Kinetic Study Of The Aqueous Polymerization Of Ethyl Acrylate Initiated By Ceric Ion-Reducing Agent System

G.V.Ramana Reddy
Polymer Division,
Central Leather Research Institute,
Adyar, Chennai-600 020 (INDIA)
E-mail: gvrr2004@yahoo.com

R.Prathipa, R.Sriram
Department of Chemistry,
Coimbatore Institute of Technology,
Coimbatore-641 014 (INDIA)

ABSTRACT

The kinetic study of the aqueous polymerization of ethyl acrylate (EA) is carried out at 30°C in nitric acid medium by employing ammonium ceric nitrate (ACN)-isopropyl alcohol (IPA) as the redox initiator system. The ceric ion consumption is found to be first order with respect to ceric ion concentration. The formation of complex between Ce(IV) and reducing agent is observed. The orders for the aqueous polymerization of EA are found to be 0.51, 0.52 and 1.43, respectively, with respect to Ce(IV), IPA and EA concentrations. The overall activation energy, $E_{overall}$, for the aqueous polymerization of EA is evaluated in the temperature region 27-40°C. A kinetic mechanism for the aqueous polymerization of EA initiated by redox initiator system is presented.   © 2005 Trade Science Inc. - INDIA

INTRODUCTION

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. The oxidation of some organic substrates by Ce(IV), believed to occur by direct attack of the ceric species on the substrate, appears to proceed by electron abstraction[1-3], while in some cases the reaction goes through an intermediate complex[4-6]. Ammonium ceric nitrate gives more intense colours with hydroxy compounds than does ceric sulphate, mostly due to the complex formation with them and the subsequent liberation of a free radical by the decomposition of the complex. This paper describes a study of the kinetics of polymerization of ethyl acrylate (EA) at 30°C in aqueous nitric acid medium by employing

ammonium ceric nitrate (ACN)-isopropyl alcohol (IPA) as the redox initiator system.

EXPERIMENTAL

Materials

The monomer, ethyl acrylate (EA) (Central Drug House Pvt. Ltd., Mumbai, India) is purified by washing with 5% sodium hydroxide followed by distilled water. The washed monomer is further purified by vacuum distillation under inert atmosphere.

Isopropyl alcohol (IPA) (AR, Fischer Chemic Ltd., Chennai, India), methanol (AR, Ranbaxy Laboratory Ltd., S.A.S.Nagar, India), tetrahydrofuran (THF) (HPLC grade, S.D.Fine Chem.Pvt.Ltd., Boisar, India), ammonium ceric nitrate (ACN) (AR, S.D.Fine Chem.Pvt.Ltd., Boisar, India), ammonium ferrous sulphate (AFS) (AR, S.D.Fine Chem.Pvt.Ltd., Boisar, India) and ferroin solution (ferrous o-phenanthroline) (AR, S.D.Fine Chem.Pvt.Ltd., Boisar, India) are used as supplied without further purification.

Methods

Aqueous polymerization of ethyl acrylate is carried out in 0.2M nitric acid at 30ºC under an inert atmosphere by using Ce(IV)-IPA redox initiator system. To an aqueous solution (27 ml) of EA and reducing agent (R) under inert atmosphere the solution (3 ml) of ACN in 2M nitric acid is added and the reaction is carried out at 30ºC. The ceric ion concentration in the reaction medium is determined volumetrically at different time intervals by adding an excess of known quantity of ammonium ferrous sulphate solution to the reaction mixture and the excess ammonium ferrous sulphate in the reaction mixture is back-titrated with standard ammonium ceric nitrate solution by using o-phenanthroline (ferroin) as an indicator. The rate of ceric ion consumption, R_{Ce}, is determined from the initial slope of the plot of the percentage consumption of Ce(IV) versus time.

The polymerization of EA in the present study is followed by gravimetry. The polymerization reaction in the reaction tube is arrested at the required time interval by adding slight excess of ammonium ferrous sulphate solution to the reaction mixture in the reaction tube. Thus, the polymer formed for different time intervals are separated by filtration in sintered crucibles and the filtered polymers are washed thoroughly in the sintered crucibles and are dried to constant weights at 60ºC in a vacuum oven. The percent conversions of polymer formed at different times is computed from the weights of the polymers obtained in these time periods. The rate of polymerization, R_p, is evaluated from the initial slope of the plot of percent conversion versus time.

