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Studies on the Solvent Effect of Aquo-DMSO Solvent Systems on the $[H^+]$ Ion Catalysed Hydrolysis of Butyl Formate

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Abstract: The solvent effect of Aquo-dipolar aprotic organic solvent systems was highlighted by studying the kinetics of the acid catalysed solvolysis of an aliphatic formate (Butyl formate) in water-DMSO media (aquo-dipolar aprotic organic solvent systems) of various composition having 20 to 80% of DMSO at five different temperatures ranging from 20 to 40°C. In the beginning, fast decrease followed by slow depletion in the rate with gradual addition of the organic co-solvent in the reaction media and also with increasing temperature of the reaction has been explained in the light of solvation of initial and transition states to different extents. The changes 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. Increase in the numerical values of free energy of activation (ΔG^*) with simultaneous enhancement in the values of enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) of the reaction, reveals that DMSO acts as enthalpy accelerator and entropy controller solvent.

Effects of ionic strength and $[H^+]$ ion on the rate of reaction have also been studied and it is concluded that the acid catalysed hydrolysis of Butyl formate is ion-dipolar reaction and it follows A_{AC}^2 mechanistic pathways in water-DMSO reaction media.

Keywords: Depletion and Enhancement, Ion-Dipolar. Sharp and smooth depletion, Mechanism, Solvation, Iso-composition, Iso-dielectric, Iso-kinetic temperature, Enthalpy dominating. Entropy controlled, Solvent-Solute Interaction

I. INTRODUCTION

Previously[1-2] and recently[3] it has been reported that the effect of dipolar aprotic solvent like DMF, dioxan, acetone etc. have widely been studied on the acid catalysed hydrolysis of lower formates, but solvent effect of a dipolar aprotic solvent DMSO having very peculiar solvating capacity on the biochemical and medicinal efficiencies of higher formate such as Butyl formate has not been given adequate attention so far.

So, in order to highlight the above noted untouched work, it has been proposed to study the effect of Dimethyl sulphoxide on the acid catalysed hydrolysis of Butyl formate.

II. EXPERIMENTAL

Purified DMSO of Merck grade and Butyl formate of USSR make were used. The kinetics of acid catalysed hydrolysis of the ester was studied as usual by adding 0.57 ml of ester with the help of syringe pipette into 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-1. Evaluated values of the two activation energies (Iso-composition, E and Iso-dielectric, E) have been mentioned in Table - II and III respectively. For deciding the mechanistic path way of the reaction, from the slopes of the plots of log k versus log [HO], the evaluated values of solvation number have been mentioned in Table - IV. The effect of [H] concentration has been studied by changing the [H] ion strength of the water-DMSO media and the evaluated values of specific rate constants have been recorded in Table - VI. The thermodynamic activation parameters of the reaction calculated by using Wynne-Jones & Eyring[4] equation has been tabulated in Table -V.

III. RESULTS AND DISCUSSION

From the values recorded in Table - I and Fig. 1, which highlights 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 followed by slow depletion in the rate of reaction after 23.75 mol % of DMSO in the reaction media. However, with increasing temperature, the rate depleting effect of solvent is found to be decreased.

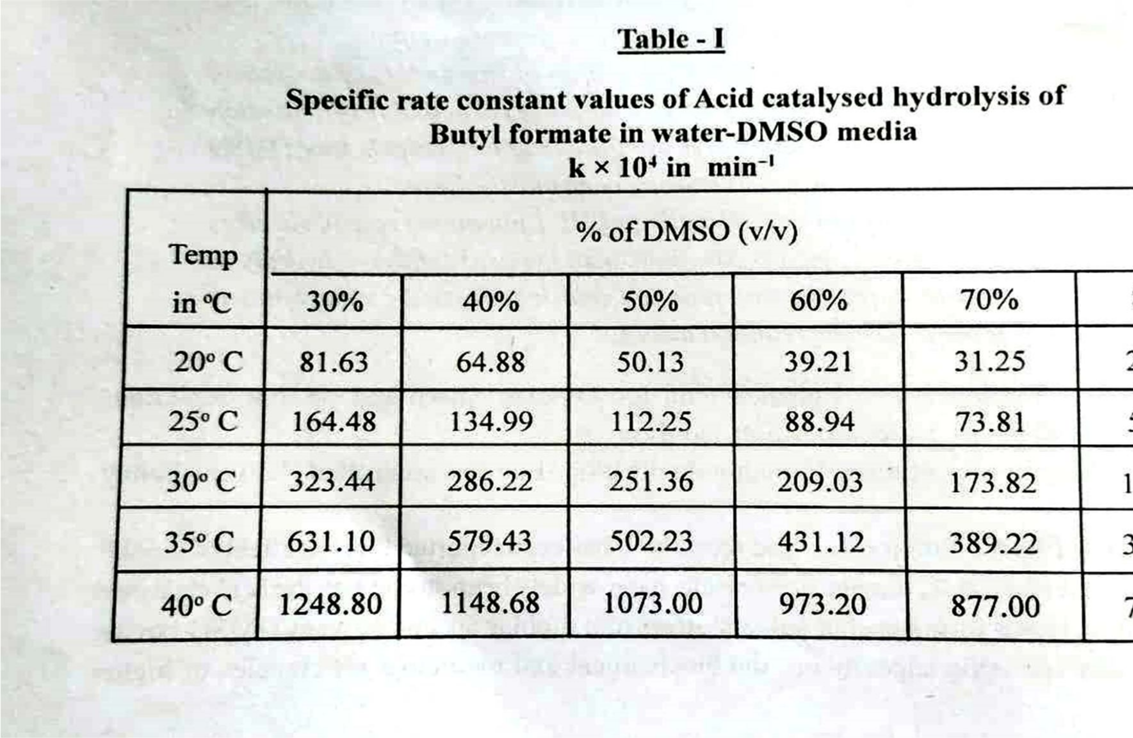


Table - I

Specific rate constant values of Acid catalysed hydrolysis of Butyl formate in water-DMSO media
$k \times 10^4$ in min^{-1}

