EFFECT OF AQUO-N-PROPANOL SOLVENT SYSTEMS ON THE MEDICINAL EFFICIENCY OF HEAVY PROPIONATES

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Abstract

For highlighting the Solvent-effect of a diapolar aprotic solvent, n-propanol on the biochemical behaviour of propionate ester, the kinetics of alkali catalysed hydrolysis of butyl propionate was carried out in aquo-n-propanol solvent systems having different concentration of the organic component (n-propanol) varying from 20 to 80% (v/v) at different temperatures ranging from 20 to 40°C.

The number of water molecules associated with the activated complex of the reaction were found to increase from 0.338 to 1.401 and from this, it is it inferred that n-propanol acts as structure breaker of water converting its dense form into bulky form and it changes the mechanistic path way of the reaction from bimolecular to unimolecular,

From the numerical value of the kinetic temperature of the reaction, which is evaluated to be 281.0, it is concluded that there is weak but appreciable interaction between solvent and solute in the reaction media.

Keywords: Heavy propionate, medicinal efficiency Bacterial Infection, Mechanism, Thermodynamic Activation parameters, Solvent-Solute Interaction.

INTRODUCTION:

The fact that the solvent affects, the rate as well as mechanism of the solvolysis reaction in water organic co-solvent media has aroused much interest and inquisitiveness in the mind of researchers.

Though a large number of works have been reported[1-5] on the solvent effect on various types of reactions but the study of solvent effect on the biochemical bahaviour of propionate ester has not been paid adequate 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 biochemical behaviour of propionates is made more effective for healing the wound on the body due to bacterial infection.

EXPERIMENTAL:

The kinetics of alkali catalysed solvolysis of Butyl propionate was studied by adding different concentration of the protic organic co-solvent (n-. propanol) from 20 to 80% (v/v) in the reaction media at five different temperatures i.e. 20, 25, 30, 35 ånd 40°C as usual methods.[6,7]. The specific rate constants were evaluated using second order kinetic equation and have been mentioned in Table - I. .

From the plots of logk values versus log [H_2O]. values as mentioned in Table - II, their slopes value were evaluated and have been inserted in Table - III. ·

From the values of the specific rate constant values, thermodynamic activation parameters namely free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) of the reaction were calculated by using Wynne Jones and Eyring[8] equation and are synchronised in Table - IV.

From the slopes of the Arrhenius plots of log k versus 1/T and log k_D (obtained from interpolation of the plots of log k against D values of water-npropanol solvent system) versul 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 - V and VI.

RESULTS AND DISCUSSION:

Determination of Mechanistic path followed by the reaction:

The mechanism of the reaction was ,determined by evaluating the number of water molecules involved in the formation of activated complex. It was done by, plotting log k against log[H_2O] by using the relation proposed by. Robertson[9], which is as;

log k= log k_0 +n log[H_2O]

where 'n' is the solvent number (number of water molecules associated with the activated complex) wich is evaluated from the slopes of the plots of log k versus log [H_2O] and tells about the criterian for studying the mechanism of the reaction.

From the values mentioned in Table - II, the plots of log k versus log [H_2O] are shown in Fig. - 1. It is obvious from Fig. - 1 that at each temperature, there come two intersecting straight lines having different values of positive slopes at each temperature are mentioned in

Table - III. : From Table - III, it is clear that below log [H_2O] value 1.456 which corresponds to 51.64% of water in water-n-propanol media, the number of water molecules associated with the activated complex increases from 0.338 to 0.778. Similarly, above log [H_2O] value 1.456 i.e. above 51.64 %, concentration of water in the reaction media, the number of water molecules involved in the formation of the activated complex increases from 0.541 to 1.401.

From the increasing number of water molecules involved in the formation of the activated complex, it is inferred that n-propanol in the reaction media acts as structure breaker and it shifts the equilibrium of water from its dense form to its bulky form and in the light of guidelines of Robertson et al[10], it is concluded that the mechanistic pathways of the reaction in presence of n-propanol is changed from bimolecular to unimolecular. Such findings and inferences are in support of the views of Upadhyay & Singh[11] and also with the recent report of Singh & Bala et al[6] and Singh & Singh et al.[12]

Solvent effect on the Thermodynamic Activation Parameters :

On perusal of the data mentioned in Table - IV, it is found that the values of free energy of activation (ΔG^*) increase with increasing npropanol content of the reaction at all the temperature at which the reaction was studied. At 30°C, values of ΔG^* were reported to increase from 87.77 kJ/mol to 90.22 kJ/mol with increasing proportion of n-propanol from 20 to 80% (v/v). Though the enhancement in ΔG^* values is not very high, however, it is up to mark for taking into consideration.

