CHAPTER - IV

OXIDATION OF CAPRAMIDE

Preliminary experiments showed that the reaction of $S_2O_8^{2-}$ ion with the amide is very slow at room temperature. In the presence of silver catalyst the reaction proceeds with a measurable rate at $35^{\circ}C$. Thus the reaction was studied at $35^{\circ}C$ taking the overall concentrations of amide as 0.1 M, $K_2S_2O_8$ as $2.0 \times 10^{-2}M$ and $AgNO_3$ as $2.0 \times 10^{-3}M$. The kinetic data is recorded in the Table B-1.

TABLE B-1

$K_2S_2O_8 = 2.0 \times 10^{-2}M$, Amide = 0.1, $AgNO_3 = 2.0 \times 10^3 M$

Temp. = $35^{\circ}C$

Time (min)	C	$k_1 \times 10^3$ min^{-1}
0	9.44	-
20	8.90	2.945
40	8.40	2.918
60	7.94	2.884
80	7.51	2.859
100	7.12	2.820
130	6.57	2.788
160	6.08	2.749
200	5.48	2.719
240	4.94	2.698
300	4.28	2.636
360	3.68	2.616
Mean $k_1 \times 10^3$ min^{-1}	-	2.784

From the results contained in Table B-1, it indicates that there is a fair constancy in the first order rate constant values, suggesting that the overall order of reaction at these concentrations of the reactants is unity. The concentration of amide was taken in excess and so the order is with respect to $S_2O_8^{2-}$.

To decide conclusively the order with respect to $S_2O_8^{2-}$ and amide, another kinetic run having equimolar concentrations (0.02 M) of the two reactants was studied. The results of these measurements are recorded in Table B-2.

TABLE B-2

$K_2S_2O_8$ = Amide = 2.0×10^{-2} M, $AgNO_3$ = 2.0×10^{-3} M

Temp. = 35° C.

Time (min)	C	$k_1 \times 10^{-3}$ min^{-}
0	9.46	-
20	8.82	3.502
40	8.23	3.482
60	7.69	3.452
80	7.20	3.412
100	6.76	3.360
130	6.14	3.324
160	5.57	3.310
200	4.91	3.278
240	4.33	3.256
300	3.58	3.239
360	2.98	3.208
Mean $k_1 \times 10^3$ min^{-1}		3.345×10^{-3}

65

Here also fairly constant values of the first
order specific rate are obtained, suggesting that the
order with respect to peroxydisulphate is one.

EFFECT OF PEROXYDISULPHATE CONCENTRATION :

In order to study the effect of peroxydisulphate
ion on the reaction rate, three more kinetic runs having
different concentrations of $S_2O_8^{2-}$ were carried out. The
following table (Table B-3) contains the results of these
kinetic runs and for the sake of comparison, the data of
Table B-1 have been included in it. These data also find
a graphic representation in Fig. B-1.

The corresponding values of the first order rate
constants for the self decomposition of $S_2O_8^{2-}$ have been
recorded directly, as already mentioned in the experimental
section of Chapter III.

TABLE B-3

Amide = 0.1 M, $AgNO_3$ = 2.0 x 10^{-3}M, Temp.=35°C

$\lceil K_2S_2O_8 \rceil$M	0.01		0.02		0.03		0.04	
Time (min)	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}
0	4.92	-	9.44	-	14.54	-	19.55	-
20	4.59	3.479	8.90	2.945	13.82	2.539	18.77	2.035
40	4.29	3.425	8.40	2.918	13.16	2.493	18.05	1.995
60	4.02	3.367	7.94	2.884	12.58	2.413	17.39	1.951
80	3.78	3.294	7.51	2.859	12.02	2.379	16.78	1.909
100	3.56	3.235	7.12	2.820	11.50	2.345	16.20	1.879
130	3.26	3.160	6.57	2.788	10.76	2.315	15.38	1.845
160	2.98	3.133	6.08	2.749	10.12	2.264	14.63	1.811
200	2.65	3.093	5.48	2.719	9.32	2.223	13.72	1.770
240	2.36	3.061	4.94	2.698	8.58	2.197	12.85	1.748
300	1.98	3.034	4.28	2.636	7.61	2.158	11.68	1.716
360	1.68	2.298	3.68	2.616	6.75	2.131	10.65	1.687
$k_1 \times 10^3 min^{-1}$		3.205		2.784		2.314		1.849
$k_2 \times 10^3 min^{-1}$		1.310		1.242		1.151		1.055
$k \times 10^3 min^{-1}$		1.895		1.542		1.163		0.794

From the above results (Table B-3), it is seen that when the concentration of $K_2S_2O_8$ was increased, there is a decrease in the first order rate constant. It must be mentioned here that in any particular run, (especially that

containing high concentration of $K_2S_2O_8$) the rate constant slightly decreases with time.

Now in order to study this effect under the conditions of constant ionic strength as well as at constant K^+ ion concentration, four kinetic runs having different concentrations of peroxydisulphate and potassium sulphate were studied. The results of these kinetic runs are recorded in Table B-4 and shown graphically in Fig. B-2.

It must be mentioned here that, in all the subsequent kinetic studies, though the self decomposition of peroxydisulphate has always been investigated under the corresponding experimental conditions, the kinetic data for these runs have been omitted due to pressure on space and hence only the corresponding values of the rate constant (viz. k_2) have been directly recorded at the end of each table.

TABLE B-4

Amide = 0.1 M, AgNO$_3$ = 2.0 x 10^{-3}M, Temp. = 35°C,

μ = 0.330

$\lceil K_2S_2O_8 \rceil$M	0.01	0.02	0.03	0.04
+				
$\lceil K_2SO_4 \rceil$M	0.09	0.08	0.07	0.06

Time (min)	Vol (in ml) of 0.02 M - Na$_2$S$_2$O$_3$used(viz.C)			
0	4.96	9.45	14.34	19.48
20	4.72	9.01	13.74	18.84
40	4.50	8.60	13.18	18.25
60	4.29	8.22	12.68	17.71
80	4.10	7.87	12.21	17.22
100	3.92	7.55	11.81	16.78
130	3.66	7.09	11.24	16.16
160	3.43	6.67	10.71	15.58
200	3.15	6.15	10.09	14.82
240	2.89	5.68	9.51	14.19
300	2.58	5.04	8.76	13.28
360	2.26	4.52	8.00	12.39

k_1 x 10^{3}min^{-1}	3.329	2.217	1.879	1.451
k_2 x10^{3}min^{-1}	0.750	0.760	0.740	0.740
k x 10^{3}min^{-1}	1.579	1.457	1.139	0.711

From the results as shown in Table B-4 it indicates that, here again the first order rate constant decreased when the concentration of $K_2S_2O_8$ were increased.

Table B-5 shows the comparison between k values with increasing concentrations of peroxydisulphate without K_2SO_4 and with K_2SO_4 to maintain constant ionic strength and constant K^+ concentration in the later case.

TABLE B-5

Amide = 0.1 M, $AgNO_3$ 2.0×10^{-3}M, Temp.=35°C

Conc. $[K_2S_2O_8]$M without K_2SO_4	k x 10^3 min^{-1}	Conc. $[K_2S_2O_8]$M with constant K^+ ionic strength	k x 10^3 min^{-1}
0.01	1.895	0.01	1.579
0.02	1.542	0.02	1.457
0.03	1.163	0.03	1.139
0.04	0.794	0.04	0.711

An examination of the above data, it indicates that at constant K^+ ionic strength, the decrease in the rate constant, with increase in $K_2S_2O_8$ concentration has been minimised.

This suggests that the effect is largely due to the increase in the ionic strength as well as due to the increase

in K^+ ion concentration, both causing inhibition. There exists a persistent rate decreasing tendency even though the reaction is carried out at constant ionic strength as well as constant K^+ ion concentration.

A plot of - Log k versus concentration of peroxydisulphate is found to be linear (Fig. B-3). The following relationship between - log k and concentration of peroxydisulphate is followed :

$$- \text{Log } k = 2.53 + 14.07 \; (S_2O_8^{2-})_o$$

provided $[S_2O_8^{2-}]_o \neq$ Zero

ORDER WITH RESPECT TO PEROXYDISULPHATE :

The order with respect to peroxydisulphate was determined by Vant Hoff's differential method. The volume of $Na_2S_2O_3$ (equivalent to $K_2S_2O_8$) was plotted against time for different intial concentration of $K_2S_2O_8$. From these curves the value of $-dc/dt$ in each case was determined from the initial slope as given in Table B-6.

TABLE B-6

Conc. $[K_2S_2O_8]$	$\frac{-dc}{dt} \times 10^{+4}$	$\text{Log}[S_2O_8^{2-}]$	$\text{Log } (\frac{-dc}{dt})$
0.01	0.61	- 2.0000	- 4.2146
0.02	1.34	- 1.6990	- 3.8728
0.03	2.03	- 1.5229	- 3.6925
0.04	2.840	- 1.3979	- 3.5466

The values of $-dc/dt$ and concentration of $[S_2O_8^{2-}]$ are substituted in the Vant Hoff's equation.

$$n = \frac{\log(-dc_1/dt) - \log(-dc_2/dt)}{\log C_1 - \log C_2}$$

and the order of the reaction is calculated thereby.

The values of $(-dc_1/dt)$ for different initial concentrations of $S_2O_8^{2-}$ and the values of n calculated thereby are recorded in Table B-7.

TABLE B-7

$[K_2S_2O_8]$ M	$(\frac{-dc}{dt}) \times 10^4$	Order of Reaction (n)
0.01	0.61	
0.02	1.34	1.135
0.01	0.61	
0.03	2.03	1.094
0.01	0.61	
0.04	2.84	1.109
0.02	1.34	
0.03	2.03	1.023
0.02	1.34	
0.04	2.84	1.083
0.03	2.03	
0.04	2.84	1.167

A plot of $\log(-dc/dt)$ versus $\log S_2O_8^{2-}$ is shown in Fig. B-4. The slope of the curve is 1.092 as such the order with respect to $S_2O_8^{2-}$ is one, which is confirmed by the values of n as shown under Table B-7.

EFFECT OF AMIDE CONCENTRATION :

The effect of capramide concentration on the rate of reaction was studied by taking different concentrations of amide. The concentrations of $S_2O_8^{2-}$ and $AgNO_3$ are kept unchanged. Table B-8 embodies the results of these kinetic runs, which have also been depicted graphically in Fig.B-5.

TABLE B-8

$K_2S_2O_8=2.0 \times 10^{-2}M$, $AgNO_3 = 2.0 \times 10^{-3}M$, Temp = $35^{o}C$

[Amide]M	0.05	0.10	0.150	0.175	0.2
Time (min)	Vol. in ml. of 0.02 M - $Na_2S_2O_3$ used (viz.C)				
0	9.45	9.44	9.46	9.45	9.45
20	8.91	8.90	8.94	8.92	8.92
40	8.41	8.40	8.45	8.43	8.41
60	7.94	7.95	7.98	7.95	7.94
80	7.49	7.51	7.53	7.51	7.52
100	7.07	7.12	7.12	7.10	7.09
130	6.47	6.57	6.54	6.53	6.50
160	5.94	6.08	6.02	6.00	5.96
200	5.28	5.48	5.38	5.36	5.33
240	4.72	4.94	4.82	4.78	4.74
300	3.98	4.28	4.06	4.04	4.02
360	3.35	3.68	3.44	3.42	3.38
$k_1 \times 10^3 min^{-1}$	2.903	2.784	2.824	2.854	2.879
$k_2 \times 10^3 min^{-1}$	1.242	1.242	1.242	1.242	1.242
$k \times 10^3 min^{-1}$	1.661	1.542	1.582	1.612	1.637

From the results of the above table (Table B-8), it indicates that when the concentration of amide was increased the rate constant remains constant indicating the zero order behaviour of the reaction.

