

A KINETIC STUDY OF DIELECTRIC EFFECT OF WATER ETHANOL REACTION MEDIA ON THE BIOCHEMICAL POTENTIAL OF SOLVOLYTIC PRODUCTS OF HIGHER PROPIONATE

RAJIV KUMAR AND R. T. SINGH

1. Research Scholar, Dept of Chemistry, V.K.S. University, Ara
2. Professor & HOD Chemistry and The Dean of the Faculty of Science, V.K.S. University, Ara

ABSTRACT

The dielectric effect of aquo-ethanol reaction media on the Biochemical potential of propionate ester was highlighted by studying the kinetics of alkali catalysed hydrolysis of butyl propionate in it (reaction media). From simultaneous increase in all the three thermodynamic parameters i.e. ΔH^ , ΔS^* and ΔG^* , it may be inferred that the solvent ethanol acts as enthalpy stimulator and entropy controller. From evaluated numerical value of Iso-kinetic temperature of the reaction i.e. 309.0, it is concluded that aquo-ethanol media may be used for manufacturing powerful ointment for removing skin diseases from the hydrolytic product of propionate ester.*

KeyWords- *Biochemical, Potential Solvolytic Products Higher Propionates, Dielectric Effect, Iso-composition, Iso-Dielectric, Iso-kinetic, Barclay-Butler Rule, Strong Interaction*

Introduction :

The studies in the kinetics of alkali catalysed hydrolysis of butyl propionate in aquo-ethanol media were proposed as the solvent effect of dipolar-Protic solvent ethanol on the biochemical potential propionate ester has not been paid even primary attention by the kineticists so far. It has been planned to study the kinetics of the solvolysis of butyl propionate in aquo-n-

propanol media having varying concentration of n-propanol from 20 to 80% (v/v) at 5 different temperatures i.e. at 20, 25, 30, 35 and 40°C.

Experimental :

Export quality of butyl propionate made in USSR and extra pure ethanol of Merck Grade were used. The kinetics of the reaction was studied as usual¹⁻² by keeping the strength of alkali 0.1 M and that of the ester (butyl propionate) 0.05 M in the reaction mixture. 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, From the recorded values of $\log k$ and $10^3/T$, in Table - II, $\log k$ values were plotted against $10^3/T$, The values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) have been mentioned in Table - III and IV respectively. The $\log k$ values were plotted against $\log [H_2O]$ from their values recorded in Table - V, the evaluated values of the slopes of these plots have been noted in Table - VI. The consolidated values of the thermodynamic activation parameters, i.e. ΔH^* , ΔG^* and ΔS^* were calculated by using Wynne-Jones and Eyring³ relation are enlisted in Table - VII.

Effect of Solvent on the Specific Rate Constant values of the Reaction :

From the survey of the data recorded in Table - I, it is obvious that the rate of the reaction decreases regularly with gradual addition of ethanol in the reaction media at all the temperatures at which the kinetics of the reaction has been studied. In order to study the variation in rate constant values with increasing concentration of ethanol in the reaction media, the $\log k$ values have been plotted against mol % of ethanol content in the reaction media as shown in Fig. - 1., Figure - 1 shows that the rate of reaction go on decreasing having different slopes due to two intersecting straight lines in the plots at about 18.25 mol % of ethanol in the reaction media. From Fig. - 1, it is also apparent that with increase in temperature, the degree of depletion in the rate become shallow (slow). Such decrease in the rate with increasing proportion of the organic co-solvent like ethanol is not new, but a number of researchers like Laidler-Landskroener⁴, Singh and Jha et al.⁵ and Akanksha & Singh et al.⁶ have also reported

similar finding and their inferences about the depletion in rate with increasing concentration of the organic co-solvent in the aquo-ethanol reaction media. However, the possible rate depleting factors in the rate may be listed as follows:

- (i) decrease in the bulk dielectric constant of the reaction media
- (ii) decreasing the polarity of the reaction media on adding less polar ethanol.

The above noted two rate depleting factors are quite in operation and this is in support of the earlier reports of Kumar, N⁷, Singh & Lal et al.⁸, and recent report of Pathak & Singh et al⁹ that the rate ought to decrease with decreasing dielectric constant value of the reaction media with addition of organic solvent to it. Thus, dielectric effect and solvation effect by the reaction media are responsible for depletion in the specific rate constants of the reaction.

