

A Kinetic Study of Alkali Catalysed Hydrolysis of Ethyl caproate in aquo-Ethylene Glycol (Aquo-EG) media

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ABSTRACT

The kinetics of alkali catalysed hydrolysis of ethyl caproate has been carried out in aquo-EG media having 20 to 80% (v/v) of ethylene glycol (EG) by volume at temperatures ranging from 20°C to 40°C. The data of specific rate constants have been tabulated in Table-1. The survey of the Table-1 apparently shows that the rate decreases regularly with gradual addition of the organic solvent (EG) in the reaction media at all the temperatures at which the kinetics has been studied.

In order to study the variation in k values with change in mol% of the organic co-solvent (EG), the logarithm of k values were noted and have been tabulated in Table-2. The plots of $\log k$ against molar composition of EG have been shown in Fig.-1 which shows that the rates of the reaction go on decreasing having different slopes after adding about 28.50 mol% of EG in the reaction media. Decreasing trend having different slopes is observed at different temperatures from 20 to 40°C. Such decrease in rate constant with increasing proportion of the organic co-solvent like EG is not new in the kinetics of solvent effect. A number of workers like Laidler-Landskroener¹ and earlier Singh² have also been able to view similar observations about depletion in rate with increase in concentration of the organic co-solvent in the reaction media. From Fig.-1 it is apparent that with increasing temperature of the reaction, the rate of depletion in the value

of specific rate constant goes on increasing (as the slope of the straight line increases).

KEYWORDS: Ethylene glycol, organic co-solvent, protic solvent, Unimolecular, bimolecular Barclay-Bulter relationship, iso-dielectric velocity constant etc..

INTRODUCTION;

In context of above noted facts, the possible rate depleting factors can be out lined as follows:

- (i) decrease in the bulk dielectric constant of the reaction medium,
- (ii) decreasing the polarity of reaction media on adding less polar solvent ethylene glycol (EG) to it.

The above noted rate depleting factors are quite in operation and this is also in agreement with the theory of Hughes and Ingold³ that the rate ought to decrease with decreasing dielectric constant of the reaction media. Moreover, similar findings and their interpretations have also been reported earlier by R. T. Singh² and in recent years by Sinha⁴ and Namrata & Singh et. al.⁵

The alkali catalysed hydrolysis of ethyl caproate in ethylene glycol (aquo-EG) media was also found to obey the Arrhenius law during the range of temperature from 20 to 40°C and composition 20 to 80% (v/v) under study. This was verified by plotting $\log k$ values against $1/T$ from the Table-3. The plots have been shown in Fig.-2. It is clear from Fig.-

2 that the plots are good straight lines. The E_c (Iso-composition or Arrhenius activation energy E_{exp}) values for different composition of aquo organic co-solvent reaction media have been calculated with the help of the slopes of the straight lines and are tabulated in Table-4.

EXPERIMENTAL

The kinetics of the alkali catalysed hydrolysis of ethyl caproate was studied by carrying out the experiments (hydrolysis) separately in two aquo-organic co-solvent media made by adding different volumes of organic co-solvent (20% to 80%). The two different aquo-organic co-solvent used were ethanol and ethylene glycol. The hydrolysis experiments were carried out at five different temperatures varying from 20°C to 40°C (20°C , 25°C , 30°C , 35°C and 40°C).

For each set of experiments, calculated quantities of the organic co-solvent, water and stock sodium hydroxide was mixed in a cleaned and dried stoppered conical flask (250ml) such that the total volume of the solution was 100ml and its basic strength became 0.1M. The conical flask containing the above solution and a small stoppered bottle having ethyl caproate were thermostated with the syringe pipette and added quickly to the alkaline solution of water-organic co-solvent mixture (water-ethanol/ water EG) followed by constant shaking. The strength of the reaction mixture in terms of the ester Ethyl caproate was 0.05M. Immediately 10ml aliquot of the reaction mixture was withdrawn with the help of a pipette and allowed to run into a flask containing 10ml of (0.1N) HCl solution so that the reaction may be quenched quickly. The excess acid of the solution was titrated by means of the standard N/20 Baryta Solution ($f=0.983$) using phenolphthalein as indicator. The moment at which half of the aliquot was added into the ice cold 0.1N HCl solution, the stop-clock was started. This time was considered as the starting time or the zero

time of hydrolysis. The corresponding titre reading was recorded as T_0 .

