4.1. Introduction

Reactions in micellar solutions are often used as models for compartmentalized systems. Such systems offer the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as of the local microenvironment on the reactivity.

According to Brown et al. [1] the effect of micelles on reactions can be ascribed to a combination of the following factors:

1. The dielectric constant in the micelle is lower than in water, which causes a solvent effect.

2. The transition state of the reaction can be stabilized by interaction with the polar head groups.

3. The reactants are concentrated relative to the surrounding water phase through interactions with the micelle surface or through insertion into the micelle itself, thus leading to an increased rate of bimolecular reactions. The acidity or basicity of ionic amphiphiles can be significantly higher on the surface of micelles than in the surrounding aqueous phase. The concentration effect can be considered as dominant in many cases.

Functional micelles containing a bound reagent (for example, the nucleophile) or a bound catalyst in the head group are of considerable interest. In this way, a high
concentration of the reactant is always ensured on the surface of the micelle and a similarity to enzymatic reactions becomes apparent which includes metallomicelles.

A large amount of kinetic data has been explained successfully in terms of the pseudo-phase model [2]. The pseudo phase model explains many features of micellar rate effects and it can be applied, atleast qualitatively, to reactions in a variety of colloidal assemblies as reverse micelles and microemulsions. Romsted et al. [3] have developed pseudophase ion exchange (PIE) model [2,4,5], wherein micellar surfaces are treated as selective ion exchangers saturated with counter ions. The number of assumptions and restrictive reaction conditions required are larger in the PIE model than in the pseudo-phase model. Analysis of various micelle catalysed reactions on the basis of the pseudo-phase kinetic model led to the conclusion that two principal factors are responsible for the efficiency of micellar reactions: concentration effects in the micellar pseudo-phase due to the hydrophobic, electrostatic and specific interactions of reactants with these micelles and changes in reactivity of reagents; on transfer from water to the micellar pseudo-phase [6] etc.

Cyclodextrins (CD) are cyclic polysugars composed of glucose units linked by 1-4α glycoside bonds [7-9]. The cyclic structure forms a hydrophobic cavity and they can include a variety of guest molecules in their cavity [10-12]. The effects of cyclodextrin inclusion on the kinetics and mechanism of ligand substitution [13,14] and electron transfer reactions of transition metal complexes in aqueous solution [15,16] have received considerable attention in recent years.
4.1.1. Electron transfer reactions of metal complexes in aqueous solution and in micelles

Electron transfer reactions involving cobalt(III) complexes are very well known because the kinetics of reduction of octahedral cobalt(III) complexes is mostly free from complications arising due to reversible electron transfer, aquation, substitution and isomerisation reactions. Diebler and Taube [17], Watts et al. [18,19] and other researchers [20] have studied the kinetics and mechanism of reduction of cobalt(III) by Fe\(^{2+}\)\(_{aq}\) in aqueous and non-aqueous media. Several transition metal complexes have been used for studying electron transfer in different environments such as micelles [21,22], vesicles [23] and DNAs [24-26]. The redox processes occurring in biological systems are controlled both by specific geometry of the inner coordination sphere, which mainly controls the operation potential of the metal center, and by the hydrophobic effect offered by the pseudo biological interfaces. Electron transfer in these restricted geometry systems attracts great deal of interest because of their potential to prolong the lifetime of charge-transfer states, a goal of electron-transfer studies aiming to utilize solar energy [27-29] and as molecular switches [30,31]. When the nature of the chemical reactions in organized system is discussed, in particular electron- and proton-transfer reactions, the influence of the driving force has to be considered.
Y. Kurimura et al, have reported the iron(II) reductions of some cobalt(III) complexes to investigate the effect of non bridging ligand on the rate of electron transfer reactions[32] and other researchers have also reported the iron(II) reductions of Co(en)$_2$XY$^{n+}$ [33] and Co(NH$_3$)$_4$XCl$^{n+}$[34,35] and electron transfer reactions between aquochromium(II) and chromium (III) complexes [36,37] to determine the effect of nonbridging ligand effect. In recent times there has been some reports on surfactant-metal complexes of various nature and their micelle forming properties [38-42].

This chapter deals with outer-sphere electron transfer reactions of the following surfactant-cobalt(III) complexes with Fe$^{2+}_{aq}$ ion in self-micelles as well as in the presence of β-cyclodextrin media.

