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A Kinetics study of miceller catalyzed oxidation of acetic acid by acidic permanganate

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Abstract

A kinetic study of oxidation of acetic 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. 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 to be in terms of mole ratio of permanganate ion and acetic acid consumed. Effect of specific ion on the reaction rate has also been reported. Activation parameters for the reaction are evaluated and the plausible mechanism is suggested.

Key words : Miceller, Oxidation, Permanganate ion.

Introduction

Kinetic study in the presence of micelles has become one of the very interesting subject of investigation now a days Surfactant have 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[1-4]. 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[5-10] hence the present work has been taken for the research. It described the detailed study on the miceller catalysed oxidation of acetic acid by acidic permanganate.

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 elucidate 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 hypotheses.

Experimental

The standard solution of acetic acid (BDH) and sodium lauryl sulphate (BDH) were prepared in double distilled water, H_2SO_4 (Analar) was used as a source of hydrogen ion. Permanganate solution was prepared as given by Vogel[11]. Standard salt solution were made by dissolving known amount of the solute in a given volume of distilled water.

Kinetic studies was performed by using systronic 104 spectrophotometer at 525nm *i.e.* at the absorbance maximum of permanganate at constant temperature. It was verified that there is no interference from other reagent at this wavelength. All kinetic measurement were conducted under pseudo first order conditions where the substrate was maintained in a large excess over the permanganate ion concentration.

Result and Discussion

(A) Dependency of reaction rate on permanganate concentration :

Dependency of reaction rate on permanganate has been studied by varying. Its 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.

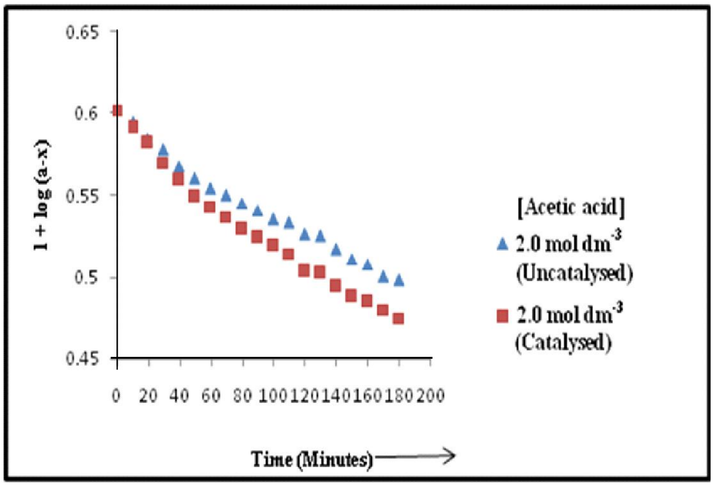

Figure 1.1 Typical run for the oxidation reaction in Sulphuric acid medium

SUMMARY Table 1.1
Dependence of rate on oxidant concentration

[Acetic Acid] = 2.0 mol dm^{-3}			[NaLS] = 1.0×10^{-4} mol dm^{-3}	
[H_2SO_4] = 4.0 mol dm^{-3}			Temperature = 298K	
$KMnO_4 \times 10^{-3}$ mol dm^{-3}	$k_1 \times 10^{-4}$ Min^{-1}		$k_1'' \times 10^{-4}$ Min^{-1}	
	Calculated	Graphical	Calculated	Graphical
0.5	24.57	23.95	13.91	13.30
0.75	24.78	25.1	13.63	12.86
1.0	24.42	24.87	13.93	13.14
1.25	24.30	24.18	13.40	13.90

(B) Dependency of reaction rate on substrate concentration :

For the determination of dependency of reaction rate on substrate concentration *i.e.* acetic acid, experiments were performed at 298K with different initial concentration of acetic 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 acetic acid. Table 1.2(A), 1.2(B).

