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A Kinetic Study of the Solvent Effect of Aquo-Dipolar Protic Solvent Systems on the Catalysed Solvolysis of Higher Hexanoates

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Abstract: ***The Kinetics of alkali catalysed hydrolysis of propyl hexanoate (a higher hexanotes) in aquo-propan-2-ol media was studies with a view to highlight the effect of a dipolar protic solvent (propan-2-ol) on the medicinal efficiency of the hydrolytic product of the ester (hexanote acid or caproic acid). The initial sharp decrease followed by slow and smooth depletion in the rate with gradual addition of the organic co solvent in the reaction media and with increasing temperature of the reaction has been explained in the light of solvation or desolvation of initial and transition state to the different extent. The increase and decrease respectively in the value of iso-composition and iso-dielectric activation energies of the reaction respectively have been observed and explained on the basis of solvation and desolvation to different extent of initial and transition states by the added solvent.***
Enhancement in the values of free energy activation ΔG* with simultaneous increase in enthalpy of activation ΔH* and entropy of activation ΔS* reveals that the specific solvation is taking place in the reaction media and propnal-2-ol acts like entropy controller and enthalpy stimulator solvent.
Keyword: Higher Hexanoate, Dipolar-protic Behaviour, Solvation and desolvation, Specific Solvation Thermodynamic Activation parameters, Iso-composition, Iso-dielectric, Iso-kinetic

I. INTRODUCTION

As reported by the different researchers[1-3] the effect of dipolar aprotic solvent like Dioxan, Acetone, DMSO, DMF etc. have widely been studied on the alkali and acidic catalysed hydrolysis of aliphatic esters but towards the study of effect of dipolar protic solvent having peculiar solvating nature on the medicinal efficiencies of the aliphatic ester having higher C-atoms even a little attention has not been paid so far. So, in order to highlight the above noted untouched research, it has been proposed to make a kinetic study of the solvent effect of propan-2-ol (dipolar protic) on the alkali catalysed hydrolysis of propyl hexanote containing higher c- atoms)

A. Experimental

Purified propan-2-ol of Merck grade and propyl Hexanoate (propyl caproate) of USSR make were taken into use. The kinetics of alkali catalysed hydrolysis of the ester was studied as usual by adding 0.90 ml of ester in 100 ml of 0.01 M NaOH solution. The values of specific rate constants were evaluated by making use of second order rate equation and are tabulated in Table 1. 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. The numerical value of water molecules associated with the activated complex have been tabulated in Table -IV and consolidated values of the three thermodynamic activation parameters have been enlisted in Table-V.

II. RESULTS AND DISCUSSION

From the plots of log k versus mol % propan-2-ol as shown in Fig. 1. it is obvious that with the gradual addition of the organic co-solvent (propan-2-ol) in the reaction media there is initially sharp followed by slow depletion in the rate of reaction at all the five different temperatures, Fig.-3.1 clearly indicates that the rate constants decrease with different slopes before and after adding 17.60 mol % of propan-2-ol in the reaction media. It is also obvious from fig. 3.1 that with increase in the temperature, the degree (or extent) of depletion in rates goes on decreasing.

The following two factors seem to be responsible for depletion in the rate of the reaction in solution, they are:

1) Decreasing the polarity of the medium as changing from polar water to less polar water-propan-2-ol medium, and
2) lowering of the bulk dielectric constant values of the medium.

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After all the deplation in the rate to different extent may be attributed pastly due to dielectric effect and pastly due to solvation effect. These finding and interpretations are in support of views of Hughes and Ingold[6] Laidler and Lanskroener[7] and also with the recent report of Rashmi & Singh et al[8] and Priyanka & Singh et al[9] .

A. Solvent Effect on Iso-Composition Activation Energy

From the slopes of the arrtenius plots of log k values 1 / T_{i} values as shown in Fig. 2, the values of iso-composition activation energy E_{exp}{C} or E_{exp} have been calculated and are mentioned in Table II.

