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Kinetic Study of Aquo-Ethylene Glycol on Alkali Catalyzed Hydrolysis of Heterocyclic Acid Ester Methylpicolinate and Thermodynamic Activation Parameters

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Abstract: A kinetic investigation was conducted to analyze the thermodynamic parameters of the hydrolysis of Methylpicolinate in water-Ethylene glycol solvent system, using different concentration of Ethylene glycol (v/V) at four different temperature 20^0C, 25^0C, 30^0C, and 35^0C. The influence of the solvent on the reaction rate was analyzed in terms of activation parameters. The decreasing trend in ΔH* and ΔS* values, coupled with the rising ΔG* with increasing concentration (mole %) of the organic co - solvent in the reaction media, inferred an enthalpy-dominated and entropy-controlled reaction. The evaluated value of Iso-kinetic temperature is very close to 300, suggesting the presence of weak but positive interaction between solvent and solute present in the reaction media.

Keywords: Methylpicolinate, aquo-Ethylene Glycol solvent, specific rate constant, thermodynamic parameters, iso-kinetic temperature.

I. INTRODUCTION

Solvents play a crucial role in determining chemical reactivity. Any change in solvent strength directly influences the rate of reaction. The effect of solvents is most commonly rationalized in terms of solvent polarity across different solvent media, which accounts for the combined influence of solvent-solute interactions, both specific and nonspecific solvation, as well as the dielectric properties of various solvent systems. Numerous researchers [1-7] have explored this rationalization with varying degrees of success. However, further research is needed to understand how the thermodynamic properties of aqueous binary solvent systems influence kinetic parameters and how activation parameters correlate with the physical properties of solvents.

To address these aspects, a kinetic study has been proposed to examine the solvent effect of ethylene glycol on the alkali-catalyzed hydrolysis of methyl picolinate, providing deeper insights into the role of solvent composition in reaction rate and mechanisms.

II. EXPERIMENTAL

Purified and high quality grade Ethylene Glycol and export quality of ester Methylpicolinate grade of high degree were used in this process. Double distilled water was used to prepare required solution. N/5 strength of NaOH was prepared in measuring flask. Aquo-Ethylene Glycol solvent was prepared varying in compositions from 10% to 60% (v/V). 8ml of solvent aquo-Ethylene Glycol (any one composition) was taken in a glass test tube and then mixed with 1ml of NaOH solution. The solution was kept in thermostat and then 1ml of ester Methylpicolinate was added to it. Then conductivity was recorded using conductivity meter. Reading was taken at regular interval of time. The process was done at different temperature 20^0C, 25^0C, 30^0C and 35^0C with all composition of solvent. Using second order kinetics, specific rate constant was calculated and tabulated in Table-1. Thermodynamic activation parameters, Enthalpy of Activation, Entropy of Activation and Free Energy of Activation were calculated with Wynne-Jones and Eyring equation [8] and tabulated in Table-3.

III. RESULT AND DISCUSSION

A. Effect of Solvent on Specific Rate Constant

To emphasize the relationship between specific rate constant and organic co-solvent, the logk values were plotted against the mole % of the organic co-solvent mentioned in Table-2 and shown in Fig.-1.

Plotted data shows a decreasing trend in the rate of the reaction with addition of Ethylene glycol to the reaction medium.

The decline in reaction rate can be attributed to the following factors:

1) Decrease in dielectric constant of the medium due to addition of bulky organic co-solvent.
2) Introduction of less polar solvent Ethylene glycol (lower polarity than water) that affects the solvation of transition state, leading to decrease in reaction rate.

These observations are in agreement with the theory proposed by Hughes and Ingold [9] which suggests that a reduction in dielectric constant and polarity of the reaction medium leads to a slower reaction rate. Recently such observation was also supported by A. K. Singh [10].

