

## **A Kinetic study of the solvent Effect of Ethanol on the Thermodynamic Parameters of Catalysed Solvolysis of Amyl Methanoate.**

**Om Prakash Upadhyay Ph.D**

Research Scholar, Dept of Physics , V.K.S. University, Ara

**Key Words-** Thermodynamic properties catalysed solvolysis Amyl, enthalpy stimulator, Entropy controller Mechanistic Pathways.

### **ABSTRACT**

For studying the solvent effect of ethanol on the thermodynamic parameters of catalysed solvolysis of amyl methanoate, the kinetics of acid catalysed hydrolysis of amyl methanoate was studied in different reaction media containing 30 to 80% of ethanol at different temperature ranging from 20°C to 40°C.

In the beginning, sharp 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 ( $\Delta G^*$ ) with simultaneous enhancement in the values of enthalpy of activation ( $\Delta H^*$ ) and entropy of activation ( $\Delta S^*$ ) of the reaction, reveals that ethyl alcohol acts as enthalpy stimulator and entropy controller.

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 is of ion-dipolar reaction and it follows  $A_{Ac}^2$  mechanistic pathways in water-EtOH media.

### **INTRODUCTION:**

In previous communications<sup>1-3</sup>, effect of dipolar aprotic solvent like DMSO, acetone, t-butanol etc. have widely been studied on the catalysed hydrolysis of aliphatic and aromatic formates but towards the verification of Barclay-Butler's<sup>4</sup> rule and evaluation of iso-kinetic temperature<sup>5</sup> for acid or base catalysed solvolysis of methanoates (formate esters) of having longer C-chains, particularly in non-aqueous solvents like ethyl alcohol, even a little attention has not been paid so far.

So, in order to highlight the above noted untouched work, it has been proposed to study the effect of ethyl alcohol on the acid catalysed hydrolysis of Amyl methanoate.

### **Experimental:**

Purified ethyl alcohol of BDH grade and Amyl methanoate of USSR make were used. The kinetics of acid catalysed hydrolysis of the ester was studied as usual by adding 0.60 ml of ester in 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. Evaluated values of the two activation energies (Iso-composition  $E_c$ , and Iso-dielectric  $E_D$ ) and thermodynamic activation parameters have been tabulated in Tables - II, III and IV respectively.

### **Results and Discussion:**

From Table - I which highlights the effect of change in concentration of the organic content of the reaction media, it is clear that there is fast followed by slow depletion in the rate of reaction after 22.5 mole % of EtOH in the reaction media. However, with increasing temperature, the effect of solvent is found to be minimised.

In our views, 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 water-EtOH medium, and
- (ii) lowering of the bulk dielectric constant values of the medium.

These explanations and interpretations have also been supported by Laidler and Landskroner<sup>6</sup> and Hughes and Ingold<sup>7</sup> and recently by Pandey and Singh.<sup>8</sup>

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

From the Arrhenius plots, the values of iso-composition activation energy ( $E_c$  or  $E_{exp}$ ) have been calculated and are mentioned in Table - II. From Table - II, it is clear that values of iso-composition activation energy go on increasing from 93.21 kJ/mole to 128.26 kJ/mole with addition of 30 to 80% of EtOH in the reaction media.

Usually, 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 in the reaction media as recorded in Table - V. These views are in support of the recent report of Kumari and Singh.<sup>9</sup>

### **Solvent Effect on Iso-dielectric Activation energy:**

From the slopes of the Arrhenius plots of  $\log k_D$  values against  $1/T$  ( $\log k_D$  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 128.04 kJ/mole to 97.35 kJ/mole

with increasing D values of the reaction media from 40 to 70. This trend of depletion in  $E_D$  values with increasing D values of the reaction media is similar to enhancement in  $E_D$  with addition of more and more EtOH in the reaction media. these interpretations have also been supported by the report of Dubey and Singh<sup>10</sup>.