- cis-[Co(en)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$
- cis-α-[Co(trien)(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$
- cis-[Co(bpy)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$·3H$_2$O
- cis-[Co(phen)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$·3H$_2$O
4.2. Experimental

4.2.1. Stoichiometry

The stoichiometry of the reaction was determined by estimating iron(III) and cobalt(II) present in the product mixture. Iron(III) was determined spectrophotometrically by Kitson’s method [43] and cobalt(II) was determined as [CoCl₄]²⁻ at 690 nm in an excess of HCl. The ratio iron(III) to cobalt(II) was found to be 1:1 in the reactions studied, indicating 1:1 stoichiometry.

4.2.2. Materials and Methods

The surfactant-cobalt(III) complexes were synthesised as reported earlier [45]. A stock solution of Fe(ClO₄)₂ was prepared by dissolving pure iron powder in a slight excess of perchloric acid. The concentration of Fe²⁺ₐq in perchloric acid solution was determined by a method similar to that reported in the literature [46].

4.2.3. Kinetic measurements

For kinetic measurements the reactant solution (containing the complex, NaClO₄, and HClO₄, omitting Fe²⁺ₐq) was thermostated. A 1 cm path length cuvette was used to achieve optimum optical densities at the concentrations chosen. All the solutions were deaerated in order to avoid any air oxidation of Fe²⁺ₐq. After thorough purging with pure N₂ for ca. 30 min, the Fe²⁺ₐq solution was transferred to the cuvette sealed with a serum cap. A pool of Hg was created on the membrane of the cap to minimize leakage of air while introducing the requisite
amount of Fe\textsuperscript{2+} \textsubscript{aq} with a hypodermic syringe to initiate reaction and the reaction was followed on a Varian Cary 500 Scan UV-Vis-NIR spectrophotometer equipped with the Water Peltier System (PCB 150). The temperature was controlled within ±0.01\textdegree C. The decrease in the absorbance was followed at 420 nm for the complexes containing bipyridine and phenanthroline ligands and at 422 nm for the complexes containing ethylenediamine and triethylenetetramine as ligands, where absorption of each cobalt(III) complex is maximum. All kinetic measurements were performed under pseudo-first order conditions with the Fe(II) in excess over the cobalt(III) complex. The concentration of Fe(ClO\textsubscript{4})\textsubscript{2} used was 0.1 mol dm\textsuperscript{-3} and the concentration of cobalt(III) complex was always chosen typically above their CMC values in the 3.0–7.0×10\textsuperscript{-4} moldm\textsuperscript{-3} region. The ionic strength was maintained at 1.0 moldm\textsuperscript{-3} in all the runs using NaClO\textsubscript{4}. The second-order rate constant, k, for the Fe(II) reduction of the cobalt(III) complex defined by \(- \frac{d[\text{Co(III)}]}{dt} = k[\text{Co(III)}][\text{Fe}^{2+} \text{aq}]\) was calculated from the concentration of Fe(II) and the slope of the pseudo first order, \(\log (A_t - A_\alpha)\) \textit{versus} time plot, which is equal to \(- \frac{k[\text{Fe(II)}]}{2.303}\), where \(A_t\) is the absorbance at time \(t\), \(A_\alpha\), the absorbance after all the cobalt(III) complex has been reduced to cobalt(II), and \(k\), the second order rate constant. Usually the value of \(A_\alpha\) was measured at times corresponding to 10 half-lives. All the first-order plots were substantially linear for at least five half-lives. Each rate constant reported was the average result of triplicate runs. Rate constants obtained from successive half-life values within a single run agreed to within ±5%. No trends indicative of systematic errors were
noted, and the average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance difference against reaction time.

4.3. Results and Discussion

4.3.1. Effect of initial concentration of the complexes

The reduction of $\textit{cis}$-$\textit{[Co(LL)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$]}^{3+}$ (LL = en or trien or bpy or phen) by Fe(II) proceeds according to the overall reaction as indicated below:

$$\textit{cis}$-$\textit{[Co(LL)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$]}^{3+} + \text{Fe}^{2+}_{\text{aq}} \rightarrow \text{Co}^{2+}_{\text{aq}} + \text{Fe}^{3+}_{\text{aq}} + 2\text{LL} + 2\text{C}_{12}\text{H}_{25}\text{NH}_2$$

