International Journal of Engineering, Science and Mathematics
Vol. 6 Issue 1, March 2017,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

STUDIES-OF THE DIELECTRIC EFFECT-OF AQUO-ETHANOL SYSTEMS ON THE INSECT-REPELLING ACTIVITY OF PHTHALATES

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ABSTRACT

Phthalate esters Possess insect repelling efficiency In order to manufacture insect repelling insecticide of desired efficiency for inereasing the field of Agricultural products the kinetics of alkali catalysed hydrolysis of diethyl phthalate was Studied in aquo-ethanol media. From enhancement and depletion obsered in the iso-composition activation and iso-dielectric activation energies respectively, in is inferred that the initial state of the reaction is solvated and the transition state is desolvated.

Simultaneous enhancement in all the three activation thermo dynanic parameters namely ΔH^*, ΔG^* and ΔS^* give sound proof of the fact that alkali catalysed hydrolysis of Diethyl phthalate in aquo-ethanol media is enthalpy dominating and entropy controlled reaction.

KeyWords **:-** *Insect Repelling, Dielectric Effect, Solvation Changes, and Bimolecular mechanistic paths Transition state, Solvation Changes uni and Bimolecular mechanist paths Transition State, Solvation number*

INTRODUCTION :

Different kineticists[1-3] have reportted their works on the different types of solvolysis reaction, but the studies on the solvent effect of aquo-primary alcohol solvent systems on the insect repelling and insecticidal potential of Phthalate ester are still remaining untouched.

Thus, in order to highlight insect rerepelling and insectisidal potential of Phthalate ester producing more and more crops, it has been proposed to study the solvent effect of aquo-ethanol solvent on the alkali catalysed hydrolysis of diethyl phatalate.

Experimental :

The kinetics of alkali catalysed hydrolysis of Diethyl phthalate was studied in aquo-ethanol reaction media having different concentration of ethanol from 20 to 80% (v/v) and at different temperatures ranging from 20 to 40°C. The reaction was found to follow the second order kinetic equation and the evaluated specific rate constants are tabulated in Table - I. The variation of log k values with temperature have been shown in Table - II. The evaluated values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) of the reaction are tabulated in Table - III and IV respectively. For deciding the mechanistic pathways of the reaction, variation of log k values of the reaction with log [H_2O] values and evaluated number of water molecules involved in the formation of activation complex of the reaction have been enlisted in Table - V and VI respectively. The thermodynamic activation parameters of the reaction have been evaluated using Absolute Reaction Rate Theory[4] and Wynne-Jones and Eyring[5] equation and are inserted in Table - VII.

DISCUSSION ON THE RESULTS:

Effect of solvent on the specific rate constants of the reaction:

With a view to explain the variation in the specific rate constants with change in mol % of ethanol, the logarithm of k values were plotted against mol% of ethanol as shown in Fig.-1. From the values recorded in Table-II and from Fig. -1, it is apparent that the rate constant values of the reaction appear to decrease with increase in the concentration of ethanol from 20 to 80% (v/v) in the reaction media at all the temperatures.

Table - I

Specific rate constant values of Alkali catalysed hydrolysis of Diethyl phthalate in water-EtOH media

$K \times 10^2$ in $(dm)^3$ $mole^{-1}$ min^{-1}

Temp in °C	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	74.41	63.42	52.46	43.61	34.05	26.63	18.56
25°C	161.73	138.10	118.88	101.88	83.20	67.27	50.11
30°C	343.64	313.40	169.22	237.74	201.74	170.84	134.52
35°C	691.19	635.48	583.71	524.93	466.87	407.19	338.92
40°C	1400.88	1321.60	1253.43	1161.98	1074.48	966.27	862.58

Table - II

Variationof log k values of the reaction at different temperatures with mol % of EtOh in water-EtOH media.

% of EtOH (v/v)	Mol % of EtOH	8+ log k values				
		20°C	25°C	30°C	35°C	40°C
20%	7.17	1.8832	2.2088	2.5361	2.8396	3.1464
25%	11.69	1.8022	2.1401	2.4909	2.8031	3.1211
30%	17.07	1.7198	2.0751	2.4301	2.7662	3.0981
40%	23.59	1.6395	2.0089	2.3761	2.7201	3.0652
50%	31.06	1.5321	1.9201	2.3048	2.6692	3.0312
60%	41.87	1.4254	1.8278	2.2326	2.6098	2.9851
70%	555.85	1.2686	1.6999	2.1288	2.5300	2.9358

