CHAPTER - IV

THERMOLUMINESCENCE BEHAVIOUR

4-1 INTRODUCTION:

Thermoluminescence (TL) has been extensively used as a technique for elucidating qualitatively the nature of electron traps and the trapping processes involved in phosphors. In thermoluminescence, on supplying thermal energy, the energy stored in a suitably excited phosphor is released in the form of light radiation. The plot of the intensity of the light emitted against temperature gives what is known as the glow curve. It can be used for estimating the activation energy E for thermal release of the trapped electron or hold and provides means of determining the escape frequency factor S. As both E and S depend sensitively upon the trapping centres, glow curve can yield valuable information about the role of various impurities present in the sample.

The object of the present investigation is to measure the activation energy and escape frequency factor for samples containing varying concentration of Zn as an activator and NaCl as a flux, and to study how these impurities influence the general features of the glow curves. The nature and origin of trapping states, and their size have also been investigated. Further, an attempt has been made to determine the type of kinetics involved in the thermoluminescence process.

4-2 THEORETICAL ASPECTS:

4-2.1 Theory of the Thermoluminescence:

Randall and Wilkins (1) were the first to consider thermoluminescence theoretically. They used a mode in which electrons in metastable states are raised thermally to an excited state from which they return to the ground state with emission of radiation. Assuming monomolecular kinetics in the luminescence process, they obtained an expression for the variation of the thermoluminescence intensity with temperature, but they neglected the retrapping of electrons in the empty traps. Later the theory was extended by Garlik and Gibson (2), who assumed bimolecular kinetics and also considered equal probabilities for the retrapping and recombination of the released electrons.

(A) Randall and Wilkin's Theory (1):

Let n be the number of trapped electrons at any time t and p the transition probability, then we have

$$\frac{dn}{dt} = -np \quad \text{-------} \quad (4.1)$$

where $p = S \exp.(-E/_{KT})$. The solution of equation (4.1) is

$$n = n_o \exp.\left[-\left(\frac{S}{\beta}\right)\int_{To}^{T} \exp.\left(-\frac{E}{KT}\right) dT\right] \text{----} 4.2$$

where n_o is the number of electrons trapped initially at $T = T_o$ and β is the uniform heating rate. The thermoluminescence intensity is given by

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

$$I = n_o S \exp.\left(-\frac{E}{KT}\right) \exp.\left[\left(-\frac{S}{\beta}\right)\int_{T_o}^{T} \exp.\left(-\frac{E}{KT}\right) dT\right] .4.3$$

(B) Garlick and Gibson's Theory (2):

Let N be the total number of electron traps of which n are filled at any time. Thus, there will be (N - n) empty traps and n empty centres. The probability that an escaping electron will recombine with an empty luminescence centre and not get trapped is given by

$$n \Big/ \Big[(N - n) + n \Big] = n/N \quad ----- (4.4)$$

The rate of escape of electrons from the trap will be equal to

$$\frac{dn}{dt} = - \frac{n^2}{N} s \ \exp. \left(- \frac{E}{KT} \right) \quad ----- (4.5)$$

The thermoluminescence intensity is given by the solution of equation (4.5) which is

$$I = n_o^2 \ s \ \exp. \left(- \frac{E}{KT} \right) \Big/ N \left\{ 1 + \frac{n_o}{N} \int_{To}^{T} \frac{s}{\beta} \exp. \left(- \frac{E}{KT} \right) dT \right\}^2 \quad ----- (4.6)$$

4-2.2 Methods for Determining the Trap Depth:

There exist several methods for determining the trap depth from glow curves and they have recently been reviewed by Shalgaonkar and Narlikar (3). With these methods, the trap depth E is estimated from either the peak temperature T_m or from the shape of the glow curve. The methods can be classified into two main types: (i) methods sensitive to the recombination kinetics, and (ii) methods independent of the recombination kinetics.

(A) Methods Sensitive to the recombination Kinetics:

(1) Randall and Wilkins' Method:

Randall and Wilkins method (1) is based on equation (4.3), which assumes monomolecular kinetics and no retrapping. In their methods, T_m corresponds to a temperature little below that at which the frequency of an electron ascaping the trap is one second, that is

$$S \ \exp. \left(\frac{-E}{KT_m} \right) \times \left\{ 1 + f(S, \beta) \right\} = 1 \ - - - \ (4.7)$$

the function $f(S, \beta) \ll 1$, and this gives the trap depth E.

$$E = T_{m\,1} + F(S, \beta) \ k \ \log S \ - - - - - - \ (4.8)$$

where $F(S, \beta)$ is another function of S and β. For $S = 2.9 \times 10^{9}$ Sec^{-1}. the above relation reduces to

$$E = 25 \ K \ T_m \ - - - - - - \ (4.9)$$

This is very similar to the relation given independently by Urbach (4), also derived from equation (4.3), which for $S = 10^{9}$ Sec^{-1} gives

$$E = \frac{T_m}{500} \ - - - - - - - \ (4.10)$$

In another approach again due to Randall and Wilkines' (1), the position of maximum is obtained by differentiating equation (4.3) with respect to T and equating to zero which yields.

$$\frac{E}{K\,T_m^2} = \frac{S}{\beta}\ \exp.\left(-\frac{E}{K\,T_m}\right) \text{ ------ } (4.11)$$

The above equation can be evaluated numerically and within an error of 1% and can be expressed (5) in the form

$$E = \frac{T_m\,(K) - T_o\,(\beta/S)}{K\,(\beta/S)} \text{ ------ } (4.12)$$

where the functions T_o and K may be obtained graphically for different values of β/S and then used for determining E (6,7,8).

It is worth mentioning that, as there are several other methods to determine E which do not require the knowledge of S, the equation (4.11) is invariably used for determining the parameter S (6,9,19), E having been determined from other methods.

(2) Method Due to Booth and Bohun:

Booth (11) and Bohun (12), independently used two heating rates β_1 and β_2 and measured the corresponding values of T_{m1} and T_{m2} of the glow maximum. Solving equation (4.11) for two different heating rates they found

$$E = \frac{K\,T_{m1}}{T_{m1} - T_{m2}} \times \log \frac{\beta_1\,T_{m2}^2}{\beta_2\,T_{m1}^2} \text{ ---- } (4.13)$$

The value of S is given by (13)

$$\log \frac{Sk}{E} = \left[T_m^2 \log \frac{T_{m\,2}^{\,2}}{\beta_2} - T_{m1} \log \frac{T_{m1}^{2}}{\beta_1}\right] \Big/ (T_{m1} - T_{m2}) \text{ --- } (4.14)$$

If T_m can be measured within an accuracy of 1°K the method is found to yield E within an error of 5%. Schon (14) has modified the equation (4.13) by replacing T_m^2 by $T_m^{3.5}$ which has resulted in a somewhat improved accuracy.

(3) Isothermal Decay Method:

In this method, after excitation, the sample is quickly heated to a specific temperature and at this temperature the luminescence decay is measured. The method, being isothermal, has the advantage that such difficulties as arising from overlapping peaks and change in the quantum efficiency or the emission spectra occuring under the non-isothermal conditions, are avoided. The decay curve obtained can be analysed and it has been shown (15) that for the first order kinetics

$$I\ (T) = n_o\ S\ \exp.\left(-\frac{E}{KT}\right) \exp.\left[-\ St\ \exp.\left(-\frac{E}{KT}\right)\right] \quad \text{--(4.15)}$$

where t is time. Thus

$$\log I\ (T) = -S\ t\ \exp.\left(-\frac{E}{KT}\right) - \frac{E}{KT} + \log\ (n_o S), \quad \text{--(4.16)}$$

and the slope m of the log I (T) versus t curve is

$$m_1 = S\ \exp.\left(-\frac{E}{KT}\right) \quad \text{------ (4.17)}$$

Taking the slope at two temperatures T_1 and T_2 , one can write

$$\log \frac{m_1}{m_2} = \left(-\frac{E}{KT}\right) \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{--- (4.18)}$$

Which can be used to determine the activation energy E. The frequency factor S may be found by the substitution of (4.18) in equation (4.17).

(4) Grossweiner's Method:

Using the equation (4.3) for the first order kinetics, Grossweiner (10) has shown that E, in terms of T_m and T_1 is given by

$$E = 1.51\, K\, T_m\, T_1 \,/\, (\, T_m - T_1\,) \text{ - - - - - - } (4.19)$$

where T_1 is the temperature at which the low temperature side of the glow peak attains one-half of the maximum intensity. According to Grossweiner, this equation is accurate within ± 5%, provided that $S/B > 10^7$ deg K^{-1} and $E/kT_m > 20$. However, Dussel and Bube (16) and Chen (9) have shown that the equation (4.19) yields values which are about 7% higher.

(5) Keating's Method:

Keating's (17), following other investigators (18,19), considered the possibility of temperature dependent frequency factor with $S = B\,T^a$, where B is a constant, and the magnitude of a is given by $-2 \leq a \leq +2$. For all values of a, Keating gave the following formula for the first-order kinetics.

$$k\,T_m \,/\, E = (1.2\,\gamma - 0.54\,)\,\left(\frac{T_2 - T_1}{T_m}\right) + 0.005 - \left[\tfrac{1}{2}\,(\,\gamma - 0.75\,)\right]^2 \text{ - - - - } (4.20)$$

In (4.20), $\gamma = (\,T_2 - T_m) \,/\, (T_m - T_1)$ and T_2 is the temperature at which the high-temperature side of the glow peak attains one-half of the maximum intensity. The formula is found to hold true for $0.75 < \gamma < 0.9$ and $10 < E/K\ T_m < 35$ (20).

(6) Method Due to Lushchik:

By assuming that the area of the half peak towards the fall-off is equal to the area of a triangle having the same height and half width, Lushchik (21) showed that the activation energy for the first-order kinetics is given by

$$E = KT_m^2 \ / \ (T_2 - T_m) \quad ----- \quad (4.21)$$

Under the same assumptions, he obtained for the second-order kinetics

$$E = 2k\ T_m^2 \ / \ (T_2 - T_m) \quad ----- \quad (4.22)$$

For better accuracy, the above two equations have been empirically modified by Chen (9) by multiplying by 0.978 and 0.853 for the first and second order kinetics respectively.

(7) Halperin and Braner's Method:

In this method, for calculating the activation energy, use is made of the symmetry of the glow peak about its maximum. Halperin and Braner (22,23) considered luminescence emission as mainly due to two kinds of recombination processes. In one process, the electron raised to an excited state within the forbidden gap below the conduction band recombines with the hole by tunnelling process and in the other the recombination takes place via a conduction band. If it is assumed that the ratio ς, of the initial concentration of trapped electrons to the trapped holes in unity, then the thermal activation energy E, can be calculated using the appropriate equation of the following.

