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# Redox Reactions of Lipophilic Cobalt Complexes in Aqueous Surfactant Media. Correlation of Rate and Electrochemical Behavior

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The effect of added surfactants, sodium dodecylsulfate (SDS), Triton X-100 ($C_8H_{17}C_6H_4(OCH_2CH_2)_xOH$, $x$ = 9, 10), and cetyltrimethylammonium bromide (CTAB), on measured rate constants for electron transfer between $Co(terpy)_2{}^{2+}$ and a series of cobalt(III) complexes, $[Co(phen)_3]^{3+}$, $[Co(5\text{-}Cl\text{-}phen)_3]^{3+}$, $[Co(5\text{-}Me\text{-}phen)_3]^{3+}$, $[Co(5,6\text{-}Me_2\text{-}phen)_3]^{3+}$, $[Co(5\text{-}SO_3\text{-}phen)_3]$, and $[Co(dipic)_2]^-$, varying in ligand structure and ionic charge, have been determined by stopped-flow spectrophotometry. The observed rate catalysis or inhibition, resulting from micellar interactions, has been rationalized using the Berezin model. Information on micellar binding, afforded by the kinetic data, correlates with electrochemical changes, particularly changes in anodic and cathodic peak currents and half-wave potentials, determined by cyclic voltammetry, that result on addition of surfactant solutions to the cobalt complexes. Strong hydrophobic interactions dominate the micellar binding of divalent cationic terpyridine and phenanthroline complexes with SDS micelles, and the enhanced stabilization of the reduced state in the micellar environment is reflected in the magnitude of the observed potential shifts. The presence of the polar $SO_3{}^-$ substituent in the neutral sulfonated cobalt(III) phenanthroline complex inhibits its association with anionic SDS. Potential shifts for the anionic $Co(dipic)_2$ complex in Triton X-100 and CTAB also appear to reflect changes in the relative stability of oxidation states in the surfactant media.

## Introduction

Diffusion-controlled peak currents and formal potentials of micellar bound complex ions are strongly dependent on surfactant and substrate structures.[1-5]. Electrochemical studies of lipophilic metal complexes in micellar solutions therefore provide a means of examining the nature of the interaction existing between surfactant micelles and complex ions used as electrochemical probes. Since such investigations yield information on mcellar binding by substrate ions in different oxidation states, they are able to provide particular insight into the delicate balance between hydrophobic and electrostatic interactions existing for lipophilic ions.

We have previously carried out an electrochemical investigation of the effect of SDS micelles on the redox behavior of the lipophilic cobalt complexes $[Co(phen)_3](ClO_4)_3$ and $[Co(terpy)_2](ClO_4)_2$, using cyclic voltammetry, chronoamperometry, and chronocoulometry.[5] The [SDS] dependence of measured diffusion coefficients was used to estimate micellar binding constants and partition coefficients for both oxidized and reduced species, and shifts in $E_{1/2}$, which accompanied the micellar associations, were rationalized in terms of the relative stabilization of the oxidation states, comprising the redox couples, in the micellar media. Semiquantitative estimates of hydrophobic and electrostatic contributions to micellar binding by the different redox states of the cobalt complexes were also made.

To explore further micellar interactions existing for complex ions, as well as their effects on reaction rates, we have made a kinetic study of the effect of added surfactants on electron transfer reactions between $Co(terpy)_2{}^{2+}$ and a series of cobalt(III) oxidants, $[Co(phen)_3]^{3+}$, $[Co(5\text{-}Me\text{-}phen)_3]^{3+}$, $[Co(5,6\text{-}Me_2\text{-}phen)_3]^{3+}$, $[Co(5\text{-}Cl\text{-}phen)_3]^{3+}$, $[Co(5\text{-}SO_3\text{-}phen)_3]$, and $[Co(dipic)_2]^-$, in which the ionic charge and hydrophobic nature of the ligands is varied. We have correlated the rate catalysis or inhibition observed kinetically with electrochemical changes that take place on addition of surfactants to the reactant complexes under similar experimental conditions. Data obtained in anionic (SDS), nonionic Triton X-100, and cationic (CTAB) surfactant solutions have been compared.

Although both kinetic and electrochemical investigations of the redox behavior of complex ions in micellar media have been carried out,[6-19] few attempts at correlation of data obtained by the two approaches have been reported. Deutsch *et al.*[20] have found that electrochemical data obtained for lipophilic cationic Tc and Re complexes containing DMPE ligands (DMPE = 1,2-bis(dimethylphosphino)ethane), in micellar solutions, do not correlate well with information obtained kinetically, and have cautioned against overinterpreting electrochemical data in surfactant solution, because of complications that can arise from the interactions of surfactants and lipophilic substrates at hetero-

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geneous electrode surfaces. Our findings enable some of the questions raised in their study to be examined over a wider range of substrate–micelle interactions. The study also extends the examination of medium effects on $Co(phen)_3^{3+}$–$Co(terpy)_2^{2+}$ electron transfer rates previously reported.[21]

## Experimental Section

**Materials.** $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$,[22] $[Co(terpy)_2](ClO_4)_2 \cdot H_2O$,[23] and the bis(dipicolinato)cobalt(III) complex $(NH_4)[Co(dipic)_2]$,[24] were prepared by literature procedures. The chloride salts $[Co(phen)_3]Cl_3 \cdot 7H_2O$, $[Co(5\text{-}Me\text{-}phen)_3]Cl_3$, $[Co(5,6\text{-}Me_2\text{-}phen)]Cl_3$, and $[Co(5\text{-}Cl\text{-}phen)_3]Cl_3$ were prepared by the method of Pfeiffer and Werdelmann.[25] $[Co(5\text{-}SO_3\text{-}phen)_3] \cdot 10H_2O$ was prepared from $CoCl_2 \cdot 6H_2O$ and the sulfonated phenanthroline ligand 5-$SO_3$-phen.[21] 5-$SO_3$-phen was obtained as cream-colored crystals by sulfonation of 1,10-phenanthroline with ammonium bisulfate at 365–370 °C for 4 h. Separation from the more soluble 3-isomer and recrystallization from water was achieved by the method of Blair and Diehl.[26] The ligands terpy (2,2′:6′,2″-terpyridine) and phen (1,10-phenanthroline) and the methyl and chloro- substituted phenanthroline complexes were obtained from the G.F.S. Co. Dipicolinic acid (2,6-pyridinedicarboxylic acid) was from the Aldrich Chemical Co. Ultrapure grade sodium dodecyl sulfate, from Mannheim Biochemicals, and Triton X-100, from Aldrich, were used as received. Cetyltrimethylammonium bromide, from the Aldrich Chemical Co., was purified by washing with diethyl ether and recrystallization from methanol.[27] $LiCF_3SO_3$ and LiCl were prepared by adding $Li_2CO_3$ to concentrated acid, $CF_3SO_3H$ and HCl, adjusting the volume with distilled water, heating the filtered solution to boiling to remove $CO_2$, and neutralizing to pH 7 with dilute acid or LiOH solution. Stock solutions were analyzed by passage of aliquot portions through Dowex 50W-X8(H) cation exchange resin and titrating the eluent with standard base. $CF_3SO_3H$, from the 3M Co., was purified by reduced pressure distillation.