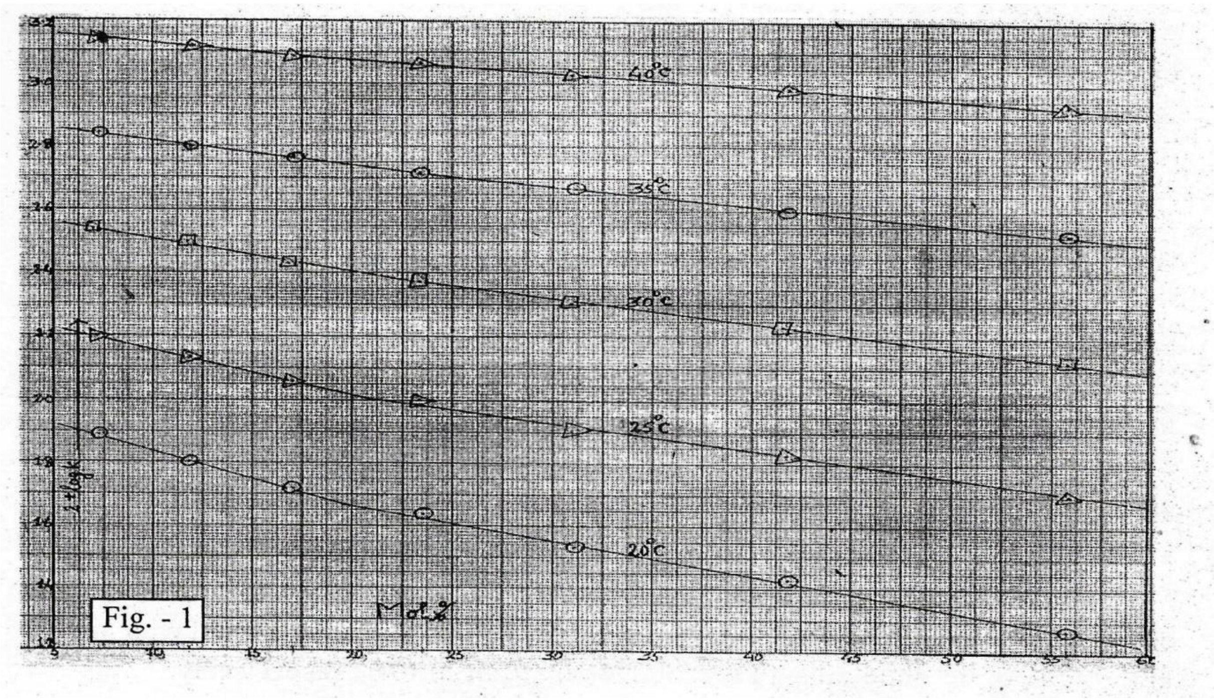

Fig. - 1

From Fig. -1, it is also clear that different decreasing trend before and after about 21.25 mol % of EtOH are observed at all temeratures from 20 to 40°C. It is also clear from Fig. -1 that with increease in temperature of the reaction, the rate of depletion in specifie rate constants becomes slower.

For retardation of the rate of reaction in aquo-ethanol media, generally the following two possible factors seem to have been responsible:

(i) Lowering of the bulk dielectric constant of medium after adding more and more ethanol to it,

(ii) Decreasing the ploarity of the medium as changing from polar water to less polar like aquo-ethanol mixture.

Both the above mentioned factores are found responsible for retardation (decrease) in the rate throughout the region of the aquo-Ethanol media in which the kinetics of the reaction were studied. Similar decrease in the rate of reaction with increasing proportion of the organic co-solvent like ethanol(EtOH) in reaction media) has also been reported earlier by Singh & Jha et al.[6], Elsemongy et al.[7] and also by Singh & Smriti et al.[8] and Monalisa & Singh et al.[9].

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

From the slopes of the plots of log k versus 1/T as shown in Fig.-2, the iso-composition activation energy (E_C) values of the reaction were evaluated which are tabulated in Table -III. From Table -III, it is observed that the values of iso-composition activation energy of the reaction go on enhancing from 112.46 kJ/ml to 147.52 kJ/mol with grradual addition of the organic content (EtOH) in the reaction media. The increase in the values of iso-composition activation energy may be attributed to the following factors:

(i) The transition state is more desolvated than the initial state,

(ii) The transition state is less solvated than the initial state, and

(iii) The transition state is desolvated and the initial state is solvated.

Out of the three possibilities, the third factor is expected to be operative in this case which gets support by the fact that the values of entropy of activation go on enhancing with increasing the concentration of Ethanol in the reaction media as recorded in Table -VII. Recently, Kumari & Singh et al.[10] and Singh & Rashmi et al.[11] have also reprted similar findings on the effect of solvent on the iso-composition activation energy.

