

Electrogenerated Chemiluminescence. 50. Electrochemistry and Electrogenerated Chemiluminescence of Micelle Solubilized Os(bpy)₃²⁺

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The oxidative electrochemistry and electrogenerated chemiluminescence (ECL) of Os(bpy)₃²⁺ were studied in the presence of sodium dodecyl sulfate (SDS), Triton X-100, and cetyltrimethylammonium bromide (CTAB) in aqueous solutions. Variation of supporting electrolyte (NaCl) concentration affected the interaction between Os(bpy)₃²⁺ and the surfactants. The measurement of oxidation peak current (*i*_{pa}) and ECL intensity at different NaCl concentrations suggested a strong interaction of Os(bpy)₃²⁺ with SDS. Above the critical micelle concentration (cmc) the strong hydrophobic interaction of Os(bpy)₃²⁺ and the SDS micelle core greatly suppresses both *i*_{pa} and the ECL intensity. The interaction of Os(bpy)₃²⁺ with CTAB micelle is much weaker because of electrostatic effects. Triton X-100 micelles do not interact with Os(bpy)₃²⁺.

We report studies of the effect of micelle-forming surfactants on the oxidative electrochemistry of Os(bpy)₃²⁺ and its ECL in the presence of oxalate. Surfactants have been used in polarographic experiments and other electrochemical experiments. Most experiments deal with *E*_{1/2} shifts and homogeneous electron-transfer kinetics of the substances solubilized in micelles.^{1–3} Micelles have also been of interest in micellar catalysis and micellar models of biological membranes.⁴ Micelles are dynamic aggregates of amphiphilic molecules and possess regions of hydrophilic and hydrophobic character.⁵ The interactions that are operative between soluble substances and host micelles include electrostatic attractions,⁶ surface adsorption,⁷ pseudophase extraction,⁸ and substrate/amphiphile coassembly to yield a unique micelle composition.⁹ The specific nature of the interaction between a soluble species and the host micelle governs the effect of micellar microenvironment on the behavior of the substrate. This study was mainly motivated by our interest in the application of Ru(bpy)₃²⁺ and other emitting centers as tags for analysis of species at low concentration.¹⁰ In certain samples, e.g., biological fluids, the addition of surfactants can be helpful in suppressing the effects of interferences.

The present experiment was designed to elucidate the microenvironment effects of micelles on the electrochemical and ECL behavior of Os(bpy)₃²⁺, which is a reasonably good luminescor.^{11,12} The one-electron oxidation near +0.6 V vs. SCE allows the study of these compounds in aqueous solutions. Sodium dodecyl sulfate (SDS), Triton X-100, and cetyltrimethylammonium bromide (CTAB) were used

as the representatives of anionic, neutral and cationic micelles, respectively. We also show that the electrolyte concentration affects the electrochemical and ECL behavior.

Experimental

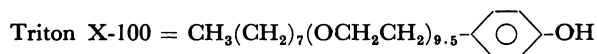
SDS, CTAB, and Triton X-100 were obtained from Aldrich Chemicals (Milwaukee, WI) and were used without further purification. Sodium chloride was purchased from MCB (reagent grade, Cincinnati, OH) and Milli-Q water (Millipore Corp. El Paso, TX) was used to prepare all solutions. Os(bpy)₃(PF₆)₂ was prepared according to the procedure of Gaudiello et al.¹³ The surface active compounds were dissolved in a very small volume of acetone to assist the solubility in water.

A three compartment cell was used to carry out all experiments. Electrochemical measurements were performed with a Princeton Applied Research (PAR) (Princeton, NJ) Model 175 universal programmer, a Model 173 potentiostat and a Model 179 digital coulometer equipped with positive feedback circuitry for IR compensation. Voltammograms were recorded on a Houston Instruments Model 2000 X-Y recorder. A BAS-100 electrochemical analyzer (Bioanalytical Systems, Lafayette, IN) was also used in the electrochemical measurements. ECL spectra were recorded on an Aminco-Bowman Spectrometer with a Hamamatsu R928 photomultiplier tube. Absorption spectra were obtained with a Hewlett-Packard Model 8450A dual-beam spectrophotometer.

Most of the experiments were performed under a purified nitrogen atmosphere. The electrochemical cell was adapted to a Schlenk line. Glassy carbon electrodes (0.07 cm²) (BAS, Lafayette, IN) were employed as working electrodes for voltammetry and ECL. The electrodes were polished with a 0.05 μm alumina/water slurry on a felt surface and sonicated. A platinum mesh was used as counter electrode and all potentials were recorded against a saturated calomel electrode (SCE).

