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# A Kinetics Study of Solvent Effect on solvent-solute interaction and mechanism of the Ion-dipolar reaction in an aquo-organic co solvent system

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**Abstract:** A kinetic study of solvolysis reaction of methyl salicylate in water-DMF solvent using different concentration of DMF (v/v) was made at four different temperatures i.e., 20<sup>o</sup> C, 25<sup>o</sup> C, 30<sup>o</sup> C, 35<sup>o</sup> C & 40<sup>o</sup> C. The rate of reaction decreases with increase of DMF content of the media. The dielectric effect and solvation change were held responsible for such depletion in the rate. The Iso-composition-Activation energy was found to be decreasing from 57.65 to 53.45 KJ/mole with gradual addition of organic co-solvent, the solvation and desolvation of transition and initial state respectively are responsible for depletion in the value of Iso-composition-Activation energy of the reaction. The number of water molecule associated with the activated complex are found to be decreasing from 1.63 to 1.41 with increase in the temperature from 20<sup>o</sup> C to 40<sup>o</sup> C and this indicated that the mechanistic path followed by the reaction change from uni-molecular to bimolecular. The Enthalpy of Activation ( $\Delta H^\ddagger$ ), Entropy of Activation ( $\Delta S^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) were also calculated.

**Keywords:** Iso-composition, Desolvation, Solvolysis, Protic, Dipolar-aprotic, Iso-Dielectric.

## I. INTRODUCTION

The dipole movement and dielectric properties have been chosen as the criteria for the classification of solvent by AJ Parker<sup>[1]</sup>, the solvent having dielectric constant values greater than 15 may contain hydrogen atom and incapable to donate the same for formation of hydrogen bond but on the other hand may be good hydrogen bond acceptors are termed aprotic or dipolar aprotic. DMSO, DMF, Sulphonale, Acetone-nitrile, Acetone etc. are good examples of dipolar aprotic solvent having peculiar chemical properties, whereas methyl alcohol, ethyl alcohol, ethylene glycol etc. are the examples of dipolar protic solvent.

In present study, the solvent DMF has been used for studying its solvent effect on the alkaline hydrolysis of methyl salicylate in water-DMF solvent system.

## II. EXPERIMENTAL

The kinetics of alkaline hydrolysis (solvolysis) of methyl salicylate was studied in a manner as reported earlier<sup>[2], [3], [4]</sup> of various water-DMF solvent mixture consisting of 30% to 70% of DMF (v/v) at different temperature rising from 20<sup>o</sup> C to 40<sup>o</sup> C at enhancing interval of 5<sup>o</sup> C. The specific rate constant value, (Tab-1) Iso-composition-Activation energy Tab-2 and the number of water molecule associated with the Activated complex of the reaction were calculated from the slopes of the plot of the logk values against log[H<sub>2</sub>O] and are enlisted in table -III. The Iso-Dielectric Activation energy (E<sub>D</sub>) was calculated by interpolation of the curve for the logk against D and mention in table-IV. The Thermodynamic activation diameter such as ( $\Delta H^\ddagger$ ), ( $\Delta G^\ddagger$ ) and ( $\Delta S^\ddagger$ ).has been evaluated using Wynne-Jones & Eyring Equation<sup>[5]</sup> and enlisted in table-V.

## III. RESULT AND DISCUSSION

From table-I and Fig-1 it is obvious that with the gradual addition of the organic co-solvent (water-DMF) in the reaction media there is the regular depletion in the rate of the reaction at all the five different temperatures.

Generally, the following two factors seem to be responsible for depletion in the rate of reaction in the solution, they are:

- A. Decreasing polarity of the medium as changing from polar water to less polar water-DMF and
- B. Lowering of bulk Dielectric constant value of the medium.

Our interpretation was also supported by Hughes and Ingold<sup>[6]</sup> and Landskroener<sup>[7]</sup>.

- 1) *Solvent Effect on Iso-composition-Activation Energy:* From the Arrhenius plots, the value of Iso-composition-Activation energy (E<sub>C</sub> or E<sub>exp</sub>) have been calculated and mentioned in table II.

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From table II, it is clear that the value of Iso-composition-Activation energy go on decreasing from 57.65 KJ/mole to 53.45 KJ/mole with increasing concentration of DMF in the reaction media.

The depletion trend in  $E_{exp}$  values may be due to either of the following three causes:

- a) Initial state is solvated less than transition state.
- b) The transition state is solvated more than the initial state.
- c) The transition state is solvated and the initial state is desolvated.

