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Permanganatic oxidation of neomycine sulphate salt in basic media: a kinetic study

Narayan V. Lawale[1], Bhagwan Singh Dobhal[2], Sandip Singh Gaur[3] and Rajendra Pardeshi*[4]

[1] Moreshwar Arts, Commerce and Science College, Bhokardan Dist Jalna, Maharashtra, India

[2] Badrinarayan Barwale, Arts, Commerce and Science College, Jalna. Maharashtra, India

[3] Sant Ramdas Arts, Science and commerce College Ghansawangi. Dist Jalna. Maharashtra, India

[4] Sant Ramdas Arts, Science and commerce College Ghansawangi. Dist Jalna. Maharashtra, India

ABSTRACT

Permanganatic oxidation of Neomycine sulphate salt has been studied at different temperatures using spectrophotometer under alkaline conditions. The effect of variation of substrate Neomycine sulphate salt (NS), oxidant (KMnO₄) and NaOH was studied under pseudo first order reaction conditions. The effect of different salts and solvents on oxidation of NS was also studied. The reaction was found to be first order with respect to oxidant, substrate and NaOH..

Keywords: Neomycine sulphate salt (NS), KMnO4 , permanganatic oxidation, alkaline permanganate

INTRODUCTION

In recent years there is increasing trends to study the oxidation of medicinal drugs by various oxidizing agents [1-3]. This is because, it is necessary to remove the pharmaceutical ingradient present in the the waste water. The oxidative degradation is one of the suitable methods. It will oxidize the medicinal drugs to some nontoxic materials. Further, it is also necessary to know oxidation for assessing the stability of drug. Neomycine sulphate is an antibiotic medicinal drug, with molecular formula $C_{20}H_{46}O_{18}$ xH_2SO_4 and molecular weight 615 g mol^{-1}.

Potassium permanganate is a widely used oxidant, works in acidic, basic and in neutral media. It has +2 to +7 oxidation states. In the present investigation, we report here with oxidation of neomycine sulphate by potassium permanganate under basic condition.

EXPERIMENTAL

For the present study distilled water was prepared in the laboratory using all quick fit glass assembly distillation units. A pinch of KOH and KMnO₄ was added the pH of the distilled water was monitor. All solutions were prepared in double distilled water a stock solution 0.01M KMnO₄ was

prepared and standardized using oxalate. A thermostat of locally assembled Dinesh make was used to maintain temperature constant. Neomycine sulphate salt was purchased from local Chemical traders of Hi-media chemicals. All kinetic runs were carried out in thermostat by champing the conditions such as variation in oxidant, variation in substrate, variation in NaOH, effect of temperature, effect of salt and effect of solvent. All kinetic runs were carried out using double beam spectrophotometer (ELICO SL 210) at 525 nm.

Equimolar solution of substrate and oxidant was taken in beaker. A small quantity of base was added the solution was left overnight. Precipitate was not observed and it was not possible to obtain product mass.

RESULT AND DISCUSSION

Effect of variation of Substrate (NS) concentration:-

To study the effect of variation of concentration of substrate the sets are prepared in which the concentration of NS was varied from 1 x 10^{-3} to 9 x 10^{-3} M, keeping constant concentration of [KMnO₄]= 1 x10^{-3} M, [NaOH] = 1 M . As the reaction has been studied under pseudo first order condition pseudo first order rate constants were calculated. It is clear

that pseudo first order rate constants were found to increase with increasing concentration [4] of NS in irregular way. When initial rate is plotted against concentration of NS, the trend line is linear with positive slope when logk versus [NS] is plotted it confirm the fractional order of reaction. Hence the reaction under pseudo first order rate depends on the concentration of substrate.

Table 1: Pseudo first order rate constant at = 25⁰C ± 0.5⁰C keeping variation in substrate (NS).

