

CHAPTER - III

OXIDATION OF CINNAMIDE

Some experiments were performed in order to decide the suitable temperature, concentration of the reactants and catalyst. It was observed that the uncatalysed reaction was extremely slow. In presence of $2.0 \times 10^{-3} \text{ M AgNO}_3$ as catalyst the reaction proceeds with a measurable velocity at 35°C . Hence, the reaction was studied at 35°C taking the overall concentrations of $\text{K}_2\text{S}_2\text{O}_8$ as 0.02 M , amide as 0.1 M and $2.0 \times 10^{-3} \text{ M AgNO}_3$ as catalyst. The kinetic data of this run is recorded in the following (Table A-1).

TABLE A-1

$\text{K}_2\text{S}_2\text{O}_8 = 2.0 \times 10^{-2} \text{ M}$, Cinnamide = 0.1 M , $\text{AgNO}_3 = 2.0 \times 10^{-3} \text{ M}$, Temp. = 35°C

Time(min)	C *	$k_1 \times 10^3 \text{ min}^{-1}$
0	9.46	-
20	8.97	2.659
40	8.52	2.616
60	8.10	2.586
80	7.71	2.556
100	7.35	2.523
130	6.83	2.505
160	6.35	2.491
200	5.77	2.472
240	5.25	2.453
300	4.54	2.447
360	3.93	2.440
Mean $k_1 \times 10^3 \text{ min}^{-1}$	-	2.522

C* denotes the volume of $\text{Na}_2\text{S}_2\text{O}_3$ (0.02 M) in ml equivalent to unreacted $\text{S}_2\text{O}_8^{2-}$

From the above results (Table A-1) it indicates that the first order rate constant goes on slightly decreasing with time. This suggests that either the reaction follows an order greater than one or the reaction is attained with inhibition during the course of the reaction leading to a decrease in the first order rate constant with time. In the experiment, the quantity of amide was taken in excess, its concentration is higher than that of $S_2O_8^{2-}$ and hence the order is with respect to $S_2O_8^{2-}$ ion.

To decide conclusively the order with respect to $S_2O_8^{2-}$ as well as with respect to the substrate, the reaction was carried out at equimolar concentrations peroxydisulphate and amide (viz 0.02 M each), keeping the temperature and concentration of the catalyst unchanged. The following table contains the results of this run (Table A-2).

TABLE A-2

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

Time(min)	C	$k_1 \times 10^3 \text{ min}^{-1}$
0	9.44	-
20	8.77	3.680
40	8.17	3.612
60	7.62	3.569
80	7.12	3.525
100	6.66	3.488
130	6.05	3.422
160	5.49	3.387
200	4.83	3.350
240	4.26	3.315
300	3.52	3.288
360	2.92	3.259
Mean $k_1 \times 10^3 \text{ min}^{-1}$	-	3.444

Here again, it is seen that the first order rate constant slightly decrease with time, which most probably may be due to some inhibition as the reaction progresses. The nearly constant values of the rate constant suggest that the order with respect to substrate may be zero.

EFFECT OF PEROXYDISULPHATE CONCENTRATION :

Before studying the effect of $K_2S_2O_8$ concentration on the reaction rate, it is necessary to study the self decomposition of peroxydisulphate without the substrate and

in the presence of silver catalyst. The results of these kinetic runs are recorded in Table A-3.

TABLE A-3

$\text{AgNO}_3 = 2.0 \times 10^{-3} \text{M}$, Temp. = 35°C

$[\text{K}_2\text{S}_2\text{O}_8] \text{M}$	0.01		0.02		0.03		0.04	
Time(min)	C	$k_2 \times 10^3$ min^{-1}	C	$k_2 \times 10^3$ min^{-1}	C	$k_2 \times 10^3$ min^{-1}	C	$k_2 \times 10^3$ min^{-1}
0	4.96	-	9.86	-	14.56	-	19.44	-
20	4.82	1.420	9.59	1.370	14.20	1.251	18.97	1.215
40	4.69	1.399	9.34	1.354	13.85	1.249	18.58	1.131
60	4.57	1.364	9.11	1.318	13.52	1.235	18.20	1.098
80	4.46	1.328	8.91	1.266	13.21	1.216	17.81	1.091
100	4.35	1.312	8.71	1.240	12.92	1.195	17.44	1.085
130	4.19	1.297	8.42	1.214	12.48	1.185	16.93	1.063
160	4.04	1.282	8.12	1.212	12.13	1.141	16.42	1.055
200	3.85	1.266	7.75	1.203	11.67	1.106	15.92	0.995
240	3.67	1.255	7.41	1.190	11.18	1.100	15.33	0.989
300	3.41	1.248	6.95	1.166	10.54	1.077	14.51	0.973
360	3.17	1.242	6.55	1.136	10.12	1.010	13.98	0.915
Mean $k_2 \times 10^3$ min^{-1}	-	1.310	-	1.242	-	1.151	-	1.055

In order to study the effect of $\text{S}_2\text{O}_8^{2-}$ ion concentration on the reaction rate, the reaction was studied at three different concentration of $\text{S}_2\text{O}_8^{2-}$ keeping the concentration of

the substrate and catalyst unchanged. Table A-4 contains the results of these kinetic runs and for comparisons sake the data of Table A-1 has been included in it.

TABLE A-4

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

$[\text{K}_2\text{S}_2\text{O}_8]^M$	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	4.95	-	9.46	-	14.42	-	19.52	-
20	4.65	3.126	8.97	2.659	13.75	2.378	18.71	2.119
40	4.37	3.115	8.52	2.616	13.13	2.342	17.98	2.054
60	4.12	3.058	8.10	2.586	12.54	2.328	17.27	2.041
80	3.89	3.012	7.71	2.556	12.01	2.285	16.61	2.017
100	3.68	2.964	7.35	2.523	11.53	2.236	16.05	1.957
130	3.39	2.911	6.83	2.505	10.83	2.200	15.24	1.903
160	3.13	2.864	6.35	2.491	10.19	2.170	14.48	1.866
200	2.84	2.777	5.77	2.472	9.38	2.150	13.64	1.792
240	2.58	2.174	5.25	2.453	8.68	2.114	12.92	1.719
300	2.23	2.657	4.54	2.447	7.76	2.065	11.94	1.638
360	1.92	2.630	3.93	2.440	6.92	2.039	10.86	1.628
$k_1 \times 10^3$ min^{-1}	-	2.893	-	2.522	-	2.209	-	1.884
$k_2 \times 10^3$ min^{-1}	-	1.310	-	1.242	-	1.151	-	1.055
$k \times 10^3$ min^{-1}	-	1.583	-	1.280	-	1.058	-	0.830

From the above results (Table A-4), it indicates that, when the concentration of $K_2S_2O_8$ was increased the first order rate constant was decreased. This decrease in the rate constant with an increase in the concentration of $S_2O_8^{2-}$ may be either due to an increase in ionic strength or due to the specific inhibitory effect of K^+ ion or due to both.

It was observed that, in any particular run, the first order rate constant decreases with time, because the reactions involving $S_2O_8^{2-}$ ions are highly susceptible to the trace impurities. Hence, all the precautions were taken to purify the substrate and all the reagents used for kinetic study. These results are recorded in the Table A-4 and also shown graphical in Fig. A-1. The rate constant k_1 at different times has been calculated by integration method. The net rate constant, (viz k) for the oxidation of the substrate is obtained after deducting the value of the rate constant (viz k_2) for the self decomposition of $S_2O_8^{2-}$ studied simultaneously (as shown in Table A-4).

It must be mention here that, in all the kinetic studies, though the self decomposition of $S_2O_8^{2-}$ has always been investigated under the corresponding experimental conditions, the kinetic data for these runs have been omitted due 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 - A-5

Amide = 0.1 M, $\text{AgNO}_3 = 2.0 \times 10^{-3} \text{M}$, Temp. = 35°C $\mu = 0.330$

$[\text{K}_2\text{S}_2\text{O}_8] \text{M}$	0.01	0.02	0.03	0.04
+ $[\text{K}_2\text{SO}_4] \text{M}$	0.09	0.08	0.07	0.06
Time (min)	Vol. (in ml.) of 0.02M, $\text{Na}_2\text{S}_2\text{O}_3$ used (viz. C)			
0	4.95	9.46	14.25	19.52
20	4.69	9.05	13.68	18.82
40	4.47	8.67	13.20	18.18
60	4.27	8.31	12.75	17.58
80	4.12	7.99	12.34	17.02
100	3.97	7.71	11.94	16.49
130	3.82	7.32	11.42	15.98
160	3.69	6.98	10.96	15.42
200	3.52	6.52	10.38	14.81
240	3.36	6.12	9.98	14.12
300	3.12	5.56	9.22	13.26
360	2.91	5.07	8.62	12.34
$k_1 \times 10^3 \text{ min}^{-1}$	2.032	1.978	1.694	1.549
$k_2 \times 10^3 \text{ min}^{-1}$	0.750	0.760	0.740	0.740
$k \times 10^3 \text{ min}^{-1}$	1.282	1.218	0.954	0.809

Again it has been observed that the first order specific rate decreases by increasing the concentration of $S_2O_8^{2-}$. However, the kinetic runs carried out above (Table A-4) do not have constant ionic strength as well as constant K^+ ion concentration. Hence, it was considered to reinvestigate this effect at constant ionic strength as well as at constant K^+ ion concentration, so the effect of both these parameters may be eliminated. Hence, the above table (Table A-5) shows the data of these kinetic runs carried out constant ionic strength and constant K^+ ion concentration which have been shown graphically in Fig. A-2. From the results contained in the above table (Table A-5) it is seen that the first order rate constant decreases.

The following table (Table A-6) shows the comparison between k values with increasing concentrations of $S_2O_8^{2-}$ with K_2SO_4 to maintain constant ionic strength and constant K^+ ion concentration in the later case.

TABLE A-6

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

Conc. $[K_2S_2O_8]M$ without $[K_2SO_4]M$	$k \times 10^3$	Conc. $[K_2S_2O_8]M$ with constant K^+ ion strength	$k \times 10^3$ min^{-1}
0.01	1.583	0.01	1.282
0.02	1.280	0.02	1.218
0.03	1.054	0.03	0.954
0.04	0.830	0.04	0.800

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From the data shown in the above table (Table A-6) it indicates that at constant K^+ ionic strength, there is a decrease in the rate constant. This suggests that the effect is due to the increase in ionic strength as well as due to the increase in K^+ ion concentration, both causing inhibition. There exists a rate decreasing tendency even though the reaction is carried out at constant ionic strength as well as at constant K^+ ion concentration which leads to the conclusion that is probably due to some trace impurity remaining in the peroxydisulphate sample itself even after repeated crystallisation which however, could not be characterised.

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

$$-\log k = 2.717 + 8.65[S_2O_8^{2-}]_0$$

provided that $[S_2O_8^{2-}]_0 \neq \text{zero}$.

ORDER WITH RESPECT TO PEROXYDISULPHATE :

The order with respect to peroxydisulphate was calculated by Van't Hoff's differential¹⁸⁷ method. The volume of $Na_2S_2O_3$ (equivalent to $K_2S_2O_8$) was plotted against time for different initial concentrations of $K_2S_2O_8$. From these curves the value of $\frac{-dc}{dt}$ in each case was determined from the initial slope as given in Table A-7.

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TABLE A-7

$[\text{K}_2\text{S}_2\text{O}_8]\text{M}$	$\frac{-dc}{dt} \times 10^{-4}$	$\text{Log}[\text{S}_2\text{O}_8^{2-}]$	$\text{Log}(\frac{-dc}{dt})$
0.01	0.51	- 2.0000	- 4.2924
0.02	1.22	- 1.6990	- 3.9136
0.03	2.07	- 1.5229	- 3.6840
0.04	2.946	- 1.3979	- 3.5307

The values of $-dc/dt$ and the concentrations of peroxydisulphate i.e. 'C' are substituted in the Van't Hoff's equation and the order of the reaction is calculated thereby.

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

The values of $(-dc/dt)$ for different initial concentration of $\text{S}_2\text{O}_8^{2-}$ and the values of 'n' calculated thereby are recorded in Table A-8.

Again a plot of $\text{Log } -dc/dt$ versus $\text{Log } [\text{S}_2\text{O}_8^{2-}]$ is shown in Fig. A-4. The slope of the graph is 1.185 as such the order with respect to $\text{S}_2\text{O}_8^{2-}$ is one which is confirmed by the values of 'n' calculated and are shown in the following table (Table A-8).

