The Effects of Nonionic Surfactants on the Tris(2,2′-bipyridyl)ruthenium(II)−Tripropylamine Electrochemiluminescence System
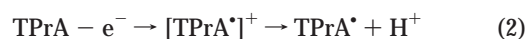
Scott Workman and Mark M. Richter*

Department of Chemistry, Southwest Missouri State University, Springfield, Missouri 65804

The electrochemistry and electrogenerated chemiluminescence (ECL) of Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridyl) were studied in the presence of the nonionic surfactants Triton X-100, Thesit, and Nonidet P40. The anodic oxidation of Ru(bpy)$_3^{2+}$ produces ECL in the presence of tri-*n*-propylamine in both aqueous and surfactant solutions. Increases in both ECL efficiency (≥8-fold) and duration of the ECL signal were observed in surfactant media. A shift to lower energies of the Ru(bpy)$_3^{2+}$ ECL emission by ∼8 nm was also observed. The one-electron oxidation of Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^{3+}$ occurs at +1.03 V vs Ag/AgCl in aqueous buffered (0.2 M potassium phosphate) solution as found by square wave voltammetry. This potential did not shift in surfactant systems, indicating that the red-shifts in ECL emission are due to stabilization of ligand π^* orbitals in the metal-to-ligand charge-transfer excited state. These results are consistent with hydrophobic interactions between Ru(bpy)$_3^{2+}$ and the nonionic surfactants.

Solubilization of molecules in aqueous, micellar surfactant solutions often leads to drastic changes in their photophysical and photochemical properties. For example, surfactants often increase the photoluminescence intensity and excited-state lifetimes of ruthenium−polypyridine complexes (e.g., Ru(bpy)$_3^{2+}$, where bpy = 2,2′-bipyridine).[1−4] Not surprisingly, interest in exploiting these phenomena has grown steadily. The interactions of transition metal complexes with surfactants continues to be of interest due to their applications in energy conversion and catalytic schemes[5,6] and as tags for the analysis of species at low concentrations.[7] Added to this is the industrial importance of surfactants in a wide range of applications (e.g., mining, oil drilling, food production).[8] Therefore, we wished to study the interactions of polypyridyl−Ru(II) complexes with various micellar systems by exploiting their long-lived metal-to-ligand charge-transfer (MLCT) emissions.

Electrochemiluminescence (ECL) involves the production of light near an electrode surface by the generation of species that can undergo highly energetic electron-transfer reactions.[9,10] One means of generating the excited states in ECL is by utilizing a coreactant, a species that can form energetic oxidants and reductants upon bond cleavage.[11,12] For example, in the Ru(bpy)$_3^{2+}$/TPrA system (TPrA = tri-*n*-proplyamine),[12] a strong reductant is generated during oxidation of TPrA that is then able to react with the oxidized form of the luminophore (i.e., Ru(bpy)$_3^{3+}$) to form the excited state:

$$Ru(bpy)_3^{2+} - e^- \rightarrow Ru(bpy)_3^{3+} \qquad (1)$$

$$TPrA - e^- \rightarrow [TPrA^\bullet]^+ \rightarrow TPrA^\bullet + H^+ \qquad (2)$$

$$TPrA^\bullet + Ru(bpy)_3^{3+} \rightarrow {}^*Ru(bpy)_3^{2+} + products \qquad (3)$$

where *Ru(bpy)$_3^{2+}$ is the light-emitting species.

The ECL of Os(bpy)$_3^{2+}$ is not affected by neutral and cationic surfactants (Triton X-100 and cetyltrimethylammonium bromide, respectively) but is attenuated by the anionic surfactant sodium dodecyl sulfate (SDS).[13] This was attributed to strong hydrophobic interactions between Os(bpy)$_3^{2+}$ and micellized SDS. Also, the ECL emissions of Ru(dp-bpy)$_3^{2+}$ and Ru(dp-phen)$_3^{2+}$ (dp-bpy = 4,4′-biphenyl-2,2′-bipyridyl and dp-phen = 4,7-diphenyl-1,10-phenanthroline) are attenuated in the presence of neutral surfactants (Triton X-100 and Tween 20), due to shielding of the

(1) Snyder, S. W.; Buell, S. L.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1989,** *93,* 5265.

(2) Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Photochem.* **1984,** *24,* 45.

(3) Hauenstein, Jr.; Dressick, W. J.; Gilbert, T. B.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1984,** *88,* 1902.

(4) (a) Mandal, K.; Hauenstein, B. L., Jr.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1983,** *87,* 328. (b) Dressick, W. J.; Hauenstein, B. L., Jr.; Gilbert, T. B.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1984,** *88,* 3337.