[NS]	[KMnO₄]	[NaOH]	k
1×10^{-3}	1×10^{-3}	1M	1.32×10^{-2}
2×10^{-3}	1×10^{-3}	1M	1.49×10^{-2}
3×10^{-3}	1×10^{-3}	1M	1.69×10^{-2}
4×10^{-3}	1×10^{-3}	1M	1.55×10^{-2}
5×10^{-3}	1×10^{-3}	1M	1.74×10^{-2}
6×10^{-3}	1×10^{-3}	1M	1.89×10^{-2}
7×10^{-3}	1×10^{-3}	1M	2.09×10^{-2}
8×10^{-3}	1×10^{-3}	1M	1.98×10^{-2}
9×10^{-3}	1×10^{-3}	1M	1.99×10^{-2}

As the reaction has been studied under pseudo first order condition using equation

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

Which is modified as:

$$k = \frac{2.303}{t} \log \frac{(OD)_\infty - (OD)_0}{(OD)_\infty - (OD)_t}$$

Effect of variation of oxidant (KMnO₄**) concentration:-**

To study the effect of variation of oxidant, we have taken substrate concentration 1×10^{-3} mol/dm³, NaOH (1M) and temperature was kept constant $25^0C \pm 0.5^0C$ in thermostat [5]. The rate constant value shows irregular trend.

*Table 2: Pseudo first order rate constant at = 25⁰C ± 0.5⁰C keeping variation in oxidant (*KMnO₄*).*

[NS]	[KMnO₄]	[NaOH]	k
1×10^{-3}	1×10^{-3}	1M	2.7×10^{-2}
1×10^{-3}	2×10^{-3}	1M	2.01×10^{-2}
1×10^{-3}	3×10^{-3}	1M	2.14×10^{-2}
1×10^{-3}	4×10^{-3}	1M	2.57×10^{-2}
1×10^{-3}	5×10^{-3}	1M	2.44×10^{-2}
1×10^{-3}	6×10^{-3}	1M	2.77×10^{-2}
1×10^{-3}	7×10^{-3}	1M	2.35×10^{-2}
1×10^{-3}	8×10^{-3}	1M	2.2×10^{-2}
1×10^{-3}	9×10^{-3}	1M	2.22×10^{-2}

Effect of variation of NaOH concentration:-

To study the effect of variation of concentration of Sodium Hydroxide (NaOH), in the experimental sets the concentration of NaOH is varied from 1×10^{-3} to 9×10^{-3} M, keeping constant concentration i.e. [NS]= 1×10^{-3} and [KMnO₄] = 5×10^{-3} M. It is clear from that pseudo first order rate constants decreases with change in concentration of NaOH confirming the first order dependence with respect to base [6]. The trend becomes irregular at higher concentration of base.

Table 3: Pseudo first order rate constant at = 25⁰C ± 0.5⁰C keeping variation in NaOH concentration:

[NS]	[KMnO₄]	[NaOH]	k
1×10^{-3}	5×10^{-3}	1×10^{-1}	2.06×10^{-2}
1×10^{-3}	5×10^{-3}	2×10^{-1}	1.81×10^{-2}
1×10^{-3}	5×10^{-3}	3×10^{-1}	1.77×10^{-2}
1×10^{-3}	5×10^{-3}	4×10^{-1}	1.58×10^{-2}
1×10^{-3}	5×10^{-3}	5×10^{-1}	1.69×10^{-2}
1×10^{-3}	5×10^{-3}	6×10^{-1}	2.01×10^{-2}
1×10^{-3}	5×10^{-3}	7×10^{-1}	2.12×10^{-2}
1×10^{-3}	5×10^{-3}	8×10^{-1}	1.98×10^{-2}
1×10^{-3}	5×10^{-3}	9×10^{-1}	2.07×10^{-2}

Effect of variation of temperature: -

The effect of temperature was studied keeping constant concentration of all reactants such as [KMnO₄] = 5×10^{-3} M, [NS] = 1×10^{-3} M and [NaOH] = 1 M. The temperature variation was done in the range of 25^0C to 50^0C. The energy of activation was calculated by plotting graph between log k verses 1/T, a straight line was obtained [7].

$$k = \frac{k_B}{T} e^{\frac{\Delta Ea^{\#}}{RT}} e^{\frac{\Delta S^{\#}}{R}}$$

The modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner sphere mechanism. The free energy change (ΔG, enthalpy changes (ΔH) and entropy change (ΔS) was determined.

