Electron Spin Resonance and Electron Spin-Echo Studies of the Photoionization of Tetramethylbenzidine in Frozen Aqueous Anionic, Cationic, and Nonionic Micellar Solutions. Effect of Micelle Type and Anionic Micelle Size

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Abstract: Electron spin resonance (ESR) and electron spin-echo studies of the photoionization of *N,N,N′,N′*-tetramethylbenzidine (TBM) to give the cation radical have been carried out in anionic (sodium octyl sulfate (S8S), sodium decyl sulfate (S10S), sodium dodecyl sulfate (S12S), and sodium tetradecyl sulfate (S14S)), cationic (dodecyltrimethylammonium chloride (DTAC) and hexadecyltrimethylammonium chloride (HTAC)), and nonionic (Triton X-100) micellar solutions frozen to 77 K. Cation–water interactions have been detected by electron spin-echo modulation (ESEM) analysis and are found to increase with decreasing alkyl chain length in anionic micelles. This is interpreted as consistent with an asymmetric solubilization site for the cation near the micellar surface and with little water penetration into the micelle. The photoionization efficiency in anionic micelles correlates with increased cation–water interactions. In cationic micelles the photoionization is about twofold more efficient than in anionic micelles of the same alkyl chain length, although the cation–water interaction is less. The overall photoionization efficiency of a micellized solute appears to depend on micellar surface charge as well as on solute location within the micelle.

Introduction

Solar photochemistry is an important and active area of energy research.[1-5] A major goal is to use visible light to carry out photoredox reactions as in photosynthesis. The key requirement is to achieve net charge separation, since efficient photoionization followed by rapid ion recombination is not a route to practical energy storage. In this work we study structural factors that affect the efficiency of light-induced charge separation in micelles as primitive models of the photosynthetic charge separation occuring in membrane bilayers.

By optical absorption studies it has been demonstrated that photoionization of organic molecules by both biphotonic[6,7] and monophotonic[8-10] processes is much more efficient in anionic micelles than in homogeneous solution. This increased efficiency is presumably related to transfer of the electron to the aqueous phase followed by rapid hydration. Although the number of molecules studied is small, it appears that biphotonic ionization is independent of the micellar surface charge whereas monophotonic ionizations strongly depends on this factor. This may be due to different photoionization mechanisms or to different locations of the photoionizable molecules within the micellar structure. Attempts have been made to study the solubilization site of various solutes in micelles, particularly pyrene, by nuclear magnetic resonance[11] (NMR) and by vibronic fluorescence intensities.[12] The NMR study suggests that pyrene is solubilized in a nonpolar part of the micelle while the fluorescence data indicate the opposite. It has been suggested that water may penetrate the micelle to give pyrene a polar environment[13] as indicated by the fluorescence data but this model does not appear to be compatible with the NMR results. It seems clear that more incisive structural studies of solubilization sites in micelles are needed. To more specifically probe the change separation process, it is necessary to study the structural location and water interactions of photoproduced cations in micelles. This work is directed toward aim.

We have recently shown how electron spin resonance (ESR) and electron spin echo modulation (ESEM) can be successfully used to deduce the surrounding structure of paramagnetic species in frozen solutions.[14-22] In a preliminary communication,[23] we have shown how ESR and ESEM can be used to obtain structural information about cations of *N,N,N′M′*-tetramethylbenzidine (TMB) produced by one-photon ionization in the anionic micelle sodium dodecyl sulfate. In this paper we extend those results to ESR and ESEM studies of TMB^+ cations in anionic micelles of different alkyl chain lengths as well as to cationic and nonionic micelles.

