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Intramicellar Electron Transfer Quenching of Excited States. Determination of the Binding Constant and Exchange Rates for Dimethylviologen[1]

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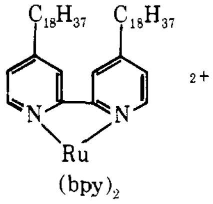
Abstract: The quenching of a water-insoluble surfactant analogue of $Ru(bpy)_3^{2+}$ by the dimethylviologen cation, DMV^{2+}, has been investigated in anionic (SDS) and cationic (CTAB) micelles. Quenching by DMV^{2+} in the former is much more effective than in homogeneous solutions; the converse is true for the latter. The quenching event in anionic micelles is dynamic and totally intramicellar. Analysis of the quenching data obtained for the SDS micelles provides an estimate for the binding constant of DMV^{2+} on the micellar surface as well as values for the rates of binding and dissociation. The rate of diffusion of the cationic DMV^{2+} on the surface of the anionic micelles has been determined to be similar to apparent intramicellar diffusional rates for quite different probes studied in several other systems.

Introduction

There has been much recent interest in excited-state phenomena occurring within organized assemblies such as micelles, vesicles, and monolayers in interfacial processes. In a number of cases recently, there has been emphasis on bimolecular processes where one or both of the substrates participating in a photoprocess is sequestered in a micelle.[2-7] In this paper a luminescent surfactant ruthenium complex is used to examine the exchange of a divalent cation with a monovalent cation on the surface of sodium dodecyl sulfate micelles by examining quenching of the luminescent probe by the divalent ion. In the present case, exchange of the dication is much faster than the rate of luminescence decay of the excited probe.

A number of kinetic expressions have been developed to describe excited state quenching processes in which both the excited species and the quencher are at least partially associated with the micelle.[8-11] In cases where both the excited complex and quencher are exclusively bound to the micelle (and the quencher is nonionic), a Poisson distribution of the quenching species results.[12] The luminescence decay observed in such cases is multiexponential and consists of components of emission from excited states in micelles containing varying numbers of quenchers. The decay at long times becomes a single exponential and corresponds to emission of the unquenched complex. A second case occurs where the quencher is partially water solubilized. In this case, multiexponential decay is also observed but the decay at long times corresponds to the emission of the complex partially quenched by the water-solubilized quencher. The kinetic analyses of these cases have been examined in detail by several groups.[8,9,13] In cases where the quenching species is ionic and the luminescent probe is micelle solubilized, results similar to those obtained for nonionic quenchers are obtained when the rate of exchange of quenchers in the Stern layer is slow on the time scale of the experiment. Several groups have examined the quenching of pyrene fluorescence by ionic quenchers in both cationic and anionic micelles.[14,15] In the present paper we examine the quenching of the surfactant ruthenium complex **1** with the dimethylviologen dication, DMV^{2+}, in both cationic and anionic micelles. Of particular interest is our finding that the exchange of DMV^{2+} is very rapid relative to the rate of decay of the excited state of **1**. A comparison of our results with those of others allows an estimation of the exchange rate of the dication with the monocationic sodium ion. We have also estimated an equilibrium constant for the exchange of DMV^{2+} with Na^+ on the micelle surface. Further, the Stern-Volmer quenching constant obtained provides a picture of the diffusional rate over the micelle surface and is compared to values obtained by others for intramicellar diffusional rates.



