STUDIES ON SOME NEW ANILS AND THEIR INTERACTION WITH LEWIS ACIDS & HEAVY METAL IONS

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by
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CERTIFICATE

Certified that the thesis entitled 'Studies on some new anils and their interaction with Lewis acids and heavy metal ions', which is being submitted by Sri Choni Lal Taploo, for the award of the degree of Doctor of Philosophy in Chemistry of the University of Roorkee, is a record of his own work, carried out under our guidance and supervision. The matter embodied in this thesis has not been submitted for the award of any other degree of any University.

This is further to certify that he has worked for a period of three years and about three months at this University to prepare this thesis.

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CONTENTS

GENERAL INTRODUCTION

GENERAL INTRODUCTION

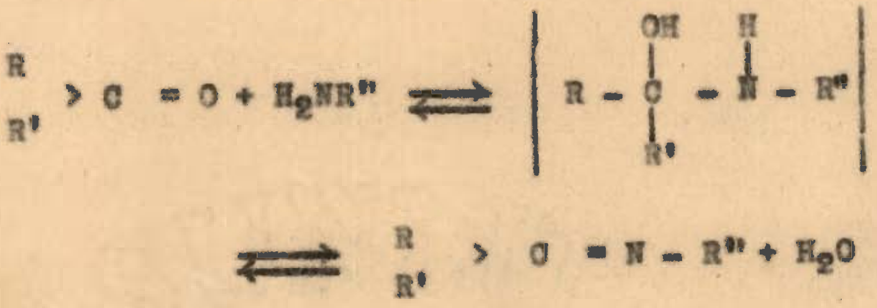
From the time of Werner(1), 1893, the chemistry of metal complexes has made such a rapid advance and has found application in so many diversified fields that it is difficult to keep pace with the day to day developments which are being added to its existing vast and enormous chemical literature. Moreover the chemistry of complex compounds does not cease to exist simply with the mention of reactions of metals with coordinating and chelating agents, having nitrogen or oxygen and even sulphur or phosphorous as donor atoms, but finds new outlets in structural problems to be solved by highly complicated theories based on quantum theory and quantum mechanics and by using extremely refined physical tools like I.R, N.M.R., E.S.R., U.V and Raman spectra , x-ray, magnetic susceptibility, mass spectroscopy, electron microscopy et. And then beyond this, it exhibits its many peculiar yet highly fascinating facets in analytical chemistry beginning with precipitates in estimating metals in volumetric analysis and colorimetry as indicator complexes, finally finding support for their identity and stability in various electro-chemical methods, e.g, pH metry, polarography, coulometry, amperometry etc. and modern analytical techniques like equilibrium dialysis, radio isotopy, liquid-liquid extraction , ion exchange, chromatography. etc.

Yet there is another aspect of the problem, viz., the type of metals which show readiness to undergo chelation or complex ion formation. It is seen that most of the investigations on complexes have been limited to the metals of transition series. Complexes of non-transition elements so far investigated are quite small in number and reactions of analytical importance (usually based on colour changes) have only been studied with dyes (substituted and unsubstituted), pigments, a few amines and halo-complexes. As such there exists enough scope for investigating new complexing and chelating agents which may be specific for non-transition elements. To one such class of reagents belong the anils which though not well recognised as chelating agents, are known for exhibiting a resonating structure when brought in contact with different Lewis acids. Study with these compounds can, therefore, form a new basis of study in the field of co-ordination chemistry.

Before introducing the subject on the interaction of metals with anils and its derivatives, it will not be out of place if a brief survey of the chemistry of anils, Lewis acids and of the different physio-chemical techniques employed to study complexes is made.

ANILS

Anils are organic compounds obtained by condensing aromatic aldehydes with aromatic amines. They are represented by a formula $RR'C = N - R''$, where R may be an alkyl, aryl or hydrogen attached to an imino carbon or nitrogen. They are often referred as Schiff's bases after the name of the discoverer, Schiff (1864)$^{(2)}$. A mechanism regarding their preparation may be given below:



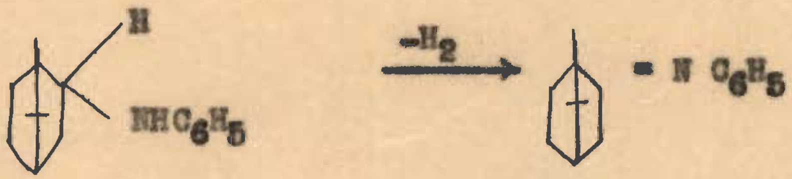
$$\begin{matrix}R\\R'\end{matrix}> C = O + H_2NR'' \rightleftharpoons \left| R - \overset{OH}{\underset{R'}{C}} - \overset{H}{N} - R'' \right| \rightleftharpoons \begin{matrix}R\\R'\end{matrix}> C = N - R'' + H_2O$$

The reaction is acid catalyzed and is generally carried out by refluxing the carbonyl compound and the amine with an azeotropic agent, like zinc chloride, if necessary. Anils show little or no tendency to polymerise spontaneously but may be polymerized by heat and acids. For example, benzalaniline, $C_6H_5-CH = NC_6H_5$, is resinified on heating with aqueous hydrochloric acid or formic acid$^{(3)}$.

PREPARATION OF ANILS

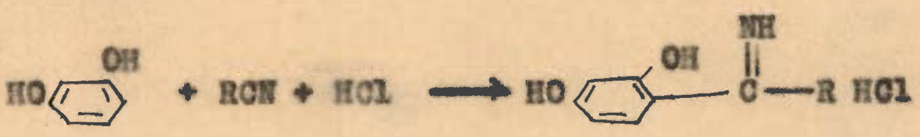
Mouren and Mignonac$^{(4)}$ synthesised various anils by the action of an aryl Grignard reagent with an aryl cyanide. Montague et al$^{(5)}$ later found that certain anilides, which may be regarded as o-hydroxy imines, react with alkyl or aryl Grignards to give the corresponding imines in about 40 % yields.

Ritter was the first to dehydrogenate amines to give imines(6). He found that isobornyl aniline is readily dehydrogenated with sulpher at 220°C to give an yield of about 89 % of the anil of camphor.



Even catalytic dehydrogenation of secondary amines over nickel, platinum or chromium catalysts at 180° gives the corresponding anils(6,7).

Hoesch and Houben(8,9) found that phenols or their ethers react with aryl cyanides when catalysed by hydrochloric acid gas or zinc chloride to give ketimines in very good yields.



Oximes of aromatic ketones can be reduced with hydrogen and nickel under pressure to give the corresponding anils. Acetophenone oximes gives an anil in 30 % yield(10)

$$R_2C = N\text{-}OH + H_2 \longrightarrow R_2C = NH + H_2O$$

Lithium aluminium hydride in tetra hydro furan reduces aromatic nitriles and gives a mixture of amines and imines(11).

$$\mathrm{Ph\ Cn} \xrightarrow{\mathrm{LiAlH_4}} \underset{(50\,\%)}{\mathrm{Ph\ CH_2\ NH_2}} + \underset{(30\,\%)}{\mathrm{Ph\ CH_2N = CH\ Ph}} + \mathrm{NH_3}$$

Nitriles can also be reduced to anils with stannous chloride in ethyl acetate containing hydrogen chloride(12).

An alkali metal or calcium salt of primary aromatic amines reacts with aromatic ketones to yield the corresponding anil(13).

Diethyl ketals also when refluxed with alkyl or aryl amines give anils(14,15).

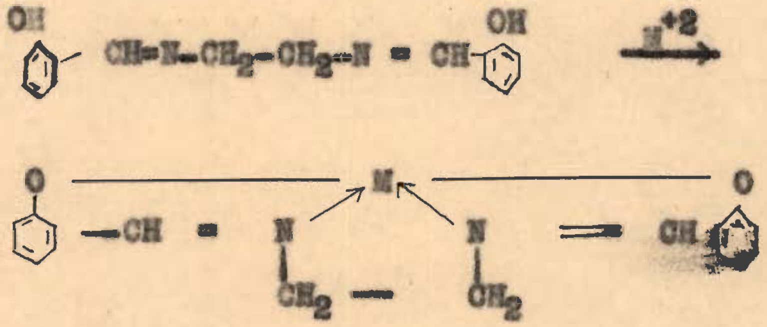
Phenyl isocyanate and p-dimethyl amino benzaldehyde at 190° give an anil in nearly quantitiative yield. Similarly phenyl isocyanate and bis(p-dimethyl amino phenyl thioketone) give the same product(16). α-amino acids react with sodium hypochlorite to give the chloro-amine intermediate which decomposes with elimination of carbon dioxide and sodium chloride and the corresponding anils are produced(17).

$$\begin{tikzcd}
\mathrm{RR'(NH\ R'')COOH + NaClO} \arrow[r, "-\mathrm{H_2O}"'] & \mathrm{RR'\ (NClR'')COONa} \arrow[d] \\
& \mathrm{RR' = NR'' + CO_2 + NaCl.}
\end{tikzcd}$$

INDUSTRIAL APPLICATIONS OF ANILS

Anils are found to have wide applications in industry, technology and medicine. A number of references are available describing their use as accelerators for vulcanization of rubber, bactericidal(18) and anticancerous material(19). Anils derived from salicylaldehyde and aromatic amines, o-amino phenol and polymethylene diamines are useful bactericidal and fungicidal agents(20). The activity of these compounds may be explained by the presence of an OH group ortho to the azomethine group. In some cases, their use has been recommended for removing traces of metals harmful for mineral oils(19). Recently it has been shown that traces of metals catalyse the oxidation and deterioration of mineral oils and gasoline. From the practical point of view, it is impossible to remove traces of metals permanently because contact with metallic processing and storage equipment would bring about further contamination.

The addition of oil soluble sequestering agents to the oil inhibits the undesirable effect of trace metal ions by formation of oil soluble metal chelates(21,22). Many types of organic chelating agents have been suggested for this application, including amines, oximes and hydroxamic acids. The anils obtained from salicyaldehyde or o-hydroxy acetophenone and diamines such as ethylene diamine or propylene diamine e.g. NN' disalicylidene diamine etc. have, however, found the widest applications. The compounds are oil soluble chelating agents:



A number of anils possess a photographic developer capacity and have been used for preparing papers for electrophotograph(23). The anils of biphenyl glyoxal and substituted amines have been used as antiviral demotherapeutics(24). It has been observed that anils from p-substituted phenyl glyoxal and 4-acetyl amino aniline produce antiviral tests. The most active compounds are derivatives of $P-H_2N\ \ C_6H_4\ \ COO\ C_2H_5$. Nylon has been stabilised against oxidative degradation by 0.01 - 1.00 % addition of Schiff's bases containing > 1 esterified or etherified -OH group or their derivatives in which azomethine group ias selectively hydrogenated. p-(3,4-methylene dioxy) benzylidene diphanylamine anil has been used for this purpose(25). Jet fuels are stabilized at a relatively high temperature by the addition of a small amount of mixture of certain esters and metal deactivating compounds. The addition contains 1-10 % by weight of a deactivator, which is an azomethine of benzylidene type(26). In dyeing polyesters and other hydrophobic textile materials, azomethine derivatives of an aromatic amine and an aldehyde containing a solubilizing group have been applied from solutions or dispersions at > 160° in order to give deep colours, especially black with good fastness to sublimation and light$^{(27)}$.

In recent years, the biochemical significance of Schiff's bases has attracted the attention of a number of workers. A number of biochemical processes are known in which Schiff's bases are formed. Vitamin B_6 catalyzed reactions have been studied by Snell and co-workers$^{(28)}$ and it has been shown that Schiff's bases are formed. Enzymatic decarboxylation$^{(29-31)}$, enzymatic aldolization$^{(32-35)}$ and perhaps the visual processes$^{(36,37)}$ all appear to involve Schiff's base formation and hydrolysis. Pyridoxal phosphate are enzymatic reactions, very probably involve both the aminolytic and hydrolytic cleavage of Schiff's bases$^{(38-40)}$.

Anils of salicylidene type are good chelating agents, e.g., 2-salicylidene amino benzo thiazole forms an orange precipitate with Ag^+ and is fairly specific for this ion$^{(41)}$. Some of the anils form chelate with heavy metal ions$^{(42)}$. Copper, nickel and uranyl chelates of salicylidene anils are suitable as light stabilizers for thermoplastic synthetic resins, when the amount of the chelate used is not more than 10 % by weight of the resin$^{(43)}$.

Solutions of the anils prepared from:

i) ethylene diamine and o-hydroxy acetophenone,

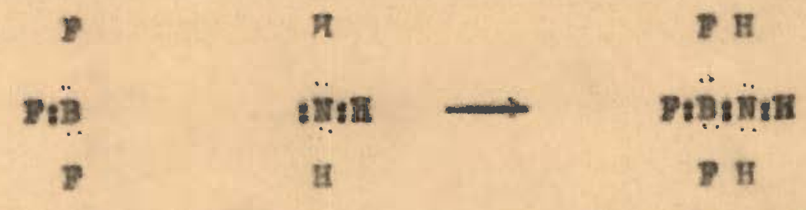
ii) ethylene diamine and formyl salicylic acid, and

iii) 1,3 diamino propan-2-ol and 3-formyl salicylic acid.

are used as indicators in the titration of ferric ions with EDTA(44).

LEWIS ACIDS

Lewis acid is the name given by G.N. Lewis(45) to compounds, both of non-metals and metals, showing tendency to accept electrons from electron donor substances (Lewis bases). Many examples in support of this type of combination can be cited, viz., reaction of boron triflouride with ammonia and diethyl ether; lithium chloride with methyl alcohol, anhydrous aluminium chloride with water, berrylium flouride with Fe^{++} (generally utilised in electrolytic melts), zinc chloride with 5-sulpho-8 hydroxy quinoline etc.



$$\begin{array}{ccccc} \text{F} & & \text{H} & & \text{F H} \\ \text{F:}\overset{..}{\underset{..}{\text{B}}} & & :\overset{..}{\underset{..}{\text{N}}}:\text{H} & \longrightarrow & \text{F:}\overset{..}{\underset{..}{\text{B}}}:\overset{..}{\underset{..}{\text{N}}}:\text{H} \\ \text{F} & & \text{H} & & \text{F H} \end{array}$$

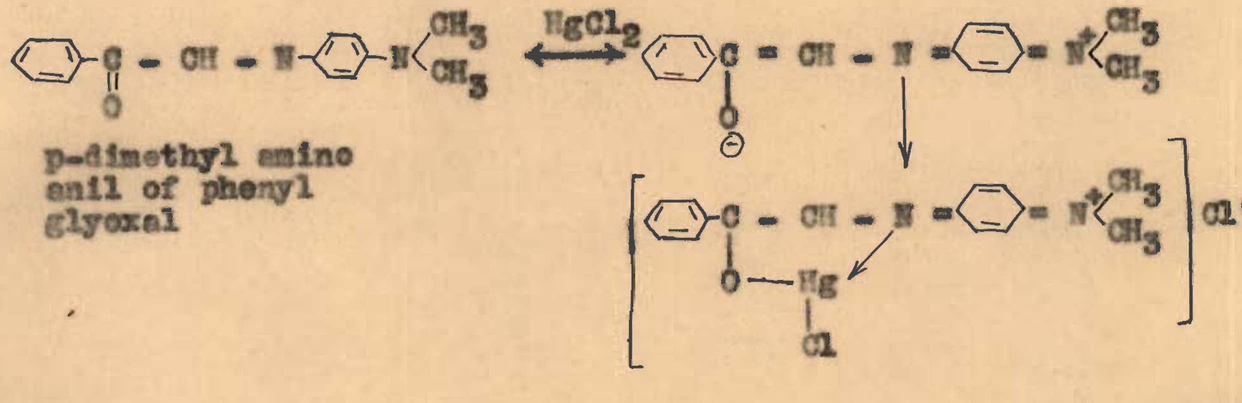
Acid Base Co-ordinated complex

Other compounds which fall under this classification are AlF_3, $SnCl_4$, $TiCl_4$, PCl_3 and SF_4. These compounds tend to form complexes with organic bases such as ethers, $R - \ddot{O} - R$.

Besides, Lewis acids can be titrated with bases in a variety of solvents. For example, BF_3 and $SnCl_4$ can be titrated against pyridine and trimethyl amine in chlorobenzene with crystal violet as an indicator.

The Lewis concept besides its theoretical impact, has greatly influenced the practice and use of acid catalysis, particularly in organic chemistry. $AlCl_3$ (anhydrous), BF_3, $FeBr_3$ are all important catalysts. Often the Lewis acid catalysts are far superior and, in some cases, are effective for reactions where Brønstead acids have little use.

Another interesting fact worth mentioning in connection with Lewis acids is that they react with certain anils to form the co-ordinated complex. The formation of complex is indicative of a sharp batho-chromic shift from yellow to violet, green etc. For example, addition of p-dimethyl amino anil of phenyl glyoxal when added to $ZnCl_2$, $AlCl_3$, $HgCl_2$ etc. solutions, results in such colour change. The probable mechanism for such reaction as suggested by Krohnke and Gross$^{(46)}$ is given below:



Further the solution of the same compound in benzene produces a sharp colour change from yellow to violet on eluting over dry silica gel. This change has been attributed to the adsorption of organic compound on the gel. The table given below describes some of the colour changes observed on silica gel.

COLOUR CHANGES ON SILICA GEL. BY ADSORPTION OF ANILS

ANIL

No	R	R'	Own colour of anil in acetonitrile	Colour on silica gel.
1.	Benzoyl	H	Bright red	Violet
2.	Benzoyl	CN	Bright red	Violet
3.	Pyridine carboxy-2	CN	Dark red	Blue violet
4.	Pyridine carboxy-3	CN	Bright red	Red Violet
5.	Pyridine carboxy-4	CN	Bright red	Dark red
6.	Quinolyl-(2)	CN	Bright red	Dark red
7.	Quinolyl-(4)	CN	Bright red	Dark red

EXPERIMENTAL METHODS USED IN INVESTIGATING METAL CHELATES

ABSORPTIOMETRIC MEASUREMENTS

The introduction of sensitive spectrophotometers, about forty years ago, has helped in the study of absorption spectra of solutions. With the improvement of the technique and instrumentation of spectrometry, it is now possible to study the absorption of the solution from ultraviolet to infra-red region with great precision and accuracy. This method, besides providing evidence for the existence of complexes, can be efficiently employed to investigate whether one or two complexes are present in solution, e.g., the phenolic ligands in combination with Fe^{3+} and phenanthroline in combination with Fe^{2+} (47). The optical measurements have also been applied in the case of complex forming dyes(48). The changes in extinction with changes in relative proportions of the metal ion and the ligand permit conclusion to be drawn regarding the composition of principal complexes formed under the reaction condition chosen.

BEER-LAMBERT LAW

Before employing spectrophotometric technique to study the coloimetric estimations or to determine the composition and stability of metal complexes it is highly desirable to know whether the solution obeys Beer-Lambert's law. The law states:

$$E = \log \frac{I_o}{I} = \varepsilon \cdot c \cdot d$$

where

E = optical density of the solution,

I_o = intensity of incident monochromatic light,

c = concentration of dissolved substance in mol/litre,

d = depth of the solution traversed by light,

ε = extinction coefficient.

When two non-reacting substances are present in solution, the total absorption is equal to the sum of absorbances of the constituents in the same thickness of the solution i.e.

$$E = \log \frac{I_o}{I} = \Sigma\, i\, \varepsilon_i = \Sigma\, i\, \varepsilon\, c_1\, d_1$$

$$= \left[\, (\varepsilon\, c_1 + \varepsilon\, c_2 + \varepsilon\, c_3 \ldots \varepsilon_i\, c_2)d \,\right]$$

Hence, it is possible to determine the concentration of a coloured complex species in solution with a fair degree of accuracy from the measurement of light absorption.

COMPOSITION OF CHELATES

A number of methods are available for the determination of the composition of chelates using absorbance measurements. A brief account of some of the methods is given below.

METHOD OF CONTINUOUS VARIATION

In recent years, a simple colorimetric method has been used to determine the composition of chelates in solution. This technique known as the method of continuous variation was introduced by Job. The basis of this method was described as early as 1910 by Ostromisslensky(49) and Denison(50) in 1912 but later on Job published the details of method along with the discussion in a series of papers and since then it has been termed as Job's method of continuous variation(51). A similar method has been employed by Cornec and Urbain(52) and Shibata, Inouye and Nakatsuka(53).

In the method of continuous variation, an additive molecular property is used as a guide, provided that this property has different values for the various species present in the solution of the metal ion(M) and ligend (L). Consider the reaction:

$$M + nL \rightleftharpoons ML_n ;$$

$$k = \frac{[M L_n]}{[M + |L|^n]|}$$

where [ ] represents activities   molar concentration, and k is the equilibrium constant. The ratio $\frac{[L]}{[M]} = n$ is satisfied at the maximum concentration of the complex compounds. Hence,

$$\frac{d[M L_n]}{d[M]} = 0 \qquad \text{for the maxima.}$$

In other words, for a constant total concentration of the metal and the chelating agent, the concentration of the chelate is greatest when the metal and the chelating agent are brought together in the same ratio in which they exist in the chelate. If the chelate is the only coloured species present, the optical density of the solution is proportional to the concentration of the chelate. The plot of the additive property e.g. optical density versus the composition of the solution would be a curve with a maximum corresponding to the composition of the chelate. Otherwise, an allowance for the absorbance of the reactants is to be made in the relevent region. This is achieved by plotting the difference between the observed optical density and theoretical optical density i.e. in the absence of complex formation, against composition of the species. The maxima of the curve gives the composition of the chelate formed, provided Beer-Lambert's law is valid throughout the course of the experiment. The method of continuous variation is applicable provided not more than one complex is formed under the given set of experimental conditions and there is no volume change on mixing the solution of the metal ion and the ligand. A modification was made by Vosburg and Cooper(54) in which they determined the nature of equilibria where more than one complex or chelate is formed.

In Job's continuous variation method, a solution M of molar concentration C, and Ke of molar concentration C' are prepared. The ratio C'/C is usually denoted by the symbol P. A volume X of the solution Ke is then mixed with a volume (1-X) of solution M where X<1. It is assumed that there is no change in volume on mixing the two solutions. Let C_1, C_2 and C_3 be the concentration of M, Ke and M_m, Ke_n respectively and K_d, the dissociation constant.

For any mixture, the following equations apply:

$$C_1^m + C_2^n = K_d\, C_3 \qquad \text{...(i)}$$

$$C_1 + m\, C_3 = C(1-X) \qquad \text{...(ii)}$$

$$C_2 + n\, C_3 = P\, C_X \qquad \text{...(iii)}$$

On differentiating (i), (ii), and (iii), we have

$$mC_2 \frac{dC_1}{dx} + nC_1 \frac{dC_2}{dx} = 0 \qquad \text{...(iv)}$$

$$\frac{dC_1}{dx} = -C \qquad \text{...(v)}$$

$$\frac{dC_2}{dx} = PC \qquad \text{...(vi)}$$

Putting the value $\frac{dC_1}{dx}$ and $\frac{dC_2}{dx}$ in (iv), we get :

$$nPC_1 - mC_2 = 0 \qquad \text{...(vii)}$$

Multiplying (ii) by n and (iii) by m and on simplification:

$$C_1 = \frac{mPC_X - nC\ (1-X)}{n\ (\ P-1)} \qquad .. \ (viii)$$

Substituting the value of C_1 in (ii)

$$C_3 = nC\ (1-X)\ (P-1) - \frac{mPC_X - nC\ (1-X)}{mn(P-1)}$$

Then substituting the values of C_1, C_2 and C_3 in (i) we get:

$$\frac{C^{m+n-1}.P^{n-1}\ |\ (Pm+n)\ X - n\ |^{m+n}}{m^{n-1}\ .\ n^{m-1}} = K_d \begin{array}{c} |(n-(m^{+n})X| \\ (P-1)^{m+n-1} \end{array}$$

If $P = 1$, the right hand side becomes zero and since C,P,n are constants then,

$$(m+n)X - n = 0$$

$$\text{or} \quad m\ X = n(1-X)$$

$$\text{or} \quad \frac{m}{n} = \frac{1-X}{X}$$

Hence, from the knowledge of the maximum value X, the composition and the formula of the chelate can be determined from the ratio of m/n , taking the simplest value of m and n.

Katsin and Gebret$^{(55)}$ gave a more general treatment for the determination of the composition of the chelate, but it had limited applicability.

A large number of workers$^{(56-60)}$ have checked the usefulness of the method of continuous variations and various modifications have been suggested from time to time. Mention may be made of Woldby(61) who found that the results obtained by this method are satisfactory only when light absorption measurements are used. Inspite of limitations, Job's continuous variation method remains a convenient tool for the study of composition of complexes in solution.

During the course of present investigations this method was found to give quite reliable results and so it was frequently employed for the determination of the composition of the complexes studied.

In Russian literature, Job's continuous variation method is known as Ostromisslensky's method(49)

SLOPE RATIO METHOD(62,63)

This method was originally used with spectrophotometric measurements and is restricted to cases where a single complex is formed at a time. The reaction $mA + nB \rightleftharpoons A_m B_n$ is considered where only one complex is formed. By making the concentration of B large and constant, the equilibrium concentration of the complex $A_m B_n$ will be proportional to analytical concentration of A added:

$$\therefore \quad | A_m B_n | = \frac{C_A}{m}$$

If the absorption spectra of the various species do not overlap seriously, one may write for the optical density at a suitable wave length:

$$As = ab \mid A_m B_n \mid$$

where a is extinction coefficient of $A_m B_n$ and b is the length of the absorption cell. Since, here Beer-Lambert's law holds good, so $As = a,b,c$ where As is the optical density, a is the extinction coefficient and b is the length of the cell and C is the concentration of the species under consideration. The proper wave length is selected so that absorption is due ohly to the complex. Substituting the value of $|A_m B_n|$ in the expression $As = ab \, |A_m B_n|$, we get:

$$As = ab \, C_A/m$$

Since, a,b and C_A are known, a plot of As versus C_A will be a straight line having a slope ab/m, from which m may be determined. Similarly, the concentration of A may be kept constant while the concentration of B is varied:

Thus $As = ab \mid A_m B_n \mid$

But $|A_m B_n| = \dfrac{C_B}{n}$

$$\therefore \quad As = ab \, \frac{C_B}{n}$$

Thus , a plot of As versus C_B under these conditions will be a straight line having a slope $\frac{ab}{n}$. The ratio of the two slopes will, therefore, be equal to $\frac{ab}{m} / \frac{ab}{n}$ $= \frac{n}{m}$. The composition of the complex may thus be determined from a knowledge of ratio of the two slopes.

Slope ratio method was modified by Vankateshwarlu and Rao(64), where the absorbances of the solutions are plotted against the concentrations of variable components from either end of the x-axis. The point of intersection of the two curves corresponds to the composition of the complex , assuming that only one complex is formed.

MOLAR RATIO METHOD

A monovariant method was described by Yoe and Jones(65,66), who termed it as a mole ratio method. It is applicable only to the reactions which are stoichiometric or nearly so.

By measuring the optical density of a solution in which a reaction was occurring, it is possible to determine the ratio of species added during complexation. By adding various amounts of the chelating agent to the constant amount of the solution of a metal ion or vice-versa, a set of data is obtained from which plot of optical density versus the ratio of chelating agent/metal ion or vice-versa may be considered. This increases to a large constant value at a ratio of the chelating agent/the metal ion or vice-versa which represents the composition of the complex. For a stable complex, when both the reactants are colourless, the curve rises from the origin as a straight line and breaks sharply to a constant absorbance at a molar ratio of the components in the complex. However, a complex that undergoes appreciable dissociation in solution, gives a continuous curve which approximately becomes parallel to molar ratio axis, only when an excess of variable component is added. Sometimes it is found that the results obtained by extrapolation of the curve are uncertain. It is observed that in many cases, such a curve may be made to break sharply at the correct molar ratio, if the ionic strength of the solution is adjusted to a suitable value by the addition of an indifferent electrolyte. Thus in such cases also it is possible to get information about the composition of the complex.

The relation of this method to continuous variation has been developed by Sidhanta(67). Mayer and Ayres(68) deduced the composition of complexes in solution by this method for situations where more than one complex exists in solution.

OTHER METHODS

Besides the above methods for determining the composition of chelates, mention may be made of Babko's method(69), the logarithmic method of Bent and French(70), Jansson's spectrophotometric method(71) and the method of isobetic points(72). There are a few, other methods which are applied to special cases such as the method of Molland(73) where more than one central ion is involved in the complexation. Stepwise complex formations have been investigated by other methods(74-76).

DETERMINATION OF STABILITY CONSTANTS

Consider the following reaction in which the metal chelate is formed from the hydrated metal ion and the most basic (most highly dissociated) form of the chelating agent:

$$M^{+n} + A^{-m} \rightleftarrows MA^{n-m}$$

$$\therefore \quad K_{MA} = \frac{|MA^{m-n}|}{|M^{+n}||A^{-m}|}$$

where the brackets indicate molar concentration and the constant applies to the specific temperature. This equilibrium constant is known as stability constant.

Just as a knowledge of dissociation constants of acids and bases has done much to systemise our understanding of the behaviour of these substances, so a sknowledge of stability constants has done much to rationalise our understanding of the behaviour of metal chelates in solution. The universal measure of the tendency towards formation of metal chelate compounds in aqeous solutions is governed by this constant, the magnitude of which gives a quantitative measure of the relative stabilities of various metal chelates. This quantity may be used in combination with other data to predict whether a metal chelate compound will or will not form under various conditions. Information about the concentration of different species of a metal complex in equilibrium mixtures is invaluable in the study of analytical separation procedures-solvent extraction, ion exchange or chromatography. It is equally important in the study of the role of metal chelates in various biological systems.

The thermodynamic constant can also be calculated from a knowledge of stability constant. However, it is doubtful whether true thermodynamic data could be determined except in very simple cases, because the method is accompanied by many difficulties. Two principal procedures are mainly followed in studying the stability constant of the chelates.

Lewis and Randell(77) first introduced the concept of ionic strength which later received theoretical justification from Debye and Huckel's theory. The classical approach for the evaluation of thermodynamic constant involved the determination of equilibrium constant in media of different low ionic strengths (infinite dilution). Some workers(78) have used the value of a single determination and attempted to correct this value to a thermodynamic equilibrium constant by the application to Debye and Huckel's theory. The second method was introduced by Biedermann and Sileen(79) and the fundamental idea of this method is to control the activity coefficient by keeping ionic strength constant, because in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of identical ionic strength. Consequently measurements of chelate formation constant are usually carried out at controled concentrations of an added inert electrolyte such as potassium nitrate or potassium chloride. For most chemical purposes, 0.10 M solutions of these electrolytes are employed, whereas for biological or medical applications 0.16M NaCl is considered to represent more closely the conditions which exist in neutral systems. When equilibrium measurements are made in a constant electroyte concentration, it is necessary that the concentration of the metal ion, ligand and the metal chelate must be lower than that of the inert electrolyte so that they will not contribute appreciably to the total electrolyte concentration.

In view of the practical difficulties encountered in the determination of true thermodynamic stability constants, Rasooti and Rasooti(80) concluded;

> 'It would, therefore, seem betterto obtain reliable values to the corresponding complexes with solvent molecules and medium ions than less

certain values of the thermodynamic constants which do not give absolute stability either, but only a stability related to the solvated molecules'.

During the present studies, the ionic strength could not be kept constant as the investigations were carried out in purely non-aqueous media. It was observed that even traces of moisture would break the complex and therefore, mixed solvents containing water and organic liquids could also not be used. Moreover, in the case of phenacylidene aniline oxime, a true solution could not be obtained even in water alcohol mixtures. Spectrophotometric investigations of these chelates were not possible at a known ionic strength. The stability constant data given in the thesis refer to arbitrary values only.

There are a number of methods for the experimental determination of stability constants. The first method was completed at the very beginning of the twentieth century(81,82). During further progress of these investigations, the work of N. Bjerrum(74) played an outstanding role. The idea of stepwise complex formation was especially fruitful. This idea was evolved in many countries, particularly in U.S.S.R. as a result of the work of A.K. Babko(69) and his co-workers. The pH-metric method of determining the equilibrium concentrations of ligends and calculating from them the formation function $(\bar{n})$, developed by J. Bjerrum(83), was also very important. Almost half of the stability constants of chelates and other coordination compounds has been extensively carried out by this method; the important contribution being the work of Laden(84) Schwarzenbach(85), Sileen(79) and others. Current interest in the formation and stability of metal ion complexes in solution is indicated by numerous reviews published since 1950(86-93) and in the proceedings of a series of international conferences(94-97).

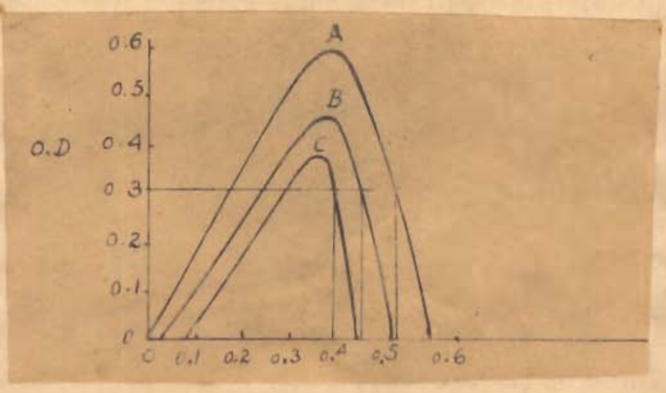
A number of methods are available for the determination of stability constants by absorption measurements, mention may, however, be made of methods of Moore and Anderson(98), Dey and co-workers(99,100), Harvey and Manning(62) and Job's method of continuous variation(51). A short account of these methods is given below.

MOORE AND ANDERSON'S METHOD(98)

This method is based on the compositions of solutions having an identical intensity of colour, i.e. the same absorbance value. In this method, both the reactants should be colourless. These authors have shown that if the magnitude of the extinction coefficient is proportional to the concentration of the complex formed, the formation constant for the equilibrium $m_A + nB \rightleftharpoons A_m \; B_n$ may be calculated as $\log K = \log \frac{A^m B^n}{A_m B_n}$ or $\log A_m \; B_n = m \log A + n \log B = \log K.$ If A is kept constant, while B is varied, $\log A_m \; B_n$ is a linear function of log B and thus the value of n can be determined from the slope of the straight line obtained by plotting log O.D. (which is proportional to log $A_m B_n$) against B. The value of m can be similarly determined by keeping B constant and varying A. From the values of m and n, the value of K can be calculated.

MODIFICATION TO ANDERSON'S METHOD(99,100)

Dey and co-workers have modified the method of continuous variation to the cases where one of the reactants may be coloured. In this method, observations obtained for the method of continuous variations are utilised and the absorbances (not the difference in absorbances) are plotted against [M]/[M]+[Ke] , where [M] is the concentration of the metal ion and [Ke] is that of the chelating agent. A typical graph obtained from the experimental observations is shown below.



[M] / [M][Ke]

Calculation of the stability constant from the curves of Continuous Variation Method.

With progressive increase of M, Ke decreases and it may be assumed that in the descending portion of the curve where metal ions are in excess, most of the chelating agent is bound up in the complex. Moreover, the chelating agent has lower absorbance than the chelate at the particular wave length of observation. Therefore, in this portion of the curve, the absorbance of the free chelating agent does not contribute substantially to the absorbance of the system as a whole. The observed absorbance may, therefore, be regarded to be due to the colour of the complex alone. We may, therefore, assume that in the above figure, where the absorbances are same (say 0.3), the respective amount of complex formed in each case are identical.

Let us consider the case of a system where a complex is formed. With the composition of the metal:chelate as 1:1, i.e. $\frac{m}{n} = 1$ or $m = n$.

For the system $mA + nB \rightleftarrows A_m B_n$

$$\therefore \quad K = \frac{X}{(a-mX)(b-nX)}$$

where $\quad m = n$,

$$\therefore \quad K = \frac{X}{(a-X)(b-X)}$$

where X is the concentration of the complex and a and b are the initial concentrations of the reactants. Taking the concentrations a_1, a_2, and b_1, b_2 of the reactants (from the two curves) having same absorbance, i.e. same value of X , we have:

$$K = \frac{X}{(a_1-X)(b_1-X)} = \frac{X}{(a_2-X)(b_2-X)}$$

or

$$X = \frac{a_1b_1 - a_2b_2}{(a_1+b_1)-(a_2+b_2)}$$

Knowing the value of X, the value of K can be found.

Next consider the case of a chelating where the ratio of the reactants is 1:2. The system can be represented as:

$$M + 2Ke \rightleftharpoons M\,Ke_2$$

or

$$K = \frac{X}{(a-X)(b-2X)^2}$$

Taking the concentrations a_1, a_2 and b_1, b_2 of the reactants having same absorbance, we have

$$K = \frac{X}{(a_1-X)(b_1-2X)^2} = \frac{X}{(a_2-X)(b_2-2X)^2}$$

or

$$4X^2(a_1+b_1) - (a_2+b_2).\ Xb_2^2 + 4(a_2b_2 - a_1b_1)+(a_1b_1^2+a_2b_2^2)=0$$

or

$$X = \frac{-|b_2^2-b_1^2+4(a_1b_1-a_2b_2)| \pm \sqrt{(b_2^2-b_1^2+4(a_2b_2-a_1b_1)^2 - 16|(a_1+b_1)-(a_2+b_2)|(ab_1^2-a_2b_2^2}}{8|(a_1+b_1)-(a_2+b_2)|}$$

Knowing the value of X from the above equation, the value of K can be found out from the equation mentioned above. Similarly in the case of a chelate where the ratio of the reactants is 2:1 , the reaction be represented as:

$$2M + Ke \rightleftharpoons M_2 Ke$$

or

$$K = \frac{X}{(a-2X)^2(b-X)}$$

or

$$X = \frac{-|a_1^2-a_2^2+4(a_1b_1-a_2b_2)| \pm \sqrt{(a_1^2-a_2^2+4(a_1b_1-a_2b_2)^2| - 4|(a_2+b_2)-(a_1+b_1)|(a_2^2b_2-a_1^2b_1)}}{8|(a_2+b_2)-(a_1+b_1)|}$$

From the value of X calculated from the experimental data, K can be calculated.

As mentioned previously (pp.   ) the instability constant of a chelate can be determined from the following equation:

$$\text{Dissociation constant } K_d = \frac{C^{m+n-1}.P^{n-1}|(Pm+n).X-n|^{m+n}}{m^{n-1}.n^{m-1}|n-(m+n).X| - (P-1)^{m+n-1}}$$

The reciprocal of K_d is the stability constant of the chelate.

MOLE RATIO METHOD$^{(65,66)}$

Consider the dissociation of a complex:

$$\begin{array}{llll} M\,Ke_n & \rightleftharpoons M & + \; nKe & \text{Initial concentration} \\ C & 0 & 0 & \\ C(1-\alpha) & \alpha.C & n\alpha.C & \text{Final concentration} \end{array}$$

C is the total concentration of the complex in moles per litre assuming no dissociation, and α is the degree of dissociation. The equilibrium constant may be written as:

$$K = \frac{(\alpha.C)\;(n\alpha C)^n}{C(1-\alpha)}$$

The value of n for the complex having been established, the value of α may be obtained from the mole ratio curves by the following relationship:

$$\alpha = \frac{E_m - E_s}{E_m}$$

where E_m is the maximum extinction obtained from the horizontal portion of the curve, indicating that the whole of the metal ion is present in the form of a complex ; E_s is the extinction at the stachiometric molar ratio of the ligand to the metal in the complex, the total concentration of the complex being the total concentration of the metal. When both the reactants are colourless, the curves generally break abruptly at the st~~e~~ochiometric ratio and α is not reliable in such cases.

CONDUCTIVITY

Conductivity measurements generally give useful information about the composition of insoluble complexes. Specific information regarding their nature cannot be obtained for soluble complexes although a number of workers have applied Job's method to determine the composition. It, however, suffers from one great drawback, viz., conductance does not respond well to additive behaviour as absorbance does.

Another drawback of conductance method in studying complexes is that it cannot be applied to systems of low conductances, especially when dealing with purely non-aqueous solutions as in the present studies. The only useful information which we could get from conductivity measurements was about the position of Cl' in Lewis acid--p-bromo phenacylidene p-dimethyl amino aniline chelates.

pH-METRY

This involves the measurement of pH during chelation when hydrogen atom of the ligand is replaced by the metal ion. A drop in pH during the chelation causes an increase in acidity. This magnitude of the observed pH change is related to the metal-ligand binding tendency and may be used to determine the stability constant of the metal chelate formed.

The increased acidity is a result of competitive binding tendencies of the two species i.e. the ligand and the metal ion. The reaction may be represented as shown below:

$$M^{+n} + H_mA \rightleftharpoons MA^{n-m} + mH^+ \qquad .. (1)$$

The equilibrium constant K' for this reaction may be defined as:

$$K' = \frac{|MA^{n-m}|\ |H^+|^m}{|M^{+n}|\ |H_mA|} \qquad .. (2)$$

If the numerator and denominator of (=n)(2) be multiplied by $|A^{-m}|$, we have

$$K' = \frac{|MA^{n-m}|\ |H^+|^m|A^{-m}|}{|M^{+n}||A^{-m}||H_mA|} = K_{MA} \cdot K_\alpha \quad .. (3)$$

where

$$K_{MA} = \frac{|MA^{n-m}|}{|M^{+m}|\ |A^{-m}|}$$

and K_α is the acid dissociation constant for the dissociation of H_mA to $m|H^+|$ and $|A^{-m}|$

i.e. $$H_mA \rightleftharpoons mH^+ + A^{-m}$$

or $$K_\alpha = \frac{|H^+|^m|A^{-m}|}{|H_mA|} \qquad .. (4)$$

Hence, if K' and K_a can be determined experimentally, equation (3) may be solved for the chelate formation constant.

These principles have been applied by Bjerrum and Schwarzenbach (locit) to the calculation of formation constant of metal chelates in aqueous solution. Bjerrum describes the stepwise formation of a series of metal-chelates of the type MA, MA_2 ... MA_n as shown below:

$$M + A \rightleftharpoons MA, \quad K_{MA} = \frac{|MA|}{|M||A|} \qquad .. (5)$$

$$MA + A \rightleftharpoons MA_2, \quad K_{MA_2} = \frac{|MA_2|}{|MA||A|} \qquad .. (6)$$

$$MA_{n-1} + A \rightleftharpoons MA_n, \quad K_{MA_n} = \frac{|MA_n|}{|MA_{n-1}||A|} \qquad .. (7)$$

Bjerrum introduced a function $\bar{n}$, which is defined as the average number of the ligand molecules bound per mole of metal. This may be expressed mathematically as :

$$\bar{n} = \frac{|MA| + 2|MA_2| + 3|MA_3| \ldots n|MA_n|}{|M| + |MA| + |MA_2| \ldots |MA_n|} \qquad .. (8)$$

Equation (8) may be obtained in terms of $|A|$ and the various formation constants K_{MA}, K_{MA_2}, ... K_{MA_n} by substitution of equation 5,6 and 7 into 8 , i.e.

$$\bar{n} = \frac{K_{MA} |A| + 2K_{MA} K_{MA_2} |A|^2 \ldots n K_{MA} K_{MA_2} K_{MA_n} |A|^n}{1+K_{MA}|A| + K_{MA} K_{A_2} |A^2| \ldots K_{MA} K_{MA_2} K_{MA_n} |A|^n} \quad .. (9)$$

Equation (9) is the so-called Bjerrum formation function. If the concentration of the unbound ligand can be determined experimentally, $\bar{n}$ can be calculated from the relation:

$$\bar{n} = \frac{At - |A|}{Mt} \quad .. (10)$$

where At and Mt denote the total concentration of the ligand and the metal respectively.

To solve equation (9), n sets of $\bar{n}$ and the corresponding $|A|$ values are required and by plotting the graph between $\bar{n}$ values as a function of $P|A|$, the negative logarithm of the free ligand concentration, $\log K_{MA}$, $\log K_{MA_2}$ and $\log K_{MA_3}$ have been calculated for P_A at $\bar{n}$ value of 0.5, 1.5 and 2.5 respectively.

Attempts were made to apply Bjerrum method to study the complexes of copper with the oxime of phenacylidene aniline anil. No fruitful information could be obtained (pp.   ) since the titration region corresponded to $\bar{n}$ values greater than 1.5. Titration at lower pH values, which could give $\bar{n}$ values < 0.5, could not be performed since addition of acid breaks the azomethine linkage (CH=N) of the ligand itself.

POLAROGRAPHIC STUDIES OF METAL CHELATES

Valuable information about the composition of the metal chelates and their behaviour in aqueous solution has been obtained from the study of their reduction at dropping mercury electrode. The underlying principle is that the reduction potentials of the metal ions are shifted, usually to more negative values, as a result of complex formation and the correlation of this displacement of potential with both the concentration of the ligand and the pH of the solution provides an excellent method for determination of the composition of the metal chelate compounds.

Two important considerations may be emphasised in studying chelate formation by polarographic techniques First, half wave potential $|E_{1/2}|$ data for the determination of the composition of the chelate and its formation constant are valid only if electrode reduction is thermodynamically reversible. Secondly, the deviation of the equation of the polarographic wave is based on the assumption that the rate controlling step of the electrode reaction is the diffusion of the reducible species to the dropping mercury electrode.

To avoid interference from the reduction of the chelating agent itself, measurement of $|E_{1/2}|$ are made generally in presence of relatively large excess of the ligand with respect to metal ion.

The following general equation may be utilised to determine the composition of chelate by knowing the coordination number of the metal ion bound with the ligand i.e.,

$$\frac{\Delta E_{1/2}}{\Delta \log|A^{-b}|} = -p\,\frac{0.0591}{n}$$

where the various symbols have usual meaning.

Thus, by plotting a graph between $|E_{1/2}|$ values and -log concentration of the ligand, the number of the ligand molecules combining with one atom of the metal can be determined and hence the composition of the chelate can be assigned.

While applying this technique to study the composition of various Lewis acid-p-bromo p-dimethyl amino anil of phenyl glyoxal, no reversible wave was obtained and hence the technique could not be employed.

AMPEROMETRIC TITRATIONS

An amperometric titration is the polarographic analogue of conductometric titration and consists of using diffusion current measurements to locate the end point of a titration with a chemical reagent. The titration performed by adding successive aliquots of a standard solution of a reagent to a solution of the sample and measuring a diffusion current after each addition. Depending upon the potential applied to the cell, the diffusion current which is measured may be proportional to the concentration of the substance being titrated or the excess of the reagent, or one of the products of the reaction. The titration curve which is a plot of this diffusion current versus the volume of the reagent added, ideally consists of two straight lines whose point of intersection corresponds to the end point of the titration. Amperometric titrations are more accurate than other polarographic methods in the great majority of the instances. They require no knowledge of the characteristics of either the capillary or the current measuring elements and they make possible the determination of such non-reduction substances such as phosphates, sulphates etc. which could otherwise be determined only by less accurate indirect methods.

An attempt was made to obtain the polarogram of the metal ion in acetone (using $LiNO_3$ as a supporting electrolyte) medium. No well defined wave with a plateau for the diffusion current was obtained. The choice of the potential at which amperometric titration could be carried out was not possible.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

At present the use of magnetic susceptibility measurements in structural studies is less common than it was a decade ago. To a large extent this is due to a greater appreciation of the difficulties associated with this method. For many years the 'magnetic criterion' was used to distinguish between ionic and covalent bonding in complexes but this general criterion has been abondoned by its originator L. Pauling(101), and no longer seems tenable. The most obvious value of this method is in the four coordinate complexes of nickel (11). Unfortunately the magnetic behaviour of ions is characteristic of their spectra and hence must be interpreted on an individual basis. In many studies it has been typical to measure the magnetic susceptibility at a single temperature and then assume that the following relations held between the measured magnetic susceptibility χ', the magnetic moment u_{eff} and the number of unpaired electrons

$$\chi' = \frac{3K\,u^2}{N\beta^2 T} = \frac{u^2}{(2.84)^2(T)}$$

$$\text{or} \quad u_{eff} = 2.84\sqrt{\chi' T} \quad \text{B.M.}$$

$$\text{or} \quad u_{eff} = \sqrt{n(n+2)} \quad \text{B.M.}$$

where K is Boltzmann constant, N the Avagadro's number, T is the absolute temperature, n is the number of unpaired electrons and B.M. is Bohr Magneton, the commonly used unit for the magnetic moment. In general, a diamagnetic correction is made for the contribution of the other parts of the molecule to the magnetic susceptibility.

A further complication may arise if there is an appreciable orbital angular momentum to the magnetic moment.

In such a case:

$$u = \sqrt{n(n+2)} = \sqrt{4S(S+1)}$$

must be replaced by a more complicated relationship.

$$u = \sqrt{L(L+D) + 4S(S+1)}$$

Fortunately for most of the first row transition elements, the simple relationship is generally a reasonable approximation and the magnetic susceptibility may then be used to determine n in the complexes. For the second and third row transition elements the simple relationship is not applicable. Keeping in view this property we have studied magnetic susceptibility of a number of chelates studied spectrophotometrically as well as by I.R. technique, and having found the nature of the metal in the chelate as well as paramagnetism of the ligand itself and its effect on complexes.

INFRARED, ULTRAVIOLET AND VISIBLE SPECTROSCOPY

Infrared spectrum measurements help to find out the actual linkage in the complexes, structure of the ligand as well as that of the complexes.

Ultra-violet spectra of the ligands and the complexes help to find out the bonding in the complexes and to locate any other charge transfer occurring within the ligand or the complex. Visible spectra of the complexes, specially those of the transition metals, help to determine the stereo-chemistry of the complexes. But if the charge transfer band is in visible region, then the visible spectra of the normal elements will also help.

THE PROBLEM

The problem under investigation has two aspects, viz., the synthesis of new anils and the study of their interaction with metals, especially the non-transitional ones.

The newly synthesised anils were characterised by preparing their derivatives and confirming the functional groups in them by recording their I.R. in solid state.

The bathochromic effect of p-bromo phenacylidene p-dimethyl amino aniline was followed by carrying out reactions with Lewis acids, $HgCl_2$, $ZnCl_2$, $FeCl_3$, $AlCl_3$, $SnCl_4$ and $SbCl_5$. Evidence for complex ion formation could only be obtained by using purely non-aqueous media. Spectrophotometric studies could only be successfully employed in elucidating their composition. Conductometric method failed to give results of any value due to low conductances. pH-metric method could partly be employed in studying Cu(II)- PAO chelate.

Polarographic reduction did not give either well defined or reversible waves with the result that both polarography and amperometry could not be successfully employed.

The complexes were isolated, analysed and their I.R and magnetic susceptibility determined in order to get an insight into the various metal-anil chelates.

The oximes of phenacylidene aniline was chosen for interaction with Cu(II) due to its specificity. Its composition, stability and structure was determined by spectrophometry, magnetic susceptibility and I.R. methods.

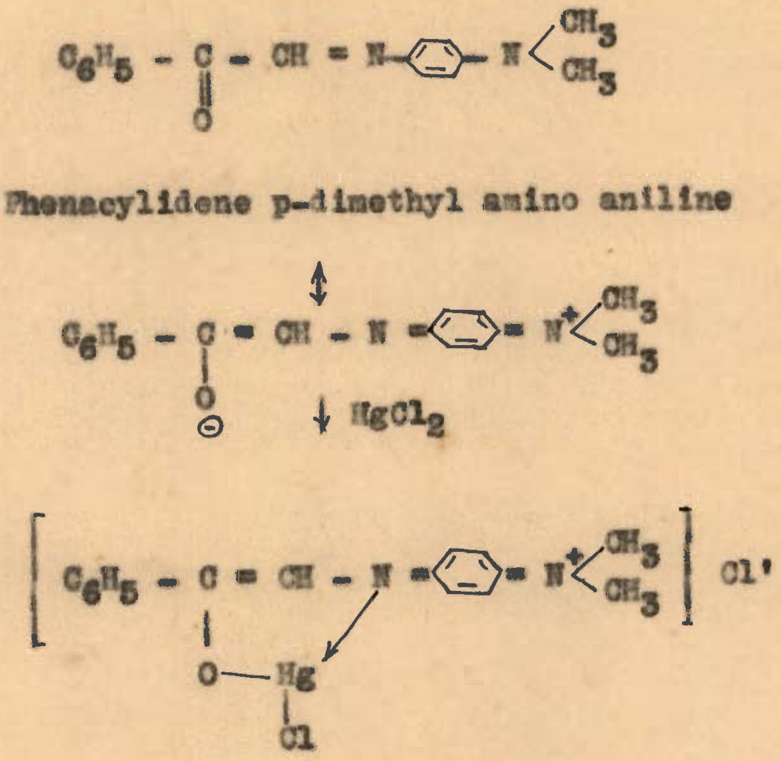
CHAPTER I

SYNTHESIS AND I.R. SPECTRA OF SOME NEW ANILS

SOME LESS FAMILIAR ANILS

Reference to the synthesis, properties and industrial applications of a large number of anils has already been made under 'General Introduction'. Other interesting compounds of the series which have attracted little attention both from the view point of their synthesis and their analytical applications are the anils of aromatic keto-aldehyde and their amino compounds. Yates(1) condensed phenyl glyoxal hydrate with aniline in 95 %, ethanol containing few drops of acetic acid. The product isolated by him melted at 164-166° and was considered by him to be a mono anil, ($C_6H_5-CO-CH=N-C_6H_5$). In 1963, Proctor et al(2) repeated the above experiment and detected five compounds by means of thin layer chromatography. Two of these compounds were isolated and were found to be a dimer, m.p. 76° and a trans anil (monomer, m.p. 145°). In 1965, the above workers repeated their own work and discovered that the monomer earlier reported by them as trans anil was in fact a dimer(3). The cis anil of phenyl glyoxal hydrate and aniline (m.p.210°) was also synthesised by Proctor et al(2) in 1965 by a different route. This too was later on found to be a dimer(3). The existence of dimers in the above syntheses may be attributed due to the presence of glacial acetic acid. An analogy may be found in the case of benzalaniline which ceases to exist as a monomer in presence of 90 / formic acid(4).

Krohnke and Gross(5) prepared a number of anils by condensing phenyl glyoxal hydrate with p-dimethyl amino aniline and found that these compounds react with Lewis acids to form the corresponding chelates as shown below:-


Phenacylidene p-dimethyl amino aniline

When such anils react with Lewis acids, there is a bathochromic shift in the molecule. It was quite interesting to observe that these compounds gave characteristics colours when coming in contact with silica gel.

In the light of the observation of Krohnke et al, it was considered worthwhile to synthesise some new anils from phenyl glyoxal hydrate, employing aromatic amino compounds instead of p-dimethyl amino aniline as the other reactant. The condensations were carried out in alcoholic media. The products were characterised by preparing various derivatives and studying the IR spectra of the pure crystalline products. One of their derivatives, viz., oximes were interesting from another view point also. They gave colour reactions with various metal ions thereby offering possibility of being used as analytical reagents.

This chapter deals with the preparation and physico-chemical studies of some new anils obtained from phenyl glyoxal hydrate with aniline, p-chloroaniline, o-, p-nitroanilines, o-, p-toluidines and α-, β-naphthylamines(6).

EXPERIMENTAL

PREPARATION OF PHENYL GLYOXAL HYDRATE

Phenyl glyoxal hydrate was prepared by earlier workers by the following methods :-

(a) From isonitroso acetophenone, by preparing its bisulphite and subsequently hydrolysing it(7,8).

(b) By oxidation of benzoyl carbinol with copper acetate(9).

(c) By heating bromo acetate with copper acetate.(10)

(d) Oxidation of acetophenone with nitrosyl chloride(11).

(e) Oxidation of α-bromo acetophenone with dimethyl sulphoxide(12).

(f) Hydrolysis of the nitrones of p-dimethyl phenacyl pyridinium halides(13).

Phenyl glyoxal hydrate was prepared following the method recommended by Riley and Gray(14) with slight modification. 600 ml. dioxane, 111 gms of SeO_2 and 20 ml. Water were taken in a three necked round bottom flash (1 litre capacity), fitted with a mercury sealed stirrer and a reflux condenser. The mixture was heated to 50-50° and stirred until a clear solution was obtained. 120 gms. of acetophenone were added in one lot and the resulting mixture was refluxed with continued stirring for four hours. The hot solution was decanted from the precipitated selenium, and dioxane and water were removed by distillation through a short column. 100 ml. of toluene were added and the distillation continued till the distilate was no more turbid. The remaining mixture was transferred to a 250 ml. Claisen flask and distilled at 95-97° / 25 m.m. Steam was passed through the Leibig condenser in order to prevent phenyl glyoxal to undergo polymerization. The yellow oil, so obtained, was immediately transferred to boiling water. On cooling, fine needles of phenyl glyoxal hydrate (m.p.85°) were obtained (m.p. recorded in the literature from 73-94°, depending upon the varying degree of hydration of the sample(15)).

PREPARATION OF ANILS

Equimolecular quantities of alcoholic solutions of phenyl glyoxal hydrate and the corresponding amines were taken in an Erlenmeyer flask. A condenser was attached and the flask was set in a hot water bath. The mixture was refluxed for about half an hour and allowed to cool. The product which solidified in a short while, was filtered and crystallized from hot alcohol. The condensation product obtained from phenyl glyoxal hydrate and aniline resulted in the formation of a solid together with a large quantity of a resinous substance. A considerable difficulty was experienced in crystallising this resinous mass. It was dissolved in a minimum quantity of ethyl acetate and then chromatographed over Brockmann alumina. The eluents were used in the order of petroleum ether, benzene, chloroform and their corresponding mixture as shown in table I. The eluents were collected in fractions of 30-40 ml. each and evaporated to dryness.

Table I

CHROMATOGRAPHY OF THE RESINOUS MASS

Fraction Number	Eluents	
1 - 2	Petroleum + Benzene (9:1 V/V)	Resinous material
3	Petroleum + Benzene (1:1 V/V)	Resinous material
4 - 10	Petroleum + Benzene (1:9 V/V)	Resinous material
11- 12	Benzene	Resinous material
13- 14	Benzene + chloroform(3:1 V/V)	Resinous material
15	Benzene + chloroform	Waxy material
16- 20	Chloroform	Yellow solid
20- 22	Nil	Nil

The fractions 1-15 were combined together and charcoalised with activated charcoal and filtered. The filterate was concentrated and rechromatographed on Brockmann Alumina. No solid was, however, obtained. The fractions 16-20 were crystallised from hot alcohol and afforded yellow crystalline plates, m.p. 124°.

On adding the alcoholic solution of phenyl glyoxal hydrate to the corresponding solutions of p-chloroaniline and α-, β-naphthylamines, condensation product were obtained immediately and no warming was necessary. The condensation product of o-toluidine, however, did not give a solid suitable for crystallization. The yields of the anils varied from 47.9 % to 99.2 %. It is rather difficult to explain why such a large variation in yield values is observed in these compounds. All these anils except phenacylidene p-chloro-aniline are coloured, crystalline compounds possessing a characteristic disagreable odour. They are soluble in methanol, ethanol, benzene, acetone and chloroform producing light yellow solutions. They are, however, insoluble in water and petroleum ether. The~~y~~ characteristics of these anils are recorded in table II. (p.52).

DERIVATIVES OF ANILS

PREPARATION OF P-NITRO PHENYL HYDRAZONES

Alcoholic solutions of p-nitrophenyl hydrazine (0.5g) and the corresponding anil (0.5g) were mixed, warmed and a drop of glaciel acetic acid was added. The mixture was left overnight, when p-nitro phenyl hydrazones separated. They were filtered, washed well with water and crystallized from nitrobenzene.

PREPARATION OF 2:4 DINITRO PHENYL HYDRAZONES

A solution of 2:4 di-nitro phenyl hydrazine in ethanol containing a few drops of concentrated sulphuric acid was warmed with equimolecular quantity of the corresponding anil. The 2:4 -dinitro phenyl hydrazones which separated, were filtered, washed well with water and crystallised from nitrobenzene.