(5) See, for example: (a) Albery, W. J. *Acc. Chem. Res.* **1982,** *15,* 142. (b) Heller, A. *Acc. Chem. Res.* **1981,** *14,* 154.

(6) See, for example: (a) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980,** *102,* 7383. (b) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum: New York, 1994; Chapter 5. (c) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992; Chapter CHS 1.

(7) Blackburn, G. F.; Shah, H. P.; Kenten, J. H.; Leland, J.; Kamin, R. A.; Link, J.; Peterman, J.; Powell, M. J.; Shah, A.; Tulley, D. B.; Tyagi, S. K.; Wilkins, E.; Wu, T.-G.; Massey, R. J. *Clin. Chem.* **1991,** *37,* 1534.

(8) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989; Chapter 1.

(9) Faulkner, L.; Bard, A. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, pp 1−95.

(10) Faulkner, L. R.; Glass, R. S. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic Press: New York, 1982; p 191.

(11) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981,** *103,* 512.

(12) Leland, J. K.; Powell, M. J. *J. Electrochem. Soc.* **1990,** *1,* 257.

(13) Ouyang, J.; Bard, A. J. *Bull Chem. Soc. Jpn.* **1988,** 61.

ruthenium luminophore during the ECL reaction.[14] However, the effects of surfactants on the ECL system of $Ru(bpy)_3^{2+}$ and TPrA have not been reported.

Due to the analytical importance of ECL[7] and the fundamental and applied importance of nonionic surfactants, we were interested in observing their effects on the commercially important $Ru(bpy)_3^{2+}$/TPrA system.

EXPERIMENTAL SECTION

Materials. $Ru(bpy)_3Cl_2$ (98%, Strem Chemical Inc, Newbury Port, MA), potassium phosphate monobasic hydrate (99.0%, EM Science, Gibbstown, NJ), Nonidet P40 (Fluka, Milwaukee, WI), Thesit (Fluka, Milwaukee, WI), and Triton X-100 (Avocado, Ward Hill, MA) were used as received. Deionized water that had been passed through a Barnstead/Thermolyne filtration system was used throughout. 0.20 M potassium phosphate (KH_2PO_4) buffer was used for all dilutions. Solutions containing 0.05 M TPrA were prepared using the potassium phosphate buffer. It was necessary to stir the solution for 10 min to completely dissolve the amine.

Methods. Solutions used to obtain ECL intensity vs concentration and time profiles were 0.1 μM $Ru(bpy)_3^{2+}$, 0.05 M TPrA, 0.2 M phosphate buffer, and 0−1.0 mM surfactant (i.e., Nonidet P40, Thesit, or Triton X-100). The pH of these solutions was adjusted to 7.5 ($\pm$0.1) with 6 M HCl or 6 M NaOH. Solutions used to obtain ECL intensity vs pH profiles were 0.1 μM $Ru(bpy)_3^{2+}$, 0.05 M TPrA, 0.2 M phosphate buffer, and 0.1 mM surfactant. The pH of these solutions was varied from 3 to 8 in increments of 1 using 6 M HCl or NaOH. Electrochemistry and ECL experiments employed a CH Instruments model 620 electrochemical analyzer (Austin, TX). ECL emission intensities were measured with a Hamamatsu HC-135 photomultiplier tube. These experiments used a platinum mesh working electrode (27 mm²), a platinum wire auxiliary, and Ag/AgCl reference (0.2 V vs NHE).[15] Electrodes were cleaned after each experiment by cycling six times between −2.0 and +2.0 V vs Ag/AgCl at 0.1 V/s in concentrated sulfuric acid solution followed by sonication for ~20 s in dilute nitric acid. ECL was obtained by sweeping from 0 to +2.0 V at 0.1 V/s using cyclic voltammetry.

Solutions used to obtain diffusion coefficients and oxidative/reductive electrochemistry were 0.01 mM $Ru(bpy)_3^{2+}$, 0.2 M phosphate buffer, and 0−20 mM surfactant in 2 mM increments. Diffusion coefficient and oxidative/reductive electrochemistry utilized a glassy carbon working electrode in place of the platinum mesh. The glassy carbon electrode was cleaned by polishing with 15-μm diamond polish (Bioanalytical Systems Inc., Lafayette, IN). For diffusion coefficients, solutions were swept from 0.9 to 1.5 V at variable scan rates in the absence of TPrA and a plot of i_{pa} vs square root scan rate ($v^{1/2}$) was developed. Due to background oxidative processes (i.e., oxidation of water), square wave voltammetry[16] was used to determine $E°$ for the metal-based oxidation $(Ru^{II}(bpy)_3^{2+} − e^- \rightarrow Ru^{III}(bpy)_3^{3+})$ by sweeping from +0.9 to +1.2 V at 0.2 V/s.