Experimental Section

The surfactants sodium octyl sulfate (S8S), sodium decyl sulfate (S10S), sodium dodecyl sulfate (S12S), sodium tetradecyl sulfate (S14S), dodecyltrimethylammonium chloride (DTAC), and hexadecyltrimethylammonium chloride (HTAC) as well as TMB were obtained from Eastman Chemicals, while *p*-di-*tert*-butylphenoxypolyethyleneoxy(9.5) ether (Trition X-100) and dodecylpolyethyleneoxy(23) ether (Brij 35)

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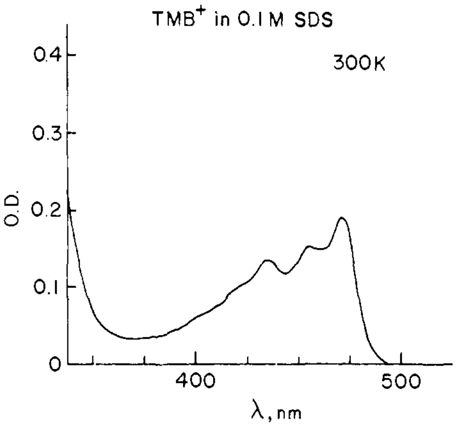

Figure 1. Optical absorption of photoproduced tetramethylbenzidine cation (TMB^+) in a 0.1 M sodium dodecyl sulfate (SDS) micellar solution.

were obtained from CalBiochem Co. Aqueous solutions of the surfactants were freshly prepared with triply distilled and deoxygenated water to 0.2 M for S8S, S10S, and S12S and to only 0.04 M for S14S due to limited solubility. The cationic surfactant concentrations were 0.1 M and the liquid nonionic surfactant concentrations were 2.5 vol %. These concentrations are above the respective critical micelle concentrations of 0.005 M or less. TMB was solubilized in these freshly prepared micelle solutions by adding as a powder and stirring the mixture gently at 60 °C for about 3 h. The concentration of solubilizate was approximately 0.1 mM based on an extinction coefficient of 34 000 at 306 nm for TMB in ethanol, which gives less than one TMB per micelle. All the samples were irradiated in 2-mm o.d. (at room temperature) or 3-mm o.d. (for frozen solutions) Suprasil quartz tubes with a high-pressure mercury lamp. The photoirradiations were coarried out by interposing a Corning filter No. 760 between the sample and the lamp to allow a band of light centered at 350 ± 30 nm to pass. The sample was exposed to a total light flux of 1.0×10^2 W m^{-2}.

All the ESR spectra were recorded at room temperature and 77 K on a Varian-E4 ESR spectrometer. The spin echo data were recorded at 4.2 K on a home-built spectrometer.[24a] The micelles were prepared in D_2O for recording the spin echo data. Optical spectra were obtained on a Cary 14 spectrophotometer.

The samples were frozen in 2–3 s by plunging tubes into liquid nitrogen. This is rapid enough that the water in the micellar surface region retains a disordered, noncrystalline structure,[24b] so it is assumed that the micellar shape is similar to that in solution.

Results

TMB^+ in Anionic Micelles. TMB in the anionic micelles of S8S, S10S, S12S, and S14S does not exhibit an ESR spectrum before photoirradiation. After photoirradiation for 100 s at room temperature a well-resolved ESR spectrum of TMB^+ is observed in S10S, S12S, and S14S micelles but not in S8S micelles. Our analysis and assignment of the ESR spectrum[23] are in good agreement with earlier work based on specifically deuterated compounds.[25] The optical absorption spectrum of TMB^+ in micellar solutions is given in Figure 1. It is similar to spectra reported in laser photolysis experiments.[10] The extinction coefficient at 475 nm is 4×10^4 M^{-1} cm^{-1}.[10] Recent research suggests that the optical bands are due to the cation dimer[26] but this seems improbable in our case since there is less than one cation per micelle.

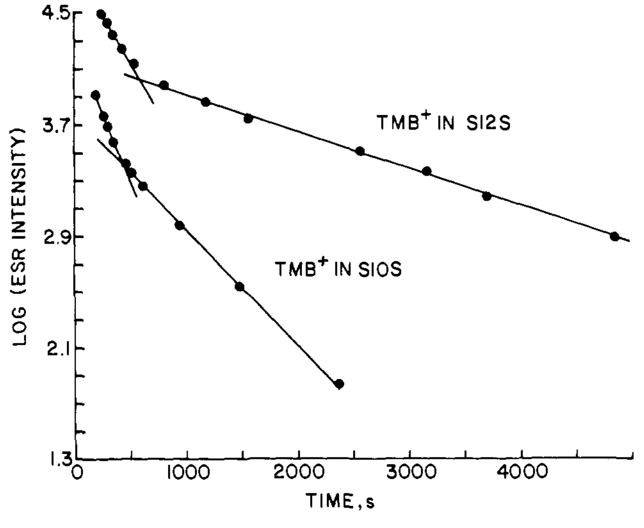

Figure 2. Variation of the ESR signal intensity at room temperature of photogenerated tetramethylbenzidine cation radical after the light source is turned off in sodium dodecyl sulfate (S12S) and sodium decyl sulfate (S10S) micelles.

