Kinetic Studies of Acid Hydrolysis of Amyl Methanoate Formate in Binary Solvent Mixture and Effect of Solvent on Activation Parameters.

Abstract

The specific rate constants for acid catalyzed hydrolysis of Amyl Mathaonate formate in water-ethylene glycol system have been determined at 20-40^0C, the solvent composition covered the range from 30-80% by weight of the organic solvent. The variation in reaction rate as well as in activation parameters have been interpreted on the basis of solvation and dielectric properties of the solvent. The thermodynamic parameters such as activation energy(E_c) free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) have been evaluated from rate conbstants using Wynne-Jones and Evring equation .All the reactions have almost negative entropy of activation which strongly support specific salvation in reaction media with change of solvent composition. Iso kinetic relationship has been determined and found to be less than 300 ($253.84K/Mole^2$) which show weak interaction in reaction media.
Keywords: Kinetics, water-ethylene glycol, activation parameter, ionic strength, Amyl Mathaonate Formate.

V.K. Singh[1], Ajay Gupta* and Suman Shekhar[2]

Author Affiliations
[1]Department of Chemistry, [2] College of Engineering,Roorkee
[2] Dept. of Chemistry, Daudnagar college,Auranggabad (Bihar)

*Corresponding Author
Dept.of Chemistry, S.R.G.I., Jhansi, India.

Email: ajay.gupt1971@gmail.com

Introduction

The acid hydrolysis of amyl mathaonate formate in binary aqueous solvent mixture revealed that the polarity of solvent surrounding the reactant greatly influence the reaction rate in activation processes. Such polarity are affected by the addition of co-solvent . However, it can be treated as mere diluents of water modifying its dielectric properties only. In this study it has been studied that solvent effect on kinetics of amyl methanoate formate catalyzed by acid. (which is used as flavoring agent in food) in varying composition of water-ethylene glycol(EG) mixture at different temperatures. In acid catalyzed reaction the aquous-solvent affect on kinetic behavior and also play a major role in controlling the reaction rate which is usually affected by interaction of solvent with transition state and also with reactant. The dielectric constant of ethylene glycol is less than water and make miscible with water in all proportions The varying composition of water- solvent mixture showing different dielectric constants values lower than water (Akerlof. G.1932, Franks F. Water: 1973, Akerlof G. and Oliver.1936) . The properties of single solvent, do not necessarily predict the reactions as reported by many workers (Singh AK. 2019,2020, Sharma Sangita et al. 2013, Magda F Fathalla. 2011), in

attempt to correlate the rate change with the nature and properties of the medium and bring confusing results. Thus Parker (Parker AJ. 1962) and Robert (Roberts DD. 1966) found that rate constants values decreases in the system with increase in dielectric constant of the solvent, as predicted by Hughes and Ingold (Hughes ED, Ingold CK. 1935) and Laidler and Landskroener (Laidler KJ, Landskroener PA.1956) . The rate of such reactions has been expected to show high values with increase of dielectric constant.

Experimental

The specific rate of hydrolysis observed volumetrically at five equidistance temperature over temperature range of 20 to 40^0 C having extraordinary attention of solvent in response mixture of water-EG media. Pure amyl methanoate (Merck) used for kinetic studies. Double distilled water is used throughout the experiment. The kinetics of acid catalyzed of ester was studied as usual by adding 0.60 ml of ester in 50 ml of 0.5M HCI solution. The values of specific rate constant were evaluated using first order rate equation and collected in Table-1. The values of rate constant for different $[H^+]$ ion concentration of the reaction media has been inserted in Table-2.The various activation parameter had been calculated using Wynne-Jones and Eyring equation (Wynne-Jones WF K, Eyring H. 1935) and given in Table-3.

Result and Discussion

Reaction rate and solvent effect:

First order kinetic equation was used to calculate the rate constant of hydrolysis of amyl methanoate in water-ethylene glycol solvent system and its value is tabulated in Table-1 It is evident from this Table that specific rate constant decreases with increasing temperature from 20 to 40^0 C. The depletion of rate to different extent with mole% in water- EG media may attributed partly due to solvation change and partly due to change in dielectric constant. The factor liable for increasing rate with temperature is because of dielectric impact and partially due to solvation in the response media. This outcome is supported through our earlier publication of Bano A. & Singh AK(Singh A K. Arjuman Bano. 2019).

