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**RESEARCH ARTICLE**

# KINETIC AND MECHANISTIC STUDIES OF MICELLER CATALYSED OXIDATION OF ISO-BUTYRIC ACID IN PERCHLORIC ACID MEDIUM BY PERMANGANATE.

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## *Abstract*

A kinetic study of oxidation of iso-butyric acid has been investigated in presence of sodium lauryl sulphate an anionic micelle and the miceller catalysed oxidation of iso butyric acid by permanganate in perchloric acid medium. The reaction is a double stage process, in which first stage is followed by second fast stage process. A first order kinetics is observed with respect to substrate and oxidant. The data will examine in the light of Zucker-Hammett, Bunnett and Bunnett-Olsen criteria of reaction mechanism. Kinetic parameters and activation have been determined. Temperature coefficient were determined by varying temperature. The stiochiometry was observed in terms of mole ration of permanganate ion and perchloric ion . salt and surface area effects have been also analysed.

## Introduction:-

Chemical kinetics is a branch of physical chemistry which deals with the rate of reaction. The study of chemical kinetics includes

- The rate of a reaction and rat laws.
- Factor affecting the rate of reaction
- The reaction's mechanism
- Kinetic and thermodynamics parameter etc.

In this work kinetic studies have been used as a tool to know the mechanism of reaction [1]. Chemical kinetic is a very extensive and important part of chemistry as a whole[2]. It's also called chemical dynamics[3]. Chemical's rates of reaction and variation with conditions have been studied for many years [4.] The correlations of reaction rate with the energies associated with the reaction molecule have been given first time by Arrhenius [5.] Inversion of cane sugar in aqueous solution in the presence of hydrogen ion studied by Wilhelmy[6], and he was the first scientist who investigated quantitative measurement of the velocity of chemical reaction. There are different types of chemical reactions and also experimental techanics used in investigation of chemical kinetics. A lot of work has been taken to study the kinetics and mechanism of the reaction in gas phase and solid phase and most of kinetics work has been done on the liquid phase especially[7-11]. The present work has been done the kinetic and mechanistic studies of miceller catalysed oxidation of iso-butyric acid in perchloric acid medium by permanganate.

The great interest of chemist in the science of chemical kinetics provides the most general method of determining the mechanism of reaction[6,12]. In recent years molecular organized assemblers viz micelles, micro-emulsions, vesicles etc. have emerged as attractive reaction media for investigation the reactivity, selectivity and catalysis of number of natural and chemical reactions[1-13].

## Experimental method:-

The kinetics of the anionic miceller catalysed oxidation of mono carboxylic aliphatic acid viz, isobutyric acid was proposed to perform under pseudo first order conditions. For finding out order of reactions Ostwald's isolation method was selected to determine the order of reactants[14].Required amount of substrate , surfactant , permanganate, acid solution and water were taken in a glass bottles which were black painted from outside to protect reaction mixture from light and were thermostated (of $^{+}_{-}0.1^{o}$C accuracy) at constant required temperature. Measured amount of potassium permanganate solution, thermostated at the same temperature, was added to the mixture solutions. Progress of the reaction was studied by measuring absorbance of unreacted permanganate spectrophotometrically at 520nm on Systronic 104 spectrophotometer with various time intervals at the maximum wavelength.

The standard solution of iso-butyric acid and sodium lauryl sulphate have been prepared in doubly distilled water. $HClO_4$ (Analar) have been used as a source of hydrogen ion. Permanganate solution has been prepared as given by Vogel[15]. Standard salt solutions have been made by dissolving known amount of the solute in a given volume of distilled water. The pseudo first order rate constants reported are the average values from two to three similar runs. The reproducibility were found to be always with $^{+}_{-}$5%.

**Result and discussion:-** The present work described the detailed kinetic and mechanism studies of miceller catalysed oxidation of iso butyric acid by permanganate in perchloric acid medium .

**Nature of the reaction:-** It has been observed that uncatalysed and miceller catalysed oxidation of iso butyric acid by potassium permanganate in perchloric acid medium is double stage process (figure 1) each of the stage being linear. First stage process is faster in comparison of second stage process.

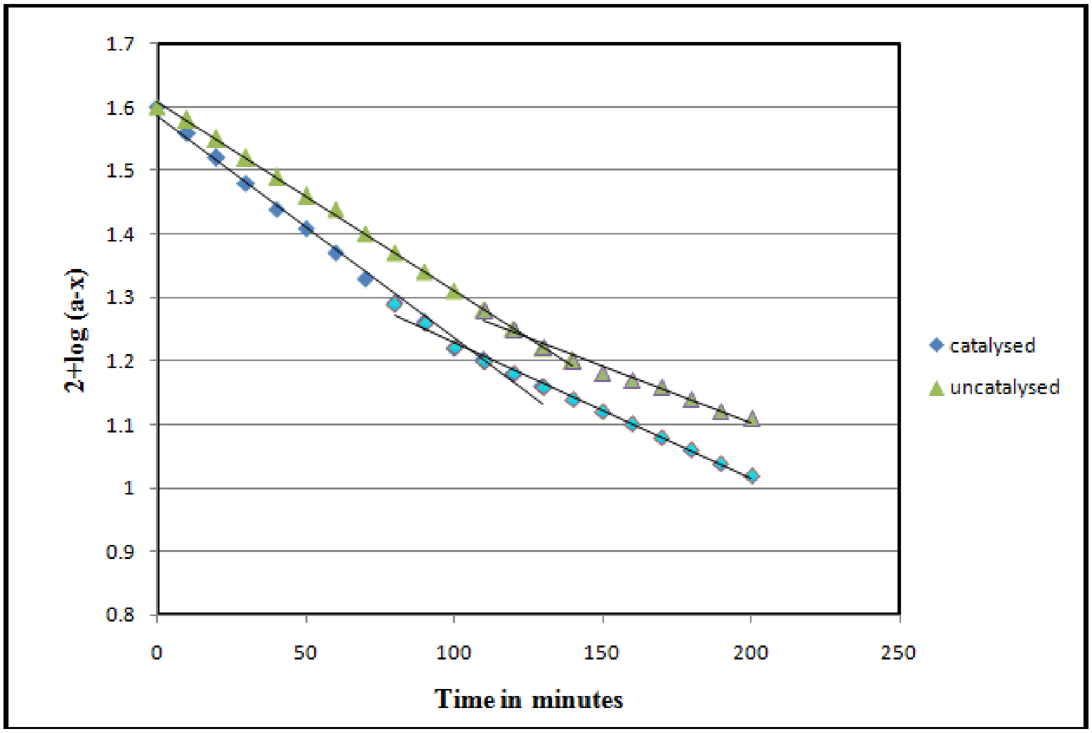


**Figure 1:**Typical run for the oxidation reaction in perchloric acid medium.

**Order of the reaction with respect to permanganate:-** It is observed that at constant concentration of perchloric acid, iso butyric acid and NaLs. The order of reaction with respect to permanganate is one according to table 1.1 and figure2. The variation of potassium permanganate concentration has practically no effect on the value of first order rate constant.

