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Initial and transition state solvent effect on Reaction Rate for Solvolysis of Ethyl Caprylate Ester in Binary Solvent System

Abstract

The kinetic reaction of ethyl caprylate in basic medium of water-acetone has been studed in different range of temperature 20 to 40^0c. The composition range of reaction mixture is 30 to 70% (v/v) of Acetone. The rate constant decreases with increase in solvent composition of reaction mixture indicate that there is destruction of charge in transition state. The trend of activation energy is found to be decrease with increasing solvent composition is an indication that initial state is desolvated and transition state is solvated. The influence of dielectric constant value of water on reaction rate has also been studied. The thermodynamic parameters (ΔG^*, ΔH^* & ΔS^*) have been determined which showed strong dependency on solvent composition.

Keywords: Ethyl Caprylate Hydrolysis, Specific rate, water- acetone, kinetic solvent effect,

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Introduction

It has been suggested that change in solvent from polar to non polar will either increase or decrease the reaction rate depending upon the type of reaction (Parker A.J. 1969). Solvent effect on reactivity in homogeneous media is explained in term of specific interaction of solvent and reactant molecules and also between solvent and transition state (Iglesias E.2005). In many physical and chemical process of solution, the solvent play very important role (Yangjeh A.H. 2005). When the magnitude of solvent in elementary reaction are changed, the rate of reaction will also change(Schmeer G et.al 1999, Kallol k Ghosh. 1999. For the understanding of solvent effect, a large effort has been made (*Panov M Yu. et al. 2003,Magdha F, Fathala. 2011, EZZ A. et al. 2017Magda F et al. 2019,*Seliverstova T S. 2020, *Seliverstova T S et al. 2020.* which are sometime succeed and also some time fail. In this context here, hydrolysis of Ethyl caprylate is presented in aqueous solvent system at different composition and in different range of temperature. Ethyl caprylate is fatty acid ethyl ester, has prominent role as metabolite. It is suitable reagent used as standard for measurement of flavour-active compound by gas chromatography. It is also used in brown cocoa, dairy savory etc.

Experimental

The kinetic of alkali catalyzed solvolysis of Ethyl caprylate in water-acetone has been studied by keeping the concentration of alkali and ester M/10 and M/20 respectively. Water used was double distilled from $KMnO_4$. Chemical used in this experiment are either BDH(Analar) or Merck grade. Acetone was purified by known procedure. The conical flask containing the solution and small stopper bottle congaing Ethyl capryalate has been thermostated for half an hour. Then 0.4 ml of ester was withdrawn with the help of pipette and added quickly to alkaline solution of water-organic co-solvent mixture by constant shaking. Immediately 10 ml of aliquot of the reaction mixture was withdrawn and allowed to run into flask containing 10 ml of N/10 HCl solution. The excess of alkali of the solution was titrated by means of standard solution using phenolphthalein as an indicator. The moment at which half of the aliquot was added into the ice cold 0.1N HCI solution, the stop clock was started. This time is considered to be zero time or starting time. Taking into account of zero time kinetics of remaining ester was estimated after quenching the 10 ml of aliquot in 10 ml of ice cold 0.1N HCl at definite interval of time followed by titration as usual.

Result and Discussion

Solvent Effect and calculated Specific Rate constant

The specific rate constant of alkali catalyzed solvolysis of Ethyl caprylate followed second order kinetics which is calculated by slope of linear plots of Log k against1/T. The values of rate data (Table-1) show that with increasing proportion of organic solvent rate decrease. The solvent effect on specific rate can also be observed when Log k is plotted against solvent composition (Table-2 and Fig-1). Dipolar protic solvent like Acetone, DMSO, DMF are powerful bases and strong hydrogen bond acceptor so it interact with solute which are hydrogen bond donors (Parker AJT. 1962.). The value of dielectric constant of the reaction media goes on decreasing with solvent composition so the result obtain in present study is against the Hugh and Ingold qualitative theory. However many instant has been reported (R Krishnanmurty P S et al. 1970, Singh L et al. 1980] in which the rate decreases in similar way as found in this case. The depletion of rate causes due to addition of Acetone in water-Acetone media, may be attributed due to combine effect of dielectric and solvation change taking place in the media. The dipolar aprotic solvent like DMSO, Acetone, DMF exerted greater effect on rate because such solvent produced inter molecular association of solvent in such aqueous solvent media. Solvent -solute interaction, solvation of reactant and transition state are also dominating factor which also exert greater effect on rate of reaction.

