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Kinetics and solvent effect on activation parameter of aquo-propanol solvent system for acid catalyzed solvolysis of propyl formate

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Abstract

Kinetic study of acid catalyzed hydrolysis of propyl formate has been carried out volumetrically in water-propanol binary solvent system having different concentration of the organic component from 30 to 70% (v/v) of propanol-2 at different temperature ranging from 20 to 40^0C. Specific rate constant values calculated by first order were found to be decreasing with increasing proportion of propanol at all temperatures. Enhancement in iso-composition activation energy(E_C) with increasing concentration of propanol-2 and depletion of dielectric activation energy(E_D) with depletion of dielectric constant of reaction media inferred that initial state is solvated and Transition state is desolvated.

The thermodynamic parameters like Enthalpy of activation **(**ΔH^*), Entropy of activation (ΔS^*) and Free energy of activation (ΔG^*) were evaluated with help of Wynne-Jones and Eyring equation and its none linear plots with mole% of propanol is indicative of specific solvation taking place in reaction media. The isokinetic temperature was calculated by linear plots of ΔH^* verses ΔS^* and its value turned out to be more than 300(621.29K/Mole^2), it shows that there is strong interaction that takes place between solvent and solute molecule.

Keywords: Propyl formate, water-propanol Activation parameter, Solvent effect, solvent-solute interaction, Iso-kinetic temperature, specific and non-specific salvation. Solvation in initial and transition state. Barclay-Butler rule

1. Introduction

To determine the chemical reactivity solvent plays a very important role. When magnitude of solvent changes the rate of elementary reaction is also changes. Solvent effect is solvent polarity which includes specific and non-specific interaction of solvent and solute in different solvent system. However, the result interpreted by different kinetics [1, 6] reaction in term of solvent polarity, sometimes succeeded and sometime failed. To make further investigation to how thermodynamic properties of mixed solvent system effect on kinetic parameter and kinetic behavior of thermodynamic parameter on physical properties of solvent, I report here the outcome of acid catalyzed hydrolysis of propyl formate in water-propanol solvent system. Propyl formats have a great medicinal application and it is also used as a flavoring agent

2. Experimental

Export quality of propyl formate grade of high degree and Pure propanol were used. The binary mixture of organic solvents and water were prepared on weight basis. The concentration of the catalyzing acid was 0.5M HCI in all mixture. The hydrolysis was carried out in glass-stoppered flask. The kinetic of the reaction was studied by adding 0.5 ML of ester through syringe pipette into 50mI of 0.5HCI solution. The reaction rates were determined by titrating the sample at different interval of time against standard of NaOH using phenolphthalein as indicator. The rate constant is calculated using first order kinetics.

3. Result and Discussion

3.1 Influence of solvent composition on rate

The variation of rate with organic solvent content in water-propanol can be seen in Table-1. From the Table-1&2 it is evident that the rate constant values of the reaction decreases with increasing proportion of propanol in the reaction media. The decreasing trend of rate is also found by plotting log k against mole% shown in fig-1.

Table 1: Specific rate constant values of acid catalysed hydrolysis of propyl formate as function of solvent composition in water-propanol system [k x10^2(dm) 3/mole/mint]

Temp in ^OC	% of propanol				
	30%	40%	50%	60%	70%
20^OC	56.23	44.66	37.93	30.90	25.40
25^OC	102.010	89.12	74.98	65.31	54.32
30^OC	194.98	194.98	153.10	128.82	112.20
35^OC	354.81	331.13	294.44	257.03	226.46
40^0C	645.65	616.59	562.34	501.18	457.08

Table 2: Variation of Log k Values against mole %, Water-propanol solvent System.

