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UNIVERSITY OF ROORKEE,
ROORKEE (U.P.)

Certified that the attached Thesis ~~Dissertation~~ on "PHYSICO CHEMICAL STUDIES ON THE INTERACTION OF ANILS WITH INORGANIC GELS & SOME LEWIS ACIDS"

was submitted by

SRI ROOP CHANDRA SAXENA

and accepted for the award of Degree of Doctor of Philosophy ~~Master of Engineering~~ in "CHEMISTRY"

vide Notification No. Ex/145/E-191

dated Nov. 9/10, 1967

(S.S.Srivastava)
Assistant Registrar (Exam.)

Dated 11.12.1967

PSUP (R) 87 Ch. 1966—1,000.

PHYSICO-CHEMICAL STUDIES ON THE INTERACTION OF ANILS WITH INORGANIC GELS & SOME LEWIS ACIDS

Thesis submitted for the award of
the Degree of
Doctor of Philosophy
in
Chemistry

by
ROOP CHANDRA SAXENA

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE
July, 1967

PHYSICO- CHEMICAL STUDIES ON THE INTERACTION OF ANILS WITH INORGANIC GELS AND SOME LEWIS ACIDS.

THESIS SUBMITTED FOR THE AWARD OF THE DEGREE
OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

Roop Chandra Saxena

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE

JULY, 1967

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Financial assistance of C.S.I.R. by providing me a fellowship on the scheme on anils is gratefully acknowledged.

Roop Chandra Saxena
(Roop Chandra Saxena)

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CERTIFICATE

Certified that the thesis entitled " Physico Chemical studies on the interaction of anils with inorganic gels and some Lewis acids", which is being submitted by Mr. Roop Chandra Saxena, 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 my 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 to prepare this thesis at this university.

Wahid U. Malik

Wahid U.Malik,
Ph.D.,D.Sc;
F.N.A.Sc; F.R.I.C.
(London)

Prof. & Head of the Chemistry
Department,
University of Roorkee, ROORKEE

ROORKEE

July 31 ,1967

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CONTENTS

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INTRODUCTORY REMARKS

INTRODUCTORY REMARKS

Investigations on the class of compounds known as anils have been carried out mainly from the synthetic view point. Here too the studies have been limited to benzylidene aniline and its derivatives and very little has been attempted at to synthesise and characterise new anils like those obtained from glyoxals and aromatic amines.

Apart from this little information is available on certain very interesting and important physico-chemical aspects, viz., their role as chelating agents, their use as colorimetric reagents, their adsorption and even possible interaction (due to bathochromic effect) with gels etc. The only work worth quoting in this direction is that of Krohnke and Gross(1) on bathochromic effect in p-dimethyl amino anil of phenyl glyoxal as observed by complex formation and adsorption.

The scanty knowledge about anils, especially about their physico-chemical behaviour, as described above, pointed towards the necessity and importance of undertaking systematic studies on these compounds. To begin with, the following aspects, which go to form the main theme of the thesis, were investigated :-

(i) β- naphthacylidene aniline, β-naphthacylidene - p-toluidene, β-naphthacylidene- p - chloroaniline, β- naphthacylidene - m - nitroaniline, β-naphthacylidene - p - nitroaniline, β-naphthacylidene, α- naphthyl amine,

β - naphthacylidene - β - naphthyl amine, p-dimethyl amino anil of β - naphthyl glyoxal, p - dimethyl amino anil of β - naphthyl glyoxal nitrile, p-dimethyl amino anil of methyl glyoxal anils, not synthesised so far were prepared and characterised by obtaining their derivatives and I.R. spectra.

(ii) The peculiar and interesting property of the above anils (as well as the previously synthesised anil, p-dimethyl amino anil of phenyl glyoxal) to undergo chelation with metals not particularly belonging to transition elements was studied in detail and the composition and structure of the complexes so obtained was investigated using methods of chemical analysis, visible spectrophotometry and I.R. spectroscopy. The metal salts chosen for these studies were the Lewis acids.

(iii) Adsorption of the anils in various non-polar solvents on inorganic gels including silica was studied and the nature of adsorption isotherm critically examined.

(iv) The behaviour of the non-aqueous solutions of some metal chelates of anils on the silica surface was studied to establish the relationship between pore availability and adsorption or surface reactions.

(v) The Appendix gives a few data on the magnetic susceptibility of the anils and its mercury, zinc and cadmium complexes to establish the phenomenon of partial charge transfer in these anils, rendering the ligand paramagnetic inspite of the lone pair of electrons associated with their structural formulae.

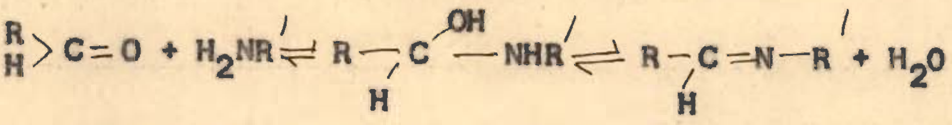
CHAPTER I

Anils formed by the condensation of β-naphthyl glyoxal hydrate and methyl glyoxal with aromatic amines.

INTRODUCTION

Anils are the condensation products of aromatic amines and the corresponding aldehydes. The first anil, benzylidene aniline, was prepared by Von Schiffs(1) by condensing benzaldehyde with aniline in presence of zinc chloride as an azeotropic reagent. They are characterised by the auxochromic grouping -CH=N due to which they owe their colour. However, the colour can be deepened by the presence of auxochromic group like - NH_2, - OH, - SO_3H, - COOH etc. The azomethine grouping - CH=N, is susceptible to mineral acids and hence the presence of mineral acid may reverse the process towards reactants.

Besides condensing aromatic aldehyde and the corresponding amine with or without solvent, anils can also be synthesised in vapour phase by passing vaporised reactants over a heated catalyst such as ThO_2. The general mechanism for their preparation is as follows:

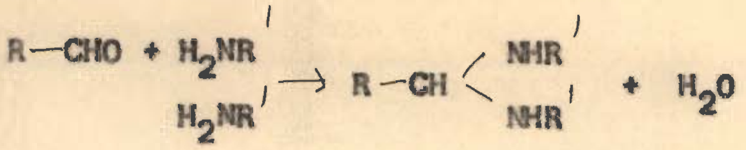


$$\begin{matrix}R\\H\end{matrix}\!>C=O + H_2NR' \rightleftharpoons R-\underset{H}{\overset{OH}{C}}-NHR' \rightleftharpoons R-\underset{H}{C}=N-R' + H_2O$$

where R and R' may be phenyl or any aryl radical.

In general the loss of water is spontaneous and the intermediate hydroxyl alkylamine does not appear.

In the preparation of anils, excess of amino compound should be avoided. For example, if two molecule of the amine be taken, then - CH=N group is not involved in the preparation, of the final product.



$$R{-}CHO + \begin{matrix} H_2NR' \\ H_2NR' \end{matrix} \rightarrow R{-}CH\left\langle \begin{matrix} NHR' \\ NHR' \end{matrix} \right. + H_2O$$

Besides the usual method of the condensation (loc. cit.), anils can also be prepared by the oxidation of the amines, such as $R'C-NHR'$, chromic acid, peroxy disulphate, $KMnO_4$ in acetone and sulphur have been recommended as the suitable oxidising agent in the process.

Industrial uses of Anils :-

The importance of anils can be judged from their use as the accelerators in the vulcanisation of rubber(2-3), jet fuel stablisers and anticancerous material. Since some of the Schiff's bases can form metal chelates with different cations, these have been used as sequestering agents in oil refining to remove harmful metals present in the crude oil during the storage of the oil. So blending the mineral oil with an appropriate Schiff's base can avoid such contamination to a large extent.

In the synthetic organic chemistry, anils are not far behind. Their use as intermediates is well known:

(i) in the preparation of carbonyl compounds, e.g. hydrolysing the Schiff's base with mineral acid, carbonyl compound are obtained,

(ii) in the alkylation of amines(4) and in the preparation of α-amino acid.

(iii) in the preparation of diphenyl methane bases, quinazolines, anils prove potential intermediate,

(iv) carbonyl compound or the corresponding amine can be isolated from the mixture by the formation of the anil and subsequently hydrolysing it, e.g. d-arginine(5) can be isolated from a gelatin hydrolyzate by the formation of the anil benzylidene arginine as an intermediate and hydrolysing this to the corresponding amino compound.

The anils of salicylaldehyde have proved specific analytic reagents for metal ions e.g. salicyledene - 2 - benzothiazole provides an orange precipitate with Ag^+ ion and is specific for it(6-10).

Anils derived from glyoxal and aromatic amines have not been investigated comprehensively so far. Few references are available on them. The only reference worth mentioning is that of Krohnke and Gross(11) who synthesised p-dimethyl amino anil of phenyl glyoxal to investigate bathochromic effect in the compound in presence of Lewis acids and silica gel.

Recently anils derived from phenyl glyoxal hydrate and primary aromatic amines have been reported(12).

The present chapter describes the synthesis of a new anil obtained from β- naphthyl-glyoxal hydrate and methyl glyoxal are reported. The methods recommended by various authors are employed in their preparation except in the case of the anil p-dimethyl amino anil of β-naphthyl - glyoxal nitrile where a different route has to be used(13). These anils have been characterised from their 2:4, dinitrophenyl-hydrazones, semi-carbazones and oximes.

EXPERIMENTAL

Preparation of Anils -

The anils listed in table No.1 were prepared by refluxing on water bath equimolar quantities of β-naphthyl glyoxal hydrate(14) and corresponding amines in a mixture of glacial acetic acid and ethanol (1:6 $\frac{v}{V}$) except in the case of p-dimethyl amino(15) anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal in which condensation was carried out in 70 % ethanol at room temperature. On cooling a yellow oil was obtained which was difficult to crystallise. The following procedure was adopted:

The oily mass was dissolved in a minimum quantity of benzene and chromatographed over Brockmann alumina. Petroleum ether (60-80°), benzene, chloroform and their mixtures were used as the eluants. Most of the fractions were found to be greasy except that from chloroform which afforded a solid mass on evaporating the solvent. The left over was charcolised and rechromatographed. But even then solid could not be obtained. The fraction obtained from chloroform was crystallised from hot methanol.

The anils reported above are soluble in benzene, xylene, toluene, acetone, chloroform and acetonitrile, but are practically insoluble in water.

Preparation of p-dimethyl amino anil of β-naphthyl - glyoxal nitrile:

Pyridinium iodide of β-naphthyl methyl ketone was synthesised by the interaction of iodine with β-naphthyl methyl ketone in presence of pyridine(17). 0.80 gm. of pyridinium iodide of β -naphthyl methyl ketone was dissolved in 10 cc of 50 % ethanol and treated with 0.33 gm. of p-nitrosodimethyl aniline in 10.0 cc[(18)] ethanol. This was followed by the addition of 1.50 gm. of sodium cyanide in 4.0 cc water, maintaining a temperature of 0-10° throughout the course of reaction. On addition of more water with subsequent chilling, scarlet red crystals of the anil were obtained which could be crystallised from glacial acetic acid.

m.P - 140°c

Derivative of anils:

2:4 - dinitrophenyl hydrazones, semicarbazones and the oximes of the anils were prepared by the usual methods and were obtained almost in theoretical yields. They were crystallised from hot alcohol. Characteristics of the derivatives are recorded in Table No.2.

p-dimethyl amino anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal give colour reaction with number of Lewis acids such as $Zncl_2$, $Fecl_3$, CdI_2, $HgCl_2$ and $SnCl_4$.

Infra red spectra of Anils :

In order to ascertain the functional groups of anils listed in table 1 their infra red spectra were recorded in potassium bromide medium by Perkin - Elmer Infra cord. The stretching frequencies of the groups are listed in table No.3.

The stretching frequency of an aryl, methyl or naphthyl ketone lies[(19)] between 1695-1715 cm^{-1}. Conjugation with respect to C=O, phenyl, methyl or naphthyl group generally decreases this frequency. Since the frequencies of the anils reported here are around the above range, it may be concluded that the anils possess a $>C = O$ group in the vicinity of β-naphthyl skeleton. Moreover, the stretching frequency of $C = N$(19) (unconju-gated) lies between 1610-1700 cm^{-1}. Since the stretching frequencies of the anils range from 1540 to 1625 cm^{-1}, evidence for the presence of C=N is thus available. The lower value may again be due to conjugation. The frequency around 820-840 cm^{-1} may be due to para disubstituted derivatives.

Table No.1

Anils derived from β -naphthyl glyoxal hydrate; methyl glyoxal and aromatic amines.

Anil	Colour	M.P	Yield	Formula	Nitrogen % Calculated	Nitrogen % Found
R- aniline	yellow	96-97	90%	$C_{18}H_{13}NO$	5.40	5.36
R- p-toluidine	Brick red	90-92	92-93%	$C_{19}H_{15}NO$	5.12	5.00
R- p-chloroaniline	Yellow	140-141	80%	$C_{18}H_{12}NOCl$	4.77	4.65
R- m-nitroaniline	Yellow	98°	70%	$C_{18}H_{12}N_2O_3$	9.21	9.16
R- p-nitroaniline	Yellow	123-124	72%	$C_{18}H_{12}N_2O_3$	9.21	9.12
R-* α-naphthylamine	Yellow	144-145	70%	$C_{22}H_{15}NO$	4.53	4.35
R-* β -naphthylamine	Gummy mass	-	-	$C_{22}H_{15}NO$	-	-
R- p-dimethyl amino aniline	Reddish orange	112-113	80%	$C_{20}H_{18}N_2O$	9.27	9.21
R- nitrile p-dimethyl amino aniline	Dark red	140-141	90%	$C_{21}H_{17}N_3O$	12.84	12.78
R′- p-dimethyl amino aniline	Pale yellow	122°	78%	$C_{11}H_{14}N_2O$	14.73	14.52

R- $C_{10}H_7COCH=$ (β -naphthacyl)

R′- $CH_3COCH=$

* - Slight warming was necessary.

Table No. 2

Characteristics of the Derivative of anils

Anil	2:4-Dinitrophenyl hydra-zones			Semi carbazones			Oximes		
	M.P. O^c	N% Calculated	Found	M.P. O^c	N% Calculated	Found	M.P. O^c	N% Calculated	Found
R- aniline	167d	15.94	15.90	130-131	17.72	17.70	105-106	10.21	10.20
R-p-toluidine	172-173	15.45	15.42	150-152	16.96	16.89	123-124	9.72	9.59
R-p-chloroaniline	130-131	14.78	14.71	110-111	15.97	15.93	117-118	9.07	9.50
R-m-nitroaniline	120-121	17.35	17.30	150-151	19.39	19.40	170-171	13.16	13.10
R-p-nitroaniline	150-151	17.35	17.32	135-136	19.39	19.36	190-192	13.16	13.13
R-α-naphthylamine	235d	14.31	14.29	210-212	15.30	15.19	153-155	8.64	8.61
R-β-naphthylamine	218-220	14.31	14.34	200-201	15.30	15.25	186-187	8.64	8.60
R^x-p-dimethyl amino aniline	150-151	17.42	17.40	180-182	19.49	19.44	181-182	13.24	13.21
R-p-dimethyl amino aniline acid nitrile	250-252	19.32	19.30	131°	21.87	21.82	145-146	16.37	16.34
R^o-p-dimethyl amino aniline	190-192	22.70	22.65	150	28.34	28.31	138	20.48	20.40

R- $C_{10}H_7CO\ CH =$ (β-naphthacyl -)

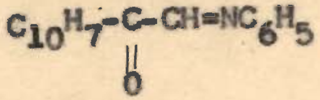
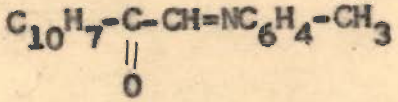
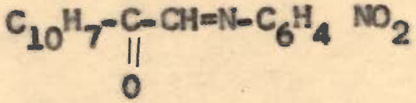
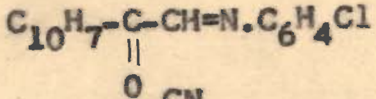
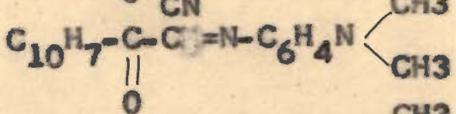
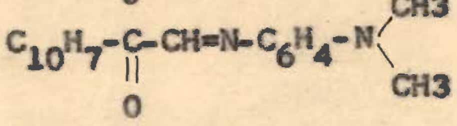
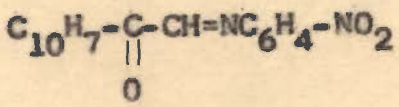
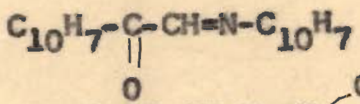
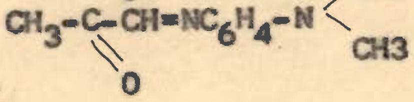
R^o- $CH_3COCH =$

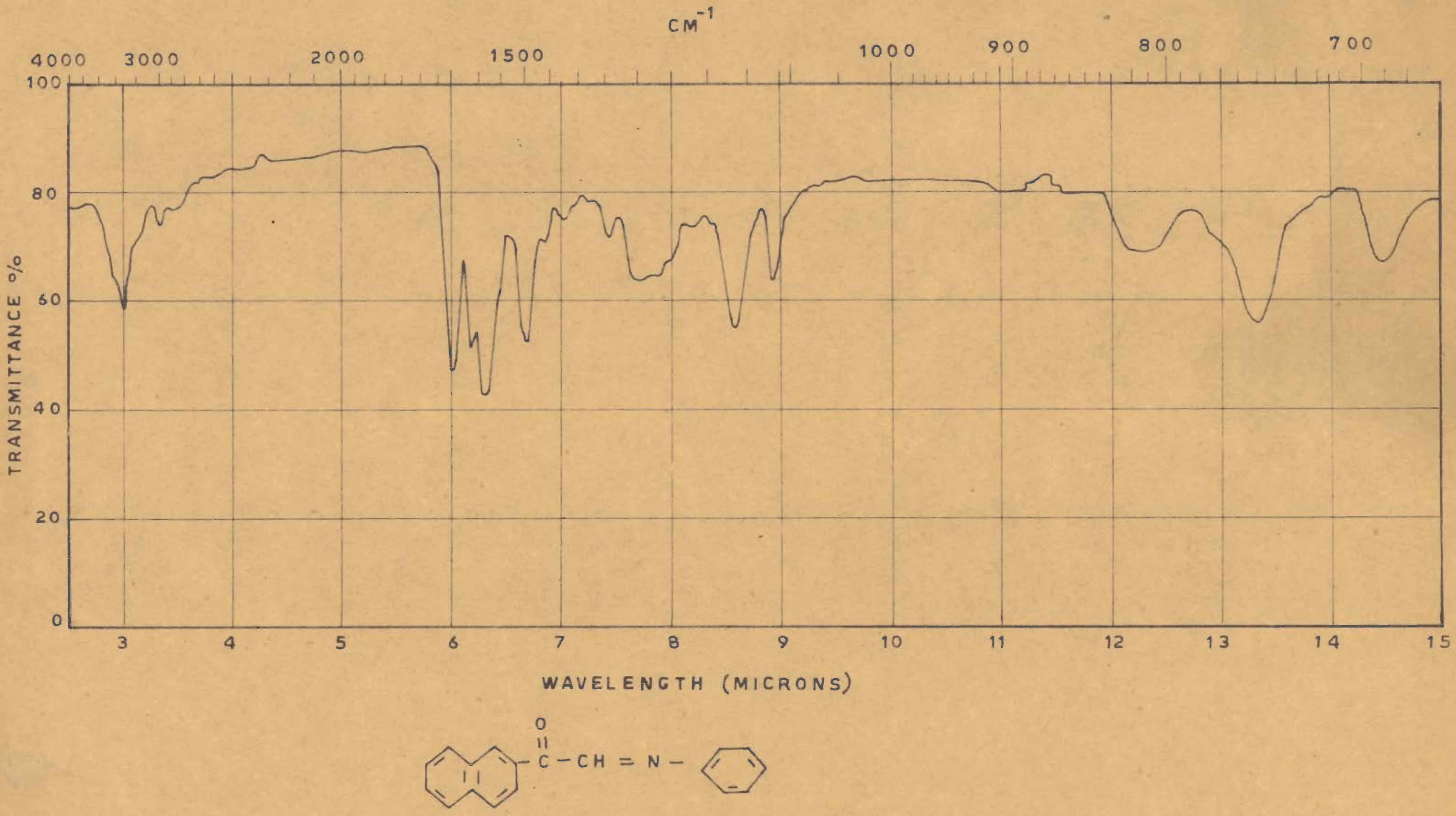
d - decompose

x - No warming was necessary.

Table No. 3

Stretching frequencies of the functional groups of the anils

Structure of anils	CH=N cm^{-1}	C=0 cm^{-1}	p-substituted groups cm^{-1}	Fig. No.
1.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=NC_6H_5$	1580	1660	-	1
2.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=NC_6H_4-CH_3$	1600	1660	820	2
3.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=N-C_6H_4\ NO_2$	1600	1640	840	3
4.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=N.C_6H_4Cl$	1600	1650	830	4
5.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-\overset{CN}{C}=N-C_6H_4N\left\langle\begin{matrix}CH3\\CH3\end{matrix}\right.$	1575	1680	825	5
6.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=N-C_6H_4-N\left\langle\begin{matrix}CH3\\CH3\end{matrix}\right.$	1625	1660	830	6
7.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=NC_6H_4-NO_2$	1540	1640	827	7
8.  $C_{10}H_7-\underset{\overset{\|}{0}}{C}-CH=N-C_{10}H_7$	1610	1680	-	8
9.  $CH_3-\underset{\overset{\|}{0}}{C}-CH=NC_6H_4-N\left\langle\begin{matrix}CH3\\CH3\end{matrix}\right.$	1600	1630	820	9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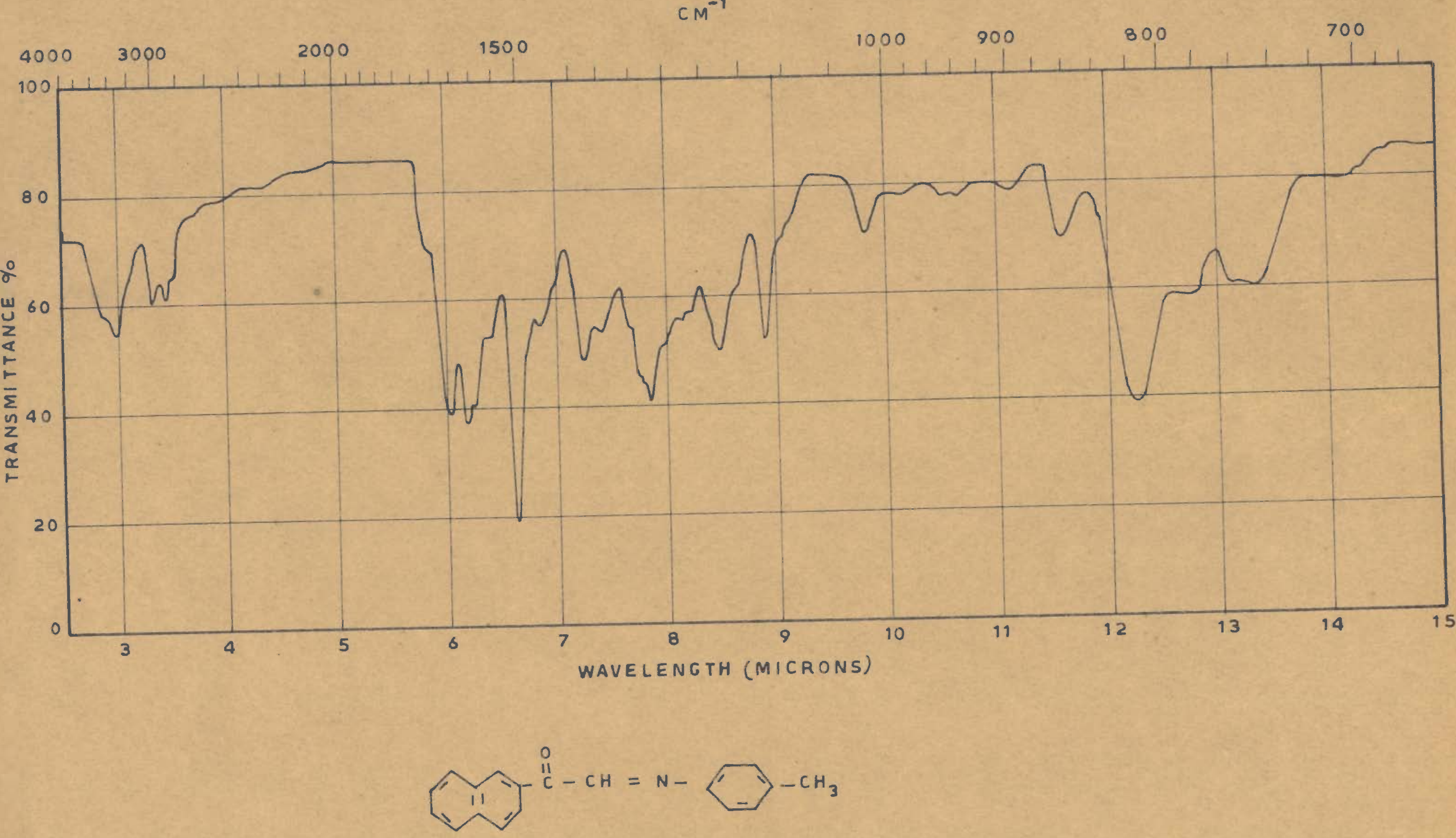
WAVELENGTH (MICRONS)
O
C – CH = N –

FIGURE_1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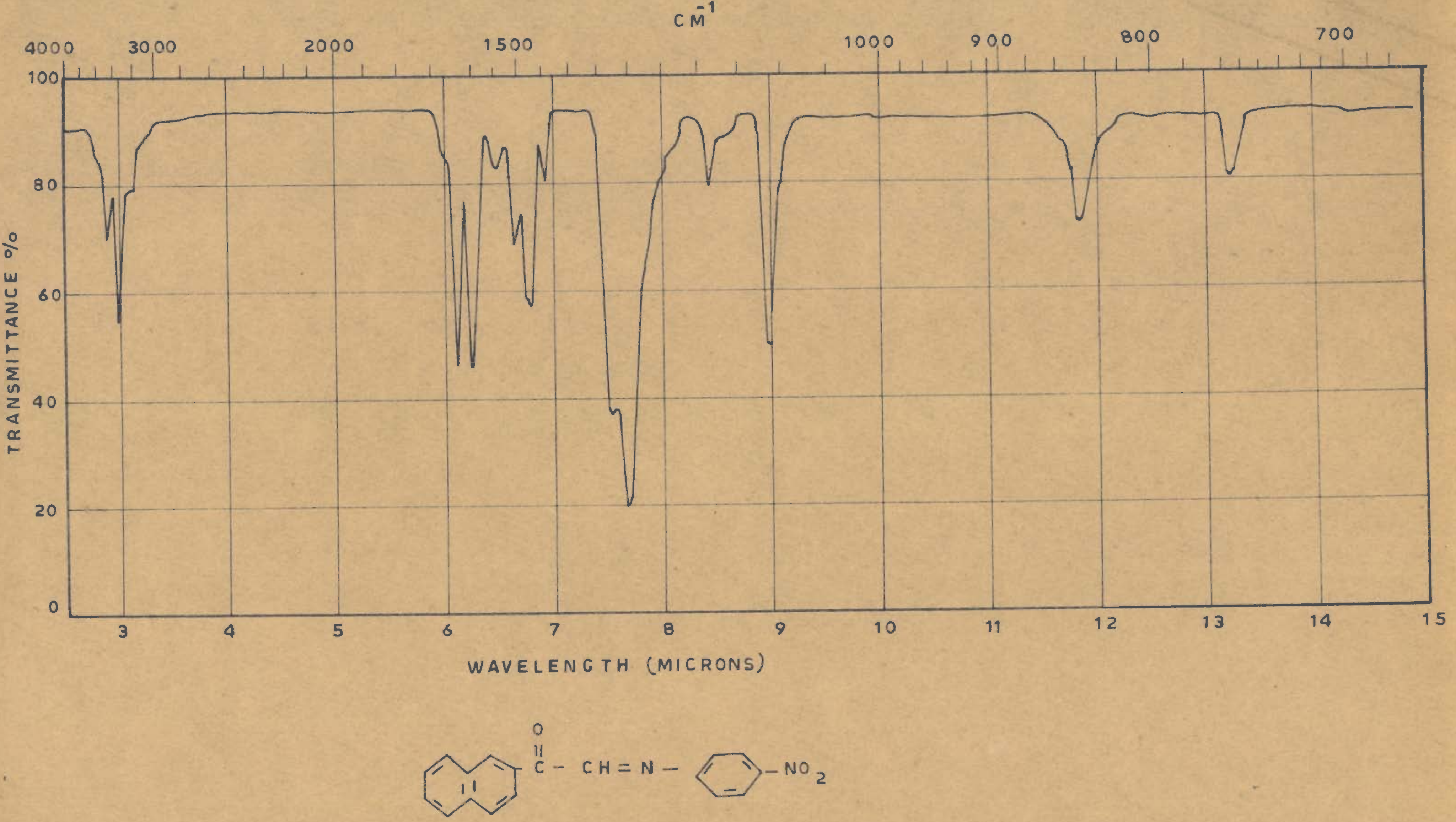
O
C – CH = N –
–CH3