Table 1 : Specific Rate Constant Values With Respect To Solvent Composition [K X10^3(Dm)3/Mole/Mint] In Acid Catalized Hydrolysis Of Amyl Methanoate Formate

Temp in ^{O}C	% of Ethylene glycol					
	30%	40%	50%	60%	70%	80%
20°C	44.66	35.07	31.62	27.86	24.54	21.37
25°C	83.17	64.56	56.88	49.54	42.65	35.39
30°C	149.62	114.81	100.00	86.09	72.44	56.88
35°C	263.02	204.17	169.82	146.21	121.61	91.20
40^{0}C	467.73	354.81	294.44	248.31	206.53	144.54

Iso-composition Activation Energy (E_c) and solvent effect

The Iso-composition Activation Energy of the reaction mixture decreases from 106.62 to 72.07 kJ/mole with increasing composition of solvent indicate that initial state is solvated and transition state is desolvated which support the recent communication of Singh AK(Singh AK. Arjuman Bano. 2019).

Iso- Dielectric Activation Energy (E_D) and solvent effect

With assist of Arrhenius plots the Iso- Dielectric Activation Energy (E_D) turned into evaluated which indicates lowering trend 84.19 to100.21 kJ/mole with increasing mole%. This is also supported by using past view of Wolford (Wolford R K, 1964) and these days view of Singh AK. et.al. (Singh AK. Arjuman Bano. 2019).

The effect of change in the concentration of [H^+] ion(acid) in the reaction media,on the kinetic of acid catalyzed solvolysis of amyl formate was studied by changing the concentration of HCI solution, keeping the ionic strength of the media constant at (μ=0.9).The value of rate constant of the reaction were found increasing with increasing[H^+] ion in the reaction media are given in Table-2. To establish the mechanism of reaction, the log k values were plotted against [H^+] and the slope of straight line was found to be 1.005 which may be treated as unity , this concluded that hydrolysis of amyl formate follow A_{AC}^2 mechanism in water-EG media as given by Zucker and Hammett(Zucker L and Hemmet LP.1939).

Table 2: **Effect Of [H^+] On The Specific Rate Constant Values Of Amyl Formate In Water-EG Media At Constant Ionic Strength**

[H^+]	[KCl]	μ	$k\times10^3$in min^{-1}	2+log[H^+]	3+logk	Values of slope

0.12	0.80	0.90	27.93	1.0000	1.4461	
0.15	0.75	0.90	41.70	1.1761	1.6201	
0.20	0.70	0.90	56.90	1.3010	1.7551	
0.25	0.65	0.90	70.34	1.3979	1.8472	1.005
0.30	0.60	0.90	84.57	1.4771	1.9272	
0.40	0.50	0.90	114.13	1.6021	2.0574	
0.50	0.40	0.90	142.20	1.6990	2.1529	
0.60	0.30	0.90	168.27	1.7782	2.2260	
0.70	0.20	0.90	198.52	1.8451	2.2978	
0.80	0.10	0.90	226.52	1.9031	2.3551	

Thermodynamic activation Parameters and solvent effect of reaction:

Activation parameter, like activation energy also plays an important role in ester hydrolysis. The enthalpy of activation (ΔH^*) free energy of activation (ΔG^*) and entropy of activation (ΔS^*) is determined using Wynne-jones and Eyring equation(Wynne-Jones WFK, Eyring H.), and the results are collected in Table-2 with increasing mole% of solvent. Although, the variation of (ΔG^*) with mole % is negligible as compared to the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) with increasing composition of reaction mixture but it cannot be ignored.

The enthalpy of activation (ΔH^*) decreases with increasing mole fraction of reaction mixture (ΔS^*), become more negative which indicated that there is polar transition state is preferentially solvated by water molecule. The plots of (ΔG^*) against mole % of EG shown in fig-1 at 25^0c is found to be increasing non-linearly with increasing concentration of EG. This gradual and non linear increase in mole fraction of organic co solvent in reaction media is indication of salvation or desolvation of reactant as reported earlier by Elsemongy et.al.(Elsemogy MM, Abu EMS, Mussa MNH 1975) and recently supported by Singh AK (Singh A K. 2017). Since among three thermodynamic enthalpy of activation (ΔH^*), (ΔS^*) and (ΔG^*) the value of (ΔG^*) increases with simultaneous decrease in (ΔH^*), (ΔS^*) with increasing mole% of organic component of reaction media. On the basis of thermodynamic co relation

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

The increase in (ΔG^*) value with decrease in ΔH^* and $\Delta S*$ is possible when the extent of depletion $\Delta S*$ is greater than ΔH^*. The greater extent of depletion in $\Delta S*$ in compare to ΔH^* in water-EG media indicate that the reaction enthalpy promoting and entropy deactivating.

