Kinetic study and Mechanism of hydrolysis of 5-chloro salicylidene - aniline Spectrophotometrically

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Abstract: **Kinetic study of hydrolysis reaction of the Schiff base, 5-chloro salicylidene - aniline (HL) have been studied in the pH range 2.86-12.30 at temperature range 293-308 K. A rate profile diagram of pH v/s rate constant shows the rate minimum in the pH range 4.51-10.22 and reaches a plateau at pH > 10.73. Suitable reaction mechanism has been suggested for the hydrolysis of the Schiff base in acidic, neutral and basic medium. From the effect of temperature on the rate, various thermodynamic parameters have been evaluated.**

Keywords: **Schiff base, hydrolysis, 5-chloro salicylidene – aniline, kinetics, Spectrophotometry.**

INTRODUCTION

The Schiff bases are also called imines. The study of formation and hydrolysis of Schiff base is an important reaction of biochemical interest[1-4]**.** The hydrolysis and formation of Schiff bases is important due to its relevance to the transformation of $>C = O$ to $>C = N$ and vice versa[5-9]. The catalytic effect of hydrogen, hydroxyl and metal ions on the formation and hydrolysis of imines have been studied by several workers[10-12].In the present work we represented here systematic study of the hydrolysis of Schiff base5-chloro salicylidene - anilineat different pH values.

MATERIALS AND METHOD

Experimental: The chemicals used such as ,5-chloro salicylidene - aniline, ethanol etc. were of AR grade. The Schiff base was prepared by condensation reaction of ,5-chloro salicylidene - anilinein ethanol medium for about three hour. On cooling the resulting yellow coloured crystals were recrystalised from ethanol, melting point = 109^{0}C. Purity was checked by TLC.

Kinetic measurements: The rate of hydrolysis of Schiff base was followed spectrophotometricallyat 434 nm by using UV/VIS, 1601, Shimadzu Spectrophotometer. Universal buffer solutions were prepared according to the reported methods[13].The pH was determined by using an Elico LI-120 pH meter. The temperature was varied between 293– 308 K. The concentration of imine was kept at 1×10^{-4} mol dm^{-3}. The ionic strength of the reaction mixture was maintained at $\mu = 0.1$ mol dm^{-3} by using KCl. All chemicals used were of A.R. grade.In a typical kinetic run, the solutions containing appropriate amounts of Schiff base and buffer solution were prepared at room temperature and allowed to equilibrate in previously adjusted thermostat. The quartz cuvettes were also allowed to equilibrate at the same temperature in the thermostatic cell block. After mixing, the reaction mixture was immediately transferred to a quartz cell and the decrease of absorbance of Schiff base with time was followed against the reagent blank kept in another quartz cell. The decrease of absorbance with time was followed at $\lambda = 434$ nm. Using spectrophotometer within 20 s of mixing the Schiff base. The plot of log (A_t-A_∞) vs time were found to be straight lines and pseudo first order rate constants were calculated from the slopes. From the effect of temperature on the reaction rate, energy of activation E, and other thermodynamic parameters were evaluated.

RESULTS AND DISCUSSION

The rate constant values in the pH range 2.86-12.30 at 303 K are listed in **Table-1**. A rate profile diagram of pH v/s rate constant at 303 K and ionic strength $\mu = 0.1$ mol dm^{-3} shows the rate minimum at 4.51<pH < 10.22**(Figure. 1).**

Table- 1: Rate constant data hydrolysis of 5-chloro salicylidene - aniline
Ethanol – water = 40 % (v/v), Temp. = 303K, $\mu = 0.1$ mol dm^{-3}.

pH	[H$^+$] x 10^6 mol dm^{-3}	[OH$^-$] x 10^6 mol dm^{-3}	k x 10^3 S^{-1}
2.86	13800.00		56.780
3.16	6918.00		31.470
4.51	2630.00		1.401
5.21	61.66		1.072
6.61	1.95		1.010

