

Studies on the effect of An Ionising Solvent containing N atom on the Reactivity of active methylene group of Maloic Acid Ester.

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Key words:- Aquo-acetonitrile, Dielectric effect, Solvation changes, Enthalpy controlled, Iso-kinetic temperature, Simulataneous enhancement

ABSTRACT

The solvent effect of aquo-acetonitrile solvet systems on a diabasic acid ester containing active methylene groups was highlighted by studying the alkali catalysed hydrolysis of diethyl malonoate in this reaction media (aquo-acetonitrile) having different composition containing acetonitrile varying from 20 to 60% (v/v)

The changes observed in its iso-composition and iso-dielectric activation energies (E_C and E_D) have been explained in the light of solvation and desolvation of the initial and transition states to different exten.

Form the evaluated values of iso-kinetic temperature which comes to be 331, it is inferred that there is appreciably strong solvent-solute interaction in aquo-acetonitrile reaction media.

Introduction :

Various Kineticists¹⁻³ have reported that the effect of dipolar aprotic solvent like DMSO, DMF, Acetone etc. have widely been used for catalysed solvolysis of different monobasic acid ester but solvent effect of a good nun polar solvent having nitrogen atom and capable of dissolving ionic compound has not been used 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 Acetonitrile on the alkali catalysed hydrolysis of a diabasic acid ester, namely diethyl malonate.

Experimental:

Purified Acetonitrile of Merck grade and diethyl malonate of Fluka AG (packed in Switzerland) were taken into use. The Kinetics of alkali catalysed hydrolysis of the ester was studied as usual by adding calculated amount(volume) with the help of the graduated syringe

pipette into 100 ml of 0.1 M NaOH solution. The reaction mixture solution was prepared such that its strength with respect to alkali became 0.1M and with respect to ester is 0.05M. The specific rate constants were evaluated by making use of second order rate equation and are tabulated in Table-I. Variation of log k values with mol% of Acetonitrile reaction media has been recorded in Table-II. The evaluated values of the Iso-composition activation energy (E_C) have been mentioned in Table-III. For deriving the mechanistic path way of the reaction, the plots of log k versus log $[H_2O]$ as their recorded values in Table-IV. The thermodynamic activation parameters of the reaction calculated by using Wynne-jones & Eyring equation⁴ has been enlisted in Table-V.

Results and Discussion :

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

In order to study the variation in k values of the reaction with change in mol % of Acetonitrile, the logarithmic values of k which have been recorded in Table - II, have been plotted against the mol % of Acetonitrile 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 with increasing concentration of Acetonitrile 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:

- (i) decreasing polarity of the medium as changing from polar water to less polar aquo - Acetonitrile medium, and
- (ii) lowering of the bulk dielectric constant values of the medium.

Among the above mentioned two rate-retarding factors, both factors are in operation and it is quite in agreement with the theory of Hughes and Ingold⁵ that the rate is bound to decrease with decreasing dielectric constants of the medium.

However, these explanations are in support of the views of Laidler and Lanskoener⁶ and earlier reports of Kumar & Singh et al.⁷ and Singh & Parveen et al.⁸. Svati & Singh et al.,⁹ and Singh & Lal et al.,¹⁰ have also reported similar findings and interpretations for depletion in the rate of solvolysis reactions.

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 45.06 kJ/mol to 83.04 kJ/mol with addition of 20 to 80% of Acetonitrile in the reaction media.

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

- (i) The greater solvation of the initial state than the transition state,
- (ii) The greater desolvation of transition state than the initial state, and
- (iii) Simultaneous solvation and desolvation of the initial and the transition state respectively.

Out of these three factors, the third 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 (Acetonitrile) in the reaction media as tabulated in Table-VII. Such changes have been found in support of the earlier views of Singh & Wats et al.¹¹ and Kumari & Singh et al.,¹². Recently, Rakesh & Singh et al.¹³ and Rashmi & Singh et al.¹⁴ have also reported similar findings.

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.¹⁵

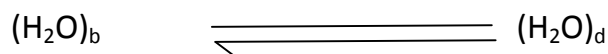
$$\log k = \log k_0 + n \log [H_2O]$$

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, straight lines

with positive slopes are obtained. The average numerical values of the slopes of straight lines is evaluated to be 1.34.

From Fig. - 3, it is also clear that with increasing temperature the slopes of the straight lines are decreasing. In other words the number of water molecules associated with the activated complex are decreasing. Thus, it can be concluded from the guidelines of Robertson et al.¹⁶ that the alkali catalysed hydrolysis of diethyl malonate in aquo-Acetonitrile media follow bimolecular mechanism with respect to water. In other words, the presence of Acetonitrile 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 Acetonitrile, the equilibrium of water shifts from its bulky form to its dense form with rise of temperature of the reaction.