Table 4: Pseudo first order rate constant at different temperatures:

Temp.	[NS]	[KMnO₄]	[NaOH]	k
25^0C	1×10^{-3}	5×10^{-3}	1M	2.99×10^{-2}
30^0C	1×10^{-3}	5×10^{-3}	1M	2.51×10^{-2}
35^0C	1×10^{-3}	5×10^{-3}	1M	2.57×10^{-2}
40^0C	1×10^{-3}	5×10^{-3}	1M	2.88×10^{-2}
45^0C	1×10^{-3}	5×10^{-3}	1M	3.2×10^{-2}
50^0C	1×10^{-3}	5×10^{-3}	1M	2.98×10^{-2}

The energy of activation was found to be -2060.23 J/mole.This activation energy was used to calculate the enthalpy of activation (ΔH) using equation

$ΔH = ΔE — RT$

The value of (ΔH) decreases with increase in temperature, which is obvious. The average (ΔS) was found to be -125.84J/mole. From this, we calculated entropy of activation using formula

$$k = \frac{k_B}{T} e^{\frac{\Delta Ea^{\#}}{RT}} e^{\frac{\Delta S^{\#}}{R}}$$

Where *k*= pseudo first order rate constant

k_B = Boltzmann constant

T = Temperature

Table 5: Thermodynamic parameter of the kinetic oxidation process:

T	k	ΔH#(J mole-1)	ΔS#(J mole-1)	ΔG#(J mole-1)
298	0.0299	-4537.8045	-125.6474	32905.1145
303	0.0251	-4579.3745	-126.2898	33686.4224
308	0.0257	-4620.9445	-126.2156	34253.4676
313	0.0288	-4662.5145	-125.8162	34717.9436
318	0.032	-4704.0845	-125.4480	35188.3832
323	0.0298	-4745.6545	-125.7180	35861.2507

The enthalpy change increase with increase in temperature. It ranges from -4537.80 J/mole to -4747.65 J/mole. The average an enthalpy was found to be -4641.72 J/mole. The free energy change also increases with temperature. The average free energy (ΔG) was then calculated using (ΔH) and (ΔS) as per the equation

$$\Delta G = \Delta H - T\Delta S$$

It was observed that (ΔG) increases with increase in temperature. The average (ΔG) was found to be 34435.42 J/mol.