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

On perusal of the data of Table-IV, it is found that the Iso-dielectric activation energy (E_D) values go on decreasing from 142.21 kJ/mol to 120.84 kJ/mol with increase in D values of the aquo-ethanol reaction media from 32 to 62 respectively.

Table – III

Evaluated values of Iso-composition Activation Energy (EC or Eexp) of the reaction in water-EtOH media.

% of EtOH(v/v)	20%	30%	40%	50%	60%	70%	80%
E_C values in K/J/mol	112.46	116.79	120.72	126.06	133.61	140.02	147.52

Table - IV

Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at Desired 'D' values of water-EtOH media.

D values	D= 32	D = 37	D = 42	D =47	D = 52	D = 57	D = 62
E_D values in kJ/mole	142.21	139.79	135.16	132.51	129.30	126.22	120.84

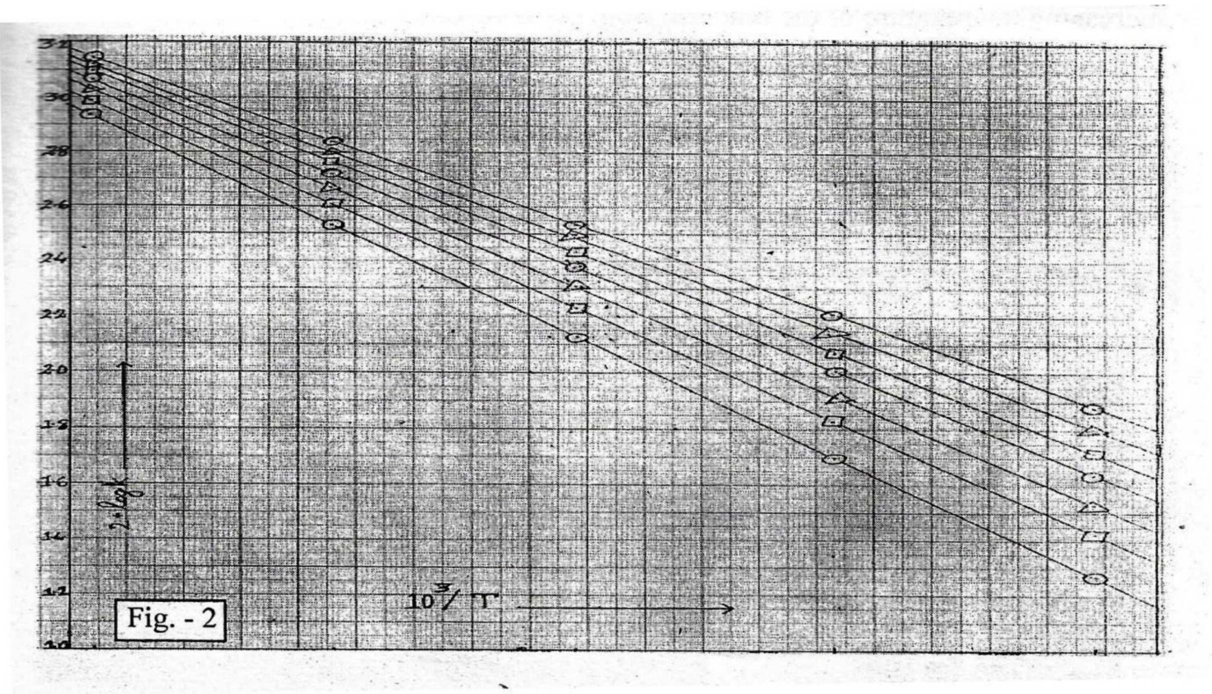

Fig. - 2

it is acceptable fact that the dielectric constants of aquo-organic cosolvent systems decreases with addition of the organic content, hence, it may be concluded that E_D values of this reaction also increase with addition of ethanol to the aquo-ethanol reaction media. Thus, E_C and E_D values of this reaction are complementary to each other.

