



iJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 4

Issue: IX

Month of publication: September 2016

DOI:

www.ijraset.com

Call:  08813907089

E-mail ID: ijraset@gmail.com

Solvent Effect on Solvolysis Rate in Alkaline Hydrolysis of Ethyl Acetate in water-methanol and water-ethanol mixed solvent system

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Abstract: *The kinetic of alkaline hydrolysis of Ethyl Acetate was investigated at different percentage of Aqueous-organic Solvent mixture with Methanol (30 to 70% v/v) and Ethanol (30 to 70% v/v) over the temperature range of 20° C to 40° C.*

The Specific Rate constant was found to be decrease in both the solvent with increasing proportion of solvent (MEOH and ETOH) at all the temperature range.

The Iso-composition Activation energy (E_c) were also evaluated which increase with solvent composition in (water-media) and decrease with solvent composition in (water-ET-OH system).

The number of water molecule associated with the activated complex are found to be decrease (1.59 to 1.42) in in water-MEOH system and increase (1.061 to 1.34) in water-MEOH media.

The Thermodynam Activation Parameter such as Enthalpy of Activation (ΔH^), Entropy of Activation (ΔS^*) and Gibb's free energy of Activation (ΔG^*) were calculated.*

I. INTRODUCTION

Although the Solvent Effect on the Rate and Mechanism of the various type of reaction has been reported.^{[1][2][3]} but very little attention has paid towards the study of the Solvent Effect on the Thermodynamic Activation Parameter and the solvent-solute interaction, particularly for an ion-dipolar reaction. In order to highlight the above noted idea, it has been proposed to make the kinetic study of the solvent effect on the alkali catalysed hydrolysis of Ethyl Acetate has not been paid even a little attention so far.

II. EXPERIMENTAL

All the chemical used were either of BDH (Analar) or merck grades. The water used was doubly distilled. The Specific Rate Constant value were calculated using second order reaction and tabulated in Table-I (Water-MEOH) and Table-II. (Water-ETOH) The Iso composition Activation energy (E_c) were evaluated and tabulated in Table-III (Water-MEOH) and Table-IV. (Water-ETOH) The number of water molecule evaluated by the slope of plot of $\log K$ and $\log(H_2O)$ and inserted in Table-V (Water-MEOH) and Table-VI. (Water-ETOH) Thermodynamic Activation Parameter were also calculated.

III. RESULT AND DISCUSSION

From table I and II (Fig. 1 & 2), it is clear that specific rate constant values of the reaction go on decreasing with increasing organic co-solvent in both the solvent (ETOH and MEOH). From the plot of $\log k$ with mole% of organic co-solvent, it was observed that plots follows decreasing trend at all temperature in both solvent. From the plot it is also apparent that the decrease is regular and follows linear trend at all the temperature in both solvent. The trend of variation in the values of specific rate constant may be discuss in light of the Hughes and Ingold^[4] theory. According to the theory of increase in Dielectric constant values of the reaction media result in increase in the rate when there is concentration of charges on the transition state and cause a decrease in the rate when there is diffusion or destruction of charges on transition state. MEOH and ETOH both being poor anion solvator. Their increase in aqueous medium will facilitate the disolvation of ions already solvated by water molecule. Since initial and transition state (both being anions differing in size and charge) cannot be equally disolvated, the rate will be affected by such specific solvation changes. Thus it appears that transition state is more disolvated than initial state in case of ETOH and MEOH as the rate decrease with increase in solvent content in the medium.

A. Effect of Solvent on Activation Energy (Iso-composition) of the reaction

From Table I and II, it is found that the value of Iso-composition Activation Energy is goes on enhancing in case of water MEOH media 62.31-64.31 where as in case of ETOH it shows decreasing trend with gradual addition of organic content. The increase in the value

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of Iso-composition Activation Energy in case of MEOH 1.06-1.34 may be attributed that initial state is solvated and transition state is dissolvated, which recently supported by Singh R T. et al^[5].