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

From the slopes of the Arrhenius plots of log k values against $10^3/T$ (from their values enlisted in Table - II) as shown in Fig.-2, the iso-composition activation energy (E_C) of the reaction were evaluated and mentioned in Table - III.

From the values recorded in Table-III, it is obvious that E_C or E_{exp} values go on increasing from 106.53 to 140.67 kJ/mol with increasing concentration of ethanol 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 as reported earlier by several researchers in this field. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for increase in E_C values with gradual addition of ethanol in the reaction media -

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

The transition state being smaller anion(ester + OH⁻) available less for ethanol molecule than the initial state, so the third factor seems to be operative in this case and it also gets support when the values of activation(ΔS^*) and enthalpy of activation (ΔH^*) go on increasing with increasing concentration of ethanol (Table-VII). Similar interpretation for enhancement in the values of Iso-composition activation energy of the reaction with gradual addition of the organic content in the reaction media have also been reported earlier by Singh & Singh et al.¹⁰, Kumari¹ & Singh et al.¹¹ and in recent years by Kishor & Singh et al.¹².

Effect of Solvent on the Iso-dielectric Activation Energy (E_D) of the reaction:

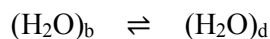
On perusal of the data of Table - IV, it is observed that the iso-dielectric activation energy (E_D) values of the reaction go on decreasing from 140.06 kJ/mol to 113.16 kJ/mol with increase in D values from D = 35 to D = 65 respectively. Such depletion in E_D values with increase in D values of the reaction media are in accordance with the increase in E_C values with increasing concentration of the organic content (ethanol) in the reaction media. Since D values of the reaction media decreases with addition of organic solvent in it, so it can also be concluded that E_D values of this reaction also increases like E_C values with decrease in D values of the reaction media. However, these findings and interpretations regarding change (decrease) in E_D values with increase in D values of the reaction media are in support of the past views of Elsemongy¹³ and Woford¹⁴ and have also been found in support of the recent report of Kumar & Singh et al.¹⁵ and Rakesh & Singh et al.¹⁶.

Effect of number of water molecules of the reaction media in the Mechanism of the Reaction:

For establishing the mechanistic pathways of the reaction, Robertson et al.¹⁷ gave an idea of solvation number 'n' which is the number or the number of water molecules involved in the formation of the activated complex and for its evaluation he proposed the equation:

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

Robertson et al¹⁷ have established the principle that the values of solvation number (n) for the reaction following unimolecular mechanistic pathway is fairly high but for the reaction following bimolecular path, it will be low. The number of water molecules 'n' involved in the formation of the activated complex of the reaction were determined by plotting log k values against log [H₂O] value for alkali catalysed hydrolysis of butyl propionate in aquo-ethanol media. The value of log k and log [H₂O] have been tabulated in Table - V and their plots have been pictured in Fig - 3. The numerical values of the slopes of plots have been recorded in Table - VI. From Fig. - 3, it is clear that at each temperature of the reaction, the plots of log k versus log [H₂O], two intersecting straight lines having, different values of slopes are obtained at log [H₂O] value at about 1.49 which corresponds to 55.60% of water in aquo-ethanol media. From the values recorded in Table - VI, it is clear that below log [H₂O] value 1.490, which corresponds to 55.60% of water in the reaction media, the number of water molecules associated with the activated complex decreases from 0.827 to 0.343 with rise in temperature of the reaction from 20 to 40°C. Similarly, in case of above, 55.60% of water concentration in the reaction media, the values of slopes decreases from 1.535 to 0.641 with increase in temperature from 20 to 40°C of the reaction. Overall, it may be inferred that number of water molecules associated with the activated complex in its formation decreases from 1.535 to 0.343. In the light of guidelines of Robertson et al.¹⁷ from the decreasing number of water molecules from 1.535 to 0.343 involved in the formation of the activated complex, it may be inferred that the mechanistic pathway followed by the reaction is changed from unimolecular to bimolecular in presence of ethanol in the reaction media and with increase in temperature of the reaction from 20 to 40°C. Regarding the changes in the structure of water, it is obvious that in presence of ethanol and with rise in temperature, water components of the reaction media, changes its structure from bulky to dense form.



