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EFFECT-OF-DMSO ON THE THERMODYNAMIC ACTIVATION PARAMETERS, ACTIVATION ENERGIES AND SOLVENT-SOLUTE INTERACTION OF CATALYSED SOLVOLYSIS OF CAPRYLATES

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ABSTRACT

The kinetics of the solvent effect of aquo-DMSO media on the catalysed hydrolysis of the ester Methyl caprylate was studied separately in different reaction media consisting of different concentration of DMSO ranging from 20 to 80% (v/v).

It has been observed that ΔH^* and ΔS^* of the reaction were found to increase simultaneously with increase in ΔG^* values and from this, it has been inferred that the reaction is enthalpy dominating and entropy deplething.

From enhancement in E_C values with increase in DMSO content of the reaction media and from depletion in E_D values with increase in D values of the aquo-DMSO media, it has been inferred that the initial state and the transition states of the reaction are solvated and desolvated respectively.

From the evaluated numerical values of the Iso-kinetic temperature of the reaction which comes to be 325.11, it is concluded that there is strong and appreciable interaction between solvent and solute in aquo-DMSO reaction media.

KEYWORDS :- *Activation Parameters, Activation Energies, Barclay- Butler Rule, Iso-kinetic temperature, Solvent-Solute Interaction*

INTRODUCTION :

Though a large number of researchers[1,2] have reported their Findings on the solvent effect on various types of reactions, but the study of solvent effect of dipolar aprotic solvent like DMSO, on the usefulness of the solvolytic product of caprylate ester i.e. Caprylic acid as dyes, drugs and synthetic flavour has not been paid even a little attention so far. So, in

order to highlight the above noted idea, it was thought essential and useful to investigate about the fact that how the uses of Caprylic acid is made more effective for manufacturing quality dyes, drugs and synthetic flavour.

Experimental :

The kinetics of alkali catalysed solvolysis of Methyl caprylate was studied by adding different concentration of the aprotic organic co-solvent (DMSO) from 20 to 80% (v/v) in the reaction media at five different temperatures i.e. 20, 25, 30, 35 and 40°C by usingh previously reported methods[3]. The specific rate constants were evaluated using second order kinetic aquation and have been mentioned in Table - 1.

The thermodynamic activation parameters namely free energy of activation (ΔG*), enthalpy of activation (ΔH*) and entropy of activation(ΔS*) of the reaction were determined by using Wynne-Jones and Eyring equation[4] and are synchronised in Table - II.from the slopes of the Arrhenius plots of log k versus 1/T and that of log K_D (obtained from interpolation of the plots of log k against D values of aquo-DMSO solvent system) versus 1/T the values of Iso-composition activation energy (E_C) and Iso-dielectric activation energy (E_D) of the reaction have been evaluated and are recorded respectively in Tables - III and IV.

Solvent effect of the Thermodynamic Activation Parameters of the Reaction:

The evaluated values of the three thermodynamic parameters namely ΔH*, ΔG* and ΔS* and synchronised in Table-II and their variation with mole % of the organic content (DMSO) of the reaction media have been observed from their plots.

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Table - I

Specific rate constant values of Alkali catalysed hydrolysis of Methyl caprylate in water-DMSO media

$K \times 10^3$ in $(dm)^3$ $mole^{-1}$ min^{-1}

Temperature in °C	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	89.08	75.61	60.70	50.13	40.11	32.46	24.67
25°C	182.05	157.98	131.86	112.80	96.52	79.41	63.07
30°C	363.50	333.73	281.13	251.36	218.73	189.71	162.67
35°C	733.50	645.80	600.76	549.79	478.41	434.91	391.02
40°C	1408.64	1318.86	1224.05	1122.28	1052.93	999.08	933.04

Table – II

Consolliaed valus of Thermodynamic Activation Parameters (ΔH*,ΔG*and ΔS*) of the reaction in water-DMSO solvent systems at different temperatures

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of DMSO (v/v)	Mol % of DMSO	ΔH* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
20%	5.94	103.38	87.59	53.87	87.36	53.75	87.12	53.64	86.81	53.80	86.56	53.73
30%	9.77	106.65	87.99	63.68	87.99	63.56	87.34	63.74	87.13	63.37	86.73	63.65
40%	14.40	111.50	88.53	78.39	88.53	78.32	87.78	78.30	87.32	78.51	86.92	78.51
50%	20.17	115.75	88.99	91.33	88.99	91.30	88.05	91.42	87.54	91.58	87.15	91.38
60%	27.49	122.24	89.54	111.61	89.54	111.73	88.40	111.67	87.90	111.49	87.38	111.57
70%	37.09	128.40	90.05	130.88	90.05	130.83	88.76	130.82	88.14	130.71	87.45	130.83
80%	50.27	135.91	90.72	154.21	90.72	154.10	89.15	154.31	88.42	154.18	87.63	154.24

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Table – III

Evaluated values of Iso-composition Activation Energy (E_C or E_{exp}) of the reactionwater-DMSO media.

% of DMSO	20%	30%	40%	50%	60%	70%	80%
E_C	105.84	109.38	115.71	118.56	123.99	130.68	138.68

Table – IV

Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at Different-Desired 'D' values of water-DMSO media.

D values	D= 60	D = 64	D = 68	D = 72	D = 76	D = 80
E_D values in kJ/mole	148.33	141.76	134.87	128.80	123.09	117.58

On perusal of the data in Table - II, it is found that the values of free energy of activation (ΔG*) increases with increasing DMSO content of the reaction at all the temperature at which the reaction was studied. AT 30°C, values of ΔG* were recorded increasing from 87.12 kJ/mol to 89.15 kJ/mol with increasing proportion of DMSO from 30 to 80% (v/v). Though the enhancement in ΔG* values is not very high, however, it is liable to be taken into consideration.

