

STUDIES ON THE SOLVENT-EFFECT OF A SECONDARY ALCOHOL ON THE EXTENSIVE THERMODYNAMIC PARAMETERS AND MECHANISM OF ACID CATALYSED SOLVOLYSIS OF ISO-PROPYL FORMATE

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ABSTRACT

For highlighting the solvent effect of a dipolar protic solvent secondary alcohol on the rate, thermodynamic activation parameters and solvent-solute interaction of a solvolysis reaction, the kinetics of acid catalysed hydrolysis of Iso-propyl formate was studied in aquo-propan-2-ol media of varying composition containing 20 to 80% propan-2-ol at five different temperatures i.e. 20, 25, 30, 35 and 40°C. The changes observed in the values of iso-composition and iso-dielectric activation energies of the reaction have also been explained in the light of solvation and desolvation of initial and transition states to different extent. From the evaluated value of iso-kinetic temperature which comes to be 328.0, it is inferred that there is strong solvent-solute interaction in aquo- propan-2-ol media. Effects of ionic strength and change in $[H^+]$ ion concentration on the rate of reaction have also been studied and it is concluded that the acid catalysed hydrolysis of Iso-propyl formate is ion-dipolar reaction and it follows A_{AC}^2 mechanistic pathways in aquo- propan-2-ol reaction media.

Introduction:

Various kineticists¹⁻³ have reported that the effect of dipolar aprotic solvent like DMF, Acetonitrile, Dioxan etc. have widely been studied on the acid catalysed hydrolysis of lower methanoates, but solvent effect of a dipolar protic solvent like propan-2-ol having very high solvating efficiency on the biochemical and medicinal efficiencies of substituted aliphatic formates such as Iso-propyl formate has not been paid adequate attention so far.

So, in order to highlight the above noted untouched piece of research work, it has been proposed to study the solvent effect of propan-2-ol on the acid catalysed hydrolysis of Iso-propyl formate.

Experimental :

Purified propan-2-ol of Merck grade and Iso-propyl formate of USSR make were taken into use. The kinetics of acid catalysed hydrolysis of the ester was studied as usual by adding 0.50 ml of ester with the help of the graduated syringe pipette into 50 ml of 0.5 M HCl solution. The values of specific rate constants were evaluated by making use of first order rate equation and are tabulated in Table - I. Variation of log k values with mol % of propan-2-ol reaction media has been recorded in Table - II. The evaluated values of the two activation energies (Iso-composition, E_C and Iso-dielectric, E_D) have been mentioned in Table - III and IV respectively. For deciding the mechanistic path way of the reaction, from the slopes of the plots of log k versus log $[H_2O]$, the evaluated values of solvation number have been mentioned in Table - V. The thermodynamic activation parameters of the reaction calculated by using Wynne-Jones & Eyring equation⁴ has been enlisted in Table -VI.

Table - I

Specific rate constant values of Acid catalysed hydrolysis of Iso-butyl formate in water-Propan-2-ol media

Temp in °C	% of Propan-2-ol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	79.10	63.07	51.27	41.70	31.52	22.79	16.87
25° C	144.64	125.23	104.76	83.21	69.23	54.98	40.19
30° C	281.96	240.05	208.35	177.75	151.39	122.35	93.37
35° C	531.13	464.09	411.62	371.62	315.28	263.69	218.93
40° C	974.77	881.25	794.51	724.60	655.54	572.93	505.01

$k \times 10^3 \text{ in } (\text{dm})^3 \text{ mol}^{-1} \text{ min}^{-1}$

The effect of $[\text{H}^+]$ concentration has been studied by changing the $[\text{H}^+]$ ion strength of the aquo- propan-2-ol media and the evaluated values of specific rate constants have been recorded in Table - VII.

Results and Discussion:

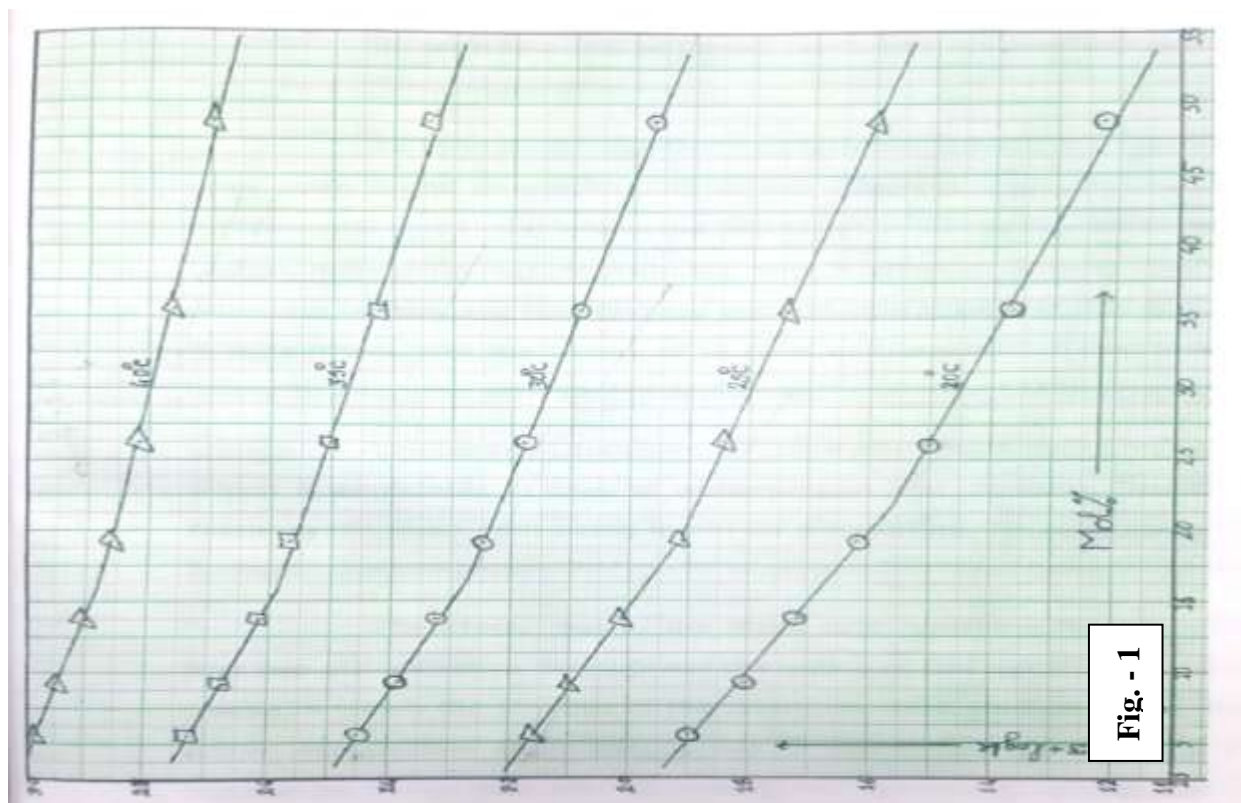
From Table - I, it is clear that specific rate constant values of the reaction decrease with increase in propan-2-ol component of the reaction media.