By taking this zero time into account, the kinetics of the reaction was studied by estimating the amount of remaining ester after quenching the 10ml ice – cold 0.1N HCl at definite desired intervals of time followed by titration as usual. These readings were noted as T_t .

The remaining reaction mixture was left stoppered for 24 hours and then it was boiled by taking it in a pressure bottle for about half an hour and then the solution was allowed to cool. 10ml of the cooled mixture was withdrawn in 10ml 0.1N HCl contained in a conical flask and was titrated against the Baryta Solution as mentioned above. This reading was called infinity reading termed as T_∞ .

10ml of 0.1N HCl was taken in a conical flask and titrated against Baryta Solution using phenolphthalein as indicator. This titre reading was mentioned as T .

The above noted process were adopted for each set of the water-organic co-solvents mixtures and from the noted readings of experiments of the value of specific rate constant of the reaction were calculated during the study using relevant method and formulae.

DISCUSSION

The data of Table-4 indicate that E_{exp} values are decreasing from 90.52 kJ/mol to 57.13 kJ/mol with increasing mol % of the organic co-solvent (EG) in the reaction media. The depletion in the E_c value may be due to either of the following three causes:

- The initial state is desolvated and the transition state is solvated,
- The initial state is more desolvated than the transition state, and
- The initial state is less solvated than the transition state.

Out of these three factors (causes), the first factor seems to be operative in this case as both ΔH^* and ΔS^* values of the reaction are found to decrease. Such findings and their

interpretations have been found in support of earlier reported works of Rakesh and Singh et. al.⁶ and also in favour of the recently reported researches by Rajiv & Singh et. al.⁷ and Renu & Singh et. al.⁸.

Effect of Solvent on Iso-Dielectric Activation energy (E_D) of the Reaction:

In order to determine the iso-dielectric activation energy, first of all, the iso-dielectric velocity constant (k_D) were evaluated by interpolation of the curve for $\log k$ against D . The interpolated values of $\log k_D$ at different temperatures and different desired dielectric constants are shown in Table-5. In order to evaluate E_D , the $\log k_D$ values were plotted against $1/T$, which have been shown in Fig.-3. These plots are found to be good straight lines and the slopes of the data give rise the value of E_D which is shown in Table-6.

On perusal of the data mentioned in Table-6, it has been found that E_D values go on increasing from 62.48 kJ/mol to 101.44 kJ/mol with increase in D values from $D=45$ to $D=70$. Such enhancement in E_D values are in accordance with the depletion in E_{exp} values with increasing mol% of the organic component (EG) in the reaction media.

However, these findings are quite natural and have been found in support of the earlier reported views of Elsemongy et.al.⁹, Wolford¹⁰ and Sharma & Singh et. al.¹¹ and also in recently reported findings of Lal & Singh et. al.¹² and Atulit¹³.

Evaluation of number of Water Molecules involved in the formation of Activated Complex and determination of Mechanism of the Reaction:

The number of water molecules involved in the formation of the activated complex were evaluated by plotting $\log k$ values against $\log[H_2O]$ for the alkali catalysed hydrolysis of ethyl caproate in water-EG media. The values of $\log k$ and $\log[H_2O]$ have been recorded and their plots are pictured that are found to follow the Robertson equation¹⁴. It is noted that at all the temperatures of the reaction the plots of $\log k$ versus $\log[H_2O]$ have two

intersecting straight lines having positive slopes. The values of the slopes of the plots are recorded in Table-7.