UV-visible spectrophotometric study

The UV-visible absorption spectra are recorded with the use of UV-visible spectrophotometer (Cary 50 Bio). The spectra are recorded for solutions: (1) Ce(IV) (0.5×10^{-3}M) in 0.2M nitric acid , (2) Ce(IV) (0.5×10^{-3}M) along with reducing agent (0.3M) in 0.2M nitric acid, and (3) Ce(IV) (0.5×10^{-3}M) along with reducing agent (0.3M) and monomer (0.1M) in 0.2M nitric acid.

Molecular weight determination

The molecular weight ($\overline{M}_w$) of the polymers formed at different time intervals are determined by gel permeation chromatography (Waters, USA) with tetrahydrofuran as eluent (TABLE 1, Figure 7).

TABLE 1: Determination of energy of activation, $E_{overall}$ and molecular weight with conversion
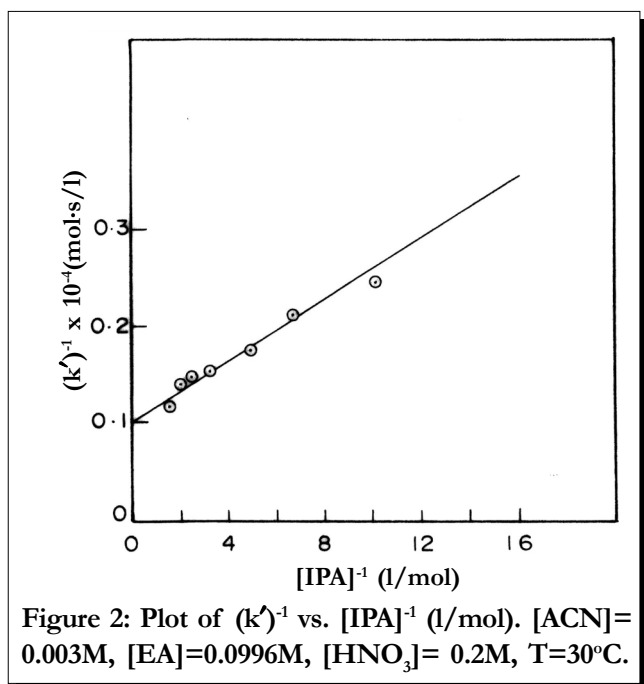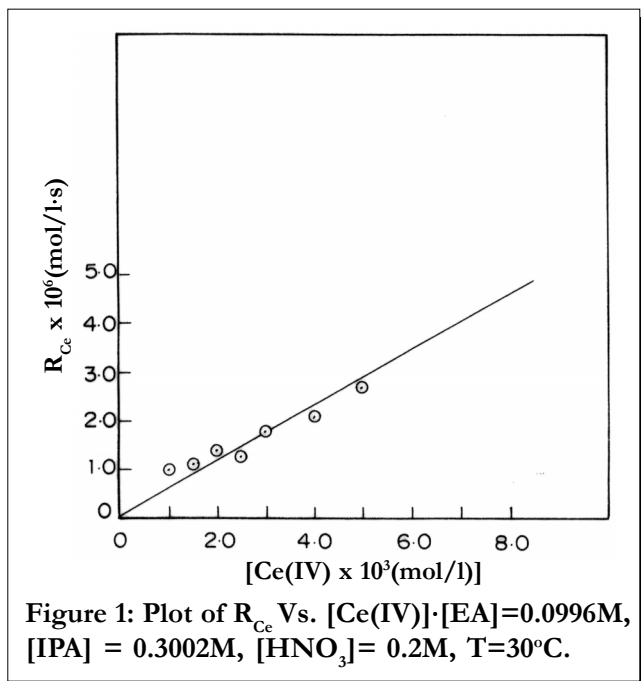
T (ºK)	$R_p \times 10^4$ (mol $l^{-1}S^{-1}$)	% Conversion	$\overline{M}_w \times 10^{-4}$
300	0.863	8.3	2.48
303	1.062	47.4	3.74
308	1.328	56.6	4.07
313	1.659	56.8	4.66
		61.8	5.26
$E_{overall} = 36.38$	KJ/mol	65.8	5.79
		67.6	5.13
		68.2	4.30

Molecular weight calibration curve is obtained with polystyrene standards in the molecular weight range 2.3×10^3 to 3.1×10^6 (Polymer laboratories, Church Stretton, Shropshire, UK).

