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# Solvent effect and kinetics on ethyl benzoate in aqueous solvent system

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## Abstract

Rate constant for the base catalyzed hydrolysis of ethyl benzoate is determined volumetrically in methanol-water mixture for the composition varying from 30 to 70% (v/v) at different temperature ranging from $20^0$ C to $40^0$ C. The initial slow but sharp decrease in rate with gradual addition organic co- solvent in the reaction media and with increasing temperature of reaction has been explained on the basis of salvation and desolvation of first and transition state to a different extent. The Iso-composition activation energy($E_C$) energy for same solution decreases as methanol content is increases while Iso- Dielectric activation energy($E_D$) with increase as the dielectric constant of the solvent increases. The trends of variation of numbers of water molecule associated with activated complex increases with increasing temperature from $20^0$ C to $40^0$ C tells about the fact that in the presence of the protic solvent(methanol) in reaction media, the bimolecular mechanistic path of reaction changed to unimolecular. The enhancement in $DG^*$ with simultaneous decrease in ($DH^*$) and ($DS^*$) values of the reaction concluded that the reaction is enthalpy stimulating and entropy control.

**Keywords:** Activated complex, solvent effect, ethyl benzoate, Hydrolysis, water-methanol mixture. Specific rate constant, Iso-composition and Iso-dielectric Activation energy

## 1. Introduction

The kinetics of hydrolysis of base catalyzed reaction has received considerably interest by

Various researches [1, 5] but the solvent effect on the rate of reaction, mechanism of the reaction and thermodynamic activation parameter of solvolysis of benzoate ester and solvent-solute interaction in the reaction media consisting of methanol have not been reported so far. The main conclusion from these studies is that the reactivity is influenced by preferential salvation of the reactant and transition state through non- specific and specific solvent-solute interaction.

Hence, in present investigation the above untouched work, it has been proposed to make a comprehensive studies of kinetic solvent effect on the alkali catalyzed hydrolysis of ethyl benzoate in water-methanol solvent system, specially benzoate ester was chosen for study in detail because its plays very active use in alcoholic beverage and has medicinal application on skin and eyes.

## 2. Experimental

Expert quality of Ethyl Benzoate of fluke AG grade packed in Switzerland and Methanol of Merck grade was used. The kinetics of the reaction was studied volumetric by keeping the strength of alkali 0.1M and that of the ester 0.5 in the reaction mixture. The reaction was found to obey second order kinetics equation and the evaluated values of specific rate constant is recorded in Table-1. The variation of Logk with mole % is shown in Table-2. With help slope of Arrhenius plot of logk verses 1/T (Table-3), the Iso-composition activation energy ($E_C$) Energy was calculated and inserted in Table-4.The values of Iso-Dielectric activation energy($E_D$) were calculated at different D are tabulated in Table-5. The variation of Logk with Log ($H_2O$) is mentioned in Table-6.The consolidated values of thermodynamic Activation Parameter i.e. ($DG^*$), ($DH^*$) and ($DS^*$) calculated with the help of Wynne-Jons and Eyring [6] equation and has been Tabulated in Table-7.

## 3. Result and Discussion

### 3.1 Solvent Effect on Specific Rate

The second order rate constant for base catalyzed hydrolysis of ethyl benzoate in water-methanol mixture were calculated at $30\text{-}40^0$ c from the slopes of linear plot of Logk against time(t). The rate constant at different temperature and composition are collected in Table-1.For showing the solvent effect on specific rate constant of the reaction, the logarithmic value of k is also plotted against the mole % of added organic solvent(methanol) in the reaction media (Tabulated in Table-2 and Fig-1), found decreasing trend with increasing composition of the solvent. The trend of variation in the values of specific rate constant (Tabe-1) can be discussed in the light of Hughes and Ingold [7] theory. According to this theory the increase in dielectric constant value causes concentration of charge on transition state with increase of rate whereas decrease in rate causes destruction or diffusion on transition state. In alkali catalyzed hydrolysis of ethyl benzoate, the dielectric constant value of reaction media increases with gradual addition of organic co solvent

a) The depletion in rate is probably due to decrease in the polarity of the reaction media by adding less polar methanol or decrease in bulk dielectric constant value of medium.

