# STUDIES ON THE EFFECT OF H-BONDINGS ON THE THERMODYNAMIC PROPERTIES AND PHARMACEUTICAL EFFICIENCY OF THE SOLVOLYSIS PRODUCTS OF HIGHER METHANOATES IN WATER-ETOH SOLVENT-SYSTEMS

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## ABSTRACT

The effect of hydrogen bondings existing in the reaction media has been highlighted by studyng the acid catalysed solvolysis of butyl methanoate in aquo-ethanol solvent systems.

The depletion and enhancement observed respectively in iso-composition and iso-dielectric activation energies reveal that the transition state is solvated and initial state is desolvated with addition of ethanol in the reaction media. Almost unity value of the slope of the plots of log k values against log [H+] values shows that the reaction follows $A_{AC}^2$ mechanism.

From the values of iso-kinetic temperature, which comes to 277.0, it is inferred that in aquo-EtOH reaction media, the reaction follows Barclay-Butler rule and there is weak but acceptable interaction between solvent and solute in aquo-EtOH(aquo-ethanol) reaction media.

**Key words:** Hydrogen bonding, phasmecentical, Efficiency, Solvent-System, Iso-dielectric, Iso-composition, Iso-kinetic Solvation number, Solvation and desolvation.

**Introduction:**

In order to explore the effect of hydrogen bondings present in aquo-dipolar-protic solvent system on the biochemical use as a flavouring agent of higher methanoate, it is has been proposed in the best interest of man kind and society to study the kinetics of [H$^+$] ion catalysed solvolysis of butyl methanoate in aquo-EtOH reaction medai.

**Experimental & Calculation:**

Export quality of butyl methanoate media in U.S.S.R. and Merck grade of ethyl alcohol of high purity (absolute alcohol) were used. The kinetics of the reaction was studied by adding 0.60ml of ester butyl methanoate through a German make graduated syring pipette into 50 ml of 0.5 M solution of HCl. The reaction was found to obey the first order kinetic equation and the evaluated valued of specific rate constants have been recorded in Table-I. The variation of log k with log [H$_2$O] of the reaction media are recorded in Table-II. From the slope of the plots of log k versus log [H$_2$O], the number of water molecules associated with the transition state of the reaction have been evaluated and are placed in Table-III.

The numerical values of thermodynamic activation parameters were calculated using Wynne-Jones and Eyring equation[1] and are synchronised in Table - IV. Effect of change in [H$^+$] ion concentration of the reaction media on the specific rate constants of the reaction has been shown in Table-V.

**Evaluation of number of water molecules involved in the formation of activated complex of the reaction and Establishment of the mechanism of the reaction :**

Robertson[2] has formulated an equation, which is as :

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

where 'n' is the salvation number i.e. the number of water molecules associated with the transition state of the reaction and is evaluated from the slopes of the plots of log k versus log [$H_2O$].

Robertson et.al.[3] have suggested that value of 'n' for unimolecular reactions is fairly high while that of bimolecular reactions, it will be low.

From the recorded values of log k and log [$H_2O$] in Table-III, the log k values were plotted against log [$H_2O$] as shown in Fig.-1 and the evaluated values of the slopes of the straight line have been enlisted in Table-IV.

From Fig.-1 it is clear that at each temperature two intersecting straight lines are obtained at log [$H_2O$] value 1.480 which corresponds to 54.40% of water concentration (v/v) in aquo-ethanol reaction media.

From the recorded values of the slopes of the plots of log k versus log [$H_2O$] in Table-IV, it is clear that below or before log [$H_2O$] values 1.480, which corresponds to 54.40% of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.366 to 0.838 with increase in temperature of the reaction from 20 to40$^o$C. Similarly, for above 54.40% water concentration in the reaction media, the number of water molecules involved in the formation of the activated complex increase from 0.587 to 1.247 with rise in temperature from 20 to 40$^o$C.

Overall, it is concluded that number of water molecules associated with the activated complex increase from 0.360 to 1.247 with rise in temperature from 20 to 40°C and from this trend, in the light of the guidelines of Robertson et.al.[3] it is inferred that the mechanistic pathway of the reaction is changed from bimolecular to unimolecular with increase in water concentration or with decrease in ethanol content of the reaction media and also with increase in the temperature of the reaction.