Such observations and inferences for the effect of solvent on the E_D values of the reaction have been reported earlier by Elsemongly et al.[12] and Wolford[13] and also recently by Singh & Bano et al.[14] and Singh & Wats et al.[15]

Involvement of water nolecules in the formation of Activated complex and Solvent effect on the Mechanism of the reaction:

By using Robertson[16] equation, the number of water molecules involved in the formation of the activated complex of the reaction were evaluated from the slopes of the plots of the log k values versus log [H_2O] values from their values recorded in Table -V. The plots are shown in Fig. -3. From Fig.-3, it is clear that the plots at each temperature have two intersecting straight lines meeting at log [H_2O] value 1.465 having positive slopes. The values of the slopes of straighht line plots have been enisted in Table-VI. From the values of the slopes mentioned in Table-VI, it is apprrent that before log [H_2O] value 1.465, which corresponds to 52.50% of water in the reaction media. Number of water molecules associated with the activated complex decreases from 0.811 to 0.316 and similarly after log [H_2O] value 1.465, the number of water molecules associated with the activated complex decreases from 1.215 to 0.439 with increasing temperature of the reaction from 20 to 40°C

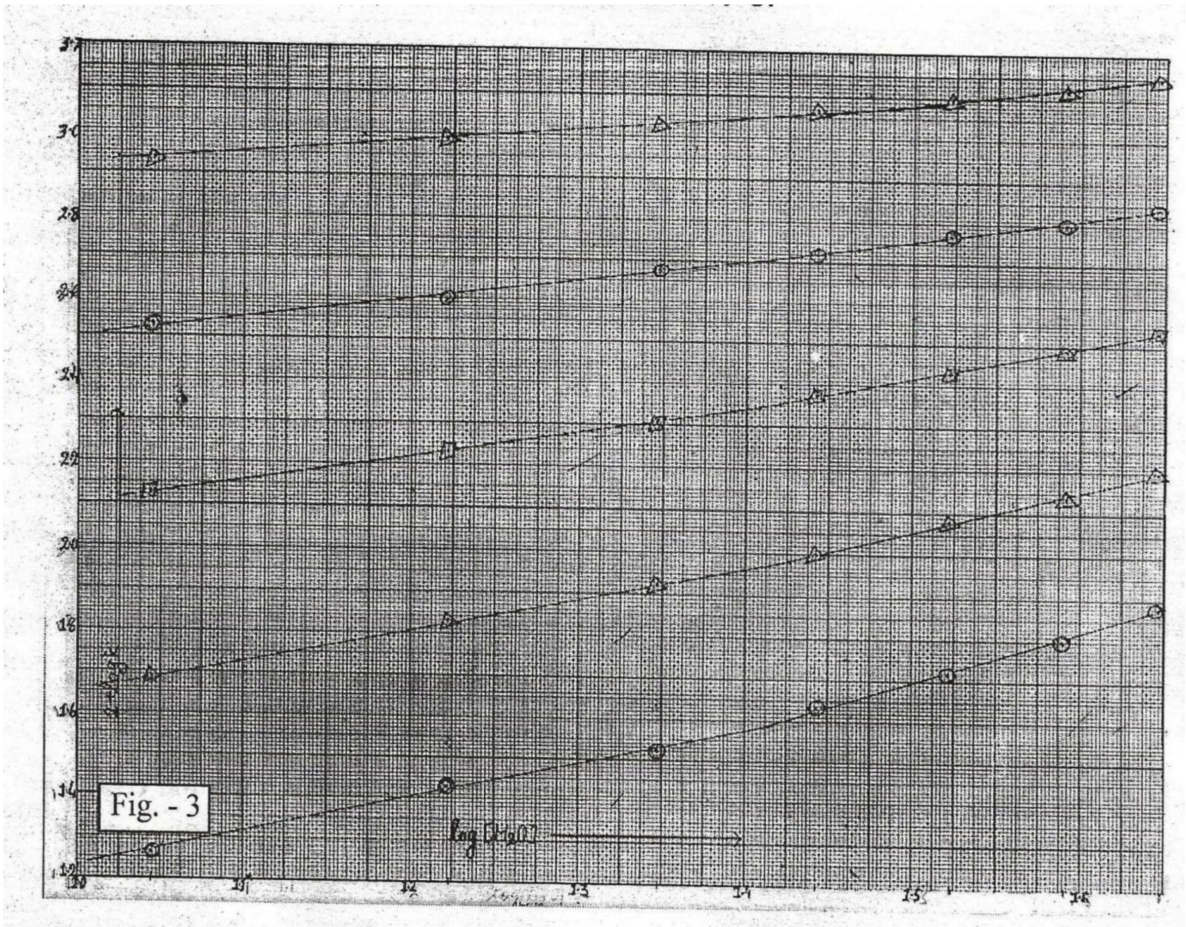

Fig. - 3

Table - V

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

% of EtOH	% of H_2O	log [H_2O]	2 + log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.8832	2.2088	2.5361	2.8396	3.1464
30%	70%	1.5898	1.8022	2.1401	2.4909	2.8031	3.1211
40%	60%	1.5229	1.7198	2.0751	2.4301	2.7662	3.0981
50%	50%	1.4437	1.6395	2.0089	2.3761	2.7201	3.0652
60%	40%	1.3468	1.5321	1.9201	2.3048	2.6692	3.0312
70%	30%	1.2218	1.4254	1.8278	2.2326	2.6098	2.9851
80%	20%	1.0458	1.2686	1.6999	2.1288	2.5300	2.9358