From Table II, it is clear that values of iso-composition activation energy go on increasing from 84.55 kJ/mol to 119.42 kJ/mol with addition of 20 to 80% of propan-2-ol in the reaction media.

Generally, the increase in the values of iso-composition activation energy may be due to:

(i) The greater desolvation of transition state than the initial state,
(ii) The greater solvation of the initial state than the transition state.
(iii) Simultaneous desolvation of the transition state and solvation of the initial state.

Out of these three factors, the third one seems to be applicable in this case and it has also been supported by the increase in the values of entropy of activation with gradual addition of the organic co-solvent in the reaction media as mentioned ahead in Table - V. Similar views have also been reported recently by Kishor &Singh et al[10].

B. Solvent Effect on Iso-dielectric Activation energy of the Reaction

From the Arrhenius plots of log k_D values against I/T (log k_D values are obtained from interpolation of the plots of log k values against D values), the values of iso-dielectric activation energy have been evaluated and are enlisted in Table - III. From this Table, it is inferred that E_D values go on decreasing from 110.89 kJ/mol to 84.57 kJ/mol with increasing D values of the reaction media from 30 to 65. This trend of depletion in E_D values with increasing D values of the reaction media has been supported earlier by Wolford[11] and in recent years by Haider & Singh el[12] aland Sinha & Singh et al[13],

C. Involvement of water molecules in the formation of transition state and Mechanism of the Reaction

The solvation number i.e. the number of water molecules associated with the transition state has been evaluted by plotting log k values, against log [H_2O] according to the relation proposed by Robertson[14]

$$\log k = \log k_o + n \log [H_2O]$$

where 'n' is the solvation number which tells about number of water molecules associated with the transition state and also hints about criterion for studying the mechanism of the reaction. On plotting log k values against log [H_2O) values as shown in Fig. 3, two straight lines having positive slop inter secting each other at log [H_2O] value 1.518 with correspond to 59.35% have been obtained at all the temperature at which the kinetic has been studied. The numerical values of slopes off all the straight lines have been tabulated in Table - IV.

From the noted values of the slopes in Table IV, it may be inferred that overall with rise of temperature of the reaction from 20°C to 40°C, the number of water molecules associated with the transition state below log [H_2O] value 1.518 which corresponds to 59-35% of water in the reaction media, decreasing from 0.908 to 0.272.

Simlary at above water conceration 59.35% in the reaction media the number of water molecules associated with the transation state decrease from 1.170 to 0.608 with rise in temperature from 20 to 40°C.

Over all it may be inferred that with increase in propan-2-ol content of the reaction media from 20 to 80%, the number of water molecules associated with the transition state decreases from 1.170 to 0.272 with rise in temperature of the reaction from 20 to 40° Such observations may be attributed to the fact that equilibrium shifts from bulky form of water to its dense from with rise of temperature of the reaction and with addition of more and more propan-2-ol the reaction media.

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

On the guidelines proposed by Robertson et al[15] and Packer & Tomillinson[16] it is also inferred that the mechanistic pathways followed by the alkali catalysed solvolysis of propyl hexanote is changed from unimolecular to bimolecular with increasing concentration of propan-2-ol in the reaction media and with increasing temperature of the reaction. Such findings and their interpretations have also been supported earlier by Singh & Namrata[17] and recently by Raghaw & Singh et al[18].

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D. Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

The famous Absolute Reaction Rate Theory[19] and Wynne & Jones Eyring[20] equation have been applied to evaluated the three thermodynamic activation parameters namely enthalpy of activation ΔH* entropy of activation ΔS* and the free energy of activation ΔG* and their evaluated values have been recorded in Table - V.

From the data mentioned in Table-V, the interesting feature comes in the light is that out of all the values of three thermodynamic parameters i.e. ΔH*, ΔS* and ΔG* values, all are increasing simultaneously with increasing proportion of propan-2-ol in the reaction media. ΔG* values go on enhancing with simultaneous increase in ΔH* and ΔS* values at all the temperature of the reaction i.e. from 20 to 40°C.

