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RESEARCH ARTICLE

A Kinetics study of miceller catalysed oxidation of propionic acid by acidic permanganate

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Abstract

A kinetic study of oxidation of propionic acid has been investigated in presence and absence of anionic micelle; sodium lauryl sulphate (NaLS). The reaction is a double stage process, in which first stage is followed by second fast stage process. It is observed that the rate was increased in the presence of surfactant used. A first order kinetics is observed with respect to substrate and oxidant. The data has been examined in the light of Zucker-Hammett, Bunnett and Bunnett-Olsen criteria of reaction mechanism.The stiochiometry was observed in terms of mole ratio of permanganate ion and propionic acid consumed. Effect of specific ions on the reaction rate has also been reported. Activation parameters for the reaction are evaluated and the plausible mechanism is suggested.

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Introduction:

Kinetic study in the presence of micelles has become one of the very interesting subject of investigation. Now a day's surfactant has attracted considerable interest in theoretical and experimental fields due to their catalytic efficiency at a certain concentration in solution. Their monomers associate to form longer aggregates known as micelles[1-5]. One of the important properties of miceller surfactant is their ability to effect the rates of chemical reaction. In present work an anionic surfactant i.e. sodium lauryl sulphate is used as miceller catalyst. The oxidation kinetics of carboxylic acids has been examined by number of workers. Since little work has been reported on the miceller catalysed oxidation of carboxylic acid by acidic permanganate and about the kinetics and mechanism of many of its important reactions[6-11], hence the present work has been taken for the research. It described the detailed study on the miceller catalysed oxidation of propionic acid by acidic permanganate. The oxidation has also been carried out by potassium dichromate from the comparative point of view[12-15].

Due to the several advantages of permanganate ions as an analytical oxidizing agent in synthetic and analytical works it is used in the present investigation. Attempts have also been made to eluciate the type of reaction mechanism based on the influence of H^+ ion and neutral salts on the rate of the reaction. The involvement of water molecule in the reaction mechanism has been explained in the light of Zucker-Hammett, Bunnett and Bunnett-Olsen hypothesis.

Experimental:

The standard solution of propionic acid (BDH) and sodium lauryl sulphate (BDH) were prepared in doubly distilled water. H_2SO_4 (Analar) was used as a source of hydrogen ion. Permanganate solution was prepared as given by Vogel[16]. Potassium dichromate solution of Analar grade from Rankem was used. Standard salt solutions were made by dissolving known amount of the solute in a given volume of distilled water.

Kinetic studies were performed by using Systronic 104 spectrophotometer at 525nm i.e. at the absorbance maximum of permanganate at constant temperature and at 420nm i.e. at the λ_{max} of dichromate. It was verified that there is no interference from other reagent at these wavelengths. All kinetic measurement were conducted under pseudo first order conditions where the substrate was maintained in a large excess over the permanganate and dichromate ion concentration.

Result and discussion:

(A) Dependency of reaction rate on permanganate concentration:

Dependency of reaction rate on permanganate has been studied by varying is initial concentration at constant concentration of other reactants. It shows that rate constant does not alter with oxidant concentration. The plot of log of optical density i.e. log(a-x) and time exhibit double stage process each being linear indicating that the order with respect to permanganate is one for each stages in acidic medium.

(B) Dependency of reaction rate on potassium dichromate at in sulphuric acid medium (chromic acid):

The oxidation has also been carried out by potassium dichromate from the comparative point of view. The reaction is double stage process. It is evident that the values of pseudo first order rate constant k_1 and k_1'' doesnot alter significantly with the concentration of dichromate

From the comparative point of view it has been confirmed that oxidation by dichromate is possible at very low concentration of sulphuric acid then in the case of permanganate. It has also been observed the rate of oxidation by dichromate is comparatively fast than by permanganate.

(C) Dependency of reaction rate on substrate concentration:

For the determination of dependency of reaction rate on substrate concentration i.e. propionic acid, experiments were performed at 298K with different initial concentration of propionic acid, keeping the concentration of all other reactants as constant. The rate both in uncatalysed and catalysed reaction was found to increase with the concentration of propionic acid. Table 1.1(A), 1.1(B).