Table - VI

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

Temperature in °C	Slope - I Where log[H_2O] value is below 1.465	Slope - II when log[H_2O] value is above 1.465
20°C	0.811	1.215
25°C	0.768	0.967
30°C	0.614	0.817
35°C	0.519	0.607
40°C	0.316	0.439

overall, it may be noted that number of water molecules involved in the formation of the activated complex of the reaction decreases from 1.215 to 0.316 with rise in temperature of the reaction from 20 to 40°C.Heance, from the depletion in the number of the water molecules, it may be inferred in the light of the guidelines of Robertson et al.[17] that with addition of ethanol in the reaction media, and also with increase in temperature of the reaction , the mechanistic pathway folllowed by the reaction from unimolecular to bimolecular and at equilibrium, the structure of water is changed from its bulky fori to dense form as:

$$(H_2O)_b \leftrightharpoons (H_2O)_d$$

Such findings have earlier been reported by parker and Tomillionson[18] and also recently by Renu & Singh et al[19]

Effect of solvent on Thermodynamic Activation Parameters of the Reaction:

For studying the solvent effect of ethanol in detail on the ΔH*, ΔG* and ΔS* values of the reaction, all the three have been plotted against mol % of ethanol as shown in Figures -4, 5 and 6 respectively. From Table-VII, which includes the consolidated values of the three thermodynamic activation parameters i.e. ΔH*, ΔS* and ΔG*, it is obvious that values of free energy of activation ΔG* enhance from 81.46 kJ/ol to 83.83 kJ/mol with gradual addition of ethanol from 20 to 80% (v/v) in the reacton media at 30°C. Though the enhancement in ΔG* values is not vety high, but, is very much liable to be taken into connsideration. Similar variatios in ΔG* values has also earlier been reported by Tommila et al.[24]. From the plots of ΔG* values with mole % of EtOH as shown in Fig.-5, a smooth curve is obtained, which is indicative of solvation or desolvation of reactants as explained by Elsemongy[12]. While variations is ΔH* and ΔS* are concerned,it is clear from Table-VII and Figures -4 and 6, that both of them increase with increasing mol % of ethanol in the reaction media, However, from Table-VII, it is interesting to observe that all the three thermodynamic activation parameters of the reaction namely ΔG*, ΔH* and ΔS* are found to increase simultaneously with gradual addition of ethanol in the reaction media.

According to the relation

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

it can easily be concluded that the simultaneous enhancement in ΔG* value with the increase in both the ΔH* and ΔS* values is only possible when the extent of enhancement in ΔH* values is greater than found in ΔS* values. The regular enhancement to the greater extent in ΔH* values in comparison to that of ΔS* values clearly indicates that the alkali catalsed solvolysis of Diethyl phthalate in aquo-ethanol media is enthalpy dominating and the organic co-solvent ethanol plays the role of entropy controller solvent. Moreover, the non-linear variation (enhancement) in ΔH* and ΔS* values with gradual addition of ethanol in the reaction media g ives information of the fact that the specific solvation is taking place in aquo-ethanol solvent systems which is in accordance with the earlier reported obseravtions of Tommila et al .[20] and Singh & Jha et al.[21]. In recent years, Singh & Bano et al.[22] and Singh & Sudhanshu et al.[23] have also

Table- VII

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

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of EtOH (v/v)	Mole% of EtOH	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%	7017	108.98	82.36	90.87	81.95	90.72	81.46	90.81	81.06	96.65	80.58	90.73
30%	11.69	112.62	82.81	101.94	82.34	101.82	81.73	102.15	81.28	103.64	80.73	102.07
40%	17.07	119.02	83.27	122.01	82.71	121.86	82.08	121.92	81.49	121.84	80.87	121.89
50%	23.59	123.70	83.72	136.42	83.09	136.27	82.39	136.31	81.77	136.14	81.07	136.20
60%	31.06	128.89	84.33	152.09	83.59	152.00	82.81	152.09	82.07	152.03	81.27	152.14
70%	41.87	133.41	84.92	165.47	84.12	165.39	83.23	165.61	82.42	165.55	81.55	165.68
80%	55.85	146.46	85.80	207.02	84.95	206.75	83.83	206.71	82.89	206.41	81.84	206.45