From the fundamental thermodynamic equation:,

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

It may be inferred that the enhancement in the values of ΔG* with simultaneous increase in ΔH* and ΔS* values is only possible when the numerical increase in the values of ΔH* is more than that found in the values of ΔS* and from this fact, it is concluded that alkali catalysed hydrolysis of propyl hexanoate in water propan-2-ol media is enthalpy dominating and entropy inhibiting or entropy controlled.

In other words, it may also be inferred that propan-2-ol by its presence in the reaction media activates the enthalpy but controls over the entropy of the reaction.

The change found in the value of the three thermodynamic activation parameters also support the fact that initial state of the reaction is solvated and the transition state is desolvated in the similar way as reported earlier by Singh & Singh et al[21] and also in recent year by Sushma & Singh et al[22].

E. Evaluation of Iso-kinetic temperature and Solvent- solute interaction:

With the help of Barclay and Butler[23] relationship between enthalpy and entropy of activation, the value of iso-kinetic temperature of the alkali catalysed hydrolysis of propyl hexanote in water-propan-2-ol media has been evaluated from the plots of ΔH* versus against ΔS* value as shown in Fig. 4. Which come to be 319.89 ≈ 320.00 and which is more than 300. From the value of iso-kinetic temperature is more than 300, it is concluded that there is a appeciable change in the structure of reactants or in the solvent or in both due to strong interaction between solvent and solute present in the reaction media consisting of propan-2-ol in the similar way as reported by Leffler[24] Earlier Madhu & Singh et al[25] and in the recent year Sushma Abhay & Singh et al[26] have also reported similar findings and their interpretation for effect of Solvent on solvent solute interaction.

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Table - I

Specific rate constant values of Alkali catalysed hydrolysis of propyl hexanote water-Propan-2-ol media

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

Temp in ^oC	% of Propan-2-ol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	83.07	72.24	60.90	50.84	41.48	31.95	22.32
25° C	146.35	129.81	111.84	96.72	81.34	65.78	49.60
30° C	257.17	230.83	207.83	184.25	159.81	136.58	110.05
35° C	436.72	398.20	365.01	336.28	303.53	269.3	233.24
40° C	741.15	684.86	649.08	616.31	569.25	542.75	492.27

Table – II

Variation of log k values of the reaction with $10^3/T$ in water- Propan-2-ol media.

Temp. ^oC	$\frac{10^3}{T}$	3 + log k values at different % of Acetone (v/v)						
		20%	30%	40%	50%	60%	70%	80%
20° C	3.413	1.9194	1.8588	1.7846	1.7062	1.6178	1.5045	1.3487
25° C	3.356	2.6154	2.1133	2.0486	1.9855	1.9103	1.8181	1.6955
30° C	3.300	2.4102	2.3633	2.3177	2.2654	2.2036	2.1354	2.0416
35° C	3.247	2.6402	2.6001	2.5623	2.5267	2.4823	2.4303	2.3678
40° C	3.195	2.8699	2.8356	2.8123	2.7898	2.7553	2.7346	2.6922

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Table – III

Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at different desired 'D' values of water propan-2-ol media.

D values	D = 30	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60	D = 65
E_D values in kJ/mol	110.89	1107.86	102.58	100.12	95.71	91.46	87.61	84.57

Table - IV

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

Temperature in ^oC	Slope - I when log[H_2O] value is below 1.518	Slope – II when log[H_2O] value is above 1.518
20^oC	0.908	1.170
25^oC	0.724	0.958
30^oC	0.583	0.881
35^oC	0.406	0.820
40^oC	0.271	0.608

