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A Kinetic Study of the Solvent Effect of Aquo-dipolar Protic Solvent systems on the Solvolysis of Iso-butyl formate

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Abstract- The solvent effect of aquo-dipolar protic solvent was highlighted by studying the kinetics of the acid catalysed hydrolysis of Iso-butyl formate in aquo-Methanol reaction media of various compositions having 20 to 80% of methanol at five different temperatures ranging from 20 to 40°C. The sharp depletion followed by slow decrease in the rate, with gradual addition of methanol in the reaction media and also with increasing temperature of the reaction has been explained in the light of solvation and desolvation of initial and transition states to different extents. The changes in the values of iso-composition and iso- dielectric activation energies of the reaction have also been explained in the light of solvation and desolvation of initial and transition states to different extent. Increase in the numerical values of free energy of activation (ΔG*) with simultaneous enhancement in the values of enthalpy of activation (ΔH*) and entropy of activation (ΔS*) of the reaction, reveals that the methanol) acts as enthalpy dominating solvent. From the evaluated value of iso-kinetic temperature which comes to he 325.0, it is inferred that there is strong solvent-solute interaction in aquo-methanol reaction media. Effects of ionic strength and change in [H^+] ion concentration on the rate of reaction have also been studied and it is concluded that the acid catalysed hydrolysis of Iso-butyl formate is ton-dipolar reaction and it follows A_{AC}^2 mechanistic pathways in aquo-MeOH reaction media.

Keywords: Formate, Iso-composition and Iso-dielectric, Solvation and Desolvation, Mechanism, Dielectric effect, Iso-kinetic temperature, Enthalpy dominating. Entropy controlled, Solvent-Solute Interaction.

I. INTRODUCTION

Various researchers have reported that the effect of dipolar aprotic solvent like DMSO, DMF, Acetone etc. have widely been studied on the acid catalysed hydrolysis of lower formates, but solvent effect of a dipolar protic solvent like Methanol having very peculiar solvating power on the biochemical and medicinal efficiencies of substituted aliphatic formate such as Iso-butyl formate has not been paid adequate attention so far.

So, in order to highlight the above noted untouched piece of research work, it has been proposed to study the solvent effect of methyl alcohol (Dipolar protic solvent) on the acid catalysed hydrolysis of Iso-butyl formate.

EXPERIMENTAL

Purified Methanol of Merck grade and Iso-butyl formate of Fluka ^{AG} (packed in Switzerland) were taken into use. The kinetics of acid catalysed hydrolysis of the ester was studied as usual by adding 0.65 ml of ester with the help of the graduated syringe pipette into 50 ml of 0.5 MHCl solution. The values of specific rate constants were evaluated by making use of first order rate equation and are tabulated in Table-1. Variation of log k values with mol% of Methanol reaction media has been recorded in Table - II. The evaluated values of the two activation energies (Iso-composition, E_C and Iso-dielectric, E_D) have been mentioned in Table III and IV respectively. For deciding the mechanistic path way of the reaction, from the slopes of the plots of log k versus log [H_2O], the evaluated values of solvation number have been mentioned in Table -V. The thermodynamic activation parameters of the reaction calculated by using Wynne-Jones & Eyring equation4 has been enlisted in Table VI.

The effect of [H^+] concentration has been studied by changing the [H^+] ion strength of the aquo-dioxan

media and the evaluated values of specific rate constants have been recorded in Table - VIL

RESULTS AND DISCUSSION

Effect of Solvent on the Specific rate constant of the Reaction:

From Table- I, it is clear that specific rate constant values of the reaction decrease with increase in dioxan component of the reaction media.

In order to study the variation in k values of the reaction with change in mol% of methanol, the logarithmic values of k which have been recorded in Table - II, have been plotted against the mol% of methanol and is shown in Fig. -1. From Fig. -1, it is clear that there is fast depletion followed by the slow decrease in the rate at 30,75 mol% of Methanol in the reaction media However, with increasing temperature, the rate depleting effect of solvent is found to be decreasing.

It is opined that the following three factors seem to be responsible for depletion in the rate of the reaction in solution, they are:

1. decreasing polarity of the medium as changing from polar water to less polar aquo-MeOH medium,
2. lowering of the bulk dielectric constant values of the aquo-MeOH reaction media, and
3. depletion of H_3O^+ ions of the solution by the organic co-solvent (Methanol) molecule due to its basic character

As Methanol is not basic, so it may not combine with H^+ and H_3O^+ ions of the acidic medium. Hence, among the above mentioned three rate retarding factors, the first two factors are in operation and it is quite in agreement with the theory of Hughes and Ingold[5] that the rate is bound to decrease with decreasing dielectric constants of the medium.

