CHAPTER III

STUDY OF PHOSPHORESCENCE DECAY

3-1 INTRODUCTION:

The study of phosphorescence decay provides information about the nature of trapping states, energy levels of luminescent materials and the type of kinetics involved in the luminescence process. The aim of the present investigation is to analyse the observations made at $300^{\circ}K$ so as to derive information about the following aspects:

1) the nature of decay law,

2) the time constant of decay,

3) the energy distribution of trap levels,

4) an insight into the mechanism responsible for decay, and

5) the effect of activator Zn and a flux on decay behaviour.

3-2 THEORETICAL BACKGROUND:

3-2.1 Decay Laws:

The phosphorescence decay may either be exponential or hyperbolic depending upon the type of kinetics involved in the luminescence process (1-6).

(A) Exponential Decay:

The exeponential decay occurs when the kinetics of luminescence is of the first order i.e., when electron traps are situated close to the luminescence centres.

. Let n be the number of excited electrons at any time
t and if p is the transition probability then,

$$\frac{dn}{dt} = -pdt \quad - - - - - - (3.1)$$

the transition probability p according to Randall and Wilkins
is given by (4,7)

$$p = S\ e^{-E/KT} \quad - - - - - - (3.2)$$

where S is the attempt to escape frequency, E the trap
depth, K the Boltzman constant and T is the absolute
temperature at which the decay takes place.

On integration, equation (3.1) gives

$$n = n_o\ \exp\ (\ -pt\ ) \quad - - - - - (3.3)$$

where n_o is the number of excited electrons at t = o, the
time when the excitation ceases.

The luminescence intensity is given by

$$I = -\ \frac{dn}{dt}$$

$$= P\ n_o\ \exp\ (\ -pt\ )$$

$$\therefore\ I = I_o\ \exp\ (\ -pt\ ) \quad - - - - - (3.4)$$

where I_o is intensity at t = o.

The equation (3.4) shows that the rate of decay depends
only upon the transition probability p.· This equation is
useful in calculating the trap depth.

(B) Hyperbolic Decay:

This type of decay results when luminescence process

is of the second order i.e., when electron traps are located away from the luminescence centres.

Let there be n impurity centres with which only n number of electrons combine at a time. If p is the probability with which an electron combines with any of the centres in time dt, then

$$p = A n dt, \qquad - - - - - (3.5)$$

A being a constant.

If all the n electrons return to the ground states at the centres through the conduction band with this probability, the rate of decay will be

$$\frac{dn}{dt} = A n^2 \qquad - - - - - - (3.6)$$

and luminescence intensity is given by

$$I = I_0 / (1 + \alpha t)^2 \qquad - - - - - - (3.7)$$

where α is another constant.

For large values of t ($t \gg 1$) the equation (3.7) can be written as

$$I = I_0 / \alpha t^2 \qquad - - - - - - (3.8)$$

Treating more generally in the light of different capture cross-sections for electrons, empty centres and traps, Andirowich (8,9) arrived at an approximate Bequerel type relation of the form

$$I = \text{const.} / (t + to)^b \qquad - - - - - (3.9)$$

where b depends on the ratio of the capture cross-

sections of traps and empty centres. However, this equation
fails in cases where well separated groups of traps exist.

3-2.2 Effect of Steady Excitation of a Phosphor on the Filling of Electron Traps:

When a phosphor is excited at a fixed temperature by
steady excitation, its luminescent intensity reaches to a
constant value. This state of phosphor is referred to as
equilibrium state and in this condition the concentration of
filled electron traps is in equilibrium.

If the phosphor contains traps of one depth, then two
cases arise:

a) When Traps Are Located Close to the Luminescence Centres (First Order Kinetics):

Let J be the intensity of excitation. Then the rate of
electrons raising to the excited state is proportional to
J, and is given by CJ, C being a constant of proportionality.
If there are n electrons in the N traps, the rate of
capture of excited electrons in traps is CJa (N-n), a being
the probability of capture per trap. The rate of escape of
electrons from traps is given by $n \, s \, e^{-E/KT}$. Under equilibrium
condition, the rate of capture of excited electrons in traps
and rate of electrons escaping from traps will be equal and
thus,

$$C \, a \, J \, (N-n) = n \, s \, e^{-(E/KT)} \quad - - - - - \quad (3.10)$$

from which we get,

$$n = \frac{N}{1 + \dfrac{Se^{-E/KT}}{A}} \quad - - - - - - (3.11)$$

where $A = C a J$ is a factor directly proportional to the intensity of excitation.

(B)   **When Traps Are Located Away From the Luminescence Centres (Second Order Kinetics):**

Let n be the number of trapped electrons and m the number in conduction band. Then (m + n) is the number cf empty luminescence centres and rate of electrons returning from the conduction band is given by

$$\frac{dm}{dt} = 0 = C J - \beta \, m \, (m+n) \, n \, s \, e^{-E/KT} - mb \, (N-m) - - -(3.12)$$

and the rate of electrons escaping from traps is

$$\frac{dn}{dt} = 0 = n \, s \, e^{-E/KT} - mb \, (N-n) \quad - - - - - (3.13)$$

where β and b are the constants and CJ is the rate of electrons rising to the excited state.

If the excitation is not of an appreciably low intensity, the number of electrons in the conduction band is much greater than the number trapped and thus m + n $\doteq$ n. Hence

$$\beta m^2 = CJ \quad - - - - - - - (3.14)$$

and therefore,

$$n = \frac{N}{1 + \dfrac{S \, e^{+E/KT}}{B}}$$

where $B = b \sqrt{C J / \beta}$ and thus is proportional to the square root of the excitation intensity.

3-2.3 The effect of Excitation Intensity on
       the Filling of Traps With Complex Distribution:

The derivations of equations (3.11) and (3.15) may be
extended to cover complex trap distributions if the form of
the specific distribution is known. In most practical cases
the number of traps, N, of different depths does not vary
rapidly with E over most of the ranges of E values. Thus
if N is assumed constant or slowly varying, the total
number of filled traps from a given excitation intensity can
be obtained. Let this number be n_T, then in most cases

$$n_T = \int_0^{E_{max}} n \ dE$$

using the equation (3.11) we obtain

$$n_T = \int_0^{E_{max}} \frac{N}{1 + \dfrac{S. \ e^{-E/KT}}{A}} \ dE \quad - - - - - (3.16)$$

For all practical exciting intensities $A \ll S$, and thus
equation (3.16) yields on integration

$$n_T = N \ K \ T \ \log (A' + 1) \quad - - - - - (3.17)$$

where $A' = A \ S^{-1} \ e^{E_{max}/KT}$ is proportional to the
excitation intensity.

At high intensities when $A' > 1$ the number of filled
traps will be a linear function of the logerithm of the
excitation intensities provided that $A \ll S$. When a approaches

s a saturation state will be reached. A similar logarithmic relation can be obtained by using equation (3.15), which includes consideration of retrapping.

3-3   RESULTS AND DISCUSSION:

3-3.1 Decay Curves:

Figs. 3.1 to 3.3 show some typical decay curves of samples studied at 300°K. They appear to be of the same general nature as reported for alkaline earth sulphide phosphors by other workers (10.14).

The first step in the analysis of decay curves is to determine which of the two main modes of decay, i.e. exponetial or hyperbolic, is operative. General shape of I - t plots, log I versus t plots and log I versus log t plots can give a useful insight into this and in addition can yield information about the nature of kinetics involved.

To examine the possibility of simple exponential decay with single trap depth given by equation (3.4), plots of log I versus t are plotted. It is found that they show deviation from straight lines. This rules out the possibility of simple exponential decay with a single trap. However, graphs of logI s versus log t (Fig.3.4 to 3.7) are found almost linear, suggesting that the decay is hyperbolic and could be represented by the equation of the form (4)

$$I = I_0 \, t^{-b} \quad - - - - - - \quad (3.18)$$

where I is the intensity at any time t, I$_0$ is at the start

of the decay, and b is the decay constant. The value of
decay constant is indicative of decay rate. Faster the decay
higher is the value of b and vice-versa. It also provides
the information about relative population of traps at various
depths.

3-3.2 Decay Constant:

The values of decay constant are calculated by the
method of least squares (15) using the relation

$$b = \frac{\Sigma x \Sigma y - n \Sigma x y}{(\Sigma x)^2 - n \Sigma x^2} \quad - - - - - - - (3.19)$$

where x = log t, y = log I and n is the number of
observations. The values of b thus obtained are given in
Table 3-1. It is seen that the values of b for all cases
are less than unity.

3-3.3 Variation of Decay Constant (b):

(1)   With Concentration of Zn:

The variation in b values with concentration of Zn
is as shown in Fig.3.8. The variation is not strictly
systematic but in general, b increases with increase in
Zn content. This implies that the incorporation of Zn alone
does not give rise to new trapping levels but modifies the
relative importance of traps responsible for phosphorescence
decay (16). An increase in amount of Zn has the effect of
populating the shallower traps in preference to the deeper
ones.

However, when an amount of Zn is varied in presence of flux (NaCl, 1.25 wt.%), the variation in b values is found to be systematic (see Fig.3.9). Thus indicating that the Zn in presence of flux, introduces new trapping levels in a phosphor (16,17).

(2)   With Concentration of Flux NaCl:

Fig.3.10 shows a variation of b with % of flux. It may be seen that the variation, here too, is systematic and indicates that the addition of flux creates new trapping levels which contribute to the phosphorescence decay (16,17).

3-3.4 Variation of Starting Contribution (Io)
       with Zn and NaCl:

The variation of Io with concentration of Zn in absence and presence of flux is shown in Figs. 3.11 and 3.12 respectively, while its variation with % of flux is given in Fig.3.13. The Io values are calculated from the intercepts on log I axis of plots between log I versus log t. As Io represents a phosphorescence intensity at 1 sec. it may be taken as a measure of phosphorescence efficiency of a phosphor.

It may be noted from the Fig.3.11 that the variation in Zn content in absence of f lux causes an increase in efficiency. However, the increase is not systematic. In presence of flux, the efficiency first decreases and then increases (Fig.3.12). The observed decrease might be due to the reduction in trapping levels for that concentration.

This has been supported by b values which also show minimum at same concentration (See Fig.3.9).

The variation observed in Io values with % of flux exhibits a maximum followed by a continuous decrease. The maximum is found at 1.25 wt.% of NaCl and is an optimum concentration of flux for better luminescence. The same concentration has been used during preparation of samples of series III (Table 2-1).

3-3.5 'Peeling off' of the Decay Curves:

In the present case, the slopes of log I-log t plots are not equal to two for $t \gg 1$, as required by the equation (3.7). This excludes the possibility of hyperbolic decay with single trap depth. However, the observed hyperbolic decay could be explained on the basis of the monomolecular superposition theory. Randall and Wilkins (4) considered the hyperbolic decay as a result of superposition of exponentials corresponding to different traps. Such a decay can be expressed by an equation of the type

$$I = Io_1 \exp (-p_1 t) + Io_2 \exp (-p_2 t) +$$

$$+ Ion \exp (-p_n t) - - - - - (3.20)$$

where Ion is the phosphorescence intensity due to electrons in the traps of energy En and P_n is the transition probability of an electron escaping from a trap of depth En.

It is possible to break up the decay cure into a set of exponentials by the method of successive subtraction as has been followed by Bube and Others (12,14,18). The same

procedure is adopted in the present case and some typical
graphs are shown in Figs. 3.14 to 3.16.

All the decay curves were split into three exponentials
and the trap depth corresponding to each exponential was
determined. The values thus obtained are listed in table 3.1.
The values of S used in the above calculations were obtained
from thermoluminescence studies to be described in chapter 4.

