Solute Partitioning in Aqueous Surfactant Assemblies: Comparison of Hydrophobic–Hydrophilic Interactions in Micelles, Alcohol-Swollen Micelles, Microemulsions, and Synthetic Vesicles[1]

John C. Russell and David G. Whitten*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received August 10, 1981*

Abstract: The structures of anionic assemblies including SLS micelles, alcohol-swollen SLS micelles, microemulsions, and vesicles of a mixture of dipalmitoyllecithin and dicetyl phosphate are investigated by using the ground-state complexation of a hydrophilic quencher (methyl viologen) with several hydrophobic fluorescent probes, including surfactant stilbenes and 1,4-diphenylbutadiene. In SLS micelles this complexation can be decreased nearly an order of magnitude by addition of 1-heptanol, indicating that the structure of the micelle can be adjusted from the highly open structure of the "pure" micelle to a much more closed structure in which hydrophobic solubilizates can be sequestered from hydrophilic reagents bound to the surface. The fluorescence quenching process in anionic vesicles is strongly dependent on temperature; at low temperatures quenching occurs, while at higher temperatures addition of methyl viologen appears to increase the stilbene fluorescence, indicating that the dicationic quencher binds to the vesicle surface, increasing the order of the system. These results indicate that the degree of organization of surfactant systems can be adjusted by simple changes in composition.

A wide variety of surfactant compounds can be dispersed in aqueous solution to form organized assemblies, either by spontaneous combination or with the aid of sonication. Their formation can be rationalized in terms of hydrophobic–hydrophilic and electrostatic interactions,[2] as well as by thermodynamic considerations.[3,4] Interest in the biological function of some of these assemblies and unusual control of reactivity has prompted a number of structural studies of the different media.[5-11] While direct investigation of some of the larger and more stable structures[12,13] by techniques such as electron microscopy has proved useful, other studies have made use of probe molecules or reactions whose spectroscopic or other properties are sensitive to the microenvironment. The precise structure[14] as well as the nature of solubilization sites[15] for "simple" micelles has been the topic of some dispute; the structural relationship between seemingly similar assemblies has also been an area of considerable concern and some controversy.

We recently reported the synthesis of a series of surfactant stilbene derivatives for use as structural probes for organized assemblies.[16] The stilbene is a nonpolar rodlike chromophore whose fluorescence and photoisomerization behavior are strongly environment sensitive;[17,18] studies of the highly water-insoluble S_{16} in films at the air–water interface indicated that the cross-sectional area and packing properties of the surfactant stilbenes are similar to those of straight-chain fatty acids.[19] We found that the *trans*-stilbene chromophore forms a ground-state complex with the dication *N,N'*-dimethyl-4,4'-bipyridinium (MV^{2+}) in both homogeneous solution and anionic sodium laurel sulfate (SLS) micelles (eq 1).[16] The observations that complexation in SLS

$$S + Q \rightleftharpoons SQ \quad (1)$$

with *trans*-stilbene and the series of surfactant stilbenes shows little dependence of K_A on the specific stilbene structure and that complex formation between highly hydrophobic and hydrophilic chromophores occurs about as readily in the SLS micelles or in acetonitrile solution led us to conclude that the SLS micelles have a highly open structure in which there is little sequestering of the stilbene from polar reagents. In the present paper we report an extension of this study to other assemblies formed from anionic surfactants. The results of this study indicate striking differences in the extent of complex formation for the assemblies investigated and underline the differences in the degree and type of organization. A particularly interesting aspect of our study is the finding that assembly properties can be "tuned" by variation of parameters such as temperature and added reagents.

Experimental Section

Materials. The synthesis of the stilbene probes S_N[16] and diphenylbutadiene[20] have been previously outlined. Sodium laurel sulfate, SLS (Biorad, electrophoresis grade), was recrystallized once from ethanol; heptanol and hexanol (Chemical Samples Co.) and dodecane (Philips) were used as received; pentanol (Aldrich) was distilled once. Dicetyl phosphate and dipalmitoyllecithin (Sigma) were used as received. Water was triply distilled, once from permanganate and once from sulfuric acid. Methyl viologen chloride (Sigma) was used as received.

Procedures. Preparation of probe-containing micellar solutions was accomplished as previously described. An appropriate amount of a 2.5×10^{-3} M benzene solution of probe was pipetted into a volumetric flask, the benzene evaporated with a steady stream of nitrogen, and sufficient