### Solvent Effect on Thermodynamic Activation Parameters:

The famous Wynne-Jones and Eyring<sup>11</sup> equation has been employed to evaluate the three thermodynamic activation parameters namely enthalpy of activation  $\Delta H^*$ , entropy of activation  $\Delta S^*$  and the free energy of activation  $\Delta G^*$  and their values have been recorded in Table-IV.

From the data mentioned in Table-IV, the interesting feature comes in the light is that out of the values of the three thermodynamic activation parameters i.e.  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  all go on increasing simultaneously with increasing proportion of ethyl alcohol in the reaction media.

From the fundamental thermodynamic equation:

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

it may be inferred that the simultaneous increase in the values of  $\Delta H^*$  and  $\Delta S^*$  with enhancement of  $\Delta G^*$  values is only possible when the quantitative increase in the values of  $\Delta H^*$  is greater than that found in the values of  $\Delta S^*$  and from this fact, it is concluded that acid catalysed hydrolysis of Amyl methanoate in water-EtOH media is enthalpy stimulating and entropy depleting.

The enhancement found in the values of enthalpy of activation  $\Delta H^*$  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 by Upadhyay and Singh<sup>12</sup> and Singh et al<sup>13</sup>.

**Table - I**

**Specific rate constant values of Acid Catalysed hydrolysis of Amyl Formate in water-EtOH media**

**$k \times 10^3$  in  $\text{min}^{-1}$**

Temp in °C	% of EtOH(v/v)					
	30%	40%	50%	60%	70%	80%
20°C	46.86	38.71	30.91	24.47	18.10	12.40
25°C	87.54	75.67	62.14	51.14	39.81	28.93
30°C	164.06	142.89	124.51	107.60	88.70	62.30
35°C	293.63	262.97	238.78	214.83	185.44	151.36
40°C	525.17	486.63	457.19	429.64	391.83	337.52

**Table - II**

**Values of Iso-composition Activation Energy of the reaction in water-EtOH media**

% of EtOH(v/v)	30%	40%	50%	60%	70%	80%
E <sub>exp</sub> value in kJ/mol	93.21	97.38	103.29	110.01	117.78	128.26

**Table - III**

**Values of Iso-Dielectric Activation Energy (E<sub>D</sub>) of the reaction at different desired**

**'D'-values of the water-EtOH media.**

D values	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60
E <sub>D</sub> values in kJ/mol	128.04	119.38	110.23	105.52	101.48	97.35

**Table- IV**

**Consolidated values of Free Energy of Activation( $\Delta G^*$ ), Enthalpy of Activation( $\Delta H^*$ ) and Entropy of Activation( $\Delta S^*$ ) of the reaction in water-EtOH media**

$\Delta H^*$  and  $\Delta G^*$  in kJ/mol,  $\Delta S^*$  in J/K/mole.

% of EtOH	Mole% of EtOH	$\Delta H^*$ in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$
30%	11.69	93.36	89.16	6.18	89.17	6.03	89.13	6.07	89.15	5.90	89.13	5.89
40%	17.07	94.23	89.62	15.71	89.53	15.74	89.47	15.67	89.43	15.56	89.32	15.66
50%	23.59	100.75	90.17	36.11	90.02	36.00	89.82	36.07	89.68	35.95	89.49	35.99
60%	31.06	107.87	90.74	58.45	90.51	58.26	90.19	58.34	89.95	58.17	89.65	58.21
70%	41.87	118.33	91.47	91.66	91.13	91.29	90.68	91.27	90.33	90.92	89.88	90.87
80%	55.25	126.08	92.39	114.95	91.92	114.63	91.57	113.89	90.85	114.38	90.27	114.38

**Table -V**

**Variation in Specific Rate constant values with  $[H^+]$  at constant  $\mu$  (ionis strength = 0.90) of the media of Acid catalysed solvolysis of Amyl formate water-EtOH media**

% of EtOH (30% v/v)

Temp. 30°C.

