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A Kinetic Study of Effect of Aquo-Dioxan Solvent Systems on the Biochemical Potential and Food Additive uses of Iso-Amyl Methanoate

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Abstract: *With an aim to highlight the solvent effect of a 1:4 dioxan (cyclic ether)on the biochemical efficiency and food additive uses of higher methanoates, the kinetics of acid catalysed hydrolysis of iso-amyl methanoate was studied in different aquo-dioxan media containing 20 to 80% (v/v) of dioxan at different temperatures from 20 to 40°C.*

Enhancement in the numerical values of free energy of activation (ΔG) with simultaneous increase in the values of enthalpy of activation (ΔH*) and entropy of activation (ΔS*) of the reaction, reveals that dioxan acts as entropy controller solvent. The iso-kinetic temperature of the reaction was evaluated to be 327.0 which infers that there is strong and appreciable solvent-solute interaction in aquo-dioxan reaction media.*

Keywords: *Biochemical potential, Food Additives Solvation, Activation Energies, Iso- kinetic, Temperature, Solvent-solute Interaction.*

1. INTRODUCTION

Though the solvent effect of various dipolar aprotic solvents like DMSO, DMF, Acetone, etc. has widely been studied on the acid and alkali catalysed solvolysis of simple esters by various kineticists[1-4], but the solvent effect of solvent containing cyclic ethereal group on the biochemical efficiency and food additives uses of the solvolysis product of the higher methanoates (methanoic acid) has not been paid even a little attention so far.

Hence, in order to highlight and elaborate the effect of a solvent cyclic ether, dioxin on the biochemical efficiencies of Iso-amyl methanoate, it has been proposed to study the effect of dioxan (cyclic ether) on the acid catalysed hydrolysis of methanoate ester.

2. EXPERIMENTAL

The solvent 1:4 dioxan of Merck grade and Iso-amyl methanoate of export quality packed in Swtzerland were taken into use. The kinetics of acid catalysed hydrolysis of the ester was studied as usual by adding 0.75 ml of ester in 50 ml of 0.5 M HCI solution. The values of specific rate constants were evaluated by making use of first order rate equation and are tabulated in Table - I. Evaluated values of the two activation energies (Iso-composition E_C and Iso-dielectric E_D) , number of water molecules associated with the activated complex and thermodynamic activation parameters have been enlisted in Tables - II, III, IV and V respectively. Effect of change of $[H^+]$ ion concentration on the specific rate constants have been mentioned in Table-VI.

3. RESULTS AND DISCUSSION

From the evaluated values of specific rate constants tabulated in Table - I and Fig.- 1, which highlight the effect of change in concentration of the organic content of the reaction media on the rate of reaction, it is clear that there is fast decrease followed by slow depletion in the rate of reaction at approx. 18.30 mol % of dioxan in the reaction media. However, with increasing temperature, the effect of solvent dioxan on degree of depletion of the rate is decreased.

Generally, the following two factors seem to be responsible for depletion in the rate of the reaction in solution, they are:

(i) Decreasing polarity of the medium as changing from polar water to less polar aquo-dioxan medium,
(ii) Lowering of the bulk dielectric constant values of the medium with gradual addition of
dioxan to it, and
(iii) Depletion of concentration of H3O+ ions of the solution by the organic content of the media due
to its basic character (if ay).

As dioxan is not basic, so it may not combine with the H+ or with H3O+ ions of the acidic solution of the reaction media .

Thus ignoring the third one only first and second factors are responsible for depletion of the rate.

Such explanations are in support of the theory of Huges & Ingold5 and views of Laidler & Landskroener6 and Elsemongy et al.7 who have predicted that rate of solvolysis reaction decreases with decrease in dielectric constants of the reaction media. In recent years Singh & Nazia et al.8 and Kumar & Singh et al.9 have also reported similar explanations for depletion in the rate of solvolysis reaction with increasing concentration of the organic constant of the reaction media.

Solvent effect on Iso-composition activation energy of the Reaction :

From the slope of the Arrhenius plots of log k versus 103/T values as shown in Fig.-2 the values of iso-composition activation energy(E_C or E_{exp}) have been calculated and are enlisted in Table – II. From Table - II, it is clear that values of iso-composition activation energy go on from increasing 91.74 to kJ/mol 125.04 kJ/mol with addition of 20 to 80% of dioxan in the reaction media.

Generally, enhancement in the values of iso-composition activation energy may be due to either of the following causes:

(i) The greater solvation of initial state than the transition state,
(ii) The greater desolvation of the transition state than the initial state, and
(iii)Simultaneous desolvation and solvation of the transition and the initial state respectively.

Out of these three factors, the third one seems to be applicable in this case and it has also been supported by the increase in the values of entropy of activation with gradual addition of the organic co-solvent dioxan in the reaction media as shown ahead in Table - V. These views are found in support of the earlier reports of Singh & Bano et al.[10], Singh & Wats et al.[11] and also of recently reported facts by Singh & Lal et al.[12] and Svati & Singh et al.[13]

Solvent Effect on the Iso-dielectric Activation Energy of the Reaction:

From the slopes of the Arrhenius plots of log k_D values against 1/T as sown in Fig. - 3 (log k_D values obtained from interpolation of the plots of log k values against D values) the values of iso-dielectric activation energy have been evaluated and are recorded in Table - III. From this table, it is inferred that E_D values go on decreasing from 123.36 kJ/mol to 91.42 kJ/mol with increasing D values of the reaction media at D = 10 and D = 60 respectively. As the dielectric constants (D values) of the reaction media decreases with increasing concentration of dioxan in it, hence the trend of depletion in E_D values of the reaction with increasing D values of the aquo-dioxan reaction media is similar to enhancement in E_C values of the reaction with increasing concentration of dioxin in the reaction media. Thus, it may be concluded that depletion in E_D values of the reaction is complimentary to enhancement in its E_C values.

