

CHAPTER-III

OXIDATION OF PYRUVAMIDE

CHAPTER - IIIOXIDATION OF PYRUVAMIDE :

Preliminary experiments were performed in order to decide the suitable temperature, catalyst and concentrations of the reactants. It was found that the uncatalysed reaction at room temperature is extremely slow, but in the presence of $2.0 \times 10^{-3} \text{ M Ag}^+$ as a catalyst, the reaction proceeds with the measurable velocity at 35°C . Hence the reaction was first carried out at 35°C , taking the overall concentration of $\text{K}_2\text{S}_2\text{O}_8$ as $2.0 \times 10^{-2} \text{ m}$ and pyruvamide as 0.1 m together with $2.0 \times 10^{-3} \text{ M}$. as silver catalyst, the kinetic data for which are recorded in the following table (Table A-1).

It must be mention here that, due to low solubility of pyruvamide in water, the solution of pyruvamide was prepared in 50 % (v/v) acetic acid.

Table A-1 : Pyruvamide = 0.1 m, $K_2S_2O_8 = 2.0 \times 10^{-2}$ m
 $AgNO_3 = 2.0 \times 10^{-3}$ M, Temp = 35°C

Time (m̄n)	C^*	$k_1 \times 10^3 \text{ min}^{-1}$
0	9.46	-
20	8.74	3.915
40	8.10	3.879
60	7.51	3.829
80	6.97	3.812
100	6.48	3.775
130	5.81	3.752
160	5.23	3.707
200	4.53	3.686
240	3.91	3.681
300	3.16	3.655
360	2.46	3.647
Mean $k_1 \times 10^3 \text{ min}^{-1}$		3.758

$[C^*$ denotes the volume of 0.02 M - $Na_2S_2O_3$
in ml. equivalent to unreacted $S_2O_8^{2-}$]

From the above data (Table A-1) it indicates that the first order rate constant goes on slightly decreasing with time. This shows 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 decrease in the first order rate constant with time. In the above experiment, the quantity of amide has been taken in excess, its concentration is more than that of $K_2S_2O_8$, hence the order is with respect to $S_2O_8^{2-}$ ion.

To decide conclusively, the order w.r.t. $S_2O_8^{2-}$ as well as w.r.t. to amide, the reaction was carried out at equimolar concentrations of $K_2S_2O_8$ and amide (viz. 0.02 m each), keeping the temperature and concentration of the catalyst unchanged. The following table (Table A-2) contains the results of this run.

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	C	$k_1 \times 10^3 \text{ min}^{-1}$
0	9.47	-
20	8.39	6.033
40	7.45	5.998
60	6.63	5.949
80	5.89	5.940
100	5.25	5.899
130	4.43	5.847
160	3.74	5.803
200	2.98	5.777
240	2.37	5.769
300	1.69	5.748
360	1.20	5.737
Mean $k_1 \times 10^3 \text{ min}^{-1}$		5.863

Here again, it has been observed that the first order rate constant slightly decreases with time, which probably may be due to some inhibition as the reaction progresses. The nearly constant values of the rate constant suggest that the order w.r.t. amide may be zero.

EFFECT OF PEROXYDISULPHATE ION CONCENTRATION :

It has been observed that, by increasing the initial concentration of $K_2S_2O_8$ the first order rate constant decreases. 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 the ionic strength or due to the specific inhibitory effect of K^+ ion or due to both.

It is seen that, in any particular run, the first order rate constant decreases with time. Since the reactions involving $S_2O_8^{2-}$ ions are highly susceptible to traces of impurities. Hence the amide was recrystallized and the effect of $S_2O_8^{2-}$ concentration was studied.

The self decomposition of $S_2O_8^{2-}$ was also studied simultaneously, the kinetic data of which are given 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	$k_2 \times 10^3 \text{ min}^{-1}$	C	$k_2 \times 10^3 \text{ min}^{-1}$	C	$k_2 \times 10^3 \text{ min}^{-1}$	C	$k_2 \times 10^3 \text{ min}^{-1}$
0	4.98	-	9.48	-	14.75	-	19.44	-
20	4.82	1.625	9.21	1.470	14.35	1.382	18.97	1.215
40	4.68	1.538	8.95	1.434	14.00	1.307	18.58	1.131
60	4.54	1.525	8.75	1.384	13.67	1.267	18.20	1.098
80	4.41	1.524	8.44	1.367	13.37	1.227	17.81	1.091
100	4.30	1.476	8.30	1.330	13.10	1.186	17.44	1.085
130	4.13	1.439	8.01	1.307	12.77	1.109	16.93	1.063
160	3.97	1.422	7.75	1.262	12.37	1.101	16.42	1.055
200	3.74	1.412	7.40	1.241	11.90	1.074	15.92	0.955
240	3.56	1.403	7.05	1.236	11.40	1.074	15.33	0.989
300	3.29	1.385	6.60	1.210	10.75	1.054	14.51	0.973
360	3.04	1.368	6.15	1.202	10.20	1.024	13.98	0.915
Mean	-	1.466	-	1.313	-	1.164	-	1.055

It must be mentioned here that in all subsequent 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 on account of pressure on space and only the corresponding values of the rate constants (viz. k_2) have been recorded directly at the end of each table.

Thus, in order to investigate the effect of $S_2O_8^{2-}$ ion concentration and . to decide the order of the reaction conclusively, the reaction was studied at three different concentrations of $S_2O_8^{2-}$, keeping the concentrations of the amide and silver catalyst unchanged. Table A-4 shows the results of these kinetic runs, and for the comparison sake the data of Table A-1 has been incorporated in it. These results have been plotted graphically in Fig. A-1. From the initial slope of the curves the first order rate constant of the reaction (viz - k_1) is evaluated. The rate constant (k_1) at different times has been calculated by the integration method. The net rate constant (viz k) for the oxidation of the reductant has been obtained after deducting the value of the rate constant (viz. k_2) for the self decomposition of $S_2O_8^{2-}$ studied simultaneously.

Table A-4 : Amide 0.1 M, $\text{AgNO}_3 = 2.0 \times 10^{-3} \text{M}$,
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	$k_1 \times 10^3$ 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	-	14.27	-	19.54	-
20	4.55	4.256	8.74	3.915	13.28	3.589	18.35	3.139
40	4.18	4.224	8.10	3.879	12.38	3.559	17.26	3.109
60	3.85	4.176	7.51	3.829	11.56	3.509	16.26	3.059
80	3.55	4.156	6.97	3.812	10.78	3.488	15.23	3.039
100	3.28	4.121	6.48	3.775	10.14	3.479	14.48	2.999
130	2.91	4.081	5.81	3.752	9.17	3.399	13.24	2.989
160	2.59	4.045	5.23	3.707	8.35	3.349	12.23	2.929
200	2.21	4.024	4.53	3.686	7.33	3.329	10.99	2.879
240	1.90	4.012	3.91	3.681	6.42	3.327	9.83	2.859
300	1.50	3.986	3.16	3.655	5.30	3.299	8.33	2.844
360	1.18	3.981	2.46	3.647	4.36	3.294	7.05	2.834
$k_1 \times 10^3 \text{min}^{-1}$	-	3.981	-	3.758	-	3.410	-	2.970
$k_2 \times 10^3 \text{min}^{-1}$	-	1.466	-	1.313	-	1.164	-	1.055
$k \times 10^3 \text{min}^{-1}$	-	2.515	-	2.445	-	2.246	-	1.925

From the above data (Table A-4) 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 do not have constant ionic strength as well as constant K^+ ion concentration, so it was considered to reinvestigate this effect at constant ionic strength as well as at constant K^+ ion concentration, so that the effect of both these parameters may be eliminated. The results of these kinetic runs are recorded in Table A-5 and also shown graphically in Fig. A-2.

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 0.02 M- $\text{Na}_2\text{S}_2\text{O}_3$ used (viz.C)			
0	4.92	9.44	14.26	19.54
20	4.60	8.85	13.43	18.58
40	4.31	8.31	12.66	17.69
60	4.05	7.82	11.97	16.88
80	3.80	7.36	11.30	16.09
100	3.57	6.94	10.71	15.38
130	3.26	6.39	9.92	14.49
160	2.98	5.86	9.19	13.63
200	2.65	5.23	8.23	12.52
240	2.35	4.65	7.43	11.48
300	1.96	3.92	6.35	10.12
360	1.64	3.31	5.43	8.91
$k_1 \times 10^3 \text{ min}^{-1}$	3.192	3.042	2.820	2.332
$k_2 \times 10^3 \text{ min}^{-1}$	0.73	0.72	0.70	0.70
$k \times 10^3 \text{ min}^{-1}$	2.462	2.322	2.120	1.632

From the above results (Table A-5), it indicates that, when the concentration of $S_2O_8^{2-}$ was increased the first order rate constant was decreased. Khan¹¹² and Srivastava observed the same type of effect while studying the oxidation of ethylene glycol by peroxydisulphate ion.

Table A-6 represents the comparison between k values with increasing concentration of $[S_2O_8^{2-}]$ without $S_2O_8^{2-}$ and with K_2SO_4 to maintain constant ionic strength and constant K^+ concentration in the later case.

Table A-6 : Amide = 0.1 M, $AgNO_3 = 2.0 \times 10^{-3} M$, Temp = 35°C.

Conc. $K_2S_2O_8$ without K_2SO_4 (M)	$k \times 10^3$ min^{-1}	Conc. $K_2S_2O_8$ with constant ionic strength (M)	$k \times 10^3$ min^{-1}
0.01	2.515	0.01	2.462
0.02	2.445	0.02	2.322
0.03	2.246	0.03	2.120
0.04	1.925	0.04	1.632

From the results contained in Table A-6 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 due to the increase in ionic strength as well as due to increase in K^+ ion concentration, both causing inhibition, This exists a persistent rate decreasing tendency even though the reaction is carried out at constant ionic strength as well as constant K^+ ion concentration which leads me to conclude that, it is probably due to some trace impurity remaining in peroxydisulphate sample even after recrystallization, which however, could not be characterized.

A plot of $-\log k$ versus concentration of $K_2S_2O_8$ is found to be linear as shown in Fig. A-3. The following relationship between $-\log k$ and concentration of $K_2S_2O_8$ is being followed.

$$-\log k = 2.525 + 5.624 [S_2O_8^{2-}]_0$$

Provided that $[S_2O_8^{2-}]_0 \neq \text{Zero}$

ORDER WITH RESPECT TO PEROXYDISULPHATE :

The order with respect to peroxydisulphate was determined by Vant Hoff's differential¹⁹³ 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.

Table A-7

Conc. $[S_2O_8^{2-}]$	$-\frac{dc}{dt} \times 10^{-4}$	$\text{Log}[S_2O_8^{2-}]$	$\text{Log}(-\frac{dc}{dt})$
0.01	0.54	- 2.0000	- 2.4676
0.02	1.26	- 1.6990	- 3.8996
0.03	2.14	- 1.5229	- 3.6696
0.04	2.868	- 1.3979	- 3.5425

The values of $-\frac{dc}{dt}$ and conc. $[S_2O_8^{2-}]$ i.e. 'C' are substituted in the Vant¹⁹³ Hoff's differential equation :

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

and the order of the reaction was calculated thereby.

The values of $(-dc/dt)$ for the different initial concentrations of $S_2O_8^{2-}$ and the values of n(order of reaction) calculated thereby are recorded in Table A-8.

Table A-8

$[\text{K}_2\text{S}_2\text{O}_8]$ M	$-\text{dc}/\text{dt} \times 10^{-4}$	Order of reaction n
0.01	0.54	1.2215
0.02	1.26	
0.01	0.54	1.2534
0.03	2.14	
0.01	0.54	1.2040
0.04	2.868	
0.02	1.26	1.1885
0.04	2.868	
0.03	2.14	1.0175
0.04	2.868	

A plot of $\log -\text{dc}/\text{dt}$ versus $\log \text{S}_2\text{O}_8^{2-}$ is shown in Fig. A-4. The slope of the curve is 1.10 as such the order with respect to $\text{S}_2\text{O}_8^{2-}$ is one, which is confirmed by the value on n as shown in the above table (Table A-8).