3-3.6 <u>Activation Energies</u>:

The values of trap depths calculated for all samples
vary from 0.70 to 1.52 eV for slowest exponential, from 0.61
to 1.42 eV for middle exponential and from 0.59 to 1.36 eV
for fastest exponential. On comparison of these values with
those determined from thermoluminescence carried out on the
same samples, it is found that the energies corresponding to
the slowest and middle exponential components show a good
agreement (see Tables 3.1 and 4.1); the thermoluminescence
values having been calculated on the assumption of the monomo-
lecular kinetics. (EH3 values). The activation energies
corresponding to the faster exponential of the decay curves
are considerably smaller. This is to be expected, since for
recording the glow curves, heating begins only after the
phosphorescence intensity has become negligible. By this time
the filled shallower traps get already empited and the
remaining deeper ones are subsequently emptied with the supply
of energy.

3-3.7 Variation of Activation Energies with Concentration of Zn and NaCl:

The values of activation energies were plotted against the concentration of Zn as well as NaCl. The plots obtained for E values of slowest exponential are as shown in Figs. 3.17 and 3.18. Similar were the nature of plots for E values corresponding to middle and faster expontials. From graphs it appears that there is no systematic change in trap depths with addition of Zn alone (see Fig.3.17 (a)). Whatever change observed, i.e. increase in E value with Zn concentration, could be due to influence of activator on distribution of trap densities (13,19,20). The variation observed in E values with Zn in presence of flux and with % of flux is however systematic in nature (Figs.3.17 (b) and 3.18), implying thereby that the introduction of Zn in presence of flux and addition of flux gives rise to new trapping levels in the phosphor (16,17). The result is in accord with the inference drawn from the b values.

3-3.8 Rate Constants and life times:

The slopes of the three straight lines obtained on the log I-t plot are P_1, P_2 and P_3 and represent the transition probabilities. The reciprocals of these transition probabilities give the values of life times T_1, T_2 and T_3 of a trapped electron contributing to slowest, middle and fastest exponential components respectively. The observed values are listed in Table 3.2.

3-3.9 <u>Kinetics of Decay</u>:

The order of kinetics involved in the decay process may be understood as follows: The decay process may be governed by monomolecular, bimolecular or intermediate kinetics depending upon the relative location of traps and luminescence centres. The monomolecular decay is exponential and is expresented by the equation (3.4), whereas the bimolecular process involves power low and is represented by equation (3.7). Thus according to these equations, a straight line on semi-log plot between I and t pepresents the first order kinetics, whereas straight line between the reciprocal of the square root of intensity and time, indicates the second order kinetics. Further, for second order kinetics, a plot between log I versus log t assumes a slope of -2 at large values of t. An examination of the decay curves obtained in the present work indicates that their form is not as per equations (3.4) or (3.7).

However, the observed nature of decay is well explained on the basis of monomolecular superposition theory, indicating that the kinetics involved is likely to be monomolecular. Thus, it may be concluded that the kinetics involved in the decay process is likely to be monomolecular.

3-3.10 <u>Distribution of trapping levels</u>:

The trapping levels in a phosphor are distributed in their depths. The distribution may be uniform, quasi-uniform,

non-uniform or exponential (21). For the present system the distribution is ascertained as follows:

For uniform trap distribution, over a wide range, the relation between phosphorescence intensity I and time t is given by the equation

$$I = \frac{Nk\,T}{t}\left[1 - \exp. \ (St)\right] \quad - - - - - (3.21)$$

where N is the number of traps with activation energies lying between E and $E + dE$. Phosphorescence in present case lasts for few minutes. Also the frequency factor S is of the order of 10^{14} Sec^{-1} (see section 4.34). Hence, we have $St \gg 1$, and above equation reduces to

$$I = \frac{N\,k\,T}{t}$$
$$= N\,k\,T\ t^{-1}$$
$$= Io\ t^{-1} \quad - - - - - - (3.22)$$

The relation is similar to $I = Io\ t^{-b}$, and for uniform trap distribution b should be unity. However, the observed values of b are not unity or even close to unity (see Table 3.1). This rules out the possibility of uniform or quasi-uniform trap distribution. On the other hand, the values of b are less than unity indicating thereby that the trap distribution is likely to be non-uniform. Now refering to equation $I = $ constant. $t^{-(\beta k\,T + 1)}$, for an exponential trap distribution $b = (\beta k\,T + 1)$, which means $b > 1$ (22). For our samples, b fluctuates between 0.24 and 0.73 and thus excludes the

probability of exponential trap distribution.

Above conclusion is supported by a plot between I.t and log t obtained for present samples. Typical plots are shown in Fig.3.19. The curves are neither straight lines parallel to log t axis nor exponential as required by uniform and exponential trap distributions respectively. However, they are increasing ones, suggesting thereby the trap distribution to be non-uniform. The curves also give an idea about the density traps at various depths. This is since, I.t is a measure of trap density while log t of trap depth.

3-4. SUMMARY:

1) Phosphorescence decay is of the form $I = Io \ t^{-b}$.

2) The decay is hyperbolic in nature and can be explained in terms of superposition of various exponentials.

3) The possible kinetics of decay process is monomo-lecular.

4) The distribution of traps responsible for the phosphorescence is likely to be non-uniform.

5) Addition of Zn in absence of flux only influences the distribution of trap densities while its introduction along with the flux gives rise to new trapping levels.

6) Incorporation of flux, NaCl, into the host lattice creates new trapping levels which contribute to the phosphorescence decay.

-0-0-0-

TABLE - 3.1

Decay Characteristics of Samples

Series No.	Sample No.	Value Io	Decay constant b	Value of E from 'Peeling off' of decay curves, eV		
				Slowest exponential.	Second exponential.	Fastest exponential.
1	2	3	4	5	6	7
	B_1	3.80	0.29	0.70	0.61	0.59
	B_2	3.71	0.28	0.84	0.75	0.73
	B_3	5.68	0.34	0.79	0.70	0.65
	B_4	15.14	0.54	0.98	0.93	0.88
I	B_5	6.83	0.42	1.18	1.10	1.06
	B_6	6.53	0.43	1.15	1.01	1.01
	B_7	14.45	0.50	1.18	1.02	0.96
	B_8	15.67	0.52	1.08	1.01	0.97
	B_9	10.00	0.47	1.46	1.37	1.34
	B_{10}	31.62	0.58	0.88	0.80	0.76
	B_{11}	80.35	0.73	1.23	1.13	1.11
	B_{12}	10.47	0.42	1.04	0.96	0.90
	B_{13}	37.15	0.65	1.01	0.94	0.88
	B_{14}	13.18	0.49	1.52	1.42	1.36
II	B_{15}	4.26	0.30	1.15	1.04	1.01
	B_{17}	3.09	0.25	1.24	1.13	1.08

Table 3.1 cont.

1	2	3	4	5	6	7
	B_{18}	4.02	0.31	1.22	1.14	1.15
	B_{19}	3.93	0.24	1.07	0.98	0.92
	B_{20}	30.55	0.63	0.96	0.88	0.83
	B_{21}	28.18	0.54	1.11	1.04	0.98
III	B_{22}	14.79	0.48	0.84	0.76	0.72
	B_{23}	22.39	0.55	1.12	1.03	0.97
	B_{24}	27.54	0.59	1.03	0.83	0.88

TABLE 3.2

Life times of samples

Sample No.	τ_1 Sec^{-1}	τ_2 Sec^{-1}	τ_3 Sec^{-1}
B_1	568.18	17.77	8.05
B_2	896.85	21.08	13.03
B_3	920.81	25.40	4.14
B_4	375.36	43.89	7.94
B_5	515.26	21.38	5.55
B_6	7547.16	39.10	10.18
B_7	21231.42	42.28	6.08
B_8	685.40	40.25	7.97
B_9	1137.65	42.68	11.41
B_{10}	1292.65	55.92	12.59
B_{11}	3343.36	88.65	35.01
B_{12}	1997.60	91.32	8.96
B_{13}	808.40	50.58	5.43
B_{14}	2020.20	41.63	4.16
B_{15}	2415.45	42.60	12.35
B_{17}	2664.53	48.48	6.56
B_{18}	918.27	49.28	7.06
B_{19}	2979.73	68.82	9.24

Table 3.2 cont.

1	2	3	4
B_{20}	1335.29	78.67	10.24
B_{21}	1481.48	81.16	9.31
B_{22}	1053.40	50.05	8.17
B_{23}	1793.07	56.85	5.20
B_{24}	1093.90	56.62	4.63

3-5. REFERENCES:

1.   Becqueral,E.,"La Lumiere", Paris (1867).

2.   Levshin,W.L.,Acta Phys.Pol.,5,301 (1936).

3.   Levshin,W.L.,and Anthony - Bomanovskii,phys.2,
      Sowj.Union,5,796 (1934).

4.   Randall,J.T. and Wilkins,M.H.F.,Proc.Roy.Soc.,
      A 184, 366 (1945).

5.   Garlick,G.F.J. and Gibson,A.F.,Proc Roy.Soc.,
      60,574 (1948).

6.   May,C.E. and Partridge,J.A.,J.Chem.Phys.,40,
      1401 (1964).

7.   Curie,D.,"Luminescence in Crystals" (Methuen and
      Co.Ltd.,London,1963).

8.   Adirowitch,E.I.,Akad.Verlag,Berlin,19 (1953).

9.   Adirowitch,E.I.,J.Phys.Rad.,17,705 (1956).

10.   Abhyankar,M.D.,Ph.D.thesis,University of Saugar,
      Sagar (1968).

11.   Sharma,D. and Amar Singh, Indian J.Pure-Appl.
      Phys.,7,310 (1919).

12.   Amar Singh,Indian J.Pure Appl.Phys.,7,367 (1969).

13.   Bhawalkar,D.R. and Malhotra,B.R.,Indian J.Pure Appl.