Temp in ^{O}C	**3 + Log k**					
	Mole%	**20^{O}C**	**25^{O}C**	**30^{O}C**	**35^{O}C**	**40^{0}C**
30%	9.33	1.750	2.010	2.290	2.550	2.810
40%	13.79	1.650	1.950	2.225	2.520	2.790
50%	19.35	1.579	1.875	2.185	2.469	2.750
60%	26.47	1.490	1.815	2.110	2.410	2.700
70%	35.90	1.405	1.735	2.050	2.355	2.660

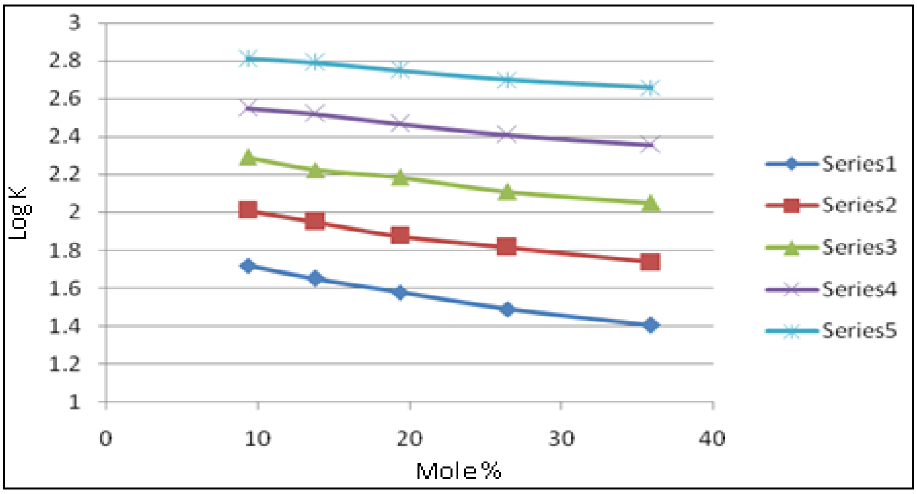

Fig. 1: Variation of log k with mole %.

3.2 The values of Iso-composition Activation Energy (E_c) on the reaction in water-propanol media was found to be increasing trend. The increased values of iso composition activation energy (94.81to112.00 KJ/Mole) as calculated by Arrhenius plots states that transition state is desolvated and initial state is solvated

3.3 Calculated values of Iso-Dielectric Activation Energy.

From the slops of the Arrhenius plots of the interpolated values of log k_D against 10^3/T, the values of k_D were evaluated and it is found to be decreasing from116.06 to 102.08 KJ/Mole with increasing D of the reaction media.

3.4 Specific rate and thermodynamic activation Parameters of reaction

For better study of kinetic solvent effect, the thermodynamic parameters Free energy of activation (ΔG^*), Enthalpy of activation (ΔH^*) & Entropy of activation (ΔS*) were taken into account as they have great significance to studying the properties of activated complex and solvating power of medium. These data are calculated with the help of Wynne-Jons and Eyiring equation [7] and are compiled in Table-3. To observe the variation of these thermodynamic parameters more clearly each of these values [(ΔG^*), (ΔH^*) & (ΔS*)] were plotted against mole% of propanol-2 which are presented in fig-2, 3&4 respectively. All these three plots follow nonlinear variation and it is indicative of specific solvation taking place in reaction media (water-propanol) as proposed by Salive and Hudson [8] and is recently supported by Singh AK [9] From Table-1, it is obvious that there is an enhancement in (ΔG^*) values with simultaneous increase in ($\Delta\Delta H^*$) and (ΔS*) values. According to thermodynamic relation of free energy and entropy. $\Delta G^* = \Delta H^*$ -ΔS*

From this relation it is evident that the simultaneous enhancement in (ΔG^*) values with increase in (ΔH^*) & (ΔS*) value is only possible when the extent of increase in (ΔH^*) value is greater than that found in (ΔS*) values and from this it may be inferred that for the reaction in water-propanol media acts as enthalpy activator and entropy inhibitor.

Table 3: Thermodynamic Activation Parameters of acid catalyzed solvolysis of propyl formate in Water- propanol Media $\Delta H^*$and ΔG^* in KJ/Mole, ΔS^*in J/K/Mole.