Summary Table 1.2 (A)
Variation of Acetic acid concentration (Uncatalysed)

[H_2SO_4] = 4.0 mol dm^{-3}			[NaLS] = 1.0×10^{-4} mol dm^{-3}	
Temperature = 298K			[$KMnO_4$] × 1.0×10^{-3} mol dm^{-3}	
[Acetic acid] 10^{-3} mol dm^{-3}	$k_1 \times 10^{-4}$ Min^{-14}		$k_1'' \times 10^{-4}$ Min^{-1}	
	By Differential	By Graphical	By Differential	By Graphical
	method	method	method	method
1.0	9.94	9.90	5.46	5.80
2.0	19.15	18.56	10.82	11.16
3.0	28.53	29.24	16.50	15.86
4.0	38.00	39.20	22.80	22.70

Table 1.2 (B)
Variation of Acetic acid concentration (Catalysed)

$[H_2SO_4]$ = 4.0 mol dm^{-3} $[NaLS]$ = 1.0×10^{-4} mol dm^{-3}
Temperature = 298K $[KMnO_4] \times 1.0 \times 10^{-3}$ mol dm^{-3}

[Acetic acid] 10^{-3} mol dm^{-3}	$k_1 \times 10^{-4}$ Min^{-1}		$k_1'' \times 10^{-4}$ Min^{-1}	
	By Differential method	By Graphical method	By Differential method	By Graphical method
1.0	12.10	12.20	6.74	6.71
2.0	24.42	24.87	13.94	13.15
3.0	38.51	38.00	21.47	20.90
4.0	52.39	50.67	29.05	28.75

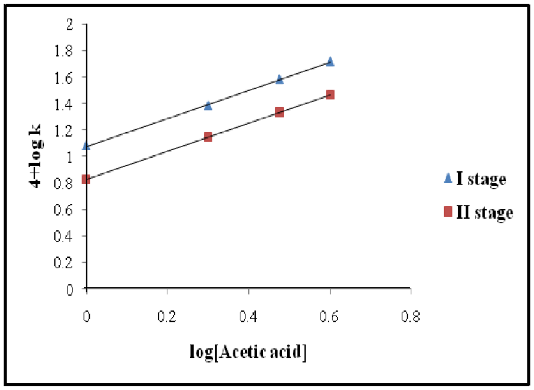

Figure1.2. log k Vs log [Acetic acid] Catalysed

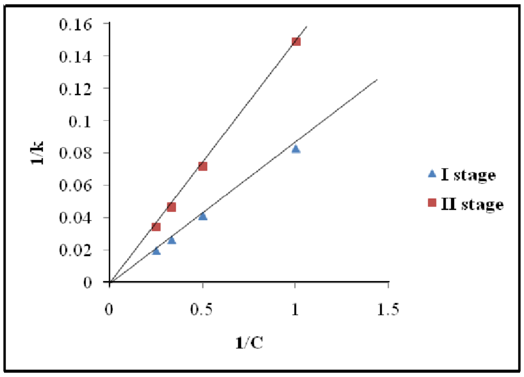

Figure 1.3. Michaelis Menten plot (Catalysed)

The plot of logarithm of [Acetic acid] with logarithm of rate constant (k_1 and k_1'') give straight line of approximately unit gradient in both the stages. These show that the order of reaction with respect to acetic 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 acetic acid, in both the stages and there is no kinetic evidence for intermediate complex formation between acetic acid and permanganate[12]. However if any complex is formed,its formation constant would be extremely small[13].

(C) 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 1.3). In the present study, the formation of premicellar aggregates are responsible for the miceller catalysis[14-17].

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 Piszkiewiez 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 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3}. Its maximum concentration used is 5.0×10^{-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 premicellar catalysis.

In present case the plot (figure 1.4) 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[18].

The results have been reported in the table 1.3 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[19-21].

