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Solvolysis Rate and Activation Parameter of Ethyl Acetate in mixed Dipolar Organic Solvent Systems – A Solvent Effect

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Abstract: ***The rate of alkaline hydrolysis of ethyl acetate were measured over the temperature range of 20° C to 40 ° C in water-methanol and water-ethanol mixture at different composition 30 to 70% (v/v). The influence of solvent variation on reaction rate was examined in term of changes in the Activation parameter. Depletion of ΔH^* and ΔS^* value with simultaneous increase in ΔG^* of the reaction in both 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.
Key Word: Activation Parameter, 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][4], 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 acetate which is important for medicinal use. It has been proposed to make a kinetic study of the solvent effect on the base catalyzed hydrolysis ethyl acetate in water-ethanol media of various compositions.

II. EXPERIMENTAL

The kinetics of base catalyzed hydrolysis of ethyl acetate has been carried out in water-methanol and water-ethanol having different concentration of solvent (ET-OH and ME-OH), varying from 30 to 70% (v/v) at five different temperature 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 and Table-II.
The evaluated thermodynamic activation parameter has been tabulated in Table-III and Table-IV.

III. RESULT AND DISCUSSION

The thermodynamics Activation parameter such as Enthalpy of Activation (ΔH^*), Entropy of Activation (ΔS^*) and free energy of Activation (ΔG^*), are better indicator of the solvent effect exerted by the solvent on the solvolysis reaction. These thermodynamics Activation parameter has been calculated with help of Wyne-Jones Eyring[5] equation and absolute rate theory.

On careful observation of the data Tabulated in table III (water-Ethanol) and table IV (water-methanol), ΔG^* value in case of water-Ethanol increases from 90.382 to 93.02 KJ/mole and 89.19 to 92.24 KJ/mole 3respectively with change of proportion of solvents from 20% to 70% at 20° C. Though the enhancement is not large, however it is quite considerable.
The report of Yagil and Anbar[6] indicate that OH^- ion of NaOH is hydrated with three molecules of water. In mixed aquo-organic co-solvent mixture, the organic component molecules are expected to contribute to the process of desolvation as they may be regarded as poor anion solvater in comparison to water. A similar variation in ΔG^* value with increasing mole % of organic co solvent has been reported by Tommila[7] and Cleave [8]
The variation of ΔG^* with mole% in both the solvent are non-linear and increase smoothly with gradual addition of both the solvent (Fig. 1 and Fig. 2). This finding is indicative of salvation or desolvation of reactant as explained by Absolute Reaction rate theory [9] and supported by Elsemongy[10] and Singh R. T. et al[11].
Moreover, as shown in Fig 1, 2, 3, 4 and 5, the non-linear curve of ΔH^*, ΔG^*, and ΔS^* with mole% in both the solvent (Et-OH and Me-OH) gives information of the fact that specific solvation is taking place in both the water-solvent mixture, as already reported by Saville and Hundson[12] and it also indicate that random distribution of the component are not acceptable. The similar non-linear variation of ΔH^*, ΔG^*, and ΔS^* value with increasing mole% of the organic component of the reaction media have also been

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reported by Tommila et. al.[13], Hyne.[14] and recently .Singh R T et al[15].

From data mention in the table III and table IV, the interesting feature comes in the light is that out of all the value of three thermodynamic parameter ΔH^*, ΔG^*, and ΔS^*, the value of ΔH^* and ΔS^* goes on decreasing with simultaneous increase in ΔG^* values with increasing proportion of Et-OH and Me-OH at all the temperature of the reaction, i.e. from 20^o C to 40^o C.

From the fundamental thermodynamic equation

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

it may be inferred that the enhancement in the value of ΔG^* with simultaneous depletion in ΔH^* and ΔS^* value is only possible when the quantitative depletion in the value of ΔH^* is less than that found in the values of ΔS^* and from this fact, it is concluded that base catalysed hydrolysis of Ethyl Acetate in water-methanol and water-ethanol media is Enthalpy dominating and Entropy controlled.

In another word, it may also be inferred that in presence of Me-OH and Et-OH in the reaction media activate the Enthalpy and control over the Entropy of the reaction.