In order to study the variation in k values of the reaction with change in mol % of propan-2-ol, the logarithmic values of k which have been recorded in Table - II, have been plotted against the mol % of propan-2-ol and is shown in Fig. -1. From Fig. -1, it is clear that there is fast depletion followed by the slow decrease in the rate at 18.70 mol % of propan-2-ol in the reaction media. However, with increasing temperature, the rate depleting effect of solvent is found to be decreasing.

Table -II

Variation of log k values of the reaction at different temperatures with mol % of Propan-2- ol in water-Propan-2-ol media.

% of Propan-2-ol (v/v)	Mol % of Propan-2-ol	3 + log k values				
		20°C	25°C	30°C	35°C	40°C
20%	5.59	1.8982	2.1603	2.4488	2.7252	2.9889
30%	9.22	1.7998	2.0977	2.3803	2.6666	2.9450
40%	13.64	1.7099	2.0202	2.3188	2.6145	2.9001
50%	19.16	1.6201	1.9202	2.2498	2.5701	2.8601
60%	26.23	1.4986	1.8403	2.1801	2.4987	2.8166
70%	35.61	1.3577	1.7402	2.0876	2.4211	2.7531
80%	48.67	1.2271	1.6041	1.9702	2.3402	2.7033



It is opined that the following three 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-propan-2-ol medium,
- (ii) lowering of the bulk dielectric constant values of the medium, and
- (iii) depletion of H_3O^+ ions of the solution by the organic co-solvent (propan-2-ol) molecule due to its basic character

As propan-2-ol is not basic, so it may not combine with H^+ and H_3O^+ ions of the acidic medium. Hence, among the above mentioned three rate retarding factors, the first two factors are

in operation and it is quite in agreement with the theory of Hughes and Ingold⁵ that the rate is bound to decrease with decreasing dielectric constants of the medium.

However, these interpretations are in support of the earlier views of Laidler and Lanskroener⁶. In the recent years, Rakesh & Singh et al.⁷, have also reported similar findings and interpretations for depletion in the rate of solvolysis reactions.

