

CHAPTER - IV

- A) VOLTAGE AND FREQUENCY DEPENDENCE  
OF EL. EMISSION;
- B) LUMINOUS EFFICIENCY

A. VOLTAGE AND FREQUENCY DEPENDENCE OF EL. EMITTANCE :

As discussed in Chapter - I, section ( 1:2:1-d), it is seen 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 ' $\eta$ ' is also a function of the applied voltage and frequency. Hence, the study of voltage and frequency dependence of EL. emittance 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 electroluminescent emission intensity 'B' of some organic compounds and powdered phosphors has been measured over wide ranges of the sinusoidal voltage, 'V' and the excitation frequency in Hzs. In the present work, the El. cell model as described in detail, in Chapter - II, Section 2:3-a, was used without any binder or dielectric. The material in the El. cell was excited by sinusoidal voltages upto 1000 V ( r.m.s. )

and with frequencies 700 - 2500 Hz. It is obvious that simultaneous excitation of a material with very high applied voltage and high frequency is impracti<sup>c</sup>able on account of high impedance and excessive 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 pure organic compounds like pyrene, anthracene, perylene and two phase organic systems, like anthracene doped by pyrene and pyrene doped by perylene, at different doping concentrations at room temperature ( 300 k ) have been studied. The spectral energy distribution ( S.E.D. ) of El. emission of these materials was also studied at selected applied voltages and frequencies.

### RESULTS

#### I) Voltage dependence of EL. emission :

Experimental results on intensity measurements as a function of applied voltages have been presented in various Table Nos. 14 - 18 and Fig.Nos. 15,19,23,25,29. In general, it is observed that the characteristics of radiations emitted by cells containing organic materials were similar with the cells containing inorganic phosphors with the exceptions that higher

Table No.14 : Voltage and frequency dependence of El. emission of pure anthracene  
 (  $\lambda_{\text{max}} = 4750 \text{ \AA}$  ).

Applied voltage volts.	El. intensity 'B'(A.U.)			
	700	1000	1500	2000
200	0.01	0.02	0.03	0.06
300	0.03	0.12	0.06	0.28
400	0.05	0.20	0.10	0.41
500	0.12	0.28	0.21	0.57
600	0.16	0.34	0.42	0.71
700	0.20	0.39	0.58	0.82
800	--	0.42	0.70	0.90
900	--	0.45	0.82	0.94
1000	--	0.48	0.88	0.95
				2200
				0.08
				0.42
				0.65
				0.94
				1.06
				1.15
				1.23
				1.29
				--

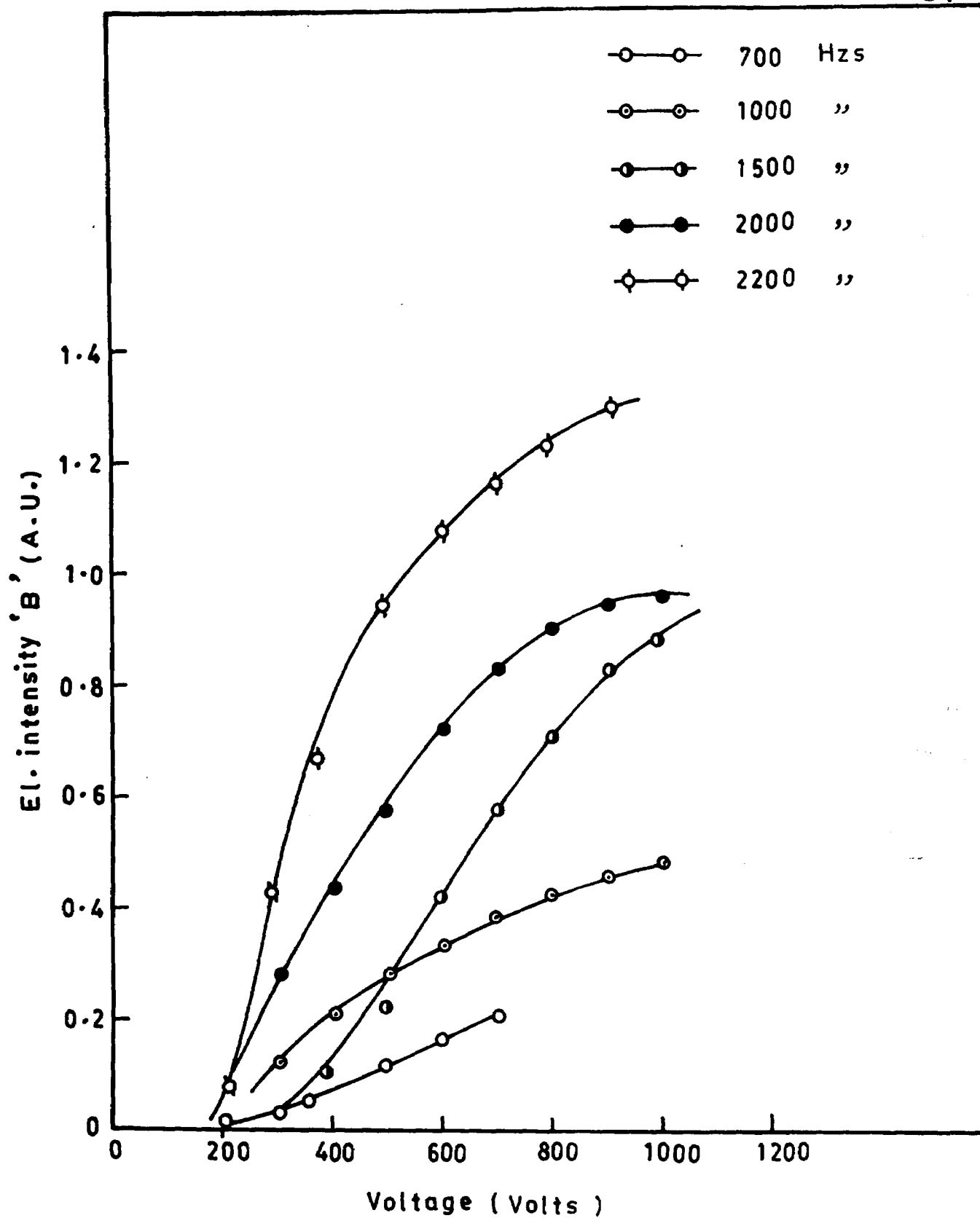


Fig. 15 — VOLTAGE DEPENDENCE OF EL. EMISSION FOR PURE ANTHRACENE AT DIFFERENT FREQUENCIES .

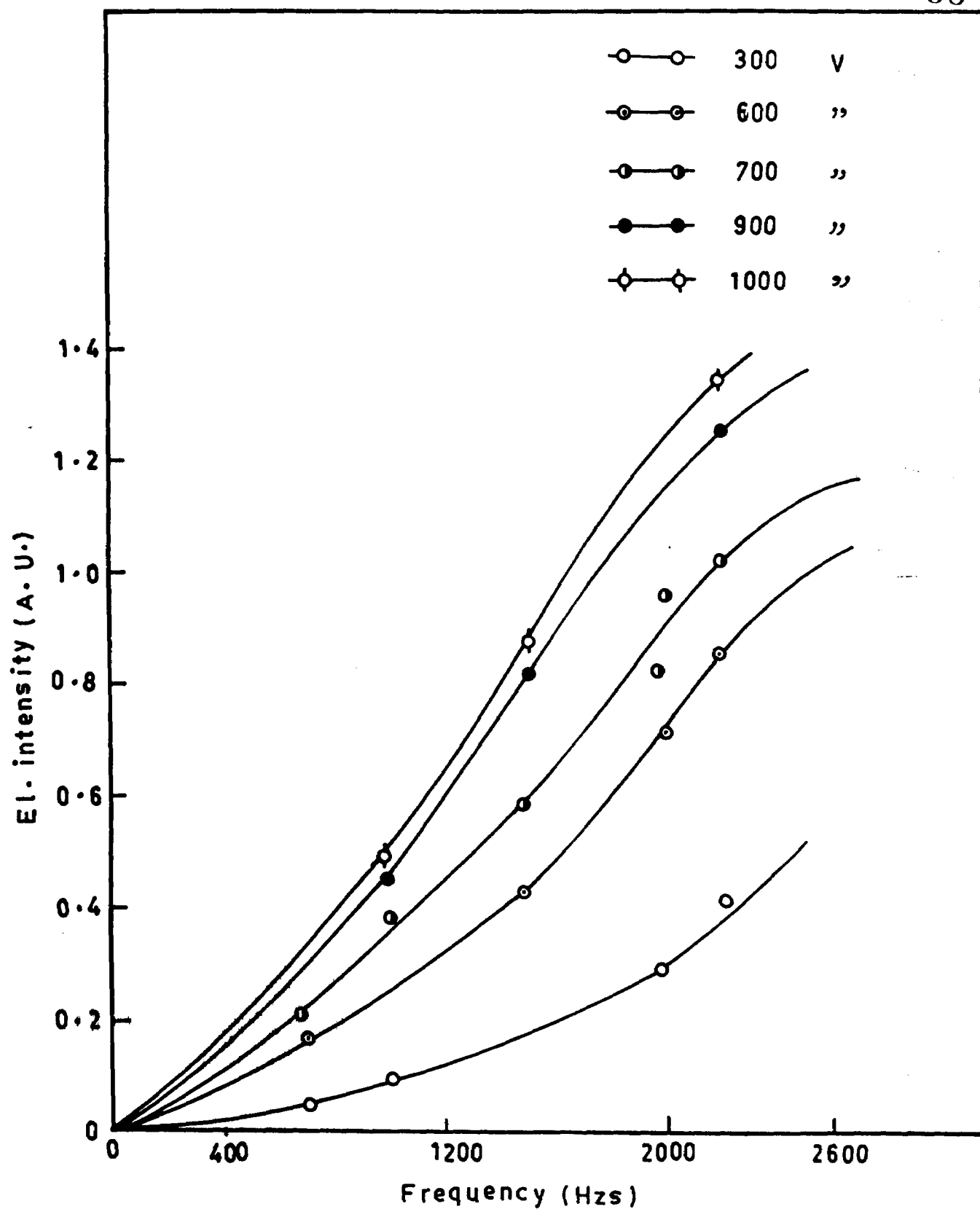


Fig. 16 — FREQUENCY DEPENDENCE OF EL. EMISSION FOR A BLUE EMITTING PURE ANTHRACENE AT DIFFERENT VOLTAGES .

