Bimolecular Electron Transfer Quenching of Neutral *Ru(phen)$_2$bps by 4,4′-Diheptyl Viologen in Water and Bound to SDS Micelles

James W. Hackett II and Claudia Turro*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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A donor/acceptor system was designed to measure the bimolecular electron transfer (ET) rate constant from a donor in the aqueous phase to an acceptor anchored to the micellar surface utilizing a simple kinetic formalism. In this system, the donor, Ru(phen)$_2$bps (phen = 1,10-phenanthroline, bps = disulfonated 4,7-diphenyl-1,10-phenanthroline), possesses an overall zero charge and does not associate with anionic or neutral surfactants, whereas the $C_7C_7V^{2+}$ (1,1′-diheptyl 4,4′-viologen) acceptor is anchored to the micellar surface through the heptyl chains. In water, the formation of a ground-state aggregate between Ru(phen)$_2$bps and $C_7C_7V^{2+}$ results in biexponential decay of the emission of the probe in the presence of quencher. The bimolecular quenching of Ru(phen)$_2$bps by $C_7C_7V^{2+}$ takes place with $k_q = 3.0 \times 10^9$ M^{-1} s^{-1}, in agreement with that measured for the related $C_1C_1V^{2+}$ (methyl viologen) 4.8×10^9 M^{-1} s^{-1}, where no aggregation was observed. Within the Ru(phen)$_2$bps−$C_7C_7V^{2+}$ aggregate the excited state of the complex is quenched with a rate of $\sim 6.3 \times 10^6$ s^{-1}. The emission decay of *Ru(phen)$_2$bps remains monoexponential in the presence of anionic SDS (sodium dodecyl sulfate) micelles, but becomes biexponential upon addition of $C_7C_7V^{2+}$. The short- and long-lifetime components have been interpreted as the reaction of aqueous *Ru(phen)$_2$bps with $C_7C_7V^{2+}$ either residing in the aqueous phase or bound to SDS ($k_q = 8.0 \times 10^7$ M^{-1} s^{-1}). The bimolecular quenching by $C_7C_7V^{2+}$ bound to the surface of SDS micelles is $\sim$ 30 times slower than in water and bound to neutral C12E8 (*n*-dodecyl octaoxyethylene glycol monoether) micelles (2.6×10^9 M^{-1} s^{-1}). Several possible explanations for the difference in the observed rates when the acceptor is bound to the SDS micellar surface are provided.

Introduction

Electron-transfer (ET) reactions in ionic microheterogeneous media,[1−3] such as micelles,[4−8] vesicles,[9−13] polymers,[14−17] starburst dendrimers,[18−20] and DNA,[21−23] have been widely investigated owing to their structural similarity to those encountered in biological assemblies and for potential use in energy conversion and storage schemes.[1−3] In the micellar systems investigated to date, either both reactants are bound to the micelle or one of the reactants possesses the same charge as the micelle surface, thus remaining in the aqueous phase.[1−8] In the latter, the repulsion between the charged reactant and the micellar surface results in slow diffusion for the formation of a reactive complex, and typically any observed redox products stem from the reaction of donor and acceptor in the aqueous phase.[24,25]

Several treatments have been developed to fit the observed kinetics when both reactants are bound to the micelle that take into account the mobility of the probe, that of the nonemissive quencher, or both.[26,27] Since the rates at which the donor and acceptor exchange with the medium are unknown, they are included as variables in the kinetic equations derived to fit the emissive decay, along with the lifetime of the probe, the quenching rate constant, and average number of quenchers per micelle.[26,27] The quenching rate constants obtained in this manner are independent of quencher concentration and are believed to be related to the mobility of the reactants along the micellar surface.[18,19c] Although this type of treatment has been widely utilized, the number of extraneous unknown variables makes it impractical to obtain information on the electron-transfer process derived from the quenching rate constants. Chemical systems can be designed to probe the role of the micelle on the ET reaction, where the decay of the probe can be fit to simpler models that provide the desired information without the inclusion of unknown variables.

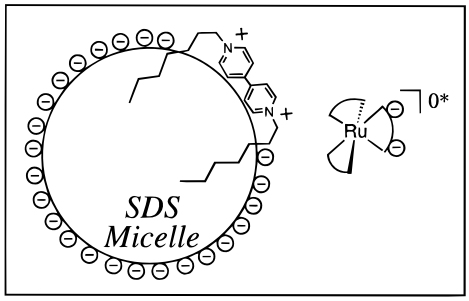

Figure 1. Schematic representation of $C_7C_7V^{2+}$ bound to an anionic SDS micelle and Ru(phen)$_2$bps in the aqeous phase.