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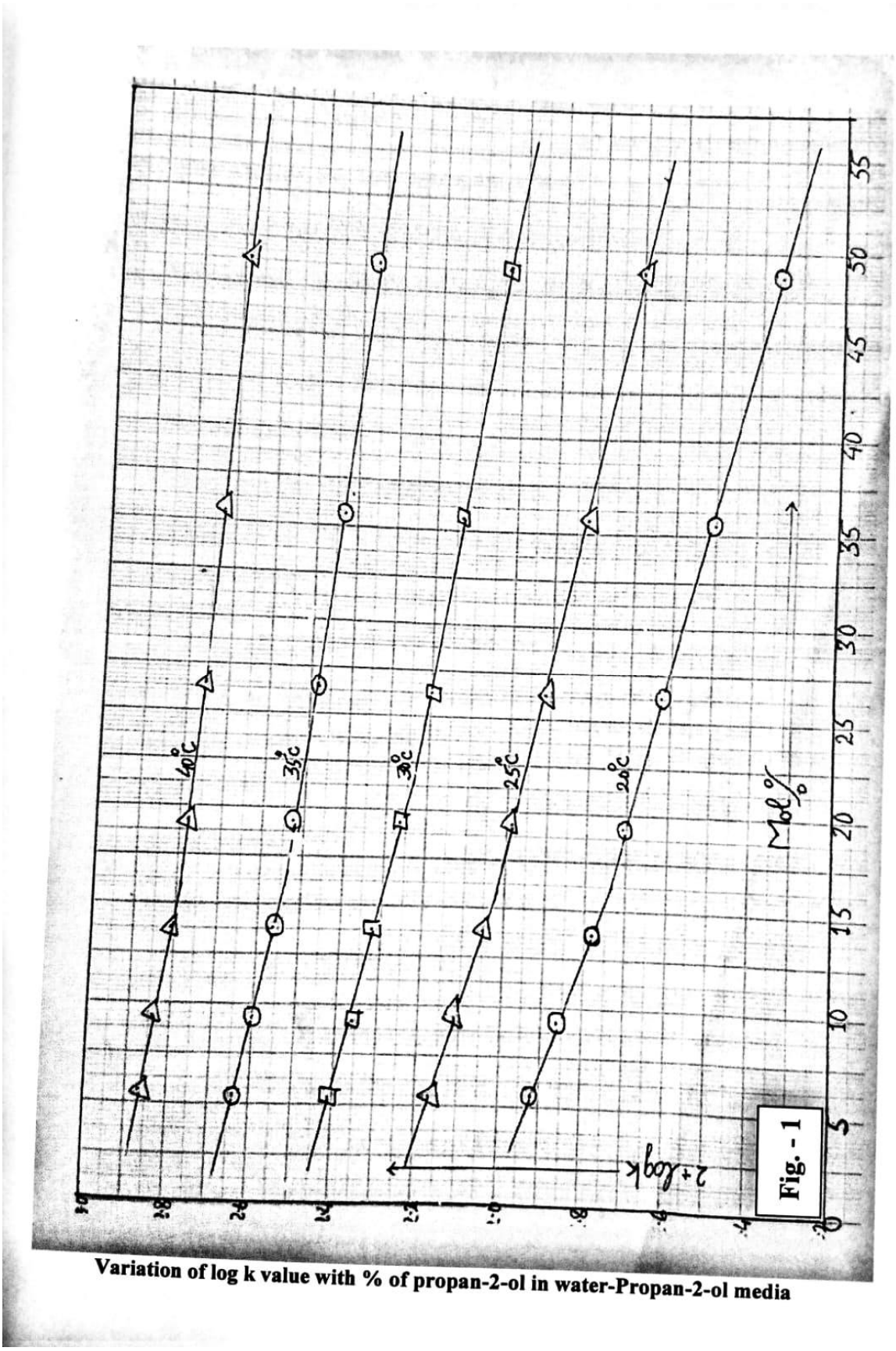
Table V

Consolidated Values of Thermodynamic Activation parameters (ΔH*, ΔG* and ΔS*) of the reaction in water-Propan-2-ol system at different temperatures.