However, these interpretations are in support of the views of Laidler and Lanskroener and earlier reports of Singh & Smriti et al.[7], and Singh & Rashmi et al.[8],. In recent years, Kumar & Singh et al9. and Singh & Kaushalendra et[10] al. have also reported similar observations ad inferences.

Solvent effect on Iso-composition activation energy of the Reaction:

From the Arrhenius plots of log k values 1/T, as shown in Fig. 2, the values of iso-composition activation energy (E_C or E_{exp}) have been calculated from the slope of the plots and are mentioned in Table - III.

From Table - III, it is clear that values of iso-composition activation energy go on increasing from 84.67 kJ/molto 128.41 kJ/mol with addition of 20 to 80% of Methanol in the reaction media.

Usually, enhancement in the values of iso-composition activation energy may be due to either of the following three causes:

(1) Simultaneous solvation and desolvation of the initial and the transition state respectively,

1. The greater solvation of the initial state than the transition state, and
2. The greater desolvation of transition state than the initial state,

Out of these three factors, the first one seems to be applicable in this case and this cause has also been supported by the increase of entropy of activation (ΔS^*) with gradual addition of the organic co-solvent (Methanol) in the reaction media as tabulated in Table - VII. Such findings have been found in support of the earlier views of Singh & Namrata et al[11]. and Singh & Wats et al[12]. In recent years, Singh & Singh et al[13]. and Kumar, N[14]. have also reported similar inferences for changes observed in Ec values of the reaction.

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

From the slopes of the Arrhenius plots of log K_D values against 1/T (log K_D values obtained from interpolation of the straight line plots of log K values against D values), the values of iso-dielectric activation energy have been evaluated and are recorded in Table - IV. From this Table, it is observed that E, values go on decreasing from 130.35 kJ/mol to 91.26 kJ/mol with increasing D values of the reaction media from 40 to 76. This trend of depletion in E_D values with increasing D values of the reaction

media is similar to enhancement in E_C values with addition of more and more Dioxan in the reaction media. These interpretations have also been supported by the earlier reports of Singh & Wats et al.[12], Kurrari & Singh et al[15]. and Singh & Sudhanshu et al[16]. However, researchers like Singh & Singh et al[13]. and Kumar, N[14] have also communicated similar interpretations for depletion changes in E_D values of the reaction.

Solvent Effect on the Participation of water molecules in the formation of Activated complex and Mechanism of the reaction:

The number of water molecules associated with the activated complex of the reaction has been determined by plotting log k values, against log [H_2O] according to the relation proposed by Robertson[17]. log K=logk_o+nlog [H_2O]

where 'n' is the solvation number which tells about the number of water molecules associated with the activated complex 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 intersecting straight lines at log [H_2O] value 1.495, with positive slopes are obtained. The numerical values of the slopes are enlisted in Table - V.

From Fig. 3 and from the values recorded in Table - V, it is clear that below log [H_2O] value 1.495 which corresponds to 56.30 % of water in the reaction media, the values of the slopes decreases from 0.997 to 0.291 with increase in temperature from 20 to 40°C. This suggests that below 56.30% of water in the reaction media, about 1.0 to 0.30 molecules of water are taking part in the formation of activated complex as the temperature rises from 20 to 40°C. Similarly, from the values of slopes, it is clear that in case of increase in water concentration (above 56.30% v/v), the numerical values of slopes decrease from 1.444 to 0.457. These values also show that approximately from 1.44 to 0.50 molecules of water are taking part in the formation of activated complex as the.

From this, it may be concluded that when concentration of water falls in aquo-Methanol media, the number of water molecules taking part in the formation of the activated complex is about half but with increase in water concentration in the reaction media, the number of water molecules associated with the formation of the activated complex becomes one and half (1.444). Thus, it can be concluded from the guidelines of Robertson et al18. that the acid catalysed hydrolysis of Iso-butyl formate in aquo-methanol media follow bimolecular mechanism with respect to water. In other words, the presence of methyl alcohol (Methanol) in the reaction media and with rise in temperature of the reaction, the mechanistic pathway of the reaction is changed from unimolecular to bimolecular.

These observations may be attributed to the fact that in presence of Methanol, the equilibrium of water shifts from its bulky form to its dense form with rise of temperature of the reaction.

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

However, Monalisa & Singh et al[3], Singh & Namrata et al[11]. Singh & Wats et al[12]. Singh & Bano et al[19]. in the past and Svati & Singh et al[20]. in recent year have also reported similar observations and inferences for effect of solvent on the mechanistic pathway of the reaction.

Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

The famous Wynne-Jones and Eyring[4] equation has been applied to evaluate the three thermodynamic activation parameters namely enthalpy of activation ΔH*, entropy of activation ΔS* and the free energy of activation ΔG* and their values have been recorded in Table - VI.

On visualising the data mentioned in Table-VI, the interesting feature comes in the that out of the values of all the three thermodynamic activation parameters ie. ΔH*, ΔG* and ΔS* all are increasing simultaneously with increasing proportion of Methanol in the reaction media from Table VI, it is clear that with increasing mole % of Methanol in the reaction media, ΔH values increases from 82.72 to 126.11 kJ/mol, ΔG* values increases from 82.14 to

84,59 kJ/mol and ΔS* values increase from 1.92 to 137.05 J/K/mol at 30°C.

For highlighting the solvent effect on the three thermodynamic activation parameters, namely ΔH*, ΔG* and ΔS*, the numerical values of all were plotted against mol% of the Methanol in the reaction as shown in Fig. 4, 5 and 6 respectively. The non-linear variation in A^H and A^S from Fig. 4 and 6 give information of the fact that specific solvation is taking place in aquo Methanol media similar to that as reported by Saville et al[21].

From the fundamental thermodynamic equation:

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

it may be inferred that the simultaneous increase in the values of ΔH* and ΔS* with enhancement of ΔG* values is only possible when the quantitative increase in the values of ΔH* is greater than that found in the values of ΔS* and from this fact, it is concluded that acid catalysed hydrolysis of Iso-butyl formate in aquo-Methanol media is enthalpy dominating and entropy inhibiting.

The enhancement found to different extent in the values of enthalpy of activation ΔH* and entropy of activation also supports the view that transition state of the reaction is desolvated and its initial state is solvated in the similar way as reported earlier by Kumar & Singh[9], Singh & Wats et al[10]. and Singh & Namrata et al[11]. Recently, Singh & Singh et al[13], Kumar[14], Svati & Singh et al[20]. and Kumar[22] have also reported.

similar interpretations for describing the effect of solvent on the changes observed in thermodynamic activation parameters of the solvolysis reaction.

Effect of Change in [H^+] ion concentration of the Reaction media on the specific rates and Mechanism of the Reaction:

The effect of change in the acid concentration on the kinetics of the reaction was studied at 30°C by changing the concentration of HCL, but the ionic strength of the reaction media was always kept fixed (μ = 0.9). The values of specific rate constant values for different [H^+] ion concentration of the reaction media have been inserted in Table - VII.

The values of the slope of straight line plots of log k versus log [H^+] as shown in Fig-7. was found to be 0.996 which is almost equal to unity and from this, it is inferred on the guidelines of Zucker and Hammett[23] that acid catalysed hydrolysis of Iso-butyl formate in aquo-Methanol media follows A_{AC}^2 mechanism. Such inferences 4. regarding the effect of concentration of [H^+] on the mechanism has been supported by the reported earlier views of Monalisa & Singh et al[24] and Singh & Navendu et al[25]. and also by the recent findings of Singh & Singh et al[26].

Solvent Effect on the Solvent-Solute Interaction in aquo-Dioxan media:

In the light of Barclay and Butler[27] relationship between enthalpy and entropy of activation, which is as:

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

where β is a constant called iso-kinetic temperature and also known as Leffler-Grunwald[28] solvent stabilizer operator.

The values of Iso-kinetic temperature of this reaction has been evaluated from the slopes of the plots of ΔH* versus ΔS* as shown in Fig.-8 and it comes to be 320.81 ≈ 321.0.

From the value of iso-kinetic temperature considerable change in the structure of reactants (above 300), it is concluded that there is a or in the solvent or in both due to strong and appreciable interaction between solvent and solute present in the aquo-Methanol media in the similar way as reported by Leffler[29]. Earlier, Kumar & Singh et al[9]. Singh & Namrata et al[11]. recently various researchers of the Singh group[13,14,20,22,26] and and findings about the solvent-solute interaction have also reported similar observations in the reaction media.

Table - I : Specific rate constant values of Acid catalysed hydrolysis of Iso-butyl formate in water-MeOH media

$k \times 10^3$ in min^{-1}

Temp in °C	% of MeOH (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	82.26	67.95	56.25	44.79	35.49	26.78	17.62
25° C	147.81	125.34	106.64	88.67	74.66	58.87	41.80
30° C	262.91	230.20	204.22	177.75	154.85	128.85	99.47
35° C	448.13	408.51	372.65	342.29	306.34	270.46	222.74
40° C	764.99	714.99	677.95	646.84	610.24	565.98	503.73

Table - II : Variation of log k values of the reaction at different temperatures with mol % of MeOH in water-MeOH media.