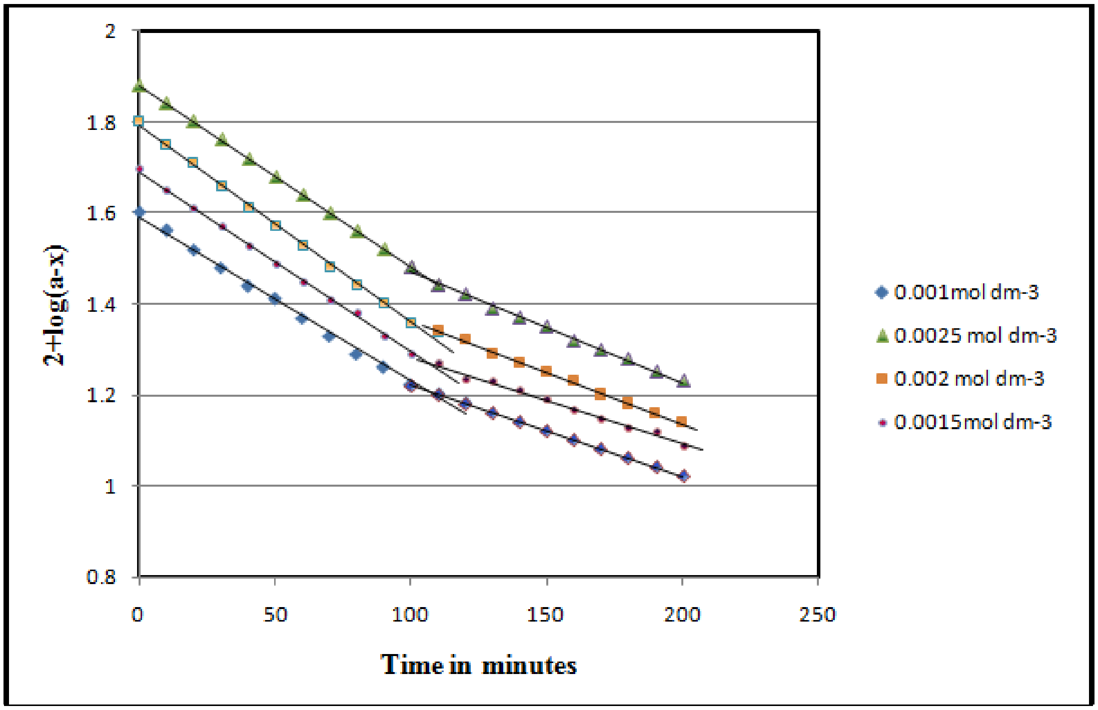


**Figure 2:**Variation of Potassium Permanganate concentration.

**Table 1.1:** Dependence of rate on oxidant concentration (Potassium Permanganate).

| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | | **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** |
|---|---|---|
| **[HClO$_4$]= 0.75 mol dm$^{-3}$** | | **Temperature= 303K** |
| **[KMnO$_4$]** | **k×10$^{-3}$ Min$^{-1}$** | **k$''_1$×10$^{-3}$ Min$^{-1}$** |
| **2.5×10$^{-3}$ mol dm$^{-3}$** | 9.212 | 5.416 |
| **2.0×10$^{-3}$ mol dm$^{-3}$** | 10.518 | 5.154 |
| **1.5×10$^{-3}$ mol dm$^{-3}$** | 9.961 | 4.786 |
| **1.0×10$^{-3}$ mol dm$^{-3}$** | 9.153 | 4.616 |

**Order of reaction with respect to iso butyric acid:-** It is observed that at constant concentration of perchloric acid, $KMnO_4$ ,and NaLs, ( According to table 1.2 and figure 3) the value of pseudo first order rate constant for both stage increases with increase in the concentration of iso butyric acid.

The plots of logarithm of iso butyric acid with logarithm of rate constant ($k_1$ and $k''_1$) are straight lines (figure 4) of approximately unit gradient in the both the stages. It show that the order of reaction with respect to iso butyric acid is one for each stages and Michaelis – Menton plots of 1/k, 1/ $k''_1$ against 1/ substrate concentration also given straight lines (Figure 5) passing through the origin for both the first and second stages. It conformed that the order of reaction with respect to iso butyric acid is one in both the stages and there is no kinetic evidence for intermediate complex formation between iso –butyric acid and permanganate[16].