FIGURE_ 2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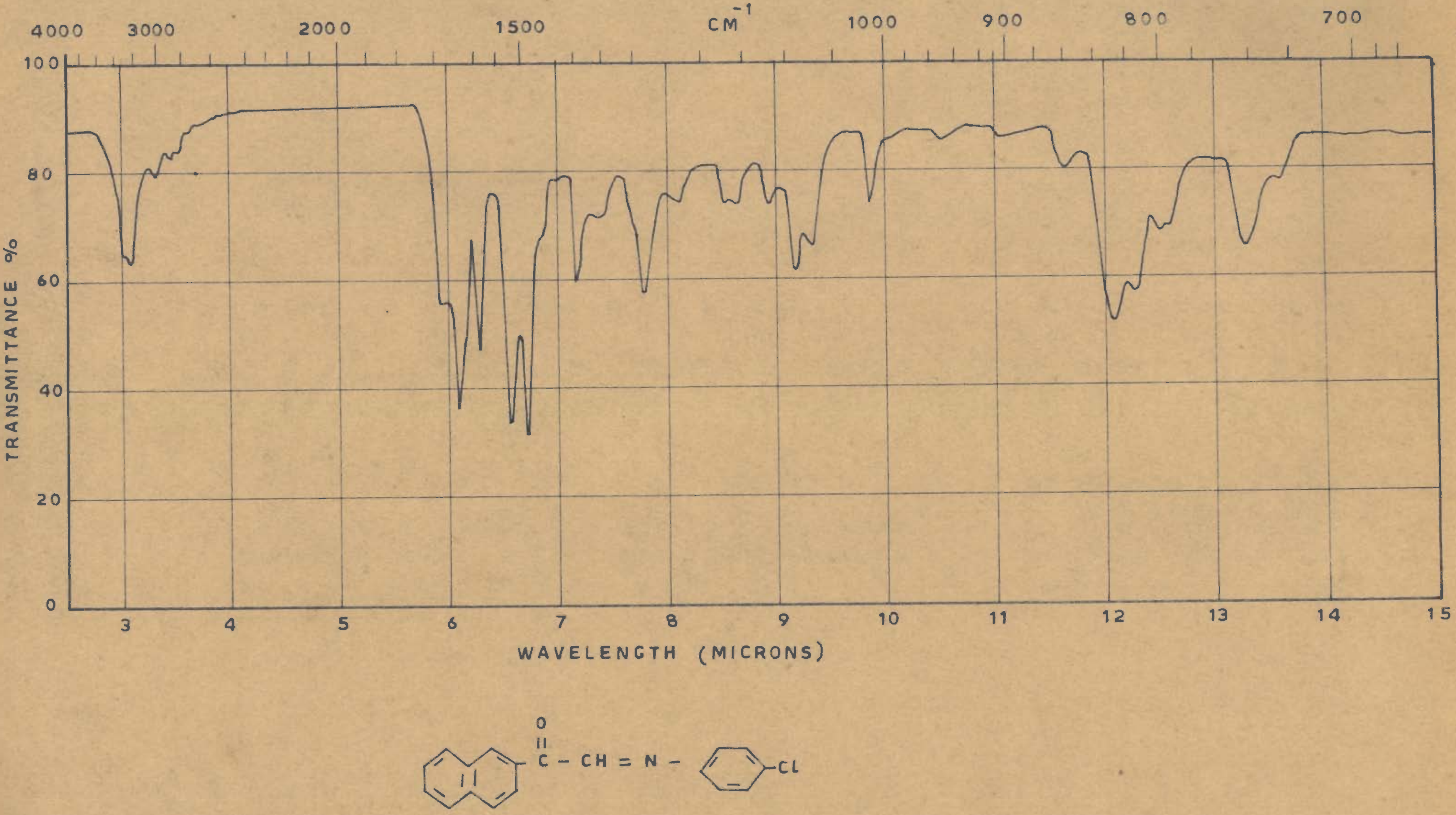
WAVELENGTH (MICRONS)
O
C - CH = N -
- NO$_2$

FIGURE _ 3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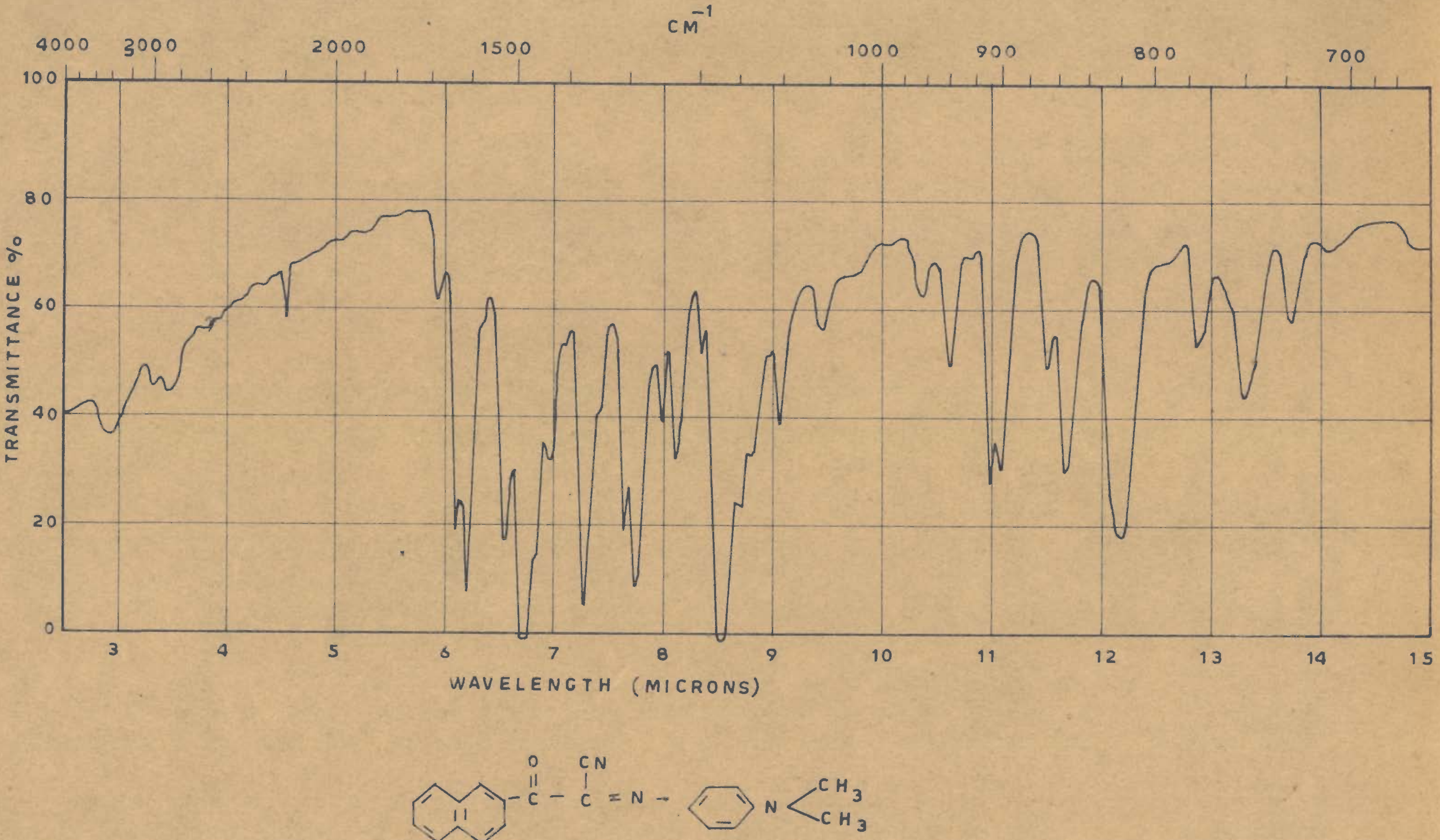
WAVELENGTH (MICRONS)
O
C – CH = N –
CL

FIGURE _ 4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WAVELENGTH (MICRONS)
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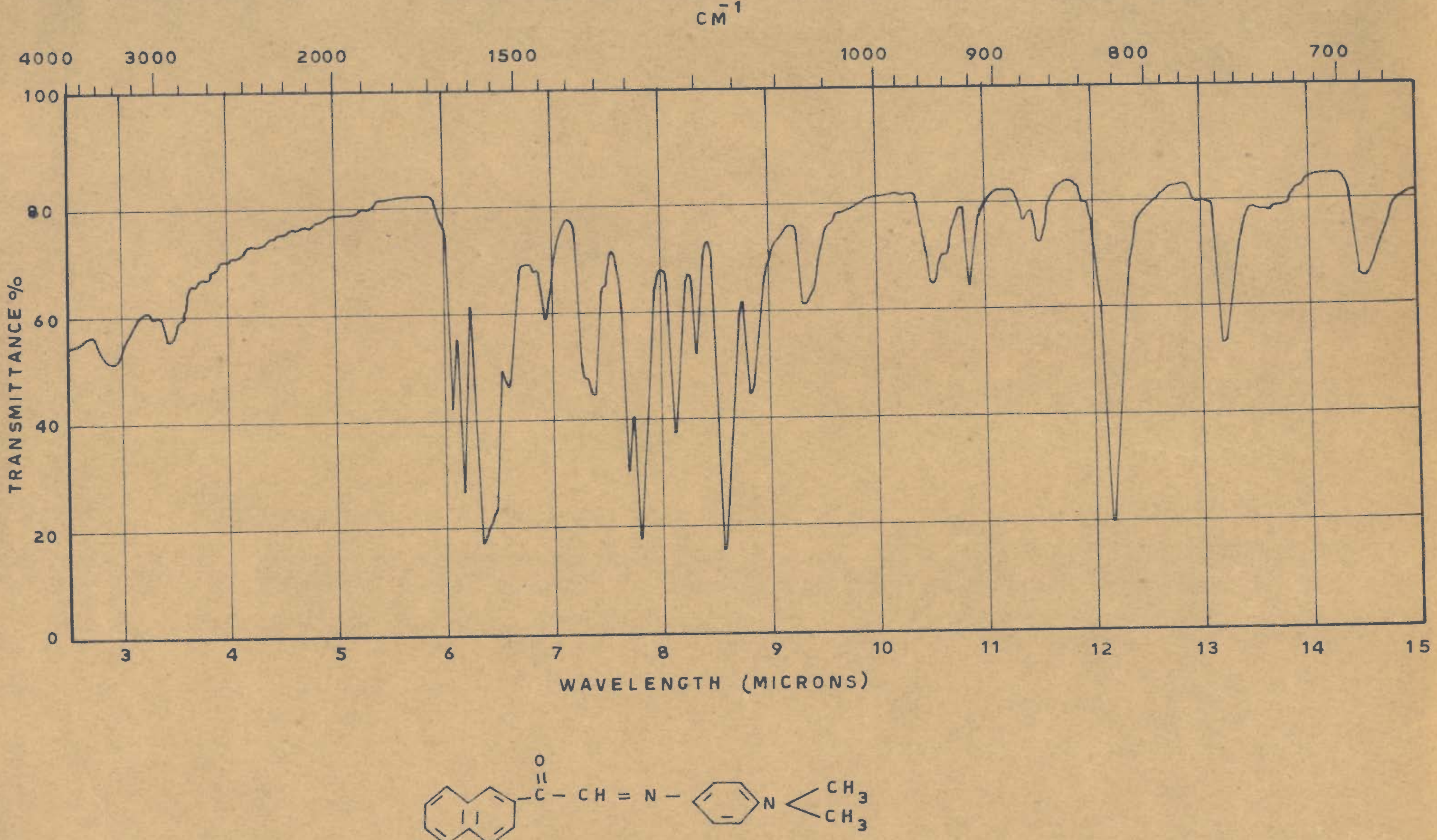
N
N
CH3
CH3

FIGURE _ 5


CM^{-1}
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TRANSMITTANCE %
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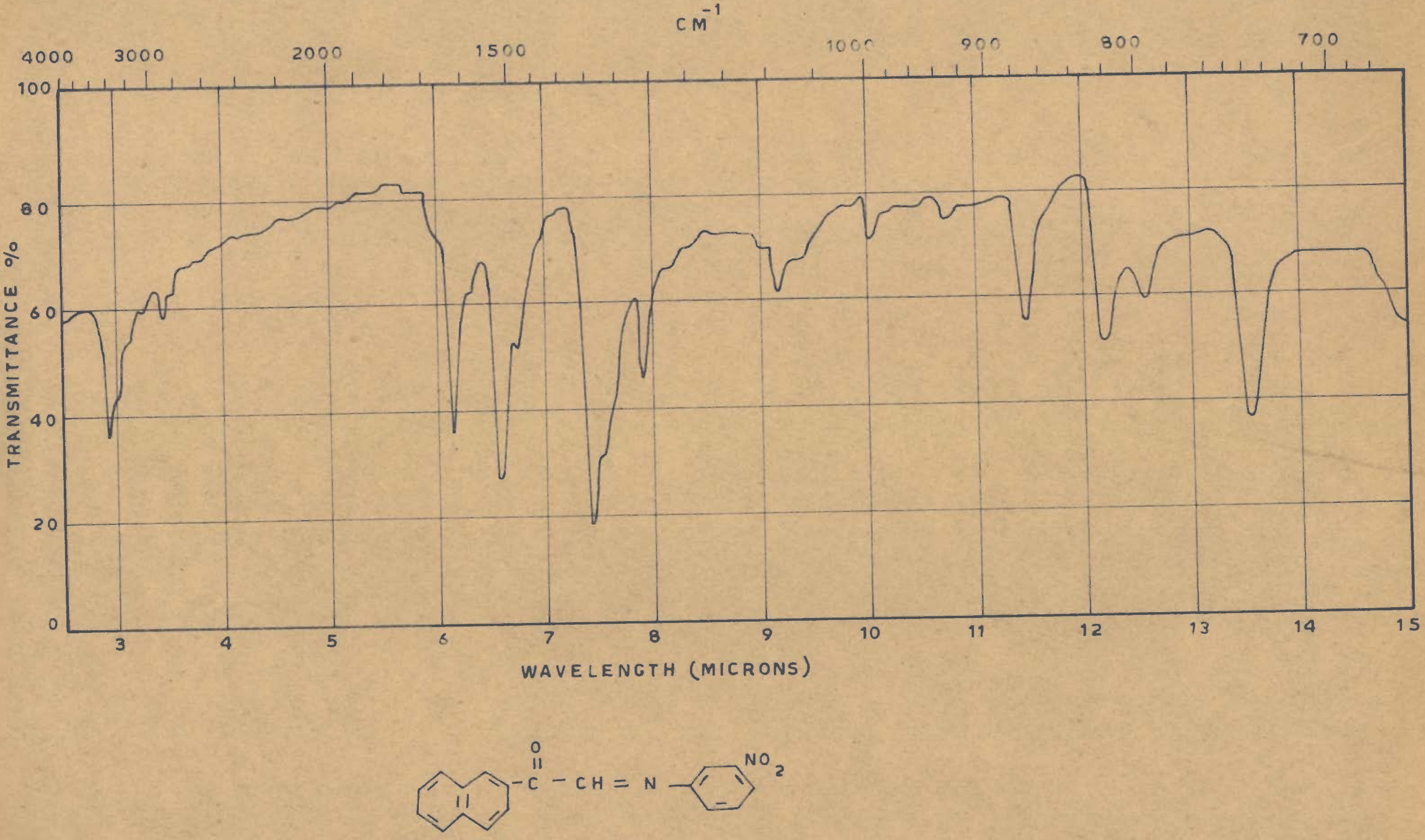
WAVELENGTH (MICRONS)
O
C
CH = N
N
CH$_3$
CH$_3$

FIGURE _ 6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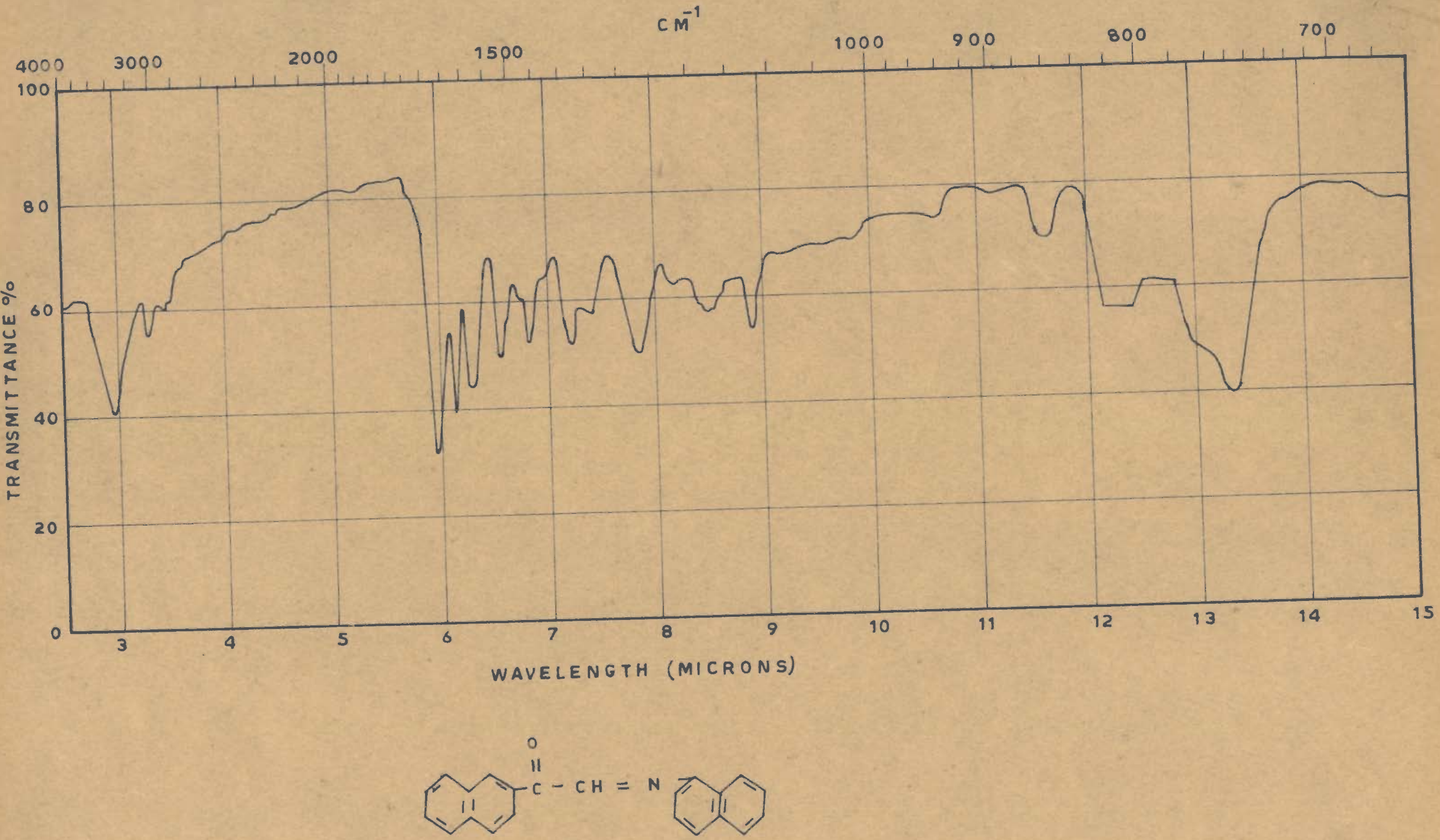
WAVELENGTH (MICRONS)
O
C
CH = N
NO2

FIGURE _ 7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TRANSMITTANCE %
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12
13
14
15
WAVELENGTH (MICRONS)
O
C – CH = N

FIGURE _ 8

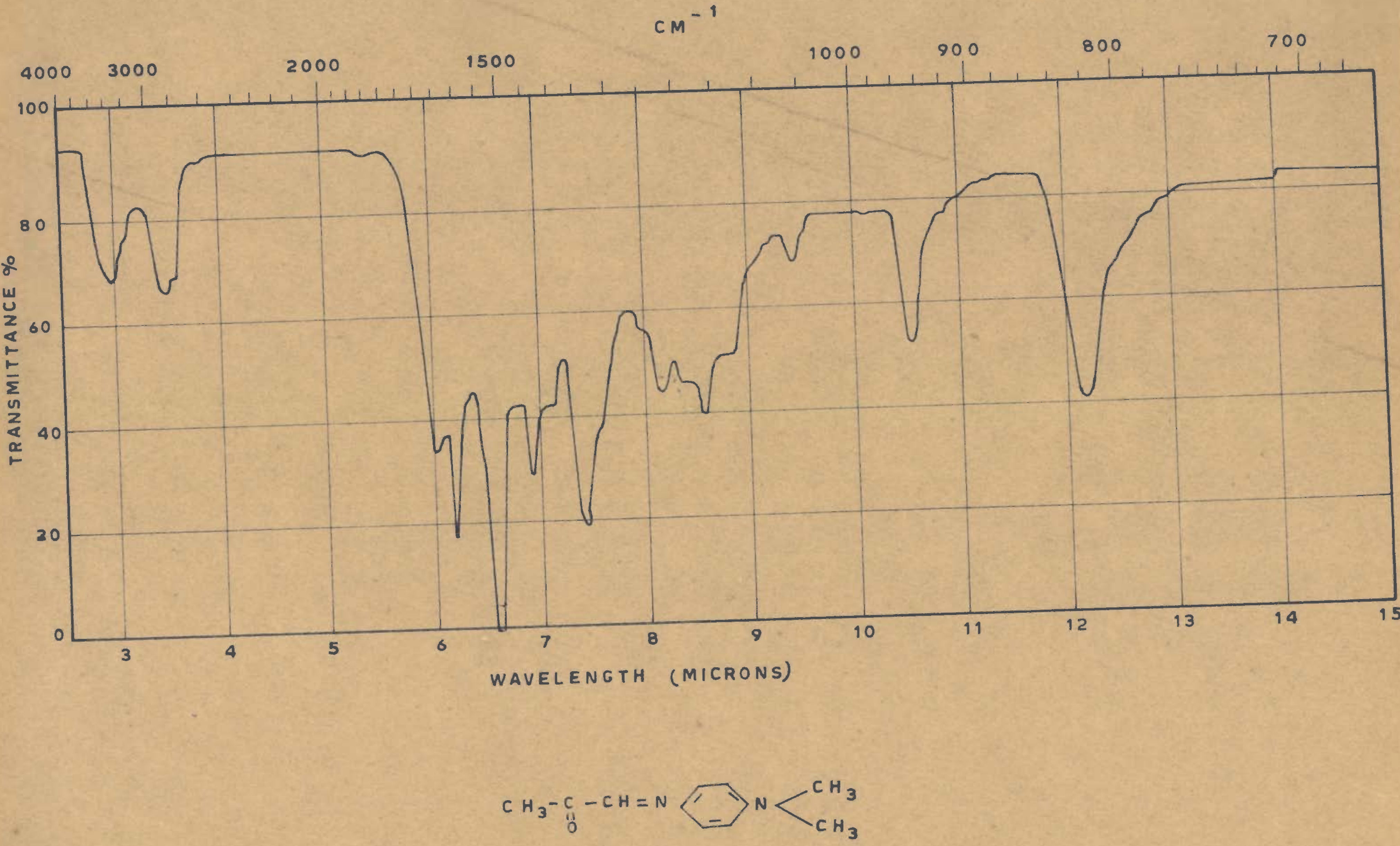

CM^{-1}
4000
3000
2000
1500
1000
900
800
700
100
80
60
40
20
0
TRANSMITTANCE %
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)
CH$_3$-C-CH=N
O
N
CH$_3$
CH$_3$

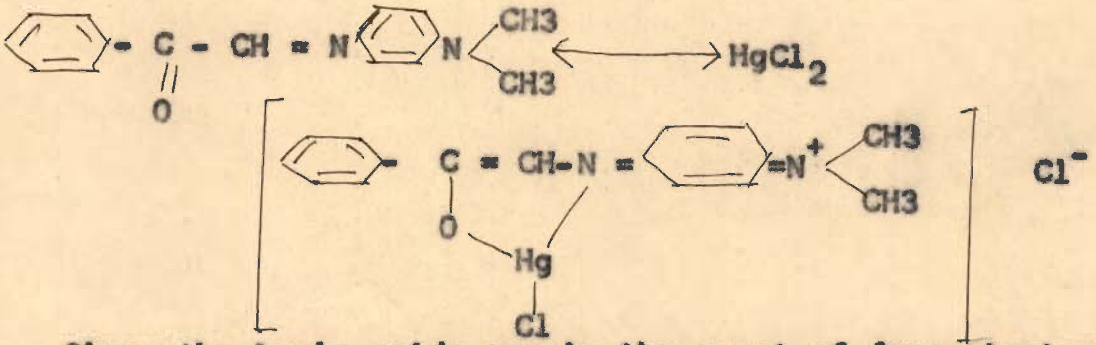
FIGURE _ 9

CHAPTER II

Spectrophotometric studies on the interaction of Lewis acids with p-dimethyl amino anil of phenyl glyoxal.

INTRODUCTION

It has been reported in the literature that various Lewis acids like $HgCl_2$, $ZnCl_2$, $Fecl_3$ etc.interact with anils such as p-dimethyl amino anil of phenyl-glyoxal an undergoing a bathochromic shift from yellow to violet, red, green etc. This large shift is an indicative of chelation as shown by the following mechanism:



Since the Lewis acids are in the quest of free electron, so they attract a pair of electron from the p-dimethyl anilino group of the anil and cause a resonance in the whole molecule. Consequently the $>C = O$ group of the ketonic skeleton becomes more electron dense or negative. Besides this there lies a pair of free electrons on the CH=N grouping of the anil which coordinates with the metal to form the chelate.

In the case of anils under investigation,addition of acetonic $ZnCl_2$,$HgCl_2$,CdI_2 and $FeCl_3$ solutins to them a shift in maxima took place. This was taken as an indication of complex ion formation. The composition and stability of these complexes, employing methods of spectrophotometry and chemical analysis, was investigated. The group or groups involved in the binding of these metals to the anil were found by recording IR spectra.

EXPERIMENTAL

(i) p-dimethyl amino anil of phenylglyoxal solution :

p-dimethyl amino anil of phenylglyoxal was prepared by the method given in Chapter 1.

Solution of p-dimethyl amino anil of phenylglyoxal was prepared by direct weighing of the pure product and dissolving it in the requisit volume of acetone.

(ii) Zinc chloride solution :

Zinc chloride (AnaLar) B.D.H. was employed during the experiments. A 0.01M solution of the salt was prepared by dissolving 0.6814 gm. of zincchloride in 500 cc doubly distilled dry acetone (B.D.H).

The strength of the zinc chloride solution was determined gravimetrically as zinc ammonium phsphate(2). Solutions of desired strengths were obtained by diluting the stock solution with doubly distilled acetone.

(iii) Cadmium Iodide solution :

Cadmium Iodide solution was prepared by dissolving the salt (B.D.H) in dry acetone.

The strength of the cadmium Iodide was determined gravimetrically as cadmium-molybdate(2).

(iv) Mercuric Chloride solution :

Stock solution of mercuric chloride was prepared by dissolving the B.D.H. salt in doubly distilled dry acetone and its strength was determined gravimetrically as mercuric thionalide(2). Solution of desired strength were obtained by diluting the stock solution with dry acetone.

(v) Ferric chloride solution : was prepared by dissolving Analar (B.D.H) sample in dry double distilled acetone, and its strength determined gravimetrically as Fe_2O_3 by hydrolysis with potassium cyanate(2).

Spectrophotometry of the Complexes

Amongst the various physical methods often employed for studying complex ion formation, spectrophotometric method is quite useful and has been found to be much more advantageous than other physical methods. The advantages of the methods lie in the fact that this method permits the study of the compositions of complexes, which are not stable enough to permit their isolation.

The method of continued variation as developed by Job(3) has been found to be of particular importance and utility in chemistry and has been frequently employed for the study of coordination compds. The great importance and versatility of this method lies in the fact that it can be applied successfully to various other physical properties like conductivity, molar heat content, refractivity etc. and makes use of any measurable additive property of the two species in solution, as long as the property has different values for the interacting species and the products. Any complex formed by the interaction of two components would give a value for the same property which is different from the mean of the values for the separate components. The application of the method may be illustrated by the simplest equilibrium of the type :

$$A + nB \rightleftharpoons AB_n$$

where A represents a metal ion, B, a coordinating group while AB_n a complex ion. Various solutions with different molefractions of the components are prepared but in each case the total sum of the moles of both the components is kept constant. The absorption of a monochromatic light by these solutions is measured and then a graph is plotted between absorption and mole fraction of one of the components. In case a complex is being formed the curve deviates from linearity, the deviation being maximum at the mole fraction corresponding to the composition of the complex while a straight line points towards no interaction. When the deviation is plotted against mole-fraction, the maximum point or the peak in the curve gives the desired composition of the complex. This conclusion can be verified by repeating the process at other wave lengths, since according to Job the position of maxima is independent of wave length.

The method of continued variation, as suggested by Job, was applicable to only those systems where the possibility of formation of only one complex exists and was not generally useful when more than one complexes were formed. This has been, however, extended by Vosburgh and Cooper(4) for systems involving more than one complexes. They have pointed out that the results are independent of the wave lengthof light used only in those cases when a single compound is formed while in systems with more than one compounds wave lengths plays an important role and hence a careful selection of wave-lengths is necessary and essential while studying complex ion formation. These authors studied the complexes of Ni^{++} with o-phenanthroline and ethylene diamine formed in 1:1, 1:2 and 1:3 proportions and copper-ammonia complexes formed in 1:2 and 1:4 proportions. Thus, they were able to confirm the validity of thei new method and the importance of the wave length of light selected for experimental measurements. They further extended the method to the study of ferric-thiocyanate, ferrous -o-phenanthroline and copper glycine systems yielding satisfactory results. Besides, this method gave other results of far reaching importance. For example, Vosburgh (loc.cit.) reported for the first time, a coordination number of six for nickel-ethylene diamine complexes and existence of ions like $(Ni\text{-}en)^{++}$ $(Ni\text{-}en_2)^{++}$ and $(Ni\text{-}en_3)^{++}$. Haendler(5) obtained similar results while studying the diethylene triamine complexes of copper.

Before performing the actual experiments on the composition of mercury-p-dimethyl amino anil of phenyl - glyoxal complexes by the spectrophotometric methods, absorption experiments were performed with complex at different wave-lengths in order to select suitable wave-length to work with and to determine the number of complexes formed. Mercuric chloride and anil (p-dimethyl amino anil of phenylglyoxal), both of strength 1.25×10^{-3} M, were mixed in the ratios mercury to anil as 2:1, 4:3, 3:2, 1:2,2:3 and

1:1.

Optical density measurements were carried out with a Bausch and Lomb 'Spectronic 20' after allowing a sufficient warming up period for the instrument. Measurements above 650 mu were made after changing to the red filter.

Selection of wave lengths :

Absorbance of mercuric chloride - anil mixtures, mixed according to Vosburgh Cooper's method.

Concn. of mercuric chloride = 1.25×10^{-3}M
Concn. of p-dimethyl amino anil
of phenyl-glyoxal = 1.25×10^{-3}M

Optical density measurements were carried out in the visible region from 325 to 625 mu. From the O-D values of various mixtures (Table No.1, Fig.1) at different wave lengths gave two maxima at 425 mu and 540 mu. The maxima at 425 is due to the excess of ligand while the other is due to complex itself. Hence the stoichiometry of the reddish violet complex could best be carried out at 540 mu.

Table No. 1

OPTICAL DENSITY

Wave length mu	Ratio of Ligand to $HgCl_2$					
	2:1	4:3	3:2	1:2	2:3	1:1
325	0.68	0.62	0.49	0.33	0.19	-
350	0.24	0.20	0.12	0.12	0.05	-
375	0.29	0.30	0.17	0.10	0.14	-
400	0.80	1.0	0.50	0.33	0.44	-
410	1.0	1.20	0.70	0.50	0.60	-
425	1.1	1.40	0.90	0.66	0.75	1.5
435	1.0	1.30	0.80	0.58	0.63	1.4
450	0.70	1.1	0.52	0.40	0.45	1.20
475	0.37	0.68	0.25	0.16	0.20	0.80
500	0.14	0.19	0.11	0.06	0.12	0.40
520	0.15	0.25	0.10	0.07	0.07	0.35
540	0.40	0.50	0.25	0.12	0.11	0.55
560	0.25	0.38	0.17	0.07	0.10	0.44
575	0.19	0.30	0.11	0.01	0.05	0.35
600	0.10	0.19	0.08	0.04	0.03	0.25
625	0.08	0.12	0.04	0.02	0.02	0.17

Fig. 1

Composition of the reddish violet complex :-

For determining the composition of reddish violet coloured mercury - anil complex by Job's method of continued variation, the following sets of mixtures were prepared. Anil and mercuric chloride solution used in all these studies was prepared in dry acetone.

Set I - 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc of mercuric chloride mixed with 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 cc of anil. The concentration of both the reactants were 0.80×10^{-3}M.

Set II - 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 cc of mercuric chloride mixed with 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc of ligand concn. of both the reactant were $1.66 \times 10^{-3}M$.

Set III - Concentration of the reactants $1.11 \times 10^{-3}M$, mixed as under Set II.

Set IV - Concentration of the reactants $1.0 \times 10^{-3}M$, mixed as under set III.

