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A COMPREHENSIVE KINETIC STUDY OF THE EFFECT OF AQUO-PRIMARY ALCOHOL SOLVENT - SYSTEMS ON THE MEDICINAL EFFICIENCY OF CAPROATE ESTER

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Abstract

The medicinal efficiencies of propyl Caproate as a pharmaceutical were quantitatively determined by evaluating the changes in extensive thermodynamic properties of its solvolysis reaction in aquo-n-propanol media.

It was observed that the values of iso- composition activation energy (E_C) go on increasing with gradual addition of the organic cosolvent, but the values of iso-dielectric activation energy (E_D) of the reaction was found decreasing with increasing dielectric constants of the reaction media.

From the evaluated value of iso kinetic temperature (327) of the reaction, it is concluded that in this reaction media (water-n-propanol), there is appreciably strong solvent-solute interaction.

Keywords:- *Solvolysis, Caproate Ester, Solvent Systems, Solvent-solute interaction, Depletion, Specific Solvation Uni and Bimolecular, Iso-kinetic temperature.*

Introduction:

On the studies of the kinetics of hydrolysis of simple amide esters, a large number of reports[1-4] are available, but the study of the effect of solvent on the hydrolysis of ester having longer carbon chain has not been paid adequate attention so far. It seems essential to study the solvent effect on the alkali catalysed solvolysis of the Propyl Caproate (Propyl caproate) as it is thought to be fruitful from industrial as well as medicinal points of views. Hence, in order to highlight the above noted untouched work, it has been proposed to study the solvent effect of n-propanol on the alkali catalysed solvolysis of Propyl Caproate in water-n-propanol media.

Experimental:

The kinetics of alkali catalysed solvolysis of Propyl Caproate was studied in water-n-propanol media having varying composition of the reaction media, separately prepared by adding 30 to 80% of n-propanol in it. The reaction mixture was prepared such that its strength in terms of ester as well as alkali were kept 0.05 M and 0.1 M respectively. The temperatures of the reaction were varied from 20 to 40°C. The reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants are recorded in Table - I. The evaluated values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) have been mentioned in Tables -II and III respectively. The evaluated values of thermodynamic activation parameters, ΔH*, ΔG* and ΔS* have been tabulated in Table-IV.

Results and Discussion:

Effect of Solvent on Iso-composition Activation Energy (E_C or E_{exp}) :

After making observation of the values of E_{exp} in Table - II, it is clear that there is enhancement in the E_{exp} values with increase in the concentration of n-propanol in the reaction media. The E_{exp} values increases from 64.18 kJ/mol to 88.89 kJ/mol. It has been established that changes in the values of activation energy are obviously noticeable only when the solvation changes take place either in the initial state level or at the transition state level or at both the levels. The increase in the activation energy of the reaction with decrease in the specific rate constant values may not seem to be quite natural. The following three possibilities may be held responsible for enhancement in the values of E_{exp}:

(i) The transition state is more desolvated than the initial state,
(ii) The initial state is more solvated than the transition state, and
(iii) The transition state is desolvated and the initial state is solvated.

Out of these three factors, the third one seems to be applicable in our case as this factor is supported by the increase in the values of entropies of activation as depicted ahead in Table - V. This conclusion has also been supported by recent works of Singh & Dubey et al[5].and Singh & Singh et al.[6].

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

From the values of E_D as tabulated in Table - III, it is apparant that there is decrease in the values of iso-dielectric activation energy (E_D) of the reaction with increase in dielectric constant values of Aquo-npropanol reaction media.

The E_D value of the reaction is 87.27 kJ/mol at D value 25 and decreases to 70.13 kJ/mol at D value 55 of the reaction media.As D values of water-n-propanol media go on decreasing with addition of n-propanol to it, so in other way, it may be inferred that like E_C or E_{exp} values of the reaction, its E, values are also increasing with addition of n-propanol in the reaction media.

However, such findings and inferences about the E_D values are quite natural and are fully in support of the views of Elsemongy[7], Wolford[8] and have also recently been supported by Singh & Singh[6], Singh and Kumari[9] and Singh & Perween[10].

Solvent Effect on the Thermodynamic Activation Parameters of the reaction:

The thermodynamic activation parameters such as enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG* are supposed to be better indicators of the solvent effects displayed by the solvent on the solvolysis reactions. These thermodynamic activation parameters have been evaluated with the help of Wynne Jones and Eyring[11] equation.

The values of all these three thermodynamic parameters i.e. ΔH*, ΔS* and ΔG* at different mol % of the organic component (n-propanol) of the reaction media have been synchronized in Table - V. The variation in ΔH*, ΔG* and ΔS* with mol % of the organic component of the watern-propanol mixtures may be studied with their plots against mol % of n-propanol in the reaction media. On careful observation of the data, it is found that ΔG* value increases from 89.45 kJ/mol to 91.01 kJ/mol with change of proportion of n-propanol from 30 to 80% (v/v) at 30°C. Though the enhancement is not very large, however it cannot be ignored rather must be taken into consideration.