(1) Photochemical Reactivity in Organized Assemblies. 24. Paper 23: Whitten, D. G.; Schmehl, R. H.; Foreman, T. K.; Bonilha, J.; Sobol, W. M.; ACS *Symp. Ser.*, in press.
(2) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd ed.; Wiley-Interscience: New York, 1980.
(3) Tanford, C. In "Micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1.
(4) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676.
(5) Menger, F. M.; Bonicamp, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 2140–2141.
(6) Atik, S. S.; Singer, L. A. *Chem. Phys. Lett.* **1978**, *59*, 519–524.
(7) Gratzel, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 6885–6889.
(8) Breslow, R.; Kitabataki, S.; Rothhard, T. *J. Am. Chem. Soc.* **1978**, *100*, 8156–8160.
(9) Czarniecki, M. F.; Breslow, R. *J. Am. Chem. Soc.* **1979**, *101*, 3675–3676.
(10) Waggoner, A. S.; Griffith, O. H.; Christenses, C. R. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *57*, 1198–1205.
(11) Fendler, E. J.; Day, C. L.; Fendler, J. H. *J. Phys. Chem.* **1972**, *76*, 1460–1466.
(12) Okahata, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1979**, *101*, 5231–5234.
(13) Kunitake, T.; Okahata, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3860–3861.
(14) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111–117.
(15) Mukerjee, P.; Cardinal, J. R.; Desai, N. R. In "Micellization, Solubilization, and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1.
(16) Russell, J. C.; Whitten, D. G.; Braun, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3219–3220.
(17) Saltiel, J.; D'Agostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445–6456.
(18) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 12–18.
(19) Russell, J. C.; Costa, S. B.; Seiders, R. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5678–5679.
(20) McDonald, R. N.; Campbell, T. W. *Org. Synth.* **1960**, *40*, 36.

0002-7863/82/1504-5937$01.25/0

0.03 M stock SLS solution added to fill the flask to approximately one-half of its capacity. This was sonicated in a bath-type sonicator and heated until a clear solution resulted, at which time the flask was filled to capacity with stock SLS solution. For S_{10} and S_{12}, addition of NaOH to a total of 1×10^{-4} M was necessary.

The probe-containing vesicular solutions were prepared by adding appropriate volumes of benzene solutions of 0.1 M vesicle-forming surfactant and 2.5×10^{-3} M probe to a 13 × 100 mm test tube, evaporating the benzene with nitrogen, adding 5.0 mL of water, and sonicating with the microtip of a Heat Systems (Model W-220F) sonicator until a clear solution formed and remained after cooling to room temperature. The solutions thus formed were centrifuged to remove titanium particles released from the sonication probe.

Fluorescence measurements were obtained with a Hitachi Perkin-Elmer MPF2A recording spectrofluorimeter with excitation at 324 nm and measurement of the emission at 358 nm. The temperature was controlled with a circulating thermostat bath. Samples of 2.0 mL of probe-containing solutions were used in all studies. Fluorescence quenching was studied by adding microliter quantities of 0.1 M aqueous MV^{2+} to a maximum of 30 μL and agitating the solution with a pipet. Addition of the same amount of water had negligible effect on the fluorescence intensity. Linear alcohols were added neat to the micellar solutions, which were agitated with a pipet and allowed to settle before the fluorescence intensity was measured.

Fluorescence quantum yields are relative to $\phi_f = 0.05$ for *trans*-stilbene in methylcyclohexane at 25 °C. Solutions were prepared about 1×10^{-5} M in S_6 and adjusted to the same optical density (relative to blanks of the unlabeled solutions). These were excited in a SLM spectrofluorimeter at several wavelengths at which the absorbances coincided, and the emission was integrated from 320 to 500 nm.

Calculation of the Association Constants, K_A

Complexation of the chromophore (S) with the quencher (Q) can be expressed as a simple equilibrium:

$$K = \frac{[S{\cdot}Q]}{[S][Q]} \tag{2}$$

If the excitation wavelength is at an isosbestic point and only the uncomplexed chromophore fluoresces, then the concentrations of complexed and free chromophore and quencher can be found from the fluorescence intensity and the amounts of reacting materials present:

$$[S] = [S]^0 I/I^0 \tag{3}$$

$$[S{\cdot}Q] = [S]^0 - [S] = [S]^0(1 - I/I^0) \tag{4}$$

$$[Q] = [Q]^0 - [S{\cdot}Q] = [Q]^0 - [S]^0(1 - I/I^0) \tag{5}$$

With substitution into eq 2 and rearrangement:

$$K = \frac{I^0/I - 1}{[Q]^0 - [S]^0(1 - I/I^0)} \tag{6}$$

Equation 6 provides the association constant for probe with quencher in homogeneous solution. In micellar solution, when both probe and quencher are tightly bound to the micelle, their effective concentrations are increased. The volume of the micellar component of the solution is

$$V_m = V^0([SLS] - CMC)V_s M + V_a \tag{7}$$

where V^0 is the total volume of the sample, V_s is the partial specific volume of the surfactant (0.889 mL/g for SLS),[21] M is the molecular weight of the surfactant (288.38 for SLS), and V_a is the added volume of alcohol. Because of the low ratio of probe to surfactant concentration, most of the micelles are not occupied by a probe molecule, and the volume in which complexation occurs must be further reduced. The Poisson distribution was used to determine the fraction of micelles occupied by probe:

$$P_n = \frac{a^n e^{-a}}{n!} \tag{8}$$

where P_n is the probability of a micelle containing n probes and a is the average number of probes per micelle in the solution. The probability of a micelle containing one or more probes is given by

$$P = 1 - P_0 = 1 - (a^0 e^{-a})/0! = 1 - e^{-a} \tag{9}$$

The average number of probe molecules per micelle is given by

$$a = \frac{[S]^0}{[\text{micelles}]} = \frac{[S]^0}{([SLS] - CMC)/N_A} \tag{10}$$