O.D. Measurements were carried out at wave-lengths 530 , 540 mμ and 550 mμ . Curves were plotted between the difference of O.D. of the mixtures and ligand against the ratios $\frac{Hg^{++}}{Hg^{++} + \text{Anil}}$. The results are given in the following tables:

Table No. 2

Set I.

Vol.of ligand ccl	Vol.of mercuric chloride	OPTICAL DENSITY					
		Mixture C	Ligand a	Difference (c-a)	Mixture C	Ligand a	Difference (c-a)
		Wave length -530 mμ			Wave length -540 mμ		
1.0	9.0	0.40	0.36	0.04	0.475	0.40	0.075
2.0	8.0	0.385	0.26	0.125	0.44	0.32	0.12
3.0	7.0	0.39	0.19	0.20	0.40	0.25	0.15
4.0	6.0	0.37	0.11	0.26	0.38	0.16	0.22
5.0	5.0	0.39	0.09	0.30	0.42	0.15	0.27
6.0	4.0	0.3555	0.08	0.275	0.36	0.13	0.23
7.0	3.0	0.26	0.06	0.205	0.275	0.10	0.175
8.0	2.0	0.175	0.05	0.125	0.19	0.09	0.10
9.0	1.0	0.09	0.04	0.05	0.12	0.07	0.05
		Fig.(2) Curve 1				Curve 2	

Table No. 3

Wave length - 550 mμ OPTICAL DENSITY

Vol. of ligand cc	Vol. of mercuric chloride cc	Mixture C	Ligand a	Difference (c-a)
1.0	9.0	0.43	0.38	0.05
2.0	8.0	0.37	0.29	0.08
3.0	7.0	0.34	0.21	0.13
4.0	6.0	0.32	0.14	0.18
5.0	5.0	0.335	0.11	0.225
6.0	4.0	0.30	0.10	0.20
7.0	3.0	0.23	0.08	0.15
8.0	2.0	0.145	0.07	0.075
9.0	1.0	0.075	0.05	0.025

Fig. 2 curve 3

Table No. 4

Set No.2

Wave length - 540 mμ OPTICAL DENSITY

Vol. of ligand cc	Vol. of mercuric chloride cc	Mixture C	Ligand a	Difference (c-a)
9.0	1.0	0.66	0.62	0.04
8.0	2.0	0.64	0.48	0.16
7.0	3.0	0.62	0.40	0.22
6.0	4.0	0.61	0.35	0.26
5.0	5.0	0.60	0.32	0.28
4.0	6.0	0.55	0.29	0.26
3.0	7.0	0.46	0.25	0.21
2.0	8.0	0.39	0.23	0.16
1.0	9.0	0.28	0.20	0.08

Fig. 3 curve 1

Table No. 5

Set No. 3

Wave length - 540 mμ OPTICAL DENSITY

Vol. of ligand cc	Vol. of mercuric chloride cc	Mixture C	Ligand a	Difference (c-a)
9.0	1.0	0.56	0.52	0.04
8.0	2.0	0.52	0.41	0.11
7.0	3.0	0.50	0.33	0.17
6.0	4.0	0.49	0.28	0.21
5.0	5.0	0.48	0.24	0.24
4.0	6.0	0.42	0.22	0.20
3.0	7.0	0.36	0.20	0.16
2.0	8.0	0.29	0.19	0.10
1.0	9.0	0.20	0.18	0.02

Fig. 3 curve 2

Table No. 6

Set No. 4

Wave length - 540 mμ OPTICAL DENSITY

Vol. of $HgCl_2$ cc	Vol. of ligand cc	Mixture C	Ligand a	Difference (c-a)
1.0	9.0	0.51	0.49	0.02
2.0	8.0	0.48	0.40	0.08
3.0	7.0	0.44	0.31	0.13
4.0	6.0	0.44	0.26	0.18
5.0	5.0	0.42	0.22	0.20
6.0	4.0	0.35	0.19	0.16
7.0	3.0	0.30	0.18	0.12
8.0	2.0	0.22	0.14	0.08
9.0	1.0	0.11	0.10	0.01

Fig. 3 curve 3

JOB'S METHOD

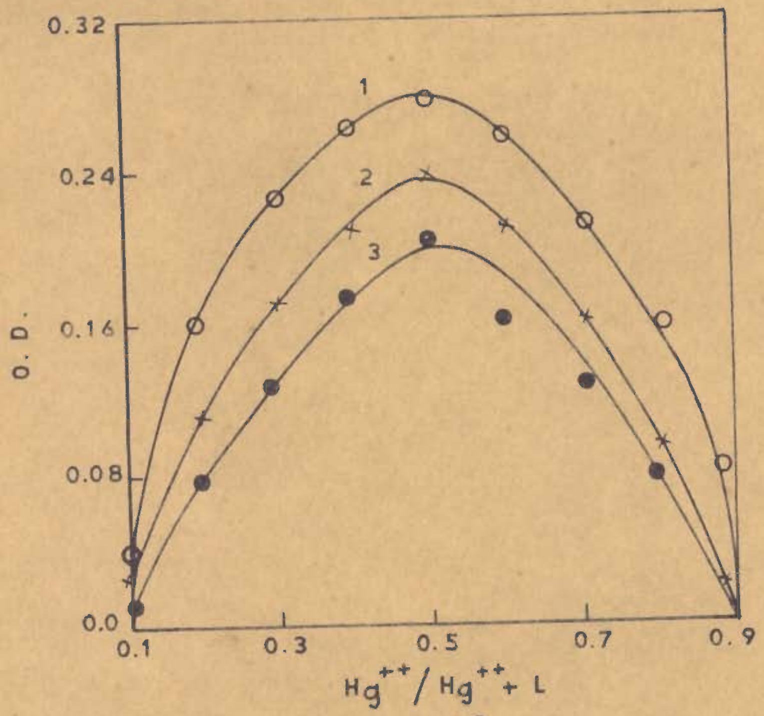


FIG. 3

JOB'S_NON EQUIMOLAR METHOD
(STABILITY CONSTANT)

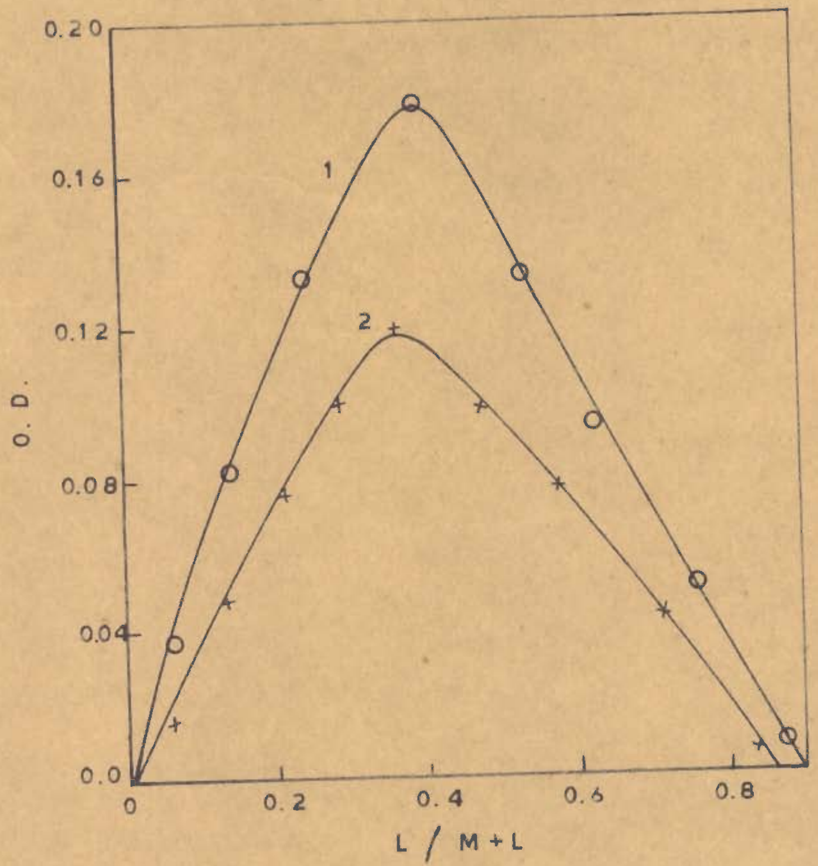


FIG. 4

Stability constants of the complexes

A number of useful methods are known for the calculation of the stability constants of the complexes formed both in aqueous and non-aqueous media, using absorbance measurements. A brief account of some of the methods is presented here.

The determination of stability constant is essential for a proper understanding of a system undergoing complex formation. It is concerned with the reaction between different solvated reactants and products. The thermodynamic constants can also be calculated from a knowledge of the stability constant. However, it is doubtful whether true thermodynamic quantities of complexes can be determined except in very simple cases, because the method is accompanied by many difficulties. Two main procedures are usually followed in studying the stability constants of the complexes.

Lewis and Randall(6) first introduced the concept of ionic strength which later received theoretical justification from the Debye-Huckel theory. The classical approach for the evaluation of thermodynamic equilibrium constants involved the determination of the equilibrium constant in media of different low ionic strengths, followed by extrapolation to zero ionic strength (infinite dilution). Some workers(7) have used the value of a single determination and attempted to correct this value to a thermodynamic equilibrium constant by the application of Debye-Huckel theory. The second method was introduced by Biedermann and Sillen(8).

The fundamental idea of the method is to control the activity coefficient by keeping ionic strength constant, because in dilute solutionsthe activity coefficient of a given strong electrolyte is the same in all the solutions of identical ionic strength. In view of the difficulties encountered in practical determination of true thermodynamic stability constants Rossotti and Rossotti(9) concluded " It would therefore seen better to obtain reliable values of stoichiometric constants (which describe the stability of species relative to the corresponding complexes with solvent molecules and medium ions) than less certain values of thermodynamic constants (which do not give absolute stability either, but only stability related to the solvated molecules)". These values of the stoichiometry constants are reliable under a given set of experimental conditions and are useful for practical purposes. The constant has been termed as stability constant in the present work.

During present studies, it has not been possible to maintain ionic strength constant by swamping with an indifferent electrolyte, because of the insolubility of electrolyte in acetone resulting in the fading of colour or precipitation of the complex. The values of the stability constants determined in this work relate to the complex species formed under given set of experimental conditions.

Method of Anderson and Coworkers :

For the calculation of the stability constant of metal complexes from absorbance data, a well known method is that described by Anderson and coworkers(10) based on a treatment of composition of solutions having an identical intensity of colour i.e. the same absorbance value. In this method, both the reactants should be colourless.

Dey and coworkers(11-12) modified this method to cases where one of the reactants may be coloured. This method is described below.

In this method observations obtained for the method of continuous variation are utilised and the absorbances (not the difference in absorbance) are plotted against $\frac{M}{M+A}$ where M is the concentration of the metal ion and A that of complexing agent when the metal solutions are coloured while the ligands are colourless. The procedure adopted with the progressive increase of M, A decreases and it may be assumed that in the ascending portions of the curve where the ligand moles are in excess, a majority of the metal is bound up in the complex. The observed absorbance may, therefore, be regarded to be due to the colour of the complex alone. Let us take the case of a system where a complex is formed with the composition of metal: complexing agent is 1:1 in the general equation

$$mM + nA = M_m A_n$$

$$m/n = 1, \text{ or } m = n,$$

the stability constant $K = \frac{x}{(a-x)(b-x)}$ .... (1)

taking two concentration as a_1, a_2 and b_1, b_2 of the reactants (from two curves) having the same absorbance i.e. the same value of x, we have

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

$$\text{or}\quad x = \frac{a_1b_1 - a_2b_2}{(a_1+b_1)-(a_2+b_2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Knowing the value of x in (2), the value of K can be found by substitution in equation (1).

Now taking the case of a complex where the ratio of the reactants is 1:2 the reaction takes place as

$$M + 2A = MA_2$$

$$K = \frac{x}{(a-x)(b-2x)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

Taking two concentrations a_1, a_2 and b_1, b_2 having the same absorbance i.e. the same value of x, we have,

$$K = \frac{x}{(a_1-x)(b_1-2x)^2} = \frac{x}{(a_2-x)(b_2-2x)^2} \quad \ldots \ (4)$$

$$x = - b2^2 - b_1{}^1 + 4(a_2b_2 - a_1b_1) \pm b2^2 + b1^2 + 4(a_2b_2 - a_1b_1)^2$$

$$- \frac{16(a_1+b_1) - (a_2+b_2)\ (a1b1^2 - a_2b_2{}^2)}{8(a_1+b_1) - (a_2+b_2)} \quad \ldots\ldots\ldots\ldots \ (5)$$

Knowing the value of x from equation (5) the value of K can be found out from equation (4) by substitution.

Comparative study of the various methods for the determination of stability constants has been made by Anderson and coworkers (loc.cit.) and they concluded that the method involving the comparison of the solution of equal absorbance yields results which are more reproducible. Several other methods for the determination of the stability constants of coloured complexes have also been made spectrophotometrically(13,14).

To determine the stability constant of the complexes under investigation non-equimolar method was employed according to Job's equation using non-equimolar solutions$^{(20)}$. Thus starting with the metal ion and ligand solutions of different molarities ($c_1/c_2 = \frac{1}{p}$) and mixing the reactants by the volumes (1-x) of M and x of L, it is found that

$$K = \frac{C_1^{m+n-1} \times p^{n-1} \left[(p_m+n)\, x - n\right]^{m+n}}{m^{n-1} \times n^{m-1} (p-1)^{m+n-n} \left[n - (m+n)\, x\right]}$$

for the reaction

$$mM + nL \rightleftharpoons M_m L_n$$

$$Ki = (M)^m (L)^n / (M_m L_n)$$

when $m = n = 1$

the above equation reduces to

$$K = \frac{C_1\left[(p+1)x - 1\right]^2}{(p-1)\,(1-2x)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

<u>Mole ratio method</u> : Stability constant can also be evaluated from mole ratio method. The dissociation of the complex may be represented by

$$MA_n = M^+ + nA^-$$

C 0 0 initial concn.

$C(1-\alpha)$ αC $n\alpha C$ equilibrium concn., where C is the total concentration of the complex ion in moles per litre assuming no dissociation, and α is the degree of dissociation, the stability constant may be written as

$$K = \frac{C(1-\alpha)}{\alpha C \times (n\alpha C)^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

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

$$\alpha = \frac{E_m - E_s}{E_m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

E_m is the maximum extinction obtained from the horizontal portion of the curve, indicating that all the reagent is present in the form of complex. E_s is the extinction of stoichiometric molar ratio of metal to reagent in the complex, the total concentration of the complex being equal to the concentration of the reagent.

In a system where the combing ratio of metal :complexing agent is 1:1, the above eqn. (7) reduces to

$$K = \frac{C(1-\alpha)}{\alpha C \times \alpha c} = \frac{1-\alpha}{C\alpha 2} \qquad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

and for a system where the combining ratio of metal :complexing agent is 1:2, the eq. (7) takes the form

$$K = \frac{C(1-\alpha)}{\alpha C \times (2\alpha C)^2} = \frac{(1-\alpha)}{4\alpha^3 C^2} \qquad \ldots\ldots\ldots\ldots\ldots (10)$$

The value of α may be obtained from the relation (8), The stability constant was calculated by the non-equimolar Job's method. Equation (6) was used for the purpose.

In actual experimentation two sets of mixtures of different concentration (Set I concn. of ligand 1.11 $\times 10^{-3}$M; concn. of mercuric chloride 0.83 $\times 10^{-3}$M, total vol. = 15 cc (Table No. 7 Fig.4 curve 1). Set II. concn. of ligand 1.0 $\times 10^{-3}$M; concn. of mercuric chloride 0.625$\times 10^{-3}$M total vol. = 20 cc (Table No.8 Fig. 4 curve 2) of reactants were prepared by mixing mercuric chloride and anil, according to the method of continuous variation. Difference in optical density of the mixture and ligand was plotted against mole fraction of $\frac{\text{mercury}}{\text{mercury + ligand}}$.

Table No. 7

Set No. 1

Wave length - 540 mμ

OPTICAL DENSITY

Vol. of ligand cc	Vol. of $HgCl_2$ cc	Mixture C	Ligand a	Difference (c-a)
1.0	11.97	0.036	0	0.036
2.0	10.64	0.082	0	0.082
3.0	9.31	0.150	0.02	0.130
4.0	7.98	0.224	0.06	0.164
5.0	6.65	0.250	0.07	0.180
6.0	5.32	0.270	0.140	0.132
7.0	3.99	0.294	0.20	0.094
8.0	2.66	0.338	0.29	0.048
9.0	1.33	0.358	0.35	0.008

Fig. 4 Curve 1

Table No. 8

Set No. 2

Wave length - 540 mμ

OPTICAL DENSITY

Vol. of ligand cc	Vol. of $HgCl_2$ cc	Mixture C	Ligand a	Difference (c-a)
1.0	14.4	0.016	0	0.016
2.0	12.8	0.048	0	0.048
3.0	11.2	0.076	0	0.076
4.0	9.6	0.10	0	0.10
5.0	8.0	0.12	0	0.12
6.0	6.4	0.140	0.04	0.100
7.0	4.8	0.178	0.10	0.078
8.0	3.2	0.242	0.20	0.042
9.0	1.6	0.256	0.25	0.006

Fig. 4 Curve 2

Dissociation const. $K = \frac{[C_1(p+1)\ x-1]^2}{(p-1)\ (1-2x\ )}$

$\frac{C1}{C2} = \frac{1}{p}$

x - maxima point (Fraction $\frac{R}{R+M}$)

C_1 = concn. of Metal ion

C_2 = concn. of Ligand.

Set No. 1 x = 0.40	**Set No. 2** x=0.36
$C_1 = 0.83\times10^{-3}M$	$C_1 = 0.625\times10^{-3}M$
$C_2 = 1.11\times10^{-3}M$	$C_2 = 1.0\times10^{-3}M$
p = 1.3	p = 1.6
$K_1 = 8.96\times10^{-5}$	$K_2 = 15.6\times10^{-5}$

$$\text{Stability constant} = \frac{1}{\text{Instability Constant}}$$

$$= \frac{1}{15.6\text{x}10^{-5}}$$

$$= 0.064\text{x}10^{5}$$

$$= 6.4\text{x}10^{3}$$

Free energy $\triangle F$ was calculated at 25°C by the relation given below:

$\triangle F = - RT \ln K$, $\triangle F$, R and T have their usual notation.

$$\triangle F = 5.224\text{x}10^{3}$$
$$= - 5.2 \text{ K cals./mole at } 25^{\circ}\text{C}$$

Isolation and chemical analysis of the mercury-p-dimethyl amino anil of phenyl-glyoxal complex :-

On mixing an equivalent amount of concentrated mercuric chloride and p-dimethyl amino anil of phenyl glyoxal solutions (acetonitrile) at once a dark blue precipitate develops. On crystallisation with acetonitrile (60 parts) a blue black metallic greenish shining prisms were obtained.

The decomposition point was 145-146°C.

For estimation of mercury, a weighed amount of dried sample of the complex was digested with aqua-regia and its mercury content was estimated gravimetrically as mercuric thionalide[2]. The chlorine or iodine present in the complex was estimated by the method of Stepanon modified by Bacon(19).

The results of analysis are as follows :-

Reported %	Found %
Hg - 38.31; Cl - 13.56	Hg - 38.47; Cl - 13.54
C - 36.68; H-3.08; N-5.35	C - 36.60; H-3.12; N-5.40
O - 3.02 (By difference)	O - 2.87 (by difference)

Estimation of nitrogen (Kjeldahl's method):-

The nitrogen estimation of the complex was carried out by Kjeldahl's method. The weighed amount of the sample was taken in dry Kjeldahl's flask containing 10 gm. of potassium sulphate and a pinch of copper sulphate. Finally 30 cc concn. H_2SO_4 (98%) containing, 1 gm. salicylic acid was added, revolving the flask as the acid was run in, to wash down any compound, which might be present in the neck. The flask was heated gently over a small flame in a fuming chamber for about half an hour, when frothing subsided, the flask was cooled a little and 4.0 gm. of sodium thiosulphate was added and the mixture was shaken. The flask was again heated with periodic shaking till the contents of the flask become pale straw coloured or colourless. The heating was continued for two hours more when in the end the contents of the flask became chalk white. The mixture was then cooled to room temperature and was diluted very slowly with 75 to 100 cc of distilled water. The clear supernatant liquid was decanted in a litre R.B. flask and the residue was washed repeatedly with four or five times distiled water, leaving as much as possible of the insoluble residue in the Kjeldahl's flask. The decanted liquid in the R.B. flask was then diluted to 300 cc and 150 cc of 50 % caustic sods solution was run slowly through the sides of the flask, so that it formed a heavy layer at the bottom. Then a few pieces of washed granulated zinc were added. From this solution ammonia was tapped out with the help of an efficient splash head in a conical flask containing 10 cc N/10 sulphuric acid diluted with 65 cc of distilled water and containing 5 dropsof methyl red indicator. When about 250 cc of the distillate has been collected, the tapping was stopped and the excess of acid was titrated with N/10 caustic soda solution, the end point being detected by the sudden change in the colour of the solution from red to yellow.

From this the amount of sulphuric acid neutralised by ammonia was obtained. Now Vcc be the volume of N/10 sulphuric acid neutralised by ammonia and W be the weight of the sample taken the percentage of total nitrogen was calculated by the following expression :

$$\frac{V \times 0.0014 \times 100}{W}$$

Since 1cc of N/10 sulphuric acid is equivalent to 0.0014 gm. of nitrogen from the eqn.

$$2NH_3 + H_2SO_4 = (NH4)_2\ SO4$$

1000 cc N-acid = 17 gm. of NH_3 = 14 gm. of N

1 cc of N/10 acid = 0.0014 gm. N

<u>Role of Salicylic acid and sodium thiosulphate</u> :-

Salicylic acid bind the nitrate - nitrogen in the organic combination.

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2\ HNO_3$$

$$HNO_3 + C6H4(OH)\ COOH \quad C6H3(OH)\ (NO2)\ COOH + H_2O$$

Salicylic acid   Nitro salicylic acid

The sodium thio-sulphate reduces the nitro-salicylic acid to amino salicylic acid from which nitrogen is easily detached out by sulphuric acid as ammonium sulphate.

$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2SO_3 + S$

$2H_2SO_3 + C_6H_3(OH)(NO_2)COOH + H_2O$

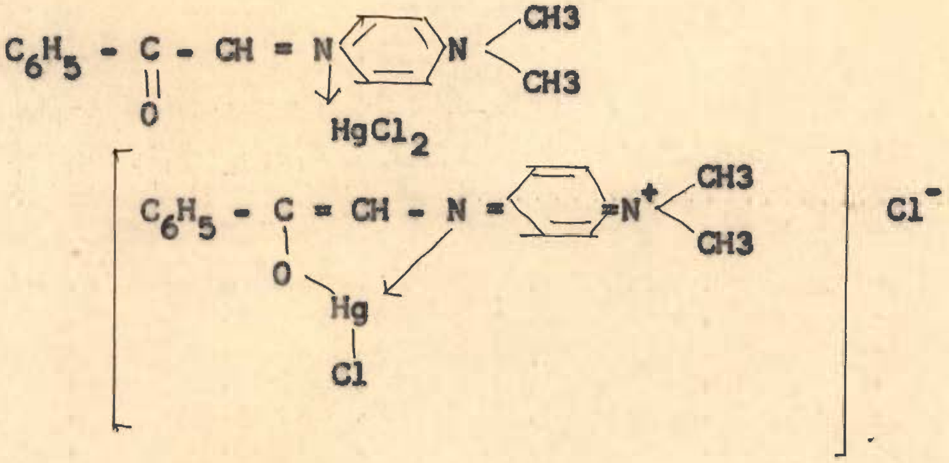
$= 3H_2SO_4 + C_6H_3(OH)(NH_2)COOH$

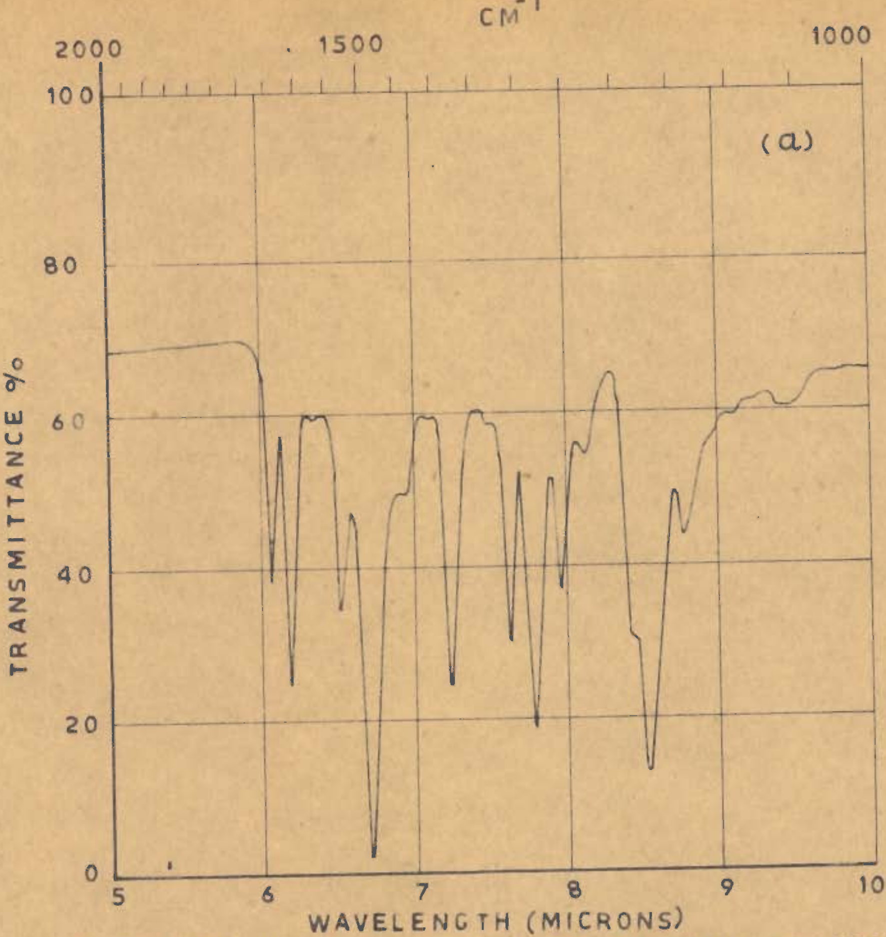
Amino salicylic acid.

Infrared Spectroscopy :-

The only donor groups to cause chelation in the anil are the $>C=O$ and $-CH=N$ groupings. On examining the spectrum of the ligand (p-dimethyl amino anil of phenyl - glyoxal), it will be seen that there are two sharp peaks around 1700 cm^{-1} and 1600 cm^{-1} respectively (fig. 5) due to the presence of above grouping. During the interaction of $HgCl_2$ and ligand, M-L bonding is created which will naturally cause a lowering of the stretching frequency of the above groups. It is quite evident that much lowering takes place in the spectrum of the chelate Hg(II) - p - dimethyl amino anil of phenyl-glyoxal (1650 and 1575 cm^{-1} respectively). The quinonoism in the chelate can be accounted for due to formation of a singlet from the doublet of the ligand around 830 cm^{-1} in p-disubstituted skeleton.

An alcoholic solution of the isolated complex produces a white precipitate of AgCl on treatment with ethanolic silver-nitrate solution. This may be possible due to ionic chlorine and not the covalent one. On the basis of the above evidences, the following structure may be assigned :


C6H5 - C - CH = N
O
N
CH3
CH3
HgCl2
C6H5 - C = CH - N =
O
Hg
Cl
=N+
CH3
CH3
Cl-



p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL

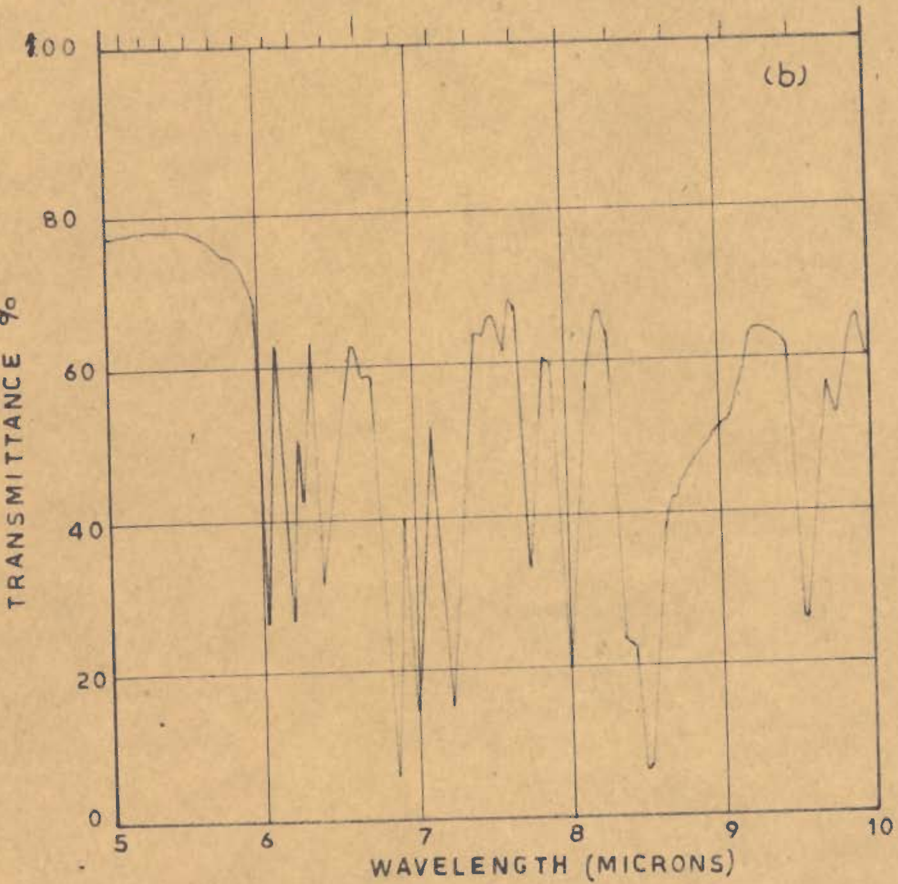


FIG. 5 – Hg^{++} – p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL COMPLEX

Composition of Ferric-p-dimethyl Amino Anil of Phenyl Glyoxal complex in Acetonic medium :

Vosburgh and Cooper's method (loc.cit.) was employed to know the number of complexes formed and for choosing wave - lengths suitable for performing further experiments ferric chloride and p-dimethyl amino anil of phenyl-glyoxal, both of strengths 0.40×10^{-3}M were mixed in the ratio of ferric chloride to ligand as 1:4, 1:3, 1:2, 2:1, 3:1 and 4:1 by mixing 2.0, 2.5, 3.33, 6.67, 7.5 and 8.0 cc of ferric chloride solution to 8.0, 7.5, 6.67,3.33, 2.5 and 2.0 cc of p-dimethyl amino anil of phenylglyoxal solution. From O.D. values at different wave-lengths, two maxima were obtained at 425 mu and 575 mu. The plot of O.D. versus wave length in the reagent itself gave only one maxima of 425 mu. Therefore, it is assumed that 425 mu maxima will be due to excess of the ligand present in the mixtures. The stoichiometry of the complex was carried out at wave-length 575 mu.

