

# Studies of Solvent Effect of Aquo-Methanol Solvent System on Kinetics and Activation Parameters of Base Catalysed Hydrolysis of Ethyl Cinnamate

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**Abstract**— The rate of alkaline hydrolysis of ethyl cinnamate was measured over the temperature range of 20° C to 40° C in water-methanol mixture at different composition 30 to 70% (v/v). The specific rate constant was calculated using second order reaction. The influence of solvent variation on reaction rate was examined in term of changes in the Activation parameter. Depletion of  $\Delta H^*$  and  $\Delta S^*$  value with simultaneous increase in  $\Delta G^*$  of the reaction in media, reveals that the reaction is Enthalpy domination and Entropy controlled. The Values of Iso-kinetic which is less than 300, clearly indicates that there is no appreciable interaction between solvent and solute present in the reaction media, i.e. reaction is not ion-dipole but ion-molecule type.

**Keywords**- Activation Parameter, Solvent effect, solvent-solute interaction, Iso-kinetic temperature, specific salvation

## I. INTRODUCTION

Though the solvent effect on the rate and mechanism of the various type of reaction has been reported [1] [2] [3] but very little attention has been paid towards the study of the solvent effect on the thermodynamic activation parameter and solvent-solute interaction, particularly solvolysis of Ethyl Cinnamate which is important for medicinal use as well as flavoring agent in cut tobacco. It has been proposed to make a kinetic study of the solvent effect on the base catalyzed hydrolysis Ethyl Cinnamate in water-methanol media of various compositions.

## II. EXPERIMENTAL

The kinetics of base catalyzed hydrolysis of ethyl acetate has been carried out volumetric in water-methanol and water-ethanol having different concentration of solvent (methanol) varying from 30 to 70% (v/v) at five different temperatures ranging from 20° C to 40° C at regular interval of 5° C. The specific rate constant calculated using second order reaction was found decrease with increase of methanol and ethanol content, tabulated in Table-I the evaluated thermodynamic activation parameter has been enlisted in Table-II.

## III. RESULT AND DISCUSSION

### A. Solvent Effect on Specific Rate

In order to highlight the effect of the solvent on specific rate constant values of the reaction, the specific rate constant were calculated with help of second order reaction and calculated values is inserted in Table-I . From Tab-1 it is observed that the values of specific rate constant is decrease with increase of temperature which is quite in agreement with theory of Hughes and Ingold[4] and Singh A K[5]

TABLE I. HYDROLYSIS OF ETHYL-CINNAMATE SPECIFIC RATE CONSTANT [K X 10<sup>3</sup>(DM)<sup>3</sup>/MOLE/MINT] VALUES OF ALKALI CATALYZED IN WATER-METHANOL MEDIA

30%	40%	50%	60%	70%
15.66	11.22	10.00	8.12	6.45
20.89	16.59	13.48	10.59	8.49
27.54	21.87	16.98	13.64	10.83
38.01	30.19	23.17	18.62	14.62
45.70	36.30	27.86	22.38	17.74

### B. Solvent effect on Thermodynamic Activation Parameters of Reaction

For better study of solvent effect on thermodynamic activation parameters, such as Enthalpy of activation ( $\Delta H^*$ ), Free energy of activation ( $\Delta G^*$ ), and Entropy of activation ( $\Delta S^*$ ) were taken into account as they have great significance. These parameters are calculated using Wynne-jones[6] and Eyring equation have been recorded in Table-II

In order to highlight the effect of solvent on these activation parameters, the value of these parameters were

plotted against mole% of methanol which is shown in figure 1, 2 & 3.

