



# Experimental and Theoretical Study of Co-Solvent Effect in Alkaline Hydrolysis of Diethyl Phthalate Ester

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## ABSTRACT

The rate constant of reaction of diethyl phthalate has been determined volumetrically using aqueous solution of ethanol covering range of 30% to 70% (v/v) at different temperature (20°C to 40°C). Whatever the experimental condition used, the reaction followed second order rate constant which decreases with increase of solvent composition. The effect of the solvent on rate and mechanism has been studied in term of solvation and desolvation concept. The relation between changes in dielectric constant due to variation of reaction mixture and change in specific rate constant has been explained on the basis of electrostatic and non-electrostatic contribution of solvent mixture. Calculated value of iso-composition activation energy is found to be increases with increase of solvent composition. The thermodynamic parameters ( $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$ ) has been determined with help of Wynne Jone and Eyring equation which show the great dependency on solvent composition.

**Keywords:** Water ethanol; Hydrolysis; Kinetic solvent effect; Diethyl phthalate; Iso composition activation energy

## INTRODUCTION

The rate of chemical reaction is change with change of solvent composition of reaction mixture which has great importance in laboratory as well as in chemical industry. Some time it is found that rate is increases by a factor  $10^9$  with change of solvent [1]. The solvent affect the reaction rate in two ways. One through static or equilibrium solvent effect and another through dynamic or fractional solvent effect [2-5]. The static solvent effect on reaction rate can be understood in term of Transition state theory. The second method are influence the rate of fast reaction. The solvent effect is also closely related to nature and extent of solvent-solute interaction. Solvent solute interaction are very much complex in mixture of the solvent than pure solvent due to possibility of specific solvation of any of solvent present in the mixture. In this investigation studies of solvent effect in hydrolysis of diethyl phthalate has been reported, which has greater use as solvent for the antimony reduction of aluminum chloride phosphorus, dichloride alkyl complex to form the corresponding alkyl phosphorus dichloride.

## MATERIALS AND METHODS

The reactions kinetics has been studied under second-order conditions. The chemical used are Merck grade or BDH (Annular). Known procedure is followed for purifying the ethanol. The diethyl ester containing in a conical flask has been thermo stated for half an hour. Immediately after then 0.4 ml of phthalate ester was withdrawn quickly and added to organic co-solvent mixture with help of pipette. Again 10 ml of aliquot has been withdrawn and allowed to pour into conical flask in which N/10 HCL solution was already present. Phenolphthalein indicator has been used to titrate the excess of alkali with standard solution. When half of aliquot into the cold 0.1 N HCl solution the stop clock was started. Rest of ester has been estimated after quenching the 10 ml of aliquot in 10 ml of 0.1 N HCl in a fixed interval of time.

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## RESULTS AND DISCUSSION

### Solvent effect dependence and rate constant

The rate of hydrolysis of diethyl phthalate has been measured in water ethanol medium by the slope of log k against time (Tables 1 and 2). The plot of log k against reciprocal of time has been found has been found to be linear. The retardation of rate with increase solvent composition may be explain on the basis of the fact that formation of polarized transition state is disfavored with increase proportion of ethanol. This fact is also supported by Hugh and in gold qualitative theory. The rate determines step of hydrolysis of ester is addition of hydroxyl ion to the

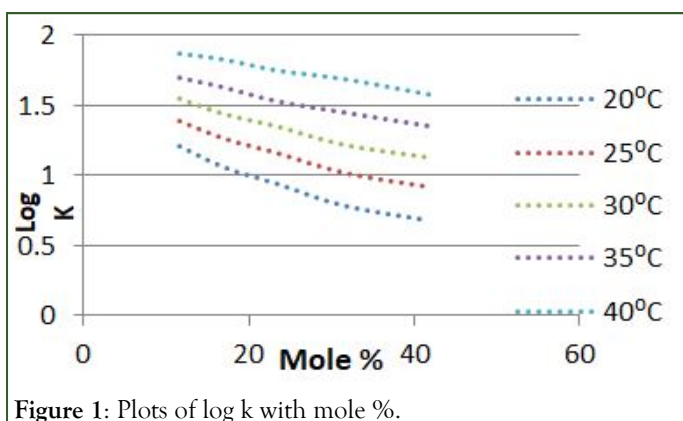
carbon of carbonyl group and after which rapid reaction with water is followed. Hence if the activity of hydroxyl ion decreases, the reaction rate must be decreases Tommila, et al. [6,7]. The lower the rate in water ethanol mixture suggested that interaction between water and ethanol increases with increase concentration of free water available for salvation of hydroxyl ion. The curve log k against mole fraction of representing smooth decrease, which implies that salvation of hydroxyl ion is stronger and hence the values of rate constant is decreases (Figure 1).

**Table 1:** Bimolecular rate constant  $k \times 10^2$  (dm)<sup>3</sup>/mole/mint.

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 different mole%.