Similar observations and inferences have also been reported earlier by Singh & Wats et al.¹⁸ and recently by Rashmi & Singh et al.¹⁹

Solvent effect on Thermodynamic Activation Parameters of the Reaction:

For better study 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 evaluated using Wynne-Jones and Eyring³ equation have been recorded in Table -VII. 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 ethanol as shown in Fig. - 4, 5 and 6 respectively. The values of ΔG^* recorded in Table -VII obviously indicate that the variation in ΔG^* is small and it increases from 87.11 to 89.42 kJ/mol with change of proportion of ethanol from 20 to 80% (v/v) at 30°C slowly with gradual addition of the organic content in water. The small but considerable increase in ΔG^* and non-linear variation in ΔH^* and ΔS^* curves with the increasing mol% of ethanol are indication of specific solvation taking place in the process of activation as already reported by Elsemongy et al.²⁰, Saville & Hudson et al.²¹ and Tomilla et al.²² Simultaneous increase in ΔG^* , ΔH^* and ΔS^* values with 148ropionate mol% of ethanol in the reaction media are only possible when the extent (degree) of enhancement in ΔH^* values is greater than that in ΔS^* values and from this, it may be inferred that in alkali catalysed hydrolysis of butyl 148ropionate aquo-ethanol media, ethanol acts as entropy controller and enthalpy stimulator solvent. Such inferences have been found in support of the earlier reported views of Monalisa & Singh et al.²³ and also of recently reported findings of Singh & Nazia et al.²⁵ and Priyanka & Singh et al.²⁵

Obedience of Barclay-Butler Relationship and Solvent-solute Interaction in aquo-Ethanol media :

This reaction is found to obey Barclay-Butler²⁶ relationship as a straight line is obtained when ΔH^* values are plotted against ΔS^* at 30°C (values mentioned in Table - VII) as shown in Fig.-

7. From the value of the slope of the plot, the values of iso-kinetic temperature of the reaction comes to be $308.95 \approx 309.0$. In the light of the reports of Leffler²⁷, high and considerable values of iso-kinetic temperature shows that in presence of ethanol, there is appreciably strong solvent-solute interaction in the reaction media (aquo-ethanol). Such observations and their interpretations have also been communicated earlier by Kumar & Singh et al.²⁸ and recently by Singh & Parween et al.²⁹.

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Table - I

Specific rate constant values of Alkali catalysed hydrolysis of Butyl nicotinate in water-EtOH media

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

Temp in °C	% of EtOH(v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	87.04	68.32	53.18	47.18	37.05	29.53	22.29
25°C	177.75	148.32	128.44	106.88	91.64	72.09	56.65
30°C	365.43	303.46	268.91	238.89	209.89	173.74	146.15
35°C	710.56	630.38	580.23	536.91	468.92	419.86	353.67
40°C	1416.45	1313.71	1192.61	1135.27	1050.03	950.17	857.24

Table - II

Variation of log k values of the reaction with $10^3/T$ in water-EtOH media.

Temp in °C	$\frac{10^3}{T}$	3+log k values at different % of EtOH (V/V)						
		20%	30%	40%	50%	60%	70%	80%
20°C	3.413	1.9397	1.8346	1.7496	1.6738	1.5688	1.4703	1.3481
25°C	3.356	2.2498	2.1712	2.1087	2.0289	1.9621	1.8579	1.7532
30°C	3.300	2.5628	2.4821	2.4296	2.3782	2.3220	2.2399	2.1648
35°C	3.247	2.8516	2.7996	2.7636	2.7299	2.6711	2.6231	2.5486
40°C	3.195	3.1512	3.1185	3.0765	3.0551	3.0212	2.9779	2.9331

Table - III

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

% of EtOH(v/v)	20%	30%	40%	50%	60%	70%	80%
E_C value in kJ/mol	106.53	112.92	117.72	121.98	126.06	133.17	140.67

Table - IV

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

D values	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60	D = 65
E_D values in kJ/mol	140.06	133.35	129.78	125.38	120.08	115.85	113.16

Table - V

Variation of log k values of the reaction with log [H₂O] values of water-EtOH system (media) at different temperatures.