TABLE A-8

$[K_2S_2O_8]M$	$-dc/dt \times 10^{-4}$	order or reaction (n)
0.01	0.51	1.25
0.02	1.22	
0.01	0.51	1.275
0.03	2.07	
0.01	0.51	1.265
0.04	2.946	
0.02	1.22	1.303
0.03	2.07	
0.03	2.07	1.226
0.04	2.946	

EFFECT OF AMIDE CONCENTRATION -

To study the effect of amide concentration on the reaction rate, the reaction was studied at five different concentrations of amide. The concentrations of $K_2S_2O_8$ and $AgNO_3$ were kept unchanged. These results are recorded in Table A-9 and shown graphically in Fig. A-5.

TABLE A-9

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

$$Temp = 35^\circ C$$

[Amide]M	0.05	0.10	0.150	0.175	0.2
Time(min)	Vol. in ml. of 0.02M- $Na_2S_2O_3$ used (viz.C)				
0	9.45	9.46	9.46	9.45	9.45
20	8.98	8.97	8.98	8.96	8.96
40	8.54	8.52	8.53	8.51	8.51
60	8.13	8.10	8.10	8.08	8.08
80	7.74	7.71	7.69	7.67	7.67
100	7.37	7.35	7.31	7.31	7.31
130	6.84	6.83	6.77	6.75	6.75
160	6.37	6.35	6.29	6.26	6.25
200	5.79	5.77	5.65	5.66	5.65
240	5.26	5.25	5.14	5.12	5.12
300	4.56	4.54	4.42	4.41	4.39
360	3.96	3.93	3.80	3.79	3.77
$k_1 \times 10^3 \text{ min}^{-1}$	2.476	2.522	2.569	2.586	2.590
$k_2 \times 10^3 \text{ min}^{-1}$	1.242	1.242	1.242	1.242	1.242
$k \times 10^3 \text{ min}^{-1}$	1.234	1.280	1.327	1.344	1.348

From the above results contained in Table A-9 it indicates that 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 C_6H_5CH governed by

$$\begin{array}{c} \text{H} \\ | \\ \text{H} - \text{C} - \text{CONH}_2 \end{array}$$

the expression.

$$k = k_{\max} \cdot \frac{(\text{Amide})_0}{b + (\text{Amide})_0}$$

In support of the above equation, a graph of $\frac{(\text{Amide})_0}{k}$ versus $(\text{Amide})_0$ is plotted (Fig. A-6).

The plot was found to be linear from which k_{\max} and b were evaluated as 0.001367 and 0.01025. From these values k was calculated and found to be equal to $k = 1.248 \times 10^{-3} \text{ min}$ was almost identical with $k = 1.280 \times 10^{-3} \text{ min}$, the calculated experimental value.

ORDER WITH RESPECT TO AMIDE :

A general behaviour of Ag^+ catalysed redox reactions involving peroxydisulphate ion is that the order with respect to substrate is zero. To confirm the order of reaction with respect to amide, the kinetic data of Table A-9 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 concentrations of amide were evaluated. These values are recorded in Table A-10.

TABLE A-10

Conc. [Amide]M	$-dc/dt \times 10^{-4}$	Log Co	Log(-dc/dt)
0.05	1.03	- 1.3010	- 3.9871
0.10	1.04	- 1.0000	- 3.9829
0.15	1.01	- 0.8239	- 3.9956
0.175	1.110	- 0.7569	- 3.9546
0.2	1.12	- 0.6021	- 3.9507

A plot of Log $(-dc/dt)$ versus Log Co is shown in Fig. A-7. The value of the slope is zero indicating that the reaction is zero order with respect to amide. Calculations were made for the order of reaction by Vant Hoff's differential method as given in Table A-11.

TABLE A-11

[Amide]M	$-dc/dtx10^{-4}$	Order of reaction (n)
0.05	1.03	0.0139
0.10	1.04	
0.05	1.03	0.0179
0.15	1.01	
0.05	1.03	0.057
0.175	1.11	
0.05	1.03	0.052
0.20	1.12	
0.10	1.04	0.072
0.15	1.01	
0.10	1.04	0.01
0.20	1.12	

From the above results (Table A-11) it is confirmed that the order with respect to amide is zero.

EFFECT OF THE CATALYST CONCENTRATION :

To study the effect of catalyst concentration on the reaction rate, the reaction was studied at five different concentrations of silver nitrate, keeping the peroxydisulphate and amide concentration unchanged. The results of these runs are recorded in Table A-12 and shown graphically in Fig.A-8.

TABLE A-12

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

$[AgNO_3] \times 10^{-3} M$	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	9.46	9.45	9.46	9.44	9.42
20	9.03	9.00	8.97	8.83	9.74
40	8.64	8.58	8.52	8.28	8.13
60	8.28	8.19	8.10	7.77	7.58
80	7.94	7.83	7.71	7.31	7.06
100	7.62	7.49	7.35	6.91	6.58
130	7.18	6.70	6.83	6.34	5.94
160	6.80	6.57	6.35	5.86	5.37
200	6.32	6.04	5.77	5.23	4.72
240	5.90	5.56	5.25	4.71	4.18
300	5.30	4.92	4.54	4.02	3.48
360	4.74	4.39	3.93	3.41	2.87
$k_1 \times 10^3 \text{ min}^{-1}$	2.107	2.293	2.522	3.067	3.516
$k_2 \times 10^3 \text{ min}^{-1}$	1.186	1.195	1.242	1.431	1.514
$k \times 10^3 \text{ min}^{-1}$	0.921	1.098	1.280	1.636	2.002

From the above results (Table (A-12)) it is observed that when the concentration of the catalyst was increased the reaction rate was also increased linearly. This indicates that the reaction is first order with respect to the catalyst.

A plot of k versus $[\text{Ag}^+]$ shown in Fig. A-9 is found to be linear and the following relationship is obeyed.

$$k = 0.53 \times 10^{-3} + 0.365 [\text{Ag}^+]$$

EFFECT OF TEMPERATURE :

In order to determine the temperature coefficient, energy of activation and other energy parameters, the reaction was studied at five different temperatures ranging from 25°C to 45°C . The results of these kinetic runs have been recorded in Table A-13 and shown graphically in Fig. A-10.

TABLE A-13

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

Temperature °C	25	30	35	40	45
Time(min)	Vol. (in ml) of 0.02 M $Na_2S_2O_3$ used (viz. C)				
0	9.45	9.45	9.46	9.42	9.42
20	9.17	9.09	8.97	8.78	8.50
40	8.92	8.77	8.52	8.19	7.72
60	8.68	8.47	8.10	7.65	7.00
80	8.49	8.19	7.71	7.16	6.36
100	8.32	7.94	7.35	6.70	5.78
130	8.06	7.56	6.83	6.08	5.02
160	7.79	7.21	6.35	5.54	4.36
200	7.46	6.77	5.77	4.89	3.61
240	7.17	6.38	5.25	4.32	3.02
300	6.74	5.82	4.54	3.58	2.28
360	6.34	5.29	3.93	2.98	1.73
$k_1 \times 10^3 \text{ min}^{-1}$	1.269	1.734	2.522	3.359	4.851
$k_2 \times 10^3 \text{ min}^{-1}$	0.650	0.820	1.242	1.623	2.504
$k \times 10^3 \text{ min}^{-1}$	0.619	0.914	1.280	1.736	2.347

From the above results (Table A-13) it indicates that the specific rate has been nearly doubled for $10^\circ C$ rise in temperature. A plot of $\log k$ versus $\frac{1}{T} \times 10^3$ is

found to be linear (Fig. A-11) showing that the reaction obeys Arrhenius relationship.

The calculated values of $1/T \times 10^3$ and $\text{Log} \left[\frac{kr}{kT/h} \right]$ are recorded in Table A-14.

TABLE A-14

Temp. °A	$1/T \times 10^3$	$Kr \times 10^3 \text{ min}^{-1}$	Log kr	$\text{Log} \left[\frac{kr}{kT/h} \right]$
298	3.356	0.619	- 3.2083	- 16.0013
303	3.301	0.914	- 3.0390	- 15.8392
308	3.246	1.280	- 2.8927	- 15.700
313	3.196	1.736	- 2.7604	- 15.5747
318	3.145	2.347	- 2.6294	- 15.4506

By making the use of Arrhenius equation at different temperatures the value of energy of activation has been calculated by the following equation :

$$\log k_1 - \log k_2 = \frac{-E}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots(1)$$

The energy of activation from the slope of the plot (Fig. A-11) is 12.420 K.Cals. mole⁻¹, which is in good agreement with the calculated value 12.384 K.Cals mole⁻¹.

The value of energy of activation was then used to calculate the frequency factor A and entropy of activation ΔS^\ddagger by the application of the following equations

$$k_r = A e^{-\Delta E/RT} \quad \dots(2)$$

and

$$A = e \left(\frac{kT}{h} \right) e^{-\Delta S^\ddagger/R} \quad \dots(3)$$

Where equation (3) is valid for reactions in solution. In the above expression k_r is the specific rate constant, k is the Boltzmann constant, h is the Plank's constant and e is a constant having a value of 2.7183 to be introduced in the equation when the reaction takes place in solution. Other symbols carry their usual meanings.

The free energy for the reaction was calculated by the equation

$$k_r = \frac{kT}{h} e^{-\Delta G/RT} \quad \dots(4)$$

Entropy of activation ΔS^\ddagger is given by the relationship

$$k_r = e \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-E/RT} \quad \dots(5)$$

$$\text{or } \ln k_r = \ln e + \ln \frac{kT}{h} + \frac{\Delta S^\ddagger}{R} - \frac{E}{RT} \quad \dots(6)$$

from which ΔS^\ddagger can be calculated.

Enthalpy of activation ΔH^\ddagger was calculated from the relation

$$kr = \frac{kT}{h} \cdot e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S^\ddagger/R} \quad \dots (7)$$

or

$$\log \frac{kr}{[kT/h]} = \frac{-\Delta H^\ddagger}{2.303 RT} + \frac{\Delta S^\ddagger}{2.303 R} \quad \dots (8)$$

The values of $\log \frac{kr}{[kT/h]}$ have been plotted against $\frac{1}{T} \times 10^3$ (Fig. A-12), from the slope of which the enthalpy change for the formation of activated complex ΔH^\ddagger has been calculated.

The values of all the Arrhenius parameters are recorded in Table A-15.

TABLE A-15

Temp. A°	$k \times 10^3$ min ⁻¹	Temp. Coe- ffi- cient	E K.Cals. mole ⁻¹	$A \times 10^{-4}$ sec ⁻¹	ΔG^\ddagger K.Cals. mole ⁻¹	ΔS^\ddagger e.u.	ΔH^\ddagger K.Cals. mole ⁻¹
298	0.619	-	-	1.249	21.816	- 33.63	
303	0.914	2.067	13.2512	1.308	22.957	- 33.58	
308	1.280	1.899	12.0865	1.310	22.123	- 33.61	11.503
313	1.736	1.833	11.8144	1.286	22.303	- 33.72	(graphi- cally)
318	2.347	-	-	1.272	22.479	- 33.61	
Mean	-	1.9332	12.384	1.285	22.335	- 33.63	

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 :

$$k = 1.285 \times 10^4 \cdot e^{-12.384/RT} \text{ sec}^{-1}$$

EFFECT OF IONIC STRENGTH :

In order to study the effect of ionic strength on the reaction rate, the reaction was studied in presence of different concentrations of potassium sulphate. The results of these kinetic runs are shown in the following table (Table A-16) and shown graphically in Fig. A-13.

TABLE A-16

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

$$\text{Amide} = 0.1 M, \quad \text{Temp} = 35^\circ C$$

$[K_2SO_4]M$	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 0.02 M- $Na_2S_2O_3$ (viz. C)						
0	9.46	9.46	9.45	9.45	9.52	9.54	9.56
20	8.97	8.97	8.99	9.02	9.07	9.19	9.24
40	8.52	8.53	8.57	8.62	8.68	8.86	8.94
60	8.10	8.13	8.17	8.25	8.31	8.55	8.66
80	7.71	7.76	7.81	7.92	7.98	8.29	8.41
100	7.35	7.51	7.47	7.59	7.67	8.03	8.15
130	6.83	6.92	6.98	7.12	7.23	7.64	7.82
160	6.35	6.46	6.54	6.68	6.25	7.29	7.49
200	5.77	5.93	6.03	6.16	6.37	6.88	7.06
240	5.25	5.44	5.56	5.66	5.92	6.52	6.73
300	4.54	4.78	4.94	5.04	5.29	5.98	6.19
360	3.93	4.19	4.43	4.62	4.72	5.48	5.71
$k_1 \times 10^3$ min^{-1}	2.522	2.425	2.313	2.181	2.129	1.702	1.559
$k_2 \times 10^3$ min^{-1}	1.242	1.235	1.219	1.190	1.167	0.882	0.774
$k \times 10^3$ min^{-1}	1.280	1.190	1.094	0.991	0.962	0.820	0.785

From the above results (Table A-16) it indicates that on increasing the ionic strength, the specific rate decreases. This shows that the salt effect is negative.

