



# Kinetics of Bimolecular Reaction on Activation Parameters for the Solvolysis of Diethyl Phthalate in Aqueous Alkaline Medium of Ethanol

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## ABSTRACT

The kinetics parameters like rate constant, iso-composition activation energy, dielectric activation energy, enthalpy of activation, entropy of activation and Gibb's free energy of activation for the alkali catalyzed hydrolysis of diethyl phthalate ester have been determined at different range of composition for mixture of water and organic solvent at different range of temperature. The effect of solvent on rate of reaction has been studied on term of solvation and desolvation concepts. The number of water molecule associated with activated complex has been found to be decreases with increase of temperature from 20°C to 40°C, this indicate the mechanistic path followed by the reaction change from unimolecular to bimolecular. The variation of  $\Delta G^*$ ,  $\Delta H^*$ ,  $\Delta S^*$  with solvent composition and the specific effect of water on the reaction rate kinetics are also discussed. Linear plots of  $\Delta H^*$  versus  $\Delta S^*$  were obtained and the isokinetic temperature (greater than 300) indicates that the reaction is entropy controlled. The results are discussed in terms of polarity of medium and the change in solvent structure.

**Keywords:** Diethyl phthalate; Kinetics solvent effect; Ethanol-water; Activation parameter

## INTRODUCTION

The physical and chemical properties of aqueous binary solvent play an important role in determination of rate of reaction as well as some other chemical properties such as solvent polarity, structuredness and hydrogen bond donation and acceptance ability. The thermodynamic parameter such as enthalpy of activation, entropy of activation and Gibb's free energy of activation are important tools to obtain the clear picture of solvation. The objective of the present research work is to calculate the contribution of each mechanism involve under different condition of temperature and composition using chemical data. Since the ester hydrolysis is ion-dipole type of reaction and assuming the predominance of electrostatic effect, Ingold as well as Laidler and Landskroener has been predicted a fall in the rates with decrease in rates with decrease in the dielectric constant of the medium [1,2]. As such attention is being made to study of effect of solvent kinetically and also to evaluate the size of the transition state according to the equation of Laidler and Landskroener. The solvent effect is closely related to extent and nature of solvent-solute interaction. Some models considered the solvent effect as continuum dielectric whereas other treated the solvent as having both bulk interaction and those arising from the particular molecular properties. In kinetic studies, the dependence of rate constant on structure of the reacting molecule or the solvent effects is expressed in terms of activation parameters. The parameters used are iso-composition Activation Energy ( $E_C$ ), enthalpy of activation ( $\Delta H^*$ ), free energy of activation ( $\Delta G^*$ ), and entropy of activation ( $\Delta S^*$ ). These values are used as convenient tools for

mechanistic evaluation of these reactions. The activation parameters, the Energy of Activation ( $E_C$ ) and entropy of activation ( $\Delta S^*$ ) are dependent on the solvent nature, nature of reaction and structure of substrate and therefore, the have often employed for the mechanism interpretations. The energy of activation is the characteristic of the substrate and does not change rapidly with change of solvent, as does the entropy of activation. The latter only govern the rate of reaction in the solution. In general, the entropy of activation has been found to be more positive that is less negative for  $SN^1$  as compare to  $SN^2$  process. For substrates which react by  $SN^1$  mechanism, increases in the size of the alkyl group at central carbon atom frequently lead to be positive shift in ( $\Delta S^*$ ), but in case of  $SN^2$  mechanism, opposite effect may be found. For a given medium, the decrease in entropy is greater for small ion than for large one because the small ion is more highly solvated than the larger ion. The loss of entropy may also found when the solvent molecule are frozen around the ionic transition state. A change in solvent from a polar solvent to a nonpolar solvent has been suggested to increase or decrease reaction rates depending on the type of reaction. In homogeneous media, solvent effect on reactivity is explained in terms of specific interaction between solvent and substrate molecule and between solvent and transition states. In course of preliminary experiments in which the reaction rate in alcoholic medium has been determine by titration process and the value obtained were found to vary with alcohol or alkaline titrating solution. Under this circumstance it is very difficult to reach at actual conclusion with respect to mechanism of activation. On the other

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hand the consistent values of rate constant can be obtained when composition of solvent maintained constant during entire course of reaction, so that only variable concentration were those of solutes present in relatively dilute solution. Under this condition a relation between activation of alcohol and dielectric strength of medium was observed. Various efforts have been put forward to explain the solvent effect in last decade but here I pay a great attention on an important ester which is used as solvent for the antimony reduction of aluminum chloride phosphorus, tri chloride alkyl complex to form the corresponding alkyl phosphorus dichloride [3-5].