% of EtOH (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	1.9397	2.2498	2.5628	2.8516	3.1512
30%	70%	1.5898	1.8346	2.1712	2.4821	2.7996	3.1185
40%	60%	1.5229	1.7496	2.1087	2.4296	2.7636	3.0765
50%	50%	1.4437	1.6738	2.0289	2.3782	2.7299	3.0551
60%	40%	1.3468	1.5688	1.9621	2.3220	2.6711	3.0212
70%	30%	1.2218	1.4703	1.8579	2.2399	2.6231	2.9778
80%	20%	1.0458	1.3481	1.7532	2.1648	2.5486	2.9331

Table - VI

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

Temperature	Slope - I When log[H ₂ O] value is below 1.49	Slope - II when log[H ₂ O] value is above 1.49
20°C	0.827	1.535
25°C	0.700	1.138
30°C	0.508	0.982
35°C	0.449	0.795
40°C	0.343	0.641

Table -VII

**Variation of ΔH^* , ΔG^* and ΔS^* values of the reaction with mol % of EtOH in water-
EtOH meida**

% of EtOH (v/v)	Mol % of EtOH	ΔH^* in kJ/mol	ΔG^* in kJ/mol at 30°C	ΔS^* in J/K/mol at 30°C
20%	7.17	104.54	87.11	51.53
30%	11.69	109.70	87.58	73.02
40%	17.07	115.47	87.88	91.66
50%	23.59	119.76	88.18	104.22
60%	31.06	125.70	88.51	122.76
70%	41.87	131.16	88.98	139.18
80%	55.85	137.99	89.42	160.31

