

Activation Parameter and Solvent Effect on Solvolysis of Ethyl Benzoate in Aquo-Organic Solvent System.

A.K. Singh

Department of chemistry (CCSIT) Teerthanker Mahaveer University, Moradabad, India

anilkumar2_singh@yahoo.com

Abstract

The rate of solvolysis of ethyl benzoate was estimated volumetrically over the temperature range of 20⁰c to 40⁰c.in water-methanol mixture at different composition. The depletion and enhancement in value of iso-composition activation energy and iso- dielectric activation shows solvation in transition state and de-solvation in initial state respectively. The effect of solvent on reaction rate was tested in term of activation parameter. Simultaneous decrease in values of ΔH^* and ΔS^* with increase in value of ΔG^* with solvent composition show that the reaction is Enthalpy domination and Entropy controlled. There is weak interaction between solvent and solute because the values of iso-kinetic temperature are less than 300 K/Mole²

Keyword: Ethyl benzoate, water-methanol Activation parameter, Solvent effect, solvent-solute interaction, Iso-kinetic temperature, specific and nonspecific solvation. Solvation in initial and transition state. Barclay-Butler rule.

Introduction

Solvent effect is most rationalized term of solvent polarity in different solvent media which attribute the sum of solvent- solute interaction, specific and nonspecific solvation and its dielectric behavior of different solvent system. Many workers [1-6] have published recently on the rationalized of solvent effect in different solvent system which some time fails and sometime succeeds. To make for further research how for the thermodynamic properties of aqueous solvent binary system are reflected in the kinetic parameter and also understand the behavior of the activation parameter in terms of the physical properties of solvents, I report the outcome of hydrolysis of ethyl benzoate in water-methanol solvent system which acts an effective use in alcoholic beverage and that can be used as medicine for treatment of skin and eye problem

Experimental

The base catalyzed hydrolysis of ethyl benzoate was estimated volumetrically in water-methanol solvent system at different degree of composition from 30 to 70% (v/v), ranging from 20° C to 40 ° at regular interval of 5° C. Pure ethyl benzoate (Merck) was used for kinetics. Distilled water is used throughout and the experiment is carried out by keeping strength of solution 0.1M with respect to NaOH and 0.05M with respect to ester the detail of procedure was mention in my previous communication [7]. Using second order kinetics, specific rate constant was calculated and inserted in Table-1.

Enthalpy of Activation, Entropy of Activation and Free Energy Activation is calculated with Wynne-Jones and Eyring equation [8] and tabulated in Table-2

Result and Discussion

(A) Effect of solvent composition on rate:

The kinetic result of hydrolysis of ethyl benzoate in water-methanol solvent system follow second order kinetic and calculated values is inserted in Table-1. The specific rate constant values decrease with increasing

temperature may be attributed partly due to dielectric effect of reaction media and partly due to solvation taking place in media which is good agreement with Hughes and Ingold [9]. and recent publication of A K Singh [10]

Table – I Rate constant as function of solvent medium composition

Temp in °C	% of Methanol				
	30%	40%	50%	60%	70%
20°C	37.15	30.54	25.70	21.87	18.62
25°C	74.13	57.54	48.97	41.68	35.48
30°C	147.91	112.20	88.10	74.13	64.56
35°C	278.61	211.34	165.95	136.45	112.20
40°C	543.25	316.22	301.99	245.47	199.52

$k \times 10^2$ (dm³/mole/mint] values of hydrolysis of Ethyl benzoate in water-methanol media

(B) Observed values of Iso-composition Activation Energy (E_D) of the reaction in water-methanol media. The iso composition activation energy is calculated with Arrhenius plot which decreases with increasing solvent composition, inferred solvation in transition state and desolvation in initial state which is supported recently by Singh A K [11]

(C) Calculated values of Iso- Dielectric Activation Energy.

The value of Iso-dielectric Activation energy (E_D) is calculated by plotting Arrhenius plot of $\log k_D$ values against $1/T$. Iso-dielectric Activation energy (E_D) values goes on increasing from 109.95 to 120.12 kJ/mole with increasing dielectric value in reaction media. This is also supported by past view of Wolford [12] recently supported by Singh R T. et al. [13]

(D) Rate and thermodynamic activation Parameters of reaction

The thermodynamic activation parameter plays an important role in determining properties of activated complex and solvating power of medium. The activation parameter (ΔG^\ddagger), ΔH^\ddagger & ΔS^\ddagger is calculated with help of Wynne-jones and Eyring equation [14] and inserted in Table-2. The nonlinear increase in (ΔG^\ddagger) and decrease in (ΔH^\ddagger) and (ΔS^\ddagger) with mole % fig-1,2 and 3 represent the specific solvation taking place in process of solvation already proposed by Saville & Hudson [15]. The non-linearity in (ΔG^\ddagger) with mole % curve in water-methanol media also indicate that random distribution of component is not acceptable. The noted data in Table-2 it is observed that Free energy of activation (ΔG^\ddagger) increases with simultaneous decrease in enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) with mole%.

