Chapter-5
Kinetic Studies of Hexacyanoferrate(II) by EDTA

Kinetics of Substitution of Hexacyanoferrate(II) by EDTA catalysed with Mercury(II)

INTRODUCTION

During the last decade, many novel methods for the determination of mercury(II) have been developed [1–6]. It has been demonstrated that of all the heavy metals, mercury(II) easily forms bond to cyanide and slowly removes it from hexacyanoferrate(II). Kinetics and mechanism of ligand replacement in low spin Fe(II) complex has been done, although it is limited to the study of pentacyano(L)ferrate(II) complex[1-7]. Few studies have been done in aqueous electrolyte and micellar media to acquire an in depth knowledge of the mechanism [8-9]. The kinetics of oxidation of the hexacyanoferrate(II) complex by various reagents in acidic and basic media have been studied and, all these investigations have been applied to specific analytical problems [10-13]. \( K_4[Fe(CN)_6^{4-}] \) hardly undergoes exchange reaction as \( CN^- \) itself is a very strong ligand although slow exchange of labelled \( CN^- \) group or aminopyridine is slow but under the action of u.v. light reversible aquation occurs leading to the formation of \( [Fe(CN)_3H_2O]^3^- \)[14]. However, only monosubstituted \( [Fe(CN)_5L]^3^- \) has been obtained either through photochemical or dissociation reaction or by metal catalysed substitution reaction[15].
Kinetic Studies of Hexacyanoferrate(II) by EDTA

\[
[\text{Fe(CN)}_6^{2-}] + \text{H}_2\text{O} \rightarrow [\text{Fe(CN)}_5\text{H}_2\text{O}]^{2-} + \text{CN}^- \quad (1)
\]

Hexacyanoferrate(II) reacts with EDTA according to the following equation

\[
[\text{Fe(CN)}_5\text{H}_2\text{O}]^{-} + \text{EDTA} \rightarrow [\text{Fe(CN)}_5\text{EDTA}]^{-} + \text{H}_2\text{O} \quad (2)
\]

\[
\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH}^- \quad (3)
\]

Mercury(II) readily forms complex with cyanide ion but decomposes in uv light.

\[
\text{Hg}^{2+} + [\text{Fe(CN)}_6^{4-}] + \text{H}_2\text{O} \rightarrow [\text{Fe(CN)}_5\text{H}_2\text{O}]^{3-} + \text{HgCN}^+ \quad (4)
\]

\[
\text{HgCN}^+ + \text{H}^+ \rightarrow \text{HCN} + \text{Hg}^{2+} \quad (5)
\]

In the present work we have studied the kinetics of substitution of \(\text{CN}^-\) by EDTA, catalysed by \(\text{Hg}^{2+}\). A probable mechanism has been proposed. Any attempt to study the substitution of \(\text{CN}^-\) by phenanthroline, pyridine, hydrazine and piperazine resulted in precipitation even in low concentration.
EXPERIMENTAL

Double distilled, de-ionized water was used throughout. The chemicals used were of analytical grade. Stock solutions of the compounds were wrapped with carbon paper to protect them from photodecomposition. The mercury(II) and hexacyanoferrate(II) solutions were diluted just before use. The desired pH= 5 of the reaction mixture was maintained by KHP-NaOH buffer [16]. The ionic strength was maintained at 0.1 M by adding appropriate amount of KNO₃.

Procedure

A mixture of 2.0 ml of each EDTA, phthalate buffer of pH = 5.0 and mercury(II) chloride were mixed in a flask thermally equilibrated for about 30 minutes at 25°C and left to stand for 10 min to ensure completion of reaction. Finally, 2.0ml of [Fe(CN)₆]⁴⁻ was added to this mixture and the wavelength of maximum absorption (365 nm) was determined (Fig.1).

RESULTS AND DISCUSSION

Effect of pH
The reaction was studied first by fixed time kinetic method in the pH range 1-13. (measured at t = 5 and 10 minutes after mixing the reagents) Fig. 2 shows plots of absorbance versus pH of the reaction mixture. It was found that, the absorbance increases with increasing pH and attains a maximum between pH 5.0 and 5.5. However, above this pH the absorption decreases which is due to the deficiency of protons. The rate is reduced at low pH due to the formation of various protonated forms of [Fe(CN)₆]⁴⁻ which are less reactive than [Fe(CN)₆⁴⁻] itself [17].

