# International Journal of Scientific Research and Reviews

# Effect of β-CD on kinetics of polymerization of acrylamide initiated by Ce (IV) – Vanillin redox system

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## ABSTRACT:

Kinetics of Polymerization of Acrylamide (AM) initiated by Ce(IV) – Vanillin redox system, was carried out two different temperatures $30^{o}C$ & $36^{o}C$ in dilute sulfuric acid medium under nitrogen atmosphere. The effect of various concentrations of monomer[AM],oxidant[Ce(IV)], reductant[van], medium[$H^{+}$] and varying ionic strengths $NaHSO_4$ on the rate of polymerization, rate of Ce(IV), consumption (-RCe) and the percentage monomer conversion were studied. The rate of polymerization (Rp) in the presence and absence of β-CD has been investigated The rate of polymerization(Rp) was also calculated by iodometry method. A suitable mechanism has been proposed.

**KEY WORDS** : Beta - cyclodextrin, ceric ammonium sulphate, Acrylamide, Rate of polymerization –Vanillin

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# I.   NTRODUCTION

Polymer is a generic name given to a vast number of materials of high molecular weight[1,2,3,4]. These materials exist in countless forms and numbers because of a very . large number and type of atoms present in this molecule. A polymer is a large molecule built by the repetition of small, simple chemical units. The individual small molecules from which the polymer is formed are known as monomers (meaning, single part) and the process by which the monomer molecules are linked to form a big polymer molecule is called *polymerization*.  A high polymer is one in which number of repeating units is in excess of about 1000.The number is termed as 'Degree of polymerization(DP)'. Metal ion used mainly for this purpose are Mn(III) and Mn(VII), Ce(IV), V(V), Co(III), Cr(VI) and Fe(III).etc. Cerium (IV) ion has been used for the oxidation of many organic compounds, in the form of ceric(IV)ammonium nitrate (CAN), Ceric (IV) ammonium sulphate (CAS), Ceric(IV) Sulphate (CS) and ceric perchlorate. Ceric ions form complexes with amines such as sulfate, nitrate and hydroxyl in aqueous solution whose relative concentrations have been found to be function of hydrogen ion, respective anion concentration and ionic strength. Numerous reducing agents have been used in combination with oxidizing metal ions to participate in general single – electron transfer reaction for free radical polymerization, The mechanism and kinetics of polymerization is involving ceric ion alone [Ananthanarayan and santappa et.al [5] and also in combination with reducing substrates such as alcohols [6] diols [7], polyols [8], aldehydes [9], ketones [10] and amines [11] etc. with different  vinyl monomers acrylonitrile, acrylamide and methyl methacrylate are studied. Vanillin(3-methoxy-1-hydroxy benzaldehyde) is a reductant, which has both phenolic and aldehyde groups and its capable of undergoing three different types of reaction those of the aldehyde groups the phenolic hydroxyl and the aromatic nucleus. The aldehydic group undergoes condensation [12] reaction that allows substitution [13] for the aldehyde reactions, such as Cannizaro's reaction,if the hydroxyl group in vanillin is protected, The aldehyde group undergoes oxidation [15] to vanillinicacid.A direct oxidation mechanism, without complex formation has been suggested for oxidation in sulfuric acid [16,17] . Some studies reported in the literature [18,19] indicate successful efforts were made to polymerize the monomer. Cyclodextrin are cyclic oligosaccharides composed of α- (1,4) linkages of a number of D-(+)glucopyronose units. A number of glucose units are designated by α- for six, β- for seven, ϒ - for eight. Many chemical reactions both in solid state [20] and solutions  are influenced by cyclodextrins due to inclusion into the apolar cavity. Reactions of these complexes are regioselcetive [21], stereospecific synthesis can be realized. Many hydrolysis reactions are observed in β-CD,bromination [22]  reaction are observed in β-CD which are stereo selective and stereospecific, many reduction [23], oxidation and photochemical reactions [24] in β-CD have been reported. The literature survey reveals that no reports of the kinetics of polymerization of Acrylamide with Ce(IV)

- vanillin in β-CD has been carried out. The rate of polymerization(Rp) of monomer in the presence and absence of β-CD were investigated.,