This reaction is postulated as outer-sphere in comparison to such type of reactions in the literature \[47,48\] involving ordinary lower primary amine coordinated cobalt(III) complexes similar to the surfactant-cobalt(III) complexes of the present study.
Accordingly the mechanism is delineated in **Scheme 1**

\[
\begin{align*}
[\text{Co(LL)}_2(DA)]^{3+} + \text{Fe}^{2+} & \overset{K_{IP}}{\longrightarrow} \{[\text{Co(LL)}_2(DA)]^{3+} ; \text{Fe}^{2+}\} \\
\{[\text{Co(LL)}_2(DA)]^{3+} ; \text{Fe}^{2+}\} & \overset{k_{et}}{\longrightarrow} \{[\text{Co(LL)}_2(DA)]^{2+} ; \text{Fe}^{3+}\} \\
\{[\text{Co(LL)}_2(DA)]^{2+} ; \text{Fe}^{3+}\} & \overset{\text{Fast}}{\longrightarrow} \text{Products}
\end{align*}
\]

\[\text{LL} = \text{en or trien or bpy or phen} \]

\[\text{DA: Dodecylamine}\]

**Scheme 1**

The observed second order rate constants k’s, are given in **Table 4.1** for the above reaction, under various initial concentrations of the surfactant–cobalt(III) complexes, at 298, 303, 308 K in aqueous solution. As seen from this Table the rate constant of the reaction goes on increasing with increase in the initial concentration of the complex from \(3 \times 10^{-4}\) moldm\(^{-3}\) to \(7 \times 10^{-4}\) moldm\(^{-3}\). As this concentration range is higher than the critical micelle concentration values [15] of these surfactant complexes all these rate constant values correspond to the rate constant values in self-micelles formed from these metal complex molecules themselves. So the increase in the rate constant of the outer-sphere electron transfer reactions with increase in initial concentration of these surfactant...
complexes (Fig. 4.1 & 4.2) can be attributed to the aggregation of these metal complexes in their own self-micelles. (With increase in initial concentration of the surfactant-cobalt(III) complexes the number of micelles present in the medium also increases. In these micelles the reactants are encountered in a small volume of stern-layer of the micelles leading to enhancement of concentration of reactants at the microlevel leading to higher rate and lower activation energy.). The structure of the complex before and after CMC are shown in scheme 2.

Scheme 2
### Table 4.1

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>[Complex] × 10^4 mol dm^-3</th>
<th>k, mol^-1 dm^3s^-1</th>
<th>298K</th>
<th>303K</th>
<th>313K</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-α-[Co(trien)(C_{12}H_{25}NH_{2})_2]^{3+}</td>
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<td>0.1</td>
<td>0.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.2</td>
<td>0.25</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.48</td>
<td>0.51</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.6</td>
<td>0.7</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.7</td>
<td>0.8</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>cis-[Co(en)<em>{2}(C</em>{12}H_{25}NH_{2})_2]^{3+}</td>
<td>3</td>
<td>4.8x10^-3</td>
<td>0.07</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.0x10^-3</td>
<td>0.16</td>
<td>0.26</td>
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<tr>
<td></td>
<td>5</td>
<td>7.5x10^-3</td>
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<td>0.28</td>
<td></td>
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<tr>
<td></td>
<td>6</td>
<td>8.4x10^-3</td>
<td>0.33</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>9.6x10^-3</td>
<td>0.48</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>cis-[Co(bpy)<em>{2}(C</em>{12}H_{25}NH_{2})_2]^{3+}</td>
<td>3</td>
<td>0.01</td>
<td>0.2</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.10</td>
<td>0.2</td>
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<td>5</td>
<td>0.15</td>
<td>0.3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.20</td>
<td>0.4</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.30</td>
<td>0.5</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>cis-[Co(phen)<em>{2}(C</em>{12}H_{25}NH_{2})_2]^{3+}</td>
<td>3</td>
<td>2.3</td>
<td>2.3</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.3</td>
<td>2.3</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.9</td>
<td>7.8</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>10</td>
<td>11.0</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>19</td>
<td>21.4</td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>

