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Effect on Dipolar protic Solvent on the [H^+] in catalysed Hydrolysis of Heavier Methanoate

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ABSTRACT

The solvent effect of ethanol on the acid catalysed solvolysis of Propyl methanoate (heavier methanoate) was studied by carrying out the hydrolysis of the ester in water-ethanol (EtOH) media of varying composition consisting of 20% to 80% (v/) at different temeratures ranging from 20 to 40°C.

The specific rate constant values of the reaction were found to decrease with increasing concentration of ethanol in the reaction media.

It was found that with increase in temperature of the reaction from 20 to 40°C from 0.252 to 1.258 molecules of water are associated with the activated complex and from this, it is inferred that medchanistic path followed by the reaction in presence of ethanol is changes from bimolecular to unimolecular. The depletion and enhancement observed respectively in iso-composition and iso-dielectric activation energies reveal that the transition state is solvated and initial state is desolvated with addition of ethanol (EtOH) in The reaction media . Form the values of iso-kinetic temperature, which comes to be 280, it may be concluded that in water-EtOH reaction media, the reaction follows Barclay-Butler rule and theere is weak but acceptable interaction between solvent and solute in the reaction media.

Key words:- Dipolar protic solvent, methanoate, Iso-dielectric, Iso-kinetic temperature . Depletion and Enhancement Barclay -Butler Rule, Leffer's guide line.

Introduction:

Earlier kinecisists[1-4] have reported on the effect of dipolar aprotic solvents like DMSO, Diaxon and DMF on the acid catalysed solvolysis of lighter medhanoate but studies on the solvent effect of dipolar protic solvent on the catalysed solvolysis of heavier methanoate are not available till today.

Heance it is thought essential to study the effect of a dipolar protic solvent ethanol on the acid catalysed hydrolysis of Propyl metthanoate, as its use as flavouring agent seems to be very useful in the food technology.

Experimental & Calculation: Export quality of Propyl methanoate, made in USSR and SISCO grade of high degree pure ethyl alcohol (99.5%) were used. The kinetics of the reaction was studied by adding 0.45 ml of ester through syringe pipette into 50 ml of 0.5 M solution of HCL. The reaction was found to obey the first order kinetic equation and the evaluated values of specific rate constants have been recorded in Table-I. The values of log k and log[H_2O] of the reaction media are recorded in Table -II. From the slope of the plots of log k versus log[H_2O], thee number of water molecules associated with the transition state of the reaction have been evaluated and are placed in Table -III. The values of both iso-composition and iso-dielectric activation energies have been mentioned in Table-IV and Table-V respectively. The values of thermodynamic activation parameters were calculated using Wynne-Jones and Eyring equation[5] and are synchronised i Table -VI.

Results and Discussion:

Table-I shows that the rate constant values of the reaction decrease with increasing proportion of ethanol in the reaction media. On plotting log k values against mole % of ethanol as shown in Fig.-1, it is obvious that up to 20.60 mol % of the ehtanol in the reaction media, the rate of the reaction falls rapidly but beyond (above) 20.60 mol% of ethanol, the depletion in the rate follows slow path. The decreasing trend in the values of the specific rate constants needs to be discussed in the light of Hughes and Ingold[6] predictions according to which an increase in the dielectric constant values of the reaction media causes an increase in the rate when there is concentration or constructions of charges on the transition stage and causes a decrease in the rate when there is diffusion or destruction of charges on the transition stage. The values of dielectric constants of the reaction media go on decreasing with gradual addition of ethanol. So our findings are fully in accordance with the qualitative

Table - 1

Specific rate constant values of Acid catalysed hydrolysis of Propyl Methanoate in water-DMSO media

$k \times 10^4$ in (dm)3 $mole^{-1}$ min^{-1}

Temp in °C	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	72.18	66.90	62.75	58.55	53.90	31.25	45.67
25°C	131.76	119.01	106.49	97.48	87.42	73.81	68.14
30°C	236.16	203.33	186.25	165.88	138.71	173.82	102.28
35°C	407.57	346.98	303.46	251.36	224.03	389.22	150.97
40°C	706.15	588.71	498.65	414.76	346.90	877.00	212.73

Table - II

Variation of log k values of the reaction at different temperetures with mol% of DMF in water-DMF media.