ECL spectra were obtained using a Shimadzu RF-5301 spectrofluorophotometer. Emission from $*Ru(bpy)_3^{2+}$ were recorded

(14) McCord, P.; Bard, A. J. *Electroanal. Chem.* **1991**, *318*, 91.
(15) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.
(16) Kissinger, P. T.; Heineman, W. R. *Laboratory Techniques in Electroanalytical Chemistry*; Dekker: New York, 1996; pp 158−159.

Chart 1. Structrues, Approximate Molecular Weights, and Critical Micelle Concentrations of the Nonionic Surfactants Studied
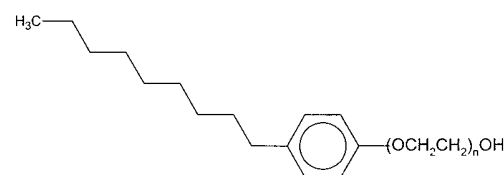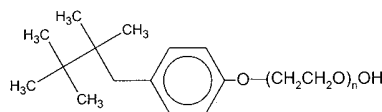

Nonidet P40® (nonylphenylpolyethylene glycol) n=9-10, MW≈646.86 g/mol.

CMC=0.75mM[32]
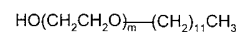
Thesit® (polyethylene glycol 400 dodecyl ether) m=9-10, MW≈600 g/mol.

CMC=0.1mM[32]

Triton X-100® (polyethylene glycol tert-octylphenyl ether) n=9-10, MW≈646.86 g/mol.

CMC=0.33mM[32]

between 550 and 650 nm. These experiments utilized a platinum working electrode (6 cm × 9 cm), platinum wire auxiliary, and Ag/AgCl reference. Solutions were composed of 0.1 mM $Ru(bpy)_3^{2+}$, 0.05 M TPrA, 0.2 M phosphate buffer, and 4 mM surfactant. Electrodes were cleaned as described above by cycling in sulfuric acid followed by sonication in dilute HNO_3. ECL was obtained by sweeping 0 to +2.0 V at 0.1 V/s via cyclic voltammetry.

RESULTS AND DISCUSSION

Electrochemistry. Square wave voltammetry experiments were used to study the effect of Triton X-100, Nonidet P-40, and Thesit (Chart 1) on the redox potentials for the oxidation of $Ru(bpy)_3^{2+}$. Oxidation peaks ($E°$) were observed in all three micellar solutions at values of 1.03 V vs Ag/AgCl ($\pm$0.01 V) due to the reversible one-electron oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ (Figure 1). The redox potentials are nearly independent of the concentration of surfactant media. Similar results were reported for $Os(bpy)_3^{2+}$ in the presence of Triton X-100 micelles.[13] The lack of an oxidative potential shift implies that the micelles do not bind more strongly to $Ru(bpy)_3^{3+}$ when compared to $Ru(bpy)_3^{2+}$. This is in contrast to $Os(bpy)_3^{2+}$ in the presence of SDS, an anionic surfactant,[13] and $Ru(bpy)_3^{2+}$ when it was bound in Nafion, a sulfonate-containing polymer.[17] In both instances, a positive potential shift was observed in the metal-based oxidation indicating that $Ru(bpy)_3^{3+}$ interacted more strongly than $Ru(bpy)_3^{2+}$ with anionic media. In binding to nonionic micelles, nonelectrostatic or hydrophobic interactions are expected to take an important role. Photoluminescence studies have shown that the binding between $Ru(bpy)_3^{2+}$ and Triton X-100 micelles is probably van der Waals or hydrophobic in nature.[18] Therefore, binding is by competition between water and the micelles for solvation of the complexes. Square wave voltammetry indicates that if an interac-

