

STUDIES ON THE KINETICS OF CATALYSED SOLVOLYSIS OF ETHYL ISO-VALERATE IN AQUEO-DIPOLAR, APROTIC SOLVENT SYSTEMS

MRITYUNJAY KUMAR* AND R.T.SINGH**

1. [Research Scholar, Dept of chemistry V.K.S. university, Ara](#)
2. [Professor and Formerly HOD Chemistry and The Dean of the Faculty of V.K.S. University, Ara](#)

ABSTRACT

Valerates and Iso-Valerates tend to Possess a lot of biochemical activities. They have pleasant odors and are used as perfumes and cosmetics. They are also used as food additives because of their Fruity odors. In order to highlight The Solvent effect on their biochemical efficiencies. The Kinetics of alkali catalysed hydrolyses of ethyl iso-Valerate was Studied in aqueo-DMF Reaction media.

Keywords :- *Iso-Valerate, Dipolar-Aprotic. Perfume Cosmetics, Flavors Food additive, Solvation specific Solvation. Solvation numbers, Entropy controller. Strong and Weak Interaction.*

Introduction :

With a view to study the solvent effect of a dipolar-protic solvent DMF, on the biochemical behaviour of Iso-valerate ester, it has been planned to study the kinetics of alkali catalysed hydrolysis of Ethyl iso-valerate in aqueo-DMF media. This kinetic study has been proposed because solvent effect of DMF on the biochemical behaviour of its hydrolytic products, valeric and iso-valeric acid as a perfume, fruit flavour intermediate, a plasticizer, vinyl stabilizer and pharmaceutical has not been paid even a little attention by the kineticists so far:

Experimental:

Export quality Ethyl iso-valerate of fluka AG grade packed in Switzerland and DMF of SISCO grade were used. The kinetics of the reaction was studied as usual^{1,2}. by keeping the strength of alkali 0.1 M and that of the ester 0.5 M in the reaction mixture. The kinetics of the solvolysis of Ethyl iso-valerate was studied in aquo-DMF media having different concentration of DMF from 20 to 80% (v/v) at five different temperatures ranging from 20°C to 40°C at an interval of 5°C. The reaction was found to obey the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table-I. The variation of $\log k$ with $\log [H_2O]$ have been mentioned in Table - II and the evaluated values of number of water molecules associated with the activated complex have been tabulated in Table -III. The evaluated values of iso-composition and iso-dielectric activation energies (E_C and E_D) have been mentioned respectively in Table-IV and Table-V and by using Wunne-Jones & Eyring equation³, the evaluated consolidated values of thermodynamic activation parameters i.e. ΔH^* , ΔG^* and ΔS^* have been enlisted in Table-VI.

Solvent Effect on the Specific Rate Constants of the Reaction :

From the data recorded in Table -I, it is clear that rate constant values of the reaction decrease with increasing concentration of DMF in the reaction media. On plotting $\log k$ values against mol % of DMF as shown in Fig. -1, it is obvious that up to approximately 22.50 mol % of the DMF in the reaction media, the rate of reaction falls rapidly but beyond 22.50 mol % of DMF, the depletion in the rate follows slow depleting path. However, the degree of depletion is found to be sharper with increase in temperature of the reaction.