## *Experimental Methods*

The polymerization was carried out in a Pyrex tube of 150 ml capacity which was sealed at the bottom and the top was fitted with a standard joint stopper having inlet and outlet tubes for the passage of nitrogen. A micro burette was fitted vertically on the stopper the aqueous solutions of Acrylamide, vanillin and sulfuric acid, sodium bisulfate (to maintain proper ionic strength) and β-CD in appropriate concentrations were taken on the reaction tube. Nitrogen gas was bubbled for about half an hour and stopcocks were closed. The solution was thermo stated to attain desired temperature and followed by addition of Ce(IV) solution from the micro burette and mixing by shaking. The volume of reaction mixture was adjusted to 20 ml. The polymerization started immediately after the addition of Ce(IV) solution. After a definite interval of time the reaction was quenched by addition of the excess standard ferrous ammonium sulfate solution. The filtrate along with washing after separation of polymer was estimated for residual Ce(IV) by titrating with standard Ce(IV) using ferroin indicator. The rate of polymerization ($R_p$) and rate of Ce(IV) consumption were calculated from the initial slope of the curve of the percentage of monomer conversion versus time and Ce(IV) consumption versus time curve respectively.

All kinetic measurements were performed under pseudo first order conditions where [Vanillin] was always in excess over [Ce(IV)] at a constant ionic strength of 0.1 mol $dm^{-3}$ in acid medium at a constant temperature of $30^oC$ and $36^oC$ respectively, unless otherwise stated. The reaction was initiated by mixing the thermo stated solutions of Ce(IV) and vanillin, which also contained the required concentration of $H_2SO_4$ and $NaHSO_4$ . The progrcess of the reaction was followed by measuring the decrease in absorbance of Ce(IV) in the reaction solution and from order slopes of plots of $log_{10}$ (Ce(IV)) versus time; the plots were linear up to 60% completion of the reaction in acidic medium and the $k_{obs}$ values were reproducible to within ±5 % and deviation from linearity was observed above 40 % of reaction due to the retarding effect of one of the products Ce(IV). The results are also interpreted in terms of the initial rate of the reaction to avoid the complexation. The order with respect to Vanillin and vanillinic Acid was found by log $k_{obs}$ versus log $_{10}$ [conc] plots these orders were obtained by varying the concentration of reductant and acid. in turn while keeping constant.

## RESULTS AND DISCUSSION

### *Effect of Ce(Iv)*

Concentration of oxidant Ce(IV) was varied from 3.14 to 7.83 x $10^{-3}$mole/dm$^3$ sec$^1$, the rate of the reaction was increased from 2.104 to 4.841 x $10^{-4}$ mole/dm$^3$ sec$^1$ from this we can concluded that the concentration of oxidant was increased, the rate of polymerization also be increased. This was also confirmed in the rate of polymerization(Rp) Vs [Ce(IV)] was increased from 1.599 to3.619 X$10^{-7}$.Then in the experiment was done by the addition of β-CD to aliquot the rate of the reaction drastically decreased from 3.852 to1.891 x $10^{-4}$ mole/dm$^3$ sec$^{1.}$.
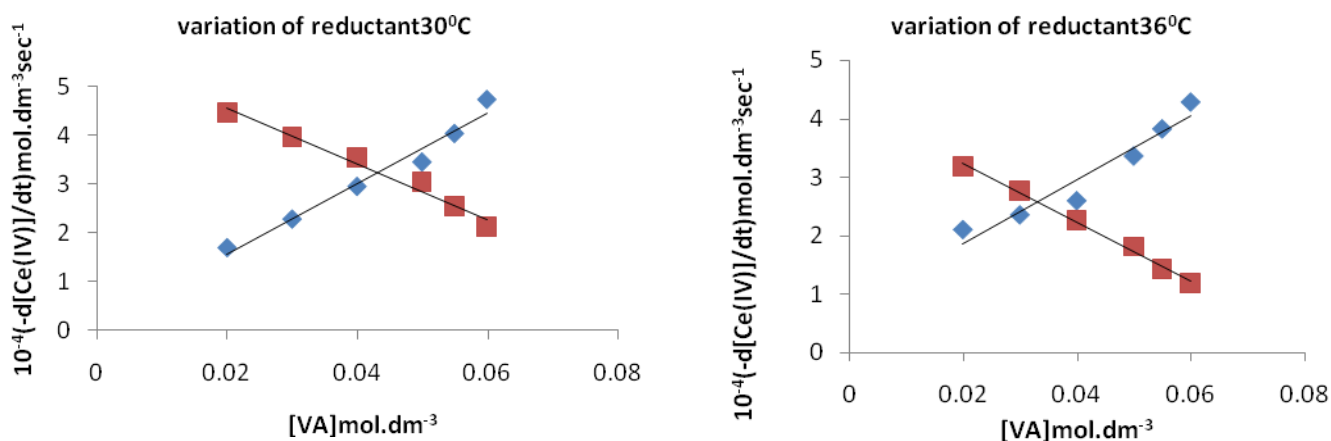