PREPARATION OF SEMICARBAZONES

A mixture of semicarbazide hydrochloride (1g) and sodium acetate (1.5g) was dissolved in a minimum quantity of water, and added to an alcoholic solution of the anil (0.5g). The mixture was refluxed over a water bath for about half an hour. It was then transferred to a beaker containing cold water and any turbidity if produced was removed by the addition of alcohol. A few drops of acetic acid were added and the whole mixture was left overnight. The precipitate of the semicarbazone was filtered, washed well with water and crystallized from alcohol.

PREPARATION OF OXIMES

A solution of hydroxylamine hydrochloride (0.5g) and sodium acetate (1g) in water was mixed with an alcoholic solution of the anil (1g) and refluxed over a water bath for about three hours. After removing most of the alcohol, the reaction mixture was transferred to ice cold water. The precipitate of the oxime was filtered, washed well with water and crystallised from alcohol.

The above derivatives were obtained in almost quantitative yields. The characteristics of the derivatives of the anils are recorded in table III. (p. 53).

REACTION WITH METAL IONS

The oximes give colour reactions with alcoholic solutions of heavy metal ions, especially copper, cobalt, nickel and iron. The colours are all green of varying shades ranging from yellow green (nickel), bright green (copper) and dark green (cobalt). With ferric iron, the colour response is given only by two of the above oximes viz. phenacylidene-β-naphthyl amine and phenacylidene-o-toluidine oximes, which give reddish orange and violet colours respectively.

PREPARATION OF ANILS FROM PHENYL GLYOXAL HYDRATE AND SOME AROMATIC AMINO COMPOUNDS

Some new anils derived from phenyl glyoxal hydrate and aromatic amines had already been described (pp. 52). A few more anils were prepared by condensing phenyl glyoxal hydrate with m-nitroaniline, p-bromoaniline, m-chloroaniline, m-toluidine, o-anisidine, o-aminophenol, sulphanilic acid, anthranilic acid, m-amino benzoic acid, p-amino benzoic acid, and sulphanilamide. These anils were characterized from their p-nitro phenyl hydrazones, 2:4 di-nitro phenyl hydrazones, semi-carbazones and oximes using the methods described previously. The anils and their derivatives are listed in tables No.IV and V respectively.(pp.54-55).

The oximes of many of these anils also produce yellow, greenish yellow and green colourations with different metal ions and they may offer a possibility for being exploited as analytical reagents.

Table II- Anils Derived from Phenyl Glyoxal Hydrate and Aromatic Amines

Name of the Anil	Colour	Formula	M.P. °C	Yield %	- Nitrogen, %	
					Calcd.	Found
R-aniline	Yellow	$C_{14}H_{11}O N$	123-124	90.9	6.69	6.73
*R-p-chloroaniline	Colourless	$C_{14}H_{10}O N Cl$	115-116	63.6	5.74	5.89
R-o-nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	105-106	82.2	11.02	11.29
R-p-nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	127-129	47.2	11.02	11.41
R-o-toluidine	Reddish Brown	$C_{15}H_{13}O N$	Gummy mass	85.5	6.28	6.12
R-p-toluidine	Yellow	$C_{15}H_{13}O N$	97-98	89.6	6.28	6.32
*R-α-naphthylamine	Yellow	$C_{18}H_{13}O N$	136-137	92.2	5.40	5.24
*R-β-naphthylamine	Yellow	$C_{18}H_{13}O N$	90-91	61.8	5.40	5.12

($R = C_6H_5 - C O - CH =$, phenacylidene radical)

* No warming was, however, necessary to obtain these anils.

Table .XII Characteristics of the Derivatives of the Anils

Name of the anils	p-nitro phenyl hydrazones			2:4 dinitro phenyl hydrazones			Semicarbazones			Oximes		
	M.P. °C	-Nitrogen		M.P. °C	-Nitrogen		M.P. °C	-Nitrogen		M.P. °C	Nitrogen	
		Calcd.	Found		Calcd.	Found		Calcd.	Found		Calcd.	Found
R-aniline	185-186	16.28	16.53	236-238	17.99	17.74	190-191	21.05	20.95	58-59	12.50	12.46
R-p-Chloro-aniline	200-201	16.16	16.46	267-269	16.52	16.46	180-181	18.63	18.44	146-147	10.83	10.35
R-o-nitro-aniline	233-234	17.99	17.61	255-256	19.35	19.12	197-198	22.50	22.31	189-201	15.61	15.42
R-p-nitro-aniline	250-252	17.99	17.54	262-263	19.35	19.40	203-205	22.50	22.25	206-207	15.61	15.48
R-o-toluidine	100-101	15.64	15.56	250-251	17.36	17.25	-	-	-	77-68	11.76	11.56
R-p-toluidine	134-135	15.64	15.32	263-265	17.36	17.16	244-245	20.00	19.95	101-102	11.76	11.43
R- -naphthyl-amine	264-265	14.21	14.13	194-195	15.94	15.63	210-211	17.72	17.86	119-120	10.22	10.20
R-B-naphthyl amine	189-190	14.21	14.09	247-249	15.94	15.83	100-101	17.72	17.43	95-96	10.22	10.32

$(R = C_6H_5 - CO - CH =)$

Table - IV Anils derived from Phenyl Glyoxal Hydrate and Aromatic Amino Compounds

Name of the anil	Colour	Formula	M.P. °C	Yield %	Nitrogen, %	
					Calcd.	Found
R-m-Nitro aniline	Yellow	$C_{14}H_{10}O_3N$	157-158	19.68	11.02	10.96
R-p-Bromo aniline	Buff	$C_{14}H_{10}ONBr$	137-138	83.33	4.68	4.49
R-m-Chloro aniline	Reddish brown	$C_{14}H_{10}ONCl$	66-67	13.69	5.74	5.62
R-m-Toluidine	Yellow	$C_{15}H_{13}ON$	113-114	19.33	6.28	6.13
R-o-Amino phenol	Dark brown	$C_{14}H_{11}O_2N$	173-174	23.33	6.22	6.05
R-p-Amino phenol	Chocolate	$C_{14}H_{11}O_2N$	125-127	40.00	6.22	6.12
R-o-Anisidine	Light yellow	$C_{15}H_{13}O_2N$	126-127	53.00	5.85	5.71
R-Sulphanilic acid	Light pink	$C_{14}H_{11}O_4NS$	244-245 d	99.20	5.01	4.98
R-Anthranilic acid	Pale yellow	$C_{15}H_{11}O_3N$	140-141	64.53	5.53	5.24
R-m-Amino benzoic acid	Buff	$C_{15}H_{11}O_3N$	245-246	39.72	5.53	5.32
R-p-Amino benzoic acid	Light yellow	$C_{15}H_{11}O_3N$	170-171	73.22	5.53	5.16
R-Sulphanilamide	Light yellow	$C_{14}H_{12}O_3N_2S$	95-96	66.63	9.72	9.48

(R = C_6H_5 - C O - CH = , Phenacylidene radical)

Table -V Characteristics of the Derivatives of the Anils

Name of the Anil	p-Nitro phenyl hydrazones			2:4 Dinitro phenyl hydrazones			Semicarbazones			Oximes		
	M.P. °C	Nitrogen,%		M.P. °C	Nitrogen,%		M.P. °C	Nitrogen,%		M.P. °C	Nitrogen,%	
		Calcd	Found		Calcd	Found		Calcd	Found		Calcd	Found
R-m-Nitro aniline	267-268	17.99	17.73	273-274	19.35	19.13	190-191	22.50	22.35	176-177	15.61	15.32
R-p-Bromo aniline	198-199	13.23	13.15	224-226	14.93	14.76	226-227	16.23	16.18	185-186	9.24	9.08
R-m-Chloro aniline	101-102	16.16	16.03	200-201	16.52	16.14	240-241	18.63	18.24	94-95	10.83	10.56
R-m-Toluidine	257-258	15.64	15.42	241-243	17.36	17.13	233-234	20.00	19.89	95-96	11.76	11.61
R-o-Amino phenol	270-272	15.55	15.23	241-242	17.45	17.28	218-219	19.82	19.71	257-258	11.66	11.34
R-p-Amino phenol	244-245	15.55	15.19	259-260	17.45	17.13	221-222$_d$	19.82	19.63	180-181	11.66	11.23
R-o-Anisidine	198-199	14.97	14.68	267-269	16.70	16.42	229-230	18.91	18.69	89-90	11.02	10.97
R-Sulphanalic acid	274-275	13.20	13.02	240-241	14.92	14.76	230-232	16.18	16.06	163-164	9.21	9.06
R-Anthranilic acid	218-219$_d$	14.43	14.18	255-256$_d$	16.16	15.98	197-198	18.06	17.98	160-161	10.44	10.28
R-m-Amino benzoic acid	208-209	14.43	14.20	203-204	16.16	15.86	265-267	18.06	18.01	185-186	10.44	10.17
R-p-Amino benzoic acid.	199-200	14.43	14.18	306-307	16.16	15.93	233-234	18.06	17.82	158-159	10.44	10.36
R-Sulphanilamide	259-260	16.54	16.48	194-195	17.65	17.42	133-134	20.28	20.13	132-133	13.86	13.65

(R = C_6H_5 - C O - CH =)

CONDENSATION OF SOME AROMATIC AMINES WITH p-BROMO PHENYL GLYOXAL HYDRATE

Krohnke et al. (loc. cit) synthesised anils derived from phenyl glyoxal hydrate and p-dimethyl amino aniline and discovered that these compounds gave metal chelates with Lewis acids. To add to our existing knowledge of these new types of anils , it was thought worthwhile to study the condensation products of p-bromo phenyl glyoxal hydrate and aromatic amines.

PREPARATION OF p-BROMO ACETOPHENONE

p-bromo phenyl glyoxal hydrate was obtained by SeO_2 oxidation of p-bromo acetophenone(14), which was prepared by acetylation of bromo benzene(16). In a 5-1 round bottomed three necked flask, fitted with mechanical stirrer, separating funnel and reflux condenser connected with gas absorption trap for disposing off hydrochloric acid gas, was placed 392 g. of bromo benzene in 1-1 of carbon disulphide. To this was added 750 g. of anhydrous aluminium chloride. The mixture was heated on a steam bath until gentle refluxing starts and then 204 g. of distilled acetic anhydride were added slowly through the dropping funnel. The time of addition was about one hour. Gentle refluxing was continued throughout the addition of the anhydride. The mixture was refluxed for one hour. The reaction was accompanied by copious evolution of hydrochloric acid gas which did entirely cease even after this subsequent heating. The condenser was then attached to one of the side necks and carbon disulphide was distilled without removing the flask from the steam bath.

After the removal of the solvent, the reaction was allowed to cool somewhat but while it was still warm, it was poured slowly with stirring over crushed ice to which concentrated hydrochloric acid was added. In this way, only a small amount of anhydrous aluminium chloride remained in the flask. This was decomposed with ice and concentrated hydrochloric acid and added to the main product. The volume was now about 5 litres. Each two litre portion was extracted twice with 300 ml. and 200 ml. portions of ether. The extracts were combined and washed twice with water, once with 10 % sodium hydroxide and twice more with water. The final water washing was practically colourless and the separation sharp.

The ethereal extract was dried for one hour with about 30 g. of fused calcium chloride and filtered, and the solvent was distilled over a water bath. The residue was distilled under reduced pressure with a short column. The distillate was found to be colourless which solidified in fine white plates, m.p. 49-50.5°. The yield was 340-395 g, 69-79 % of the theoretical amount.

The oxidation of p-bromo acetophenone was carried out as already mentioned (pp.56) by SeO_2 oxidation of the ketone. After the oxidation was complete, the hot solution was decanted from the precipitated selenium and distilled under atmospheric pressure until most of the alcohol was removed. 100 ml. of xylene was now added and the solution again distilled under atmospheric pressure till the distillate was no longer turbid. The remaining mixture was transferred to a 250 ml. Claisen flask under reduced pressure. This modification was necessary in order to prevent the formation of p-bromo phenyl glyoxal hydrate which could also distil along with the solvent. The residue was then distilled under reduced pressure (at 7 m.m.) and the distillate was dissolved in hot water. On cooling p-bromo phenyl glyoxal hydrate was obtained in fine needles, m.p.132°.

PREPARATION OF ANILS FROM p-BROMO PHENYL GLYOXAL

The anils described in table VI (p. 59) were obtained by refluxing on a water bath equimolecular quantities of p-bromo phenyl glyoxal hydrate and the corresponding amino compounds in 95 % ethanol. On cooling, the solid products obtained were separated and crystallized from hot alcohol. The anils are soluble in ethanol, methanol acetone, acetonitrile, benzene and toluene while they are practically insoluble in water and petroleum ether.

DERIVATIVES OF THE ANILS

p-nitro phenyl hydrazones, 2:4 di-nitro phenyl hydrazones, semicarbazones and oximes of the anils were prepared

Table -VI Anils derived from p-bromo Phenyl Glyoxal Hydrate and Aromatic Amines

Name of the Anils	Colour	Formula	M.P. °C	Yield %	Nitrogen % Calcd.	Nitrogen % Found
R- Aniline	Light yellow	$C_{14}H_{10}ONBr$	60-61	78.21	4.86	4.81
R-Toluidine	Brown	$C_{15}H_{12}ONBr$	76-77	56.32	4.63	4.59
R-m-Toluidine	Brown	$C_{15}H_{12}ONBr$	74-75	52.35	4.63	4.62
R-p-Toluidine	Yellow	$C_{15}H_{12}ONBr$	86-87	64.52	4.63	4.57
R-o-Chloroaniline	Brown	$C_{14}H_9ONClBr$	Gummy	-	4.34	-
R-m-Chloroaniline	Dark Brown	$C_{14}H_9ONClBr$	82-83	56.52	4.34	4.29
R-p-Chloroaniline	Black	$C_{14}H_9ONClBr$	65-66	73.42	4.34	4.31
R-Sulphanilamide	Brown	$C_{14}H_{11}O_3N_2SBr$	112-113	68.23	7.63	7.60

R = ($Br-C_6H_4-CO-CH=$, p-bromo phenacylidene radical)

Table - VII Characteristics of the Derivatives of the Anils

Anil	P-nitrophenyl Hydrazones			2:4 Dinitrophenyl Hydrazones			Semi-carbazones			Oximes		
	M.P. °C	Nitrogen,%		M.P. °C	Nitrogen, %		M.P. °C	Nitrogen,%		M.P. °C	Nitrogen, %	
		Calcd	Found		Calcd	Found		Calcd	Found		Calcd	Found
R-Aniline	267-268	13.24	13.21	258.260	14.95	14.86	231-232	16.24	16.18	155-156	9.25	9.12
R-o-Toluidine	290-291	12.86	12.46	250-251	14.52	14.32	142-143	15.61	15.59	Gummy	8.83	-
R-m-Toluidine	250-251	12.86	12.58	245-247	14.52	14.42	183-184	15.61	15.62	Gummy	8.83	-
R-p-Toluidine	281-282	12.86	12.67	286-288	14.52	14.48	207-209	15.61	25.44	128-129	8.83	8.79
R-o-Chloroaniline	231-233	12.22	12.13	246-248	13.90	13.82	196-197	14.74	14.68	193-195	8.28	8.23
R-m-Chloroaniline	221-223$_d$	12.22	12.05	215-217	13.90	18.75	238-239	14.74	14.72	Gummy	8.28	8.19
R-p-Chloroaniline	219-220	12.22	12.18	284-285	13.90	18.64	232-234	14.74	14.69	143-144	8.28	8.23
R-Sulphanilamide	282-284	13.94	13.84	272-274	12.73	12.68	240-241	16.51	16.48	Gummy	11.00	-

R = (Br-C_6H_4-CO-CH = , p-bromo phenacylidene radical) in the usual manner, and were obtained almost in quantitative yields. p-nitro phenyl hydrazones and 2:4 di-nitro phenyl hydrazones were crystallised from nitrobenzene while semicarbazones and oximes from alcohol. The characteristics of these derivatives are given in Table VII (p.60). The oximes of these anils also give sharp colour changes with various metal ions and may offer a possibility of being used as chelating agents.

I.R. SPECTRA STUDIES OF THE ANILS AND SOME THEIR DERIVATIVES (17)

The I.R. spectra of the above listed anils (including some of their derivatives) were recorded in solid state by KBr technique in order to ascertain the presence of the functional groups. Perkin-Elmer infracord and Beckmann I.R-4 spectro-photometers were used for this purpose (courtesy: Saldtler Research Laboratories, U.S.A.). The stretching frequencies of the functional groups of such compounds are listed in tables VIII to XI (pp. 66 TO 71).

ANILS

Phenacylidene aniline, p-chloro phenacylidene aniline and phenacylidene m-toluidine possess an azomethine linkage to characterise them as anils. Their stretching frequencies are given in table VIII.

The spectra of these compounds show a sharp band around 1700 cm.$^{-1}$, characteristic of an aryl absorption band (1700-1670 cm.$^{-1}$). I, M, steric effect and conjugation of the > C = O group with respect to phenyl or naphtyl skeleton lowers such frequency. CH=N group shows characteristic band between 1630-1613 cm.$^{-1}$. From the spectra of the compounds (1-3), there is an evidence of -CH=N because the frequencies lie around this range. However, lowering of frequency in (2) may be due to — I effect which generally lowers this value. The stretching frequency at 2930 cm.$^{-1}$ in the compound (3), cannot be other than C-CH_3 situated in the meta position since there are usually three peaks due to this group in the range of 2970-2850 cm.$^{-1}$ of which the most useful for diaganosis is near 2960 cm.$^{-1}$. A compound having single C-Cl link attached to a phenyl skeleton shows stretching frequency in the range of 750-700 cm.$^{-1}$. In the spectrum of the compound (2) the frequency 705 cm.$^{-1}$ falls well within this range and hence the evidence for such a linkage is forthcoming. The C=C stretching frequencies of benzene derivatives are in the ranges 1520-1480 cm.$^{-1}$ and 1630-1590 cm.$^{-1}$ respectively. 1:4 disubstituted derivatives reveal the frequency around 830 cm.$^{-1}$. The peaks of the spectra (1-3) of the anils also give evidence for such grouping or linkages.

2:4- DI-NITRO PHENYL HYDRAZONES AND p-NITRO PHENYL HYDRAZONES OF THE ANILS

Some of the anils synthesised (loc.cit) have been characterised by 2:4 di-nitro phenyl hydrazones and p-nitrophenyl hydrazones and the stretching frequencies of their functional groups are given in table IX.(

Aromatic nitro compounds show a band in the range of 1560-1350 cm.$^{-1}$ due to C-NO_2 group. Presence of an electron-attracting group in para position or a bulky group in ortho position (steric effect) tends to move the C-NO_2 frequency out of aromatic plane and is consequently raised from 1350 to 1540 cm.$^{-1}$ On the other hand when the substituents are electron-donating , the frequency is lowered from 1560 to 1490 cm.$^{-1}$ Further, in aromatic compounds containing two or more nitro groups, multiple frequencies are observed. In the spectra of the compound (4 to 27) the stretching frequencies of C-NO_2 group or groups fits well in this range as well as multiplication of bonds is observed in 2:4 di-nitro derivatives due to the above influence. The higher or lower value than the normal range may be accounted for due to aforesaid influences. NH group has characteristic frequency between 3400-3000 cm.$^{-1}$ The spectra of all the hydrazones show a sharp peak round about this region.

The azomethine linkage in such type derivatives lies in the normal range of — CH=N. Besides, most of the derivatives are p-disubstituted whose frequency is in the range of 840-820 cm.$^{-1}$ On examining all such spectra, there is a broad peak around 830 cm^{-1} which can be assigned to such grouping. There is a peak at 1080 cm^{-1} in the compound (4) which can be attributed to S=O group of p-substituted sulphonic ($-SO_3H$) constituent. p-bromo phenyl skeleton of some of the derivatives (16,17,18) possess C-Br skeleton around 690-645 cm^{-1} range and C-Cl linkage in p-chloro substituted compound at 750-700 cm^{-1}(17,19).

SEMICARBAZONES

The characteristic groups of semicarbazones of the anils, which determine their structure, are > $CONH_2$, CH=N, NH etc. The frequencies of such compounds are listed in table X.

In the compounds (28 to 37) CH=N linkage around 1600 cm^{-1} is quite evident. The NH stretching frequency of such grouping lies in the range of 3400-3000 cm^{-1} and is a sharp diagonisable peak. Above 3000 cm^{-1} there is a sharp peak due to NH_2 group of $-CONH_2$. However, >C=O group of such compound lies near 1700 cm^{-1}. Like 2:4 di-nitro and phenyl hydrazones of the anils, such compound possess 1:4 disubstituted group. The frequencies 3200 cm^{-1} and 3000 cm^{-1} in the compounds (28 and 35) is due to $C-CH_3$ grouping attached to phenyl skeleton, 1450 cm^{-1} in the compound (19) is because of $C-NO_2$ and S=O group of para substituted-SO_3H group in (31) is around 1080 cm^{-1}.

OXIMES

Oximes of the anils were prepared to exploit them as chelating agent for metal ions. Besides -CH=N group of the anil, there are characteristic OH and C=N grouping in such compounds due to oximino C=N=OH linkage. Some of the oximes are tabulated in table XI.

From the spectra of such oximes (38 to 41), -CH=N and p-disubstituted stretching frequencies fall well within their respective ranges. The OH frequency of =N-OH group shows such frequency in the vicinity of 3200 cm^{-1} as also depicted from the respective spectra. C=N frequency of C=N=OH group is in the range of 1650-1680 cm^{-1} which is also shown by spectra (Table XI). However, in one case(41) there is 1300 cm^{-1} frequency which has been also reported in the literature(18) due to weak bond of such grouping. The oxime (39) shows S=O frequency at 1150 $cm.^{-1}$ due to $-SO_2NH_2$ p-substituted group.

Table-VIII Infrared stretching frequencies of the functional groups of the Anils

Cm^{-1}

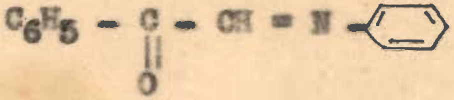
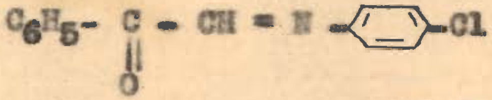
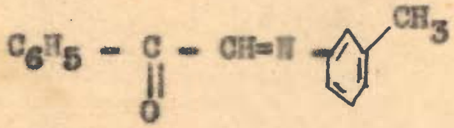
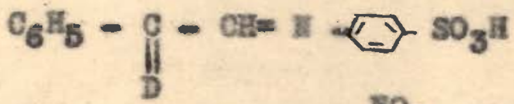
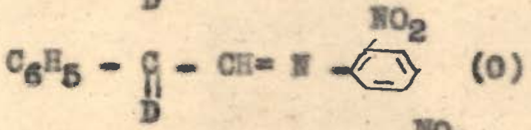
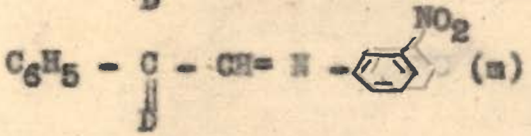
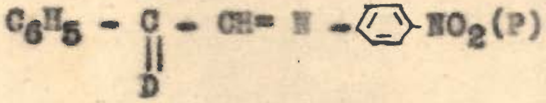
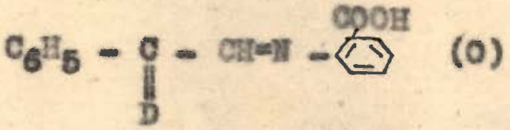
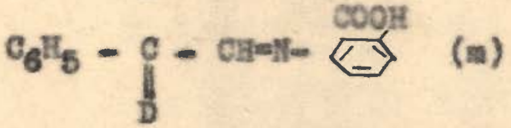
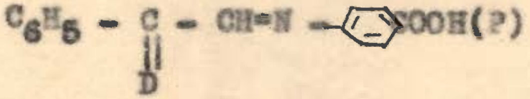
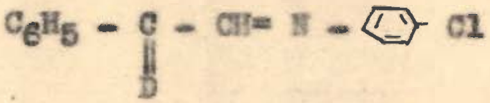
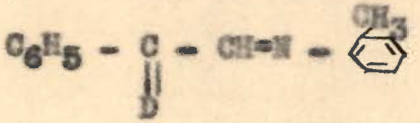
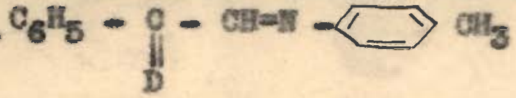
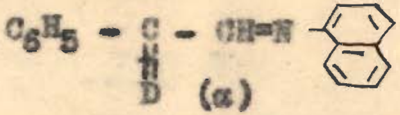
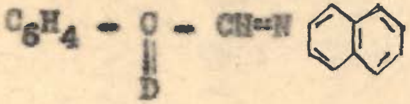
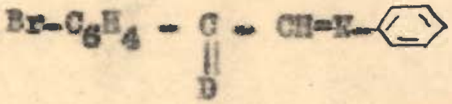
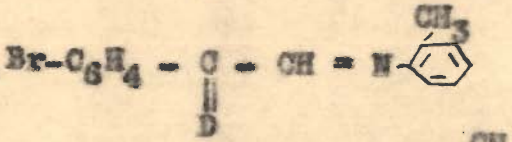
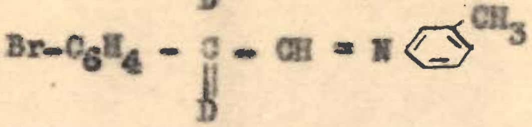
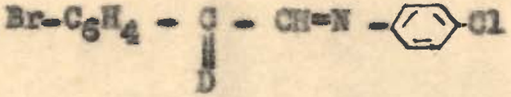
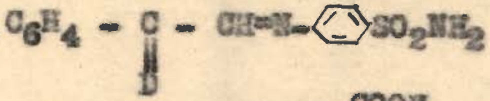
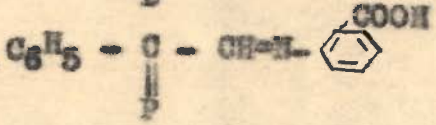
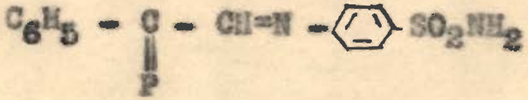
Structure	>C=O	CH=N	1:4 Di. substituted	$C-CH_3$	C-Cl.	Fig. No.
1. 	1690	1600	860	-	-	I
2. 	1690	1590	815	-	705	II
3. 	1700	1600	850	2930	-	III

Table IX- Infrared Stretching Frequencies of 2:4 -dinitro Phenyl Hydrazones and P-nitro Phenyl Hydrazones of the Anils

Cm^{-1}

		CH=N	$C-NO_2$	-NH	-OH	1:4 di-substituted	SO_2NH_2	Fig.
4.		1610, 1530	1420, 1440	-	-	820	-	IV
5.		1600, 1620	1420, 1500	3350	-	820, 845	-	V
6.		1610	1440, 1490	3260	-	830	-	VI
7.		1600, 1640	1420, 1500	3290	-	835	-	VII
8.		1585, 1610	1420, 1500	3300	3440	-	-	VIII
9.		1590, 1610	1410, 1440	3370	3100	-	-	IX
10.		1585, 1605	1415, 1490	3280	3450	825	-	X
11.		1575, 1600	1340, 1425	3350	-	835	-	XI
12.		1580 1600	1440, 1490	3290	840	-	($C-CH_3$) 3100	XII

Structure	CH=N	C-NO$_2$	-NH	1:4	SO$_2$-NH$_2$	C-CH$_3$	Fig.
13. 	1580, 1600	1440, 1490	3290	830	-	3100	XIII
14. 	1605, 1640	1370, 1490	3320	835	-	-	XIV
15. 	1600, 1620	1430, 1500	3300	840	-	-	XV
16. 	1585, 1610	1420, 1490	3280	830	-	-	XVI
17. 	1580, 1600	1415, 1490	3280	830	-	3100	XVII
18. 	1575, 1600	1440, 1500	3440	830	-	3090	XVIII
19. 	1525 1600	1425, 1500	3440	830	-	-	XIX
20. 	1550, 1600	1450, 1570	3500	830	1340		XX
21. 	1590, 1550	1490	3260	835	-		XXI
22. 	1550, 1595	1490	3260	840	1160, 1315		XXII

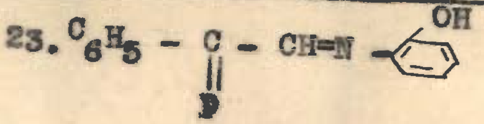
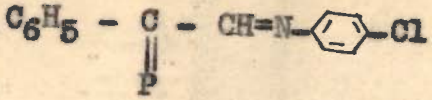
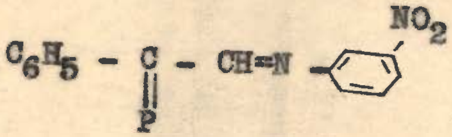
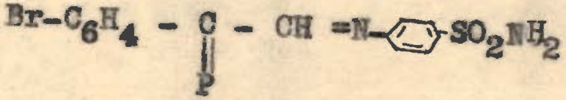
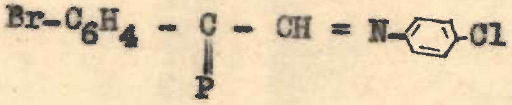
Structure	CH=N	C-NO_2	-NH	1:4	-SO_2 NH_2	Fig.
23. 	1580, 1600	1500	3200	830	-	XXIII
24. 	1610, 1650	1465	3330	855	-	XXIV
25. 	1580, 1600	1450, 1495	3400	840	-	XXV
26. 	1550, 1590	1490	3280	830	1150, 1320	XXVI
27. 	1540, 1590	1490	3260	830	-	XXVII

Table -X Infrared Stretching frequencies of Semi-carbazones of the Anil Cm^{-1}

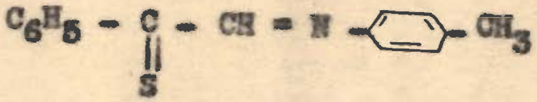
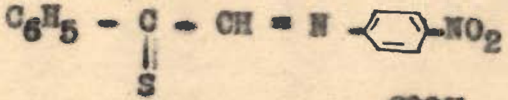
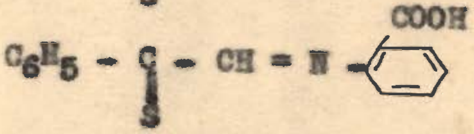
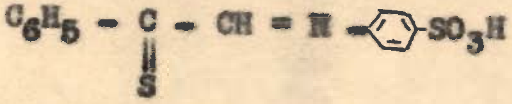
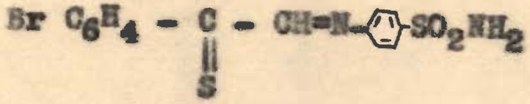
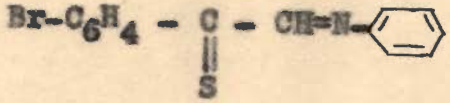
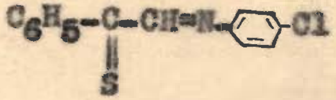
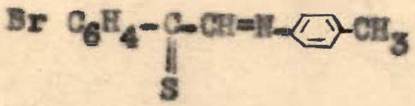
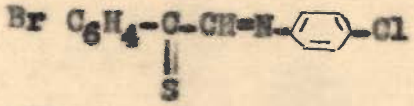
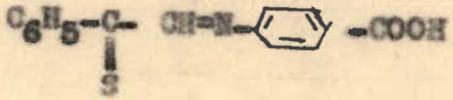
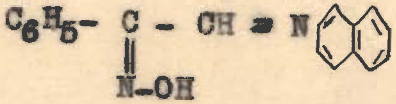
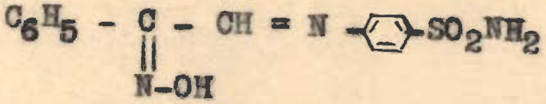
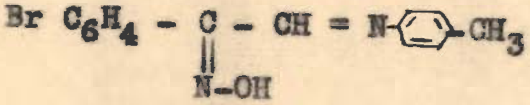
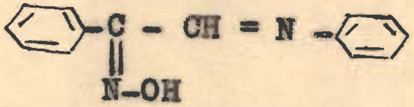
		C=O	CH=N	NH	-CO NH_2	1:4 di-substituted	Fig.
28.		1700	1525 1600	3225	3500	-	XXVIII
29.		1700	1600	3300	3500	840	XXIX
30.		1700	1575, 1600	3200	-	-	XXX
31.		1700	1600	3180	3500	810	XXXI
32.		1700	1600	3200	3440	-	XXXII
33.		1730	1650	3210	3500	-	XXXIII
34.		1700	1650	3280	3500	-	XXXIV
35.		1725	1600	3200	3575	840	XXXV
36.		1700	1605	-	3400	855	XXXVI
37.		1700	1550, 1600	3210	3500	-	XXXVII

Table -XI Infrared Spectra of the Oxime

Cm^{-1}

		C=N(oxime)	CH=N(Imine)	OH	1:4 di-substituted	SO_2NH_2	Fig.
38.		1640	1600	3500	—	—	XXXVIII
39.		1620	1600 1645	3550	825	1150 1320	XXXIX
40.		1630	1600	3275	830	-	XL
41.		1300 (w)	1600 1575	3400	830	-	XLI
42.		1650 (b)	1475	3375	820	-	XLII

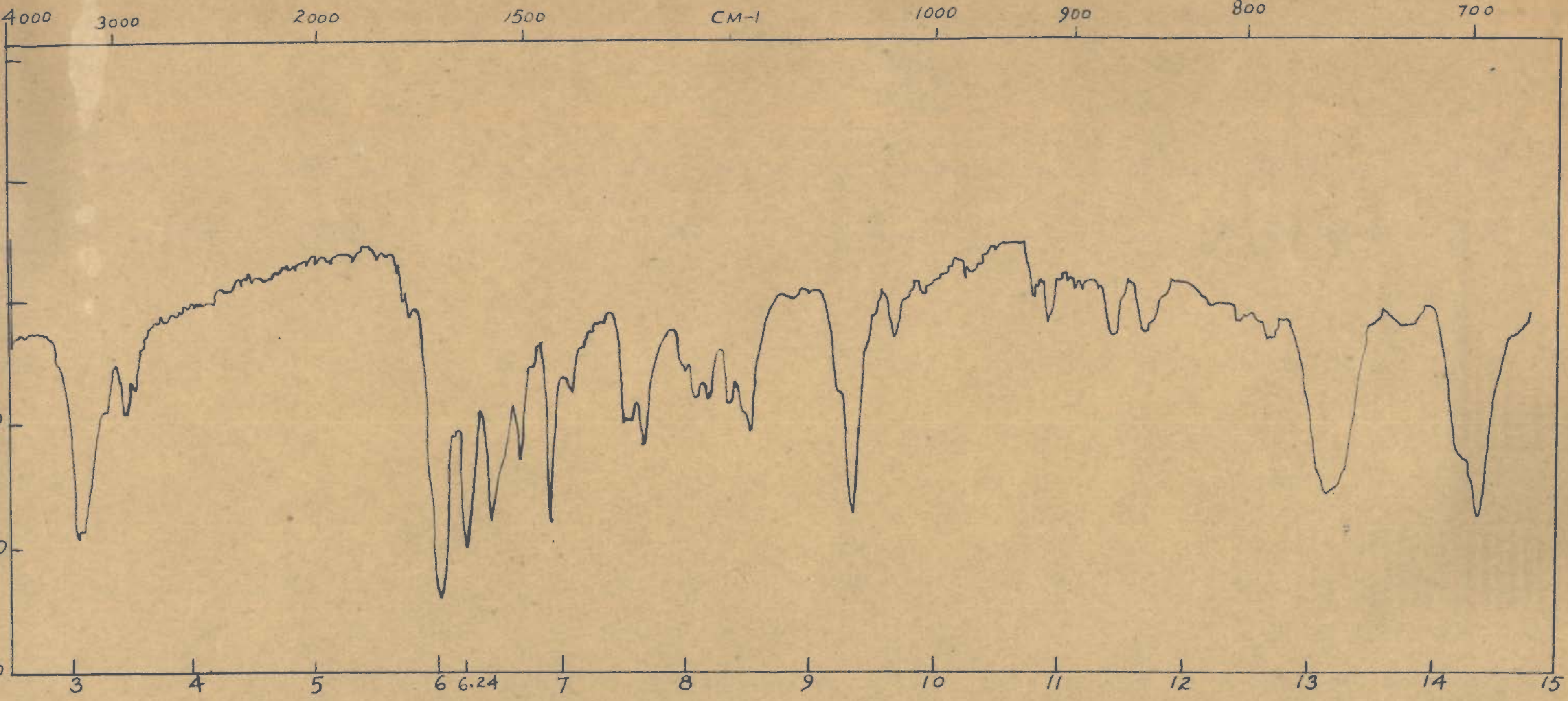
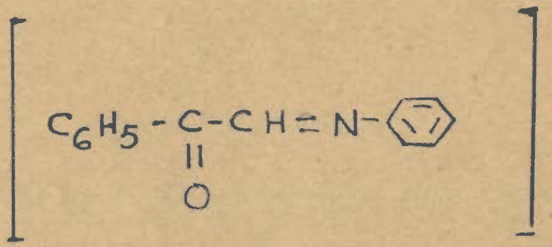


FIG - I



$$\left[C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-CH=N-C_6H_5 \right]$$

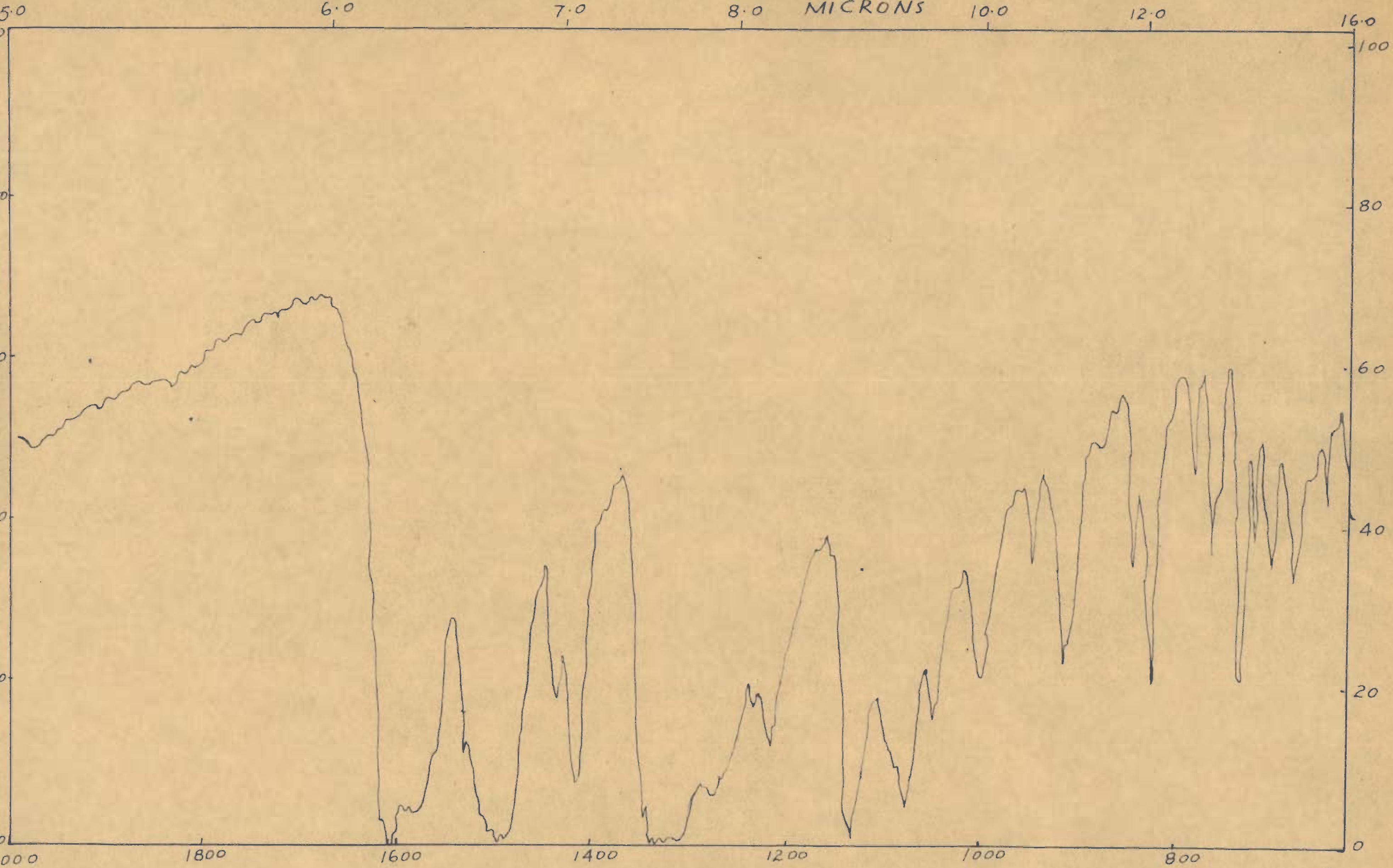
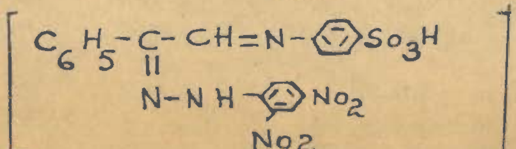


FIG. $IV_{(A)}$



$C_6H_5-\underset{\underset{N-NH-C_6H_3(NO_2)_2}{\|}}{C}-CH=N-C_6H_4-SO_3H$

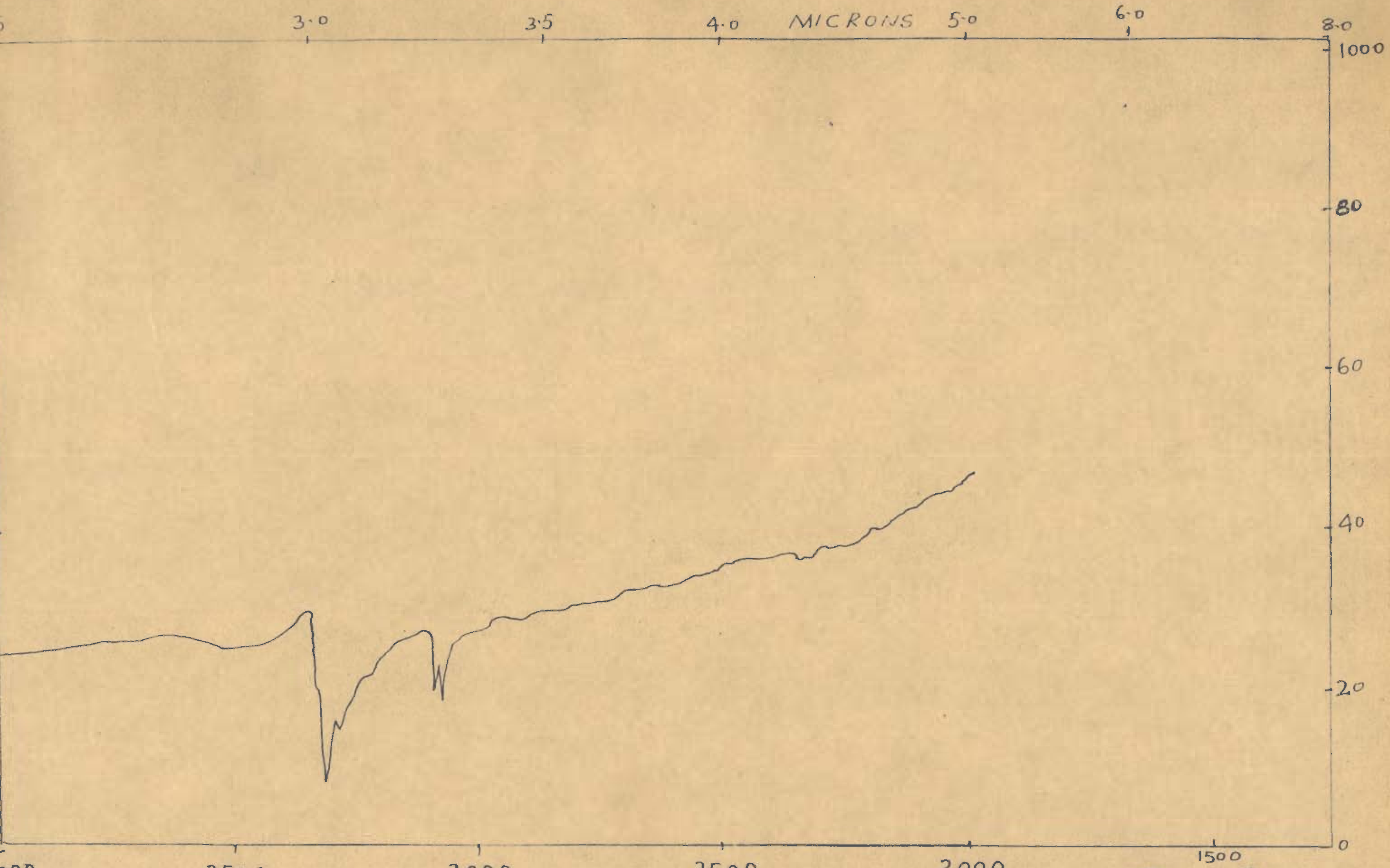
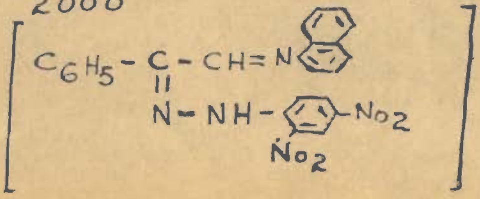

3·0
3·5
4·0
MICRONS
5·0
6·0
8·0
1000
80
60
40
20
0
3500
3000
2500
2000
1500
FREQUENCY (CM-1)

FIG. IV(B)



C6H5 - C - CH = N
N - NH -
NO2
NO2

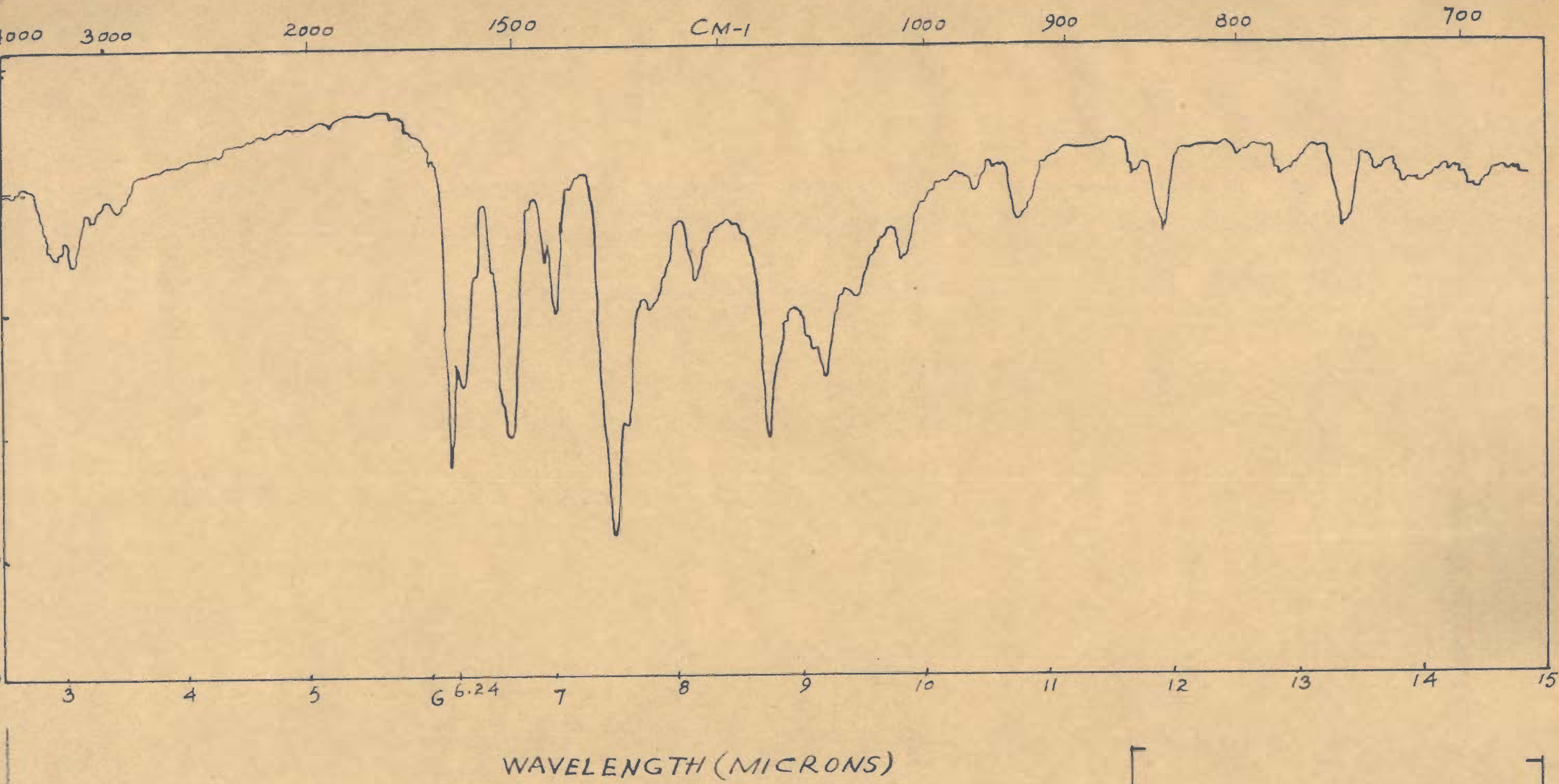
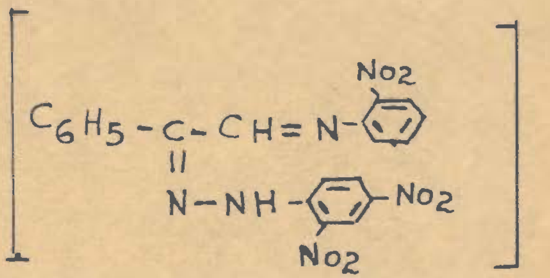

000
3000
2000
1500
CM-1
1000
900
800
700
3
4
5
6
6.24
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

FIG - V


C6H5 - C - CH = N -
N - NH -
NO2
NO2
NO2

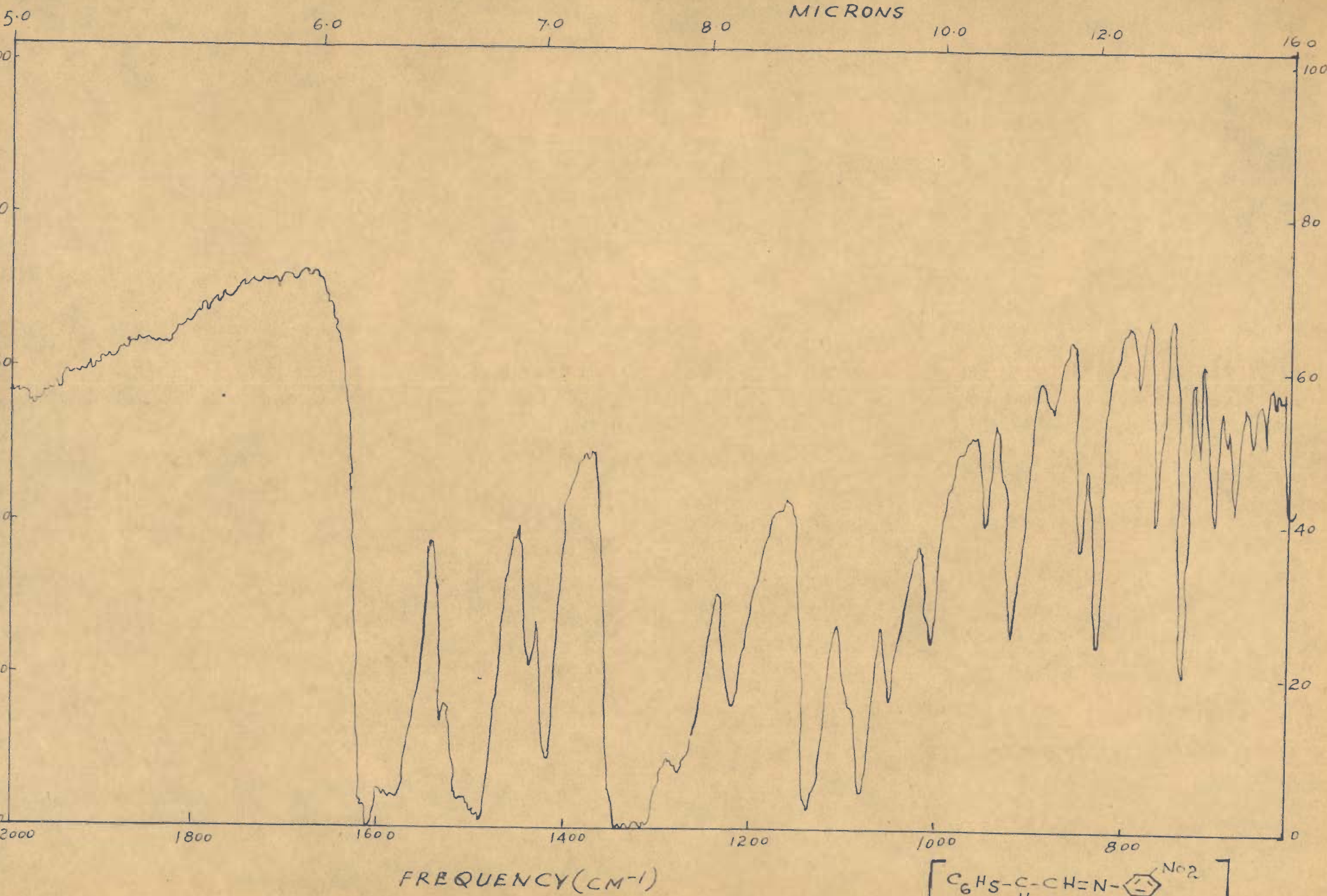
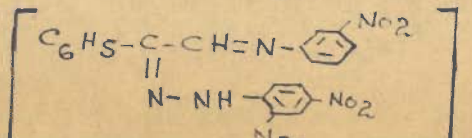
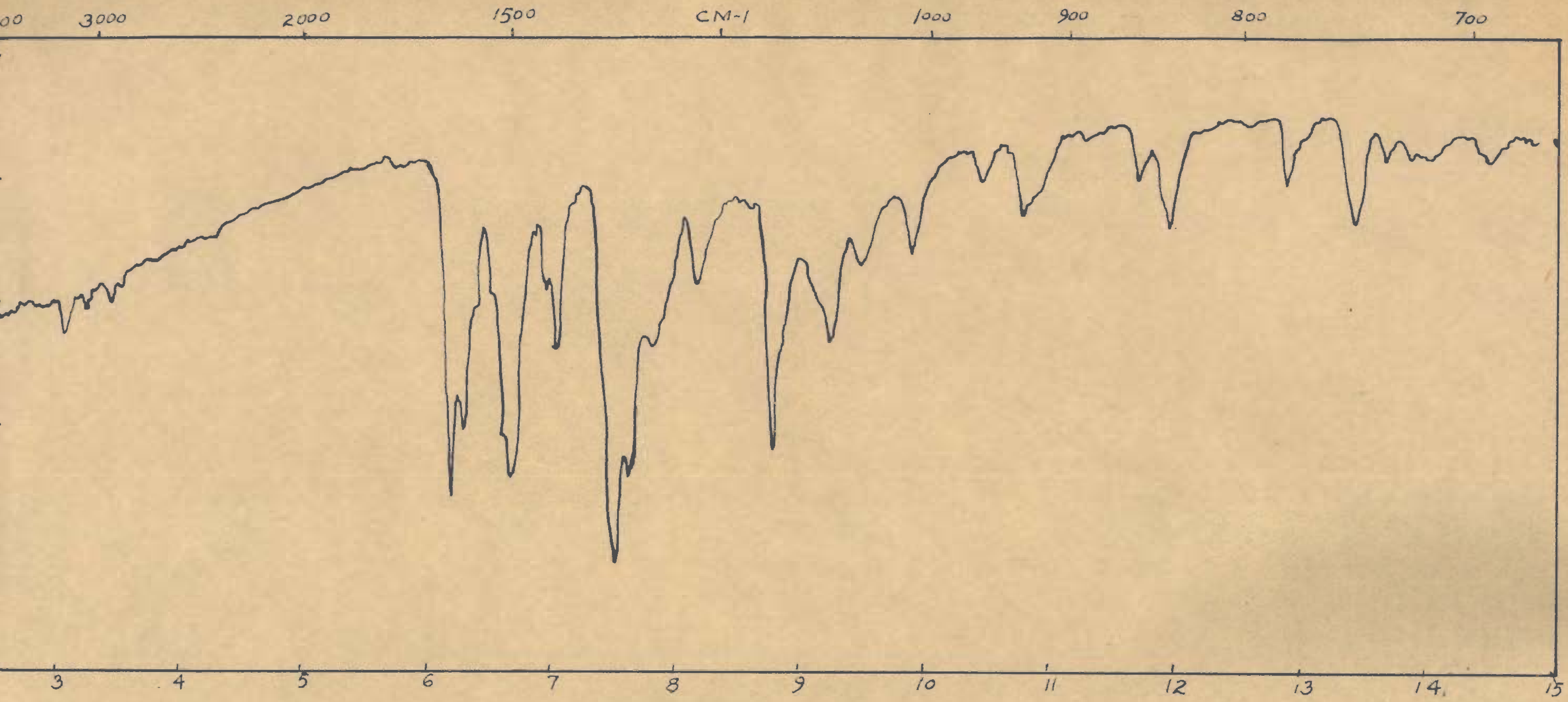

MICRONS
5.0
6.0
7.0
8.0
10.0
12.0
16.0
100
80
60
40
20
0
2000
1800
1600
1400
1200
1000
800
FREQUENCY(CM-1)

FIG- VI


C6H5-C-CH=N-
No2
N-NH-
No2



WAVELENGTH (MICRONE)