To this end, we have designed a system aimed at obtaining electron transfer quenching rate constants at the micellar surface without the use of the complex equations discussed above. In addition, the role of electrostatic repulsion and attraction by the excited electron donor to the micellar surface and to the acceptor have been minimized through the use of a neutral Ru(II) complex. The positions of the donor and acceptor are shown in Figure 1, where the highly water soluble excited-state electron donor, *Ru(phen)$_2$bps (phen = 10-phenanthroline, bps = disulfonated 4,7-diphenyl-1,10-phenanthroline), resides in the aqueous phase and possesses overall zero charge. The electron acceptor, $C_7C_7V^{2+}$ (1,1′-diheptyl-4,4′-bipyridinium), is expected

* To whom correspondence should be addressed.

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to be anchored to the hydrophobic interior of micelle through its heptyl chains, with its charged redox-active group at the anionic SDS (sodium dodecyl sulfate) or neutral C12E8 (*n*-dodecyl octaoxyethylene glycol monoether) surface.[28] The electron transfer takes place from the triplet metal-to-ligand charge transfer (MLCT) excited state of Ru(phen)$_2$bps in the aqueous phase to the micelle-bound $C_7C_7V^{2+}$. In the system shown in Figure 1, the simpler Stern−Volmer treatment has been utilized to determine quenching rate constants, since the donor does not associate with SDS micelles and the acceptor remains bound to the micelle during the lifetime of the probe.

Experimental Section

Materials. The ligands 1,10-phenanthroline (phen) and disulfonated 4,7-diphenyl-1,10-phenanthroline (bps), as well as $RuCl_3$ and sodium dodecyl sulfate (SDS), were purchased from Aldrich. Dodecyl trimethylammonium bromide (DTAB) and *n*-dodecyl octaoxyethylene glycol monoether (C12E8) were purchased from Sigma and were used without further purification. 1,1′-Diheptyl-4,4′-bipyridinium ($C_7C_7V^{2+}$) dibromide was purchased from Aldrich, and its tetrafluoroborate salt was prepared by precipitation and filtration of AgBr from methanol upon addition of $AgBF_4$. Any remaining Ag^+ was precipitated by gradual addition of NaCl dissolved in methanol, followed by removal of AgCl by filtration. All quenching experiments reported in this work were performed with the BF_4^- salt. Ru(phen)$_2$bps was prepared from the reaction of Ru(phen)$_2$Cl$_2$ with bps ligand as described in detail previously.[29]

Methods. All solutions were bubbled with nitrogen for 5 min immediately prior to data collection, and each measurement was conducted with a fresh solution. Owing to the propensity of micellar solutions to form bubbles during the deoxygenation procedure, a quartz cell with a large reservoir and a stopcock was utilized, where the bubbles either dissipated or were able to expand without flowing out of the vessel. In the experiments performed here the micelle concentration was kept constant as quencher was added. However, the ratio of quencher to micelle[30] concentrations did not exceed 1.5, in an effort to minimize the disruption to the micellar system by the presence of bound viologens.

Instrumentation. Absorption measurements were performed in a Hewlett-Packard diode array spectrometer (HP 8453) with HP8453Win System software installed in an HP Vectra XM 5/120 desktop computer. Emission spectra were collected on a SPEX FluoroMax-2 spectrometer equipped with a 150 W xenon source, a red-sensitive R928P photomultiplier tube, and DataMax-Std software on a Pentium microprocessor. The decay of the emission was measured following sample excitation with the 532 nm output from a frequency-doubled Spectra-Physics GCR-150-10 Nd:YAG laser (fwhm ∼ 10 ns, 3 mJ/pulse). The emission was collected through a 570 nm cutoff filter (Oriel OG-570), collimated, and focused with two fused silica plano-convex lenses (*f*/4, 1 in. diameter) into the entrance slit of a Spex H-20 single monochromator (1200 gr/mm grating blazed at 500 nm). The luminescence was detected utilizing a Hamamatsu R928 photomultiplier tube powered by a Stanford Research PS325 power supply; the signal was digitized on a Tektronics 400 MHz oscilloscope (TDS 380). A PowerMac 7600/132 (Apple) equipped with a National Instruments GPIB interface (NI-488.2) and a National Instruments data acquisition board (PCI-1200) was programmed with LabView 4.1 software to control the data acquisition by the oscilloscope and the PMT voltage. The fits of the data were performed utilizing Kaleidagraph plotting software. Attenuated scattered laser light yielded an overall instrument response function with fwhm = 12.5 ns.