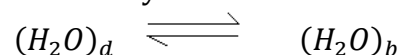
Robertson et. al.¹⁴ has established that the value of salvation number 'n' which is evaluated from the slopes of the plots of $\log k$ versus $\log[H_2O]$ following Robertson equation:

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

for unimolecular reaction, it will be fairly high while that of bimolecular reaction, it will be low. In the present study, it is clearly found that the values of slopes of the plots, when water concentration in the reaction media is below 45.75% (at $\log[H_2O] = 1.405$ which is point of intersection of the two straight lines), are found to increase from 0.291 to 0.783 with rise of temperature of the reaction. With above 45.75% of water concentration in the reaction media, the values of slopes enhance from 0.507 to 1.238 with rise of temperature of the reaction from 20°C to 40°C.

In the light of the inferences of Robertson et. al.¹⁵, from the values of the slopes of the plots, it may be concluded that with rise of temperature, the mechanistic path of the reaction changes from bimolecular to unimolecular with gradual increase of the water content in the reaction media. In other words, it may be opined that with gradual addition of the organic co-solvent (EG) in the reaction media and with rise in temperature of the reaction, the mechanistic path of the alkali catalysed hydrolysis of ethyl caproate is changed from bimolecular to unimolecular.

About the changes in the structure of water, it is obvious that in presence of EG with rise in temperature, water components of the reaction media changes its structure from dense form to bulky form:



Similar findings and their interpretations have also been reported earlier by Abhay & Singh et. al.¹⁶ and in recent years by Priyanka & Singh et. al.¹⁷ and K. Sushma¹⁸ for effect of solvent on the mechanistic path followed by the solvolysis reaction.

Evaluation of Iso-kinetic Temperature and Study of Solvent-Solute Interaction in the aquo-EG Reaction Media:

In order to evaluate Iso-kinetic temperature by using the iso-kinetic relationship formulated by Barclay & Butler¹⁹, ΔH^* was plotted against ΔS^* . Their values are recorded in Table-8. It is found that the variation is well linear in accordance with Barclay-Butler relationship¹⁹. The numerical value of the slope was found to be $291.80 \approx 292.0$ (less than 300) and from it is clearly opined that there is weak but considerable interaction between solvent and solute present in the reaction media as already reported by Leffler²⁰.

Earlier Singh & Singh et. al.²¹, Kumar & Singh et. al.²² and in recently year Ojha & Singh et. al.²³ and Sushma & Singh et. al.^{24,25} have also reported similar findings and their interpretations for weak solvent - solute interactions in different Aquo-Organic co-solvent reaction media.

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Table-1

Specific rate constant values of Alkali Catalysed Hydrolysis of Ethyl Caproate in Water EG media

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

Temp in °C	% of EG (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	90.45	83.62	79.30	72.94	67.33	61.00	55.23
25°C	165.88	150.42	137.34	122.35	107.13	94.43	80.00
30°C	305.21	269.34	244.46	205.21	172.90	146.93	117.44
35°C	541.12	467.95	399.76	332.74	269.84	219.94	167.73
40°C	961.83	81.04	674.68	538.39	420.53	331.59	239.83

Table-2

Variation of log k values of the reaction at different temperatures with mol% of EG in water-EG media

% of EG (v/v)	Mole% of EG	3+ log k values				
		20°C	25°C	30°C	35°C	40°C
20%	6.96	1.9564	2.2198	2.4846	2.7333	2.9831
30%	12.16	1.9223	2.1773	2.4304	2.6702	2.9087
40%	17.73	1.8993	2.1378	2.3882	2.6018	2.8291
50%	24.42	1.8603	2.0876	2.3122	2.5221	2.7311
60%	32.64	1.8282	2.0299	2.2378	2.4311	2.6238
70%	42.94	1.7853	1.9751	2.1671	2.3423	2.5206
80%	56.34	1.7422	1.9031	2.0698	2.2246	2.3799

