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

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Abstract

The solvent effect of ethanol on the alkali catalyzed solvolysis reaction was studied by carring out of the hydrolysis of ester namely ethyl cinnamate in water-methanol media of varying composition consisting of 30 to 70% of methanol (v/v) at different Temperature ranging from 20°c to 70°c. The Specific rate constant values of the reaction were found to depleted with increasing concentration of methanol in reaction media. Enhancement in ΔG^* with simultaneous depletion in ΔH^* and ΔS^* of the reaction, it has been concluded that reaction is enthalpy stimulating and entropy inhibiting and specific salvation take place in water methanol media. From the evaluated value of Iso kinetic temperature, which is less than 300 indicates that this reaction in water-methanol media obey Barclay-Butler rule and there is weak but considerable solvent-solute interaction taking place in reaction media.

Keywords: Solvent effect; Solvent-solute interaction; Iso-kinetic temperature; Specific salvation; Ethyl cinnamate; Base catalyzed; Activation parameter

Introduction

Study of solvent effect of protic and aprotic solvent on the reaction such as hydrolysis of ester and amide have been carried out by numbers of workers but explanation put forward are not quite satisfactory particularly solvolysis of Ethyl Cinamate which is important for medicinal use as well as flavoring agent in cut tobacco [1-3]. There for kinetic study of the solvent effect on the base catalyzed hydrolysis Ethyl Cennamate in water-methanol media of various compositions are needed to investigate which has not studies so far.

Experimental

The hydrolysis of ethyl cinnamate has been carried out volumetric in water-methanol having different concentration of solvent (methanol) varying from 30 to 70% (v/v) at five different temperatures ranging from 20°C to 40°C. The reaction was found to follow second order kinetics equation and evaluated value of specific rate constant has tabulated in TABLE 1 the evaluated thermodynamic activation parameter has been enlisted in TABLE 2.

Result and Discussion

Solvent Effect on Rate of reaction

The specific rate constant was calculated with help of second order kinetics and calculated values is inserted in TABLE. 1 From TABLE. 1 it is observed that the values of specific rate constant are decrease with increase of temperature which is quite in agreement with theory of Hughes and Ingold [4] and Singh AK [5].

TABLE 1. **Hydrolysis of Ethyl-Cinnamate Specific rate constant [k $\times$ 10^3(dm)3/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

Effect of salvation power of reaction media on thermodynamic activation parameters of reaction

It is a great significance to study of solvent effect on thermodynamic activation parameters, such as Enthalpy of activation (ΔH^*), Free energy of activation (ΔG^*), and Entropy of activation (ΔS^*). These parameters are calculated using Wynne-jones [6] and Eyring equation have been recorded in TABLE 2.

To explain the effect of solvent on these activation parameters, the value of these parameters was plotted against mole% at 300c of methanol which is shown in FIG. 1, FIG. 2 and FIG. 3.

From FIG. 2 and the value s of ΔG^* recorded in TABLE. 2, obviously indicate that the variation in ΔG^* 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 ΔG^* and nonlinear variation in ΔH^* and $\square\Delta S^*$ curves with the increasing mole% as shown in FIG. 1 and FIG. 3 are indication of specific salvation 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 ΔG^* values. Increase in ΔG^* with simultaneous decrease in ΔH^* and $\square\Delta S^*$ values are only possible when extent (degree) of depletion in ΔS^* value is greater than ΔH^* values and from this, it may be inferred that alkali catalyzed hydrolysis of ethyl cinnamate in water-methanol media act as Entropy inhibitor and Enthalpy stimulator solvent. Such inference has also recently been supported by recent view of Singh AK [11].

TABLE 2. **Thermodynamics activation parameters of the reaction in water- acetone media ΔH* and ΔG* in KJ/Mole, ΔS* in J/K/Mole.**

| % of MEOH	Mole %	ΔH* in Kj/Mole	20˚C		25˚C		30˚C		35˚C		40˚C	
			ΔG*	-ΔS*	ΔG*	-ΔS*	ΔG*	-ΔS*	ΔG*	-ΔS*	ΔG*	-ΔS*
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