EFFECT OF AMIDE CONCENTRATION :

In order to study the effect of amide concentration on the reacting rate, the reaction was studied at five different initial concentrations of amide (varying from 0.025 M to 0.125 M) keeping the concentrations of $\text{K}_2\text{S}_2\text{O}_8$ and AgNO_3 constant. The results of these kinetic runs 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	0.1	0.150	0.175	0.20
Time (min)	Vol. (in ml) of $0.02 M-Na_2S_2O_3$ used (viz.C)				
0	9.45	9.46	9.44	9.46	9.45
20	8.78	8.74	8.71	8.73	8.74
40	8.17	8.10	8.04	8.07	8.10
60	7.61	7.51	7.44	7.47	7.51
80	7.09	6.97	6.88	6.91	7.14
100	6.62	6.48	6.39	6.42	6.48
130	5.98	5.81	5.73	5.78	5.87
160	5.42	5.23	5.15	5.18	5.28
200	4.74	4.53	4.44	4.49	4.61
240	4.14	3.91	3.83	3.88	3.99
300	3.38	3.16	3.07	3.12	3.24
360	2.27	2.46	2.47	2.51	2.63
$k_1 \times 10^3 \text{ min}^{-1}$	3.530	3.758	3.865	3.829	3.708
$k_2 \times 10^3 \text{ min}^{-1}$	1.313	1.313	1.313	1.313	1.313
$k \times 10^3 \text{ min}^{-1}$	2.217	2.445	2.552	2.516	2.395

From the above results (as shown in Table A-9), it indicates that, when the concentration of amide was increased, there is no effect on the reaction rate. The rate constant does not show any variation and practically remains constant indicating the zero order behaviour of the reaction.

The specific rate is seen to be a function of the initial concentration of both $S_2O_8^{2-}$ and $CH_3 \cdot CO \cdot CONH_2$ governed by the expression.

$$k = k_{\max} \cdot \frac{(CH_3 \cdot CO \cdot CONH_2)_0}{b + (CH_3 \cdot CO \cdot CONH_2)_0}$$

In support of the above equation, a plot of $\frac{(CH_3 \cdot CO \cdot CONH_2)_0}{k}$ versus $(CH_3 \cdot CO \cdot CONH_2)_0$ was found to be linear (Fig A-6) from which the values of k_{\max} and b were calculated. The values of k_{\max} was 0.002381 and b was 0.02856. From these values k was calculated and was found to be equal to $k = 2.215 \times 10^{-3}$ which was almost identical with 2.445×10^{-3} the experimental value.

ORDER WITH RESPECT TO AMIDE :

A general behaviour of Ag^+ catalysed redox reactions involving peroxydisulphate is that, the order with respect to the reductant is zero. To confirm the order of the 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 $-\frac{dc}{dt}$ corresponding to various initial concentration of amide were evaluated. These values are recorded in Table A-10.

Table A-10

Conc. of Amide (M)	$-\frac{dc}{dt} \times 10^{-4}$	$\text{Log}[C_0]$	$\text{Log}(-\frac{dc}{dt})$
0.05	1.05	- 1.3010	- 3.9789
0.1	1.06	- 1.0000	- 3.9747
0.150	1.03	- 0.8239	- 3.4872
0.175	1.05	- 0.7569	- 3.9790
0.20	1.11	- 0.6021	- 3.9547

A plot of $\log \left(-\frac{dc}{dt}\right)$ versus $\log (\text{Amide})$ is shown in fig. A-7. It gives the values of the slope as zero, which suggests that the reaction is of Zero Order w.r.t. amide. Calculations were made for the order of reaction by Van't Hoff's differential method as given in Table A-11.

Table A-11

[Amide]M	$\left(-\frac{dc}{dt}\right) \times 10^{-4}$	Order of reaction (n)
0.05	1.05	0.1478
0.1	1.06	
0.05	1.05	0.1259
0.150	1.03	
0.05	1.05	0.0555
0.2	1.11	
0.10	1.06	0.1011
0.15	1.03	
0.10	1.06	0.02956
0.20	1.11	

This confirms that the order w.r.t. amide is zero.

EFFECT OF SILVER CATALYST CONCENTRATION :

In order to study the effect of different concentrations of the catalyst on the reaction rate, the reaction was studied at five different concentrations of Silver nitrate, keeping the concentrations of peroxydisulphate and amide unchanged. These results have been recorded in Table A-12 and shown graphically in Fig A-8.

Table A-12 : $K_2S_2O_8 = 2.0 \times 10^{-2} M$, Amide = 0.1 M,
Temp = $35^\circ C$

$(AgNO_3) \times 10^{-3}$	1.0	1.5	2.0	3.0	4.0
Time (min)	Vol (in ml) of 0.02 M- $Na_2S_2O_3$ used (viz. C)				
0	9.44	9.44	9.46	9.45	9.43
20	8.96	8.85	8.74	8.51	8.28
40	8.53	8.31	8.10	7.67	7.27
60	8.13	7.81	7.51	6.93	6.41
80	7.74	7.35	6.97	6.26	5.65
100	7.39	6.92	6.48	5.67	4.99
130	6.91	6.36	5.81	4.92	4.17
160	6.48	5.85	5.23	4.25	3.48
200	5.92	5.21	4.53	3.50	2.73
240	5.40	4.63	3.91	2.88	2.13
300	4.73	3.91	3.16	2.15	1.48
360	4.13	3.29	2.46	1.61	1.03
$k_1 \times 10^3 \text{ min}^{-1}$	2.415	3.060	3.758	5.060	6.120
$k_2 \times 10^3 \text{ min}^{-1}$	1.238	1.292	1.313	1.526	1.683
$k \times 10^3 \text{ min}^{-1}$	1.177	1.768	2.445	3.534	4.500

From the above results as shown in Table A-12, it shows that when the concentration of Silver Catalyst was increased the reaction rate was also increased linearly. The plot of k versus (Ag^+) shown in Fig. A-9 is found to be linear and the following relationship is being followed.

$$k = 0.125 \times 10^{-3} + 1.433 [\text{Ag}^+]$$

Mishra and Ghosh¹¹³ have reported a non-linear behaviour for this reaction, but have failed to account for this abnormal behaviour.

EFFECT OF TEMPERATURE :

In order to determine the temperature coefficient, energy of activation and various other energy parameters, the reaction was studied at five different temperatures ranging from 25°C to 45°C. These results have been recorded in the following table and shown graphically in Fig. A-10.

Table A-13 : $K_2S_2O_8 = 2.0 \times 10^{-2} M$, Amide = 0.1 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	9.44	9.46	9.45	9.43
20	9.03	8.89	8.74	8.47	8.12
40	8.70	8.39	8.10	7.60	7.00
60	8.36	7.93	7.51	6.83	6.06
80	8.04	7.49	6.97	6.15	5.23
100	7.75	7.10	6.48	5.54	4.53
130	7.33	6.56	5.81	4.77	3.68
160	6.97	6.08	5.23	4.10	2.93
200	6.49	5.48	4.53	3.34	2.25
240	6.03	4.91	3.91	2.71	1.49
300	5.43	4.20	3.16	2.00	1.11
360	4.87	3.59	2.46	1.48	0.73
$k_1 \times 10^3 \text{ min}^{-1}$	1.959	2.797	3.758	5.293	7.273
$k_2 \times 10^3 \text{ min}^{-1}$	0.750	0.900	1.313	1.653	2.561
$k \times 10^3 \text{ min}^{-1}$	1.209	1.897	2.445	3.640	4.712

From the above results as shown in Table A-13, it indicates that the specific rate has been nearly doubled for 10°C rise in temperature. The calculated values of $\frac{1}{T} \times 10^3$ and $\log \frac{kr}{kT/h}$ are recorded in Table A-14.

Table A - 14

Temp A°	$\frac{1}{T} \times 10^3$	$kr \times 10^3$ min ⁻¹	log kr	$\log\left[\frac{kr}{kT/h}\right]$
298	3.356	1.209	- 2.9176	- 15.7347
303	3.301	1.897	- 2.7219	- 15.5463
308	3.246	2.445	- 2.6117	- 15.4433
313	3.196	3.640	- 2.4389	- 15.2771
318	3.145	4.712	- 2.3268	- 15.1721

The energy of activation was calculated from the plot of $-\log k$ versus $\frac{1}{T}$ (Fig. A-11) is 13.155 K.cals. mole⁻¹ which is in good agreement with the calculated value, 12353 K.cals. mole⁻¹.

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

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

The value of energy of activation was then used to calculate the frequency factor A and entropy of activation by the application of the following equation :

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

and

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

where equation (3) is valid for the reactions in solution. In the above expressions k_r is the specific rate constant, k is the Boltzmann constant, h is the Planck's constant and e is a constant having a value of 2.718 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

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

Entropy of activation is given by the relationship :

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

or

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

from which ΔS^\ddagger can be calculated.

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

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

or

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

The values of $\log \frac{kr}{[kT/h]}$ have been plotted against $\frac{1}{T}$ in Fig. A-12 from the slope of which the enthalpy change for the formation of the activated complex H has been calculated.

The values of all the energy parameters are recorded in the following table (Table A-15).

Table A - 15

Temperature A°	$k \times 10^3$ min^{-1}	Temp. coe- ffi- cient	E K. Cals. mole^{-1}	$A \times 10^4$ litre mole^{-1} sec^{-1}	ΔG^\ddagger K. Cals. mole^{-1}	ΔS^\ddagger E.U.	ΔH^\ddagger K.Cals. mole^{-1}
298	1.209	-	-	2.010	21.582	-	32.88
303	1.897	2.02	12.843	3.156	23.211	-	32.16
308	2.445	1.918	11.415	2.028	21.370	-	33.00 13.155 (graphically)
313	3.640	1.927	12.802	2.280	20.720	-	3288
318	4.712	-	-	2.104	23.42	-	33.00
Mean	-	1.955	12.353	2.315	22.060		32.784

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.

$$k = 2.315 \times 10^4 \cdot e^{-12353/RT} \text{ Sec}^{-1}$$

EFFECT OF IONIC STRENGTH :

In order to study the effect of ionic strength, the reaction was studied in presence of varying concentrations of potassium sulphate. The results of these kinetic runs are recorded in Table A-16 and shown graphically in Fig. A-13.

Table A-16 : $K_2S_2O_8 = 2.0 \times 10^{-2} M$, Amide = 0.1 M,

$AgNO_3 = 2.0 \times 10^{-3} M$, 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 0.02 M- $Na_2S_2O_3$ used (viz. c)						
0	9.46	9.47	9.47	9.48	9.46	9.45	9.46
20	8.74	8.77	8.81	8.92	8.94	8.95	9.03
40	8.10	8.13	8.20	8.41	8.46	8.50	8.63
60	7.51	7.56	7.65	7.94	8.02	8.07	8.27
80	6.97	7.02	7.14	7.50	7.60	7.67	7.92
100	6.48	6.54	6.68	7.10	7.22	7.31	7.61
130	5.81	5.88	6.05	6.57	6.73	6.86	7.15
160	5.23	5.29	5.49	6.07	6.26	6.42	6.76
200	4.53	4.60	4.81	5.46	5.68	5.86	6.24
240	3.91	3.99	4.22	4.90	5.15	5.33	5.76
300	3.16	3.24	3.48	4.19	4.46	4.64	5.13
360	2.46	2.62	2.86	3.57	3.85	4.04	4.55
$k_1 \times 10^3 \text{ min}^{-1}$	3.758	3.685	3.462	2.850	2.645	2.505	2.155
$k_2 \times 10^3 \text{ min}^{-1}$	1.313	1.292	1.235	1.180	1.163	1.125	0.850
$k \times 10^3 \text{ min}^{-1}$	2.445	2.393	2.227	1.670	1.482	1.380	1.305

On comparing the rate constants at various ionic strength, it is seen that on increasing the ionic strength, the specific rate decreases. This shows that the salt effect is negative. The reaction however, retains its first order behaviour.

In order to decide the nature of the observed negative salt effect, graphs were plotted between $\log k$ versus $(\mu)^{1/2}$ as well as between $\log k$ versus μ as shown in Fig. 14(A) and Fig. 14(B) respectively. It has been observed that, a linear relationship is maintained between $\log k$ and $(\mu)^{1/2}$ whereas there exists no linearity between k and μ . The linearity between $\log k$ and $(\mu)^{1/2}$ exists only in the the region of low ionic strength (< 0.2). Thus it follows that, the negative salt effect is of the 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

Conc. K_2SO_4 (M)	μ	$k \times 10^3$ min^{-1}	$\sqrt{\mu}$	$\log k$
0.00	0.008	2.445	0.08944	- 2.6118
0.005	0.023	2.393	0.1517	- 2.6811
0.01	0.038	2.227	0.1949	- 2.7523
0.015	0.053	1.670	0.2302	- 2.7773
0.02	0.068	1.482	0.2607	- 2.8292
0.03	0.098	1.380	0.3130	- 2.8602
0.04	0.128	1.305	0.3578	- 2.8844

It may be stated that the ionic strength employed is rather high for Bronsted¹⁹⁴ relationship to be strictly quantitatively applicable, but still the agreement is found to be fairly good.