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

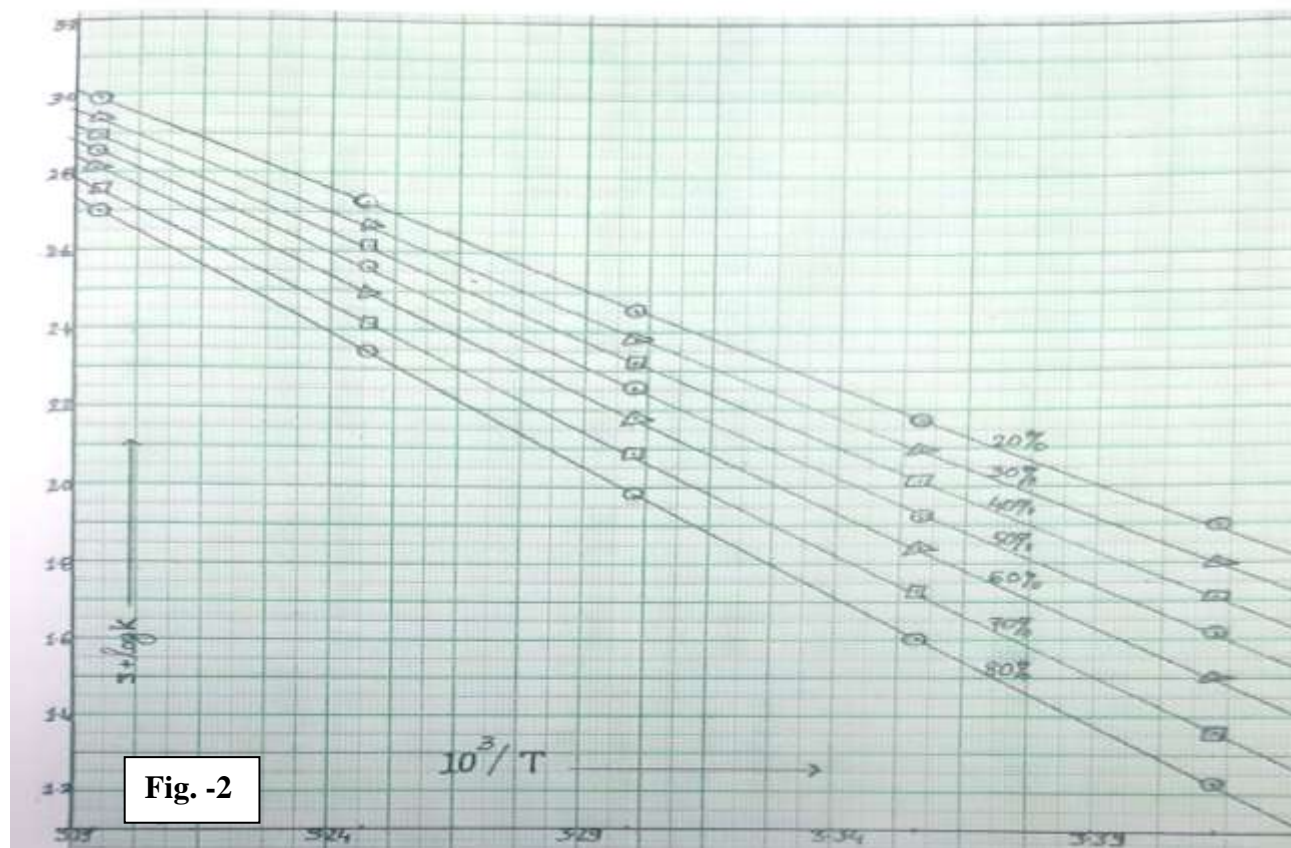
From the Arrhenius plots of $\log k$ values $1/T$, as shown in Fig. - 2, the values of iso-composition activation energy (E_c or E_{exp}) have been calculated from the slope of the plots and are mentioned in Table - III.

Table - III
Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-Propan-2-ol media.

% of Propan-2-ol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c value in KJ/mol	96.89	100.71	104.60	110.56	116.53	122.71	130.25

From Table - III, it is clear that values of iso-composition activation energy go on increasing from 96.89 kJ/mol to 130.25 kJ/mol with addition of 20 to 80% of propan-2-ol in the reaction media. Usually, enhancement in the values of iso-composition activation energy may be due to either of the following three causes:

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



Out of these three factors, the first one seems to be applicable in this case and this cause has also been supported by the increase of entropy of activation (ΔS^*) with gradual addition of the organic co-solvent (propan-2-ol) in the reaction media as tabulated in Table - VII. Such changes have been found in support of the earlier views of Singh & Singh et al⁸. In this connection, recently Singh & Wats et al⁹. and Rashmi & Singh et al.¹⁰, have also reported similar findings.

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

From the slopes of the Arrhenius plots of $\log k_D$ values against $1/T$ ($\log k_D$ values are obtained from interpolation of the straight line plots of $\log k$ values against D values), the values

of iso-dielectric activation energy have been evaluated and are recorded in Table - IV. From this Table, it is observed that E_D values go on decreasing from 132.96 kJ/mol to 96.74 kJ/mol with increasing D values of the reaction media from 30 to 65. This trend of depletion in E_D values with increasing D values of the reaction media is similar to enhancement in E_C values with addition of more and more propan-2-ol in the reaction media. These interpretations have also been supported by the earlier reports of Singh & Singh et al.⁸. However, Singh & Wats et al.⁹ and Priyanka & Singh et al.¹¹ have also gone through similar findings respectively.

Table - IV

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

D values	D = 30	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60	D = 65
E_D values in kJ/mol	132.96	129.39	123.56	117.53	112.90	109.33	101.76	96.74

Solvent Effect on the Participation of water molecules in the formation of Activated complex and Mechanism of the reaction:

The number of water molecules associated with the activated complex of the reaction has been determined by plotting log k values, against log [H₂O] according to the relation proposed by Robertson.¹²