(17) Martin, C. R.; Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4817.
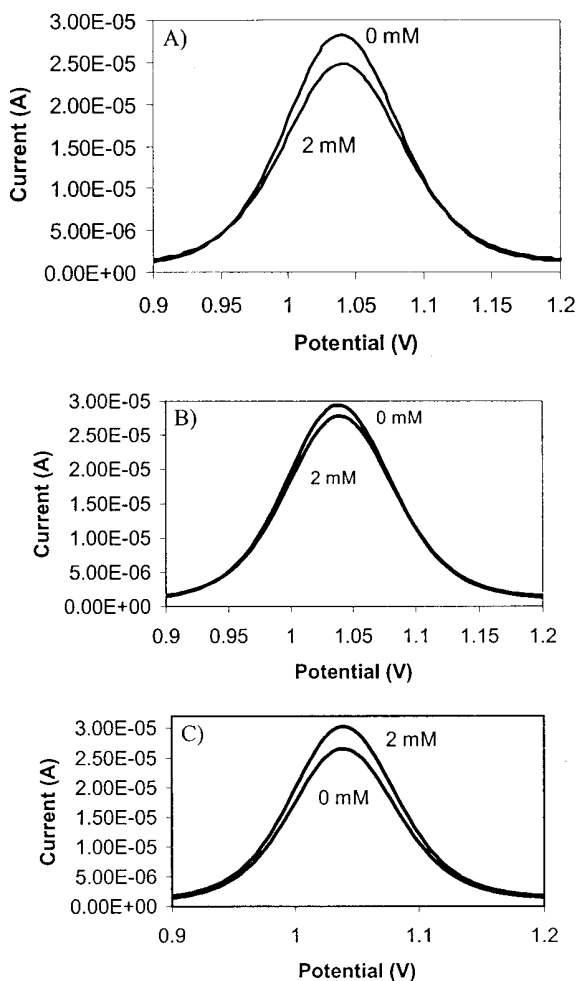(18) Mandal, K.; Hauenstein, B. L., Jr.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1983**, *87*, 328

Figure 1. Square wave voltammogram varying the concentration of surfactant (0 and 2 mM) for ∼0.01 mM $Ru(bpy)_3^{2+}$ and 0.05 M TPrA in 0.2 M phosphate buffer: (A) Nonidet P-40; (B) Triton X-100; (C) Thesit.

Figure 2. Intensity vs concentration of surfactant plots for Ru-$(bpy)_3^{2+}$ (0.1 μm), $C_9H_{21}N$ (0.05 M), and potassium phosphate buffer (0.2 M). Error bars are ±10%.

tion between $Ru(bpy)_3^{2+/3+}$ and micelles is occurring, it is weak. However, the depression in peak current for the oxidation of Ru-$(bpy)_3^{2+}$ at Nonidet P-40 and Triton X-100 concentrations greater than 2 mM indicates that $Ru(bpy)_3^{2+}$/micelle aggregates are formed. Surprisingly, the oxidative peak current for $Ru(bpy)_3^{2+}$ increases in the presence of Thesit. The reasons for this are unclear, but seem to indicate weaker interactions between Ru-$(bpy)_3^{2+}$ and Thesit micelles as compared to Triton and Nonidet. Due to background reductive processes, it was not possible to successfully isolate the ligand reductions of the $Ru(bpy)_3^{2+}$ complex in purely aqueous or aqueous surfactant solutions.

Diffusion coefficients (D_o), the rate at which electroactive molecules diffuse to the surface of an electrode, are one measure of the association of electroactive molecules with surfactants and micelles. A plot of i_{pa} vs the square root of the scan rate ($v^{1/2}$) for $Ru(bpy)_3^{2+}$ in the presence and absence of surfactant is linear.[19] This indicates that the oxidation of $Ru(bpy)_3^{2+}$ in aqueous solution

($Ru(bpy)_3^{2+}{}_{(aq)}$) and $Ru(bpy)_3^{2+}$ in micellar solution ($Ru(bpy)_3^{2+}{}_{(m)}$) is diffusion-controlled.[20] Diffusion coefficients for $Ru(bpy)_3^{2+}{}_{(m)}$ are 4.70×10^{-8} cm²/s for Triton, 3.76×10^{-8} cm²/s for Nonidet, and 3.30×10^{-8} cm²/s for Thesit, determined from the slope of i_{pa} vs $v^{1/2}$. These are significantly smaller than $Ru(bpy)_3^{2+}{}_{(aq)}$ (7.33×10^{-8} cm²/s), indicating that the electrochemically active species in the presence of surfactant is micelle-solubilized $Ru(bpy)_3^{2+}{}_{(m)}$ in the bulk solution.[21] This is consistent with other studies involving association of electroactive molecules with surfactants and micelles.[13,22−24] From the slopes of i_{pa} vs $v^{1/2}$, the diffusion coefficients appear to be affected the most by Nonidet P40 and Triton X-100, consistent with the voltammetric studies.

