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Topological quenching of 2,4,6-triphenylpyrylium tetrafluoroborate in anionic micelles

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Abstract

Topological quenching of the excited states of the photosensitizer 2,4,6-triphenylpyrylium tetrafluoroborate bound to an anionic SDS micelle has been observed by fluorescence spectroscopy. Spectroscopic data suggests that the triphenylpyrylium cation is micellized with the cationic pyrylium moiety slightly projecting out, experiencing the aqueous polar environment. Accordingly, the quenching mechanism varied from static for neutral quenchers and dynamic for the cationic quenchers whereas no quenching was observed for anionic quenchers. Upon irradiation, micellized TP⁺ undergoes a photoinduced hydrolysis to 1,3,5-triphenyl-1-pentene-1,5-dione, possibly through an electron transfer between triplet excited pyrylium cation and water molecules. This electron transfer leads to the generation of hydroxyl radicals producing the build-up of 10⁻² M hydrogen peroxide. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

We have earlier reported the use of the zeolite encapsulated 2,4,6-triphenylpyrylium cation (TP⁺) in the photocatalytic splitting of water generating reactive hydroxyl radicals [1–4]. In contrast, an unsupported pyrylium cation not embedded within the zeolites was found to undergo a fast nucleophilic ring opening reaction at pH = 7 to form a 1,5-diketone, which makes TP⁺ unsuitable to be used as a photosensitizer in aqueous solutions. Here we have investigated the use of micelles in stabilizing the cationic pyrylium salt in aqueous solution at neutral pH as well as at pH = 4.7 and its effect in the topological control of fluorescence

quenching process. Pyrylium ions are efficient electron transfer sensitizers and find ample use in a variety of photochemical reactions in non-aqueous solutions [5]. However, reports dealing with the use of pyrylium ions in aqueous or other microheterogeneous media and particularly on micelles are rare [6,7].

SDS is an amphiphilic molecule with a hydrophobic tail and an anionic head group. These molecules are known to undergo aggregation to form micelles having an inner hydrophobic domain. Micellar solutions define a microheterogeneous medium and the studies in this area have showed that these are efficient media for carrying out various chemical reactions, thereby one could achieve selectivity and specificity in the product distributions [8–10]. Micelles have been used in photochemistry to control the course of the reaction or to enforce a separation between the donor

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and acceptor in a photoinduced electron transfer reaction, thereby controlling the undesired back electron transfer reaction [11–20]. Here we report the variations in the photophysical properties of TP^+ in micellar aqueous solutions and the result of the topological photosensitizer–quencher interaction in TP^+ bound in anionic SDS micelle.

2. Results and discussion

2.1. Absorption and emission studies

Since the pyrylium salts are found to be unstable in neutral aqueous solutions we have used sodium acetate–acetic acid buffer solutions (pH = 4.7). We found that these solutions were stable for a period long enough to carry out absorption and fluorescence measurements. Fig. 1 shows the absorption spectra of TP^+ in the buffer solution and in micelle. The absorption and the emission spectra of TP^+ in the buffer solution were found to be similar to those in acetonitrile solutions. Our control experiments using UV–Vis absorption spectroscopy rule out any ground state association with SDS molecules at concentrations below critical micellar concentration. Upon addition of SDS at concentrations above critical micellar concentration (0.5×10^{-3} M) the absorption spectrum of TP^+ showed a significant

bathochromic shift. Such a shift in the absorption maximum is reported for pyrylium salts when going from polar to non-polar solvents [5,21,22]. This reflects the changes in the relative solvation energy of the excited state depending on the polarity of the solvent, due to the slow solvent reorganization compared to the instantaneous charge redistribution associated with excitation. Since pyrylium molecule is cationic, the effects observed in the absorption spectrum upon micellization can be rationalized assuming that the polar pyrylium moiety is aligned with the negatively charged sulphate groups and the hydrophobic phenyl group at the 4-position with the alkyl chain of the surfactant molecule as shown in Scheme 1.