The specific rate is seen to be a function of $S_2O_8^{2-}$ and $CH_3(CH_2)_8 CONH_2$ governed by the expression.

$$k = k_{max} \cdot \frac{[Amide]_o}{b + [Amide]_o}$$

In support of the above equation a graph of $\frac{[Amide]_o}{K}$ versus concentration of amide is plotted. (Fig. B-6) and was found to be linear from which kmax and b were evaluated as 0.001721 and 0.01032 respectively. From these values k is calculated and was found to be equal to $k = 1.560 \times 10^{-3}$ was almost identical with $k = 1.542 \times 10^{-3}$ the experimental value.

ORDER WITH RESPECT TO AMIDE :

To confirm the order with respect to amide, the data of Table B-8 was subjected to Vant Hoff's differential method. From the initial slope of the concentration versus time curves, the values of -dc/dt corresponding to various initial concentration of amide were evaluated which are given in Table B-9.

TABLE B-9

Conc.[Amide]M	$\frac{-dc}{dt} \times 10^4$	Log C_o	Log $\frac{-dc}{dt}$
0.05	1.04	- 1.3010	- 3.9829
0.10	1.04	- 1.000	- 3.9829
0.15	1.03	- 0.8239	- 3.9871
0.175	1.02	- 0.7569	- 3.9913
0.2	1.03	- 0.6021	- 3.9871

A plot of Log (-dc/dt) versus Log C_o is shown in Fig. B-7. It gives the value of the slope as zero, which suggests that the reaction is of zero order with respect to amide. Calculations were made for the order of the reaction by Vant Hoff's' method and are given in Table B-10.

TABLE B-10

[Amide]M	-dc/dt×10^4	Order of reaction (n)
0.05 0.1	1.04 1.04	0.00
0.05 0.15	1.04 1.03	0.008
0.05 0.175	1.04 1.02	0.0154
0.05 0.2	1.04 1.03	0.006
0.10 0.15	1.04 1.03	0.024
0.15 0.2	1.03 1.03	0.00

This confirms that the order with respect to amide is zero.

EFFECT OF CATALYST CONCENTRATION :

The effect of varying concentrations of the catalyst on the reaction rate was studied at 35°C. The kinetic data of these runs are recorded in Table B-11 and shown graphically in Fig. B-8.

TABLE B-11

$[AgNO_3] \times 10^{-3}$M	1.0	1.5	2.0	3.0	4.0
Time (min)	Vol.(in ml) of $0.02M-Na_2S_2O_3$ used (viz.C)				
0	9.45	9.45	9.44	9.42	9.42
20	9.02	8.96	8.90	8.75	8.64
40	8.62	8.51	8.40	8.14	7.95
60	8.26	8.10	7.94	7.58	7.32
80	7.92	7.72	7.51	7.07	6.76
100	7.60	7.38	7.12	6.60	6.25
130	7.14	6.68	6.57	5.97	5.56
160	6.72	6.44	6.08	5.40	4.96
200	6.29	5.92	5.48	4.72	4.28
240	5.75	5.43	4.94	4.14	3.69
300	5.12	4.78	4.28	3.38	2.95
360	4.57	4.19	3.68	2.78	2.36
$k_1 \times 10^3$min^{-1}	2.165	2.442	2.784	3.527	4.058
$k_2 \times 10^3$min^{-1}	1.186	1.195	1.242	1.431	1.514
$k \times 10^3$min^{-1}	0.979	1.247	1.542	2.096	2.544

The data (Table B-11) indicates that the specific rate increases with increasing concentration of silver nitrate. The plot of k versus $[Ag^+]$ concentration is found to be linear

as shown in Fig. B-9 and the following relationship is obeyed.

$$k = 0.4 \times 10^{-3} + 0.586[Ag^+]$$

EFFECT OF TEMPERATURE :

The reaction was studied at five different temperatures ranging from $25^\circ C$ to $45^\circ C$. The concentrations of all the reactants were kept constant. These kinetic runs are recorded in Table B-12 and shown graphically in Fig. B-10.

TABLE B-12

Amide = 0.1 M, $AgNO_3 = 2.0 \times 10^{-3}M$, $K_2S_2O_8 = 2.0 \times 10^{-2}M$

Temp.	$25^\circ C$	$30^\circ C$	$35^\circ C$	$40^\circ C$	$45^\circ C$
Time (min)	Vol in (ml.) of $0.02M-Na_2S_2O_3$ used (viz-C)				
0	9.45	9.44	9.44	9.45	9.46
20	9.15	9.06	8.90	8.74	8.42
40	8.87	8.71	8.40	8.09	7.51
60	8.61	8.38	7.94	7.50	6.71
80	8.38	8.08	7.51	6.97	6.02
100	8.15	7.81	7.12	6.49	5.41
130	7.83	7.41	6.57	5.83	4.59
160	7.55	7.05	6.08	5.23	3.92
200	7.19	6.60	5.48	4.53	3.17
240	6.85	6.19	4.94	3.94	2.56
300	6.36	5.62	4.28	3.17	1.86
360	5.96	5.12	3.68	2.56	1.36
$k_1 \times 10^3$ min^{-1}	1.443	1.868	2.784	3.743	5.577
$k_2 \times 10^3$ min^{-1}	0.650	0.820	1.242	1.623	2.504
$k \times 10^3$ min^{-1}	0.793	1.048	1.542	2.120	3.073

The calculated values of $\frac{1}{T} \times 10^3$ and $\log \frac{kr}{kT/h}$ are recorded in Table B-13.

TABLE B-13

Temp.A^o	$\frac{1}{T} \times 10^3$	kr x 10^3 min^{-1}	Log kr	Log $[\frac{kr}{kT/h}]$
298	3.356	0.793	- 3.1007	- 15.8938
303	3.301	1.048	- 2.9796	- 15.7577
308	3.246	1.542	- 2.8119	- 15.6192
313	3.196	2.120	- 2.6736	- 15.4880
318	3.145	3.073	- 2.5124	- 15.3208

A plot of log kr versus $\frac{1}{T} \times 10^3$ is found to be linear (Fig. B-11) showing that the reaction obeys Arrhenius relationship.

The energy of activation from the slppe of the curve is 12.926 K.cals. mole^{-1} which is in good agreement with the calculated value. Similarly, from the slope of the curve obtained by plotting log ($\frac{kr}{kT/h}$) versus $\frac{1}{T} \times 10^3$ (Fig. B-12) the value of the enthalpy change for the formation of an activated complex ($\Delta H^{\neq}$) is calculated. The values of E and $\Delta H^{\neq}$ along with other thermodynamic parameters are recorded in Table B-14.

TABLE B-14

Temp. $\overset{\circ}{A}$	$k \times 10^3$ min^{-1}	Temp. Coefficient	E. K.cals. mole^{-1}	$A \times 10^{-4}$ litre mole^{-1} sec^{-1}	$\Delta G^{\neq}$ K.Cals mole^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta H^{\neq}$ K.Cals. mole^{-1}
298	0.793	-	-	3.977	21.669	- 31.305	
303	1.048	1.944	12.100	3.713	21.875	- 31.500	
308	1.542	2.022	13.275	3.871	22.009	- 31.458	11.440 (graphically)
313	2.120	1.992	12.932	3.791	22.179	- 31.529	
318	3.073	-	-	3.968	22.308	- 31.471	
Mean	-	1.986	12.769	3.864	22.008	- 31.452	

A large negative value of entropy of activation is indicative of the formation of an activated complex involving either two oppositely charged ions or an ion and a neutral molecule.

The rate constant for this reaction may be expressed by the following relation

$$K = 3.864 \times 10^4 . e^{-12.769/RT} \quad Sec^{-1}$$

EFFECT OF IONIC STRENGTH :

The effect of varying ionic strength on the reaction rate was studied by adding different amounts of K_2SO_4 to the reaction mixture. The results of these kinetic runs are recorded in Table B-15 and shown graphically in Fig. B-13.

TABLE B-15

Amide = 0.1 M, $AgNO_3 = 2.0 \times 10^{-3}$ M, $K_2S_2O_8 = 2.0 \times 10^{-2}$ M

Temp. = $35^{\circ}C$

K_2SO_4(M)	Nil	0.005	0.01	0.015	0.02	0.03	0.04
μ	0.008	0.023	0.038	0.053	0.068	0.098	0.128

Time (min)	Vol.(in ml) of $0.02M-Na_2S_2O_3$ used (viz.C)						
0	9.44	9.48	9.48	9.46	9.46	9.45	9.45
20	8.90	8.96	8.97	8.99	9.00	9.07	9.12
40	8.40	8.48	8.50	8.56	8.58	8.71	8.81
60	7.94	8.04	8.07	8.17	8.19	8.40	8.52
80	7.51	7.63	7.67	7.80	7.84	8.09	8.25
100	7.12	7.24	7.30	7.46	7.53	7.81	8.00
130	6.57	6.73	6.78	6.98	7.04	7.42	7.65
160	6.08	6.25	6.32	6.56	6.62	7.07	7.32
200	5.48	5.66	5.73	6.04	6.10	6.62	6.93
240	4.94	5.13	5.23	5.54	5.62	6.23	6.58
300	4.28	4.43	4.54	4.91	4.95	5.68	6.06
360	3.68	3.83	3.96	4.34	4.37	5.18	5.62

$k_1 \times 10^3$ min^{-1}	2.784	2.653	2.581	2.338	2.287	1.856	1.620
$k_2 \times 10^3$ min^{-1}	1.242	1.235	1.219	1.148	1.167	0.882	0.774
$k \times 10^3$ min^{-1}	1.542	1.418	1.362	1.190	1.120	0.974	0.846

From the results given in Table B-15 it indicates that the salt effect is negative.

On plotting log k against $\mu^{1/2}$ as well as k against μ as shown in Fig. 14(A) and 14(B) respectively, it is found that log k versus $\mu^{1/2}$ curve is linear in the region of low ionic strength (< 0.20), while there exists no linearity in the plot of k versus μ. This suggests that the salt effect is of primary exponential type in the region of low ionic strength indicating that the rate determining process involves a reaction between the oppositely charged ions.

TABLE B-16

$[K_2SO_4]$ M	μ	$k \times 10^3$ min^{-1}	$\sqrt{\mu}$	Log k
Nil	0.008	1.542	0.08944	- 2.8119
0.005	0.023	1.418	0.1517	- 2.8433
0.01	0.038	1.362	0.1949	- 2.8658
0.015	0.053	1.148	0.2302	- 2.9400
0.02	0.068	1.100	0.2607	- 2.9586
0.03	0.098	0.974	0.3130	- 3.0114
0.04	0.128	0.846	0.3578	- 3.0726

It may be stated that the ionic strength employed is rather high for Bronsted relationship to be strictly applicable quantitatively, but still the agreement is found to be fairly good.

SPECIFIC IONIC EFFECT :

The following table (Table B-17) includes the results of the kinetic runs investigating the effect of various cations on the rate of this reaction. These data have also been shown graphically in Fig. B-15. This study has been carried out at constant ionic strength.

TABLE B-17

$K_2S_2O_8$=2.0 x 10^{-2}M, $AgNO_3$ = 2.0 x 10^{-3}M, Amide = 0.1 M

Temp = 35°C, μ=0.212

Salt added	Nil	K_2SO_4	Na_2SO_4	Li_2SO_4	$MgSO_4$	$ZnSO_4$
(Concentration) M	0.00	0.05	0.05	0.05	0.0375	0.0375
Time(min)	Vol. (in ml) of 0.02 M - $Na_2S_2O_3$ used (viz.C)					
0	9.44	9.48	9.46	9.45	9.48	9.48
20	8.90	9.16	9.07	9.05	9.03	8.98
40	8.40	8.86	8.71	8.68	8.61	8.52
60	7.94	8.59	8.38	8.34	8.23	8.10
80	7.51	8.33	8.09	8.02	7.88	7.71
100	7.12	8.09	7.82	7.73	7.55	7.35
130	6.57	7.76	7.41	7.32	7.09	6.86
160	6.08	7.46	7.06	6.95	6.67	6.42
200	5.48	7.11	6.62	6.49	6.14	5.86
240	4.94	6.82	6.21	6.07	5.67	5.36
300	4.28	6.35	5.64	5.48	5.04	4.69
360	3.68	5.78	5.11	4.94	4.48	4.12
k_1x10^3min^{-1}	2.784	1.523	1.884	1.968	2.246	2.499
k_2x10^3min^{-1}	1.242	0.750	0.820	0.820	0.840	0.960
k x10^3min^{-1}	1.542	0.773	1.064	1.148	1.406	1.539

It is seen that the specific inhibitory effect of the various ions is in the order

$$K^+ > Na^+ > Li^+ > Mg^{2+} > Zn^{2+}$$
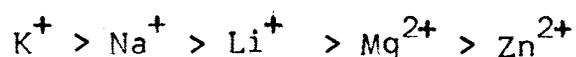
EFFECT OF HYDROGEN ION CONCENTRATION :

The solution of substrate was prepared in acetic acid medium and hence it was not possible to study the effect of pH on reaction rate, but it was observed that the reaction was not catalysed by acetic acid.

