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Studies on the Solvent Effect of Aquo-n-propanol Solvent systems on the Kinetic of Catalysed Solvolysis of Aliphatic Caprate Ester

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Abstract: The kinetics of the alkali catalysed hydrolysis of aliphatic caproate (Propyl caproate) were studied in aquo-n-propanol solvent systems and the specific rate constants of the reaction were found decreasing with increasing concentration of the organic content (n-propanol) of the media It is inferred that dielectric effect and the solvation changes are the causes of depletion in the rate of the reaction.

The iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) of the reaction were found to increase and decrease respectively and from this, it is inferred that the transition state of the reaction is desolvated and its initial state is solvated.

From the deletion observed in the solvation number of the water content of the aquo-n-propanol solvent systems with increase in the temperature of the reaction it is inferred that unimolecular mechanistic path of the reaction is changed to bimolecular mechanistic path. Increase observed in free energy of activation with simultaneous increase in the values of both the ΔH* and ΔS*, it is inferred that in the presence of n-propanol with reaction media, the reaction becomes enthalpy dominating and entropy inhibiting.

From the evaluated values of iso-kinetic temperature of the reaction which comes to be 328, it is concluded that Barclay-Butler rule is obeyed by the reaction and there is strong solvent-solute interaction in presence of n-propanol in the reaction media.

Keywords: Caprate ester, Dipolar protic solvent, Longer C-chain Iso-composition and Iso-dielectric activation energy, Transition state, Entropy controlled, Enthalpy dominating, Specific salvation

I. INTRODUCTION

The kinetics of alkali catalysed hydrolysis of Propyl caproate (having longer carbon chain) in water-n-propanol media has been carried ut, as this reaction is very useful from commercial as well as medicinal points of views and also that it has not been paid adequate attention by the researcher so far.

The solvolysis of the said ester was studied in water-n-propanol media having varying concentration of n-propanol fro 30-80% (v/v) at five different temperatures ie. 20,25, 30, 35 and 40°C.

II. EXPERIMENTAL

Export quality of Propyl caproate ester packed in Switzerland and Merck grade of n-propanol were taken in use. The kinetics of alkali catalysed hydrolysis of Propyl caproate were studied keeping the strength of alkali and easters as 0.1 M and 0.05 M respectively. The concentration of the organic solvent n-propanol was varied from 30 to 80% (v/v) and hydrolysis was carried out at five different temperatures at 20, 25, 30, 35 and 40°C. The reaction was found to follow second order kinetic equation and the evaluated values of the specific rate constants were enlisted in Table - 1. The evaluated values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) have been recorded respectively in Table-II and III. From the slopes of the plots of log k value versus log [H_2O] values as recorded in Table - IV, the evaluated values of number of water molecules associated with the activated complex of the reaction have been tabulated in Table V. The three thermodynamic activation parameters namely ΔH*, ΔG* and ΔS* were calculated by applying Wynne-Jones and Eyring equation[1] and their values are synchronised in Table - VI.

III. RESULTS AND DISCUSSION

1) *Solvent Effect on the Rate of Reaction:*

Table-I shows that the specific rate constant values of the reaction decrease with increasing proportion of n-propanol in the reaction media. On plotting log k values against mol% of n-propanol as shown in Fig.-1, it is obvious that rates of reaction go on depleting with gradual addition of n-propanol in the reaction media. The depletion in the rate follows smooth depleting path. From the plots of log k versus mol% of n-propanol in the reaction media, two intersecting straight lines having different values of slopes are obtained. The decrease in the rate with increasing mol% of n-propanol at all the five temperatures are found to follow deep depletion path up to 18.75 mol % of the n-propanol in the reaction media and after its 18.75 mol% in the reaction media, the rate of depletion becomes slow. From Fig. 1, it is clear that sharpness in the depletion of the rate becomes slow with increase in temperature of the reaction. This decreasing trend in the values of the rate constants needs to be discussed in the light of Hughes and Ingold[2] predictions and the theory of Laidler and Landskroener[3]. The values of dielectric constant of the reaction media go on decreasing with gradual addition of n-propanol. So our findings are fully in accordance with the qualitative prediction of Hughes and Ingold[2].