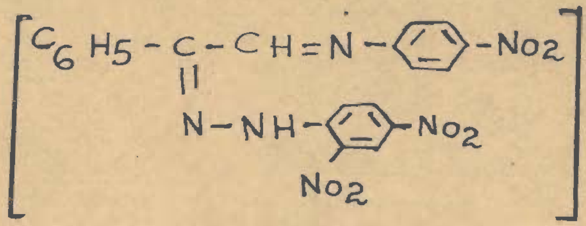
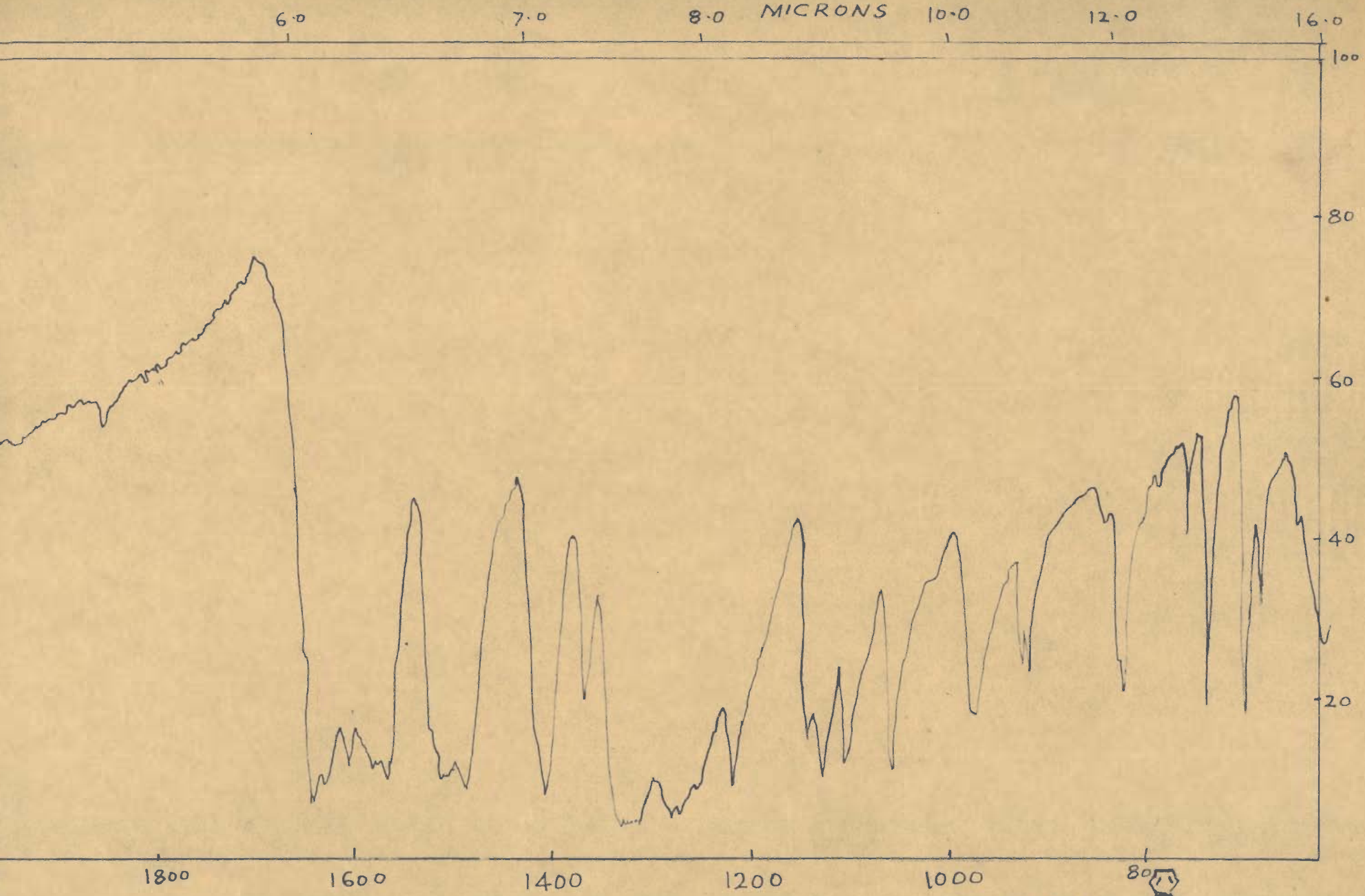


FIG- VII



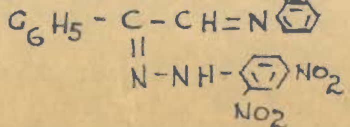


FIG - $\mathrm{XIV_A}$

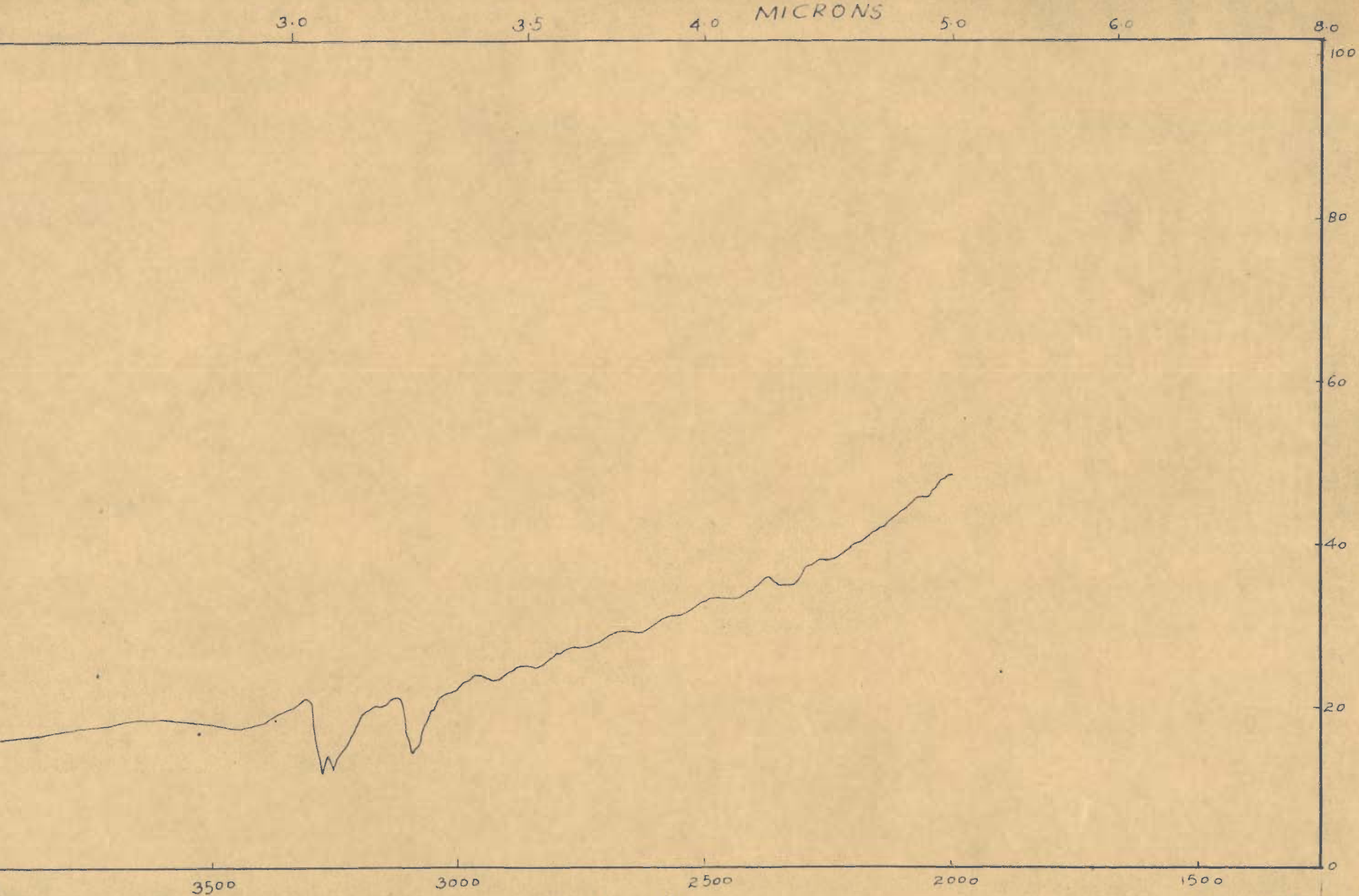
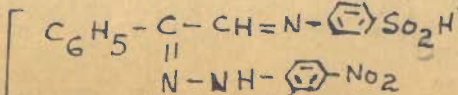


FIG. XIV(a)



$$\left[C_6H_5-\underset{\underset{N-NH-C_6H_4-NO_2}{\|}}{C}-CH=N-C_6H_4-SO_2H \right]$$

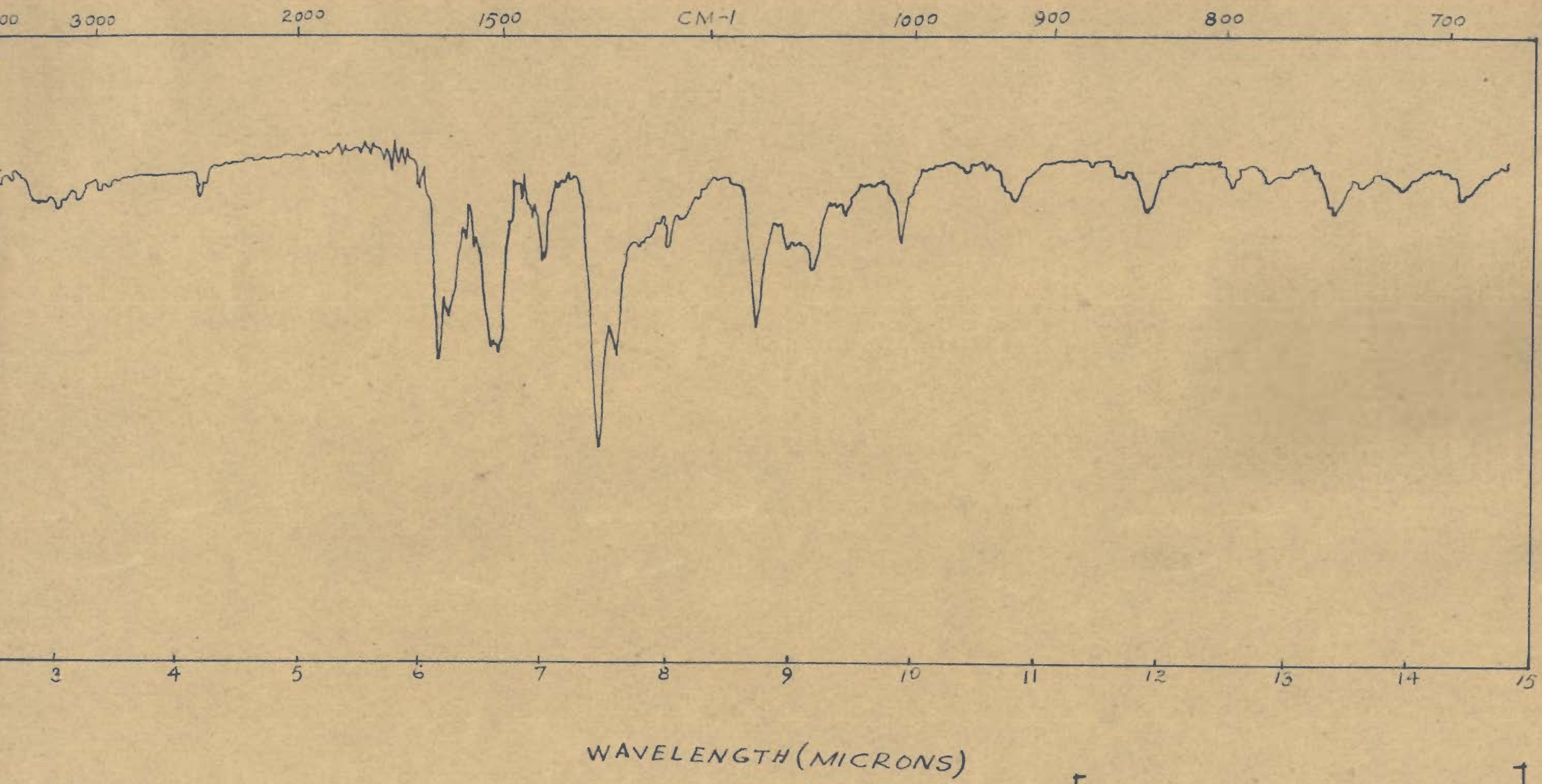
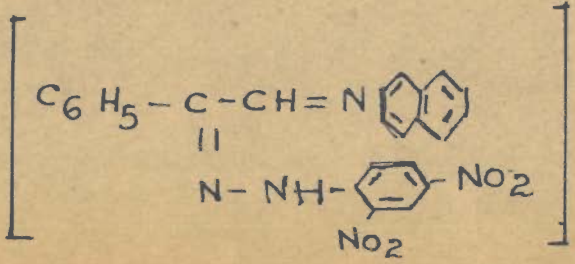

00
3000
2000
1500
CM-1
1000
900
800
700
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

FIG. XV.


C6 H5 - C - CH = N
N - NH -
NO2
NO2

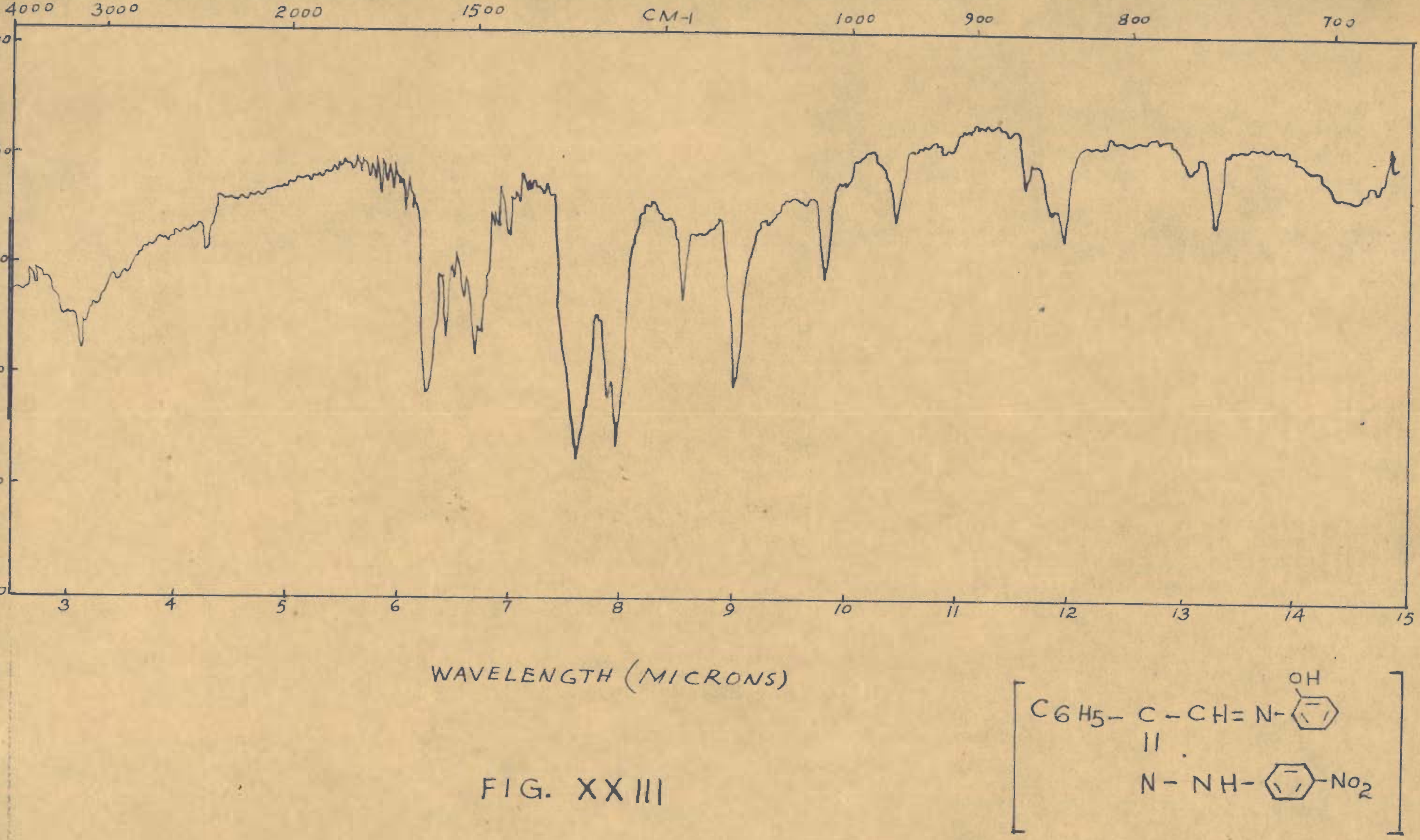

4000
3000
2000
1500
CM-1
1000
900
800
700
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)
OH
C6H5 - C - CH = N -
N - NH -
-NO2

FIG. XXIII

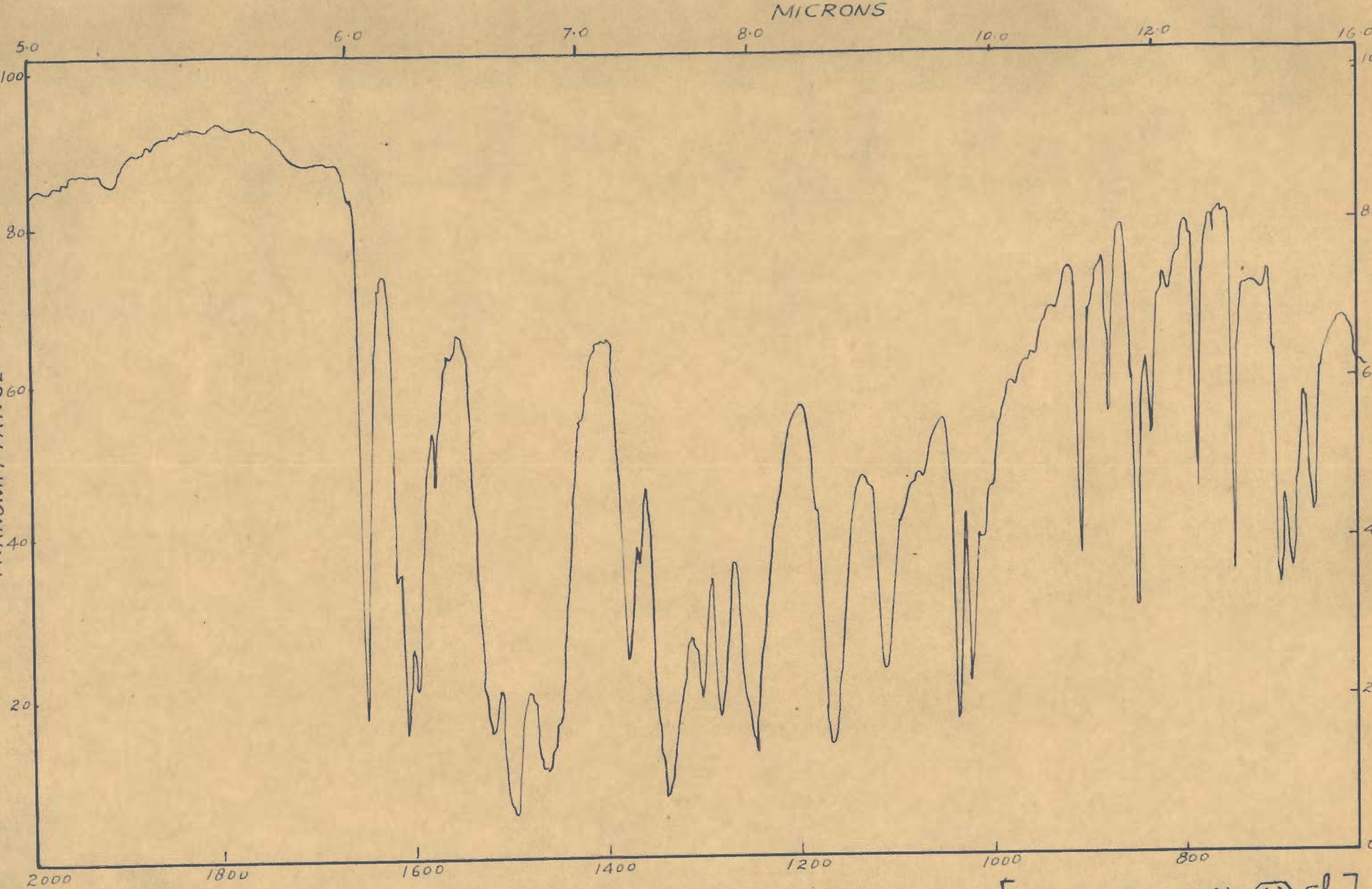
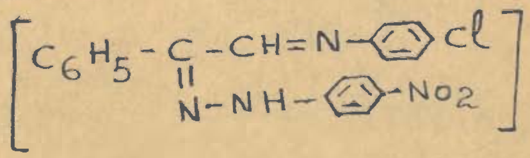

MICRONS
5.0
6.0
7.0
8.0
10.0
12.0
16.0
100
80
60
40
20
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM-1)

FIG. XX IV(A)


C6H5-C-CH=N-
Cl
N-NH-
-NO2

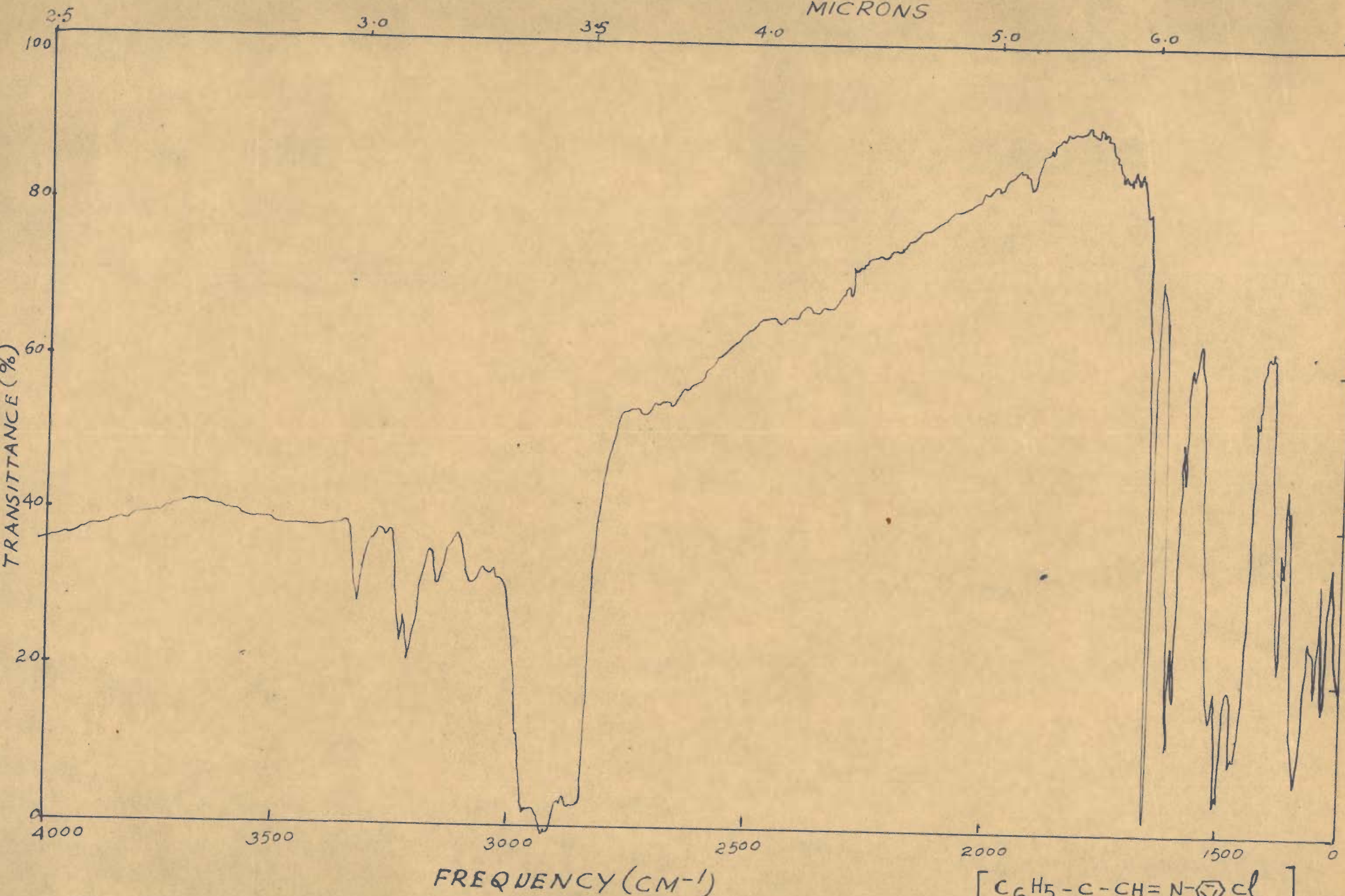
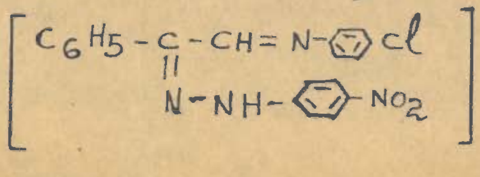
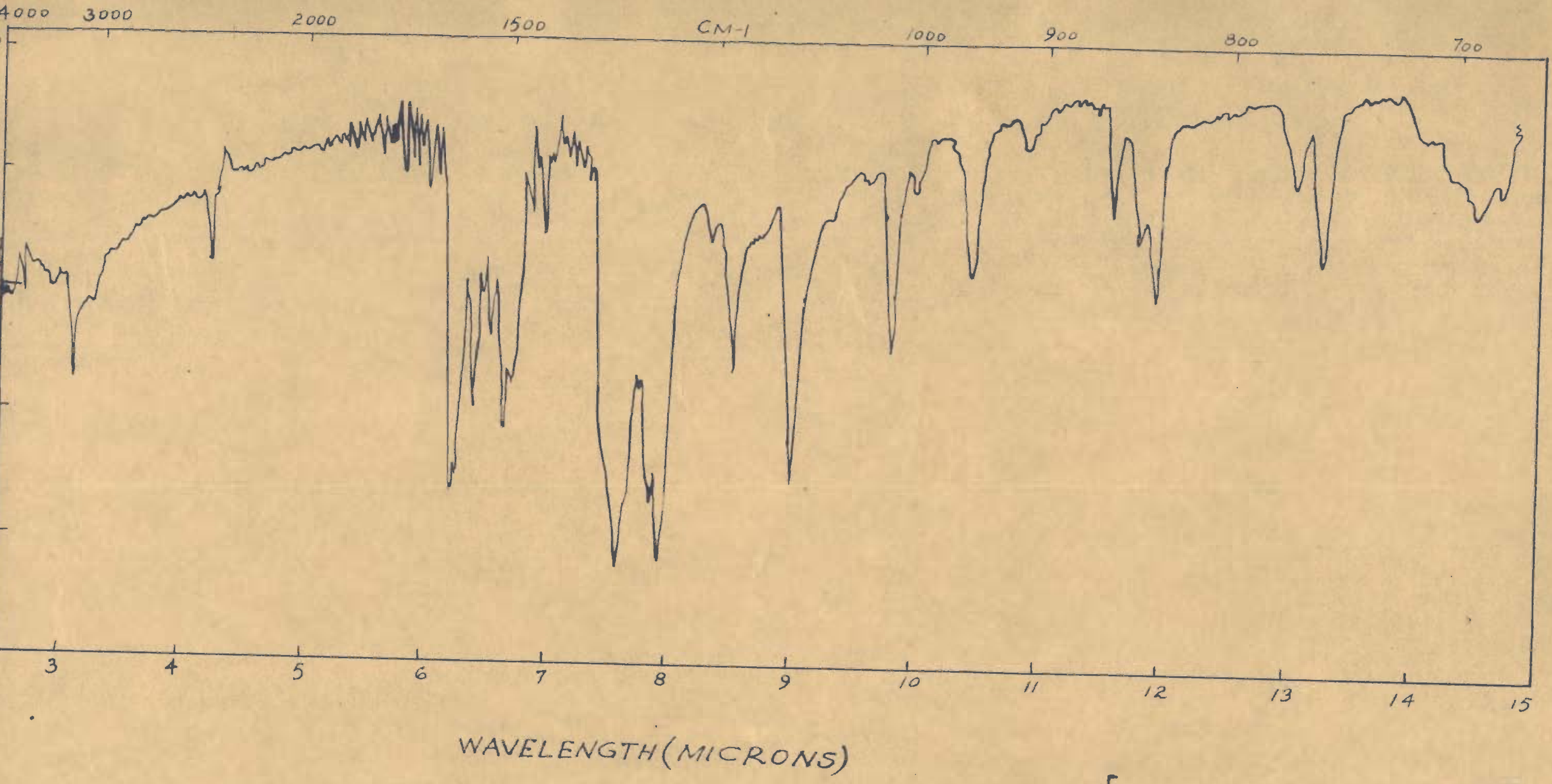

MICRONS
2·5
3·0
3·5
4·0
5·0
6·0
100
80
60
40
20
0
TRANSITTANCE (%)
4000
3500
3000
2500
2000
1500
0
FREQUENCY (CM-1)

FIG XXIV(B)


C6H5 - C - CH = N - Cl
N - NH - NO2


4000
3000
2000
1500
CM-1
1000
900
800
700
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

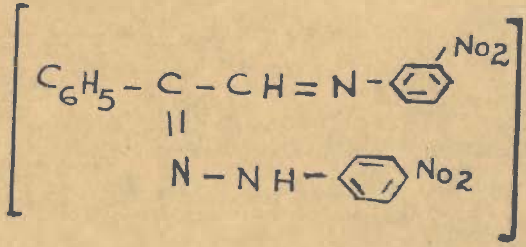

C6H5 – C – CH = N –
NO2
N – NH –
NO2

FIG. XXV

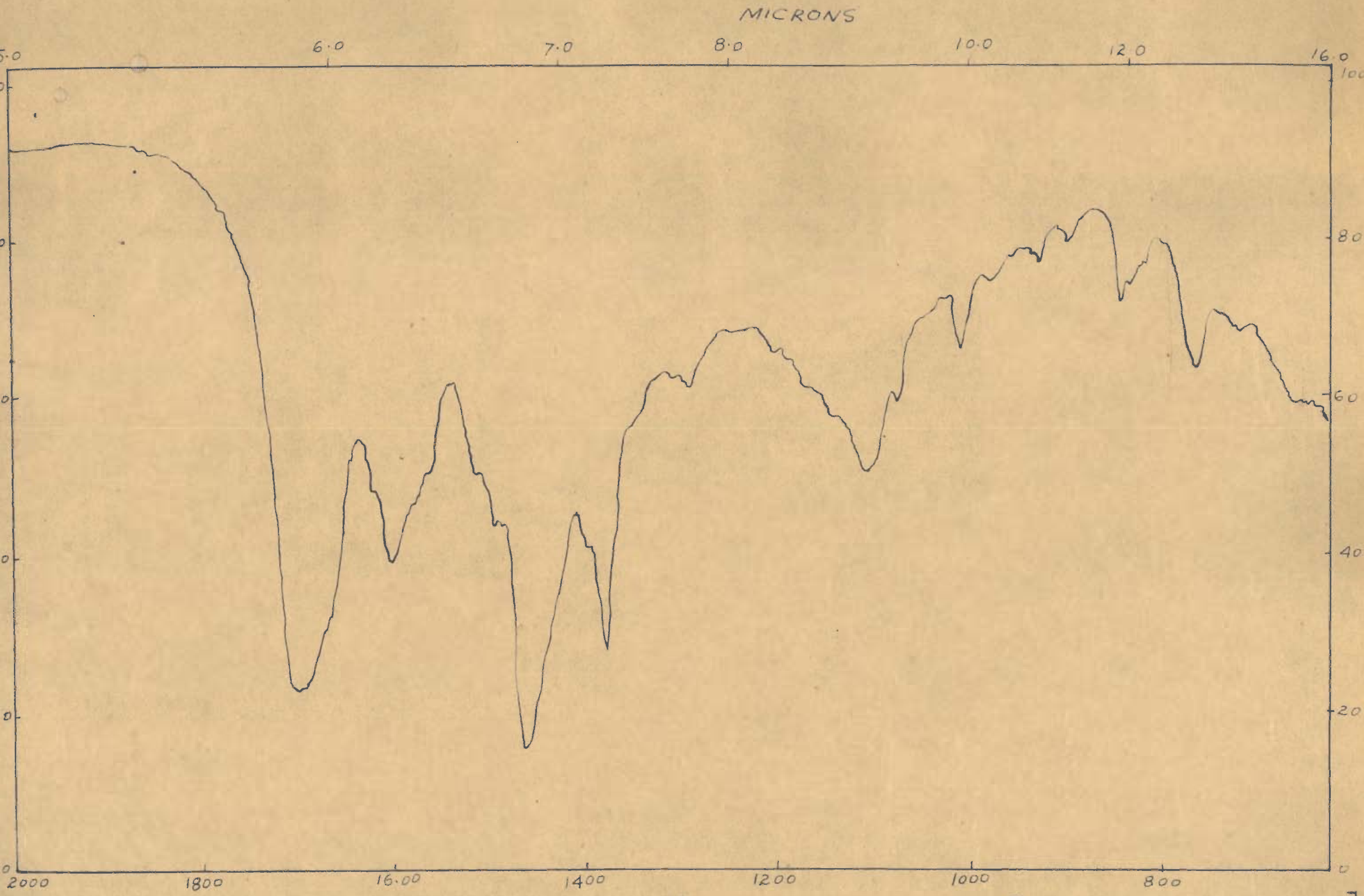
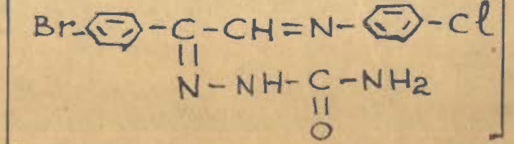


FIG. XXXVI (A)



$$\left[\mathrm{Br{-}C_6H_4{-}\underset{\underset{N{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH_2}{\|}}{C}{-}CH{=}N{-}C_6H_4{-}Cl}\right]$$

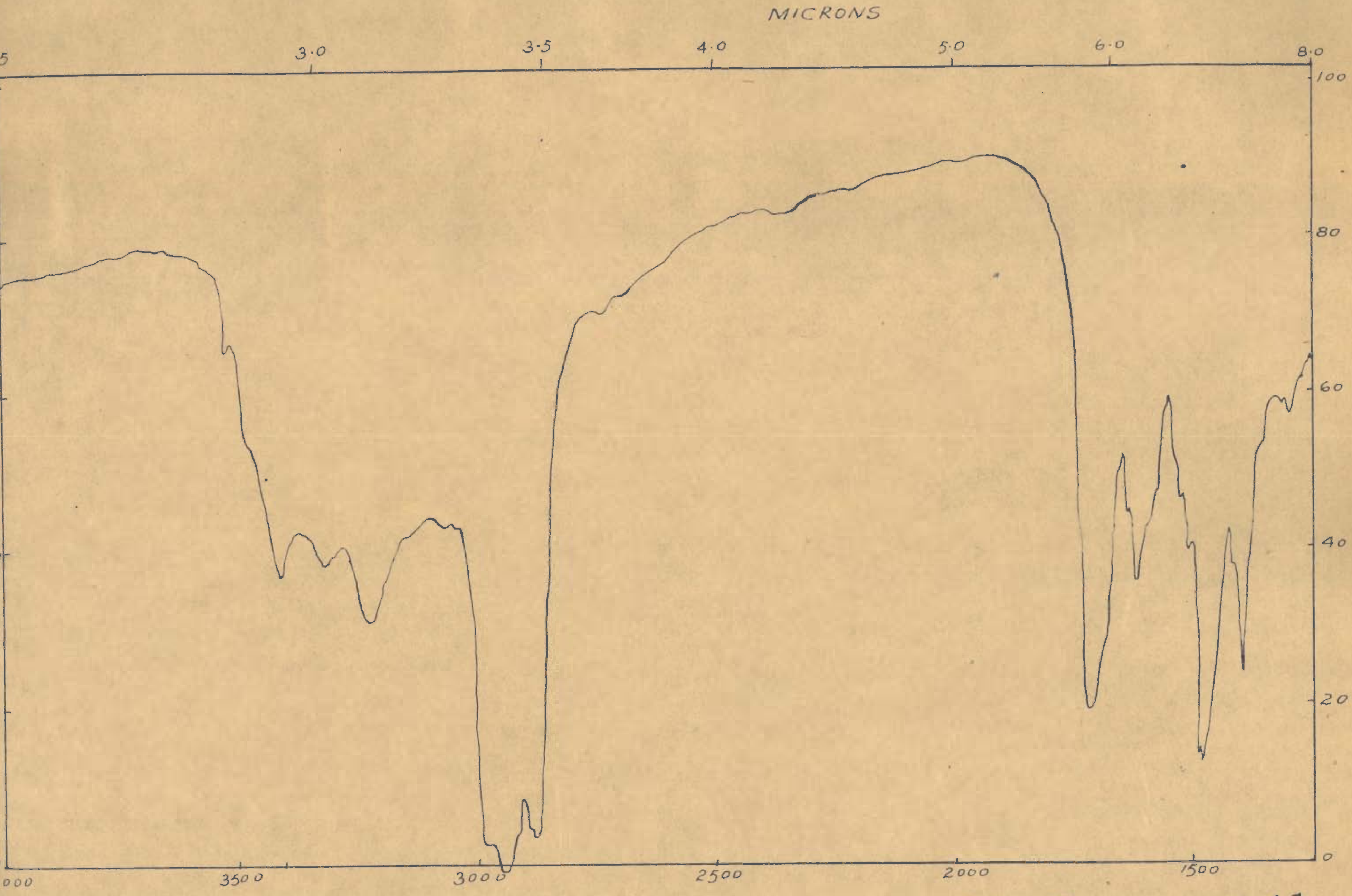
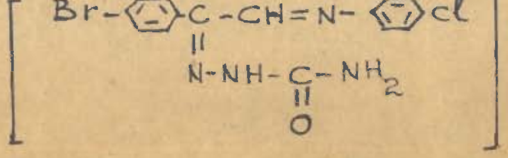

MICRONS
5
3·0
3·5
4·0
5·0
6·0
8·0
100
80
60
40
20
0
000
3500
3000
2500
2000
1500
FREQUENCY (CM^{-1})

FIG. XXXVI$_B$


Br-
C-CH=N-
Cl
N-NH-C-NH$_2$
O

CHAPTER II

SPECTROPHOTOMETRIC STUDIES OF PHENACYLIDENE ANILINE OXIME WITH COPPER(II)

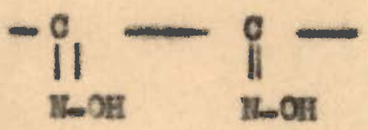
INTRODUCTION

Many oximes are known to possess valuable analytical applications(1-6). These compounds are supposed to enter into reaction with metal ions in the following two ways:-

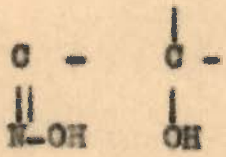
- i) Complexation takes place through coordination by nitrogen atom of the group =N-OH of the oxime.
- ii) Salt formation takes place by replacement of the hydrogen atom of the oxime by the metal ion.

Many of these salts are insoluble, and usually coloured, which makes them important in analytical procedures. Most of the analytically important oximes belong to the following classes:-

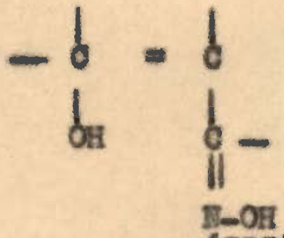
1. The ortho dioxime - (I)
2. The acyloin oxime - (II)
3. Ortho-hydroxy aromatic oxime - (III)
4. The monoxime of α-diketone- - (IV)
5. Nitroso-substituted hydroxylamine - (V)

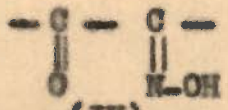

$-\underset{\|}{C}\underset{N-OH}{}-\underset{\|}{C}\underset{N-OH}{}-$

(I)

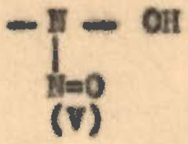

$\underset{N-OH}{\underset{\|}{C}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$

(II)


(III)


$-\underset{O}{\underset{\|}{C}}-\underset{N-OH}{\underset{\|}{C}}-$

(IV)

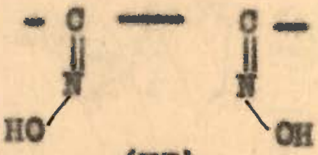

$-\underset{N=O}{\underset{|}{N}}-OH$

(V)

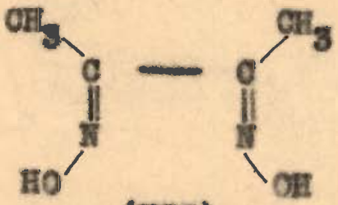
THE ORTHO DIOXIME

The dioximes of α-β diketones form metallic derivatives in which one of the oxime groups functions as an acid and the other as the coordinating group e.g. dimethyl glyoxime, α-furaldioxime and cyclohexane dione dioxime etc. In 1905 , the Russian chemist, Tschugaeff(7) discovered for the first time the reaction between nickel salts and dimethyl glyoxime, which possesses an ortho-dioxime grouping. It yields a brilliant scarlet red insoluble complex $Ni(C_4 H_7 O_2 N_2)_2$. This composition indicates that one of the hydrogen atoms of each of the two molecules of dimethyl glyoxime has been replaced by the bivalent nickel atom (IX). The dioxime group-C(=N-OH)-C(=NOH)-(VI)-selectively precipitates nickel ions provided the group is a part of an aliphatic molecule and is attached to alkyl groups, and has α or anti configuration (XI). These dioximes also yield yellow precipitates with palladium salts, but not with salts of any other metal. The ortho-dioxime group may, therefore, be considered as a specific group for nickel and palladium. When this group is attached to an aromatic system, its behaviour is similar to that of a dibasic acid e.g. α-benzil dioxime, which forms salts with metal ions.

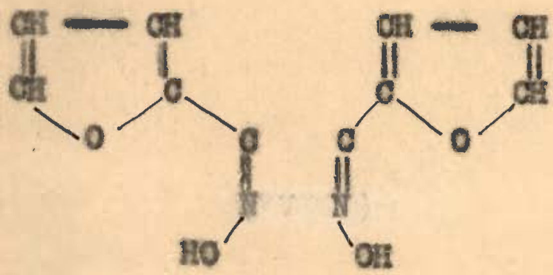
The sensitivity of the reagent may be increased by the introduction of different substituents in the molecule. For instance, the replacements of methyl groups in dimethyl glyoxime (VII) with furan groups in the form of furildioxime (VIII), increases the sensitivity of the reagent for nickel to about three-fold.



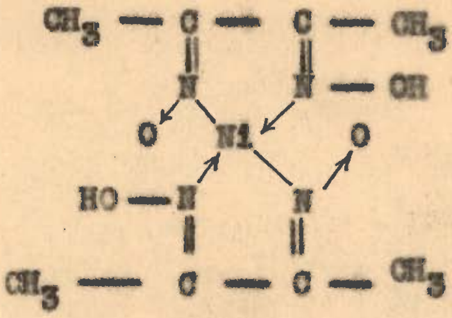
(VI)



(VII)

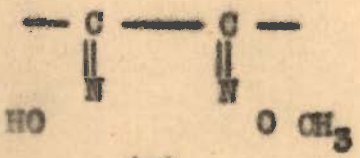


(XVIII)

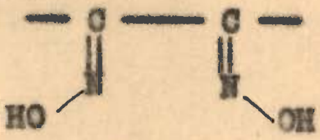


(IX)

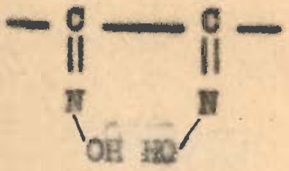
The structure IX for dimethyl glyoxime-nickel chelate has been proved beyond doubt. If one of the OH groups of the oxime be methylated, no change in precipitation characteristics takes place(8,9). Further, it has been shown that no precipitation takes place when the dioxime grouping possesses a syn-or β-configuration (XII). However, or amphi dioxime (XIII) reacts with nickel to give a yellow or yellowish green compound, in which one molecule of the dioxime reacts with one atom of nickel where hydrogen atoms of both the oxime grouping are replaced by the metal to give a six membered ring (XIV)



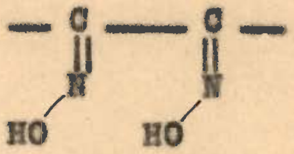
(X)



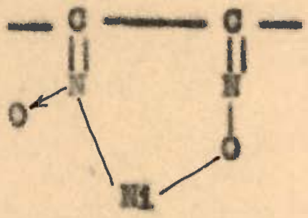
(XI)
Anti



(XII)
Syn



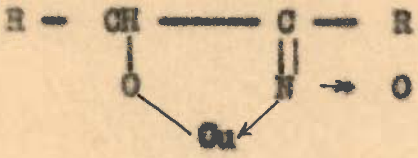
(XIII)



(XIV)

THE ACYLOIN OXIME

A number of compounds containing the group > C(OH)-C(=N-OH)- possess valuable analytical applications.These substances which are known as α-acyloin oximes react with cupric salts to form green water-insoluble complexes.There is some difficulty in assigning a definite structure to the copper complex, since available evidence indicates three possible structures. While reacting with copper, the molecule may act as a dibasic acid in which both hydroxyl and oxime groups are acidic, or it may function as a monobasic acid with either of the hydroxyl or the oxime groups reacting while the other functioning as a coordinating group. The The available evidence, however, seems to indicate that the α-acyloin oximes react as dibasic acids towards cupric salts to form compounds of the type XV.

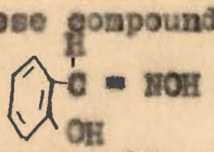


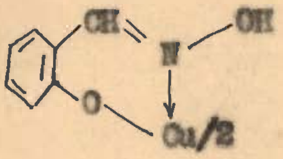
(XV)

Under special conditions, α-benzoin oxime reacts with cobalt, nickel, bivalent platinum and palladium to form complex compounds in which the oxime functions as a monobasic acid^(10^).The acid character of the hydroxyl group is greatly enhanced by the proximity of the oxime group, and this structure appears to be essential for the hydroxy oximes to function as a dibasic acid. α-benzoin oxime ($C_6H_5 - \underset{OH}{CH} - C = N - OH$) is the most commonly used analytical reagent amongst acyloin oximes^(11). Copper is precipitated from a neutral or ammonical solution, even in presence of tartarate ions. It should be emphasized that all the hydroxy oximes of pentanol-2-one-4, $CH_3-CH(OH)-CH_2-C(=N-OH)-CH_3$ and chloral acetophenone, $CCl_3-CH(OH)-CH_2-C(=N-OH)-C_6H_5$ do not form water insoluble salts , since the structures of these compounds are such that the formation of a five membered chelate ring with copper is impossible.

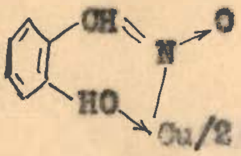
It may, therefore, be inferred that the copper specificity of the acyloin oxime depends in part upon a structure which makes it possible for the formation of such a ring system.

THE ORTHO-HYDROXY AROMATIC OXIMES

These compounds , which are characterized by the presence of  grouping, form bright yellow to greenish copper salts, insoluble in dilute acetic acid. The most readily available compound of this class is salicylaldoxime $OH-C_6H_4-CH=N=OH$, which was first employed by Ephraim$^{(1)}$ for the detection and gravimetric estimation of copper. In the formation of the copper salt, salicylaldoxime functions as a monobasic acid in which the hydrogen atom of either the phenolic group or the oxime group may be replaced by an equivalent amount of the metal. The copper atom, in turn, is a coordinated to the other group to form typical complex compounds such as (XVI) or (XVII)



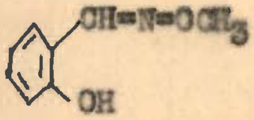
or



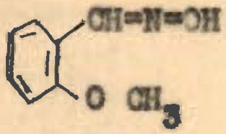
(XVI)

(XVII)

Ephraim(loc.cit) assumed that it is the phenolic hydrogen atom which is replaced, and this view has been supported by the investigations of Feigl and Bendi$^{(12)}$ on the reactions of the isomeric methyl ethers of salicylaldoxime (XVIII) or (XIX).

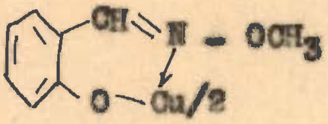


and



(XVIII) (XIX)

The compound containing the free hydroxyl group reacts with copper acetate to form a dark brown salt, while the isomeric phenolic ether does not react.



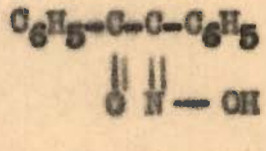
(XX)

A number of other metals also react with this reagent to form salts in a neutral or slightly alkaline medium(13). The insolubility of the copper complex of this type of oxime has made it selective and hence it can be separated from the other metal ions. The grouping $HO - \overset{H}{\overset{|}{C}} - C - C = N - OH$, which is present in salicylaldoxime and other o-hydroxy oximes is not in itself sufficient to give a specific copper reaction. Pentanol-2-one-4 oxime $CH_3-CH(OH)-CH_2-C(=N-OH)-CH_3$, and chloral acetophenone oxime, $CCl_3-CH(OH)-CH_2-C(=N-OH)-C_6H_5$, which contains the same grouping, neither yields insoluble copper salts nor produces any characteristic colouration with copper salts. From this it is evident that the enhanced acidity of the phenolic group because of its linkage to aromatic ring and lack of any steric hindrance between the =N-OH and an OH group seem to be respohsible for their interaction with metal ions.

THE MONOXIME OF α-DIKETONES

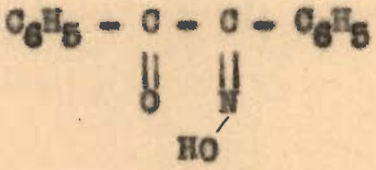
The grouping, -CO-C(=N-OH)-, which is present in the monoxime of the diketones, is important from analytical point of view as it confers upon the molecule the property of inner complex formation with metal ions. One of the most important reactions of compounds of this type is the so called 'iron blue reaction', which was first observed by Whitely. Ferrous salts in solutions buffered with an acetate form inner complex salts with numerous isonitroso compounds, which give the oxime group after enolisation. The compounds are generally deep blue in colour, soluble in water and many organic solvents.

In order to establish the relationship between structure and 'iron blue reaction' with ferrous iron, Feigl and co-workers investigated the reactions of monoximes of a number of carbonyl compounds. Theyfound that isonitroso acetone, isonitroso acetylacetone, isonitroso acetophenone, isonitroso benzoylacetone, isonitroso acetoacetic ester, bromo isonitroso acetoacetic ester etc. produce blue colours with ferrous salts. On the other hand tribromo acetoacetic ester, chloro isonitroso acetophenone etc., which are incapable of undergoing enolization, do not give any reaction with ferrous salts. From the above observations it is evident that 'iron blue reaction' is given only by those compounds which contain an enolisable carbonyl group in proximity with an oxime grouping. For example, α-benzil monoxime (XXI) reacts with ferrous salts to give a blue colour, while β-benzil monoxime (XXII) does not.



$C_6H_5-C(=O)-C(=N-OH)-C_6H_5$

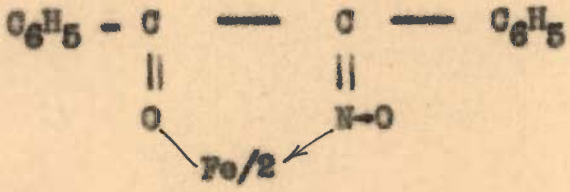
(XXI)



$C_6H_5-C(=O)-C(=N-OH)-C_6H_5$

(XXII)

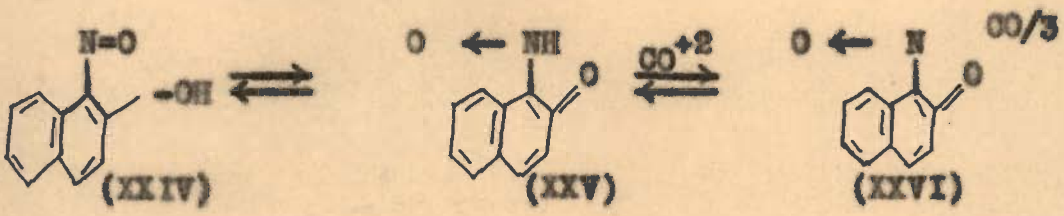
There is no possibility of enolisation in either of the compounds, but the configuration of the oxime group in (XXI) is such that the complexation takes place as shown in (XXIII).



(XXIII)

The configuration of the β-isomer is such that it does not give similar complex. A number of analytically important compounds containing the grouping -CO-C(=N-OH) are known in which the two carbon atoms form a part of a ring system. Best known of this class of compounds are α-nitroso β-naphthol, β-nitroso-α-naphthol and ortho nitrosophenol. These compounds form intensely coloured complexes with almost all the heavy metals. The cobaltic salt of α-nitroso-

-β-naphthol, for example , is derived from the tautomeric form of the quinone oxime(14,15)



The conversion of CO(II) to CO(III) is probably due to the oxidising nature of the reagent or the oxidising action of the air. This reagent also forms precipitate of $Cu(C_{10}H_6O(NO_2)_2$ with copper salts. This reaction has been employed for the microchemical detection(16) and separation(17) of copper. The photometric determination of cobalt can also be undertaken by this reagent and it can be estimated even in the presence of nickel.

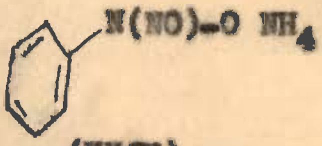
THE NITROSO-SUBSTITUTED HYDROXYLAMINES

These compounds (XXVII) exist in tautomeric equilibria with the corresponding enol forms (XXVIII) and can, therefore, be classed as oximes.

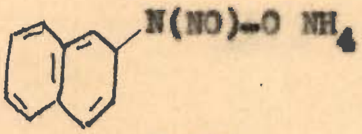
$$-N(NO - OH \rightleftharpoons - N(\rightarrow O) = N - OH$$

(XXVII) (XXVIII)

The two well-known compounds, cupferron and neocupferron belong to this group have been extensively used as anlytical reagents.



(XXIX)
Cupferron

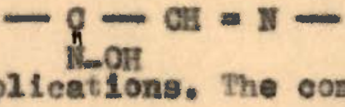


(XXX)
Neocupferron

Traces of copper in water can be detected with the help of cupferron which forms copper cupferronate[18]. It is then extracted with chloroform and the residue obtained on evaporation of the solvent is treated with alizarin blue.

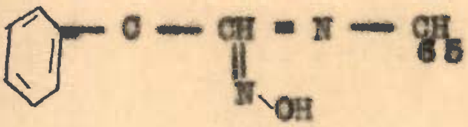
From the foregoing survey of oximes, it is evident that oximes are potential analytical reagents. There is further scope for the development of this field involving the synthesis of a large number of analytically important oximes putting them to use for the detection and determination of various metal ions.

The author has synthesised a group of new oximes containing an oxime group in proximity with an azomethine grouping i.e.

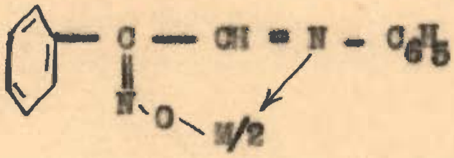


$-\underset{\underset{N-OH}{\|}}{C}-CH=N-$

and examined their analytical applications. The complexation takes place by the salt formation due to the replacement of the hydrogen atom of the oxime group and coordination from the nitrogen atom of the azomethine grouping as shown in XXXII.



(XXXI)



(XXXII)
M=bivalent metal

From this group, the author selected phenacylidene aniline oxime and investigated its complexes with copper.

PHENACYLIDENE ANILINE OXIME AS AN ANALYTICAL REAGENT

Schiff's bases like salicylaldimine (salicyldehyde-ammonia Schiff's base)$^{(19)}$, β-hydroxy naphthaldimine, o-hydroxy acetophenone imine$^{(20)}$, ethylene diamine bis-sulphosalicyldehyde, salicyldehyde-glycine-hydroxamic acid$^{(21)}$, ethylene diamine bis-o-hydroxy acetophenone$^{(22)}$ have been employed by a number of workers for the determination of copper, nickel and iron (III). It may, however, be pointed out that Schiff's bases obtained from phenyl glyoxal hydrate have not been tried so far as chelating agents.

Preliminary studies showed that none of these gave suitable colour reactions with metals so as to be usefully employed for colorimetric estimations. Surprisingly enough, when the above anils were changed into their corresponding Oximes, very sensitive colour reactions with metals were observed. Phenacylidene aniline oxime (PAO) was, therefore, synthesised and its copper complexes were also investigated.

The spectrophotometric study of this reagent in aqueous medium could not be undertaken on account of its extremely low solubility in water. The compound is, however, soluble in water-ethanol mixture (1:1), but the solution so obtained fails to give a clear solution when reacted with the metal. The most favourable condition for the interaction was found to be 90 per cent alcoholic solution of copper (II) and absolute alcoholic solution of the chelating agent. The reaction of the two resulted in the formation of a dark brown coloured complex.

EXPERIMENTAL

A solution of copper nitrate (A.R), $5x10^{-2}$M was prepared in 90 per cent ethanol and standardised iodometrically. $5x10^{-2}$M solution of phenacylidene aniline oxime was prepared in absolute alcohol. Absorbance measurements were carried out with a 'spectronic-20'- Bausch and Lomb spectrophotometer. I.R. spectra were carried out by Perkin-Elmer Infracord spectrophotometer.

PREPARATION OF PHENACYLIDENE ANILINE

Phenyl glyoxal hydrate was prepared by the oxidation of acetophenone with selenium dioxide (pp.   ). Equimolar quantities of phenyl glyoxal hydrate and aniline were dissolved in 95 per cent alcohol and the mixture was refluxed over a water bath for about half an hour. The reaction product, which got solidified after a short time, was separated and crystallized from hot alcohol.

PREPARATION OF PHENACYLIDENE ANILINE OXIME

An aqueous solution of hydroxylamine hydrochloride (0.5g) and sodium acetate (1g) was mixed with an alcoholic solution of phenacylidene aniline (1g) and refluxed over a water bath for about two hours. After evaporating most of the alcohol, the reaction mixture was transferred to an ice cold water. The precipitated oxime was filtered, washed well with water and crystallised from hot alcohol.

NATURE OF THE COMPLEX

In order to ascertain the number of complexes formed, Vosburg and Cooper's method(54) was employed. On mixing the solutions of the oxime and the copper(II) ion, a dark brown coloured complex was obtained. An interval of twenty four hours was found sufficient for equilibration. Copper (II) and PAO (both .005M) were mixed in different ratios, i.e., 1:1, 1:2, 1:3 ... 2:1 etc. The total volume of 10 ml. was kept constant throughout the measurements. The absorbance of the solution was measured at different wave lengths. By plotting the graph between the optical density and wave lengths, only one λ max at 35 mu was obtained indicating thereby the formation of one complex. The optical density of either the metal ion or the ligand at this wavelength was small in comparison to that of the complex.

In the table 1, the optical densities tabulated were calculated from the % transmittances of the mixtures.

Thus from Fig.I, it is evident that the maximum absorbance for the complex is observed at 350 mu. This wave length was chosen to determine the composition and other thermodynamic data of the chelate.

STOICHIOMETRY OF THE COMPONENTS

Job's continued variation method(51) was employed for the determination of the composition of the complex. The following sets of solutions were taken for investigations.

1,2,3 ..... 9 ml. of $5x10^{-3}M$ copper nitrate solutions
9,8,7 ..... 1 ml. of $5x10^{-3}M$ PAO solution.

The total volume of each set was kept constant at 10 ml. Same volumes of the solutions of the metal ion and the ligand were taken and the total volume was made upto 10 ml. in each case. The absorbance of different complimentary mixtures, ligand and the metal ion solutions was determined at 350 mu , and the difference of O.D. between the mixtures and the sum of the ligand and the metal ion was plotted against mole fraction of the components. The peaks of the curves a, and b in Fig.2 show that the ratio of the metal to the ligand is 1:2.

The composition of copper (II)-PAO chelate was further confirmed by slope ratio method.

THE SLOPE RATIO METHOD(63,62)

Varying volumes of copper nitrate solution (.005M) were added to a constant volume of the ligand (6 ml. of 0.0005M). The total volume was kept constant at 10 ml. by addition of ethanol. In another set, different volumes of the ligand (0.005M) were added to 6 ml. of 0.0005M Copper(II) solution and the total volume was kept constant at 10 ml. Their O.D. were measured and plotted against varying amounts of the metal ion as well as that of the ligand. The composition of the complex formed was determined by the ratio of the slopes of the two curves (Fig.3,4 and 5).

All measurements were carried out after 24 hours of equilibration. The composition of the copper (II)-PAO chelate was also confirmed by mole ratio method.