EFFECT OF ALLYL ACETATE ON REACTION RATE :

The reaction was carried out in the absence of and at three different initial concentrations of allyl acetate. The results of these kinetic runs are summarised in Table B-18 and shown graphically in Fig. B-16.

TABLE B-18

$K_2S_2O_8 = 2.0 \times 10^{-2}M$, $AgNO_3 = 2.0 \times 10^{-3}M$, Amide = 0.1 M,
Temp = $35^{\circ}C$

[Allyl acetate]M	Nil	0.001	0.005	0.01
Time (min)	Vol(in ml.)of $0.02M-Na_2S_2O_3$ used(viz.C)			
0	9.44	9.48	9.46	9.48
20	8.90	9.01	9.07	9.16
40	8.40	8.58	8.73	8.86
60	7.94	8.18	8.41	8.59
80	7.51	7.81	8.12	8.33
100	7.12	7.46	7.86	8.08
130	6.57	6.98	7.48	7.75
160	6.08	6.54	7.12	7.43
200	5.48	6.02	6.66	7.05
240	4.94	5.52	6.23	6.68
300	4.28	4.86	5.64	6.18
360	3.68	4.34	5.12	5.75
$k \times 10^3$ min^{-1}	2.784	2.353	1.848	1.553

From the data contained in Table B-18, indicates that allyl acetate inhibits the rate of reaction. So the reaction involving $S_2O_8^{2-}$ are greatly inhibited by allyl acetate which acts as a sulphate radical trapping reagent. The radical trapping may be due to the polymerisation of allyl acetate by sulphate ions formed from the catalysed decomposition of peroxydisulphate ion.

MOLE RATIO :

For determining the mole ratio between $K_2S_2O_8$ and amide, two kinetic runs were carried out simultaneously, one in the

absence of presence of amide and the other in the absence of amide. In both the kinetic runs the concentration of $K_2S_2O_8$ was the same and was five times the concentration of amide. The concentration of the catalyst was the same in both the runs. At suitable intervals of time 5 ml of the reaction mixture was pipetted out and estimated for unreacted $S_2O_8^{2-}$. These results are recorded in Table B-19 and shown graphically in Fig. B-17.

TABLE B-19

$K_2S_2O_8 = 0.05$, $AgNO_3 = 2.0 \times 10^{-3}M$, Temp=$35^{\circ}C$

(Amide) M	0.01	Nil
0	24.36	24.25
30	22.41	23.42
60	20.92	22.40
90	19.98	21.85
120	18.34	20.87
150	17.21	20.42
180	16.16	19.52
210	14.98	19.04
240	13.81	18.21
270	13.03	17.41
300	12.52	16.97
330	11.95	15.86
360	11.34	15.83
390	11.02	15.10
420	10.62	14.45
450	10.30	14.12
480	9.86	13.54

The curve (Fig. B-17) consists of two portions - the first for the oxidation of amide and second for self decomposition of peroxydisulphate ion. Now tangents are drawn at portion of the curve which intersect at point P. From this point of intersection the value of $K_2S_2O_8$ consumed in the complete oxidation of 5 ml of 0.01 amide is calculated. The point Q on the curve B at the same time gives the value corresponding to self decomposition of $K_2S_2O_8$.

From the graph (Fig. B-17) it indicates that the two plots become parallel at P. At this point log c = 1.08 which corresponds to 12.02 ml.

The corresponding value of log c at the same time on the self decomposition curve is shown by point Q. At this point log C = 1.23 which corresponds to 16.98 ml.   .

The difference between the two values is 4.96 ccs.

