

A Kinetics Study of Solvent Effect on Thermodynamics Activation Parameter on alkali catalyzed Solvolysis of Methyl Salicylate in water-DMF Media

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Abstract

A kinetic study on Thermodynamic parameter of solvolysis reaction of methyl salicylate in water-DMF solvent system using different concentration of DMF (v/v) was made at four different temperature i.e. 20° C, 25° C, 30° C, 40° C.

It was observed that with increasing concentration (mole %) of the organic co-solvent in the reaction media, the ΔH^* and ΔS^* values of the reaction goes on descending while ΔG^* value goes on enhancing. Hence, it was inferred that the reaction was entropy control.

The evaluated values of Iso-kinetic temperature are come to 202.62, which is less than 300, indicate weak interaction between solvent and solute present in the reaction media.

I. Introduction

By the previous research[1][2][3] on the effect of dipolar aprotic solvent, like DMF, DMSO, dioxane, Acetone have widely been studied on the acidic and basic hydrolysis of aliphatic ester but towards the study of solvent effect and mechanistic path of aromatic ester like methyl salicylate so far has paid very little attention.

So, in order to highlight the above noted idea, it has been proposed to make a kinetic study of the solvent effect of DMF on the alkali catalyzed hydrolysis of methyl salicylate.

2. Experiment

Purified Di-methyl formamide (DMF) of BDH grade and methyl salicylate of USSR grade were taken into use.

The kinetic of alkali catalyzed hydrolysis of ester was studied as usual[4][5] the values of specific rate constant were evaluated by making use of second order rate equation and are tabulated in table I.

Result and Discussion:

From the plot of $\log k$ versus mole%, table 2 and Fig 2 it is obvious that with the gradual addition of the organic co-solvent (DMF) in the reaction media, there is gradual depletion in the rate of reaction at all five different temperatures.

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

- (i) Decreasing the polarity of the medium as changing from polar water to less polar water-DMF medium
- (ii) Lowering of the bulk dielectric constant values of the medium.

Our interpretation has also been supported by Hugh and in gold [6], Laidler and Landskroener [7] and recently [8] [9].

3. Solvent effect on the Thermodynamic

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3.1 Activation Parameter

Similar to the ISO-composition Activation Energy (E_c) and ISO- dielectric Activation Energy (ED), The other thermodynamic Parameter such as enthalpy of activation (ΔH^*), Entropy of activation ΔS^* and free energy of activation ΔG^* are also the better indicator of the solvent effect displayed by the solvent on the solvolysis reaction.

The values of all the three thermodynamic parameter i.e. ΔH^* , ΔS^* and ΔG^* at different mole of the organic component of the reaction media (DMF) have been synchronized in table-III On careful observation of the data it is found that ΔG^* value increase from 98.26 kJ/mole to 101.05 kJ/mole with change in proportion of DMF from 30 to 70% (v/v) at 200C. Though the enhancement is not very large, however, it cannot be overlooked.

The report of Yagil and Anbar [10] indicate that OH ion of NaOH is hydrated with three molecule of water. In mixed aquo-organic co-solvent mixture, organic component molecule are expected to contribute to the process of dissolvent as they may be regarded as poor anion solvator in ΔG^* values with increasing mole% of organic co-solvent has been reported by Tommila [11] and cleave [12] on plotting ΔG^* value against mole% of DMF as shown in fig-1

The gradual increase in mole% of organic component of the reaction media with ΔG^* is indicative of solvation or desolvation of reactant as explained by Absolute Reaction Rate Theory and also reported by Elsemongy et al [13]

So far as the variation in ΔH^* and ΔS^* are concerned, it has been found from the plot of ΔH^* and ΔS^* against mole% as shown in fig-3 and fig-4 that both of them decrease with increase mole% of DMF. However on perusal of the Tab- IInd. It is interestingly observed. that out of all the three thermodynamic parameter of the reaction namely ΔG^* , ΔH^* and ΔS^* only ΔH^* and ΔS^* are found to decrease with Simultaneous increase in ΔG^* as well as with

increase in mole% of the organic component of the reaction media. According to relation