MOLE RATIO METHOD(64,65)

Varying volumes of copper (II) were added to a constant volume of PAO i.e. 1 ml. (both equimolar). The total volume was made upto 10 ml. by addition of alcohol. The optical densities of all these solutions were plotted against the different amounts of the metal ion or PAO added. The composition of the chelate was determined from the curves a, b and c in Fig.6.

CHEMICAL ANALYSIS

The complex was prepared by mixing equimolecular solutions of the metal ion and the ligand in the ratio of 1:2. It was dried in vacuum. The solid so obtained was repeatedly crystallised from alcohol to give dark brown crystals. A weighed quantity of the complex was fused with fusion mixture and copper oxide, thus obtained was converted into copper sulphate, in which the metal was estimated iodometrically. Nitrogen was estimated by Kjeldhal's method.

Found: Cu, 11.50 % ; N, 12.21 % , $C_{28}H_{22}N_4O_2Cu$

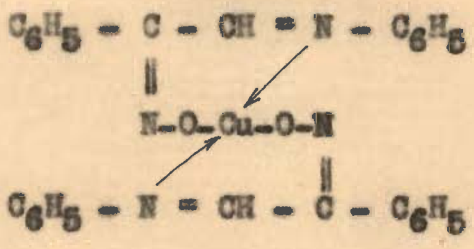
Theoretical: Cu, 12.47 % ; N, 12.50 % .

STRUCTURE OF THE CHELATE

The infrared spectra of the ligand and the complex were determined in Nujol using a Perkin-Elmer infracord spectrophotometer. The ligand shows the presence of two C=N groupings at 1670 cm^{-1} and 1600 cm^{-1}, (Fig.7). The first frequency shows very little shift (1670 cm^{-1} to 1660 cm^{-1}) on complex ion formation but the second one is markedly shifted (1600 cm^{-1} to 1540 cm^{-1}). From latter shifts it may be inferred that binding takes place through nitrogen of azomethine linkage (Fig.8). The band at 1175 cm^{-1} shifts to 1170 cm^{-1} which may be due to N - O vibration.

In the parent compound 3370 cm^{-1} under shoulder 3400 cm^{-1} (Fig.7) is due to an OH stretching vibration of = N - OH group. The complex does not show such a sharp peak at 3370 cm^{-1} (Fig.8) indicating the absence of the OH group in the chelate.

On the basis of the above data the structure of the chelate may be represented as follows:-



pH-METRY OF THE COMPLEX

Attempts to study the stability of the complex by Bjerrum methods met with little success because of the small drop in pH on the addition of metal ion to the ligand. Moreover the pH range available for titration against the alkali was also small due to the slightly acidic nature of the ligand (pH 6.0). Titration with acid, done with the aim of getting a range towards the lower pH side could also not be performed because of the decomposition of the azomethine linkage of the ligand by acids. The results of one particular study (Fig.9) are given in table 10-12.

The values of $\bar{n}$ were too high to enable calculation of stability constant.

However, the above results provide definite qualitative information about the binding of the metal ion through a covalent linkage by the release of H^+ from the oxime grouping of the ligand.

STABILITY CONSTANT AND FREE ENERGY CHANGE(64,65)

Considering the following reaction between copper(II) and phenacylidene aniline oxime (PAO).

$$Cu\,R_2 \longrightarrow Cu + 2R$$

C $\quad$ 0 $\quad$ 0 (Initial concentration)

$C(1-\alpha)$ $\quad$ $C\alpha$ $\quad$ $2C\alpha$ (Equilibrium concentration)

where C is the total concentration of the complex in moles per litre and α is the degree of dissociation. The stability constant is given by:

$$Es = \frac{C(1-\alpha)}{\alpha C\ (2C\alpha)^2} = \frac{C(1-\alpha)}{4\alpha^3\ C^2} = \frac{1-\alpha}{4\alpha^3\ C^2}$$

The value of α was obtained from the curve a, Fig.6.

$$\alpha = \frac{E_m - E_s}{E_m}$$

$$= \frac{1.60 - 1.52}{1.60} = .05$$

where E_m is the maximum extinction coefficient obtained from the horizontal portion of the curve, indicating that the whole of copper (II) is converted into the complex. E_s is the extinction coefficient of the solution containing stoichiometric molar ratio of the two reactants present in the complex.

$$\therefore \quad E_s = \frac{1-.05}{4(.05)^3(.0005)^2} = 0.7547\text{x}10^{10}$$

The standard free energy of the complex has been calculated from the following expression at 16°:

$$-\triangle F = RT\ \ln Es$$

$$\therefore \triangle F = 1.987 \text{ x } 289 \text{ x } 2.303 \log 0.7597 \text{ x } 10^{10}$$

$$= 13070 \text{ cals.} = 13.07 \text{ K cals./mol.}$$

Table-1 Vosburg and Cooper's Method for Cu(II) and PAO (Both $5 \times 10^{-3} M$)

Concentration of $Cu(NO_3)_2$ solution = $5 \times 10^{-3} M (C)$

Concentration of PAO solution = $5 \times 10^{-3} M (C')$

$$P = \frac{C'}{C} = 1$$

(Ratio of the metal to the ligand)

Wave length	1:1 (a)	1:2 (b)	1:3 (c)	3:1 (d)	2:1 -
330	1.55	1.60	1.77	1.22	1.34
335	1.52	1.69	1.82	1.26	1.39
340	1.60	1.82	2.00	1.26	1.45
345	1.60	1.82	2.00	1.18	1.45
350	1.69	2.00	2.00	1.07	1.39
360	1.60	1.82	2.15	0.93	1.26
370	1.45	1.82	2.30	0.73	1.04
375	1.39	1.82	2.00	0.64	0.93
400	0.85	1.30	1.69	0.36	0.53
425	0.51	0.82	1.18	0.20	0.31
450	0.30	0.53	0.78	0.11	0.17
475	0.18	0.34	0.54	0.06	0.09
500	0.10	0.22	0.38	0.04	0.06
525	0.07	0.16	0.29	0.02	0.04
575	0.06	0.115	0.21	0.02	0.025

Fig.1

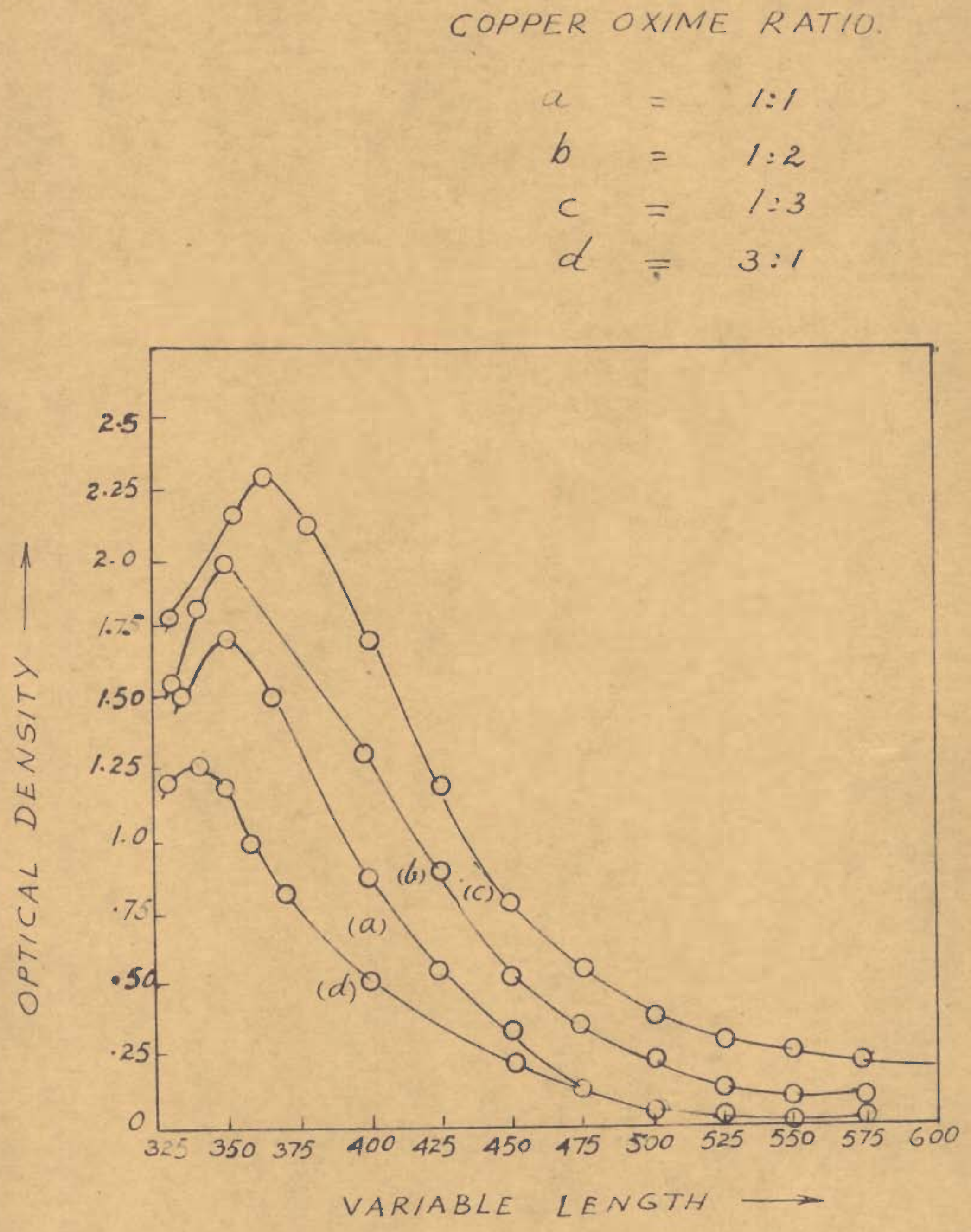


FIG. 1. ABSORPTION SPECTRA OF COPPER COMPLEX.

Table 2- Job's Method for Cu(II) and PAO (Both $5x10^{-3}M$)

Concentration of $CU(NO_3)_2$ Solution = $5x10^{-3}M(C)$

Concentration of PAO solution = $5x10^{-3}M(C')$

Wave length = 350 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2:: Cu(II) : PAO

Vol.of Cu(II) ml.	Vol. of PAO ml.	O.D.of the mixture	O.D. of Cu(II)	O.D. of PAO	Difference -D
-	-	C	a	b	|C-(a+b)|
1	9	2.000	0.030	1.602	0.368
2	8	2.000	0.035	1.523	0.442
3	7	2.000	0.035	1.456	0.509
4	6	1.884	0.045	1.347	0.492
5	5	1.699	0.055	1.184	0.457
6	4	1.523	0.060	1.046	0.417
7	3	1.155	0.065	0.80	0.29
8	2	0.9208	0.075	0.63	0.213
9	1	0.4500	0.08	0.27	0.10

Fig. 2 Curve (a)

Table 3- Job's Method for Cu(II) and PAO(Both $2.50x10^{-3}M$)

Concentration of $Cu(NO_3)_2$ solution = $2.50x10^{-3}M(C)$

Concentration of PAO solution = $2.50x10^{-3}M(C')$

Wave length = 350 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2::Cu(II):PAO

Vol.of Cu(II) ml.	Vol.of PAO ml.	O.D. of the mixture	O.D.of Cu(II)	O.D. of PAO	Difference -D
-	-	C	a	b	|C-(a+b)|
1	9	1.824	0.0362	1.155	0.6328
2	8	1.824	0.03	1.071	0.7230
3	7	1.824	0.035	0.9788	0.8102
4	6	1.755	0.065	0.85	0.8450
5	5	1.602	0.055	0.7328	0.8142
6	4	1.456	0.06	0.61	0.7860
7	3	1.301	0.075	0.48	0.746
8	2	1.022	0.0675	0.3275	0.627
9	1	0.59	0.065	0.18	0.3450

Fig.2 , Curve (b)

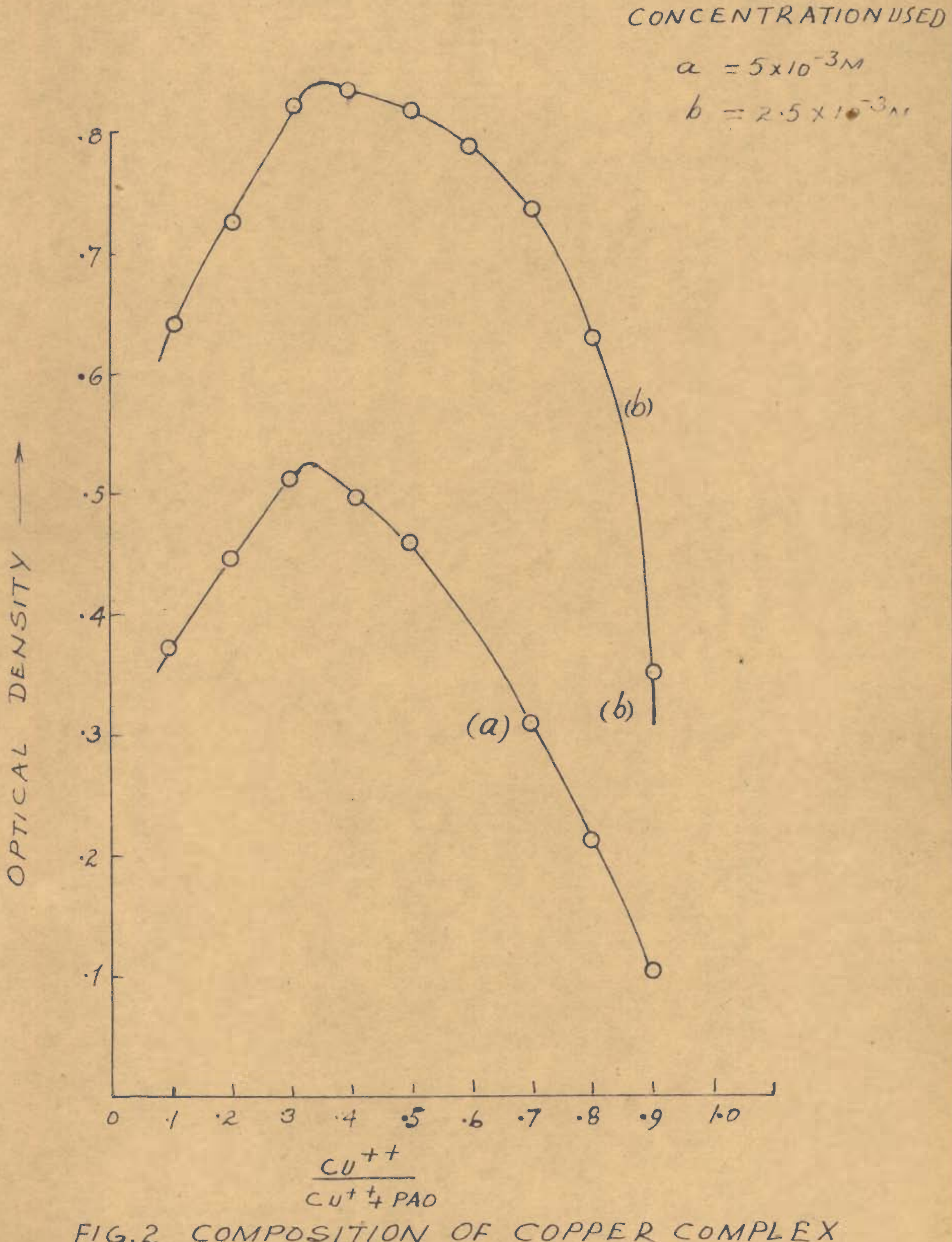


FIG.2 COMPOSITION OF COPPER COMPLEX

BY JOB'S METHOD

Table 4- Composition of the Complex by Slope Ratio Method

Set I Volume of 0.5×10^{-3}M PAO solution = 6 ml.

Strength of Cu(II) solution = 5×10^{-3}M

Set II Volume of 0.5×10^{-3}M Cu(II) solution = 6 ml.

Strength of PAO solution = 5×10^{-3}M

Wave length = 350 mu

Set I		Set II	
Vol. of Cu(II) ml.	O.D.	Vol. of PAO ml.	O.D.
0.00	0.175	0.00	0.075
0.10	0.46	0.30	0.54
0.20	0.62	0.60	0.80
0.30	0.80	0.90	1.22
0.40	0.87	1.20	1.60
0.50	0.95	1.80	1.70

Curve (a) Fig-3 Curve (b)

Table 5- Composition of the Complex by Slope Ratio Method

Set I Volume of 0.25 x 10^{-3}M PAO = 6 ml.
Strength of Cu(II) Solution = 2.5x10^{-3}M

Set II Volume of 0.25x10^{-3}M Cu(II) Solution = 6 ml.
Strength of PAO solution = 2.5x10^{-3}M
Wave length = 350 m

Set I		Set II	
Vol. of Cu(II) ml.	O.D.	Vol. of PAO ml.	O.D.
0.00	0.120	0.00	0.015
0.10	0.180	0.20	0.145
0.20	0.280	0.40	0.250
0.30	0.330	0.60	0.365
0.40	0.400	0.80	0.475
-	-	1.00	0.680
-	-	1.20	0.680

Curve (a) Fig.4 Curve (b)

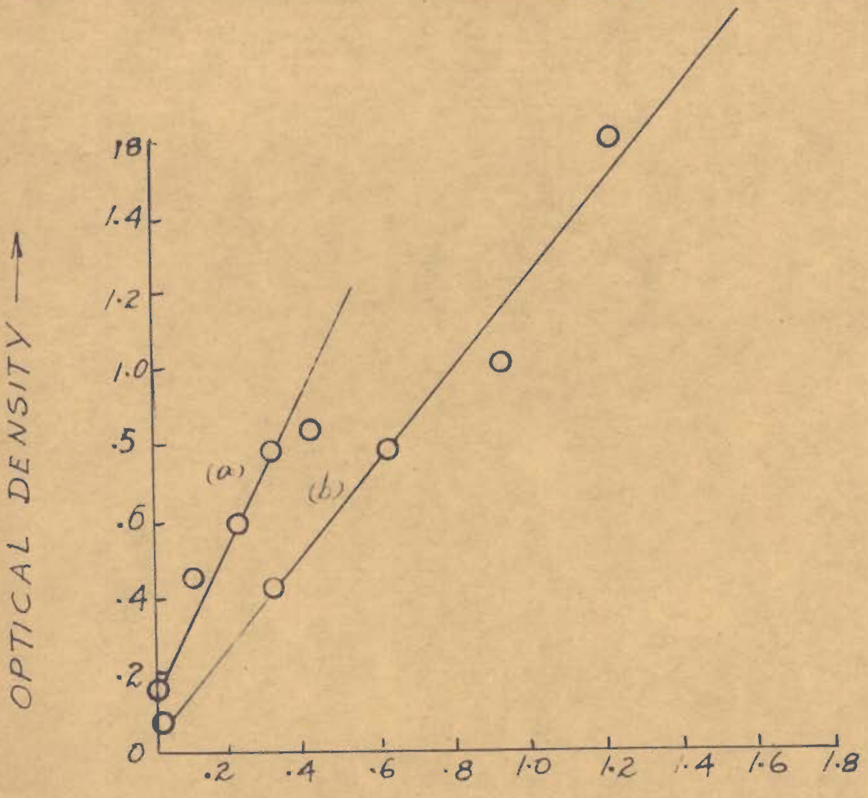


FIG. 3 COMPOSITION OF THE COMPLEX. SLOPE RATIO METHOD.

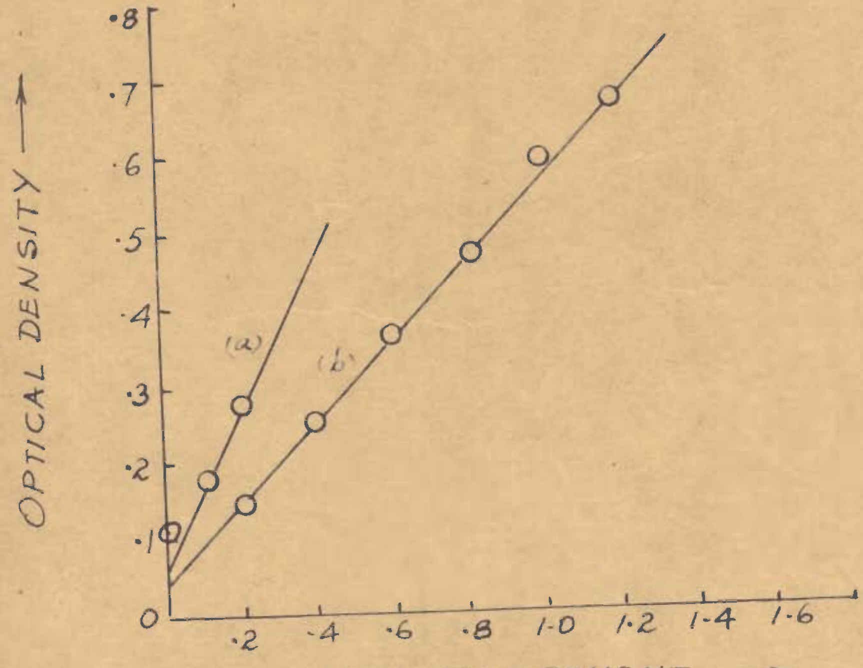


FIG. 4 COMPOSITION OF THE COMPLEX BY SLOPE RATIO METHOD.

Table 6- Composition of the complex by Slope Ratio Method

Set I Volume of 0.125×10^{-3}M PAO = 6 ml.

Strength of Cu(II) solution = 1.25×10^{-3}M

Set II Volume of 0.125×10^{-3}M Cu(II) solution = 6 ml.

Strength of PAO solution = 1.25×10^{-3}M

Wave length = 350 m

Set I		Set II	
Vol. of Cu(II)	O.D.	Vol.of PAO	O.D.
0.00	0.05	0.00	0.005
0.10	0.09	0.20	0.05
0.20	0.12	0.40	0.08
0.30	0.13	0.60	0.14
0.40	0.14	0.80	0.19
0.50	0.16	1.00	0.21
-	-	1.20	0.25

Curve (a) Fig.5 Curve (b)

Table 7- Composition of the Complex by Mole Ratio Method

Strength of Cu(II) or PAO solution = 5 x 10^{-3}M

Constant Volume of Cu(II) or PAO solution = 1 ml.

Wave length = 350 mu

Set I		Set II	
Vol.of Cu(II) ml.	O.D.	Vol.of PAO ml.	O.D.
0.00	0.295	0.00	0.045
0.10	0.590	0.40	0.52
0.20	0.825	0.80	0.93
0.30	1.046	1.20	1.260
0.40	1.097	1.60	1.456
0.50	1.125	2.00	1.523
0.60	1.555	2.40	1.602
0.80	1.555	2.80	1.602
0.90	1.555	3.20	1.602

Fig.6 Curve (a)

Table 8- Composition of the Complex by Mole Ratio Method

Strength of Cu(II) or PAO solution = $2.5x10^{-3}M$

Constant Volume of Cu(II) or PAO solution. = 1 ml.

Wave length = 350 mu

Set I		Set II	
Vol.of Cu(II) ml.	O.D.	Vol.of PAO ml.	O.D.
0.00	0.175	0.00	0.015
0.10	0.280	0.40	0.31
0.20	0.40	0.80	0.55
0.30	0.520	1.20	0.77
0.40	0.540	1.60	1.00
0.50	0.600	2.00	1.26
0.60	0.610	2.40	1.30
0.70	0.610	2.80	1.30
0.80	0.610	3.20	1.30

Fig.6 Curve (b)

Table 9- Composition of the Complex by Mole Ratio Method

Strength of Cu(II) or PAO solution = 1.25×10^{-3}M

Constant volume of Cu(II) or PAO Solution = 1 ml.

Wave length = 350 mμ

Set I		Set II	
Vol. of Cu(II) ml.	O.D.	Vol. of PAO ml.	O.D.
0.00	0.08	0.00	-
0.10	0.085	0.40	0.03
0.20	0.09	0.80	0.17
0.30	0.12	1.20	0.30
0.40	0.137	1.60	0.40
0.50	0.20	2.00	0.50
0.60	0.21	2.40	0.52
0.70	0.21		
0.80	0.21	2.80	0.52
0.90	0.21	-	-

Fig.6 Curve (c)

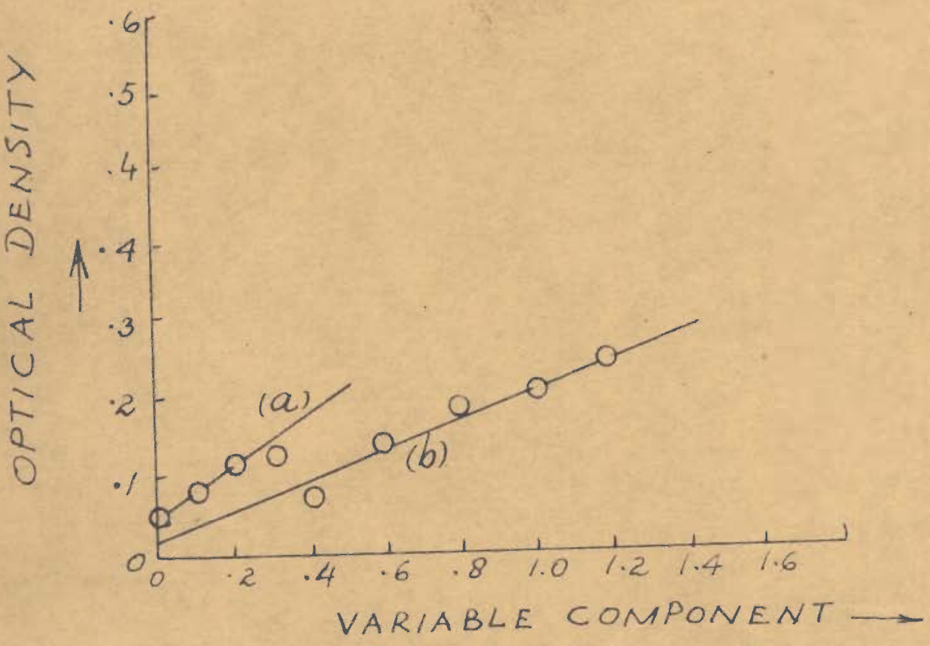


FIG.5 COMPOSITION OF THE COMPLEX BY SLOPE RATIO METHOD

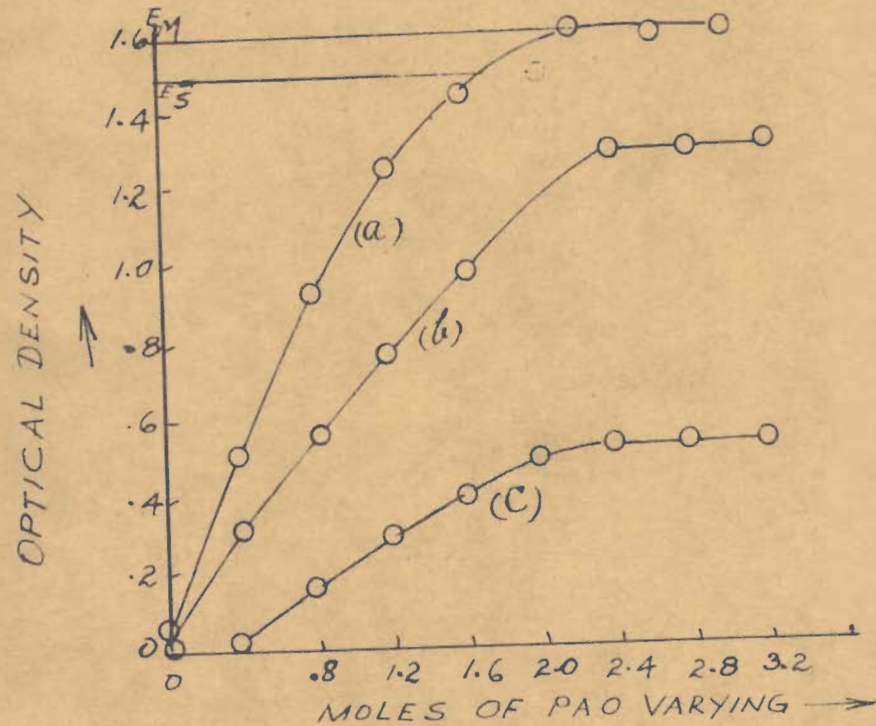


FIG. 6. COMPOSITION OF COMPLEX BY MOLE RATIO METHOD

Table -10 Titration of 2.50×10^{-3} M PAO against 2.50×10^{-3} MKOH

pH	Vol.of KOH (ml.)	pH	Vol.of KOH (ml.)
6.0	0.0	9.00	6.00
6.1	0.40	9.10	6.80
6.3	0.80	9.15	7.20
6.55	1.20	9.20	7.60
6.75	1.60	9.25	8.00
7.00	2.00		
7.35	2.40		
7.70	2.80		
7.95	3.20		
8.15	3.60		
8.30	4.00		
8.50	4.40		
8.60	4.80		
8.75	5.20		
8.85	5.60		
9.00	6.00		

Fig.9 , Curve (a)

Table -11 Titration of (2.50x10^{-3}M PAO + 10x10^{-3}M Cu(II)) against 2.50x10^{-3} KOH

Volume of 2.5x10^{-3}M PAO = 20 ml.
Volume of 10x10^{-3}M Cu(II) = 1 ml.

pH	Vol. of KOH (ml.)	pH	Vol.of KOH (ml.)
5.15	0.0	6.50	7.6
5.30	0.4	6.55	8.0
5.40	0.8	6.60	8.4
5.50	1.2	6.65	9.2
5.60	1.6	6.75	10.0
5.70	2.0	6.90	10.4
5.75	2.4	6.90	10.8
5.82	2.8	7.00	11.2
5.90	3.2	7.05	11.6
6.00	3.6	7.25	12.2
6.05	4.0	7.25	12.4
6.10	4.4	7.40	12.6
6.15	4.8	7.40	12.8
6.20	5.2	7.40	13.0
6.30	6.0		
6.35	6.4		
6.40	6.8		
6.45	7.2		

Fig. 9, Curve (b)

Table -12 Determination of $\bar{n}$ of Cu(II)-PAO Complex

pH	2.5x10^{-3}M KOH (ml)	$\bar{n}$	Average $\bar{n}$
6.5	6.8	1.70	
7.0	9.2	2.30	2.19
7.5	10.3	2.57	

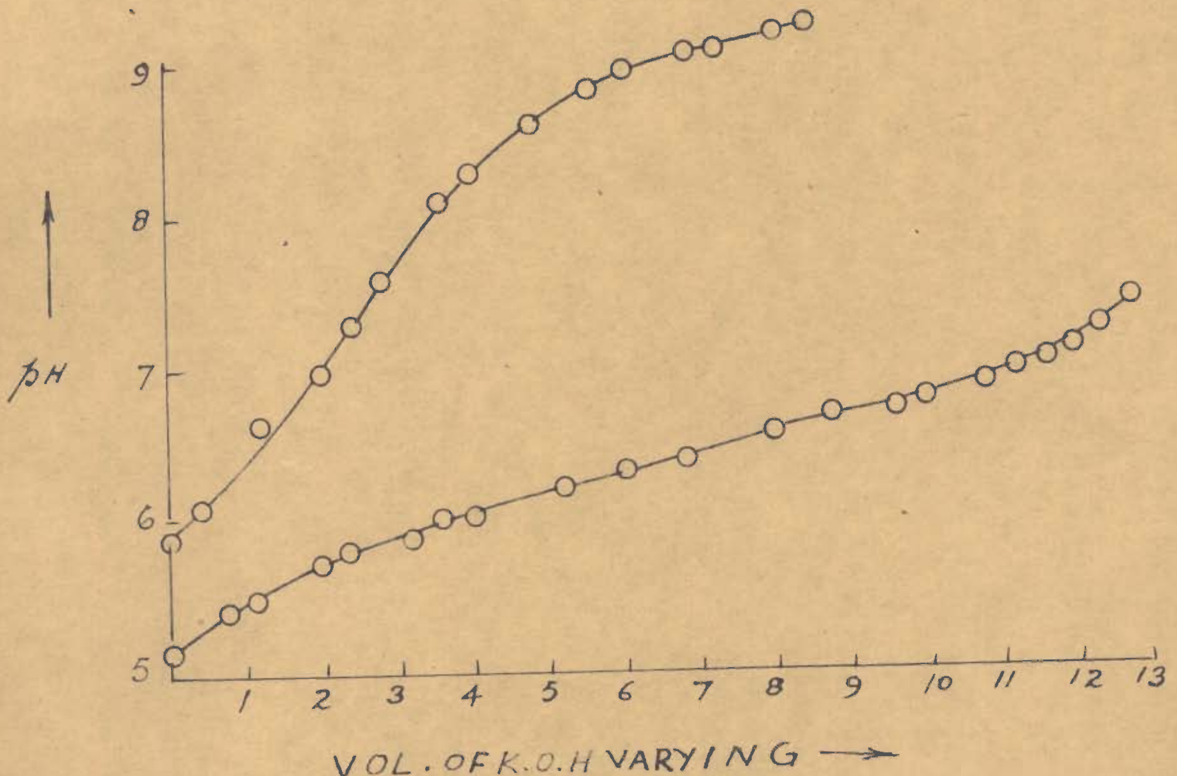


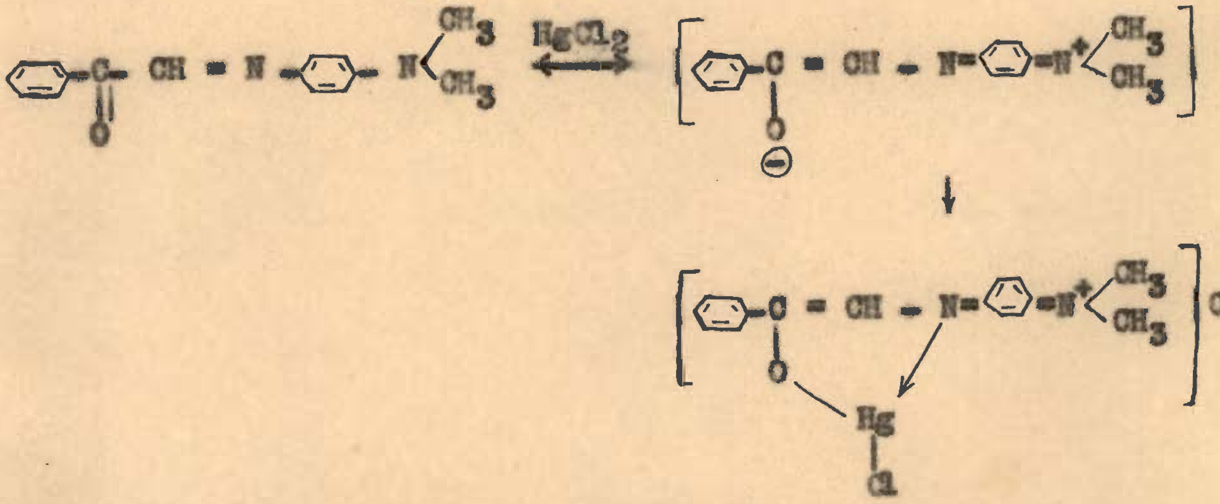
FIG- 9

CHAPTER - III

COMPOSITION OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE LEWIS ACIDS-HALIDES OF Fe(III), Al(III), Hg(II), Zn(II), Sn(IV) AND Sb(V) COMPLEXES.

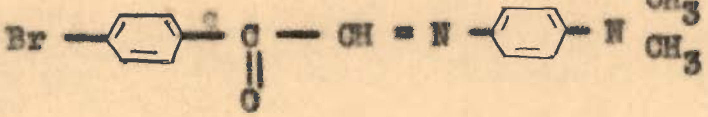
IRON (III) COMPLEX OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

It is a well known fact that the presence of an auxochromic group increases the basic character of a molecule. When such compounds react with Lewis acids, they experience resonance and one of the benzenoid rings is transformed into a quinonoid one. This re-arrangement is then responsible for the chelation of Lewis acids with the ligand. Such effects have rarely been reported for anils. In this connection the reference worth mentioning is that of Krohnke and Gross, (loc cit) who on the basis of color changes only, proposed the possibility of bathochromic effect in anils prepared from phenyl glyoxal hydrate with p-dimethyl amino aniline (pp. 10). The chelation takes place with a typical Lewis acid, is shown below:



Since anil obtained from p-bromo phenyl glyoxal hydrate with p-dimethyl amino aniline is expected to behave in a similar manner, it was considered worthwhile to study comprehensively the reaction of this compound with Lewis acids. Preliminary experiments exhibited the following colour changes with different Lewis acids of p-bromo phenacylidene p-dimethyl amino aniline.

Anil



LEWIS ACID	OWN COLOUR OF THE REAGENT	CHANGE IN COLOUR
1. $FeCl_3$	Yellow	Bluish green
2. $AlCl_3$(Anhydrous)	Yellow	Violet
3. $HgCl_2$	Yellow	Green
4. $ZnCl_2$	Yellow	Bluish green
5. $SnCl_4$	Yellow	Violet
6. $SbCl_5$	Yellow	Violet

The results on the interaction of p-bromo phenacylidene p-dimethyl amino aniline with Fe(III) studied spectrophotometrically are given below:

SYNTHESIS OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

The synthesis of the compound involved the following stages:

(i) Preparation of p-bromo acetophenone,

(ii) Preparation of p-bromo phenyl glyoxal hydrate,

(iii) Condensation of p-bromo phenyl glyoxal hydrate with p-dimethyl amino aniline.

p-bromo acetophenone was synthesised from bromo-benzene with Friedal-Crafts reaction as described previously (pp. 56).

p-bromo acetophenone was oxidised with selenium dioxide (pp. 57). Equimolar quantities of p-bromo phenyl glyoxal hydrate and p-dimethyl amino aniline were dissolved in 95 % alcohol and refluxed on a water bath for about one hour. A solid mass was separated which was crystallised from alcohol (m.p. 108°C)

EXPERIMENTAL

REAGENT AND APPARATUS

Acetone (B.D.H) was redistilled before use. A stock solution of ferric chloride (A.R.) was prepared in acetone and Fe(III) estimated gravimetrically as Fe_2O_3.

0.05 M solution of p-bromo phenacylidene p-dimethyl amino aniline was also prepared in acetone.

The absorbance measurements were carried out with a 'Spectronic 20' Bausch and Lomb spectrophotometer. I.R. measurements were carried out by Perkin-Elmer Infracord spectrophotometer.

NATURE OF THE COMPLEX

The number of the complexes formed during the course of interaction of ferric chloride solution with the ligand was ascertained by Vosburg and Cooper's method. $\lambda_{max.}$ of $\frac{M}{3200}$ solution of the ligand was found to be at 425 mu while that of $\frac{M}{2000}$ $FeCl_3$ at 350 mu. The sharp change in colour was evidenced instantaneously. The colour did not fade even after a week. The solutions of Fe(III) and of p-bromo phenacylidene p-dimethyl amino aniline (both 0.5×10^{-3}M) were mixed in different ratios i.e. 1:1, 1:2... 4:1 and the total volume was kept constant at 10 ml. The plots of O.D. against wave length gave two peaks; one at 350 mu found only in mixtures containing excess of iron and the other at 600 mu (Fig.10). The latter wave length was chosen for all the subsequent studies.

STOICHIOMETRY OF THE COMPONENTS

Job's continued variation method (loc cit) was employed for the determination of the number of metal ions got bound to the ligand. The following sets of mixtures were prepared and their optical densities measured at 600 mu

1,2,3 .... 8,9 ml. of Fe(III) solution.
9,8,7 .... 2,1 ml. of the ligand.

Same volume of the metal ion and the ligand were taken and the total volume in every set was kept constant at 10 ml. By plotting a graph between the composition of the mixtures and the difference between the O.D. of the mixtures and the sum of the ligand and the metal ion, a peak was realised which gave the composition of the chelate. The ratio metal to ligand was found to be 1:2.

From the curves, it is evident that the ratio of the metal ion to the ligand is 1:2 (Table 14 to 15 and Fig.11).

SLOPE RATIO METHOD

This method was employed at three different concentrations. The composition of the complex was found to be 1:2 (metal:ligand) as in case of Job's continued variation method (Tables 17 to 19 and Figs. 12 and 13).

MOLAR RATIO METHOD

This method was employed with a view to determine the composition, stability constant and other thermodynamic properties of the complex (Table 20 to 21 and Fig.14).

CHEMICAL ANALYSIS

When acetonic solutions of ferric chloride and p-bromo phenacylidene p-dimethyl amino aniline (0.5M each) were mixed together in the ratio of 1:2, a green solution was obtained. The mixture was concentrated under reduced pressure, when a sticky mass was obtained. On washing this mass several times with petroleum ether (60-80^{o}), a violet solid was left which was crystallized from acetonitrile.

A weighed quantity (0.5002 gm.) of the chelate was heated with concentrated nitric acid several times to ensure the decomposition of the organic matter. The residue was dissolved in distilled water and Fe(III) estimated as Fe_2O_3 gravimetrically.

ESTIMATION OF Fe(III) IN THE CHELATE

(a) Weight of Fe(III)- Complex = 0.5000 gm.

Weight of Fe_2O_3 found = 0.0475 gm.

Theoretical weight of Fe_2O_3 in the complex. = 0.0481 gm.

Calcd.	Found	Error %
0.0481 gm.	0.0475 gm.	1.24

(b) Weight of Fe(III)- Complex = 0.8539 gm.

Weight of Fe_2O_3 found = 0.0815 gm.

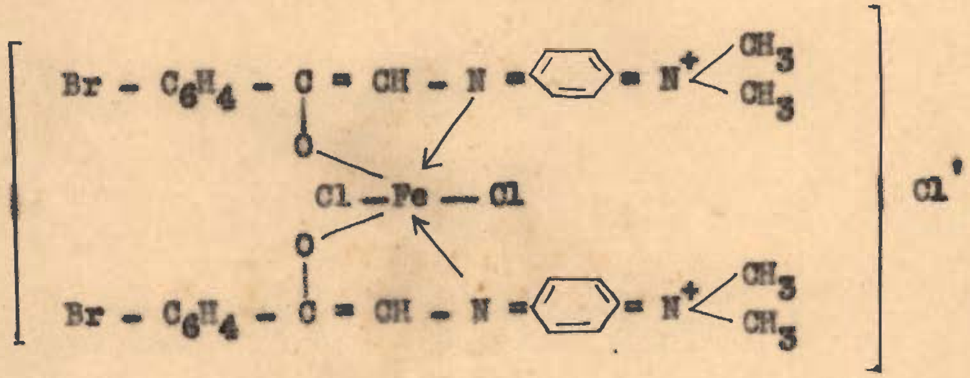
Theoretical weight of Fe_2O_3 in the complex. = 0.0822 gm.

Calcd.	Found	Error %
0.0822 gm.	0.0815 gm.	0.96

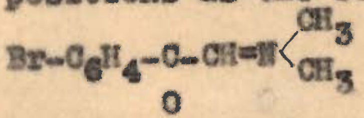
The gravimetric analysis gave results in accordance with the composition determined by spectrophotometric methods.

STRUCTURE OF THE CHELATE

From the above data and assuming a coordination number 6 of Fe(III) , the following structure may be given for the chelate:



On adding alcoholic solution of silver nitrate to an alcoholic solution of the isolated chelate, a white precipitate of silver chloride was obtained, indicating the presence of ionic chlorine.

The structure of the complex was also confirmed by infrared studies. In the ligand, (Fig. 15) the stretching vibration of an aryl ketone, found at 1700 cm.$^{-1}$ and that of a C=N at 1600 cm^{-1} are the centres of the binding of Fe(III) ion. From the Fig.16 it is found that these two vibrations shift to lower frequencies viz., 1590 cm.$^{-1}$ and 1540 cm^{-1} respectively, thereby confirming the above positions as the seats for chelation. Further the ligand  $Br-C_6H_4-\underset{O}{C}-CH=N\langle^{CH_3}_{CH_3}$ shows out of plane vibration of p-disubstituted benzene around at 830 cm^{-1} as a doublet. In the chelate, this band becomes a singlet. It is possible that the two peaks found in the ligand are due to the two p-disubstituted units. On chelation, one of the 830 cm.$^{-1}$ peaks vanishes due to change from benzonoid to quinonoid. The spectrum of the complex also shows some perturbation in the phenyl group skeleton vibration region between 1550 cm.$^{-1}$ and 1400 cm.$^{-1}$ which is expected from the type of structure proposed for the chelate.

DETERMINATION OF THE STABILITY CONSTANT AND FREE ENERGY CHANGE

The stability constant of the chelate was determined by mole ratio method which enabled to calculate free energy change.

Consider the reaction between Fe(III) and the ligand.

$$FeR_2 \rightarrow Fe + 2\,R$$

C	0	0	Initial concentration.
C(1-α)	Cα	2Cα	Equilibrium concentration.

THE STABILITY CONSTANT

$$E_S = \frac{C(1-\alpha)}{(\alpha C)\ (2\alpha C)^2} = \frac{1-\alpha}{4\alpha^3\ C^2}$$

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{1.42 - 1.38}{1.42}$$

$$= \frac{0.04}{1.42}$$

$$= 0.028 \text{ (Fig.14, Curve a)}$$

where E_m and E_s have usual significance.

$$\therefore E_S = \frac{1 - \alpha}{4\alpha^3 C^2} = \frac{1 - 0.028}{4(.028)^3(.002)^2}$$

$$= 0.2767 \times 10^{12}$$

Temp. = 26°C

Change in free energy

$$-\Delta F = R\,T \ln E_S = 1.987 \times 299 \times 2.303 \log 0.2767 \times 10^{12}$$

$$= 15660 \text{ cals.} = 15.66 \text{ K Cals./mol.}$$

Table -13 Vosburg and Cooper's Method for Fe(III) and p-Bromo Phenacylidene p-dimethyl Amino Aniline (Both $0.5x10^{-3}M$)

Concentration of Fe(III) solution = $0.5x10^{-3}M(C)$

Concentration of the ligand = $0.5x10^{-3}M(C')$

$$P = \frac{C'}{C} = 1$$

(Ratio of the metal ion to the ligand)

Wave length mu	1:1 (a)	1:2 (b)	1:3 (c)	4:1 (d)	3:1 (e)	2:1 (f)
330	1.92	2.00	2.00	1.52	1.52	1.70
350	2.00	2.30	2.30	1.70	1.70	1.82
375	1.92	2.00	2.00	1.60	1.60	1.65
400	1.02	1.39	1.70	0.97	0.82	0.88
425	0.74	1.22	1.60	0.41	0.44	0.52
450	0.65	1.12	1.52	0.32	0.35	0.44
475	0.58	0.90	1.15	0.29	0.32	0.40
500	0.56	0.72	0.77	0.27	0.31	0.39
525	0.60	0.72	0.72	0.26	0.30	0.39
550	0.65	0.79	0.7214	0.2450	0.29	0.39
575	0.70	0.85	0.70	0.22	0.27	0.37
600	0.72	0.89	0.62	0.18	0.22	0.34
625	0.70	0.88	0.53	0.135	0.17	0.29
650	0.56	0.68	0.40	0.09	0.11	0.17
675	0.46	0.56	0.32	0.07	0.08	0.13
700	0.31	0.38	0.22	0.06	0.06	0.09
725	0.18	0.22	0.15	0.04	0.04	0.07

Fig.10

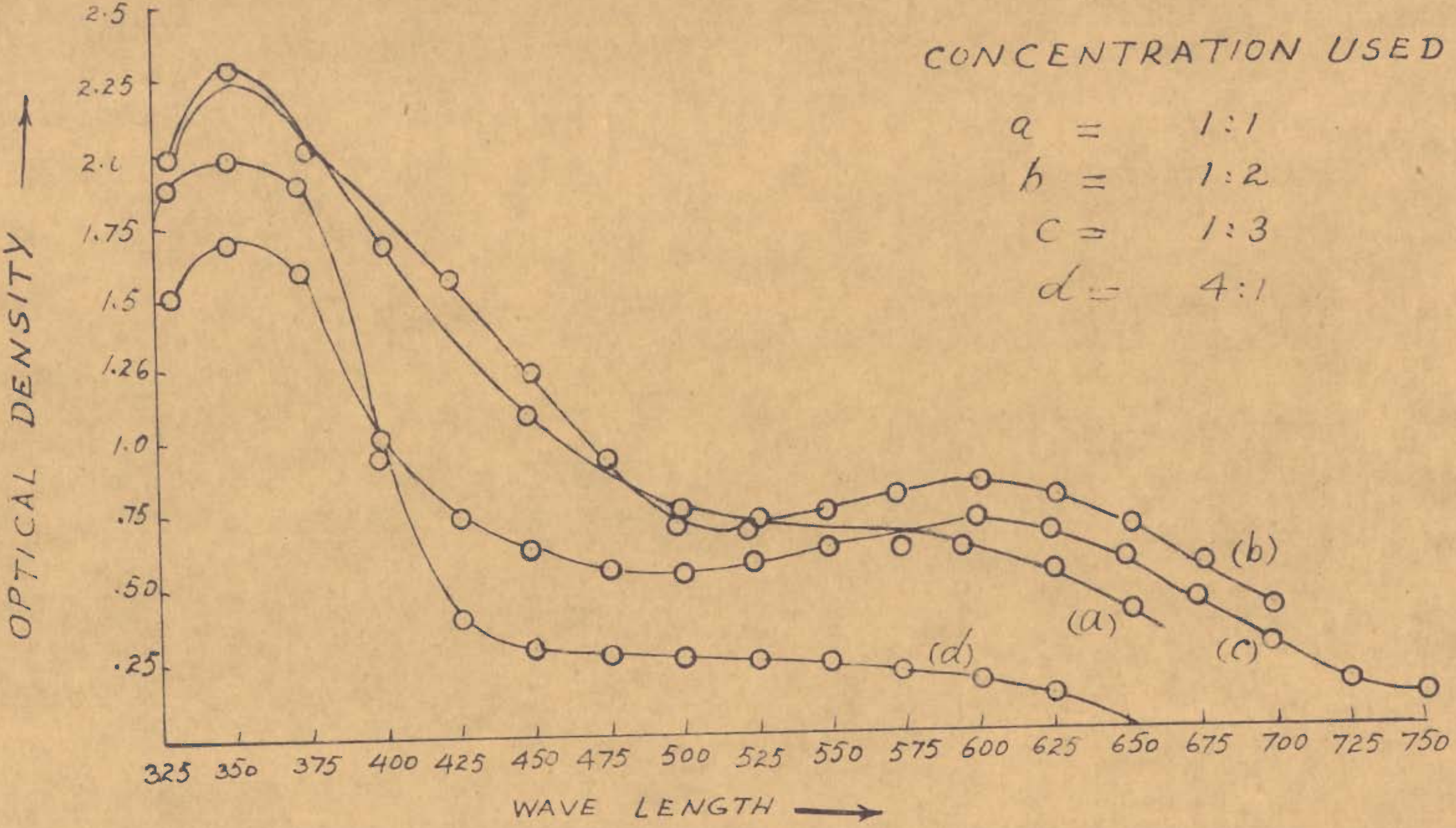


FIG. 10 - ABSORPTION SPECTRA OF FERRIC CHLORIDE COMPLEX.

Table -14

Job's Method for Fe(III) and the Ligand (Both 0.33×10^{-3}M)

Concentration of $FeCl_3$ Solution = 0.33×10^{-3}M(C)

Concentration of the Ligand solution = 0.33×10^{-3}M(C')

Wave length = 600 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Fe(III) : the ligand.

Vol.of Fe(III) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of Fe(III)	O.D. of the ligand	Difference - D
-	-	C	a	b	$\vert C-(a+b)$
1	9	0.37	0.01	0.325	0.035
2	8	0.44	0.01	0.300	0.130
3	7	0.56	0.01	0.240	0.310
4	6	0.62	0.01	0.210	0.400
5	5	0.45	0.02	0.175	0.265
6	4	0.31	0.02	0.135	0.155
7	3	0.23	0.025	0.110	0.095
8	2	0.16	0.03	0.07	0.06
9	1	0.095	0.03	0.03	0.035

Fig.11, Curve (a)

Table -15 Job's Method for Fe(III) and the Ligand
(Both 0.25×10^{-3}M)

Concentration of $FeCl_3$ solution = 0.25×10^{-3}M(C)
Concentration of the ligand solution = 0.25×10^{-3}M(C')
Wave length = 600 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Fe(III): the ligand

Vol.of Fe(III) ml.	Vol.of the ligand. ml.	O.D. of the mixture	O.D. of Fe(III)	O.D. of the ligand	Difference -D
–	–	C	a	b	C–(a+b)
1	9	0.30	0.000	0.285	0.015
2	8	0.275	0.005	0.255	0.020
3	7	0.320	0.005	0.220	0.095
4	6	0.410	0.005	0.180	0.225
5	5	0.370	0.015	0.150	0.205
6	4	0.285	0.015	0.120	0.150
7	3	0.185	0.015	0.085	0.085
8	2	0.09	0.015	0.045	0.030
9	1	0.04	0.02	0.020	0.000

Fig.11, Curve (b)

Table -16 Job's Method for Fe(III) and the ligand (Both 0.285×10^{-3}M)

Concentration of Fe(III) solution = 0.285×10^{-3}M (C)

Concentration of the ligand solution = 0.285×10^{-3}M (C')

Wave length = 600 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Fe(III) : the ligand

Vol.of Fe(III) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of Fe(III)	O.D. of the ligand	Differen
-	-	C	a	b	|C-(a+b)
1	9	0.31	0.01	0.285	0.015
2	8	0.36	0.01	0.230	0.080
3	7	0.39	0.015	0.210	0.165
4	6	0.575	0.025	0.170	0.390
5	5	0.550	0.025	0.140	0.38
6	4	0.470	0.025	0.115	0.33
7	3	0.375	0.030	0.085	0.260
8	2	0.270	0.035	0.05	0.185
9	1	0.135	0.040	0.03	0.065

Table -17 Slope Ratio Method for 1.25×10^{-3}M Fe(III) and 0.125×10^{-3} M ligand, and Vice-Versa

Set I Volume of 0.125×10^{-3}M ligand = 8 ml.
Strength of Fe(III) Solution = 1.25×10^{-3}M

Set

Set II Volume of 0.125×10^{-3}M Fe(III) solution = 8 ml.
Strength of the ligand = 1.25×10^{-3}M

Set I Vol.of Fe(III) ml.	O.D.	Set II Vol.of the ligand ml.	O.D.
0.00	0.105	0.00	0.010
0.10	0.110	0.10	0.030
0.20	0.140	0.20	0.065
0.30	0.190	0.30	0.080
0.40	0.230	0.40	0.120
0.50	0.280	0.50	0.145

Curve (a) Fig.12 Curve (b)

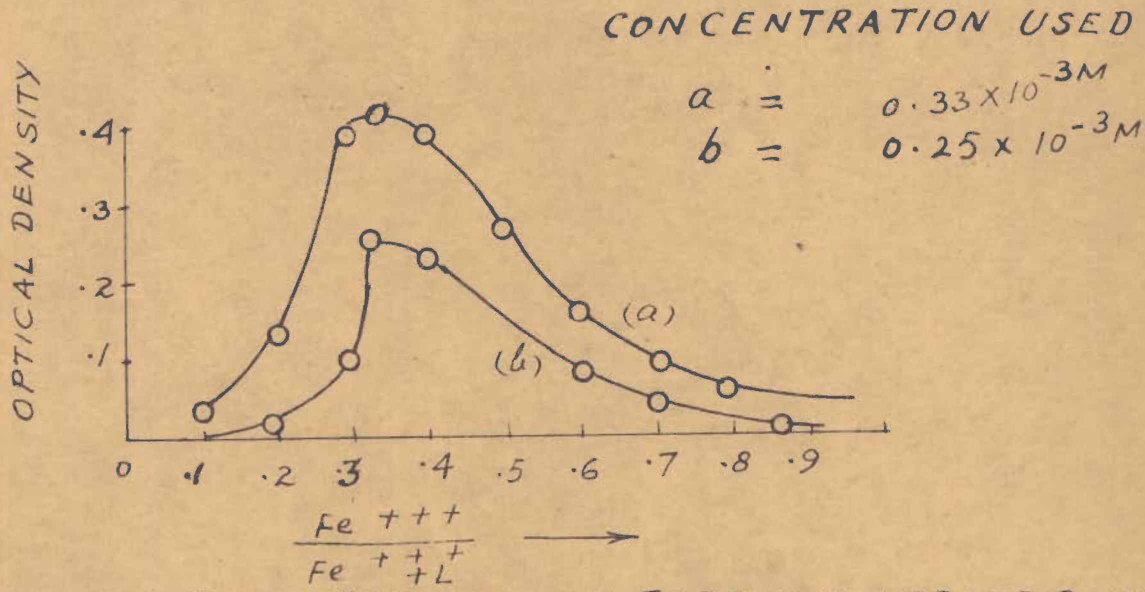


FIG. 11 COMPOSITION OF FERRIC CHLORIDE COMPLEX BY JOB'S METHOD.

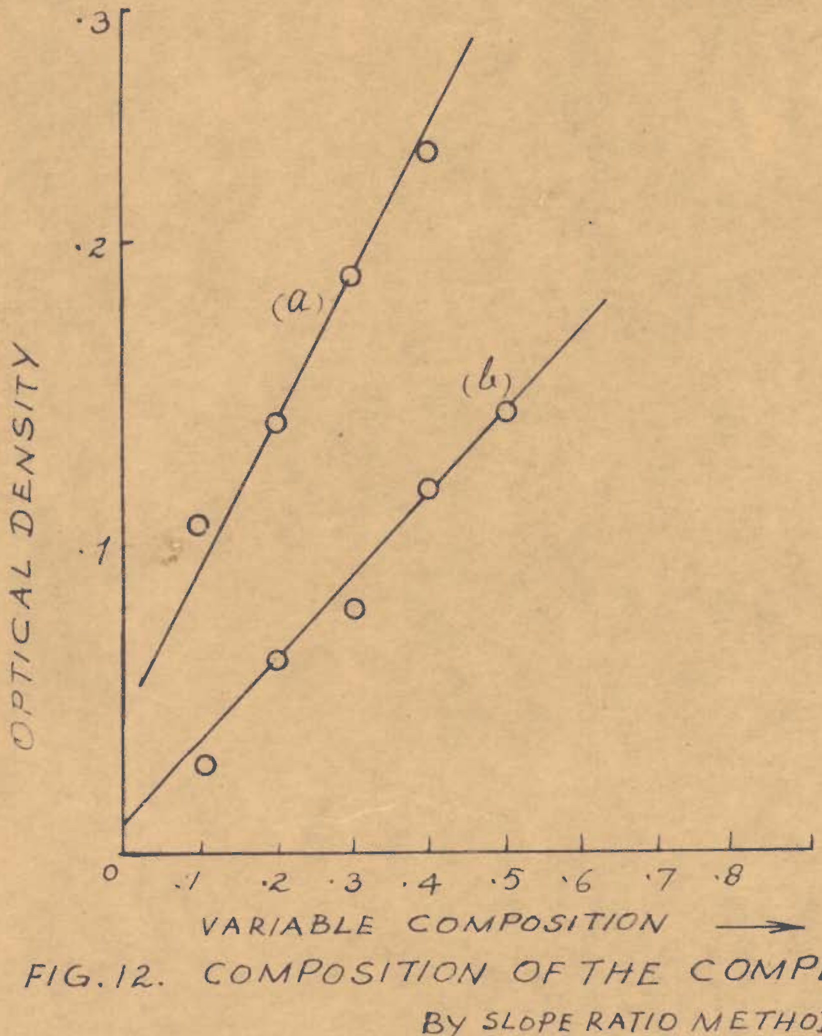


FIG. 12. COMPOSITION OF THE COMPLEX BY SLOPE RATIO METHOD.