**Fig : 1 Van [2 x $10^{-1}$moldm$^{-3}$], AM [2 x $10^{-4}$moldm$^{-3}$], H$^+$[2.5 moldm$^{-3}$**

We also found that Rp was decreased from 4.341 to 2.397 at 30$^0$C. This was due to β-CD encapsulated the monomer in its cavity which is not available for polymerization; therefore the rate and Rp were decreased even though we increase the concentration of oxidant. The same trend was also observed when we increased the temperature to 36$^0$C the rate was increased from 3.267 to

6.512x $10^{-4}$ and the Rp was increased 2.169 to 4.234x$10^{-7}$ . But in the presence of β-CD the rate was decreased from 4.630 to 2.693x$10^{-4}$ mole/dm$^3$ sec$^1$ and also Rp was decreased from 3.273 to 0.984 x $10^{-7}$.Therefore β-CD a smal entity which separates the monomer from oxidant. So β-CD was actually decreased the polymerization Fig 1

## VARIATION OF REDUCTANT

By increasing the concentration of vanillin from 2 x $10^{-1}$moldm$^{-3}$ to 6 x $10^{-1}$moldm$^{-3}$, increase in the rate of reaction from 1.683 to 4.741x$10^{-4}$ mole/dm$^3$sec $^{-1}$and rate of polymerization from1.2605 to 4027 X$10^{-7}$at 30$^0$C was observed. Therefore increasing the concentration of vanillin, increase in both the rate of reaction and rate of polymerization was observed. When we added β-CD to the reaction mixture the rate was decreased from 4.462 to 2.104 x $10^{-4}$ mole/dm$^3$ sec$^1$ and the Rp was decreased from 2.801 to 2..089 x$10^{-7}$. The same trend was followed at higher temperature (36$^0$C) the rate of reaction was increased from 2.104 to 4.294X$10^{-4}$ mole/dm$^3$ sec$^1$ and Rp was increased from 3.260 to 4.362 x $10^{-7}$. Therefore as we increased the concentration of vanillin, the rate of the reaction was increased. But β-CD was added in the reaction medium, the rate of reaction was decreased from 3.1887 to1.183x $10^{-4}$ mole/dm$^3$ sec$^{-1}$ and Rp4.421 to 0.995 x $10^{-7}$. When we compared 30$^0$C and 36$^0$C, as the temperature increases both the rate was also increased in without β-CD. But with β- CD the rate was decreased. This observation indicates that as we increased the temperature the rate of the reaction in the presence of β-CD was slightly changed and as we increased the concentration of vanillin a sudden decreased. From this observation we can concluded that more and more vanillin molecule were occupied in β-CD cavity. Thus β-CD prevents polymerization .Fig 2
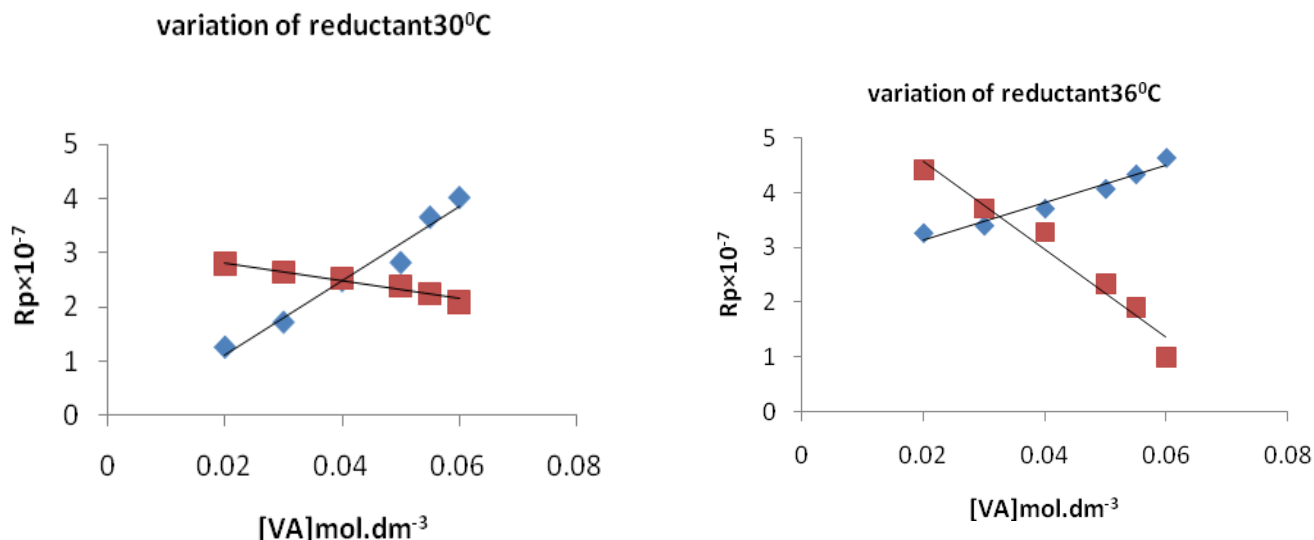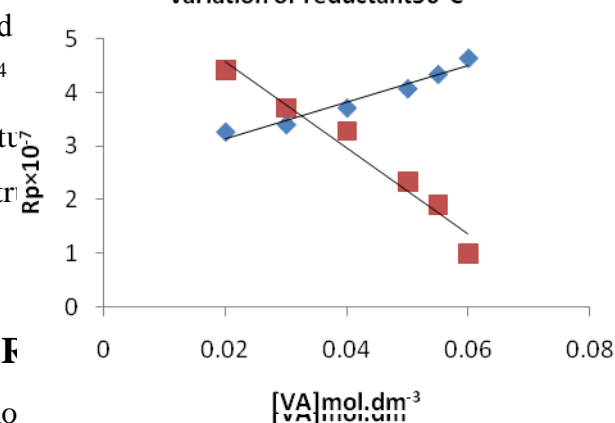
variation of reductant30⁰C