where N_A is the aggregation number of the surfactant; hence

$$P = 1 - \exp\left(\frac{-[S]^0 N_A}{[SLS] - CMC}\right) \tag{11}$$

With 5×10^{-5} M probe in 0.03 M SLS, assuming a CMC of 0.008 M and a N_A of 63, P is 0.133, which corresponds to about one probe for every seven micelles. When the effective micellar concentration of probe and quencher is determined, only those micelles that contain at least one probe are considered:

$$[S_m] = \frac{[S]^0 V^0}{V_m P} \tag{12}$$

The quencher is considered to be distributed evenly among all the micelles; its effective micellar concentration is

$$[Q_m]^0 = [Q]^0 V^0/V_m \tag{13}$$

Substituting these values into eq 11 yields

$$K_a = \frac{I^0/I - 1}{\frac{[Q]^0 V^0}{V_m} - \frac{[S]^0 V^0}{V_m P}(1 - I/I^0)}$$

$$K_a = \frac{V_m(I^0/I - 1)}{V^0([Q]^0 - ([S]^0/P)(1 - I/I^0))} \tag{14}$$

A similar method was used for calculation of K_a for DPB with quencher in the microemulsion system tested.

Equation 6 provides K_a in terms of known quantities. In the presence of a large excess of quencher, the uncomplexed quencher may be considered equal to the added quencher:

$$[Q] = [Q]^0 \tag{15}$$

In terms of known quantities eq 2 becomes

$$K = \frac{[S{\cdot}Q]}{[S][Q]} = \frac{[S]^0(1 - I/I^0)}{([S]^0 I/I^0)[Q]^0}$$
$$= (I^0/I)(1 - I/I^0)/[Q]^0$$
$$= (I^0/I - 1)/[Q]^0 \tag{16}$$

Rearranged, this becomes the Stern–Volmer equation:

$$I^0/I = 1 + K[Q]^0 \tag{17}$$

Results

The aromatic hydrocarbon probes used in this study, S_N, *trans*-stilbene, and *trans,trans*-1,4-diphenyl-1,3-butadiene (DPB), are water insoluble at neutral pH. As reported previously for stilbene and S_N[16] and other aromatic hydrocarbons,[22,23] DPB forms a ground-state complex with MV^{2+} both in acetonitrile ($K_A = 5.1$) and in aqueous SLS ($K_A = 23$, Figure 1). This complex has an ultraviolet absorption spectrum quite similar to that of uncomplexed DPB; a weak charge-transfer absorbance band is seen in the visible region.[24] Thus while charge-transfer interactions undoubtably play a role in its formation, the complex is probably best described as a weakly perturbed DPB chromophore.

(21) Mukerjee, P. *J. Phys. Chem.* **1962**, *66*, 1733.

(22) From the Doctoral Thesis of Franciscus Margaretha Martens, Universitat van Amsterdam, 1981.

(23) Martens, F. M.; Verhoeven, J. W. *J. Phys. Chem.* **1981**, *85*, 1773–1777.

(24) Otruba, J. P., personal communication.

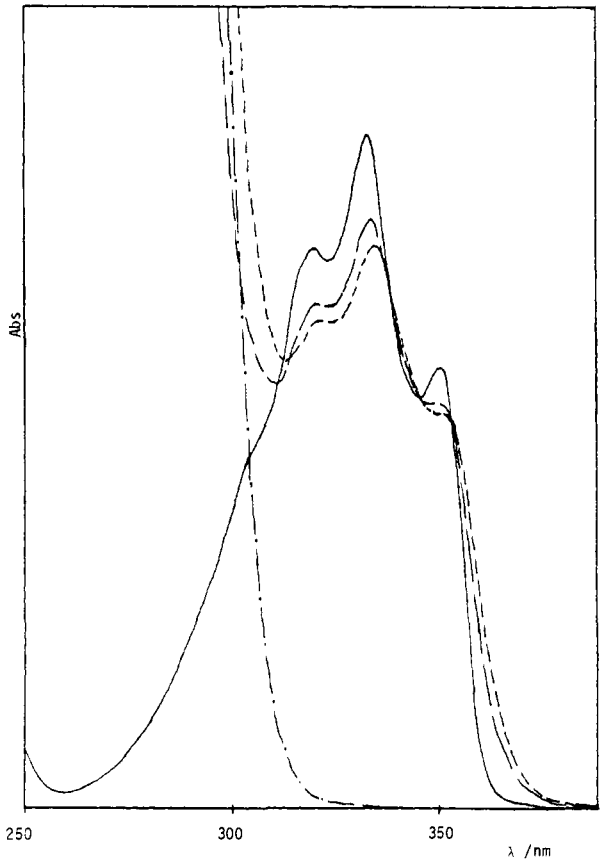


Figure 1. Absorbance spectra in 0.03 M SLS containing 5×10^{-5} M DPB. $[MV^{2+}] = 0$ (—), 5×10^{-4} M (– –), 1×10^{-3}) M (3 ---). (—•—•) shows the spectrum of 1×10^{-3} M MV^{2+} in 0.03 M SLS.

