iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH
IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 14 **Issue:** I **Month of publication:** January 2026

DOI: https://doi.org/10.22214/ijraset.2026.77207

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.538
Volume 14 Issue I Jan 2026- Available at www.ijraset.com

A Kinetic Study of the Solvent Effect of Aquo-Dipolar Aprotic Organic-Solvent Systems on the Biochemical Efficiency of Caprate Ester

Dr. Kumari Priyanka
Department of Chemistry, K. B. Jha College, Katihar, Purnea University Purnea

Abstract: For studying the Solvent-effect of a dipolar aprotic solvent, DMSO on the biochemical efficiency of Caprate ester, the kinetics of alkali catalysed hydrolysis of Propyl caprate was carried out in aquo-DMSO solvent systems having different concentration of the organic component (DMSO) varying from 30 to 80% (v/v) at different temperatures ranging from 20 to 40°C

The mumber of water molecules associated with the activated complex of the reaction were found to decrease from 1.339 to 0.324 and from this, it is inferred that DMSO acts as structure reformer of water converting its bulky form into dense form and it changes the mechanistic path way of the reaction from unimolecular to bimolecular.

With gradual addition of DMSO to the reaction media, enthalpy of activation (ΔH*) and entropy of activation (ΔS*) were found increasing with simultaneous increase in free energy of activation (ΔG*). On the basis of this observation, it has been inferred that the enthalpy of activation enhances to greater extent than entropy of activation and initial state of the reaction is solvated and the transition state is desolvated,

The Iso-composition activation energy (E_C) values of the reaction were found to be enhancing from 102.11 kJ/mol to 130.53 kJ/mol with increasing concentration of DMSO in the reaction media. From this enhancement in E_C it has been confirmed that the initial state of the reaction is solvated and its transition state is desolvated.

From the depletion observed in iso-dielectric activation energy (E_D) of the reaction with increase in D values of the reaction media, it is concluded that E_C and E_D values of the reaction are complementary to each other.

From the numerical value of the iso-kinetic temperature of the reaction, which is evaluated to be 331.44, it is opined that there is strong and appreciable interaction between solvent and solute in water-DMSO reaction media.

Keywords: Caprate Ester, Dipolar Aprotic, Activation Parameters, Biochemical, Iso-kinetic, Transition state, Barclay-Butler Rule, Enthalpy dominating. Entropy controlled.

I. INTRODUCTION

The observation that the solvent affects, the rate as well as mechanism of the solvolysis reaction in water-organic co-solvent media has aroused much interest and inquisitiveness in the mind of researchers. Though a large number of works have been reported[1-4] on the solvent effect on various types of reaction but the study of solvent effect on the biochemical and industrial uses of heavy caprate ester has not been paid adequate attention so far. So, in order to highlight the above noted idea, it was thought essential and useful to investigate about the fact that how the biochemical and industrial uses of Propyl caprate are more effective for manufacturing perfumes to be used as cosmetics as well as flavours, which is widely used as food additive for human beings.

II. EXPERIMENTAL

The kinetics of alkali catalysed solvolysis of Propyl caprate was studied by adding different concentration of the aprotic organic co-solvent (DMSO) from 30 to 80% (v/v) in the reaction media at five different temperatures i.e. 20, 25, 30, 35 and 40°C using previously adopted methods[5,6]. The specific rate constants were evaluated using second order kinetic equation and have been mentioned in Table - I. From the plots of log k values versus log [H_2O] values, as mentioned in Table - II, their slopes value were evaluated and have been inserted in Table - III.

From the slopes of the Arrhenius plots of log k versus 1/T and that of log k (obtained from interpolation of the plots of log k against D values of water-DMSO solvent system) versus the values of Iso-composition activation energy (E_C) and Iso-dielectric activation energy (E_D) of the reaction have been evaluated and are recorded respectively in Tables IV and V.

From the values of the specific rate constant values, thermodynamic activation parameters namely free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) of the reaction were determined by using Wynne-Jones and Eyring equation[7] and are synchronised in Table - VL.

III. RESULTS & DISCUSSION

A. Evaluation of Solvation number and Determination of Mechanistic path Followed by the Reaction

The mechanism of the reaction was determined by evaluating the number (n) i.e. the solvation number of water molecules involved in the formation of activated complex. It was done by plotting logk against log[HO] by using the relation proposed by Robertson[8]. which is as:

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

where 'n' is the solvent number (number of water molecules associated with the activated complex) which is evaluated from the slopes of the plots of log k versus log [H_2O] and