Results and Discussion

Photophysical Properties of Ru(phen)$_2$bps. The absorption spectrum of Ru(phen)$_2$bps in water is similar to that recorded for related Ru(II) complexes with maxima (molar extinction coefficient) at 265 nm (62 900 M^{-1} cm^{-1}), 277 nm (sh), 423 nm (10 100 M^{-1} cm^{-1}), and 430 nm (10 500 M^{-1} cm^{-1}), where the 265 nm peak and the shoulder at 277 nm correspond to the ligand-centered (LC) $\pi\pi^*$ transitions of phen and bps, respectively.[31,32] The broad absorption in the 400−450 nm range is attributed to metal-to-ligand charge transfer (MLCT) transitions from Ru(II) to phen and bps. The emission of Ru(phen)$_2$bps possesses a maximum, λ_{em}, at 626 nm in water and decays monoexponentially with a lifetime, τ, of 4.6 μs at 20 °C. Comparison of the emission properties of Ru(phen)$_2$bps to those of Ru(phen)$_3^{2+}$ (λ_{em} = 606 nm, τ = 1.1 μs) and Ru(bps)$_3^{4-}$ (λ_{em} = 629 nm, τ = 4.6 μs) leads to the conclusion that the emission in Ru(phen)$_2$bps stems from the lower-lying Ru → bps MLCT state.[29] This finding is in agreement with that observed for other mixed-ligand complexes of Ru(II).[33]

The maximum and intensity of the Ru(phen)$_2$bps emission and absorption do not change significantly in the presence of premicellar and micellar concentrations of the anionic SDS and neutral C12E8 surfactants at a given temperature, consistent with little or no interaction between the complex and the micelles.[29] However, changes in the absorption and emission characteristics of the complex with cationic DTAB surfactant (DTAB = dodecyltrimethylamonium bromide) at premicellar concentrations (0.05−10 mM) was observed, indicative of ground-state association. From a comparison of the results obtained with the neutral Ru(phen)$_2$bps to those of charged Ru(II) complexes in the presence of micelles, it was recently concluded that the bps ligand makes the complex very hydrophilic.[29] This property, in addition to the overall zero charge, aids in keeping Ru(phen)$_2$bps in the aqueous phase, without significant association to the anionic SDS or neutral C12E8 micelles.

Quenching of Ru(phen)$_2$bps by $C_7C_7V^{2+}$. *Water.* The emission intensity and lifetime of the MLCT excited state of Ru(phen)$_2$bps are efficiently quenched by the electron acceptor methyl viologen ($C_1C_1V^{2+}$) and the related 1,1′-diheptyl-4,4′-bipyridinium ($C_7C_7V^{2+}$) in water and in the presence of various concentrations of NaCl and Na_2SO_4. The driving force, ΔG, for the electron transfer from the MLCT excited state of Ru(phen)$_2$bps to $C_7C_7V^{2+}$ is −0.42 V, calculated utilizing $E_{1/2}(Ru^{III/II*}) = -0.83$ V vs NHE and $E_{1/2}(C_7C_7V^{2+/+\bullet}) = -0.41$ V vs NHE with BF_4^- as the counterion.[34] The excited-state oxidation potential of Ru(phen)$_2$bps was estimated from the complex's excited-state energy, $E_{00} \sim 2.1$ eV, and the measured ground-state oxidation potential, $E_{1/2}(Ru^{III/II}) = +1.27$ V vs NHE.[35]

Upon addition of $C_7C_7V^{2+}$ to aqueous solutions of Ru(phen)$_2$bps, the emission decay becomes biexponential, with a short-lifetime component whose percent contribution increases with increasing $C_7C_7V^{2+}$ concentration. The measured lifetimes and their percent contributions to the total emission are listed in Table 1, where the short-lifetime component accounts for 5%−65% of the total emission from 0.25 to 0.88 mM $C_7C_7V^{2+}$ in water. Such biexponential decays were not observed upon addition of $C_1C_1V^{2+}$, where the emission decay of the complex remained monoexponential.

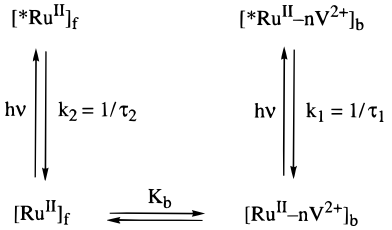
The kinetics of the excited Ru(phen)$_2$bps in the presence of $C_7C_7V^{2+}$ can be interpreted utilizing Scheme 1, where a ground-

TABLE 1: Fit Parameters for the Emission Decay of *Ru(phen)$_2$bps upon Addition of $C_7C_7V^{2+}$ in Water, 0.05 M NaCl, and 0.5 M NaCl[a]