SPECIFIC IONIC EFFECT :

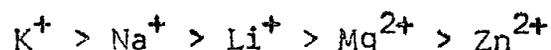
In order to determine the specific ionic effect the reaction was studied in presence of different salts at constant ionic strength. The results of these kinetic runs are recorded in Table A-18 and shown graphically in Fig. A-15.

Table A-18 : Amide = 0.1 M, $K_2S_2O_8 = 2.0 \times 10^{-2} M$,

$AgNO_3 = 2.0 \times 10^{-3} M$, Temp = 35°C. $\mu = 0.212$

Salt added	No Salt	K_2SO_4	Na_2SO_4	Li_2SO_4	$MgSO_4$	$ZnSO_4$
Conc. (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	9.45	9.46	9.48	9.45	9.48
20	8.74	9.04	8.96	8.95	8.87	8.86
40	8.10	8.65	8.50	8.46	8.34	8.29
60	7.51	8.30	8.08	8.01	7.86	7.78
80	6.97	7.96	7.68	7.58	7.40	7.28
100	6.48	7.66	7.31	7.19	7.00	6.84
130	5.81	7.23	6.82	6.69	6.46	6.23
160	5.23	6.86	6.37	6.21	5.96	5.70
200	4.53	6.37	5.81	5.63	5.34	5.03
240	3.91	5.90	5.27	5.08	4.78	4.48
300	3.16	5.28	4.60	4.37	4.05	3.71
360	2.46	4.72	4.00	3.76	3.44	3.09
$k_1 \times 10^3 \text{ min}^{-1}$	3.758	2.064	2.530	2.711	2.957	3.237
$k_2 \times 10^3 \text{ min}^{-1}$	1.313	0.850	0.860	0.880	0.920	0.960
$k \times 10^3 \text{ min}^{-1}$	2.445	1.214	1.670	1.831	2.037	2.277

On comparing the rate constants from the data of Table A-18, it is seen that the specific inhibitory effect of the various ions is in the order



This is almost the same order as represented by Khan and Srivastava in the case of oxidation of glycols by peroxydisulphate ion.

EFFECT OF HYDROGEN ION CONCENTRATION :

The amide solution was prepared in 50 % acetic acid, hence no attempt was made to study the effect of acid such as sulphuric acid on the reaction rate.

EFFECT OF ALLYL ACETATE :

It is well known that the reaction involving $S_2O_8^{2-}$ ion is inhibited by allyl acetate. It has been shown by Kolthoff¹⁹⁵ and co-workers, Wiberg,¹⁹⁶ Ball¹⁹⁷ and coworkers that allyl acetate is an efficient capture of sulphate ion radical (SO_4), which is known to be formed in oxidation reactions involving $S_2O_8^{2-}$ ion. Hence, it was considered to investigate the effect of allyl acetate on peroxydisulphate oxidation of organic compounds studied in this thesis.

To study the effect of allyl acetate on the reaction rate, the reaction was studied in the presence of 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 : Amide = 0.1 M, $K_2S_2O_8 = 2.0 \times 10^{-2} M$,
 $AgNO_3 = 2.0 \times 10^{-3} M$, Temp = $35^\circ C$

Allyl acetate (M)	Nil	0.001	0.005	0.01
Time (min)	Vol. (in ml.) of 0.02 M $Na_2S_3O_3$ used (viz.C)			
0	9.46	9.48	9.45	9.45
20	8.74	9.06	9.09	9.19
40	8.10	8.67	8.76	8.94
60	7.51	8.31	8.47	8.72
80	6.97	7.97	8.17	8.50
100	6.48	7.66	7.91	8.31
130	5.81	7.23	7.56	8.09
160	5.23	6.84	7.23	7.85
200	4.53	6.33	6.80	7.54
240	3.91	5.86	6.38	7.23
300	3.16	5.23	5.82	6.79
360	2.46	4.66	5.31	6.38
$k \times 10^3 \text{ min}^{-1}$	3.758	2.099	1.743	1.230

From the above results (Table A-19) it is seen that allyl acetate inhibits the rate of reaction. It may be pointed out that allyl acetate does not act as a very efficient radical capture reagent in this case. The radical capture may be due to polymerization of allyl acetate by sulphate radical ions formed from the catalysed decomposition of peroxydisulphate ion.

MOLE RATIO :

In order to determine the number of moles of $S_2O_8^{2-}$ reaction with one mole of amide, the graphical method was used. $K_2S_2O_8$ was taken in excess as compared to amide. Simultaneously a blank run was also performed. At suitable intervals of time 5 ml of the reaction mixture was pipetted out and estimated for unreacted $K_2S_2O_8$. These results are recorded in Table A-20 and shown graphically in Fig. A-17.

The curves consist of two portions - the first for the oxidation of amide and the second for the self decomposition of peroxydisulphate ion. Now tangents are drawn on the 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 0.01 M amide is calculated. The point Q on the curve at the same time gives the value corresponding to self decomposed $K_2S_2O_8$.

Table A-20

Reaction mixture Overall concentration

 $K_2S_2O_8 = 0.05 M$ $AgNO_3 = 0.002 M$ Temperature = $35^\circ C$

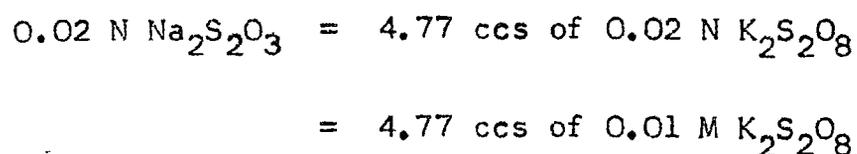
Amide	0.01 M	0.00M
Time (min)	Vol. in ml of 0.02 M- $Na_2S_2O_3$ used (viz. C)	
0	24.22	24.15
30	23.95	23.42
60	22.14	22.31
90	19.85	21.49
120	18.46	20.71
150	17.41	20.40
180	16.10	19.53
210	15.35	19.11
240	13.82	18.24
270	13.16	17.34
300	12.56	16.95
330	11.47	15.84
360	10.75	15.83
390	10.66	15.15
420	10.51	14.40
450	9.95	14.10
480	9.81	13.56

From the graph (Fig. A-17) it indicates that the two plots become parallel at P. At this point $\log C = 1.06$ which corresponds 11.48 ml.

The corresponding value of $\log C$ at the same time on the self decomposition curve is shown by point Q. At this point $\log C = 1.06$, which corresponds to 16.21 ml.

The difference between the two values is 4.77 ccs.

Therefore, 4.77 ccs of



Hence 5 ml of 0.01 M amide = 4.77 ccs of 0.01 M $\text{K}_2\text{S}_2\text{O}_8$. Thus one mole of amide consumes one mole of peroxydisulphate for completion of the reaction.

FIG.- A1
EFFECT OF $K_2S_2O_8$

AMIDE - 0.1M
 $AgNO_3$ - $2.0 \times 10^{-3} M$
TEMP. - $35^\circ C$

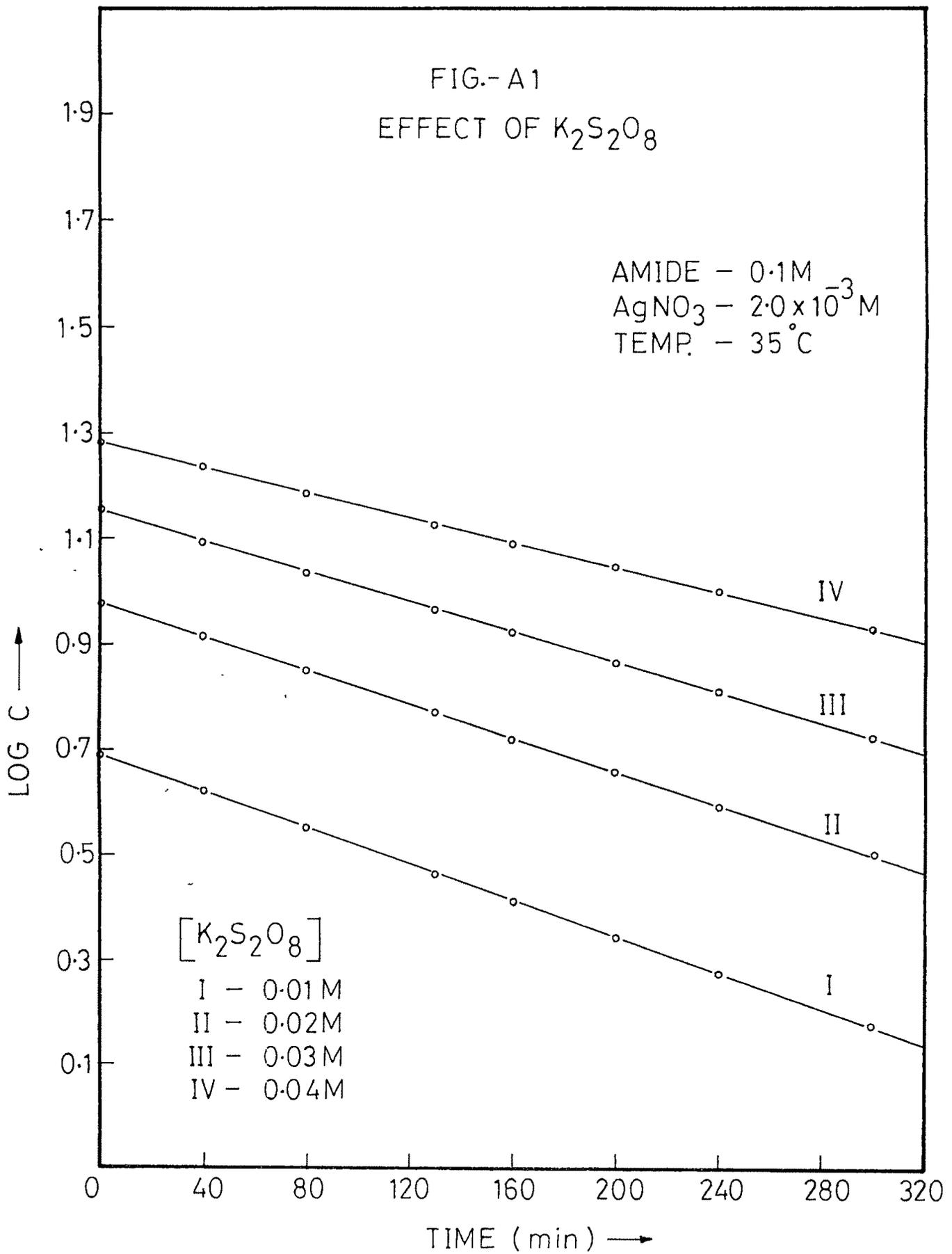


FIG.- A2

EFFECT OF $K_2S_2O_8$ AT CONSTANT μ .