Type of process	Equation	Condition
Tunneling, $\varsigma = 1$.		
(a) Recombination dominant	$E_1 = kT_m^2 / (T_2 - T_m)$,	$\mu g \simeq e^{-1}$ -- (4.23)
(b) Retrapping dominant	$E_2 = 2kT_m^2 / (T_2 - T_m)$,	$\mu g = 0.5$ - - (4.24)
- Via conduction band, $\varsigma \simeq 1$		
(a) First Order	$E_3 = \frac{1.72\ kT_m^2}{(T_m - T_1)} (1 \frac{-5.16}{\Delta})$,	$\mu g \leq e^{-1} (1 + \frac{2}{\Delta})$ (4.25)
(b) Second Order	$E_4 = \frac{2k\ T_m^2}{(T_m - T_1)} (1 - \frac{6}{\Delta})$,	$\mu g \geq e^{-1} (1 + \frac{2}{\Delta})$ --(4.25)

where $1/\Delta = kT_m / E << 1$ is a correction factor and T_1 is the temperature on low temperature side of glow peak at which intensity is one half of its peak value.

The factor $\mu g = \delta / W = (T_2 - T_m) / (T_2 - T_1)$ is called the symmetry factor and is a characteristic of the type of kinetics involved in the process. The values of μg equal to or less than $e^{-1} (1 + \frac{2}{\Delta})$ should be obtained for first order process while values greater than $e^{-1} (1 + \frac{2}{\Delta})$

(usually about 0.5) correspond to second order process. Thus the advantage of this method lies in the fact that the first half of the peak is sufficient for the evalution of E and it also points a way of determining the kinetics of the process involved. But many times, the presence of weak shoulders at the high temperature side of a glow peak causes an apparent increase in the ug values which may wrongly indicate the process to be of the second order (24).

When the ratio, ρ , is greater than unity, the activation energy is given by

$$E = \frac{kT_m^{\,2}}{(T_2 - T_m)}\left[1 + \frac{(T_2 - T_1)}{(T_m - T_1)}\right] \text{ - - - - } (4.27)$$

with the condition $\mu g = 0.5$

(8) <u>Method due to Chen</u>:

The method suggested by Chen (9) to determine E, follows from Randall and Wilkins formula with the same assumptions as made by Lushchik. For first order kinetics E is given by

$$E = 2kT_m\left[\frac{1.25\ T_m}{(T_2 - T_1)} - 1\right] \text{ - - - - - } (4.28)$$

and for second order kinetics,

$$E = 2kT_m\left[\frac{1.756\ T_m}{(T_2 - T_1)} - 1\right] \text{ - - - - } (4.29)$$

Here the numerical constants are chosen empirically to have a better estimation of E and $E/kT_m >> 1$.

Moreover, Chen (25) showed that the symmetry factor $\mu g \simeq 0.42$ is a characteristic of the first order peak while $\mu g \simeq 0.52$ corresponds to second order one. On correlating the symmetry factor and order of kinetics , he gave the following equations to evaluate E for general order of kinetics,

$$E_\tau = \left[1.51 + 3.0\ (\mu g - 0.42)\right] \frac{kT_m^2}{T_m - T_1} - \left[1.5 + 4.2\ (\mu g - 0.42)\right] 2kT_m \quad \text{- - (4.30)}$$

$$E_\delta = \left[0.976 + 7.3\ (\mu g - 0.42)\right] \frac{kT_m^2}{T_2 - T_m} \quad \text{- - - - (4.31)}$$

$$E_W = \left[2.52 + 10.2\ (\mu g - 0.42)\right] \frac{kT_m^2}{T_2 - T_1} - 2\,k\,T_m \quad \text{- - - (4.32)}$$

In addition, Chen suggested corrections to the formulae suggested by other workers and are as follows:

(a) <u>Chen's modification to method due to Gressweiner:</u>

Chen (9) modified the Grossweiner's relation (equation 4.19) empirically giving

$$E = C_1\, k\, T_m\, T_1 \,/\, (T_m - T_1) \quad \text{- - - - (4.33)}$$

where $C_1 = 1.41$ for first order kinetics and $C_1 = 1.68$ for second order; which yields E values with a better accuracy over a wide range of S values.

(b) Chen's modification to method due to Lushchik:

Chen (9) suggested that if the area under the glow curve is not exactly equal to the area of a triangle approximated, then Lushchik's method needs correction. Accordingly he gave corrected formulae as

$$E = c_6\, k\, T_m^2 \,/\, (T_2 - T_m) \text{ - - - - - - - } (4.34)$$

with $C_6 = 0.976 \pm 0.004$ for first order kinetics, and

$$E = C_7\, k\, T_m^2 \,/\, (T_2 - T_m) \text{ - - - - - - } (4.35)$$

with $C_7 = 0.853 \pm 0.0012$ for second order kinetics.

(c) Chen's correction to method due to Halperin and Braner:

Applying some corrections to method due to Halperin and Braner, Chen (9) suggested the equation for first order kinetics case as

$$E = \frac{1.52\, k\, T_m^2}{(T_m - T_1)} - (1.58 \times 2\, k\, T_m) \text{ - - - - } (4.36)$$

and for case of second order kinetics as

$$E = \frac{1.81\, k\, T_m^2}{(T_m - T_1)} - 2\, k\, T_m \text{ - - - - - } (4.37)$$

(9) Inflection Point Method:

This method, proposed by Land (26), makes use of the inflection temperature T_1 of the glow curve for evaluating E. The inflection temperature is given by setting $d^2I/dT^2 = 0$ for the intensity temperature relation. The equation obtained for E is

$$E = \frac{k\, T_m\, T_1}{|T_1 - T_m|} \quad \log \quad \frac{A}{(T_1 / T_m)^2} \quad ---- (4.38)$$

where A = 0.77 and 2.66 respectively for $T_1 < T_m$ and $T_1 > T_m$ for the first-order kinetics, and A = 0.24 and 3.43 respectively for $T_1 < T_m$ and $T_1 > T_m$ for the second-order kinetics. Thus, by measuring T_1 and T_m, E can be determined.

(B) Methods Independent of the Recombination Kinetics:

(1) Method due to Hoogenstraaten:

Using equation (4.11), Hoogenstraatan (27) has shown that the peak temperature T_m is related to E by the equation

$$\log_e (T_m^2 / \beta) = \frac{E}{k\, T_m} + \log_e \frac{E}{SK} \quad --- (4.39)$$

Thus, the plot between $\log_e (T_m^2 / \beta)$ versus $1/ T_m$ is linear with a slope equal to E/K and making an intercept of log Sk/E. Thus both E and S can be determined (20).

(2) Initial Rise Method:

The method of initial rise, suggested by Garlick and Gibson (2), is based on the fact that for all types of kinetics, the intensity in the initial part of the glow curve can be expressed in the form

$$I = F \ \exp.\ ({}^{-E}/kT) \text{ - - - - - } (4.40)$$

F being a sunction of the number of completely filled traps and empty centres, which takes into account the transition probabilities involved. Assuming F to be constant (23) in the initial part of the glow curve, the equation (4.32) takes the form

$$\log_e I = {}^{-E}/\ kT + \text{constant} \text{ - - - - - } (4.41)$$

A plot of $\log_e$ I against $^1/T$ should give a straight line, and the slope of which yields the value of E.

(3) Numerical Kinetics Method:

This method of analysis (28) involves a numerical computation which proceeds in small arbitrary time steps. During each step the concentration of trapped charge, the carrier concentrations, the radiative relaxations of excited centres, etc. are adjusted in accordance with the physical process involved. When used to analyse the experimental data, some initial approximate values of E and S are chosen and they are suitably varied to determine the values giving the best last-square fit to the experimental data.

(4) Method Due to Muntoni et al:

The method proposed by Muntoni et al (29) for activation energy is based on the measurement of area under the glow curve. The kinetic equation proposed by Antonov- Romanovsii (30) and Lushchik (21) is of the form

$$I \propto - \frac{dm}{dt} = A\, m^{\alpha}\, e^{-E/kT} \text{ - - - - } (4.42)$$

where m is the density of the recombination centres, A is a proportionality constant and a suitable numerical parameter representing the kinetic order. For constant warming rate β, the above equation can be written as

$$I = a\,\beta\, \frac{dm}{dt} \text{ - - - - - - - - - - } (4.43)$$

where a is a factor depending on the efficiency of the light detector and on units. On integration, the above equation takes the form

$$m\,(T) = S\,(T)\,/\,(a/\beta) \text{ - - - - - } (4.44)$$

where S (T) is the integrated area of the curve in the interval from T to T_f, being the temperature corresponding to the end of the glow curve. The above equation may be expressed as

$$\log \frac{I}{[S\,(T)]^{\alpha}} = \left(- \frac{E}{kT}\right) + C \text{ - - - - - - } (4.45)$$

where $C = \log\,(A\, a^{1-\alpha}\, \beta^{\alpha})$. The value of which results in linear plot of $\log\,(I\,/\,(S\,(T))^{\alpha}$ versus 1/T represents the order of kinetics involved, and the slope of the straight line thus obtained gives the value of the activation energy.

(5) Method Due to Maxia et al:

Another method involving area measurement is due to Maxia et.al.(31) who have, starting from the kinetic equation

(4.42), shown that

$$\log \left\{ I\ (T) \ \frac{\cos\theta + \sin\theta\ S\ (T)}{S^2\ (T) + \Delta S\ (T)} \right\} = (\ -E/kT\ ) + \mu \quad \text{--}(4.46)$$

$$\text{or}\quad Y = \frac{EX}{K} + \mu \quad \text{------}\ (4.47)$$

where Y is the term on the left hand side and $X = \frac{1}{T}$, θ is a function of the area of the glow curve and the probability factors for recombination and retrapping which determines the linear behaviour of Y and X. Except for O all quantities on the left hand side of the above equation can be determined from TL spectrum.

