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Micellar Effect on Electron Transfer.[1] 3. Kinetics of Substituted 1,10-Phenanthroline Complexes of Iron(III) with Iron(II) in the Presence of Sodium Dodecyl Sulfate

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In a previous paper,[1a] the effect of the micelle-forming surfactant sodium dodecyl sulfate (SDS) on the electron-transfer rate between tris(2,2'-bipyridine)ruthenium(III), Ru(bpy)$_3^{3+}$, and negatively charged complexes like Mo(CN)$_8^{4-}$ and Fe(CN)$_6^{4-}$ was reported: a decrease of 2–3 orders of magnitude was observed.

The study of the reaction between Ru(bpy)$_3^{3+}$ and Fe^{2+}(aq) in the presence of SDS provided only an estimate of a lower limit of the reaction rate, since its half-time is much shorter than the mixing time of our stopped-flow apparatus.

In the present note, the effect of SDS on the electron-transfer reactions between substituted 1,10-phenanthroline complexes of iron(III), FeL$_3^{3+}$, and Fe^{2+}(aq) according to

$$\text{FeL}_3^{3+} + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{FeL}_3^{2+} + \text{Fe}^{3+}(\text{aq}) \qquad (1)$$

is reported. Since these reactions exhibit a smaller driving force,[2] the catalytic effect of micelles can be followed over a large concentration range of surfactant.

Experimental Section

Reagents. The following tris(1,10-phenanthroline)iron(II) derivatives were prepared and recrystallized as perchlorate according to the procedure described in the literature:[2] 5,6-dimethyl- (5,6-Me$_2$phen), 4,7-dimethyl- (4,7-Me$_2$phen), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me$_4$phen). The corresponding FeL$_3^{3+}$ were prepared by electrooxidation or PbO$_2$ oxidation.[2] FeSO$_4$ solutions were standardized by oxidimetric titration. Sodium dodecyl sulfate (Merck) was recrystallized several times. All other reagents were of the highest purity available. Doubly distilled water was used.

Procedure. The kinetic runs were followed at the wavelength of maximum absorption of the FeL$_3^{2+}$ complexes,[2] by means of a Durrum–Gibson stopped-flow spectrophotometer. [FeL$_3^{3+}$] was in the range (3–5) × 10^{-6} M, while [Fe^{2+}(aq)] was from 6 × 10^{-6} M to 1 × 10^{-4} M, depending on the half-time of the reactions. SDS was added to both solutions before mixing. The rate constants were evaluated according to first- or second-order rate laws. Also the method proposed by Corbett gave satisfactory results.[3] Each value reported in Tables I–IV (supplementary material) was averaged over four to eight separate measurements. The data were analyzed by using a weighted least-squares method, and weights were assigned on the
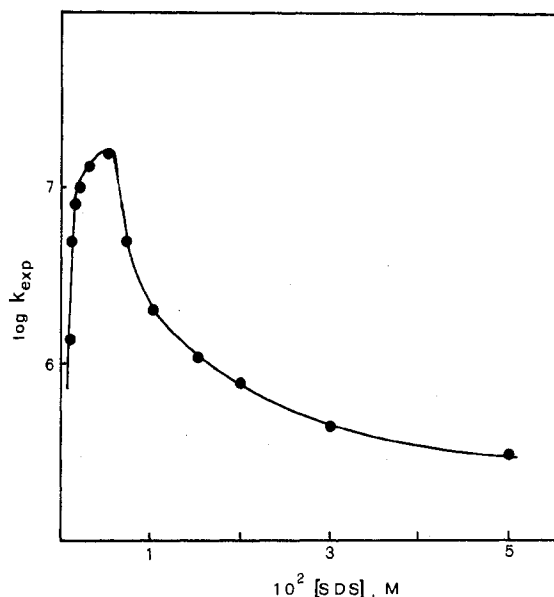

Figure 1. Plot of the observed second-order rate constants as a function of SDS concentration, for the reaction of Fe(Me$_4$phen)$_3^{3+}$ with Fe^{2+}(aq) ([H$_2$SO$_4$] = 0.005 M, 25.0 °C).

basis of the standard deviation of each point. All measurements were carried out at 25.0 °C.

