

# KINETIC STUDY OF POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY Ce(IV) – VANILLIN REDOX SYSTEM IN THE PRESENCE $\beta$ -CD AND MICELLAR PHASE

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**Abstract:** Kinetics of Polymerization of methylmethacrylate (MMA) initiated by Ce(IV) – Vanillin redox system have been carried out at two different temperatures 30°C & 36°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 monomer [MMA], oxidant [Ce(IV)], reductant [vanillin], medium [H<sup>+</sup>] and varying ionic strengths NaHSO<sub>4</sub> on the rate of polymerization, rate of Ce(IV) consumption (-R<sub>Ce</sub>) and the percentage monomer conversion were examined. Further, the rate of polymerization (R<sub>p</sub>) in  $\beta$ -CD and micellar (SLS, CTAB and Tx-100) phase at constant concentration has been investigated. The kinetic study of Michalis-menton mechanism for the formation of intermediate complex between reactants allows the oxidation data to be calculated from the plot of Line Weaver-Burk. The varying rate and thermodynamic parameters were studied by Arrhenius and Eyring plot. The rate of polymerization can be calculated. A suitable mechanism has been proposed based on the experimental results.

**Key words :** MMA-methylmethacrylate,  $\beta$ -CD-Beta-cyclodextrin, Ce(IV) –ceric ammonium sulphate, SLS-Sodium lauryl sulphate, CTAB-cetyltrimethyl ammonium bromide Tx-100- Triton-X-100

## 1. INTRODUCTION

Kinetic studies on aqueous polymerization of MMA have been reported[1,2]. Several reports have 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 monomer radicals with ceric ion[12]. Vanillin is a very powerful flavoring reagent in the food industry and widely used in the synthesis of drugs, 40% of vanillin is consumed in manufacturing drug

as Aldomet, L-Dopa[13] and Trimethaprin 2A. It is also used in the preparation of perfume and as a catalyst to polymerize methyl methacrylates [14]. Vanillin (3-methoxy-1-hydroxy benzaldehyde) 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<sup>15</sup> reaction that allows substitution[16] for the aldehyde reactions, likes Cannizaro's reaction. If the hydroxyl group in vanillin is protected, Aldehyde group undergoes oxidation[17] to vanillin acid. A direct oxidation mechanism, without complex formation has been suggested for oxidation in sulfuric acid[18,19]. The kinetics of polymerization of MMA with Ce(IV) and vanillin has been reported[20] The literature survey reveals that no reports of the kinetics of polymerization of MMA with Ce(IV) - vanillin in  $\beta$ -CD and micellar phase has been carried out.

## 2. 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 MMA, vanillin and sulfuric acid, sodium bisulfate (to maintain ionic strength) and SDS in appropriate concentrations were taken on the reaction tube. Nitrogen gas was bubbled for about half an hour. 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 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 0.25 mol d<sup>-3</sup> in acid medium at a constant temperature of 30°C and 36°C respectively, unless otherwise stated. The reaction was initiated by mixing the thermostated solutions of Ce(IV) and vanillin, which also contained the required concentration of H<sub>2</sub>SO<sub>4</sub> and NaHSO<sub>4</sub>. The process of the reaction was followed by measuring the decrease in concentration of Ce(IV) in the reaction solution and from order slopes of plots of log<sub>10</sub> (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 vanillic Acid was found by log  $k_{obs}$  versus log<sub>10</sub> (concentration) plots these orders were obtained by varying the concentration of reluctant and acid in turn while keeping constant. The acid formation is confirmed by I.R. data[21]

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of Ce(IV)

The concentration cerium(IV) was varied from 3.14 x 10<sup>-3</sup> to 7.83 x 10<sup>-3</sup> mol dm<sup>-3</sup> at constant [vanillin] (2 x 10<sup>-1</sup> mol dm<sup>-3</sup>), [H<sup>+</sup>] 2.5 (mol dm<sup>-3</sup>), [NaHSO<sub>4</sub>] (2 mol dm<sup>-3</sup>). The rate of the reaction is increased with increase in the concentration Ce(IV) from 6.907 to 10.855 for 30°C and 5.328 to 12.343 for 36°C as shown in the fig 1 and table 1. The observed that  $R_p(obs)$  increase with increasing Ce(IV) concentration from 2.907 to 3.013 for temp 30°C and 2.658 to 3.013 for temp 36°C as shown in the plot of  $R_p(obs)$  Vs Ce(IV) fig 2 table 2 shows a straight line.