      Phys., 7,163 (1969).

14.   Powar,S.H.,Lawangar,R.D.,Shalgaonkar,C.S. and
      Narlikar,A.V.Phil.Mag.,24,727, (1971).

15. Kenney,J.F. and Keeping,E.S., "Mathematics of Statistics" (Van Ngtrand Co.Ltd.,1959).

16. Sinha,O.P. and Sivaraman,S.,Indian J.Pure.Appli. Phys.,10,135 (1972).

17. Lawangar,R.D. and Narlikar,A.V.,J.Luminescence, 11, 135 (1975).

18. Bube,R.H.,Phys.Rev.,80,655 (1950).

19. Bhawalkar,D.R. and Muley,K.,Indian J.Pure Appl. Phys.,8,476 (1970).

20. Pathak,G.R. and Kamra,P.C.,Indian J.Pure.Appl. Phys.,10,318 (1972).

21. Randal, J.T. and Wilkins,M.H.F.,Proc.Roy.Soc., (London) A 184 390 (1945).

22. Garlik,G.F.J.,Encyclopedia of Physics,Edt.by S.Flugg; Vol.XXVI light and matter II, edition (1958).

...
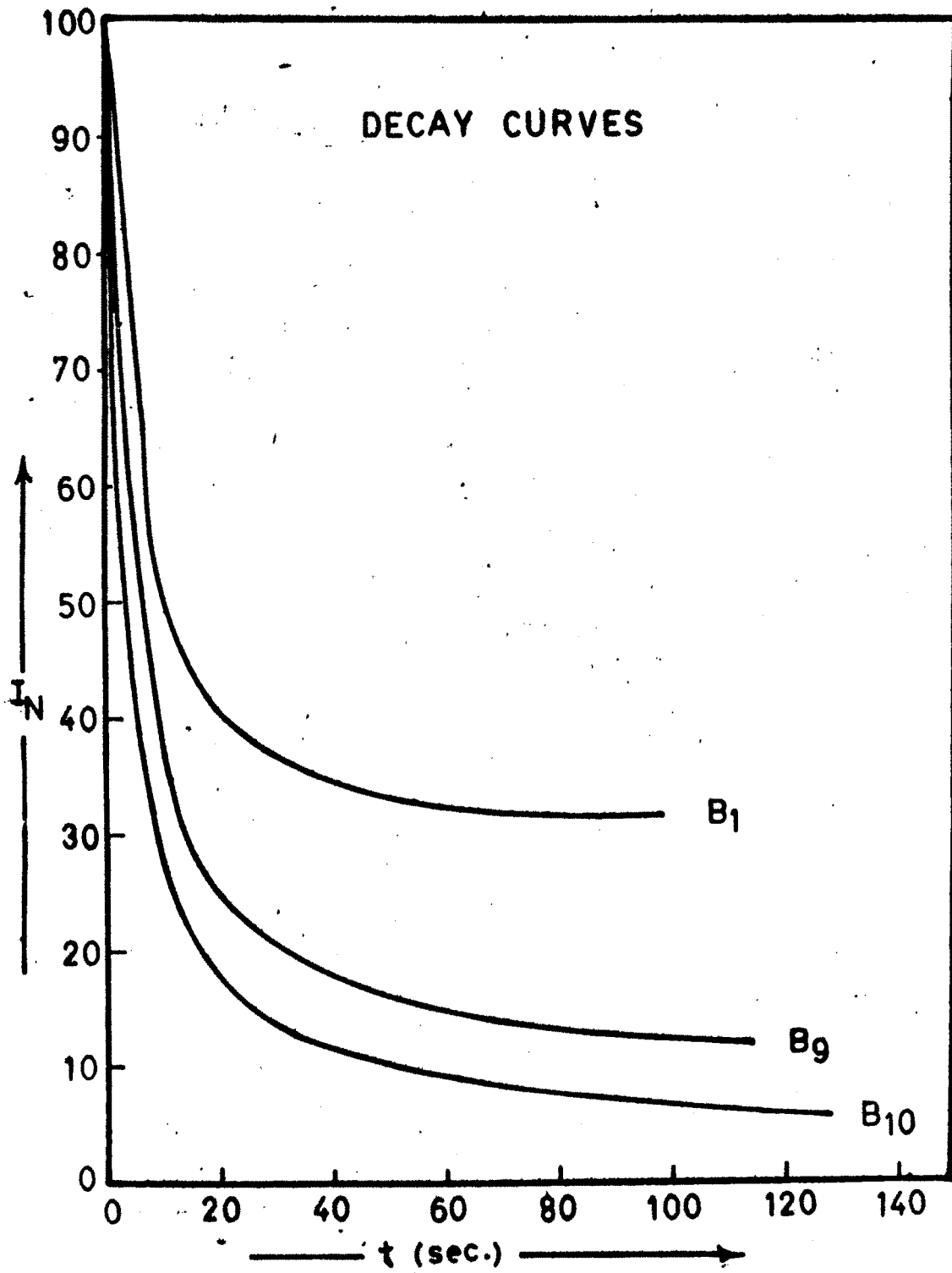
Fig. 3·1
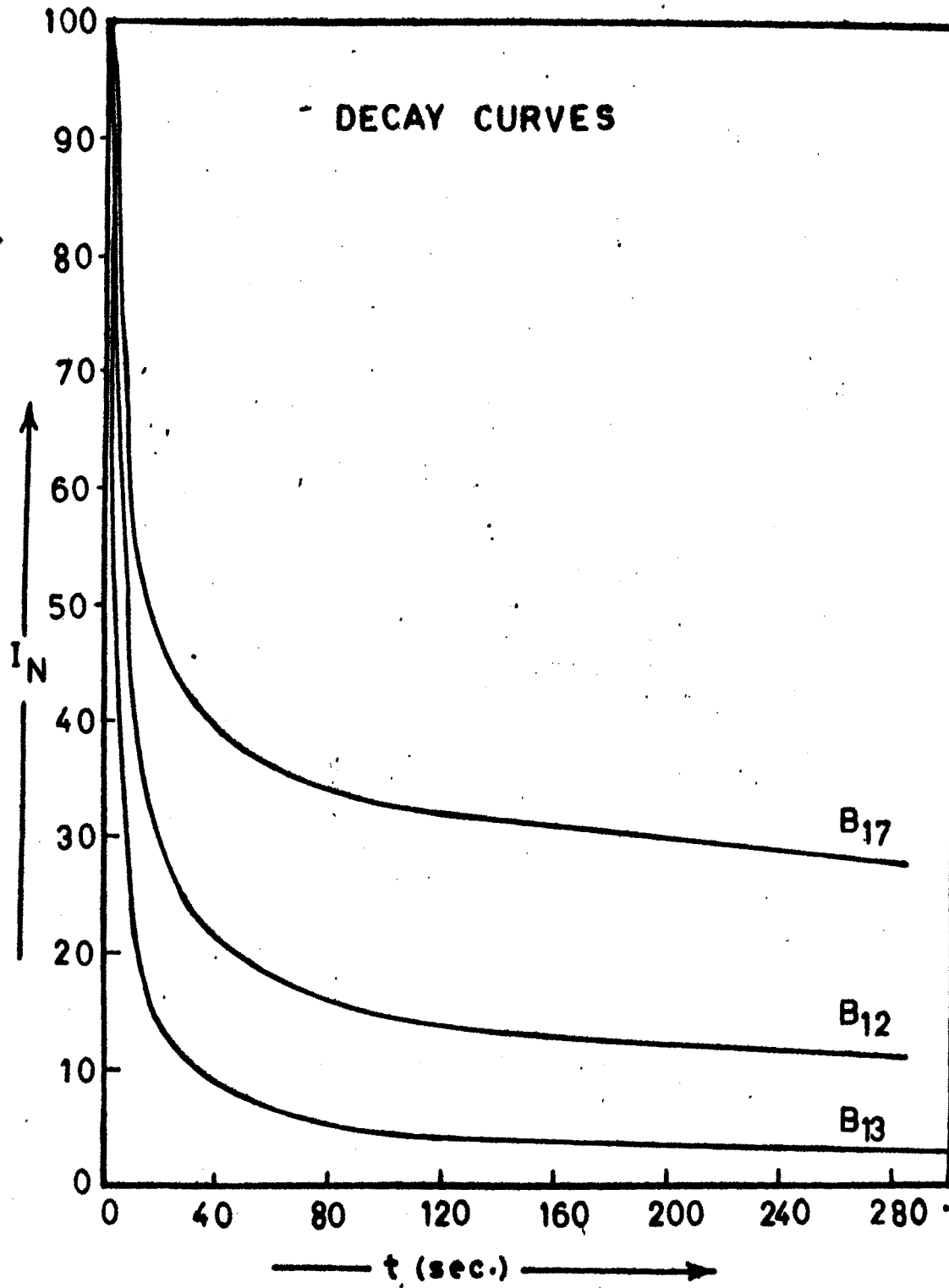
Fig. 3.2
