Potassium K (I) Catalyzed Oxidation of L- Leucine by Cerium (IV) In Sulfuric Acid Medium – A Kinetic Study.

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Abstract: *The kinetics of oxidation of L-Leucine by cerium (IV) in presence of catalytic amount of potassium (K^+) in acid medium has been studied significantly in the temperature range of (300-315) K. The reaction proceeds through the formation of an intermediate complex formation followed by the radical formation mechanism. The reaction followed first order kinetics with respect to L-Leucine, inverse order with respect to Ce(IV), and a positive fractional order with respect to potassium(K^+). The major oxidation products are identified by spot test and FT-IR. The polymerization of acrylonitrile indicates the generation pf free radicals in the reaction system. A suitable mechanism has been proposed for the above reaction.*

Key Words: *acid medium, catalytic, free radicals, intermediate complex, mechanism, order, polymerization, Potassium, temperature*

I. Introduction

The oxidative decarboxylation of essential amino acids is an interesting field in modern bio-chemistry to study the metabolism in living organism. As an essential amino acid , L-Leucine can not be synthesized by animals, thus it must be ingested usually as a component of proteins. Actually L-Leucine is classified as a hydrophobic amino acid due to its aliphatic isobutyl side chain. Plants and microorganisms synthesized L-Leucine from pyruvic acid by a series of enzymes [1]. Leucine is utilized in the liver, adipose tissue and muscle tissue. Among the essential amino acids leucine is the only dietary amino acid that has the capacity to simulate muscle protein synthesis [2]. Being as an essential amino acid, leucine is an active site residues of enzymes and help in maintaining the correct conformation of enzymes by keeping them in their proper ionic states. The oxidation of amino acids is more interesting because of the products differ depending on the oxidants [3,4].

Metal ions play an important role in the oxidative decarbonylation of amino acids. However our preliminary literature review and observations suggests that the oxidation of some organic compounds by Ce(IV) in sulfuric acid medium can be efficiently catalyzed by various metal ions even at trace concentration. Among the different metal ions, potassium(I) has been used as catalyst for the oxidation of L-Leucine. Kinetics of oxidation of amino acids by a variety of oxidants such as Mn(III), Co(III), Os(VIII), $Fe(CN)_6^{-3}$, Chloramine – T, 1-Chlorobenzotriazole, N - bromo succinimide , Peronomono sulfate(P.M.S) [5,6,7,8,9,10,11] in acid and alkaline media in presence of catalytic amount of different metal ion such as Cr(IV), Ir(III), Ag(I), Rh(VI), Mn(VI) has been reported elsewhere [12,13,14,15,16].

Ce (IV) is a well known oxidant [17] in acid media having the reduction potential [18] of Ce(IV)/Ce(III) = 1.70V . In General the oxidation of organic compounds by Cerium(IV) seems to proceed via the formation of intermediate complex [19,20]. The oxidation reaction of L-Leucine by Ce(IV) is catalyzed by a small amount of (10^{-8} mol dm^{-3}) of K^+ to accelerate the overall reaction in aqueous sulfuric acid medium. In sulfuric acid and sulfate media, several sulfate complexes of Ce(IV) have been reported [21,22,23,24] such as $Ce(SO_4)^{+2}$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$ and $HCe(SO_4)_3^-$, but the role of these compounds have not received much consideration so far. Thus the cause of decrease in rate of reaction with increase in sulfuric acid concentration has not been understood. The reaction proceeds through the quite complicated mechanism due to the formation of different Ce (IV) active complexes. Thus oxidation of L-leucine may help in understanding enzyme kinetics and a variety of mechanisms are possible. Herein, we describe the results of the title reaction in order to determine the active species of oxidant, reductant catalyst in such media and to arrive at plausible mechanism.

II. Experimental

Stock solution of L- leucine (sigma Aldrich) was prepared by dissolving the requisite amount of L-leucine in doubly distilled water. The Ce(IV) stock solution was prepared by dissolving Cerium(IV)ammonium sulfate (sigma Aldrich) in 1 mol dm^{-3} sulfuric acid and standardized with iron(II)ammonium sulfate solution [25]. The other chemicals and reagents such as potassium nitrate, sodium sulfate, sulfuric acid, acetonitrile etc used are of analytical grade with 99.9% purity.

III. Kinetic Measurements

Kinetic studies were carried out in the temperature range of (300 – 315)K under pseudo-first order condition with a large excess of L-leucine over Ce(IV). The reaction was followed by estimating the unreacted Ce(IV) as a function of time. The titration was done against ferrous ammonium sulfate solution and ferroin as indicator [26]. There were no precautions to exclude the diffused light entering into the reaction mixture [27]. The Ce(IV) solution was thermally quite stable [28] in the visible region and undergoes a photochemical decomposition [29] only in the UV – region. Since the oxidation of [30] water even at 333K by Ce(IV) was immeasurably slow and insignificant, no further precautions were taken to account for this. The plots of log[Ce(IV)] v/s time were plotted against the decrease of reaction rate from the titre values and from the slope, the pseudo first order rate constants K_{obs} were obtained. K_{obs} values have been calculated by taking 6 – 8 values at least upto 8o% completion of the reaction. The observed rate constants were reproducible within the experimental error $\pm$ 5% .