TABLE - 1.1 (A) :Variation of propionic acid concentration (Uncatalysed)

$[H_2SO_4]$ = 3.0 mol dm^{-3} **Temperature = 298K**			**$[KMnO_4]$ = 1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = Nil**	
[propionic acid] mol dm^{-3}	**k_1× 10^{-3}Min^{-1} (First stage)**		**k_1'' × 10^{-3} Min^{-1} (Second stage)**	
	By Differential method	**By Graphical method**	**By Differential method**	**By Graphical method**
0.10	3.40	3.24	1.11	1.20
0.15	5.06	4.90	1.63	1.67
0.20	6.79	6.80	2.25	2.35
0.25	8.40	8.20	2.71	2.68
0.30	10.65	11.17	3.34	3.36

TABLE 1.1 - (B) :Variation of propionic acid concentration (Catalysed)

$[H_2SO_4]$ = 3.0 mol dm^{-3} **Temperature = 298K**			**$[KMnO_4]$ = 1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 × 10^{-4} mol dm^{-3}**	
[propionic acid] mol dm^{-3}	**k_1× 10^{-3}Min^{-1}**		**k_1'' × 10^{-3}Min^{-1}**	
	By Differential method	**By Graphical method**	**By Differential method**	**By Graphical Method**
0.10	4.13	4.13	1.75	1.74
0.15	6.13	6.10	2.58	2.55
0.20	8.40	8.17	3.45	3.39
0.25	10.26	9.44	4.25	4.33
0.30	12.32	11.28	5.28	5.22

Plot of logarithm of [propionic acid] with logarithm of rate constant (k_1 and k_1”) give straight line approximately of unit gradient in both the stages. These show that the order of reaction with respect to propionic acid is one for each stages and plots of 1/k_1, 1/k_1” against 1/Substrate concentration (i.e. Michaelis-Menten plots) give straight lines passing through the origin for both the first and second stages. These confirm the first order dependence of reaction rate with respect to propionic acid, in both the stages and there is no kinetic evidence for intermediate complex formation between propionic acid and permanganate[17]. However if any complex is formed, its formation constant would be extremely small.

(D)i: Effect of the variation of the sulphuric acid and perchloric acid concentration :

The reaction was studied at different sulphuric acid and perchloric acid concentrations, keeping the constant concentration of propionic acid, potassium permanganate and sodium lauryl sulphate. The variation of the $[H^+]$ concentration on the reaction rate has been investigated between 2.0 mol dm^{-3} to 4.0 mol dm^{-3} concentration range of the sulphuric acid and 1.0 mol dm^{-3} to 3.0 mol dm^{-3} concentration range of the perchloric acid medium.The experimental results obtained are summarized in table 1.2 and 1.3.

TABLE - 1.2: Dependence of rate on sulphuric acid concentration [H^+]

[propionic acid] = 0.20 mol dm^{-3} **Temperature = 298K**			**[$KMnO_4$]=1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 ×10^{-4} mol dm^{-3}**	
[H^+] mol dm^{-3}	**-H_0**	$-\log a_{H_2O}$	**k_1×10^{-3} Min^{-1}**	**k_1''×10^{-3} Min^{-1}**
2.0	0.84	0.043	5.88	2.45
2.5	1.12	0.063	6.77	3.16
3.0	1.38	0.085	8.41	3.45
3.5	1.62	0.111	11.00	4.18
4.0	1.85	0.142	13.70	4.97

TABLE 1.3 : Dependence of rate on perchloric acid concentration [H^+]

[propionic acid] = 0.20 mol dm^{-3} **Temperature = 298K**			**[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 ×10^{-4} mol dm^{-3}**	
[H^+] mol dm^{-3}	**-H_0**	$-\log a_{H_2O}$	**k_1×10^{-3} Min^{-1}**	**k_1''×10^{-3} Min^{-1}**
1.0	0.22	0.018	3.44	1.56
1.5	0.53	0.030	3.88	2.00
2.0	0.78	0.043	4.61	2.66
2.5	1.01	0.060	5.46	3.39
3.0	1.23	0.081	6.33	4.21