Table-1

Specific rate constant K values of alkali, catalyzed hydrolysis of Methylpicolinate in aquo - ethylene glycol system;

Temp. in ^{0}C	% of Ethylene glycol					
	10%	20%	30%	40%	50%	60%
20^0C	30.61	29.51	28.18	27.54	26.30	25.70
25^0C	36.30	34.197	31.91	30.19	28.18	26.91
30^0C	41.68	38.90	35.48	32.658	29.71	27.54
35^0C	49.20	44.87	40.17	35.97	31.62	28.84

Table- 2

Variation of logk value of the reaction with mole % of Ethylene Glycol in aquo-Ethylene Glycol media at different temperature;

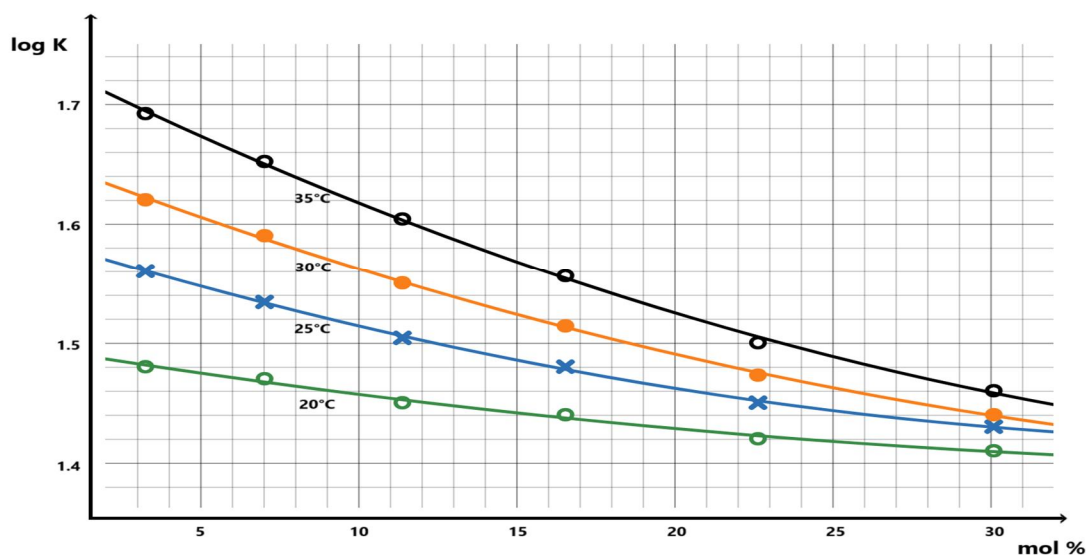| % of Ethylene glycol (v/V)	Mole % of Ethylene glycol	log k			
		20^0C	25^0C	30^0C	35^0C
10%	3.27	1.48	1.56	1.62	1.692
20%	7.04	1.47	1.534	1.59	1.652
30%	11.40	1.45	1.504	1.55	1.604
40%	16.56	1.44	1.48	1.514	1.556
50%	22.65	1.42	1.45	1.473	1.50
60%	30.11	1.41	1.43	1.44	1.46

Fig. 1: Variation of logk value with mole % of Ethylene Glycol in water ethylene glycol media.

B. Effect of solvent on thermodynamic activation parameters

The thermodynamic activation parameters play a crucial role in understanding the properties of the activated complex and the solvating power of the medium.

To gain a comprehensive understanding of the kinetic and solvent effect, the thermodynamic activation parameters, Free Energy of activation (ΔG^*), Enthalpy of activation (ΔH^*), and Entropy of activation (ΔS^*) were analyzed. These parameters were determined using the Wynne-Jones and Eyring equations [8] and are presented in Table-3.

Table 3

Evaluated values of thermodynamic activation parameter (ΔH^* ΔG^* and ΔS^*) of the base catalyzed hydrolysis of Methylpicolinate in aquo - Ethylene glycol media at different mole percentage of Ethylene glycol and different temperatures.