AMIDE - 0.1M
 $AgNO_3$ - 2.0×10^{-3} M
TEMP. - 35°C
 μ - 0.301

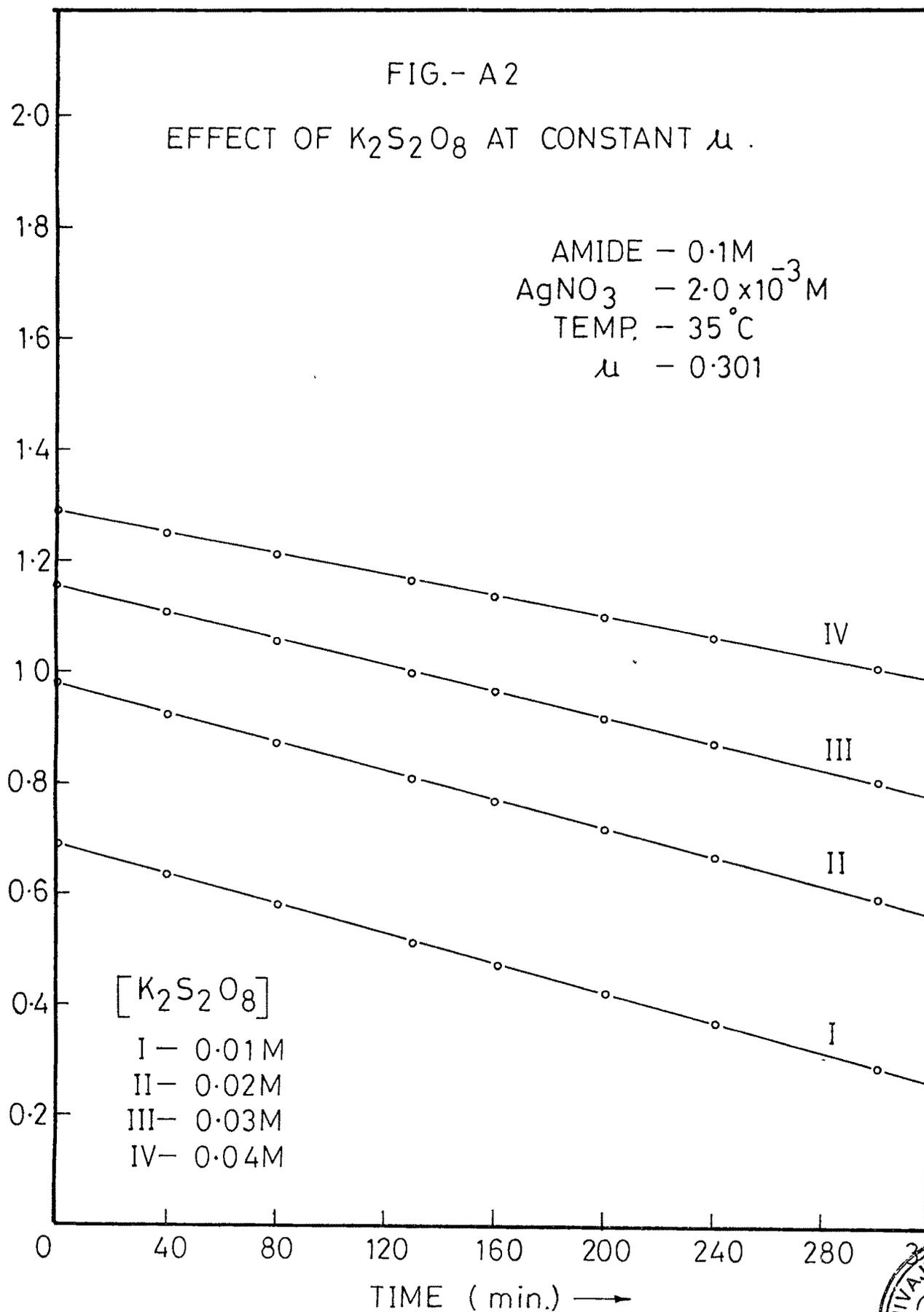


FIG.- A3
PLOT OF LOG k VERSUS CONC. $K_2S_2O_8$.

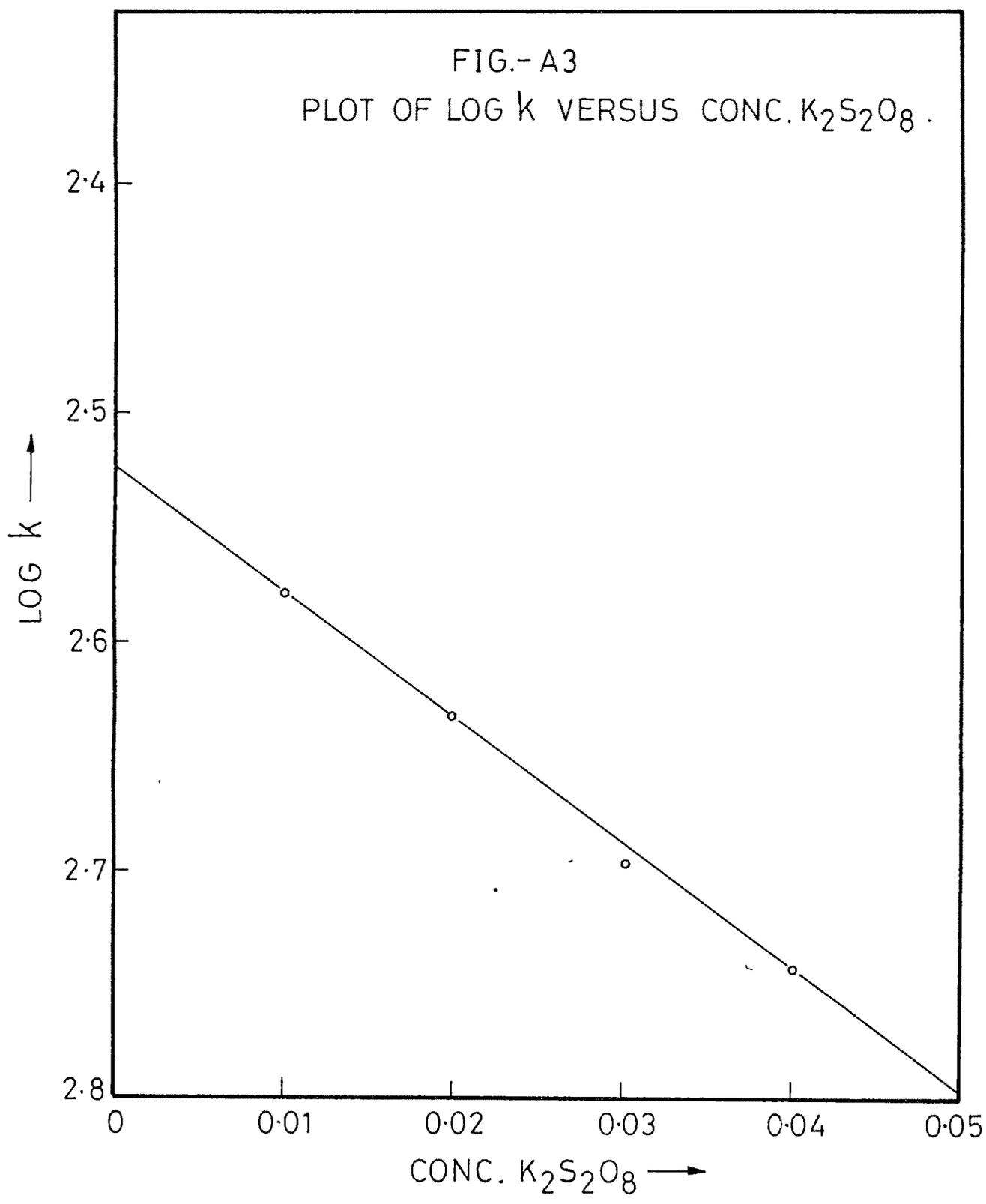


FIG.-A4

PLOT OF LOG (-dc/dt) VERSUS ($S_2O_8^{2-}$)

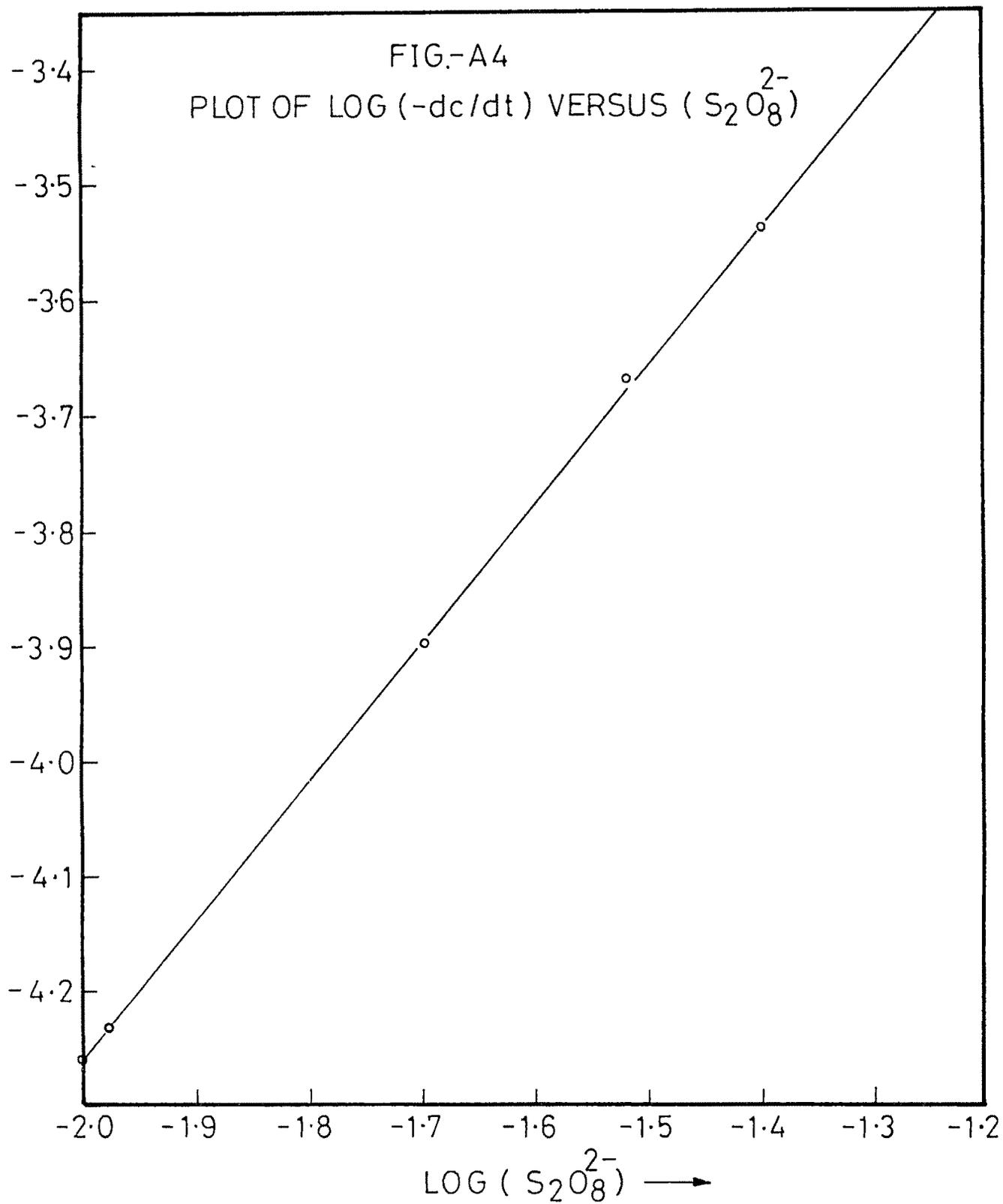


FIG.- A5

EFFECT OF AMIDE CONCENTRATION

$K_2S_2O_8^-$ $2.0 \times 10^{-2} M$
 $AgNO_3^-$ $2.0 \times 10^{-3} M$
TEMP. - $35^\circ C$