The correction coefficient

$$\rho = \frac{\mathrm{cov}\,(\ X,\ Y\ )}{V\ (x)\ \ V\ (Y)^{1/2}} \quad \text{-----}\ (4.48)$$

can be numerically computed as a function of θ, and θ is conditioned for ρ or ρ^2 attaining unity. From this the activation energy is given by

$$E = -K\ \frac{\mathrm{cov}\ (X,Y)}{V\ (X)} = -\,k\ \frac{\mathrm{cov}\,(X,Y)}{V\ (Y)} \quad \text{----}\ (4.49)$$

4-3 RESULTS AND DISCUSSION:

4-3.1 Glow Curves:

Glow curves for various samples containing different concentrations of Zn and a flux NaCl are shown in Figures 4.1 to 4.4. The curves are obtained at a heating rate of 0.47°k/sec and measurements have been carried out in the temperature range of 300°k to 400°k. It may be seen from the figures that the general features of the glow curves are markedly influrenced by the concentrations of Zn and NaCl. The curves in the figures are plotted after normalising the maximum intensity of a peak to a value 100 and suitably shifting their ordinates to avoid overlaping and to render their comparison easier.

(i) Glow curves for unfluxed SrS:Zn phosphors:

Figures- 4.1 and 4.2 show the glow curves for unfluxed samples containing varing concentration of Zn. A glow curve for undoped SrS is also shown in the Fig.4.1 for comparison. From these figures it is evident that, all the curves exhibit single glow peak (peak-B) in the temperature region studied and addition of an activator do not gives rise to new glow peak. However, increase in concentration of Zn modifies the relative shape of the glow curves and shifts the peak position towards the low temperature side. This implies that the addition of activator do not introduces new trapping levels but changes the relative population of traps of different depths. An increase in concentration of Zn has the effect of populating the shallower traps in preference to the deeper ones.

(ii) Glow curves for samples containing flux NaCl:

Glow curves for sample containing different amount of NaCl are as shown in Fig.4.3. The addition and increase in percentage of NaCl significantly influences the general features of the glow curves. At low concentrations glow curves exhibit single glow peak while that at high ones two peaks. The first one (Peak-A) is around $325^{\circ}K$ and second (Peak-B) around $340^{\circ}K$. This indicates that the addition of high concentration of NaCl gives rise to new trapping levels in the temperature region studied.

(iii) Glow curves for fulxed SrS:Zn Phosphors:

Fig.4-4 shows a set of five glow curves obtained for samples containing a fixed concentration (1.25 wt.%) of NaCl and varing concentration of Zn. At low concentrations of Zn, nature of glow curves is similar to that obtained with Zn alone. However, at high concentrations two peaks appear and they overlap on each other. Thus suggesting that high concentration of Zn, in presence of flux, creates new trapping levels responsible for thermoluminescence.

The conclusions of the glow curve measurements are in accord with those obtained from decay studies.

4-3.2 Activation energies of the glow peaks:

Activation energy, E, of a glow peak can be evaluated in several ways as described in section 4-2.2. In the present case, however, methods due to (i) Garlick and Gibson, (ii) Grossweiner, (iii) Halperin and Braner, (i) Chen, and (v) Urbach are used to calculate the value of E.

To compute the activation energy by these methods, it is necessary that the peaks be isolated. There exist several methods for isolation of glow peaks. However, in the present case, the method suggested by Bettinalli et.al (32) is followed and an example of procedure is illustrated in Fig.4.5.

It should be mentioned that certain glow peaks could not be satisfactorily isolated as they were weak/broad and as such activation energies corresponding to them can not be evaluated unambigiously.

The first method followed, which is due to Garlick and Gibson (2), is the initial rise method. Here the logarithm of TL intensity is plotted as a function reciprocal of temperature. The plot is fairly linear (see figs.4.6 and 4.7) with its slope equal to $^{-E}/k$. The activation energies determined in this way for peak-B denoted by E; and are listed in Tables 4-1.

The second method followed is due to Grossweiner (10). As pointed out by Chen (9), the method yields E values about 7% higher, hence the modified formulae suggested by him viz. equation 4.33 with Cl = 1.41 and 1.68, are used to evaluate E. The values calculated accordingly and designated as $^{E}G1$ and $^{E}G_2$, for the first and second order kinetics respectively, are shown in Tables 4.1.

The third method followed is due to Halperin and Braner (22,23) and is a more general means of evaluating E values.

It also gives a clue to the type of kinetics involved in the process. The values of E obtained using equations 4.23- to 4.26 are listed in Tables 4.1. It is observed that the values of E calculated using equations 4.23 and 4.24 are inconsistant with E values calculated by other methods. Thus the possibility of sub-model I, in which the recombination takes place by tunneling process, is ruled out. On the other hand, consistency of E values calculated by equations 4.25 and 4.26 assure the validity of sub-model II, wherein recombination take place via a conduction band.

The fourth method used in due to Chen (25) and is for general order of kinetics. The values of E computed according to equation 4.32 are designated as E_{W}' and are shown in Tables 4.2.

The final method followed is due to Urbach. The E values estimated as per equation 4.10 are denoted by Eu and are given in Table 4.2.

A comparison of activation energies contained in Tables 4.1 and 4.2 indicates that E values calculated by different methods are consistent.

4-3.3 Effect of variation in concentration of Zn and NaCl on activation energy:

Fig.4.8 to 4.10 exhibit the variation of E value (EH_3) corresponding to a glow peak B with concentration of Zn and NaCl for various samples. From Fig. 4.8 it may be

·seen that the activation energy does not vary significantly with Zn concentration. The trap depths of effective levels are distributed from 0.59 eV to 1.46 eV. The observed variation is also not systematic in character. However, when Zn is varied in presence of flux the variation is found to be systematic (Fig.4.9). The curve exhibits two maxima. Similar is the situation with variation in % of flux.

4-3.4 Escape Frequency Factor:

The escape frequency factor S is evaluated using Randall and Wilkins formula based on monomolecular kinetics (1) viz.

$$\frac{\beta E}{k T_m^2} = S \exp.\left(- \frac{E}{k T_m} \right) \text{ - - - - } (4.11)$$

know E, β and T_m, S can be readily evaluated. The values of E obtained from the formula (4.25) are used in the above equation to obtain S. The values of S thus calculated are listed in Table 4.3. For all samples studied, S varies from 10^9 to 10^{22} Sec^{-1}. However, the observed variation is not systematic with respect to the activator and flux concentrations.

4-3.5 Size of traps:

The capture cross-section (6) of each type of trapping centre can be evaluated from the knowledge of escape frequency factor. Mott and Gurency (33) proposed the following equation on the assumption that the density of free electrons (or holes in case of hole traps) is equal to the density of empty traps.

$$\frac{1/\tau}{\sigma} = \frac{2\pi m\,(kT)^2\sqrt{6\pi}}{h^3}\exp.(-{}^{E}/_{kT}) \text{ - - } (4.50)$$

On combining this equation with equation

$p = \frac{1}{\tau} = S \exp.\,(-{}^{E}/_{kT})$, we have numerical equation of the type

$$\sigma = \frac{S}{1.63 \times 10^{21} \times T^2} \text{ - - - - } (4.51)$$

which in its simplest form be given as (34),

$$\frac{S}{\sigma} \simeq 1.5 \times 10^{26} \text{ - - - - } (4.52)$$

The values of σ, estimated by making the use of S values obtained from Randall and Wilkins formula, are listed in Table 4.3. The estimated values are found to vary from 1.66×10^{-16} Cm^2 to 1.29×10^{-4} Cm^2.

The capture cross- section, estimated for various substances, has values from 10^{-11} Cm^2 to 10^{-24} Cm^2 (35). M.Lax (18) has given the name to the traps with large capture cross-section, such as in case of Sb 1 10^{-12}, as giant traps; while those with a value 10^{-17}Cm^2 for SrS:Ho phosphors as of medium size by Jain and Sinha (34). Thus the traps of present investigation can be regarded as giant traps.

4-3.6 Kinetics of Luminescence:

The kinetic equation for a glow curve is of the form,

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

$$= S\,n^{\alpha}\ \exp.\,(-{}^{E}/_{kT}) \text{ - - - - - } (4.53)$$

where I is the glow intensity, S is the pre-exponential factor, n is the concentration of trapped carriers and α is a suitable numerical parameter representing the order of kinetics. Usually $1 \geqslant \alpha \leqslant 2$. For $\alpha = 1$, the order of kinetics is said to be monomolecular (first order), and for $\alpha = 2$, it is said to be bimolecular (second order), while non-integer values of $\alpha (1 > \alpha < 2)$ indicate it to be an intermediate. In the present study, the conclusion as regards the order of kinetics is drawn from the comparison of E values, symmetry factor of glow curves and a method due to Muntoni et al.

On comparison of E values determined, by different methods and listed in Tables 4.1 and 4.2, it is seen that the E values calculated on the assumption of the first order kinetics (E_{G1} and E_{H3}) agree most with Ei (independent of kinetics) indicating the kinetics to be first order. However, these values do not agree with those estimated by Chen's method (general order of kinetics). Thus the order of kinetics thought to be monomolecular is suspicious.

The summetry factor $\mu g = \delta / \omega$, is also a characteristic of the type of kinetics involved in the process. The values of μg obtained for present glow peaks and listed in Table 4.2 is seen to be greater than $e^{-1} (1 + \frac{2}{\Delta})$, indicating the kinetics to be bimolecular; contradicting the above conclusion. However, as discussed earlier (see section 4.2.2), any such conclusion drawn from the magnitude of μg is likely to be erroneous.

To establish a certainty in the result, another method is followed and is one proposed by Muntoni et.al (29). According to this method, a plot of log $\frac{I\ (T)}{[S\ (T)]^{\alpha}}$ versus $\frac{1}{T}$ results in a straight line for specific value of α, which represents the order of kinetics; while for other values it is being concave or convex. Here α, which represents the order of kinetics, is an index of the integrated area of the curve in the interval from T to T_f, T_f being the temperature corresponding to the end of the glow peak.

Fig.4.11 shows the log $\frac{I\ (T)}{[S\ (T)]^{\alpha}}$ versus $\frac{1}{T}$ plot obtained for sample No.B20 with values of α being equal to 1, 1.5 and 2. It may been seen from the figure that the plot is not linear for $\alpha = 1$ or $\alpha = 2$. However, it is almost linear for intermediate value of α, such as 1.5, indicating thereby the order of kinetics to be an intermediate. For glow peaks of other samples, similar results were obtained and an average value of α comes to be 1.5 ± 0.2. Non-integer values of α were also observed by Muntoni et.al. (29) for ZnS and NaCl and by Kathruid and Sunta (36) for Lif TLD-100. Thus, taking into consideration non-agreement of E values and also unreliability of conclusions drawn from μg values, here it may be concluded that the kinetics involved in TL process is not uniquely monomolecular or bimolecular, but likely to be intermediate whose order is about 1.5 ± 0.2.

4-4. SUMMARY:

1. Glow curves depend sensitively upon the concentration of Zn and NaCl.

2. Addition of Zn, in absence of flux, does not give rise to new glow peaks in the temperature region studied. The trap depths of effective levels are insensitive to the added concentration.

