acidities, as well as ab initio calculations, for phenol and related aliphatic compounds lead to the same conclusion.[14]

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**Appendix**

**Estimation of Differential Atomic Relaxation.** The atomic portion of the relaxation energy arises because of the shrinkage of the atomic orbitals on the ionized atom toward the core hole. In comparisons of the same type of atom in different environments, contributions from identically occupied orbitals will cancel. We will be concerned only with the differentially occupied valence orbitals. For an atom with a valence occupancy of $n$ electrons there will be a potential at the core equal to $kn$. After core ionization, this will change to $k^F n$ and, according to the relaxation potential model,[9] the contribution to the relaxation energy from this source will be $n(k^F - k)/2$. The differential atomic relaxation in two different environments will be $\Delta n(k^F - k)/2$.

The value of $k$ can be readily estimated by using $\langle 1/r \rangle$ expectation values from Hartree–Fock calculations or from Slater orbitals and Slater's screening rules.[20] For $k^F$, the same procedures can be used, but we must take into account that $\langle 1/r \rangle$ is affected not only by the removal of the core electron but also by the additional valence electrons that are attracted to the atom in response to the newly created core-hole. Using Slater's rules we estimate $(k^F - k)$ to be 5.8 eV for $F(1s2s^22p^5)^+$ and 3.4 eV for $F(1s2s^22p^6)$. The average value of 4.6 eV agrees reasonably well with the equivalent-cores quantity $k_{Ne} - k_F$ (4.4 eV from Slater's rules and Slater orbitals and 4.5 from Desclaux's values of $\langle 1/r \rangle$.)[25] Similarly we estimate 2 eV for sulfur and chlorine, 1.2 eV for bromine, and 0.9 eV for iodine.

Combining these values with either the theoretical or experimental values for $\Delta q = -\Delta n$ (Tables II and III, respectively) gives differential atomic relaxation energies between −0.02 and −0.07 eV, as noted in the text.

**Registry No.** $C_6H_5F$, 462-06-6; $C_6H_{11}F$, 372-46-3; $C_6H_5Cl$, 108-90-7; $C_6H_{11}Cl$, 542-18-7; $C_6H_5Br$, 108-86-1; $C_6H_{11}Br$, 108-85-0; $C_6H_5I$, 591-50-4; $C_6H_{11}I$, 626-62-0; $C_6H_5SH$, 108-98-5; $C_6H_{11}SH$, 1569-69-3; $C_4H_4S$, 110-02-1; $C_4H_8S$, 110-01-0.

(25) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 312.

# Electron Spin Resonance and Electron Spin Echo Modulation Studies of *N,N,N′,N′*-Tetramethylbenzidine Photoionization in Frozen Micellar Solutions: Structural Effect of 1-Butanol Addition to Sodium and Tetramethylammonium Dodecylsulfate and Dodecyltrimethylammonium Chloride Micelles

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**Abstract:** The electron spin echo modulation (ESEM) and electron spin resonance (ESR) spectra of the photogenerated *N,N,N′,N′*-tetramethylbenzidine cation radical ($TMB^+$) in frozen micellar solutions of sodium and tetramethylammonium dodecylsulfate (SDS and TMADS, respectively) as well as dodecyltrimethylammonium chloride (DTAC) have been studied as a function of 1-butanol (1-BuOH) concentration from 0 to 200 mM. A 5-doxylstearic acid spin probe has also been used in the ESEM experiments. The efficiency of TMB photoionization has been determined from ESR data, while ESEM analysis has given information about micelle hydration and aqueous interactions of $TMB^+$. The variations observed with 1-BuOH addition depend on the micellar charge and the nature of the counterion in dodecylsulfate micelles. The main findings are that (1) hydration of TMADS micelles decreases from 0 to 200 mM 1-BuOH, while hydration of SDS and DTAC micelles increases somewhat from 0 to 100 mM and remains constant from 100 to 200 mM 1-BuOH, and (2) the efficiency of charge separation upon photoionization of TMB can be increased by alcohol addition in SDS micelles but not in TMADS and DTAC micelles. The results are interpreted primarily in terms of the effect of added alcohol on the surfactant headgroup density.