From the enhancing trend of number of water molecules involved in the formation of the activated complex, it is also inferred that on addition of EtOH in the reaction media, the equilibrium of water is shifted from its dense form bulky from.

$$(H_2O)_d \rightleftharpoons (H_2O)_b$$
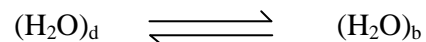
Such observations, inferences and their interpretations have been reported earlier by Singh & Singh et al.[4] and also recently Sinha & Singh et al.[5]

**Solvent Effect on Thermodynamic Activation Parameters of the Reaction:**

The three thermodynamic activation parameters namely enthalpy of activation ($\Delta H^*$), free energy of activation ($\Delta G^*$) and entropy of activation ($\Delta S^*$) of the reaction were evaluated using Absolute rate theory and Wynne-Jones and Eyring euqation[1] and have been mentioned in Table-V. it is clear that $\Delta G^*$ values of the reaction go on increasing with simultaneous decrease in both the $\Delta H^*$ and $\Delta S^*$ values of the reaction.

In order to study the variation in these thermodynamic parameters more clearly, they were plotted against the mol% of EtOH which have been shown in Fig.-2, 3 and 4 and for $\Delta H^*$, $\Delta G^*$ and $\Delta S^*$ respectively. From Fig.-2, 3 and 4, it is clear that all of them very non-linearly to the considerable extent with the increasing concentration(mol %) of EtOH  and this is the indication of specific salvation taking place in the reaction media according to Saville and Hudson[6]. The $\Delta H^*$ and $\Delta S^*$ are complimentary to each other as the resulting net property of $\Delta G^*$ in Table-VII is a well behaved function.

From the values of $\Delta G^*$ in Table-VII and also from the Fig.-6, it is clear that $\Delta G^*$ is being little affected by the solvent composition (mol%). However, there is considerable enhancement in $\Delta G^*$ values.

From Table-V, it is also clear that $\Delta G^*$ values are found to increase simultaneously with depletion in both the $\Delta H^*$ and $\Delta S^*$ values.

From the thermodynamic relation-

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

It is apparent that enhancement in $\Delta G^*$ values with simultaneous decrease in both of $\Delta H^*$ and $\Delta S^*$ values of the reaction is only possible when the extent of depletion in $\Delta S^*$ values is greater than in $\Delta H^*$ values. From these findings, it is concluded that the acid catalysed hydrolysis of butyl methanoate in aquo-ethanol media is entropy controlled and enthalpy dominated reaction. Similarly findings and their interpretations have also been reported recently by Kumar and Singh et al.[7] and Sharma & Singh et al.[8]

**Solvent Effect on Solvent-Solute Interaction in the quo-EtOH Reaction media:**

For evaluating the solvent-solute interaction for a solvolysis reaction, Barclay and Butler[9] have correlated the enthalpy of activation ($\Delta H^*$) and the entropy of activation ($\Delta S^*$) by means of the relationship-

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

Where $\beta$ is a constant called iso-kinetic temperature and it is evaluated from the slope of plots of $\Delta H^*$ values against $\Delta S^*$ value.

From the recorded values of $\Delta H^*$ and $\Delta S^*$ in Table-VII, $\Delta H^*$ values were plotted against $\Delta S^*$ (at $30^oC$) which is shown in Fig. 5. The plot consists of a straight line whose slope value has been evaluated to be 284.0 which is less than 300. Following the guidelines of Lefller[10], It is concluded that there is weak but considerable solvent-solute iteraction for acid catalysed hydrolysis of butyl-methanoate in aquo-ethanol reaction media.

Similar interpretations for weak solvent-solute interaction have also been reported earlier by Singh & Singh et.al.[11] and recently also by Dheeraj & Singh et.al.[12].

**Effect of change of [H$^+$] in concentration of the reaction media on the Mechanism of the Reaction:**

In order to investigate the effect of change in acid concentration of reaction media (H$^+$) in concentration on the specific rate constants of the acid catalysed hydrolysis of Iso-propyl formate in aquo-ethanol media, experiments were performed to study the kinetics at various concentrations of HCl (from 0.1 M to 0.8M), keeping the temperature, solvent composition and ionic strength of the reaction media constant. The reactions were carried out at 25$^o$C in the reaction media having 20% (v/v) concentration of ethanol and the evaluated values of specific rate constants have been tabulated in Table-VI. From the tabulated values

of log k and log [H$^+$] in Table-VI, log k values were plotted against log [H$^+$] and has been shown in Fig.-4. From Fig.-6, it is clear that the plot is an excellent straight line showing linear dependence of rate of reaction on [H$^+$] ion concentration. The slope of the log k versus log [H$^+$] plot is evaluated to be  which is almost equal to unity.  From this value of slope (unity), it may be inferred on the basis of the hypothesis of Zucker and Hammett[13] that acid catalysed hydrolysis of butyl methanoate  in aquo-ethanol media follows A$_{AC}^2$ mechanism. Similar observation, inference and their interpretations have also been reported earlier by Tauheed & Singh et.al.[14] and in the recent years also by Sushma and Singh et.al.[15].