Complex: surfactant-cobalt(III) complex ion
4.3.2. Effect of Nonbridging Ligand

Nonbridging ligand effect was previously classified\cite{49} in the following three categories; (a) effects of geometry—relative rates of reduction of various pairs of cis and trans isomers; (b) effects of changing the nature of one nonbridging ligand—variation in rates along a series of constant geometry cis or trans; (c) effects of chelation—change in rate upon substitution of ammonia by ethylenediamine. In such reactions of cobalt(III) complexes, it has been suggested that the effect of nonbridging cis-ligand on the rate is of minor importance\cite{50}. However in the case of complexes containing ordinary alkylamine ligands when going from methylamine to butylamine\cite{51}, the second order rate constant successively decreases with increase in the size of the amine ligand. But in the present study, in the case of surfactant-metal complex containing triethylenetetramine ligand the second order rate constant is higher compared to complex containing ethylenediamine ligand in all the initial concentrations studied. This is due to the lower cmc value for trien containing complex. Increasing the size of the amine ligand decreases the cmc value of the complex due to the high hydrophobicity which facilitates the formation of micelles. So more number of micelles will be available which enhances the overall rate of the reaction. This suggests that the introduction of a higher alkylamine group into the nonbridging cis-ligand also facilitates the reaction in contrast to complexes with ordinary ligands.
4.3.3. Effect of β-cyclodextrin

It is known that the binding of many simple phenyl derivatives is stronger to β-cyclodextrin [52-54], these trends depend to the cavity sizes of the cyclodextrins which increase as $\alpha$-CD $<$ β-CD $<$ γ-CD[54]. β-cyclodextrin has the ability to form complex with host molecules, that the complex forms when a suitable hydrophobic molecule displaces water from the cavity[55]. The effects of presence of cyclodextrin in the medium on the kinetics of the electron transfer reactions between the same surfactant-cobalt(III) complexes and $\text{Fe}^{2+}_{\text{aq}}$ have also been investigated. In the presence of cyclodextrin in the media also the reduction of the surfactant-cobalt(III) complexes with $\text{Fe}^{2+}_{\text{aq}}$ proceeds with second order reaction and the results are listed in the Table 4.2. As seen from this Table addition of increasing concentrations of cyclodextrin has resulted in significant decrease in the second order rate constant. It is well known fact that β-cyclodextrin is a good structure breaker of micelles[53]. As the long aliphatic chains of surfactants can be included into the cavities of cyclodextrin the formation of micelles will be difficult leading to increase of CMC values of surfactants in presence of cyclodextrin. So in the present case the decrease of rate constant with increase in the concentration of cyclodextrin in the media can be attributed to the inclusion of long aliphatic chain present in one of the ligands into cyclodextrin (Fig.4.9) which ultimately decreases the micelle formation of the surfactant complexes leading to lowering of
rate constant. This effect of presence of cyclodextrin in the media also supports the earlier conclusion on the effect of initial concentration of the complexes on rate constant (Fig. 4.3 & 4.4).

**Table 4.2**

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>[β-CD]× 10³, mol dm⁻³</th>
<th>k× 10³ mol⁻¹ dm³s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-α-[Co(trien)(C₁₂H₂₅NH₂)₂]³⁺</td>
<td>0.10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>17</td>
</tr>
<tr>
<td>cis-[Co(en)₂(C₁₂H₂₅NH₂)₂]³⁺</td>
<td>0.10</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>25</td>
</tr>
<tr>
<td>cis-[Co(bpy)₂(C₁₂H₂₅NH₂)₂]³⁺</td>
<td>0.10</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>2.0</td>
</tr>
<tr>
<td>cis-[Co(phen)₂(C₁₂H₂₅NH₂)₂]³⁺</td>
<td>0.10</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>2.6</td>
</tr>
<tr>
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<td>0.20</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.8</td>
</tr>
</tbody>
</table>
4.3.4. Activation parameters and isokinetic plots

The effect of temperature on rate was studied at three different temperatures viz., 298, 303 and 308 K at various initial concentrations of the surfactant complexes in order to obtain the activation parameters for the reaction between cobalt(III) surfactant complexes and Fe(II). From the transition state theory [40], it is known that \( \ln k/T = \ln k_B/h + \Delta S^\# / R - \Delta H^\# /RT \).

The values of \( \Delta S^\# \) and \( \Delta H^\# \) determined by plotting \( \ln(k/T) \) vs \( 1/T \) are shown in Table 4.3. As seen from this Table both \( \Delta H^\# \) and \( \Delta S^\# \) values decrease with increasing the initial concentration of the surfactant-cobalt(III) complexes, this is due to the presence of more number of micelles at higher initial concentration of surfactant-cobalt(III) complexes.