$$\log k = \log k_0 + n \log [H_2O]$$

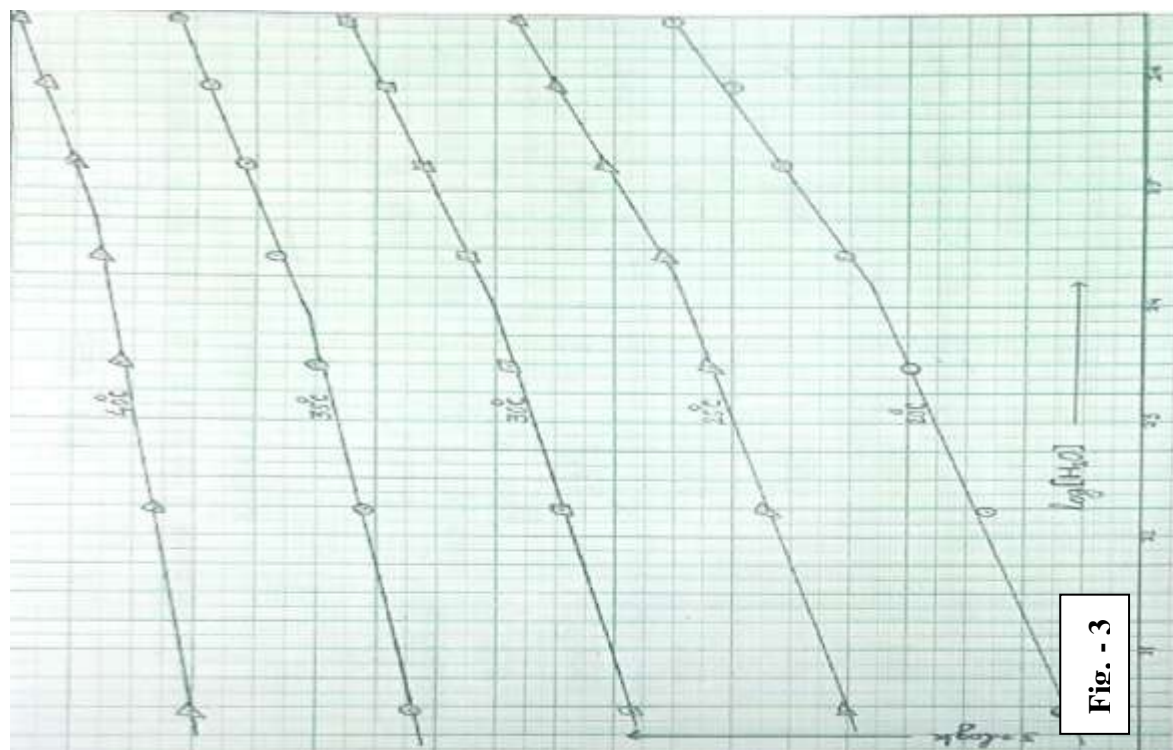
where 'n' is the solvation number which tells about the number of water molecules associated with

the activated complex and also hints about criterion for studying the mechanism of the reaction. On plotting log k values against log [H₂O] values as shown in Fig. - 3, two intersecting straight lines at log [H₂O] value 1.413, with positive slopes are obtained. The numerical values of the slopes are enlisted in Table - V.

Table - V

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

Temperature in °C	Slope - I when log[H ₂ O] value is below 1.413	Slope - II when log[H ₂ O] value is above 1.413
20°C	0.926	0.935
25°C	0.817	1.226
30°C	0.682	0.996
35°C	0.497	0.893
40°C	0.387	0.785



From Fig. - 3 and from the values recorded in Table - V, it is clear that below $\log [H_2O]$ value 1.413 which corresponds to 46.60% of water in the reaction media, the values of the slopes decreases from 0.926 to 0.387 with increase in temperature from 20 to 40°C. This suggests that below 46.60 % of water in the reaction media, about 1.0 to 0.50 molecules of water are taking part in the formation of activated complex as the temperature rises from 20 to 40°C. Similarly, from the values of slopes, it is clear that in case of increase in water concentration (above 46.60 % v/v), the numerical values of slopes decrease from 1.456 to 0.785. These values also show that approximately from 1.50 to 1.0 molecules of water are taking part in the formation of activated complex as the temperature of the reaction rises from 20 to 40°C. From this, it may be concluded that when concentration of water falls in aquo- propan-2-ol media, the number of water molecules taking part in the formation of the activated complex is about half but with increase in

water concentration in the reaction media, the number of water molecules associated with the formation of the activated complex becomes one. Thus, it can be concluded from the guidelines of Robertson et al.¹² that the acid catalysed hydrolysis of Iso-butyl methanoate in aquo- propan-2-ol media follow bimolecular mechanism with respect to water. In other words, the presence of propan-2-ol in the reaction media and with rise in temperature of the reaction, the mechanistic pathway of the reaction is changed from unimolecular to bimolecular.

These observations may be attributed to the fact that in presence of propan-2-ol, the equilibrium of water shifts from its bulky form to its dense form with rise of temperature of the reaction.



al.⁹, Singh & Bano et al.¹³ and Sharad & Singh et al.¹⁴, in recent years have also reported similar observations and inferences.

Thermodynamic Activation Parameters of the Reaction :

The famous Wynne-Jones and Eyring⁴ equation has been applied to evaluate the three thermodynamic activation parameters namely enthalpy of activation ΔH^* , entropy of activation ΔS^* and the free energy of activation ΔG^* and their values have been recorded in Table - VI. On visualising the data mentioned in Table-VI, the interesting feature comes in the light is that out of the values of all the three thermodynamic activation parameters i.e. ΔH^* , ΔG^* and ΔS^* are increasing simultaneously with increasing proportion of propan-2-ol in the reaction media. For highlighting the solvent effect on the three thermodynamic activation parameters, namely ΔH^* , ΔG^* and ΔS^* , the numerical values of all were plotted against mol % of the propan-2-ol in the reaction as shown in Fig. - 4, 5 and 6 respectively. The non-linear variation in ΔH^* and ΔS^* from Fig. - 4 and 6 give information of the fact that specific solvation is taking place in aquo-propan-2-ol media similar to that as reported by Saville et al.¹⁵. From the fundamental thermodynamic equation:

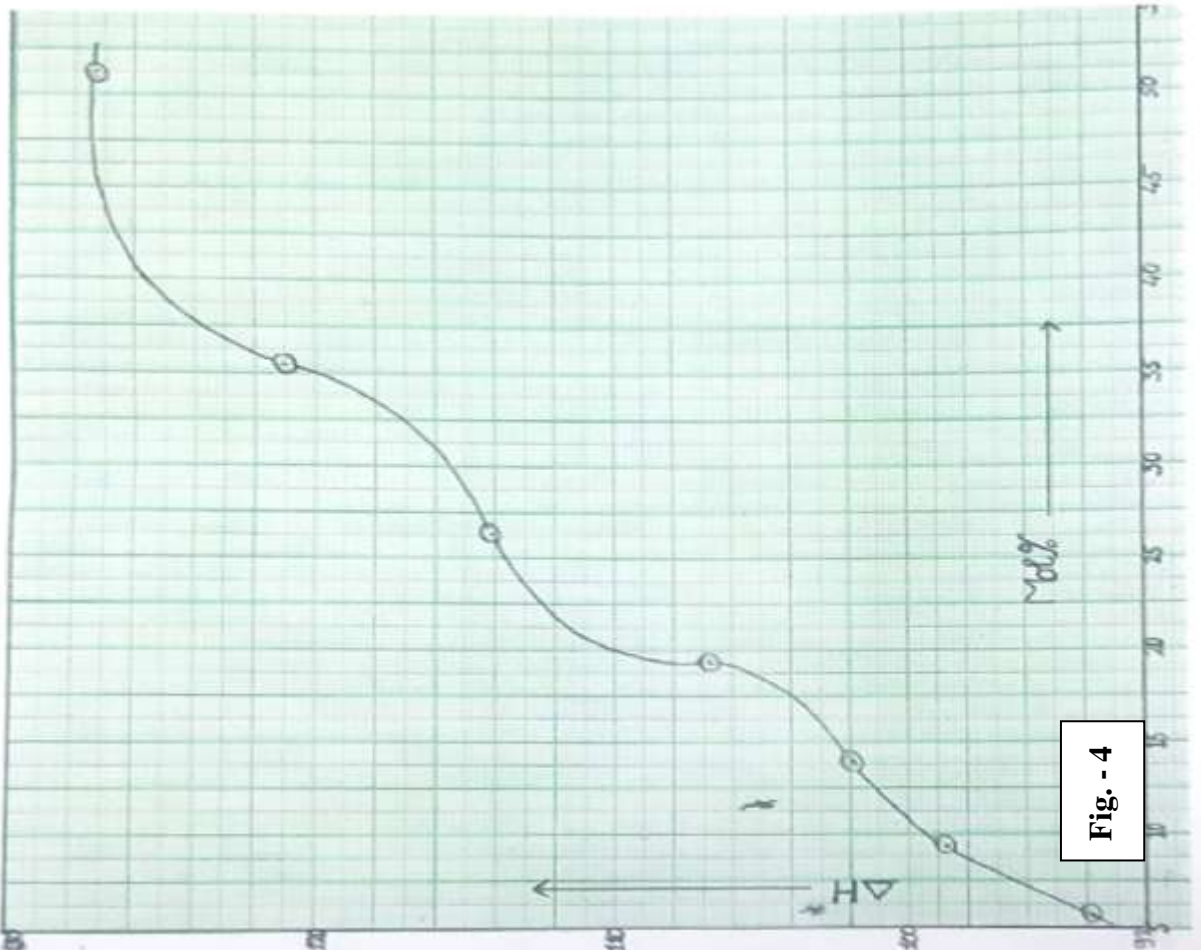
$$\Delta G^* = \Delta H^* - T\Delta S^*$$

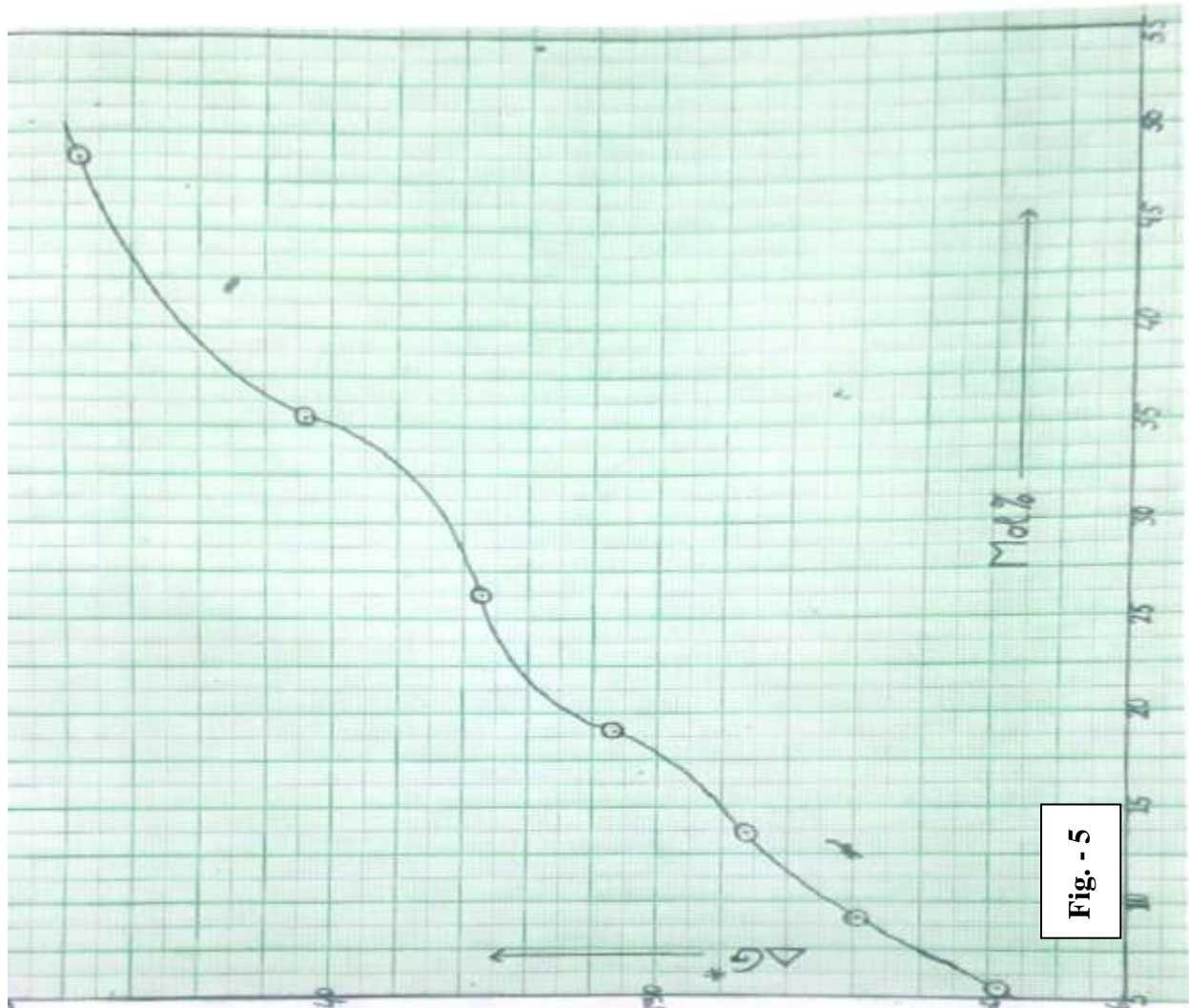
it may be inferred that the simultaneous increase in the values of ΔH^* and ΔS^* with enhancement of ΔG^* values is only possible when the quantitative increase in the values of ΔH^* is greater than that found in the values of ΔS^* and from this fact, it is concluded that acid catalysed hydrolysis of Iso-