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of Propan-2-ol (v/v)	Mole % of Propan-2-ol	Δ H* in kJ/mol	20° C		25° C		30° C		35° C		40°C	
			Δ G*	Δ S*	Δ G*	Δ S*	Δ G*	Δ S*	Δ G*	Δ S*	Δ G*	Δ S*
20 %	5.59	81.54	82.15	-2.08	82.19	-2.08	82.19	-2.14	82.24	-2.25	82.24	-2.21
30%	9.22	84.99	82.49	8.52	82.49	8.39	82.47	8.33	82.47	8.17	82.44	8.14
40%	13.64	89.44	82.91	22.27	82.86	22.07	82.73	22.13	82.70	21.88	82.58	21.90
50%	19.16	94.24	83.35	37.17	83.22	36.98	83.03	36.98	82.75	37.32	82.72	36.81
60%	26.23	99.66	83.85	53.96	83.65	53.72	83.39	53.67	83.17	53.53	82.92	53.46
70%	35.61	106.67	84.48	75.72	84.17	75.47	83.79	75.50	83.47	75.30	83.05	75.46
80%	48.67	118.34	85.35	112.58	84.87	112.30	84.33	112.23	83.84	112.0	83.03	112.94

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Variation of log k value with % of propan-2-ol in water-Propan-2-ol media

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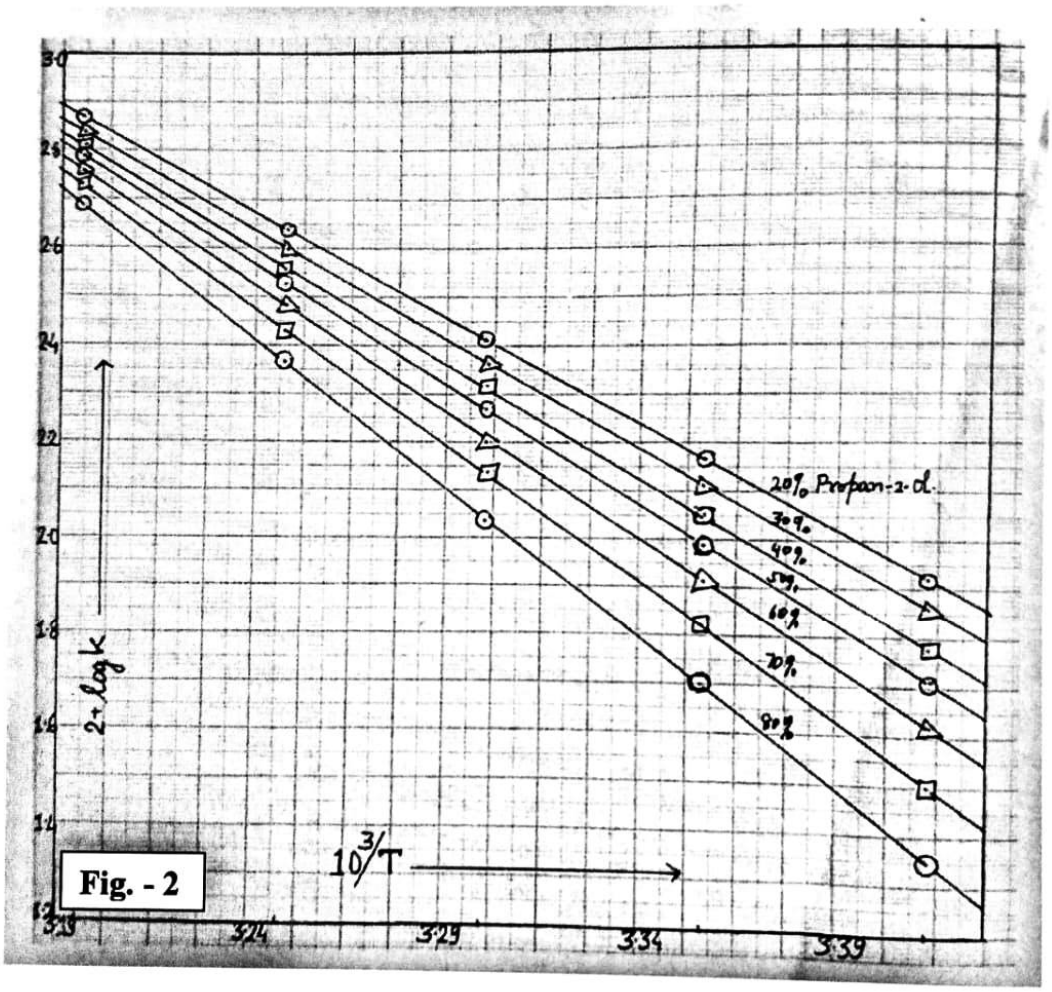