Table -18 Slope Ratio Method for 1.00×10^{-3}M Fe(III) and 0.10×10^{-3}M ligand, and Vice-Versa

Set I Volume of 0.10×10^{-3}M ligand = 8 ml.
Strength of Fe(III) solution = 1.0×10^{-3}M

Set II Volume of 0.10×10^{-3}M Fe(III) solution = 8 ml.
Strength of the ligand =1.0×10^{-3}M

Set I		Set II	
Vol.of Fe(III) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.00	0.010	0.00	0.01
0.10	0.060	0.10	0.03
0.20	0.115	0.20	0.05
0.30	0.165	0.30	0.06
0.40	0.220	0.40	0.08
0.50	0.270	0.50	0.105

Curve (a) Fig.13 Curve (b)

Table-19 Slope Ratio Method for 0.833×10^{-3}M Fe(III) and 0.0833×10^{-3}M Ligand, and Vice=Versa

Volume of 0.0833×10^{-3}M ligand = 8 ml.
Strength of Fe(III) solution = 0.833×10^{-3}M

Volume of 0.0833×10^{-3}M Fe(III) = 8 ml.
Strength of the ligand = 0.833×10^{-3}M

Set I		Set II	
Vol. of Fe(III) ml.	O.D.	Vol. of the ligand ml.	O.D.
0.00	0.06	0.00	0.00
0.10	0.07	0.10	0.02
0.20	0.08	0.20	0.04
0.30	0.09	0.30	0.07
0.40	0.10	0.40	0.10
0.50	0.12	0.50	0.13

Table -20 Composition of the Complex by Mole Ratio Method

Strength of Fe(III) or the ligand solution = $2x10^{-3}M$

Constant Volume of Fe(III) or the ligand = 1 ml.

Wave length = 600 mu

Set I		Set II	
Vol.of Fe(III) ml.	O.D.	Vol. of the ligand. ml.	O.D.
0.00	0.42	0.00	0.065
0.20	0.47	0.20	0.140
0.40	0.56	0.40	0.250
0.60	0.68	0.60	0.52
0.80	0.85	0.80	0.68
1.20	1.05	1.00	0.83
1.40	1.222	1.20	0.96
1.60	1.347	1.40	1.12
1.80	1.347	1.80	1.35
-	-	2.0	1.380
-	-	2.2	1.420
-	-	2.4	1.420

Fig.14 Curve (a)

Table 21- Composition of the Complex by Mole Ratio Method

Strength of Fe(III) or the ligand solution=1.25x10^{-3}M
Constant Volume of Fe(III) or the ligand = 1 ml.
Wave length = 600 mu

Set I		Set II	
Vol.of Fe(III) ml.	O.D.	Vol. of the ligand.	O.D.
0.00	0.27	0.00	0.02
0.20	0.30	0.20	0.065
0.40	0.36	0.40	0.13
0.60	0.42	0.60	0.19
1.00	0.52	1.00	0.245
1.20	0.70	1.20	0.385
-	-	1.40	0.54
-	-	1.60	0.66
-	-	1.80	0.79
-	-	2.00	0.90
-	-	2.20	0.94
-	-	2.40	0.94

Fig.14 Curve (b)

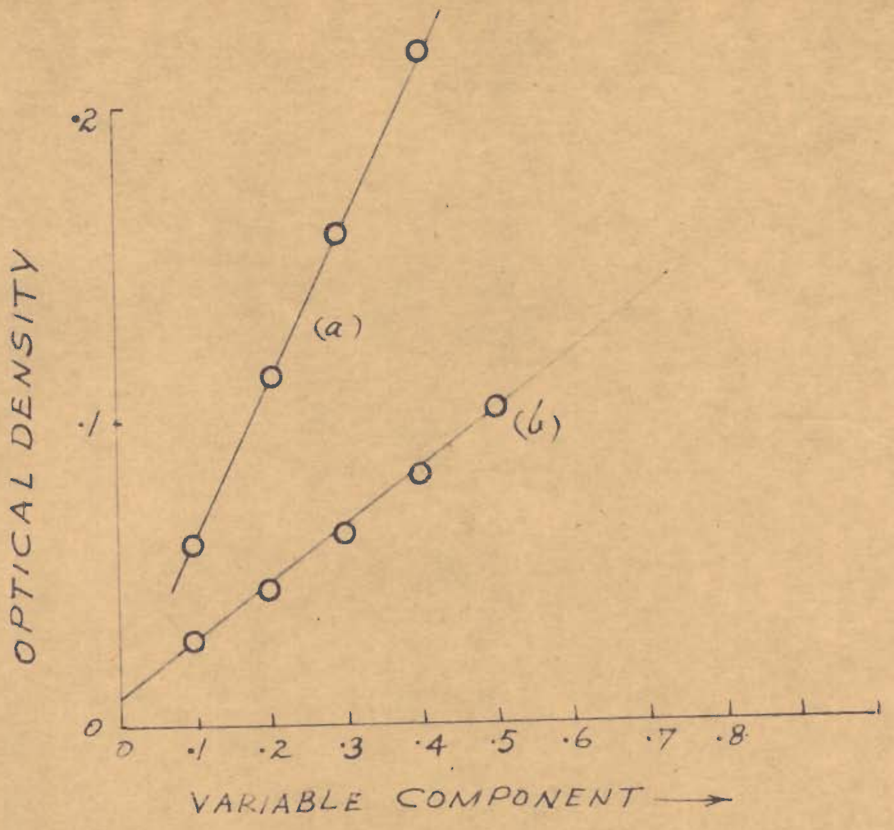


FIG. 13 COMPOSITION OF THE COMPLEX
BY SLOPE RATIO METHOD

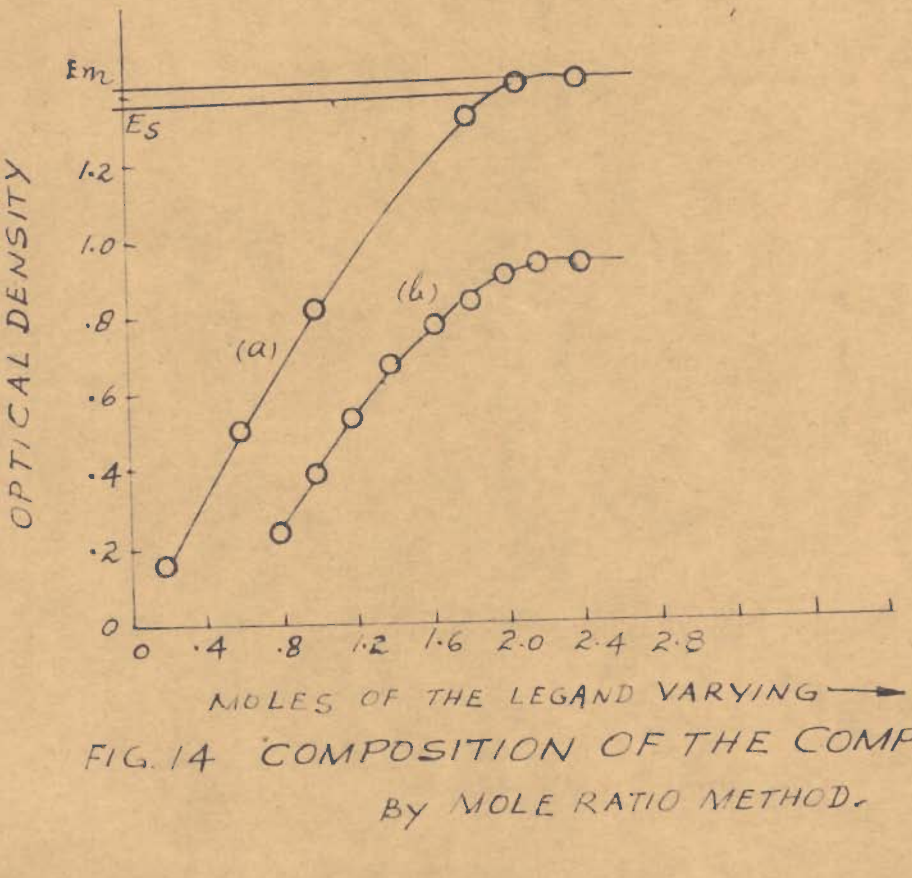
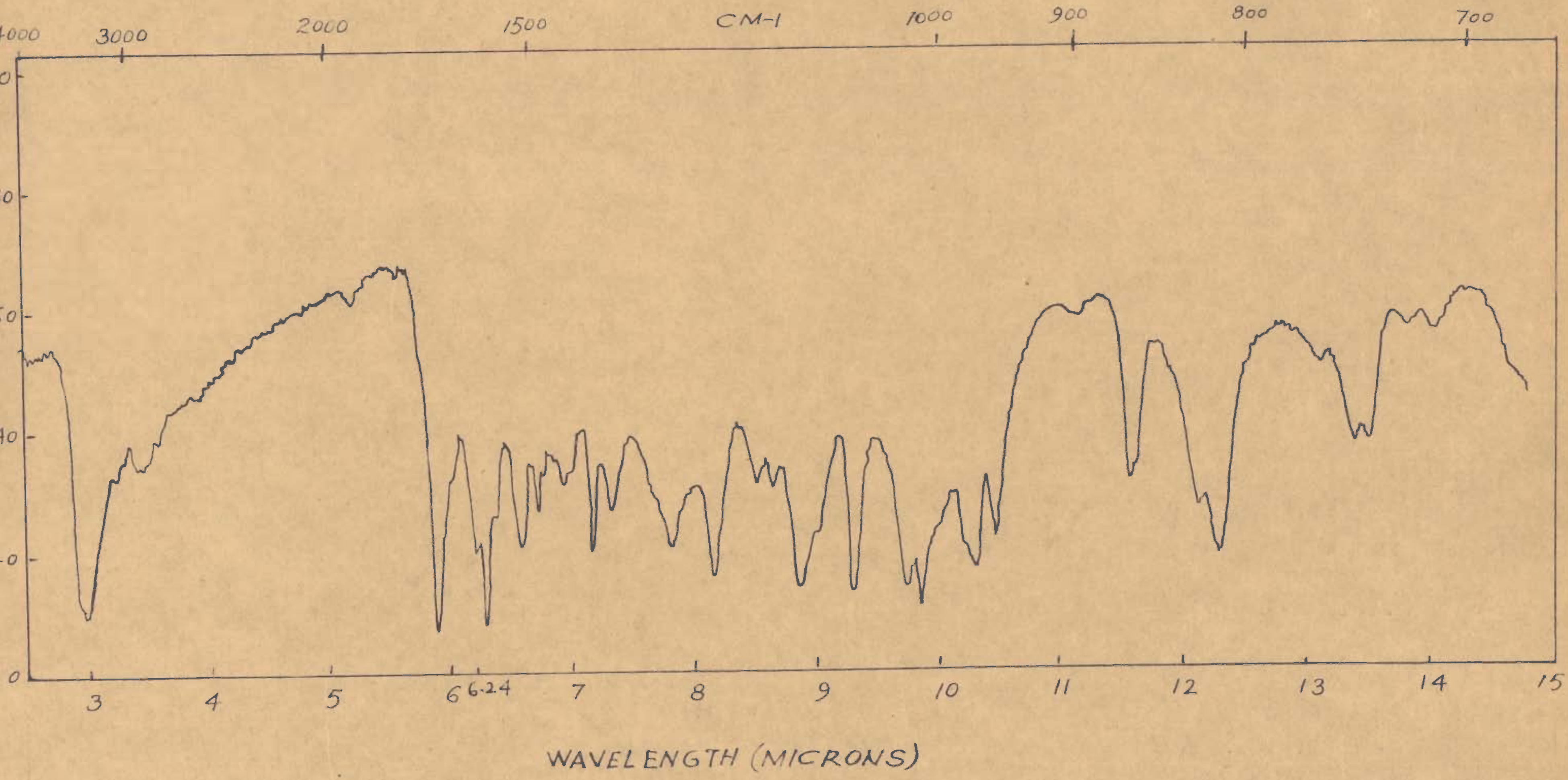


FIG. 14 COMPOSITION OF THE COMPLEX
BY MOLE RATIO METHOD.



I.R. SPECTRUM OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

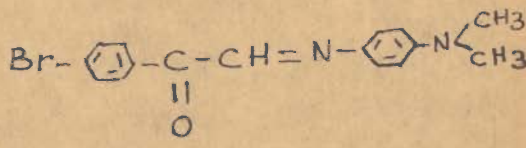
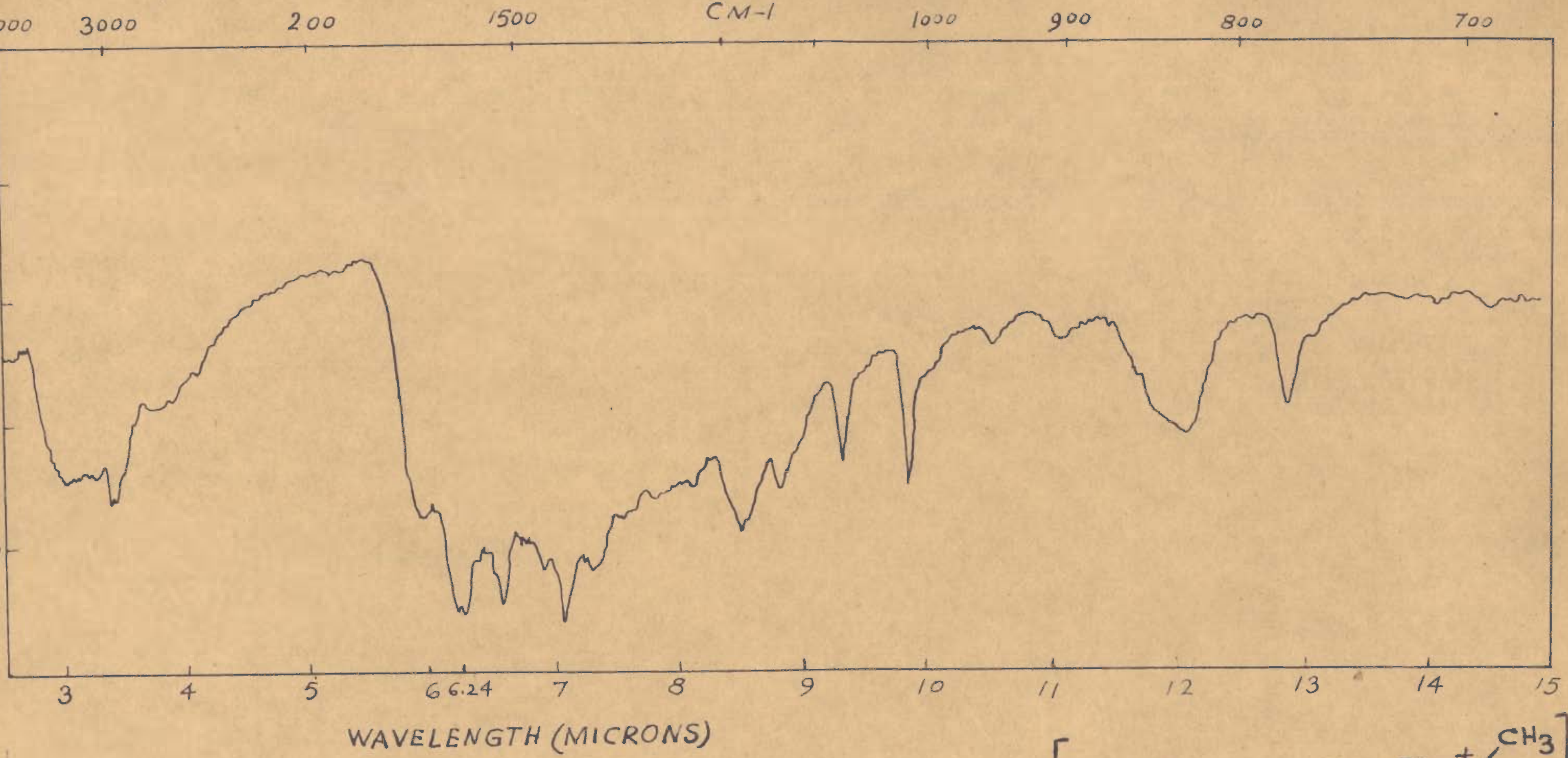
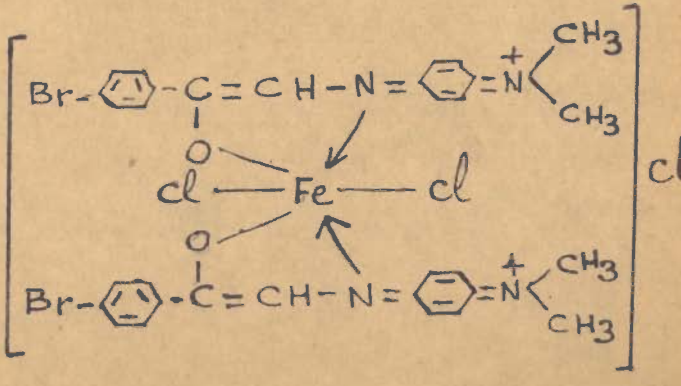


FIG. 15





I. R. SPECTRUM OF p-BROMO PHENACYLIDENE

p-DIMETHYL AMINO ANILINE-Fe (III) CHELATE

FIG-16

ALUMINIUM (III) COMPLEX OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

Like other Lewis acids, anhydrous aluminium chloride also forms chelates on reaction with p-bromo phenacylidene p-dimethyl amino aniline. During the formation of this chelate the ligand molecule experiences a bathochromic shift where one of the benzene rings rearranges from the benzenoid to the quinonoid form.

EXPERIMENTAL

A stock solution of the ligand (0.05M) was prepared in acetone. Anhydrous aluminium chloride was dissolved in acetone and Al(III) estimated gravimetrically as Al_2O_3. When dilute solutions of Al(III) and the ligand were mixed together, a sharp change in colour from yellow to violet was observed. The absorbance and I.R. measurements were carried out with Bausch and Lomb 'Spectronic 20' spectrophotometer, and Perkin-Elmer Infracord spectrophotometer respectively.

NATURE OF THE COMPLEX

Vosburg and Cooper's method was used for the determination of the possible number of chelates formed during the interaction. Two $\lambda_{max.}$ at 425 mu and 535 mu were obtained (Fig.17). The first maxima was realised in mixtures containing excess of the ligand while the second corresponded to the chelate formed. The wave length 535 mu could, therefore, be employed for spectrophotometric study of the complex. The studies were, however, carried out at 550 mu, the wave length at which largest difference between the O.D. values of the ligand and the chelate could exist.

STOICHIOMETRY OF THE COMPONENTS

Job's method of continued variation was used for the determination of the composition of the chelate. A peak was observed when the ratio of the metal to the ligand was as 1:2. The following sets of the mixtures were prepared. The metal ion being colourless, the absorbance of the ligand was only deducted. Throughout the investigations the total volume was kept constant at 10 ml. (Table 23-24), Fig.18.

SLOPE RATIO METHOD

This method was also employed to deduce the composition of the chelate as already determined by Job's continued variation method (Table 25 and Fig.19).

From the ratio of the slopes of the two curves, the composition of the metal to the ligand was determined as 1:2.

MOLAR RATIO METHOD

To a fixed volume of Al(III) solution (2 ml. of $1x10^{-3}M$) varying volumes of the ligand ($1x10^{-3}M$) were added. The absorbance plotted at 535 mu against volume of the variable components showed a sharp break at a molar ratio of the components. Similar results were obtained on adding varying volumes of the metal ion to a constant volume (2 ml. of $1x10^{-3}$M) of the ligand. The results are summarised in tables 26-27 , Fig. 20.

CHEMICAL ANALYSIS

On mixing equimolar quantities of Al(III) and p-bromo phenacylidene p-dimethyl amino aniline solutions (0.05 M each) in the ratio of 1:2, a sharp change of the colour from yellow to violet was observed. The resulting violet solution was concentrated in vacuum when a violet sticky mass was obtained. This was washed several times with petroleum ether (60-80°) to remove the adhering sticky mass. The solid thus obtained was then dried and crystallized from acetonitrile. The resulting chelate was extremely hygroscopic.

A known weight of the chelate was heated with concentrated nitric acid and the solution evaporated to dryness. The process was repeated several times in order to ensure the complete decomposition of the organic matter. The residue was dissolved in water and Al(III) estimated gravimetrically as Al_2O_3. The observations are recorded as shown below:

ESTIMATION OF Al(III) IN THE CHELATE

(i)	Weight of aluminium complex	= 0.3492 gm.
	Weight of Al_2O_3 obtained	= 0.0218 gm.

Theoretical weight of Al_2O_3 in complex = 0.0222 gm.

Calcd.	Found	Error %
0.0222 gm.	0.0218 gm.	1.83

(ii) Weight of Al(III) complex = 0.7972 gm.

Weight of Al_2O_3 obtained = 0.0511 gm.

Theoretical weight of Al_2O_3 in the complex. = 0.0550 gm.

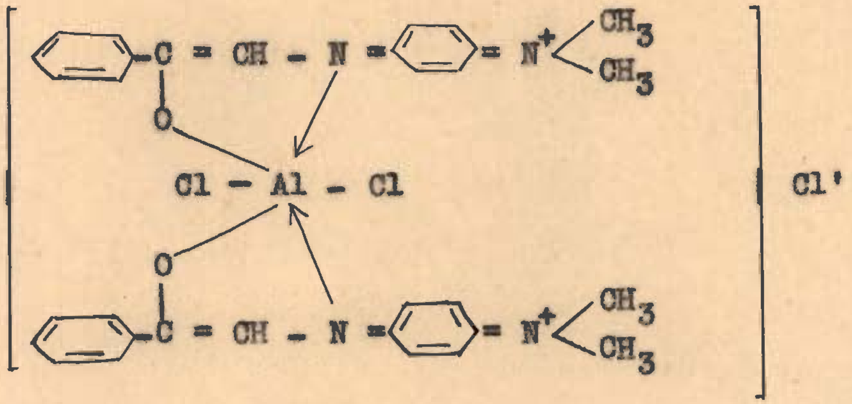
Calcd.	Found	Error %
0.0511 gm.	0.0550 gm.	1.20

From the chemical analysis it is evident that one Al(III) ion is bound with two molecules of the ligand.

STRUCTURE OF THE CHELATE

When anhydrous Al Cl_3 reacts with p-bromo phenacylidene p-dimethyl amino aniline, a lone pair of electrons shifts from the nitrogen of $-\ddot{N}\langle^{CH_3}_{CH_3}$ to the nucleus benzene and then to $>C=O$ group, resulting in the transformation of benzenoid to quinonoid structure.

Due to resonance, $-\underset{\underset{O}{|}}{C}=$ and $-CH=\ddot{N}$ are likely the seats of interaction. On this basis , the following structure may be given for the chelate:



On adding alcoholic solution of silver nitrate to an alcoholic solution of the isolated chelate, a white precipitate of silver chloride was obtained, indicating the presence of ionic chlorine outside the coordination sphere.

The seats of interaction of the ligand with the metal ion could be confirmed by considering the I.R. spectra of the ligand and complex. In the ligand (Fig.15), the stretching vibration of an aryl ketone is found at 1700 $cm.^{-1}$ while that of -CH=N at 1600 $cm.^{-1}$. On chelation these two frequancies are shifted to 1650 cm^{-1} and 1525 cm^{-1} respectively (Fig.21) confirming thereby these two positions to offer seats for binding with the metal ion to cause chelation. Further, the ligand shows out of plane vibration of p-disubstituted benzene around at 830 $cm.^{-1}$ as a doublet. As observed for the iron chelate, here too one band vanishes and only one band remains on chelation. Further, there is a perturbation in the phenyl group skeleton vibration region between 1660 cm.$^{-1}$ and 1400 cm.$^{-1}$ in the complex. All these observations confirm the above structure.

DETERMINATION OF STABILITY CONSTANT AND FREE ENERGY CHANGE.

Consider the dissociation of Al(III) chelate. As the chelation takes place with one part of the metal ion and two parts of the ligand, it may be represented as:

$$\begin{array}{cccccl} Al\,R_2 & \longrightarrow & Al & + & 2\,R & \\ C & & 0 & & 0 & \text{(Initial concentration)} \\ C(1-\alpha) & & C\alpha & & 2\alpha C & \text{(Equilibrium concentration)} \end{array}$$

where

C = Concentration of the complex in moles per litre.

α = Degree of dissociation

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{0.66-0.46}{0.66} = 0.303 \text{ (Fig.20, Curve a)}$$

where E_m and E_s have usual significance.

$$\therefore E_s = \frac{1-\alpha}{4\alpha^3\ C^2} = \frac{1-0.303}{4(0.303)^3(0.0002)^2}$$

$$= 0.1566 \times 10^{-9}$$

Temp. = 27°C

$\therefore$ Change in free energy

$$-\Delta F = R\,T \ln E_s = 1.987 \text{x} (300) \text{x} 2.303 \log.\ 0.1566 \text{x} 10^9$$

$$= 11250 \text{ cals/mol} = 11.25 \text{ K cals/mol.}$$

Table -22 Vosburg and Cooper's Method for Al(III) and p-bromo phenacylidene p-dimethyl Amino Aniline (Both 1×10^{-3}M)

Concentration of Al(III) solution = 1×10^{-3}M (C)

Concentration of the ligand = 1×10^{-3}M(C')

$$P = \frac{C'}{C} = 1$$

(Ratio of the metal to the ligand)

Wave length mu	1:1 (a)	1:2 (b)	1:3 (c)	1:4 (d)	4:1 (e)	3:1 (f)	2:1 (g)
325	1.34	1.70	1.82	1.82	0.75	0.8861	0.99
350	0.98	1.30	1.45	1.52	0.52	0.61	0.64
375	0.84	1.09	1.26	1.30	0.45	0.54	0.57
400	0.82	1.07	1.22	1.30	0.40	0.48	0.51
425	0.81	1.09	1.26	1.34	0.39	0.47	0.52
450	0.79	1.04	1.22	1.30	0.39	0.47	0.52
475	0.72	0.94	1.07	1.15	0.36	0.44	0.47
500	0.64	0.81	0.92	0.98	0.35	0.41	0.44
525	0.62	0.77	0.87	0.92	0.34	0.40	0.43
535	0.65	0.78	0.88	0.94	0.34	0.44	0.44
550	0.63	0.76	0.85	0.92	0.35	0.41	0.43
565	0.58	0.75	0.82	0.88	0.34	0.39	0.42
575	0.56	0.69	0.78	0.81	0.29	0.35	0.38
600	0.47	0.58	0.49	0.68	0.24	0.28	0.31
625	0.36	0.43	0.48	0.50	0.17	0.22	0.23
650	0.22	0.30	0.31	0.33	0.11	0.135	0.15

Fig.17

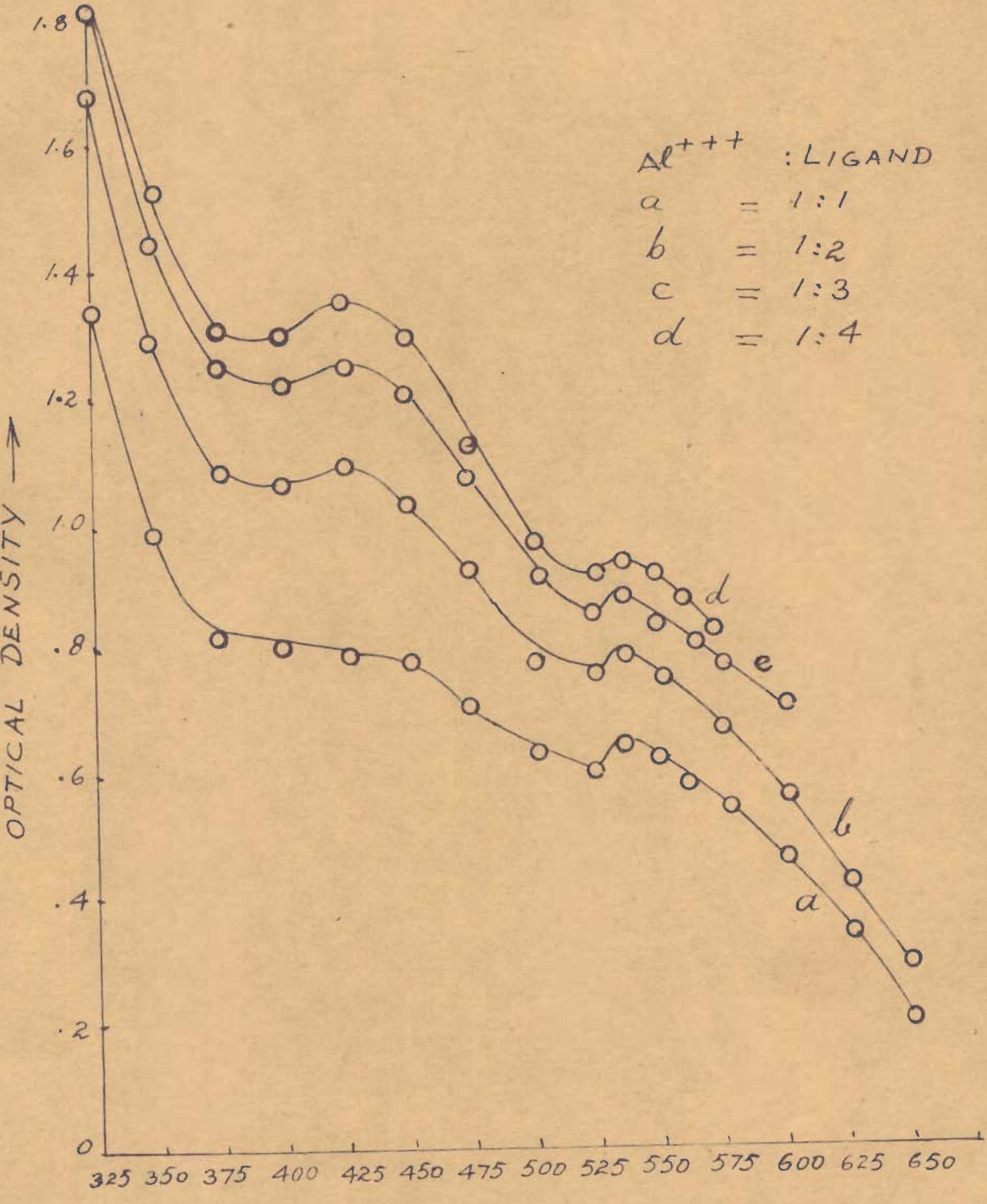


FIG-17

ABSORPTION SPECTRUM OF Al(III) CHLORIDE ANHYDROUS COMPLEX.

Table -23 Job's Method for Al(III) and the Ligand
(Both 0.66×10^{-3}M)

Concentration of $AlCl_3$ solution = 0.66×10^{-3}M(C)
Concentration of the ligand = 0.66×10^{-3}M(C')
Wave length = 550 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Al(III) : the Ligand

Vol. of Al(III) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of the ligand	Difference
-	-	C	b	(C-b)
1	9	1.14	1.085	0.055
2	8	0.90	0.820	0.08
3	7	0.84	0.743	0.097
3.33	6.67	0.75	0.650	0.100
4	6	0.67	0.574	0.096
5	5	0.60	0.512	0.088
6	4	0.57	0.491	0.079
7	3	0.42	0.365	0.068
8	2	0.31	0.257	0.053
9	1	0.16	0.137	0.025

Fig.18, Curve (a)

Table -24 Job's Method for Al(III) and the Ligand (Both 0.50×10^{-3}M)

Concentration of $AlCl_3$ solution = 0.50×10^{-3}M(C)

Concentration of the ligand = 0.50×10^{-3}M(C')

Wave length = 550 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Al(III) : the Ligand

Vol.of Al(III) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of the ligand	Differe
1	9	0.54	0.51	0.03
2	8	0.49	0.437	0.05
3	7	0.42	0.35	0.07
3.33	6.67	0.40	0.325	0.07
4	6	0.38	0.308	0.07
5	5	0.34	0.276	0.06
6	4	0.25	0.197	0.05
7	3	0.18	0.14	0.04
8	2	0.109	0.083	0.02
9	1	0.068	0.061	0.00

Fig.18 , Curve (b)

Table -25 Slope Ratio Method for 0.125×10^{-3}M Al(
1.25×10^{-3} M ligand, and vice-versa.

Set I Volume of 0.125×10^{-3}M ligand = 8 ml.
Strength of Al(III) solution = 1.25×10^{-3}M

Set II Volume of 0.125×10^{-3}M Al(III) solution = 8 ml.
Strength of the ligand = 1.25×10^{-3}M

Set I		Set II	
Vol.of Al.(III) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.10	0.26	0.10	0.035
0.20	0.27	0.20	0.065
0.30	0.29	0.30	0.095
0.40	0.30	0.40	0.130
0.50	0.315	0.50	0.160

Curve (a) Fig.19 Curve (b)

CONCENTRATION USED

$a = 0.66 \times 16^{-3} M$
$b = 0.50 \times 10^{-3} M$

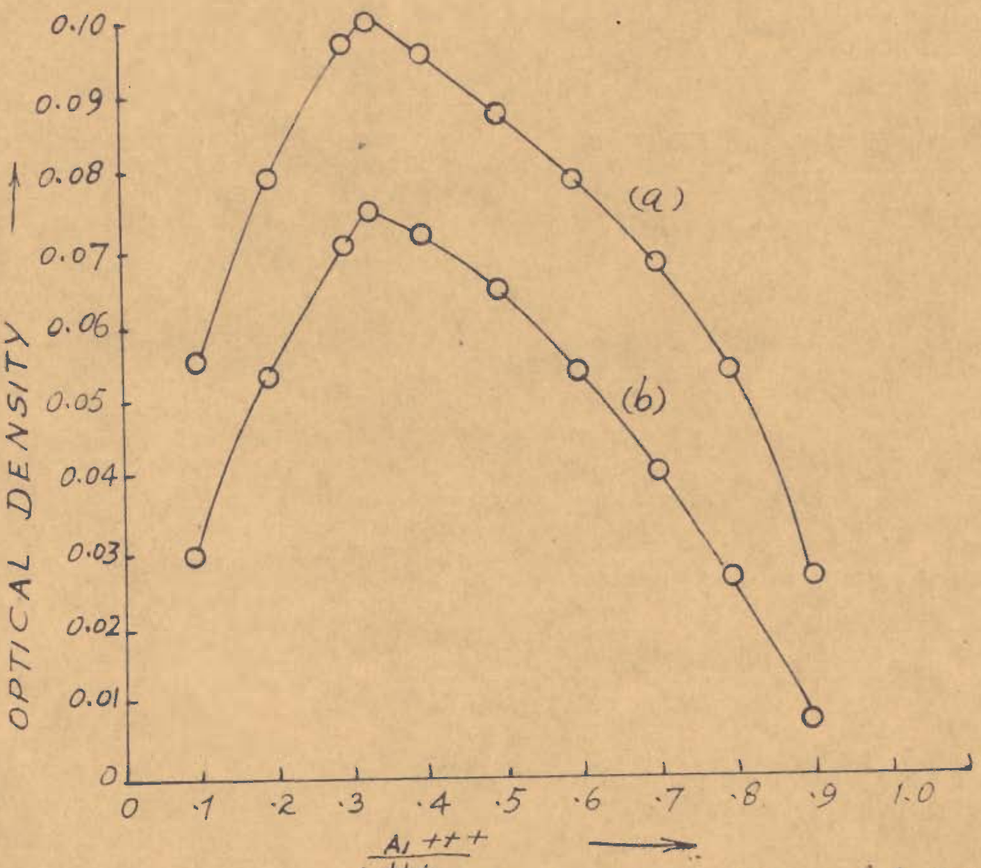


FIG. 18– COMPOSITION OF $AlCl_3$ COMPLEX BY JOBS METHOD

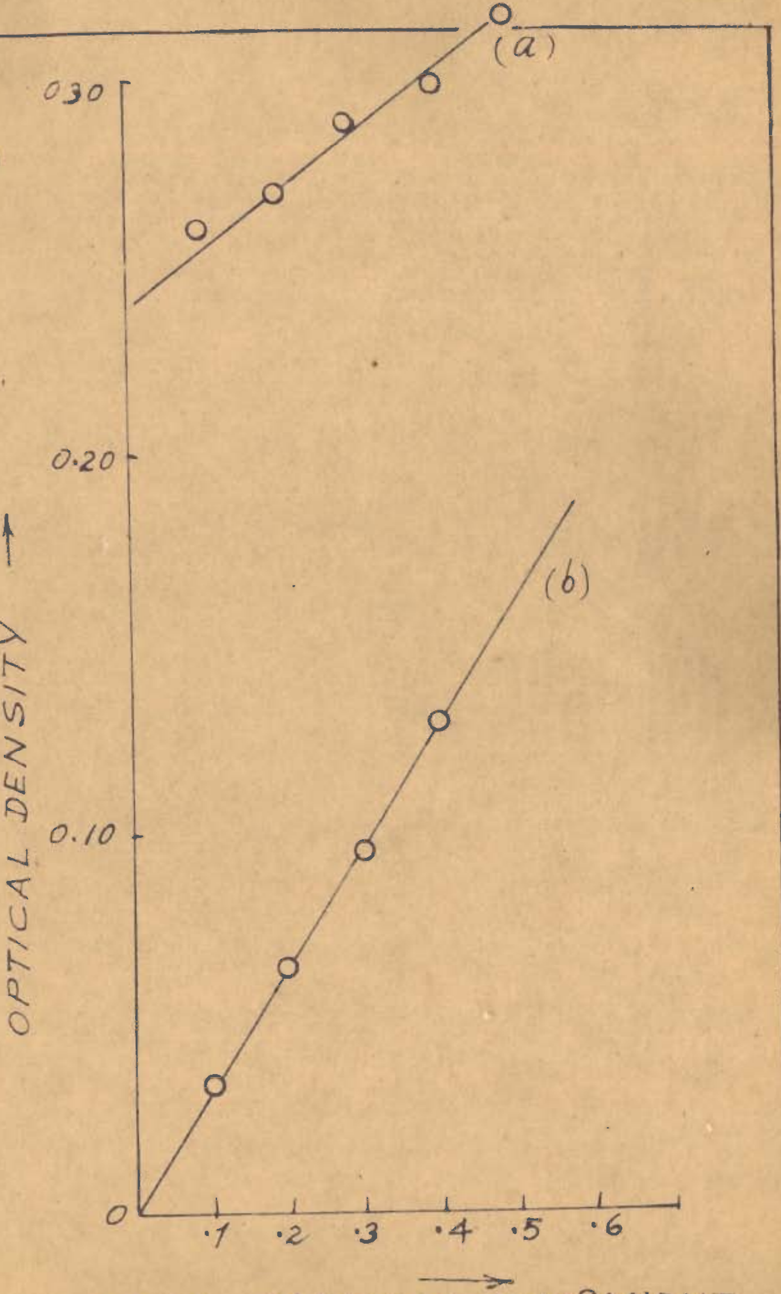


FIG. 19 VARIABLE COMPONENT COMPOSITION OF $AlCl_3$ COMPLEX

Table -26 Composition of the Complex by Mole Ratio Method

Strength of Al(III) or the ligand = 1.0×10^{-3}M

Constant Volume of Al(III) or the ligand. = 2 ml.

Wave length = 535 mu .

Set I		Set II	
Vol.of Al(III) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.20	0.21	0.80	0.10
0.40	0.22	1.60	0.19
0.80	0.24	2.40	0.28
1.00	0.25	3.20	0.37
1.20	0.25	4.00	0.46
1.20	0.25	4.80	0.55
-	-	5.60	0.66
-	-	5.80	0.665
-	-	6.0	0.665

Fig.20 Curve (a)

Table -27 Composition of the Complex by Mole Ratio Metho

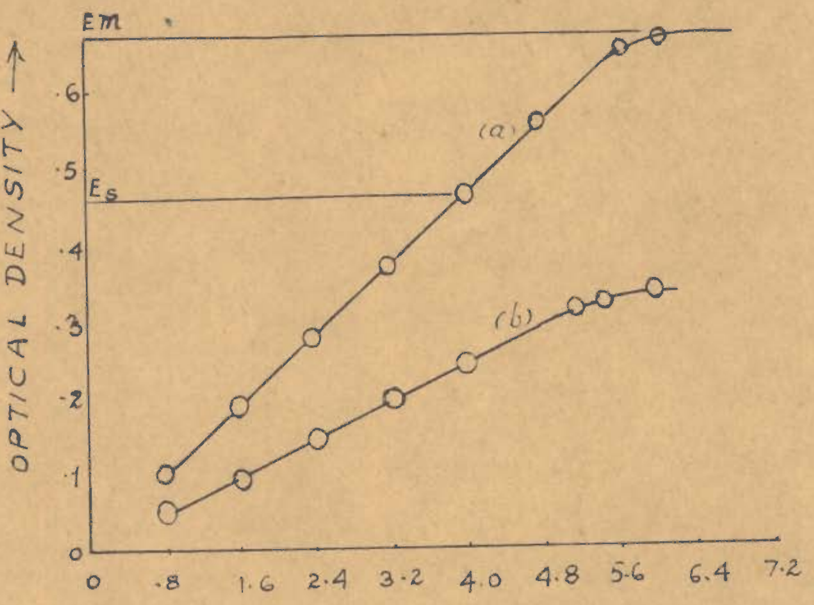
Strength of Al(III) or the ligand solution = 0.66×10^{-3}M

Constant volume of Al(III) or the ligand. = 2 ml.

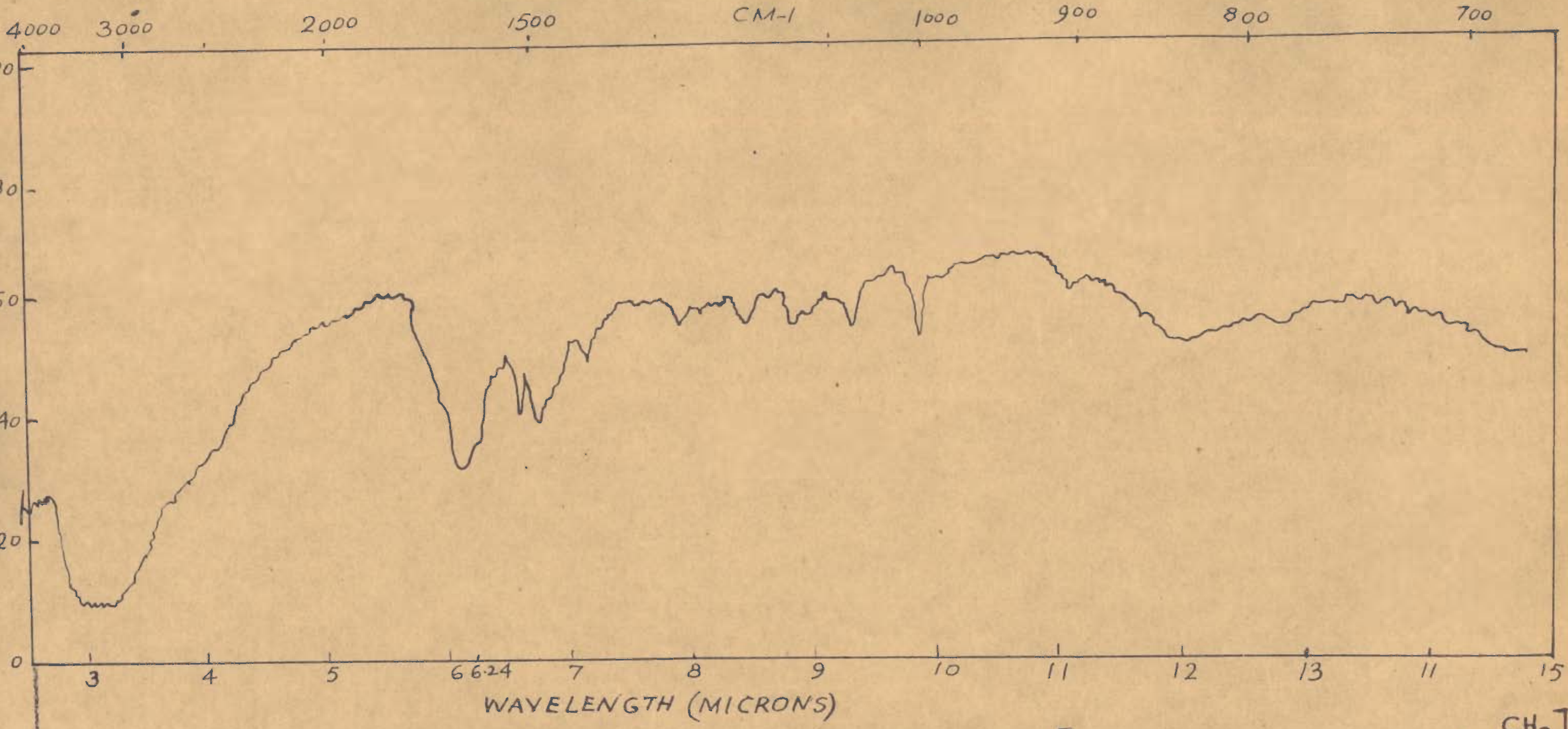
Wave length = 535 m

Set I		Set II	
Vol.of Al(III) ml.	O.D.	Vol.of the ligand ml.	O.D
0.20	0.08	0.80	0.05
0.40	0.09	1.60	0.09
0.60	0.10	2.40	0.14
0.80	0.11	3.20	0.19
1.00	0.115	4.00	0.24
1.20	0.12	4.80	0.29
1.40	0.12	5.00	0.31
1.60	0.12	5.40	0.325
-	-	6.00	0.33

Fig.20 Curve (b)

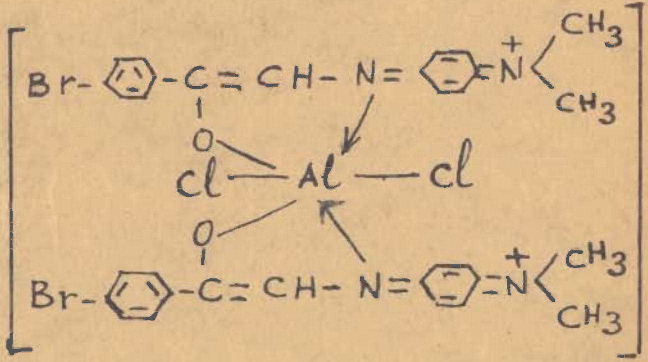


FIG– 20 Moles of the Ligand Varying →
COMPOSITION OF THE COMPLEX BY
MOLE RATIO METHOD.



I.R SPECTRUM OF p. BROMO PHENACYLIDENE p. DIMITHYLAMINO ANILINE - Al(III) CHELATE.

FIG- 21



MERCURY (II) COMPLEX OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

An acetonic solution of mercuric chloride when added to solution of p-bromo phenacylidene p-dimethyl amino aniline brings about a bathochromic shift in its molecule together with the formation of the chelate. The composition and nature of this chelate was determined by spectrophotometry.

EXPERIMENTAL

Stock solutions (0.05 M) of mercuric chloride and the ligand were prepared in acetone. The absorbances and I.R. measurements were carried out with the help of 'spectronic 20' Bausch and Lomb spectrophotometer and Perkin-Elmer Infracord respectively.

NATURE OF THE COMPLEX

When the solutions of p-bromo phenacylidene p-dimethyl amino aniline and mercuric chloride were mixed, a sharp colour change from yellow to green was instantaneously observed which was indicative of the fact that chelation took place. To ascertain the number of chelates formed in complexation, Vosburg and Cooper's method was employed. $\lambda_{max.}$ for different mixtures was found at 575 mu (Fig.22) and this wave length was selected to study the nature of the complex formed. In the case of Job's continuous variation method, wave length 585 mu was chosen in order to have marked difference in absorbance values of the chelate and the ligand.

STOICHIOMETRY OF THE COMPONENTS

Job's continued variation method gave a peak at 1:1 (the ratio of the metal and the ligand). Since Hg(II) solution showed no absorbance at 585 mu, so the optical density of the ligand was deducted from that of the mixture. The total volume was kept constant at 10 ml. (Table 29-30 and Fig.23).

Slope and molar ratio methods were also employed to ascertain the above composition. These methods could not, however, be employed successfully. For determining the stability constant of the chelate, Job's continued variation method with non-equimolar ratio was employed (Tables 30-32, Fig.24).

CHEMICAL ANALYSIS

The chelate was prepared and isolated by concentrating equimolar solutions of Hg(II) and the ligand. It was washed several times with petroleum ether (60-80°) to remove adhering sticky mass. The solid thus obtained was crystallised from acetonitrile.

0.2 to 0.5 gms. of the complex was decomposed by subsequent treatment with concentrated nitric acid and aqua-regia. The mixture was evaporated to dryness and the residue dissolved in concentrated hydrochloric acid and diluted with 50 ml. of distilled water. The solution was saturated with hydrogen sulphide gas in order to precipitate mercury as mercuric sulphide. The precipitate was filtered through a sintered crucible, washed well with cold water, dried at 105-110° and finally weighed as HgS.

ESTIMATION OF Hg(II) IN THE CHELATE

(i) Weight of the complex = 0.5020 gm.

Weight of mercuric sulphide obtained. = 0.1924 gm.

Theoretical weight of HgS in the complex. = 0.1938 gm.

Calcd.	Found	Error %
0.1938 gm.	0.1924 gm.	0.7

(ii) Weight of Hg(III) complex = 0.4670 gm.

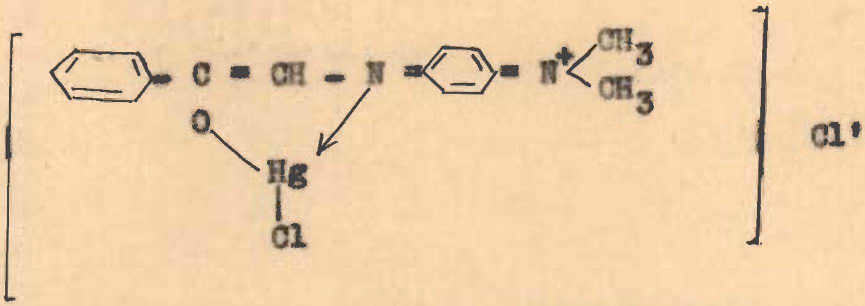
Weight of HgS obtained = 0.1792 gm.

Theoretical weight of HgS in the complex. = 0.1802 gm.

Calcd.	Found	Error %
0.1802 gm.	0.1792 gm.	0.55

STRUCTURE OF THE CHELATE

As in the case of other Lewis acids, mercuric chloride also introduces conjugation on account of the resonance effects in the ligand. This results in a bathochromic shift and the chelation takes place due to increasing negative tendency at the >C=O group of the ligand. The following possible structure may be assigned to the chelate:



An alcoholic solution of the chelate gave a white precipitate of silver chloride with an alcoholic solution of silver nitrate, thereby indicating the presence of ionisable chloride ion. The structure of the complex was further confirmed by I.R. studies.

The ligand shows a >C=O stretching frequency at 1700 cm.$^{-1}$ due to an aryl ketone and another at 1600 cm.$^{-1}$ characteristic of an azomethine grouping (-CH=N) Fig.15. From Fig.25, it may be seen that these frequencies shift to 1670 cm.$^{-1}$ and 1575 cm.$^{-1}$ respectively after chelation. This lowering of frequencies at these centres indicate the seats of the interaction of the metal ion with the ligand. Around 830 cm.$^{-1}$, a doublet is shown in the spectrum of the ligand, while only one peak is shown in the spectrum of the chelate. This also indicates that one of the two benzenoid rings might have changed to a quinonoid one. Further, there is some perturbation in the phenyl group skeleton vibration region between 1550 cm^{-1}

and 1400 cm^{-1} in the chelate as expected from the proposed structure.

STABILITY CONSTANT AND FREE ENERGY CHANGE OF THE CHELATE

The molar ratio method was not applicable to this chelate but Job's equation could be employed for the determination of the stability constant and other thermodynamic data of the chelate.

Non-equimolar solutions of the ligand and the metal ion were prepared and the curves between difference in O.D. of the mixture and the ligand against $\frac{M}{M+L}$ were drawn. From the following general equation , the instability constant and hence stability constant of the chelate was determined:

$$\frac{C^{m+n-1}\ P^{n-1}\ |\ (Pm + n)\ x - n)|^{\ m+n}}{m^{n-1}\ n^{m-1}\ (P-1)^{m+n-1}} = K|n-(m+n)X|$$

or

$$K = \frac{C^{m+n-1}\ P^{n-1}\ |(Pm + n)\ x - n)|^{m+n}}{m^{n-1}\ n^{m-1}\ (P-1)^{m+n-1}|n-(m+n).x|}$$

where C stands for the concentration of Hg(II) ions, Pc stands for the concentration of the ligand, i.e. $P = \frac{C'}{C}$ and X is the amount of the ligand used as determined from the maximum in the curves.

DETERMINATION OF INSTABILITY CONSTANT OF THE Hg(II)-CHELATE

Fig.	Curve	Concentration of Hg(II) solution	X	P	λ	Instability constant K	Mean K
24	a	$.625\times10^{-3}$M	0.64	0.66	575	2.607×10^{-5}	2.6825×10^{-5}
24	b	$.66\times10^{-3}$M	0.725	0.50	575	2.76×10^{-5}	

Since stability constant $K' = \frac{1}{K}$

$$\therefore \quad K' = \frac{1}{2.6825\times10^{-5}} = 0.3729\times10^{5}$$

$$-\Delta F = RT \ln K'$$

$$= 1.987\times308\times2.303 \log 0.3729\times10^{5}$$

$$= 6443 \text{ cals/mol} = 6.443 \text{ K Cals/mol.}$$

Table -28 Vosburg and Cooper's Method for Hg(II) and p-Bromo Phenacylidene P-dimethyl Amino Aniline (Both 1.25×10^{-3}M)

Concentration of Hg(II) Solution = 1.25×10^{-3}M (C)
Concentration of the ligand = 1.25×10^{-3}M (C')

$$p = \frac{C'}{C} = 1$$

(10 C.C. of the Mixture diluted to 15 C.C)

(Ratio of the metal to the Ligand)

Wave length mμ	1:1 (a)	2:1 (b)	3:1 (c)	4:1 (d)	1:3 (e)
325	1.30	0.85	0.70	0.58	2.000
350	1.18	0.75	0.60	0.50	1.824
375	1.15	0.72	0.58	0.47	1.770
400	1.30	0.80	0.64	0.51	1.824
415	1.35	0.82	0.68	0.53	2.000
425	1.34	0.82	0.68	0.54	2.000
435	1.34	0.82	0.68	0.53	2.000
450	1.26	0.79	0.64	0.50	2.000
475	1.04	0.66	0.54	0.43	1.700
500	0.82	0.53	0.44	0.34	1.301
525	0.78	0.51	0.42	0.33	1.187
550	0.81	0.53	0.43	0.34	1.222
565	0.82	0.54	0.44	0.345	1.222
575	0.82	0.54	0.45	0.35	1.155
585	0.79	0.53	0.43	0.34	1.125
600	0.77	0.52	0.41	0.33	1.109
625	0.65	0.44	0.36	0.29	0.920
650	0.60	0.40	0.30	0.25	0.800

Fig.22

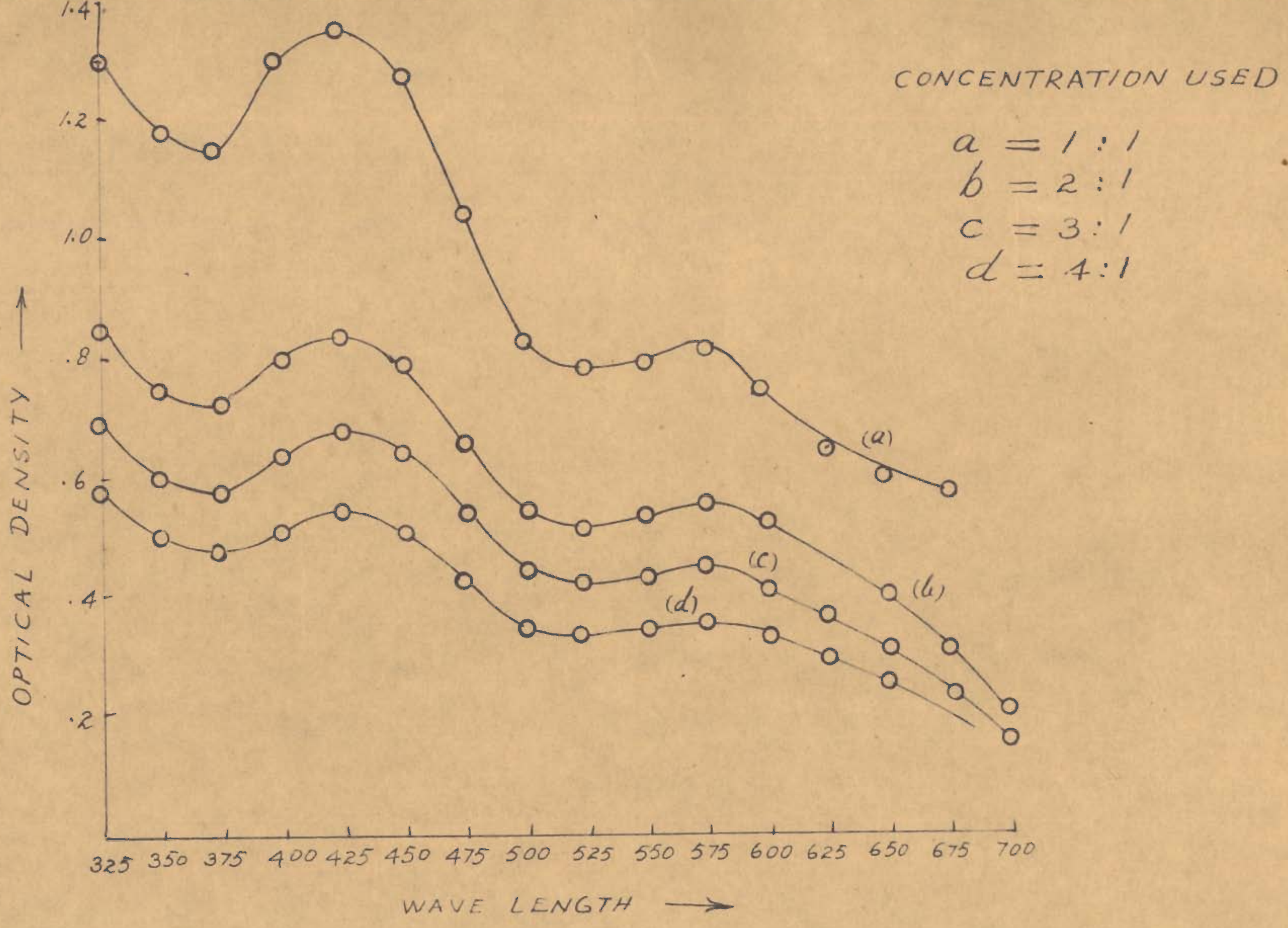


FIG. 22. ABSORPTION SPECTRA OF $Hgcl_2$ COMPLEX.