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Experimental Section

The sodium dodecyl sulfate used (Aldrich) was purified by Soxhlet extraction with hexane for 25 h to remove dodecanol followed by crystallization from acetone/water (95/5). Cetyltrimethylammonium bromide (Aldrich) was twice recrystallized from acetone. The

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Table I. Quenching of the Luminescence of **1** in Various Media

medium	μ	obsd quenching constant	
		I^0/I	τ_0/τ
CH_3CN	0.20	260	
0.024 M SDS	0.20	2403	2250
0.024 M SDS	0.10	2950	
0.036 M SDS	0.20	1540	1300
0.042 M SDS	0.20	1170	1000
0.00125 M CTAB	0.20	<1	

ruthenium complex was generously provided by Dr. W. H. F. Sasse and was pure by LC. Sodium chloride (Fisher Certified) and dimethylviologen dichloride (Aldrich) were used as received. Water was triply distilled as described previously.[32]

Micellar solutions were prepared by sonication (Branson sonicator, 80 W) of the solid complex **1** in the aqueous detergent solution for 20–30 min; samples were then centrifuged on a desk top centrifuge for 15 min. When detergent concentrations below the cmc were used, centrifugation of sonicated solutions resulted in the precipitation of most of the complex **1**. At concentrations of surfactant greater than the cmc concentrations of **1** of approximately 10^{-5} M were obtained in CTAB; in SDS concentrations of **1** greater than 5×10^{-5} M were obtained with no precipitation occurring.

Steady-state luminescence was measured using an MPF-2A spectrofluorimeter including a Hamamatsu R-446 red-sensitive photomultiplier. Both aerated and FPT degassed samples were used in the quenching experiments and results obtained by both methods agreed within 3%.

Transient measurements were made using a Molectron 400 nitrogen laser (337 nm) of pulse width 8 ns as the excitation source. Emission was measured at right angles; photomultiplier output was input into a Tektronix 7A26 (20 MHz) vertical amplifier of the Tektronix 7912 transient digitizier. The digitizer was interfaced to a PDP-11 computer which stored the output signal. Each sample represented the average signal of 80 pulses.

Results and Discussion

The complex **1** proved to be completely insoluble in water in the absence of surfactant and did not significantly offset the critical micelle concentration of either surfactant. Solubilization of **1** into both sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) micelles was accomplished by sonicating a suspension of the solid complex in the micellar solution for 15–25 min. Only a small amount of the complex could be incorporated into CTAB solutions; a concentration of **1** of approximately 10^{-5} M was obtained in 7.5×10^{-4} M micelles (cmc = 0.000 25 M, $\bar{n}$ = 95).[16] A variety of SDS concentrations were studied ranging from 2.5×10^{-4} to 4.5×10^{-4} in micelles (cmc = 0.008, $\bar{n}$ = 65 at μ = 0.20);[17] the concentration of **1** in all the SDS solutions was 1.50×10^{-5} M. A small increase in the aggregation number with increasing surfactant concentration has been observed for SDS;[18] we have assumed this variation to be negligible.

In the cationic micelles the charge transfer absorption band of the complex was red shifted by *20* nm relative to acetonitrile solution. The emission spectrum was unaffected by the change in environment. Solutions of **1** solubilized in SDS have absorption and emission spectra very similar to those in acetonitrile. The emission lifetime does not vary significantly for a variety of solutions containing different surfactant concentrations, indicating that no self-quenching of the complex is occurring.

Intensity quenching of the luminescence of **1** by DMV^{2+} was found to follow approximate Stern–Volmer relationships in homogeneous solution and both aqueous detergents; Table I gives the Stern–Volmer constants. Owing to Coulombic repulsion the DMV^{2+} is almost certainly not bound to the cationic micelles; the low K_{SV} also reflects a Coulombic barrier lowering the quenching rate constant by two orders of magnitude. The reduction in quenching efficiency in these micelles may be compared to the "hydrophobic effect" produced by surrounding the $Ru(bpy)_3{}^{2+}$ chromophore with large alkyl groups.[19] In contrast the effective quenching ability of DMV^{2+} is greatly enhanced when **1** is bound in anionic micelles. The observed Stern–Volmer quenching constant obtained, however, is dependent upon both the surfactant concentration and the ionic strength. Increases in surfactant concentration lead to decreases in the quenching constant indicating that micelle-bound DMV^{2+} participates in the quenching process. Indeed a plot of I^0/I vs. quenchers/micelle (Figure 1) shows that the data fall very nearly on a single line in which the points correlate well independent of surfactant concentration. An increase in salt concentration leads to rather dramatic decreases in K_{SV} and demonstrates that the quenching species competes with sodium ions for binding sites available at the micelle surface.