Results: Factors influencing the rate of oxidation of L-leucine by Ce(IV) are -

[L-leucine]   (ii) [Ce(IV)]   (iii) [H$^+$]   (iv) ionic strength
(v) Effect of [HSO$_4^-$]   (vi) Di- electric constant   (vii) Potassium K(I)

3.1   Effect of [L- leucine] :

The Kinetic runs were carried out at various concentrations of L- Leucine (1×10^{-3} – 10×10^{-3} mol dm^{-3})at [Ce(IV)] (5×10^{-4} mol dm^{-3}) [H$^+$] (0.05mol dm^{-3}), [Na$_2$SO$_4$] (0.1 mol dm^{-3}) and [K(I)] (2×10^{-8} mol dm^{-3}) which yielded rate constants whose values depend on   [L- Leucine]. The pseudo – first order rate constants values were found to be increased with L- Leucine (shown in Table 1). This shows that the reaction obeys the first order kinetics with respect to [L- Leucine]. This was confirmed by the linear plot of K_{obs} v/s [L – Leucine] (Fig.1). The plot of $1/k_{obs}$ v/s 1/[L- Leucine] exhibits excellent linearity (Fig.3) with a positive slope . The values of K_2 (mol d m^{-3}s^{-1}) obtained from such plots (Table 2) were in agreement with the corresponding values calculated from the factor K_{obs} (S^{-1}) / [L- Leucine].

3.2 Effect of [Ce(IV)] :

The rate of the reaction was measured with various [Ce(IV)] (1×10^{-4} – 10×10^{-4}) at [L- Leucine] (5×10^{-3}) ,[H$^+$] (0.05 mol dm^{-3}) , Na$_2$SO$_4$(0.1 mol dm^{-3}) and [K (I)] (2×10^{-8} mol dm^{-3}). The rate of the reaction decreased with the increase in [Ce(IV)] indicating that the order with respect to [Ce(IV)] and the possible reason behind this was the formation of some less reactive polymeric Ce(IV) at higher [Ce(IV)] [30-35]. It is supported by a linear plot of K_{obs} v/s [Ce(IV)].

3.3 Effect of [H$^+$] :

The rate of the reaction were measured with various [H$^+$] (3.5×10^{-2} – 7.5×10^{-2} mol dm^{-3}) at [L- Leucine] (5.0×10^{-3} mol dm^{-3}) [Ce(IV)] (5.0×10^{-4} mol dm^{-3}) , [Na$_2$SO$_4$] (0.1mol dm^{-3}) and K(I) (2×10^{-8} mol dm^{-3}). The rate of the reaction decreased with increase in hydrogen in concentration (Table 3). The order of the reaction respect to [H$^+$]   was found to be negative obtained from the plot of   logK_{obs} v/s log [H$^+$] (Fig.5).

3.4 Effect of [ionic strength]:

The effect of ionic strength was studied by the addition of sodium sulfate on the reaction rate. The rate of the reaction decreased with increase in [µ] (Table 4). The effect of sulfate ion can be explained on the basis of removal of reactive species as Ce(SO$_4$)$_3^{-2}$ [31].

$$Ce(SO_4)_2 + SO_4^{-2} \rightarrow Ce(SO_4)_3^{-2}$$
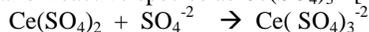
3.5 Effect of [HSO4$^-$]:

The rate of the reaction were measured with various [HSO$_4^-$] (5×10^{-3} – 5×10^{-2} mol dm^{-3}) at L- Leucine(5×10^{-3} mol dm^{-3}), [Ce(IV)] (5×10^{-4} mol dm^{-3}), [H$^+$](.05 mol dm^{-3}), Na$_2$SO$_4$ (0.1 mol dm^{-3}) and [K(I)] (2×10^{-8} mol dm^{-3}).

The reaction rate decreased with incease in [HSO$_4^-$] indicating that the order of the reaction with respect to [HSO$_4^-$] was negative. This can be confirmed by the linear plot of 1/ K_{obs} v/s [HSO$_4^-$]. The plot of $1/K_{obs}$ v/s [HSO$_4^-$] was found to be linear with positive intercept and positive slope.
The hydrogen sulfate dependence can be represented as

$K_{obs} = $ a/ b+c[HSO$_4^-$]   -------(i)

3.6 Effect of Di-electric constant :

To study the effect of dielectric constant of the medium on the rate of reaction , the oxidation of L-Leucine by Ce(IV) was studied in acronitrile as well as acetone mixtures of various concentrations and compositions (Table-5). The data obtained from the study clearly evident that the rate of the reaction decreased

with increase in acetonitrile and acetone content of solvent i.e the dielectric constant of the solvent mixture decrease. The fact behind this is due to the development of charge in the transition state involving a more polar activated complex than the reactants [32]. Actually here the reaction proceed through the involvement of a neutral molecules and an ion irrespective of involvement of ion-ion or dipole- dipole type mechanism.