A plot of (ΔH) verses (ΔS) is linear which is followed by this equation

$$(\Delta H) = \beta \, \Delta S$$

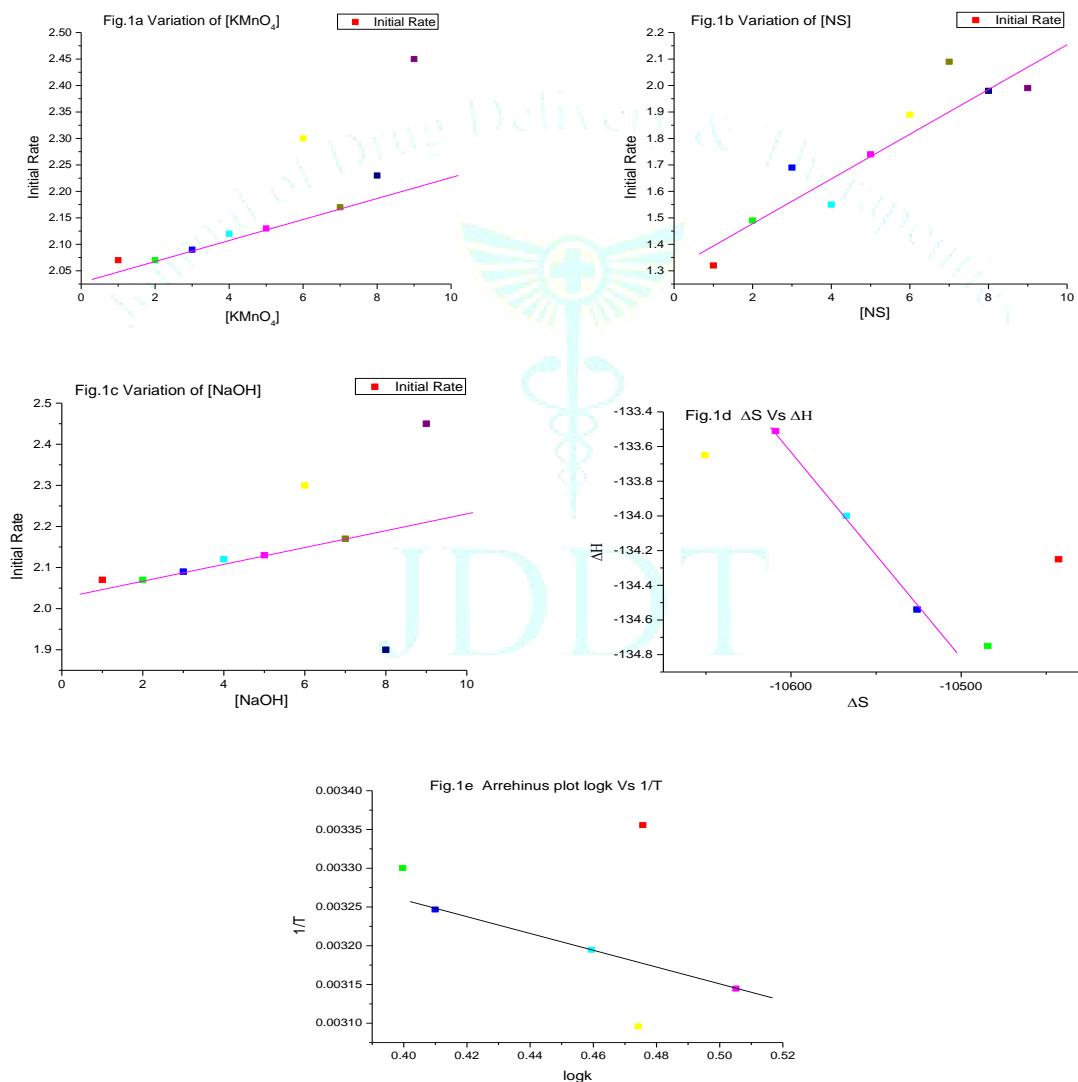Where β is called iso kinetic temperature, for NS it is=**36.88 k**

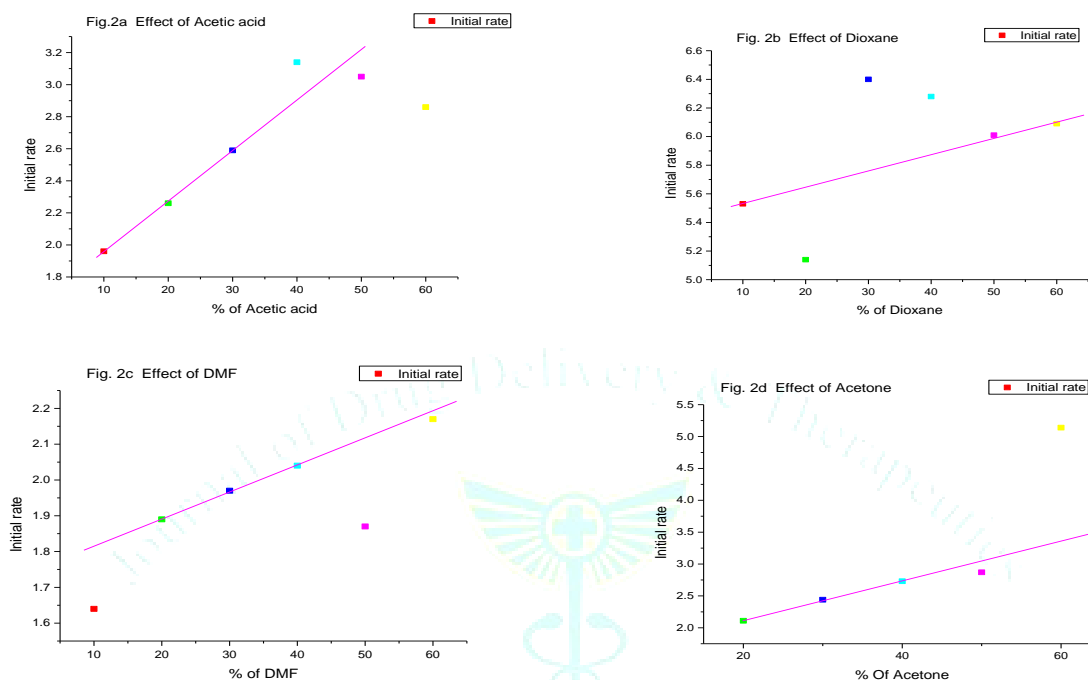*Figure 1: Pseudo first order rate constant at variation in oxidant, substrate, base and temperature.*