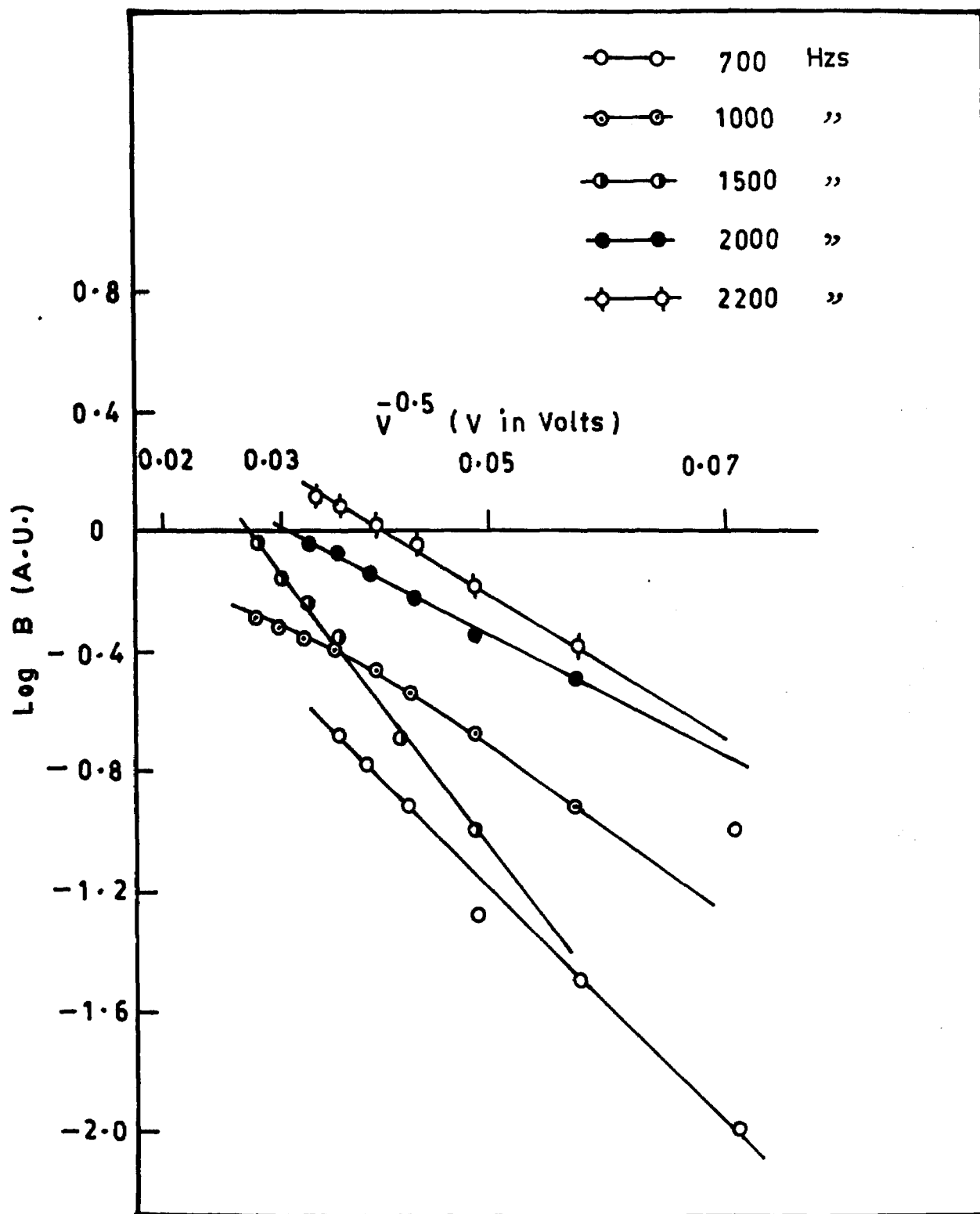


Fig.17 — DEPENDENCE OF Log B AS A FUNCTION OF  $V^{-0.5}$   
FOR VARIOUS FREQUENCIES BLUE EL. ANTHRACENE.

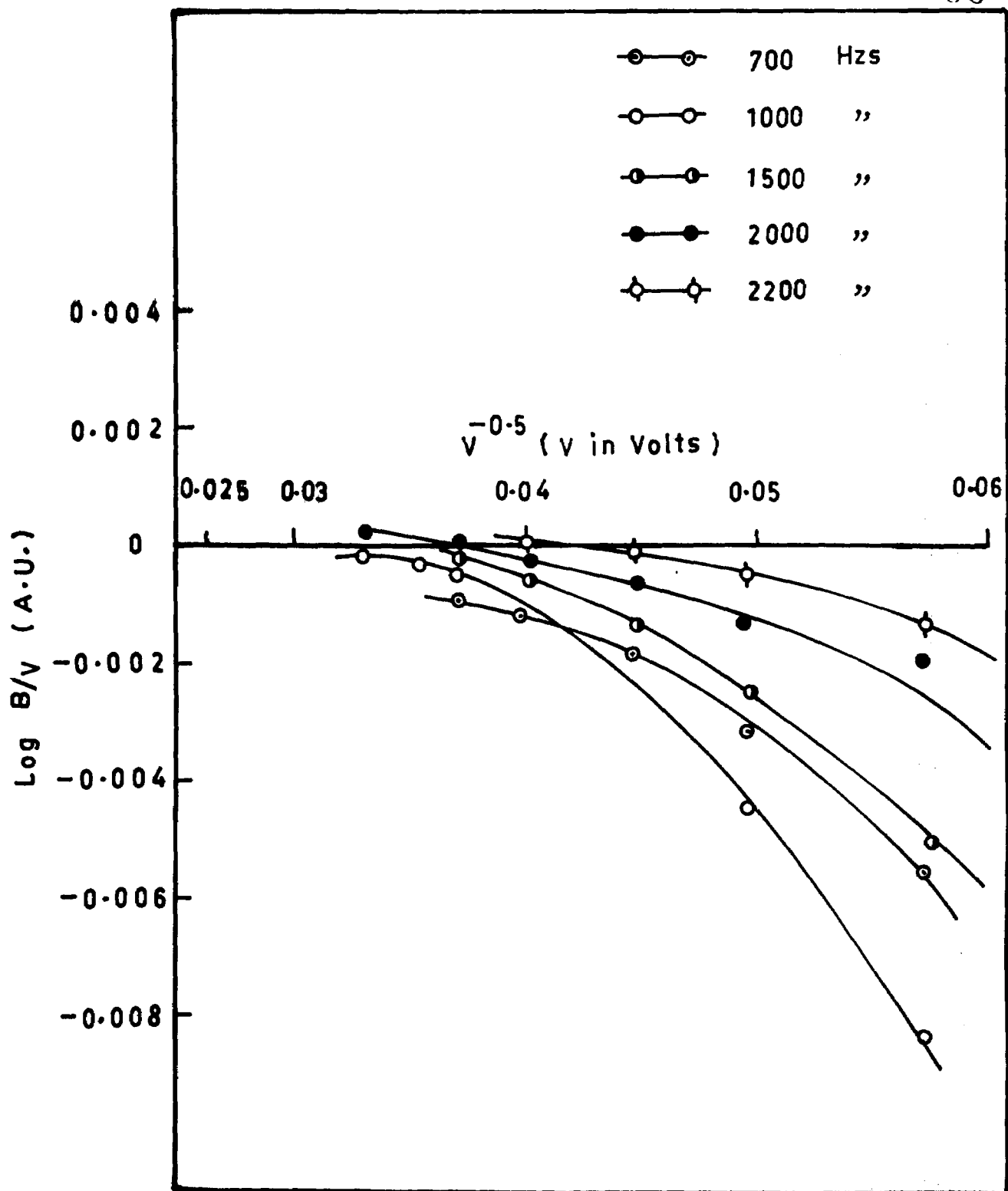


Fig. 18 — DEPENDENCE OF  $\text{Log } B/V$  AS A FUNCTION OF  $V^{-0.5}$  FOR VARIOUS FREQUENCIES [BLUE EL. OF PURE-ANTHRACENE] .



Table No.15 : Voltage and frequency dependence of El.emission of pure pyrene  
 (  $\lambda_{\text{max}} = 5100 \text{ \AA}$  )

Applied voltage volts.	El.intensity 'B' (A.U.)				
	1000	1500	1700	2000	3000
	Applied frequency (Hz)				
300	-	0.20	0.50	1.00	2.40
400	0.10	0.40	1.00	1.90	3.50
500	0.20	0.60	1.40	2.90	5.30
600	0.25	0.90	2.00	3.80	7.30
700	0.30	1.00	2.20	4.60	9.60
800	0.40	1.10	2.90	5.60	11.60
900	0.50	1.40	3.50	6.10	12.00
1000	-	-	3.90	6.50	12.10