Table - 1

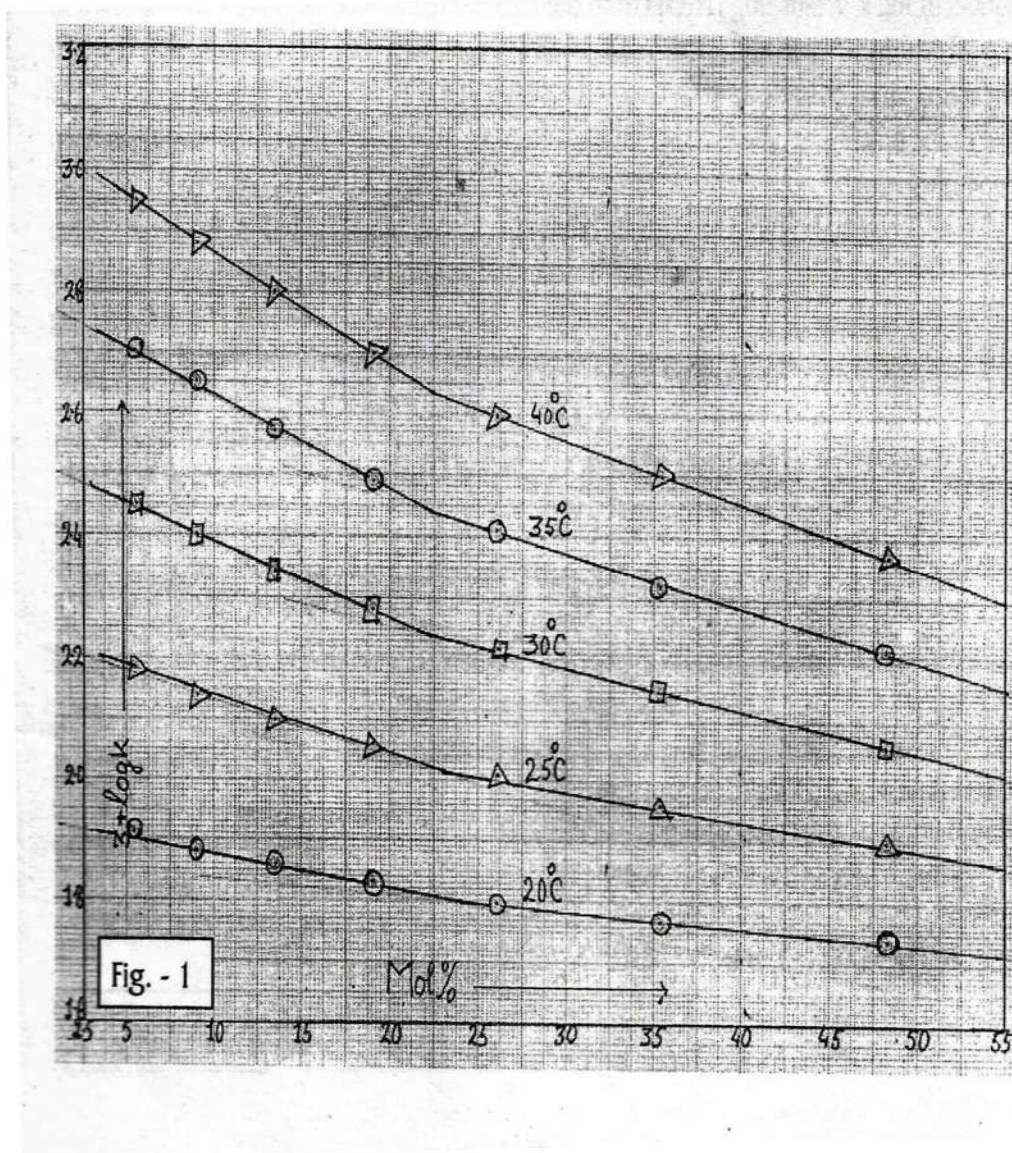
**Specific rate constant values of Alkali catalysed hydrolysis of Ethyl
Iso-valerate in water-DMF media
 $k \times 10^3$ in (dm)³ mol⁻¹ min⁻¹**

Temp in °C	% of DMF (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	80.64	75.84	71.81	67.64	63.12	59.03	54.60
25°C	150.38	136.84	125.34	113.79	101.67	90.82	79.40
30°C	279.38	248.37	218.88	191.91	164.66	140.22	115.37
35°C	501.30	442.69	371.36	310.67	255.92	209.03	164.74
40°C	893.51	758.75	620.93	506.41	398.20	314.20	233.94

Table – II

**Variation of log k values of the reaction with log [H₂O] values of water-DMF
solvent systems(media) at different temperetures**

% of DMF	% of H ₂ O	log [H ₂ O]	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
20%	5.53	7017	1.9066	2.1772	2.4462	2.7001	2.9511
30%	9.12	11.69	1.8799	2.1362	2.3951	2.6461	2.8801
40%	13.50	17.07	1.8562	2.0981	2.3402	2.5698	2.7986
50%	18.96	23.59	1.8302	2.0561	2.2831	2.4923	2.7045
60%	25.99	31.06	1.8002	2.0072	2.2166	2.4081	2.6001
70%	35.27	41.87	1.7711	1.9582	2.1469	2.3202	2.4972
80%	48.29	55.85	1.7372	1.8998	2.0621	2.2168	2.3691



Such decreasing trends in specific rate constant having different slopes are not new in the kinetic research field. However, our findings are in agreement with the qualitative prediction of Laidler and Landskroener⁴ and recent reports of Akanksha & Singh et al.⁵ and Kuamri & Singh et al.⁶ who predicted that the rate of ion-dipolar reaction decreases with the decrease in

the dielectric constant values of the reaction media. Overall, it has been concluded that the depletion in the rate of hydrolysis of Ethyl iso-valerate in aquo-DMF media is due to both the dielectric effect of the reaction media and the solvation effect by the dipolar-aprotic solvent DMF.

Evaluation of the Solvation number of the activated complex and Solvent Effect on the Mechanism of the reaction :

The effect of concentration of Water [H₂O] of the aquo-DMF media (mixture) on the rate and mechanism of alkali catalysed hydrolysis of Ethyl iso-valerate has been studied in the guide lines and observations rendered by Tommila et al.⁷, Lane⁸ and Elsemongy et al.⁹. They have established an idea of number of water molecules taking part in the formation of the activated complex which is also called the solvation number of the activated complex. It is evaluated using the relation proposed by Robertson¹⁰ which is-