Results

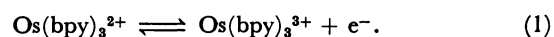
Cyclic Voltammetry. Cyclic voltammetry (CV) experiments were carried out to study the effect of



Structures of Surfactants

SDS, Triton X-100, and CTAB micelles on the redox potentials and peak currents (i_p) for the oxidation of $\text{Os}(\text{bpy})_3^{2+}$. The cyclic voltammogram of a 0.2 mM[†] aqueous solution of $\text{Os}(\text{bpy})_3^{2+}$ in 50 mM NaCl in the absence and presence of surfactants is shown in Fig. 1. The waves observed are due to the one-electron oxidation¹²⁾ of $\text{Os}(\text{bpy})_3^{2+}$, and, on reversal, the

reduction of the +3 species:



CV waves were observed in all three micellar solutions as shown in Fig. 1b–d. The value of ΔE_p , the separation between anodic and cathodic peak potentials ($E_{pa} - E_{pc}$), shows that the waves are essentially reversible in all solutions. ΔE_p is listed in Table 1 for all media. There are variations in the redox potentials associated with half reaction 1 in SDS media. In the presence of SDS, the $E_{1/2}$ (formal standard potential)

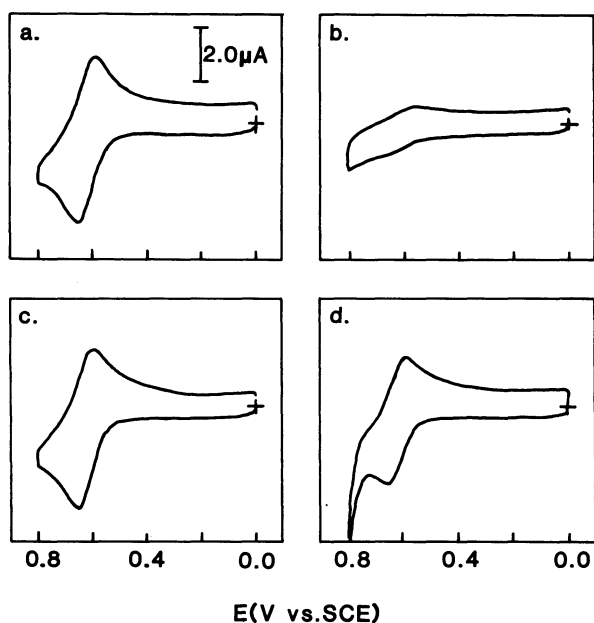


Fig. 1. Cyclic voltammogram for the oxidation of 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$, 50 mM NaCl, at a GC electrode. Scan rate, 100 mV s⁻¹. (a) Aqueous solution; (b) 70 mM SDS; (c) 5% (w/v) Triton X-100; (d) 70 mM CTAB.

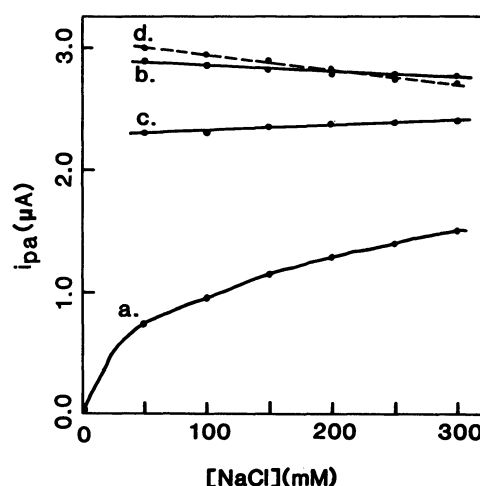


Fig. 2. Electrolyte (NaCl) concentration dependence of peak current for the oxidation of 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$ at GC electrode. Scan rate, 100 mV s⁻¹. (a) 70 mM SDS; (b) 5% (w/v) Triton X-100; (c) 70 mM CTAB; (d) pure aqueous.

Table 1. Variations of Half-Wave Potentials for $\text{Os}(\text{bpy})_3^{3+}/\text{Os}(\text{bpy})_3^{2+}$ ($C=0.2$ mM) in Different Media at Different NaCl Concentrations

	50 mM				100 mM				150 mM			
	E_{pa}^a	E_{pc}^a	ΔE_p^b	$\frac{E_{pa} + E_{pc}}{2}$	E_{pa}	E_{pc}	ΔE_p	$\frac{E_{pa} + E_{pc}}{2}$	E_{pa}	E_{pc}	ΔE_p	$\frac{E_{pa} + E_{pc}}{2}$
Aqueous	0.655	0.590	65	0.623	0.650	0.585	65	0.618	0.650	0.585	65	0.618
70 mM SDS	0.650	0.580	70	0.615	0.656	0.590	66	0.623	0.680	0.610	70	0.645
70 mM CTAB	0.655	0.588	67	0.622	0.650	0.580	70	0.615	0.648	0.580	68	0.614
5% (w/v) Triton X-100	0.655	0.595	60	0.625	0.652	0.590	62	0.621	0.648	0.582	66	0.615
	200 mM				250 mM				300 mM			
	E_{pa}	E_{pc}	ΔE_p	$\frac{E_{pa} + E_{pc}}{2}$	E_{pa}	E_{pc}	ΔE_p	$\frac{E_{pa} + E_{pc}}{2}$	E_{pa}	E_{pc}	ΔE_p	$\frac{E_{pa} + E_{pc}}{2}$
Aqueous	0.645	0.585	60	0.615	0.640	0.580	60	0.610	0.640	0.580	60	0.610
70 mM SDS	0.690	0.618	72	0.654	0.695	0.625	70	0.660	0.705	0.630	75	0.668
70 mM CTAB	0.640	0.578	62	0.609	0.638	0.576	62	0.607	0.638	0.572	66	0.605
5% (w/v) Triton X-100	0.640	0.580	60	0.610	0.645	0.582	63	0.614	0.642	0.578	64	0.610

a) E_{pa} and E_{pc} in V vs. SCE. b) ΔE_p in mV.