Summary Table 1.3.
Dependence of rate on NaLS Concentration and catalytic constant :

[Acetic acid] = 2.0 mol dm^{-3} $[H_2SO_4]$ = 4.0 mol dm^{-3}		$[KMnO_4]$ = 1.0×10^{-3} mol dm^{-3} Temperature = 298K		
[NaLS] mol dm^{-3}	$k_1\times10^{-4}$ Min^{-1}	$k_c \times 10^4$ (litre $mol^{-1}Min^{-1}$)	$k''_1\times 10^{-4}Min^{-1}$	$k''_c\times 10^4$ (litre $mol^{-1}Min^{-1}$)
Uncatalysed (Absent)	19.20	---	10.80	---
1.0×10^{-4}	24.42	5.20	13.90	3.10
2.0×10^{-4}	29.53	5.15	17.20	3.20
3.0×10^{-4}	34.80	5.20	20.28	3.13
4.0×10^{-4}	40.30	5.27	23.90	3.25
5.0×10^{-4}	44.33	5.02	27.56	3.34

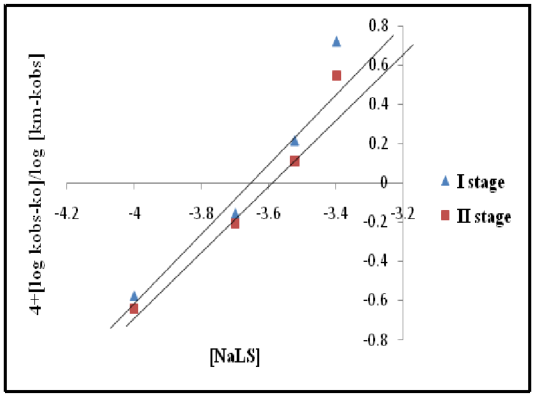

Figure 1.4. Piszkiewicz plots

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

The reaction were studied at different sulphuric acid and perchloric acid concentrations, keeping the constant concentration of acetic 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 1.4 and 1.5.

Summary Table 1.4.
Dependence of rate on Sulphuric acid concentration [H$^+$]

<table>
<tr><td colspan="3">[Acetic acid] = 2.0 mol dm^{-3}
Temperature = 298K</td><td colspan="2">[NaLS] = 1.0 ×10^{-4} mol dm^{-3}
[KMnO$_4$] = 1.0 × 10^{-3} mol dm^{-3}</td></tr>
<tr><td>[H$^+$] mol dm^{-3}</td><td>- H$_0$</td><td>-log a$_{H2O}$</td><td>k$_1$ × 10^{-4} Min^{-1}</td><td>k_1'' × 10^{-4} Min^{-1}</td></tr>
<tr><td>2.0</td><td>0.84</td><td>0.043</td><td>10.42</td><td>4.74</td></tr>
<tr><td>2.5</td><td>1.12</td><td>0.063</td><td>13.32</td><td>7.10</td></tr>
<tr><td>3.0</td><td>1.38</td><td>0.085</td><td>16.36</td><td>10.64</td></tr>
<tr><td>3.5</td><td>1.62</td><td>0.111</td><td>20.47</td><td>12.00</td></tr>
<tr><td>4.0</td><td>1.85</td><td>0.142</td><td>24.42</td><td>13.93</td></tr>
</table>

Summary Table 1.5.
Dependence of rate on perchloric acid concentration [H$^+$]

<table>
<tr><td colspan="3">[Acetic acid] = 2.0 mol dm^{-3}
Temperature = 298K</td><td colspan="2">[NaLS] = 1.0 ×10^{-4} mol dm^{-3}
[KMnO$_4$] = 1.0 × 10^{-3} mol dm^{-3}</td></tr>
<tr><td>[H$^+$] mol dm^{-3}</td><td>- H$_0$</td><td>-log a$_{H2O}$</td><td>k$_1$ × 10^{-4} Min^{-1}</td><td>k_1'' × 10^{-4} Min^{-1}</td></tr>
<tr><td>1.0</td><td>0.22</td><td>0.018</td><td>19.89</td><td>12.26</td></tr>
<tr><td>1.5</td><td>0.53</td><td>0.03</td><td>24.48</td><td>16.29</td></tr>
<tr><td>2.0</td><td>0.78</td><td>0.043</td><td>31.12</td><td>21.40</td></tr>
<tr><td>2.5</td><td>1.01</td><td>0.06</td><td>37.51</td><td>26.21</td></tr>
<tr><td>3.0</td><td>1.23</td><td>0.081</td><td>43.62</td><td>32.25</td></tr>
</table>