## METHODOLOGY

The kinetic procedure of reaction of alkali catalyzed of diethyl pathalate ester has been studied in aqueous solvent system in which calculated amount of ester was added. The mixture of ester, solvent and water has been thermostated for half an hour. From beginning of time consider as zero time, rest of the reaction mixture has been titrated in some interval of time. The second order rate equation has been used to determine the rate constant which is summarized in Table 1.

## RESULTS AND DISCUSSION

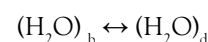
### Reaction rate

The hydrolysis of diethyl Pathalate ester in presence of alkali has been found to be second order kinetic. The specific rate constant has been calculated from the plots of  $\log k$  against the reciprocal of absolute temperature in various composition of reaction mixture. The rate of reaction decreases with increase of solvent composition of reaction media as evident from the Table 1. This decreasing trend of reaction rate is in accordance with earlier report which accounts in the favor of more polarized transition state in reaction media with high dielectric constant [6-8]. Here the retardation in rate with solvent composition is due to diffusion or distraction of charge on transition state similar as Ingold C. K. Hughes. Since the value of dielectric constant value of the reaction media goes on decreasing with gradual addition of solvent, hence it is fully

supported by qualitative prediction of Ingold C. K. Hughes [1].

### Water molecule involved decides the mechanism of reaction

The rate can also be expressed in term of involvement of water molecule in reaction media. This can explain by plotting  $\log k$  against different logarithmic mole fraction of water molecule. The calculation of number of water molecule (solvation number) involve in transition state has been determined by the slope of line obtained by plots of  $\log k$  and different water concentration as suggested by Tommila [9] and Lane [10] and inserted in Table 3 and there graph has been pictured in Figure 1. From the Figure1, it been shown that, for each temperature of the reaction, two intersecting line are obtained having different value of slopes value at about 1.44 which correspond to 49.57 % of water molecule in ethanol. From the Table 3 it has been shown that, below 1.44 values of  $\text{Log}(\text{H}_2\text{O})$ , the number of water molecule involve in activated complex decrease from 1.302 to 0.904 with increase of temperature. Similarly, the value of slope above than 1.44 decreases from 2.454 to 1.153 at different values of temperature 20°C to 40°C. Overall it has been inferred from the above result that number of water molecules involved in formation of activated complex from 1.425 to 0.904. On the basis of past invention Robertson et al., [11] has been established that the decrease in number of water molecule from 2.454 to 0.904 involve in formation of activated complex, the mechanistic pathways followed by the reaction change from unimolecular to bimolecular in presence of ethanol in the reaction media with increase of temperature. Regarding the change in structure of water, it is obvious that in presence of ethanol with rise of temperature, the water component of the reaction media changes its structure from bulky to dense form.



As per earlier report of Robertson, et al., [12] is found that the reaction mechanism change from uni-molecular to bimolecular [13,14] with increase in water concentration.

**Table 1:** Specific rate constant ( $k \times 10^3(\text{dm}^3/\text{mole}/\text{min})$ ) values at different composition of solvent.

Temp in °C	% of Ethanol				
	30%	40%	50%	60%	70%
20°C	16.21	11.48	8.7	6.09	4.78
25°C	24.54	18.4	14.45	10.47	8.31
30°C	35.48	27.54	22.38	16.59	13.48
35°C	50.11	42.65	33.88	28.31	22.64
40°C	74.47	67.45	56.23	48.97	38.01

**Table 2:** Log k values with  $\log(\text{H}_2\text{O})$  at different temperature.

% of Ethanol	% of $\text{H}_2\text{O}$	$\text{Log}(\text{H}_2\text{O})$	2+Log k				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.569	1.21	1.39	1.55	1.7	1.872
40%	60%	1.522	1.06	1.265	1.44	1.63	1.829
50%	50%	1.4437	0.94	1.16	1.35	1.53	1.75
60%	40%	1.346	0.785	1.02	1.22	1.452	1.69
70%	30%	1.221	0.68	0.92	1.13	1.355	1.58

