CHAPTER V
DISCUSSION

In this chapter, the experimental results obtained in the redox polymerization of acrylamide (AAM) using a series of initiating systems constituted by cerium (IV) and amino acid ligands (L) namely valine (Val), serine (Ser), asparagine (Aspn), proline (Pro), dihydroxyphenylalanine (Dopa) and histidine (His) are presented and discussed. On the basis of the experimental results, the kinetic expressions and mechanisms are proposed. The results are compared critically with those obtained by earlier workers. Attempts have been made to draw a correlation between the reactivity of the above ligands and a general conclusion from the results.

5.1 STEADY STATE ATTAINMENT AND PERCENTAGE CONVERSION

The polymerization of acrylamide, initiated by Ce(IV)-amino acid redox systems involving ligand (L) (L=Val, Ser, Aspn, Pro, Dopa and His) at 45°C, was carried out in aqueous acidic solution under deaerated condition. To check the presence of the photochemical activity, the reaction vessel was kept for 6 h exposing to diffused light at about 50°C in an ice bath. About 2% of the monomer, had been polymerized. As this percentage is insignificant, all the polymerization experiments were carried out by covering the reaction vessel with a black cloth at 45°C.
The monomer solution in 0.075 mol dm$^{-3}$ of H$_2$SO$_4$ was mixed with Ce(IV) and the ligand (amino acid) in a reaction vessel and kept in a thermostat at 45°C. After polymerization was over, the unreacted monomer concentration was determined by the methods of bromine addition to the double bond and the rate of monomer disappearance ($R_p$) had been calculated.

No induction period has been observed for all the systems. In the presence of oxygen under aerated condition the induction period is found to vary from 3 min to 10 min for all the systems$^{128}$. Addition of hydroquinone inhibited the polymerization reaction$^{134}$ showed that the polymerization proceeds through a free–radical mechanism. Epr spectra (Fig. 7 - Fig. 12) also proved that the reaction proceeds through a free radical mechanism$^{137-139}$.

In the present study the polymerization reaction was carried out by varying time from 10 min to one hour and keeping $[M]=0.2$ mol dm$^{-3}$, $[\text{Ce(IV)}]= [L] = 2.0 \times 10^{-3}$ mol dm$^{-3}$, and kept in a thermostat. The results obtained in this experiment are shown in Tables 1 to 6. The period of polymerization is plotted against the percentage conversion as well as the rate of polymerization and the results are shown in the Graphs (1A to 6A and 1B to 6B).

It is evident that the rate of polymerization is decreased and percentage conversion of the monomer is increased with increase of time. In order to compare the reactivity of the ligands, the rate of
polymerization and percentage conversion of monomer are calculated after 20 min of polymerization and are shown in the Table 7. It is clear that under identical conditions the reactivities depending on amino acid ligands follow the order:

His > Dopa > Pro > Aspn > Ser > Val

It can be seen (Tables 1 – 6) that the percentage conversion is higher for ligands namely His, Dopa, Pro and it is lower for the ligands Aspn, Ser and Val. In the polymerization of AN using Mn(III) and a series of carboxylic acid systems Nayak et al. found the following order of reactivity:

citric > tartatic > ascorbic > oxalic > succinic > glutaric > adipic acids

They explained this observation by statistical consideration of the carboxylic groups. In the present system +I groups accelerate the polymerization. The statistical number of OH and COOH groups on the reducing ligand has been reported to increase the rate of polymerization.