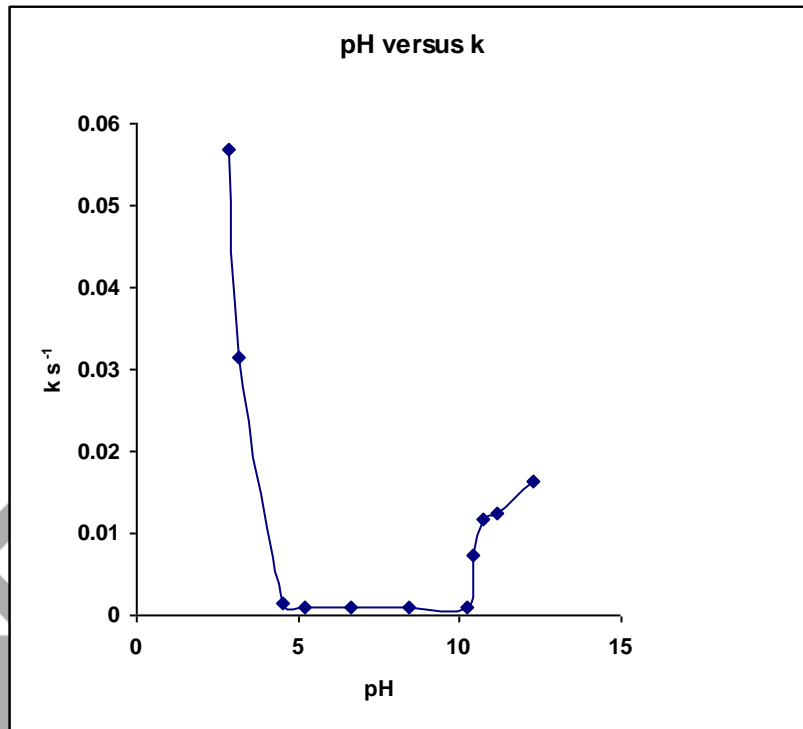| 8.40		2.53	0.971
10.22		1660.00	1.008
10.42		2630.00	7.220
10.73		5370.00	11.792
11.15		14130.00	12.331
12.30		19250.00	16.220

Fig. 1: Plot of k against pH at 303 K for the hydrolysis of 5-chloro salicylidene - aniline at $\mu = 0.1$ mol dm^{-3}.

Rate - limiting pathways: In the pH range 2.86-12.30, the Schiff base (HL) may be assumed to undergo hydrolysis by four rate determining pathways.

1. The acid catalysed addition of water to the imine linkage of protonated Schiff base, H_2L^+ (k_1).
2. A spontaneous path involving the addition of water to the imine likage of the neutral imine, HL (k_2).
3. The addition of water to the imine anion, L^- (k_3).
4. The addition of hydroxyl ion to the imine anion, L^- (k_4).

The last step in which the hydroxyl ion predominates may be eliminated as the rate constant was found to be almost independent of the hydroxyl ion concentration at pH > 10.22 **(Table 1).** Thus the overall rate of hydrolysis will be,

$$\text{Rate} = k_1 (H_2L^+) + k_2 (HL) + k_3 (L^-) \quad ...1$$

The deprotonation and protonation equilibria of the imine (HL) may be represented

$$H_2L \xrightarrow{ k_1 } HL + H^+$$

$$HL \xrightarrow{ k_2 } \bar{L} + H^+$$
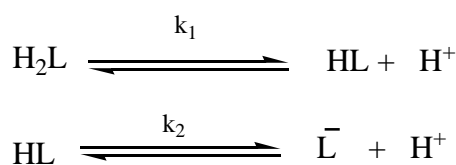
**Hydrolysis of Schiff base in acidic and neutral range of pH**