The emission spectral maximum remained unchanged upon micellization but an enhancement in the emission intensity was observed. The change in the fluorescence intensity upon addition of SDS is shown in Fig. 2. The increase in the fluorescence intensity reached a plateau at concentration equal to the critical micellar concentration of SDS. The fluorescence quantum yield (Φ_f) in buffer solution in the presence and absence of micelle was determined by relative actinometry using optically matched solutions of TP^+ tetrafluoroborate in dichloromethane as the reference. The observed quantum yield value in buffer solution ($\Phi_f = 0.25$) was less compared to that in non-aqueous solutions ($\Phi_f = 0.52$) [5]. Upon micellization the

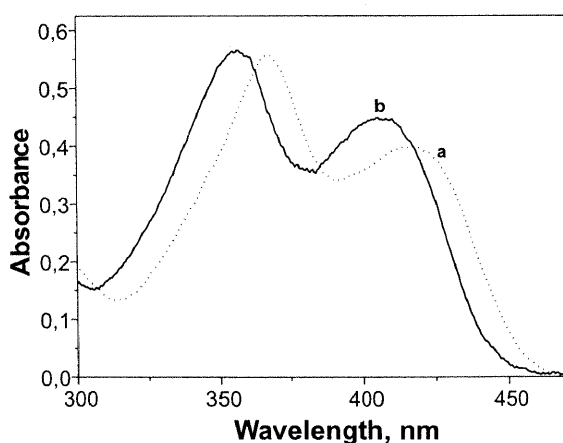
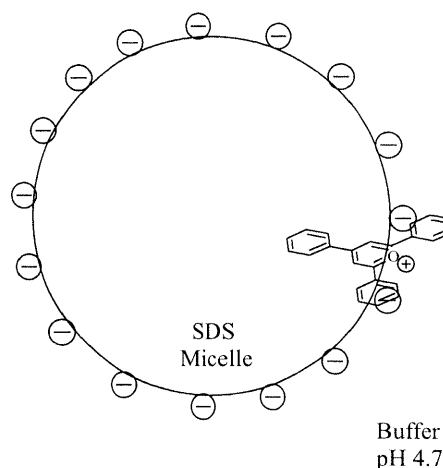


Fig. 1. UV–Vis absorption spectra of TP^+ (2×10^{-5} M) in presence (a) and absence (b) of SDS.



Scheme 1.

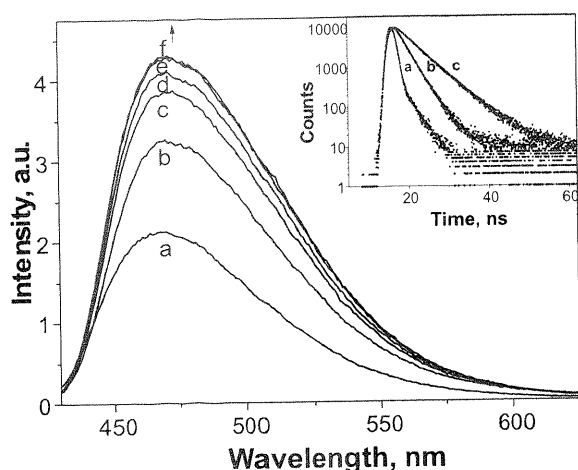


Fig. 2. Fluorescence emission spectra of TP⁺ at various concentrations of SDS. (a) 0; (b) 5×10^{-4} ; (c) 7.5×10^{-4} ; (d) 1×10^{-3} ; (e) 5×10^{-3} and (f) 1×10^{-2} M. Inset shows the fluorescence decay profiles of TP⁺ recorded in the presence and absence of SDS: (a) lamp profile; (b) in AcOH/NaOAc buffer pH-5 and (c) in AcOH/NaOAc buffer pH-5 and SDS (0.01 M).