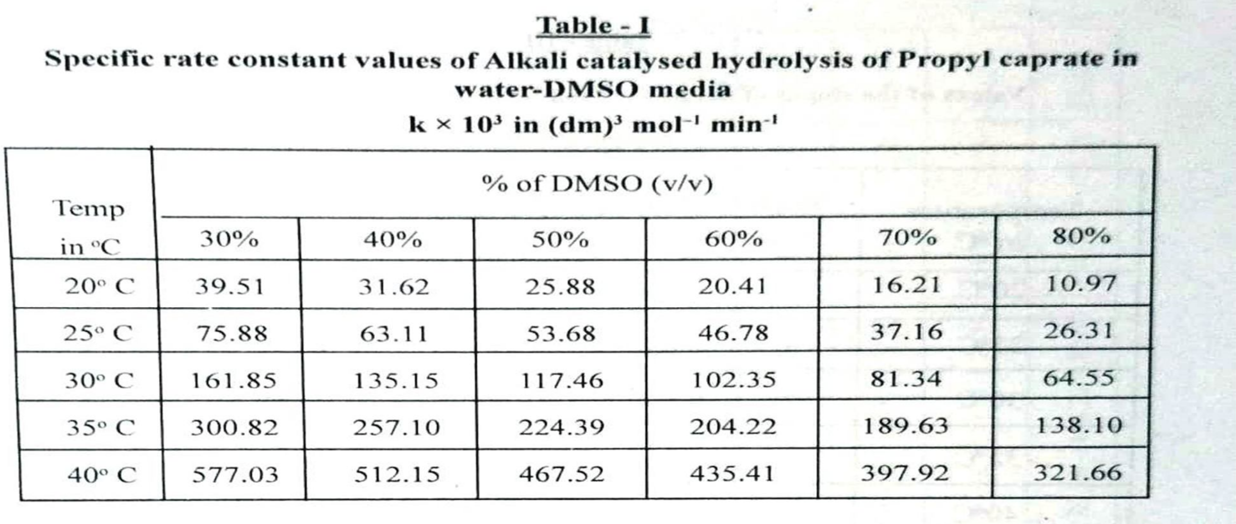

Table - I

Specific rate constant values of Alkali catalysed hydrolysis of Propyl caprate in water-DMSO media

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

Temp in °C	% of DMSO (v/v)					
	30%	40%	50%	60%	70%	80%
20° C	39.51	31.62	25.88	20.41	16.21	10.97
25° C	75.88	63.11	53.68	46.78	37.16	26.31
30° C	161.85	135.15	117.46	102.35	81.34	64.55
35° C	300.82	257.10	224.39	204.22	189.63	138.10
40° C	577.03	512.15	467.52	435.41	397.92	321.66

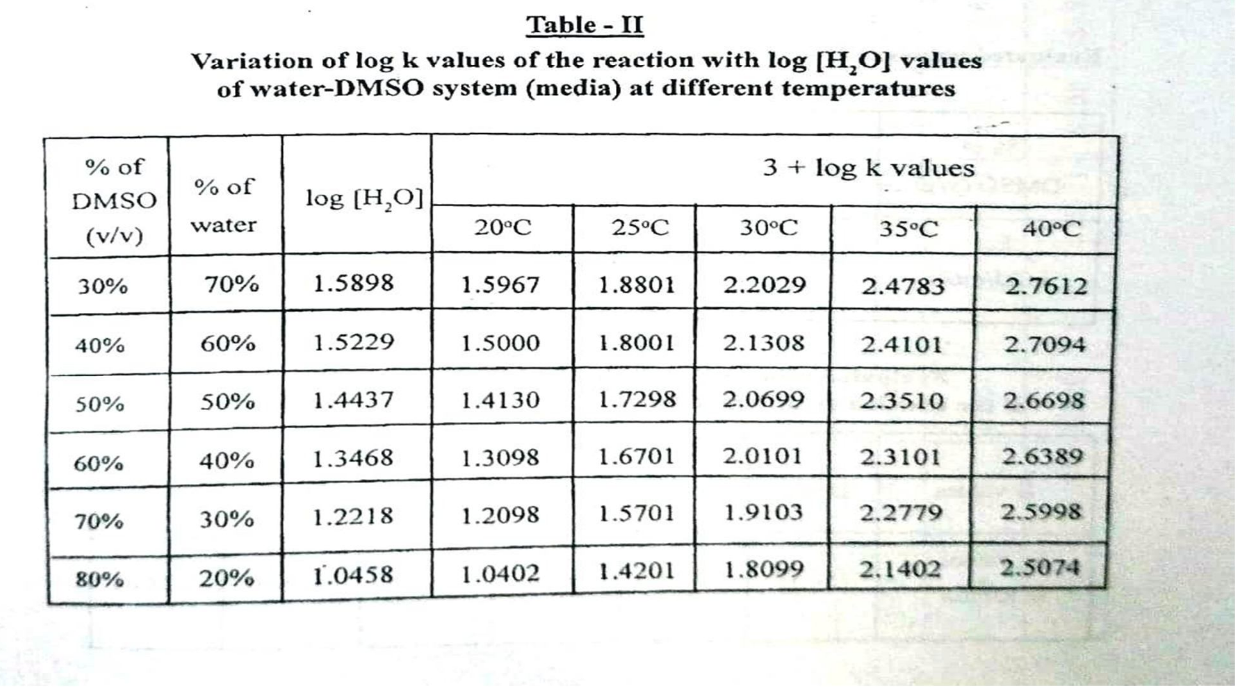

Table - II

Variation of log k values of the reaction with log [H_2O] values of water-DMSO system (media) at different temperatures

% of DMSO (v/v)	% of water	log [H_2O]	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.5898	1.5967	1.8801	2.2029	2.4783	2.7612
40%	60%	1.5229	1.5000	1.8001	2.1308	2.4101	2.7094
50%	50%	1.4437	1.4130	1.7298	2.0699	2.3510	2.6698
60%	40%	1.3468	1.3098	1.6701	2.0101	2.3101	2.6389
70%	30%	1.2218	1.2098	1.5701	1.9103	2.2779	2.5998
80%	20%	1.0458	1.0402	1.4201	1.8099	2.1402	2.5074

