A Kinetic Study of the Solvent Effect of Aquo-Aprotic Solvent Systems on the Food Additive Efficiency of Iso-Butyl Formate Ester

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ABSTRACT

WIth a view to highlight the solvent effect of aquo-aprotic Solvent Systems on the food additive efficiency of the ester iso-butyl formate, its acid catalysed hydrolysis has been studied in aquo-DMF reaction media having different concentration of aprotic solvent (DMF) ranging from 20% to 80% (v/v) and at different temperatures increasing from 20 to 40°C.

The specific rate constant values of the reaction were found to be decrease with increasing concentration of DMF in the reaction media. It was found that from 0.172 to 1.290 molecules of water are involved in the formation of activated complex and from this, it is inferred that in the presence of DMF in the reaction media, the mechanistic pathways of the reaction is changed from bimolecular to unimolecular.

The depletion observed in the values of iso-composition activation energy of the reaction shows that the transition state is solvated and initial stage is desolvated with addition of DMF in reaction media. The unity value of slope of the plots of log k *values against* $\log [H^+]$ *values shows that the reaction follows* $A_{AC}2$ *mechanism. From the evaluated values of iso-kinetic temperature i.e. 290.0, it may be inferred that in water-DMF reaction media, there is weak but favourably considerable solvent – solute interaction.*

KEYWORDS: Food additive, iso-butyl formate, Aprotic, Solvent, Extensive property, Iso-dielectric, Solvent-Solute Interaction, Iso-kinetic temperature, Specific Solvation.

INTRODUCTION

It has been highlighted that the ester iso-butyl formate is used as in fruit-flavours such as pear, raspberry and other berry flavoures with applications in beverages, ice-cream, candy and baked goods. The main hydrolysis products of iso-butyl formate is formic acid which is used as preservative and antibacterial agents. It is also useful in the manufacturing of leather and rubber. It is useful as a miticide by beekeepers.

In order to get fruit flavours, preservatives, antibacterials and miticide of desired efficiency it has been planned and proposed to study the kinetics of acid catalysed hydrolysis of iso-butyl formate in different aquo-DMF reaction media having different concentration of DMF varying from 20 to 80% (v/v) at five different temperatures ranging from 20 to 40^0C.

EXPERIMENTAL & CALCULATION:

Export quality of butyl formate, made in USSR and Dimethyl Formamide (DMF) make were taken into use. The kinetics of the reaction was studied by adding 0.60 ml of the ester into 50ml of 0.5 M HCl solution in thermostated condition at desired temperature. The reaction was found to obey the first order kinetic equation and the evaluated values of specific rate constants have been recorded in Table – I. The values of both iso-composition and iso-dielectric activation energies have been mentioned in Table-II and Table-III respectively.

The evaluated values of the water molecules involved in the formation of transition state of the reaction at different temperatures have been tabulated in Table – IV. The consolidated values of thermodynamic activation parameters $\Delta G^*, \Delta H^*$ and ΔS^* were evaluated using Wynne-Jones and Eyring[1] equation and are enlisted in Table – V.

Results and Discussion

Table – I shows that the specific rate constant values of the reaction decrease with increasing proportion of DMF in the reaction media. On plotting log k value against mol% of MDF as shown in Fig. – 1, it is obvious that up to 18.50 mol% of DMF in the reaction media, the rate of reaction falls rapidly but beyond 18.5 mol% of DMF, the depletion in the rate follows shallow path.

From the plots it is apparent that on gradual addition of DMF in the reaction media at lower temperature, the depletion in the rate of reaction is slow but it becomes sharper with increase in temperature of the reaction.

The decreasing trend in the values of rate constants needs to be discussed in the light of Hughes and Ingold[2] predictions according to which an increase in the dielectric constant values of the reaction media causes an increase in the rate when there is concentration or constructions of charges on the transition state and causes a decrease in the rate when there is diffusion or destruction of charges on the transition state. The values of dielectric constants of the reaction media go on decreasing with gradual addition of DMF, so these findings are fully in accordance with the qualitative prediction of Hughes and Ingold. However, these findings are also in agreement with the qualitative prediction of Laidler and Landskroener[3] and also with the recent reports of Upadhyay[4], Namrata & Singh et. al.[5] and Atulit[6] who predicted that the rate of ion-dipolar reaction decreases with the decrease in the dielectric constant values of the reaction media. However, it has been concluded that in this case, both the dielectric effect and solvation effect (solvation of the transition state) are responsible for shallow and sharp depletion.