% of MEOH	**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%	9.33	38.47	88.01	169.07	89.06	169.76	88.98	166.69	88.85	163.57	88.85	160.95
40%	13.79	40.75	89.53	166.48	89.40	163.69	89.36	160.42	89.08	156.91	88.97	154.05
50%	19.35	42.98	89.93	160.23	89.80	157.11	89.59	153.82	89.39	150.68	89.21	147.69
60%	26.47	44.13	90.43	158.02	90.63	156.04	90.03	151.48	90.06	149.12	89.75	145.75
70%	35.90	44.67	90.91	157.87	91.03	155.16	90.38	150.85	90.39	148.44	90.07	145.04

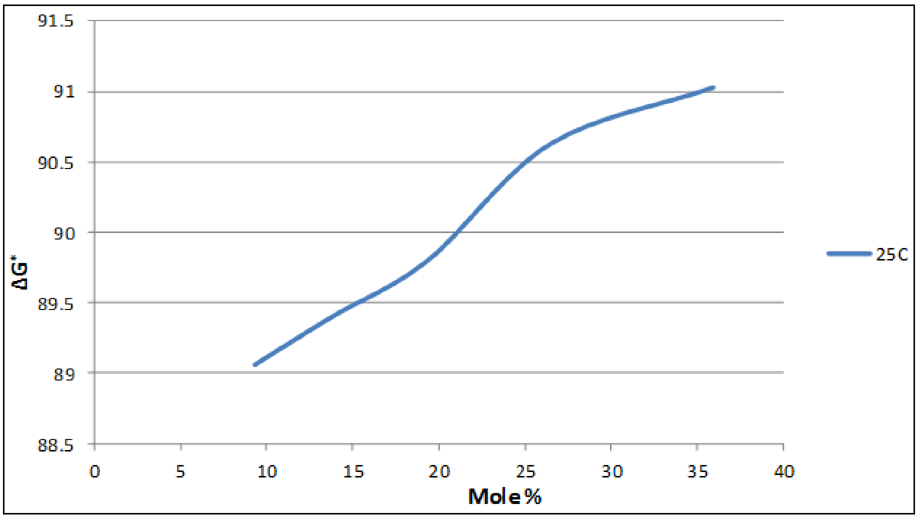

Fig 2: Variation of ΔG^* with mole % at 25^0c (water-propanol)

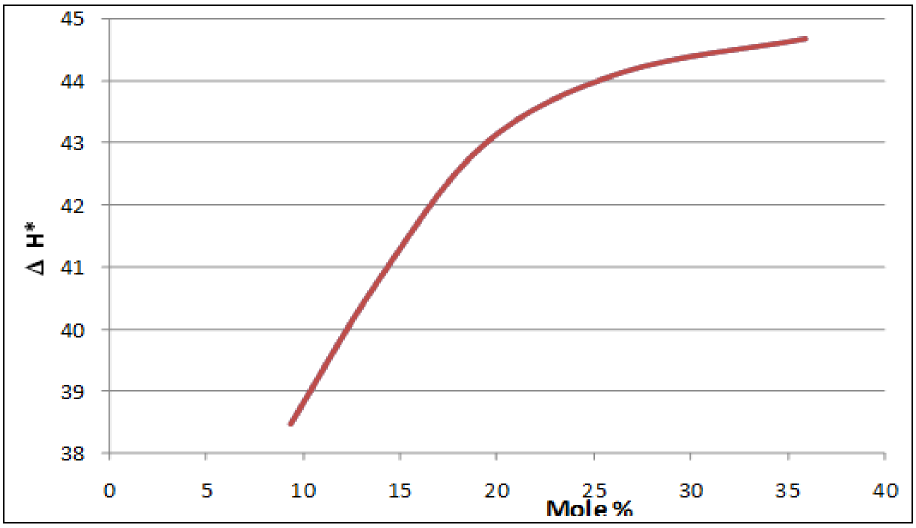

Fig 3: Variation of ΔH^* with mole % at 25^0c (water-propanol)