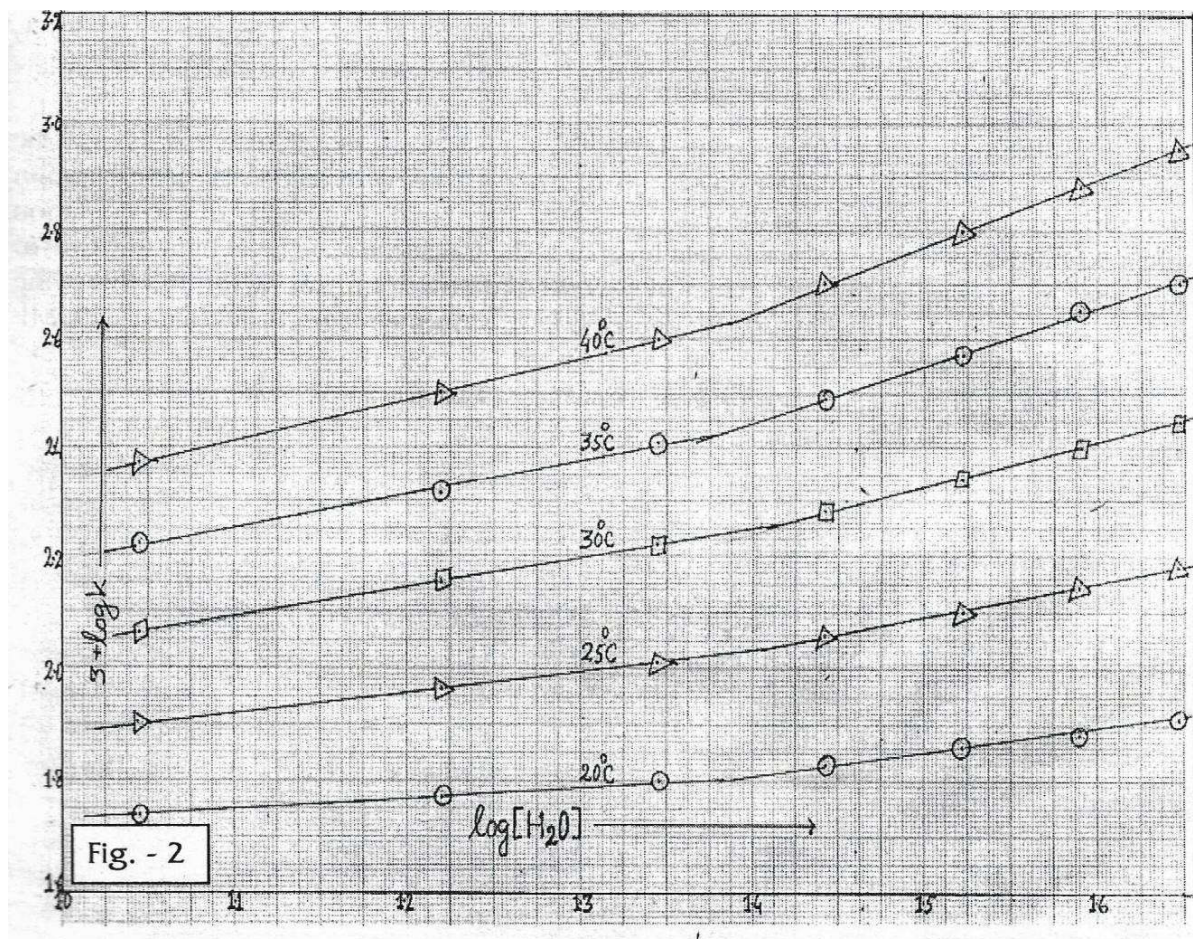
$$\log k = \log K_0 + \log[\text{H}_2\text{O}]^n$$

Where 'n' is the solvation number which tells about the criterion for studying the mechanism of the plots of log k versus log[H₂O] (from their values mentioned in Table -II) as shown in Fig. -2 and have been recorded in Table -III. From Fig. -2, it is obvious that the two intersecting straight lines meet at log[H₂O] values 1.398 which corresponds to 45.00% of water in the reaction media at almost all the 5 temperatures at which the reaction has been carried out. From the values recorded in Table -III, it is obvious that before log[H₂O] values 1.398, i.e. before 45.00% concentration of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.174 to 0.761 and after log [H₂O] value 1.398 (i.e. after 45.00% of water concentration in the reaction media) the number

Table - VI

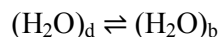
Values of the slopes of the plots of log k versus log [H₂O] values at different temperatures

Temperature in °C	Slope - I when log[H₂O] is below 1.398	Slope - II when log[H₂O] is above 1.398
20°C	0.174	0.444
25°C	0.397	0.611
30°C	0.570	0.863
35°C	0.629	1.062
40°C	0.761	1.236



of water molecules associated with the activated complex increase from 0.444 to 1.236 with increase in temperature from 20 to 40°C. Overall, 'n' values are found to increase from 0.174 to 1.236 with increase in temperature of the reaction from 20 to 40°C. Robertson et al.¹¹ have established that value of slopes (n) for unimolecular reaction is fairly high while that for bimolecular reaction will be low. From the evaluated increasing number of water-molecules associated with the activated complex, it is concluded on the guide lines of Robertson et al.¹¹ that in presence of DMF, the reaction alkali catalysed hydrolysis of ethyl iso-valerate changes its mechanistic pathway from bimolecular to unimolecular with increase in temperature of the reaction. In the light of findings and report of Parker and Tomillinson¹², from increasing

number of water molecules it is also concluded that in presence of DMF, water present in aquo-DMF media changes its structure at equilibrium from dense form to its bulky form with rise in temperature of the reaction from 20 to 40°C.