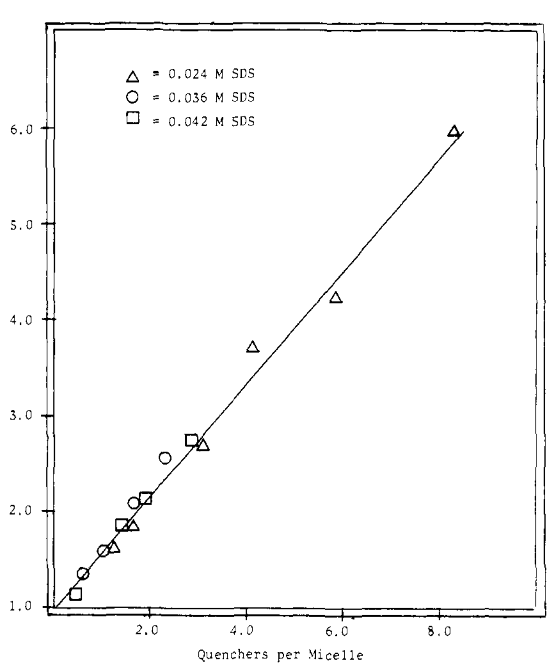

Figure 1. Emission quenching of **1** vs. the average number of DMV^{2+} molecules per micelle for 2.0×10^{-5} M **1** and 0.024 M SDS (△), 0.036 M SDS (○), and 0.042 M SDS (□).

Stern–Volmer constants obtained by transient methods are only slightly lower (12%) than those obtained in steady-state experiments and indicate that, although there may be a small amount of static quenching, the primary quenching process is dynamic in nature (Table I). In Figure 2 semilogarithmic transient decay plots of the luminescence of **1** both in the absence and presence of DMV^{2+} are shown. As can be seen, the transient decay of partially quenched samples is clearly monoexponential. This is the case for quencher concentrations between 0.2 and 2 mM. Thus the DMV^{2+} must be binding and dissociating from the micelle at a rate rapid relative to the rate of decay of the excited state of **1** (1.5×10^6 s^{-1}). It is interesting to note that biexponential decay of luminescence is observed in the quenching of pyrene fluorescence by DMV^{2+} in SDS where the decay rate of pyrene singlets is 5.6×10^6 s^{-1}.[14] Since both the steady-state and transient experiments yield Stern–Volmer quenching constants that are similar and the transient decay is monoexponential, the quenching must be occurring by a dynamic process.

Scheme I represents the events leading to and competing with the quenching event. Initially an equilibrium is established between micelle-bound and water-solubilized DMV^{2+}. Since the rate of dissociation is greater than the sum of the rates of radiative and nonradiative decay for the complex **1**, the number of quencher molecules per micelle corresponds to the average number, $[DMV_b{}^{2+}]/[\text{micelle}]$, on the time scale of this experiment and does not appear as a statistical distribution over

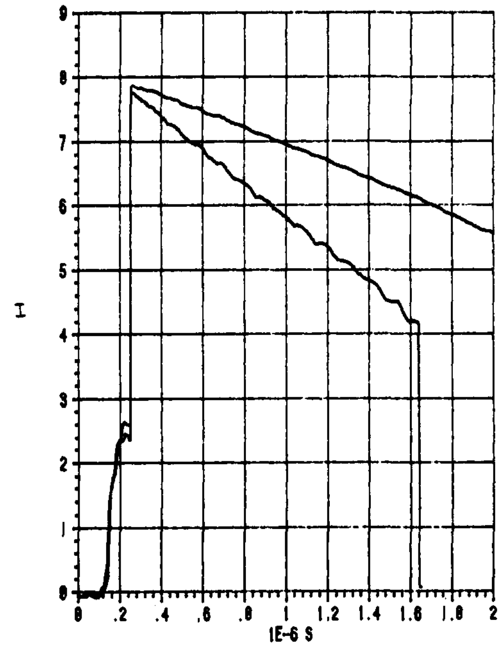

Figure 2. Semilogarithmic emission decay of **1** in the presence and absence of quencher: 0.036 M SDS; upper line; 0.036 M SDS and 5.0×10^{-4} M DMV^{2+}, lower line.