$[H^+]$	[KCl]	$\mu$	$k \times 10^3$ in $\text{min}^{-1}$	$2 + \log[H^+]$	$3 + \log k$	Slope
0.10	0.80	0.90	32.22	1.0000	1.5081	
0.15	0.75	0.90	49.32	1.1761	1.6930	
0.20	0.70	0.90	64.88	1.3010	1.8121	
0.25	0.65	0.90	81.32	1.3979	1.9102	
0.30	0.60	0.90	96.61	1.4771	1.9850	1.0004
0.35	0.50	0.90	132.77	1.6021	2.1231	
0.40	0.40	0.90	164.60	1.6990	2.2150	
0.60	0.30	0.90	201.74	1.7782	2.3048	
0.70	0.20	0.90	226.57	1.8451	2.3552	
0.80	0.10	0.90	264.36	1.9031	2.4222	

**Effect of change of  $[H^+]$  ion concentration on the rate of thi Reaction on the Rate of the Reaction**

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 -V.

The values of the slope of straight line plots of  $\log k$  versus  $\log [H^+]$  as shown in Fig. - 3 was found to be 1.004 which is almost equal to unity and from this, it is inferred on the guidelines of Zucker and Hammett<sup>14</sup> that acid catalysed hydrolysis Amyl methanoate in waterEtOH media follows  $A_{Ac}^2$  mechanism. Similar reported have been reported recently by Rakesh & Singh et al<sup>15</sup>.

**Evaluation of Iso-kinetic temperature and Solvent-Solute Interaction:**

In the light of Barclay and Butler relationship between enthalpy and entropy of activation, the value of iso-kinetic temperature of the acid catalysed hydrolysis of Amyl methanoate in water-EtOH media has been evaluated which comes to be 324.31.

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 appreciable and strong interaction between solvent and solute present in the reaction mixture in the similar way as reported by Leffler<sup>5</sup>. This conclusion is found to be in support of the earlier reports of Singh et al<sup>16</sup>. and also of the earlier reported of Tauheed & Singh et al<sup>17</sup>.

### References

1. Singh, Lallan, Singh, R. T. and Jha, R. C.: J. Indian Chem. Soc., **57**, 1089, 1980
2. Srivastava, S.P., Singh, P., Mishra, S. K. and Singh, R. T.:ARJ Phys.Sci., **11**, No.(1-2) 129-132, 2008
3. Dubey, R., Singh, A. K.,Singh, P.K. and and Singh, R. T:NIRJ Sci., **4**, 133-139,2010
4. Barclay, I. M. and Butler, J. A. : Trans. Faraday Soc., **34**, 1445, 1938
5. Leffler, J. E.: J. Org. Chem., **20**, 1201, 1955
6. Laidler, K. J. and Lanskroener, P.A.: Trans. Faraday Soc., **52**,200,1956
7. Hughes, E. D. and Ingold, C.K. :J. Chem. Soc., **244**, 255, 1935
8. Pandey, R. S., Kumar, P.,Pathak, P.. and Singh, R. T. : NIRJ Sci., **5**, 67-74, 2010
9. Kumari, S., Singh, S. K., Singh, D. K. and Singh, R. T.: NIRJ. Sci., **8**, 95-99, 2012
10. Dubey, R., Singh, A. K.,Singh, P. and Singh, R. T.: NIRJ Sci., **4**, 121-128, 2010
11. Wynne-Jones, W.F.K. and Eyring, H.: J. Chem. Phys., **3**, 492, 1953
12. Upadhyay, M. K., Kumar, A.,Singh, V. K. and Singh, R. T.:ARJ Phys.Sci., **11**, No. (1-2) 133-136, 2008 .
13. Singh, R. T., Singh, S.N.,Singh, P. and Singh, R. I. : NIRJ Sci., **8**, 133-138, 2012
14. Zucker, L. and Hammett, L.P.: J.Am. Chem. Soc., **61**,2791, 1939
15. K. Rakesh and Singh RT. : NIRJ Sci **22**, 39-51, 2016(Dec)
16. Srivastava, S.P., Singh, P., Mishra, S. K. and Singh, R. T.:ARJ Phys. Sci., **11**, No. (1-2)129-132, 2008
17. Tauheed S, Haider SR and Singh RT : NIRJ Sci **24**, 67-84, 2017(Sept)