In case of ET-OH the value of Activation Energy decrease from 59.56 to 56.52 Kj/mole with increase proportion of ETOH in water-ETOH media.

The depleting trend in the E_{exp} values can be explained by any of the following three situations.

- 1) The transition state is less desolvated than the initial state.
- 2) The initial state is less solvated than the transition state.
- 3) The initial state is disolvated and the transition state is solvated.

Out of three situation the third factor seems to be operative as both ΔH^* and ΔS^* values of the reaction were found decreasing with increasing ET Content in water-ETOH media. Our this inference has also been in favour of the finding of Singh A K^[6]. On the basis of enhancement (water-MEOH media) and depletion (water-ETOH media) it is inferred that methyl alcohol has the solvating power to solvate the initial state and to desolvate the transition state where ethanol has the opposite trend that of methanol. Our this finding is also supported by Singh, R T et al., Singh, A K^[5,6]

B. Effect of solvating power on the number of water molecules associated with the Activated complex and on mechanistic path of the reaction.

The effect of water concentration $[H_2O]$ of water-MEOH media and water-ETOH media on rate and mechanism of alkaline hydrolysis of ethyl acetate has been studied in light of guideline and observation render by Tommil-E^[8], Lane-C.A.^[9], Eismongy et al^[10] – they have established on idea of the number of water molecule associated with the Activated complex has been determined by plotting $\log k$ against by $[H_2O]$ according to the relation proposed by Robertson.^[11]

$$\log k = \log k_0 + n \log [H_2O]$$

Here n is the solvation number which tells about the criteria for studying about the mechanism of reaction.

It is obvious from the plots of $\log k$ versus $\log [H_2O]$ that at all the five temperature at which kinetics were studied, straight lines with different values as mentioned in table-IV table IV (Fig3&4).

From the value of slope as mention table-IV table IV (Fig.3&4) the number of water molecules associated with Activated complex varies from (1.59 to 1.42) in case of water-ETOH media with rise of temperature where as in case of water-MEOH varies from (1.06 to 1.34).

From the above values of slope mention in table IV it is inferred that equilibrium shifted from bulky form (b) of water to dense form (d) in case of water-ETOH media, with rise of temperature.



Where as in case of water-MEOH media, the equilibrium shift from dense form (d) to bulky water (b) with rise of temp.



In the light of finding of Robertson^[11] and from above noted trend, it is concluded that solvating power of ETOH change the mechanism of the reaction from unimolecular to bio-molecular, where as in case MEOH the change in mechanism of reaction are opposite manner i.e. from bimolecular to unimolecular. Recently supported by singh, A K^[12]

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Table - I
 Specific rate constant [$k \times 10^3$ (dm)³/mole/mint] values of alkali catalyzed
 Hydrolysis of ethyl-acetate in water-MEOH media

Temp in °C	% of MEOH				
	30%	40%	50%	60%	70%
20°C	40.27	30.19	23.44	18.40	14.79
25°C	58.88	44.66	34.67	26.85	21.13
30°C	89.12	69.98	52.36	41.20	33.11
35°C	133.35	112.20	79.43	62.95	50.11
40°C	199.06	151.35	117.48	91.20	73.28

Table - II
 Specific rate constant values ($k \times 10^3$) in (dm)³/mole/mint in water-ETOH media

Temp in °C	% of ETOH				
	30%	40%	50%	60%	70%
20°C	31.62	25.11	18.62	14.28	10.71
30°C	56.23	45.18	33.11	25.70	18.19
35°C	75.85	58.88	43.65	33.11	23.98
40°C	97.72	77.62	57.54	40.73	31.62

Table - III
 Values of Iso-composition Activation Energy (water-MEOH media)

% of ME-OH	30%	40%	50%	60%	70%
E _{exp} in KJ/mole	62.31	62.51	63.67	64.26	64.88

Table - IV
 Values of Iso-composition Activation Energy (water-ETOH media)