**Kinetic Measurements.** An Aminco stopped-flow spectrophotometer, coupled to a Nicolet 2090 digital oscilloscope and a Hewlett Packard Vectra ES/12 computer was used for data collection and calculation of rate constants. Reactions were carried out under pseudo-first-order conditions with cobalt(III) oxidants, at *ca.* $4 \times 10^{-4}$ M in excess of $Co(terpy)_2^{2+}$ at *ca.* $4 \times 10^{-5}$ M. First-order plots were linear to at least 3 half-lives. Reactions were followed at 505 nm, where $Co(terpy)_2^{2+}$ has its maximum visible absorbance ($\epsilon$ = 1400 $M^{-1}$ $cm^{-1}$).[22,23] Three rate determinations were usually carried out for each filling of the stopped flow instrument.

**Electrochemical Measurements.** Cyclic voltammetry was performed using a BAS voltammograph and a Houston Instrument Model 2000 Omnigraphic recorder. Potentials were measured, in deoxygenated solutions under argon, using a glassy-carbon working electrode (BAS, MF2112), a Pt-wire auxiliary electrode, and a BAS saturated calomel (SCE) or Ag/AgCl reference electrode. The working electrode was polished with an alumina–water suspension on a felt surface and sonicated prior to use. The BAS electrochemical cell was thermostated at 25.0 ± 0.1 °C. Solutions at different surfactant concentrations were generated by adding small volumes of stock surfactant solution to the cobalt complex in the electrochemical cell, using a microsyringe. Under the experimental conditions, the effect of free surfactant and surfactant micelles on liquid junction potentials is negligible due to their low concentrations compared to that of the supporting electrolyte (0.20 M $LiCF_3SO_3$ or 0.20 M LiCl). Open circuit potential measurement of the glassy-carbon working electrode, with respect to a Ag/AgCl, saturated KCl, reference electrode with a Vycor junction, shows a potential of 226 ± 1 mV over the entire range of *SDS* concentrations used in this study.

## Results and Discussion

**Kinetics of $Co(terpy)_2^{2+}$ Reduction of Cationic Cobalt(III) Phenanthroline Complexes in SDS Solutions.** The kinetic data for electron transfer between $Co(terpy)_2^{2+}$ and cobalt(III) phenanthroline complexes, $CoL_3^{3+}$ (L = phen, 5-Me-phen, 5,6-$Me_2$-phen, 5-Cl-phen), in SDS solutions is typical of micellar catalysis involving both reactants residing predominantly in the micellar phase. Data, summarized in Table 1 and illustrated in Figure 1, show second-order rate constants for $Co(phen)_3^{3+}$–$Co(terpy)_2^{2+}$ electron transfer, measured as a function of surfactant concentration, passing through a maximum near the cmc. The data conforms to the Berezin model which considers surfactant solutions, above the critical micelle concentration, as a two phase system with the reactants partitioned between the aqueous and micellar pseudophases.[28]

**Table 1.** Rate Data for the $Co(terpy)_2^{2+}$–$Co(phen)_3^{3+}$ Electron Transfer in SDS[a]

| [$LiCF_3SO_3$] = 0.10 M | | | | [$LiCF_3SO_3$] = 0.20 M | |
|---|---|---|---|---|---|
| [SDS], M | $10^{-3}k_{2(obs)}$, $M^{-1}$ $s^{-1}$ | [SDS], M | $10^{-3}k_{2(obs)}$, $M^{-1}$ $s^{-1}$ | [SDS], M | $10^{-3}k_{2(obs)}$, $M^{-1}$ $s^{-1}$ |
| 0.0 | 0.240 | 0.045 | 7.12 | 0.0 | 0.876 |
| 0.0005 | 3.84 | 0.0052 | 5.23 | 0.00101 | 6.90 |
| 0.0010 | 9.68 | 0.0060 | 3.34 | 0.00200 | 9.43 |
| 0.0015 | 11.5 | 0.0080 | 1.59 | 0.00252 | 10.6 |
| 0.0020 | 13.3 | 0.0100 | 1.08 | 0.00310 | 8.94 |
| 0.0020 | 12.8 | 0.0100 | 1.13 | 0.00400 | 6.21 |
| 0.0025 | 11.5 | 0.0150 | 0.498 | 0.00800 | 1.34 |
| 0.0030 | 10.9 | 0.0200 | 0.304 | 0.0100 | 0.844 |
| 0.0035 | 10.2 | 0.0300 | 0.189 | 0.0180 | 0.310 |
| 0.0037 | 9.64 | 0.0500 | 0.104 | 0.0240 | 0.219 |
| 0.0040 | 8.40 | | | 0.0360 | 0.143 |
| | | | | 0.0502 | 0.0695 |

[a] 25.0 °C.

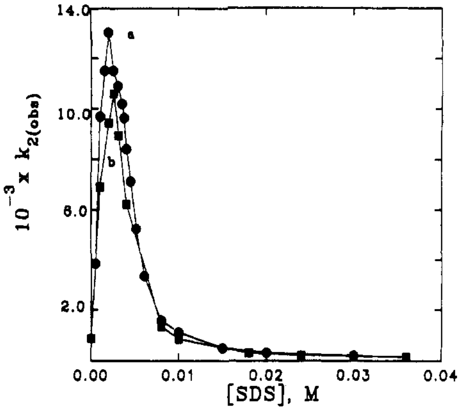

**Figure 1.** Effect of SDS on second-order rate constants for $Co(terpy)_2^{2+}$ reduction of $Co(phen)_3^{3+}$ in $LiCF_3SO_3$: (a) 0.10 M $LiCF_3SO_3$; (b) 0.20 M $LiCF_3SO_3$.

$$\begin{tikzcd}
Co(phen)_3{}^{3+}{}_{(w)} + Co(terpy)_2{}^{2+}{}_{(w)} \arrow[r, "k_w"] \arrow[d, shift left, "K_A" swap] & Co(phen)_3{}^{2+}{}_{(w)} + Co(terpy)_2{}^{3+}{}_{(w)} \\
Co(phen)_3{}^{3+}{}_{(m)} + Co(terpy)_2{}^{2+}{}_{(m)} \arrow[r, "k_m"] \arrow[u, shift left, "K_B" swap] & Co(phen)_3{}^{2+}{}_{(m)} + Co(terpy)_2{}^{3+}{}_{(m)}
\end{tikzcd}$$

Observed bimolecular rate constants, $k_{2(obs)}$, are related to rate constants for electron transfer in the aqueous ($k_w$) and micellar ($k_m$) phases, as well as at the micelle-water interface between the micellar bound cobalt(III) oxidant, $Co(phen)_3{}^{3+}{}_{(m)}$, and $Co(terpy)_2{}^{2+}{}_{(w)}$ ($k_m'$), and between the micelle bound reductant, $Co(terpy)_2{}^{2+}{}_{(m)}$, and $Co(phen)_3{}^{3+}{}_{(w)}$ in the bulk aqueous phase ($k_m''$).