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

It can easily be concluded that Simultaneous increase ΔG^* values with decrease in ΔH^* and ΔS^* value is only possible when the extent of depletion in ΔS^* values is greater than that found in ΔH^* . The regular depletion to the great extent in ΔS^* values in comparison to that of ΔH^* values clearly indicate that alkali catalyzed hydrolysis of methyl salicylate in water-DMF Enthalpy promoting and Entropy deactivating one. More over as found non-linear enhancement in ΔH^* value with Mole % in fig-3, give information of the fact that specific solvation is taking in water-DMF media as already reported by savile[14] et al. and it is also indicate that random distribution of the component are not acceptable.

The similar nonlinear variation in ΔG^* , ΔH^* and ΔS^* values with increase mole% of the organic co-solvent (DMF) in reaction media have also been reported by Tommila et al.[15] Hyne at al[16] and recently by singh et.al. [17]

3.2 Evaluation of ISO-kinetic Temperature and Solvent-Solute Interaction

In the light of Barclay and Butler[13] relationship between enthalpy and entropy of Activation, the value of Iso-kinetic temperature of alkali catalyzed hydrolysis of methyl salicylate in DMF media has been evaluated which comes to be 202.62 which is much less than 300(Fig-6).

From the value of ISO-kinetic temperature, it is concluded that there is a slow change in the structure of the reactant or in solvent or in both due to weak interaction between solvent and solute present in the reaction media consisting of DMF in similar ways as reported by Lefler [14]. Our this conclusion has also been recently reported by [15][16].

Table: 1. Specific Rate Constant [k x10³(dm)³/mole/mint]

Temp in °C	4 + log K				
	30%	40%	50%	60%	70%
20°C	12.58	9.81	7.16	5.24	4.01
25°C	19.27	14.45	10.47	7.58	5.75
30°C	28.18	20.41	14.96	10.83	8.12
35°C	40.73	29.51	21.13	15.48	11.35
40°C	57.54	41.97	29.17	21.33	15.81

Values of Alkali Catalyzed Hydrolysis of Methyl-salicylate in Water-DMF Media

Table: 3

Table: 3. Thermodynamics Activation Parameters of the Reaction in Water- DMF Media ΔH^* and ΔG^* in KJ/Mole, ΔS^* in J/K/Mole

% of DMF	Mole %	ΔH^* in KJ/Mole	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	$-\Delta S^*$								
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

Fig: 1. Variation of 4 + logK with 1/T (Water-DMF Media)

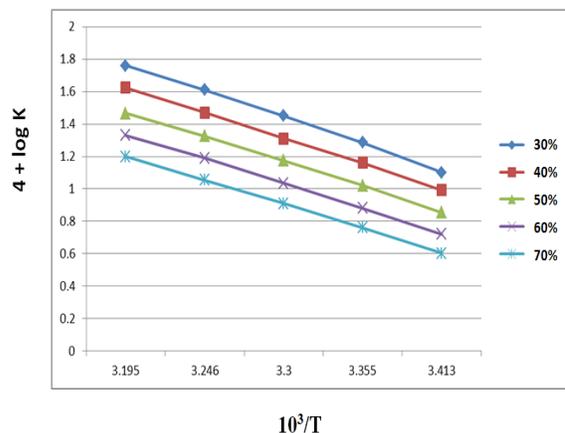


Table: 2. Variation of 4+logK values with mole % (Water-DMF media) of Alkaline Hydrolysis of Methyl Salicylate

% of DMF	Mole %	4+log K				
		20°C	25°C	30°C	35°C	40°C
30 %	9.12	1.100	1.285	1.450	1.610	1.760
40 %	13.50	0.992	1.160	1.310	1.470	1.623
50 %	18.96	0.855	1.020	1.175	1.325	1.465
60 %	25.98	0.720	0.880	1.035	1.190	1.329
70 %	35.27	0.604	0.760	0.910	1.055	1.199

Fig: 2.