quantum yield increased to 0.55. The reduction in fluorescence quantum yield in buffer solution indicates the quenching of singlet states by water molecules. Fluorescence lifetime measurements in aqueous buffer solutions yielded single exponential decay profiles with a lifetime of 2 ns. The fits of fluorescence decay in the presence of SDS were predominantly single exponential and reasonably good with $\chi^2 \leq 2$. Usually the fitting procedure of a micellized fluorophore requires the use of complex equations that take into account the dynamics of the association–disassociation mechanism of molecules with micelles [13,18,19,23]. Taking into consideration of the possible strong electrostatic binding of TP⁺ with the anionic micelle and the short lifetime of the TP⁺ we assumed that disassociation process is less significant to affect the decay kinetics. At surfactant concentrations above the critical micellar concentration the fluorescence lifetime was 4.3 ns slightly longer than that observed in non-aqueous solutions ($\tau = 3.5$ ns) [5]. Inset in Fig. 2 shows the fluorescence decay profiles of TP⁺ recorded in the presence and absence of SDS. Thus, micellization in anionic SDS protects pyrylium nucleus from nucleophilic attack by water molecules as revealed by the longer persist-

tence of TP⁺ and provides an apolar environment to TP⁺ as indicated by the luminescence quantum yield and lifetime values.

2.2. Fluorescence quenching studies

In order to assess the topology and accessibility of the micellized pyrylium cation we have undertaken fluorescence quenching studies with neutral, anionic and cationic quencher molecules. We have used naphthalene as neutral quencher and Br⁻ and Co(II) as the anionic and cationic quenchers, respectively. Concentration of TP⁺ used was 7×10^{-6} M and SDS 0.01 M at which the concentration of the micellar assemblies was 3.2×10^{-5} M, calculated by using the equation, $[M] = ([S] - \text{cmc})/N_{\text{agg}}$, where [S] is the concentration of the surfactant, cmc is the critical micellar concentration and N_{agg} is the aggregation number. Thus, under conditions of lower occupancy one can realize a Poisson distribution for quenchers which can be solubilized by the micelle [13,16,19]. The rate of fluorescence decay of TP⁺ is much faster compared to the rate of quencher migration to and from the micellar assemblies ($\sim 10^5$ to 10^6 s⁻¹) and also, the rate of TP⁺ migration is expected to be slow due to the electrostatic association of TP⁺ with the anionic surfactant. Hence overall quenching process can be analysed by a simpler model such as Stern–Volmer model. Hackett and Turro have used such a treatment for quenching of the fluorescence of a neutral Ru(phen)₂ bps by 4,4'-diheptyl viologen [20]. Here the cationic viologen moiety is strongly bound to the SDS micelle and quenching process was well described using the Stern–Volmer treatment. Fig. 3A,B shows the Stern–Volmer plots obtained for the fluorescence quenching of TP⁺ by Br⁻, Co(II) and naphthalene. Results of fluorescence quenching studies in the absence of micelles showed that the quenching mechanism is diffusion controlled under homogeneous conditions. Table 1 summarizes the Stern–Volmer quenching constants and the fluorescence quenching rate in the absence and presence of SDS. Importantly no fluorescence quenching was observed with Br⁻ in the presence of SDS (see Fig. 3A) as compared to diffusion-controlled quenching in the absence of

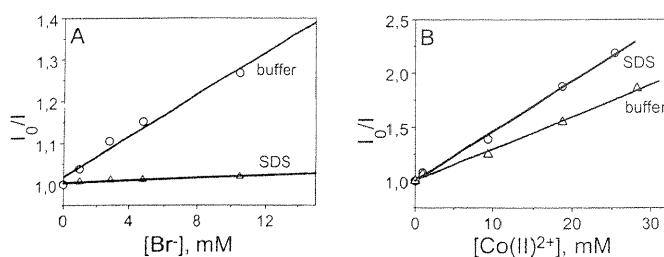


Fig. 3. Stern–Volmer plots for the fluorescence quenching of TP^+ with bromide (A) and Co^{2+} (B) in the presence (Δ) and absence (O) of SDS (0.01 M).