3. Introduction of Zn in presence of flux gives rise to a new glow peak aroung 3.25^{o}K. Similar is the result with addition of flux to the host lattice.

4. Escape frequency factor varies from 10^{9} to 10^{22}Sec^{-1}. for.various samples studied. But variation is not systematic with Zn and NaCl concentration.

5. Average size of traps responsible for thermoluminescence is of the order of 10^{-10} Cm^{2} and traps may be termed as jiant traps.

6. The probable type of kinetics involved in thermoluminescence process is intermidiate whose order is about 1.5 ± 0.2.

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TABLE 4.1

Activation Energy of glow peak-B for different samples

Sample No	Method of analysis, Activation energy (eV)						
	Garlick and Gibson	Grossweiner		Halperin and Braner ($\rho = 1$)			
		First Order.	Second Order.	Tunneling		Via conduction band	
				First order	Second order.	First Order.	Second Order.
	Ei	E_{G1}	E_{G2}	EH_1	EH_2	EH_3	EH_4
1	2	3	4	5	6	7	8
B_1	0.57	0.59	0.71	0.59	1.19	0.59	0.76
B_2	0.69	0.84	1.00	0.58	1.17	0.85	1.07
B_3	0.86	0.78	0.93	0.60	1.20	0.79	1.00
B_4	1.33	0.97	1.15	0.64	1.28	1.00	1.24
B_5	1.23	1.16	1.38	0.81	1.63	1.20	1.48
B_6	1.40	1.05	1.25	0.74	1.49	1.09	1.34
B_7	1.58	1.06	1.26	0.69	1.38	1.09	1.35
B_8	1.19	1.05	1.25	0.77	1.55	1.09	1.34
B_9	1.54	1.40	1.67	0.92	1.84	1.46	1.79
B_{10}	1.41	0.83	0.99	0.69	1.38	0.85	1.06
B_{11}	1.08	1.15	1.37	0.84	1.69	1.19	1.47
B_{12}	1.38	0.99	1.18	0.73	1.46	1.01	1.26
B_{13}	1.08	0.98	1.17	0.78	1.57	1.01	1.25
B_{14}	1.41	1.50	1.78	0.98	1.96	1.56	1.92
B_{15}	1.26	1.11	1.32	0.67	1.35	1.15	1.42
B_{17}	1.38	1.19	1.41	0.80	1.60	1.23	1.52
B_{18}	1.27	1.20	1.43	0.74	1.49	1.25	1.54
B_{19}	1.54	1.04	1.24	0.87	1.74	1.07	1.33

TABLE 4.1 cont..

1	2	3	4	5	6	7	8
B_{20}	1.15	0.92	1.10	0.68	1.37	0.95	1.18
B_{21}	1.15	0.99	1.18	0.73	1.46	1.11	1.37
B_{22}	1.38	0.83	0.98	0.76	1.52	0.84	1.06
B_{23}	1.13	1.08	1.28	0.65	1.31	1.11	1.38
B_{24}	1.38	1.00	1.19	0.73	1.47	1.03	1.27

TABLE 4-2

Activation Energy and Symmetry Factor of Glow Peaks for Different Samples

Sample No.	Glow Peak A Activation Energy, eV $E_u \doteq T_m/500$	Glow Peak B			
		Activation Energy, eV,		Symmetry Factor μ_g	
		Chen E_N	$E_u = \frac{T_m}{500}$	Experimental δ/W	Calculated $e^{-1}(1+\frac{2}{\Delta})$
B_1	-	0.45	0.69	0.34	0.40
B_2	-	1.01	0.68	0.52	0.39
B_3	-	0.90	0.68	0.48	0.39
B_4	-	1.18	0.65	0.55	0.38
B_5	-	1.39	0.66	0.52	0.38
B_6	-	1.26	0.65	0.52	0.38
B_7	-	1.29	0.65	0.55	0.38
B_8	-	1.23	0.65	0.50	0.38
B_9	-	1.71	0.65	0.55	0.38
B_{10}	-	0.89	0.65	0.44	0.39
B_{11}	-	1.35	0.65	0.50	0.38
B_{12}	-	1.35	0.66	0.50	0.38
B_{13}	-	1.08	0.66	0.45	0.38
B_{14}	0.65	1.83	0.67	0.55	0.38
B_{15}	0.65	1.37	0.67	0.58	0.38
B_{17}	0.64	1.44	0.66	0.54	0.38
B_{18}	0.65	1.48	0.67	0.57	0.38
B_{19}	0.65	1.10	0.68	0.43	0.38
B_{20}	-	1.08	0.66	0.50	0.39
B_{21}	-	1.30	0.66	0.53	0.38
B_{22}	0.65	0.76	0.67	0.38	0.39
B_{23}	-	1.33	0.66	0.58	0.38
B_{24}	0.65	1.17	0.66	0.50	0.38

TABLE 4.3

Escape Frequency Factor and Size of Traps of glow Peak-B for different samples

Sample No	Escape frequency factor, Sec^{-1} s Randall and Wilkins method	Size of Trap, Cm^{2} σ
B_1	1.10×10^{9}	0.73×10^{-17}
B_2	1.99×10^{11}	1.32×10^{-15}
B_3	2.50×10^{10}	1.66×10^{-16}
B_4	1.08×10^{14}	0.72×10^{-12}
B_5	1.62×10^{17}	1.08×10^{-9}
B_6	2.90×10^{15}	1.93×10^{-11}
B_7	3.30×10^{15}	2.20×10^{-11}
B_8	2.90×10^{15}	1.93×10^{-11}
B_9	3.03×10^{21}	$2.02 \times 10^{-\text{[illegible]}5}$
B_{10}	5.47×10^{11}	3.65×10^{-15}
B_{11}	1.41×10^{17}	0.94×10^{-9}
B_{12}	1.53×10^{14}	1.02×10^{-12}
B_{13}	1.36×10^{14}	0.91×10^{-12}
B_{14}	1.94×10^{22}	1.29×10^{-4}
B_{15}	8.71×10^{15}	5.80×10^{-11}
B_{17}	2.81×10^{17}	1.87×10^{-9}
B_{18}	3.71×10^{17}	2.47×10^{-9}
B_{19}	4.41×10^{14}	2.94×10^{-12}
B_{20}	1.10×10^{13}	0.73×10^{-13}
B_{21}	4.25×10^{15}	2.83×10^{-11}
B_{22}	1.64×10^{11}	1.09×10^{-15}
B_{23}	4.83×10^{15}	3.22×10^{-11}
B_{24}	1.94×10^{14}	1.29×10^{-12}

REFERENCES:

1. Randall, J.T. and Wilkins, M.H.F., Proc.Roy Soc. (London), A 184, 366 (1945).
2. Garlick, G.F.J. and Gibson, A.F., Proc.Roy.Soc (London), A 60, 574 (1948).
3. Shalgaonkar, C.S. and Narlikar, A.V., Materials Sci., 7, 1465 (1972).
4. Urbach, F., Cornell Symposium (Wiley, New York), 115 (1946).
5. Curie, D. " Luminescence in Crystalls " (Methuen, London), 162 (1963).
6. Power, S.H., Lawangar, R.D., Shalgaonkar, C.S. and Narlikar, A.V., Phil.Mag.24,727 (1971).
7. Sharma, and Singh, A., Indian J.Pure Appl.Phys., 7,130 (1969).
8. Agnihotri, V.B. and Ranade, J.D., Indian J.Pure. Appl.Phys., 6,70 (1968).
9. Chen, R.J., Appl.Phys., 40, 570 (1969).
10. Grossweiner, L.T., J.Appl.Phys., 24,1306 (1953).
11. Booth, A.H., Cand.J.Chem., 32,214 (1954).
12. Bohun, A., Zech.J.Phys., 4,19 (1954).
13. Wrezesinka, A., Acta Phys.Polonica, 15,151 (1956).
14. Schon, M., Tech.Wiss Abhand Osram-Ges., 7,173 (1958).

15, Garlick, G.F.J.," Luminescent Materials " (Oxford University Press, New York, (1949).