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| Temp in $^oC$ | % of EtOH (v/v) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 20% | 30% | 40% | 50% | 60% | 70% | 80% |
| 20$^o$ C | 75.42 | 67.95 | 64.15 | 59.62 | 54.65 | 49.90 | 42.78 |
| 25$^o$ C | 138.10 | 123.37 | 111.94 | 100.48 | 89.60 | 79.20 | 64.60 |
| 30$^o$ C | 251.14 | 219.89 | 194.89 | 169.90 | 147.94 | 125.83 | 97.41 |

<u>**Table -1**</u>

**Specific rate constant values of Acid catalysed hydrolysis of Butyl methanoate in water-EtOH media**

$$k \times 10^4 \text{ in } (dm)^3 \text{ mol}^{-1} \text{ min}^{-1}$$

| | | | | | | |
|---|---|---|---|---|---|---|
| **35⁰ C** | 446.27 | 381.24 | 330.29 | 281.00 | 233.51 | 194.49 | 143.48 |
| **40⁰ C** | 788.50 | 666.04 | 562.08 | 462.49 | 373.42 | 299.71 | 212.23 |

**Table - II.**

**Variation of log k with log [H$_2$O] values of water-EtOH system temperatures.**

values of the reaction

(media)  at different

| Temperature in ⁰C | Slope - I when log[H$_2$O] value is below 1.480 | Slope - II when log[H$_2$O] value is above 1.480 |
|---|---|---|
| **20⁰C** | 0.366 | 0.587 |
| **25⁰C** | 0.432 | 0.704 |
| **30⁰C** | 0.607 | 0.895 |

**Table – III**

Values of the log k versus log [H$_2$O] at different temperatures

slopes of the plots of

| % of EtOH (v/v) | % of H$_2$O | log [H$_2$O] | log k values | | | | |
|---|---|---|---|---|---|---|---|
| | | | **20⁰C** | **25⁰C** | **30⁰C** | **35⁰C** | **40⁰C** |
| 20% | 80% | 1.6478 | 1.8774 | 2.1401 | 2.3999 | 2.6495 | 2.8968 |
| 30% | 70% | 1.5898 | 1.8321 | 2.0912 | 2.3422 | 2.5811 | 2.8235 |
| 40% | 60% | 1.5229 | 1.8071 | 2.0489 | 2.2897 | 2.5188 | 2.7497 |
| 50% | 50% | 1.4437 | 1.7753 | 2.0020 | 2.2301 | 2.4487 | 2.6651 |
| 60% | 40% | 1.3468 | 1.7375 | 1.9523 | 2.1700 | 2.3683 | 2.5701 |
| 70% | 30% | 1.2218 | 1.6981 | 1.8987 | 2.099 | 2.2889 | 2.4767 |
| 80% | 20% | 1.0458 | 1.6312 | 1.8102 | 1.9886 | 2.1567 | 2.3268 |

| | | |
|---|---|---|
| **35⁰C** | 0.730 | 1.078 |
| **40⁰C** | 0.838 | 1.247 |

**Table – IV**

Variation of ∆H*, ∆G* and ∆S* values of the reaction

with mol % of EtOH in water-EtOH media

| % of EtOH (v/v) | Mol % of EtOH | $\Delta H^*$ in kJ/mol | $\Delta G^*$ in kJ/mol at 30⁰C | $\Delta S^*$ in J/K/mol at 30⁰C | $(\Delta S^* + 150)$ in J/K/mol at 30⁰C |
|---|---|---|---|---|---|
| **20%** | 7.17 | 87.04 | 93.86 | -22.51 | 127.49 |
| **30%** | 11.69 | 83.82 | 94.19 | -34.23 | 115.77 |
| **40%** | 17.07 | 80.00 | 94.50 | -47.86 | 102.14 |
| **50%** | 23.59 | 75.56 | 94.84 | -63.63 | 86.37 |
| **60%** | 31.06 | 70.48 | 95.19 | -81.57 | 68.43 |
| **70%** | 41.87 | 66.88 | 95.60 | -94.79 | 55.21 |
| **80%** | 55.85 | 96.24 | 96.24 | -122.21 | 27.79 |