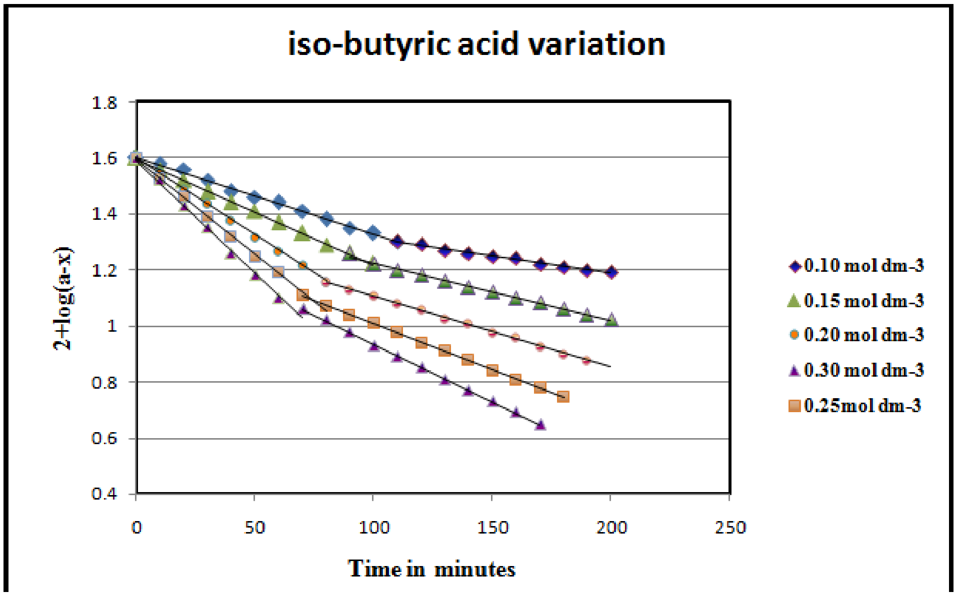


**Figure 3:** Variation of iso- butyric acid concentration.

**Table 1.2:** Variation of iso-butyric acid concentration.

| **[$HClO_4$]= 0.75 mol dm$^{-3}$** | | **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** |
|---|---|---|
| **[$KMnO_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | | **Temperature= 303K** |
| **[Iso-butyric acid]** | **k×10$^{-3}$ Min$^{-1}$** | **k$''_1$×10$^{-3}$ Min$^{-1}$** |
| **0.10 mol dm$^{-3}$** | 6.3093 | 2.9806 |
| **0.15 mol dm$^{-3}$** | 9.1534 | 4.6160 |
| **0.20 mol dm$^{-3}$** | 12.4716 | 5.965 |
| **0.25 mol dm$^{-3}$** | 15.9842 | 7.6452 |
| **0.30 mol dm$^{-3}$** | 19.3098 | 9.3267 |

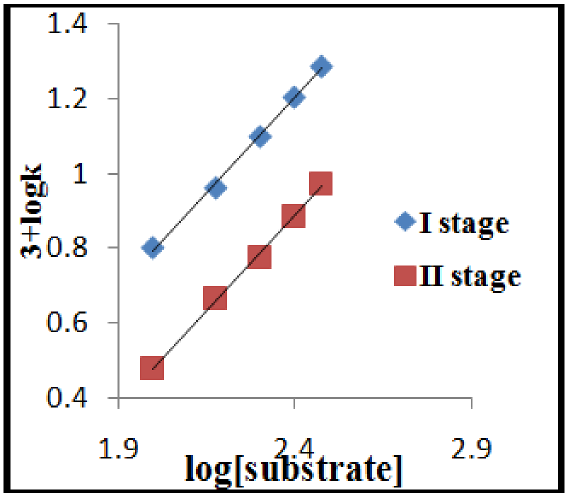


**Figure 4:** log k Vs log [substrate].

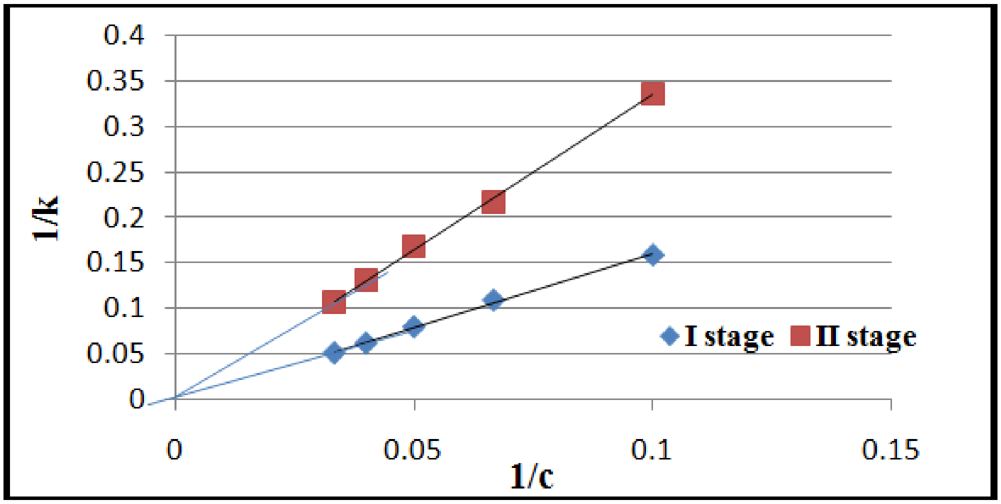


**Figure 5:** Michaelis Menten plot.

**Second order rate constant:-** The second order rate constant have been obtained by dividing the pseudo first order rate constant $k_1$ by the actual concentration of iso butyric acid for a given constant acid concentration at a particular temperature. The value of $k_s$ obtained from this relation are recorded in the table 1.3.The result reported in the table 1.3 indicate that the value of the second order rate constant , $k_s$ (first stage) and $k'_s$(second stage) for different iso butyric acid concentration , are constant for a particular temperature at given concentration of iso butyric acid.

**Table 1.3:**Second order rate constant.

| **$[HClO_4]$= 0.75 mol $dm^{-3}$** | | | **[NaLs]=$1.0\times10^{-4}$ mol $dm^{-3}$** | |
|---|---|---|---|---|
| **$[KMnO_4]$=$1.0\times10^{-3}$ mol $dm^{-3}$** | | | **Temperature= 303K** | |
| **[Iso-butyric acid]** | **$k\times10^{-3}$ $Min^{-1}$** | **$k''_1\times10^{-3}$ $Min^{-1}$** | **Second order rate constant $k_s\times10^{-3}$ liters $mol^{-1}$,$min^{-1}$** | **Second order rate constant $k'_s\times10^{-3}$ liters $mol^{-1}$,$min^{-1}$** |
| 0.10 mol $dm^{-3}$ | 6.3093 | 2.980 | 63.093 | 29.806 |
| 0.15 mol $dm^{-3}$ | 9.1534 | 4.616 | 61.022 | 30.773 |
| 0.20 mol $dm^{-3}$ | 12.471 | 5.965 | 62.358 | 29.825 |
| 0.25 mol $dm^{-3}$ | 15.984 | 7.645 | 63.936 | 30.580 |
| 0.30 mol $dm^{-3}$ | 19.309 | 9.326 | 64.366 | 31.089 |

**Effect of variation of perchloric acid concentration:-** It is observed that at constant concentration of iso butyric acid,$KMnO_4$ and NaLs(According to table 1.4 and figure 6) the rate of oxidative decarboxylation of iso butyric acid increase with increase in the concentration of perchloric acid medium . Zucker-Hammett, Bunnett's and Bunnett-Olsen plots have been applied to investigate the role of $H_2O$ and activity of $H^+$ ion on the oxidation reaction [17-20]. The slope values of all plots have been calculated for each stages given in the table 1.5 and plots also given in figure 6.1 to 6.4. These show that water molecule is involved as a proton abstracting agent in the rate determine step.