Table -29 Job's Method for Hg(II) and the ligand
(Both 0.416×10^{-3}M)

Concentration of 0.416×10^{-3} Hg(II) solution = 0.416×10^{-3}M(

Concentration of 0.416×10^{-3} ligand = 0.416×10^{-3}M(

Wave length = 585 m

$$P = \frac{C'}{C} = 1$$

Peak at 1:1::Hg(II):the ligand

Vol.of Hg(II) ml.	Vol.of the ligand ml.	O.D.of the mixture m	O.D. of the ligand	Difference
-	-	C	b	(C-b)
1	9	0.59	0.53	0.06
2	8	0.51	0.43	0.08
3	7	0.46	0.37	0.091
4	6	0.39	0.29	0.101
5	5	0.36	0.25	0.110
6	4	0.26	0.16	0.102
7	3	0.20	0.11	0.092
8	2	0.18	0.10	0.08
9	1	0.10	0.034	0.066

Fig. 23, Curve (a)

Table -30 Job's Method for Hg(II) and the Ligand

(Both 0.20×10^{-3}M)

Concentration of 0.20×10^{-3}M Hg(II) solution = 0.20×10^{-3}M (c)

Concentration of 0.20×10^{-3}M ligand = 0.20×10^{-3}M (C')

Wave length = 585 m

$$P = \frac{C'}{C} = 1$$

Peak at 1:1 :: Hg(II): the ligand

Vol.of Hg(II) ml.	Vol.of the ligand ml.	O.D.of the mixture	O.D. of the ligand	Differenc
-	-	c	b	(c-b)
1	9	0.28	0.27	0.01
2	8	0.25	0.213	0.037
3	7	0.235	0.184	0.051
4	6	0.190	0.128	0.062
5	5	0.160	0.090	0.070
6	4	0.130	0.070	0.059
7	3	0.09	0.046	0.044
8	2	0.06	0.03	0.03
9	1	0.03	0.02	0.01

Fig.23 , Curve (b)

Table 31- Job's Method for Hg(II) and the Ligand (Non-equimolar)

Concentration of $HgCl_2$ solution = 0.625×10^{-3}M(C)

Concentration of the ligand = 0.416×10^{-3}M(C')

Wave length = 575 mu

$$P = \frac{C'}{C} = 0.66$$

Vol.of Hg(II)	Vol.of the ligand	O.D. of the mixture	O.D. of the ligand	Difference
-	-	C	b	(C-b)
1	9	0.47	0.38	0.09
2	8	0.45	0.34	0.11
3	7	0.42	0.30	0.12
4	6	0.37	0.25	0.12
5	5	0.31	0.20	0.11
6	4	0.26	0.16	0.10
7	3	0.20	0.12	0.08
8	2	0.13	0.08	0.05
9	1	0.07	0.04	0.03

Fig.24, Curve (a)

Table -32 Job's Method for Hg(II) and the Ligand (Non-Equimolar)

Concentration of $HgCl_2$ solution = 0.66×10^{-3} M(C)

Concentration of the ligand = 0.33×10^{-3} M(C')

Wave length = 575 mu

$$P = \frac{C'}{C} = 0.5$$

Vol.of Hg(II) ml	Vol.of the ligand ml	O.D. of the mixture	O.D. of the ligand	Difference
-	-	C	b	(C-b)
1	9	0.35	0.33	0.02
2	8	0.32	0.295	0.025
3	7	0.285	0.2571	0.027
4	6	0.24	0.22	0.02
5	5	0.205	0.19	0.015
6	4	0.165	0.15	0.015
7	3	0.12	0.11	0.01
8	2	0.09	0.08	0.01
9	1	0.05	0.045	0.005

Fig.24, Curve (b)

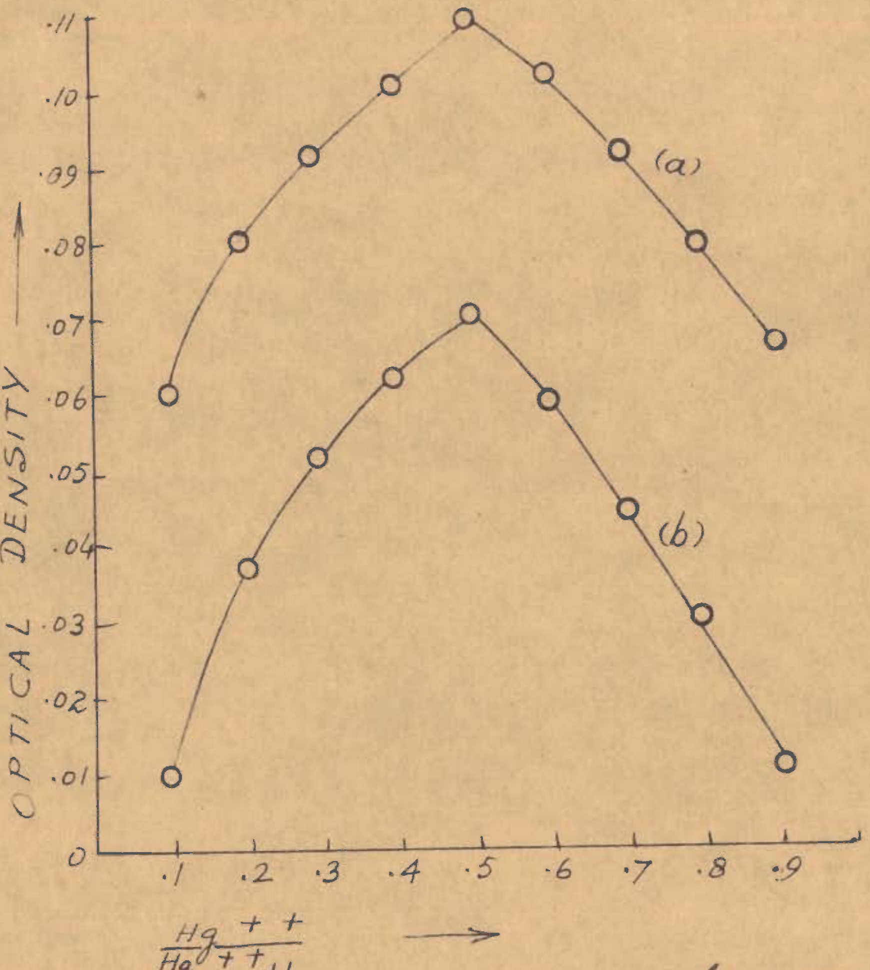


FIG. 23 COMPOSITION OF $Hgcl_2$ COMPLEX BY JOBS METHOD

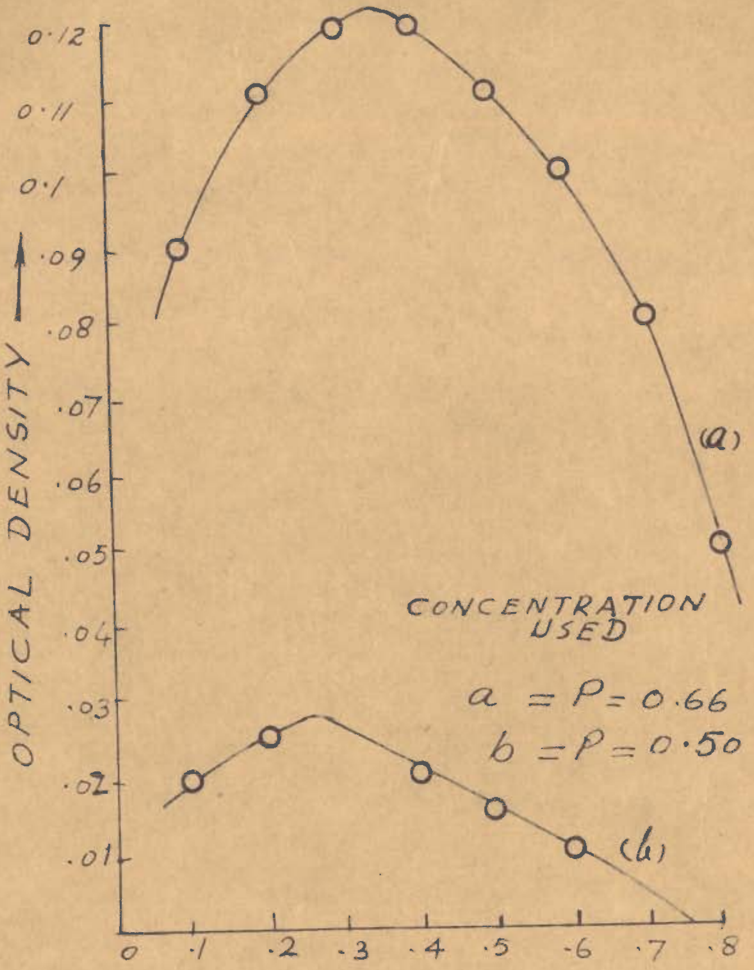
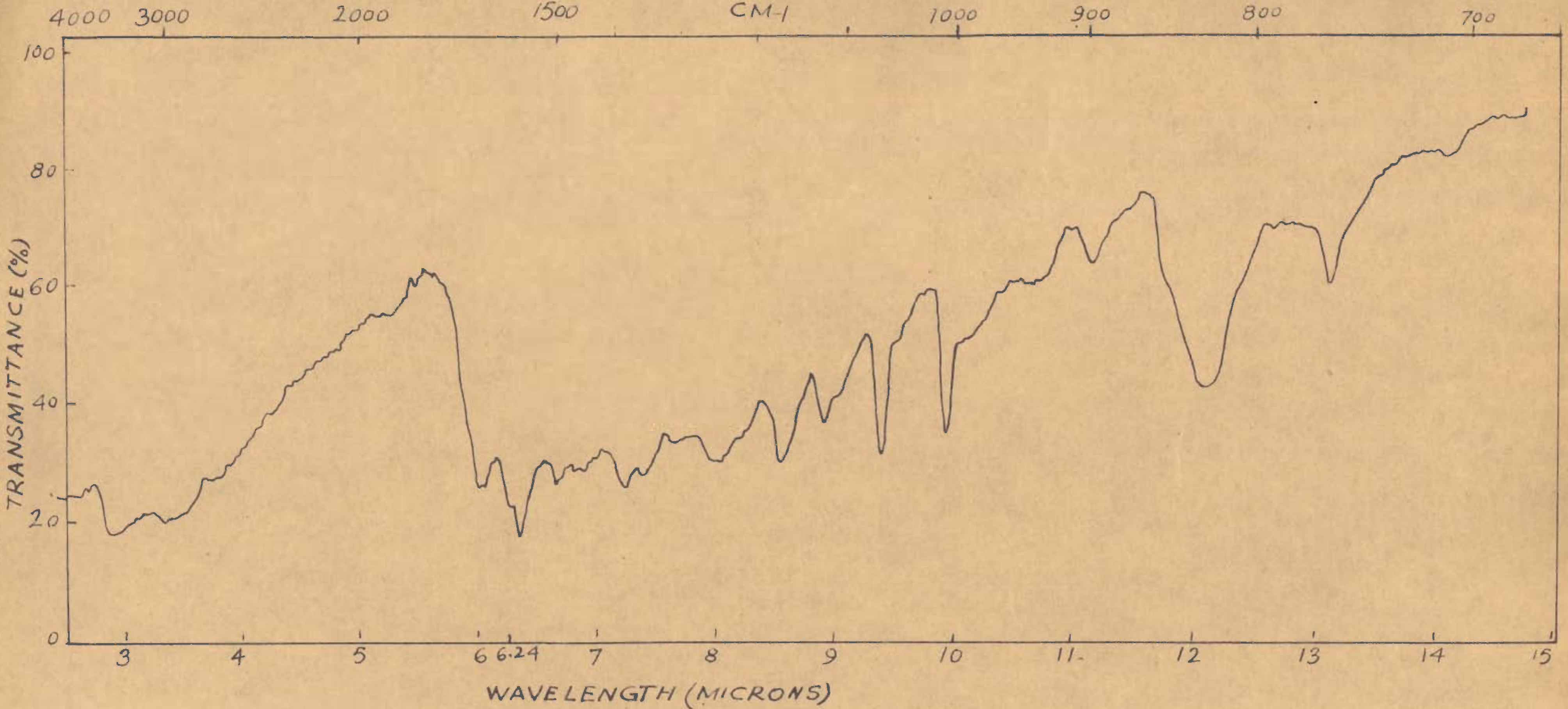


FIG. 24 STABILITY CONSTANT DETERMINATION OF $Hgcl_2$ COMPLEX BY JOBS METHOD



I.R. SPECTRUM OF p-BROMOPHENACYLIDENE p. DIMETHYLAMINO ANILINE - Hg (II) CHELATE.

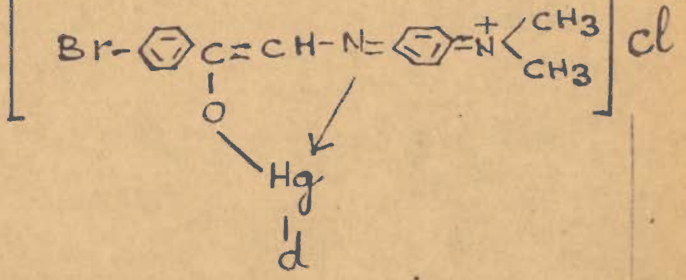


FIG-25.

ZINC(II) COMPLEX OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

A sharp colour change from yellow to green takes place when the acetonic solutions of zinc chloride and p-bromo phenacylidene p-dimethyl amino aniline are mixed together. Like other Lewis acids, bathochromic shift in this case from 425 mu to 600 mu takes places. Besides, the possibility of the formation of the chelate also exists.

EXPERIMENTAL

A stock solution of zinc chloride was prepared in acetone and Zn(II) estimated gravimetrically as $Zn(NH_4)PO_4$. A solution of the ligand in acetone (0.05M) was prepared. The absorbances were measured with the help of Bausch and Lomb 'spectronic 20'. I.R. spectra were taken with the help of Perkin-Elmer Infracord.

NATURE OF THE COMPLEX

Plots between O.D. and wave lengths of 0.312×10^{-3}M ligand give $\lambda_{max.}$ at 425 mu. By Vosburg and Cooper's method (loc cit), $\lambda_{max.}$ of the olive green chelate was observed at 600 mu (Fig.26). This wave length was, therefore, selected as the suitable wave length for the determination of the composition except in the case of Job's continuous variation method where wave length of 610 m was chosen in order to have maximum difference in absorbance. The green colour did not fade even on keeping it for a week.

STOICHIOMETRY OF THE COMPONENTS

To ascertain the composition of the chelate, Job's continued variation method was employed at two different concentrations. The peak was found at 1:1 (metal: ligand) Table 34-35 and Fig. 27. 2 ml. of each mixture was diluted to 10 ml. and O.D. determined. The same dilution was made for the ligand also. As zinc chloride is colourless, only the absorbance of the ligand was subtracted from that of the mixture.

By this method, the composition of the chelate was found to be as 1:1 (Metal ion: ligand).

From the slopes of the curves (Figs. 28 and 29, Curves a and b) clearly the existence of 1:1 complex is indicated.

MOLAR RATIO METHOD

This method also provides evidence for the formation of 1:1 complex (Fig.30, curves a and b).

CHEMICAL ANALYSIS

Equimolar solutions in acetone of Zn(II) and p-bromo phenacylidene p-dimethyl amino aniline were mixed together. The mixture afforded on concentration in vacuum a violet coloured sticky mass. It was repeatedly washed with petroleum ether (60-80°) to free it from the sticky mass. The solid thus obtained was crystallized from acetonitrile. Zn(II) was estimated gravimetrically as zinc ammonium phosphate.

A weighed amount of the complex was heated with concentrated nitric acid repeatedly till whole of the organic matter was destroyed. The residue obtained after evaporating the mixture to dryness was dissolved in water and Zn(II) was estimated as $Zn(NH_4)\ PO_4$.

ESTIMATION OF Zn(II) IN THE CHELATE

(i) Weight of zinc (II) complex = 0.2876 gm.

Weight of $Zn(NH_4)PO_4$ obtained = 0.1089 gm.

Theoretical weight of $Zn(NH_4)PO_4$ in the complex. = 0.1097 gm.

Calcd.	Found	Error %
0.1097 gm.	0.1089 gm.	.72

(ii) Weight of zinc (II) complex = 0.2792 gm.

Weight of $Zn(NH_4)PO_4$ found = 0.1056 gm.

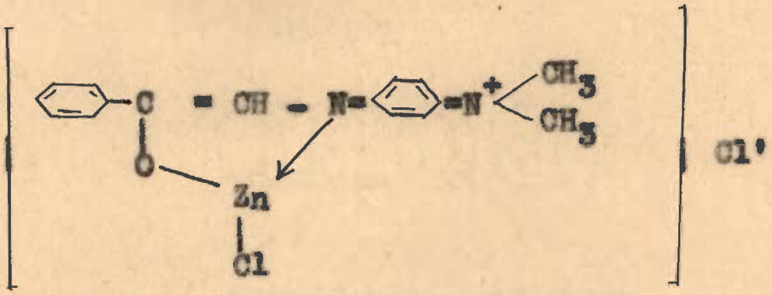
Theoretical weight of $Zn(NH_4)PO_4$ in the complex. = 0.1065 gm.

Calcd.	Found	Error %
0.1065 gm.	0.1056 gm.	.85

The above determination shows that one molecule of Zn(II) reacts with 1 molecule of the ligand to give the corresponding chelate.

STRUCTURE OF THE CHELATE

From the spectrophotometric data and chemical analysis, the following structure may be assigned to the Zn(II)-p-bromo phenacylidene p-dimethyl amino aniline chelate:



An alcoholic solution of the complex produces a white precipitate of silver chloride with an alcoholic solution of silver nitrate indicating the presence of chloride ion along with the complex.

The structure given above gets support from I.R. studies. The stretching vibrations of an aryl ketone & -CH= are at 1700 cm.$^{-1}$ and 1600 cm.$^{-1}$ respectively (Fig.15). In the spectrum of the chelate (Fig.31), the stretching frequency of the aryl ketone is lowered to 1625 cm.$^{-1}$ and of the -CH=N group to 1575 cm.$^{-1}$. This lowering of stretching frequencies evidently proves that these are the locations for interaction to form the corresponding chelate.

STABILITY CONSTANT AND FREE ENERGY CHANGE:

Consider the reaction between Zn(II) and p-bromo

Phenacylidene p-dimethyl amino aniline

$$ZnR \longrightarrow Zn + R$$

$C \qquad 0 \qquad 0$ (Initial concentration)

$C(1-\alpha) \qquad \alpha C \qquad \alpha C$ (Equilibrium concentration)

where C = concentration of the complex in mols. per litre, assuming no dissociation, while α is the degree of dissociation.

$\therefore$ Stability constant of the chelate(1:1):

$$K_S = \frac{C(1-\alpha)}{\alpha \cdot C \cdot \alpha . C} = \frac{(1-\alpha)}{C\alpha^2}$$

From the mole ratio curve b, Fig. 30

$$\alpha = \frac{0.58-0.49}{0.58} = 0.155$$

$$\therefore K_S = \frac{1-\alpha}{C\alpha^2} = \frac{1-0.155}{(.00025)(0.155)^2}$$

$$= 0.1407 \times 10^6$$

Temp. $= 29^\circ$

Change in Free Energy:

$$-\Delta F = R\,T \ln K_S = 1.987 x 302 x 2.303 \log 0.1407 x 10^6$$

$$= 7128 \text{ Cals/mol.} = 7.128 \text{ K cals/mol.}$$

Table -33 Vosburg and Cooper's Method for Zn(II) and P-Bromo phenacylidene P-dimethyl Amino Aniline (Both 0.625×10^{-3}M)

Concentration of Zn(II) solution = 0.625×10^{-3}M(C)

Concentration of the ligand = 0.625×10^{-3}M(C')

$$P = \frac{C'}{C} = 1$$

Ratio of metal to the ligand

Wave length mu	1:1 (a)	1:2 (b)	1:3 (c)	4:1 (d)	3:1 (e)	2:1 (f)
325	1.00	1.40	1.60	0.43	0.52	0.77
350	0.77	1.09	1.30	0.32	0.40	0.56
375	0.74	1.07	1.34	0.25	0.37	0.43
400	0.81	1.26	1.52	0.24	0.42	0.41
410	0.92	1.30	1.65	0.25	0.44	0.42
425	0.96	1.30	1.69	0.26	0.45	0.43
435	0.92	1.04	1.65	0.26	0.44	-
450	0.88	1.30	1.60	0.25	0.43	-
475	0.72	1.04	1.30	0.25	0.36	0.46
500	0.56	0.94	0.96	0.26	0.30	0.48
525	0.54	0.74	0.88	0.28	0.29	0.51
550	0.56	0.75	0.88	0.30	0.31	0.52
575	0.57	0.76	1.12	0.36	0.32	0.53
585	0.57	0.74	-	0.37	0.34	0.53
600	0.58	0.70	0.79	0.39	0.35	0.55
625	0.50	0.59	0.65	0.36	0.32	0.53

Fig. 26

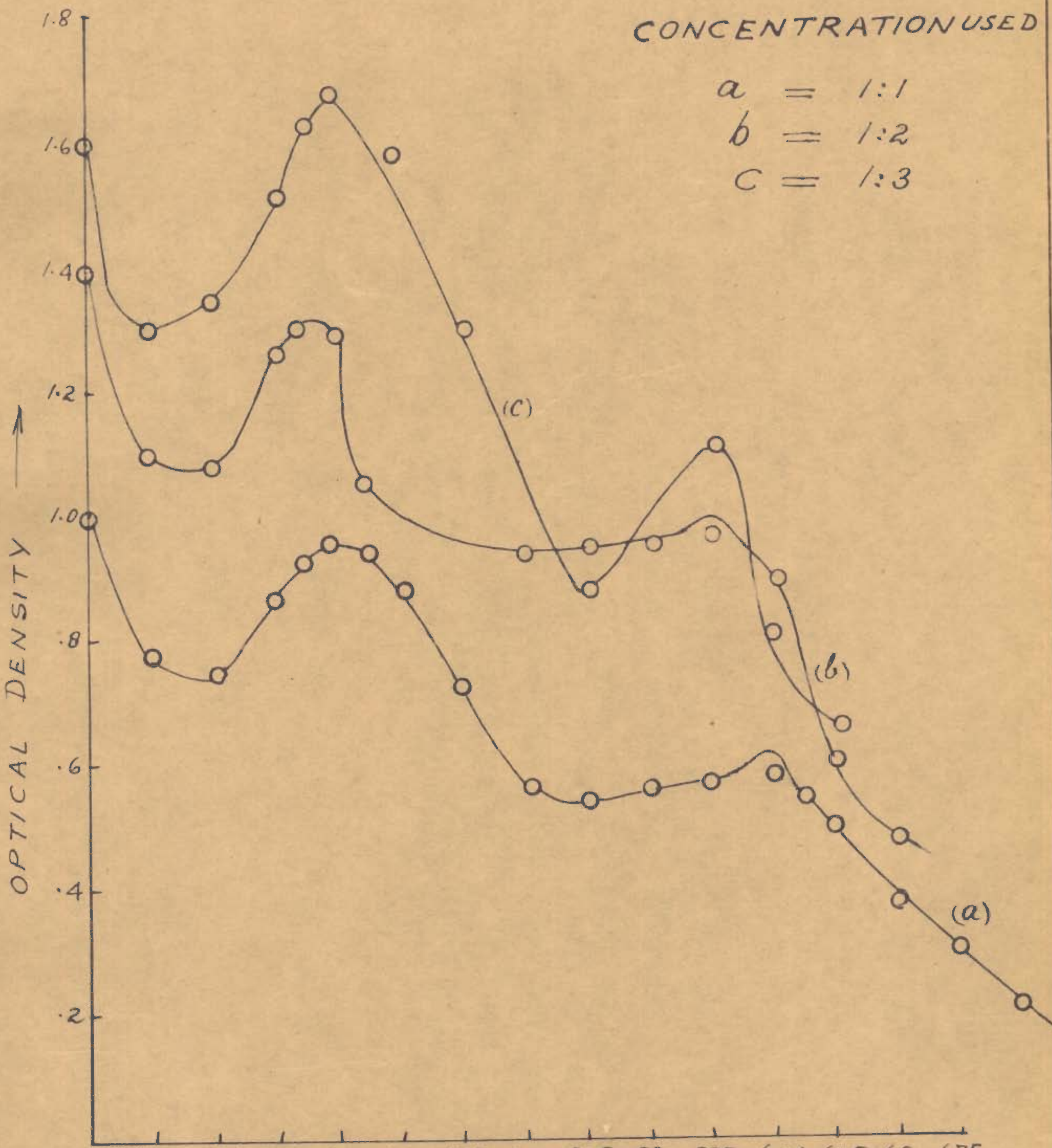


FIG. 26. ABSORPTION SPECTRA OF $ZnCl_2$ COMPLEX.

Table -34 Job's Method for Zn(II) and the ligand
(Both 1.25×10^{-3}M)

Concentration of 1.25×10^{-3}M Zn(II) solution = 1.25×10^{-3}M(

Concentration of the ligand = 1.25×10^{-3}M(

Wave length = 610 mu

(2 C.C. of the Mixture diluted to 10 ml.)

$$P = \frac{C'}{C} = 1$$

Peak at 1:1 :: Zn(II) : the ligand

Vol.of Zn(II) ml.	Vol.of the ligand	O.D. of the mixture	O.D. of the ligand.	Difference
-	-	C	b	(C-b)
1	9	0.41	0.36	0.05
2	8	0.385	0.314	0.071
3	7	0.375	0.290	0.085
4	6	0.275	0.180	0.095
5	5	0.22	0.12	0.100
6	4	0.20	0.107	0.093
7	3	0.16	0.077	0.083
8	2	0.13	0.062	0.068
9	1	0.100	0.049	0.051

Fig.27, Curve (a)

Table -35 Job's Method for Zu(II) and the Ligand (Both $1x10^{-3}M$)

Concentration of Zn(II) solution = $1x10^{-3}M(C)$

Concentration of the ligand = $1x10^{-3}M(C')$

(2 C.C. of the mixture diluted to 10 ml)

$$P = \frac{C'}{C} = 1$$

Peak at 1:1 :: Zu(II):the ligand

Vol.of Zu(II) ml.	Vol.of the ligand ml.	O.D. of the mixture C	O.D. of the ligand b	Difference (C-b)
1	9	0.36	0.34	0.02
2	8	0.34	0.30	0.04
3	7	0.27	0.217	0.053
4	6	0.23	0.167	0.063
5	5	0.20	0.13	0.070
6	4	0.175	0.107	0.066
7	3	0.12	0.062	0.058
8	2	0.09	0.046	0.044
9	1	0.06	0.035	0.025

Fig.27, Curve (b)

Table -36 Slope Ratio Method for $0.125\times10^{-3}M$ Zn(II) and $1.25\times10^{-3}M$ ligand, and vice-versa.

Set I
Volume of $0.125\times10^{-3}M$ ligand = 5 ml.
Strength of Zn(II) solution = $1.25\times10^{-3}M$

Set II
Volume of $0.125\times10^{-3}M$ Zn(II) solution = 5 ml.
Strength of the ligand. = $1.25\times10^{-3}M$

Set I		Set II	
Vol.of Zn(II) ml.	O.D.	Vol.of the ligand. ml.	O.D.
0.10	0.095	0.10	0.05
0.20	0.10	0.20	0.06
0.30	0.11	0.30	0.07
0.40	0.12	0.40	0.08
0.50	0.13	0.50	1.00

Curve(a) Fig.28 Curve (b)

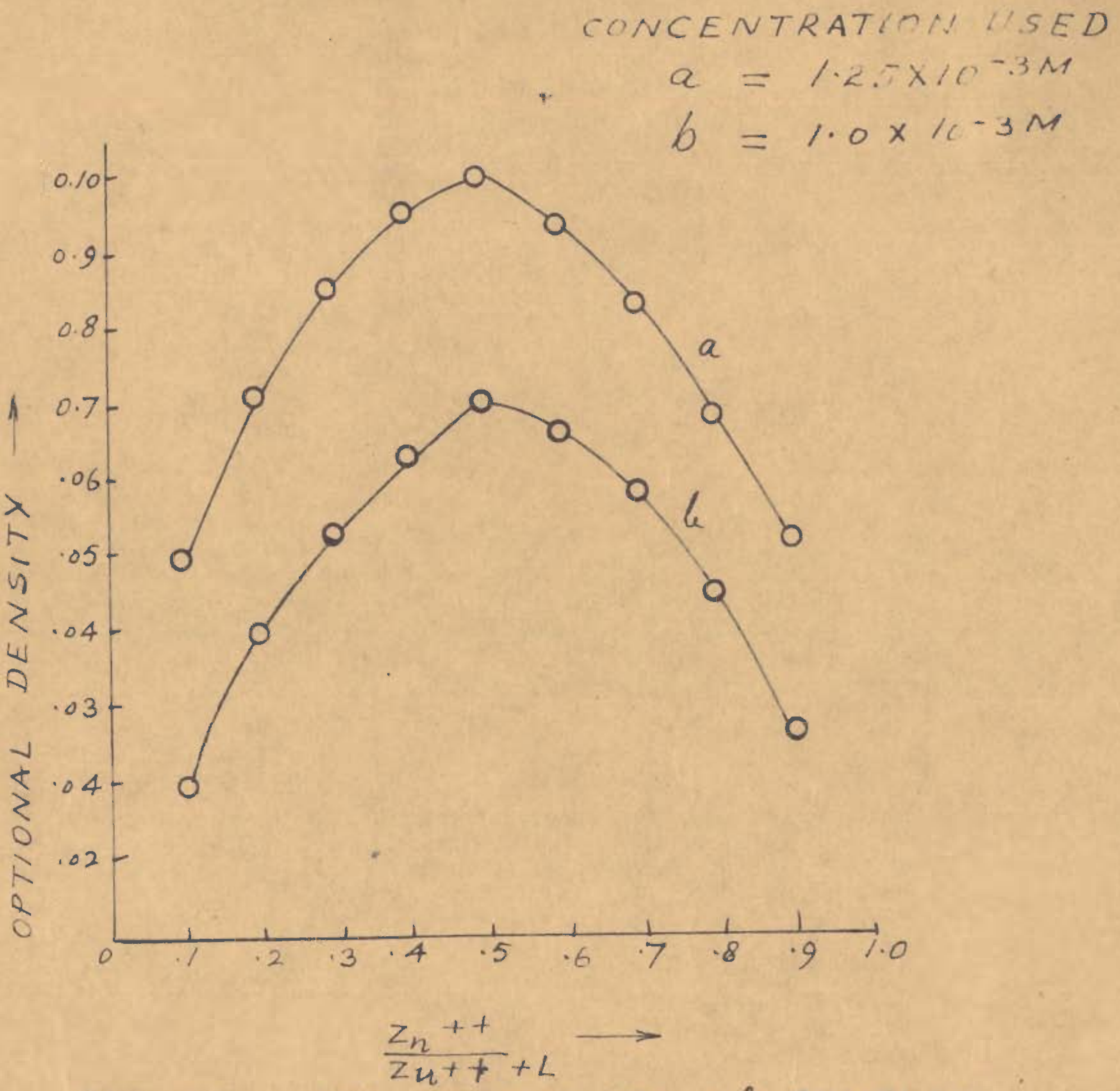


FIG. 27— COMPOSITION Zn Cl_2 COMPLEX BY JOB METHOD.

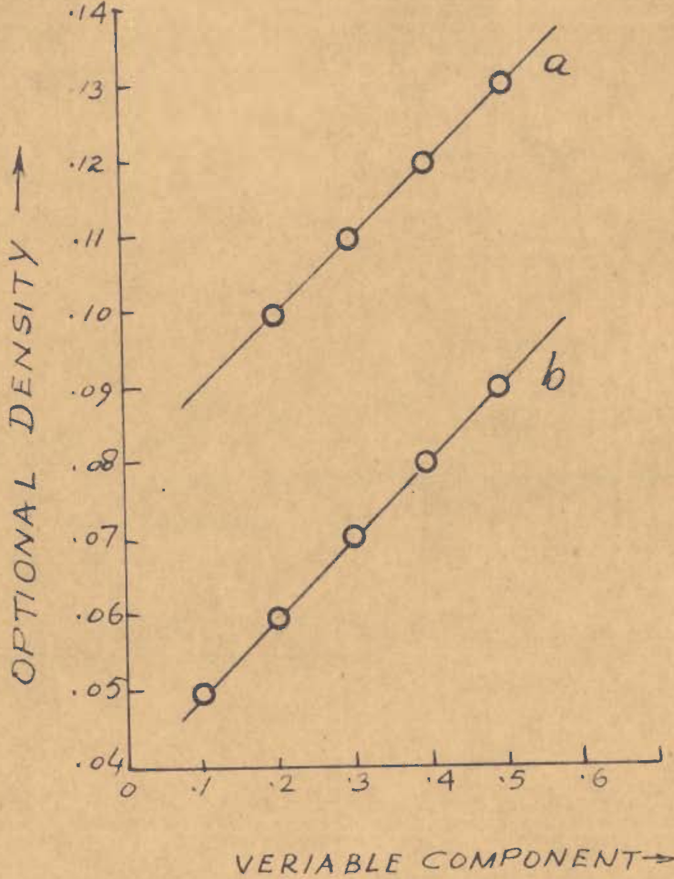


FIG. 28— COMPOSITION OF THE Zn Cl_2 COMPLEX BY SLOPE RATIO METHOD

Table-37 Slope Ratio Method for 0.10×10^{-3}M Zn(II) and 1.0×10^{-3}M ligand, and vice versa.

Set I Volume of 0.10×10^{-3}M ligand = 5 ml.
Strength of Zn(II) solution = 1.0×10^{-3}M

Set II Volume of 0.10×10^{-3}M Zn(II) solution = 5 ml.
Strength of the ligand = 1.0×10^{-3}M

Set I		Set II	
Vol. of Zn(II) ml.	O.D.	Vol. of the ligand ml.	O.D.
0.10	0.07	0.10	0.03
0.20	0.09	0.20	0.05
0.30	0.11	0.30	0.07
0.40	0.115	0.40	0.09
0.50	0.13	0.50	0.11

Curve (a) Fig.29 Curve (b)

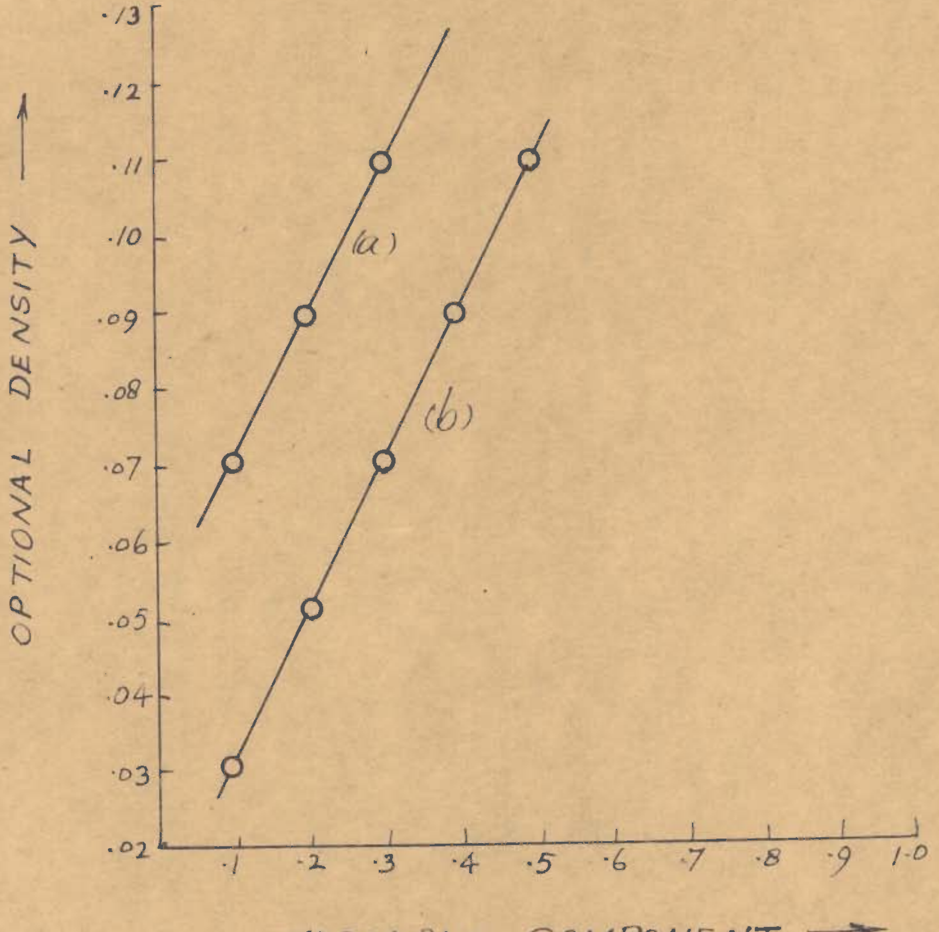


FIG. 28 – COMPOSITION OF THE $ZnCl_2$ COMPLEX BY [redacted] METHOD.

SLOPE RATIO

Table -38 Composition of the Complex by Mole Ratio Me

Strength of Zn(II) or the ligand solution = 1.25×10^{-3}M

Constant Volume of Zn(II) or the ligand = 2 ml.

Wave length = 600 mu

Set I		Set II	
Vol.of Zn ml.	O.D.	Volume of the ligand ml.	O.D.
0.40	0.21	0.40	0.09
0.80	0.23	0.80	0.19
1.00	0.24	1.00	0.23
1.20	0.245	1.20	0.29
1.60	0.25	1.60	0.39
2.00	0.27	2.00	0.49
2.40	0.29	2.40	0.55
2.80	0.295	2.80	0.58
3.20	0.295	2.80	0.585

Fig.30 Curve (a)

Table-39 Composition of the Complex by Mole Ratio Method.

Strength of Zn(II) or the ligand = 0.625x10^{-3}M

Constant volume of Zn(II) or the ligand. = 2 ml.

Wave length = 600 ml.

Set I		Set II	
Vol.of Zn(II) ml.	O.D.	Vol.of the ligand. m.l.	O.D.
0.40	0.07	0.40	0.20
0.80	0.14	0.80	0.22
1.20	0.21	1.20	0.24
1.60	0.26	1.60	0.26
2.00	0.28	2.00	0.28
2.40	0.36	2.40	0.29
2.80	0.36	2.80	0.295
3.00	0.39	3.00	0.295

Fig.30 Curve (b)

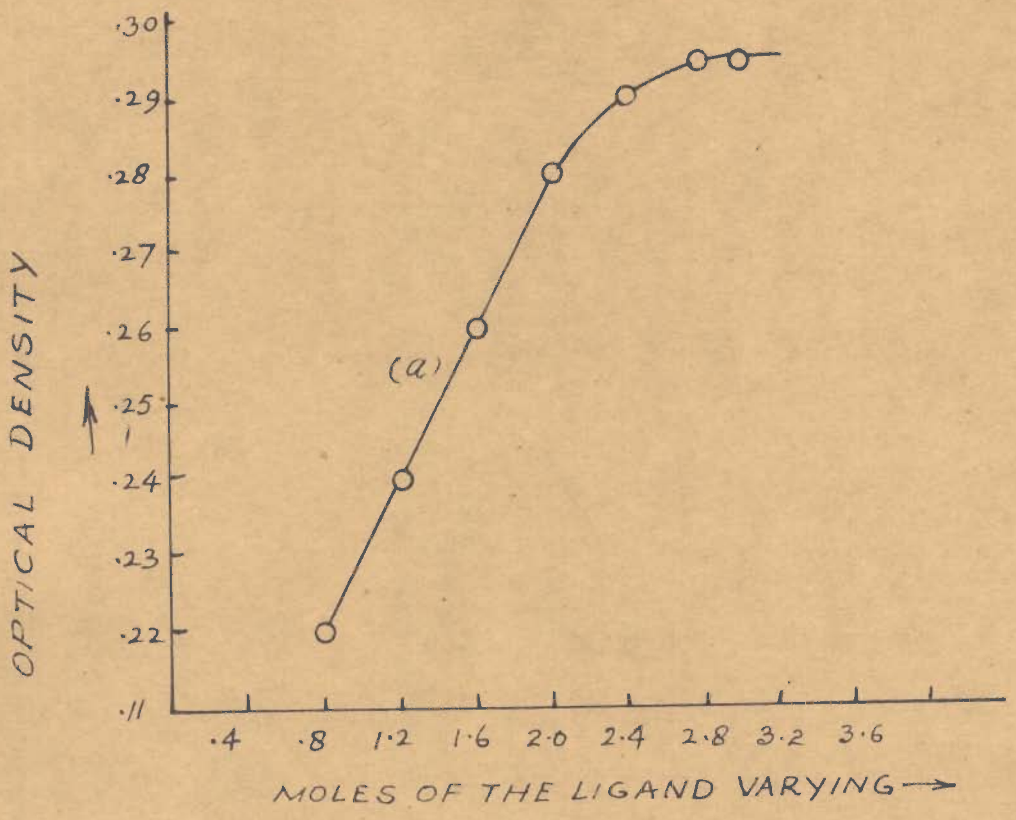


FIG.30(a)

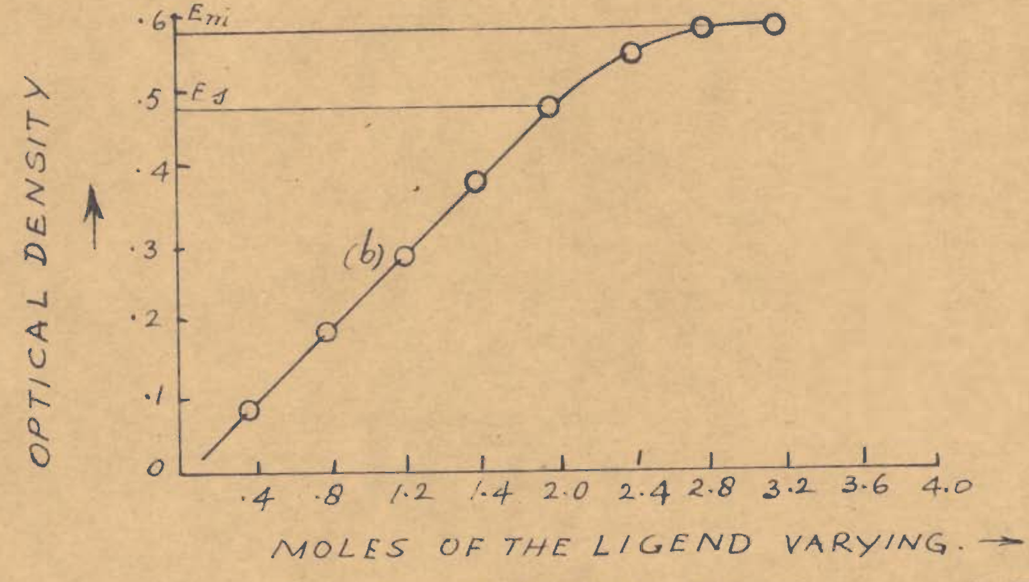
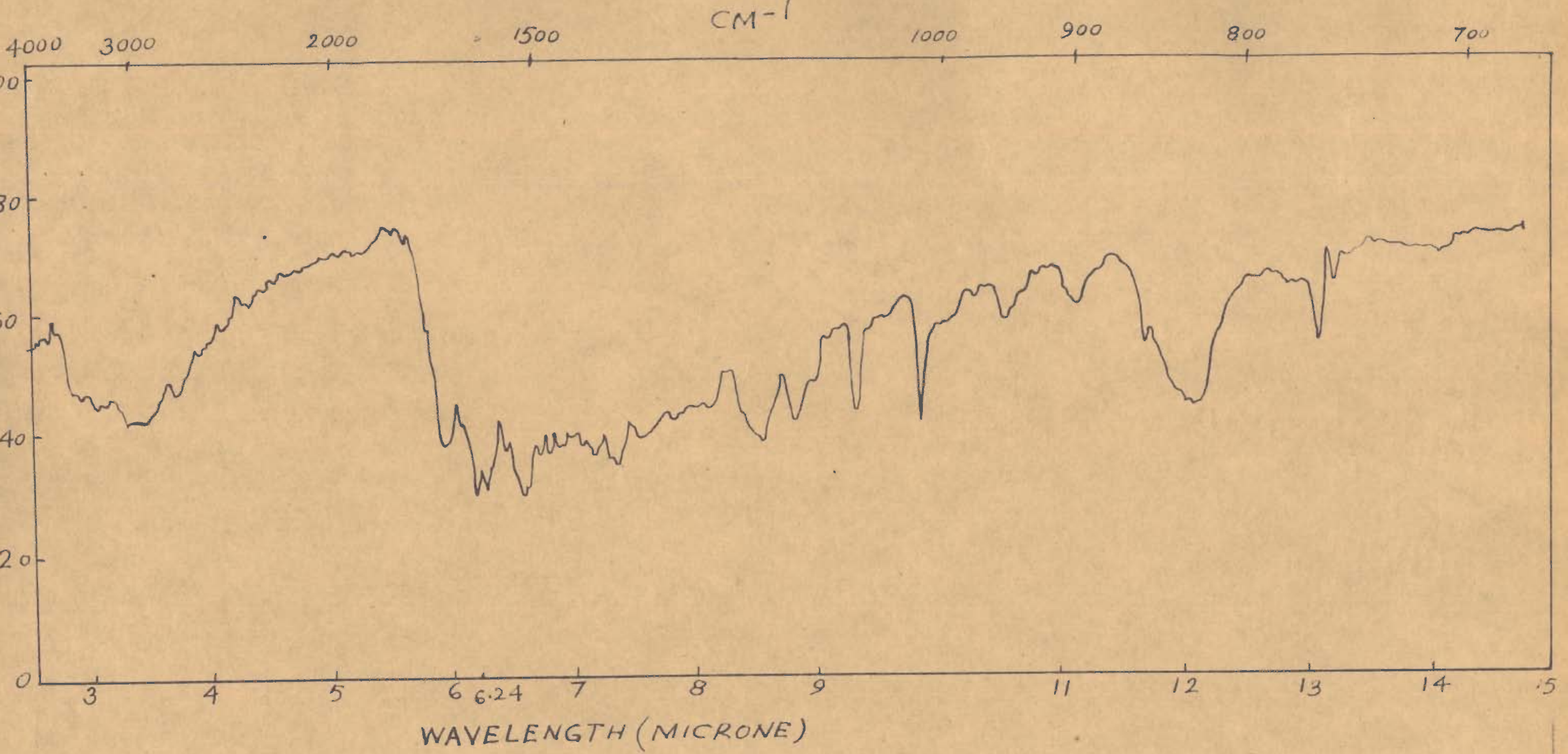


FIG. 30(b) COMPOSITION OF THE COMPLEX BY MOLE RATIO METHOD.



I.R. SPECTRUM OF p- BROMO PHENACYLIDENE p- DIMETHYL AMINO ANILINE-ZnII CHELATE.

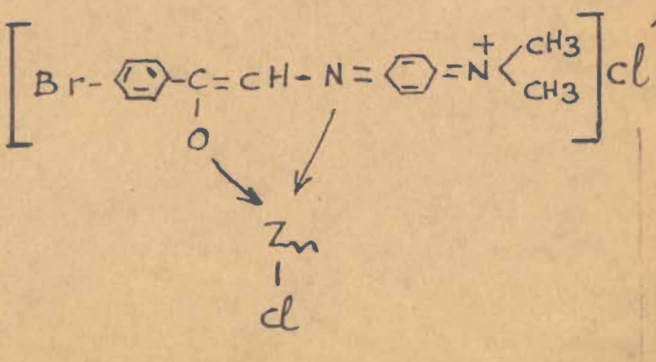


FIG- 31

TIN(IV) COMPLEX OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

Stannic chloride, like other Lewis acids, react with p-bromo phenacylidene p-amino dimethyl aniline to give a green coloured chelate where $\lambda_{max.}$ of the ligand shifts from 425 mu to 600 mu due to bathochromic effect. The composition of the chelate was determined by spectrophotometry.

EXPERIMENTAL

A stock solution of the ligand (.05M) was prepared in acetone. Stannic chloride solution was prepared by dissolving stannic chloride pentahydrate (E.Merck) in acetone and Sn(IV) estimated gravimetrically as SnO_2.50 ml. of the solution was diluted with water to 100 ml. It was then neutralised by ammonium hydroxide till a slight permanent white precipitate was formed. 50 ml. of saturated ammonium nitrate was added to dissolve metastannic acid and this was diluted to 400 ml. The contents were boiled and stirred constantly. The precipitate so formed was digested, filtered, dried, ignated and finally weighed as SnO_2.

NATURE OF THE COMPLEX

Vosburg and Cooper's method was applied to ascertain the number of chelates formed. $\lambda_{max.}$ due to the ligand was found to be at 425 mu while that of the chelate at 600 mu. (Fig.32). Therefore, 600 mu was selected as the appropriate wave length to study the composition. Absorbance measurements were carried out with the help of Bausch and Lomb 'spectronic 20' spectrophotometer while I.R. was recorded on Perkin-Elmer infracord.

STOICHIOMETRY OF THE COMPONENTS

For determining the composition of the Sn(IV) chelate, the methods of continuous variation, slope ratio and mole ratio were employed.

In the continuous variation method, optical densities of a series of solutions prepared by mixing X ml. of $0.55\text{x}10^{-3}$M $SnCl_4$ solution with (10-X)ml. of $0.555\text{x}10^{-3}$M of the ligand solution. The total volume was kept constant at 10 ml. (where X varied by 1.0-9 ml.) were determined at 600 mu, employing acetone as a blank. The peak in the curve a (Fig.33) shows the molar composition of the $SnCl_4$ and p-bromo phenacylidene p-dimethyl amino aniline complex as 1:2. The O.D. of Sn(IV) solution was negligible at 600 mu (Table 41, Fig.33).

SLOPE RATIO METHOD

This method gave similar results as obtained from Job's continuous variation method for the composition of the chelate. (Table 43-45, Figs. 34-36).

MOLAR RATIO METHOD

This method was employed to determine the composition stability constant and change in free energy of the chelate.

The results are given in Table 46-48, Fig. 37 and Curves a, b and c.

CHEMICAL ANALYSIS

The chelate was prepared and isolated by concentrating 1:2 (mole) mixture of Sn(IV) and the ligand. It was crystallised from acetonitrile. A known amount of it was decomposed by concentrated nitric acid. The mixture was evaporated to dryness and the residue dissolved in concentrated hydrochloric acid. It was diluted with water and Sn(IV) was estimated from the solution as SnO_2 gravimetrically.

ESTIMATION OF Sn(IV) IN THE COMPLEX

(i) Weight of the complex = 0.6946 gm.
Weight of SnO_2 obtained = 0.1125 gm.
Theoretical weight of SnO_2 in the complex. = 0.1134 gm.

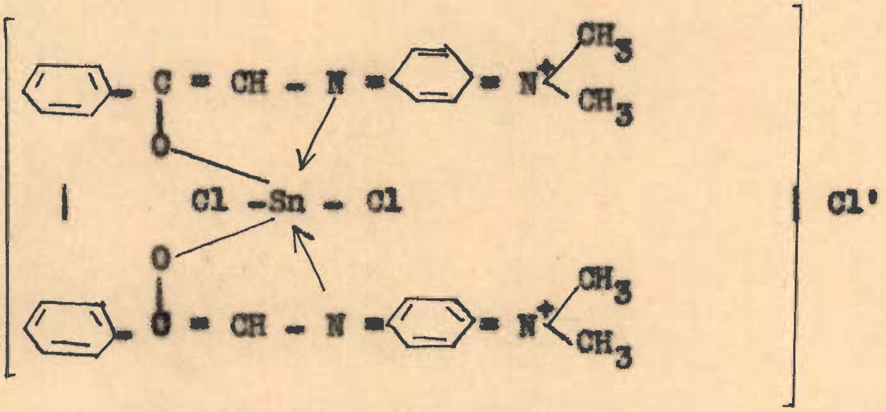
Calcd.	Found	Error %
0.1134 gm.	0.1125 gm.	0.80

From the chemical analysis, it may be concluded that one molecule of Sn(IV) combines with two molecules of the ligand to form the chelate.

STRUCTURE OF THE CHELATE

As in the case of other Lewis acids stannic chloride also introduces conjugation on account of resonance. This results in a bathochromic shift and the chelation takes place due to the increasing negative tendency at the >C=O group of the ligand.

In accordance with the composition, the following possible structure may be assigned to the chelate.



This structure clearly shows that Sn(IV) has a coordination number six in the chelate.

An alcoholic solution of the chelate gave a white precipitate of silver chloride with an alcoholic solution of silver nitrate, thereby indicating the presence of ionisable chloride ions.

I.R. spectra of the ligand shows a >C=O stretching frequency at 1700 cm^{-1} characteristic of an aryl ketone and another stretching frequency at 1600 $cm.^{-1}$ due to presence of a C=N group. From the spectrum of the chelate (Fig.38) , it is seen that the lowering of the frequencies 1575 $cm.^{-1}$ and 1525 $cm.^{-1}$ respectively takes place. The lowering of frequencies at these centres indicates the seats of the interaction of the metal ion with the ligand. The spectrum of the ligand also exhibits doublets around 830^{-1} (Fig.15) while only one peak is shown in the spectrum of the chelate. This may be due to the change of one of the two benzenoid rings to a quinonoid one. Further, there is some perturbation in the phenyl group skeleton vibration region between 1550 $cm.^{-1}$ and 1400 cm^{-1} in the chelate. This is expected from the proposed structure.

STABILITY CONSTANT AND FREE ENERGY CHANGE

From various methods of absorption measurements, it has been found that 1 mole of Sn(IV) combines with 2 moles of the ligand to form the corresponding chelate. The dissociation constant of the complex may be expressed as:

$Sn\ R_2 \longrightarrow$	Sn	$+2R$	
C	0	0	(Initial concentration)
$C(1-\alpha)$	$C\alpha$	$2C\alpha$	(Equilibrium concentration)

The stability constant was deduced from the following equation:

$$K_S = \frac{C(1-\alpha)}{C\alpha\ (2C\alpha)^2} = \frac{C(1-\alpha)}{C\alpha\ 4C^2\ \alpha^2} = \frac{1-\alpha}{4\alpha^3\ C^2}$$

where C is the concentration of the complex in moles per litre and α is the degree of dissociation.

The value of α can be deduced from the relationship:

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{0.30 - 0.28}{0.30} = .066 \text{(Fig.37 Curve a)}$$

where E_m is the maximum absorbance of a given amount of Sn(IV) in the presence of a large excess of the ligand, which assures that all the Sn(IV) is bound as the complex. E_s is the value obtained when the same amount of Sn(IV) is mixed with two moles of the ligand i.e. 1:2.

$$\therefore \quad E_S = \frac{1 - \alpha}{4\alpha^3 C^2} = \frac{1 - 0.066}{4(0.066)^3(.000125)^2}$$

$$= 0.5199\text{x}10^{11}$$

Temperature=33°C

Change in free energy:

$$- \Delta F = \text{R.T.ln } E_S = 1.987 \times 306 \times 2.303 \log 0.5199\text{x}10^{11}$$

$$= 15000 \text{ cals/mol.}$$

$$= 15.00 \text{ K cals/mol.}$$

Table -40 Vosburg and Cooper's Method for Sn(IV) and P-Bromo Phenacylidene P-dimethyl Amino Aniline (Both 1x10^{-3}M)

Concentration of Sn(IV) solution = 1x10^{-3}M(C)
Concentration of the ligand = 1x10^{-3}M(C')

$$P = \frac{C'}{C} = 1$$

Wave length m	1:1 (a)	1:2 (b)	1:3 (c)	1:4 (d)	4:1 (e)	3:1 (f)	2:1 (g)
330	1.02	1.45	1.70	1.70	0.44	0.50	0.72
350	0.90	1.30	1.52	1.60	0.38	0.43	0.63
375	0.75	1.15	1.34	1.45	0.31	0.36	0.52
400	0.70	1.15	1.39	1.52	0.27	0.31	0.47
425	0.68	1.15	1.40	1.52	0.26	0.30	0.45
450	0.64	1.09	1.30	1.45	0.24	0.29	0.42
475	0.56	0.90	1.09	1.15	0.21	0.25	0.39
500	0.50	0.70	0.81	0.85	0.20	0.24	0.26
525	0.54	0.69	0.79	0.82	0.22	0.26	0.38
550	0.59	0.75	0.82	0.85	0.25	0.30	0.43
575	0.66	0.76	0.83	0.83	0.28	0.33	0.46
585	0.67	0.75	0.80	0.81	0.29	0.34	0.48
600	0.68	0.72	0.77	0.75	0.29	0.35	0.49
615	0.64	0.65	-	0.67	0.28	0.34	0.47
625	0.62	0.60	-	0.59	0.28	0.32	0.45
650	0.54	0.45	0.44	0.37	0.24	0.29	0.40
675	0.43	0.33	0.32	0.25	0.19	0.24	0.34

Fig.32

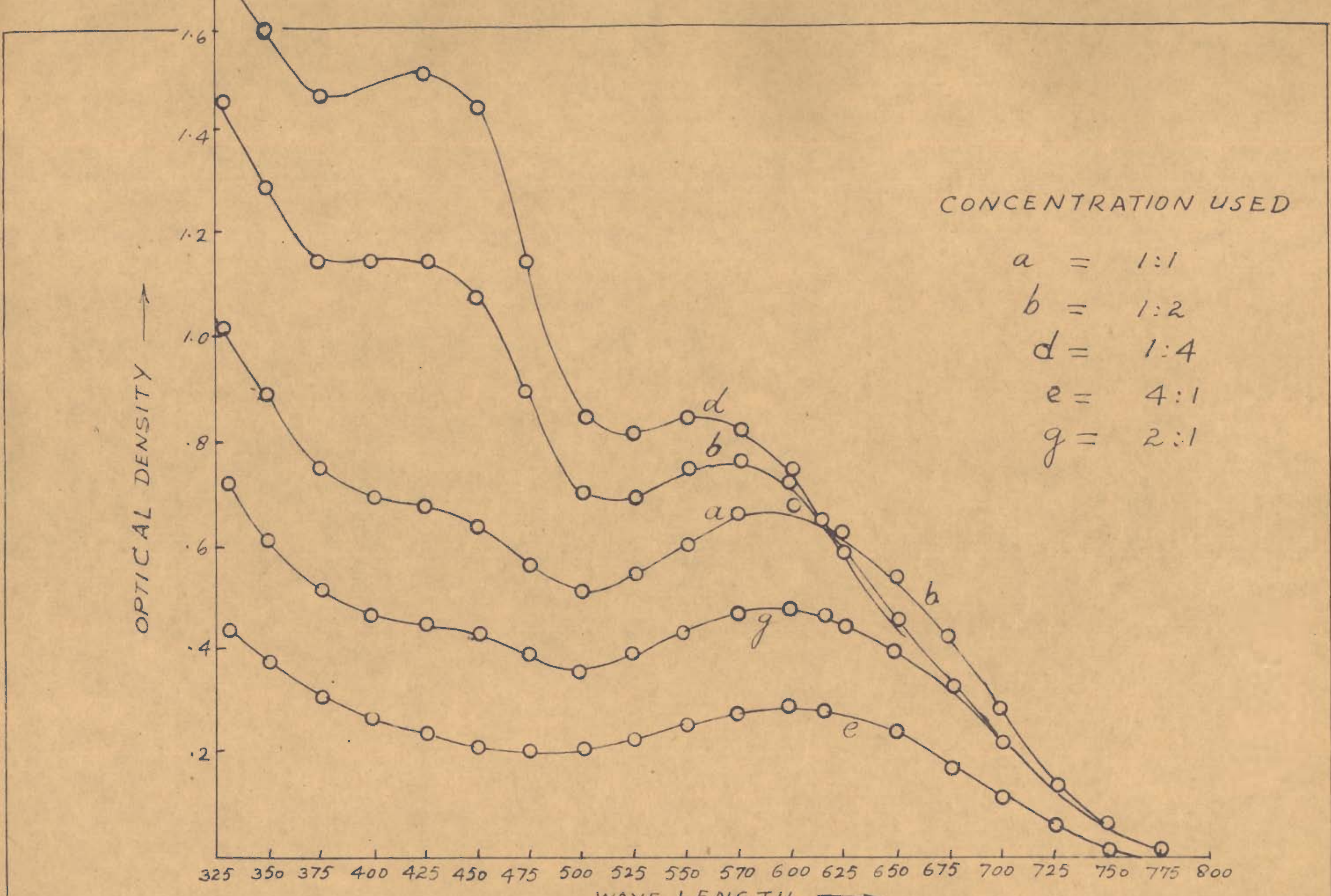


FIG. 32 ABSORPTION SPECTRA OF $SnCl_4$ COMPLEX.