RESULTS

The effect of ceric ion concentration on R_{Ce} is

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Figure 1: Plot of R_{Ce} Vs. [Ce(IV)]·[EA]=0.0996M, [IPA] = 0.3002M, [HNO$_3$]= 0.2M, T=30°C.

Figure 2: Plot of $(k')^{-1}$ vs. [IPA]$^{-1}$ (l/mol). [ACN]= 0.003M, [EA]=0.0996M, [HNO$_3$]= 0.2M, T=30°C.

Figure 3: UV-vis absorption spectra. (1) ACN in 0.2M HNO$_3$, (2) ACN with IPA in 0.2M HNO$_3$, (3) ACN with IPA and EA in 0.2M HNO$_3$; reference solution is water
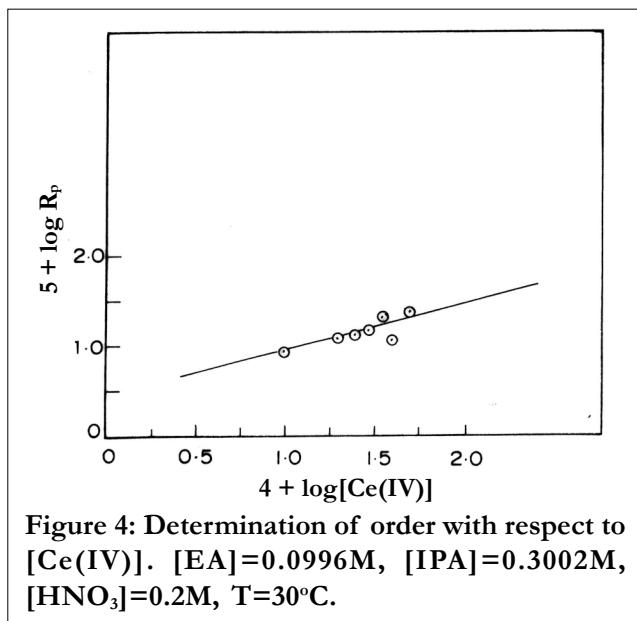
studied by varying the ceric ion concentration in the reaction medium in the range 1.0 - 5.0x10^{-3} moll^{-1} and by keeping all other variables in the reaction medium constant. The effect of reducing agent concentration on R_{Ce} is also studied by varying