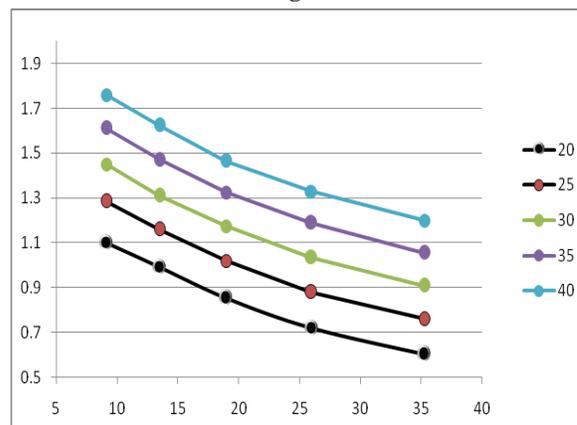
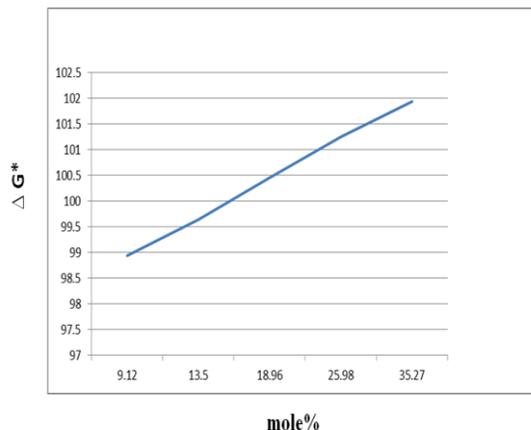
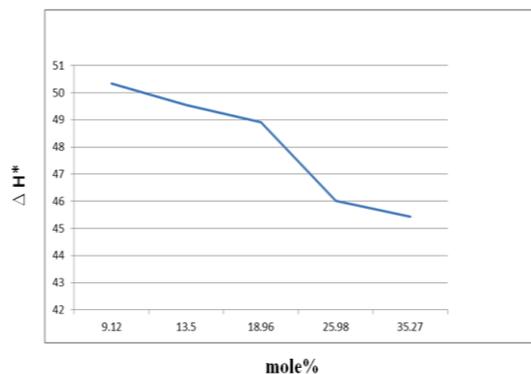
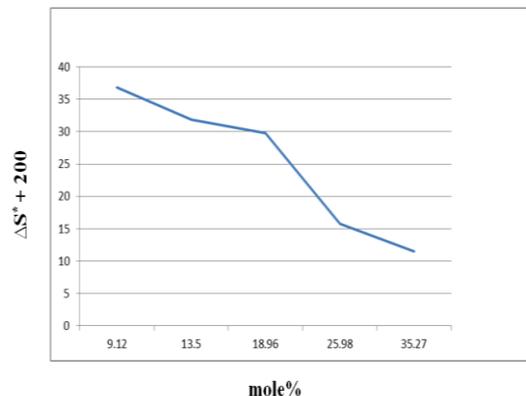
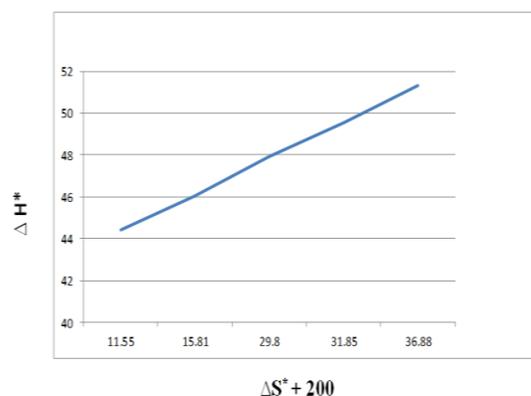


Fig: 3. Variation of ΔG^* with Mole % (Water-DMF Media)**Fig: 4.** Variation of ΔH^* with Mole % (Water-DMF Media)**Fig: 5.** Variation of $\Delta S^* + 200$ with Mole % (Water-DMF Media)**Fig: 6.** Variation of ΔH^* with $\Delta S^* + 200$ with Mole % (Water-DMF Media)

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