Table 1 Effect of Ce (IV)

[Ce(IV)] mol. dm <sup>-3</sup>	10 <sup>-7</sup> [-d [Ce(IV)]/dt] mol. dm <sup>-3</sup> . sec <sup>-1</sup>	
	30°C	36°C
0.00314	6.9079	5.3289
0.00418	7.6974	7.5
0.00523	8.2895	8.8816
0.00627	8.8816	10.8553
0.00732	10.0658	12.2368
0.00783	10.8553	12.34342

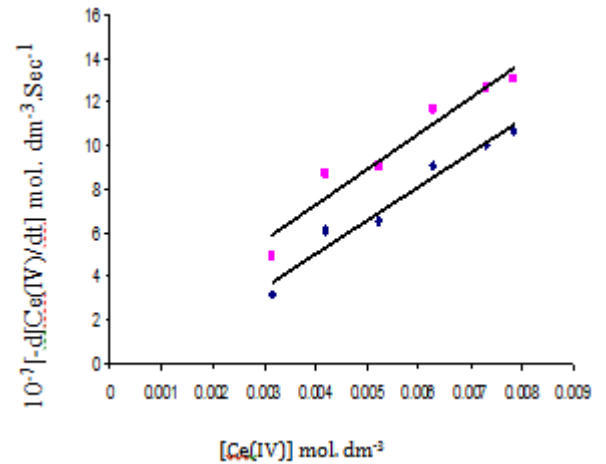


Fig - 1: Effect of Ce (IV)

Table 2 Effect of Ce (IV)

[Ce(IV)] mol. dm <sup>-3</sup>	$R_p \times 10^{-7}$	
	30°C	36°C
0.00314	2.9076	2.6588
0.00418	2.9243	2.8360
0.00523	2.9423	2.9068
0.00627	3.0297	2.9423
0.00732	3.0658	2.9778
0.00784	3.1017	3.0133

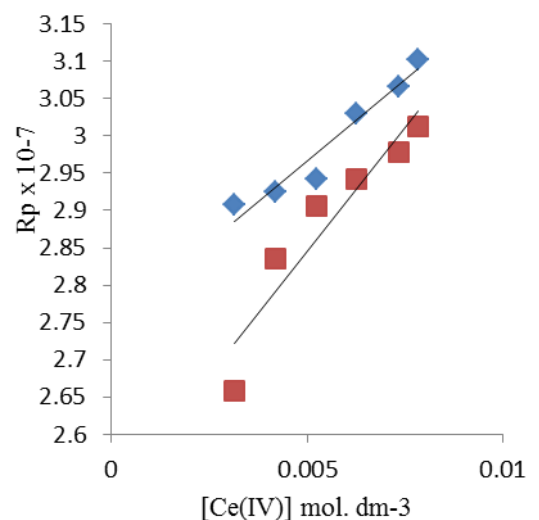
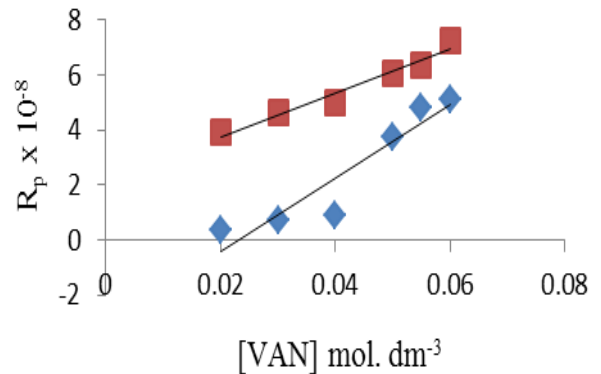


Fig 2

**Effect of [Vanillin]**

The concentration of vanillin was varied from  $(2 \times 10^{-2} \text{ mol dm}^{-3})$  to  $(6 \times 10^{-2} \text{ mol dm}^{-3})$  at constant  $[\text{Ce(IV)}]$   $0.0284 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{NaHSO}_4]$   $(2 \text{ mol dm}^{-3})$ . The rate of the reaction is increased with increase in the concentration  $[\text{Van}]$  from 14.013 to 17.96 for  $30^\circ\text{C}$  and 14.605 to 20.132 for  $36^\circ\text{C}$  as shown in the fig 3 and table 3. The observed that  $R_p(\text{obs})$  increase with increasing  $[\text{Van}]$  concentration from 0.360 to 5.132 for temp  $30^\circ\text{C}$  and 3.8981 to 7.2663 for temp  $36^\circ\text{C}$ . The plot of  $k(\text{s}^{-1})$  vs  $[\text{vanillin}]$  yielded linear indicating first order dependence with respect to vanillin (table4,fig4) Table 3 Effect of  $[\text{VAN}]$