[†] 1 M=1 mol dm⁻³.

shifted to slightly more positive values (see Table 1), especially at higher supporting electrolyte concentration; e.g., $E_{1/2}$ was 0.668 V vs. SCE at 300 mM NaCl with 70 mM SDS compared to 0.610 V in 300 mM NaCl alone. Both i_{pc} and i_{pa} were depressed about four times in the presence of SDS (50 mM NaCl in solution) and reduced slightly in the presence of Triton X-100 micelles and of CTAB micelles compared to that in an aqueous solution in the absence of surfactant (Fig. 2).

The supporting electrolyte concentration affects the oxidation of $\text{Os}(\text{bpy})_3^{2+}$ as shown by i_{pa} vs. concentration of NaCl plots in Fig. 2. The variation of electrolyte concentration caused different responses for the three different micellar solutions. In 70 mM SDS (Fig. 2a), when the concentration of NaCl increased from 50 mM to 300 mM, the formal standard potential shifted from 0.615 to 0.688 V vs. SCE and the i_{pa} increased from 0.75 to 1.5 μA . In the absence of added NaCl, a solution with 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$ shows an $i_{pa}=1.6 \mu\text{A}$ (with positive feedback iR compensation). However, under the same conditions in the presence of 70 μM SDS, no oxidation wave is seen ($i_{pa}\approx 0$). This indicates that all of the $\text{Os}(\text{bpy})_3^{2+}$ in the SDS micelles becomes completely electrochemically inactive in the absence of supporting electrolyte. The peak current increased slightly upon the successive addition of NaCl with CTAB micelles, as shown in Fig. 2c. In the presence of Triton X-100 micelles, as well as without any surfactant added, the peak current decreased slightly as the concentration of NaCl increased.

The voltammetry was also studied at various

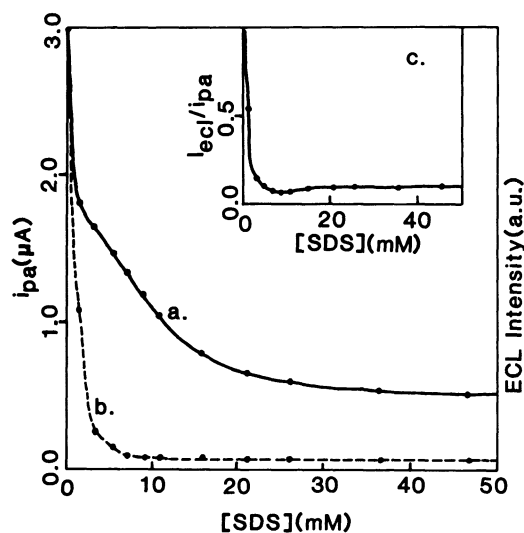


Fig. 3. (a) SDS concentration dependence of peak current for 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$ in 50 mM NaCl solution at GC electrode. Scan rate, 100 mV s^{-1} . (b) SDS concentration dependence of ECL intensity of $\text{Os}(\text{bpy})_3^{2+}$ in 50 mM NaCl, 20 mM $\text{C}_2\text{O}_4^{2-}$; (c) ratio of the ECL intensity by the current at corresponding SDS concentration.

concentrations of SDS. A plot of peak current vs. concentration of SDS is shown in Fig. 3a. SDS was gradually added to an aqueous solution containing 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$ and 50 mM NaCl. The oxidation peak current dropped from 3.0 to 1.9 μA upon the addition of 1.7 mM SDS, then continued decreasing, roughly linearly proportional to the SDS concentration, up to about 12 mM. Addition of more SDS depressed the peak current further until 30 mM SDS had been added. The peak current then leveled at 0.55 μA for SDS concentration up to 50 mM. The same phenomenon is observed for MV^+ reduction at different concentrations of SDS,¹⁴ where the reduction current was depressed continually as the SDS concentration was raised above the critical micelle concentration (cmc) (which is 2.25 mM at 50 mM NaCl).