16. Dussel, G.A. and Bube, R.H., Phys.Rev., 1955, 764, (1967).

17. Keating, P.N. Proc.Phys.Soc., 68, 1408 (1961).

18. Lax, M., Phys.Rev., 119, 1502 (1960).

19. Bemski, G., Phys.Rev., 111, 1515, (1952).

20. Nicholas, K.H. and Woods, J.Brit.J.Appl.Phys., 15, 785 (1964).

21. Lushchik, G.B., Soviet Phys.JETP, 3, 390 (1956).

22. Halperin, A. and Braner, A.A., Phys.Rev., 117, 408 (1960.)

23. Halperin, A., Braner, A.A., Ben-Zvi, A. and Kristianpoller, N., Phys.Rev., 117, 416 (1960).

24. Lawangar, R.D., Shalgaonkar, C.S., Pawar, S.H., and Narlikar A.V., Solid St.Comm., 10, 1241 (1972).

25. Chen R., J.Elec.Chem.Soc., 116, 1254 (1969).

26. Land.P.L., J.Phys.Chem.Solids.30, 1681 (1959).

27. Hoogenstraaten, W., Philips Res.Reports, 13, 515 (1953).

28. Chemmy, P.J., Townsend, P.D. and Levy, P.W., Phys. Rev., 155, 917 (1967).

29. Muntoni, C., Rucci, A. and Serpi, A., Ricarca Sci., 38, 762 (1968).

30. Antonov-Romancvakii, V.V., Izvest-Akad.Nauk, SSSR. Fiz.Ser.10, 477 (1946).

31. Maxia,V.,Onnis,O. and Rucci,A.,J.Luminescence, 3, 378 (1971).

32. Bettinali,C.,Ferraresso,G. and Manconi,J.W.,J.Chem. Phys.,50,3957 (1969).

33. Mott,N.F. and Gurney R.W.,Electronic Processes in Ionic Crystals (Oxford: Clarendon,1948), p.108.

34. Jain,S.K. and Sinha,O.P.,Indian J.Phys.48, 1100 (1974).

35. Bube,R.H. and Cardon,F.,J.Appl.Phys.35,2712 (1964).

36. Kathuria,S.P.and Sunta,C.M.,J.Phys.D.Appl.Phys, 12, 1 (1979).

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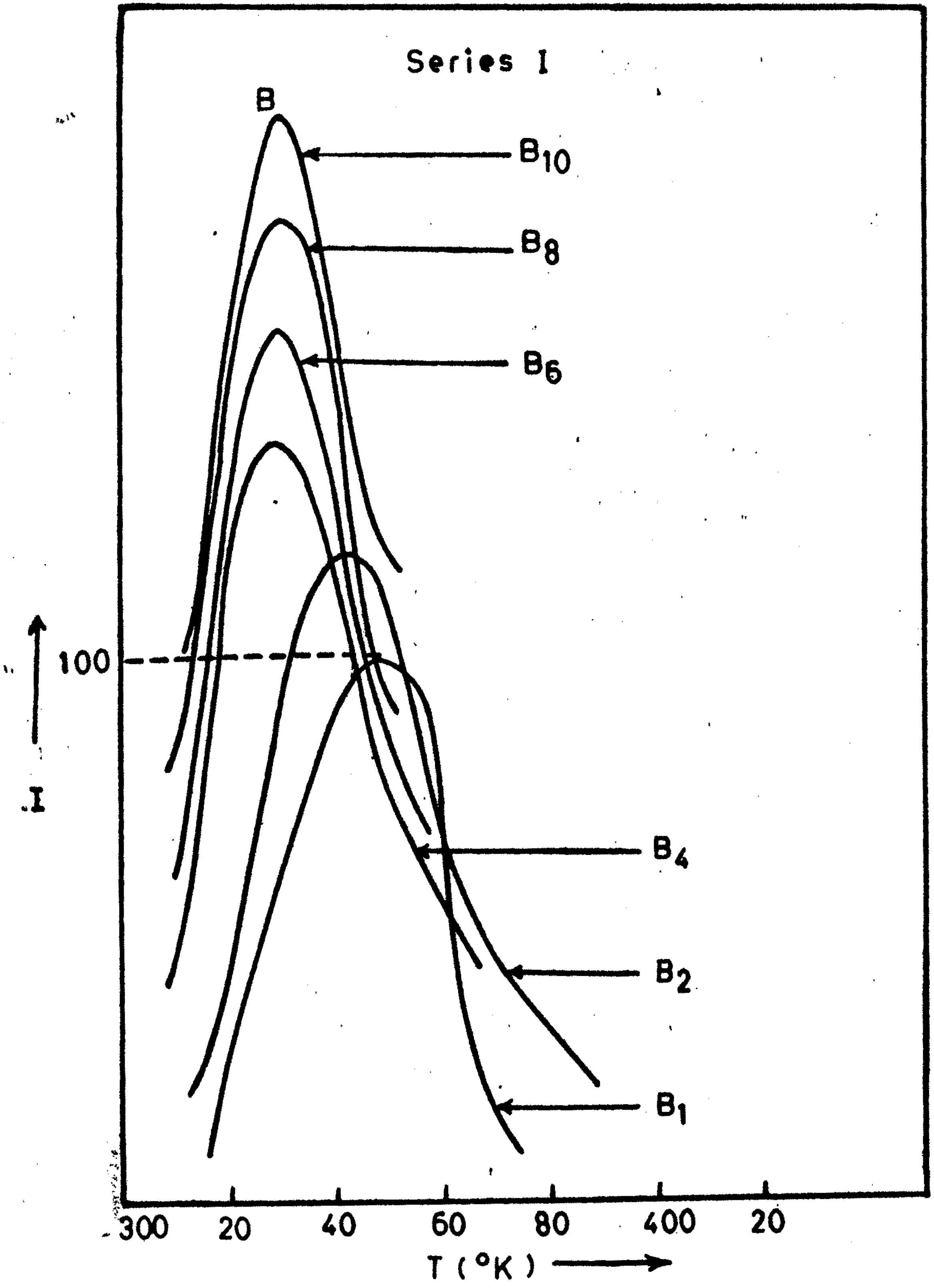
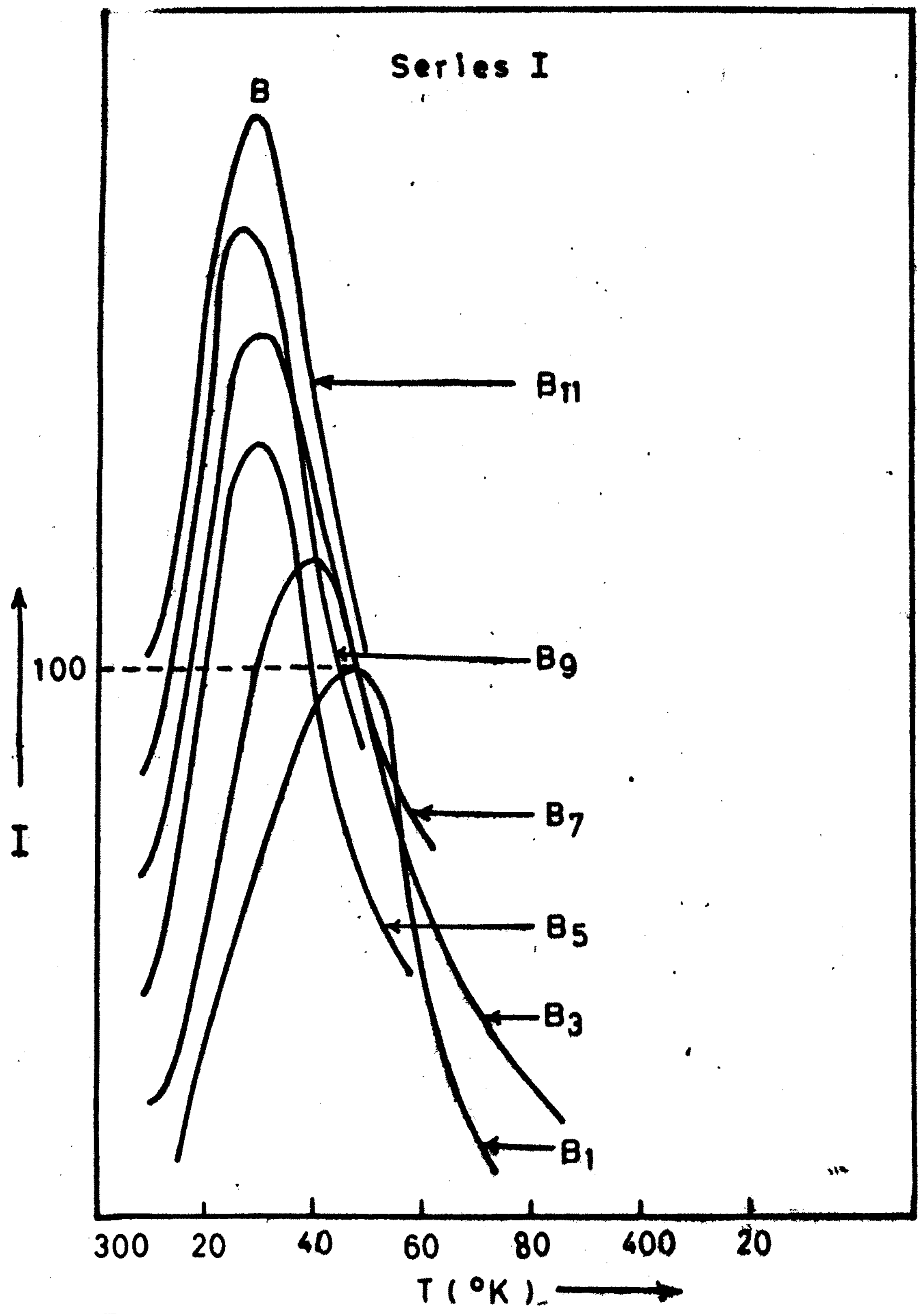


Fig. 4.1



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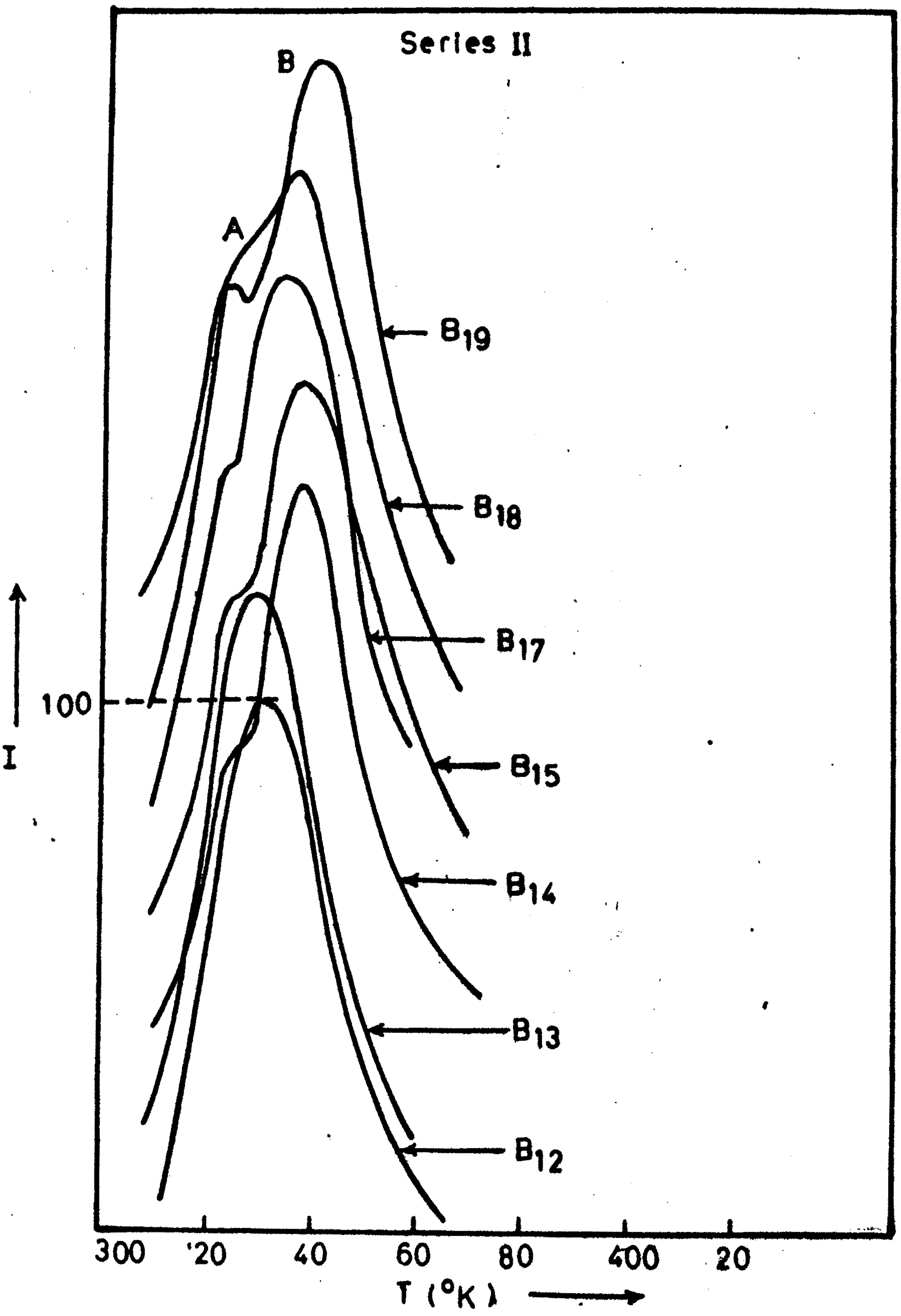
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Fig. 4·3