### Table - V

### Effect of [H$^+$] on the Specific rate constant values of

### Acid Catalysed Hydrolysis of Butyl methanoate in water-EtOH media at constant ionic strength ($\mu$ = 0.9)

| [H$^+$] | [KCl] | $\mu$ | k x 10$^4$ in min$^{-1}$ | 2 + log [H$^+$] | 4+ log k | value of the slope of the plot of log k vesus log [H$^+$] |
|---|---|---|---|---|---|---|
| 0.10 | 0.80 | 0.90 | 5098 | 1.0000 | 1.7074 | |
| 0.15 | 0.75 | 0.90 | 75.82 | 1.1761 | 1.8798 | |
| 0.20 | 0.70 | 0.90 | 100.65 | 1.3010 | 2.0028 | |
| 0.25 | 0.65 | 0.90 | 125.81 | 1.3979 | 2.0997 | |
| 0.30 | 0.60 | 0.90 | 150.49 | 1.4771 | 2.1775 | 1.002 |
| 0.40 | 0.50 | 0.90 | 199.57 | 1.6021 | 2.3001 | |
| 0.50 | 0.40 | 0.90 | 251.14 | 1.6990 | 2.3999 | |

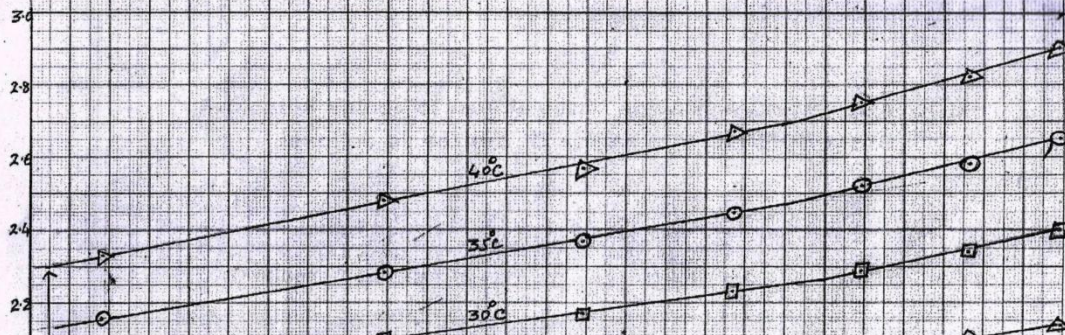| | | | | | | |
|------|------|------|--------|--------|--------|--|
| 0.60 | 0.30 | 0.90 | 301.23 | 1.7782 | 2.4789 | |
| 0.70 | 0.20 | 0.90 | 348.66 | 1.8451 | 2.5424 | |
| 0.80 | 0.10 | 0.90 | 398.47 | 1.9030 | 2.6004 | |