Diffusion Coefficients. The diffusion coefficient, D_o , is a measure of the association of electroactive molecules with the surfactant and micelles. Plots of i_{pa} vs. the square root of the sweep rate ($v^{1/2}$) in different media (Fig. 4) are linear, indicating that the electrode reaction of $\text{Os}(\text{bpy})_3^{2+}$ is diffusion-controlled in the absence and presence of surfactant. This suggests that the electrochemically active species in the presence of SDS is the micelle-solubilized $\text{Os}(\text{bpy})_3^{2+}$ in the bulk solution, since the slope of the i_{pa} vs. $v^{1/2}$ line corresponding to the SDS solution is significantly smaller than those corresponding to the other media. This observation is also clear from the decreased i_{pa} value in CV for a 0.2 mM solution of $\text{Os}(\text{bpy})_3^{2+}$ in the presence of SDS micelles as compared to i_{pa} -values in the other media. D_o was $7.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 50 mM NaCl aqueous solution, while D_o was $3.3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ in a 70 mM SDS and 50 mM NaCl solution. The decrease in D_o agrees with previous results of other species due to association with surfactants and in micellar assemblies^{1a,3a,15} and an increase in the effective radius of the substrate.¹⁶

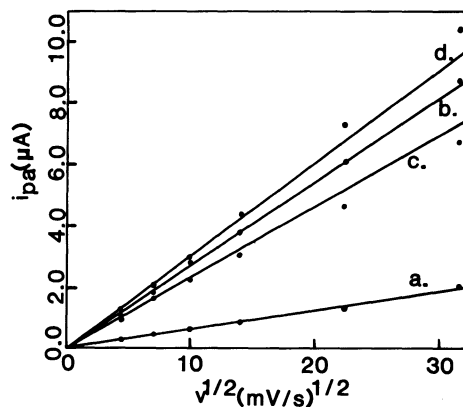


Fig. 4. Scan rate dependence of the anodic peak current for the oxidation of 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$. (a) 50 mM NaCl + 70 mM SDS; (b) 50 mM NaCl + 5% Triton X-100; (c) 50 mM NaCl + 70 mM CTAB; (d) 50 mM NaCl aqueous.

The slopes of the i_p vs. $v^{1/2}$ lines in the presence of CTAB and Triton X-100 (50 mM NaCl) deviate little from those in aqueous solution and yield D_o -values of 4.4×10^{-6} and $5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $\text{Os}(\text{bpy})_3^{2+}$, respectively.

In general, the addition of electrolytes increases the size of ionic micelles.¹⁷⁾ As shown by other experiments¹⁸⁾ with no added salt, the SDS micelles are monodisperse with an aggregation number of 55. The aggregation numbers are 98.6 with 0.189 M NaCl and 162 with 0.424 M NaCl. The larger size of the micelles would suggest a smaller value for D_o . This is contrary to what is shown in Fig. 5, where the slopes of the i_p vs. $v^{1/2}$ line become steeper at higher concentration of NaCl in the presence of SDS micelles. The magnitude of i_{pa} in CV also increases with an increase in NaCl concentration in the presence of SDS. Thus, for example, the diffusion coefficient increased from 3.3×10^{-7} to $1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ when the NaCl concentration increased from 50 to 300 mM. An explanation for this effect is proposed in the Discussion section. In all other media (surfactant-free solution, CTAB and Triton X-100 micellar solution), the addition of more NaCl caused only slight changes in the slopes of i_p vs. $v^{1/2}$ lines; i.e., diffusion coefficients showed only minor changes at higher concentrations of NaCl.

Electrogenerated Chemiluminescence. ECL of $\text{Os}(\text{bpy})_3^{2+}$ has been observed¹²⁾ upon the annihilation reaction between electrogenerated $\text{Os}(\text{bpy})_3^{3+}$ and $\text{Os}(\text{bpy})_3^{2+}$ in acetonitrile solution. Because of the limited potential range of water, an alternative method, using oxalate oxidation,¹⁹⁾ to generate the ECL of $\text{Os}(\text{bpy})_3^{2+}$ was tried. When the potential was scanned to positive values in solutions of $\text{Os}(\text{bpy})_3^{2+}$ and $\text{C}_2\text{O}_4^{2-}$, $\text{Os}(\text{bpy})_3^{2+}$ was oxidized to $\text{Os}(\text{bpy})_3^{3+}$ and

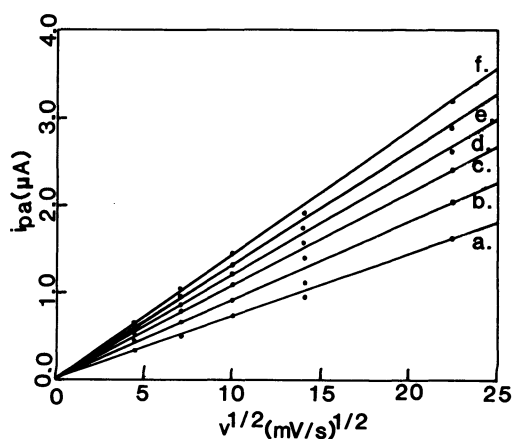


Fig. 5. Scan rate dependence of the anodic peak current for the oxidation of 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$ at GC electrode in the presence of 70 mM SDS at the concentration of (a) 50 mM NaCl; (b) 100 mM NaCl; (c) 150 mM NaCl; (d) 200 mM NaCl; (e) 250 mM NaCl; (f) 300 mM NaCl.