Temp in °C	% of DMSO (v/v)					
	30%	40%	50%	60%	70%	80%
20° C	81.63	64.88	50.13	39.21	31.25	20.65
25° C	164.48	134.99	112.25	88.94	73.81	52.80
30° C	323.44	286.22	251.36	209.03	173.82	133.35
35° C	631.10	579.43	502.23	431.12	389.22	323.67
40° C	1248.80	1148.68	1073.00	973.20	877.00	724.77

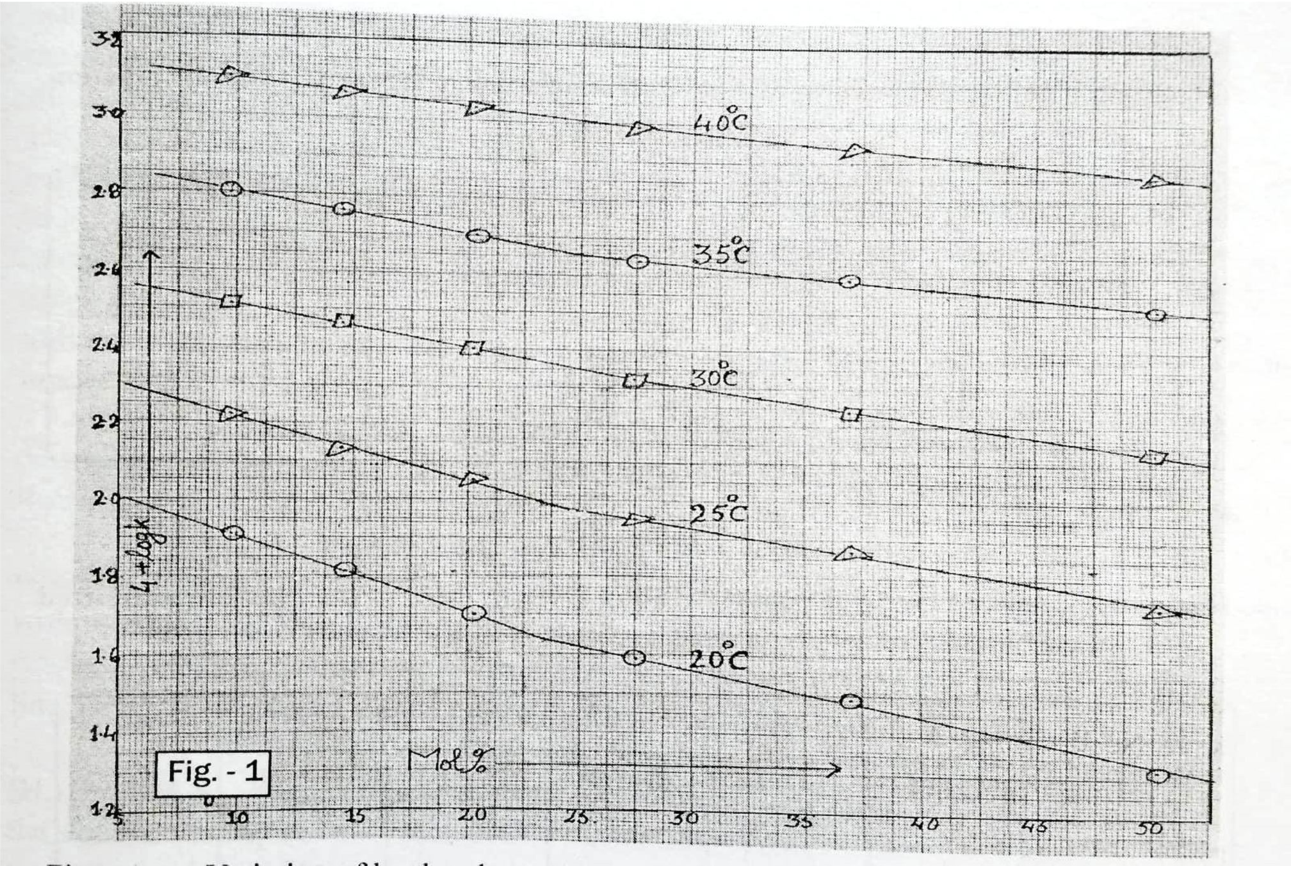


Fig.1: Variation of log k values with mol % of DMSO in water-DMSO media

In our views, the folowing three factors seem to be responsible:
For depletion in the rate of the reaction in solution, they are:

1) decreasing polarity of the medium as changing from polar water to less polar water-DMSO medium,
2) lowering of the bulk dielectric constant values of the medium, and
3) depletion of H_3O^+ ions of the solution by the organic co-solvent molecule due to its basic character

As DMSO 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 Ingold[5] that the rate is bound to decrease with decreasing dielectric constants of the medium.
Our these explanations are also in support of the views of Laidler and Lanskroener[6] and are also supported by the recent reports of Singh & Namrata et al[7]. and Kumar & Singh[8].

A. *Solvent effect on Iso-composition Activation Energy*

From the Arrhenius plots of log k values 1/T, 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 - II.