According to thermodynamic relation of free energy and entropy

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

On the basis of above thermodynamic relation it is clear that increase in ΔG^\ddagger with simultaneous decrease in ΔH^\ddagger and ΔS^\ddagger possible only when extent of depletion in ΔS^\ddagger is greater than ΔH^\ddagger . The regular decrease in these

activation parameters that is entropy of activation and enthalpy of activation also indicate that the reaction is enthalpy dominating and entropy control which also supported by recent communication of Singh A K [16]

Table-II Activation Parameters as a function of composition for reaction in Water- Methanol 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	90.68	84.42	21.36	84.15	21.91	83.85	22.54	83.58	23.05	82.04	23.36
40%	22.90	89.65	84.83	16.45	84.76	16.48	84.55	16.83	84.32	17.30	84.55	17.57
50%	30.82	89.64	85.25	14.98	85.16	15.03	85.08	14.78	84.94	15.25	84.27	17.15
60%	40.06	89.06	85.65	11.63	85.56	11.74	85.60	11.41	85.44	11.75	84.82	13.54
70%	50.97	88.47	86.04	8.2	85.96	8.45	85.95	8.31	85.95	8.18	85.36	9.90

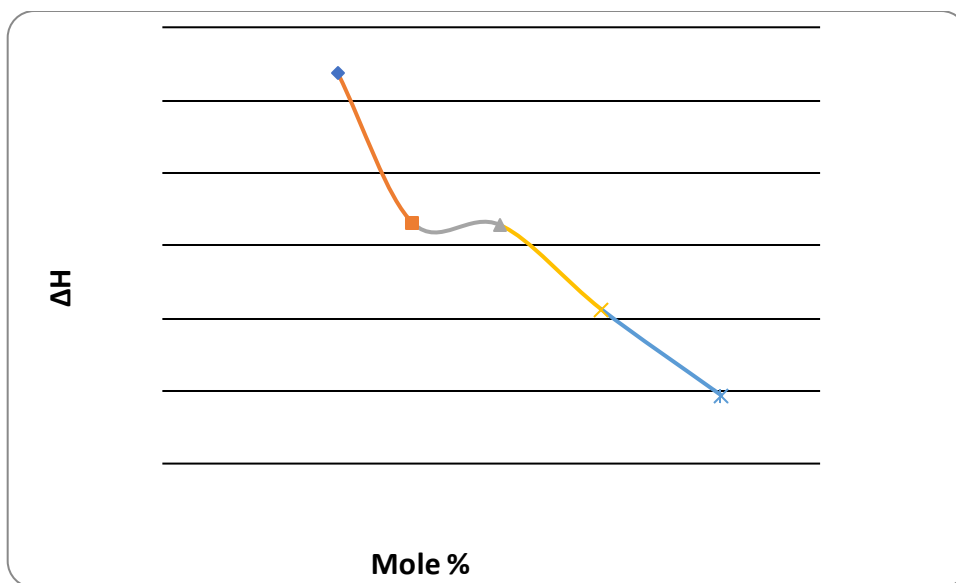


Fig (1)- Variation of ΔH^* with mole % at 25⁰c (water-methanol)

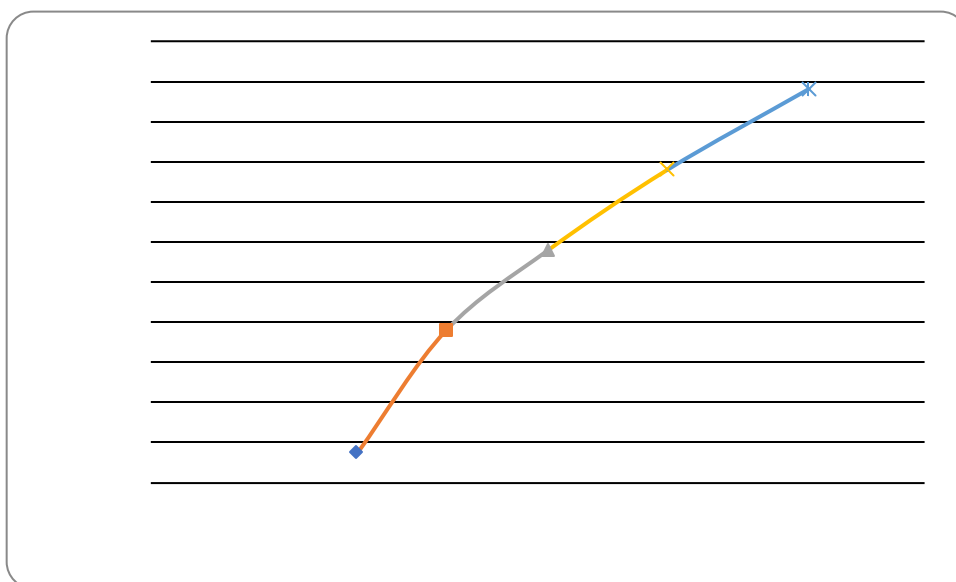
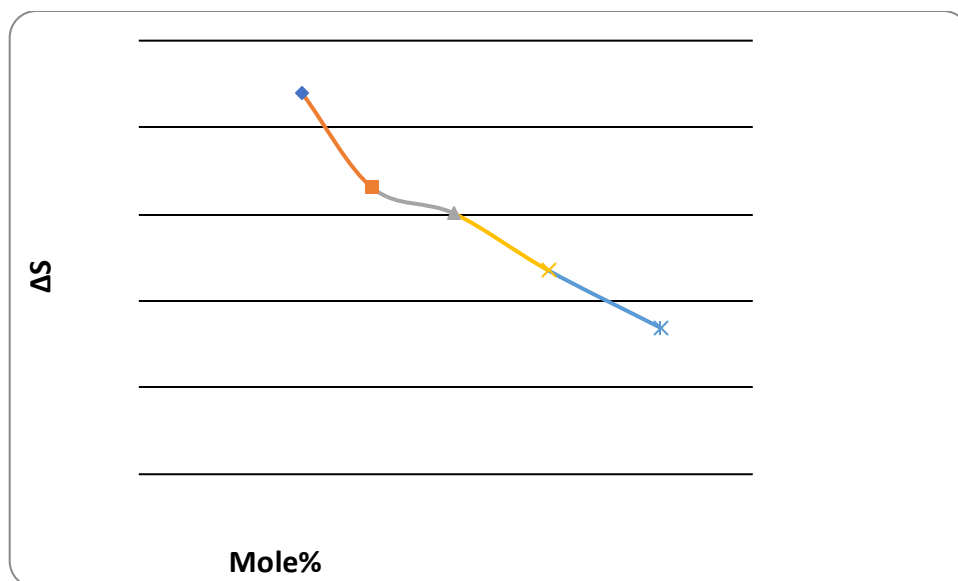


