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Ionic Strength Effects on the Reduction of $CoEDTA^-$ by $Fe(CN)_6^{4-}$

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The effect of ionic strength on the reduction of $CoEDTA^-$ *by* $Fe(CN)_6^{4-}$ *is reported. The results are in direct contrast to expected behavior in that the rate constant initially increases, reaches a maximum at ionic strength 0.11* M, *and then begins to decrease. The results are discussed in terms of ion-pairing between* Na^+ *and* $Fe(CN)_6^{4-}$ *with the proposal that the observed decrease can be attributed to the increasing presence of the unreactive ion-triplet* $Na_2Fe(CN)_6^{2-}$ *at higher ionic strengths. The effect of the cyclic polyether 18-crown-6 is reported.*

Introduction

Two studies have been reported on the reduction of cobalt(III) chelate complexes ($Co^{III}Y$ where Y = EDTA, CyDTA and PDTA) by iron(II)–cyanide complexes ($Fe(CN)_6^{4-}$ and $Fe(CN)_5P(C_6H_5)_3^{3-}$). In the initial study by Haim *et al.* [1] a value of 0.21 M^{-1} s^{-1} was reported for k_f in the reaction at 25 °C and

$$CoEDTA^- + Fe(CN)_6^{4-} \overset{k_f}{\rightleftharpoons} CoEDTA^{2-} + Fe(CN)_6^{3-} \qquad (1)$$

ionic strength 0.59 *M*. The second study by Huchital and Lepore [2] expanded this work to other systems. A value of 0.297 M^{-1} s^{-1} was reported for k_f in reaction (1) at 25 °C and ionic strength = 0.26 *M*.

The effect of ionic strength on the rates of reactions between ions in aqueous solution at 25 °C is given by the equation

$$\log k = \log k_o + \frac{1.02\, Z_a Z_b I^{1/2}}{1 + I^{1/2}} \qquad (2)$$

where Z_a and Z_b are the charges of the reactant ions, k_o is the rate constant at zero ionic strength, and k is the rate constant at some finite ionic strength, I. This equation, which has been used quite successfully for reactions at high ionic strengths [3] predicts a positive salt effect (increasing rate constant) when the reactants are of the same sign. The variation of k_f at the two ionic strengths given above is in direct contrast to its expected behavior.

This paper reports the results of a more detailed study on the ionic strength dependence of reaction (1). The study was performed at 25 °C and pH 6.00. The results are indicative of strong ion-pairing between the alkali metal ion and the $Fe(CN)_6^{4-}$ reductant. This aspect will be developed and expanded to alkali metal ion effects on electron-transfer reactions in general.

Experimental

Materials

Potassium Ethylenediaminetetraacetatocobaltate(III), $K[Co^{III}EDTA]$, was prepared and analyzed as previously described [2]. $Na_4Fe(CN)_6 \cdot 10H_2O$, NaOH and ascorbic acid were purchased as the Fisher reagent grade chemicals and used without further purification. $NaClO_4$, used to control the ionic strength, was purchased as the hydrated salt from G. F. Smith. The cyclic polyether 18-crown-6 was purchased from Aldrich Chemicals.

Kinetic Measurements

All runs were carried out under pseudo-first-order conditions using the iron(II) complex in excess. Sample solutions were prepared to be at pH = 6.0 using excess EDTA and NaOH. The ionic strength was adjusted to the reported value using $NaClO_4$ as the added external electrolyte. The concentration of $Co^{III}EDTA$ was calculated from the weights and volumes used and checked spectrophotometrically (our values of wavelength for maximum absorbance and molar absorptivity at this maximum are 536 nm (ϵ = 317 M^{-1} cm^{-1}) and 382 nm (ϵ = 213 M^{-1} cm^{-1})). Hexacyanoferrate(II) stock solutions were analyzed spectrophotometrically after oxidation to the iron(III) complex with peroxydisulfate using a molar absorptivity of 1023 M^{-1} cm^{-1} at 420 nm for $Fe(CN)_6^{3-}$.