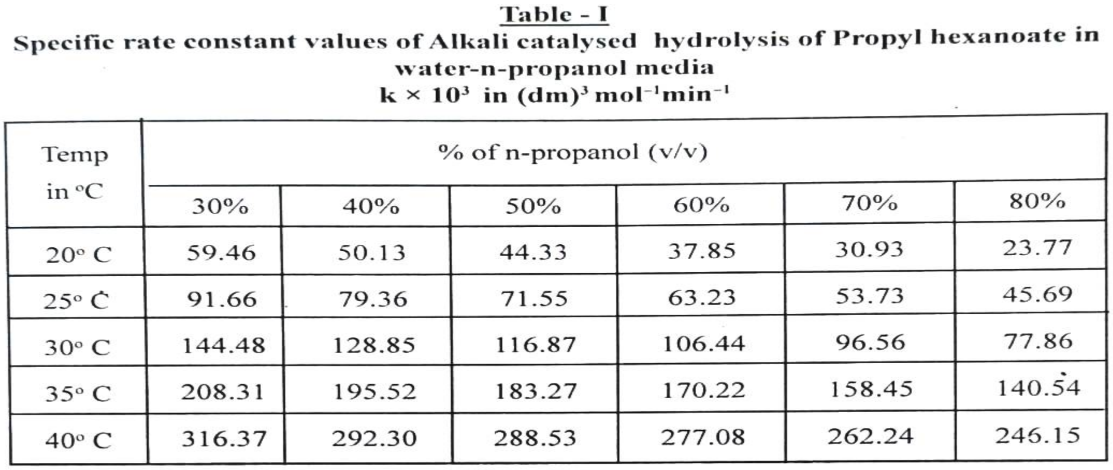


Table - I

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

$k \times 10^3$ 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

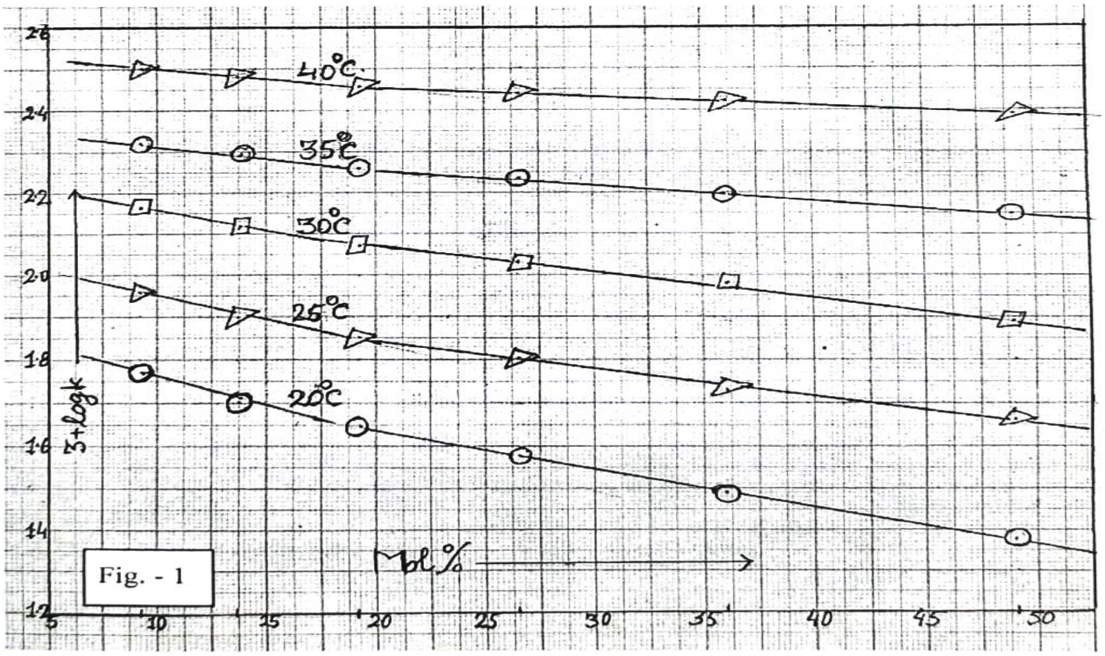


Fig. - 1 : Variation of log k values with mol % of n-propanol in water-n-propanol media

However, our findings are also in agreement with the qualitative prediction of Singh et al[4-5] and recent reports of Singh & Perween et al[6]. and Kumar & Singh et al[7]. Who predicted that the rate of ion dipolar reaction decreases with decrease in the dielectric constant values of the reaction media and partly due to the solvation changes taking place in the reaction media.

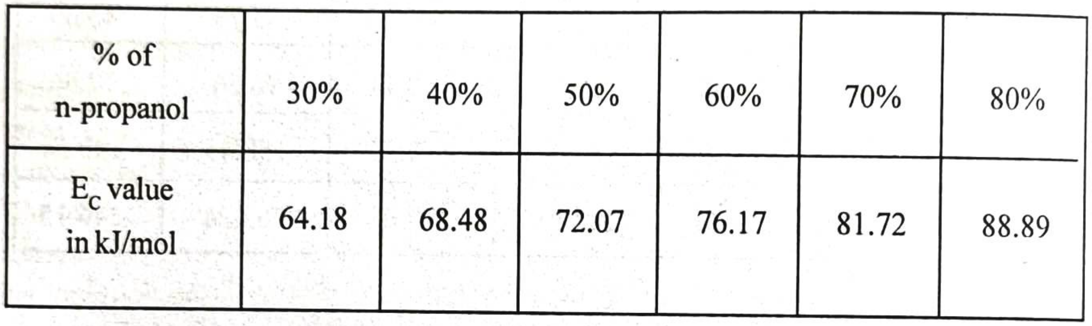
2) *Solvent effect on the Iso-composition Activation Energy of the reaction:*

The values of iso-composition activation energy (E_C) of the reaction were evaluated from the Arrhenius plots of log k values of the reaction against $10^3/T$ which is shown in Fig.-2 and have been tabulated in Table-II.