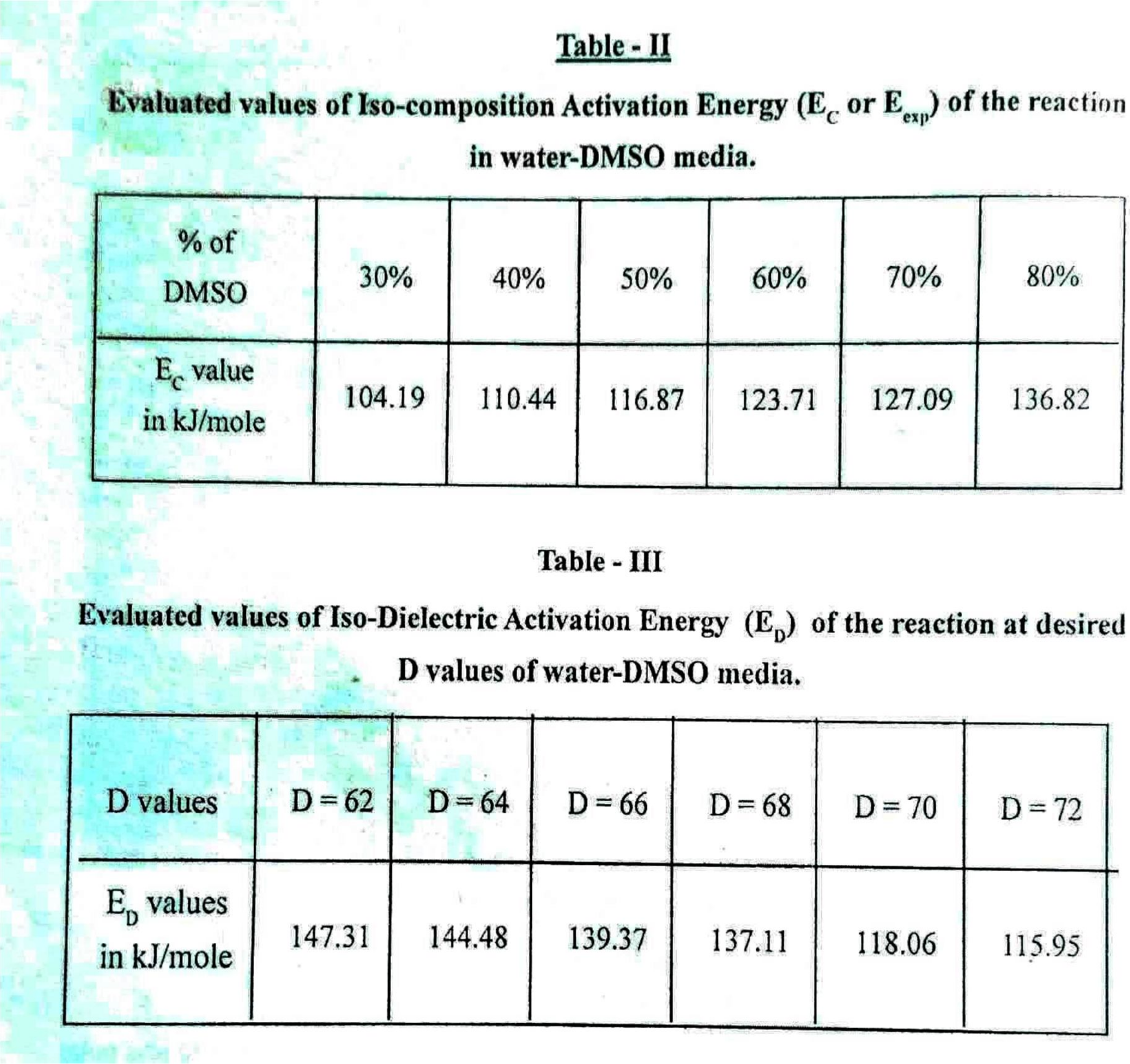


Table - II

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

% of DMSO	30%	40%	50%	60%	70%	80%
E_C value in kJ/mole	104.19	110.44	116.87	123.71	127.09	136.82

Table - III

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

D values	D = 62	D = 64	D = 66	D = 68	D = 70	D = 72
E_D values in kJ/mole	147.31	144.48	139.37	137.11	118.06	115.95

From Table-II, it is clear that values of iso-composition activation energy go on increasing from 104.19 kJ/mol to 136.82 kJ/mol with addition of 20 to 80% of DMSO in the reaction media.

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

1) The greater desolvation of transition state than the initial state,
2) The greater solvation of the initial state than the transition state, and
3) Simultaneous solvation and desolvation of the initial and the transition state respectively.

Out of these three factors, the third one seems to be applicable in our case and it has also been supported by the increase of entropy of activation with gradual addition of the organic co-solvent in the reaction media as recorded in Table - IV. Our such views are in support of the recent report of Singh & Namrata[7] and Kumar & Singh et al[8].

B. Solvent Effect on Iso-dielectric Activation Energy

From the slopes of the Arrhenius plots of log K_D values against I/T (log k overline o

values 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 -III. From this Table, it is inferred that E_D values go on decreasing from 147.31 kJ/mol to 115.95 kJ/mol with increasing D values of the reaction media from 62 to 72. 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 DMSO in the reaction media. Our these interpretations have also been supported by the recent reports of Singh & Perween[9] and Singh & Kumari et al[10].

C. Solvent Effet on the Participation of water Molecules in the Transition state and Mechanism of the Reaction

The number of water molecules associated with the transition state has been determined by plotting log k values, against log $[H_2O]$ according to the relation proposed by Robertson[11].

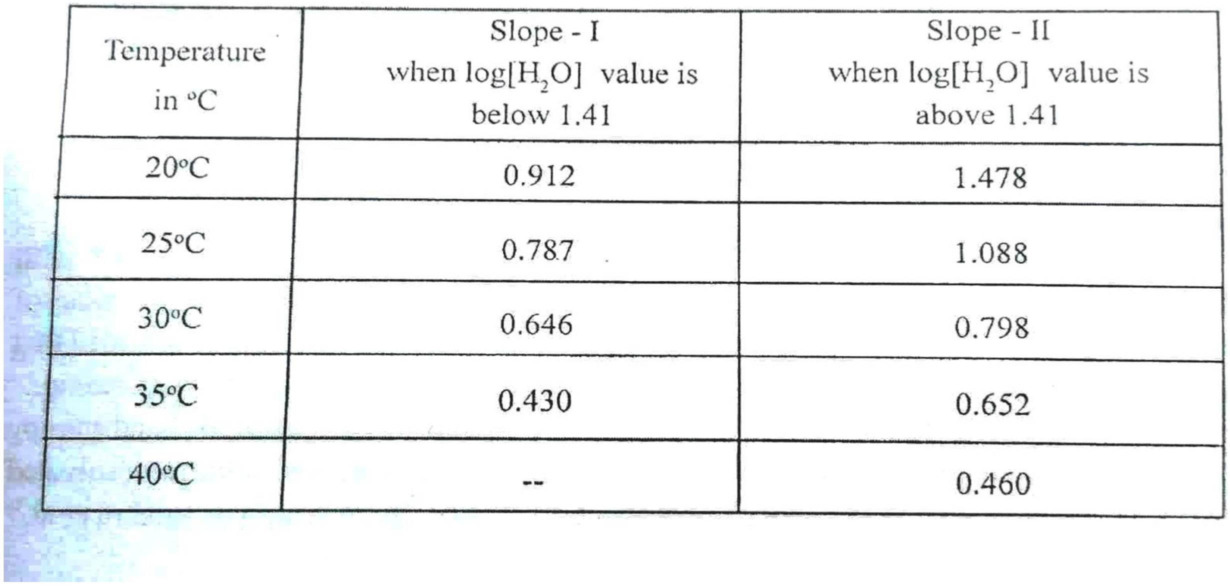
$$\log k=\log k_o + \log [H_2O]$$

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 the mechanism of the reaction. On plotting log k values against log [HO] values as shown in Fig. - 2, a straight line, with positive slopes are obtained which are recorded in Table - IV.