However, earlier Bencel et al.¹⁷, Singh & Bano et al.¹⁸ and in recent years Singh & Zeba et al.,¹⁹ have also reported similar observations and inferences.

Solvent Effect on Thermodynamic Activation Parameters of the Reaction :

The famous Wynne-Jones and Eyring⁴ 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 - V.

On visualising the data mentioned in Table-V, the interesting feature comes in the light is that out of the values of all the three thermodynamic activation parameters i.e. ΔH^* , ΔG^* and ΔS^* all are increasing simultaneously with increasing proportion of Acetonitrile in the reaction media.

For highlighting the solvent effect on the three thermodynamic activation parameters, namely ΔH^* , ΔG^* and $-T\Delta S^*$, the numerical values of all were plotted against mol % of the Acetonitrile in the reaction as shown in Fig. - 4. The non-linear variation in ΔH^* and ΔS^* from Fig. - 4 gives information of the fact that specific solvation is taking place in aquo-Acetonitrile media similar to that as reported by Saville et al.²⁰

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 alkali catalysed hydrolysis of diethyl methanoate in aquo-Acetonitrile 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 fact that transition state of the reaction is more desolvated than that of its initial state in the similar way as reported earlier by Singh & Zeba et al.¹⁹ Saville and Hndson²⁰ Singh & Kaushalendra²¹. Recently, Singh & Singh et al.²² have also reported similar interpretations for describing the effect of solvent on the changes found in thermodynamic activation parameters of the solvolysis reaction.

Solvent Effect on the Solvent-Solute Interaction in aquo-Acetonitrile Reaction Media:

In the light of Barclay and Butler²³ relationship between enthalpy and entropy of activation, which is as:

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

where ' β ' is a constant called iso-kinetic temperature and also known as Leffler-Gruunwald²⁴ 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^* at 35⁰Cas shown in Fig.-5 and it comes to be 331.0.

From the value of iso-kinetic temperature (above 300), it is concluded that there is a considerable change in the structure of reactants or in the solvent or in both due to strong and appreciable interaction between solvent and solute present in the aquo-Acetonitrile media in the similar way as reported by Leffler²⁵. Earlier Singh & Parween et al.⁸, and in recent years sharad & Singh et al²⁶. Sushma & Singh et al²⁶. and Sushma-Abhay & Singh et al²⁷ have also reported similar observations and findings about the solvent-solute interaction in different reaction media.

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Table - 1

Specific rate constant values of Alkali catalysed hydrolysis of diethyl malonate in aquo-acetonitrile media

$k \times 10^2$ in lit. mol⁻¹min⁻¹

Temp in °C	% of Acetonitrile (v/v)				
	20%	30%	40%	50%	60%
20°C	62.0	37.9	24.0	16.9	13.3
25°C	73.8	60.4	37.7	31.7	22.3
30°C	102.8	74.5	57.7	47.0	38.2
35°C	139.0	111.7	80.9	73.6	65.8
40°C	191.6	156.3	132.7	115.6	98.4

Table - II

Variation of log k values with mol % of acetonitrile at different temperatures for alkali catalysed hydrolysis of diethyl malonate aquo-acetonitrile media.

% of Acetonitrile (v/v)	Mol % of Acetonitrile	2 + log k values				
		25°C	30°C	35°C	40°C	45°C
20%	7.90	1.792	21.868	2.012	2.143	2.2883
30%	12.81	1.579	1.781	1.872	2.048	2.194
40%	18.61	1.380	1.588	1.761	1.908	2.123
50%	25.53	1.228	1.501	1.672	1.867	2.063
60%	33.96	1.124	1.348	1.582	1.818	1.993

Table - III

Evaluated values of iso-composition Activation Energy (E_c or E_{exp}) of the reaction in aquo-acetonitrile media.