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

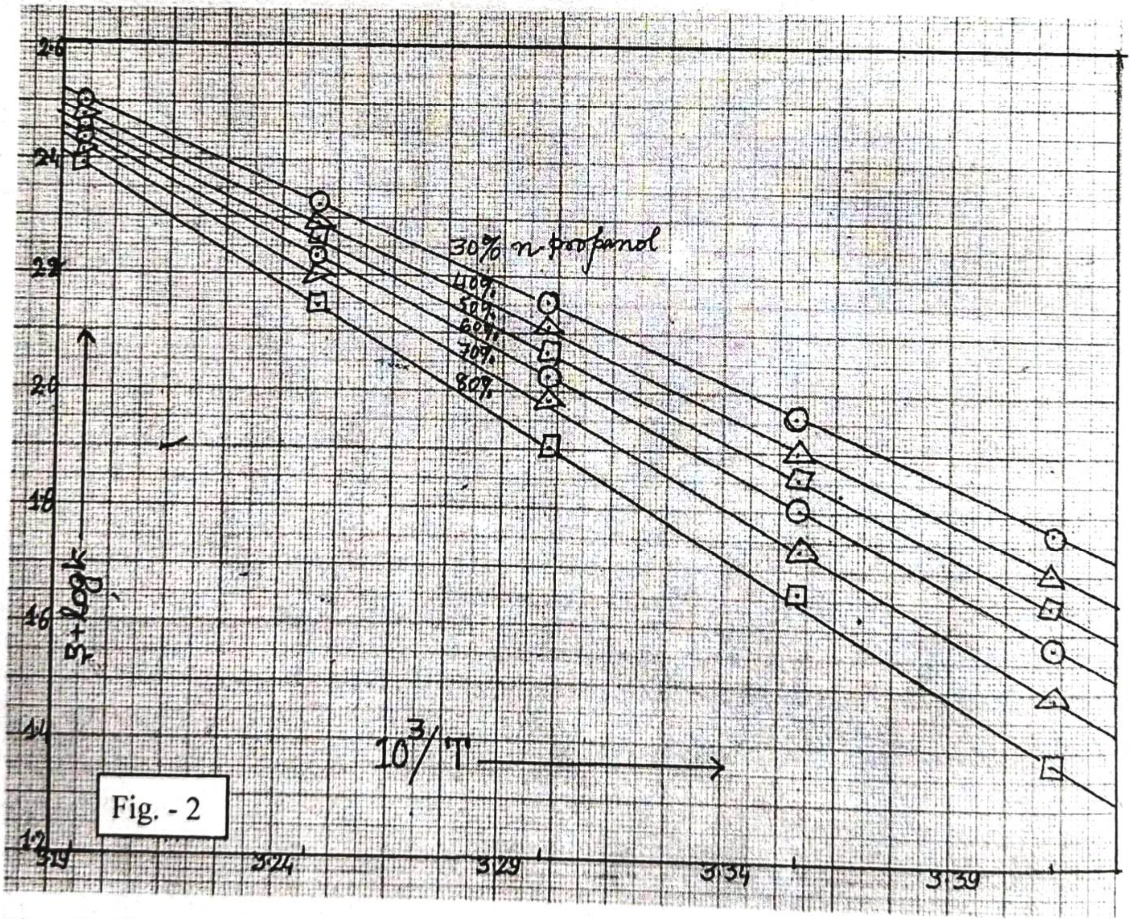


Fig. - 2 : Plots of log k values versus $10^3/T$ in water-n-propanol media

From Table-II, it is obvious that E_C values go on increasing from 64.18 kJ/mol to 88.89 kJ/mol with increase in concentration of n-propanol from 30 to 80% (v/v) in reaction media. This change is probably due to solvation changes taking place either at initial state level or at the transition state level or at the level of both the states as reported earlier by several researchers[8-9] and recently by Kumar & Singh[10] and Singh & Dubey[11] in this field. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for increase in E_C values with gradual addition of n-propanol in the reaction media:-
(i) The initial state is solvated more than the transition state,
(ii) The transition state is desolvated more than initial state. and
(iii) The initial state is solvated and the transition state is desolvated..
The transition state being large anion (ester $+H^+$) not available more for solvation by n-propanol molecule than the initial state, so the third factor seems to be operative in this case and it also gets support when the values of entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) go on increasing with concentration with n-propanol as shown in Table VI.. These inferences have also been supported by the recent findings by Singh & Perween[6], Kumar & Singh[7], Singh & Namrata[12] and Kumar & Singh et al[13].