**Concentration of EtOH = 20% (v/v)**                    **Temp. - 30°C**
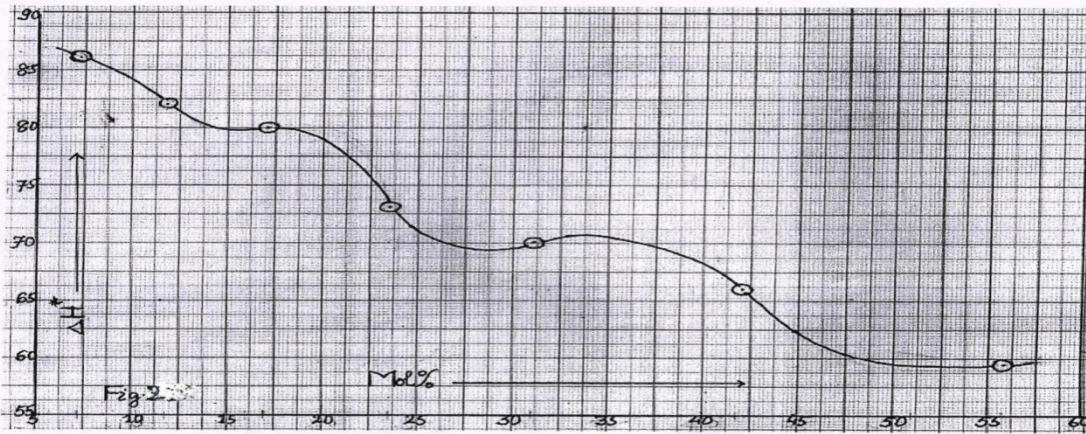
Fig. - 2. : Variation of ΔH* values with mol % of EtOH in water-EtOH media
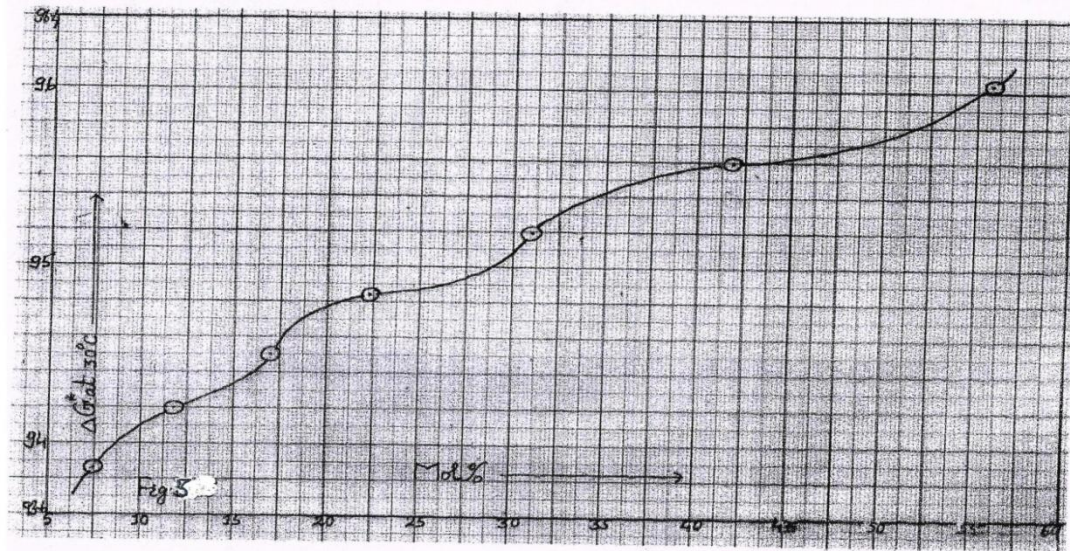
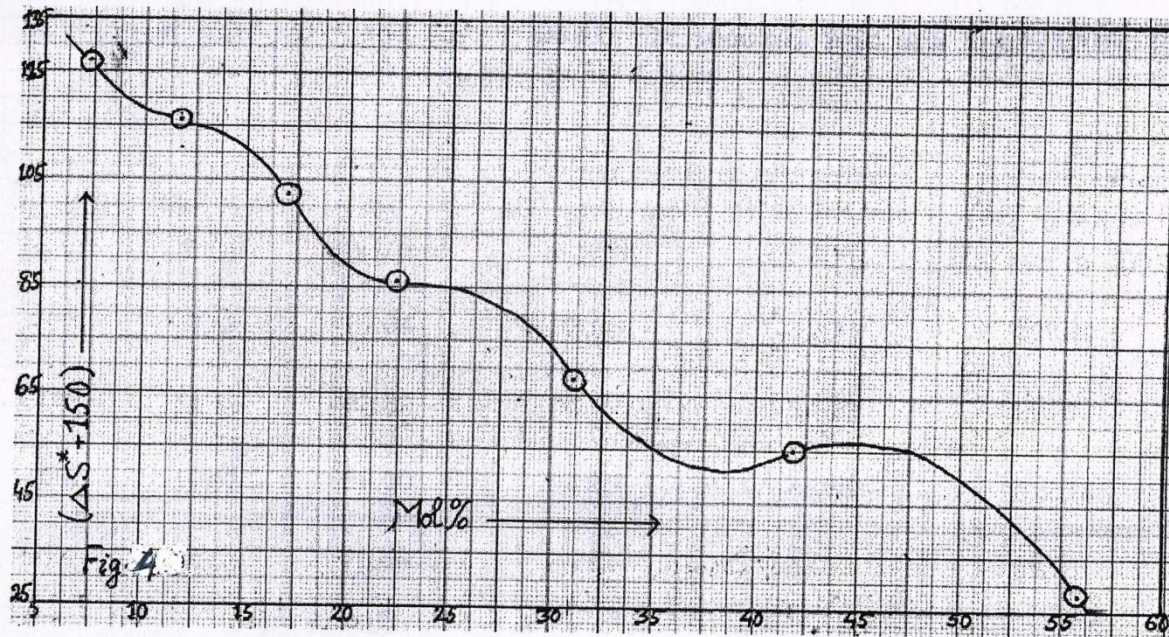Fig. - 3 : Variation of ∆G* values with mol % of EtOH in water-EtOH media
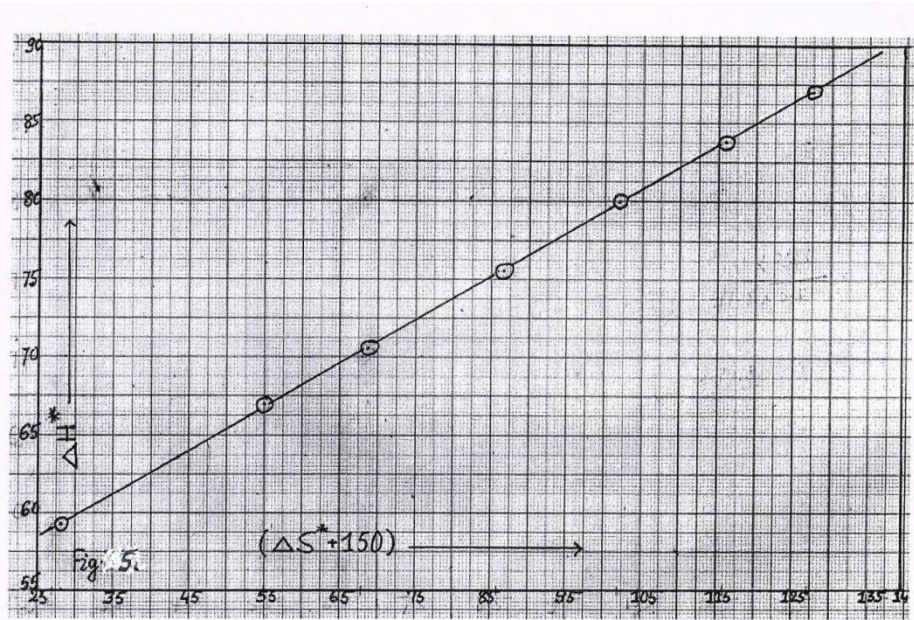
Fig. - 4 : Variation of ΔS* values with mol % of EtOH in water-EtOH media