Fig. - 2

Plots of log k values versus $10^3/T$ in water-Propan-2-ol media.

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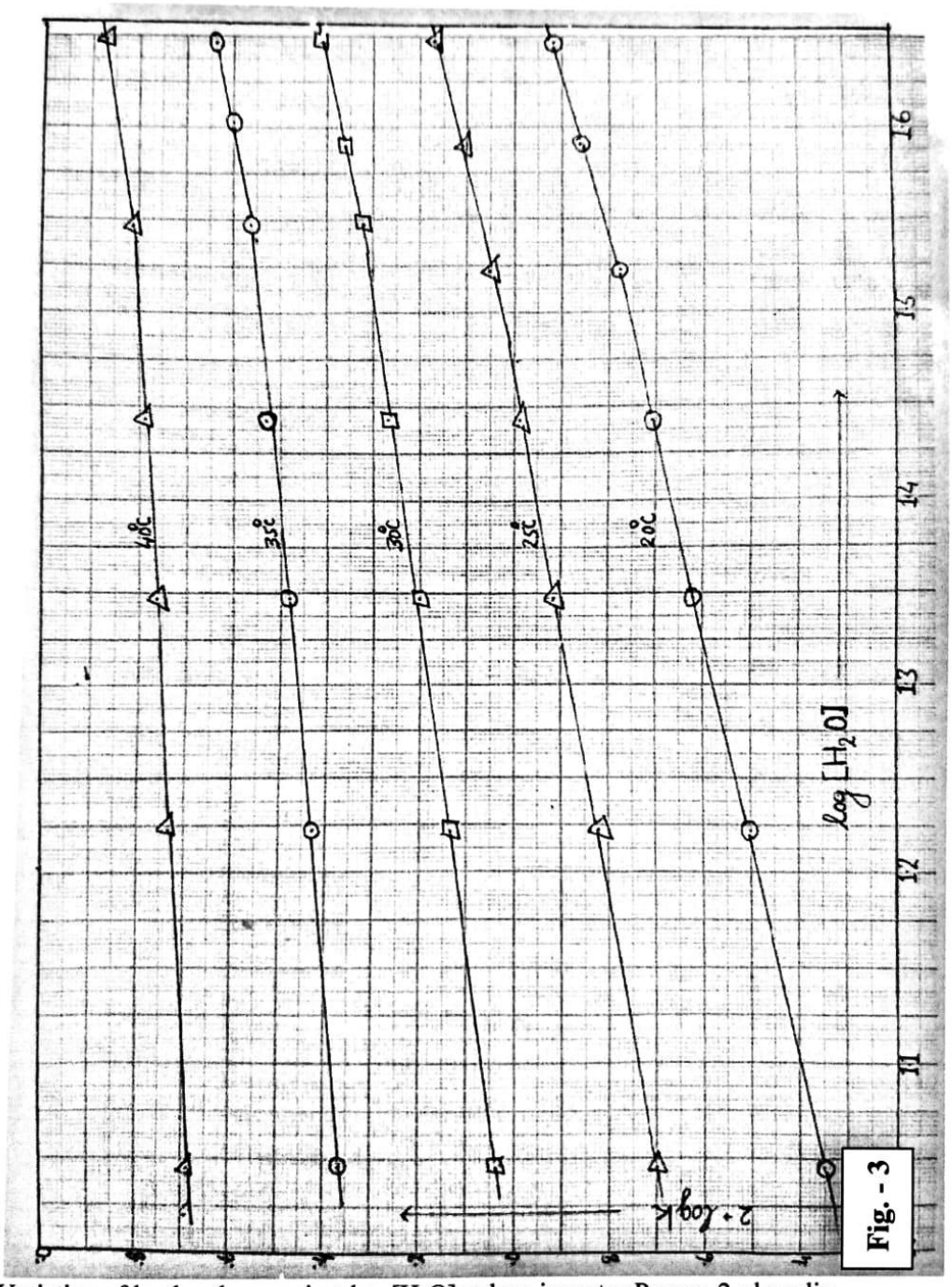
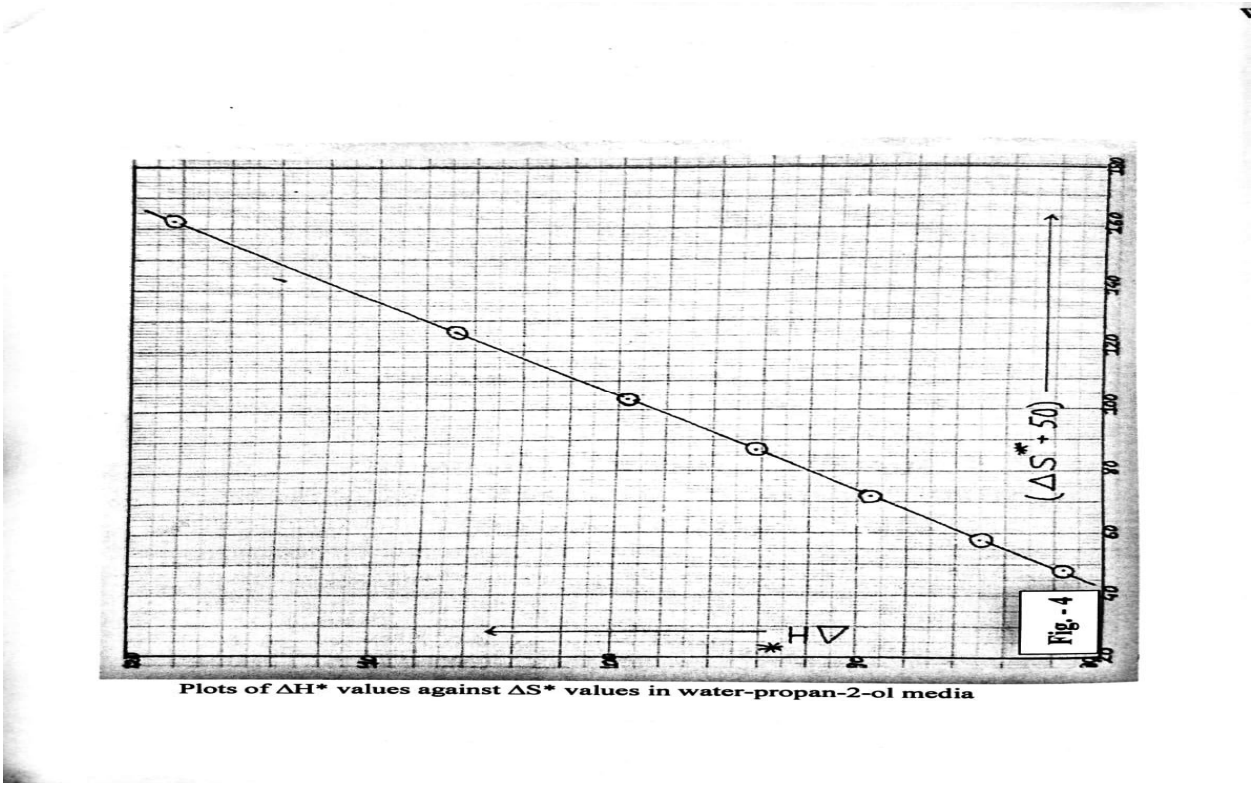