Electrogenerated Chemiluminescence. ECL was generated as outlined in eqs 1−3. The intensity of the $Ru(bpy)_3^{2+}$ ECL emission depends on the concentration of nonionic surfactant (Figure 2). In all cases, at concentrations well below the reported critical micelle concentrations (cmc) of 0.75, 0.10, and 0.33 mM for Nonidet P40,[13] Thesit,[13] and Triton X-100,[13] respectively, the ECL signal increases. This indicates binding is occurring between the $Ru(bpy)_3^{2+}$ molecule and surfactant molecules.[4,5]

(19) $Ru(bpy)_3^{2+}$ (0.01 mM), $C_9H_{21}N$ (0.05 M), buffer (0.2 M), surfactant (2 mM). With no surfactant, $y = 2.074 \times 10^{-6}x - 0.0254 \times 10^{-6}$ and $R^2 = 0.9921$; with Thesit, $y = 1.6594 \times 10^{-6}x - 0.0137 \times 10^{-6}$ and $R^2 = 0.9978$; with Triton X-100, $y = 1.3905 \times 10^{-6}x - 0.0098 \times 10^{-6}$ and $R^2 = 0.9966$; and with Nonidet P40, $y = 1.4855 \times 10^{-6}x - 0.0139 \times 10^{-6}$ and $R_2 = 0.9963$.
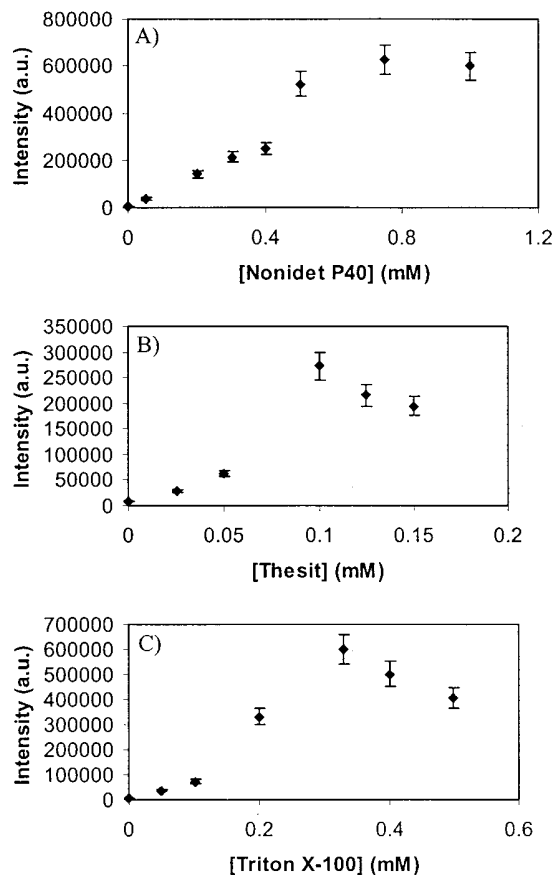
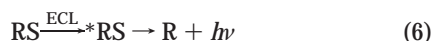(20) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 218.
(21) Lee, S. K.; Bard, A. J. *Anal. Lett.* **1998**, *31*, 2209.
(22) Ohawa, Y.; Shimazaki, Y.; Aoyagui, S. *J. Electroanal. Chem.* **1980**, *114*, 235.
(23) McIntire, G. L.; Chiapppardi, D. M.; Casselberry, R. L.; Blount, H. N. *J. Phys. Chem.* **1982**, *86*, 2632.
(24) Kaifer, A. E.; Bard, A. J. *J. Phys. Chem.* **1985,** *89*, 4876.

Equations 4–8 describe some of the possible interactions between a reporter molecule (R) and a surfactant monomer (S) or micelle (M):

$$R \xrightarrow{ECL} {}^*R \rightarrow R + h\nu \qquad (4)$$

$$R + S \rightleftharpoons RS \qquad (5)$$

$$RS \xrightarrow{ECL} {}^*RS \rightarrow R + h\nu \qquad (6)$$

$$R + M \rightleftharpoons RM \qquad (7)$$

$$RM \xrightarrow{ECL} {}^*RM \rightarrow RM + h\nu \qquad (8)$$

It is assumed that R or *R can interact with S or M to form association species RS and *RS or RM and *RM. Unfortunately, these ECL measurements can only monitor species containing *R. Also, there is very little information available concerning photoluminescence or ECL emission in the pre-cmc region (i.e., RS or *RS), making definitive conclusions about the reasons for the observed increases impossible. However, it is known that organic and transition metal complexes may serve as nucleating sites for surfactant micelle formation. The concept of induced micelle formation or the formation of premicellar aggregates[25] (formation of micelles in the presence of an added solute at surfactant concentrations below the normal cmc) has been used to describe spectral changes in a number of systems (e.g., pinacyanol in sodium lauryl sulfate solution[14]).[18,26] These assemblies are believed to form as a result of nucleation rather than as a result of binding of the reporter molecule to existing micelles that may form in bulk solution at the normal cmc of the surfactant.