the reducing agent concentration in the range 0.1 - 0.5M while keeping constant all the other parameters in the reaction medium. No induction period is observed for the reaction between ceric ion and reducing agent.
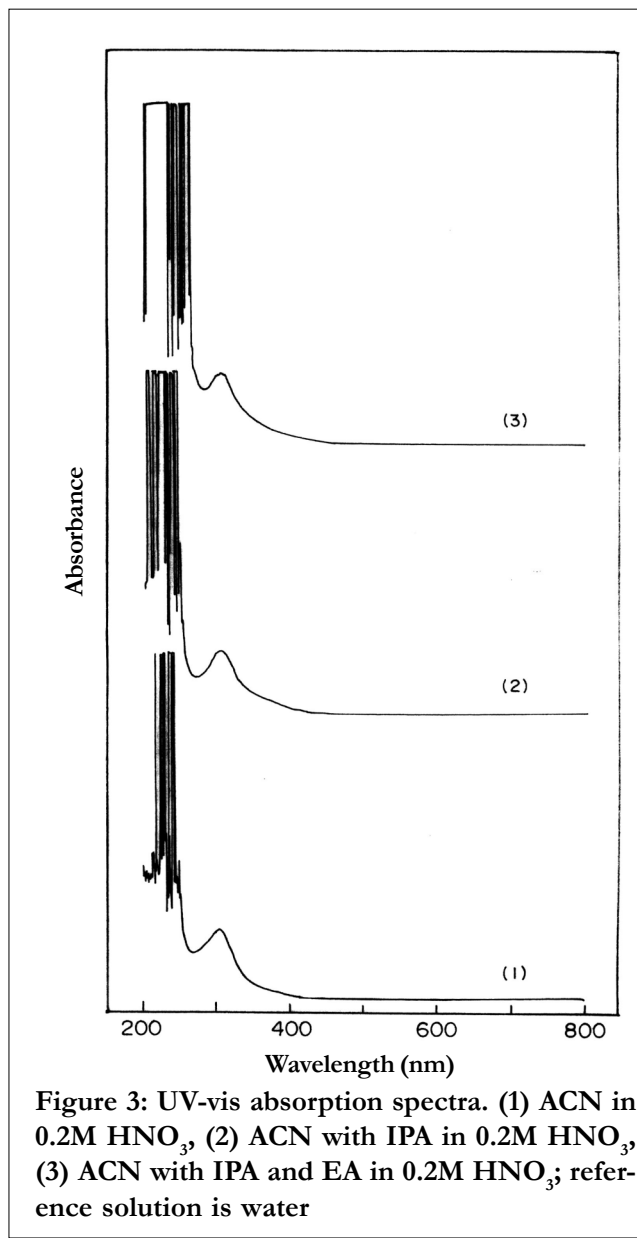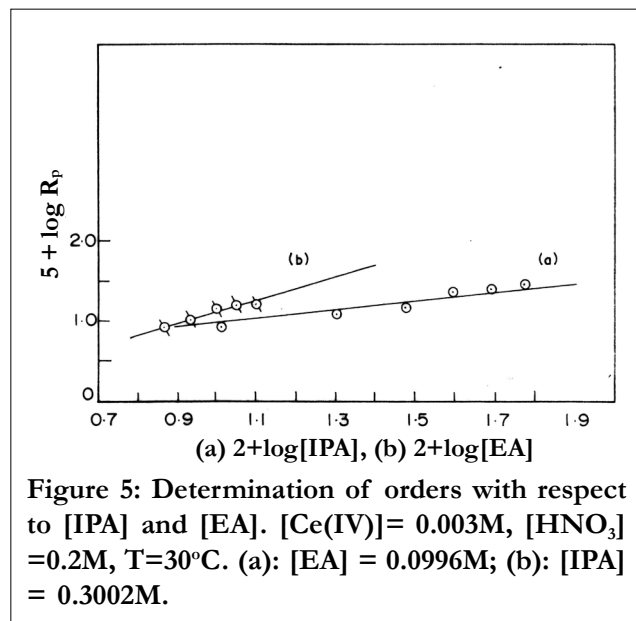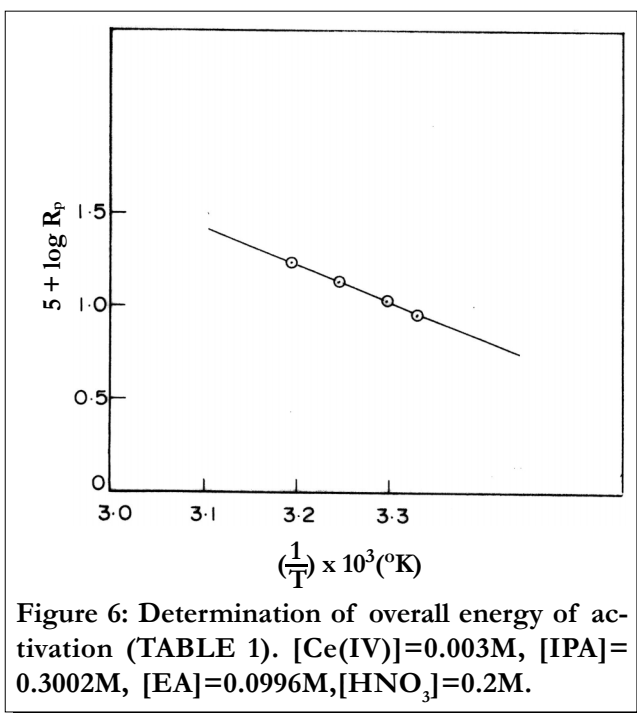
The dependence of R_{Ce} on Ce(IV) is first order under present experimental conditions (Figure 1). The pseudo-first-order rate constant, k^1, for ceric ion consumption is evaluated from the slope of the plot of log[Ce(IV)] versus time. The plot of inverse of pseudo-first-order rate constants, $(k^1)^{-1}$, versus reciprocal of reducing agent concentrations, $[R]^{-1}$, yields straight line with non-zero intercept on the ordinate (Figure 2).

