



ISSN 0973-3450

(Print)

JUC Vol. 16(5), 63-71 (2020). Periodicity 2-Monthly

(Online)



ISSN 2319-8036

9 772319 803009



Estd. 2005

JOURNAL OF ULTRA CHEMISTRY

An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering

website:- www.journalofchemistry.org

Studies on the effect of Aquo-Dioxan Solvent System on the biochemical behaviour of the Substituted Valerates

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Acceptance Date 15th October, 2020,

Online Publication Date 22nd October, 2020

Abstract

Valerates and Substituted Valerates have been found to be useful for human beings as its hydrolysis product i.e. valeric acid is used in the society in the form of perfumes, flavours, plasticizer, vinyl stabilizer and pharmaceuticals.

With a view to study the solvent effect of 1:4 dioxan on the biochemical behaviour of the hydrolysis product of a substituted valerate, the kinetic of Alkali catalysed of methyl iso-valerate was studied in aquo-dioxan media.

Increase observed in free energy activation with simultaneous increase in the value of both the activation ΔH^* and ΔS^* , it is concluded that in the presence of dioxan with reaction media, the reaction becomes enthalpy dominating and entropy controlled.

From the evaluated values of the reaction which comes to be 329.0, it is inferred that Barclay-Butler rule is obeyed by the reaction and there is strong solvent-solute interaction in presence of dioxan the reaction media.

Key words : Mechanism, Solvation and desolvation, , Barclay-Butler rule, Valerate, Thermodynamic Parameters, Solvent-Solute Interaction.

Introduction

The kinetics of alkali catalysed hydrolysis of methyl iso-valerate in water-dioxan media has been carried out, as this reaction is very useful from biochemical and food preservation points of view and also that it has not been paid adequate

attention by the researchers so far. Moreover the study of solvent effect on the catalysed hydrolysis of methyl iso-valerate is useful and beneficial for human beings as the hydrolysis products of the ester i.e. valeric acid has been found extensively useful for the modern society in the form of perfume, flavours, plasticizer, vinyl stabilizer and Pharmaceuticals.

Experimental

Export quality of methyl Iso-valerate ester packed in Switzerland and Marck grade of dioxan were taken in use. The kinetics of alkali catalysed hydrolysis of Iso-valerate was studied as usual¹ keeping the strength of alkali and ester as 0.1 M and 0.05 M respectively. The concentration of organic solvent dioxan was varied from 20 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 the second order kinetic equation and the evaluated values of specific rate constants were enlisted in Table 1. The evaluated values of Iso-composition activation energy (E_c) and Iso-dielectric energy (E_D) have been recorded in Table -2 and 3 respectively. The three thermodynamic activation parameters namely ΔH^* , ΔG^* and ΔS^* were calculated by applying Wynne-Jones and Eyring equation² and their values have been synchronised in Table-4.

Results and Discussion

Solvent Effect on the Specific Rate Constants of the Reaction:

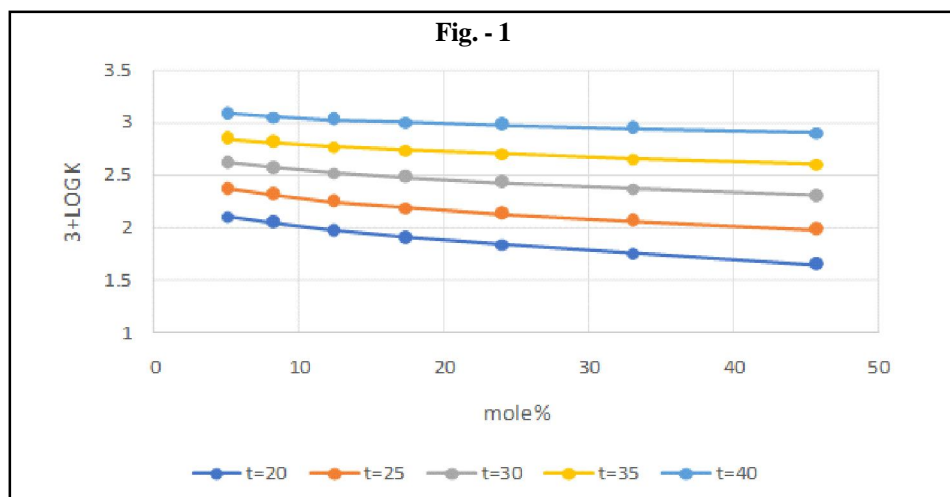
Table - 1, shows that specific rate constant values of the reaction decreasing with increasing proportion of dioxan in the reaction media. On plots of $\log k$ values against mol % of dioxan as shown in Fig.-1. It is obvious that rates of reaction go on