From prior photophysical[4–6] and ECL[13,14,21] studies in micellar media, we assume that the changes in ECL intensities are caused by partitioning of the complexes between free and surfactant-bound forms and that the different forms exhibit different intensities. Since the ECL intensity increases with increasing concentration of surfactant up to the cmc, it appears the bound forms have higher intensities. The cmc is the concentration at which species equilibria favor formation of micelles over unassociated surfactant molecules.[8] Below the cmc, complexes can be formed between dissolved species (e.g., $Ru(bpy)_3^{2+}$) and surfactant molecules while above the cmc the surfactant exists in solution primarily as micelles, and dissolved species may partition between the micellar and water phases. These observations, coupled with detailed photochemical and photophysical studies,[1–3] strongly suggest that the surfactants interact with the reporter molecules and that there is an equilibrium between the bound and unbound forms of the complex. The interaction is sufficiently strong to influence surfactant assembly and ECL emission intensities at surfactant concentrations well below the cmc. Surfactant concen-

trations of 0.5–1 mM and $[Ru(bpy)_3^{2+}] \approx 1 \times 10^{-5}$ M also ensure that >99% binding of $Ru(bpy)_3^{2+}$ in micelles occurs and that >99% of these micelles contain only one $Ru(bpy)_3^{2+}$ molecule.[27] It is also apparent that the coreactant and solubilized $Ru(bpy)_3^{2+}$ react across the surfactant micelles and are not solubilized in separate microenvironments. This is in contrast to the ECL of diphenyl-substituted derivatives (i.e., $Ru(dp\text{-}bpy)_3^{2+}$ and $Ru(dp\text{-}phen)_3^{2+\prime\prime}$) in the presence of the neutral surfactants Triton X-100 and Tween 20 using TPrA as a coreactant.[14] Decreased ECL in the diphenyl systems was attributed to shielding of the luminophores by micelles during the ECL reaction.[14] The reason for the contrasting behavior of $Ru(bpy)_3^{2+}$ and $Ru(dp\text{-}bpy)_3^{2+}$ and $Ru(dp\text{-}phen)_3^{2+}$ is unclear. Theoretical models based on changes in excited-state lifetimes and fluorescence spectra indicate that the degree of binding of ruthenium polypyridyl compounds in micelle structures depends on the nature and degree of ligand substitution.[4,18] The increased hydrophobicity of the diphenyl-substituted compounds may lead to greater binding as compared to $Ru(bpy)_3^{2+}$ or binding of $Ru(dp\text{-}bpy)_3^{2+}$ and $Ru(dp\text{-}phen)_3^{2+}$ in a region that is shielded from the electrode and/or the coreactant.[14]

TPrA was also used to generate ECL for the heptamethine cyanine dye IR-144 ($C_{56}H_{73}N_5O_8S_2$) in SDS surfactant media.[21] Increased intensities were observed (compared to solutions containing no SDS) and attributed to enhanced solubility of IR 144 and decreased aggregation of the dye molecules in SDS media.[21] Due to the hydrophobic nature of the micelle, and the organic nature of the reporter and coreactant molecules, the increased ECL intensity with $Ru(bpy)_3^{2+}$ may be due to the exclusion of water from the emitting environment[1,2,13,23] and the increased solubility of $Ru(bpy)_3^{2+}$ and TPrA in surfactant media.

The observed increases in ECL may also be due to incorporation of TPrA into the surfactant assemblies. Unfortunately, these experiments cannot probe the extent of TPrA "micellization" and its effects on ECL properties. However, TPrA was used as a coreactant in aqueous media containing Triton X-100 in the present work, as well as in both the diphenyl-substituted[14] and heptamethine cyanine dye[21] studies discussed above. The contrasting behavior between the studies, most notably the decreases observed in the diphenyl systems and the increases observed in the present work, make it apparent that changes in TPrA solubility cannot solely account for the dramatic changes observed in ECL properties and that surfactant/luminophore interactions clearly play a role.

ECL intensity vs time transients are shown in Figure 3. The potential of the working electrode was stepped to +2.0 V, and the ECL intensity measured. As expected, there was a sharp increase in light intensity due to the higher concentrations of coreactant and $Ru(bpy)_3^{2+}$ near the electrode surface. At times longer than 7 s (there is a 5-s delay before the onset of ECL to allow for a stable background measurement in Figure 4), the ECL becomes diffusion controlled and the $Ru(bpy)_3^{2+}{}_{(m)}$ solutions decay to background levels at a slower rate than $Ru(bpy)_3^{2+}{}_{(aq)}$. The magnitude of the increases in both ECL intensity and duration of the signal (i.e., rate of decay) depend on the identity of the nonionic surfactant.