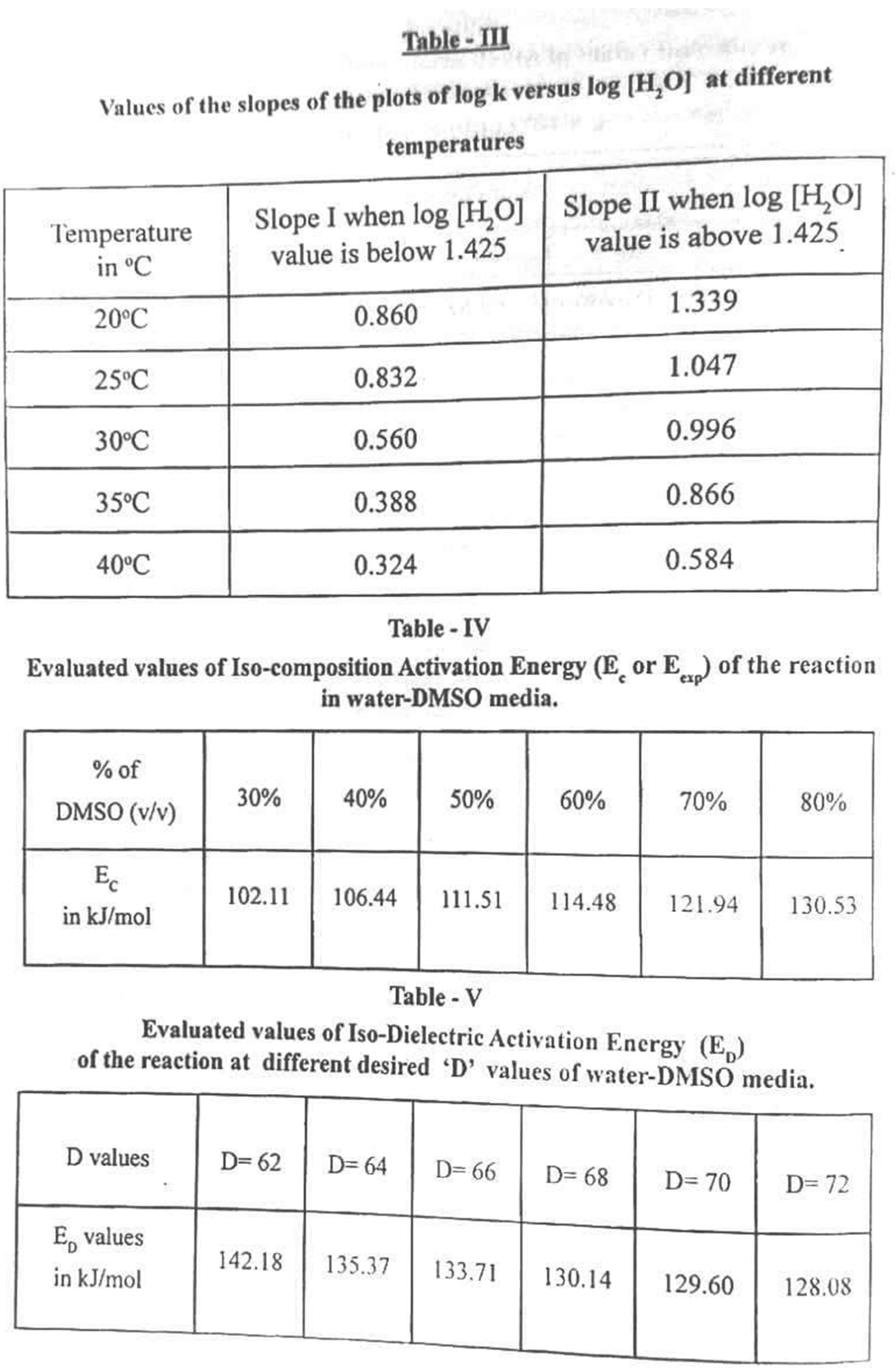

Table - III

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 1.425	Slope II when log [H_2O] value is above 1.425
20°C	0.860	1.339
25°C	0.832	1.047
30°C	0.560	0.996
35°C	0.388	0.866
40°C	0.324	0.584

Table - IV

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

% of DMSO (v/v)	30%	40%	50%	60%	70%	80%
E_C in kJ/mol	102.11	106.44	111.51	114.48	121.94	130.53

Table - V

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

D values	D= 62	D= 64	D= 66	D= 68	D= 70	D= 72
E_D values in kJ/mol	142.18	135.37	133.71	130.14	129.60	128.08