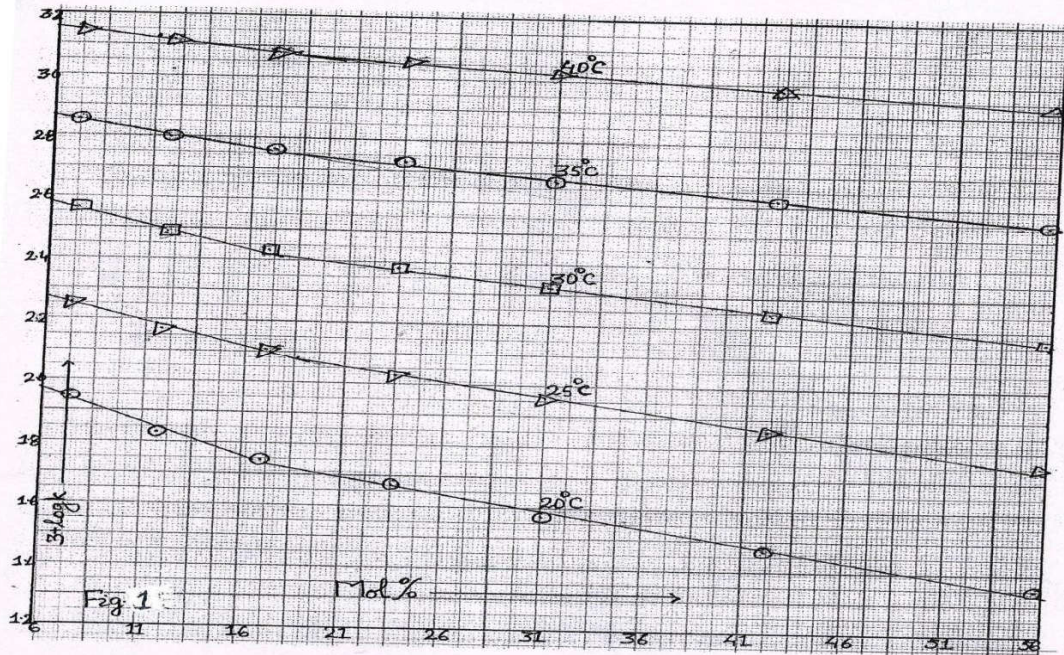
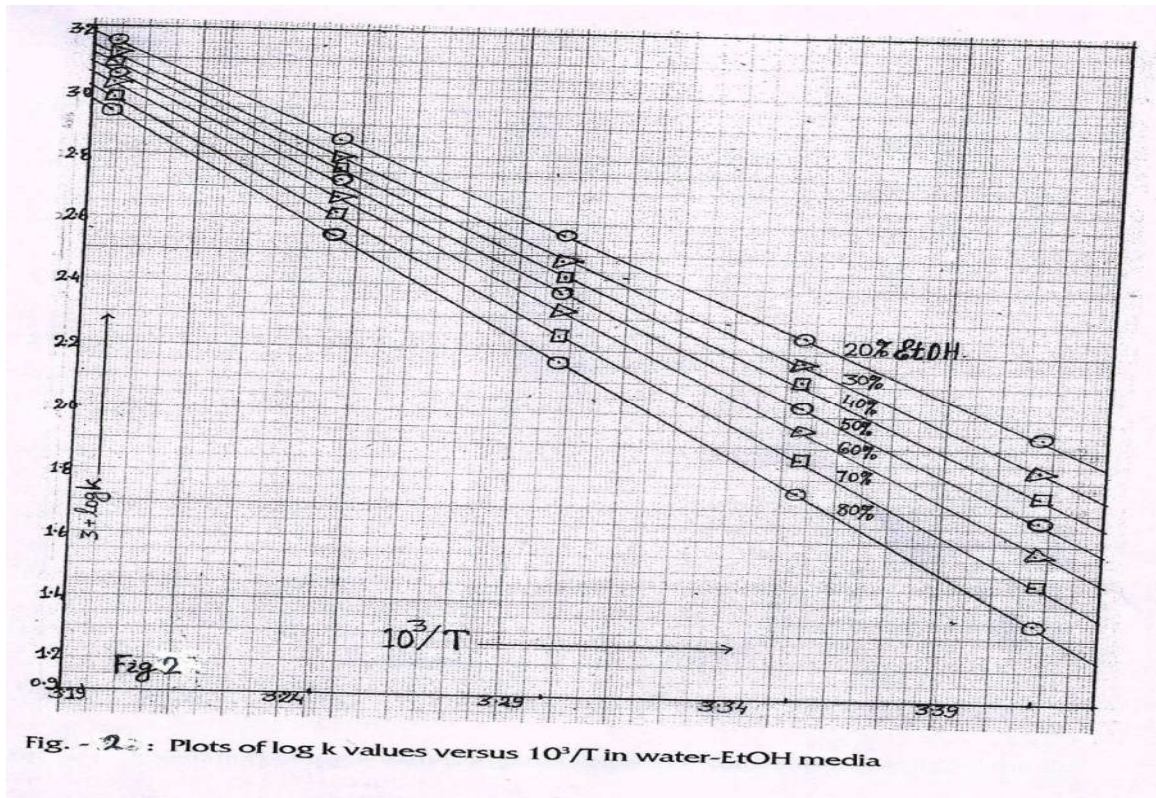