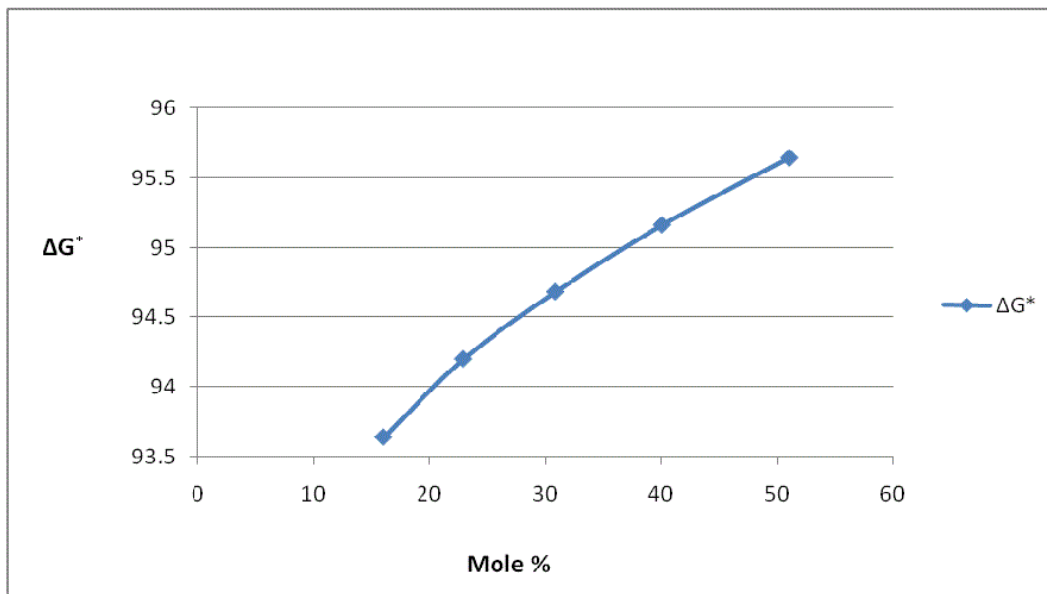FIG. 1. **Variation of ΔH* with mole % at 200c (water-methanol).**

3
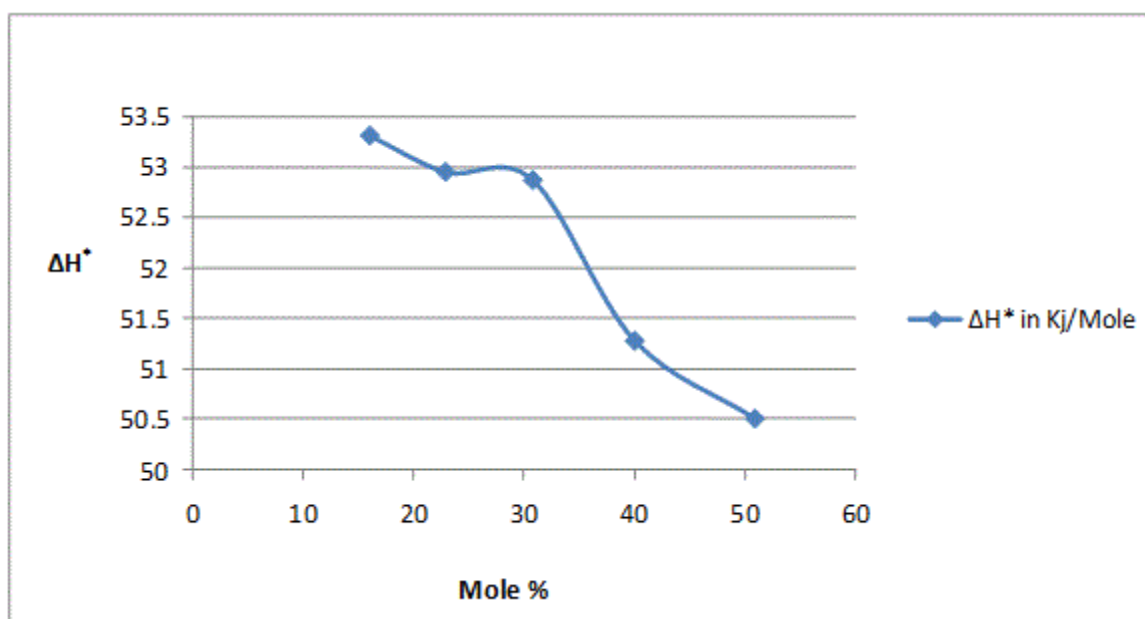
FIG. 2. **Variation of ΔG* with mole % at 300c (water-methanol).**
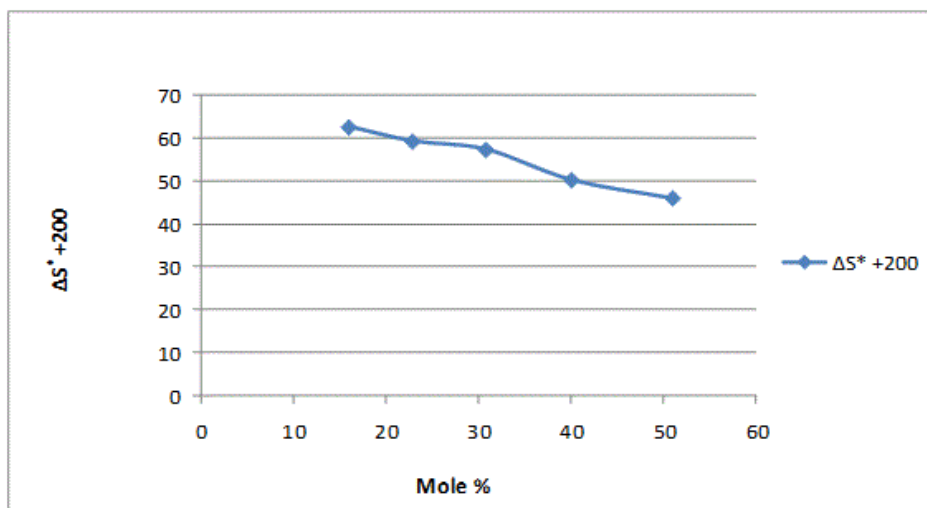