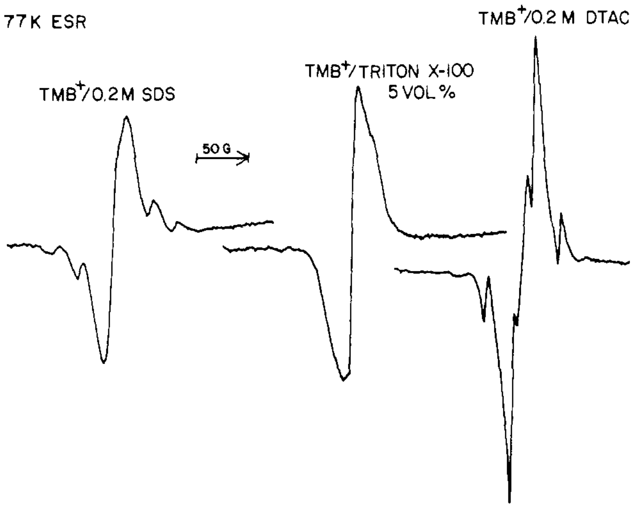

Figure 3. ESR spectra at 77 K of tetramethylbenzidine cation (TMB^+) in anionic (sodium dodecyl sulfate), nonionic (Triton X-100, and cationic (dodecyltrimethylammonium chloride) frozen micellar solutions.

The micelle-to-TMB ratio is about 1:1 in S14S and about 10:1 in S12S, S10S, and S8S. The steady-state ESR intensity of TMB^+ decreases twofold from S12S to S10S and is not observable in S8S. The intensity in S14S is similar to that in S12S but this is due to less complete solubilization of TMB due to the small micelle-to-TMB ratio. The general trend observed is that the TMB^+ intensity decreases with decreasing alkyl chain length. This trend reflects a decreasing TMB^+ lifetime as the alkyl chain decreases. Figure 2 shows that the TMB^+ decay in S12S is slower than in S10S after the light is turned off. In both cases the decay seems characterized by two concomitant first-order processes. Analysis gives rate constants of 2.6×10^{-4} and 8.4×10^{-4} s^{-1} for the slow decay of TMB^+ in S12S and S10S, respectively. After substraction of this slow decay the remaining faster decay at short times gives a linear semilog plot with rate constants of 1.1×10^{-3} and 1.2×10^{-3} s^{-1} for S12S and S10S, respectively.

We have previously shown that the micellar structure is retained in solutions rapidly frozen to 77 K.[23] Photoirradiation at 77 K generates ESR spectra of TMB^+ in S10S, S12S, S14S as well as in S8S. Figure 3 shows a spectrum in S12S. At this temperature decay of TMB^+ does not occur and the TMB^+ intensity for constant photoirradiation time should reflect the photoionization efficiency. The TMB^+ intensity is largest in S8S and decreases by factors of 0.86, 0.75, and 0.28 in S10S, S12S, and S14S, respectively.

To probe TMB^+–water interactions two-pulse electron spin echo experiments[27] were run in D_2O micellar solutions at 4.2 K; the results are shown in Figure 4. The echo intensity is recorded vs. the time between the two applied microwave pulses, τ. In general, the echo intensity decreases with τ according to transverse re-

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Figure 4. Two-pulse electron spin echo decay envelopes at 4.2 K of photogenerated TMB$^+$ in S14S, S12S, S10S, and S8S anionic micelles prepared in D_2O. The vertical axes are offset to avoid overlap. Both proton and deuterium modulations are seen on close analysis; in S14S the proton modulation has been largely suppressed by using longer pulse lengths.