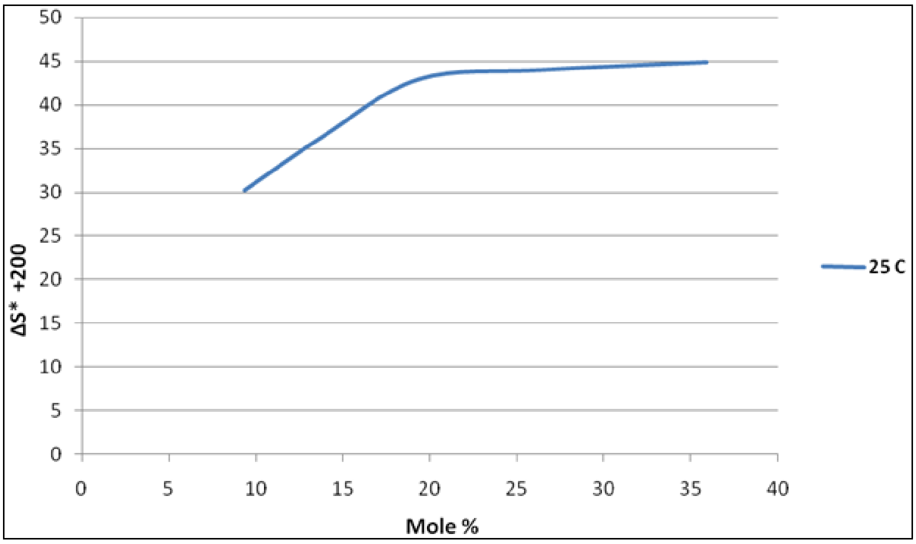

Fig 4: Variation of ΔS +200 with mole % at 25^0c (water-propanol)

3.5 Solvent-Solute Interaction and Iso-kinetic Temperature

For verifying the abeyance of Barclay and Butler [10], the slope of the plots of ΔH^* against ΔS^* were determined in the light of relation

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

Where β is a constant called iso kinetic temperature.

Laffler [11] has pointed out that iso-kinetic relation has been examined in much solvolysis reaction and yielded slope should lie between 300 to 400, when there is considerable interaction between solvent and solute in the reaction media. In this study also, the plots of ΔH^* against ΔS^* was found to be in a straight line as shown in fig-4 with this, its slope value was evaluated to be 621.29 K/mole^{2}inferred that there is strong interaction between solvent and solute. Same trend of result was recent found by Singh RT [12]

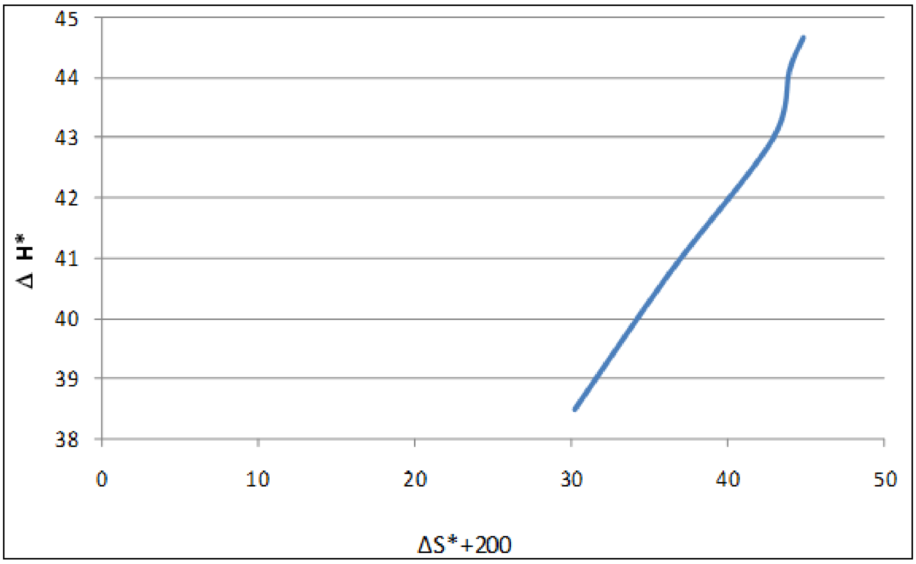

Fig 5: Variation of ΔH* with ΔS*+200 at 25^{0}C (water-propanol) system

4. Conclusion

By observing the analysis of above result, it has been found that

1. There is depletion of specific rate constant values with increasing proportion of co-solvent at all temperature.
2. The increasing trend of iso composition energy (E_c) shows that transition state is desolvated whereas initial state is solvated
3. None linear plots of $\Delta G,^*\Delta H^*$ & ΔS^* with mole % of solvent indicate that specific solvation take place in reaction media.
4. The value of iso kinetic temperature is greater than than 300 indicate that there is considerable interaction take place between solvent and solute in the reaction media

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