$\text{C}_2\text{O}_4^{2-}$ generated $\text{CO}_2^{\cdot -}$, which in turn produced $\text{Os}(\text{bpy})_3^{2+*}$.¹⁹⁾ Figure 6 shows the ECL intensity-potential profile for the system of 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$, 20 mM $\text{C}_2\text{O}_4^{2-}$, 50 mM NaCl in aqueous solution. ECL was first observed at the potential where $\text{Os}(\text{bpy})_3^{2+}$ is oxidized. No emission was observed at this sensitivity in the absence of $\text{Os}(\text{bpy})_3^{2+}$ (Fig. 6a). The addition of 70 mM SDS reduced the ECL intensity twenty-fold. When 5% (w/v) Triton X-100 or 70 mM CTAB was added (50 mM NaCl in solution), the ECL intensity decreased to two-thirds the value found in the absence of surfactant.

The effect of electrolyte concentration on the ECL intensity is shown in Fig. 7. In the SDS micellar media, increasing the NaCl concentration resulted in more intense ECL (Fig. 7a), in the same way that the

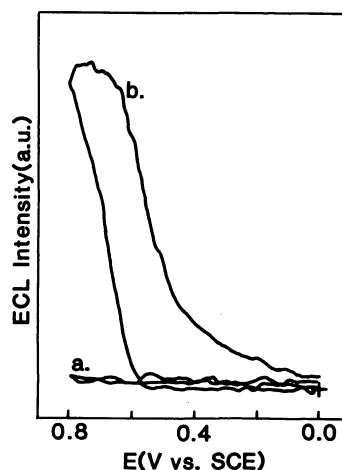


Fig. 6. Potential dependence of ECL intensity. (a) Background, 50 mM NaCl + 20 mM $(\text{NH}_4)_2\text{C}_2\text{O}_4$; (b) system (a) + 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$.

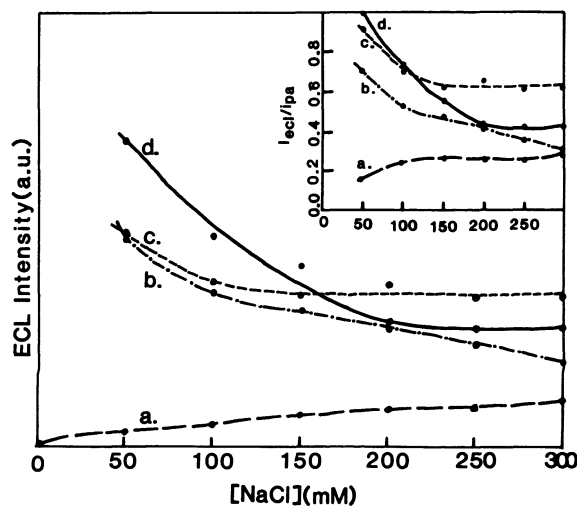


Fig. 7. NaCl concentration dependence of ECL intensity of 0.2 mM $\text{Os}(\text{bpy})_3^{2+}$, 20 mM $\text{C}_2\text{O}_4^{2-}$. (a) 70 mM SDS; (b) 5% Triton X-100; (c) 70 mM CTAB; (d) pure aqueous.

i_{pa} -value increased with the electrolyte concentration. A zero ECL intensity was obtained by extrapolation to zero electrolyte concentration, which is expected from the zero peak current at zero electrolyte concentration (Fig. 2a). For CTAB solutions, the ECL intensity decreased as the NaCl concentration increased from 50 mM to 100 mM and reached a constant value at higher NaCl concentration (Fig. 7c). Similarly the ECL intensity decreased with an increase in NaCl concentration in the Triton X-100 micellar solution (Fig. 7b), which was similar to the ECL intensity change in aqueous solution (Fig. 7b).

The ratio of ECL intensity to peak current (I/i_{pa}) is much lower in an SDS solution than that in all other media at lower NaCl concentration as shown by the insert in Fig. 7. As the NaCl concentration increased, the I/i_{pa} ratio increased at higher NaCl concentration in SDS micellar solution. The ratio decreased for all other media as the NaCl concentration increased, except in the CTAB micellar solution, where the ratio reached a constant value and was larger than that in all other media at higher NaCl concentrations.

The ECL intensity vs. SDS concentration dependence is shown in Fig. 3b. It shows the same trend as the i_{pa} -SDS concentration plot. The presence of 1.7 mM SDS greatly reduced the ECL intensity. The greater the SDS concentration, the weaker was the ECL intensity. At an SDS concentration of 7 mM or higher, only very weak ECL was observed, and the intensities became essentially independent of SDS concentration. Figure 3c is a plot of the ratio of ECL intensity (Fig. 3b) to i_{pa} (Fig. 3a) at each SDS concentration.