$$k_{2(obs)} = \frac{((k_m/V)K_AK_B + k_m'K_A + k_m''K_B)C + k_w(1 - CV)}{(1 + K_AC)(1 + K_BC)} \qquad (1)$$

$K_A$ and $K_B$ are binding constants for the association of $Co(phen)_3^{3+}$ and $Co(terpy)_2^{2+}$ respectively with SDS micelles, *C* is the concentration of added surfactant in excess of the cmc (*C* =

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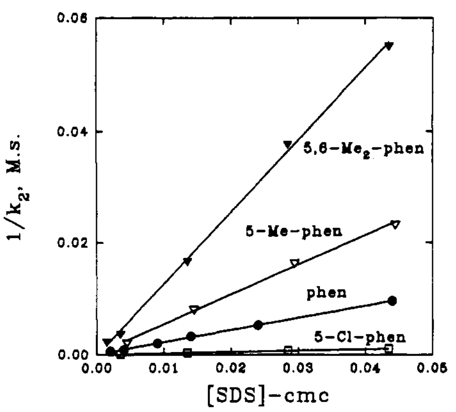

**Figure 2.** Reciprocal plot of $1/k_{2(obs)}$ vs $C$ for $Co(terpy)_2^{2+}$ reduction of 1,10-phenanthroline complexes of Co(III), $CoL_3^{3+}$, in 0.10 M $LiCF_3SO_3$, where L = 5-Cl-phen, phen, 5-Me-phen, and 5,6-$Me_2$-phen.

**Table 2.** Electrochemically Determined Micellar Association Constants and Partition Coefficients for $Co(phen)_3^{3+}$ and $Co(terpy)_2^{2+}$ in SDS[a]

| | $Co(terpy)_2^{2+}$ | $Co(phen)_3^{3+}$ |
|---|---|---|
| $K_1$, $M^{-1}$ | 441 ± 57 | 550 ± 19 |
| cmc,[b] mM | 1.6 ± 0.1 | 3.3 ± 0.6 |
| $K_d$ | 2400,[c] 4240[d] | 2710[c] ± 105 |

[a] $K_1 = [S_n{\cdot}P]/[S_n][P]n$, where $S_n$ is the SDS micelle composed of n surfactant molecules, P is the electrochemical probe, $Co(phen)_3^{3+}$ or $Co(terpy)_2^{2+}$, and $S_n{\cdot}P$ is the bound probe. $K_d = [F_b/V_m]/[F_f/(V_s - V_m)]$, where $F_f$ and $F_b$ are the fractions of free and bound probes, $V_m$ = volume of micelle phase, and $V_s$ = total volume of solution. Temperature = 25 °C. $[LiCF_3SO_3]$ = 0.20 M. [b] cmc = critical micelle concentration in presence of complex. [c] [SDS] = 4.95 mM. [d] [SDS] = 10.1 mM.

[SDS] - cmc) and $V$ is the partial molar volume of the surfactant in the micelle. The binding constants are defined by the equations $K_A = (P_A - 1)V$ and $K_B = (P_B - 1)V$, where $P_A$ and $P_B$ are partition coefficients ($P_A = [A]_m/[A]_w$; $P_B = [B]_m/[B]_w$). It is assumed that the exchange of molecules between the phases is very rapid and the reaction does not affect the partition equilibrium.

With both reactants strongly associated with the micellar phase, reaction rates involving the $k_w$, $k_m'$, and $k_m''$ paths are assumed negligible relative to $(k_m/V)K_AK_B$, and with $K_AC$ and $K_BC \gg 1$, eq 1 reduces to

$$k_{2(obs)} = \frac{(k_m/V)K_AK_B}{(K_A + K_B) + K_AK_BC} \qquad (2)$$

**Table 3.** Kinetic Data for $Co(terpy)_2^{2+}$ Reduction of Substituted Phenanthroline Complexes, $CoL_3^{3+}$,[a] in SDS at 25 °C[b]

| | $k_{2(obs)}$, $M^{-1}$ $s^{-1}$ | | |
|---|---|---|---|
| [SDS], M | L = 5-Me-phen | 5,6-$Me_2$-phen | 5-Cl-phen |
| 0.050 | 42.9 | 18.2 | 942 |
| 0.035 | 60.9 | 26.5 | 1350 |
| 0.020 | 123 | 59.9 | 2950 |
| 0.010 | 453 | 265 | 9700 |
| 0.0080 | | 442 | |

[a] Perchlorate salts. [b] 0.10 M $LiCF_3SO_3$.

**Table 4.** Summary of Rate and Electrochemical Data for $Co(terpy)_2^{2+}$ Reduction of Co(III) Phenanthroline Complexes in SDS Micellar Solutions[a]

| oxidant | $k_m$,[b] $M^{-1}$ $s^{-1}$ | $E_{1/2(m)}$,[c] V vs SCE |
|---|---|---|
| $[Co(phen)_3]^{3+}$ | 1.16 | 0.181 |
| $[Co(5\text{-}Me\text{-}phen)_3]^{3+}$ | 0.473 | 0.148 |
| $[Co(5,6\text{-}Me_2\text{-}phen)_3]^{3+}$ | 0.154 | 0.0825 |
| $[Co(5\text{-}Cl\text{-}phen)_3]^{3+}$ | 10.3 | 0.308 |

[a] All data at 25 °C. [b] In 0.10 M $LiCF_3SO_3$. [c] In 0.20 M LiCl.

This equation predicts that, above the cmc, $1/k_{2(obs)}$ should be linearly dependent on $C$, with a slope of $V/k_m$ and a slope/intercept ratio = $K_AK_B/(K_A + K_B)$. Plots of $1/k_{(obs)}$ vs $C$ for the $Co(terpy)_2^{2+}$ reduction of $Co(phen)_3^{3+}$ as well as for reduction of the substituted phenanthroline complexes, $Co(5\text{-}Me\text{-}phen)_3^{3+}$, $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$, and $Co(5\text{-}Cl\text{-}phen)_3^{3+}$ (Figure 2) are linear, consistent with the Berezin model. Quantitative data on micellar binding is difficult to obtain from the plots, however, because of the uncertainty in the value of cmc applicable to these reactions, and the small intercepts involved. The kinetic data obtained in 0.20 M LiCF3SO3, using a cmc value of 6.5 mM, yields a value of 460 for the slope/intercept ratio. Lower cmc values result in higher ratios, though positive intercepts are only obtained with cmc > 4.4 mM. The value of 460 for $K_AK_B/(K_A + K_B)$ is in good agreement with a value, between 412 and 318, obtained from the electrochemically determined partition coefficients, $K_d$, shown in Table 2.[5] Electrostatic contributions to micellar binding can be estimated through the equation $P = e^{-z\varphi/25.7}$,[28] which relates the partition coefficient $P$, for an ionic species of charge $Z$, distributed between aqueous and micellar phases, to the micellar surface potential $\varphi$ (mV) at 25 °C. Using a value of -75 mV for the SDS surface potential, reported by Fernandez and Fromherz in 0.20 M LiCl,[29] gives partition coefficients of 6.4 × $10^3$ and 343, for 3+ and 2+ cations, respectively. Corresponding values of 1.6 × $10^3$ and 86 $M^{-1}$ for $K_A$ and $K_B$, obtained using the value $V$ = 0.25 $M^{-1}$ for the partial molar volume of SDS above the cmc,[30,31] lead to $K_AK_B/(K_A = K_B)$ = 82. The difference between this value and the experimentally determined values provides further support for the finding of our electrochemical study[5] that, for the lipophilic cationic cobalt complexes involved in this study, strong micellar binding is occurring through both electrostatic and specific hydrophobic interactions. Significant hydrophobic contributions to micellar binding by cobalt phenanthroline complexes has been indicated previously in kinetic data for ferrocene–cobalt(III) electron transfer reactions[12] in SDS solutions. The greater SDS induced rate enhancement in 0.10 M $LiCF_3SO_3$, illustrated in Figure 1, is consistent with the stronger electrostatic interaction expected at the lower salt concentration.