The change found in the value of three thermodynamic Activation parameter also support the fact that initial state of the reaction is desolvated and the transition state in the similar ways as recently reported by Singh R T et al. [16].

Evaluation of Iso-kinetic Temperature and Solvent-Solute Interaction:

In the light of Barclay[17] 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. β is the Iso-kinetic temperature.

From the data available in the table III and IV, the plot of ΔH^* and ΔS^* 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 244 (water-EtOH) and 141.99 (water-MeOH) which is less than 300.

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[18]. Our this conclusion has been recently supported by Kumari Madhu et al.[19].

Table - I

Specific rate constant[k x10^3(dm)^3/mole/mint]values of alkali catalysed Hydrolysis of ethyl-acetate in water-ME-OH media

Temp in ^{O}C	% of ME-OH				
	30%	40%	50%	60%	70%
20^{O}C	40.27	30.19	23.44	18.40	14.79
25^{O}C	58.88	44.66	34.67	26.85	21.13
30^{O}C	89.12	69.98	52.36	41.20	33.11
35^{O}C	133.35	112.20	79.43	62.95	50.11
40^{0}C	199.06	151.35	117.48	91.20	73.28

Table - II

Specific rate constant values (k x10^3) in (dm)^3/mole/mint in water-ET-OH media

Temp in ^{O}C	% of ET-OH				
	30%	40%	50%	60%	70%
20^{O}C	31.62	25.11	18.62	14.28	10.71
30^{O}C	56.23	45.18	33.11	25.70	18.19
35^{O}C	75.85	58.88	43.65	33.11	23.98
40^{0}C	97.72	77.62	57.54	40.73	31.62

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Table-III

Thermodynamics Activation Parameters of the Reaction in Water- Me-OH Media ΔH^* and ΔG^* in KJ/Mole, ΔS^* in J/K/Mole.

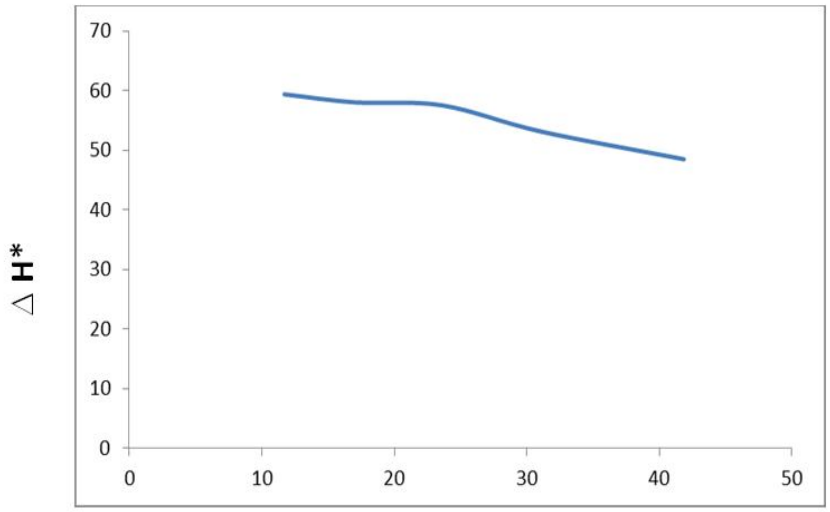
% of Me-OH	Mole %	ΔH^* in Kj/Mole	20^0C		25^0C		30^0C		35^0C		40^0C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
30%	16.03	65.15	89.82	84.19	90.43	84.83	90.96	85.18	91.42	85.29	91.92	85.52
40%	22.90	62.75	90.49	94.67	91.12	94.20	91.57	95.11	91.87	96.78	92.64	95.49
50%	30.82	62.06	91.06	98.97	91.80	99.78	92.30	99.80	92.75	99.64	93.30	99.80
60%	40.06	61.84	91.70	101.91	92.38	102.48	92.91	102.54	93.35	102.30	93.96	102.61
70%	50.97	61.15	92.24	106.10	92.98	106.81	93.52	106.83	93.94	106.46	94.53	106.64

Table-IV

Thermodynamics Activation Parameters of the Reaction in Water- Et-OH Media ΔH^* and ΔG^* in KJ/Mole, ΔS^* in J/K/Mole.