Thus, in order to decide the nature of the observed negative salt effect, graphs were plotted between $\log k$ and $\mu^{1/2}$ as well as between k and $\mu^{1/2}$ as shown in Fig. 14(A) and 14(B) respectively. It is observed that a linear relationship is maintained between $\log k$ and $\mu^{1/2}$ whereas there exists no linearity between k and $\mu^{1/2}$. The linearity between $\log k$ and $\mu^{1/2}$ exists only in the region of low ionic strength (< 0.2). Thus it follows that the negative salt effect is of primary exponential type in the region of low ionic strength. This suggests that the rate determining process may be between two oppositely charged ions.

TABLE A-17

$[K_2SO_4]M$	μ	$k \times 10^3$ min^{-1}	$\sqrt{\mu}$	Log k
Nil	0.008	1.280	0.08944	- 2.8927
0.005	0.023	1.190	0.1517	- 2.9225
0.01	0.038	1.094	0.1949	- 2.9609
0.015	0.053	0.991	0.2302	- 3.0039
0.02	0.068	0.962	0.2607	- 3.0168
0.03	0.098	0.820	0.3130	- 3.0861
0.04	0.128	0.785	0.3578	- 3.1051

It may be stated that the ionic strength employed is rather high for Bronsted¹⁸⁸ relationship to be strictly quantitatively applicable but still the agreement is found to be fairly good.

SPECIFIC IONIC STRENGTH :

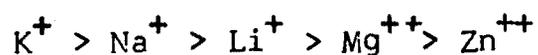
To determine the specific ionic effect on the reaction rate, the reaction was studied in presence of different salts at constant ionic strength. These results are recorded in the following table (Table A-18).

TABLE A-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°C,
 $\mu = 0.212$

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	9.46	9.52	9.55	9.54	9.54	9.55
20	8.97	9.21	9.22	9.19	9.18	9.13
40	8.52	8.94	8.90	8.86	8.85	8.74
60	8.10	8.71	8.61	8.58	8.55	8.39
80	7.71	8.50	8.34	8.32	8.29	8.08
100	7.35	8.31	8.09	8.05	8.03	7.79
130	6.83	8.02	7.74	7.71	7.64	7.40
160	6.35	7.76	7.46	7.38	7.29	7.03
200	5.77	7.42	7.16	6.96	6.88	6.56
240	5.25	7.09	6.82	6.61	6.52	6.16
300	4.54	6.68	6.42	6.11	5.98	5.58
360	3.93	6.23	6.06	5.68	5.48	5.14
$k_1 \times 10^3 \text{ min}^{-1}$	2.522	1.355	1.567	1.650	1.709	1.985
$k_2 \times 10^3 \text{ min}^{-1}$	1.242	0.750	0.820	0.820	0.840	0.960
$k \times 10^3 \text{ min}^{-1}$	1.280	0.655	0.747	0.830	0.869	1.025

From the results contained in Table A-18, it is observed that the specific inhibitory effect of the various ions is in the order



Thus we can conclude that the salt effect is negative.

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 definitely observed that the reaction was not catalysed by the addition of acetic acid.

EFFECT OF ALLYL ACETATE ON REACTION RATE :

To study the effect of allyl acetate on the reaction rate, the reaction was studied in the absence of allyl acetate and at three different initial concentrations of allyl acetate. The results of these kinetic runs are recorded in Table A-19 and shown graphically in Fig. A-16.

TABLE A-19

$K_2S_2O_8 = 2.0 \times 10^{-2} M$, $AgNO_3 = 2.0 \times 10^{-3} M$, Amide = 0.1 M,
Temp = 35°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	9.46	9.46	9.46	9.45
20	8.97	9.05	9.11	9.16
40	8.52	8.67	8.79	8.89
60	8.10	8.32	8.50	8.66
80	7.71	7.98	8.23	8.43
100	7.35	7.66	7.96	8.22
130	6.83	7.30	7.58	7.95
160	6.35	6.91	7.24	7.69
200	5.77	6.41	6.85	7.32
240	5.25	5.98	6.45	7.00
300	5.54	5.35	5.96	6.57
360	3.93	4.81	5.48	6.14
$k \times 10^3 \text{ min}^{-1}$	2.280	2.032	1.691	1.355

From the above results (Table A-19) it is seen that allyl acetate inhibits the rate of reaction. Thus the reactions involving $S_2O_8^{2-}$ are greatly inhibited by allyl acetate which acts as a sulphate radical capture agent. In this case allyl acetate does not act as a very efficient radical

capture¹⁸⁹⁻¹⁹¹ agent. The radical capture may be due to the polymerisation of allyl acetate by sulphate ions formed from the catalysed decomposition of peroxydisulphate ion.

MOLE RATIO :

To determine the number of moles of peroxydisulphate with one mole of substrate (amide), the graphical method was used. This method is described as given below.

$K_2S_2O_8$ was taken in excess as compared to amide. Simultaneously a blank run was also carried out. At suitable intervals of time 5 ml of the reaction mixture was pipetted out and unreacted $K_2S_2O_8$ was estimated. The results of these kinetic runs are recorded in Table A-20, and shown graphically in Fig. A-17.

TABLE A-20

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

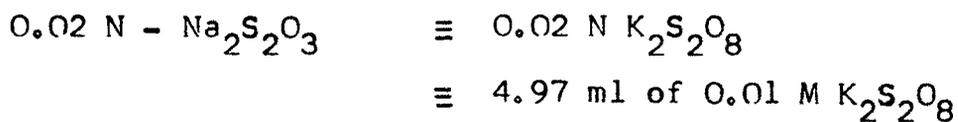
[Amide] M	0.01	Nil
Time (min)	Vol. (in ml.) of $0.2 \text{ M-Na}_2\text{S}_2\text{O}_3$ used (viz.C)	
0	23.94	24.02
30	22.43	23.48
60	21.16	22.45
90	19.58	21.83
120	18.46	20.91
150	17.05	20.31
180	15.98	19.55
210	14.83	18.92
240	13.87	18.24
270	12.95	17.30
300	12.12	16.83
330	11.58	16.44
360	10.98	15.81
390	10.56	15.05
420	10.27	14.42
450	10.03	14.14
480	9.59	13.73

As shown in the Fig. A-17 it is observed that curve consist of two portions. The first portion is for the

oxidation of amide and the second portion for the self decomposition of $K_2S_2O_8$. Now the tangents are drawn on portions 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 10 ml of amide (0.01 M) 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 shown in Fig. A-17 it is seen that the two plots become parallel (for some time) upto P (see graph). At this point $\log C = 1.05$ which corresponds to 11.22 ml. At the same time the corresponding value of $\log C$ on the self decomposition curve is shown by the point Q. At this point $\log C = 1.21$ which corresponds to 16.22 ml. The difference between these two values is 4.97 ml.

Therefore 4.97 ml of



Hence, 5 ml of 0.01 M amide \equiv 4.97 ml.

of 0.01M $K_2S_2O_8$.

So one mole of amide approximately consumes one mole of $K_2S_2O_8$ for complete reaction.

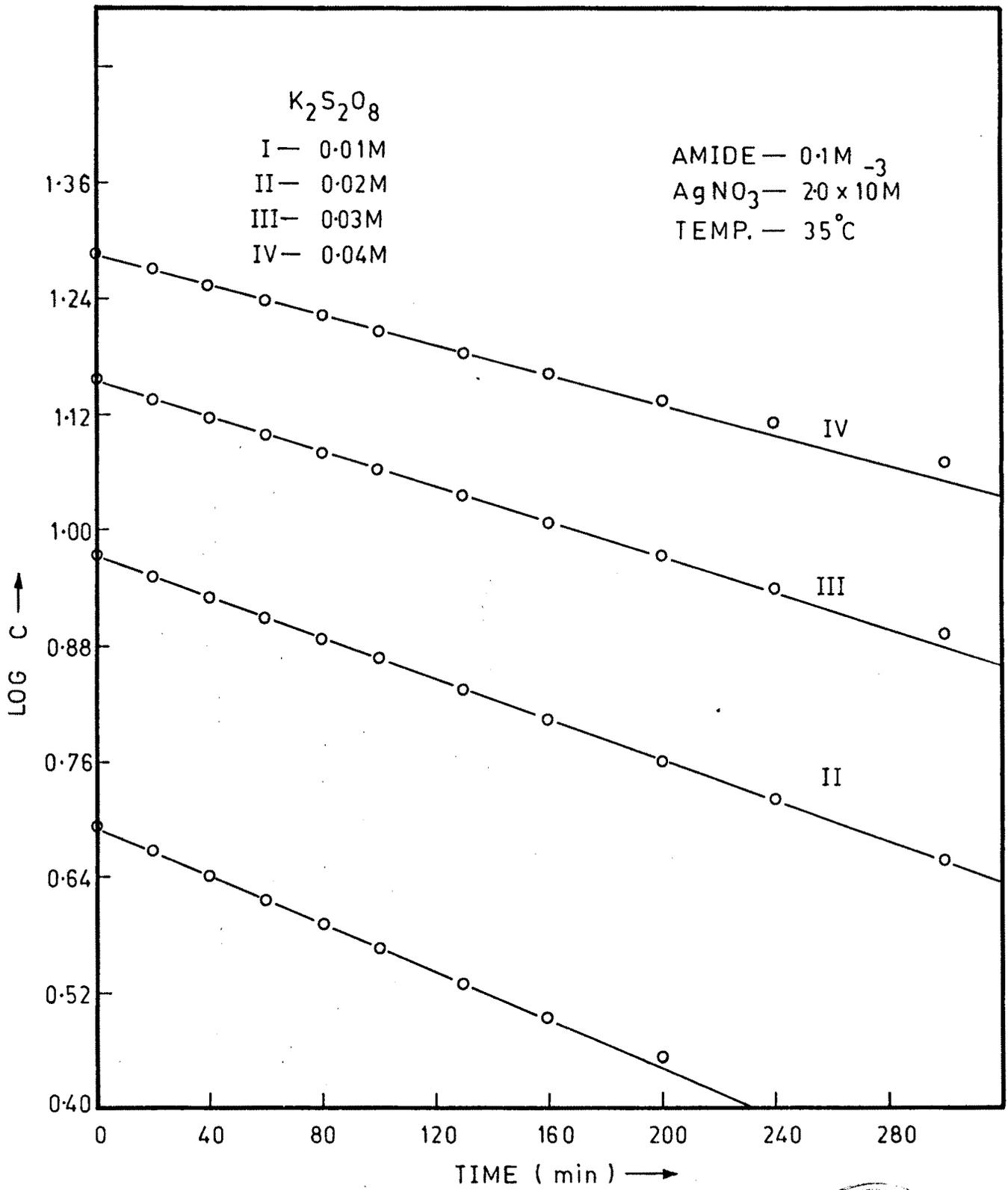


FIG. A-1 EFFECT OF $K_2S_2O_8$



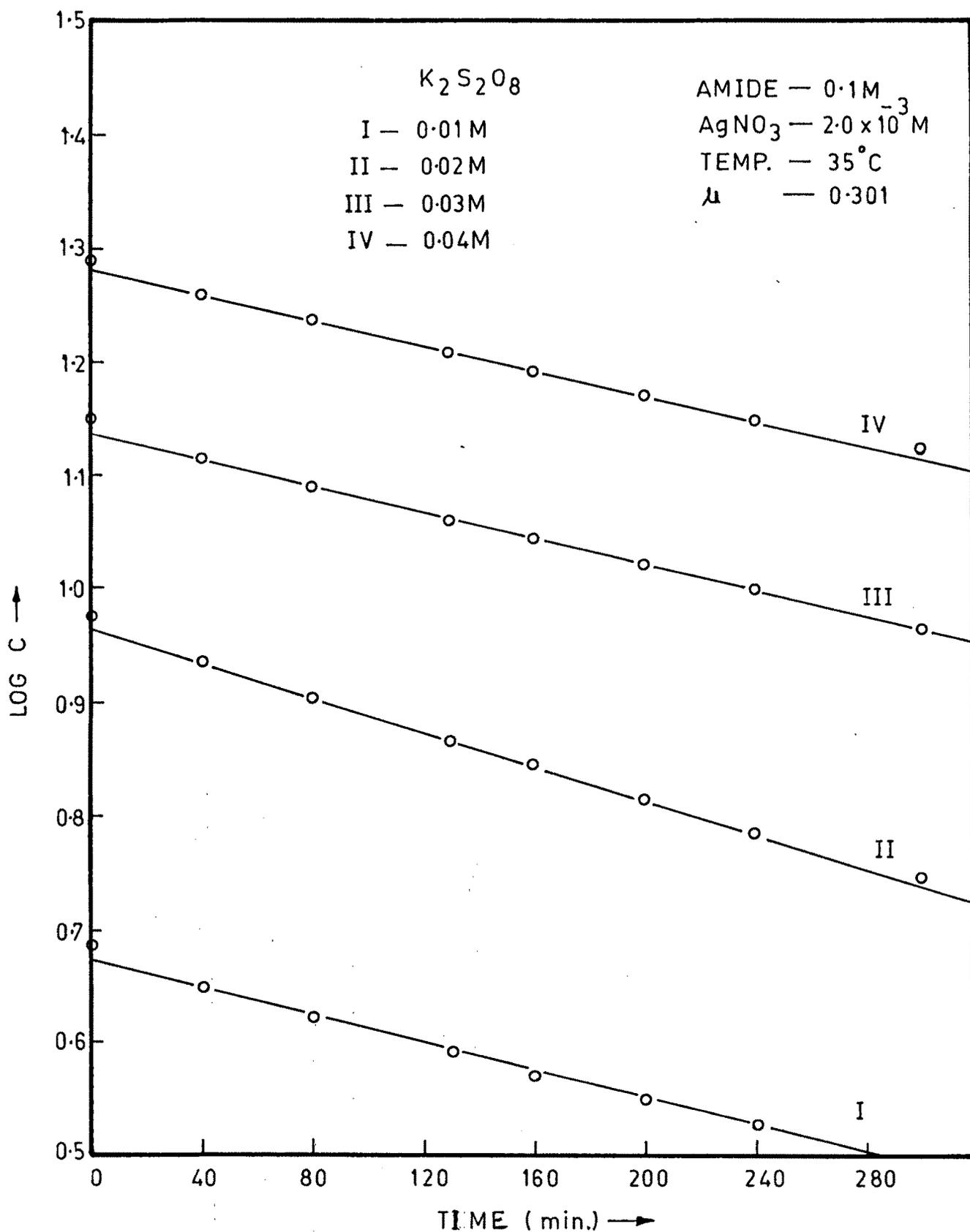


FIG. A-2 EFFECT OF $K_2S_2O_8$ AT CONSTANT μ .