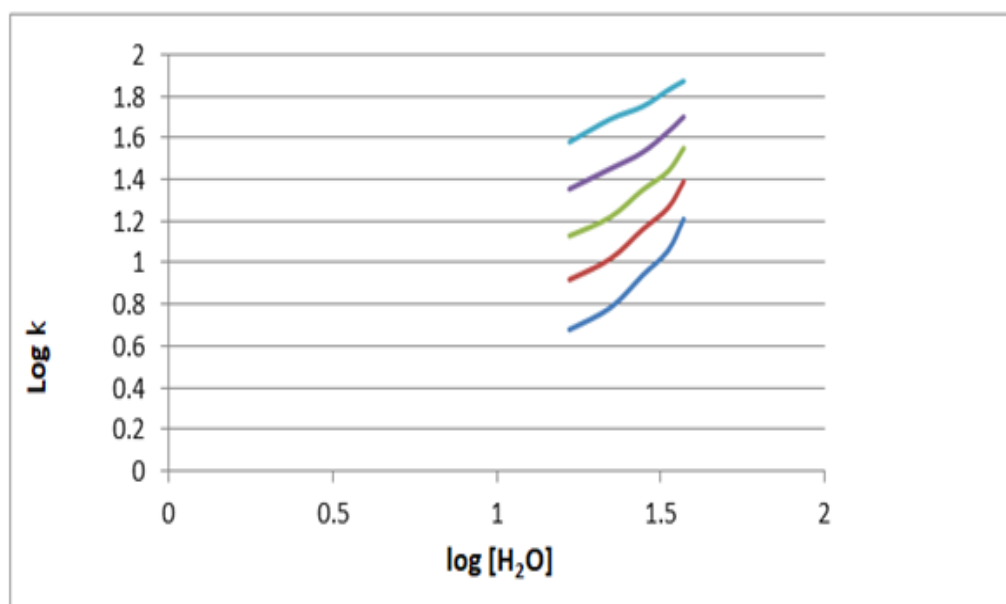


Figure 1: Variation of  $\log (H_2O)$  with  $\text{Log } k$ . Note: ( — ) 20°C; ( — ) 25°C; ( — ) 30°C; ( — ) 35°C; ( — ) 40°C

Table 3: Different values Slopes of  $\log k$  verses  $\log (H_2O)$  Water-ethanol media.

Temp°C	Slope-1	Slope-2
20°C	1.302	2.454
25°C	1.181	2.222
30°C	1.168	1.888
35°C	1.012	1.747
40°C	0.904	1.153

### Activation parameters of reaction ( $\Delta H^*$ , $\Delta G^*$ and $\Delta S^*$ )

The value of activation parameters like free energy of activation ( $\Delta G^*$ ), enthalpy of activation ( $\Delta H^*$ ) and entropy of activation ( $\Delta S^*$ ) have a great role in hydrolysis of ester. All the different result of activation parameters are calculated with help of Wynne-jones and Eyring equation, [15] and inserted in Table 4. The variation of ( $\Delta G^*$ ) and ( $\Delta H^*$ ) with mole% of organic component of has been shown in Figures 2 and 3 respectively while that of ( $\Delta S^*$ ) has been picture in Figure 4. On careful observation of data, it has been found that, ( $\Delta G^*$ ) values increases from 87.51 to 90.49 kJ/mole with change of proportion of solvent at 20°C. Though enhancement is not very large, however cannot be overlooked. The report of Yagil and Anbar [16] indicate that OH<sup>-</sup> ion of the NaOH is hydrated with three molecule of water. From the Figure 2, it is obvious that ( $\Delta G^*$ ) values increase linearly with increasing mole% of ethanol indicate that solvation or desolvation of reactant as earlier explained by Absolute Reaction Rate theory. So far as variation of ( $\Delta H^*$ ) and  $\Delta S^*$  is concern, it is clear from Figure 3 and 4, that both of them are increases with increases of mole% ethanol in reaction mixture.

From the Table 4, it is apparent that ( $\Delta H^*$ ) and ( $\Delta S^*$ ) value of the reaction increases with increase of mole% in similar ways as ( $\Delta G^*$ ). On the basis of fundamental thermodynamic equation.