Summarized in Table 3 is representitive kinetic data for the $Co(terpy)_2^{2+}$ reduction of the substituted phenanthroline complexes, $Co(5\text{-}Me\text{-}phen)_3^{3+}$, $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$, and $Co(5\text{-}Cl\text{-}phen)_3^{3+}$ in 0.10 M $LiCF_3SO_3$. Data was only obtained at [SDS] > *ca.* 0.060 M, as precipitation of the substituted phenanthroline complexes by SDS occurred at surfactant concentrations prior to the cmc. In all cases, the data conforms to eq 2 with reciprocal plots of $1/k_{2(obs)}$ *vs* $C$, shown in Figure 2, linear for a range of SDS concentrations employed above the cmc.

Values of $k_m$, the electron transfer rate constant in the micellar pseudophase, obtained using $V$ = 0.25 $M^{-1}$, are shown in Table 4. If the reactants are restricted to a smaller effective micellar volume concentrated near the Stern layer, a value of 0.14 for $V$ would be more appropriate.[32] In either case, the $k_m$ values obtained are smaller than $k_w$ by about 2 orders of magnitude. Similar effects have been demonstrated previously.[11,12,32] The finding of $k_m < k_w$ suggests that the overall reorganization energy required of the precursor complex in the micellar environment is greater than in water. This is despite reduced outer-sphere reorganizational energies and electrostatic work terms that would be expected to result from charge neutralization for the cationic reactants near the anionic head groups. The lowered rate constants could be a consequence of geometric constraints on encounter between complexes bound to the micelle surface or partially embedded in the micellar interior, or of stronger

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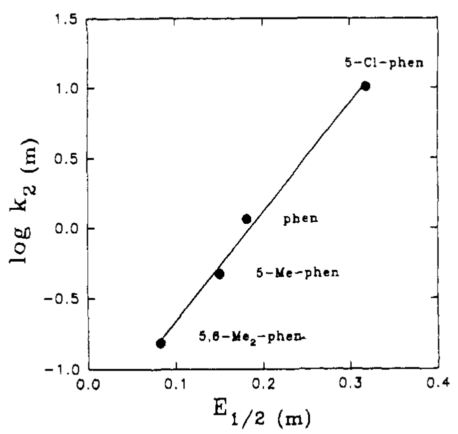

Figure 3. Linear free energy relationship for $Co(terpy)_2{}^{2+}$ reduction of Co(III) phenanthroline complexes in SDS micellar media.

interreactant repulsions resulting from lowered dielectric in the micellar interior.

Correlation of the $k_m$ values with the thermodynamic driving force of the reaction is illustrated in Figure 3, where log $k_m$ is plotted against $E_{1/2(m)}$, the half-wave potential of the Co(III) oxidants in the micellar solutions. The slope corresponds to a value of 0.48 for $\Delta\Delta G^*/\Delta\Delta G^*$, in excellent agreement with the value of 0.5 predicted by Marcus theory. Driving force dependences (log $k_w$ vs $E_{1/2}$) have previously been reported for electron transfer reactions in SDS solutions involving Os and Ru complexes, $OsL_3{}^{3+}$ and $RuL_3{}^{2+}$, containing similar hydrophobic ligands (L = chloro- or methyl-substituted 1,10-phenanthroline or 2,2'-bipyridine). Both reduction of $OsL_3{}^{3+}$ by $Fe(H_2O)_6{}^{2+}$, electrostatically bound to the SDS surface,[14] and electron transfer quenching of micellar bound $RuL_3{}^{2+}$ by $HgCl_3{}^-$ anions in the aqueous phase[33,34] display such behavior. The existence of free energy relationships in SDS solutions, with reactants experiencing diverse micellar interactions including strong hydrophobic association, electrostatic binding, and electrostatic repulsion, strongly suggests that thermodynamic factors are the principal determinant of reaction rates in micellar solutions. Environmental changes, resulting from specific interactions with anionic head groups or the micellar subphase, would appear to control reaction rates principly as a consequence of their influence on thermodynamic properties of reactants, reflected in their operating redox potentials.

**Electrochemical Behavior of Cationic Cobalt Phenanthroline and Terpyridine Complexes in SDS Solutions.** Electrochemical data for cationic cobalt phenanthroline complexes in 0.20 M LiCl at SDS concentrations between 0 and 0.0204 M is summarized in Table 5. Lithium chloride was used as electrolyte, because of the limited solubility of the substituted phenanthroline complexes in 0.20 M $LiCF_3SO_3$. Close to reversible electrochemical behavior was found in all cases with anodic and cathodic peak separations of 70–90 mV and peak currents linearly dependent on the square root of the scan rate for scan rates studied between 20 and 250 mV/s. The addition of SDS caused a gradual reduction in the anodic and cathodic peak currents, and shifts in the peak potentials to more positive values (Figure 4a). The decrease in peak currents, due to partial solubilization of the complex by the surfactant micelle and a slower rate of diffusion to the electrode of the larger micelle solubilized complex ion, results in the values for apparent diffusion coefficients, calculated by the Randles-Sevcik equation, shown in Table 5. We have previously reported similar effects for $Co(phen)_3{}^{3+/2+}$ and $Co(terpy)_2{}^{3+/2+}$ in 0.20 M $LiCF_3SO_3$.[5] Data are summarized in Table 6. Maximum potentials were observed with [SDS] = 5 mM, near to the cmc, and were followed by small decreases at higher surfactant concentrations. The magnitude of the shift, $E_{1/2(m)} - E_{1/2(w)}$, varying between 60 and 105 mV, appears to correlate with the hydrophobic nature of the ligands involved (Figure 5). It suggests a greater net stabilization of the divalent cations in micellar solutions than for their oxidized counterparts. This would appear to be contrary to that expected if electrostatic interactions dominate the micellar binding of the cationic complexes to the anionic micellar surface, as was found