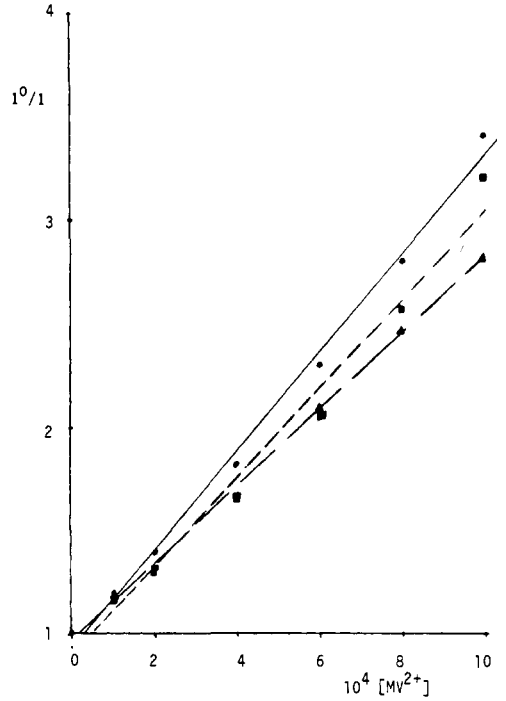


Figure 2. Plot for Stern–Volmer quenching of 5×10^{-5} M S_N in 0.028 M SLS at 20 °C. S_6 (●) (—); S_{10} (■) (----); S_{12} (▲) (– –). Lines fit by linear regression.

The stilbene fluorescence is quenched in the presence of methyl viologen, and the nature of this quenching in SLS micelles was studied by laser flash techniques. While the fluorescence intensity was quenched, the fluorescence lifetime was unchanged in the presence of MV^{2+}, indicating that quenching results only from

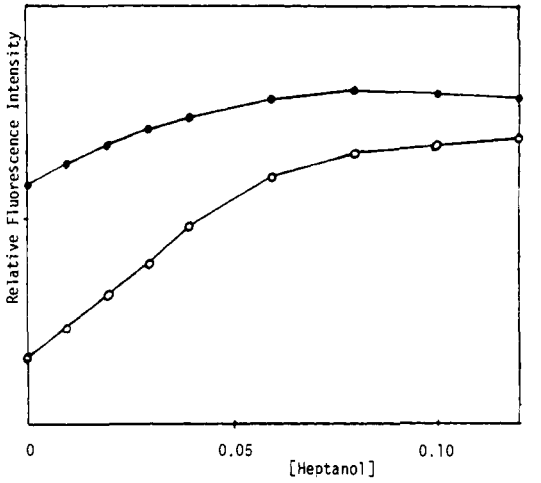


Figure 3. Plot of measured emission intensity of S_6 (5×10^{-5} M) in SLS (0.03 M) as a function of added heptanol concentration. $[MV^{2+}] = 0$ (●); $[MV^{2+}] = 1 \times 10^{-3}$ M (○).

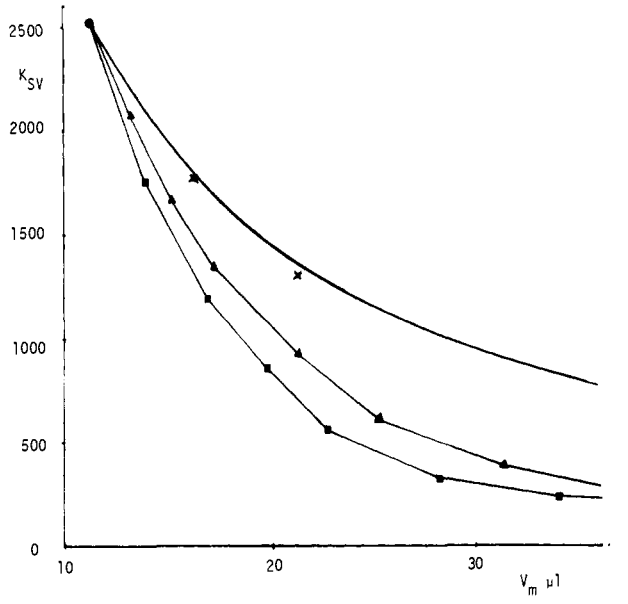


Figure 4. Plot of quenching constant K_{SV} for quenching of S_6 fluorescence in 0.03 M SLS by MV^{2+} as a function of micellar volume. V_m is increased by increasing the concentration of SLS (×) or by addition of linear alcohols (hexanol (▲) or heptanol (■).

complexation and has little, if any, dynamic component.[25] Fluorescence quenching was used throughout to obtain association constants K_A.

Figure 2 shows a plot of Stern–Volmer quenching of some of the probes in SLS solution. The small upward curvature seen can be rationalized as resulting from the assumption, made in eq 15, that the concentration of complexed quencher in solution is small compared to that of the uncomplexed quencher. High quenching constants are obtained for all the probes, indicating their accessibility to interaction with the quencher.

Addition of water-insoluble linear alcohols to SLS micelles has been asserted to cause a "swelling" of the micelles;[26-28] up to a 4-fold excess of 1-heptanol can be added without causing turbidity. Figure 3 shows the fluorescence intensity of S_6 in micellar SLS as a function of added heptanol concentration. In the absence

(25) Braun, A. M., private communication.
(26) Thomas, J. K. *ACS Symp. Ser.*, in press.
(27) Jain, A. K.; Singh, R. P. B. *J. Colloid Interface Sci.* **1981**, *81*, 536–539.
(28) Almgren, M.; Lofroth, J.-E. *J. Colloid Interface Sci.* **1981**, *81*, 486–499.