Kinetic measurements and spectra were obtained using a Cary 15 spectrophotometer. Reactions were

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TABLE I. Variation[a] of k_f with Ionic Strength for the Reduction of $CoEDTA^-$ by $Fe(CN)_6^{4-}$.

10^2I M	$10^3[Fe(CN)_6^{4-}]$ M	k_f M^{-1} sec^{-1}
0.193[b]	0.103	0.105
0.389[b]	0.265	0.129
0.706[b]	0.529	0.143
1.10[b]	1.06	0.171
1.28[b]	1.06	0.171
1.70[b]	1.06	0.209
1.73[b]	1.06	0.205
3.29[b]	2.64	0.237
4.46	2.64	0.255
5.89	2.64	0.278
6.00	5.28	0.261
6.04	2.64	0.267
7.26	2.64	0.307
7.26	2.64	0.306
7.33	2.64	0.300
11.3	2.64	0.316
11.4	2.64	0.330
14.0[b]	13.2	0.314
17.8	2.64	0.302
19.9	2.64	0.315
23.0	2.64	0.314
26.0	2.64	0.301
33.5	2.64	0.267
36.0	2.64	0.258
43.5	2.64	0.234
63.6	2.64	0.194
66.0	2.64	0.191
104.	2.64	0.111

[a] pH = 6.0, T = 25.0, $[CoEDTA^-] = 2.0 \times 10^{-4}$ M. [b] No $NaClO_4$ added.

conducted in 10 cm cylindrical cells. These cells were filled with a solution containing the iron(II) complex and the proper amount of ascorbic acid. The ionic strength of this solution was adjusted so that the proper value would be obtained when the desired volume of the cobalt(III) chelate solution was added.

The reactions were followed by monitoring the absorbance decrease of the $Co^{III}EDTA$ complex at 536 nm. Rate constants were obtained from the slopes of standard first order plots of ln $(A_t - A_\infty)$ *versus* time by least squares analyses. These plots were linear for 3 to 4 half lives.

Results

TABLE II. Effect of Na^+ on k_f for the $CoEDTA^-/Fe(CN)_6^{4-}$ Reaction.[a]

$10^3[Fe(CN)_6^{4-}]$[b] M	10^4 k_{obs} sec^{-1}	k_f M^{-1} sec^{-1}	$10^2[Na^+]$ M
2.66	5.34	0.201	1.08
2.65	5.29	0.199	1.08
2.53	5.31	0.209	1.22
1.59	3.67	0.231	1.73
1.52	3.48	0.229	1.74
1.06	2.50	0.238	2.06
0.53	1.30	0.245	2.35

[a] Rate constants were obtained from initial rates. No ascorbic acid was added. T = 25.0 °C, I = 0.0268 M, pH = 6.0. [b] $[CoEDTA^-] = 2.38 \times 10^{-4}$ M.

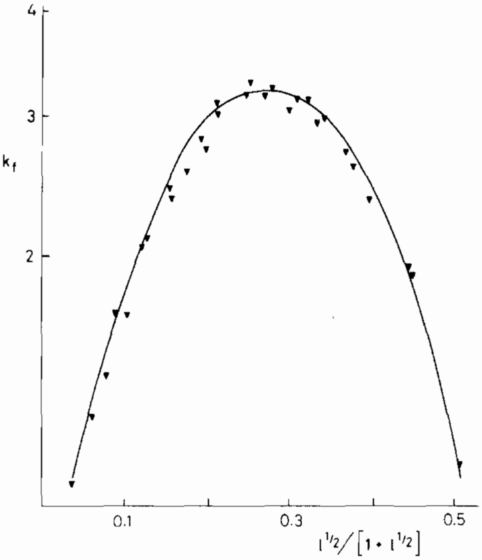

Fig. 1. Plot of $\log k_f$ *versus* $I^{1/2}/(1 + I^{1/2})$ for the reduction of $CoEDTA^-$ by $Fe(CN)_6^{4-}$.