As observed from the values recorded in Table - IV, it is clear that below log [HO] value1.41 which corresponds to 46.30% of water in the reaction media, the values of the slopes decreases from 0.912 to 0.430 with increase in temperature from 20 to 40°C. This suggests that below 46.30% 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 46.30% v/v), the numerical values of slopes decrease from 1.478 to

Table-IV

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



Temperature in °C	Slope - I when $\log[H_2O]$ value is below 1.41	Slope - II when $\log[H_2O]$ value is above 1.41
20°C	0.912	1.478
25°C	0.787	1.088
30°C	0.646	0.798
35°C	0.430	0.652
40°C	--	0.460

0.460. These values show that approximately from 1.50 to 0.50 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 water-DMSO media, the number of water molecules taking part in the formation of the activated complex is about one 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 and half. Thus, it can be concluded from the guidelines of Robertson et al[12]. that the acid catalysed hydrolysis of Butyl formate in water-DMSO media follow bimolecular mechanism with respect to water. In other words, the presence of DMSO in the reaction media and with rise in temperature of the reaction, the mechanistic pathway of the reaction is changed from unimolecular to bimolecular.

Our these observations may be attributed to the fact that in presence of DMSO, the equilibrium of water shifts from its dense form to its bulky form with rise of temperature of the reaction.

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

The recent reports of Singh & Singh et al[13,14] has been found to support our above interpretations on the findings about the mechanistic pathways followed by the reaction.

D. Solvent Effect on Thermodynamic Activation Parameters

The famous Wynne-Jones and Eyring[4] 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 - V. From the data mentioned in Table-V, the interesting feature comes in the light is that out of the values of all the three thermodynamic activation parameters ie. AH, AS* increase with simultaneous increasing in AG with increasing proportion of DMSO in the reaction media.

For highlighting the solvent effect on the three thermodynamic activation parameters, namely AH, AG and AS*, the values of all were plotted against mol % of the dimethyl suphoxide (DMSO) in the reaction as shown in Fig. 3, 4 and 5 respectively. The non-linear variation in AH and AS from Fig.3 and 5 give information of the fact that specific solvation is taking place in water-DMSO 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 AH is greater than that found in the values of ΔS* and from this fact, it is concluded that acid catalysed hydrolysis of Butyl formate in water-DMSO media is enthalpy dominating

The enhancement found 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 intial state in the similar way as reported recently by Singh & Mishra et al[16].

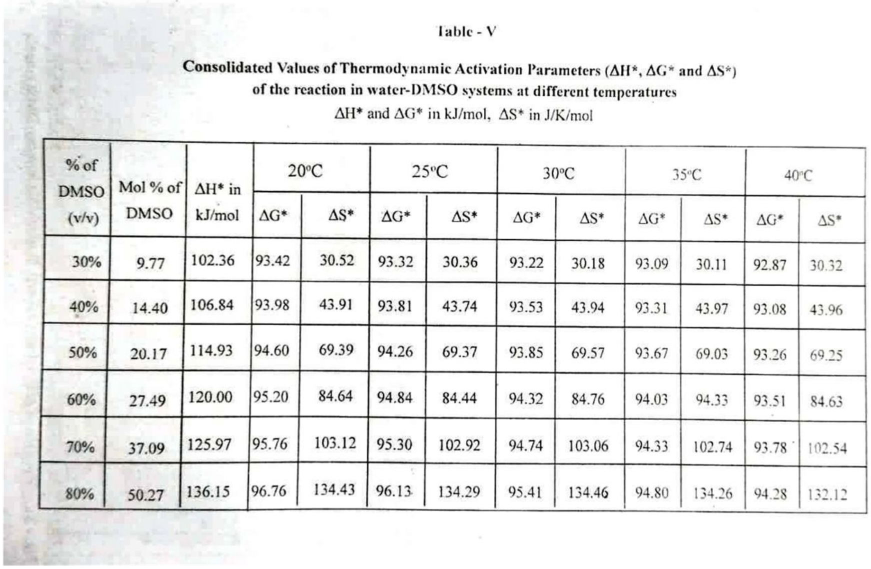


Table - V

Consolidated Values of Thermodynamic Activation Parameters (ΔH*, ΔG* and ΔS*) of the reaction in water-DMSO systems at different temperatures

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of DMSO (v/v)	Mol % of DMSO	ΔH* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
30%	9.77	102.36	93.42	30.52	93.32	30.36	93.22	30.18	93.09	30.11	92.87	30.32
40%	14.40	106.84	93.98	43.91	93.81	43.74	93.53	43.94	93.31	43.97	93.08	43.96
50%	20.17	114.93	94.60	69.39	94.26	69.37	93.85	69.57	93.67	69.03	93.26	69.25
60%	27.49	120.00	95.20	84.64	94.84	84.44	94.32	84.76	94.03	94.33	93.51	84.63
70%	37.09	125.97	95.76	103.12	95.30	102.92	94.74	103.06	94.33	102.74	93.78	102.54
80%	50.27	136.15	96.76	134.43	96.13	134.29	95.41	134.46	94.80	134.26	94.28	132.12