**Table 1.4:**Dependence of rate on perchloric acid concentration $[H^+]$.

| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | | | **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** | | |
|---|---|---|---|---|---|
| **[$KMnO_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | | | **Temperature= 303K** | | |
| **[$H^+$] mol dm$^{-3}$** | **-$H_0$** | **-log a$H_2O$** | **Log [$H^+$]** | **k×10$^{-3}$ Min$^{-1}$** | **$k''_1$×10$^{-3}$ Min$^{-1}$** |
| 0.75 | 0.04 | 0.012 | -0.12493 | 9.1534 | 4.6160 |
| 1.00 | 0.22 | 0.018 | 0 | 12.1296 | 5.2071 |
| 1.50 | 0.53 | 0.030 | 0.17609 | 14.9014 | 8.9453 |
| 2.00 | 0.78 | 0.043 | 0.30102 | 20.3322 | 10.7218 |
| 2.50 | 1.01 | 0.060 | 0.39794 | 28.4285 | 17.4300 |

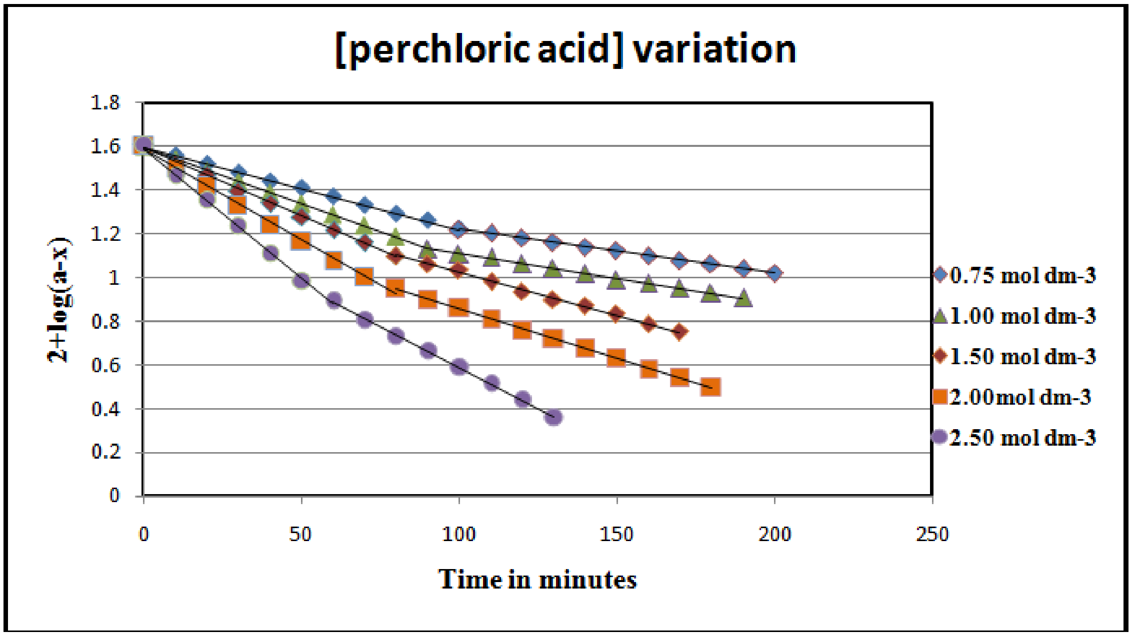
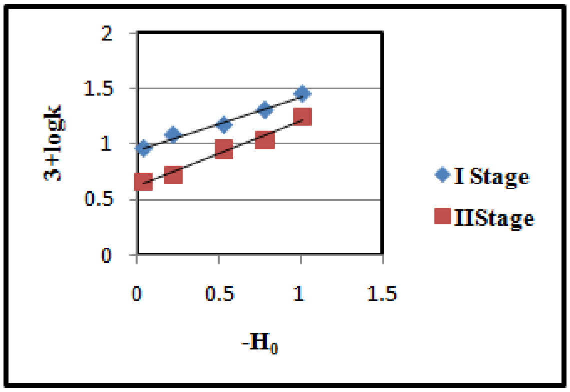