Absorption and Luminescence Spectra. The spectroscopic properties of molecules are usually influenced by the environment. Since micelle formation produces a different environment for the solubilized $\text{Os}(\text{bpy})_3^{2+}$, the spectroscopic behavior of $\text{Os}(\text{bpy})_3^{2+}$ should change upon addition of SDS. Figure 8 shows

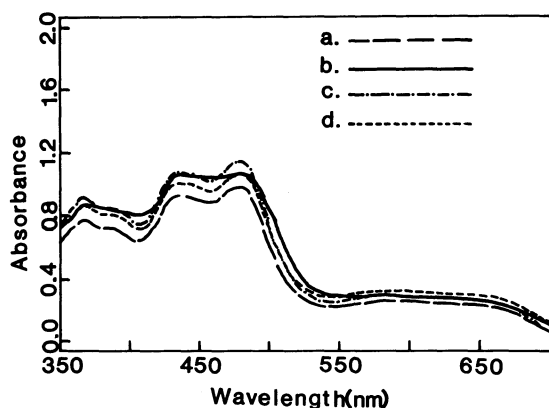


Fig. 8. Absorption spectra of $\text{Os}(\text{bpy})_3^{2+}$, in (a) aqueous solution, (b) 70 mM SDS solution; (c) 5% Triton X-100 solution; (d) 70 mM CTAB solution. 1 cm path length cell.

the absorption spectra of $\text{Os}(\text{bpy})_3^{2+}$ in different media. The spectra in CTAB and Triton X-100 micellar solutions were essentially the same as those in the pure aqueous solution. The absorption spectrum changed slightly upon addition of SDS, with the minimum at 460 nm becoming flat. The absorption spectra did not change when the NaCl concentration was varied.

The luminescence spectra (Fig. 9) were also affected to a greater extent in the presence of SDS. The emission spectra of $\text{Os}(\text{bpy})_3^{2+}$ in 70 mM CTAB and 5% (w/v) Triton X-100 micelle solution were identical to that in aqueous solution with a maximum at about 730 nm. The position of the emission peak was shifted to 765 nm in a 70 mM SDS micellar solution. Since the concentration of $\text{Os}(\text{bpy})_3^{2+}$ was the same in all of the solutions of different surfactants and in a 50 mM NaCl aqueous solution alone, and because the absorbances were the same, the fact that the emission intensities were about the same indicates that the quantum yields are about the same in different solutions. Variation of concentration of NaCl did not change the absorption or luminescence spectra in any of the solutions, nor did it affect the absorbance or emission intensities.

The shift in the emission peak for $\text{Os}(\text{bpy})_3^{2+}$ in the SDS solution clearly shows an interaction between these species. The effect on the $\text{Os}(\text{bpy})_3^{2+}$ emission depends upon whether the SDS concentration is above or below the cmc. The spectrum has a peak at 730 nm in pure aqueous solution. Addition of up to 3.4 mM SDS shifted the peak to 710 nm (a blue shift) (Fig. 9b). The turning point concentration of SDS for the large red spectral shift was near the critical micelle concentration of SDS (2.25 mM); i.e., when the concentration of SDS changed from below the cmc to above it, a large shift in peak position towards longer wavelengths (to 765 nm) resulted. As a comparison, the luminescence spectrum of $\text{Os}(\text{bpy})_3^{2+}$ in hexane

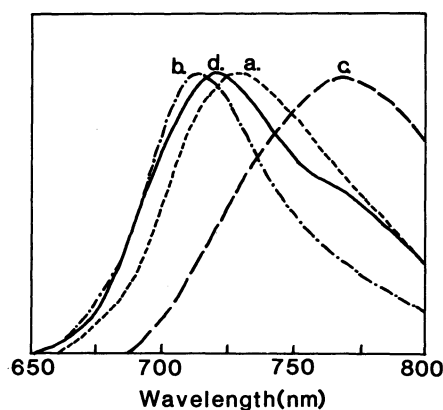
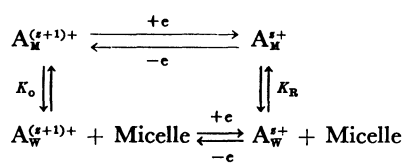


Fig. 9. Luminescence spectra of $\text{Os}(\text{bpy})_3^{2+}$, in (a) pure aqueous, or 70 mM CTAB or 5% Triton X-100 solutions; (b) 2 mM SDS solution; (c) 70 mM SDS solution; (d) hexane solution. $\lambda_{exc}=470$ nm.

was measured; a shoulder appeared at 767 nm in addition to a peak at 720 nm. Note that a similar emission spectrum shift was reported for [11-(3-hexyl-1-indolyl)undecyl]trimethylammonium bromide around the cmc in an aqueous solution.²⁰⁾

Discussion

Dissolved species associate with surfactant molecules in different ways at different surfactant concentrations.²¹⁾ Below the critical micelle concentration (cmc), complexes can be formed between dissolved species and surfactant molecules (premicellar aggregates).^{14, 21)} Above the cmc the surfactant exists in solution as micelles, and dissolved species, A, can partition between the micellar and the water phase. Scheme 1 is often used to describe a redox couple in which the oxidized and reduced forms interact with micellar aggregates (when the surfactant concentration is above the cmc).^{1a)}



Scheme 1.