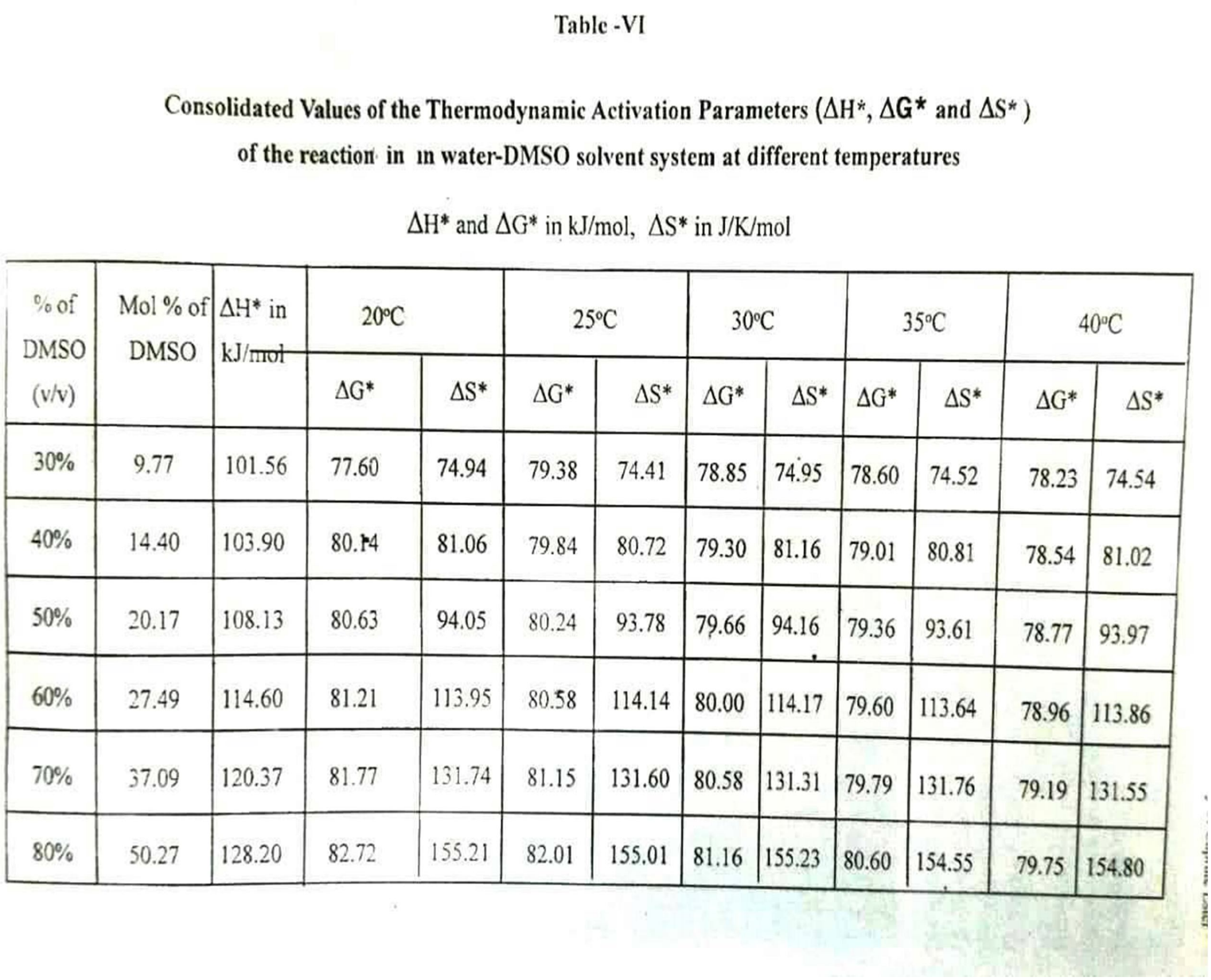

Table -VI

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

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of DMSO (v/v)	Mol % of DMSO	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%	9.77	101.56	77.60	74.94	79.38	74.41	78.85	74.95	78.60	74.52	78.23	74.54
40%	14.40	103.90	80.14	81.06	79.84	80.72	79.30	81.16	79.01	80.81	78.54	81.02
50%	20.17	108.13	80.63	94.05	80.24	93.78	79.66	94.16	79.36	93.61	78.77	93.97
60%	27.49	114.60	81.21	113.95	80.58	114.14	80.00	114.17	79.60	113.64	78.96	113.86
70%	37.09	120.37	81.77	131.74	81.15	131.60	80.58	131.31	79.79	131.76	79.19	131.55
80%	50.27	128.20	82.72	155.21	82.01	155.01	81.16	155.23	80.60	154.55	79.75	154.80

tells about the criterian for studying about the mechanism of the reaction.

From the values mentioned in Table - II, the plots of log k versus log [H_2O] are shown in Fig. 1. It is obvious from Fig. 1 that at each temperature, there come two intersecting straight lines having different values of positive slopes at each temperature are mentioned in Table - IIIL

From Table-III, it is clear that below log [H_2O] value 1.425 which corresponds to 47.90% of water in water-DMSO media, the number of water molecules associated with the activated complex decreases from 0.860 to 0.324. Similarly, above log [H_2O] value 1.425 ie. above 47.90%, concentration of water in the reaction media, the number of water molecules involved in the formation of the activated complex decreases from 1.339 to 0.584.