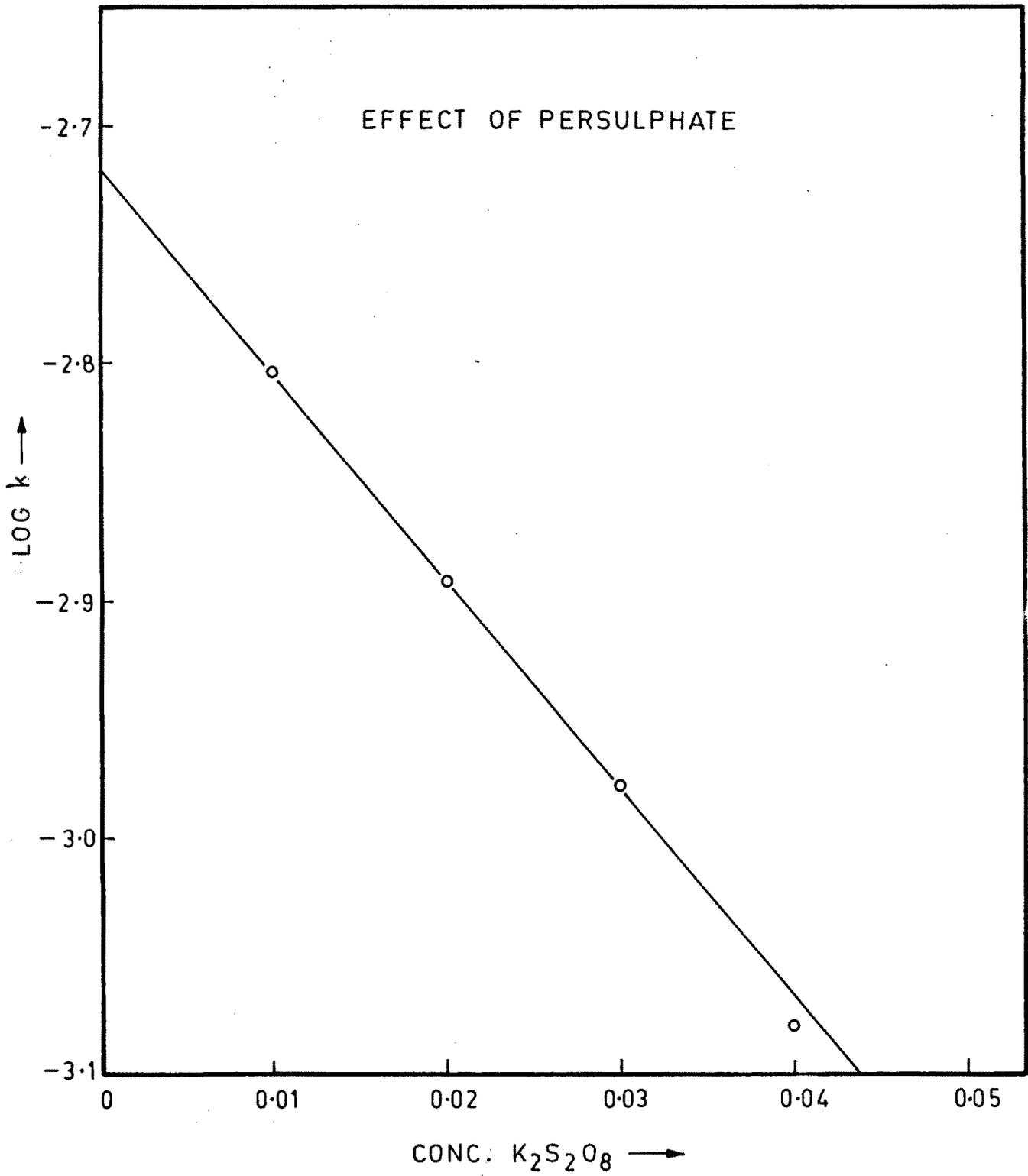


FIG. A-3 PLOT OF $\text{LOG } k$ VS. CONC OF $K_2S_2O_8$.

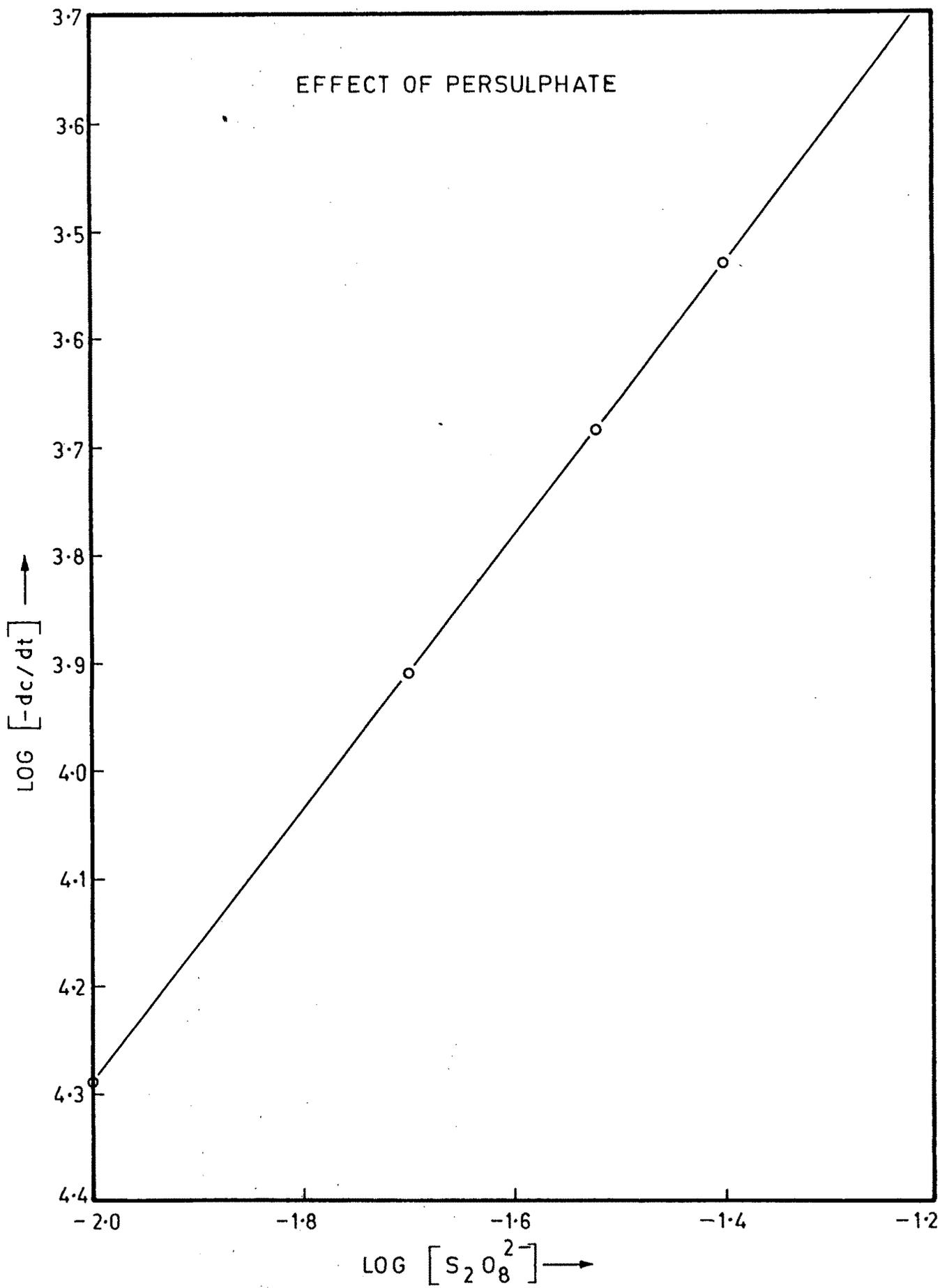


FIG. A-4 PLOT OF $\text{LOG} [-dc/dt]$ vs $\text{LOG} [S_2O_8^{2-}]$

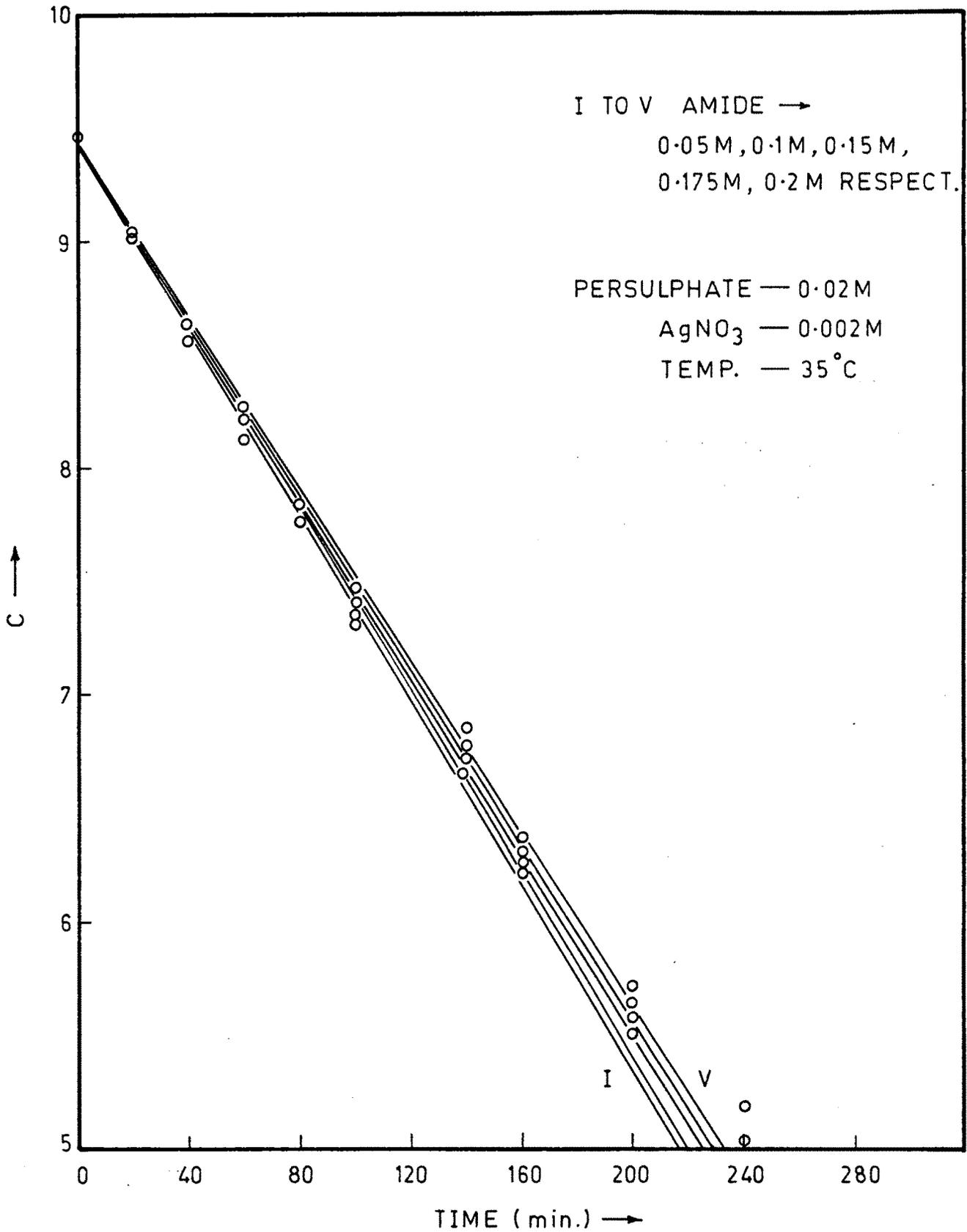


FIG. A-5 EFFECT OF AMIDE ['C' VS. TIME] .