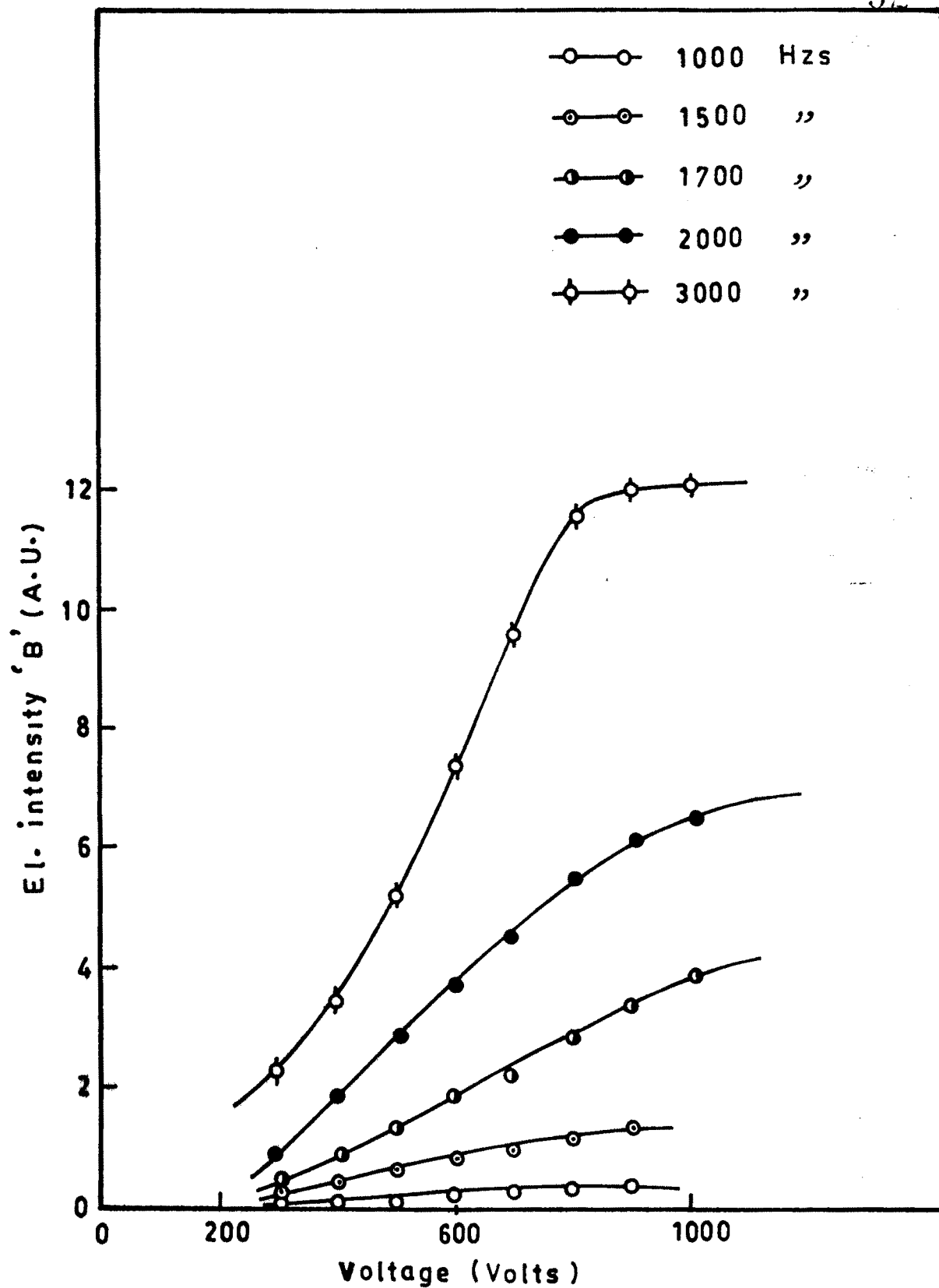


Fig. 19 — VOLTAGE DEPENDENCE OF EL-EMISSION FOR PURE PYRENE AT DIFFERENT FREQUENCIES.

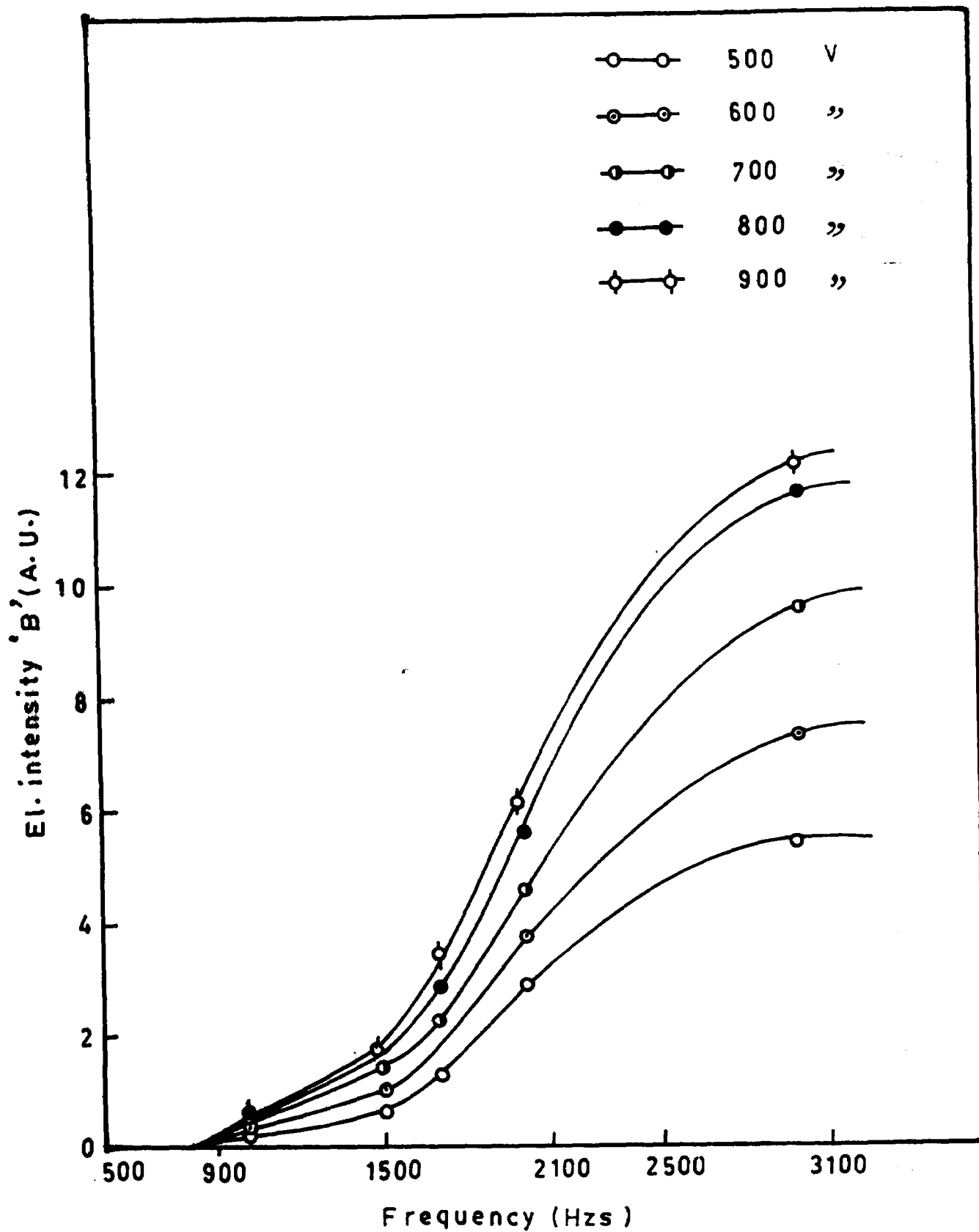


Fig.20 — FREQUENCY DEPENDENCE OF EL EMISSION FOR PURE PYRENE AT DIFFERENT VOLTAGES.

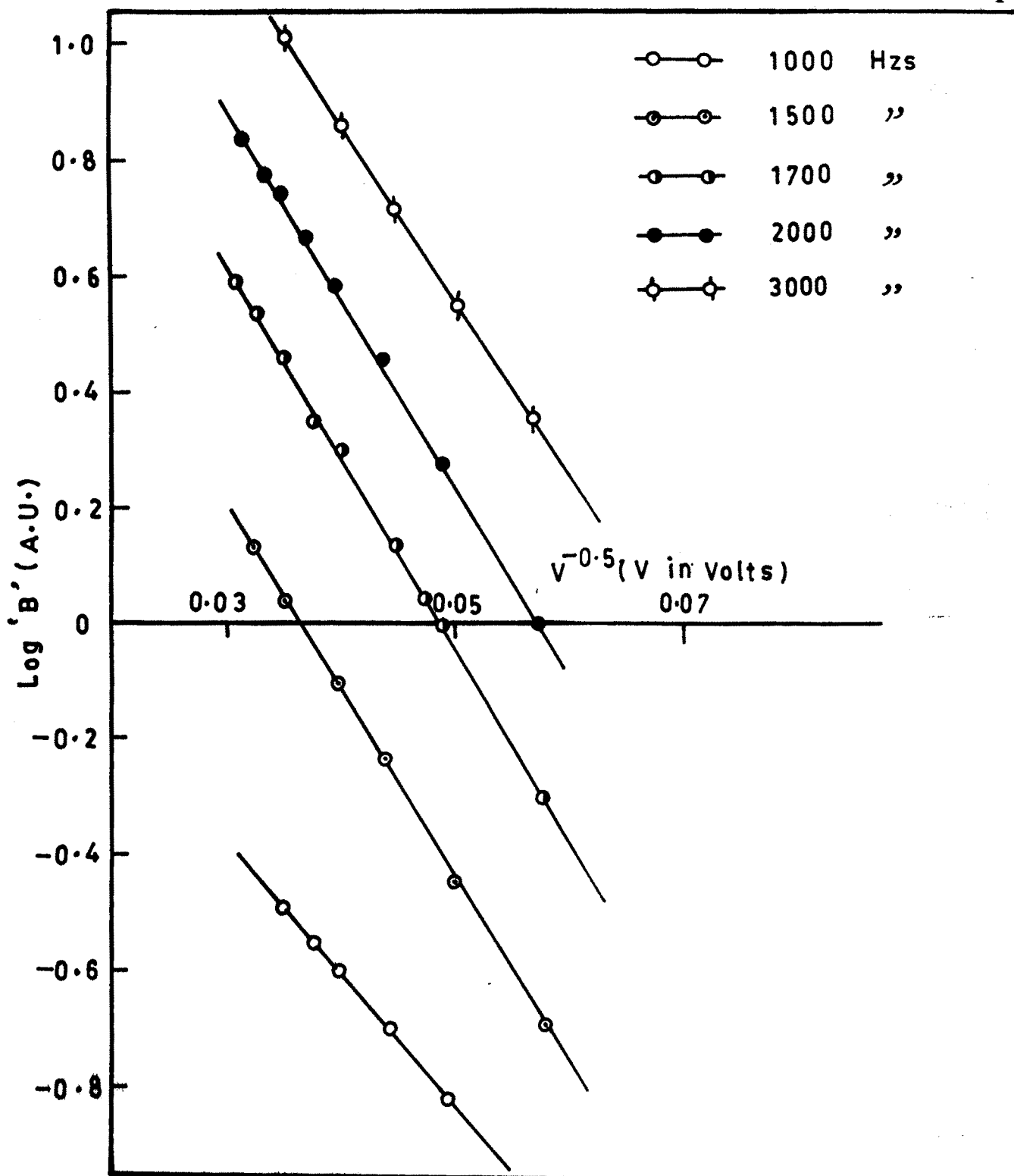


Fig. 21 — DEPENDENCE OF LOG 'B' AS A FUNCTION OF  $V^{-0.5}$  FOR VARIOUS FREQUENCIES. (PURE PYRENE)