% of Et-OH	Mole %	ΔH^* in Kj/Mole	20^0C		30^0C		35^0C		40^0C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
30%	11.69	59.38	90.38	105.80	91.37	108.05	92.87	108.73	93.78	109.90
40%	17.07	58.03	90.94	112.32	92.68	114.35	93.52	115.22	94.90	117.79
50%	23.59	57.54	91.67	116.48	93.46	118.54	94.29	119.31	95.16	120.19
60%	31.06	53.15	92.32	133.68	94.10	135.14	94.94	135.68	95.88	136.51
70%	41.87	48.49	93.02	151.97	94.80	152.83	95.63	153.05	96.73	154.12

Fig. 1



Variation of ΔH^* with mole % (in water Et-OH Media)

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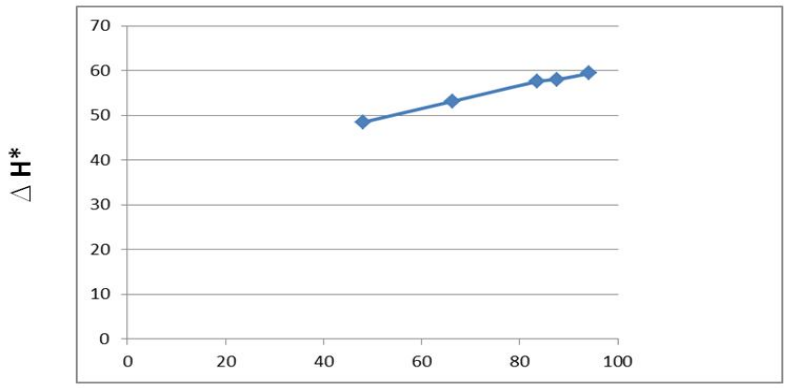
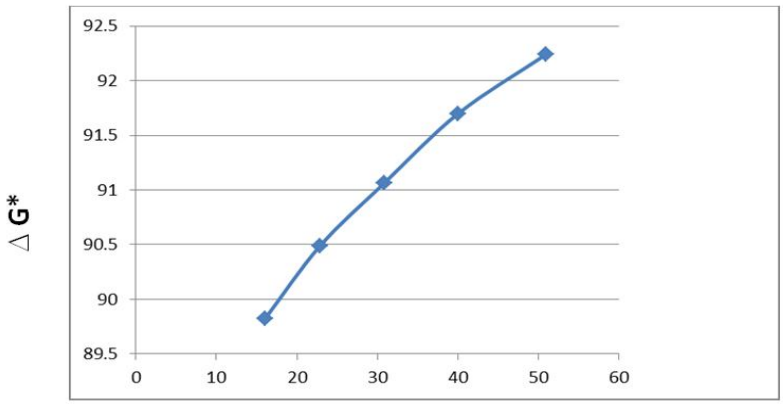
Fig. 2



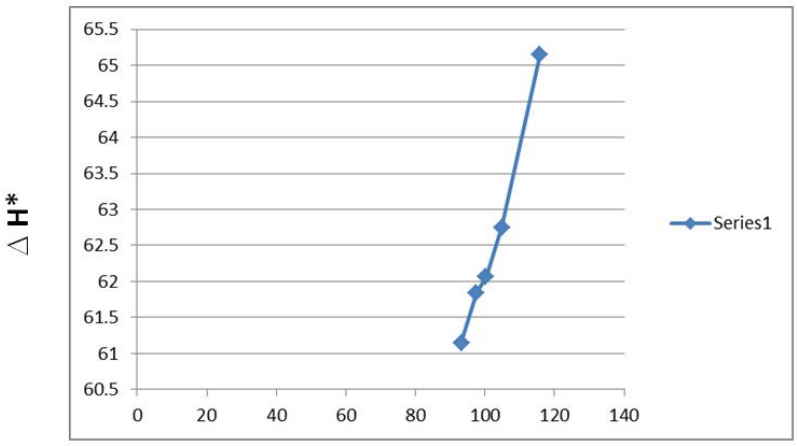
Variation of ΔH^* with ΔS^* +200 (in water Et-OH Media)