3.7 [K (I)] Dependence:
The reaction rates measured with various [K(I)] (2×10^{-8} – 9×10^{-8} mol dm^{-3}) at [L-Leucine] (5.0×10^{-3} mol dm^{-3}), [Ce(IV)](5.0×10^{-4} mol dm^{-3}), [Na$_2$SO$_4$] (0.1 mol dm^{-3}) and [H$^+$] (5.0 $\times 10^{-2}$ mol dm^{-3}). The rate of the reaction increased with increase in [K$^+$]. (Table-6). A plot of K$_{obs}$ v/s [Ag(I)] yields a straight line [33]. The plot of K$_{obs}$ v/s [K$^+$] showed a good linear plots (Fig.6) and it is passing nearly through origin.

3.8 Test for free radical intermediate :
A known quantity of acrylonitrile scavenger polymer had been added to the reaction mixture and the mixture was kept for 2h in an inert atmosphere. Then the reaction mixture was diluting by adding methanol, while precipitate has been formed, indicating the generation of free radicals in the reaction.

3.9 Rate and Activation parameters :
The effect of temperature on K$_{obs}$ (S^{-1}) was studied in the temperature range of (300-315)K and the detailed results are shown in Table-7. The value of energy of activation was calculated from Arrhenius plot (Fig.7). The value of entropy of activation (S*), enthalpy of activation (H*) and free energy change of activation (G*) was calculated from Eyrings plot (Fig.8). The large negative value of entropy of activation (S*) obtained is attributed to the severe restriction of solvent molecules (electrostriction) around the transition state [34] and from this it may be concluded that the complex is more ordered than the [35]

4.0 Stoichiometry and Product analysis :
The reaction mixture containing an excess of [Ce(IV)] over [L-Leucine] at constant ionic strength, acidity and at constant concentration of catalyst were kept for 24h at 303K in an inert atmosphere. The unreacted Ce(IV) was titrated against standard ferrous ammonium sulfate by using ferroin as an indicator.
and ammonia [36] by Nessler's reagent. CO$_2$ was qualitatively detected by bubbling N$_2$ gas through the acidified reaction mixture and passing the liberated gas through a tube ,containing limewater [37]. The product aldehyde was estimated qualitatively and is evidenced by its 2,4-D.N.P derivative [38]. The nature of the aldehyde was confirmed by its I.R spectrum [39] carbonyl stretching at 1729 cm^{-1} and a band at 2928 cm^{-1} [40] due to the aldehydic –CH stretching. It was also studied that the aldehyde does not undergo further oxidation under the present optimum kinetic conditions. The stoichiometry of the reaction under kinetic study is

$$\underset{\underset{NH_2}{|}}{R-CH-COOH} + 2Ce(SO_4)_2 + H_2O \xrightarrow{K^+} R-CHO + NH_3 + CO_2 + 2Ce(III) + 2SO_4^{-2} + 2H^+$$

Where R => -CH-CHMe$_2$
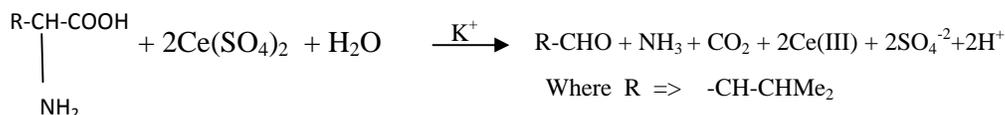
5.0 Meachanism of the reaction : :- scheme -1
Amino acids are reported to form an adduct with the metal ion due to the avalibility of electron pair on oxygen atoms [41]. Similarly due small size and strong ionization activity potassium form an adduct initially with isoleucine. Due to the presence of excess Ce(IV) species in the reaction medium an another bridged adduct is formed. The linear plot of 1/K$_{obs}$ v/s 1/[L –leucine] with non- zero intercepts confirms the formation complex between K(I) and L –leucine in the first step (Fig.2). This shows Michaelis – Menton type of reaction mechanism. The formation of such type of complex was also proved kinetically by the plot of [Ce(IV)][K$^+$]/rate v/s 1/[L-leucine] (Fig7). Such type of complex formation has been reported elsewhere [42,43]The experimental results suggest that [L –isoleucine] forms adduct with catalyst K(I). In the next step the adduct combines with excess amount of Ce(SO$_4$)$_2$ in a slow step to form an Cerium activated complex, which undergoes dissociation in the next step to regenerate the K(I) catalyst and a free radical intermediate. Again on the next step the radical reacts with Ce(SO$_4$)$_2$ to give final products as shown in the scheme1.