b) The decrease in the polarity of reaction media due to addition of a less polar solvent and also decrease in bulk dielectric constant, is in good agreement with the theory of Hughes and Ingold Such decrease in rate constant with increasing proportion of organic co-solvent like methanol was also reported by Elsemongy [8], and recently by Singh A K [9]

**Table 1:** Specific rate constant k $10^2$(dm) $^3$/mole/mint] values of alkali catalyzed Hydrolysis of Ethyl-benzoate in water- Methanol

| Temp in $^{O}$C | % of Methanol | | | | |
|---|---|---|---|---|---|
| | 30% | 40% | 50% | 60% | 70% |
| 20$^{O}$C | 37.15 | 30.54 | 25.70 | 21.87 | 18.62 |
| 25$^{O}$C | 74.13 | 57.54 | 48.97 | 41.68 | 35.48 |
| 30$^{O}$C | 147.91 | 112.20 | 88.10 | 74.13 | 64.56 |
| 35$^{O}$C | 278.61 | 211.34 | 165.95 | 136.45 | 112.20 |
| 40$^{0}$C | 543.25 | 398.10 | 301.99 | 245.47 | 199.52 |

**Table 2:** Variation of 2 + Log k Value against mole %,( Water-methanol) System.

| Temp in $^{O}$C | | 2 + Log k | | | | |
|---|---|---|---|---|---|---|
| | Mole% | 20$^{O}$C | 25$^{O}$C | 30$^{O}$C | 35$^{O}$C | 40$^{0}$C |
| 30% | 16.03 | 1.570 | 1.870 | 2.170 | 2.445 | 2.735 |
| 40% | 22.90 | 1.485 | 1.760 | 2.050 | 2.325 | 2.500 |
| 50% | 30.82 | 1.410 | 1.690 | 1.960 | 2.220 | 2.480 |
| 60% | 40.06 | 1.340 | 1.620 | 1.870 | 2.135 | 2.390 |
| 70% | 50.97 | 1.270 | 1.550 | 1.810 | 2.050 | 2.300 |

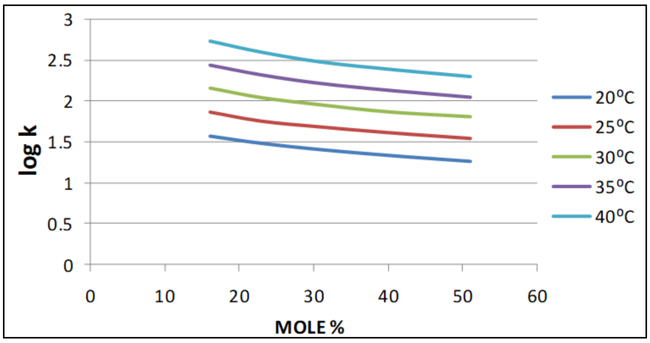

**Fig 1:** Variation of log k with mole %.

### 3.2 Evaluated values of Iso-composition Activation Energy ($E_c$) of the reaction

The value of of Iso-composition activation energy ($E_c$) of the reaction has been evaluated from Arrhenius plots of logk values of the reaction against $10^3$/T. The plots are shown in figure-2 and the numerical values of $E_c$ of the reaction are enlisted in Tab-4. The depletion of $E_c$ values from 96.09 to90.15 kj/mol with increase concentration of MEOH has been established that changes the value of activation energies and this is noticeable only when the salvation changes take place in either initial state level or at transition state level or both levels. The decrease in activation energy of the reaction with decrease in specific rate constant values may seem to be quite natural. The following three possibilities can be hold responsible for depletion in the values of $E_c$.

a. Transition state is more solvated than initial state.
b. The transition state is less desolvated than initial state, and
c. The transition state is solvated and the initial state is desolvated.