The rate constant varies linearly with hydrogen ion concentration in the pH range 4.51-8.40. In this pH range, equation (1) reduces to (2),

$$Rate = k_1 \, (H_2L^+) + k_2 \, (HL)$$

$$K = (k_1/K_1) \, [H^+] + k_2 \qquad \qquad ...2$$

A plot of k vs $[H^+]$ was found to be a straight line with slope k_1/K_1 from which k_1 was calculated to 2.902×10^2 at 303K. Since the intercept of the plot is zero, k_2 is taken as zero. In the acidic pH range, the proton catalysed attack of water on the reactive imine linkage of (HL) is suggested to be the rate- limiting step for the hydrolysis **(scheme 1)**. The extremely low rates in the neutral pH range are due to   negligible protonation of (HL). Consequently, the attack of water on the protonated imine is very slow. The addition of water to the neutral imine is therefore suggested to be rate – limiting step.

5-Chloro Salicyaldehyde   Aniline

Products
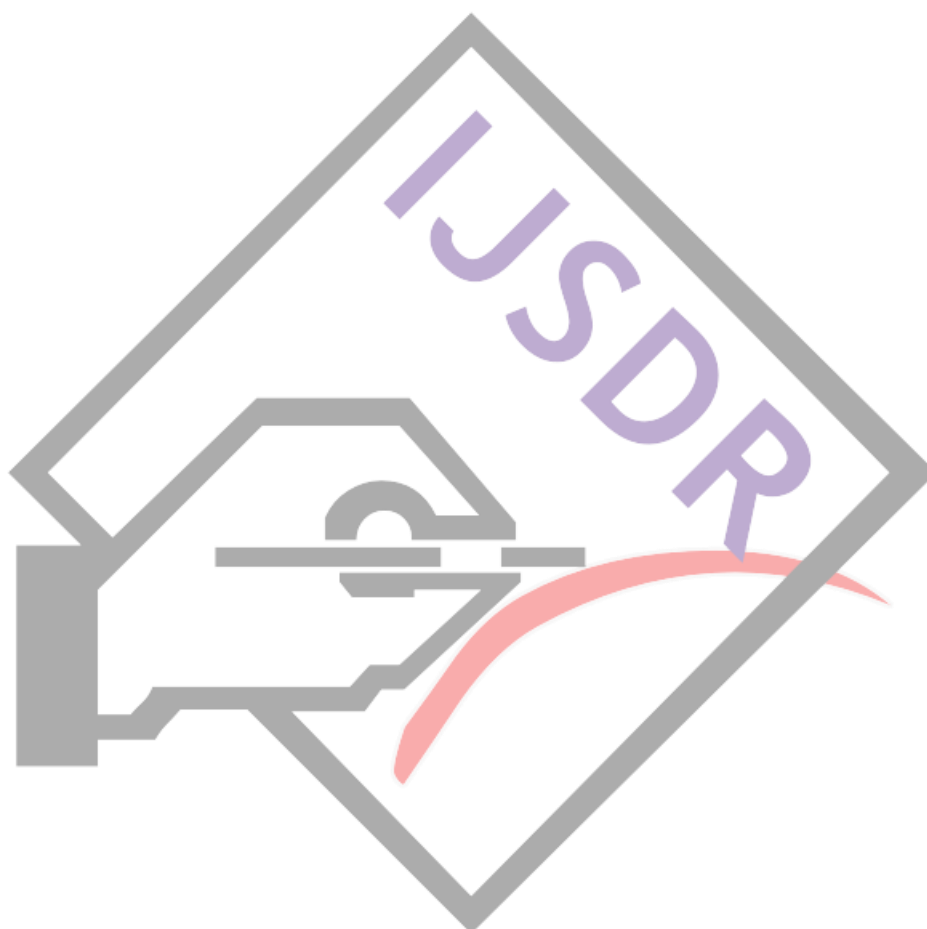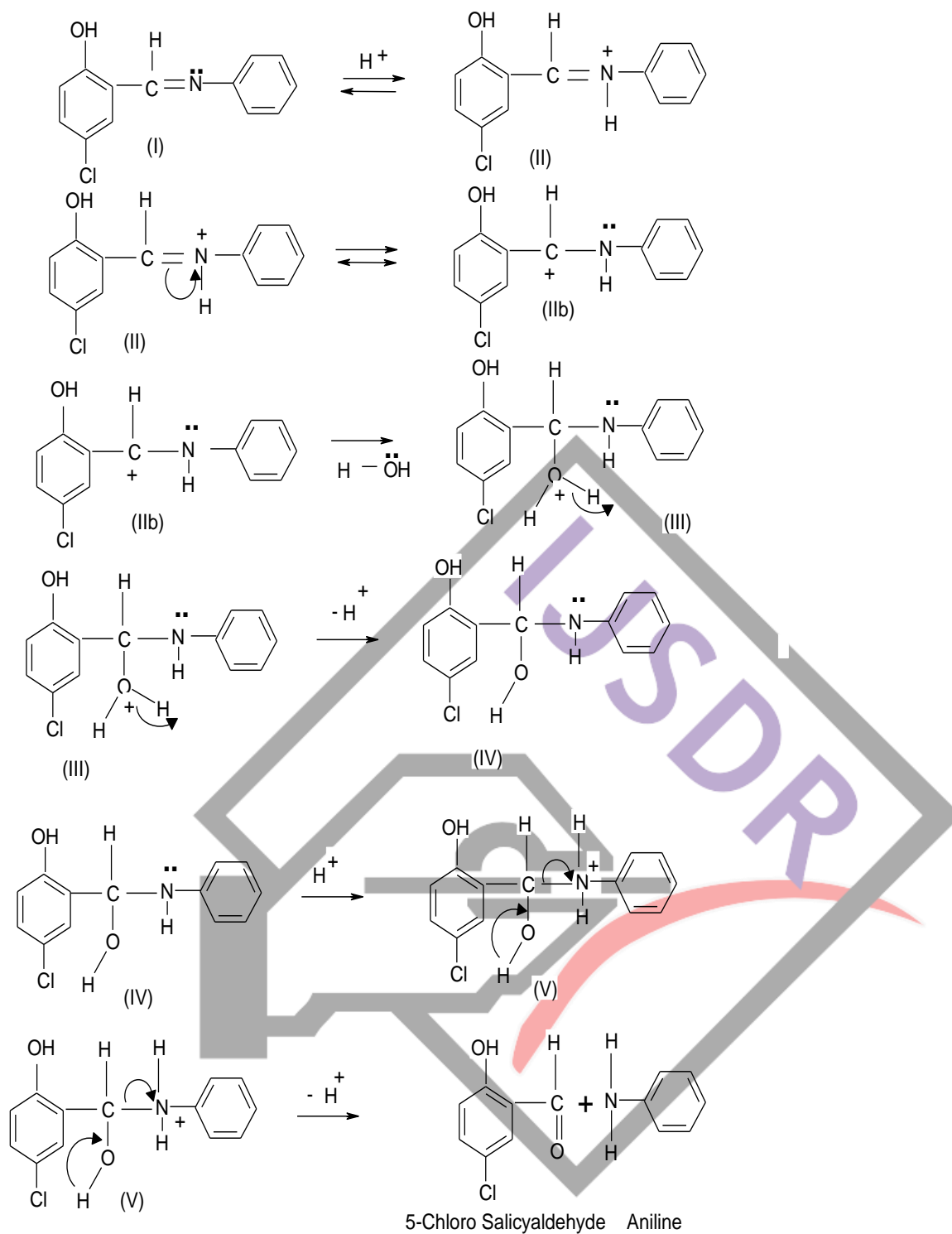
Scheme-I

Hydrolysis of Schiff base in basic medium:

In the basic range, pH >10.22, the rate constant initially increases with increase in pH and is nearly independent of hydroxyl ion concentration at pH > 11.15. In this pH range, the Schiff base may be assumed to be exclusively in the anionic form L⁻ due to the neutralization of the phenolic proton of the ortho- hydroxy group by the OH⁻ ion of alkali[10].The above observations lead to the assumption that the complex formed may be Arrheninus complex. In the presence of excess catalyst, Arrhenius complex leads to specific hydroxyl ion catalysis at low hydroxyl concentration and the rate reaches a limiting value at high hydroxyl ion concentration[12].