Scheme 1 :
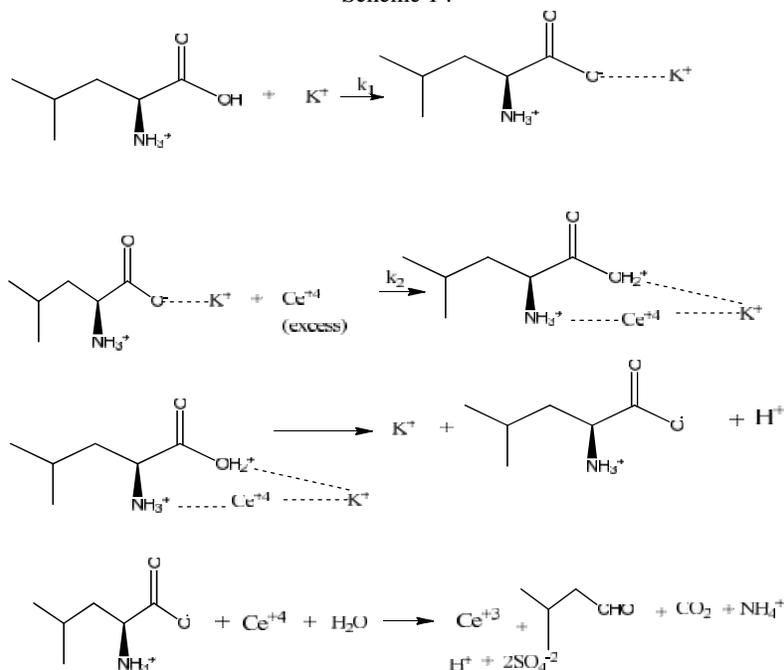
IV. Results And Discussion

The rate expression may be represented by the following equation :-

$$k_{obs} = \frac{k_2 f k_1 [\text{L-Leucine}][K^+]}{k_1 [\text{Ce (IV)}][H^+][\text{L-Leucine}] + 1} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(ii)$$

The above rate equation can be written as follows :-

$$\frac{1}{k_{obs}} \quad \frac{[\text{Ce (IV)}][H^+]}{k_2 f [K^+]} \quad + \quad 1/k_2 f k_1 [K^+][\text{L-Leucine}] \quad \dots\dots\dots\dots(iii)$$

$$\frac{1}{k_{obs}} \quad - \quad \frac{[\text{Ce (IV)}][H^+]}{k_2 f [K^+]} \quad + \quad \frac{1}{k_2 f k_1 [K^+]} \quad \frac{1}{[\text{L-Leucine}]} \quad \dots\dots\dots\dots (iv)$$

$$\frac{1}{k_{obs}} \quad = \quad \frac{[\text{Ce (IV)}][H^+]}{k_2 f [K^+]} \quad + \quad \frac{1}{k_2 k_1 [\text{L-Leucine}]} \quad \frac{1}{[K^+]} \quad \dots\dots\dots\dots (v)$$

Equation (ii) suggested that $n_{ap} = 1.0$, $0 < n_{ap}$ [L- Leucine] which is consistent with the results of our experiments. Equation (iv) suggests that at constant [H^+] and [K^+] the plot of $1/K_{obs}$ v/s $1/$[L-Leucine] should be linear with positive intercept as shown in (Fig.2). Equation (v) which suggests that at constant [H^+] and [L- Leucine] the plot of $1/K_{obs}$ v/s $1/[K^+]$ should yield good linear plots through origin as shown (Fig.5).

4.1 Kinetically active Cerium species:

Under the experimental condition in aqueous Sulfuric acid medium, the important Ce(IV)-Sulfato complexes are $Ce(SO_4)^{+2}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$ and the relevent equilibria are [44,45]

$$Ce^{+4} + HSO_4^- \quad \rightleftharpoons \quad Ce(SO_4)^{+2} + H^+ \qquad _1 = 3500 \quad \dots\dots\dots(vi)$$

$$Ce(SO_4)^{+2} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+ \qquad \beta_2 = 200 \quad ....(vii)$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \qquad \beta_3 = 3.4 \quad ....(viii)$$
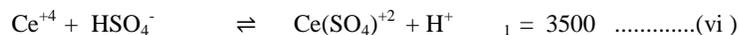
Among the different sulfato species, the kinetically active species should be inferred on the basis of kinetic data , not according to the magnitude of concentration [46]. From the relationship between hydrogen sulfate and K_{obs} , $Ce(SO_4)_2$ has been found as the kinetically active species in the present study. According to the mass balance equation (ix) is obtained -

$$[Ce(IV)]_T = [Ce^{+4}] + [Ce(SO_4)^{+2}] + [Ce(SO_4)_2] + [HCe(SO_4)_3^-] \qquad --------(ix)$$