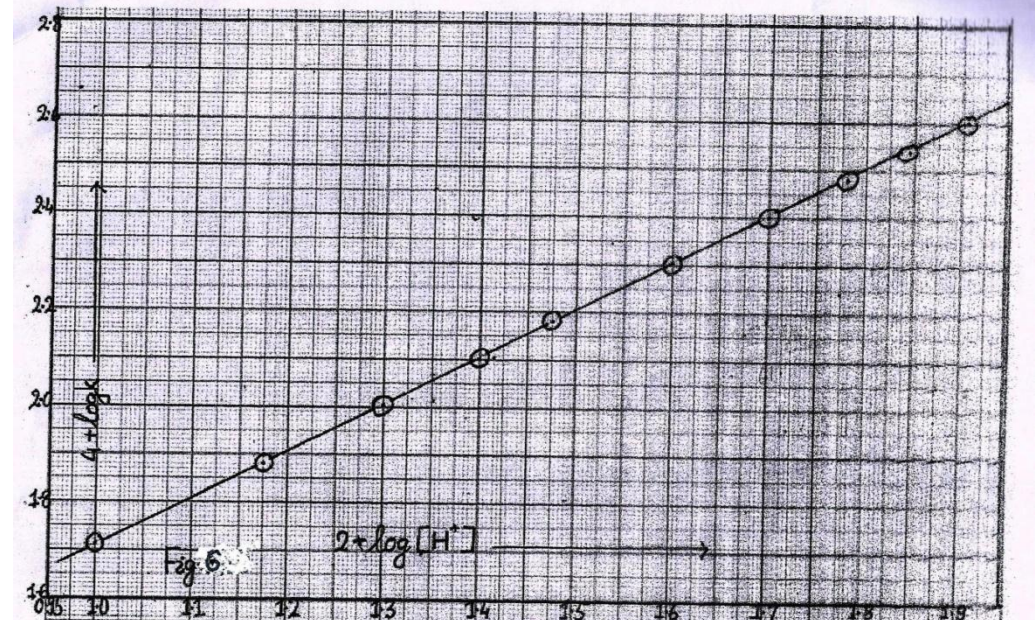Fig. - 5 : Plots of ΔH* values against ΔS* values in water-EtOH media



Fig. - 6 : Plots of log k values against log [H⁺] in water-EtOH media