Reprinted from The Journal of Physical Chemistry, 1990, 94.

A Luminescence Quenching Study on the Localization Problem of $Ru(bpy)_3^{2+}$ in Micelles and Hemimicelles

Joy T. Kunjappu,[†,‡] P. Somasundaran,*[,‡] and N. J. Turro[§]

Langmuir Center for Colloids and Interfaces and Chemistry Department, Columbia University, New York, New York 10027 *(Received: May 19, 1989; In Final Form: June 8, 1990)*

Quenching studies on the luminescence emission of $Ru(bpy)_3^{2+}$ with ferrocyanide ion, 9-methylanthracene, and doxylstearic acids have been carried out in hemimicellar and micellar aggregates to gain insight into the location of this Raman and luminescence probe. $Ru(bpy)_3^{2+}$ is bound to a more nonpolar hemimicellar hydrophobic region as evidenced from the observed larger Stokes shift in this case than in the case of a micellar environment. Stern–Volmer constants for the doxylstearic acid quenching of $Ru(bpy)_3^{2+}$ luminescence in micelles indicated that the optical electron in the MLCT state of the probe molecule resides in a bipyridyl ring which appears to be close to position 7 of the stearic acid chain.

Introduction

Determination of the exact location of probe molecules in organized assemblies is essential in interpreting the results of spectroscopic studies with those probes. Spectroscopic methods (luminescence, ESR, etc.) using probes have been applied in understanding the interior structure and dynamics of micelles, vesicles, microemulsions, etc.;[1] a variety of tailor-made probes, chiefly of aromatic hydrocarbon types and their derivatives,[2] are successfully employed for this purpose.

In a recent study we reported the use of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl) as a Raman[3] and luminescence[4] probe to study the structure and evolution of anionic surfactant aggregates in solution and in the adsorbed state on solids. (These aggregates are referred to as hemimicelles or more appropriately by the generic term *solloid*.[3b] Shifts in frequencies and enhancement in intensities of the excited-state Raman spectra of $Ru(bpy)_3^{2+}$ in sodium dodecyl sulfate (SDS) micelles and Al_2O_3/SDS hemimicelles were remarkable responding to the general course of the aggregation process.

$Ru(bpy)_3^{2+}$ has been the focus of many studies owing to its projected potential in solar energy conversion.[5] A few studies address the problem of localization of $Ru(bpy)_3^{2+}$ in micellar solutions: Meisel et al.[6] inferred that $Ru(bpy)_3^{2+}$ in SDS micelles is embedded in a highly negatively charged microenvironment; Warr and Grieser[7] observed that the alkylbipyridyl derivatives of $Ru(bpy)_3^{2+}$ are effectively quenched in SDS micelles only if the alkyl chain length is 12 carbon atoms or fewer; Colaneri et al.[8] studied the ESR spectra of alkylviologen monocation radical formed by the quenching of $Ru(bpy)_3^{2+}$ and inferred that the binding site of the ruthenium complex at the micellar interface depends on the alkyl chain length of the viologen and ruthenium complex. Another study[9] indicated that $Ru(bpy)_3^{2+}$ is less hydrated in SDS micelles than in water.

It is, thus, generally recognized that both electrostatic and hydrophobic factors play a role in deciding the binding site of $Ru(bpy)_3^{2+}$ in SDS micelles. This study seeks answers to the question of the location of this probe in micelles with a special reference to the nature of its excited state in a micellar environment and to throw light into this problem in the context of hemimicelles. We employ the luminescence quenching method for this purpose with a variety of quenchers. The quencher molecules chosen were potassium ferrocyanide, 9-methylanthracene, and a series of isomeric doxylstearic acids.

Experimental Section

Sodium dodecyl sulfate (SDS) was obtained from Biorad Laboratories, 9-methylanthracene (9-MA) and tris(2,2′-bipyridyl)ruthenium(II) chloride were obtained from Alfa Products, and 5-, 7-, 12-, and 16-monosubstituted isomeric doxylstearic acids (5-D, 7-D, 12-D, and 16-D) were from Molecular Probes. Linde A alumina (particle size 0.3 μm; surface area 15 m^2/g) from Union Carbide was the substrate. All of these materials were used without further purification. Aqueous samples were prepared in triply distilled water.