Therefore, 4.96 ccs of

0.02 N $Na_2S_2O_3$ $\equiv$ 4.96 ccs of 0.02 N $K_2S_2O_8$

$\equiv$ 4.96 ccs of 0.01 M $K_2S_2O_8$
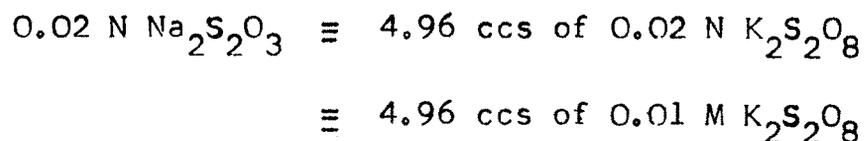
Hence 5 ml of 0.01 M amide $\equiv$ 4.96 ml of 0.01 M $K_2S_2O_8$. Thus one mole of amide consumes one mole of peroxy-disulphate for completion of the reaction.
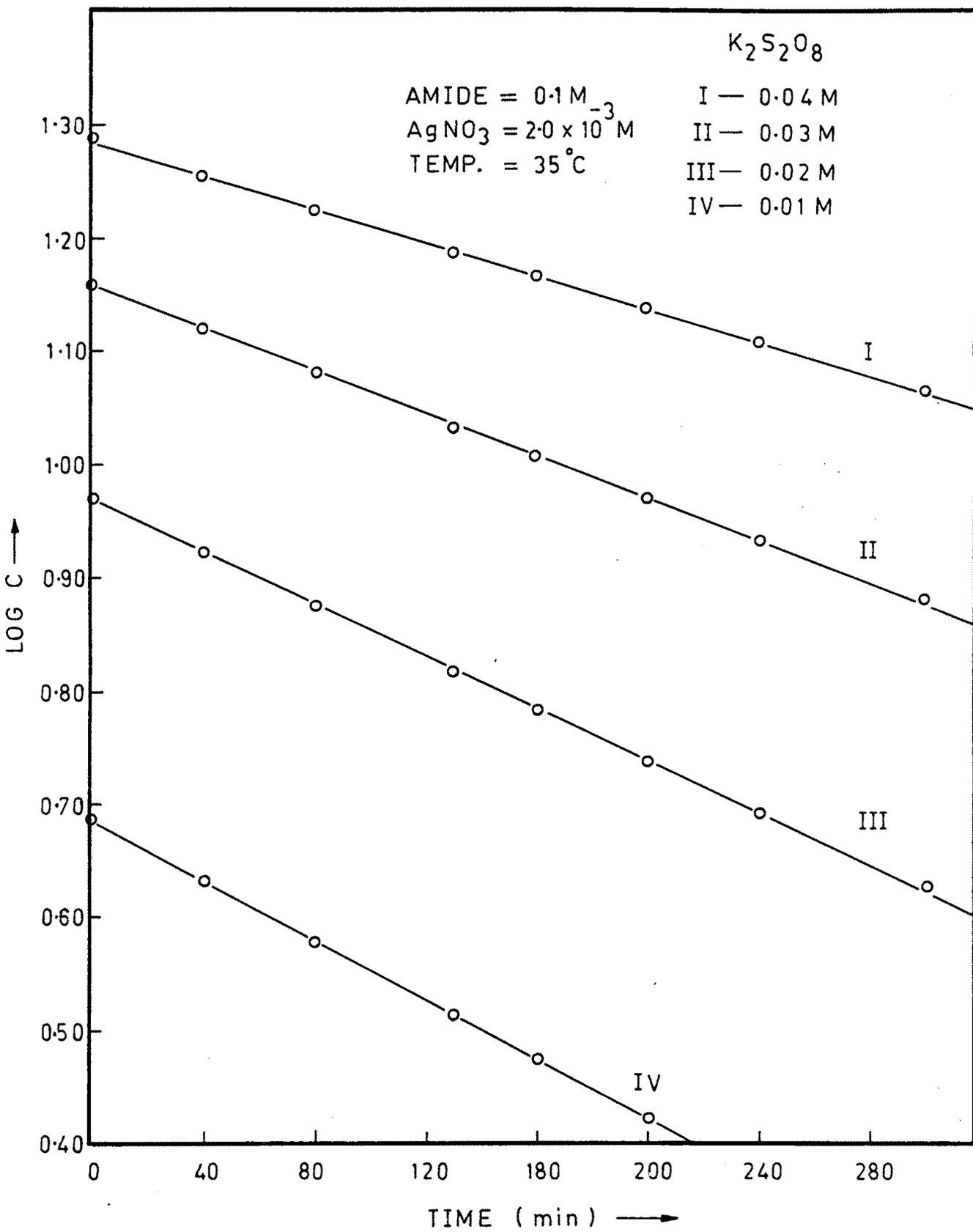
FIG. B-1 EFFECT OF $K_2S_2O_8$
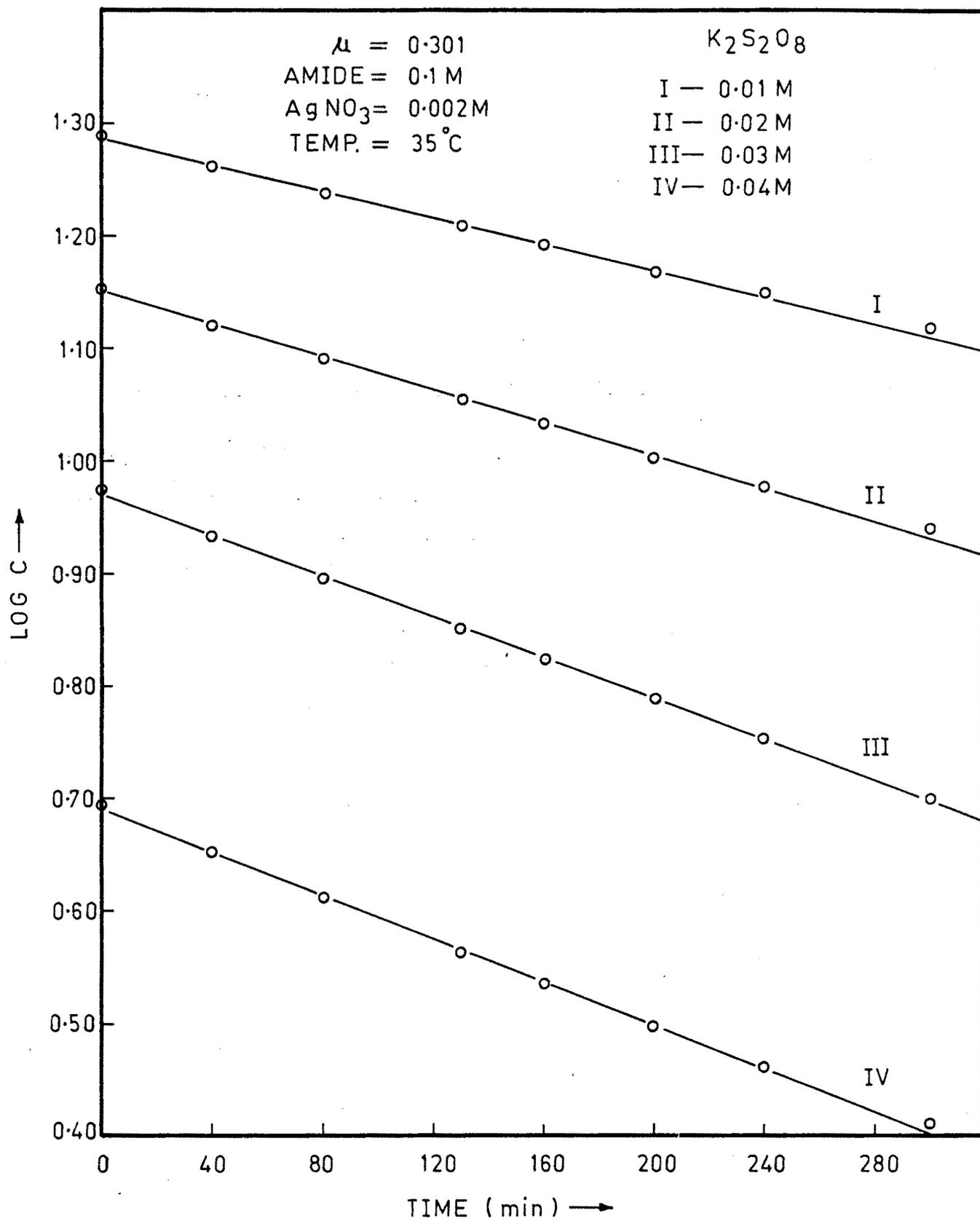
FIG. B-2 EFFECT OF $K_2S_2O_8$ AT CONSTANT μ
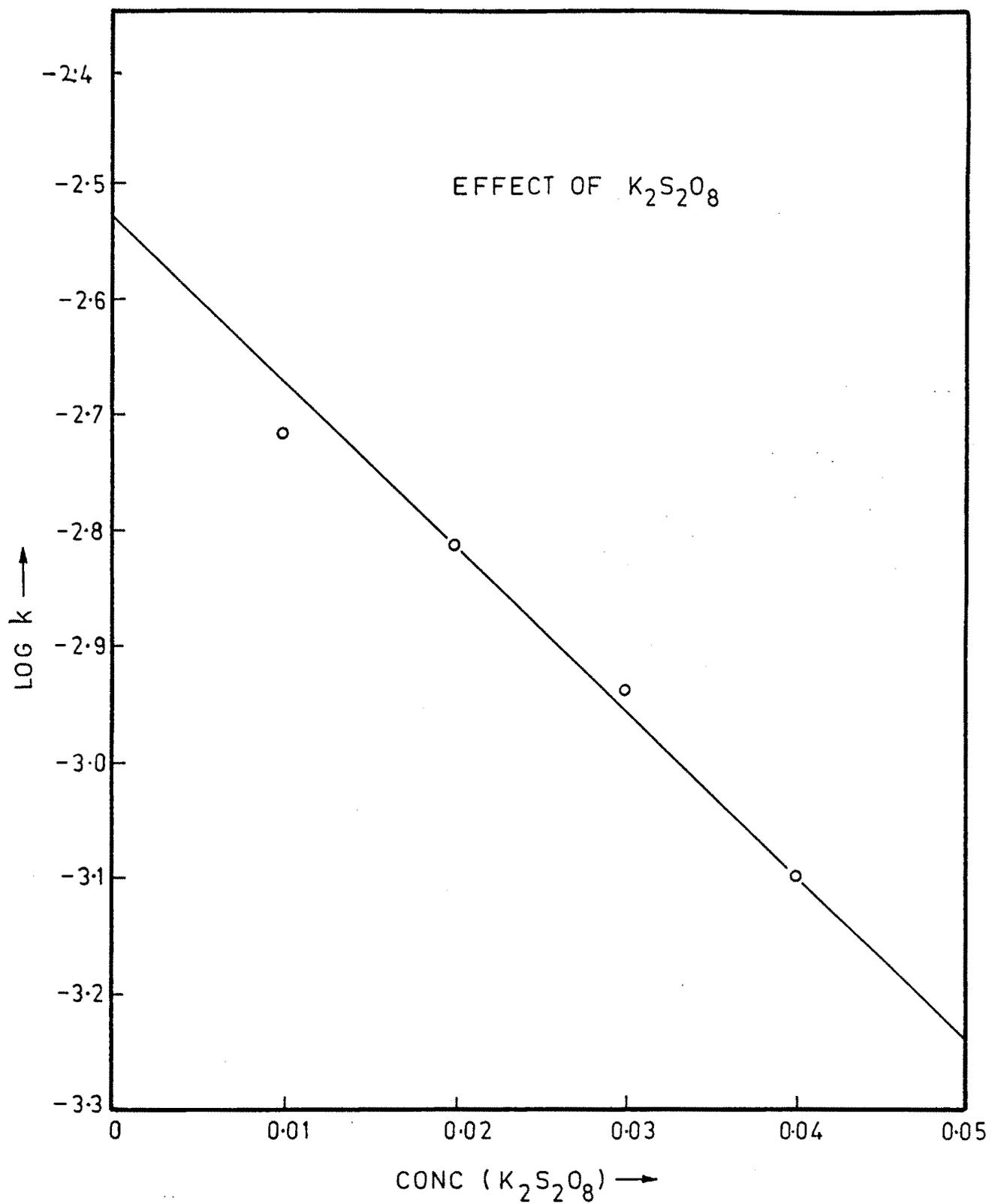
FIG. B-3: PLOT OF LOG k VERSUS CONC ($K_2S_2O_8$)
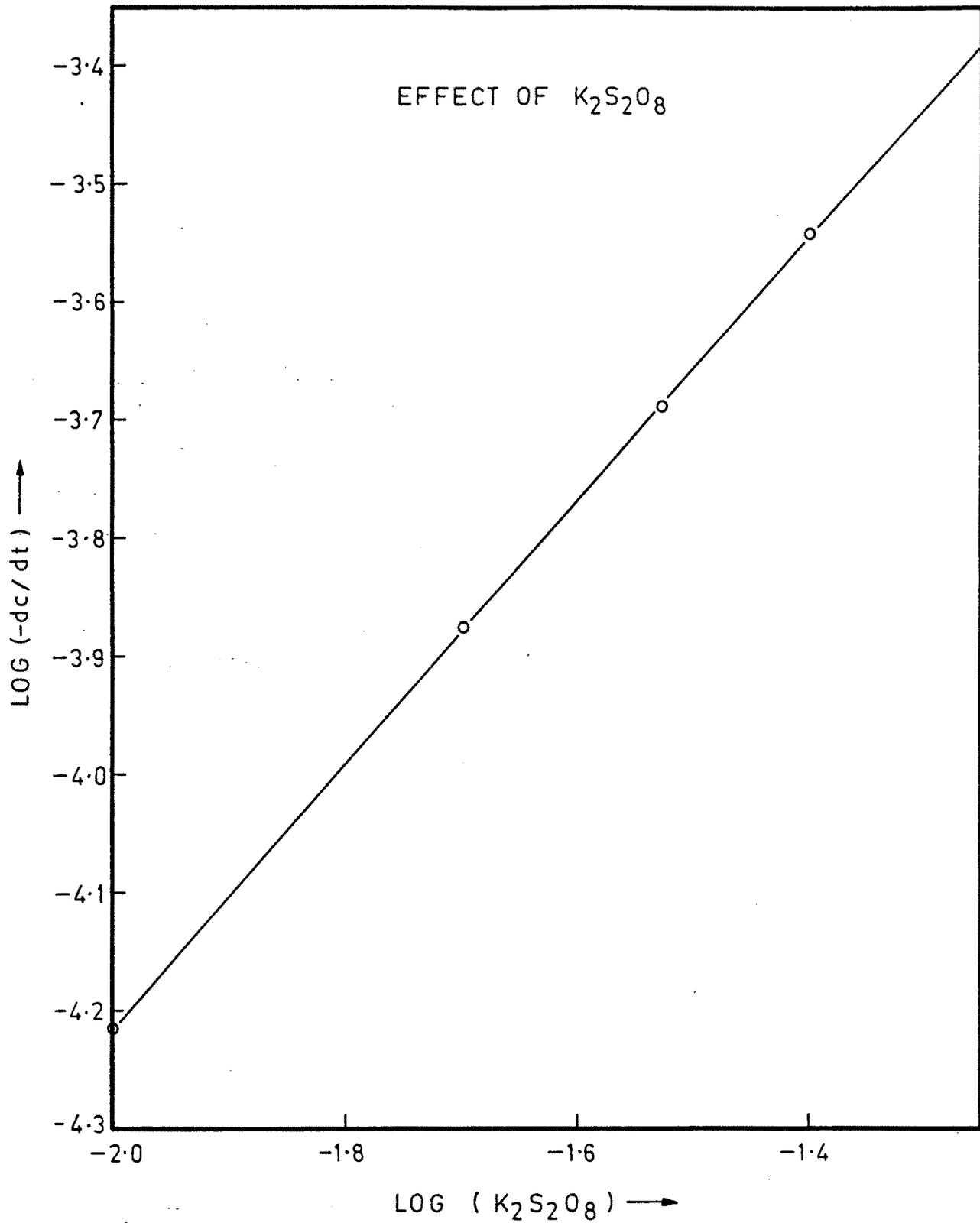
EFFECT OF $K_2S_2O_8$