Table-3

Variation of log k value of the reaction with $10^3/T$ in water EG media

Temp in °C	$10^3/T$	3+ log k values at different % (v/v) of EG						
		20%	30%	40%	50%	60%	70%	80%
20°C	3.413	1.9564	1.9223	1.8993	1.8603	1.8282	1.7853	1.7422
25°C	3.356	2.2148	2.1773	2.1378	2.0876	2.0299	1.9757	1.9031
30°C	3.300	2.4846	2.4303	2.3882	2.3122	2.2378	2.1671	2.0698
35°C	3.247	2.7333	2.6702	2.6018	2.5221	2.4311	2.3423	2.2246

40°C	3.195	2.9831	2.9087	2.8291	2.7311	2.6238	2.5206	2.3799
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Table-4

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

% of EG (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c values of kJ/mol	90.52	87.18	82.32	76.90	70.70	65.73	57.13

Table-5

Variation of Interpolated log k_D values at different desired D value of Water-EG media with Temperature

Temp in °C	$10^3/T$	log k_D values						
		D=35	D=40	D=45	D=50	D=55	D=60	D=65
20°C	3.413	1.7031	1.7489	1.7899	1.8306	1.8721	1.9165	3.413
25°C	3.356	1.8588	1.9252	1.9888	2.0579	2.1234	2.1899	3.356
30°C	3.300	2.0492	2.1362	2.2211	2.3076	2.3972	2.4902	3.300
35°C	3.247	2.2099	2.3321	2.4346	2.5478	2.6604	2.7902	3.247
40°C	3.195	2.3936	2.5346	2.6733	2.8128	2.9498	3.0876	3.195

Table-6

Evaluated Values of Iso-Dielectric Energy (E_D) of the reaction in Different Desired 'D' values of the water - EG media.

D Values	D=45	D=50	D=55	D=60	D=65	D=70
E_D values of kJ/mol	62.48	68.13	75.35	85.2	93.17	101.44

Table-7

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

Temp. in °C	Slope - I when log [H ₂ O] value is below 1.405	Slope - II when log [H ₂ O] value is above 1.405
20°C	0.291	0.507
25°C	0.505	0.698
30°C	0.577	0.901
35°C	0.694	1.007
40°C	0.783	1.238

Table-8

Variation of ΔH^* , ΔG^* and ΔS^* values of the reaction with mol% of EG in Water EG media

% of EG (v/v)	Mol% of EG	ΔH^* in kJ/mol	ΔG^* in kJ/ mol at 30°C	ΔS^* in J/K/ mol at 30°C	($\Delta S^* + 150$) in J/K/ mol at 30°C
20%	6.96	88.65	87.56	3.60	153.60
30%	12.16	84.40	87.88	-11.49	138.51
40%	17.73	80.21	88.12	-26.11	123.89
50%	24.42	74.41	88.56	-47.36	102.64
60%	32.64	67.56	89.00	-70.76	79.24
70%	42.94	63.18	89.41	-86.57	63.43
80%	56.34	54.06	89.97	-118.51	31.49