The adsorption samples were prepared by shaking alumina preconditioned in water at a pH of 6.5 and a NaCl concentration of 0.1 M with an appropriate SDS solution as described earlier.[10] The integrity of the isotherm was checked by tracing the adsorption isotherm in the presence of 5.3×10^{-5} M $Ru(bpy)_3^{2+}$. For quenching studies with ferrocyanide, fresh solutions of potassium ferrocyanide were prepared and mixed thoroughly with SDS micellar solution or Al_2O_3/SDS hemimicellar slurry immediately before the luminescence measurements. Stock methanolic solutions of 9-MA (for micelles and hemimicelles) and doxylstearic acids (for micelles) were used as quenchers; the methanol content of the samples did not exceed more than 1% of the total volume. In this concentration level, methanol does not have any serious interference with the micellar[7] and hemimicellar[11] properties.

Emission and excitation spectra of $Ru(bpy)_3^{2+}$ in different cases were recorded with a SPEX FLUOROLOG spectrofluorometer at an excitation wavelength of 450 nm for the emission studies and at an emission wavelength of 638 and 678 nm for the excitation studies. The residual concentration of $Ru(bpy)_3^{2+}$ in the supernatant was determined by measuring its absorption at 450 nm using a Beckman UV/vis spectrophotometer.

Results and Discussion

Figure 1 shows the adsorption isotherm of SDS on alumina in the presence and absence of $Ru(bpy)_3^{2+}$. (The method of analyzing the adsorption samples for the residual surfactant con-

[†] On leave of absence from Chemistry Division, BARC, India.
[‡] Langmuir Center for Colloids and Interfaces.
[§] Chemistry Department.

(1) (a) Somasundaran, P.; Kunjappu, J. T. *Miner. Metall. Process.* **1988** (May), 68. (b) Zana, R. *Surfactant Solutions*; Marcel Dekker: New York, 1987; Vol. 22, p 241. (c) Mishra, B. K.; Valaulikar, B. S.; Kunjappu, J. T.; Manohar, C. *J. Colloid Interface Sci.* **1989**, *127*, 373.
(2) (a) Malliaris, A. *Adv. Colloid Interface Sci.* **1987**, *27*, 153. (b) Ranby, B. In *ESR Spectroscopy in Polymer Research*; Rabek, J. F., Ed.; Springer-Verlag: Berlin, 1977.
(3) (a) Somasundaran, P.; Kunjappu, J. T.; Kumar, C. V.; Turro, N. J.; Barton, C. V. *Langmuir* **1989**, *5*, 215. (b) Somasundaran, P.; Kunjappu, J. T. In *Innovations in Materials Processing Using Aqueous, Colloid and Surface Chemistry*; Doyle, F. M., Raghavan, S., Somasundaran, P., Warren, G. W., Eds.; The Minerals, Metals and Materials Society: Warrendale, PA, 1988; p 31.
(4) Kunjappu, J. T.; Somasundaran, P. *Colloids Surf.*, in press.
(5) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(6) Meisel, D.; Matheson, M. S.; Rabani, J. *J. Am. Chem. Soc.* **1978**, *100*, 117.
(7) Warr, G. G.; Greiser, F. *Chem. Phys. Lett.* **1985**, *116*, 505.
(8) Colaneri, M. J.; Kevan, L.; Schmehl, R. *J. Phys. Chem.* **1989**, *93*, 397.
(9) Havenstein, B. L., Jr.; Dressick, W. J.; Buell, S. L.; Demas, J. N.; Degraff, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 4251.
(10) Chandar, P.; Somasundaran, P.; Turro, N. J. *J. Colloid Interface Sci.* **1987**, *117*, 31.
(11) Somasundaran, P. Unpublished results.