Table 1.Bimolecular rate constant k x10^3(dm)^3/mole/mint]

Temp in ^{O}C	% of Acetone				
	30%	40%	50%	60%	70%
20^{O}C	26.91	23.71	21.33	18.48	15.84
25^{O}C	55.59	46.66	39.81	33.11	26.30
30^{O}C	107.15	89.12	72.44	58.74	42.65
35^{O}C	208.92	164.05	127.35	100.00	67.60
40^{0}C	398.10	305.49	229.08	175.79	107.15

Table 2.Change in Log k Value with mole %

Temp in ^{O}C	**Mole%**	**3 + Log k**				
		20^{O}C	**25^{O}C**	**30^{O}C**	**35^{O}C**	**40^{0}C**
30%	9.56	1.430	1.745	2.030	2.320	2.600
40%	14.11	1.375	1.669	1.950	2.215	2.485
50%	19.77	1.329	1.600	1.860	2.105	2.360
60%	26.99	1.265	1.520	1.769	2.000	2.245
70%	36.52	1.200	1.420	1.630	1.830	2.030

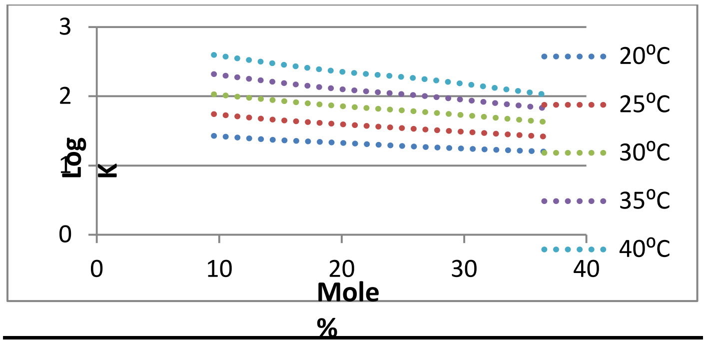

Fig. 1: Plots of log k with mole %.

Thermodynamic Activation Energy (Ec) of bimolecular reaction.

With the help of slopes (**Fig-2**) of linear plots of (Logk against 1/T) of Arrhenius equation , the numerical value of activation energy(E_c) has been calculated and tabulated in Table-4. The depleting trend of iso composition activation energy with enhancement in solvent composition,indicate that solvation in transition state and desolvation in initial state, because transition state possess more cation (ester+H^+) available by the salvation of acetone molecule than initial state (Varma DK et al. 2020, Sundhansu NS. 2020). The decrease in value of ΔH^* and ΔS^* also indicate the decrease in disorderness of the reaction media.

Table 3. Logk Values with different Temperature, Water- acetone media

Temp in ^{O}C		**3 + Logk**				
	10^3/T	**30%**	**40%**	**50%**	**60%**	**70%**
20^{O}C	3.412	1.430	1.375	1.329	1.265	1.200
25^{O}C	3.355	1.745	1.669	1.600	1.520	1.420
30^{O}C	3.300	2.030	1.950	1.860	1.769	1.630
35^{O}C	3.247	2.320	2.215	2.105	2.000	1.830
40^{0}C	3.195	2.600	2.485	2.360	2.245	2.030

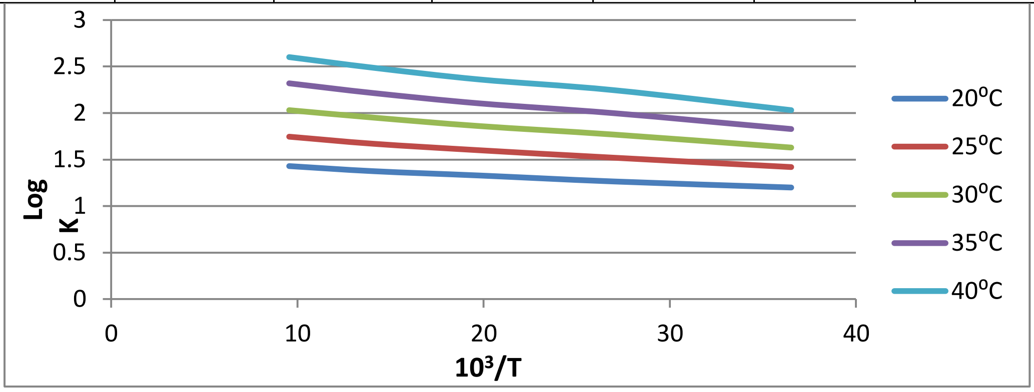

Fig. 2: Plots of Log K with 10^3/T.

