CHAPTER — IV

VOLTAGE AND FREQUENCY DEPENDENCE
OF ELECTROLUMINESCENCE EMISSION

4.1   VOLTAGE AND FREQUENCY DEPENDENCE OF
ELECTROLUMINESCENCE EMISSION.

It is evident from the discussion in Chapter-I, section (1.2.1-d),that the intensity of El. emission is greatly varied with the voltage and frequency of the applied field. Similarly,it is observed that the luminous efficiency 'η' is also a function of the applied voltage and frequency. Hence, the study of voltage and frequency dependence of El.emission is of prime importance in determining the optical characteristics of a given material. This study also helps to establish conditions for maximum El. efficiency for the system under consideration. The El. emission depends upon the type of an El. cell and the dielectric used in its construction. By keeping these parameters identical for different materials,valuable information regarding voltage-frequency dependence and the El. efficiency can be obtained.

The El. emission intensity 'B' of some organic metal chelate complexes has been measured over wide ranges of the sinusoidal voltage,'V' and the excitation frequency in Hz. In the present work, the El. cell was used as described before (Chapter -II ,Section - 2.3-a)with the various dielectrics and without any dielectric. The material in the El.cell was excited by sinusoidal voltages upto 2500 V (r.m.s) and with frequencies 600-2000 Hz. Simultaneous excitation of a material with very high applied voltage and

frequency produce high impedence and excess local heating which leads to breakdown of the cell and total loss of brightness. However, special attempts were made to cover wide ranges of voltages and excitation frequencies as large as possible.

The voltage-frequency dependence of El. emission of some organo-metallic chelate complexes like magnesium,calcium zinc, cadmium and aluminium oxinates at room temperature(300 ^{o}K) have been studied. The spectral intensity distribution of El. emission of these materials was also studied at selected applied voltages and frequencies.

R E S U L T S :

4. 1- I) VOLTAGE DEPENDENCE OF ELECTROLUMINESCENCE EMISSION

Experimental results on intensity measurements as a function of applied voltages have been presented in various Table Nos. 6-10 and Fig.Nos. 8,13,18,23,28. In general,it is observed that the charactaristics of radiations emitted by cells containing organic materials were similar with the cells containing inorganic phosphors with the exceptions that higher voltages were needed to stimulate emission. It is invariably observed,that for a constant higher values of frequency (> 1000 Hz) the brightness (B) increases rather rapidly (exponentially) with increasing applied voltage (v), and the general form of the plots indicates that the El. intensity seems to saturate at high voltages.

Several equations for voltage dependence of El.brightness

TABLE NO.6   VOLTAGE AND FREQUENCY DEPENDENCE OF EL. EMISSION OF

MAGNESIUM OXINATE (λ MAX = 490 nm).

Applied Frequency (Hz)	El. Intensity 'B' (A.U.) Applied Voltage (V)				
	400	540	660	780	900
1000	24	70	102	120	128
1100	32	76	112	133	149
1200	47	88	127	155	178
1300	62	118	155	190	208
1400	77	135	190	217	238
1500	100	162	220	250	275
1600	120	192	250	282	305
1700	138	212	274	305	329
1800	162	232	292	324	350
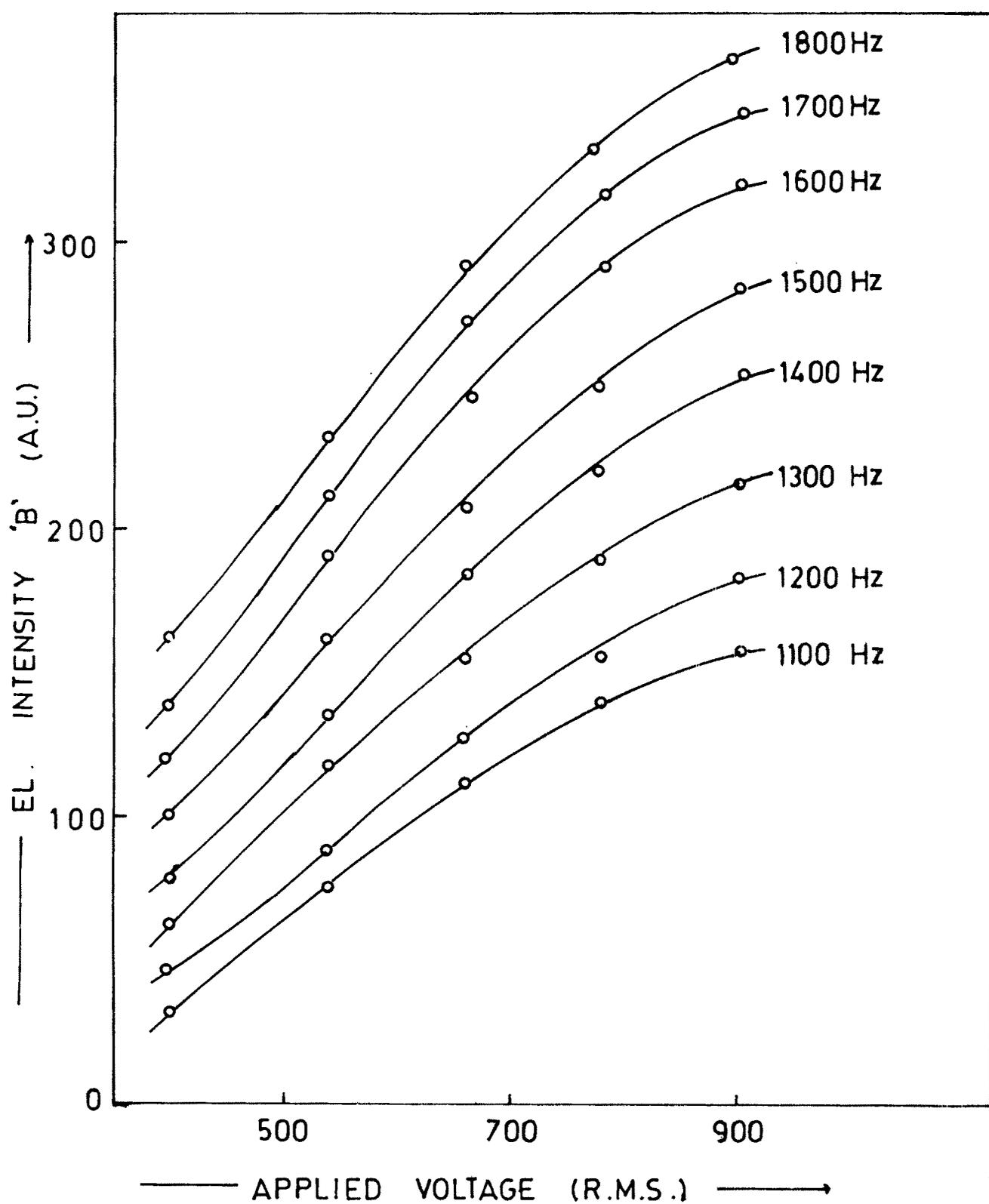
FIG · 8 VOLTAGE DEPENDENCE OF EL . EMISSION FOR
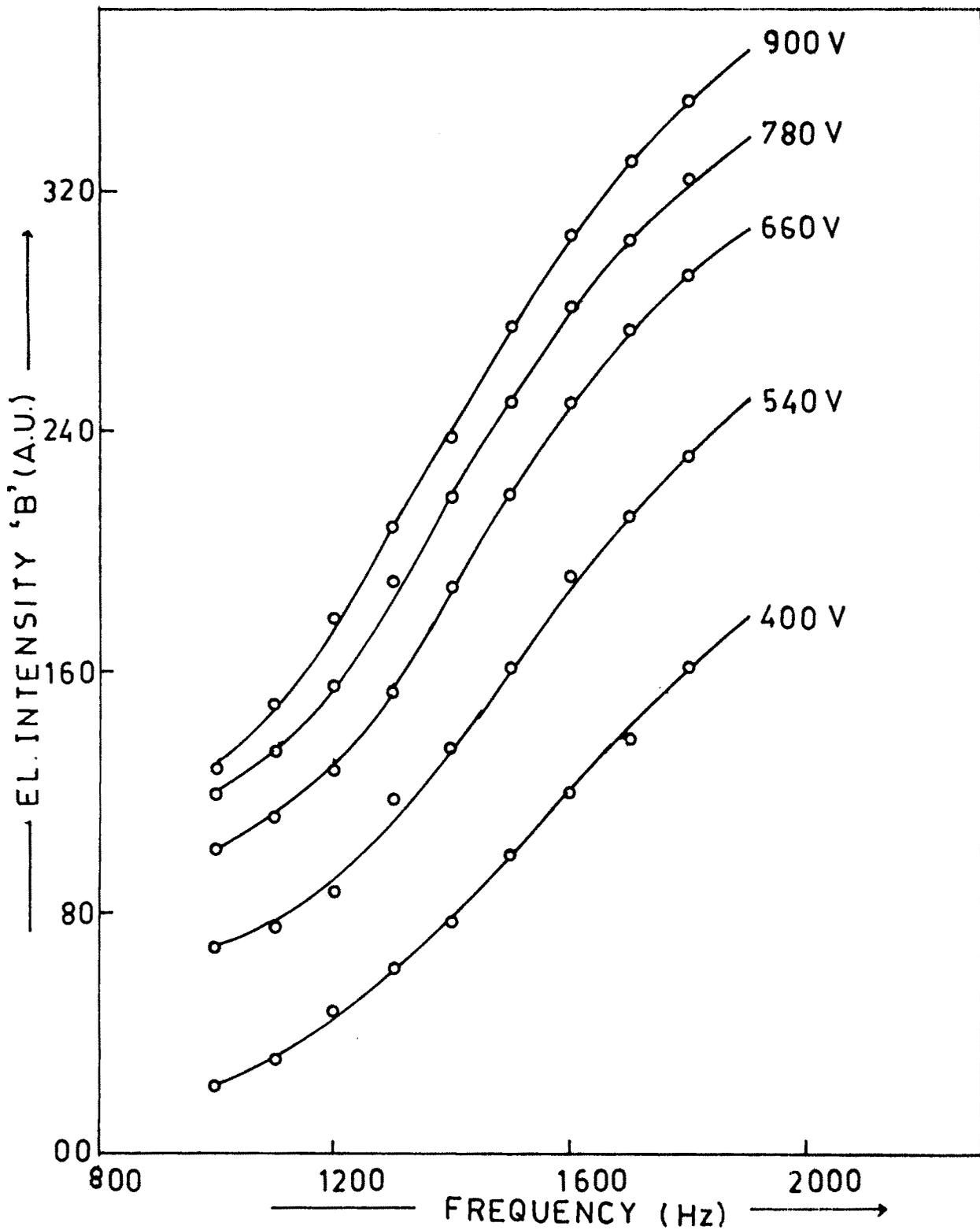
MAGNESIUM OXINATE AT DIFFERENT FREQUENCIES .

FIG: 9 FREQUENCY DEPENDENCE OF EL.EMISSION
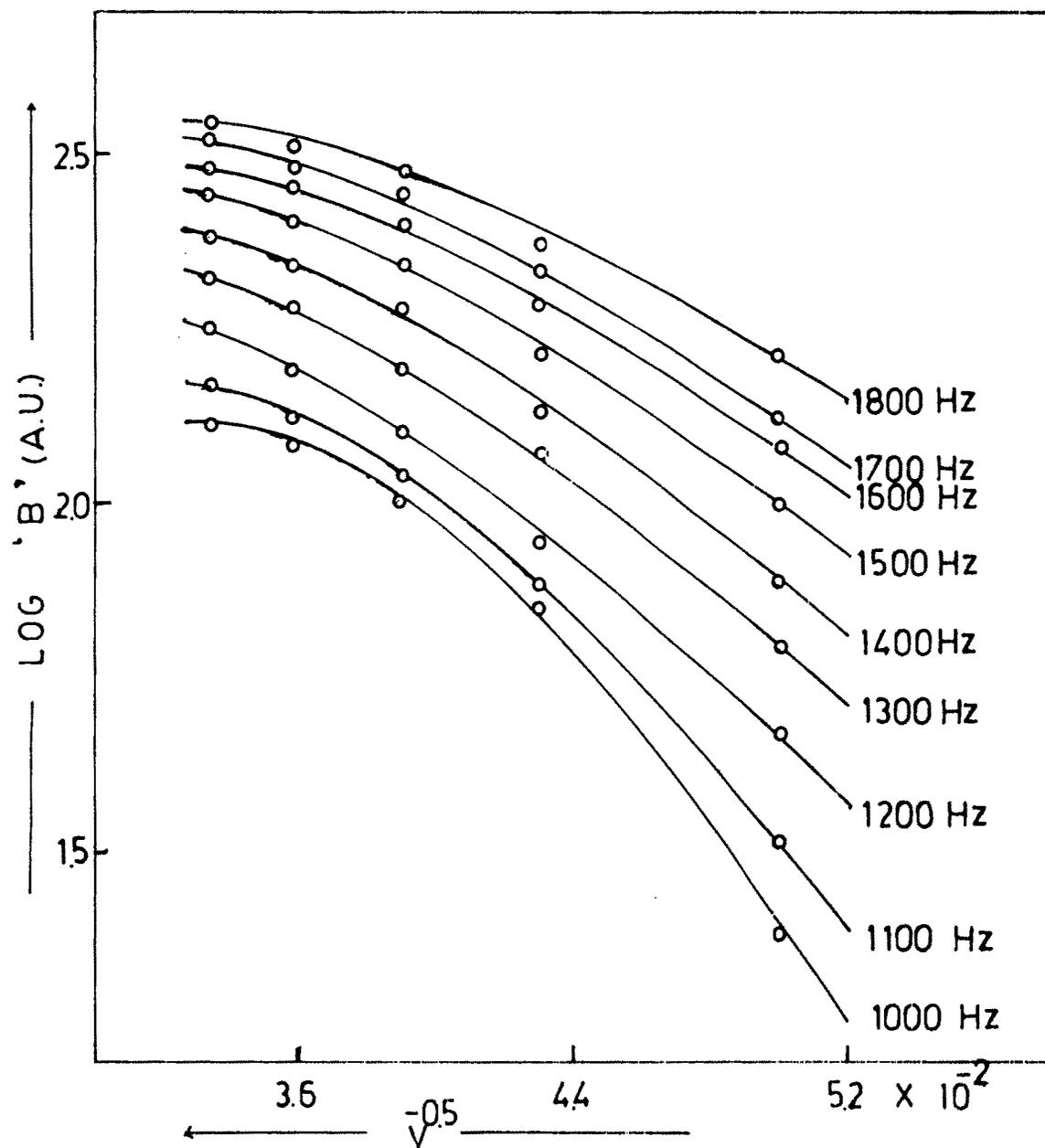FOR MAGNESIUM OXINATE AT DIFFERENT
VOLTAGES.