(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[22] 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[23] *i.e.* the Bunnett relationships (log [rate constant] + log $[H_o]$) against log a_{H2O}, log ([rate constant]– log $[H^+]$) against log a_{H2O} and (log [rate constant]–log $[H^+]$- H_o) against log a_{H2O} have been obtained. In the same way the Bunnett- Olsen plot[24] *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 1.6 and 1.7. The values of $-H_0$ and a_{H2O} have been taken from Bunnett[24], Paul and Long[25] respectively.

Summary Table 1.6.

Acid catalysis and different correlation (H_2SO_4 medium):

[Acetic acid] = 2.0 mol dm^{-3} Temperature = 298K		[NaLS] = 1.0×10^{-4} mol dm^{-3} $[KMnO_4]$ = 1.0×10^{-3} mol dm^{-3}		
S.No	Correlation	Parameters	Slope values	
			I stage	II stage
1	**Zucker- Hammett plots**			
(a)	log rate constant against $-H_0$	Slope	0.367	0.468
(b)	log rate constant against log $[H^+]$	Slope	1.23	1.58
2	**Bunnett's plots**			
(a)	log [rate constant] + log $[H_o]$ against log a_{H2O}	(ω)	- 6.40	- 5.52
(b)	log [rate constant] – log $[H^+]$ against log a_{H2O}	(ω*)	0.729	1.62
(c)	log [rate constant] – log $[H^+]$ - H_o against log a_{H2O}.	Slope	10.85	11.73
3	**Bunnett - Olsen plot (L.F.E.R)**			
(a)	log [rate constant] +H_0 against H_0 + log $[H^+]$	(ϕ)	0.899	0.762

Summary Table 1.7.

Acid catalysis and different correlation ($HClO_4$ medium):

[Acetic acid] = 2.0 mol dm^{-3} Temperature = 298K		[NaLS] = 1.0×10^{-4} mol dm^{-3} [$KMnO_4$] = 1.0×10^{-3} mol dm^{-3}		
S.No	Correlation	Parameters	Slope values	
			I stage	II stage
1	**Zucker- Hammett plots**			
(a)	log rate constant against $-H_0$	Slope	0.348	0.420
(b)	log rate constant against log [H^+]	Slope	0.730	0.882
2	**Bunnett's plots**			
(a)	(log [rate constant] + log [H_o]) against log a_{H2O}	(ω)	a	-9.09
(b)	(log [rate constant] – log [H^+]) against log a_{H2O}	(ω*)	-1.834	-0.712
(c)	(log [rate constant] – log[H^+] - H_o) against log a_{H2O}.	Slope	12.75	13.87
3	**Bunnett - Olsen plot (L.F.E.R)**			
(a)	(log [rate constant] +H_0 against (H_0 + log [H^+])	(ϕ)	1.22	1.09

(E) 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 constant the concentration of all the reactants. The result have been recorded in the table 1.8.

Summary table 1.8. Effect of temperature variation

[Acetic acid] = 2.0 mol dm^{-3} [H_2SO_4] = 4.0 mol dm^{-3}			[$KMnO_4$]= 1.0×10^{-3} mol dm^{-3} Temperature = 298K	
Temperature (K)	Velocity constant for Uncatalysed NaLS = Nil		Velocity constant for Catalysed [NaLS = 1.0×10^{-4}M]	
	$k_1 \times 10^{-4} Min^{-1}$	$k_1'' \times 10^{-4} Min^{-1}$	$k_1 \times 10^{-4} Min^{-1}$	$k_1'' \times 10^{-4} Min^{-1}$
298	19.15	10.82	24.42	13.93
303	26.86	15.99	30.06	20.01
308	40.55	22.41	49.51	27.55
313	54.27	32.03	59.87	38.03
Temperature Range (K)	Temperature coefficient for Uncatalysed		Temperature coefficient for Catalysed	
	I stage	II stage	I stage	II stage
298-308	2.12	2.07	2.02	1.97
303-313	2.04	2.01	1.99	1.90

Form 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 1.9 obtained. The values of energy of activation have also been obtained from the slopes of Arrehenius plots and have been reported in the respective tables.