Similar findings and their interpretations have been reported earlier by Singh & Singh et al.¹³ and Singh & Hafizee et al.¹⁴ and recently by Priyanka & Singh et al.¹⁵ and Singh & Rashmi et al.¹⁶.

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

From the values of the slopes of the plots of log k versus 1/T as shown in Fig. -3, the values of iso-composition activation energy were evaluated and are inserted in Table -IV. From the values recorded in Table-IV, it is obvious that E_C or E_{exp} values of the reaction go on decreasing from 91.56 kJ/mol to 56.10 kJ/mol with increasing concentration of DMF from 20 to 80% (v/v) in the reaction media. This trend 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. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for decrease in E_C values with gradual addition of DMF in the reaction media:-

- (1) The transition state is more solvated than the initial state,
- (2) The initial state is more desolvated than the transition state, and
- (3) The transition state is solvated and the initial state is desolvated.

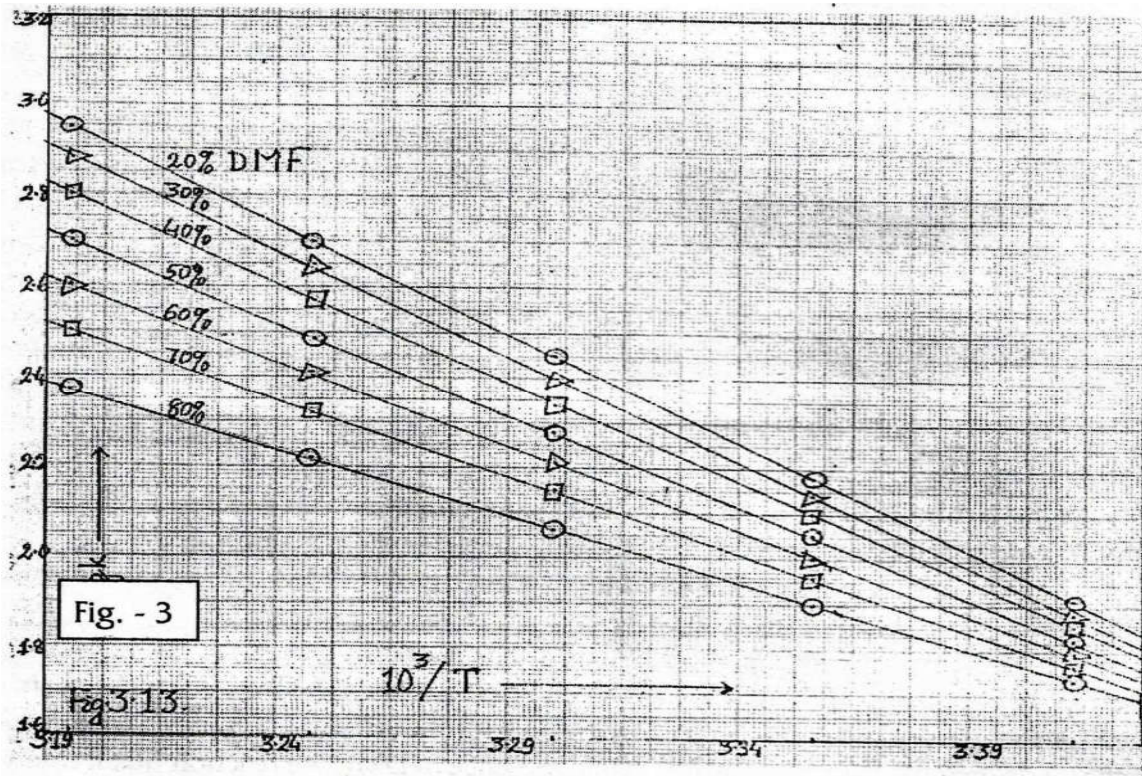


Table - IV

Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-DMF media.

% of DMF (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c value in kJ/mol	91.56	88.27	83.72	77.44	71.25	65.03	56.10

Table - V

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

D values	D = 50	D = 55	D = 60	D = 65	D = 70	D = 75
E_c value in kJ/mol	62.35	70.65	79.15	87.18	94.43	103.61

The transition state being large anion(ester + OH) available more for solvation by DMF molecule than the initial state, so the third factor seems to be operative in our case and it also gets support when the values of entropy of activation(ΔS^*) and enthalpy of activation (ΔH^*) go on depleting with increasing concentration of DMF as reported in Table-VI.

Similar depletion and its causes in the values of activation energy of the reaction with gradual addition of the organic content in the reaction media have earlier been reported by Singh & Hafizee et al.¹⁴ and Singh & Singh et al.¹⁷ and also recently by Singh & Bano et al.¹⁸ and Singh & Wats et al.¹⁹.