% of MeOH (v/v)	Mol % of MeOH	3 + log k values				
		20°C	25°C	30°C	35°C	40°C
20%	10.02	1.9152	2.1697	2.4198	2.6574	2.8837
30%	16.03	1.8322	2.0981	2.3621	2.6112	2.8543
40%	22.90	1.7501	2.0279	2.3101	2.5713	2.8312
50%	30.82	1.6512	1.9478	2.2498	2.5344	2.8108
60%	40.06	1.5501	1.8731	2.1899	24862	2.7855
70%	50.97	1.4278	1.7699	2.1101	2.4321	2.7528
80%	64.45	1.2460	1.6212	1.9977	2.3478	2.7022

Table - III

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

% of MeOH	20%	30%	40%	50%	60%	70%	80%
E_c value in kJ/mol	84.67	90.21	95.04	101.91	109.33	116.12	128.41

Table - IV

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

D values	D = 40	D = 45	D = 50	D = 55	D = 60	D = 65	D = 70
E_D values in kJ/mol	130.35	123.49	117.75	111.09	104.86	97.61	91.26

Table - V

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 1.495	Slope - II when log[H_2O] value is above 1.495
20°C	0.997	1.444
25°C	0.837	1.163
30°C	0.647	0.963
35°C	0.452	0.682
40°C	0.291	0.457

Table - VI

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

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of MeOH (v/v)	Mol % of MeOH	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%	10.02	82.72	82.18	1.8614	82.17	1.86	82.14	1.92	82.17	1.79	82.15	1.81
30%	16.03	87.74	82.64	17.39	82.58	17.31	82.47	17.37	82.41	17.30	82.33	17.27
40%	22.90	93.65	83.10	35.98	82.98	35.80	82.78	35.88	82.64	35.72	82.47	35.71
50%	30.82	100.42	83.66	57.21	83.43	57.00	83.13	57.08	82.86	57.01	82.59	56.96
60%	40.06	106.40	84.23	75.69	83.76	75.97	83.47	75.68	83.15	75.51	82.74	75.59
70%	50.97	115.28	84.91	103.64	84.45	103.45	83.94	103.44	83.46	103.29	82.94	103.32
80%	69.45	126.11	85.93	137.14	85.30	136.97	84.59	137.05	83.96	136.86	83.24	136.97

Table - VII

Effect of $[H^+]$ on the Specific rate constant values of Acid Catalysed Hydrolysis of Iso-butyl formate in water-MeOH media at constant ionic strength (μ = 0.9)

Temp. - 30°C

$[H^+]$	[KCl]	μ	$k \times 10^3$ in min^{-1}	$2 + \log[H^+]$	$3 + \log k$	value of the slope of the plot of log k vesus log $[H^+]$
0.10	0.80	0.90	53.24	1.0000	1.7262	
0.15	0.75	0.90	79.09	1.1761	1.8981	
0.20	0.70	0.90	105.49	1.3010	2.0232	
0.25	0.65	0.90	132.37	1.3979	2.1218	
0.30	0.60	0.90	158.09	1.4771	2.1989	0.996
0.40	0.50	0.90	210.43	1.6021	2.3231	
0.50	0.40	0.90	262.91	1.6990	2.4198	
0.60	0.30	0.90	319.23	1.7782	2.5041	
0.70	0.20	0.90	370.00	1.8451	2.5682	
0.80	0.10	0.90	426.48	1.9030	2.6299	