5.2. VARIATION OF MONOMER CONCENTRATION AND ITS EFFECT ON THE RATE OF POLYMERIZATION

The polymerization reaction was carried out by varying the monomer concentration from 0.050 mol dm$^{-3}$ to 0.500 mol dm$^{-3}$ and keeping [Ce(IV)] = [L] = 2.0 x 10$^{-3}$ mol dm$^{-3}$  [H$_2$SO$_4$] = 0.075 mol dm$^{-3}$ for 20 min at 45° ±0.5°C under deaerated condition. The amino acid ligands used are Val, Ser, Aspn, Pro, Dopa and His.
The rate of polymerization has been determined and the results are shown in Tables 8-13. The values of log[M] are plotted against log $R_p$ and are shown in Graphs 7A-12A and 7B-12B. It can be seen from the graphs that straight lines are obtained for all the systems. The slope of the straight line for each ligand system has been calculated and presented (Tables 8-13). It is evident from the above results that the order is about one for all the ligands.

The first order dependence of [M] with respect to $R_p$ has been reported in the vinyl polymerization with the redox systems Ce(IV)-lactic acid,\textsuperscript{109} Ce(IV)-citric acid,\textsuperscript{105} Ce(IV)-thiourea,\textsuperscript{107} Mn(III)-ethoxyacetic acid (EAA)\textsuperscript{68} and Mn(III)-glycerol and Ce(IV)-glycine\textsuperscript{128} systems.

The first order dependence of monomer concentration in the present study has been explained by assuming (i) no involvement of monomer in the radical production and that (ii) the growing polymer radicals undergo combination with monomer for termination. Therefore it appears that the metal ion interacts with ligands more easily than with the monomer and hence the production of the radical due to the reaction between monomer and metal ion is absent.

5.3 THE EFFECT OF ACID CONCENTRATION ON $R_p$

The amino acidate ions are chelating agents and they form complexes with most metal ions. These ligands use –COO\textsuperscript{-} group and the lone pair on nitrogen for chelation with metal ion. Both –COO\textsuperscript{-} and
nitrogen site possess greater affinity for protons and this capacity is characterized by definite ionization constants $K_a$ or $pK_a$ values (Table 33). It can be seen from Table 33 that at low pH values most of the COO$^-$ and nitrogen sites are protonated in the amino acidate ions and as the pH is increased the above sites gradually lose the protons. It is inherent that the protons in nitrogen site are lost only at about pH 9 in all the cases as indicated by the high $pK_a$ values. Therefore it is clear that at pH 11, the ligation sites are comparatively deprotonated and this pH appears to be most favourable to form coordination complex with the metal ion. Most of the transition metal ions are hydroxylated even at acidic pH and at basic pH they get precipitated as hydroxides. Hence stable complexation has been found to occur at moderately acidic pH values.

In aqueous acidic medium the metal ion and the ligand are present together. But a competition between the proton and the metal ion to add to the ligation sites prevails. When the pH is increased, the OH$^-$ ions may also tend to add into the coordination sphere of the complex. It is reported that when the pH is higher, the ligand gets protonated preferentially over the complexation with metal ion. At the same time when the pH is increased the metal ion becomes unfavourable though the ligation sites are free by deprotonation. Thus, the pH value plays a vital role in the complex formation process between the metal ion and the ligand. In this investigation, attention
has been paid to compare the reactivity of the amino acid ligands through polymerization technique. Hence the estimations of $R_p$ value of each ligand at varying pH values by the following experiments are conducted.

The reaction solutions were prepared such that $[M]=0.2 \text{ mol dm}^{-3}$, $[\text{Ce(IV)}] = [L] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and varying concentrations in the range between 0.005 mol dm$^{-3}$ and 0.1250 mol dm$^{-3}$ of sulphuric acid. The experiment was conducted in a thermostat at 45°C for 20 min and the $R_p$ was determined. The results are shown in the Tables 14-19 and the plots are drawn between $[\text{H}^+]$ and $R_p$ and shown in Graphs 13-18.

It can be seen from Graphs 13-18 that the $R_p$ value increases as the $[\text{H}^+]$ increases and after reaching a maximum it decreases with further increase of $[\text{H}^+]$. This observation may be explained on the basis of two factors:

(i) At very low $[\text{H}^+]$, the ligand may be deprotonated so that the coordination becomes easier for the metal ion. Though this fact favours the higher $R_p$ value due to high complexation probability, the metal ion is significantly olated$^{121}$ as Ce(OH)$^{3+}$ and Ce(OH)$_2^{2+}$, and the complexation is affected. Of these two behaviours the latter predominates and hence the $R_p$ value is gradually decreased.