The results of the study of the effect of ionic strength on the reduction reaction (1) are shown in Table I. A plot of $\log k_f$ against $I^{1/2}/(1 + I^{1/2})$, according to equation (2), is shown in Fig. 1. The values of k_f show an initial increase reaching a maximum at ionic strength 0.11 M, and then decrease with increasing ionic strength.

The effect of sodium ions on the reduction of $CoEDTA^-$ by $Fe(CN)_6^{4-}$ was investigated since cations are known to affect other reactions involving the ferrocyanide ion [4–6]. Reactions were conducted at an ionic strength of 0.0268 M. The concentration of $Fe(CN)_6^{4-}$ ranged from 0.53×10^{-3} M to 2.66×10^{-3} M. The ionic strength and pH were adjusted with sodium hydroxide and sodium perchlorate. To avoid complications from potassium ion, solutions of KCoEDTA were converted to the sodium form on a Bio-Rad AG 50 W-X8 cation exchange column. The resultant values of k_f under these experimental conditions are shown in Table II.

Under experimental conditions of the present work, the $Fe(CN)_6^{4-}$ complex can exist in three different forms [7]: the unassociated ferrocyanide ion, the ion-pair and the ion-triplet. These forms are related by the following equations

$$Na^+ + Fe(CN)_6^{4-} \overset{K_a^0}{\rightleftharpoons} NaFe(CN)_6^{3-} \qquad (3)$$

$$Na^+ + NaFe(CN)_6^{3-} \overset{K_b^0}{\rightleftharpoons} Na_2Fe(CN)_6^{2-} \qquad (4)$$

The thermodynamic association constant (K_a^0) for the ion-pair formation, (eqn. (3)), is known to be 120 M^{-1}. The value for the ion-triplet (K_b^0) formation, eqn. (4), is not known but has been estimated [8] as 15 M^{-1}. If the unassociated ferrocyanide, the ion-pair and the ion-triplet are all reactive, with rate constants k^0, k^a and k^b, in the reduction of $CoEDTA^-$, then the rate law can be written as

$$R = [CoEDTA^-][Fe(CN)_6^{4-}] \times [k^0 + k^aK_a[Na^+] + k^bK_aK_b[Na^+]^2] \qquad (5)$$

(this assumes that ion pair formation between $CoEDTA^-$ and Na^+ is negligible). Here K_a and K_b are the values of the association constants at a particular value of ionic strength. They can be evaluated from their thermodynamic values and their ionic strength dependencies [9, 10] as given by eqn. (6).

$$\log K = \log K^0 - \frac{Z_aZ_bI^{1/2}}{1 + 1.5\,I^{1/2}} \qquad (6)$$

The value of Z_aZ_b is equal to 4 and 3 for the processes given by eqns. (3) and (4) respectively.

The total ferrocyanide concentration can be expressed as

$$Fe(CN)_6^{4-}]_T = [Fe(CN)_6^{4-}] + [NaFe(CN)_6^{3-}] + [Na_2Fe(CN)_6^{2-}] \qquad (7)$$

Representing the concentration of the ion-pair and ion-triplet in terms of $[Na^+]$ and $[Fe(CN)_6^{4-}]$ leads to

$$[Fe(CN)_6^{4-}]_T + [Fe(CN)_6^{4-}] \times (1 + K_a[Na^+] + K_aK_b[Na^+]^2) \qquad (8)$$

Solving for the concentration of $Fe(CN)_6^{4-}$, substituting into eqn. (5) and rearranging leads to

$$\frac{R(1 + K_a[Na^+] + K_aK_b[Na^+]^2)}{[CoEDTA^-][Fe(CN)_6^{4-}]_T} = K^0 + k^aK_a[Na^+] + k^bK_aK_b[Na^+]^2 \qquad (9)$$

and since

$$k_f = R/[CoEDTA^-][Fe(CN)_6^{4-}]_T$$

eqn. (9) can be written as

$$k_f(1 + K_a[Na^+] + K_aK_b[Na^+]^2) = k^0 + k^aK_a[Na^+] + k^bK_aK_b[Na^+]^2 \qquad (10)$$

The constants K_a and K_b can be calculated using eqn. (6) to be 36 and 6.1 respectively at $I = 0.0268$ *M* and 25 °C. Using these values and the data in Table II, the lefthand side of equation (10) can be evaluated. Linear regression by the method of least squares of the resultant values against the sodium ion concentration yields 15.6 M^{-2} sec^{-1} and 0.12 M^{-1} sec^{-1} for the slope and intercept, respectively, with a correlation coefficient of 0.999.