Recent work from this laboratory[1-5] has been directed toward elucidation of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies such as micelles and vesicles. Electron spin resonance (ESR) studies of the photoproduced *N,N,N′,N′*-tetramethylbenzidine cation radical ($TMB^+$) in frozen micellar solutions have indicated that the photoionization efficiency depends on such factors as micelle size and charge, the nature of the counterion, and the ionic strength of the solution. Electron spin echo modulation (ESEM) analysis has shown that the photoionization efficiency in anionic micelles is greater for stronger $TMB^+$ interactions with water nominally outside the micelle.[3-5]

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(1) Narayana, P. A.; Li, A. S. W.; Kevan, L. *J. Am. Chem. Soc.* **1981**, *103*, 3603.
(2) Narayana, P. A.; Li, A. S. W.; Kevan, L. *J. Am. Chem. Soc.* **1982**, *104*, 6502.
(3) Li, A. S. W.; Kevan, L. *J. Am. Chem. Soc.* **1983**, *105*, 5752.
(4) Maldonado, R.; Kevan, L.; Szajdzinska-Pietek, E.; Jones, R. R. M. *J. Chem. Phys.* **1984**, *81*, 3958.
(5) Szajdzinska-Pietek, E.; Maldonado, R.; Kevan, L.; Jones, R. R. M. *J. Am. Chem. Soc.* **1984**, *106*, 4675.

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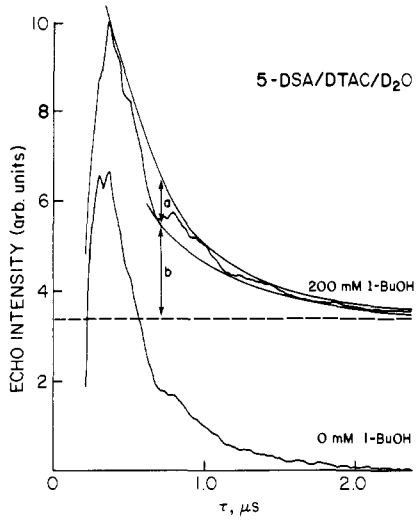


**Figure 1.** Relative yields of TMB cation photoproduced at 77 K in 100 mM SDS, TMADS, and DTAC micellar solutions vs. 1-BuOH concentration.

In the present work, ESR and ESEM studies are extended to micellar solutions containing 1-butanol (1-BuOH). The addition of a medium-chain-length alcohol to micellar solutions changes many micellar properties due to concentration of significant alcohol in the micellar surface region.[6-16] Changes in the environment of a micelle-solubilized substrate[13,15,16] may affect the photoionization process.[17] Here, the efficiency of TMB photoionization and the interactions of $TMB^+$ and a 5-doxylstearic acid spin probe (5-DSA) with water are studied in sodium and tetramethylammonium dodecylsulfate (SDS and TMADS, respectively) anionic micellar solutions and in dodecyltrimethylammonium chloride (DTAC) cationic micellar solutions as a function of the 1-BuOH concentration.

## Experimental Section

SDS and TMB from Eastman Kodak Co. and 5-DSA from Molecular Probes Inc. as well as 1-BuOH (99%) from Aldrich Chemical Co. were used as received as justified previously.[4,5] DTAC from Eastman Kodak Co. was recrystallized twice from a mixture of 10% ethanol in acetone. TMADS was prepared as described previously.[5] Triply distilled $H_2O$ and $D_2O$ from Aldrich Chemical Co. were used to make 0.1 M surfactant solutions for ESR and ESEM studies, respectively. The water was deoxygenated by nitrogen bubbling, and the samples were prepared in a nitrogen atmosphere.

Stock solutions containing 0.2 mM TMB or 0.4 mM 5-DSA and 0.1 M SDS, TMADS, or DTAC were prepared by procedures given elsewhere.[2,18] 1-BuOH was added to portions of these solutions to give a 200 mM concentration. Less concentrated 1-BuOH solutions were obtained by dilution with the original stock solutions.

The samples were sealed in 2 mm o.d. Suprasil quartz tubes for the ESR studies and in 3 mm o.d. Suprasil quartz tubes for the ESEM studies. They were rapidly frozen by plunging into liquid nitrogen. The TMB samples were irradiated with 370 ± 40 nm light using a 900-W high-pressure mercury lamp and a Corning filter No. 7-60 to give a flux of $1 \times 10^2$ W m$^{-2}$. Irradiation times were 8 and 15 min for the ESR and ESEM experiments, respectively.