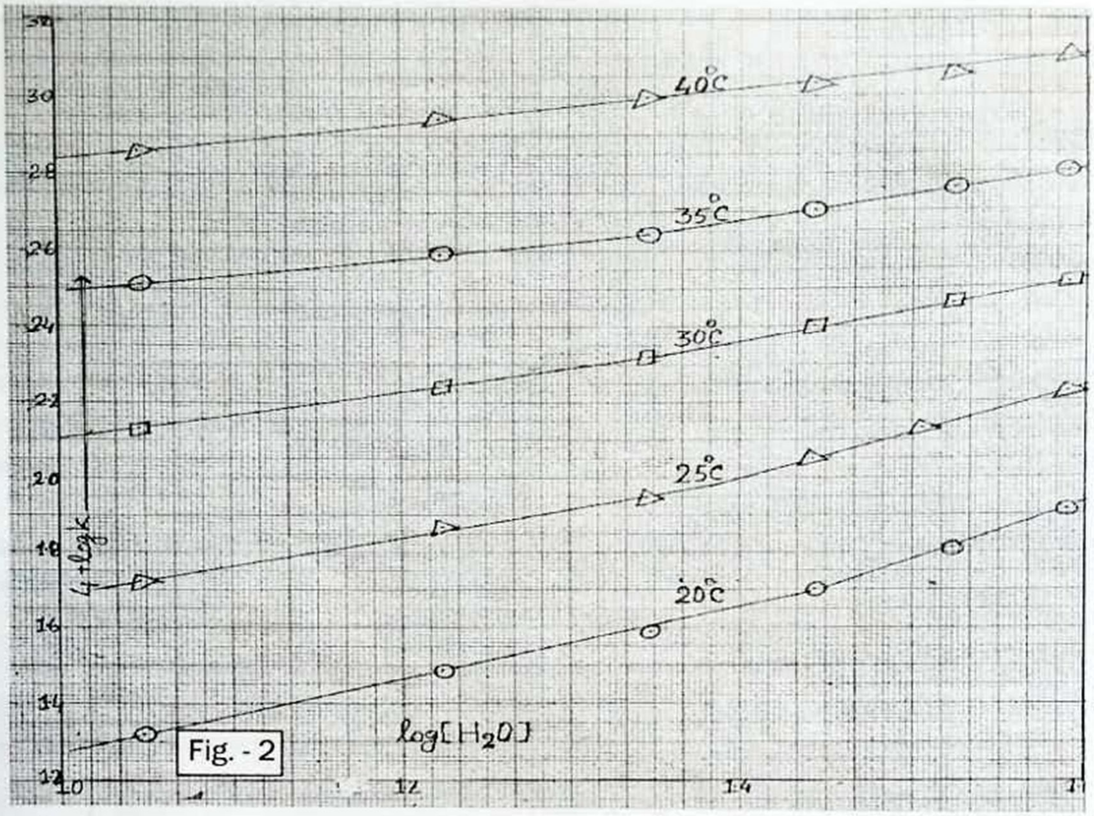


Fig. - 2 : Variation of log k values against log [H_2O] values in water-DMSO media