(ii) At higher $[\text{H}^+]$, the Ce(IV) is not olated and the complexation may be more effective. However, the carboxylate groups and the
nitrogen centers of the ligand become protonated and they are not readily available for complexation. This behaviour predominates and hence the complexation is not effective which is reflected in the low $R_p$ values. Therefore the protonation of the ligand and the olation of the metal ion in combination determine the extent of complexation between the metal and ligand.

In the Ce(IV)-His redox system the $R_p$ value is maximum in the range $[H^+] = 0.025$ to $0.1150 \text{ mol dm}^{-3}$ and it appears that the complexation is higher in the above $[H^+]$ range. The different pK$_a$ values of His (Table 33) also suggest that the ligand is almost completely protonated at $[H^+] > 0.1050$ and centers may be deprotonated at $[H^+] < 0.025 \text{ mol dm}^{-3}$. This fact also supports the general shape of the curve.

Likewise the plots of $R_p$ vs $[H^+]$ of other systems can be compared with the above His system. It is evident from Graphs 13-18 that the general behaviour of the curve is similar in all these systems.

The above concepts of protonation of ligands and olation of metal ion in influencing the $R_p$ values have also been reported by many workers. In the polymerization of MMA using Ce(IV)-methanol redox system$^{120}$ the decreasing $R_p$ value at increasing $[H^+]$ has been attributed to the protonation of methanol which results in the formation of a weak complex since the positive CH$_3$–OH$_2^+$ is repelled by the positive metal ion. Like this Fernandez and Guzman reported the effects of nitric acid on
the polymerization of MMA initiated by Ce(IV)- isopropylalcohol\textsuperscript{121} and isobutyl alchohol\textsuperscript{119} redox systems. In that study the $R_p$ value initially increases rapidly on increasing the nitric acid concentration and then decreases with further increase of $[H^+]$. This observation is explained on the basis of olation of the metal ion that ceric ions in the higher acid concentration consist of different species such as Ce$^{4+}$, (CeOH)$^{3+}$ and (Ce-O-Ce)$^{6+}$ whose relative amounts depend on the $[H^+]$ according to the following equilibria:

\[
\begin{align*}
2\text{Ce}^{4+} + \text{H}_2\text{O} & \rightleftharpoons 2(\text{CeOH})^{3+} + \text{H}^+ \\
2(\text{CeOH})^{3+} & \rightleftharpoons (\text{Ce-O-Ce})^{6+} + \text{H}_2\text{O}
\end{align*}
\]

when the metal ion is hydroxylated, then it is unfavourable for complexation which is reflected in the decrease of $R_p$ values.

5.4 **EVALUATION OF FORMATION CONSTANT AND DISPROPORTIONATION CONSTANT**

The amino acidoate ions are chelating ligands which form complexes with many metal ions.\textsuperscript{140} It is expected that these ligands form stable complexes with Ce(IV) in the polymerization reaction mixture. In the presence of monomer, this complex gets decomposed by transfer of electron from the ligand to metal ion in which the ligand radical ($R^*$) is formed and polymerization is initiated. Such a type of system is characterized by the formation constant $K$ and decomposition constant $k_d$ (also called as disproportionation constant).
\[
\text{Ce(IV) + Ligand} \xrightarrow{K} [\text{Ce(IV) – Ligand}] \xrightarrow{k_d} \text{Complex C}
\]

\[
[\text{Ce(IV) – Ligand}] \rightarrow \text{Ce(III) + Ligand}^* + H^+
\]