**Figure 6:**Variation of perchloric acid concentration.



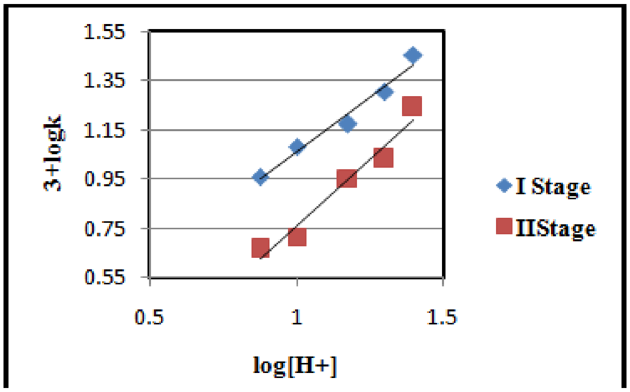


**Figure 6.1:** Zucker-Hammett plot I.

**Figure 6.2:** Zucker-Hammett plot II.

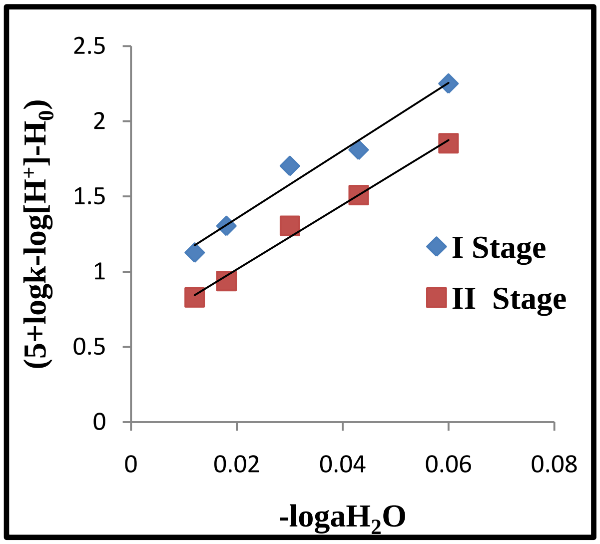


**Figure 6.3:** Bunnett's plot I

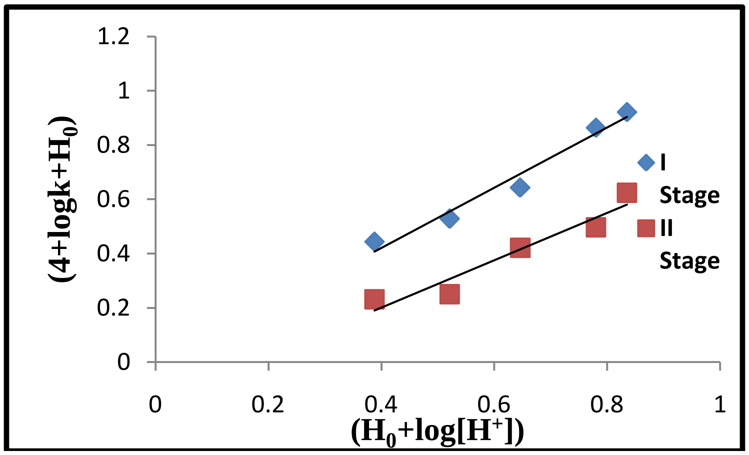


**Figure 6.4:** Bunnett- Olsen plot II

**Table 1.5:** Correlation of reaction rate with perchloric acid concentration.

| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | | **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** | | |
|---|---|---|---|---|
| **[KMnO$_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | | **Temperature= 303K** | | |
| **S.No.** | **Correlation** | **Parameters** | **Slope values** | |
| | | | **I Stage** | **II Stage** |
| | **Zucker- Hammett plots** | | | |
| (a) | (log Rate constant) against –$H_0$ | Slope | 0.479 | 0.589 |
| (b) | (log Rate constant) against log[$H^+$] | Slope | 0.882 | 1.081 |
| | **Bunnett's plots** | | | |
| (a) | (log Rate constant+$H_0$) against –log$aH_2O$ | (ω) | a | a |
| (b) | { (log Rate constant)-log[$H^+$]} against –log$aH_2O$ | (ω$^*$) | a | a |
| (c) | (log Rate constant-log [$H^+$]-$H_0$) against –log$aH_2O$ | Slope | 22.51 | 21.50 |
| | **Bunnett's Olsen plots (L.F.E.R.)** | | | |
| (a) | (log Rate constant+$H_0$) against ($H_0$+log[$H^+$]) | (Φ) | 1.111 | 0.871 |

a = not obtained

**Effect of variation of surfactant concentration:-**It is observed that at constant concentration of iso butyric acid,$KMnO_4$ and perchloric acid(According to table 1.6 and figure 9) the pseudo first order rate constant for the given concentration range of NaLs, increase with the increase concentration of NaLs and value of velocity constant are high in comparison to the uncatalysed reaction. The plots of k & $k''_1$ against NaLs concentration are also straight line in both the stages showing the catalytic activity of NaLs (figure 7).

In the present investigation maximum NaLs concentration is 5×10$^{-4}$ mol dm$^{-3}$. The reaction rate increases with increase concentration of NaLs from 1×10$^{-4}$ mol dm$^{-3}$ to 5×10$^{-4}$ mol dm$^{-3}$. This is well below the reported CMC of NaLs which is available in the literature as **8.1×10$^{-3}$mol dm$^{-3}$** at 298K. This phenomena which is observed in present case is of premiceller catalysis .The plot [Figure8(a) and 8(b)] are good straight lines with slpoe value below 20. The 'n' value obtained for first and second stages are **1.958** and **2.489**. These are between the expected value for premiceller catalysis i.e between 1 to 6, while in the case of miceller catalysis this value should be more than 20. This is according to the binding parameter as suggested by Piszkiewicz[21]. The n value of positive cooperativity also supports the substrate promoted micellization[22-24].