depleting with gradual addition of dioxan in the reaction media. The depletion in the rate follows smooth depletion path. From the plots of $\log k$ versus mol % of dioxan in the reaction media, two intersecting straight lines having different values of slopes are obtained. The decrease in the rate with increasing mol % of dioxan at all the five temperatures are found to follow deep depletion path up to mol % of dioxan in the reaction media and after its 15.25 mol% in the reaction media, the rate of depletion becomes slow. It is clear that sharpness in the depletion of rate becomes slow with increase in temperature of the reaction. This decreasing trend in the values of the rate constants need to be discussed in the light of the Hughes and Ingold³ predictions and theory of Laidler and Landskroener⁴. The values of dielectric constant of the reaction media go on decreasing with gradual addition of dioxan. So, such findings are fully in accordance with the qualitative prediction of Hughes and Ingold².

However, similar findings are also in agreement with the qualitative prediction of Hughes and Ingold³ and Singh & Jha *et.al.*⁵ and earlier reports of Singh & Parween *et.al.*⁶ Recently Savati & Singh *et.al.*⁷ and Reshmi & Singh *et.al.* have been reported 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.

Table -1
Specific rate constant values of Alkali catalysed hydrolysis of Methyl iso-valerate
in water-Dioxan media
 $k \times 10^3$ in (dm)³ mole⁻¹ min⁻¹

Temp in °C	% of Dioxan (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	127.44	111.22	92.70	79.58	68.74	57.04	44.65
25°C	231.53	202.63	174.30	154.13	135.27	116.23	94.91
30°C	410.49	366.61	328.55	296.55	267.67	234.31	198.98
35°C	699.20	640.47	587.22	546.39	500.96	450.61	398.02
40°C	1196.19	1121.50	1062.18	1001.38	939.94	873.37	793.60



Plots of log k values against mol % of dioxan

Solvent Effect on the Iso-composition Activation Energy of the reaction :

The values of iso-composition activation energy (E_c) of the reaction were Evaluted from the slopes of Arrhenius plots of log k values of the reaction against $10^3/T$ as shown the Fig.-2 and have been tabulated in Table-2.

From Table - 2 it is obvious that E_c values go on increasing from 85.12 kJ/mol to 110.22 kJ/mol. With increase in concentration of dioxan from 20 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 state as reported earlier by Priyanka & Singh *et. al.*⁹ and Singh & Singh *et.al.*¹⁰ in this field. Considering the extent of solvation to be dominant factor, the following three factors seem to be

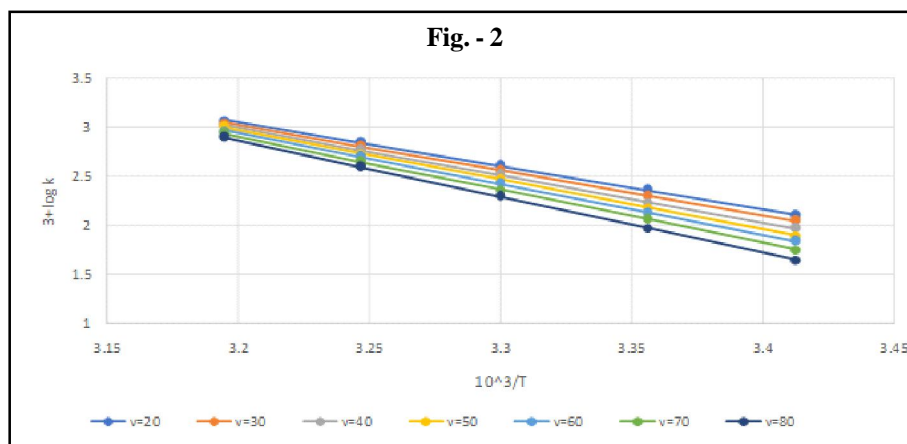
responsible for increase in E_c values with gradual addition of Dioxan in the reaction media :