Out of three factor, in our case the third (III) factor seem to be operative as  $\Delta H^*$  and  $\Delta S^*$  values of reaction as calculated are found decrease with increase concentration of DMF in reaction media. i.e., disorderness in reaction media. This conclusion has also been supported by singh et al <sup>[8]</sup>

- 2) *Effect of Solvent on Iso-Dielectric-Activation energy  $E_D$* : From the slopes of the Arrhenius plots of  $\log k_D$  values (obtained from interplotation of  $\log k$  value of the reaction against D values of the reaction media) versus  $10^3/T$ . The value of Iso-Dielectric-Activation energy of reaction have been recorded in table III.

From the table-III and Fig-2, it is obvious that  $E_D$  values goes on decreasing with decreasing Dielectric constant values of reaction media.

These finding and interpretation about the change observe is not supported by Wolford <sup>[9]</sup> but recently supported by singh et al <sup>[10]</sup>

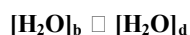
- 3) *Solvent Effect on the Mechanistic Pathways of the Reaction*: The mechanism of the reaction was decided by evaluating the number of water molecule involved in the formation of Activated complex. It was done by plotting  $\log k$  against  $\log[H_2O]$  following the reaction proposed by Robertson <sup>[11]</sup> which is as

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

where n is the solvent number (number of water molecule associated with the Activated complex) which is evaluated from the slopes of the plots of  $\log k$  versus  $\log [H_2O]$  and tells about the criterion for studying the mechanism of the reaction.

From the table-IV and Fig-3, it is clear that in water-DMF media, the number of water molecule associated with the Activated complex decrease from 1.63 to 1.41 with rise of temperature in the reaction from 20<sup>o</sup> C to 40<sup>o</sup> C.

From above noted observation, the clear picture come in the light that the depletion in number of water molecule attached with activated or transition state with rise of temperature is found because the equilibrium of the reaction shifts from bulky form of water to its dense form in presence of DMF in reaction media.



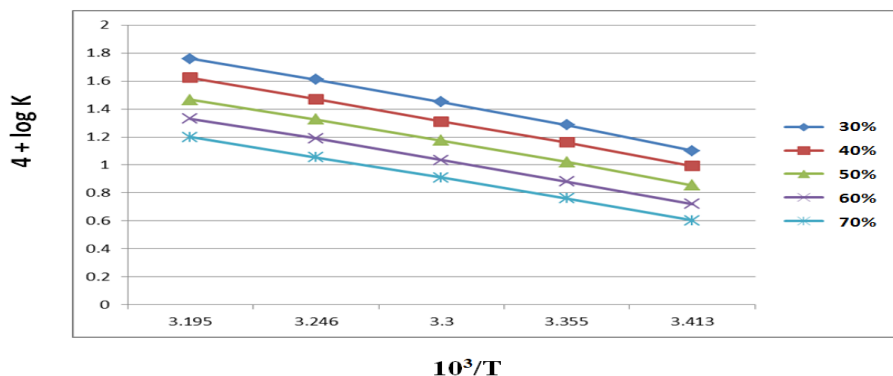
After all, it is clear that at all temperatures, the number of water molecules associated with the activated complex decreases as the temperature of water-DMF mixture go on increasing. It explain that bulky form of water is changed to its dense form also when temperature is enhanced in similar ways as reported on the guideline of Tommila et. al. <sup>12</sup> it is concluded that with addition of DMF and also with increasing path changed from uni-molecular to biomolecular. Our this conclusion has also been supported recently by singh et al <sup>[13]</sup>

Table - I  
Specific rate constant [ $k \times 10^3$  (dm)<sup>3</sup>/mole/mint] values of alkali catalyzed  
Hydrolysis of methyl-salicylate in water-DMF media

Temp in <sup>o</sup> C	% of DMF (v/v)				
	30%	40%	50%	60%	70%
20 <sup>o</sup> C	12.58	9.81	7.16	5.24	4.01
25 <sup>o</sup> C	19.27	14.45	10.47	7.58	5.75
30 <sup>o</sup> C	28.18	20.41	14.96	10.83	8.12
35 <sup>o</sup> C	40.73	29.51	21.13	15.48	11.35
40 <sup>o</sup> C	57.54	41.97	29.17	21.33	15.81

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Fig. 1



Variation of 4 + log K with 1/T (water-DMF media)

Table-ii

Value of Iso-composition Activation Energy of reaction in water-DMF media

Percentage of DMF	E <sub>EXP</sub> in KJ/mole
30%	57.65
40%	56.17
50%	54.14
60%	54.27
70%	53.45