In the present study, the rate increases with the hydroxyl ion concentration at low hydroxyl ion concentrations(**Table-2**). Further the rate reaches a limiting value at higher hydroxyl ion concentrations. All these facts indicate that the rate- limiting step is the slow reactions of Schiff base anion L⁻ water (k_4) [10, 14.] The average value of the rate constants at pH > 11.15 is taken as $k_4 = 13.26 \times 10^{-3}$ at 303 K (**Fig.2a and Fig.2b**).

Table- 2: Rate constant (Order) date of hydrolysis of 5-chloro salicylidene - aniline
Medium-(ethanol - water) Temp. = 30 ^{0}C ; Buffer-Acetate; pH = 3.16;μ = 0.1 M

Time	O.D.	A_0-A_∞	A_t-A_∞	Log($A_0-A_\infty/A_t-A_\infty$)	$k \times 10^2$ s⁻¹
0	1.120				
15	1.108	0.032	0.020	0.2041	3.1339
30	1.100	0.032	0.012	0.4259	3.2700
45	1.096	0.032	0.008	0.6021	3.0812
60	1.093	0.032	0.005	0.8062	3.0944
75	1.091	0.032	0.003	1.0280	3.1567
90	1.090	0.032	0.002	1.2041	3.0812
∞	1.088				
				k_{mean}	3.1473
				k $_{Graph}$	3.1100

Time vs Log (A₀-A∞)/(Aₜ-A∞)

y = 0.0135x
R² = 0.9993
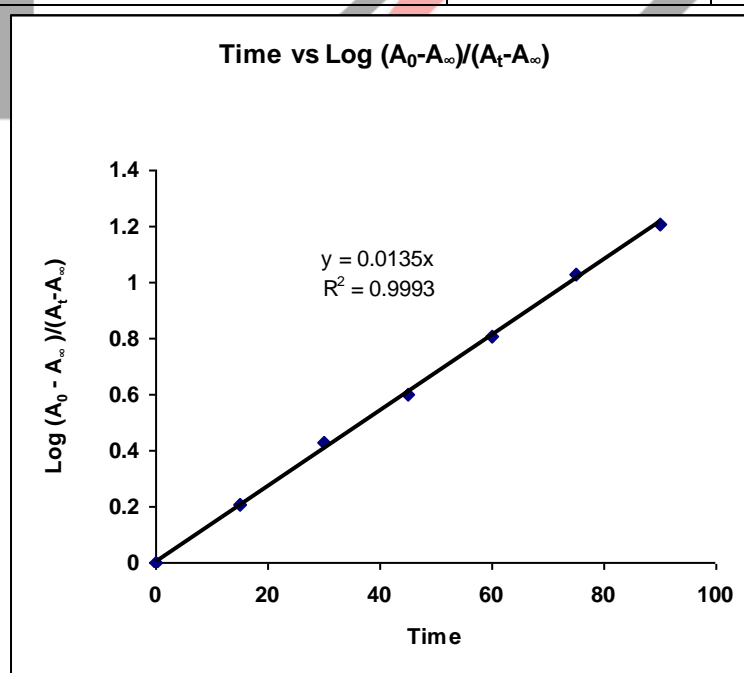
Fig. 2(a): Plot of Time versus Log (A₀-A∞/Aₜ- A∞) at 30 ^{0}C for hydrolysis of 5-chloro salicylidene - anilineat pH = 3.16

Time versus Log(A$_t$- A$_\infty$)