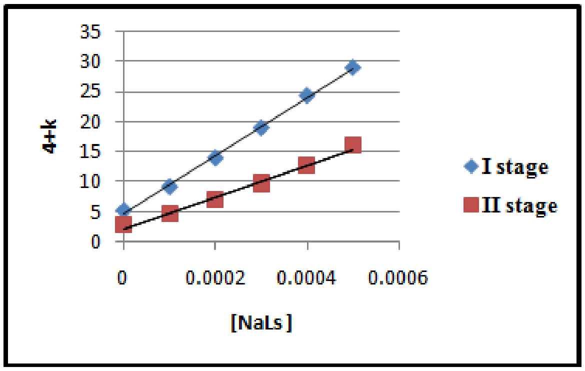


**Figure 7:**k against NaLs concentration.

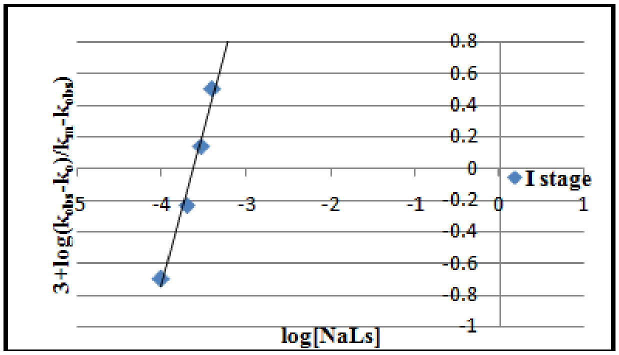


**Figure 8 a:** Piszkiewiez plot (For I Stage).

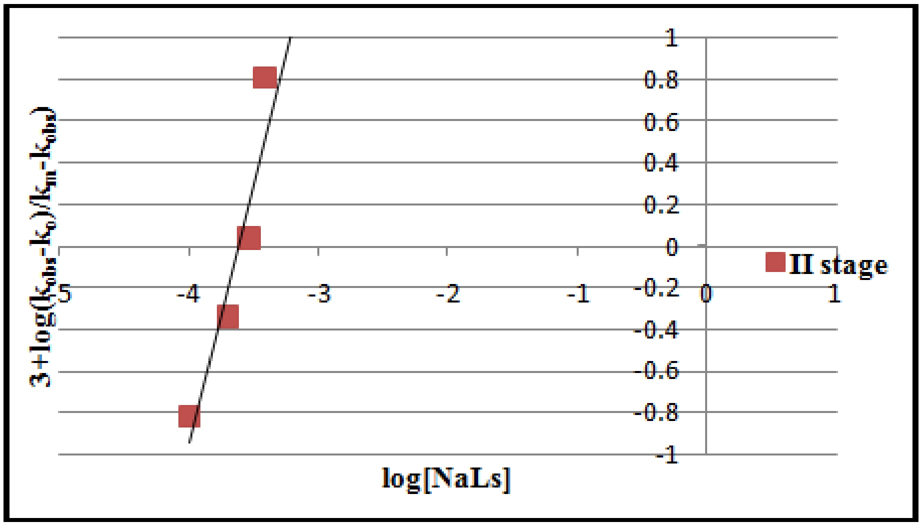


**Figure 8 b:** Piszkiewiez plot (For IIStage).

**Table 1.6:**Dependence of rate on[NaLs] concentration and catalytic constant.

| **[KMnO$_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | | **Iso-Butyric acid= 0.15 mol dm$^{-3}$** | | |
|---|---|---|---|---|
| **[HClO$_4$]= 0.75 mol dm$^{-3}$** | | **Temperature= 303K** | | |
| **NaLs mol dm$^{-3}$** | **k×10$^{-3}$ Min$^{-1}$** | **$k_c$×10$^{-3}$ Min$^{-1}$** | **$k''_1$×10$^{-3}$ Min$^{-1}$** | **$k_c''$×10$^{-3}$ Min$^{-1}$** |
| uncatalysed | 5.2278 | ----- | 2.8787 | ------ |
| 1×10$^{-4}$ | 9.1534 | 3.9256 | 4.6160 | 1.7373 |
| 2×10$^{-4}$ | 13.940 | 4.3561 | 6.9523 | 2.0368 |
| 3×10$^{-4}$ | 18.943 | 4.5717 | 9.652 | 2.2577 |
| 4×10$^{-4}$ | 23.276 | 4.5120 | 12.6554 | 2.4441 |
| 5×10$^{-4}$ | 28.928 | 4.7400 | 15.945 | 2.61326 |

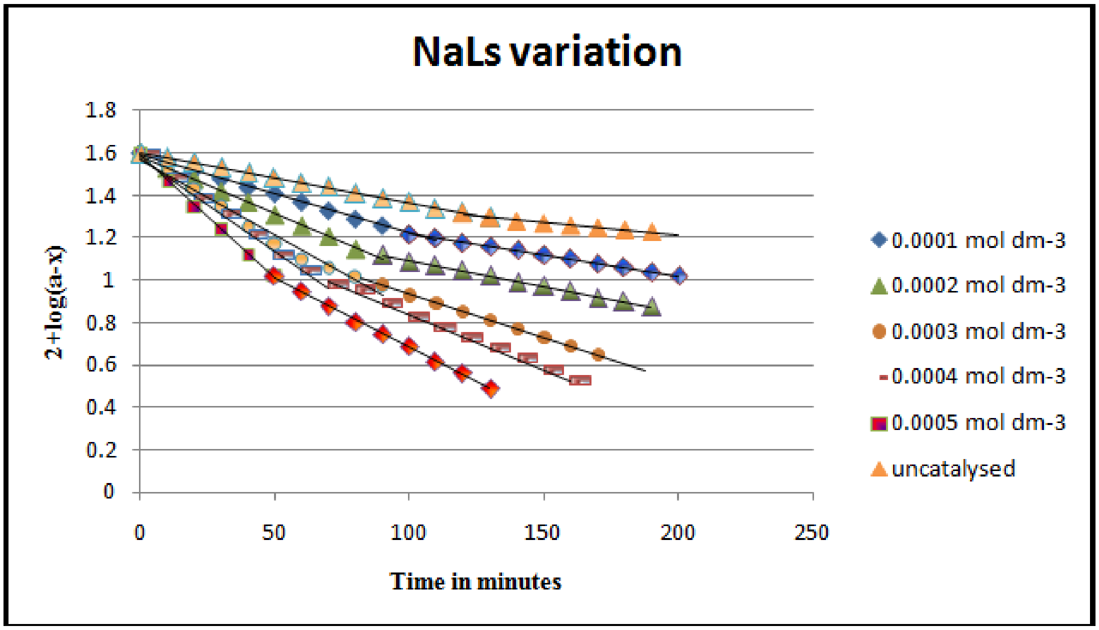


**Figure 9:**Variation of surfactant concentration.

**Effect of variation of temperature:-** Temperature variation is observed at constant concentration of iso butyric acid,$KMnO_4$ , perchloric acid and NaLs. (According to table 1.7and figure 10). It is studied at 303K, 308K, 313K, and at 318K. The value of temperature coefficient have been given in (table 1.8) , Arrhenius plots[25] are also given (figure 11) for calculation of activation energy. The experimental results in forms of kinetic and thermodynamic parameter are recorded in table1.9. The values of all parameter reported are in favor of normal oxidation reaction.