% of Acetonitrile	20%	30%	40%	50%	60%
E_c value in kJ/mol	40.06	55.99	66.15	73.79	83.04

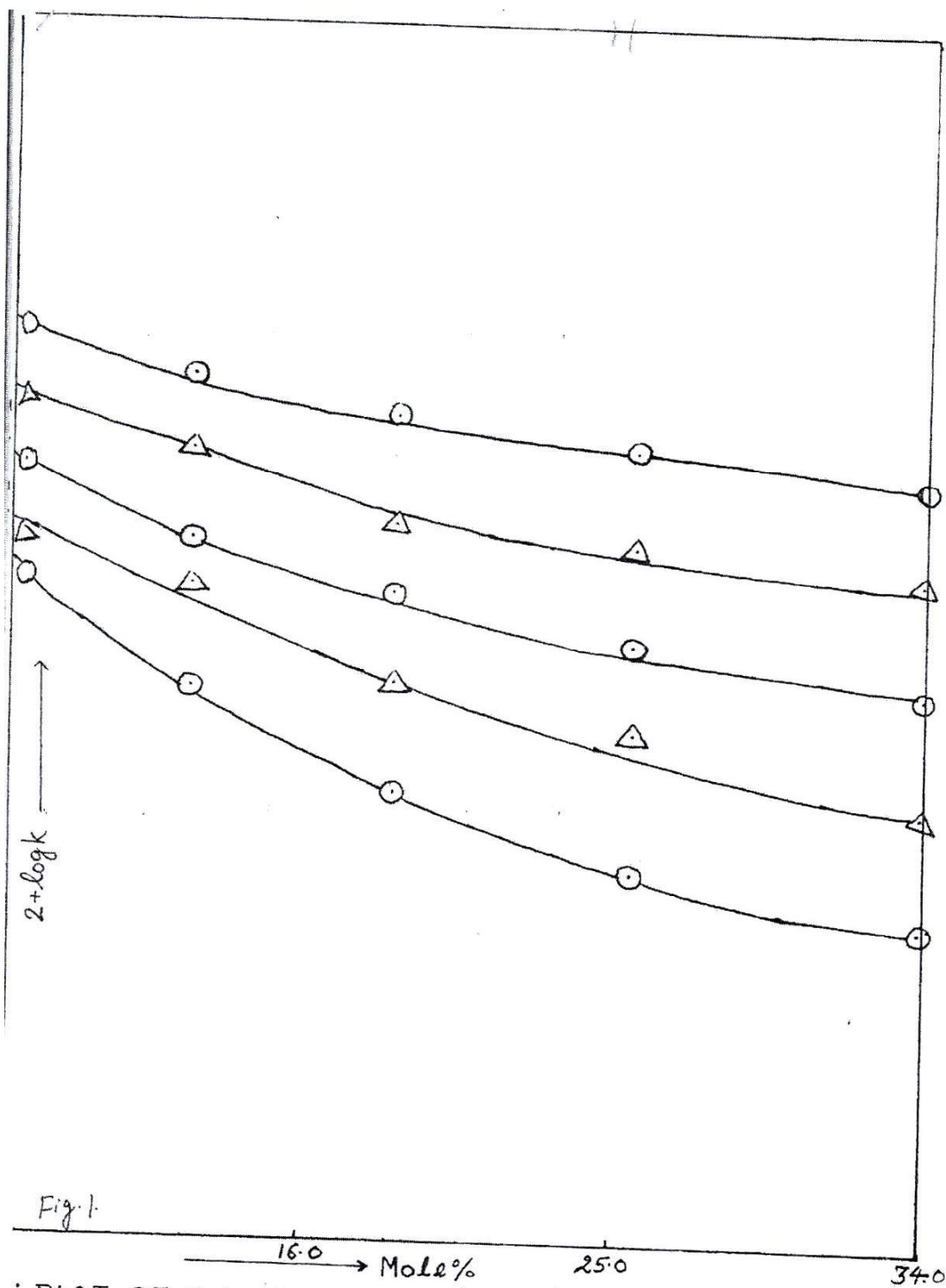
Table - IV

Variation of log k values with mol % of acetonitrile at different temperatures for alkali catalysed hydrolysis of diethyl malonate aquo-acetonitrile media.

% of Acetonitrile (v/v)	Mol % of water	log[H ₂ O]	2+log k values				
			25 °C	30 °C	35 °C	40 °C	45 °C
20%	80	1.648	1.792	1.868	2.012	2.143	2.283
30%	70	1.590	1.579	1.781	1.872	2.048	2.194
40%	60	1.523	1.380	1.588	1.761	1.908	2.123
50%	50	1.444	1.228	1.501	1.672	1.867	2.063
60%	40	1.347	1.124	1.348	1.582	1.818	1.993

Table - V**Consolidated Values of Thermodynamic Activation parameters (ΔH^* , ΔG^* and ΔS^*)****of the reaction in water-Acetone system at different temperatures,** **ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol**