Table 1

Stern–Volmer quenching constants and the bimolecular quenching rate constants for the quenching of the fluorescence of TP^+ with naphthalene, Co^{2+} and Br^- quenchers in the presence and absence of SDS

Quencher	Buffer		SDS (0.01 M)	
	K_{sv} (M^{-1})	k_q ($M^{-1}s^{-1}$)	K_{sv} (M^{-1})	k_q ($M^{-1}s^{-1}$)
Naphthalene	105	4.5×10^{10}	1310	3.0×10^{11}
Co^{2+}	27	1.2×10^{10}	45	1.0×10^{10}
Br^-	26	1.1×10^{10}	–	–

SDS. This shows that TP^+ is micellized completely with high association constant and the exit rate has to be much lower than the fluorescence decay. The electrostatic repulsion between the surface negative charges and the bromide ions makes collisional quenching impossible.

With cationic quencher cobalt(II) acetate the quenching involves collisional quenching between $Co(II)$ ions and excited TP^+ both having positive charges and bound to the shallow sulphonic layer of the micelle. The bimolecular quenching constant calculated from the lifetime and Stern–Volmer constants in aqueous and micellar solutions were similar. The rate constants obtained were in the diffusion limit predicted by the modified Smoluchowsky equation [24]. In principle, one would expect a reduction in the rate of bimolecular quenching in the presence of micelles under conditions in which probe and quencher have restricted mobility due to the electrostatic binding to the micelle negative layer. However, the restricted diffusion is counterbalanced by the fact that the effective volume in which probe and quencher can be located is much smaller than the total micellar solution volume. This ‘concentration effect’ that locates probe and quencher in proximity due to the

interaction with the sulphonic groups of the micelle compensates the predicted restricted mobility of probe and quencher. We studied the fluorescence quenching at higher surfactant concentration (0.1 M) at which the concentration of the micellar assemblies is much higher than the concentration of TP^+ . At this concentration the chances of the quencher and the TP^+ being in the same micelle will be lower. However, we observed no change in the rate of fluorescence quenching at this concentration. This can be rationalized assuming that the barrier to diffusion offered by the micelle is compensated by the increase in the fluorescence lifetime of TP^+ . Alternatively, quenching could also occur when probe and quencher located on the external layer of two different micelles collide. Fig. 3b shows the Stern–Volmer plots recorded for the fluorescence quenching of TP^+ by $Co(II)$ in the presence and absence of SDS.

However, the Stern–Volmer constants obtained for neutral quenchers such as naphthalene ($1310 M^{-1}$) and anisole ($450 M^{-1}$) were very high compared to those obtained in the absence of micelles. Also at surfactant concentrations of 0.01 M and at higher quencher concentrations ($\sim 0.1 M$) it is likely that every micelle has one or more

quencher molecules present. But the observed quenching constants obtained from the Stern–Volmer plot were unusually high, while the lifetime of the residual weak emission was the same as that of the unquenched micellized TP^+ . This situation corresponds to a static quenching of fluorescence by naphthalene or anisole molecules probably due to the formation of a ground state complex between the TP^+ and the quencher. The Stern–Volmer constant thus obtained should be similar to the association constant for these quenchers in SDS micelles. In fact, the observed value is just an order less compared to the one reported for the association constant of naphthalene in SDS at higher concentrations [14]. Such a model was proved from the non-observance of a decrease in the fluorescence lifetime with increase in the concentration of naphthalene [25].

In contrast, at higher surfactant concentrations (0.1 M) the quenching mechanism was changed to dynamic quenching as seen in the drastic reduction in the quenching constant. Here it is unlikely that the TP^+ and the quencher are in the same micelle and the only possibility that exists for the fluorescence quenching is by the intermicellar diffusional quenching. Fig. 4 shows the Stern–Volmer plot obtained for the fluorescence quenching of the TP^+ with naphthalene in the absence and presence of SDS. Thus, SDS micellization of TP^+ strongly

influences its quenching behaviour as compared to aqueous solutions. Micellization may also control the rate of back electron transfer due to the different polarities of pyranil radicals and relocation of this transient could be possible.