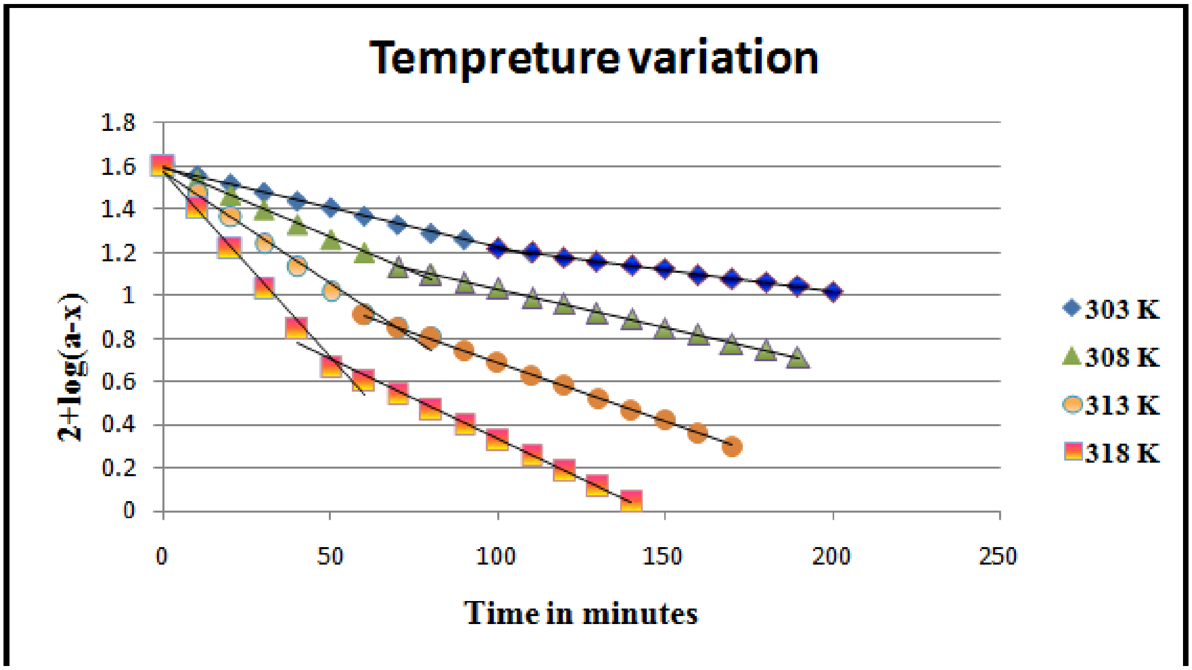


**Figure 10**:Variation of Temperature.

**Table 1.7:** The values of temperature coefficient for 10°C rise in temperature are summarized in following table ,

| **Temperature Coefficients** | | |
|---|---|---|
| **Temperature range K** | **Stage I** | **Stage II** |
| 303K-313K | 2.9790 | 2.7596 |
| 308K-318K | 2.8324 | 2.0208 |

**Table 1.8:** Effect of the Temperature variation.

| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | | **[$HClO_4$]= 0.75 mol dm$^{-3}$** |
|---|---|---|
| **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** | | **[$KMnO_4$]=1.0×10$^{-3}$ mol dm$^{3}$** |
| **Temperature** | **k×10$^{-3}$ Min$^{-1}$** | **k$''_1$×10$^{-3}$ Min$^{-1}$** |
| 303K | 9.1534 | 4.6160 |
| 308K | 15.4318 | 7.8348 |
| 313K | 27.2686 | 12.7386 |
| 318K | 43.7104 | 15.8331 |

**Arrhenius plots:-**

The Arrhenius plot has been drawn between logk and 1/T to determine activation of energy by slope measurement.

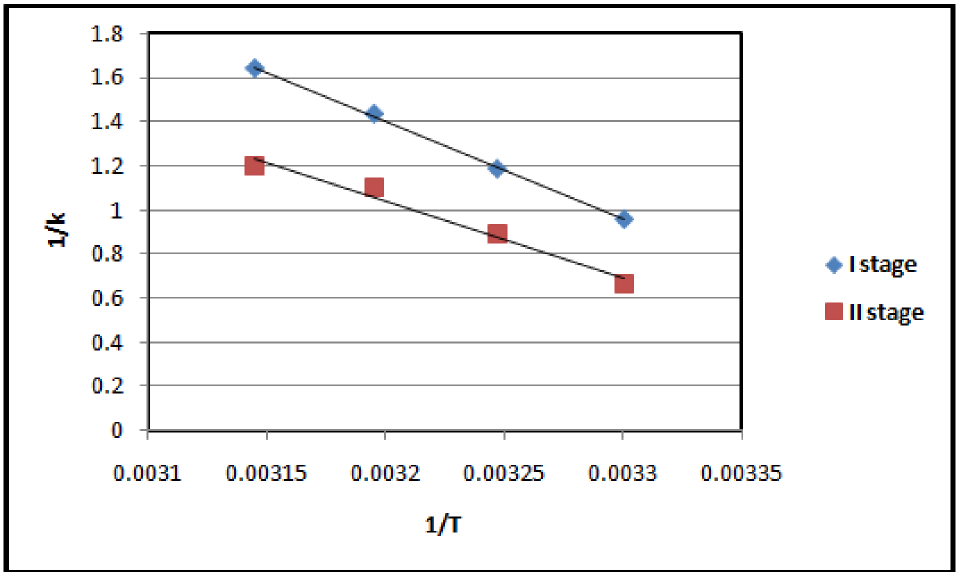


**Figure 11 :**Arrhenius plots logk against 1/T

**Table 1.9:** Thermodynamic and activation parameters.

| | | | | | | |
|---|---|---|---|---|---|---|
| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | | | **[$HClO_4$]= 0.75 mol dm$^{-3}$** | | | |
| **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** | | | **[$KMnO_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | | | |
| **Temperature= 303K** | | | | | | |
| **Kinetic Parameter** | | | | | | |
| **Stage** | **Energy of activation ( ΔEa$^{\#}$) KJ Mol$^{-1}$** | | **Enthalpy of activation (ΔH$^{\#}$)KJmol$^{-1}$** | **Entropy of activation (ΔS$^{\#}$) Jmol$^{-1}$K$^{-1}$** | **Frequency factor (pZ$^{\#}$) dm$^{3}$ mol$^{-1}$ sec$^{-1}$** | **Free Energy of activation (ΔG$^{\#}$) KJmol$^{-1}$** |
| | **Cal.** | **Gra.** | | | | |
| **For First Stage** | 83.5027 | 84.285 | 80.9835 | -5.945 | 12.93×10$^{12}$ | 79.183 |
| **For Second Stage** | 65.8304 | 67.1873 | 63.3112 | -68.06 | 7.37×10$^{9}$ | 42.689 |

**Effect of natural salt and specific ionic effects on reaction rates:-** The primary kinetic salt effect was not observed within the concentration limits as demanded for the applicability of Bronsted-Bjerum equation[26]. Hence specific ionic effect is observed and results have been reported. The linear plots of logk and $k^{\prime\prime}_{1}$ against ionic strength**(μ)** are in favor of specific ionic effect. The specific effect of cations.

