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POLYMERIZATION OF METHYLACRYLATE INITIATED BY CE(IV) – VANILLIN REDOX SYSTEM IN THE PRESENCE AND ABSENCE OF B-CD : A KINETIC STUDY

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Abstract - *Kinetics of Polymerization of methylacrylate (MA) initiated by Ce(IV) – Vanillin redox system was carried out at two different temperatures 30^{o}C & 36^{o}C in dilute sulfuric acid medium under nitrogen atmosphere. The rate of oxidation of Vanillin by Ce(IV) in the presence and absence of monomer, were studied. The effect of various concentrations of [MA], [Ce(IV)], [vanillin], $[H^+]$and varying ionic strengths on the rate of polymerization, rate of Ce(IV) consumption (-Rce) and the percentage monomer conversion were examined. The rate of polymerization in the presence and absence of β-CD has been investigated The kinetic study of Michelis –menton mechanism for formation of intermediate complex between reactants allows the oxidation data to be calculated from the plot of Line Weaver-Burk.and the activation parameters were computed using Arrhenius and Eyringplots. The rate of polymerization was also calculated by iodimetry method. A suitable mechanism has been proposed based on the experimental results.*

***Key words** :Beta-cyclodextrin, ceric ammonium sulphate, Methylacrylate rate of polymerization -Vanillin*

Introduction

A chemical compound containing one or more polymerizable structural units is known as monomer. The process by which the monomer molecules are bonded together to form a macro size molecule (polymer) called polymerization [1-2]. The macromolecules consisting of identical monomers are called homopolymers. When different types of monomers are used, the resulting polymer is called copolymer or mixed polymer. Many reports have been appeared on the mechanism and kinetics of vinyl polymerization initiated by variety of initiators [3-6]. Ceric ion has been widely used in vinyl polymerization in the presence of various organic reducing agents such as alcohols [7], acids [8], amides [9], amines [10] *etc*. Rout *et al*. [11] have proposed a linear termination step involving interaction of polymer radicals with ceric ion [12[.Vanillin (3-methoxy-1-hydroxy benzaldehyde) has both phenolic and aldehyde groups and it is 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 [13] reaction and give Canizaro's reaction [14]. If the hydroxyl group in vanillin is protected, then aldehyde group undergoes oxidation [15] to vanillin acid. A direct oxidation mechanism, without complex formation has been suggested for oxidation in sulfuric acid [16,17].The kinetics of polymerization of MMA with Ce (IV) and vanillin has been reported [18]. Some studies reported in the literature [19]' indicate successful efforts were made to polymerize the monomer in the presence of 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 [21] are influenced by cyclodextrins due to inclusion into the a polar cavity. Reactions of these complexes are regioselcetive [22], stereo specific synthesis can be realized. Many hydrolysis reactions are observed in β-CD. Many bromination [23] reaction are observed in β-CD which are stereo selective and specific, many reduction [24], oxidation and photochemical reactions [25] in β-CD have been reported. The literature survey reveals that no reports of the kinetics of polymerization of MA 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. The literature survey reveals that no reports of the kinetics of polymerization of MA with Ce (IV) - vanillin in the presence and absence of β-CD has been carried out.

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 funnel was fitted vertically on the stopper the aqueous solutions of MA, 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 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 stared 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 d^{-3} in acid medium at a constant temperature of 30°C and36°C 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 process of the reaction was followed by measuring the decrease in absorbance of Ce(IV) in the reaction solution and from the 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 $_{10}$ (concentration) plots these orders were obtained by varying the concentration of reductant and acid in turn while keeping constant.