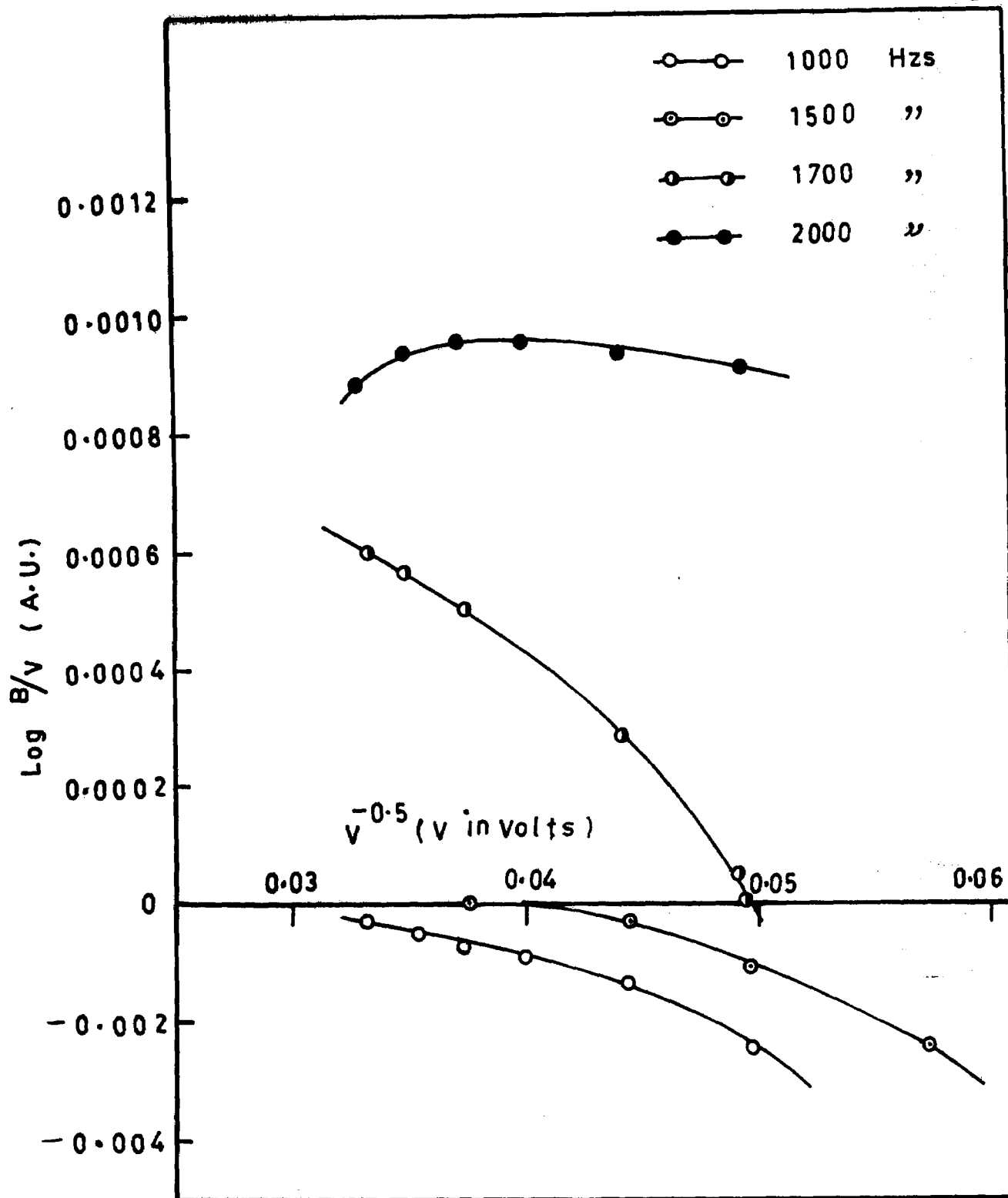


Fig.22 — DEPENDENCE OF  $\text{LOG } B/V$  AS A FUNCTION OF  $V^{-0.5}$  FOR VARIOUS FREQUENCIES [BLUISH-GREEN EL. OF PYRENE]

Table No.16: Voltage dependence of El. emission of Anthracene (ACN) at different concentrations of pyrene (Py.) as dopant

Voltage applied in volts	El. intensity 'B'(A.U.)					
	10 <sup>-2</sup> mole py. per mole ACN		5x10 <sup>-2</sup> mole py. per mole ACN		10 <sup>-1</sup> mole py. per mole ACN	
	800 Hzs	1500 Hzs	800 Hzs	1500 Hzs	800 Hzs	1500 Hzs
300	0.02	0.06	0.01	0.03	0.01	0.04
400	0.05	0.10	0.03	0.08	0.02	0.07
500	0.07	0.16	0.06	0.13	0.04	0.12
600	0.10	0.22	0.08	0.18	0.05	0.16
700	0.12	0.30	0.10	0.25	0.06	0.21
800	0.13	0.60	0.11	0.35	0.08	0.27
900	0.14	0.70	0.12	0.45	0.09	0.32

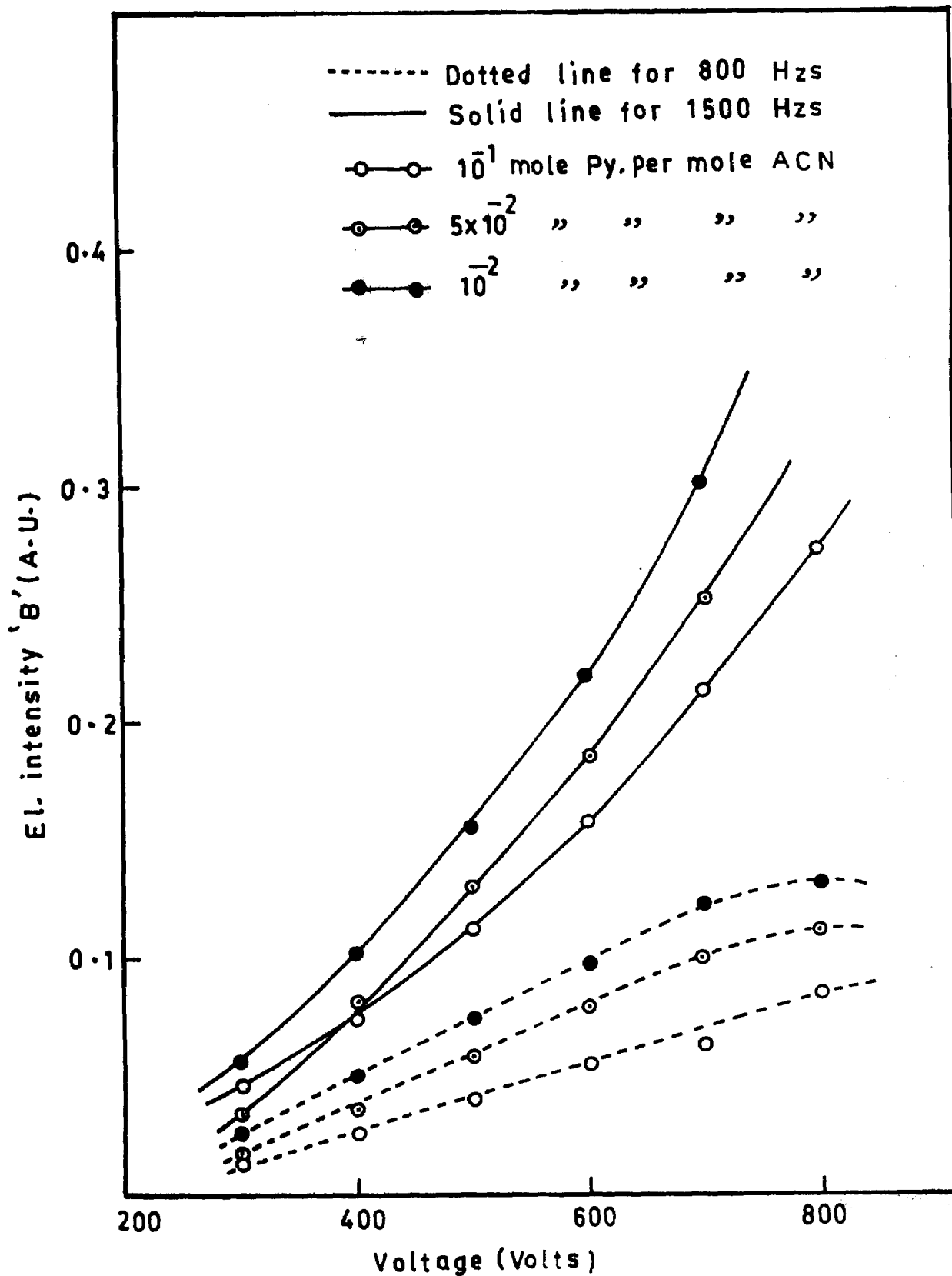


Fig. 23 — VOLTAGE DEPENDENCE OF EL. EMISSION OF ANTHRACENE AT DIFFERENT CONCENTRATIONS OF PYRENE AS A DOPANT.

Table No.17: Voltage and frequency dependence of El. emission of pure perylene  
 (  $\lambda_{\text{max}} = 5400 \text{ \AA}$  ).

Applied Voltage volts.	El. intensity 'B' (A.U.)			
	1000	1500	2000	2300
300	-	0.04	0.15	0.28
400	0.01	0.10	0.27	0.38
500	0.06	0.17	0.33	0.52
600	0.10	0.26	0.55	0.71
700	0.17	0.34	0.67	1.00
800	0.22	0.44	0.77	1.22
900	-	0.52	0.82	1.25
1000	-	0.59	0.84	1.27