laxation mechanisms. It may also decrease due to cation decay but that does not occur in this system on a nanosecond time scale. In addition, there is a periodic intensity variation called nuclear modulation. This modulation is due to weak electron-nuclear hyperfine interaction with molecules near the cation and gives structural information about the environment of the cation. The observed modulation occurs in periods of 0.08 and 0.5 μs. The former period is characteristic of protons in the applied field and arises due to interaction of the cation with the protons on the surfactant molecules while the latter period is characteristic of deuterons and arises due to interactions of the cation with the deuterium nuclei of water molecules. It can be seen from Figure 4 that the depth of deuterium modulation decreases as the alkyl chain length increases. Analysis give average interaction distances of 0.40, 0.44, 0.48, and 0.50 nm for S8S to S14S.

TMB$^+$ in Cationic Micelles. TMB dissolved in dodecyltrimethylammonium chloride (DTAC) and hexadecyltrimethylammonium chloride (HTAC) micelles does not exhibit any ESR spectrum, even after photoirradiation at room temperature. This is consistent with the rapid reaction of hydrated electrons with cationic micelles.[13] But after photoirradiation at 77 K strong ESR signals assignable to TMB$^+$ are seen as shown in Figure 3. The steady-state TMB$^+$ intensities are comparable between DTAC and HTAC in contrast to anionic micelle systems. A quantitative comparison of the intensities of the steady-state ESR spectra from TMB$^+$ in the anionic and cationic micelle systems indicates that the yield of TMB$^+$ in cationic micelles is at least 2 times larger than in anionic micelles with the same alkyl chain length.

The two-pulse electron spin echo decay curves from TMB$^+$ in DTAC and HTAC are shown in Figure 5. These echo envelopes were recorded at 4.2 K for samples prepared in D_2O. The echo envelopes exhibit proton modulation and only a hint of deuterium modulation. The deuterium modulation in DTAC is significantly weaker than in the comparable S12S anionic system.

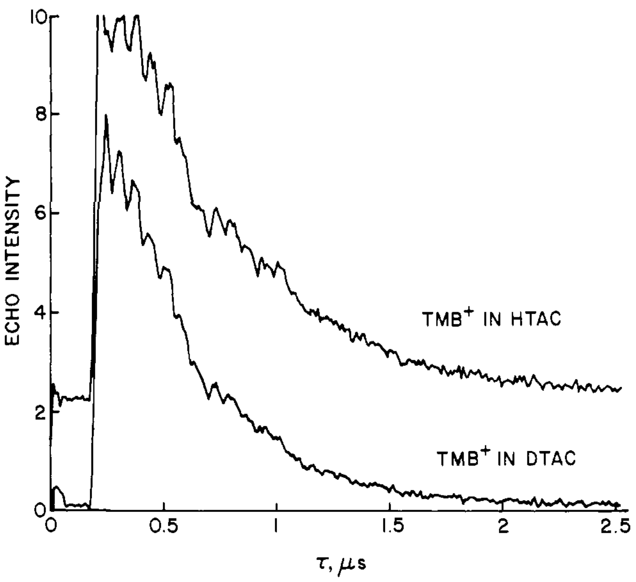

Figure 5. Two-pulse electron spin echo decay envelopes at 4.2 K of photogenerated TMB$^+$ in DTAC and HTAC cationic micelles. The vertical axes are offset to avoid overlap. Proton modulation is seen along with very weak deuterium modulation.

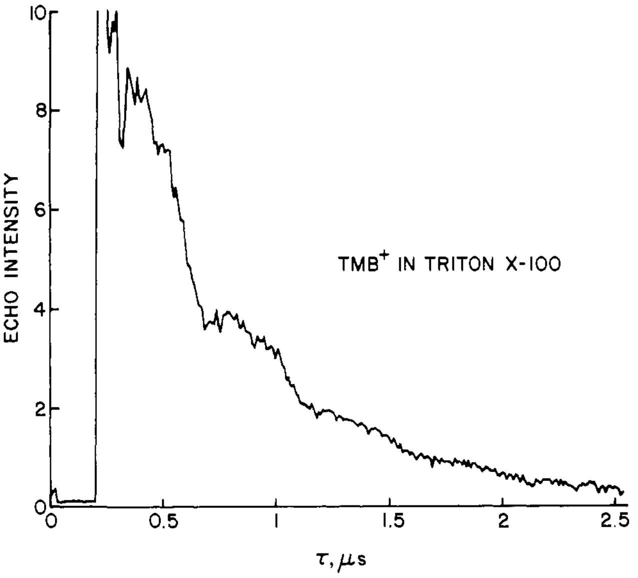

Figure 6. Two-pulse electron spin echo decay envelope at 4.2 K of photogenerated TMB$^+$ in Triton X-100 micelle prepared in D_2O. Both proton and deuterium modulations are seen.