A similar variations in ΔG^* values with increasing mol % of organic solvent has also been reported by Singh & Singh et al.[12]. From the plot of ΔG^* against mol % of organic co-solvent (as shown in Fig. - 2) it is found that ΔG^* values increases smoothly and non-linearly with gradual addition of n-propanol in the reaction media. This finding is indicative of desolvation of reactants as explained and also supported by Elsemongy et al.[13]

So far as the variation in ΔH^* and ΔS^* values are concerned, on going through Table - IV, it is interestingly observed that both of them decrease with gradual increase in the concentration of npropanol in the reaction media at all the temperatures.

On the basis of the relation:

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

it can be concluded that simultaneous enhancement in ΔG^* values with depletion in the values of both ΔH^* and ΔS^* values is only possible when the extent of depletion in ΔS^* is more than that of ΔH^*. The regular depletion to the greater extent in ΔS^* values in

comparison to that of ΔH* values clearly indicates that the alkali catalysed hydrolysis of Butyl propionate in water-n-propanol media is entropy controlled. Moreover, non-linear variation in ΔS* and ΔH* values with increasing mol % of n-propanol in the reaction media, as shown in Fig. - 3 and 4 respectively, gives information of the fact that the specific solvation is taking place in water-n-propanol systems, similar to that as reported by Saville et al[14] and it also indicates that the random distribution of the components are not permissible. The similar nonlinear variations in AS* and AH* values with increasing mol % of the organic component in the reaction media have also been reported recently by Singh & Perween et al[15] and Kumari & Singh et al.[16] The depletion in both ΔH* and ΔS* values justifies that transition state is less desolvated in comparison to initial state in water-n-propanol media.

Solvent Effect and evaluation of Isocomposition Activation Energy:

From Table - V, it is obvious that iso-composition activation energy values of the reaction go on decreasing from 101.19 kJ/mol to 80.94 kJ/ mol with increasing concentration of n-propanol in the reaction media.

The decreasing trend in the E value may be due to either of the following three causes:

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

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

   (iii)   The transition state is less desolvated than the initial state.

Out of these three causes, the third factor seems to be operative in this case as both ΔH* and ΔS* values of the reaction as mentioned in Table - IV, are found to decrease. Similar findings have also been reported recently by Singh & Bala et al.[6]. Singh & Priyanka et al.[7] and Monalisa & Singh et al.[17].

Solvent Effect on the Iso-dielectric Activation Energy (EP) pf the Reaction:

From the recorded values of the Iso-dielectric activation energy (E_D) of the reaction in Table - VI, it is apparant that with increase in D values of the reaction media from D=25 to D= 60, the E_D values go on increasing from 91.85 kJ/ mol to 112.82 kJ/mol respectively.

Since with increase in n-propanol content of the reaction media there is decrease in its dielectric (D) values, hence in reverse way it may be inferred that with decrease in D values of the reaction media or with increasing n-propanol concentration in the reaction media, E_D

values also decrease similar to decrease in E_C values. Thus, E_C and E_D values are complementary to each other.

Similar interpretation for such effect of concentration of the added organic content of the media or of the effect of change in dielectric constants of the reaction media have also been reported recently by Monalisa & Singh et al.[17] and Singh & Singh et al.[18].

Solvent effect on Iso-kinetic Temperature:

The values of the Iso-kinetic temperature of the reaction was evaluated by using Barclay and Butler[9] relationship which is as follows:

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

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 - IV, the plots of ΔH^* versus ΔS^* at 30°C were made and from the slope of the obtained straight line, the value of isokinetic temperature was found to be $281.21 \approx 281$. In the light of Leffler's[20] guidelines, from the value of iso-kinetic temperature which is less than the standard value 300, it is concluded that in water n-propanol media, there is weak but appreciable solvent-solute interaction for alkali catalysed solvolysis of Butyl propionate. Similar findings have also earlier been reported earlier by Kumari Singh et al.[21] and recently by Namrata & Singh et al.[22].

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Table - I

Alkali catalysed hydrolysis of Butyl propionate in water-n-propanol media.