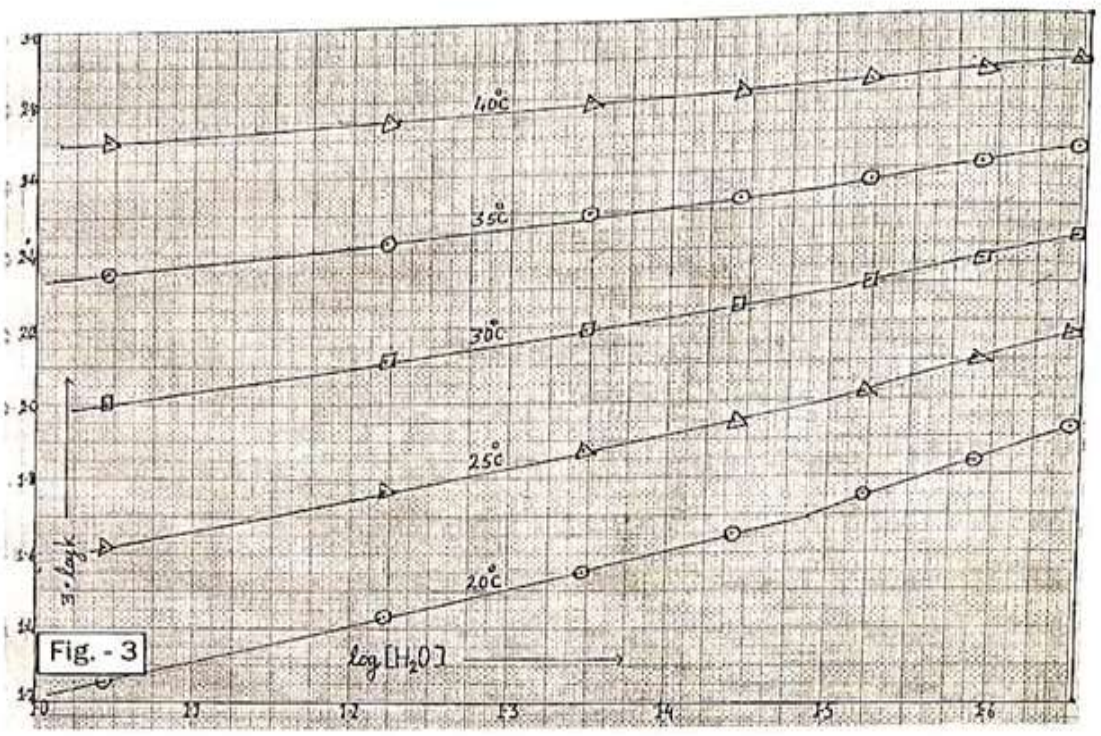


Fig. - 3

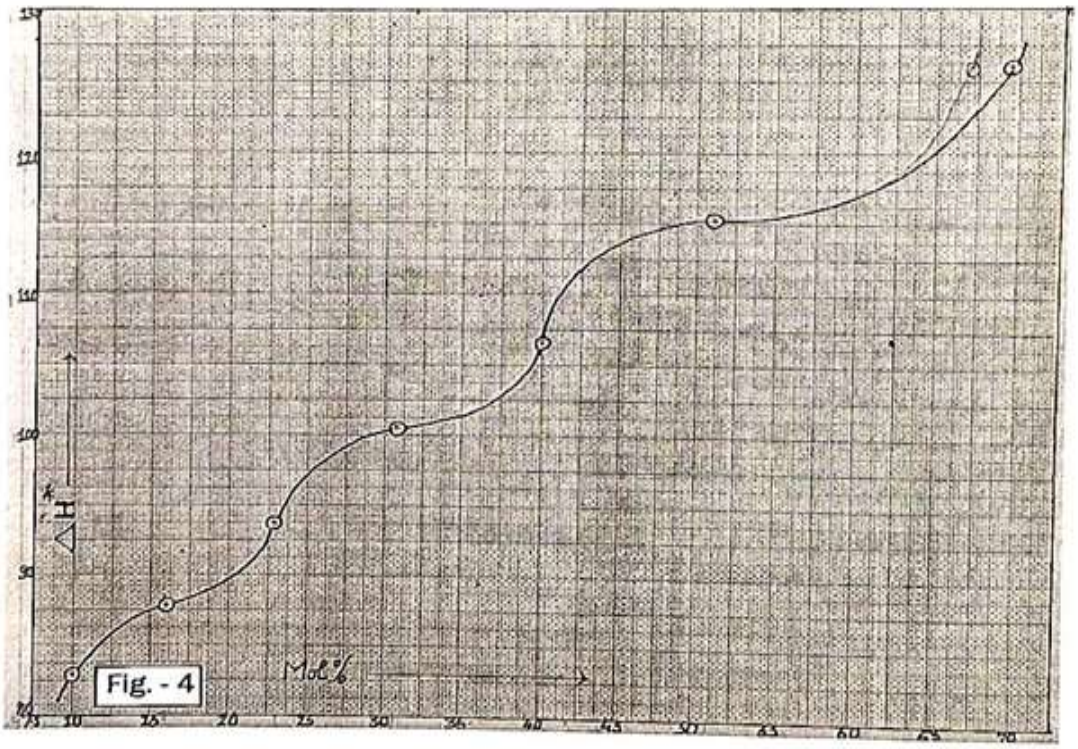