ΔH^* and ΔG^* in KJ/mole, ΔS^* in J/K/mole

% of Ethylene glycol (v/V)	Mole % of Ethylene glycol	ΔH^* in KJ/mole	20^0C		25^0C		30^0C		35^0C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
10%	3.27	20.67	63.39	-145.80	64.08	-145.70	64.85	-145.83	65.54	-145.69
20%	7.04	17.99	63.472	-155.23	64.23	-155.19	65.03	-155.25	65.78	-155.16
30%	11.40	14.74	63.20	-166.72	64.42	-166.71	65.26	-166.74	66.06	-166.64
40%	16.56	10.41	63.39	-181.67	64.54	-181.66	65.47	-181.72	66.34	-181.60
50%	22.65	6.47	63.751	-195.50	64.71	-195.45	65.70	-195.51	66.67	-195.47
60%	30.11	2.99	63.81	-207.58	64.83	-207.52	65.90	-207.62	66.91	-207.54

To better illustrate the variations in these thermodynamic parameters, ΔG^*, ΔH^*, and ΔS^* were plotted against the mole percentage of Ethylene glycol, as depicted in Fig. 2, 3, and 4 respectively. All these three plots follow nonlinear variation and it is indicative of specific solvation taking place in reaction media (water-Ethylene glycol) as proposed by Elsemongy et al.[11] and Saville & Hudson[12] and recently supported by Singh AK[13].
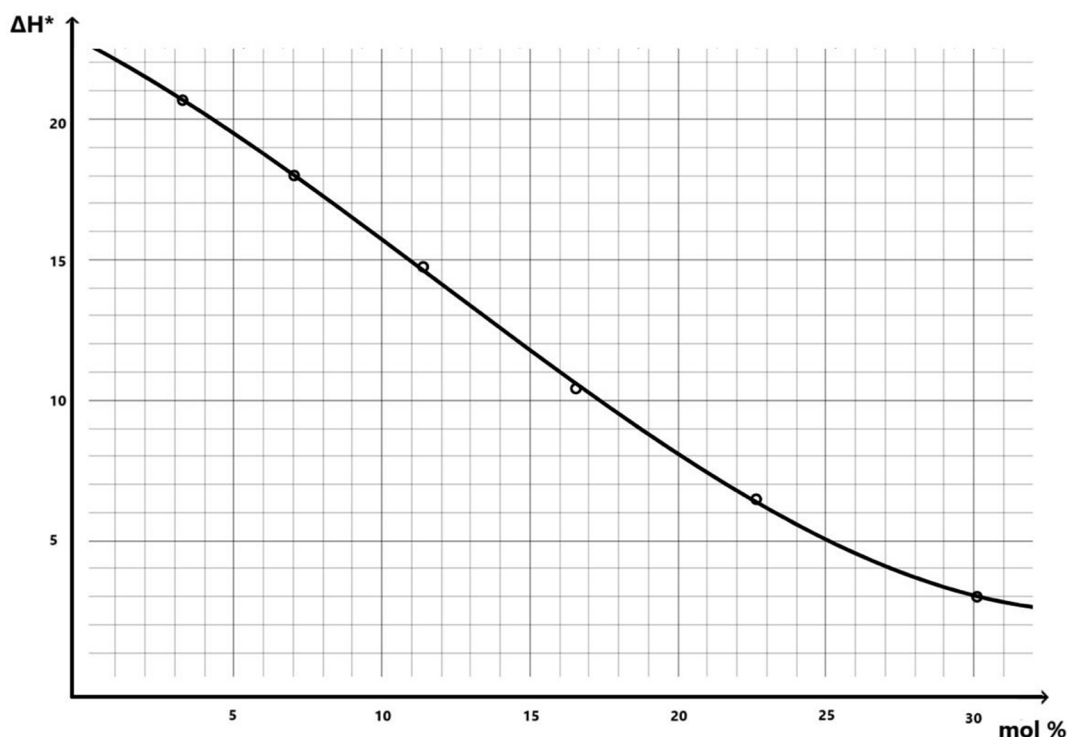