Solvent Effect on activation energies (iso-composition and iso-dielectric) of the reaction

From the slope of the Arrhenius plots of log k values against 10^3/T as shown in fig. -2, E_C values of the reaction have been evaluated and are placed in Table – II. From Table – II, it is obvious that E_C values go on decreasing from 89.65 to 58.25 kJ/mol with increasing concentration of DMF in 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 Rai & Singh et. al.[7] and Srivastav & Singh et. al.[8] in this field. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for decrease in E_C values with gradual addition of DMF in the reaction media:-

(i) The transition state is desolvated less than initial state,
(ii) The transition state is solvated more than the initial state, and
(iii) The transition state is solvated and the initial state is desolvated.

The transition state being large cation(ester $+H^+$) is available more for solvation by DMF molecule than the initial state, so the third factor seems to be operative in this case and it has also been found in support of the recent report of Rajiv & Singh[9], Renu & Singh et. al.[10] and Priyanka & Singh et. al.[11].

Solvent Effect on Iso-dilectric Activation Energy (E_D) of the Reaction:

With a view to minimize the dielectric effect, the iso-dielectric activation energy was evaluated from the Arrhenious plot of log k_D values (obtained from interpolation of the plots of log k values against D values of the reaction media) against 1/T adopting the methods of Elsemongy et. al.[12] and the value thus obtained have been tabulated in Table – II. From the table, it was found that E_D values go on increasing from 66.89 to 88.47 kJ/mol with increase in D values from D=55 to 70 respectively. This trend of increase in E_D values is quite in agreement with changes in E_C values of this reaction and also with the findings of Wolford[13] and also with that of Rajiv & Singh,[9] Renu & Singh et. al.[10], Priyanka & Singh et. al.[11] and Lal & Singh et. al.[14].

Evaluation of Solvation number and the Effect of Solvent on the Mechanism of the Reaction:

The solvation number i.e. the number of water molecules involved in the formation of activated complex evaluated from the slopes of the plots of log k versus log [H_2O] as shown in fig. -3 and have been recorded in Table – IV.

From Table – IV it is apparent that before and after log [H_2O] value approx. 1.408 which corresponds to 46.05% of water in the reaction media, the values of the slopes of the two intersecting straight lines are different.

Before log [H_2O] value 1.408 which corresponds to approx. 46.05% of water in the reaction media, the values of the solvation number (n) i.e. the number of water molecules associated with the Transition state (activated complex of the reaction increases from 0.172 to 0.594, whereas after log [H_2O]

value 1.408, the values of n increases from 0.373 to 1.296 with increase in temperature of the reaction from 20 to 40°C.

Thus, the guidelines of Robertson et. al.[15] which suggests that the value of 'n' for unimolecular reaction is fairly high while that for bimolecular reaction it will be low, it is inferred that the mechanistic pathways of the acid catalysed hydrolysis of iso-butyl formate is changed from bimolecular to unimolecular in presence of DMF in the reaction media and also with increasing temperature of the reaction from 20 to 40°C.

It is also inferred that on gradual addition of DMF in the reaction media at equilibrium, the dense form of water is changed to its bulky form.

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

Our such interpretations and inferences have earlier been found in support of the report by Singh & Bala et. al.[16], Kumar & Singh et. al.[17] and also in favour of the recently reported findings of Renu & Singh et. al. [10], Priyanka & Singh et. al.[11] and Sushma[18].