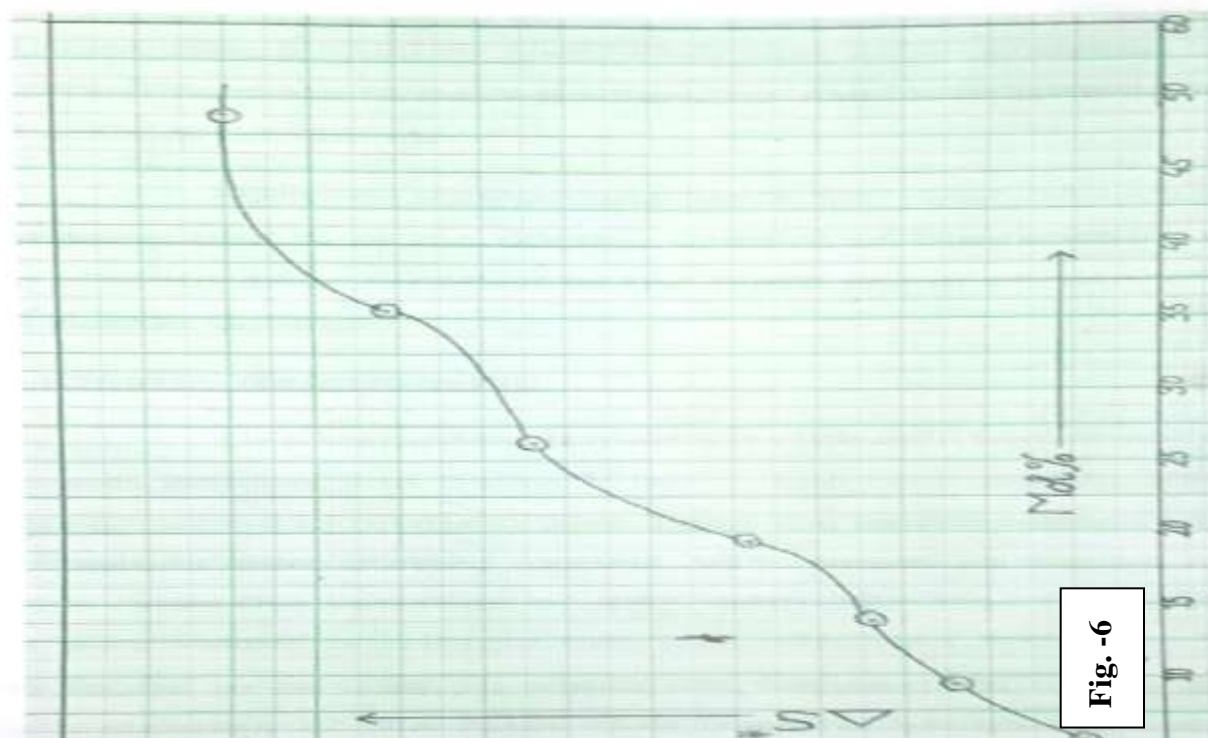
Table - VI
Variation of ΔH^* , ΔG^* and ΔS^* values of the reaction with mol % of Ethanol in water-Ethanol media

% of Propan-2-ol (v/v)	Mol % of Propan-2-ol	ΔH^* in kJ/mol	ΔG^* in kJ/mol at 30°C	ΔS^* in J/K/mol at 30°C
20%	5.59	93.86	81.97	39.24
30%	9.22	98.60	82.37	53.57
40%	13.64	101.81	82.72	62.99
50%	19.16	106.71	83.12	77.82
60%	26.23	113.96	83.53	100.42
70%	35.61	120.90	84.07	121.56
80%	48.67	127.23	84.79	140.22

propyl formate in aquo- propan-2-ol media is enthalpy dominating and entropy controlling reaction. The enhancement found to different extent in the values of enthalpy of activation ΔH^* and entropy of activation also supports the fact that transition state of the reaction is more desolvated than that of its initial state in the similar way as reported earlier by Singh & Singh et al⁸. Recently, Namrata & Singh et. al¹⁶. have also reported similar interpretations for describing the effect of solvent on the changes found in thermodynamic activation parameters of the solvolysis reaction.