3) *Solvent Effect on the Iso-dielectric Activation Energy (ED) of the Reaction:*

On perusal of the data of Table -III, it is found that iso-dielectric energy (E_D) values of the reaction are decreasing from 87.27 kJ/mol to 70.13 kJ/mol with increase in dielectric constant values of the reaction media from D 25 to D65 respectively. Since D values of the water-n-propanol reaction media go on decreasing with gradual addition of n-propanol to it, hence it may also be concluded that like E_C values E_D values are also increasing with decrease in D values of the reaction media or with adding more and more n-propanol to it. Thus it also may be inferred that E_C and E_D values of the solvolysis reactions are complimentary to each other.
Such findings and their interpretations are also in support of the past views of Elsemongy et al[14], Wolford[15] and are supported by the recent reports of Singh & Perween[6] Singh & Namrata[12] and Singh & Kumari et al[16].

4) *Effect of Solvent on the Solvation number and on the Mechanistic pathways of the reaction:*

The solvation number i.e. the number of water molecules involved in the formation of the activated complex of the reaction were evaluated from the slopes of log k values of the reaction against log [H_2O) value of the reaction media. By using Robertson[17] equation which is -
where 'n' is the solvation number.

$$\mathbf{\log k = \log k_o + n \log [H_2O]}$$

The log k and log [H_2O] are enlisted in Table - IV and their plots are shown in Fig. -3 and the numerical values of the slopes of the plots have been enlisted in Table - V.
Robertson et al[18]. have established that the numerical value of solvation number 'n' i.e. the number of water molecules associated with the activated complex in its formation are fairly high for reaction following unimolecular mechanistic pathway and are low for reaction following bimolecular mechanistic pathway.

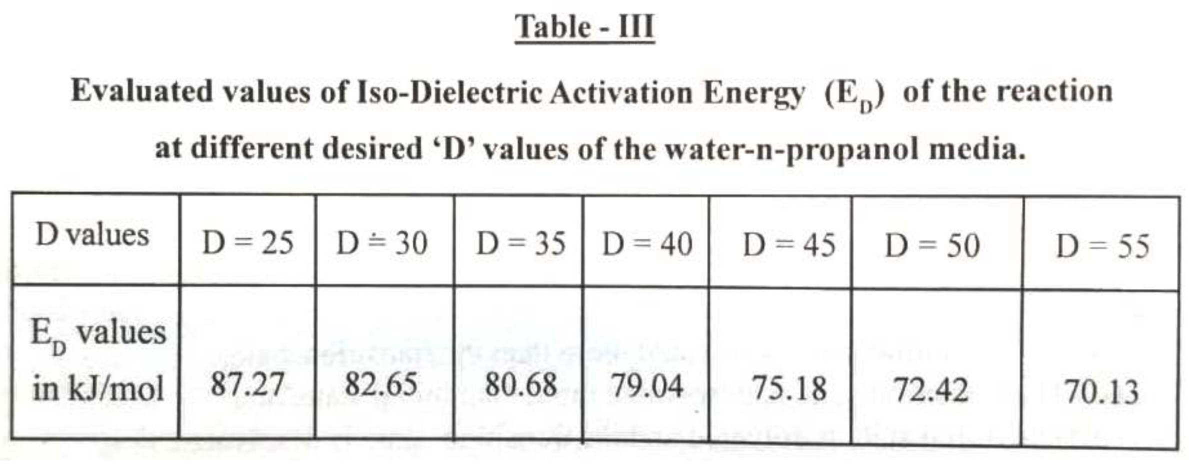


Table - III

Evaluated values of Iso-Dielectric 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 values in kJ/mol	87.27	82.65	80.68	79.04	75.18	72.42	70.13

From Fig. 3 and from the values recorded in Table - V, it is clear that at all the temperatures of the reaction, the plots of log k versus log [H,O], there are two straight lines having different slopes which meet at log [H_2O] value 1.40 which corresponds to 47.30% of water in water-n-propanol media.