TMB$^+$ in Nonionic Micelles. TMB samples dissolved in nonionic micelles of Brij 35 and Triton X-100 do not exhibit ESR spectra, even at 77 K, before photoirradiation. These samples also do not show any ESR spectra after photoirradiation at room temperature. However, an ESR spectrum is observed from TMB$^+$ in Triton X-100 after photoirradiation at 77 K as shown in Figure 3, although none is observed in Brij 35.

The two-pulse electron spin echo decay envelope of TMB$^+$ in Triton X-100 prepared in D_2O is shown in Figure 6. Prominent deuterium modulation is observed in addition to proton modulation.

Discussion

Anionic Micelles. For S12S micelles the average diameter is about 4 nm and the approximate length of TMB$^+$ is about 1 nm. The structure of TMB is $(CH_3)_2N$–Ph–$N(CH_3)_2$ where Ph is a phenyl ring. To minimize molecular interactions it seems probable that both TMB and TMB$^+$ will be located with their long axes parallel to the long axes of the surfactant molecules. Thus, although the cation is relatively large, it can be located symmetrically or asymmetrically within a roughly spherical micelle. Figure 7 shows an asymmetric position which we will argue is most probable. The hyperfine coupling constants of TMB$^+$ indicate that the bulk of the unpaired electron spin density is located on the two ends of the cation on the nitrogen and methyl carbons.[25] The deuterium modulation detected by electron spin echo indicates that TMB$^+$ interacts with D_2O. Previous analysis of such deu-

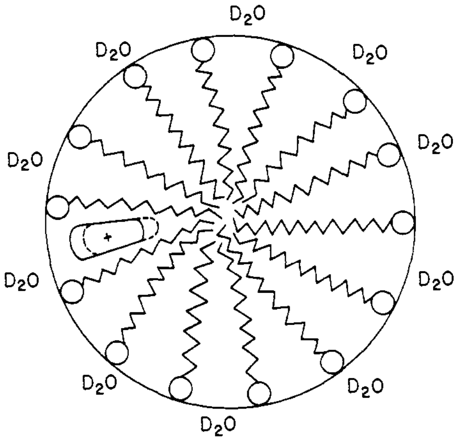

Figure 7. Schematic diagram of an ordered micelle model composed of surfactant molecules with polar head groups (circles) and nonpolar alkyl chain tails (wiggly lines) showing an asymmetric location for a photogenerated solute cation. The dashed lines show an alternate cation location indicating that a small distribution of locations is probable.

terium modulation[27] shows that such modulation is only detectable for interaction distances less than about 0.6 nm. Thus, if the water does not penetrate the micelle surface significantly as suggested originally,[28,29] TMB^+ must be located asymmetrically within the roughly spherical micelle and the deuterium modulation reflects interaction with one end of the TMB^+. On the other hand, some recent work has been interpreted to indicate that water penetrates deeply into the micelle,[30] although this interpretation is open to dispute.[31] If this were so, the location of TMB^+ becomes ambiguous. However, our observation of changing deuterium modulation with changing alkyl chain length of the surfactants indicates to us that water does not penetrate deeply into the micelles. If water did penetrate the micelle, TMB^+ would be in relatively close contact with it regardless of alkyl chain length, and a change in the surfactant alkyl chain length would not change the average cation–water interaction.