Similar findings and their interpretations for depletion in E_D values of the reaction with increasing D values of the reaction media have also been reported earlier by N. Kumar[14], Kumar & Singh et al.[15] and recntly by Priyanka & Singh et al.[16].

Evaluation of water molecules involved in the formation of transition state and mechanism of the reaction :

The number of water molecules involved in the formation of the transition state has been determined by plotting log k values against log [H_2O] according to the relation proposed by Robertson[16]:

$$\log k = \log k_o + n \log [H_2O]$$

where 'n' is the solvation number which tells about the number of water molecules associated with the transition state and also hints about criterion for studying about the mechanism of the reaction. From the plots of log k values against log [H_2O] values as shown in Fig. - 4, it is clear that at each temperature two inersecting straight lines with positive slopes are obtained and their slope values have been recorded in Table-IV.

From the value of the slopes, as recorded in Table-IV, it is clear that below log [H_2O] value 1.445 (intersection point of the two straight lines) which corresponds to 50.20 % of water in aquo-dioxan media, the values of slopes are decreasing from 0.845 to 0.335 with increase in temperature from 20° to 40°C. Similarly, after log [H_2O] value 1.445 i.e. in case of water concentration above 50.20% in the reaction media, the values of slopes decrease from 1.285 to 0.406 with increase in temperature of the reaction from 20° to 40°C.

Overall, it may be concluded that when water concentration fall below 50.20 % in the reaction media, the number of water molecules taking part in the formation of activated complex is about half (0.335), but with increasing concentration of water in the reaction media (above 50.20%) the number of water molecules associated with the activated complex become above 1 (1.285).

However, from decreasing number of water molecules from 1.285 to 0.335 assiciated with the activated complex with increase in temperature from 20° to 40°C, it may be inferred in the light of findings of Robertson et al.[18] that mechanistic path of the reaction is changed from unimolecular to bimolecular in presence of dioxan in the reaction media.

It has also been concluded that in presence of dioxan in the reaction media at equilibrium the structure of water is changed from its bulky form to dense form.

$$(H_2O)_b \rightleftharpoons (H_2O)_d$$

Such findings inferences and their explanations have also been reported earlier by Monalisa & Singh et al.[19], Chandra & Singh et al.[20] and recently by Kumar, N.[21] and Kishor & Singh et al.[22]

Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

By using the Absolute Reaction Rate Theory[23] and the famous Wynne-Jones and Eyring[24] equation, the values of three thermodynamic activation parameters namely enthalpy of activation ΔH*, entropy of activation ΔS* and the free energy of activation ΔG* have been evaluated and are recorded in Table - V.

From the data mentioned in Table - V, the interesting feature comes in the light is that out of the three thermodynamic activation parameters i.e. ΔH*, ΔS* and ΔG* values, all the three go on increasing with increasing proportion of dioxan in the reaction media. Variations in ΔH*,ΔG* and ΔS* values of the reaction with mol % of dioxan in aquo-dioxan media have been shown in figures 5, 6 and 7 respectively.

From the fundamental thermodynamic equation :

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

it may be inferred that the simultaneous increase in the values of ΔH* and ΔS* with enhancement in ΔG* values is only possible when the quantitative increase in the values of ΔH* is greater than that found in ΔS* and from this, it is concluded that acid catalysed hydrolysis of Iso-amyl methanoate in aquo-dioxan media is enthalpy dominating and entropy controlled one.

The enhancement observed in the values of enthalpy of activation ΔH* and entropy of activation ΔS* also supports the fact that the transition state of the reaction is desolvated and the initial state is solvated in the similar way as reported earlier by Singh & Wats et al.[25] and recently also by Rashmi & Singh et al.[26] and Singh & Lal et al.[27].

Effect of change of [H^+] ion-concentration of the reaction media on the rate and Mechanism of the reaction :

The effect of change in the acid concentration of the reaction media kinetics of the reaction was studied by changing the concentration of HCl, but the ionic strength of the reaction media was always kept fixed ($\mu = 0.9$). The evaluated values of the specific rate constant at different [H^+] strength of the media has been tabulated in Table - VI.

The value of the slope of straight line plots of log k versus log [H^+] as shown in Fig.- 8 was found to be 0.998 which is almost equal to unity and from this, it is inferred on the guidelines of Zucker and Hammett[28] that this hydrolysis follows A_{AC}^2 mechanism. Similar inferences have also been reported earlier by Upadhyay & Singh et al.[29], Singh & Navendu et al.[30] and recently by Abhay & Singh et al.[31] for the effect of [H^+] ion concentration of the reaction media on the rate and mechanism of the acid catalysed solvolysis reaction.

Evaluation of Iso-kinetic temperature and Solvent-solute Interaction in aquo-dioxan reaction media:

In the light of Barclay & Butler[32], relationship between enthalpy and entropy of activation, the value of iso-kinetic temperature of the acid catalysed hydrolysis of Iso-amyl methanoate in aquo-dioxan media has been evaluated from the slopes of the plots of ΔH^* versus ΔS^* as shown in Fig.- 9. The plot is straight line and its slope value is evaluated to be 327.0.

From the value of iso-kinetic temperature (much above 300), it is concluded that there is a considerable change in the structure of reactants or in the solvent or in both due to appreciable and strong interaction between solvent and solute present in the reaction mixture in the similar way as reported by Leffler[33]. Earlier Kumar & Singh et al.[34,35] and recently Pathak & Singh et al.[36] have also reported similar findings and explanations for solvent-solute interaction in the different reaction media.