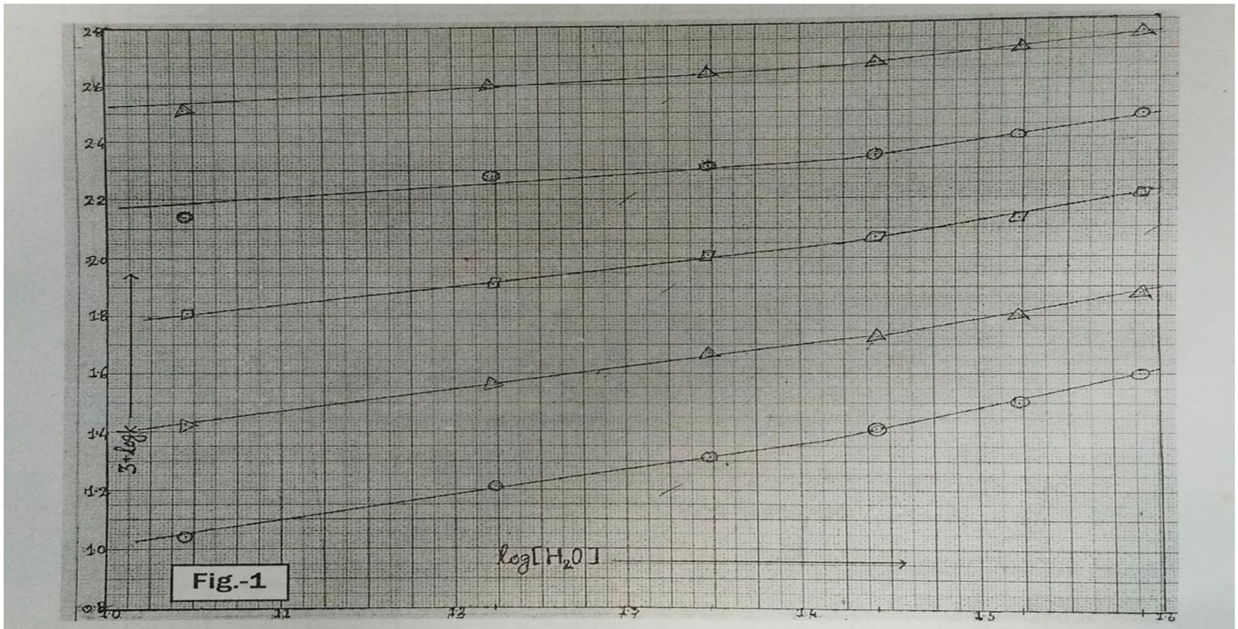

Fig. - 1 : Plots of log k values versus log [H_2O] values in water-DMSO media

From the decreasing number of water molecules involved in the formation of the activated complex, it is inferred that DMSO in the reaction media acts as structure reformer and in doing so, it shifts the equilibrium of water from its bulky form to its dense form and in the light of guidelines of Robertson et al[9] it is concluded that the mechanistic pathways of the reaction in presence of DMSO is changed from unimolecular to bimolecular. Our such findings and inferences are in support of the recently reported views of Singh & Kumari et al[11].

B. Solvent effect on the Thermodynamic Activation Parameters:

On perusal of the data mentioned in Table-IV, it is found that the values of free energy of activation (ΔG*) increases with increasing DMSO content of the reaction at all the temperature at which the reaction was studied. At 30°C, values of ΔG* were reported to increase from 78.85 kJ/mol to 81.16 kJ/mol with increasing proportion of DMSO from 30 to 80% (v/v). Though the enhancement in ΔG* values is not very high, however, it is up to mark for taking into consideration.

A similar variations in ΔG* values with increasing mol % of organic solvent has also been reported by Singh & Kumar[12] and Kumari & Singh[13]. From the plot of ΔG* against mol % of organic co-solvent (as shown in Fig. 2) it is found that ΔG* values increases smoothly and non-linearly with gradual addition of DMSO in the reaction media. This finding is indicative of desolation of reactants as explained and also supported by Elsemongy et al[14].

So far as the variation in ΔH* and ΔS* values are concerned, on going through Table - IV, it is interestingly observed that both of them decrease with gradual increase in the concentration of DMSO in the reaction media at all the temperatures.

On the basis of the relation:-

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

it can be concluded that simultaneous enhancement in ΔG* values with increase in the values of both the ΔH* and ΔS* values is only possible when the extent of increase in ΔH* is more than that of ΔS* The regular enhancement to the greater extent in ΔH*