The spectrophotometric studies are done with Varian UV-visible spectrophotometer (Cary 50 Bio) which show shift in the absorption maximum of ceric ion in 0.2M nitric acid from 245nm to 248nm when

Figure 4: Determination of order with respect to [Ce(IV)]. [EA]=0.0996M, [IPA]=0.3002M, [HNO₃]=0.2M, T=30°C.

(a) 2+log[IPA], (b) 2+log[EA]

Figure 5: Determination of orders with respect to [IPA] and [EA]. [Ce(IV)]= 0.003M, [HNO₃] =0.2M, T=30°C. (a): [EA] = 0.0996M; (b): [IPA] = 0.3002M.

the reducing agent IPA is added to it. When monomer is also added along with the reducing agent to the ceric solution in nitric acid medium, the absorption maximum of ceric ion at 245nm shifts to 251nm (Figure 3).

Induction periods are observed with all the polymerization reactions and these are found to vary inversely with the rate of initiation. The order with respect to (w.r.t.) [Ce(IV)] for EA polymerization is evaluated as the slope of the logarithmic graph of

Figure 6: Determination of overall energy of activation (TABLE 1). [Ce(IV)]=0.003M, [IPA]= 0.3002M, [EA]=0.0996M,[HNO₃]=0.2M.

R_p versus [Ce(IV)] (Figure 4). The order w.r.t. [Ce(IV)] under present experimental conditions is found to be 0.51. The order w.r.t. [R] for EA polymerization under present experimental conditions is evaluated from the slope of the logarithmic plot of R_p versus [R] and is found to be 0.52 (Figure 5). The order w.r.t. [EA] under present experimental conditions is found to be 1.43 (Figure 5).

The overall activation energy, $E_{overall}$, for EA polymerization under present experimental conditions is evaluated from the Arrhenius plot of $\log R_p$ versus $1/T$ in the temperature region 27-40°C and is found to be 36.38 KJ/mol (TABLE 1, Figure 6).

The variation of molecular weight ($\overline{M}_w$) with percent conversion is observed and is found to increase up to 65.8 percent conversion and then falls (TABLE 1).

DISCUSSION

Spectrophotometric observations indicate that both the reducing agent and the monomer complex with the ceric species in the nitric acid medium as there is shift in the absorption maximum when the monomer is added to the solution of ceric ion and reducing agent in nitric acid medium (Figure 3). The plot of $(k^1)^{-1}$ versus $[R]^{-1}$ (Figure 2) yields a straight line which is indicating the formation of complex

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between ceric ion and reducing agent, and the complex formation between ceric ion and reducing agent may be maximum compared to the monomer liganding with the ceric ion[7,8].

Since the tetravalent cerium is known to have a coordination number of six, the reaction between cerate and the reducing agent (R) presents the possibility of the formation of coordinate intermediates as indicated[6].

$$Ce(X)_6 + R \rightleftarrows Ce(X)_x(R)_y$$
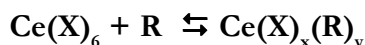
X's, the groups coordinated with tetravalent cerium in nitric acid solution which may be OH^-, NO_3^- and/ or H_2O. x lies between 0 and <6, and y lies between >0 and 6. When monomer is also complexing with cerate along with reducing agent in the reaction medium, the coordinate intermediates can be presented by the equilibrium reaction

$$Ce(X)_6 + R + M \rightleftarrows Ce(X)_x(R)_y(M)_z$$
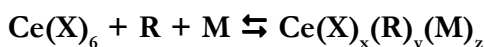
Where x lies between 0 and <6, y lies between >0 and <6, and z may be a small fraction lying between >0 and <1.