(D)(ii). Applicability of Zucker-Hammett, Bunnett and Bunnett-Olsen hypothesis: Different hypothesis have been applied to investigate the role and activity of H^+ ion on the oxidation reaction. In order to correlate the rate of oxidation with acid concentration, the two Zucker-Hammett[19] plots i.e. the plot of (log rate constant against – H_0) and the plot of (log rate constant against log [H^+]), show linear correlations of rate with the acid concentration. This shows that the reaction is acid catalysed. However, none of the straight line of this Zucker-Hammett plots in both the cases of sulphuric and perchloric acid produces the ideal slope value of unity. Deviation from the ideal slope value of unity suggest that the water molecule may be involve in some way in the rate determining step. Since the ideal slope values (i.e. unity) of two Zucker-Hammett plots are not obtained

hence the Bunnett's plots[20] i.e. the Bunnett relationships (log[rateconstant] + log [H_o]) against log a_{H2O}, log([rate constant] – log[H^+]) against loga_{H2O} and (log [rate constant] – log[H^+] - H_o) against log a_{H2O} have been obtained. In the same way the Bunnett-Olsen plot[21] i.e. the plot of linear free energy relationship, i.e. (log [rate constant] + H_0) against (H_0 + log [H^+]) has also been obtained. On the basis of Bunnett and Bunnett-Olsen empirical observations the reported slope values of these plots confirms that in the [H^+] catalysed reactions the water molecule should act as a proton abstracting agent in the rate determining step. The slope values of two Bunnett plots ω and ω* and of one Bunnett-Olsen plots 'ϕ' have been reported in the table 1.4 and 1.5. The values of -H_0 and a_{H2O} have been taken from Bunnett[20], Paul and Long[22] respectively.

TABLE – 1.4 : Correlation of reaction rate with sulphuric acid concentration

[propionic acid] = 0.20 mol dm^{-3} **Temperature = 298K**		**[$KMnO_4$] =1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 ×10^{-4} mol dm^{-3}**		
S.No	**Correlation**	**Parameters**	**Slope value**	
			I stage	**II stage**
1.	**Zucker-Hammett plot**			
(a)	(log Rate constant) against –H_0	Slope	0.373	0.291
(b)	(log Rate constant) against log [H^+]	Slope	1.23	0.977
2.	**Bunnett's plots**			
(a)	(log Rate constant + H_0) against $-\log a_{H_2O}$	(ω)	-6.283	-7.163
(b)	(log Rate constant – log [H^+]) against $-\log a_{H_2O}$	(ω*)	0.847	-0.026
(c)	(log Rate constant – log [H^+] – H_0) against	Slope	10.976	10.096

	$- \log a_{H_2O}$.			
3.	**Bunnett-Olsen plot (L.F.E.R)**			
(a)	(log Rate constant $+H_0$) against (H_0 + log $[H^+]$)	(ϕ)	0.889	1.007

TABLE - 1.5 : Correlation of reaction rate with perchloric acid concentration

[propionic acid] = 0.20 mol dm^{-3} **Temperature = 298K**		**$[KMnO_4]$ =1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 ×10^{-4} mol dm^{-3}**		
S.No	**Correlation**	**Parameters**	**Slope value**	
			I stage	**II stage**
1.	**Zucker-Hammett plot**			
(a)	(log Rate constant) against $–H_0$	Slope	0.269	0.435
(b)	(log Rate constant) against log $[H^+]$	Slope	0.558	0.908
2.	**Bunnett's plots**			
(a)	(log Rate constant + H_0) against $- \log a_{H_2O}$	(ω)	a	-8.839
(b)	(log Rate constant – log $[H^+]$) against $- \log a_{H_2O}$	(ω*)	-2.999	-0.431
(c)	(log Rate constant] – log $[H^+]$ – H_0) against $- \log a_{H_2O}$	Slope	12.676	15.214
3.	**Bunnett's - Olsen plot (L.F.E.R)**			
(a)	(log Rate constant + H_0) against (H_0 + log $[H^+]$)	(ϕ)	1.374	1.066

Where 'a' is for absent

(E) Dependency of reaction rate on NaLS concentration:

Effect of variation of concentration of anionic surfactant i.e. sodium lauryl sulphate (NaLS) has been studied keeping the other reactants constant at given constant temperature.

It is clear that the pseudo first order rate constant for the given concentration range of NaLS increases with the increase in NaLS Concentration (Table 1.6). In the present study, the formation of premiceller aggregates are responsible for the miceller catalysis[23-26].