Table-41 Job's Method for Sn(IV) and the ligand (Both 0.5×10^{-3}M)

Concentration of $SnCl_4$ solution = 0.5×10^{-3}M(C)

Concentration of the ligand = 0.5×10^{-3}M(C')

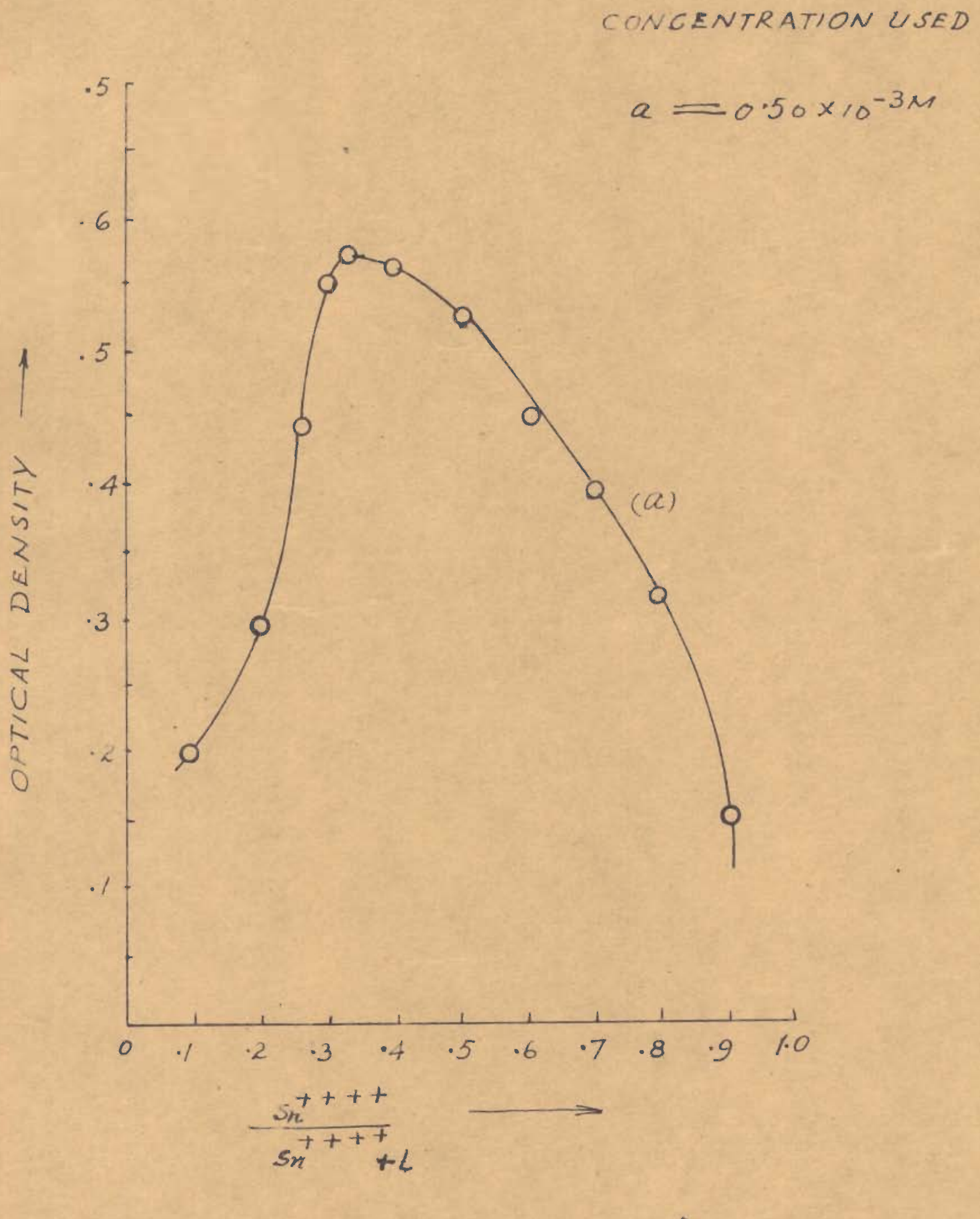
Wave length = 600 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Sn(IV): the ligand

Vol.of sn (IV) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of the ligand	Difference
-	-	C	b	(C-b)
1	9	0.42	0.38	0.04
2	8	0.415	0.355	0.06
3	7	0.410	0.30	0.11
3.33	6.67	0.405	0.29	0.115
4	6	0.372	0.26	0.112
5	5	0.305	0.20	0.105
6	4	0.26	0.17	0.09
7	3	0.225	0.145	0.08
8	2	0.145	0.08	0.065
9	1	0.065	0.03	0.035

Fig.33, Curve (a)



CONCENTRATION USED

$a = 0{\cdot}50 \times 10^{-3}M$

FIG. 33 – COMPOSITION OF $S_n\,Cl_4$ COMPLEX BY JOB'S METHOD.

Table -42 Job's Method for Sn(IV) and the ligand
(Both $0.555x10^{-3}M$)

Concentration of $SnCl_4$ solution = $0.555x10^{-3}M(C)$

Concentration of the ligand = $0.555x10^{-3}M(C')$

Wave length = 600 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2:: Sn(N) : the ligand

Vol.of Sn(IV) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of the ligand	Difference
-	-	C	b	(C-b)
1	9	0.465	0.420	0.045
2	8	0.475	0.365	0.11
3	7	0.45	0.32	0.13
3.33	6.67	0.44	0.30	0.14
4	8	0.37	0.275	0.095
5	5	0.32	0.23	0.09
6	4	0.31	0.225	0.085
7	3	0.21	0.14	0.07
8	2	0.145	0.08	0.065
9	1	0.06	0.02	0.04

Table -43 Slope Ratio Method for 0.5×10^{-3}M Sn(IV) and 5×10^{-3}M ligand, and vice versa.

Set I Volume of 0.5×10^{-3}M ligand = 8 ml.
Strength of Sn(IV) solution = 5×10^{-3}M

Set II Volume of 0.5×10^{-3}M Sn(IV) solution = 8 ml.
Strength of the ligand = 5×10^{-3}M

Set I		Set II	
Vol. of Sn(IV)	O.D.	Vol. of the ligand.	O.D.
0.10	0.16	0.10	0.39
0.20	0.31	0.20	0.52
0.30	0.47	0.30	0.58
0.40	0.58	0.40	0.65

Curve (a) Fig.34 Curve (b)

Table -44 Slope Ratio Method for 0.33×10^{-3}M Sn(IV) and 3.33×10^{-3}M Ligand, and Vice-Versa.

Set I- Volume of 0.33×10^{-3}M ligand = 8 ml.
Strength of Sn(IV) solution = 3.33×10^{-3}M

Set II- Volume of 0.33×10^{-3}M Sn(IV) solution. = 8 ml.
Strength of the ligand = 3.33×10^{-3}M

Set I		Set II	
Vol. of Sn(IV) ml.	O.D.	Vol. of the ligand.	O.D.
0.10	0.25	0.10	0.09
0.20	0.29	0.20	0.18
0.30	0.33	0.30	0.27
0.40	0.36	0.40	0.36

Curve (a) Fig-35 Curve (b)

Table -45 Slope Ratio Method for 0.25×10^{-3}M Sn(IV) and 2.5×10^{-3}M ligand, and vice-versa.

Set I Volume of 0.25×10^{-3}M ligand = 8 ml.
Strength of Sn(IV) solution = 2.50×10^{-3}M

Set II Volume of 0.25×10^{-3}Sn(IV) solution = 8 ml.
Strength of the ligand = 2.50×10^{-3}M

Set I		Set II	
Vol.of Sn(IV) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.10	0.18	0.10	0.05
0.20	0.22	0.20	0.145
0.30	0.265	0.30	0.22
0.40	0.28	0.40	0.29

Curve (a) Fig.36 Curve (b)

Table -46 Composition of the Complex by Mole Ratio Method

Strength of Sn(IV) or the ligand solution = 1.25×10^{-3}M
Constant volume of Sn(IV) or the ligand = 1 ml.
Wave length = 600 mu

Set I		Set II	
Vol.of Sn(IV) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.10	0.09	0.40	0.05
0.20	0.10	0.80	0.11
0.30	0.11	1.20	0.165
0.40	0.115	1.60	0.22
0.50	0.12	2.00	0.28
0.60	0.12	2.20	0.29
0.70	0.12	2.40	0.30
0.80	0.12	2.60	0.30

Fig. 37 Curve (a)

Table -47 Composition of the Complex by Mole Ratic Metho

Strength of Sn(IV) or the ligand = 2.0×10^{-3}M

Constant Volume of Sn(IV) or the ligand. = 1 ml.

Wave length = 600 mu

Vol.of Sn(IV) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.10	0.10	0.10	0.04
0.20	0.20	0.20	0.05
0.30	0.21	0.30	0.09
0.40	0.22	0.40	0.11
0.50	0.225	0.50	0.15
0.60	0.235	1.00	0.28
0.70	0.260	1.50	0.40
0.80	0.265	2.00	0.41
0.90	0.27	2.50	0.56
1.00	0.27	3.00	0.58
-	-	3.20	0.58

Fig.37 Curve (b)

Table 48 Composition of the Complex by Mole Ratio Method

Strength of Sn(IV) or the ligand = 2.5×10^{-3}M

Constant Volume of Sn(IV) or the ligand. = 1 ml.

Wave Length = 600 mu

Set I		Set II	
Vol. of Sn(IV) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.10	0.24	0.40	0.10
0.20	0.25	0.80	0.245
0.30	0.27	1.20	0.37
0.40	0.275	1.60	0.45
0.50	0.290	2.00	0.57
0.60	0.290	2.20	0.62
0.70	0.290	2.30	0.64
0.80	0.290	2.40	0.66

Fig.37 Curve (C)

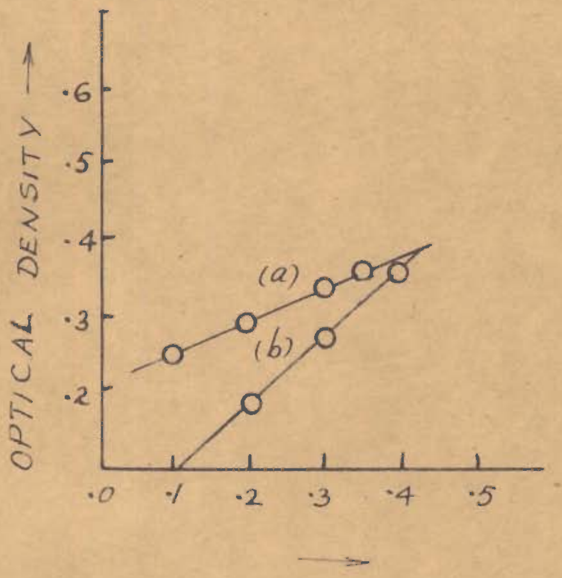


FIG. 35 VARIABLE COMPONENT

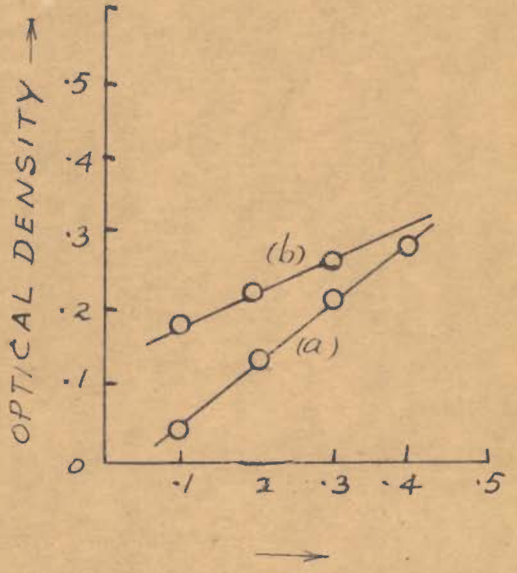


FIG-36 VARIABLE COMPONENT

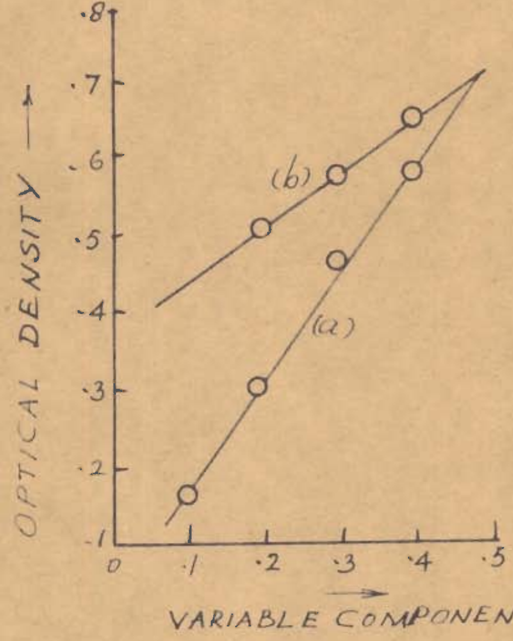


FIG. 34. COMPOSITION OF THE COMPLEX BY STOPE RATIO METHOD.

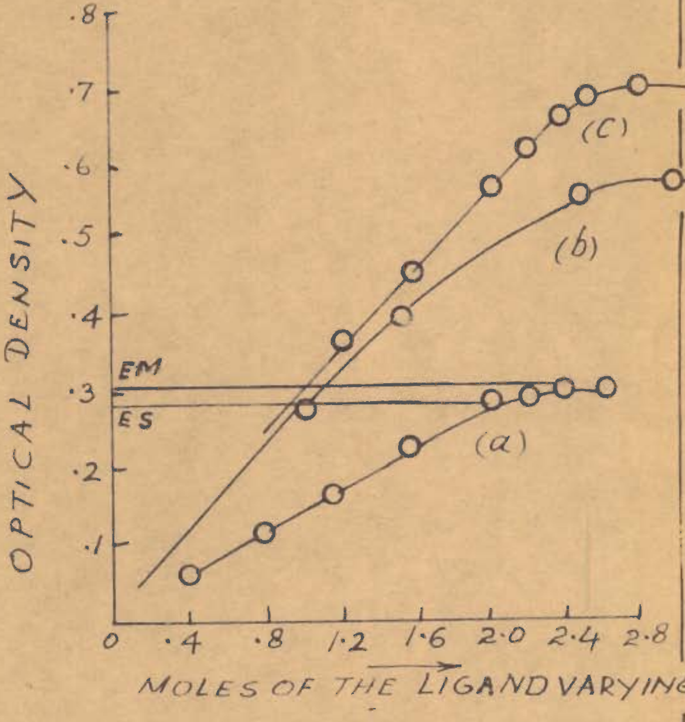
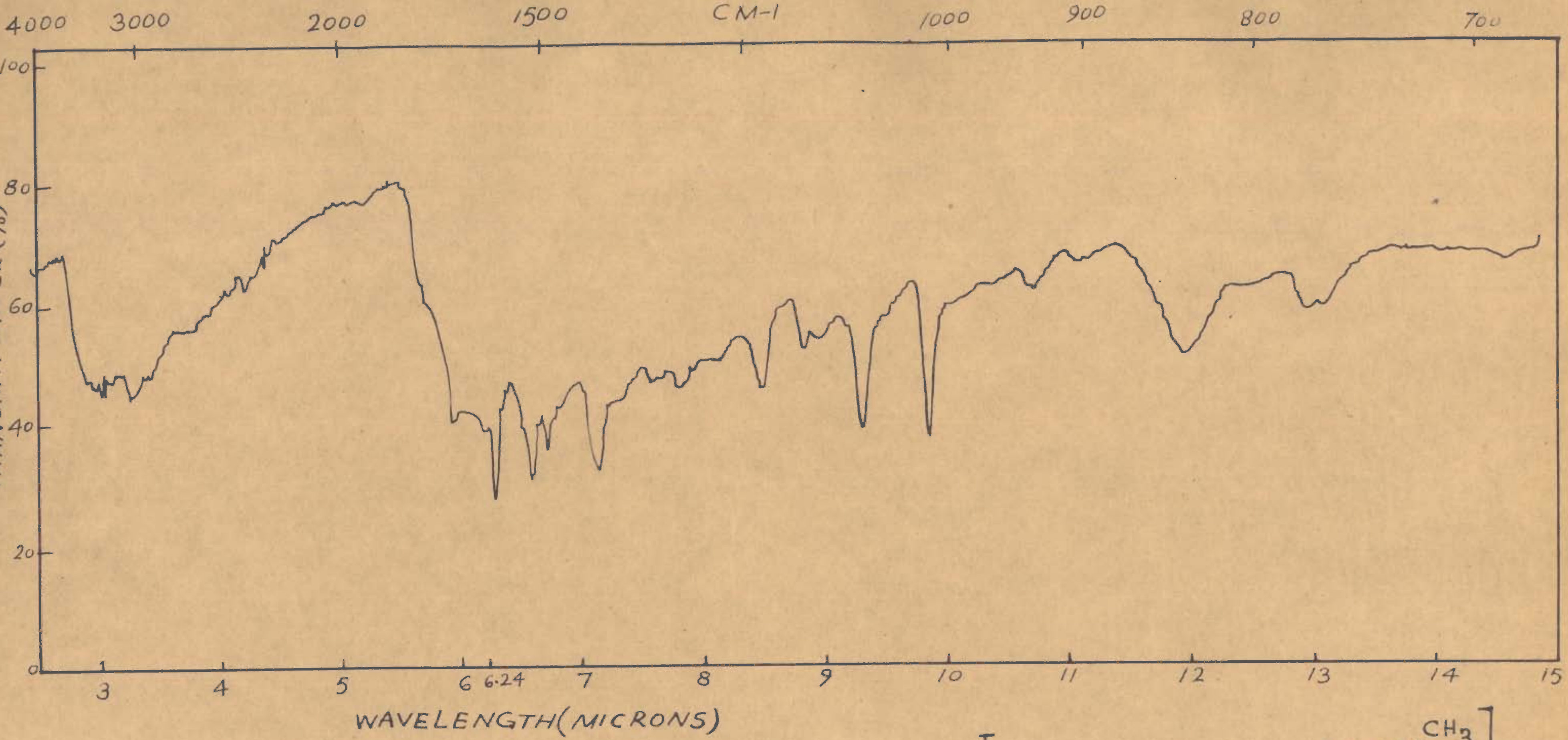
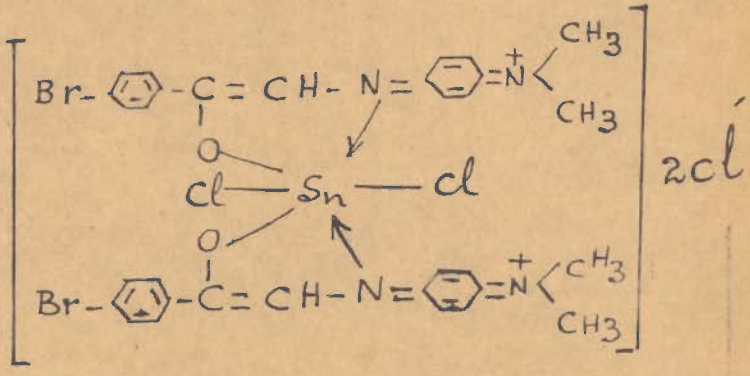


FIG. 37 COMPOSITION OF THE COMPLEX BY MOLE RATIO METHOD





I. R. SPECTRUM OF p.BROMO PHENACYLIDENE p.DIMETHYLAMINO ANILINE– Sn(IV) CHELATE.

FIG-38

ANTIMONY(V) COMPLEX OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

Antimony penta chloride interacts with p-bromo phenacylidene p-dimethyl amino aniline to form a violet chelate. During this reaction, the electronegativity of the >C=O group of the ligand is enhanced and consequently it becomes more reactive towards the metal ion. A bathochromic shift from 425 mu to 550 mu takes place. The latter wave length was selected to study the composition of the chelate.

EXPERIMENTAL

A stock solution of the ligand (0.05M) was prepared in acetone. Antimony penta chloride (.01M) solution was also prepared in acetone and Sb(V) contents estimated gravimetrically as Sb_2S_3(1).

NATURE OF THE COMPLEX

Vosburg and Cooper's method was employed to find out the number of chelates formed during complexation. By plotting optical densities of the ligand against wave lengths, $\lambda_{max.}$ was obtained at 425 mu. Solutions of Sb(V) and the ligand were prepared in different ratios and their absorbances measured at different wave lengths. From the curve the $\lambda_{max.}$ for the chelate was observed at 600 mu (Fig. 39), which was selected as the proper wave length to find out the composition, stability constant and other thermodynamic properties of the chelate formed. Since only one $\lambda_{max.}$ was observed for the above solution, it is evident that only one chelate has been formed.

STOICHIOMETRY OF THE COMPONENTS

Job's continuous variation, slope ratio and molar ratio methods were employed for studying the composition of the chelate and it was concluded from these methods that one mole of Sb(V) combines with two moles of the ligand to form the corresponding chelate.

In Job's continued variation method, the following sets of mixtures were prepared and their optical densities measured at 600 mu.

1,2,3 ... 8,9 ml. of 0.555×10^{-3}M Sb(V) solution.
9,8,7 ... 2,1 ml. of 0.555×10^{-3}M ligand solution.

Same volumes of Sb(V) and the ligand were taken and the total volume in all the solutions were kept constant at 10 ml. The optical density of the metal ion at 600 mu was negligible. By plotting a graph between the difference of the optical densities of the above mixtures and the corresponding value of the ligand against the composition of Sb(V) and the ligand, a peak was obtained which showed that the composition was 1:2 (Sb(V):the ligand). Similar results were obtained at different concentrations of the metal ion and the ligand, (Fig.40, curves a and b).

SLOPE RATIO METHOD

This method gave similar results as obtained from Job's continuous variation method for determining the composition of the chelate (Table 52-53 and Figs. 41-42).

MOLAR RATIO METHOD

This method was employed for determining the composition, the stability constant and other thermodynamic data of the chelate (Table 54-55, Fig.43).

CHEMICAL ANALYSIS

When solutions of Sb(V) and p-bromo phenacylidene p-dimethyl amino aniline were mixed in the ratio of 1:2, a green solution was obtained which on concentration in vacuum afforded a violet sticky mass. This was washed several times with petroleum ether (60-80°) to free it from the resinous mass and a solid was obtained. It was then crystallized from acetonitrile. A known amount of the chelate was decomposed by boiling with concentrated nitric acid and then evaporated to dryness. After cooling, the residue was triturated with water and then diluted. Sb(V) contents in the resulting solution were estimated gravimatrically as Sb_2S_3.

ESTIMATION OF Sb(V) AS Sb_2 S_3 IN THE COMPLEX

(i) Weight of the complex = 0.8004 gm.
Weight of Sb_2S_3 obtained = 0.1272 gm.
Theoretical weight of Sb_2S_3 = 0.1281 gm.

Calcd.	Found	Error %
0.1281 gm.	0.1272 gm.	0.70

(ii) Weight of the complex = 0.6674 gm.

Weight of Sb_2S_b obtained = 0.1062 gm.

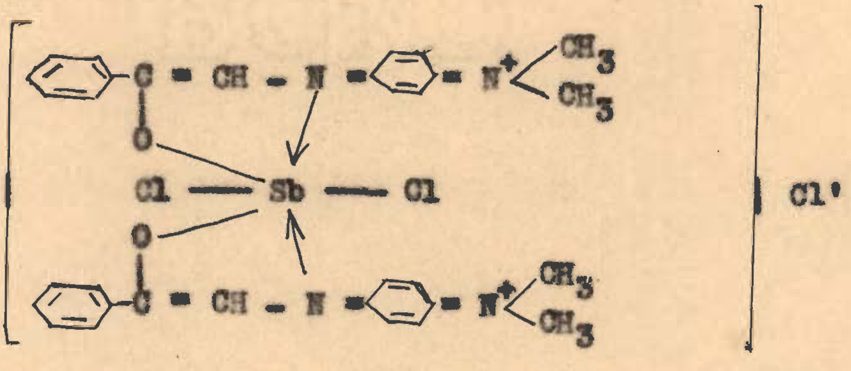
Theoretical weight of Sb_2S_3 = 0.1802 gm.

Calcd.	Found	Error %
0.1068 gm.	0.1062 gm.	0.56

From the chemical analysis as well as absorption measurement studies , it is quite evident that one molecule of Sb(V) combines with 2 molecules of the ligand to form the chelate.

STRUCTURE OF THE CHELATE

From the above data, the following structure may be assigned to the chelate:-



An alcoholic solution of silver nitrate gave a white precipitate with an alcoholic solution of the complex, indicating thereby the presence of chloride ions.

The above structure for the chelate was further confirmed by I.R. Study of the ligand and the chelate. In Fig.15 the stretching vibration characteristic of an aryl ketone is exhibited at 1700 cm^{-1} and that of a C=N at 1600 cm^{-1}. For the complex (Fig.44) these frequencies are lowered to 1625 cm^{-1} and 1555 cm^{-1} respectively. This lowering of stretching frequencies indicates that the > C=O and the C=N are the only positions for the chelation. Around 830 cm^{-1}, the ligand exhibits out of plane vibration as a doublet which on complexation appears as a singlet. This may be due to conversion of one of the benzenoid rings into a quinonoid.

STABILITY CONSTANT AND FREE ENERGY CHANGE

The different absorption measurements have shown that 1 mole of Sb(V) combines with 2 moles of the ligand to form the corresponding chelate. Consider the dissociation of Sb(V)-the ligand chelate:

$SbR_2 \longrightarrow$	Sb	+2R	
C	0	0	(Initial concentration)
$C(1-\alpha)$	$C\alpha$	$2C\alpha$	(Equilibrium concentration)

Where C is the concentration of the complex and α is the degree of dissociation.

$$\alpha = \frac{E_m - E_s}{E_m}$$

Where E_m and E_s has

where E_m and E_s have usual significance.

$$\therefore \quad \alpha = \frac{0.53-0.47}{0.53} = 0.113 \text{ (Fig.43, Curve a)}$$

$$\therefore \quad E_S = \frac{C(1-\alpha)}{C\alpha(2C\alpha)^2} = \frac{1-\alpha}{4\alpha^3\ C^2}$$

$$= \frac{1 - 0.113}{4(0.113)^3\ (0.00025)^2} = 0.2459\text{x}10^{10}$$

$$C = \frac{1\text{x}2.50 \text{ x } 10^{-3}}{10}$$

$= .00025$ gm/litre.

Temp. $= 23^0$

$\therefore$ Change in free energy:

$$- F = RT \ln E_S$$

$= 1.987 \text{ x } 296 \text{ x } 2.303 \log 0.2459\text{x}10^{10}$

$= 12720$ cals./mol.

$= 12.72$ K Cals/mol.

Table-49 Vosburg and Cooper's Method for Sb(V) and p-Bromo Phenacylidene p-dimethyl Amino Aniline
(Both 0.5×10^{-3}M)

Concentration of Sb(V) solution = 0.5×10^{-3}M
Concentration of the ligand = 0.5×10^{-3}M

$$P = \frac{C'}{C} = 1$$

Wave length	1:1 (a)	1:2 (b)	1:3 (c)	1:4 (d)	4:1 -	3:1 -	2:1 -
325	0.89	1.09	1.22	1.301	0.53	0.56	0.67
350	0.72	0.92	1.02	1.114	0.42	0.45	0.54
375	0.58	0.79	0.88	0.98	0.31	0.325	0.41
400	0.54	0.79	0.91	0.99	0.25	0.28	0.37
415	0.54	0.81	0.94	1.00	0.23	0.27	0.36
425	0.54	0.80	0.93	1.01	0.22	0.28	0.35
435	0.52	0.79	0.92	0.99	0.21	0.25	0.33
450	0.50	0.77	0.88	0.95	0.20	0.26	0.32
475	0.43	0.63	0.72	0.78	0.18	0.23	0.28
500	0.37	0.48	0.53	0.59	0.16	0.20	0.25
525	0.37	0.46	0.49	0.56	0.16	0.18	0.25
535	0.37	0.47	0.51	0.58	0.16	0.18	0.25
550	0.41	0.49	0.53	0.62	0.17	0.18	0.26
565	0.38	0.48	0.52	0.60	0.16	0.18	0.26
575	0.38	0.46	0.49	0.53	0.16	0.18	0.24
600	0.36	0.42	0.44	0.53	0.14	0.16	0.24
625	0.31	0.33	0.35	0.42	0.11	0.13	0.24

Fig. 39

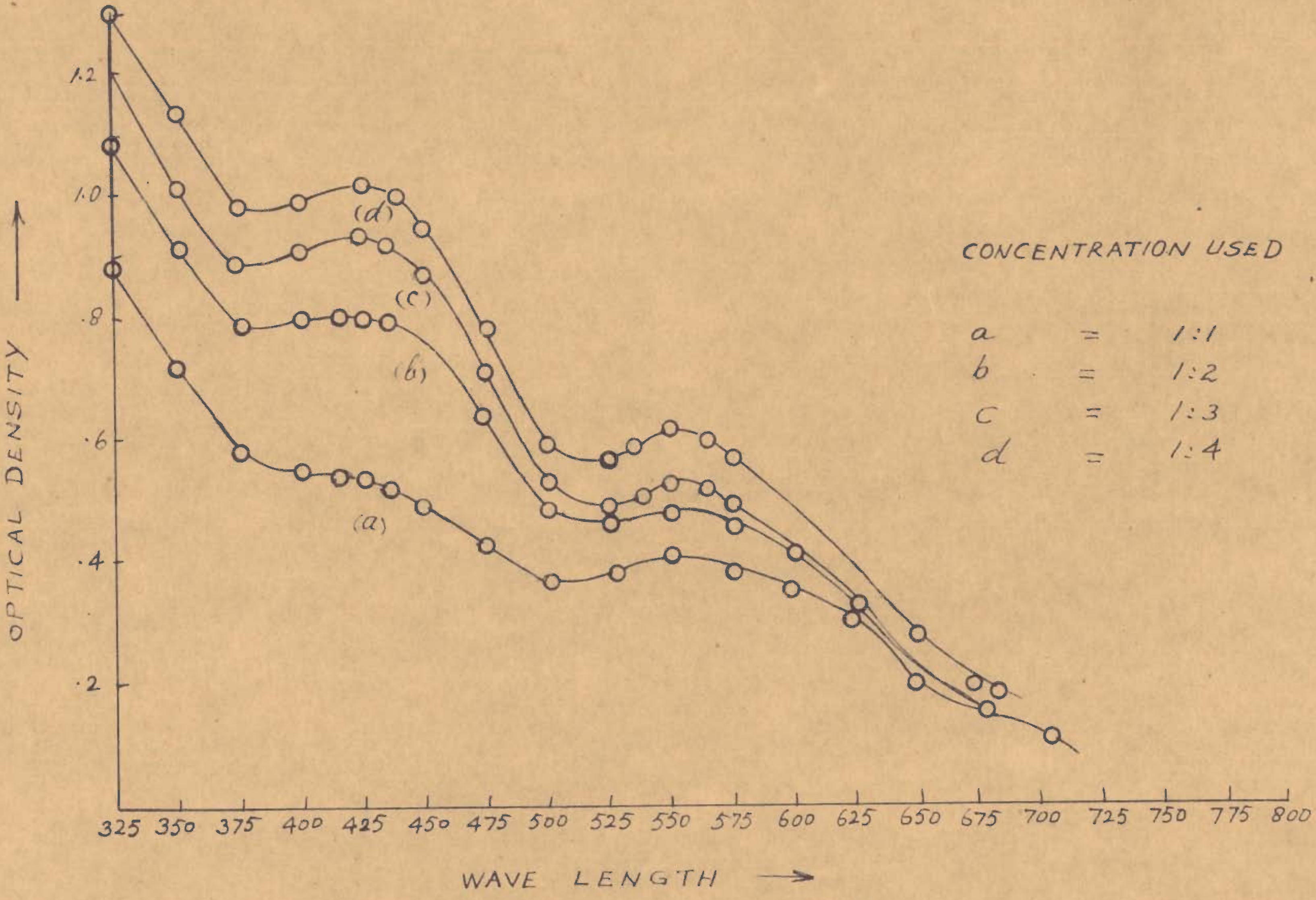


FIG. 39 ABSORPTION SPECTRA OF $Sbcl_5$ COMPLEX.

Table -50 Job's Method for Sb(V) and the Ligand
(Both $0.555 x 10^{-3}$M)

Concentration of $SbCl_5$ solution = $0.555x10^{-3}$M(C)
Concentration of the ligand solution = $0.555x10^{-3}$M(C')
Wave length = 550 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Sb(V) : the ligand

Vol.of Sb(V) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of the ligand	Difference
1	9	0.54	0.50	0.04
2	8	0.49	0.44	0.05
3	7	0.465	0.39	0.075
3.33	6.67	0.46	0.38	0.08
4	6	0.39	0.33	0.06
5	5	0.345	0.29	0.055
6	4	0.25	0.21	0.04
7	3	0.21	0.17	0.04
8	2	0.16	0.125	0.035
9	1	0.10	0.07	0.03

Fig.40, Curve (a)

Table -51 Job's Method for Sb(V) and the ligand

Concentration of $SbCl_5$ solution = 0.50×10^{-3}M(C)

Concentration of the ligand solution = 0.50×10^{-3}M(C')

Wave length = 550 mu

$$P = \frac{C'}{C} = 1$$

Peak at 1:2 :: Sb(V) : the ligand

Vol.of Sb(V) ml.	Vol.of the ligand ml.	O.D. of the mixture	O.D. of the ligand	Difference
1	9	0.54	0.52	0.02
2	8	0.48	0.45	0.03
3.	7	0.44	0.39	0.05
3.33	6.67	0.43	0.375	0.055
4	6	0.39	0.35	0.04
5	5	0.35	0.32	0.03
7	3	0.25	0.23	0.02
8	2	0.21	0.19	0.02
9	1	0.18	0.17	0.01

Fig. 40, Curve (b)

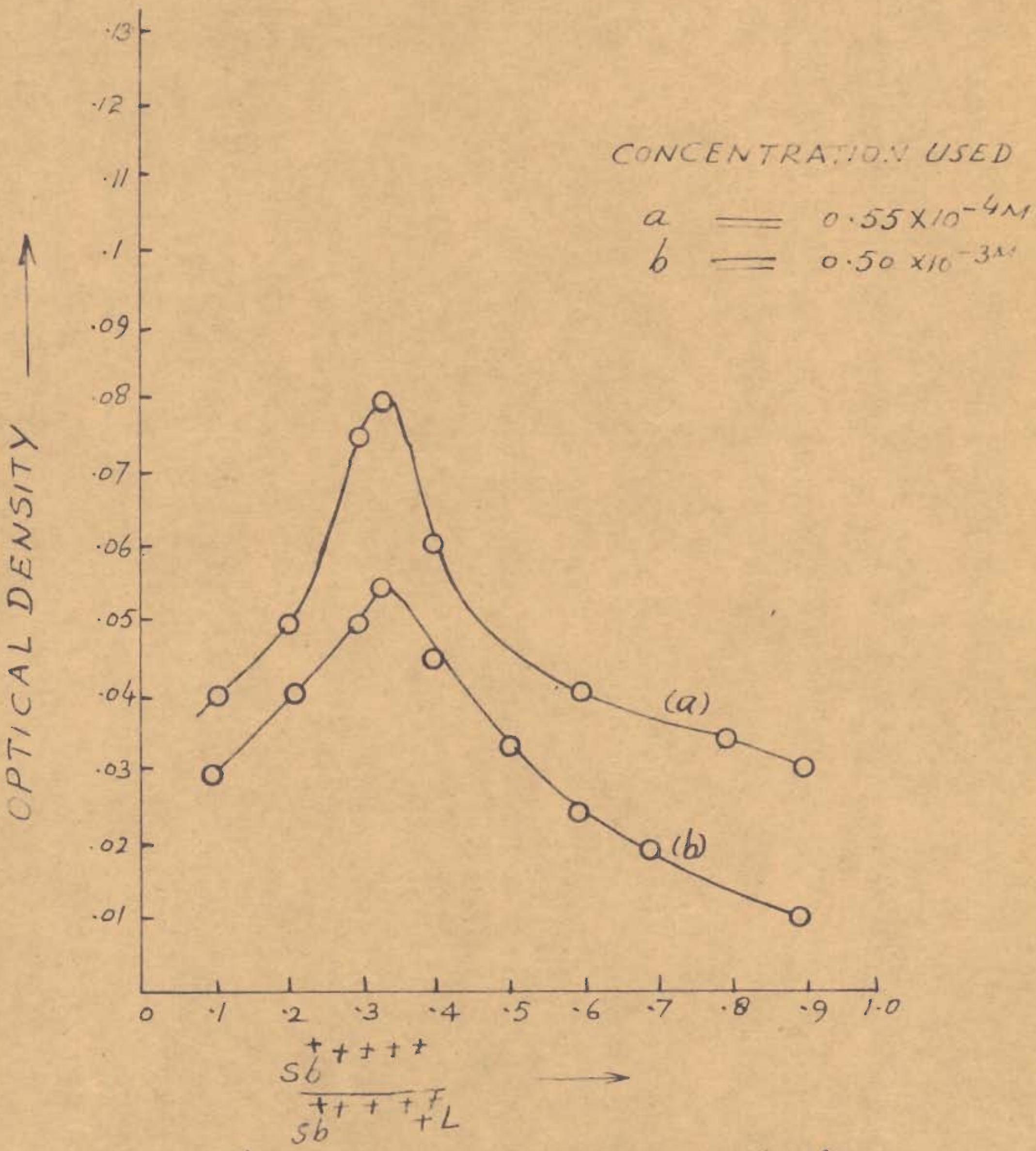


FIG. 40- COMPOSITION OF $SbCl_5$

BY JOBS METHOD.

Table -52 Slope Ratio Method for $4x10^{-3}M$ Sb(V) and $0.4x10^{-3}M$ ligand, and vice-versa

Set I Volume of $0.4x10^{-3}M$ ligand = 8 ml.
Concentration of Sb(V) solution. = $4x10^{-3}M$

Set II Volume of $0.4x10^{-3}M$ Sb(V) Solution = 8 ml.
Concentration of the ligand = $4x10^{-3}M$

Set I		Set II	
Vol.of Sb(V) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.00	0.355	0.00	0.04
0.10	0.36	0.20	0.14
0.20	0.365	0.40	0.25
0.30	0.37	0.60	0.355
0.40	0.385	0.80	0.44
0.60	0.44	1.00	0.53
0.80	0.46	1.20	0.61
1.00	0.49	1.40	0.70
-	-	1.60	0.73

Curve (a) Fig.41 Curve (b)

Table -53 Slope Ratio Method for 0.33×10^{-3}M Sb(V) and 3.33×10^{-3} Ligand, and Vice-versa.

Set I- Volume of 0.33×10^{-3}M ligand = 8 ml.
Concentration of Sb(V) solution = 3.33×10^{-3}M

Set II-Volume of 0.33×10^{-3}M Sb(V) solution = 8 ml.
Concentration of the ligand = 3.33×10^{-3}M

Set I		Set II	
Vol.of Sb(V) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.00	0.265	0.00	0.04
0.10	0.27	0.20	0.11
0.20	0.28	0.40	0.20
0.30	0.29	0.60	0.27
0.40	0.30	0.80	0.34
0.60	0.33	1.00	0.425
0.80	0.35	1.20	0.495
1.00	0.39	1.40	0.56
-	-	1.60	0.64

Curve (a) Fig.42 Curve (b)

Table -54 Composition of the Complex by Mole Ratio Method.

Strength of Sb(V) or the ligand solution = 2.5×10^{-3}M

Constant volume of Sb(V) or the ligand = 1 ml.

Wave length = 550 mu

Set I		Set II	
Vol.of Sb(V) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.00	0.18	0.00	0.03
0.10	0.195	0.40	0.13
0.20	0.215	0.80	0.22
0.30	0.215	1.20	0.30
0.40	0.22	1.60	0.40
0.50	0.23	2.00	0.47
0.60	0.23	2.10	0.50
0.70	0.235	2.20	0.53
0.80	0.24	2.30	0.53
0.90	0.24	2.40	0.53

Fig.43 Curve (a)

Table -55 Composition of the Complex by Mole Ratio Metho

Strength of Sb(V) or the ligand	= $2x10^{-3}M$
Constant volume of Sb(V) or the ligand.	= 1 ml.
Wave length	= 550 ml.

Set I		Set II	
Vol.of Sb.(V) ml.	O.D.	Vol.of the ligand ml.	O.D.
0.00	0.14	0.00	0.02
0.10	0.15	0.40	0.09
0.20	0.16	0.80	0.165
0.30	0.17	1.20	0.24
0.40	0.175	1.60	0.31
0.50	0.175	2.00	0.385
0.60	0.1775	2.10	0.395
-	-	2.20	0.410
-	-	2.30	0.410
-	-	2.40	0.410

Fig.43 Curve (b)

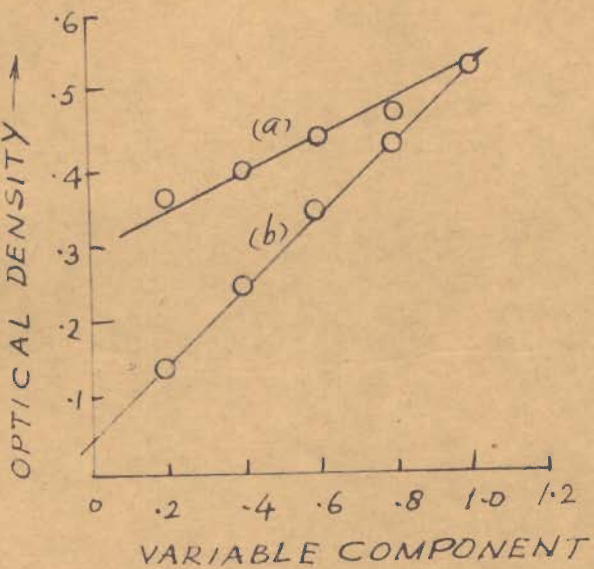


FIG. 41 COMPOSITION OF COMPLEX BY SLOPE RATIO METHOD.

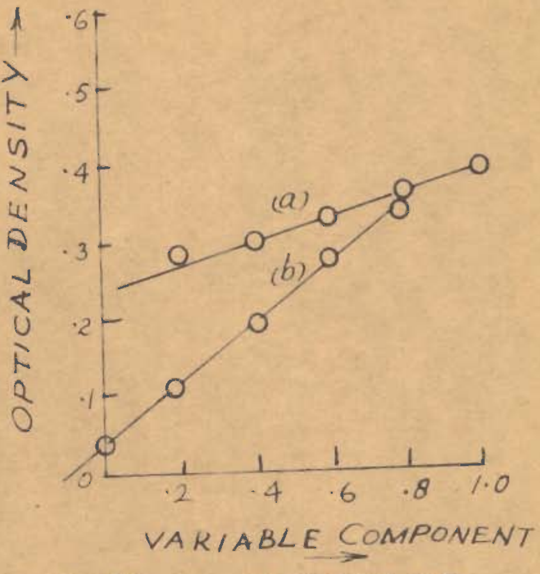


FIG. 42. COMPOSITION OF COMPLEX BY SLOPE RATIO METHOD.

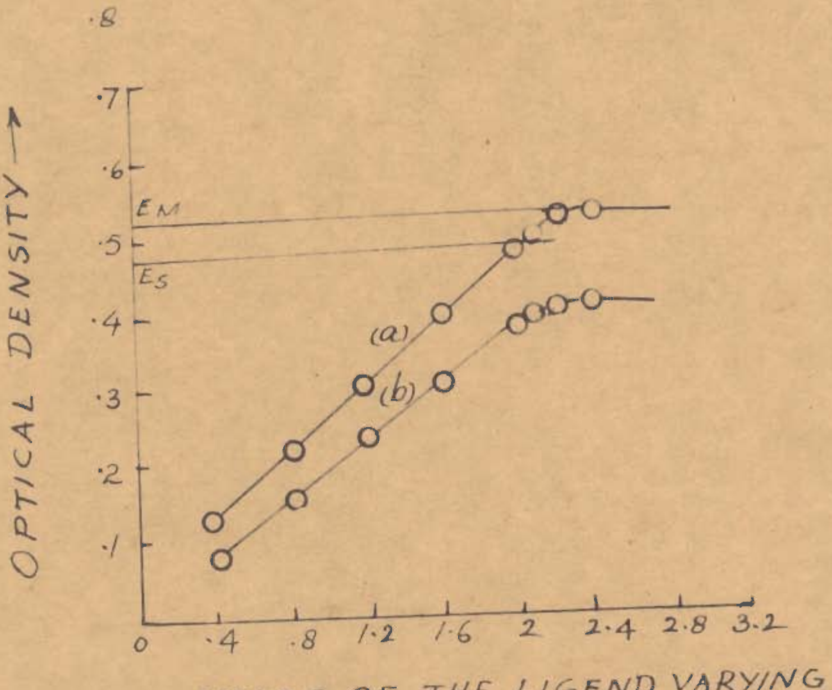
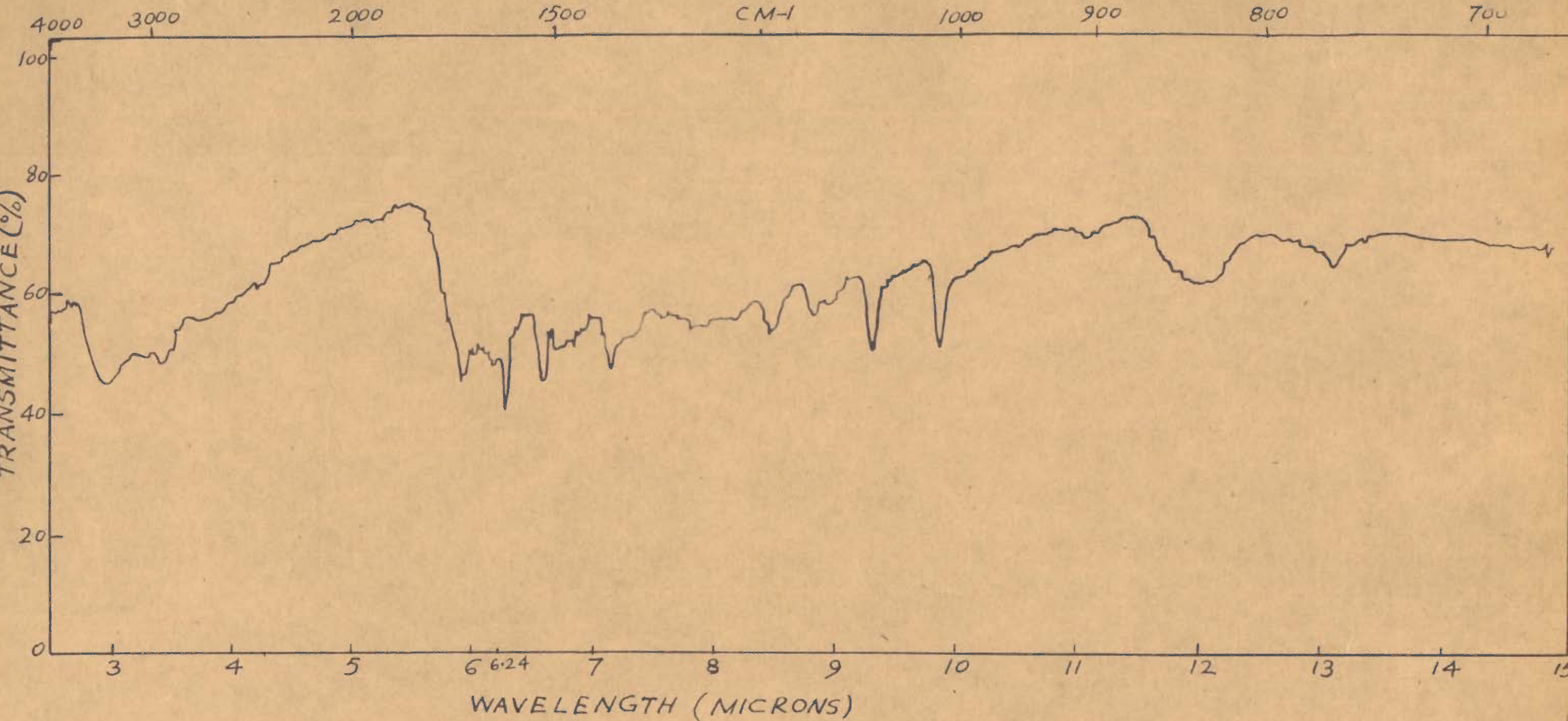


FIG. 43 COMPOSITION OF THE COMPLEX BY MOLE RATIO METHOD.



I. R. SPECTRUM OF p- BROMO PHENACYLIDENE

p. DIMETHYL AMINO ANILINE-Sb(V) CHELATE.

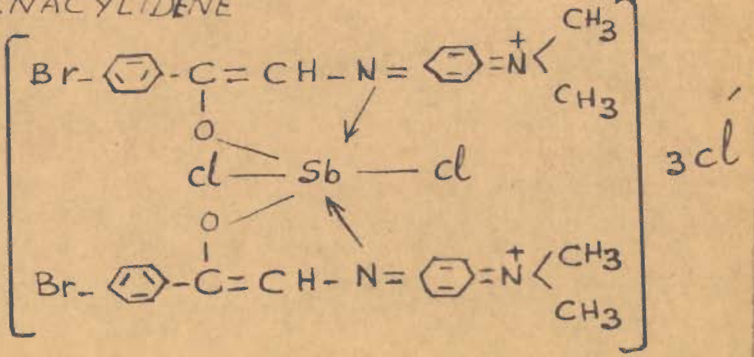
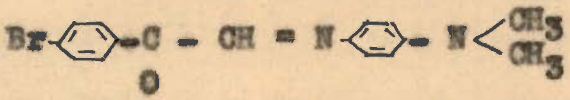


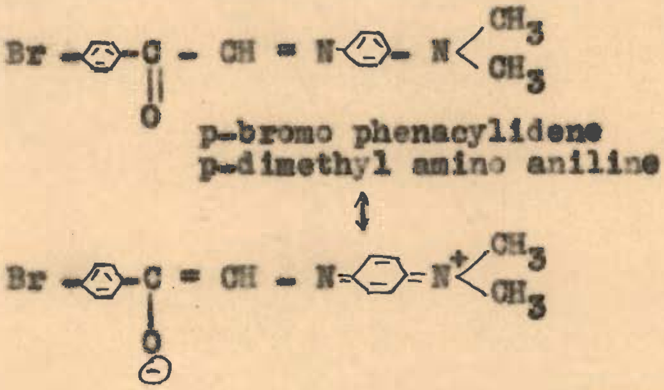
FIG. 44

CHAPTER - IV

MAGNETIC PROPERTIES, CONDUCTIVITY MEASUREMENTS U.V. AND VISIBLE SPECTRA OF THE COMPLEXES

MAGNETIC PROPERTIES OF Cu(II),Hg(II), Fe(III), Sn(IV) AND Sb(V)COMPLEXES

The ligand p-bromo phenacylidene p-dimethyl amino aniline  has a possibility of existing in a resonating and switter ion structures by which process the phenyl ring attached to the substituted anilino group may take a quinonoid structure as shown below:



p-bromo phenacylidene p-dimethyl amino aniline

On the other hand there is a possibility that both intra and intermolecular charge transfer may take place. The latter possibility may render the ligand molecule partially paramagnetic. Since the chelates under discussion are of the Lewis neutralisation type, the studies of the magnetic properties is expected to provide interesting and useful information.

As described earlier (Chapters II and III), some of the isolated complexes are quite stable and non-hygroscopic. Magnetic susceptibility measurements of these complexes were possible by Gouy's method.

EXPERIMENTAL

DETERMINATION OF MAGNETIC SUSCEPTIBILITIES

Magnetic susceptibility measurements were carried out in this laboratory by Gouy's balance consisting of a semimicro Mettler balance for suspending and weighing the sample in a magnetic field 8.5×10^3 Gauss generated by an electromagnet which was fed from the A.C. mains via rectifier cum current stabilizer (UNICO). Measurements were carried out at only one temperature, viz. the room temperature.

Firstly the constant of the tube, C, was determined, using copper sulphate (A.R.) as a standard and then copper sulphate was replaced by the ligand or the complex under investigation.

CALCULATIONS

DETERMINATION OF THE CONSTANT OF THE TUBE

The change in weight , $\triangle W$, of copper sulphate under the influence of magnetic field was found from the following data:

Weight of the empty tube + Field off $= W_1$

Weight of the empty tube + Field On $= W_2$

Weight of the empty tube + copper sulphate + Field off. $= W_3$

Weight of the empty tube + Copper sulphate + Field on $= W_4$

Change in weight $\triangle W$ $= (W_4-W_3)-(W_2-$

The total magnetic force on the tube containing copper sulphate or any other standard substance is given by

$$F = \frac{1}{2} AK \left(H^2 - H_o^2\right)$$

where H is the field at the centre of pole gap of a magnet, H_o is the field in the region out of influence of the magnet and A is area of cross section of the tube.

Since $H < H_o$

$$\therefore \quad F = \frac{1}{2} AKH^2$$

But $F = g. \Delta W$

or $K = \frac{2g.\Delta W}{AH^2}$

Since specific susceptibility

$$\chi = \frac{K}{\rho}$$

$$\therefore \quad = \frac{2g\,\Delta W}{AH^2\,\rho} = \frac{2g}{H^2}\frac{\Delta W}{A\rho}$$

But $\rho = \frac{W}{V}$, where V is the volume and W the total weight of the substance.

$$\therefore \chi = \frac{2g}{H^2}\frac{\Delta W}{A}.\frac{V}{W}$$

But $V = A.l$, where l is the length of the tube to which the specimen has been filled up.

$$\therefore \chi = \frac{2g}{H^2}\frac{\Delta W}{A}.\frac{A.l}{W} = \frac{2g}{H^2}.\, l\, .\frac{\Delta W}{W}$$

But g, H and l are constant for a particular tube at a particular place under a constant magnetic field.

$$\therefore \quad \chi = \frac{C.\Delta W}{W}$$

where C is the constant of the tube. In the above expression ΔW is expressed in mg. and W in gms. After determining the constant, C, of the tube, the specific and thence molar susceptibility χ_M is determined. ΔW of the complex was also determined in the similar manner as carried above, replacing copper sulphate by the complex under investigation.

DIAMAGNETIC CORRECTION

The values of the Pascal's constant, to determine the diamagnetic corrections of the ligands were taken from Magnetochemistry by Shelwood, and Bhatnagar and Mathur$^{(1,2)}$. The diamagnetic corrections for the ligands under investigations are given below:

DIAMAGNETIC CORRECTION OF PHENACYLIDENE ANILINE OXIME

Moleculer formula of the ligand under interaction

$= C_{14}H_{11}N_2O$

$C = 14x6.00x10^{-6} \quad = 84.00 \times 10^{-6}$

$H = 11x2.93x10^{-6} \quad = 32.23 \times 10^{-6}$

$O = 1x4.61x10^{-6} \quad = 4.61 \times 10^{-6}$

$N = 2 \times 2.11x10^{-6} \quad = 4.22 \times 10^{-6}$

Constitutive Correction | $C = N = 2(-8.2)10^{-6} = -16.40 \times 10^{-6}$

Carbon in two phenyl rings $= 2(-1.4)10^{-6} = -2.80 \times 10^{-6}$

Total 105.86×10^{-6}

DIAMAGNETIC CORRECTION OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

Molecular formula of the ligand under interaction

$= C_{16}H_{15}N_2O\,Br$

$C = 16 \times 6.00 \times 10^{-6} = 96.00 \times 10^{-6}$

$H = 15 \times 2.93 \times 10^{-6} = 43.95 \times 10^{-6}$

$O = 1 \times 4.61 \times 10^{-6} = 4.61 \times 10^{-6}$

$N = 2 \times 2.11 \times 10^{-6} = 4.22 \times 10^{-6}$

$Br = 1 \times 30.60 \times 10^{-6} = 30.60 \times 10^{-6}$

Constitutive Correction | $C = N\text{-}R = 1(-8.20)10^{-6}$

$= -8.20 \times 10^{-6}$

Carbon in two phenyl rings $= 2(-1.40)10^{-6}$

$= -2.80 \times 10^{-6}$

$C = C = 1(-5.5)10^{-6}$

$= -5.50 \times 10^{-6}$

Total 162.88×10^{-6}

DERIVATION OF THE FORMULA FOR MAGNETIC SUSCEPTIBILITY

As shown above , the constant

$$C = \frac{\chi_s W}{\Delta W}$$

where W is the weight of the specimen under investigation,

ΔW the change in wt. under the influence of applied magnetic field and χ is the specific susceptibility

$$.\dot{}.\ \chi = \frac{C.W}{W}$$

From Gouy's method both W, W and C can be determined and hence the specific susceptibility can be calculated. Knowing the molecular weight of the complex, molar susceptibility of the complex $\chi_M = \chi$.Mol.wt.of the complex. By applying diamagnetic correction of the ligand portion, χ_M can be determined. Therefore, the effective magnetic moment of the ion bound in the complex is:

$$u\ eff = 2.84\sqrt{\chi'_M T}\ \text{B.M.}$$

RESULTS

MAGNETIC SUSCEPTIBILITY OF THE COMPLEXES

Constant of the Tube:

Wt. of the empty tube + Field off = 12.58345 gm.

Wt. of the empty tube + Field on = 12.58245 gm.

Wt. of the empty tube + Copper sulphate + Field off = 13.18815 gm.

Wt. of the empty tube + Copper sulphate + Field on = 13.19395 gm.

.·. Wt. of copper sulphate = 13.18815-12.58345 = 0.60470 gm.

.·. ΔW = (13.19395-13.18815)-(12.58245-12.58345)

= (0.00580)-(-0.00100) gm.

= 5.8 mg. + 1.0 mg = 6.8 mg.

$\therefore$ Constant of the tube $C = \frac{1460\times10^{-6}}{249.69} \times \frac{0.60470 \text{ gm.}}{6.8 \text{ mg.}}$

$= 5.2 \times 10^{-7}$

MAGNETIC SUSCEPTIBILITY OF THE COPPER COMPLEX

Wt. of the empty tube + Field off = 12.58345 gm.

Wt. of the empty tube + Field on = 12.58245 gm.

Wt. of the empty tube + Copper complex + field off. = 12.89905 gm.

Wt. of the empty tube + copper complex + field on. = 12.89960 gm.

$\therefore$ Weight of the complex(12.89905-12.58345)= 0.31560 gm.

$\therefore \Delta W = (12.89960-12.89905)-(12.58245-12.58345)$ gm.

$= (0.00055) - (-0.0010)$ gm. = (0

$=$ .55mg. + 1 mg. = 1.55 mg.

$$\therefore \chi_{\text{complex}} = \frac{C.\Delta W \text{ mg.}}{W \text{ gm.}} = \frac{5.2\times10^{-7}\times1.55}{0.31560}$$

$$= 2.554 \times 10^{-6}$$

Molecular weight of the complex = 510.056

$$\therefore \chi_M = \text{Mol. wt.} \times \chi_{\text{complex}}$$
$$= 510.056 \times 2.554\times10^{-6}$$
$$= 1.304 \times 10^{-3}$$
$$= 1304 \times 10^{-6}$$

Diamagnetic correction for each ligand molecule

$= 105.86\times10^{-6}$

$\therefore$ Diamagnetic correction for the two ligand molecules $= 2(105.86\times10^{-6})$

$= 211.72\times10^{-6}$

$\therefore \chi'_M = \chi_M +$ (Diamagnetic correction) x 2 for each ligand molecule

$= 1304 \times 10^{-6} + 211.72 \times 10^{-6}$

$= 1515.72 \times 10^{-6}$

Temp. $= 33^\circ C$

u eff $= 2.84 \sqrt{T \chi'_M}$

$= 2.84 \sqrt{(273+33) \times 1515.72 \times 10^{-6}}$

$= 1.934$ B.M.