The order with respect to [Ce(IV)] for EA polymerization is found to be 0.51 under present experimental conditions (Figure 4) which is nearer to the theoretical value (0.5) for [Ce(IV)] exponent in the rate equation.
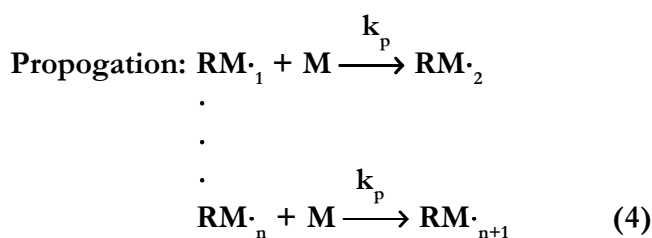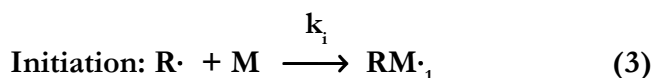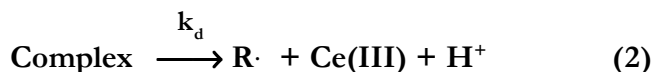
The orders for EA polymerization with respect to [IPA] and [EA] are evaluated from the log- log plots, and are found to be 0.52 and 1.43, respectively (Figure 5). The exponent (0.52) for [IPA] is found nearer to the power (0.5) of [IPA] in the rate equation. The higher value (1.43) for [EA] exponent may be due to the linear termination (monomolecular termination with ceric species) of the growing chains as well as bimolecular termination of the growing chains[12]. The higher order with respect to [EA] gives support to the complex nature of the initiation reactions involving monomer molecules as participating reactants to generate initiating free radicals[7].

The overall activation energy, $E_{overall}$, for EA polymerization is found to be 36.38 KJ/mole (TABLE 1, Figure 6). This is the same order as those found in other aqueous polymerization systems[9-11].

The experimental results indicate that the aqueous polymerization of EA under the experimental conditions used, at the early stages of the reaction, obey homogeneous free-radical polymerization kinetics. The following reaction scheme explains satisfactorily the kinetic results obtained.

Primary radical formation

$$Ce(IV) + R \overset{K}{\rightleftarrows} complex \tag{1}$$

$$Complex \overset{k_d}{\longrightarrow} R\cdot + Ce(III) + H^+ \tag{2}$$

$$Initiation: R\cdot + M \overset{k_i}{\longrightarrow} RM\cdot_1 \tag{3}$$

$$Propogation: RM\cdot_1 + M \overset{k_p}{\longrightarrow} RM\cdot_2$$

$$\vdots$$

$$RM\cdot_n + M \overset{k_p}{\longrightarrow} RM\cdot_{n+1} \tag{4}$$

Bimolecular termination:

$$RM\cdot_n + RM\cdot_m \overset{k_t}{\longrightarrow} Polymer \tag{5}$$

Monomolecular termination with Ce(IV) (linear termination):

$$RM\cdot_n + Ce(IV) \overset{k_t^1}{\longrightarrow} Polymer + Ce(III) + H^+ \tag{6}$$

Oxidative termination of primary radicals:

$$R\cdot + Ce(IV) \overset{k_o}{\longrightarrow} Products + Ce(III) \tag{7}$$

Where $R\cdot$ is a primary radical, and $RM\cdot_n$ is the growing primary radical. By applying the steady-state principle to the active intermediates $R\cdot$ and $RM\cdot_n$, and considering only the mutual type of termination as effective under our experimental conditions, the following equations for R_p and R_{Ce} were derived[9]:

$$R_p = \frac{-d[M]}{dt} = \frac{k_p}{k_t^{1/2}} \left\{ \frac{k_i k_d K[R][Ce(IV)]_{eq}}{k_i[M] + k_o[Ce(IV)]_{eq}} \right\}^{1/2} [M]^{3/2} \tag{8}$$

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = k_d K[R][Ce(IV)]_{eq} \left\{ 1 + \frac{k_o[Ce(IV)]_{eq}}{k_i[M] + k_o[Ce(IV)]_{eq}} \right\} \tag{9}$$