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Table - I

Specific rate constant values of Acid catalysed hydrolysis of Iso-amyl methanoate in water-Dioxan media

k x 10^{3} in min^{-1}

Temp in °C	% of Dioxan (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	97.02	82.72	68.28	56.52	45.32	36.12	26.16
25° C	180.32	158.93	136.58	115.43	96.01	79.45	60.24
30° C	334.58	303.11	269.96	237.41	204.74	176.28	141.35
35° C	602.28	552.20	512.63	459.52	410.58	367.71	310.17
40° C	1062.69	1015.08	969.62	891.66	829.66	768.42	674.37

Table - II

Evaluated values of Iso-composition Activation Energy(E_C or E_{exp}) of the reaction in water-Dioxan media.

% of Dioxan (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C value in kJ/mol	91.74	96.64	101.42	104.69	109.25	115.22	125.04

Table - III

Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at different desired 'D' values of the water-Dioxan media.

D values	D = 10	D = 20	D = 30	D = 40	D = 50	D = 60
E_D values in kJ/mol	123.36	115.06	108.50	101.86	97.61	91.42

Table - IV

Values of the slopes of the plots of log k versus log [H2O] at differen temperatures

Temperature in °C	Slope - I when log[H_2O] value is below 1.445	Slope - II when log[H_2O] value is above 1.445
20°C	0.845	1.285
25°C	0.636	1.024
30°C	0.588	0.760
35°C	0.441	0.699
40°C	0.335	0.406

Table - V

Variation of ΔH^*, ΔG^* and ΔS^* values of the reaction with mol % of Dioxan in water-Dioxan media

% of Dioxan	Mol % of Dioxan	ΔH^* in kJ/mol	ΔDG^* in kJ/mol at 30°C	ΔS^* in J/K/mol at 30°C
20%	5.02	89.36	87.33	6.68
30%	8.31	93.17	87.58	18.45
40%	12.36	98.78	87.87	35.99
50%	17.46	102.76	88.20	48.05
60%	24.08	108.68	88.57	66.37
70%	38.04	114.37	88.95	83.90
80%	45.83	121.18	89.50	104.53

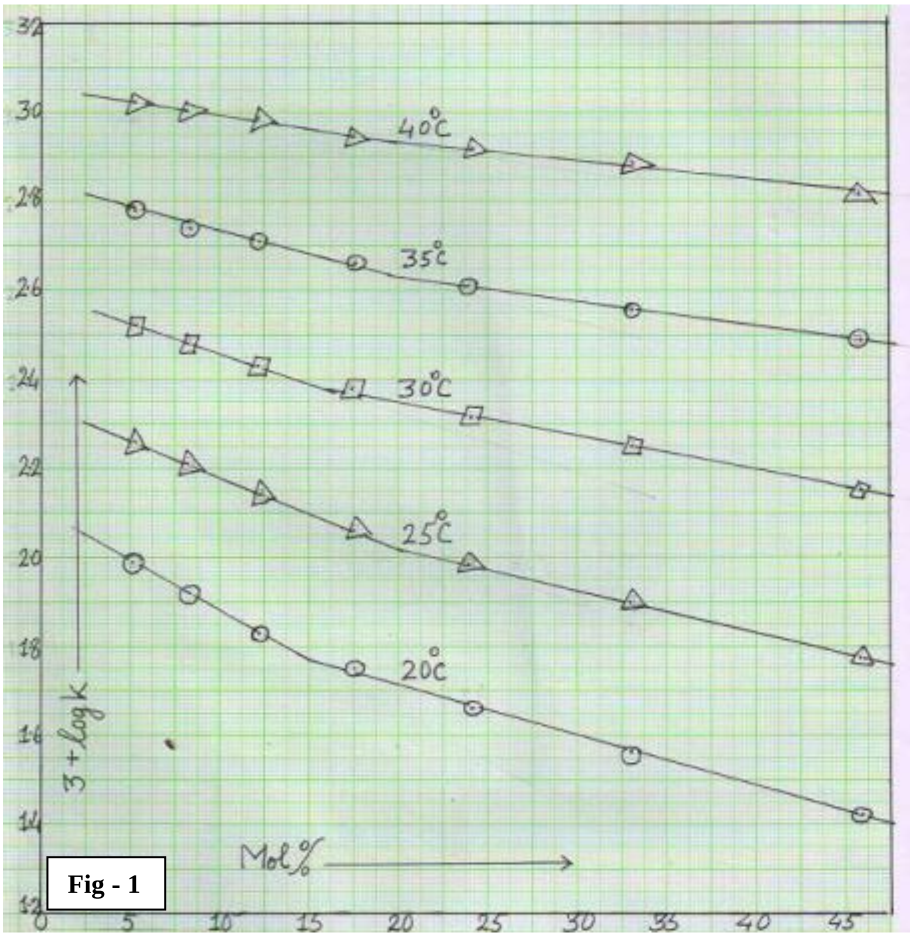
Table - VI

Effect of $[H^+]$ on the Specific rate constant values of Acid Catalysed Hydrolysis of Iso-amyl methanoate in water-Dioxan media at constant ionic ($\mu = 0.9$)

Concentration of Dioxan = 20% (v/v)