% of Acetonitrile(v/v)	Mole % of Acetonitrile	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
20%	7.90	38.79	84.32	152.81	85.34	153.65	85.95	153.11	86.59	152.74	87.16	152.14
30%	12.81	52.47	85.54	110.97	85.84	110.15	86.77	111.37	87.16	110.84	87.71	110.82
40%	18.61	63.11	86.68	79.10	86.96	78.74	87.43	78.95	88.00	79.54	88.14	78.72
50%	25.53	71.33	87.54	54.41	87.47	53.29	87.95	53.97	88.25	54.07	88.51	54.044
60%	33.96	80.65	88.14	25.41	88.35	25.43	88.48	25.44	88.54	25.24	88.93	26.06



: PLOT OF $2+\text{Log}k$ VS MOLE% OF ACETONITRILE FOR ALKALINE HYDROLYSIS OF DIETHYL MALONATE IN

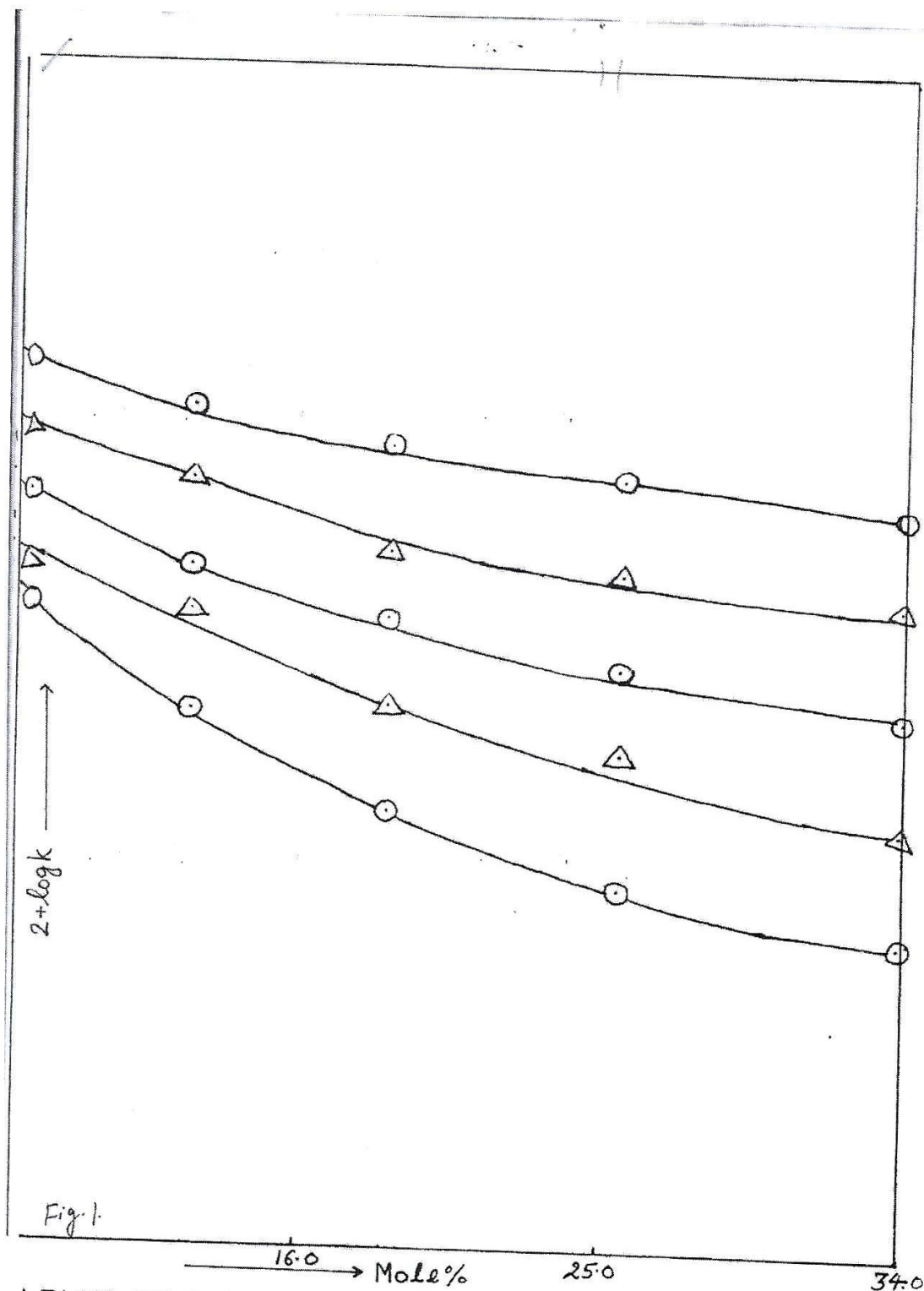
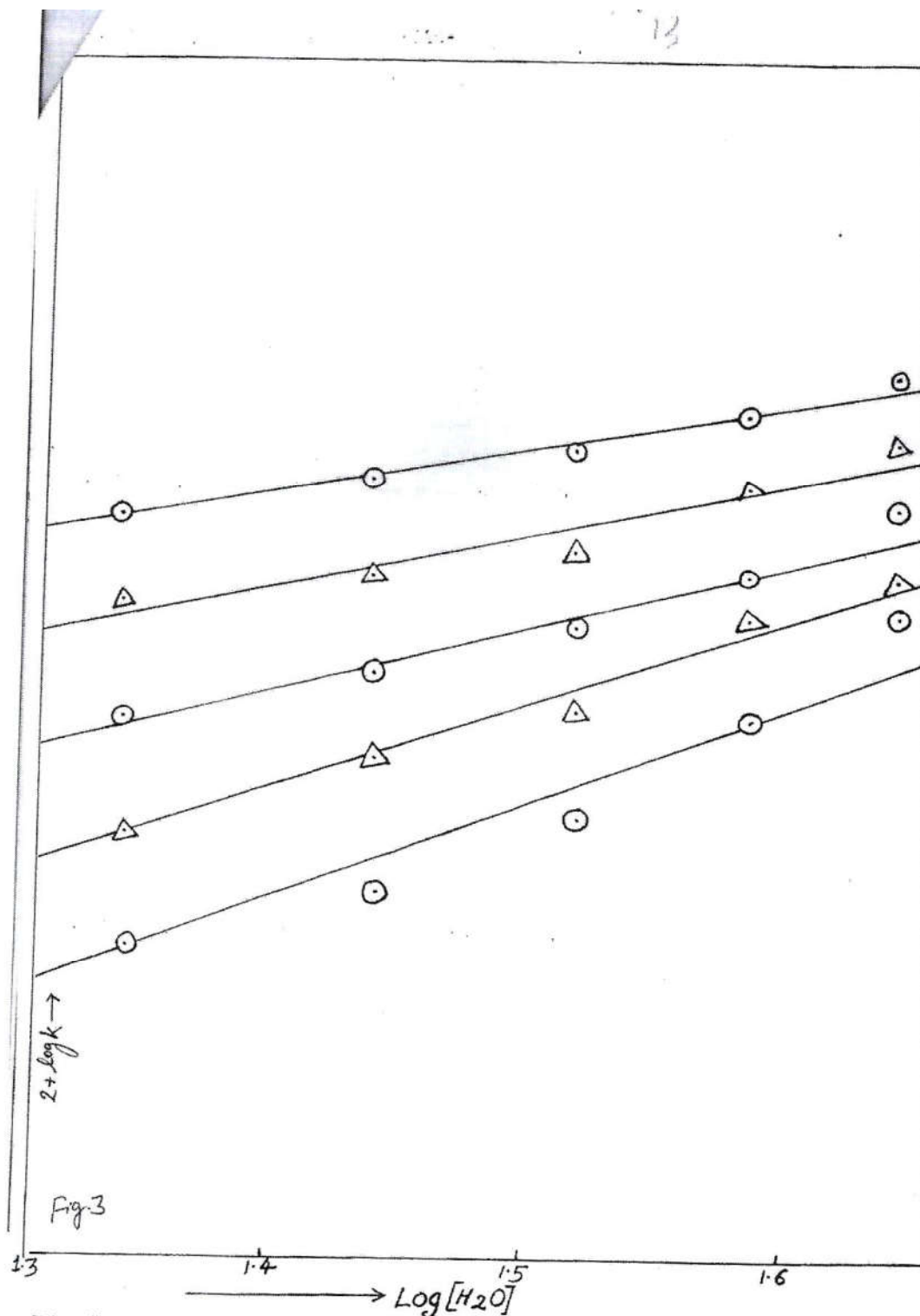


Fig. 1
 : PLOT OF $2 + \log k$ VS MOLE% OF ACETONITRILE FOR ALKALINE HYDROLYSIS OF DIETHYL MALONATE IN



PLOT OF $2 + \log k$ VS $\log [H_2O]$ FOR ALKALINE HYDROLYSIS OF DIETHYL MALONATE IN AQUO-ACETONITRILE MEDIA