The catalysis by the concentration of micelle which is below their cmc (i.e. critical micelles concentration) value is also possible as reported in the literature. It is termed as premiceller catalysis. It has been determined graphically by plotting a Piszkiewicz graph between log $[k_{obs} - k_o] / [k_m - k_{obs}]$ and log [NaLS]. Here k_o is the velocity constant in absence of NaLS, k_{obs} is the velocity constant at different NaLS concentration, while k_m is the maximum velocity constant in presence of NaLS used. The concentration of NaLS varied from 5.0×10^{-4} to 9.0×10^{-4} mol dm^{-3}. Its maximum concentration used is 9.0×10^{-4} mol dm^{-3}. This is well below the reported cmc of sodium lauryl sulphate which is reported in the literature as 8.1×10^{-3} mol dm^{-3} at 298K. This confirms that the observed phenomenon is a case of premiceller catalysis.

In present case the plot is good straight line. The slope value 'n' obtained from this graph for first and second stages are 2.05 and 1.88.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 parameters as suggested by Piszkiewicz[27].

The result have been reported in the table 1.6 for both the stages. The 'n' value of positive cooperativity also supports the substrate promoted micellization which is analogous to positive cooperativity in case of enzymatic reactions[28-30].

TABLE - 1.6 : Dependence of rate on NaLS Concentration and Catalytic Constant

[Propionic Acid] = 0.15 mol dm^{-3} **[H_2SO_4] = 3.0 mol dm^{-3}**			**[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3}** **Temperature = 298K**	
[NaLS] mol dm^{-3}	**$k_1 \times 10^{-3}$ Min^{-1}**	**$k_c \times 10^3$ litre mol^{-1} min^{-1}**	**$k''_1 \times 10^{-4}$ Min^{-1}**	**$k''_c \times 10^3$ litre mol^{-1} min^{-1}**
Uncatalysed (Absent)	5.06	----	1.63	----
5.0 ×10^{-4}	6.11	2.10	2.58	1.90
6.0 ×10^{-4}	6.56	2.40	2.80	1.95
7.0 ×10^{-4}	6.93	2.67	3.03	2.01
8.0 ×10^{-4}	7.24	2.72	3.21	1.97
9.0 ×10^{-4}	7.74	2.93	3.45	2.20

(F) Effect of variation of temperature :

The reaction was studied at different temperature i.e. 298, 303, 308 and 313K in order to observe the effect of temperature on reaction rate at the constant concentration of all the reactants. The result have been recorded in the table 1.7:

TABLE - 1.7 : Effect of Temperature variation

[propionic acid] = 0.15 mol dm^{-3} **[H_2SO_4] = 3.0 mol dm^{-3}**			**[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3}** **Temperature = 298K**	
Temperature (K)	**Velocity constant forUncatalysed NaLS = Nil**		**Velocity constant for Catalysed NaLS = 5.0× 10^{-4}mol dm^{-3}**	
	$k_1 \times 10^{-3}$Min^{-1}	**$k''_1 \times 10^{-3}$Min^{-1}**	**$k_1 \times 10^{-3}$Min^{-1}**	**$k''_1 \times 10^{-3}$Min^{-1}**
298	5.06	1.63	6.11	2.58
303	7.48	2.96	9.54	3.53
308	11.11	3.75	12.83	5.53
313	15.89	6.66	19.57	7.48
Temperature Range (K)	**Temperature coefficient for Uncatalysed**		**Temperature coefficient for Catalysed**	
	I stage	**II stage**	**I stage**	**II stage**
298-308	2.19	2.30	2.09	2.14
303-313	2.12	2.25	2.05	2.09

From the temperature variation studies, the various kinetic and activation parameters such as Energy of activation $\Delta E^{\neq}$, Enthalpy of activation $\Delta H^{\neq}$, Entropy of activation $\Delta S^{\neq}$, Frequency factor pZ and Free Energy $\Delta G^{\neq}$ have been calculated by their standard equations and reported in the table 1.8. The values of energy of activation have also been obtained from the slopes of Arrehenius plots[31] and have been reported in the respective table.