(25) See, for example: (a) Brauenstein, C. H.; Baker, A. P.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857. (b) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849. (c) Cooper, J. B.; MacQueen, D. B.; Petersen, J. D.; Wertz, D. W. *Inorg. Chem.* **1990**, *29*, 3701. (d) Dose, E. V.; Wilson, L. *Inorg. Chem.* **1978**, *17*, 2660. (e) Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 2827.

(26) (a) Green, F. A. *J. Colloid Interface Sci.* **1972**, *41*, 124. (b) Chaimovich, H.; Blanco, A.; Chayet, L.; Costa, L. M.; Monteiro, P. M.; Bunton, C. A. *Tetrahedron* **1975**, *31*, 1139. (c) Kasumoto, Y.; Sato, H. *Chem. Phys. Lett.* **1979**, *68*, 13.

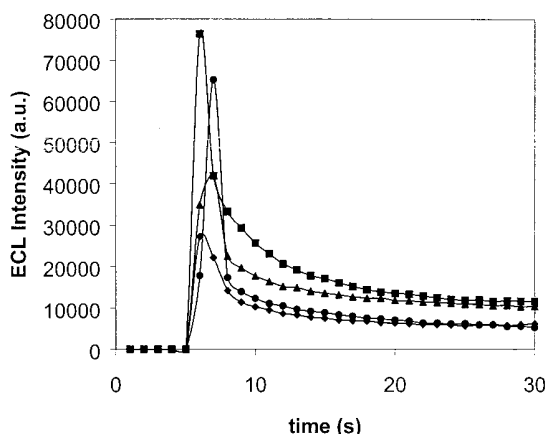(27) Dressick, W. J.; Cline, J., III; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 7567–7574.

Figure 3. Intensity vs time plot for $Ru(bpy)_3^{2+}$ (0.1 μM), TPrA (0.05 M), buffer (0.2 M), and surfactant (0.1 mM): (■) Nonidet P40; (●) Triton; (▲) Thesit; (◆) no surfactant. Error bars are omitted for claity.
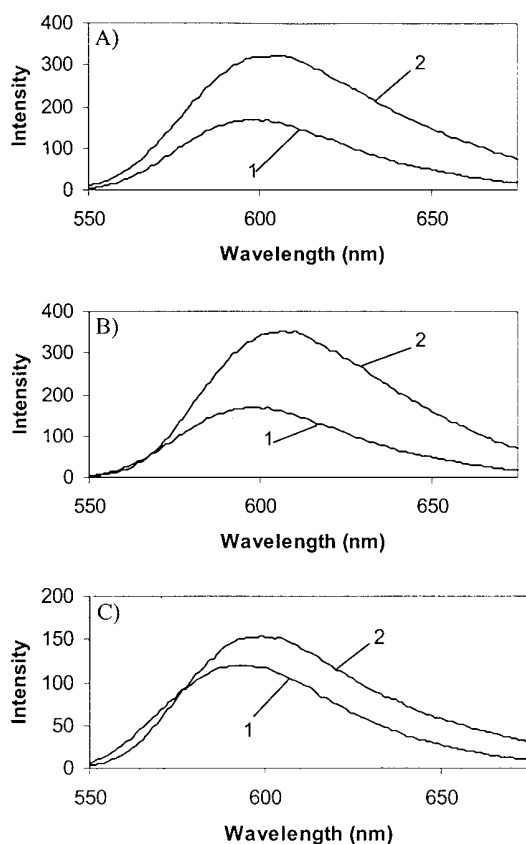

Figure 4. ECL Intensity vs wavelength for 0.1 mM $Ru(bpy)_3^{2+}$, 0.05 mM TprA, and 0.2 M phosphate buffer: (A) Nonidet P40 (1) 0 and (2) 4 mM; (B) Thesit (1) 0 and (2) 4 mM; (C) Triton X-100 (1) 0 and (2) 4 mM. Slit widths, 3 nm.