RESULTS AND DISCUSSION

Variation of oxidant

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 5.68 to 9.07 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 2.49 to 5.26 x10^{-7} .Then in the experiment was done by the addition of β-CD to aliquot the rate of the reaction drastically decreased from 4.8 to 0.887 x 10^{-4} mole/dm^3 sec$^{1.}$. We also found that Rp was decreased from 4.1 to 3.28 x 10^{-7}. This was due to β-CD complexation of the monomer in its cavity which was 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 from 30^{0}C to 36^{0}C the rate was increased from 2.853 to 5.821 x 10^{-4} and the Rp was increased 3.185 to 7.89 x10^{-7} . But in the presence of β-CD the rate was decreased from 7.70 to 4.69 x10^{-4} mole/dm^3 sec^1 and also Rp was decreased from 3.74 to2.832 x 10^{-7}. Therefore β-CD a smal entity which separates the monomer to form polymer. So β-CD was actually decreased the polymerization Fig 1

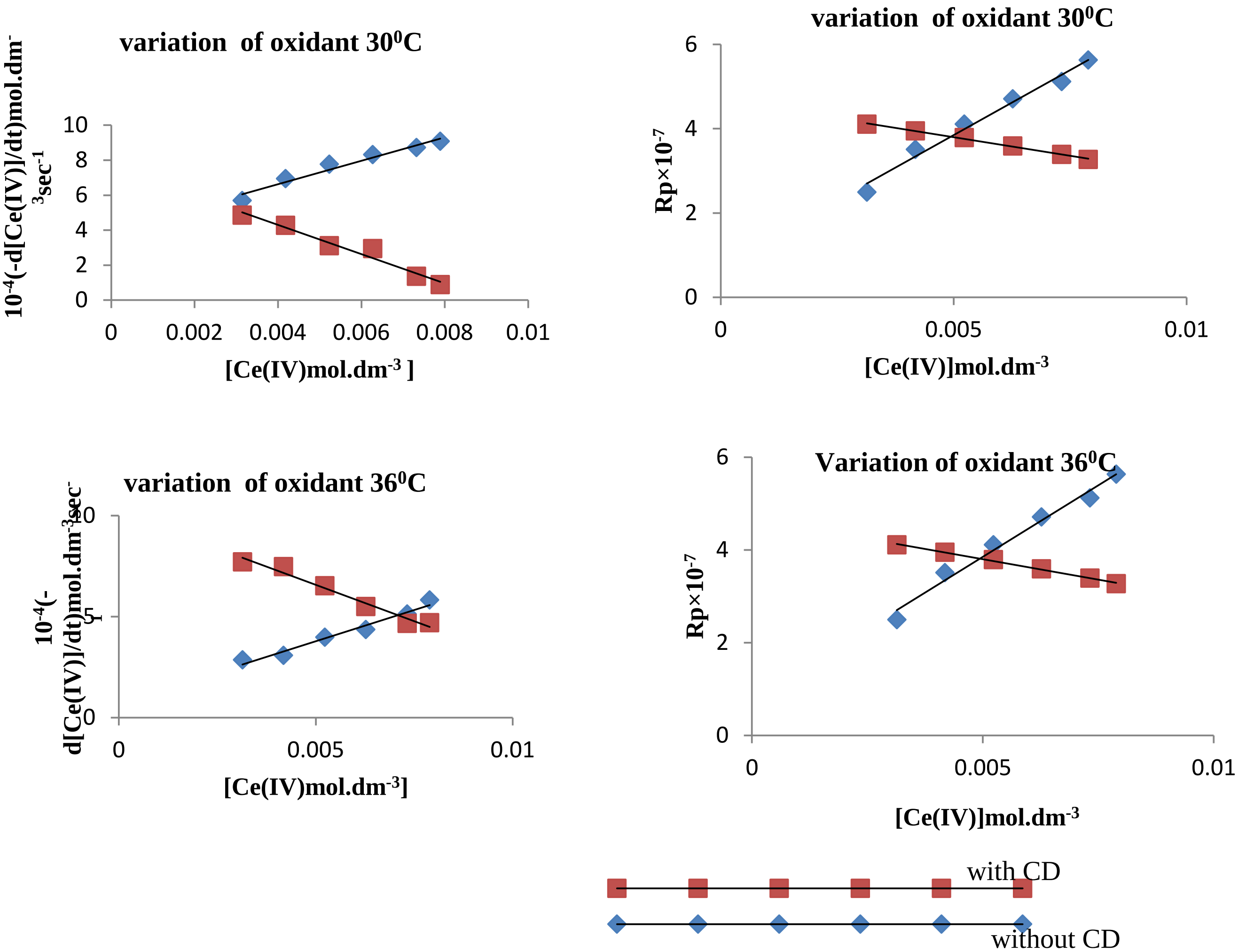


Fig1 Van [2 x 10^{-1}moldm^{-3}], MA[2 x 10^{-4}moldm^{-3}], H^+[2.5 moldm^{-3}]