Solvent effect on the Iso-dielectric Activation energy of the reaction:

On perusal of the data mentioned in Table-V, it is clear that the value of iso-dielectric activation energy (E_D) of the reaction are found to increase from 62.35 kJ/mol to 103.61 kJ/mol with increasing dielectric constants of aquo-DMF media from D = 50 to D 75 respectively. As dielectric constants of aquo-DMF media decrease with addition of the organic solvent(DMF) to it, so in other way it may be concluded that like iso-composition activation energy, the values of iso-dielectric activation energy of the alkali catalysed hydrolysis of Ethyl iso-valerate in aquo-DMF media are also decreasing with gradual addition of DMF in the reaction media. This trend of variation is in good agreement with that

of Wolford²⁰. However, such variation in E_D values of the reaction with increasing D values of the reaction media has also been found in support of the recently reported views of Singh & Bano et al.²¹ and Singh & Singh et al.²².

Solvent effect on Thermodynamic Activation Parameters of the reaction:

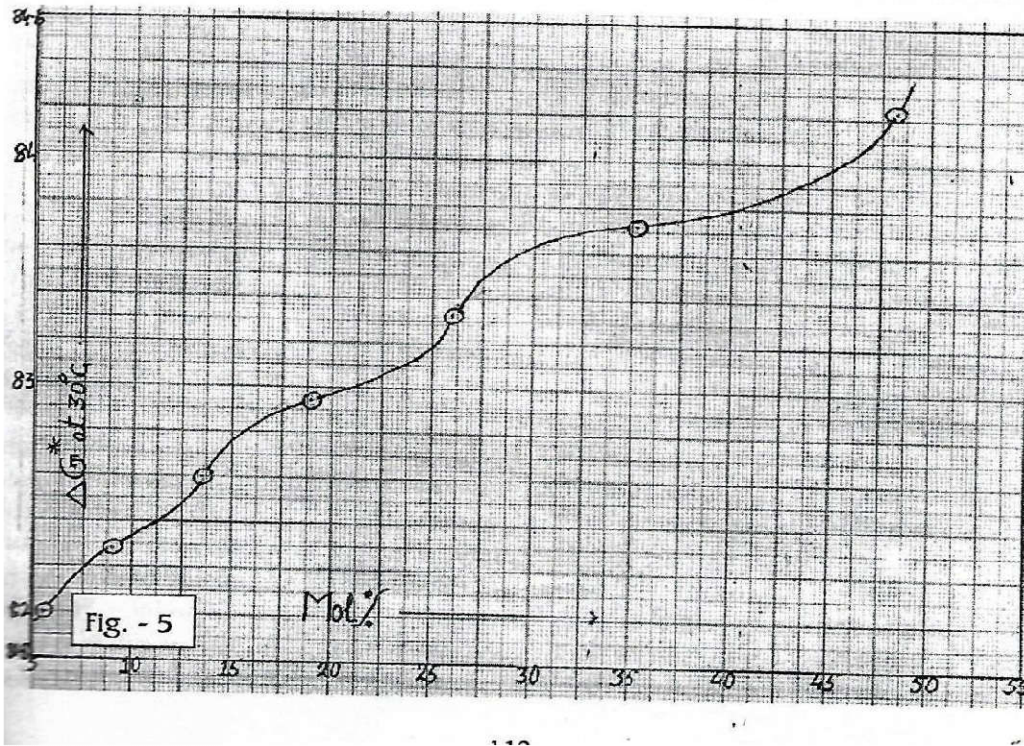
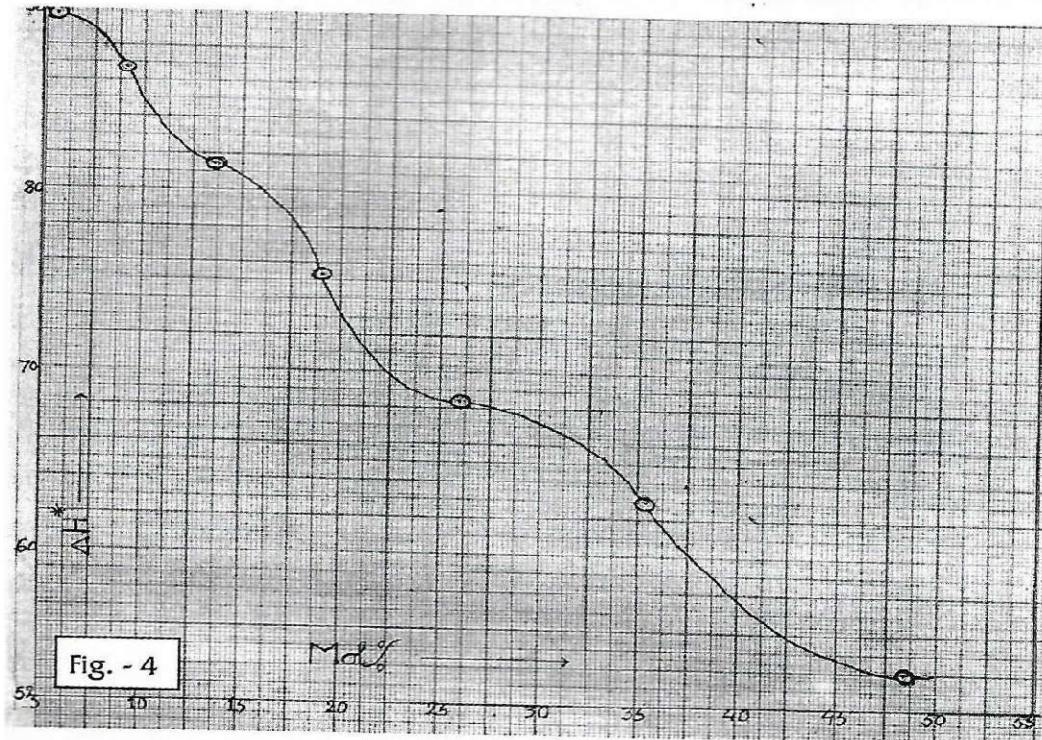
For better understanding and knowledge of the effects of solvent, the thermodynamic activation parameters, such as enthalpy of activation ΔH^* , entropy of activation ΔS^* and free energy of activation ΔG^* were taken into account as they have great significance. These parameters were evaluated using Wynne-Jones and Eyring³ equation and have been recorded in Table-VI. In order to highlight the effect of solvent concentration on these thermodynamic parameters more clearly, ΔH^* , ΔG^* and ΔS^* values were plotted against mol % of DMF which are shown in figures 4, 5 and 6 respectively. Fig. -5 and the values of ΔG^* recorded in Table-VI obviously indicate that the variation in ΔG^* is small and it increases from 81.99 to kJ/mol with increase of