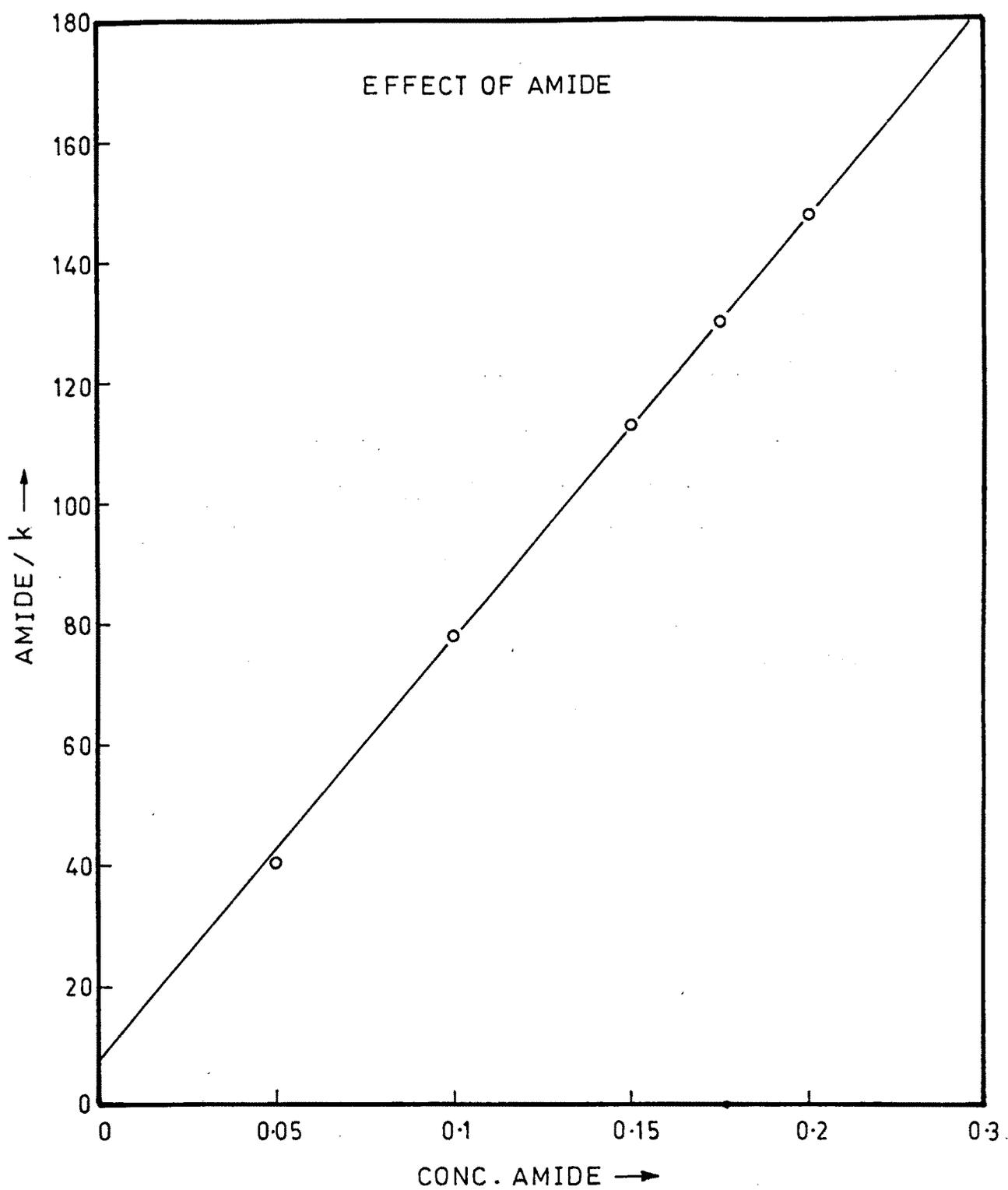


FIG. A-6 PLOT OF AMIDE / k VS. k .

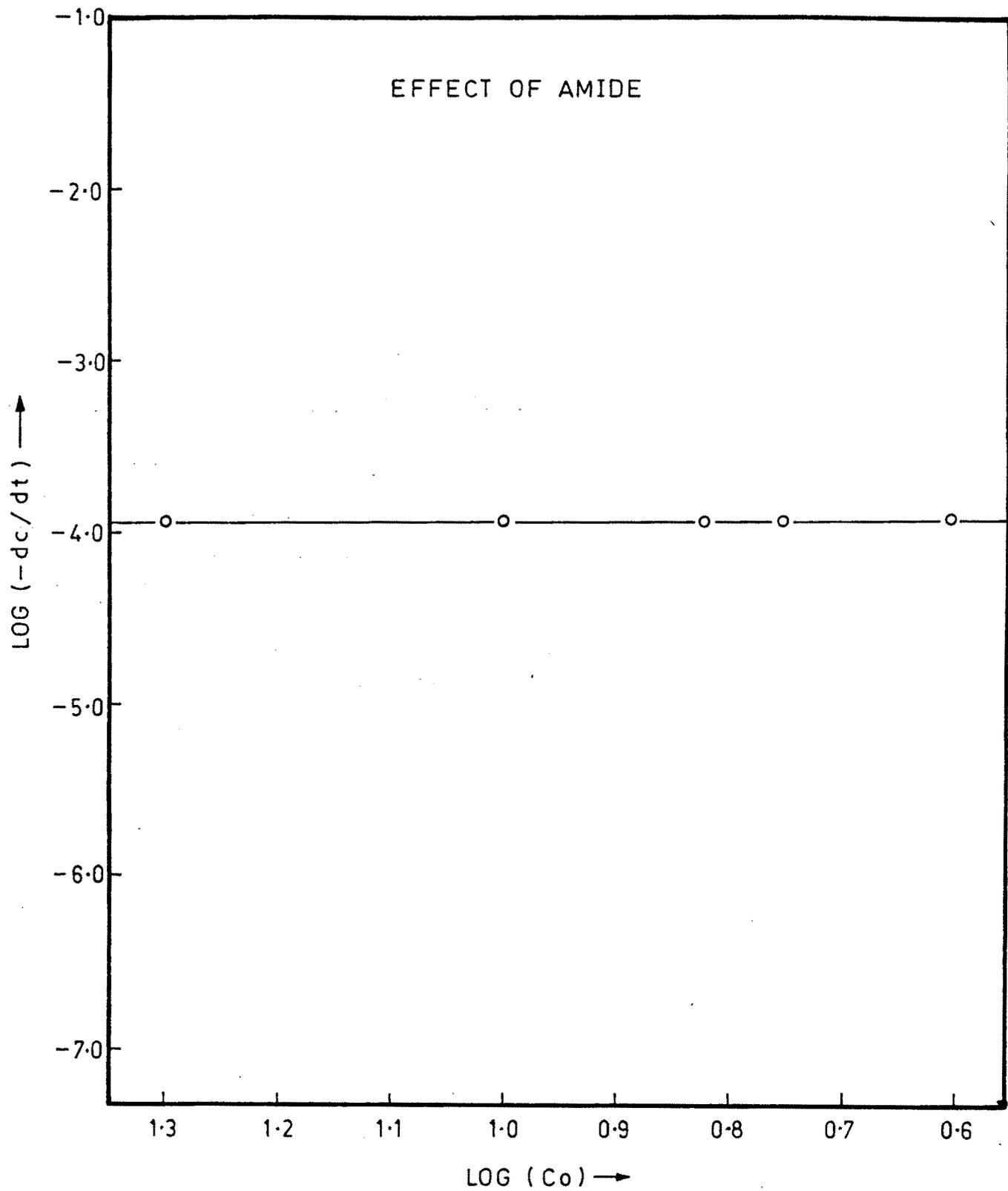


FIG. A-7 PLOT OF $\text{LOG}(-dc/dt)$ VS $\text{LOG}(C_0)$.