$[C_7C_7V^{2+}]_o$/ mM	water				0.05 M NaCl				0.50 M NaCl			
	$\%\tau_1$[b]	τ_1/ns	$\%\tau_2$[b]	τ_2/ns	$\%\tau_1$[b]	τ_1/ns	$\%\tau_2$[b]	τ_2/ns	$\%\tau_1$[b]	τ_1/ns	$\%\tau_2$[b]	τ_2/ns
0.00			100	3370[c]			100	3380[c]			100	3335[c]
0.12	3.0	93	97.0	1560	5.0	75	95.0	1480				
0.25	5.0	129	95.0	960	4.0	93	96.0	998	6.1	82	93.9	975
0.38	8.2	155	91.8	700	5.0	217	95.0	797	6.0	90	94.0	739
0.50	8.4	163	91.6	578	8.6	246	91.4	619	6.0	108	94.0	579
0.65	10.7	166	89.3	472	14.6	246	85.4	519	6.5	128	93.5	491
0.75	56.9	123	43.1	406	8.2	116	91.8	425	7.9	109	92.1	413
0.88	65.0	172	35.0	354	14.9	169	85.1	387	11.6	186	88.4	371

[a] Measured at (27.5 °C). [b] Percentages calculated as the integrated emission for each component from the preexponential factors in the equation $a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where $\%\tau_1 = a_1\tau_1/(a_1\tau_1 + a_2\tau_2)$ and $\%\tau_2 = a_2\tau_2/(a_1\tau_1 + a_2\tau_2)$. [c] Decay fit a monoexponential kinetics.

SCHEME 1



state adduct between Ru(phen)$_2$bps and $C_7C_7V^{2+}$ is formed. In the absence of quencher, *Ru(phen)$_2$bps decays with a rate constant given by $k_o = 1/\tau_o$. Owing to the amphiphilic features of the quencher, it is likely that it forms micelles at millimolar concentrations. The critical micelle concentration (cmc) of the related series of viologens $C_1C_nV^{2+}$ (n = 12, 14, 16) range from 4.2 mM (n = 16) to 20 mM (n = 12).[25] Therefore, in the concentration range utilized in this study (Table 1), only premicellar $C_7C_7V^{2+}$ adducts are expected. Since the donor Ru(II) complex is also amphiphilic, with one ligand that possesses two anionic groups and two hydrophobic ligands, it can associate with the $C_7C_7V^{2+}$ premicellar adducts to form the bound Ru(phen)$_2$bps, $[Ru^{II}-nV^{2+}]_b$ (Scheme 1). The quenching of $[*Ru^{II}-nV^{2+}]_b$ within the aggregates is expected to be independent of $C_7C_7V^{2+}$ concentration and to take place with the bound ET rate constant k_{et}^b. The excited state of free Ru(phen)$_2$bps, $[*Ru^{II}]_f$, is subject to bimolecular quenching by $C_7C_7V^{2+}$, which can be interpreted utilizing Stern−Volmer kinetics with quenching rate constant k_q.[36] Therefore, the two excited-state decay rate constants k_1 and k_2 are related to the lifetime components τ_1 and τ_2, respectively, and are given by

$$k_1 = 1/\tau_1 = k_o + k_{et}^{\ b} \quad (1)$$

$$k_2 = 1/\tau_2 = k_o + k_q[V^{2+}]_o \quad (2)$$

In this model the ground-state adduct, $[Ru^{II}-nV^{2+}]_b$, is excited by light and decays with rate constant k_1 (=$1/\tau_1$), which reflects the intra-aggregate quenching, k_{et}^b, by $C_7C_7V^{2+}$. This interpretation is supported by the relative insensitivity of τ_1 to quencher concentration and the increase in the percent contribution of τ_1 as the $C_7C_7V^{2+}$ concentration is increased (Table 1). Addition of NaCl does not greatly affect the intra-aggregate quenching rate constant (k_{et}^b) but leads to a lower concentration of the adduct, as reflected by the lower percent contribution of τ_1 at 0.05 and 0.5 M NaCl listed in Table 1. Utilization of the $\%\tau_1$ values to calculate ground-state binding constants of the Ru/V^{2+} adduct leads to values of 195, 184, and 137 M^{-1} in 0.00, 0.05, and 0.5 M NaCl, respectively.[37] From the average value of τ_1 (151 ns), an intra-adduct ET rate, k_{et}^b, of 6.3×10^6 s^{-1} can be calculated (eq 1). This rate appears slow for an aggregate, although it is possible that aggregation takes place in a geometry that is not optimal for the ET event.