Under the present experimental situation, if the

condition $k_i[M] >> k_o[Ce(IV)]_{eq}$ obeys, then eqns. 8 and 9 reduce to

$$R_p = \frac{-d[M]}{dt} = k_p(\frac{k_d K}{k_t})^{1/2}[R]^{1/2}[Ce(IV)]_{eq}^{1/2}[M] \quad (10)$$

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = k_d K[R][Ce(IV)]_{eq} \quad (11)$$

Since the measured rate $-d[Ce(IV)]/dt$ applies to total $[Ce(IV)]$, and since $[Ce(IV)]_T = [Ce(IV)]_{eq}(1+K[R])$, one obtains

$$R_p = \frac{-d[M]}{dt} = (k_p/k_t^{1/2})(k_d K)^{1/2}\{\frac{[R]^{1/2}[Ce(IV)]_T^{1/2}}{(1+K[R])^{1/2}}\}[M]$$

$$(12)$$

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = (k_d K\{\frac{[R][Ce(IV)]_T}{1+K[R]}\} \quad (13)$$

On the other hand, if under the present experimental conditions the situation is $k_o[Ce(IV)]_{eq} >> k_i[M]$, then eqns. 8 and 9 reduce to

$$R_p = (k_p/k_t^{1/2})(k_i/k_o)^{1/2}(k_d K)^{1/2}[R]^{1/2}[M]^{3/2} \quad (14)$$

$$R_{Ce} = \frac{2k_d K[R][Ce(IV)]_T}{(1+K[R])} \quad (15)$$

The variation in molecular weight with percent conversion is observed in the present study (TABLE 1, Figure 7). This may be due to the fact that the

Figure 7: $\overline{M}w$ Vs. %Conversion. [Ce(IV)]=0.003M, [IPA]=0.3002M, [EA]=0.128M, [HNO₃]=0.2M, T=30°C.
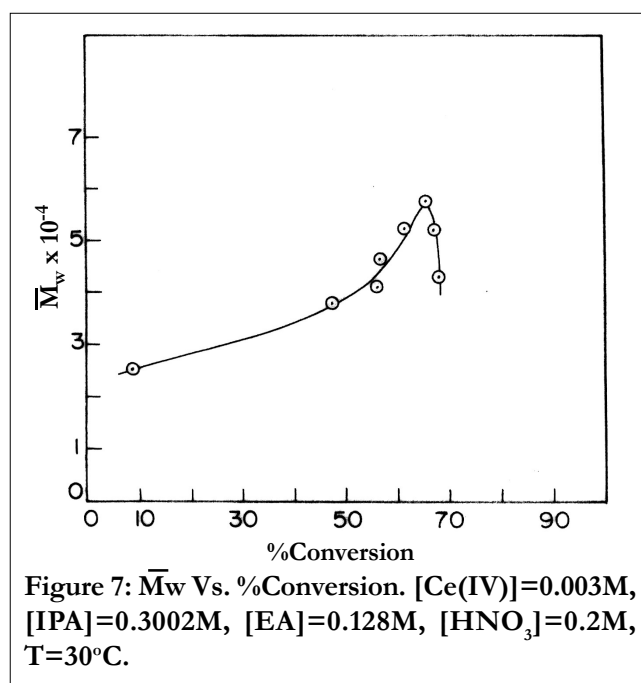
polymerization of EA in aqueous medium initially follows homogeneous polymerization kinetics, then emulsion polymerization kinetics for some period in the intermediate stage when the charge-stabilized small particles are dispersed in the aqueous phase where the monomer is soluble in the polymer and is transferred into these particles, and finally reaches a pseudo-homogeneous-type reaction where EA is situated in the insoluble phase, coarse particles. This type of kinetics can show an effect on the molecular weight of the polymer formed, which varies with conversion[9].

The degree of polymerization can be expressed by the following eqn.16

$$\overline{DP} = \frac{R_p}{\Sigma R_t} = \frac{k_p[M]}{k_t[M_n^\cdot]+k_t^1[Ce(IV)]} \quad (16)$$

Where k_t^1 is the rate constant for linear termination of growing chains with ceric species.