variation of reductant36⁰C



**Fig : 2 Ce(IV) [2.84 x 10⁻⁵moldm⁻³], AM[2 x 10⁻⁴moldm⁻³], H⁺[2.5moldm⁻³]**

## VARIATION OF $H_2SO_4$

In the $H^+$ ion variation we observed that the rate of reaction was slightly increased from 2.462 to 5.104 x10⁻⁴ mole/dm³ sec¹ and Rp 1.260 to 4.357x 10⁻⁷ at 30⁰C when β-CD was added to the medium abruptly changed and the rate of reaction was decreased from 4.925 to 2.205X10⁻⁴ mole/dm³ sec¹and Rp2.273 to 0.962. From this we observed as increase the concentration of $H^+$ normal kinetics was slightly increased but in the presence of β-CD the rate of the reaction was suddenly decreased. It was due to acid will affect the β-CD structure and tend to hydrolyses β-CD and more and more glucose molecule will prevent polymerization. The same trend was observed for temperature 36⁰C.When we compared the rate of the reaction at 30 and 36⁰C without β-CD, the rate of the reaction at 36⁰C was increased from 0.137 to 2.643x10⁻⁴ mole/dm³ sec¹ and Rp1.882 to 2.594 was also increased. From this it may be concluded that as the temperature was increased, the movement ions was increased, which was good

CD the rate was decreased from 2.337 to 0.946x 10⁻⁴ 0⁻⁷ From this we can conclude that at higher temperatu h the movement of ions were faster rate but β-CD str cose units which hindered the polymerization. Fig 3

## VARIATION OF MONOMER

The rate and Rp of the reactio mole/dm³ sec¹3.466 to6.732x 10⁻⁷ respectively as we were increased the concentration of monomer at 30⁰C. This increase in the rate and Rp was due to more and more number of molecules of monomer