Table 5. Effect of SDS on Electrochemical Parameters from Cyclic Voltammetry for $[CoL_3]^{3+/2+}$ Couples,[a] in 0.20 M LiCl at 25 °C

| [SDS], M | $E^{1/2}$, V[b] | $\Delta E_p$, mV[b] | $10^7 D_{Pc}$,[c] cm²/s | $10^7 D_{Pa}$,[d] cm²/s |
|---|---|---|---|---|
| | | L = phen | | |
| 0 | 0.113 | 75 | 23.6 | 27.3 |
| 0.00437 | 0.185 | 60 | 9.60 | 6.20 |
| 0.00820 | 0.184 | 72 | 2.19 | 0.873 |
| 0.0130 | 0.180 | 80 | 0.184 | 0.305 |
| 0.0208 | 0.175 | 100 | 0.053 | 0.134 |
| | | L = 5-Me-phen | | |
| 0 | 0.0605 | 71 | 15.8 | 22.0 |
| 0.00437 | 0.150 | 50 | 7.19 | 6.77 |
| 0.00820 | 0.133 | 65 | 0.836 | 0.667 |
| 0.0130 | 0.120 | 80 | 0.234 | 0.246 |
| 0.0208 | 0.115 | 70 | 0.103 | 0.113 |
| | | L = 5,6-$Me_2$-phen | | |
| 0 | –0.0200 | 80 | 7.14 | 14.4 |
| 0.00437 | 0.0850 | 60 | 4.82 | 4.82 |
| 0.00820 | 0.0625 | 75 | 0.367 | 0.340 |
| 0.0130 | 0.0450 | 90 | 0.130 | 0.261 |
| 0.0208 | 0.0400 | 80 | 0.0846 | 0.204 |
| | | L = 5-Cl-phen | | |
| 0 | 0.258 | 95 | 16.9 | 21.8 |
| 0.00658 | 0.318 | 75 | 4.60 | 3.06 |
| 0.00980 | 0.298 | 55 | 1.21 | 0.904 |
| 0.0130 | 0.285 | 70 | 0.431 | 0.667 |
| 0.0208 | 0.270 | 80 | 0.176 | 0.210 |

[a] Chloride salts. [b] Scan rate ($v$) = 25 mV/s; $E_{1/2} = (E_{Pa} + E_{Pc})/2$, and $\Delta E_p = E_{Pa} - E_{Pc}$; V vs SCE. [c] Determined at each surfactant concentration from slope of cathodic peak current, $i_{Pc}$, vs $v^{1/2}$. [d] Determined from anodic peak current, $i_{Pa}$, vs $v^{1/2}$.

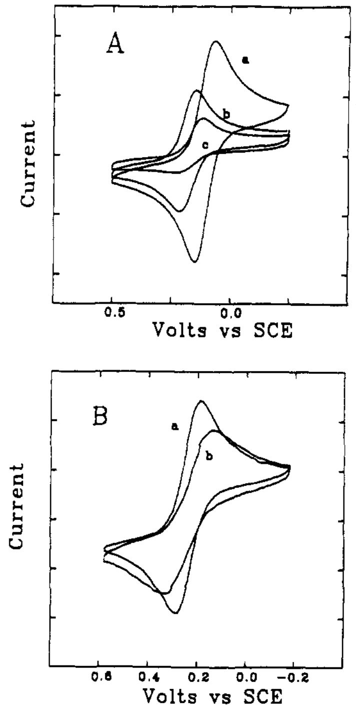

Figure 4. A. Effect of SDS on cyclic voltammetry of $[Co(phen)_3]^{3+}$ in 0.20 M $LiCF_3SO_3$: (a) [SDS] = 0 M; (b) [SDS] = 4.95 mM; (c) [SDS] = 0.0204 M. Scan rate = 50 mV/s. B. Effect of Triton X-100 on cyclic voltammetry of $[Co(5\text{-}SO_3\text{-}phen)_3]$ in 0.10 M $LiCF_3SO_3$: (a) [TX-100] = 0 mM; (b) [TX-100] = 0.32 mM. Scan rate = 20 mV/s.

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**Table 6.** Effect of SDS on Half-Wave Potentials of $[Co(phen\text{-}X)_3]^{3+/2+}$ and $[Co(terpy)_2]^{3+/2+}$ Redox Couples at 25 °C

| medium | ligand | $E_{1/2(w)}$[a] | $E_{1/2(m)}$[a] | $E_{1/2(w)} - E_{1/2(w)}$[b] |
|---|---|---|---|---|
| 0.20 M $LiCF_3SO_3$ | phen | 0.105 | 0.177[c] | 72 |
| | terpy | 0.006 | 0.068[c] | 62 |
| 0.20 M LiCl | 5-Cl-phen | 0.262 | 0.308[d] | 46 |
| | phen | 0.112 | 0.181[e] | 69 |
| | 5-Me-phen | 0.060 | 0.148[e] | 88 |
| | 5,6-$Me_2$-phen | –0.0225 | 0.0825 | 105 |

[a] V *vs* SCE. [b] mV. [c] 5.0 M SDS. [d] 6.6 mM SDS. [e] 4.4 mM SDS.

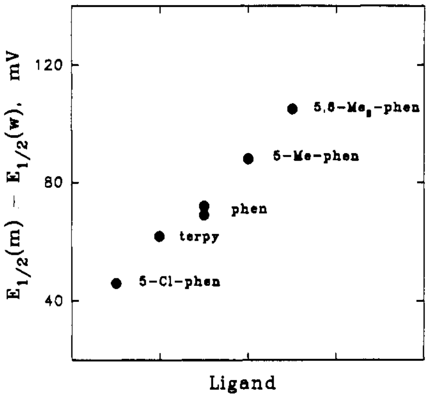


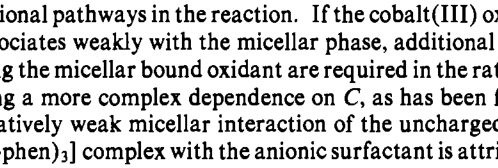
**Figure 5.** Shift in half-wave potential for $CoL_3^{3+/2+}$ (L = phen, 5-Cl-phen, 5-Me-phen, 5,6-$Me_2$-phen) and $CoL_2^{3+/2+}$ (L = terpy) redox couples in SDS surfactant media.

for DMPE complexes of Tc and Re,[20] and suggests strong hydrophobic association of the reduced Co(II) complexes with the SDS interior. Similar positive shifts have been reported for related Os(III)/Os(II), Ru(III)/Ru(II) and Fe(III)/Fe(II) couples, with hydrophobic diimine ligands, in both ground and excited states,[33,34] and Aoyagui and co-workers have previously attributed variation in $\Delta E_{1/2}$ values, for complexes of like charge, to differences in hydrophobic character.[14] For a redox couple in which both the oxidized and reduced forms interact with micellar aggregates, the formal potentials in the absence and presence of micelles are related to association constants, $K_O$ and $K_R$, for oxidized and reduced species, through the equation, $E°_{(m)} - E°_{(w)} = (RT/F) \ln (K_R/K_O)$. Applying $E_{1/2}$ values from Table 5 leads to $K_R/K_O$ ratios of 60, 33, 10, and 17 for the 5,6-dimethyl-, 5-methyl-, and 5-chloro-substituted and unsubstituted 1,10-phenanthroline complexes respectively, accepting the error introduced into the equation through the use of $E_{1/2}$ values in place of formal potentials.