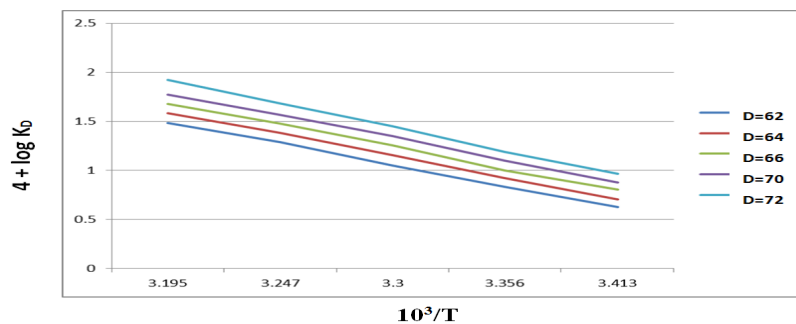
Table- III

Value of Iso-Dielectric Activation Energy (E<sub>D</sub>) of different

Dielectric constant (D) in water-DMF media

Dielectric Constant (D)	D=62	D=64	D=66	D=70	D=72
E <sub>D</sub> in KJ/mole	82.11	82.36	83.02	84.79	86.71

Fig. 2



Variation of log K<sub>D</sub> value with 1/T (water-DMF media)

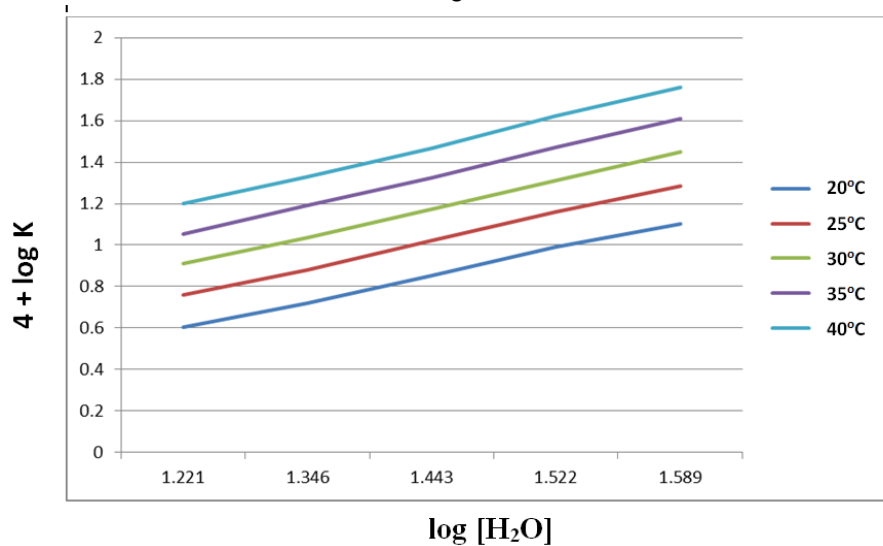
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Table-IV

The value of slope of plote of log k verses log[H<sub>2</sub>O]  
Of reaction in water-DMF media

Temp <sup>0</sup> C	Slope
20 <sup>0</sup> c	1.63
25 <sup>0</sup> c	1.51
30 <sup>0</sup> c	1.49
35 <sup>0</sup> c	1.44
40 <sup>0</sup> c	1.41

Fig. 3



Variation of 4 + logK value with log [H<sub>2</sub>O] (water-DMF media)

Table-V

Thermodynamics Activation Parameters of the Reaction in Water- DMF Media  $\Delta H^*$  and  $\Delta G^*$  in KJ/Mole,  $\Delta S^*$  in J/K/Mole.

% of DMF	Mole %	$\Delta H^*$ in KJ/Mole	20 <sup>0</sup> C		25 <sup>0</sup> C		30 <sup>0</sup> C		35 <sup>0</sup> C		40 <sup>0</sup> C	
			$\Delta G^*$	$-\Delta S^*$	$\Delta G^*$	$-\Delta S^*$	$\Delta G^*$	$-\Delta S^*$	$\Delta G^*$	$-\Delta S^*$	$\Delta G^*$	$-\Delta S^*$
30%	9.12	50.33	98.26	163.58	98.94	163.12	99.69	162.90	100.45	162.72	101.24	162.65
40%	13.50	49.54	98.87	168.36	99.64	168.15	100.51	168.21	101.28	167.98	102.06	167.79
50%	18.96	48.92	99.64	173.10	100.46	172.91	101.52	173.59	102.14	172.79	103.01	172.81
60%	25.98	46.02	100.40	187.30	101.25	185.33	102.11	185.11	102.94	184.80	103.83	184.69
70%	35.27	45.44	101.05	189.79	101.94	189.59	102.84	189.43	103.74	189.28	104.61	189.04

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