Fig. 1 : Variation of log k values with mole % of EtOH in water-EtOH media



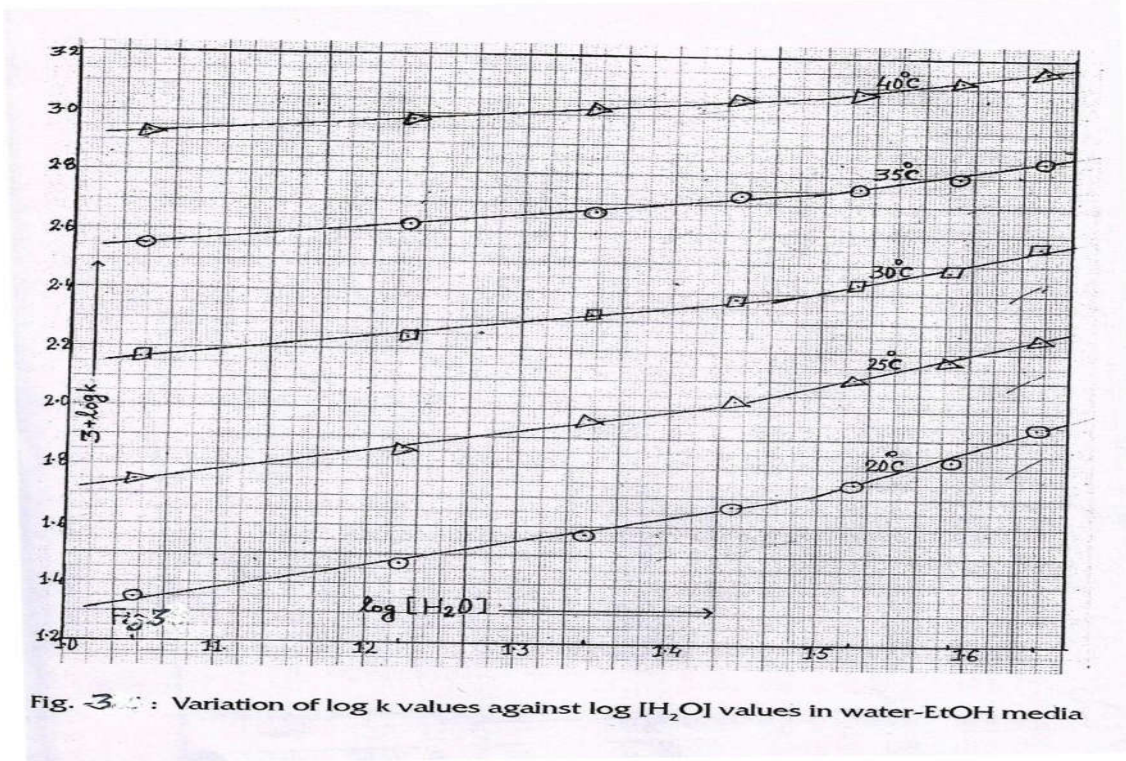


Fig. 3 : Variation of log k values against log [H₂O] values in water-EtOH media