Although changes in half-wave potential on micellization have often been discussed in terms of electrostatic effects,[35-38] for diimine 3+/2+ complexes and other strongly lipophilic cationic substrates,[1,14] shifts in potential in SDS surfactant media do not appear attributable primarily to electrostatic factors. The good correlation between potential shift and hydrophobic ligand structure points strongly to specific hydrophobic interactions being involved in the relative stabilization of the redox states. In particular, the enhanced association of the lower oxidation state with the micellar interior appears to outweigh electrostatic considerations when strongly hydrophobic ligands are involved. The hydrophobic ligand structure could effectively weaken Coulombic forces by promoting solubilization in the micellar interior. Changes in solvent polarity in the micellar media could also influence the thermodynamic driving force of a redox couple on micellization. The reduced dielectric constant at the micellar surface, estimated as 32 for SDS micelles,[29] could be contributing to the observed potential shifts through the greater loss of solvation energy experienced by the more highly charged oxidant. For ions partially embedded in the micelle or completely solubilized in the micellar interior, loss of coulombic solvation energy would be even more dramatic. Kajer and Ulstrup report $E_{1/2}$ for $Co(phen)_3^{3+/2+}$ shifted by +300 mV in ethylene glycol,[21] and we have found both $Co(phen)_3^{3+/2+}$ and $Co(terpy)_2^{3+/2+}$ potentials to be sensitive to the dielectric contant of a range of dipolar organic solvents.[39] Although reference electrode solution junction potentials contribute to potential changes in non-aqueous solvents, in the range of SDS concentrations employed in this study, the micellar volume never accounts for more than 0.37% of the total solution volume and an effective aqueous medium is maintained throughout. There is also no evidence of SDS-induced adsorption on the glassy-carbon working electrode[5] or of surfactant induced changes in the reference electrode junction potentials.[1-4,38,40]

**Redox Behavior of $[Co(5\text{-}SO_3^-\text{-}phen)_3]$ and $[Co(dipic)_2]^-$.** In view of the high degree of hydrophobic participation in the micellar binding of cationic cobalt(III) phenanthroline complexes with SDS micelles, it was of interest to examine the redox behavior of the electrically neutral, $[Co(5\text{-}SO_3\text{-}phen)_3]$, and anionic, $[Co(dipic)_2]^-$, complexes under similar conditions. Information on micellar binding obtained from kinetic data for the reduction of $[Co(5\text{-}SO_3\text{-}phen)_3]$ and $[Co(dipic)_2]^-$ by $Co(terpy)_2^{2+}$ was again compared with that indicated by cyclic voltammetry. Data was obtained in anionic SDS, nonionic Triton X-100, and cationic CTAB surfactant solutions.

**(i) Kinetic Data in SDS and Triton X-100.** Rapid second-order rate constants $1.59 \times 10^4$ $M^{-1}$ $s^{-1}$ and $5.33 \times 10^4$ $M^{-1}$ $s^{-1}$ were obtained for the $[Co(terpy)_2]^{2+}$ reduction of $[Co(5\text{-}SO_3\text{-}phen)_3]$ and $[Co(dipic)_2]^-$, respectively, in 0.20 M $LiCF_3SO_3$ with no added surfactant. The $Co(5\text{-}SO_3\text{-}phen)_3$ rate constant is in good agreement with the value, $1.20 \times 10^4$, previously reported in 0.050 M sodium *p*-tolenesulfonate.[21] Both reactions are strongly inhibited by added surfactant, and second-order rate constants are decreased 20- and 100-fold respectively, at SDS concentrations beyond the cmc (Table 7). The marked rate inhibition suggests that only one reactant, $Co(terpy)_2^{2+}$, is partitioned into the micellar phase, where it reacts much more slowly with the cobalt(III) oxidant residing predominantly in the aqueous phase. With both micelle-bound and aqueous $Co(terpy)_2^{2+}$ species undergoing electron transfer with $Co(5\text{-}SO_3\text{-}phen)_3$



eq 1 reduces to $k_{2(obs)} = (k_m''K_BC + k_w)/(1 + K_BC)$, which predicts a lienar dependence of $k_{2(obs)}$ on 1/[C], provided $K_BC \gg 1$. Such a plot, shown in Figure 6, is not linear over the range of SDS concentrations employed, however, suggesting the involvement of additional pathways in the reaction. If the cobalt(III) oxidant also associates weakly with the micellar phase, additional terms involving the micellar bound oxidant are required in the rate law, requiring a more complex dependence on *C*, as has been found. The relatively weak micellar interaction of the uncharged $[Co(5\text{-}SO_3\text{-}phen)_3]$ complex with the anionic surfactant is attributed to electrostatic repulsion resulting from the fairly high negative density associated with the $-SO_3^-$ substituent. This is consistent with the even more marked rate inhibition observed with the anionic oxidant, $[Co(dipic)_2]^-$, where reaction is again occuring at the micelle–water interface between micelle-solubilized reductant and $Co(dipic)_2^-$ in the aqueous phase. Similar

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**Table 7.** Effect of SDS on Electron Transfer Rate Constants[a] for $Co(terpy)_2^{2+}$ Reduction of $[Co(5\text{-}SO_3\text{-}phen)_3]$ and $[Co(dipic)_2]^-$

| $[Co(5\text{-}SO_3\text{-}phen)_3]$ | | $[Co(dipic)_2]^-$ | |
|---|---|---|---|
| [SDS], mM | $k_{2(obs)}$,[b] $M^{-1}$ $s^{-1}$ | [SDS], mM | $k_{2(obs)}$,[b] $M^{-1}$ $s^{-1}$ |
| 0 | 15900 | 0 | 53300 |
| 0.40 | 15850 | 0.5 | 41900 |
| 1.00 | 1990 | 1.0 | 14200 |
| 2.39 | 902 | 2.0 | 572 |
| 3.18 | 786 | 4.0 | 183 |
| 3.97 | 704 | 5.0 | 174 |
| 5.34 | 700 | 10.0 | 138 |
| 5.93 | 688 | 20.0 | 131 |
| 9.42 | 581 | | |
| 11.7 | 547 | | |
| 13.6 | 483 | | |
| 16.4 | 481 | | |
| 19.2 | 439 | | |
| 23.8 | 425 | | |

[a] All data at 25.0 °C. [b] $[LiCF_3SO_3]$ = 0.20 M.