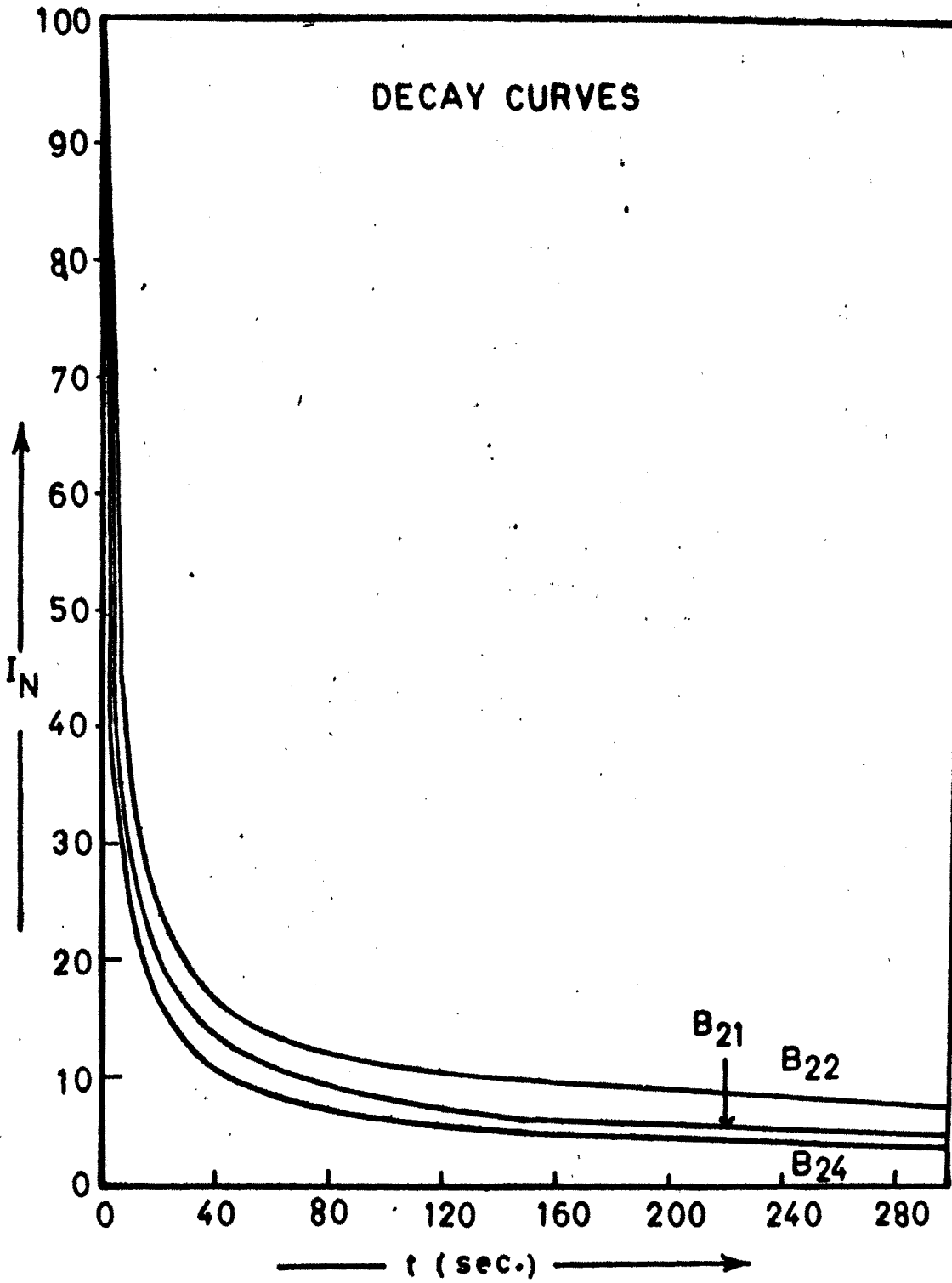
Fig. 3·3
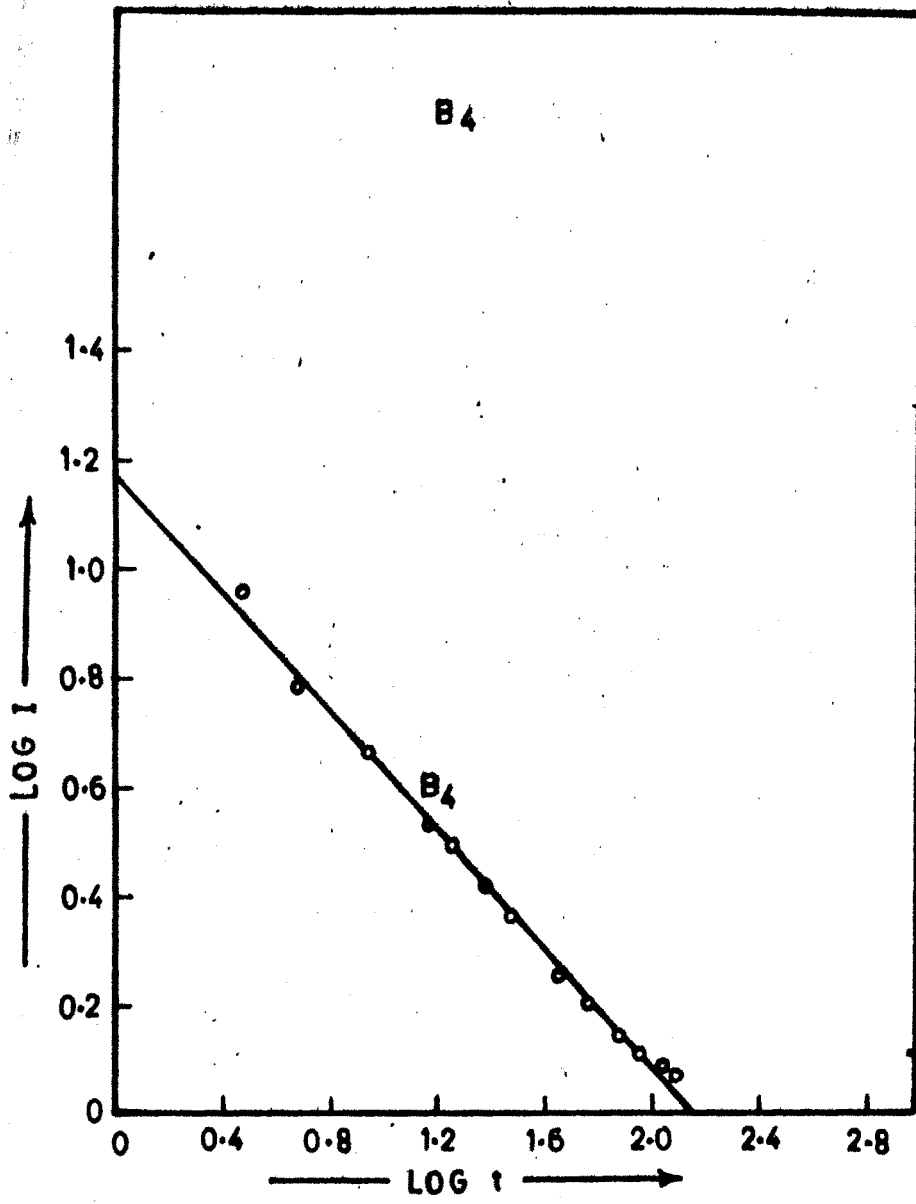
Fig. 3.4
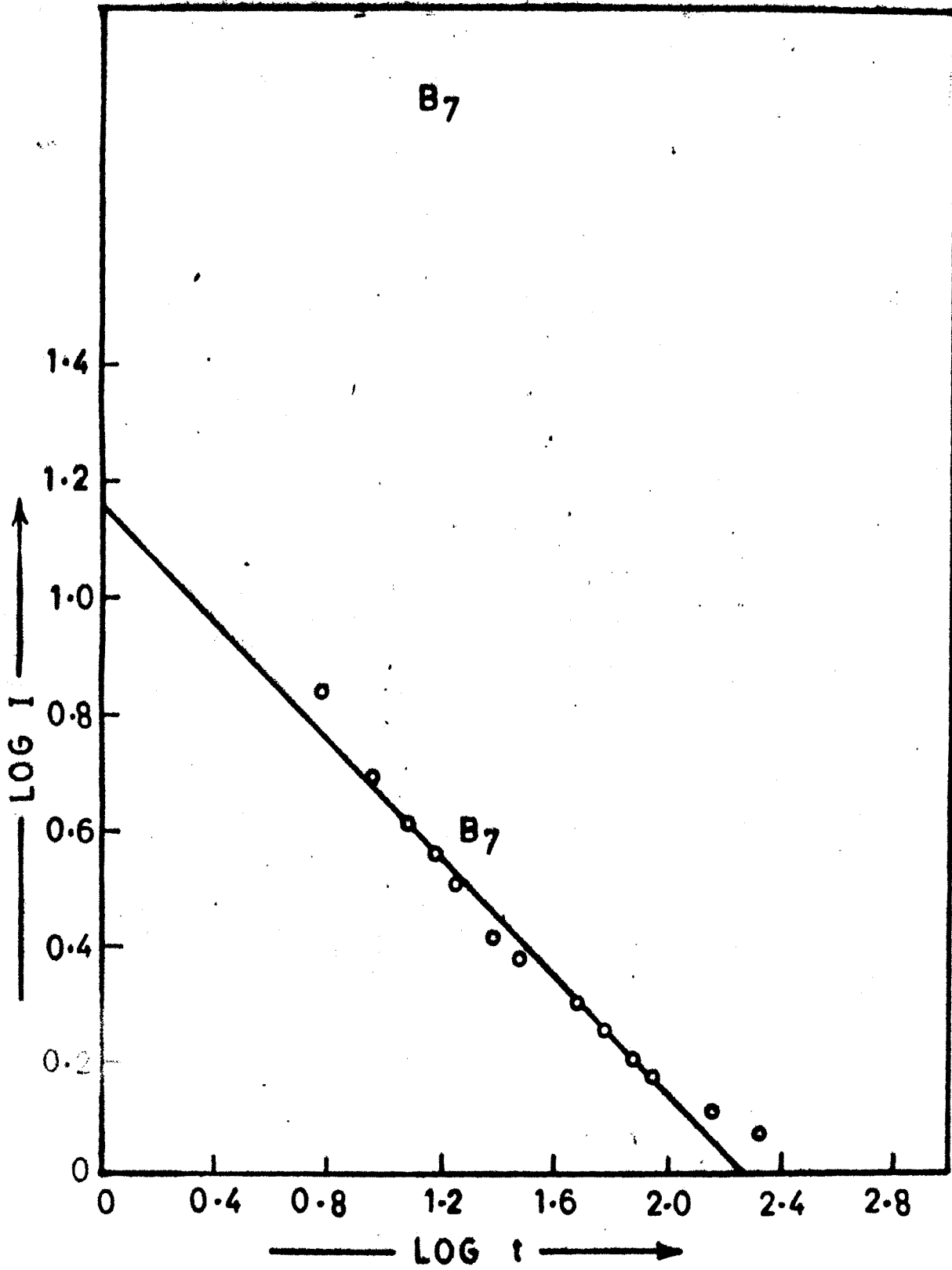
Fig. 3.5
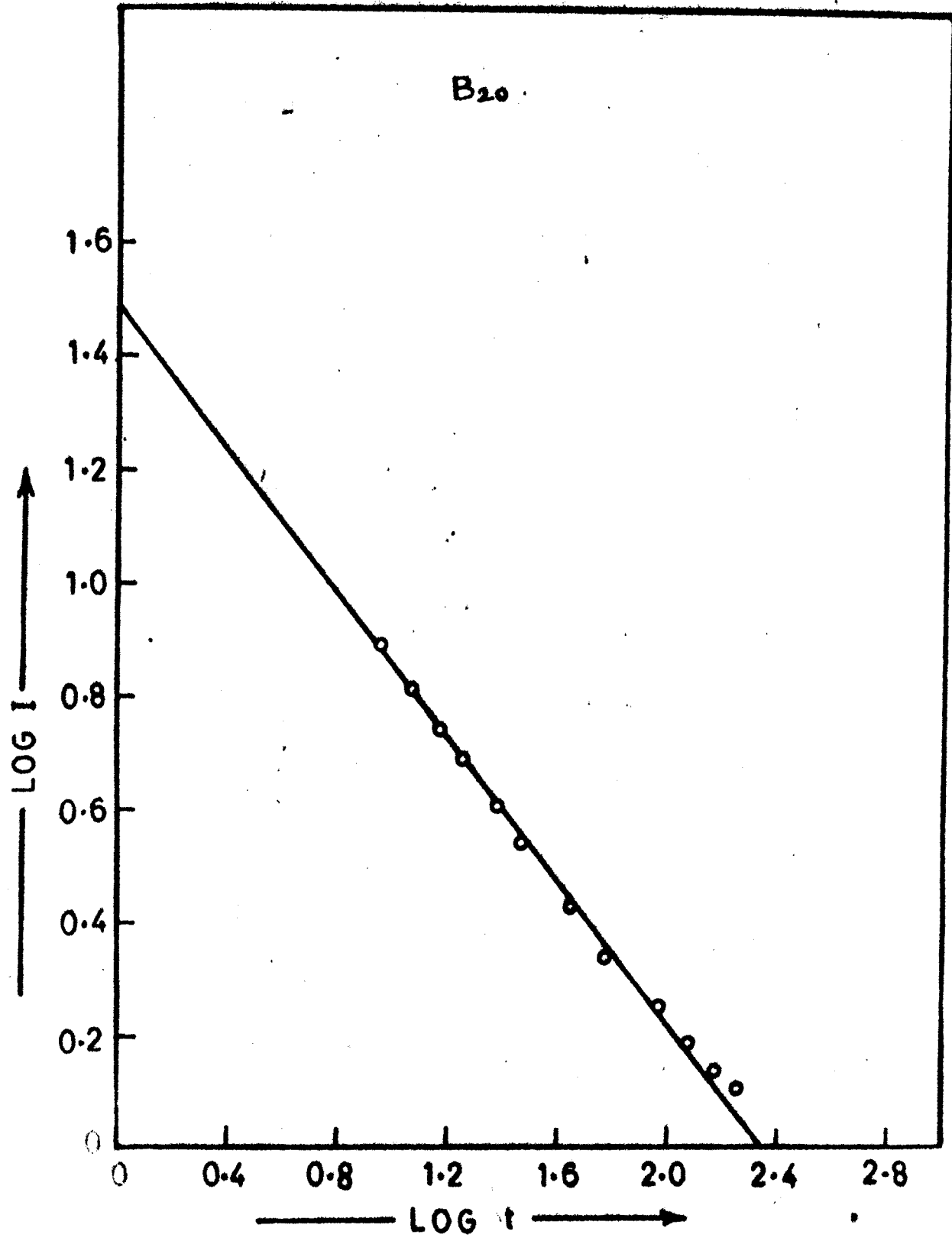
Fig. 3·6
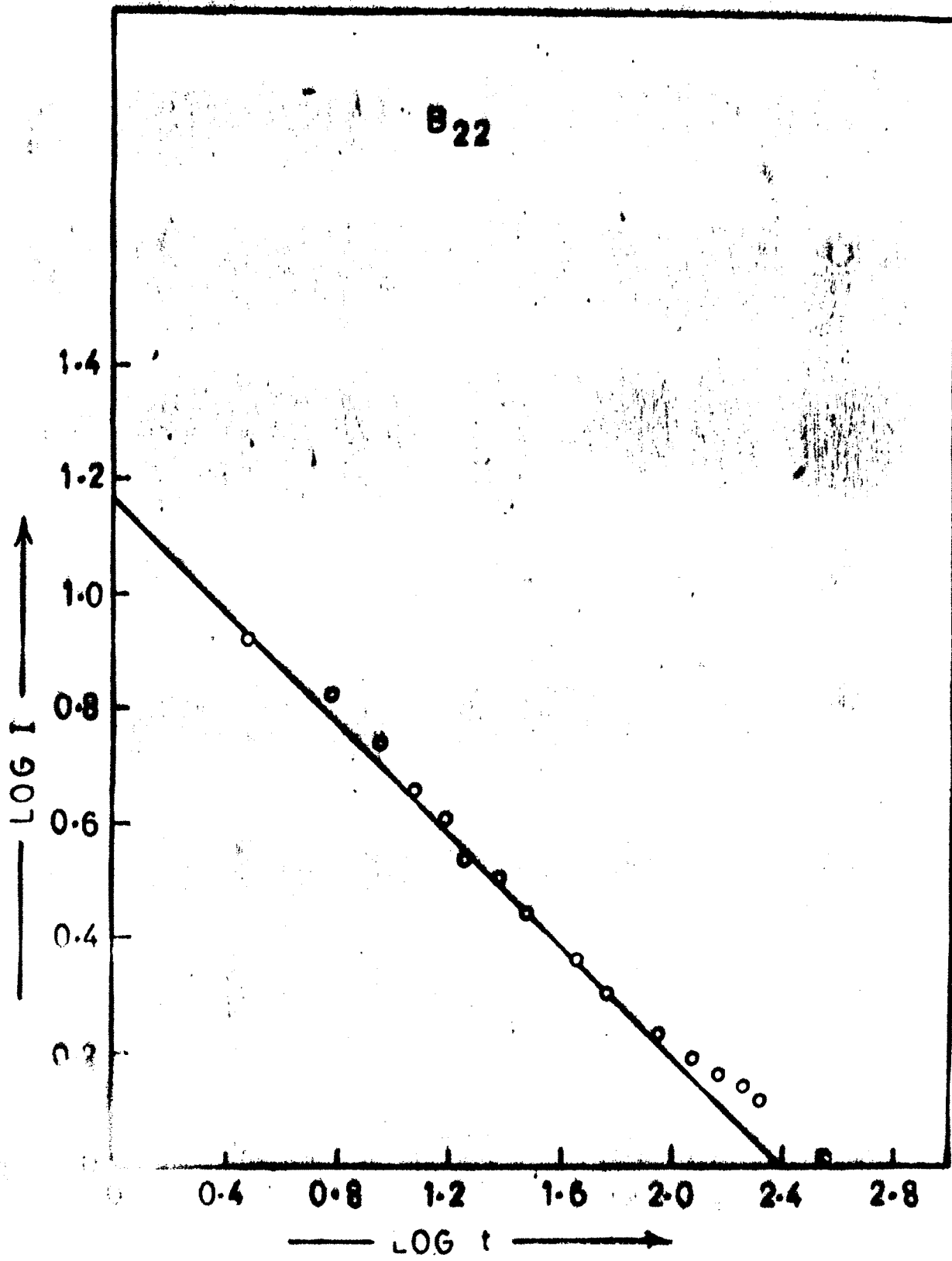
Fig. 3·7
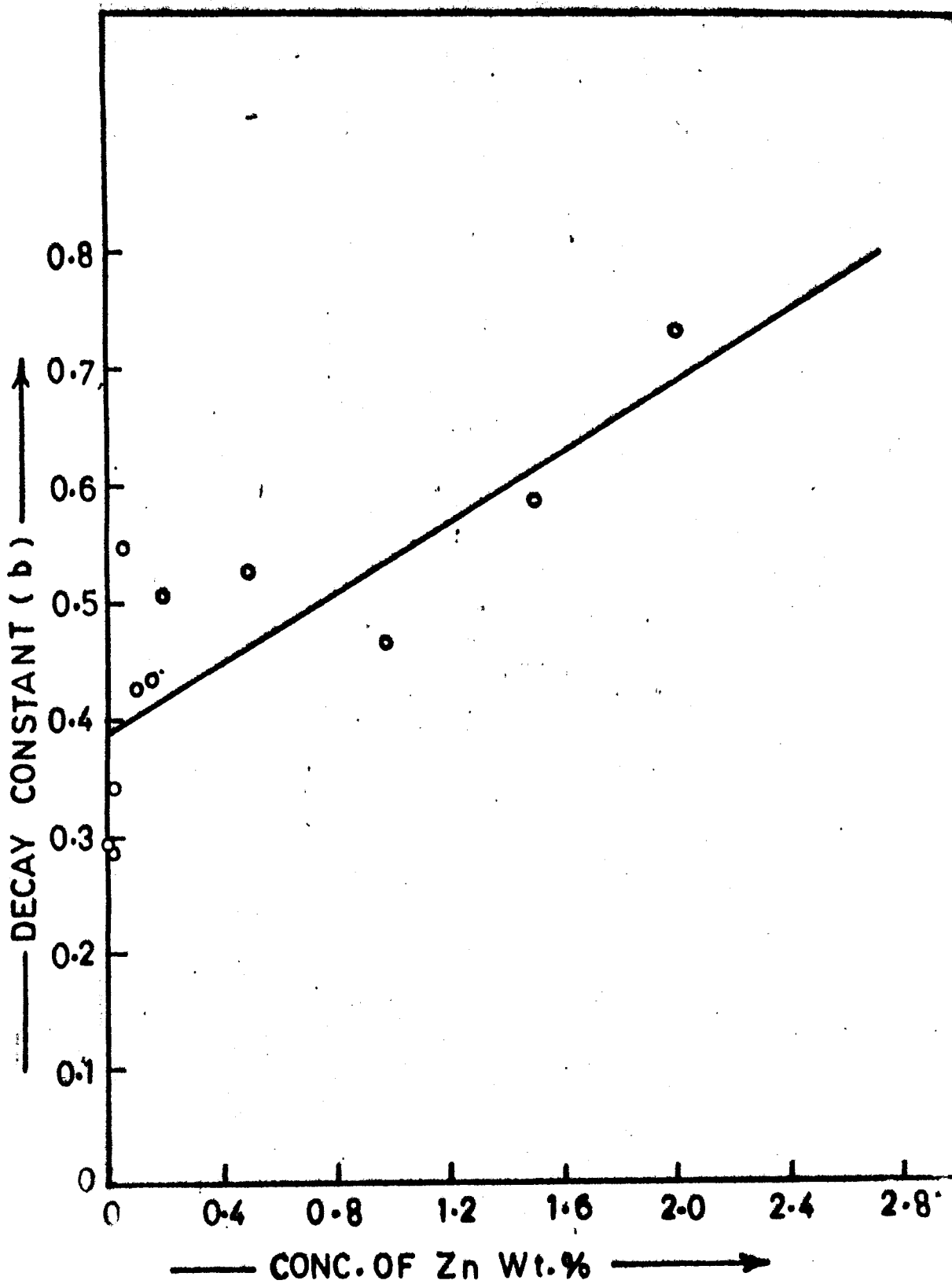
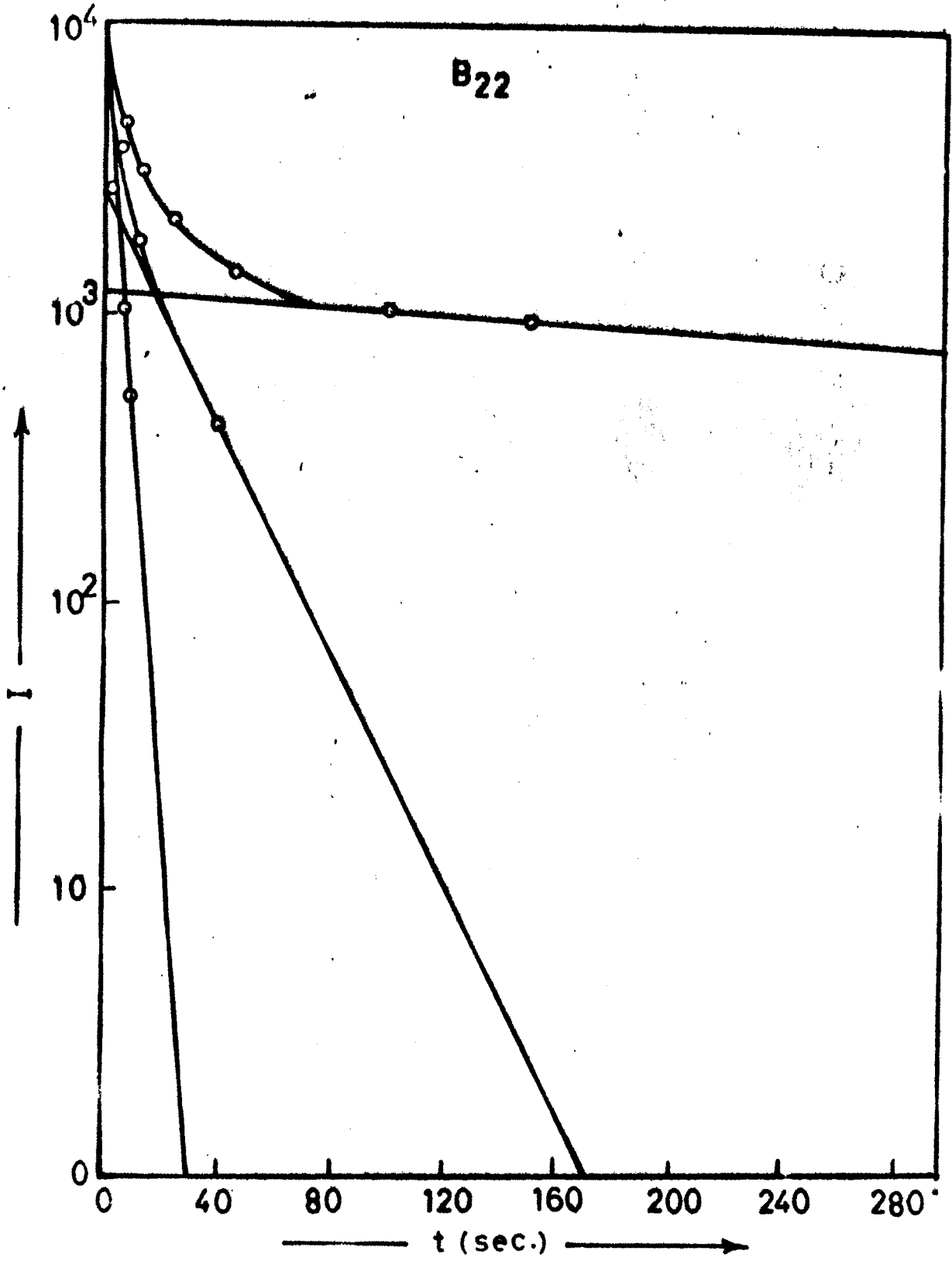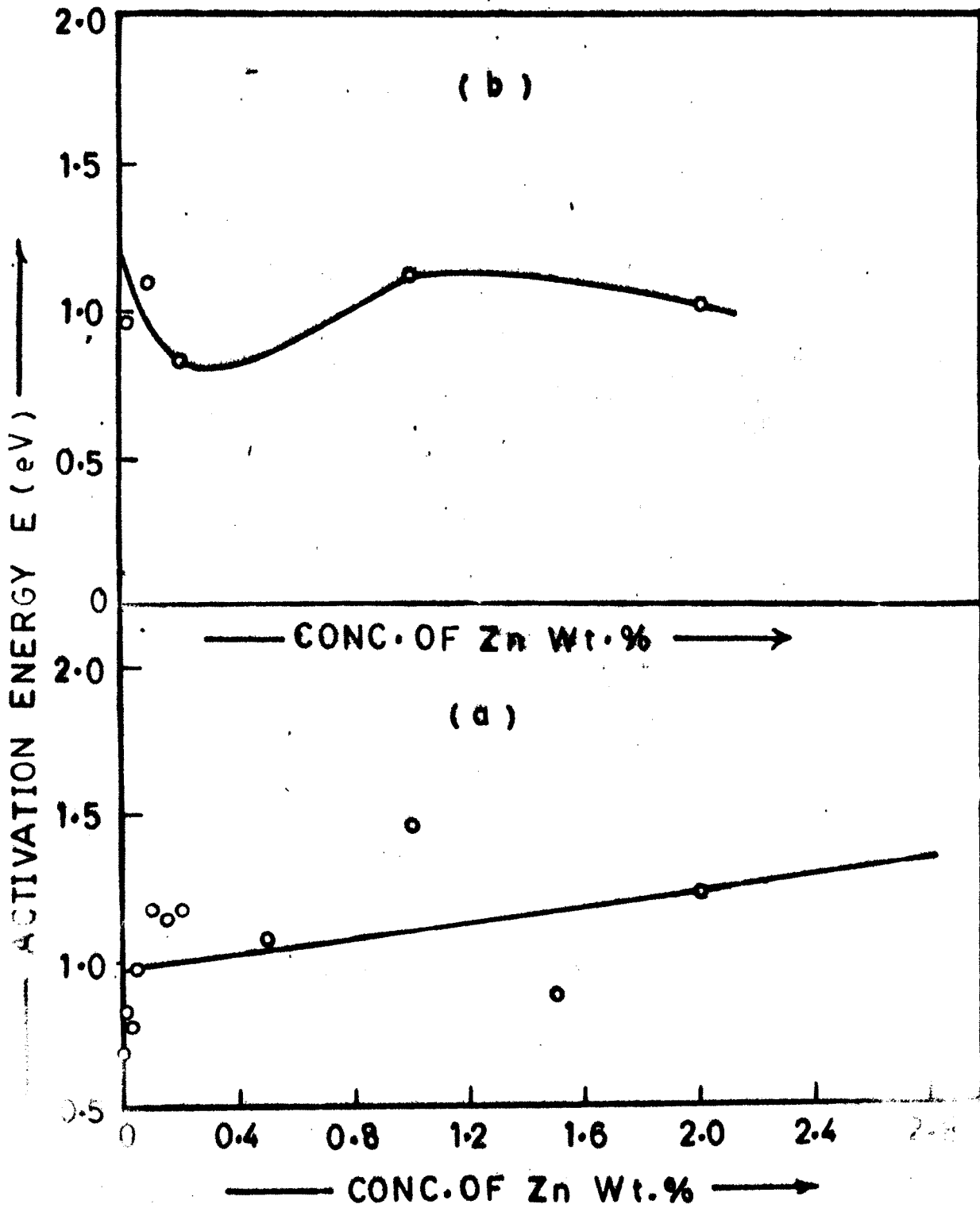Fig. 3·8
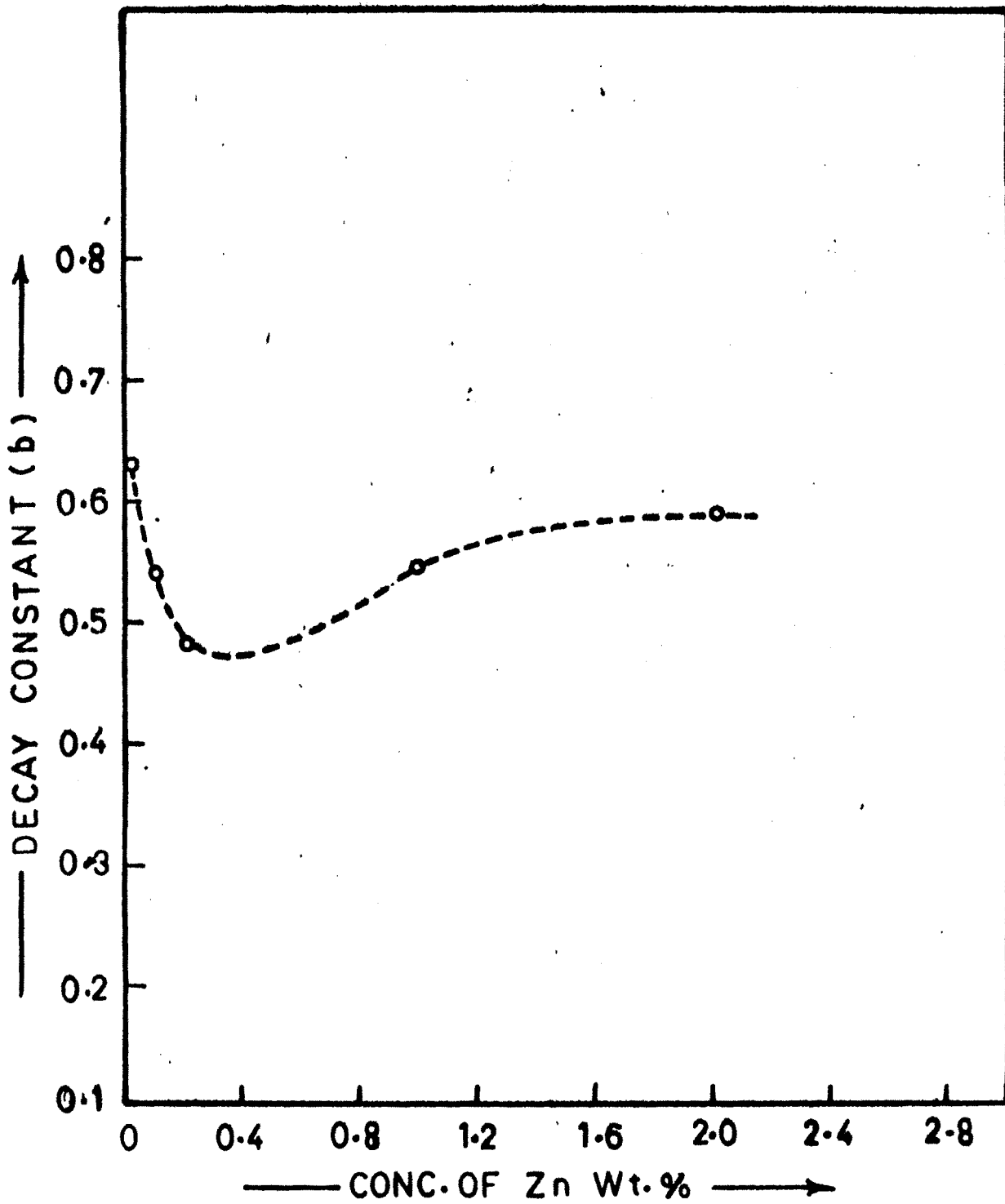