Selection of wave lengths :-

Absorbance of ferric chloride - p - dimethyl amino anil of phenyl glyoxal mixtures, mixed according to Vosburgh Cooper's method.

Table No. 9 Fig.6

Concentration of ferric chloride = 0.40×10^{-3}M
Concentration of ligand = 0.40×10^{-3}M
Maxima of $FeCl_3$ (300) mμ

Wave length curve No mμ	Ratio of ferric chloride to ligand 1:4	1:3	2:1	3:1	4:1	1:2
	1	2	3	4	5	6
325	0.90	0.78	0.70	0.60	0.40	-
350	0.35	0.20	0.13	0.13	0.05	-
375	0.28	0.17	0.09	0.12	0.02	-
400	0.80	0.50	0.25	0.15	0.13	-
415	1.07	0.80	0.60	0.40	0.44	-
425	1.18	1.0	0.78	0.83	0.32	1.2
435	1.10	0.90	0.75	0.70	0.12	1.1
450	0.91	0.50	0.30	0.30	0.13	0.90
475	0.30	0.20	0.12	0.05	0.02	0.50
500	0.18	0.17	0.03	0.04	0.01	0.25
525	0.18	0.13	0.07	0.08	0.03	0.31
550	0.25	0.17	0.08	0.12	0.07	0.34
560	0.30	0.23	0.12	0.17	0.08	0.47
575	0.37	0.39	0.27	0.31	0.19	0.32
590	0.30	0.25	0.14	0.21	0.10	0.21
605	0.22	0.12	0.05	0.08	0.01	0.10
615	0.10	0.05	0.0	-	-	0.04
625	0.04	0.03	-	-	-	-

Fig. 6

Composition of the complex :

Job's method (loc.cit.) of continued variation was followed for determining the composition of the yellow green complex. Equimolar solutions of ferric chloride and p-dimethyl amino anil of phenyl-glyoxal were mixed as under: $FeCl_3$: 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0, 10.0 11.0 cc and Anil : 11.0, 10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc and O.D. of mixtures were measured at two wave-lengths (565 mu and 575 mu). Such two sets of experiments were carried out at two concentrations viz. 0.55×10^{-3}M and 0.50×10^{-3}M. The difference in O.D. of the mixtures and ligand was plotted against mole fraction of $\frac{Fe^{+++}}{Fe^{+++}}$. The O.D. of the ferric chloride was negligible at this concentration. The results of Job's method are given below:

Table No.10

Set I

Wave length - 565 mμ 575 mμ

Vol.of Ferric chloride cc	Vol.of Ligand cc	O.D. Mixture c	O.D. Ligand a	Difference (c-a)	O.D. Mixture c	O.D. Ligand a	Difference (c-a)
1.0	11.0	0.262	0.23	0.032	0.238	0.22	0.018
2.0	10.0	0.252	0.19	0.066	0.23	0.17	0.06
3.0	9.0	0.22	0.09	0.13	0.21	0.03	0.18
4.0	8.0	0.18	0	0.18	0.20	0	0.20
5.0	7.0	0.162	0	0.162	0.186	0	0.186
6.0	6.0	0.160	0	0.160	0.16	0	0.160
7.0	5.0	0.100	0	0.10	0.134	0	0.134
8.0	4.0	0.072	0	0.072	0.106	0	0.106
9.0	3.0	0.044	0	0.044	0.08	0	0.08
10.0	2.0	0.024	0	0.024	0.052	0	0.052
11.0	1.0	0.006	0	0.006	0.03	0	0.03

Fig.7 curve 1 Fig. 8 curve 1

Table No. 11

Set No.2

Wave length - 565 mμ 575 mμ

1.0	11.0	0.17	0.15	0.02	0.182	0.17	0.012
2.0	10.0	0.14	0.10	0.044	0.178	0.15	0.028
3.0	9.0	0.11	0.02	0.09	0.170	0.11	0.06
4.0	8.0	0.150	0	0.150	0.166	0	0.166
5.0	7.0	0.114	0	0.114	0.152	0	0.152
6.0	6.0	0.088	0	0.088	0.124	0	0.124
7.0	5.0	0.064	0	0.064	0.10	0	0.10
8.0	4.0	0.04	0	0.04	0.076	0	0.076
9.0	3.0	0.02	0	0.02	0.048	0	0.048
10.0	2.0	0.08	0	0.008	0.03	0	0.03
11.0	1.0	-	-	-	0.014	0	0.014

Fig. 7 curve 2 Fig. 8 curve 2

Mono Variation method :

The method was developed by Yoe and Jones(16)

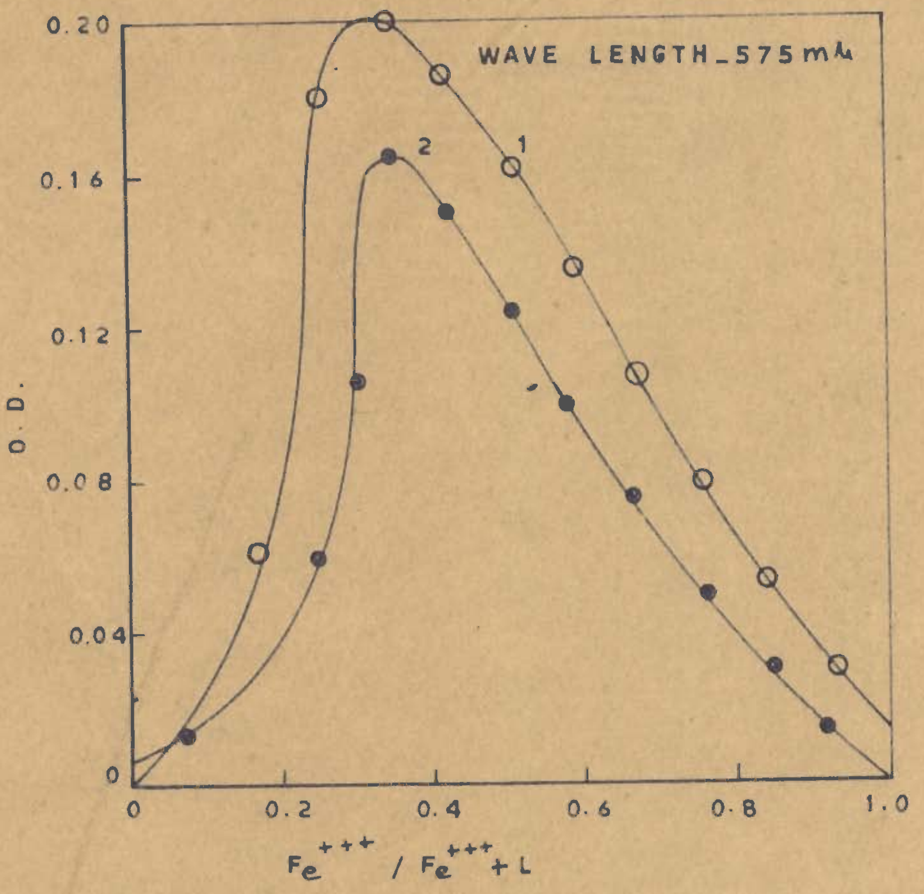


FIG. 8

MOLAR RATIO METHOD

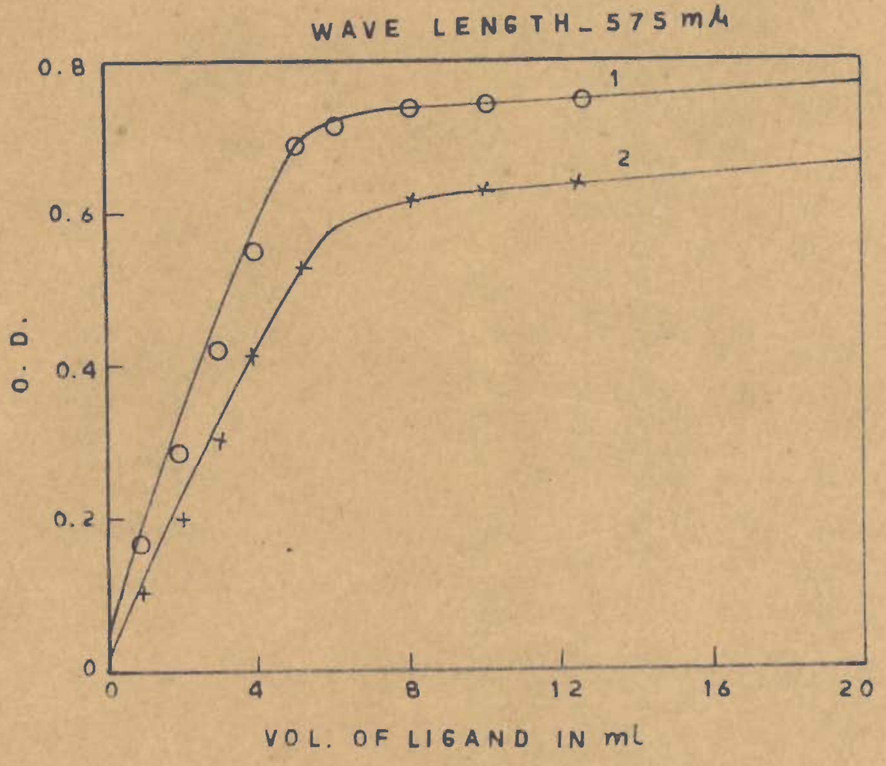


FIG. 9

and was termed the mole ratio method. A series of solutions of increasing ratios of the metal to the reagent or Vice - Versa are prepared and the absorbance of the mixture is measured. The plots of O.D. against molar ratio give inflexion corresponding to complexion formation. When both the reactants are colourless, the curve rises from the origin as a straight line and breaks sharply to a constant absorbance at the molar ratio of the components in the complex. However, for complexes that undergo dissociation in solution, a continuous curve which becomes approximately parallel to the molar ratio axis is obtained, only when an excess of the variable component is added.

Sometimes it is found that the results obtained by extrapolation of this 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 addition of an indifferent electrolyte (this is however difficult to achieve in non-aqueous medium). Thus in such cases also, it is possible to get information about the composition of the complex by this method. Recently Mayer and Ayres(17) deduced the stoichiometry of complexes in solution for situation in which several complexes exist under a given set of conditions from the mole ratio method.

Experiments for the mole ratio method (keeping constant amount of ferric chloride and varying the concentration of p-dimethyl amino anil of phenyl-glyoxal and vice versa) were performed at two different concentrations.

The O.D. measurements are carried out at 565 $m\mu$ and 575 $m\mu$. The results are given below:

Table No. 12

Absorption values for molar ratio method

Concentration of ligand = 1.11×10^{-3}M

Concentration of ferric chloride = 0.55×10^{-3}M

Total volume = 20 cc

Fig. 10 - curve 1 Fig. 9 curve -1

Vol. of ligand cc	Vol. of $FeCl_3$ cc	O.D. at 565 $m\mu$	O.D. at 575 $m\mu$
1.0	5.0	0.13	0.17
2.0	5.0	0.30	0.29
3.0	5.0	0.40	0.42
4.0	5.0	0.54	0.55
5.0	5.0	0.65	0.70
6.0	5.0	0.66	0.71
8.0	5.0	0.67	0.73
10.0	5.0	0.68	0.74
12.5	5.0	0.69	0.75

Table No. 13

Set No. 2

Concentration of ligand = 0.90×10^{-3}M

Concentration of Ferric chloride = 0.45×10^{-3}M

Total volume = 20.0 cc

Fig. 10 curve 2 Fig. 9 curve 2

1.0	5.0	0.08	0.10
2.0	5.0	0.20	0.19
3.0	5.0	0.32	0.31
4.0	5.0	0.40	0.41
5.0	5.0	0.52	0.53
6.0	5.0	0.54	0.57
8.0	5.0	0.56	0.62
10.0	5.0	0.57	0.63
12.5	5.0	0.58	0.64

Slope ratio method :

The slope ratio method, which is in common with other spectrophotometric methods, not only confirms the results obtained by Job's method of continued variation and Molar ratio method but also helps in establishing the ratio of colour forming radicals to the metal ions. In the reaction

$$mA + nB \rightleftharpoons Am\ Bn$$

If the concentration of B is constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex Am Bn will be essentially proportional to the analytical concentration of A, added in the reaction so that

$$(Am\ Bn) = CA/m \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{1}$$

where the bracket term denotes equilibrium concentration while C represents the analytical or total concentration.

According to Beer's Law,

$$E = ed\ (Am\ Bm) \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{2}$$

where E-denotes measured extinction, e the molecular extinction coefficient and d, the thickness of the cell in Cm. Substituting the value of (Am Bn) from equation (1) in equation (2) $E = ed.\ C_A|m \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$

E is plotted against different analytical concentrations of A, keeping the concentration of B constant and in excess. The equation (3) is valid over the straight line portion of the curve and the slope of the line is given by the relation,

$$slope_1 = ed/m \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{4}$$

Similarly, if A is the component inconstant excess and the concentration of B is varied, then

$$(Am\ Bn) = C_B/n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

On plotting E against C_B, the slope of the straight line portion of the curve will be :

$$\text{Slope}_2 = ed/n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes and can be expressed as follows :

$$\text{slope}_1 / \text{slope}_2 = n/m$$

This method was tried in order to get confirmation of the results obtained earlier by Job's and Molar ratio method regarding the composition of complex. The results are summarised below :

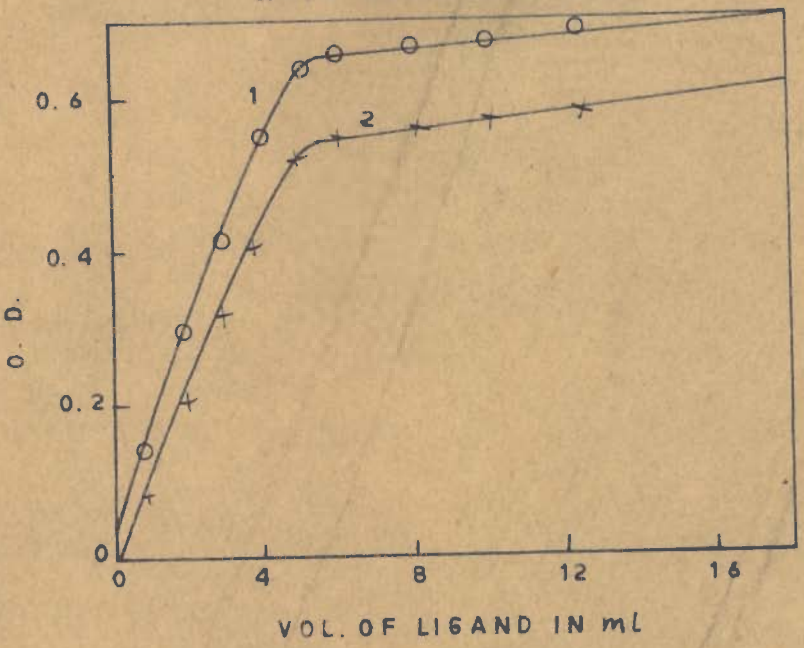
Set 1 - where the volume of ferric chloride was kept constant and that of p-dimethyl amino anil of phenyl glyoxal varied. The curves were plotted between O.D. and volume of the variant in ml. (Table No. 14. Fig. 11. Curve 2).

Set 2 - volume of ligand constant, while that of ferric chloride varying, the results are tabulated in the following tables (Table No. 15. Fig. 11 - curve 1).

Table No. 14

Vol. of $FeCl_3$ cc	Vol. of Ligand cc	O.D. at 575 mμ
5.0	1.0	0.12
5.0	2.0	0.14
5.0	3.0	0.17
5.0	4.0	0.18
5.0	5.0	0.20
5.0	6.0	0.22

Fig. 11 curve 2


MOLAR RATIO METHOD

WAVE LENGTH_565 mμ

FIG. 10

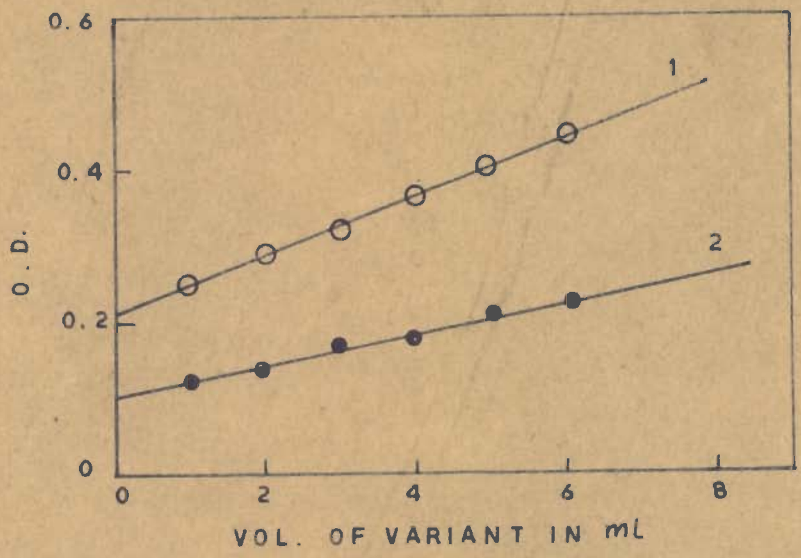

SLOPE RATIO METHOD

FIG. 11

Table No. 15

Set No. 2

Absorbance values for slope ratio method.

Concentration of Ligand = 0.50×10^{-3}M

concentration of ferric chloride = 1.0×10^{-3}M

Total volume = 15.0 cc

Vol. of $FeCl_3$ cc	Vol. of ligand cc	O.D. at 575 mμ
1.0	5.0	0.25
2.0	5.0	0.29
3.0	5.0	0.32
4.0	5.0	0.36
5.0	5.0	0.40
6.0	5.0	0.44

Fig. 11 - curve 1

Stability constant of ferric-p-dimethyl amino anil of phenyl glyoxal complex :

Stability constant was evaluated from molar ratio method. The dissociation of the complex can be written as

$FeR_2 \rightleftharpoons Fe + 2R$ ....Initial concentration

$C(1-\alpha) \quad \alpha C \quad 2\alpha C$ ....Final concentration

where 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 K is given by the equation:

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

The value of α ,may be obtained by the following relationship:

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

where E_m is the maximum absorption obtained from the horizontal portion of the curve, when all the iron is present in the form of complex and E_s is the observed absorption of the stoichiometric molar ratio of the reagent to iron in the complex.

The stability constant K^1 of the complex is the reciprocal of the dissociation constant.

$$\text{i.e. stability constant} = \frac{1}{\text{Dissociation constant}}$$

For determination of the stability constant, data given in Table No. 12 Fig. 9 curve 1 was used.

$E_m = 0.74$

$E_s = 0.70$ $\qquad C = 0.137 \times 10^{-3}$M

$\alpha = 0.05$

Instability constant $K_1 = 98.7 \times 10^{-14}$

Stability constant $K_s = \frac{1}{K_1} = \frac{1}{98.7 \times 10^{-14}} = 1.012 \times 10^{12}$

Free energy $\triangle F$ was calculated by the following relationship

$\triangle F = - RT \ln K$

$= - 16.50$ Kcals./mole at 25°C

Isolation and chemical analysis of the bluish green iron - p-dimethyl amino anil of phenylglyoxal complex :

100 cc of 0.005 M acetonic solution of ferric chloride was taken in a beaker and 100 cc of 0.005M reagent solution was added to it. The resulting mixture was concentrated in a vacuum dessicator over calcium chloride, when the bluish green crystals of Iron-p-dimethyl amino anil of phenylglyoxal complex were isolated. These crystals were

washed several times with acetonitrile in order to remove adhering impurities of ferric chloride and the reagent, and then dried in a vacuum dissicator.

Decomposition point - 190°d.

For estimation of iron, a weighed amount of the complex was, decomposed with aqua regia and its metal content wasestimated gravimetrically as iron oxide by the hydrolysis of potassiumcyanate.

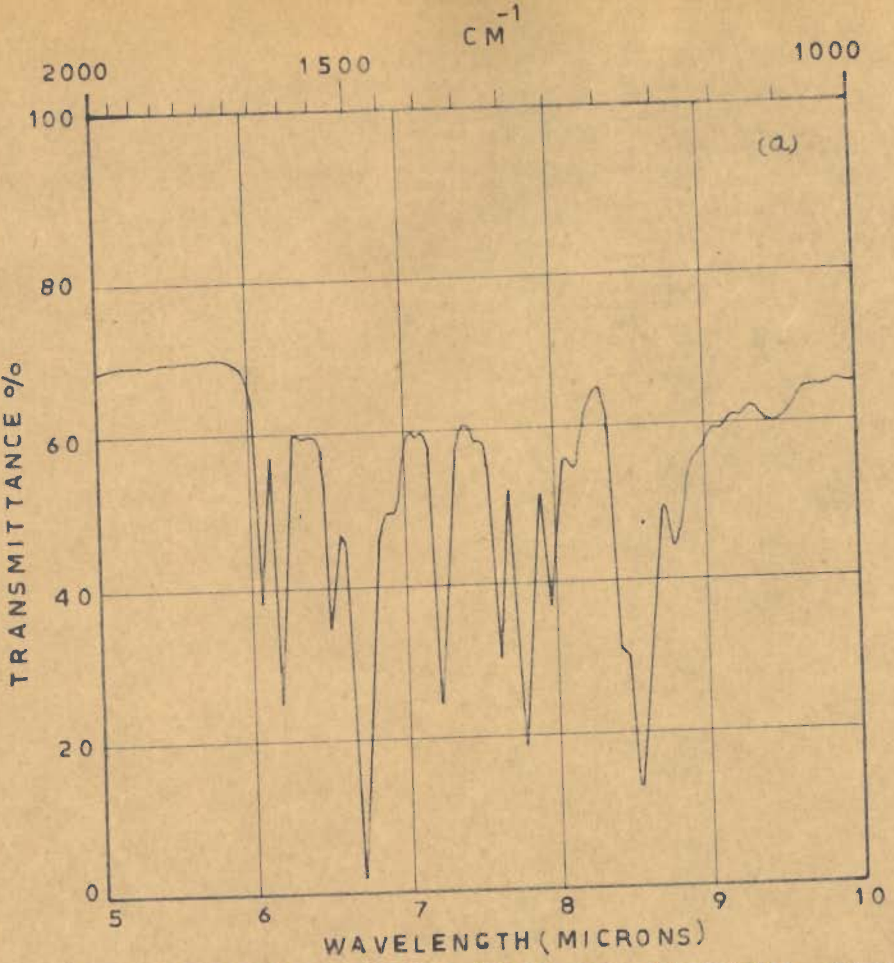
The results of analysis are as follows :

Reported	Found
Fe - 8.38; Cl-15.98;	Fe-8.47; Cl-15.69
C - 57.62; H-4.80;	C-57.60; H-4.78;
N - 3.34 and	N-3.38 and
O - 9.88 (By difference)	O-10.08 (By difference)

Structure of the complex :

The $>C = O$ and - CH=N group of the ligand p-dimethyl amino anil of phenyl glyoxal lies around 1700 cm^{-1} and 1600 cm^{-1} respectively.

The interaction of the Lewis acid ferric chloride causes bathochromic effect and makes the $>C=O$ group more reactive. In the ligand the other location for the inter-action can only be the nitrogen of -CH=N grouping due to presence of lone pair of electron. In the spectra of the complex the stretching frequencies lower to 1630 and 1580 cm^{-1} respectively (Fig. 12) this can only be possible when inter-action at these two positions viz. $>C=O$ and -CH=N grouping, takes place.



p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL

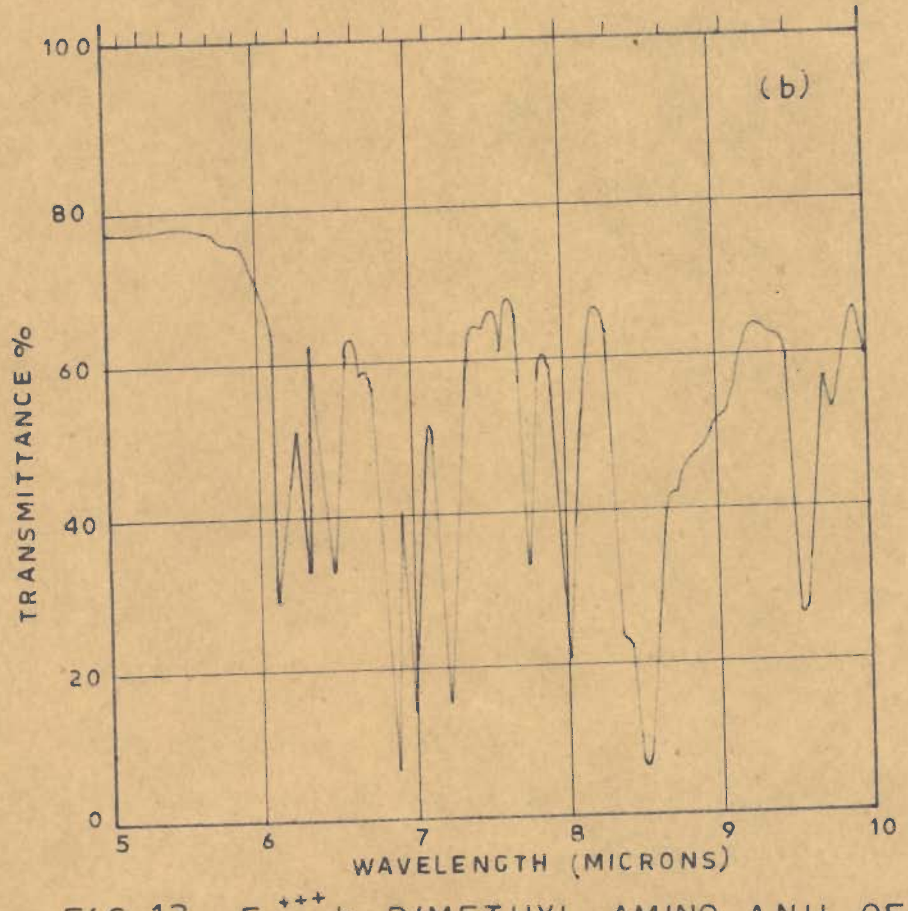
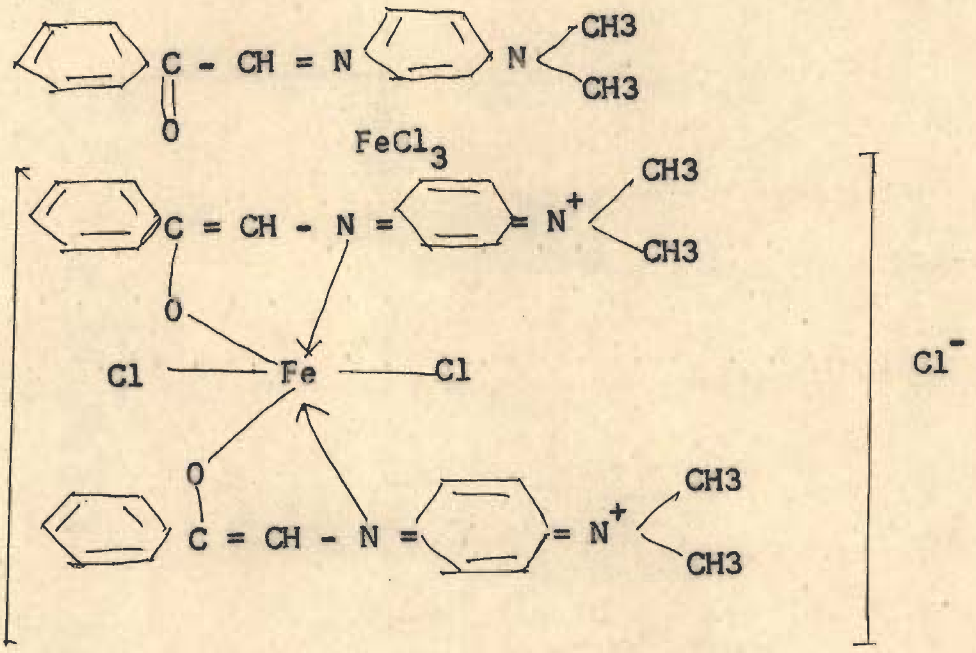


FIG. 12 _ Fe^{+++} - p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL COMPLEX

The ionic chlorine outside the coordination sphere of the chelate was confirmed by the formation of a white precipitate of AgCl by mixing ethanolic solutions of $AgNO_3$ and the isolated product on the basis of the above results, the following structure may be assigned to the chelate.



Studies on the Zn (ii)-p-dimethyl Amino Anil of Phenyl-glyoxal complex :

In order to determine the number of complexes formed by the interaction of zinc chloride and p-dimethyl amino anil of phenyl-glyoxal, the method of Vosburgh and Cooper (loc. cit.) was followed.

Equimolar solutions of the reactants (ZnCl$_2$ and p-dimethyl amino anil of phenyl glyoxal) of concentration 0.66 x 10^{-3}M were mixed in the ratio 4:3, 3:2, 3:1, 2:1 and 1:1. The O.D. were measured in the wave length range of 325 mμ to 625 mμ by Bausch and Lomb "Spectromic 20".

Absorption experiments carried out in the range 325 mμ to 625 mμ showed one maxima at 425 mμ and another at 560 mμ (Table No. 16 fig. 13). The former is due to the excess of ligand and later due to the complex. Therefore all the absorption measurements were carried out at 560 mμ.

Table No. 16 Fig. 13

Vosburgh and Cooper's method

Wave length mμ	Ratio of Ligand to Zinc chloride				
	4:3	3:2	3:1	2:1	1:1
curve No.	1	2	3	4	5
325	0.40	0.30	0.23	0.17	0.15
350	0.35	0.28	0.18	0.15	0.13
375	0.45	0.37	0.26	0.17	0.13
400	0.75	0.65	0.50	0.30	0.17
415	0.87	0.78	0.64	0.53	0.20
425	0.90	0.82	0.66	0.60	0.20
435	0.87	0.78	0.64	0.54	0.20
450	0.80	0.65	0.52	0.40	0.17
475	0.50	0.40	0.30	0.20	0.12
500	0.25	0.25	0.14	0.18	0.10
525	0.20	0.23	0.27	0.38	0.20
550	0.55	0.60	0.61	0.72	0.45
560	0.63	0.67	0.70	0.75	0.52
575	0.59	0.65	0.66	0.70	0.47
600	0.45	0.57	0.60	0.50	0.34
625	0.20	0.34	0.30	0.20	0.12

For determining the composition of the olive green complex formed between zinc chloride and p-dimethyl amino anil of phenyl-glyoxal, Job's method of continuous variation was employed. The following sets of mixture were prepared :

Set I - 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 cc of $ZnCl_2$ were mixed with 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc of ligand respectively. The concentration of both the reactant was $1.25 \times 10^{-3}M$

Set II - Concentration of the reactants being $1.11 \times 10^{-3}M$ curves were plotted between the difference of O.D. and the ratio $\frac{M}{M + L}$ (M and L represent metal and ligand) at two different wave lengths 550 $m\mu$ and 560 $m\mu$ respectively.