I TO V AMIDE \rightarrow
0.05M, 0.1M, 0.15M,
0.175M, 0.02M, RESPECT

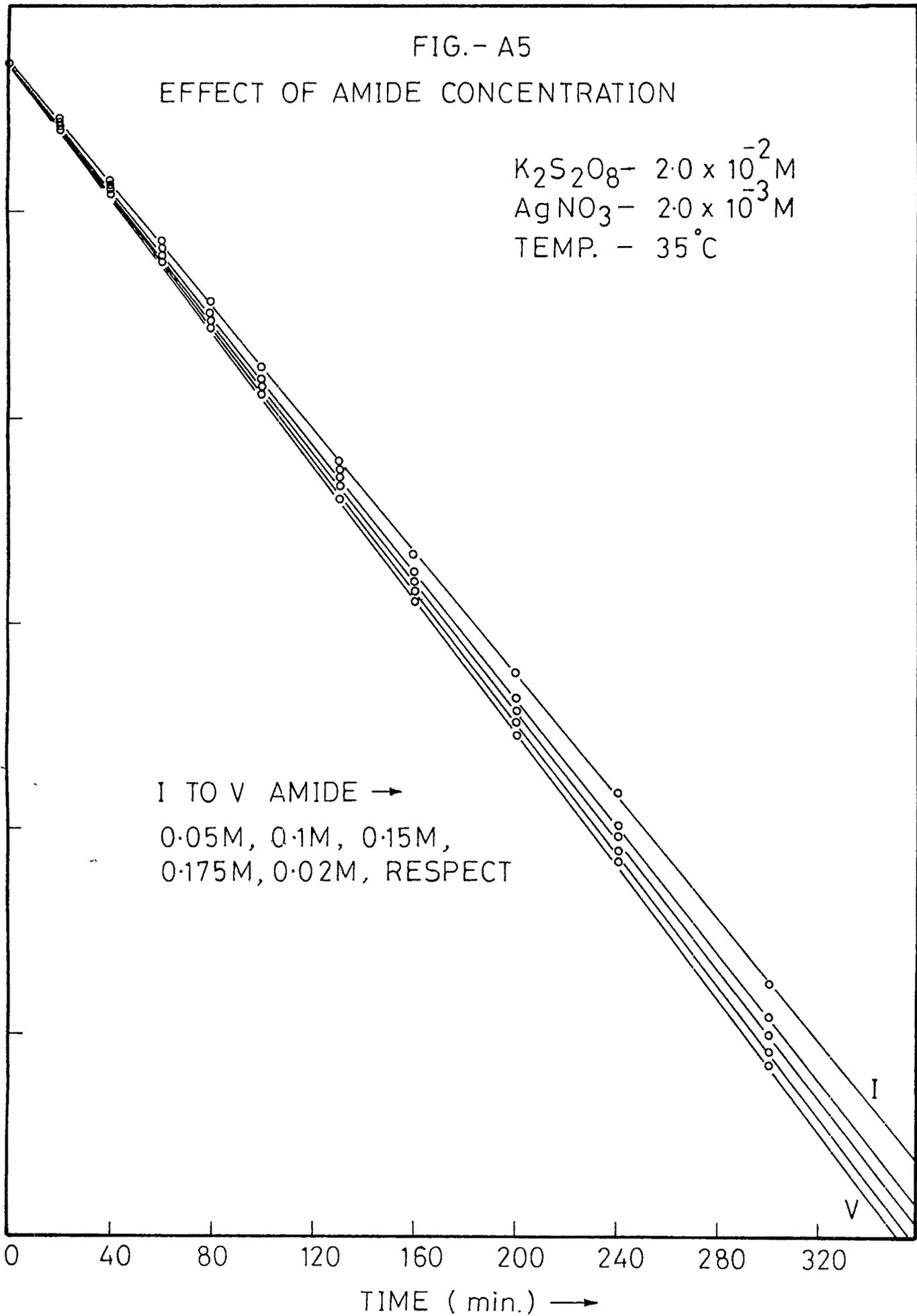


FIG.- A6

PLOT OF CONC. OF AMIDE VERSUS AMIDE / k

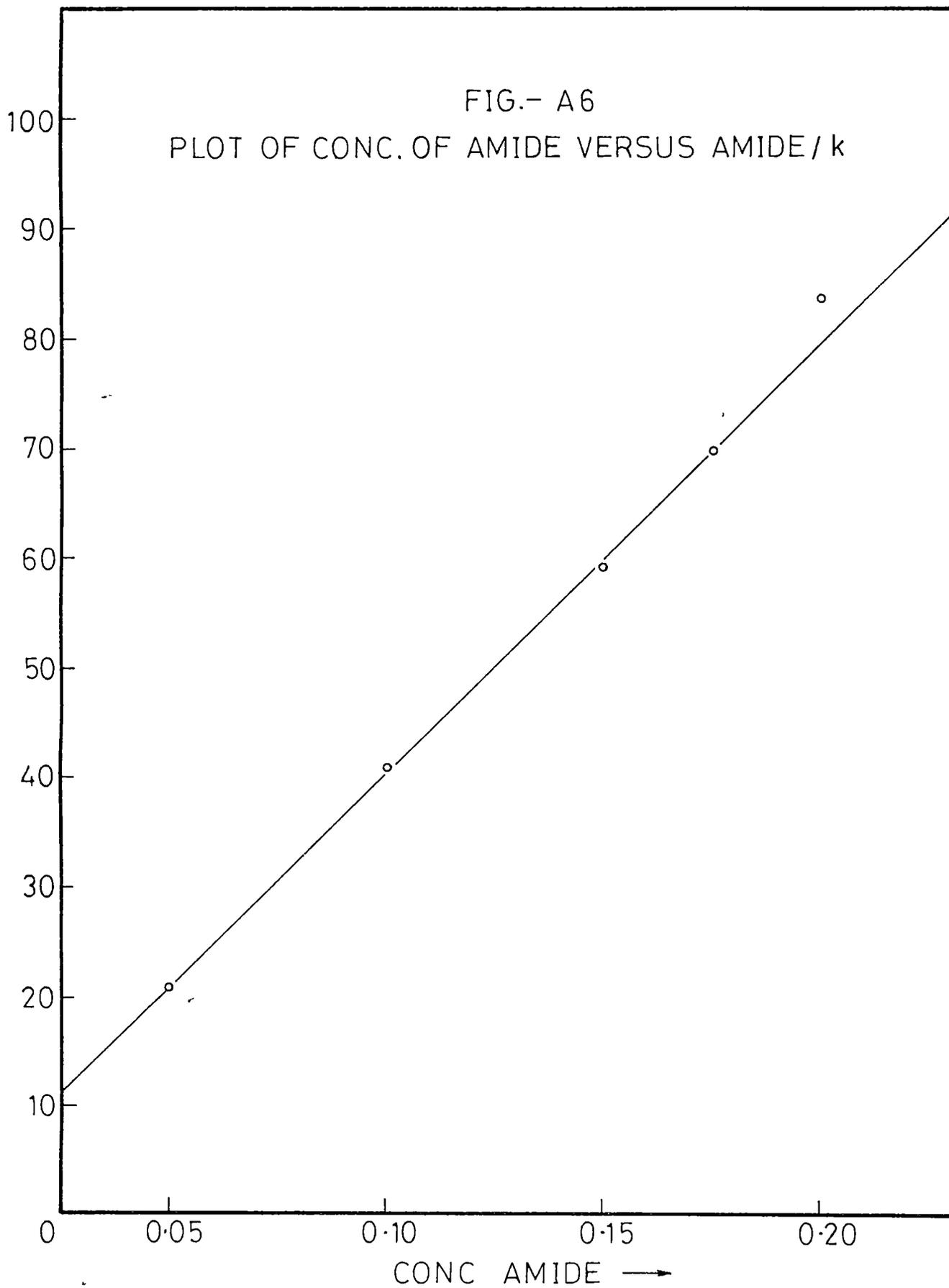


FIG.- A7

PLOT OF LOG (-dc/dt) VERSUS LOG (Co).

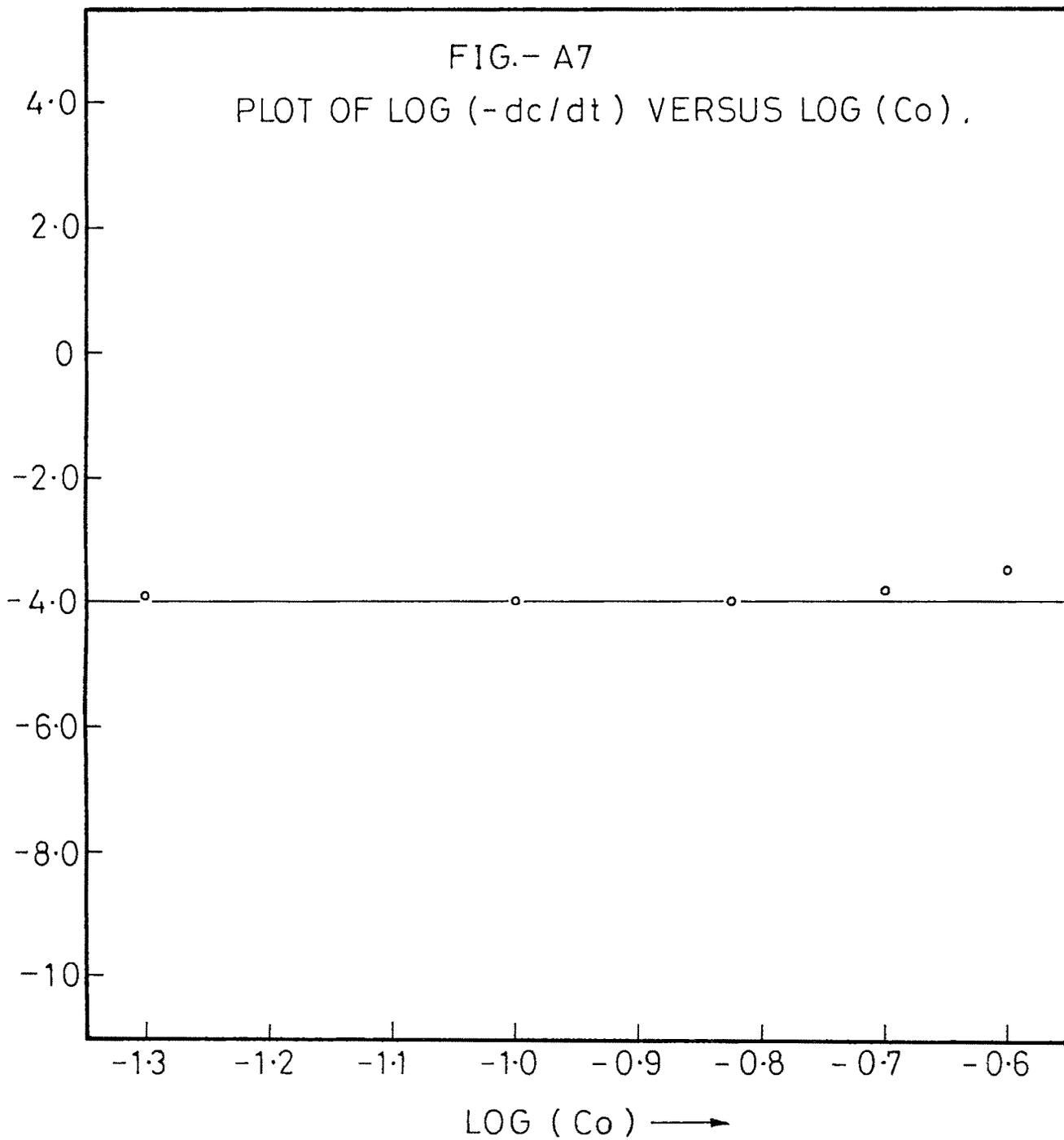


FIG.- A8

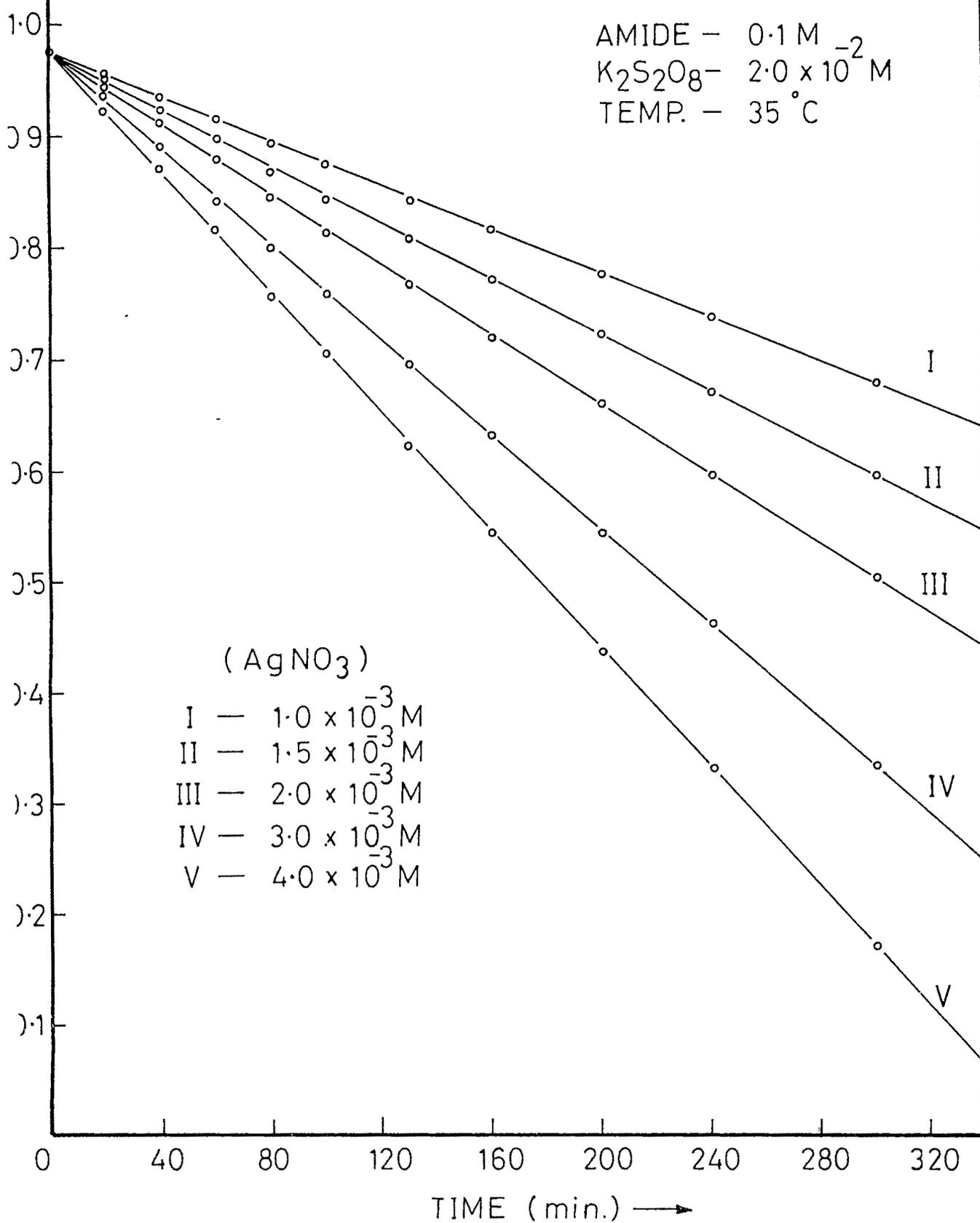


FIG.-A9

PLOT OF $k \times 10^3 \text{ min}^{-1}$ VERSUS (Ag^+)