increase the rate and polymerization of the reaction. When we add β-CD the rate of the reaction was decreased from 2.852 to 0.0945x $10^{-4}$ mole/dm$^3$ sec$^1$ and Rp 4.966 to2.279x $10^{-7}$
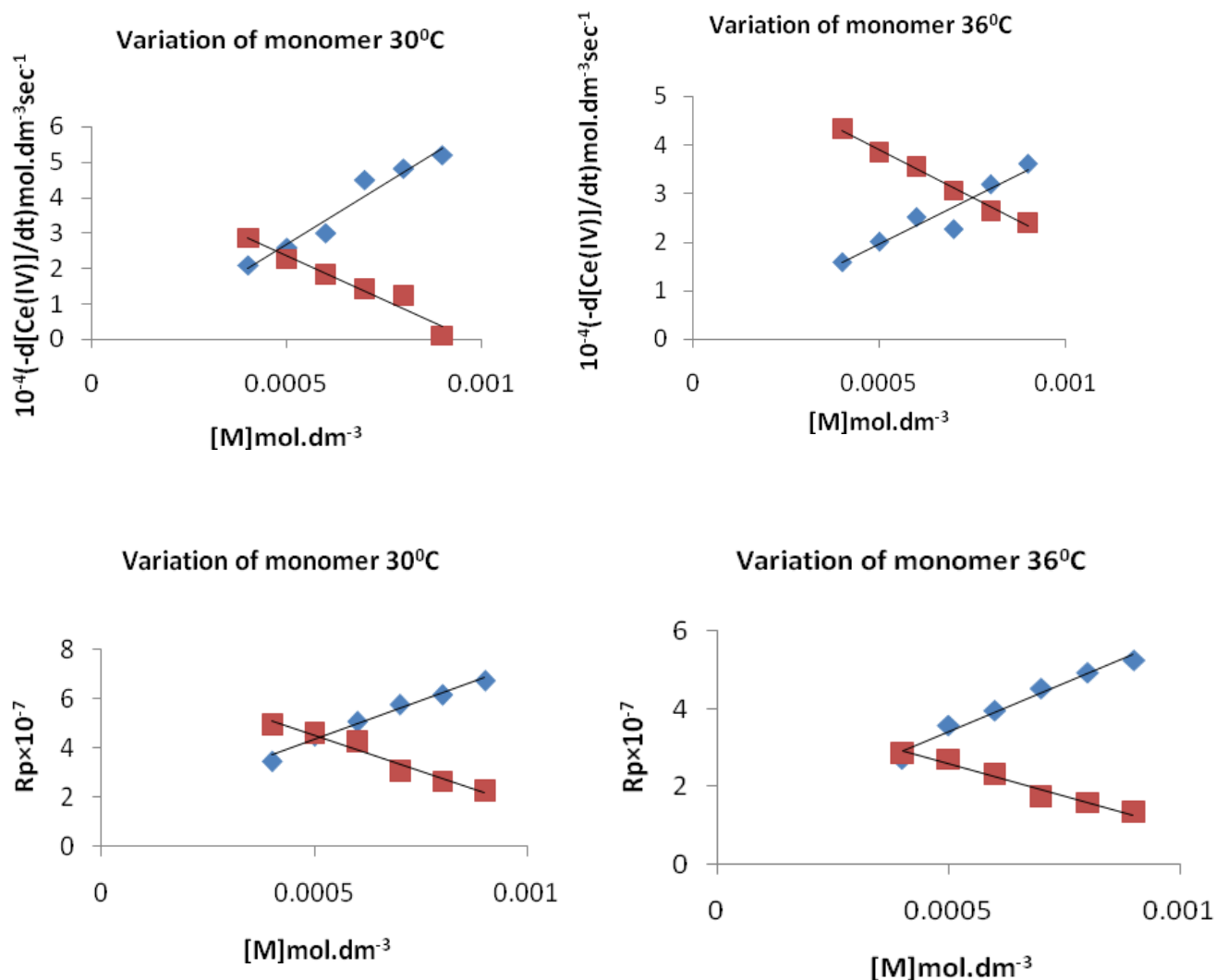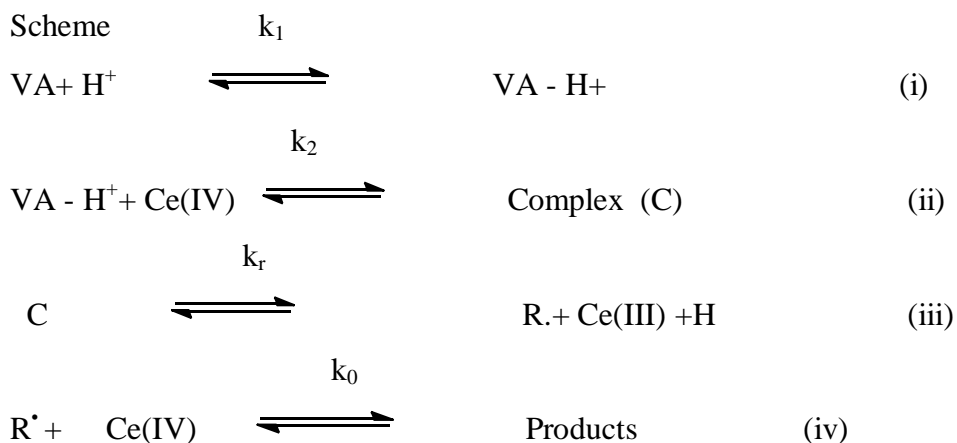