$y = -0.0134x - 1.5056$
$R^2 = 0.999$

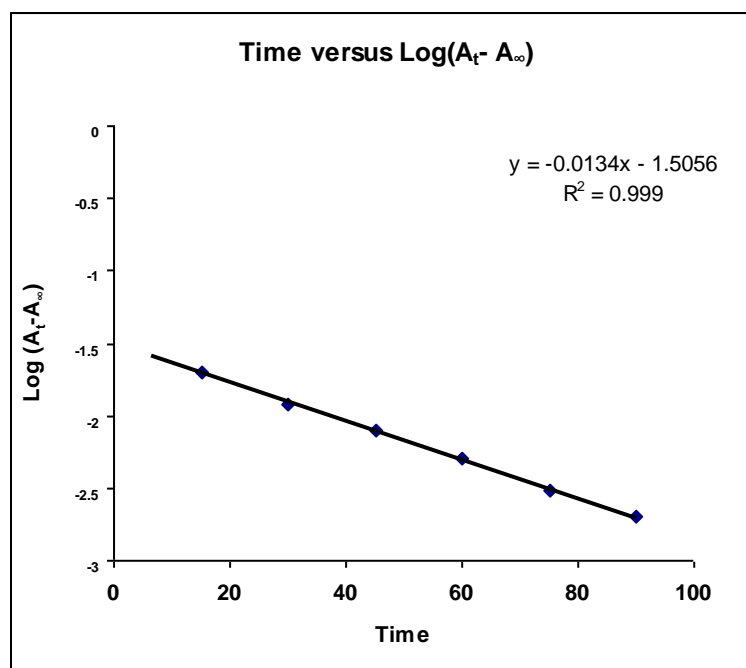*(Y-axis: Log (A$_t$-A$_\infty$); X-axis: Time)*

Fig. 2(b): Plot of Time versus Log (A$_t$- A$_\infty$) at 30 ^{0}C for hydrolysis Of 5-chloro salicylidene - aniline

VARIATION OF REACTION RATE WITH TEMPERATURE

In order to examine the effect of temperature on reaction rate, the reaction was carried out at different temperatures, 293,298,303and308 K. The activation parameters were calculated [15-16] Ea, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are given in the **Table- 3**.The plot of $(3 + \log k)$ v/s $1/T$ is linear (**Fig.-3 a and Fig. 3 b**).

Table- 3: Rate constants and activation parameters for 5-chloro salicylidene - aniline

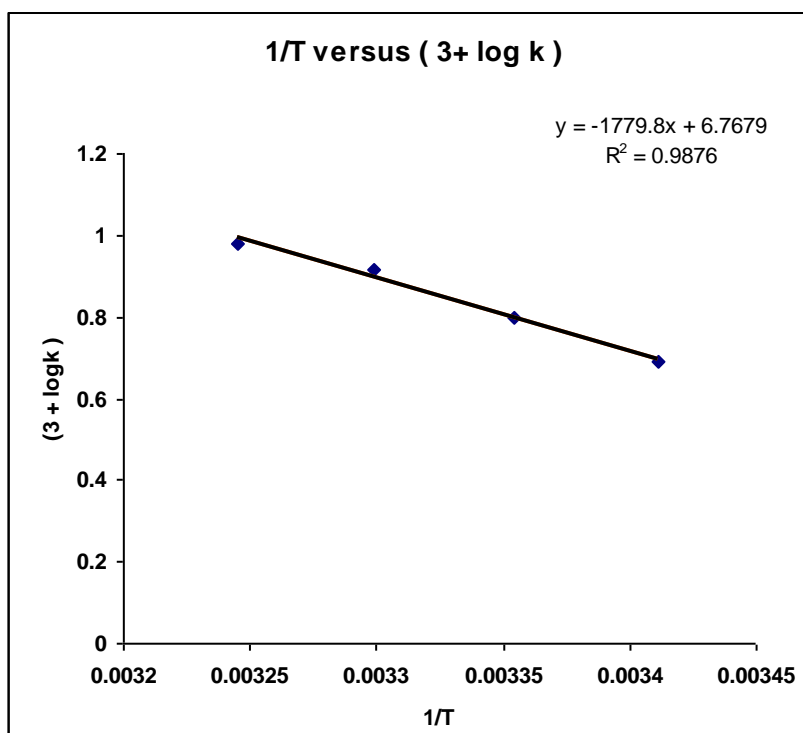| Temperature	10^3 x k s^{-1}	Ea cal mol^{-1}	$\Delta S^{\neq}$ cal mol^{-1}	$\Delta G^{\neq}$ cal mol^{-1}	$\Delta H^{\neq}$ cal mol^{-1}	Log A
293 K	2.704					
298 K	3.440					
303 K	4.497	7917.249	- 43.968	20452.51	7324.805	6.768
308 K	6.524					

