6$ s^{-1}. It should be noted that in Scheme I the boxes identify species contained in the *local* aggregates (7-10 surfactant molecules) mentioned before. Examination of the residual optical density at 540 nm, about 1 μs after laser excitation, suggests that about 20% of the radical pairs separate, while the other 80% undergo intersystem crossing processes. For comparison, in the benzophenone–SDS system, around 7% of the radical pairs undergoes separation.[24]

C2. Effect of 1,4-Cyclohexadiene on the Photochemistry of Benzophenone. As in earlier studies involving micelles,[24,43,48,50] we added 1,4-cyclohexadiene, which is a remarkably efficient hydrogen donor toward triplet benzophenone. Under these conditions, R in Scheme I is the cyclohexadienyl radical. As pointed out in section B5 the triplet lifetime can be reduced to 44 or 12 ns by addition of 4.5 or 12 mM 1,4-cyclohexadiene, respectively. Under these conditions the formation of the triplet radical pair approaches an "instantaneous" process. When this condition is met the leftmost box in Scheme I can be ignored. Figure 13 (top) shows a trace obtained in the presence of 4.5 mM 1,4-cyclohexadiene, which illustrates that in this case the residual optical density is rather large, reflecting extensive radical-pair separation; at least 44% of the radical pairs separate under these conditions.[57] Since the behavior of $(C_6H_5)_2\overset{.}{C}OH$ is not expected to change drastically upon addition of 1,4-cyclohexadiene, one is forced to conclude that the increased efficiency of separation process in this system is due to the exit of the cyclohexadienyl radical.

C3. Magnetic Field Effects. Earlier work from this and other laboratories has demonstrated that application of moderate fields can have a drastic effect on the behavior of geminate radical pairs in compartmentalized systems.[24,43,55,56] The main cause of this effect is the Zeeman splitting of the triplet sublevels which leads to a slowdown, and eventual shut-off, of intersystem crossing channels from the T_+ and T_- sublevels.
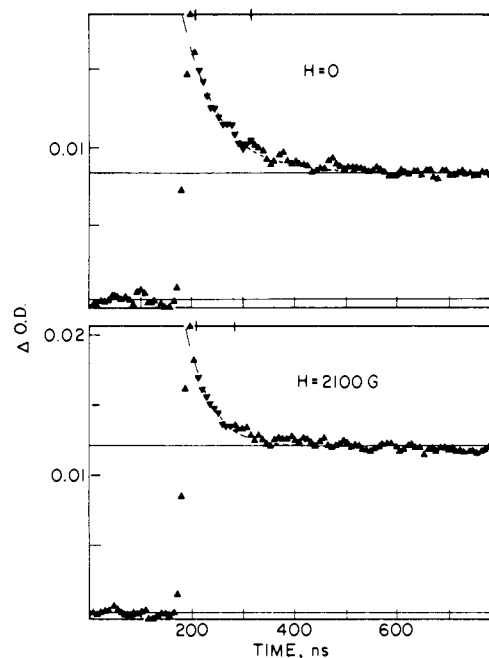

Figure 13. Decay trace monitored at 540 nm for a sample of benzophenone in PSS/DTB containing 4.5 mM 1,4-cyclohexadiene in the absence (top) and presence (bottom) of an external magnetic field.

Comparison of the two traces in Figure 13 shows an increase in residual absorption, which in turn reflects increased importance of radical exit processes in the presence of an external magnetic field. Analysis of the data in Figure 13 leads to at least 58% escape at 2100 G, compared with 44% in the absence of an applied field.[57] Thus, the effect is qualitatively the same as in micellar solution, though perhaps not as pronounced. Unfortunately, reducing the triplet lifetime to the point where it can be confidently regarded as an "instantaneous" decay, a necessary condition for a simplified analysis of the data, proved difficult. In principle this can be achieved by adding large concentrations of 1,4-cyclohexadiene; however, for concentrations of around 12 mM as in one of the examples above (compare with DTB 14 mM) it is questionable whether one could assume that the nature of the aggregates has not been substantially modified.