Results and Discussion

Kinetics. The linear dependence of the pseudo-first-order rate constants on [Fe^{2+}(aq)], as well as the linearity of the second-order plots, both in absence of surfactant and over the presently studied SDS concentration range, supports that for reaction 1 the following rate law holds:

$$-d[\text{FeL}_3^{3+}]/dt = k_{\text{exptl}}[\text{FeL}_3^{3+}][\text{Fe}^{2+}(\text{aq})] \qquad (2)$$

In the absence of surfactant ([H$_2$SO$_4$] = 0.02 M, [NaNO$_3$] = 0.04 M) the following rate constants were obtained: Fe-(5,6-Me$_2$phen)$_3^{3+}$, k = (6.0 ± 0.3) × 10^4 M^{-1} s^{-1}; Fe(4,7-Me$_2$phen)$_3^{3+}$, k = (9.0 ± 0.4) × 10^3 M^{-1} s^{-1}; Fe(Me$_4$phen)$_3^{3+}$, k = (3.3 ± 0.2) × 10^3 M^{-1} s^{-1}. These values are comparable with the results in 0.5 M H$_2$SO$_4$, previously reported.[2] For Fe(Me$_4$phen)$_3^{3+}$ the rate constant measured in [H$_2$SO$_4$] = 0.005 M was (4.1 ± 0.2) × 10^3 M^{-1} s^{-1}.

General Features of Micellar Catalysis. Since both reactants can interact with anionic micelles, Berezin's approach[4] can be adopted in the analysis of the present results. According to this model

$$k_{\text{exptl}} = \frac{(k_{\text{M}}P_{\text{A}}P_{\text{B}} + k_{\text{M}}'P_{\text{A}} + k_{\text{M}}''P_{\text{B}})C\bar{V} + k_{\text{w}}(1 - C\bar{V})}{(1 + K_{\text{A}}C)(1 + K_{\text{B}}C)}$$

$$(3)$$

where P_i and K_i are the partition coefficient and the binding constant, respectively, and $\bar{V}$ is the partial volume of the surfactant monomer; these three parameters are interconnected by the equation $K_i = (P_i - 1)\bar{V}$. The subscripts M, w, A, and B refer to the micellar and aqueous phases and to the reactants (in the present report A refers to FeL$_3^{3+}$ and B to Fe^{2+}(aq)). k_{M} and k_{w} are the rate constants for the reaction when both reactants are in micellar and aqueous phases, respectively; k_{M}' refers to the reaction between compound A in the micellar phase with B in aqueous phase and k_{M}'' to the reverse situation; C is the stoichiometric surfactant concentration minus the critical micelle concentration (cmc). A relevant extension of the Berezin approach has been recently given by Romsted,[5]

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(2) Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830.
(3) Corbett, J. F. *J. Chem. Educ.* **1972**, *49*, 663.

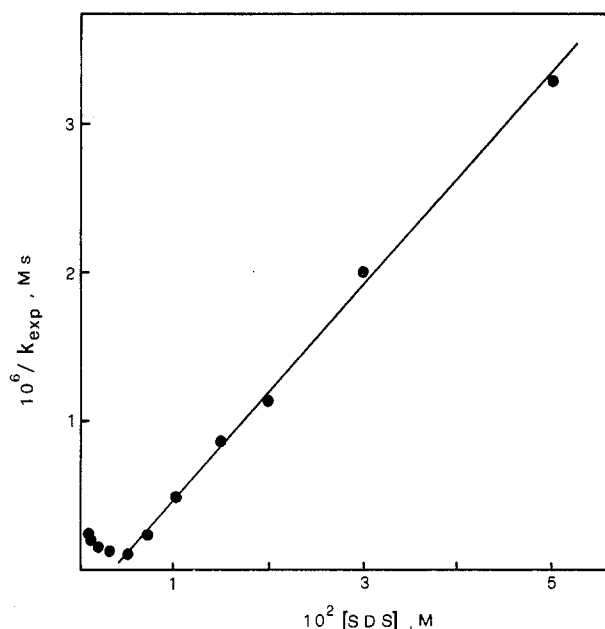(4) Berezin, I. V.; Martinek, K.; Yatsimirskii, A. K. *Russ. Chem. Rev. (Engl. Transl.)* **1973**, *42*, 787.