0022-3654/90/2094-8464$02.50/0

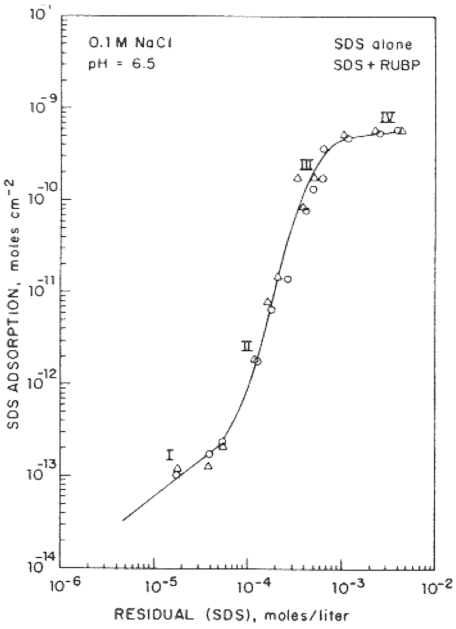

Figure 1. Adsorption isotherm of sodium dodecyl sulfate on alumina with and without $Ru(bpy)_3^{2+}$; pH = 6.5, [NaCl] = 10^{-1} M, and [$Ru(bpy)_3^{2+}$] = 5.3×10^{-5} M. (I, II, III, and IV are the different regions.)

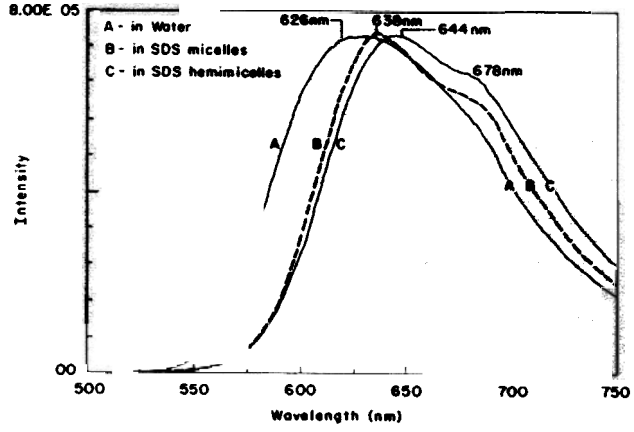

Figure 2. Emission spectra of $Ru(bpy)_3^{2+}$ in water (A), SDS micelles (B), and Al_2O_3/SDS hemimicelles (C); [NaCl] = 10^{-1} M and [$Ru(bpy)_3^{2+}$] = 5.3×10^{-5} M; [SDS] = 10^{-2} M in micelles; excitation wavelength = 450 nm. The intensities are normalized at the emission maxima of the samples.

centration is detailed elsewhere.[10]) The isotherm is not perturbed by the presence of the probe in the level used by us. This isotherm is characteristic of the adsorption of an anionic surfactant on oxide minerals, and the significance of inflections (regions I, II, III, and IV) in it has been interpreted earlier.[1a] Hemimicellization (surfactant aggregation on the solid) occurs at the first sharply increasing point (transition between I and II) of the isotherm, and the continued surfactant adsorption takes place up to region IV, which marks the onset of micellization in the bulk of aqueous phase. Different points in these regions were chosen for the quenching studies with ferrocyanide and 9-MA.

Figure 2 shows the emission spectra of $Ru(bpy)_3^{2+}$ in water, SDS micelles ([SDS] = 10^{-2} M), and Al_2O_3/SDS hemimicelles in region III. (In region IV, the probe partitions between micelles and hemimicelles.) The emission intensities are normalized at their maximum in each case. In fact, the emission intensity in the micellar case at its maximum was ~35% more than the aqueous case. It may be seen that the emission maxima and the spectra themselves shift to longer wavelengths in micelles and hemimicelles. The emission maxima in water, micelles, and hemimicelles are 626, 638, and 644 nm, respectively. It may be noted that the emission maxima reported in some of the earlier

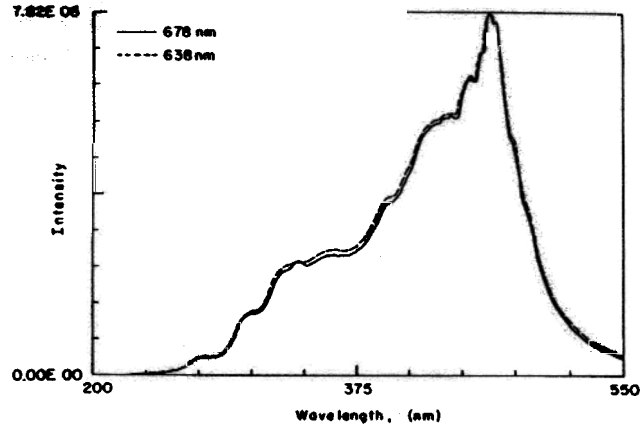

Figure 3. Excitation spectra (uncorrected) or $Ru(bpy)_3^{2+}$ in sodium dodecyl sulfate micelles at emission wavelengths of 638 nm (---) and 678 nm (—); [$Ru(bpy)_3^{2+}$] = 5.3×10^{-5} M; [SDS] = 10^{-2} M, [NaCl] = 10^{-1} M.