% of ME-OH	30%	40%	50%	60%	70%
E _{exp} in KJ/mole	59.56	59.25	57.50	57.49	56.52

Table-V
 The value of slope of plot of log k verses log[H₂O]
 of reaction in water-MEOH media

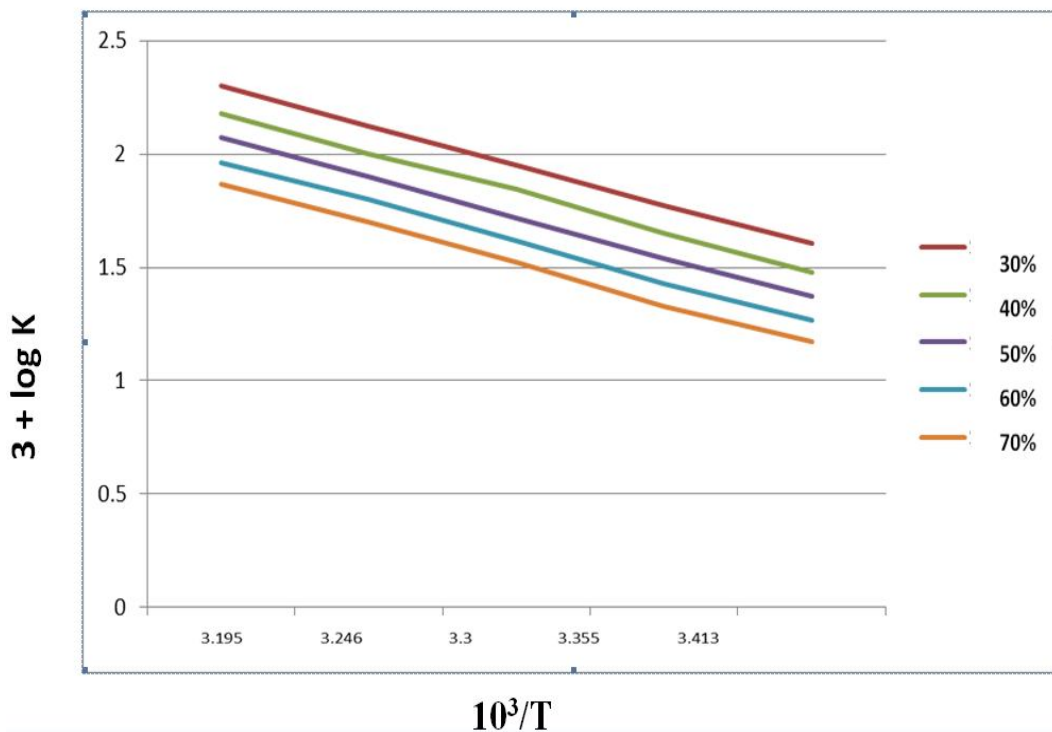
Temp ⁰ C	20 ⁰ c	25 ⁰ c	30 ⁰ c	35 ⁰ c	40 ⁰ c
Slope	1.061	1.081	1.186	1.282	1.349

Table-VI
 The value of slope of plote of log k verses log [H₂O] Of reaction in water-ETOH media