MAGNETIC SUSCEPTIBILITY OF THE MERCURIC CHLORIDE COMPLEX

Constant of the tube $C = \frac{1460 \times 10^{-6}}{249.69} \times \frac{0.60470}{6.8 \text{ mg}}$

$= 5.2 \times 10^{-7}$

Weight of the empty tube + Field off = 12.58345 gm.

Weight of the empty tube + Field on = 12.58245 gm.

Weight of the empty tube + $HgCl_2$ complex + Field off = 13.09840 gm.

Weight of the empty tube + $HgCl_2$ complex + Field on = 13.09755 gm.

$\therefore$ Weight of the complex (13.09840-12.58345 gm.)

= 0.51495 gm.

$\therefore \Delta W = (13.09755-13.09840)-(12.58245-12.58345)$

$= (-0.00085)-(-0.00100)$ gm.

$= -0.85$ mg + 1 mg.

$= 0.15$ mg.

$$\chi_{complex} = \frac{C.\Delta W_{complex}}{W_{complex}} = 5.2 \times 10^{-7} . \frac{0.15 \text{ mg.}}{0.51495 \text{ gm.}}$$

$= 0.1514 \times 10^{-6}$

Molecular weight of the complex = 602.752

$\therefore \chi_M' = \chi_{complex}$ .mol.wt. of the complex

$= 0.1514 \times 10^{-6} \times 602.752$

$= 91.29 \times 10^{-6}$

Diamagnetic correction of each organic portion

$= 162.88 \times 10^{-6}$

2Cl' $= 2\times20.16 \times 10^{-6}$

$= 40.20 \times 10^{-6}$

Total diamagnetic correction $= 203.08\times10^{-6}$

$\chi_M' = 91.29\times10^{-6}+203.08\times10^{-6}$

$= 294.37\times10^{-6}$

Temp. $= 26^{0}C$

u eff.$= 2.84\sqrt{T \chi_M'}$ B.M.

$= 2.84\sqrt{(273+26)\times294.37\times10^{-6}}$

$= 0.8423$ B.M.

MAGNETIC SUSCEPTIBILITY OF THE $FeCl_3$ COMPLEX

CONSTANT OF THE TUBE

Weight of the empty tube + Field off	= 12.66720 gm.
Weight of the empty tube + Field on	= 12.66620 gm.
Weight of the empty tube + Copper sulphate + Field off	= 13.20070 gm.
Weight of the empty tube+copper sulphate + Field on	= 13.20625 gm.

$\therefore$ Weight of copper sulphate = (13.20070 - 12.66720) gm.=0.53350 gm.

$\therefore \Delta W = (0.00555)-(-0.0010)$ gm.
= 5.55 mg. + 1 mg. = 6.55 mg.

$\therefore$ Constant of the tube $C = \frac{1460\times10^{-6}}{249.69} \times \frac{0.5335\text{ gm.}}{6.55\text{ mg.}}$

$= 4.763\times10^{-7}$

Weight of the empty tube+Field off = 12.66720 gm.

Weight of the empty tube + Field on = 12.66620 gm.

Weight of the empty tube +$FeCl_3$ complex + field off = 12.98780 gm.

Weight of the empty tube + $FeCl_3$ complex + Field on = 13.00610 gm.

$\therefore$ Weight of $FeCl_3$ complex = (12.98780-12.667

= 0.32060 gm.

$\therefore$ W = (13.00610-12.98780) - (12.66620-12.66720) = (0.0183gm.)-(.00

= (18.3+1)mg.

= 19.3 mg.

$\chi_{complex} = \frac{C\Delta W}{W\text{ gm}}$ mg. $= \frac{4.763\times10^{-7}\times19.3}{0.3206\text{ gm.}}$

$= 28.68\times10^{-6}$

Moleculer weight of the iron complex = 824.677

$\therefore \chi_M = \chi_{complex}\cdot$ Mol.wt.of the complex

$= 28.68\times10^{-6}\times824.677$

$= 23650 \times 10^{-6}$

Diamagnetic correction of each ligand molecule

$= 162.88\times10^{-6}$

$\therefore$ Diamagnetic correction of two ligand molecules $= 2(162.88\times10^{-6})$

$= 325.76\times10^{-6}$

3 Cl' $= 3\times20.10\times10^{-6}$ $= 60.30\times10^{-6}$

$\therefore$ Total diamagnetic correction

$= 325.76\text{x}10^{-6}+60.30\text{x}10^{-6}$

$= 386.06\text{x}10^{-6}$

$\chi'_M \quad = 23650 \text{ x } 10^{-6}+386.06 \text{ x } 10^{-6}$

$= 240360.06\text{x}10^{-6}$

Temp. $= 24^{0}$

u eff. $= 2.84\sqrt{T.\ \chi'_M}$

$= 2.84\sqrt{(273+24)\text{x}240360.06\text{x}10^{-6}}$

$= 7.588$ B.M.

MAGNETIC SUSCEPTIBILITY OF THE STANNIC CHLORIDE COMPLEX

Constant of the tube $C = \frac{1460\text{x}10^{-6}}{249.69} \text{ x } \frac{0.5335 \text{ gm.}}{6.55 \text{ mg}}$

$= 4.763\text{x}10^{-6}$

Weight of the empty tube + Field off = 12.66720 gm.

Weight of the empty tube + Field on = 12.66620 gm.

Weight of the empty tube + $SnCl_4$ complex + Field off. = 13.06425 gm.

Weight of the empty tube + $SnCl_4$ complex + Field on. = 13.06340 gm.

$\therefore$ Weight of the complex

= (13.06425-12.66720)gm. = 0.39705 gm.

$\therefore \triangle W = (13.06340 - 13.06425)-$

$(12.66620-12.66720)=(-0.00085)-(-0.0010)\text{gm}$

$= (-0.85+1.0)$ mg

$= 0.15$ mg.

$$\chi_{complex} = \frac{C.\Delta W_{mg.}}{W_{gm.}} = \frac{4.763x10^{-7}x0.15\ mg.}{0.39705\ gm.}$$

$$= 0.1797x10^{-6}$$

Mol.weight of the complex = 922.76

$$\therefore \chi_M = \chi_{complex} \text{ x Mol. wt. of the complex}$$

$$= 0.1797x10^{-6}x922.76$$

$$= 165.80x10^{-6}$$

Diamagnetic correction for two molecules of the ligand $2x162.88x10-6$ $= 325.76x10^{-6}$

$4\ Cl' = 4x20.10x10^{-6}$ $= 80.40\ x\ 10^{-6}$

Total diamagnetic correction $= 325.76x10^{-6}+80.40x10$

$= 406.16x10^{-6}$

$$\chi_M' = \chi_M + \text{Total diamagnetic correction}$$

$$= 165.80\ x\ 10^{-6} + 406.16x10^{-6}$$

$$= 571.96x10^{-6}$$

Temp. = 35°

$$\therefore u\ eff. = 2.84\sqrt{T\ \chi_M'}\ \text{B.M.}$$

$$= 2.84\sqrt{(273+35)x571.96x10^{-6}}$$

$$= 1.192\ \text{B.M.}$$

MAGNETIC SUSCEPTIBILITY OF THE $SbCl_5$ COMPLEX

$$\text{Constant of the tube C} = \frac{1460x10^{-6}}{249.69} \text{ x } \frac{0.5335\ gm.}{6.55\ mg.}$$

$$= 4.763\ x\ 10^{-6}$$

Weight of the empty tube + Field off = 12.66720 gm.

Weight of the empty tube + Field on = 12.66620 gm.

Weight of the empty tube + $SbCl_5$ complex + field off. = 13.03265 gm.

Weight of the empty tube + $SbCl_5$ complex + field on. = 13.03185 gm.

∴ Weight of the complex

= 13.03265 − 12.66720 = 0.36545 gm.

∴ ΔW = (13.03185−13.03265)−(12.66620−12.66720)

= (−0.00080)−(−0.0010)gm.

= (−0.80+1) mg.

= 0.20 mg.

$$\chi_{complex} = \frac{C.\Delta W\ mg.}{W\ gm.} = \frac{4.763\times10^{-7}\times0.20mg.}{0.36545\ gm.}$$

$= 0.2607\times10^{-6}$

Molecular weight of the complex = 961.377

∴ $\chi_M = \chi_{complex}$ x Mol. wt. of the complex.

$= 0.2607\times10^{-6}\times961.377 = 250.60\times10^{-6}$

Diamagnetic correction for two ligand molecules = 2x162.88 $= 325.76\times10^{-6}$

5 Cl' = 5x20.10 $= 100.50\times10^{-6}$

Total diamagnetic correction

$= 325.76\times10^{-6}+100.50\times10^{-6} = 426.26\times10^{-6}$

∴ $\chi'_M = \chi_M$ + Diamagnetic correction

$= 250.60\times10^{-6}+426.26\times10^{-6} = 676.86\times10^{-6}$

Temp. = 35°

$$u\ \text{eff.} = 2.84\sqrt{T\ \chi'_M}$$

$$= 2.84\sqrt{(273+35)\times676.86\times10^{-6}}$$

$$= 1.296\ \text{B.M.}$$

DISCUSSION

COPPER-PHENACYLIDENE ANILINE OXIME COMPLEX

The effective magnetic moment of the copper complex is 1.93 B.M. which is well within the range, (1.70 to 2.20, expected for the copper complexes. The orbital contributions in the copper complexes are all quenched.

From the data (obtained at one temperature) it appears that there is not much reduction of the constant in the complex from the free ion value. However, one thing is certain that there is not much antiferro-magnetic interaction. From these results it may be concluded that the possibility of the complex existing in form of a polynuclear complex is very remote.

LEWIS ACIDS-p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE COMPLEXES

The most interesting feature of these studies is the paramagnetic behaviour of the ligand itself. The ligand is found to show the effective magnetic moment of 1.61 B.M. The ligand consists of even number of electrons and this is obviously not a free radical. Hence a paramagnetic behaviour should not normally be expected in the ligand. The paramagnetic behaviour may, therefore, come if there is some partial charge transfer. The paramagnetic behaviour is well manifested in the complex Hg(II), Sn(IV) and Sb(V), which would normally give a diamagnetic behaviour. Hg(II) complex which contains only one ligand molecule gives effective magnetic moment of 0.84 B.M. whereas Sn(IV) and Sb(V) complexes, which contain two ligands each, give effective magnetic moment of 1.19 and 1.30 B.M. respectively.

The fact that the ligand itself shows higher moment value suggests that either the ligand gets associated or it possesses more effective charge transfer property being cut off in the complexes by the metal-ligand bond. Probably it is for this reason that $HgCl_2$ gives a lower magnetic moment and the other two complexes containing two ligand molecules give values nearly equal to those of the ligand. In the free ligand it seems that the effective spin-free electron is one but in these complexes it seems to be half while in Sn(IV) and Sb(V) complexes, the effective spin electron is nearly one. This supports our contention that in the free ligand the effective charge transfer is more(This has been amply demonstrated in the electronic spectra).

In Fe(III) complex the charge transfer will be more effective than the complexes described above. The net result is that the iron complex may retain one effective spin-free electron per ligand besides the five usual spin-free electron in Fe(III) ion. The effective magnetic moment of iron complex is 7.5 B.M. which is just short of the spin only value of

7.9 free electrons. As the magnetic moment of iron complexes are independent of their stereochemistry, orbital contribution and spin-orbit coupling constant, the higher value has not other explanation.

This peculiar magnetic behaviour is the only example of its type. It appears that the paramagnetism of the ligand has been carried to the complexes to a reduced degree. But the reduction is wiped off if the Lewis acid becomes an active participitant as in the case of Fe(III) complex.

CONDUCTIVITY MEASUREMENTS OF THE COMPLEXES

Further confirmation regarding the position of Cl' ion in the coordination sphere of the Lewis acid complexes of p-bromo phenacylidene p-dimethyl amino aniline was done by conductivity method. Measurements were carried out at 25°±1C with Mullard's conductance bridge. The observations are recorded below:-

1. MOLAR CONDUCTIVITY OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

Wt. of p-bromo phenacylidene p-dimethyl amino aniline and the weighing tube	= 4.16473 gm.
Wt. of empty tube	= 4.15940 gm.
.˙. Wt. of the ligand	0.00533 gm.

.˙. 0.00533 gm. dissolved in 10 ml. of acetone has molarity
$= 1.609\times10^{-3}M$

.˙. Conductance = $3.45\times1\times10^{-6}$ Mhos.

.˙. Molar conductivity = $\dfrac{\text{Specific conductivity}\times10^{3}}{\text{concentration}}$

$$\text{or } \triangle_M = \frac{K\times10^{3}}{C} = \frac{1.9515\times10^{3}\times3.45\times10^{-6}}{1.609\times10^{-3}}$$

= 4.18 Mhos

Thus when the concentration is of the order 10^{-3}, the molar conductance is 4.18 mhos.

When the concentration is of the order of 10^{-4}, the molar conductance is found to be 6.6 Mhos.

MOLAR CONDUCTIVITY OF Hg(II)-p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE

Wt. of weighing tube + Hg(II) complex = 4.01955 gms.

Wt. of weighing tube = 4.00100 gms.

∴ Wt. of complex 0.01855 gms.

Volume of the solution = 10 ml.

∴ Molar concentration = $2.986\text{x}10^{-3}$M

Conductance = $0.638\text{x}10^{-4}$ Mhos.

Specific conductance = Cell constant x conductance

$$= 1.4515\text{x}0.638\text{x}10^{-4}$$

$$\therefore \quad M = \frac{K\text{x}10^{3}}{C} = \frac{1.4515\text{x}0.638\text{x}10^{-4}\text{x}10^{3}}{2.986\text{x}10^{-3}}$$

$$\therefore \quad M = 41.69 \text{ Mhos.}$$

When the solution was diluted 10 times the conductance obtained was found to be $6.45\text{x}10^{-6}$ Mhos.

$$\therefore \quad M = \frac{1.4515\text{x}6.45\text{x}10^{-6}\text{x}10^{3}}{2.986\text{x}10\text{-}4} = 42.15 \text{ Mhos.}$$

MOLAR CONDUCTIVITY OF Sn(IV)-p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE CHELATE

Wt. of weighing tube+the Sn(IV) complex = 3.98350 gm.

Wt. of weighing tube = 3.97237 gm.

∴ Wt. of the complex 0.0113 gm.

Since 0.0113 gm. have been dissolved in 10 c.c.

∴ Molar concentration $= 1.206\times10^{-3}M$

Conductance $= 0.230\times10^{-4}$ Mhos

$$\therefore \Lambda_M = \frac{K.10^3}{C} = \frac{1.4515\times0.230\times10^{-4}\times10^3}{1.206\times10^{-3}}$$

$$= 37.21 \text{ Mhos.}$$

When the dilution has been done 10 times the conductance observed 2.9×10^{-6} Mhos.

$$\therefore \Lambda_M = \frac{1.415\times2.9\times10^{-6}\times10^3}{1.206\times10^{-4}}$$

$$= 46.92 \text{ Mhos.}$$

MOLAR CONDUCTIVITY OF Sb(V)-p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE COMPLEX

Weight of weighing tube + Sb(V) chelate = 4.01797 gm.

Weight of weighing tube = 3.99973 gm.

∴ Weight of the chelate in 10 ml.solvent = 0.01824 gm.

∴ Molar concentration $= 1.897\times10^{-3}$

Conductance measured = 0.335x10-4 Mhos.

$$\therefore \Lambda_M = \frac{1.4515\times0.335\times10^{-4}\times10^3}{1.897\times10\text{-}3} = 34.46 \text{ Mhos}$$

When molar concentration is 1.897×10^{-4}

Conductance is $4.1x10^{-6}$ Mhos

$$\therefore \Lambda M = \frac{1.4515x4.1x10^{-6}x10^{3}}{1.897x10^{3}} = 42.17 \text{ Mhos}$$

MOLAR CONDUCTIVITY OF Cu(II)-PHENACYLIDENE ANILINE OXIME

Weight of the Cu(II)-PAO Oxime = 0.01305 gm/10 ml.

Mol. concentration = $2.558x10^{-3}$

$$\therefore \quad \Lambda M = \frac{K.10^{3}}{C} = \frac{1.4515x0.197x10^{-4}x10^{3}}{2.558x10-3}$$

$$= 15.03 \text{ Mhos}$$

When the solution has been diluted 10 times

$$\Lambda M = 21.36 \text{ Mhos}$$

DISCUSSION

The molar conductance of the ligand p-bromo phenacylidene p-dimethyl amino aniline in acetone was expected to be a little higher than what was found. The lower value be possibly due to ion association. A ten-fold dilution increases the ΛM values by 50 % which may also supports ion association. The complexes on the other hand show a limited conductahce, not even comparable to 1:1 electrolytes. This partial conductivity may be due to either solvation or the positively charged amino nitrogen combining with the anion i.e. Cl'. A decrease in dissociation may also give a low value. Except the Hg(II)-complex, the increase in ΛM values is fairly considerable with ten-fold dilution.

Even then solvation cannot be ruled out at all.

On the other hand Cu(II)-phenacylidene aniline oxime complex shows a limited conductance. The conductance of this neutral complex cannot be other than some solvolysis. In that complexes are found to be very stable units.

The conductance of the solvent acetone was also determined and was found to be negligible as compared to the conductance of complexes in solution. The observed conductance may, therefore, be taken as the conductance of the complexes for all practical purposes.

ABSORPTION SPECTRA OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE AND ITS COMPLEXES IN U.V. AND VISIBLE REGION

The U.V. spectra of the ligand p-bromo phenacylidene p-dimethyl amino aniline in acetonitrile shows a broad and at the same time few sharp peaks at 220 mu (Fig.45, Curve a). The band at the lowest wave length is π-π^* band due to the carbonyl group, suggesting effective delocalisation. The broad bands around 250 mu is due to the benzene ring as well as the quinonoid structure but in the process of the formation of the quinonoid unit the partly allowed bands have been rendered allowed, (Fig.46, Curves a and b). No n-π^* band could be detected and hence their change on complex formation could not be properly characterised. The ligand shows a charge transfer band also. The band at about 430 mu is nearly absent in complex but the 570 mu is retained. It seems that we have located both the inter molecular and intra molecular charge transfer bands (Fig.47, Curve a). Both these bands are weakened on undergoing complex information but the intra-molecular one weakens more.

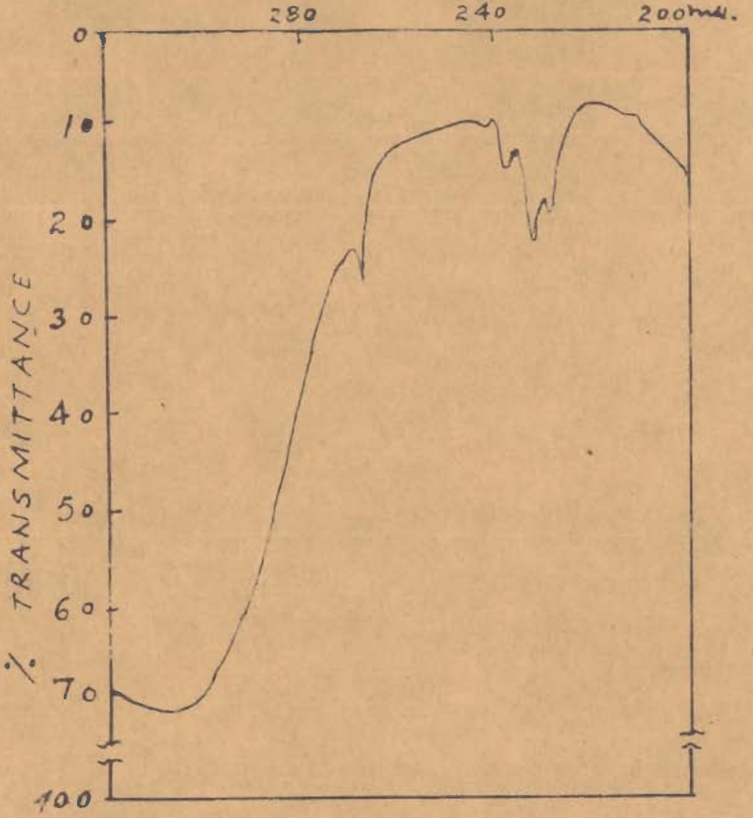


FIG. 45 - ABSORPHIAN SPECTRUM OF
p-BROMO PHENACYLIDENE
P-DIMETLYL ANILINE
(Br-L) IN U.V. REGION

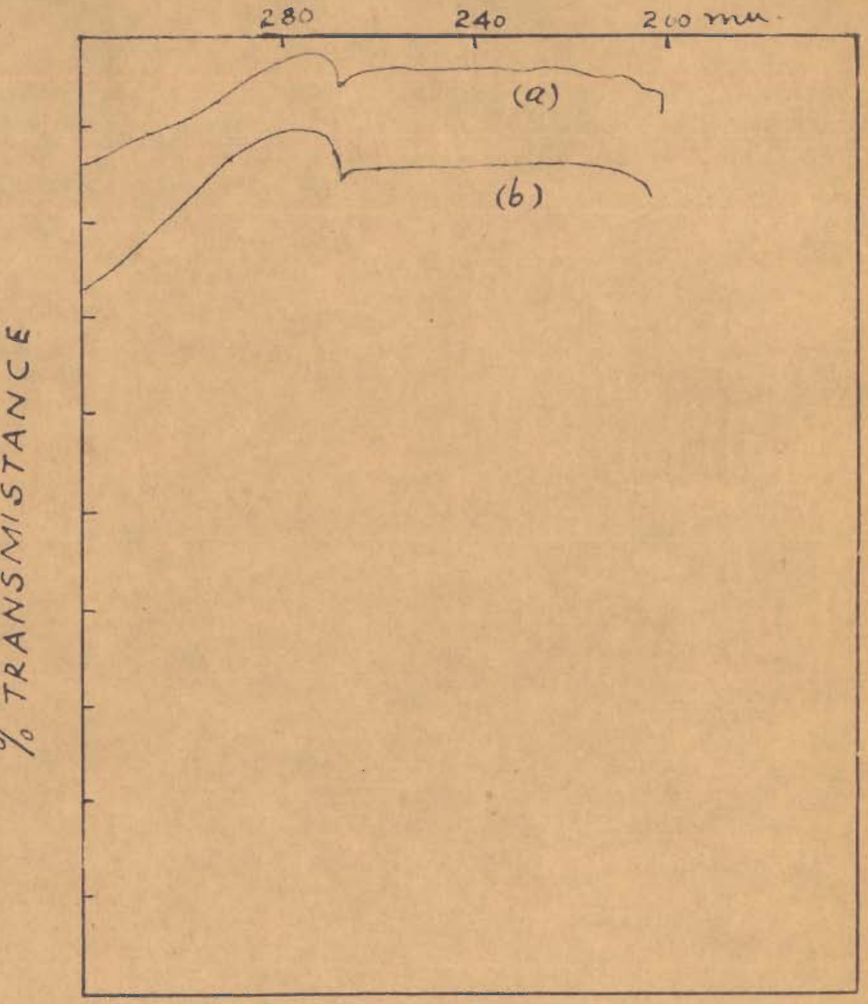


FIG-46 ABSORPTION SPECTRUM OF
(a) Fe(III)-Br-L,(b) Sn(IV)-Br-L) COMPLEXE
IN U.V. REGION.

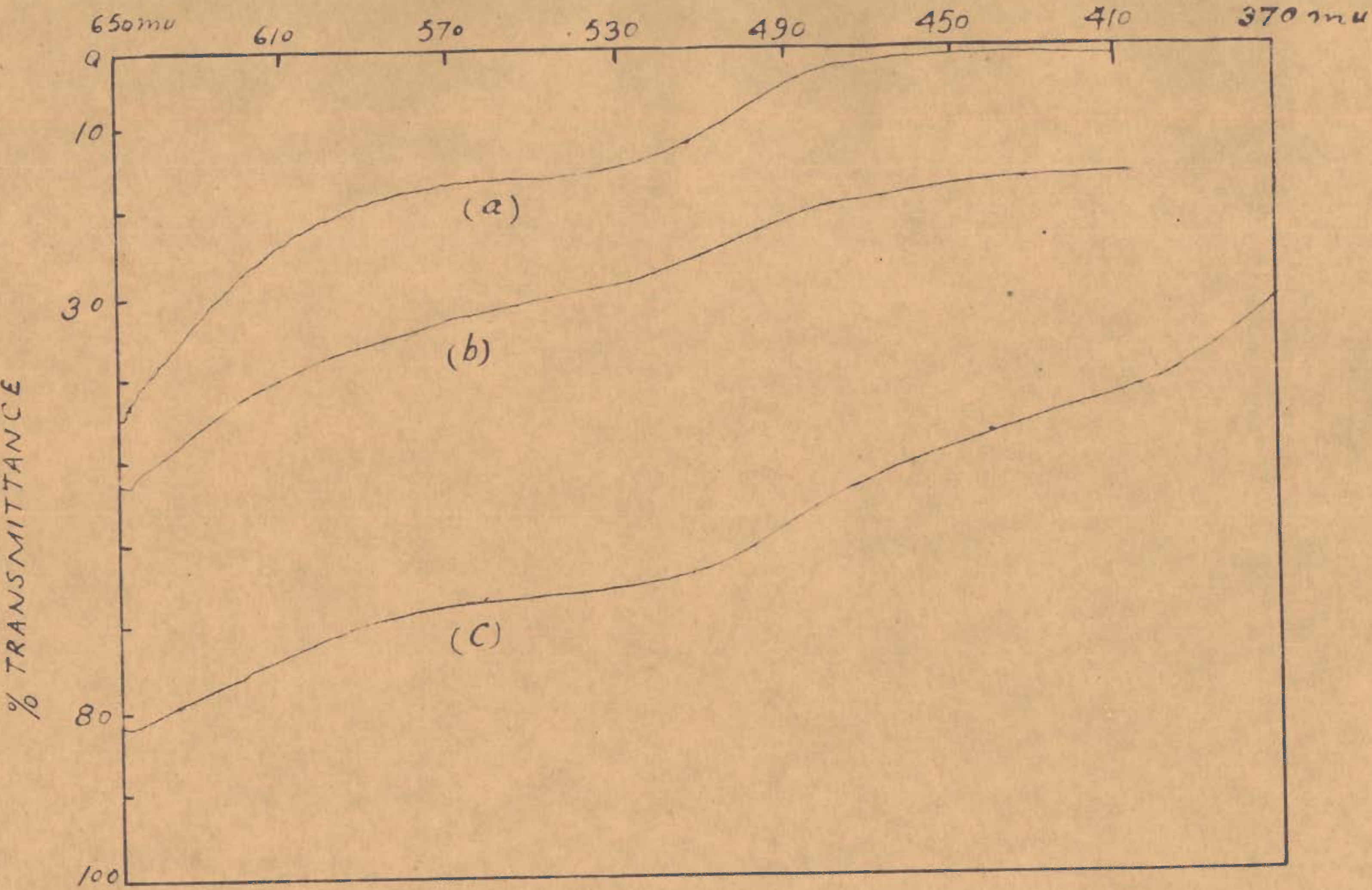


FIG.47 ABSORPTION SPECTRA OF;
(a) Br-L; (b) Fe(III)-Br-L AND (C) Sn(IV)-Br-L COMPLEXES IN VISIBLE REGION

SUMMARY

Out of the large number of complexing and chelating agents cited in the chemical literature, anils find very little mention. These compounds, besides containing nitrogen and oxygen which can serve as coordination sites, have the unique property of exhibiting colour changes (due to bathochromic effect) when brought in contact with metal ions, especially those belonging to non-transition series. Krohnke and Gross observed such changes in p-dimethyl amino anil of phenyl glyoxal when brought in contact with silica gel or certain Lewis acids. The nature and composition of the product or products found by such interaction have not yet been investigated. An attempt in this direction was considered worth investigating and forms the theme of the thesis.

To begin with a number of anils besides the one mentioned by Krohnke and Gross were synthesised and fully characterized in the laboratory. Having obtained the anils and their oximes in pure form, their acetonic or alcoholic solutions were made to react with some Lewis acids. The Lewis acids chosen for this purpose are the halides of Hg(II), Zn(II), anhydrous Al(III), Sn(IV), Sb(V) and Fe(III). Moreover,a characteristic colour change was observed in the case of phenacylidene aniline oxime with cupric ions and was studied for the sake of complexation.

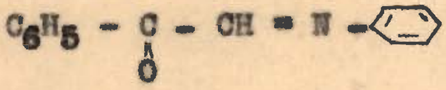
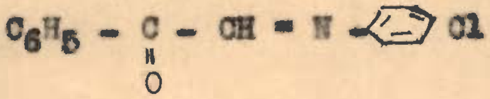
SYNTHESIS AND I.R. SPECTRA OF SOME NEW ANILS

Some new anils were prepared by condensing phenyl glyoxal hydrate with aniline, m-, p-chloroanilines, o-, m-, p-nitroanilines, p-bromoaniline, o-, m-, p-toluidines, α-,β-naphthylamines, o-, p-aminophenols, o-anisidine, sulphanilic acid, anthranilic acid, m-, p-amino benzoic acids and sulphanilamide.

Similarly p-bromo phenyl glyoxal hydrate was synthesised by SeO_2 oxidation of p-bromo acetophenone. This keto aldehyde hydrate was then condensed with aniline, o-, m-, p-toluidines, o-, m-, p-chloroanilines and sulphanilamide.

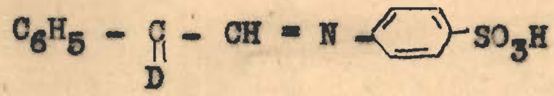
Nitrogen contents of the above anils were estimated and were characterized by preparing their p-nitro phenyl hydrazones, 2:4-dinitro phenyl hydrazones, semicarbazones and oximes. The oxime of many of these anils gave colour reaction with a number of metal ions and thereby offered a possibility of being used as chelating agents.

The functional groups in some of the anils and their derivatives were confirmed by recording their I.R. spectra in solid state. Typical structures of some of the new anils and their derivatives are given below.(For other structures,vide pp. 66-71).

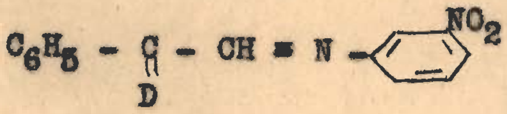
<u>Name of the Anil or the derivative</u>	<u>Structure</u>
1. Phenacylidene aniline	
2. Phenacylidene p-chloro-aniline	

2:4-dinitro phenyl hydrazones of:

3. Phenacylidene sulphanilic acid

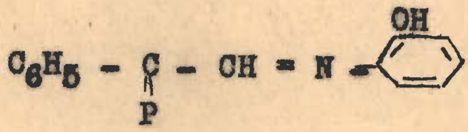


4. Phenacylidene m-nitroaniline

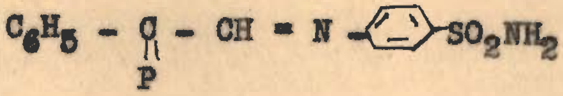


P-nitro phenyl hydrazones of:

5. Phenacylidene o-aminophenol

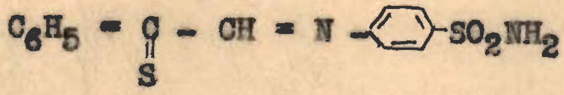


6. Phenacylidene sulphanilamide

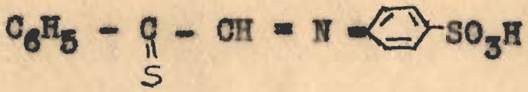


Semicarbazones of:

7. Phenacylidene sulphanilamide

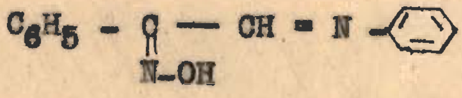


8. Phenacylidene sulphanilic acid

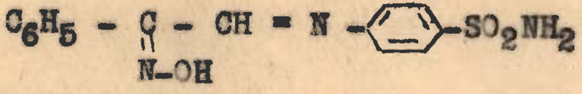


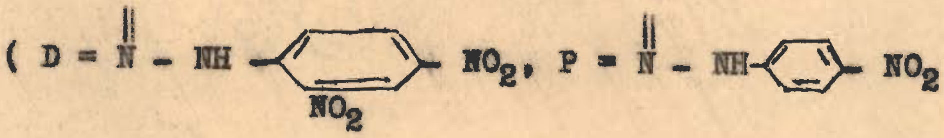
Oximes of:

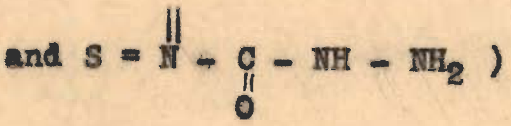
9. Phenacylidene Aniline



10. Phenacylidene sulphanilamide







$$\text{and } S = \overset{\parallel}{N} - \underset{\underset{O}{\parallel}}{C} - NH - NH_2 \text{)}$$

SPECTROPHOTOMETRIC STUDIES ON COPPER (II) - PHENACYLIDENE ANILINE OXIME COMPLEX

Oximes have proved analytically important chelating agents and are classified as:

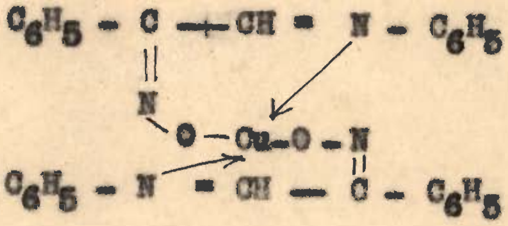
Orthodioxime, acyloin oxime, ortho-hydroxy aromatic oxime, monoxime of α-diketone and nitroso substituted hydroxylamines. These compounds react with metal ions either by replacement of hydrogen of the oxime group by metal or through nitrogen of such grouping to give chelates. Under suitable conditions the oxime can be made to react quite selectively and can prove to be of analytical importance.

The alcoholic solution of Cu(II) with phenacylidene aniline oxime gave a soluble complex of wine colour. The composition, stability and thermodynamic data of this chelate were determined by spectrophotometric and chemical methods. A 1:2 complex was found to be formed with stability constant and free energy formation change values as 0.7547×10^7 and 13.07 K Cals/mole respectively.

Equimolar ethanolic solutions of Cu(II) and phenacylidene aniline oxime were mixed in 1:2 ratio when a colour change was observed, resulting in the formation of wine coloured complex. This was concentrated in a vacuum dessicator when a solid mass was obtained. The solid was then crystallised from alcohol. The metal content was estimated iodometrically(pp. 89)

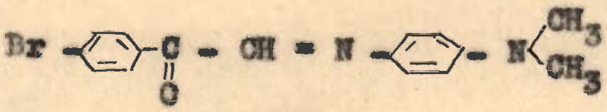
The infrared spectrum of the complex showed the absence of OH stretching frequency thereby providing evidence for the existance of a covalent binding through oxygen.

A drop in pH was also noticed when the metal ion and the ligand were mixed. This fact further confirmed the above view point. The following structure is proposed for the chelate:



COMPOSITION OF p-BROMO PHENACYLIDENE p-DIMETHYL AMINO ANILINE-LEWIS ACIDS-HALIDES OF Fe(III), Al(III), Hg(II), Zn(II), Sn(IV) AND Sb(V) COMPLEXES

When acetonic solution of p-bromo phenacylidene p-dimethyl amino aniline was added to either of these Lewis acids, a bathochromic shift was experienced in the whole system. This shift caused mesomerism of the ligand in situ with chelation. The reaction mixture decomposed even with traces of moisture, liberating the ligand as an isolated species. The following changes were obtained on the interaction of the Lewis acids with the ligand.

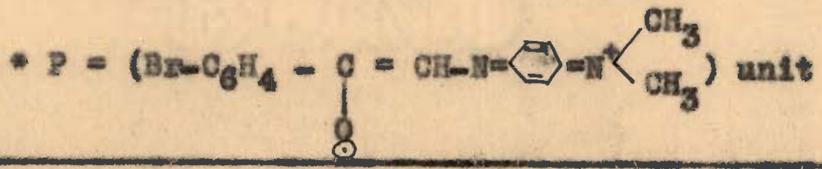


ANIL

Lewis acid	Own colour of the reagant	Change in colour
1. $FeCl_3$	Yellow	Bluish green
2. $AlCl_3$	Yellow	Violet
3. $HgCl_2$	Yellow	Green
4. $ZnCl_2$	Yellow	Bluish green.
5. $SnCl_4$	Yellow	Violet
6. $SbCl_5$	Yellow	Violet

Job's Method of Continuous Variation was employed to determine the composition of Fe(III), Al(III), Hg(II), Zn(II), Sn(IV) and Sb(V) complexes in purely non-aqueous medium, following their chemical analysis and I.R. spectra. However, stability constants and changes in free energy of these chelates were determined by mole ratio method except in the case of Hg(II) chelate where Job's method was found to be more suitable. The data for the chelates are tabulated below.

No.	Name of the chelate	Ratio L:M	Stability constant	Change in free energy K Cals/mole
1.	$^{*}P-FeCl_3$	2:1	0.2757×10^{12}	15.66
2.	$P-AlCl_3$	2:1	0.1566×10^{9}	11.25
3.	$P-HgCl_2$	1:1	0.3729×10^{5}	6.44
4.	$P-ZnCl_2$	1:1	0.1407×10^{6}	7.13
5.	$P-SnCl_4$	2:1	0.5199×10^{11}	15.00
6.	$P-SbCl_5$	2:1	0.2459×10^{10}	12.72



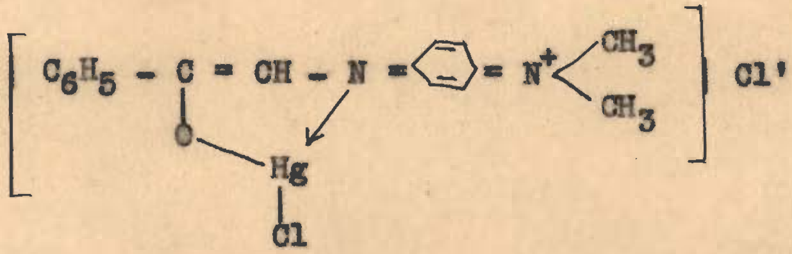
$* P = (Br-C_6H_4-\underset{\underset{O}{|}}{C}=CH-N=C_6H_4=N^{+}(CH_3)_2)$ unit

The chelates in their solid state were isolated by evaporating the reaction mixtures in a vacuum dessicator. The resinous mass thus obtained was washed several times by petroleum ether (60-80°) and the solid so obtained was crystallised from acetonitrile. The metal contents |pp.Fe(III) 108, Al(III) 124, Hg(II) 135, Zn(II) 146, Sn(IV) 158, and Sb(V) 17 were estimated by the usual methods.

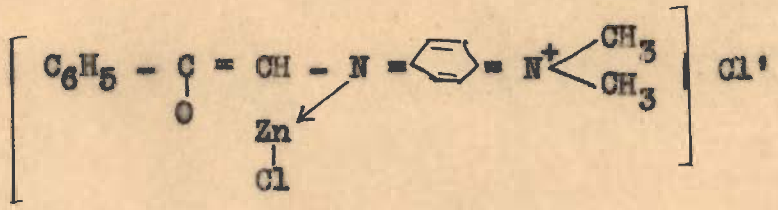
The actual linkages involved in chelate formation to form M-L bonds was studied by I.R. spectra. Perkin-Elmer Infracord spectrophotometer was used. In the spectra of the chelates lowering of stretching frequencies of >C=O and CH=N groupings from those of their normal values 1700 cm^{-1} and 1600 cm^{-1} in the ligand was observed. This lowering can only be due to binding uf the Lewis acids by coordination through oxygen and nitrogen of >C=O and CH=N groupings of the anil.

These chelates differ from those of Cu(II)-Phenacylidene aniline oxime complex that unlike cupric ion, the whole Lewis acid enter into complex formation (vide infra). Some typical structures of the Lewis acid chelates are given below.

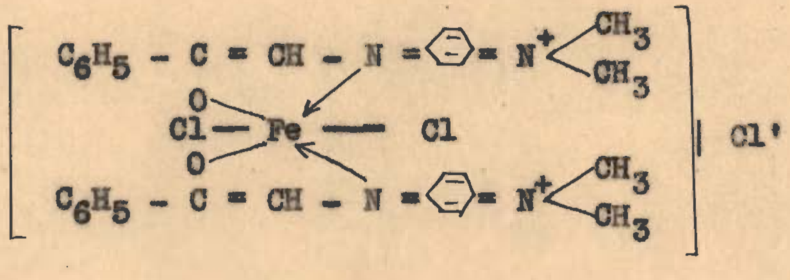
1.



2.



3.



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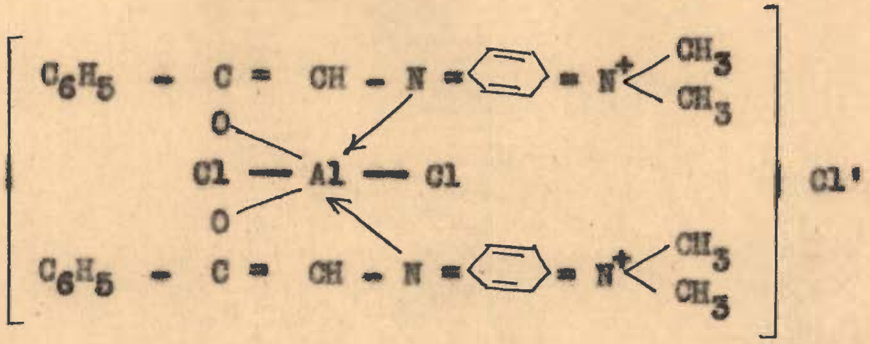
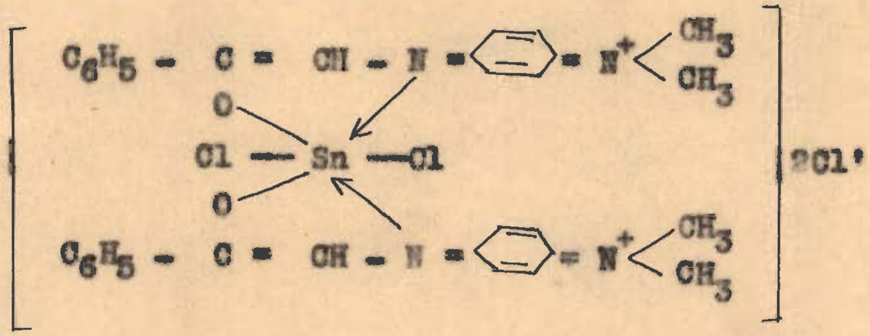
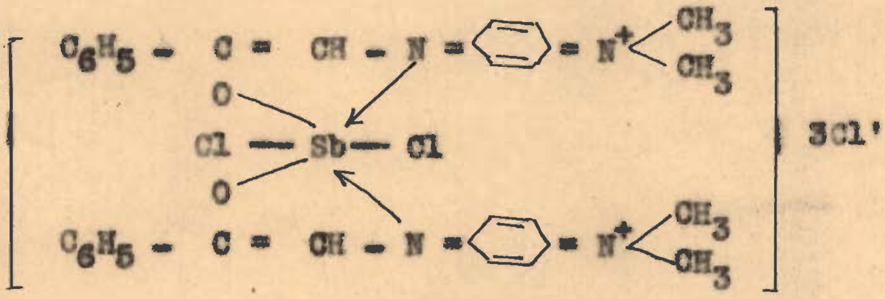


5.



6.



MAGNETIC PROPERTIES, CONDUCTIVITY MEASUREMENTS, U.V. AND VISIBLE SPECTRA OF THE COMPLEXES

The chelates Cu(II) - PAO, Hg(II), Zn(II), Sn(IV), Sb(V) and Fe(III) - p-bromo- phenacylidene p-dimethyl amino aniline were isolated as solids and kept in a vacuum dessicator to avoid the effect of moisture. Their magnetic susceptibilities were determined using A.R. copper sulphate pentahydrate as the calibrant. Magnetic moments were calculated from the relation:

$$u\ \text{eff.} = 2.84\sqrt{\chi'_M \times T} \quad \text{B.M.}$$

where T is absolute temperature.

These results, besides providing the information about the quanta state of the chelates, also gives evidence of the para-magnetism of p-bromo phenacylidene p-dimethyl amino aniline itself and its effect on complexes by charge transfer in the formation of M-L bond.

The effective magnetic moment of Cu(II)-PAO complex is 1.93 B.M. which is well within the range (1.70 - 2.20), expected for the copper complexes.

Hg(II), Sn(IV) and Sb(V) complexes are generally diamagnetic in character. But this peculiar paramagnetism in such type of complexes may be due to the induced magnetism carried out by the metal from that of the ligand to form charge transfer complexes.

Evidence for the formation of charge transfer complexes was available from U.V. spectra.

That the Lewis acids as such and not the metal ion alone coordinate with the ligand could be seen from conductivity measurements. The molar conductances (pp.200-203) of the complexes in acetone solution are of the same order as that of acetonic solution of the ligand. But some conductance showed that chlorine ion in the complexes, therefore, exists outside the coordination sphere.

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LIST OF PUBLICATIONS

1. Condensation of Some Aromatic Amines with Phenyl Glyoxal Jour. Chem. and Engg.Data , Vol.11, No.2, April 1966.

2. Preparation of Anils from Phenyl Glyoxal Hydrate and Aromatic Amino Compounds.(Indi Jour. Chem. (in press)

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ndensation of Some Aromatic Amines with Phenyl Glyoxal

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ME NEW ANILS have been prepared by condensing
nyl glyoxal hydrate (*1*) with aniline, *p*-chloroaniline,
nd *p*-nitroanilines, *o*-, and *p*- toluidines, and α-, and
phthylamines. They have been characterized by pre-
ng their *p*- nitrophenyl hydrazones, 2,4-dinitrophenyl
razones, semicarbazones, and oximes. The oximes give
r reactions with a number of metal ions and offer the
ibility of being used as analytical reagents.

EXPERIMENTAL

Preparation of Anils. Equimolar quantities of phenyl glyoxal hydrate and the corresponding amines in 95% ethanol were refluxed on a water bath. The solid products, which separated on cooling, were crystallized from absolute alcohol and gave anils listed in Table I. These anils are soluble in methanol, ethanol, benzene, acetone, and chloro-

Table I. Anils Derived from Phenyl Glyoxal and Aromatic Amines

Anil	Color	Formula	M.P., ° C.	Yield, %	Nitrogen, %	
					Calcd.	Found
R-[a]Aniline	Yellow	$C_{14}H_{11}ON$	89–90	90.9	6.69	6.73
R- *p*-Chloroaniline[b]	Colorless	$C_{14}H_{10}ONCl$	115–116	63.6	5.74	5.89
R- *o*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	105–106	82.2	11.02	11.29
R- *p*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	127–129	47.2	11.02	11.41
R- *o*-Toluidine	Reddish brown	$C_{15}H_{13}ON$	Gummy mass	85.5	6.28	6.12
R- *p*-Toluidine	Yellow	$C_{15}H_{13}ON$	97–98	89.6	6.28	6.32
R- α-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	136–137	92.2	5.40	5.24
R- β-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	90–91	61.8	5.40	5.12

[a] R = C_6H_5—CO—CH= (phenacylidene radical). [b] No warming necessary to obtain these anils.

Table II. Characteristics of the Derivatives of Anils

Anil	*p*-Nitro Phenyl Hydrazones			2,4-Dinitro Phenyl Hydrazones			Semicarbozones			Oximes		
	M.P., ° C.	Nitrogen, %		M.P., ° C.	Nitrogen, %		M.P., ° C.	Nitrogen, %		M.P., ° C.	Nitrogen, %	
		Calcd.	Found		Calcd.	Found		Calcd.	Found		Calcd.	Found
Aniline	185–186	16.28	16.53	236–238	17.99	17.74	190–191	21.05	20.95	58–59	12.5	12.46
p-Chloroaniline	200–201	16.16	16.46	267–269	16.52	16.46	180–181	18.63	18.44	146–147	10.83	10.35
o-Nitroaniline	233–234	17.99	17.61	255–256	19.35	19.12	197–198	22.50	22.31	189–201	15.61	15.42
p-Nitroaniline	250–252	17.99	17.54	262–263	19.35	19.40	203–205	22.50	22.25	206–207	15.61	15.48
o-Toluidine	100–101	15.64	15.56	250–251	17.36	17.25	. . .	. . .	. . .	77–78	11.76	11.56
p-Toluidine	134–135	15.64	15.32	263–265	17.36	17.16	244–245	20.00	19.95	101–102	11.76	11.43
α-Naphthylamine	264–265	14.21	14.13	194–195	15.94	15.63	210–211	17.72	17.56	119–120	10.22	10.20
β-Naphthylamine	189–190	14.21	14.09	247–249	15.94	15.83	100–101	17.72	17.43	95–96	10.22	10.32

C_6H_5—CO—CH=.

Preparation of Anils from Phenyl Glyoxal Hydrate and Aromatic Amino Compounds.*

WAHID U. MALIK, D. R. GUPTA[x] AND C. L. TAPLOO
Department of Chemistry, University of
Roorkee, Roorkee.

Some new anils derived from phenyl glyoxal hydrate and aromatic amines were reported earlier(1). The present communication deals with the preparation of anils from phenyl glyoxal hydrate and m-nitroaniline, p-bromoaniline, m-chloroaniline m-toluidine, o-aminophenol, p-aminophenol, o-anisidine, sulphanilic acid, anthranilic acid, m-aminobenzoic acid, p-aminobenzoic acid and sulphanilamide. These anils have been characterized from their p-nitro phenyl hydrazones, 2:4-dinitro phenyl hydrazones, semicarbazones and oximes.

Preparation of Anils:

The anils listed in table I were prepared by refluxing on a water bath equimolar quantities of phenyl glyoxal hydrate and the corresponding amino compounds in 95 % ethanol. On cooling, the solid products obtained were separated and crystallized from hot alcohol. These anils are soluble in methanol, acetone, acetonitrile, benzene and toluene; while they are practically insoluble in water and petroleum ether.

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[*] Indian Journal of Chemistry (In press).

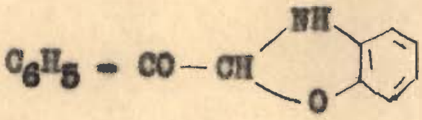
[x] Professor of Chemistry, U.P. Agricultural University, Pantnagar, Nainital.

Table 1- Anils Derived from Phenyl Glyoxal Hydrate and Aromatic Amino Compound.

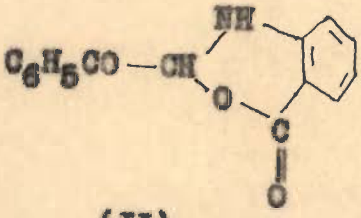
Name of the Anil	Colour	Formula	M.P. °C	Yield %	Nitrogen Calcd.	Nitrogen Found
R-m-Nitro aniline	Yellow	$C_{14}H_{10}O_3N$	157-158	19.68	11.02	10.96
R-p-Bromo aniline	Buff	$C_{14}H_{10}ONBr$	137-138	83.38	4.68	4.49
R-m-Chloro aniline	Reddish Brown	$C_{14}H_{10}ONCl$	66-67	18.69	5.74	5.62
R-m-Toluidine	Yellow	$C_{15}H_{13}ON$	113-114	19.33	6.28	6.13
R-o-Amino phenol	Dark Brown	$C_{14}H_{11}O_2N$	173-174	93.33	6.22	6.05
R-p-Amino phenol	Chocolate	$C_{14}H_{11}O_2N$	125-127	40.00	6.22	6.12
R-o-Anisidine	Light Yellow	$C_{15}H_{13}O_2N$	126-127	53.00	5.85	5.71
R-Sulphanilic acid.	Light Pink	$C_{14}H_{11}O_4NS$	244-245d	99.20	5.01	4.98
R-Anthranilic acid.	Pale Yellow	$C_{15}H_{11}O_3N$	140-141	64.53	5.53	5.24
R-m-Amino benzoic acid	Buff	$C_{15}H_{11}O_3N$	245-246	39.72	5.53	5.32
R-p-Amino benzoic acid	Light Yellow	$C_{15}H_{11}O_3N$	170-171	73.22	5.53	5.16
R-Sulphanilamide	Light Yellow	$C_{14}H_{12}O_3N_2S$	95-96	66.63	9.72	9.48

(R = C_6H_5 - CO - CH = , Phenacylidene radical)

Although in the synthesis of the aniles of phenyl glyoxal hydrate-o-aminophenol and anthranilic acid the following two alternative structures can be envisaged, but their possibility is ruled out on the following observation:



(I)



(II)

The structure I should not give a phenolic test while structure II would not respond to the carboxylic group test. It is, however, observed that alcoholic solution of the condensation product of phenyl glyoxal hydrate and o-aminophenol gives red colouration with alcoholic ferric chloride solution, confirming the presence of a free phenolic group, while the condensation product of phenyl glyoxal hydrate and anthranilic acid is soluble in sodium hydroxide solution indicating the presence of a free-COOH grouping. The possibility of the existence of structure I and II is, therefore , very remote.

2:4:6 tribromo aniline, however, gave no condensation product with phenyl glyoxal hydrate probably due to steric hindrance caused by bromine atoms in the ortho positions.

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Condensation of Some Aromatic Amines with Phenyl Glyoxal

WAHID U. MALIK, D. R. GUPTA, and C. L. TAPLOO
Chemical Laboratories, University of Roorkee, Roorkee, India

SOME NEW ANILS have been prepared by condensing phenyl glyoxal hydrate (*1*) with aniline, *p*-chloroaniline, *o*-, and *p*-nitroanilines, *o*-, and *p*- toluidines, and *α*-, and *β*-naphthylamines. They have been characterized by preparing their *p*- nitrophenyl hydrazones, 2,4-dinitrophenyl hydrazones, semicarbazones, and oximes. The oximes give color reactions with a number of metal ions and offer the possibility of being used as analytical reagents.

EXPERIMENTAL

Preparation of Anils. Equimolar quantities of phenyl glyoxal hydrate and the corresponding amines in 95% ethanol were refluxed on a water bath. The solid products, which separated on cooling, were crystallized from absolute alcohol and gave anils listed in Table I. These anils are soluble in methanol, ethanol, benzene, acetone, and chloro-

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Anil	Color	Formula	M.P., ° C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
R-[a]Aniline	Yellow	$C_{14}H_{11}ON$	89–90	90.9	6.69	6.73
R- *p*-Chloroaniline[b]	Colorless	$C_{14}H_{10}ONCl$	115–116	63.6	5.74	5.89
R- *o*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	105–106	82.2	11.02	11.29
R- *p*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	127–129	47.2	11.02	11.41
R- *o*-Toluidine	Reddish brown	$C_{15}H_{13}ON$	Gummy mass	85.5	6.28	6.12
R- *p*-Toluidine	Yellow	$C_{15}H_{13}ON$	97–98	89.6	6.28	6.32
R- *α*-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	136–137	92.2	5.40	5.24
R- *β*-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	90–91	61.8	5.40	5.12

[a] R = C_6H_5—CO—CH= (phenacylidene radical). [b] No warming necessary to obtain these anils.

Table II. Characteristics of the Derivatives of Anils

Anil	*p*-Nitro Phenyl Hydrazones M.P., ° C.	Nitrogen, % Calcd.	Nitrogen, % Found	2,4-Dinitro Phenyl Hydrazones M.P., ° C.	Nitrogen, % Calcd.	Nitrogen, % Found	Semicarbozones M.P., ° C.	Nitrogen, % Calcd.	Nitrogen, % Found	Oximes M.P., ° C.	Nitrogen, % Calcd.	Nitrogen, % Found
R-[a] Aniline	185–186	16.28	16.53	236–238	17.99	17.74	190–191	21.05	20.95	58–59	12.5	12.46
R- *p*-Chloroaniline	200–201	16.16	16.46	267–269	16.52	16.46	180–181	18.63	18.44	146–147	10.83	10.35
R- *o*-Nitroaniline	233–234	17.99	17.61	255–256	19.35	19.12	197–198	22.50	22.31	189–201	15.61	15.42
R- *p*-Nitroaniline	250–252	17.99	17.54	262–263	19.35	19.40	203–205	22.50	22.25	206–207	15.61	15.48
R- *o*-Toluidine	100–101	15.64	15.56	250–251	17.36	17.25	. . .	. . .	. . .	77–78	11.76	11.56
R- *p*-Toluidine	134–135	15.64	15.32	263–265	17.36	17.16	244–245	20.00	19.95	101–102	11.76	11.43
R- *α*-Naphthylamine	264–265	14.21	14.13	194–195	15.94	15.63	210–211	17.72	17.56	119–120	10.22	10.20
R- *β*-Naphthylamine	189–190	14.21	14.09	247–249	15.94	15.83	100–101	17.72	17.43	95–96	10.22	10.32

[a] R = C_6H_5—CO—CH=.

Derivatives of Anils

p-nitro phenyl hydrazones, 2:4-dinitro phenyl hydrazones, semicarbazones and oximes of the anils were prepared by the usual methods and were obtained almost in theoretical yields. p-nitro phenyl hydrazones and 2:4 -dinitro phenyl hydrazones were crystallised from nitro benzene. Semicarbazones and oximes were, however, crystallised from ethanol. The characteristics of these derivatives are recorded in table II.

The oximes of many of these anils produce yellow, greenish yellow and green colouration with metal ions and offer a possibility for being used as analytical reagents.

Thanks are due to C.S.I.R., New Delhi, for the grant of a research scheme No.I(205)/63-E.II under which this work has been carried out.

Reference

(1) Malik, W.U., Gupta, D.R. and Taploo, C.L., J. Chem. Eng. Data, 11 (1966), 210.

Table -II   Characteristics of the Derivatives of Anils

Name of the anil	p-Nitro phenyl hydrazones			2:4 Dinitro phenyl hydrazones			Semi-carbazones			Oximes		
	M.P. °C	Nitrogen, %		M.P. °C	Nitrogen, %		M.P. °C	Nitrogen, %		M.P. °C	Nitrogen, %	
		Calcd	Found		Calcd	Found		Calcd	Found		Calcd	Found
R-m-Nitro aniline.	267-268	17.99	17.73	273-274	19.35	19.13	190-191	22.50	22.35	176-177	15.61	15.32
R-p-Bromo aniline	198-199	13.23	13.15	244-226	14.93	14.76	226-227	16.23	16.18	185-186	9.24	9.08
R-m-Chloro aniline	101-102	16.16	16.03	200-201	16.52	16.14	240-241	18.63	18.24	94- 95	10.83	10.56
R-m-Toluidine	257-258	15.64	15.42	241-243	17.36	17.13	233-234	20.00	19.89	95-96	11.76	11.61
R-o-Amino phenol	270-272	15.55	15.23	241-242	17.45	17.28	218-219	19.82	19.71	257-258	11.66	11.34
R-p-Amino phenol	244-245	15.55	15.19	259-260	17.45	17.13	221-222$_d$	19.82	19.63	180-181	11.66	11.23
R-o-Anisidine	198-199	14.97	14.68	267-269	16.70	16.42	229-230	18.91	18.69	89-90	11.02	11.97
R-Sulphanilic acid	274-275	13.20	13.[illegible]	240-241	14.92	14.76	230-232	16.18	16.06	163-164	9.21	9.06
R-Anthranilic acid	218-219$_d$	14.43	14.18	255-256$_d$	16.16	15.98	197-198	18.06	17.98	160-161	10.44	10.28
R-m-Amino Benzoic acid	208-209$_d$	14.43	14.20	203-204	16.16	15.86	265-267	18.06	18.01	185-186	10.44	10.17
R-p-Amino Benzoic acid	199-200	14.43	14.18	306-307	16.16	15.93	233-234	18.06	17.82	158-159	10.44	10.36
R-Sulphanilamide	259-260	16.54	16.48	194-195	17.65	17.42	133-134	20.28	20.13	132-133	13.86	13.65

($R = C_6H_5 - C O - CH =$)