Temp. - 25°C

$[H^+]$	[KCl]	μ	$k \times 10^3$ in min^{-1}	2 + log $[H^+]$	3 + log k	value of the slope of the plot of log k vesus log $[H^+]$
0.10	0.80	0.90	34.38	1.0000	1.5376	
0.15	0.75	0.90	56.39	1.1761	1.7512	
0.20	0.70	0.90	74.78	1.3010	1.8738	
0.25	0.65	0.90	93.28	1.3979	1.9698	
0.30	0.60	0.90	109.98	1.4771	2.0413	0.990
0.40	0.50	0.90	144.91	1.6021	2.1611	
0.50	0.40	0.90	180.32	1.6990	2.2560	
0.60	0.30	0.90	217.67	1.7782	2.3378	
0.70	0.20	0.90	251.88	1.8451	2.4012	
0.80	0.10	0.90	282.03	1.9030	2.4503	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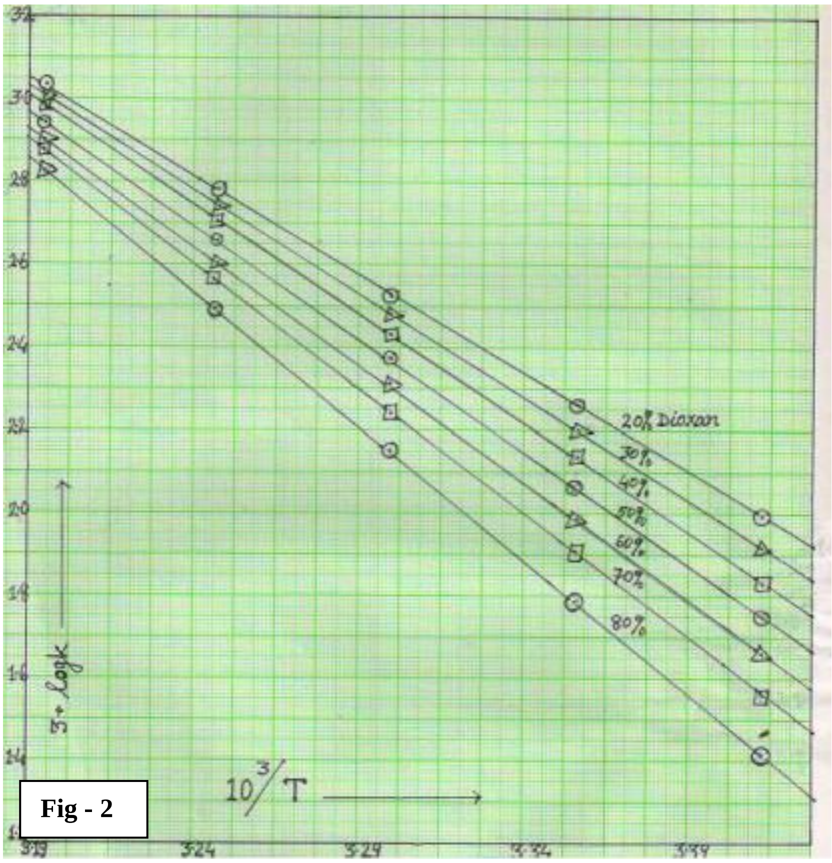
3 + log K
Mol%

Fig - 1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14
12
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3.24
3.29
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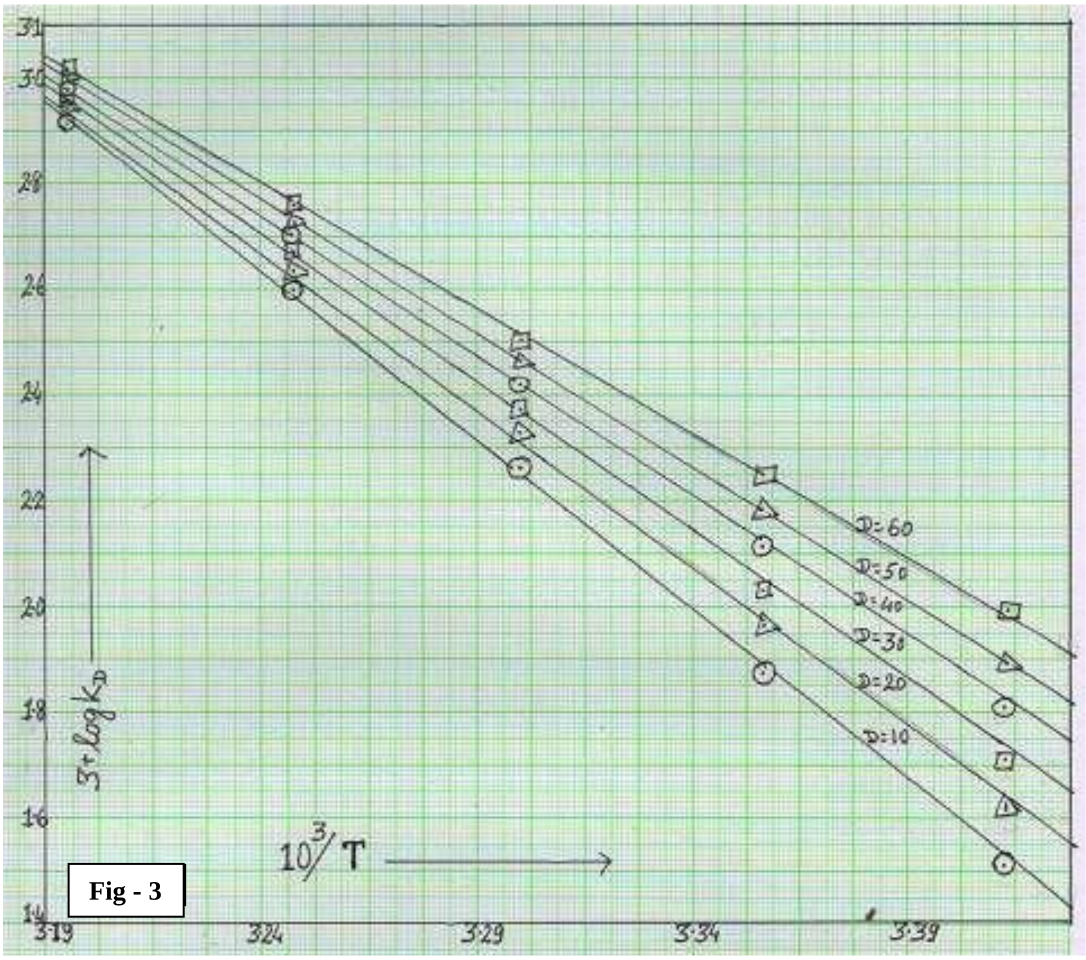
30%
40%
50%
60%
70%
80%
3 + log K
10³/T