In the polymerization of vinyl monomers using Ce(IV) and L (L = triethanolamine, diethanolamine, triethylamine and diethylamine series) Saha et al. have evaluated \(k_dK\) value\(^9\). Nayak et al. and Samal et al. assume the constants \(K\) and \(k_d\) in the initiating systems Mn(III)-G (G = 1-propanol, 2 – propanol, glycols, glycerols and cyclo alcohols) and Mn(III)-A (A = formamide, acetamide, succinamide and thioacetamide) respectively, but the values have not been reported\(^62 \& 63\). However, in the vinyl polymerization by Ce(IV) and EDTA Wen-Cheng et al. evaluated \(K\) and \(k_d\) values\(^12\). In the present study \(K\) and \(k_d\) values for the series of amino-acidate ligands are evaluated, following the method of Wen-Cheng.

\[
\text{Ce(IV) + Amino acid} \xrightarrow{k_l} [\text{Ce(IV) – Amino acid}] \xrightarrow{k_d} \text{Complex C}
\]

\[
[\text{Ce(IV) – Amino acid}] \rightarrow \text{R}^* + \text{Ce(III)} + H^+
\]

\[
\frac{-d[\text{Ce(IV)}]}{dt} = k_d[C]
\]
k_1 [Ce(IV)] [Amino acid] = k_{-1} [C]

\[ \frac{k_1}{k_{-1}}[Ce(IV)][Amino\ acid] = [C], \text{ since } k_1/k_{-1} = K \]

using Eq. (1) as well as the material balance on the [Ce(IV)], i.e.,

\[ K [Ce(IV)]_i[Amino\ acid] = [C] \]  \hspace{1cm} (4)

and

\[ [Ce(IV)] = [C] + [Ce(IV)]_f \]  \hspace{1cm} (5)

where [C] and [Ce(IV)]_f represent the concentrations of the chelated complex and of the unchelated cerium ion, respectively.

Substituting the value of [C] from Eq. (4)

\[ [Ce(IV)] = K [Ce(IV)]_f[Amino\ acid] + [Ce(IV)]_f \]  \hspace{1cm} (6)

\[ [Ce(IV)] = [Ce(IV)]_f[K[Amino\ acid] + 1] \frac{[Ce(IV)]}{1 + K[Amino\ acid]} = [Ce(IV)] \]  \hspace{1cm} (7)

Substituting Eq. (7) in Eq. (4)

\[ [C] = \frac{K[Ce(IV)][Amino\ acid]}{1 + K[Amino\ acid]} \]  \hspace{1cm} (8)

Substituting Eq. (8) in Eq. (3)

\[ \frac{-d[Ce(IV)]}{dt} = k_a K[Ce(IV)] + [Amino\ acid] \]

\[ \frac{1 + K[Amino\ acid]}{k_a K[Amino\ acid]} \frac{[Ce(IV)]}{-d[Ce(IV)]} \]

\[ \frac{dt}{dt} \]
\[ \frac{1}{k_d K [\text{Amino acid}]} + \frac{1}{k_d} = \frac{[\text{Ce(IV)}]}{dt} \]

where \( K \) = formation constant and \( k_d \) = disproportionation constant.

From Eq. (10), it is evident that the constant \( K \) and \( k_d \) can be evaluated by determining the rate of disappearance of Ce(IV) in the polymerization experiment in which the concentration of the ligand is varied keeping [Ce(IV)] as constant. In practice the reaction mixture containing 0.2 mol dm\(^{-3}\) of monomer and 2.0 x 10 mol dm\(^{-3}\) of Ce(IV) and the ligand concentration is varied from 0.5 x 10\(^{-4}\) to 1.9 x 10\(^{-3}\) mol dm\(^{-3}\) for all the systems. The results are shown in Tables 20-25 and plots are drawn taking 1/[aminoacid] in X axis and [Ce(IV)]/d([Ce(IV)]/dt) in Y axis and straight lines are obtained (Graphs 19-24). From the values of slopes and intercepts, the values of \( K \) and \( k_d \) are calculated and are shown in Table 26.