Effect of Change in $[H^+]$ ion concentration of the Reaction media on the specific rates and Mechanism of the Reaction :

The effect of change in the acid concentration on the kinetics of the reaction was studied at $25^{\circ}C$ by changing the concentration of HCl, but the ionic strength of the reaction media was always kept fixed ($\mu = 0.9$). The values of specific rate constant values for different $[H^+]$ ion concentration of the reaction media have been inserted in Table - VII.

Table - VII

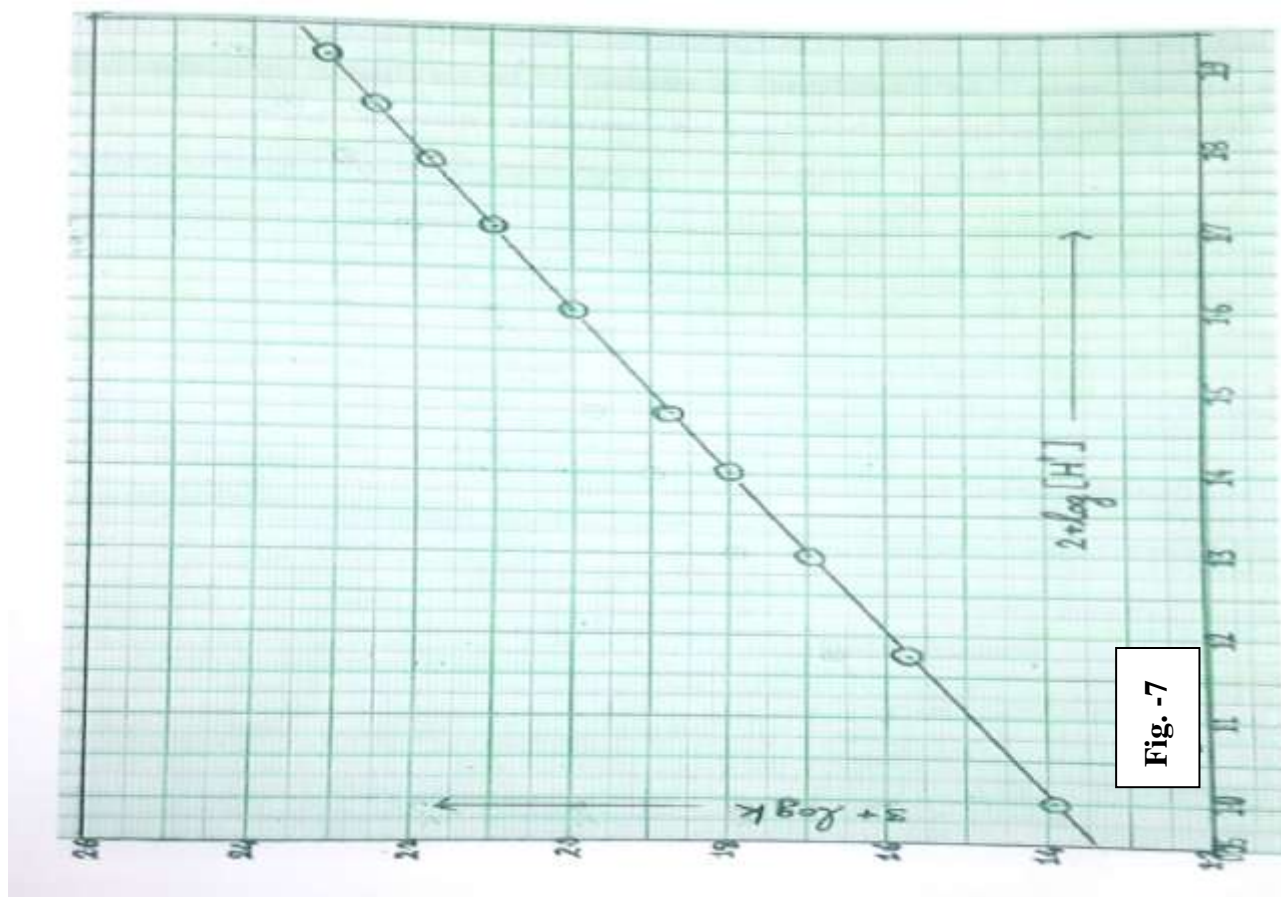
Effect of $[H^+]$ on the Specific rate constant values of
 Acid Catalysed Hydrolysis of Isobutyl methanoate in water-EtOH media
 at constant ionic strength ($\mu = 0.9$)

Temp. - 25°C

$[H^+]$	[KCl]	μ	$k \times 10^4$ in min^{-1}	$2 + \log[H^+]$	$2 + \log k$	value of the slope of the plot of $\log k$ versus $\log [H^+]$
0.10	0.80	0.90	24.48	1.0000	1.3889	
0.15	0.75	0.90	37.13	1.1761	1.5701	
0.20	0.70	0.90	49.73	1.3010	1.6966	
0.25	0.65	0.90	62.94	1.3979	1.7989	
0.30	0.60	0.90	74.52	1.4771	1.8723	
0.40	0.50	0.90	99.59	1.6021	2.9982	
0.50	0.40	0.90	125.23	1.6990	2.0977	1.005
0.60	0.30	0.90	153.23	1.7782	2.1801	
0.70	0.20	0.90	176.93	1.8451	2.2478	
0.80	0.10	0.90	202.86	1.9030	2.3072	