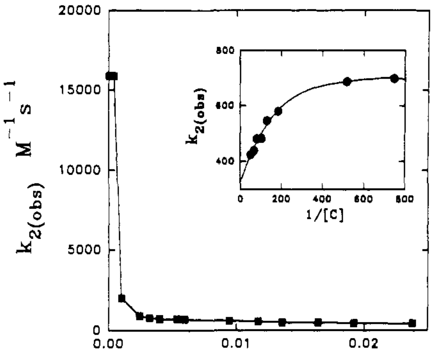
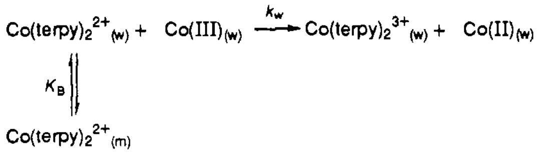


**Figure 6.** Effect of SDS on second-order constants for $Co(terpy)_2^{2+}$–$[Co(5\text{-}SO_3\text{-}phen)_3]$ electron transfer in 0.20 M $LiCF_3SO_3$.

kinetic behavior has been reported for reaction of $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ with $Ru(bpy)_3^{3+}$ and iron(III) phenanthroline complexes in SDS solutions.[8a,b]

Rate inhibition was also found with the nonionic surfactant, Triton X-100. Table 8 shows representative kinetic data for the effect of Triton X-100 on the $[Co(terpy)_2]^{2+}$ reduction of $[Co(phen)_3]^{3+}$, $[Co(5\text{-}SO_3\text{-}phen)_3]$, and $[Co(dipic)_2]^-$ in $LiCF_3SO_3$. In all cases the measured rate constants decrease on addition of surfactant, though less sharply than for $[Co(5\text{-}SO_3\text{-}phen)_3]$ and $[Co(dipic)_2]^-$ in SDS. The data are consistent with one of the reactants weakly associating with micellar pseudophase, but with the reaction taking place almost entirely in the bulk aqueous phase. If $Co(terpy)_2^{2+}$ is the micellar bound reactant



$$\begin{tikzcd} Co(terpy)_2{}^{2+}_{(w)} + Co(III)_{(w)} \arrow[r, "k_w"] \arrow[d, shift left, "K_B"'] & Co(terpy)_2{}^{3+}_{(w)} + Co(II)_{(w)} \\ Co(terpy)_2{}^{2+}_{(m)} \arrow[u, shift left] & \end{tikzcd}$$

equation 1 reduces to $k_{2(obs)} = k_w/(1 + K_BC)$, and $k_{2(obs)}$ is expected to fall with added surfactant, as $Co(terpy)_2^{2+}$ is partitioned into the micellar phase. The observed linear dependences of $1/k_{2(obs)}$ on $C$, illustrated in Figure 7, yields values for $K_B$ and $k_W$ summarized in Table 9. The cmc of Triton X-100, $2 \times 10^{-4}$ M in salt-free solutions, is assumed to be negligible under the experimental conditions.

**(ii) Comparative Electrochemistry of $Co(5\text{-}SO_3\text{-}phen)_3$ and $Co(phen)_3^{3+}$ in SDS and Triton X-100.** The weak association of $Co(5\text{-}SO_3\text{-}phen)_3$ with both SDS and Triton X-100 micelles was further indicated by the electrochemical data. In the absence of surfactants, cyclic voltammetry on $Co(5\text{-}SO_3\text{-}phen)_3$ in 0.10 M $LiCF_3SO_3$ showed a peak separation of 103 mV, at 25 mV/s, indicative of quasi-reversible behavior. The observed half-wave potential of 0.239 V vs SCE, compares to a value of 0.254 V previously reported in 0.05 M sodium *p*-toluenesulfonate.[21] Addition of SDS, up to 0.0204 M, resulted in no significant changes in either peak currents or half-wave potentials, consistent with negligible micellar association. This contrasts to substantial shifts in $E_{1/2}$ of $[Co(5\text{-}SO_3\text{-}phen)_3]$ in organic solvents, reported by Ulstrup, and accords with essentially aqueous solvation of the complex being maintained in the SDS micellar solutions. Successive additions of Triton X-100 to $Co(5\text{-}SO_3\text{-}phen)_3$ at low concentrations caused a decrease in both peak currents, by *ca.* 28–36% of their original values at [Triton X-100] = 0.32 mM, accompanied by an increase in the peak separation to 0.205 V (Figure 4b). The half-wave potential remained essentially

**Table 8.** Electron Transfer Rate Constants for the $Co(terpy)_2^{2+}$ Reduction of Co(III) Complexes in Triton X-100 Surfactant Solutions at 25 °C

| oxidant | [Triton X-100], mM | $k_{2(obs)}$, $M^{-1}$ $s^{-1}$ |
|---|---|---|
| $[Co(phen)_3]^{3+}$ [a] | 0.00 | 522 |
| | 0.403 | 535 |
| | 2.02 | 529 |
| | 4.03 | 495 |
| | 8.07 | 467 |
| | 20.2 | 380 |
| | 40.3 | 317 |
| | 66.5 | 259 |
| | 80.7 | 232 |
| | 99.7 | 184 |

| oxidant | [Triton X-100], mM | $10^{-4}k_{2(obs)}$, $M^{-1}$ $s^{-1}$ |
|---|---|---|
| $[Co(5\text{-}SO_3\text{-}phen)_3]$[a] | 0.00 | 1.36 |
| | 0.501 | 1.05 |
| | 1.01 | 0.988 |
| | 2.98 | 0.970 |
| | 5.94 | 0.938 |
| | 11.7 | 0.864 |
| | 19.1 | 0.756 |
| | 36.5 | 0.594 |
| $[Co(dipic)_2]^-$ [b] | 0.00 | 5.32 |
| | 4.02 | 4.54 |
| | 8.04 | 4.09 |
| | 14.1 | 3.76 |
| | 20.1 | 2.91 |
| | 40.2 | 2.26 |

[a] 0.10 M $LiCF_3SO_3$. [b] 0.20 M $LiCF_3SO_3$.

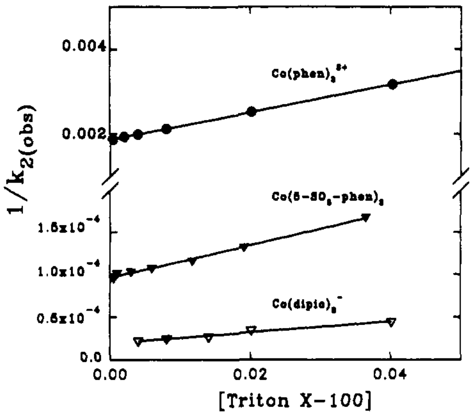


**Figure 7.** Reciprocal plot for $Co(terpy)_2^{2+}$ reduction of $Co(phen)_3^{3+}$, $Co(5\text{-}SO_3\text{-}phen)_3$, and $Co(dipic)_2^-$ in Triton X-100 surfactant media.