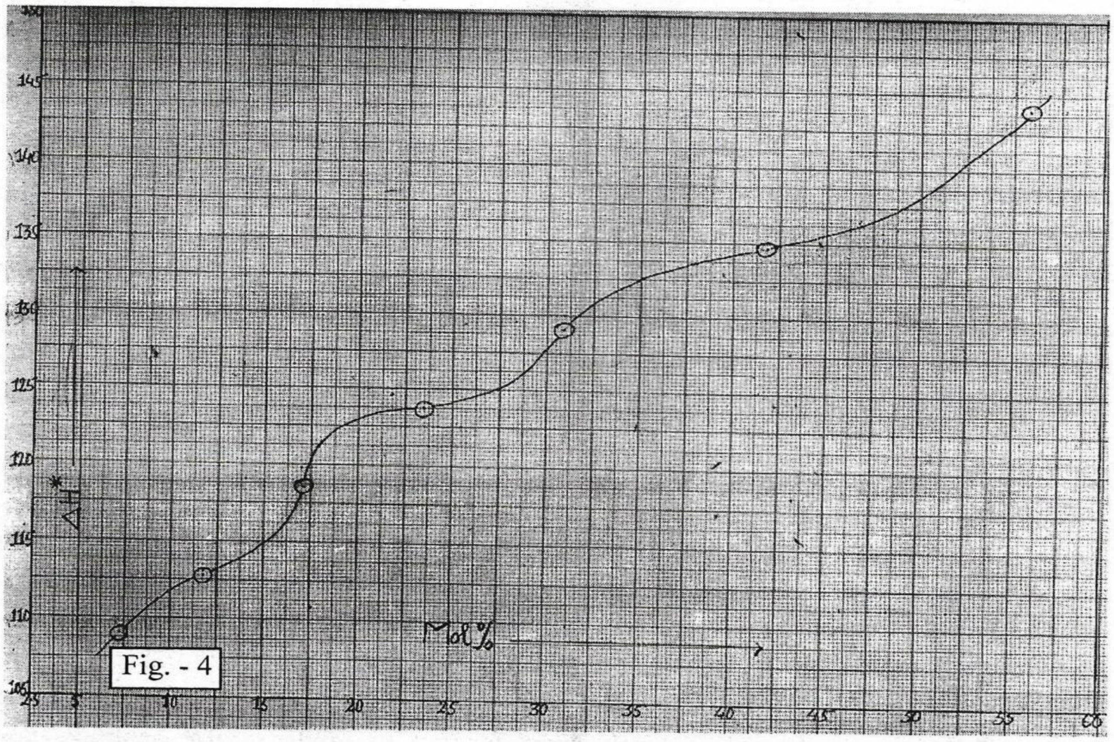
150
145
140
135
130
125
120
115
110
106
ΔH*
Mol%
5
10
15
20
25
30
35
40
45
50
55
60

Fig. - 4

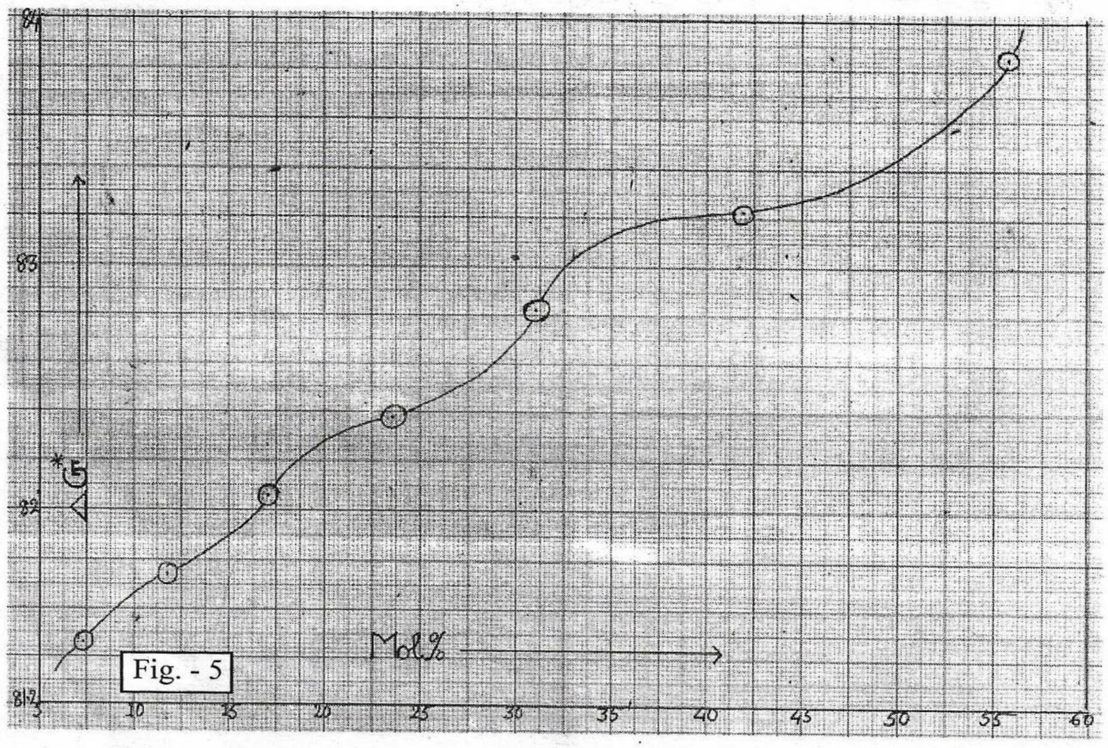
84
83
82
81.7
ΔG*
Mol%
5
10
15
20
25
30
35
40
45
50
55
60