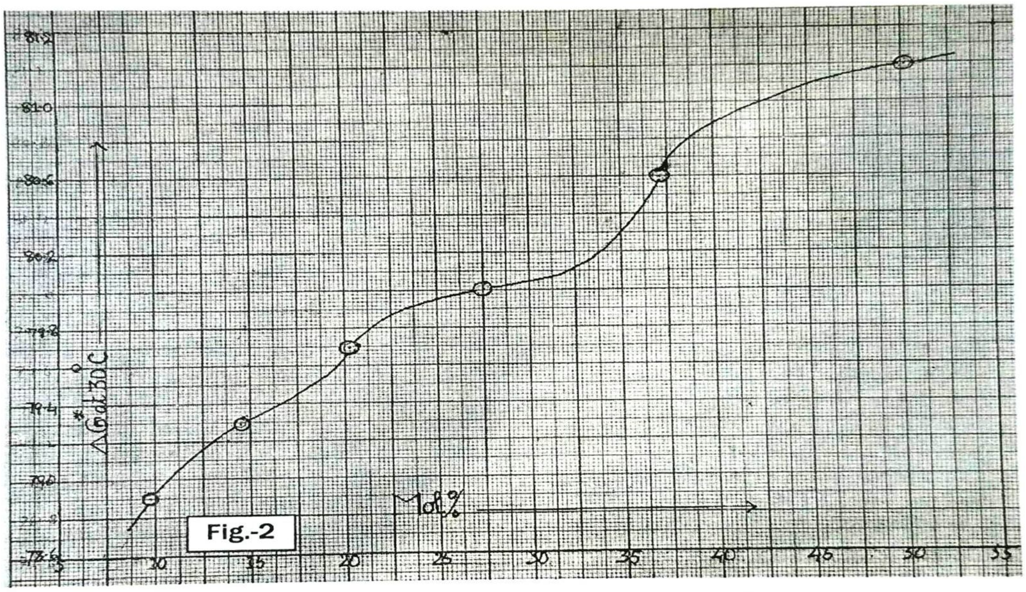

Fig. - 2: Plots of ΔG* values against mole % of DMSO in water-DMSO media

values in comparison to that of ΔS* values clearly indicates that the alkali catalysed hydrolysis of Propyl caprate in water-DMSO media is enthalpy dominated and entropy controlled. Moreover, non-linear variation in ΔS* and ΔH* values with increasing mol % of DMSO in the reaction media, as shown in Fig. 3 and 4 respectively, gives information of the fact that the specific solvation is taking place in water-DMSO systems, similar to that as reported by Saville et al[15] and it also indicates that the random distribution of the components are not permissible. The similar non-linear variations in ΔS* and ΔH* values with increasing mol % of the organic component in the reaction media have also been reported recently by Singh & Singh et al[16] and Singh & Hafizee[17]. The depletion in both ΔH* and ΔS* values justifies that transition state of the reaction is desolvated and its initial state is solvated in water-DMSO media.

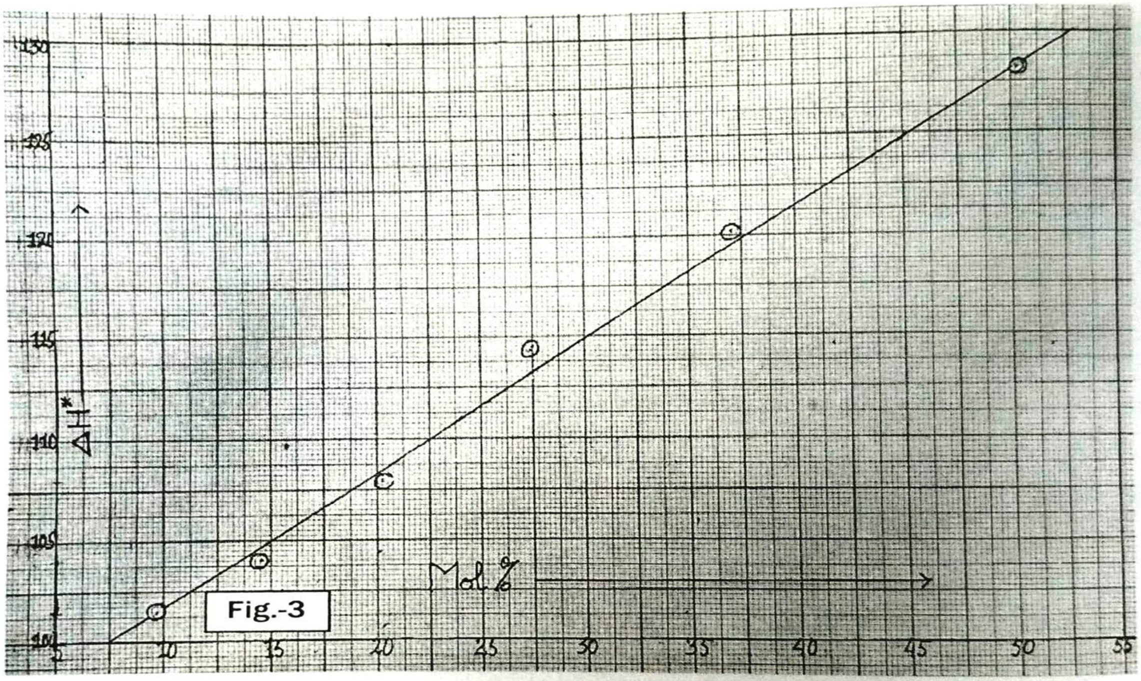

Fig. - 3 : Plots of ΔH* values against mole % of DMSO in water-DMSO media

C. *Solvent Effect and evaluation of Iso-composition Activation Energy*

From Table-IV, it is obvious that iso-composition activation energy values of the reaction go on increasing from 102.11 kJ/mol to 130.64 kJ/mol with increasing concentration of DMSO in the reaction media.

The enhancing trend in the E_{exp} value may be due to either of the following three causes:

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

Out of these three causes, the third factor seems to be operative in this case as both ΔH* and ΔS* values of the reaction as mentioned in Table IV, are found to increase. Similar findings have also been reported recently by Singh & Perween[18] and Kumari & Singh[19].

D. *Solvent Effect on the Iso-dielectric Activation Energy (E_D) of the Reaction:*

From the recorded values of the Iso-dielectric activation energy (E_D) of the reaction in Table V, it is apparent that with increase in D values of the reaction media from D 62 to D72, the E_D values go on decreasing from 142.18 kJ/mol to 128.08 kJ/mol respectively.

Since with increase in DMSO content of the reaction media there is decrease in its dielectric (D) values, hence in reverse way it may be inferred that with decrease in D values of the reaction media or with increasing DMSO concentration in the reaction media, E_D values also increase similar to increase in E_C values. Thus, E_C and E_D values are complementary to each other.