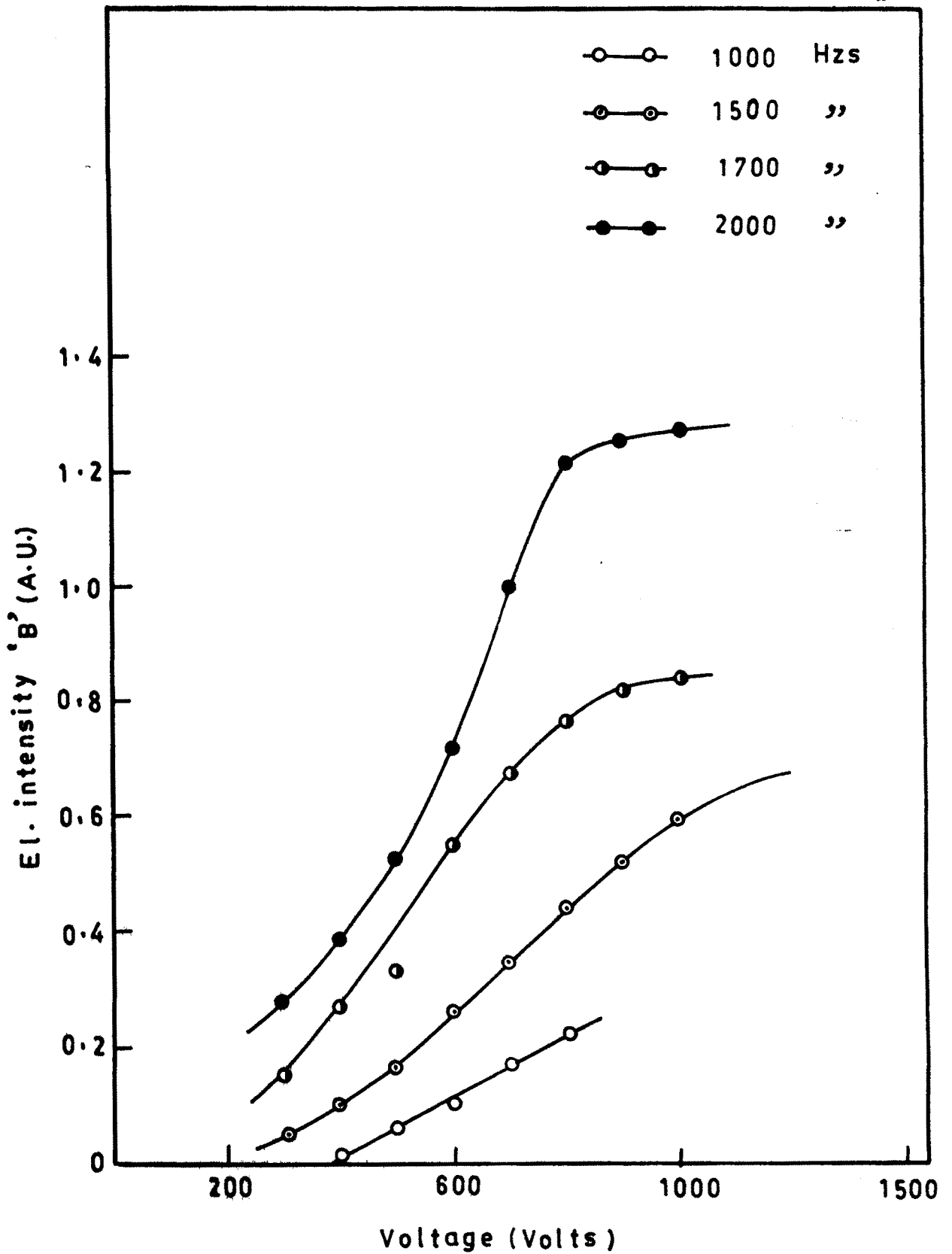


Fig. 25—VOLTAGE DEPENDENCE OF EL-EMISSION FOR PURE PERYLENE AT DIFFERENT FREQUENCIES.

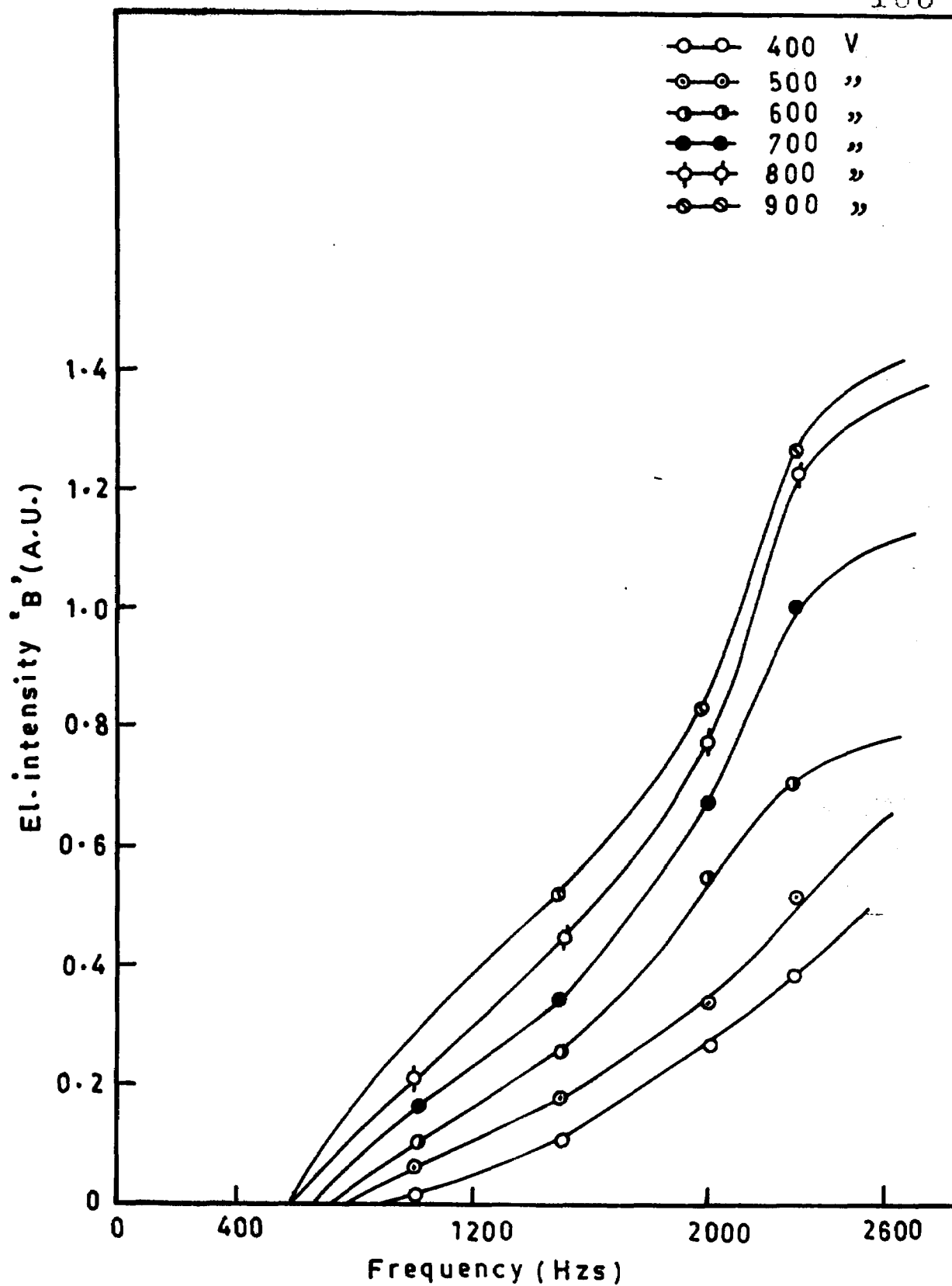


Fig. 26 — FREQUENCY DEPENDENCE OF EL. EMISSION FOR A PURE PERYLENE AT DIFFERENT VOLTAGES .

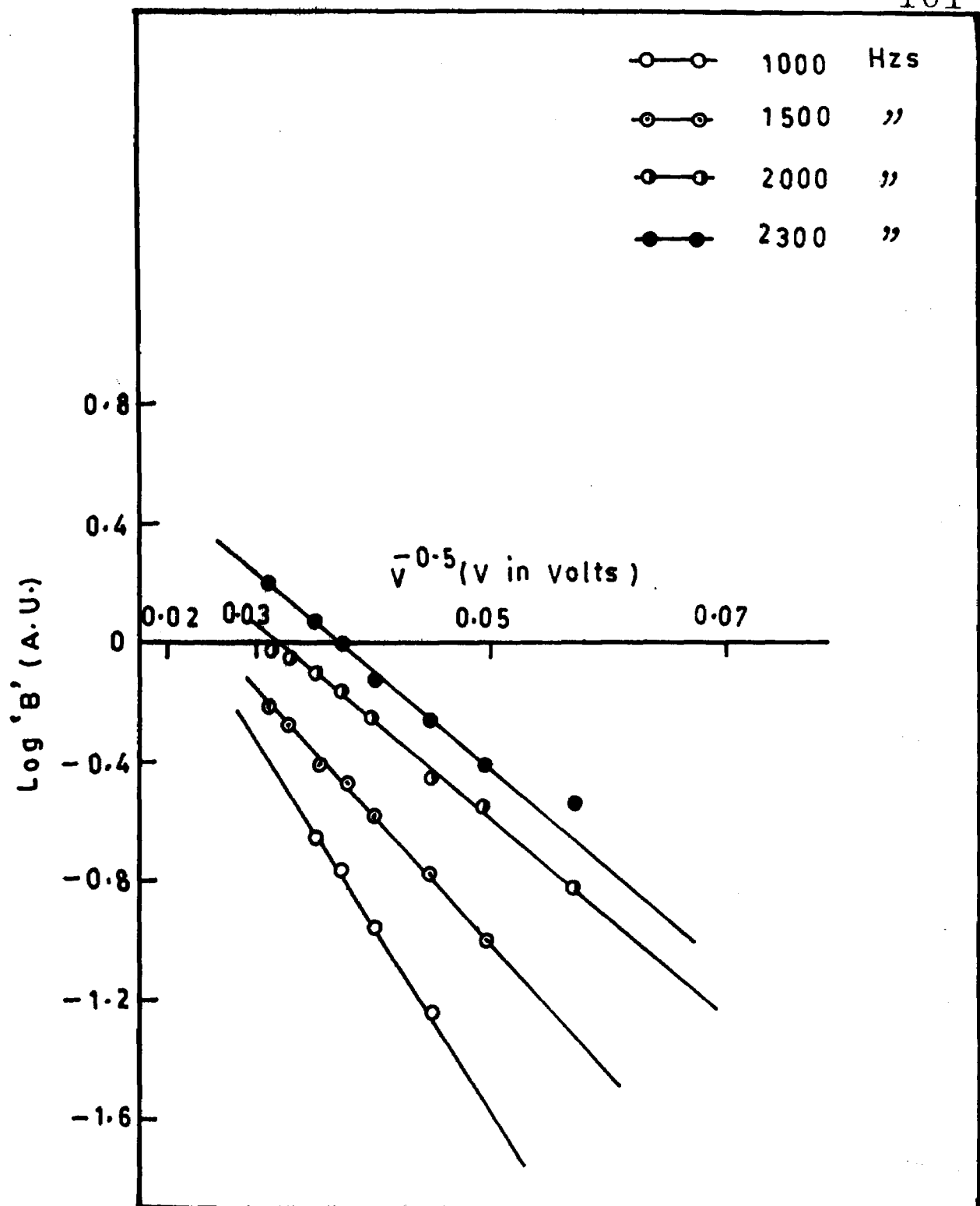


Fig. 27— DEPENDENCE OF LOG B AS A FUNCTION OF  $V^{-0.5}$  FOR VARIOUS FREQUENCIES. [PURE PERYLENE].