Job's Method - Table No. 17

Set No.1

		Wave length = 550 $m\mu$			560 $m\mu$		
Vol. of $ZnCl_2$ cc	Vol. of ligand cc	O.D. Mixture c	O.D. Ligand a	Difference (c-a)	O.D. Mixture c	O.D. Ligand a	Difference (c-a)
1.0	9.0	0.65	0.57	0.08	0.71	0.60	0.11
2.0	8.0	0.64	0.48	0.16	0.70	0.50	0.20
3.0	7.0	0.62	0.40	0.22	0.66	0.40	0.26
4.0	6.0	0.605	0.34	0.265	0.65	0.36	0.29
5.0	5.0	0.57	0.27	0.30	0.61	0.29	0.325
6.0	4.0	0.49	0.21	0.28	0.53	0.23	0.30
7.0	3.0	0.43	0.18	0.25	0.46	0.20	0.26
8.0	2.0	0.34	0.16	0.18	0.39	0.20	0.19
9.0	1.0	0.24	0.14	0.10	0.24	0.18	0.06
			Fig. 15 Curve 1			Fig. 14 curve 1	

Table No. 18

Set No. 2 Wave length - 550 mμ Wave length - 560 mμ

Vol. of $ZnCl_2$ cc	Vol. of ligand cc	O.D. Mixture c	O.D. Ligand a	Difference (c-a)	O.D. Mixture c	O.D. Ligand a	Difference (c-a)
1.0	9.0	0.53	0.50	0.03	0.58	0.52	0.06
2.0	8.0	0.50	0.40	0.10	0.58	0.44	0.14
3.0	7.0	0.48	0.32	0.16	0.54	0.34	0.20
4.0	6.0	0.48	0.28	0.20	0.53	0.29	0.24
5.0	5.0	0.45	0.22	0.23	0.50	0.25	0.25
6.0	4.0	0.40	0.18	0.22	0.44	0.22	0.22
7.0	3.0	0.345	0.17	0.175	0.38	0.20	0.18
8.0	2.0	0.26	0.16	0.10	0.305	0.18	0.125
9.0	1.0	0.17	0.14	0.03	0.22	0.17	0.05

Fig.15 curve 2 Fig. 14 curve 2

Molar ratio method :

The composition of the complex was further investigated by molar ratio method (loc. cit.) keeping the volume of zinc chloride constant and that of ligand varying at two different concentration of the reactants.

Set No. 1 - concentration of reactants = 1.0×10^{-3}M

Total volume = 15 cc

Table No. 19 Fig. 16-17 curve 1.

Set No. 2 - concentration of reactants = 2.0×10^{-3}M

Total volume = 15 cc

Table No. 20 Fig. 16-17 curve-2

JOB'S METHOD

WAVE LENGTH – 550 mμ

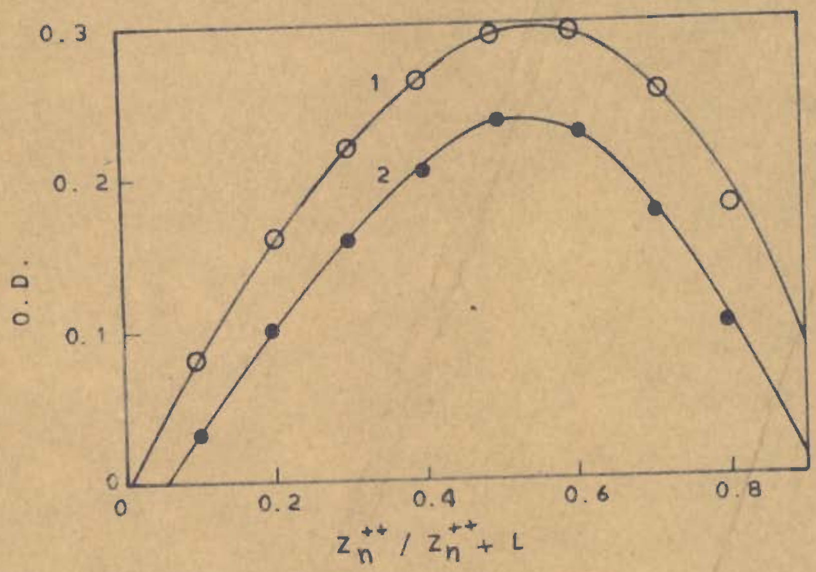


FIG. 15

MOLAR RATIO METHOD

WAVE LENGTH – 560 mμ

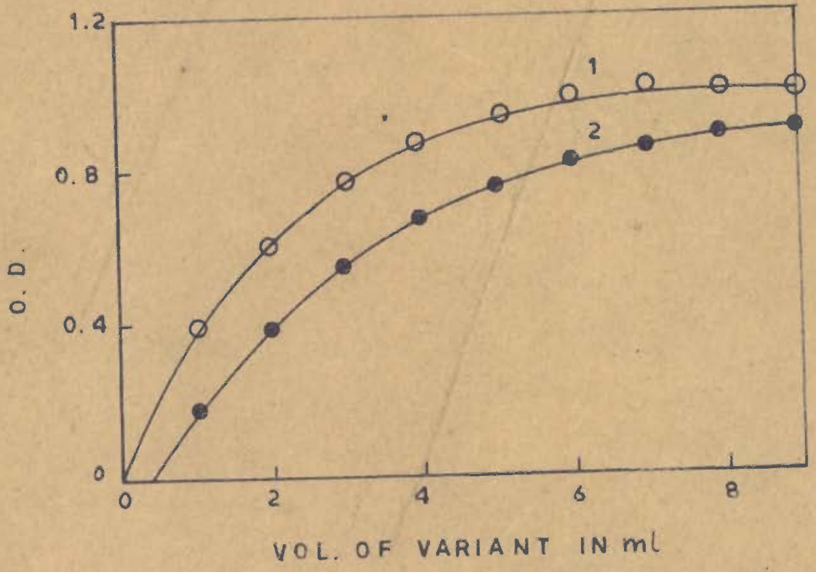


FIG. 16

Table No. 19

Molar ratio method

Fig. 16 curve 1 Fig. 17 curve 1

Volume of $ZnCl_2$ cc	Volume of ligand cc	O.D. at 560 $m\mu$	O.D. at 550 $m\mu$	O.D. at 570 $m\mu$
5.0	1.0	0.40	0.10	0.08
5.0	2.0	0.60	0.36	0.20
5.0	3.0	0.76	0.60	0.36
5.0	4.0	0.86	0.80	0.50
5.0	5.0	0.94	0.90	0.60
5.0	6.0	1.0	0.96	0.66
5.0	7.0	1.01	0.98	0.70
5.0	8.0	1.01	0.98	0.72
5.0	9.0	1.01	1.0	0.74

Set No.2

Table No. 20

Fig. 17 curve 2 Fig. 16 curve 2

5.0	1.0	0.08	0.19	0.08
5.0	2.0	0.26	0.40	0.24
5.0	3.0	0.44	0.54	0.32
5.0	4.0	0.58	0.66	0.50
5.0	5.0	0.70	0.76	0.60
5.0	6.0	0.78	0.80	0.70
5.0	7.0	0.80	0.86	0.72
5.0	8.0	0.82	0.88	0.74
5.0	9.0	0.84	0.90	0.75

Table No. 21

Set No.1

Concentration of ligand = 2×10^{-3}M

Concentration of Zinc chloride = 1×10^{-3}M

Total volume = 10.0 cc

Volume of ligand cc	Volume of zinc chloride cc	O.D. at 550 mμ	O.D. at 560 mμ	O.D. at 570 mμ
5.0	0.20	0.56	0.72	0.38
5.0	0.40	0.68	0.82	0.50
5.0	0.60	0.80	0.96	0.62
5.0	0.80	0.94	1.10	0.76
5.0	1.0	1.1	1.2	0.90
5.0	1.2	1.2	1.34	1.02
5.0	1.4	1.34	1.46	1.20
5.0	1.6	1.48	1.6	1.30
5.0	1.8	1.60	1.70	1.40
Fig. 18 curve		(2)	(1)	(3)

Table No. 22

Set No. 2

Concentration of Ligand = 1×10^{-3}M

Concentration of Zinc chloride = 2×10^{-3}M

Total volume = 10.0 cc

Volume of zinc chloride cc	Volume of ligand cc	O.D. at 550 mμ	O.D. at 560 mμ	O.D. at 570 mμ
5.0	0.20	0.12	0.24	0.10
5.0	0.40	0.24	0.36	0.12
5.0	0.60	0.36	0.50	0.24
5.0	0.80	0.48	0.64	0.36
5.0	1.0	0.60	0.74	0.50
5.0	1.2	0.70	0.86	0.60
5.0	1.4	0.84	1.0	0.72
5.0	1.6	0.98	1.1	0.80
5.0	1.8	1.1	1.24	0.96
Fig. 18 curve		5	4	6

MOLAR RATIO METHOD

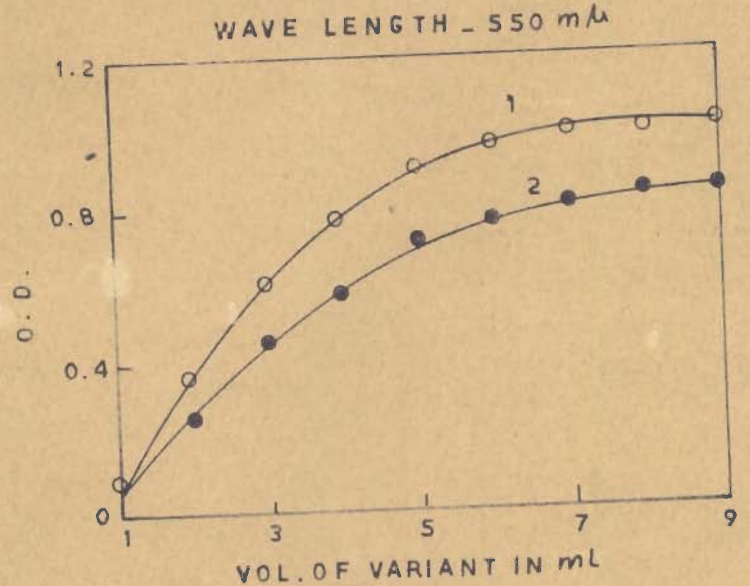


FIG. 17

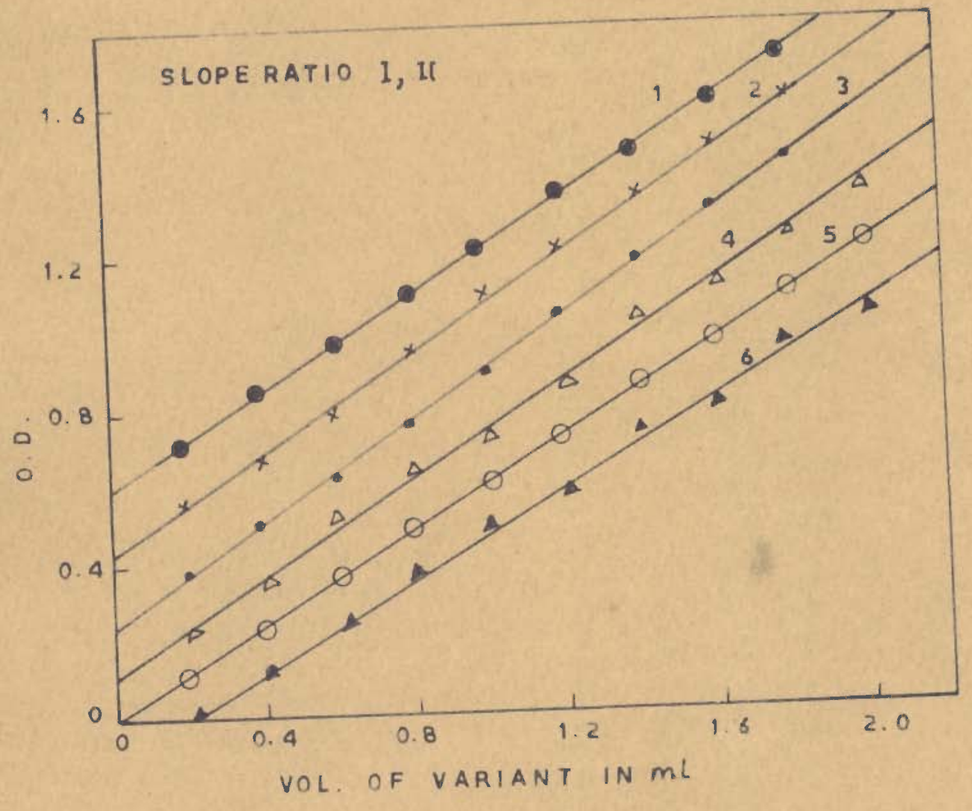


FIG.18 _ Zn^{++} + p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL

Slope ratio method :

The composition of the complex obtained by Job's and molar ratio method, was further confirmed by slope ratio method. The results are as follows :

Set No. 1 - concentration of ligand = 2.0×10^{-3}M
concentration of Zinc chloride = 1.0×10^{-3}M
Total volume = 10.0 cc

Table No. 21 Fig. 18

Set No. 2 - concentration of ligand = 1.0×10^{-3}M
concentration of Zinc chloride = 2.0×10^{-3}M
Total volume = 10 cc

Table No.22 Fig. 18

Stability constant :

It was determined by the molar ratio method (loc. cit.) using data (Fig. 16 curve 1 Table No. 19) by the equation $= \frac{E_m - E_s}{E_m}$ and $K_s = \frac{(1-\alpha)}{C\alpha^2}$

where α, E_m, E_s and C have their usual significance.

$E_m = 1.0$ $C = 0.33\times10^{-3}$M

$E_s = 0.85$

$\alpha = 0.15$

$K_s = 1.1\times10^5$

Free energy $-\Delta F = RT \ln K$

$= -6.8$ K cals.

Isolation and chemical analysis of the Zn-p-dimethyl amino anil of phenyl glyoxal complex :

50 cc of zinc-chloride (0.0025M) solution was added to 50 cc of p-dimethyl amino anil of phenyl-glyoxal

solution of strength 0.0025M (both solutions were prepared in acetonitrile). The blue black, crystalline precipitate of Zn-p-dimethyl amino anil of phenyl-glyoxal was obtained.

Decomposition point -230° C.

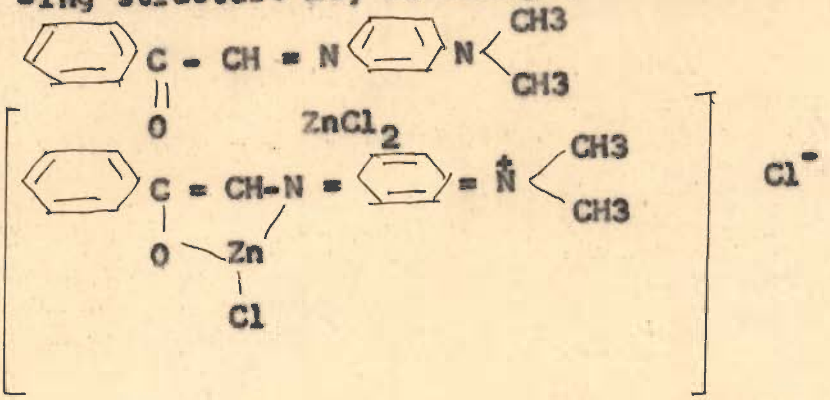
For estimation of zinc, a weighed amount of sample of the complex was digested with aqua regia and its zinc content was estimated gravimetrically by diammonium hydrogen phosphate.

Chemical analysis of this complex was done by the methods described earlier. The results of analysis are as follows :

Calculated	Found
Zn-16.83; Cl-18.28	Zn-16.79; Cl-18.70
C-49.44; H-4.12;	C-49.53; H-4.30;
N-7.20 and	N-7.8 and
O-4.13 (By difference)	O-2.88 (By difference)

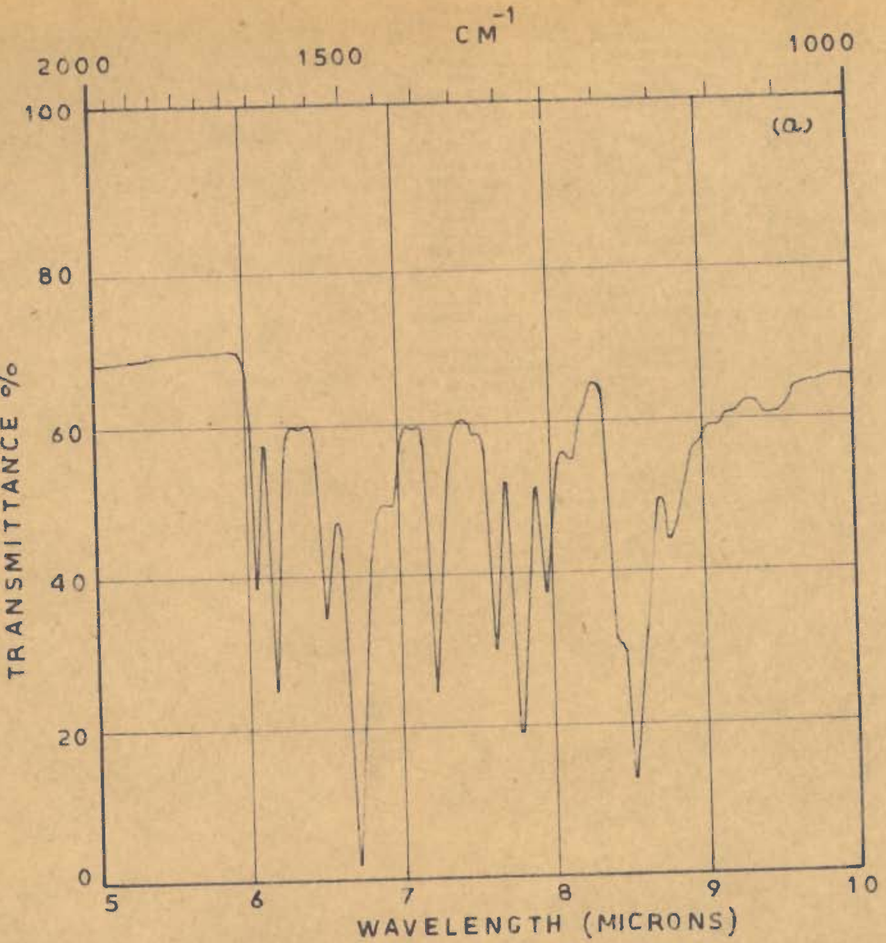
Structure of the complex :

From the above data it is evident that one mole of zinc chloride combines with one mole of the p-dimethyl amino anil of phenyl glyoxal to form the chelate. The following structure may be assigned to the complex :



The ionic chlorine outside the co-ordination sphere of the anil chelate was confirmed by the formation of white precipitate of AgCl, on adding ethanolic solution of silver nitrate to the solution of the complex.

From the spectra of the ligand and the complex (Fig. 19) a marked lowering of the frequencies of its functional groups i.e. $>C = O$ and $-CH=N$ was observed. This lowering cannot be other than the positions where binding takes place.



þ- DIMETHYL AMINO ANIL OF PHENYL GLYOXAL

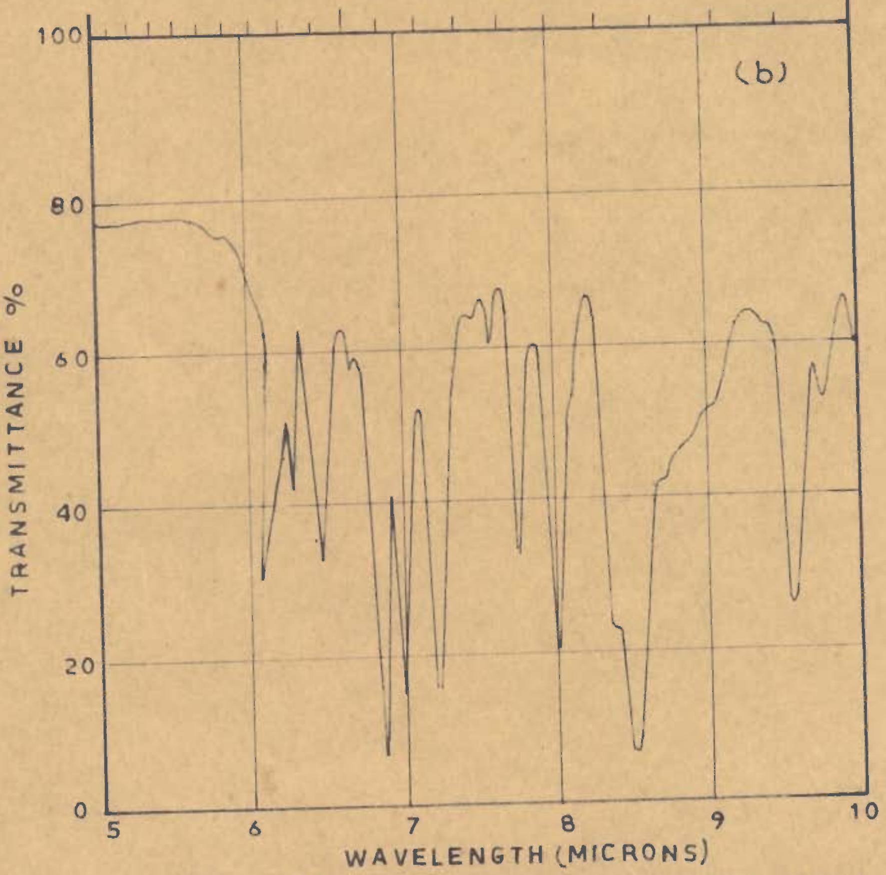


FIG. 19 _ Z_n^{++} - þ - DIMETHYL AMINO ANIL OF PHENYL GLYOXAL COMPLEX

COMPOSITION OF CADMIUM (II) p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL COMPLEX IN ACETONIC MEDIUM :-

Nature of the Complex :

In order to ascertain the number of complexes formed in the course of reaction Vosburgh and Copper method was employed. Different mixtures of the metal ion eg; cd(II) and the ligand were mixed in different ratio and their optical densities were measured. A plot of the O.D. and the wave length gave a curve (Fig. 20) having two maxima e.g. at 425 mμ and 540 mμ respectively. The plot of O.D. versus wave length in the reagent itself gave only one max. at 425 mμ. Therefore it is assumed that 425 mμ maxima will be due to excess of the reagent present in the mixtures. Thus 540 mμ was choosen as the proper wave length to study the different aspects of the violet chelate (Table No.23 Fig.20).

Stoichiometry of the complex :

Job's method of continued variation was employed to determine the composition of the complex. Equimolecular solutions of cadmium Iodide and p-dimethyl-amino anil of phenyl glyoxal were mixed and their optical density measured at wave length 540 mμ. The difference in optical densities of the mixtures and the ligand were plotted against the molar fraction i.e. $\frac{M}{M + L}$ of the components. The results are given below :

Table No. 23

Concentration of cadmium Iodide = 0.83×10^{-3}M
Concentration of Ligand = 0.83×10^{-3}M

Fig. 20

Wave length mμ	Ratio of cadmium iodide to ligand 1:1	1:2	1:3	2:1	3:1
325	0.100	0.60	0.48	0.32	0.22
350	0.95	0.26	0.20	0.10	0.05
375	0.80	0.25	0.17	0.09	0.03
405	0.78	0.68	0.30	0.25	0.20
415	0.65	0.82	0.64	0.36	0.45
425	0.65	0.88	0.70	0.47	0.52
435	0.60	0.86	0.66	0.42	0.47
450	0.58	0.78	0.50	0.25	0.35
475	0.35	0.26	0.15	0.10	0.10
500	0.17	0.12	0.07	0.03	0.04
525	0.30	0.22	0.13	0.04	0.07
540	0.43	0.38	0.28	0.15	0.24
555	0.40	0.36	0.23	0.13	0.18
575	0.23	0.20	0.13	0.05	0.12
600	0.10	0.08	0.01	0.02	0.10
625	0.08	0.02	0.02	0	0.07

Table No. 24

Job's Method concn. of reactants = 1.11×10^{-3}M
Wave length - 540 mμ. Total volume = 10.0 cc

Vol. of CdI_2 cc	Vol. of ligand cc	O.D. Mixture C	O.D. Ligand a	Difference (c-a)
1.0	9.0	0.64	0.52	0.12
2.0	8.0	0.628	0.41	0.218
3.0	7.0	0.60	0.33	0.270
4.0	6.0	0.58	0.28	0.30
5.0	5.0	0.56	0.24	0.32
6.0	4.0	0.525	0.24	0.285
7.0	3.0	0.442	0.20	0.242
8.0	2.0	0.365	0.20	0.165
9.0	1.0	0.27	0.19	0.08

Fig. 21 Curve 1

Table No. 25

Concentration of reactants = 1.0×10^{-3}M
Wave length - 540 mμ Total volume = 10.0 cc

Vol. of ligand cc	Vol. of CdI_2 cc	O.D. Mixture C	O.D. ligand a	Difference (c-a)
9.0	1.0	0.56	0.49	0.07
8.0	2.0	0.53	0.40	0.13
7.0	3.0	0.49	0.32	0.17
6.0	4.0	0.47	0.26	0.21
5.0	5.0	0.46	0.22	0.240
4.0	6.0	0.418	0.20	0.218
3.0	7.0	0.34	0.18	0.16
2.0	8.0	0.24	0.14	0.10
1.0	9.0	0.14	0.10	0.04

Fig. 21 curve 2

Molar ratio method :

To confirm the results obtained by Job's method, molar ratio method was also performed. Solution were mixed according to the method described earlier (keeping constant volume of cadmium Iodide and varying the concentration of p-dimethyl amino anil of phenyl glyoxal). Here too two concentrations of metal ion were used for determining the composition of the complex. Following results are obtained :

Table No. 26

Concentration of CdI_2 = 2×10^{-3}M

Concentration of Ligand= 1×10^{-3}M

Total volume = 10.0 cc

Fig. 22 curve 1

Fig.23 curve 1

Vol. of CdI_2 cc	Vol. of ligand cc	O.D. at 540 mμ	O.D at 550 mμ
2.0	1.0	0.20	0.15
2.0	~~0.38~~ 2.0	0.38	0.30
2.0	3.0	0.53	0.45
2.0	4.0	0.61	0.57
2.0	5.0	0.66	0.58
2.0	6.0	0.67	0.60
2.0	7.0	0.67	0.60
2.0	8.0	0.67	0.60

Table No. 27

Concentration of CdI_2 = 1.66×10^{-3}M
Concentration of ligand = 0.83×10^{-3}M
Total volume = 10 cc

Fig. 22 curve 2 Fig.23 curve 2

Vol. of CdI_2 cc	Vol. of ligand cc	O.D. at 540 mμ	O.D. at 550 mμ
2.0	1.0	0.10	0.09
2.0	2.0	0.23	0.24
2.0	3.0	0.41	0.35
2.0	4.0	0.52	0.47
2.0	5.0	0.57	0.50
2.0	6.0	0.57	0.51
2.0	7.0	0.58	0.51
2.0	8.0	0.58	0.51

Slope ratio method :

The composition of cadmium Iodide - anil complex was further investigated by slope ratio method.

Set No. 1

concn. of Ligand = 2.0×10^{-3}M
concn. of cadmium Iodide = 1.0×10^{-3}M
Total volume = 10.0 cc
Table No. 28

Set No. 2

concentration of Ligand = 1.0×10^{-3}M
concentration of cadmium Iodide = 2.0×10^{-3}M
Total volume = 10.0 cc
Table No. 29

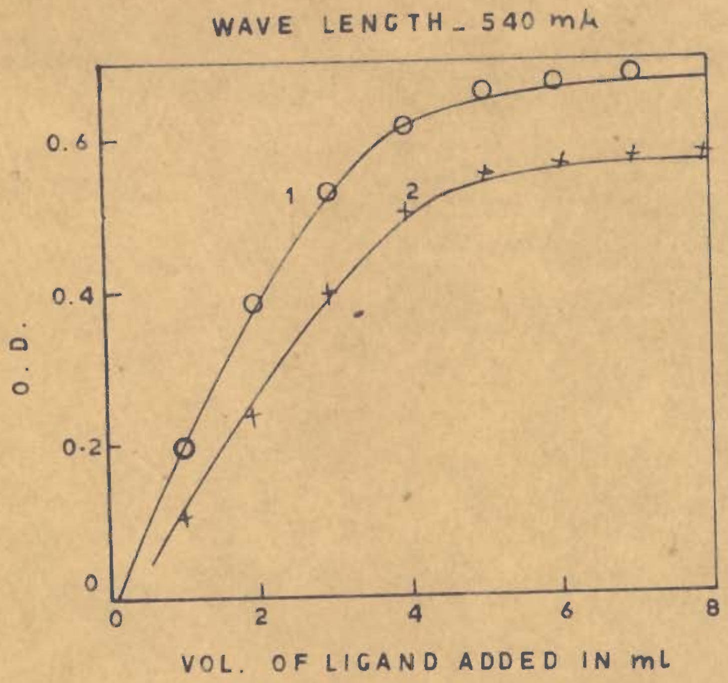


FIG. 22

MOLAR RATIO METHOD

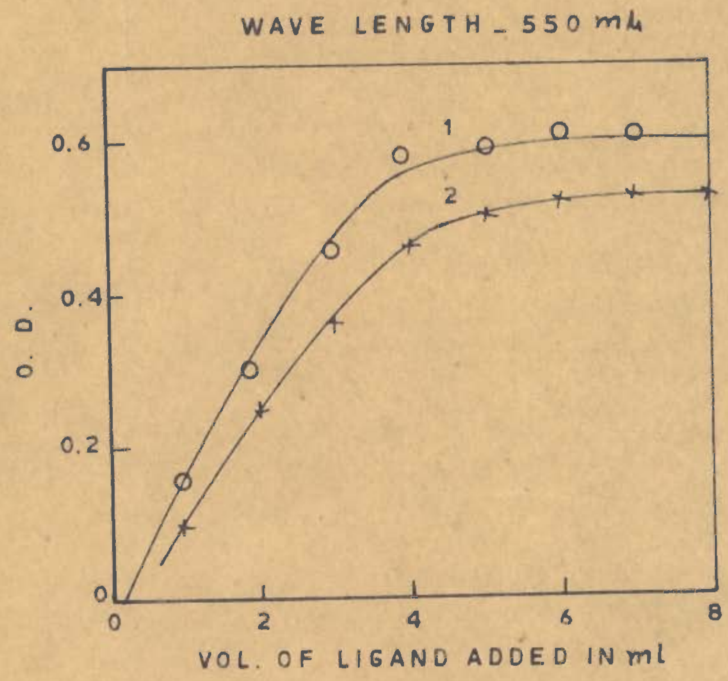


FIG. 23

Table No. 28

Set No. 1

Concentration of ligand = $2 \times 10^{-3}M$
Concentration of cadmium iodide = $1 \times 10^{-3}M$
Total volume = 10 cc

Fig. 24 curve 1 2 3

Volume of ligand cc	Volume of CdI_2 cc	O.D. at 530 $m\mu$	O.D. at 540 $m\mu$	O.D. at 550 $m\mu$
5.0	0.20	0.10	0.10	0.125
5.0	0.40	0.13	0.15	0.22
5.0	0.60	0.25	0.30	0.325
5.0	0.80	0.35	0.35	0.41
5.0	1.0	0.45	0.475	0.50
5.0	1.1	0.50	0.525	0.54
5.0	1.2	0.55	0.55	0.575

Table No. 29

Set No.2

Concentration of ligand = $1 \times 10^{-3}M$
Concentration of CdI_2 = $2 \times 10^{-3}M$
total volume = 10.0 cc

Fig. 24 curve 4 5 6

Volume of CdI_2 cc	Volume of ligand cc	O.D. at 530 $m\mu$	O.D. at 540 $m\mu$	O. D. at 550 $m\mu$
5.0	0.20	0.175	0.13	0.15
5.0	0.40	0.26	0.22	0.25
5.0	0.60	0.36	0.30	0.35
5.0	0.80	0.45	0.40	0.45
5.0	1.0	0.55	0.50	0.49
5.0	1.1	0.57	0.55	0.53
5.0	1.2	0.62	0.58	0.63

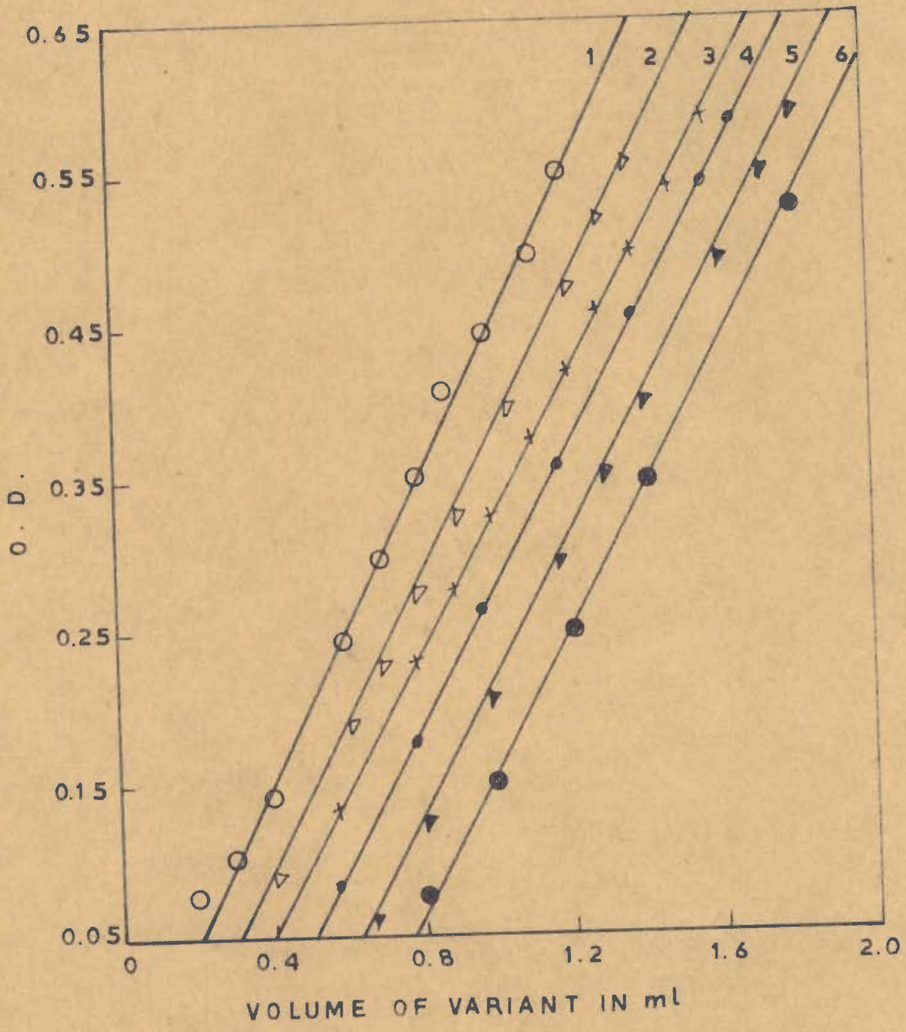


FIG. 24 _ SLOPE RATIO METHOD: Cd-p-DIMETHYL
AMINO ANIL OF PHENYL GLYOXAL
SET I AND II.