2.3. Photoinduced electron transfer sensitized hydroxyl radical generation

As we have reported in an earlier publication, TP^+ encapsulated within the supercages of zeolite Y is an efficient photocatalyst to bring about oxidation of water molecules to hydroxyl radicals [1–4]. This is possible because of the low oxidation potential of water (1.28 V vs SCE) and the electron transfer reaction between TP^+ and water is exoergonic as predicted by the Rehm–Weller formulation [26]. In practice, this reaction cannot be carried out in aqueous solution due to instability of the TP^+ in water at neutral pH. Our attempts to do this reaction using SDS micellized TP^+ were successful and we obtained an appreciable yield of hydrogen peroxide or hydroperoxides (1.1×10^{-2} M) determined by iodimetric titration [27]. We have irradiated TP^+ (1×10^{-4} M) in buffered (pH = 5) SDS (0.05 M) solutions using pyrex filtered light from a 200 W mercury lamp and the solutions were thoroughly degassed prior to irradiation. However, we observed a complete

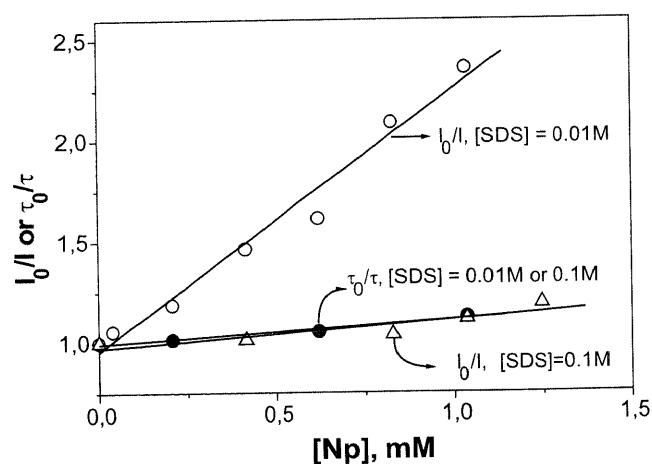


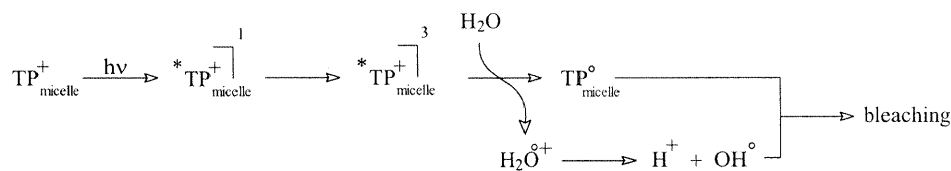
Fig. 4. Stern–Volmer plots for the fluorescence quenching of TP^+ with naphthalene: plot of I_0/I vs. $[\text{Np}]$ (O) 0.01 M SDS, (Δ) 0.1 M SDS and (\bullet) a plot of τ_0/τ vs. $[\text{Np}]$ at 0.01 M or 0.1 M SDS. (The difference between the I_0/I and the τ_0/τ plots for a 0.01 M SDS evidences the operation of a static quenching.)

degradation of TP^+ at the irradiation conditions. A likely rationalization for this photochemical process is the attack of hydroxyl radicals either to the TP radicals formed during the electron transfer reaction or to other TP^+ in its ground state (Scheme 2). This is in contrast to the total absence of photobleaching when TP^+ is incorporated within the zeolite.

To learn about this electron transfer process in micelle-bound TP^+ and to get evidence for the intermediacy of TP radicals, laser flash photolysis studies were carried out using TP^+ (1×10^{-4} M) in buffered SDS solutions (0.1 M) using a dynamic flow cell under nitrogen. Although the intensity of the transient spectrum was weak, we could not observe any triplet state absorption for the micellized TP^+ under these conditions, instead we obtained a band at 550 nm corresponding to TP^\bullet radicals (Fig. 5) [5]. This shows that photoinduced electron transfer to generate TP^\bullet radical is the only detectable process. Our attempts to detect

indirectly hydroxyl radicals by scavenging with methyl viologen (cationic) and benzene (neutral) as probes were unsuccessful. This indicates that the decay of $\cdot OH$ radicals in micelles is very fast and the possibility for trapping it with probe molecules is negligible due to its short lifetime.