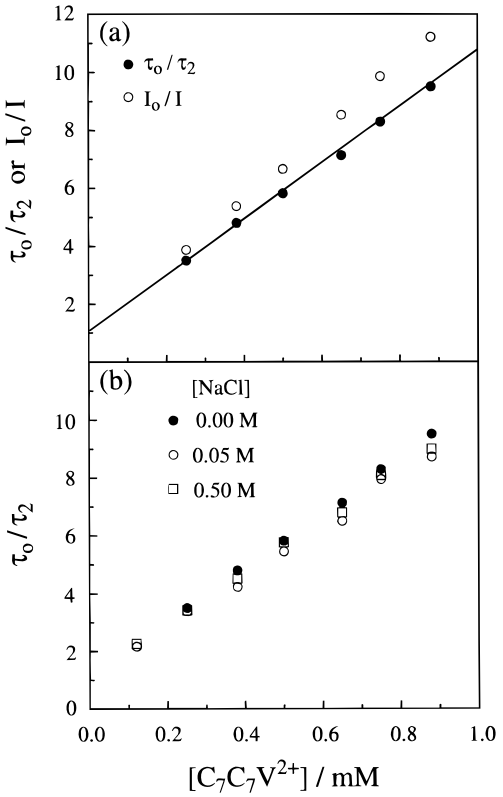


Figure 2. Stern−Volmer plots for the quenching of 5 μM Ru(phen)$_2$bps by $C_7C_7V^{2+}$ (data from Table 1) (a) in water showing τ_o/τ_2 and I_o/I and (b) the comparison of the τ_o/τ_2 points in water, 0.05 M NaCl, and 0.50 M NaCl.

The bimolecular quenching of *Ru(phen)$_2$bps by $C_7C_7V^{2+}$ yields a linear plot of τ_o/τ_2 vs $[C_7C_7V^{2+}]_o$ (Figure 2a), consistent with the Stern−Volmer equation (eq 3) obtained from multiplication of eq 2 by τ_o.

$$\tau_o/\tau_2 = 1 + \tau_o k_q[V^{2+}]_o \quad (3)$$

The bimolecular quenching rate constant, k_q, determined in this manner (eq 3) in water was 3.0×10^9 M^{-1} s^{-1}. As shown in Figure 2a, the values of I_o/I are slightly greater than those of τ_o/τ_2 owing to the loss in emission intensity from the aggregated Ru(phen)$_2$bps. As expected from the similar reduction potentials of the acceptors, the quenching rate constant for $C_7C_7V^{2+}$ (3.0×10^9 M^{-1} s^{-1}) is similar to that obtained for $C_1C_1V^{2+}$ (4.8×10^9 M^{-1} s^{-1}) in water.

TABLE 2: Fit Parameters for the Emission Decay of *Ru(phen)$_2$bps upon Addition of $C_7C_7V^{2+}$ in 72 mM SDS[a]

$[C_7C_7V^{2+}]_o$/mM	$\%\tau_1$[b]	τ_1/ns	$\%\tau_2$[b]	τ_2/μs
0.00			100	3.30[c]
0.05			100	3.20[c]
0.10	2.6	418	97.4	3.09
0.20	4.1	412	95.9	3.06
0.40	7.4	374	92.6	2.91
0.60	10.0	329	90.0	2.78
0.80	11.9	261	88.1	2.32
1.0	16.1	238	83.9	2.05
1.5	25.2	198	74.8	1.73

[a] Measured at (27 °C). [b] Percentages calculated as the integrated emission for each component from the preexponential factors in the equation $a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where $\%\tau_1 = a_1\tau_1/(a_1\tau_1 + a_2\tau_2)$ and $\%\tau_2 = a_2\tau_2/(a_1\tau_1 + a_2\tau_2)$. [c] Decay fit a monoexponential kinetics.

The quenching of the long-lifetime component, τ_2, in the presence of NaCl is consistent with the model presented in Scheme 1. The ionic strength is not expected to play a significant role in bimolecular quenching when one of the reactants is neutral, where screening of electrostatic forces between the reactants does not play a role in the diffusion rate constant. As shown in Figure 2b, the plots of τ_o/τ_2 vs $[C_7C_7V^{2+}]_o$ (from Table 1) in the presence of NaCl are similar to that in water, yielding quenching rate constants, k_q, of 3.0×10^9 and 2.6×10^9 M^{-1} s^{-1} in 0.05 and 0.5 M NaCl, respectively.