The resultant value of k^0 (0.12 M^{-1} sec^{-1}) can be used in rearranged form of the last equation

$$\frac{k_f(1 + K_a[Na^+] + K_aK_b[Na^+]^2) - k^0}{[Na^+]} = k^aK_a + k^bK_aK_b[Na^+] \qquad (11)$$

to substantiate the non-contribution of the ion-triplet to the observed reactivity. Calculation of the first term of eqn. (11) at the various sodium ion concentrations leads to constant value of 15.2 ± 0.3 M^{-2} sec^{-1}.

These results indicate that the first terms in eqns. (10) and (11) are independent of the sodium ion concentration. This implies that the ion-triplet does not contribute to the reduction of $CoEDTA^-$, or, alternately, its concentration under the present experimental condition is not sufficient to contribute to the observed reactivity. In either case the data indicate that the value of k^0 and k^a are 0.12 M^{-1} sec^{-1} and 0.42 M^{-1} sec^{-1}, respectively.

In a further, perhaps more definitive, effort to explore the role of sodium ions in the $CoEDTA^-$–$Fe(CN)_6^{4-}$ redox reaction, some experiments were conducted in the presence of a cyclic polyether, 18-crown-6. The choice of this compound was based on its solubility in water and its ability to form a stable 1:1 complex [11] with sodium ions. The log K value for complex formation is reported [12] to be 0.80. Reactions were conducted at an ionic strength near the maximum of Fig. 1 ($I = 0.12$ *M*) and pH of 6.00.

In the absence of 18-crown-6, the value of the second order rate constant, k_f was 0.319 M^{-1} sec^{-1}, but in the presence of 0.125 *M* crown compound, the value of k_f was found to have undergone a significant increase to 0.396 M^{-1} sec^{-1}. Thus the ability of 18-crown-6 to reduce the concentration of free sodium ions in solution has also caused an increase in the rate constant of the reaction. The implications of these results will now be considered.

Discussion

The apparent ionic strength dependence of the reduction of $CoEDTA^-$ by $Fe(CN)_6^{4-}$ can probably be best explained in terms of a specific cation effect. Such effects are well documented [4–6, 13] in reactions involving the tetranegatively charged ferrocyanide ion. For example, the redox reaction between [6] $Fe(CN)_6^{4-}$ and $S_2O_3^{2-}$ increases with increasing concentration of K^+ at constant ionic strength. Also, Wahl [4] and coworkers showed that the electron-exchange reaction between hexacyanoferrate(II) and -(III) ions depends on the nature and concentration of the cation present but shows very little dependence on ionic strength.

It is conceivable that, under the present experimental conditions, the electrostatic interaction of Na^+ with $Fe(CN)_6^{4-}$ can produce both the ion-pair $NaFe(CN)_6^{3-}$, and ion-triplet, $Na_2Fe(CN)_6^{2-}$. Cohen and Plane [7] have postulated the existence of the ion-triplet $K_2Fe(CN)_6^{2-}$ at an ionic strength as low as 0.02 *M*; thus the existence of such a species at the ionic strengths used in these studies is entirely reasonable [14].

