

because of the ease of NMR assignments even for complicated molecules such as chlorophylls. On the other hand, just as in NMR line broadening studies,⁹ it yields only ratios of hyperfine coupling constants and needs at least one ENDOR frequency to convert the ratios to absolute values.

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Hydrophobic-Hydrophilic Interactions in Sodium Dodecyl Sulfate Micelles. Stilbene-Viologen Complex Formation as a Probe of the Micelle Interior¹

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The formation of organized assemblies such as micelles, vesicles, and other bilayer systems is commonly attributed to hydrophobic effects which result in the organized media existing as a micro-heterogeneous phase separate from the bulk solution and consisting of discrete hydrophobic and hydrophilic regions.²⁻⁶ Although there has been controversy as to the distinctness of these regions and the site of various species solubilized in or interacting with them, it is clear that these organized assemblies can act variously as carriers, barriers, or reaction media toward different reagents. Unresolved problems concerning micelles in particular center around features such as the size, shape, amount of water incorporated in hydrophobic regions, and "tightness", or integrity of the structure.³⁻⁵ In recent studies we have used surfactant molecules incorporating relatively nonpolar chromophores as probes for the hydrophobic regions of micelles, vesicles, and other assemblies.⁷⁻¹⁰ A molecule of particular utility has been the surfactant *trans*-stilbene, S₁₆, which can be incorporated into a variety of media and whose fluorescence and photoisomerization behavior provides a sensitive index of the microenvironment.¹⁰ In

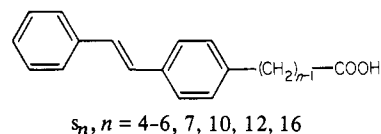
Table I. Stern-Volmer Constants for Quenching of Surfactant Stilbene Fluorescence by Methyl Viologen (MV²⁺) in SLS Micelles

<i>trans</i> -stilbene derivative ^a	K_{sv}^{20}	r
S ₄	2150 ± 200 ^b	0.992
S ₅	2060	0.997
S ₆	2440	0.997
S ₇	2120	0.998
S ₁₀	2250	0.996
S ₁₂	1870	0.998
S ₁₆	1020	0.999
<i>trans</i> -stilbene	2450	0.997

^a Surfactant stilbene concentration 5×10^{-5} M in each case, [SLS] = 0.028. ^b Error limits in each case are ± 200 or less.

the present paper we report a study of complex formation between a series of surfactant stilbenes, S_n, and the organic dication dimethyl viologen, MV²⁺, in micellar media. In the generally accepted model for micelle structure the stilbene chromophore in most, if not all, of these compounds would be expected to be buried relatively deep in a hydrophobic hydrocarbon core, while the viologen dication should be located in the more polar surface region or Stern layer.²⁻⁴ However, much recent work has suggested that most polar molecules and even aromatic hydrocarbons tend to occupy surface sites or at least regions moderately polar.^{5,11-13} This has been attributed variously to the high surface/volume ratio present in the micelle and the inadequacy of the headgroups to "cover" the surface as well as to a high internal Laplace pressure within the micelle interior.^{5,11} The results of this study are noteworthy in that we find complex formation occurs readily regardless of where the stilbene chromophore is located in the surfactant molecules. This, together with other results presented herein, indicates that the entire micelle is available for complex formation and is in accord with a developing picture that in many cases micelles have a very open structure with extensive hydrocarbon-water interfaces.

The synthesis of the surfactant *trans*-stilbenes, S_n, was relatively straightforward. Toluene was acylated under Friedel-Crafts



conditions with the acid chloride monomethyl ester of the appropriate diacid to give the toluene keto ester precursors of S₄, S₅, S₆, S₁₀, and S₁₆. In the case of S₇ and S₁₂, the Grignard reagent from 4-bromotoluene was condensed with cycloheptanone and cyclododecanone, respectively, and the resulting tertiary alcohol cyclododecanone, respectively, by refluxing with *p*-toluenesulfonic acid in toluene. The cyclic styrene thus formed was cleaved by ozonolysis and the product refluxed in methanol-sulfuric acid to give the toluene keto ester. The keto esters were brominated at the aromatic methyl with *N*-bromosuccinimide and then treated with triphenylphosphine to give Wittig reagents. Condensation with benzaldehyde by using potassium carbonate yielded the corresponding *trans*-stilbene keto esters which were reduced to the S_n esters by refluxing with zinc amalgam in hydrochloric acid. The esters were saponified by refluxing with potassium hydroxide in aqueous acetone. Satisfactory NMR, IR, and UV spectra and elemental analyses were obtained for all the stilbene acids or the corresponding methyl ester precursors for those acids too insoluble to analyze as such. Sodium dodecyl sulfate (SLS, Biorad) was recrystallized once from ethanol. Methyl viologen dichloride hydrate (Aldrich) and LTAC were used as received. The surfactant *N*-methyl-*N'*-hexadecyl-4,4'-bipyridinium²⁺ (MV16²⁺) was synthesized as described previously.¹⁴