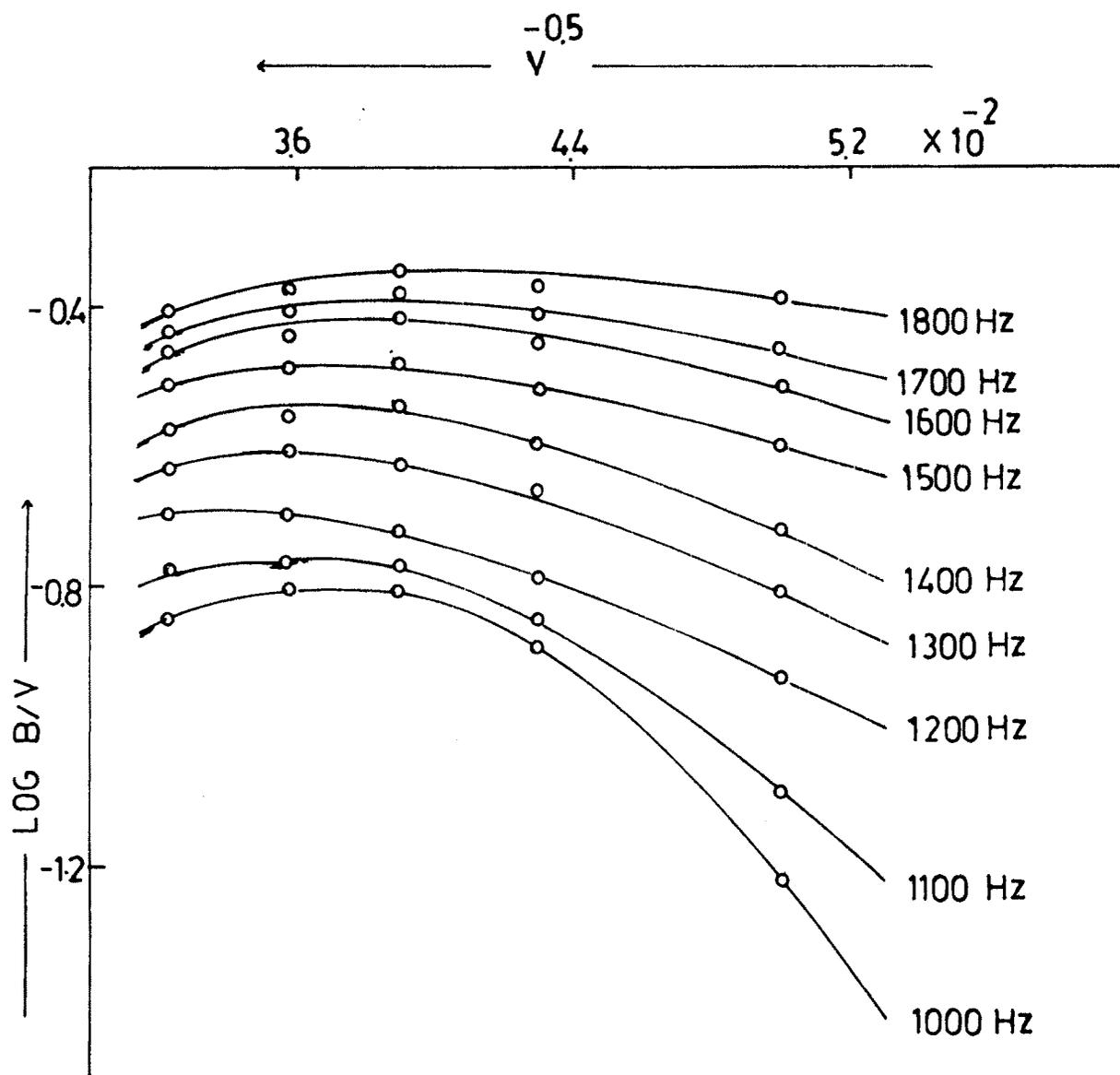FIG·10 DEPENDENCE OF LOG B AS A FUNCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR MAGNESIUM OXINATE .

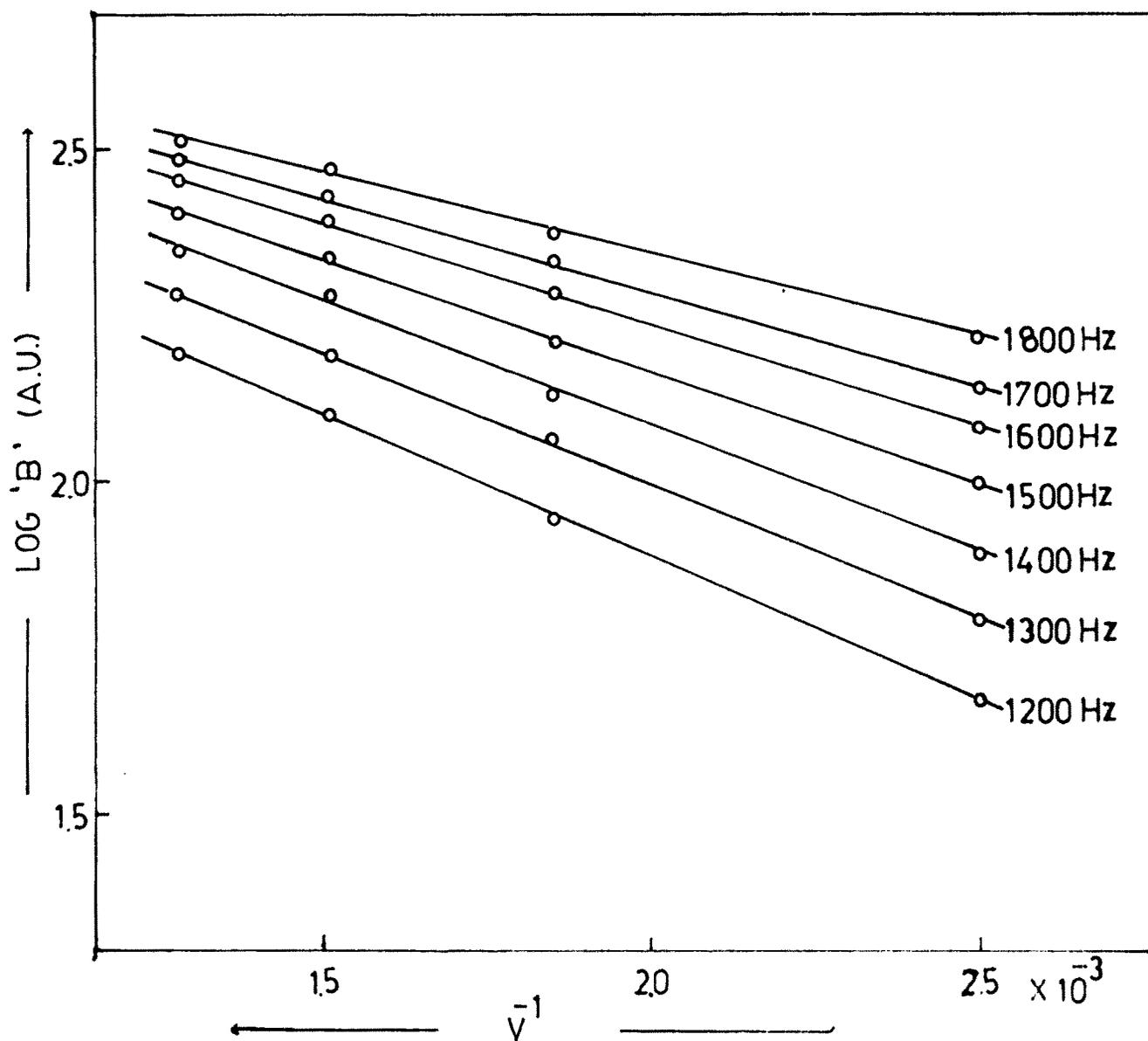FIG·11 DEPENDENCE OF LOG B/V AS A FUNCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR MAGNESIUM OXINATE.

FIG·12 DEPENDENCE OF LOG B AS A FUNCTION OF $\bar{V}^1$ FOR VARIOUS FREQUENCIES FOR MAGNESIUM OXINATE.

TABLE NO. 7   VOLTAGE AND FREQUENCY DEPENDENCE OF EL. EMISSION OF

CALCIUM OXINATE   (λ max = 475 nm).

El. Intensity 'B' (A.U.)

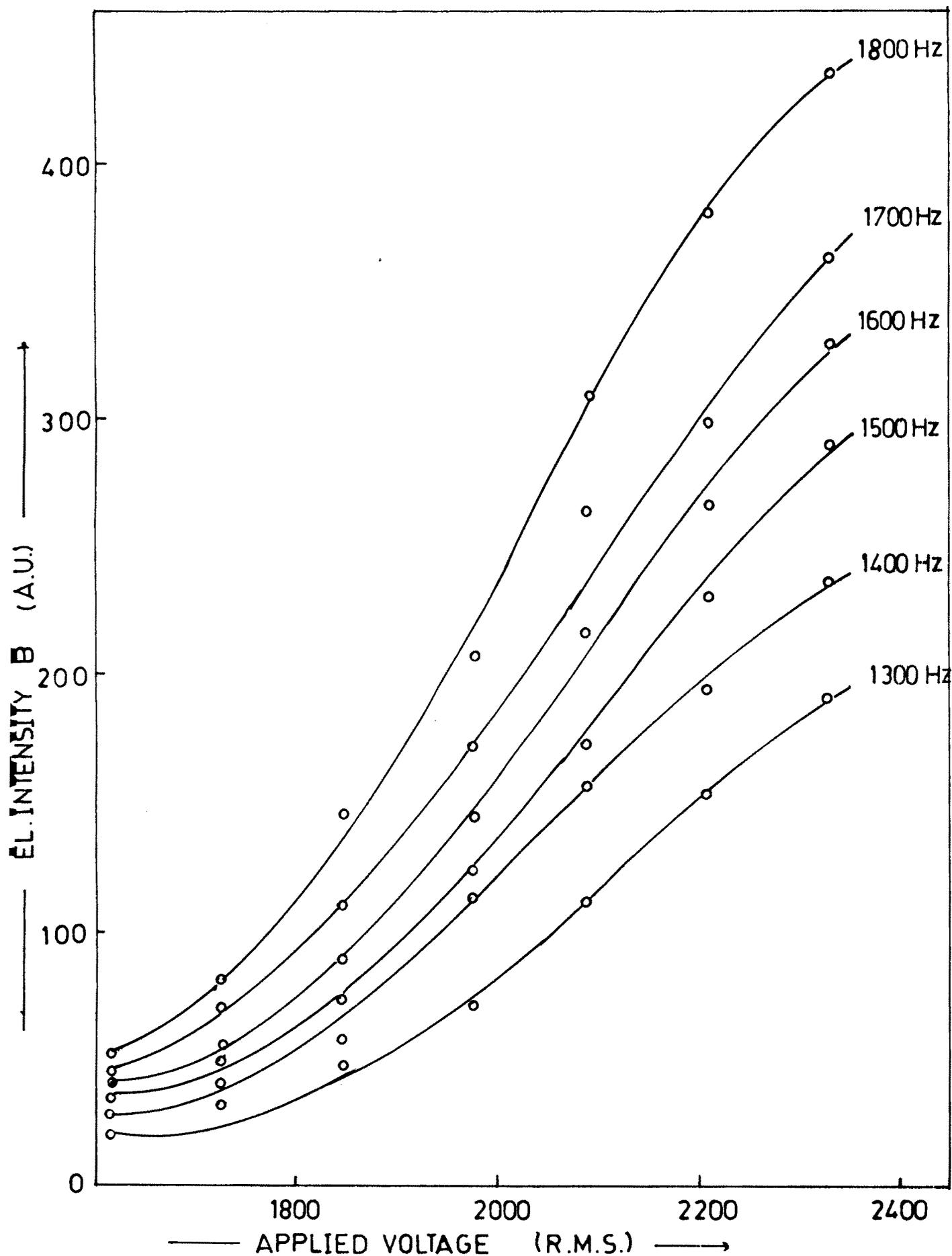| Applied Frequency (Hz)	Applied Voltage (V)						
	1620	1730	1850	1980	2090	2210	2330
1300	20	32	48	73	113	155	192
1400	26	40	57	100	148	196	238
1500	30	49	74	125	174	232	282
1600	35	56	91	145	218	268	316
1700	46	69	111	174	265	300	364
1800	52	83	150	224	310	382	436

FIG·13 VOLTAGE DEPENDENCE OF EL.EMISSION FOR CALCIUM
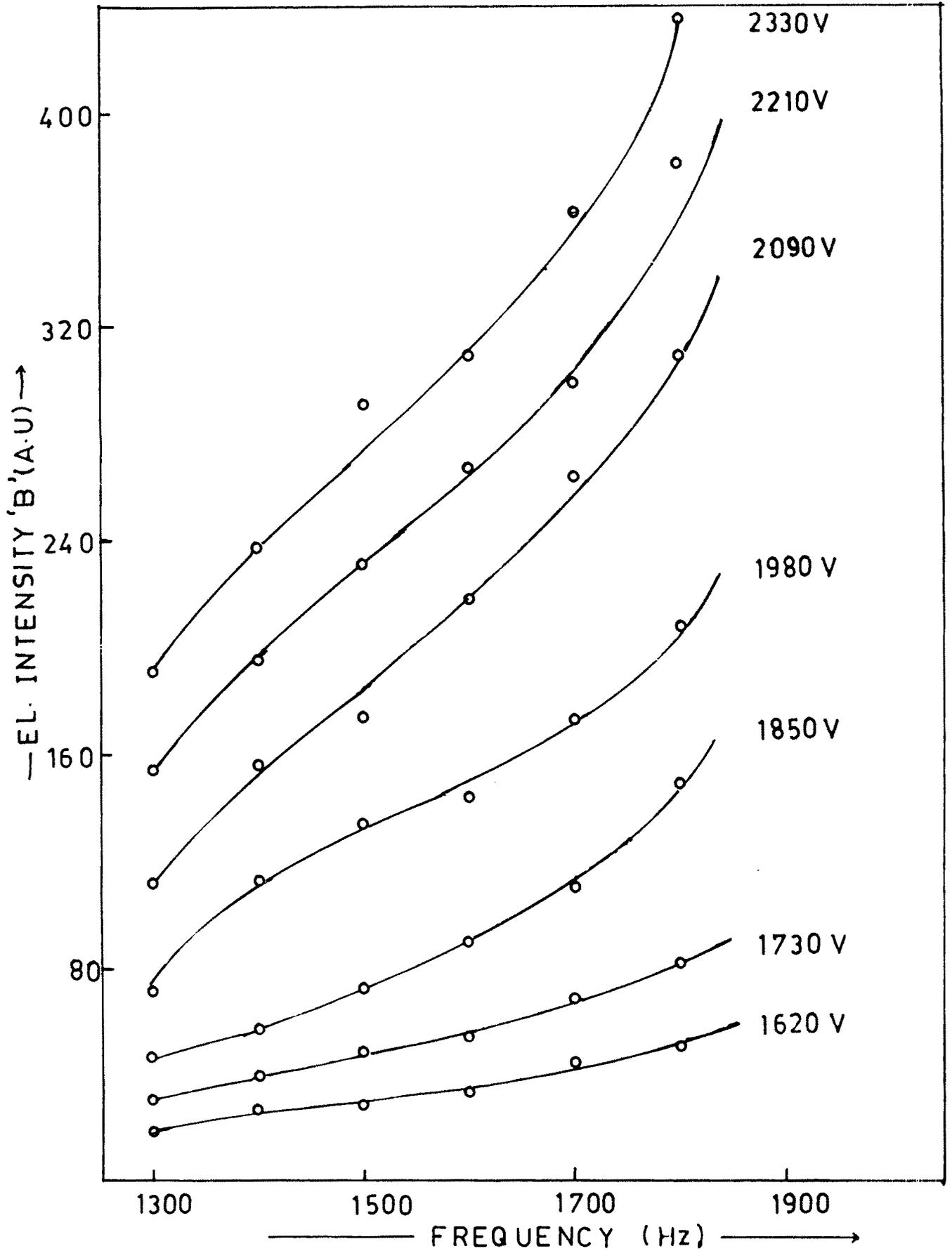
OXINATE AT DIFFERENT FREQUENCIES.