Summary table 1.9. Thermodynamic and Activation Parameters
(for uncatalysed and catalysed reactions)

<table>
<tr><td colspan="4">[Acetic acid] = 2.0 mol dm^{-3}
[H_2SO_4] = 4.0 mol dm^{-3}</td><td colspan="3">[$KMnO_4$]= 1.0 × 10^{-3} mol dm^{-3}
[NaLS]= 1.0 × 10^{-4} mol dm^{-3}
Temperature = 298K</td></tr>
<tr><td colspan="7">Kinetic Parameters</td></tr>
<tr><td rowspan="2">Stages</td><td colspan="2">Energy of activation ($\Delta E^{\neq}$) KJ mol^{-1}</td><td rowspan="2">Enthalpy of activation ($\Delta H^{\neq}$) KJ mol^{-1}</td><td rowspan="2">Entropy of activation ($\Delta S^{\neq}$) Jmol^{-1}K^{-1}</td><td rowspan="2">Frequency factor (pZ) dm^{3}mol^{-1} Sec^{-1}</td><td rowspan="2">Free Energy of activation ($\Delta G^{\neq}$) KJ mol^{-1}</td></tr>
<tr><td>Cal.</td><td>Gra.</td></tr>
<tr><td>Uncatalysed I stage (Without NaLS)</td><td>59.2719</td><td>55.7965</td><td>52.5920</td><td>-111.812</td><td>38.15×10^6</td><td>18.1587</td></tr>
<tr><td>Uncatalysed II stage (Without NaLS)</td><td>57.5292</td><td>55.8687</td><td>51.7496</td><td>-119.472</td><td>15.14×10^6</td><td>15.9529</td></tr>
<tr><td>Catalysed I stage (With NaLS)</td><td>54.0029</td><td>49.0214</td><td>50.9263</td><td>-115.562</td><td>24.30×10^5</td><td>15.3564</td></tr>
<tr><td>Catalysed II stage (With NaLS)</td><td>52.0724</td><td>51.8001</td><td>50.6658</td><td>-121.281</td><td>12.17×10^6</td><td>13.3111</td></tr>
</table>

Note: The graphical values of $\Delta E^{\neq}$ have been used for determination of other activation parameters wherever required.

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

In the case of oxidation of acetic 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[26]. Hence the results obtained in term of specific ionic effect are summarized in the following tables. Total ionic strengths of (*i.e.* μ) in the reaction mixture has also been given.

Specific effect of cations :

In order to know the specific effect of cations, sulphates and nitrates of cations were taken at their identical molar concentrations. The variation of cations with common anions (SO_4^{2-}, NO_3^{2-}) has been given in table 1.10.