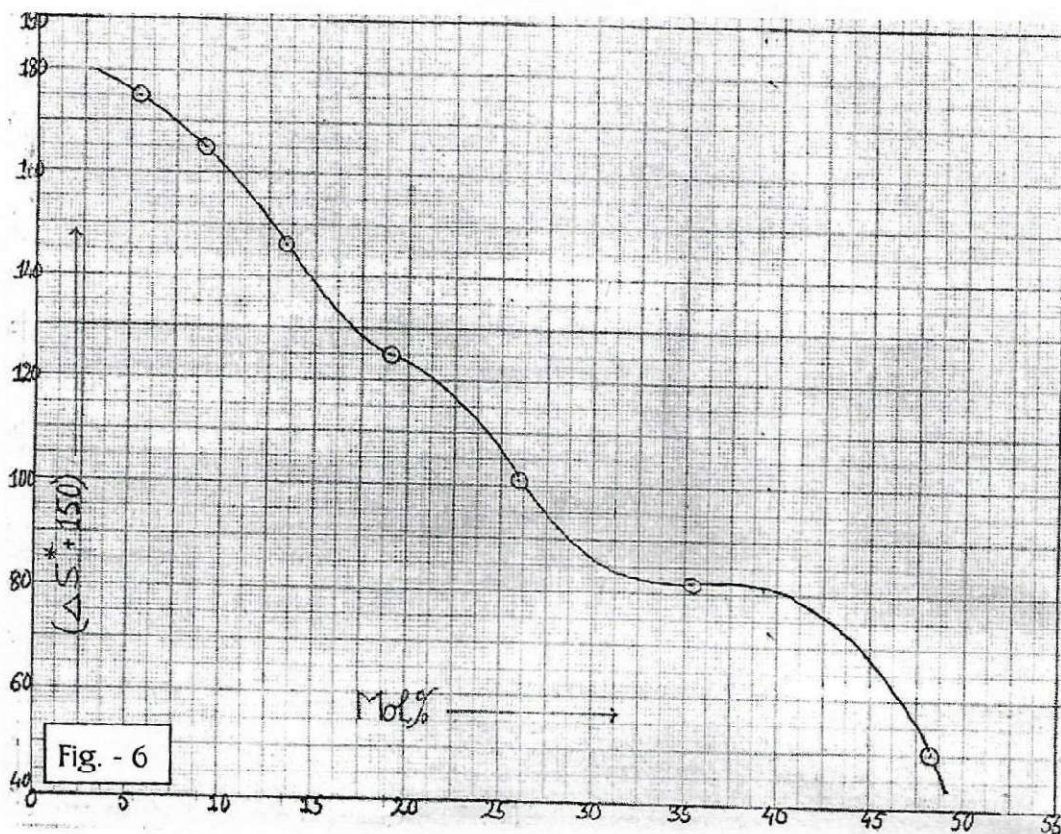
Table - VI

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

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

% of DMF (v/v)	Mole % of DMF	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20%	5.53	89.71	82.23	25.54	82.13	25.44	81.99	25.48	81.88	25.40	81.75	25.42
30%	9.12	86.72	82.38	14.82	82.36	14.62	82.88	14.64	82.21	14.66	82.18	14.51
40%	13.50	81.46	82.51	-3.57	82.58	-3.74	82.60	-3.75	82.65	-3.86	82.66	-3.83
50%	18.96	75.39	82.65	-24.79	82.82	-24.92	82.93	-24.89	83.11	-25.06	83.23	-25.04
60%	25.98	68.48	82.82	-48.95	83.10	-49.05	83.3	-48.97	83.61	-49.11	83.85	-49.12
70%	35.27	63.01	82.99	-68.17	83.38	-68.34	83.72	-68.35	84.12	-68.55	84.47	-68.56
80%	48.29	53.91	83.18	-99.88	83.71	-99.99	84.21	-100.1	84.73	-	85.24	-100.8

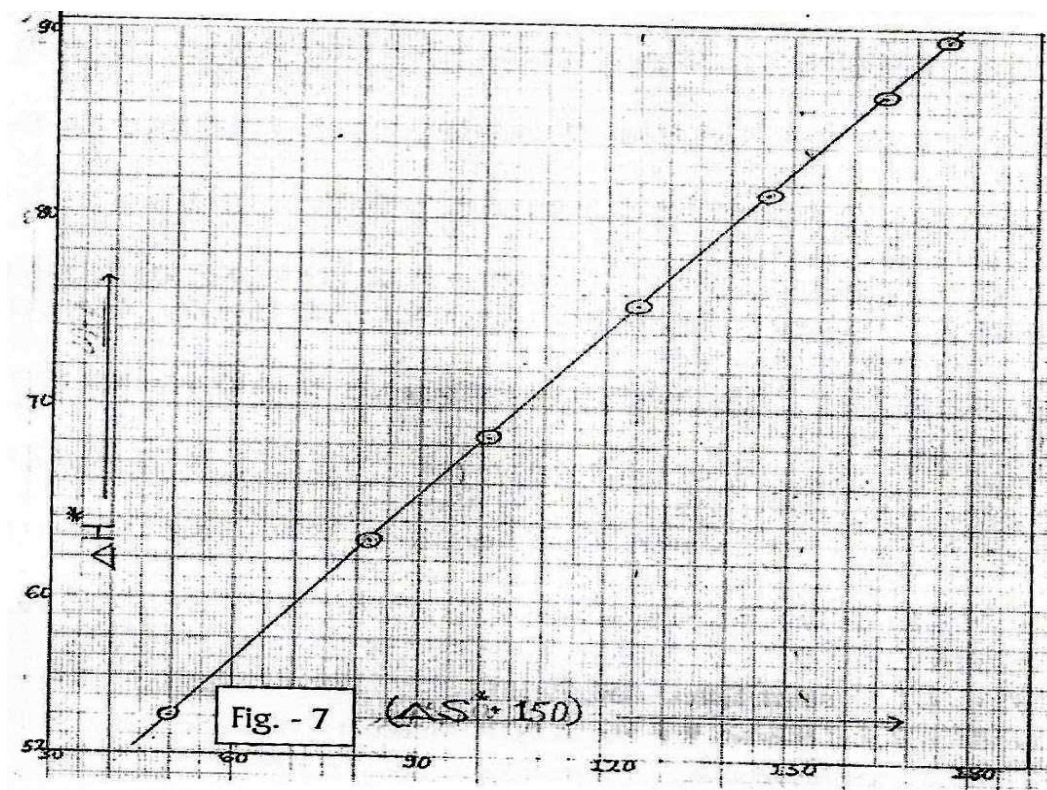




proportion of DMF from 20% to 80%(v/v) at 30°C. gradually in water. The small but considerable increase in ΔG^* and non-linear variation in ΔH^* and ΔS^* curves with the increasing mol % of DMF as shown in Figs. -4 and 6, are indication of specific solvation taking place in the process of activation as already reported by Cleve²³, Saville & Hudson²⁴ and Tomilla et al.²⁵ and Elsemongy et al.