From fig-2 and the value s of  $\Delta G^*$  recorded in Tab-II, obviously indicate that the variation in

$\Delta G^*$  is small and it increases from 94.98 to 97.19 kJ/mole at 30°C with change of proportion of methanol from 30% to 70% (v/v). The small but considerable increase in  $\Delta G^*$  and non linear variation in  $\Delta H^*$  &  $\Delta S^*$  curves with the increasing mole% as shown in figure-1 and fig-3 are indication of specific solvation taking place in process of activation as already proposed by Saville & Hudson [7], Tomilla et al. [8],

Esemongy [9] and Cleve [10] have also observe the similar increase in  $\Delta G^*$  values. Increase in  $\Delta G^*$  with simultaneous decrease in

$\Delta H^*$  &  $\Delta S^*$  values is only possible when extent (degree) of depletion in  $\Delta S^*$  value is greater than  $\Delta H^*$  values and from this, it may be inferred that alkali catalysed hydrolysis of ethyl cinnamate in water-methanol media act as Entropy inhibitor and Enthalpy stimulator solvent. Such inference have also recently been supported by recent view of Singh A K [11]

TABLE II. THERMODYNAMICS ACTIVATION PARAMETERS OF THE REACTION IN WATER- ACETONE MEDIA  $\Delta H^*$  AND  $\Delta G^*$  IN KJ/MOLE,  $\Delta S^*$  IN J/K/MOLE

% of MEOH	Mole %	$\Delta H^*$ in KJ/Mole	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%	16.03	53.31	93.64	137.64	94.27	137.44	94.98	137.52	95.60	137.30	96.31	137.38
40%	22.90	52.95	94.20	140.78	94.91	138.42	95.65	140.89	96.31	140.77	97.03	140.83
50%	30.82	52.87	94.68	142.6	95.44	140.30	96.23	143.10	96.96	143.14	97.75	143.38
60%	40.06	51.28	95.16	149.76	95.88	147.24	96.72	149.96	97.43	149.83	98.23	150.00
70%	50.97	50.51	95.64	154.02	96.39	151.44	97.19	154.05	97.96	152.56	98.77	154.18

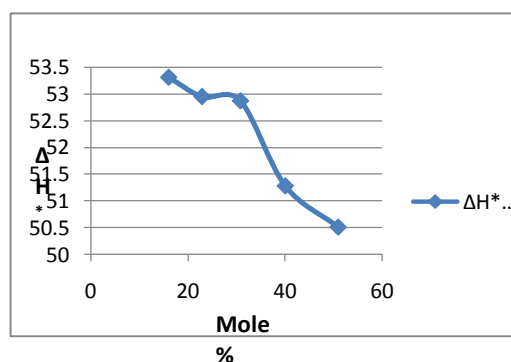


Figure 1. Variation of  $\Delta H^*$  with mole % at 20°C (water-methanol)

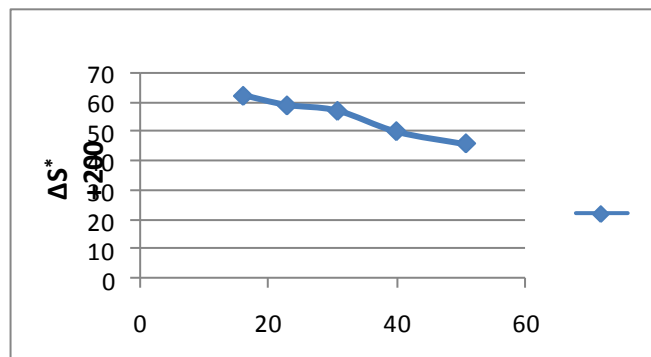


Figure 3. Variation of  $\Delta S^*$  with mole % at 20°C (water-methanol)

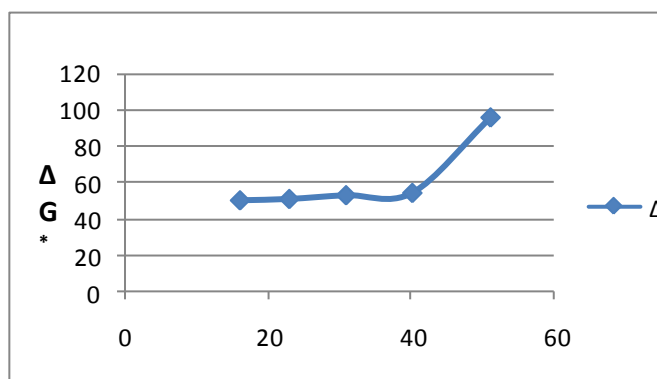


Figure 2. Variation of  $\Delta G^*$  with mole % at 20°C (water-methanol)

C. Evaluation of Iso-kinetic Temperature and Solvent-Solute Interaction

In the light of Barclay [12] and Butler relationship between Enthalpy and Entropy of Activation, which is as follows?