From the evaluated values of slopes as recorded in Table - V, it is clear that

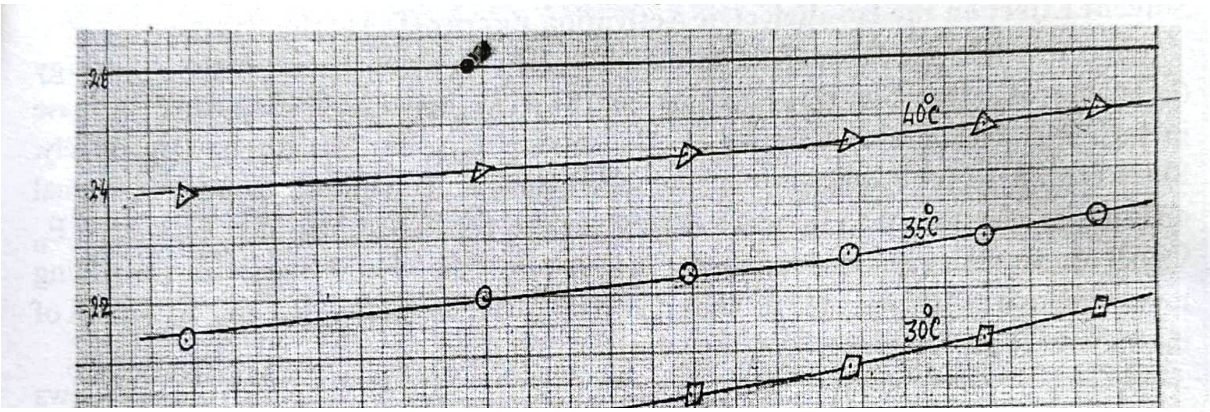


Table - IV

Variation of log k values with log [H_2O] values of water-n-propanol solvent system (media) at different temperatures.

% of n-propanol (v/v)	% of H_2O (v/v)	log [H_2O]	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.5898	1.7742	1.9622	2.1598	2.3187	2.5002
40%	60%	1.5229	1.7001	1.8996	2.1101	2.2912	2.4761
50%	50%	1.4437	1.6467	1.8546	2.0677	2.2631	2.4602
60%	40%	1.3468	1.5781	1.8009	2.0271	2.2310	2.4426
70%	30%	1.2218	1.4904	1.7302	1.9848	2.1999	2.4187
80%	20%	1.0458	1.3761	1.6598	1.8913	2.1478	2.3912

Table - V

Values of the slopes of the plots of log k versus log [H_2O] at different temperatures

Temperature in °C	Slope - I when log[H_2O] value is below 1.40	Slope - II when log[H_2O] value is above 1.40
20°C	0.667	0.842
25°C	0.439	0.759
30°C	0.404	0.634
35°C	0.289	0.477
40°C	0.160	0.278

before log [H_2O] value 1.40 which corresponds to 47.30% of water concentration in the reaction media, their values are decreasing from 0.667 to 0.160 with rise in temperature of the reaction from 20 to 40 °C Similarly, after log [H_2O] value 1.40 i.e. above 47.30% of water in the reaction media, the numerical values of the slopes i.e. the number of water molecules associated with the activated complex in its formation decrease from 0.842 to 0.278 with increase in temperature from 20 to 40 ° C

Overall, it may be concluded that number of water molecules associated with the activated complex of the reaction in the formation decrease from 0.842 to 0.160.

Thus, on the guidelines of Robertson et al.[18], it may be inferred that with rise in temperature of the reaction, the mechanistic pathways of the reaction is changed from unimolecular to bimolecular in presence of n-propanol in the reaction media.

About the change in the structure of water in presence of n-propanol and with rise in temperature of the reaction, water components of the reaction media changes its structure from its bulky form to dense form at equilibrium.

$$(H_2O)_b \rightleftharpoons (H_2O)_d$$

These findings and their such interpretations have also been supported by Singh & Perween[6] and Kumar & Singh et al[7]. and Singh & Singh[19]in their recent publica-tions.

5) Effect of Solvent on the Thermodynamic Activation Parameters of the Reaction:

The three thermodynamic activation parameters namely ΔH*, ΔG* and ΔS* of the alkali catalysed hydrolysis of Propyl caproate were evaluated using Wynne-Jones and Eyring equation[1] and their values have been synchronised in Table - VI.

From Table VI, it is clear that out of the three thermodynamic activation parameters ΔH*, ΔG* and ΔS* all of them are found increasing with increasing mol % of n-propanol in the reaction media.

For better understanding of the effect of solvent n-propanol on these three thermodynamic activation parameters, their values were plotted against mol% of the solvent(n-propanol) which have been shown in Fig. 4, 5 and 6 showing the variation in ΔH*, ΔG* and ΔS* respectively with mol % of n-propanol in the reaction media

The reasonable and considerable increase in ΔG* values (from 89.45 to 91.01 kJ/mol at 30°C) as found in Table - VI and non-linear variation in ΔH*, ΔG* and ΔS* with mol% of n-propanol as shown in Fig. 4, 5 and 6 respectively are indication of specific solvation taking place in the process of activation as reported by Saville and Hudson[20], Tommila et al[21]. and Hyne et al[22]. Enhancement observed in both the ΔH* and ΔS* values also justifies that transition state of the reaction is desolvated and the initial state of the reaction is solvated. Simultaneous increase in ΔG* values with increase in ΔH* and ΔS* values is only possible when the extent (degree) of enhancement in ΔH* values is more than that of ΔS* values and from this, it may be inferred that alkali catalysed hydrolysis of Propyl caproate is entropy suppressing or controlled and enthalpy dominating reaction. Such findings and interpretations have also recently been reported by Singh & Perween[6] Singh & Namrata[12] and Singh & Kumari et al[23] and Singh & Mishra et al[24].

6) Solvent Effecton Iso-kinetic temperature and Solvent-Solute Interaction:

This reaction is found to obey Barclay and Butler[25] rule and straight line is obtained when ΔH* values of the reaction is plotted against ΔS* as shown in Fig. - 7 and from their values tabulated in Table - VII.