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Table II. Temperature Effect on Fluorescence Quenching of S_6 by MV^{2+} and $MV16^{2+}$ in SLS Micelles

$T, ^\circ\text{C}$	MV^{2+}		$MV16^{2+}$	
	K_{sv}	r	K_{sv}	r
10	3430 ± 200^a	0.998	1220	0.997
20	2520	0.997	910	0.997
30	1890	0.996	790	0.996

^a Precision limits ± 200 or less in each case.

Table III. Quenching of Surfactant Stilbene Fluorescence by Viologen Derivatives in Various Media

stilbene	viologen	medium	$T, ^\circ\text{C}$	K_{sv}
S_6	MV^{2+}	SLS	20	2440
S_6	MV^{2+}	acetonitrile	20	15.5
S_6	MV^{2+}	LTAC	28	0
S_6	$MV16^{2+}$	LTAC	28	285
S_6	$MV16^{2+}$	SLS	30	790
S_{10}	$MV16^{2+}$	LTAC	38	285

trans-Stilbene and all the surfactant stilbenes were dissolved in 0.028 M SLS to give clear solutions¹⁵ showing the characteristic stilbene absorbance in the UV region. The absorption spectra of all the surfactant stilbenes are red shifted by about 6 nm in both homogeneous (CH_2Cl_2) and micellar (SLS) solutions. A moderately strong fluorescence similar to that of stilbene but red shifted is observed in each case. Addition of low concentrations of MV^{2+} ($1-10 \times 10^{-4}$ M) results in quenching of the fluorescence in micellar SLS; plots of I^0/I vs. $[MV^{2+}]$ are nearly linear in each case (Table I).¹⁶

Both the surfactant stilbenes and the methyl viologen are expected to be strongly bound to the SLS micelle. In this situation two modes of fluorescence quenching are possible: quenching may occur as a result of intramicellar diffusion or, alternately, quenching due to formation of a ground-state complex between stilbene and MV^{2+} may occur. Examination of the UV spectra reveals that a ground-state complex is formed; on addition of MV^{2+} to S_6 in SLS micelles the absorption maximum at 316 nm decreases in intensity, while the longest wavelength band is observed to tail off at yet longer wavelengths. Isobestic points are observed at 323 and 332 nm. The observation that K_{sv} decreases with increasing temperature (Table II) for S_6 quenched by MV^{2+} or the surfactant viologen $MV16^{2+}$ strongly suggests that most, if not all, of the quenching is due to the ground-state complex.^{17,18} Although a ground-state complex is evidently responsible for most of the fluorescence quenching, a dynamic process may still account for some. A modified Stern-Volmer relationship developed by Balzani¹⁹ predicts an upward curvature of the plot of I^0/I vs. $[Q]$ in this case and a slight upward curvature is observable in several of the plots. However, the curvature is very small, and any dynamic component would be expected to be minimal due to the extremely short fluorescence lifetime of the chromophore.

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(15) Solubilization of S_4 , S_5 , S_6 , and S_7 in SLS occurred readily upon sonication of an appropriately measured amount in SLS solution, though heating was occasionally necessary to effect complete solution. S_{10} , S_{12} , and S_{16} micellar solutions were prepared by slow addition of a 2.5×10^{-3} M benzene solution of the surfactant stilbene to a warm stirred SLS solution containing about 0.001 M NaOH. The benzene was then allowed to evaporate.