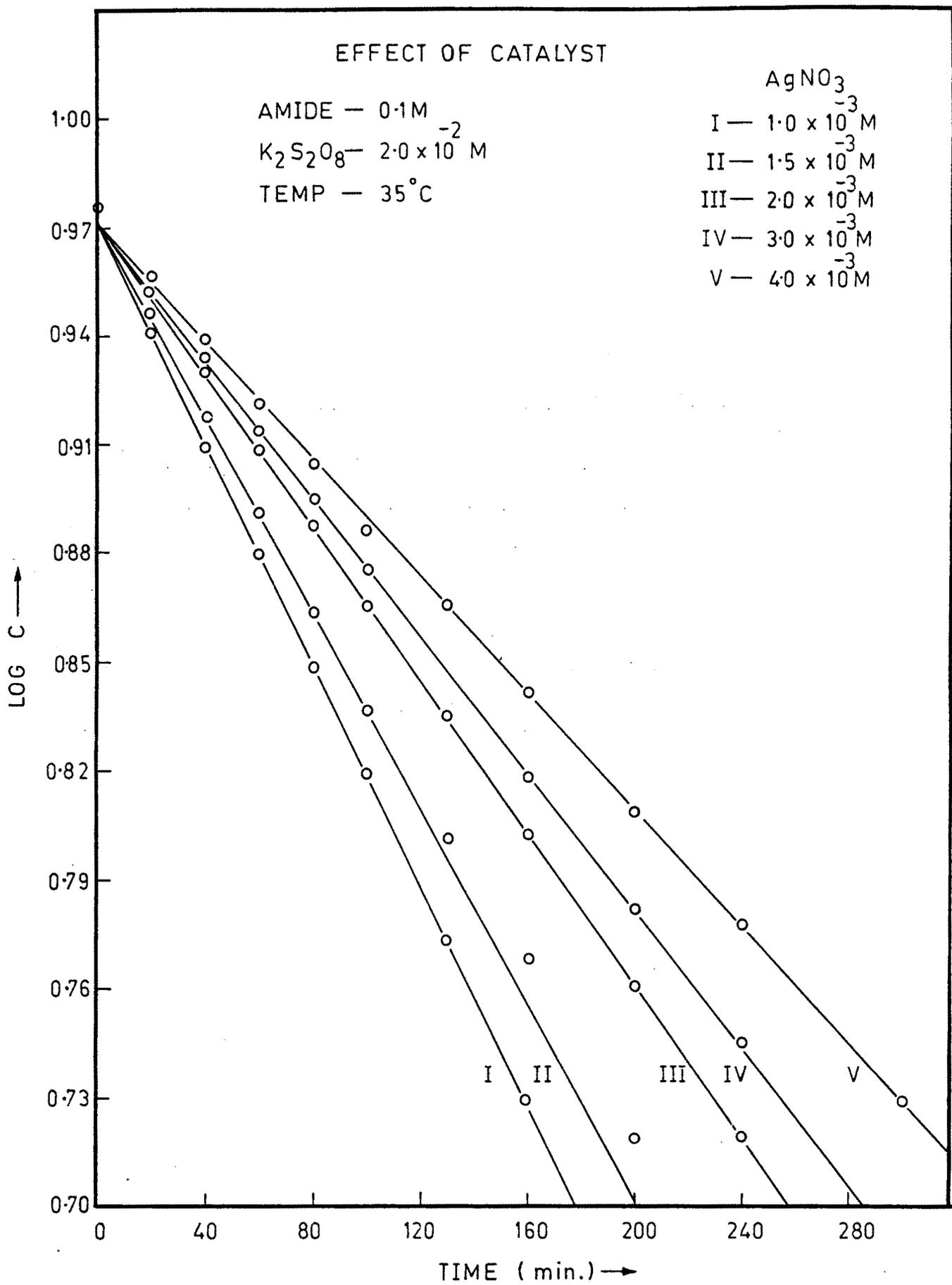


FIG. A-8

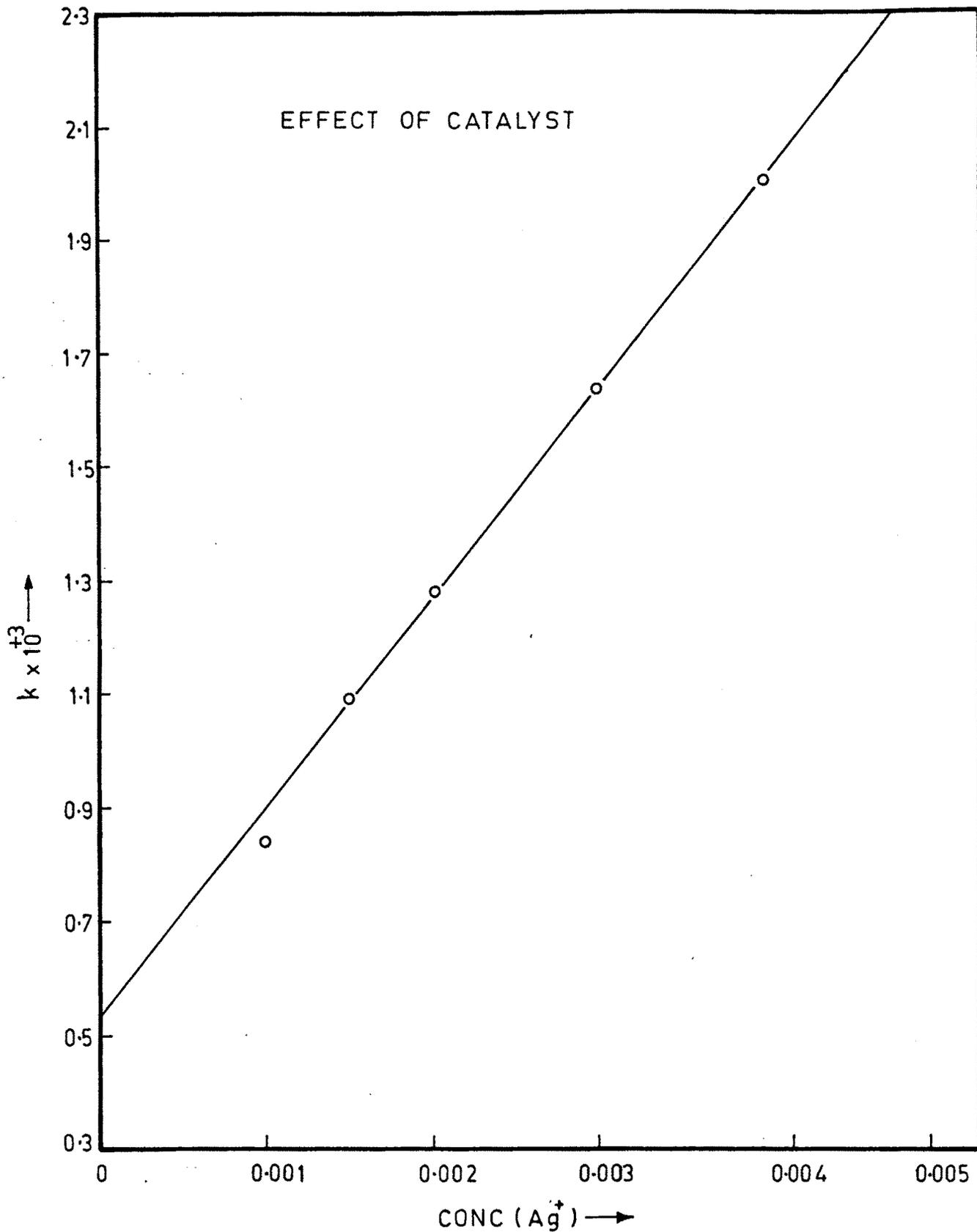


FIG. A-9 PLOT OF $k \times 10^3$ VS. CONC (Ag⁺) .

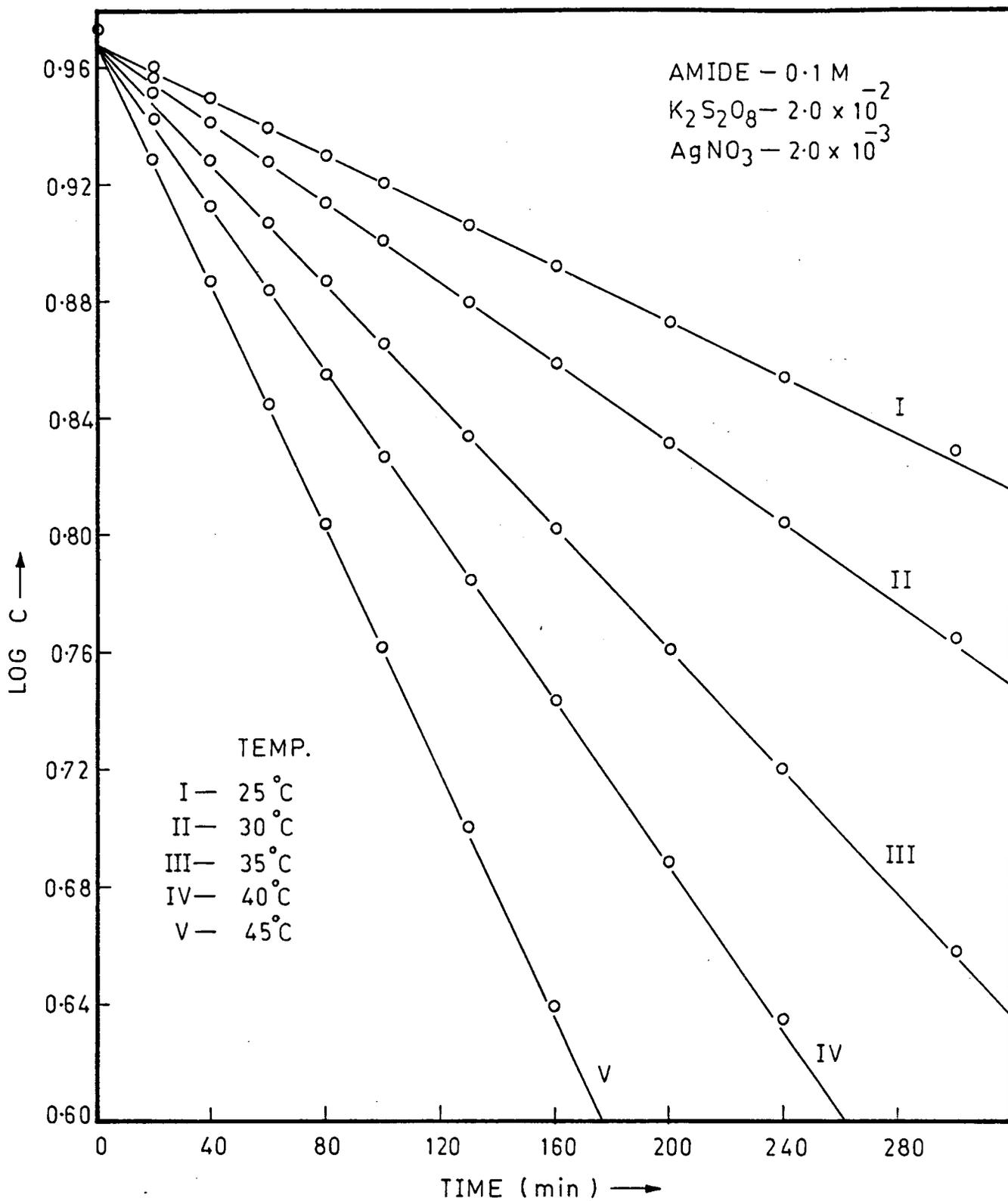


FIG. A-10 EFFECT OF TEMPERATURE .