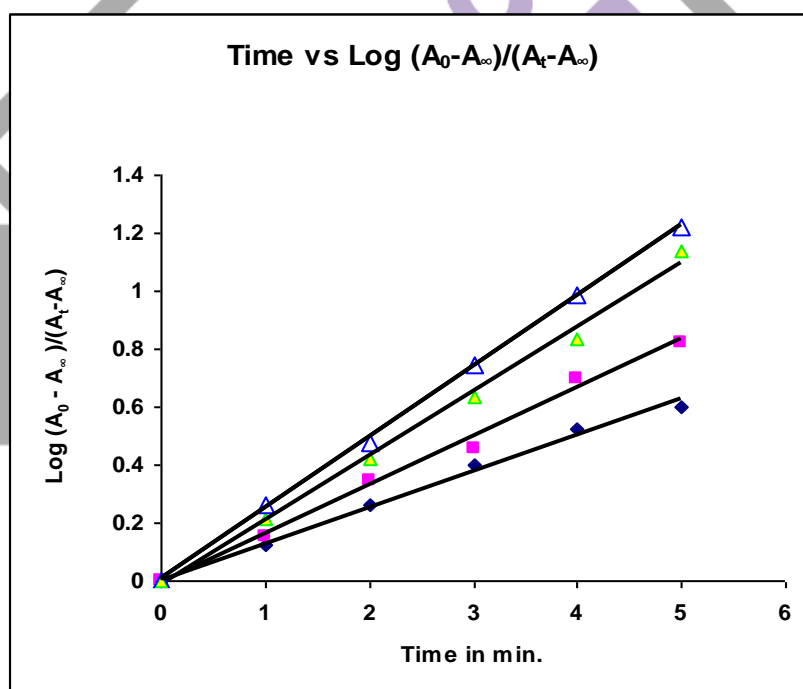**Fig.3 (a): Plot of (3+ log k) against 1/T for hydrolysis of 5-chloro salicylidene - aniline**

Fig. 3(b): Plot of log $(A_0-A_\infty)/(A_t-A_\infty)$ against Time For Hydrolysis of 5-chloro salicylidene - aniline

From the values of thermo dynamic parameters it is observed that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the important parameters in controlling the rates of reactions[17]. The negative values of entropy of activation indicate that activated complex is probable. The high negative values of entropy of activation suggest that the reaction may occur between like charged ions or ions and neutral molecules and may generate rigid intermediate transition state resulting in slow rate of the reaction. The values of frequency factor lies below 10^{10} and hence present reaction may be taking place between ions of like charges[18]. Activation entropy values are negative. This is because the protonated water molecule is held up at the nitrogen atom of imine linkage. The large negative values of $\Delta S^{\neq}$ also indicate an extensive reorientation of the solvent molecules as a result of the formation of the activated complex[19-20] .A negative value of $\Delta S^{\neq}$ means that the activated complex is more ordered than the reactants. A more negative $\Delta S^{\neq}$ may indicate that frequency factor A, will have smaller value and the reaction will be slower. For slower reactions a higher value of $\Delta G^{\neq}$ will be observed at given temperature. The rate of hydrolysis was increased with increase in temperature. Relatively constant values of $\Delta G^{\neq}$ suggest similar mechanism of all the reactions.

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