The evaluated values of three thermodynamic activation parameters i.e. $\Delta G^*, \Delta H^*$ and ΔS^* are depicted in Table – V. From their values in Table – V, it is evident that enhancement observed in ΔG^* values is followed by simultaneous depletion in both the values of ΔH^* and ΔS^*. The non-linear variation observed in $\Delta H^*, \Delta G^* and\, \Delta S^*$ were observed with mol% of DMF in water DMF media. The non-linear variation is sign of specific solvation and desolvation of transition and initial state respectively as reported earlier by Tommila et. al.[19], Saville et. al.[20] and Hyne et. al.[21].

Simultaneous increase in ΔG^*value followed by decrease in ΔH^* and ΔS^* is only possible when the extent of depletion in ΔS^* value is greater than that observed in ΔH^*values. From this, it may be inferred that acid catalysed hydrolysis of iso-butyl formate in presence of DMF in reaction media is enthalpy stimulator and entropy deactivator or controller. These findings are found in support of earlier reports of Kumari & Singh et. al.[22], and also of recent reports of Priyanka & Singh et. al.[11] and Rekesh & Singh et. al.[23].

Effect of [H+] ion on the rate and Mechanism of the Reaction:

The effect of change in hydrogen ion concentration [H+] has also been studied by keeping the ionic strength, % of DMF and temperature of the reaction constant at $\mu = 0.90$, 20% DMF (v/v) and 25°C respectively. The evaluated k values at different [H+] ion strength in the reaction have been mentioned in Table – VI.

The plot of log k values against log [H+] as shown in Fig. -4 are found to have a good straight line with the value of slope equal to 0.997 which may be treated as almost equal to unity. This value of slope (equal to unity) indicates that acid catalysed hydrolysis of iso-butyl formate in water DMF media follows the pathway of $A_{AC}2$ mechanism as reported by Zucker and Hammett[24].

Similar conclusions and inferences have also been reported earlier by Pandey and Singh et. al.[25] and recently by Sunita & Singh et. al.[26] and Singh & Singh et. al.[27].

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Table – I

Specific rate constant values of Acid Catalysed Hydrolysis of Butyl Formate in Water-DMF media [HCl]=0.5M

$\mathbf{k \times 10^4} \, \boldsymbol{in} \, \mathbf{min^{-1}}$

Temp in ^{0}C	% of DMF (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20^{0}C	79.01	75.52	70.93	68.33	64.50	62.24	58.51
25^{0}C	143.28	132.46	122.41	112.18	102.83	95.74	85.86
30^{0}C	262.24	234.37	211.54	184.12	164.48	146.59	129.01
35^{0}C	461.01	398.20	345.78	293.16	251.07	218.73	182.01
40^{0}C	810.59	677.80	570.43	465.69	388.96	329.69	263.69

Table – II

Values of Iso-composition Activation Energy (E_C or E_{exp}) of the reaction in water-DMF media

% of n-DMF (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C in kJ/mol	89.65	84.89	79.86	74.32	69.22	64.17	58.25

Table – III

Values of Iso-dielectric Energy (E_D) of the reaction at desired 'D' values of water-DMF media

Dielectric constant values	D=55	D=57.50	D=60.00	D=62.50	D=65.00	D=67.50	D=70.00
E_D values in kJ/mol	66.89	70.82	73.69	76.01	79.56	83.14	88.47

Table – IV

Values of the slopes of the plots of log k versus log [H_2O] in water-DMF media at different temperatures

