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A Kinetic Study of the Solvent Effect of DMF on the Medicinal Efficiency of Salicylate Ester

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Abstract: ***For highlighting the solvent effect of a peculiar dipolar aprotic solvent, DMF, on the medicinal efficiency of Salicylate ester, the kinetic studies of the alkali catalysed solvolysis of Butyl salicyate in aquo-DMF medium of various compositions starting from 30 to 80 vol. % of DMF at temperatures ranging from 20 to 40°C have been carried out. The specific rate constant values were found to decrease with increasing proportion of DMF at all the temperatures and thus the prediction of Parker has not been found applicable. The numerical values of iso-composition activation energy E_C and iso-dielectric energy E_D were found to be changed in opposite direction to each other. The values of iso-composition energy of the reaction are found to increase with increasing concentration of DMF in the reaction media. On the other hand, the values of iso-dielectric activation energy were found decreasing with increasing the dielectric constant value of the reaction media. These changes observed in the two types of activation energies have been interpreted in the light of solvation and desolvation of initial and transition states to different extent. Variations in thermodynamic activations parameters ΔS^*, ΔH^* and ΔG^* have also been evaluated and interpreted on the basis of specific solvation taking place in the reaction media.***

From the evaluated value of Iso-kinetic temperature of the reaction, which is 336.7, it is inferred that there is strong solvent-solute interaction in water-DMF media.

Keywords: Efficiency, Salicylate ester, Electrostatic effect, Iso-dielectric, Iso-composition, Activation parameters, Solvation phenomenon, Mobile transition state, Ion-molecular.

I. INTRODUCTION

The effect of solvent on the alkali catalysed hydrolysis of esters have received a large number of attention from time to time[1-2] but the explanations put forward for them are not satisfactory. Considering ester hydrolysis as ion-dipole type and assuming the predominance of electrostatic effects, Ingold[3] as well as Laidler[4] have predicted a decrease in rate with decreasing dielectric constant of the medium, for which there is general experimental evidence. However, on the basis of solvation phenomenon, Parker[5] predicted a rate enhancement in case of ester hydrolysis by dipolar-aprotic solvents like DMSO etc. and this view has been supported by Reberts[6] However, the decrease in rate of ester hydrolysis upon addition of these solvents has also been observed earlier[7-9] and recently[10] and therefore, more works are needed to establish the mechanism of solvation and the effect of dielectric constant. Among the esters studied thoroughly so far, the esters having medicinal efficiency like salicylates appear to have received very little attention in this regard. Therefore, it is thought worthwhile to study the effect of a typical dipolar aprotic solvent DMF on the rate as well as on the various activation parameters of alkali catalysed hydrolysis of Butyl salicylate at different temperatures to arrive at some definite conclusions regarding the effect of DMF on the medicinal potential of salicylate particularly in removing the joint pain of living being.

II. EXPERIMENTAL

All the chemicals used were either of BDH (AnalR) or Merck (CP) grade and all were purified before their use. The kinetics of alkali catalysed hydrolysis of Butyl salicylate was studied in water-DMF media having varying concentration of DMF from 30 to 80% (v/v) at five different temperatures ranging from 20 to 40°C. The strength of reaction mixture was fixed 0.1M and 0.05 M with respect to alkali (NaOH) and ester respectively.

The reaction was found to obey 2nd order kinetic equation and the evaluated value of specific rate constants of the reaction have been recorded in Table - 1. The value of Iso-composition activation energy (E_C). Iso-dielectric activation energy (E_D) and

Table - I
Specific Rate Constant values of Alkali Catalysed Hydrolysis of Butyl Salicylate in water-DMF media.
$kx10^3$ in $(dm)^3$ $mole^{-1}$ min^{-1}

Temp in °C	% of DMF (v/v)					
	30%	40%	50%	60%	70%	80%
20° C	56.29	44.88	36.64	29.25	23.81	17.74
25° C	111.71	96.36	79.03	65.74	54.94	42.54
30° C	228.88	196.43	71.83	147.16	128.00	109.91
35° C	426.27	393.37	353.83	315.21	279.96	230.25
40° C	869.16	794.15	732.99	674.37	613.34	524.93

thermodynamic activation parameters of the reaction have been enlisted in Table - II, III and IV rtespectively

III. RESULTS AND DISCUSSION

A. Solvent Effect on the rate of reaction:

From Table-1, it is obvious that rate constant values are markebly decreas-ing with the progressive addition of DMF at all the temperatures. Since DMF has a lower dielectric constant value than water, the bulk dielectric constant of the medium will be found to decrease and this will disfavour the formation of higher polar transition state.