FIG B-4 PLOT OF LOG (-dc/dt) VERSUS LOG ($K_2S_2O_8$)
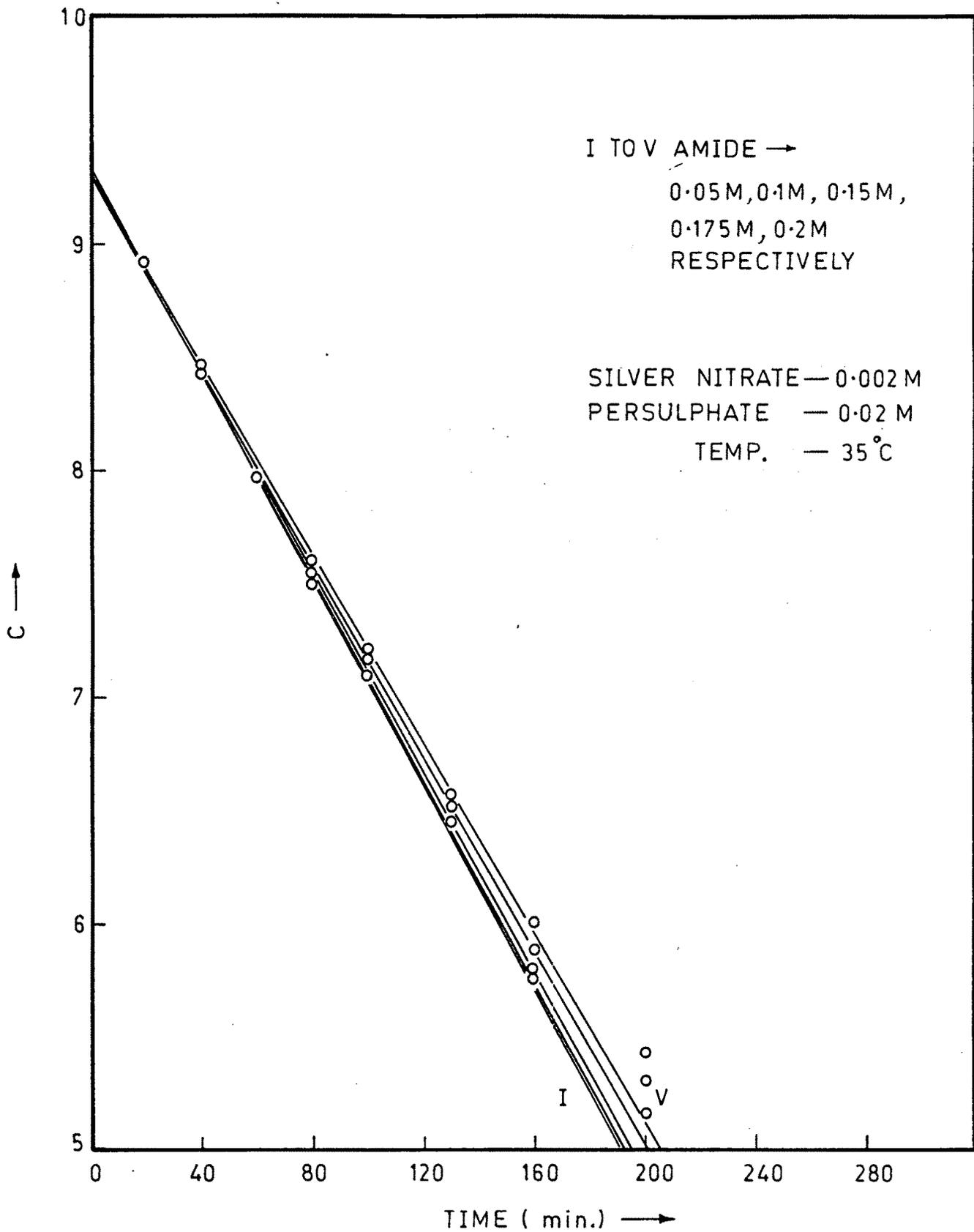
FIG. B-5 EFFECT OF AMIDE
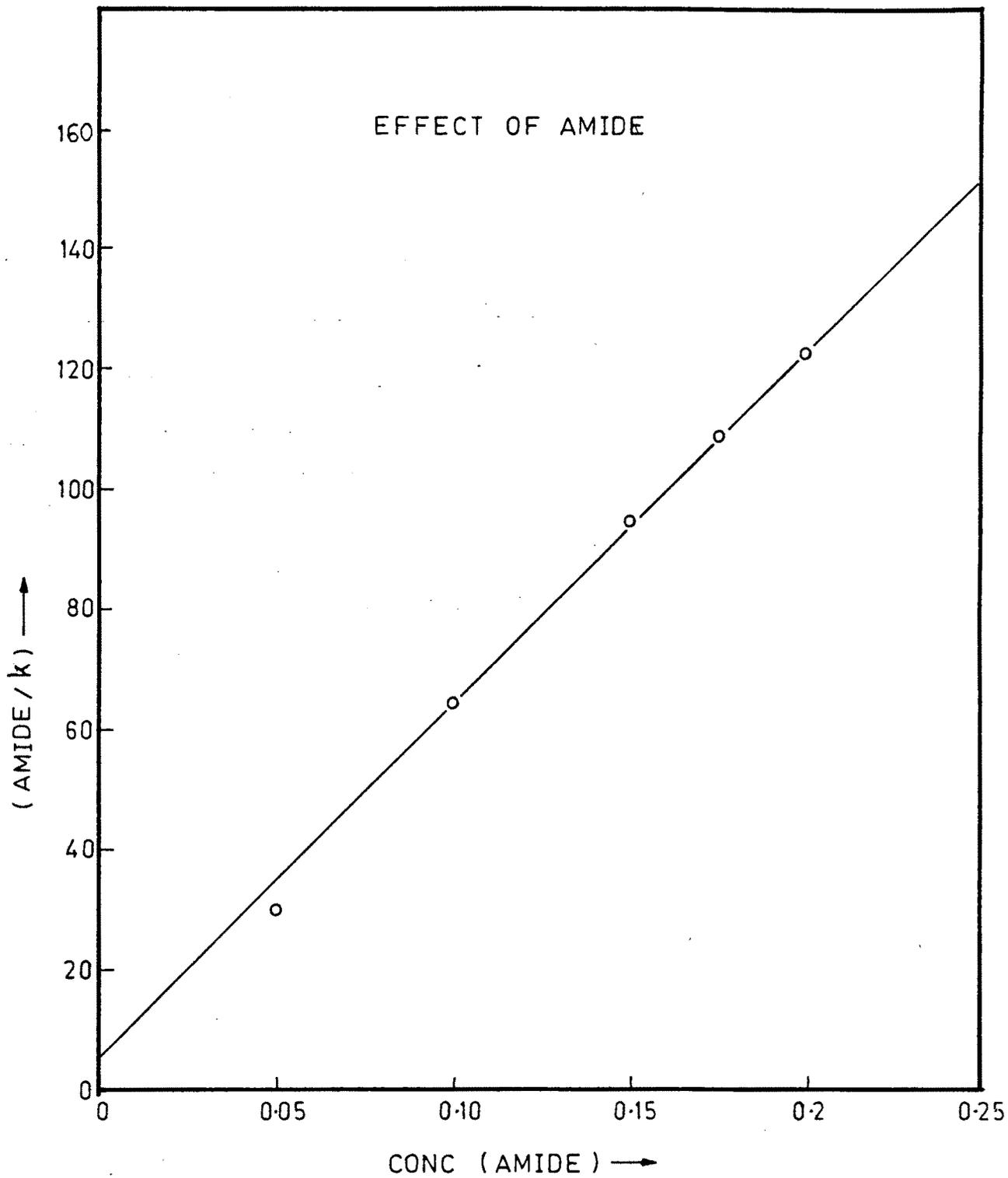
EFFECT OF AMIDE

FIG. B-6 : PLOT OF (AMIDE/k) VERSUS (AMIDE)
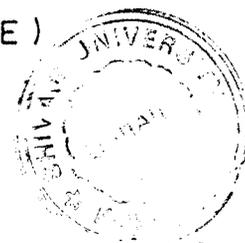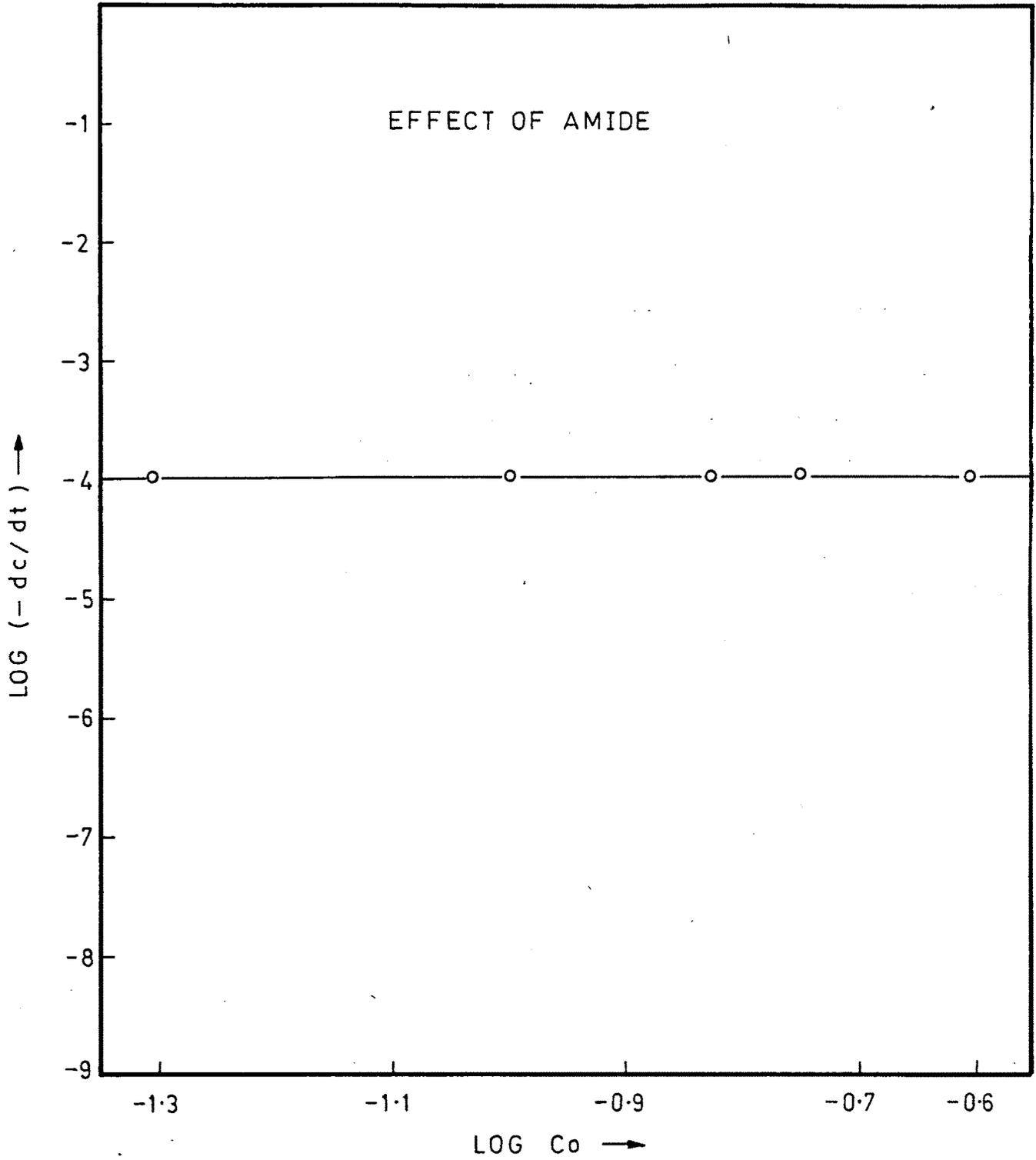
EFFECT OF AMIDE

FIG. B—7: PLOT OF LOG (-dc/dt) VERSUS LOG (Co)

EFFECT OF CATALYST

AMIDE = 0·1 M

$K_2S_2O_8 = 0·02 M$

TEMP. = 35 °C

(Ag^+)

I — 0·004 M
II — 0·003 M
III — 0·002 M
IV — 0·015 M
V — 0·001 M

LOG C

TIME (min)