Fig - 2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3·29
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D=20
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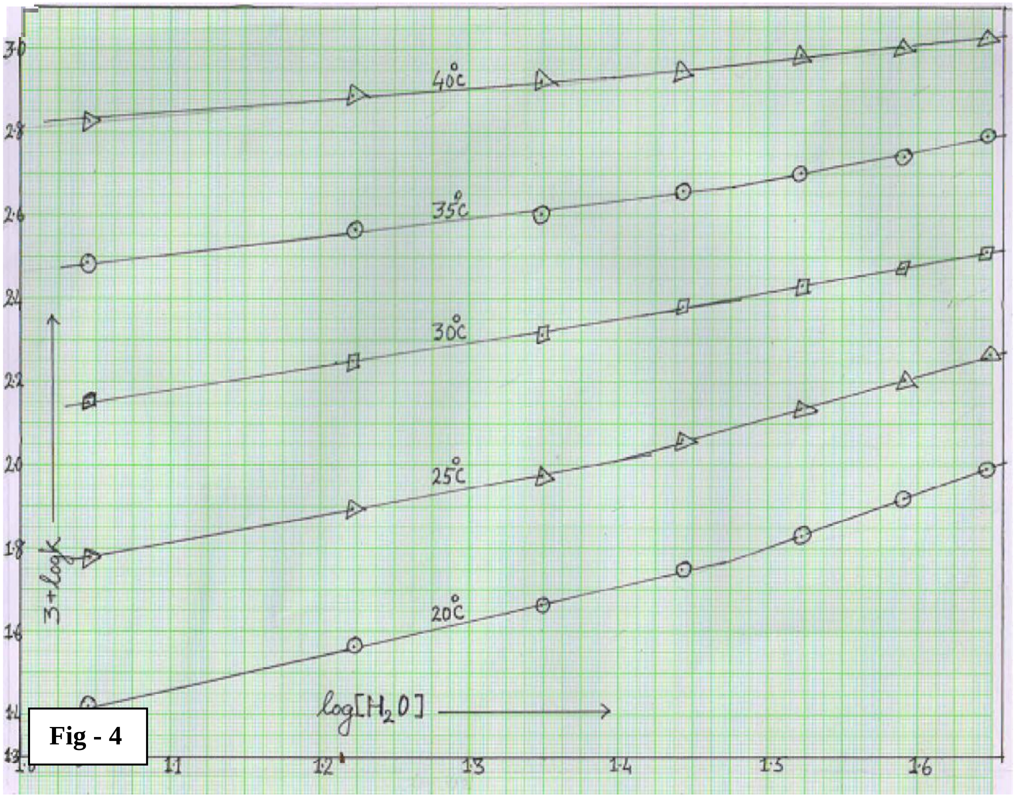
Fig - 3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1·3
1·4
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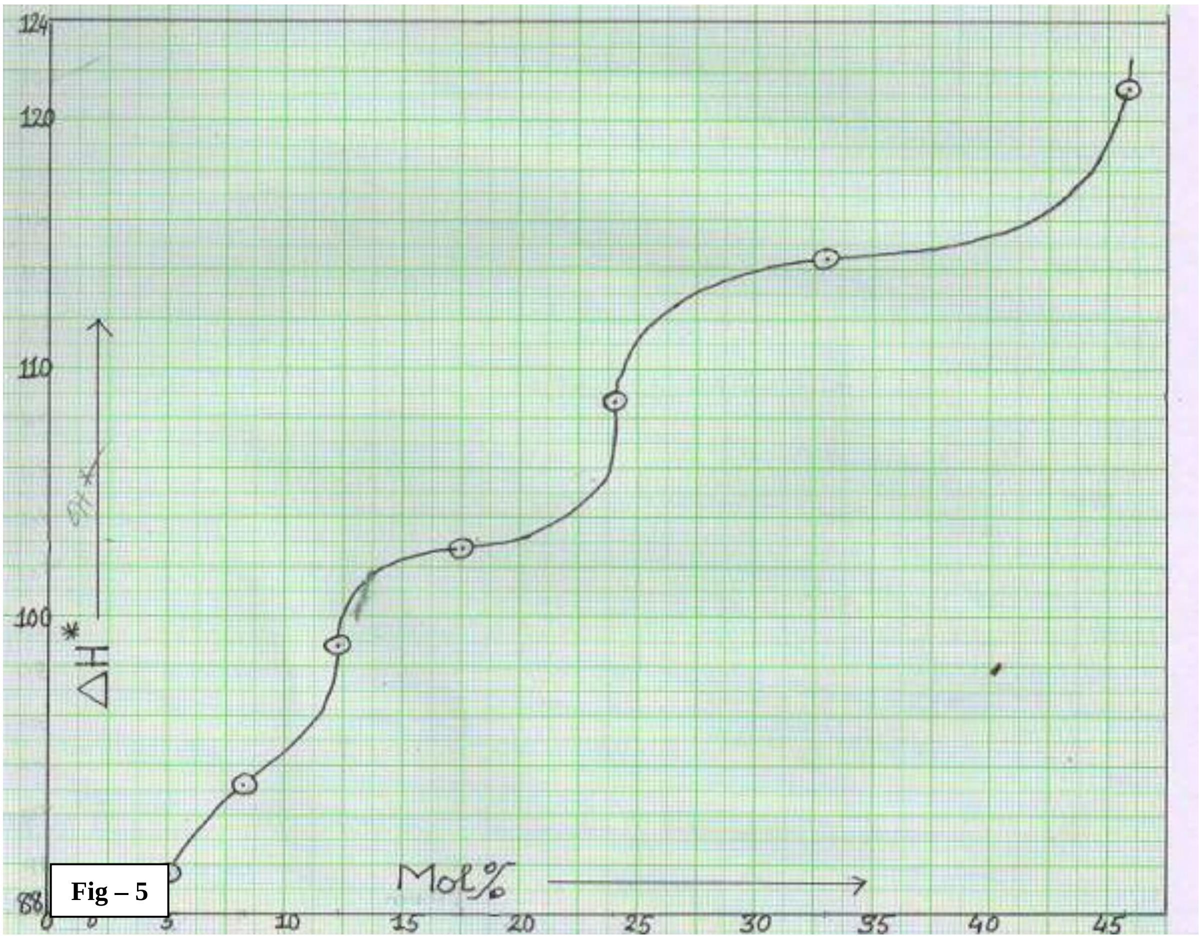
40°C
35°C
30°C
25°C
20°C
3+log k
log[H_2O]