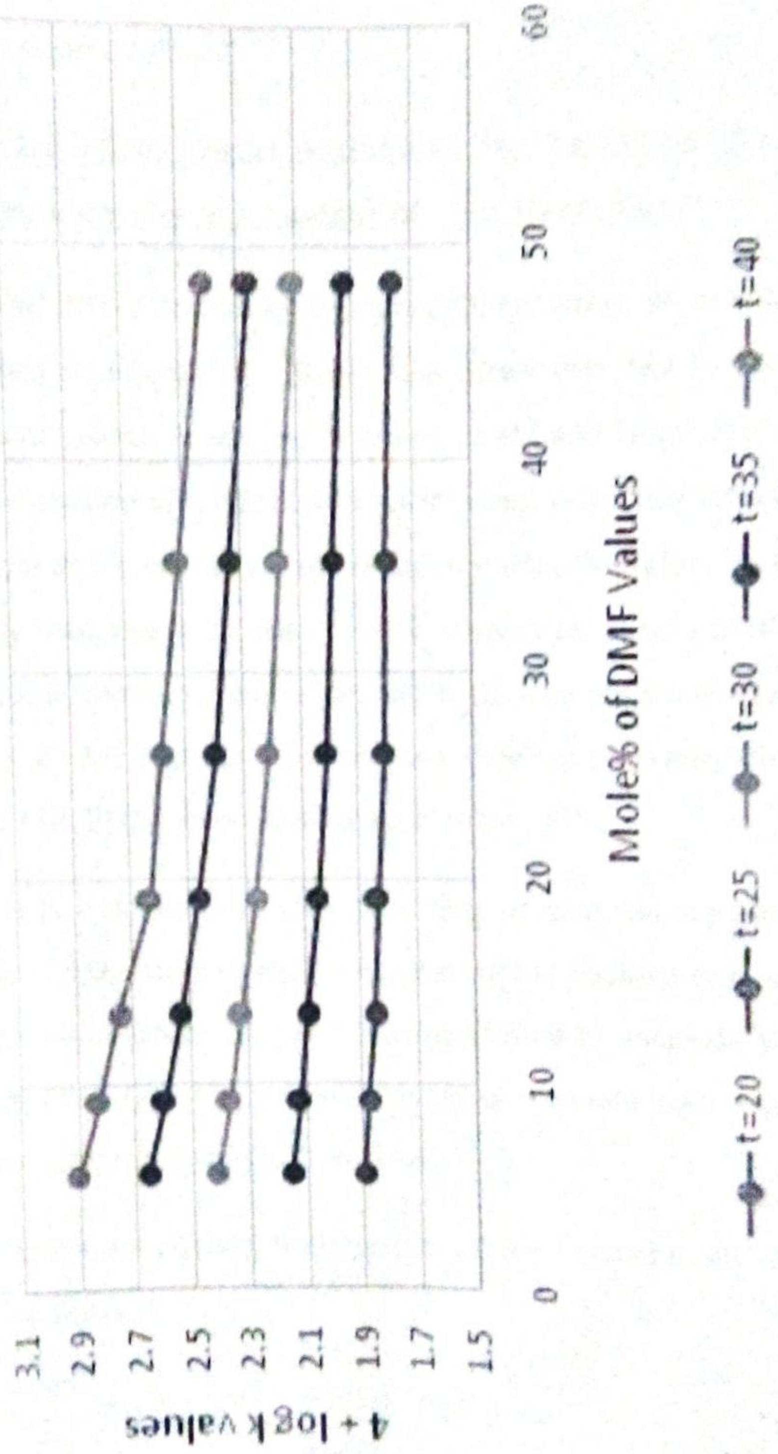
Temp. in ^{0}C	Slope – I where log [H_2O] is below 1.408	Slope – II when log [H_2O] is above 1.408
20^{0}C	0.172	0.373
25^{0}C	0.295	0.569
30^{0}C	0.398	0.740
35^{0}C	0.499	0.979
40^{0}C	0.594	1.290

Table – V

Thermodynamic Activation Parameters of Alkali Catalysed Hydrolysis of Butyl Formate in Water-DMF Solvent System

ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol

% of DMF (v/v)	Mole% of DMF	ΔH* in kJ/mol	30^{0}C		
			ΔG* in kJ/mol	ΔS* in J/K/mol	(ΔS*+100) in J/K/mol
20%	05.53	87.07	82.15	16.24	116.24
30%	09.12	81.65	82.43	-02.77	97.23
40%	13.50	78.02	82.69	-15.41	84.59
50%	18.96	71.96	83.04	-36.57	63.43
60%	25.98	66.30	83.32	-56.17	43.83
70%	35.37	62.95	83.61	-68.10	31.82
80%	48.29	55.90	83.97	-92.64	07.36