% of EtOH (v/v)	% of H_2O	log $[H_2O]$	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.8584	2.1198	2.3732	2.6102	2.8489
30%	70%	1.5898	1.8254	2.0756	2.3082	2.5403	2.7699
40%	60%	1.5229	1.7976	2.0273	2.2701	2.4821	2.6978
50%	50%	1.4437	1.7675	1.9889	2.2198	2.4003	2.6178
60%	40%	1.3468	1.7316	1.9416	2.1421	2.3503	2.5402
70%	30%	1.2218	1.7001	1.8899	2.0933	2.2816	2.4578
80%	20%	1.0458	1.6596	1.8334	2.0098	2.1789	2.3278

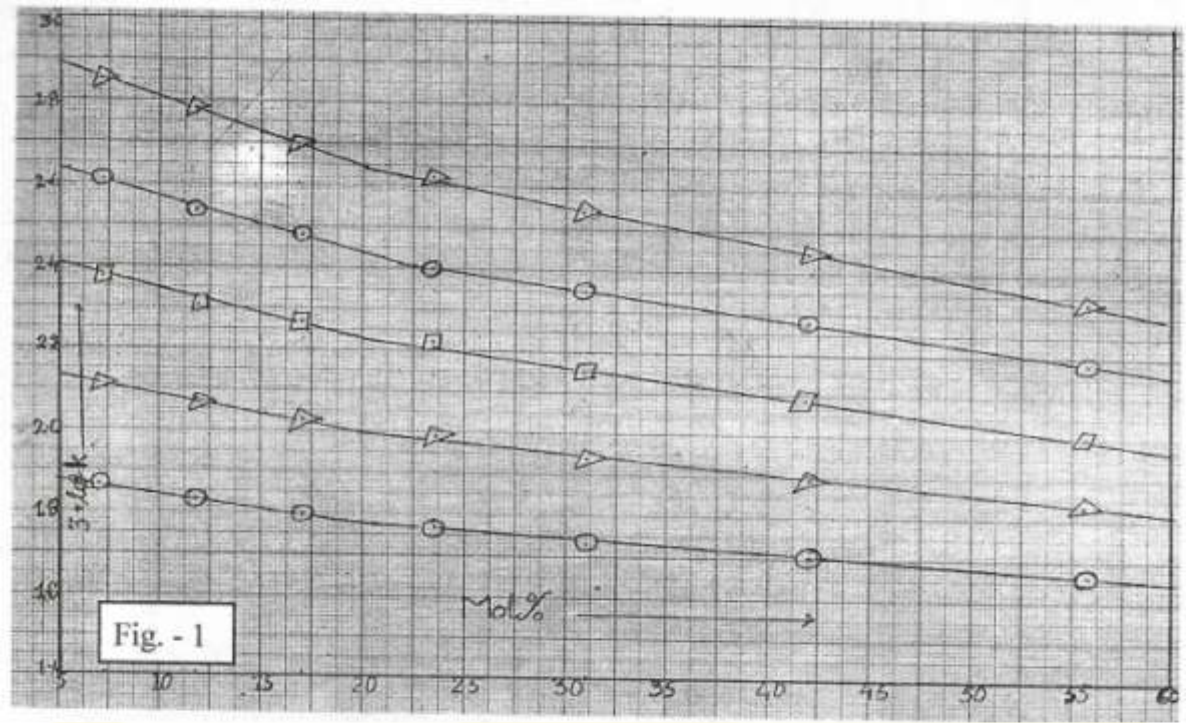


Fig.- 1 : Variation of log k values with mol % of EtOH in water-EtOH media

prediction of Hughes and Ingold. Howeve, our findings are also in agreement with the qualitative prediction of Laidler and Landskroenel[7] and with the earlier reports of Singh & Kumari et al [8] Kumar & Singh et al [9] and also with recent repon of R.T. Singh[10] , who predicted that the rate of ion dipolar reaction decreases with decrease in the dielectric constant values of the reaction media.

Evaluation of Sovation number and Determination of mechanistic pathways followed by the reaction:

Solvation number 'n' is the number of water molecules associated with transition state of the reaction. Robertson[11] has derived an equation, which is as:

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

where 'n' is the solvation number and is evaluated from the slopes of the plots of log k versus log $[H_2O]$.

Robertson et al.[12] suggested that values of 'n' for unimolecular reactions is fairly high while that of bimolecular reactions, it will be low.

From the recorded values of log k and log$[H_2O]$ in Table -II, the log k values were plotted against log$[H_2O]$ as shown in Fig. -2 and the evaluated values of the slopes of the straight lines have been enlisted in Table-III.

From Fig.-2 it is clear that at each temperature two intersecting straight lines are obtained at log[H_2O] value 1.415 which corresponds to 46.80% of water concentration (v/v) in water-EtOH reaction media.