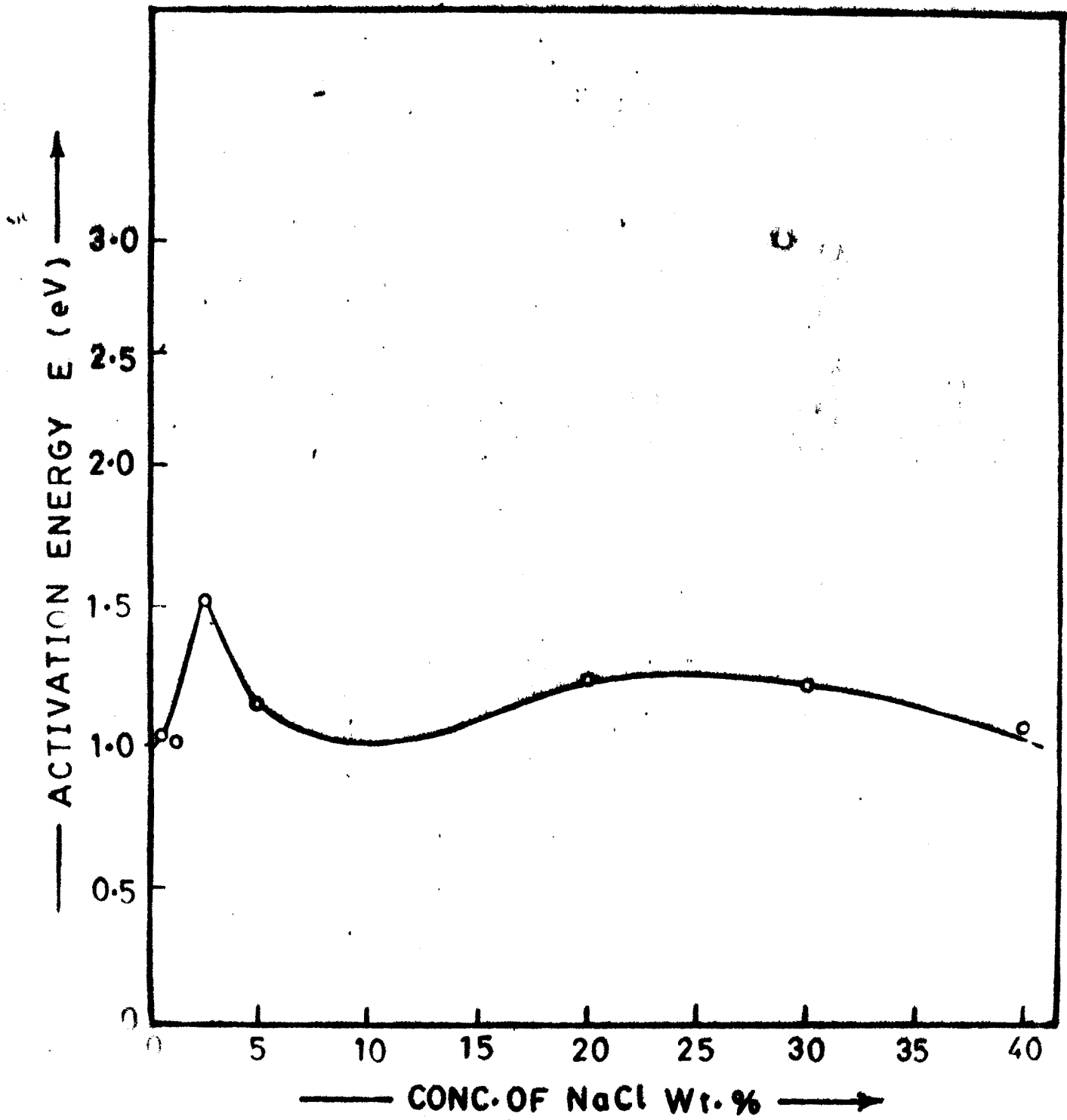Fig. 3.9
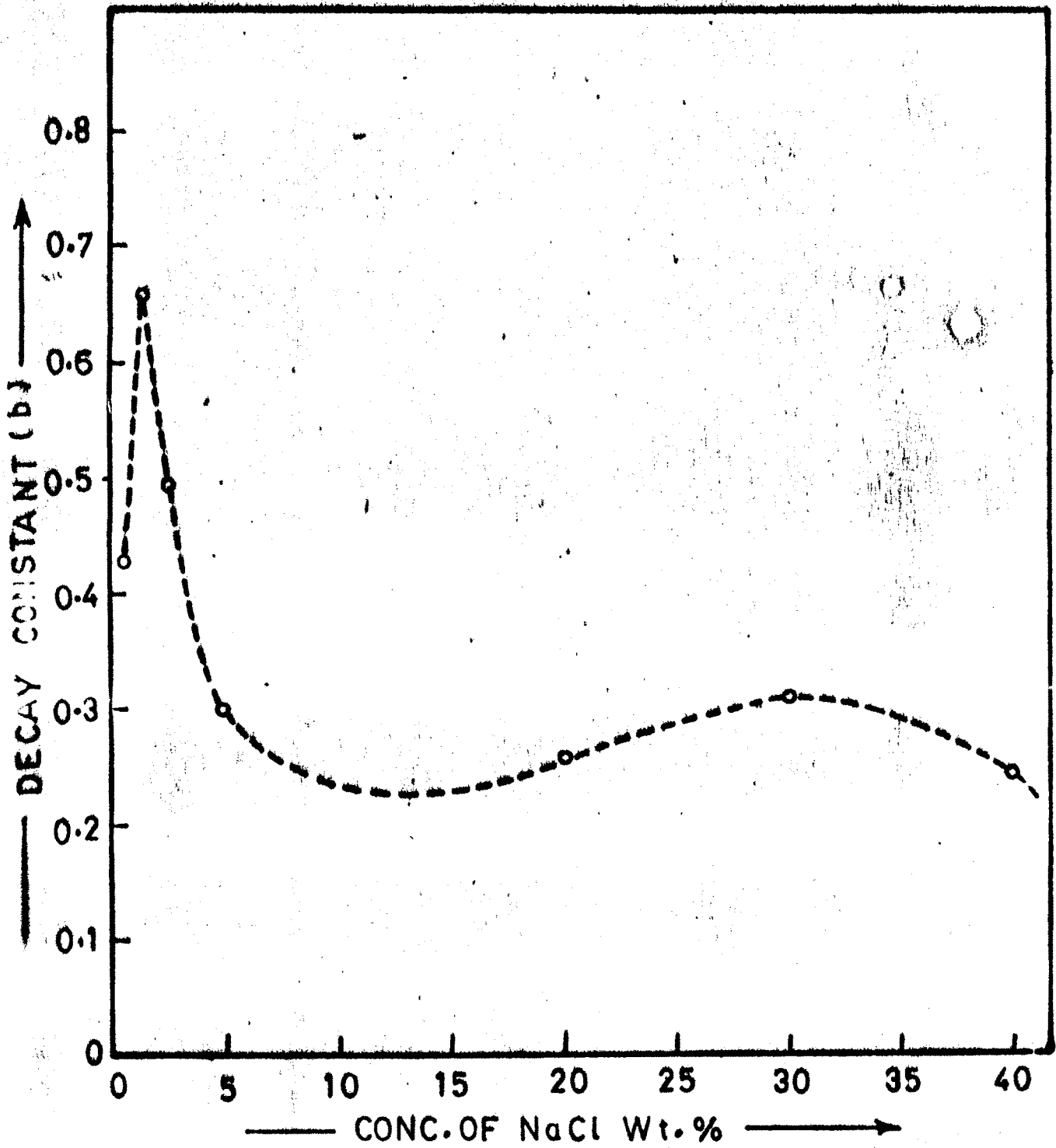
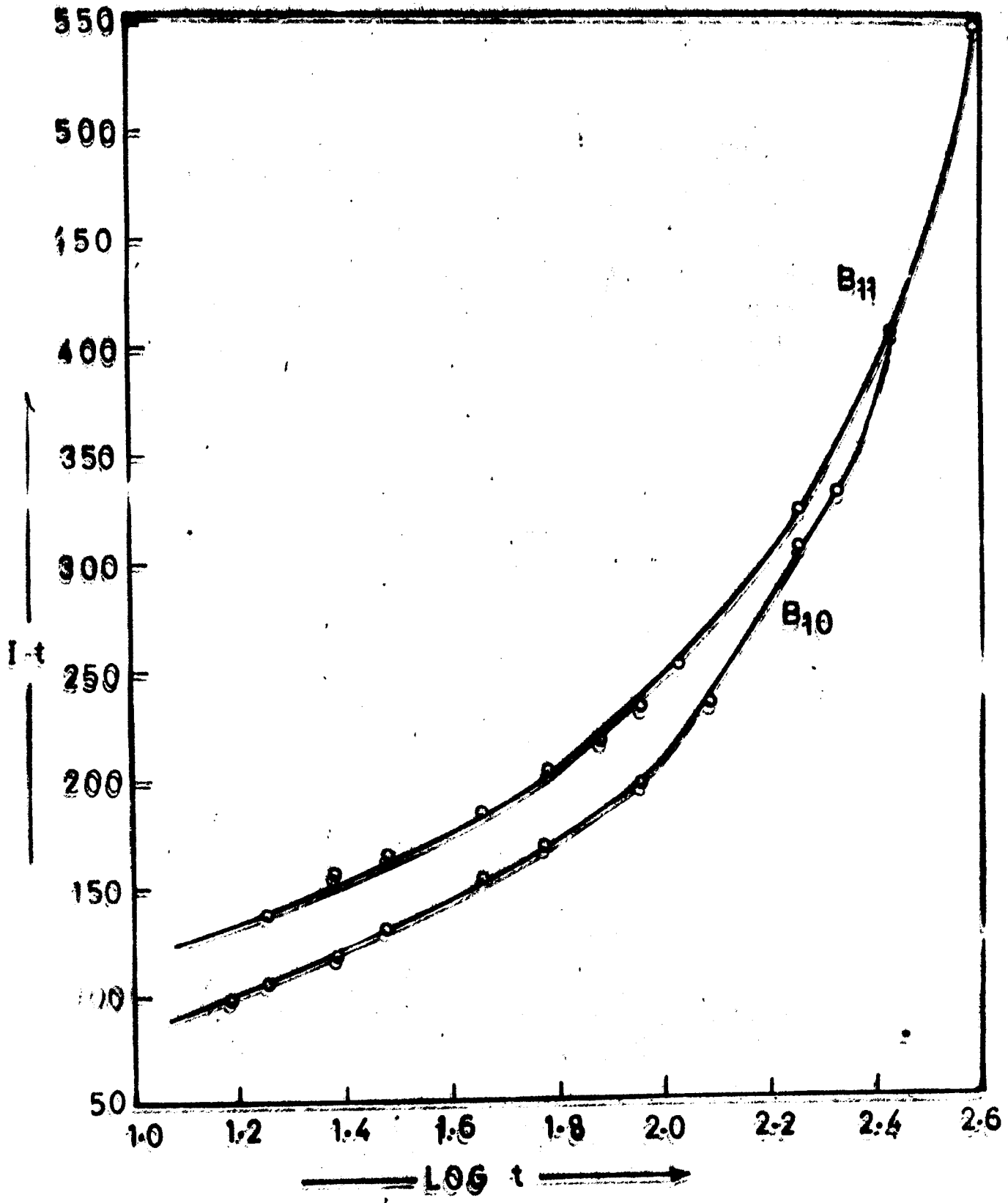Fig. 3.10
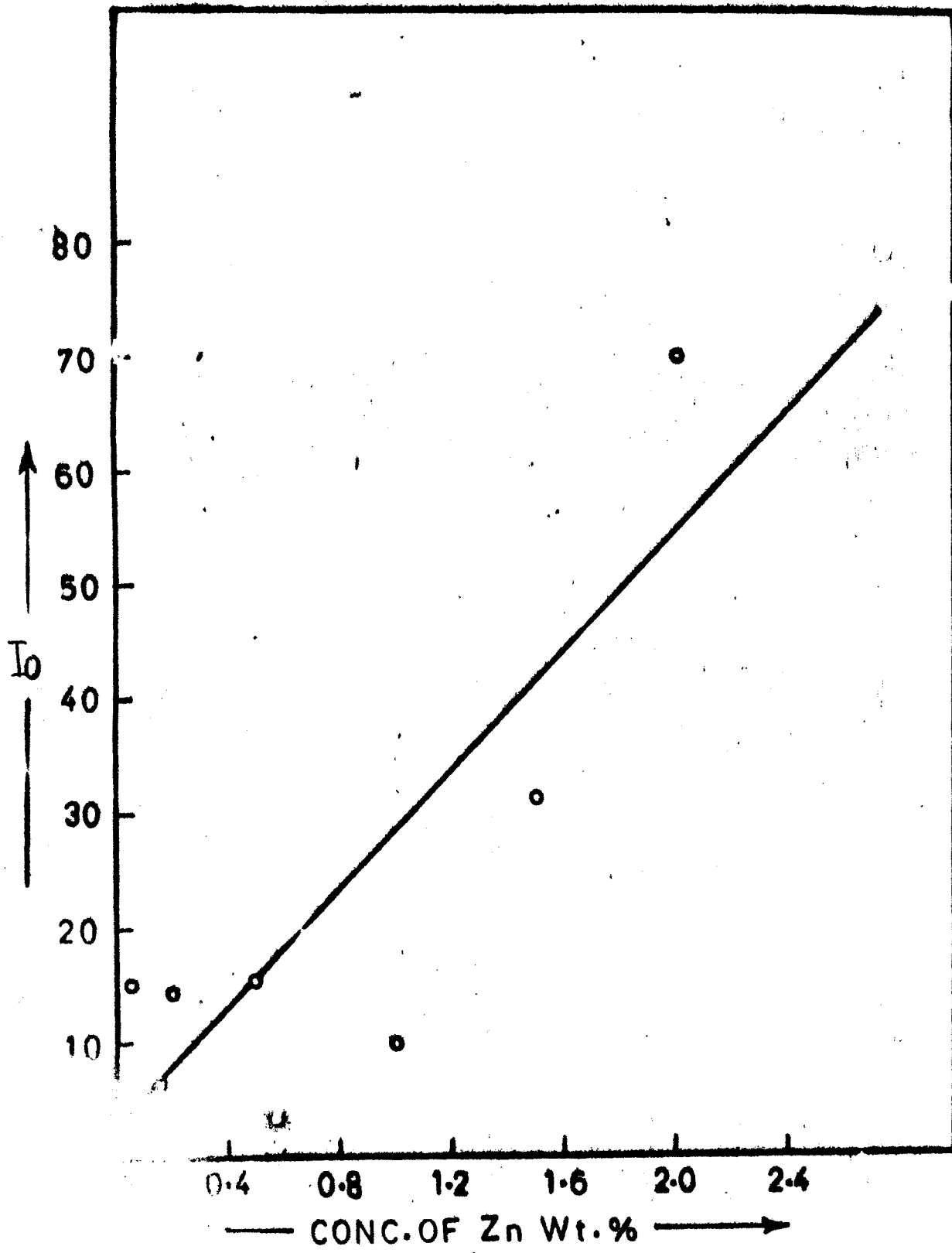
Fig. 3·11
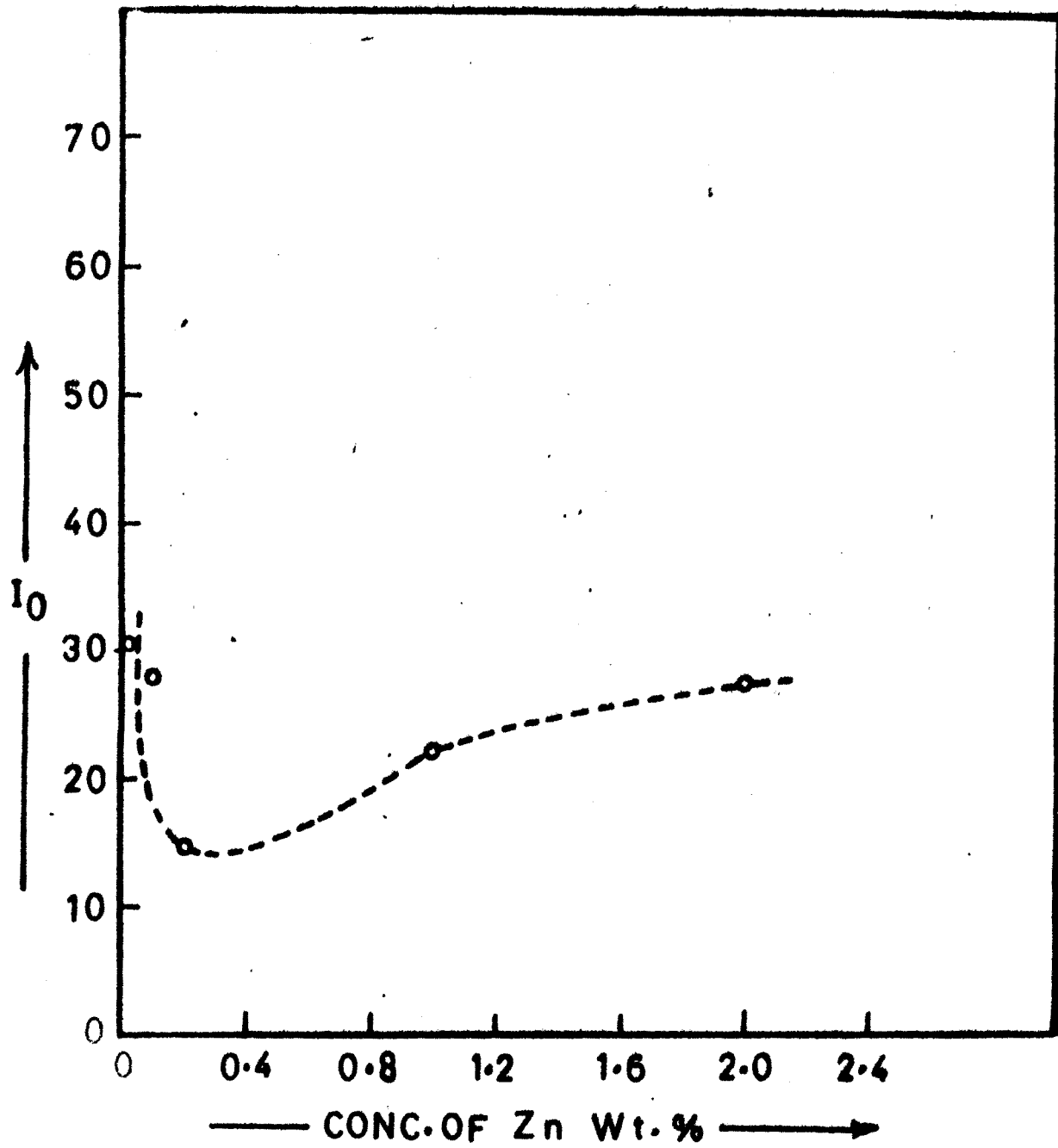
Fig. 3.12
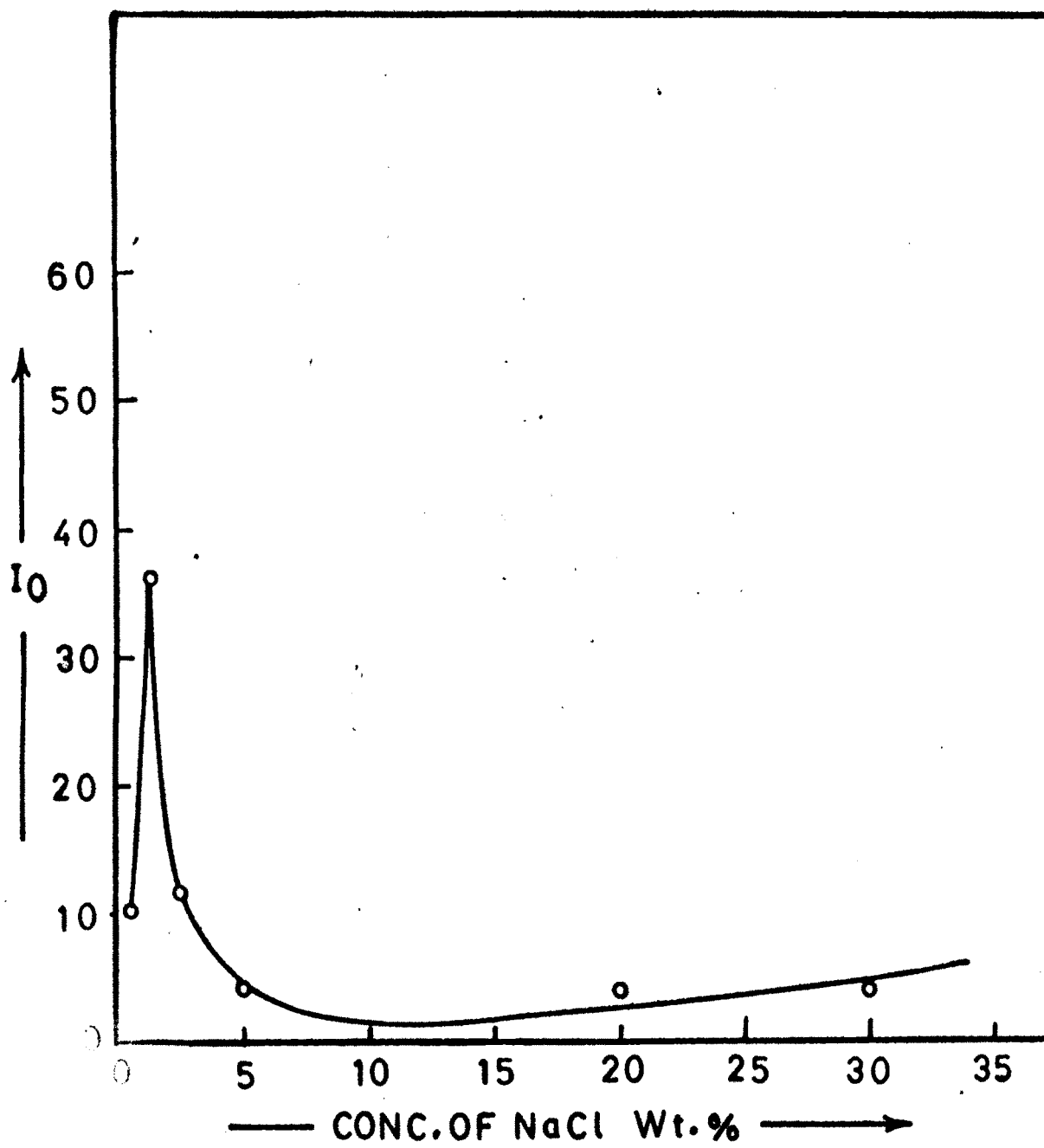
Fig. 3·13
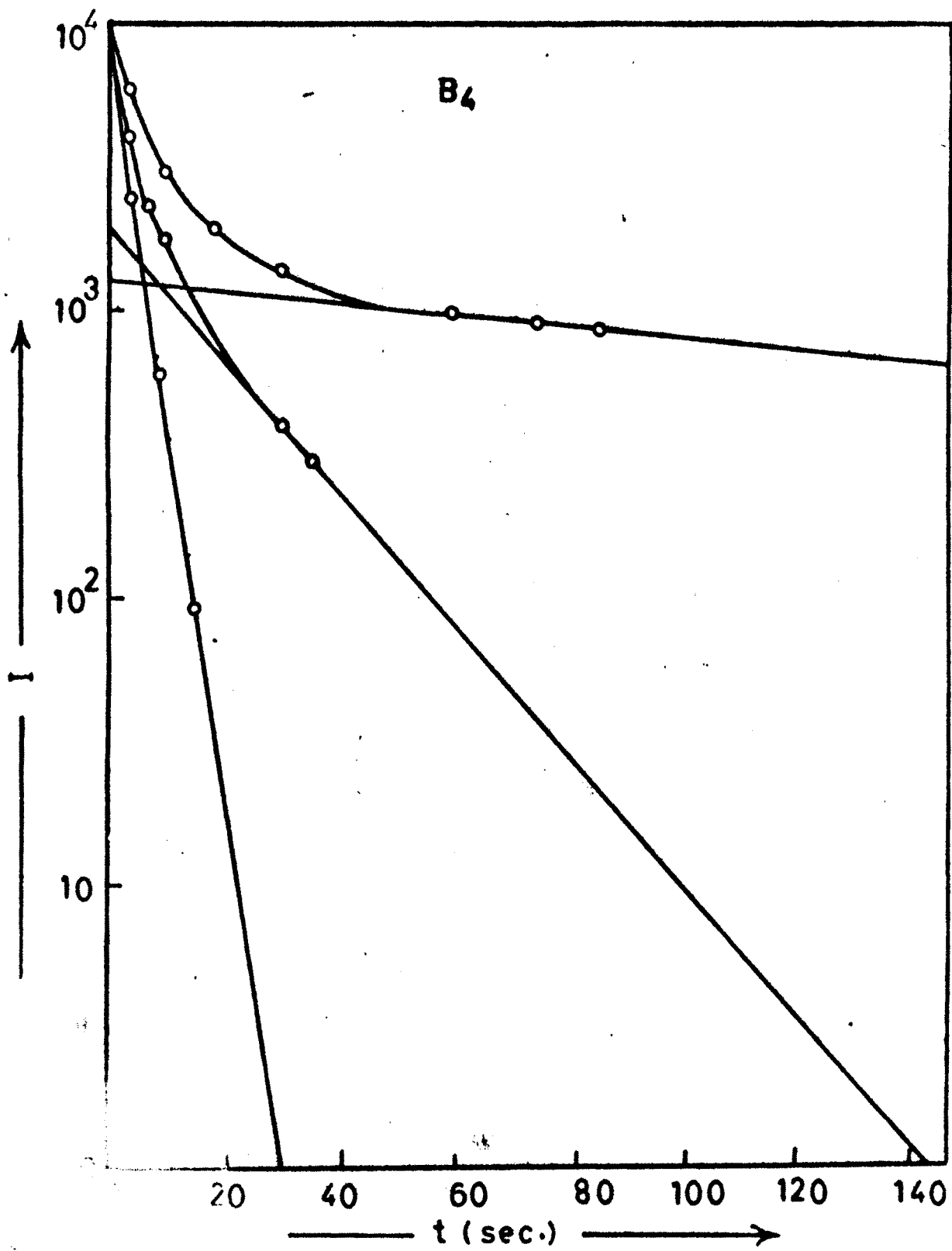
Fig. 3·14
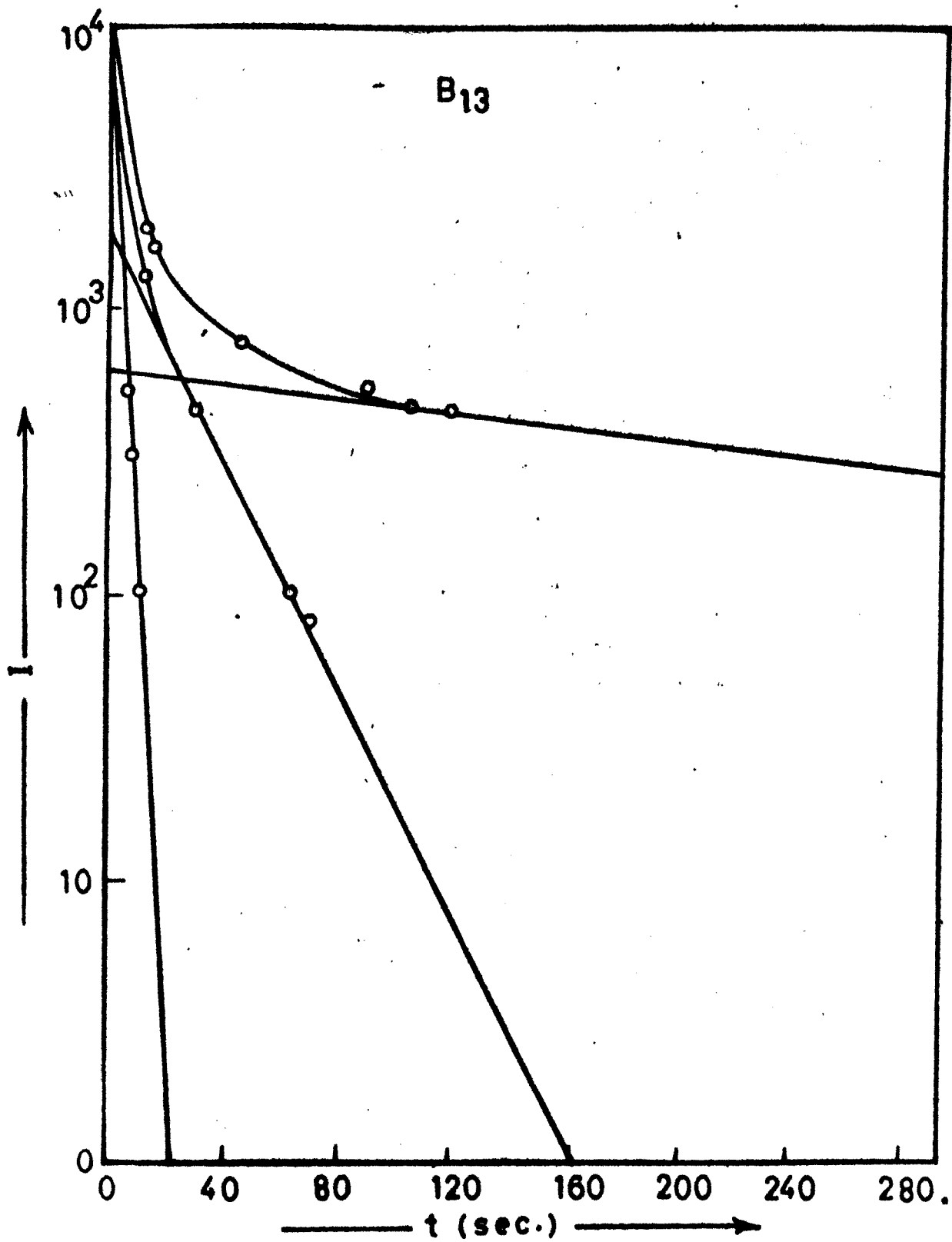
Fig. 3.15

Fig. 3·16

Fig. 3·17

Fig. 3.18

Fig. 3.19