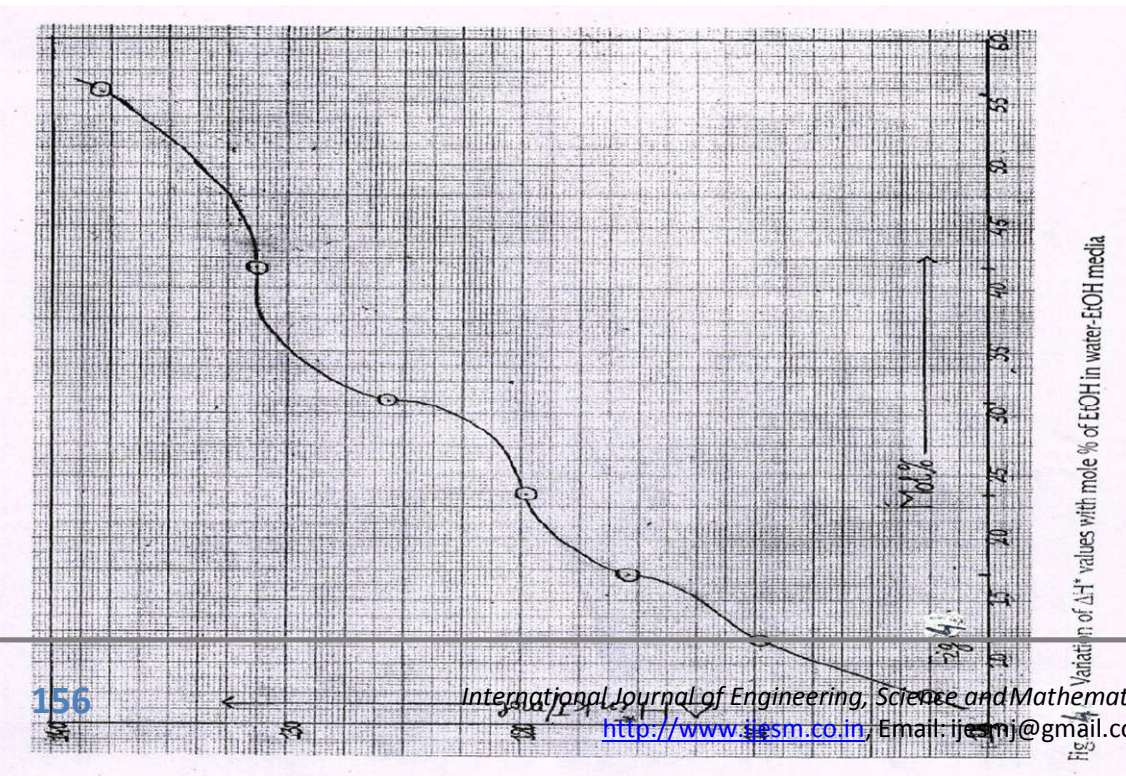


Fig. 4 : Variation of ΔH^+ values with mole % of EtOH in water-EtOH media

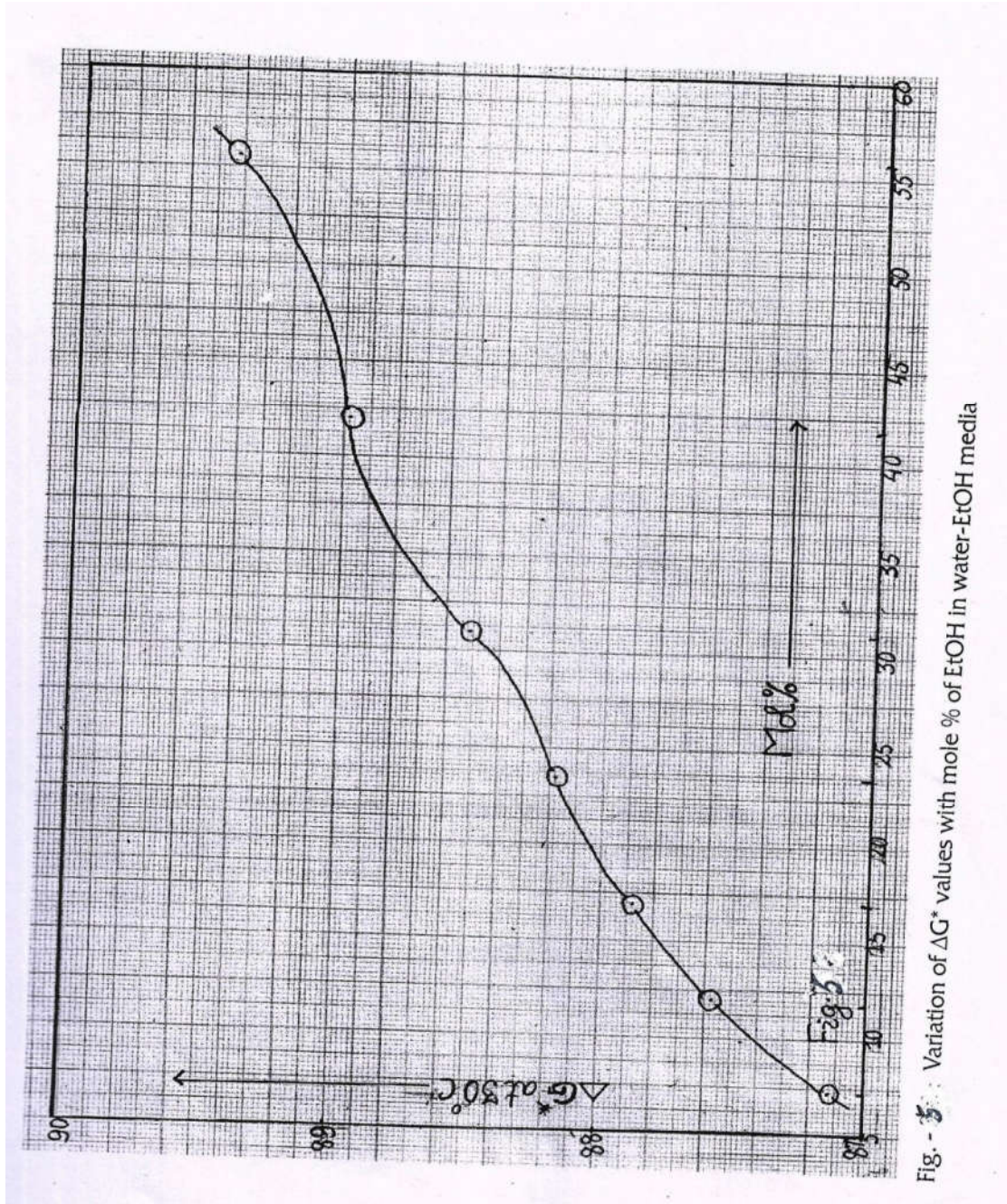