Out of these three factors, the third seems to be applicable in our case, as this factor is by decrease in the values of Entropy of activation ($\Delta S^*$) and Enthalpy of activation ($\Delta H^*$) with gradual addition of organic co- solvent (methanol) in the reaction media, as mention in Table-8 This conclusion is also supported recently by Singh R. T. *et al.* [10]

**Table 3:** Variation of Logk Values against $10^3$/T, Water- methanol System.

| Temp in $^{O}$C | | 2 + Logk | | | | |
|---|---|---|---|---|---|---|
| | $10^3$/T | 30% | 40% | 50% | 60% | 70% |
| 20$^{O}$C | 3.412 | 1.570 | 1.485 | 1.410 | 1.340 | 1.270 |
| 25$^{O}$C | 3.355 | 1.870 | 1.760 | 1.690 | 1.620 | 1.550 |
| 30$^{O}$C | 3.300 | 2.170 | 2.050 | 1.960 | 1.870 | 1.815 |
| 35$^{O}$C | 3.247 | 2.445 | 2.325 | 2.220 | 2.135 | 2.050 |
| 40$^{O}$C | 3.195 | 2.735 | 2.600 | 2.480 | 2.395 | 2.300 |

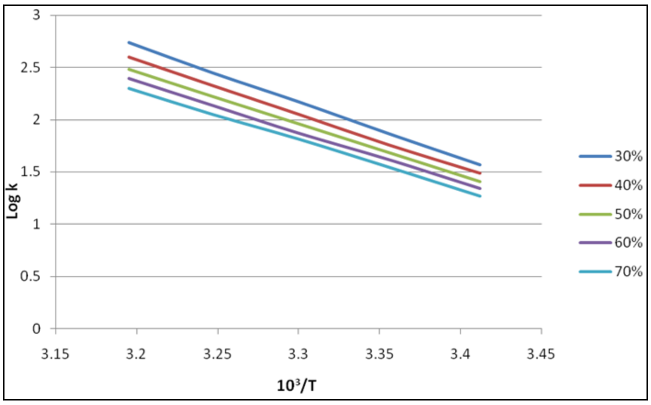

**Fig 2:** Variation of Log K with $10^3$/T.

**Table 4:** Values of Iso-composition activation energy with increasing percentage of solvent (water-MEOH media)

| % of MEOH | 30% | 40% | 50% | 60% | 70% |
|---|---|---|---|---|---|
| $E_{exp}$ in KJ/mole | 96.09 | 92.66 | 92.99 | 91.15 | 90.15 |

### 3.3 Effect of Solvent on Iso- Dielectric Activation Energy

The value of of Iso-dielectric Activation energy($E_D$) is calculated by plotting Arrhenius plot of log$k_D$ values against 1/T and evaluated values are recorded in Table-5. This table shows that, $E_D$ value goes up from 109.95to120.12 kj/mole, with increasing dielectric value in the reaction media. This interpretation was supported by past view of Wolford [11] and recently it is supported by Singh R T. *et al.* [12]

**Table 5:** Values of Iso-Dielectric Activation Energy (water-methanol)

| Dielectric constant(D) | D=45 | D=50 | D=55 | D=60 | D=65 |
|---|---|---|---|---|---|
| $E_D$ in KJ/mole | 109.95 | 112.11 | 113.13 | 117.78 | 120.12 |

### 3.4 Effect of Solvent on Salvation number and mechanistic path of the reaction

Salvation number (n) that is the number of water molecule associated with activated complex is evaluated by using Robertson [13] relation.

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

The salvation number (n) is determined by plotting logk against log [$H_2O$]. The slope of plot give the number of water molecule associated with activated complex and tabulated in Table-6. By the observation of tabulated value of slope it is indicated that the value of slopes increases from 0.008 to 1.120 which attributes to the fact that equilibrium of water molecule by addition of methanol, is shifted from dense form to bulky form with rise of temperature.

**$[H_2O]_d \leftrightarrow [H_2O]_b$**

It shows that, with addition of methanol to water the mechanistic path of reaction is changed from bimolecular to unimolecular in similar way as observed by Parker and Tomilinson [14] and recently by Singh A K [1].