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 1.46 to 5.94 x10^{-4} mole/dm^{3} sec $^{-1}$ and rate of polymerization from 3.20 to 6.83 x10^{-7} at 30^{0}C were observed. Therefore increasing the concentration of vanillin, increase in both the rate of reaction and rate of polymerization were observed. When we added β-CD to the reaction mixture the rate was decreased from 7.95 to 3.03 x 10^{-4} mole/dm^{3} sec^{1} and the Rp was decreased from 4.51 to 1.66 x10^{-7}. The same trend was followed at higher temperature (36^{0}C) the rate of reaction was increased from0.7 to4.3 x10^{-4} mole/dm^{3} sec^{1} and Rp was increased from 2.51 to3.6 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 6.79 to3.32 x 10^{-4} mole/dm^{3} sec $^{-1}$ and Rp5.11 to 4.22 x 10^{-7}. When we compared 30^{0}C and 36^{0}C, as the temperature increases the rate was also increased in without β-CD. But in 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 decrease in the rate was observed. From this we can concluded that more and more vanillin molecule were occupied in β-CD cavity. Thus β-CD was prevents polymerization .Fig 2

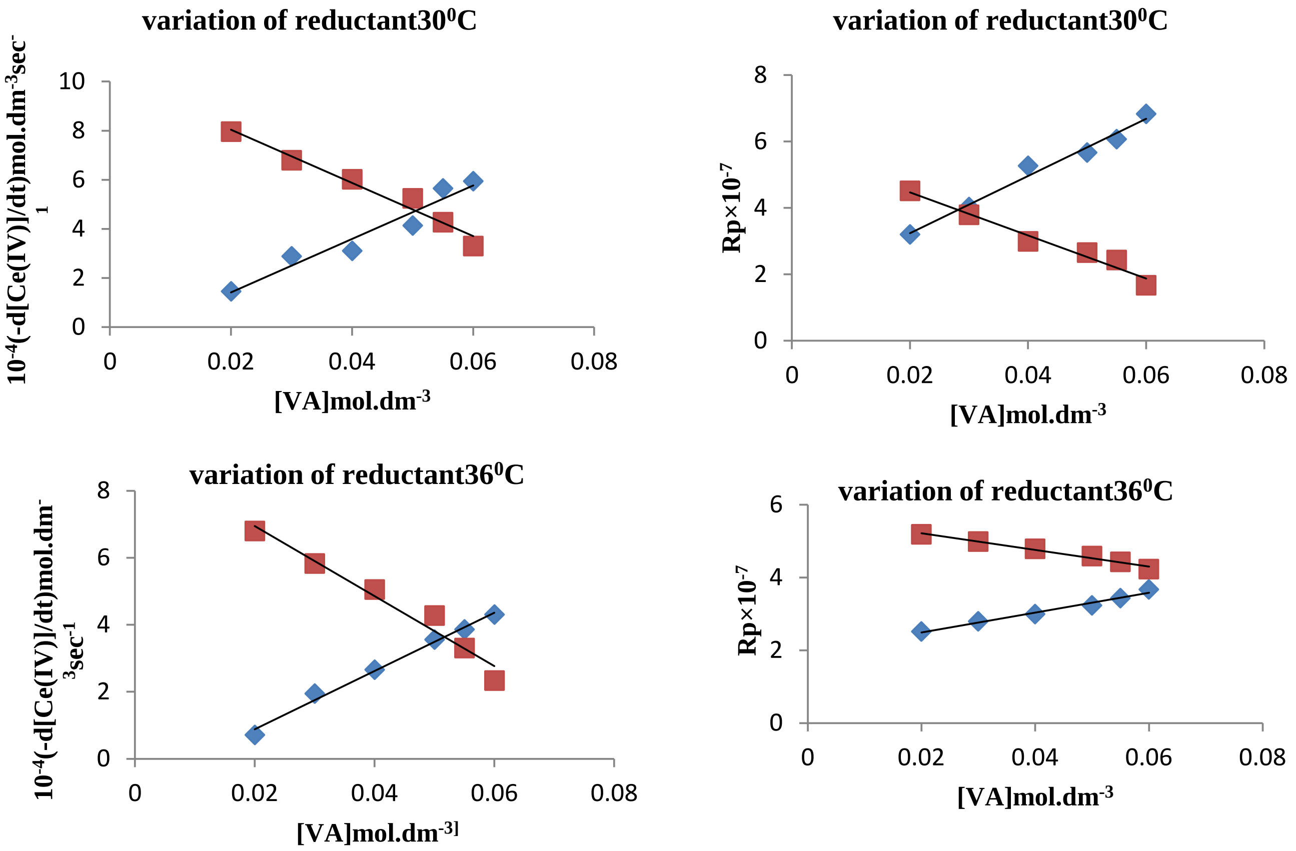