(16) The fluorescence intensities were measured at excitation wavelengths of 316, 322, and 328 nm and emission wavelengths of 358 and 274 nm. The MV^{2+} and $MV16^{2+}$ had only negligible absorbance at these wavelengths. A slight upward curvature of the plots of I^0/I vs. $[MV^{2+}]$ was noted for most of the experiments; however, this effect was small enough that it may result from an effect of the presence of the dication MV^{2+} on the micelle structure. Repeated measurements indicated that no permanent photochemical change occurred in the samples on the time scale of the experiments.

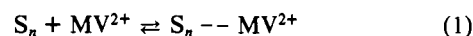
(17) Analysis of a plot of $\ln K_c$ vs. $1/T$ gives $\Delta S^\circ = -12$ eu.

(18) The cmc and N_A of SLS should not be much affected over the temperature range employed.³

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Examination of the absorption spectra indicates that ground-state complex formation occurs for S_6 and MV^{2+} in acetonitrile, resulting in a much lower extent (Table III) of fluorescence quenching. Although MV^{2+} was not observed to quench the fluorescence of the stilbenes in cationic (LTAC) micelles, as would be expected due to mutual repulsion of the quencher and micelle, some quenching was observed for S_6 and S_{10} by the surfactant viologen $MV16^{2+}$ (Table III).

The results obtained in this study are noteworthy for several reasons. The formation of the ground-state complex (eq 1) in the



$$K_{sv} \propto K_c = \frac{[S_n \cdots MV^{2+}]}{[S_n][MV^{2+}]} \quad (2)$$

micelle is anticipated to involve bringing together two chromophores of rather disparate hydrophobicity; clearly if either chromophore is tightly sequestered in a hydrophilic or hydrophobic site, the magnitude of K_c , and hence K_{sv} , should reflect the energies of desolvation associated with one or both monomers and the solvation of the complex. However, as the data in Table I indicate, there is only a factor of 2 separating what is perhaps the most hydrophobic stilbene, S_{16} , from free *trans*-stilbene which would be expected to reside at a "surface site". This remarkably small variation in the K_{sv} values suggests there is little sequestering of the stilbene chromophore from the polar viologen in any of the compounds studied. The intramicellar equilibrium constant, K_c , can be calculated by using the cmc (8.13×10^{-3} M) and aggregation number (62) of the SDS micelles to calculate the intramicellar concentrations of S_n , MV^{2+} , and $S_n \cdots MV^{2+}$.^{20,21} For S_6 at 20 $^\circ\text{C}$, we obtain $K_c = 16.4 \text{ M}^{-1}$ which is strikingly close to the value obtained for homogeneous acetonitrile solution (here $K_{sv} = K_c = 15.5$ at 20 $^\circ\text{C}$). This indicates essentially that the entire volume of the micelle is available for complex formation and suggests that the solvent reorganization energies involved within the micelle are relatively small for MV^{2+} and the various stilbenes.

It is interesting to note that the surfactant viologen gives lower values for K_{sv} in both anionic and cationic micelles. The lower values for anionic micelles might be attributed to preferential association of oppositely charged viologen and sulfate head groups; however, this explanation is unattractive, since even lower values for K_{sv} are obtained for the cationic micelles. A more reasonable explanation of the differential quenching observed between $MV16^{2+}$ and MV^{2+} might be the preferential solubilization of the latter at hydrophilic-hydrophobic sites in the "micelle interior" compared to "head group" sites for the chromophore in the surfactant. Taken together, the results of this study are most consistent with a highly open structure for at least the SLS micelles in which the distinction between polar and nonpolar sites is small. These results imply strongly that micelles have a less ordered structure than is generally accepted and that there is not a well-ordered phase boundary between "Stern layer" and hydrocarbon core and are in accord with conclusions obtained in other recent studies by using quite different techniques to probe micelle structure.^{5,11,23,24}

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE7823126) and the Swiss National Science Foundation (Project No. 4.337.0.79.4) for support of this work.

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(21) These data indicate a micelle concentration of 3.21×10^{-4} M and an average occupation [with 5×10^{-5} M stilbene probe (S_6)] of 0.156 S_6 /micelle. The Poisson distribution was used to calculate the fraction of occupied micelles (0.144), the difference being due to doubly and triply occupied micelles. Mukerjee²² has measured 0.889 mL/g as the partial specific volume of SLS which means that, after correcting for the cmc, in a 0.028 M SLS solution 5.12×10^{-3} is the fraction of the volume in the form of micelles.

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