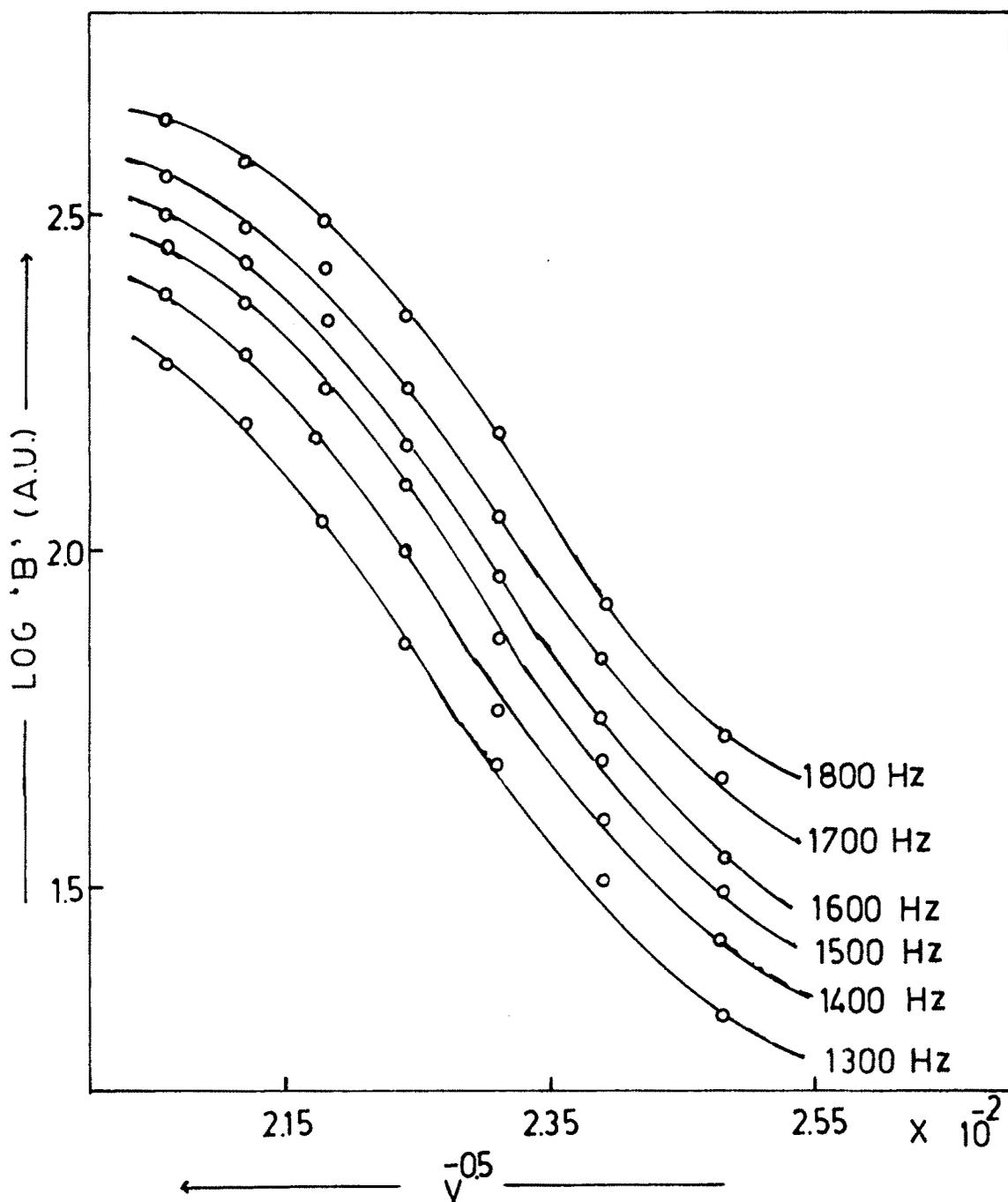FIG·14 FREQUENCY DEPENDENCE OF EL.EMISSION FOR CALCIUM OXINATE AT DIFFERENT VOLTAGES·

FIG·15 DEPENDENCE OF LOG B AS A FUNCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR CALCIUM OXINATE .
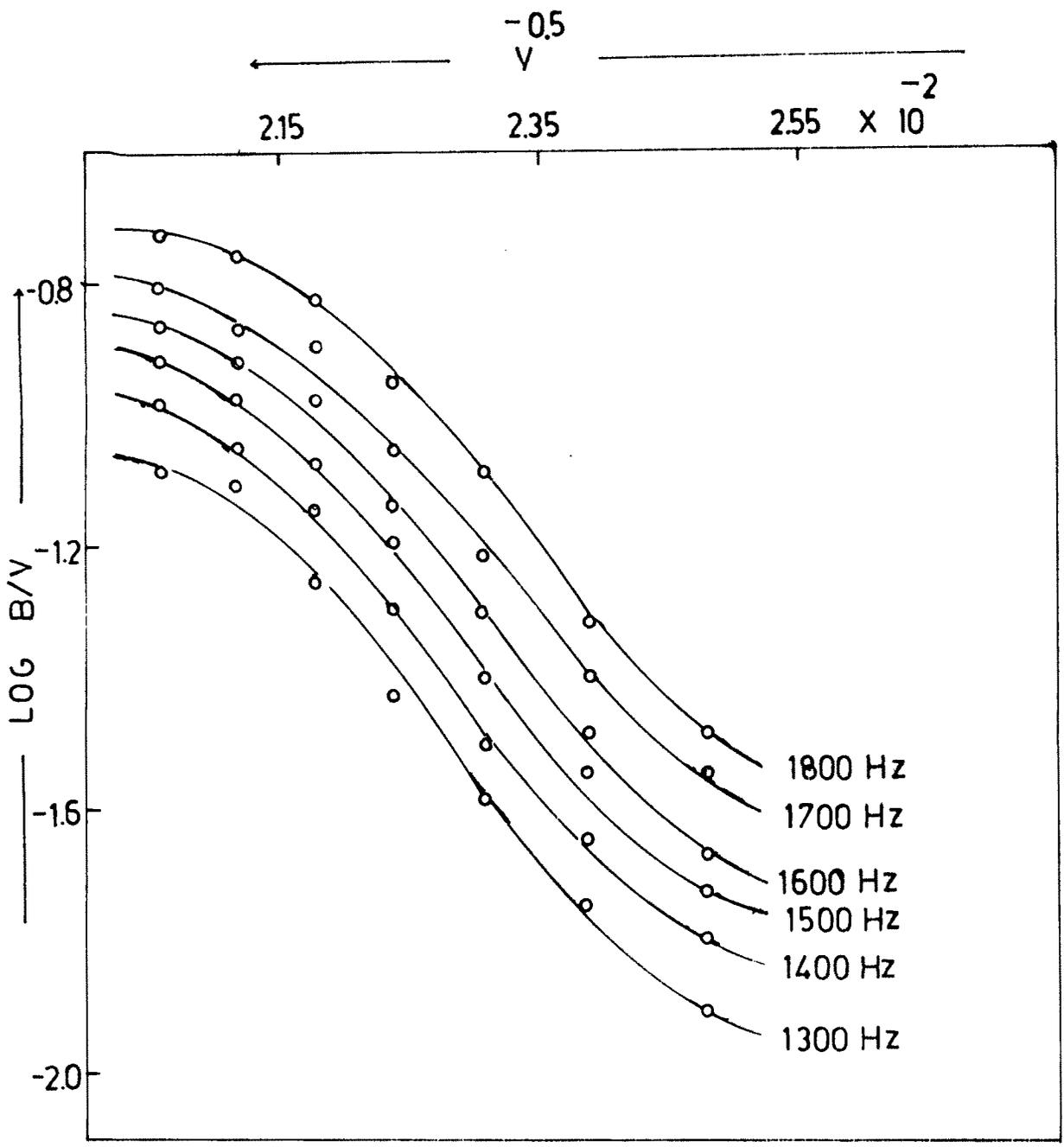
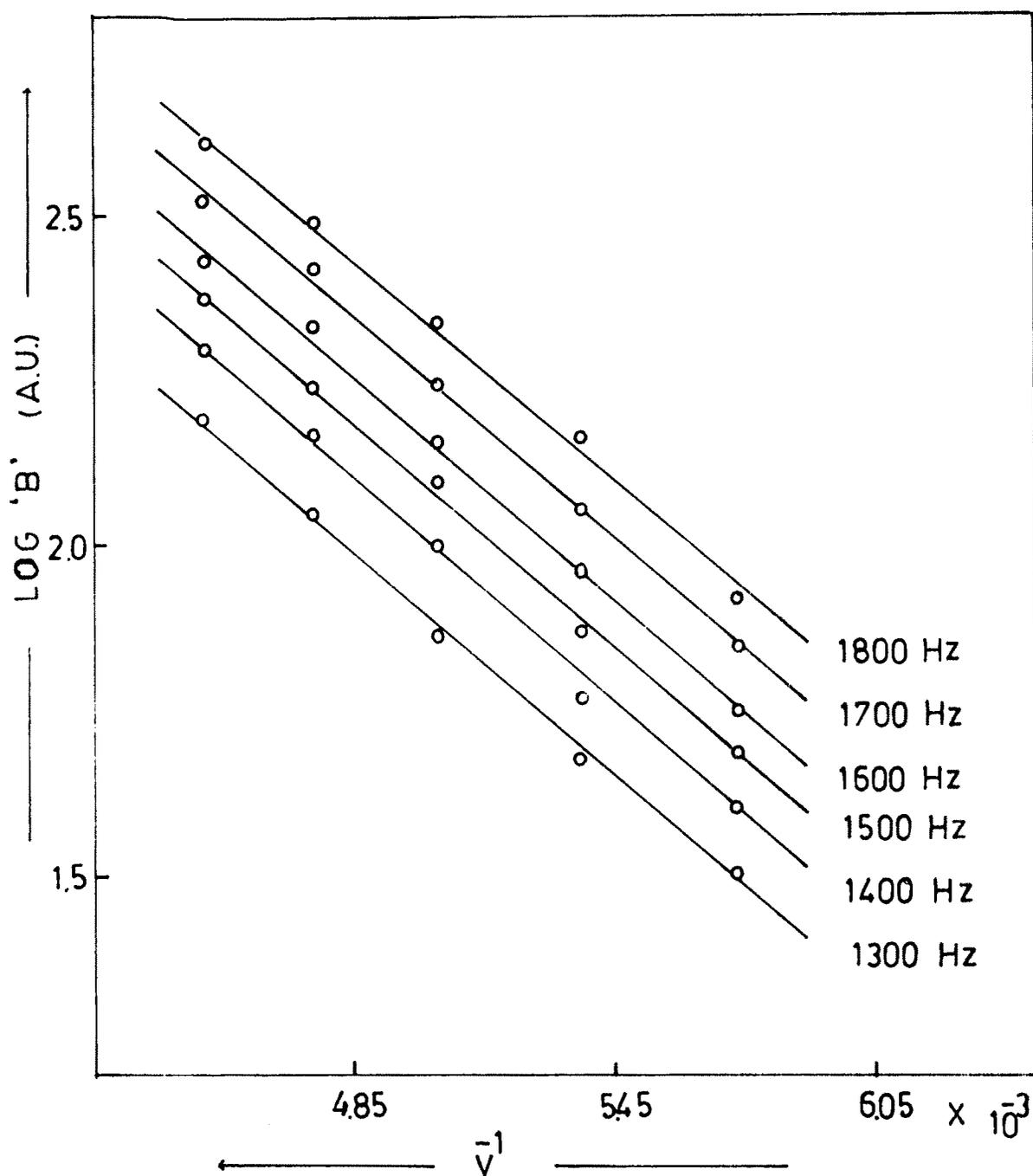FIG·16 DEPENDENCE OF LOG B/V AS A FUNCTION OF V$^{-0.5}$ FOR VARIOUS FREQUENCIES FOR CALCIUM OXINATE.

FIG·17 DEPENDENCE OF LOG B AS A FUNCTION OF $\bar{V}^1$ FOR VARIOUS FREQUENCIES FOR CALCIUM OXINATE .

TABLE NO.8   VOLTAGE AND FREQUENCY DEPENDENCE OF EL. EMISSION OF ZINC OXINATE (λ max = 515 nm).

EL.   Intensity 'B' (A.U.)

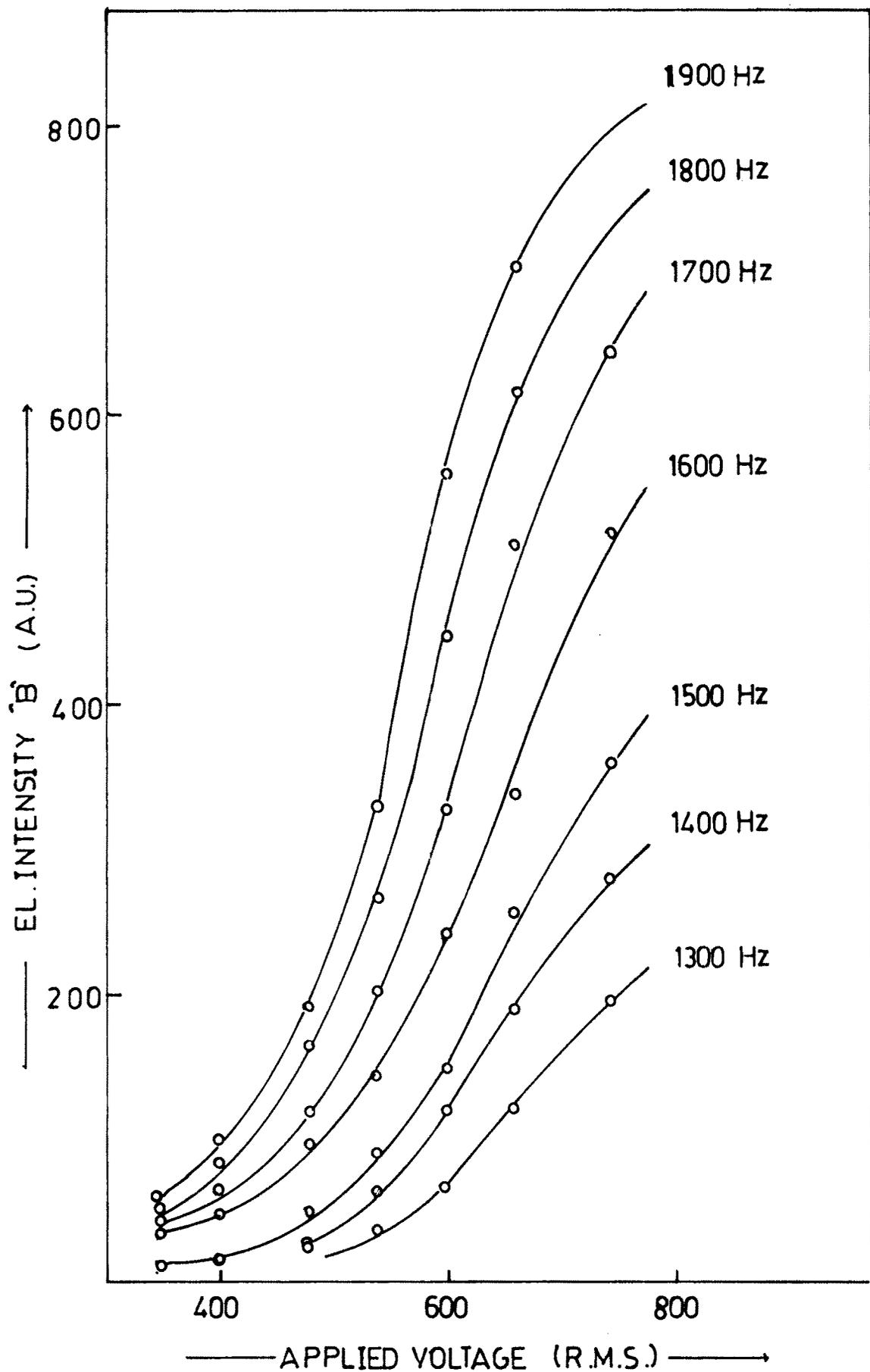| Applied Frequency (Hz)	Applied Voltage (V)						
	350	400	480	540	600	660	720
1300	-	-	23	37	66	120	196
1400	-	-	25	64	118	190	278
1500	-	-	40	95	163	256	358
1600	-	26	83	144	269	384	520
1700	14	43	120	226	328	508	643
1800	43	71	170	301	448	620	760
1900	52	98	219	363	560	703	-