Table-3: Calculated Values Activation Parameters of the Reaction in Water-n-propanol Media [$\Delta H^*$and ΔG^* in KJ/Mole, ΔS^*in J/K/Mole.]

| % of propanol	Mole %	ΔH^* in Kj/Mole	20^{0}C		25^{0}C		30^{0}C		35^{0}C		40^{0}C	
			ΔG^*	-ΔS^*	ΔG^*	-ΔS^*	ΔG^*	-ΔS^*	ΔG^*	-ΔS^*	ΔG^*	-ΔS^*
30%	12.16	87.89	89.53	5.59	89.57	5.05	89.65	5.80	89.68	5.81	89.69	5.75
40%	17.73	83.76	86.58	22.59	90.20	21.61	90.32	21.65	90.33	21.33	90.41	21.24
50%	24.42	82.84	90.38	25.73	90.52	25.30	90.67	25.84	90.80	25.84	90.78	25.36
60%	32.42	82.09	90.96	30.27	90.86	27.75	91.04	29.53	91.19	31.88	91.44	29.87
70%	42.94	78.84	91.00	41.50	91.23	41.57	91.48	41.71	91.66	41.62	91.70	41.08
80%	56.34	77.41	91.33	47.50	91.70	47.95	92.09	48.44	92.40	48.66	92.64	48.65
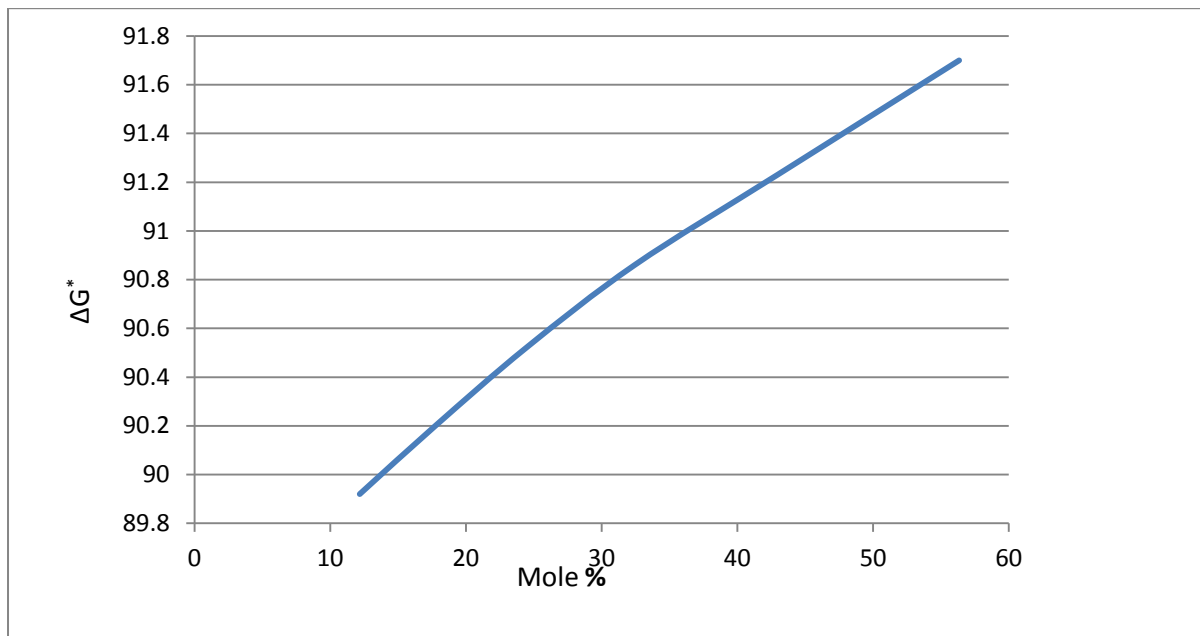
Fig (1)- Variation of ΔG^* with mole % at 25^0c (water-ethylene glycol)
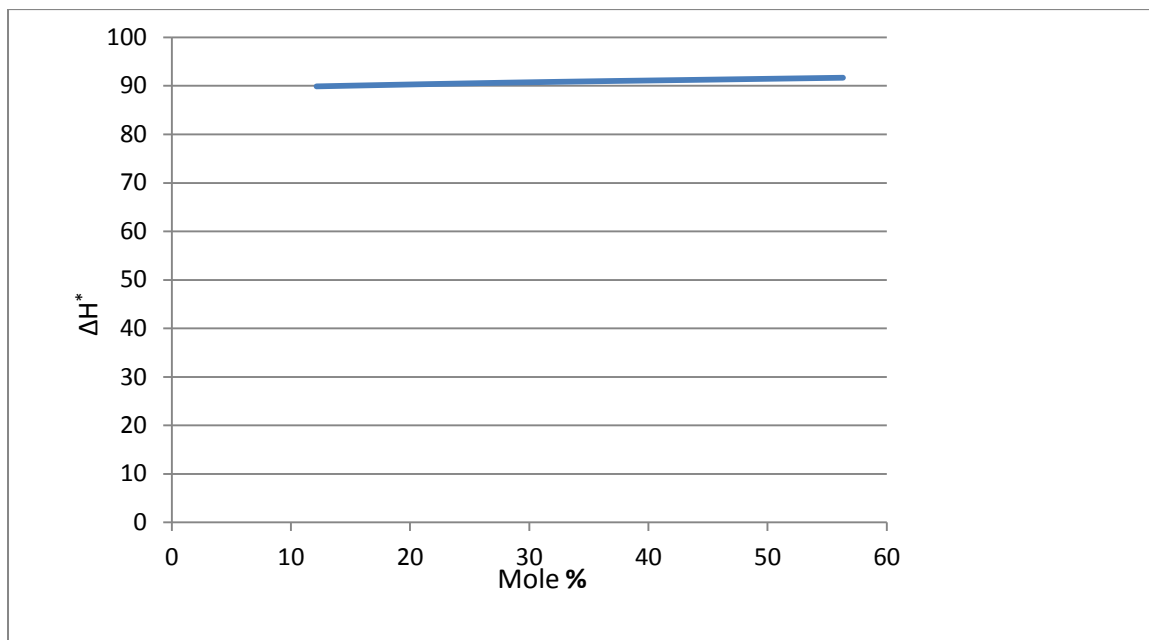