It can be seen from the table that the \( K \) value for His is higher than that of Val. It has been known that more stable complexes initiate vinyl polymerization effectively in the Ce(IV)- amino acid ligand systems. In the above study +I groups accelerate the polymerization owing to increased electron density thereby increased case of complex formation.
The statistical number of OH groups on the reducing ligand has been reported to increase the rate of polymersation.\textsuperscript{62}

Thus, the initiation of polymerization occurs by free radicals which are produced by the decomposition of complex and the easiness of the decomposition is characterized by the constant $k_d$. The higher the $k_d$ value, the higher the reactivity of complex for initiation. The $k_d$ value for His is higher and for Val, lower. It is reasonable to assume that the electron transfer reaction from ligand to metal is faster in the case of His and is lower in the case of Val.

The reactivity may depend upon the combined result of complex formation, inductive effect of adjacent groups and the statistical effect of reactive centers. The above facts may act collectively or individually in influencing the formation of the complex and subsequent decomposition to produce initiating radicals for the polymerization reaction.

\textbf{5.5 \hspace{1em} EFFECT OF EXCESS OF CERIUM ON THE RATE OF POLYMERIZATION}

In the polymerization of acrylamide Wen-Cheng et al.\textsuperscript{125} always kept the molarity of Ce(IV) a few times greater than the molarity of EDTA. It appears that after the formation of 1:1 complex between Ce(IV) and EDTA, the excess cerium(IV), if any, increases the complexity of the system. Though Ce(IV) alone is not known to oxidise water and initiate polymerization, one is not sure about the reactivity of Ce(IV) which is present in excess along with the complex in the polymerization
mixture. Hence it would be of interest to keep the concentration of the complex as constant and vary the excess [Ce(IV)].

Contrarily, in the redox polymerization of vinyl monomers by Ce(IV)-lactic acid (LA), it has been shown that $R_p$ increased with the increase of the ratio $(LA)/[Ce(IV)]$ from 0.1 to 1.0 and beyond the ratio 1.0 the $R_p$ remained constant. This shows that the excess of Ce(IV) ions is not involved in the initiation of polymerization. Similar results are also reported for the system Ce(IV)-glucose.

In view of the above facts it is interesting to study the effect of excess of cerium on $R_p$. The polymerization solution was prepared by taking $[M] = 0.2 \text{ mol dm}^{-3}$, $[H^+] = 0.075 \text{ mol dm}^{-3}$, $[L] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[Ce(IV)]$ varying from $1.0 \times 10^{-4}$ to $2.0 \times 10^{-3} \text{ mol dm}^{-3}$. After deaeration with nitrogen, it was polymerized at $45^\circ\text{C}$ for 20 min. The $R_p$ values were determined and are reported in Tables 27-32. The plots were drawn between the ratio $[L]/[Ce(IV)]$ and $R_p$, and between $\log[L]/[Ce(IV)]$ and $\log R_p$ (Graphs 25A – 30A and 25B-30B).

From Graphs 25A – 30A, it is evident that when the ratio $[L]/[Ce(IV)]$ is less than about 0.5 polymerization is very low and after which the $R_p$ steadily increases. It is maximum when the ratio $[L]/[Ce(IV)]$ is nearly 1 and beyond which the $R_p$ remains constant. These observations indicate that as the ratio is less the Ce(IV) ions being present in large excess are involved in the termination process and hence the $R_p$ is significantly low. Moreover, as the ratio $[L]/[Ce(IV)]$
is nearly equal to one, such termination process is insignificant and the $R_p$ is maximum. The complex concentration also increases as the ratio is increased which is reflected in the increasing $R_p$ values. Beyond the ratio 1.0 the $R_p$ is constant showing no influence of excess ligand concentration on $R_p$.

In the present systems and in other systems like Ce(IV)-citric acid and Ce(IV)-glucose\textsuperscript{110}, the complex decomposes to give ligand free radicals to initiate polymerization. The Ce(IV) ions are involved in the termination process in these systems.