Fig.-2: Variation of values of ΔH^* with mole% of Ethylene Glycol in aquo-Ethylene glycol media
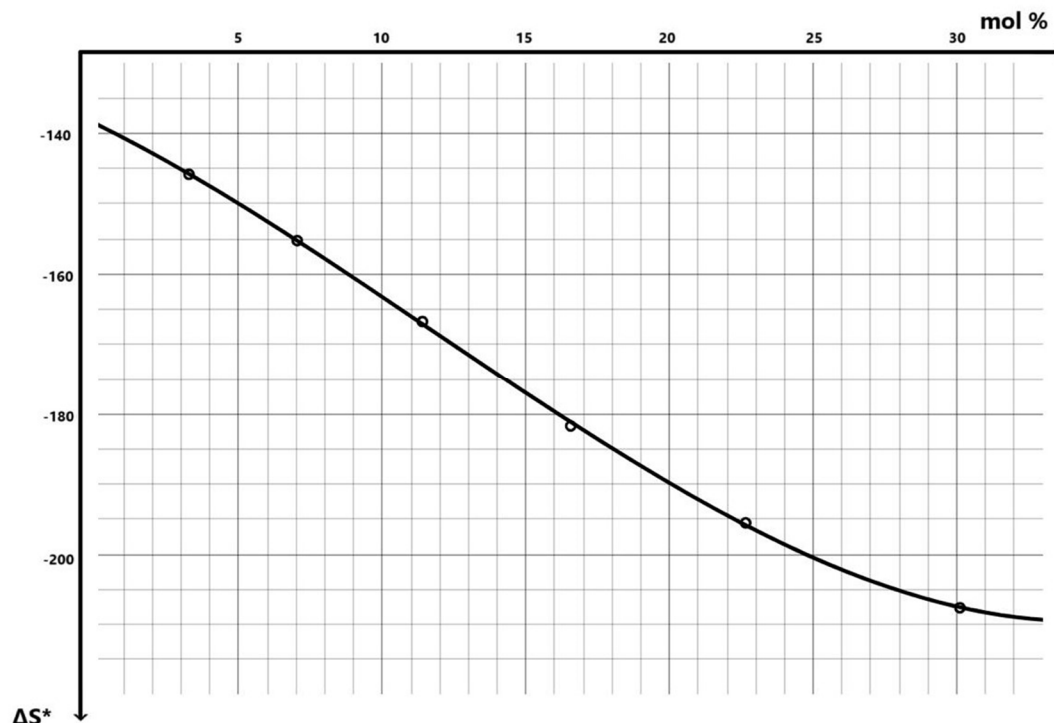
Fig. 3: Variation of values of ΔS^* values with mole% of Ethylene Glycol in aquo-Ethylene glycol media
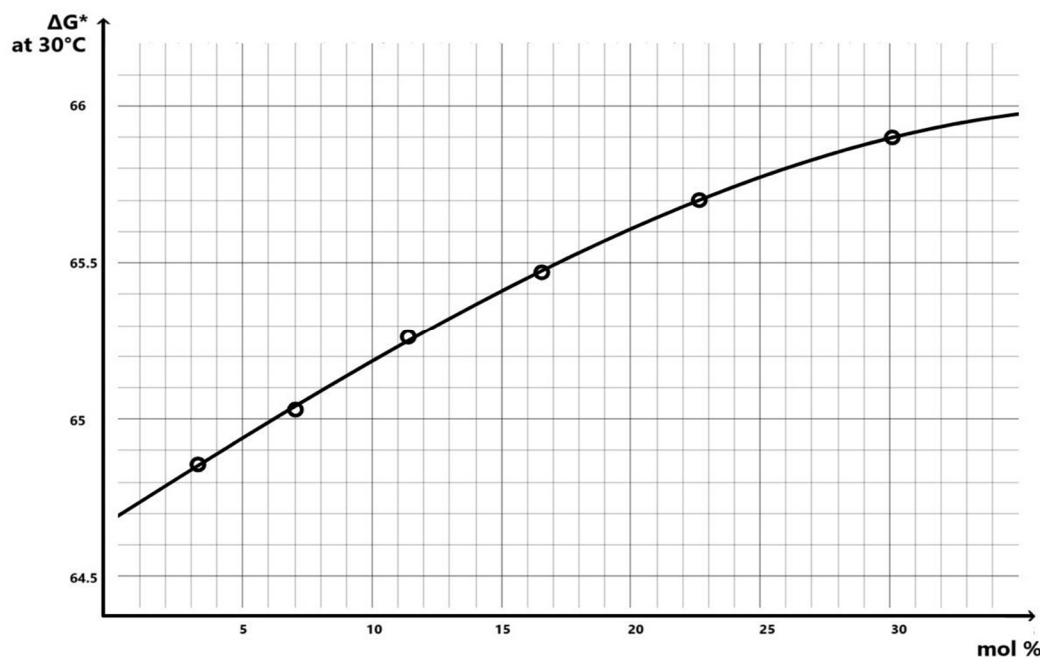