C4. Generation of "Light Absorbing Transients". Among the products of the photoreduction of benzophenone are the so-called "light absorbing transients" LATs, which are an isomeric mixture of ortho and para coupling products.[24,58] While LATs are only

LAT
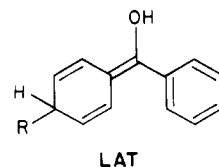
responsible for a small percentage of the products, they account for almost all the absorption changes observed in the near-UV region in the photochemistry of benzophenone.

In earlier work we have shown that the yield of LATs is much larger in micellar than in homogeneous solution.[24] The absorptions due to LATs are readily monitored at 320 nm, following irradiation of benzophenone samples for short intervals (typically 20 s). Figure 14 shows the increases in optical density observed in the PSS/DTB system. Control experiments showed that the initial rate of formation of LATs was very similar to that in sodium

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(57) The figure of 44% is based on the ratio of OD at the top and after the decay is complete; the actual efficiency of separation would be slightly higher if the value at the top still incorporates some signal from the triplet state.

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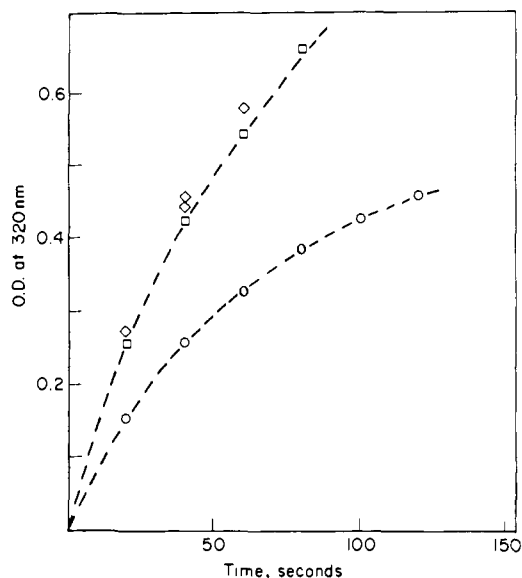6282 *J. Am. Chem. Soc., Vol. 106, No. 21, 1984*

Abuin and Scaiano

Figure 14. Formation of LATs (see text) upon irradiation of benzophenone for several 20-s intervals in aggregates of PSS (20 mM) and DTB (10 mM) in the absence (□) and presence (○) of air and in SDS micelles (◊) under nitrogen ([SDS] = 0.05 M).

Figure 15. Illustration of the interaction of the surfactant molecules with the polyelectrolyte, showing the formation of many small local aggregates.

dodecyl sulfate micelles but at least 1 order of magnitude faster than in DTB micelles, where the predominant process is triplet quenching by the bromide counterions. As in some of the examples presented before (vide supra) these results indicate an essentially complete substitution of the bromide ions by the polyelectrolyte in PSS/DTB aggregates. Our earlier experiments had suggested that the increase in LAT yields in micellar systems was due to the orientation of the reagents (i.e., the radical pair) within these aggregates. The example is far from unique; for example, de Mayo et al. and Wolff[59] found other systems involving photodimerizations where similar effects are observed. If, as in the case of micelles, we assume that this indicates the presence of accessible hydrophilic sites, we have to conclude that despite the nonpolar character of local aggregates (see section A3), some water penetrates the aggregate as a whole.

While the LAT yields in deaerated solutions are similar in sodium dodecyl sulfate micelles and in PSS/DTB aggregates, the yields in aerated samples are substantially higher in PSS/DTB aggregates, and the LATs are longer lived. Quite possibly, these results are mainly due to LAT differences in stability and to a laser extent to triplet-state protection.