Temp ⁰ C	20 ⁰ c	30 ⁰ c	35 ⁰ c	40 ⁰ c
Slope	1.59	1.48	1.43	1.42

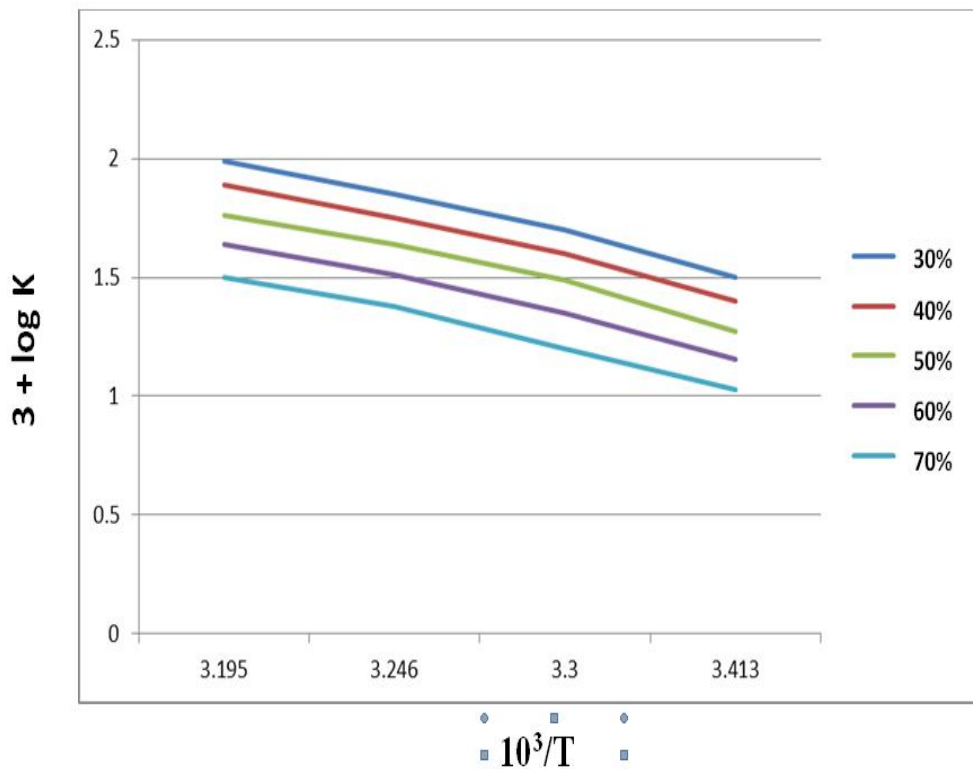
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Fig. 1



Variation of $3 + \log K$ value with $10^3/T$ (water-MEOH media)

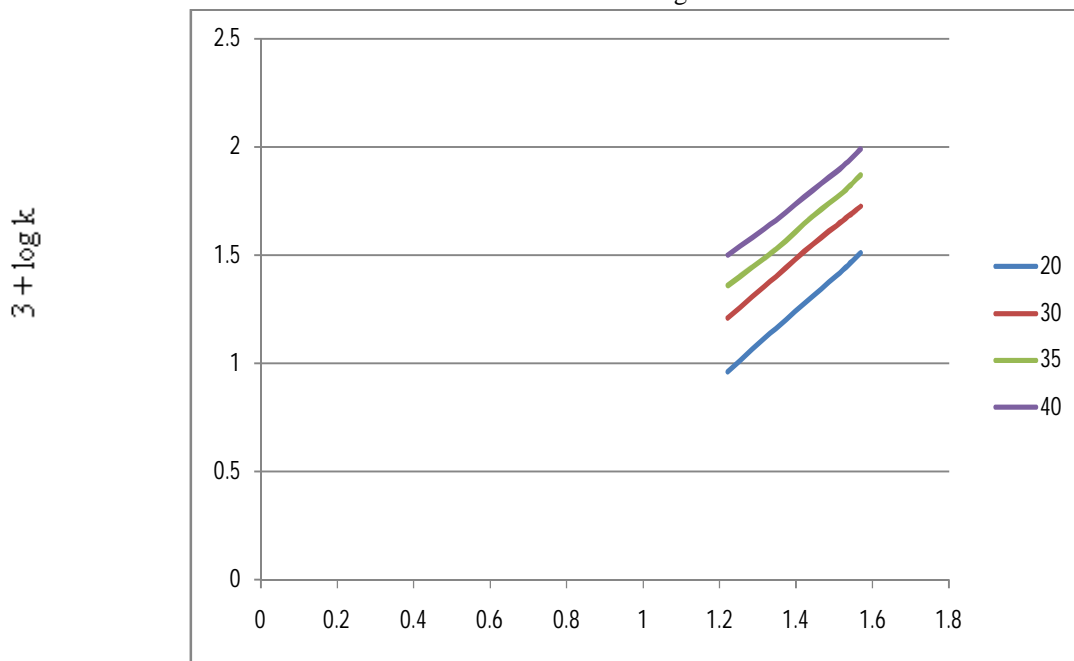
Fig. 2



Variation of $3 + \log K$ value with $10^3/T$ (water-ETOH media)