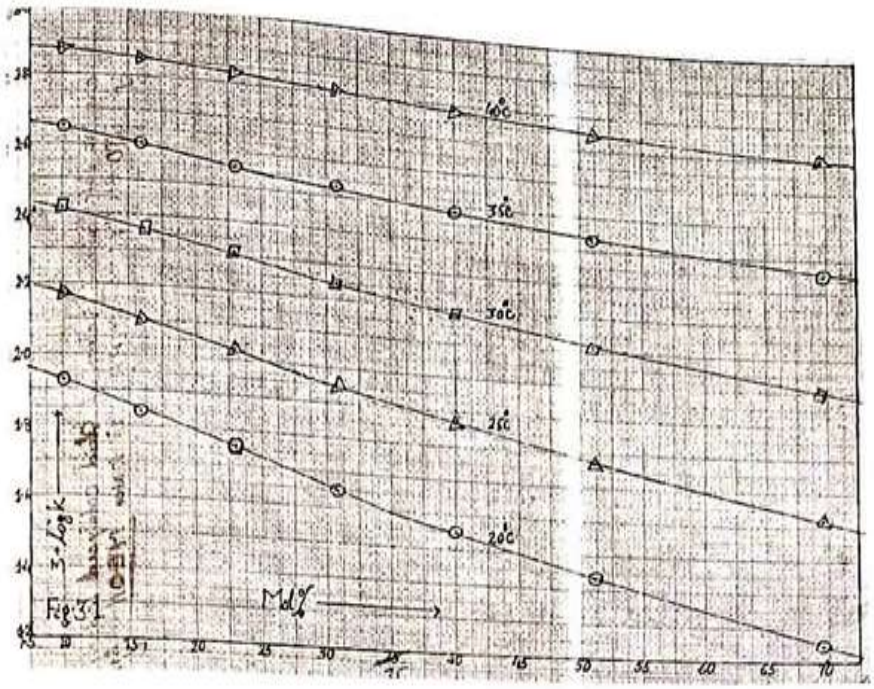
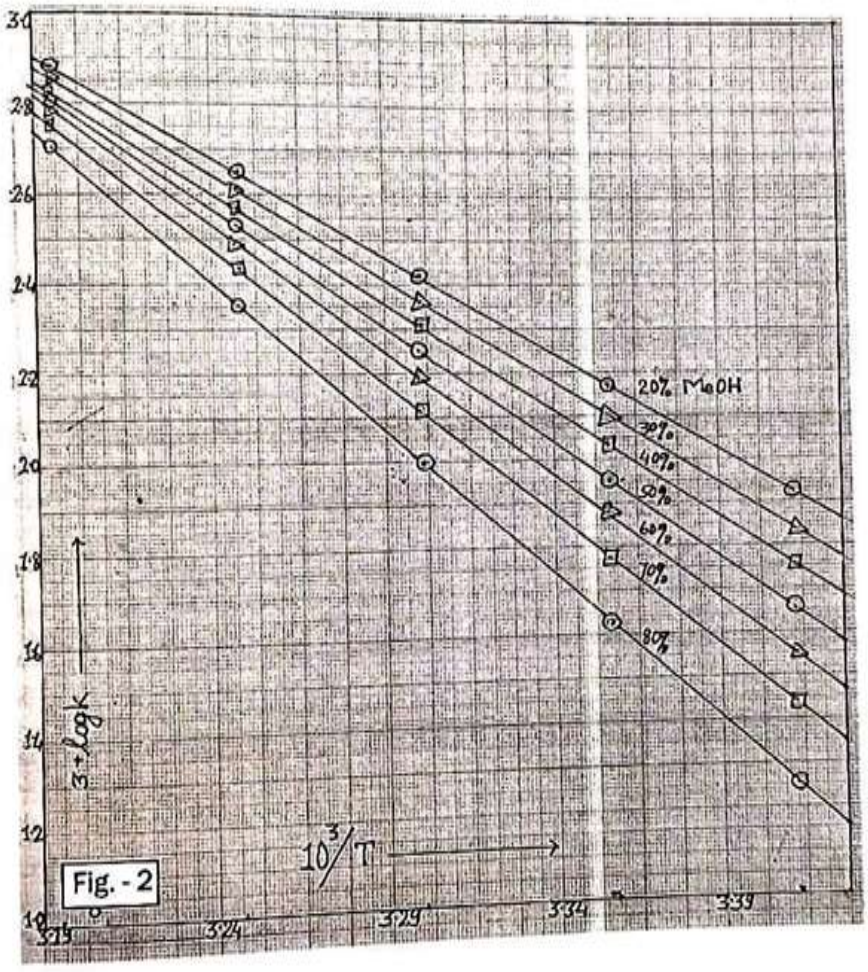
