THERMODYNAMIC STABILITY OF METAL THIOACID COMPLEXES - A POLAROGRAPHIC STUDY

By

VINOD KUMAR

Thesis submitted to the Haryana Agricultural University in partial fulfilment of the requirements for the degree of:

MASTER OF SCIENCE

in

CHEMISTRY

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HISAR

1987

DEDICATED TO

VIRENDER AND KAMAL

WHOSE INSPIRATION AND COOPERATION

BROUGHT ME

HERE

UPTO

LIST OF ABBREVIATIONS

By	=	2,2' Dipyridyl
DME	=	Dropping mercury electrode
DPP	=	Differential pulse polarography
$(E_{\frac{1}{2}})$	=	Half-wave potential
K	=	Stability constant
K_c	=	Instability constant
M	=	Molar
mS	=	Milli second
TEP	=	2-(2-Thienyl)pyridine
TLA	=	Thiolactic acid
TP	=	Thioproline
TPA	=	2-Thiophene acetic acid
TSA	=	Thiosalicylic acid
V	=	Volts

CERTIFICATE - I

This is to certify that this thesis entitled, "Thermodynamic Stabilities of Metal Thioacid Complexes - A Polarographic Study" submitted for the degree of Master of Science in the subject of Chemistry to the Haryana Agricultural University, is a bonafide research work carried out by Shri Vinod Kumar under our supervision and no part of this thesis has been submitted for any other degree.

The assistance and help received during the course of investigation have been fully acknowledged.

P S Relan
Major Advisor

K. Kumar
Co-major Advisor

CERTIFICATE - II

This is to certify that the thesis entitled, "Thermodynamic Stabilities of Metal Thioacid Complexes - A Polarographic Study" submitted by Shri Vinod Kumar to the Haryana Agricultural University in partial fulfilment of the requirements for the degree of Master of Science in the subject of Chemistry has been approved by the Student's Advisory Committee after an oral examination on the same, in collaboration with an External Examiner.

External Examiner

Major Advisor

Co-major Advisor

Head of the Department

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Vinod Kumar

(VINOD KUMAR)

Hisar
November 3, 1987

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CHAPTER - I

INTRODUCTION

The multifarious research work done in the field of Coordination Chemistry during the last four to five decades has led to the recent extraordinary fast development not only in the field of Chemistry but also in other branches like biological sciences. The investigations include the studies on the conditions governing the formation of complex compounds, the interpretation of electronic structure of complexes as a function of their stereochemistry, the nature of metal-ligand bonds, the thermodynamic stability and the kinetics and mechanism of complex forming processes. Studies aimed to determine stabilities in aqueous and non-aqueous media have been developing quite successfully over the past few decades. It is evident from the fact that huge literature has piled up on purely scientific to modern physico-chemical to biochemically relevant compounds. This includes books (Bailar and Busch, 1956; Chaberek and Martell, 1959; Figgis, 1967; Lever, 1968; Orgel, 1960 and Sacconi, 1970), international conferences (1961), international symposia (1957), national symposia (1979) and the research papers published during the past years.

The concept of formation constants was introduced at the end of nineteenth century (Abegg and Bodlander, 1899). The major development in this field was initiated by Jannik Bjerrum (1941) who gave a general method of determining the

stability constants of metal amine complexes. Systematic studies on the determination of stepwise constants were carried out at about the same time by Babko (1935). Leden (1941) and Fronaeus (1950) also forwarded their own methods of determining the stepwise formation constants. Sullivan and Hindman (1952) have made a comparison and critical analysis of Bjerrum (1941), Leden (1941), Fronaeus (1950) and others, the Swedish chemist Sillen (1959) evolved an experimental procedure for studying the hydrolytic and polymerisation equilibria in solution, leading to the formation of polynuclear complexes. A fundamental mathematical treatment for the complex equilibria was given by Rossotti and Rossotti (1961). Zharkov (1978) suggested that the stability of complexes is governed not only by the nature and relative position of electron donating groups but also by the binding sites of the ligand.

Coordination chemistry has become a field of interest not only to inorganic chemists but also to organic, analytical and physical chemists, biochemists, biologists, chemical crystallographers and technologists in various fields. In fact, the applications of coordination compounds are many more and some of these are being discussed below.

Several careful studies revealed that the complexes, particularly the mixed ligand are the intermediates in ligand displacement (Janes and Margerum, 1966 and Carr et al., 1967)

and ligand catalyzed complex formation reactions (Beck, 1960). In these reactions the oxidation is accompanied by migration of a coordinated anion from the oxidising agent to reducing agents (Taube, 1952 and 1959). The rate of reduction of permanganates and ferrates by hydroxyl ions has been reported (Jezowska-Trzebiatowska, 1957) in the presence of alkali metal cations. A general conclusion derived from such kinetic studies is that the lability or inertness of complexes is determined not only by the nature of the central atom and the geometry of the complex, but also by the nature of the ligand and the solvent in which the reaction takes place. Thus, the formation of complexes and their studies are crucial from the point of view of the kinetic effect and also as catalysts or intermediate products in a variety of organic syntheses (Basole and Pearson, 1958).

In most of the analytical methods, complexes are involved as sensitive and specific reagents or indicators for the determination of cations and anions. They are finding ever-increasing applications for the separation and purification of lanthanides and actinides. The technology of platinum group metals and extraction of gold from its ores is entirely based on the formation of complex compounds. An interesting example of mixed ligand complex formation of analytical importance is the spectrophotometric determination of fluoride ion. Schilt and Fritsch (1966) reported different cyano-1,

10-phenanthroline complexes of iron (II, III) as indicators and reagents in spectrophotometric analysis. The studies on complexones in analytical chemistry opened a new horizons in volumetric (Manns et al., 1952), gravimetric (Hure et al., 1952), colorimetric (Sweetser and Bricher, 1954), polarographic (Velenta and Zumau, 1954) and other methods of analysis (Pribil and Simon, 1949). Over 60 elements of the periodic table can be determined by direct or indirect methods. The complexones are important in purification and separation of various elements and compounds. One of the most difficult task, the separation of the rare earth elements, has been solved by the use of complexones (Marsh, 1950; Vickery, 1951 and Marsh, 1955). These compounds indeed form the nucleus of modern volumetric analysis, which means of analytical chemistry as a whole.

In the biological systems the stabilities of complexes are of extensive use, as many metabolic and toxicological functions are derived from them. The metal complex formation is deeply involved in normal life processes, which has led to a number of reviews such as "The Effects of Chelating Agents on Organisms" (Albert, 1967), "Chelation in Medicine" (Schubert, 1966), "Metal Binding in Medicine" (Seven and Johnson, 1960), "Metal Chelates in Biological Systems" (Dwyer and Mellor, 1964) and "Structure and Bonding in Biochemistry" (Collection of Metalloenzyme Reviews, 1970). The complexones are quite effective in removing toxic metals

from the body, including radioactive isotopes and their fission products (Rubin et al., 1953). The metal content of the soil can be regulated by these complexing agents (Jacobson, 1951). Complexones have been widely used in the textile, leather, food and paper industries, in the production of metals, varnishes, paints and rubbers. It is also used in the purification of petroleum, wax fats etc. (Hylaniki, 1962).

The biological aspects of coordination chemistry are being studied in a new branch of chemistry 'Bio-inorganic Chemistry' (Spitsyn and Dunaeva, 1978). The principal tasks in this field are the study of the nature of the coordination compounds present in living organisms, determination of their composition, structure, properties and role in biological processes. Bio-inorganic chemistry further includes the development of new effective chemo-therapeutic agents, including antitumor preparations based on the use of coordination compounds of metals and biologically active ligands, the production of the best forms of microfertilizers and study of processes leading to the pollution of the environment by compounds of toxic metals.

Organic-sulphur compounds have been well recognised in agricultural, medicine and industrial fields. Sulphur plays an important role in plant growth. Organic-sulphur compounds are being used as fungicides and acaricides. A review of Sigel (?) clearly brings out biological significance

of sulphur containing mixed ligand complexes.

In view of the significant role of thermodynamic stability and role of sulphur complexes as fungicides and acaricides discussed above, the studies were undertaken with the following objectives:

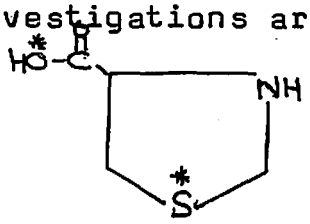
1. Thermodynamic stabilities of Zn(II), Ni(II) and Cd(II) with thioacids, viz., Thioproline, 2-Thiophene acetic acid and 2-(2-Thienyl) pyridine were determined.

2. To evaluate antifungal activities of some mixed ligand complexes containing organic-sulphur, viz., Thiolactic acid and Thiosalicylic acid with Ni(II), Zn(II), Mn(II), Fe(II), Co(II) against Macrophomina phaseolina, Rhizoctonia solani and Fusarium oxysporium fungi.

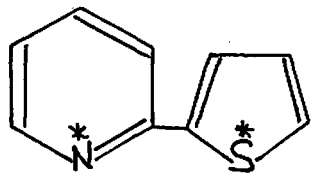
C H A P T E R - II

REVIEW OF LITERATURE

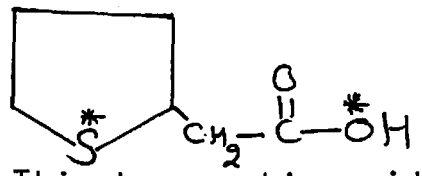
The structures of the thioacids used in the present investigations are:

1. 

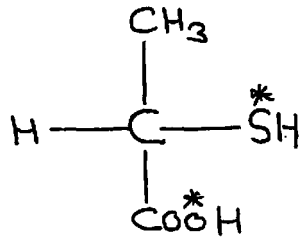
Thioproline

2. 

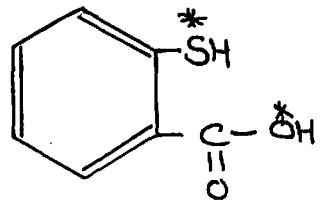
2-(2-Thienyl) pyridine

3. 

2-Thiopheneacetic acid

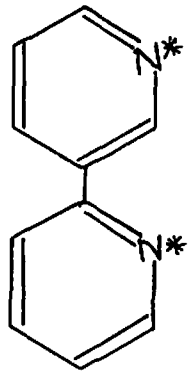
4. 

Thiolactic acid

5. 

Thiosalicylic acid

The structure of the 2,2'-bipyridal used in the present investigations is:



2,2'-Bipyridal

The atoms responsible for donation of electron pair in complex formation are marked in estrik.

Chacko et al. (1981) studied the structure of L-thioproline hydrochloride by X-ray crystallographic method. The title compound was monoclinic. Bond angles and bond lengths were determined. The N is protonated, while the carbonyl group remains unionized. The thioproline ring has an envelope confirmation. All 3H-bonds possible are formed with Cl atoms. Cis-ML_2X_2 [M=Pt, Pd; L=thioproline] (X=Cl,Br) were prepared from $K_2[MX_4]$ and L in aqueous EtOH. Cis-PtL_2I_2 was prepared from $K_2[PtCl_4]$ KI, and L. $[PtX_6][HL_2]$ were prepared from $H_2[PtX_6]$ and L in HX solution, whereas $[RhL_4X_2]X$ were prepared from $Na_3[RhX_6]$ in HX with L in 1:4 molar ratio by Craciunescu et al. (1982). The antitumor activity of these thioproline complexes against the L_{1210} and P_{388} systems and their cytotoxicity against KB cells were determined. Only the neutral Pt[II] complexes and Pt[IV] complex salt developed significant cytostatic activity. None of the complex showed significant antitumor activity in vivo.

According to Tahira et al. (1985) the rate of the

reaction of nitration of thioproline increased with decrease in pH and was Ist order with respect to nitrite concentration. The reaction rate was proportional to the concentration of total thioproline (free plus protonated), not to that of free thioproline. Thioproline acted as a nitrite scavenger, and supressed the formation of a carcinogen, N-nitroso-N-benzyl-methyl amine from N-benzyl-methylamine and nitrite. More than 90 per cent of the formation of N-nitroso-N-benzyl-methylamine was inhibited by adding 20mM thioproline to a reaction mixture containing 20mM N-b enzyl methyl amine and 20mM $NaNO_2$ at pH 3.0 and 37^{o}. Yuan and Wang (1985) gave a method for improvement of the synthesis of thioproline from formaldehyde.

Sarnatskaya et al. (1986) investigated that the thioproline and its derivatives inhibited the growth of the tobacco tissue and differentiated the normal and tumor tobacco tissue. Yang et al. (1986) reported that in isolating papillary muscles of guinea pigs, thiproline antagonized a frequency dependent block, induced by large concentrations of lidocaine and alone thioproline had no effect on the amplitude, duration and V_{max} of the action potential but prolonged the functional refractory period. Cho (1985) showed that thioproline influenced the germination and mycelial growth of Candido albicans in germ tube formation media containing L-proline. Antitumor property with respect

to their low toxicities and mechanisms of thioproline and its derivatives were discussed by Yuan et al. (1985).

Cao et al. (1985) studied the effect of thioproline on the immune system of mice. The delayed type hypersensitivity reaction to thioproline were higher than the controls. The phagocytic percentage, phagocytic index and bacterial killing percentage in response to thioproline were higher than in controls. The macrophase-thymocyte autorosetting tests in response to thioproline also were higher than in controls. These results showed that thioproline had a beneficial effect on phagocyte and bactericidal activities in addition to tumor-inhibiting properties.

Divalent platinum and palladium complexes with 2-(2-thienyl) pyridine of general formula $M[TP]_2X_2$ (X=Cl,Br) have been reported by Giordano et al. (1978). The structure has been established and the crystal data obtained. Sagitdinov and Schubert (1979) discussed the liquid-crystalline properties of trans-2-(5-n-alkyl-2-thienyl) acrylic acids. The cathodic reduction of 4-(2'-thienyl) quinazoline (4-TQ) was carried out at the dropping mercury electode in aqueous MeOH solutions of varying compounds in the pH range 1.30-11.70 by Antony et al. (1979). Two polrographic waves were observed in the buffered and unbuffered media which was found to be diffusion controlled. The first wave was reversible in acid solutions in all solvent compounds, mechanism for the reduction of 4-TQ leading to the formation of 3,4-dihydro-4-(2'-thienyl) quina-

zoline is proposed in acid, neutral and alkaline media.

Patel (1980) prepared ML_2 [M=Mn, Co, Ni, Zn, Cu, Pd, HL=4,4,4-Trifluoro-1-(2-thienyl) 1-3 butanedione] and $ML_2.2H_2O$ [M=Mn,Fe,Co,Ni,Zn] and complexes were characterized by magnetic susceptibility at 80-300° and UV reflectance spectra. MnL_2 showed an antiferromagnetic interactions where as NiL_2 showed a ferromagnetic interaction. The S atom of the thienyl ring did not bond to the metals. Therefore, the stereochemistry of the complexes resembled those of the corresponding acetylacetones. For the physico-chemical studies of metal β-diketones Patel and Adimado (1980) prepared ML_2 [M=Al,Cr,Mn,Fe and Co; HL=1-(2-Thienyl)- and 4,4,4-Trifluoro -1-(2-thienyl)-1,3 butonedione] complexes and were characterized by magnetic moments, IR, UV spectra. The IR band assignments suggested that substitution of a CF_3 group in Thenoyl acetone for a Me group increased the C=O and C=C bond strength and decreased that of the M-O bond of the chelate ring.

Maestri et al. (1985) illustrated luminescence of Pt[II]-2-(2-thienyl) pyridine and compared with that of the C-protonated neutral ligand. The strong and structured luminescence emission was observed at 500-600nm. The Pt[II]-2(2-thienyl) pyridine complex, where 2-(2-Thienyl) pyridine is ortho C-deprotonated form of 2-(2-Thienyl) -2-pyridine, is a photoluminescent species reported by Bonafede et al. (1986). In DMF solution, this complex undergoes 2-1 electron reversible reduction process

(E_{pc} = - 1.80 and-2.11 V vs SCE) and one reversible reduction process (E_{pc} = + 0.82 V vs SCE). In DMF solution electro generated chemiluminescence was observed. In a.c. electrolysis experiments stepping the potential between -1.80 and +0.82 V. In the presence of N,N'-diphenyl-1,4-phenylenediamine (E_{pc} = + 0.42 V.), chemiluminescence was observed. On pulsing of the poential between -1.80 and + 0.50 V when $S_2O_8^{2-}$ ions were present in the solution, chemiluminescence was observed in a.c. electrolysis experiments. The chemiluminescence spectrum was always identical with the photoluminescence spectrum indicating that the chemical reaction that followed the electrochemical process led to the same metal to ligand charge transfer excited state that was generated by light excitation of Pt(II)-2(2'-Thienyl) pyridine. The mechanism of the chemiluminescence process is discussed.

The stability constants and thermodynamic functions of Thiophene-2-carboxylic acid and the stability constants of its 1:1 complexes with several alkaline earth elements were determined by Sandhu et al. (1976) in aqueous medium using Calvin-Bjerrum pH titration technique. The free energy change, enthalphy change and entropy change of the complexes were calculated using Gibbs-Helmholtz equation. Lumme and Korvolo (1975) reported the preparation of some complexes of salicylaldoxime, 2-Indolecarboxylic acid and 2-Thiophene carboxylic acid with Co(II), Ni(II) and Cu(II)

and discussed their thermal behaviour by thermogravimetric, differential thermogravimetric, differential thermal analysis and mass spectrometric methods. Kinetic parameters were calculated for the decomposition reaction.

Chaudhury and Ghosh (1976) have reported a new simpler method of calculation of free ligand concentration and formation constants for metal complexes applied to Cu(II) -acetate, Cu(II)-thiophene-2- carboxylic acid and Cu(II) -salicylaldehyde in aqueous 50 volume per cent aqueous EtOH and 50 volume per cent aqueous dioxane at $30^{o}C$ in 0.1M $NaClO_4$. Small discrepancies were observed in the values of $[L]$ and K_n in mixed aqueous media but excellent correlations were obtained in aqueous media. Cu(II)-furoate and Cu(II) -thiophene-2-carboxylate were synthesized and formulated as dimeric species with 4 carboxylate bridges by Richardson et al. (1977). The furan and thiophene moiety give use to polymeric structures, ESR spectra and magnetic susceptibility measurements showed that the dimer had a singlet ground state and a thermally populated triplet state. The exchange coupling constants were -322 and -312 cm^{-1} for the furoate and thiophene-2-carboxylate. Spectral and magnetic properties were also discussed.

Sandhu et al. (1976) determined the proton-ligand stability constants and stepwise formation constants of the complexes of Be^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Uo^{2+} with Thiophene -2-carboxylic acid in aqueous medium at 30^{o}, 40^{o}, 50^{o} and

0.2M ionic strength by the Calvin-Bjerrum pH titration technique as used by Irving-Rossotti. The thermodynamic functions ΔG^0, ΔH^0 and ΔS^0 were calculated from temperature coefficients and Gibb's-Helmholtz equations. De, Basudev and Chaudhury (1976) investigated formation constants, at 30^o in 0.1M $NaClO_4$ 50 volume per cent aqueous dioxane, of ligands, thiophene-2-carboxylic acid [T_2CA] (I); tetrahydro-thiophene-2-carboxylic acid [THT_2CA] (II); acetic acid (III); m-nitrobenzoic acid (IV) and O-chlorobenzoic acid (V) with metal ions, viz., Ag(I), Hg(II), Fe(II), Co(II), Mn(II) and Ti(I). M-S π interaction in complexes between I and Fe(II) and between II and Ag(I), Hg(II) and Fe(II) has been suggested. Irving and Williams order is violated by Fe(II) in complexes with I and II.

Heats and entropies of complex formation of thiophene -2-carboxylate ion with Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were determined directly by calorometery as reported by Aruga (1979). The formation constant values were known in the literature. The values of the thermodynamic quantities for thiophene -2-carboxylate, compared with (ethyl thio) acetate and (phenyl thio) acetate, indicated a greater tendency for aromatic sulphur to form bond with the above metals than for aliphatic sulphur. The causes of this behaviour have been discussed. Shvedov et al. (1985) prepared several derivatives of 2-thiophene acetic acid.

Oxidation kinetics of thiosalicylic acid by ferricyanide ion in 60 per cent EtOH-H_2O system in 1M HCl was investigated colorimetrically by Panpalia et al. (1974) and determined that the order of reaction with respect to thiosalicylic acid was two but it was one with respect to ferricyanide ion. The rate increased with decrease in $[H^+]$ and dielectric constant of the medium. Addition of dithiosalicylic acid or electrolytes had no effect on the rate. However, the addition of $[Fe(CN)_6]^{4-}$ retarted the rate but its formation during the oxidation of thiol did not have any detectable effect on the rate before first half life. In the polarography of thiosalicylic acid in 40 per cent EtOH and in the presence of KNO_3 at the DME, well defined anodic waves were obtained by Tiwari and Sharma (1974) at pH 1.60-13.50. The reversible wave, involving a 1-electron transfer process was diffusion controlled, proportional to the concentration, and did not correspond to the formation of $[2\text{-}HO_2C\ C_6H_4]_2S_2$ but to the formation of $[2\text{-}HO_2C\ C_6H_4SHg]$. The diffusion coefficients were 5.248×10^{-6} and 5.105×10^{-6} cm^2 sec^{-1} and the temperature coefficients of the diffusion current 1.215 and 1.127 per cent per degree at 20-45^0 and pH 5.70 and 9.20, respectively. The dissociation constant obtained from the plot of the half wave potential vs pH was 9.80.

Nair and Nigam (1974) prepared and characterized the complexes of Ni(II), Cu(II), Rh(II), Pd(II) and Pt(IV) complexes of thiosalicylic acid. Complexes of Ni(II) and

Cu(II) were paramagnetic whereas those of Rh(II), Pd(II) and Pt(IV) were dimagnetic. They have discussed stereochemistry of these complexes and relevant ligand-field parameters were calculated. Al-Niaimi and Al-Saadi (1974) reported the acid dissociation constants of thiosalicylic acid $[LH_2]$ in 75 per cent (volume) dioxane-H_2O at 30°, and complex formation of LH_2 with M(II) [M=Zn(II), Cd(II), Hg(II) and Pb(II)] were studied potentiometrically in the same medium. $Hg[LH]Cl$, $Hg[LH]_2$ and ML [M=Zn, Cd, Pb] were isolated and characterized and concluded that thiosalicylic acid coordinated through S and O atoms.

Kumari, Vinod et al. (1975) studied the formation constants and free energies of coordination for Ni^{2+}-thiosalicylic acid-glycine [Tiron, ethylenediamine, propylenediamine] 1:1:1 ternary complexes at 25° and ionic strength 0.117M KNO_3 in 20 volume per cent EtOH by potentiometric studies. Log K values for ternary complexes were 5.125 ± 0.15, 7.88 ± 0.15, 6.09 ± 0.05, 3.40 ± 0.18 and ΔG^o values were 6.97, 10.71, 8.28 and 4.62 Kcal/mole, respectively.

Thermal decomposition of thiosalicylamide complexes of Co(II), Ni(II) and Mo(VI) was investigated by Wesolowski and Lewicka (1976) upto 700°C. Thiosalicylamide [HL] reacted with $Co(NO_3)_2 \cdot 2H_2O$ and $Ni(NO_3)_2 \cdot 2H_2O$ in H_2O and with $(NH_4)_2MoO_4$ in 0.1M $HClO_4$ to form the complexes $ML_2 \cdot H_2O$ [M=Co, Ni] and $MoO_2\ L_2 \cdot 2HL,\ 1.5\ H_2O$. Use of thiosalicylic acid, salicylic acid and phthalic acid as complexing agent for the extraction of Cr(III) from aqueous solution was made by Sebastian and

Hilderbrand (1978). The BuOH was used as the organic solvent and the extraction efficiency was optimized with respect to pH, heating period, choice of buffer and concentrations of the salting out agent. An extraction efficiency of greater than 97 per cent was obtained using a mixed phthalic-thiosalicylic complexing system.

Kumari, Vinod et al. (1978) cited potentiometric evidences for the formation of Zn(II)-TSA-en/Pn/gly/tiron (where TSA= thiosalicylic acid, en=ethylenediamine, Pn=1, 2-dipropylened-diamine, gly=glycine, Tiron=1,2-dihydroxy benzene-3,5 disulfonic acid disodium salt). The order of stability in terms of secondary ligands was Tiron > en > gly > Pn.

Puri and Patil (1978) prepared and characterized the complexes CeL_4 and $LnL_2Cl(H_2O)$ [HL=2-amino thiophenol; Ln=La, Pr,Nd,Sm,Gd] and $H_3[LnL'_3(H_2O)_3]$ [H_2L'=O-HSC_6H_4COOH; Ln=La,Nd, Sm,Gd,Y] by chemical analysis, electric conductance and IR spectra. Studies revealed that both ligands were bidentate. Biswas and Chaudhuri (1984) reported the synthesis and characterization of isomers of bis-(thiosalicylohydrazidato) Ni(II) and kinetics and mechanism of their interconversion reactions in solutions.