Figure 2. Plot of $1/k_{exptl}$ as a function of SDS concentration for the data of Figure 1.

by introducing the assumption of the saturation of the Stern layer of the micelle with respect to its counterion; this treatment allows one to predict and to explain several experimental features of micellar effects on the reaction rates.

Effect of SDS on the Electron Transfer between Fe-$(Me_4phen)_3^{3+}$ and $Fe^{2+}(aq)$ in $[H_2SO_4] = 0.005$ M. Figure 1 shows the variation of the observed rate constants as a function of SDS concentration. The maximum of increase is reached at about 5×10^{-3} M SDS, very near the cmc in the present experimental conditions.[6] Above the maximum the reaction rate constant starts to decrease sharply and then gradually (Table I). This feature is clearly accounted for by the Berezin[4] and Romsted[5] treatments.

Since FeL_3^{3+} complexes are strongly associated with the micelles,[1] the terms including k_w and k_M'' can be assumed to be negligible with respect to the other terms appearing in the numerator of eq 3, and since $K_A C \gg 1$, eq 3 is reduced to

$$k_{exptl} = \frac{\bar{k}_M K_B + k_M'}{1 + K_B C} \quad (4)$$

where $\bar{k}_M = k_M / \bar{V}$. Equation 4 can be rearranged into

$$\frac{1}{k_{exptl}} = \frac{1}{\bar{k}_M K_B + k_M'} + \frac{K_B}{\bar{k}_M K_B + k_M'} \quad (5)$$

As shown in Figure 2, a plot of $1/k_{exptl}$ as a function of SDS concentration gives a good straight line, thus supporting the applicability of eq 5 to the present reactions.

From the plot of Figure 2, the ratio of slope to intercept should give K_B. However, only a semiquantitative estimate can be obtained, since the value of the exact cmc is not accurately known. In fact, it is known that the cmc of surfactants is a function of the concentration of inert salt and of the nature of the counterions present in solution.[7] If cmc = 5×10^{-3} M is tentatively assumed (that is near the maximum of the rate enhancement), $K_B \approx 1 \times 10^3$ M^{-1} can be obtained.

The partition coefficient of an ionic species between an aqueous phase and micellar pseudophase can be estimated through

$$P = e^{-Z\psi/25.7} \quad \text{at } 25.0 \text{ °C}$$

where Z is the ionic charge and ψ the surface potential of micelle.[4,8] Since also ψ is extremely sensitive to several factors (ionic strength, pH, nature of counterions, etc.), the proper value of ψ is also problematic.

From electrophoretic data,[9] as well as from change in apparent dissociation constants of indicators,[10] a value of $\psi = 110$–120 mV seems reasonable. This allows the estimate $P = 5 \times 10^3$–1×10^4. Since $K = P\bar{V}$, by assuming $\bar{V} = 0.246$ M^{-1},[11] the binding constant for a bivalent ion would range between 1.2×10^3 and 2.5×10^3 M^{-1}, comparable with the present estimate.