FIG·18 VOLTAGE DEPENDENCE OF EL·EMISSION FOR ZINC
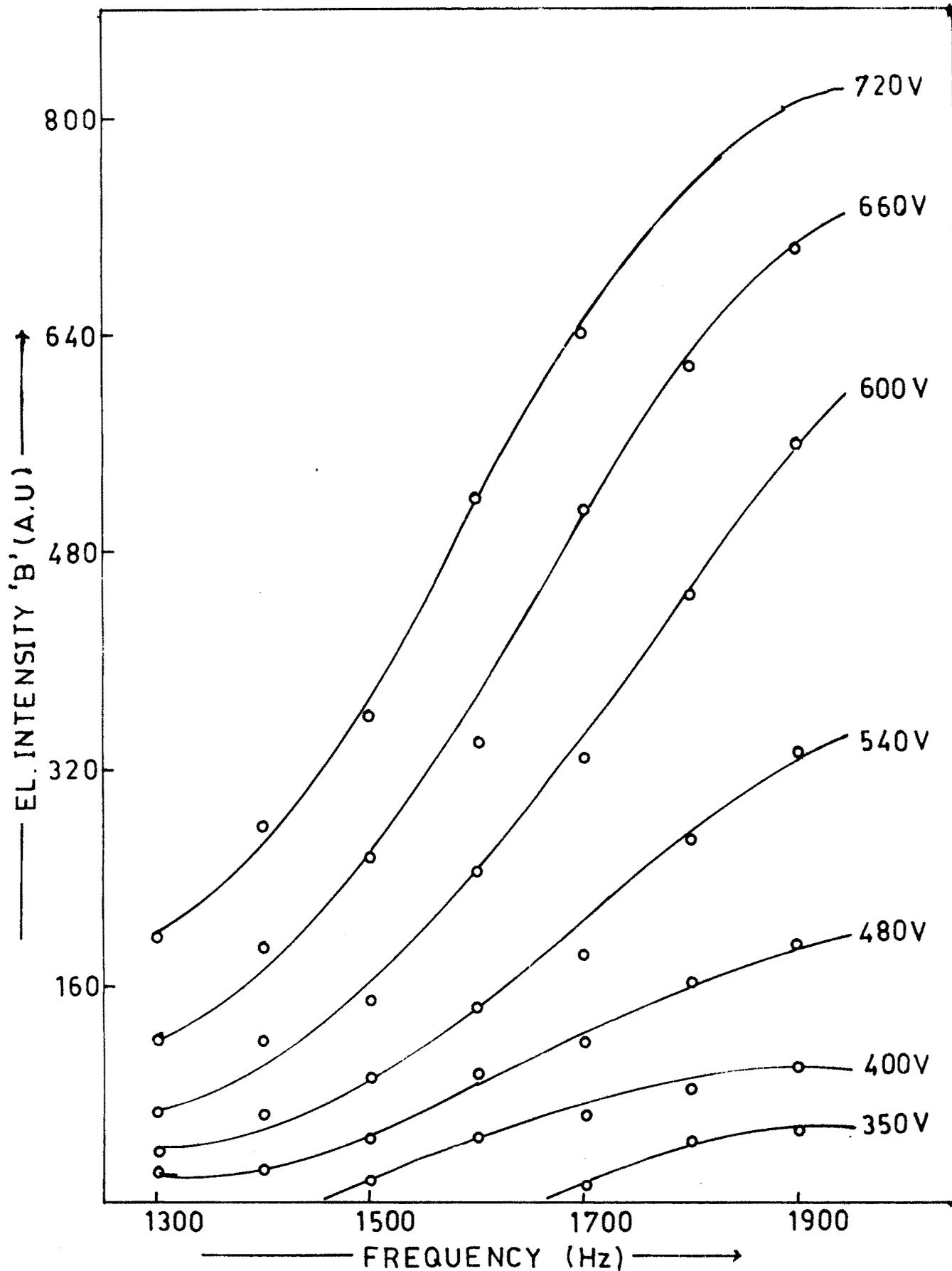
OXINATE AT DIFFERENT FREQUENCIES.

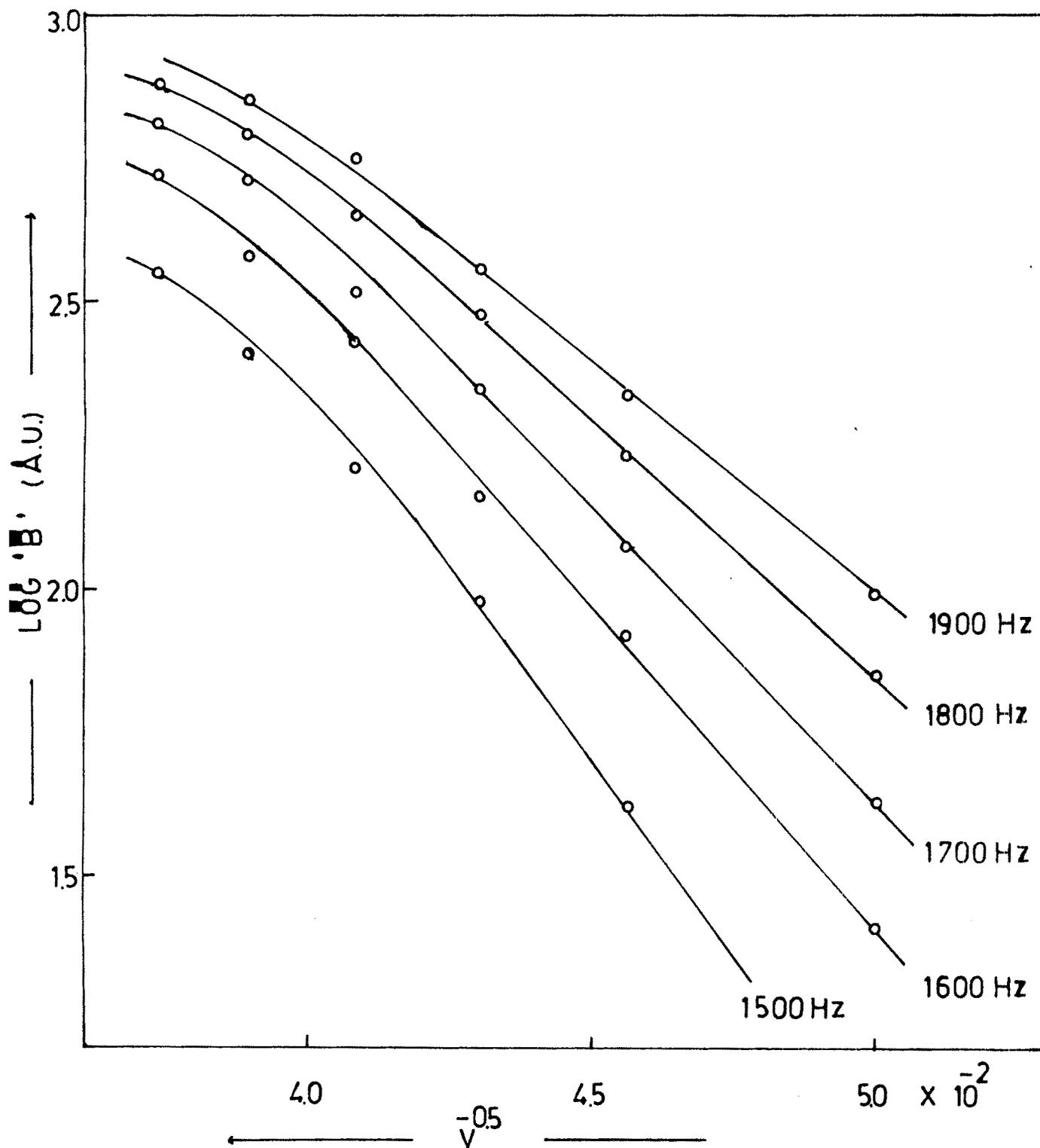FIG·19 EREQUENCY DEPENDENCE OF EL.EMISSION FOR ZINC OXINATE AT DIFFERENT VOLTAGES.

FIG·20 DEPENDENCE OF LOG B AS A FUNCTION OF $V^{-0.5}$
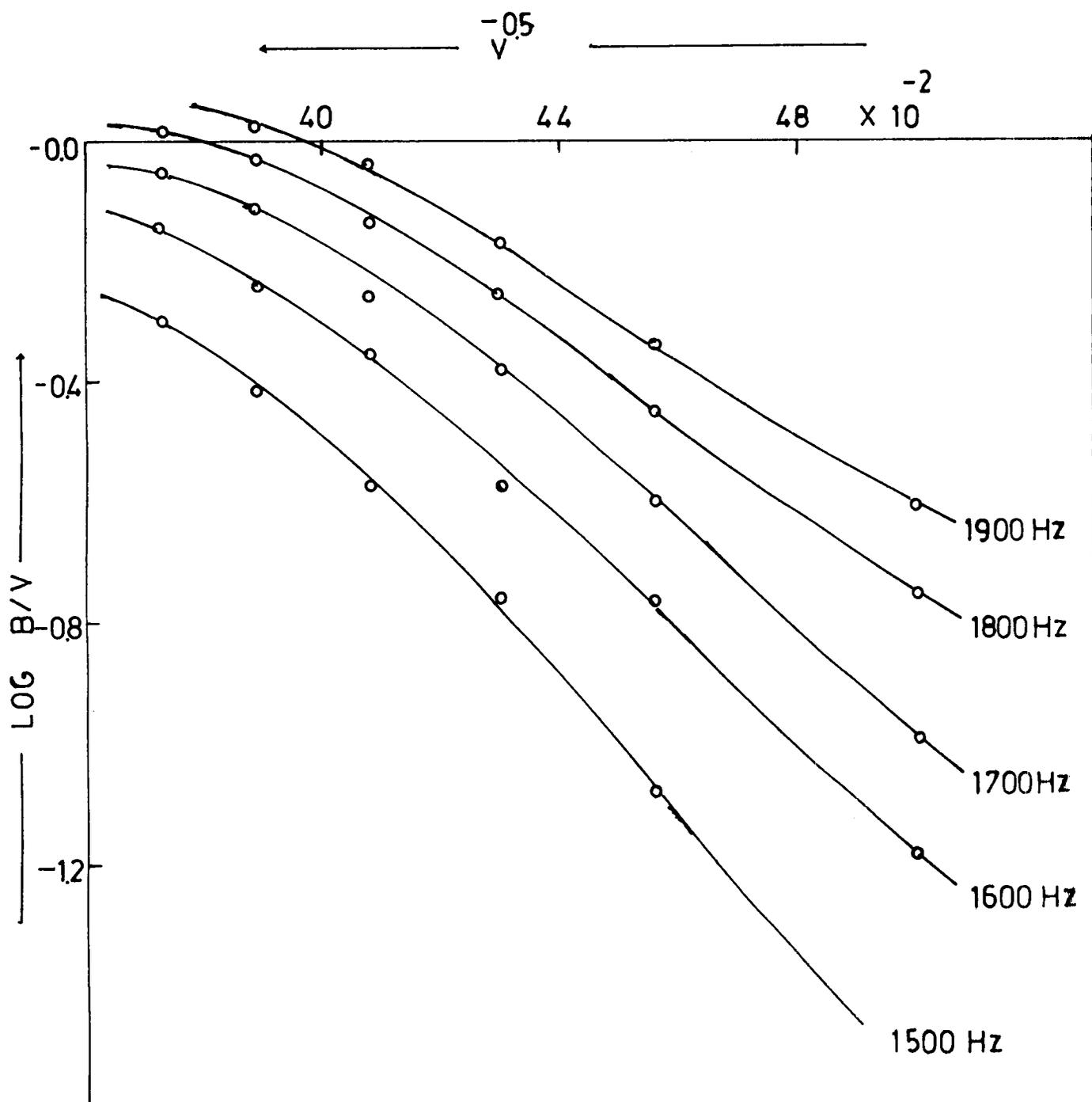
FOR VARIOUS FREQUENCIES FOR ZINC OXINATE .

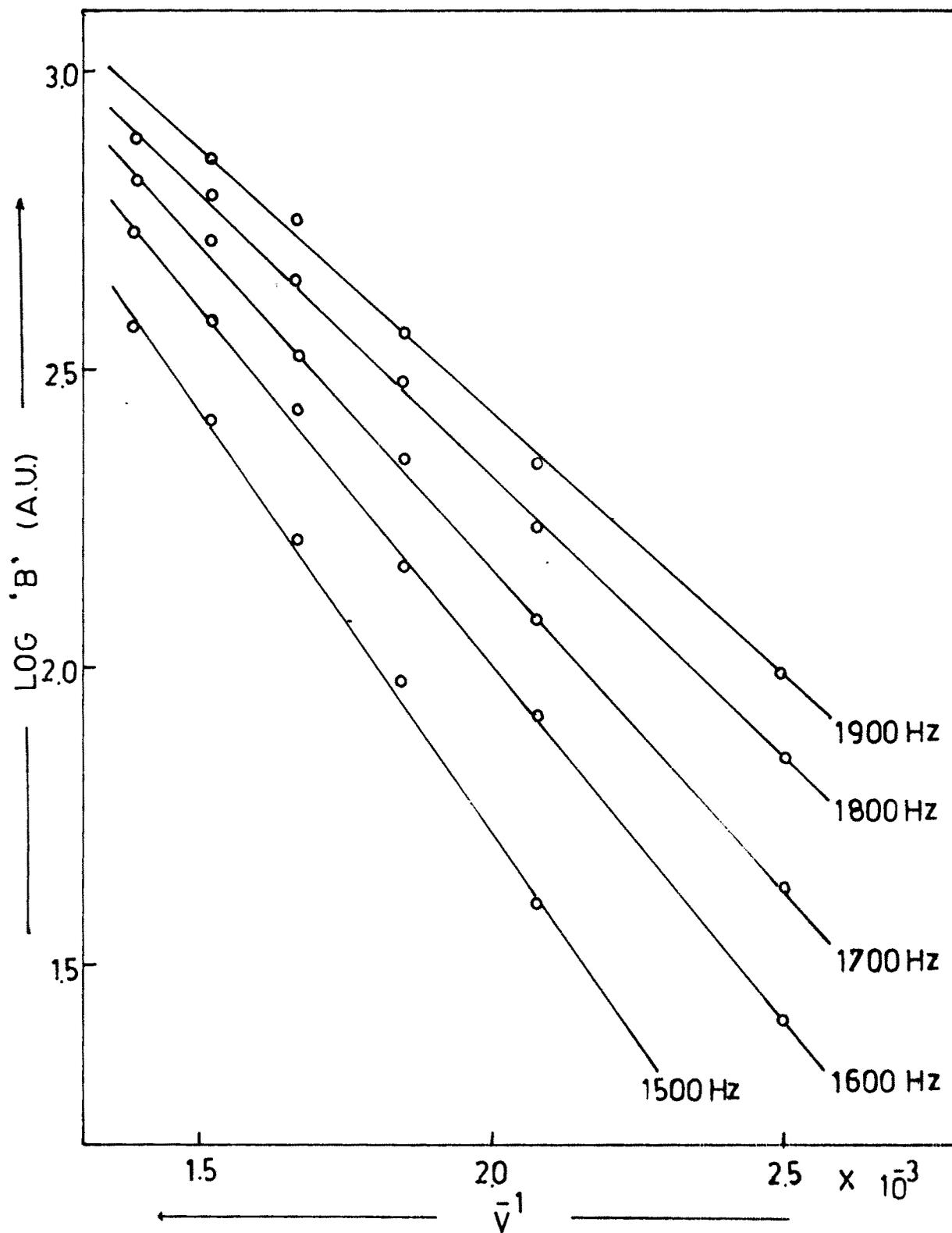FIG·21 DEPENDENCE OF LOG B/V AS A FUNCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR ZINC OXINATE.