By keeping $SO_4^{2-}$ ion as common and by varying cations, the following relative order is observed.
**$Al^{3+} > Mg^{2+} > Na^{+}$**

The specific effect of anions:
By keeping $Na^{+}$ ion as common and by varying anions, the following relative order is observed.
**$F^{-} > CH_3COO^{-}$**

**Catalytic effect of Mn (II):-** The catalytic effect of manganous sulphate have also been the studied. The effect of Mn(II) as a catalyst in the case of oxidation of permanganate is well known [27,28,]. It is assumed that in the present case Mn (II) forms a complex with isobutyric acid which may then be oxidized by active molecular oxidizing species $HMnO_4$ or Mn(II) may react with Mn(VII) to give Mn(III) which may accelerate the rate of reaction[29].
All metals are lewis acids. Catalytic activity of metals in acid catalysed reaction may be due to it's addition to the substrate in such a way that makes it able to drain electrons towards the site of attachment [30].

**Table 1.10:** Effect of Mn(II).

| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | | **[$KMnO_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | |
|---|---|---|---|
| **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** | | **[$HClO_4$]= 0.75 mol dm$^{-3}$** | |
| **Temperature= 303K** | | | |
| **[$MnSO_4$ ]mol dm$^{-3}$** | **μ** | **k×10$^{-3}$ Min$^{-1}$** | **$k^{\prime\prime}_{1}$×10$^{-3}$ Min$^{-1}$** |
| 0.00 | 4.0000 | 9.1534 | 4.6160 |
| 0.0001 | 4.0004 | 11.4577 | 5.2858 |
| 0.0002 | 4.0008 | 14.3857 | 6.2470 |
| 0.0003 | 4.0012 | 17.6998 | 6.7088 |
| 0.0004 | 4.0016 | 23.7088 | 7.8396 |

**10.Effect of change in surface area :** The effect of change in surface area on the reaction have been also studied . The oxidation reactions have been carried out with addition of glass balls of same size and different number at constant concentration of other reactant. The result have been given in the table 1.11 and it has been observed that the change in area with increasing the numbers of balls, retards rate of oxidation[30].

**Table 1.11:** Surface area variation.

| **[Iso-butyric acid]= 0.15 mol dm$^{-3}$** | **[$HClO_4$]= 0.75 mol dm$^{-3}$** | |
|---|---|---|
| **[NaLs]=1.0×10$^{-4}$ mol dm$^{-3}$** | **Temperature= 303K** | |
| **[$KMnO_4$]=1.0×10$^{-3}$ mol dm$^{-3}$** | | |
| **No. of Glass balls** | **k×10$^{-3}$ Min$^{-1}$** | **$k^{\prime\prime}_{1}$×10$^{-3}$ Min$^{-1}$** |
| Without glass balls | 9.1534 | 4.6160 |
| 5 | 7.4541 | 4.3001 |
| 10 | 6.1443 | 3.6595 |
| 15 | 4.6771 | 3.2538 |
| 20 | 3.4623 | 2.8229 |

**Stoichiometry of the Reaction, Free radical, and Product analysis:-** The stoiciometry of the reaction was determined by analytical method. In this method the reaction mixture containing known excess of $KMnO_4$ over the iso butyric acid were allowed to stand at room temperature sufficiently long time(36 hour). After the time the amount of unreactant permanganate was estimated idometrically. It has been found that the five mole of substrate consumes one mole of potassium permanganate. On the basis of literature available and the work performed[30,31], the catalysed reaction is proceeds as follow:

$$5(CH_3)_2CHCOOH + 2MnO^{-}_4 + 6H^{+} \longrightarrow 5(CH_3)_2CHOH + 2Mn^{2+} + 5CO_2 + 3H_2O$$

It is also observed that alcohol and carbon dioxide have been determined as the end product. Identification of $CO_2$ is carried out by lime water test. It has been observed that the lime water turns milky within 4 to 6 hour of oxidation. Iso propyl alcohol was detected as oxidation product of surfactant catalysed oxidation of iso butyric acid. Respective alcohol was identified by spot test method as given by Figel[32]. Active organic free radical's formation has been also confirmed by the formation of white precipitate of mercurous chloride as a result of addition of mercuric chloride [16].

**Mechanism:-** Following mechanism is proposed for the studied reaction which has been reported by earlier worker for oxidation of iso butyric acid in different medium[79].

$$(CH_3)_2CHCOOH + H^+ \rightarrow (CH_3)_2CHCOOH_2^+$$

$$MnO_4^- + H^+_{aq} \underset{}{\overset{K_2}{\rightleftharpoons}} HMnO_4$$

(Molecular)

$$n\,(NaLS) \rightleftharpoons (NaLS)_n$$

(n is below CMC)

$$(NaLS)_n + (CH_3)_2CHCOOH_2^+ \xrightarrow{k_3} (NaLS)_n\text{--------}(CH_3)_2CHCOOH_2^+$$

(n = below 20) Substrate – Surfactant association (without covalent bonds) (NaLS)n---

$$(CH_3)_2CHCOOH_2^+ + HMnO_4 + H_2O \xrightarrow{k_2\ \textit{slowest step}} (NaLS)_n\text{---}(CH_3)_2CHCOO^\bullet + HMnO_4^- + H_3O^+$$

Purely physical premiceller catalysis

$$(NaLS)_n\text{----}(CH_3)_2CHCOOH_2^+ \xrightarrow{\textit{Fast}} (NaLS)_n\text{ ---- }(CH_3)_2CH^\bullet + CO_2$$

$$(NaLS)_n\text{ ---- }(CH_3)_2CH^\bullet + HMnO_4 \xrightarrow{\textit{Fast}} (NaLS)_n + (CH_3)_2CH^+ + HMnO_4^-$$

$$(CH_3)_2CH^+ + H_2O \xrightarrow{\textit{Fast}} (CH_3)_2CHOH + H^+$$

## Conclusion:-

On the basis of kinetic result and observation it is evident the rate of oxidative decarboxylation of iso butyric acid is increase in the presence of micelles and perchloric acid medium . Zucker-Hammett, Bunnett's and Bunnett-Olsen plots have been applied to investigate the role of $H_2O$ and activity of $H^+$ ion on the oxidation reaction. It shows that water molecule is involved as proton abstracting agent in the rate determining step.

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