**Table 9.** Summary of Micellar Binding Constants and Electron Transfer Rate Constants obtained for $Co(terpy)_2^{2+}$ Reduction of Co(III) Oxidants in Triton X-100 Surfactant Media

| complex | redox partner | $K_B$, $M^{-1}$ | $k_w$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|
| $Co(terpy)_2^{2+}$ | $Co(phen)_3^{3+}$ | 18[a] | 538 |
| $Co(terpy)_2^{2+}$ | $Co(5\text{-}SO_3\text{-}phen)_3$ | 29[a] | $1.1 \times 10^4$ |
| $Co(terpy)_2^{2+}$ | $Co(dipic)_2^-$ | 33[b] | $5.2 \times 10^4$ |

[a] 0.10 M $LiCF_3SO_3$. [b] 0.20 M $LiCF_3SO_3$. All data at 25.0 °C.

unchanged at *ca.* 0.238 V. Subsequent additions of surfactant, up to 0.020 M, resulted in negligible further change in either peak current or peak potential. The lowered peak currents and increased electrochemical irreversibility of the $[Co(5\text{-}SO_3\text{-}phen)_3]^{0/-1}$ couple in Triton X-100 suggests greater micellar solubilization of the uncharged Co(III) complex by the nonionic surfactant that was apparent in anionic SDS media. Triton X-100 induced electrochemical changes were also determined for the cationic cobalt(III) complexes, $Co(phen)_3^{3+}$, $Co(terpy)_2^{2+}$, and $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$. Reversible behavior was maintained in all cases on addition of Triton X-100 up to 0.083 M, with anodic and cathodic peak separations of 65–70 mV and linear $i_p$ *vs* $v^{1/2}$ plots, for scan rates between 20 and 250 mV/s. Diffusion coefficients were unchanged for $Co(terpy)_2^{2+}$, compared to 24 and 65% decreases in $D_0$ determination for $Co(phen)_3^{3+}$ and $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$. In the case of the dimethylphenanthroline complex, the reduction in anodic and cathodic peak currents was also accompanied by a small anodic shift in $E_{1/2}$. The electrochemical changes in Triton X-100 again point to reduced diffusion currents and potential shifts as reliable monitors of micellar interactions. Equilibrium association constants for Triton X-100 and several ruthenium(II) and osmium(II) phenanthroline complexes have been reported by Demas and co-workers.[41] They indicate relatively weak interactions for divalent $Ru(phen)_3^{2+}$ and $Os(terpy)_2^{2+}$ complexes, but show micellar binding substantially increased by methyl substituents in the phenanthroline ring. The Triton X-100 induced electrochemical changes above suggest greater micellar interaction with the cobalt(III) oxidants $Co(phen)_3^{3+}$ and $Co(5\text{-}SO_3\text{-}phen)_3^{3+}$ than with $Co(terpy)_2^{2+}$. If this is so, the $K_b$ values in Table 9 would reflect micellar binding to Triton X-100 by the cobalt(III) phenanthroline oxidants rather than by the $Co(terpy)_2^{2+}$ reductant.

**(iii) Electrochemistry of $[Co(dipic)_2]^-$ in SDS, Triton X-100, and CTAB.** To extend the effect of surfactants on the electrochemical behavior of cationic and nonionic complexes to anionic substrates, cyclic voltammetry was carried out on the anionic $Co(dipic)_2^-$ complex in SDS, Triton X-100, and CTAB. In 0.10 M $LiCF_3SO_3$ with no surfactant present, $(NH_4)[Co(dipic)_2]$ displayed irreversible behavior at 250 mV/s with cathodic and anodic peaks separated by 0.30 V. The anodic wave receded at slower scan rates, presumably due to the substitutional lability of the cobalt(II) dipic complex giving rise to mixed aquo–dipic Co(II) species, and was almost negligible at 10 mV/s. An additional cathodic peak was found at –0.53 V at slow scan rates. Although the addition of SDS produced negligible change in the cyclic voltammogram of $Co(dipic)_2^-$ solutions, complex behavior was observed in both Triton X-100 and CTAB. In both cases, added surfactant produced strong transient cathodic currents which decayed rapidly, resulting in a cyclic voltammogram comparable to that present initially, but with a shifted cathodic peak: the peak was shifted in a negative direction with Triton X-100 and a positive direction with CTAB (Figure 8). Such strong transient currents are characteristic of surfactant induced adsorption effects at the electrode surface and may involve rapid structural reorganization of adsorbed surfactant–$Co(dipic)_2^-$ species. With CTAB this may be associated with the adsorption of $CTAB^+{:}Co(dipic)_2^-$ ion pairs, and $Co(dipic)_2^-$–surfactant aggregates also appear to be involved in the adsorption process in Triton X-100, as no evidence for Triton X-100 adsorption was apparent with the other cobalt(III) oxidants. Surfactants induced adsorption at electrode surfaces have been reported previously,[40,42] and we have noted similar effects with the anionic cobalt complexes $Co(edta)^{2-}$ and $Co(hedta)^{2-}$ in CTAB.

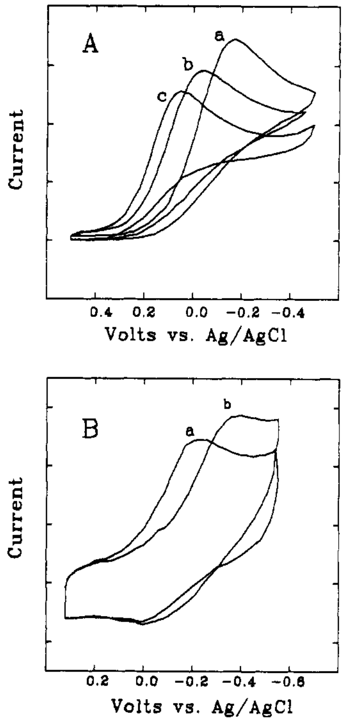


**Figure 8.** A. Effect of CTAB on cyclic voltammetry of 5 mM $(NH_4)[Co(dipic)_2]$ in 0.20 M $LiCF_2CO_2$: (a) [CTAB] = 0 mM; (b) [CTAB] = 0.10 mM; (c) [CTAB] = 1.23 mM. Scan rate = 100 mV/s. B. Effect of Triton X-100 on cyclic voltammetry of 0.50 mM $(NH_4)[Co(dipic)_2]$ in 0.10 M $LiCF_3SO_3$: (a) [TX-100] = 0 M; (b) [TX-100] = 0.0276 M. $(NH_4)[Co(dipic)_2]$ = 0.50 mM. Scan rate = 100 mV/s.

If the cathodic potential shifts reflect changes in the relative stability of the $Co(dipic)_2^{-/2-}$ redox states as a result of micellar interactions, the reduced $Co(dipic)_2^{2-}$ anion is stabilized relative to its oxidized counterpart in the cationic CTAB surfactant, whereas the $Co(dipic)_2^-$ oxidant, of lower ionic charge, is stabilized relative to the reduced dianion in nonionic Triton X-100. The cathodic shift observed for $Co(dipic)_2^-$ in CTAB would be consistent with electrostatic interactions dominating the micellar binding of $Co(dipic)_2^{-/2-}$ ions with CTAB micelles, which would not be unexpected in view of the open nonhydrophobic structure of the dipicolinate ligand. Although we recognize that any conclusions regarding potential shifts for cobalt dipicolinate species in Triton X-100 and CTAB solutions are tentative, since $E_{1/2}$ values may be influenced by surfactant induced adsorption on the electrode, the inferences made above would add support to the conclusions from the SDS data that surfactant induced changes in formal potentials of Co(III)/Co(II) redox couples are principally due to changes in the relative stability of oxidation states resulting from specific micellar associations.

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