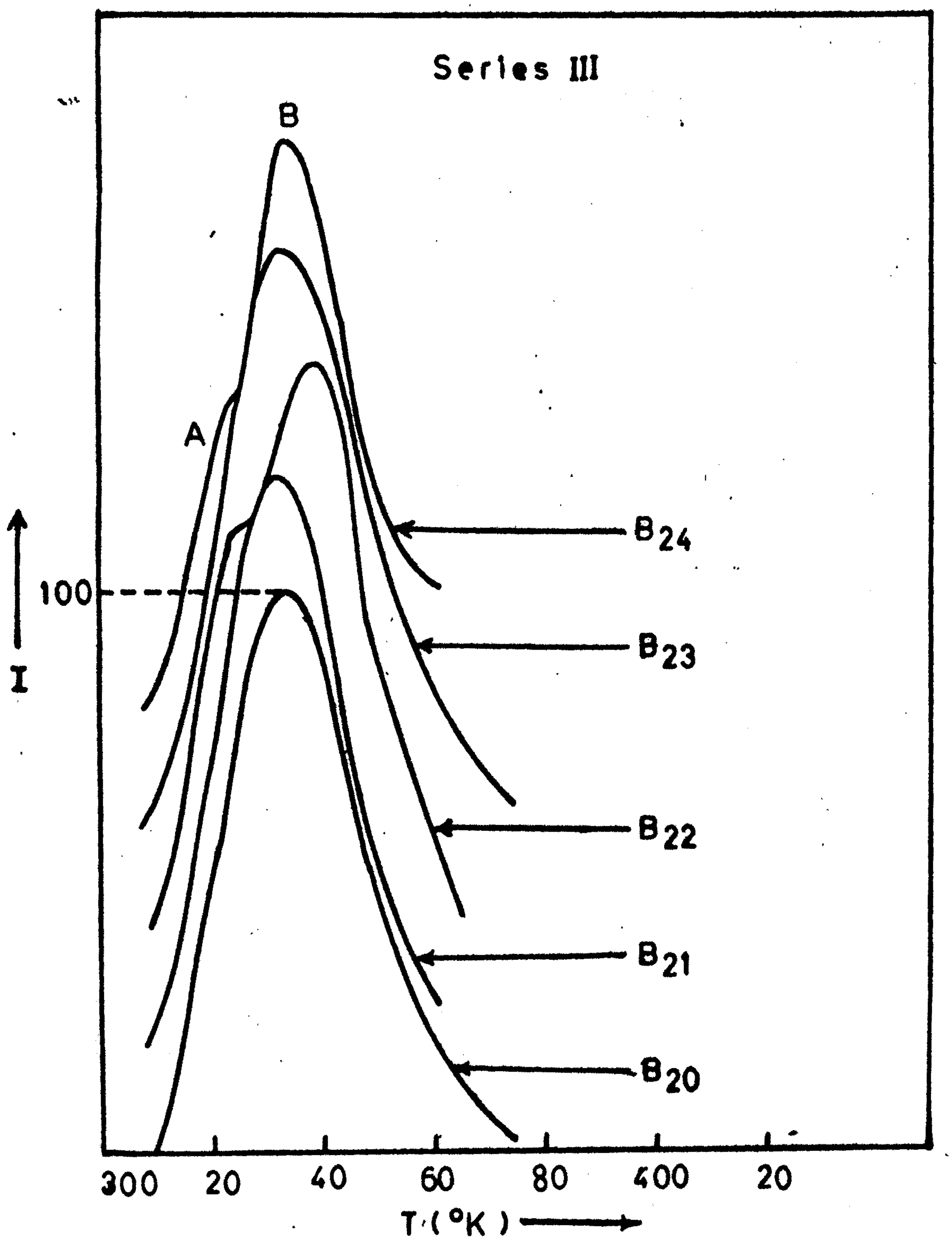

Fig. 4.4

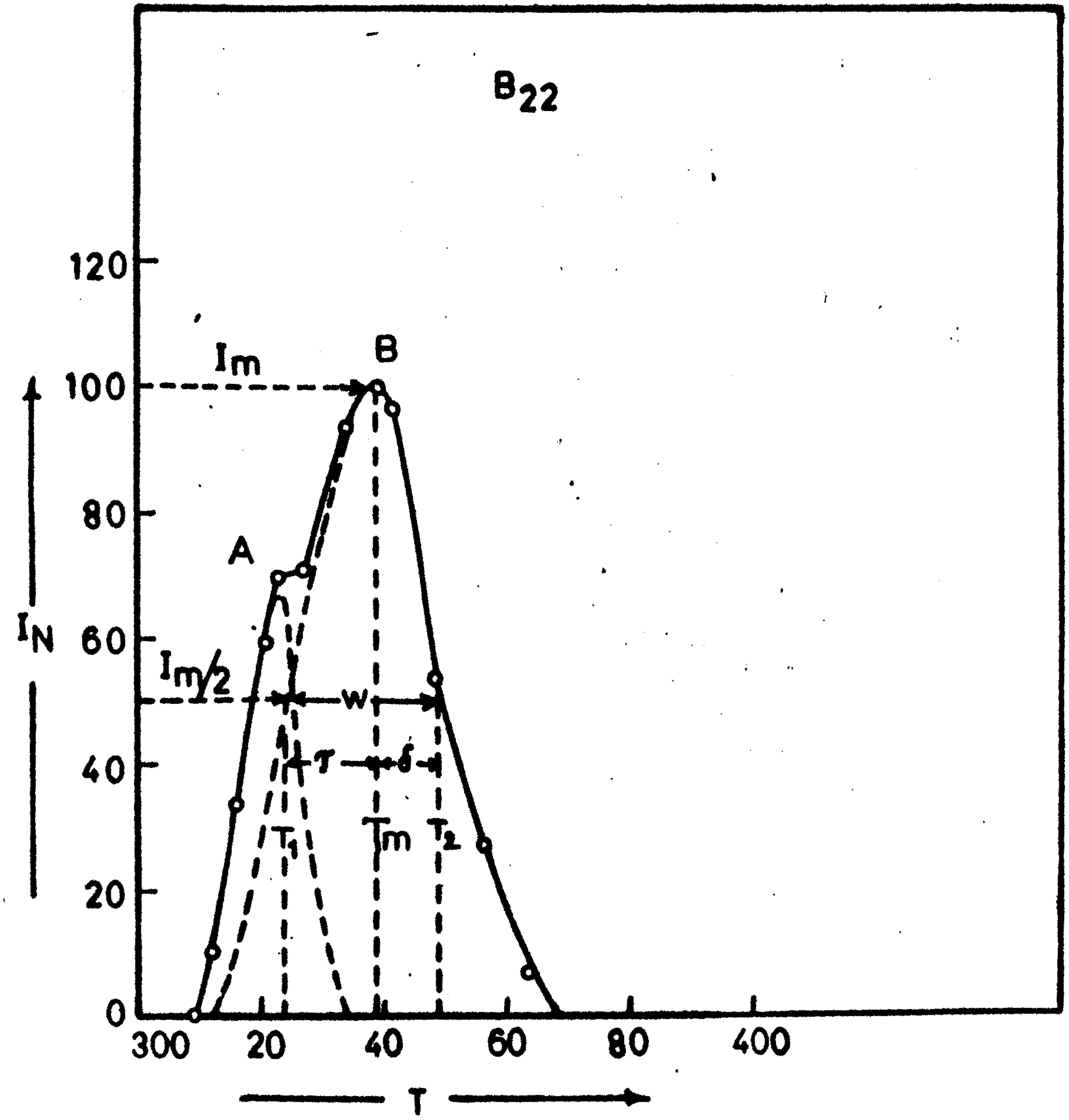
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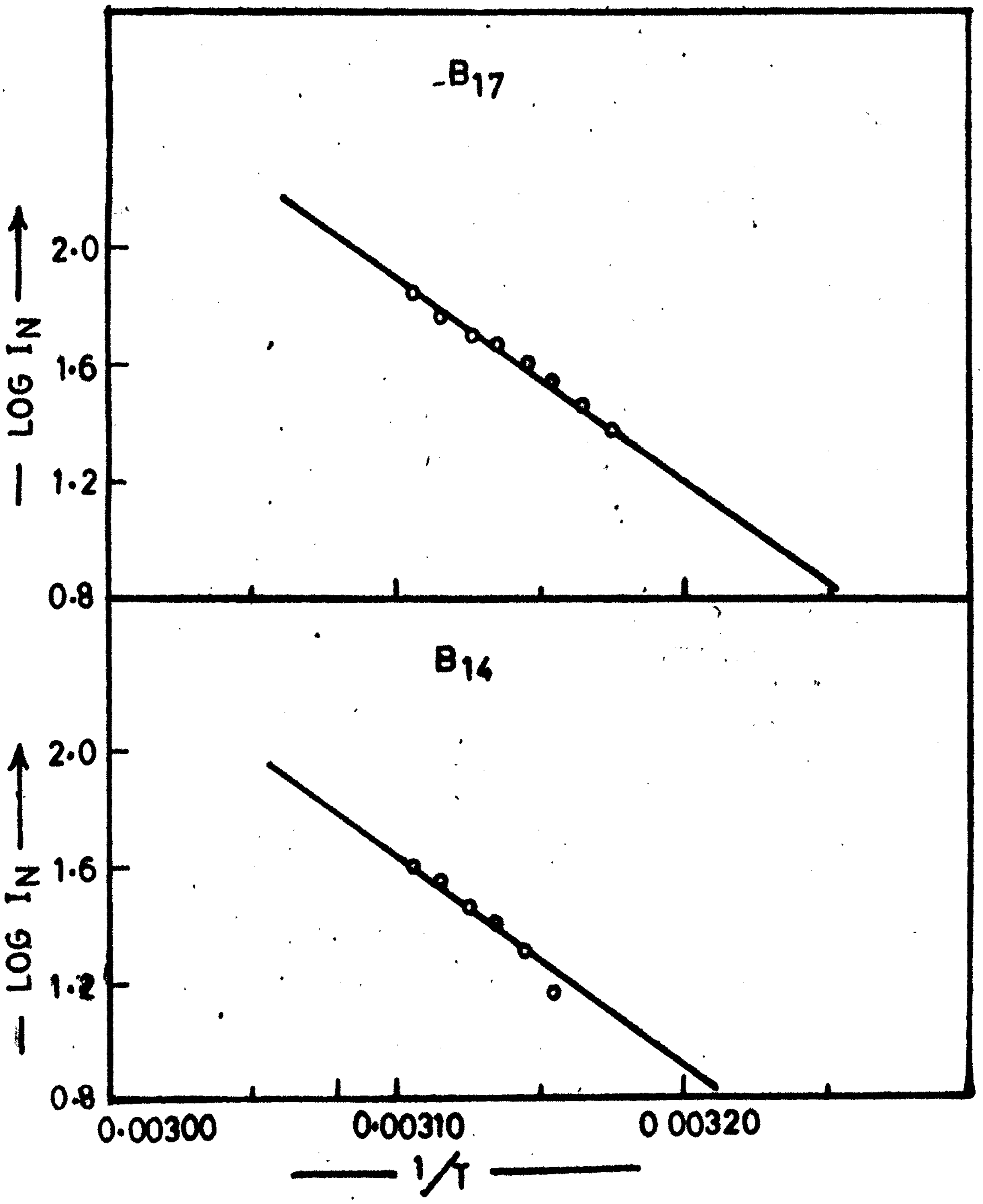
Fig. 4.5