On the basis of the asymmetric solubilization model for TMB^+ portrayed in Figure 7 and the lack of significant water penetraction into the micelle, the alkyl chain length effect on deuterium modulation can be explained as follows. As the alkyl chain length increases, the TMB^+ has a little greater region for asymmetric localization as shown by the dashed line in Figure 7, and its average distance from the micelle surface increases. Recall that we observe a distribution of TMB^+ localization positions in the frozen solution. If we make the reasonable assumption that TMB^+ interacts with the same number of waters as the surfactant alkyl chain length increases, we can estimate approximate average interaction distances of 0.40, 0.44, 0.48, and 0.50 nm for S8S to S14S. This range of distance is significantly less than the increase in alkyl chain lengths, which is about 0.9 nm for S8S to S14S, as expected. These semiquantitative extimates do not allow us to specify an average distance from the polar head groups of the surfactant molecules to one end of TMB^+ since the average position of the interacting water molecules relative to the polar head groups is unknown.

The photoionization efficiency of TMB also varies with the alkyl chain length of the surfactant. The variation is such that the photoionization efficiency increases as the TMB^+–water interaction increases; both occur as micelle size decreases. In solution at least some of the photoionization-produced electrons become hydrated, apparently after leaving the micelle.[13] Thus, our finding about the photoionization efficiency correlates with a shorter average travel distance for those photoelectrons that become hydrated. This is not inconsistent with a tunneling mechanism for the photoionization.[9]

Recently, more disordered micelle models have been suggested in which there is no water penetration but part of the alkyl chains are exposed to the micelle surface through gauche links in the alkyl chains and greater disorder near the micelle surface.[32,33] This allows portions of the alkyl chains to interact with the water phase as suggested by some experiments.[34] In the framework of these models our results also indicate that TMB^+ is solubilized asymmetrically because of the lack of water penetration.

Cationic Micelles. The most interesting result about photoionization of TMB in cationic micells at 77 K is that it occurs at about twice the efficiency as in anionic micelles. If photoionization is aided by strong cation–water interactions, this could imply that TMB is solubilized closer to the micelle surface in cationic micelles as compared to anionic micelles. However, this is not supported by the smaller magnitude of the deuterium modulation in D_2O solutions of the cationic micelles. We must conclude that the photoionization efficiency depends on both the location in the micellar structure relative to external water and on the micellar surface charge.

The role of micellar surface charge is not clearly understood. One possible explanation is that in cationic micelles the electron can escape in any direction from the cation but in anionic micelles the electron can only escape toward the nearest surface. This would account for a somewhat larger photoionization efficiency in cationic micelles and a greater dependence on the strength of cation–water interactions in anionic micelles. In accordance with this the limited data available on DTAC and HTAC micelles indicate little if any alkyl chain length effect on the photoionization efficiency or deuterium modulation in cationic micelles.

It is interesting to note that in room-temperature solutions the initial TMB^+ yield in flash photolysis experiments is less in cationic than in anionic micelles.[8,9] This was attributed to a fast back-reaction due to hydrated electron attraction back to the cationic micellar surface. This enhanced back-reaction does not seem to occur in the frozen solutions. It is also not observed for pyrene photoionization in cationic micelles at room temperature.[6,7]

Nonionic Micelles. It is unclear why TMB^+ is stabilized at 77 K in Triton X-100 but not in Brij 35 micelles. These two surfactants do have a rather different structure. Brij 35 has an alkane end and a longer polyethyleneoxy end. In micellar form the polyethyleneoxy chain is thought to be hydrated. Thus, if TMB^+ were intially localized in this semipolar, hydrated region, it may not be stable. Triton X-100 has a di-*tert*-butylphenoxy end which is like an alkane end and a much longer polyethyleneoxy end. Perhaps simply is localizd in the hydrophobic core or perhaps it is simply more deeply buried into the longer polyethyleneoxy chains than is possible in Brij 35.

The relatively strong deuterium modulation observed indicates strong TMB^+ –water interactions. NMR studies show that water penetrates into the sizable region of the long polyethyleneoxy chains but does not penetrate into the nonpolar core region.[35,36] If TMB^+ is located near the phenoxy end of the polyethyleneoxy chain, it would be in a region of strong TMB^+–water interactions.

Further work with a variety of nonionic micelles is necessary to be much more definitive about the TMB^+ location or the origin of the cation–water interactions. Unfortunately few nonionic surfactants are available.

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