The ECL results indicate that, whatever the nature of the pre-cmc complexes, the interaction is sufficiently strong enough to (1) influence ECL (and surfactant assembly) at Nonidet P40, Thesit, and Triton X-100 concentrations below the cmc and (2) result in a ≥8-fold increase in ECL intensity at the cmc. Also, ECL intensities appear to be the most affected by Nonidet P40 and Triton X-100, consistent with voltammetric and diffusion coefficient studies. This is probably due to the structure of the micelles and micelle/substrate complexes.[24,28] Triton, Thesit, and Nonidet

surfactant molecules all have a common poly(ethylene oxide) hydrophilic region (Chart 1). However, the hydrophobic regions of Triton and Nonidet differ from that of Thesit. Triton and Nonidet contain a branched hydrocarbon-substituted phenoxy group while Thesit possesses long-chain *n*-alkyl or alkene groups. Despite these differences, all surfactants are assumed to form micelles of similar structure consisting of a dry central hydrocarbon or aromatic core and a wet outer sheath of hydrated poly(ethylene oxide) units.[29] Therefore, it is likely that the aromatic region of the Triton and Nonidet are better solvents for the aromatic ligands than the alkane chain system of Thesit.

With the addition of surfactant, there is a shift in peak emission maximums toward longer wavelengths by approximately 8−10 nm (Figure 4). This red-shift for $Ru(bpy)_3^{2+}$ ECL emission in surfactant solution clearly shows an interaction between these species and suggests that the ligand $\pi-\pi^*$ energy gap decreases due to interactions of the ligand π^* orbitals with the hydrophobic regions of the micelles. Due to background reductive processes, it was not possible to successfully isolate the ligand reductions of the $Ru(bpy)_3^{2+}$ complex in purely aqueous or aqueous surfactant solutions. However, no shift in the metal-based $Ru^{II/III}$ oxidation peak potential occurs as the concentration of surfactant is increased. Since the separation between the metal-based oxidation $(Ru^{II}(bpy)_3^{2+} - e^- \rightarrow Ru^{III}(bpy)_3^{3+})$ and the first ligand-based reduction $(Ru^{II}(bpy)_3^{2+} + e^- \rightarrow Ru^{II}(bpy^{\bullet-})(bpy)_2^+)$ is a rough measure of the MLCT energy gap,[6,25] the most likely mechanism for the shift of ECL spectra is stabilization of the ligand-based orbitals.

The ECL emission is pH dependent, with maximum intensities observed at pH ∼8. Similar trends are observed in the absence of surfactants[12,30] and indicate that the micelles do not interact directly in ECL generation. This is also important for ECL applications since the pH of environmental and biological systems is ∼7.5 and would require less sample preparation prior to analysis.

CONCLUSIONS

Interactions of the $Ru(bpy)_3^{2+}$ ECL excited with nonionic surfactants have yielded significant, and potentially useful, changes in emission properties. For example, addition of surfactant at or below the cmc has resulted in a ≥8-fold increase in ECL intensity, a red-shift in the emission, and increases in the duration of the emission from ∼2 to 5 s upon application of a potential pulse. These changes reflect the substantial variations in the environment of the emitting MLCT state.

Clearly, binding of $Ru(bpy)_3^{2+}$ to nonionic surfactants containing poly(ethylene)oxide units is a general phenomenon. Several factors appear to affect the ECL intensities: the amount of $Ru(bpy)_3^{2+}$ oxidized to $Ru(bpy)_3^{3+}$, the reaction of the strong reductant (TPrA•) with $Ru(bpy)_3^{3+}$ to form *$Ru(bpy)_3^{2+}$, and the nature of the $Ru(bpy)_3^{2+}$/micelle microenvironment. Other factors, including $Ru(bpy)_3^{2+}$ binding mode, orientation, and solvent accessibility may affect the chemistry and ECL of the bound ECL

(28) Rusling, J. F. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, pp 1−88.

(29) (a) Robson, R. J.; Dennis, E. A. *J. Phys. Chem.* **1977**, *81*, 1075 (b) Tanford, C.; Nozaki, Y.; Rhode, M. F. *J. Phys. Chem.* **1977**, *81*, 1555. (c) Paradies, H. H. *J. Phys. Chem.* **1980**, *84*, 599. (d) Tanford, C.; Nozaki, Y.; Rhode, M. F. *J. Phys. Chem.* **1977**, *81*, 1555.

(30) Alexander, C.; McCall, J.; Richter, M. M. *Chem. Educ.* **1998**, *3*, 1.

luminophores. However, a full understanding of these micelle-substrate interactions in ECL systems is currently lacking. Detailed studies of derivatized ruthenium systems (e.g., $Ru(bpy)_2$-$(R\text{-}bpy)^{2+}$, where R-bpy is a substituted bipyridine ligand) are underway to investigate the role of ligand modification on ECL in surfactant solution. On the basis of photochemical and photophysical precedents,[1-3] the introduction of substituents to the polypyridyl rings will affect the way in which the reporter complex interacts with the micelles, allowing us to further probe micelle/reporter interactions.