DMF being a poor anion solvent[10] its increase in the aqueous mixture will naturally facilitate the desolvation of ions already solvated by water, forming a DMF-water associated species[11]. Since the initial and the transition states (all being anions differing in size and charge) cannot be equally desolvated, the rate will naturally be effected by such specific solvation changes. Experimentally it has been observed that the rate decreases with increas-ing DMF in the medium and thus, it appears that the phenomenon of desolvation is more dominant in the transition state than that in the initial state and that is why the activation energy has been found to increase. Similar findings have also been reported recently by Singh & Kumari[12] and Singh and Sing[13]

B. Effect of temperature and solvent on the Iso-composition Activation Energy

Rate constant values of the reaction were found to increase with increasing temperature in accordance to the Arrhenius law, yielding a good straight line for the plots of log k against 1/T. The E_{exp} or E_C (Iso-composition activation energy) values are shown in Table - II. The E_C values increase from 104.63 to 129.96 kJ/mole with increasing proportion of DMF from 30 to 80% (v/v) in the reaction $media_{exp}$

The probable causes for enhancement in the value of iso-composition activa-tion energy of the reaction is desolvation and solvation of the transition and initial states respectively, which is also supported by the increase in the values of entropy of activation as recorded in Table - IV. Such finding and their interpretations have also been supported by Singh et al[14]. and recently by Singh & Mishra et al[15].

C. Solvent Effect on the Iso-dielectric Activation Energy of the reaction

The values of Iso-dielectric Activation Energy of the reaction at different desired dielectric constant values of the media have been evaluated by the process reported by Esemongy et al[16] and are recorded in Table III.

From the values recorded in Table - III, it is obvious that E_D values are found to decrease from 134.23 to 107.45 kJ/mole with increasing D values from 55 to 70 respec-

Table - II
Iso-composition Activation Energy (E_c or E_{exp}) of the reaction

% of DMF (v/v)	30%	40%	50%	60%	70%	80%
E_{exp} value kJ/mole	104.63	108.88	114.85	120.18	123.23	129.96

tively of the reaction media. This trend of change (depletion) in E_D values is in harmony with the enhancement in E_C values with increasing concentration of DMF in the reaction media.
Such findings are quite natural and are supported by the report of Dubey and Singh[17] and also by recent researches of Singh & Kumari et al[18].

D. Solvent Effect on the Thermodynamic Activation Parameters of the reaction
The evaluated consolidatd values of the thermodynamic activation param-eters, ΔH*, ΔG* and ΔS* are mentioned in Table IV. The increase in ΔG* is a sign of specific desolvation of the transition state. This is in agreement with our view that the tran-sition state is less solvated or desolvated with addition of DMF in the mixture. Elsemongy[16] and Cleve[19] have observed a similar increase in ΔG* values. Thus from Table - IV. it is apparent that ΔH* and ΔS* values of the reaction are increasing with simultaneous en-hancement in ΔG* values. According to one of the fundamental thermodynamic equations

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

the above noted observation is only possible when enhancement in ΔH* is greater than that observed in ΔS* and thus the reaction is enthalpy dominating. Such observations and infer-ences have been found to be supported by the recent reports of Singh & Kumari[20]

E. Obeyancy of Barclay - Butler Rule and Solvent-solute interaction in the water-DMF Reaction Media
As recorded in Table IV, both the values of ΔH* and ΔS* are found increasing and the increase being quite smooth. Iso-kinetic relationship between ΔH* and ΔS* are obeying Barclay and Butler[21] rule giving an excellent straight line when ΔH* is plotted against ΔS*. The numerical value of slope of the plots which determine the value of Iso-kinetic temperature is found to be 336.70.
The increase in ΔH* and ΔS* values suggests the formation of more mobile transition state which supports the contention of desolvation of the transition state. On the guidelines of Leffler[22], from the evaluated value of Iso-kinetic temperature of the reaction which is greater than 300 (336.70), it is inferred that there is appreciable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to much stronger interaction between solvent and solute present in the water-DMF reaction media.
Similar observations and inferences have also been reported recently by Singh & Kumari et al[23].

F. Effect of Ionic strength on the rate of reaction
There is negligible influence of the ionic strength on the reaction rate. This suggest that the reaction is not ion-ion, but ion-molecular in nature.