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

The transition state being large anion (ester + OH^-) not available more for solvation by dioxan molecule than the initial state, so the first 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 increasing of dioxan as shown in Table- VI. Theses inferences have also been supported by the earlier finding by Rakesh & Singh¹¹ and also in recent years by Sushma & Singh *et.al.*¹²

Table – 2
Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-Dioxan media

% of Dioxan (v/v)	20%	30%	40%	50%	60%	70%	80%
EC value in kJ/mol	85.12	88.24	93.42	96.84	100.29	104.27	110.22



Plots of log k values of the reaction against $10^3/T$

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

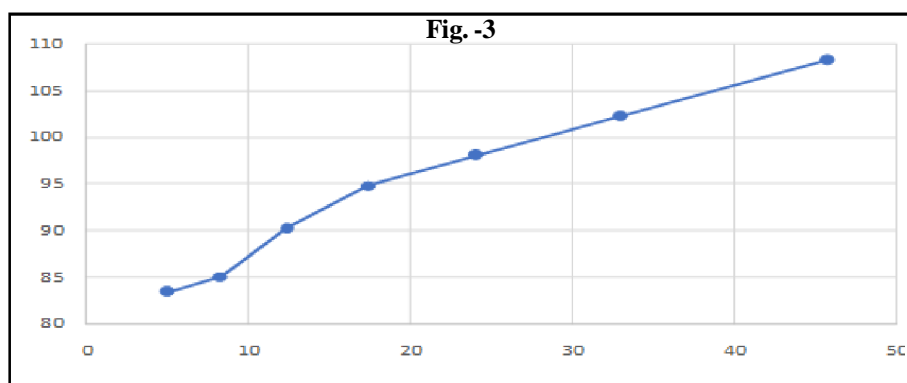
On perusal of the data of Table - 3, it is found that the value of iso-dielectric energy (E_D) values of the reaction are decreasing from 107.38 kJ/mol to 82.58 kJ/mol with increase in dielectric constant values of the reaction media from $D = 10$ to $D = 66$ respectively. Since D values of the water – dioxan reaction media go on decrease with gradual addition of dioxan 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 dioxan to it. Thus it also may be inferred that E_C and E_D values of the solvolysis reaction are complimentary to each other.

Such findings and interpretations are also in supported by the past views of Elsemongy *et.al.*¹³, Wolford¹⁴ and are supported by the earlier reports of Kishor & Singh *et.al.*¹⁵ and the recent findings of Sushma & Singh *et.al.*¹² and Haider & Singh *et.al.*¹⁶.

Table - 3
Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at different desired ' D ' values of water-Dioxan media.

D values	D = 10	D = 20	D = 30	D = 40	D = 50	D = 60
E_D values in kJ/mol	107.38	102.89	98.70	92.76	86.59	82.58



variation of ΔH^* with mol % of dioxan in the reaction media.

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 methyl isovalerate were evaluated using Wynne Jones and Eyring²² equation and their values have been synchronised in table 4.

From Table-4, it is clear that out of the three thermodynamic activation parameters ΔH^* , ΔG^* and ΔS^* all of them are found increasing with increasing mol % in the reaction media.

For better understanding of the effect of solvent dioxan these three thermodynamic activation parameters their values were plotted against mol % of the solvent dioxan which have been shown in Fig- 3, 4 and 5 showing the variation ΔH^* , ΔG^* and ΔS^* respectively with mol % of dioxan in the reaction media.

