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Micellar Effect on Electron Transfer. V [1]. The Kinetics of Reactions of Substituted 1,10-Phenanthroline Complexes of Iron(III) with Octacyanomolibdate(IV) and Hexacyanoferrate(II) in the Presence of Sodium Dodecyl Sulphate

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Introduction

Electron transfer reactions occurring in biological systems frequently involve proteins containing transition metal ions [2]. In comparison with the behavior of less complicated transition metal complexes, the influence of the environment on the reactivity of the metal centers has to be considered.

The micelles, aggregates of amphiphilic molecules in which the interior contains the hydrophobic parts of the amphiphiles while the hydrophilic residues are located at the surface in contact with the bulk water, can be adopted as suitable models for more complex bioaggregates [3].

In a previous paper, the remarkable effect of the anionic micelles on the outer-sphere electron transfer between tris(2,2'-bipyridine)ruthenium(III), [Ru(bpy)$_3^{3+}$], and Mo(CN)$_8^{4-}$ or Fe(CN)$_6^{4-}$ was reported [1a].

In the present note, the title reactions were investigated in order to assess the influence of the free energy change on such systems in the pressence of surfactants.

Experimental

The following tris(1,10-phenanthroline)iron(II) complexes, (FeL$_3^{2+}$), were prepared and recrystallized as perchlorate according to the procedure described in the literature [4]: 1,10-phenanthroline (phen), 5-chloro- (clphen), 5-methyl- (mphen), 5,6-dimethyl- (dmphen), and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen). The corresponding FeL$_3^{3+}$ were prepared by PbO$_2$ oxidation. Sodium dodecyl sulphate (SDS, Merck) was recrystallized several times. Potassium hexacyanoferrate(II) was C. Erba reagent and potassium octacyanomolibdate(IV) was synthetized according to the literature [5].

The kinetic runs were performed by means of a Durrum–Gibson stopped-flow spectrophotometer, with [FeL$_3^{3+}$] = 3–5 × 10^{-6} *M* and [Mo(CN)$_8^{4-}$] = 5 × 10^{-6}–2 × 10^{-5} *M*; [H$_2$SO$_4$] = 8.3 × 10^{-3} *M* (for Fe(clphen)$_3^{3+}$, [H$_2$SO$_4$] = 3.2 × 10^{-2} *M*) at 8.0 °C. SDS concentrations were 0.010, 0.030 and 0.050 *M*.

The rate constants were evaluated according to a second order rate law by following the reaction progress at the wavelength of maximum absorption of FeL$_3^{2+}$ [4]. The reported values were averaged over 5–8 separate measurements.

Results and Discussion

The reactions between FeL$_3^{3+}$ and Mo(CN)$_8^{4-}$ or Fe(CN)$_6^{4-}$ in the absence of micelles occur at very fast rates [6]. In the presence of anionic micelles (the present SDS concentrations are above the critical micellar concentration) [7], the electron transfer rates are strongly decreased (see Tables I and II), as previously observed for the reactions of Ru(bpy)$_3^{3+}$ with the same reactants [1a].

TABLE I. Rate Constants at Different SDS Concentrations for the Reactions between FeL$_3^{3+}$ and Mo(CN)$_8^{4-}$ (8.0 °C; [H$_2$SO$_4$] = 8.3 × 10^{-3} *M*).

Oxidant	[SDS], *M*			
	0	0.010	0.030	0.050
Ru(bpy)$_3^{3+}$	3.2 × 10^9 [a]	1.6 × 10^7 [b]		
Fe(clphen)$_3^{3+}$	3.1 × 10^9 [a]	1.5 × 10^7 [c]		
Fe(phen)$_3^{3+}$	3.2 × 10^9 [a]	8.2 × 10^6	1.5 × 10^7	2.1 × 10^7
Fe(mphen)$_3^{3+}$	3.2 × 10^9 [a]	5.6 × 10^6	1.2 × 10^7	1.9 × 10^7
Fe(dmphen)$_3^{3+}$	3.1 × 10^9 [a]	3.0 × 10^6	6.5 × 10^6	8.7 × 10^6
Fe(tmphen)$_3^{3+}$		8.6 × 10^5	2.1 × 10^6	2.5 × 10^6

[a] 23 °C; [HClO$_4$] = 1 *M* [6]. [b] 8.0 °C; [HClO$_4$] = 0.015 *M* [1a]. [c] 8.0 °C; [H$_2$SO$_4$] = 0.032 *M* [this work].

TABLE II. Rate Constants at Different SDS Concentrations for the Reactions between FeL_3^{3+} and $Fe(CN)_6^{4-}$ (8.0 °C; $[H_2SO_4] = 8.3 \times 10^{-3}$ *M*).