The behavior of the plot of log k_f *versus* $I^{1/2}/(1 + I^{1/2})$ can be rationalized in terms of ionic strength effects and in terms of the presence of complexed and noncomplexed forms of $Fe(CN)_6^{4-}$. The initial portion of Fig. 1 rises rapidly with a slope of 3.8, indicative that at very low ionic strengths the reactive species *are* $CoEDTA^-$ and $Fe(CN)_6^{4-}$. As the ionic strength increases, the concentration of Na^+ also increases and associated species of ferrocyanide are formed. Each of these new species can react with $CoEDTA^-$ with its own characteristic rate constant. A complete analysis of the system would now demand a knowledge of the association constants and reaction rate constants along with the ionic strength dependence of each quantity. This is an insurmountable task since the association constant of Na^+ with $Fe(CN)_6^{4-}$ is not known and theories of ionic strength dependencies are rarely applicable [15] at values of I much greater than 0.010 *M*, particularly in the reaction of highly charged species.

A qualitiative description of the system can be given in terms of two reactive iron(II) species, $Fe(CN)_6^{4-}$ and $NaFe(CN)_6^{3-}$, and one non-reactive species, $Na_2Fe(CN)_6^{2-}$. This assumption would explain the decrease in rate constant at values of I greater than 0.15 *M*, since further addition of sodium perchlorate to increase the ionic strength would result in the formation of greater amounts of the ion-triplet and a decrease in the concentration of the reactive species. This argument also explains the results of Rawoof and Sutter [13] on the reduction of MnO_4^- by $Fe(CN)_6^{4-}$ at pH 6.0 and I = 0.093 *M*. These workers observed that an increase in ionic strength or cation concentration caused a slight decrease in the rate constant of the reaction. The maximum value of the rate constant occurred at a value of I = 0.1 *M*. Under these conditions, these authors stated, the ion-pair would be present to an extent greater than 95%. It was concluded that the rate determining step is between the permanganate ion and the ion-pair (assuming the equilibrium in eqn. (3) is fast compared to the rate determining step), $KFe(CN)_6^{3-}$ or $NaFe(CN)_6^{3-}$, since both cations gave the same kinetic results.

The lack of reactivity of the ion-triplet is also indicated by the increase in k_f when the reaction was conducted in the presence of 18-crown-6, which forms a 1:1 complex with Na^+ and effectively lowers the concentration of free sodium ions in solution. The results of removing some of the cations would be to reduce the concentration of the triplet and thereby transform the iron(II) reductant into more reactive species. An increase in k_f could also be the result of an increase in ionic strength caused by the addition of 18-crown-6. However, a simple calculation using eqn. (10) would require almost a doubling of the ionic strength to account for the increase in k_f if the reactive species is assumed to be $NaFe(CN)_6^{3-}$. Thus, the former explanation is preferred.

Wahl [4] and coworkers stated that it appears that the catalytic effects of these cations level off or decrease at higher concentrations. This suggests that the rate constant for paths involving several cations are not especially large. If the reactivity of the triplet is negligible, as also indicated by the dependence of eqn. (10) and the independence of eqn. (11) on the concentration of sodium ions, the rate law can be expressed in terms of two reactive species, $Fe(CN)_6^{4-}$ and $NaFe(CN)_6^{3-}$,

$$\text{Rate} = [CoEDTA^-]\,[Fe(CN)_6^{4-}]\; k^{o} + k^{a}K_a[Na^+]) \qquad (14)$$

whose second order rate constants are 0.12 M^{-1} sec^{-1} and 0.42 M^{-1} sec^{-1} respectively at I = 0.0268 *M*.

The observed initial acceleration of k_f upon addition of added electrolyte, $NaClO_4$, is then partially due to ionic strength effects. Reduction of electrostatic repulsion by ion-pair formation should also play a major role. The very recent work of Okamoto and coworkers [16] on the oxidation of N-propyl-1,4-dihydronicotinamide (a neutral molecule) by ferricyanide showed that the reaction is accelerated by alkalimetal ions in the orders $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ = Et_4N^+$. This order suggests the acceleration of the electron transfer process correlates with the polarizability of the cation [17].

Thus it seems that the effect of alkali-metal ions on electron-transfer reactions can be described in terms of: (1) ionic strength effects, (2) a decrease in electrostatic interactions and (3) an acceleration of the electron-transfer step by a polarizable species which behaves as an electron-conductor.

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