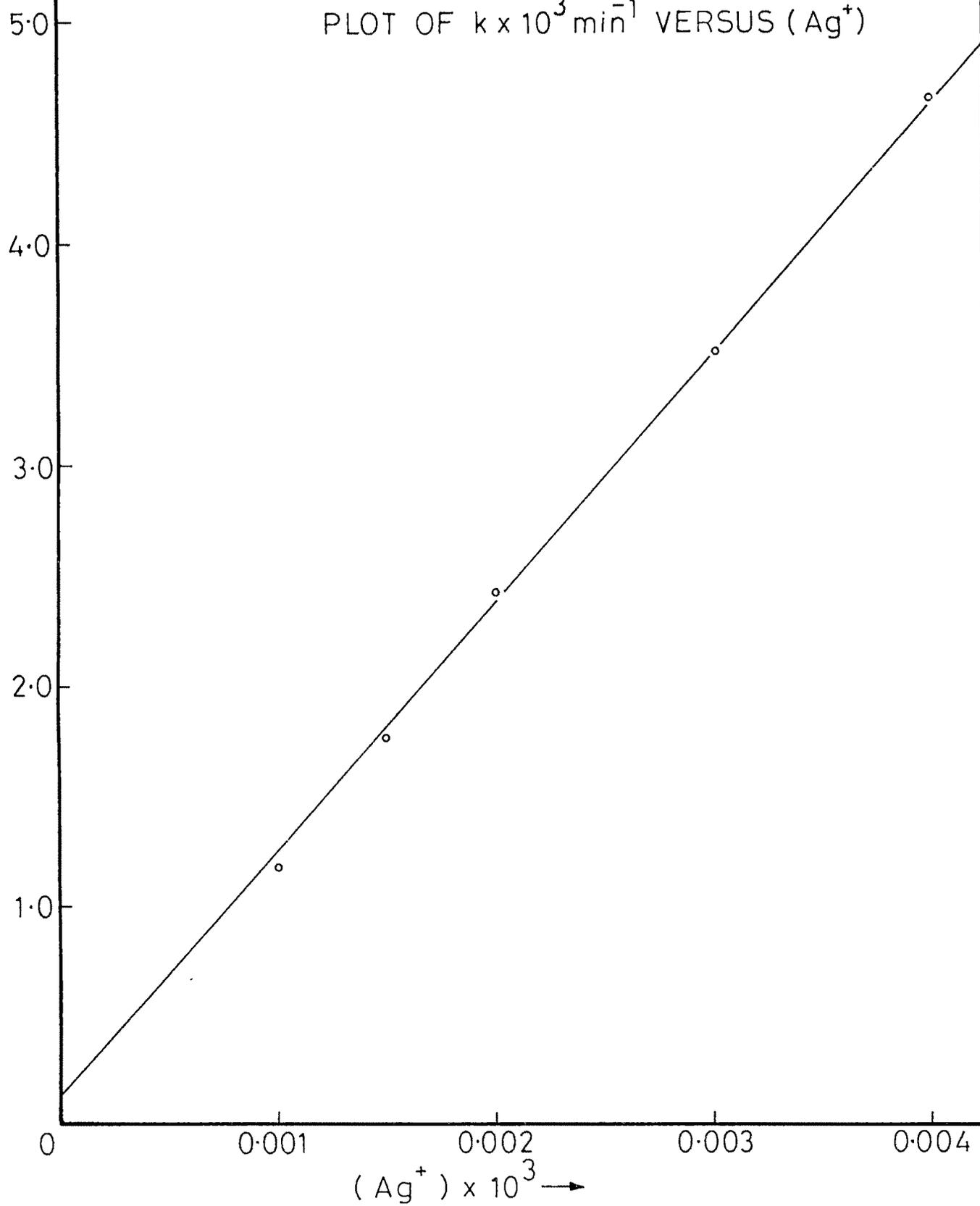


FIG.- A 10

EFFECT OF TEMPERATURE

AMIDE - $0.1M$
 $K_2S_2O_8 - 2 \times 10^{-2} M$
 $AgNO_3 - 2.0 \times 10^{-3} M$