4 + log k values
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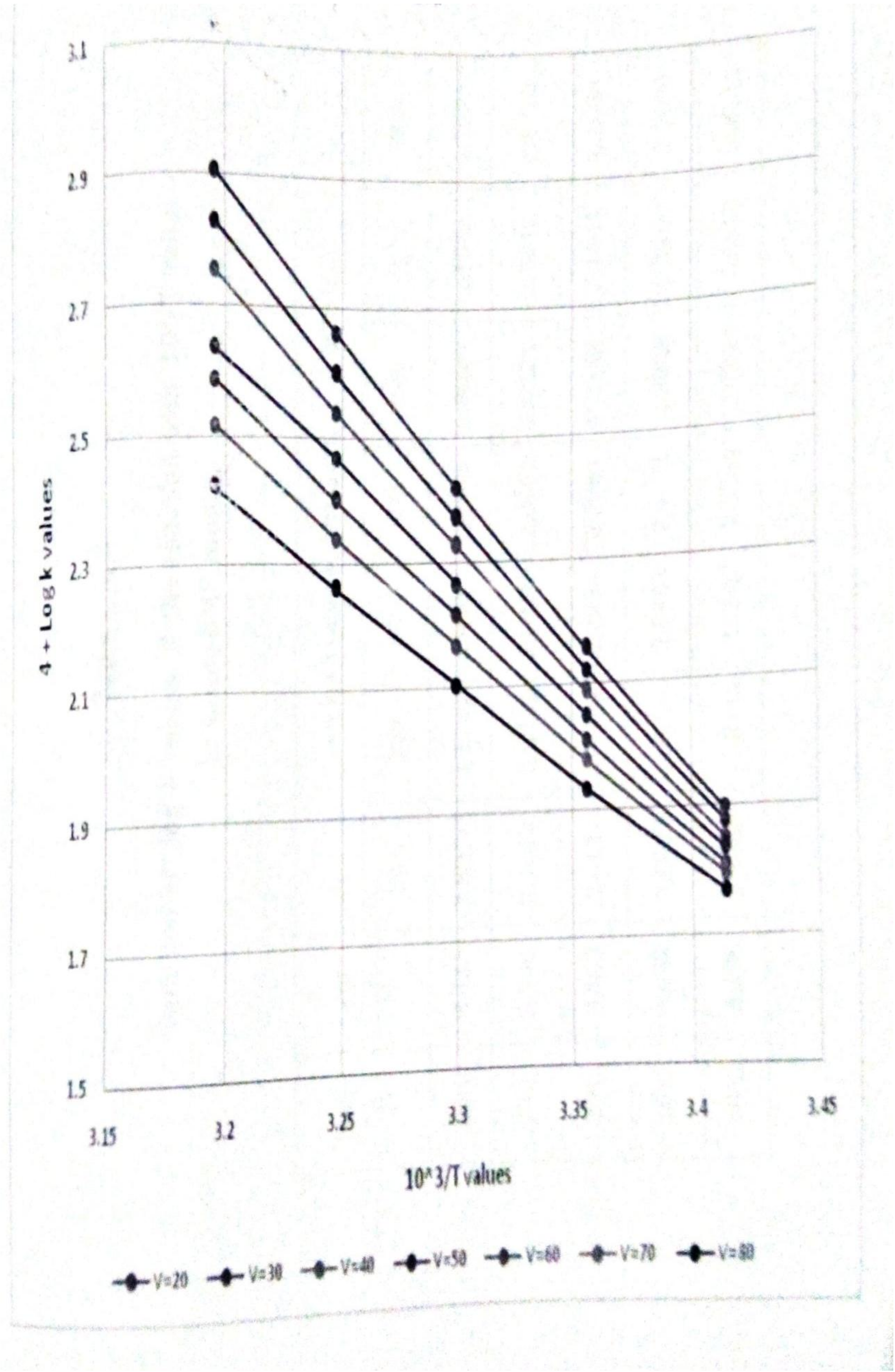
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
0
10
20
30
40
50
60
Mole% of DMF Values
t=20
t=25
t=30
t=35
t=40