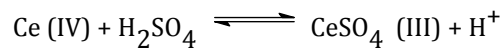
**Table 3**

[VAN] mol. dm <sup>-3</sup>	10 <sup>-7</sup> [-d [Ce(IV)/dt] mol. dm <sup>-3</sup> . Sec <sup>-1</sup>	
	30 <sup>o</sup> c	36 <sup>o</sup> c
0.02	14.013	14.605
0.03	15.395	15.395
0.04	15.987	16.974
0.05	16.579	17.961
0.055	17.566	19.145
0.06	17.961	20.132

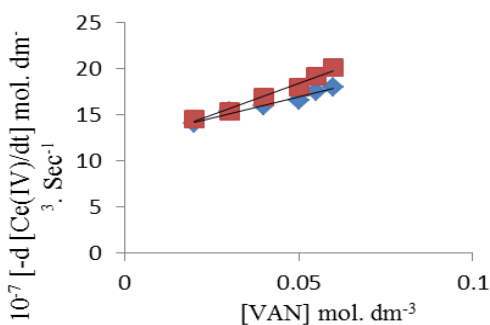
**Fig 4**

**Effect of [H<sup>+</sup>]**

The increase in concentration of acid leads to a slight change in the rate  $R_p(\text{obs})$  at constant ionic strength. But  $R_p(\text{obs})$  was independent of  $[\text{H}^+]$ . This may be attributed to formation of less active  $\text{Ce(IV)}$  species given by the following equilibrium.



At constant  $[\text{H}_2\text{SO}_4]$ , the increase in  $[\text{H}^+]$  will lead to a decrease in the ratio  $\text{Ce}[\text{SO}_4] \text{ (III)} / \text{Ce(IV)}$ . Hence with lower  $[\text{H}^+]$  the reactivity of  $\text{CeSO}_4 \text{ (III)}$  predominates where as at higher  $[\text{H}^+]$  the effect was reversed. The rate of reaction increased from 1.299 to 0.779 for  $30^\circ\text{C}$  and 1.178 to 0.858 for  $36^\circ\text{C}$  fig 5 table 5. The observed that  $R_p(\text{obs})$  slight change with increasing  $[\text{H}^+]$  concentration from 2.273 to 2.962 for temp  $30^\circ\text{C}$  and 3.373 to 2.479 for temp  $36^\circ\text{C}$ . The plot of  $k(\text{s}^{-1})$  vs  $[\text{H}^+]$  yielded linear and indicating first order dependence with respect to  $[\text{H}^+]$  ( fig6 table 6)



**Fig.3**

**Table 4 Effect of [VAN]**

[VAN] mol. dm <sup>-3</sup>	R <sub>p</sub> × 10 <sup>-8</sup>	
	30 <sup>o</sup> c	36 <sup>o</sup> c
0.02	0.3607	3.8981
0.03	0.7214	4.6083
0.04	0.8878	4.9634
0.05	3.7455	6.0288
0.055	4.7859	6.3806
0.06	5.1327	7.2663

**Table 5 Effect of [H<sup>+</sup>]**

[H <sub>2</sub> SO <sub>4</sub> ] <sup>-1</sup> (mol. dm <sup>-3</sup> ) <sup>-1</sup>	10 <sup>6</sup> [-d [Ce(IV)/dt] <sup>-1</sup> mol. dm <sup>-3</sup> . Sec <sup>-1</sup>	
	30 <sup>o</sup> c	36 <sup>o</sup> c
20	1.2992	1.1783
3.33	1.1259	1.1014
1.818	1.034	1.0555
1.25	0.9559	0.9744
0.952	0.8587	0.9212
0.769	0.7795	0.8587







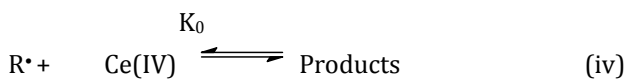
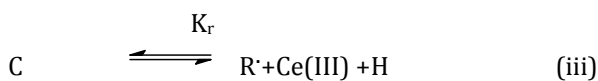
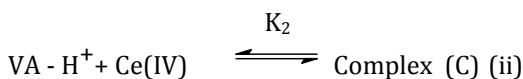
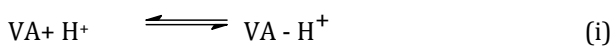


**Kinetics of oxidation in presence of monomer**

The Kinetics of oxidation of Vanillin (VA) by Ce(IV) in the presence and absence of monomer was carried out at the temperature 30°C and 36<sup>0</sup>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 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)<sup>-1</sup> vs [H<sup>+</sup>]<sup>-1</sup> were also found to be linear.