studies[6] in water and micelles were ~10 nm blue-shifted, probably due to differences in the correction factors applied. However, the nature of $Ru(bpy)_3^{2+}$ emission in hemimicelles is reported in detail for the first time.

One interesting aspect of the shifts in the maximum of the above spectra is that the probe senses a relatively more nonpolar environment in hemimicelles than in micelles. That a red shift in the emission maximum of the phosphorescent triplet state of the metal–ligand charge-transfer (MLCT, d transition) band of $Ru(bpy)_3^{2+}$ indicates a nonpolar environment is documented earlier.[6] Note that the micropolarities estimated earlier with pyrene, based on changes in the intensities of the vibrational fine structures (I_1 and I_3) in micelles and hemimicelles, yielded almost the same values.[10] This suggests the potential of $Ru(bpy)_3^{2+}$ as a reliable probe to monitor the changes in hemimicellar polarity.

We also performed experiments to determine the direct adsorption of $Ru(bpy)_3^{2+}$ on alumina from aqueous solution at different surface charges. The test samples were prepared at different pH values ranging from 4 to 10. The point of zero charge of the mineral falls around a pH value of ~8.5.[12] The observation that the probe did not adsorb directly on alumina even at negative ζ potentials indicates the importance of hydrophobic factors in its binding to hemimicelles also. The hemimicellar region chosen in the present study corresponded to negative ζ potential at the interface. One of our recent studies[4] had clearly shown that the binding of $Ru(bpy)_3^{2+}$ in hemimicelles takes place only after the aggregation process on the surface reaches somewhere around midway in region II (Figure 1). This observation has been considered to be supportive of the adsorption of some of the surfactant molecules in a reverse orientation on the already formed aggregates. This results in the development of negative charge on the aggregates, permitting the binding of the positively charged probe. It may be argued that the probe senses a more nonpolar environment in hemimicelles than in micelles, owing to the strong hydrophobic interaction among the tail groups of the surfactant molecules. High microviscosities in the hemimicelles as reported by us earlier also corroborate this observation.[13]

A further look at Figure 2 shows that the shifted emission spectra in micellar and hemimicellar cases exhibit a broad shoulder at ~678 nm. Such a distortion may be considered as a manifestation of the immobilization of the probe in surfactant aggregates. To test the possibility of more than one type of bound species being present in the above cases, the excitation spectra of $Ru(bpy)_3^{2+}$ were recorded at the emission maximum in each case and at 678 nm. The excitation spectra (uncorrected) in these cases did not show any significant difference. The excitation

(12) Somasundaran, P.; Fuerstenau, D. W. *J. Phys. Chem.* **1966**, *70*, 90.
(13) (a) Somasundaran, P.; Turro, N. J.; Chandar, P. *Colloids Surf.* **1986**, *20*, 145. (b) Waterman, K. C.; Turro, N. J.; Chandar, P.; Somasundaran, P. *J. Phys. Chem.* **1986**, *90*, 6830. (c) Chandar, P.; Somasundaran, P.; Waterman, K. C.; Turro, N. J. *J. Phys. Chem.* **1987**, *91*, 150.