Fig - 4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ΔH*
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Fig – 5

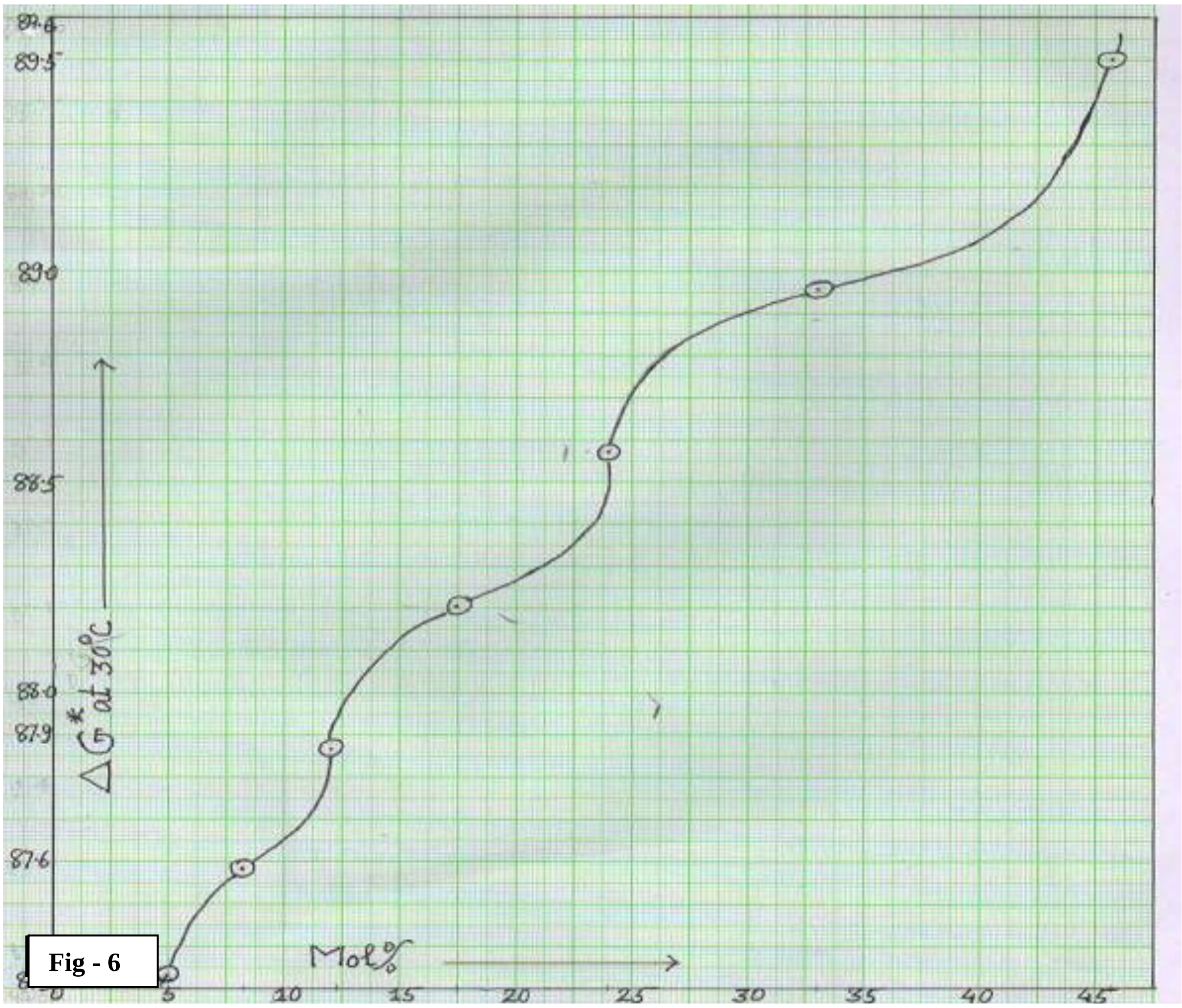
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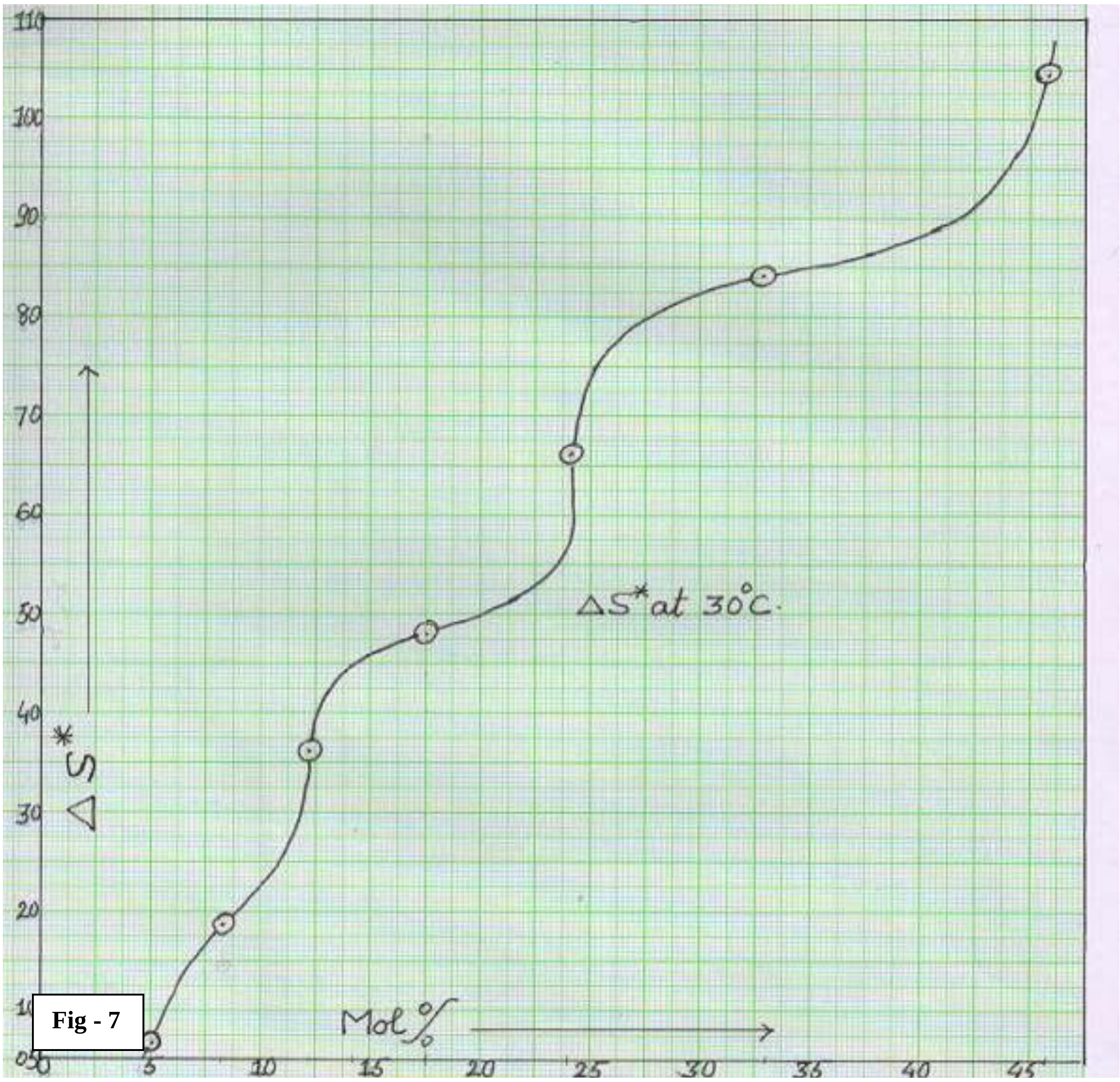