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

It is straight line equation representing the relationship between Enthalpy and Entropy of Activation.  $\beta$  is the Iso-kinetic temperature.

From the data available in the table II, the plot of  $\Delta H^*$  and  $\Delta S^*$  in both the solvent system in Fig. 4 and from the slope of straight line, the value of Iso-kinetic temperature was calculated to be 200 (water-Methanol) media.

From the value of Iso-kinetic temperature which is much less than 300, it is concluded that there is slow change in the structure of the reactant or in the solvent or in both due to weak interaction between solvent and solute present in both the reaction media in similar way as reported by Lefler [13]

Our this conclusion has been recently supported by Singh A K.[14]

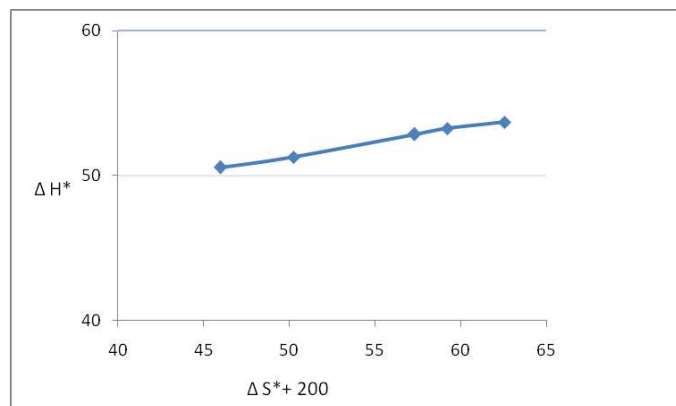


Figure 4. Variation of  $\Delta H^*$  with  $\Delta S^*$  at 25°C (water-methanol) system

#### IV. CONCLUSION

The result of this work indicate that the rate of hydrolysis of Ethyl cinnamate, decreasing trend at all temp with increasing mole% of co-solvent which appear that transition state is more desolvated than initial state. The enhancement in the value of and  $\Delta G^*$  with simultaneous decrease in  $\Delta H^*$  &  $\Delta S^*$  for the hydrolysis ethyl cinnamate in water- Methanol is enthalpy dominating and Enthalpy control. The Values of Iso-kinetic which is less than 300, clearly indicates that there is no appreciable interaction between solvent and solute present in the reaction media, i.e. reaction is not ion-dipole but ion-molecule type.

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**Dr. A. K. Singh** is working as Asst. Professor of Chemistry in College of Engineering of Teethankar Mahaveer University, Moradabad, India since 2010. He holds Master of Science in Physical Chemistry, awarded in 1989, from Magadh University, Gaya followed by Doctor of Philosophy (Ph.D.) in Kinetic Solvent Effect, awarded in 2009 from VKS University Ara, India. He has studied different solvation capacity of different reaction media (e.g. Water-DMSO, Water-DMF, Water-Aceton. Water-Methanol etc) on the Specific Rate Constant value of the Reaction, the Iso- Composition, Iso- Dielectric Activation Energy, the Number of Water and Solvent Molecules Associated the Activated complex of the Reaction in order to decide the Nature of Mechanistic path of the Reaction, Thermodynamic Activation Parameter of the Reaction, the value of Iso Kinetic Temp on the Reaction in order to Explore the Idea of Solvent-Solute Interaction in More Media. He has published seventeen research articles in his credits.



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