ESR spectra were recorded at 77 K on a Varian E-4 spectrometer. The two-pulse electron spin echo signals were recorded at 4.2 K on a home-built spectrometer[19] by using 50-ns exciting pulses.

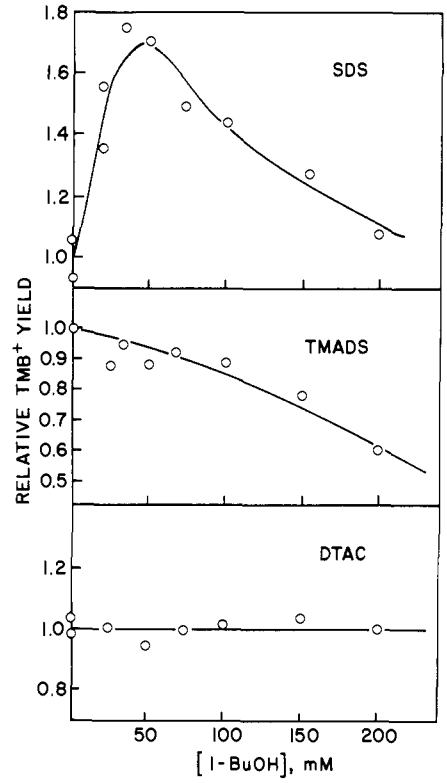


**Figure 2.** Two-pulse electron spin echo decay curve at 4.2 K of 5-DSA in DTAC/$D_2O$ micellar solution. The base lines have been offset vertically to avoid overlap, and the maxima of each decay curve are normalized to the same values.

## Results

**ESR Studies of TMB Photoionization Efficiency.** In the absence of 1-BuOH, the same ESR spectra of the TMB cation at 77 K were observed as previously.[1,2] The concentration of $TMB^+$ in SDS was taken as proportional to the ESR signal intensity, while in TMADS and DTAC micelles, because of changes in the line shapes, it was determined by double-integration of the ESR lines. Figure 1 presents the relative yields of $TMB^+$ vs. the 1-BuOH concentration in the examined systems. In anionic SDS micelles, the yield initially increases, reaches a maximum at 50 mM 1-BuOH, and then decreases so that the value obtained for 200 mM 1-BuOH is close to that for the sample containing no 1-BuOH. In TMADS anionic micelles, the $TMB^+$ yield decreases approximately linearly over the range from 0 to 200 mM 1-BuOH. In cationic DTAC micelles, 1-BuOH addition from 0 to 200 mM does not seem to affect the photoionization efficiency.

**ESEM Studies of $TMB^+$ and 5-DSA Interactions with $D_2O$.** Figure 2 shows the two-pulse ESEM spectra obtained for the 5-doxylstearic acid spin probe in DTAC micelles in $D_2O$ with 0 and 200 mM added 1-butanol. The echo decay curves exhibit detectable modulation with a period of 0.5 μs, corresponding to electron–deuteron hyperfine interactions. Additionally, a 0.08-μs modulation period can be distinguished which is due to interactions with protons of the surfactant and alcohol molecules. Similar modulation periods were observed in all the 5-DSA and $TMB^+$ samples prepared in $D_2O$.

The normalized deuterium modulation depth was determined in the manner described previously[4,5,20] as $a/a + b$ as shown in

(6) Shirama, K.; Kashiwabara, T. *J. Colloid Interf. Sci.* **1971**, *36*, 65.
(7) Hayase, K.; Hayano, S. *J. Colloid Interf. Sci.* **1978**, *63*, 446.
(8) Vikingstad, E.; Kvammen, O. *J. Colloid Interf. Sci.* **1980**, *74*, 16.
(9) Zana, R.; Yiv, S.; Strazielle, C.; Lianos, P. *J. Colloid Interf. Sci.* **1981**, *80*, 208.
(10) Larsen, J. W.; Tepley, L. *J. Colloid Interf. Sci.* **1974**, *49*, 113.
(11) Jain, A. K.; Singh, R. P. B. *J. Colloid Interf. Sci.* **1981**, *81*, 536.
(12) Almgren, M.; Swarup, S. *J. Colloid Interf. Sci.* **1983**, *91*, 256.
(13) Lianos, P.; Zana, R. *Chem. Phys. Lett.* **1980**, *72*, 171.
(14) Grieser, F. *J. Phys. Chem.* **1981**, *85*, 928.
(15) Lianos, P.; Lang, J.; Strazielle, C.; Zana, R. *J. Phys. Chem.* **1982**, *86*, 1019.
(16) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188.
(17) Grand, D.; Hautecloque, S.; Bernas, A.; Petit, A. *J. Phys. Chem.* **1983**, *87*, 5236.
(18) Bales, B. L., Kevan, L. *J. Phys. Chem.* **1982**, *86*, 3836.
(19) Ichikawa, T.; Kevan, L.; Narayana, P. A. *J. Phys. Chem.* **1979**, *83*, 3378.
(20) Szajdzinska-Pietek, E.; Maldonado, R.; Kevan, L.; Berr, S. S.; Jones, R. R. M. *J. Phys. Chem.* **1985**, *89*, 1547.