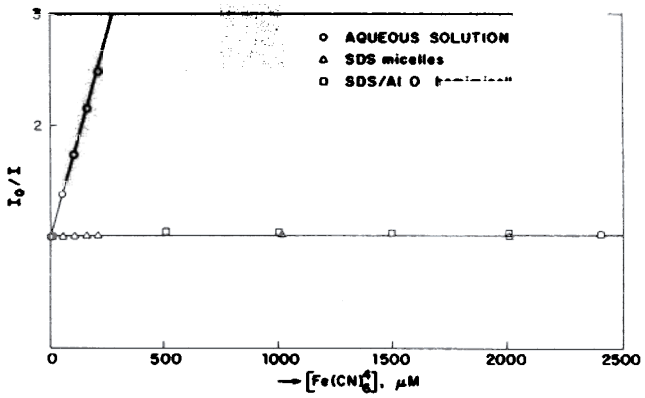

Figure 4. Stern–Volmer plot for the quenching of $Ru(bpy)_3^{2+}$ by ferrocyanide in (○) water, (△) SDS micelles, and (□) Al_2O_3/SDS hemimicelles; [NaCl] = 10^{-1} and $[Ru(bpy)_3^{2+}] = 5.3 \times 10^{-5}$ M; [SDS] = 10^{-2} M in micelles.

spectra are shown in Figure 3 for the micellar case. Even though the shoulder at 678 nm is more prominent in hemimicelles than in micelles, it does not suggest that $Ru(bpy)_3^{2+}$ is more strongly bound to hemimicelles than to micelles; in fact, at higher surfactant concentrations in the bulk, $Ru(bpy)_3^{2+}$ prefers to remain in the micellar phase than in the hemimicellar phase.[4]

It is possible that the probe, a positively charged species, may be bound to SDS micelles or to Al_2O_3/SDS hemimicelles as a counterion in the electric double layer. If it were so, the excited state of $Ru(bpy)_3^{2+}$ may be quenched by anionic ions like ferrocyanide. Protection from ferrocyanide quenching of the luminescence of ruthenium polypyridyl complexes in the bound state on DNA has been reported.[14] Figure 4 shows the Stern–Volmer plots for the quenching of $Ru(bpy)_3^{2+}$ by ferrocyanide in water, micelles, and hemimicelles. The Stern–Volmer constant for the ferrocyanide quenching in aerated aqueous 10^{-1} M NaCl solution is 7.4×10^3 dm^3 mol^{-1}. While efficient quenching was observed in aqueous solution, practically no quenching was observed in the micellar and hemimicellar cases. This reinforces the earlier suggestion that both the electrostatic and hydrophobic factors are important in the binding of this probe. It is interesting to note that the probe is embedded within the surfactant aggregates in the hemimicellar case as well. However, it may be argued that lack of ferrocyanide quenching alone cannot be taken as proof to conclude that the probe is not surface bound since the negatively charged quencher may be strongly repelled by the negative micelle surface. But, other evidences to follow tend to suggest that hydrophobic factors also have a decisive role in holding the probe in the aggregates. It was mentioned earlier that the probe did not adsorb directly on alumina even at negative ζ potentials.

$Ru(bpy)_3^{2+}$/9-MA is a donor–quencher pair demonstrated to be eminently suitable for determining the aggregation number of anionic surfactants in micellar solutions.[15] Though the same quenching method may not be successfully applied to determine the aggregation number of hemimicelles, the relative quenching efficiency can help test the location of $Ru(bpy)_3^{2+}$ in the hemimicellar aggregates. The location of aromatic hydrocarbons like pyrene and dinaphthylpropane in the hemimicellar case has been conjectured to be in its hydrophobic region.[10] The same argument may be extended to fix the position of 9-MA in hemimicelles. In a typical set of experiments, the probe and the quencher were incorporated in the hemimicellar aggregates at a fixed probe level of 2×10^{-5} M and varying quencher levels of 10^{-4}–10^{-5} M at an adsorption density of $\sim 10^{-11}$ mol cm^{-2} of SDS on alumina under the adsorption conditions described earlier.

The log (I_0/I) vs [quencher] plot yielded linearity for the hemimicellar case. The fluorescence intensity of 9-MA ($I_{391\ nm}$) was determined in each adsorption sample to ensure that the