3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
4 + Log k values
3.15
3.2
3.25
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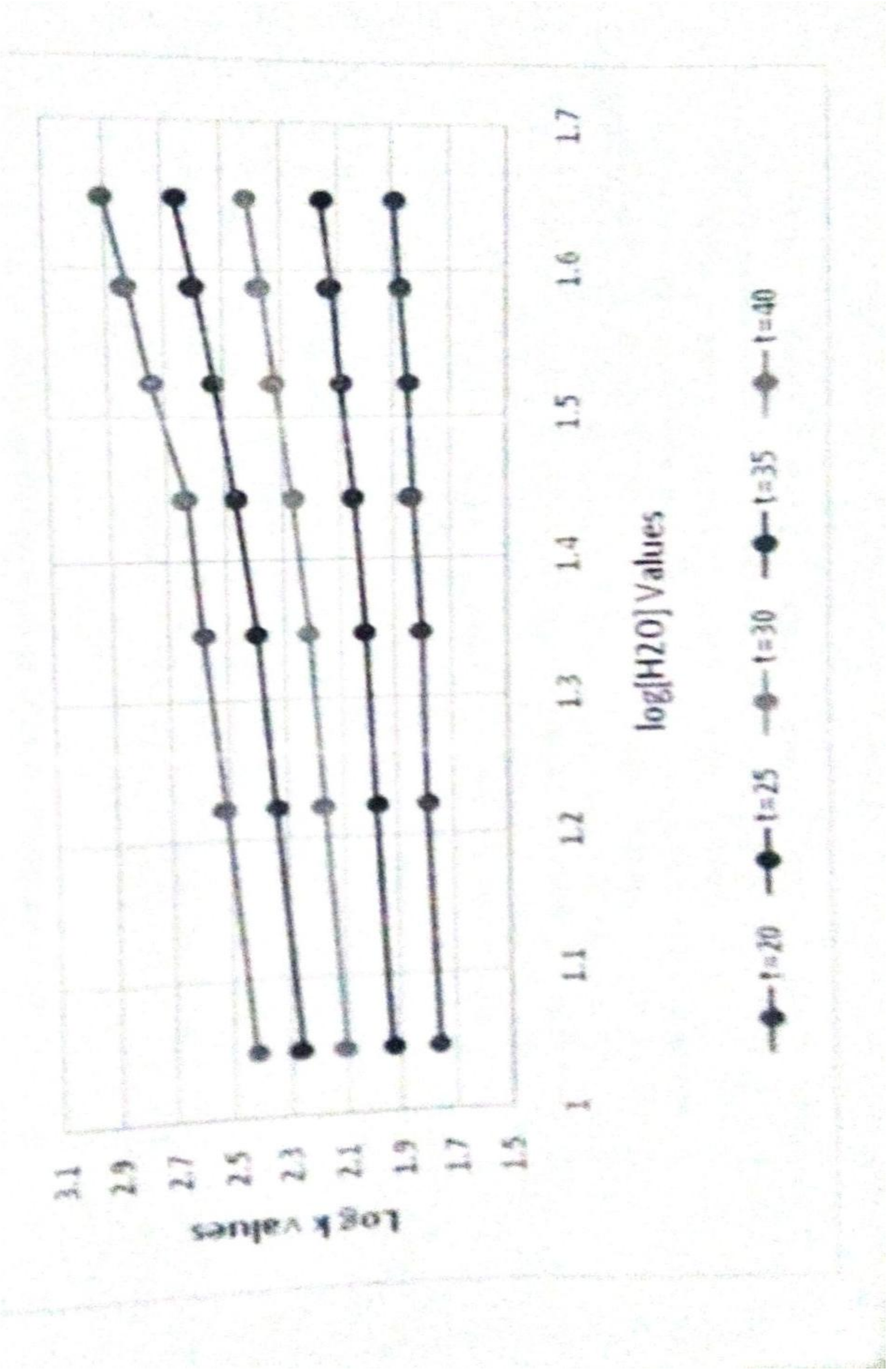
Log k values
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2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