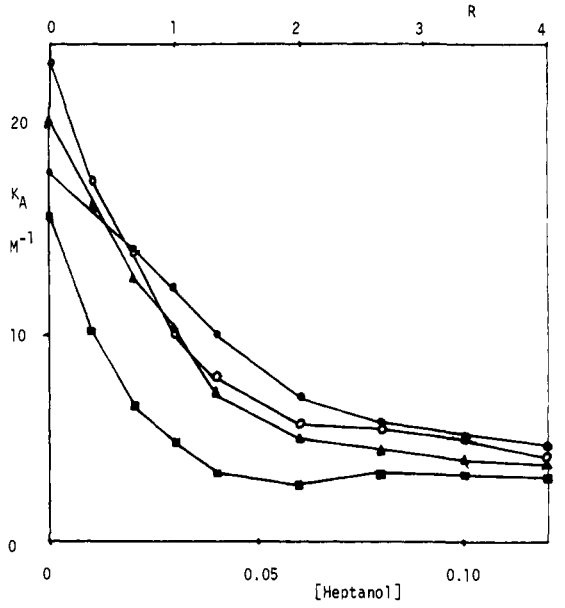


Figure 5. Plot of K_A for association of fluorescent probe with MV^{2+} in 0.03 M SLS as a function of added 1-heptanol at 20 °C. (○) *trans,trans*-1,4-Diphenyl-1,3-butadiene; (●) S_4; (▲) S_6; (■) S_{10}. The upper abscissa indicates the heptanol/SLS ratio.

Table I. Association Constants, K_A, for Fluorescent Probes with MV^{2+} in 0.03 M SLS at 20 °C with Various Concentrations of 1-Heptanol

	[heptanol]/[SLS]			
probe	0	1.0	2.0	4.0
DPB	22.9	10.0	5.6	4.1
S_4	17.8	12.2	7.0	4.6
S_6	20.3	10.3	5.0	3.6
S_{10}	15.8	4.8	2.7	3.1

of quencher, the fluorescence intensity increases to a maximum at a molar ratio of heptanol to SDS of about $R = 2$, where it levels out and begins to decrease. With MV^{2+} present, the fluorescence intensity starts at a much lower level, due to the complexation, but increases rapidly with heptanol concentration, eventually leveling out at an intensity not much below that of the unquenched solution. With eq 17 these data can be used to calculate quenching constants, K_{SV} for the various solutions. K_{SV} is dependent on the volume of the micellar portion of the medium, which increases with alcohol addition. Figure 4 shows K_{SV} for quenching of S_6 fluorescence by MV^{2+} plotted vs. the volume of the micellar component of a solution of SLS (calculated from eq 7) in which the micellar volume is increased by adding 1-hexanol and 1-heptanol and by increasing the SLS concentration. As expected, increasing the SLS concentration decreases the quenching constant in an inverse proportion to the amount of SLS present in the form of micelles. Addition of the alcohols decreases K_{SV} more rapidly than can be accounted for by the simple increase in micellar volume, indicating that there must be some additional effect on the structure of the aggregate that prevents the interaction of probe with quencher.

To separate the effects of the micellar structure, we developed eq 14, which corrects the quenching constant for the volume increase by determining the actual association constant of the fluorescent probe and quencher in the aggregate. Figure 5 shows K_A for several of the probes plotted as a function of heptanol concentration in SLS solution, and Table I gives representative values for K_A at several heptanol concentrations. All the hydrophobic probes show a rapid decrease in K_A with initial addition of heptanol; however, the decrease levels out after a concentration of about two heptanols per SLS molecule. The shortest chain of the surfactants, S_4, shows the slowest decrease in K_A, whereas the longest chain member tested, S_{10}, shows the sharpest decrease,

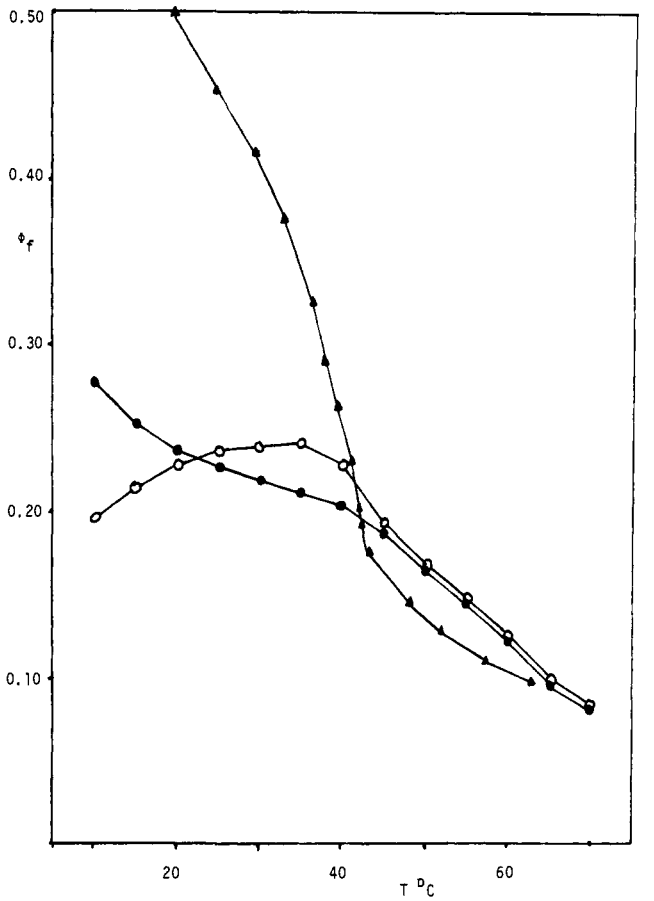


Figure 6. Fluorescence quantum yield of stilbene probe in vesicles as a function of temperature. (●) [DPL] = [DCP] = 2.5×10^{-3} M, [S_6] = 1×10^{-5} M. (○) Same solution with 1.5×10^{-3} M MV^{2+} added. (▲) 1×10^{-5} M S_4 in 1×10^{-3} M DPL.