From the recorded values of the slopes of the plots of log k versus log[H_2O] in Table -III, it is clear that below or before log[H_2O] value 1.415, which corresponds to 46.80% of water concentration in the reaction media, the number of water molecules involved in the formation of the activated complex increase from 0.252 to 0.945 with rise in temperature from 20 to 40°C. Similarly after 46.80 % of water concentration in the section media the number of water molecules in the activated complex in creases from 0.510 to 1.258 with rise in temperature from 20 to 40°C.

Overall, it is concluded that number of water molecules associated with the activatted complex increase from 0.252 to 1.258 with rise in temperature from 20 to 40°C and from this trend, in the light of the guidelines of Robertson et al.[12] it is inferred that the mechanistic pathway of the reaction is changed from bimolecular to unimolecular with

Table - VI

Values of the slopes of the plots of log k versus log [H_2O] values at different temperatures

Temperature in °C	Slope - I Where log[H_2O] value is below 1.415	Slope - II Where log[H_2O] value is above 1.398
20°C	0.252	0.510
25°C	3.375	0.657
30°C	0.494	0.798
35°C	0.564	1.047
40°C	0.745	1.258

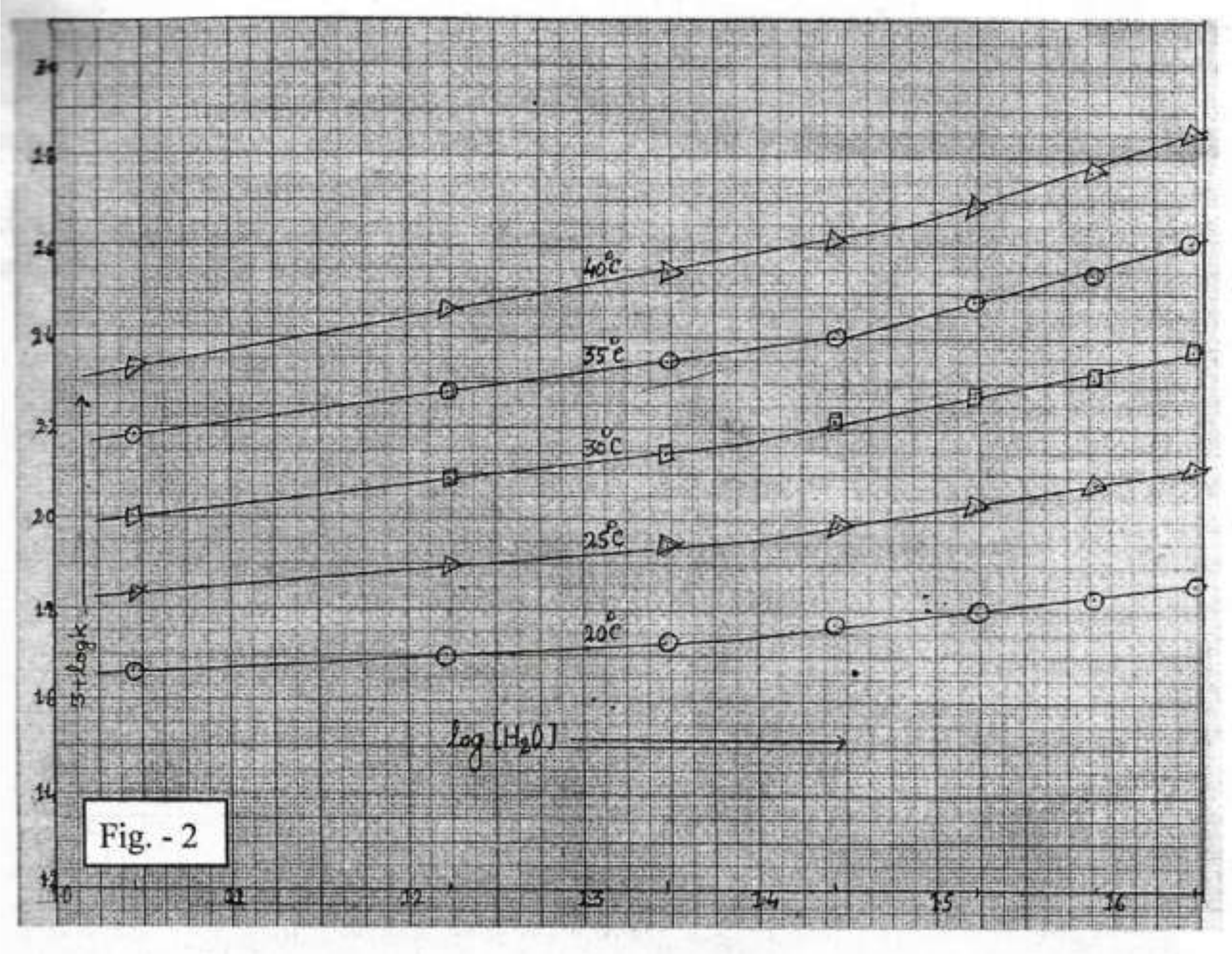


Fig. - 2

Fig. - 2: Variation of log k values against log[H_2O] values in water-EtOH media

increase in water concentration or with decrease in ethanol content of the reaction media and also with increase in the temperature of the reaction.