From equation (vi) – (viii) the following equation can be derived

$$[Ce^{+4}] = \frac{[Ce(SO_4)_2][H^+]^2}{\beta_1\beta_2[HSO_4]^2} \qquad ----------(x)$$

$$[Ce(SO_4)^{+2}] = \frac{[Ce(SO_4)_2][H^+]}{\beta_2[HSO_4^-]} \qquad ------------(xi)$$

$$[Ce(SO_4)_2] = \frac{[HCe(SO_4)_3^-]}{\beta_3[HSO_4^-]} \qquad ---------(xii)$$

$$[HCe(SO_4)_3^-] = \beta_3[HSO_4^-][Ce(SO_4)_2] \qquad ---------(xiii)$$

Substituting the above equation into equation (ix), we get

$$[Ce(IV)_T] = \frac{[Ce(SO_4)_2][H^+]^2}{\beta_1\beta_2[HSO_4^-]^2} + \frac{[Ce(SO_4)_2][H^+]}{\beta_2[HSO_4]} + [Ce(SO_4)_2] + \beta_3[HSO_4^-][Ce(SO_4)_2]$$

$$...................... (xiv)$$

By considering the relative magnitudes of the successive equilibrium constants which are in the order $\beta_1 >> \beta_2 >> \beta_3$ the value of $\frac{[Ce(SO_4)_2][H^+]^2}{\beta_1\beta_2[HSO_4^-]^2}$ and $\frac{[Ce(SO_4)_2][H^+]}{\beta_2[HSO_4^-]}$

are much less than the other two terms.
Therefore, we get equation (xv) from equation (xiv).

$$[Ce(IV)]_T = [Ce(SO_4)_2] + \beta_3[HSO_4^-][Ce(SO_4)_2]$$
$$= [Ce(SO_4)_2](1 + \beta_3[HSO_4^-]) \qquad ---------(xv)$$

So $[Ce(SO_4)^{+2}] = \dfrac{[Ce(IV)]_T}{(1 + \beta_3[HSO_4^-])} = f[Ce(IV)_T] \qquad ------(xvi)$

Where $f = \dfrac{1}{(1 + \beta_3[HSO_4^-])}$ ....(xvii)

where f – denotes the fraction of kinetically active species to the total Cerium(IV).
Substituting the equation (xvii) into equation (ii) we get

$$k_{obs} = \frac{k_2 k_1 [\text{L-Leucine}][K^+]}{k_1[Ce(IV)][H^+][\text{L-Leucine}] + 1 (1 + _3 [HSO_4^-])} \quad \ldots\ldots\ldots.(xviii)$$

Assuming that $\quad m = \dfrac{k_2 k_1 [\text{L-Leucine}][K^+]}{k_1[Ce(IV)][H^+][\text{L-Leucine}] + 1} \quad \ldots\ldots. (xix)$

So equation (xviii) may be written as

$$k_{obs} = \frac{m}{(1 + _3 [HSO_4^-])} \quad \ldots\ldots\ldots..(xx)$$

or,

$$1/k_{obs} = \frac{1}{m} + \frac{_3}{m} \quad [HSO4^-] \quad ....(xxi)$$

The equation (xxi) is same as equation (i) which can be able to explain the negative order dependence on $[HSO_4^-]$. Equation (xxi) suggests that $1/K_{obs}$ v/s $[HSO_4^-]$ should be linear and matches with the experimental data. According to the principle of salt effect , there must be a neutral molecule in rate determining step, which confirms $Ce(SO_4)_2$ as the kinetically active species. The rate constants decreased with increase in $[H^+]$ (Table-3) due to the formation of an active inhibitor $H_2Ce(SO_4)_2^{-2}$ [47,48,49]. The order of the reaction with respect to $[H^+]$ was negative. Increased in the sulfuric acid concentration in the reaction mixture leads to increase in $[H^+]$, but there is also a corresponding increase in $[HSO_4^-]$. If the rate is inversely dependent on the $[HSO_4^-]$ to a great extent the overall effect of adding sulfuric acid would be lower the rate (table3). Similar behavior has been reported in the oxidation of antimony(II)) [50,51], mandelic acid [52, 53,54], malic acid [56], fructose [57], by Cerium(IV). Addition of Cerium(III) retarded the reaction appreciably due to the formation of Ce^{+4}, Ce^{+3} ion pairs. In the oxidation of tellurium(IV) by Ce(IV), the product Ce(III) also retarded the reaction [58]. In the oxidation of glutamic acid [59], lactic acid [60,61], and mandelic acid [62,] by Cerium(IV) in sulfuric acid – sulfate media reported. In addition to that ionic strength has little effect on K_{obs} .

V.   Conclusion
The reaction between Cerium(IV) and L-Leucine is sluggish in sulfuric acid medium at 300K. The reaction proceeds through a measurable velocity in presence of small amount of (10^{-8} mol dm^{-3}) of silver. The main active species of Ce(IV) is considered to be $Ce(SO_4)_2$ although others species might be active to a much lesser extent. The role of hydrogen ion is crucial to reaction. the description of the mechanism is consistent with all the experimental evidence.