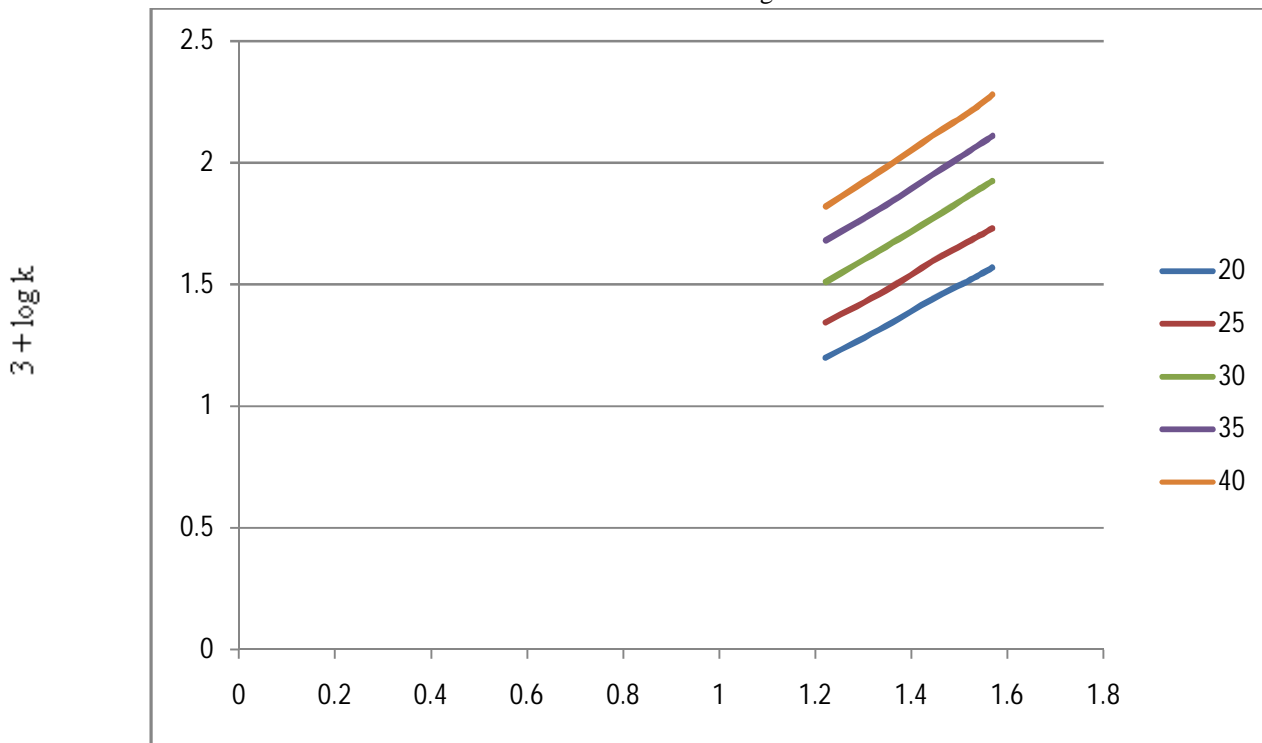
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Fig. 3



Log (H₂O)
Variation of 3 + logK value with log[H₂O](water-ETOH media)

Fig. 4



Log(H₂O)
Variation of 3 + logK value with log(H₂O)(water-MEOH media)

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