Saxena and Singh (1974) determined the stability constants of Zn^{2+} and Uo_2^{2+} 1:1 and 1:2 complexes with thiolactic acid by potentiometric and pH titration at 20, 30 and 40^{o} in 0.1M $NaClO_4$ by the Calvin and Melchior version of the Bjerrum method. The

thermodynamic parameters for complex formation were also calculated. The formation of complexes between Mo(IV) and thiolactic acid, thioglycolic acid and thiomalic acid was studied by Lamache (1976) using spectrophotometric and polarographic methods. In solution, 3 monomeric 1:1 complexes were formed and their stability constants were determined at pH 4.7. At the same pH, $MoO\left[H_2O\right]_2\left[SCH_2COO\right]$, $MoO\left[H_2O\right]_2\left[SCH\ Me\ COO\right]$ and $MoO\left[H_2O\right]_2\left[SCH(CH_2COOH)\ COO\right]$ were isolated and characterized by elemental analysis and IR spectroscopy. Kaur and Gupta (1979) reported the stability constants for the mixed ligand complexes of the Pb^{2+} and Tl^{+} with thiolactic acid $\left[H_2L\right]$ and oxalic acid $\left[H_2L'\right]$ in aqueous KNO_3 solution at 30^{o} using a polarographic method. The only species detected were $\left[PbLL'\right]^{2-}$ and $\left[TlLL'\right]^{3-}$, with stability constants log K=6.55 and 4.69, respectively. The kinetics of vandyl complex formation with vanillomandelic, madelic and thiolactic acids were studied at 25^{o} and ionic strength 0.5M KNO_3 by temperature jump and the complex stability constant for thiolactic acid with vandyl was determined by utilizing the Bjerrum titration technique by Che and Kustin (1980). Due to unavailability of acid dissociation constants for the α-OH groups, the complex stability constants for vanillomandelic and mandelic acids with vanadyl could not be directly determined byBjerrum method. For all three ligand systems an iterative procedure was carried out in which apparent forward and reverse rate constants for the complexation reaction were used to

calculate the complex stability constants. The stability constants obtained were $(4.45 \pm 0.37)\times10^{-3}$, $(6.14 \pm 0.33)\times10^{-3}$ and $(1.79 \pm 0.06)\times10^{-3}$ for the Vo^{2+}-vanillomandelic acid, Vo^{2+}-mandelic acid and Vo^{2+}-thiolactic acid complexes, respectively. Vanadyl complexation with all 3 ligands occurred with the loss of two protons, indicating bidentate chelation. For all the three formation rate constants were studied. The complexation reaction of the Ni^{2+} with the monovalent bidentate ligands vanillomandelic, mandelic and thiolactic acid were studied at 25^{o} and ionic strength 0.5M KNO_3 by temperature jump and stopped flow method and the formation rate constants were determined by Che and Kustin (1981). Stability constants for formation of the metal monocomplexes were detected by utilizing the Bjerrum titration equation. The kinetics of the complex formation is discussed in terms of 2 different rate determining steps sterically controlled substitution and internal H-bonding, as the results do not support the more usual dissociative substitution mechanism on Ni(II).

Saxena et al. (1983) investigated the precise nature of complexation of Cd^{2+} and Pb^{2+} with mixed ligand system, viz., thiolactic acid and glutamic acid by polarographic method and found that only a single mixed ligand species was formed. They also (1983) reported that the stability constants(log K)for Cd[Thiolactate]$_2$ glutamate=12.86, Pb[thiolactate]$_2$ glutamate =10.80 and Tl[thiolactate]$_2$ glutamate=3.47. Stability constants were determined by polarographic method.

Block (1955) attempted to correlate the stability of the mixed ligand complexes with their antimicrobial activity and reported that chelate lost its ability to chelate as the pH was lowered and also lost its toxicity effect. The order of toxicity to A.niger of the oxine chelates was Cu > Zn > Fe > Mg. Gourley (1960) reported that salicylic acid, thiosalicylic acid and their derivatives were potential antimicrobial agents and drugs. Gershon and Parmegiani (1963) found that the activity of the metal chelates of 8-quinolinol, its salt with salicylic acid and 3-hydroxy-2-nephthoic acid and Cu(II) was considerably increased as compared to that of the free metal and the ligands alone on their complexation.

Williams (1972) reported that some drugs had increased activity when administered as metal complexes and a number of metal chelates inhibited tumor growth. Albert (1973) reported the toxic effect of an organic molecule would be diminished by the chelation of metal ions in some cases. Further the introduction of nitro group enhanced the antifungal activity. Chattopadhyay and Nandi (1975) studied the growth inhibition of Fusarium moniliforme by some metallic cations and anions. They found mycelical growth was completely inhibited in Cu, Co, Zn, and CN at concentrations above 10^{-4}, 10^{-3}, 10^{-2}M, respectively. Toxic actions of cations and the anions were considered to act as inhibitors by inactivating the enzymes. All the metallic cations have, however, been found to promote growth at very low concentrations (10^{-7}M) revealing thereby

their importance as micronutrients. Satpathy *et al.* (1981) attempted to prepare a few metal complexes of Co(II), Ni(II) and Cu(II) with N-Benzoyl-N'-O-aminophenylthiocarbamide (BAPTC) and to evaluate their antifungal activities against *A.niger*, *F.oxysporium* and *H.oryzae* by the method of Horsfall (1945) using the agar plate technique. The evaluation was carried out at 1000 μg ml^{-1} in dioxane. The fungicidal data revealed that all the complexes except $\left[Co_2(BAPTC)_2(NO_3)_4\right]$ were physiologically more active then the ligand. It might be due to the presence of >C=O and >C=S groups in the ligand as well as in the complex. Nayak *et al.* (1981) synthesised Co(II) complexes with 2-pyrazoline-5-one derivatives and screened these complexes for their antifungal activity against the rice blast pathogen *P.oryzae* and brown leaf spot pathogen *H. oryzae* using spore germination tests at various concentrations. All the complexes showed encouraging fungicidal activity against these two pathogens. By comparing the fungicidal activities of the complexes with that of the free ligands it was seen that the activity of the ligands increased considerably when they were coordinated with the metal ion Co(II). Fungicidal activities of the prepared complexes were compared with the standard fungicides, viz., Hinosan 50% EC, Difolatan 50% WP, Derosal 60% WP at 1000 μg ml^{-1} concentration. It was seen that complexes inhibited spore germination in the range of the above standard fungicides.

Surya Rao and Ganorkar (1981) synthesised complexes of general formulae ML_2 and $M'L_2.2H_2O$ [where M=Ni(II), Cu(II), Zn(II) and M'=Mn(II), Fe(II) and Co(II) and L=furfurylidene benzoyl hydrazone (FBHZ) or 5-nitro-FBHZ (5-NFBHZ)]. These schiff bases and their metal chelates were screened against Rhizoctonia solani in PDA medium, using three sclerotial bodies in each petri plate. All metal chelates exhibited significant fungitoxicity at 250 μg ml^{-1} but FBHZ and 5-NFBHZ showed activity at 500 μg ml^{-1} and some of the metal chelates exhibited more fungitoxicity when compared to Dithane, M-45. The fungitoxicity had varied with metal ion and Cu(II) chelate had exhibited maximum fungistatic activity. The fungistatic activity of the metal chelates was found to be in the following order

$$Cu > Ni > Fe > Zn > Mn > Co$$

The insoluble binuclear mixed ligand complex Cu(II)-CDTA-HQ (where CDTA=1,2 diaminocyclohexanetetraacetic acid, HQ=8-hydroxy quinoline) has been isolated and tested for its antifungal activities against P.chrysogenum, A.terrus and A.alternata and antibacterial activities against Staphallococcus and Streptococcus by Khanna, Sujata et al. (1982). The biocidal activity of the mixed ligand chelate was considerably higher as compared to that of the free ligands, metal ions and binary complexes. Higher activity of mixed ligand complex might probably be attributed either to the combined bioactive effects of both the ligands present in the complex or due to their

increased liposoluble nature as a result of coordination to the metal ion. Besides these factors the rapid diffusion of the metal complex through the cell membrane of fungi and bacteria might be one of the important factors.

Srivastava et al. (1982) prepared the complexes of N-cyclo hexyl benzothiazole sulphonamide with Cu(II), Mn(II), Ni(II), Co(II) and Fe(II) and screened for fungitoxicity against D. tetramera, A. alternata and F. oxysporium. All the complexes exhibited significant fungitoxicity at 500, 200 and 100 $\mu g\ ml^{-1}$, the inhibition ranging from 60 to 88 per cent, 31 to 60 per cent and 24 to 35 per cent, respectively. The toxicity of the metal chelates in the descending order was as follows:

$$Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II)$$

Vasudha et al. (1982) studied the fungicidal activities of the complexes of Cu(II), Ni(II), Co(II), Fe(III), Mn(II) and Zn(II) with schiff base derived from 2-hydrazinobenzoxazole and salicylaldehyde against Curvularia sp., Fusarium sp. and Alternaria sp. by spore germination method at three different concentrations, i.e., at 1000, 500 and 200 $\mu g\ ml^{-1}$. It was found that the inhibition by the metal chelates was more than that by the ligand. In general the order of inhibition was:

$$Cu(II) > Zn(II) > Fe(III) > Ni(II) > Co(II) > Mn(II)$$

Bahel et al. (1982) evaluated fungitoxicity of the Zn(II), Ni(II), Cu(II) and Co(II) complexes with

3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazoles against H. oryzae by agar-plate method at three different concentrations, i.e. 1:1000, 1:10000, 1:100000 $\mu g\ ml^{-1}$. Fungicidal screening data indicated that the complexes were more fungitoxic than free ligand. Bajpai and Shukla (1982) reported that the toxicity, anti-amoebic, antibacterial and antifungal activities were inversely proportional to the radius of the metal ion.

Satpathy et al. (1983) assayed the antifungal activities of Ni(II), Co(II) and Cu(II) complexes with p-p'-bis (benzoylthiourea) bipyridyl and free ligands against A. niger, F. oxysporium and H. oryzae at 1000 $\mu g\ ml^{-1}$ in dioxane. The fungicidal activities displayed by various compounds revealed that most of the complexes were physiologically more active than the free ligand. Bandiwar et al. (1983) evaluated fungitoxicity of Co(II), Ni(II) and Cu(II) complexes with pyrrolidinate against Alternaria solani, Rhizopus nodosus and Botryodiplodia theopbromae and concluded that three metal complexes differed in their fungitoxic action. Among cobalt complexes cobalt-pyrrolidinate tetrahydrate was more toxic than the 'pn' complex. The extent of the antifungal activity induced by the former was about six times higher than that induced by the later. Nickel complexes with 'pn' or 'en' ligands were more or less equally toxic. Cu^{2+} mixed ligand complexes induced quite varied inhibitory effects. Cu^{2+} complex with 'pn' as secondary ligand was most effective against test (ED_{50}=640 $\mu g\ ml^{-1}$) while the Cu^{2+}-pyrrolidinate dihydrate alone (without 'pn' as secondary ligand) could not

suppress even 50 per cent of the fungal growth at a far higher concentration (i.e. 10000 $\mu g\ ml^{-1}$). In general, the inhibition of fungal growth increased gradually with the increase of concentration of complex. Co(III), Ni(II) and Cu(II) chloride complexes with ethoxythiocarboxyl had been found to exhibit pronounced antifungal activity as reported by Singh et al. (1983).

Oberoi, Madhu et al. (1984) isolated and characterized the insoluble ternary complex 1:1:1, Cu(II)-DPHC-HQ (DPHC= 2-carboxy,2'-hydroxy diphenylamine; HQ=8-hydroxy quinoline) and studied antifungal activity against D.tetramera, A.nigricans and C.albicans and antibacterial activity against B.substilis, S.aureus and E.coli. A comparison of the activity of the above ternary species had been made with the activities of the ligands involved and that of binary 1:1, Cu(II)-HQ complex. The biocidal activity of the mixed ligand chelate was found to be considerably higher as compared to that of the free metal ion, ligands and binary complexes. The growth inhibition of the tested fungi and bacteria might be due to the exchange of trace metals of the metalloenzymes with the metal of the complex.

Tripathi et al. (1984) reported the antifungal activity of La(III)-tartaric acid-8-hydroxy quinoline complex, tartaric acid, hydro quinoline and free metal ion against A.niger and A.flavus. The observations revealed that the complex had been found to be more toxic as compared to the free metal and ligands

involved. The increased activity of the complex was probably due to their combined activity effect of both the ligands in metal chelate due to their more liposoluble nature on being coordinated with the metal ion forming a stable metal chelate or due to a comparatively faster diffusion of the metal complex as a whole through the cells of the fungi.

$Cu(TH)_2(OH)_2$, $Cu(TH-H)(OH)2.H_2O$ and $Cu(TH)_2Cl_2$ (where TH=Tyrosine hydrazide) complexes and the parent ligand were screened for antifungal activity against Rhizoctonia solani at four different concentrations, i.e., 50, 100, 200 and 400 $\mu g\ ml^{-1}$ by Rao et al. (1984). The data revealed that the complex $Cu(TH)_2(OH)_2$ exhibited enhanced activity at all the four concentrations while $Cu(TH)_2Cl_2$ and $Cu(TH-H)(OH).2.H_2O$ showed a lesser activity compared to the ligand with a marked difference at particularly low concentrations.

Thiosemicarbazides and their metal complexes show a variety of biological activities. Singh et al. (1984) reported that the metal complexes of thiosemicarbazides with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) showed significant antifungal activity against A.niger and R.oryzae at 10000, 5000, 1000 $\mu g\ ml^{-1}$ concentration. The antifungal activity shown by these complexes was associated with $>N-C=S$ moiety. Singh et al. (1985) prepared and characterized the complexes of Co(II), Cu(II), Hg(II), Cd(II) with N-(p-tolyl)-N'-benzoylthiocarbamide and screened for fungitoxicity against

R. solani. The data showed that ligand and all the complexes except CdL_2Cl_2 were inactive at 50 and 100 $\mu g\ ml^{-1}$ concentrations but all the complexes except CuL_2Cl_2 and $Co(L-H)_2(H_2O)_2$ were more active than the ligand at 300 $\mu g\ ml^{-1}$.

Anjaneyulu *et al*. (1985) found that in general the antimicrobial activity of 8-hydroxy quinoline was intensified by 25 times or more, when it was chelated with Cu. The salicylic acid, thiosalicylic acid even their copper complexes possessed very little activity against the growth of fungi and bacteria even at relatively higher concentrations but the ternary complexes of Cu(II) with 8-hydroxy quinoline and salicylic acid or thiosalicylic acid were found to possess very effective toxic action against *A. niger*, *A. fumigatus* and *T. rubrum*.

C H A P T E R - III

MATERIALS AND METHODS

1. Polarographic Study

Water

The whole work was carried out by the conductivity water prepared as follows. The glass distilled water was redistilled over potassium permanganate. The resulting distilate was boiled, cooled and kept in well stoppered corning flasks.

Ligands

Freshly prepared ligand solutions were used. Solutions of the ligands, viz., Thioproline, 2-(2-Thienyl)pyridine and 2-Thiophene acetic acid were prepared by direct weighing. Potassium nitrate (0.1M) solution was used to make the volumes. All the ligands used were analytical grade, viz., Thioproline (Sigma, T-0631), 2-Thiophene acetic acid (Sigma, T-3896) and 2-(2-Thienyl)pyridine (Aldrich, 19,890-0). The purity of the solid compounds was tested by determining their melting point which were found to agree with ..... given in literature.

Potassium nitrate solution

Analytical grade potassium nitrate (S.M.) was used for preparing 0.1M solution in conductivity water.

Gelatin

A calculated amount of supporting electrolyte, gelatin, was added to 0.1M potassium nitrate solution, so that the gelatin concentration was 0.01 per cent in that.

Hydrochloric acid

Analytical grade of the acid was used. The acid was standardized against standard alkali and diluted to obtain 0.5M solution.

Metal salt solution

Zinc sulphate (Sarabhi, GR), Nickel sulphate (BDH, AR) and Cadmium acetate (BDH, AR) were used. Salts were kept in a oven at 110-120°C to remove moisture and solutions were prepared by dissolving a known weighed amount of the salt in conductivity water. The purity of the metal ions was tested by usual known methods.

Apparatus

pH meter and accessories

An Eltop digital pH meter, 3020, was used in the present investigations for pH adjustment. The pH-meter had a limit of error of ± 0.01 pH and a reproducibility of 0.01 pH. Combined glass and calomel electrode was used. The current supply was stabilized by AC voltage stabilizer with a frequency of 1000 cycles per second.

Polarographic analyzer and accessories

The model 174A polarographic analyzer from EG&G Princeton Applied Research (Photograph-B) was used for recording the polargrams. A high-compliance potentiostat (+80 V, 20 mA) with high electrometer input impedance (10" ohms), the 174A, extends

the usefulness of the differential pulse technique in high resistance media, such as, non aqueous solution or aqueous solutions of low conductivity.

In the M174A, the programmer output (ramp, pulses or pulse-modulated ramp) is summed with the initial potential and with a feedback signal taken from a reference electrode positioned as close as possible to the working electrode double-layer. The potentiostat in turn applies a potential to the auxiliary electrode and drives it to whatever potential is required to make the reference electrode equal to (but of opposite polarity to) the sum of the programmed and initial potentials. It should be noted that the programmed potential is that of the working electrode with respect to the reference electrode. However, because the working electrode is always at ground potential, the required relationship is achieved by driving the auxiliary electrode with a potential opposite to that selected. If a programmed potential of -1 V were selected, the working electrode would, as expected, be at -1 V with respect to the reference electrode. To do this, however, the auxiliary electrode would be driven to some higher positive voltage, the reference electrode would at +1 V with respect to ground, and the working electrode would be at ground potential. Two-electrode operation, in which the reference electrode lead is connected to the auxiliary electrode, is also possible.

Any current that flows through the working electrode is

double-banana connector. One binding post is at ground. The other carries the X-axis deflection signal, a zero to +1.5 V ramp at a source resistance of nominally 30 ohms.

Y-axis recorder output

Pair of binding posts spaced to accept standard double-banana connector. One binding post is at ground. The other carries the Y-axis output, identically the M174A output. A full scale cell current (corresponds to full scale panel-meter indication) gives +10 V output. The output polarity can be reversed with the display direction switch. As with the X-axis recorder output, the output resistance is nominally 30 ohms.

Drop timer

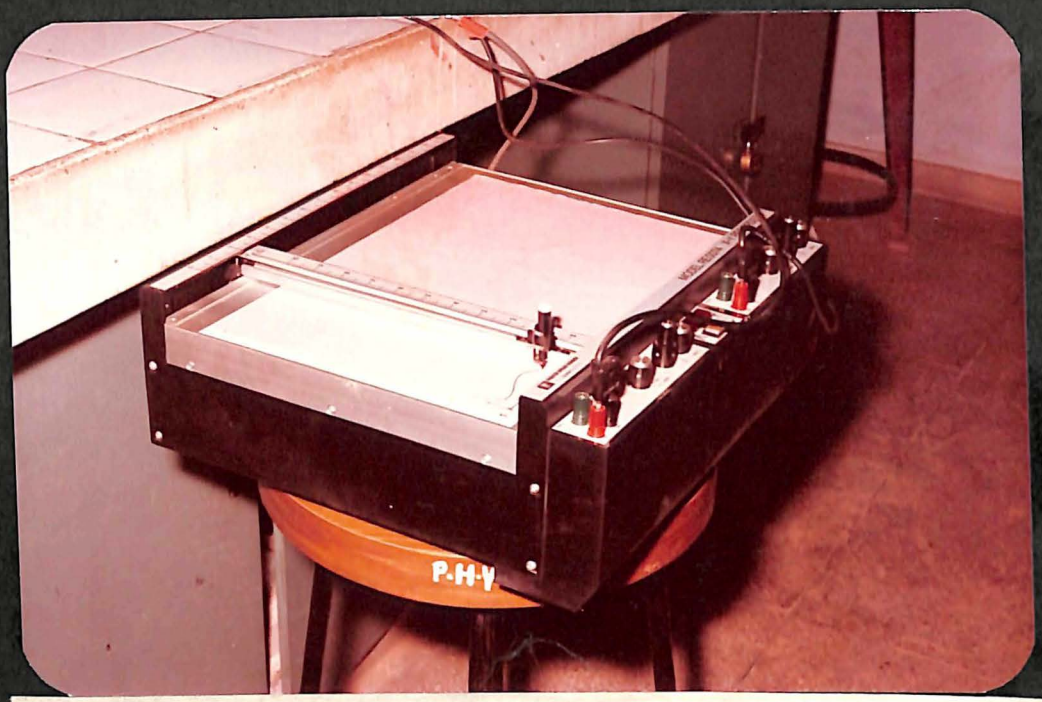
The M174/70 drop timer head is included with the M174A. This head mounted on a stand and assembled together with certain additional items to form a dropping mercury electrode, which allows mercury drops to be dislodged at the time intervals selected by the M174A front-panel drop time switch.

Mercury drop electrode (DME)

The model 303A SMDE from EG&G Princeton Applied Research (Photograph-A) was used. The model 303A SMDE produces a mercury droplet whose size remains constant over the course of current measurement rather than growing continually. Because the mercury drop is electromechanically dispensed, current-sampling operations such as occur with differential pulse polarography are performed on an electrode of constant surface area. This

Photograph - A: The model 303A Static Mercury Drop Electrode (SMDE)

Photograph - B: The model 174A Polarographic Analyser



Photograph - C: The model RE0088-XY Recorder

factor reduces baseline distortions in differential pulse polarography and thus enhances sensitivity. A further increase in sensitivity is due to the large drop size afforded by this model.

Capillary

The model 1601-0199 capillary was used.

Titration Procedure

The following titration solutions were prepared.

(a) Metal solutions

(i)	Zn(II)	1×10^{-5}M
(ii)	Ni(II)	1×10^{-7}M
(iii)	Cd(II)	1×10^{-3}M

(b) Ligand solutions

(i)	Thioproline	1×10^{-2}M
(ii)	2-Thiophene acetic acid	1×10^{-2}M
(iii)	2-(2-Thienyl) pyridine	1×10^{-2}M

(c) Potassium nitrate solution 0.1M

The titration solutions consisted of 0.25 ml of metal solution and another solution containing 0.25 ml of metal solution and graded amounts of ligand ranging from 1.00 to 20.00 ml (Table 2 to 10) in each of the ligand. The resulting volume was made upto 25.00 ml by adding appropriate amount of

potassium nitrate solution, giving the desired ionic strength of 0.1M. The titrations were carried out in a specially designed beaker of capacity 25.00 ml made of corning glass. The beaker was fitted with an inlet for passing nitrogen gas and also fitted with the dropping mercury electrode, calomel electrode and platinum electrode. The nitrogen gas was passed for 8 minutes to remove dissolved oxygen gas. The gelatin was added to suppress the maxima. The following conditions were set before recording the polarograms.

Electrode	:	DME
Display direction	:	"+ve"
Initial potential	:	0.70V for Zn(II) system 0.70V for Ni(II) system 0.40V for Cd(II) system
Drop time	:	1.0 second
Scan rate	:	5mV/second
Scan direction	:	"-ve"
Scan range	:	1.5 volts
Modulation amplitude	:	25 or 50 mV
Low pass filter	:	Off
Output off set	:	Zero
Current range	:	1mA
Current off	:	"+ve"
Operating mode	:	DPP

Recorder

X-axes : 100-50mV

Y-axes : 1V to 5V

Adjusted the recorder controls so that the pen was located at the lower left hand corner of the polarogram chart paper. Set the sensitivity of the recorder.

X-axes : 50mV

Y-axes : 50mV

The following polarograms were obtained:

(i) Metal solution

(ii) Metal + ligand with graded amounts

The following metal + ligand systems were studied:

(a) Zn(II)+Thioproline system

(b) Zn(II)+2-Thiophene acetic acid system

(c) Zn(II)+2-(2-Thienyl)pyridine system

(d) Ni(II)+Thioproline system

(e) Ni(II)+2-Thiophene acetic acid system

(f) Ni(II)+2-(2-Thienyl)pyridine system

(g) Cd(II)+2-Thiophane acetic acid system

(h) Cd(II)+Thioproline system

(i) Cd(II)+2-(2-Thienyl)pyridine system

The experiments were performed in duplicate so as to ensure the reproducibility of results. The DPP mode was selected because it yielded large easily defined peaks for low concentrations of metal ions.

$E_{\frac{1}{2}}$ and $(\frac{di}{dE})$ values (Table 1A to 10) were selected from the polarograms. The value of $(\frac{di}{dE})$ is always small at potentials preceding the wave, increases to a maximum at the half-wave potential and then decreases again to a very small value on the plateau.

The following expression for the maximum value of $(\frac{di}{dE})$ is:

$$(\frac{di}{dE})_{max} = -\frac{\nu F}{Rt} \cdot \frac{id}{4} \qquad \text{(Meites, 1967)}$$

Where $\nu = n$ if the wave is reversible or αn if it is totally irreversible and it involves a single rate determining step. From this equation, id, can be calculated.

Determination of Stability Constants

The complexes are usually formed in stages according to the following sets of equations and the corresponding equilibrium expressions can be written:

$$M + L \rightleftharpoons ML \quad ; \quad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \quad ; \quad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$ML_{n-1} + L \rightleftharpoons ML_n \quad ; \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad \ldots (1)$$

By successive substitution, we get

$$\begin{aligned}
[ML] &= K_1[M][L] \\
[ML_2] &= K_1K_2[M][L]^2 \\
&\vdots \\
[ML_n] &= K_1K_2 \ldots K_n[M][L]^n \qquad \ldots (2)
\end{aligned}$$

Writing β for the products of the stepwise stability constants, we get

$$\begin{aligned}
\beta_1 &= \frac{[ML]}{[M][L]} = K_1 ; \\
\beta_2 &= \frac{[ML_2]}{[M][L]^2} = K_1K_2; \\
&\vdots \\
\beta_n &= \frac{[ML_n]}{[M][L]^n} = K_1K_2 \ldots K_n = \prod_1^n K_i \qquad \ldots (3)
\end{aligned}$$

β_n is known as the overall stability constant of the $_n$th complex. In general, the value of the first stability constant is the largest and the values of the successive stability constants decrease i.e. $K_1 > K_2 > \ldots\ldots > K_n$. In solution, stability constants can be determined if the composition of the system is known.

The total concentration of the metal ion in solution, whether complexed or not, is given by

$$[T_M] = [M] + [ML] + [ML_2] + \ldots = \sum_{i=0}^{i=N} [ML_i]$$

Using Eqs. 2 and 3

$$T_M = [M] + \beta_1[M][L] + \beta_2[M][L]^2 \quad \ldots\ (4)$$

Then, Eq. 4 can be expressed as

$$T_M = [M] \sum_{i=0}^{i=N} \beta_i [L]^i \quad \ldots\ (5)$$

The total concentration of the ligand can be expressed as

$$T_L = [L] + [ML] + 2[ML_2] + \ldots = L + \sum_{i=1}^{i=N} i[ML_i]$$

or, by inserting the overall stability constants:

$$T_L = [L] + \beta_1[M][L] + 2\beta_2[M][L]^2 + \ldots$$
$$= [L] + [M] \sum_{i=1}^{i=N} i\,\beta_i [L]^i \quad \ldots\ (6)$$

Where N indicates the maximum number of ligands.

Bjerrum (1941) has introduced a quantity $\bar{n}$, the average ligand number for expressing the degree of complex formation. The average ligand number gives the mean number of ligands bound (in whatever form) per metal ion, i.e.

$$\bar{n} = \frac{T_L - [L]}{T_M} \quad \ldots\ (7)$$

For monodentate ligands, $\bar{n}$ gives the average coordination number.

Using equations 4 and 6 in Eq. 7,

$$\bar{n} = \frac{\beta_1[M][L] + 2\beta_2[M][L]^2 + \ldots\ldots}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \ldots}$$

Cancelling M, we get

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \ldots\ldots}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots} = \frac{\sum_1^N i\beta_i[L]^i}{1 + \sum_1^N \beta_i[L]^i} \quad \ldots(8)$$

Equation (8) was named the formation function of the system by Bjerrum.

Thus it appears

$$\bar{n} = f[L]$$

Where $[L]$ is the free ligand concentration.

It should be emphasized that if the ligand is the anion of an acid like HL, $[L]$ denotes the concentration of the free ligand anion L. Therefore, one can write

$$\bar{n} = \frac{[HL]_t - L}{[M]_t} \quad \ldots(9)$$

Where $[HL]_t$ = total analytical concentration of HL,

$[M]_t$ = total analytical concentration of metal M in the system.

Factors Affecting Complex Formation

A quite brief account of the factors influencing the formation and stability of complex compounds is given below:

The nature of the central ion: Alkali metals, alkaline earth metals, lanthanides and actinides are in general, poor complex former, with mainly electrostatic bonding. As the bonds are mainly ionic the stability increases with increase in the ionic potential on the central ion e.g. for the same ligand in general stability trend is as follows:

$$Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+} \quad ;$$

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} \quad ;$$

$$Lu^{3+} > Tm^{3+} > \ldots\ldots > Pr^{3+} > Ce^{3+} > La^{3+} \; .$$

The charge and the radius of the metal ion as well as the orbital splitting determine the complex stability in case of transition metal ions with partially filled d-orbitals. The covalency of the bond and the stability of the complex formed generally increases with increase in oxidation state of the metal ion. For a given ligand, the stability constants of the complexes formed by some bivalent metal ions of the first transition series usually follow the order:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This order, known as Irving and Williams (1953) order, can be accounted for by the decrease in size of metal ion from Mn(II) to Zn(II) and the crystal-field stabilization energy increasing from Fe(II) to Cu(II).

Nature of the ligand: The important characteristics of the ligands affecting the stability of complexes are: (i) proton

affinity of the ligand (ii) the nature of the donor atom (iii) chelation and size of chelate ring (iv) number of metal chelate rings per ligand (v) steric effect (vi) effect of substitution on the ligand (vii) resonance effect, and (viii) entropy effect.

The basicity of a ligand is an important factor which determines how easily it can donate electrons. In general, the stability of metal complexes increases as pKa of the ligand increases. The donor atoms in the ligands are elements on the right hand side of the periodic table. They have been arranged in order of increasing electro-negativity.

$$As,\ P < C,\ Se,\ S,\ I < Br < N,\ Cl < O < F$$

Sidgwick (1941) has explained the tendencies of various donor groups to form complexes with metals. The donor atom donates a lone pair of electrons to the acceptor metal atom. This donation may involve some π-character, which arises from the back donation of d-electrons from metal atoms to $p\pi$ - or $d\pi$ - antibonding orbitals of the ligand.

Multidentate ligands have chelating ability to form more stable complexes than monodentate ones. The stability of chelate also depends on the number of atoms in the ring formed. Chelates with 5- or 6- membered rings are the most stable. The stability also depends on the number of chelate rings per ligand. For example, the order of stability of Cu(II) complexes in terms of the following ligands is

triethylenetetramine (trien) > diethylenetriamine (dien) > ethylenediamine (en) > ammonia(NH_3).

Stability of complex also depends on the steric factor. The ethylenediamine complexes are more stable as compared to alkylated ethylenediamines. Though alkylated ethylenediamine is a stronger base than ethylenediamine, it is a weaker complexing agent because of the hindrance caused by the alkyl group in ring formation. Effect of substitution on the ligand may prevent it from acquiring the orientation about the central metal ion and thus affects the stability. In general, increased stability of the chelate is due to an increase in the value of entropy.

Reversible Processes involving Simple or Complex Metal Ions and Metals Soluble in Mercury

The reduction of a simple (i.e. aquo-complex) metal ion to give metal atoms soluble in the mercury may be described by the equation.

$$M^{n+} + ne + Hg = M(Hg) \qquad \ldots\ (1)$$

If thermodynamic equilibrium is very rapidly attained, the concentrations of the metal ions and the metal atoms at the drop surface must conform to the Nernst equation.

$$E_{d.e.} = E^0_S - \frac{RT}{nF} \ln \frac{f_a C^0_a}{a^0_{Hg}\, f_s C^0_S} \qquad \ldots\ (2)$$

Where E^0_S is the standard potential of the half reaction, C^0_S and C^0_a are the molar concentrations of the dissolved ion and of the

metal in the amalgam, both at the surface of drop, f_s and fa are the corresponding activity coefficients, and a^0_{Hg} is the activity of the mercury in the amalgam at the drop surface. The standard potential E^0_s differs from the standard potential of the half-reaction.

$$M^{n+} + ne = M$$

Because it includes the free energy of solution of the metal in mercury. Since the amalgams formed are quite dilute, a^0_{Hg} is practically equal to the activity of pure mercury, which will be taken as unity.

It is assumed that the rate of diffusion of the metal ion M^{n+} to the drop surface, and hence the current i, is proportional to the difference between the concentrations of M^{n+} in the bulk of the solution and at the electrode surface.

$$i = k_s(C_s - C^0_s) \qquad \ldots\ (3)$$

Throughout this equation, it is taken for granted that every current has been corrected for the residual current that flows at the same potential.

At any potential on the plateau of the wave, C^0_s is virtually zero because the ions are reduced so rapidly as they reach the electrode surface, while the current is equal by definition to the diffusion current id. Hence ...

$$id = k_s C_s \qquad \ldots\ (4)$$

So that according to the Ilkovic equation, k_s is equal to

$$607 n_S D_S^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}}$$

Since i, id and k_S all fluctuate as the drops grow and fall, it is most convenient to speak of the average values of these quantities during the drop life.

Meanwhile the concentration of the metal atoms in the amalgam at the drop surface is also proportional to the current

$$i = -k_a C_a^0 \qquad \text{.... (5)}$$

Where k_a has the same form as k_S but involves the diffusion coefficient of the metal atoms in the amalgam instead of that of the metal ions in the solution. The negative sign here and in the following equations reflects the fact that k_a is negative, as will be exaplined in connection with Eq. (11). Combining Eqs. (2) through (5) yields

$$E_{d.e.} = E_S^0 - \frac{RT}{nF} \ln \left(- \frac{f_a k_S}{f_S k_a} \right) - \frac{RT}{nF} \ln \frac{i}{id-i} \qquad \text{.... (6)}$$

When the potential of the dropping electrode is equal to the half-wave potential $E_{\frac{1}{2}}$, $i = \frac{id}{2}$ by definition, and since the last term of Eq. (6) then becomes zero one has

$$E_{d.e.} = E_{\frac{1}{2}} = E_S^0 - \frac{RT}{nF} \ln \left(- \frac{f_a k_S}{f_S k_a} \right) \qquad \text{.... (7)}$$

Which may also be written

$$E_{\frac{1}{2}} = E_S^{0'} - \frac{RT}{nF} \ln \left(- \frac{k_S}{k_a} \right) \qquad \text{.... (8)}$$

Where $E_S^{0'}$ is the formal potential of the half-reaction under the experimental conditions (ionic strength, temperature, etc.) employed.

Eq. (6) may now be written

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{id-i} \quad \ldots (9)$$

or, at 25^{o}

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.05915}{n} \log \frac{i}{id-i} \quad \ldots (10)$$

In the above equations i is the cathodic current resulting from the reduction of M^{n+}. For a dropping metal-amalgam electrode in a solution of the supporting electrolyte alone, an anodic (negative) current will be obtained from the oxidation of the metal atoms. In this case

$$i_a = k_a (C_a - C_a^0) \quad \ldots (11)$$

Where i_a is the anodic current and C_a is the concentration of the metal atoms in the interior of the drop. It is evident that k_a must be negative, for a negative current is obtained if C_a exceeds C_a^0 (that is, if metal atoms are being oxidized at the drop surface), and this is why a negative sign appeared in Eq. (5). The anodic diffusion current $(id)_a$ is given by

$$(id)_a = k_a C_a \quad \ldots (12)$$

While

$$i_a = -k_S C_S^0 \quad \ldots (13)$$

Here the negative sign arises because i_a is negative while both k_S and C_S^0 are positive. Combining Eqs. (11) through (13) with Eq. (2) yields

$$E_{d.e.} = E^0_S - \frac{RT}{nF} \ln \left(- \frac{f_a \, k_S}{f_S \, k_a} \right) - \frac{RT}{nF} \ln \frac{(id)_a - i_a}{i_a} \quad .. (14)$$

At the half-wave potential of the anodic wave

$$i_a = \frac{(id)_a}{2} , \quad \text{and}$$

$$E_{d.e.} = E_{\frac{1}{2}} = E^0_S - \frac{RT}{nF} \ln \left(- \frac{f_a \, k_S}{f_S \, k_a} \right) \quad .. (15)$$

The half-wave potentials of reversible and irreversible processes predict the chemical, thermodynamic and structural information of the reaction.

The half-wave potential of an aquo-metal ion is usually shifted in the direction of more negative potential when a ligand species with which it may complex is present in solution. From a knowledge of free ligand concentration and measurement of the half-wave potential shift it is possible to calculate the stability constant and coordination number of complex species for reversible and now for irreversible processes. In addition to the effects of irreversibility, there are many systems of complexes where polarographic analysis is complicated by kinetic effects, such as the rates of dissociation of some species being slower than the diffusion rate also, the equilibrium between some, successivelly formed, complexes may be less mobile than between others, polarographic technique has been applied as a useful tool for the determination of the structure of complexes.

For the reversible reduction of a simple ion

$$M^{n+} + ne + Hg = M(Hg) \qquad \ldots (1A)$$

The half-wave potential is given by

$$(E_{\frac{1}{2}})_S = E^0_S - \frac{RT}{nF} \ln \left(- \frac{f_a \, k_S}{f_S \, k_a}\right) \qquad \ldots (2A)$$

Where E^0_S is the standard potential of the metal ion-metal amalgam complex, f_a and f_S are the activity coefficients of the metal atoms in the amalgam and the metal ions in the solution, k_a is the ratio of the anodic diffusion current to the concentration of metal in the amalgam, and k_S is the ratio of the cathodic diffusion current to the concentration of metal ion in the solution.

According to Ilkovic equation

$$- \frac{k_S}{k_a} = \frac{D_S^{\frac{1}{2}}}{D_a^{\frac{1}{2}}} \qquad \ldots (3A)$$

For the reversible reduction of a complex ion

$$MX_p^{(n-pb)} + ne + Hg = M(Hg) + pX^{-b} \qquad \ldots (4A)$$

The half-wave potential $(E_{\frac{1}{2}})_C$ is given by

$$(E_{\frac{1}{2}})_C = E^0_S - \frac{RT}{nF} \ln \left(- \frac{f_a \, k_c}{f_c \, k_a}\right) + \frac{RT}{nF} \ln K_C - \frac{RT}{nF} p \ln C_x f_x \qquad \ldots (5A)$$

Where the subscript C denotes the complex ion; K_C is the overall dissociation constant of the predominating complex $MX_p^{(n-pb)+}$, and C_x is the concentration of the ligand X, which

is assumed to be so large that it does not vary at the drop surface as the current changes.

Substracting Eq. (2) from Eq. (5) at 25^{o} is given by

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.05915}{n} \left[\log K_C - \log \frac{f_s k_c}{f_c k_s} - p \log C_x f_x \right] \quad \ldots (6A)$$

It is assumed here that K_C is much smaller than C_X^p, so that the concentrations of the simple ion and of any possible lower complex can be neglected in the presence of the excess of ligand. When it is satisfied, the half-wave potential of the complex ion will be at least $0.1/nV$ more negative than that of the simple ion. The following correction term is added to the R.H.S. of Eq. (6A) when a small difference is encountered.

$$- \frac{RT}{nF} \ln \left[1 - \frac{k_c f_c k_a}{(f_x C_x) p f_a k_c} \right]$$

Differentiation of equation (6A) gives

$$\frac{d(E_{\frac{1}{2}})_c}{d(\log C_x)} = - \frac{0.05915}{n} p \quad \ldots (7A)$$

Provided that the activity coefficients f_s, f_c and f_x and the liquid-junction potential all remain constant as C_x is varied, and that the ratio $\frac{k_c}{k_s}$ also remains constant.

As long as C_x does not exceed about 1M, neither k_c nor k_s is likely to vary greatly. Usually $\frac{k_c}{k_s}$ will be constant

over a wide range of experimental conditions. Constant values of f_x, of the ratio $\frac{f_s}{f_c}$, and of the liquid-junction potential are more difficult to ensure. So far as the activity coefficients are concerned the usual course is to maintain a constant ionic strength as C_x is varied. Thus Eq. (6A) may now be written for C_x = 1M.

$$(E_{\frac{1}{2}})_{c,C_{x=1}} - (E_{\frac{1}{2}})_s = \frac{0.05915}{n}\left[\log K_c - \log\frac{f_s}{f_c} - \log\frac{k_c}{k_s} - p\log f_x\right] \quad \ldots (8A)$$

To obtain K_c it is necessary to evaluate or make some assumptions about each of the last three terms on the right hand side of this equation. The ratio $\frac{k_c}{k_s}$ is given, according to the Ilkovic equation by

$$\frac{k_c}{k_s} = \frac{D_c^{\frac{1}{2}}}{D_s^{\frac{1}{2}}} = \frac{I_c}{I_s} \quad \ldots (9A)$$

So that it can be calculated by the corresponding diffusion current constants. An error of ± 10 per cent in this ratio correspondes to an error of only ± 2.4/nmV, in the difference between the two half-wave potentials. This is small enough to be ignored. The activity coefficient can be best given by the extended Debye-Huckel equation.

$$\log f_i = -\frac{0.51Z_i^2\sqrt{\mu}}{1+0.33^0 a_i\sqrt{\mu}} + \beta_i \quad \ldots (10A)$$

Assuming for want of anything better, that the distance

of closest approach a_i^0 , is equal to the typical value $4.5A^0$, for each of the ionic species and that the salting-out coefficients β_i are also equal, one obtains

$$\log(f_s/f_c) = (Z_c^2 - Z_s^2)L \qquad \ldots (11A)$$

Where

$$L = 0.51\mu^{\frac{1}{2}}/(1+1.5/\mu^{\frac{1}{2}}) \qquad \ldots (11B)$$

2. Biocidal Activity

Material Used

The ligands, viz., Thiosalicylic acid and thiolactic acid both from sigma were used as supplied without further purification. The purity of the compounds was tested by determining their melting points which were found to agree with that given in literature. Analytical grade metal sulphates, viz., Nickel sulphate, Zinc sulphate, Ferrous sulphate, Manganese sulphate and Cobalt sulphate were used for the preparation of the complexes supplied by BDH. All the chemicals were dried in a hot air oven at a temperature 110^0 to 120^0 before use.

Dehydrated alcohol B.P. (extra pure, BDH) was used without further purification. Double distilled water was used throughout the investigations in washing and solution preparation etc.

Preparation of Complexes

Simple complexes of $\left[M(A)(H_2O)_4\right]SO_4$ type where (M=Zn(II), Ni(II), Mn(II), Fe(II) and Co(II); A=2,2' dipyridyl) were prepared as described by Panchal and Bhattacharya (1973).

To 10.00 ml of 1M aqueous metal sulphate solution was added 10.00 ml of 1M alcoholic dipyridyl solution with stirring. The mixture was refluxed for half an hour and alcohol was added to precipitate out the solid. The precipitates were filtered and washed with alcohol + water (1:1) mixture. They were dried in the oven at 80°C. The analysis of the compounds corresponded to the composition $\left[M(A)(H_2O)_4\right]SO_4$. Zn(II) complexes are white in colour, Ni(II) complexes have green colour, Fe(II) complexes have brick red colour, Mn(II) complexes have yellow colour and Co(II) complexes have pinkish colour.

Preparation of $\left[M(A)L(H_2O)_2\right]$ Type Mixed Ligand Complexes containing M(II) + 2.2'-dipyridyl and thio acids

(Where M=Zn(II), Ni(II), Mn(II), Co(II) and Fe(II), Thio acids are thiosalycylic acid & Thiolactic acid, A=2,2'-dipyridyl)

To 5.00 ml of 1M aqueous solution of the above solids was added 5.00 ml of 1M aqueous solution of Thioacid with constant stirring. The mixture was concentrated to reduce the volume. To this mixture alcohol was added to precipitate out the solid. The precipitates were washed with alcohol + water (1:2) mixture. They were dried at 80°C in the oven. The analysis of the compounds corresponded to the composition $\left[M(A)L(H_2O)_2\right]$.

The compounds were analysed for metal, nitrogen and sulphur contents and the values are similar as reported by Panchal and Bhattacharya (1973).

Evaluation of Anti Fungal Activity

Test fungi

Pathogenic isolates of the following fungi were used:

1. Macrophomina phaseolina (Tassi) Goid
2. Rhizoctonia solani Kuhn from cowpea seedlings
3. Fusarium oxysporium

Their cultures were maintained on Czapek's agar slants at $5^{o}C$.

Among several methods available the most commonly used technique is food-poisoned technique (Horsfall, 1945) which consists of the following steps:

Sterilization of the Apparatus

All the glass apparatus was cleaned with chromic acid followed by distilled water and then sterillized at $180^{o}C$ in a hot air oven for at least 2 hours.

Preparation of the Medium

Czapek's nutrient agar medium was used which consisted of the following:

1.	Sucrose	30 g
2.	Agar Agar	20 g
3.	$NaNO_3$	3 g
4.	K_2HPO_4	1 g
5.	$MgSO_4$	0.5 g
6.	KCl	0.5 g
7.	$FeSO_4$	10 mg
8.	Double distilled H_2O	1000 ml
9.	Streptopenicillin	50 mg/1000 ml Medium

All the components dissolved in distilled water and made the volume 1000 ml. Streptopenicillin was used to prevent the growth of unwanted bacteria.

Test of Fungitoxicity

The test fungi were grown on Czapek's agar medium (pH 6.0) containing logrithmic concentration series of each compound (1-100 µg/ml medium). The required amount of compound dissolved in 1 ml of distilled water was incorporated aseptically into 99 ml aliquotes of sterilised Czapek's agar medium cooled to 45°C. After brief shaking each lot of medium was poured into six petridishes and allowed to solidify. Each dish was inoculated centrally with a 10 mm mycelial disc cut from the periphery of 2-3 days old fungal colonies. Inoculated petridishes were inocubated in the dark at 30±1°C and colony diameter was measured periodically till the control dishes were nearly completely covered with fungus growth. Three replicate dishes were used for each concentration of a chemical together with three dishes containing toxicant free medium. The degree of inhibition of growth (Photograph E, F, G & H) was calculated from the mean differences between treatments and control as percentage of the latter, by using the formula

$$\% \text{ Inhibition} = \frac{C-T}{C} \times 100$$

Where

C = Mycelial growth in control

T = Mycelial growth in treated plate

Fungicidal Potency

Fungicidal value concerns itself with quality factors- availability and inherent toxicity. The fungicidal value is its ability to kill the mycelium. Availability is concerned with the making of a fungicide out of an insoluble residue. It is concerned with the speed of solubility. A material with small particles is more available than one of the same kind with large particles.

Inherent toxicity is the ability of the toxicant once made available to the fungus concerned. It is desirable to use a series of doses for each material and to determine the percentage of mortality for each dosage. From such data a dosage, its plot is usually a straight line on logarithmic probability paper. If it does not, all elements of technique, such as volatility, diffusion, and coverage, should be scrutinized before deciding that the line is really other than straight.

Such a line provides ED values and slopes, that is, the lethal dose for any given level of response, such as ED_{50} or ED_{90} value and the angle of the line. ED values measure the dose factors of quantity of deposite and also availability since availability is really a dose factor. ED values, therefore, are important in quality control of a fungicide. They show differences in particle size etc.

Slope is measure of inherent toxicity. If compounds act

differently, they will show different slopes. Slope, however, may measure coverage also. Thus fungicidal potency may be discussed either by the dosage-response curve or by action of percentage response (Horsfall, 1945).

The Dosage-Response Curve

In this experiment a series of dosage of each material is taken and in each case inhibition from each dose is determined. Dose is an independent variable, is plotted on the X-axis, and inhibition, being the dependent variable is plotted on the Y-axis. The result is a sigmoid curve. The upper half of the curve is fatter than the lower, and the upper end of the curve tails off slowly towards the ceiling of response. Thus the relation between dose and response is flexible.

Action of Dose

In nature processes follow the law of diminishing returns, according to biology or physics, which means that an increase in stimulus will not result in an equivalent increase in response. It means that an increase in response requires a geometric increase in dose. Therefore, the fattened upper portion of the curve is due to the law of diminishing returns. It can be reduced to normal shape by expressing the dose logarithms instead of in arithmetic units.

Action of Percentage Response

Having eliminated the bulbous upper portion of the curve,

it is apparent that the S shape must be caused by irregularities in the weight of the values on the other axis. It turns out that this is due to the rubber nature of the percentage scale. The percentage scale is least sensitive in the middle range or at 50 per cent and its sensitivity increases rapidly as it approaches the ceiling and the floor of response. The percentage numbers remain at equal intervals despite the fact that the sensitivity increases. It is necessary to stretch the space between the percentage values if we are to use the response scale as a firm ruler. This has been done graphically on probability paper and statistically by the use of probits which are so arranged that they measure response in equal steps. In bioassays by stating that data plotted on logarithmic-probability paper will give a straight line, which means that the data are now measured by a firm ruler. Data so treated provide two useful values, ED_{50} and slope.

C H A P T E R - IV

RESULTS AND DISCUSSION

1. Polarography

Polarograms were scanned by Differential Pulse Polarography technique. It is a technique in which a linearly increasing dc ramp is applied to the chemical cell and a fixed height pulse is superimposed on this ramp near the end of the life of each drop. The current flow is sampled just before application of the pulse and again at the end of the pulse. The read out presented to the recorder is the difference between these two currents. Such a differential signal provides the derivative of polarographic curve in a peak presentation.

Derivative voltammetry consists of recording the rate of change, (di/dt), of the current flowing through a voltammetric cell against the potential E of the indicator electrode, which is varied at a constant rate (dE/dt). The value of (di/dE) is small at potentials preceding the wave, increases to a maximum at the half-wave potential, if the wave obeys either equation (9) or equation (10), and then decreases again to a very small value on the plateau. By differentiating either of these equations one obtains the following expression for the maximum value of (di/dE)

$$(di/dE)_{max} = \frac{\nu E}{Rt} \cdot \frac{id}{4}$$

Where ν is equal to n if the wave is reversible or to αn_a if it is irreversible and involves a single rate-determining step.

The maximum deflection of the galvenometer or recorder occurs at the half-wave potentials. It is proportional to the diffusion current (and hence to the concentration of electroactive substance responsible for maxima) and increases as the rate of polarization increases. It is larger for reversible wave than for an irreversible one involving the same overall number of electrons.

Zn(II) complexes

The pH at which Zn(II-Thioproline, Zn(II)-2-Thiophene acetic acid and Zn(II)-2-(2-Thienyl)pyridine have been studied are 8.15±0.1; 8.10±0.1 and 8.00±0.1, respectively, in 0.1M potassium nitrate, with 0.01 per cent gelatin being used as maximum suppressor. In the case of dc polarography the diffusion controlled reduction nature of the polarographic wave can be established by considering (i) direct proportionality with concentration, (ii) dependence of the height of the mercury column, and (iii) low temperature coefficient. Reversibility of the process can be established by complete retracing of the path and diffusion controlled reduction by the same height of the wave in case of differential pulse polarography. The nature of the waves for Zn(II) ion and its complexes were well defined and were found to be diffusion controlled. The reduction of Zn(II) ion at pH 8.15 vs SCE was -0.895 V.

The half-wave potentials shifted to more negative values

on increase of ligand concentration. A Lingane treatment of the data revealed the formation of complexes with p=2 (where p=number of ligands attached to the central metal ion in any form) in each of case consequently, the predominating complex under these conditions was ZnL_2. For the equation for the straight line curve through experimental points (Fig. 1 to 3), it is found that $(E_{\frac{1}{2}})_{c,cx=1}$ is -1.082 V, -1.116 V and -1.117 V vs SCE for Zn(II)-Thioproline, Zn(II)-2-Thiophene acetic acid and Zn(II)-2-(2-Thienyl)pyridine, respectively.

It is assumed here that the liquid-junction potential between the saturated potassium chloride in the SCE and 0.1M potassium nitrate will be essentially identical containing the ligand. To calculate the instability constant from Lingane Eq. (8A) the ratio k_c/k_s, according to Ilkovic equation is

$$\frac{k_c}{k_s} = \frac{I_c}{I_s}$$

So that it can be calculated from the corresponding diffusion current constants. In differential pulse polarography, the diffusion current constants are related with $(di/dE)_{max}$ values as given by (Meites, 1967). Thus

$$\frac{k_c}{k_s} = \frac{(\frac{di}{dE})_{c,cx=1}}{(\frac{di}{dE})_s} = \frac{I_c}{I_s}$$

The activity coefficients 'f_i' were determined by extended Debye-Huckel equation.

A perusal of the data in the Table 2 to 4 indicate the formation constant values to be 6.22, 8.19 and 7.33 in case of Zn(II)-Thioproline, Zn(II)-2-Thiophene acetic acid and Zn(II)-2-(2-Thienyl)pyridine, respectively. The following stability order is observed.

2-Thiophene acetic acid > 2-(2-Thienyl)pyridine > Thioproline

Ni(II) complexes

The pH at which Ni(II)-Thioproline, Ni(II)-2-Thiophene acetic acid and Ni(II)-2-(2-Thienyl)pyridine systems have been studied are 6.80±0.1; 6.95±0.1 and 6.52±0.1, respectively in 0.1M potassium nitrate, with 0.01 per cent gelatin as maximum suppressor. Reversibility of the process can be established by complete retracing of the path and diffusion controlled reduction by the same height of the wave in differential pulse polarography. The nature of the wave for Ni(II) ion and its complexes were well defined and were found to be diffusion controlled. The reduction of Ni(II) ion at pH 6.52 vs SCE was -1.04 V.

The half-wave potentials shifted to more negative values on increase of ligand concentration. A Lingane treatment of the data revealed the formation of complexes with p=2 in each of case consequently, the predominating complex under these conditions was $Ni(II)L_2$. For the equation for the straight line curve through experimental points (Fig. 4 to 6), it is found that $(E_{\frac{1}{2}})_{c,cx=1}$ is -1.2575 V, -1.2570 V and -1.2960 V vs SCE for Ni(II)-Thioproline, Ni(II)-2-Thiophene acetic acid

TABLE 1A: $\left(\frac{di}{dE}\right)_S$ VALUES FOR METAL IONS

TEMPERATURE = 25°C

Sr. No.	Name of metal ion	$\left(\frac{di}{dE}\right)_S$	Current(i)
1.	Zn(II)	1.44	10 μA
2.	Ni(II)	3.00	10 μA
3.	Cd(II)	7.30	0.02mA

TABLE 1B: $\left(\frac{di}{dE}\right)_{c,cx=1}$ VALUES FOR METAL+LIGAND SYSTEMS

TEMPERATURE = 25°C

Sr. No.	Name of metal+ligand system	$\left(\frac{di}{dE}\right)_{c,cx=1}$	Current
1.	Zn+TP	13.94	10 μA
2.	Zn+TPA	2.10	10 μA
3.	Zn+TEP	16.45	10 μA
4.	Ni+TP	6.90	10 μA
5.	Ni+TPA	21.88	10 μA
6.	Ni+TEP	4.30	10 μA
7.	Cd+TP	32.08	0.02mA
8.	Cd+TPA	12.86	0.02mA
9.	Cd+TEP	9.80	0.02mA

TABLE 2: METAL-LIGAND STABILITY CONSTANT OF Zn(II)-THIOPROLINE SYSTEM, AT μ =0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 8.15± 0.1

Sr. No.	Concentration of ligand (1×10^{-3}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf_x	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s]\times 2}{0.05915} + \text{plog}f_x + \log\frac{k_c}{k_s}$
0.	0.00	-0.695	-	-	-	
1.	0.20	-0.845	2	-0.878	0.986	
2.	0.40	-0.860	2	-0.878	0.986	$K_c = 6.08\times10^{-7}$
3.	0.80	-0.850	2	-0.878	0.986	
4.	1.00	-0.880	2	-0.878	0.986	
5.	1.20	-0.890	2	-0.878	0.986	
6.	1.40	-0.895	2	-0.878	0.986	
7.	1.60	-0.895	2	-0.878	0.986	$\log K = -\log K_c = 6.22$
8.	1.80	-0.900	2	-0.878	0.986	
9.	2.00	-0.905	2	-0.878	0.986	
10.	2.20	-0.910	2	-0.878	0.986	
11.	2.40	-0.915	2	-0.878	0.986	
12.	2.60	-0.915	2	-0.878	0.986	
13.	2.80	-0.910	2	-0.878	0.986	

TABLE 3: METAL-LIGAND STABILITY CONSTANT OF Zn(II)-THIOPHENE ACETIC ACID SYSTEM, AT μ =0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 8.10±0.10

Sr. No.	Concentration of ligand (1×10^{-4}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf$_x$	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{\left[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s\right] \times 2}{0.05915} + p\log f_x + \log \frac{k_c}{k_s}$
0.	0.00	-0.895	-	-	-	
1.	4.00	-0.945	2	-0.878	0.163	
2.	8.00	-0.960	2	-0.878	0.163	$K_c = 6.49\times10^{-9}$
3.	12.00	-0.970	2	-0.878	0.163	
4.	20.00	-0.980	2	-0.878	0.163	
5.	24.00	-0.985	2	-0.878	0.163	
6.	40.00	-0.995	2	-0.878	0.163	$\log K = -\log K_c = 8.19$
7.	44.00	-0.995	2	-0.878	0.163	
8.	48.00	-1.00	2	-0.878	0.163	
9.	52.00	-1.00	2	-0.878	0.163	
10.	60.00	-1.05	2	-0.878	0.163	

TABLE 4: METAL-LIGAND STABILITY CONSTANT OF Zn(II)-2-(2-THIENYL)PYRIDINE SYSTEM AT μ=0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 8.00±0.10

Sr. No.	Concentration of ligand (1×10^{-5}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf$_x$	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s]\times 2}{0.05915} + p\log f_x + \log \frac{k_c}{k_s}$
0.	0.00	-0.895	-	-	-	
1.	1.00	-0.900	2	-0.878	1.058	$K_c = 4.70\times10^{-8}$
2.	2.00	-0.910	2	-0.878	1.058	
3.	3.00	-0.920	2	-0.878	1.058	
4.	4.00	-0.925	2	-0.878	1.058	
5.	4.80	-0.925	2	-0.878	1.058	$\log K = -\log K_c = 7.33$
6.	6.00	-1.050	2	-0.878	1.058	
7.	7.00	-1.055	2	-0.878	1.058	
8.	9.00	-0.940	2	-0.878	1.058	

TABLE 5: METAL-LIGAND STABILITY CONSTANT OF Ni(II)-THIOPROLINE SYSTEM AT μ=0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 6.80±0.1

Sr. No.	Concentration of ligand (1×10^{-4}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf$_x$	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{\left[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s\right] \times 2}{0.05915} + p\log f_x + \log \frac{k_c}{k_s}$
0.	0.00	-1.040	-	-	-	
1.	1.00	-1.085	2	-0.878	0.362	
2.	2.00	-1.095	2	-0.878	0.362	$K_c = 1.35\times10^{-8}$
3.	4.00	-1.105	2	-0.878	0.362	
4.	6.00	-1.140	2	-0.878	0.362	
5.	8.00	-1.220	2	-0.878	0.362	
6.	10.00	-1.250	2	-0.878	0.362	$\log K = -\log K_c = 7.87$
7.	12.00	-1.130	2	-0.878	0.362	
8.	16.00	-1.135	2	-0.878	0.362	
9.	20.00	-1.140	2	-0.878	0.362	
10.	24.00	-1.220	2	-0.878	0.362	

TABLE 6: METAL-LIGAND STABILITY CONSTANT OF Ni(II)-2-THIOPHENE ACETIC ACID SYSTEM AT μ =0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 6.95±0.10

Sr. No.	Concentration of ligand (1×10^{-4}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf_x	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{\left[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s\right]\times 2}{0.05915} + \text{plog}f_x + \log\frac{k_c}{k_s}$
0.	0.00	-1.040	-	-	-	
1.	8.00	-1.050	2	-0.878	0.863	$K_c = 4.45\times10^{-8}$
2.	16.00	-1.065	2	-0.878	0.863	
3.	24.00	-1.065	2	-0.878	0.863	
4.	32.00	-1.090	2	-0.878	0.863	
5.	40.00	-1.070	2	-0.878	0.863	
6.	48.00	-1.1075	2	-0.878	0.863	
7.	56.00	-1.105	2	-0.878	0.863	$\log K = -\log K_c = 7.35$
8.	64.00	-1.110	2	-0.878	0.863	
9.	72.00	-1.115	2	-0.878	0.863	
10.	80.00	-1.120	2	-0.878	0.863	
11.	88.00	-1.1225	2	-0.878	0.863	
12.	96.00	-1.125	2	-0.878	0.863	

TABLE 7: METAL-LIGAND STABILITY CONSTANT OF Ni(II)-2-(2-THIENYL)PYRIDINE SYSTEM AT μ=0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 6.52±0.10

Sr. No.	Concentration of ligand (1×10^{-5}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf$_x$	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s] \times 2}{0.05915} + \text{plogf}_x + \log\frac{k_c}{k_s}$
0.	0.00	-1.040	-	-	-	
1.	1.60	-1.030	2	-0.878	0.156	$K_c = 4.19\times10^{-10}$
2.	3.20	-1.0425	2	-0.878	0.156	
3.	4.80	-1.060	2	-0.878	0.156	
4.	6.40	-1.070	2	-0.878	0.156	
5.	8.00	-1.0725	2	-0.878	0.156	
6.	9.60	-1.050	2	-0.878	0.156	
7.	11.20	-1.075	2	-0.878	0.156	$\log K = -\log K_c = 9.38$
8.	14.40	-1.075	2	-0.878	0.156	
9.	16.00	-1.080	2	-0.878	0.156	
10.	17.60	-1.080	2	-0.878	0.156	
11.	19.20	-1.090	2	-0.878	0.156	

TABLE 8: METAL-LIGAND STABILITY CONSTANT OF Cd(II)-THIOPROLINE SYSTEM AT μ=0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C, pH = 11.50±0.10

Sr. No.	Concentration of ligand (1×10^{-4}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf$_x$	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s] \times 2}{0.05915} + \text{plogf}_x + \log \frac{k_c}{k_s}$
0.	0.00	-0.6250	-	-	-	
1.	4.00	-0.6250	2	-0.878	0.643	
2.	8.00	-0.6250	2	-0.878	0.643	$K_c = 2.86\times10^{-6}$
3.	12.00	-0.6325	2	-0.878	0.643	
4.	16.00	-0.6375	2	-0.878	0.643	
5.	20.00	-0.6450	2	-0.878	0.643	
6.	24.00	-0.6500	2	-0.878	0.643	
7.	28.00	-0.6525	2	-0.878	0.643	
8.	32.00	-0.6550	2	-0.878	0.643	$\log K = -\log K_c = 5.46$
9.	36.00	-0.6500	2	-0.878	0.643	
10.	40.00	-0.6600	2	-0.878	0.643	
11.	44.00	-0.6550	2	-0.878	0.643	
12.	48.00	-0.6650	2	-0.878	0.643	

TABLE 9: METAL-LIGAND STABILITY CONSTANT OF Cd(II)-2-THIOPHENE ACETIC ACID SYSTEM AT μ=0.1M POTASSIUM NITRATE, TEMPERATURE = 25°C; pH = 11.05±0.10

Sr. No.	Concentration of ligand (1×10^{-4}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf_x	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{\left[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s\right]x2}{0.05915} + \text{plog}f_x + \log\frac{k_c}{k_s}$
0.	0.00	-0.625	-	-	-	
1.	4.00	-0.8625	2	-0.878	0.2460	
2.	12.00	-0.880	2	-0.878	0.2460	$K_c = 4.56\times10^{-16}$
3.	20.00	-0.90	2	-0.878	0.2460	
4.	28.00	-0.905	2	-0.878	0.2460	
5.	40.00	-0.9175	2	-0.878	0.2460	
6.	48.00	-0.940	2	-0.878	0.2460	
7.	60.00	-0.930	2	-0.878	0.2460	$\log K = -\log K_c = 15.34$
8.	72.00	-0.935	2	-0.878	0.2460	
9.	80.00	-0.960	2	-0.878	0.2460	
10.	88.00	-0.9425	2	-0.878	0.2460	
11.	96.00	-0.9625	2	-0.878	0.2460	

TABLE 10: METAL-LIGAND STABILITY CONSTANT OF Cd(II)-2-(2-THIENYL)PYRIDINE SYSTEM AT μ =0.1M POTASSIUM NITRATE; TEMPERATURE = 25°C, pH = 11.58±0.10

Sr. No.	Concentration of ligand (1×10^{-4}M)	$(E_{\frac{1}{2}})$ (Volts)	p	plogf_x	log $\frac{k_c}{k_s}$ at cx=1	$\log K_c = \frac{\left[(E_{\frac{1}{2}})_{c,cx=1} - (E_{\frac{1}{2}})_s\right] \times 2}{0.05915} + \text{plog}f_x + \log\frac{k_c}{k_s}$
0.	0.00	-0.625	-	-	-	
1.	4.00	-0.670	2	-0.878	0.128	$K_c = 4.24\times10^{-10}$
2.	8.00	-0.700	2	-0.878	0.128	
3.	12.00	-0.660	2	-0.878	0.128	
4.	16.00	-0.670	2	-0.878	0.128	
5.	20.00	-0.710	2	-0.878	0.128	———————
6.	24.00	-0.720	2	-0.878	0.128	
7.	28.00	-0.725	2	-0.878	0.128	$\log K = -\log K_c = 9.63$
8.	32.00	-0.730	2	-0.878	0.128	
9.	36.00	-0.735	2	-0.878	0.128	
10.	40.00	-0.740	2	-0.878	0.128	

FIG.1 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Zn(II)-THIOPROLINE SYSTEM.

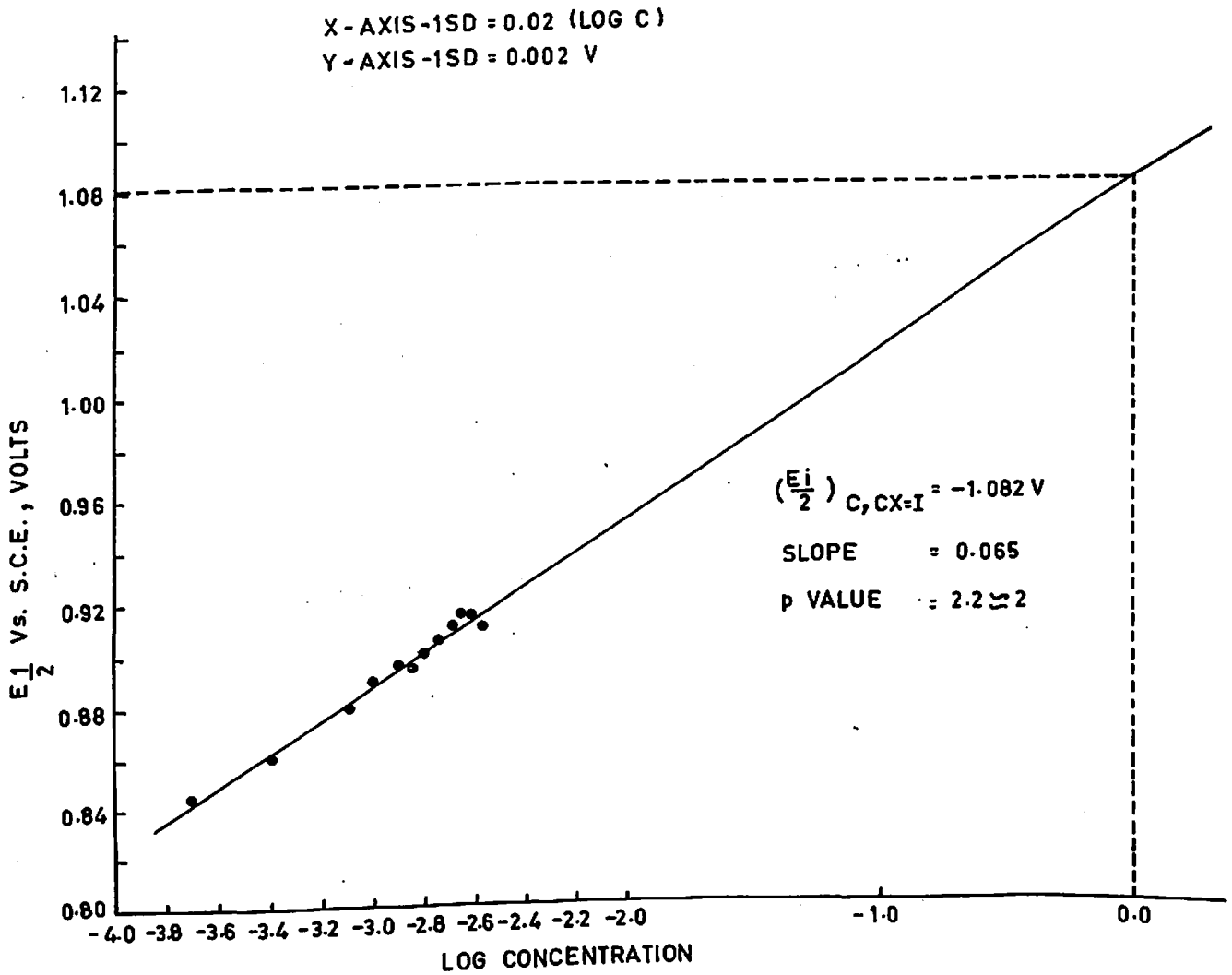


FIG.2 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Zn(II)-2-THIOPHENE ACETIC ACID.

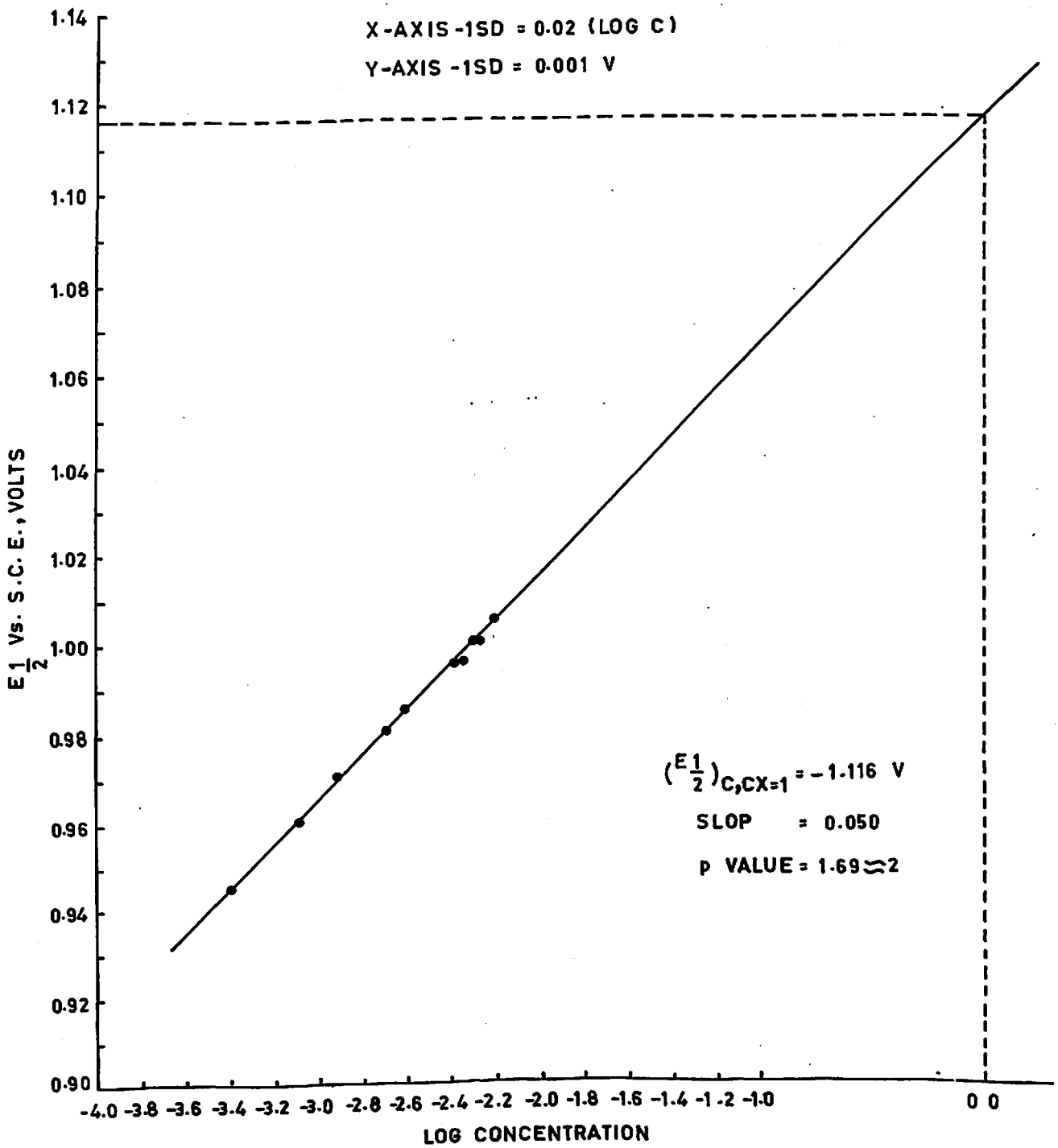


FIG.3 A CURVE BETWEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Zn(II)-2-(2-THIENYL) PYRIDINE SYSTEM.

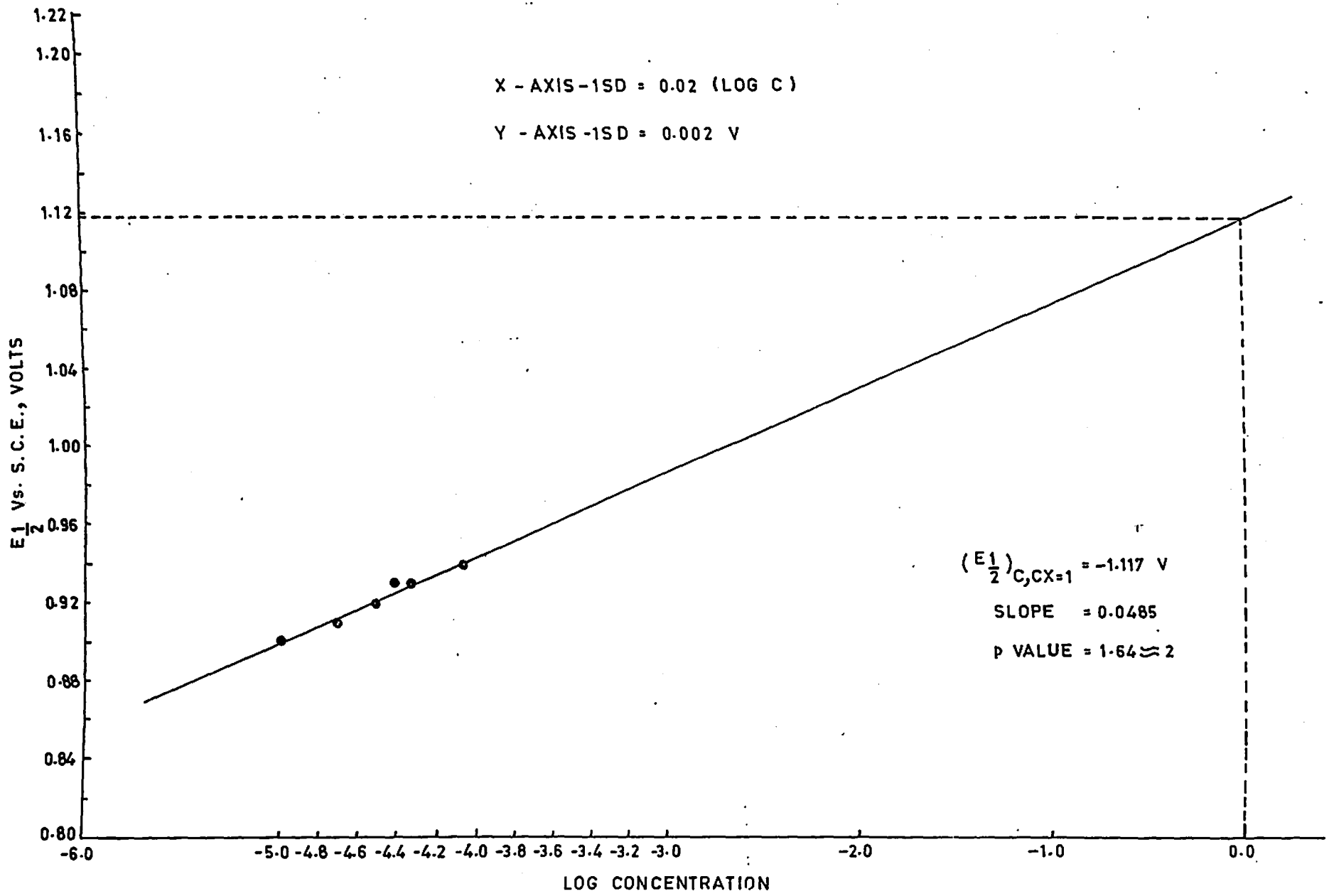


FIG.4 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Ni(II)-THIOPROLINE SYSTEM.

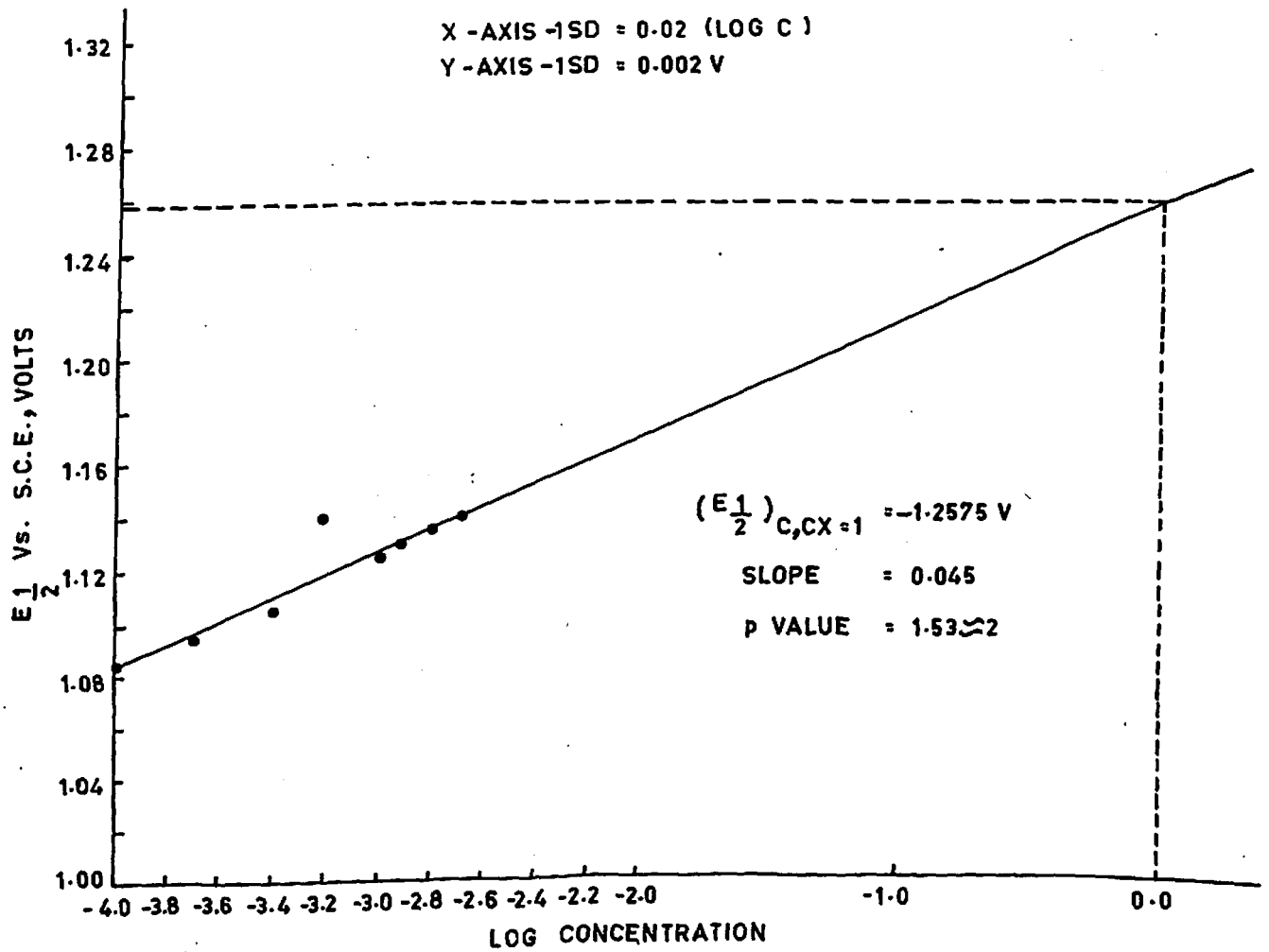
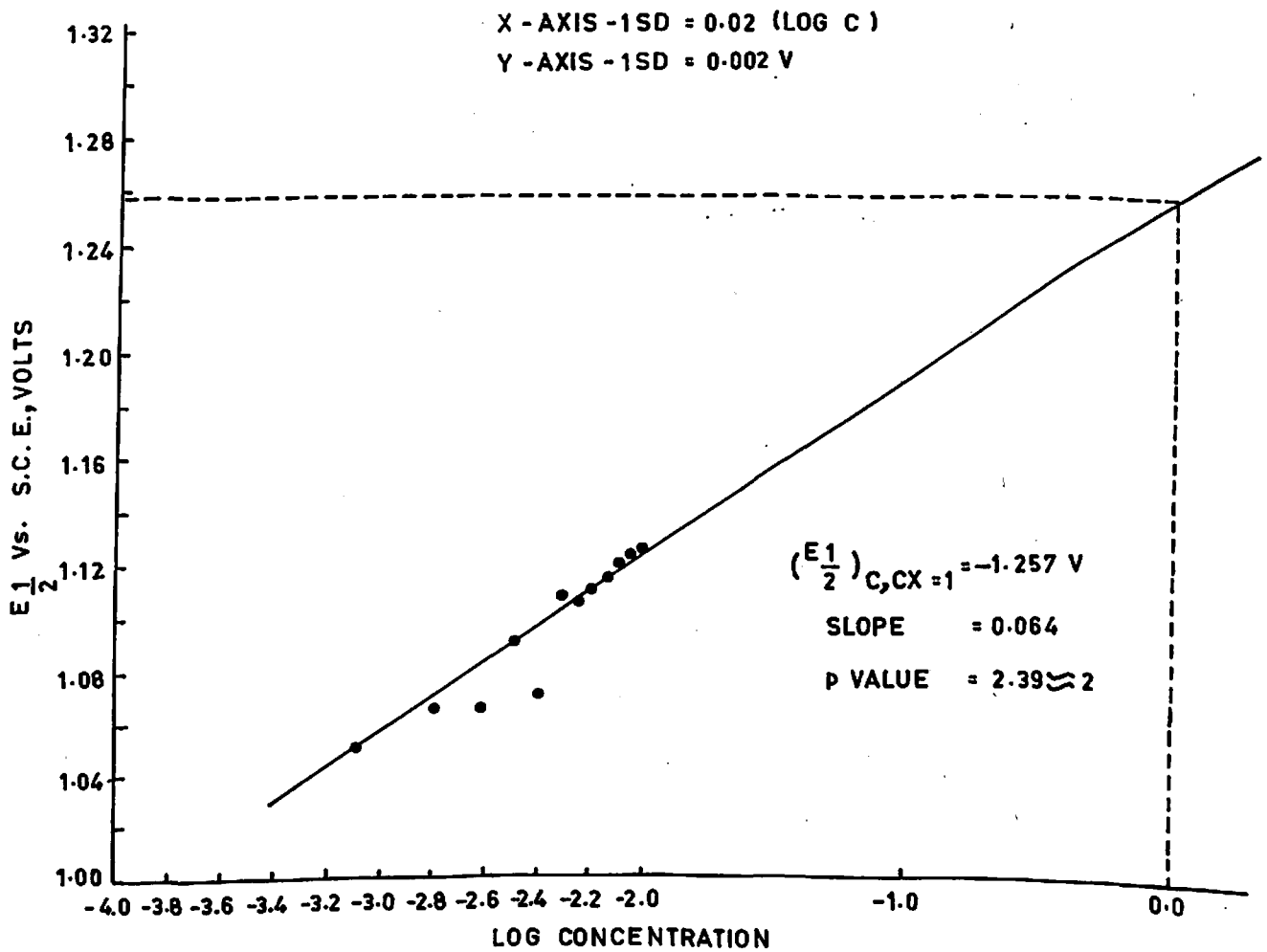


FIG.5 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Ni(II)-2-THIOPHENE ACETIC ACID SYSTEM.



G.6 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Ni(II)-2-(2-THIENYL) PYRIDINE SYSTEM.

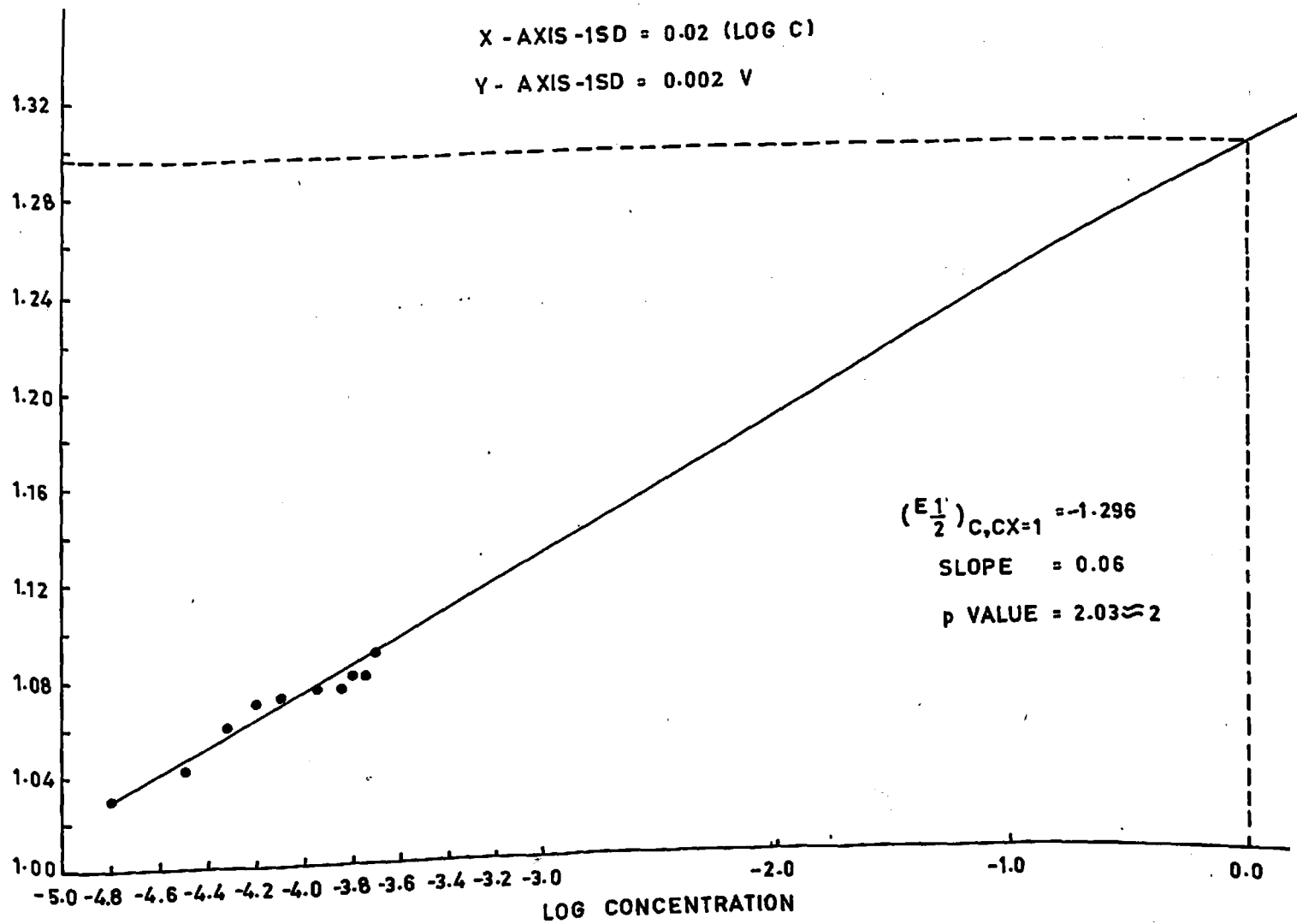


FIG.7 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCEN-TRATION OF LIGAND OF Cd(II)-THIOPROLINE SYSTEM.

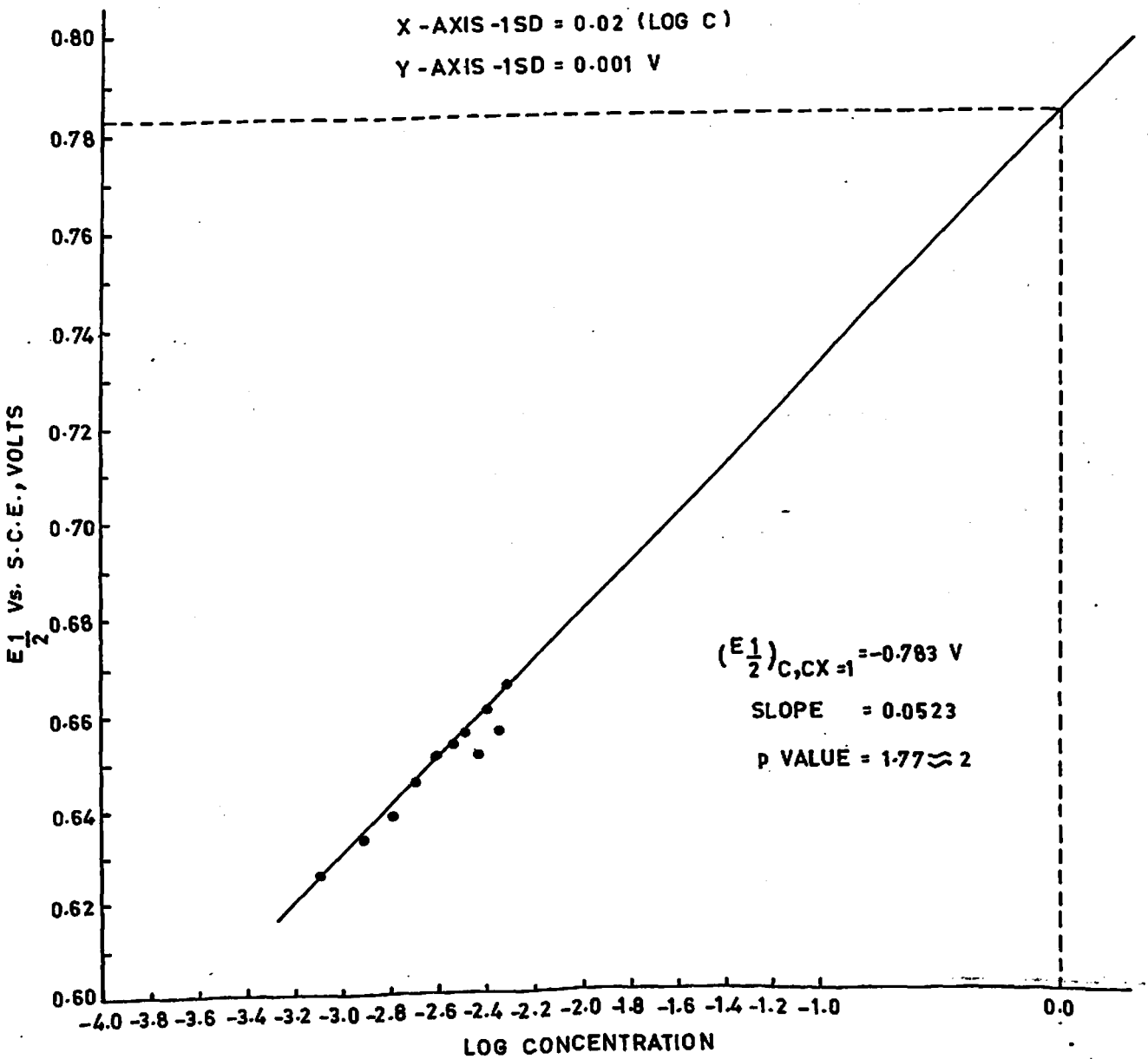


FIG. 8 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCENTRATION OF LIGAND OF Cd(II)-2-THIOPHENE ACETIC ACID SYSTEM.

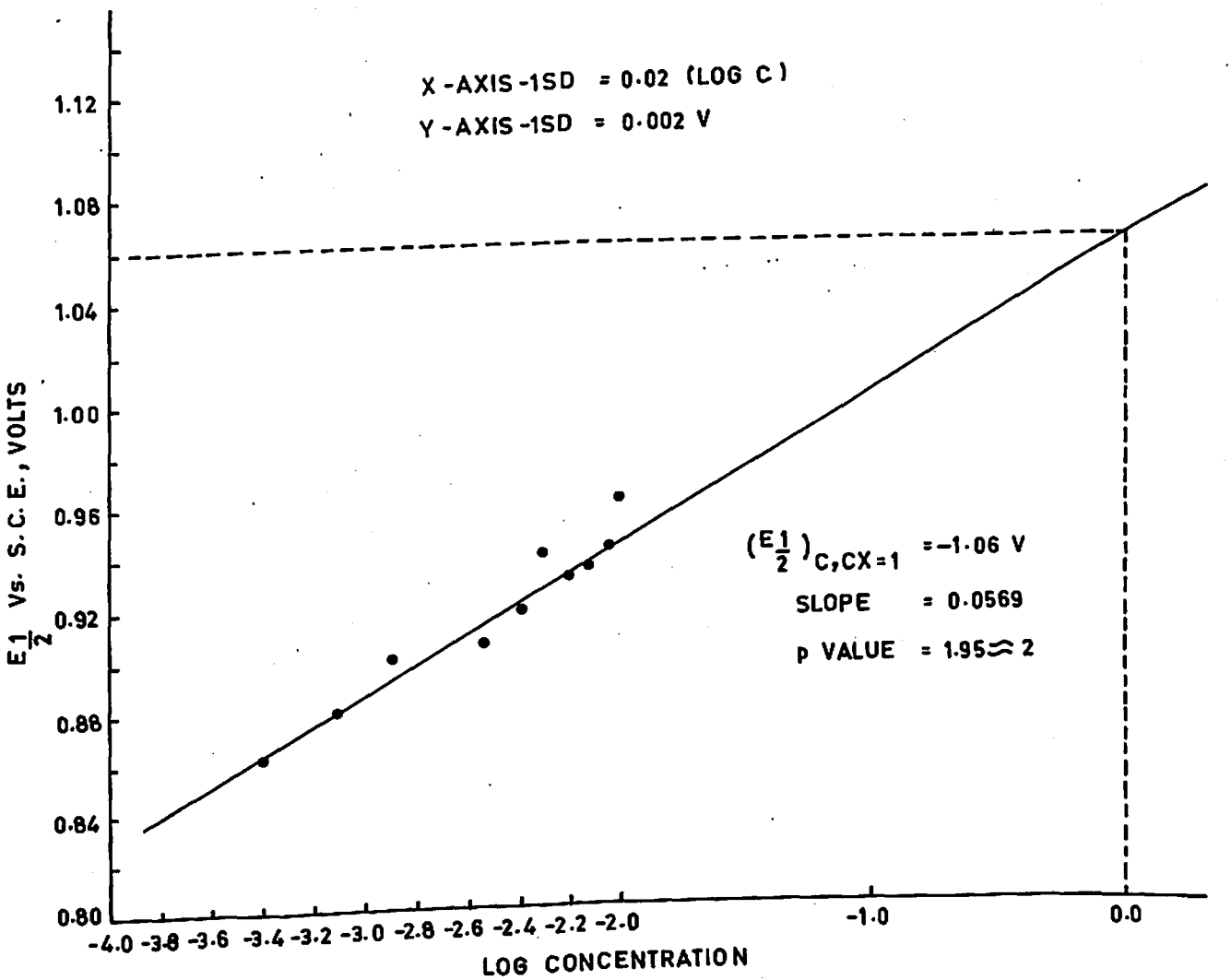
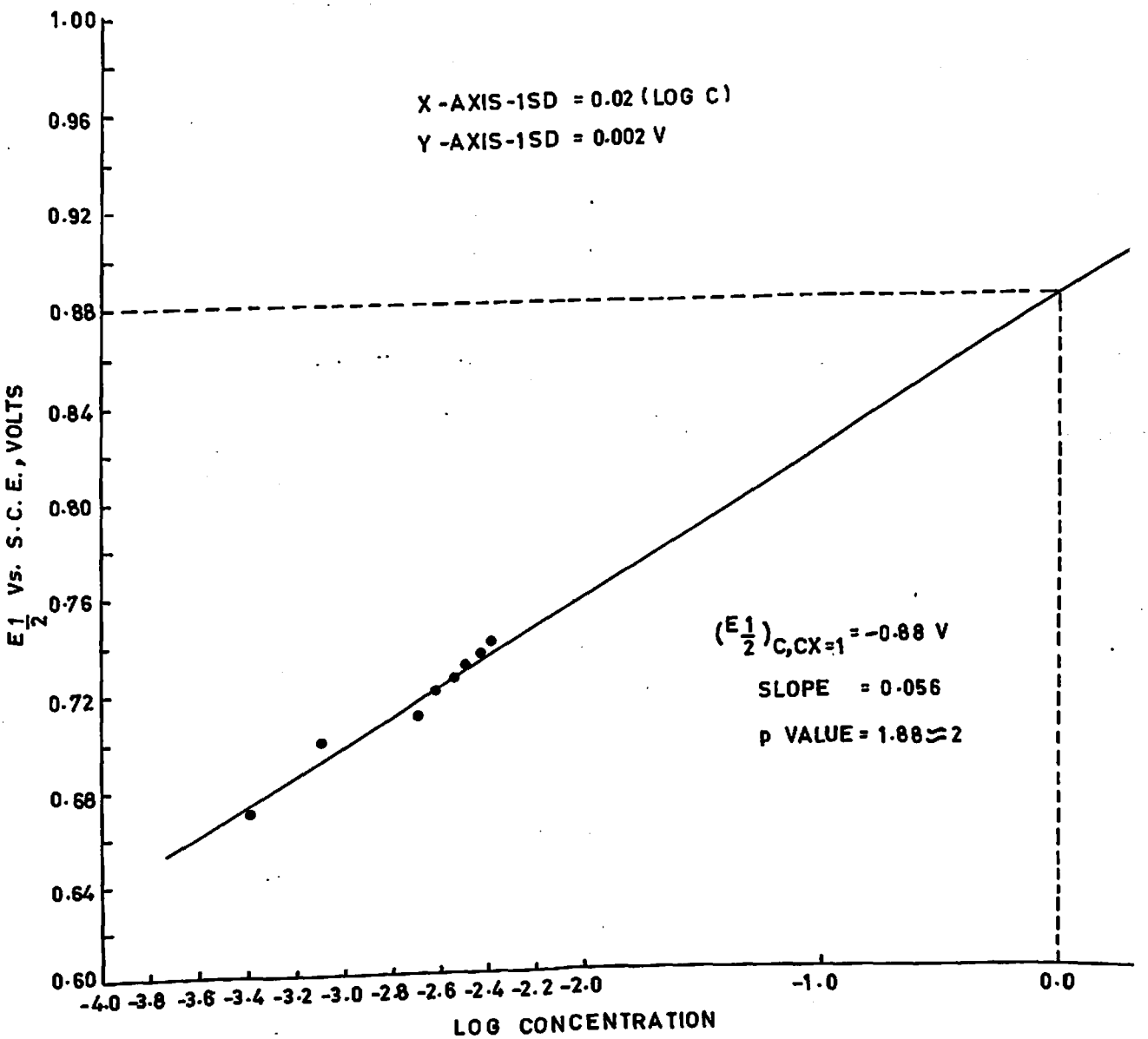
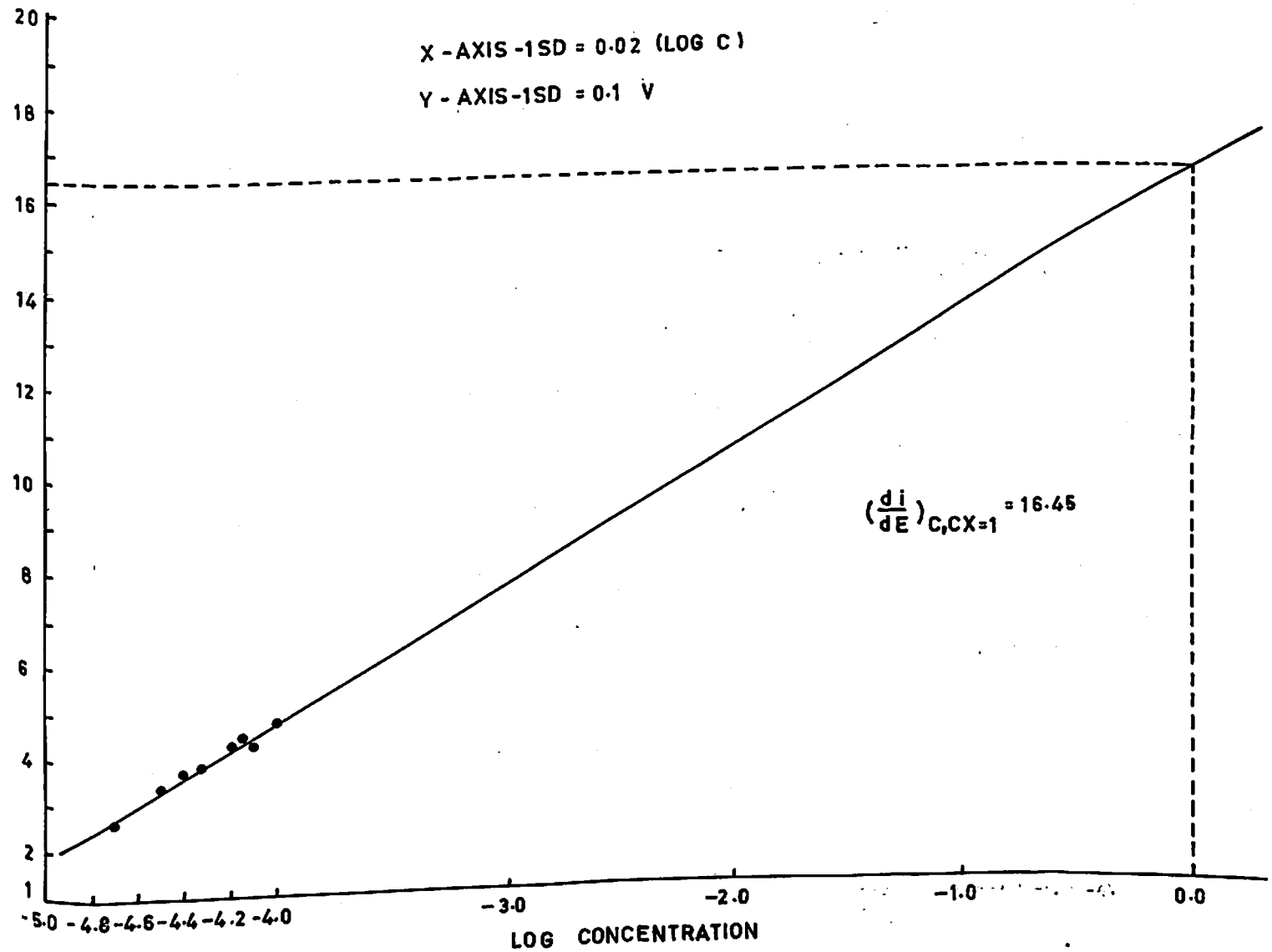


FIG.9 A CURVE BETWEEN HALF-WAVE POTENTIAL AT VARYING CONCEN-TRATION OF LIGAND OF Cd(II)-2-(2-THIENYL) PYRIDINE SYSTEM.



IG.10 A CURVE BETWEEN (di/dE) AT VARYING CONCENTRATION OF LIGAND OF Zn(II)-2-(2-THIENYL) PYRIDINE SYSTEM.



and Ni(II)-2-(2-Thienyl)pyridine, respectively.

A perusal of the data in the Table 5 to 7 indicate the formation constant value to be 7.87, 7.35 and 9.38 in case of Ni(II)-Thioproline, Ni(II)-2-Thiophene acetic acid and Ni(II)-2-(2-Thienyl)pyridine, respectively. The following stability order is observed.

2-(2-Thienyl)pyridine > Thioproline > 2-Thiophene acetic acid

Cd(II) complexes

The pH at which Cd(II)-Thioproline, Cd(II)-2-Thiophene acetic acid and Cd(II)-2-(2-Thienyl)pyridine system have been studied are 11.50±0.10, 11.05±0.10 and 11.58±0.1, respectively, in 0.1M potassium nitrate, with 0.01 per cent gelatin as maximum suppressor. Reversibility of the process can be established by complete retracing of the path and diffusion controlled reduction by the same height of the wave in differential pulse polarography. The nature of the wave for Cd(II) ion and its complexes were well defined and were found to be diffusion controlled. The reduction of Cd(II) ion at pH 11.00 vs SCE was -0.625 V.

The half-wave potentials shifted to more negative values on increase of ligand concentration. A Lingane treatment of the data revealed the formation of complexes with p=2 in each of case consequently, the predominating complex under these conditions was $Cd(II)L_2$. For the equation for the straight line curve through experimental points (Fig. 7 to 9) it is found that $(E_{\frac{1}{2}})_{c,cx=1}$ is -0.783 V, -1.060 V and -0.860 V vs

SCE for Cd(II)-Thioproline, Cd(II)-2-Thiophene acetic acid and Cd(II)-2-(2-Thienyl)pyridine, respectively.

A perusal of the data in Table 8 to 10 indicate the formation constant value to be 5.46, 15.34 and 9.63 in case of Cd(II)-Thioproline, Cd(II)-2-Thiophene acetic acid and Cd(II)-2-(2-Thienyl)pyridine, respectively. The following stability order is observed.

2-Thiophene acetic acid > 2-(2-Thienyl)pyridine > Thioproline

Thioproline, a saturated ring structure, with sulphur and carboxylato groups for coordinating with the metal ion, will probably provide carboxylate oxygen for coordination in preference to sulphur, as sulphur is not charged. The possibility of the chelate formation is also ruled out, as in that case a six membered structure molecule is formed and will be most unstable as strain will be maximum due to distorted form. Thus there is probability of M(II)-$(Thioproline)_2$ complex, i.e. 1:2 complex existing in solution.

2-Thiophene acetic acid and 2-(2-Thienyl)pyridine both act as bidentate ligands. Both have unsaturated benzene molecules. 2-Thiophene acetic acid complex with M(II) ion may be six membered and that of 2-(2-Thienyl)pyridine will be five membered structures. Chelation explains the higher stabilities over thioproline, which may be acting as a monodentate ligand. The stability of 2-Thiophene acetic acid over 2-(2-Thienyl) pyridine may be explained as five membered rings are less stable than six membered rings.

2. Biocidal Activity

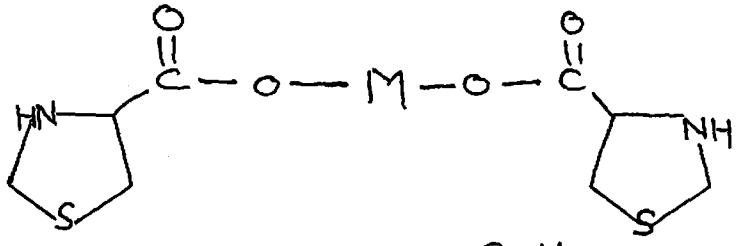
The metal ions, the ligands, the binary complexes and mixed ligand complexes of 2,2'-bipyridyl (By) and thioacids, viz., thiosalicylic acid (TSA) and thiolactic acid (TLA) were screened for their antifungal activity against Macrophomina phaseolina, Fusarium oxysporium and Rhizoctonia solani by food poisoned technique. The screening was done at 1, 10, 50 and 100 $\mu g\ ml^{-1}$ in aqueous medium. All the experiments were carried out in triplicate. The results are given in Tables 11, 12, 13 and 14. The perusal of the data revealed mixed ligand complexes showing encouraging fungicidal activity against M. phaseolina and F. oxysporium but simple metal ions were found to be ineffective against all the tested fungi. Fungitoxicity varied not only among the mixed ligand complexes, binary complexes and metal ions, but also varied with the different kinds of test fungi.

Nickel complexes

The nickel ion exhibited fungitoxicity at 100 $\mu g\ ml^{-1}$ level against M. phaseolina and R. solani as compared to F. oxysporium in which inhibition was observed even at 100 $\mu g\ ml^{-1}$ level. It showed 6.00 and 14.60 per cent mycelial growth inhibition in case of M. phaseolina and R. solani, respectively and varied from 2.64 to 32.00 per cent in case of F. oxysporium with increasing concentrations of metal ion. Metal complexes with ligands containing nitrogen and sulphur atoms find use as pesticides and fungicides. The fungicidal activity of bipyridyl

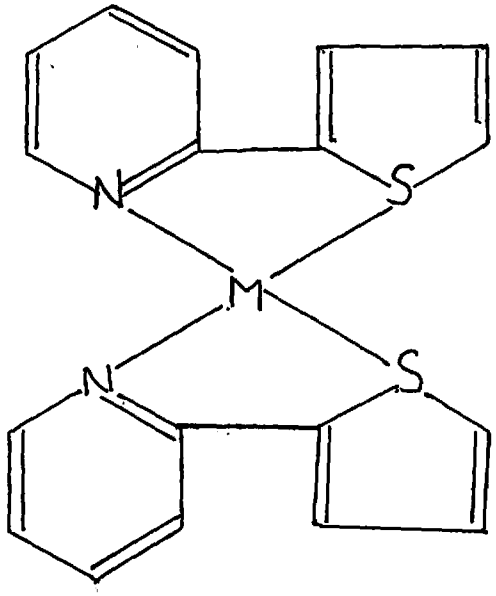
The complexes of TP, TPA and TEP with M(II) M=Zn(II), Ni(II), and Cd(II) may be represented as:

1.



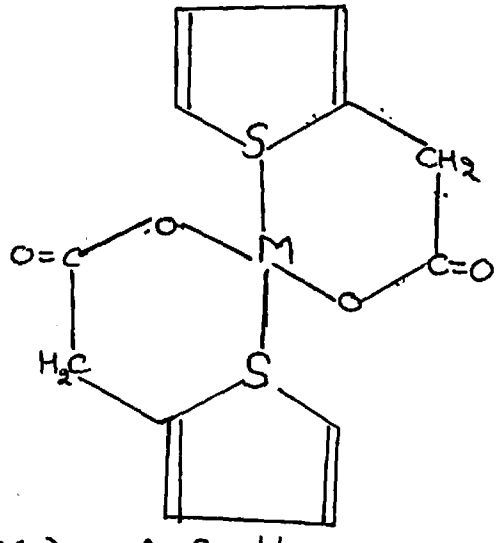
M(II)-TP Complex

2.



M(II)-TEP Complex

3.



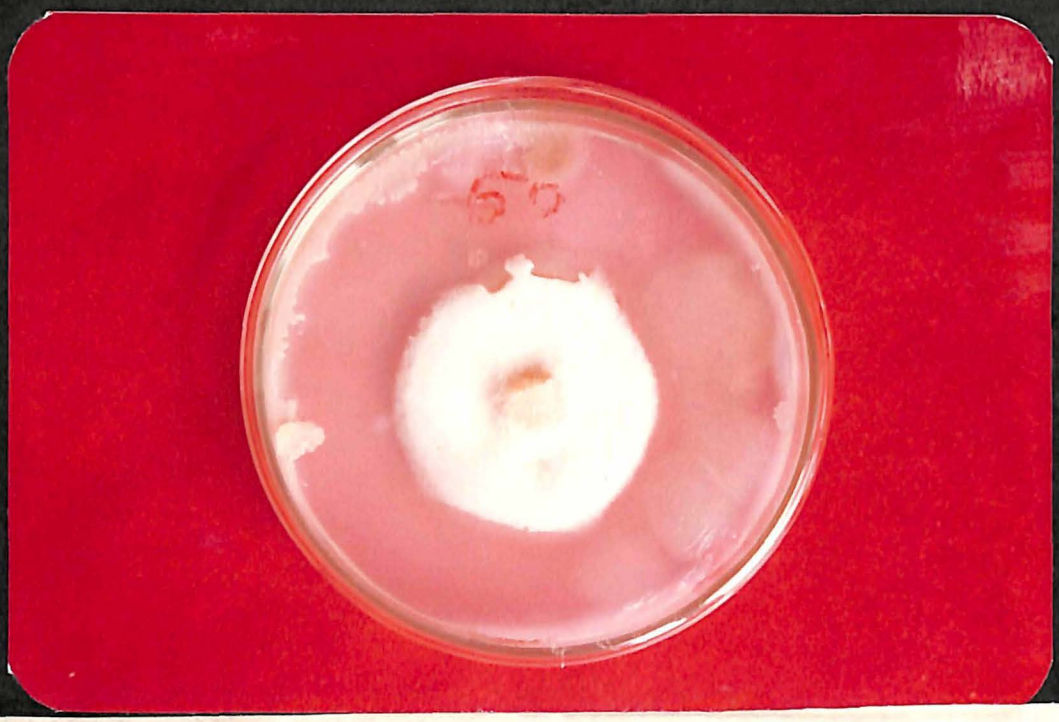
M(II)-TPA Complex

may be due to nitrogen atoms. The per cent inhibition observed in case of bipyridyl is 4.00, 14.68, 22.65, 35.32; 8.33, 12.66, 20.67, 25.33 and 0.00, 0.00, 2.66, 6.67 against F. oxysporium, M. phaseolina and R. solani at 1, 10, 50 and 100 μg ml^{-1} levels, respectively. The data indicate that nitrogen donor ligand is least effective against R. solani. The inhibition of fungal growth by Ni(II)-(By) binary complex showed the order F. oxysporium > M. phaseolina > R. solani. The per cent growth inhibition was 54.00, 34.66 and 29.33, respectively, in the three test fungi at 100 μg ml^{-1} level. It indicates Ni(II)-(By) complex to be more effective against F. oxysporium. The per cent inhibition by sulphur ligands, viz., TSA and TLA at 1, 10, 50 and 100 μg ml^{-1} level against M. phaseolina, F. oxysporium and R. solani are 6.68, 12.60, 20.00, 28.00; 6.66, 17.31, 25.33, 32.00; 0.00, 0.00, 0.00, 4.00 and 12.00, 14.00, 26.66, 30.64; 9.31, 18.58, 26.66, 38.64; 0.00, 2.66, 6.67, 13.34, respectively. TSA and TLA were more potent against M. phaseolina and F. oxysporium fungi. Mixed ligand complexes of Nickel, i.e., Ni-(By)-TSA and Ni-(By)-TLA exhibited mycelial growth inhibition as 39.31, 51.66, 62.34, 69.14; 36.00, 50.62, 57.52, 67.38, 6.67, 22.66, 39.62, 49.35, and 28.39, 49.00, 64.00, 70.33; 40.00, 50.64, 58.68, 62.38; 9.34, 32.00, 41.34, 57.31, respectively against the tested fungi at four concentrations, viz., 1, 10, 50 and 100 μg ml^{-1}, respectively. The following decreasing order of fungitoxicity was observed.

M. phaseolina > F. oxysporium > R. solani

Photograph - E: Percentage Inhibition shown by Zn-By-TLA complex against F. oxysporium at 1 μg ml^{-1} level after 120 hours

Photograph - F: Percentage Inhibition shown by Zn-By-TLA complex against F. oxysporium at 10 μg ml^{-1} level after 120 hours



Photograph - G: Percentage Inhibition shown by Zn-By-TLA complex against F. oxysporium at 50 µg ml^{-1} level after 120 hours

Photograph - H: Percentage Inhibition shown by Zn-By-TLA complex against F. oxysporium at 100 µg ml^{-1} level after 120 hours

2.32 and 6.67 per cent mycelial growth inhibition in case of M. phaseolina and R. solani, respectively, and varied from 4.00 to 30.62 per cent in case of F. oxysporium with increasing concentration of metal ion. The inhibition of fungal growth by Zn(II)-(By) complex showed the order F. oxysporium > M. phaseolina > R. solani. The per cent growth inhibition was 49.00, 38.34 and 29.34, respectively, in the three test fungi. It indicates Zn(II)-(By) complex to be more effective against F. oxysporium. Mixed ligand complexes of TSA and TLA, i.e., Zn(II)-By-TSA and Zn(II)-By-TLA exhibited mycelial growth inhibition as 36.00, 45.33, 54.62, 62.66; 23.20, 44.00, 53.00, 62.38; 1.34, 13.28, 20.00, 37.38, and 25.28, 42.00, 54.64, 64.67; 17.42, 28.00, 54.84, 60.67; 0.00, 16.00, 26.66, 37.34, respectively, against the three tested fungi at four concentrations, viz., 1, 10, 50 and 100 $\mu g\ ml^{-1}$. The following decreasing order of fungitoxicity was observed.

M. phaseolina > F. oxysporium > R. solani

Manganese complexes

The manganese ion exhibited no fungitoxicity even at 100 $\mu g\ ml^{-1}$ level against M. phaseolina and R. solani as compared to F. oxysporium in which inhibition was observed at 10 $\mu g\ ml^{-1}$. It showed no growth inhibition in case of M. phaseolina and R. solani and varied from 3.65 to 15.67 per cent in case of F. oxysporium with increasing concentration of metal ion. The inhibition of fungal growth by Mn(II)-(By) complex showed the order F. oxysporium > M. phaseolina > R. solani. The per cent

growth inhibition was 46.67, 33.33 and 13.34, respectively, in the three tested fungi. It indicates Mn(II)-(By) complex to be more effective against F.oxysporium. Mixed ligand complexes of TSA and TLA, i.e., Mn(II)-By-TSA and Mn(II)-By-TLA exhibited mycelial growth inhibition as 18.00, 36.00, 50.59, 60.00; 26.58, 36.00, 46.74, 54.66; 2.64, 12.67, 23.28, 34.67 and 28.68, 42.62, 49.31, 58.66; 26.64, 36.00, 44.00, 52.00; 0.00, 2.45, 10.67, 36.00, respectively, against the three tested fungi at four concentrations, viz., 1, 10, 50 and 100 $\mu g\ ml^{-1}$. The following decreasing order of fungitoxicity was observed.

M.phaseolina > F.oxysporium > R.solani

Cobalt complexes

The cobalt ion exhibited no fungitoxicity even at 100 $\mu g\ ml^{-1}$ level against M.phaseolina and R.solani as compared to F.oxysporium in which inhibition was observed at 10 $\mu g\ ml^{-1}$. It showed no growth inhibition in case of M.phaseolina and R.solani and varied from 4.59 to 12.38 per cent in case of F.oxysporium with increasing concentration of metal ion. The inhibition of the fungal growth Co(II)-By complex showed the order M.phaseolina > F.oxysporium > R.solani. The per cent growth inhibition at 100 $\mu g\ ml^{-1}$ was 33.38, 31.32 and 12.00 in the three tested fungi. It indicates Co(II)-(By) complex to be more effective against M.phaseolina. The mixed ligand complexes of TSA and TLA, i.e., Co(II)-By-TSA and Co(II)-By-TLA exhibited mycelial growth inhibition as 30.68, 38.64, 50.66, 57.34; 22.00, 34.48, 44.00, 50.64; 0.00, 13.33, 20.00, 28.00 and

TABLE 11: FUNGICIDAL SCREENING : AVERAGE % INHIBITION AFTER 120 HOURS; Organism = Macrophomina phaseolina; Medium = Czapek's Agar Medium; Temperature = 30±1°C

Compound Number	Name of Compound	*1	10	50	100
1.	Zn(By)TSA	36.00	45.33	54.62	62.66
2.	Ni(By)TSA	39.31	51.66	62.34	69.14
3.	Mn(By)TSA	18.00	36.00	50.69	60.00
4.	Co(By)TSA	30.68	38.64	50.66	57.34
5.	Fe(By)TSA	35.34	48.65	56.64	66.34
6.	Zn(By)TLA	25.28	42.00	54.64	64.67
7.	Ni(By)TLA	28.39	49.00	64.00	70.33
8.	Mn(By)TLA	28.68	42.62	49.31	58.66
9.	Co(By)TLA	25.30	39.38	49.36	54.32
10.	Fe(By)TLA	27.58	45.60	58.32	66.61
11.	Zn(By)	6.66	14.64	27.33	38.34
12.	Ni(By)	9.33	16.00	22.61	34.66
13.	Mn(By)	14.00	20.00	27.00	33.33
14.	Co(By)	12.00	18.67	25.46	33.38
15.	Fe(By)	11.28	18.58	29.33	38.55
16.	$ZnSO_4 . xH_2O$	0.00	0.00	0.00	2.32
17.	$NiSO_4 . xH_2O$	0.00	0.00	0.00	6.00
18.	$MnSO_4 . xH_2O$	0.00	0.00	0.00	0.00
19.	$CoSO_4 . xH_2O$	0.00	0.00	0.00	0.00
20.	$FeSO_4 . xH_2O$	0.00	0.00	0.00	4.06
21.	TSA	6.68	12.60	20.00	28.00
22.	TLA	12.00	14.00	26.66	30.64
23.	By	8.33	12.66	20.67	25.33

*Concentrations used in $\mu g\ ml^{-1}$

TABLE 12: FUNGICIDAL SCREENING : AVERAGE % INHIBITION AFTER 120 HOURS; Organism = *Fusarium oxysporium*
Medium = Czapek's Agar Medium; Temperature = 30±1°C

Compound Number	Name of Compound	*1	10	50	100
1.	Zn(By)TSA	23.20	44.00	53.00	62.38
2.	Ni(By)TSA	36.00	50.62	57.52	63.36
3.	Mn(By)TSA	26.58	36.00	46.74	54.66
4.	Co(By)TSA	22.00	34.48	44.00	50.64
5.	Fe(By)TSA	33.33	46.67	60.00	65.00
6.	Zn(By)TLA	17.42	28.00	54.84	60.67
7.	Ni(By)TLA	40.00	50.64	58.68	62.38
8.	Mn(By)TLA	26.64	36.00	44.00	52.00
9.	Co(By)TLA	13.34	25.00	30.54	46.62
10.	Fe(By)TLA	25.36	33.33	60.66	64.00
11.	Zn(By)	14.68	26.67	42.56	49.00
12.	Ni(By)	17.38	33.32	48.66	54.00
13.	Mn(By)	10.71	26.54	34.64	46.67
14.	Co(By)	1.34	9.45	18.65	31.32
15.	Fe(By)	12.64	27.35	32.59	51.00
16.	$ZnSO_4 \cdot xH_2O$	4.00	12.66	26.68	30.62
17.	$NiSO_4 \cdot xH_2O$	2.64	13.36	25.32	32.00
18.	$MnSO_4 \cdot xH_2O$	0.00	3.65	11.62	15.67
19.	$CoSO_4 \cdot xH_2O$	0.00	4.59	8.65	12.38
20.	$FeSO_4 \cdot xH_2O$	0.00	3.67	13.33	16.34
21.	TSA	6.66	17.31	25.33	32.00
22.	TLA	9.31	18.58	26.68	38.64
23.	By	4.00	14.68	22.65	35.32

*Concentrations used in $\mu g\ ml^{-1}$

TABLE 13: FUNGICIDAL SCREENING : AVERAGE % INHIBITION AFTER 120 HOURS; Organism = Rhizoctonia solani; Medium = Czapek's Agar Medium; Temperature = 30±1°C

Compound Number	Name of Compound	*1	10	50	100
1.	Zn(By)TSA	1.34	13.28	20.00	37.38
2.	Ni(By)TSA	6.67	22.66	39.62	49.35
3.	Mn(By)TSA	2.64	12.67	23.28	34.67
4.	Co(By)TSA	0.00	13.33	20.00	28.00
5.	Fe(By)TSA	8.00	16.00	25.33	36.00
6.	Zn(By)TLA	0.00	16.00	26.66	37.34
7.	Ni(By)TLA	9.34	32.00	41.34	57.31
8.	Mn(By)TLA	0.00	2.45	10.67	36.00
9.	Co(By)TLA	4.00	15.00	23.32	33.35
10.	Fe(By)TLA	1.05	12.00	26.67	49.33
11.	Zn(By)	0.00	12.00	25.32	29.34
12.	Ni(By)	0.00	13.34	22.66	29.33
13.	Mn(By)	0.00	0.00	4.00	13.34
14.	Co(By)	0.00	1.34	6.67	12.00
15.	Fe(By)	0.00	0.00	9.34	17.38
16.	$ZnSO_4 \cdot xH_2O$	0.00	0.00	2.64	6.67
17.	$NiSO_4 \cdot xH_2O$	0.00	0.00	0.00	14.60
18.	$MnSO_4 \cdot xH_2O$	0.00	0.00	0.00	0.00
19.	$CoSO_4 \cdot xH_2O$	0.00	0.00	0.00	0.00
20.	$FeSO_4 \cdot xH_2O$	0.00	0.00	0.00	5.33
21.	TSA	0.00	0.00	0.00	4.00
22.	TLA	0.00	2.66	6.67	13.34
23.	By	0.00	0.00	2.66	6.67

*Concentrations used in $\mu g\ ml^{-1}$

FIG. 11 DOSAGE-GROWTH RESPONSE CURVE OF Ni-By-TSA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI.

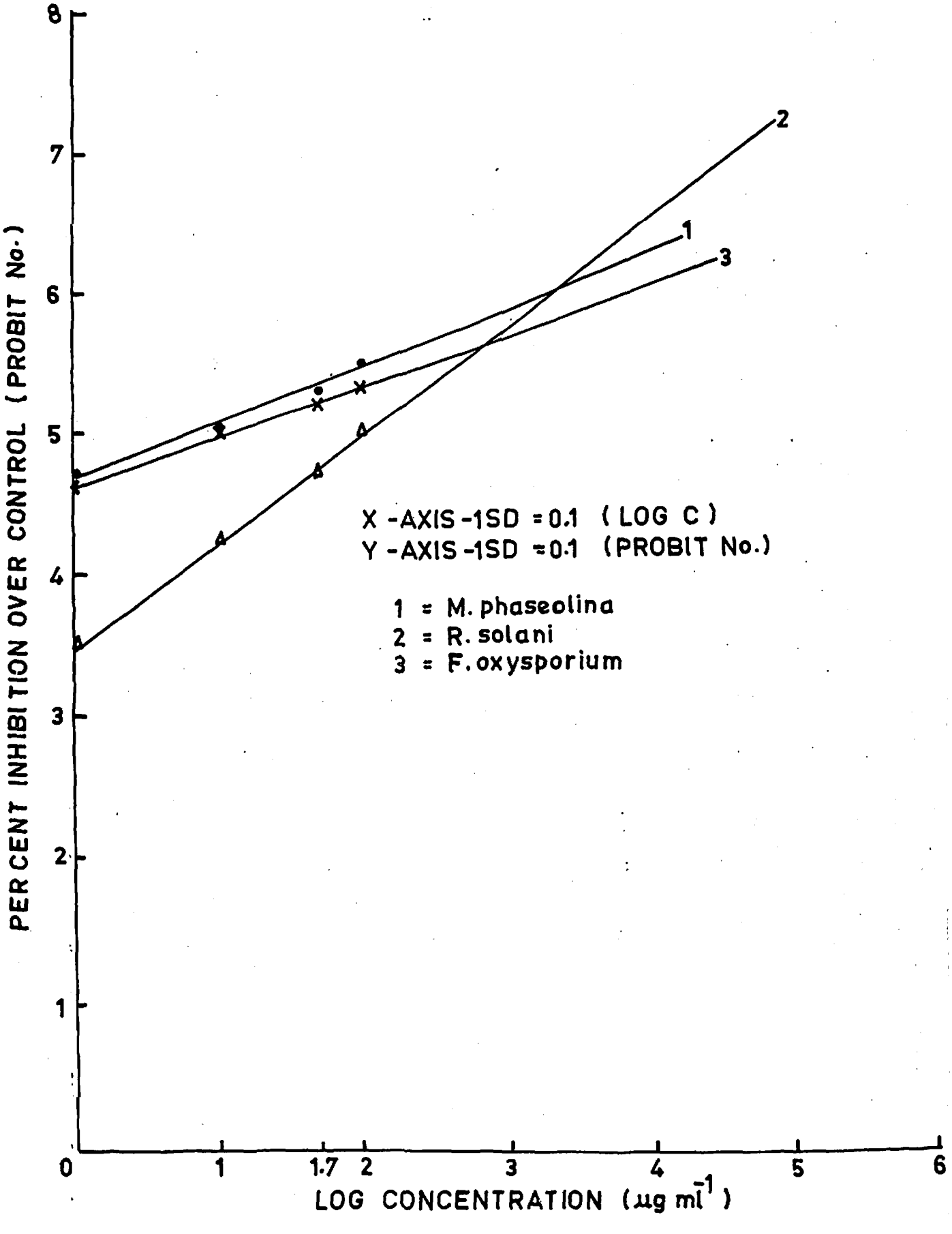


FIG. 12 DOSAGE-GROWTH RESPONSE CURVE OF Zn-By-TSA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI.

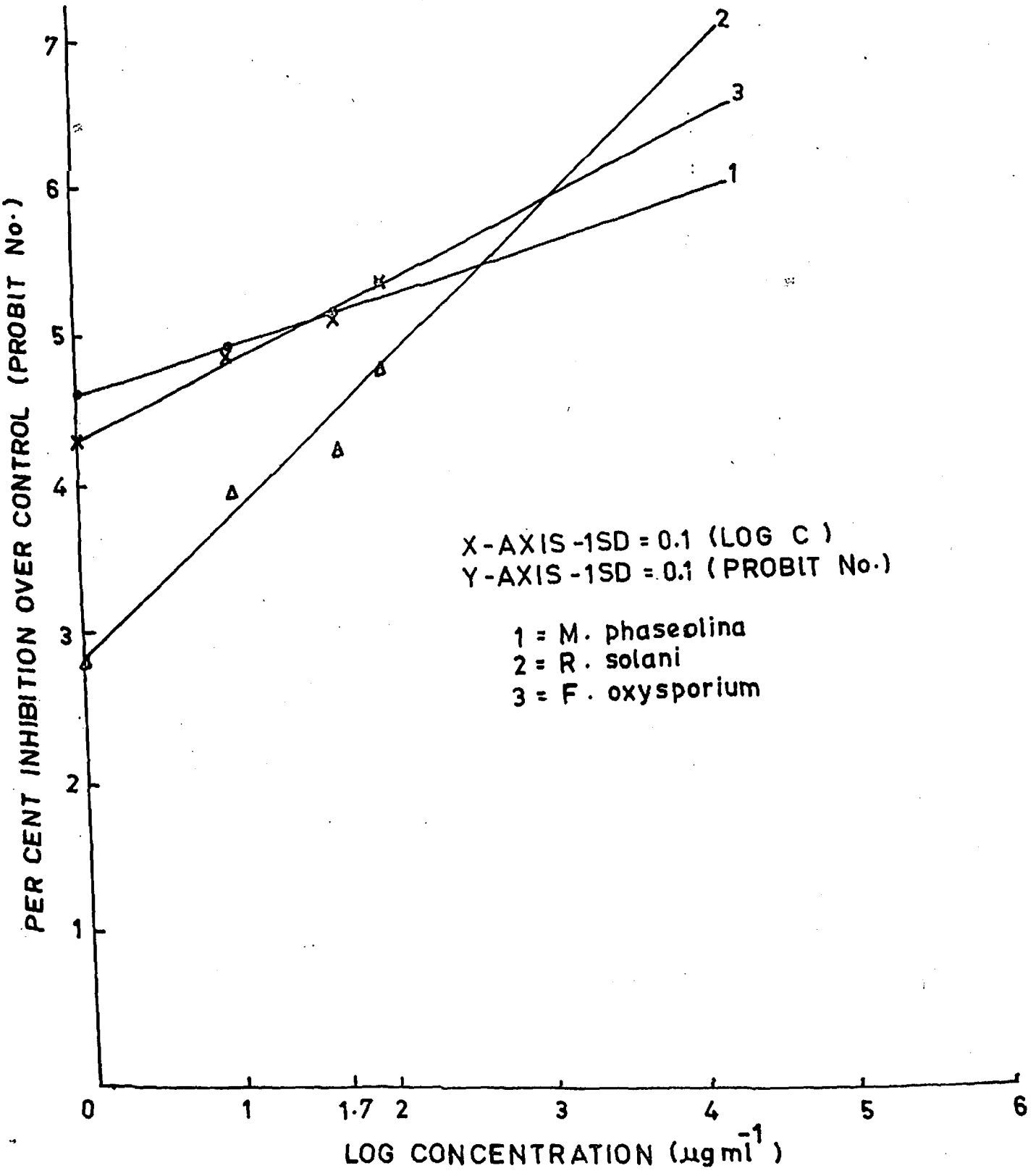


FIG.13 DOSE-GROWTH RESPONSE CURVE OF Fe-By-TSA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI.

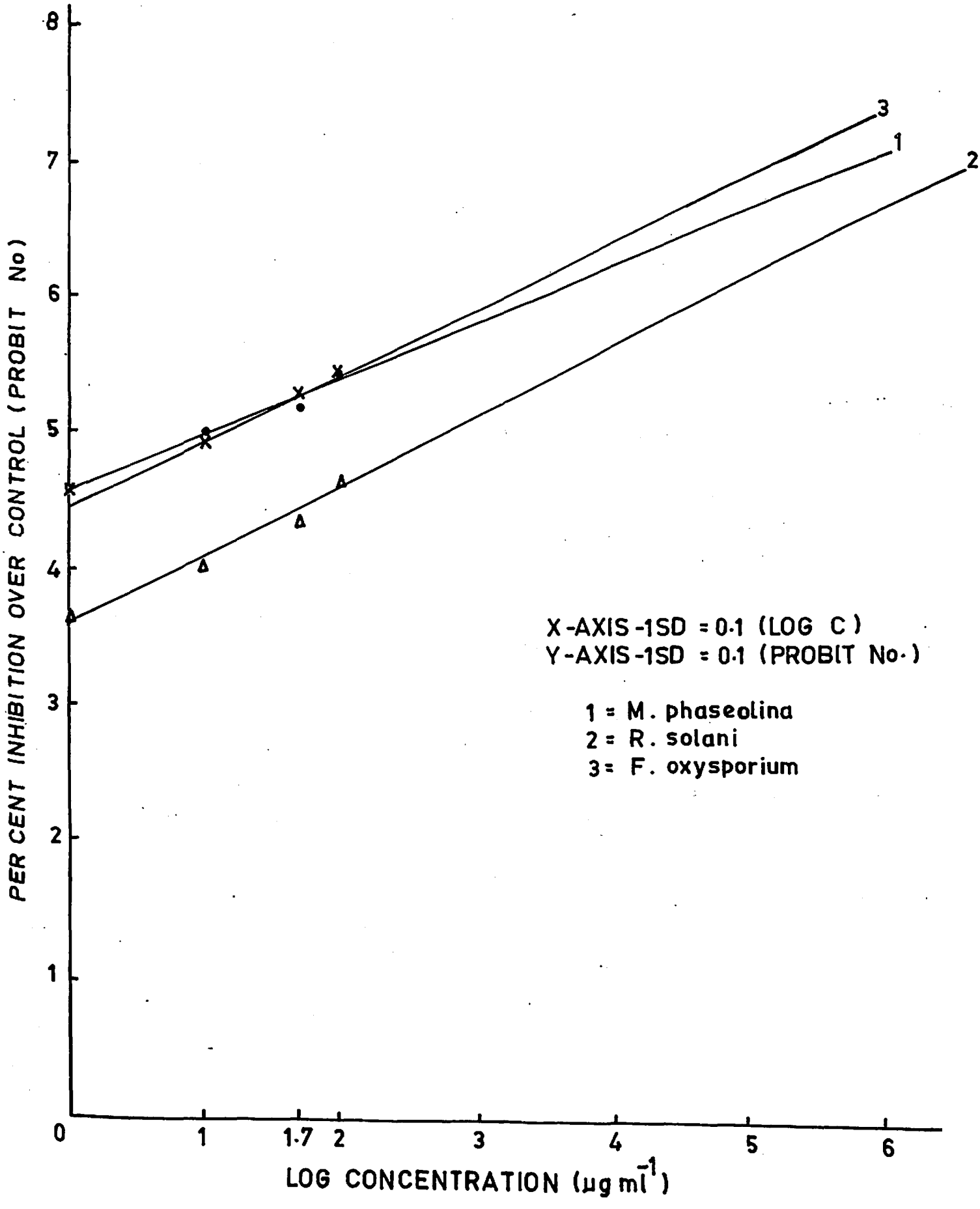


FIG.14 DOSE-GROWTH RESPONSE CURVE OF Mn-By-TSA MIXED LIGAND COMPLEX AGAINST *M. phaseolina*, *R. solani* AND *F. oxysporium* FUNGI.

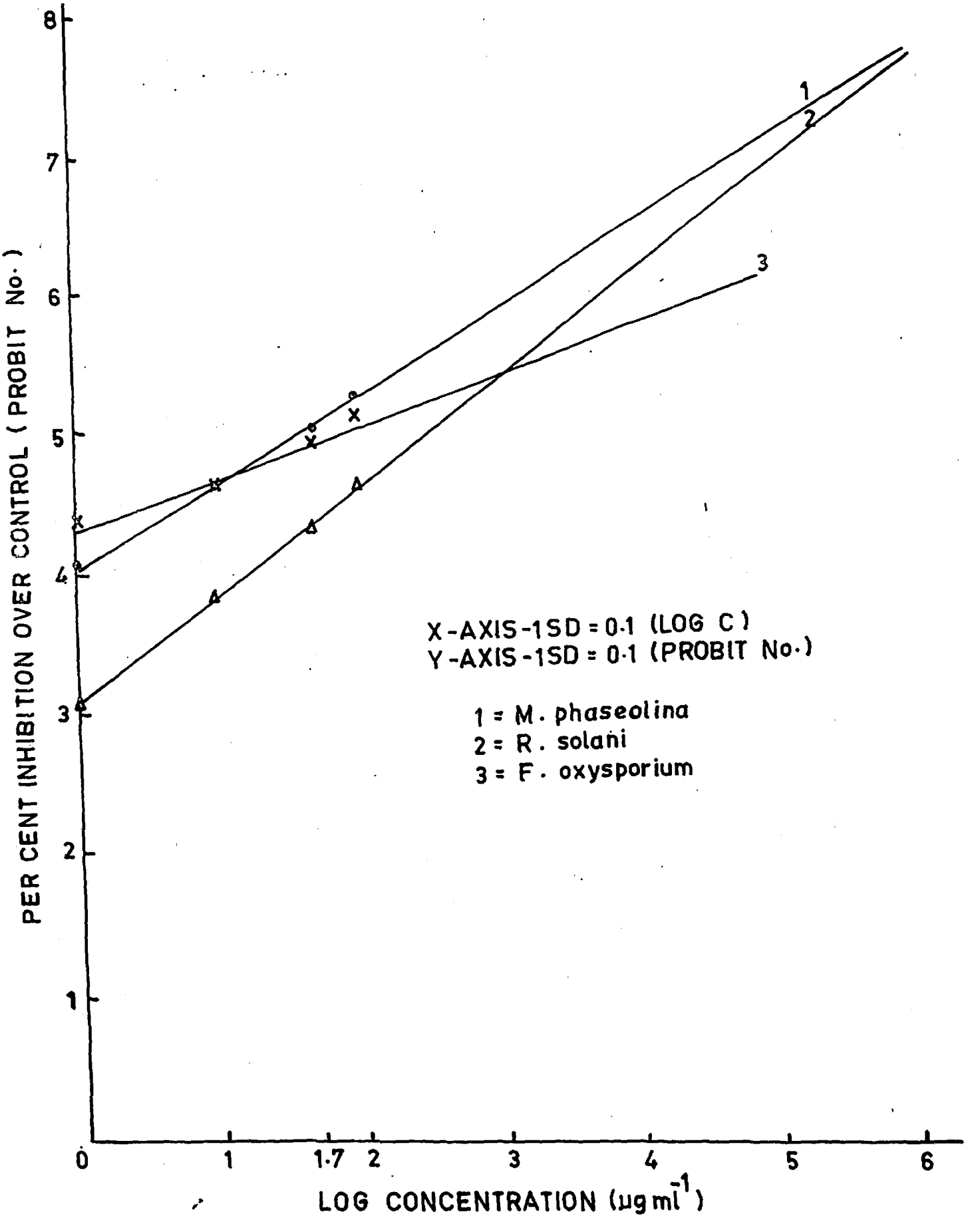


FIG.15 DOSE-GROWTH RESPONSE CURVE OF Co-By-TSA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI.

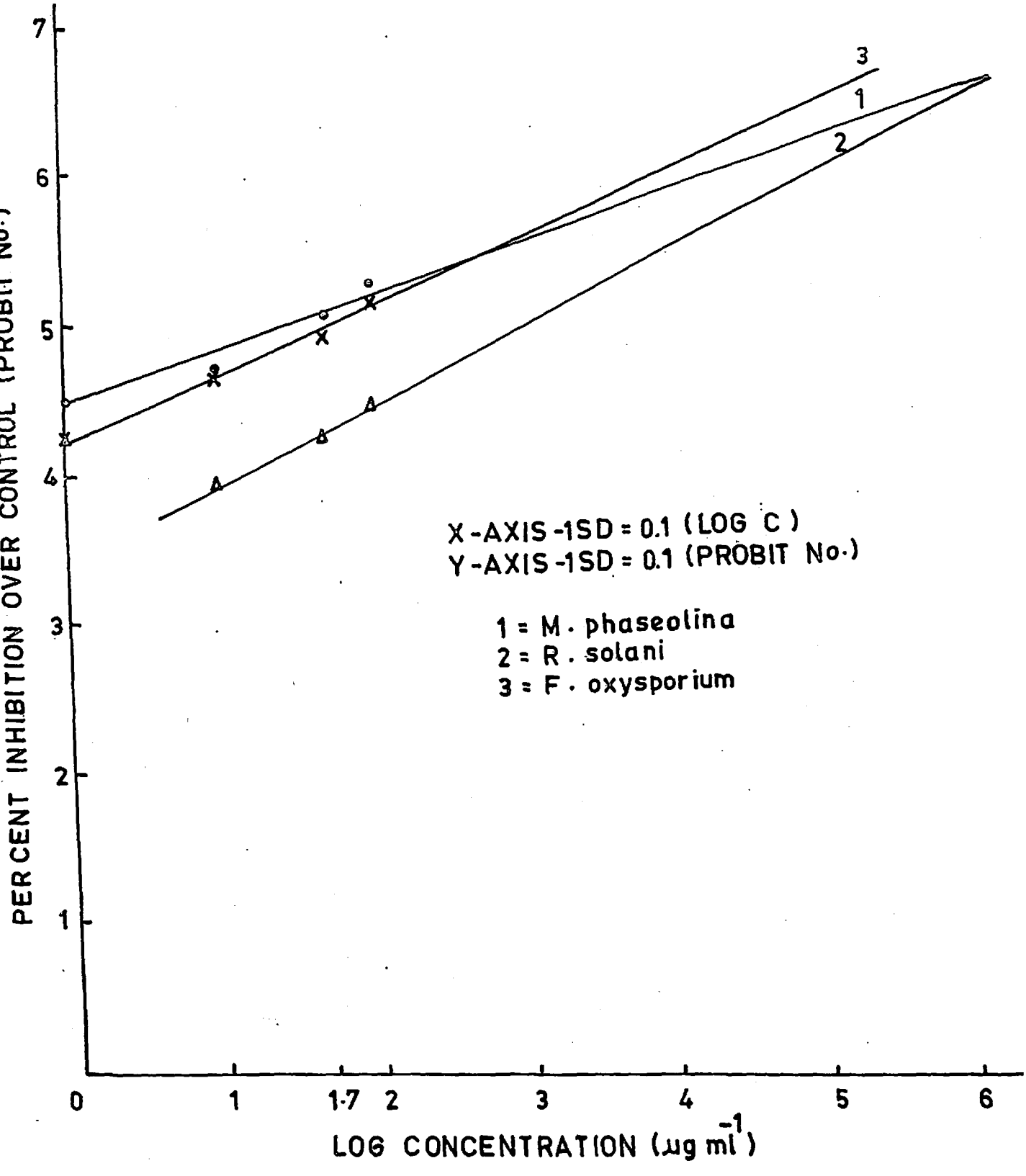


FIG.16 DOSE-GROWTH RESPONSE CURVE OF Ni-By-TLA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI.

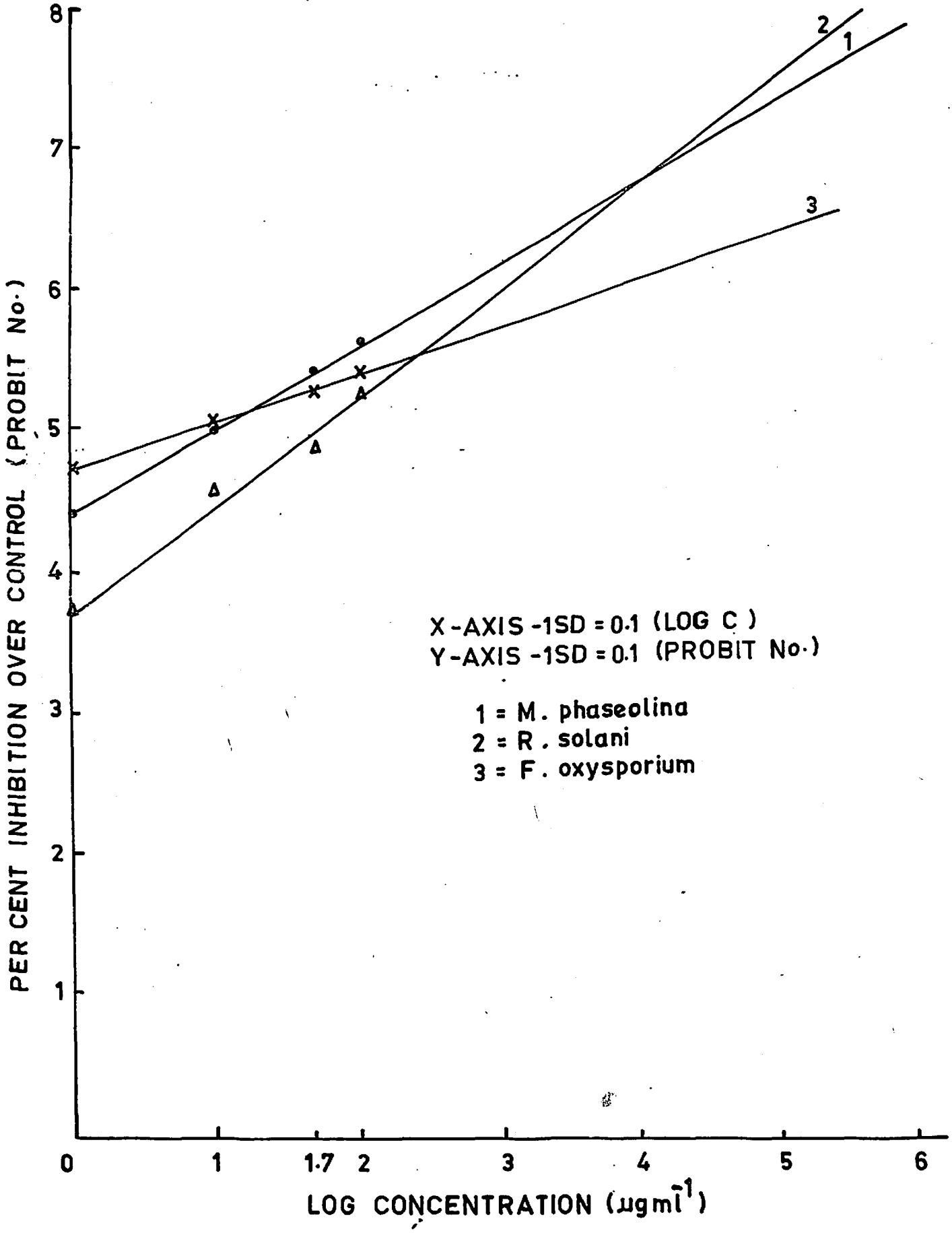


FIG.17 DOSE-GROWTH RESPONSE CURVE OF Zn-By-TLA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI

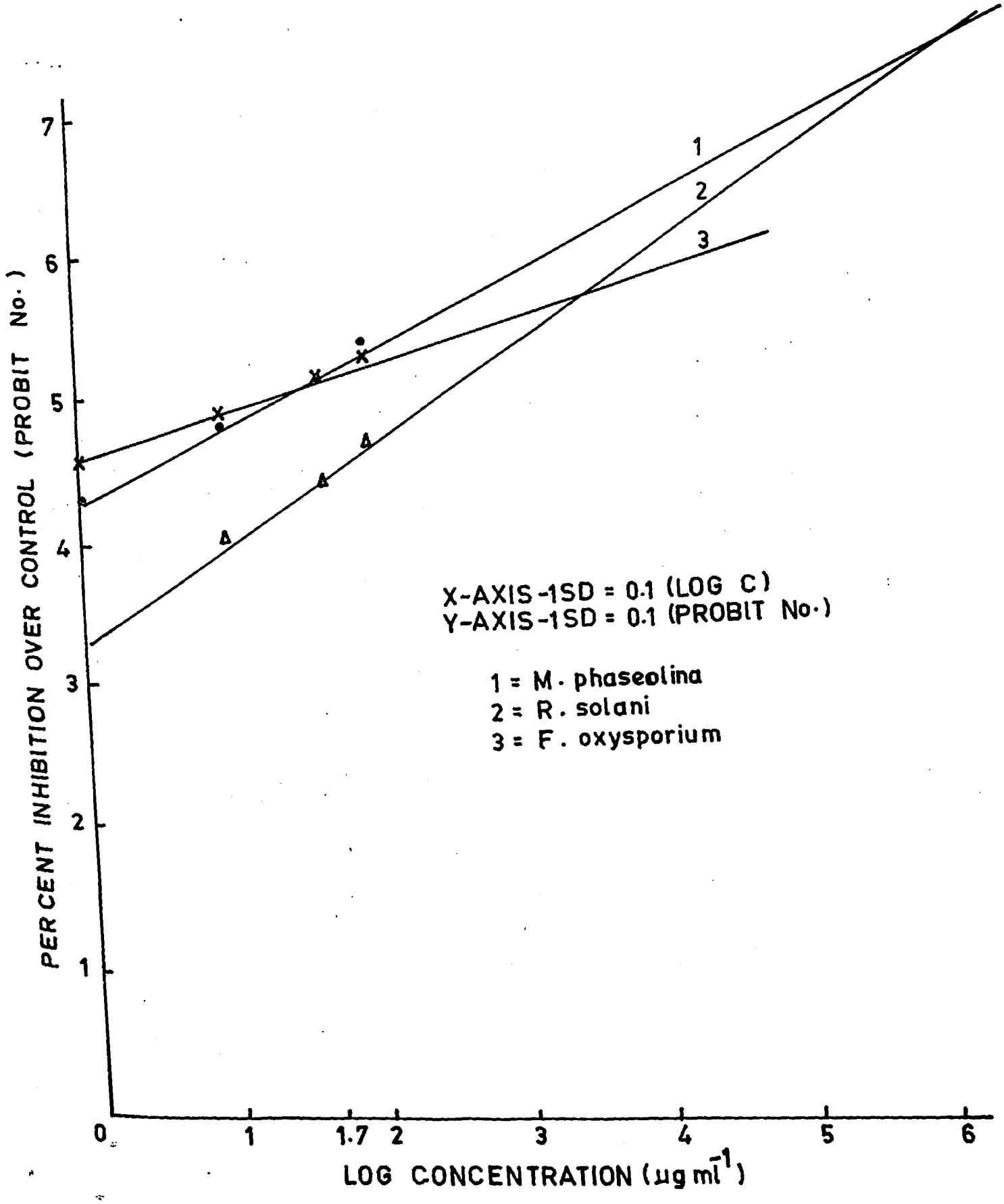


FIG.18 DOSAGE-GROWTH RESPONSE CURVE OF Fe-By-TLA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R. solani AND F. oxysporium FUNGI.

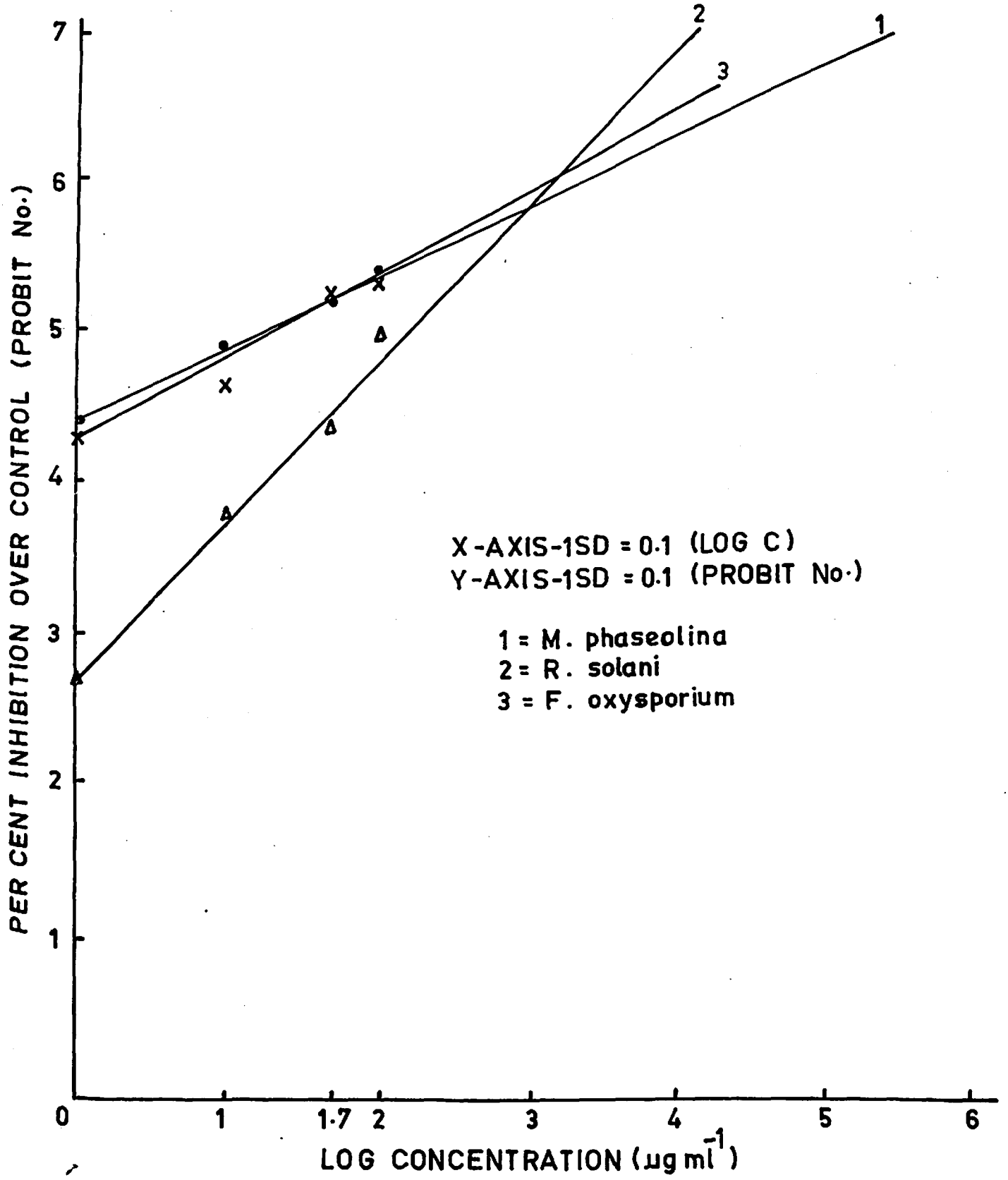


FIG. 19 DOSAGE-GROWTH RESPONSE CURVE OF Mn-By-TLA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R.solani AND F. oxysporium FUNGI.

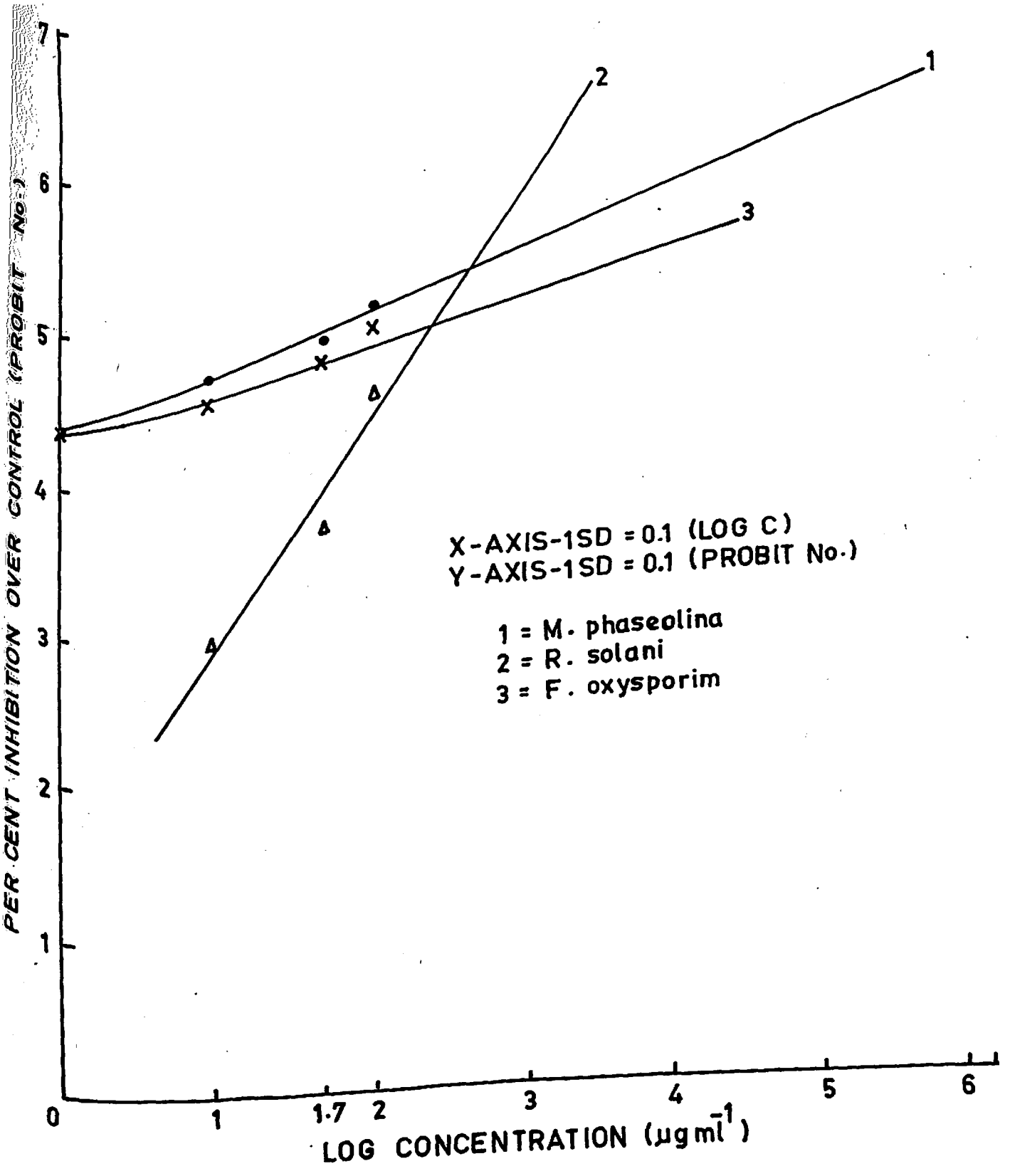


FIG.20 DOSAGE-GROWTH RESPONSE CURVE OF Co-By-TLA MIXED LIGAND COMPLEX AGAINST M. phaseolina, R.solani AND F. oxysporium FUNGI.

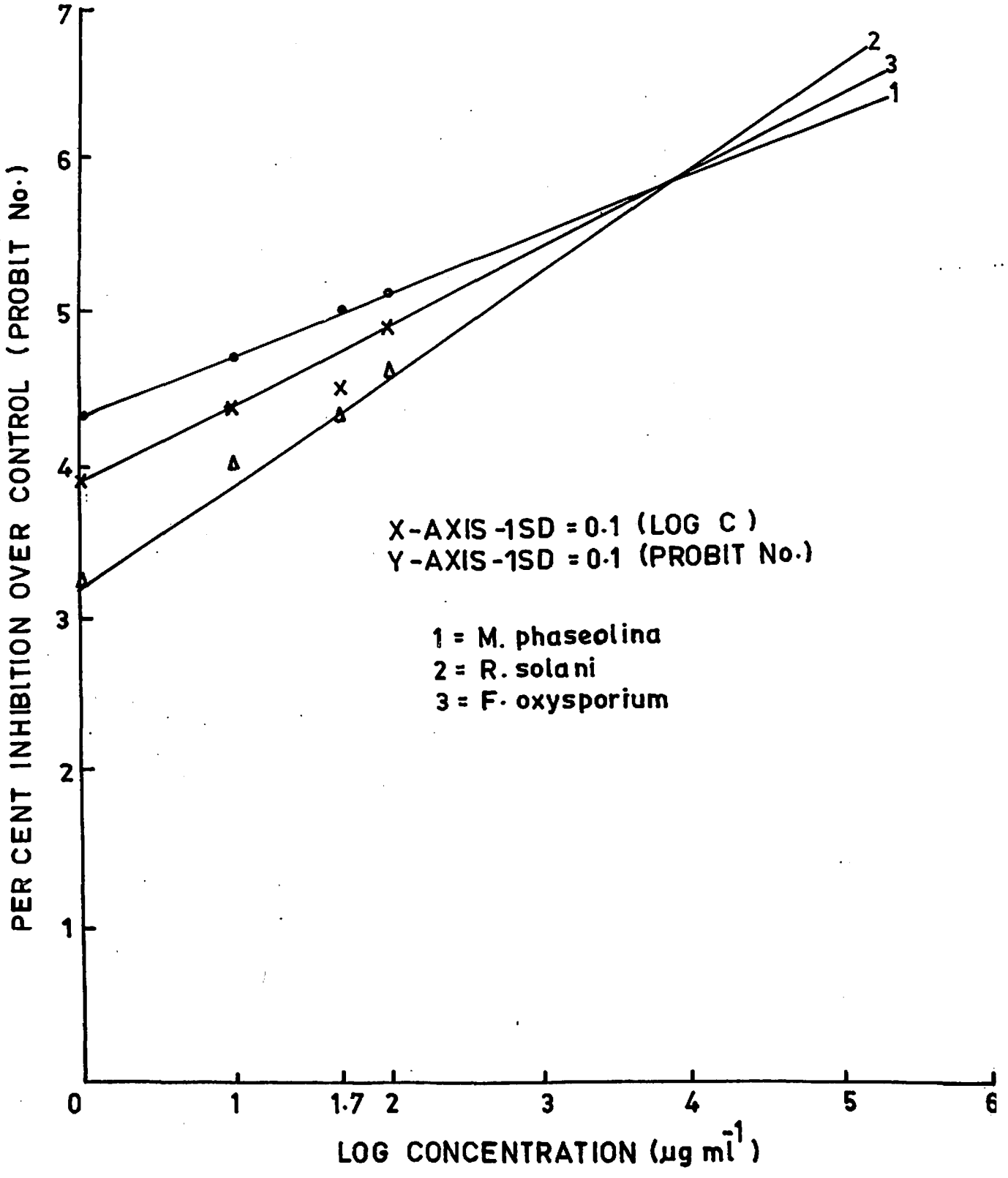


TABLE 14: *ED_{50} VALUES OF MIXED LIGAND COMPLEXES, BINARY COMPLEXES, METAL IONS AND LIGANDS; Temperature = 30±1°C

Compound Number	Name of Compound	M. phaseolina	F. oxysporium	R. solani
1.	Zn(By)TSA	16	32	> 224
2.	Ni(By)TSA	7	12	> 112
3.	Mn(By)TSA	40	63	> 398
4.	Co(By)TSA	45	> 100	a **
5.	Fe(By)TSA	12	16	> 120
6.	Zn(By)TLA	32	43	> 316
7.	Ni(By)TLA	15	10	50
8.	Mn(By)TLA	50	90	> 320
9.	Co(By)TLA	71	> 142	> 355
10.	Fe(By)TLA	20	22	> 100
11.	Zn(By)	a	> 125	a
12.	Ni(By)	a	71	a
13.	Mn(By)	a	> 200	a
14.	Co(By)	a	> 400	a
15.	Fe(By)	a	> 100	a
16.	$ZnSO_4 \cdot xH_2O$	a	> 892	a
17.	$NiSO_4 \cdot xH_2O$	a	> 630	a
18.	$MnSO_4 \cdot xH_2O$	NA***	a	NA
19.	$CoSO_4 \cdot xH_2O$	NA	a	NA
20.	$FeSO_4 \cdot xH_2O$	a	a	a
21.	TSA	a	> 1000	a
22.	TLA	a	> 602	a
23.	By	a	> 447	a

* Concentration required to inhibit 50% mycelial growth in $\mu g\ ml^{-1}$

** > 1000 $\mu g\ ml^{-1}$

*** Not effective even at 100 $\mu g\ ml^{-1}$

25.30, 39.38, 49.36, 54.32; 13.34, 25.00, 30.54, 46.62; 4.00, 15.00, 23.32, 33.35; respectively, against the three tested fungi at four concentrations, viz., 1, 10, 50 and 100 $\mu g\ ml^{-1}$. The following decreasing order of the fungitoxicity was observed.

M. phaseolina > *F. oxysporium* > *R. solani*

By comparing the fungicidal activities of the mixed ligand complexes with that of binary complexes, free ligands and metal ions, it is seen that the activity of the ligands increases considerably when they are coordinated with the metal ions and further enhances when mixed ligand complexes are formed. All the mixed ligand complexes exhibited significant fungitoxicity at 100 $\mu g\ ml^{-1}$ level. The fungitoxicity has varied with the nature of metal ion too. Ni(II) complexes have exhibited maximum fungistatic activity.

The fungicidal data reveal that the physiological activity may perhaps be due to the presence of N, >C=O and >C=S groups in the ligands as well as in the complexes. This observation is more or less in accordance with the observation of Horsfall and Rich (1951). The increased activity of the mixed ligand complexes may probably be attributed either to the combined bioactive effects of the metal ion and both the ligands present in the complexes or to the increased liposoluble nature of the complex. Besides, increased diffusion of the metal complex through the cell membrane of fungi may also play a significant role in increasing the fungicidal activity of the metal

complexes (Tripathi et al., 1984). The growth inhibition of the tested fungi may also be due to the exchange of trace metals of the metalloenzymes (present in the cell fluids and responsible for growth) with the metal of the complex under test. This may bring about a change in the nature of enzyme activity (Zentmyer et al., 1960).

Data indicate that the ten mixed ligand complexes differed in their fungitoxic action. Among TSA and TLA complexes, Ni(II)-By-TLA was more toxic than the Ni(II)-By-TSA complex, i.e., the toxicity induced by the TLA was higher than TSA. Comparing the toxicity depending upon the nature of metal ion, the following decreasing order of antifungal activity was obtained.

Fungi	Order	Ligand order
M. phaseolina	Ni > Fe > Zn > Mn > Co	By > TLA > TSA
F. oxysporium	Ni > Fe > Zn > Mn > Co	TLA > By > TSA
R. solani	Ni > Fe > Zn > Mn > Co	TLA > By > TSA

Data also indicate that in general the inhibition of fungal growth increased gradually with the increase in concentration of the complexes. The ED_{50} values, i.e., the concentration required to inhibit 50 per cent of fungi growth, have been presented in Table 14.

The dosage growth response curves against thiosalicylic acid and thiolactic acid mixed ligand metal complexes with M. phaseolina, R. solani and F. oxysporium fungi cross one another

(Fig. 11 to 20). The different fungicides have different slopes for same fungus as well as same fungicide has different slopes for different fungi. Slopes measure inherent toxicity of that portion of material that is available (Horsfall, 1945). Thus it is an indicative of the mode of toxic action. From Fig. 11 to 20 it is also clear that for doses below the point of crossing, the compound is less active for a fungus, is more active for the same fungus above the point of crossing and vice versa.

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C H A P T E R - V

SUMMARY

1. Polarographic study

The present study deals with the determination of thermodynamic stabilities of bivalent metal cations with thioacids. It also aims at the evaluation of fungicidal effects of mixed ligand complexes containing organic sulphur.

The thermodynamic stabilities were determined by polarographic technique. Polarograms were scanned by differential pulse polarography technique. The differential pulse polarography provides the derivative of polarographic curve in a peak presentation. The value of (di/dE) is small at potentials preceding the the wave, increases to a maximum at half-wave potential, Thus the maximum deflection occurs at the half-wave potential and is proportional to diffusion current. The reversibility of the process was established by the complete reversal of the path and diffusion controlled reduction by the same height of the wave when repeated. The half-wave potential shifted to more negative value on increase of ligand concentration. A Lingane treatment of the data was applied to calculate the number of ligands attached with central metal ion and thermogynamic stability constant value calculated.

Zn(II)-Thioproline, Zn(II) 2-Thiophene acetic acid and Zn(II)-TEP were studied at pH range 8.10 to 8.15 $\pm$ 0.10 in 0.1M KNO_3, with 0.01 per cent gelation being used as a maximum suppressor. The predominating complex under these conditions was ZnL_2. The stability constant values were 6.22, 8.19 and

7.33 in case of Zn(II)-TP, Zn(II)-TPA, Zn(II)-TEP, respectively. The order of stability was

$$TPA > TEP > TP$$

Ni(II)-TP, Ni(II)-TPA and Ni(II)-TEP were studied at pH range 6.52 to 6.95 $\pm$ 0.1, in 0.1M KNO_3, 0.01 per cent gelatin being used as a maximum suppressor. The predominating complex under these conditions was NiL_2. The stability constant values were 7.87, 7.35 and 9.38 in case of Ni(II)-TP, Ni(II)-TPA and Ni(II)-TEP, respectively. The order of stability was

$$TEP > TP > TPA$$

Cd(II)-TP, Cd(II)-TPA and Cd(II)-TEP were studied at pH range 11.05 to 11.58 $\pm$ 0.1, in 0.1M KNO_3, 0.01 per cent gelatin being used as a maximum suppressor. The predominating complex under these conditions was CdL_2. The stability constant values were 5.46, 15.34 and 9.63 in case of Cd(II)-TP, Cd(II)-TPA and Cd(II)-TEP, respectively. The order of stability was

$$TPA > TEP > TP$$

2. Biocidal activity

Five metal ions, viz., Ni(II), Fe(II), Zn(II), Mn(II) and Co(II), their binary complexes with 2,2' bipyridyl and mixed ligand complexes with TSA and TLA as secondary ligands were screened for their fungicidal action against three fungi, namely, M. phaseolina, F. oxysporium and R. solani. TLA complexe

were found to be more toxic than TSA. The toxicity dependent also on the nature of metal ion. The following decreasing order of antifungal activity was observed

Fungi	Order	Ligand order
M. phaseolina	Ni> Fe> Zn> Mn> Co	By >TLA>TSA
F. oxysporium	Ni> Fe> Zn> Mn> Co	TLA>By >TSA
R. solani	Ni >Fe> Zn> Mn >Co	TLA>By> TSA

The inhibition of fungal growth increased gradually with increase in the concentration of the complexes. ED_{50} values have also been determined. The dosage growth response curves indicated different slopes and for the different fungi with the same complexes, the ourves crossed one another. So the toxicity action was different above and the point of crossing. This is an indicative of mode of toxic action. For dosage below the point of crossing, the complex was less active for a fungus was more active for the same fungus above the point of crossing.

The physiological activity of the complexes might be due to the presence of N, $>C=O$, $>C=S$ groups. The different factors responsible for inhibition might be: i) bioactive effects of metal ions and ligands, ii) increased liposoluble nature of complexes, iii) increased diffusion of metal complexes through the cell membrane of the fungi or iv) exchange of trace metals of the metalloenzymes. The concentration of the metal complexes and the nature of metal ion played important roles for inhibition.

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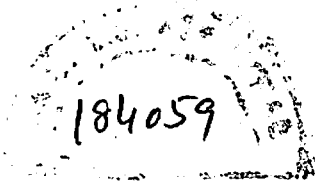

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