FIG. 3. **Variation of ΔS*+200 with mole % at 300c (water-methanol).**

Barclay and Butler relationship and Solvent-Solute Interaction

Barclay and Butler relationship between Enthalpy and Entropy of Activation, which is as follows [12].

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

This reaction is found to follow the above Barclay and Butler relation where β represent iso kinetic temperature. It is also known as Leffer-Grunwald solvent stabilizer operator. From the value of slope of plot (FIG. 3), the value of iso kinetic

4

temperature was evaluated which come to less than 300 (FIG. 4). (200 aprox), it shows that change in structure of reactant or solvent is due to weak interaction between solvent and solute in similar way as reported by Leffer [12] and recently supported by Singh AK [13].
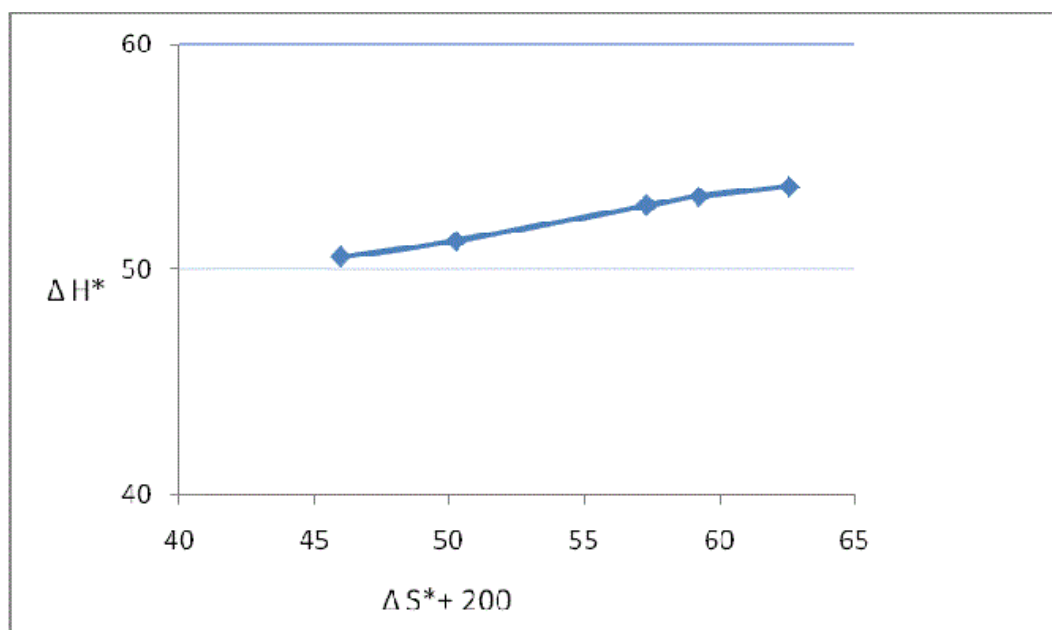

FIG. 4. **Variation of ΔH* with ΔS* at 300C (water-methanol) system.**

Conclusion

In this research work, namely hydrolysis of cinnamate ester the specific rate constant show decreasing trend at all specify temperature indicate that transition state is more desolveted than initial state. The increase in the value of and ΔG^* with simultaneous decrease in ΔH^* & ΔS^* 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.

Acknowledgement

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