The Barclay and Butler equation is-$\boldsymbol{\delta m (\Delta H^*) = ß\delta m (\Delta S^*)}$

It is a relation between enthalpy (ΔH*) and entropy (ΔS*) of activation values of reaction and ß is called iso-kinetic temperature of the reaction which is also called Leffler-Grunwald solvent stabilizer operator[26]. From the value of slope of the plot, the value of iso-kinetic temperature was evaluated which came to be 327.08≈ 327.

Table - VI

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)	Mol % 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	–40.71
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

Table - VII

Variation of ΔH^*, ΔG^* and ΔS^* values of the reaction with mol % of n-propanol in water-n-propanol media

% of n-propanol	Mol % of n-propanol	ΔH^* in kJ/mol at 30°C	ΔG^* in kJ/mol at 30°C	ΔS^* in J/K/mol at 30°C	$(\Delta S^* + 100)$ in J/K/mol at 30°C
30%	9.33	62.11	89.45	–90.23	9.77
40%	13.79	65.33	89.74	–79.59	20.41
50%	19.35	68.80	89.98	–69.91	30.09
60%	26.47	73.52	90.22	–55.13	44.87
70%	35.90	78.19	90.46	–40.50	59.50
80%	48.98	86.08	91.01	–16.26	83.74

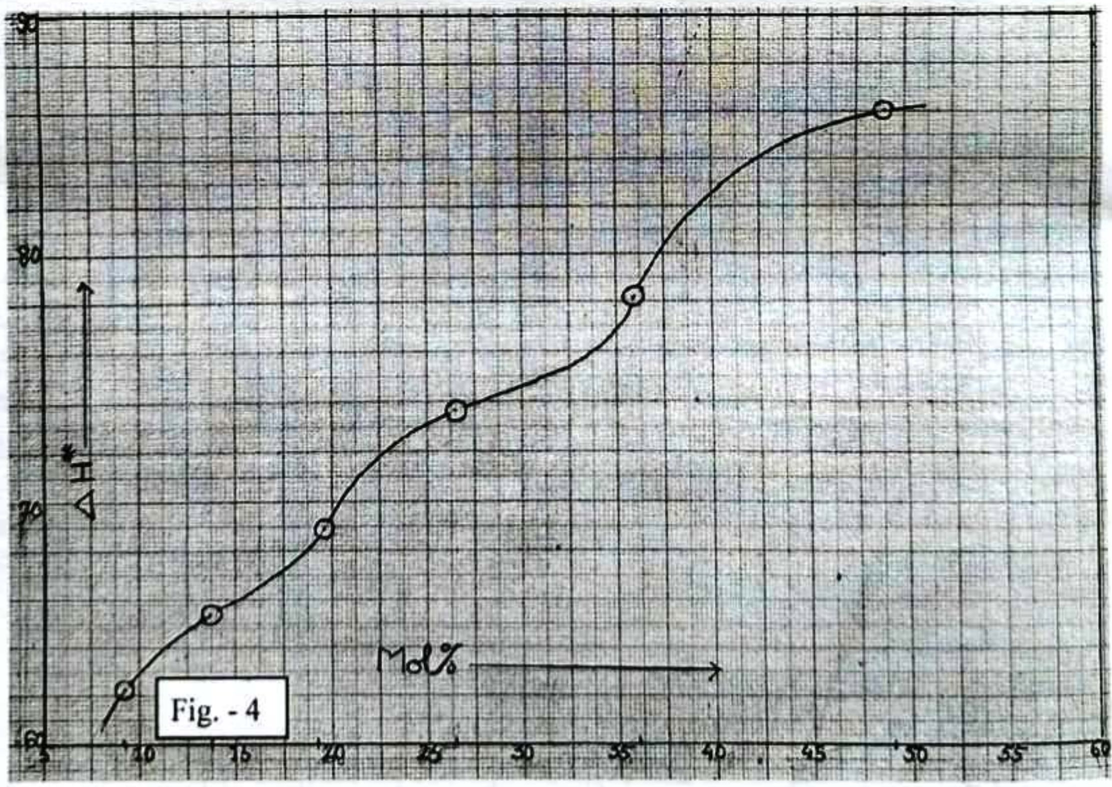


Fig. - 4 : Variation of ΔH^* values with mol % of n-propanol in water-n-propanol media