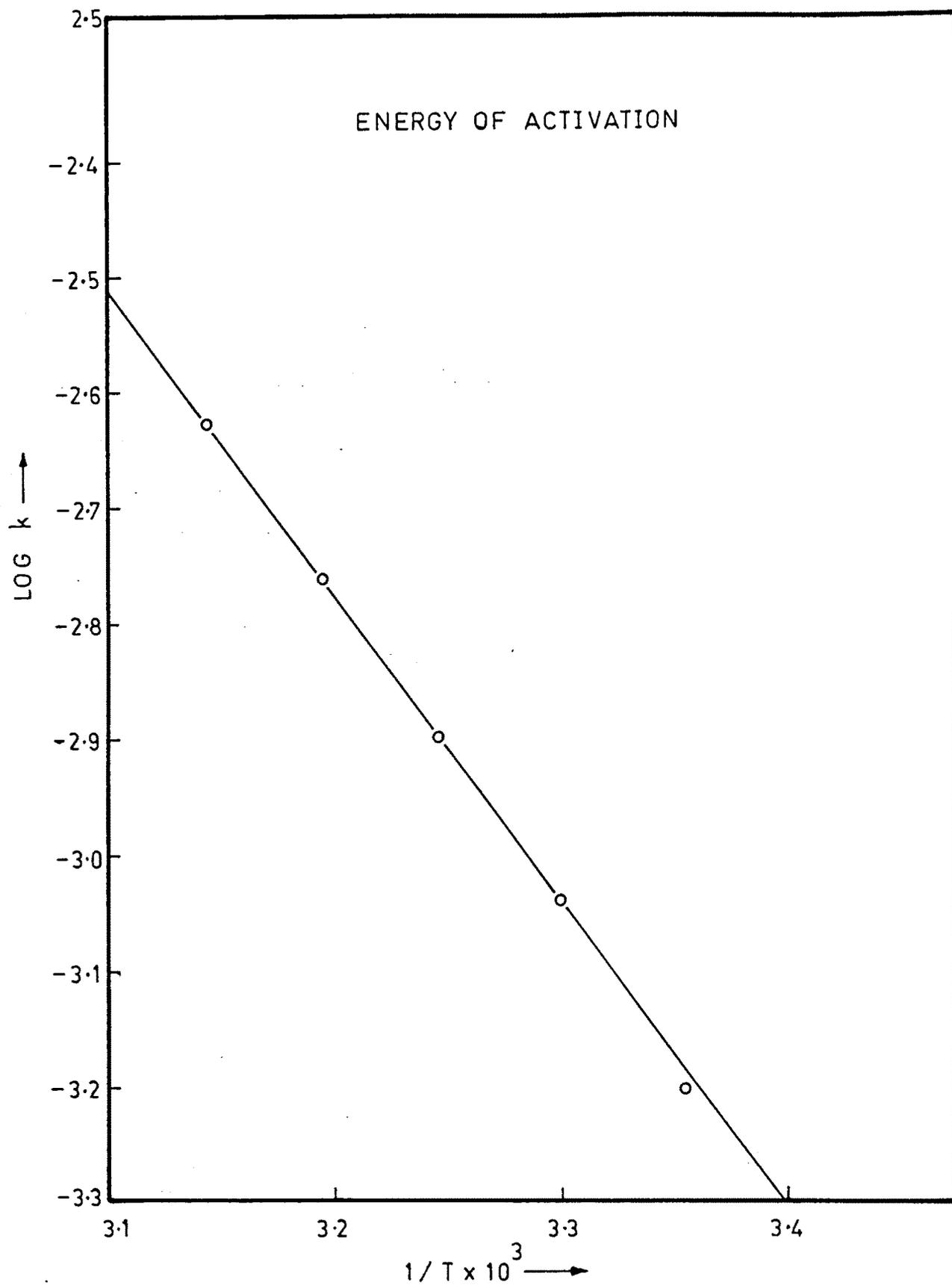


FIG A-11 PLOT OF $\log k$ VS $1/T \times 10^3$

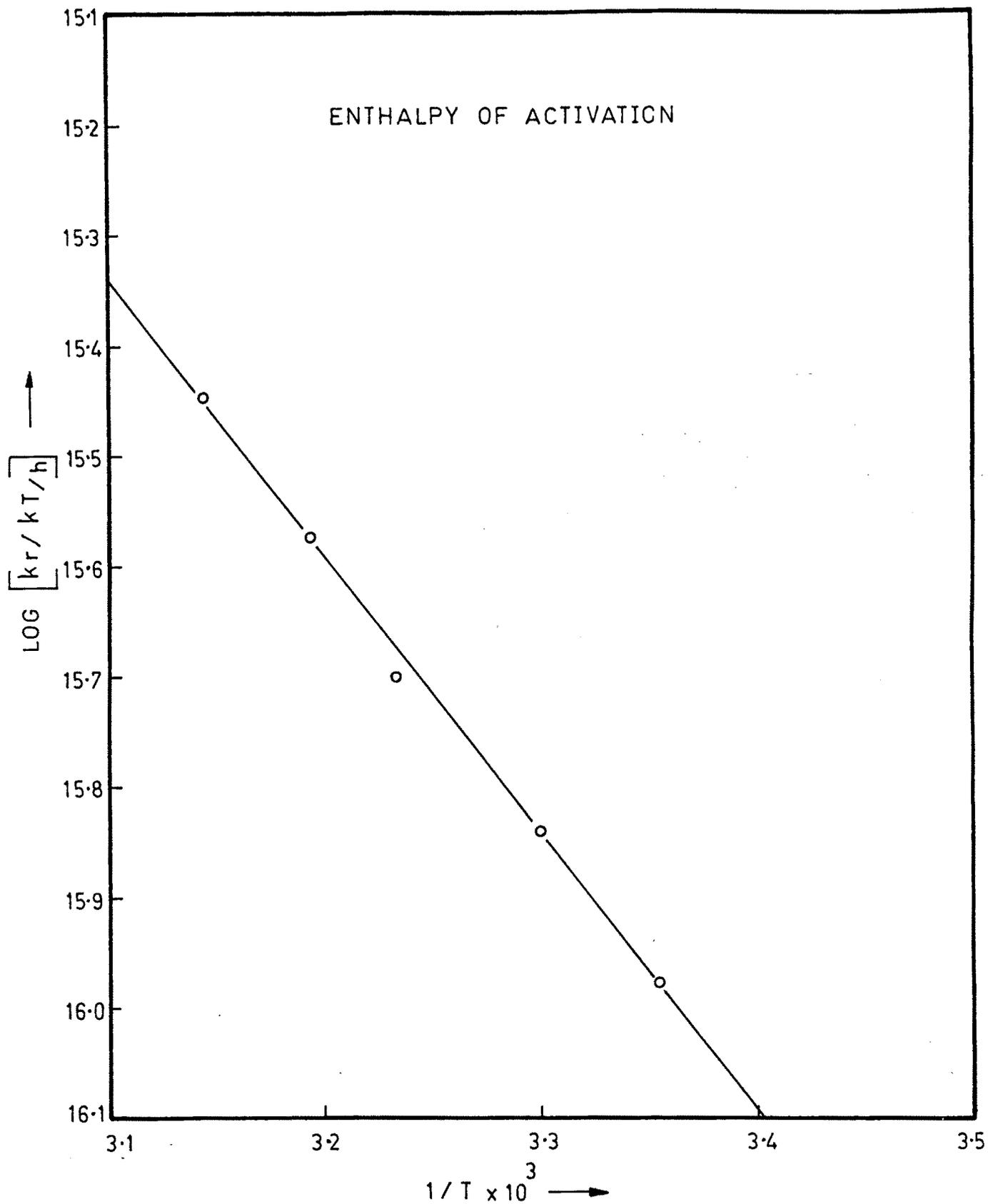


FIG A-12 PLOT OF $\text{LOG} \left[\frac{k_r}{kT/h} \right]$ VS $1/T \times 10^3$.

EFFECT OF IONIC STRENGTH

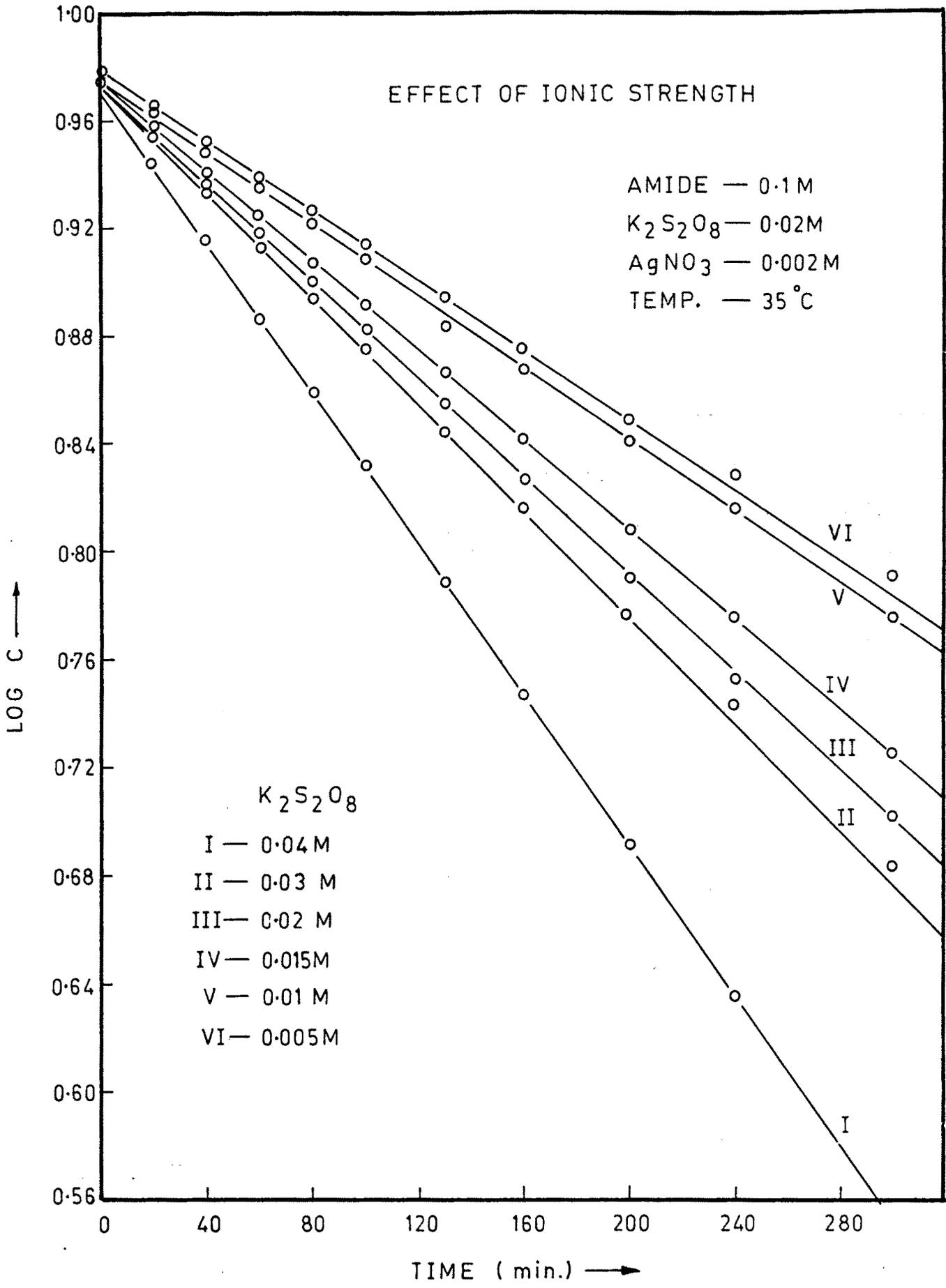


FIG. A-13

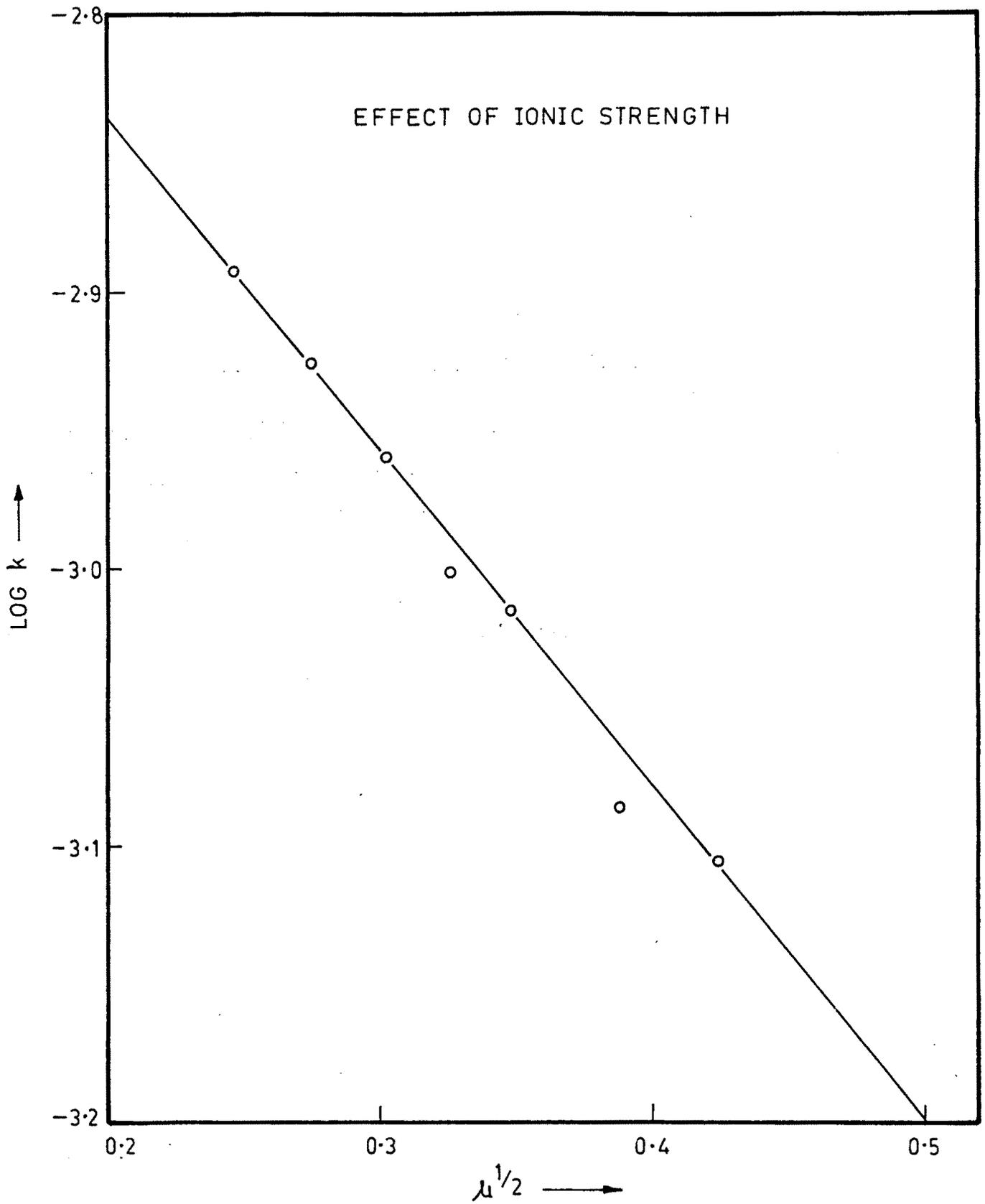


FIG A-14(a) PLOT OF LOG k VS $\mu^{1/2}$.

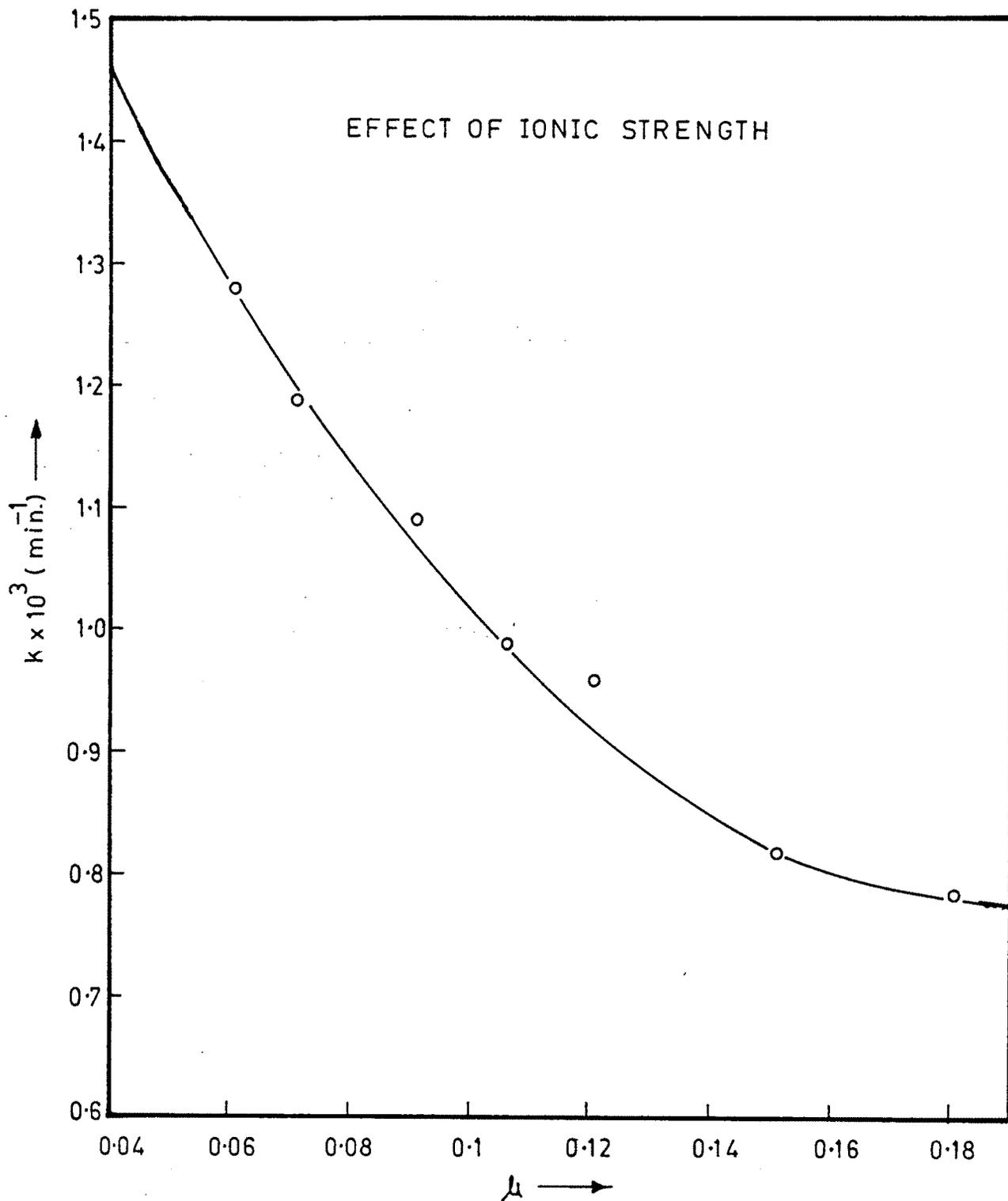


FIG. A-14(b) PLOT OF k VS. μ .