FIG·22 DEPENDENCE OF LOG B AS A FUNCTION OF $\bar{v}^1$ FOR VARIOUS FREQUENCIES FOR ZINC OXINATE.

TABLE NO. 9   VOLTAGE AND FREQUENCY DEPENDENCE OF EL. EMISSION OF CADMIUM OXINATE (λ Max = 520 nm).

El. Intensity 'B'(A.U.)

Applied Frequency (Hz)	Applied Voltage (V)							
	400	540	660	780	900	1020	1130	1250
600	4	11	18	23	27	30	32	34
800	7	20	33	44	52	58	62	68
1000	9	27	47	62	68	77	82	85
1200	13	37	55	70	85	94	102	108
1400	23	59	87	110	125	136	145	153
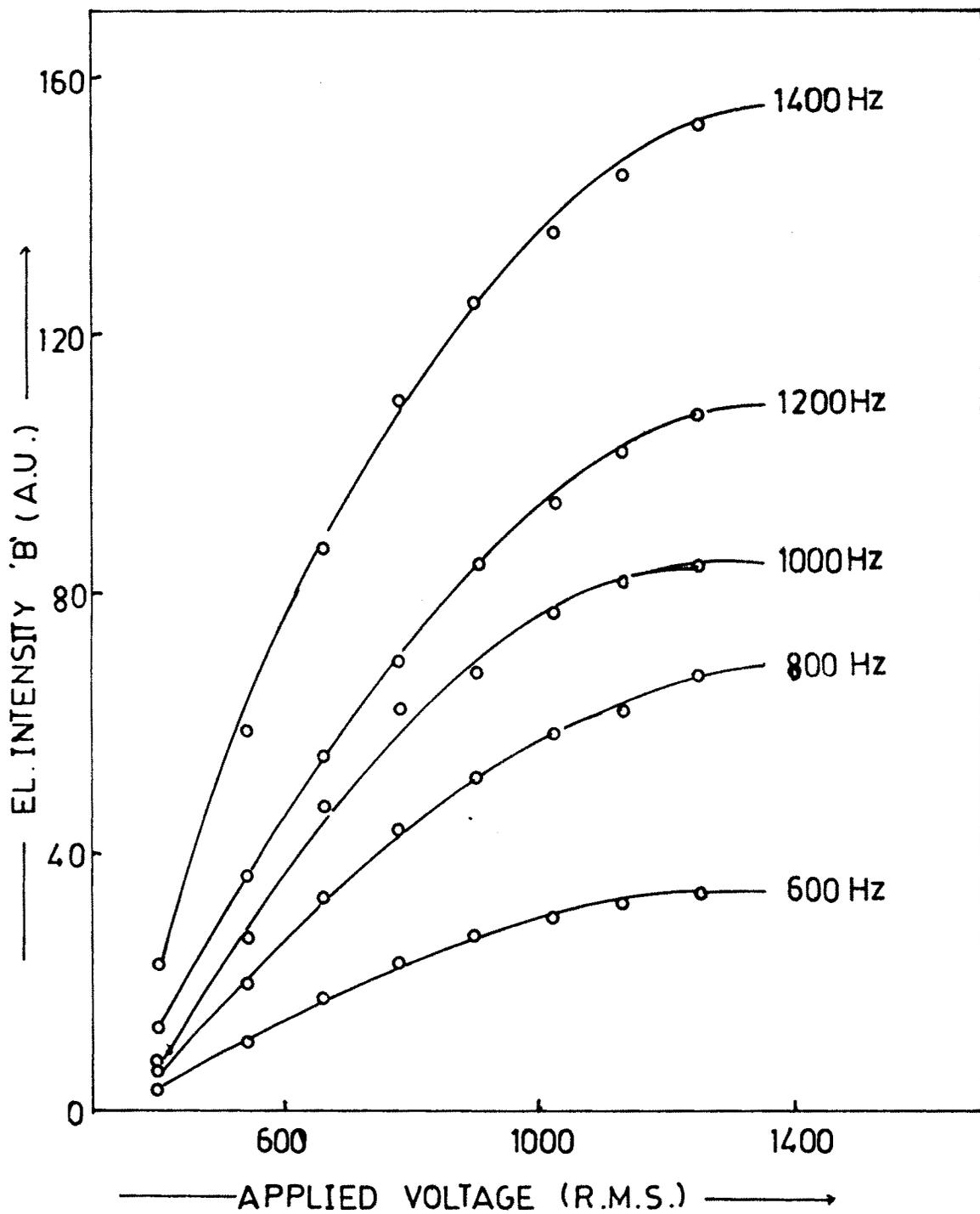
FIG·23 VOLTAGE DEPENDENCE OF EL.EMISSION FOR CADMIUM
OXINATE AT DIFFERENT FREQUENCIES.

FIG·24 FREQUENCY DEPENDENCE OF EL.EMISSION FOR CADMIUM OXINATE AT DIFFERENT VOLTAGES.

FIG·25 DEPENDENCE OF LOG B AS A FUNCTION OF $\overline{V}^{.05}$ FOR VARIOUS FREQUENCIES FOR CADMIUM OXINATE.

FIG·26 DEPENDENCE OF LOG B/V AS A FUNCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR CADMIUM OXINATE .

FIG·27 DEPENDENCE OF LOG B AS A FUNCTION OF $\bar{V}^1$ FOR VARIOUS FREQUENCIES FOR CADMIUM OXINATE.

TABLE NO. 10   VOLTAGE AND FREQUENCY DEPENDENCE OF EL. EMISSION OF

ALUMINIUM OXINATE   (λ Max = 510 nm).

El.Intensity 'B' (A.U.)

Applied Voltage (V)

| Applied Frequency (Hz)	280	400	540	660	780	900	1020	1130
1000	0	2	18	50	98	148	182	218
1200	1	4	27	71	127	181	219	245
1400	2	11	47	101	159	205	247	275
1600	4	17	69	128	180	219	263	293
1800	5	27	85	143	195	245	285	317
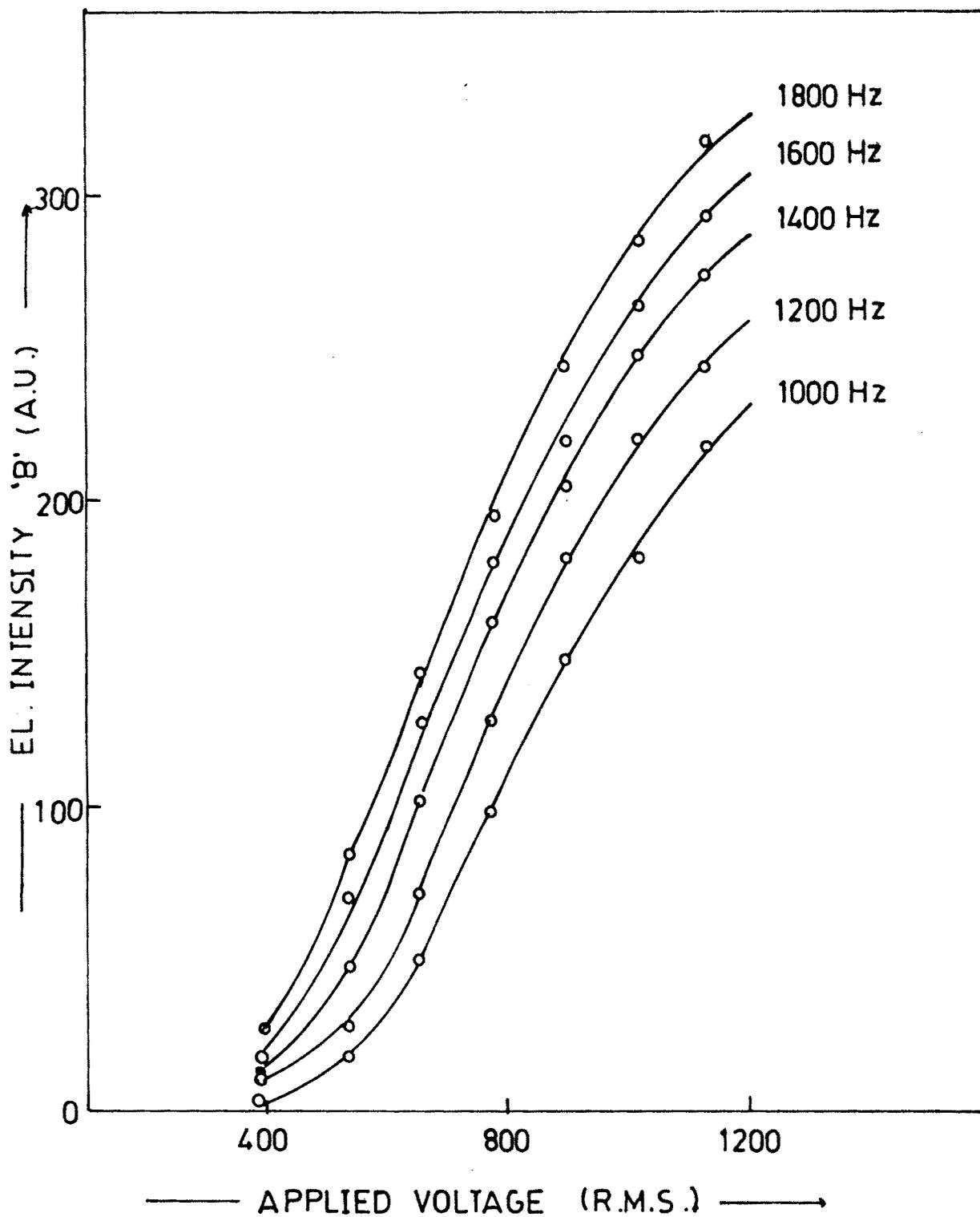
FIG ·28 VOLTAGE DEPENDENCE OF EL.EMISSION FOR ALUMINIUM OXINATE AT DIFFERENT FREQUENCIES.
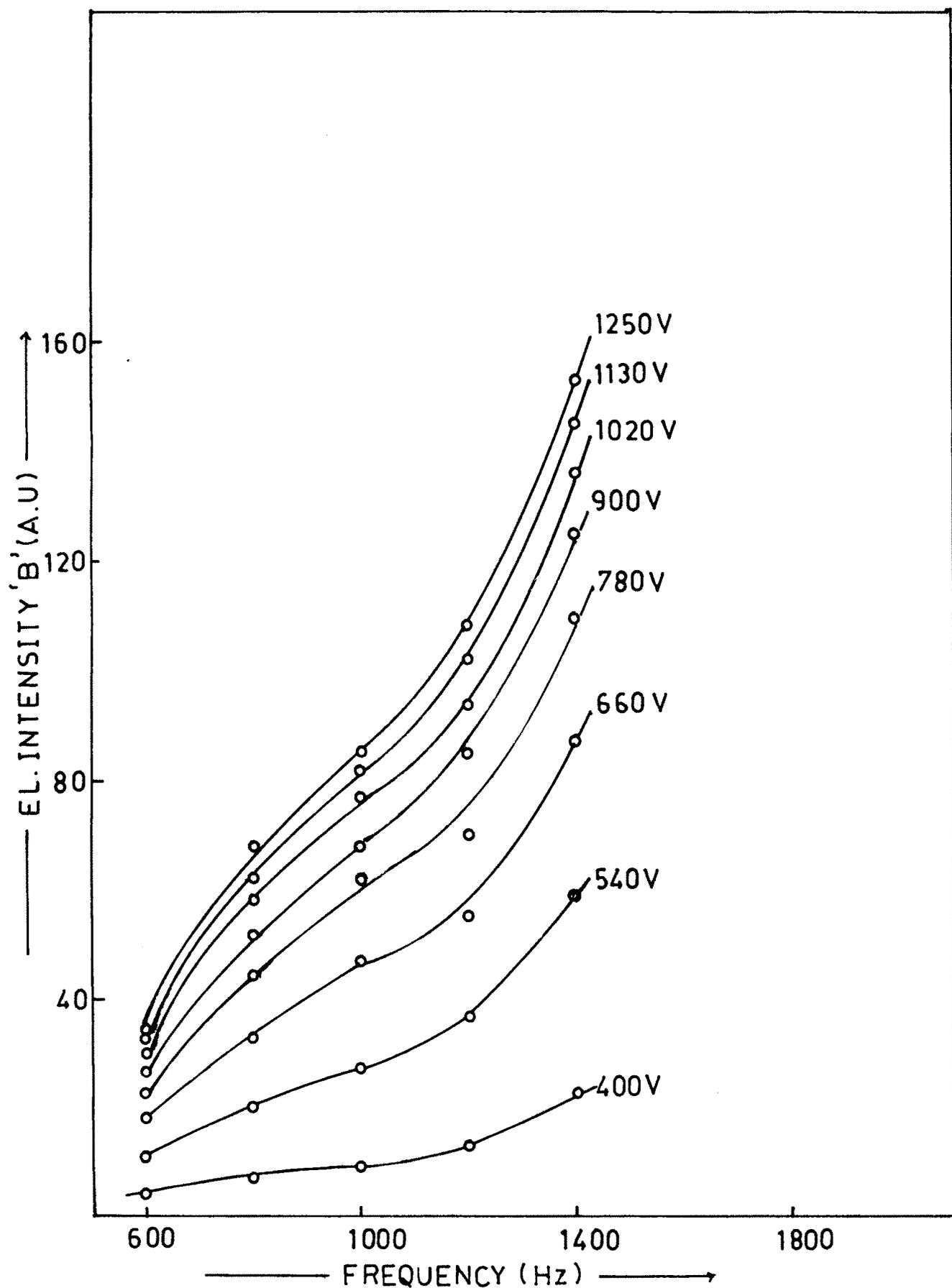
FIG·29 FREQUENCY DEPENDENCE OF EL.EMISSION FOR
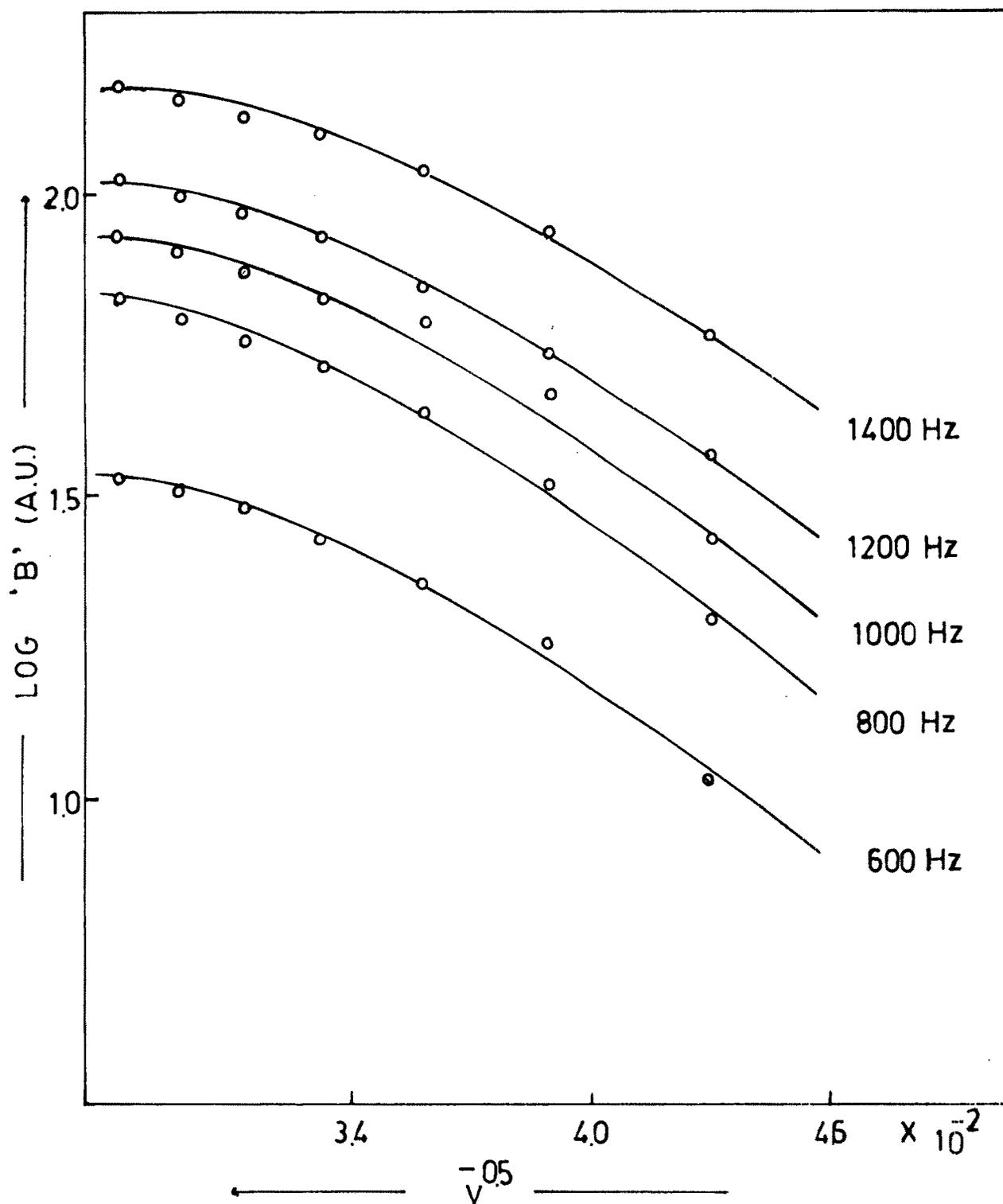ALUMINIUM OXINATE AT DIFFERENT VOLTAGES.