Fig - 6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ΔS*
ΔS* at 30°C.
Mol %
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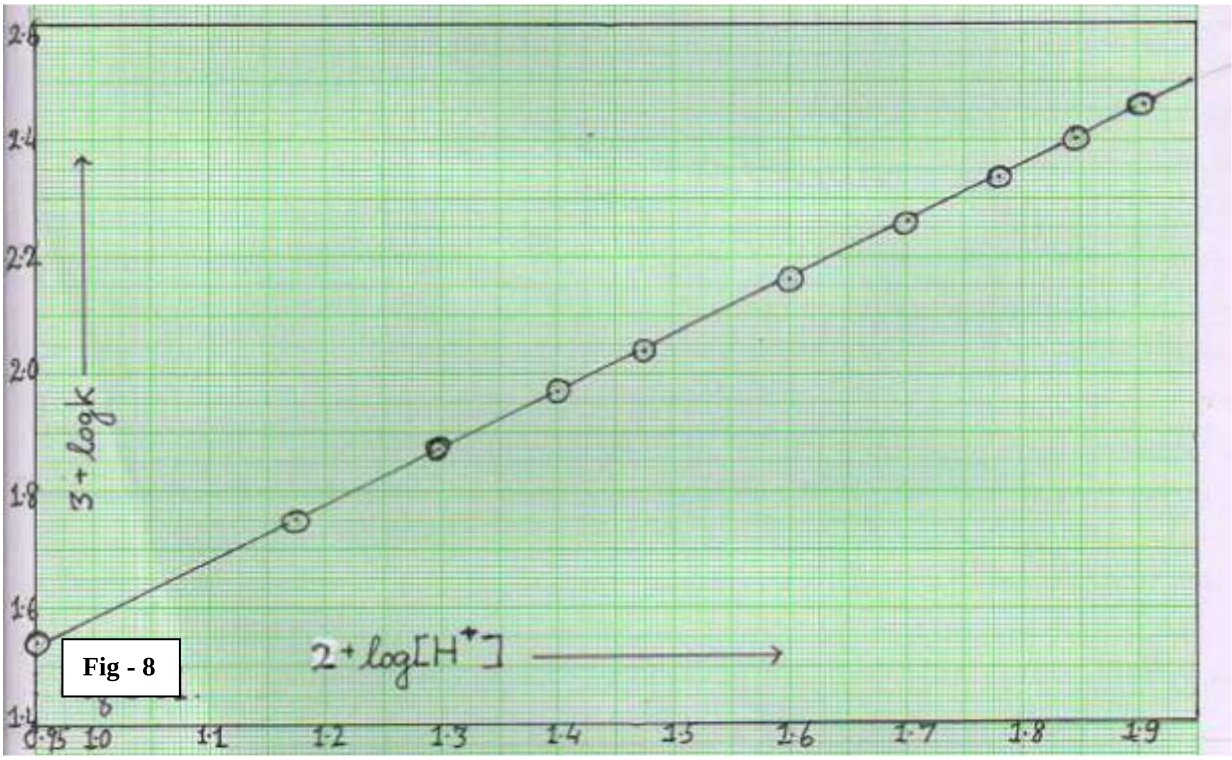
Fig - 7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2 + log[H+]
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Fig - 8