Fig. - 5

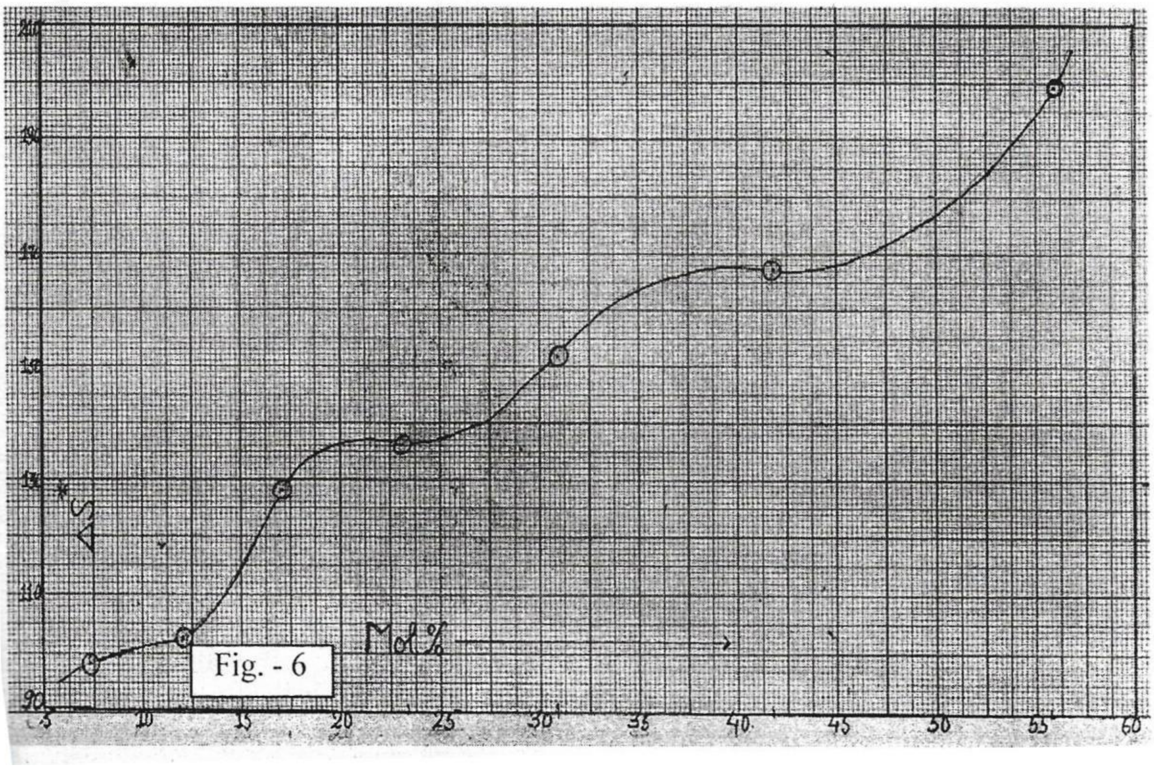

Fig. - 6

reported similar inferences.

Evaluation of Iso-kinetic Temperature and Solvent effect on the Solvent-solute Interaction in aquo-Ethanol media:

With the help of iso-kinetic relationnship developed by Barclay and Butler[24], the value of iso-kinetic temperature was eevaluated.