Fig 2 Fig1 Ce(IV) [2.84 x 10^{-5}moldm^{-3}], MA[2 x 10^{-4}moldm^{-3}], H^{+}[2.5 moldm^{-3}];

Variation of H_2SO_4

In the H^{+} ion variation we observed that the rate of reaction was slightly increased from1.59 to 2.38 x10^{-4} mole/dm^{3} sec^{1} and Rp4.14 to 5.43 x 10^{-7} at 30^{0}C when β-CD was added to the medium abruptly changed and the rate of reaction was decreased from 3.26 to 1.36 X10^{-4} mole/dm^{3} sec^{1}and Rp 4.10 to 3.07. 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 36^{0}C.When we compared the rate of the reaction at 30 and 36^{0}C without β-CD, the rate of the reaction at 36^{0}C was increased from 3.35 to 4.26 x10^{-4} mole/dm^{3} sec^{1} and Rp 2.79 to 5.42 was also increased. From this it may be concluded that as the temperature was increased, the movement ions was increased, which was good for polymerization. But in the presence of β-CD the rate was decreased from 5.58 to 4.54 x 10^{-4} mole/dm^{3} sec^{1} and Rp from 4.07 to1.48 x 10^{-7} From this we can conclude that at higher temperature (36^{0}C) in the presence of β-CD even though the movement of ions were faster rate but β-CD structure hydrolyzed to give more number of glucose units which hindered the polymerization. Fig 3