C5. Photocleavage of Dibenzyl Ketone. The photochemistry of dibenzyl ketone in micellar and other organized systems has been extensively studied by Turro and his co-workers.[55,56] It has been known for a number of years that the cleavage of the triplet to yield $PhCH_2$ and $PhCH_2CO$ is an extremely fast ($\leq$10 ns) and efficient process.[55,56] Recent studies from Turro's and our laboratory have shown that the phenylacetyl radical decarbonylates with rate constants of around or slightly under 10^7 s^{-1}.[60,61]

When dibenzyl ketone is photodecomposed in PSS/DTB aggregates, using for excitation the pulses from an excimer laser (308 nm), we observe the characteristic spectrum of the benzyl radical ($\lambda_{max} \sim$ 317 nm). In relatively long time scales (tens of microseconds) the decay follows clean, homogeneous-like second-order kinetics, with $2k_t/\epsilon_{317} = 4.2 \times 10^6$ cm s^{-1}. Second-order analysis of the data typically leads to correlation coefficients in excess of 0.99. In the short time scales the transient phenomena observed is relatively complex and not unlike that observed in this
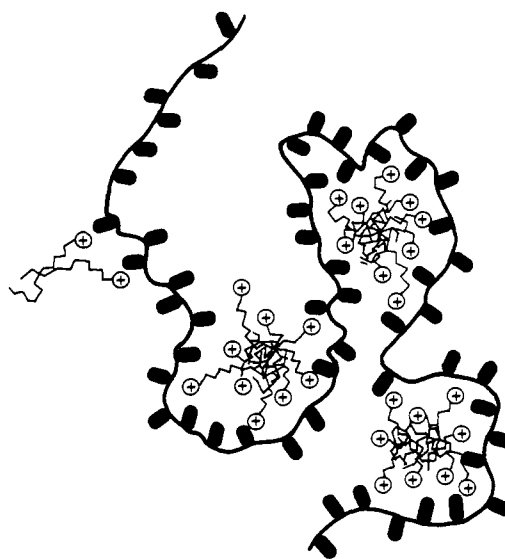
and other laboratories in the case of sodium dodecyl sulfate micelles.[62] That is, we observe a fast decay, with $k_{decay} \sim 10^7$ s^{-1}, followed by a growth occurring in a few 100 ns, probably reflecting decarbonylation. The fast decay is believed to result from intersystem crossing and separation of the $PhCH_2-PhCH_2CO$ radical pair.

Conclusion

In this section we address the question as to how the photochemical behavior in PSS/DTB aggregates compares with processes in homogeneous solution and in other organized systems, particularly micelles. Figure 15 shows a model for the PSS/DTB aggregates; naturally, this is only a rough description, useful only as a working model for PSS/DTB aggregates.

The results presented in section A show that (i) for DTB-PSS ratios of at least up to 0.5, not less than 90% of the detergent is polymer bound and that this aggregation takes place well below the cmc of the surfactant, (ii) formation of this aggregate is accompanied by coiling of the polymer chain, this is in fact consistent with the cooperative binding effect reported,[13,63,64] which usually indicates the presence of aggregates (which have been referred to as "micelle-like")[65] on the polymer, and (iii) the local order present is capable of providing a relatively nonpolar environment to many of the guest probes, such as pyrene.

It is important to emphasize that aggregation takes place when the free-detergent concentration is very low, typically $\sim$2 orders of magnitude below the cmc for the surfactant. In this sense these aggregates are clearly not conventional micelles. Electron spin resonance studies in related systems[66] show that the aggregation number of a surfactant on a polymer (i.e., cluster size) may be smaller than the ordinary micellar aggregation number. This is consistent with our estimate of 7–10 molecules per local cluster.