The Barclay and Butler equation is :

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

It is a relationship between ehthalpy and entropy of activation and 'β' is called iso-kinetic temperature which is also called Leffler-Grunwald[25] solvent stabilizer operator. In the light of the above mentioned relationship, the value of iso-kinetic temperature was evaluated from the slope of the plots of ΔH* against ΔS* as shown in Figure - 7 and it comes to 332.46 ≈ 333 (more than 300). In thee light of Leffler's[26]. guidelines, it is concluded from the value of the slope that there is considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to strong interaction between solvent and solute present in aquo-ethanol reaction media.

Similar inferences and their interpretations regarding the Solvent-solute interaction have also been reported recently by Singh & Navendu et al.[27] and Singh & Wats et al.[28] and Sushma & Singh et al[29]

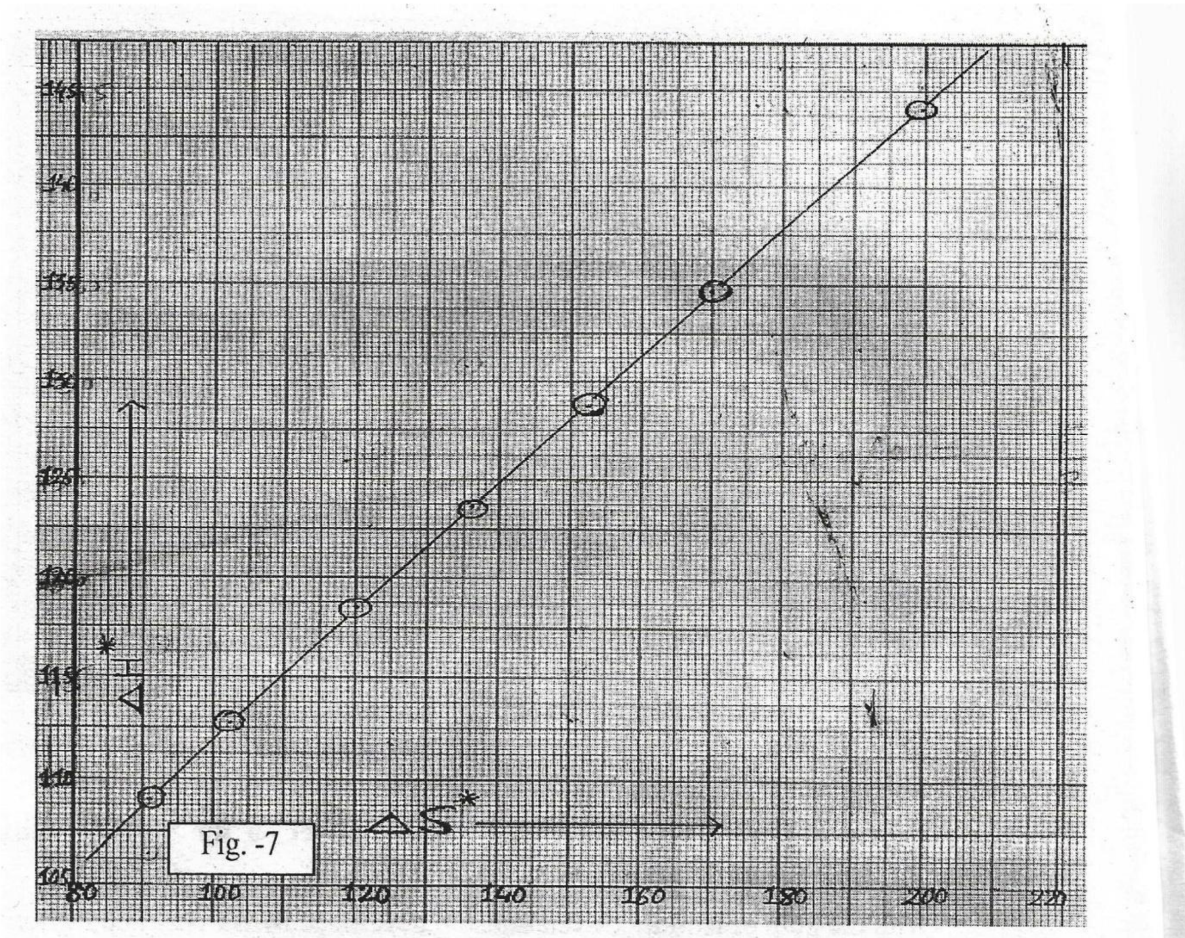

Fig. -7

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