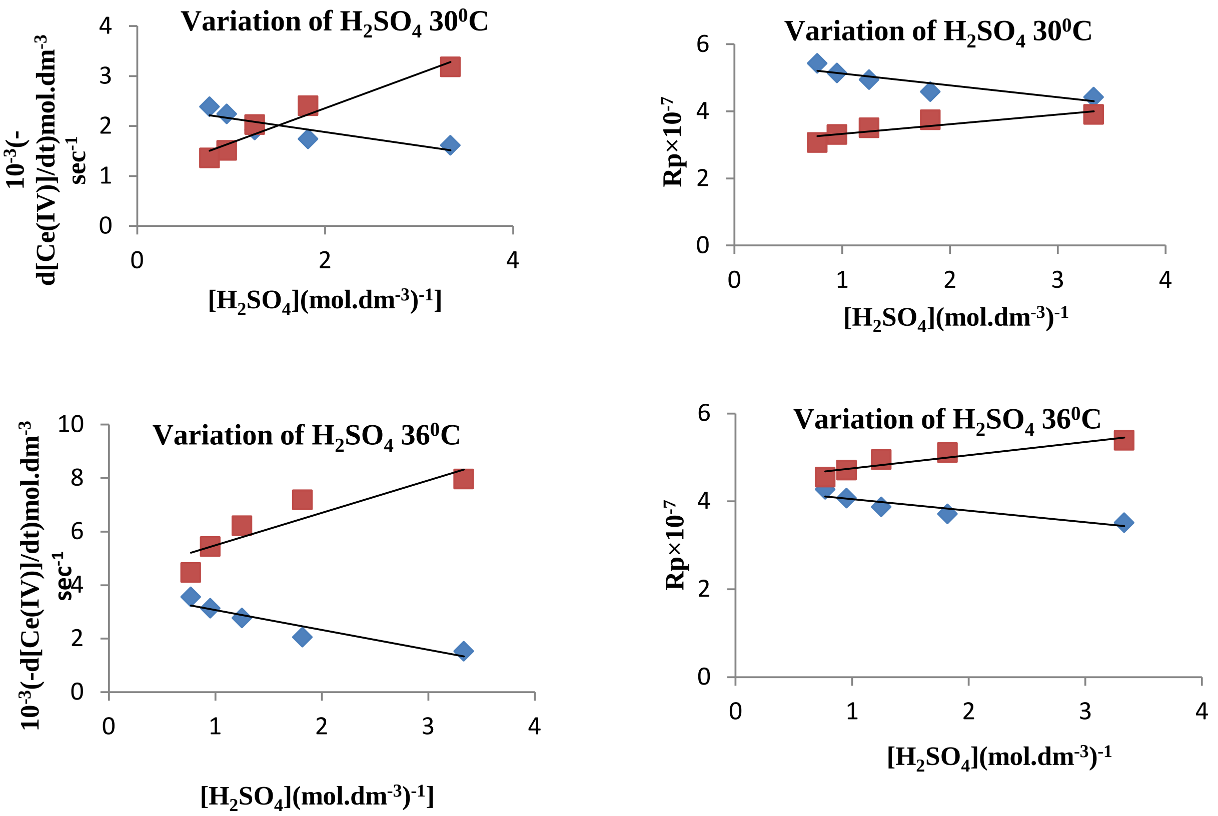
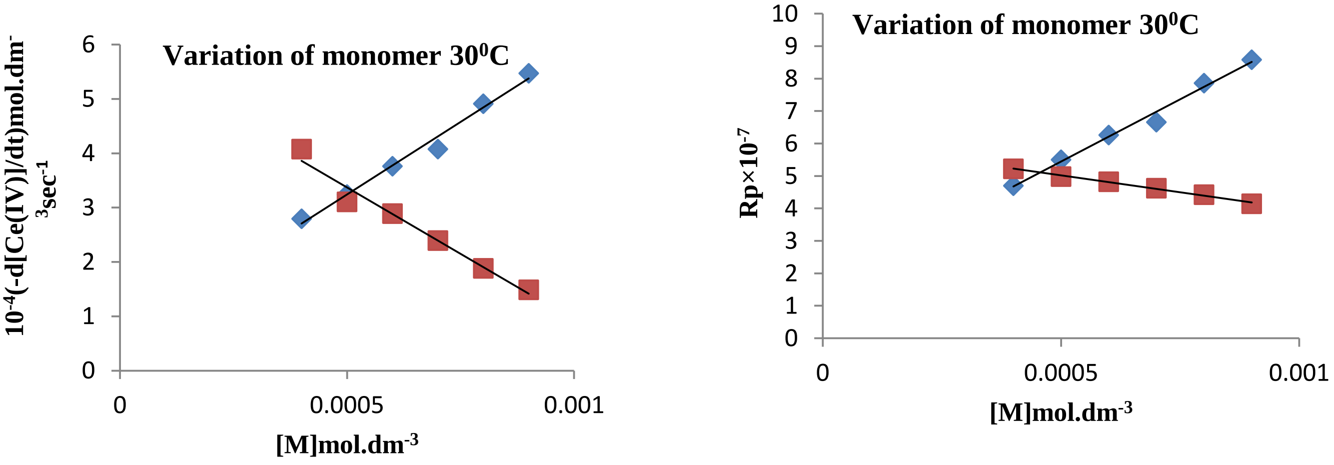