A similar variation in ΔG* values with increasing mol % of organic co-solvent has also been reported recently by Singh & Perween[10] and Singh & Kumari[12]. This gradual non-linear increase in ΔG* values with increase in mol % of the organic component in the reaction media is indicative of solvation or desolvation of reactants as explained by Absolute Reaction Rate Theory[13].

So far as the variation in ΔH* and ΔS* are concerned, it is clear from Table - V that both of them increase with increasing mol % of n-propanol in the reaction media. However, on perusal of the Table - V, it is interestingly observed that out of all the three thermodynamic parameters of the reaction namely ΔG*, ΔH* and ΔS*, all are found to be enhanced simultaneously with increase in mol % of n-propanol of the reaction media.

According to the relation,

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

it can be easily concluded that increase in ΔG* values with simultaneous enhancement in ΔH* and ΔS* values is only possible when the extent of enhancement in ΔS* values is less than that of ΔH*. The regular enhancement to the lesser extent in ΔS* values in comparison to the ΔH* values clearly indicates that the alkali catalysed hydrolysis of Propyl Caproate in watern-propanol media is enthalpy dominating and entropy controlled. Moreover non linearity in ΔH* and ΔS* curves give information of the fact that specific solvation is taking place in water-n-propanol systems as reported by Saville et al.[14] and it also indicates that the random distributions of the components are not acceptable. The similar non linear variations in ΔH* and ΔS* values with increasing mol % of the organic component in the reaction media have earlier been reported by Tommila et al.[15], Upadhya & Singh[16] and recently by Singh & Kumari[12] and Rai & Singh et al[17].

Verfication of Iso-Kinetic Relationship and Solvent Effect on SolventSolute Interaction in the reaction:

Barclay and Butler[18] have developed iso-kinetic relationship between enthalpy of activation ΔH* and entropy of activation ΔS* as follows:

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

where 'β' is a constant called iso-kinetic temperature. Leffler[19] has pointed out that plot of ΔH* against ΔS* results in a straight line and the slope of the line gives the value of iso-kinetic temperature. He pointed out that in many solvolysis reaótions, the values of slope of plots of ΔH* versus ΔS* come in between 300 and 400 and this foretells about the considerably strong interaction between solvent and solute of the reaction mixture.

In the present study also, plots of ΔH* versus ΔS* has been found linear, which is conformity with Barclay-Butler relationship. The numerical value of the slope of the straight line is found to be 327.08 ≈ 327.0 which is much higher than 300. Thus, in light of Leffler's guidelines, from the value of the slope, it can easily be concluded 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 strong interaction between solvent and solute present in the reaction mixture (water-n-propanol media) in the similar way as reported by Leffler[19]. The structural changes with increasing proportion of the n-propanol in water-n-propanol solvent system are responsible for the decrease in the specific rate constant values. However, our this conclusion has also been supported recently by Singh & Priyanka[20], Singh & Singh et al.[21] and Singh & Kumari[22].

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Table - 1

Specific rate constant values of Alkali catalysed hydrolysis of Propyl Caproate in water-n-propanol media

k x 10^3 in (dm)3 mol^{-1} min^{-1}

Temp in °C	% of n-propanol (v/v)					
	30%	**40%**	**50%**	**60%**	**70%**	**80%**
20°C	59.46	50.13	44.33	37.85	30.93	23.77
25°C	91.66	79.36	71.55	63.23	53.73	45.69
30°C	144.48	128.85	116.87	106.44	96.56	77.86
35°C	208.31	195.52	183.27	170.22	158.45	140.54
40°C	316.37	292.30	288.53	277.08	262.24	246.15

Table - II

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)	30%	40%	50%	60%	70%	80%
E_c value in kJ/mol	64.18	68.48	72.07	76.17	81.72	88.89

Table - III

Evaluated values of Iso-composition Activation Energy (E_D) of the reaction at Different Desired 'D' values of the water-n-propanol media.

D values	D = 25	D = 30	D = 35	D = 40	D = 45	D = 50	D = 55
E_D value in kJ/mol	87.27	82.65	80.68	79.04	75.18	72.42	70.13

Table - IV

Consolidated Values of Activation Parameters (ΔH*, ΔG* and ΔS*) of the reaction in water-n-propanol system at different temperatures.

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of n-propanol (v/v)	Mole % of n-propanol	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%	9.33	62.11	88.58	-90.34	89.06	-90.44	89.45	-90.23	90.03	-90.66	90.45	-90.53
40%	13.79	65.33	88.60	-79.41	89.42	-80.81	89.74	-79.59	90.19	-80.71	90.59	-80.69
50%	19.35	68.80	89.29	-69.95	89.67	-70.05	89.98	-69.91	90.35	-69.98	90.68	-69.90
60%	26.47	73.52	89.68	-55.16	89.98	-55.25	90.22	-55.13	90.55	-55.30	90.79	-55.19
70%	35.90	78.19	90.17	-40.88	90.38	-40.91	90.46	-40.50	90.73	-40.74	90.93	-40.17
80%	48.98	86.08	90.81	-16.15	90.78	-15.79	91.01	-16.26	91.04	-16.10	91.10	-16.04