log[H2O] Values
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t=25
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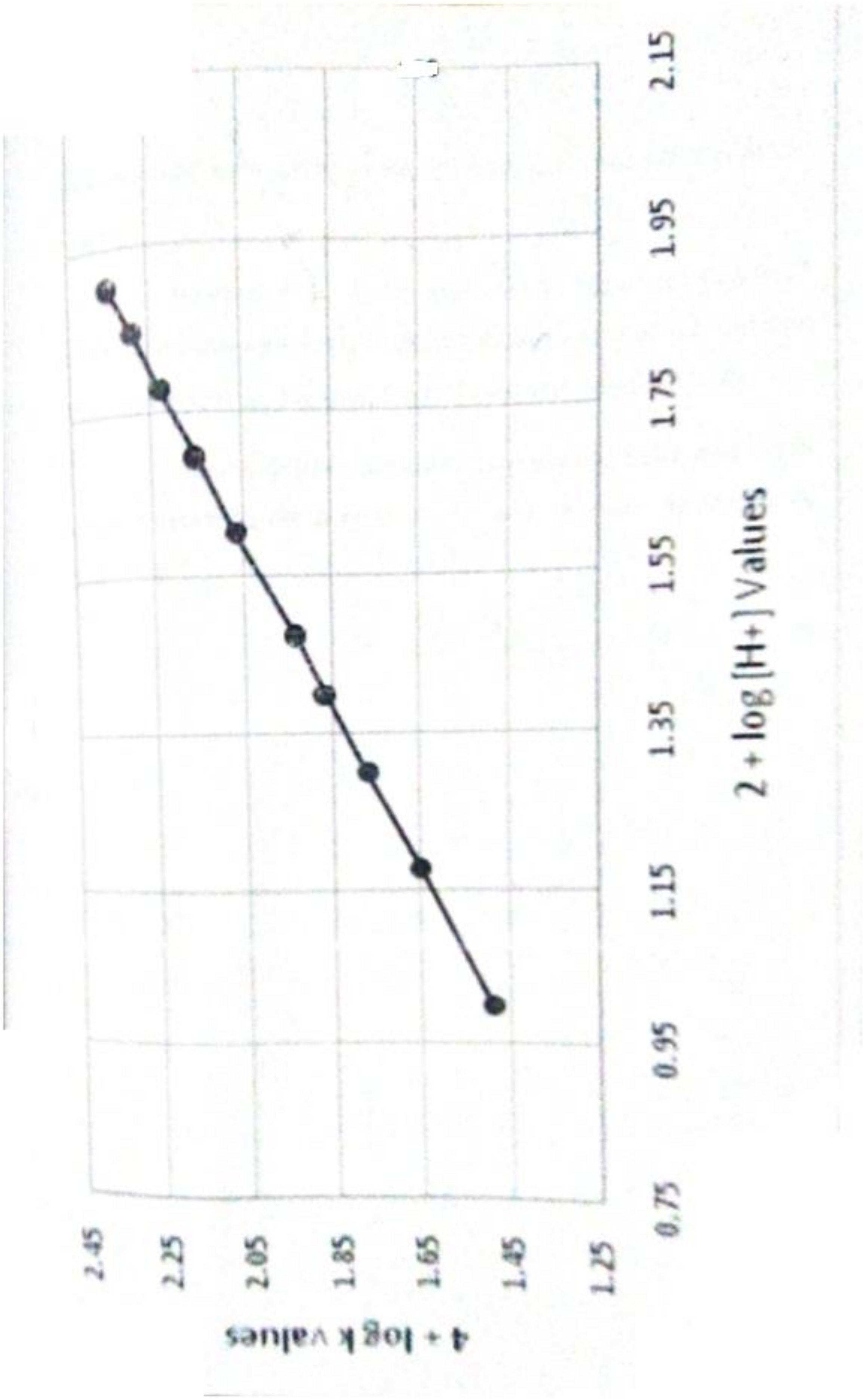
t=35
t=40


4 + log k values
2.45
2.25
2.05
1.85
1.65
1.45
1.25
0.75
0.95
1.15
1.35
1.55
1.75
1.95
2.15
2 + log [H+] Values