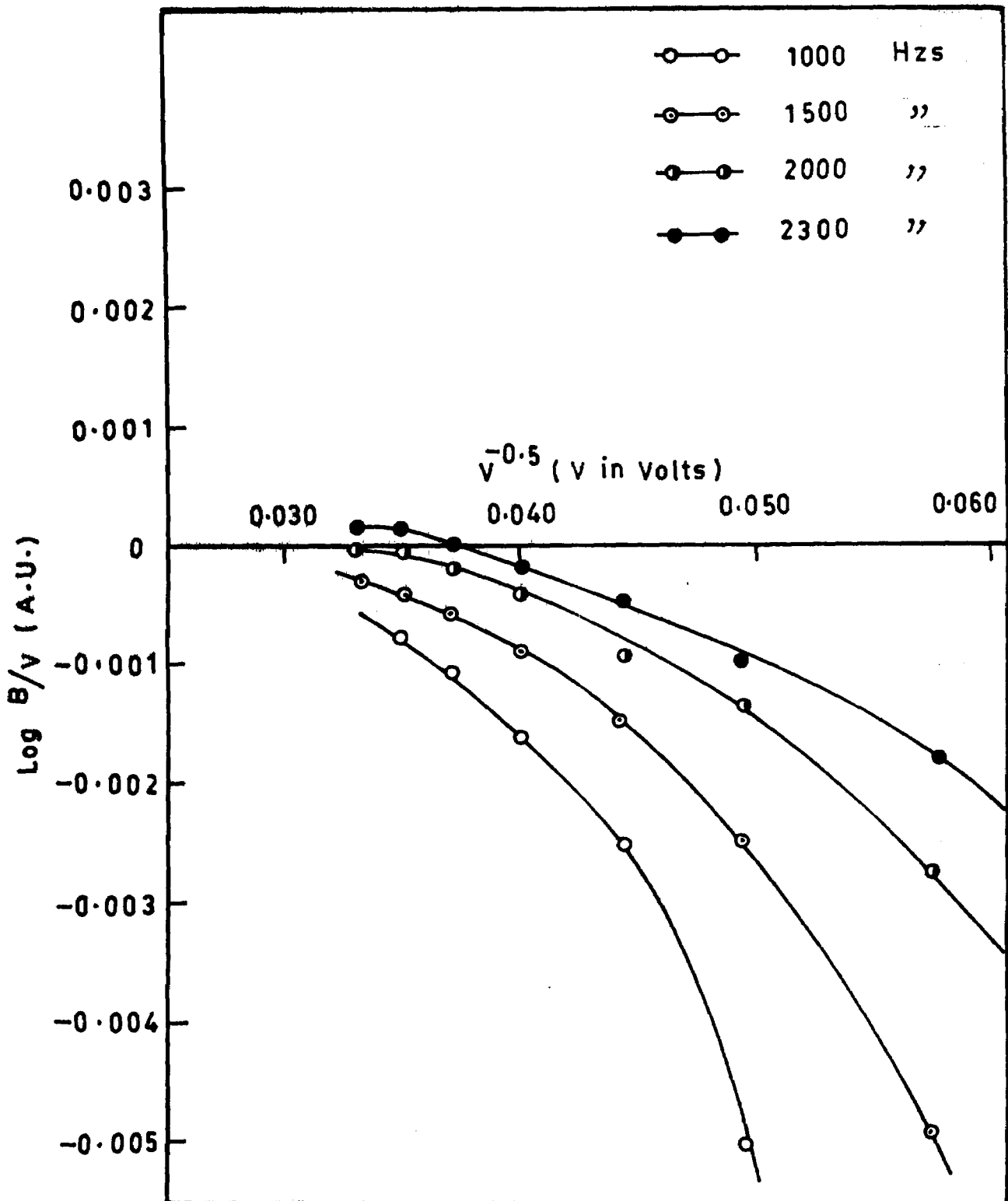


Fig. 28 — DEPENDENCE OF  $\text{LOG } B/V$  AS A FUNCTION OF  $V^{-0.5}$  FOR VARIOUS FREQUENCIES. [YELLOW EL. OF PURE PERYLENE].

Table No. 18: Voltage dependence of El. emission of pyrene (Py) at different concentrations of perylene as dopant

Voltage applied in volts	El. intensity 'B'(A.U.)					
	10 <sup>-2</sup> mole perylene per mole py.		5x10 <sup>-2</sup> mole perylene per mole py.		10 <sup>-1</sup> mole perylene per mole py.	
	800 Hzs	1500 Hzs	800 Hzs	1500 Hzs	800 Hzs	1500 Hzs
300	0.10	0.15	0.05	0.05	0.02	0.03
400	0.15	0.30	0.08	0.15	0.04	0.08
500	0.20	0.80	0.13	0.37	0.06	0.25
600	0.26	1.50	0.15	0.80	0.07	0.45
700	0.32	1.80	0.19	1.21	0.08	0.70
800	0.35	2.10	0.23	1.50	0.10	1.00
900	0.40	3.00	0.24	1.80	0.12	1.25

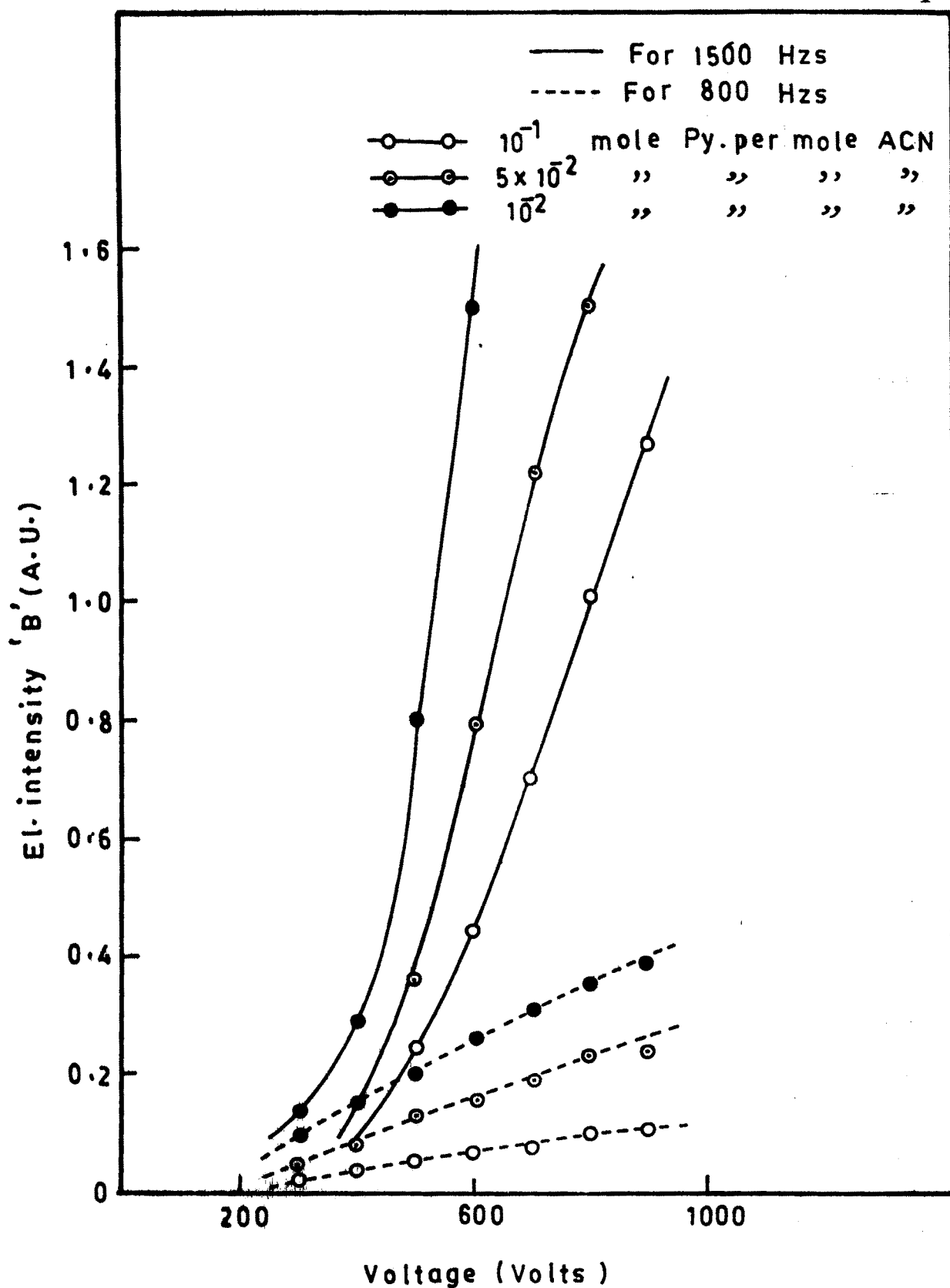


Fig. 29 — VOLTAGE DEPENDENCE OF EL. EMISSION OF PYRENE AT DIFFERENT CONCENTRATIONS OF PERYLENE AS DOPANT .

Table No.19: Frequency dependence of El. emission of Anthracene (ACN )at different concentration of pyrene (Py)as dopant.