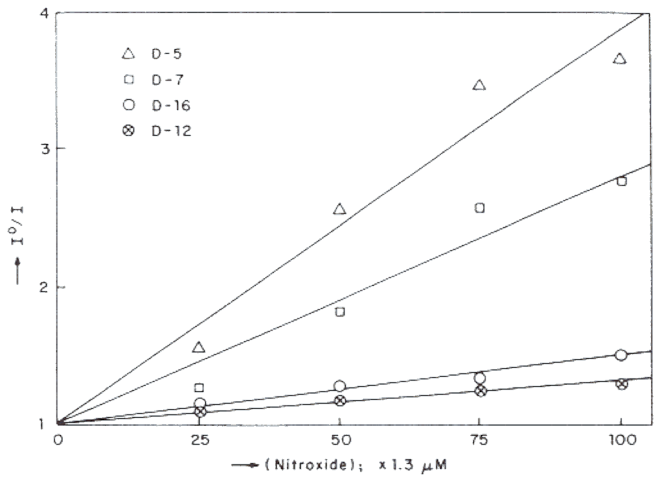

Figure 5. Stern–Volmer plot for the nitroxide quenching of $Ru(bpy)_3^{2+}$ by doxylstearic acids in aqueous solution; [NaCl] = 10^{-1} M and $[Ru(bpy)_3^{2+}] = 5.3 \times 10^{-5}$ M; [SDS] = 10^{-2} M.

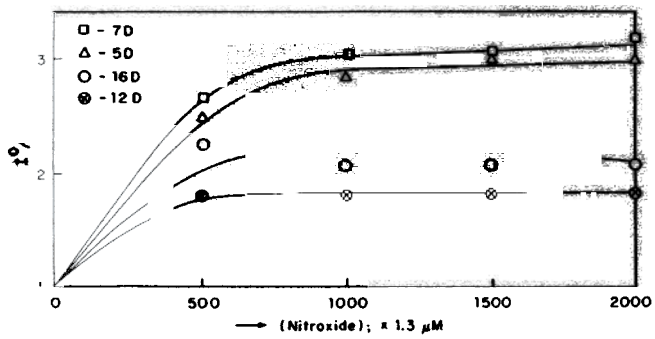

Figure 6. Stern–Volmer plot for the nitroxide quenching of $Ru(bpy)_3^{2+}$ by doxylstearic acids in SDS micelles; [NaCl] = 10^{-1} M, $[Ru(bpy)_3^{2+}] = 4 \times 10^{-6}$ M, and [SDS] = 10^{-2} M. At low concentration levels, there was a great degree of scatter in the experimental data for the quenching efficiency of all the four quenchers (not shown in the graph).

quencher is solubilized in the hemimicelles. The logarithmic dependence of the ratio of the luminescence intensities with quencher concentration is characteristic of the statistical distribution of the probe and the quencher molecules in hemimicelles. The ratio of luminescence intensities (I/I_0) with and without the quencher Q is related to the surface aggregate concentration M as

$$I/I_0 = \exp\{-[Q]/[M]\}$$

Here, the normal Stern–Volmer relation is no more valid. These results may be taken as a direct evidence to infer that the probe $Ru(bpy)_3^{2+}$ in hemimicellar aggregates also resides in the hydrophobic region. Attempts to calculate the aggregation number of hemimicelles from the $Ru(bpy)_3^{2+}$/9-MA quenching data resulted in its gross underestimation compared to the numbers reported from fluorescence lifetime studies with pyrene.[10] The aggregation number determined with $Ru(bpy)_3^{2+}$/9-MA was about 10–20, which is less by an order of magnitude than the solution case. Perhaps the assumptions concerning static quenching may not be fully applicable in the hemimicellar case; i.e., the rate constants for quenching and decay of luminescence of $Ru(bpy)_3^{2+}$ in micelles may be of comparable magnitude.

Another aspect of the localization problem of $Ru(bpy)_3^{2+}$ in micelles that is of consequence to the nature of its excited state is directed toward the distribution of excitation energy in the bipyridine rings. Insight into this may be obtained from quenching studies using fixed quencher centers on molecules similar to the surfactant itself. A number of isomeric doxylstearic acids (5-D, 7-D, 12-D, and 16-D) were chosen for this purpose. Such molecules can form mixed micelles with the surfactant. The quenching properties of these nitroxides were studied in aqueous and SDS micellar solutions: Figures 5 and 6 show the Stern–Volmer plots

(14) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518.
(15) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.