The rate of disappearance of Ce(IV) ($R_{Ce}$) values determined in each system is shown in the respective Tables 27-32. The $R_{Ce}$ values remain almost constant when the ratio $[L]/[\text{Ce(IV)}]$ is increased from 0.1 to 2.0. Assuming the formation of the complex between Ce(IV) and ligand, it is expected that $R_{Ce}$ value should increase with the above ratio and hence the complex concentration is increased. But it appears that at low complex concentrations the Ce(IV) is produced by decomposition of the complex and Ce(IV) is as well involved in the termination process. But at high ratio the termination process is absent and the extent of complex decomposition is more. Thus the Ce(III) formation is compensated by the termination process at low concentration and enhanced decomposition of the complex at high concentrations. This aspect results in a constant $R_{Ce}$ value during polymerization.
5.6 VARIATION OF INITIATOR CONCENTRATION AND ITS EFFECT ON $R_p$

In the present study, the polymerization mixture was prepared by mixing respective solutions of $[M] = 0.200$ mol dm$^{-3}$, $[H_2SO_4] = 0.075$ mol dm$^{-3}$ and varying the concentrations of Ce(IV) and the ligands and the reaction was carried out at 40°C for 20 min. The polymerization reactions were continued by increasing the complex concentrations from $19 \times 10^{-3}$ to $9 \times 10^{-3}$ mol dm$^{-3}$ and keeping the ratio of [Ce(IV)] and [L] as 1:1. The $R_p$ values were determined under deaerated conditions. The results were shown in the Tables 34-39. The plots are drawn between log $R_p$ and log[C] and are shown in Graphs 31-36.

It is evident from the values of the experimental results that the $R_p$ value gradually increases as the concentration of the complex is increased regularly and reaches a maximum value, beyond which it decreases on further increase of complex concentrations. Similar observations were made by earlier workers in the polymerization of vinyl monomers using Ce(IV)-isobutyl alcohol$^{119}$ and Mn(III)-glycol$^{62}$ systems. The initial increase of $R_p$ is attributed to the increased radical production. The ligand radicals may disappear by initiation of polymerization and also by reduction of the metal ion. When the radical concentration is low, the reduction of the metal ion is insignificant but at the high concentration of complex, they are utilized mostly in reducing the metal ion. Therefore the $R_p$ value decreases after reaching
a maximum. This type of observation has been made in all the ligand systems of this investigation.

This kind of decrease of $R_p$ with the increase of complex concentration has been observed in the polymerization of MMA with Ce(IV)-methanol redox system$^{120}$ and the polymerization of AN with Cr(IV)-thiourea$^7$ system. In the polymerization of MMA with Ce(IV)-isobutyl alcohol$^{119}$ redox system, Fernandez et al. reported that the $R_p$ values gradually increase on increasing the concentration of Ce(IV) and IBA, but decrease at high complex concentration.

5.7 EFFECT OF TEMPERATURE

The temperature of the redox polymerization of acrylamide by the Ce(IV)-amino acid redox systems was varied from 25°C to 55°C, keeping the [monomer]=0.20 mol dm$^{-3}$, [Ce(IV)]=[Ligand]=$2.0 \times 10^{-3}$ mol dm$^{-3}$ [H$^+$]=0.075 mol dm$^{-3}$ and the period of polymerization was kept at 20 min. The results obtained for all the systems (Tables 40-45) and the corresponding Arrhenius plots are shown (Graphs 37-42). The activation energies and activation parameters were determined. The activation energies for the polymerization using redox systems of Ce(IV)-L, where L = Val, Ser, Aspn, Pro, Dopa and His were 76.607 kJmol$^{-1}$, 73.525 kJmol$^{-1}$, 70.840 kJmol$^{-1}$, 63.453 kJmol$^{-1}$, 55.407 kJmol$^{-1}$, 52.151 kJmol$^{-1}$ respectively.
It is clear from the various activation energies that Ce(IV)-His redox system is the most reactive and Ce(IV)-Val is the least reactive among the series of redox systems which are considered for the studies. The reactivities based on ligand difference, follow the order:

His > Dopa > Pro > Aspn > Ser > Val

These values of activation energies are found to be in the range of values reported for similar systems. Wen Cheng et al.\textsuperscript{125}, who studied the vinyl polymerization initiated by Ce(IV)-EDTA redox system have reported an activation energy value of 62.0 kJ mol\textsuperscript{-1}, Riaz Ahamed et al.\textsuperscript{102} in the polymerization of acrylonitrile initiated by Ce(IV) – acetaldehyde redox system reported an activation energy value of 67.3 kJ mol\textsuperscript{-1}.

Dong Jianhya et al.,\textsuperscript{121} who studied the polymerization of acrylamide in the presence of Ce(IV)-acetoactanilide redox system, have reported the activation energy of 57.0 kJ mol\textsuperscript{-1} and in the Ce(IV)-thiourea redox system, Pramanick et al.\textsuperscript{118} reported an activation energy value of 50.62kJ mol\textsuperscript{-1}.

The values of activation parameters, enthalpy of activation, entropy of activation and free energy of activation for polymerization of acrylamide initiated by Ce(IV)-aminoacid ligand systems are presented (Table 46).
5.7.1. Isokinetic Relationship

The dependence of rate on the structure of the reacting molecules is related to activation parameters. Leffler\textsuperscript{143} deduced the following isokinetic equation in modification of the Hammet equation.

\[
E_a = E_0 - 2.303R\beta\log A
\]

\[
\Delta H^\# = \Delta H^0 + \beta\Delta S^\#
\]

which holds good for a series of related reactions. The validity of the isokinetic relation was tested by plotting $\Delta H^\#$ versus $\Delta S^\#$. This linear relationship between activation enthalpies and activation entropies in a series of related reaction is called isokinetic relationship. The slope of the plot, $\Delta H^\#$ versus $\Delta S^\#$ is the isokinetic temperature, '$\beta$' and it has an important physical meaning. It represents a temperature at which all reactions of the series should proceed at the same rate and same mechanism and the reaction constant attains the value of zero at the temperature\textsuperscript{144}.

The plot of $\Delta H^\#$ versus $\Delta S^\#$ (isokinetic plot) for the systems Val, Sen, Aspn, Pro, Dopa and His is shown in Graph (43). The slope of the plot gives the value of '$\beta$' as 298.0 K.

5.8 ABSORPTION SPECTRA OF Ce(IV) – AMINO ACID LIGAND COMPLEXES

The amino acids, Val, Ser, Aspn and Pro are bidendate ligands. Dopa is an ambidentate and His is a tridentate ligand\textsuperscript{141,142}.
In the polymerization reaction, it is assumed that the complex between the metal and the reducing ligand is first formed which then decomposes to give initiating radicals. The formation constant (K) and also the decomposition constant (kd) for such complexes were evaluated in many systems.\textsuperscript{96,125}

In the polymerization of acrylamide using Ce(IV) and EDTA redox system, Wen-Cheng et al.\textsuperscript{96} determined the K and kd values. They followed the disappearance of Ce(IV) by measuring the optical density at 350 nm at which Ce(IV) absorbs strongly. Though the above authors assume the formation of complex, no evidence except the evaluation of K value has been provided for that. The complex formation can be easily identified by comparing the absorption spectra of free metal ion and the mixture of the solution of the metal ion with the ligand\textsuperscript{128}. Hence, in the present study, the absorption spectra of aminoacids, Ce(IV), a mixture of these two and free Ce(III) are recorded and shown in Figures (1-6). It is evident from the figures that the amino acids, Val, Ser, Aspn and Pro absorb in the UV region but have no $\lambda_{\text{max}}$ value. The other two amino acids viz., Dopa and His show $\lambda_{\text{max}}$ around 212 and 225 nm respectively. The Ce(IV) absorbs strongly in the region between 280 to 400 nm in the form of a broad peak with $\lambda_{\text{max}}$ at 320 nm. It is evident that these systems strongly absorb at about 300 nm with peaks indicating the complex formation in solution. The absorption spectra of the mixture of the solution of Ce(IV) and an amino acid are completely
different from those of Ce(IV) alone (Fig. 1-5). These observations indicate the formation of the coordination complex between Ce(IV) and EDTA. The absorption spectrum of Ce(III) shows a well defined $\lambda_{\text{max}}$ at 260, 252 and 223 nm.