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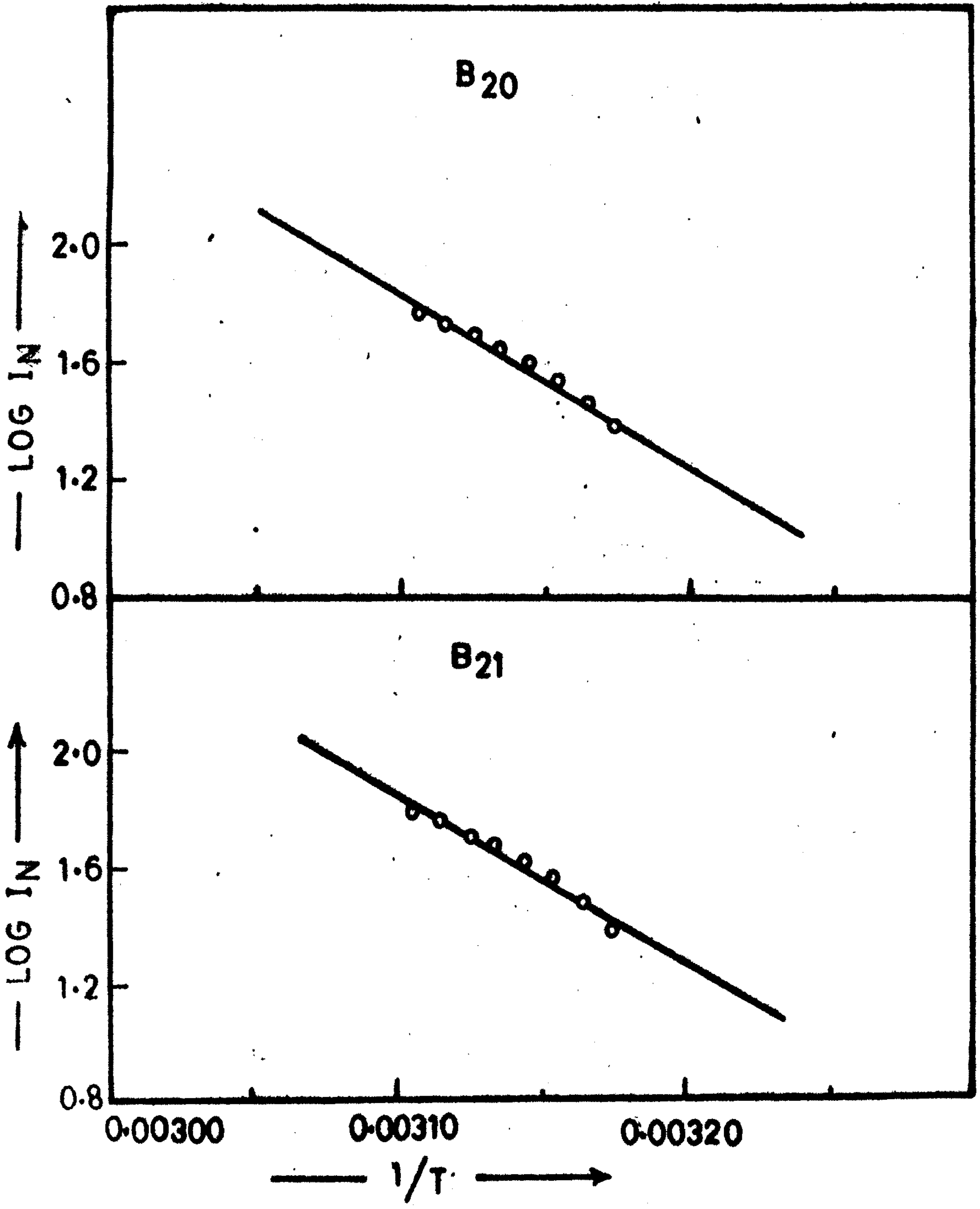

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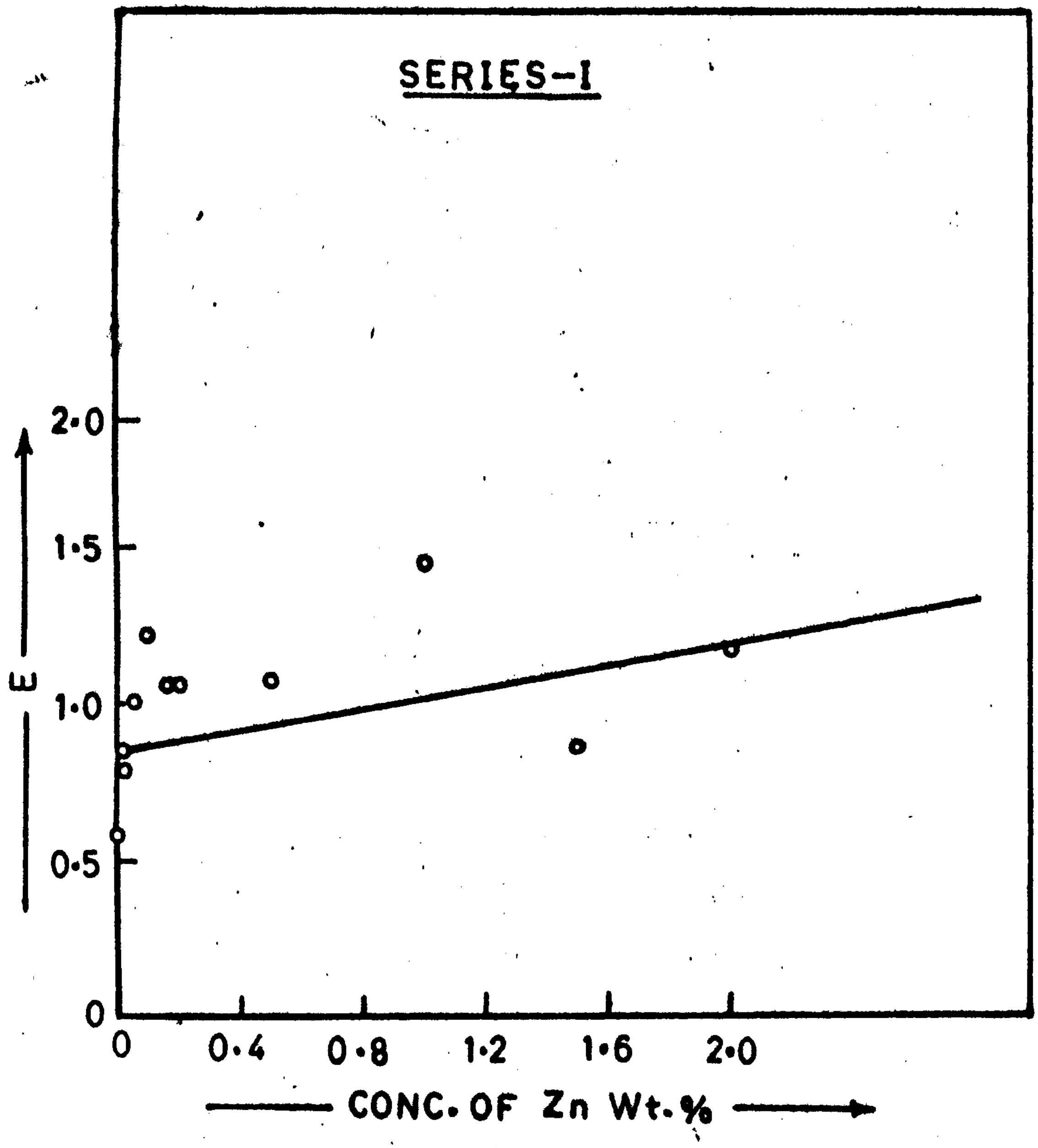