⁹ have also observed the similar increase in ΔG^* values, Increase in ΔG^* with simultaneous decrease in ΔH^* and ΔS^* values are only possible when the extent(degree) of depletion in ΔS^* values is greater than that in ΔH^* values and from this, it may be inferred that in alkali catalysed hydrolysis of ethyl iso-valerate in aquo-DMF media, DMF acts as entropy controller (inhibitor) and enthalpy stimulator solvent. Such observations and inferences have been reported earlier by Monalisa & Singh et al.²⁶ and recently also by chandra & Singh et al.²⁷ and Kumar & Singh et al.²⁸.

Varification of Barclay-Butler relationship and Solvent Effect on Solvent-solute interaction in the aquo-DMF solvent systems :

This reaction is found to obey Barclay-Butler²⁹ relationship as a straight line is obtained when ΔH^* values are plotted against ΔS^* values at 30°C (values mentioned in Table-VI) as shown in Fig. -7 and from the value of the slope of the plot, the evaluated values of iso-kinetic temperature of the reaction comes to be $284.34 \approx 284.0$. In the light of the reports of Leffler³⁰, low (below 300) but considerable value of iso-kinetic temperature shows tht in presence of DMF, there is weak but appreciable solvent-solute interaction in the reaction media(aquo-DMf). Similar findings and interpretations for Solvent-solute interaction in the reactin media have also been reported by Monalisa & Singh et al.³¹, Singh & Navendu et al.³² and Singh & Wats et al.³³.