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Figures & Tables Captions :
Fig.1 The linear plot of k_{obs} (S^{-1}) v/s [L-Leucine] at different temperature.
Fig.2 The linear plot of $5+log[Ce(IV)]$ v/s Time.
Fig.3 The linear plot of $1/k_{obs}$ v/s $1/[L-Leucine]$.
Fig.4 The plot of $logk_{obs}$ v/s $log[Ce(IV)]$.
Fig.5 The linear plot of $logk_{obs}$ v/s $log[H^+]$.
Fig.6 The linear plot of k_{obs} v/s catalyst(K^+).
Fig.7 The linear plot of $logk_2$ v/s $1/T$ [To calculate energy of activation (Ea)].
Fig.8 The Eyring's plot $[5+logk_2/T$ v/s $1/T$ x$10^{-3}]$
Table 1 Effect of concentration of L-Leucine and Ce(IV) on the pseudo first order rate constant (k_{obs}) and second order rate constant (k_2).
Table 2 The comparison between graphically and experimentally calculated value of k_2.
Table 3 Effect of concentration of $[H^+]$ on the pseudo first order rate constant (k_{obs}).
Table 4 Effect of ionic strength (μ) on the pseudo first order rate constant (k_{obs}).
Table 5 Effect of di-electric constant on the pseudo first order rate constant (k_{obs})
Table 6 Effect of variation of temperature on pseudo first order rate constant (k_{obs}) and second order rate constant (k_2).
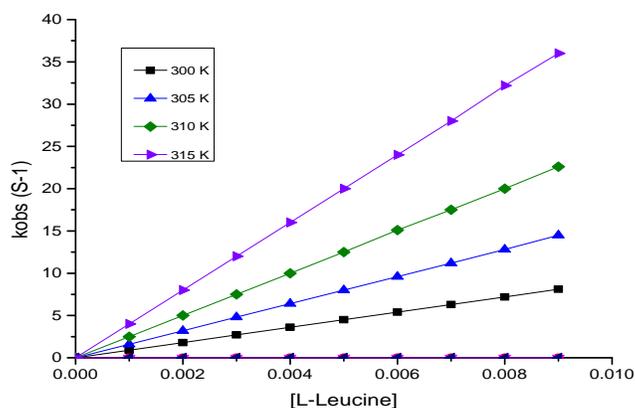
Fig. 1
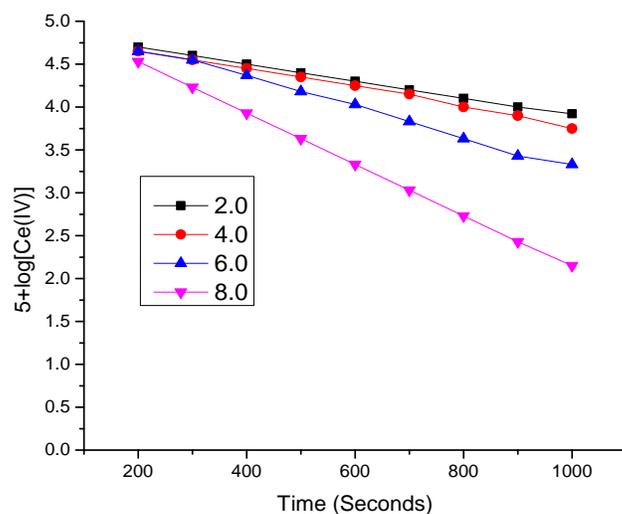
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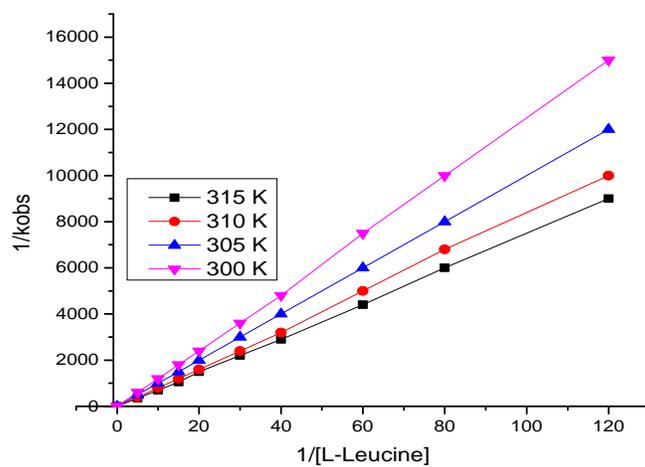
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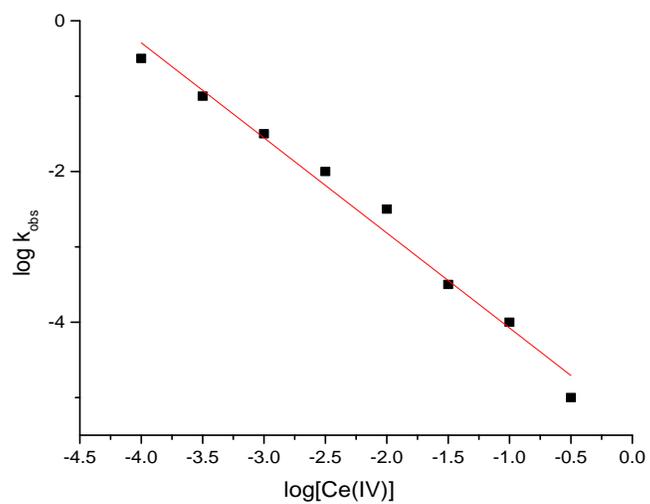
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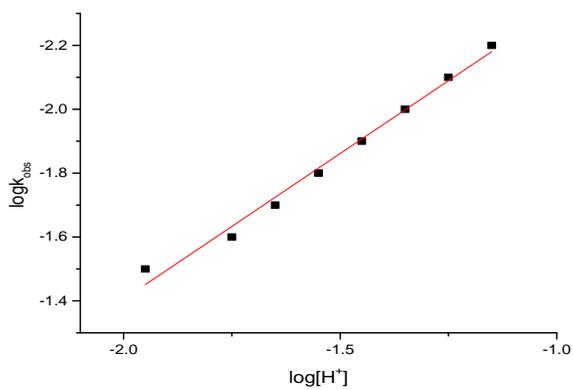
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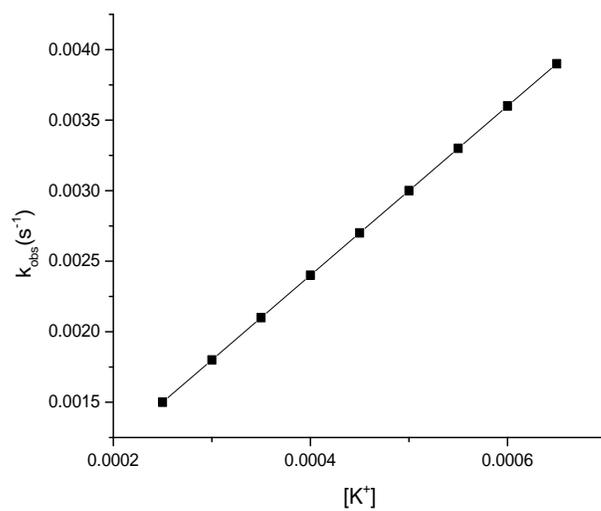
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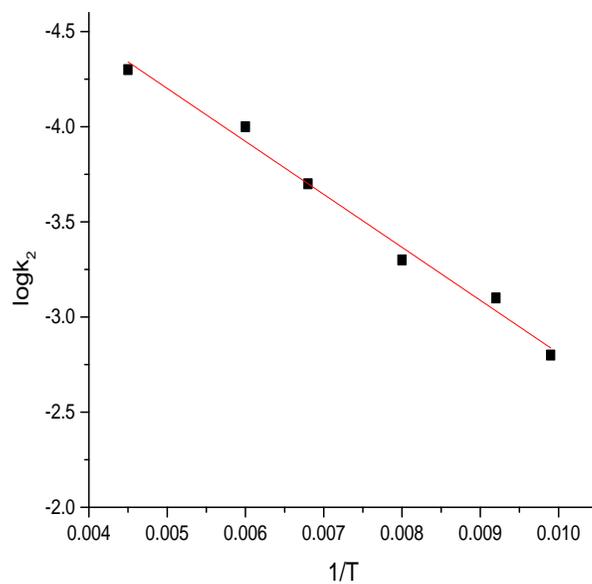
Fig. 7
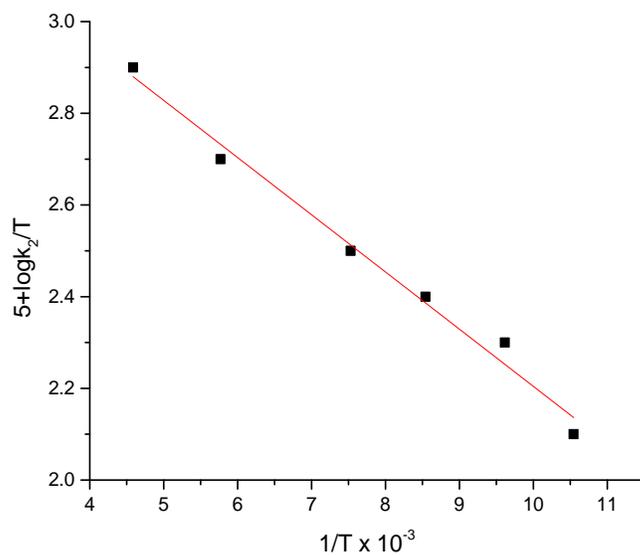
Fig. 8