$k \times 10^3$ in $(dm)^3$ mol^{-1} min^{-1}

Temp in °C	% of n-propanol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	62.94	56.26	53.69	49.45	49.81	39.77	35.33
25°C	126.07	112.25	104.66	94.65	86.10	70.73	61.35
30°C	281.77	237.79	199.71	177.87	151.60	134.99	101.19
35°C	541.25	455.93	396.92	346.82	281.77	230.04	170.26
40°C	1083.18	848.98	726.27	629.22	518.08	405.70	303.11

Table - II

Variation of log k values of the reaction with log [H$_2$O] values of water-n-propanol system (media) at different temperatures.

% of n-propanol (V/V)	% of water	log [H$_2$O]	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.7989	2.1006	2.4499	2.7334	3.0349
30%	70%	1.5898	1.7502	2.0502	2.3762	2.6589	2.9209
40%	60%	1.5229	1.7299	2.0198	2.3004	2.5987	2.8611
50%	50%	1.4437	1.6942	1.9761	2.2801	2.5401	2.7988
60%	40%	1.3468	1.6416	1.9358	2.1801	2.4499	2.7144
70%	30%	1.2218	1.5996	1.8496	2.1303	2.3618	2.6082
80%	20%	1.0458	1.5482	1.7878	2.0261	2.2311	2.4816

Table -IV

Thermodynamic Activation parameters of the reaction in water-n-propanol media

ΔH^* and ΔG^* in kJ/mole, ΔS^* in J/K/mole

% of n-propanol (v/v)	Mole % of n-propanol	ΔH^* in kJ/mole	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20%	5.66	106.99	88.57	63.06	88.27	62.82	87.77	63.45	87.58	63.01	87.24	63.10
30%	9.33	103.02	88.71	48.84	88.56	48.55	88.19	48.95	88.02	49.18	87.88	48.39
40%	13.79	98.18	88.83	31.96	88.73	31.75	88.63	31.55	88.38	31.86	88.28	31.66
50%	19.35	64.64	89.03	19.16	88.86	19.41	88.92	18.86	88.72	19.20	88.66	19.12
60%	26.67	91.14	89.32	06.01	89.21	06.60	89.33	05.97	89.26	06.11	89.16	06.32
70%	35.90	87.01	89.56	-8.70	89.70	-9.34	89.62	-8.62	89.78	-8.98	89.80	-8.91
80%	48.98	78.90	89.85	-37.37	90.05	-37.44	90.22	-37.39	90.55	-37.83	90.56	-37.25

Table – V

Values of the slopes of the plots of log k versus log [H₂O] values at different temperatures

Temperature in °C	Slope - I Where log[H₂O] value is below 1.456	Slope - II when log[H₂O] value is above 1.456
20°C	0.338	0.541
25°C	0.488	0.693
30°C	0.583	0.962
35°C	0.738	1.153
40°C	0.778	1.401

Table - VI

Evaluated Values of Iso-composition Activation Energy (E_C or E_{exp}) of the reaction in water-n-propanol media.

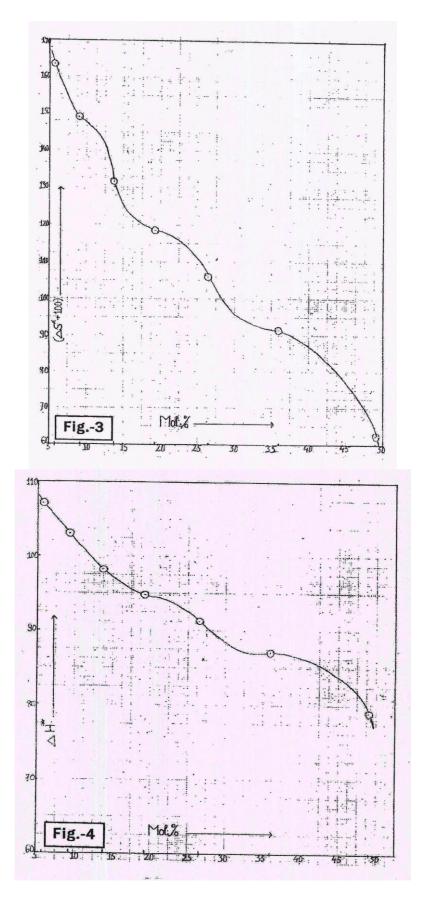| % of n-propanol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C values in k/J/mol	109.19	105.11	99.66	97.14	93.25	88.97	80.94

Table - VII

Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at desired 'D' values of the water-n-propanol media.

D values	D= 25	D = 30	D = 35	D =40	D = 45	$\frac{D}{50}=$	D=55	D=60
E_D values in kJ/mole	91.85	95.71	98.43	100.31	102.75	105.48	109.82	112.82

Fig.-1

Fig.-2

Fig.-3

Fig.-4