Frequency in Hz	El.intensity 'B'(A.U.)					
	10 <sup>-2</sup> mole py. per mole ACN		5x10 <sup>-2</sup> mole py. per mole ACN		10 <sup>-1</sup> mole py. per mole ACN	
	500 V	900 V	500 V	900 V	500 V	900 V
800	0.19	0.80	0.10	0.58	0.02	0.40
1000	0.60	1.40	0.48	1.04	0.28	0.85
1200	0.90	2.00	0.70	1.60	0.54	1.30
1400	1.80	2.50	0.82	2.10	0.68	1.73
1600	1.20	2.80	1.00	2.44	0.78	2.10
1800	1.28	3.00	1.80	2.60	0.88	2.32

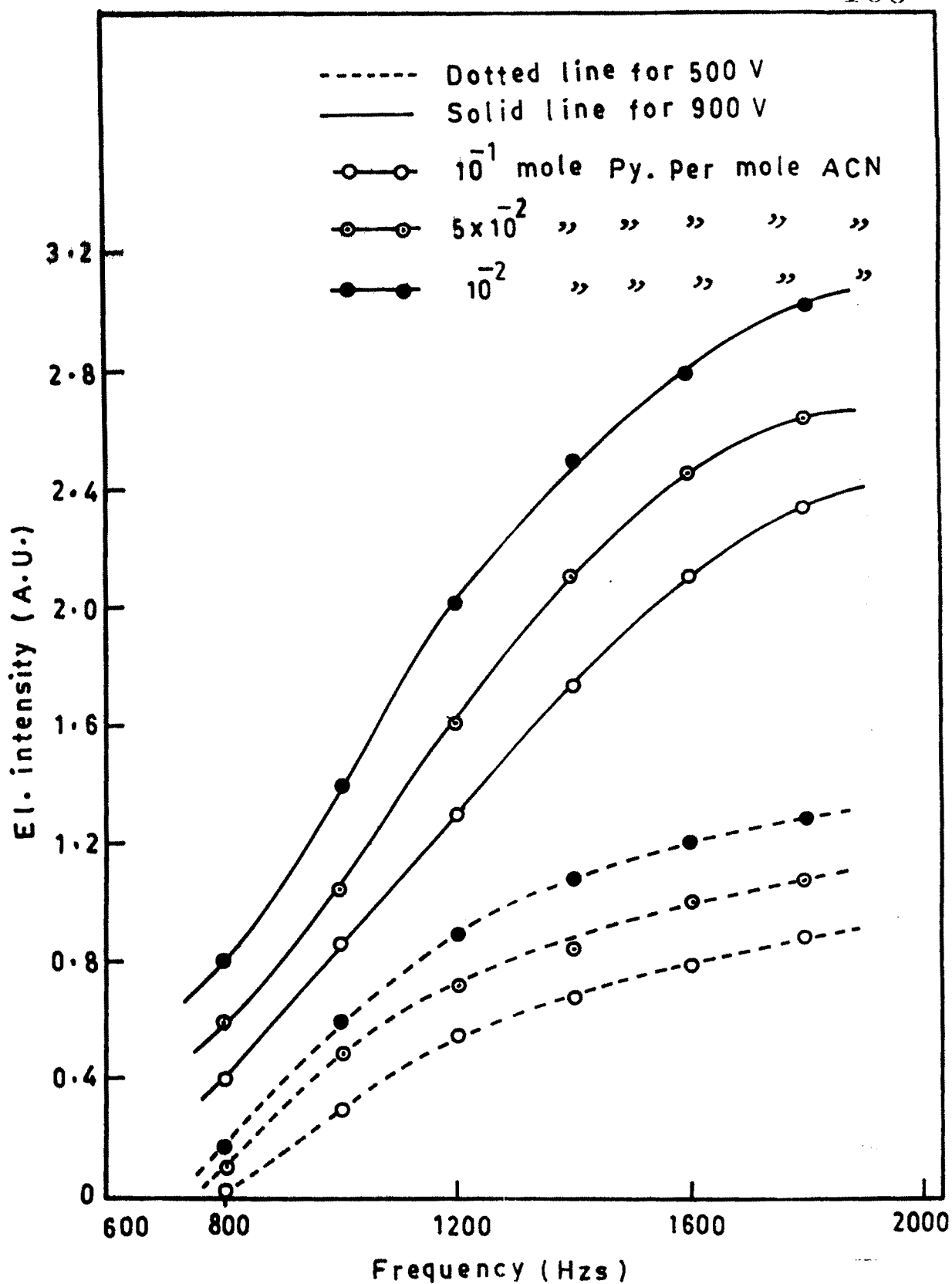


Fig. 24 — FREQUENCY DEPENDENCE OF EL. EMISSION OF ANTHRACENE AT DIFFERENT CONCENTRATIONS OF PYRENE AS DOPANT .



Table No. 20 : Frequency dependence of El. emission of pyrene (Py) at different concentrations of perylene as dopant.

Frequency in Hzs	El. intensity 'B'(A.U.)					
	10 <sup>-2</sup> mole % per mole py.		5x10 <sup>-2</sup> mole perylene per mole py.			
	500 V	900 V	500 V	900 V		
800	-	0.05	-	0.04	-	0.03
1000	0.03	0.09	0.02	0.07	0.01	0.05
1200	0.06	0.13	0.04	0.10	0.02	0.08
1400	0.07	0.18	0.06	0.15	0.05	0.12
1600	0.08	0.25	0.07	0.22	0.06	0.17
1800	0.10	0.32	0.07	0.27	0.07	0.23
2000	0.12	0.33	0.07	0.28	0.07	0.27

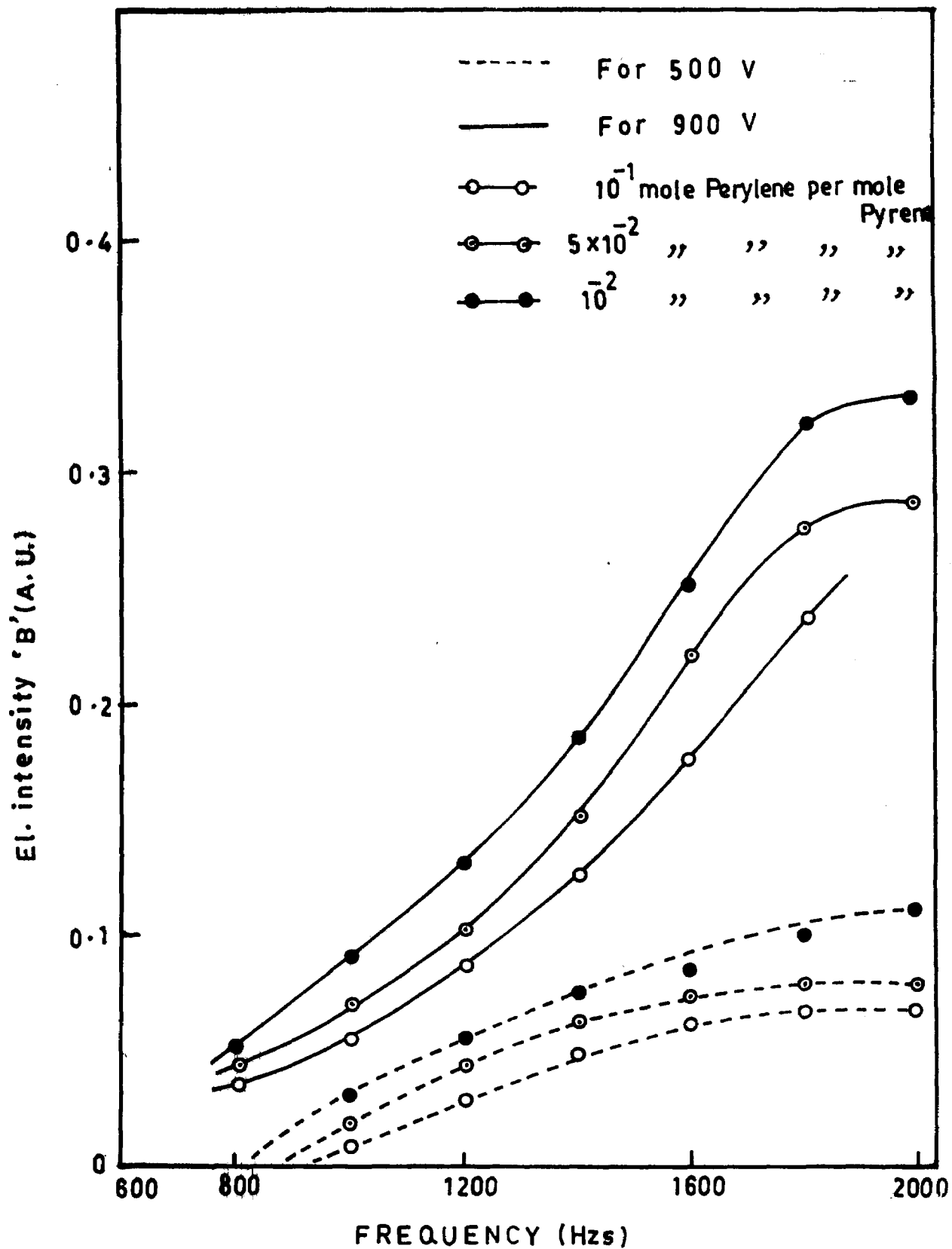


Fig. 30 — FREQUENCY DEPENDENCE OF EL EMISSION OF PYRENE AT DIFFERENT CONCENTRATIONS OF PERYLENE AS DOPANT.

voltages were needed to stimulate emission. It is invariably observed, that for a constant higher values of frequency (  $> 1000$  Hzs ) 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. However, for a constant smaller frequencies (  $\leq 1000$  Hzs ) the brightness ( B ) increases linearly with increasing applied voltages. The results obtained on anthracene are in very good agreement with previous workers<sup>13,86</sup>.

Several equations for voltage dependence of EL. brightness 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 without any claim to a theoretical background. In order to decide the exact nature of the B-V relationship, the two equations were tested, namely.

$$B = a \cdot \exp \left[ \frac{-b}{\sqrt{V^{0.5}}} \right] \quad \dots ( 1 )$$

and

$$B = a \cdot V \cdot \exp \left[ \frac{-b}{\sqrt{V^{0.5}}} \right] \quad \dots ( 2 )$$

where 'a' and 'b' are constants.

The equation ( 1 ) describes the variation of B with V when B approaches a definite value with infinite voltage.

W. Lehmann<sup>18-d</sup> has shown that this equation is identical with the following equation, given by Ivey<sup>51</sup>,

$$B = a. \exp \left[ \frac{-b}{V-V_0} \right] \quad .. \quad ( 3 )$$

The equation ( 3 ) describes the variation of B with V when B becomes infinite for infinite voltages. Thus, equation ( 1 ) is a saturation equation while ( 2 ) is an unsaturation equation. Here attempts has been made to verify the validity of both these equations, Fig.Nos.16,22 and 28, show the plots of log B/v against  $v^{-0.5}$ ; while Fig.No.17,21 and 27, represent the plots of log B against  $v^{-0.5}$  for anthracene, pyrene and perylene respectively.

It is seen that the plots of log B/V Vs  $v^{-0.5}$  are not linear for various frequencies studied, the values of log B/v falling short of those expected from linear behaviour. However, the plots of log B against  $v^{-0.5}$  are straight lines over the range of voltages ( 300-1000V ) and frequencies ( 700-2500 Hzs ).

It is seen from the plots of log B Vs  $v^{-0.5}$  that the values of constants 'a' ( intercept ) and 'b' ( slope ) are slightly frequency dependent, thus confirming the validity of equation (1) i.e.

$$B = a. \exp \left[ \frac{-b}{v^{0.5}} \right]$$

At smaller values of frequencies, the relation (1) fails and the EL. brightness increases linearly in accordance with the relation given by Maxia et. al.<sup>87</sup>, i.e.,

$$B = \sqrt{V} \quad \dots (4)$$

where ' $\sqrt{V}$ ' is a parameter which depends on the frequency.