TABLE - 1.8 : Thermodynamic and Activation Parameters
(For Uncatalysed and Catalysed reaction)

[propionic acid] = 0.15 mol dm^{-3} **[H_2SO_4]=3.0moldm^{-3} Temperature = 298K**			**[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 × 10^{-4} mol dm^{-3}**			
Kinetic Parameters						
Stages	**Energy of activation ($\Delta E^{\neq}$) KJ mol^{-1}**		**Enthalpy of activation ($\Delta H^{\neq}$) KJ mol^{-1}**	**Entropy of activation ($\Delta S^{\neq}$) J mol^{-1} K^{-1}**	**Frequency factor (pZ) dm^3 mol^{-1}Sec^{-1}**	**Free Energy of activation ($\Delta G^{\neq}$) KJ mol^{-1}**
	Cal.	**Gra.**				
Uncatalysed I stage (Without NaLS)	62.021	57.438	54.878	-96.11	25.52×10^7	25.276
Uncatalysed II stage (Without NaLS)	65.703	60.919	58.358	-93.84	33.58×10^7	29.455

Catalysed I stage (With NaLS)	56.618	55.696	53.136	-100.58	14.92×10^{7}	22.154
Catalysed II stage (With NaLS)	58.185	53.957	50.665	-123.82	32.67×10^{6}	15.795

(G) Effect of Neutral salt and specific ionic effects on reaction rates:

In the case of oxidation of propionic acid by potassium permanganate in the sulphuric acid medium, the primary kinetic salt effect was not observed by adding the neutral salts within the concentration limits as demanded for the applicability of Bronsted-Bjerum equation[32]. Hence the results obtained in term of specific ionic effect.

Specific effect of cations and anions:

In order to know the specific effect of cations, sulphates and nitrates of cations were taken at their identical molar concentrations and in order to know the specific effect of anions, sodium salt of anions were taken at their identical molar concentration. The order of the effectiveness of univalent, bivalent and trivalent ions has been found as:

For cations $Al^{3+} > Zn^{2+} > Mg^{2+} > Na^{+}$ (as their sulphate)
$Na^{+} > K^{+}$ (as their nitrates)
For anions $NO_3^{2-} > SO_4^{2-}$

It has been observed that the CH_3COO^{-} and F^{-} anions have the negative effect on the reaction velocity. The rate of both the stages decreases with the increases in the concentration of CH_3COO^{-} and F^{-} in the order $F^{-} > CH_3COO^{-}$.

(H) Effect of Manganous Mn(II) ion:

The effect of Mn(II) as a catalyst in the case of oxidation of permanganate is well known[33-34]. The catalytic effect of manganous sulphate in the present oxidation reaction has been studied and results have been reported in the table 1.9.

TABLE - 1.9 : Effect of Mn(II)

[propionic acid] = 0.15 mol dm^{-3} **[H_2SO_4] = 3.0 mol dm^{-3}** **Temperature = 298K**		**[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3}** **[NaLS] = 5.0 × 10^{-4} mol dm^{-3}**	
[$MnSO_4$]	**μ**	**$k_1 \times 10^{-3}$ Min^{-1}**	**$k_1'' \times 10^{-3}$ Min^{-1}**
0.0000	3.000	6.11	2.58
0.0001	3.0004	10.99	4.15
0.0002	3.0008	13.87	4.50
0.0003	3.0012	16.58	5.00
0.0004	3.0016	19.34	5.51

(I) Stoichiometry and product analysis:

Stoichiometry of the reaction was determined by analytical method. In this method the reaction mixture containing known excess of $KMnO_4$ over the substrate i.e. propionic acid were allowed to stand at room temperature for a sufficiently long time (36 hours). After that the amount of unreacted permanganate was estimated iodometrically using starch as an indicator. 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, the catalysed reaction is proceeds as follows:

$$5\,CH_3CH_2COOH + 2MnO_4^{-} + 6\,H^{+} \longrightarrow 2Mn^{2+} + 5CH_3CH_2OH + 5CO_2 + 3H_2O$$

Ethyl alcohal was identified by spot test method as given by Figel[35] and Carbon dioxide have been determined by routine test as the end products.The formation of intermediate free radical is confirmed by induced reduction of mercuric chloride. Low value of energy of activation also supports the same.

(J) Mechanism :

On the basis of the results of kinetic measurements facts and discussion the following mechanism for the oxidation reaction of propionic acid in the absence and presence of sodium lauryl sulphate as catalyst has been suggested.