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

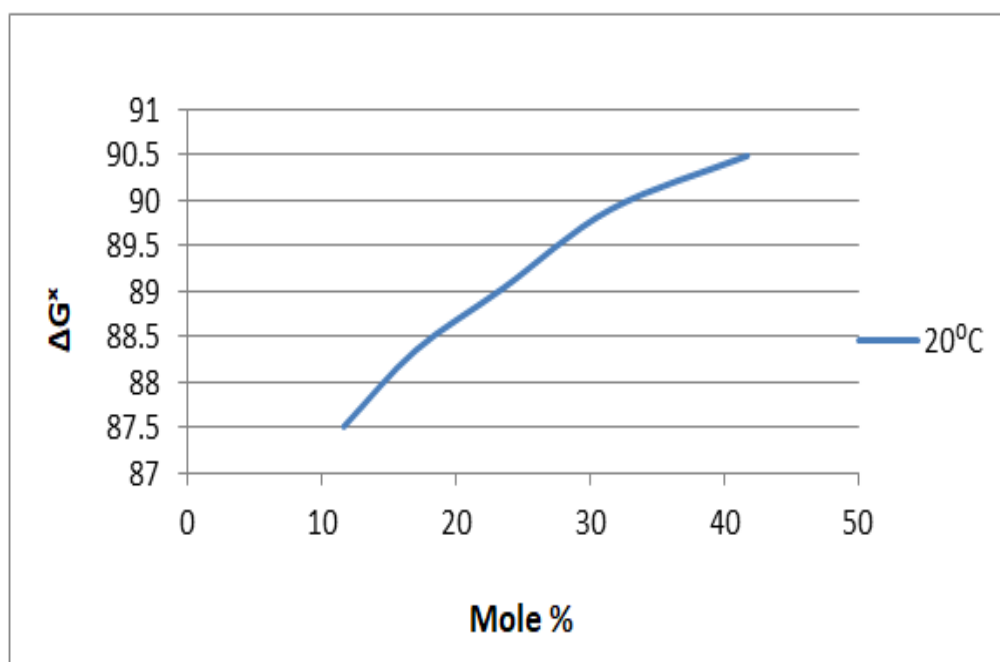
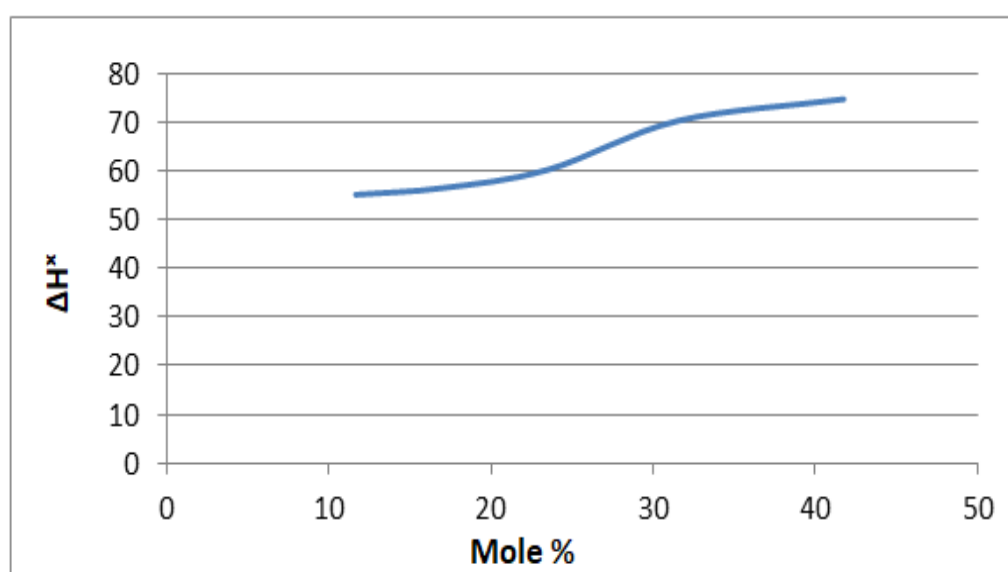
On the basis of above relation, enhancement in ( $\Delta H^*$ ) is only possible when its value is more than  $\Delta S^*$  and hence the reaction is entropy dominating. This observation is also found by many previous reports [17,18].

### Iso-kinetic temperature

Negligible change in ( $\Delta G^*$ ) and large change in ( $\Delta H^*$ ) and ( $\Delta S^*$ ) with different composition of reaction mixture usually show enthalpy- entropy compensation effect. This compensation effect is usually result in linear relationship between  $\Delta H^*$  and  $\Delta S^*$ . The plots of  $\Delta H^*$  and  $\Delta S^*$  is found to be liner, which follow Barclay and Butler rule [19]. The slope of the line which is also known as Iso-kinetic Temperature is found to be 372.24 suggests strong interaction between solvent and solute. Previous reports also support this suggestion [20,04].