Table 4.Activation Energy at different composition of solvent

% of EG	**30%**	**40%**	**50%**	**60%**	**70%**
E_{exp} in KJ/mole	103.75	99.41	99.03	88.36	74.09

Table 5. $\log k_D$ Values with different Temperature at constant D for Water- acetone media.

Temp in ^{O}C	10^3/T	D=40	D=45	D=50	D=55	D=60
20^{O}C	3.412	1.189	1.240	1.299	1.355	1.410
25^{O}C	3.355	1.420	1.500	1.580	1.660	1.740
30^{O}C	3.300	1.695	1.770	1.850	1.930	2.015
35^{O}C	3.247	1.895	2.015	2.140	2.260	2.385
40^{0}C	3.195	2.152	2.280	2.410	2.539	2.669

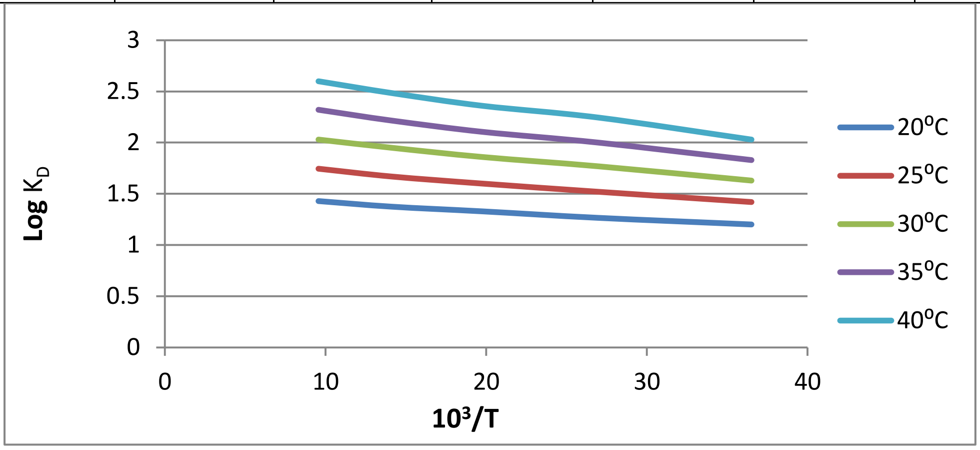

Fig. 3 Plots of Log K_D with 10^3/T.

Effect of Dielectric Activation Energy

An alternative aspect of solvent effect can be tested by considering the influence of dielectric constant D on reaction rate. Thus, an increase in D causes a consequent increase in rate. By the interpolation of (Akerlof G. 1932) data, the dielectric constant values of reaction mixture have been obtained. When dielectric constant D of the medium is lowered, there is a considerably decrease in rate is found. The plots of log k and D-1/2D+1 give linear relation which indicate that reaction have dipole-dipole interaction(Lanndskroner(Laidler and Landskroener1956) .If the reaction is considered as ion-dipole interaction, linear relation is obtained by plotting Logk against1/D, other liner relationship obtained for Logk vs LogD (Fayez Yet.al. 1978). Graphical application of different electrostatic theory for dipole-dipole as well as ion-dipole showed that the best linear plots are obtained when Logk is plotted as a function of D. Departure from linearity at low dielectric constant at low dielectric constant is however still preserved. In case of preferential solvation or solvation shortening of activated complex by water, with the higher component of solvent mixture there is deviation in linearity is observed. However, in the present study of alkaline hydrolysis of caprylate ester is based on dielectric constant effect and can better be treated as an ion dipole interaction, in which ester represent the actual dipole rather than dipole interaction. Here Iso-dielectric activation energy was calculated by the slopes of interpolation of Logk against different temperature [Fig-3] and the calculated values of dielectric activation energy are inserted in Table-6. The decreasing trend of (E_D) values with decreasing D is similar as previous views of (Wolford RK.1964, Singh AK. 2020)

Table 6. Dielectric Activation Energy values at different D.

Dielectric constant(D)	D=40	D=45	D=50	D=55	D=60
E_D in kJ/mole	86.62	91.62	94.66	99.64	106.39

Conclusion

The rate of hydrolysis of alkali catalyzed hydrolysis of ethyl caprylate decreases with increase composition of organic solvent at different temperature range. The increase in value of Iso-composition energy with decreasing solvent proportion, indicate that the solvation takes place in initial state and desolvation in transition state. The result of this project was to analyze the solvent-solute interaction and solvation change in initial and transition state. Dielectric values also play important role in observing solvent effect in aqueous solvent media.

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