Other recent investigations, concerning bivalent ions in SDS, like $Ru(bpy)_3^{2+}$ (in this case also hydrophobic contributions could be operating),[12] Ni^{2+},[10] and VO^{2+},[13] concluded that virtually all the bivalent ions are at the micellar surface, at concentrations only slightly above the cmc.[14]

From the intercept, it follows that $\bar{k}_M K_B + k_M' \approx 2 \times 10^7$ M^{-1} s^{-1}. If only the pathway referred to $\bar{k}_M$ is operating, then $k_M \approx 5 \times 10^3$ M^{-1} s^{-1}. This is virtually the same as the value observed in the absence of surfactant; in such a case the enhancement for the outer-sphere electron transfer should be due to a concentration effect at the micellar interface. The same conclusion has been reached in recent studies on the effect of surfactant in electron-transfer reactions involving manganese(II) and cobalt(II) aminopolycarboxylate complexes[15] and in metal complex formation, both on the basis of a simple phenomenological method[10] as well as through a numerical calculation based on the nonlinearized Poisson–Boltzmann equation.[16]

On the other hand, if also the pathway represented by k_M' is contributing to the reaction progress, the increase would be due to a favorable electrostatic effect (the reverse has been observed for the reaction of $Ru(bpy)_3^{3+}$ with $Mo(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$ in SDS)[1a] as well as to the change in dielectric constant near the micellar surface or loss of solvation of the reactants: these factors could influence the outer-sphere reorganizational energy required in the electron-transfer act.[17]

The reaction rates of $Fe(5,6-Me_2phen)_3^{3+}$ and $Fe(4,7-Me_2phen)_3^{3+}$ with $Fe^{2+}(aq)$ in the presence of SDS under the same conditions of ionic strength and acidity have been found to proceed faster than the mixing time of our stopped-flow apparatus, particularly at the lower SDS concentrations.

Effect of SDS on the Electron Transfer between FeL_3^{3+} and $Fe^{2+}(aq)$ in $[H_2SO_4] = 0.02$ M and $[NaNO_3] = 0.04$ M. Under these experimental conditions the maximum rate enhancement is about 500 times, for all three phenanthroline complexes, and occurs around $(1.0$–$1.5) \times 10^{-3}$ M of SDS (see Figure 3 and Tables II–IV). Since the cmc is decreased by the addition of

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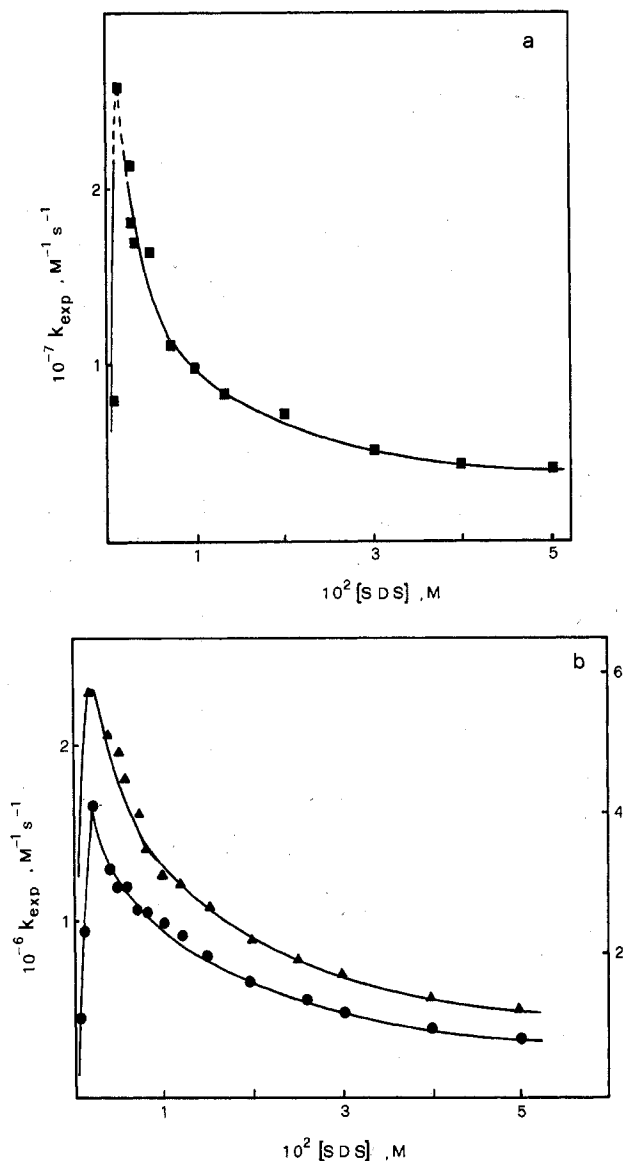(17) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