**Fig :4 Ce(IV) [2.84 x $10^{-5}$moldm$^{-3}$], Van [2 x $10^{-1}$moldm$^{-3}$] AM[2 x $10^{-4}$moldm$^{-3}$],**

Here when increase monomer concentration more molecules were occupied inside the β-CD cavity. At 36$^o$C the rate of polymerization was increased from 1.599 to3.619 x $10^{-4}$ mole/dm$^3$sec$^1$and the Rp 2.719 to 5.264 x $10^{-7}$.This was similar observation as above increasing the temperature increase in the Rp observed. When the kinetics was followed in the presence of β-CD. the rate decreased from 4.341 to 2.397x $10^{-4}$ mole/dm$^3$ sec$^{-1}$ and Rp 2.89 to1.350x $10^{-7}$. This was also similar observation that was by increasing the temperature increase in the mobility of ions and increase in the polymerization. But increase in the monomer concentration more monomer molecule will occupy β-CD cavity. Thus β-CD deaccelerated the polymerization. Fig 4

## *Kinetics of oxidation in presence of β-CD*

Kinetics of oxidation of Vanillin (VA) by Ce(IV) in the presence and absence of β-CD was carried out at the temperature $30^0$C and $36^0$C. The rate of oxidant consumptio(-d[Ce(IV)]/dt) were proportional to [Ce(IV)], Variation of rates with substrate concentration suggested the formation of 1:1 complex intermediates prior to oxidation. The plots of (-d [Ce(IV)]/dt) against [VA] were linear the complex formation between the oxidant and the substrate in the redox pair and reciprocal plots of $(-d[Ce(IV)]/dt)^{-1}$vs $[H^+]^{-1}$ were also found to be linear.

Scheme    $k_1$

VA+ $H^+$  ⇌    VA - H+     (i)

      $k_2$

VA - $H^+$+ Ce(IV) ⇌   Complex (C)   (ii)

     $k_r$

 C    ⇌    R.+ Ce(III) +H  (iii)

      $k_0$

$R^•$ + Ce(IV)  ⇌   Products  (iv)

Where, C represents the complex formation between the substrate and the oxidant.

The two equilibrium $k_1$ and $k_2$ were treated separately so that,

$k_1$=([ - H+]eq) / ([VA]eq[H+])  and        (1)

[VA]T = [VA - H+]eq+ [VA]eq        (2)

From equation(1),

[VA - H+]eq= $k_1$ [VA]eq[H+]

Introducing this value in equation (2),We get,

[VA]T=$k_1$[VA]eq[H+]+[VA]eq

=[VA]eq(1 + $k_1$[H+])        (3)

Where [VA]eq denotes the equilibrium concentration of VA also,

[Ce (IV)]T = [Ce(IV)]eq+ [C]       (4)

From the kinetic step (2)

$k_2$ = [C] / ([VA - H+]eq[Ce (IV)] eq)[C]

= $k_2$ [VA -H+]eq[Ce (IV)]$_{eq}$        (5)

Substituting equation (5) in equation (4),

[Ce(IV)]T=[Ce(IV)]eq+$k_2$[VA-H+]eq[Ce(IV)]eq=[Ce(IV)]eq(1+$k_2$[VA-H+]eq) (6)

Where [Ce(IV)]eq represents the equilibrium concentration of ceric ion.