For anthracene-pyrene and pyrene-perylene systems, the variation in the EL. brightness with voltage, 'V' for various frequencies and dopant concentrations are shown in Fig. Nos.23 and 29 respectively. At higher dopant concentrations enhanced quenching effect was observed. Thus, light out put is strongly quenched when anthracene is doped by more than  $10^{-1}$  mole of pyrene per mole and when pyrene is doped by more than  $10^{-1}$  mole of perylene per mole. At higher value of frequency ( $> 1000$  Hz) the relation,

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

holds good, where 'a' and 'b' are constants and 'V' is the voltage applied. At smaller frequencies ( $< 1000$  Hz) this relation fails and a linear variation of brightness with voltage occurs, i.e.

$$B = \sqrt{V}$$

as observed in above organic compounds.

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 the El. process.

The assumption of existence of a 'Mott -Schottky' barrier at the surface of the microcrystalline grain of the El. material gives the equation:

$$B = B_0 \exp \left[ \frac{-b}{V^{0.5}} \right] \quad \dots (5)$$

or

$$B = B_0 \exp \left[ \frac{-b}{V_0 + V} \right] \quad \dots (6)$$

which are identical with equations (1) and (3) <sup>as</sup> above.

Model for a.c. electroluminescence as developed by Bonfiglioli and Brovotto<sup>88</sup> gives a similar relation between B and V.

Since the El. emission of the organic materials and phosphors studied here seems to obey invariably the saturation equation (1) or (5), it seems that either the 'Mott Schottky' barrier mechanism or 'a defective border' mechanism given by Bonfiglioli and Brovatto is prevailing.

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 result 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 microcrystalline, 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. Here, the local field strength is considerably higher than the average electric field. A rectifying exhaustion barrier of the Mott-Schottky type exists at the interface of base matrix conductor. The occurrence of Mott-Schottky exhaustion barrier necessitates that the electrons must be located in the electrode surface adjacent to the barrier, leaving behind the positive space charge in the barrier region.

The positive space charge will induce a negative space charge in the conducting phase adjacent to it, so that the thin layer of conducting phase on the other surface remains an equipotential surface. Due to the positive space charge in the barrier region, the field strength at the localized spot is enhanced and other electrons penetrate the potential barrier or are released from surface donor levels and produce secondaries, enlarging the space charge and so on, thus starting an avalanche, until the voltage drop across such a spot reaches a maximum. Thus, the theory supports the validity of equation.

$$B = a \cdot \exp \left[ \frac{-b}{V^{0.5}} \right]$$

II) Frequency-dependence of El. intensity

As discussed in earlier section the brightness of an electroluminescence is a function not only of the applied alternating voltage but also of the frequency. The experimental results, as shown in Fig. Nos. 16,20,23,26,30 for frequency dependence of El. emittance of various organic materials show that the El. emittance (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. emittance increases linearly with frequency. It is easy to vary the frequency and to hold constant the voltage applied (if not very high ) to the cell. Furthermore, any process of electroluminescence 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-homogeneous 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.

However, an attempt have been made to explain our experimental results on the basis of the phenomenological treatment



of electroluminescent build-up process. There are similarities between this process and build-up of photoluminescence under ultra-violet stimulation. One of the characteristics 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 electroluminescence, 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 then assume that the electroluminescent brightness can be regarded as being due to the instantaneous concentration  $N_L$  of light emitting point sources. After excitation, these sources would decay and, in the simplest case, the decay rate would be  $N_L / \tau_0$  where  $\tau_0$  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  $N - N_L$  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 average 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 ;

$$\frac{dN_L}{dt} = \frac{-N_L}{\tau_0} + \frac{\alpha \omega}{2\pi} (N - N_L) \quad \dots (7)$$

where  $\omega$  is the angular frequency and ' $\alpha$ ' a constant of proportionality which must be presumed to be voltage dependent, though invariant with frequency. The solution under the condition  $N_L = 0$  at  $t = 0$  and  $dN_L/dt = 0$  at  $t = \infty$ , is

$$N_L = N_{L\infty} \left[ 1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad \dots (8)$$

where  $N_{L\infty} = N \left( \frac{\alpha \omega \tau}{2\pi} \right)$  .. (9)

and  $\tau$  is a new effective time constant, given by

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{\alpha \omega}{2\pi} \quad \dots (10)$$

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 conditions can be simply discussed in terms of equations ( 8 ) and ( 10 ) which gives

$$N_{L\infty} = \frac{N}{1 + 2\pi/\omega\tau_0} \quad \dots (11)$$

which at very low frequencies approximate to

$$N_{L\infty} \approx N\omega\tau_0 f \quad \dots (12)$$

'f' being the frequency.  $N_{L\infty}$  may be taken as proportional to the brightness B, thus establishing the initially linear relationship with frequency. The rate at which system saturates at higher frequencies is evidently dependent on  $\tau_0$  and  $\omega$ .

#### B) Luminous Efficiency :

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

$$\eta = \frac{B}{W} \quad \dots (13)$$

Lehmann has given the expression for  $\eta$  as

$$\eta = \frac{B}{W} = \frac{(B/f)}{aV^2K_0'' + b(B/f)^{1/2}} \quad \dots (14)$$

where a, b and  $K_0''$  are constants.

For the calculation of luminous efficiency the values of constants, 'a' and 'b' obtained from the plots of  $\log B$  vs  $V^{-0.5}$

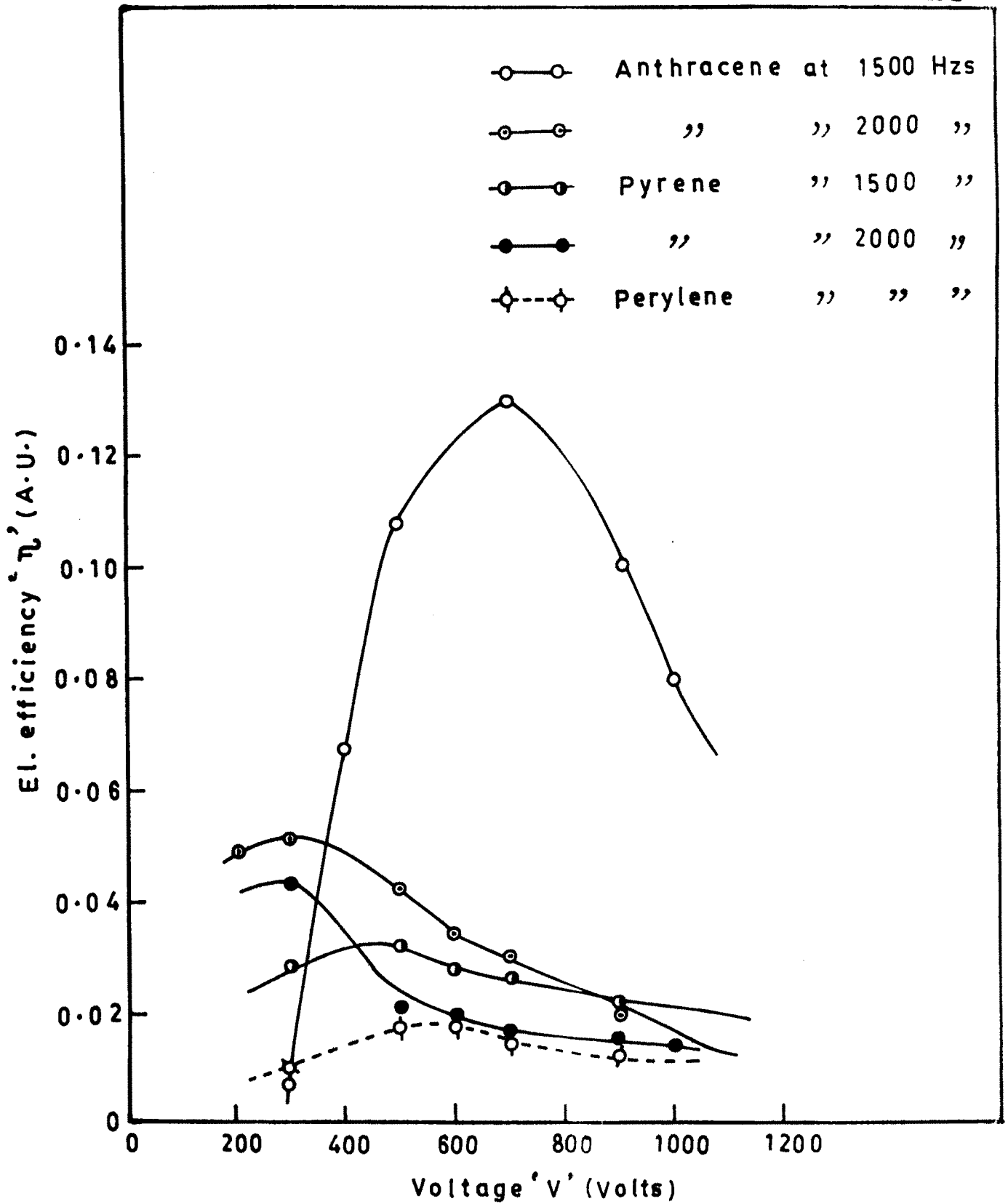


Fig. 31—VOLTAGE DEPENDENCE OF EL. EFFICIENCY OF VARIOUS ORGANIC COMPOUNDS AT VARIOUS FREQUENCIES .

were used. The value of  $K_0''$  was taken to be unity. However, since the El. intensity 'B' was measured in arbitrary units, the values of ' $\eta$ ' are also in arbitrary units. The values of ' $\eta$ ' obtained at various voltages and frequencies are plotted in Fig. No.31.

Voltage dependence of ' $\eta$ ' :

In general, the dependence of luminous efficiency on the applied voltage is quantitatively the same for all frequencies and for all types of materials. Thus, the efficiency is increased with voltage reaches a saturation value and after a broad maximum, decreases slightly. However, the voltage range in which optimum efficiency is obtained seems to be dependent on frequency. Thus, at low frequencies, optimum efficiency is obtained at higher voltages while at higher frequencies, optimum efficiencies are obtained at lower voltages. Similarly, the El. efficiency, also seems to depend upon the frequency. As the frequency is increased, El. efficiency also increases. In the range of frequency between 800-1700 Hzs, the efficiency is maximum and then decreases sharply at still higher frequencies.

Thus, it is seen that for a given organic compound the EL efficiency seems to be optimum at a specific voltage and frequency only.