Similar interpretation for such effect of concentration of the added organic content of the media or of the effect of change in dielectric constants of the reaction media have also been reported recently by Singh & Perween[18] Kumari & Singh[19] Singh & Namrata[20] and Kumar & Singh et al[21].

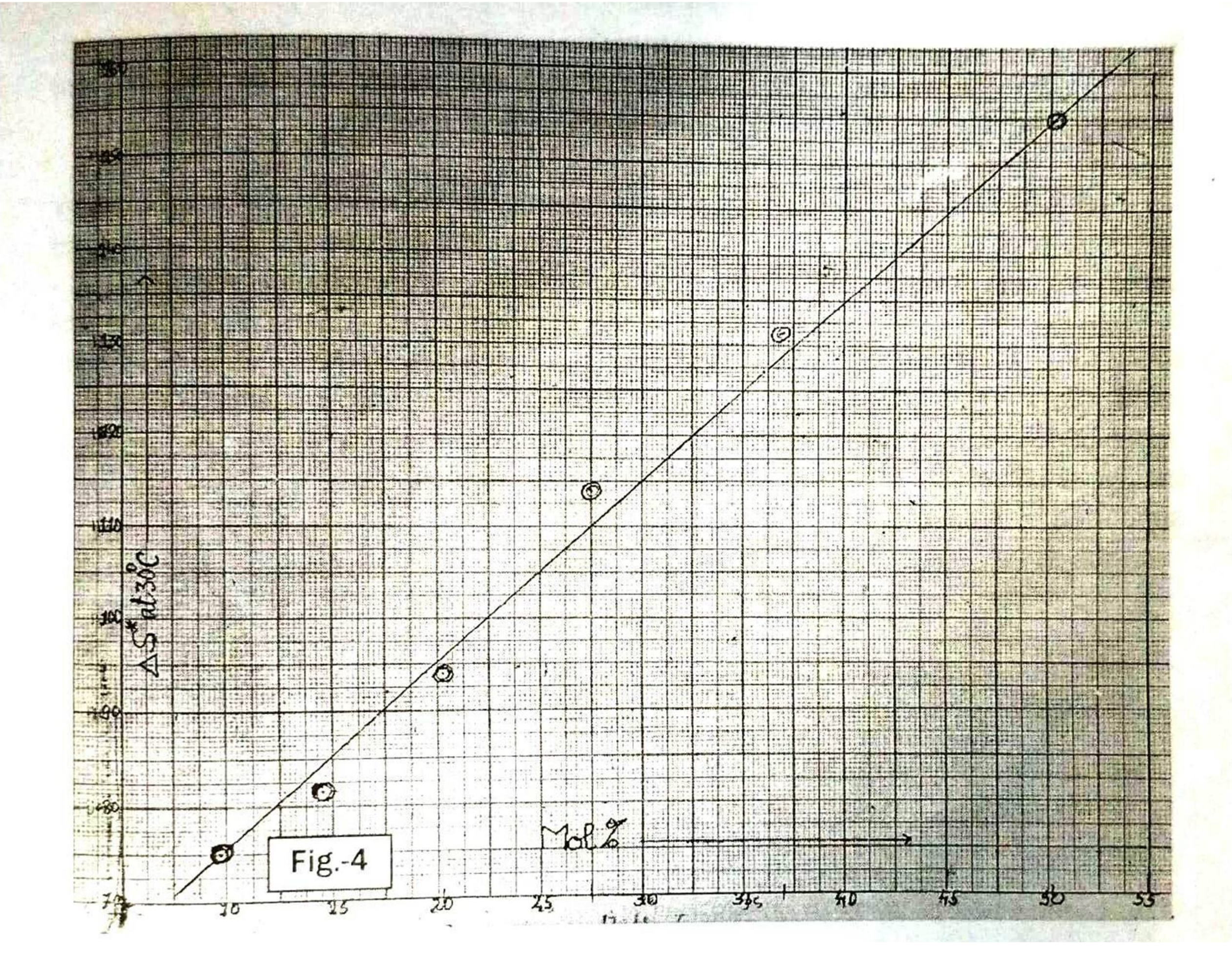

Fig. -4: Plots of ΔS* values against mole % of DMSO in water-DMSO media

E. Solvent effect on Iso-kinetic Temperature

The values of the Iso-kinetic temperature of the reaction was evaluated by using Barclay and Butler[22] relationship which is as follows:

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

It is a straight line equation presenting the relationship between enthalpy and entropy of activation. 'b' is iso-kinetic temperature. From the data available in Table-VI, the plots of ΔH* versus ΔS* at 30°C were made which is shown in Fig. -5. From the slope of the obtained straight line, the value of iso-kinetic temperature was found to be 331.44 In the light of Leffler's[23] guidelines, from the value of iso-kinetic temperature which is much higher than the standard value 300, it is concluded that in water-DMSO media, there is appreciably strong solvent-solute interaction for alkali catalysed solvolysis of Propyl caprate. Our such findings have also recently been supported by Kumar & Singh et al[24].