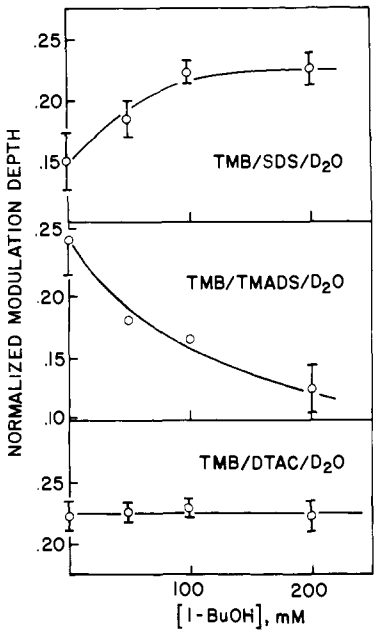


**Figure 3.** Normalized depth of deuterium modulation of $TMB^+$ vs. 1-BuOH concentration in 100 mM SDS, TMADS, and DTAC micellar solutions in $D_2O$. The error bars represent standard deviations for replicate experiments.

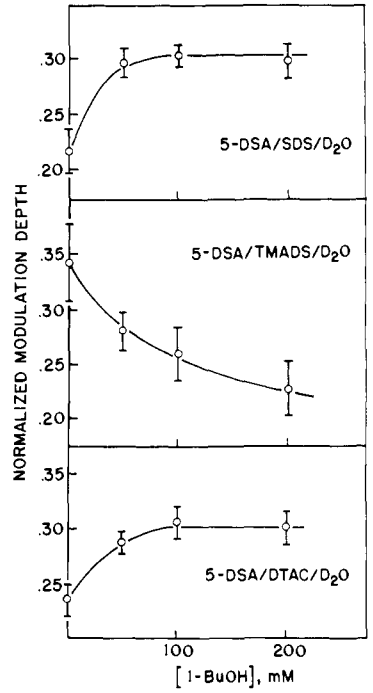


**Figure 4.** Normalized depth of deuterium modulation of 5-doxylstearic acid spin probe vs. 1-BuOH concentration in 100 mM SDS, TMADS, and DTAC micellar solutions in $D_2O$. The error bars represent standard deviations for replicate experiments.

Figure 2. The normalized modulation depths are plotted vs. the 1-BuOH concentration in Figure 3 for $TMB^+$. In anionic SDS micelles, the modulation depth increases from 0 to 100 mM 1-BuOH and then remains constant to 200 mM 1-BuOH. In anionic TMADS micelles, however, it decreases monotonically from 0 to 200 mM 1-BuOH. For cationic DTAC micelles, no change of deuterium modulation depth with 1-BuOH content is observed.

The dependence of the normalized deuterium modulation depth vs. 1-BuOH concentration for 5-DSA is shown in Figure 4. For anionic SDS and TMADS micelles, the same trends are observed as in the experiments with $TMB^+$. In cationic DTAC micelles, the modulation depth for 5-DSA increases from 0 to 100 mM and then remains constant to 200 mM 1-BuOH; this increase contrasts with no change observed for $TMB^+$.