Stability constant of the complex :

Stability constant of violet complex K was calculated by the molar ratio method. The dissociation of the complex may be represented by

$$\begin{array}{llll} MA = & M & + A & \\ C & 0 & 0 & \text{initial concentration} \\ C(1-\alpha) & \alpha C & \alpha C & \text{Eq. concentration} \end{array}$$

Where C is the total concentration of the complex ion in moles per litre and α is the degree of dissociation, the stability constant may be written as :

$$K = \frac{C(1-\alpha)}{\alpha C \, \alpha C} = \frac{(1-\alpha)}{\alpha^2 C}$$

α may be obtained from the molar ratio curve (Fig.22 curve 1 Table No. 26) as :

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

where E_m is the maximum extinction obtained from the horizontal portion of the curve, indicating that while the reagent is complex, E_s is the extinction of stoichiometric molar ratio of metal to reagent.

Free energy change was calculated by the relationship $-\Delta F = RT \ln K$

where R - the gas constant

T - Absolute temperature

ΔF - Change in free energy

Stability constant by molar ratio method :

$$\alpha = \frac{E_m - E_s}{E_m} \qquad K = \frac{1-\alpha}{C\alpha^2}$$

Set No. 1 - Fig. 22 curve 1 (Table No. 26)

$E_m = 0.67$

$E_s = 0.61$ $\qquad$ $K_s = 3.5 \times 10^{+5}$

$\alpha = 0.08$

$C = 0.4 \times 10^{-3}$

$-\triangle F = RT \ln K$

$= 7.6$ Kcals/mole. at 25°C

Isolation and chemical analysis of the dark-blue coloured Cadmium-p-dimethyl amino anil of phenylglyoxal complex :

Since 1:1 complex was indicated by the spectrophotometric methods concentrated equimolar acetonitrolic solutions of cadmium Iodide and the reagent were mixed. The resulting precipitate so obtained was thoroughly washed with acetonitrile. It was then dried in a vacuum dessicator over calcium chloride.

Decomposition point - 205°C

Chemical analysis :

A weighed amount of the dried sample was digested with Aqua regia, evaporated till whole of the organic matter was destroyed and cadmium contents were estimated - gravimetrically as cadmium-molybdate.

The results of chemical analysis are as follows:-

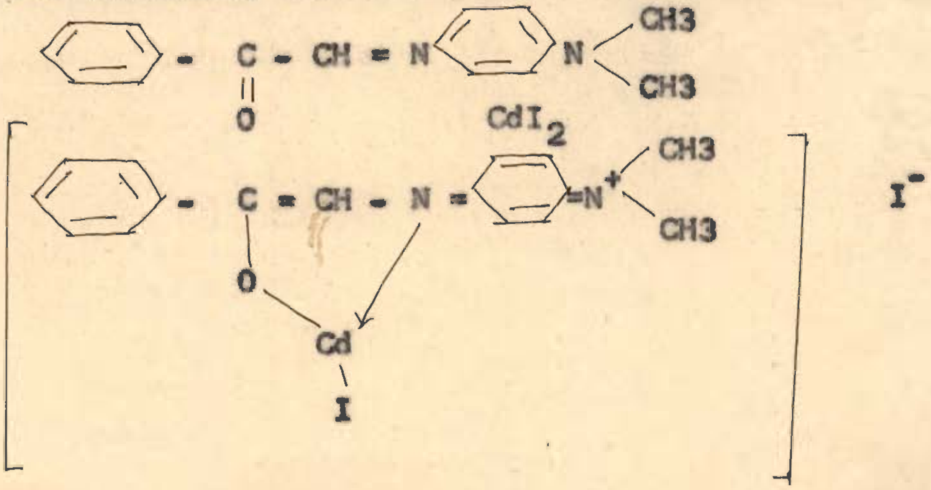
Calculated	Found
Cd-18.17; I-41.06; 2	Cd-18.00; I-41.31;
C - 31.05; H -2.58	C-31.13; H - 2.53;
N - 4.52 and	N - 4.35 and
O - 2.67 (By diff.)	O - 2.68 (By diff.)

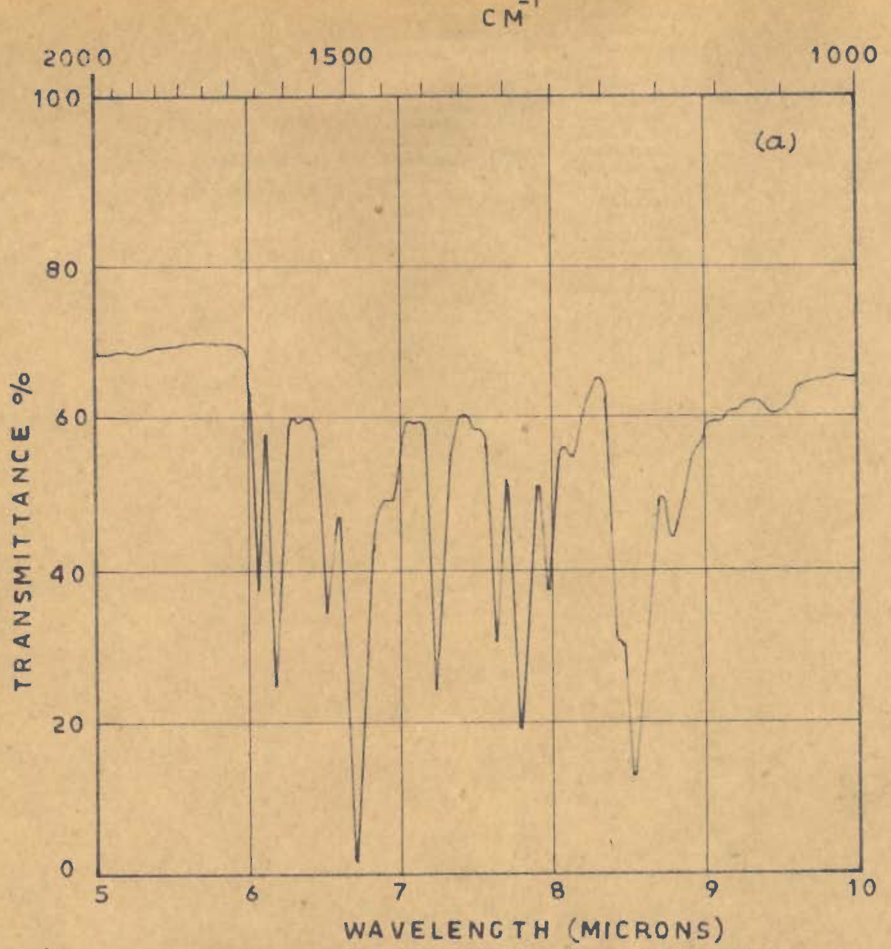
From the above analysis it is clear that chelate is 1:1 (p-dimethyl amino anil of phenyl glyoxal - Cd I_2).

Structure of the complex -

In order to ascertain the seats of interaction in course of the chelation, I.R. measurements were recorded in solid state by KBr technique. The $>C=O$ and - CH=N grouping show characteristic frequencies around 1700 cm^{-1} and 1600 cm^{-1} respectively. From the spectrum of the complex, (Fig. 25). These frequencies are lowered to (1680 cm^{-1}, 1570 cm^{-1}) respectively. This lowering of the frequencies can only be responsible for M-L binding in the chelation. Around 830 cm^{-1} there is a doublet (1:4 disubstituted) which becomes a singlet in the chelate. This may be attributed to one of the benzenoid changing to quinonoid unit. The conjugation in the chelation is also revealed by perturbation in phenyl skeleton frequencies(1400-1500 cm^{-1}).

The ionic Iodine outside the coordination sphere of the chelate was confirmed by the formation of a yellowish precipitate of AgI by mixing ethanolic solutions of $AgNO_3$ and the isolated product. On the basis of the above results, the following structure may be assigned to the chelate.





p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL

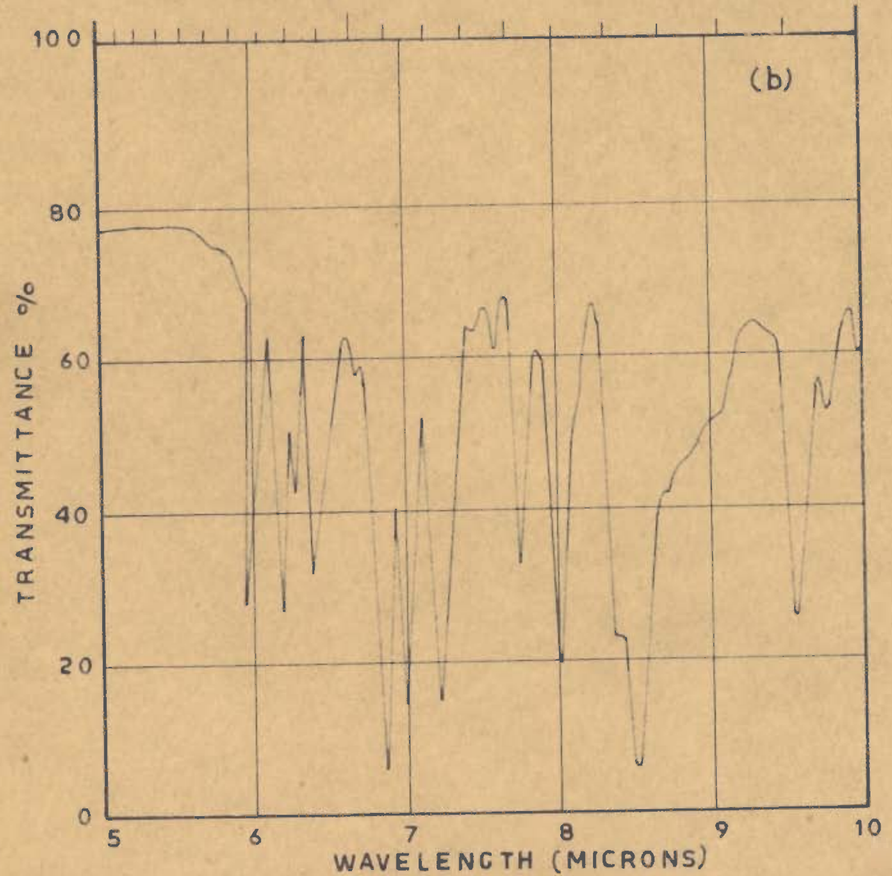


FIG. 25 _ Cd^{++}-p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL COMPLEX

CHAPTER III

Spectrophotometric studies on the interaction of Lewis acids with p-dimethyl amino anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal.

INTRODUCTION:-

The application of Schiff's bases for analytical purposes has not been widely studied. Duke(1) reported the gravimetric estimation of copper in brass and bronze with salicyl-aldimine. Mukherjee(3) has used β-hydroxy-naphthal--dimine and orthohydroxy acetophenone for gravimetric determination of copper and nickel. The same author has also studied the application of ethylene diamine-bis-sulphosalicy--laldehyde and salicyl-aldehyde-glycine - hydroxamic acid(3) in the colorimetric estimation of ferric ion. Singh and Kumar(4) have recently studied the reactions of different metal ions with bis-salicylaldehyde ethylene diamine and also developed a method for the estimation of copper with base. Poddar and Dey(5-6) have reported the colorimetric estimation of Fe (III) with the Schiff's base derived from ortho-hydroxy acetophenone and ethylene diamine, and the use of Schiff's base derived from 1,3-diamino propanol -2 and salicylaldehyde as a reagent for the spectrophotometric determination of Fe (III).

The survey of the literature would, however, show that the bathochromatic effect in anils has not been exploited either to study complex ion formation or in estimating metal ions with this reagent. One of the earliest references concerned the work of Krohnke and Gross(7) who studied the interaction of the anil, p-dimethyl amino anil of phenyl-glyoxal with mercuric chloride.

In this Chapter the composition and stability of the complexes of Zn^{++}, $Cd,^{++}$ $Hg,^{++}$ Fe^{+++} with p-dimethyl amino anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl-glyoxal in acetonic medium employing spectrophotometric methods, has been investigated. The results of the spectrophotometric studies have been further confirmed by I.R. spectra and chemical analysis of the isolated products.

Mercury-p-dimethyl amino anil of β-naphthyl-glyoxal complex in acetonic medium :-

Vosburgh and Cooper's method (loc. cit.) has employed to know the number of complexes formed by the interaction of mercuric chloride with p-dimethyl amino anil of β-naphthyl-glyoxal, in acetonic medium. The solutions of the reactants prepared in acetone (both of strength 5.0×10^{-4}M) were mixed in the ratios of mercuric chloride to reagent as 1:4, 2:3, 3:2, 1:2, 2:1 and 1:1. optical density was measuredat different wave lengths, ranging from 325 $m\mu$ to 625 $m\mu$.

Table No. 1

Concentration of $HgCl_2 = 5 \times 10^{-4}$M
Concentration of ligand = 5×10^{-4}M

Wave length $m\mu$	Ratio of ligand to mercuric chloride					
	1:4	2:3	3:2	1:2	2:1	1:1
325	0.90	0.70	0.58	0.50	0.31	-
350	0.25	0.20	0.15	0.17	0.09	-
375	0.30	0.23	0.16	0.11	0.05	-
400	0.75	0.55	0.40	0.25	0.15	-
425	1.30	1.1	0.80	0.55	0.40	-
435	1.50	1.25	1.00	0.70	0.53	1.6
450	1.20	0.90	0.70	0.45	0.30	1.30
475	0.57	0.40	0.26	0.14	0.07	1.70
500	0.16	0.10	0.10	0.08	0.01	0.36
525	0.20	0.12	0.07	0.03	0.01	0.30
550	0.35	0.23	0.12	0.08	0.05	0.40
565	0.45	0.35	0.26	0.17	0.11	0.50
580	0.35	0.24	0.15	0.10	0.06	0.40
600	0.20	0.10	0.05	0.02	0.01	0.25
625	0.05	0.03	0.02	-	-	0.13

Fig. 1

Two peaks at 435 mμ and 565 mμ were obtained. The former one was realised in mixtures containing excess of ligand (435 mμ). At this wave length the absorbance of the ligand was greater than that of the mixtures. Since in complexation the absorbance of the chelates should be greater than either of the components, this wave length could not be taken as a suitable one to apply Job's method. All experiments to determine the composition of the complex were, therefore, carried out 565. mμ

Job's method of continued variation -

Job's method was followed for determining the composition of the violet complex. Equimoleculer solutions of mercuric chloride and reagent, of concentrations 1.25×10^{-3}M and 1.0×10^{-3}M were mixed according to the method of continuous variation and O.D. measurements were carried out at three different wave length 555, 565 and 575 mμ. As the O.D. of the ligand is appreciable on the above wave length, the difference of O.D. of mixture and ligand was plotted against the ratio, $\frac{Hg^{++}}{Hg^{++} + L}$.

Table No. 2

Set No. 1

Concentration of reactants - 1.25x10^{-3}M

Wave length - 555 mu   Wave length - 565 mu

Vol. of ligand cc	Vol. of $HgCl_2$ cc	O.D. Mixt. c	O.D. Ligand a	Difference (c-a)	O.D. Mixt. c	O.B. Ligand a	Difference (c-a)
9.0	1.0	0.69	0.55	0.14	0.746	0.60	0.146
8.0	2.0	0.64	0.47	0.172	0.70	0.50	0.20
7.0	3.0	0.62	0.40	0.22	0.67	0.43	0.24
6.0	4.0	0.60	0.35	0.25	0.65	0.38	0.27
5.0	5.0	0.57	0.30	0.27	0.61	0.32	0.29
4.0	6.0	0.538	0.28	0.258	0.56	0.30	0.26
3.0	7.0	0.49	0.25	0.24	0.49	0.27	0.22
2.0	8.0	0.428	0.22	0.208	0.40	0.24	0.16
1.0	9.0	0.32	0.17	0.15	0.34	0.20	0.14

Fig. 3 curve 1   Fig.2 curve 1

Table No. 3

Wave length 575 mu

Vol. of $HgCl_2$ cc	Vol. of ligand cc	O.D. of mixture c	O.D. of ligand a	Difference (c-a)
1.0	9.0	0.65	0.52	0.13
2.0	8.0	0.602	0.45	0.152
3.0	7.0	0.56	0.38	0.180
4.0	6.0	0.53	0.32	0.21
5.0	5.0	0.51	0.26	0.25
6.0	4.0	0.48	0.25	0.234
7.0	3.0	0.44	0.23	0.21
8.0	2.0	0.38	0.20	0.18
9.0	1.0	0.29	0.16	0.13

Fig. 4 curve 1

Set No. 2 - concentration of reactants = 1.0x10^{-3}M

(Fig.2,3,4 curve 2)

JOB'S METHOD

WAVE LENGTH - 555 mμ

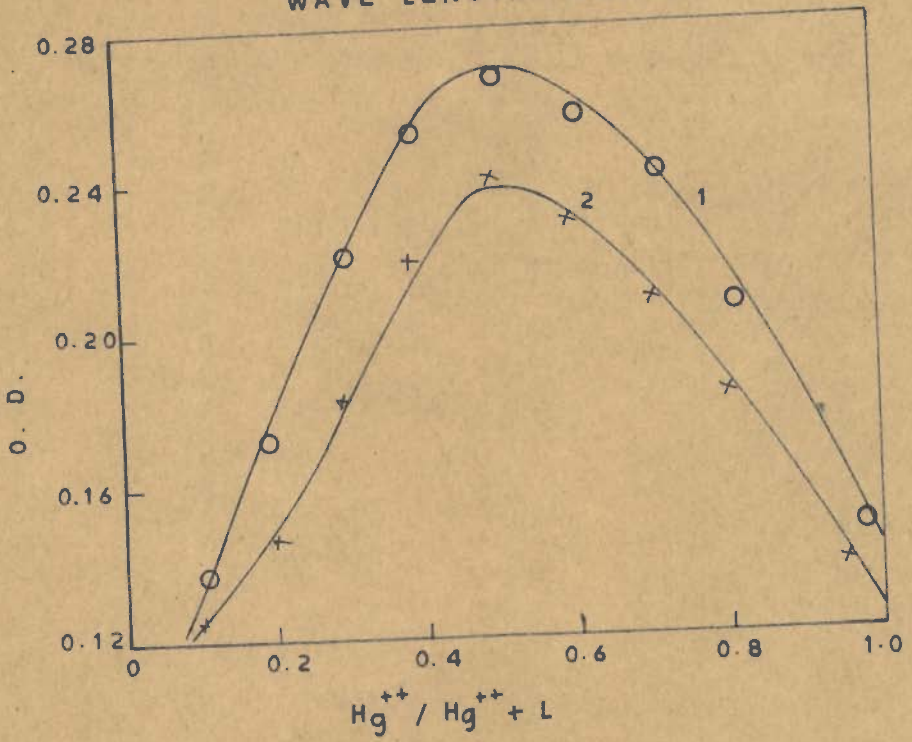


FIG. 3

WAVE LENGTH - 575 mμ

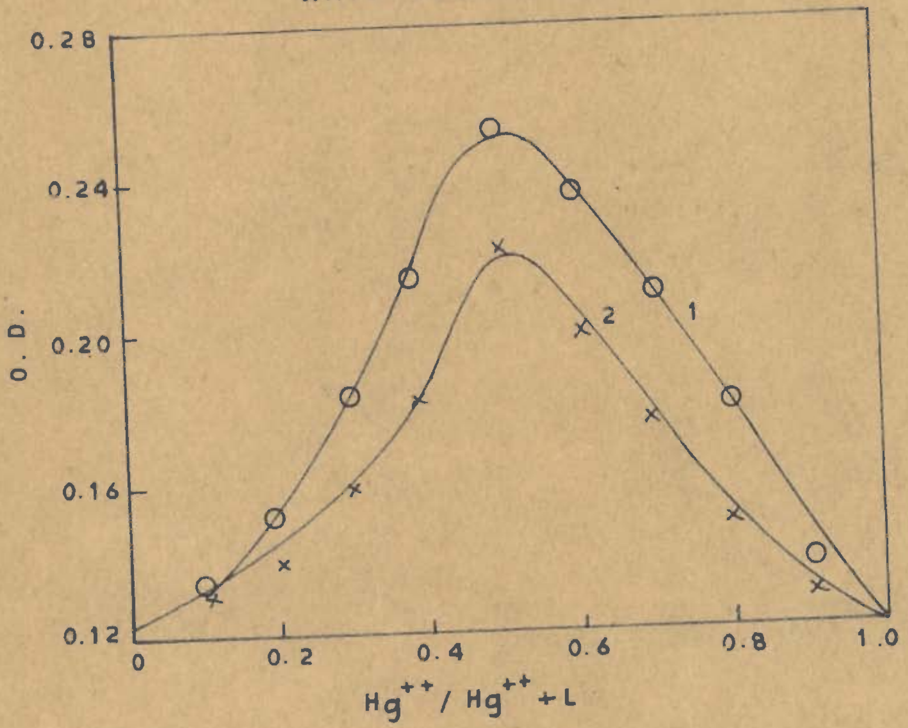


FIG. 4

Stability constant of the complex -

Attempt was made to apply slope and molar ratio method to elucidate the composition and stability of the complex. It was found that both the methods failed and hence the stability constant of the metal chelate was calculated by applying Job's equation when the reactants are mixed in nonequimolar proportion (loc. cit.). Thus starting with the metal-ion and ligand solutions of different molarities ($c_1/c_2 = \frac{1}{p}$) and mixing the reactants by the volumes $(1 - x)$ of M and x of L, it was found that, dissociation constant

$$\frac{K = C_1^{M+n-1} \text{ x } p^{n-1} \left[(pm + n)\, x - n \right]^{m+n}}{m^{n-1} \text{ x } n^{m-1} \, (p-1)^{m+n-n} \left[(n-(m+n)\, x \right]} \quad \text{............} \quad (1)$$

For the reaction

$$mM + nL \rightleftharpoons M_m L_n \; ;$$

$$\text{Instability constant Ki} = \frac{(M)^m \, (L)^n}{(M_m \, L_n)} \quad \text{...........} \quad (2)$$

The above equation (1) for 1:1 complex by putting m = n = 1, reduces to

$$\frac{K = c_1 \left[(p + 1)\, x - 1 \right]^2}{(p-1)\,(1-2x)}$$

where x - value of maxima,

Job's method (Non equimolar solution)

Table No. 4

Concentration of ligand = $0.83\times10^{-3}M$
Concentration of $HgCl_2$ = $0.66\times10^{-3}M$
Wave length - 565 mμ Total volume 15 cc

Vol. of ligand cc	Vol. of $HgCl_2$ cc	O.D. of Mixture c	O.D. of ligand a	Difference (c-a)
1.0	11.25	0.032	0	0.032
2.0	10.00	0.066	0	0.066
3.0	8.75	0.096	0	0.096
4.0	7.5	0.120	0	0.120
5.0	6.25	0.128	0	0.128
6.0	5.0	0.186	0.08	0.106
7.0	3.75	0.208	0.12	0.08
8.0	2.50	0.216	0.17	0.046
9.0	1.25	0.314	0.30	0.014

Fig. 5 Curve 1

Set No.2

Table No. 5

Concentration of ligand = $0.714\times10^{-3}M$
Concentration of $HgCl_2$ = $0.625\times10^{-3}M$
Wave length - 565 mμ Total volume - 15 cc

1.0	10.26	0.016	0	0.016
2.0	9.12	0.038	0	0.038
3.0	7.98	0.064	0	0.064
4.0	6.84	0.082	0	0.082
5.0	5.70	0.086	0	0.086
6.0	4.56	0.106	0.04	0.066
7.0	3.42	0.126	0.080	0.046
8.0	2.28	0.144	0.120	0.024
9.0	1.14	0.162	0.160	0.002

Fig. 5 Curve 2

JOB'S METHOD

NON EQUIMOLAR CONCN.

(STABILITY CONSTANT)

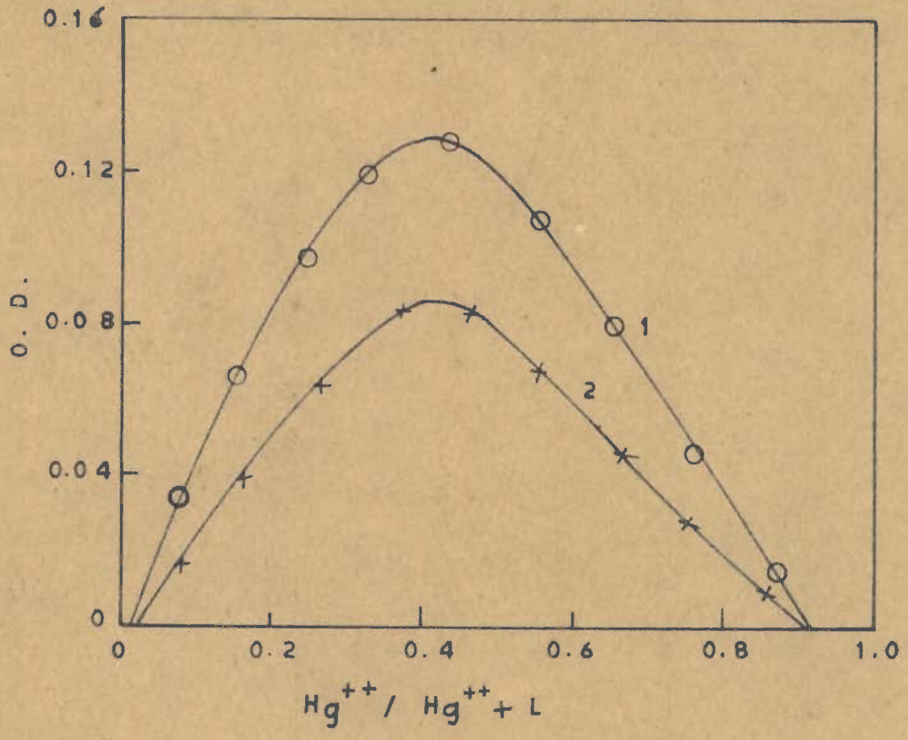


FIG. 5

By putting the value of $x = 0.43;\ c_1 = 0.625 \times 10^{-3} M$

$c_2 = 0.714 \times 10^{-3} M$ and

$p = 1.14$

From the data of Fig. 5 curve 2 (Table No.5), the value of instability constant comes to be 2.54×10^{-4}. Therefore the stability constant = (instability constant)$^{-1}$ = 3.9×10^{5}. Change in free energy of the complex formation was calculated by the equation at 25° C $\Delta F = -RT \ln K$

where ΔF, R and T, have their usual significance. By substituting $R = 2$, $T = 298°$, and $K = 3.9 \times 10^{5}$.

ΔF comes to be = - 7.6 Kcals/mole at 25°C. The considerable decrease in free energy during the complex ion formation, showed the spontaneous nature of complex formation.

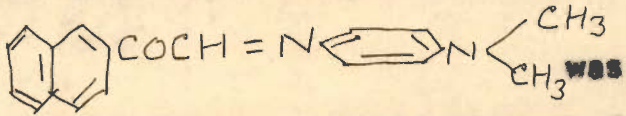
Isolation and Chemical analysis :-

Equal volumes of an acetonitrolic solutions of reactants of concentrations (0.005M) were mixed. When a bluish green coloured complex was obtained, the ppt. obtained was washed with acetonitrile, and dried under vacuum. Decomposition point 168°.