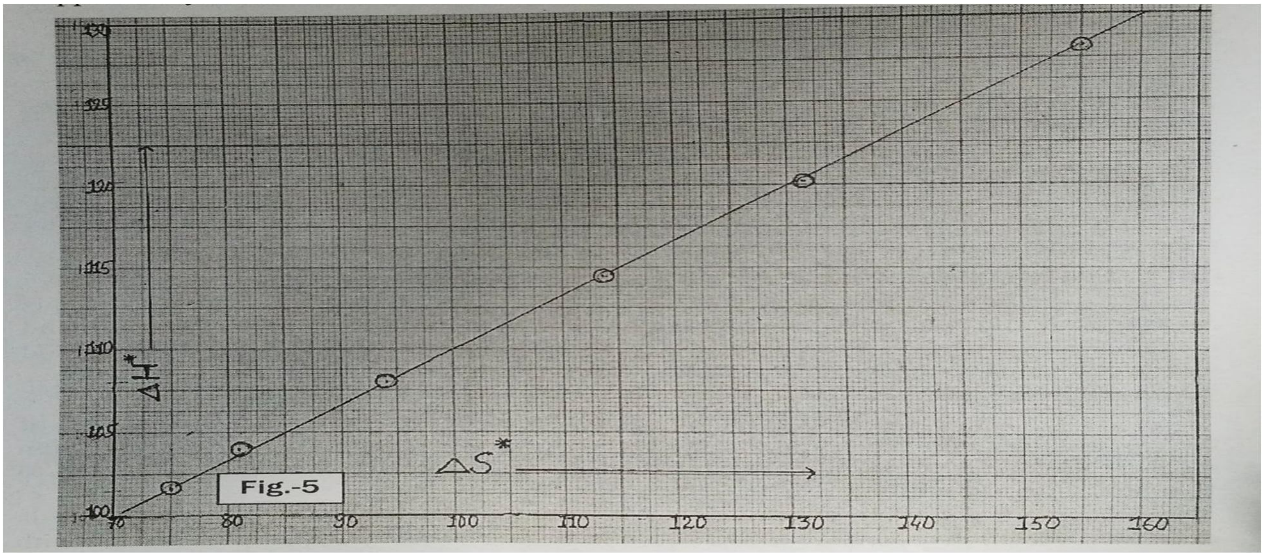

Fig. 5: Plots of ΔH* versus ΔS* in water-DMSO media

REFERENCES

[1] Laidler, K. J. and Eyring. H. and Moussa M. N. H.: Am. N. Y. acad. Sci., 39, 303, 1940
[2] Singh, Lallan., Singh, R. T..Singh, R. K. and Jha, R. C.: J. Indian. Chem.. Soc., 55, 375, 1978
[3] Singh, Lallan., Gupta, A. K., Singh, R. T., Verma, D. K.and Jha, R. C.: React. Kinet mCasal. Lett. 24, No. (1-2), 161-165, 1984
[4] Singh, B., Gupta, A. K., Pathak, D. B., Singh, Y. P., and Singh, R. T.: J. Indian Chen. Soc., 66, 372-379, 1989
[5] Singh, R.T., Ojha, R. P. Singh, R. K. and Kumari,, M.: ARJ Phys. Sci., 14, No. (1-2), 81-861.2011
[6] Singh, R. T., Singh, A. K., Singh, P. K. and Dubey, R. NIRJ Sci., 8, 87-93, 2012
[7] Wynne Jones W. F. K. and Eyring H.: J. Chem. Phys., 3, 492, 1953
[8] Robertson R. E. Prog. Phy. Org. Chem. 1, 213, 1976
[9] Robertson R. E. Hippolitile, R. L. and Scott, J. M. W.: Canad, J, Chem. Soc., 1959, 37, 383-1959
[10] Singh, R. T., Kumari, R., Singh, P. and Kumari,, A..: ARJ Phys. Sci., 14, No. (1-2), 127-135, 2011
[11] Singh, R. T., Singh, D. K., Puja and Kumari, M. NIRJ Sci., 12, 77-85, 2013
[12] Singh R. T., Singh, P., Kishore, K. and Kumar, R.: ARJ Phys. Sci., 14, No. (1-2), 87-95,2011
[13] Kumari, S., Singh, S. K., Singh, D. K. and Singh R. T.: NIRJ Sci., 8, 95-99,2012
[14] Elsemongy M. M., Elamayam M. S. and Moussa M. N. H. Z. Physik Chem. (Neue Folge), 94, 69, 1975
[15] Saville B. J. and Hudson R. F.: J. Chem. Soc., 4114, 1955.
[16] Singh, R. T., Kumari, S., Singh, D. and Singh, R. I..: ARJ Phys. Sci., 16, No.(1-2), 129-137, 2013
[17] Singh, R. T., Navendu, K. S., Henry, W. and Hafizee, N. K. NIRJ Sci., 14,53-61, 2014
[18] Singh R. T., Kumar, S., Perween, Z. and Singh, R. I.: ARJ Phys. Sci., 16, No. (1-2), 117-128,2013
[19] Kumari, S., Kishore, K., and Singh R. T.: NIRJ Sci., 10, 105-110, 2012
[20] Singh R. T., Kumari, M., Chaudhary, K.K. and Namrata: ARJ Phys. Sci., 16, No. (1-2). 105-115, 2013
[21] Kumar, P., Rai, R. M., Rai, C. L. and Singh R. T. NIRJ Sci., 8, 95-99, 2012
[22] Barclay, I. A.and Butler, J. A.: Trans Faraday, Soc., 34, 1445,1938
[23] Leffler, J. E.: J. Org. Chem., 20, 1201, 1955
[24] Kumar, S., Mishra, S. K., Dubey, R. and Singh, R. T.: NIRJ Sci., 15, 29-38,2014.

******