Other systems have been previously reported where either the donor or the acceptor possessed a long alkyl chain and could therefore act as a surfactant. In systems containing Ru(II) complexes whose ligands possessed long alkyl chain substituents, biexponential decays were observed at premicellar concentrations in the presence of $C_1C_1V^{2+}$, although the decay rate was not reported.[38] In the $Ru(bpy)_3^{2+}/C_1C_{16}V^{2+}$ (bpy = 2,2′-bipyridine) system a premicellar (cmc = 4.2 mM) quenching rate constant of 6.7×10^8 M^{-1} s^{-1} was measured, and the formation of reduced viologen as the quencher concentration increased remained constant above the cmc.[25] The lower bimolecular quenching rate constant observed in $Ru(bpy)_3^{2+}/C_1C_{16}V^{2+}$ compared to our $Ru(phen)_2bps/C_7C_7V^{2+}$ system can be explained in terms of electrostatic repulsion between the reactants in the former, leading to a lower rate of diffusion of the reactants to their closest-contact ET distance.

Micellar Media. The emission decay of $Ru(phen)_2bps$ fits monoexponential kinetics in 40 and 72 mM SDS (cmc = 8.0 mM), with lifetimes of 3.9 and 3.3 μs, respectively. This observation is consistent with the highly soluble complex residing in the aqueous phase with little or no interaction with the anionic SDS micelles. One of the goals of the present study was to utilize an acceptor that remained bound to the SDS micelles during the excited-state lifetime of the Ru(II) complex, with a large enough binding constant to SDS micelles to ensure a negligible quencher concentration in the aqueous phase. Such a scenario would result in monoexponential decays of $Ru(phen)_2bps$ as a function of added quencher at a constant micelle concentration and would avoid the utilization of a large number of unknown variables as fit parameters, including the exchange rate of the probe and quencher.[26,27] However, when $C_7C_7V^{2+}$ is added at concentrations above 0.05 mM to $Ru(phen)_2bps$ solutions containing 40 and 72 mM SDS, the decay of the complex becomes biexponential with short- and long-lifetime components, τ_1 and τ_2, respectively. The parameters obtained from the monoexponential and biexponential fits of the decays as a function of quencher concentration are listed in Table 2 for 72 mM SDS.

Although the interpretation of the observed kinetics in the micellar system can be complex, some possibilities can be ruled out. The two decays cannot be correlated to binding of the Ru complex to SDS or to $C_7C_7V^{2+}$, since various concentrations of $Ru(phen)_2bps$ at constant quencher and micelle concentrations resulted in similar lifetimes and preexponential factors. The short- and long-lifetime components, τ_1 ($\%\tau_1$) and τ_2 ($\%\tau_2$), for solutions containing 40 mM SDS and 0.2 mM $C_7C_7V^{2+}$were 443 ns (5.8%) and 3.2 μs (94.2%), 458 ns (5.9%) and 3.4 μs (94.1%), and 381 ns (3.6%) and 3.3 μs (96.4%), for 5, 10, and 20 μM $Ru(phen)_2bps$, respectively. Since a 4-fold increase in the concentration of the Ru(II) complex does not result in significant changes in the lifetimes or their preexponential factors, it can be concluded that binding of the complex to the micelles or the quencher is not a factor that contributes to the observed decay kinetics.

The $C_7C_7V^{2+}$ acceptor is known to bind tightly to SDS micelles with exchange rates with the aqueous medium slower than the lifetime of the excited state of Ru(II) complexes; therefore a minimal fraction of the viologen is expected in the aqueous phase and the contributions from exchange to the decay can be neglected.[26−28] In addition, the donor is expected to remain in the aqueous phase with little or no interaction with the micelles.[29] The biexponential decays can be explained in terms of quenching of the $*Ru(phen)_2bps$ excited state by $C_7C_7V^{2+}$ molecules not bound to SDS and those bound to the micelles that are not in fast exchange. The preexponential factors would then be associated with the percentage of $*Ru(phen)_2bps$ quenched by free viologen ($\%\tau_1$) and by micelle-bound $C_7C_7V^{2+}$ ($\%\tau_2$). This interpretation is consistent with lower $\%\tau_1$ values observed at 72 mM SDS ($\%\tau_1 = 10.0\%$ at $[C_7C_7V^{2+}] = 0.6$ mM) compared to those measured at 40 mM SDS ($\%\tau_1 = 15.3\%$ at $[C_7C_7V^{2+}] = 0.5$ mM), indicating that a lower fraction of the *Ru(II) is quenched by free viologen in the presence of the greater micelle concentration.