The epr spectral peaks (Fig. 7 – Fig. 12) indicate the probability of formation of free radicals viz., acrylamide free radical polycrylamide free radical along with Val / Ser / Aspn / Pro / Dopa / His and Ce(III) ion. This observation indicates the free-radical mechanism for the polymerization reactions.

### 5.9 REACTION SCHEMES AND RATE EXPRESSIONS

The experimental results presented in section 5.2 may be subjected to a detailed kinetic analysis, in the light of the undermentioned probable reaction schemes.

#### 5.9.1 Polymerisation of Acrylamide Initiated by the Redox Systems Ce(IV)-Aminoacid ligands

The aminoacid ligands form complexes with Ce(IV)

$$\text{Ce(IV)} + \text{Amino acid} \overset{K}{\underset{\text{Complex}}{\leftrightarrow}} C$$  \hspace{1cm} (1)

where aminoacids (L) represent the valine (Val), serine (Ser), asparagine (Aspn), proline(Pro), dihydroxyphenylalanine(Dopa) and histidine (His).
The complex C may decompose to give the aminoacid ligand radical, Ce(III) and proton.

\[
C \xrightarrow{k_d} L^\cdot + \text{Ce(III)} + H^+ \quad (2)
\]

where \(L^\cdot\) are the aminoacid ligand radicals like Val, Ser, Asp, Pro, Dopa and His.

a) **Initiation**

The amino acid ligand radicals initiate the polymerization to give the monomer radical \(M_1^\cdot\).

\[
\text{Amino acid}^\cdot + M \xrightarrow{k_1} M_1^\cdot \quad (3)
\]

b) **Propagation**

\[
M_n + M \xrightarrow{k_p} M_{n+1}^\cdot \quad (4)
\]

c) **Termination**

\[
M_{n+1}^\cdot + M \xrightarrow{k_t} \text{polymer} \quad (5)
\]

Applying the steady state approximation for \([M_n^\cdot]\)

\[
k_1[M][\text{aminoacid}^\cdot] = k_t[M_n^\cdot] [M] \quad (4)
\]

\[
[M_n^\cdot] = \frac{k_1 [M][\text{Amino acid}]}{k_t [M]} \quad (5)
\]

since \([\text{Amino acid}] = k_d[C]\)
\[ [M_{n}^{\star}] = \frac{k_{f}k_{d}[C]}{k_{i}} \] (6)

The rate of polymerization,

\[ R_p = k_p[M_{n}^{\star}][M] \]

Substituting the value of \( [M_{n}^{\star}] \) from Eq. (6) in Eq. (7)

\[ [R_p] = \frac{k_{p}k_{f}k_{d}}{k_{i}}[C][M] \] (8)

The above rate expression accounts for the observed kinetic results, that is, a first order dependence on the monomer concentration and a first order dependence on the complex concentration for all the systems. The complex formation between Ce(IV) and these amino acid ligands is supported by the absorption spectra given in Figures 1-5.

Further the complex formation constant, \( K \) is evaluated in all the cases and the values are presented in Tables 14-19. The decomposition constant \( k_d \) of the complex is also evaluated and the values are given in Table 20. The discussion on the formation constants and the decomposition constants for the Ce(IV) and Val, Ser, Aspn, Pro, Dopa and His systems has already been presented in section 5.3.