Summary Table 1.10.
Specific effect of cations

[Acetic acid] = 2.0 mol dm^{-3} [H_2SO_4] = 4.0 mol dm^{-3} Temperature = 298K				[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3} [NaLS] = 1.0 × 10^{-4} mol dm^{-3}			
Na_2SO_4				**$MgSO_4$**			
Na_2SO_4 mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}	$MgSO_4$ mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}
0.00	4.000	24.42	13.94	0.00	4.000	24.42	13.94
0.001	4.003	28.79	17.19	0.001	4.004	31.33	21.46
0.002	4.006	33.39	19.22	0.002	4.008	37.87	24.48
0.003	4.009	37.87	23.26	0.003	4.012	41.97	29.02
0.004	4.012	43.18	27.46	0.004	4.016	47.79	32.15
$ZnSO_4$				**$Al_2(SO_4)_3$**			
$ZnSO_4$ mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}	$Al_2(SO_4)_3$ mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}
0.00	4.000	24.42	13.94	0.00	4.000	24.42	13.94
0.001	4.004	35.82	25.17	0.001	4.015	38.26	28.36
0.002	4.008	42.61	29.07	0.002	4.03	46.64	32.47
0.003	4.012	47.21	34.17	0.003	4.045	54.12	38.17
0.004	4.016	53.54	38.3	0.004	4.06	59.88	42.41
KNO_3				**$NaNO_3$**			
KNO_3 mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}	$NaNO_3$ mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}
0.00	4.000	24.42	13.94	0.00	4.000	24.42	13.94
0.001	4.0025	28.16	15.41	0.001	4.0025	33.27	17.23
0.002	4.005	33.27	17.41	0.002	4.005	39.28	20.38
0.003	4.0075	38.51	20.17	0.003	4.0075	45.48	24.35
0.004	4.01	43.18	23.57	0.004	4.01	49.51	28.35

Specific effect of anions :

In order to know the specific effect of anions, sodium salt of anions were taken at their identical molar concentration. The variation of anions with common cations (Na^+) has been given in table 1.11.

Summary table 1.11.
Specific effect of anions :

[Acetic acid] = 2.0 mol dm^{-3} [H_2SO_4] = 4.0 mol dm^{-3} Temperature = 298K				[$KMnO_4$] = 1.0 × 10^{-3} mol dm^{-3} [NaLS] = 1.0 × 10^{-4} mol dm^{-3}			
Na_2SO_4				**$NaNO_3$**			
Na_2SO_4 mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}	$NaNO_3$ mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}
0.00	4.000	24.42	13.94	0.00	4.000	24.42	13.94
0.001	4.003	28.79	17.19	0.001	4.0025	33.27	17.23
0.002	4006	33.39	19.22	0.002	4.005	39.28	20.38
0.003	4.009	37.87	23.26	0.003	4.0075	45.48	24.35
0.004	4.012	43.18	27.46	0.004	4.010	49.51	28.35
NaF				**CH_3COONa**			
NaF mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}	CH_3COONa mol dm^{-3}	μ	$k_1 \times 10^{-4}$ Min^{-1}	$k_1'' \times 10^{-4}$ Min^{-1}
0.00	4.000	24.42	13.94	0.00	4.000	24.42	13.94
0.001	4.001	22.29	12.00	0.001	4.001	23.01	12.57
0.002	4.002	19.91	11.07	0.002	4.002	21.03	11.64
0.003	4.003	16.97	9.53	0.003	4.003	17.41	10.55
0.004	4.004	14.26	8.06	0.004	4.004	15.08	10.20

The tables shows that the cations and anions do exert their specific effect on the reaction velocity. 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 anion $NO_3^{2-} > SO_4^{2-}$

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 $F^- > CH_3COO^-$.

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

The effect of Mn(II) as a catalyst in the case of oxidation of permanganate is well known[27-28]. The catalytic effect of manganous sulphate in the present oxidation reaction has been studied and results have been reported in the table 1.12.

Summary Table 1.12.
Effect of Mn (II)

<table>
<tr><td colspan="2">[Acetic acid] = 2.0 mol dm^{-3}
[H_2SO_4] = 4.0 mol dm^{-3}
Temperature = 298K</td><td>[$KMnO_4$] = 1.0×10^{-3} mol dm^{-3}
[NaLS] = 1.0×10^{-4} mol dm^{-3}</td></tr>
<tr><td colspan="3">[$MnSO_4$]</td></tr>
<tr><td>μ</td><td>$k_1 \times 10^{-4}$ Min^{-1}</td><td>$k_1^{''} \times 10^{-4}$ Min^{-1}</td></tr>
<tr><td>4.000</td><td>24.42</td><td>13.94</td></tr>
<tr><td>4.0004</td><td>42.61</td><td>32.91</td></tr>
<tr><td>4.0008</td><td>51.82</td><td>35.02</td></tr>
<tr><td>4.0012</td><td>59.88</td><td>41.95</td></tr>
<tr><td>4.0016</td><td>69.09</td><td>45.37</td></tr>
</table>