Fig. 4: Variation of values of ΔG^* values with mole% of Ethylene Glycol in aquo-Ethylene glycol media

From Table-3, it is interestingly observed that out of all the three thermodynamic parameter of the reaction namely ΔG^*, ΔH^* and ΔS^* only ΔH^* and ΔS^* are found to decrease with increase in mole% of the organic component of the reaction media. Based on the thermodynamic relation:

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

It can be inferred that the simultaneous rise in ΔG^* alongside the decline in ΔH^* and ΔS^* is only feasible if the reduction in ΔS^* is more pronounced than that of ΔH^*.

The regular depletion to the great extant in ΔS^* values in comparison to that of ΔH^* values clearly indicate that alkali catalyzed hydrolysis of Methylpicolinate in water-Ethylene glycol media is Enthalpy promoting and Entropy deactivating.

The similar nonlinear variation in ΔG^*, ΔH^* and ΔS^* values with increase in mole% of the organic co-solvent (Ethylene Glycol) in reaction media have also been reported by Tommila et al.[14] and Hyne et al.[15] and recently by Singh et.al.[16].

C. Iso-kinetic temperature and solvent solute interaction

The slope of plots ΔH^* against ΔS^* shown in Fig.-5, give the value of iso-kinetic temperature (β) in the light of relation proposed by Barclay and Butler [17].

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

The slope of the straight line was found to less than 300 ($286K/mole^2$) conclude that there is slight weak but position solvent-solute interaction in the reaction media.

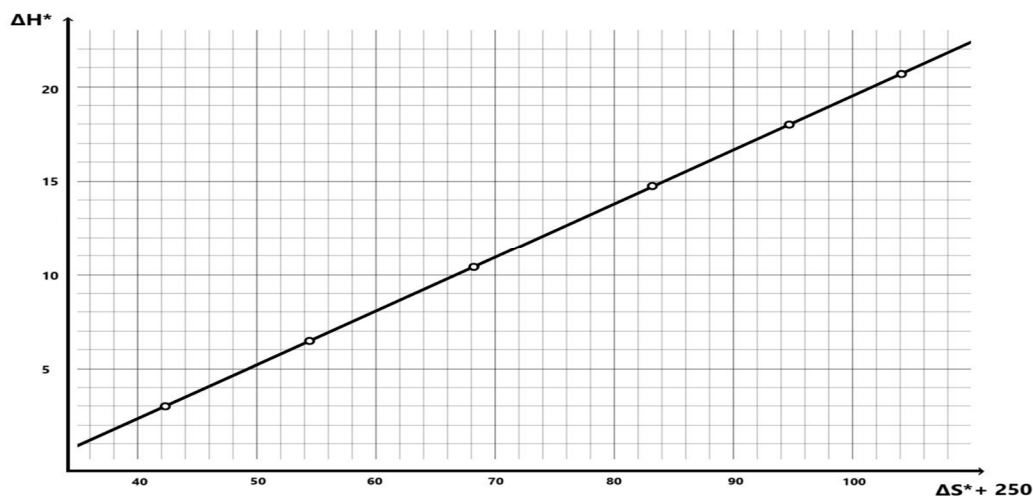This conclusion is earlier supported by Lefler [18] and recently by Singh RT et al. [19].

Fig. 5: Plots of ΔH^* values against ΔS^* values in aquo-Ethylene Glycol media

IV. CONCLUSION

Based on the analysis of the results, the following findings have been observed:

1) The specific rate constant values exhibit a decreasing trend with an increasing proportion of the co-solvent across all temperatures.
2) The nonlinear plots of ΔG^*, ΔH^*, and ΔS^* against the mole percentage of the solvent suggest the occurrence of specific solvation in the reaction medium.
3) The simultaneous decrease in ΔH^* and ΔS^* values, along with an increase in ΔG^*, indicates that the reaction is enthalpy-stimulated and entropy-inhibited.
4) The iso-kinetic temperature, though slightly below 300, suggests significant interactions between the solvent and solute within the reaction medium.

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