While the aggregates (assuming they contain only one PSS molecule) contain typically about 300 detergent molecules, all experiments suggest that the guest molecules actually "see" or sense very small units, probably containing less than 10 surfactant molecules. Thus, as shown in Figure 15 we picture these local aggregates as small islands having only a few detergent units. The suggestion of small aggregates is consistent with the observation that exit and radical-pair intersystem crossing in PSS/DTB aggregates are somewhat faster than in micellar solutions. In the

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latter we have observed that these processes are faster in the smaller micelles.[24]

The results with pyrene and xanthone show that PSS/DTB aggregates provide a nonpolar environment to these probes; however, the relocation of xanthone, the quenching by ions for a variety of probes, and the high yield of LATs in the case of benzophenone all seem to indicate that hydroxylic regions are readily accessible to the probe molecules. Thus, we suggest that water intercalates between the DTB islands or clusters and that in this sense, while the polymer has a coiled structure, it remains sufficiently open to allow water to penetrate in the system. This is not surprising in view of the fact that only about half of the charges have been neutralized.

The relocation of xanthone, presented in section B3, is believed to be the first example of its nature. In this sense it is important to note that xanthone is rather special only in that those changes are easily detectable, but the same type of phenomena may take place in many other systems. Quite frequently kinetic and equilibrium parameters for exit–entry processes in organized systems are measured for ground, singlet or triplet states and then used without any consideration for the type of electronic state. Our results indicate that solubility properties for ground and excited states may be quite different, particularly when significant changes in dipole moment occur upon excitation.

The behavior of radical pairs is quite similar to that observed in *small* micelles, with the competition between intersystem crossing and radical escape taking place in the hundreds of nanoseconds time domain.

Perhaps the most significant difference between the local DTB clusters in PSS/DTB aggregates, and conventional micelles, is that while the latter offer probe protection from *positive* quenchers, the PSS/DTB aggregates protect from *negative* species, thus reflecting the overall negative charge of the aggregates; in this sense, while local clusters seem to control the luminescent properties of the probes, static quenching phenomena, and radical-pair behavior, this is not the case of intermolecular processes involving species in the aqueous phase. These seem to be largely controlled by the total aggregate, particularly its charge.

SAC–CI Calculations for Rydberg Levels of the Ammonium Radical

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Abstract: A highly accurate computational determination for Rydberg states of NH_4 is made with the cluster expansion of the wave function theory. The theory confirms the recent assignment of the Schüler band to $^2T_2(3p) \rightarrow {}^2A_2(3s)$. However, for the Schuster band, there is a 4510-cm⁻¹ discrepancy between Herzberg's assignment and the present calculation.

The NH_4 radical is a molecule of special interest because its Rydberg states are expected to be bound and corresponding Rydberg spectra are the subject of wide recent discussion. In this paper a highly accurate computational determination for Rydberg states of NH_4 is made with cluster expansion of the wave-function theory.

The bands occurring in discharges through NH_3 have been observed by a number of investigators in the last 100 years, but none have obtained a definite identification.[1,2] Recent study by Herzberg[3–6] has established that the diffuse bands at 13 040, 15 390, 17 630, 17 730, and 18 930 cm⁻¹ are of the Rydberg spectrum of NH_4, and he has given them the name Schuster bands. He has assigned the Schuster band system to $^2T_2(3d) \rightarrow {}^2A_1(3s)$. A further band, the so-called Schüler band, is observed in the region 15050–15210 cm⁻¹. Herzberg tentatively assigns the

Table I. NH_4^+ Ground-State Energies (au)

	ground-state energy	correlation energy
SCF	−56.551275	
CI(S+D)	−56.664884	−0.113609
SAC	−56.669148	−0.117872

Schüler band to $^2E(3d) \rightarrow {}^2T_2(3p)$. However, there exist serious conflicts between theoretical[7–9] and experimental results. There is a need for further improvement in the ab initio calculations with consideration of electron-correlation effects. Recently we have developed the symmetry-adapted-cluster (SAC) expansion theory and the SAC-CI theory[10,11] as an approach specifically designed to study the correlation effect both for the ground state and various excited states. Thus it seemed to be of particular interest to apply these theories to the NH_4 radical.

First we have performed the SAC calculation on the ground state of NH_4^+. We employed a basis set with the description

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