Effect of variation of solvent concentration: -

The reaction was monitored in four different solvents, namely 1,4 dioxane ,Acetic acid ,DMF ,Acetone. The rate constant of acetone was found to be less compared to other solvent. The rate constant in acetone decreases with increase in percentage of solvent. In DMF rate constant increases with increases in percentage of solvent. For acetic acid also the rate constant decreases, but no regular trend was observed for 1, 4 dioxane.

Table 6: Pseudo first order rate constant at = $25^0C \pm 0.5^0C$ keeping variation in solvent concentration:

[NS] = 1 X10⁻³; [KMnO₄] = 5 X 10⁻³; [NaOH] = 1M   ; [Temp.] = $25^0C \pm 0.5^0C$

Percentage of Solvent	Rate constant (sec⁻¹)			
	1,4 dioxane	Acetic Acid	DMF	Acetone
10 %	2.53×10^{-1}	1.96×10^{-1}	1.64×10^{-1}	--
20 %	5.14×10^{-1}	2.26×10^{-1}	2.19×10^{-1}	3.44×10^{-1}
30 %	6.4×10^{-2}	2.59×10^{-2}	1.97×10^{-2}	5.14×10^{-2}
40 %	6.28×10^{-2}	3.14×10^{-2}	3.17×10^{-2}	2.73×10^{-2}
50 %	6.01×10^{-2}	3.05×10^{-2}	1.87×10^{-2}	2.87×10^{-2}
60 %	5.13×10^{-2}	2.86×10^{-2}	2.83×10^{-2}	5.14×10^{-2}

Figure 2: Pseudo first order rate constant at variation in solvent and its concentration.

Effect of variation of salts:-

To study the effect of variation of salts, the concentration of salts was varied from 1 x 10⁻³ to 9 x 10⁻³ M, keeping constant concentration of reactants such as [KMnO₄] = 5 x 10⁻³ M, [NS] = 1 x 10⁻³ M, [NaOH] 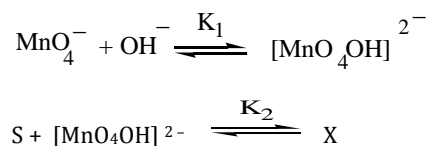= 1 M. From the obtained results, it is clear that pseudo first order rate constant k_{obs} increases with the increase in concentration of salts. A plot of log k_{obs} vs $\sqrt{\mu}$, according to extended Bronsted Debye-Huckel equation was found to be linear with negative slopes (NaCl, CaCl₂, AlCl₃, Na₂SO₄ and Na₃PO₄) indicating negative salt effect.
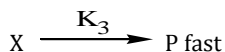
Table 7: Pseudo first order rate constant at = $25^0C \pm 0.5^0C$ keeping variation in salts concentration:

[NS] = 1 X10⁻³; [KMnO₄] = 5 X 10⁻³; [NaOH] = 1M ; [Temp.] = $25^0C \pm 0.5^0C$

Conc. Of Salt	Rate Const.(sec⁻¹)				
	NaCl	CaCl₂	AlCl₃	Na₂SO₄	Na₃PO₄
1×10^{-2}	2.29×10^{-2}	1.84×10^{-2}	1.79×10^{-2}	2×10^{-2}	2.18×10^{-2}
2×10^{-2}	1.62×10^{-2}	2.12×10^{-2}	1.91×10^{-2}	1.82×10^{-2}	2.8×10^{-2}
3×10^{-2}	1.89×10^{-2}	2.34×10^{-2}	1.94×10^{-2}	1.64×10^{-2}	2.09×10^{-2}
4×10^{-2}	1.95×10^{-2}	2.35×10^{-2}	2.07×10^{-2}	1.61×10^{-2}	2×10^{-2}
5×10^{-2}	1.79×10^{-2}	2.34×10^{-2}	2.01×10^{-2}	1.6×10^{-2}	1.98×10^{-2}
6×10^{-2}	2.69×10^{-2}	2.42×10^{-2}	2.17×10^{-2}	1.41×10^{-2}	1.9×10^{-2}
7×10^{-2}	2.63×10^{-2}	2.81×10^{-2}	2.27×10^{-2}	1.42×10^{-2}	1.43×10^{-2}
8×10^{-2}	1.86×10^{-2}	2.88×10^{-2}	2.6×10^{-2}	1.32×10^{-2}	1.19×10^{-2}
9×10^{-2}	1.86×10^{-2}	2.79×10^{-2}	2.67×10^{-2}	1.09×10^{-2}	1.48×10^{-2}

Mechanism:

The mechanism of basic oxidation of Neomycine sulphate introduce the formation of hydroxyl ion in the first step, which then reacts with substrate to form a complex. The complex formed convert into product. The last step is a fast process.

$$MnO_4^- + OH^- \xrightleftharpoons{K_1} [MnO_4OH]^{2-}$$

$$S + [MnO_4OH]^{2-} \xrightleftharpoons{K_2} X$$

$$X \xrightarrow{K_3} P \text{ fast}$$

Therefore the rate of reaction can be given as:

Rate = K_3 [X]   -------------- (1)

Applying law of mass action:

$$K_1 = \frac{[MnO_4OH]^{2-}}{[MnO_4]^- [OH]}$$ -------------- (2)

$$K_2 = \frac{[X]}{[S][MnO_4OH]^-}$$ -------------- (3)

The total of MnO_4^- i.e. $[MnO_4^-]_T$ is given as;

$[MnO_4^-]_T = [MnO_4^-] + [X]$ -------------- (4)

Substituting (3) in (4)

$[MnO_4^-]_T = [MnO_4^-] + K_2 [S] [MnO_4OH]^{2-}$ ------------- (5)

Substituting equation (2) in (5)

$[MnO_4^-]_T = [MnO_4^-] + K_1K_2 [S] [MnO_4^- [OH^-]$

$\qquad = [MnO_4^-] \{1 + K_1K_2 [S] [OH^-]\}$

$\therefore [MnO_4^-] = \dfrac{[MnO_4^-]_T}{1 + K_1K_2[S] [OH^-]}$ -------------- (6)

Similarly for base OH^-,

$[OH^-]_T = [OH^-] + [MnO_4OH]^{2-} + [X]$ -------------- (7)

Substituting equation (3) in (7);

$[OH^-]_T = [OH^-] + [MnO_4OH]^{2-} + K_2 [S] [MnO_4OH]^{2-}$ ------ (8)

Substituting equation (2) in (7)

$[OH^-]_T = [OH^-] + K_1[MnO_4^-] [OH^-] + K_1K_2 [S] [MnO_4^-] [OH^-]$

$\qquad = [OH^-] \{1 + K_1 [MnO_4^-] + K_1K_2 [S] [OH^-]\}$

$\therefore [OH^-] = \dfrac{[OH^-]_T}{1 + K_1[MnO_4^-] + K_1K_2[S] [OH^-]}$ ----- (9)

But rate of reaction can be given as:

Rate $\quad = K_3$ [X]

$\qquad = K_3K_2$ [S] $[MnO_4OH]^{2-}$

$\qquad = K_3K_1K_2$ [S] $[MnO_4^-]$ $[OH^-]$ ------ (10)

Substituting equation (6) and (9) in (10)

Rate $= \dfrac{K_3K_1K_2[S][MnO_4^-] + [OH^-]_T}{(1 + K_1K_2[S][OH^-](1 + K_1[MnO_4^-] + K_1K_2[S] [OH^-]}$