Temp in °C	Mole%	2+Log k				
		20°C	25°C	30°C	35°C	40°C
30%	7.13	1.21	1.39	1.55	1.7	1.872
40%	11.63	1.06	1.265	1.44	1.63	1.829
50%	17	0.94	1.16	1.35	1.53	1.75
60%	31.54	0.785	1.02	1.22	1.452	1.69
70%	41.75	0.68	0.92	1.13	1.355	1.58



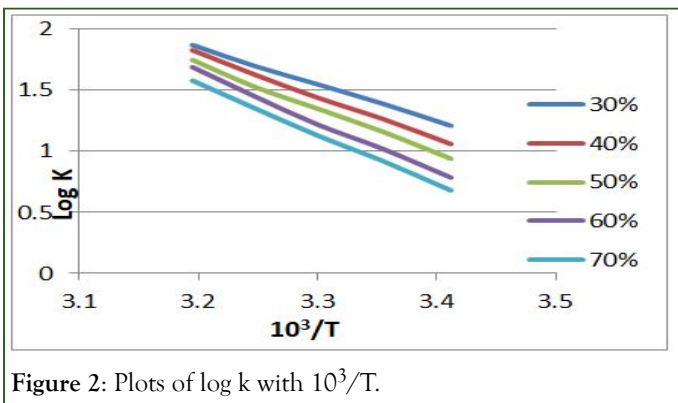
### Activation Energy ( $E_c$ ) and rate of reaction

Arrhenius plots (Log k against  $1/T$ ) has been used to calculate value of activation Energy ( $E_c$ ) (Table 3 and Figure 2). Table 4 collects the obtained values of activation energies under different solvent composition. The increase in ( $E_c$ ) values with increase in solvent composition has been noticeable because it will only happened when there is salvation change take place either in initial level or transition level or both.

The increasing value of ( $E_c$ ) as a function of solvent composition indicate that there is salvation take place at initial level where as desolation at transition level (Table 5 and Figure 3) [8-12].

**Table 3:** Different log k values as a function of temperature.

Temp in °C	$10^3/T$	2 + Logk				
		30%	40%	50%	60%	70%
20°C	3.412	1.21	1.06	0.94	0.785	0.68
25°C	3.355	1.39	1.265	1.16	1.02	0.92
30°C	3.3	1.55	1.44	1.35	1.22	1.13
35°C	3.247	1.7	1.63	1.53	1.452	1.355
40°C	3.195	1.872	1.829	1.75	1.69	1.58

**Table 4:** Iso composition activation energy at different solvent fraction.

% of $E_c$	30%	40%	50%	60%	70%
$E_{exp}$ in KJ/mole	61.64	68.56	74.25	82	82.36

**Table 5:** The values  $\log k_D$  at different D.

Temp in °C	$10^3/T$	D=40	D=45	D=50	D=55	D=60
20°C	3.412	0.75	0.85	0.94	1.04	1.14
25°C	3.355	0.94	1.04	1.145	1.25	1.35
30°C	3.3	1.16	1.275	1.39	1.501	1.62
35°C	3.247	1.428	1.519	1.61	1.7	1.79
40°C	3.195	1.655	1.74	1.831	1.92	2.01

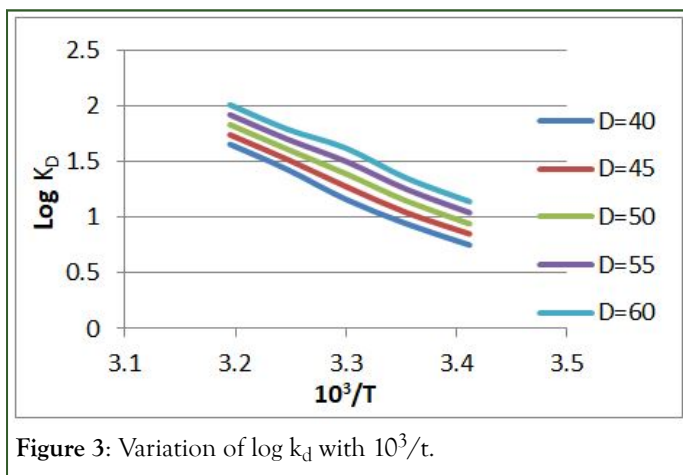


Figure 3: Variation of  $\log k_d$  with  $10^3/T$ .

### Dielectric effect on reaction rate

The another aspect of effect solvent may be also be consider by observing the effect of dielectric constant D on reaction rate.

Table 6: calculated values of  $(E_D)$  at constant D.

Dielectric constant(D)	D=40	D=45	D=50	D=55	D=60
$E_D$ in KJ/mole	83.76	80.62	79.64	78.84	77.31

## CONCLUSION

The gradual decrease of rate constant is found with increase proportion of solvent composition due to increase concentration of free water available for salvation of hydroxyl ion. The increase of activation energy with increasing composition of solvent indicates desolation in transition state and salvation in initial state. Dielectric value follow similar trend as iso composition activation energy.

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There is an increase in rate is found to increase in D whereas the rate is decreases with decrease in D. The dielectric constant value is obtained by interpolation of aklerof data. Linear relationship is obtained between  $\log k$  and  $D-1/2D+1$  for dipole dipole interaction Lanndskroner. However for ion dipole linear relation is obtain by plotting  $\text{Log}k$  and  $\text{Log}D$  or  $\text{Log}k$  against  $1/D$ . With help of slope of plots of  $\text{Log} kD$  against reciprocal of absolute temperature, the iso dielectric values has been calculated with help of slope of different linear line. The depletion in  $(E_D)$  with decreasing D, showed that depletion in  $(E_D)$  values followed similar trend as  $(E_C)$  vales with increasing proportion of solvent composition (Table 6) [13].