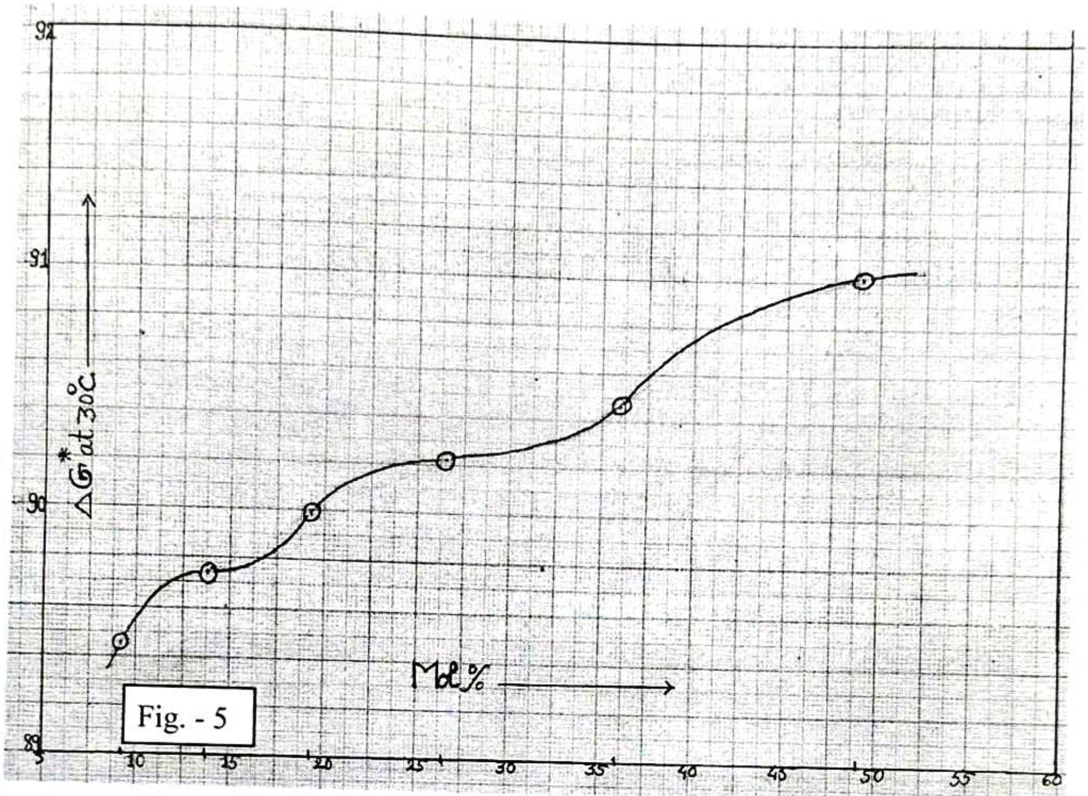


Fig. - 5 : Variation of ΔG* values with mol % of n-propanol in water-n-propanol media

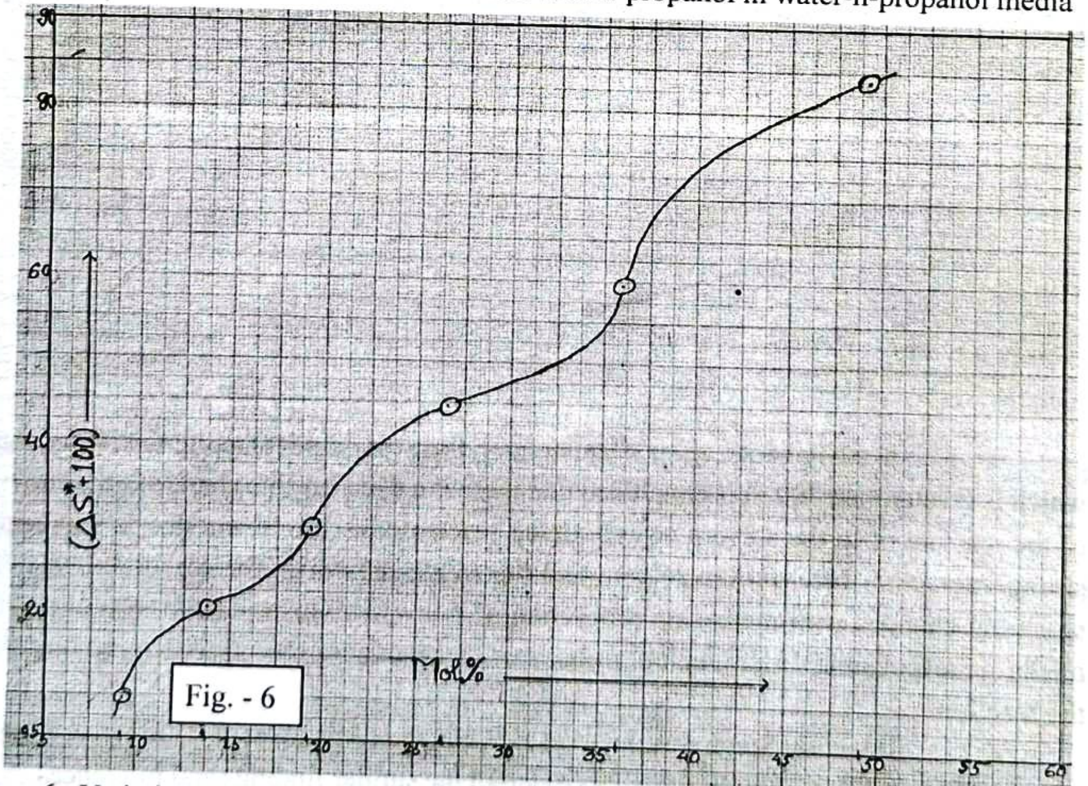


Fig. - 6 : Variation of ΔS* values with mol % of n-propanol in water-n-propanol media