$K_O = [A_W^{(z+1)+}][\text{micelle}]/[A_W^{(z+1)+}]$ and $K_R = [A_W^{z+}][\text{micelle}]/[A_M^{z+}]$ are equilibrium constants, the subscripts M and W indicate the micellar and aqueous phases, respectively; and O and R indicate constants appropriate for the oxidant and reductant, respectively. For a simple reversible one-electron process, the formal standard potential can be represented as $E_W^0 + (RT/F)\ln K_O(1+K_R)/K_R(1+K_O)$. When $A^{(z+1)+}$ and A^{z+} exist predominantly in the micelles, $K_O, K_R \ll 1$, the formal standard potential becomes $E_W^0 + (RT/F)\ln[K_O/K_R]$. When $A^{(z+1)+}$ and A^{z+} exist predominantly in the water phase, $K_O, K_R \gg 1$, the logarithmic term disappears and the potential is E_W^0 , which represents the formal standard potential of the redox couple in the absence of micelles. The electrochemical evidence presented here indicates predominant existence of $A^{(z+1)+}$ and A^{z+} in the SDS micelles. The positive potential shift implies that $K_O > K_R$ and SDS micelles associate more strongly with $\text{Os}(\text{bpy})_3^{2+}$ than with $\text{Os}(\text{bpy})_3^{3+}$. Higher electrolyte concentrations resulted in a more positive potential shift, which indicates that the association of SDS with $\text{Os}(\text{bpy})_3^{2+}$ was enhanced relative to that of $\text{Os}(\text{bpy})_3^{3+}$; i.e., $(K_O/K_R)' > K_O/K_R$ where the prime denotes a higher electrolyte concentration. Two types of interactions can be considered between the Os-species and the SDS molecules: electrostatic and hydrophobic. The stronger interaction of the Os(II) species suggests that the hydrophobic interaction, involving the bpy ligands and the hydrocarbon chains on the SDS, is

important. A similar phenomenon has been observed for association of SDS with methyl viologens of different oxidation states;^{14, 15)} i.e., SDS associates more strongly with MV^+ than with the MV^{2+} form. Similarly $\text{Ru}(\text{bpy})_3^{2+}$ is bound into Nafion more strongly than $\text{Ru}(\text{bpy})_3^{3+}$.²²⁾ This was also explained by the importance of hydrophobic interactions between the complex and the nonpolar regions of the Nafion.

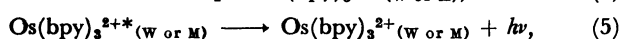
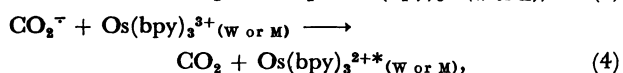
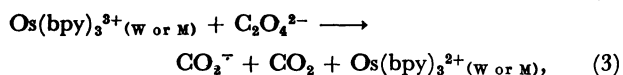
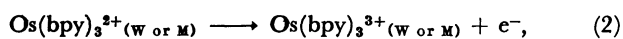
The observed depression of the peak current for the oxidation of $\text{Os}(\text{bpy})_3^{2+}$ at SDS levels below the cmc indicates that $\text{Os}(\text{bpy})_3^{2+}$ -surfactant aggregates are formed. By the same argument that has been applied to explain, for example, the shift in standard potential for 10-methylphenothiazine at premicellar concentrations of SDS,²¹⁾ the near independence of peak potentials for the oxidation of $\text{Os}(\text{bpy})_3^{2+}$ at these levels of SDS indicates that $\text{Os}(\text{bpy})_3^{2+}$ -SDS and $\text{Os}(\text{bpy})_3^{3+}$ -SDS complexes have essentially equal formation constants.

At concentrations of SDS above the cmc, the aggregation number of the micelles can be altered by changing the electrolyte concentration in solution.¹⁸⁾ In general, both theoretical treatments²³⁾ and experimental studies¹⁸⁾ show that higher electrolyte concentrations result in larger aggregation numbers. Thus with an increase of electrolyte (e.g., NaCl) concentration, the size of the micelle should increase and its diffusion coefficient should decrease. If the $\text{Os}(\text{bpy})_3^{2+}$ contained in the micelle was reduced directly at the electrode, one would predict that the oxidation peak current and the measured D_R would decrease with an increase in NaCl concentration. However, the experimental results showed that i_{pa} (Fig. 2a) and D_R (Fig. 5) both increased with an increase of NaCl concentration. This finding can be explained, however, using the same model as that of Saji et al.,²⁴⁾ for a similar finding for the oxidation of (11-ferrocenylundecyl)trimethylammonium bromide in the presence of SDS micelles. These authors showed that the ferrocenyl moiety incorporated in the micelle is not electroactive in the absence of added electrolyte. Earlier studies of others, given in this paper,²⁴⁾ have similarly found that a species incorporated in a micelle could become electroinactive. In the case described here, when $\text{Os}(\text{bpy})_3^{2+}$ penetrates the micellar surface, it associates strongly with the hydrocarbon core via hydrophobic interactions. This $\text{Os}(\text{bpy})_3^{2+}$ would not be electroactive, since the micelle would prevent it from coming within electron transfer distance to the electrode and small anions would not be available to maintain electroneutrality. These micelle-bound $\text{Os}(\text{bpy})_3^{2+}$ species would make no contribution to the anodic current. As found here, increasing the NaCl concentration increases the electroactivity of the micelle-bound $\text{Os}(\text{bpy})_3^{2+}$, presumably because of a greater availability of anions to

balance the positive charge formed during the electrode reaction and maintain electroneutrality.