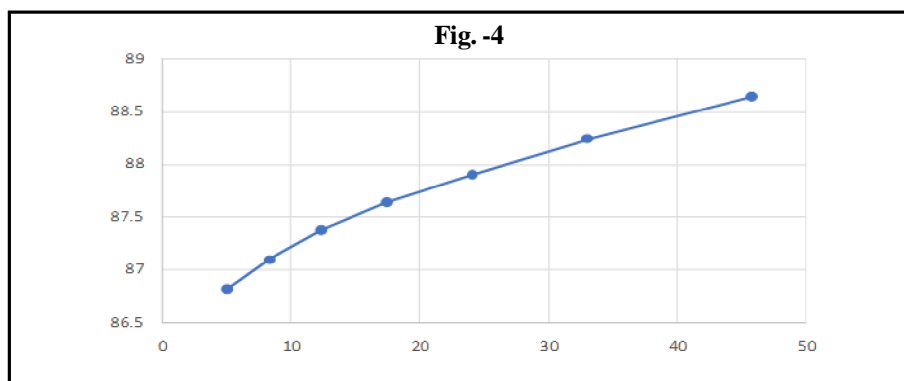
The reasonable and considerable increase in

ΔG^* values (from 86.86 to 88.64 kJ/mol at 30°C) as found in Table 4 and non-linear variation in ΔH^* , ΔG^* and ΔS^* with mol % of dioxan as shown in fig 3, 4, and 5 respectively are indication of specific solvation taking place in the process of activation as reported by Saville and Hudson¹⁶, Tonnala *et.al.*¹⁷ and Hyne *et.al.*¹⁸. Enhancement observed in both the ΔH^* , ΔG^* and ΔS^* values also justifies that transition state of the reaction is desolvated and 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 methyl isovalerate is entropy suppressing or controlled and enthalpy dominating reaction. Such findings and interpretations have been reported earlier by Singh & Mishra *et.al.*²⁰ and in recent years also Sinha and Singh *et.al.*²¹

Table – 4
Variation of ΔH^* , ΔG^* and ΔS^* values of the reaction with mol % of Dioxan in water-Dioxan media

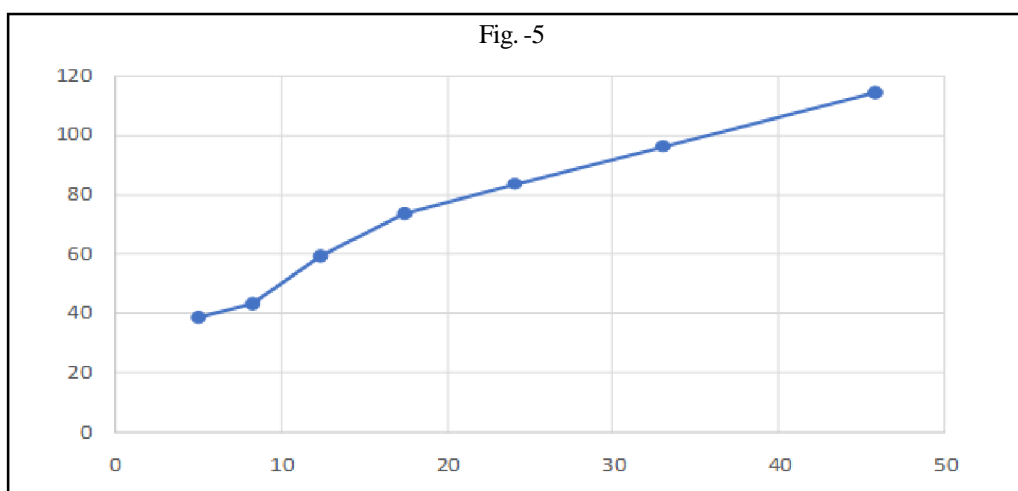
% of Dioxan (v/v)	Mol % of Dioxan	ΔH^* in kJ/mol	ΔG^* (at 30°C) in kJ/mol	ΔS^* at 30°C in J/K/mol	($\Delta S^* + 50$) at 30°C J/K/mol
20%	5.02	83.41	86.86	-11.39	38.61
30%	8.31	85.06	87.10	-6.73	43.21
40%	12.36	90.18	87.38	9.24	59.24
50%	17.46	94.78	87.64	23.56	73.56
60%	24.08	98.04	87.90	33.47	83.47
70%	33.04	102.22	88.24	46.14	96.14
80%	45.83	108.22	88.64	64.62	114.22