**Effect of EDTA**

The complex formation with EDTA is influenced by a change in pH of the solution which is either perhaps due to ionization of the metal complex at low pH or hydrolysis of the metal ion at higher pH. The effect of EDTA was examined as a function of its concentration at 5 pH. A plot of initial rate versus EDTA shows slow change in rate constant (Fig. 3) in varied 2 × 10⁻⁵ to 7×10⁻⁵ M and finally decreases at still higher concentrations. A fixed concentration of 4×10⁻⁴ M was thus selected as optimum.

**Effect of [Fe(CN)₆]⁴⁻ on the initial rate**

The initial rate were evaluated as a function of [Fe(CN)₆⁴⁻] by changing its concentration from 5×10⁻⁴ to 2×10⁻² M, keeping all other parameters constant. The plot of log Vi versus log [Fe(CN)₆⁴⁻] (Fig 4) indicates variable
order of dependence in \([\text{Fe(CN)}_6{}^{4-}]\) is exhibited ranging from first order to higher concentration but certainly not tending towards zero order.

**Effect of \([\text{Hg}^{2+}]\) on initial rate**

The concentration of mercury(II) was varied between \((1 \times 10^{-5} \text{ to } 2 \times 10^{-3} \text{ M})\) and those of the \(\text{[Fe(CN)}_6{}^{4-}]\) and EDTA were kept constant. The pH and temperature were maintained at 5 and, 25°C respectively (Fig. 5). The large variation in \([\text{Hg}^{2+}]\) was selected in order to test the linearity between initial rate and \([\text{Hg}^{2+}]\) for its analytical application. A plot of the absorbance measured at an interval of one min versus \([\text{Hg}^{2+}]\) as a function of pH (Fig. 5) indicates that the rate increases linearly until the ratio of the \(\text{[Fe(CN)}_6{}^{4-}]\) and \([\text{Hg}^{2+}]\) reaches 1:1. When the concentration of \([\text{Hg}^{2+}]\) exceeds that of \(\text{[Fe(CN)}_6{}^{4-}]\) the absorption begins to diminish and follows a non-linear pattern. The intercept computed from the initial linear portion of the Fig. 5 provides the rate due to the uncatalyzed path. However, decline in the rate of reaction at higher \([\text{Hg}^{2+}]\) is probably due to the formation of a binary adduct, \(\text{[Fe(CN)}_6{}^{4-} \cdot 2\text{HgCl}_2]\). In a separate experiment it was observed that a white precipitate is formed immediately after mixing \(\text{[Fe(CN)}_6{}^{4-}]\) with \([\text{Hg}^{2+}]\) in 1:2 molar ratio which rapidly turned blue, confirming the formation of a binuclear complex. A similar observation has also been made by Beck [18].
Effect of temperature and ionic strength

The rate of the [Hg$^{2+}$] catalyzed ligand exchange between [Fe(CN)$_6^{4-}$] and EDTA was studied as a function of temperature in the range 20-30°C. The higher temperature was avoided due to the possibility of decomposition of [Fe(CN)$_5$EDTA]$^{3-}$. The Arrhenius equation was used to determine the activation energy (Ea) for the catalyzed reaction. The enthalpy ($\Delta H^\dagger$) and entropy of activation ($\Delta S^\dagger$) were calculated using Eyring equation. The values of activation parameters were found to be $E_a = 78.2$ KJ mol$^{-1}$, $\Delta S^\dagger = -48.67$ KJ mol$^{-1}$ and $\Delta H^\dagger = -52.5$ KJ mol$^{-1}$. The effect of ionic strength on the initial rate of reaction was also studied by varying the ionic strength between 0.015 and 0.2 M range. The higher ionic strength was avoided due to the limited solubility of (KNO$_3$). When KCl was used to maintain the ionic strength the rate was found to decrease considerably. This is probably due to a subsequent decrease in [Hg$^{2+}$] or [HgCl$^+$] along with the ion-pair formation between [Fe(CN)$_6^{4-}$] and [Hg$^{2+}$] [19].