Oxidant	[SDS], *M*		
	0	0.010	0.030
$Ru(bpy)_3^{3+}$	2.8×10^{9} [a]	3×10^{7} [b]	
$Fe(clphen)_3^{3+}$		2.2×10^{7} [c]	
$Fe(phen)_3^{3+}$	1.7×10^{9} [d]	2.0×10^{7}	2.4×10^{7}
$Fe(mphen)_3^{3+}$		1.5×10^{7}	1.8×10^{7}
$Fe(dmphen)_3^{3+}$		1.2×10^{7}	1.5×10^{7}
$Fe(tmphen)_3^{3+}$		2.5×10^{6}	3.8×10^{6}

[a] 23 °C; $[H_2SO_4]$ = 1 *M* [6]. [b] 8.0 °C; $[HClO_4]$ = 0.015 *M* [1a]. [c] 8.0 °C; $[H_2SO_4]$ = 0.032 *M* [this work]. [d] 23 °C; $[HClO_4]$ = 0.5 *M* [10].

The experimental results can be explained if we assume that FeL_3^{3+} (represented by A in the scheme) strongly interact with the anionic micelles [1a, c] while $Mo(CN)_8^{4-}$ or $Fe(CN)_6^{4-}$ (B) are in the bulk [8]

$$\text{mic} + A_w \underset{}{\overset{K_1}{\rightleftarrows}} A_{mic} \qquad (1)$$

$$A_w + B_w \xrightarrow{k_w} \text{products} \qquad (2)$$

$$A_{mic} + B_w \xrightarrow{k_m} \text{products} \qquad (3)$$

hence if (1) is always equilibrated and k_{obs} is the observed second order rate constants

$$k_{obs} = \frac{k_w + k_m K_1 [\text{mic}]}{1 + K_1 [\text{mic}]} \qquad (4)$$

Since $K_1 [\text{mic}] \gg 1$ [1a, c], it follows that

$$k_{obs} = k_w K_1^{-1} [\text{mic}]^{-1} + k_m \qquad (5)$$

In the present case, the observed rate constants slightly increase with increasing the surfactant concentration (probably due to a salt effect), thus ruling out the contribution of k_w to the reaction progress. Then the main reaction pathway is at the micelle–water interface, as previously suggested [1a].

The peculiarity of the present results is shown in Fig. 1, where the values of k_{obs} (at [SDS] = 0.010 *M*) are reported as a function of the reduction potentials of the oxidizing complexes. Particularly for $Mo(CN)_8^{4-}$, a depedence of the reaction rate on the driving force of the reaction can be observed. In the absence of surfactant, as reported in Table I, the reaction rates involving $Mo(CN)_8^{4-}$ exhibit virtually the same value, namely the diffusion controlled rate (k_{diff}) is reached.

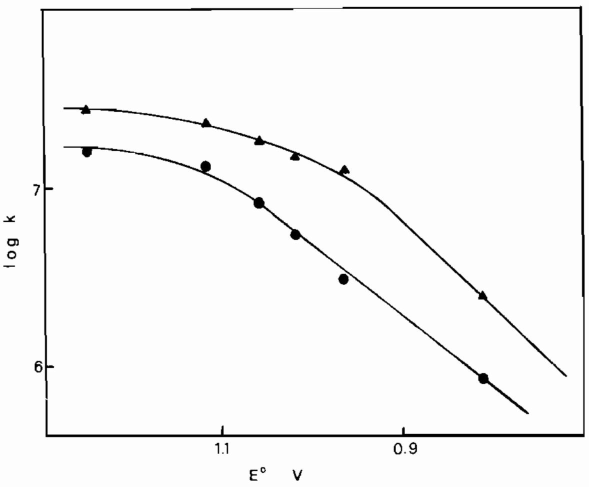

Fig. 1. Plots of logk as a function of the reduction potentials of $FeL_3^{3+/2+}$ [4, 11]: (▲) $Fe(CN)_6^{4-}$; (●) $Mo(CN)_8^{4-}$. ([SDS] = 0.010 *M*; 8.0 °C).

The Marcus theory [2, 9] for outer-sphere electron transfers, allows to estimate the electron transfer rate (k_{et}), being the activation free energy expressed by a coulombic contribution and another term related to the free energy of the reaction; it follows that, in absence of surfactant, $k_{et} \gg k_{diff}$: then the coulombic term (which refers to species with opposite charges) has a levelling effect on the reaction rates.

On the contrary, in the presence of anionic micelles, FeL_3^{3+} are imbedded in a negatively charged atmosphere, and an electrostatic repulsion with the negatively charged cyano complexes is operating. It is then probable that, at least in some cases, $k_{diff} > k_{et}$; as a consequence also the term including the free energy change is now influencing the reaction rates, as usual for the outer-sphere electron transfers [2].

In conclusion, the micellar aggregates can largely affect the rates and the controlling factors of the electron transfer reactions.

Acknowledgements

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