Fig. - 3

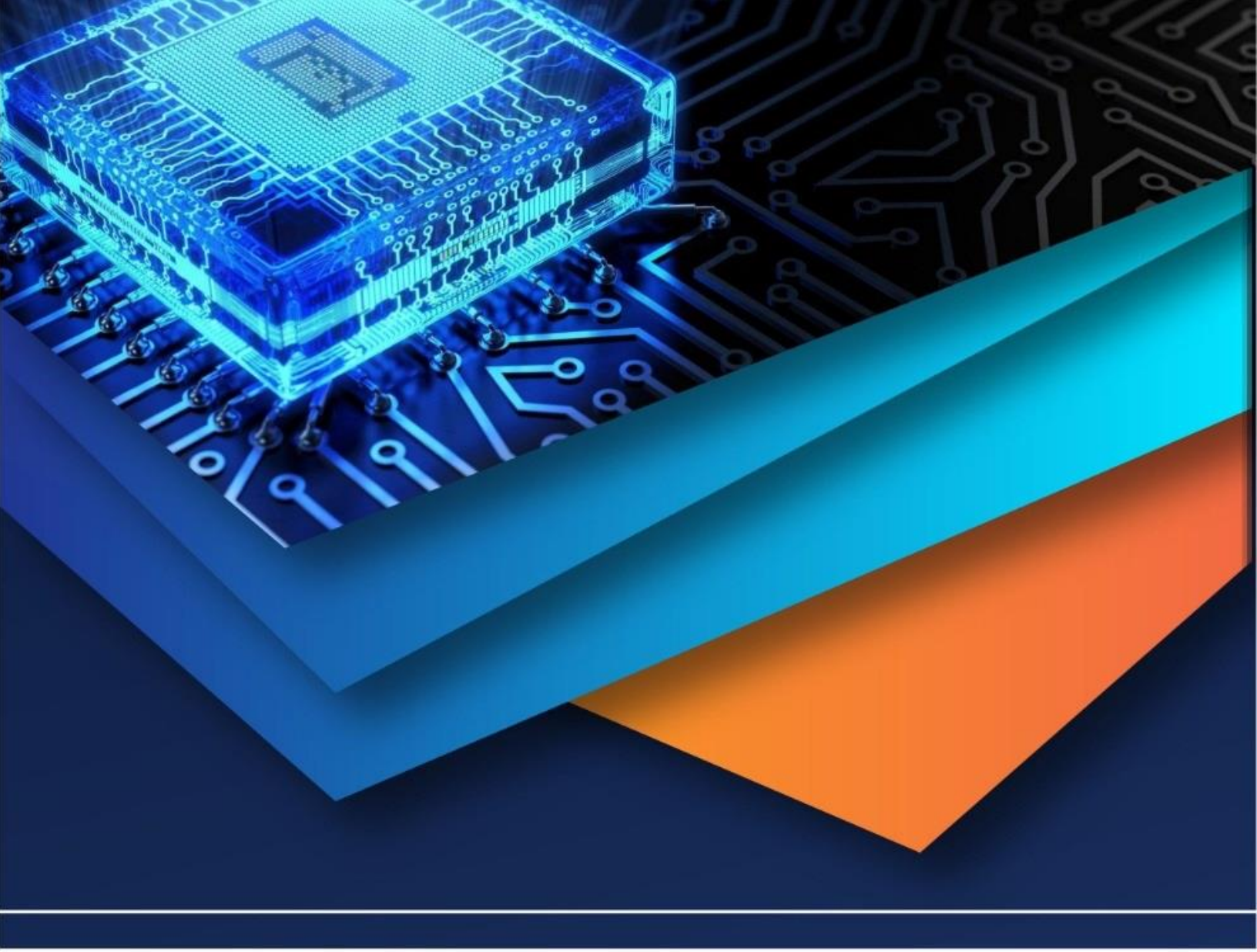
Variation of log k values against log [H_2O] values in water-Propan-2-ol media



Plots of ΔH* values against ΔS* values in water-propan-2-ol media

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