Table –III
Iso-dielectric Activation Energy(E_D) of the Reaction

D valus of Aquo-DMF mixture	D = 55	D = 57.5	D = 60	D = 62.5	D = 65	D = 67.5	D = 70
E_D kJ/mole	134.93	127.97	125.42	122.96	114.85	111.19	107.45

Table - IV

Activation Parameters of Alkali Catalysed Hydrolysis of Butyl Salicylate in water - DMF solvent system
ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of DMF (v/v)	Mol % of DMF	ΔH* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
30%	9.12	103.35	83.08	69.18	82.86	68.75	82.49	68.84	882.18	68.73	81.82	68.78
40%	13.58	106.32	83.65	77.37	83.23	77.48	82.87	77.39	82.50	77.34	82.05	77.53
50%	18.96	112.27	84.15	95.97	83.72	95.80	83.16	96.07	82.77	95.77	82.27	95.84
60%	25.98	117.50	84.69	111.97	84.18	111.81	83.60	111.88	83.07	111.78	82.48	116.88
70%	35.27	122.48	85.18	127.30	84.68	126.84	83.95	126.16	83.37	126.98	82.72	127.02
80%	49.28	126.19	85.91	137.47	85.26	137.35	84.34	138.12	83.87	137.40	83.13	137.57

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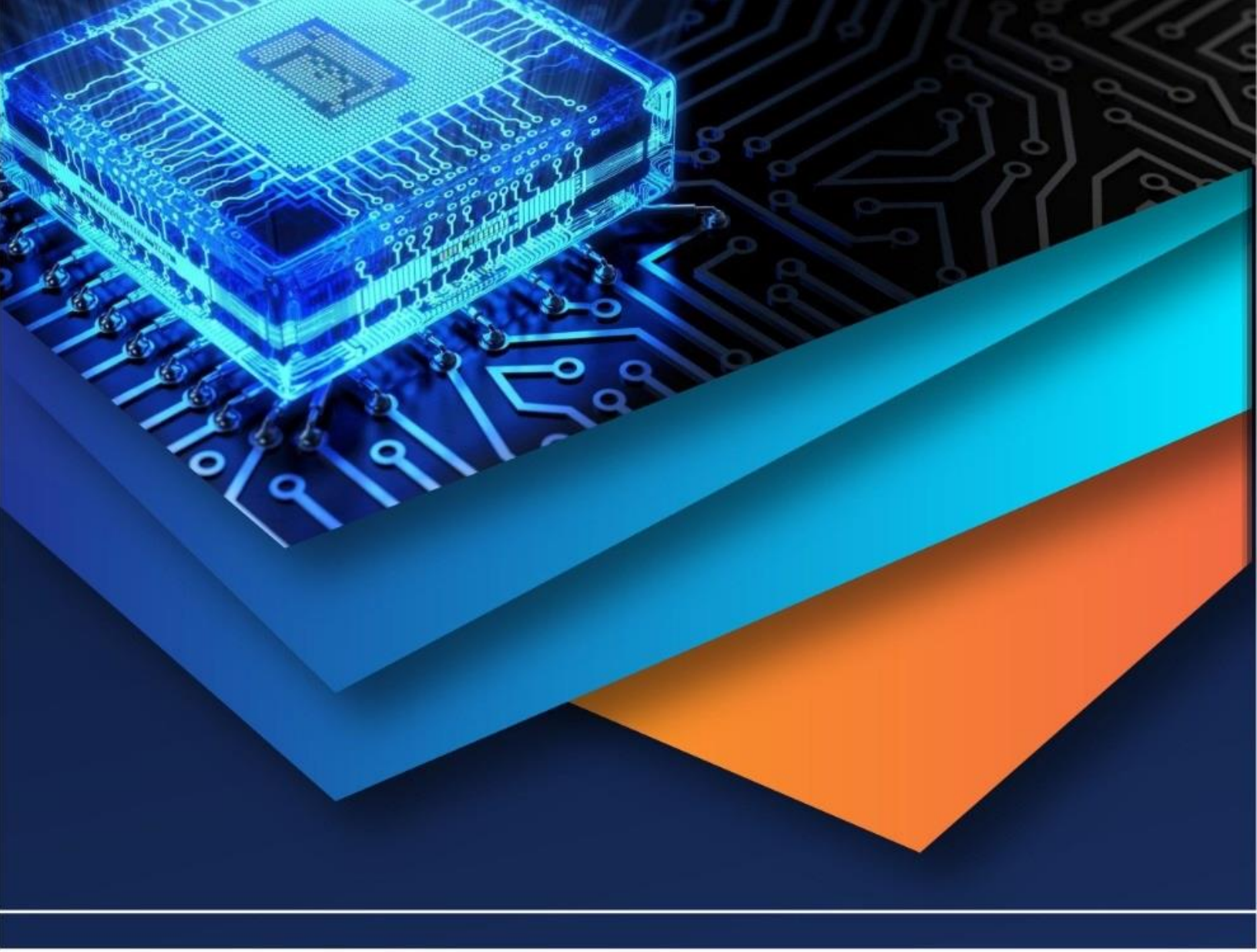

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