FIG·30 DEPENDENCE OF LOG B AS A FUNCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR ALUMINIUM OXINATE.
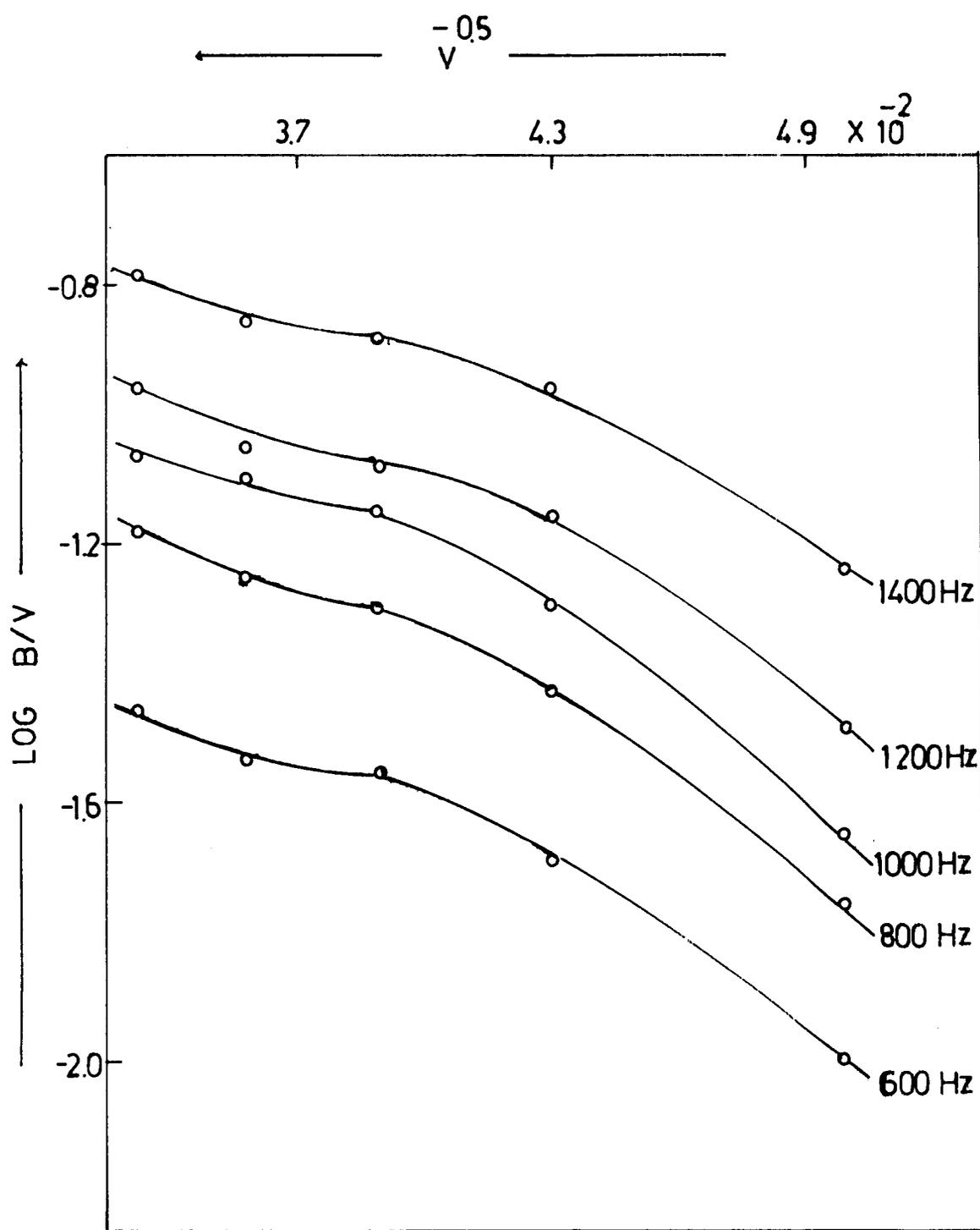
FIG·31 DEPENDENCE OF LOG B/V AS A FUCTION OF $V^{-0.5}$ FOR VARIOUS FREQUENCIES FOR ALUMINIUM OXINATE.

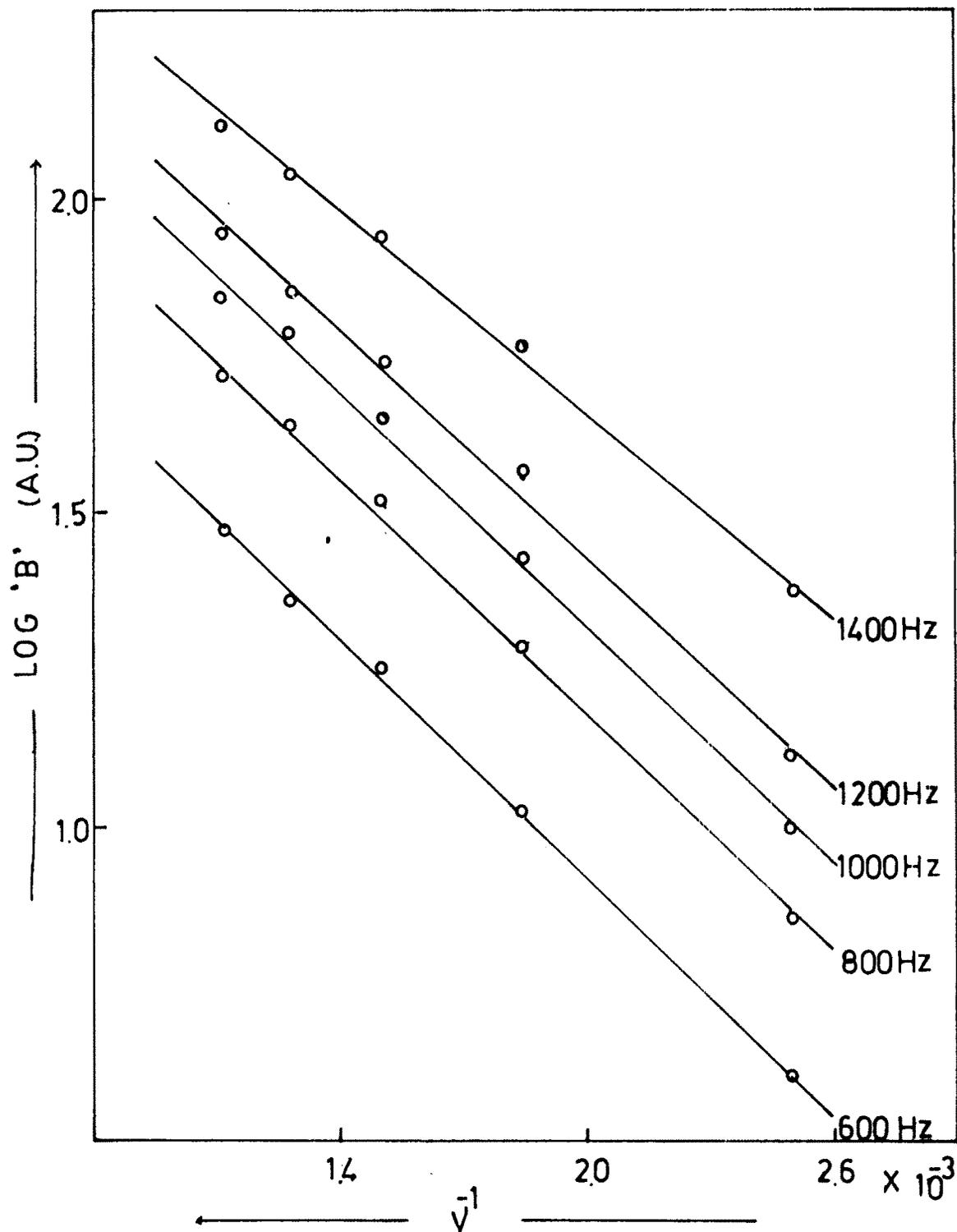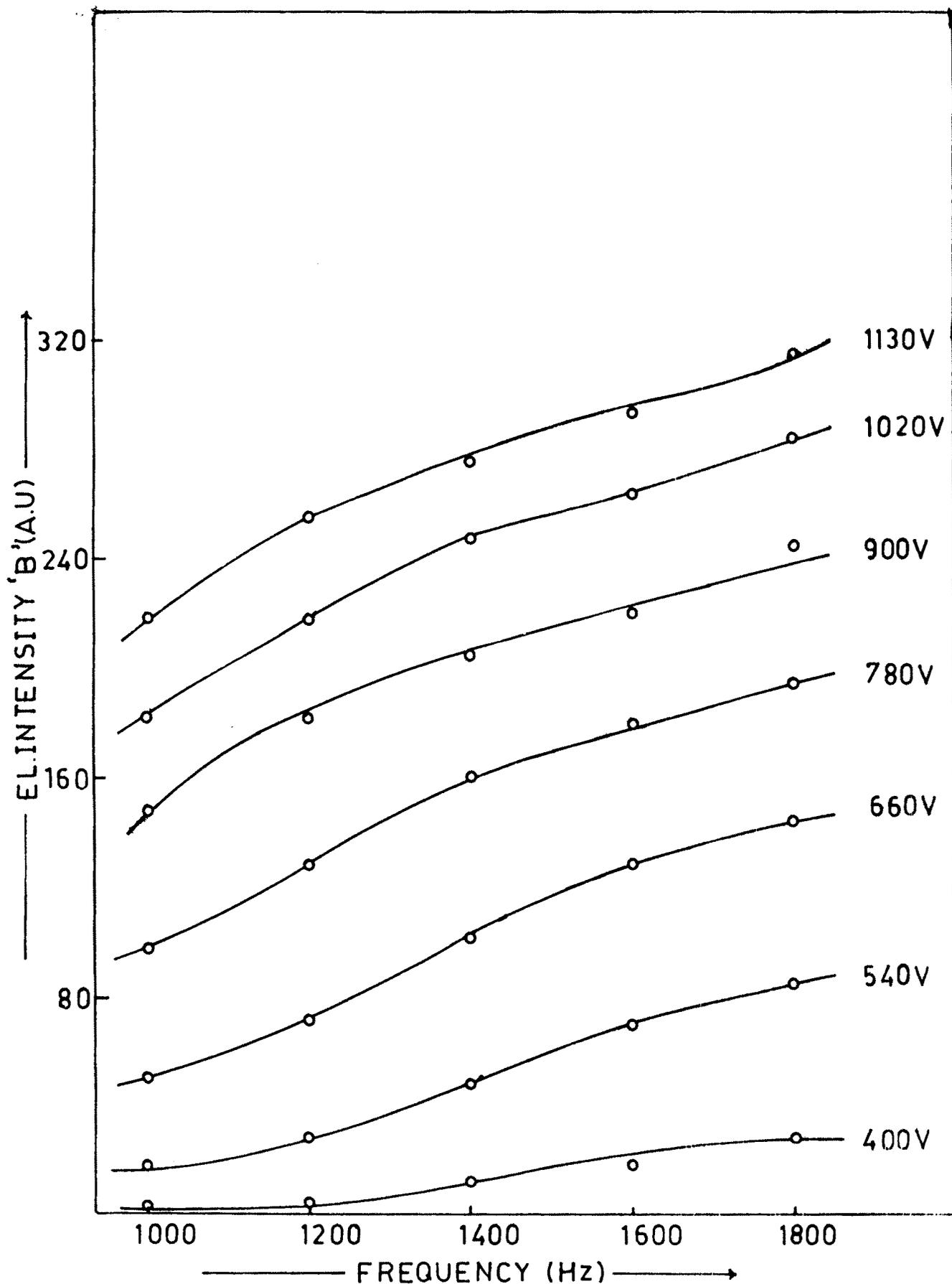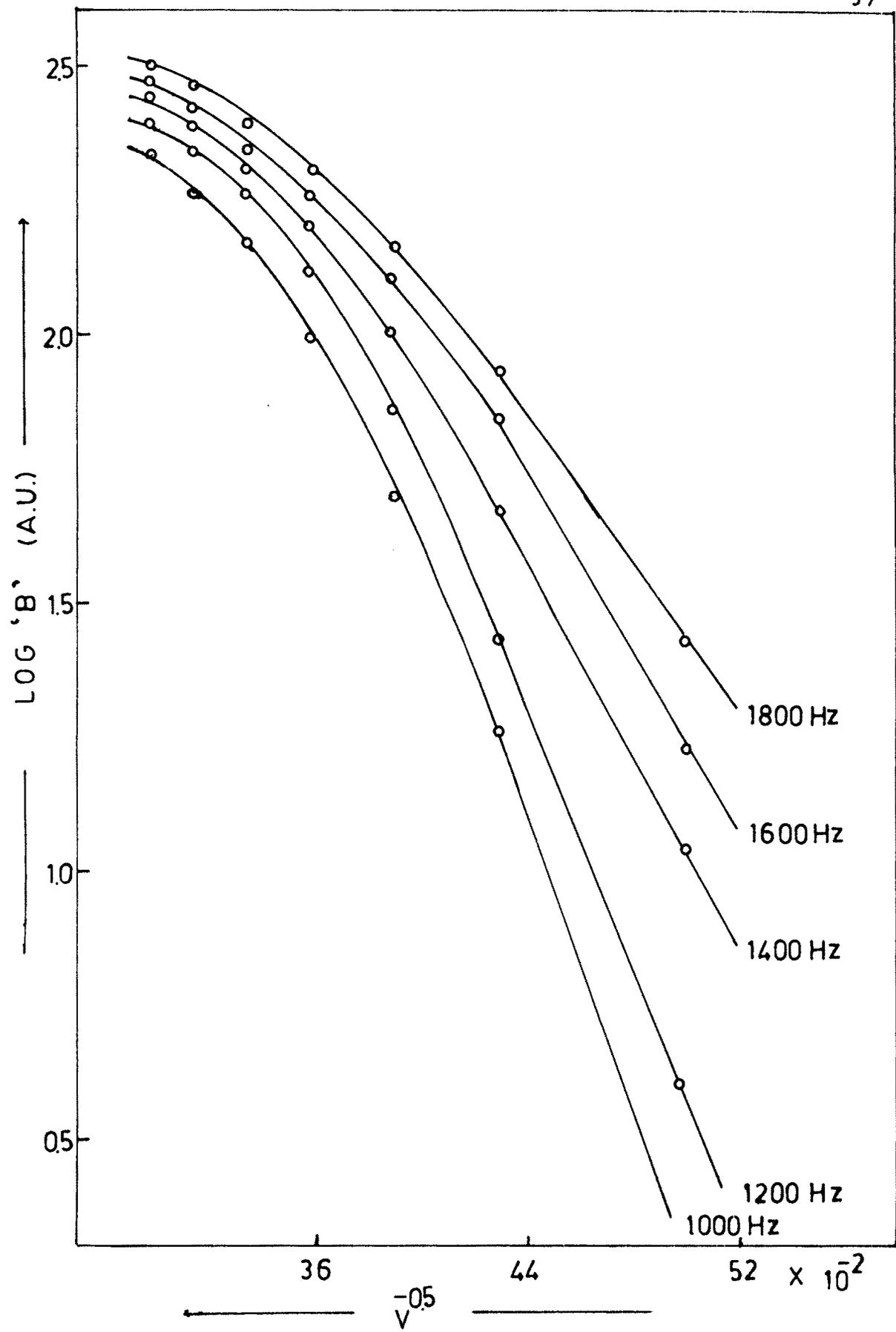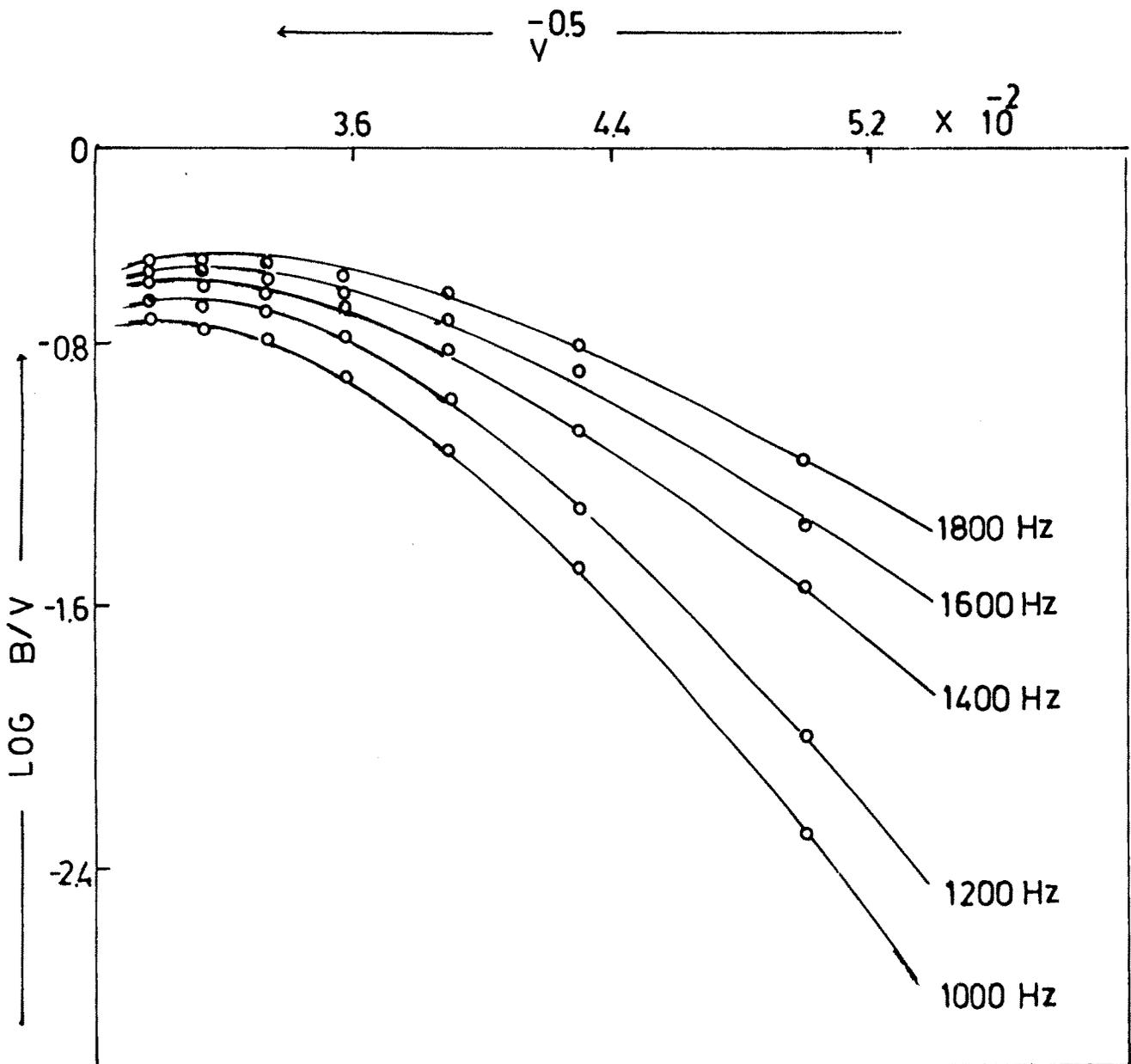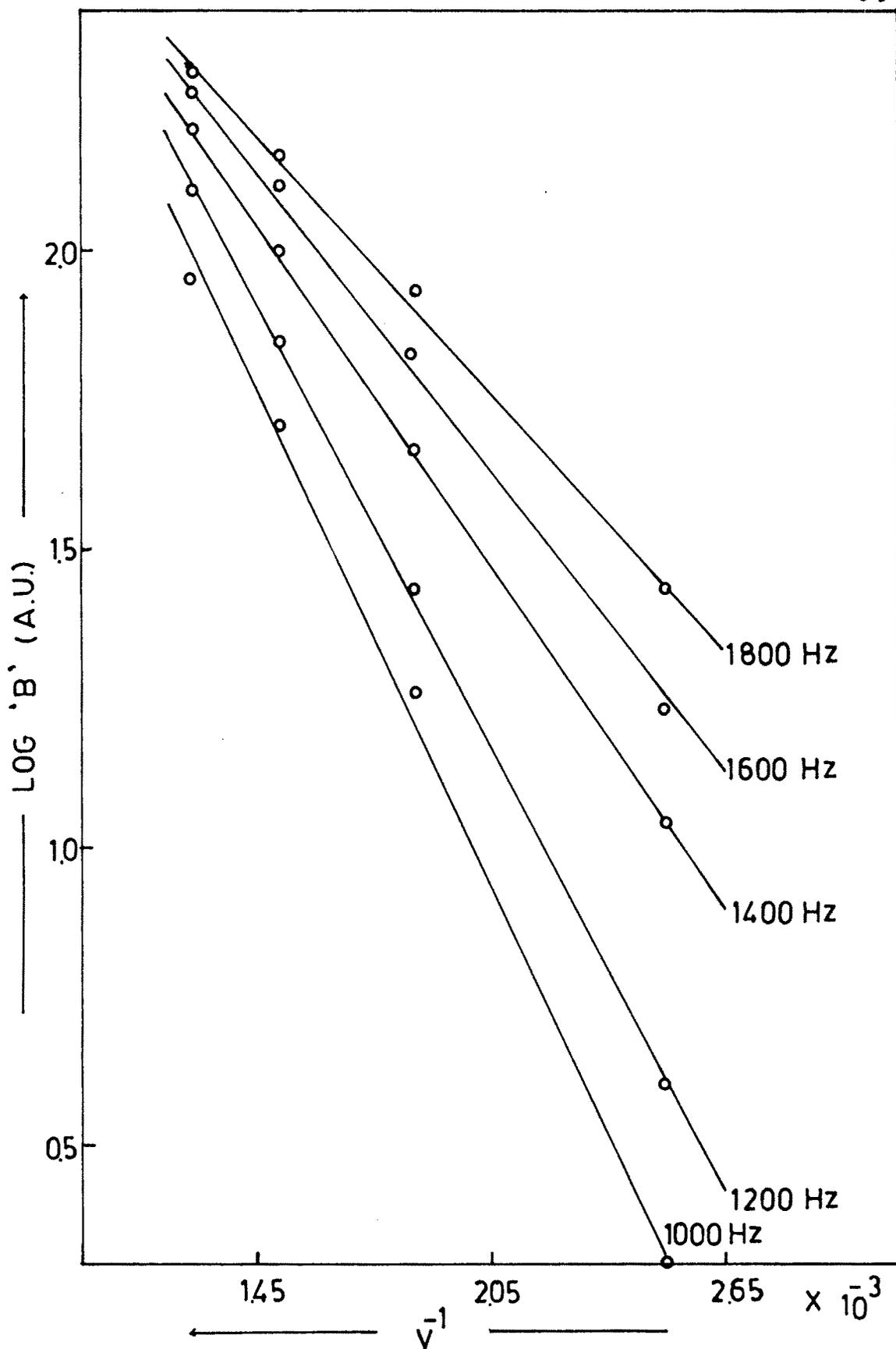FIG·32 DEPENDENCE OF LOG B AS A FUNCTION OF $\bar{V}^{1}$ FOR VARIOUS FREQUENCIES FOR ALUMINIUM OXINATE.