References

1. Singh, R.T., Singh, A.K., Kuamri, V. and Perveen, M. : ARJ Phys. Sci., **15**, No.(1-2), 151- 160,2012
2. Kumari, S., Singh, D.K., Singh, S.K. and Singh,S.K. and Singh, RT.: NIRJ Sci. **10**, 73-82, 2012
3. Wynne Jones W.F.K. and Eyring, H. : J. Chem. Phys.,**3**, 492, 1953
4. Laidler, K.J. and Lanskroener, P.A. : Trans Faraday Sov. **52**, 200, 1956
5. Akanksha, Kumari, R.,Kumar, R. and Singh, R.T. : ARJ Phy. Sci. **17**, Nos. (1-2), 105-116, 2014
6. Kumar,S., Kumari, Sushma, Kumari,S. and Singh, R.T. : NIRJ Sci. **16**, 63-70, 2014
7. Tommila, A., Paakhala, E., Vertanen, V.K. Ervaad, A. and Viapio : Am. Acad. Sci. Fennical, A-2, 91, 1959
8. Lane, C.A. : J. Am. Che., Soc. 86, 2521, 1964
9. Elsemongy, M.M., Elamayem, M.S. and Moussa, M.N.H. : Z. Physik. Chem. Neue Folge, 95, 215, 1975
10. Robertson, R.E. : Prog. Phy. Org. Chem., **4**, 213, 1967 11. Robertson, R.E., Heppolitile, R.L. and Scott, J.M. : Canad.J.Chem. Soc., **37**, 803, 1959
12. Packer, K.J. and Tomillinson, D.J. : Trans. Faraday Soc., **67**, 1302, 1971
13. Singh, R.T., Mishra,S.K., Singh, S.B, and Singh, S. : ARJ Phys. Sci., 15, No.(1-2), 141-150, 2010

14. Singh, R.T., Navendu, K.S., Henry, W. and Hafizee, N.K. : NIRJ. Sci., 14, 53-61, 2014
15. K. Priyanka, S. Nazia, Vishal Kumar and R.T. Singh : ARJ Phy. Sci. **17**, No. (1-2), 117-128, 2014
16. Singh, R.T., Rashmi, Sinha, P.K. and Singh, A.K. : NIRJ Sci. **16**, 25-32, 2014
17. Singh, R.T., Kumar, S., Singh, D. and Singh, R.I. : ARJ Phy. Sci. 16, No. (1-2), 117-128, 2013
18. Singh, R.T., Singh, U.N., Singh, A.K. and Bano, H.N. : ARJ Phy. Sci. **17**, Nos. (1-2), 129-140, 2014
19. Singh, R.T., Wats, K., Kishor, K. and Kumar, d. : NIRJ Sci. **16**, 33-42, 2014
20. Wolford, R.K. : J. Phys. Chem.,. 68, 3392, 1964
21. Singh, A., Bano, H.N., Kuamri, V. and Singh, R.T. : ARJ Phys. Sci; **17**, No.(1-2), 153-165, 2014
22. Singh, R.K., Sudhanshu, N.K.,Kumar, M. and Singh, R.T. : NIRJ Sci. **16**, 43-52, 2014
23. Cleave N.J. : Soumen Kemi, 458, 79, 1953
24. Saville, B.J. and Husdan, R.F. and M.N.H. Moussa : J. Chem.Soc., 20, 120, 1955
25. Tomilla, E., and Mevikallio, E. : Somun Kemi, 26C, 79, 1953
26. Monalisa, Singh, R.N., Sudhanshu, N.S, and Singh, R.T. : NIRJ Sci. **12**, 89-99, 2013
27. Chandra, P., Rai, R.M., Rai, C.L. and Singh, R.T. : ARJ Phys. Sci., **17**, No. (1-2), 167-172, 2014

28. Kumar, S., Kumari, Sushma, Kumari, S. and Singh, R.T. : NIRJ Sci. **16**, 63-70, 2014
29. Barclay, I.M. and Butler, J.A.V. : Trans. Faraday Soc. 1938, 34, 1445
30. Leffler, J.E. : J. Org. Chem., 20, 1201, 1955
31. Monalisa, Verma, S., Singh, D.K. and Singh, R.T. : NIRJ Sci. **17**, 35-47, 2015(Jan.)
32. Singh, R.T., Navendu, K.S. Lal, V.K. and Singh, R.I. : ARJ Phys. Sci; **17**, No (1-2), 187-200, 2014
33. Singh, R.T., Wats, K., Kumari, R. and Kaushalendra, K. : NIRJ Sci. **18**, 33-43, 2015(June)