variation of ΔG^* with mol % of dioxan in the reaction media.

Table - 5
Variation of log k values of the reaction with log [H₂O] values of water-Dioxan System
(media) at different temperatures

% of Dioxan (v/v)	% of H ₂ O	log [H ₂ O]	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	2.1053	2.3646	2.6133	2.8446	3.0778
30%	70%	1.5898	2.0462	2.3067	2.5642	2.8065	3.0498
40%	60%	1.5229	1.9671	2.2413	2.5166	2.7688	3.0262
50%	50%	1.4437	1.9008	2.1879	2.4721	2.7375	3.0006
60%	40%	1.3468	1.8372	2.1312	2.4276	2.6998	2.9731
70%	30%	1.2218	1.7562	2.0653	2.3698	2.6538	2.9412
80%	20%	1.0458	1.6498	1.9773	2.2988	2.5999	2.8996



variation of ΔS* with mol % of dioxan in the reaction media.

Effect of Solvent on the Solvent number and on the Mechanism 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 [H₂O] value of the reaction media. By using Robertson²² equation which

$$\log k = \log k + n \log [\text{H}_2\text{O}]$$

(Here 'n' is the solvation number)

The log k and log [H₂O] are enlisted in Table 5 and their plots are shown in Fig. -6 and numerical values of the slopes of the plots have been enlisted in

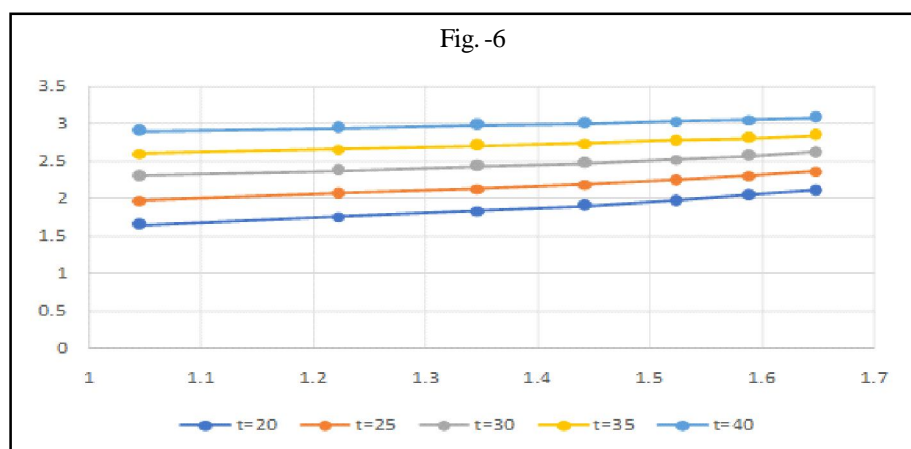
Table 6.

Robertson *et.al.*²³ 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.

From the values recorded in Table VI, it is clear that at all the temperature of the reaction the plots of log k versus log [H₂O], There are two straight lines having different slopes which meet at log [H₂O] values 1.439 which corresponds to 49.50% of water in water- dioxan media.