## Discussion

In recent papers, we have shown that micellar structure is retained in these rapidly frozen aqueous solutions.[1-5,20,21] The cation radical of *N,N,N',N'*-tetramethylbenzidine (TMB) is readily photogenerated in anionic micellar solutions and is stable for tens of minutes.[1] In homogeneous solutions, it has a lifetime of only a few microseconds. It is possible to generate $TMB^{+}\cdot$ in frozen micellar solutions, thaw the solution, and still observe $TMB^{+}\cdot$ by electron spin resonance, thus indicating that the micellar structure was retained upon freezing.[1] Rather similar TMB photoionization results have been obtained in frozen micellar and vesicle solutions.[3] Since the vesicle structure is much less dynamic than that of micelles, one expects that vesicular structure should be retained more easily upon rapid freezing. Thus, the similarity of photoionization results supports the retention of micellar structure in rapidly frozen solutions. Hashimoto and Thomas[22] have obtained independent evidence supporting the retention of micellar structure in rapidly frozen solutions. They recently used luminescence quenching to measure micellar aggregation numbers and found similar aggregation numbers for SDS micelles in liquid and in 77 K frozen ethylene glycol–water solutions. This directly indicates that the micellar sizes and hence the gross structure are the same in liquid and rapidly frozen solutions.

The question of the solubilization locus of $TMB^+$ in micelles has been discussed in previous publications.[1-5] $TMB^+$ has an asymmetric location in the micelle interior and the water molecules do not penetrate the micelle surface significantly. The doxylstearic acid molecules are comicellized with the surfactant molecules with their carboxylate groups in the outer Stern layer of the micelle and the hydrocarbon chain in the micelle interior.[20,21] The 5-doxyl moiety is thus expected to be in the micelle interior but close to the micellar interface region; this has recently been supported by ESEM measurements.[5,20,21]

The deuterium modulation depth reflects the magnitude of the dipolar interaction between the unpaired electron in $TMB^+$ or 5-DSA and the water deuteriums.[23] The measured modulation depth changes inversely with the average distance between the unpaired electron and surrounding deuteriums and with deuterium density. For realistic deuterium densities, modulation can be detected to about 0.6 nm.

In the absence of 1-BuOH, the unpaired electron–water interactions monitored for 5-DSA and $TMP^+$ decrease in the order TMADS > DTAC > SDS, which is consistent with the previously deduced low hydration of SDS and DTAC micelle interfaces and greater hydration of the interface region in TMADS micelles.[2,5,21] The observed changes of deuterium modulation depth with 1-BuOH addition can be due to changes of water content in the probe neighborhood by opening up the micelle interface structure and/or by replacement of water by butanol molecules.

In TMADS micellar solution, deuterium interactions with both $TMB^+$ and the nitroxide group of 5-DSA decrease with 1-BuOH concentration. The simplest explanation is that 1-BuOH molecules displace water from the highly hydrated micellar surface so that the average number of deuteriums interacting with the spin probe decreases. Even though 1-BuOH will become 1-BuOD in $D_2O$ solutions, the average number of deuteriums in the interface environment will decrease since water has two deuteriums per molecule and since 1-BuOD displaces more than one water molecule on the average.

In contrast, in SDS micellar solution, 1-BuOH addition causes an increase in the 5-DSA and $TMB^+$ interactions with deuteriums. It has been concluded from ESEM measurements that SDS micellar surfaces are less densely or deeply hydrated than are

(21) Szajdzinska-Pietek, E.; Maldonado, R.; Kevan, L.; Jones, R. R. M.; Coleman, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 784.
(22) Hashimoto, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 5230.
(23) Kevan, L. In "Time Domain Electron Spin Resonance", Kevan, L., Schwartz, R. N., Eds.; Wiley-Interscience: New York, 1973; Chapter 8.

TMADS micellar surfaces.[5,20] This was based on the picture of the tetramethylammonium counterion acting as a spacer intercalated in the negative headgroup region in TMADS micelles. In SDS micelles, added 1-BuOH may also act as a headgroup spacer due to its alkyl tail seeking a hydrophobic environment. In a similar fashion as in TMADS micelles, this can lead to increased water interactions in the micellar surface region as observed at low 1-BuOH concentrations. At higher concentrations of added 1-BuOH, some of the water is replaced by 1-BuOH. These opposing effects can lead to the observed saturation of the deuterium modulation at higher 1-BuOH concentration.