From the enhancing trend of number of water molecules invoved in hte formation of the activated complex, it is also inferred that on addition of ethanol in the reaction media, the equilibrium of water is shifted from its dense form to bulky form.

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

These observations and interpretations have also earlier and recently Kumar & Singh.[13] and Abhay & Singh et al [14] respectively,

Solvent effect on activation energies (Iso-composition and Iso-dielectric) of the reaction:

From Table-IV, it is obvious that E_C values go on decreasing with increasing the concentration of EtOH in reaction media. This trend is probably due to solvation changes taking place either at initial state level or at the transition state level or at the level of both the initial and transition states as reported earlier by several researchers[13-14] in this field. Considering the extent of solvation to be a dominat factor, the following three factors seem to be responsible for decrease in E_C values with gradual addition of EtOH in the reaction media:-

(i) The transition state is desolvated less than the initial state,

(ii) The transition state is solvated more than the initial state. and

Table - IV

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

% of EtOH (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C value in kJ/mol	89.96	83.48	79.07	75.00	71.24	66.42	59.66

Table - V

Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at Desired "D" values of the water-EtOH media.

D values	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60	D = 65
E_D value in kJ/mol	70.53	72.12	76.52	80.14	84.18	88.64	92.38

(iii) The transition state is solvated and the initial state is desolvated.

The transition state being large cation (ester+H^+) is available more for solvation by EtOH molecule than the initial state, so the third factor seems to be operative in our case and it is also supported by the decrease in entropy of activation (ΔS^*) of the reaction as shown in Table - VI. So situation third is the more plausible explanation for decrease in E_C values of the reaction go on decreasing due to solvation of the transition state and desolvation of initial state. This view has also been supported recently by Sushma & Singh et al[15]

Effect of Solvation on the Iso-dielectric Activation Energy (E_D) of the Reaction:

With a view to minimise the dielectric effect, the iso-dielectric activation energy was evaluated from the slopes of the Arehenius plots of log K_D values (Obtained from interpolation of the plots of log k values against D values of the reaction media) against 1/T following the guidelines of Wolford[16] and Elsemongy et al.[17] and the value thus obtained have been tabulated in Table-V. From the Table-V, it is found that E_D values go on increasing from

70.53. to 92.38 kJ/mol with increase in D values from D = 35 to D = 75. This trend of increase in E_D values is quite in agreement with changes (decrease) in E_C values of this reaction and also with the findings of Wolford[16]. and Sinha & Singh et al [18]

Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

The three thermodynamic parameters namely enthalpy of activation(ΔH^*), free energy of activation(ΔG^*) and entropy of activation(ΔS^*) of the reaction were evaluated using Wynne-Jones and Eyring equation[5] and have been mentioned in Table -VI. From the values enlisted in Table-VI, it is clear that ΔH^* and ΔS^* values of the reaction.

In order to observe the variation in these thermodynamic parameters more clearly, they were plotted against the mol % of ethanol which have been shown in Fig. -3, 4 and 5 for ΔH^*, ΔG^* and ΔS^* respectively. From Fig. -3,4 and 5, it is clear that ΔH^*, ΔG^*