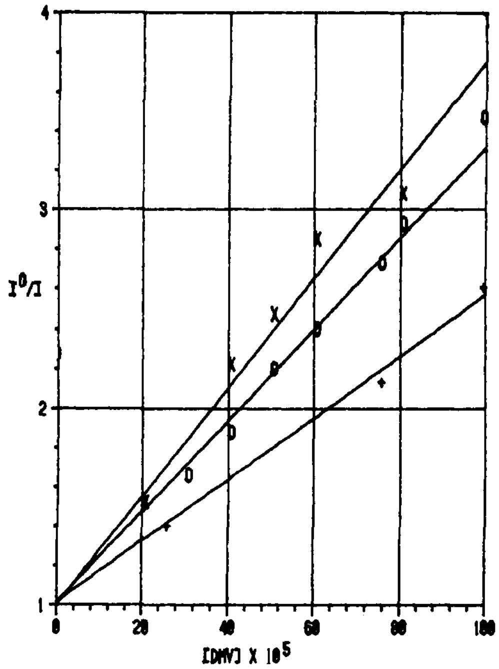

Figure 3. Emission quenching of **1** vs. DMV^{2+} concentration: (+), 0.036 M SDS and μ = 0.20; (O) 0.024 M SDS and μ = 0.20; (×) 0.024 M SDS and μ = 0.10. Solid lines represent quenching calculated from eq 3.

Scheme I

$$2n\mathrm{Na_b}^+ \; n\mathrm{DMV_{aq}}^{2+} \underset{K_b}{\overset{K_f}{\rightleftarrows}} n\mathrm{DMV_b}^{2+} + 2n\mathrm{Na_{aq}}^+ \tag{1}$$

$$\mathrm{Ru}^{2+}, \mathrm{M}, n\mathrm{DMV}^{2+} \xrightarrow{h\nu} \mathrm{Ru}^{2+*}, \mathrm{M}, n\mathrm{DMV}^{2+} \tag{2}$$

$$\mathrm{Ru}^{2+*}, \mathrm{M}, n\mathrm{DMV}^{2+} \xrightarrow{k_d + k_r} \mathrm{Ru}^{2+}, \mathrm{M}, n\mathrm{DMV}^{2+} + \Delta + h\nu \tag{3}$$

$$\mathrm{Ru}^{2+*}, \mathrm{M}, n\mathrm{DMV}^{2+} \xrightarrow{k_q} \mathrm{Ru}^{3+}, \mathrm{M}, \mathrm{DMV}^{+}, (n-1)\,\mathrm{DMV}^{2+} \tag{4}$$

the micelles. Rapid exchange rates have been observed for monoanionic species (Br^-, I^-, NO_3^-, Cl^-, OH^-) in CTAB micelles and pyrene triplets exhibit single exponential decay even when the quenching ion is bound at $t = 0$.[20]

The decay of the luminescence of **1** may be described by assuming that the concentration of quencher equals the concentration of bound DMV^{2+} in the total micellar volume, $[DMV_b]$ (not the solution volume).[21] Simple kinetic analysis leads to the expression below for the decay of **1** excited states in the presence of DMV^{2+}.

$$[\mathrm{Ru}^{2+*}](t) = [\mathrm{Ru}^{2+*}](0)\exp[-(K_f + K_d + K_q[\mathrm{DMV_b}])t] \tag{5}$$