Fig 3 Ce(IV) [2.84 x 10^{-5}moldm^{-3}], Van [2 x 10^{-1}moldm^{-3}] MA[2 x 10^{-4}moldm^{-3}],

Variation of monomer

The rate and Rp of the reaction was increased from and 2.79 to 5.74 x10^{-4} mole/dm^3 sec^1 and 4.70 to 8.58 x 10^{-7} respectively as we were increased the concentration of monomer at 30^{o}C. 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 4.70 to 1.48 x 10^{-4} mole/dm^3 sec^1 and Rp5.22 to4.14 x 10^{-7}. 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 4.65 to8.95 x 10^{-4} mole/dm^{3}sec^1 and the Rp4.98 to 8.98 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 9.70 to 5.2 x 10^{-4} mole/dm^3 sec $^{-1}$ and Rp4.34 to1.3.43 x 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 de-accelerated the polymerization. Fig 4.



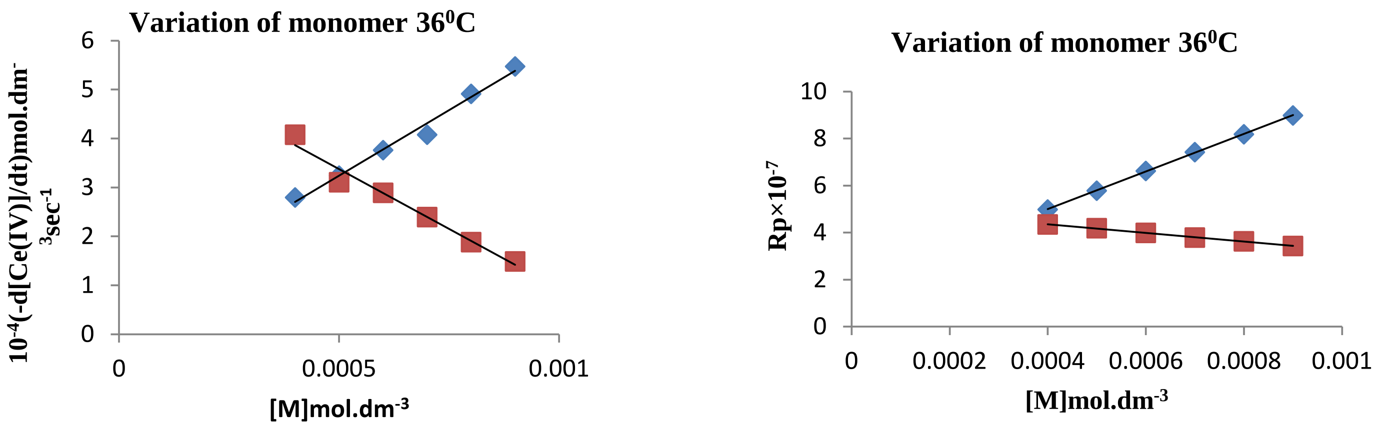


Fig 4 Ce(IV) [2.84 x 10^{-5}moldm^{-3}], Van [2 x 10^{-1}moldm^{-3}],H^+[2.5moldm^{-3}

Kinetics of oxidation in presence of monomer

The Kinetics of oxidation of Vanillin (VA) by Ce(IV) in the presence and absence of monomer was carried out at the temperature 30^{0}C and 36^{0}C. The rate of oxidant consumption(-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 (-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

$$VA + H^+ \overset{K_1}{\rightleftharpoons} VA - H^+ \qquad \text{(i)}$$

$$VA - H^+ + Ce(IV) \overset{K_2}{\rightleftharpoons} \text{Complex (C)} \qquad \text{(ii)}$$

$$C \overset{K_r}{\rightleftharpoons} R^{\cdot} + Ce(III) + H \qquad \text{(iii)}$$

$$R^{\bullet} + Ce(IV) \overset{K_0}{\rightleftharpoons} \text{Products} \qquad \text{(iv)}$$