Combining the information from fluorescence measurements with that of laser flash photolysis, a more complete knowledge of the photoprocesses undergone by SDS – micelle-bound TP^+ can be obtained. Thus, fluorescence quantum yield and fluorescence lifetime data obtained for TP^+ in the SDS micelle are similar to those observed in non-aqueous solvents. These emission properties prove that the singlet excited state of the micellized TP^+ is not affected by the presence of water molecules. Thus, it has to be the triplet excited state which is involved in the electron transfer quenching reaction with water molecules to generate the hydroxyl radicals. In this context, the fact that in aqueous micellar solutions the triplet excited state is not



Scheme 2.

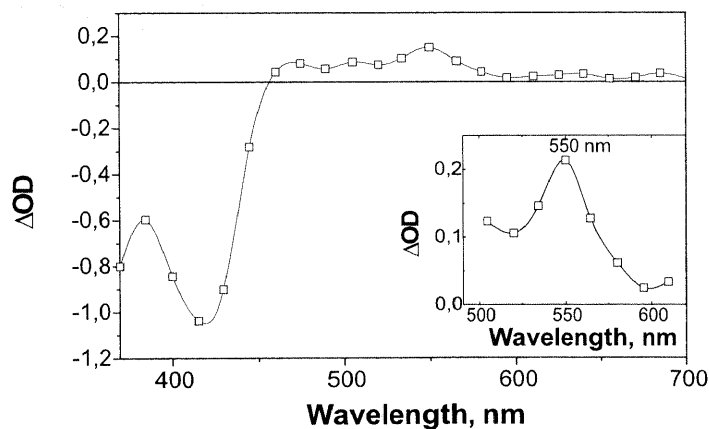


Fig. 5. Transient absorption spectra of a solution of TP^+ (1×10^{-4} M) in SDS (0.1 M) recorded 0.6 μ s after the laser flash. The negative region of the transient spectrum corresponds to the bleaching of the TP^+ ground state. Inset shows the enlarged spectrum in the range 500–600 nm.

detected by laser flash photolysis indicates that this excited state is the one that undergoes a fast and efficient quenching by water molecules.

3. Conclusion

It has been observed that TP⁺ shows appreciable stability in buffered micellar solutions. Micellization leads to a bathochromic shift in the absorption maxima, and an increase in the fluorescence quantum yield and fluorescence lifetime. Analysis of the fluorescence quenching data with quencher molecules having different charges reveals that TP⁺ is incorporated in the micelle with the cationic pyrylium moiety located at the hydrophilic sulphonic layer with the 4-phenyl substituent pointing towards the core of the micelle and aligned with the alkyl chains of the SDS molecules experiencing a non-polar environment. Topological-quenching of micelle-bound TP⁺ in which the interaction with the quencher depends on the quencher location with respect to the anionic boundary of the micelle has been observed: (i) for neutral molecules, the quenching mechanism varies from static to dynamic with increase in the surfactant concentration; (ii) anionic molecules do not quench and (iii) a 'concentration effect' occurs for cationic quenchers. The use of this microheterogeneous system as a hydroxyl radical generator is limited due to the sensitizer degradation reaction under prolonged irradiation.

4. Experimental

Triphenylpyrylium tetrafluoroborate (TP⁺), sodium dodecylsulphate, naphthalene and anisole were obtained from Aldrich and used as received. The micellar solutions were subjected to ultrasound for constant intervals before measurements. Absorption spectra were recorded on a Shimadzu Model UV 2101 PC spectrophotometer and fluorescence spectra or fluorescence lifetime were recorded on an Edinburgh Analytical Instruments FL900 spectrophotometer. Laser flash photolysis studies were carried out using 355 nm third harmonic output from a Spectra

Physics Nd:YAG laser and an Oriel kinetic spectrometer set-up which has been described elsewhere [28]. Photoirradiations were carried out using Pyrex filtered light from a 200 W mercury lamp and the solutions were thoroughly degassed prior to irradiation.

Acknowledgements

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