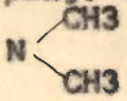
A weighed amount of the dried sample was digested with aqua-regia and its mercury content was estimated gravimetrically as mercuric thionalide. The results of the chemical analysis are as follows :-

Calculated	Found
Hg -34.97; Cl-12.37	Hg-34.34; Cl-12.30;
C -41.84; H- 3.13;	C-40.93; H-3.31;
N - 4.88 and	N-4.23 and
O - 2.89 (By difference)	O-4.89 (By difference)

Structure of the complex -



was synthesised in order to exploit it as a chelating agent for the interection of the different Lewis acids (which create a bathochromic shift from yellow to green, violet, blue etc.). This ligand is characterised by the functional groups such as -CH=N, $>C=O$ attached to naphthyl skeleton and 1:4 p-di-substituted grouping. The auxochromic group responsible for quinonoism is



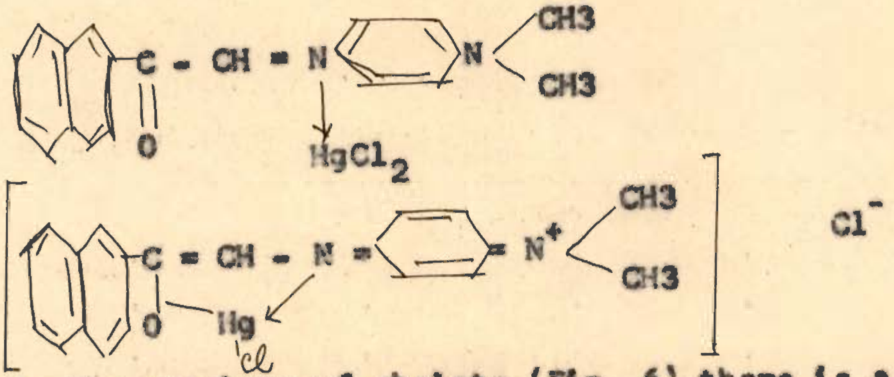
$N(CH_3)_2$.

There is a sharp peak at 1640 cm^{-1} under shoulder 1680 cm^{-1} which can only be due to naphthyl ketone. Since there is conjugation of $>C=O$ group with respect to naphthyl skeleton so lowering of the stretching frequency from its normal range is evident. Another seat of interaction can be the azomethine grouping of -CH=N, which coordinates during chelation. This grouping which is a characteristic of anil is around 1600 cm^{-1}. The auxochromic group in the ligand shows an absorption band at 2825 cm^{-1} which fits in well within the range of 2829-2810 cm^{-1}, characteristic of such grouping in the aromatic system.

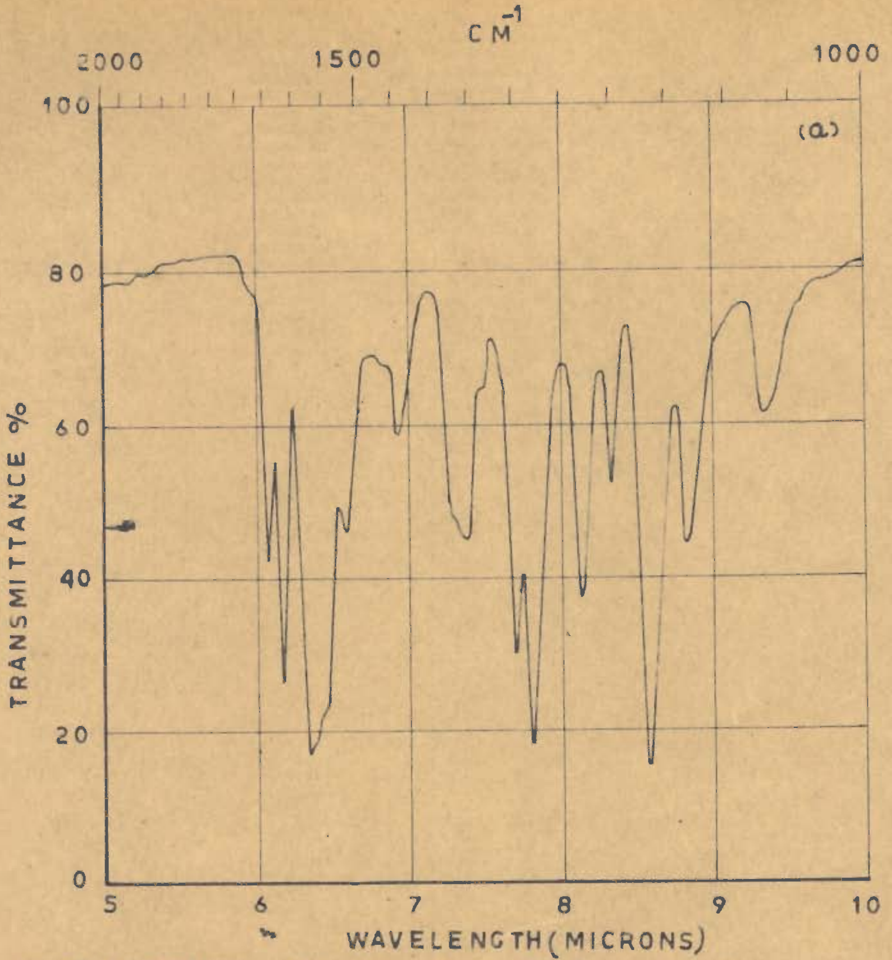
The C=C bands are quite clear in the range of its phenyl skeleton (1620-1580 cm^{-1}). 1:4 disubstituted grouping in this ligand cannot be ignored since there is a sharp peak around 830 cm^{-1}.

C-N stretching frequency of a phenyl skeleton lies from 1068 - 1090 cm^{-1}. In the ligand there is a peak at 1070 cm^{-1} due to this grouping.

From the spectrophotometric data and chemical analysis, it has been found that one mol. of $HgCl_2$ combines with one mol. of the ligand to form the corresponding chelate, on this basis the following structure may be assigned to such type of chelate.



In the spectrum of chelate (Fig. 6) there is a lowering of stretching frequency of >C=0 grouping from 1640 to 1600 cm^{-1} and that of - CH=N from 1600 cm^{-1} to 1545 cm^{-1}. This lowering can be accounted for due to the M - L binding in the complex ion. In the range of 800-870 cm^{-1}, there is a sharp doublet in the ligand while only a singlet is observed in Hg (II) complex. This maybe due to the conversion of one of the benzenoid ring changing to quinonoid unit. The rearrangement in bands as shown by the structure is itself revealed by the perturbation of the frequencies in the aromatic plane. From I.R. studies it is quite clear that - CH=N and >C=0 can be the only seats of interaction.



p-DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL

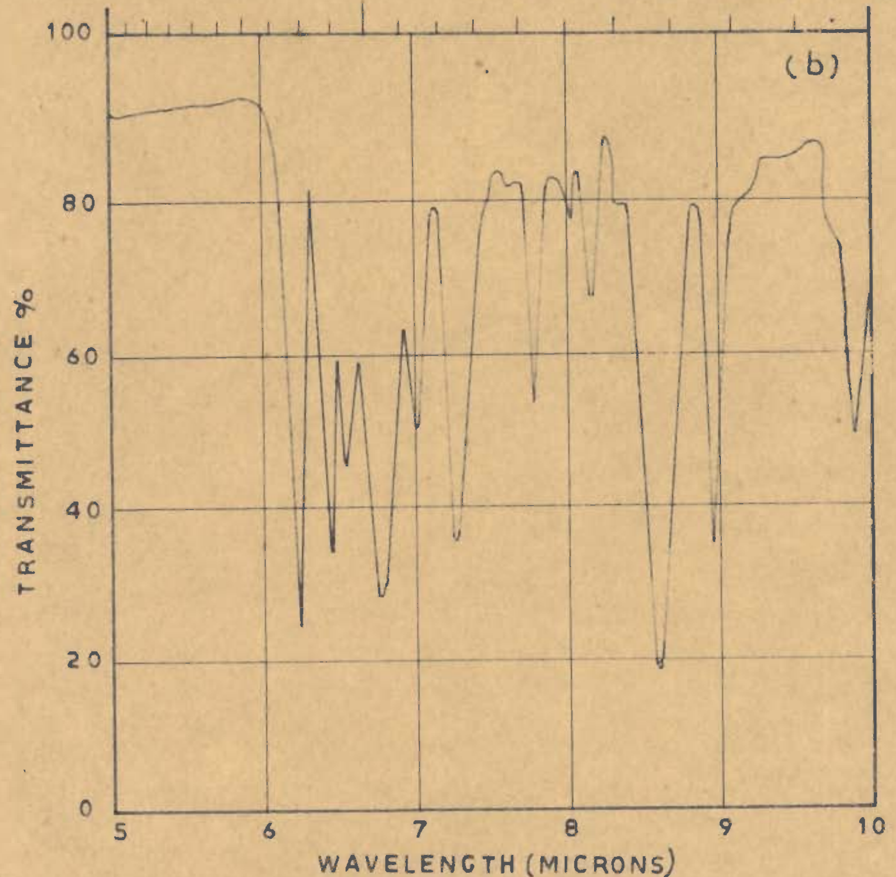


FIG. 6 _ Hg^{++} – p-DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL COMPLEX

Studies on ferric chloride - p-dimethyl amino anil of β-naphthyl glyoxal complex :-

Spectrophotometric measurements were carried out with Bausch and Lomb 'spectronic 2o'.

Before carrying out absorption experiments on the composition of the complex, Vosburgh and Coopers' method was employed to know the number of complexes formed. Equimolar solution of ferric-chloride and reagent of concentration 0.33×10^{-3}M were mixed in the ratio 1:4, 2:3, 1:1, 3:2, 2:1 and 1:2 respectively and their absorbances were noted at different wave lengths in the range of 325 mu to 625 mu. The ligand p-dimethyl amino anil of β-naphthyl glyoxal in acetonic solution shows λmax at 435 mu. In certain mixtures, where there is excess of ligand, two λmax. are shown at 435 mu and 600 mu, 600 mu was choosen as the wave length to study the composition of the bluish green complex and its other thermodynamic data.

Job's method - The composition of the complex was determined by Job's method (loc.cit.) of continuous variation. Mixtures of equimolar solution of ferric-chloride and reagent were mixed according to the following scheme :

Set No. 1 concentration of ferric chloride and reagent (0.50×10^{-3}M). The solutions were mixed in the following order :-

1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9;0 cc of ferric chloride were mixed with 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc of reagent respectively and their optical

Table No.6

Vosburgh and Cooper's method.

Concentration of ferric chloride = $0.33x10^{-3}M$
Concentration of ligand = $0.33x10^{-3}M$

Fig. 7

Wave length mu	Ratio of ligand to ferric chloride 1:4	2:3	1:1	3:2	2:1	1:2
325	0.60	0.45	0.23	0.30	0.32	-
350	0.18	0.15	0.04	0.07	0.10	-
375	0.15	0.11	0.05	0.08	0.05	-
405	0.45	0.50	0.20	0.26	0.10	-
415	0.66	0.85	0.60	0.40	0.20	-
425	0.90	1.0	0.75	0.57	0.32	-
435	1.1	1.02	0.85	0.66	0.50	-
450	1.0	0.95	0.80	0.62	0.44	1.1
475	0.80	0.70	0.52	0.35	0.24	0.92
500	0.50	0.37	0.20	0.14	0.07	0.63
525	0.20	0.10	0.05	0.05	0.05	0.34
550	0.08	0.05	0.07	0.02	0.02	0.20
575	0.24	0.18	0.18	0.07	0.02	0.32
585	0.33	0.22	0.28	0.12	0.03	0.42
600	0.42	0.32	0.35	0.22	0.13	0.47
605	0.38	0.27	0.30	0.17	0.10	0.45
615	0.20	0.11	0.20	0.10	0.02	0.40
625	0.10	0.09	0.11	0.01	0.01	0.30

densities were noted at 590, 600 and 610 mu.

9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc of reagent (0.50×10^{-3}M) were mixed with 1.0, 2.0, 3.0, 4.0 5.0, 6.0, 7.0, 8.0 and 9.0 cc of acetone respectively and their optical densities were measured at three different wave length.

Set No. II - concentration of ferric chloride and p-dimethyl amino anil of β-naphthyl glyoxal = 0.45×10^{-3}M, all other details being the same as in set I.

Set No. III - concentration of reactants 0.40×10^{-3}M, all other details being the same as in set I.

The O.D. of ferric chloride at these concentration was found to be negligible.

curves were plotted between the difference in O.D. (O.D. of the mixture - O.D. of ligand) versus $\frac{Fe^{+++}}{Fe^{+++} + R}$.

Table No. 7

Job's method - Set No.1
concentration of ferric chloride = 0.50×10^{-3}M
concentration of ligand = 0.50×10^{-3}M
wave length - 590 mu - Fig. 8 curve 1 Wave length 600 mu

Vol.of ferric chloride cc	Vol.of ligand cc	O.D. mixture c	O.D. ligand a	Difference (c-a)	O.D. mixture c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.30	0.22	0.08	0.34	0.24	0.10
2.0	8.0	0.29	0.12	0.176	0.328	0.12	0.208
2.8	7.2	0.278	0.06	0.218	0.308	0.07	0.238
3.33	6.67	0.26	0.03	0.23	0.28	0.04	0.24
4.0	6.0	0.23	0.01	0.22	0.254	0.02	0.234
5.0	5.0	0.19	0	0.19	0.20	0	0.20
6.0	4.0	0.14	0	0.14	0.16	0	0.16
7.0	3.0	0.10	0	0.10	0.116	0	0.116
8.0	2.0	0.06	0	0.06	0.07	0	0.07

Fig.8 curve 1 Fig.9 curve 1

JOB'S METHOD

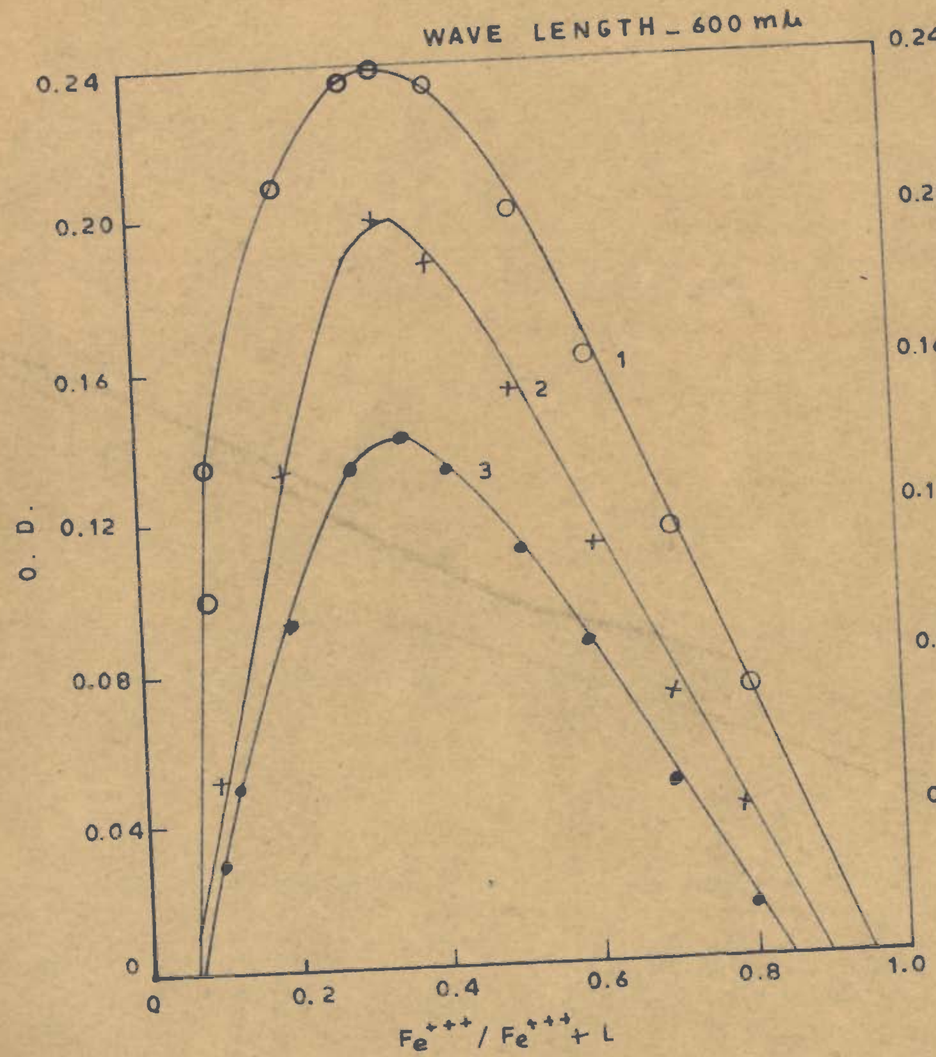


FIG. 9

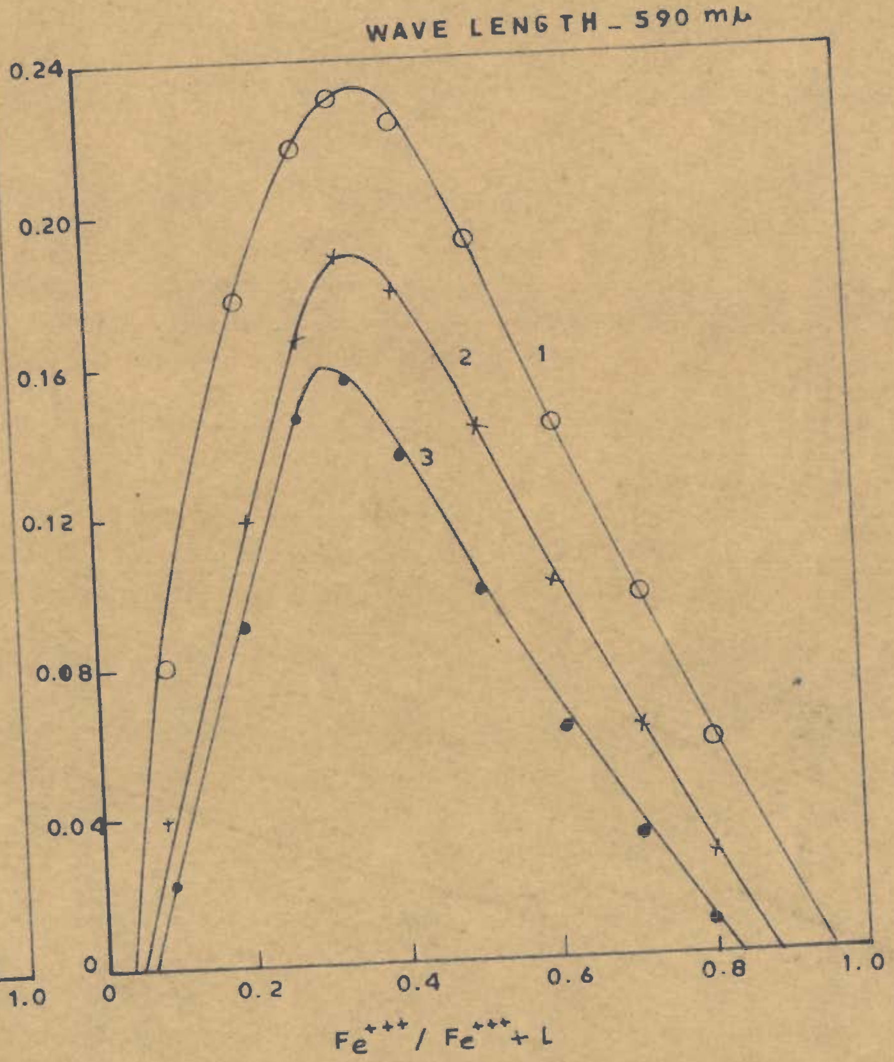


FIG. 8

Set No. 2 - Concn.of ferric chloride = 0.45×10^{-3}M
Concn. of ligand = 0.45×10^{-3}M
Fig.8,9,10 Curve 2

Table No. 8

Wave length - 610 mu

Volume of ferric chloride cc	Volume of ligand cc	O.D. mixture c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.27	0.19	0.08
2.0	8.0	0.25	0.09	0.16
2.8	7.2	0.238	0.02	0.218
3.33	6.67	0.23	0.01	0.224
4.0	6.0	0.208	0	0.208
5.0	5.0	0.18	0	0.18
6.0	4.0	0.14	0	0.14
7.0	3.0	0.094	0	0.094
8.0	2.0	0.04	0	0.04

Fig. 10 Curve 1

Set No. 3 - Concn.of ferric chloride=0.40×10^{-3}M
Concn.of ligand =0.40×10^{-3}M
Fig.8,9,10 Curve 3

Molar ratio method -

For obtaining confirmation of the results of Job's method, experiments employing molar ratio method were also performed. Solution were mixed according to the method described earlier (keeping constant amount of ferric chloride and varying the concentration of reagent). Following results were obtained:

Molar ratio method :

Set No. 1 - concentration of ligand = 1.0×10^{-3}M
concentration of ferric chloride = 0.50×10^{-3}M
total volume - 20.0 cc

Set No. 2 - concentration of ligand = 0.66×10^{-3}M
concentration of ferric chloride = 0.33×10^{-3}M
total volume - 20 cc

Table No. 9

		Set No. 1		Set No. 2	
vol. of ligand cc	vol.of $FeCl_3$ cc	O.D. at 590 mu	O.D. at 600 mu	O.D. at 590 mu	O.D. at 600 mu
1.0	5.0	0.17	0.19	0.14	0.13
2.0	5.0	0.33	0.35	0.25	0.26
3.0	5.0	0.51	0.54	0.38	0.42
4.0	5.0	0.66	0.75	0.50	0.57
5.0	5.0	0.77	0.86	0.61	0.64
6.0	5.0	0.79	0.88	0.62	0.71
8.0	5.0	0.80	0.90	0.67	0.71
10.0	5.0	0.81	0.92	0.68	0.72
12.5	5.0	0.82	0.94	0.70	0.75
		Fig.12 curve 2	Fig.11 curve 1	Fig.12 curve 2	Fig.11 curve 2

Slope ratio method -

The results arrived at by Job's and molar ratio methods were further confirmed by slope ratio method. Two series of solutions were prepared by varying the concentration of one of the reactants in presence of constant amount of the other. Two sets of experiments were carried out.

Set No. I -

concentration of ligand = 0.83×10^{-3}M

concentration of ferric chloride = 0.41×10^{-3}M

total volume = 15 cc

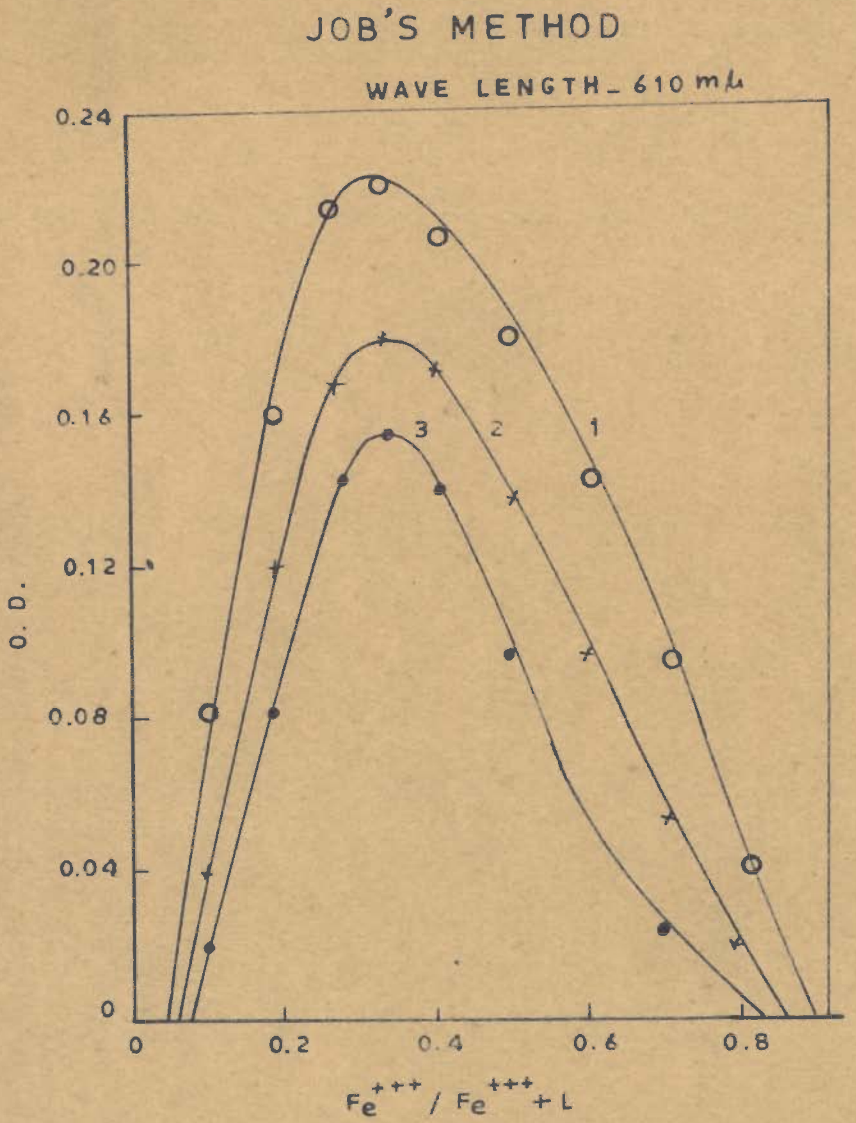

JOB'S METHOD
WAVE LENGTH _ 610 mμ
0.24
0.20
0.16
0.12
0.08
0.04
0
O. D.
0
0.2
0.4
0.6
0.8
3
2
1
Fe+++ / Fe+++ + L

FIG. 10

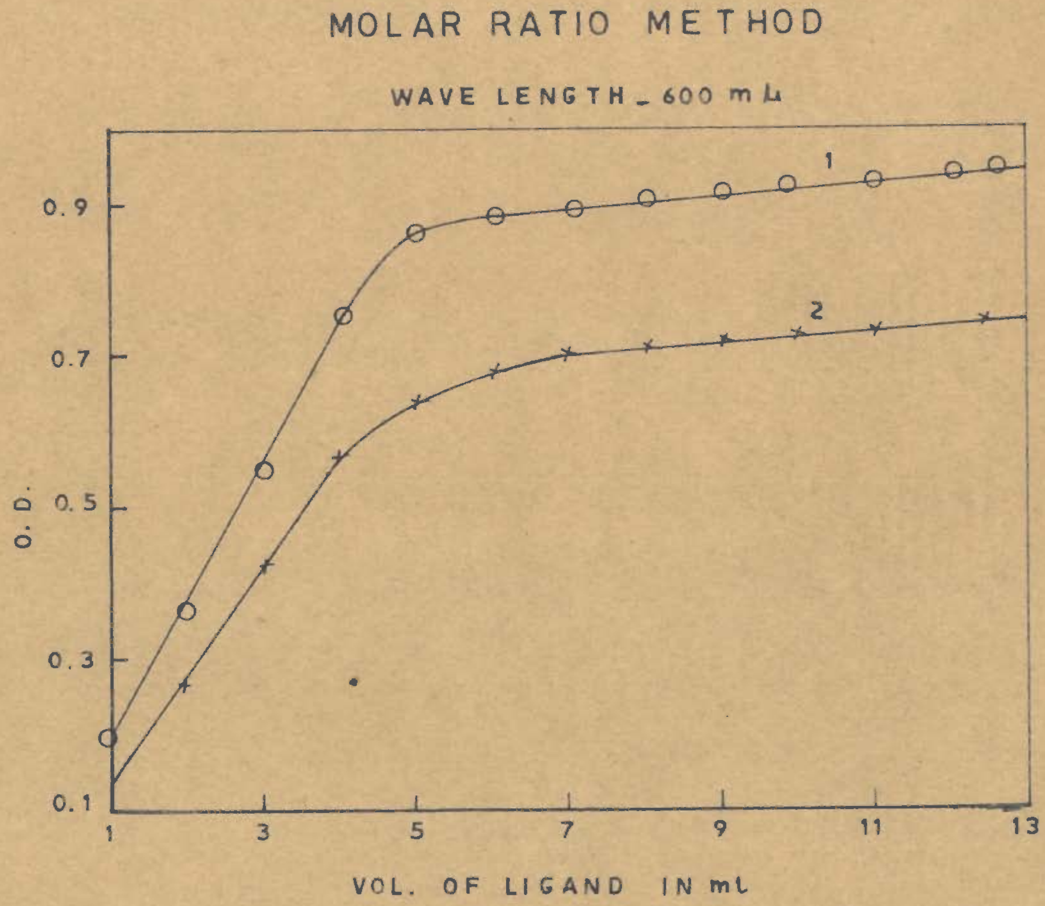

MOLAR RATIO METHOD
WAVE LENGTH _ 600 mμ
0.9
0.7
0.5
0.3
0.1
O. D.
1
3
5
7
9
11
13
1
2
VOL. OF LIGAND IN ml

FIG. 11

MOLAR RATIO METHOD

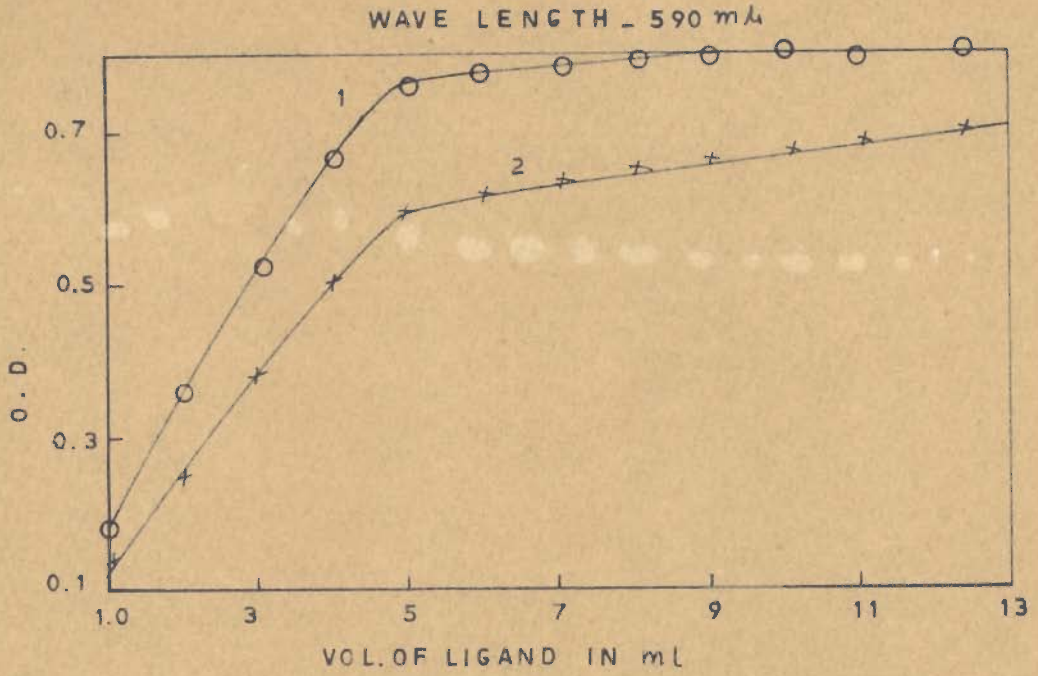


FIG. 12

SLOPE RATIO METHOD

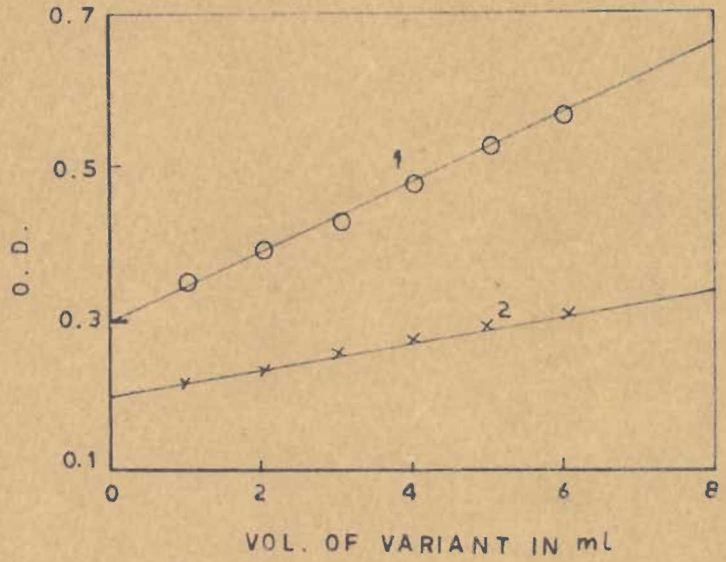


FIG. 13

Table No. 10

Set No. 1 - concentration of ligand = 0.83×10^{-3}M
concentration of ferric chloride = 0.415×10^{-3}M
total volume = 15 cc.