The decrease in i_{pa} in the presence of CTAB, as well as the effect of NaCl concentration on i_{pa} , is much smaller than for SDS. This suggests a much weaker interaction, perhaps because of the electrostatic repulsion between CTAB and $\text{Os}(\text{bpy})_3^{2+}$, with the bulk of the current observed in the presence of CTAB originating from $\text{Os}(\text{bpy})_3^{2+}$ present in solution. By similar arguments, the interaction of $\text{Os}(\text{bpy})_3^{2+}$ and Triton X-100 is even weaker or absent.

In the present experiment, ECL was generated by the following mechanism:¹⁹



where the subscripts W and M represent the aqueous and micellar phases, respectively. If we assume the luminescence yields of $\text{Os}(\text{bpy})_3^{2+*}$ in the water and micellar phases are the same, there are two main factors affecting the ECL intensities: the amount of $\text{Os}(\text{bpy})_3^{2+}$ oxidized to $\text{Os}(\text{bpy})_3^{3+}$ and the nature of the environment of the reaction of $\text{CO}_2^{\cdot -}$ with $\text{Os}(\text{bpy})_3^{3+}$ to generate $\text{Os}(\text{bpy})_3^{2+*}$. In aqueous solution in the absence of surfactant and in Triton X-100 micellar solution, the NaCl concentration strongly affected the observed ECL intensity (Fig. 7). While we have not investigated the mechanism of this decrease in intensity with NaCl concentration, it probably involves perturbation of the reaction of $\text{CO}_2^{\cdot -}$ with $\text{Os}(\text{bpy})_3^{3+}$ [or $\text{Os}(\text{bpy})_3^{2+}$]. The ECL intensity of $\text{Os}(\text{bpy})_3^{2+*}$ emission in an acetonitrile solution produced by generation of the +1 and +3 species, increases 2.5 times with an increase in tetrabutylammonium hexafluorophosphate from 50 mM to 200 mM. In SDS micellar solution the ECL intensity was lower than that in the other media. As discussed above, the amount of $\text{Os}(\text{bpy})_3^{3+}$ generated, i.e., the oxidation current, is decreased in the presence of SDS. This leads to a strong decrease in the ECL intensity. The oxidation current was larger at higher NaCl concentrations, and in addition, the reaction of $\text{CO}_2^{\cdot -}$ with $\text{Os}(\text{bpy})_3^{3+}$ may take place in an environment that is less strongly perturbed by increases in ionic strength. This can account for the increase in ECL intensity as the NaCl concentration increased. The addition of CTAB decreased the intensity of ECL in 50 mM NaCl. In this case this decreased with added NaCl. The rate of decrease with increasing NaCl was not as high in the presence of CTAB as in aqueous NaCl solutions alone (Fig. 7), so that at NaCl concentrations above 200 mM, the ECL intensity in

the presence of CTAB was larger than in its absence.

The luminescence spectra also indicate an interaction of $\text{Os}(\text{bpy})_3^{2+}$ and SDS; the spectra strongly depend upon the SDS concentration. At the pre-cmc concentration level, the luminescence spectrum shows a peak wavelength at 710 nm, which is blue-shifted with respect to that at 730 nm in an aqueous solution without SDS. We ascribe this spectrum to an $\text{Os}(\text{bpy})_3^{2+}$ -SDS aggregate. When the SDS concentration was increased above the cmc, the spectrum showed a red shift with the peak wavelength at 765 nm. This apparently indicates a different type of interaction of $\text{Os}(\text{bpy})_3^{2+}$ with SDS micelles than in premicellar aggregates. While the luminescence spectrum has only one peak at 730 nm in aqueous solution, there is additional shoulder at 767 nm in a hexane solution of $\text{Os}(\text{bpy})_3^{2+}$. Thus the observed emission peak in SDS micelles at 765 nm can probably be attributed to a hydrophobic interaction.

Conclusion

Electrochemical techniques and ECL were used to study the interactions of the surfactants SDS, CTAB, and Triton X-100 with $\text{Os}(\text{bpy})_3^{2+}$ at different concentrations of electrolyte. The $\text{Os}(\text{bpy})_3^{2+}$ interacted most strongly with SDS, and at concentrations of SDS above the cmc and in the absence of added electrolyte (NaCl), both the electrochemical response and ECL (in the presence of oxalate) were suppressed. Addition of NaCl caused increases in both anodic current and ECL emission, although the levels remained below those under similar conditions in the absence of SDS. The interaction of $\text{Os}(\text{bpy})_3^{2+}$ with CTAB was much weaker, while that with Triton X-100 was almost absent.

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