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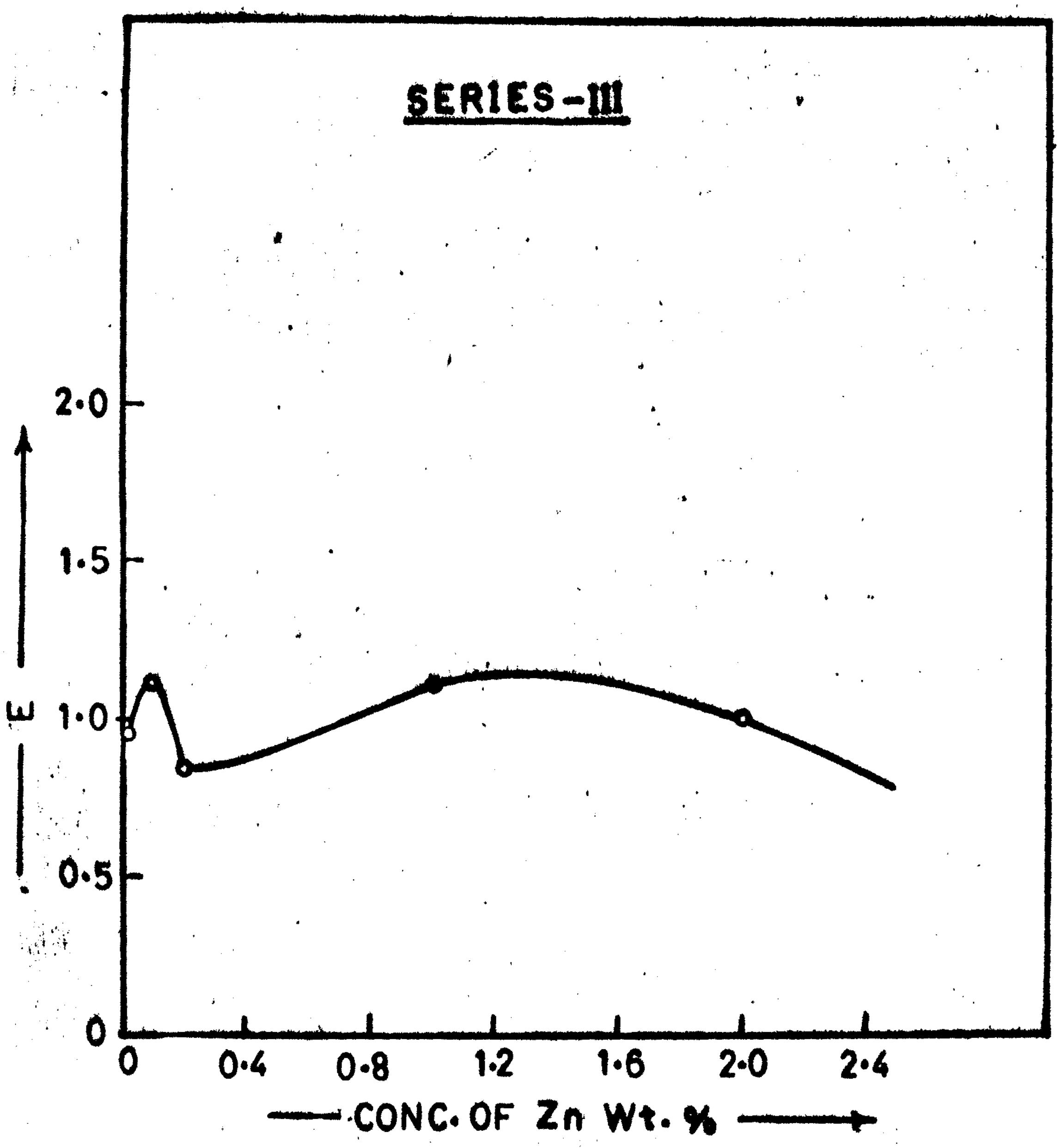

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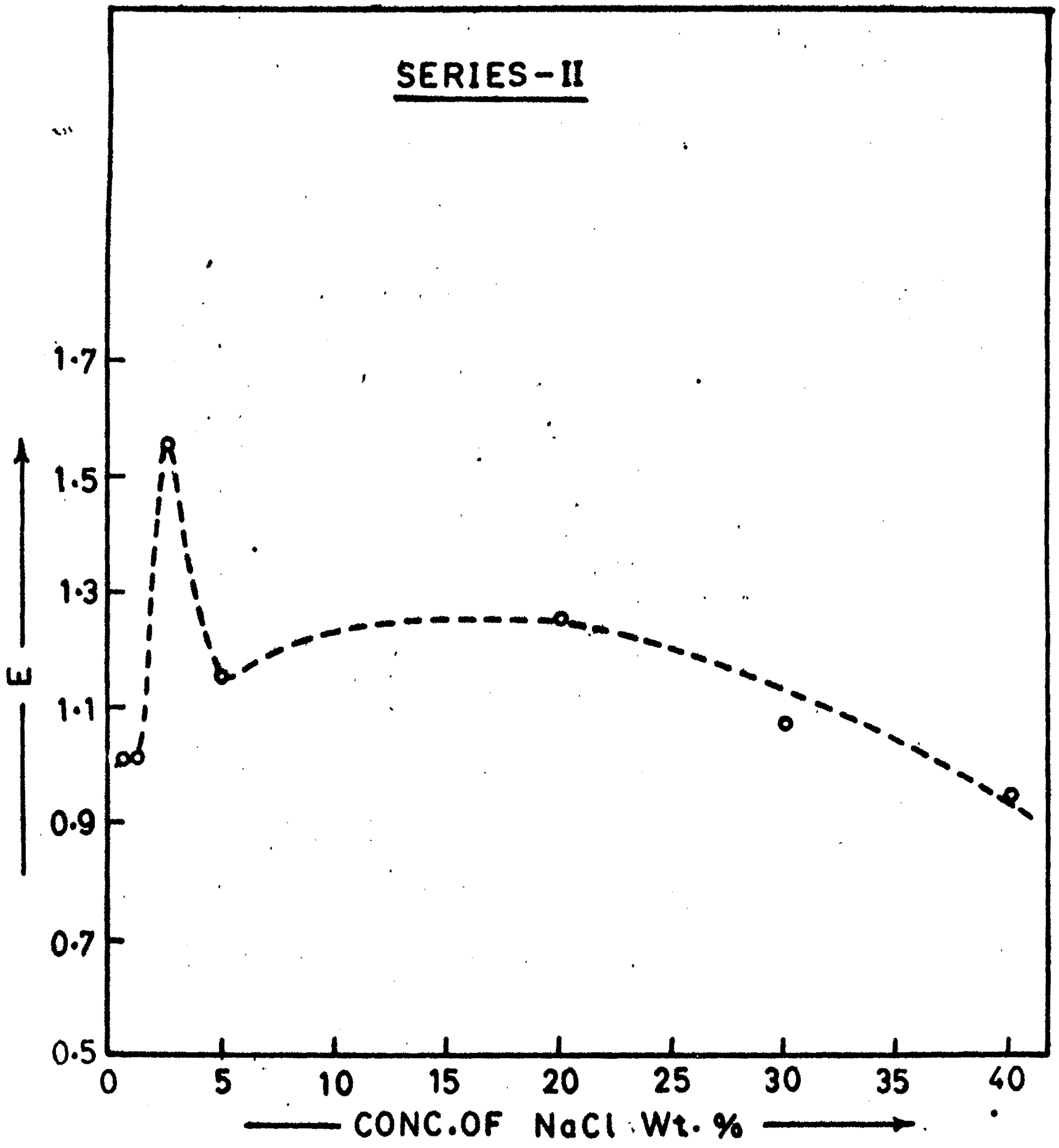
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1·5
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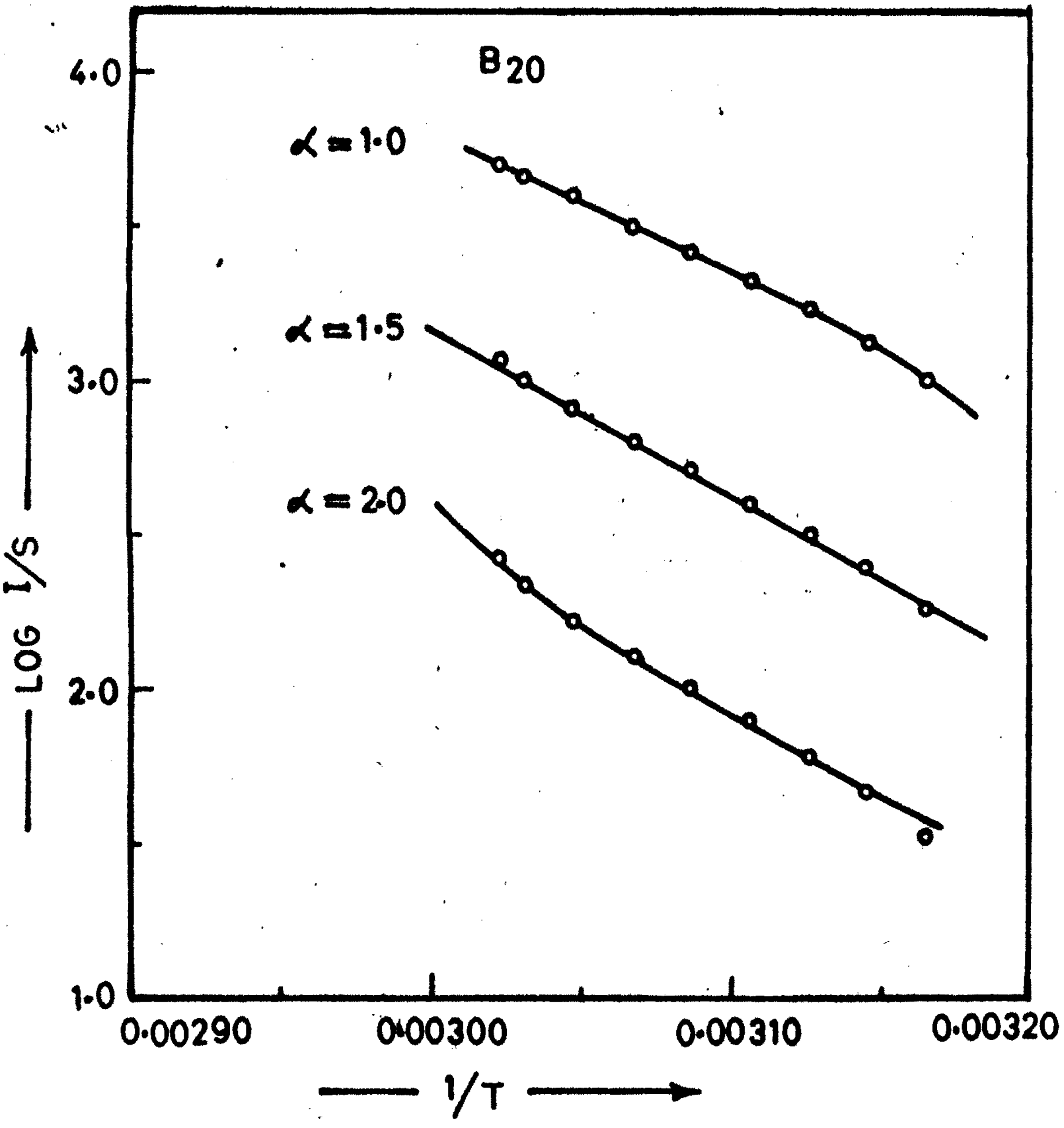
CONC.OF NaCl Wt. %

Fig. 4·10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α = 1·5
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4·0
3·0
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1·0
LOG I/S
0·00290
0·00300
0·00310
0·00320
1/T

Fig. 4·11