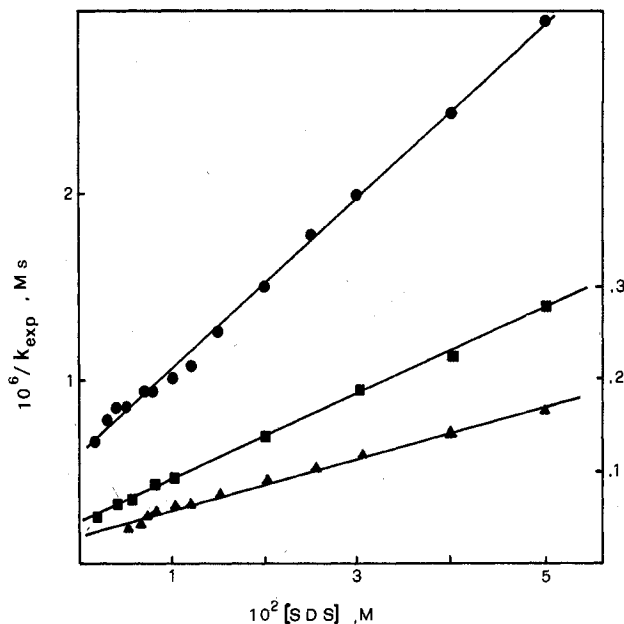**Figure 4.** Plot of $1/k_{exptl}$ as a function of SDS concentration for the data of Figure 3: $Fe(5,6-Me_2phen)_3^{3+}$ (■, right-hand scale), Fe-$(4,7-Me_2phen)_3^{3+}$ (▲, left-hand scale), $Fe(Me_4phen)_3^{3+}$ (●, left-hand scale).

From the intercepts, the following values of $\bar{k}_M K_B + k_M'$ can be obtained: $Fe(5,6-Me_2phen)_3^{3+}$, $(2.6 \pm 0.6) \times 10^7$ M^{-1} s^{-1}; $Fe(4,7-Me_2phen)_3^{3+}$, $(6.2 \pm 0.5) \times 10^6$ M^{-1} s^{-1}; Fe-$(Me_4phen)_3^{3+}$, $(1.6 \pm 0.2) \times 10^6$ M^{-1} s^{-1}.

If the pathway represented by $\bar{k}_M$ is operating, the values of k_M, for all the three different FeL_3^{3+}, are, also under these experimental conditions, practically the same as determined in the absence of surfactant. This leads us to conclude that the present reactions are again controlled by their driving force and that the increase in rate can be due to other factors, mainly the concentration effect at the micellar surface, although the change of environmental properties and the electrostatic effect can play an important role.

It is evident from the present and previous results[1,12,18] that the rates of the simplest electron-transfer reactions, that is the outer-sphere ones, can be largely enhanced or inhibited by the micellar systems.

Figure 3. Plot of the observed second-order rate constant as a function of SDS concentration ($[H_2SO_4]$ = 0.02 M, $[NaNO_3]$ = 0.04 M, 25.0 °C) for the reaction of Fe^{2+}(aq) with: (a) $Fe(5,6-Me_2phen)_3^{3+}$; (b) $Fe(4,7-Me_2phen)_3^{3+}$ (▲, right-hand scale), $Fe(Me_4phen)_3^{3+}$ (●, left-hand scale).

inert electrolytes,[6] the maximum is again around the cmc. Plots according to eq 5 are linear (see Figure 4) and from the ratios of slope to intercept, K_B = 80-100 M^{-1}, under these experimental conditions.

The surface potential of micelles is strongly reduced upon addition of excess electrolyte.[9] If, in the present conditions, ψ is assumed to be 75-80 mV,[9,10] K_B = 90-130 M^{-1}.

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