(1) Mechanism and rate law for uncatalysed oxidation:

The mechanism proceeds with the formation of molecular $HMnO_4$ in sulphuric acid medium

$$MnO_4^- + H^+_{aq} \underset{}{\overset{K_2}{\rightleftharpoons}} HMnO_4 \text{ --------(1)}$$

This step is consistant with the spectroscopic evidence of existence of molecular $HMnO_4$. Now substrate reacts with $HMnO_4$, (that is more powerful oxidizing species of MnO_4^-) in the presence of water molecule.

$$CH_3CH_2COOH + HMnO_4 + H_2O \xrightarrow[\text{slow}]{k_1} CH_3CH_2COO^{\bullet} + HMnO_4^- + H_3O^+ \text{ -------- (2)}$$

This three body collision is difficult and thus explains the cause of slowness in the slowest reaction. It is rate determining step. All subsequent steps are very fast and not of kinetic importance, are as follows;

$$CH_3CH_2COO^{\bullet} \xrightarrow{\text{fast}} CH_3CH_2^{\bullet} + CO_2 \text{ -------(3)}$$

$$CH_3CH_2^{\bullet} + HMnO_4 \xrightarrow{\text{fast}} CH_3CH_2^{+} + HMnO_4^- \text{ --------(4)}$$

$$CH_3CH_2^{+} + H_2O \xrightarrow{\text{fast}} CH_3CH_2OH + H^+$$

$$CH_3CH_2^{\bullet} + CH_3CH_2^{\bullet} \xrightarrow{\text{fast}} C_4H_{10}$$

The above mechanism leads to suggest the rate expression as follow for uncatalysed reaction; in which the concentration of hydrogen ion and water have been withdrawn from main equation.

$$-\frac{d[MnO_4^-]}{dt} = K_S\,[CH_3CH_2COOH]\;[MnO_4^-]$$

Where

$$K_S = \frac{k_1\,K_1\,K_2\,[H^+]^2\,[H_2O]}{\{\,1 + K_2\,[H^+]\,\}}$$

(2) Mechanism and rate law for catalysed reaction:

The reaction rates have been found substantially increased in presence of anionic sodium lauryl sulphate surfactant. It is assumed that due to the electrostatic interaction between propionic acid and micelles of surfactant leads the increase in effective concentration which is responsible for the increase in reaction rate. The very low number ‘n’ of surfactant molecules i.e. below 20 is expected in micelles. The mechanism proposed, therefore involve the substrate – surfactant interaction, with the premiceller catalysis phenomenon as the n, calculated has the value below 20.

$$CH_3CH_2COOH + H^+_{aq} \overset{K_1}{\rightleftharpoons} CH_3CH_2COOH_2^+$$

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

(Molecular)

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

(n is below CMC)

$$(NaLS)_n + CH_3CH_2COOH_2^+ \xrightarrow{K_3} (NaLS)_n\text{-------}CH_3CH_2COOH_2^+$$

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

$$(NaLS)_n\text{-------}CH_3CH_2COOH_2^+ + HMnO_4 + H_2O \xrightarrow[\text{Slowest step}]{K_2} (NaLS)_n\text{--}CH_3CH_2COO^{\bullet} + HMnO_4^- + H_3O^+$$

Purely physical premiceller catalysis

$$(NaLS)_n\text{-------}CH_3CH_2COOH_2^+ \xrightarrow{\text{fast}} (NaLS)_n\text{----}CH_3CH_2^{\bullet} + CO_2$$

$$(NaLS)_n\text{----}CH_3CH_2^{\bullet} + HMnO_4 \xrightarrow{\text{fast}} (NaLS)_n + CH_3CH_2^{+} + HMnO_4^-$$

$$CH_3CH_2^{+} + H_2O \xrightarrow{\text{fast}} CH_3CH_2OH + H^+$$

The following rate law expression may be derived from above discussed steps considering that catalysed and uncatalysed reactions proceeds simultaneously.