Fig. 3



Variation of ΔG^* with mole% (in water Me-OH Media)

Fig. 4



Variation of ΔH^* with ΔS^*+200 (in water Me-OH Media)

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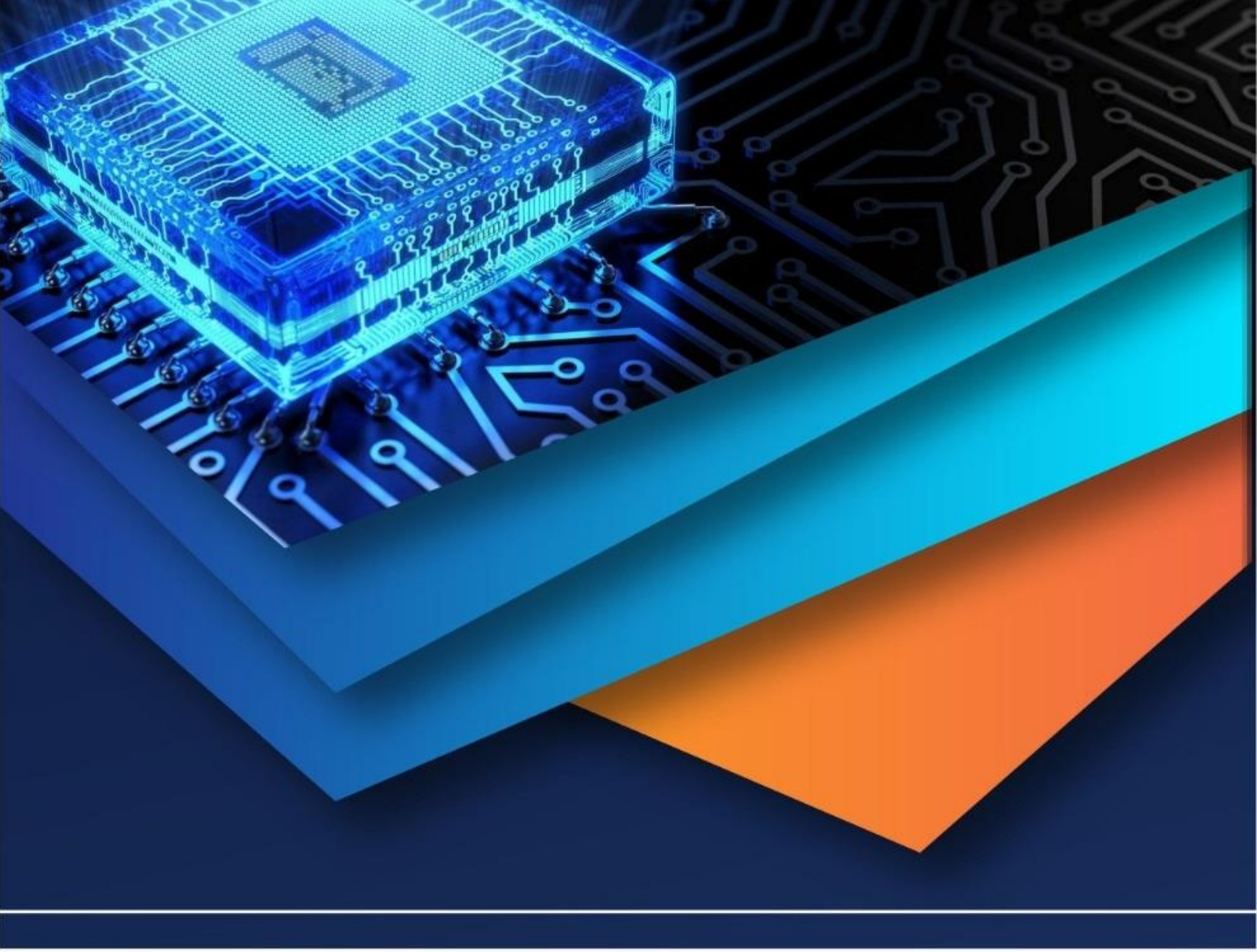

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