have been mentioned in chapter I, section 1:2:1- d. Some

of them have identical forms,some differ but slightly,

whereas others have a bearing on experimental data and

hence empirical in nature. In view of this confusing

situation,it may be useful to describe here the voltage-

behaviour of the brightness by a suitable equation with-

out any claim to a theoretical background. Inorder to

decide the exact nature of the B-V relationship, the

three equations were tested,namely,

$$B = a. \exp \left[\frac{-b}{V^{0.5}} \right] \quad \text{---} \quad 1$$

$$B = a. V.\exp \left[\frac{-b}{V^{0.5}} \right] \quad \text{----} \quad 2$$

$$\text{and} \quad B = a. \exp. \left[\frac{-b}{V} \right] \quad \text{----} \quad 3$$

where 'a' and 'b' are constants.

The equation (1) describes the variation of B with

V when B approaches a definate value with infinite voltage.

W. Lehmann[147] has shown that,this equation is identical with

the following equation,given by Ivey[102].

$$B = a. \exp \left[\frac{-b}{V-Vo} \right] \quad \text{-----} \quad 4$$

The equation (4) describes the variation of B with V

when B becomes infinite for infinite voltages. Thus,equation

(1) is a saturation equation while (2) and (3) are unsatura-

tion equations. Here attempts have been made to verify the

validity of all the three equations. Fig.Nos. 10,15,20,25

and 30,show the plots of log B against $V^{-0.5}$; while Fig.Nos.

11,16,21,26 and 31, show the plots of log B/V against
$V^{-0.5}$ and Fig.Nos.12,17,22,27 and 32 represents the plots
of log B against V^{-1}, for magnesium,calcium,zinc,cadmium
and aluminium oxinate respectively.

It is seen that the plots of log B Vs $V^{-0.5}$ and log
B/V   Vs $V^{-0.5}$ are not linear. Whereas, the plots of log
B   Vs V^{-1} at different frequencies are linear thus confir-
ming the validity of the equation:

$$B = a.\ exp \left[\frac{-b}{V} \right].$$

For a microcrystalline powder material it has been
observed that El. emission is not uniform through out the
bulk but restricted to localized spots on the surface. This
non-uniformity of El.emission makes the voltage-brightness
relation more complicated and hence it is difficult to
explain it on any theoretical basis. However,attempts have
been made to present these results on the basis of mechanism
of El.process.

On the basis of existance of a 'Mott-Schottky' barrier
at the surface of the microcrystalline grain of the El.
material gives the equation:

$$B = Bo.\ exp \left[\frac{-b}{V^{0.5}} \right] \quad ------ \quad 5$$

$$or \quad B = Bo.\ exp \left[\frac{-b}{Vo +V} \right] \quad ----- \quad 6$$

which are identical with equations (1) and (4). Bonfiglioli

and Brovotto[148] gives a similar relation between B and V.
Therefore, the 'Mott-Schottky' barrier mechanism or 'a
defective border' mechanism given by Bonfiglioli and Brovotto
must be operating in inorganic and some organic El.materials.
This behaviour is usually interpreted by saying that the
rate of exciting electrons from bound states is proportional
to exp. (-constant /E), where E is the electric field strength,
would be proportional to $V^{1/2}$ in the vicinity of a junction or
a Schottky barrier.

It is of interest to see how the applied a.c.voltage
is distributed in the organic material and phosphor system
composed of microcrystallites. The results of a voltage
saturation of El. brightness seems to be important,since it
indicates that only a very limited number of carriers can be
excited during each cycle of the applied a.c. voltage even
if this voltage becomes infinite. In the case of microcrysta-
lline,powder phosphors, the excitation process is restricted
to a small fraction of the grains in the neighbourhood of
the contact of base matrix with a conducting phase or a
metal conductor.

From our plots of log B Vs V^{-1} at different frequencies,
it was found that the formula

$$B = a \cdot \exp\left[\frac{-b}{V}\right]$$

fitts better than the formula

$$B = a \cdot \exp\left[\frac{-b}{V^{\frac{1}{2}}}\right]$$

indicating that the E, the electric field strength,operating

must be proportional to V^1 rather than $V^{\frac{1}{2}}$, as in the vicinity of a junction or a Schottky barrier. In the case of metallic salts of 8- hydroxyquinoline studied, if there are no junctions or barriers, E would be proportional to V^1. Thus, it seems that electrons are introduced by the field, either from the electrodes or from bound states within the material, at a rate proportional to V^1. These electrons may excite luminescence centres in the material and thus light is produced.

4.1 - II)   **FREQUENCY — DEPENDENCE OF ELECTROLUMINESCENCE EMISSION.**

The brightness of an El. is a function not only of the applied a.c. voltage but also of the frequency. The experimental results, as shown in Fig.Nos. 9,14,19,24,29 for frequency dependence of El. emission of magnesium, calcium, zinc, cadmium and aluminium oxinate respectively. The El. brightness (B) is approximately linearly increasing with frequency at low frequencies and a distinct saturation occurs at high frequencies and high voltages. It is also observed that higher the applied voltage greater is the frequency range in which El. brightness increases linearly with frequency. It is easy to vary the frequency and to hold constant voltage applied (if not very high) to the cell. Furthermore, any process of El. in the phosphor occurs with exactly the same frequency as that applied to the cell.

But field strength at any point in the phosphor particle,
is not known, nor is its dependence on frequency,even
when the voltage to the cell remains constant,because of
the complicated and non-homogenious structure of the
particle. This may be one reason for the complicated behaviour
of the El. brightness during frequency variation,as long
as finite voltages are used.

An attempt have been made to explain our experimental
results on the basis of electroluminescent build-up process.
There are similarities between this process and build-up of
photoluminescence under ultra-violet stimulation. One of
the charactaristics of photoluminescent build-up is the
increase in build-up rate with increasing intensity of
excitation. One would perhaps expect this to be true also
for El; but as far as is known,such an effect has not been
confirmed. In terms of time, the build-up rate is distinctly
greater at higher frequency,but considered in terms of the
number of brightness waves needed to reach a certain intensity
level,the rate is actually lower.

The excitation of electrons, their trapping and their
subsequent release involve a relaxation time and this provides,
in most general sense, the possibility of frequency dependent
behaviour. Let us assume that the El.brightness can be regarded
as being due to the instantaneous concentration Nl of light
emitting point sources. After excitation,these sources would
decay and,in the simplest case, the decay rate would be Nl/To,

where Υ_0 is an effective relaxation time. In opposition to the decay, the excitation voltage would produce new emitting localities, at a rate which we may presume to be proportional to the concentration N- Nl of unexcited sources, where 'N' being the total concentration of sources which are capable of participating in the process.