The constant modulation depth in the DTAC/$D_2O$/1-BuOH system observed for the $TMB^+$ probe can be reconciled by assuming that TMB, initially located relatively close to the micelle surface, moves deeper into the hydrophobic core as 1-BuOH is added. This is expected to occur more readily in DTAC than in SDS since the modulation depth at zero 1-butanol concentration is larger in DTAC than in SDS. Thus, expected increases in the modulation depth, as seen for SDS, may be balanced out. This explanation seems supported by the 5-DSA probe results in Figure 4. The 5-DSA probe is more or less anchored near the micelle surface by the carboxyl headgroup and cannot readily move deeper into the DTAC micelle due to added 1-BuOH. Thus, 5-DSA shows similar modulation depth trends in both DTAC and SDS micelles.

A few photoionization efficiency experiments were also done with cetyltrimethylammonium chloride micelles; in general the efficiency was independent of 1-BuOH concentration as found for DTAC micelles. From the explanation advanced above for the net photoionization efficiency effect in DTAC micelles, one expects such agreement.

The effect of 1-BuOH on the TMB photoionization efficiency also varies with the micelle type. In past studies[4,5] a general correlation between the degree of $TMB^+$–water interaction measured by ESEM and the photoionization efficiency was found. This also holds for the photoionization efficiencies measured in TMADS and DTAC micelles as shown in Figure 1. In TMADS and DTAC miceles, the changes in $TMB^+$ yields with 1-BuOH concentration parallel the change in cation–water interactions as measured by the normalized modulation depths in Figure 3. The interpretation of this correlation with water interactions is that efficient charge separation occurs if the photoelectron is hydrated fast enough to slow its back reaction with the photoproduced $TMB^+$.

In SDS micelles, the $TMB^+$–water interactions increase with 1-butanol concentration to 50–100 mM 1-BuOH as shown in Figure 3. The yield of photoproduced $TMB^+$ also increases up to 50 mM 1-BuOH but then it decreases at higher 1-BuOH concentrations. In the higher concentration region, water is being displaced by 1-BuOH so net water interactions with $TMB^+$ decrease, correlating with the decrease in the $TMB^+$ yield. This effect also contributes to the decrease observed for TMADS. Alcohol also reacts slowly with $TMB^+$ in anionic micelles to regenerate TMB.[24] This reaction can also contribute to the decreases observed for both SDS and TMADS.

The effect of 1-BuOH on the photoionization yield of perylene in SDS micelles at room temperature has been studied recently by Grand et al.[17] They observed an increase in the hydrated electron yield vs. 1-BuOH concentration up to 150 mM followed by a decrease at higher 1-BuOH concentration. Our results with TMB in SDS micelles closely resemble this, but because we have several experimental points between 0 and 150 mM 1-BuOH, the maximum in the $TMB^+$ yield is observed to occur at 50 mM 1-BuOH. The results of Grand et al.[17] were interpreted in terms of the effect of 1-BuOH on the micelle surface charge which affects the electron–cation recombination probability. It was assumed that the surface charge initially increases with 1-BuOH concentration due to an increase in the degree of counterion dissociation and then decreases due to intercalation of 1-BuOH among the surfactant headgroups to reduce the surface charge density. Thus, the back reaction of the solvated electron with the photoproduced cation would be inhibited at low 1-BuOH concentration and enhanced at higher 1-BuOH concentration.

For SDS solutions containing 150 and 300 mM 1-BuOH, significant counterion dissociation occurs.[11] For tetradecyltrimethylammonium bromide micelles, the increase in the degree of counterion dissociation was only detectable at 1-BuOH concentrations higher than 100 mM.[9] Also, there is no change in conductivity of 20 mM SDS micellar solution with addition of 100 mM 1-BuOH.[14] Thus, for 50 mM 1-BuOH, one expects only a minor increase in counterion dissociation compared to the alcohol-free solution. Electrostatic interactions at the micelle surface could account for changes in the $TMB^+$ yield at high alcohol concentration but probably not at concentrations below 50 mM. We suggest that the initial increase in the photoionization yield with 1-BuOH in SDS micelles is primarily due to the enhancement of the TMB–water interactions as discussed above.

In summary, the effect of 1-BuOH on the photoionization efficiency of micelle solubilizate depends on the micelle charge and on the kind of counterion in dodecylsulfate micellar solutions. In SDS micelles, the charge separation can be enhanced by 70% by addition of 50 mM 1-BuOH.

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**Registry No.** $TMB^+$, 21296-82-2; 5-DSA, 29545-48-0; 1-BuOH, 71-36-3.

(24) Jones, R. R. M., unpublished results.