Figure 7. Visualization of doxylstearic acid molecule and $Ru(bpy)_3^{2+}$ in water. Note that the actual molecules contain only one doxyl group as substituent.

for the aqueous and micellar cases, respectively. The quenching behavior of these molecules in homogeneous solution itself seems to be interesting (Figure 5). The Stern–Volmer constants for 5-D, 7-D, 12-D, and 16-D cases in the aqueous case were 2.3×10^4, 1.4×10^4, 3.9×10^3, and 2.7×10^3 (±5%) $dm^3\ mol^{-1}\ s^{-1}$. The quenching efficiency in solution follows the order

$$5\text{-D} > 7\text{-D} > 16\text{-D} > 12\text{-D}$$

Such a sequence may be understandable by considering the probability for the close proximity between the positively charged probe and the carboxylic acid group (as is known in the case of methylviologen/poly(acrylic acid) system[16]) and the probability of folding of the long hydrocarbon chain. This may be visualized as shown in Figure 7. The bending of the hydrocarbon chain explains the reversal in the sequence of quenching efficiencies of 12-D and 16-D doxylstearic acids.

Quenching of $Ru(bpy)_3^{2+}$ by doxylstearic acids in SDS micelles (Figure 6) shows the order

$$7\text{-D} > 5\text{-D} > 16\text{-D} > 12\text{-D}$$

The Stern–Volmer constants for the above sequence are 3.1×10^3, 2.3×10^3, 1.6×10^3, and 1.4×10^3 (±5%) $dm^3\ mol^{-1}\ s^{-1}$, the slope being calculated from the tangents of individual curves. Although the quenching efficiency of the different nitroxides is different, saturation is reached at about the same quencher concentration in all the cases. Here also a reversal in the quenching efficiencies of 12-D and 16-D is observed, probably due to the same reasons noted earlier. In addition, there is a reversal in the quenching efficiencies of 5-D and 7-D. Such a sequence points to the closeness of the excited state of $Ru(bpy)_3^{2+}$ to the nitroxide group of the quencher molecule. A static rather than dynamic picture of the donor and quencher molecules in the aggregates is assumed to be valid in the interpretation of the quenching results. Even though the dynamic nature of the surfactants (both SDS and nitroxide quencher molecules) and the probe is associated with a definite micellar exit/entry ratio, this ratio may remain more or less the same for the quenching scenarios in the individual SDS/$Ru(bpy)_3^{2+}$/doxylstearic acid cases. In other words, the quenching rate constants should indicate a mean position between the excitation center in the probe and the nitroxide center of the quencher on a time-averaged basis. This leads us to the question of distribution of the excitation energy in the pyridine ring subsequent to the formation of the MLCT state.

The luminescent state of $Ru(bpy)_3^{2+}$ has been a subject of much controversy. Though various studies support models in which the optical electron is delocalized[17] or localized[18] in bipyridine rings, time-resolved resonance Raman[19] and picosecond luminescence[18] studies are in favor of a localization model. The localization model means that the optical electron in the charge-transfer state is strongly localized in a single ligand rather than distributed in all the three ligands equally. Quenching by nitroxide radical is shown to be predominated by the electron-exchange-induced intersystem crossing and/or vibrational deactivation mechanisms.[20] The former mechanism necessitates in complex formation between the excited state and the nitroxide doublet prior to quenching. The

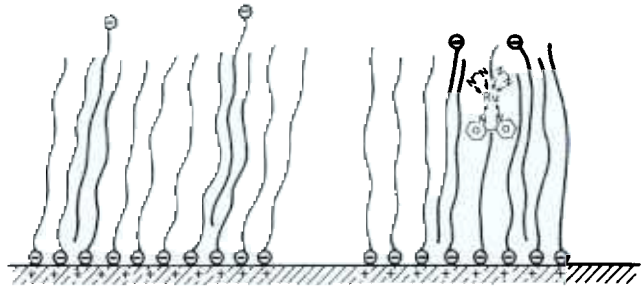

Figure 8. Visualization of the location of $Ru(bpy)_3^{2+}$ in Al_2O_3/SDS hemimicellar aggregate. The probe is incorporated in the hemimicelle after some of the surfactant molecules adsorb with a reverse orientation. (The molecular structures are not drawn to scale.)