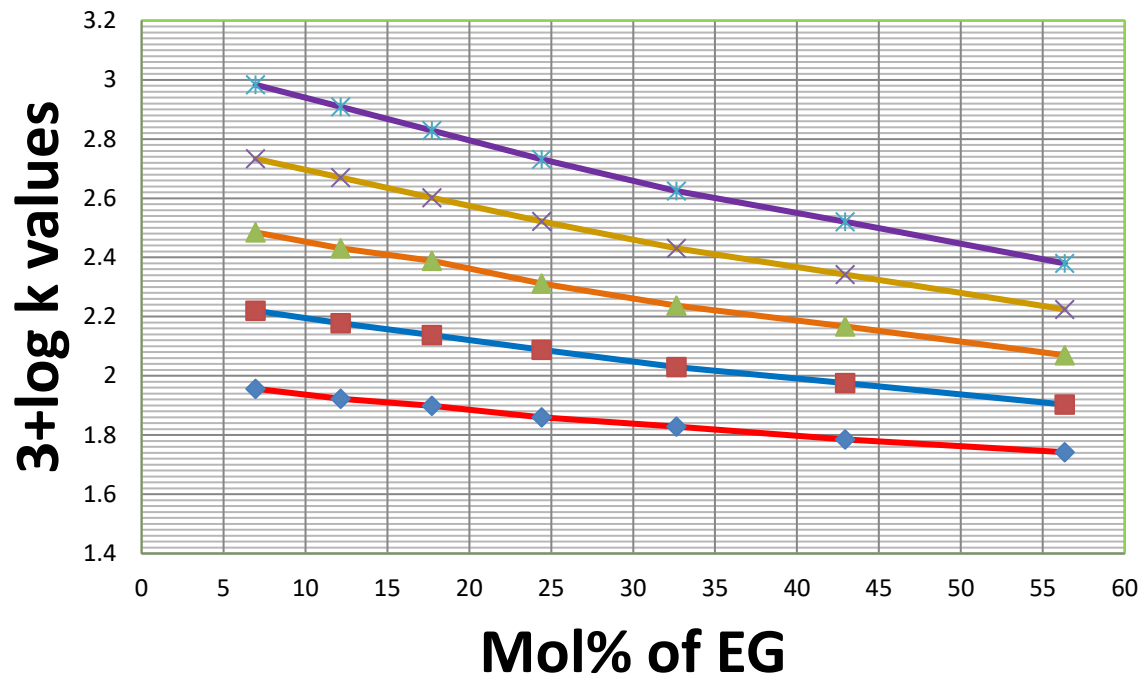


Fig.-1

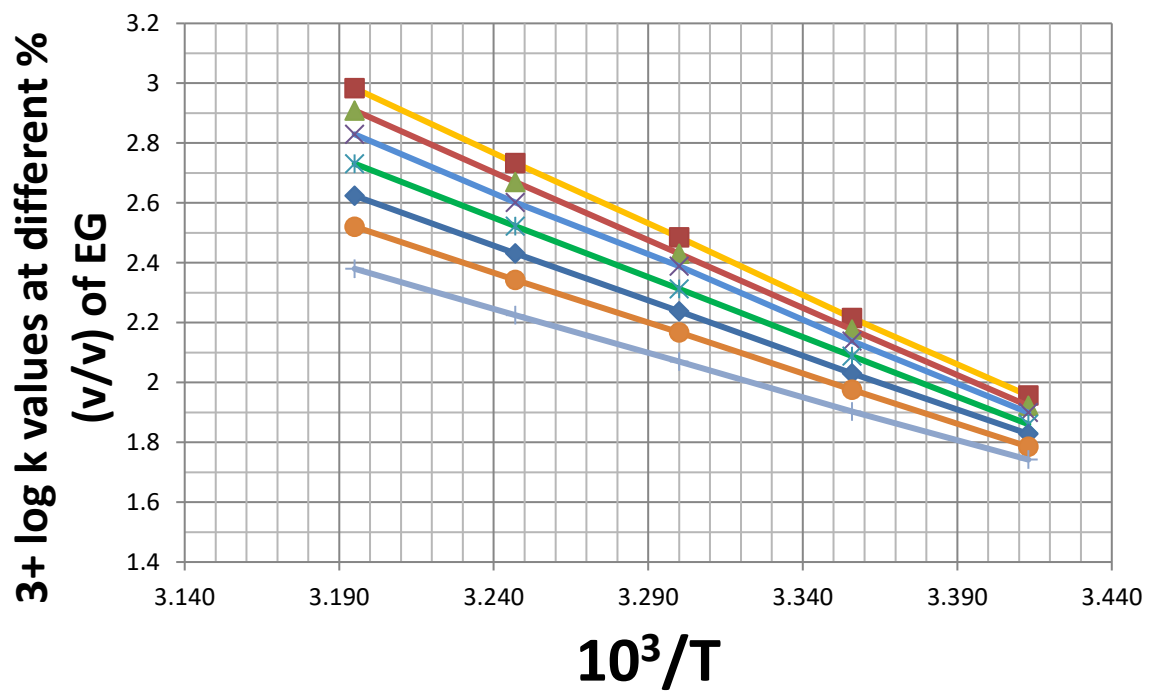


Fig.-2