Fig (2)- Variation of ΔH^* with mole % at 25^0c (water- water-ethylene glycol)
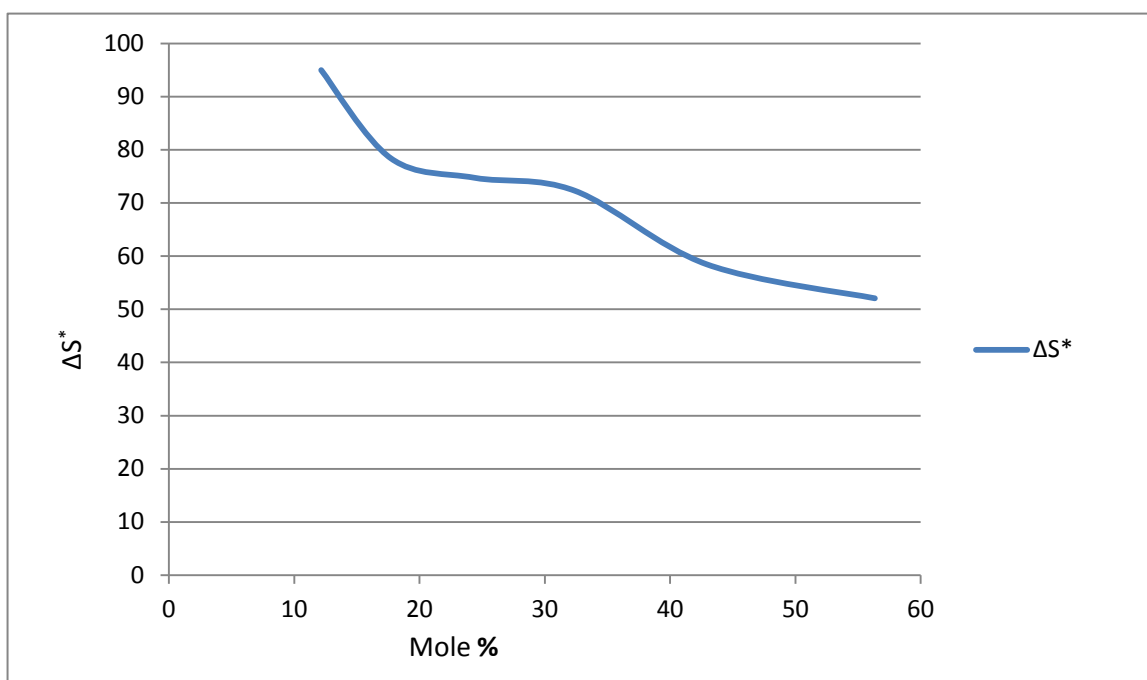
Fig (3)- Variation of ΔS^*+100 with mole % at 25^0c (water-ethylene glycol)