The values of the slope of straight line plots of $\log k$ versus $\log [H^+]$ as shown in Fig - 7. was found

to be 1.005 which is almost equal to unity and from this, it is inferred on the guidelines of Zucker and Hammett¹⁷ that acid catalysed hydrolysis of Iso-propyl formate in aquo- propan-2-ol media follows A_{AC}^2 mechanism. Such inferences regarding the mechanism has also been supported by the recently reported views of Sinha & Singh et al¹⁸. And Sushma, Abhay and Singh et.al.¹⁹



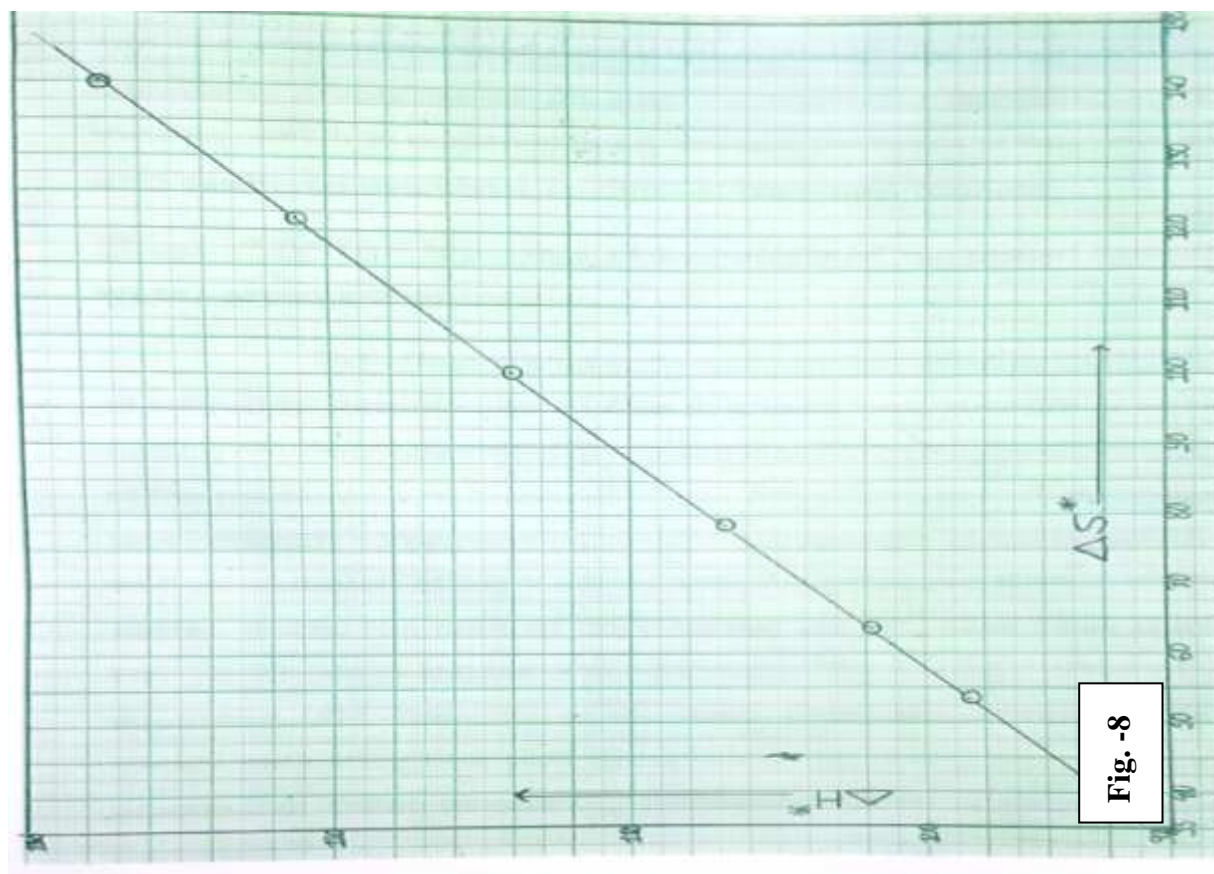
Solvent Effect on the Solvent-Solute Interaction in aquo-Ethanol media:

In the light of Barclay and Butler²⁰ relationship between enthalpy and entropy of

activation, which is as:

$$\delta m (\Delta H^*) = \beta \delta m (\Delta S^*)$$

where 'β' is a constant called iso-kinetic temperature and also known as Leffler-Grunwald²¹ solvent stabilizer operator. The values of Iso-kinetic temperature of this reaction has been evaluated from the slopes of the plots of ΔH^* versus ΔS^* as shown in Fig.-8 and it comes to be $324.50 \approx 325.0$. From the value of iso-kinetic temperature (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 strong and appreciable interaction between solvent and solute present in the aquo- propan-2-ol media in the similar way as reported by Leffler²². Earlier Singh & Singh et al⁸. and in recent years Raghaw & Singh et al²³. and Sushma, Abhay & Singh et.al.¹⁹ have also reported similar observations and findings about the solvent-solute interaction in the different reaction media.



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