The expression is very simple compared to luminescence decay expressions derived for other similar systems where a statistical distribution of quenchers is required.[8]

To determine the concentration of bound DMV^{2+}, an evaluation of the initial equilibrium (eq 1) of Scheme I is required. If one assumes that the concentration of bound DMV^{2+} is small relative to the total concentration of associated surfactant, an approximation of the total concentration of bound DMV^{2+} may be derived.[25]

$$[\mathrm{DMV_b}^{2+}] = K_{eq}/(K_{eq} + N^2) \tag{6}$$

$$\text{where} \quad (N)^2 = \left(\frac{\mathrm{Na_{aq}}}{\mathrm{Na_b}}\right)^2 \approx \left(\frac{\alpha C_D + \mathrm{cmc} + [\mathrm{NaCl}]}{(1-\alpha)C_D}\right)^2 \tag{7}$$

In the above expression for $(N)^2$, α represents the concentration of surfactant that is dissociated in solution, C_D is the concentration of micellized surfactant, and cmc is the critical micelle concentration. The steady-state Stern–Volmer type expression obtained for the case where the DMV^{2+} concentration is the concentration of quencher in the total volume of micelles[21] as in solution is given below.

$$I^0/I = 1 + k_{sv}[\mathrm{DMV_b}] = 1 + \left[\frac{K_{eq}}{(K_{eq} + N^2)\,C_D\bar{V}}\right][\mathrm{DMV_t}^{2+}] \tag{8}$$

Here the term $1/C_D\bar{V}$ represents the micellar volume[23] and DMV_T^{2+} is the analytical quencher concentration. The slope of a plot of I^0/I vs. $[DMV_T^{2+}]$ has K_{SV} and K_{eq} as variables. The value of K_{eq} may be determined by solving simultaneous equations from the slopes at two different salt concentrations. Table II lists the K_{eq} values obtained from the slopes of the Stern–Volmer (S–V) plots of the salt concentrations examined in 0.024 M SDS. It should be noted that, although K_{eq} may be determined by varying the surfactant concentration at constant ionic strength, small changes in the value of the observed Stern–Volmer slopes result in very large changes in K_{eq}.

The fraction of DMV^{2+} bound to the micelle at any surfactant concentration may be determined given the value of K_{eq} and is simply equal to $K_{eq}/(K_{eq} + N^2)$. For the various surfactant concentrations examined in 0.2 M salt the fractions are 0.77 (0.024 M), 0.91 (0.036 M), and 0.94 (0.042 M) assuming that $K_{eq} = 914$. Thus in Figure 1 the data all appear to fall very nearly on a single line even when it is assumed that all the DMV^{2+} is bound to the micelles.

The second-order k_{SV} can be calculated from the observed slope and the binding constant of DMV^{2+}. The average value obtained using 914 as K_{eq} was $11.93 \pm 0.82\ M^{-1}$. Figure 3 shows the correlation between the experimental points and the derived expression (8) using $K_{eq} = 914$ and $k_{SV} = 11.9\ M^{-1}$. The second-order quenching constant k_q has a value of $1.5 \times 10^7\ M^{-1}\ s^{-1}$ and represents the intramicellar diffusion and quenching events.[26]

As noted earlier, the exchange rate of the DMV^{2+} species with the micelles must be greater than $1.5 \times 10^6\ M^{-2}\ s^{-1}$. This corresponds to k_b (Scheme I) and, since K_{eq} is known, limits for the rate of association k_f can be estimated to be between

Table II. Values of K_{eq} Determined from Observed Quenching Constants

	[SDS]	μ	$(N)^2$	k_{obsd}	$K_{eq}{}^a$
1	0.024	0.05	23	3064	1016 (1,2)
2	0.024	0.10	75	2918	844 (2,3)
3	0.024	0.20	272	2403	882 (1,3)

[a] The average value obtained, 914 ± 90, was used in other calculations.