**Table 6:** Variation of 2+ Log k with log $[H_2O]$ (water-methanol) at different temperature

| % of Acetone | % of $H_2O$ | Log $[H_2O]$ | 2 + Log k | | | | |
|---|---|---|---|---|---|---|---|
| | | | $20^0C$ | $25^0c$ | $30^0c$ | $35^0c$ | $40^0c$ |
| 30% | 70% | 1.5690 | 1.590 | 1.870 | 2.139 | 2.400 | 2.750 |
| 40% | 60% | 1.5229 | 1.485 | 1.760 | 2.025 | 2.275 | 2.53 |
| 50% | 50% | 1.4437 | 1.410 | 1.690 | 1.945 | 2.220 | 2.455 |
| 60% | 40% | 1.3468 | 1.350 | 1.620 | 1.890 | 2.135 | 2.390 |
| 70% | 30% | 1.2218 | 1.270 | 1.550 | 1.810 | 2.050 | 2.300 |

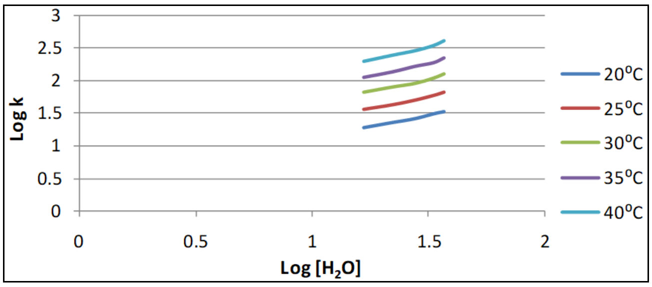

**Fig 3:** Variation of log $[H_2O]$ with Log K.

**Table 7:** Evaluated values of slopes (Plot of log k verses log $[H_2O]$) of Water-methanol media

| $Temp^0C$ | $20^0c$ | $25^0c$ | $30^0c$ | $35^0c$ | $40^0c$ |
|---|---|---|---|---|---|
| Slope | 0.800 | 0.856 | 0.862 | 0.967 | 1.120 |

**Table 7:** Thermodynamics Activation Parameters ($\Delta H^*$and $\Delta G^*$ in KJ/Mole, $\Delta S^*$in J/K/Mole) of the reaction in Water- methanol Media.

| % of Meoh | Mole % | $\Delta H^*$ in Kj/ Mole | $20^0C$ | | $25^0C$ | | $30^0C$ | | $35^0C$ | | $40^0C$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\Delta G^*$ | $\Delta S^*$ | $\Delta G^*$ | $\Delta S^*$ | $\Delta G^*$ | $\Delta S^*$ | $\Delta G^*$ | $\Delta S^*$ | $\Delta G^*$ | $\Delta S^*$ |
| 30% | 16.03 | 101.83 | 84.35 | 59.65 | 84.13 | 59.39 | 83.85 | 59.33 | 83.64 | 59.05 | 83.04 | 60.03 |
| 40% | 22.90 | 96.96 | 84.83 | 41.39 | 84.76 | 41.63 | 84.55 | 41.71 | 84.32 | 41.03 | 84.45 | 39.96 |
| 50% | 30.82 | 94.74 | 85.25 | 32.38 | 85.16 | 32.14 | 85.08 | 31.88 | 84.94 | 31.81 | 84.58 | 32.46 |
| 60% | 40.06 | 88.70 | 85.65 | 10.04 | 85.56 | 10.53 | 85.60 | 10.23 | 85.44 | 10.58 | 85.12 | 32.70 |
| 70% | 50.97 | 87.79 | 86.04 | 5.97 | 85.96 | 6.14 | 85.95 | 6.07 | 85.95 | 5.97 | 85.66 | 17.60 |

## 5. Conclusion

In hydrolysis of ethyl benzoate, the decrease in rate constant with mole percentage of co solvent t either decreases in bulk dielectric constant value or it decreases in polarity of reaction media by the addition of less polar methanol to it.

Decreasing trend of activation energy ($E_c$) with increase co-solvent inferred the salvation in transition state and desolvation in initial state. The increasing number of water molecule associated with activated complex with increasing temperature shows that the mechanism of reaction media changes from bio molecular to unimolecular with addition of the solvent (methanol).

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