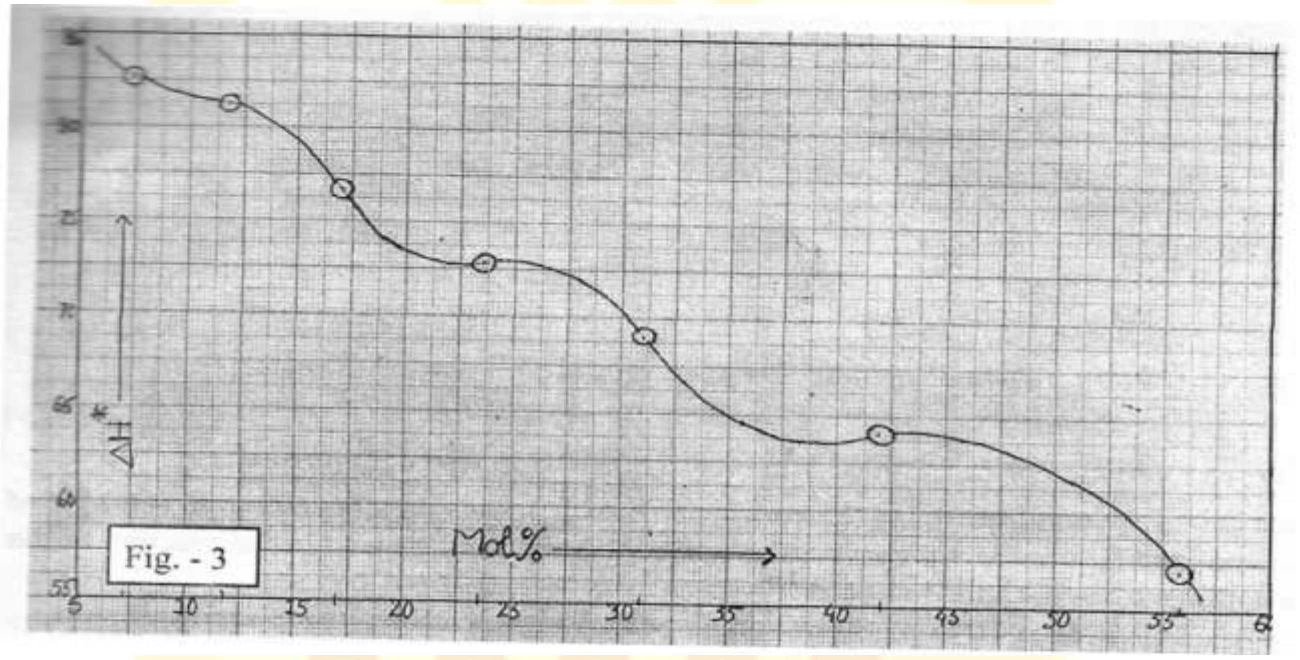


Fig. -3 : Variation of ΔH^* values with mol % of EtOH in water-EtOH media

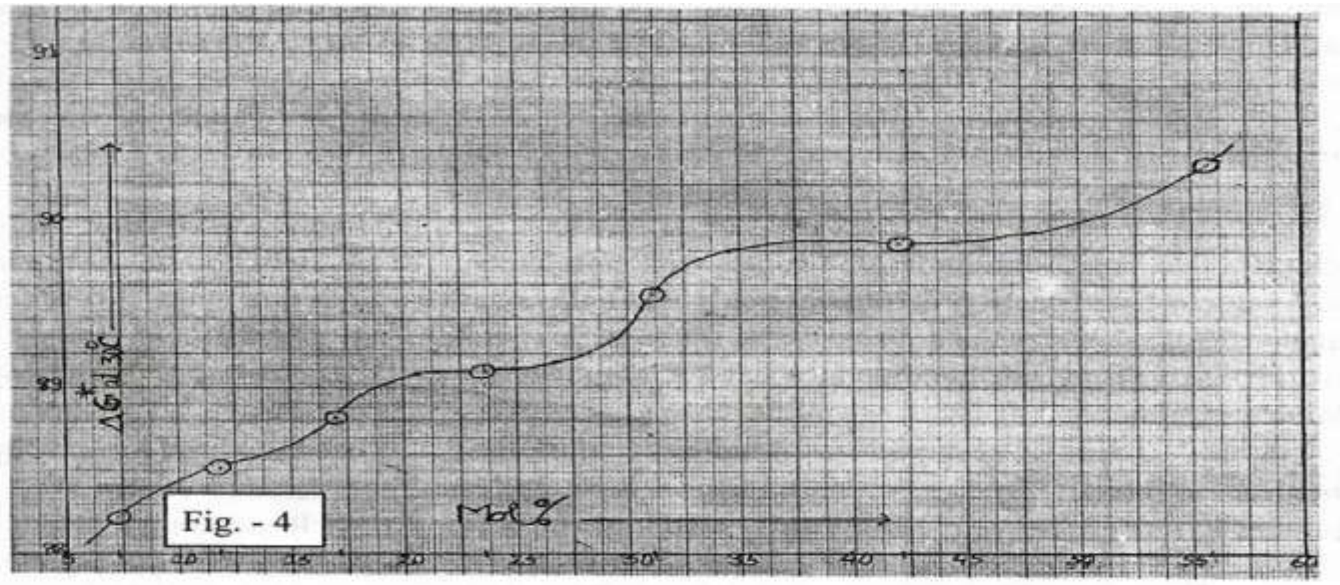


Fig. -4 : Variation of ΔG* values with mol % of EtOH in water-EtOH media

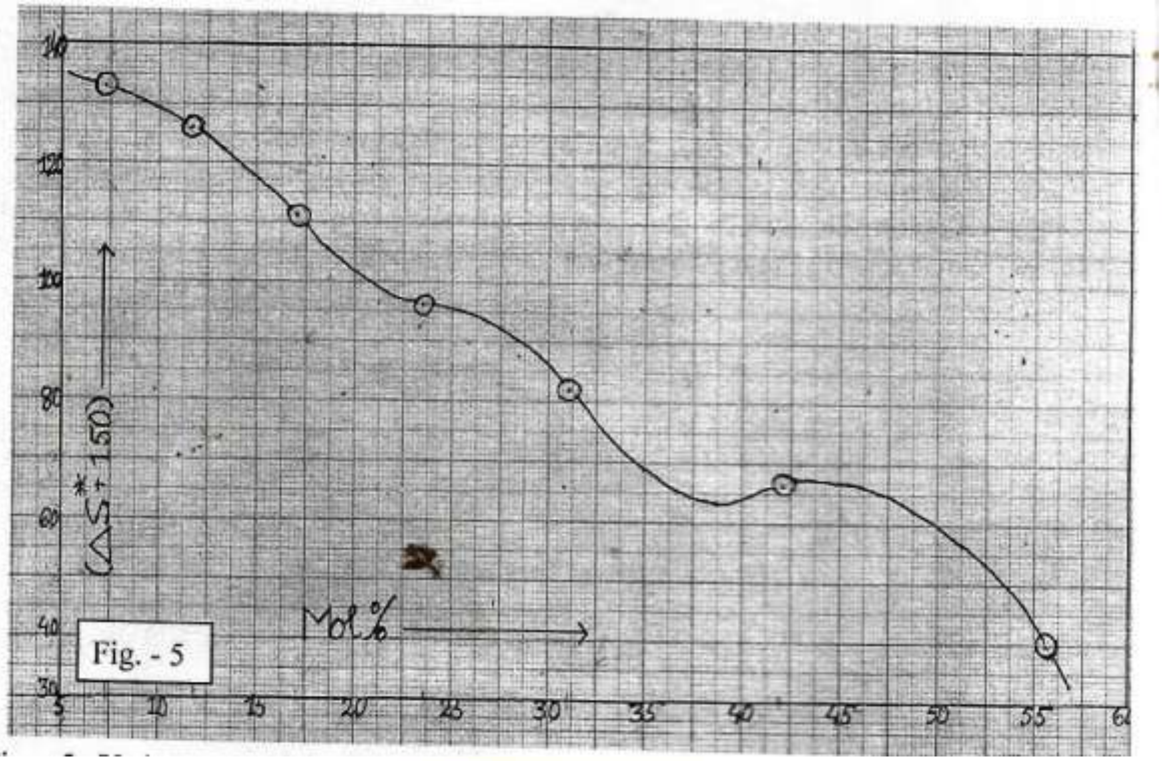


Fig.-5 : Variation of ΔS* values with mol % of EtOH in water-EtOH media and ΔS* vary non-linearly to the considerable extent with the concentration (mol %) of ethanol and this is the indication of specific solvation taking place in the reaction media according to Saville and Hudson.[19]

The ΔG^* in Table-VI is as well behaved function. From the values of ΔG^* in Table-VI and also from the Fig.-4, it is clear that ΔG^* is being little affected by the solvent composition (mol %). However, there is considerable enhancement (from 88.21 to 90.32 kJ/mol at 30°C) in ΔG^* values.

From Table -VI, is is also clear that ΔG^* values are found to increase simultaneously with depletion in both the ΔH^* and ΔS^* values (as seen in Table -VI).

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

it is clear that enhancement in ΔG^* values with simultaneous decrease in both of ΔH^* and ΔS^* values of the reaction is possible only when the extent of depletion in ΔS^* values is greater than in ΔH^* values. From these findings, it is concluded that the acid catalysed hydrolysis of Propyl methanoate in water-EtOH media is entropy controlled and enthalpy dominating reaction.

Similar observations and interpretations have also been reported recently by Dheeraj & Singh et al[20].