1.18 and 5.12 $M^{-2}\ s^{-1} \times 10^9\ M^{-2}\ s^{-1}$. This is close to the diffusion-controlled rate (1.1×10^{10}) and is certainly reasonable given our results. Rates of entry and exit have been determined for diiodomethane in SDS and are somewhat faster than those for the DMV^{2+} dication. The association constant for diiodomethane is approximately three times that for DMV^{2+}.[27] The much higher association constant is to be expected for the reasonably hydrophobic diiodomethane which resides almost exclusively in the micellar medium.

In summary we have shown that the quenching behavior clearly shows that both the quencher and the substrate, **1**, reside at the micelle surface and that all the quenching occurs by bound quenchers. However, at the same time, the quencher is rapidly exchanging such that all excited substrate molecules have the same possibility of being quenched and a nonstatistical approach is justified. It is certainly reasonable that in other systems employing either neutral water-soluble organic quenchers or soluble quenchers having charges opposite to the surfactant[20] similar behavior should obtain. Since our results indicate that only bound DMV^{2+} is quenching the excited state of **1**, the Stern–Volmer constant for the quenching of **1** by DMV^{2+} is analogous to the quenching constant obtained in homogeneous solution; in the micellar case the total solution volume is the volume of micelles in the bulk solution. One important aspect of reactions occurring in micellar systems is the question of diffusion in different regions, particularly in the core or on the surface. Several studies have used intramicellar luminescence quenching in attempts to define diffusion–viscosity relationships within the micelle and it is worthwhile to examine results of the present study in this context. The quenching of analogous ruthenium complexes by DMV^{2+} in solution has been shown to occur primarily by electron transfer; from this it may be assumed that the process occurs by either (1) tunnelling, (2) diffusion or hopping on the surface of the micelle, or (3) desorption of DMV^{2+} followed by resorption at a site close enough to the Ru^{2+*} center for electron transfer to occur. A diffusional mechanism seems most reasonable in this case. In order to compare the k_q obtained here with values determined with other substrate–quencher combinations it must be considered that the k_q measured can be regarded as a product of some diffusional or hopping rate, k_{diff}, and the probability that quenching will occur once close proximity is attained. From solution studies we can infer that the probability of quenching in a nonviscous solvent is about 2%; however, it could be argued that in the micellar media a somewhat higher value might be expected for the probability since the resonance time for encounter of **1** and DMV^{2+} may increase in the anionic environment of the micelle. The maximum value of 1 for the probability of electron transfer would indicate that the intramicellar diffusional rate equals the quenching rate of $1.5 \times 10^7\ M^{-1}\ s^{-1}$. However, recent findings of Meisel et al. indicate that for $Ru(bpy)_3{}^{2+}$ quenching by $Cu^{2+}{}_{aq}$ in a poly(vinyl sulfate) potential field the quenching process is directly analogous to that occurring in homogeneous solution.[29] Thus, assuming a probability of 2%, a diffusional rate constant of $7.5 \times 10^8\ M^{-1}\ s^{-1}$ is obtained, which is reasonably close to those obtained ($1.9 \times 10^8\ M^{-1}\ s^{-1}$, Singer;[11] $1.2 \times 10^8\ M^{-1}\ s^{-1}$, Thomas[28]) for quite different probes. Since the apparent rate constant obtained in the present case, where the diffusion is clearly on the surface, is similar to the other values, it is tempting to conclude that the other values also indicate diffusion over the surface of the aggregate and not through the interior. Thus this finding lends further support to much recent evidence which seems to indicate that probe molecules solubilized in micelles reside on or near the surface of the aggregate.[30,31]

In conclusion, the above-described system allows for an analysis of the rate of association and dissociation of an ionic species with the curved potential field of oppositely charged micellar surface. Further, the diffusional rate of the Stern region that is obtained is very close to other rates obtained in which the position of both the substrate and/or quencher could not be clearly defined, suggesting that other results may also reflect surface diffusion rather than bulk micellar diffusion.

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