The increase of molecular weight with conversion seems to be related with the loci of polymerization. In the initial stages of homogeneous polymerization in aqueous medium, the termination rate between two oligomeric radicals is higher, which results in lower molecular weight polymer particles. During the intermediate stage when most of the monomer shifts to charge-stabilized discrete particles dispersed in the aqueous phase because of the solubility of the monomer in the polymer, sol phase polymerization occurs in these particles where bimolecular termination is slower due to the unavailability of a second radical within each particle and also due to the gel effect[14] and hence, the molecular size of the polymer particles is larger. At higher conversions in coarse precipitated polymer particles to which most of the monomer is shifted are big enough to permit the coexistence of more than one polymer radical within them and hence, the termination rate can be higher to cause the reduction in molecular size. Depletion of monomer and initiator concentrations together with bimolecular termination all influence the degree of polymerization at higher conversions (eqn.16).

Evaluation of rate constants

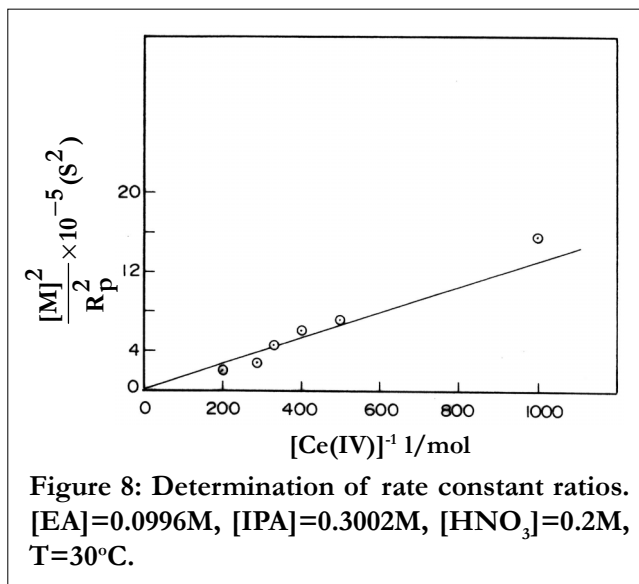In the present study k_d and K are obtained[9] from

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Figure 8: Determination of rate constant ratios. [EA]=0.0996M, [IPA]=0.3002M, [HNO$_3$]=0.2M, T=30ºC.

TABLE 2: Rate constants for the polymerization of EA at 30ºC.

Initiator system	K (lmol^{-1})	(ki/ko)	k$_d$x10^3 (s^{-1})	(k$_p$/k$_t^{1/2}$) (l$^{1/2}$mol$^{-1/2}$s$^{-1/2}$)
Ce(IV) - IPA	6.15	0.229	1.00	1.089

the relationship

$$1/k^1 = 1/(k_d K[R]) + 1/k_d \qquad (17)$$

and the values are reported in TABLE 2 (Figure 2).

When there is a dependence of R$_p$ on [Ce(IV)], the following equation can be used to evaluate the rate constants ratios[10], (k$_i$/k$_o$) and (k$_p$/k$_t^{1/2}$)

$$\frac{[M]^2}{R_p^2} = (\frac{k_t}{k_p^2})\{ \frac{1}{k_d K[R]} + \frac{1}{k_d} \} \frac{1}{[Ce(IV)]_T} +$$

$$(\frac{k_t}{k_p^2})\{ \frac{k_o}{k_i k_d K[R][M]} \} \qquad (18)$$

The values obtained are reported in TABLE 2 (Figure 8) and these are comparable to the literature results[10-13].

CONCLUSIONS

The reduction of ceric ion shows first order with respect to ceric ion concentration. The spectrophotometric observations show that the monomer also complexes with the ceric ion along with the reducing agent. The plot of inverse of pseudo-first-order rate constants with the inverse of reducing agent concentrations yield straight line with positive intercepts on the ordinate, which support the maximum complex formation of reducing agent with ceric ion. Higher order with respect to monomer concentration supports the proposal of linear termination of the growing chains as well as bimolecular termination of the growing chains. The overall activation energy obtained is comparable with the literature results.

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