Solvent Effect on Solvent-Solute Interaction in the water-EtOH Reaction Media:

For highlighting solvent-solute interaction for a solvolysis reaction, Barclay and Butler[21] have correlated the enthalpy of activation (ΔH^*) and the entropy of activation

Table - VI

Consolidated Values of Thermodynamic Activation (ΔH^*, ΔG^* and ΔH^*), of the reaction, in water-EtOH system at different temperatures

ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol

% of EtOH (v/v)	Mole % of EtOH	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	**ΔS^***	**ΔG^***	**ΔS^***	**ΔG^***	**ΔS^***	**ΔG^***	**ΔS^***	**ΔG^***	**ΔS^***
20%	7017	82.65	88.11	-18.61	88.16	-18.48	88.21	-18.34	88.31	-18.37	88.36	-18.22
30%	11.69	81.19	88.29	-24.23	88.41	-24.23	88.55	-24.27	88.72	-24.45	88.83	-24.40
40%	17.07	76.89	88.48	-39.53	88.69	-39.58	88.81	-39.33	89.07	-39.53	89.26	-39.52
50%	23.59	72.74	88.62	-54.20	89.91	-54.26	89.10	-54.01	89.55	-54.69	89.74	-54.33
60%	31.06	68.96	88.82	-67.76	89.18	-67.83	89.55	-67.95	89.84	-67.80	90.21	-67.87
70%	41.87	64.33	88.99	-84.18	89.47	-84.37	89.93	-84.18	90.25	-84.16	90.70	-84.25
80%	55.85	56.90	89.22	-110.32	89.97	-110.99	90.32	-110.30	90.85	-110.25	91.48	-110.48

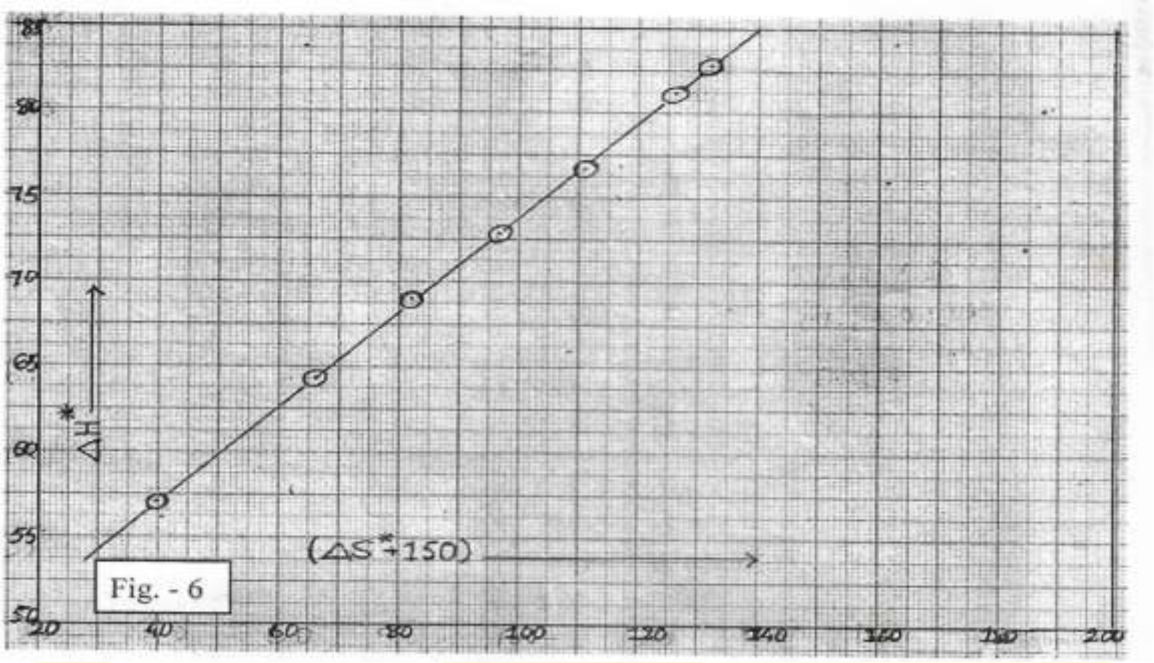


Fig.-6 : Plots of -ΔH* values against ΔS* values in water-EtOH media

Table -VII

Effect of $[H^+]$ on the Specific rate constant values of Acid Catalysed Hydrolysis of Propyl formate in water-EtOH medi

at constant ionic strength ($\mu = 0.9$)

$[H^+]$	[KCL]	μ	$k \times 10^3$ in min^{-1}	2 log$[H^+]$	3 + log k	values of the slope of the plot of log k vesus log$[H^+]$
0.10	0.80	0.90	47.76	1.0000	1.6770	
0.15	0.75	0.90	70.78	1.1761	1.8499	
0.20	0.70	0.90	94.15	1.3010	1.9738	
0.25	0.65	0.90	118.33	1.3979	2.0731	
0.30	0.60	0.90	140.48	1.4771	2.1476	
0.40	0.50	0.90	187.72	1.6021	2.2731	1.003
0.50	0.40	0.90	236.16	1.6990	2.3732	
0.60	0.30	0.90	283.60	1.7782	2.4527	
0.70	0.20	0.90	330.60	1.8451	2.5192	
080	0.10	0.90	377.83	1.9030	2.5773	

(ΔS^*) by means of the relationship-

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

where β is a constant called iso-kinetic temperature and it is evaluated from the slope of plots of ΔH^* values against ΔS^* value.