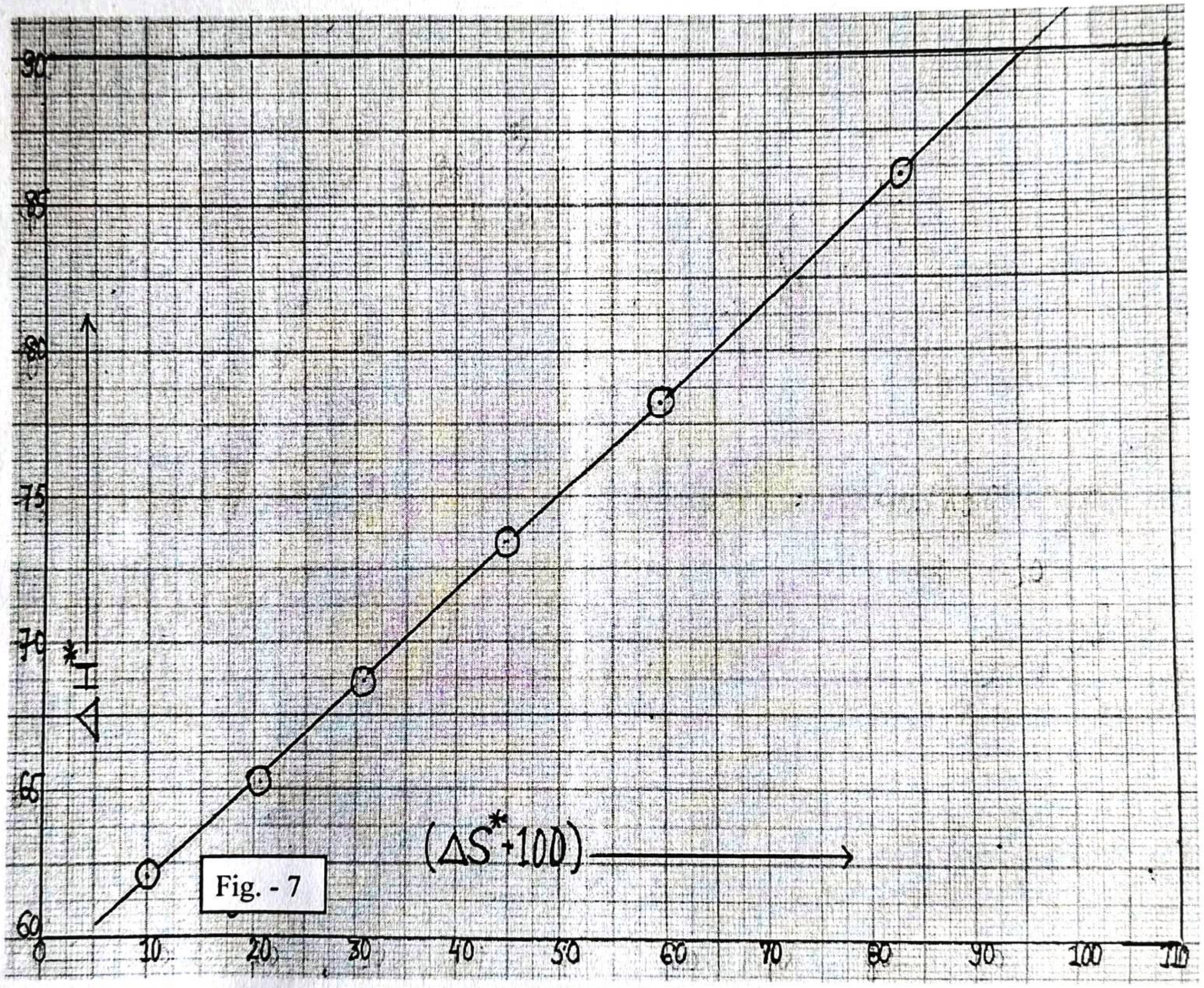


Fig. - 7 : Plots of ΔH* values against ΔS* values in water-n-propanol media

In the light of Leffler's[27] guidelines, from the values of iso-kinetic temperature which is greater than 300, it is concluded that there is a considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to appreciably strong interaction between the solvent and the solute present in the reaction media. The structural changes with increasing proportion of n-propanol in water-n-propanol reaction media are responsible for the depletion observed in the values of the specific rate constant of the reaction.

Recently Singh & Kumari et al[23] Singh & Mishra et al[24], Singh & Singh et al[28] and Singh & Kumari et al[29] have also reported the similar findings and inferences.

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