**Table 4:** Different values of thermodynamics Activation Parameters ( $\Delta H^*$  and  $\Delta G^*$  in KJ/Mole,  $\Delta S^*$  in J/K/Mole)

% of EG	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%	11.63	55.12	87.51	110.54	86.88	106.57	87.46	106.7	88.08	107	88.47	106.54
40%	17	56.48	88.35	108.77	87.6	104.42	88.1	104.4	88.49	103.9	88.73	103.03
50%	23.5	60.24	89.03	98.25	88.2	93.82	88.63	93.69	89.08	93.63	89.21	92.55
60%	31.54	70.3	89.9	66.89	89	65.77	89.39	63	89.55	63.25	89.57	61.56
70%	41.75	74.74	90.49	53.75	89.57	49.76	89.91	50.06	90.12	49.93	90.23	49.48

**Figure 2:** Plot of  $\Delta G^*$  versus mole % at 20°C .**Figure 3:** Plot of  $\Delta H^*$  against mole %.

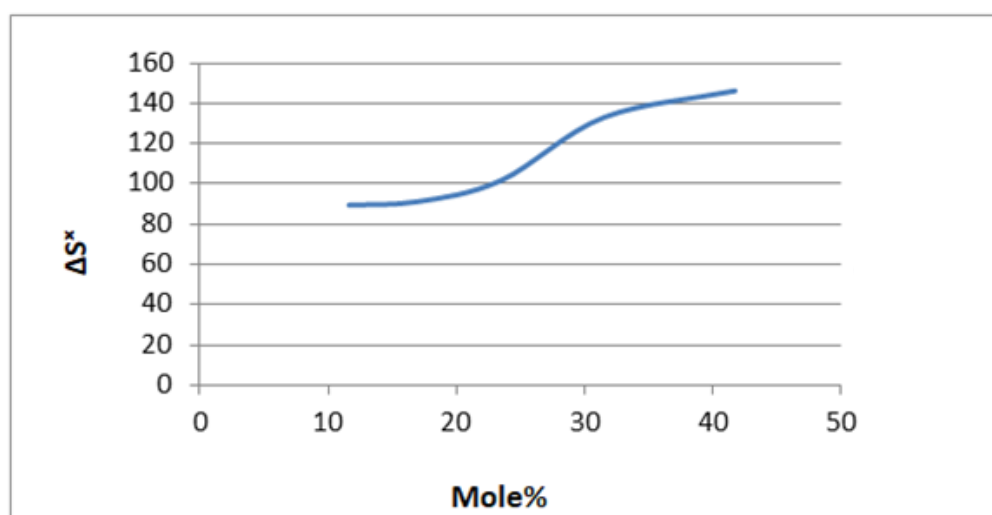


Figure 4: Plot of  $\Delta S^*+200$  versus mole% at 20°. Note: (—) 20°C

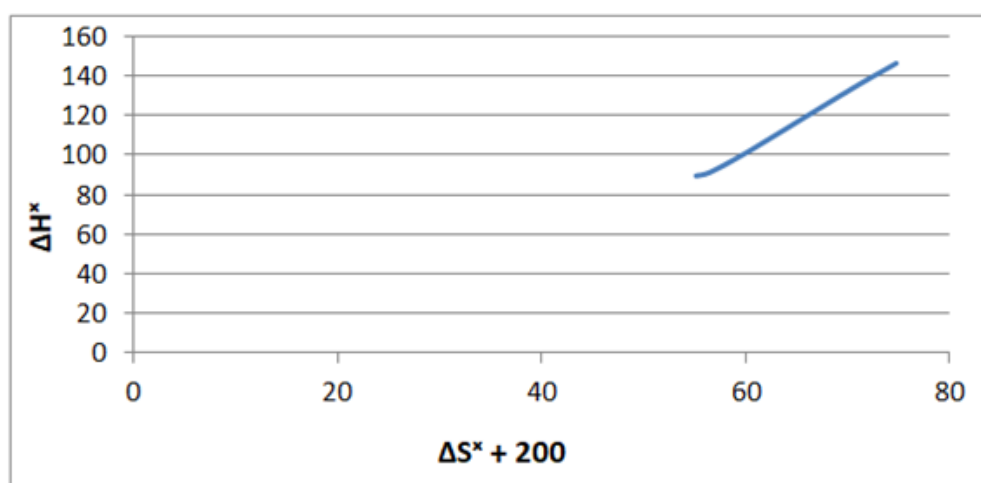


Figure 5: Variation of  $\Delta H^*$  with  $\Delta S^*+200$  at 20°C (water-ethanol) system.

## CONCLUSION

The objective of this investigation is to find out the solvent-solute interaction and solvation of reactant as well as transition state during the hydrolysis of ester. In this project the rate of reaction decreases with increases of solvent composition at different temperature. The calculated values of solvation number represent the involvement of number of water molecule in formation of activated complex. The entropy-enthalpy compensation effect is appeared due to small change in  $\Delta G^*$  and large change in ( $\Delta H^*$ ) and ( $\Delta S^*$ ). Strong solvent-solute interaction is shown due to greater values of slope more than 300°C; indicate the reaction is enthalpy control

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