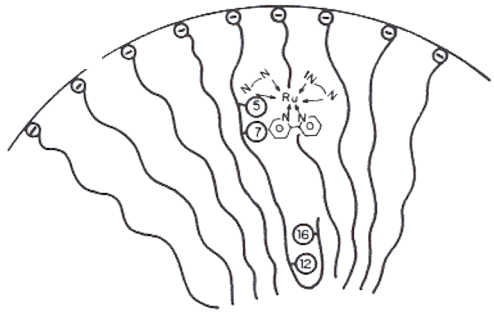

Figure 9. Visualization of $Ru(bpy)_3^{2+}$ and doxylstearic acid in SDS micelles. The MLCT state of the probe is assumed to be localized in the bipyridine ring that is close to position 7 of doxylstearic acid quencher. (The molecular structures are not drawn to scale.)

close proximity of the excited state with the quenching group would determine the ease of such a complex formation. In fact, an interaction distance of 4–6 Å is estimated to be necessary to attain diffusion-controlled quenching rates.[21] The quenching results described above imply that the excitation center in $Ru(bpy)_3^{2+}$ is close to position 7 of the alkyl chain of the stearic acid. A situation like this can be envisaged if a distorted ruthenium complex is assumed to be formed in the bound state such that a bipyridine ring "sees" position 7 of stearic acid closely. Evidently, this bipyridine ring of $Ru(bpy)_3^{2+}$ would be farther away from the negative micellar surface, and the localization of the negative electron must be strongly favored. It is debatable whether position 7 of stearic acid is the point of closest approach to the bipyridyl ring localizing the excited electron in the MLCT state of $Ru(bpy)_3^{2+}$, since we could not test the quenching efficiencies with other isomers with doxyl substituents between positions 8 and 11. However, the bimolecular quenching rate constant calculated for 7-D, assuming the luminescence lifetime value for $Ru(bpy)_3^{2+}$ in aerated solutions, approached diffusion-controlled limiting values. This suggests that the position 7 may be close to the excitation center in the ruthenium complex. Such an argument is also in line with recently published results[3a] from our laboratories in which we observed enhancement in intensity and shifts in frequencies of the excited-state resonance Raman spectrum of $Ru(bpy)_3^{2+}$ in SDS micelles relative to its aqueous spectra. It is believed that the changes in the total symmetry properties of the $Ru(bpy)_3^{2+}$ molecule, rather than the differences in the micropolarity and microviscosity of the medium, play a role in the observed spectral changes. The distorted bipyridine suggested in this case may also be like an earlier model proposed by Krenske et al.[22] for $Ru(bpy)_3^{2+}$ adsorption onto clay membranes where one of the pyridine rings of the bipyridine ring is assumed to be in a twisted state owing to the free rotation of the C–C bond joining the pyridine rings. The location of the probe in the hemimicelles and micelles may be represented as in Figures 8 and 9.

(16) Stramel, R. D.; Thomas, J. K. *J. Colloid Interface Sci.* **1986**, *110*, 121.
(17) Ferguson, J.; Herren, F. *Chem. Phys. Lett.* **1982**, *89*, 376.
(18) Krausz, E. *Chem. Phys. Lett.* **1985**, *116*, 501.
(19) (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (b) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.
(20) Green, II, J. A.; Singer, L. A.; Parks, J. H. *J. Chem. Phys.* **1973**, *58*, 2690.
(21) Bieri, V. G.; Wallach, D. F. H. *Biochim. Biophys. Acta* **1975**, *389*, 413.
(22) Krenske, D.; Abdo, S.; Van Damme, H.; Cruz, M.; Fripiat, J. J. *J. Phys. Chem.* **1980**, *84*, 2447.

In conclusion, while attempting to expose the location of the probe, $Ru(bpy)_3^{2+}$, in micellar and hemimicellar environments, our study has provided useful insights into the problem of localization of excitation energy itself. In general, the bound probe molecule resides within the surfactant aggregates rather than as counterions, in both micellar and hemimicellar cases.

Acknowledgment. The authors thank the National Science Foundation, the Department of Energy, and IBM for their financial support.

Registry No. SDS, 151-21-3; 5-D, 29545-48-0; 7-D, 40951-82-4; 12-D, 29545-47-9; 16-D, 53034-38-1; 9-MA, 779-02-2; $Ru(bpy)_3^{2+}$, 15158-62-0; Al_2O_3, 1344-28-1; ferrocyanide, 13408-63-4.