The positive value of \( \Delta S^\# \) clearly indicates the presence of electrostatic repulsion between the reductant and the surfactant-cobalt(III) complex in self micelles in the micellar phase. Also the ion pair formed in the transition state is due to association of \( \textit{cis}^{-}[\text{Co(II)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+} \) and \( \text{Fe}^{2+}_{\text{aq}} \) and is presumed to possess a net positive charge. Such a transition state, the magnitude of repulsion is relatively more, hence the bulkier ion pair is not adequately hydrated thus leaving more number of solvent molecules to remain free than in the reactants, hence there is possibly an increase in entropy in going from reactants to the ion pair stage. Thus \( \Delta S^\# \) is positive.
The plots of activation enthalphy \textit{versus} activation entropy (isokinetic plots) values for the series of initial concentration of the complexes give straight lines (\textbf{Fig. 4.5-4.8}) for all the complexes indicating that a common mechanism exists in all the initial concentrations of the complexes studied.

\textbf{Table 4.3}

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>[Complex] x 10^4 moldm^{-3}</th>
<th>(\Delta H^\circ) kJmol^{-1}</th>
<th>(\Delta S^\circ) JK^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{cis}-[Co(trien)(C_{12}H_{25}NH_{2})_2]^{3+}</td>
<td>3</td>
<td>202.3</td>
<td>587.3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>160.6</td>
<td>453.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
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<td>123.3</td>
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</tr>
<tr>
<td></td>
<td>7</td>
<td>137.8</td>
<td>386.9</td>
</tr>
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<td>\textit{cis}-[Co(en)<em>2(C</em>{12}H_{25}NH_{2})_2]^{3+}</td>
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</tr>
<tr>
<td></td>
<td>7</td>
<td>118</td>
<td>306</td>
</tr>
<tr>
<td>\textit{cis}-[Co(bpy)<em>2(C</em>{12}H_{25}NH_{2})_2]^{3+}</td>
<td>3</td>
<td>83.1</td>
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<td>7</td>
<td>43.6</td>
<td>43.0</td>
</tr>
</tbody>
</table>

Complex: surfactant-cobalt(III) complex ion
Plot of $k$ against [Complex] under various temperatures viz 298, 303, 313 K. 
$\text{Fe}^{2+}_{\text{aq}} = 0.1 \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$

(a) cis-$[\text{Co(trien)}(\text{C}_{12}\text{H}_{25}\text{NH}_{2})_{2}]^{3+}$
(b) cis-[Co(en)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$]$^{3+}$

Fig. 4.1
Plot of $k$ against [Complex] under various temperatures viz 298, 303, 313 K. 
$\text{Fe}^{2+}_{\text{aq}} = 0.1 \text{ mol dm}^{-3}, \mu = 1.0 \text{ mol dm}^{-3}$

(a) cis-[$\text{Co(bpy)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$
(b) cis-[Co(phen)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$]$^{3+}$

Fig. 4.2
Plot of $[\beta\text{-CD}]$ vs $k$, Temperature = 305 K

a) cis-$\text{[Co(trien)(C}_{12}\text{H}_{25}\text{NH}_{2})_{2}]^{3+}\$

b) cis-$\text{[Co(en)_{2}(C}_{12}\text{H}_{25}\text{NH}_{2})_{2}]^{3+}\$

Fig. 4.3
Plot of $[\beta\text{-CD}]$ vs $k$, Temperature = 305 K

a) cis-$[\text{Co(bpy)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$
b) cis-$[\text{Co(phen)}_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$

Fig. 4.4
An isokinetic plot of the activation parameters for the reduction of cis-[Co(trien)(C_{12}H_{25}NH_{2})_{2}]^{3+} \text{ by } \text{Fe}^{2+_{aq}}
Isokinetic plot of the activation parameters for the reduction of cis-[Co(en)\(_2\)(C\(_{12}H\(_{25}\)NH\(_2\))\(_2\)]^{3+} \text{ by } Fe^{2+}_{\text{aq}}$

\[ \Delta H^\neq \text{kJmol}^{-1} \]
\[ \Delta S^\neq \text{Jmol}^{-1}K^{-1} \]

**Fig.4.6**
Isokinetic plot of the activation parameters for the reduction of 
cis-[Co(bpy)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$]$^{3+}$ by Fe$^{2+}_{aq}$

Fig. 4.7
Isokinetic plot of the activation parameters for the reduction of cis-[Co(phen)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$]$^{3+}$ by Fe$^{2+}_{aq}$

Fig. 4.8
Fig. 4.9

[Co(phen)$_2$(DA)$_2$]$^{3+}$

[Co(bpy)$_2$(DA)$_2$]$^{3+}$
References:


