RESULTS AND DISCUSSION

III RESULTS AND DISCUSSION

III. 1. Chelate polymers of 2,5-dihydroxy-p-benzoquinone :

2,5-Dihydroxy-p-benzoquinone is known to form chelate polymers. Jain and Singhal[258] studied the precipitation of various metal ions by the ligand and suggested that 6-coordinate M(III) and 8-coordinate M(IV) might form cross-linked chelate polymers whereas bivalent cations might form linear chelate polymers. Kanda and coworkers[120,123,240,259] prepared chelate polymers of Cu(II), Ni(II) and Cd(II) and made extensive studies on the copper (II) chelate polymer. Frank and coworkers[247] studied the preparation of a number of its metallic complexes and chelate polymers. Recently Rose, Block and Davis[260] studied the degree of polymerisation of Zn derivatives and Bottei and Fangman[261] studied thermal and spectral properties of Co (II), Ni(II), Cu(II) and Zn(II) chelate polymers of the ligand. The complexes and chelate polymers formed by Co(II), Ni(II), Cu(II) and Fe(II) with the above ligand in presence of amines and the complexes formed by organic bases are included in the present studies.

(i) Co(II) Chelate polymers :

The magnetic moments of Co(II) chelate polymers calculated from magnetic susceptibilities are presented in table -40 and some important IR bands of BQCo B are given in table- 41. Plots of $\log_{10}\rho$ of the chelate polymers vs. reciprocal temperature are given in fig. 21.

Table 40

Magnetic moments of cobalt (II) chelate polymers

No.	Compound	Molar magnetic susceptibility (per Co- atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per Co- atom) $X_m' \times 10^6$	Magnetic moment (per Co- atom) (μ) B.M.
1.	BQCo	10930	11010	5.20
2.	BQCo Py	10640	10760	5.14
3.	BQCo B	11060	11250	5.25
4.	BQCo A	10690	10870	5.19
5.	BQCo B (f)	10640	10790	5.15
6.	BQCo P	9500	9640	4.87

Table 41

Some characteristic IR frequencies (cm^{-1}) of BQCo B

3300 m	1360 s	965 m
3200 m	1288 w	930 m
3100 w	1252 s	838 w
1610 m	1185 w	822 m
1510 vs (b)	1095 w	793 m
1400 m	1015 m	

Table 42

No.	Compound	Energy gap (E ev.)	Resistivity at infinite temperature (ρ_∞ ohm.cm.)
		(a)	
1.	BQCo	0.52	1.11×10^{10}
2.	BQCo B	1.23	8.37×10^{4}
3.	BQCo A	2.50	3.97×10^{-4}
		(b)	
1.	BQCo B	0.94	1.82×10^{5}
2.	BQCo P	1.86	7.14×10^{-1}
3.	BQCo T	2.06	7.31×10^{-2}

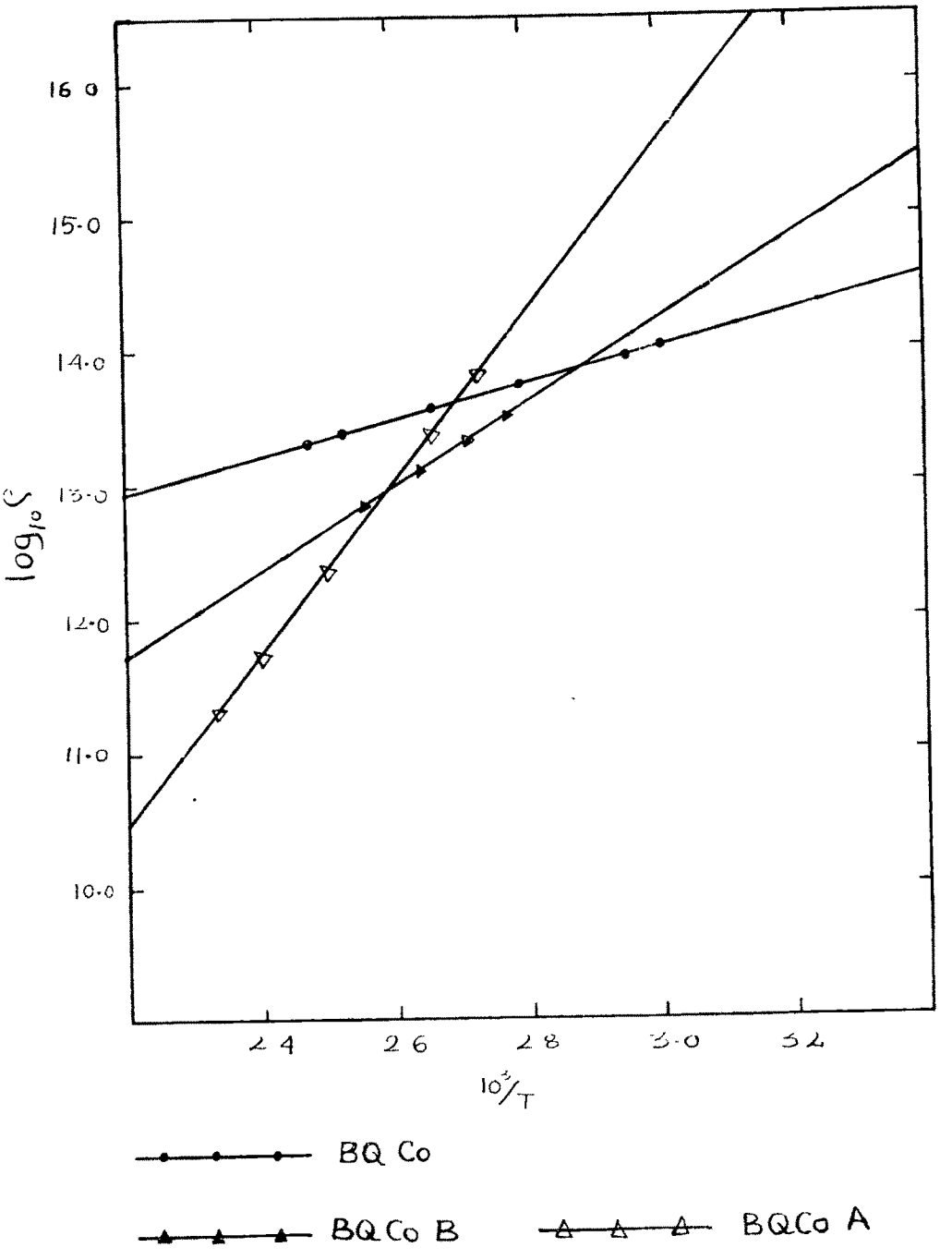
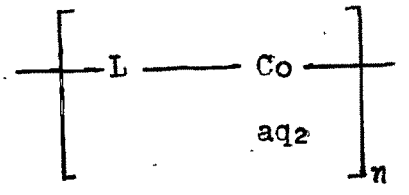


FIG. 21: Log RESISTIVITY vs. $10^3/T$ FOR COBALT CHELATE POLYMERS.

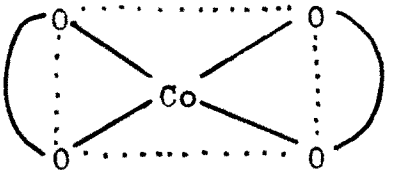
The analysis of BQCo shows that the ratio of metal to ligand is 1 : 1 ; hence the chelate is represented as a linear polymeric chain (1)



(1)

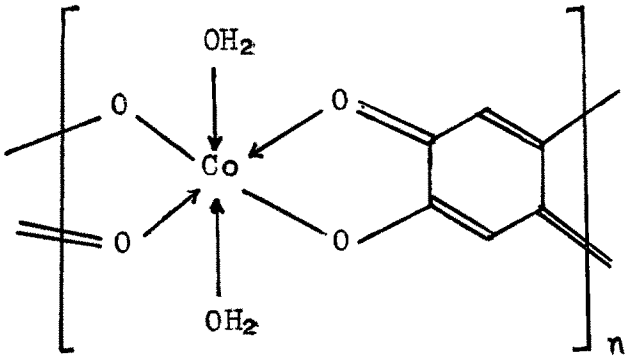
where LH_2 represents 2,5-dihydroxy-p-benzoquinone and aq represents water.

Its magnetic moment per cobalt atom is calculated as 5.20 B.M. The chelate monomer may, therefore, be considered to have an octahedral configuration, with four oxygen atoms of the ligands lying in the same plane with metal atom as in (2).



(2)

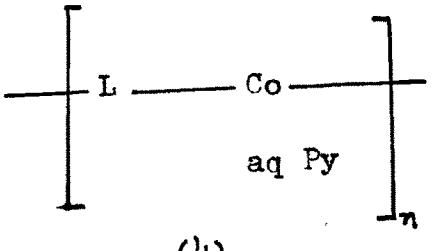
It is suggested that the chelate monomer is a trans octahedral one and be formulated as (3).



(3)

Bottei and Fangman suggested, on the basis of elemental analysis and thermogravimetric investigations, that the cobalt chelate be represented as $Co(C_6H_2O_4)(H_2O)_2$. They also studied IR spectra of the ligand and its Co-chelate. From these studies they concluded that (1) the ligand molecule may possibly be present as an end-group in the polymer, (2) both carbonyl groups of the ligand have functioned as coordinating groups and (3) both phenolic hydrogens are absent in the chelate polymer.

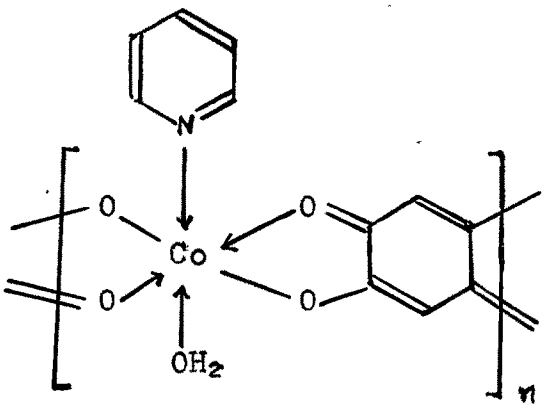
The analysis of the pyridinated complex BQCo Py shows that the ratio of metal to pyridine is 1 : 1. The chelate is, therefore, represented as a linear polymer (4).



(4)

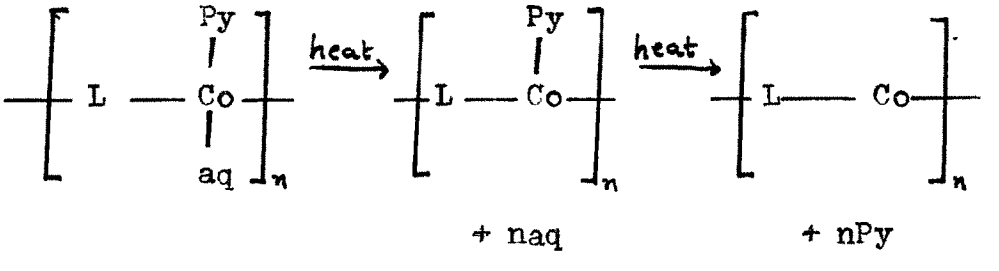
where Py represents pyridine.

The magnetic moment of the chelate polymer per cobalt atom is found to be 5.14 B.M. It indicates octahedral nature of the chelate monomer which may be formulated as a trans octahedral one (5).



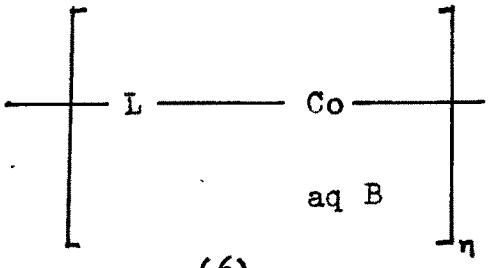
(5)

Its thermal analyses (D.T.A. and T.G.A.) (cf.fig.17) show that the polymer (1) is losing water and pyridine over a temperature range of 150-400°C,(2) melts at 550-60°C and (3) undergoes depolymerisation at 640-50°C. On the basis of D.T.A. it is possible to suggest that loss of water and pyridine molecules is a two-step process ; water is given out first, followed by the evolution of pyridine. The thermal decomposition reactions may be represented as follows :



However, it may be noted that both thermograms indicate high unstability of 5-coordinate Co system and the possible overlap of the two decomposition reactions.

The analysis of the chelate polymer with benzidine shows that the ratio of metal to benzidine is 1 : 1. Hence it is represented as (6)

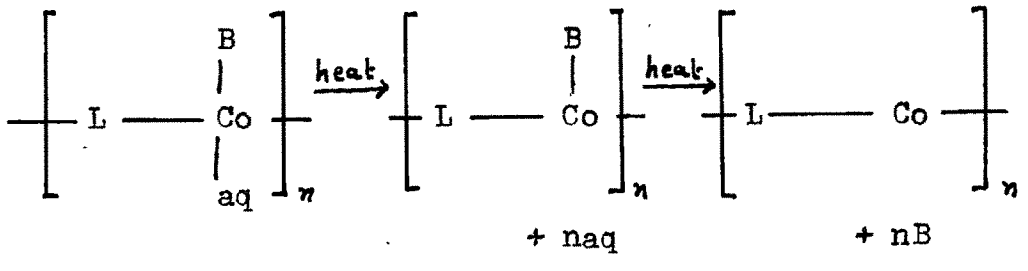


(6)

where B represents benzidine.

Its magnetic moment per cobalt atom is calculated as 5.25 B.M. and the chelate monomer is represented as a trans octahedral one similar to (5).

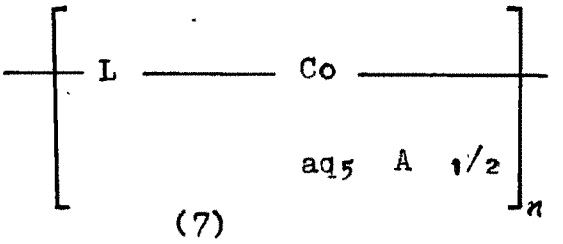
Its thermal analyses (D.T.A. and T.G.A.) (cf. fig. 16) show that the polymer (1) is losing water at 110-220 ^{o}C, (2) is losing benzidine over a wide range of temperature, (3) melts at 550-60 ^{o}C and (4) undergoes depolymerisation at 640-50 ^{o}C. The two step decomposition reactions may be represented as follows :



The results suggest that BQCo Py and BQCo B have the same melting point indicating the formation of the same product after the thermal loss of water and amine. The possibility that benzidine may be forming two coordinate links to cobalt atoms, is not completely eliminated on the basis of these observations. The decision can be reached from IR spectrum. Two bands at 3300 and 3200 cm^{-1} in the IR spectrum of BQCo B suggest the presence of free and coordinated amino groups. It eliminates the possibility of both amino groups being coordinated to cobalt and confirms its structure similar to (5).

The absorption band for chelated carbonyl group, not coordinated to metal is observed at 1610 cm^{-1}, indicating the presence of the ligand as the end molecule of the chain. Further, Bottei and Fangman observed the band for chelated carbonyl group, coordinated to cobalt at 1529 cm^{-1}. We find a broad band at 1520–1490 cm^{-1}.

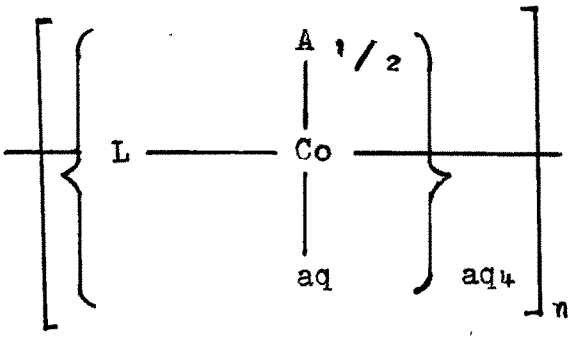
The analysis of the chelate polymer with azoaniline shows the ratio of metal to amine as 1 : 1/2. Hence it is represented as (7)



(7)

where A represents azoaniline.

Its magnetic moment per cobalt atom is found to be 5.19 B.M. and the chelate monomer is represented as a trans octahedral one (8).



(8)

In the absence of any further studies, it is not possible to decide whether azoaniline molecule links the two cobalt atoms or is present as a molar fraction.

Thus all these chelate polymers are considered to have the octahedral configuration and to contain the amino ligand coordinated to metal rather than present as lattice molecule, or as impurity.

The electrical resistivities (ρ) of these chelate polymers show a wide varation. When the electrical resistivities of the "di-aquo " chelate polymer are compared with those of the " ammino " chelate polymers, it is generally observed that the di-aquo polymer has smaller resistivity at room temperature and greater resistivity at a temperature above 150^{o}C than the ammino-polymers.

The plots of log ρ vs. $10^{3}/T$ for these polymers

are linear as required by the equation,

$$\rho = \rho_0 \times e^{\frac{E}{2kT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(a)$$

where E and ρ_0 are the energy gap and a constant respectively.

From the plots are calculated E and ρ_0 values and are presented in table - 42 (a).

E values are increasing in order,

water < benzidine < 1/2 azoaniline

ρ_0 values are decreasing in order,

water > benzidine > 1/2 azoaniline

Thus E and ρ_0 values appear to be inter-related. To find out the relation, $\log_{10}\rho_0$ is plotted against E in fig. 22. A straight line is obtained. Hence,

$$\rho_0 = \gamma \times e^{-\beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(b)$$

where γ and β are constants.

Substituting the value of ρ_0 in equation (a) we get,

$$\rho_0 = \gamma \times e^{-\beta E + \frac{E}{2kT}}$$

$$= \gamma \times e^{E\left(\frac{1}{2kT} - \beta\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(c)$$

This expression makes it clear that the exponential term consists of temperature dependent and temperature independent terms.

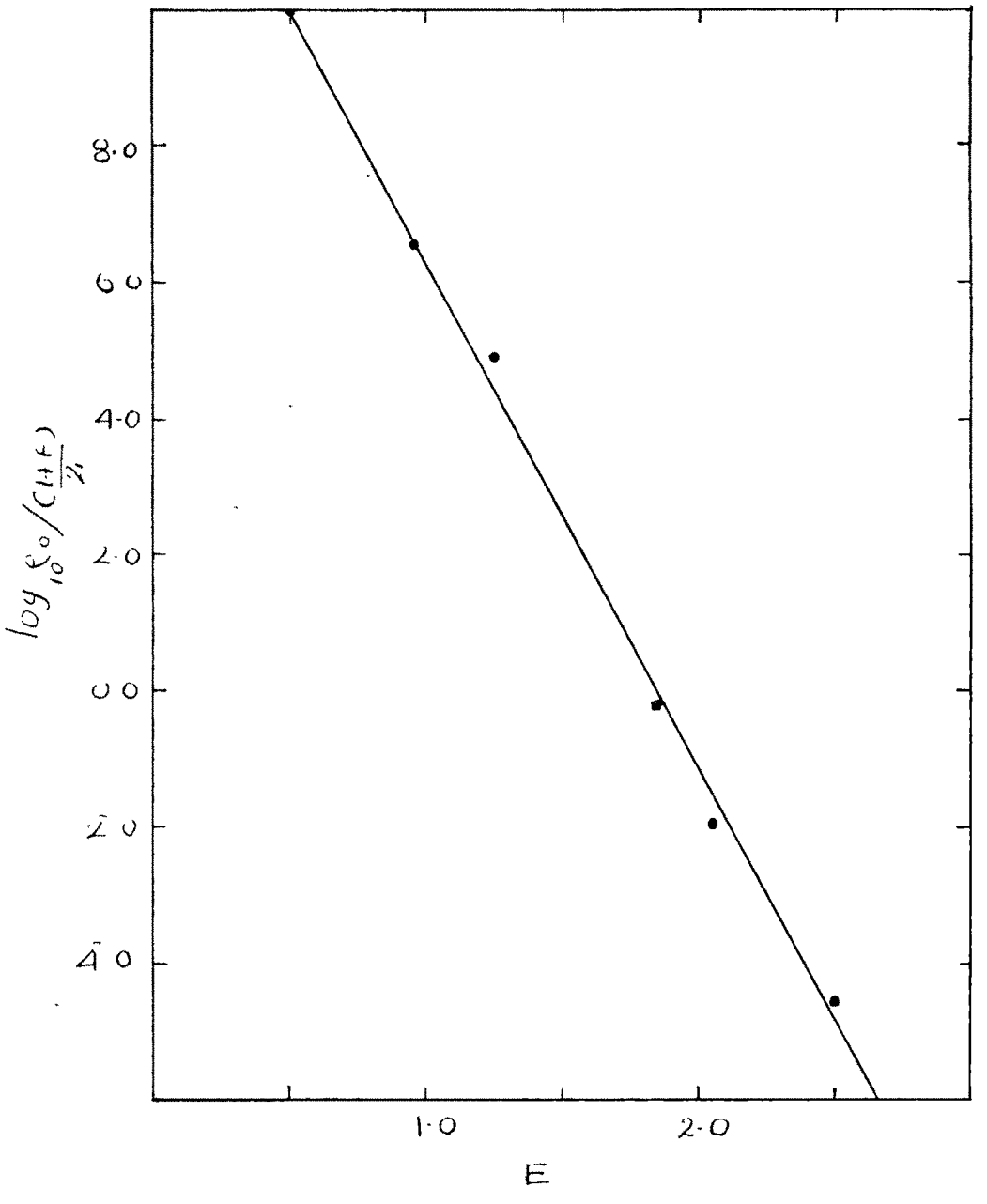


FIG. 22: $\log_{10} \varepsilon_0/(\frac{1+\varepsilon}{2})$ VS E FOR COBALT CHELATE POLYMERS

While attempting to prepare ammino chelate polymers containing simple ratio of chelate polymer to amine, some products were isolated containing molar fractional amounts of amines. These have been studied with a view to understand their influence on the electrical conductivity of the polymeric systems.

On the basis of analyses, the Co-chelate polymers with molar fractional amounts of benzidine, p-phenylenediamine and thioaniline mayb be represented as follows :

$$\left[(CoL)_5 \quad B_3 \quad aq_{10} \right]_n$$

(9)

$$\left[(CoL)_5 \quad P_4 \quad aq_{10} \right]_n$$

(10)

$$\left[(CoL)_5 \quad T \quad aq_5 \right]_n$$

(11)

where P and T represent p-phenylenediamine and thioaniline respectively.

The above formulations indicate that the minimum degree of polymerisation calculated taking n = 1, will be 5.

The magnetic moments of (9) and (10) per cobalt atom are found to be 5.15 and 4.87 B.M. respectively. Hence octahedral configurations for these chelate monomers

are suggested.

Log ρ of these chelate polymers is plotted against reciprocal temperature in fig. 23. From the curves, E and ρ_o values are calculated and presented in table 42 (b).

E and ρ_o values for these polymers were found to be inter-related. When a graph of $\log_{10} \rho_o / \frac{1+F}{2}$ for ammino polymers is plotted vs. E in the earlier fig. 22, points were found to lie on the same straight line. Hence, for ammino polymers,

$$\frac{\log_{10} \rho_o}{\frac{(1+F)}{2}} = \log_{10} \gamma - \frac{\beta E}{2.3}$$

$$\text{i.e} \quad \rho_o = \gamma^{\frac{(1+F)}{2}} \times e^{-\beta E \frac{(1+F)}{2}} \qquad \ldots\ldots\ldots\ldots(d)$$

Where F is the molar fraction of the amino ligand coordinated per Co-atom and γ and β are constants. When F = 0, the relation (b) holds good. Values of γ and β are calculated as 10^{14} and 17.16 respectively. Hence the resistivities (ρ) of the ammino chelate polymers over a range of temperature may be represented by the relation (e)

$$\rho = \rho_o \times e^{\frac{+E}{2kT}}$$

$$= \gamma^{\frac{(1+F)}{2}} \times e^{E\left[\frac{1}{2kT} - \beta \frac{(1+F)}{2}\right]} \qquad \ldots\ldots\ldots(e)$$

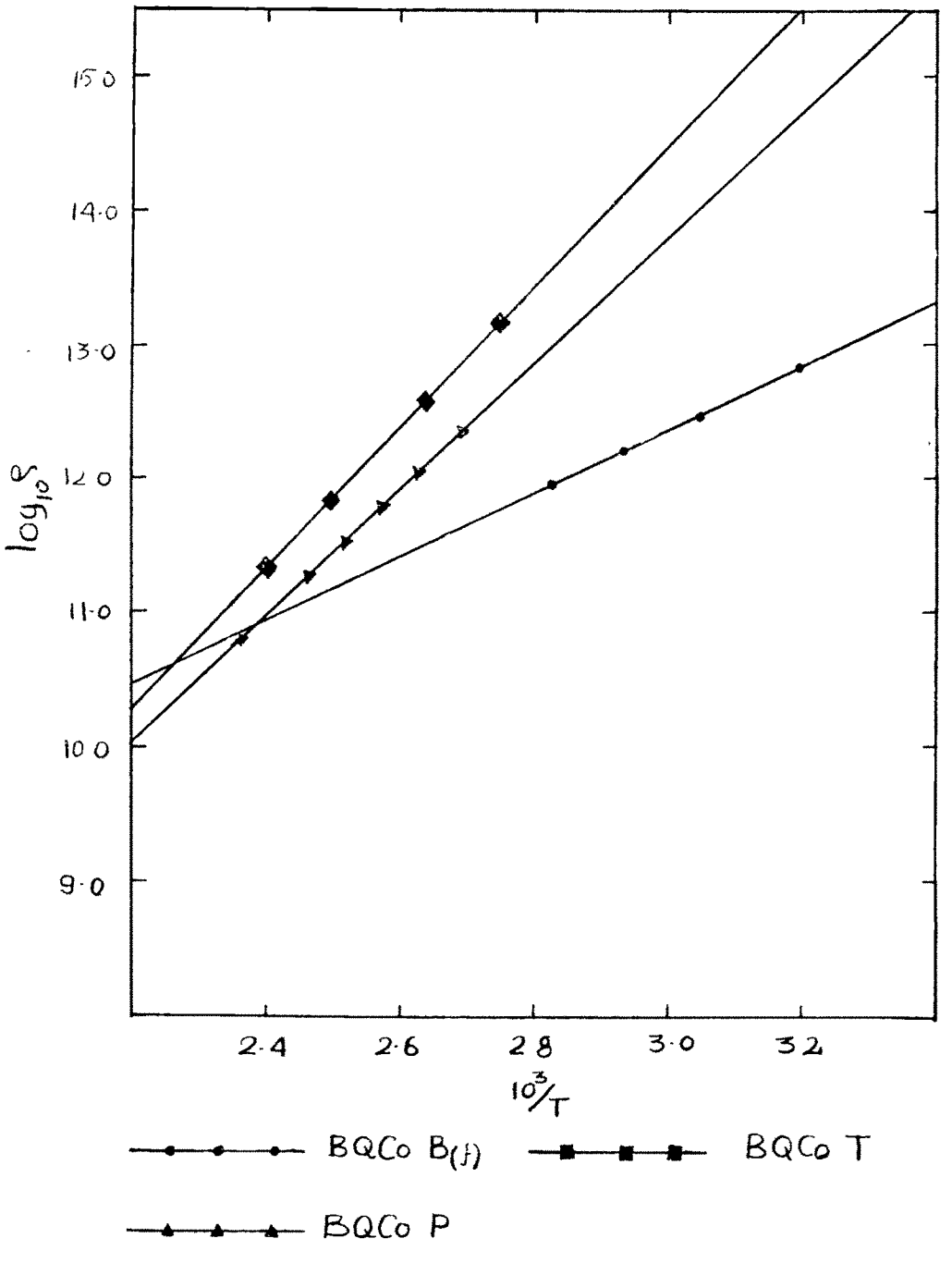


FIG: 23: Log RESISTIVITY vs. $10^3/T$ FOR COBALT CHELATE POLYMERS

When F = 0, the relation (c) holds good.

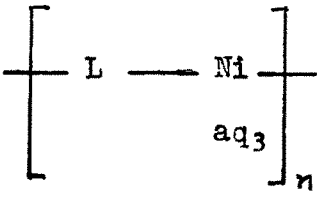
Values of resistivities calculated at 30°C and 150°C using the above values of γ and β and known values of F and E for each chelate polymer are presented in table 43 and compared with the corresponding values of resistivities observed from the graphs of $\log_{10} \rho$ vs. 1/T. Close agreement between the values is observed.

The results were encouraging and hence in subsequent studies complexes and chelate polymers containing molar fractional amounts of amines were also investigated.

(ii) Nickel (II) chelate polymers :

The magnetic moments of nickel chelate polymers calculated from magnetic susceptibilities are presented in table 44 and some important IR bands of BQNi are given in table 45. Plots of $\log_{10} \rho$ of the chelate polymers vs. reciprocal temperature are given in figs. 24 and 25.

The analysis of BQNi shows that the ratio of metal to ligand is 1 : 1 ; hence the polychelate is represented as a linear polymeric chain (12),



(12)

Table 43

Electrical resistivities of cobalt chelate polymers at 30°C and 150°C

No.	Compound	F =	$\log_{10}\rho$ at 30°C		$\log_{10}\rho$ at 150°C	
			observed (graph)	calculated (eqn.c or e)	observed (graph)	calculated (eqn. c or e)
1.	BQCo	-	14.42	14.45	13.15	13.21
2.	BQCo B	1.0	15.16	15.07	12.20	12.15
3.	BQCo A	0.5	17.45	17.34	11.45	11.40
4.	BQCo $B_{(f)}$	0.6	13.08	13.40	10.85	11.19
5.	BQCo P	0.8	15.20	15.59	10.85	11.20
6.	BQCo T	0.2	16.05	16.35	11.15	11.45

Table 44

Magnetic moments of nickel (II) chelate polymers

No.	Compound	Molar magnetic susceptibility (per Ni- atom) $Xm \times 10^6$	Corrected molar magnetic susceptibility (per Ni- atom) $Xm' \times 10^6$	Magnetic moment (per Ni- atom) (μ) B.M.
1.	BQNi	4440	4530	3.34
2.	BQNi Py	3900	4060	3.17
3.	BQNi P	3960	4090	3.18
4.	BQNi T	4120	4330	3.28
5.	BQNi A	4380	4650	3.40

Table 45

Some characteristic IR frequencies (cm^{-1}) of BQNi

3280 s	1250 s
1530 vs(b)	845 w
1370 s	815 m
1285 w	770 w

Table 46

No.	Compound	Energy gap (E ev.)	Resistivity at infinite temperature (ρ_∞ ohm.cm.)
1.	BQNi	2.80	1.07×10^{-5}
2.	BQNi Py	2.85	9.77×10^{-6}
3.	BQNi P	1.59	3.40×10^{2}
4.	BQNi T	2.33	1.06×10^{-3}
5.	BQNi A	2.31	3.81×10^{-4}

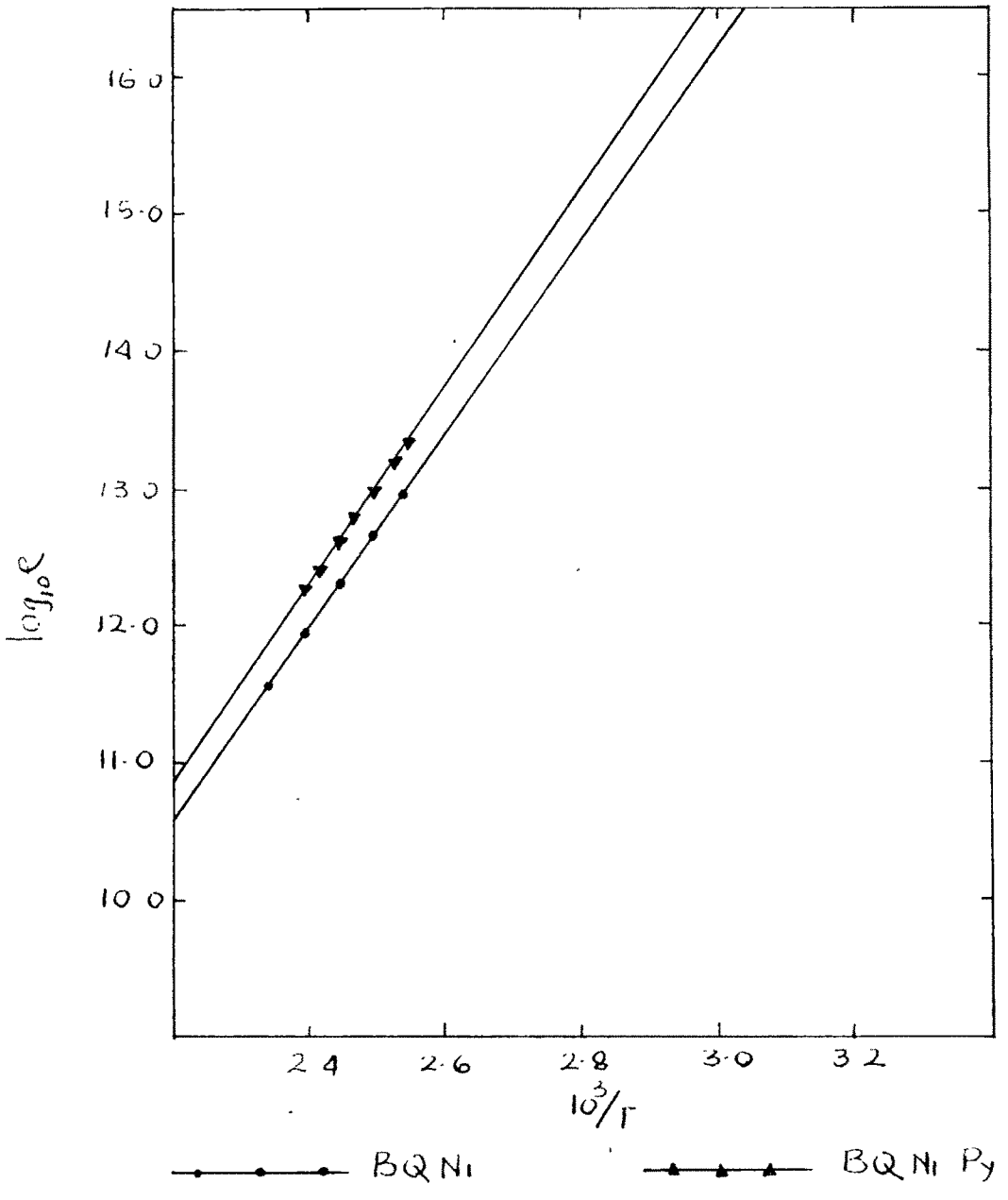


FIG 24: Log RESISTIVITY vs. $10^3/T$ FOR NICKEL CHELATE POLYMERS.

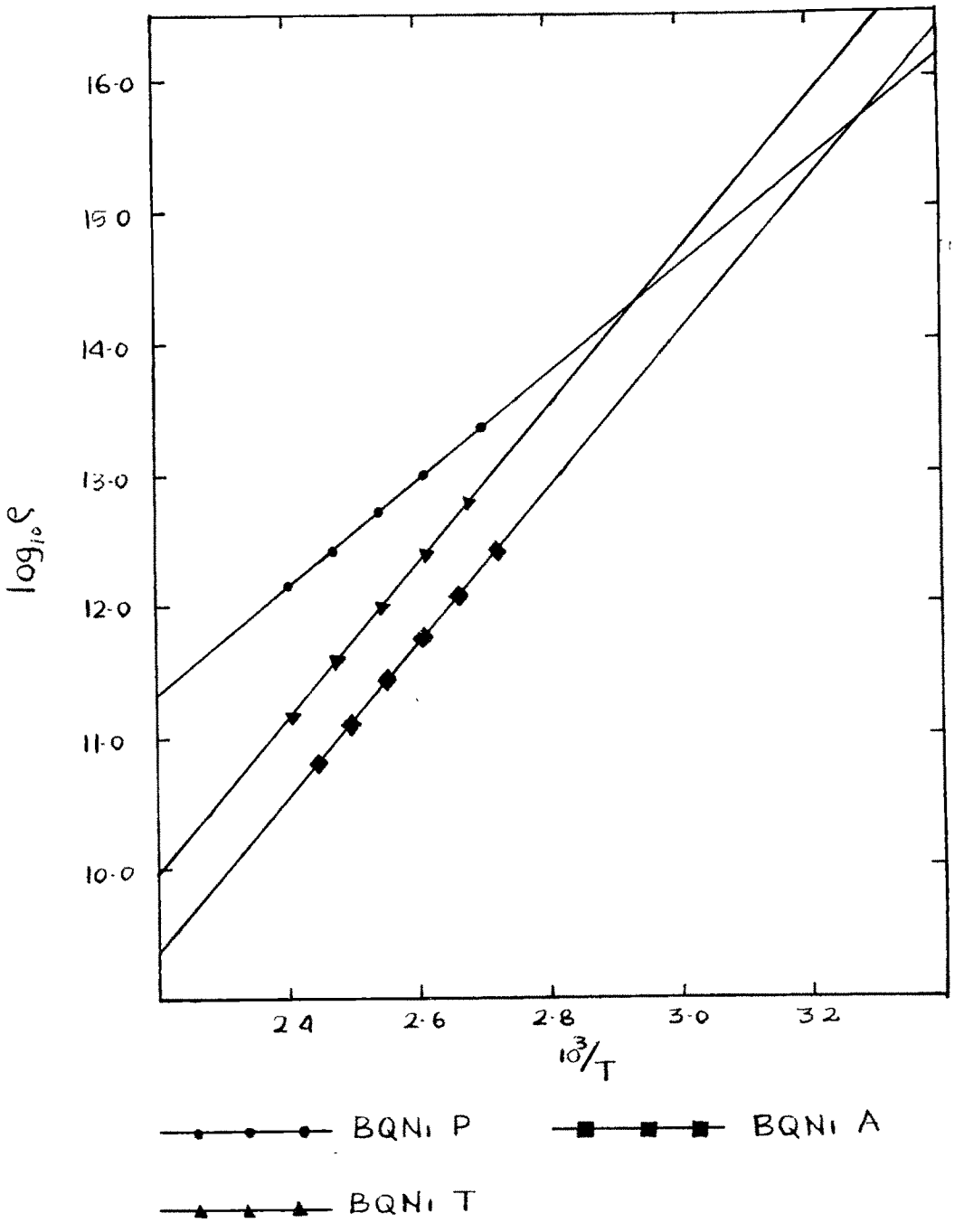
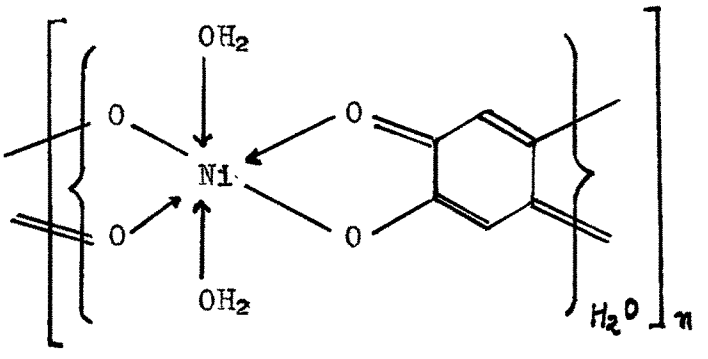


FIG. 25: Log RESISTIVITY *vs* $10^3/T$ FOR NICKEL CHELATE POLYMERS.

Its magnetic moment per nickel atom is found to be 3.34 B.M. The chelate monomer may, therefore, be considered to have an octahedral configuration (13)



(13)

Kanda has shown that the complex is a linear polymer with metal : ligand ratio of 1 : 1. Bottei and Fangman have suggested that the (analytical) data be corrected for adsorbed water and the complex be formulated as ,

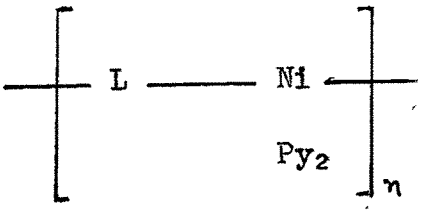
$$Ni\ (C_6H_2O_4)\ (H_2O)_2$$

From the thermogravimetric studies they concluded that the loss of water and the decomposition of the complex occurred simultaneously. They also suggested from the IR spectral studies that both carbonyl groups of the ligand functioned as coordinating groups and both phenolic groups were involved in complex formation.

The IR spectrum obtained by us is almost identical with the one presented by Bottei and Fangman in their paper. It may be noted here that the paramagnetic nature of the chelate monomer and its pink

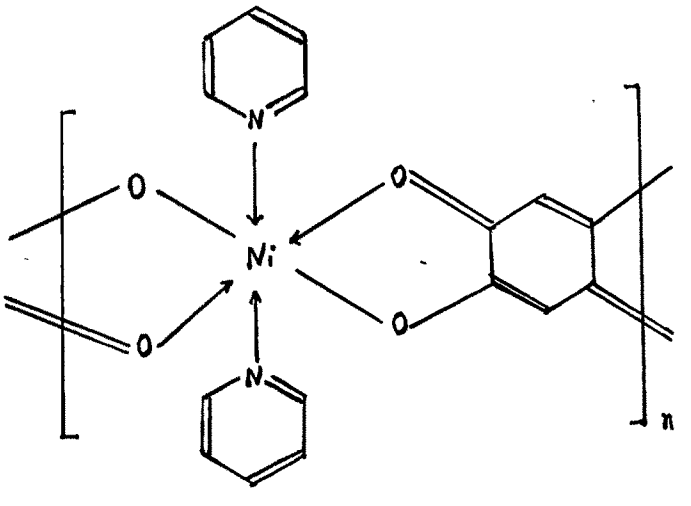
colour are contrary to the usual colour rule for nickel (II) complexes.

The analysis of the pyridinated complex BQNi Py shows that the ratio of metal to pyridine is 1 : 2 ; the polychelate is therefore represented as (14),



(14)

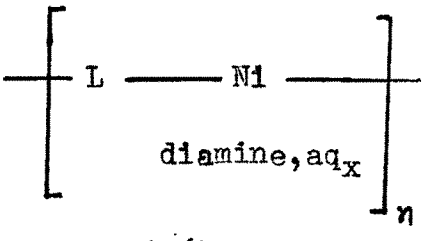
Its magnetic moment per nickel atom is calculated as 3.17 B.M. It indicates octahedral nature of the chelate monomer which may be formulated as a trans octahedral one (15),



(15)

When a diamine such as p-phenylenediamine, or azoaniline is used for the formation, the ratio of metal to diamine is found to be 1 : 1 from analyses.

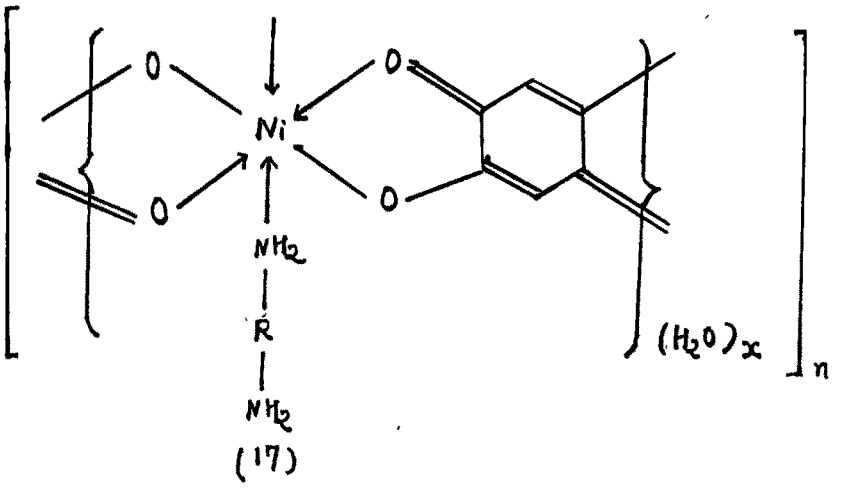
The polychelates are therefore represented as (16),



(16)

where diamine = ,	x =
(a) p-phenylenediamine	0
(b) azoaniline	7

The magnetic moments of 16(a) and 16(b) per nickel atom are 3.18 and 3.40 B.M. respectively. The results indicate octahedral nature of the monomeric chelates which may be represented as (17)



(17)

where R =,	x =
(a) C_6H_4	0
(b) $C_6H_4N{=}NC_6H_4$	7

The analysis of BQNi T shows that the ratio of amine to metal is 7 : 10 ; hence the polychelate is represented as (18)

$$\left[(NiL)_{10}\, T_7\, aq_{50} \right]_n$$

(18)

Its magnetic moment per nickel atom is calculated as 3.27 B.M. It indicates octahedral nature of the chelate monomer.

The plots of $\log_{10} \varrho$ of these chelate polymers vs. reciprocal temperature are linear, as required by equation (a). From the plots are calculated E and ϱ_o values and are presented in table 46.

E values are increasing in order,

p-phenylenediamine < thioaniline ~ azoaniline < water < pyridine

ϱ_o values are decreasing in order,

p-phenylenediamine > thioaniline > azoaniline > water ~ pyridine

Thus E and ϱ_o values appear to be inter-related. When a graph of $\log_{10} \varrho_o / n(\frac{1+F'}{2})$ for ammino polymers ($\log_{10} \varrho_o$ for aquo polymer) is plotted vs. E (in fig. 26) , a straight line is obtained, satisfying equation (d') for ammino polymers.

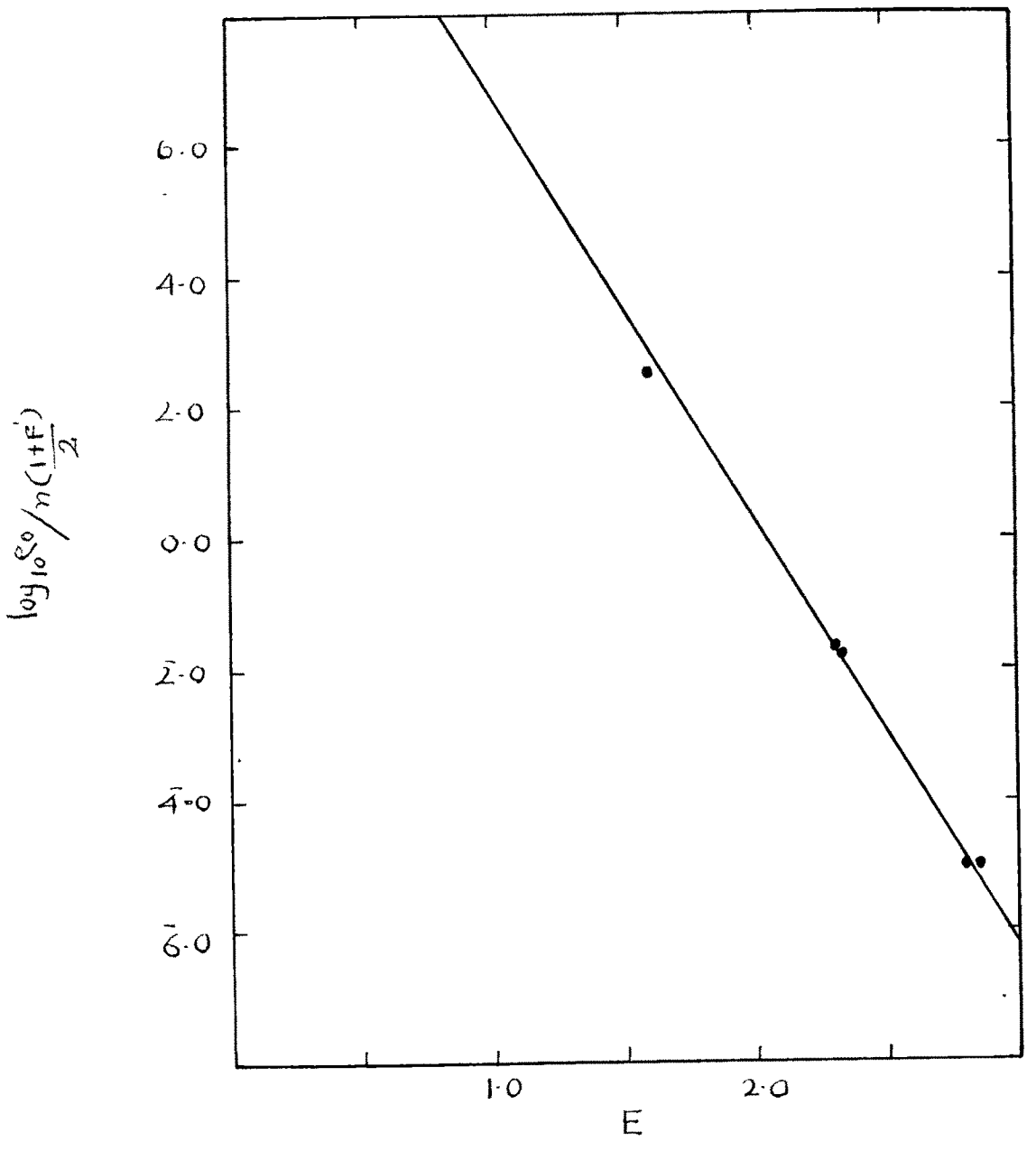


FIG. 26: $\log_{10}\epsilon_0/n\frac{(1+F')}{2}$ vs E FOR NICKEL CHELATE POLYMERS.

$$\frac{\log_{10} \rho_0}{n\left(\frac{1+F'}{2}\right)} = \log_{10} \gamma - \frac{\beta E}{2.3}$$

$$\text{i.e. } \rho_0 = \gamma^{n\left(\frac{1+F'}{2}\right)} \times e^{-\beta E n\left(\frac{1+F'}{2}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (d')$$

Where F' is the fraction of half the amino groups coordinated per nickel atom, n is the number of rings associated with the amine molecule, and γ and β are constants. When F'=0, relation (b) will hold good.

$$\rho_0 = \gamma \times e^{-\beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots (b)$$

Values of γ and β are calculated as $10^{13.3}$ and 14.95 respectively. Hence the resistivity of ammino nickel chelate polymers over a range of temperature may be represented by the relation (e')

$$\rho = \gamma^{n\left(\frac{1+F'}{2}\right)} \times e^{E\left[\frac{1}{2kT} - \beta n\left(\frac{1+F'}{2}\right)\right]} \quad \ldots\ldots\ldots\ldots\ldots (e')$$

when F'=0, the relation (c) will hold good.

$$\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots (c)$$

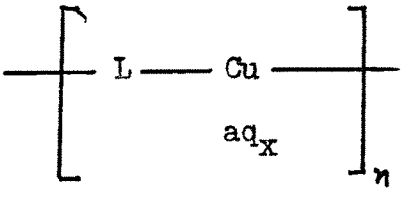
Values of resistivities calculated at 30°C and 150°C using the above values of γ and β and known values of n, F' and E for each chelate polymer are presented in

table 47 and compared with the corresponding values of resistivities obtained from the graphs of $\log_{10}\rho$ vs. $10^3/T$. Close agreement between the values is observed.

(iii) Copper (II) chelate polymers :

The magnetic moments of the Cu(II) chelate polymers calculated from the magnetic susceptibilities are presented in table 48, and some important IR bands of BQCu A are presented in table 49. Plots of $\log_{10}\rho$ of the chelate polymers vs. reciprocal temperature are given in figs.27 and 28.

Molar composition (metal:ligand) of the copper chelate (BQCu) was found by Jain and Singhal[258] to vary from 1:0.72 to 1:1.25. We prepared BQCu by two methods. These complexes may be represented by (19).



(19)

where x =

(a) 1/2

(b) 3/2

BQCu has been studied extensively by Kanda and coworkers.[120,123,240,259] From X-ray diffraction and magnetic studies they suggested that the polymer would have one dimensional chain structure with a degree of polymerisation of 9-10. They found that the polymer

Table 47

Electrical resistivities of nickel chelate polymers at 30°C and 150°C

No.	Compound	F =	$\log_{10}\rho$ at 30°C		$\log_{10}\rho$ at 150°C	
			observed (graph)	calculated (eqn.c or e)	observed (graph)	calculated (eqn. c or e)
1.	BQNi	-	18.30	18.43	11.70	11.81
2.	BQNi Py	1.0	18.79	18.52	12.00	11.79
3.	BQNi P	1.0	15.77	16.21	12.00	12.45
4.	BQNi T	0.7	16.40	16.28	10.90	10.76
5.	BQNi A	1.0	15.80	15.83	10.35	10.37

Table 48

Magnetic moments of copper (II) chelate polymers

No.	Compound	Molar magnetic susceptibility (per Cu- atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per Cu-atom) $X_m' \times 10^6$	Magnetic moment (per Cu- atom) (μ) B.M.
1.	BQCu	1460	1540	1.94
2.	BQCu Py	1760	1860	2.13
3.	BQCu B	1580	1730	2.07
4.	BQCu T	1250	1440	1.89
5.	BQCu A	1870	2090	2.28

Table 49

Some characteristic IR frequencies (cm^{-1}) of BQCu A

3450 m (b)	1475 s (b)	1070 m (b)
3190 m	1340 s	860 w
1600 m	1280 m	843 m
1555 m	1245 s	832 m

Table 50

No.	Compound	Energy gap (E ev.)	Resistivity at infinite temperature (ρ_∞ ohm.cm.)
1.	BQCu	0.73	1.59×10^{4}
2.	BQCu Py	0.76	1.87×10^{5}
3.	BQCu B	1.93	1.88×10^{-2}
4.	BQCu T	2.04	2.24×10^{-2}
5.	BQCu A	2.04	5.98×10^{-2}

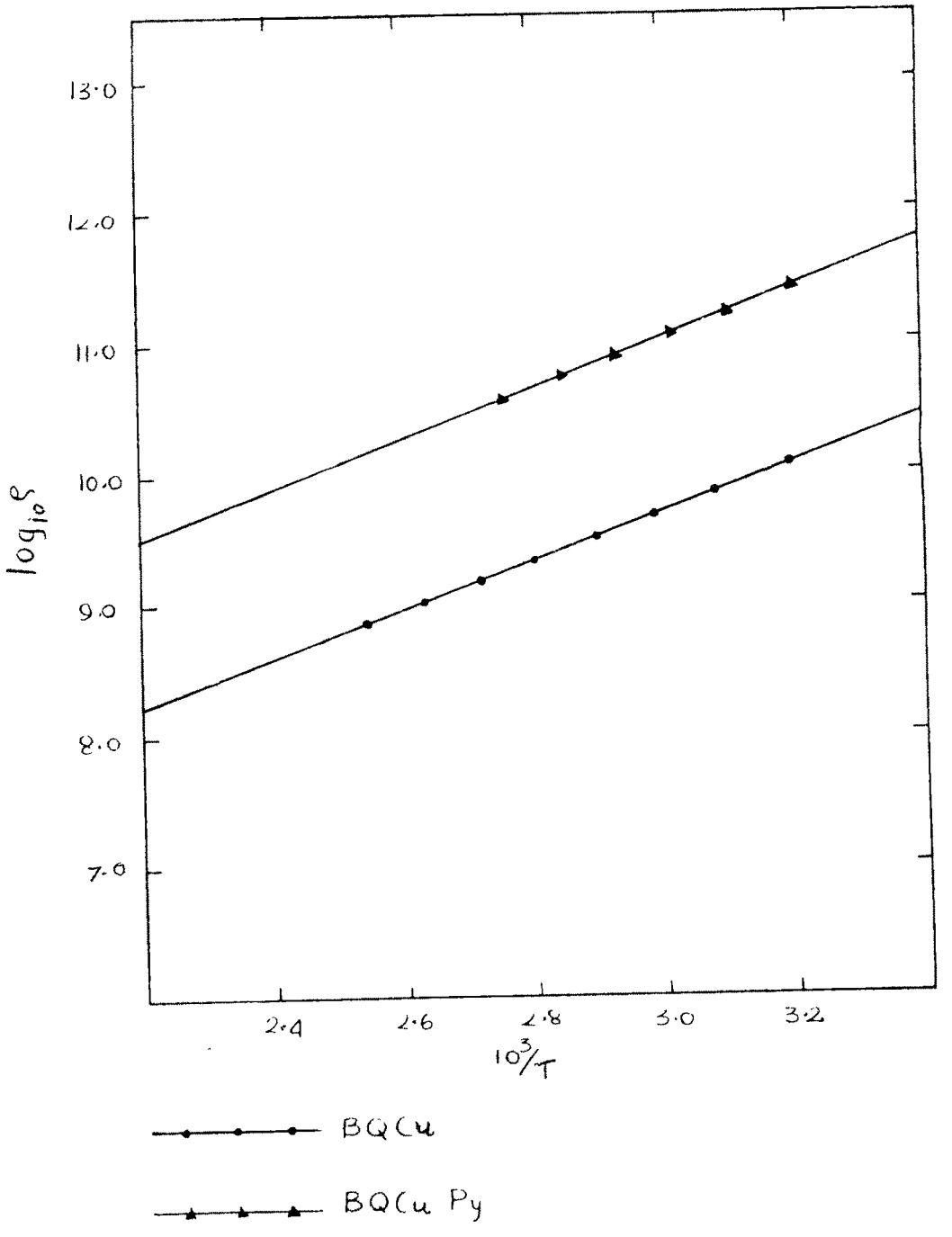


FIG 27: Log RESISTIVITY vs $10^3/T$ FOR COPPER CHELATE POLYMERS

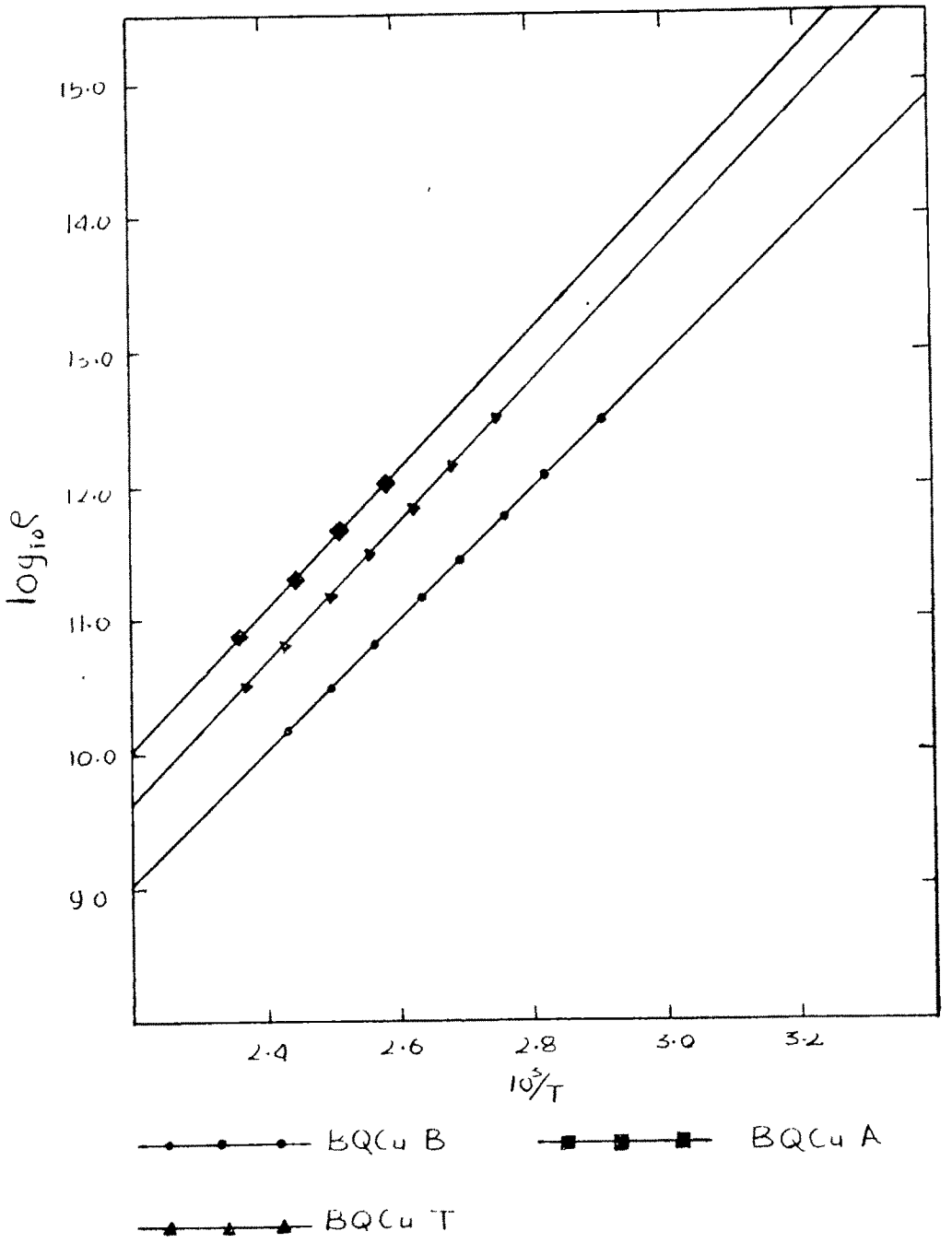


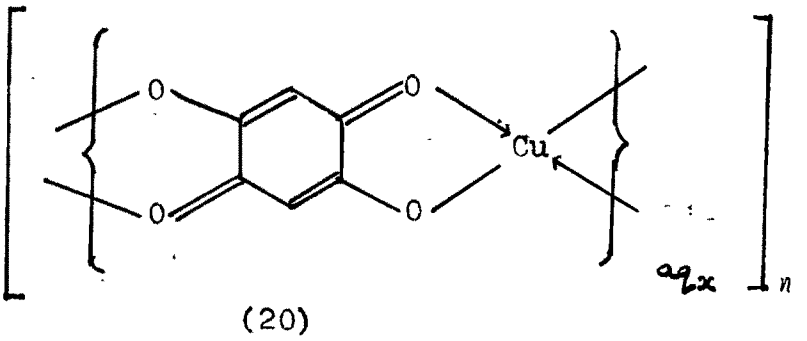
FIG. 28: LOG RESISTIVITY VS. $10^3/T$ FOR COPPER CHELATE POLYMERS.

yielded no reproducible values of resistivity with either a.c. or d.c. measurements[4]. They further studied the antiferro magnetic behaviour of the complex. We also find that the resistivities vary to a considerable extent. The values presented here are one set of values which appear to be the mean of the various determinations.

Bottei and Fangman suggested that the complex be represented as ($C_6H_2O_4Cu$) containing adsorbed water ; they concluded from thermogravimetric and IR spectral studies that the complex is not hydrated.

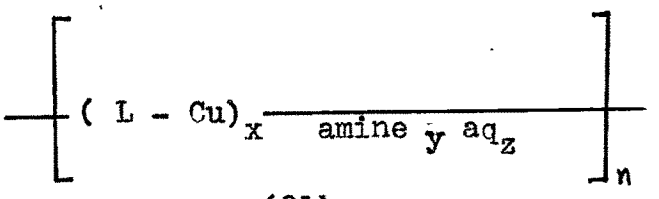
The mean magnetic moment of the chelate polymer per Cu-atom is found by us as 1.94 B.M.

On the basis of the above observations, the polymer may be represented as (20)



(20)

The analyses of BQCu Py, BQCu B and BQCu T show that molar fractions of amines are present in these polymers. They may be represented by (21).

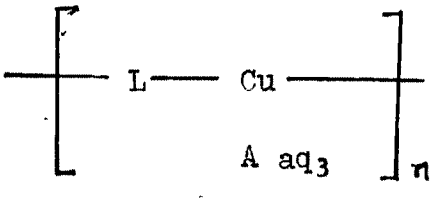


(21)

where amine = ,	x =	, y =	, z =
(a) pyridine	4	3	4
(b) benzidine	3	2	3
(c) thioaniline	4	3	9

The magnetic moments of these polymers BQCu Py, BQCu B and BQCu T per copper atom are calculated as 2.13, 2.07 and 1.89 B.M. respectively. The introduction of amine molecules in these polymers do not show any abnormality in their values of magnetic moments at room temperature.

The analysis of BQCu A shows the ratio of copper to amine as 1 : 1 ; hence it may be represented as (22).



(22)

Its magnetic moment per copper atom has been calculated as 2.28 B.M. The absorption band for chelated carbonyl group coordinated to metal is found at 1475 cm^{-1}.

Plots of $\log_{10}\rho$ of chelate polymers vs.reciprocal temperature are found to be linear as expected by equation (a), hence values of Eg and ρ_o are calculated and presented in table 50.

When $\log_{10} \rho_o / \left(\frac{2}{1+F}\right)^2$ for ammino polymers ($\log_{10} \rho_o$ for aquo polymer) is plotted vs. E in fig.29, a straight line is obtained satisfying the equation(d")

$$\frac{\log_{10} \rho_o}{\left(\frac{2}{1+F}\right)^2} = \log_{10} \gamma - \frac{\beta E}{2.3}$$

$$\text{i.e. } \rho_o = \gamma \left(\frac{2}{1+F}\right)^2 \times e^{\beta E \left(\frac{2}{1+F}\right)^2} \quad \ldots\ldots\ldots\ldots (d")$$

Where F is the molar fraction of the amine molecule per copper atom and γ and β are constants. When F=0, the relation (b) will hold good.

$$\rho_o = \gamma \times e^{-\beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots (b)$$

Values of γ and β are calculated as $10^{7.25}$ and 9.66 respectively. Hence the resistivity (ρ) of ammino copper chelate polymers may be represented by the relation (e")

$$\rho = \gamma \left(\frac{2}{1+F}\right)^2 \times e^{E\left[\frac{1}{2kT} - \beta \left(\frac{2}{1+F}\right)^2\right]} \quad \ldots\ldots\ldots (e")$$

when F=0, the relation (c) will hold good.

$$\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]} \quad \ldots\ldots\ldots\ldots\ldots (c)$$

Values of resistivities calculated at 30°C and 150°C using the above values of γ and β and known values

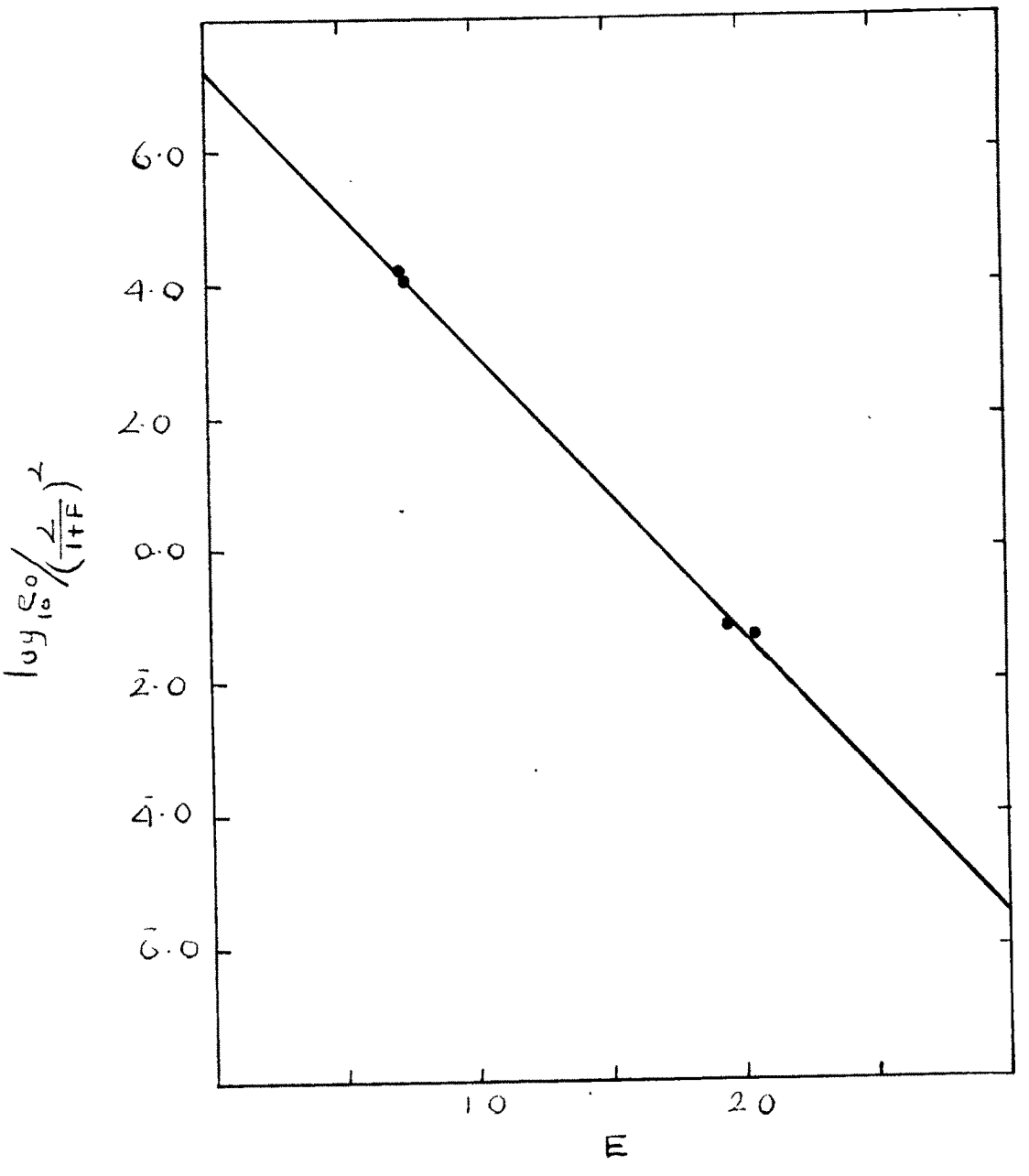


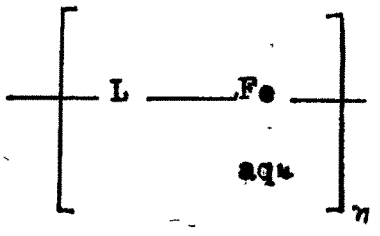
FIG. 29: $\log_{10} \varepsilon_0/(\frac{2}{1+F})^2$ vs. E FOR COPPER CHELATE POLYMERS

of F and E for each chelate polymer are presented in table 51 and compared with the corresponding values of resistivity obtained from the graph of $\log_{10}\varrho$ vs. $10^3/T$. Close agreement between the values is observed.

(iv) Iron (II) chelate polymers :

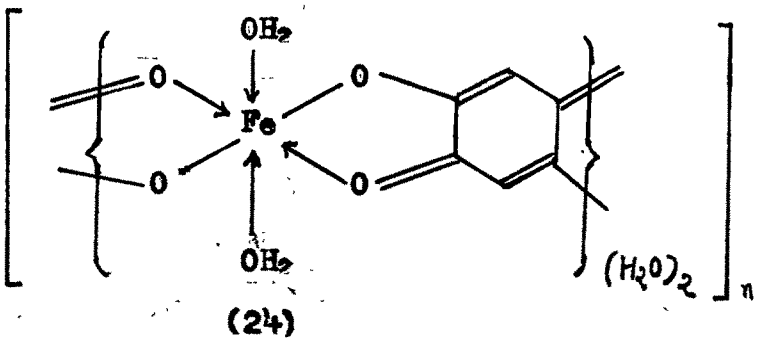
The magnetic moments of iron chelate polymers calculated from their magnetic susceptibilities are presented in table 52 and some important IR bands of BQ Fe are presented in table 53. Plots of $\log_{10}\varrho$ of these chelate polymers vs. reciprocal temperature are given in fig. 30.

From the analysis of BQ Fe, the ratio of metal to ligand is found to be 1 : 1 ; hence it may be represented as (23)



(23)

Its magnetic moment per iron atom is found to be 5.25 B.M. indicating high spin octahedral nature of the chelate monomer. Hence it is considered to have trans octahedral structure and is represented as (24)



(24)

Table 51

Electrical resistivities of copper chelate polymers at 30°C and 150°C

No.	Compound	F =	$\log_{10}\rho$ at 30°C		$\log_{10}\rho$ at 150°C	
			observed (graph)	calculated (eqn.c or e)	observed (graph)	calculated (eqn. c or e)
1.	BQCu	-	10.27	10.37	8.55	8.54
2.	BQCu Py	0.75	11.63	11.63	9.82	9.83
3.	BQCu B	0.66	14.40	14.86	9.85	10.30
4.	BQCu T	0.75	15.35	15.27	10.45	10.45
5.	BQCu A	1.0	15.75	15.66	10.85	10.84

Table 52

Magnetic moments of iron (II) chelate polymers

No.	Compound	Molar magnetic susceptibility (per Fe-atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per Fe-atom) $X_m' \times 10^6$	Magnetic moment (per Fe-atom) (μ) B.M.
1.	BQFe	11010	11150	5.25
2.	BQFe Py	12640	12770	5.57
3.	BQFe T	10530	10780	5.16
4.	BQFe A	10750	10990	5.21

Table 53

Some characteristic IR frequencies (cm^{-1}) of BQFe

3450 m	1240 vs
3050 w	858 w
1485 vs	835 m
1335 vs	

Table 54

No.	Compound	Energy gap (E ev.)	Resistivity at infinite temperature (ρ_∞ ohm.cm.)
1.	BQFe	1.22	6.78×10^{1}
2.	BQFe Py	0.93	4.69×10^{2}
3.	BQFe T	1.03	1.16×10^{1}
4.	BQFe A	1.08	2.24×10^{1}

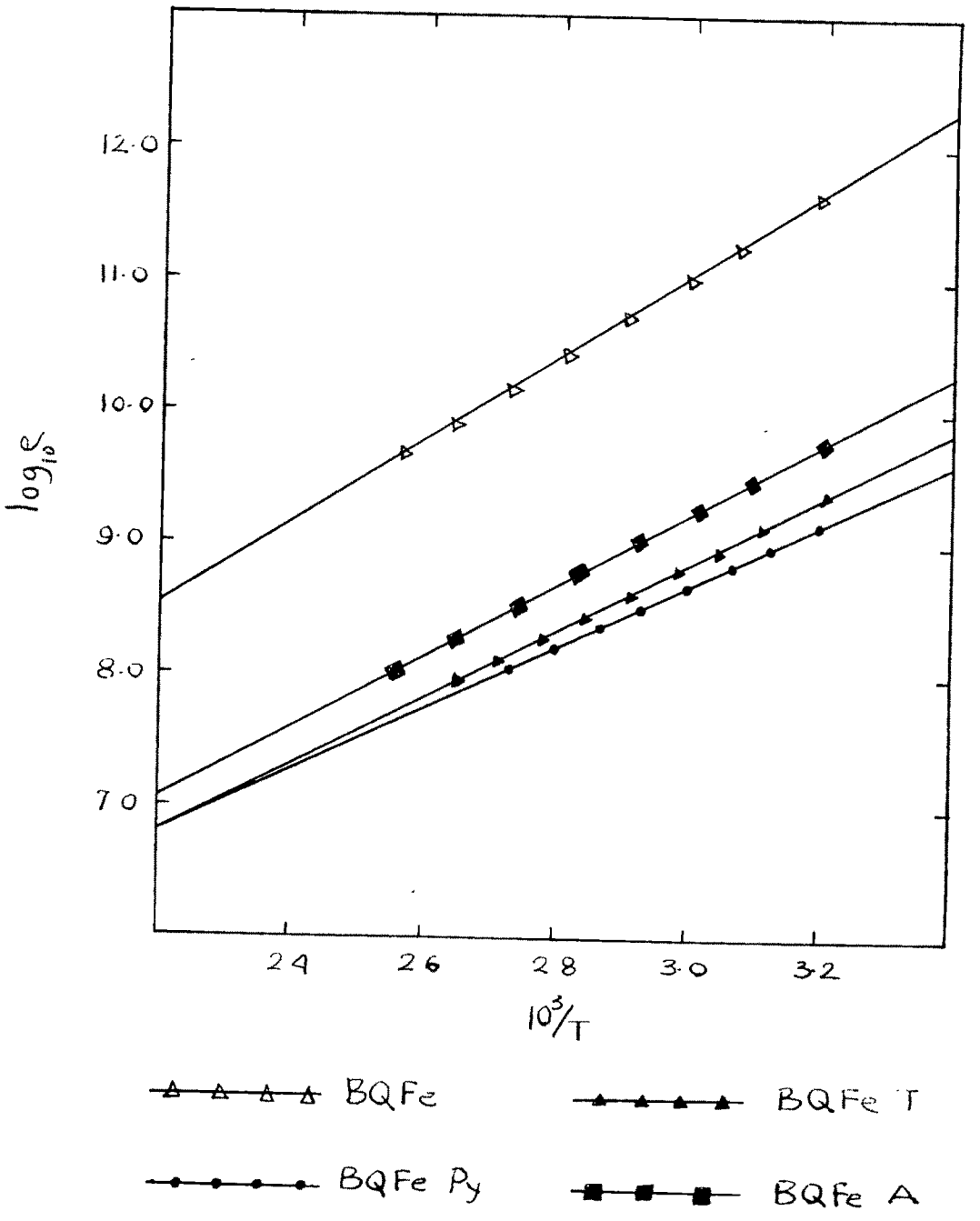
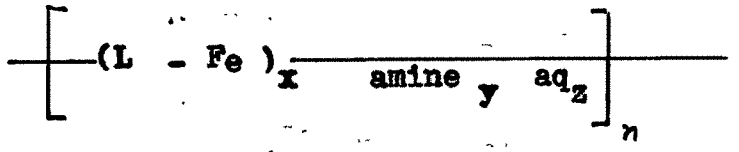


FIG. 30: Log RESISTIVITY vs. $10^3/T$ FOR IRON CHELATE POLYMERS.

On the basis of analyses BQFe Py, BQFe T and BQFe A may be represented as (25)



(25)

where amine = ,	x = ,	y = ,	z =
(a) pyridine	2	1	8
(b) thioaniline	4	3	32
(c) azoaniline	5	4	35

The magnetic moments of the polymers BQFe Py, BQFe T and BQFe A are found to be 5.57, 5.16 and 5.21 B.M. respectively. They are all considered to have trans octahedral nature.

Plots of $\log_{10}\varrho$ of these chelate polymers vs. reciprocal temperature are linear as expected for the equation (a). From the plots are calculated the values of E and ϱ_o and are presented in table 54.

When a graph of $\frac{\log_{10}\varrho_o}{\frac{1}{1+F}}$ is plotted vs. E (fig.31), a straight line is obtained, satisfying equation (d) for iron chelate polymers.

$$\frac{\log_{10}\varrho_o}{\frac{1}{1+F}} = \log_{10}\gamma - \frac{\beta E}{2.3}$$

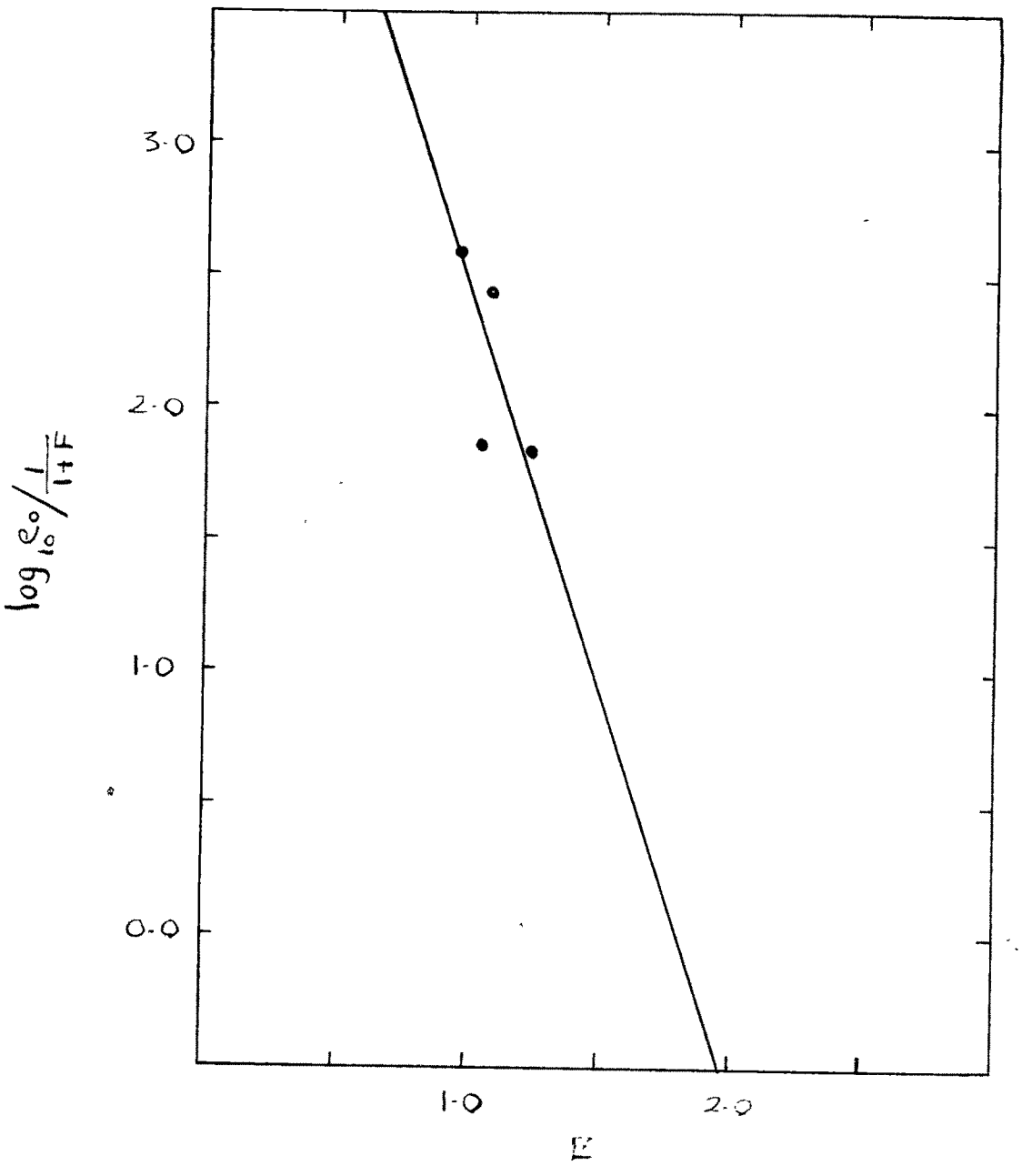


FIG 31: Log $\varepsilon_0/\frac{1}{1+F}$ vs. E FOR IRON CHELATE POLYMERS

i.e. $$\rho_0 = \gamma^{\frac{1}{1+F}} \times e^{-\beta E\left(\frac{1}{1+F}\right)} \quad \text{.....(d)}^{\#}$$

where F is the molar fraction of the amino ligand coordinated per iron atom, and γ and β are constants.

Values of γ and β are calculated as $10^{5.4}$ and 6.9 respectively. Hence the resistivity of iron chelate polymers over a range of temperature may be represented by the equation (e#)

$$\rho = \gamma^{\frac{1}{1+F}} \times e^{E\left[\frac{1}{2kT} - \beta\left(\frac{1}{1+F}\right)\right]} \quad \text{.....(e)}^{\#}$$

Values of resistivities calculated at $30^{\circ}C$ and $150^{\circ}C$ using the above values of γ and β and known values of F and E for each chelate polymer are presented in table 55 and compared with the corresponding values of resistivities obtained from the graph of $\log_{10}\rho$ vs. $10^3/T$. Close agreement between the values is observed.

(v) Complexes with organic bases :

Schawartz[262] showed that 2,5-dihydroxy-p-benzoquinone forms a complex with pyridine melting at $275^{\circ}C$ (decomp.). We have studied the formation of complexes by 2,5-dihydroxy-p-benzoquinone with benzidine, p-phenylenediamine and azoaniline.

Table 55

Electrical resistivities of iron chelate polymers at 30°C and 150°C

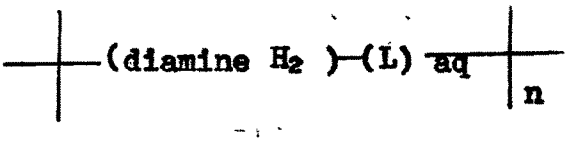
No.	Compound	F =	$\log_{10} \rho$ at 30°C		$\log_{10} \rho$ at 150°C	
			observed (graph)	calculated (eqn. c or e)	observed (graph)	calculated (eqn. c or e)
1.	BQFe	-	12.00	11.90	9.05	9.02
2.	BQFe Py	0.5	9.40	9.49	7.15	7.29
3.	BQFe T	0.75	9.60	9.90	7.15	7.47
4.	BQFe A	0.8	9.90	10.20	7.50	7.65

On the basis of analysis, they are formulated as, (26)

$$\left[(LH_2 . \text{diamine})\ aq \right]$$

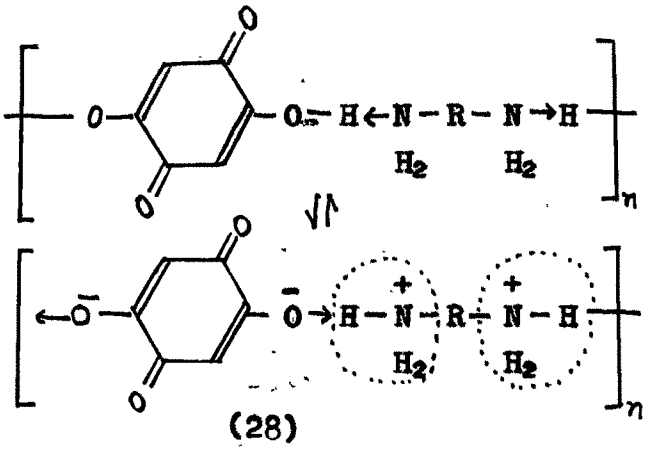
(26)

Their absorption spectra in the ultra-violet region are presented in fig. 32. The wave-length maxima (λ max) and the corresponding E values of these compounds are presented in table 56. These spectra are similar to the spectrum of sodium 2,5-dihydroxy-p-benzoquinonate, hence it is suggested that these complexes may be represented as (27)



(27)

The electrical conductivity of BQ B is studied in methanol solution. Calculation of the equivalent conductivity shows that the value is less than $10\ cm^2\ equiv^{-1}\ ohm^{-1}$, indicating that BQ B may be considered to be almost a non-electrolyte. Other complexes may be considered similar to BQ B and they may be represented as a linear polymeric chain (28) and its chelated forms.



(28)

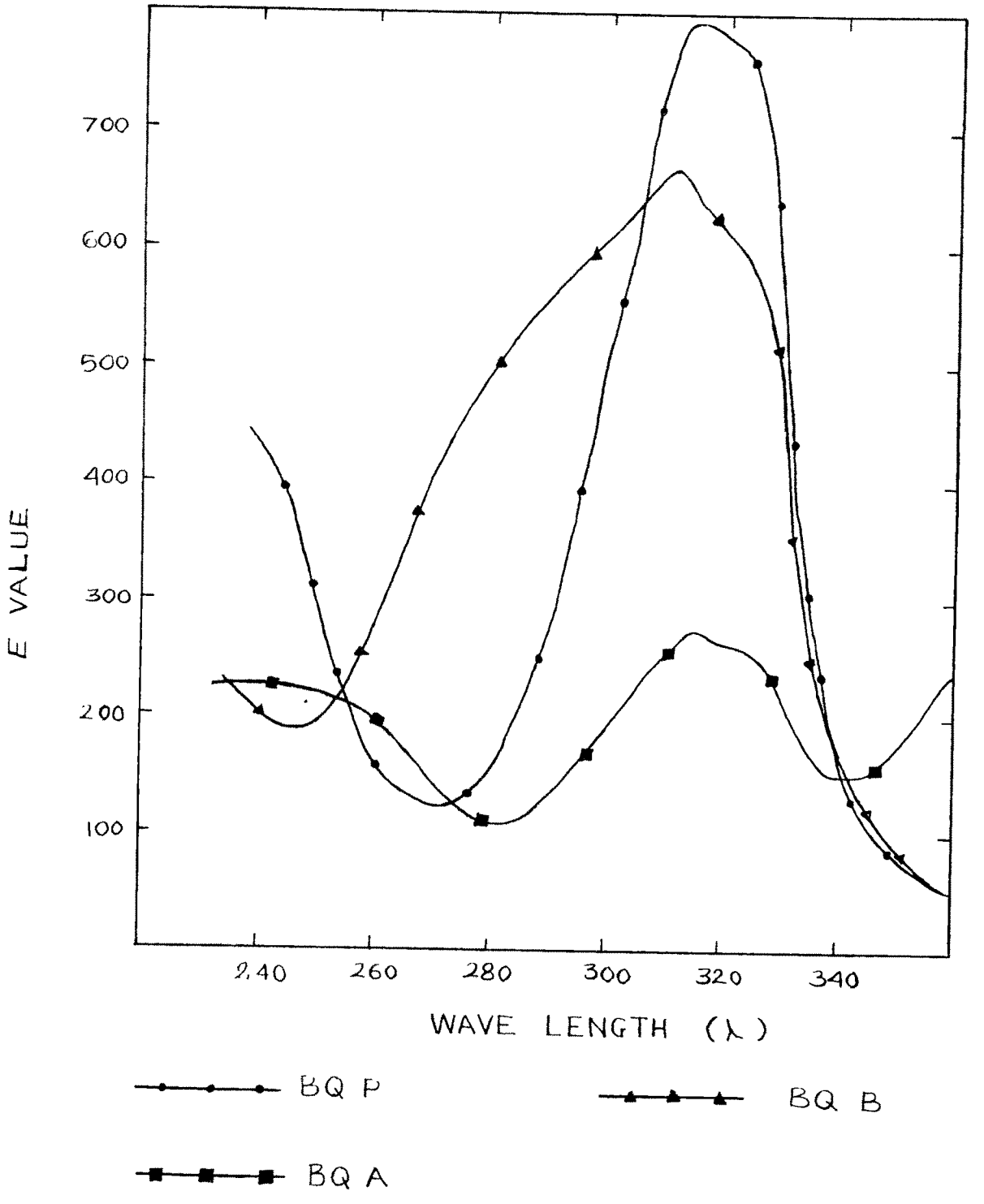


FIG. 32: UV SPECTRA OF ADDITION PRODUCTS.

Table 56

Ultra-violet absorption spectra of addition products

No.	Compound	λ max. (mμ)	E -value
1.	BQ B	312	668
		246-48	192
2.	BQ P	314-16	792
		272	122
		238	458
3.	BQ A	340	149
		314	270
		280-82	108

Table 57

No.	Compound	Energy gap (E ev.)	Resistivity at infinite temperature (ϱ_0 ohmcm.)
1.	BQ B	1.53	9.40×10^{2}
2.	BQ P	1.87	1.29×10^{1}
3.	BQ A	2.26	3.24×10^{-5}

Graphs of $\log_{10}\rho$ of these complexes vs. reciprocal temperature are plotted in fig. 33. Linear curves are observed as expected for equation (a). Hence the E and ρ_0 values are calculated from the curves and are presented in table 57.

$\text{Log}_{10}\rho_0$ of these complexes is plotted vs. E in fig.34. A straight line is obtained, satisfying equation (b)

$$\log_{10}\rho_0 = \log_{10}\gamma - \frac{\beta E}{2.3}$$

$$\text{i.e. } \rho_0 = \gamma \times e^{-\beta E} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(b)$$

where γ and β are constants. Values of γ and β are calculated as $10^{18.3}$ and 23.0 respectively. Hence the resistivities of the compounds over a range of temperature may be represented by the equation (c)

$$\rho = \rho_0 \times e^{\frac{E}{2kT}}$$

$$= \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(c)$$

Values of resistivities calculated at $30^{\circ}C$ and $150^{\circ}C$ using the above values of γ and β and known values of E for each compound are presented in table 58, and compared with the corresponding values of resistivities obtained from the graphs of $\log_{10}\rho$ vs. $10^3/T$. Close

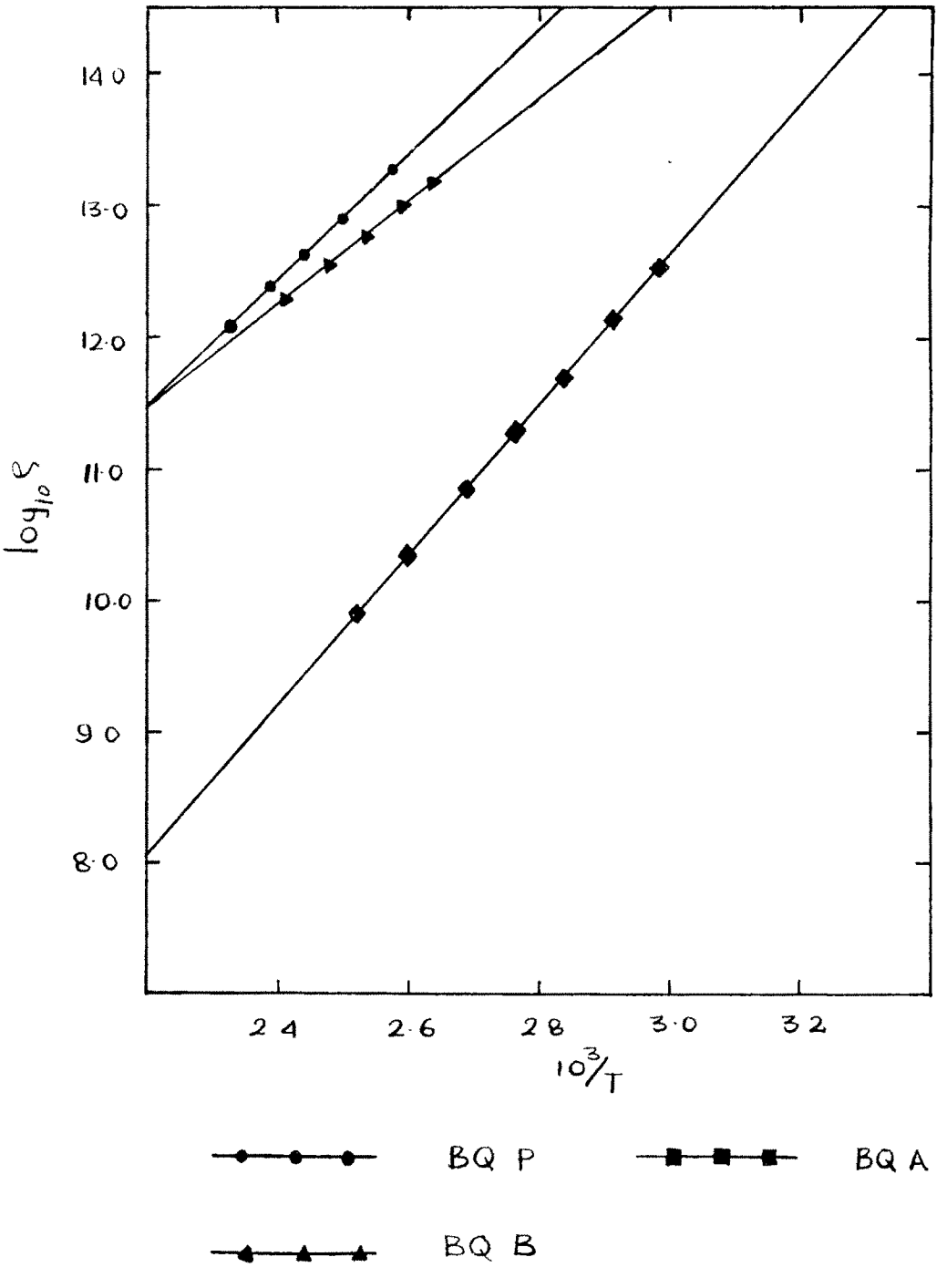


FIG. 33: Log RESISTIVITY VS. $10^3/T$ FOR ADDITION PRODUCTS.

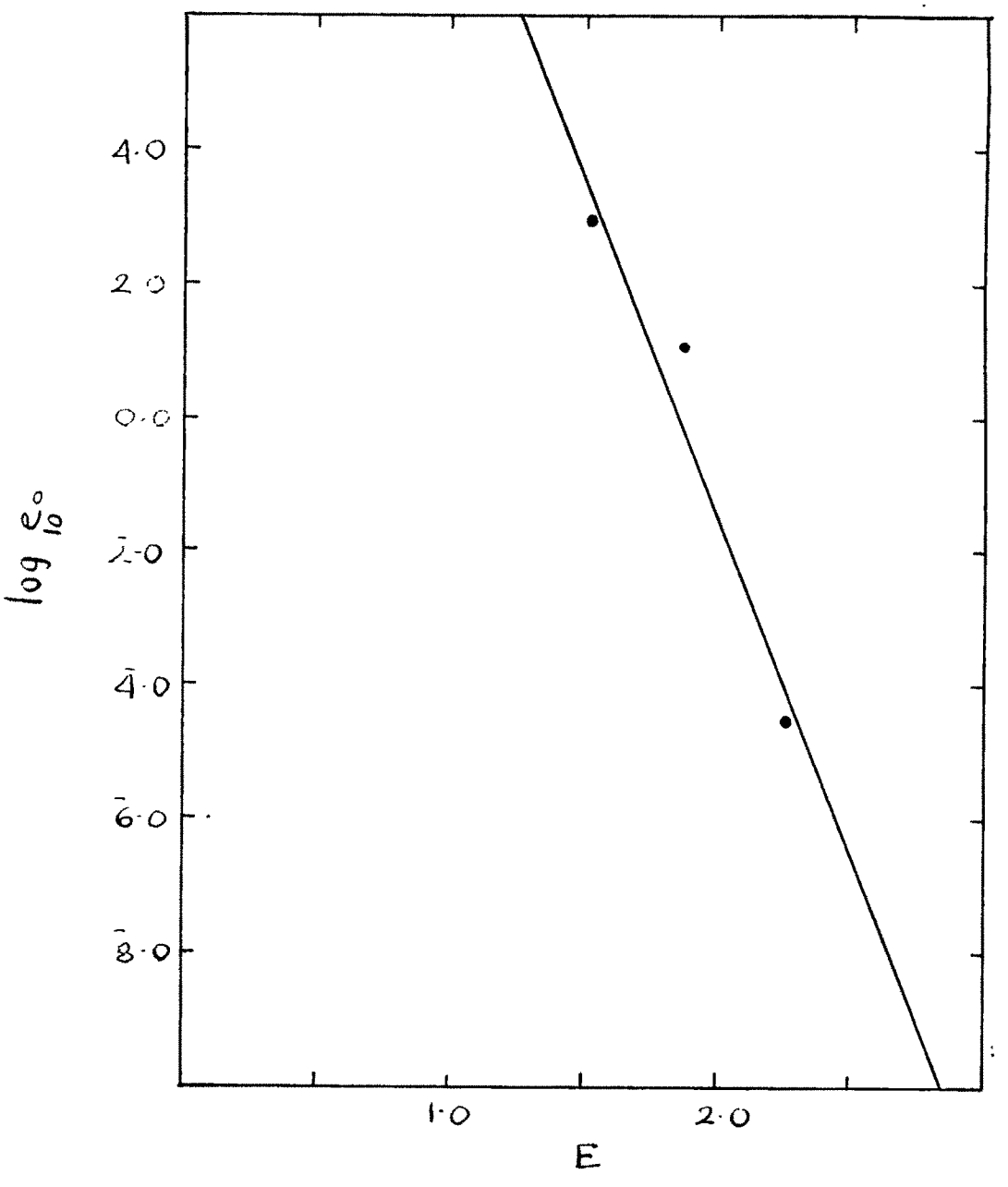


FIG 34: $Log_{10}\varepsilon_0$ vs. E FOR ADDITION PRODUCTS.

Table 58

Electrical resistivities of addition products at 30°C and 150°C

No.	Compound	$\log_{10}\rho$ at 30°C		$\log_{10}\rho$ at 150°C	
		observed (graph)	calculated (eqn. c or e)	observed (graph)	calculated (eqn. c or e)
1.	BQ B	15.78	15.75	12.10	12.13
2.	BQ P	16.75	15.18	12.25	10.76
3.	BQ A	14.35	14.53	8.95	9.19

agreement between the values is observed except for BQ P.

(vi) General :

There is a wide variation regarding the nature of the compounds investigated. Fe,Co and Ni are in octahedral ligand fields, whereas Cu is in square or square pyramidal ligand field. Organic complexes are considered to consist of one dimensional linear chains. Amines are present as " cations " in organic complexes, but as coordinated molecules in metal compounds.

Amine molecules are not considered to form impurity centres in these compounds. Hence conductivity is considered to be essentially intrinsic in all the cases.

While preparing the chelate polymers, it was observed that introduction of amines into the chelates during chain formation was difficult and often a few of the metal atoms of the chain would get coordinated to amines.

Further, when diamines are used, both amino groups may or may not be coordinated to metal atoms. Thus one amino group of the diamine was found coordinated to Co atom in the case of Co-chelate polymers and was considered to be coordinated to Fe and Cu atoms in the case of Fe and Cu chelate polymers. However, both amino groups of the diamine or two amino groups of a monoamine were found coordinated to metal atom in the case of nickel chelate polymers. This is reflected in the correlation between $\log_{10}\rho$ and E by the factor (1+F) or (1+F'). Factor (1+F) is useful when both amino groups of the diamine were

not coordinated to the metal atom and (1+F') when both amino groups were coordinated to metal atom. Further, when both the amino groups of the diamine or two amino groups of the monoamine are used, in bond formation, the size factor (n) of the amine ligand influences the relation between $\log_{10}\rho$ and E.

It is possible to correlate $\log_{10}\gamma$ or β with the atomic numbers of metal atoms. When graphs of $\log_{10}\gamma$ or β vs. atomic number are plotted (fig. 35), curves are obtained which have the same nature as the CF stabilisation energy curves. Thus metal atoms appear to have a definite influence on the conduction process in chelate polymers.

When the values of E of aquo polymers (BQCo, BQNi, BQCu and BQFe) are compared, we find they are increasing in the order,

$$BQCo < BQCu < BQFe < BQNi$$

For the ammino polymers, a generalised equation (f) showing the relation between ρ_o and E for various metal chelate polymers be written as

$$\rho_o = \gamma^{Z} \times e^{-Z\beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots (f)$$

where β and γ are constants depending on the nature of the metal atom in the chelate polymer and Z will be a factor depending on the mole fraction and size of the amine ligand and metal atom. It has been found that for "aquo" chelate polymers, the equation (b) is satisfactory.

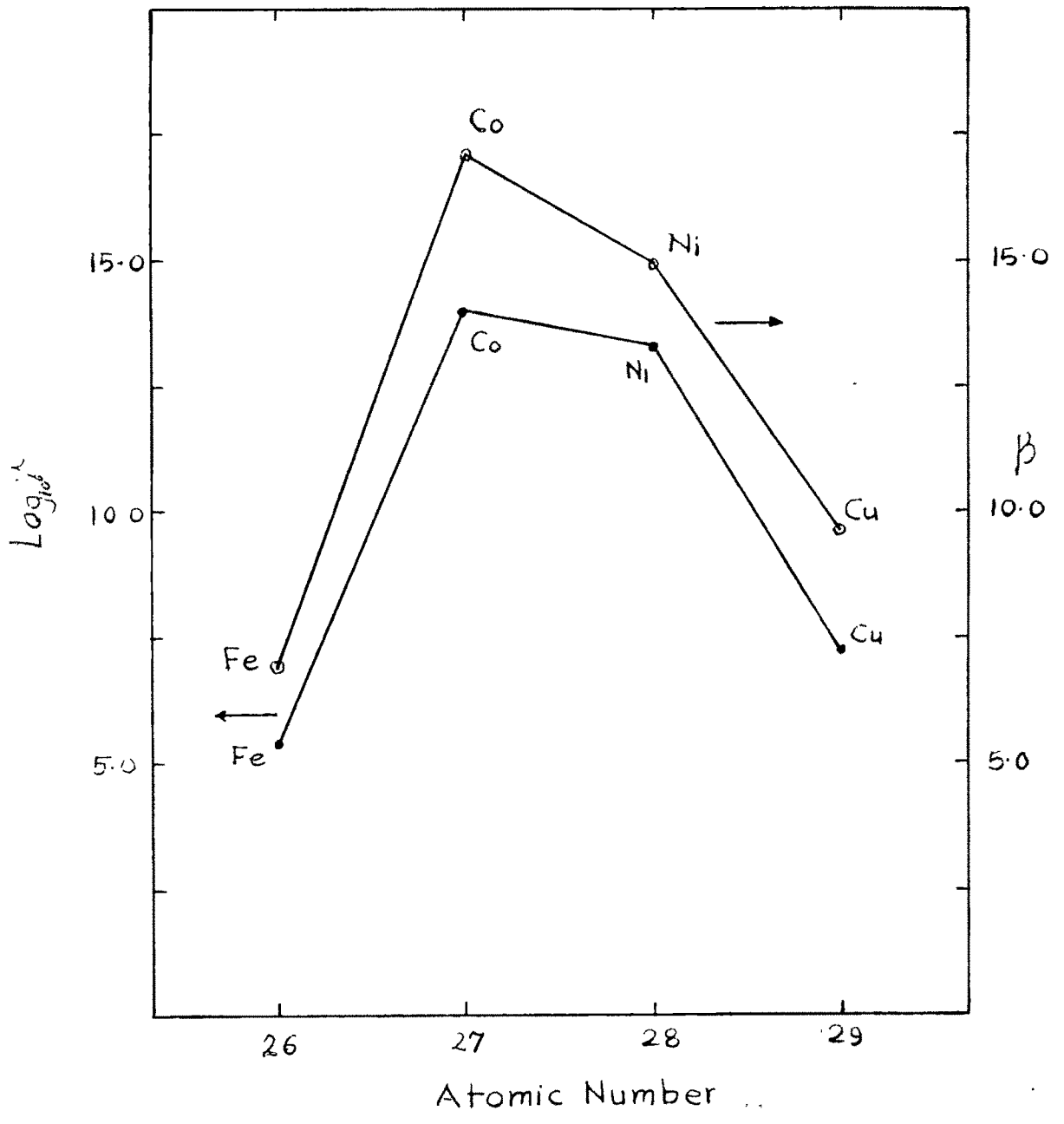


FIG. 35: $Log_{10}\gamma$ OR β VS ATOMIC NUMBER.

$$\rho_o = \gamma \times e^{-\beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (b)$$

It appears that this is a special case of a generalised equation (g)

$$\rho_o = \gamma \times e^{-U \beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (g)$$

where U would be a correlation factor and would depend primarily on the nature of the ligand.

The equation (g) can be treated for chelate polymers obtained from various quinonoid and non-quinonoid ligands. For that purpose, the values of β and γ obtained from the studies of chelate polymers of 2,5-dihydroxy-p-benzoquinone may be considered applicable to the study of chelate polymers of other ligands. Use of these values will lead to the determination of the correlation factor (U). A constant value of (U) will be anticipated for the chelate polymers of the same ligand and also for the chelate polymers of similar ligands. This has been attempted in subsequent investigations and reported in the following pages.

III. 2. <u>1,4-Dihydroxy naphthoquinone (naphthazarin) and its transition metal chelate polymers</u> :

Underwood, Toribara and Neuman[263] found from spectroscopic studies at different pH by continuous variation method that two complexes were formed by naphthazarin(NQ) with Berryllium corresponding to the ratios of 1 : 1 and

2 : 1. The reaction has been investigated for the detection of Be by Mustafin and Kul'berg[264] and for the colorimetric determination of Be by Przheval'skii, et al[265] and Karanovich[266].

Moeller and Tecotzky[267] found from spectroscopic studies by Job's method that rare earth metals, titanium and thorium formed complexes with NQ wherein the ratio of metal to NQ was 1 : 2 ; they also investigated the use of NQ as analytical reagent for Be.

Mangini and Stratta[268] prepared Cu (II), Ni(II) and Co(II) chelate polymers of NQ wherein the ratio of metal to ligand was found to be 1 : 1. Bailes and Calvin[269] prepared Co(II) chelate polymer of NQ with two molecules of water and studied its oxygen-carrying properties. Bottei and Gerace[270] prepared chelate polymers of Co(II), Ni(II), Cu(II), Zn(II) and Be(II) with NQ and studied their IR spectral and thermal properties.

Recently Akiyama and Mizutani[271] prepared Cu chelate polymer of NQ and studied its electrical resistivity.

We have prepared the chelate polymers of Co(II) and Cu(II) with NQ. The magnetic moments of the chelate polymers calculated from the magnetic susceptibilities are presented in table 59(a) and plots of $\log_{10}\rho$ of these polymers vs. reciprocal temperature are given in fig.36.

(a) Cobalt chelate polymer of naphthazarin(NQCo) :

From the analyses of NQCo, the ratio of metal to ligand is found as 1 : 1 ; hence the chelate polymer is

Table 59

Magnetic moments of transition metal chelate polymers of Naphthazarin and Quinizarin

No.	Compound	Molar magnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $X_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
			(a)	
1.	NQCu	1870	1980	2.21
2.	NQCo	10440	10560	5.09
			(b)	
1.	AQCu (Am)	2160	2300	2.37
2.	AQCu (Ac)	2090	2220	2.33
3.	AQCo (Ac)	9690	9830	4.92

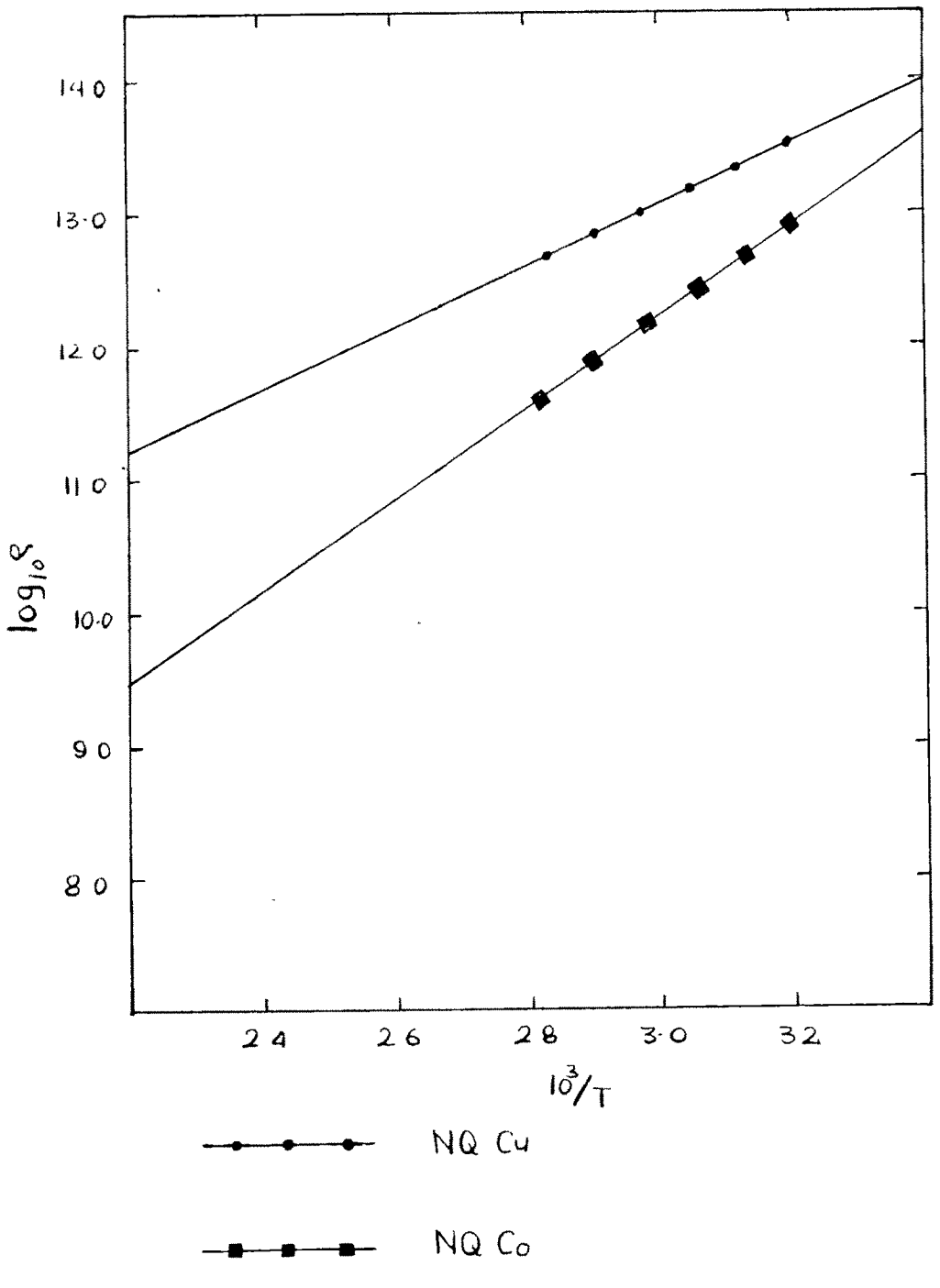
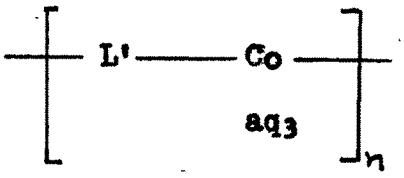


FIG 36: Log RESISTIVITY vs $10^3/T$ FOR. CHELATE POLYMERS OF NAPHTHAZARIN.

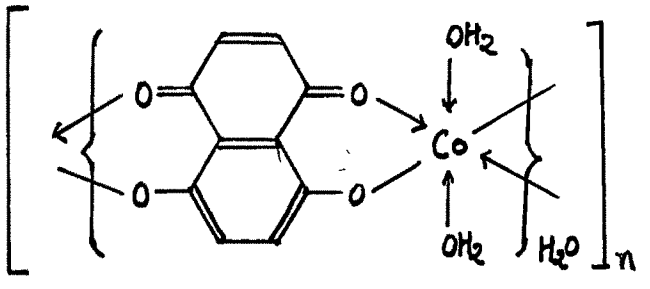
represented as a linear polymeric chain (29)



(29)

where $L'H_2$ represents naphthazarin.

Magnetic moment of NQCo per cobalt atom is found to be 5.09 B.M., indicating octahedral nature of the chelate polymer. The monomer may therefore be represented as a trans octahedral one (30).



(30)

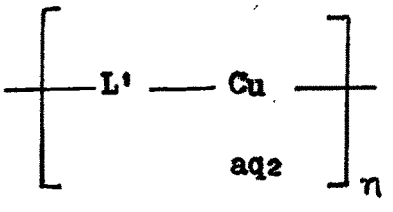
Bottei and Gerace suggested that cobalt complex is octahedral in which NQ and Co alternate to form a linear chain with the water molecules occupying the remaining two trans positions. The thermal investigations (TGA) showed that % loss in water was greater than would correspond to the presence of two water molecules and it was attributed to the presence of adsorbed water in the complex. Further, they also suggested from IR spectroscopic studies that NQ was present as an end-molecule in the polymeric chain.

Plot of $\log_{10} e$ vs. reciprocal temperature is linear as expected for the equation (a). From the graph

the values of E and log $_{10}$ ϵ_{max} are calculated as 1.36 ev. and 1.9 respectively. On substituting these values in the equation (g), the value of the correlation factor U is calculated as 1.19.

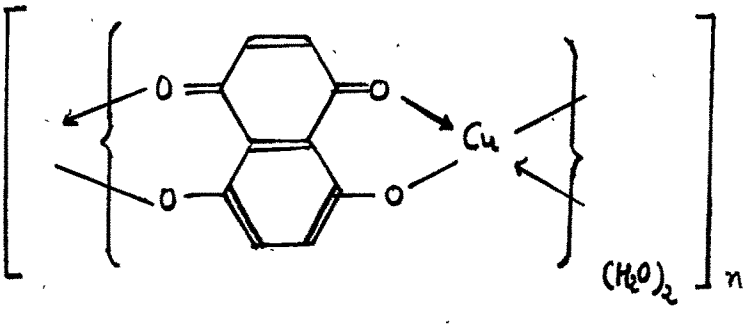
(b) Copper chelate polymer of naphthazarin (NQCu) :

From the analysis of NQCu, the ratio of metal to ligand is found as 1 : 1 ; hence the chelate polymer is represented as a linear polymeric chain (31).



(31)

Magnetic moment of NQCu per copper atom is found to be 2.21 B.M., indicating square planar nature of the monomer. Hence it may be represented as (32).



(32)

Bottei and Gerace found that although two water molecules were coordinated to cobalt in the Co-chelate polymer, no water was coordinated to Cu in copper chelate polymer.

Plot of $\log_{10} \rho$ vs. reciprocal temperature is linear as expected by the equation (a). The values of E and $\log_{10} \rho_0$ are calculated from the graph as 0.924 ev. and 6.05 respectively. On substituting these values in the equation (g), the value of the correlation factor U is found as 0.31.

Akiyama and Mizutani found that E for copper complex of NQ was close to that for NQ but that the conductivity of the complex was greater than that for NQ.

(c) General :

Values of E of the chelate polymers of NQ are increasing in the order,

Cu < Co

Value of U is found to be 1.19 (and not 1.00) for Co-chelate polymer. Increase in value may be attributed to the increase in the number of fused rings or in the number of π-bonds in the quinonoid ligand. The value of U for copper chelate polymer appears to be anomalous.

III.3. Dihydroxy anthraquinones and their transition metal chelate polymers :

Mustafin and Kul'berg[264] studied the analytical detection of Be with 1,4-dihydroxy anthraquinone (quinizarin) and its 5,8-dichloro derivative. Przheval'skii et al[265] developed colorimetric method for the detection of Be with quinizarin (AQ) and its 5,8-dichloro derivative.

White, Haffman and Magee[272] studied the fluorescence emision spectra, fluorescence excitation spectra and absorption spectra of Be complex with AQ. Fletcher[273] utilised Be-AQ system to study the performance of a filter fluorometer. White, Ho and Weimer[274] compared the absorption and fluorescence spectra of Al,Be,Th,Zr,B and Li with AQ.

Suemitsu[275] found from spectroscopic studies by Job's method that Mg formed a chelate polymer with AQ wherein the ratio of metal to ligand was 1 : 1. Korenman, Kurina and Emelin[276] investigated the colour reaction of Ge with AQ and 1,5-dihydroxy anthraquinone (anthrarufin) (AQR).

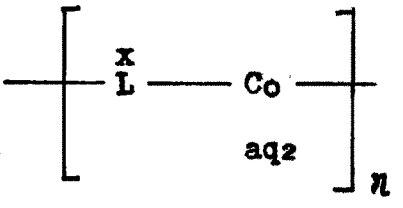
Flumiani and Bajic'[277] prepared Cu(II) chelate polymers of AQ and AQR. Knobloch and Ranscher[278] prepared chelate polymers of Cu(II) and Ni(II) with AQ and studied their IR spectra. Korshak and coworkers[279] (i) prepared chelate polymers of AQ with Mn(II), Co(II),Ni(II),Cu(II), Zn(II) and Cd(II) and studied their thermomechanical properties, crystal structures and approximate molecular weights, (ii) prepared homogeneous chelate polymers of AQ with Be,Mg and Ca and copolymers of AQ and 4,4'-bis (acetoacetyl) diphenyl ether with Be,Mg,Mn,Co,Ni,Cu and Zn and studied their magnetic properties. Slinkin,Dulov and Rubinstein[280] investigated the catalytic properties of chelate polymers of AQ with Mn,Co,Ni,Cu and Zn and found that (i) Zn and Co polychelates showed no catalytic activity and (ii) with other polychelates, the activity was $Cu^{2+} > Mn^{2+} > Ni^{2+}$.

Inoue and coworkers[122] prepared chelate polymers of AQ and AQR with Fe(II),Co(II),Ni(II),Cu(II),Zn(II), Sn(II),Pb(II) and studied their heat resistivities and electrical conductivities.

We have prepared the chelate polymers of AQ with Co(II) and Cu(II) and of AQR with Co(II),Ni(II) and Cu(II). The magnetic moments of these chelate polymers are presented in table 59(b) and plots of $\log_{10} \varrho$ vs. reciprocal temperature are shown in figs. 37 and 38.

(a) Cobalt chelate polymer with quinizarin : (AQCo):

From the analysis of AQCo, the ratio of metal to ligand is found as 1 : 1 ; hence it is represented as a linear polymer (33)



(33)

where $\overset{x}{LH_2}$ represents quinizarin.

The magnetic moment of AQCo per Co-atom is calculated as 4.92 B.M., indicating octahedral structure. Hence the monomeric chelate may be represented as a trans octahedral one (34)

Korshak and coworkers have suggested from the studies of magnetic moment that Co(II) chelate polymer with AQ would be octahedral involving sp^3d^2 hybrid orbitals.

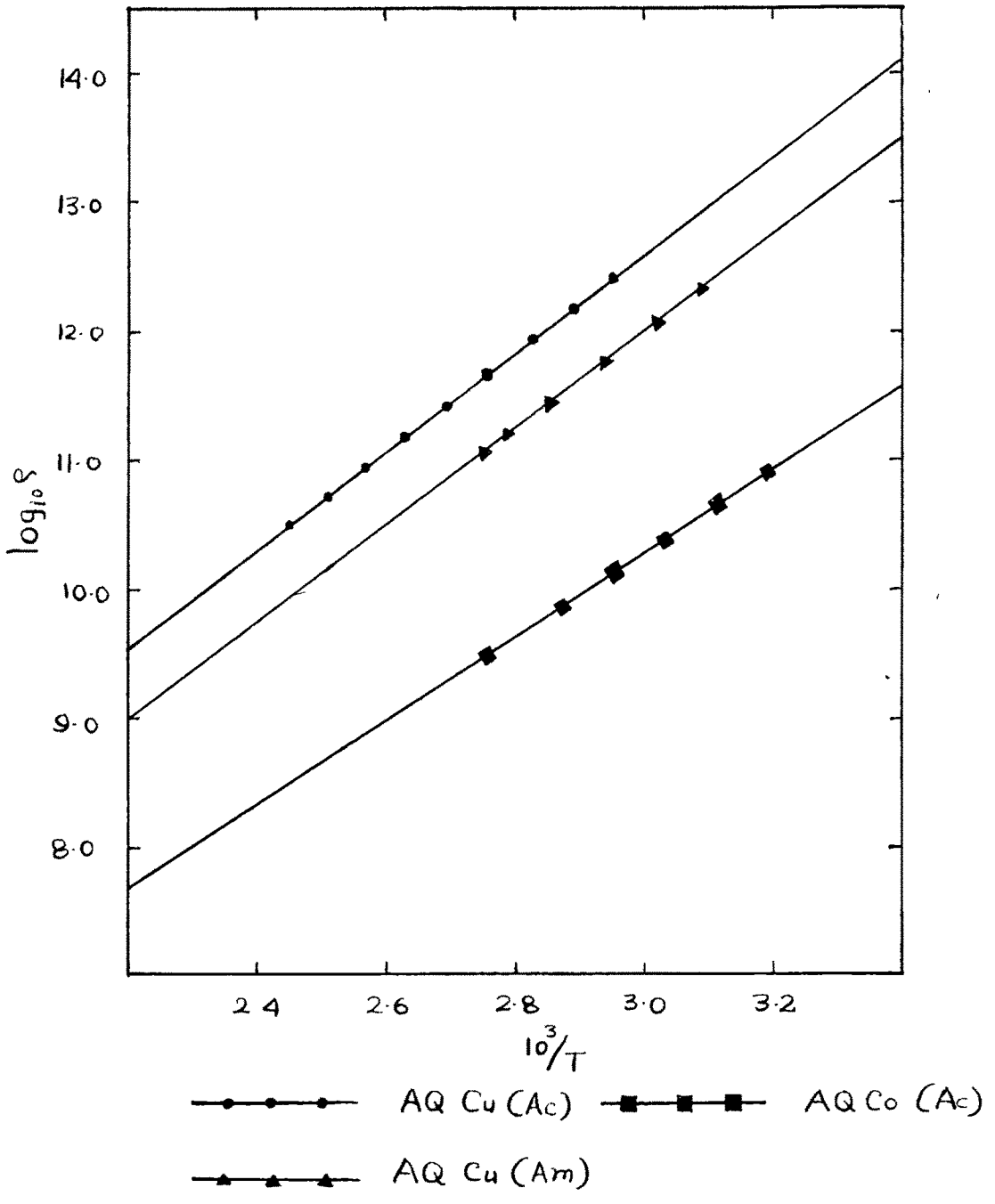


FIG. 37: Log RESISTIVITY vs. $10^3/T$ FOR CHELATE POLYMERS OF QUINIZARIN.

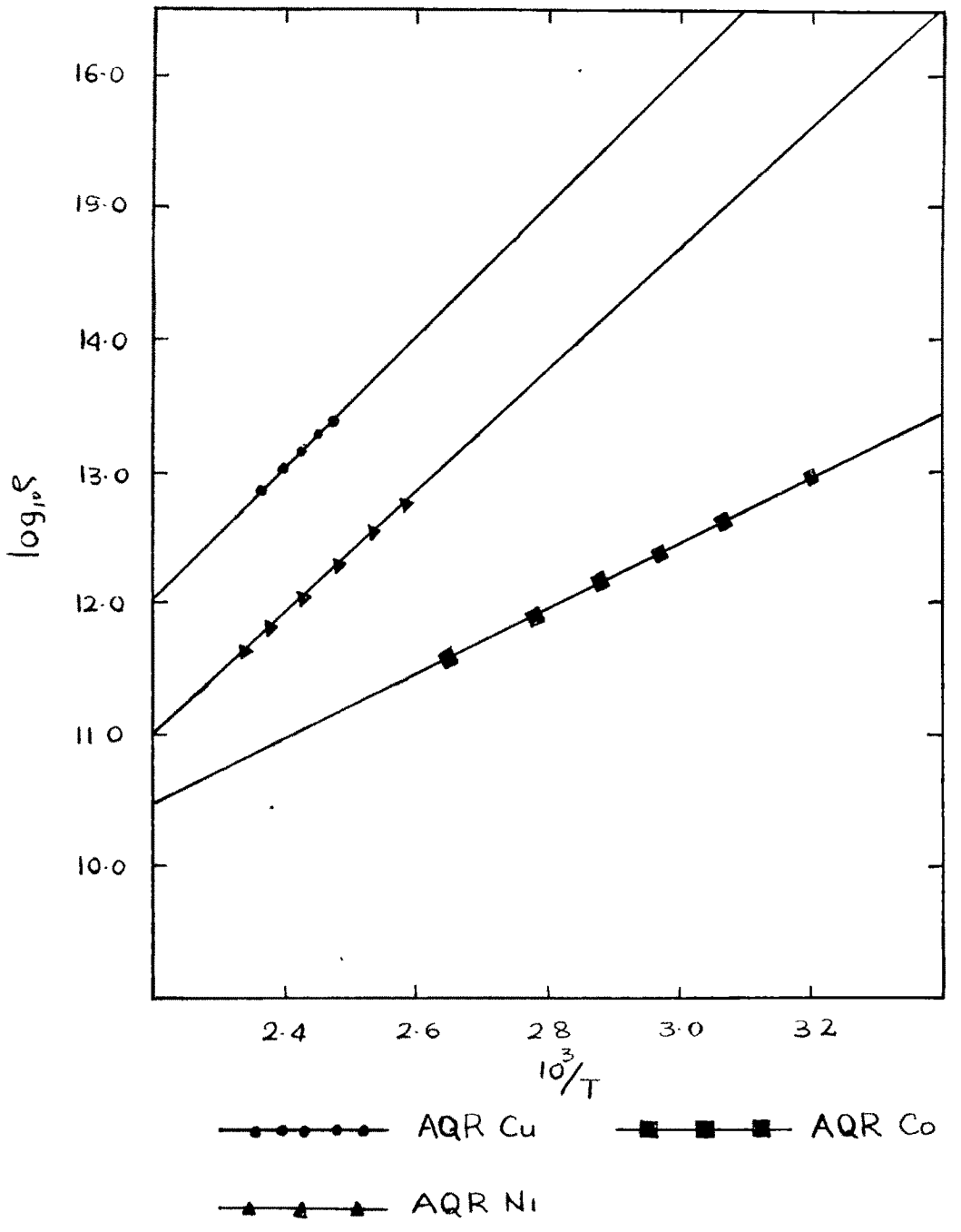
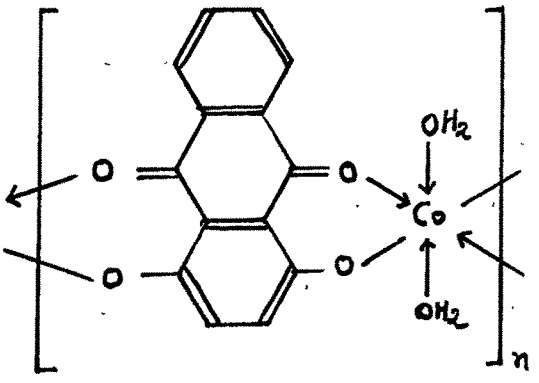


FIG. 38: Log RESISTIVITY vs. $10^3/T$ FOR CHELATE POLYMERS OF ANTHRARUFIN.

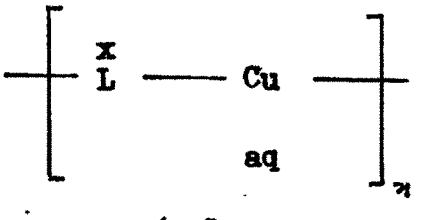


(34)

Plot of $\log_{10}\rho$ vs. reciprocal temperature is linear as expected for the equation (a). The values of E and $\log_{10}\rho_0$ are calculated from the graph as 1.28ev and 0.60 respectively. When these values are substituted in the equation (g), the value of the correlation factor U is found to be 1.40.

(b) Copper(II) chelate polymers with quinizarin :(AQCu):

Copper polychelates were prepared under different conditions:(i) in presence of ammonia and (ii) in presence of acetic acid. The analysis of both polychelates gave the ratio of metal to ligand as 1 : 1. Hence they may be represented as a linear chain (35)



(35)

The magnetic moments of these polychelates are found to be 2.37 B.M. and 2.33 B.M. respectively. Korshak and coworkers have suggested sp^2d hybridisation for

the bonding orbitals of copper in the polychelate from magnetic studies.

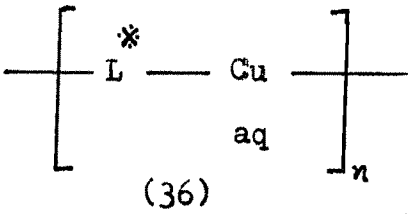
The plots of $\log_{10}\varrho$ vs. reciprocal temperature are linear as expected for the relation (a). The values of E and $\log_{10}\varrho_0$ are calculated from the graph as follows.

	E(ev)	$\log_{10}\varrho_0$
AQCu (Am)	1.485	0.75
AQCu (Ac)	1.48	1.30

When these values are substituted in the equation (g) the values of the correlation factor U for AQCu(Am) and AQCu(Ac) are found to be 1.04 and 0.96 respectively.

(c) Copper chelate polymer of anthrarufin: (AQRCu):

From the analysis of AQRCu the ratio of metal to ligand is found to be 1:1 ; hence it is represented as a linear polymer (36)



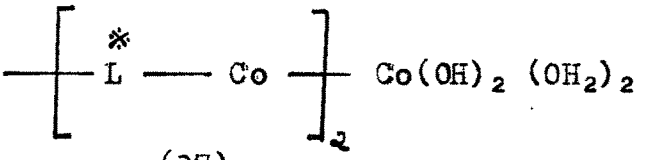
(36)

where $\overset{*}{L}H_2$ represents anthrarufin molecule.

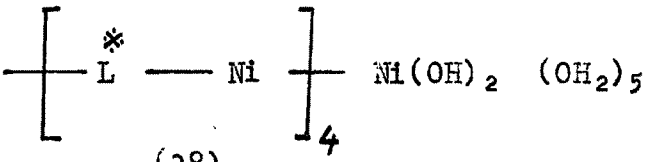
Plot of $\log_{10}\varrho$ vs. reciprocal temperature is linear as expected. From the graph are calculated the values of E and $\log_{10}\varrho_0$ as 1.99 ev. and 0.93 respectively. When these values are substituted in the equation (g) the value of the correlation factor U is found to be 0.76.

(d) Cobalt and nickel chelate polymers of anthrarufin : (AQRCo and AQRNi) :

The analysis of these polymers indicate that (i) the degree of polymerisation of these polymers is low and (ii) the metal is the end group in the polymeric chain. They may be represented as (37 and 38)



(37)



(38)

Plots of $\log_{10} \rho$ vs. reciprocal temperature are linear as expected. From the graphs are calculated the values of E and $\log_{10} \rho_0$ as follows.

	E(ev)	$\log_{10} \rho_0$
AQRCo	0.99	4.97
AQRNi	1.83	0.81

When these values are substituted in the equation (g) the values of the correlation factor U for AQRCo and AQRNi are found to be 1.22 and 1.05 respectively.

(e) General :

The values of E for the chelate polymers of AQ and AQR are increasing in order;

AQ : Co < Cu

AQR : Co < Ni < Cu

It may be noted here that the degree of polymerisation of Co and Ni chelate polymers of AQR is low.

The value of U for AQCo is 1.40 and may be related to the number of fused rings or the number of π-bonds in the ligand. The value of U for AQRCo, however, is somewhat low as its anticipated value would correspond to that for AQCo . It may be attributed mainly to the low value of the degree of polymerisation of AQRCo .

A graph of the correlation factor vs. the number of π-bonds in the ligand for the cobalt chelate polymers of BQ, NQ and AQ is a straight line (fig.39). Hence,

$$U = \omega\pi + Z \qquad \text{.....(h)}$$

where ω and Z are constants and π represents the number of π-bonds per Co-atom. If it is assumed that for the Co-chelate polymers of low degree of polymerisation, the presence of metal atom or ligand as the end-molecule and the coplanarity of the metal and ligand would influence the effective numbers of π-bonds per metal atom along a plane, explanation can be put forth for the low value of U for such polymers. Thus for AQRCo, the degree of polymerisation can be calculated from analysis as two, with Co-atom as the end-group ; hence the effective number of π-bonds per Co-atom along a plane would be 5.33 ; and

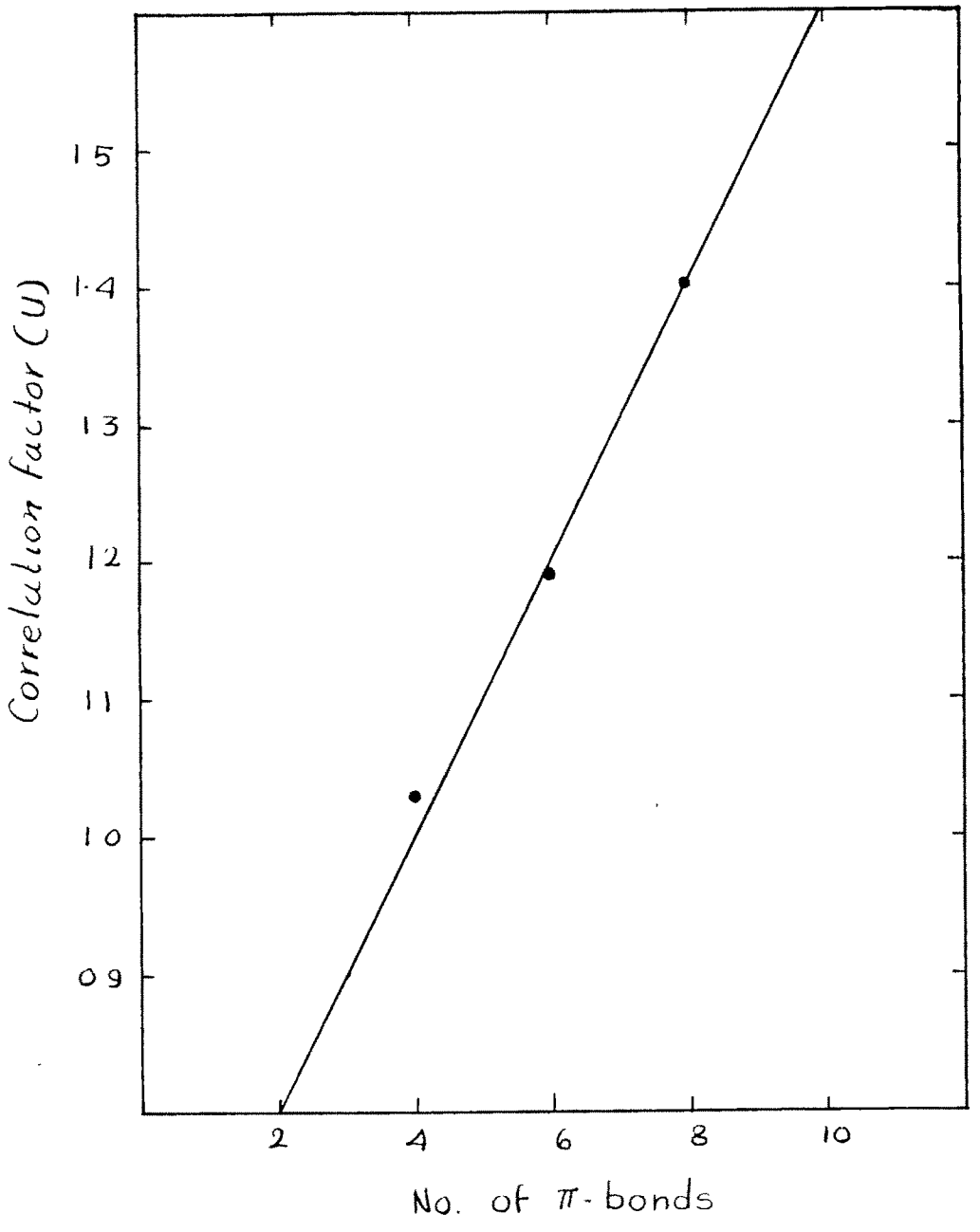


FIG. 39: CORRELATION FACTOR (U) VS. NO. OF π-BONDS.

the value of U would be 1.13. If the above graph (fig.39) is considered the known value of U (i.e. 1.22) will suggest the effective number of π-bonds per Co-atom as 6 and the degree of polymerisation to be 3. Thus the effective number of π-bonds per Co-atom along a plane appears to be an important guide in fixing the value of U.

In the case of nickel chelate polymers, the value of U does not change appreciably with the change in the number of fused rings or the number of π-bonds in the ligand.

The values of U for copper chelate polymers are not constant and are also not changing as in the case of cobalt chelate polymers ; very low values of U are found for NQCu and AQRCu.

For further comparison other ligand systems which may or may not have apparent resemblance to quinonoid ring system are now considered.

III.4. 1,5-Disubstituted 2,6-dihydroxy naphthalene and their chelate polymers :

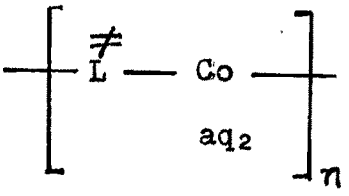
Dewar and Talati[121] prepared dioximes of 1,5-diacetyl and 1,5-diformyl derivatives of 2,6-dihydroxy naphthalene and their chelate polymers with Cu(II), Ni(II) and Pd(II) and studied their electrical conductivity.

We have prepared the Co(II) and Cu(II) chelate polymers of the dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene and also the Co(II) chelate polymer of

1,5-diamino-2,6-dihydroxy naphthalene. The plots of $\log_{10} e$ vs. reciprocal temperature are given in fig. 40.

(a) Cobalt chelate polymer of the dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene : (ONCo) :

From the analysis of ONCo the ratio of metal to ligand is found as 1:1 ; hence it may be represented as (39)



(39)

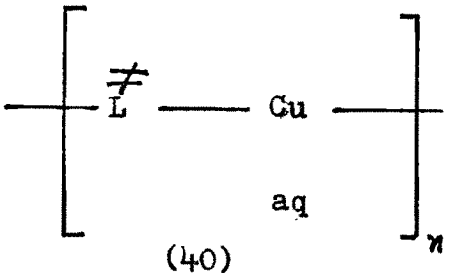
where $\overset{\neq}{L}H_2$ represents the dioxime ligand.

It is considered to have trans octahedral structure for the monomeric unit.

Plot of $\log_{10} e$ vs. reciprocal temperature is linear as expected. From the graph are found the E and $\log_{10} e_0$ values as 1.28 ev. and 1.85 respectively. When these values are substituted in the equation (g), the value of the correlation factor U is found to be 1.27.

(b) Copper chelate polymer of the dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene : (ONCu) :

From the analysis of ONCu, the ratio of metal to ligand is found as 1:1, hence it may be represented as (40).



(40)

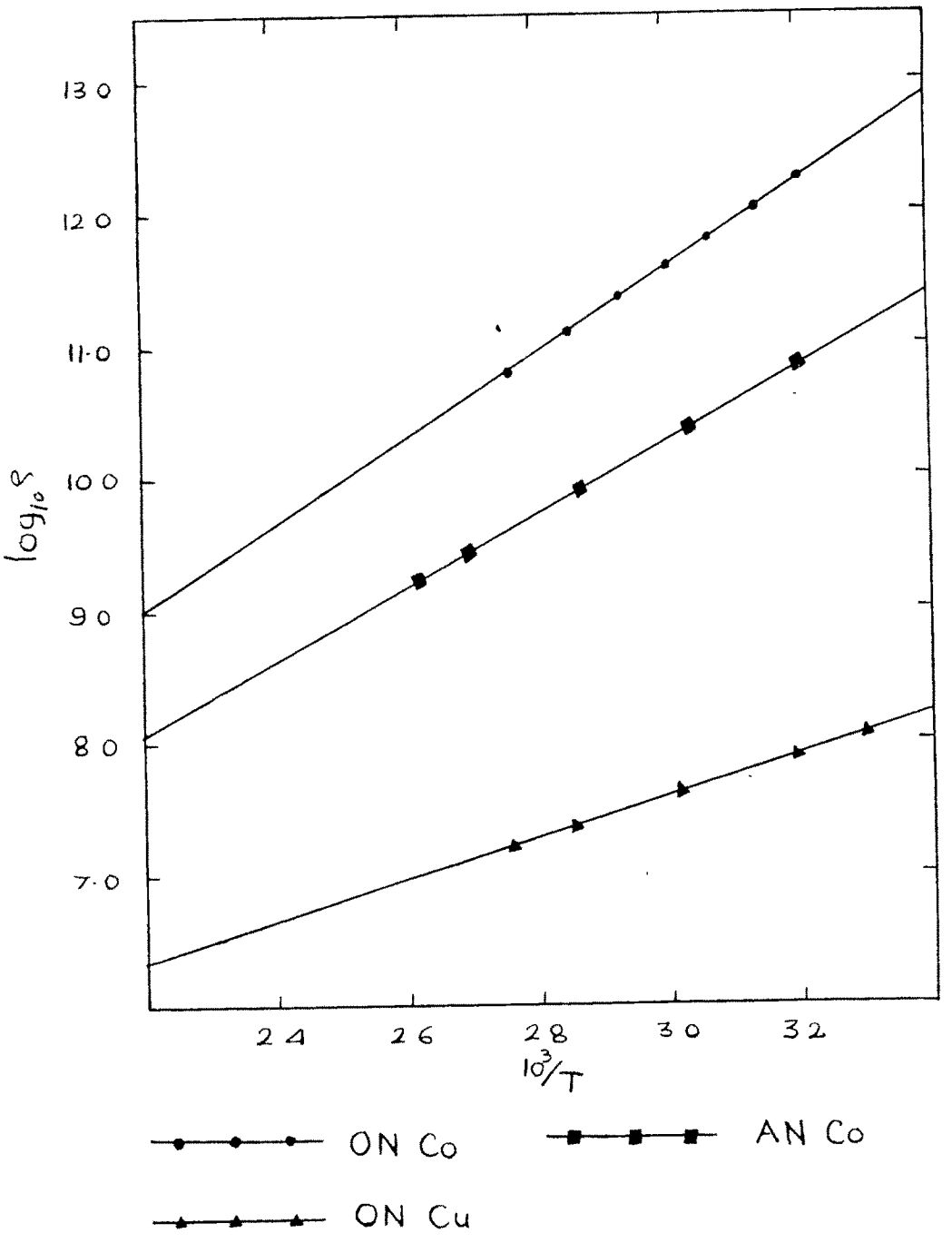
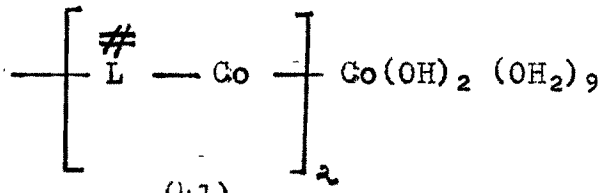


FIG 40: Log RESISTIVITY vs $10^3/T$ FOR ON Co, ON Cu AND AN Co.

Plot of $\log_{10} \rho$ vs. reciprocal temperature is linear as expected. From the graph are calculated the values of E and $\log_{10} \rho_o$ as 0.61 ev. and 1.97 respectively. Dewar and Talati have found the values of E and $\log_{10} \rho_o$ as 0.73 ev. and 1.72 respectively for the anhydrous copper chelate polymer. When the values of E and $\log_{10} \rho_o$ are substituted in the equation (g), the value of the correlation factor U is found as 2.06.

(c) Cobalt chelate polymer of 1,5-diamino-2,6-dihydroxy naphthalene : (ANCo) :

From the analysis of ANCo, it is found that (i) the degree of polymerisation is low, and (ii) metal atom is the end-group in the polymeric chain. Hence it is represented as (41)



(41)

where $L^{\#}H_2$ represents 1,5-diamino-2,6-dihydroxy naphthalene.

Plot of $\log_{10} \rho$ vs. reciprocal temperature is linear as expected. From the graph are calculated E and $\log_{10} \rho_o$ values as 1.10 ev. and 2.97 respectively. When these values are substituted in the equation (g), the value of the correlation factor U is obtained as 1.34.

III.5. 5,8-Dihydroxy quinoxaline and its chelate polymers :

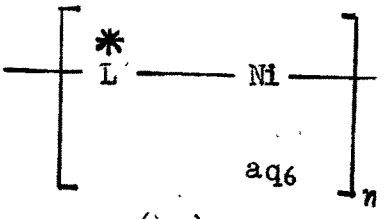
Kawai[281] investigated the colour reactions of Cu, Zn, Pb and Bi and precipitation reactions of Fe, Co, Ni, Cu and Zn with 5,8-dihydroxy quinoxaline (Q). Adachi[251] also

investigated the precipitation and colour reactions of various ions in aqueous and acetone solutions.

We have prepared Cu, Ni and Co chelate polymers of Q. The plots of $\log_{10}\varrho$ vs. reciprocal temperature are given in fig. 41.

(a) Nickel chelate polymer of 5,8-dihydroxy quinoxaline: (QNi) :

From the analysis of QNi, the ratio of metal to ligand is found as 1:1 ; hence the chelate polymer is represented as a linear polymeric chain (42),



(42)

where $\overset{*}{L}H_2$ represents 5,8-dihydroxy quinoxaline.

Plot of $\log_{10}\varrho$ vs. reciprocal temperature is linear as expected. From the graph are calculated the values of E and $\log_{10}\varrho_0$ as 1.46 ev. and 1.5 respectively. When these values are substituted in the equation (g), the value of the correlation factor U is found to be 1.24.

(b) Cobalt chelate polymer of 5,8-dihydroxy quinoxaline: (QCo) :

The analysis of this polymer indicates that (i) the degree of polymerisation is low and (ii) the metal is the end -group in the polymeric chain. It may be represented as (43).

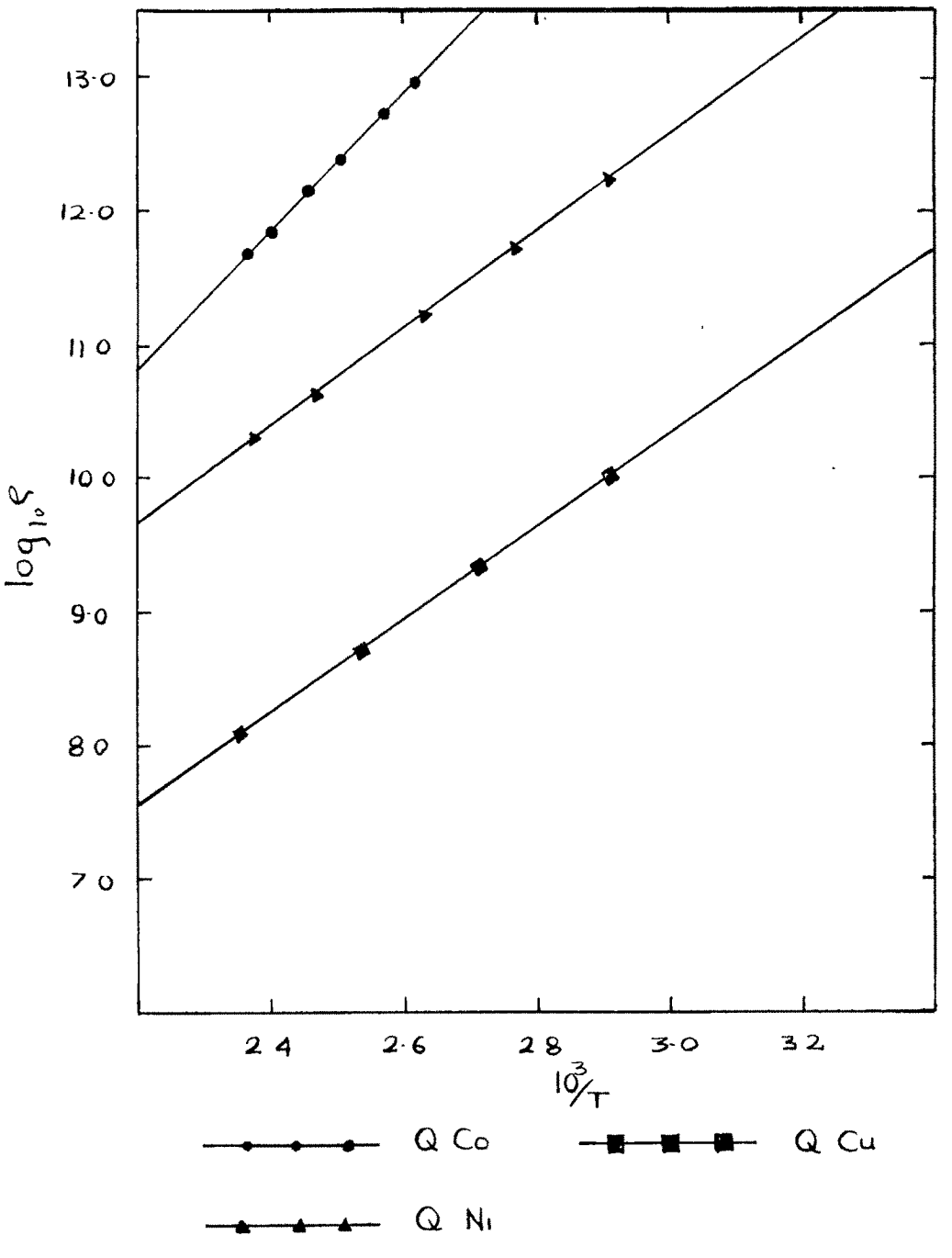
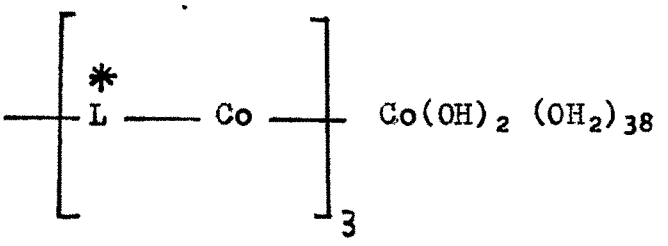


FIG 41 : Log RESISTIVITY Vs. $10^3/T$ FOR CHELATE POLYMERS OF 5,8 - DIHYDROXY QUINOXALINE.

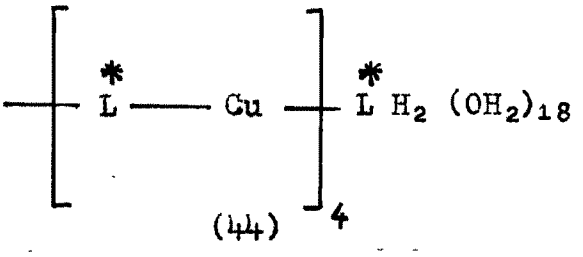


(43)

Plot of $\log_{10}\varrho$ vs. reciprocal temperature is linear as expected. From the graph are calculated the values of E and $\log_{10}\varrho_o$ as 2.06 ev. and $\bar{1}.37$ respectively. When these values are substituted in the equation (g), the value of the correlation factor U is found to be 0.95.

(c) Copper chelate polymer of 5,8-dihydroxy quinoxaline:(QCu):

The analysis of this polymer indicates that (i) the degree of polymerisation is low and (ii) the ligand is the end -molecule in the polymeric chain. It may be represented as (44).



(44)

Plot of $\log_{10}\varrho$ vs. reciprocal temperature is linear as expected. From the graph are calculated the values of E and $\log_{10}\varrho_o$ as 1.36 ev. and 0.025 respectively. When these values are substituted in the equation (g), the value of the correlation factor U is found to be 1.26.

(d) General :

The ligand ON can be represented in the quinonoid form. Hence the equation (h) relating U with the (effective) number of π-bonds per Co-atom should be applicable to ONCo. The value of U calculated using the equation (h) is 1.30, whereas that obtained from the equation (g) is 1.27.

The ligand AN cannot be represented in the quinonoid form ; and the value of U for ANCo appears to be much higher than anticipated for the effective number of π-bonds per Co-atom. Further the ligand Q, cannot be represented in the quinonoid form. Even then, the equation (h) appears suitable in calculating the value of U for QCo. The degree of polymerisation of QCo is low i.e. 3 ; hence the effective number of π-bonds per Co-atom along a plane may be calculated as 3.75 and the value of U would be 0.975. The value of U obtained using the equation (g) is 0.95. Thus for Co-chelate polymers a correlation factor is obtained which can be evaluated from the effective number of π-bonds per Co-atom along a plane in the polymer.

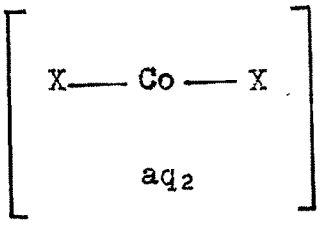
Non-polymeric Co and Ni complexes are investigated with a view to understand the nature of U for such complexes.

III.6. 4,6-Diacetyl resorcinol and its cobalt complex : (DARCo) :

Inoue et al.[122] prepared Zn,Cu,Ni,Co,Fe,Pb and Sn complexes of 2,4-diacetyl resorcinol and its dioxime and studied their electrical conductivity. Ramaswamy and Sen[282] studied Cu,Ni,Co and Zn chelate polymers of

2,4-diformyl resorcinol and Cu chelate polymer of resorcinol 2,4-dialdoxime. Bailes and Calvin[269] have reported the preparation of Co-chelate polymer of 4,6-diformyl resorcinol. Baker[283] studied 2,4-diacetyl and 4,6-diacetyl resorcinols. He showed that 2,4-diacetyl resorcinol is completely intramolecularly H-bonded, while 4,6-diacetyl resorcinol exhibits only partial intramolecular H-bonding ; IR spectrum of 4,6-diacetyl resorcinol showed two distinct CO frequencies corresponding to the normal and H-bonded CO groups.

We have prepared cobalt complex of 4,6-diacetyl resorcinol. On the basis of analysis, DARCo may be represented as (45)



(45)

where XH represents 4,6-diacetyl resorcinol.

Plot of $\log_{10} \epsilon$ vs. reciprocal temperature (fig.42) is linear as expected. From the graph are calculated the values of E and $\log_{10} \epsilon_0$ as 2.01 ev. and 1.75 respectively. When these values are substituted in the equation (g) the value of U is found to be 0.95. When this value of U is considered for equation (h), the effective number of π-bonds per Co-atom along a plane can be calculated as 3.5. Hence it can be suggested that the two ligand molecules are not coplanar and even one of the two CO groups is also out of plane of the ligand ring.

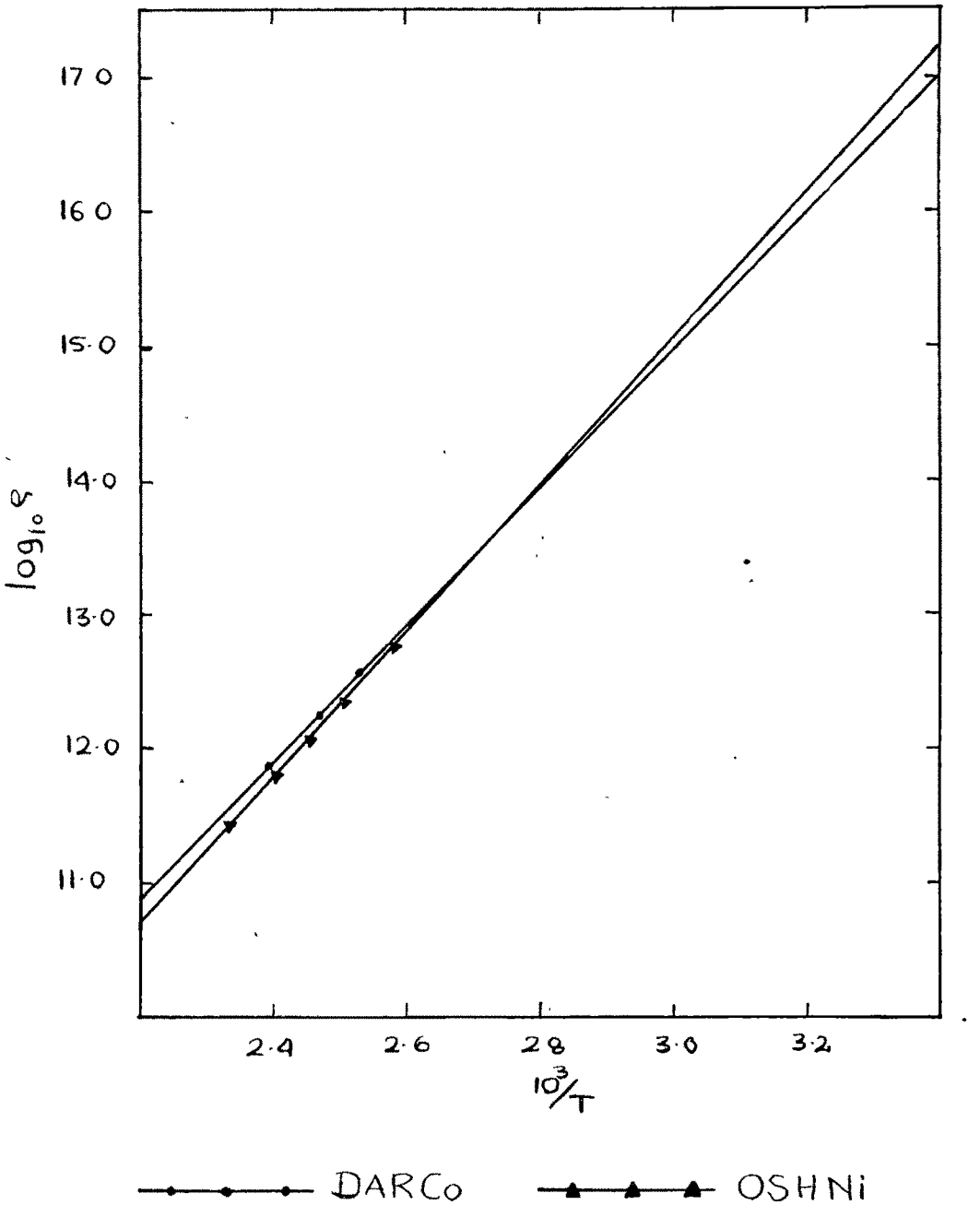
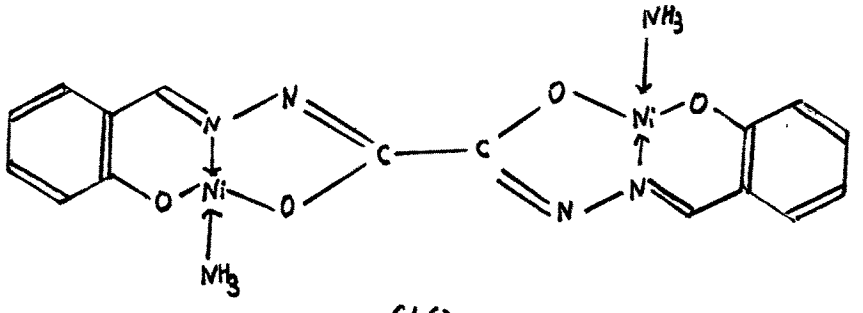


FIG. 42: Log RESISTIVITY vs. $10^3/T$ FOR DARCo AND OSHNi

III.7. Oxalyl bis (salicylidene hydrazide) and its nickel complex (OSH Ni) :

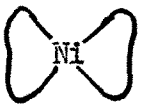
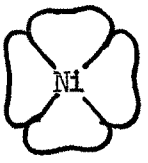
Sacconi[254] prepared nickel complex of oxalyl bis (salicylidene hydrazide) and represented it as (46) :



(46)

We prepared the nickel complex by the same method and obtained similar analysis for the complex OSH Ni.

The plot of $\log_{10}\epsilon$ vs. reciprocal temperature (fig.42) is linear as expected. From the graph are found E and $\log_{10}\epsilon_0$ values as 2.16 ev. and 2.73 respectively. When these values are substituted in the equation (g) the value of U is found to be 1.04. The results indicate that monomeric or polymeric nature of the complex does not affect the value of (U). It has been observed by us from the comparative studies of other Ni-complexes of aromatic and heterocyclic ligands that the value of U is influenced by the number of rings formed by the ligands with the Ni-atom. The values of U for the different systems, together with characteristic examples are as follows :

System	U	example	U (obs.)
	1.0	Ni BQ	0.98
		Ni AQR	1.05
	1.25	Ni salphen	1.20
		Ni salen	1.22
	1.50	Ni phthalo-cyanine	1.52

III.8. <u>The halogen adducts of the transition metal complexes of glyoximes</u> :

Bhat and coworkers[119] studied the semiconductivity behaviour of bis(dimethyl glyoximates) of nickel and palladium (DMGNi and DMGPd) . Thomas and Underhill[284] investigated the semiconductivity of the single crystals of DMGNi. Foust[285] prepared the bromine and iodine adducts of bis(diphenyl glyoximates) of nickel and palladium and studied the semiconductivity and other properties of the iodine adduct of bis(diphenyl glyoximato) nickel (DPGNi I).

We have prepared the bromine and iodine adducts of the bis(glyoximates) of Ni, Co and Cu and studied their electrical conductivity. The plots of $\log_{10}\rho$ vs. reciprocal temperature for the adducts over a small range of temperature are presented in figs. 43 and 44 and their magnetic moments are presented in table 60.

Co and Ni complexes of diphenyl glyoxime (DPGCo, DPGNi), Ni complex of dimethyl glyoxime (DMGNi) and

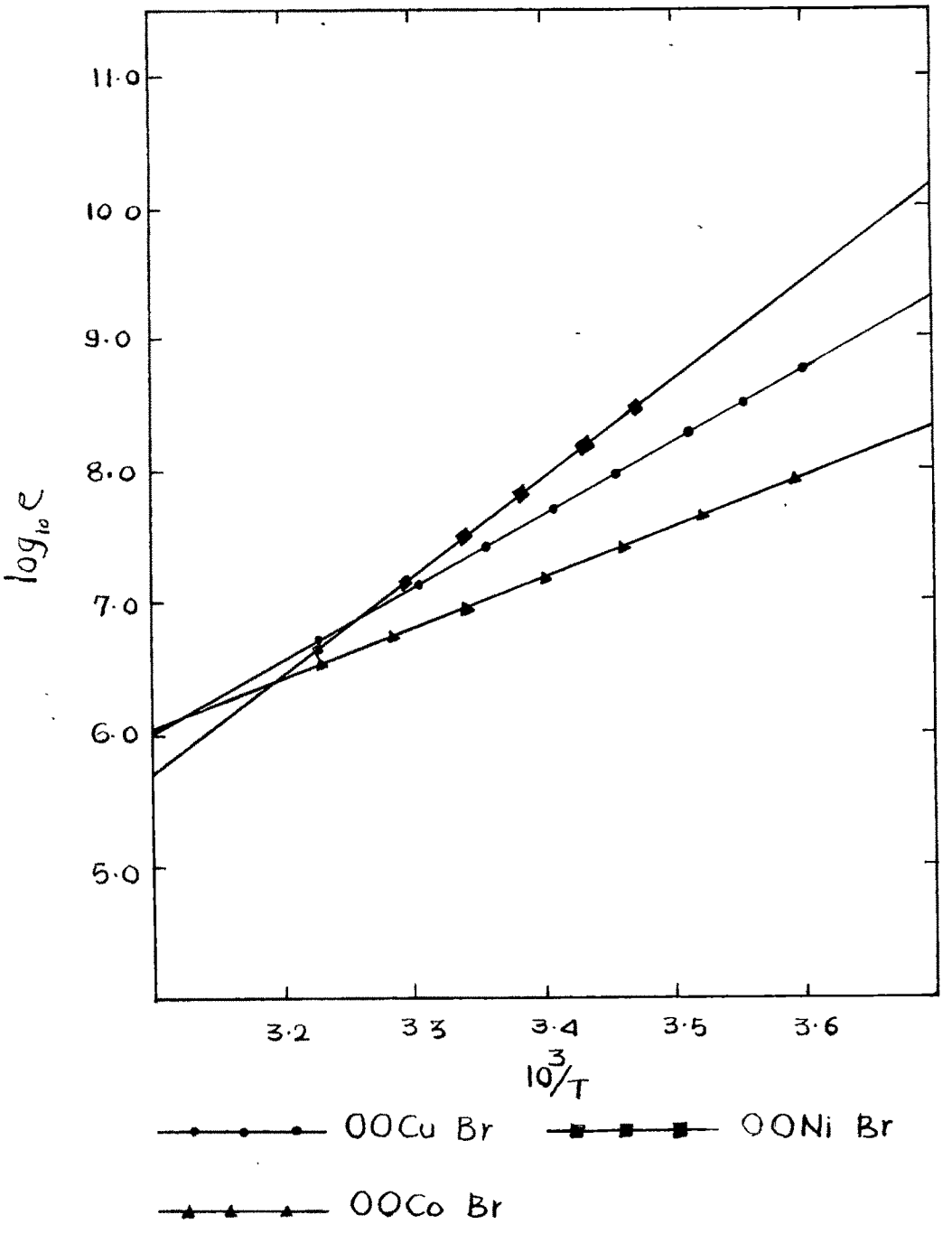


FIG. 43: Log RESISTIVITY vs. $10^3/T$ FOR HALOGEN ADDUCTS.

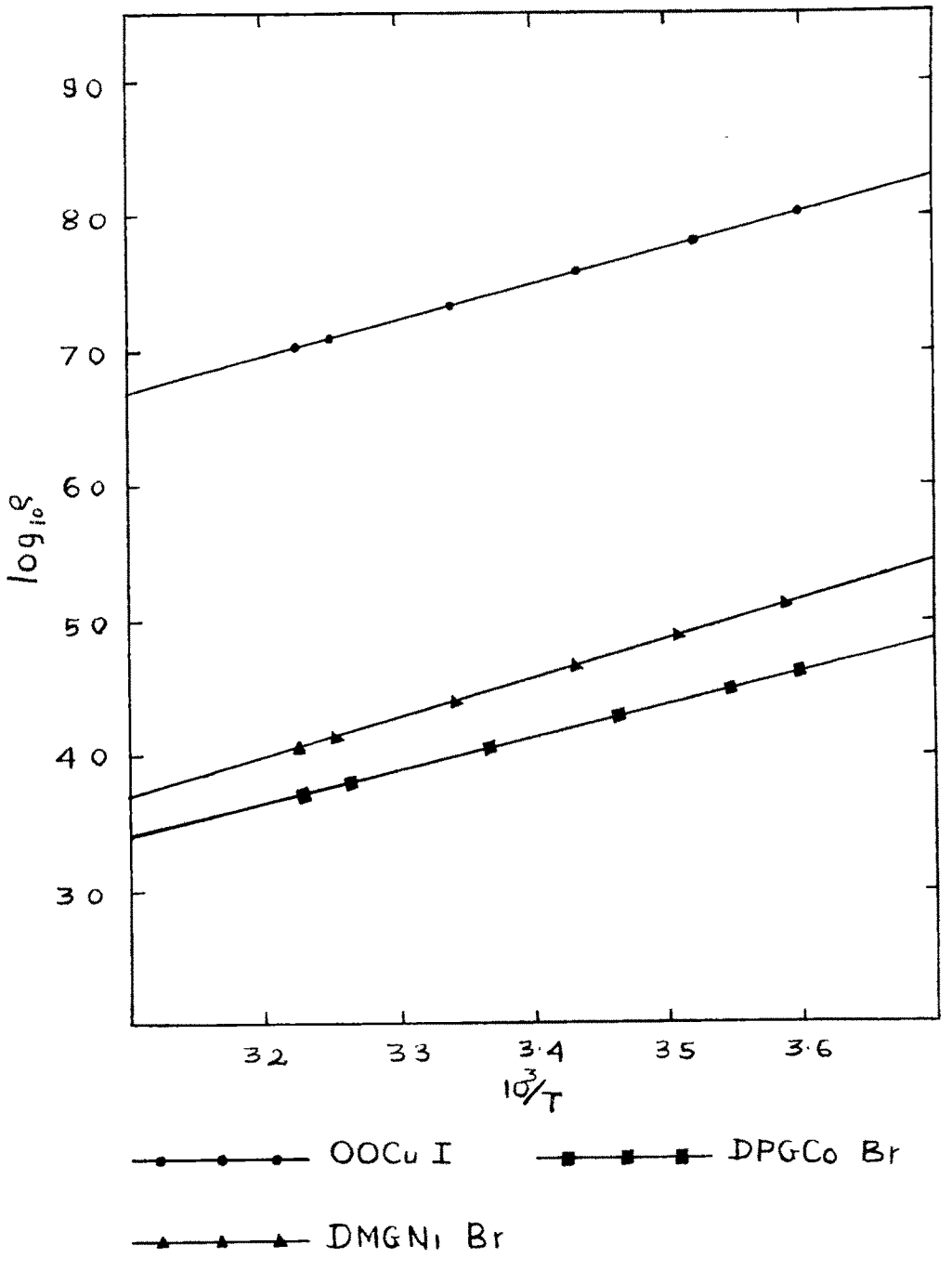


FIG. 44: Log RESISTIVITY vs. $10^3/T$ FOR HALOGEN ADDUCTS.

Table 60

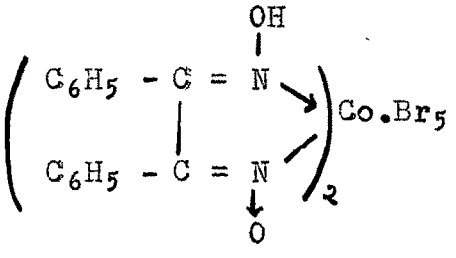
Magnetic moments of halogen adducts

No.	Compound	Molar magnetic susceptibility (per metal atom) $Xm \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $Xm' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1.	OOCu Br	2060	2340	2.40
2.	OOCo Br	2030	2440	2.45

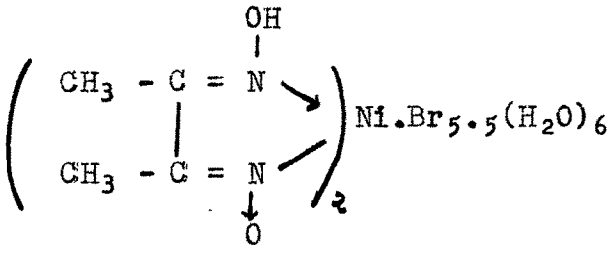
Cu,Ni and Co complexes of 2,3-dioxobutyranilide dioxime (OOCu,OONi,OOCo) were prepared by the known methods.

The bromine adducts of DPGNi and DPGCo were prepared in carbon tetrachloride,while the iodine adduct of DPGNi was prepared in benzyl alcohol. The bromine adducts of DMGNi,OOCu,OOCo and OONi were prepared in chloroform and the iodine adduct of OOCu was prepared in o-dichlorobenzene. The products DPGNi Br and DPGNi I are known and hence are not investigated further.

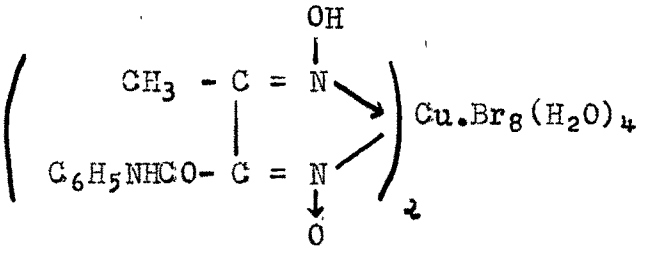
Large excess of bromine was used in all experiments. As a result, adducts containing large proportions of bromine were obtained. On the basis of analyses the products are formulated as



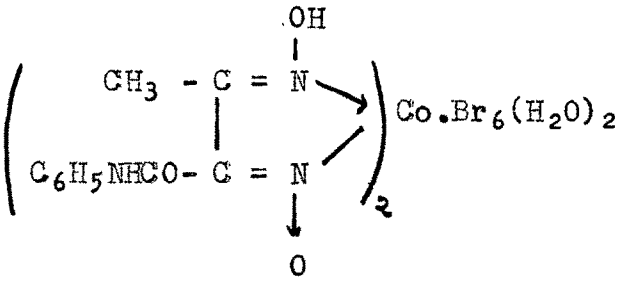
(47)



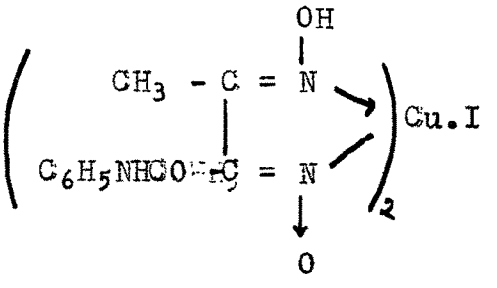
(48)


OH
CH3 - C = N
C6H5NHCO- C = N
O
2
Cu.Br8(H2O)4

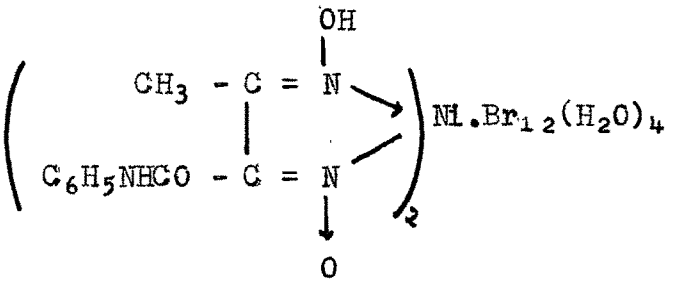
(49)


OH
CH3 - C = N
C6H5NHCO- C = N
O
2
Co.Br6(H2O)2

(50)


OH
CH3 - C = N
C6H5NHCO- C = N
O
2
Cu.I

(51)


OH
CH3 - C = N
C6H5NHCO - C = N
O
2
Ni.Br12(H2O)4

(52)

Foust studied in detail, the structure of DPGNi I. He suggested that it is an inclusion-type molecular complex stabilised by charge transfer interaction. He found from X-ray studies that I -atoms lie in channels which are parallel to DPGNi stacks.

OOCu I may be considered to have a structure similar to DPGNi I. In the case of bromine adducts, bromine may be present (i) as forming molecular complex,(ii) as anion and (iii) as impurity atoms. If bromine was present as anion, saline nature of the product would be observed and the metal ion would be present in the higher oxidation state. The magnetic studies showed that both Cu and Co are in bivalent state and are not oxidised to the tervalent state. Further, the products do not exhibit saline nature. Hence bromine is not considered to be present as an anion. Further, if bromine was present as impurity, it would have been washed off during the preparation. Hence all bromine atoms are considered to form inclusion - type molecular complexes, although different bromine atoms may not be present in the same way in the system.

The plots of $\log_{10} \varrho$ vs. $10^3/T$ are linear as expected. From the curves are calculated the values of E and ϱ_0 and are presented in table 61. The values of E for the adducts containing the same ligand and halogen are increasing in order.

$$Co < Cu < Ni$$

and for the adducts containing different halogens but the

Table 61

No.	Compound	Energy gap (E ev.)	Resistivity at infinite temperature (ρ_0 ohm.cm.)
1.	DPGCo Br	1.04	1.8×10^{-5}
2.	DMGNi Br	1.12	1.0×10^{-5}
3.	OOCu I	1.16	3.5×10^{-3}
4.	OOCu Br	2.24	4.5×10^{-12}
5.	OOCo Br	1.56	8.9×10^{-7}
6.	OONi Br	2.96	6.3×10^{-18}

Table 62

No.	Compound	Correlation factor (U)
1.	DPGCo Br	2.42
2.	DMGNi Br	2.51
3.	OOCu I	1.99
4.	OOCu Br	1.98
5.	OOCo Br	1.72
6.	OONi Br	1.58

same ligand, the value of E is increasing in order.

$$I < Br$$

The correlation factor (U) is calculated by substituting the values of E and ϵ_o for the different adducts in the equation (g) and are presented in table 62. Substituting these values of (U) in the equation (h), the effective number of π-bonds per Co-atom along a plane are calculated, as 18 for DPGCo Br and 11 for OOCo Br. The number of π-bonds calculated on the basis of their structures are 16 for DPGCo Br and 12 for OOCo Br. Thus the equation (h) appears to be applicable to the Co-complexes of different types.

III.9. General Discussion :

(a) Conjugation :

Eley[286] suggested that conductivity will be higher as the electrons become more delocalised and a ring system like benzene or a conjugated bond chain may be considered to behave like internal super conductor. Pohl, however, pointed out that such superconductivity would result only if the system contains appreciable density of unpaired electrons. Generally the conductivity rises as the amount of unsaturation increases.

Our investigations deal with chelate polymers of various metals and ligands. For cobalt chelate polymers, we find that the conductivity is increasing in order,

$$BQ < NQ < AQ$$

we have correlated this effect to the factor (U). However, in the case of copper chelate polymers, we find that conductivity is increasing in order,

$$AQR < AQ \sim NQ < BQ$$

The results indicate that factors other than conjugation are of greater importants in deciding the conductivity of the system.

(b) Metal :

Gooden[2] showed that copper chelates are less conducting than the corresponding nickel chelates of schiff bases. It is also observed that conductivities of metal substituted phthalocyanines[49] increase in order,

$$Cu < Ni < Co$$

and those of metal rubeanates[127] are increasing in order,

$$Co < Ni < Cu$$

We find that in the case of chelate polymers of Cu and Co, the conductivity shows a variation with the ligands as follows,

BQ: Cu > Co

NQ: Cu ~ Co

AQ: Cu < Co

ON: Cu > Co

Q : Cu > Co

(c) Anisotropy :

Conduction anisotropy[43,211,287] has been observed for phenanthrene, poly-iodides, layer compounds, free radicals, copper-phthalocyanine etc. The present investigations on conductivity were carried out using pressed powder. Hence the effect of anisotropy has been averaged out. If single crystal can be prepared and investigated, the influence of anisotropy can be evaluated. It is seen that, good correlations are possible in the case of cobalt chelate polymers ; but not in the case of copper chelate polymers. It may be suggested, therefore, that anisotropy may be exerting considerable influence on the conductivity of copper chelate polymers of different ligands.

(d) Long range order :

It is often considered that high degree of polymerisation of conducting units leading to long range order may improve upon the conductivity of the system. The degree of polymerisation obtainable in the case of conducting chelate polymers is often low and may have a value of less than 10. Long range order can give rise to carrier transport but is not essential to it. This short range order is found sufficient for conductivity considerations.

(e) Mobility :

Many, Harnik and Gerlich[288] suggested that a rough correlation exists between the mobilities and the

corresponding activation energies. The higher mobilities correspond, on the whole, to higher activation energies. Their results are generalised by the relation

$$\log \sigma_o \approx 10\, E' - 13$$

We find that a correlation exists between ϱ_o and E,

$$\varrho_o = \gamma \times e^{-U\beta E}$$

where U,β and γ are constants. We suggest that U,β and γ are not having the same value for different systems, but have different values, depending on the nature of the metal and the conjugated ligand system and on the mode of linkage. Values of β and γ have been established for cobalt and nickel chelate polymers ; and the factor (U) is related to the number of π- bonds per Co-atom in the case of cobalt chelates and chelate polymers and to the number of rings formed by the ligands with nickel atom in the case of nickel chelates and chelate polymers.