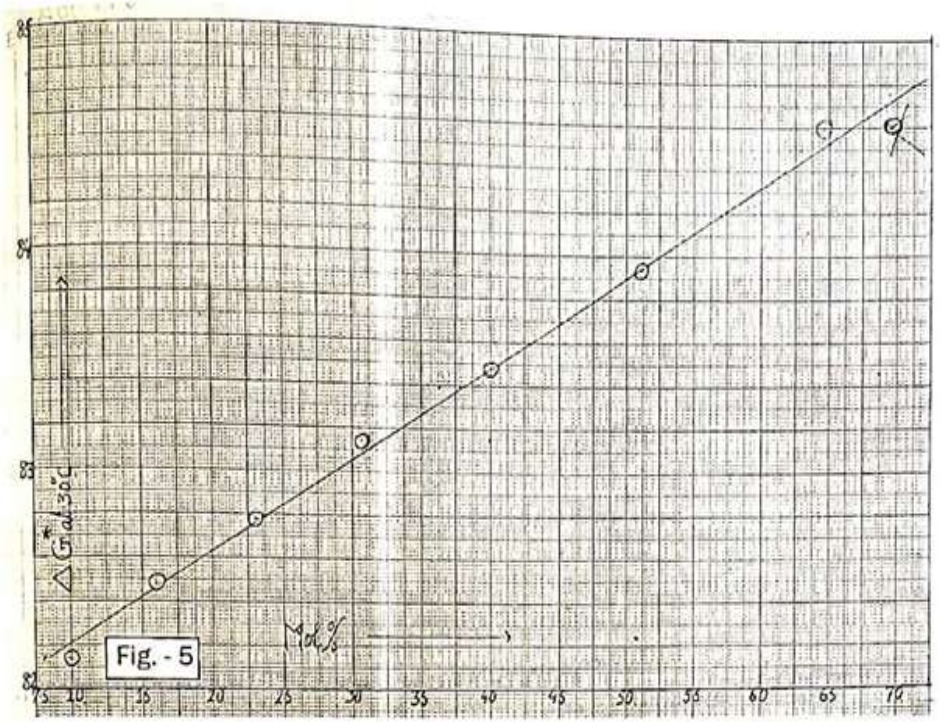
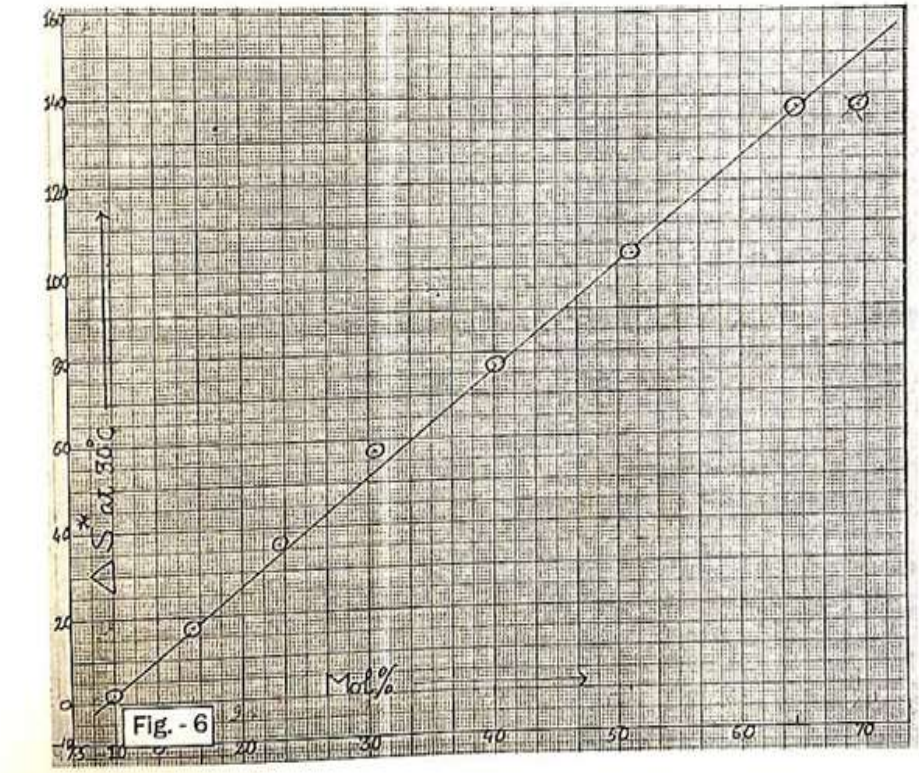