Similar variation in ΔG* values with increasing mol % of organic solvent of the reaction media have also been reported earlier by Singh & Singh et al.[5] and recently by kishor & Singh et al.[6] From the plot of ΔG* against mol % of organic co-solvent,it is found that ΔG* values increases smoothly and non-linearly with gradual addition of DMSO in the reaction media. This finding is indicatiove of desolvation of reactants as explained and also supported

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by Elsemongy et al.[7]So far as tha variation in ΔH* and ΔS* values are concened, on going through Table-IV, it is interestiongly observed that both of them decrease with gradual increase in the concentration of DMSO in the reaction media at all the temperatures.

On the besis of the relation

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

it can be concluded that simultaneous enhancement in ΔG* values with increase in the values of both the ΔH* and ΔS* is only possible when the extent of increase in ΔH* is more than that of ΔS*. The regular enhancement to the greater extent in ΔH* values in comparisoon to that of ΔS* values clearly indicates that the alkali catalysed hydrolysis of Methyl caprylate in aquo-DMSO media is enthalpy dominated and entropy inhibited. Moreover, non-linear variation in ΔH* and ΔS* values with increasing mol % of DMSO in the rection media, gives information of the fact that the specific solvation is taking place in aquo-DMSO systems, similar to that as reported by Saville et al.[8] and it also indicates that the random distribution of the components are not permissible. The similar non-linear varriations in ΔS* and ΔH* values with increasing mol % of the organic component in the reaction media have been reported easlier by Kumar[9], Singh & Lal et al.[10] and recently also by Singh & Singh[11] The enhancement in both ΔH* and ΔS* values also justifies that transition state of the reaction is desolvated and its initial state is solvated in aquo-DMSO reaction media.

Solvent Effect on the Iso-composition Activation Energy (E_C) of the Reaction: From the slopes of the Arrhenius plots of log k versus $10^3/T$ the values of Iso-composition activation energy (E_C) of the reaction have been evaluated and recorded in Table-III. From Table -III, it is obvious that iso-composition activation energy values of the reaction go on increasing from 105.84 kJ/mol to 138.68 kJ/mol with increasing concentration of DMSO in the reaction media from 20 to 80% (v/v).

The enhancing trend in the E_{exp} value may be due to either of the following three causes:

(i) The initial state is more solvated than the transition state,

(ii) The transition state is more desolvated than the initial state, and

(iii) The initial state is solvated and the transtion state is desolvated.

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Out of these three causes, the factor seems to be operative in this case as both ΔH* and ΔS* values of the reaction as mentioned in Table - II, are found to increase. Such findings have been reported earlier by Singh & Perween et al.[12] and Wats & Singh et al.[13]. Similar interpretations have also been support of the recent reports of Sushma & Singhet al.[14]

Solvent Effect on the Iso-dielectric Activation Energy (E_D) of the Reaction:

Similar to Iso-composition activation energy (E_C), the values of Iso-dielectric activation energy (E_D) were also calculated from the slopes of the Arrhenius plots of log k_D versus $10^3/T$. From the recorded values of the Iso-dielecttric activation energy (E_D) of the reaction in Table - IV, it is apparent that with increase in D values of the reaction media from D = 60 to D = 80, the E_D values go on decreasing from 148.33 kJ/mol to 117.58 kJ/mol respectively. Since with increase in DMSO content of the reaction media there is decrease in its dielectric (D) values, hence in reverse way it may be inferred that with

Table - V

Variation of ΔH*, ΔG* and ΔS* values of the reaction with mole % of DMSO inwater-DMSO media

% of DMSO (v/v)	Mol % of DMSO	ΔH* in kJ/mol	ΔG* (at 30°C) in kJ/mol	ΔS* at 30°C in J/K/mol
20%	5.94	103.38	87.12	53.64
30%	9.77	106.65	87.34	63.74
40%	14040	111.50	87.78	78.30
50%	20.17	115.75	88.05	91.42
60%	27.49	122.24	88.40	111.67
70%	37.90	128.40	88.76	130.82
80%	50.27	135.91	89.15	154.31

decrease in D values of the reaction media or with increasingh DMSO concentration in it, E_D values also increase similar to increase in E_C values. Thus, E_C and E_D values are complementary to each other. Similar interpretations for such effect of concentration of the added organic content of the media or of the effect of change in dielectric sonstants of the reaction media have also been reported earlier by Kumar & Singh et al.[15] and recently by Raghaw & Singh et al.[16]

Solvent effect on the Iso-kinetic Temperature of the Reaction and Solvent-solute Interaction in the Aquo-DMSO Reaction Media:

The values of the Iso-kinetic temperature of the reaction was evaluated by using Barclay and Butler[17] relationship which is as follows:

$$\delta m\,(\Delta H^*) = \beta\,\delta\,m\,(\Delta S^*)$$

It is a straight line equation presenting the relationship between enthalpy and entropy of activation. 'β' is iso-kinetic temperature. From the data available in Table - V, the plots of ΔH* versus ΔS* at 30°C were made. From the slope of the obtained straight line, the value of iso-kinetic temperature was found to be 325.11 ≈ 325.0. In the light of Leffler's[18] guidelines, from the value of iso-kinetic temperature which is much higher than the standard value 300, it is concluded that in aquo-DMSDO media, there is appreciably strong solvet-solute interaction for alkali catalysed solvolysis oxf Methyl caprylate. Similar observation, inferences and interpretations have also been reported earlier by Navendu & Singh et al.[19] and recently by Sushma-Abhay & Singh et al.[20]

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