FIG. B-8

EFFECT OF CATALYST
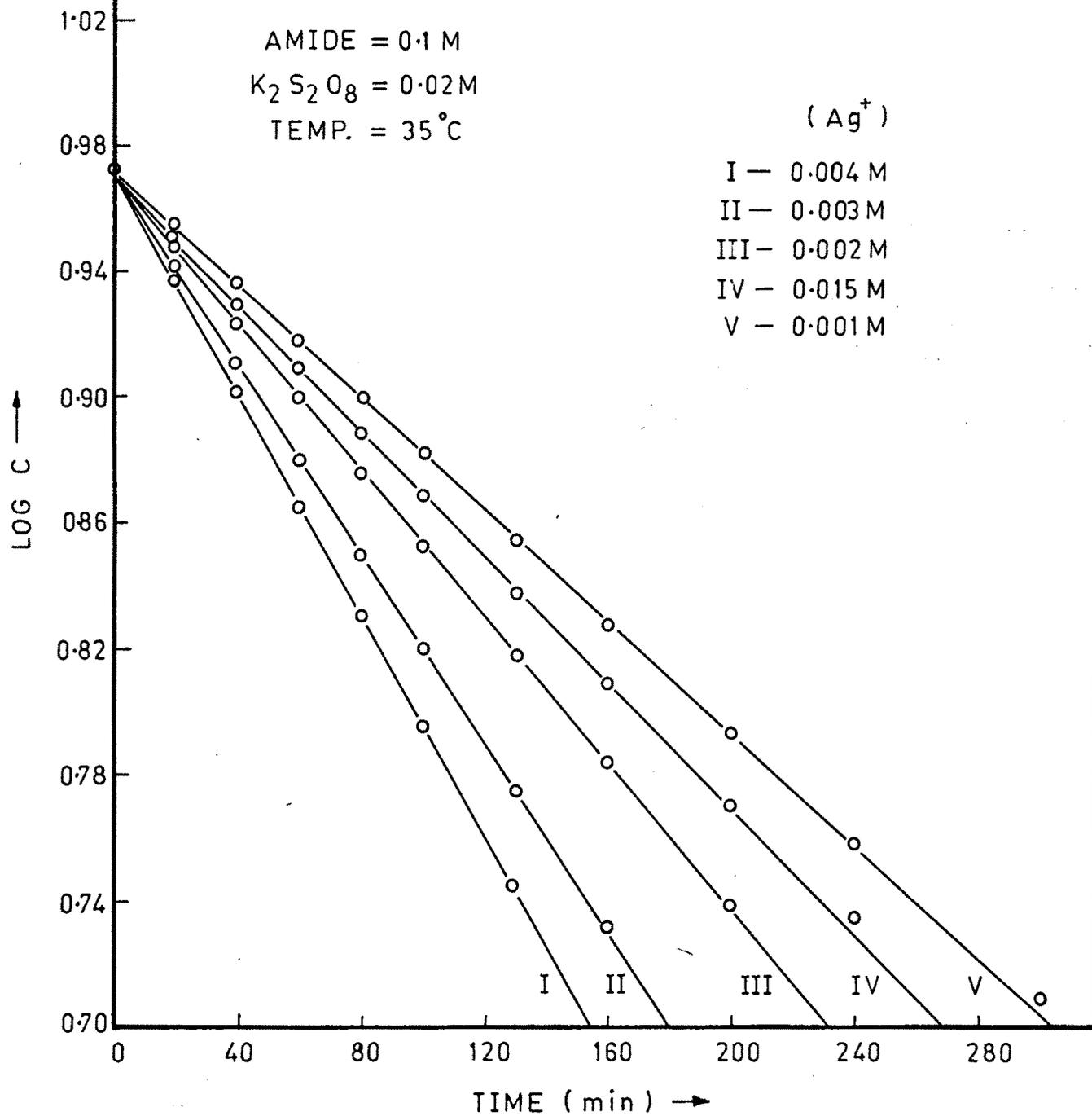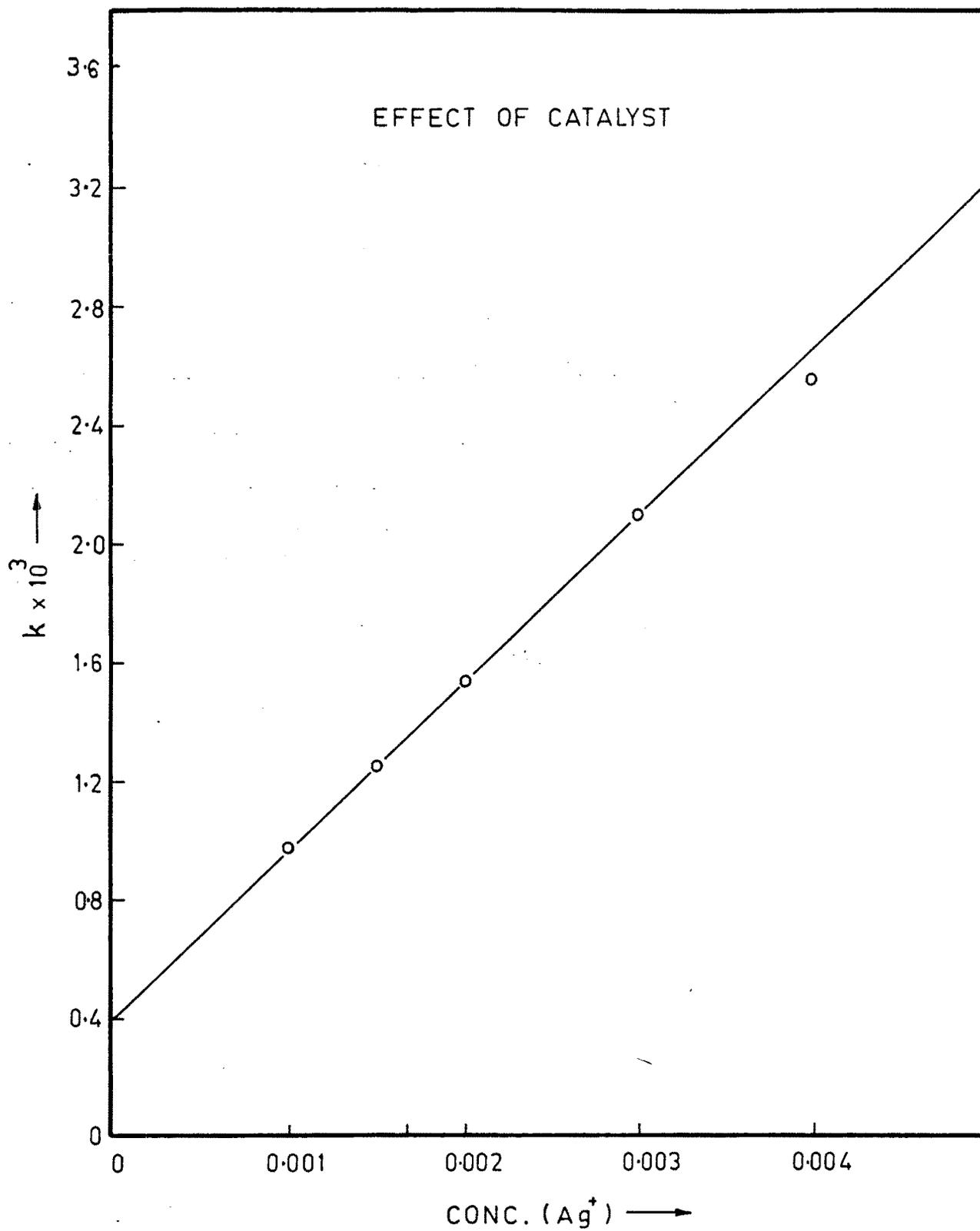
FIG. B-9 : PLOT OF $k \times 10^3$ VERSUS CONC.(Ag^+)

FIG. B —10

FIG B—11   PLOT OF LOG k VS $1/T \times 10^3$

ENTHALPY OF ACTIVATION
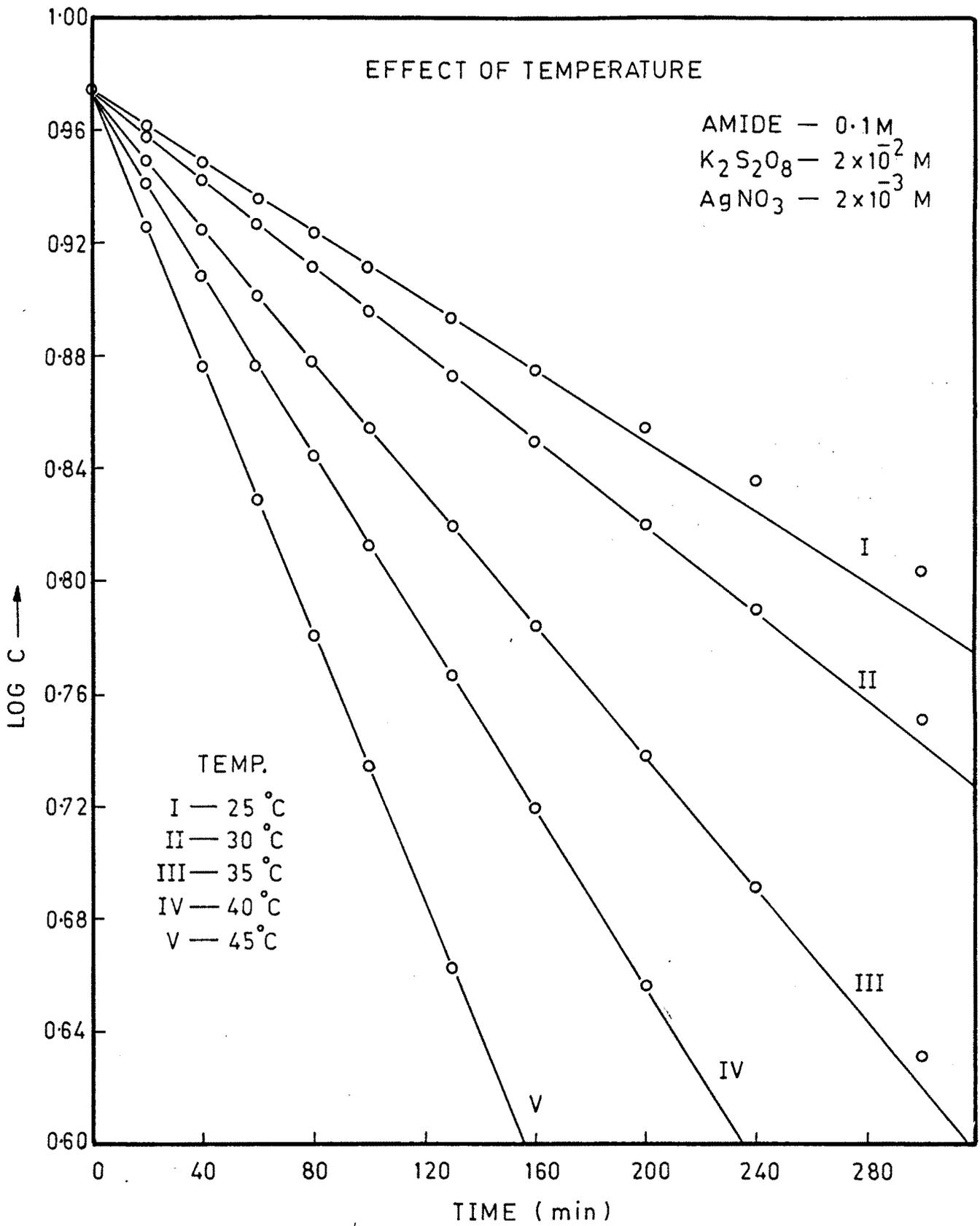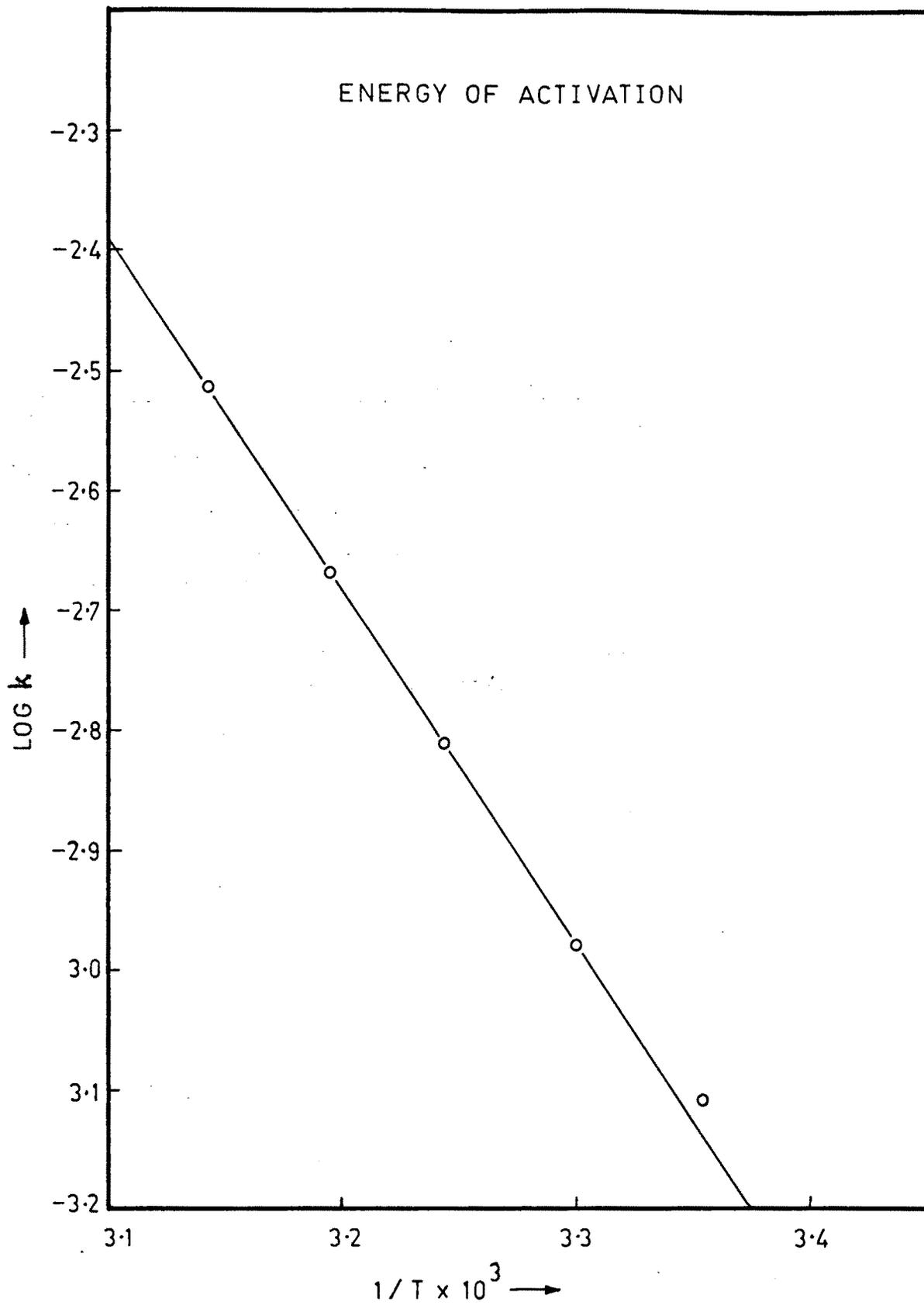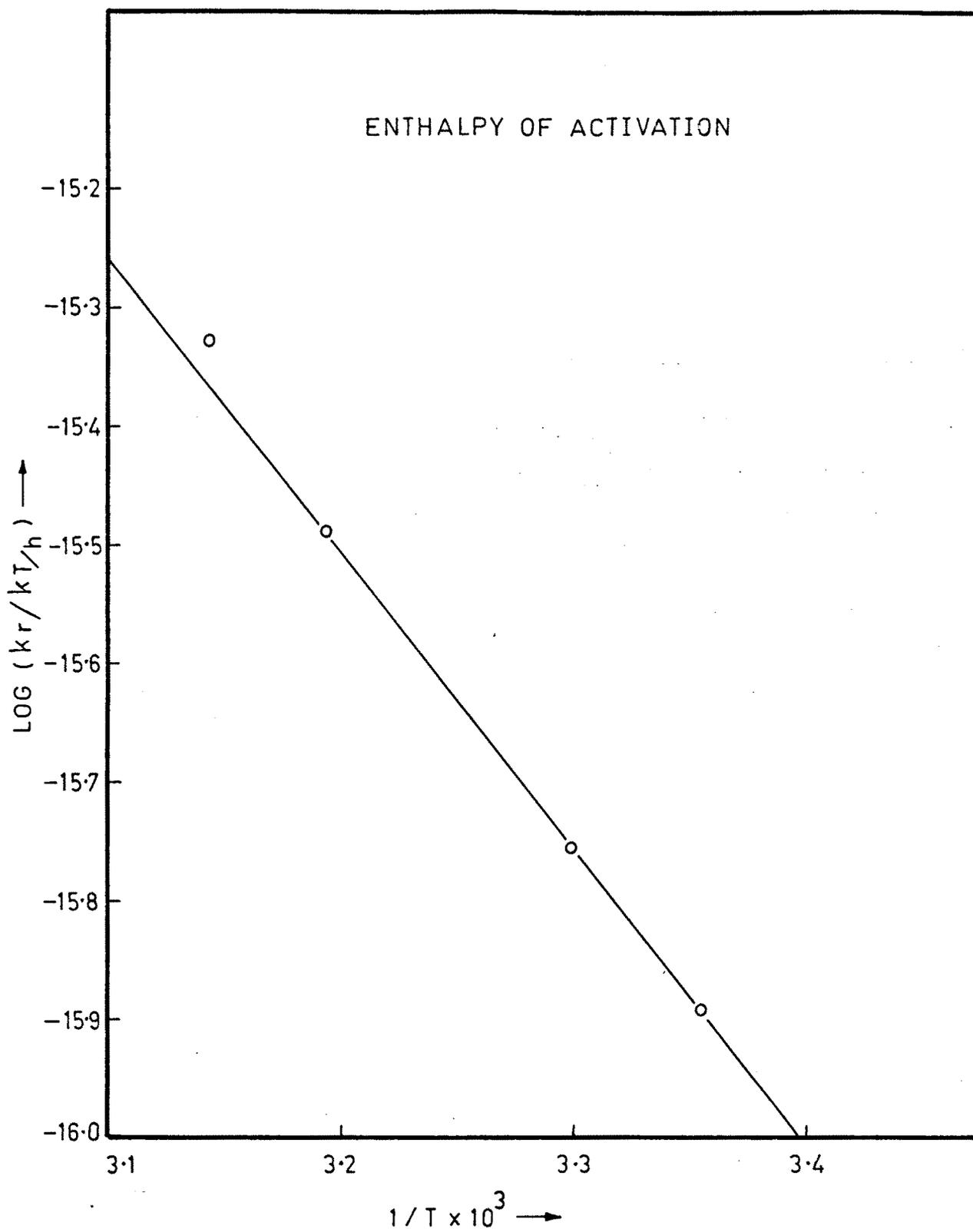
FIG. B-12 : PLOT OF LOG ($kr/kT/h$) VARSUS $1/T \times 10^3$