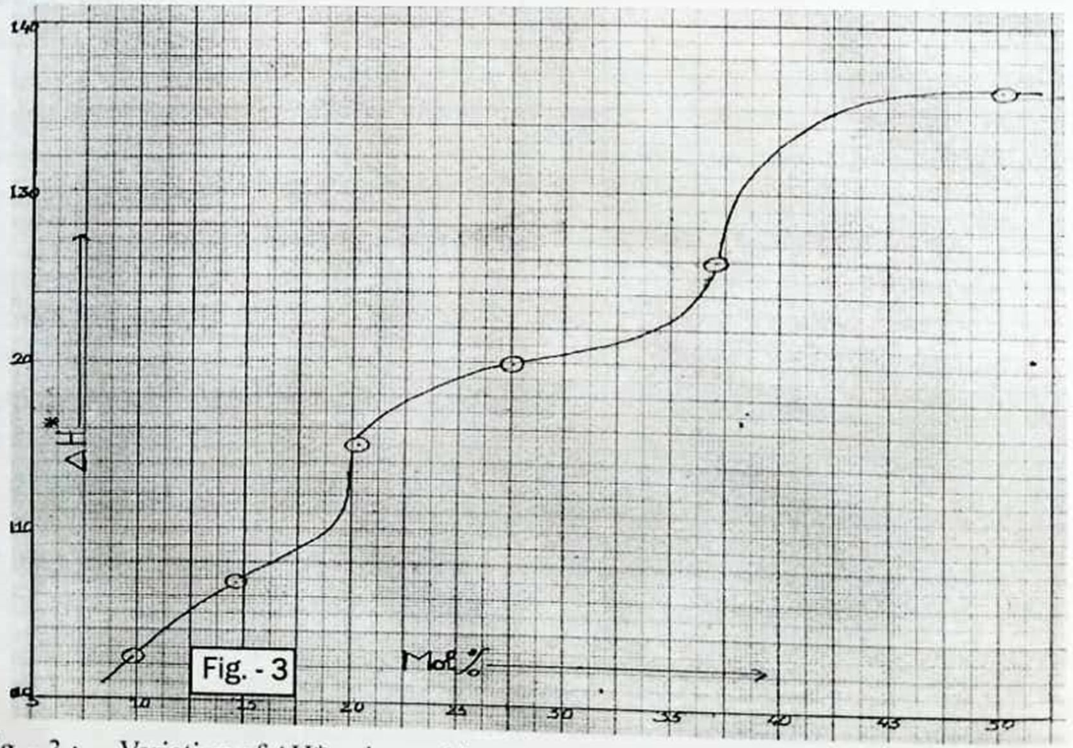


Fig. - 3 : Variation of ΔH* values with mol % of DMSO in water-DMSO media

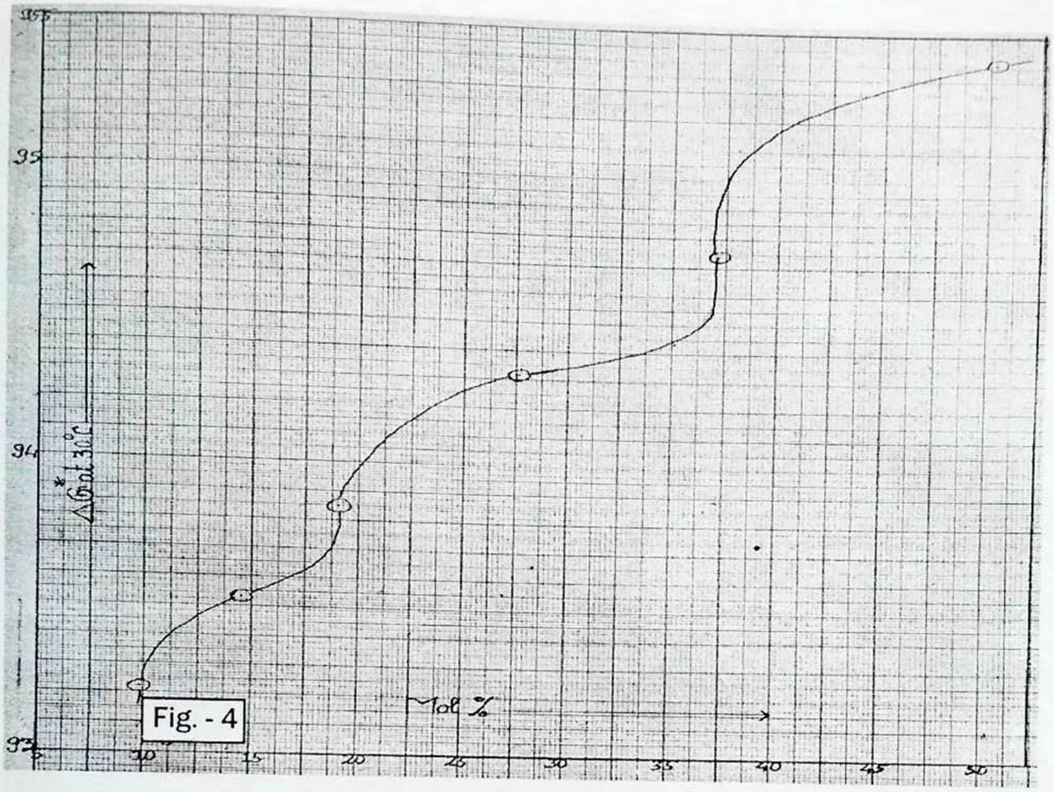


Fig. - 4 : Variation of ΔG* values with mol % of DMSO in water-DMSO media

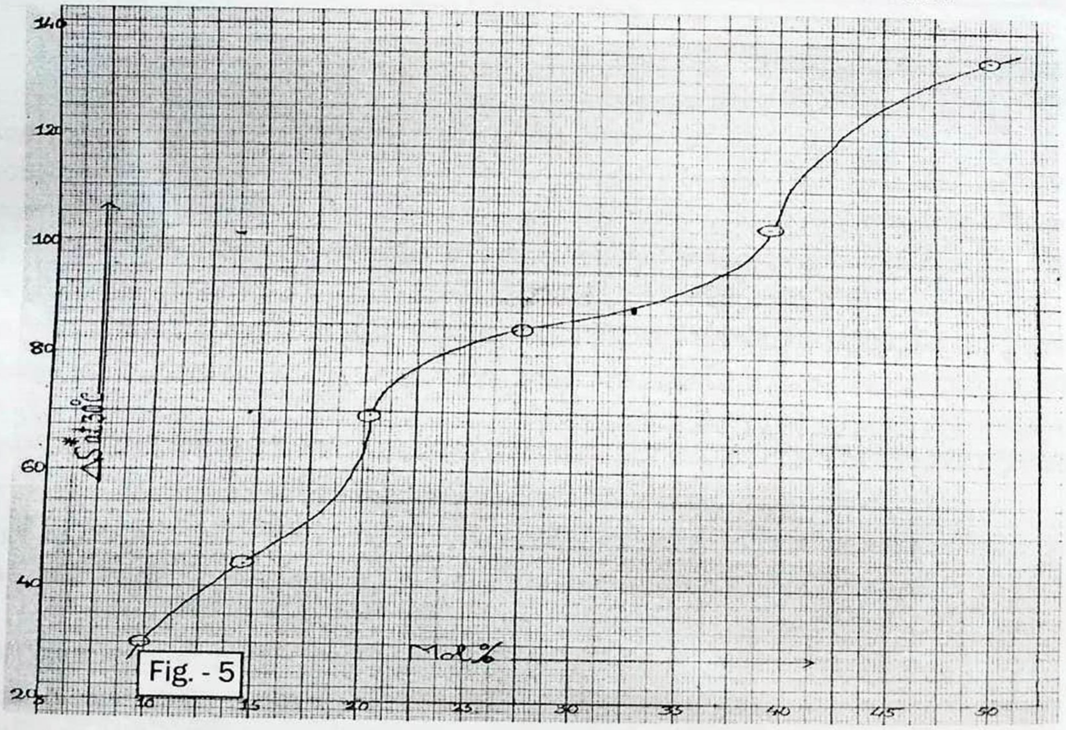


Fig. - 5 : Variation of ΔS* values with mol % of DMSO in water-DMSO media

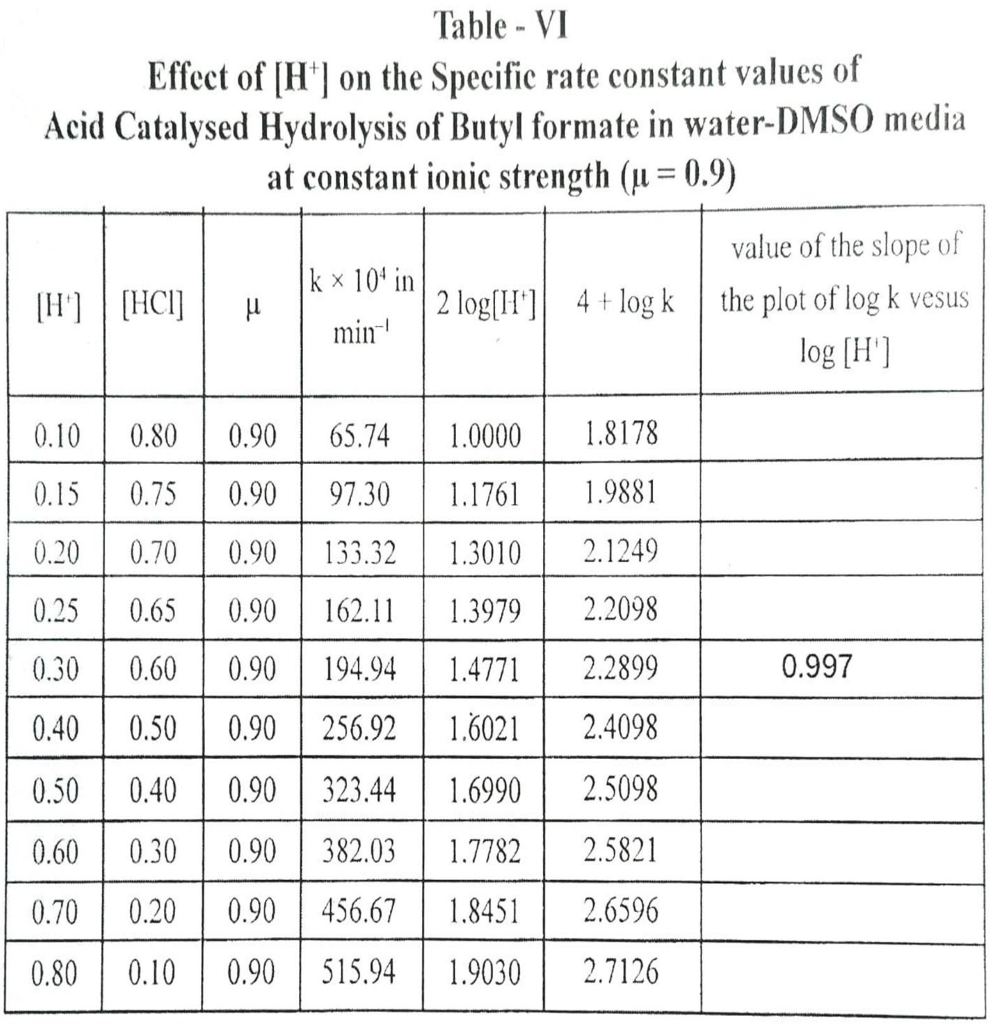


Table - VI
Effect of $[H^+]$ on the Specific rate constant values of
Acid Catalysed Hydrolysis of Butyl formate in water-DMSO media
at constant ionic strength ($\mu = 0.9$)

$[H^+]$	[HCl]	μ	$k \times 10^4$ in min^{-1}	$2 \log[H^+]$	4 + log k	value of the slope of the plot of log k vesus log $[H^+]$
0.10	0.80	0.90	65.74	1.0000	1.8178	
0.15	0.75	0.90	97.30	1.1761	1.9881	
0.20	0.70	0.90	133.32	1.3010	2.1249	
0.25	0.65	0.90	162.11	1.3979	2.2098	
0.30	0.60	0.90	194.94	1.4771	2.2899	0.997
0.40	0.50	0.90	256.92	1.6021	2.4098	
0.50	0.40	0.90	323.44	1.6990	2.5098	
0.60	0.30	0.90	382.03	1.7782	2.5821	
0.70	0.20	0.90	456.67	1.8451	2.6596	
0.80	0.10	0.90	515.94	1.9030	2.7126	

and Kumar & Singh et al[17].

E. Effect of Change of [H+] ion concentration