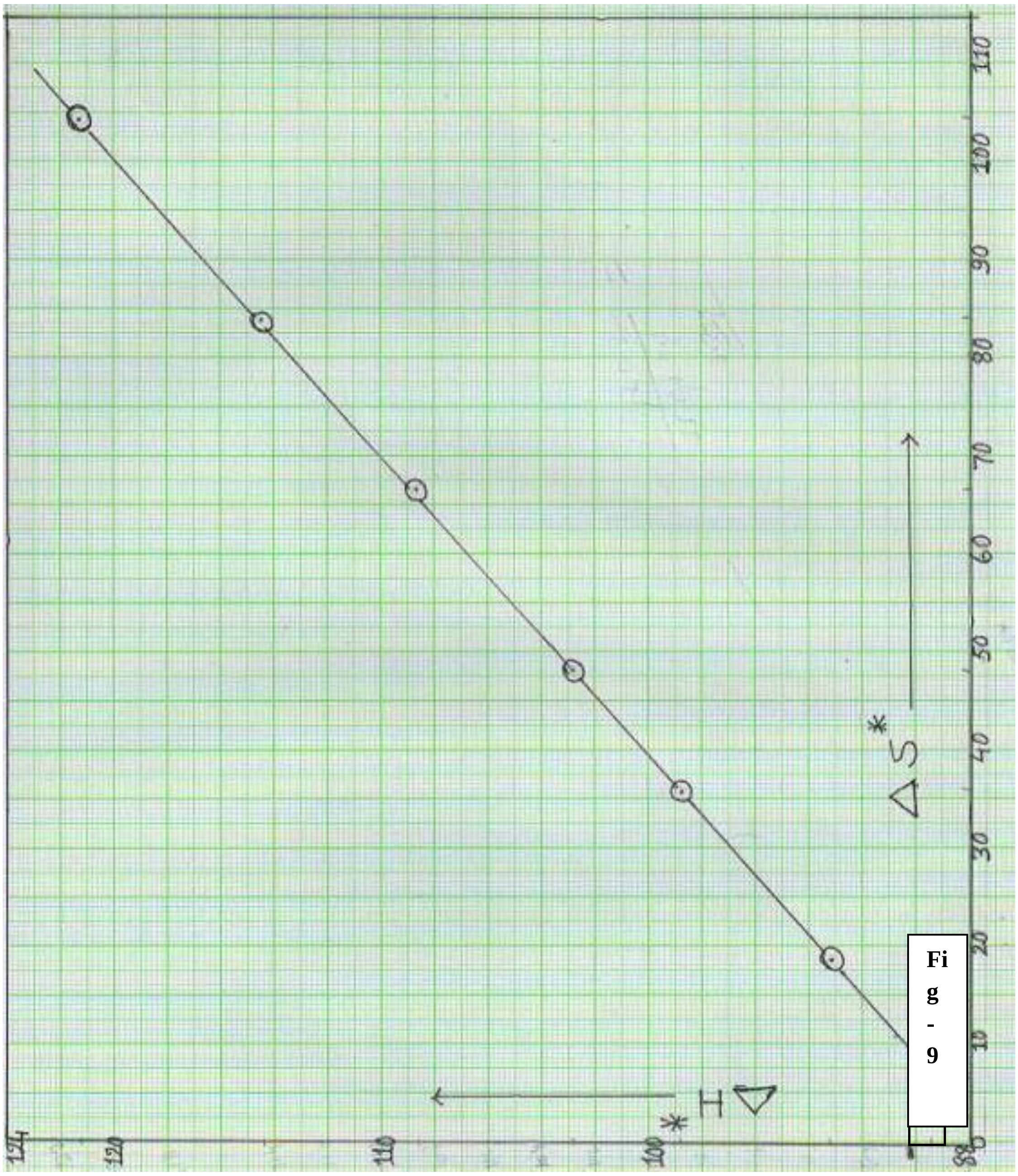

Fig-9