Scheme K<sub>1</sub>



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

The two equilibrium K<sub>1</sub> and K<sub>2</sub> were treated separately so that,

$$K_1 = \frac{[VA - H^+]_{eq}}{[VA]_{eq} [H^+]_{eq}} \quad (1)$$

and

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

From equation(1),

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

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

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

Where [VA]<sub>eq</sub> denotes the equilibrium concentration of LA

also,

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

From the kinetic step (2)

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

Substituting equation (5) in equation (4),

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

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

By applying steady-state approximation to the intermediate(R\*), the following expression can be derived from the kineticscheme steps(iii)and(iv):

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

therefore

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

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

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

From the Kinetic steps,

$$-d [Ce(IV)] / dt = K_r [C] + K_0 [Ce(IV)]_{eq} [R^*] \\ = K_r [C] + K_0 [Ce(IV)]_{eq} K_r [C] / (K_0 [Ce(IV)]_{eq}) \\ = 2K_r [C]$$

From the equation(5),

$$-d [Ce(IV)] / dt = 2K_r K_2 [VA - H^+]_{eq} [Ce(IV)]_{eq}$$

By using the equation (1),

$$-d [Ce(IV)] / dt = 2K_r K_1 K_2 [VA]_{eq} [H^+]_{eq} [Ce(IV)]_{eq}$$

Applying the equation (3) and (6)

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

The above equation explain the dependence of the rate on Ce(IV) concentration and also variable with substrate concentration. The observation of Michelis - Mentonkinetics, 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:

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

$$= \frac{(2K_r K_1 K_2 [\text{LA}]_T [\text{Ce(IV)}]_T [\text{H}^+])}{(1+K_1 K_2 [\text{VA}]_T [\text{H}^+]) / (1+K_1 [\text{H}^+])}$$

$$= \frac{(2K_r K_1 K_2 [\text{VA}]_T [\text{Ce(IV)}]_T [\text{H}^+])}{(1+K_1 [\text{H}^+] + K_1 K_2 [\text{VA}]_T [\text{H}^+])}$$

$$= \frac{(2K_r K_1 K_2 [\text{VA}]_T [\text{Ce(IV)}]_T [\text{H}^+])}{(1+K_1 [\text{H}^+] + K_1 K_2 [\text{VA}]_T [\text{H}^+])}$$

Taking reciprocal rate is given by,  
 $d[\text{Ce(IV)}]/dt = 1/(2K_r K_1 K_2 [\text{VA}]_T [\text{Ce(IV)}]_T [\text{H}^+]) + 1/(2K_r K_2 [\text{VA}]_T [\text{Ce(IV)}]_T) - 1/(2K_r [\text{Ce(IV)}]_T) \quad (8)$

This equation explains the linear plot of  $(-d[\text{Ce(IV)}]/dt)^{-1}$  vs  $[\text{H}^+]^{-1}$ ,  $(-d[\text{Ce(IV)}]/dt)^{-1}$  vs  $[\text{VA}]^{-1}$ . Equation (8) explain the dependence of rate on  $[\text{Ce(IV)}]$ .

Thus  $K_r$  could be evaluated from the plots of  $(-d[\text{Ce(IV)}]/dt)^{-1}$  vs  $[\text{VA}]^{-1}$  from the intercepts of the plots of  $(-d[\text{Ce(IV)}]/dt)^{-1}$  vs  $[\text{H}^+]^{-1}$ ,  $K_2$  could be evaluated. The value of  $K_1$  can be

determined from the slope of the plots of  $(-d[\text{Ce(IV)}]/dt)^{-1}$  vs  $[\text{H}^+]^{-1}$  by knowing the values of  $K_r$  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  $R_p$  increases the reductant concentration also be the same results on rate and  $R_p$

## CONCLUSION

Kinetics of polymerization of methyl methacrylate initiated by Ce(IV) – vanillin redox system was carried out two different temperature 30°C and 36°C in dilute sulfuric acid medium under nitrogen atmosphere. The rate of oxidant and reductant were studied in the presence and absence of monomer. 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 overall activation energy varying rate and thermodynamic parameters are studied by Arrhenius and Eyring plot. The rate of polymerization is also calculated by iodometry method. The effect of rate by using cationic surfactant rate increases, anionic surfactant the rate decreases and non ionic surfactant no effect on rate. Effect of  $\beta$ -CD rate of polymerization increases. Particle size decreases due to hydrophobic interaction.

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