The effect of change in the acid concentration on the 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 values of specific rate constant values for different $[H^+]$ ion concentration of the reaction media have been inserted in Table - VI.

The values of the slope of straight line plots of log k versus log $[H^+]$ as shown in Fig-6. was found to be 0.997 which is almost equal to unity and from this, it is inferred on the guidelines of Zucker and Hammett[18] that acid catalysed hydrolysis of Butyl formate in water-DMSO media follows A_{AC}^2 mechanism.

F. Solvent Effect and Evaluation of Iso-kinetic temperature and Solvent-Solute Interaction

In the light of Barclay and Butler[19] relationship between enthalpy and entropy of activation, the value of iso-kinetic temperature of the acid catalysed hydrolysis of Butyl formate in water-DMSO media has been evaluated from the slopes of the plots of ΔH^* versus ΔS^* as shown in Fig. 7 which came to be 323.57 ≈approx 324

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 reaction mixture

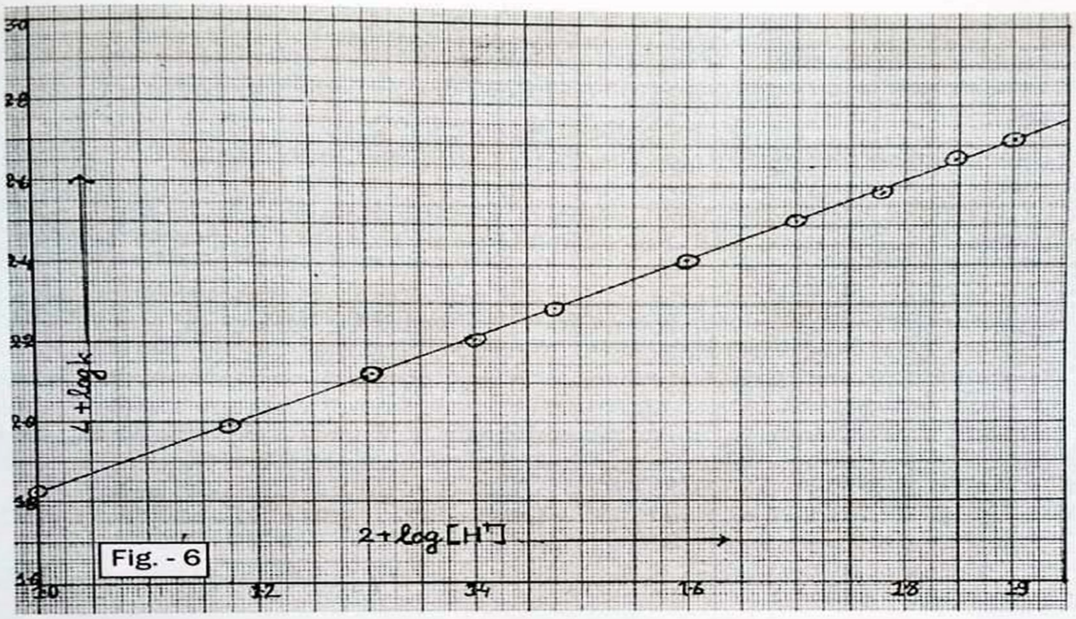


Fig. - 6 : Plots of log k values against log [H⁺] values in water-DMSO media.