The following scheme for the mercury(II) catalyzed ligand exchange between [Fe(CN)$_6^{4-}$] and EDTA has been proposed:
Formation of the complex, \([\text{Fe(CN)}_5\text{EDTA}]^{3-}\) through the catalyzed path can be written as:
while that for the uncatalyzed path the

$$\text{rate} = k'[\text{Fe(CN)}_6^{4+}] \quad (13)$$

where, $k'$ is a composite rate constant involving a concentration term. If the rate determining step is taken to be the composition of the activated complex ($A^+$), the activity of the mercury(II) at low concentration can be easily explained by the above mechanism. The overall rate for uncatalyzed reaction can be expressed through equation (13) using a non limiting concentration of EDTA.

$$\text{Rate} = \frac{d}{dt} [\text{Fe(CN)}_5\text{EDTA}]^{3^-} = k'[\text{Fe(CN)}_6^{4+}] \quad (14)$$

$$+ \frac{k_2 K [\text{Fe(CN)}_6^{4+}][\text{Hg}^{2+}][\text{H}_2\text{O}]}{1+K[\text{Fe(CN)}_6^{4+}]}$$

The second term in the above equation refers to the rate of the catalyzed reaction and explains the variable order dependence in $[\text{Fe(CN)}_6^{4+}]$. $K$ is defined as the equilibrium constant for the association of the mercury(II) with water and $[\text{Fe(CN)}_6^{4-}]$. Since water is in a large excess, the equation (14) is reduced to equation (15)

$$\text{Rate} = k'[\text{Fe(CN)}_6^{4+}] + k'_2 K[\text{Hg}^{2+}][\text{Fe(CN)}_6^{4-}] \quad (15)$$

Now equation (15) yields the observed rate constant ($k_{obs}$) as expressed by equation (16)
Kinetic Studies of Hexacyanoferrate(II) by EDTA

\[ k_{\text{obs}} = k' + k'_2 K[Hg^{2+}] \]  
(16)

where, \( k'_2 = k_2 + [H_2O] \).

A plot of the initial rate versus \([Hg^{2+}]\) at low \([Fe(CN)_6^{4-}]\) is given in fig.6.

In case of higher \([Fe(CN)_6^{4-}]\), equation (14) takes the form of equation (17).

\[ \text{Rate} = k' [Fe(CN)_6^{4-}] + k'_2 [Hg^{2+}] \]  
(17)

The value of the initial rate \( (V_i) \) as a function of \([Hg^{2+}]\) at low \([Fe(CN)_6^{4-}]\) is listed in table 1. The \( k' \) and \( k'_2 \) have been calculated from fig.6 of initial rate versus \([Hg^{2+}]\) using equation (17) at specified experimental condition. The rate constant \( k' \) and \( k_2 \) are found to be \( 4.17 \times 10^{-3} \text{ S}^{-1} \) and \( 2.50 \text{ S}^{-1} \) respectively, at \( I = 0.1 \text{ M}, \text{pH} = 5, \text{temp} = 25^\circ \text{C} \). The value of \( k'_1 \) and \( k_2 \) so obtained are substituted in equation (17) to evaluate the equilibrium constant \( K \) at various \([Hg^{2+}]\) at low \([Fe(CN)_6^{4-}]\). The \( K \) (Table 1) and the average value of \( \log K \) (2.80) in our case is comparable with that reported by Beck for \([Fe(CN)_6^{4-} \cdot Hg(CN)_2] \) complex (log = 2.38) [17]. Although the values of \( k_2 \) have been calculated employing high \([Fe(CN)_6^{4-}]\) using equation (17) it can be obtained even at low \([Fe(CN)_6^{4-}]\) using equation (18).

\[ k_2 = \frac{\text{Rate} - k'[Fe(CN)_6^{4-}]}{K[Fe(CN)_6^{4-}][Hg^{2+}][H_2O]} \]  
(18)
However, the values calculated from this equation are almost identical. The ionic behavior of $[\text{Hg}^{2+}]$ may be represented by the following reactions.

$$
\text{Hg}^{2+} + \text{Cl}^- \rightleftharpoons k_1 \text{HgCl}^+
$$

$$
\text{HgCl}^+ + \text{Cl}^- \rightleftharpoons k_2 \text{HgCl}_2
$$

It has been shown that when Hg(NO$_3$)$_2$ reacts with $[\text{Fe(CN)}_6^{4-}]$ in solution the resultant was $\text{Hg}_2[\text{Fe(CN)}_6^{4-}]$ [20], which has also been verified from the absorption spectra of both the reacting components and the eventual product. This is quite obvious because the $[\text{Hg}^{2+}]$ is more electropositive than K$^+$ ion. The activation energy calculated for this reaction is lower than those reported [21-22] for the replacement of CN$^-$ in nearly similar reaction systems. The entropy of activation is negative which is obvious if the virtual solvations of the activated complex and its highly charged dissociation products are considered. Thus, the activation parameters provide further support to the proposed mechanism.