EFFECT OF IONIC STRENGTH

AMIDE = 0·1 M
$K_2S_2O_8$ = 0·02 M
$AgNO_3$ = 0·002 M
TEMP. = 35 °C

K_2SO_4

I — 0·04 M
II — 0·03 M
III — 0·02 M
IV — 0·015 M
V — 0·01 M
VI — 0·005 M

LOG C

TIME (min)
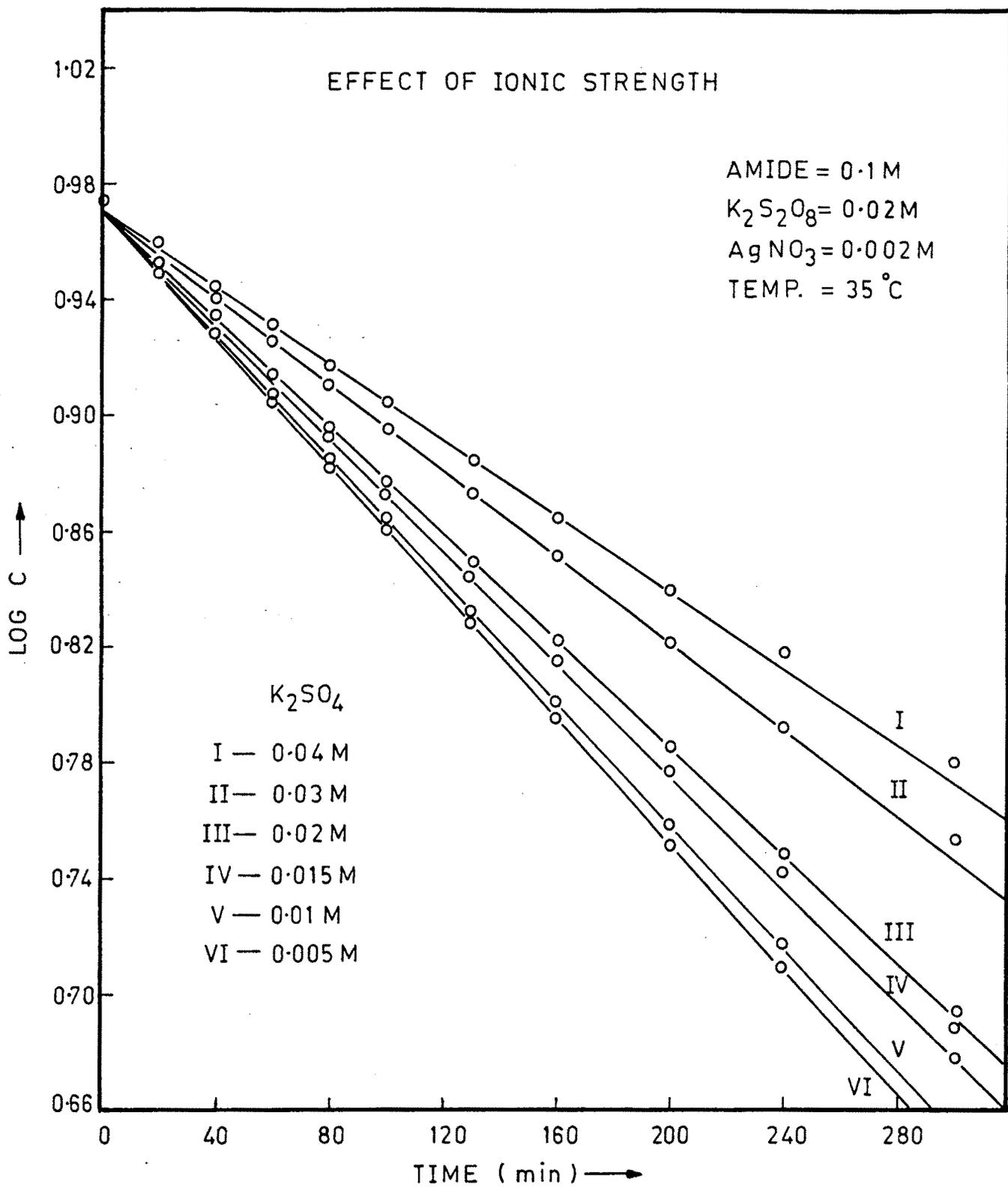
FIG B —13   PLOT OF LOG C VS. TIME .

EFFECT OF IONIC STRENGTH
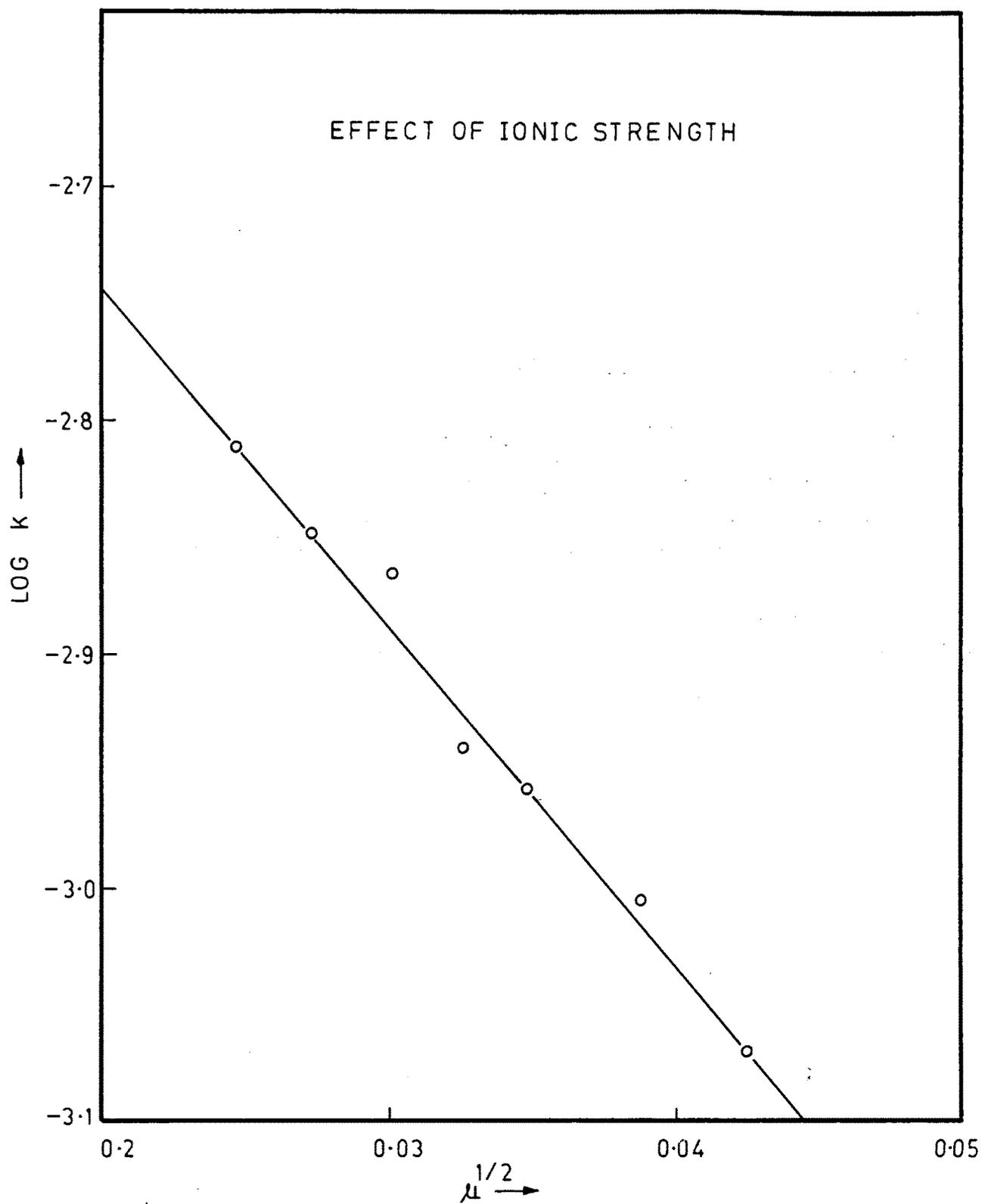
FIG. B-14(a)   PLOT OF LOG k VS '$\mu^{1/2}$.'