with the intermediate S_6 and the nonsurfactant probe DPB showing intermediate results.

Closely related oil/water microemulsions have been prepared with SLS, the same alcohols, and hydrocarbons such as dodecane. Using a system well characterized by Almgren, Grieser, and Thomas[29] (5.53% SLS, 10.28% 1-pentanol, 5.14% *n*-dodecane, 79.05% H_2O), we find results somewhat similar to those obtained for the alcohol-swollen micelles. Here, K_A was calculated for the association of DPB with MV^{2+}; DPB was used in this case because the low value for K_A and the large effective aggregate volume make it necessary to use concentrations of MV^{2+} high enough to cause significant absorbance near the excitation wavelength of the stilbene probes. The measured value of 2.9 is very close to those found in SLS at large heptanol concentrations.

The fluorescence of these probes is similar in SLS micelles, microemulsions, and hydrocarbon solution; however, in the more highly organized vesicular media the fluorescence is much higher, indicating an environment much more restrictive to the twisting of the excited stilbene chromophore.[17] For the two systems shown, pure dipalmitoyllecithin and 1:1 dipalmitoyllecithin:dicetyl phosphate, rather different fluorescence behavior is observed. Figure 6 shows a plot of fluorescence quantum yield of the probe as a function of temperature for the two systems. For DPL there is a clear discontinuity in the vicinity of the phase-transition temperature;[30] below this the fluorescence continues to increase steeply. For DPL/DCP a similar indication of T_C can be inferred from the plot; here, however, the increase below T_C is less steep. The quenching of fluorescence by MV^{2+} was also studied in this system.[16] Since the vesicle surface is anionic, MV^{2+} is expected to bind, and this does appear to be the case. At low temperatures

(29) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188–3193.
(30) Reference 2, p 132.

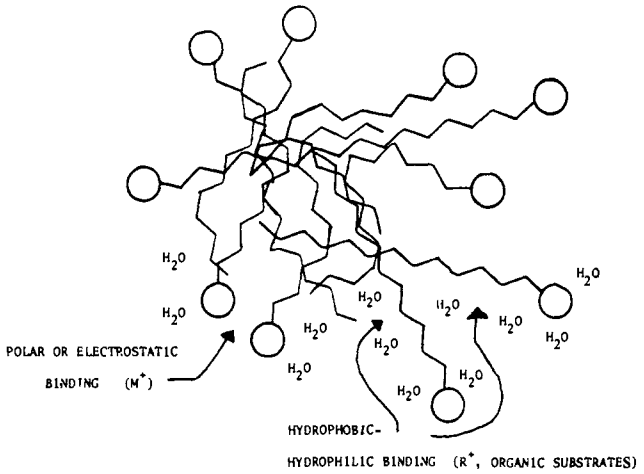


Figure 7. "Open" model for SLS micelle.

probe fluorescence is quenched significantly; at moderate temperatures, however, the quenching disappears, and the fluorescence actually increases in the presence of MV^{2+}, while at higher temperatures MV^{2+} has no effect whatever. This indicates that, while low temperatures favor the interaction of the probe and quencher, at higher temperatures the interaction is prevented.

Discussion

Micelles, Swollen Micelles, and Oil/Water Microemulsions. This study involves the complexation of a highly hydrophobic fluorescent probe with a highly hydrophilic quencher. In the organized media used, the stilbene probe should be located in the most hydrophobic region, associating with the surfactant alkyl groups.[31] Because the surfactants contain anionic head groups, the dicationic methylviologen should be associated with the interfacial region of the organizate, where the head groups are located.

The finding that K_{SV} is large for all probes in SLS micelles indicates the accessibility of the probe to the quencher. This, along with a number of recent findings,[14] is consistent with a very open structure for the SLS micelle, with little capacity for separating hydrophobic from hydrophilic regions. Figure 7 shows a possible structure for such an open micelle. The micelle contains binding sites for both hydrophobic and hydrophilic solutes, but no structural feature of the aggregate prevents interaction of the two. Regardless of the length of the hydrocarbon chain of the stilbene probe, the chromophore should be easily accessible to the quencher.

The addition of heptanol to SLS micelles was observed to cause an increase in fluorescence intensity of S_6 in the absence of MV^{2+} out to a ratio of heptanol to SLS of about 2, after which it leveled out and began to decrease (Figure 3). This increase suggests a "tightening" of the environment of the chromophore in the presence of the alcohol. The most likely explanation for this is that the alcohol binds to the micelle, its hydroxy group hydrogen bonding to the surfactant head groups, increasing the distance between them and so decreasing the repulsion between them.[32] The surfactants making up the aggregate are more tightly associated, increasing the resistance to molecular motion necessary for photoisomerization of the stilbene chromophore, thus favoring fluorescence.[17] Observations that the addition of alcohols decreases the CMC of micellar surfactants support this interpretation; a lower CMC indicates a stronger drive toward aggregation and a tighter structure.