From the recorded values of ΔH^* and Δs^* in Table - VI, ΔH^* values were plotted against ΔS^* which is shown in Fig. -6. the plot consists of a straight line whose slope values has been evaluated to be 280.33 ≈

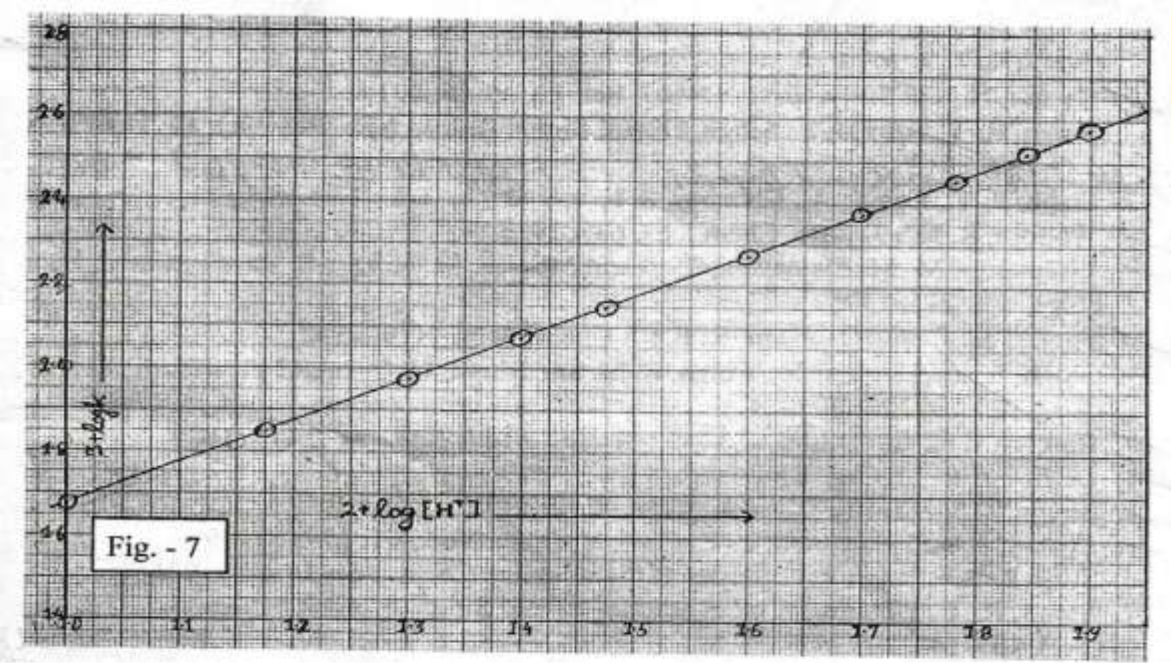
280 which is less than 300. On the guidelines of Leffler[22], it is concluded that there is weak but considerable solvent-solute interaction for acid catalysed hydrolysis of Propyl methanoate in aquo-EtOH reaction media.

Such conclusions has also been supported earlier recently by Sushma- Abhay and Singh et al[23]

Effect of $[H^+]$ on the rate and mechanism of the reaction:

In order to investigate the effect of acid concentration (H^+ in concentration on the acid catalysed hydrolysis of Propyl methanoate in water ethanol media, experiments were performed to study the kinetics at various concentrations of HCl (from 0.1M to 0.8 M), keeping the temperature, solvent composition and ionic strength of the reaction media constant. The reaactions were carried out at 30°C in the reaction media having 30% (v/v) concentration of EtOH and the evaluated specific rate constants have been tanulated in Table -VII. From the tabulated values of log k and log $[H^+]$ in Table -VII, log k values were plotted against log$[H^+]$ and has been shown in Fig.-7. From Fig. -7, it is clear that the plot is an excellent straight line showing linear dependence of rate of reaction on $[H^+]$ ion concentration. The slope of the log k versus log$[H^+]$ plot is evaluated to be 1.003 which is

Fig. - 7 : Plots of log k values against log$[H^+]$ in water-EtOH media



almost equal to unity. From this value of slope (unity), it may be inferred on the basis of the hypothesis of Zucker and Hammett[24] that acid catalysed hydrolysis of Propyl methanoate in water-ethanol media follow $A_{AC}2$ mechanism.

Similar conclusious have also been reported recently by Sushma - Abhay & Singh et al[25]

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