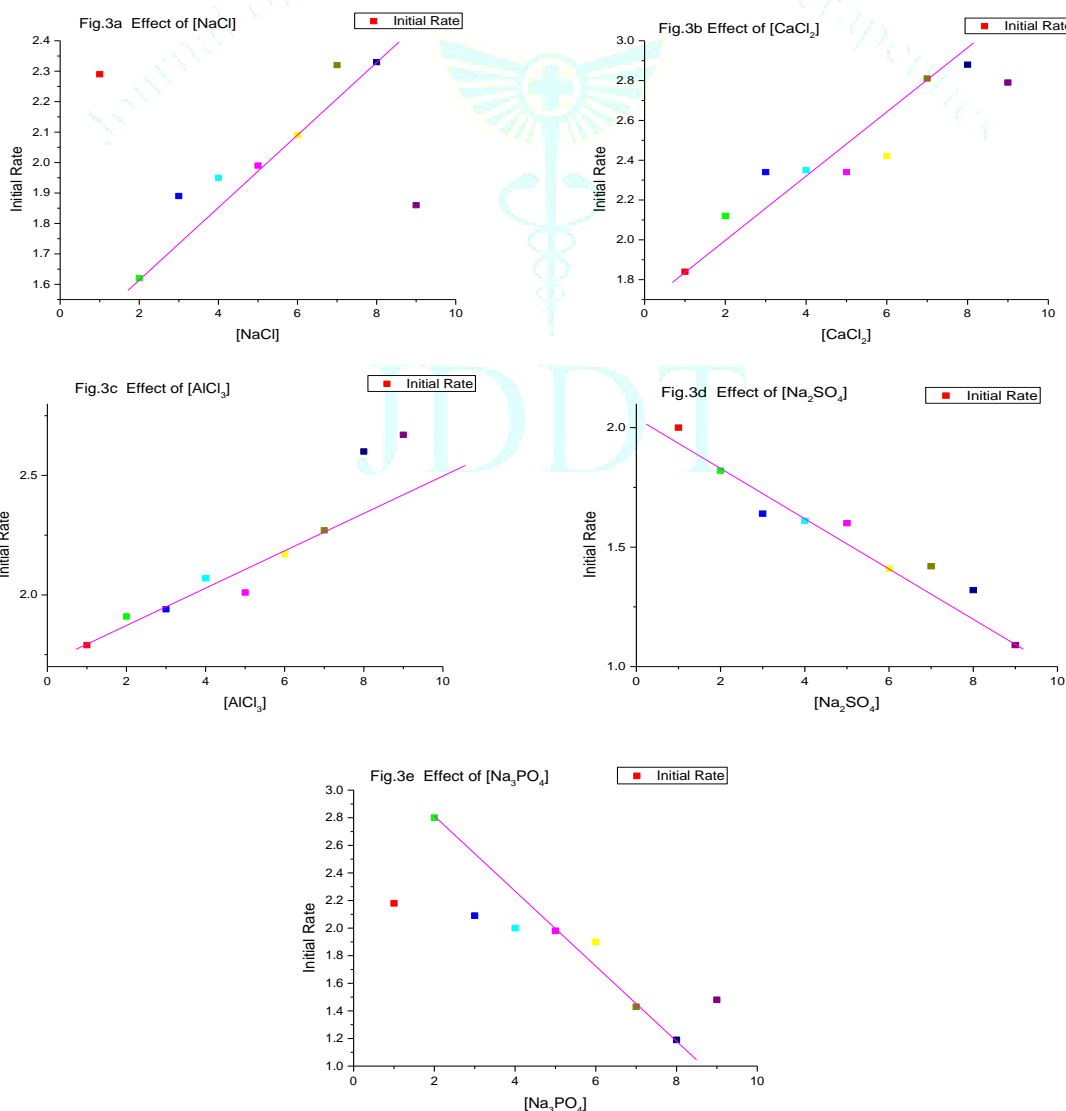The rate of reaction hence directly proportional to concentration of substrate and to the concentration of $KMnO_4$.

Figure 3: Pseudo first order rate constant at variation in salts and its concentration.

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