Table - 1

[L-Leucine]x10³ (mol dm⁻³)	[Ce(IV)] x 10⁴ (mol dm⁻³)	K_{obs} x10³ (S⁻¹)				k_2 x 10² (mol dm⁻³ s⁻¹)			
		300 K	305 K	310 K	315 K	300 K	305 K	310K	315 K
1.0	5.0	0.9	1.6	2.55	4.0	11.0	17.5	27.0	40.0
2.0	5.0	1.82	3.10	5.15	8.25	11.25	17.8	27.5	38.1
3.0	5.0	2.75	4.9	7.5	11.5	11.79	17.2	25.9	37.7
4.0	5.0	3.65	5.85	9.76	15.37	10.87	16.9	26.6	39.2
5.0	5.0	4.58	8.15	13.18	1.1	11.28	16.6	27.5	36.83
6.0	*5.0*	5.5	9.8	15.8	22.47	11.63	17.9	26.3	37.5
7.0	5.0	6.4	11.5	17.85	26.58	10.5	18.5	25.7	39.63
8.0	5.0	7.5	12.38	19.29	29.20	10.78	17.75	24.5	38.6
9.0	5.0	8.5	13.7	21.0	32.28	11.1	17.5	25.5	37.8
10.0	5.0	9.9	1.48	23.1	36.98	10.85	17.85	26.2	39.12
5.0	1.0		1310						
5.0	2.0		250.8						
5.0	3.0		175.8						
5.0	4.0		87.5						
5.0	5.0	5.29	40.3	16.0	23.1	11.3	17.9	27.5	39.5
5.0	6.0		18.75						
5.0	7.0		9.8						
5.0	8.0		3.5						

Table -2

Temperature(K)	K_2 x 10³ mol dm⁻³s⁻¹	
	Graphical	calculated
300K	10.9	10.87
305K	17.86	17021
310K	25.57	26.6
315K	37.83	39.1

Table-3

[L-Leucine] x 10³ mol dm⁻³	[Ce(IV)] x 10⁴ mol dm⁻³	[H⁺] mol dm⁻³	[K⁺] x 10⁸ mol dm⁻³	μ[Na₂SO₄] mol dm⁻³	K_{obs} x 10⁴ Sec⁻¹ 300K
5.0	*5.0*	.020	2.0	0.1	32.3
5.0	5.0	.025	2.0	0.1	20.01
5.0	5.0	.030	2.0	0.1	15.83
5.0	5.0	.035	2.0	0.1	13.5
5.0	5.0	.040	2.0	0.1	11.79
5.0	5.0	.045	2.0	0.1	9.21

Table - 4

[L-Leucine] x 10^3 mol dm^{-3}	[Ce(IV)] x 10^4 mol dm^{-3}	[HSO$_4^-$] mol dm^{-3}	[Na$_2$SO$_4$] mol dm^{-3}	K$_{obs}$ x 10^4 sec^{-1} 300K
5.0	5.0	----	.05	7.75
5.0	5.0	-----	.10	6.33
5.0	5.0	-----	.20	5.45
5.0	5.0	-----	.30	4.61
5.0	5.0	------	.40	3.60
5.0	5.0	.05	------	10.45
5.0	5.0	.10	-------	8.75
5.0	5.0	.20	------	7.39
5.0	5.0	.30	-------	6.51
5.0	5.0	.40	------	5.23

Table -5

[H$^+$] mol dm^{-3}	[K$^+$] x10^8 mol dm^{-3}	[μ] [Na$_2$SO$_4$] mol dm^{-3}	Acetonitrile (% v/v)	Acetone (% v/v)	K$_{obs}$ x 10^4 Sec^{-1}
.05	2.0	0.1	30	---	3.31
.05	2.0	0.1	40	---	2.68
.05	2.0	0.1	50	---	1.92
.05	2.0	0.1	60	---	1.32
.05	2.0	0.1	----	30	4.7
.05	2.0	0.1	---	40	3.8
.05	2.0	0.1	---	50	2.53
.05	2.0	0.1	---	60	1.75

Table -6

[L-Leucine] x10^3 mol dm^{-3}	[Ce(IV)] X 10mol dm^{-3}	K$_{obs}$ x 10^4 (S^{-1})				K$_2$ x 10^2 mol dm^{-3} s^{-1}			
		300K	305K	310K	315K	300K	305K	310k	315K
1.0	5.0	0.9	1.6	2.55	4.0	11.0	17.5	27.0	40.0
2.0	5.0	1.82	3.10	5.15	8.25	11.25	17.8	27.5	38.1
3.0	5.0	2.75	4.9	7.5	11.5	11.79	17.2	25.9	37.7
4.0	5.0	3.65	5.85	9.76	15.37	10.87	16.9	26.6	39.2
5.0	5.0	4.58	8.15	13.18	18.1	11.28	16.6	27.5	36.83
6.0	5.0	5.5	9.8	15.8	22.47	11.63	17.9	26.3	37.5
7.0	5.0	6.4	11.5	17.85	26.58	10.5	18.5	25.7	39.63
8.0	5.0	7.5	12.38	19.29	29.20	10.78	17.75	24.5	38.6
9.0	5.0	8.5	13.7	21.0	32.28	11.1	17.5	25.5	37.8
10.0	5.0	9.9	14.8	23.1	36.98	10.85	17.85	26.2	39.12