Comparison of the kinetics of our system to those previously reported is difficult since, to our knowledge, a system where the excited donor remains on the aqueous phase while the acceptor is bound to the micellar surface (possessing slow exchange with the aqueous medium) has not been reported. Multiexponential decays have been observed in micellar systems for excited micelle-bound probes in the presence of $C_1C_1V^{2+}$ quenchers. The decays of the different components were interpreted as the lifetime of the probe quenched by micelle-associated viologens located at various positions with respect to the probe.[27] In SDS micellar systems where the Ru(II) probe is tightly bound to the surface through the utilization of ligands substituted with $-n$-$C_{17}H_{35}$ chains, monoexponential decays were observed in the presence of $C_1C_1V^{2+}$ owing to the fast on−off rates of the quencher and no Ru(II) complex present in the aqueous phase.[39] Biexponential decays were observed for $Ru(phen)_3^{2+}$ associated with starburst dendrimers (SBD) in the presence of dendrimer-bound $Co(phen)_3^{3+}$ quenchers.[19b] At high SBD concentrations (>5 mM) where all the probe (10 μM) was bound to the dendrimer surface and the SBD-to-$Co(phen)_3^{3+}$ ratio was greater than 500, the two decays were believed to arise from $*Ru(phen)_3^{2+}$ that was bound to a host that either contained $Co(phen)_3^{3+}$ (quenched decay) or was free of quencher.[19b] In our system, we cannot attain such high host concentrations, since surfactants are known to form aggregates other than micelles at high concentrations, although the decays are indeed monoexponential at low $C_7C_7V^{2+}$ concentrations.

The changes in the short-lifetime component, τ_1, cannot be directly correlated to the quencher concentration in the presence

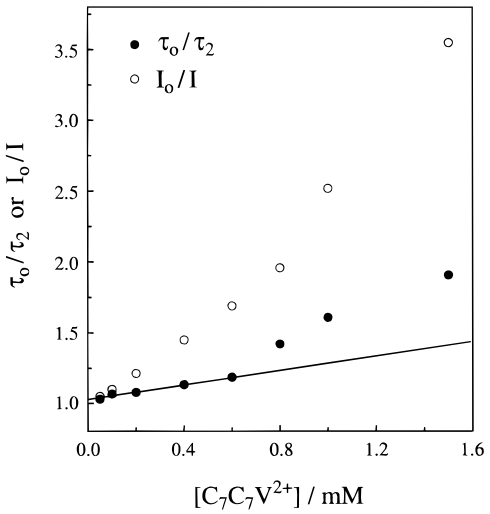


Figure 3. Stern−Volmer plots of τ_o/τ_2 and I_o/I for the quenching of 5 μM Ru(phen)$_2$bps by $C_7C_7^{2+}$ in 72 mM SDS (data from Table 2). The linear fit for points $[C_7C_7^{2+}] \leq 0.6$ mM is shown (see text).

of SDS micelles. It is possible that bimolecular quenching of *Ru(phen)$_2$bps by quencher in the aqueous phase is taking place (with $k_q = 3.0 \times 10^9$ M^{-1} s^{-1}), coupled with the formation of the Ru−V^{2+} aggregates observed in the absence of micelles discussed above ($K \sim 200$ M^{-1}). In addition, the concentration of free viologen is unknown, especially since micellar properties including critical micelle concentration and aggregation number are likely to vary as $C_7C_7V^{2+}$ is added. Therefore, at this time no attempt to obtain kinetic information from τ_1 will be made, although from the arguments presented above it is believed to be associated with the quenching of *Ru(phen)$_2$bps in the aqueous phase by $C_7C_7V^{2+}$ not bound to SDS.

The decrease in the long-lifetime component, τ_2 (Table 2), is interpreted as the bimolecular quenching of *Ru(phen)$_2$bps in the aqueous phase by $C_7C_7V^{2+}$ bound to SDS micelles, as depicted in Figure 1. If indeed the quenching results from the reactants as shown in Figure 1, the system should follow Stern−Volmer kinetics and the plot of τ_o/τ_2 vs $[C_7C_7V^{2+}]$ should be linear. Such a Stern−Volmer plot is shown in Figure 3, where the changes in I_o/I are included for comparison. The value of I_o/I is slightly greater than that of τ_o/τ_2 stemming from the lower overall emission intensity of the short-lifetime component, τ_1. It is evident from Figure 3 that deviations from linearity occur in the Stern−Volmer plot above 0.6 mM quencher. From the data listed in Table 2 it is apparent that above 0.6 mM $C_7C_7V^{2+}$ in 72 mM SDS the percentage of *Ru(phen)$_2$bps quenched by viologen not bound to SDS is greater than 10% (from $\%\tau_1$). Since the concentration of micelles is approximately 1.0 mM at 72 mM SDS monomers,[30] it is possible that at the higher viologen concentrations the properties of the micellar system are disturbed enough such that the Stern−Volmer treatment is no longer applicable. These disturbances may include more than one viologen present per micelle, changes in the SDS micellar properties such as cmc and aggregation number, or micellization (or some other aggregation) of the diheptyl viologens themselves. To ensure the model presented in Figure 1, it is reasonable to consider only the data points for which the percent of Ru complex quenched by viologen in solution is less than 10%. Fitting the τ_o/τ_2 points in Figure 3 for $[C_7C_7V^{2+}]_o \leq 0.6$ mM to a line results in a quenching rate constant, k_q^{SDS}, of 8.0×10^7 M^{-1} s^{-1}.