Iso-kinetic Temperature and solvent effect: The values of iso-kinetic temperature of the reaction was evaluated using Barclele-Butler (Barclay and Butlar JAV. 1938) relationship which is expressed as

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

It is relation between enthalpy and entropy of activation, β is known as iso-kinetic temperature or Laffler-Grunwald solvent stabilizer operator (Laffler J E. ,Grundwald E. 1963). The value of iso-kinetic temperature was evaluated from the slopes of straight line ploting between $\Box$ H^* verses $\Box S^*$ at 25^0c which is shown in fig-4.

From the slope of straight line of the plots, the value of iso-kinetic temperature was evaluated to be 253.84K/Mole$^{2.}$(less than300). Thus, in the light of Lefler(Lefler JE. 1955) guiding communication, it can be concluded that there may be no appreciable exchange in structure of reactant or in the solvent or in each the reactant or in solvent or both the reactant and solvent due to weak interaction between solvent and solute present in reaction media in similar ways as reported by Singh AK (Singh AK. **2020**).
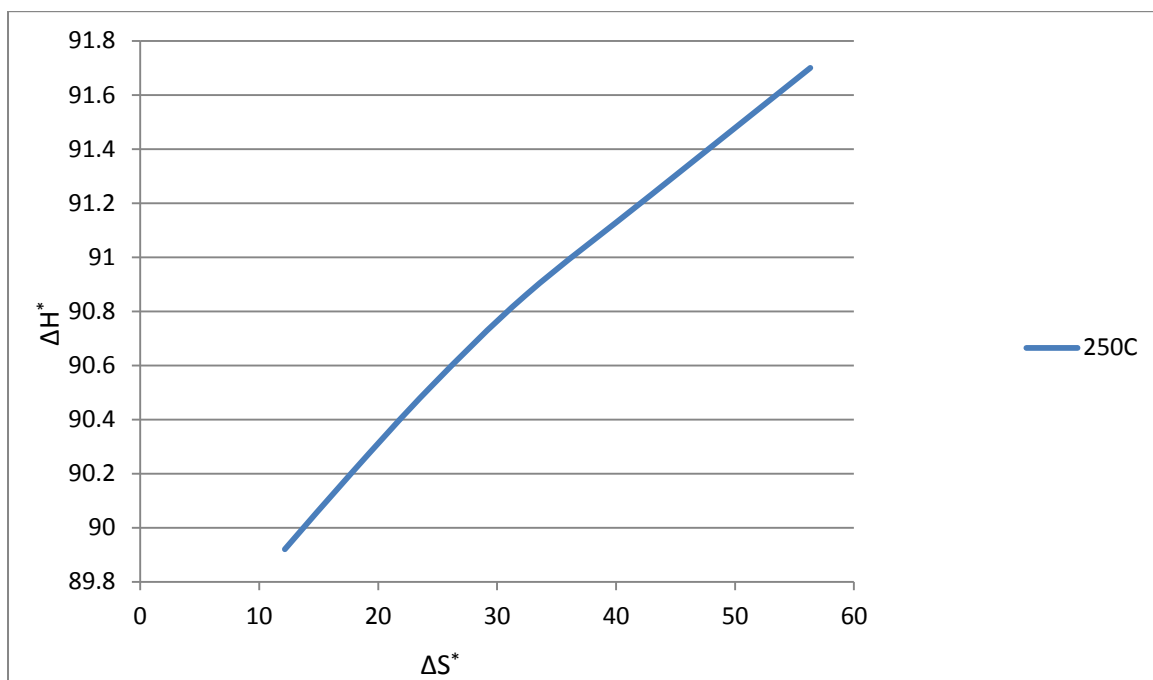
Fig. 4: Variation of ΔH* with ΔS*+100 (wate- water-ethylene glycol) system

Conclusion

The results of above project hydrolysis of Amyl Formate in water-EG media, following conclusion are found as: the solvent effect was discussed considering the dielectric constant of the medium and water water concentration effect on the reaction rate. Activation parameters calculated with help of Wynne-jones and Eyring equation and there is considerably change was found which shows that there is specific change taking place during the hydrolysis of amyl methanoate. The lower values of ionic strength shows weak interaction between solvent ant solute in the reaction media.The value of ionic strength the mechanism followed by hydrolysis is A_{AC}^2 type.

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