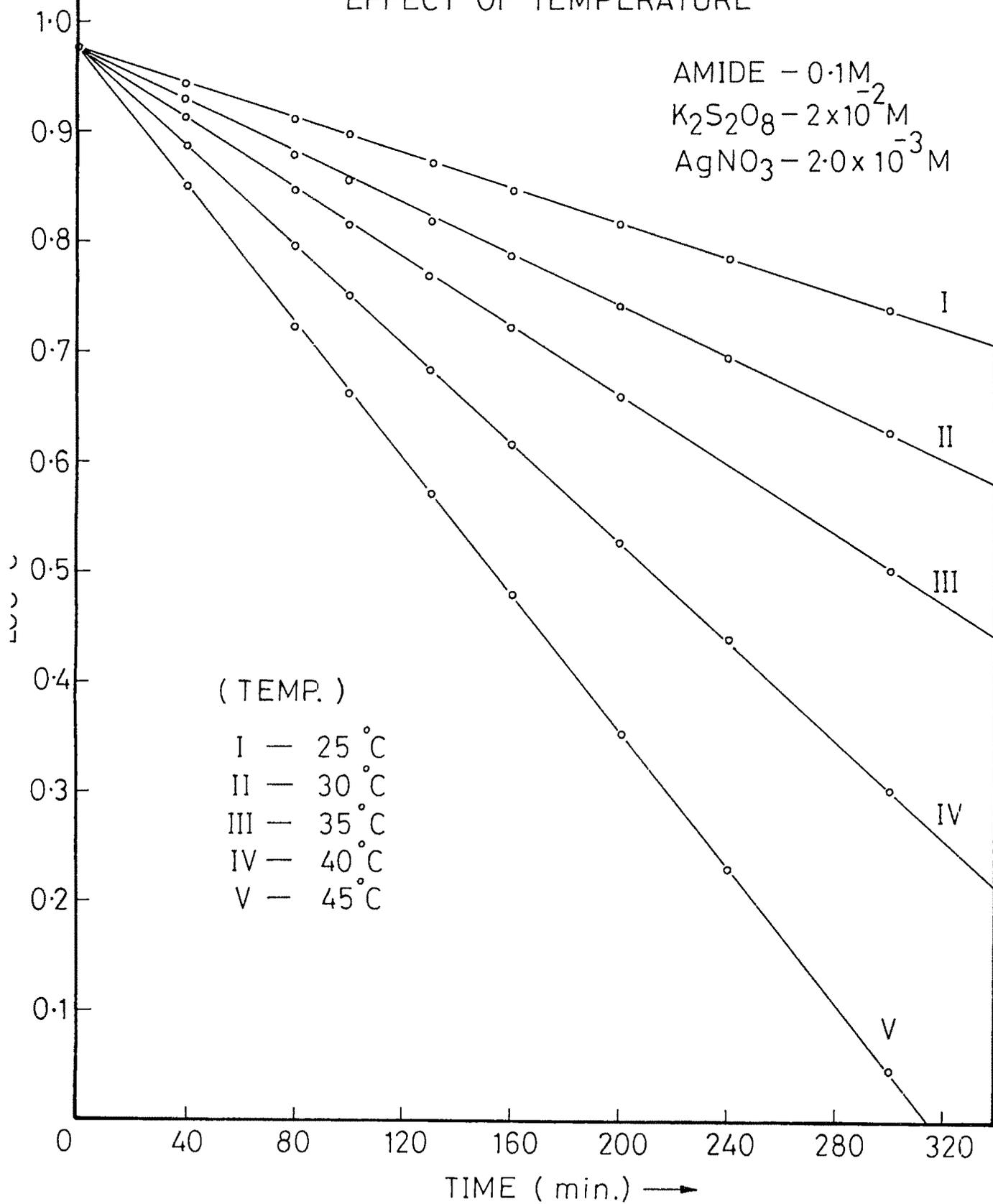


FIG.- A11

PLOT OF LOG k VERSUS $1/T \times 10^3$

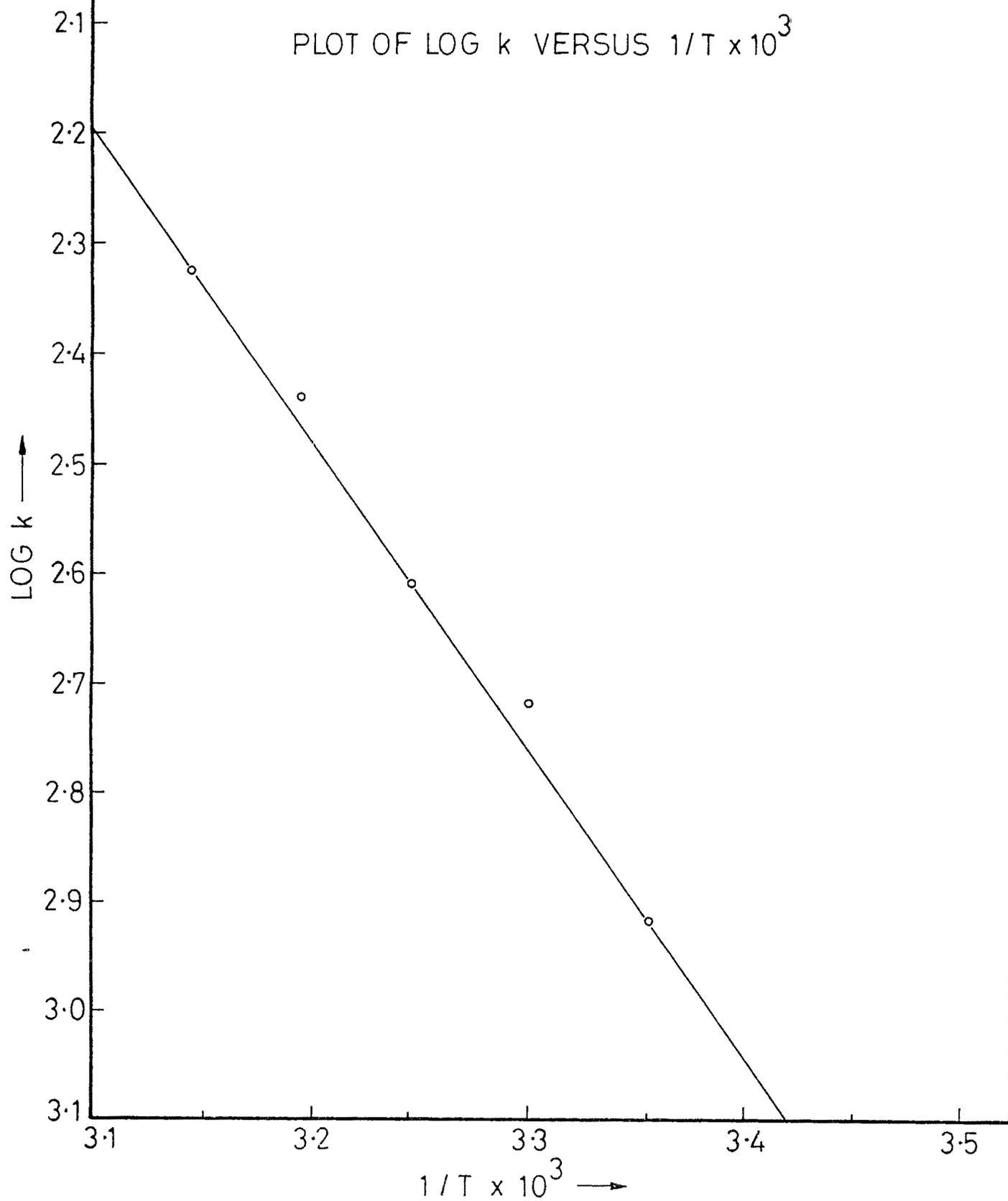


FIG.- A12

PLOT OF LOG $\left[\frac{kr}{KT/h} \right]$ VERSUS $1/T \times 10^3$

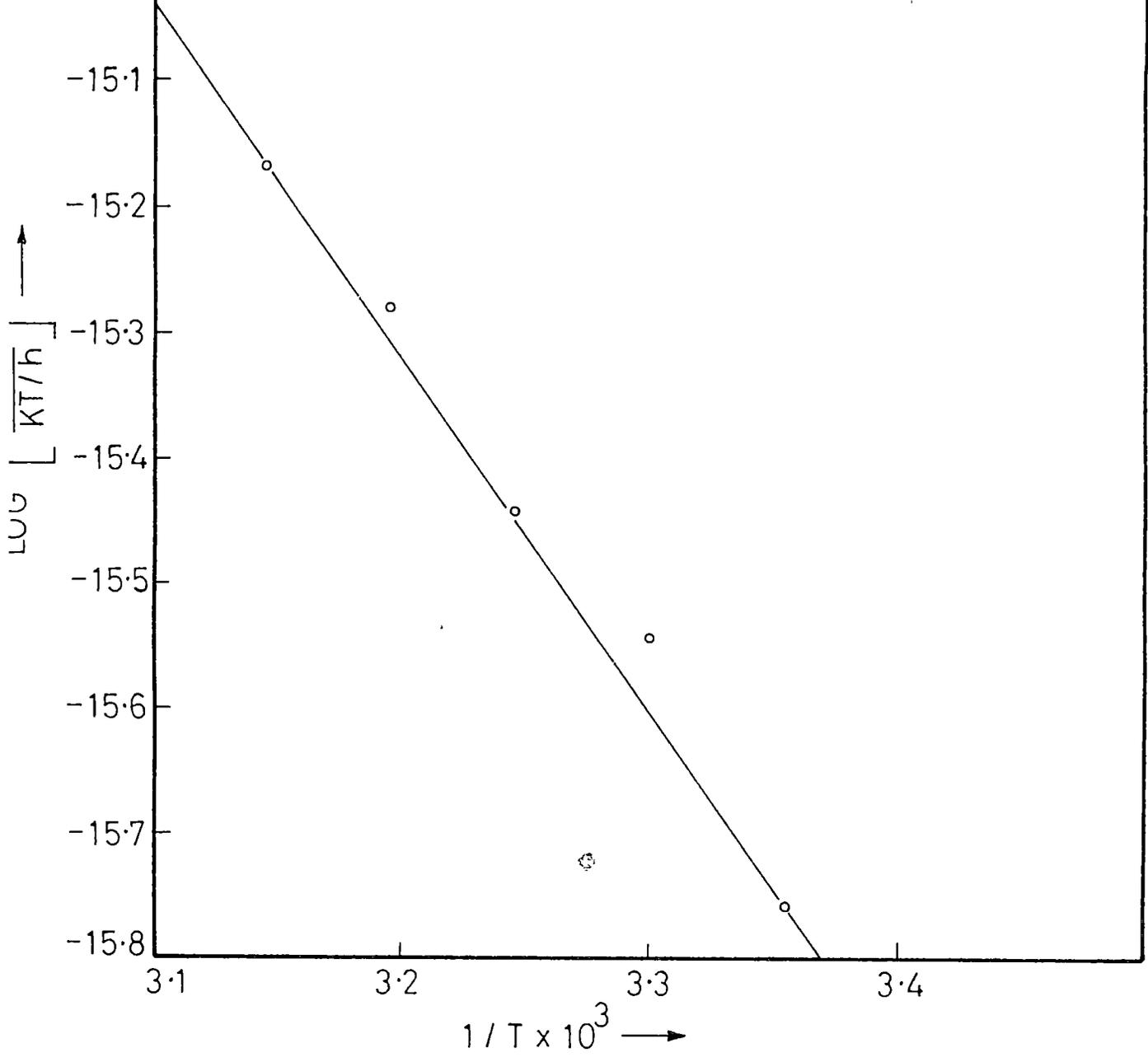


FIG.— A13

EFFECT OF IONIC STRENGTH

AMIDE — 0.1M
 $K_2S_2O_8$ — $2.0 \times 10^{-2} M$
 $AgNO_3$ — $2.0 \times 10^{-3} M$
TEMP. — 35°C

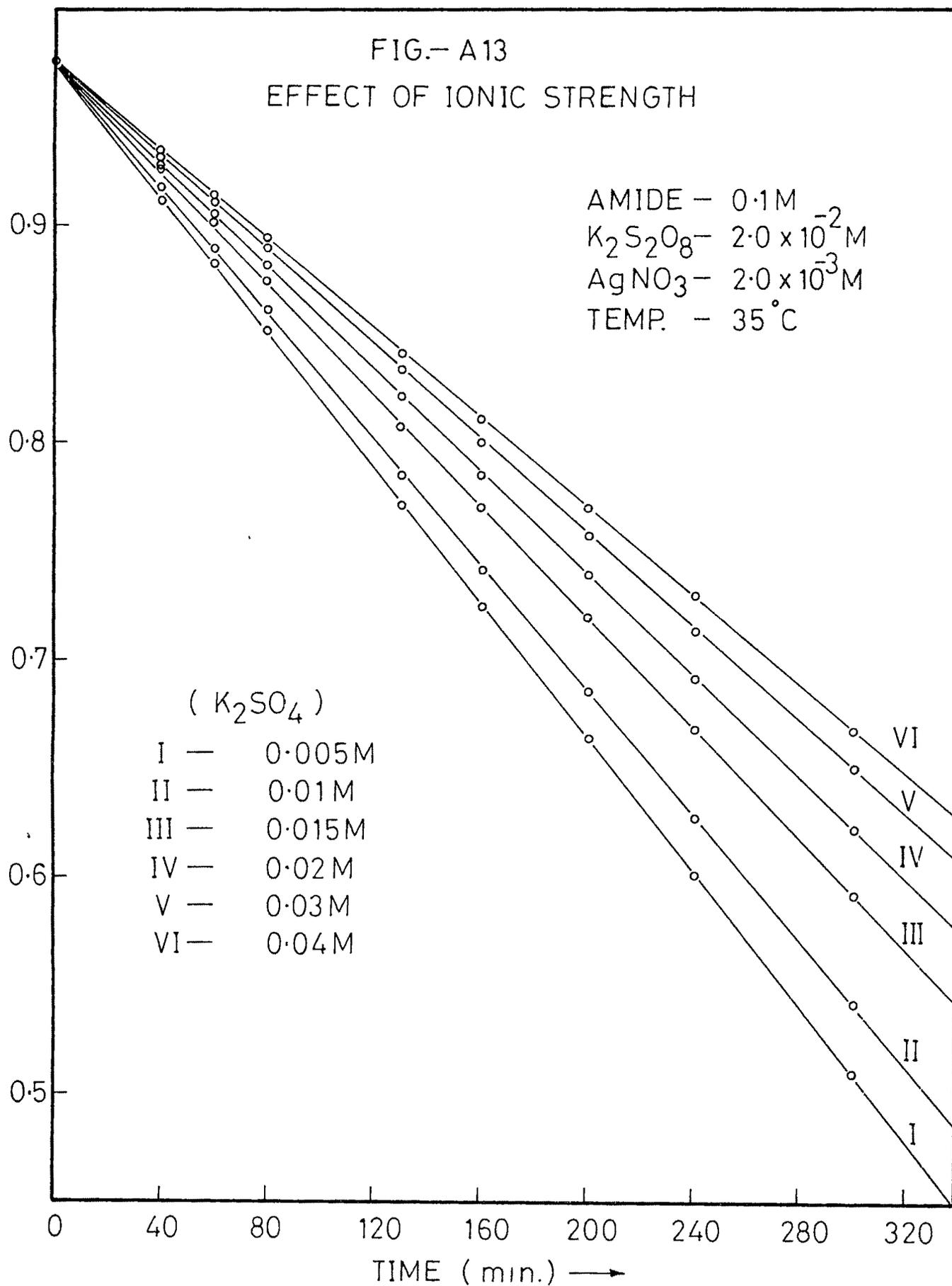


FIG.- A14 (a)