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,

$$K_1 = ([\ - H^+]_{eq}) / ([VA]_{eq}[H^+]) \quad \text{and} \qquad (1)$$

$$[VA]_T = [VA - H^+]_{eq} + [VA]_{eq} \qquad (2)$$

From equation(1),

$$[VA - H^+]_{eq} = K_1[VA]_{eq}[H^+]$$

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

$$[VA]_T = K_1[VA]_{eq}[H^+]+[VA]_{eq}$$

$$= [VA]_{eq}(1 + K_1[H^+]) \qquad (3)$$

Where $[VA]_{eq}$ denotes the equilibrium concentration of VA also,

$$[Ce\ (IV)]_T = [Ce(IV)]_{eq} + [C] \qquad (4)$$

From the kinetic step (2)

$$K_2 = [C] / ([VA - H^+]_{eq}[Ce\ (IV)]_{eq})[C]$$

$$= K_2[VA\text{-}H^+]_{eq}[Ce(IV)]_{eq} \qquad (5)$$

Substituting equation (5) in equation (4),

$$[Ce(IV)]_T = [Ce(IV)]_{eq} + K_2[VA - H^+]_{eq}[Ce(IV)]_{eq} = [Ce(IV)]_{eq}(1+K_2[VA - H^+]_{eq}) \qquad (6)$$

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 kineticscheme steps(iii)and(iv):

$$-d[R^\bullet] / dt = K_0[Ce(IV)]_{eq}[R^\bullet] - K_r[C] = 0$$

therefore

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

$$[R^\bullet] = [K_r[C]) / (K_0[Ce(IV)]_{eq}) \qquad (7)$$

The rate law for the oxidation could then be derived as follows.
From the Kinetic steps,

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

$$= K_r[C]+K_0[Ce(IV)]_{eq}K_r[C] / (K_0[Ce(IV)]_{eq})$$

$$= 2K_r[C]$$

From the equation (5),

$$-d[Ce(IV)] / dt = 2K_rK_2[VA\text{-}H^+]_{eq}[Ce(IV)]_{eq}$$

By using the equation (1),

$$-d[Ce(IV)] / dt = 2K_rK_1K_2[VA]_{eq}[H^+][Ce(IV)]_{eq}$$

Applying the equation (3) and (6)

$$-d[Ce(IV)]/dt=(2K_rK_1K_2[VA]_T[Ce(IV)]_T[H^+]/(1+K_1[H^+])x(1+K_2[VA\text{-}H^+]_{eq})=R_0$$

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 equation can be written as follows:

$$-d[Ce(IV)]/dt = \frac{(2K_rK_1K_2[VA]_T[Ce(IV)]_T[H^+])}{(1+K_1[H^+])(1+K_2K_1[VA]_{eq}[H^+])}$$

$$= \frac{(2K_rK_1K_2[LA]_T[Ce(IV)]_T[H^+])}{(1+K_1K_2[VA]_T[H^+])/(1+K_1[H^+])}$$

$$= \frac{(2K_rK_1K_2[VA]_T[Ce(IV)]_T[H^+])}{(1+K_1[H^+]+ K_1K_2[VA]_T[H^+])}$$

Taking reciprocal rate is given by

$$d[Ce(IV)]/dt)=1/(2K_rK_1K_2[VA]_T[Ce(IV)]_T[H^+])+1/(2K_rK_2[VA]_T[Ce(IV)]_T)1/(2K_r[Ce(IV)]_T \qquad \text{-(8)}$$

This equation explains the linear plot of$(-d[Ce(IV)]/dt)^{-1}$ vs$[H^+]^{-1}$,$(-d[Ce(IV)]/dt)^{-1}$ vs$[VA]^{-}$Equation (8) explain the dependence of rate on[Ce(IV)].Thus Kr 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 K1 can be determined from the slope of the plots of (-d[Ce(IV)]/dt)-1vs $[H+]^{-1}$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 Rpincreases the reductant concentration also be the same results on rate and Rp

Conclusion

Kinetics of polymerization of initiated by methyl cry late Ce (IV) – vanillin redox system was carried out two different temperature 30^0C and 36^0C in dilute sulphuric 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. 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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