Fig (2)- Variation of ΔG^* with mole % at 25⁰c (water-methanol)



The enhancement in the value of and $\cdot G^*$ with

Fig (3)- Variation of ΔS with mole % at 25⁰c (water-methanol)

(F) Solvent-Solute Interaction and Iso-kinetic Temperature:

The Iso kinetic temperature is calculated by plotting $\cdot H^*$ against $\cdot S^*$ [fig-4] and its slope of straight line which come to less than 300(265 K/Mole²) conclude that there is weak interaction between solvent and solute present in reaction mixture and no any considerable change take place in structure of reactant or solvent or both. Which is earlier supported by Lefler [17] The above conclusion is based on Barclay [18] and Butler relationship between Enthalpy and Entropy of Activation,

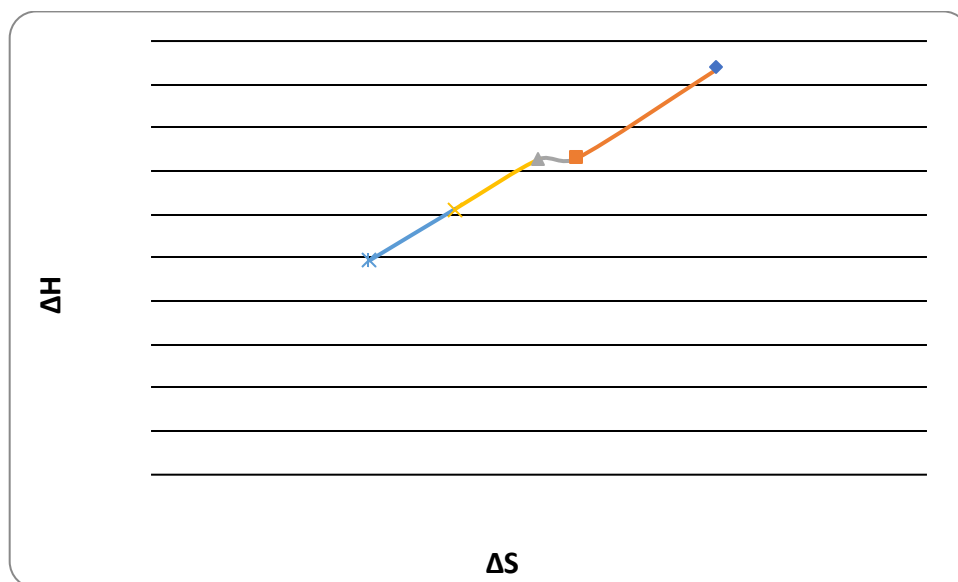


Fig. 4: Variation of ΔH^* with ΔS^* at 25⁰C (water-methanol) system

(G) Conclusion

By comparing the result of above project hydrolysis of ethyl benzoate in water-methanol media, following conclusion are found as:

1. The specific rate constant is decreases with increases temperature.
2. The iso composition energy and iso-dielectric activation energy are on opposite trend that one (E_c) is depleting where another (E_D) is enhancing.
3. Simultaneous decrease in ΔH^\ddagger & ΔS^\ddagger with values with increase in ΔG^\ddagger with for the hydrolysis ethyl benzoate in water- methanol is enthalpy stimulator and entropy inhibitor solvent.
4. The value of iso kinetic temperature is less than 300 indicate that reaction is not ion-dipole but ion-molecule type.

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