Fig. - 5 : Variation of ΔG^* values with mole % of EtOH in water-EtOH media

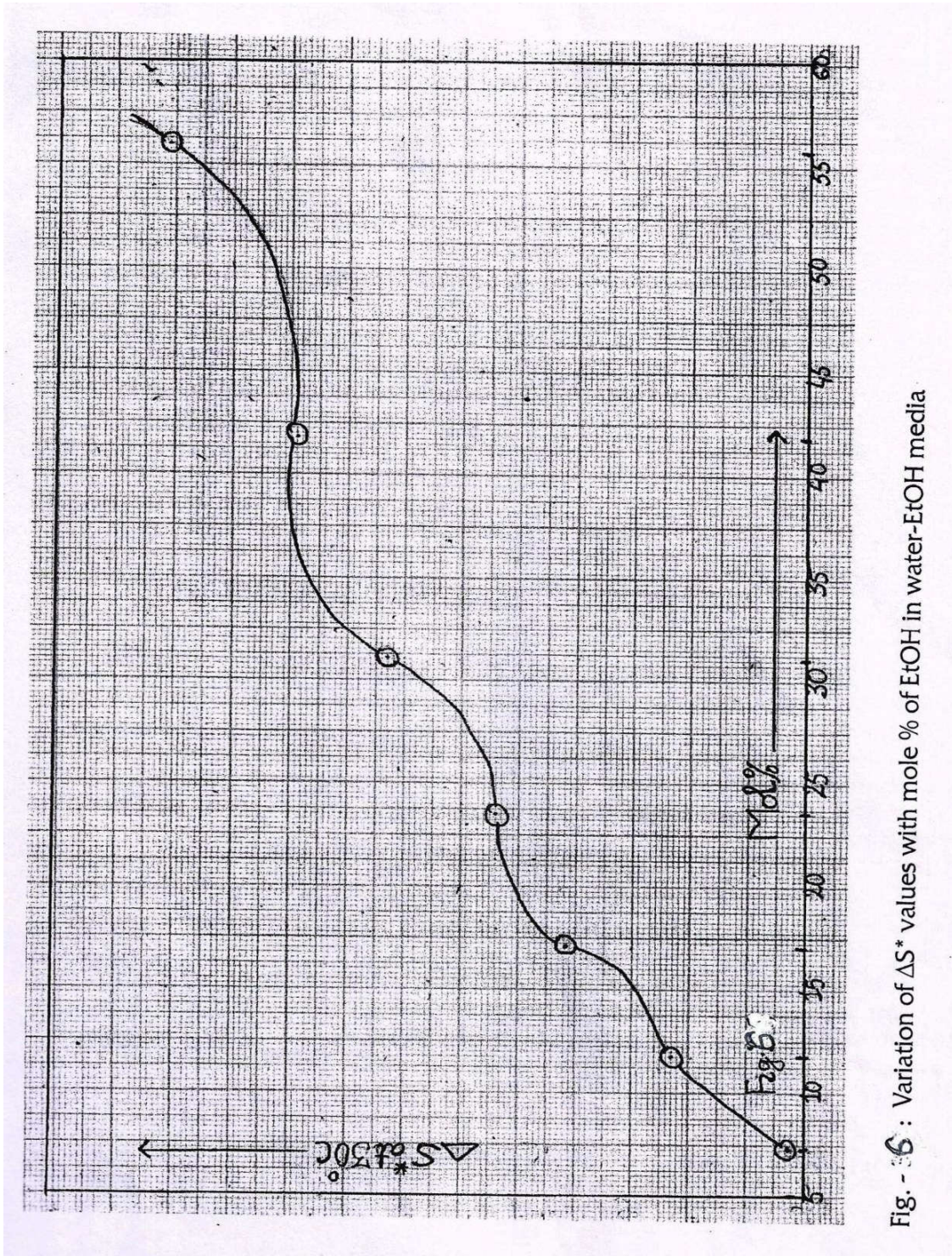


Fig. - 6 : Variation of ΔS^* values with mole % of EtOH in water-EtOH media