The magnitude of the quenching rate constant by $C_7C_7V^{2+}$ acceptors bound to SDS micelles, $k_q^{SDS} = 8.0 \times 10^7$ M^{-1} s^{-1}, is significantly slower than that measured in water (3.0×10^9 M^{-1} s^{-1}), in the presence of 0.05 and 0.5 M NaCl (3.0×10^9 and 2.6×10^9 M^{-1} s^{-1}, respectively), and when $C_7C_7V^{2+}$ is bound to neutral C12E8 micelles (2.6×10^9 M^{-1} s^{-1}). One possible explanation for this effect is that owing to the negative charges at the micellar surface, the reduction potential of the micelle-bound viologen is more negative. Electrochemical experiments have shown that the reduction potential of $C_{16}C_1V^{2+}$ bound to SDS was 0.2 V more negative than that bound to neutral micelles.[40] The quenching reaction presented here consists of a bimolecular system where the quenching rate constant in water is near the diffusion limit. The difference in the reduction potential in the micelle-bound viologen would result in a lowering of the driving force of the electron-transfer reaction by 0.2 V, which would not account for the large difference in the quenching rate constants in water and bound to SDS micelles.[36,41−43] The diffusion coefficient of the larger viologen−micelle ($r \sim 18$ Å) aggregate is expected to be approximately 3 times slower than for the quencher in water;[44] however, this factor is not large enough to account for the observed differences. Furthermore, the quenching rate constant measured in neutral C12E8 micelles, where similar diffusion arguments can be made, was 2.6×10^9 M^{-1} s^{-1}.

Another possible explanation for the difference in quenching rate constants in the presence and absence of SDS micelles arises from the localization of the electron on the bps ligand in the reactive MLCT excited state of Ru(phen)$_2$bps. Therefore, the fastest electron-transfer rate would be expected for encounter complexes where the bps ligand is closest to the viologen. In the presence of SDS micelles, it is unlikely that Ru(phen)$_2$bps would approach the quencher bound to the anionic micellar surface with the bps ligand owing to repulsion by the $-SO_3^-$ groups. If this is the case, then the electron-transfer distance would be greater when $C_7C_7V^{2+}$ is bound to SDS micelles than in water or in the presence of C12E8, where closest contact between the quencher and the bps ligand of Ru(phen)$_2$bps is not hindered by electrostatic repulsion, thus permitting the most favorable orientation and closest distance for the electron-transfer event.

It is possible that a combination of the factors described above plays a role in the observed differences in the presence and absence of SDS micelles. To address this question, neutral hydrophilic complexes where the electron is not localized on the anionic ligand in the MLCT excited state are currently being prepared.

Conclusions

A donor/acceptor system was designed to measure the micellar effects on bimolecular electron-transfer kinetics, and the quenching rate constants in water and SDS micelles were measured. The donor, Ru(phen)$_2$bps, possesses an overall zero charge and resides in the aqueous phase, whereas the $C_7C_7V^{2+}$ acceptor is anchored to the micellar surface through the heptyl chains. In water, the formation of an aggregate between Ru(phen)$_2$bps and $C_7C_7V^{2+}$ results in biexponential decay of the emission of the probe in the presence of quencher. The quenching rate constant of the nonaggregated Ru(phen)$_2$bps by $C_7C_7V^{2+}$ was 3.0×10^9 M^{-1} s^{-1}, whereas the intra-adduct ET rate was $\sim 6.3 \times 10^6$ s^{-1}.

The emission decay of *Ru(phen)$_2$bps remains monoexponential in the presence of SDS micelles, but becomes biexponential upon addition of $C_7C_7V^{2+}$. In this case the short-lifetime

component has been interpreted as quenching of the Ru(II) excited state by $C_7C_7V^{2+}$ not bound to SDS, whereas the long-lifetime component results from the quenching of *Ru(phen)$_2$bps by viologen bound to the micelles. The quenching rate constant of the latter was 8.0×10^7 M^{-1} s^{-1}. Possible explanations for the significantly slower quenching rate constant for SDS-bound $C_7C_7V^{2+}$ include the shift in the reduction potential of the viologen bound to SDS, slower diffusion coefficient of the quencher−micelle adduct, and an orientation effect of the reactive intermediate driven by electrostatic repulsion between the bps $-SO_3^-$ groups and the micellar surface charges.

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