PLOT OF LOG k VERSUS $(\mu)^{1/2}$

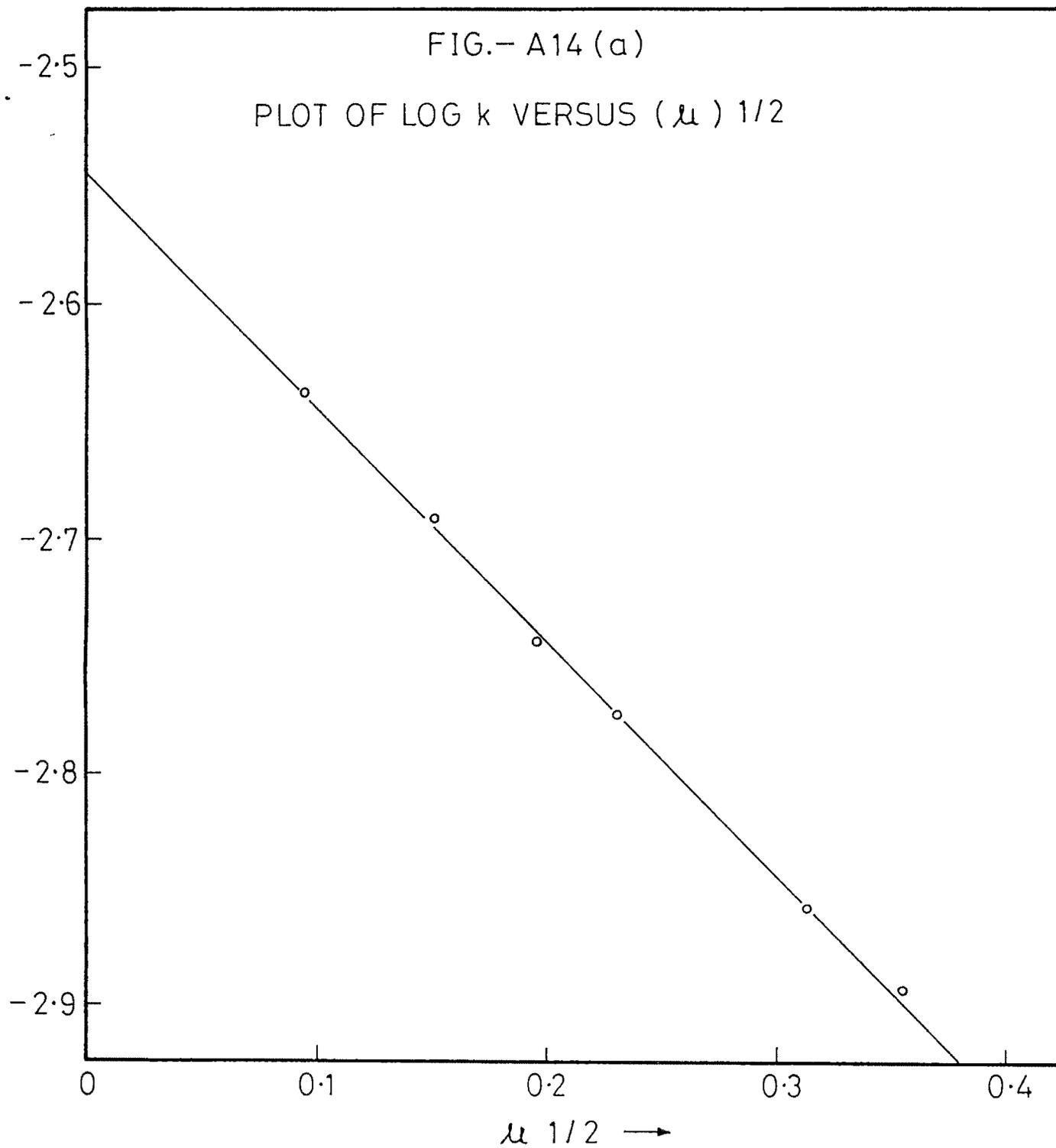


FIG.- A14(b)
PLOT OF $k \times 10^3 \text{ min}^{-1}$ VERSUS μ

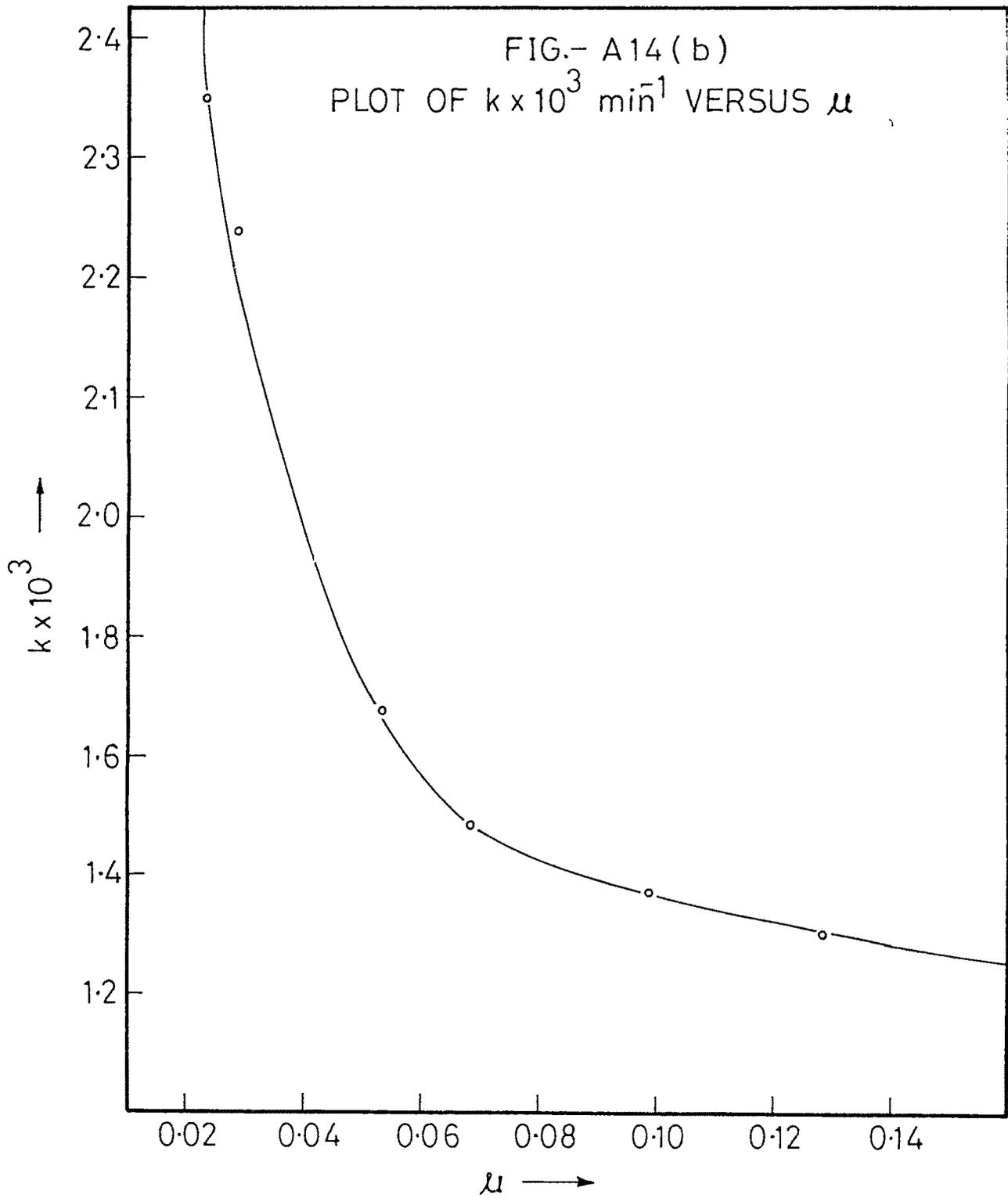


FIG.-A15
SPECIFIC ION EFFECT

AMIDE - 0.1 M
 $K_2S_2O_8$ - 2.0×10^{-2} M
 $AgNO_3$ - 2.0×10^{-3} M
TEMP. - 35°C

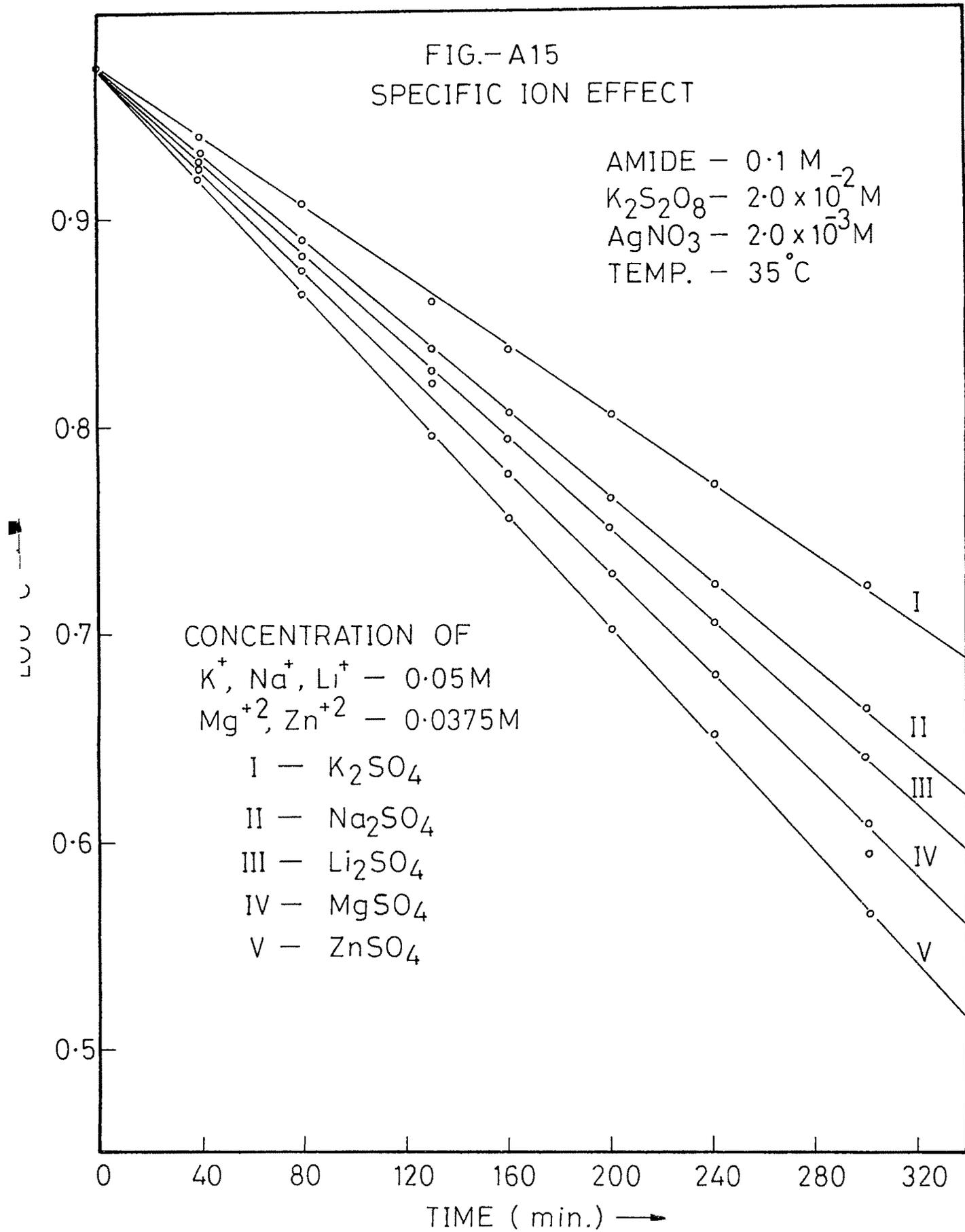


FIG.-A16
EFFECT OF ALLYL ACETATE

AMIDE - 0.1M
 $K_2S_2O_8$ - $2.0 \times 10^{-2} M$
 $AgNO_3$ - $2.0 \times 10^{-3} M$
TEMP. - $35^\circ C$

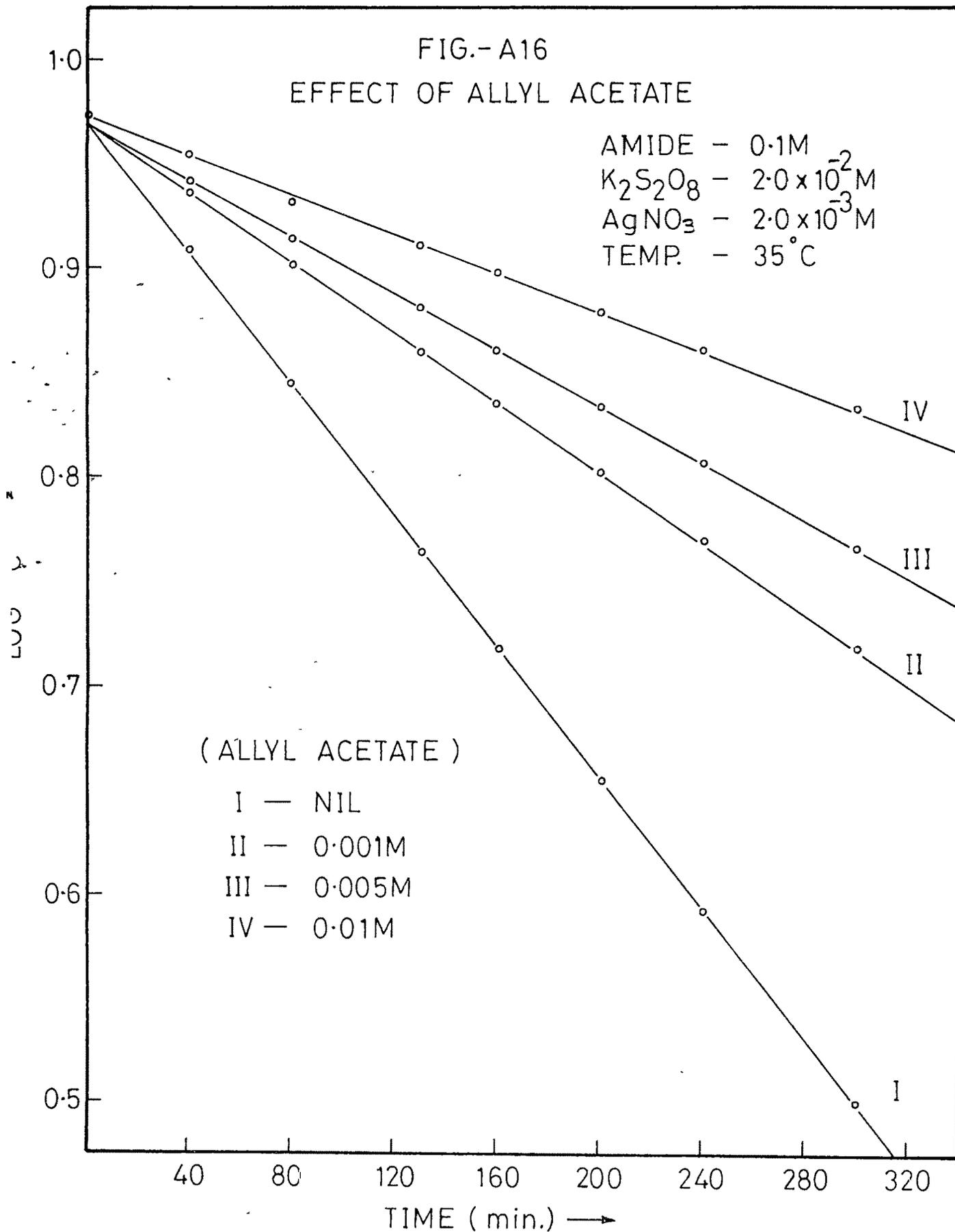


FIG.- A17
MOLE RATIO

$K_2S_2O_8$ - $5.0 \times 10^{-2} M$
 $AgNO_3$ - $2.0 \times 10^{-3} M$
TEMP. - $35^\circ C$