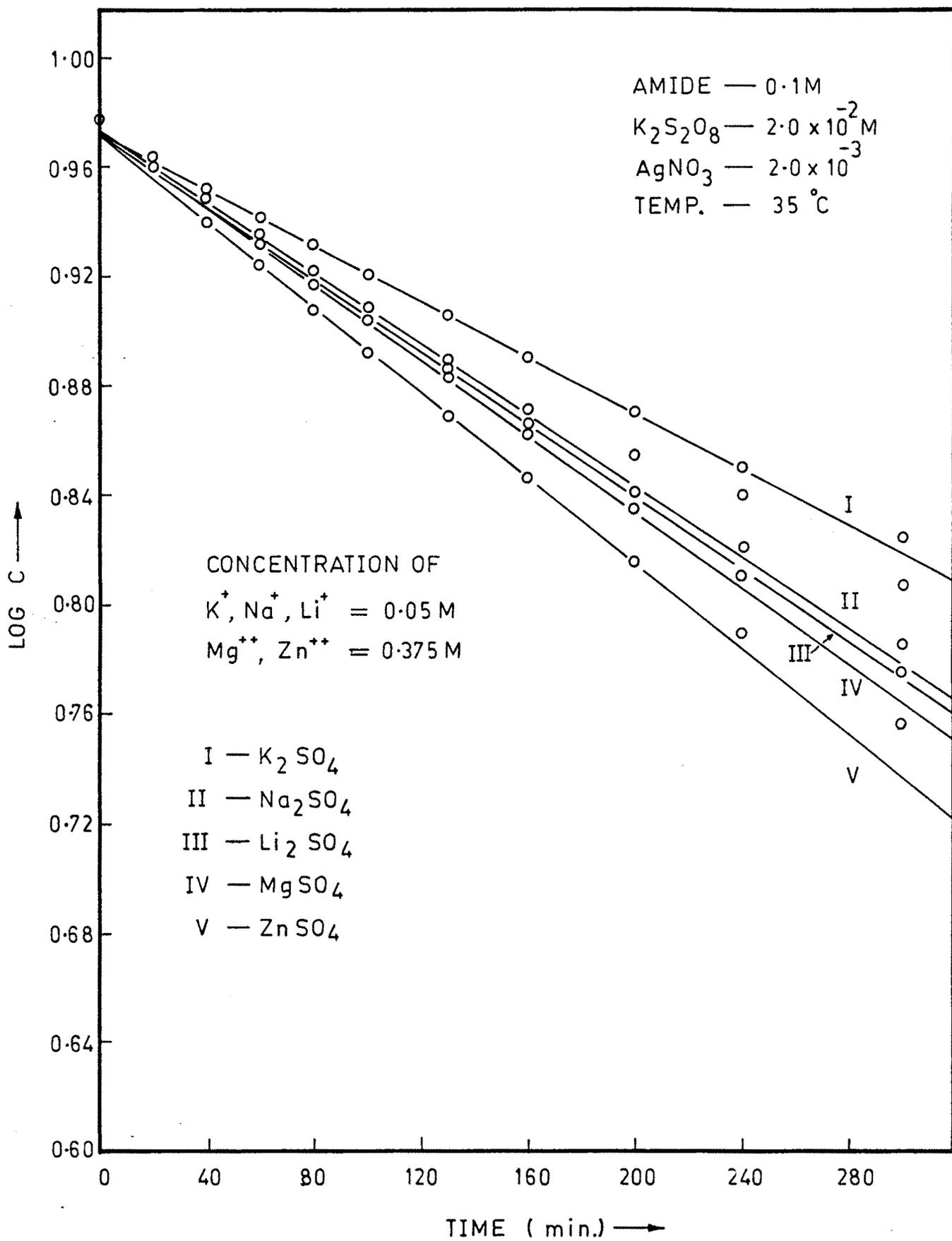


FIG. A-15

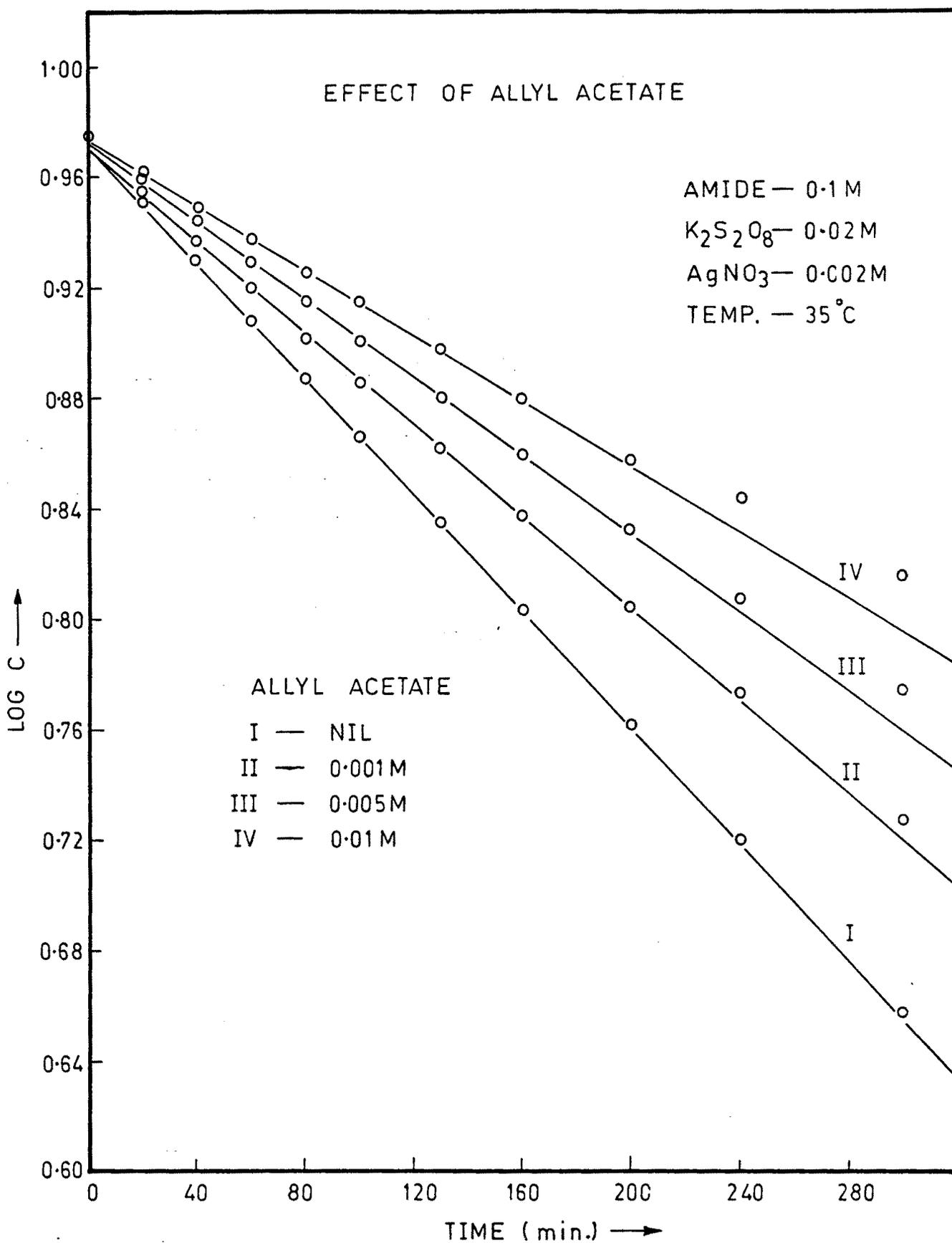


FIG. A-16

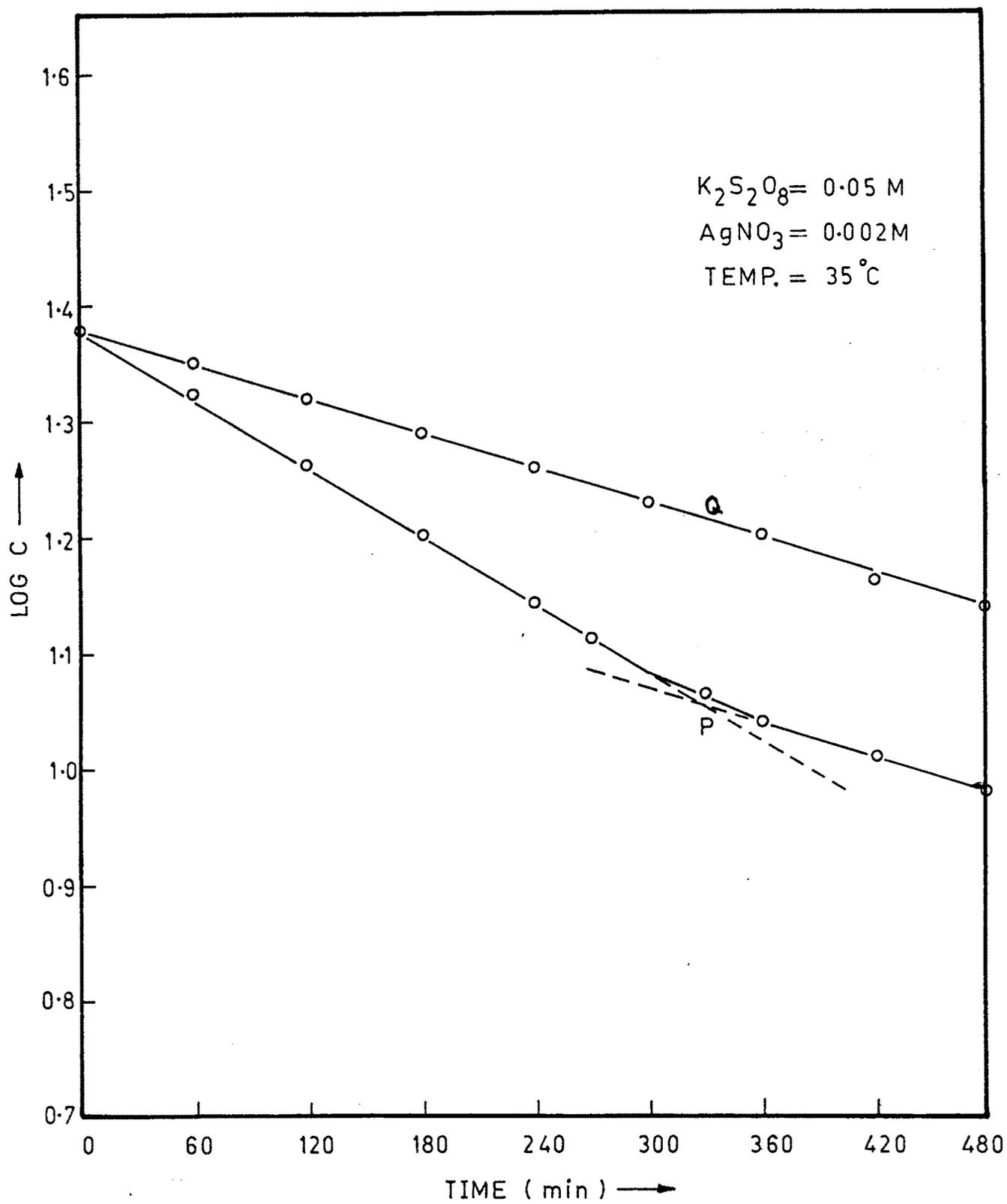


FIG. A-17 MOLE RATIO .