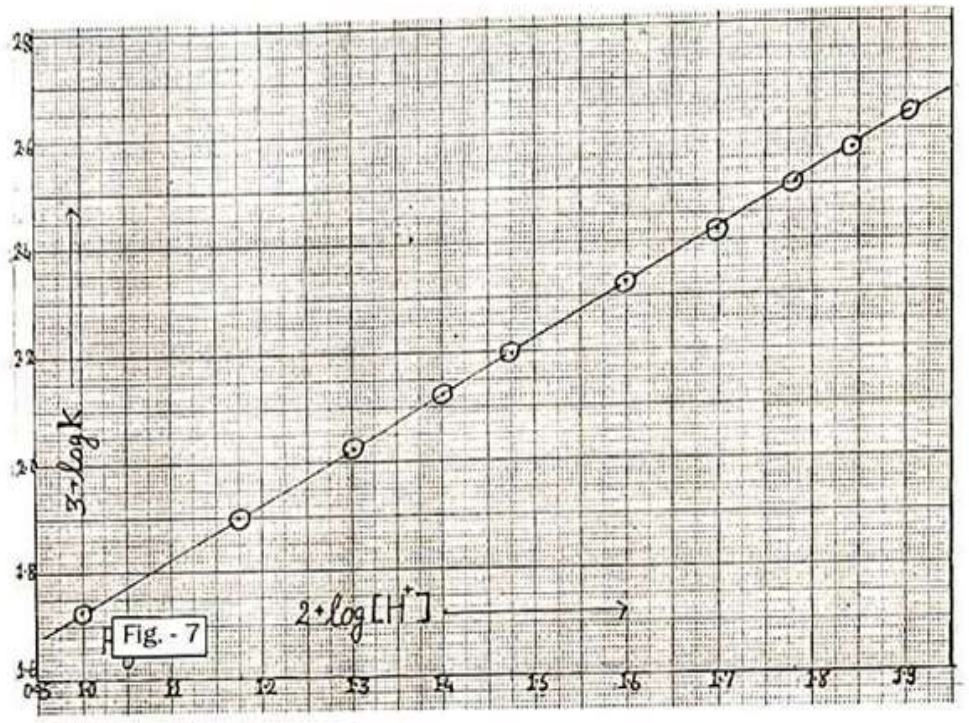
Fig. - 4

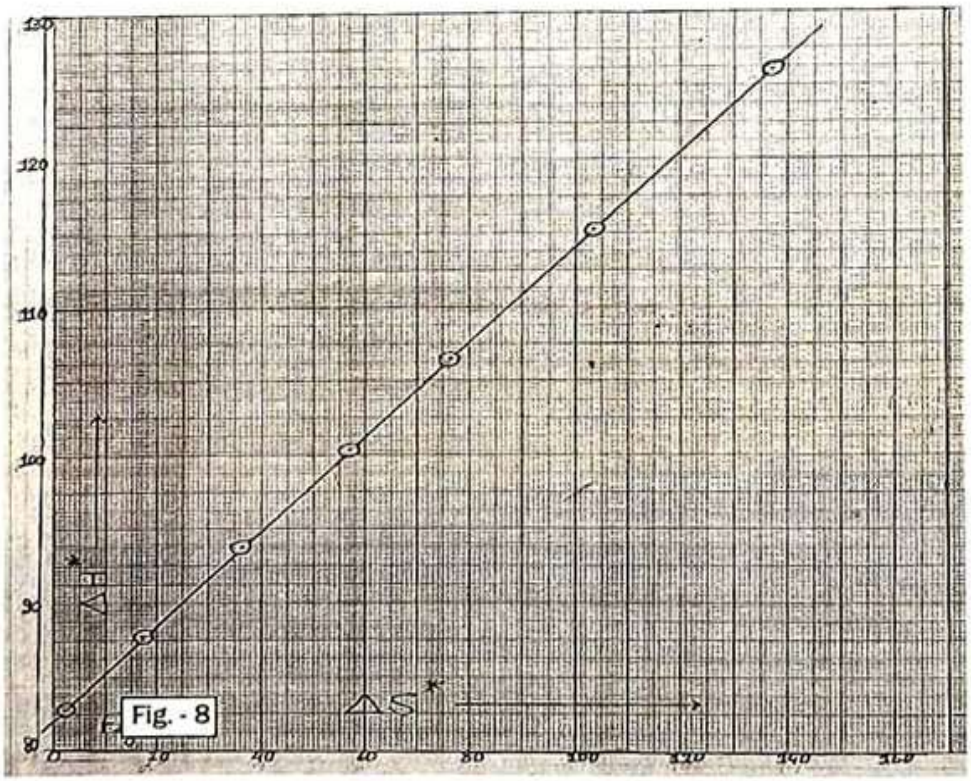

40°C
35°C
30°C
25°C
20°C
3-Log K
Mol%
Fig:3.1


20% MeOH
30%
40%
50%
60%
70%
80%
3+Log K
10³/T
Fig. - 2


Mol%
Fig. - 5


Mol%
Fig. - 6


3+log K
2+log [H+]
Fig. - 7


ΔH*
ΔS*
Fig. - 8

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