In addition to increasing the fluorescence intensity of the probes, the addition of linear alcohols also decreases their quenching by MV^{2+}. Figure 4 shows that some of this decrease is due to an increase in the aggregate volume decreasing the effective concentrations of the probe and quencher. Because of this dependency of quenching on aggregate volume, values for the association constant K_A of the two were calculated.[33] When these are plotted vs. heptanol concentration (Figure 5), they show a significant decrease with increasing heptanol, indicating that some change in the aggregate other than the increase in volume is decreasing the accessibility of probe to quencher. It seems most likely that, in addition to tightening the aggregate, the presence of heptanol causes some structural organization such that hydrophobic and hydrophilic portions become more separated from each other. The most ready explanation is that the stilbene chromophore is now sequestered within the hydrophobic "swollen" micellar interior, while the cationic MV^{2+} is associated with the charged surface. The finding that the longer chain probes are more affected than the shorter chain probes suggests that there are different "depths" to which the chromophores may be solubilized in the aggregate; the chromophore of S_4, which is located near the surface of the aggregate, is more accessible to the quencher than is that of S_{10}, which is buried deeper.

This interpretation might be objected to on the grounds that the binding of alcohols might interfere with the binding of MV^{2+} to the aggregate; a decrease in MV^{2+} binding to the aggregate on addition of the heptanol would also explain the decrease in apparent K_A. That methyl viologen does associate strongly with SLS micelles was shown in a previous study in this laboratory.[34] Molar ratios of MV^{2+} to SLS of up to 1:3.0 were observed in micellar SLS systems before a significant amount of unbound MV^{2+} could be detected in the solution.[25] In a preliminary study of alcohol-swollen micelles, we observed that a 0.02 M SLS solution shows a ratio of 1:2.7 in the presence of 0.07 M heptanol, indicating that the heptanol actually increases the capacity of the aggregate to bind MV^{2+}.[35]

The microemulsion system tested was shown to give a value for association of DPB with MV^{2+} of 2.9 M^{-1}. This value is close enough to those found in SLS micelles at large heptanol concentrations (Table I) to suggest a similar sequestering behavior. The assumption usually made for microemulsion systems, that they have a well-defined hydrophobic–hydrophilic interface appears well founded in this case.

Vesicles. The behavior of the stilbene fluorescence in DPL/DCP vesicles in the presence of added methyl viologen is interesting and somewhat complicated. At temperatures well above the phase transition (40 °C), there is no quenching whatsoever for the stilbene probes S4, S6, S10, S12, and S16 in DPL/DCP. Since we have established that methyl viologen binds well to these vesicles, these results suggest that the stilbene and viologen chromophores are separated from each other in the liquid crystalline phase of these vesicles. This result is not unexpected since several other studies suggest that the vesicles retain their ability to entrap hydrophilic reagents in this phase and retain much of their overall structure.[36] It is interesting to note that there is no quenching even with the shortest chain stilbene, S4, where the distance between the edge of the stilbene chromophore and the hydrophilic region should be only several angstroms at most. Since electron transfer from the excited singlet state of the stilbene to methyl viologen should be a highly favored process, one might anticipate that a long-range process, perhaps via tunneling, could occur for S4 and perhaps for the other stilbenes.[36] The lack of any quenching for these probes suggests that no long-range electron transfer is occurring in these cases; comparison with recent studies using other excited substrates in which such long-range electron transfer to methyl viologen was indicated[36] may suggest that the much shorter lifetime of the stilbene singlet prevents the observation of such a process.

(31) However, a case could be made that the stilbenes, as with other nonsurfactant aromatics, has some preference for a "surface" site. See ref 14.
(32) Zana, R.; Yiv, S.; Strazielle, C.; Lianos, P. *J. Colloid Interface Sci.* **1981**, *80*, 208.
(33) K_A was calculated as in ref 15, assuming that the CMC and aggregation number remain constant with addition of heptanol. Both of these values have been shown to decrease with addition of linear alcohols (ref 27 and 28); however, the effect on our calculations should be minimal.
(34) Foreman, T. K.; Sobol, W. M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 5333–5336.
(35) Foreman, T. K.; Bonilha, J. B.; Russell, J. C.; Whitten, D. G., unpublished results.
(36) Tunuli, M. S.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507.

The behavior of the stilbene–viologen system in DPL/DCP at lower temperatures is somewhat more complicated. The actual *increase* in stilbene probe fluorescence in the presence of viologen in the phase-transition region is probably attributable to a "tightening" of the vesicle structure brought about by interaction of the added cation with the anionic head groups of the assembly. The quenching of stilbene fluorescence observed at lower temperatures is more difficult to understand. As pointed out above, the sharp increase in stilbene fluorescence in DPL alone at low temperatures is best attributed to location of the stilbene probe in a highly ordered environment in which the effective "microviscocity" is very high. Studies with other probes more hydrophilic than stilbene also suggest that the functionalized surfactants should be retained in the hydrocarbon portion of the vesicles. The contrast between the behavior of the stilbene probes in DPL alone and in DPL/DCP (Figure 6) may indicate that in the mixed vesicles the stilbene occupies a "different" site at low temperatures. This could explain the quenching by MV^{2+}. Alternatively, if we assume the stilbene remains "within" the bilayer interior, the observed quenching could be due either to a static phenomenon whereby the viologen is also incorporated into a relatively hydrophobic site such that some stilbene–viologen contacts are possible or to a quenching over greater distances such as has been proposed for other vesicle systems.[36] Studies are currently under way to distinguish between these possibilities.