EFFECT OF IONIC STRENGTH
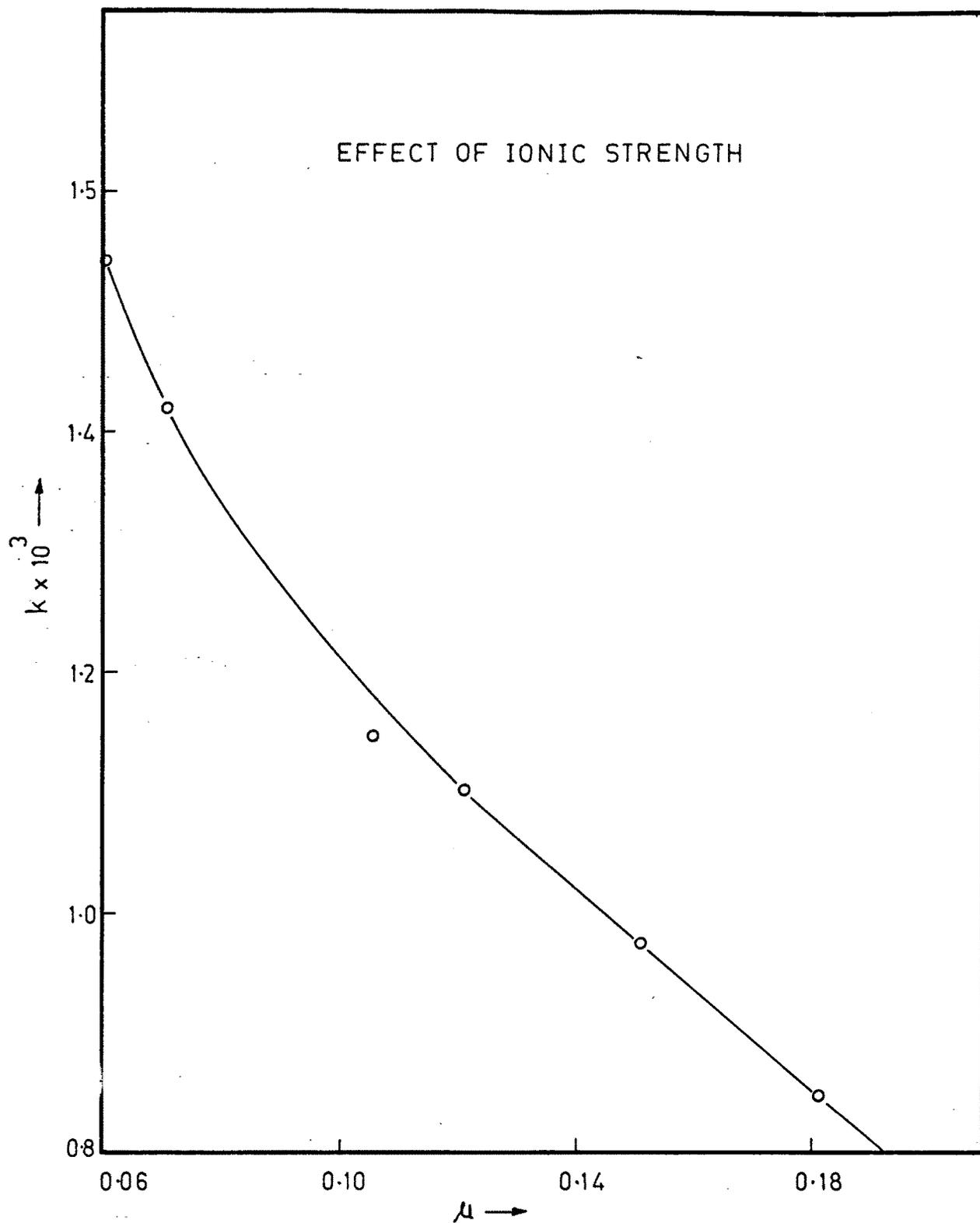
FIG. B −14 (b) PLOT OF $k \times 10^3$ VS. 'μ'.
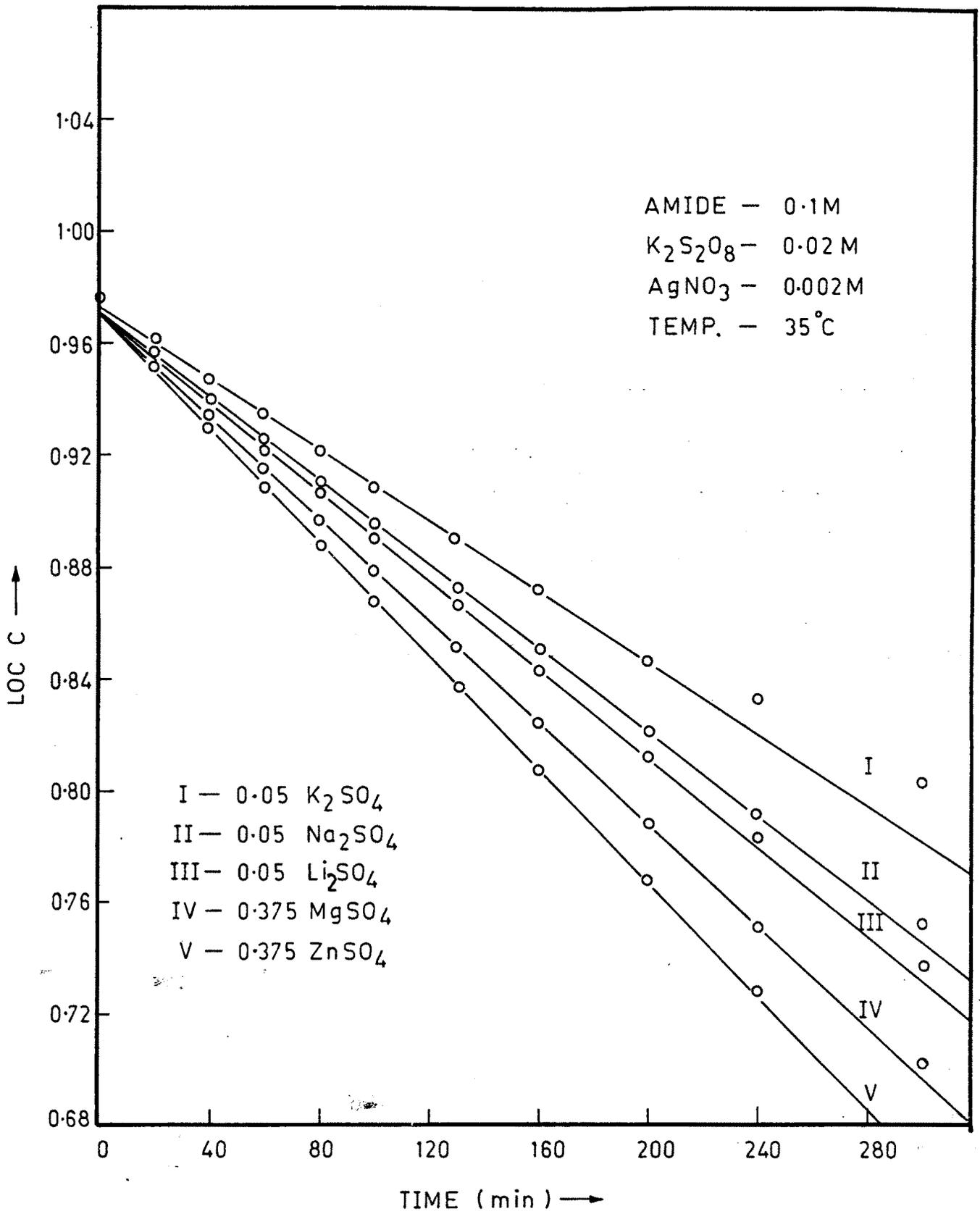
FIG. B-15   EFFECT OF SPECIFIC ION.
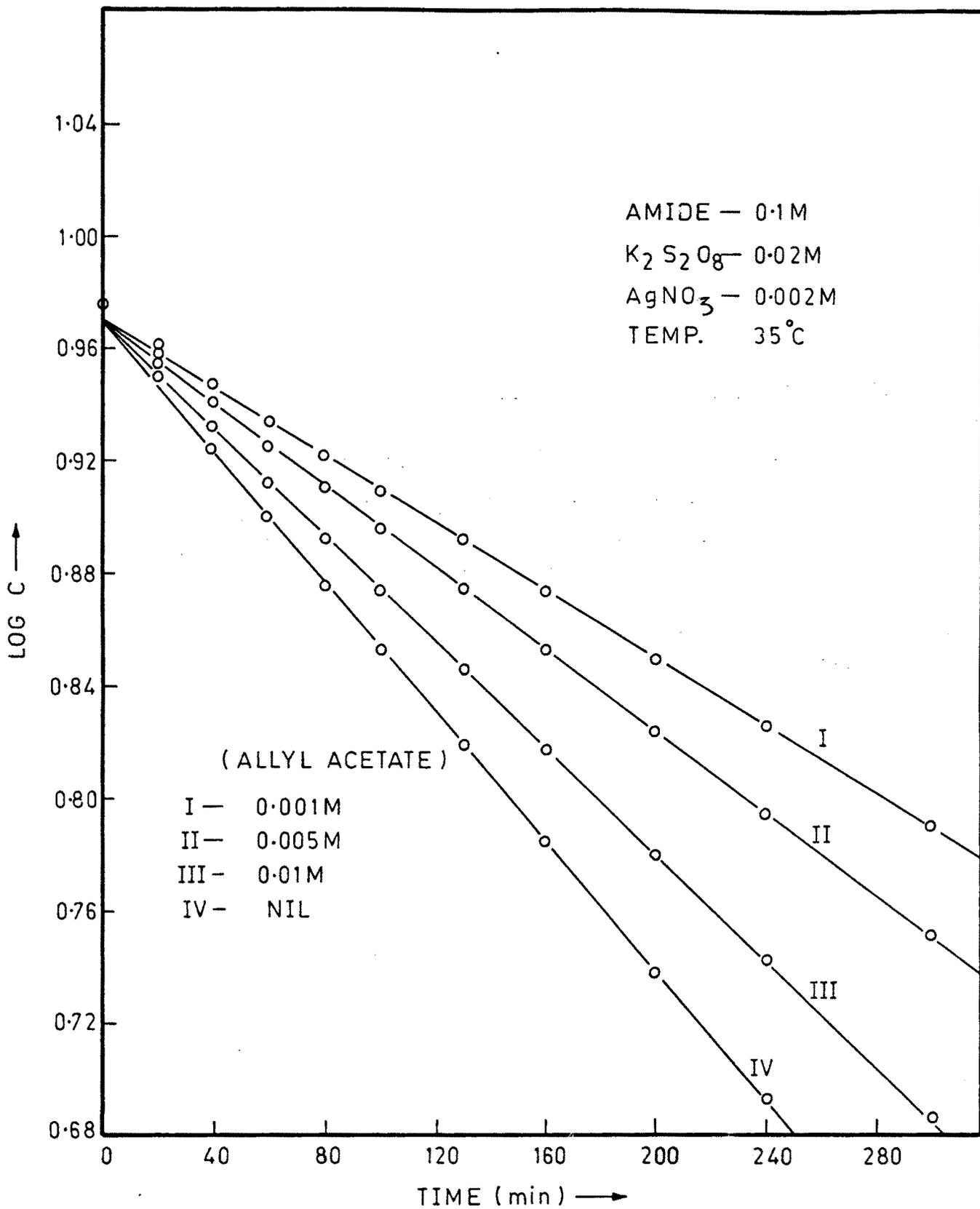
FIG. B—16   EFFECT OF ALLYL ACETATE

FIG. B-17   MOLE RATIO