Table – 6 Variation of log k values of the reaction with log [H₂O] values of water-Dioxan System (media) at different temperatures

Temperature in °C	Slope - I when log[H ₂ O] value is below 1.439	II when log[H ₂ O] value Slope - is above 1.439
20°C	0.651	1.051
25°C	0.533	0.743
30°C	0.461	0.705
35°C	0.322	0.536
40°C	0.264	0.442



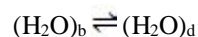
From the evaluated values of slopes as recorded in Table- 6, it is clear that before log [H₂O] values 1.439 which corresponds to 49.50% of water concentration in the reaction media, their values are decreasing from 0.651 to 0.264 with rise in temperature of the reaction from 20 to 40°C. Similarly, after log [H₂O] value 1.439 *i.e.* above 49.50% 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 decreases from 1.051 to 0.442 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 decreases from 1.051 to 0.264.

Thus on the guidelines of Robertson *et.al.*²³ 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 dioxan in the reaction media.

About the change in the structure of water in presence of dioxan 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.



Similar findings and their such interpretations have also been supported by earlier findings of Singh & Sinha *et.al.*²⁴ and also recently by Raghaw & Singh *et.al.*²⁵

Effect of Solvent on the Solvent – solute Interaction in Aquo-DMSO reaction Media :

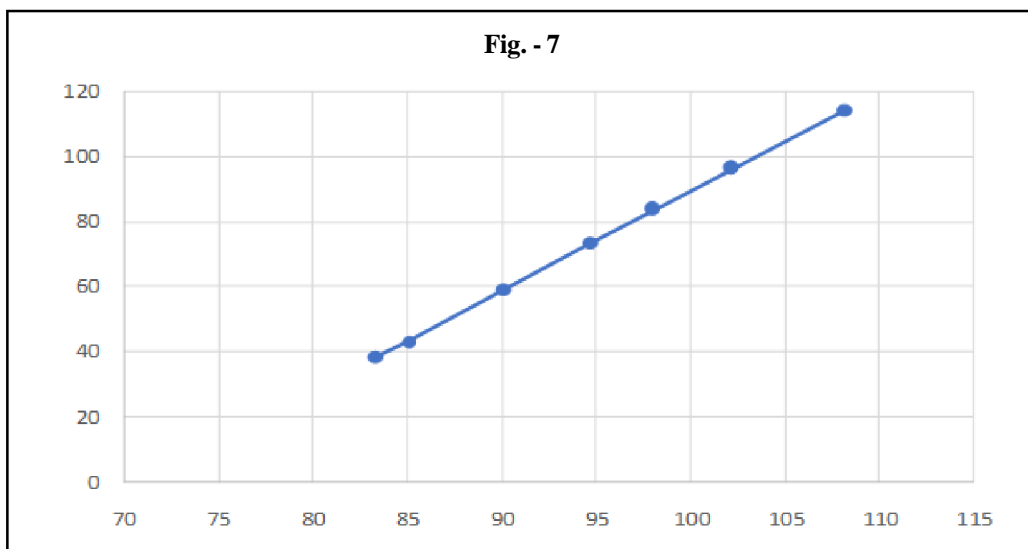
Following the Barclay and Butler²⁶ relationship :

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

(where ' β ' is the iso-kinetic temperature)

That plot of ΔH^* against ΔS^* was found to be straight line as shown in Fig 7 and from its slope the Iso-kinetic temperature of the reaction was evaluated to $328.78 \approx 329.0$. From the numerical value

of the Iso – kinetic temperature of the reaction which is greater than 300, it is concluded in the light of Leffler²⁷ that there is considerable change in the structure of the reactant or with the solvent or in both the reactant and solvent due to strong interaction between solvent and solute present in the reaction media in presence of dioxan.



That plot of ΔH^* against ΔS^* was found to be straight line

However similar findings and their interpretations for solvent-solute interactions in the different reaction media have also been reported earlier by Singh & Navendu *et al.*²⁸ and recent by Namrata & Singh *et al.*³⁰ and Sushma, Ashutosh & Singh *et al.*³¹

Scope of future work and Conclusion

Future Studies on the solvolysis of different valerates are open to the researchers of the kinetic field as it has wide applications and uses particularly for the people of the modern societies.

Acknowledgement

The authors would like to thank the anonymous reviewers for their valuable comments and suggestions to improve the quality of the paper.

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