By applying steady-state approximation to the intermediate($R^\bullet$),the following expression can be derived from the kinetic scheme steps(iii)and (iv):

$-d[R^\bullet] / dt = k_0 [Ce (IV)]eq[R^\bullet] - K_r [C] = 0$

therefore

$K0 [Ce (IV) ]eq[R^\bullet] = k_r[C]$

$[R^\bullet] = [K_r [C] ) / (K_0[Ce (IV)]_{eq})$

(7)

The rate law for the oxidation could then be derived as follows.

From the Kinetic steps,

$-d [Ce (IV)] / dt = k_r[C]+k_0[Ce(IV)]eq[R^\bullet]$

$=k_r[C]+k_0[Ce(IV)]eqk_r[C] / (k0[Ce(IV)]eq)$

$= 2k_r[C]$

From the equation(5),

$-d[Ce(IV)] / dt = 2krK_2 [VA -H+]eq[Ce(IV)]eq$

By using the equation (1),

$-d[Ce(IV)] / dt = 2krk_1k_2[VA]eq[H^+][Ce(IV)]eq$

Applying the equation (3) and (6)

$-d[Ce(IV)]/dt=(2k_rk_1K_2[VA]T[Ce(IV)]T[H+]/(1+k1[H+])x(1+k_2[VA -H+]eq)=R0$

The above equation explain the dependence of the rate on Ce(IV) concentration and also variable with substrate concentration.

The observation of Michelis-Menton kinetics, i.e. The formation of a complex between the reactants allow the oxidation data to be treated according to the method of Line Wearer and Burk.

Thus the above equations can be written as follws:

$$-d[Ce(IV)]/dt = \frac{(2k_rk_1k2[VA]T[Ce(IV)]T[H+])}{(1+k_1[H+])(1+k_2k_1[VA]_{eq}[H+])}$$

$$= \frac{(2k_rk_1k_2[ VA]T[Ce(IV)]T[H+])}{(1+k_1k_2[VA]_T[H+])/(1+k_1[H+])}$$

$$= \frac{(2k_rk_1k_2[VA]T[Ce(IV)]T[H+])}{(1+k_1[H+]+ k_1k_2[VA]T[H+])}$$

Taking reciprocal rate is given by,

$d[Ce(IV)]/dt)=1/(2k_rk_1k_2[VA]T[Ce(IV)]T[H+])+1/(2krk_2[VA]T[Ce(IV)]T)1/(2kr[Ce(IV)]T)-(8)$

Taking reciprocal rate is given by,

$d[Ce(IV)]/dt = 1/(2k_r k_1 k_2[VA]T[Ce(IV)]T[H+]) + 1/(2k_r k_2[VA]T[Ce(IV)]T)1/(2kr[Ce(IV)]T) -$ (8)

This equation explains the linear plot $(-d[Ce(IV)]/dt)^{-1}$vs$[H+]^{-1}$,$(-d[Ce(IV)]/dt)^{-1}$ vs $[VA]^{-1}$

Equation (8) explain the dependence of rate on$[Ce(IV)]$.

Thus $k_r$ could be evaluated from the plots of $(-d[Ce(IV)]/dt)^{-1}$vs$[VA]^{-1}$ from the intercepts of the plots of$(-d[Ce(IV)]/dt)-1$vs$[H+]^{-1}$ , $k_2$ could be evaluated The value of $k_1$ can be determined from the slope of the plots of $(-d[Ce(IV)]/dt)^{-1}$vs $[H+]^{-1}$ by knowing the values of kr and $k_2$.

 The disappearance concentration of Ce(IV)  at given time  which determine the rate of reaction, The cerium (IV) ion  concentration  increases  the rate  and Rp increases,  the reductant     concentration also be the same  results on rate and Rp

## CONCLUSION

Kinetics of polymerization of  initiated by Acrylamide Ce(IV) – vanillin redox system was carried out two different temperature $30^0C$ and $36^0C$ in dilute sulfuric acid medium under nitrogen atmosphere.  The rate of oxidant, reductant ,medium and monomer were studied in the presence and absence of β-CD . In the absence of β-CD  the rate and Rp were increases and in the presence of β-CD  the rate and Rp were decreases, this due to the polar groups present in monomers is involved in hydrogen bonding with hydroxyl group of cyclodextrin making them less reactive toward the polymerization reaction. The observation of  Michelis-menton kinetics the formation of intermediate complex between reactants allows the oxidation data to be treated according to the method of Line Weaver – Burk plot.  The rate of polymerization was also calculated by iodimetry method. The effect of rate by β-CD rate of polymerization decreases.

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