The overall results of this study emphasize the variability of the structures of different surfactant assemblies. Moreover, they indicate how controlled modulation can be obtained, especially in the case of charged micelles, by the use of additives. Thus SLS micelles can be adjusted from loose aggregates with little separation of hydrophobic from hydrophilic regions to well-organized assemblies capable of sequestering nonpolar solubilizates in a hydrophobic interior, much less accessible to polar solutes. This ability to modify the sequestering action of surfactant assemblies should be especially useful in developing surfactant systems for control and modification of reactivity.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-8121140) for financial support of this work.

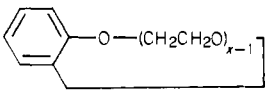
Registry No. SDS, 151-21-3; MV^{2+}, 4685-14-7; *trans,trans*-DPB, 538-81-8; S_4, 77814-46-1; S_6, 77814-47-2; S_{10}, 77824-98-7; S_{12}, 77814-49-4; S_{16}, 74392-06-6; heptyl alcohol, 111-70-6; dicetyl phosphate, 2197-63-9; *trans*-stilbene, 103-30-0.

Monte Carlo Study of Macrocyclization To Form Benzo-Crown Ethers

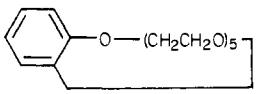
Wayne L. Mattice* and George R. Newkome

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received January 21, 1982*

Abstract: A Monte Carlo study has been conducted of the formation of benzo-crown ethers (**1**) from an acyclic precursor.



1



2

The range of x is 2 to 16 inclusive. Limiting behavior is obtained at $x \geq 7$. As x falls below 7, calculated cyclization constants fall below the extrapolation of the limiting behavior. The cyclization constants pass through a minimum when x is about 4. The major features of the computed cyclization constants are in harmony with trends observed in kinetic constants reported recently by Illuminati et al.[11] The presence of an ortho-fused benzo moiety has a marked effect on the relative ease of cyclization to form $(CH_2CH_2O)_6$ and **2**.

Calculations based on a rotational isomeric state model[1-3] for unperturbed poly(oxyethylene) have provided insight into configuration-dependent properties of macrocycles formed from this polymer. The model that predicts cyclization to form $(OCH_2CH_2)_{2y}$, y = 2–10, is most readily achieved with $(OCH_2CH_2)_6$,[4] a conclusion which stands in harmony with experiment.[5,6] Among the most favored conformations calculated[4] for $(OCH_2CH_2)_6$ is the one seen in its complex with potassium ion.[7,8] The most favorable conformation calculated[4] for $(OCH_2CH_2)_8$ is the one found experimentally in the crystalline state.[7] Larger poly(oxyethylene) macrocycles are sufficiently flexible so that no one conformation dominates the configuration partition function. Cyclization of the larger poly(oxyethylene) chains is found to require a contraction in the average distribution of chain atoms along the major principal axis of the gyration tensor, with little change perpendicular to this axis.[4,9]

Origin of the large macrocyclization equilibrium constants for $(OCH_2CH_2)_6$ and $(OCH_2CH_2)_8$ becomes clear upon comparison with macrocyclization equilibrium constants for the formation of $(SCH_2CH_2)_{2y}$ from poly(thiaethylene).[10] Macrocyclization equilibrium constants are found to be smaller in the sulfur series. Furthermore, the macrocyclization equilibrium constants calculated for the members of the sulfur series with y = 3 and 4 follow the trend established by molecules with higher y, but the molecules with y = 3 and 4 in the oxygen series have significantly higher macrocyclization equilibrium constants than the results predicted by this trend. The special behavior of $(OCH_2CH_2)_6$ and $(OCH_2CH_2)_8$, as opposed to the unremarkable behavior of $(SCH_2CH_2)_6$ and $(SCH_2CH_2)_8$, might conceivably be attributed to either of two factors: (a) geometric constants (bond lengths and bond

(1) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1415.
(2) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 3702.
(3) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(4) Mattice, W. L. *Macromolecules* **1979**, *12*, 944.
(5) Greene, R. N. *Tetrahedron Lett.* **1972**, 1793.
(6) Cook, F. L.; Caruso, T. C.; Byrne, M. P.; Bowers, C. W.; Speck, D. H.; Liotta, C. L. *Tetrahedron Lett.* **1974**, 4029.
(7) Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1972**, *26*, 1471.
(8) Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerly, R. P. *Acta Crystallogr., Sect. B* **1974**, *30*, 2722.
(9) Mattice, W. L. *Macromolecules* **1980**, *13*, 506.
(10) Mattice, W. L. *J. Am. Chem. Soc.* **1980**, *102*, 2242.

0002-7863/82/1504-5942$01.25/0