**CONCLUSION**

In the present work we have studied the kinetics of substitution of CN$^-$ by EDTA catalyzed by $[\text{Hg}^{2+}]$. A probable mechanism of the reaction has been
proposed. The results presented here clearly demonstrate that the chelating agent EDTA was used for the neutralization of CN⁻ in complex formation which is more effective and inexpensive. The values of thermodynamic parameters are $E_a = 78.2 \text{ KJ mol}^{-1}$, $\Delta S^\circ = -48.67 \text{ JK}^{-1} \text{ mole}^{-1}$ and $\Delta H^\circ = -52.5 \text{ KJ mole}^{-1}$. The negative value of the parameters show the exothermic nature of reaction.
Fig. 1 Absorption spectra of reactants and products: (A) [EDTA] = $1 \times 10^{-3}$ M; 
(B) $[\text{Fe(CN)}_6^{3-}] = 5 \times 10^{-4}$ M (C) $[\text{Fe(CN)}_6^{4+}] (4 \times 10^{-4}$ M) + [EDTA]($4 \times 10^{-3}$ M) 
+ [$\text{Hg}^{2+}](3 \times 10^{-5}$ M) at pH = 5.0
Fig. 2 Effect of pH on Hg$^{2+}$ catalysed substitution of CN in hexacyanoferrate(II) by EDTA. $[\text{Fe}($CN$)_6^{4-}] = 5 \times 10^{-3} \text{M}$, EDTA = $1 \times 10^{-5} \text{M}$, $[\text{Hg}^{2+}] = 3 \times 10^{-5} \text{M}$, Temp = 25°C and I = 0.1M (KNO$_3$).
**Fig. 3** Effect of EDTA on initial rate, $[\text{Fe(CN)}_6^{4-}] = 3.5 \times 10^{-2} \text{ M}$, $[\text{Hg}^{2+}] = 3 \times 10^{-5} \text{ M}$, pH = 5, Temp = 25°C and I = 0.1 M (KNO₃).

**Fig. 4** Dependence of the initial rate on $[\text{Fe(CN)}_6^{4-}]$ in presence of $[\text{Hg}^{2+}]$ 
$[\text{EDTA}] = 3 \times 10^{-4} \text{ M}$, $[\text{Hg}^{2+}] = 3 \times 10^{-5} \text{ M}$, pH 5.0, temp = 25°C and 0.2 M (KNO₃).
Kinetic Studies of Hexacyanoferrate(II) by EDTA

Fig. 5 Dependence of the initial rate of substitution of CN⁻ in [Fe(CN)₆⁴⁺] by EDTA on [HgCl₂], [Fe(CN)₆⁴⁺] = 3.5 × 10⁻³ M, [EDTA] = 3 × 10⁻⁴ M, pH = 5, temp = 25°C and I = 0.1 M (KNO₃).

Fig. 6 Effect of variation of [Hg²⁺] on initial rate (Vi) at high concentration of [Fe(CN)₆⁴⁺] under the condition [Fe(CN)₆⁴⁺] = 8 × 10⁻⁴ M, [EDTA] = 5 × 10⁻⁴ M, pH = 5, temp. = 25°C, I = 0.1 M (KNO₃).
Table 1. Calculation of $K$ by varying $[\text{Hg}^{2+}]$ at constant $[\text{Fe(CN)}_6^{4-}]$.

$[\text{Fe(CN)}_6^{4-}] = 8 \times 10^{-4}$ M, $[\text{Hg}^{2+}] = 5 \times 10^{-4}$ M, $pH = 5$, temp = 25°C and $I = 0.1$ M (KNO$_3$).

<table>
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<th>$[\text{Hg}^{2+}] \times 10^{-4}$ (M)</th>
<th>$V_i \times 10^4$</th>
<th>$K$(calcld.)</th>
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Average log $k = 2.80$
REFERENCES