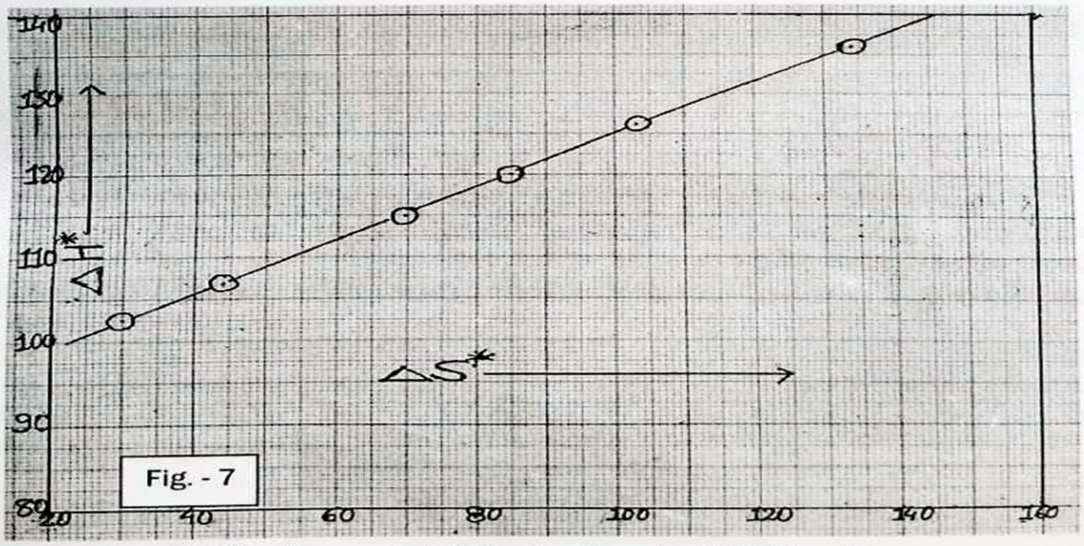


Fig. - 7 : Plots of ΔH* values against ΔS* values in water-DMSO media

in the similar way as reported by Leffler[20] Recently Singh & Namrata et al[7], Kumar & Rai et al[17] and Singh & Kumar[21] have also reported similar observations and findings as that of ours in this research.

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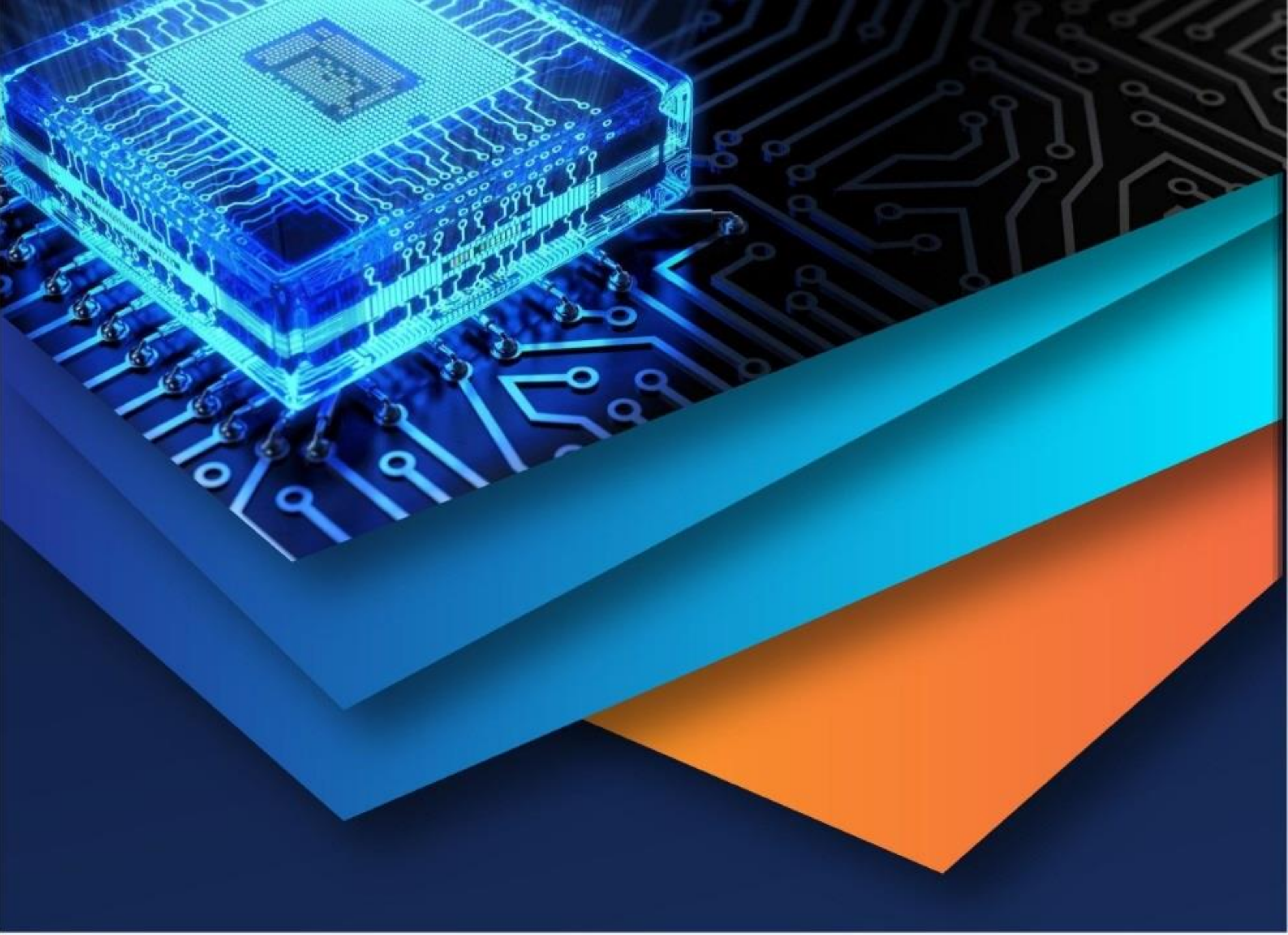

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