(H) 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.* acetic 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:

$$5\ CH_3COOH + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + CH_3OH + 5CO_2 + 3H_2O$$

Methyl alcohol was identified by spot test method as given by Figel[29] and Carbon dioxide have been determined as the end products by lime water test. The evolution of gas give the positive test for CO_2 as the limewater turns milky after 4 to 6 hours in each case. The formation of intermediate free radical is confirmed by induced reduction of mercuric chloride. Low value of energy of activation also supports the same.

(I) Mechanism :

Keeping in the results of kinetic measurement facts and discussion an humble attempts has been made to envisage a mechanism for the oxidation reaction of acetic acid in the absence and presence of sodium lauryl sulphate as catalyst.

(1) Mechanism and rate law for uncatalysed oxidation

$$CH_3COOH + H^+_{aq} \underset{}{\overset{K_1}{\rightleftharpoons}} CH_3COOH_2^+ \text{ --------(1)}$$

$$MnO_4^- + H^+_{aq} \overset{K_2}{\rightleftharpoons} HMnO_4 \text{ --------(2)}$$

This step is consistant with the spectroscopic evidence of existence of molecular $HMnO_4$, therefore cumulative effect explains the catalysis by mineral acid[30]. Now protonated substrate reacts with $HMnO_4$, (that is more powerful oxidizing species of MnO_4^-) in the presence of water molecule.

$$CH_3COOH + HMnO_4 + H_2O \xrightarrow[\text{slow}]{k_1}$$

$$CH_3COO^{\bullet} + HMnO_4^- + H_3O^+ \text{ --------(3)}$$

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;

$$RCH_3COO^{\bullet} \xrightarrow{\text{fast}} CH_3^{\bullet} + CO_2 \text{ -------(4)}$$

$$CH_3^{\bullet} + HMnO_4 \xrightarrow{\text{fast}} CH_3^+ + HMnO_4^- \text{ --------(5)}$$

$$CH_3^+ + H_2O \xrightarrow{\text{fast}} CH_3OH + H^+$$

$$CH_3^{\bullet} + CH_3^{\bullet} \xrightarrow{\text{fast}} C_2H_6$$

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 withdraw from main equation.

$$-\frac{d[MnO_4^-]}{dt} = K_S\,[CH_3COOH]\,[MnO_4^-]$$

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 acetic 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.

$$CH_3COOH + H^+_{aq} \overset{K_1}{\rightleftharpoons} CH_3COOH_2^+$$

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

(Molecular)

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

(n is below CMC)

$$(NaLS)_n + CH_3COOH_2^+ \xrightarrow{K_3} (NaLS)_n\text{-------}CH_3COOH_2^+$$

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

$$(NaLS)_n\text{-------}CH_3COOH_2^+ + HMnO_4 + H_2O \xrightarrow[\text{Slowest step}]{k_2} (NaLS)_n\text{----}CH_3COO^{\bullet} + HMnO_4^{\bullet} + H_3O^+$$

Purely physical premiceller catalysis

$$(NaLS)_n\text{----}CH_3COO^{\bullet} \xrightarrow{\text{fast}} (NaLS)_n\text{----}CH_3^{\bullet} + CO_2$$

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

$$CH_3^+ + H_2O \xrightarrow{\text{fast}} CH_3OH + H^+$$

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

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_1\,k_2\,K_1\,K_2\,K_3[H^+]^2\,[H_2O][CH_3COOH_2^+][MnO_4^-]}{\{1 + K_2\,[H^+]\}}$$

Here

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

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 and Bunnett-Olsens Hypotheses.

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