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_1 k_2 K_1 K_2 K_3 [H^+]^2 [H_2O][CH_3CH_2COOH_2^+][MnO_4^-]}{\{1 + K_2 [H^+]\}}$$

$$-\frac{d[MnO_4^-]}{dt} = k'' \ [NaLS]_n \ [CH_3CH_2COOH_2^+][MnO_4^-]$$

Here

$$k'' = \frac{k_1 k_2 K_1 K_2 K_3 [H^+]^2 [H_2O]}{\{1 + K_2 [H^+]\}}$$

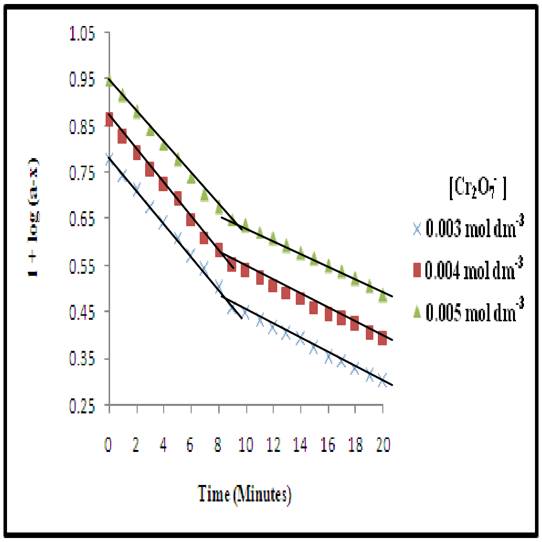


Figure - 1.2: variation of [Dichromate]

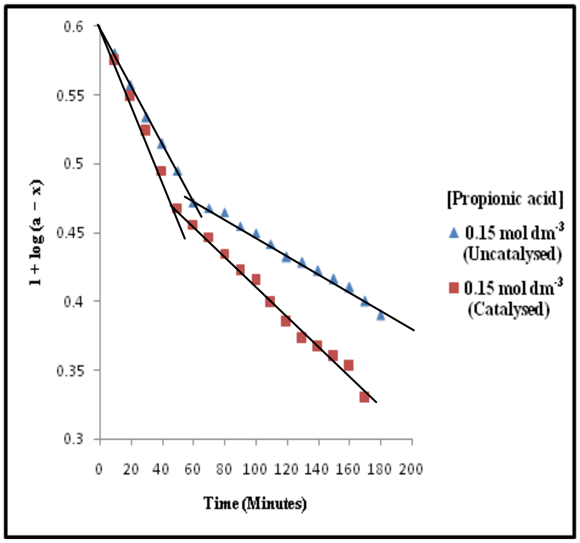
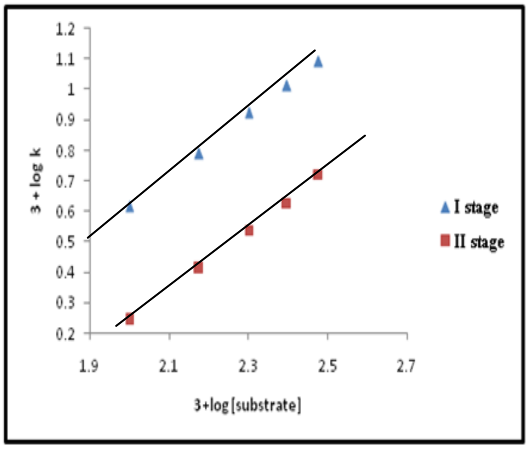


Figure – 1.1: Typical run for the oxidation reaction in sulphuric acid medium



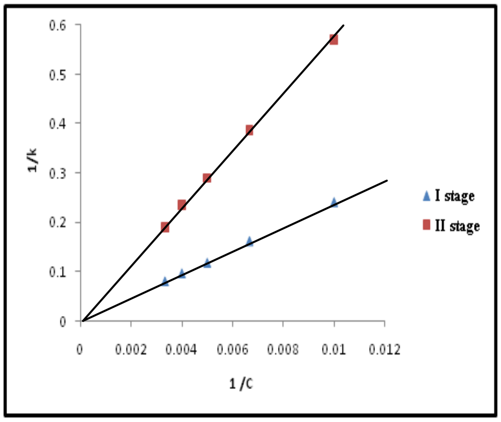


Figure - 1.4: Michaelis-Menten plot (Catalysed) **Figure - 1.3: log k Vs log [Substrate] Catalysed**

Conclusion:

It is evident from the rate law that reaction is first order with respect to substrate and oxidant. The role of surfactant is only as premiceller physical catalyst with no covalent bond formation between surfactant – substrate association.Rate law involve the acid concentration term and water molecule which has been explained in the light of Zucker-Hammett, Bunnett's and Bunnett-Olsen Hypothesis.

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