It is now necessary to consider how the avarage rate of emitting localities should depend on frequency. It is evidently true that the light output depends not so much on the duration of high voltage but on the number of times (per second) the voltage is applied or removed. As a first rough approximation we shall here assume that the generation rate is actually proportional to that number over a useful range of frequencies. Accordingly we shall write:

$$\frac{dN1}{dt} = \frac{-N1}{\Upsilon_0} + \frac{\alpha w}{2\pi}(N - N1) \ ---- \ 7$$

where 'w' is angular frequency and 'α' a constant of proportionality which must be presumed to be voltage dependent, though invariant with frequency. Under the condition N1=o at t = o and dN1/ dt = o at t = ∞ , is

$$N1 = N1\infty \left(1 - \exp\left(\frac{-t}{\Upsilon}\right)\right) \ ----- \ 8$$

Where $N1\infty = N(\alpha w\Upsilon / 2\pi)$ 9
and Υ is a new effective time constant, given by

$$\frac{1}{\Upsilon} = \frac{1}{\Upsilon_0} + \frac{\alpha w}{2\pi} \ ------10$$

As long as frequency is low enough,the individual

flashes of which the brightness wave is composed have time to subside to zero (or almost so) before the system is reactivated by the next voltage peak. The peak values of the light output are not strongly frequency dependent and neither is the time width of the flashes, Over a certain range, an increased excitation frequency thus means an increased number of equivalent light flashes per second and thus a linearly increasing time average. As frequency continues to rise,successive excitation pulses must begin to interact and the linear relation cannot continue to hold. These condtions can be simply discussed in terms of equations (8)and (10) which gives

$$Nl_\infty = \frac{N}{1+2\pi \, / \, \alpha \, w \, T_0} \qquad ----- \quad 11$$

which at very low frequencies approximate to

$$Nl_\infty \simeq N \alpha \, T_0 \, f \qquad ---- \quad 12$$

'f' being the frequency. Nl_∞ may be taken as proportional to the brightness B, thus establishing the initially linear relation-ship with frequency. The rate at which system saturates at higher frequencies is evidently dependent on T_0 and α .

4.2   LUMINOUS EFFICIENCY,

The luminous efficiency, η is essentially a ratio of the emission intensity 'B' to the effective power absorption(W)i.e.

$$\eta \simeq \frac{B}{W} \qquad ------- \quad 13$$

Lehmann has given the expression for η as

$$\eta = \frac{B}{W} = \frac{(B/f)}{aV^2\left(K_0 + b(B/f)^{\frac{1}{2}}\right)} \quad ---14$$
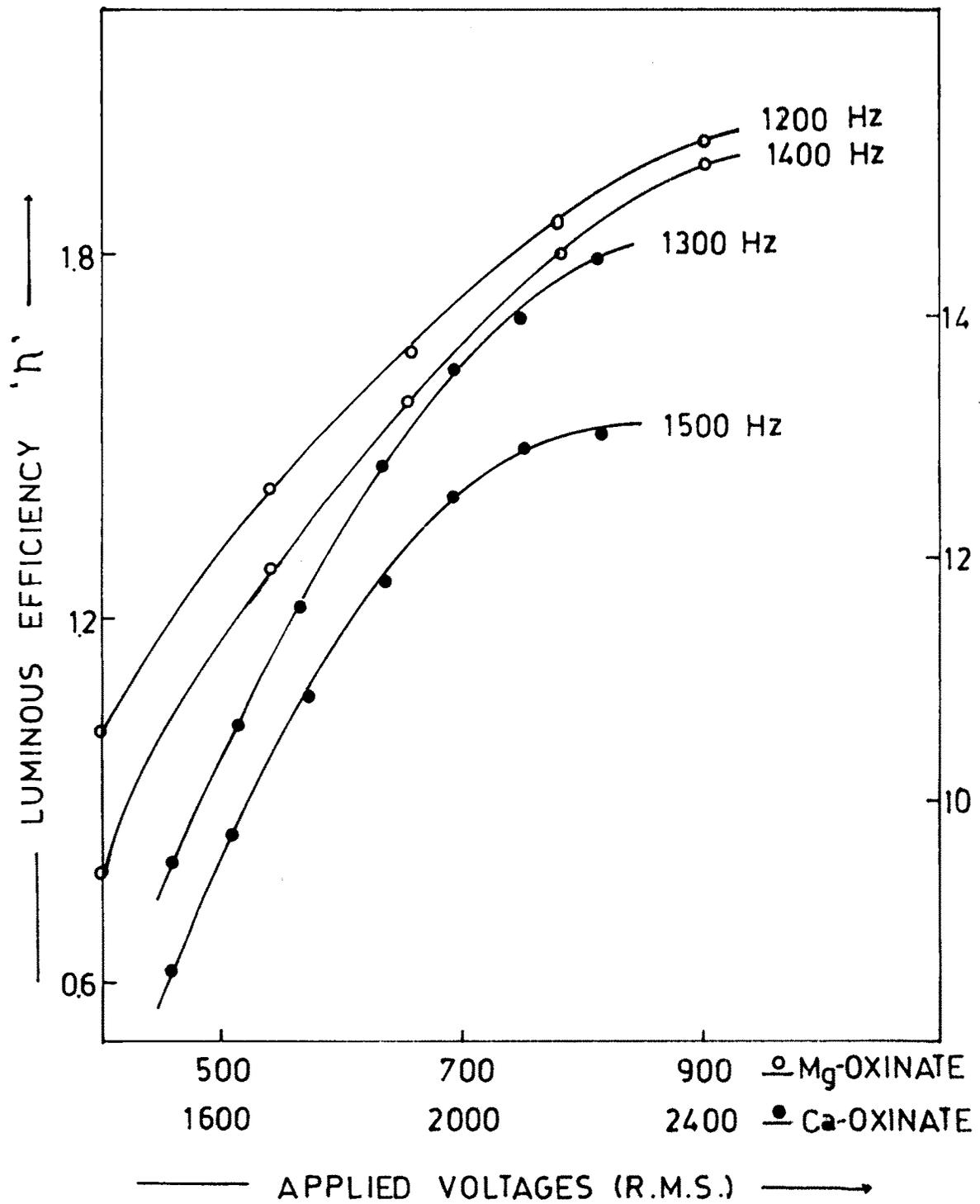
FIG · 33   VOLTAGE AND FREQUENCY DEPENDENCE OF LUMINOUS EFFICIENCY FOR MAGNESIUM AND CALCIUM OXINATE.
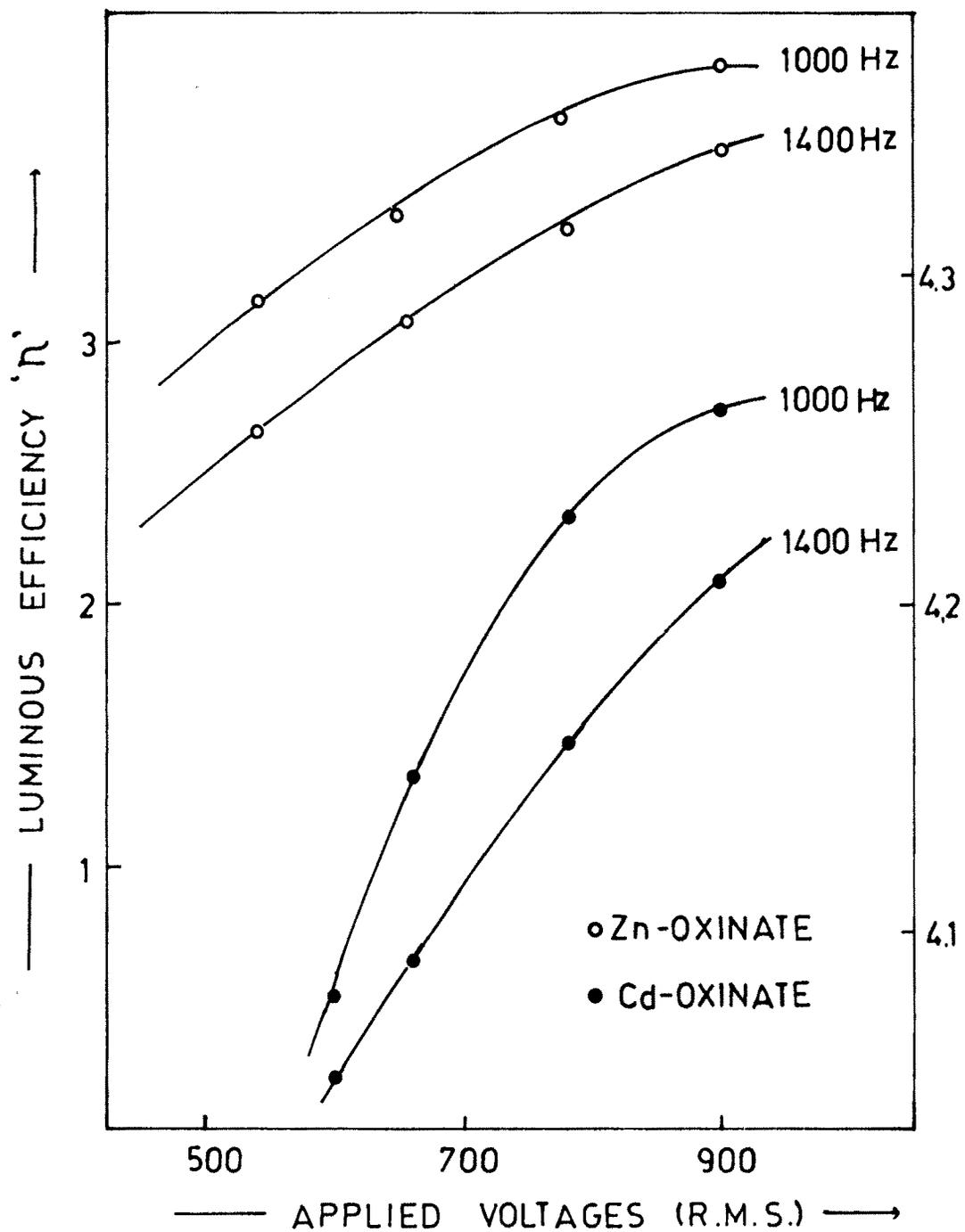
FIG · 34   VOLTAGE AND FREQUENCY DEPENDENCE
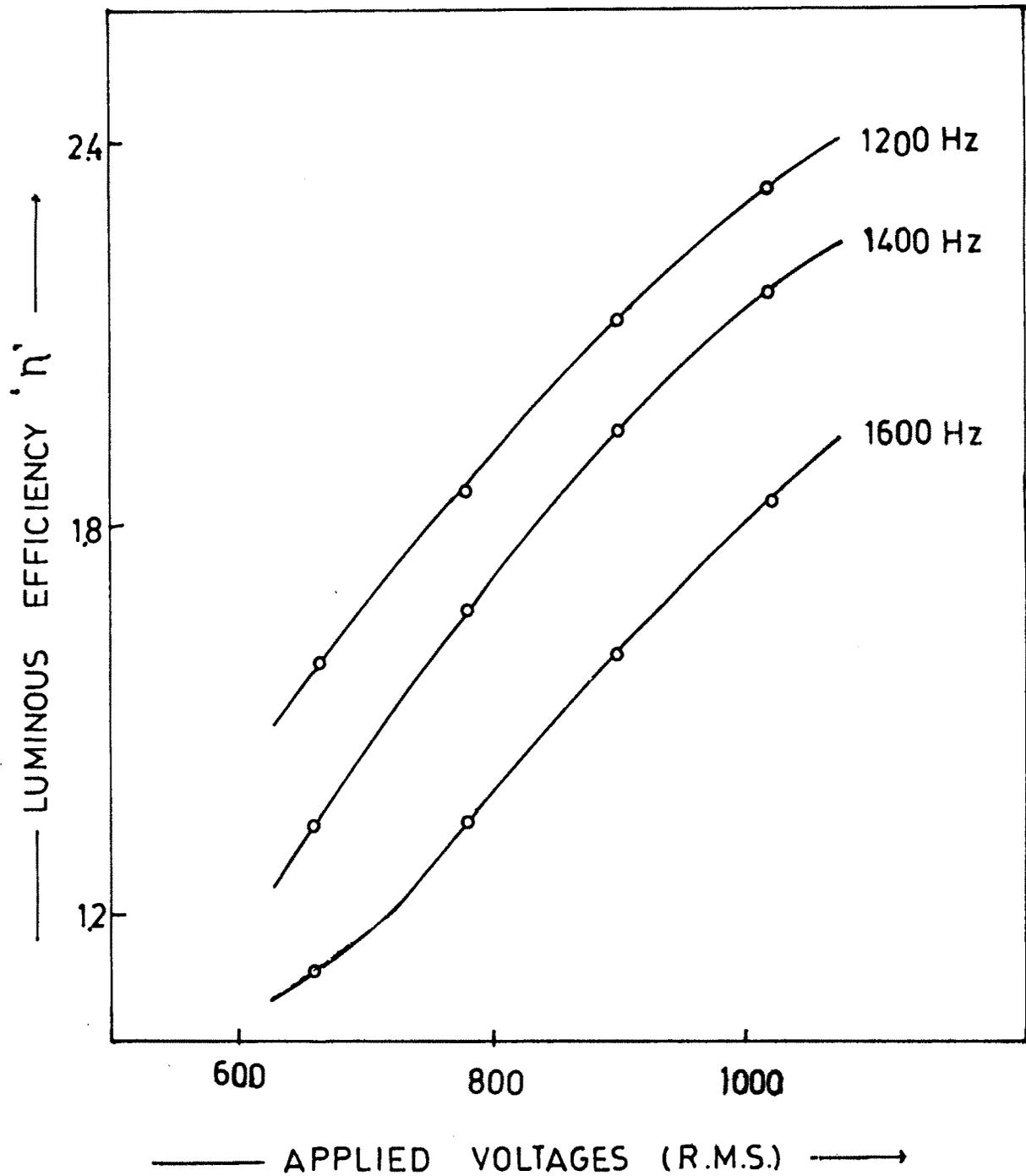OF   LUMINOUS   EFFICIENCY   FOR   ZINC
AND   CADMIUM   OXINATE .

FIG · 35 VOLTAGE AND FREQUENCY DEPENDENCE OF

LUMINOUS EFFICIENCY FOR ALUMINIUM

OXINATE .

where a,b and K_0'' are constants.

For the calculations of luminous efficiency the values of constants, 'a' and 'b' are obtained from the plots of Log B Vs $\bar{V}^{-1}$. The value of K_0'' was taken to be unity. However, since the El. intensity 'B' was measured in arbitrary units, the values of 'η' are also in arbitrary units. The values of 'η' obtained at various voltages and frequencies are plotted in Fig.Nos. 33,34 and 35.

VOLTAGE AND FREQUENCY DEPENDENCE OF 'η'

In general, the dependence of luminous efficiency on the applied voltage is qualitatively the same for all frequencies and for all types of metal oxinates. The brightness increases with increasing voltage upto the highest applied voltages. However, the efficiency is very low in the region of low voltages, due to very low brightness B. With increasing applied voltage, the efficiency increases due to the rapidly increasing brightness, and seems to be saturate at moderate voltages. This behaviour of El.is quite contrary to that of other light sources (electric bulbs, incandescent filament lamps, fluorescent tubes,etc.);since, in them, high brightness and high efficiency do not appear simultaneously. This very behaviour of El. lamps facilitates practical applications, since it is not necessary to increase the voltage upto the breakdown point, in order to obtain highest efficiency. Instead,it should be nearly half the breakdown voltage.

* * * * *