Volume of ferric chloride cc	Volume of ligand cc	O.D. at 600 mu
5.0	1.0	0.22
5.0	2.0	0.23
5.0	3.0	0.25
5.0	4.0	0.27
5.0	5.0	0.28
5.0	6.0	0.30

Fig. 13 curve 2

Set No. 2 - concentration of reagent = 0.415×10^{-3}M
concentration of ferric chloride = 0.83×10^{-3}M
total volume = 15.0 cc

Table No. 11

Volume of ferric chloride cc	Volume of ligand cc	O.D. at 600 mu
1.0	5.0	0.34
2.0	5.0	0.39
3.0	5.0	0.43
4.0	5.0	0.47
5.0	5.0	0.52
6.0	5.0	0.57

Fig. 13 curve 1

Stability constant -

It was determined by molar ratio method. The dissociation of the complex can be written as

$$FeR_2 \overset{1}{\rightleftharpoons} Fe + 2R \text{ -----Initial concentration}$$

$$C(1-\alpha) \quad \alpha C \quad 2\alpha C \text{ ----Final concentration}$$

where 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 K is given by the equation,

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

The value of α, may be obtained by the following relationship :

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

where E_m is the maximum absorption obtained from the horizontal portion of the curve, when all the iron is present in the form of complex and E_s is the observed absorption of the stoichiometric molar ratio of the reagent to iron in the complex.

Data from Hg.11 curve 1 (Table No. 9) was used for calculating the formation constant,

$$E_m = 0.90 \quad \alpha = 0.05 \text{ and } c = 0.125 \times 10^{-3}$$

$$E_s = 0.85$$

$$\therefore K = 81.9 \times 10^{-14}$$

$$\text{Stability constant} = \frac{1}{(\text{Instability Constant})}$$

$$= 1.2\text{x}10^{12}$$

Change in free energy was calculated by the relationship,

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

where R, T, and ΔF have their usual significance. By putting the value of $K = 1.2\text{x}10^{12}$

$$R = 2 \text{ and } T = 298^{\circ}A;$$

the value of ΔF comes out to be

$$= - 16.61 \text{ K cals/mole at } 25^{\circ}C$$

The reaction is followed with a considerable decrease of free energy at room temperature, indicating the spontaneous nature of complex formation.

Isolation and chemical analysis of the ferric-p-dimethyl amino anil of β-naphthyl glyoxal complex :-

80 cc of 0.005M acetonic solution of ferric chloride was taken in a beaker and 80 cc of 0.005M reagent solution was added to it. The resulting mixture was concentrated in a vacuum dessicator over calcium chloride, when the bluish green crystals of Fe^{+++} - p-dimethyl amino anil of β-naphthyl glyoxal complex were isolated. These crystals were washed several times with acetonitrile in order to wash out the adhering impurities of ferric chloride and the reagent, and then dried in a vacuum dessicator.

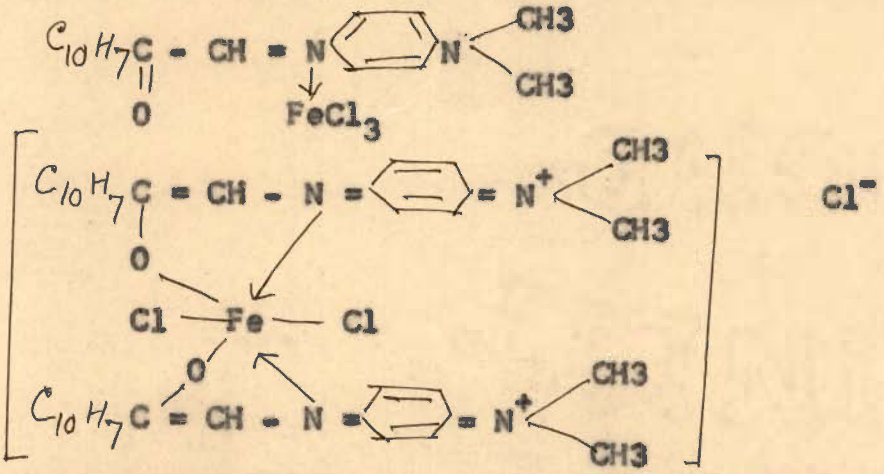
Decomposition point - 200°C.

Iron was estimated by the usual method. The results of chemical analysis are as follows :-

Calculated	Found
Fe - 7.28; Cl-13.90;	Fe - 7.08; Cl-13.12;
C - 62.63; H- 4.69;	C - 62.36; H- 4.61;
N - 7.30 and	N - 6.98 and
O - 4.20 (by difference)	O - 5.85 (by difference)

Structure of the complex :-

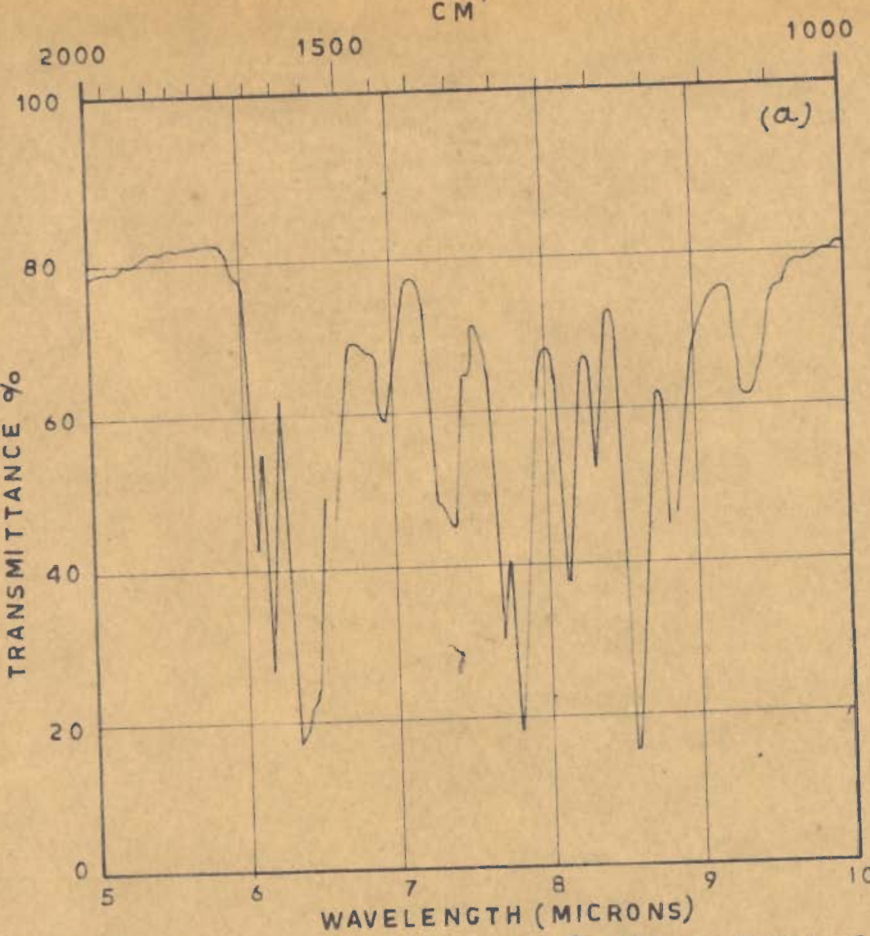
The various methods of adsorption measurements as discussed above shows that the stoichiometric ratio of ferric chloride and the ligand is as 1:2. Assuming a coordination number of six for Fe (III), the following structure can be assigned on the basis of the stoichiometric ratio.



From the structure it is quite clear that the species is not a neutral complex, but an ionic one. Qualitative evidence in support of Cl negative being outside the coordinating sphere is forthcoming from the fact that a white precipitate formed when the ethanolic solution of $AgNO_3$ is added to the ethanolic solution of the complex.

I.R. Studies -

Like Hg(II) complex, in this complex too the sites of interaction are keto and azomethine groupings. It appears that a resonance is experienced by the ligand under the influence of ferric chloride which makes the $\rangle C = O$ more electron dense to facilitate the binding. In this type of chelate there is lowering of frequencies from those of $\rangle C = O$ and - CH=N groupings (1670-1700 cm^{-1}, 1580-1600 cm^{-1}) Fig. 14. The conjugation caused in the resonating structure is itself revealed by the spectrum of the chelate due to perturbation in the phenyl group skeleton.



p- DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL

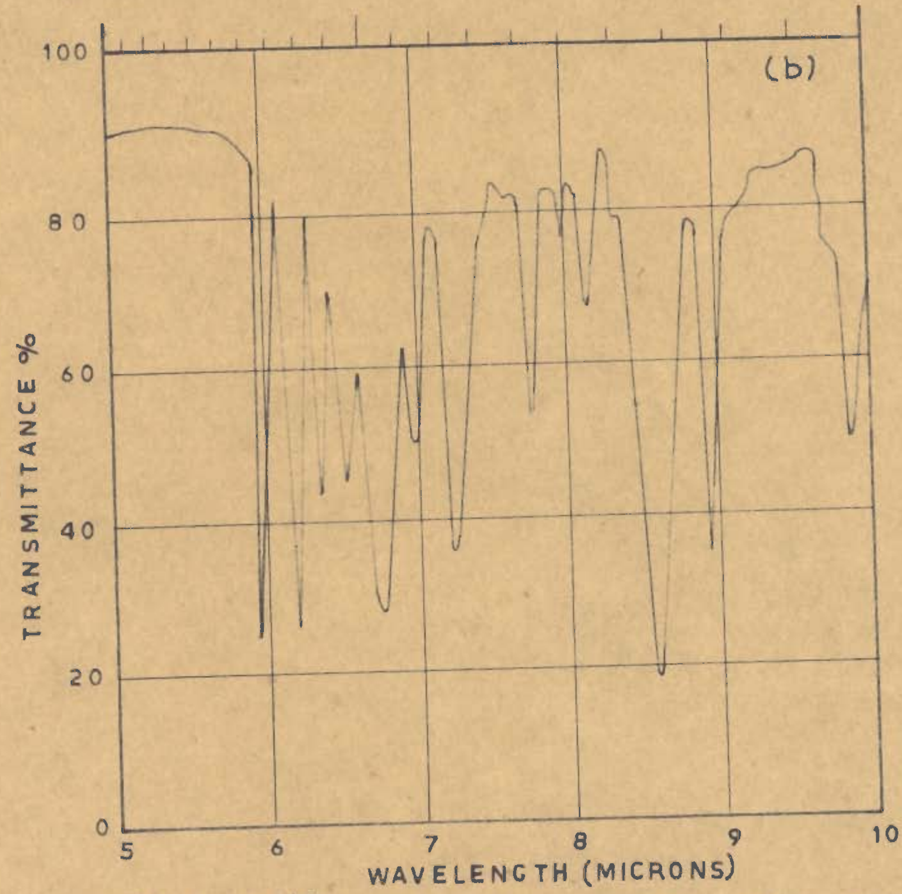


FIG. 14 _ Fe^{+++} - p- DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL COMPLEX

Zinc chloride - p - dimethyl amino anil of β-naphthyl - glyoxal complex :-

In order to determine the number of complexes formed by the interaction of zinc chloride and p-dimethyl amino anil of β-naphthyl glyoxal the method of Vosburgh and Cooper was followed. Equimolar solution (0.714×10^{-3}M) of zinc chloride and the reagent were mixed in the ratio of 4:3, 2:1, 3:1 and 1:1 respectively and the absorbance were measured in the wave length range 325mμ to 625mμ O.D measurements reveal two maxima at 435mμ and 580mμ respectively. The former peak was realised only in mixtures containing excess of the ligand (Fig. 15). The wave length 580mμ was, therefore, chosen for further studies.

Table No. 12

Concentration of zinc chloride = 0.714×10^{-3}M
Concentration of ligand = 0.714×10^{-3}M
Fig. 15

Wave length mμ	Ratio of ligand to zinc chloride			
	4:3	2:1	3:1	1:1
325	0.50	0.40	0.28	0.18
350	0.22	0.13	0.10	0.07
375	0.22	0.12	0.08	0.05
400	0.50	0.34	0.26	0.20
415	0.74	0.55	0.45	0.37
425	0.90	0.75	0.60	0.47
435	1.0	0.85	0.70	0.55
450	0.95	0.80	0.66	0.54
475	0.66	0.60	0.45	0.30
500	0.25	0.22	0.18	0.10
525	0.20	0.13	0.10	0.07
550	0.43	0.34	0.30	0.20
570	0.60	0.50	0.50	0.40
580	0.62	0.57	0.53	0.44
600	0.45	0.40	0.37	0.30
625	0.10	0.18	0.06	0. 10

Job's method was followed for determining the composition of the complex. Equimolar solutions of zinc chloride and p-dimethyl amino anil of β-naphthyl glyoxal of three different concentrations, viz., 1.11×10^{-3}M; 1.0×10^{-3}M and 0.83×10^{-3}M, were mixed according to the method of continuous variation and O.D. was measured at 580 mμ. The absorption of solution containing the ligand was also measured. The difference in O.D. was plotted against the ratio $\frac{Zn^{++}}{Zn^{++}+R}$

Table No. 13

Job's method Set No.1

Concentration of zinc chloride - 1.11×10^{-3}M
Concentration of ligand - 1.11×10^{-3}M
Wave length - 570 mμ

Vol. of zinc chloride cc	Volume of ligand cc	O.D. Mixture c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.58	0.48	0.10
2.0	8.0	0.56	0.35	0.21
3.0	7.0	0.55	0.26	0.29
4.0	6.0	0.54	0.22	0.32
5.0	5.0	0.52	0.17	0.35
6.0	4.0	0.49	0.16	0.33
7.0	3.0	0.43	0.15	0.28
8.0	2.0	0.38	0.14	0.24
9.0	1.0	0.25	0.13	0.12

Fig. 17 Curve 1

Set No. 2

Concentration of $ZnCl_2$ = $1.0\times10^{-3}M$

Concentration of ligand = $1.0\times10^{-3}M$

Total volume = 10.0 cc

Fig. 16,17, 18 Curve 2.

Set No. 3

Concentration of $ZnCl_2$ = $0.83\times10^{-3}M$

Concentration of ligand = $0.83\times10^{-3}M$

Total volume = 10.0 cc

Fig.16,17,18 curve 3

Wave length - 580 $m\mu$

Vol. of zinc chloride cc	Volume of ligand cc	O.D. Mixture c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.64	0.52	0.12
2.0	8.0	0.62	0.39	0.23
3.0	7.0	0.59	0.30	0.29
4.0	6.0	0.56	0.22	0.34
5.0	5.0	0.54	0.18	0.36
6.0	4.0	0.52	0.17	0.35
7.0	3.0	0.47	0.17	0.30
8.0	2.0	0.40	0.16	0.24
9.0	1.0	0.36	0.16	0.20

Fig. 16 curve 1

Table No. 14

Wave length - 590 $m\mu$

1.0	9.0	0.59	0.50	0.09
2.0	8.0	0.57	0.37	0.20
3.0	7.0	0.54	0.27	0.27
4.0	6.0	0.53	0.20	0.31
5.0	5.0	0.51	0.18	0.33
6.0	4.0	0.465	0.16	0.305
7.0	3.0	0.42	0.14	0.28
8.0	2.0	0.33	0.13	0.20
9.0	1.0	0.21	0.13	0.08

Fig. 18 curve 11

Slope ratio method -

In order to get conclusive information regarding the composition of the complex, the method of slope ratio

JOB'S METHOD

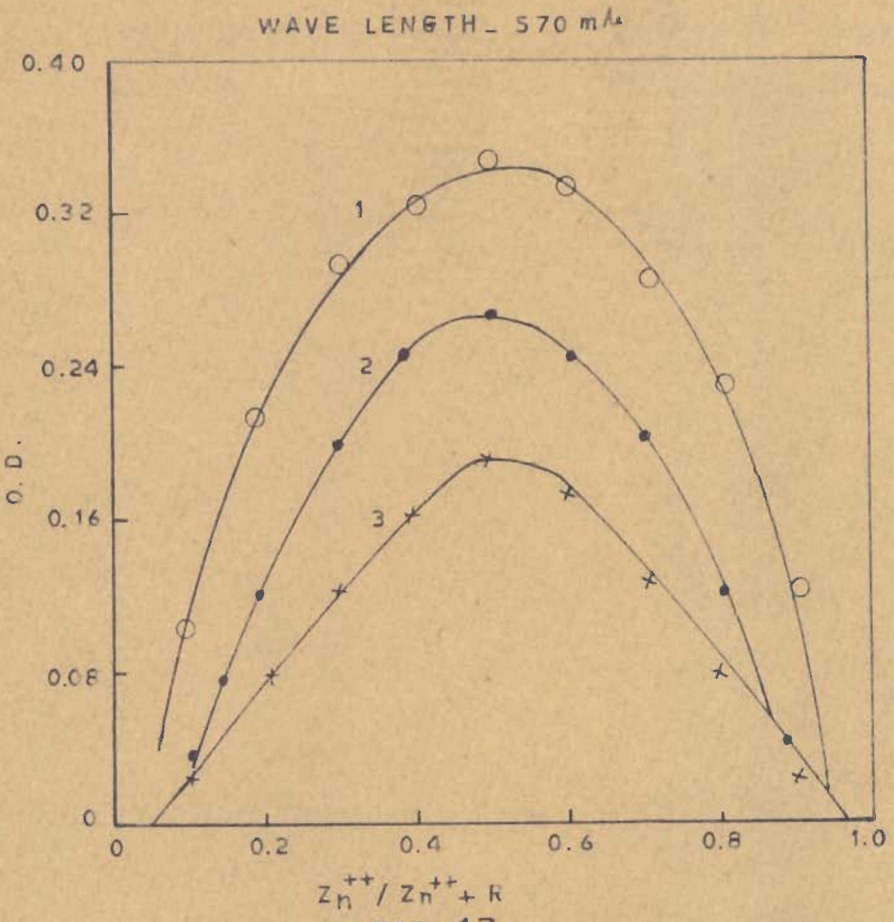


FIG. 17

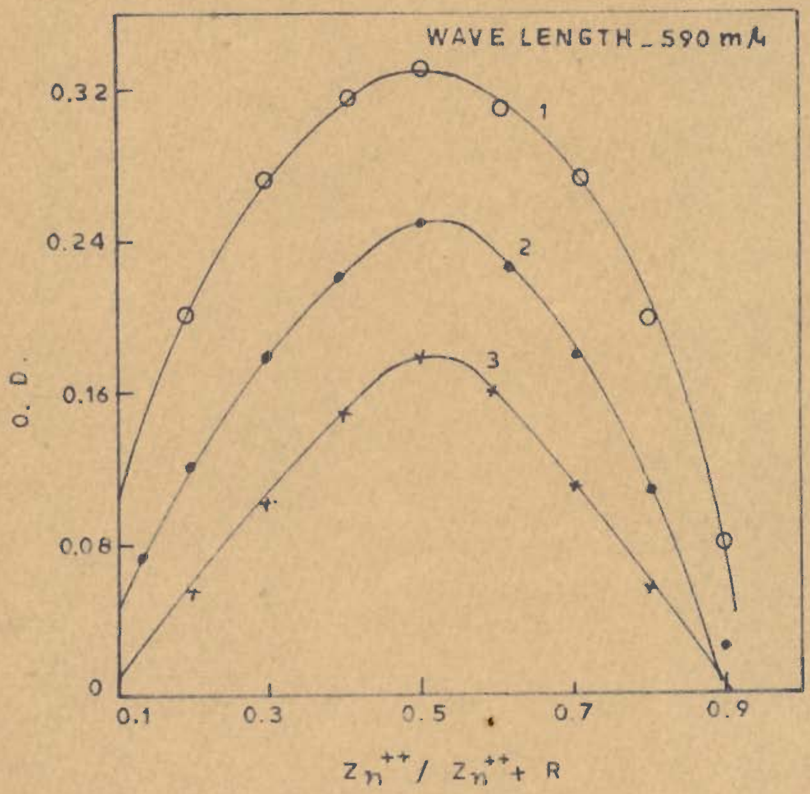


FIG. 18

was also attempted. Two sets were prepared. In the first set the concentration of zinc chloride was kept constant and that of p-dimethyl amino anil of β-naphthyl glyoxal was varied while in the other set the mixing was done in the reverse order.

Table No. 15

Slope ratio method -Set No.1

Concentration of ligand = 1×10^{-3}M
Concentration of zinc chloride = 5×10^{-3}M
Total volume = 5.0 cc

Fig. 21 curve (2) (1) (3)

Volume of zinc chloride cc	Volume of ligand cc	O.D. at 570 mu	O.D. at 580 mu	O.D. at 590 mu
2.5	0.10	0.16	0.30	0.12
2.5	0.20	0.20	0.34	0.13
2.5	0.30	0.24	0.36	0.14
2.5	0.40	0.30	0.44	0.20
2.5	0.60	0.40	0.52	0.30
2.5	0.80	0.50	0.60	0.38
2.5	1.0	0.58	0.72	0.44
2.5	1.2	0.70	0.80	0.56
2.5	1.4	0.80	0.90	0.66
2.5	1.6	0.88	1.0	0.76

Table No. 16

Set No. 2

Concentration of ligand = 5×10^{-3}M
Concentration of zinc chloride = 1×10^{-3}M

Total volume = 5.0 cc

Fig. 21 curve (6) (5) (4)

Volume of zinc chloride cc	Volume of ligand cc	O.D. at 570 mu	O.D. at 580 mu	O.D. at 590 mu
0.10	2.5	0.05	0.07	0.06
0.20	2.5	0.12	0.10	0.10
0.30	2.5	0.16	0.16	0.14
0.40	2.5	0.20	0.26	0.20
0.60	2.5	0.30	0.30	0.28
0.80	2.5	0.34	0.40	0.40
1.0	2.5	0.50	0.54	0.44
1.2	2.5	0.54	0.64	0.50
1.4	2.5	0.62	0.74	0.62
1.6	2.5	0.64	0.76	0.63

Molar ratio method -

Molar ratio method was employed to confirm the results obtained by Job's and slopes ratio methods. Two sets containing different concentrations of the reactants were used. In first set the concentration of the zinc chloride was kept constant and that of the reagent varied. In the second set mixing was done in the reverse order. The curves were plotted between O.D. and the volume of variant in ml.

Set No. 1 - Concentration of reagent = $2.0\times10^{-3}M$

Concentration of zinc chloride = $2.0\times10^{-3}M$

Total volume = 15.0 cc.

Table No. 17

Volume of ligand cc	Volume of zinc chloride cc	O.D. at 570 mu	O.D. at 580 mu
1.0	5.0	0.10	0.15
2.0	5.0	0.23	0.26
3.0	5.0	0.32	0.35
4.0	5.0	0.38	0.41
5.0	5.0	0.42	0.43
6.0	5.0	0.44	0.46
7.0	5.0	0.46	0.47
8.0	5.0	0.47	0.49
9.0	5.0	0.48	0.50
10.0	5.0	0.50	0.51

Fig. 19 Curve 1 Fig. 20 curve 1

Set No. 2 - Concentration of ligand = $1.25\times10^{-3}M$

Concentration of zinc chloride = $1.25\times10^{-3}M$

Total volume = 15.0 cc

Table No. 18

Volume of ligand cc	Volume of $ZnCl_2$ cc	O.D. at 570 mu	O.D. at 580 mu
1.0	5.0	0.04	0.05
2.0	5.0	0.12	0.15
3.0	5.0	0.21	0.24
4.0	5.0	0.27	0.30
5.0	5.0	0.32	0.35
6.0	5.0	0.36	0.38
7.0	5.0	0.40	0.40
8.0	5.0	0.42	0.41
9.0	5.0	0.43	0.42
10.0	5.0	0.44	0.42

Fig. 19 curve 2

Fig. 20 curve 2

MOLAR RATIO METHOD

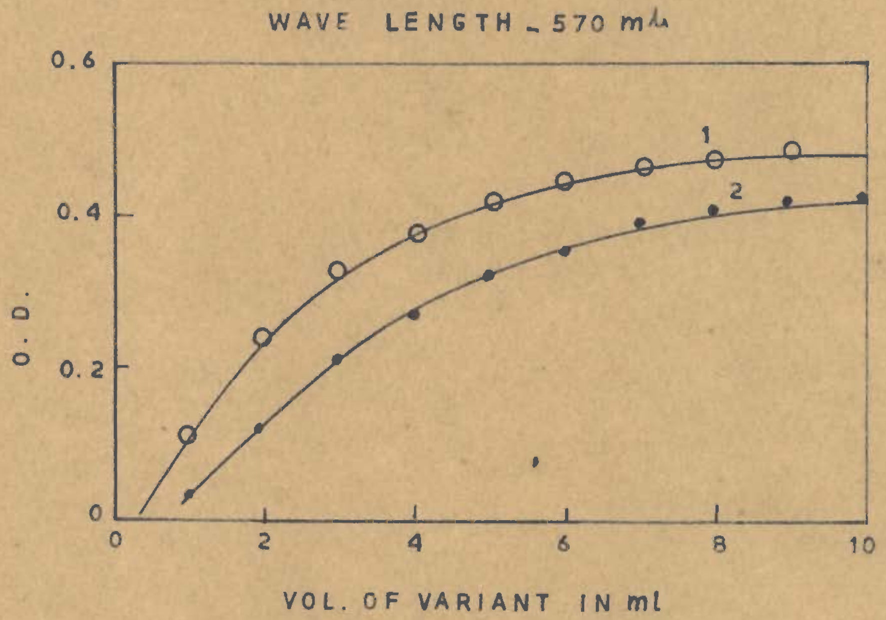


FIG. 19

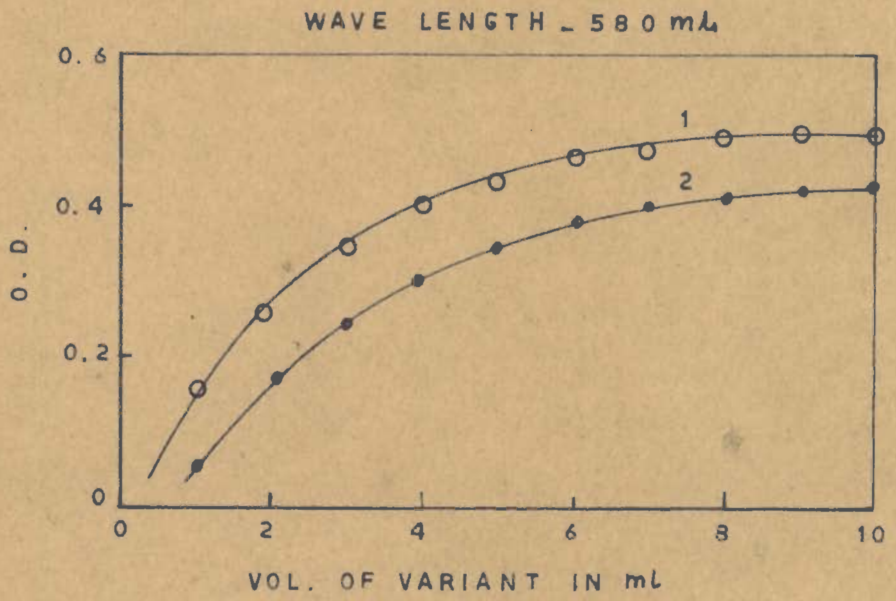


FIG. 20

SLOPE RATIO METHO

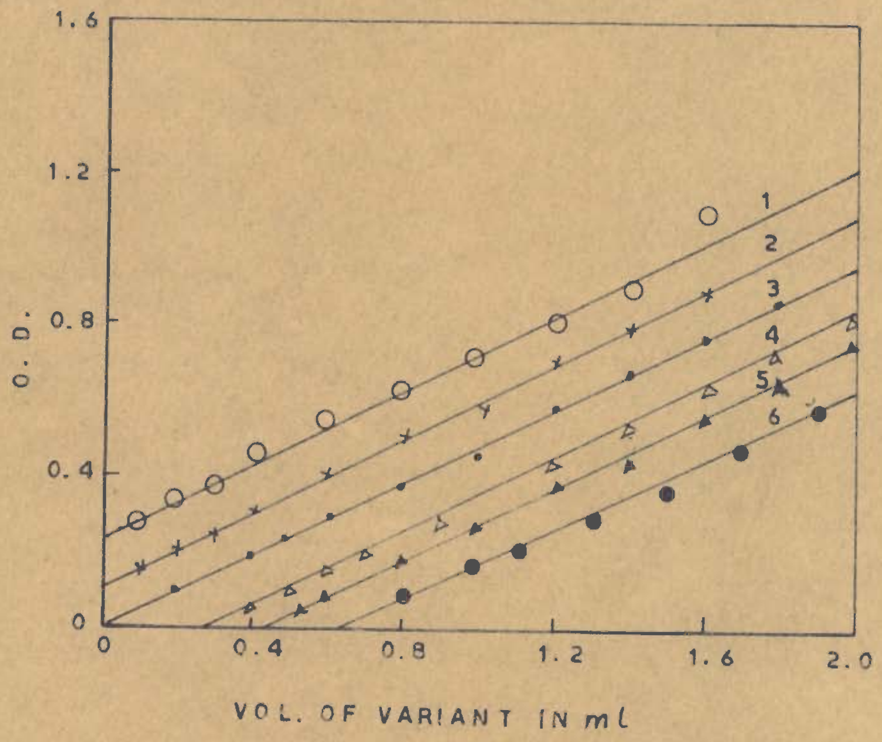


FIG. 21

Formation constant -

The formation constant of Zn -p-dimethyl amino anil of β-naphthyl glyoxal complex was determined by the molar ratio method. For 1:1 complex, the equation used being

$$\alpha = \frac{E_m - E_s}{E_m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

and $$K = \frac{(1 - \alpha)}{C \alpha 2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

By putting the value of $E_m = 0.50$, $E_s = 0.43$ $\alpha = 0.14$ and $C = 0.66 \times 10^{-3}$M, the value of $K_s = 6.6 \times 10^4$ (set 1, Fig.19 curve 1, Table No.17). Change in free energy was calculated by the expression;

$\triangle F = - RT \ln K$, inserting the value of $R = 2$, $T = 298^\circ$A and $K = 6.6 \times 10^4$,

$\triangle F = - 6.61$ Kcals/moles at 25°C, the reaction is accompanied with a considerable decrease of free energy at room temperature indicating the spontaneous nature of the reaction.

Isolation and chemical analysis of zinc-p-dimethyl amino anil of β-naphthyl - glyoxal complex :-

Equal volume of acetonitrolic solutions of reactants of concentration 0.0025M were mixed. On mixing, blue black, precipitate of Zn-p-dimethyl amino anil of β -naphthyl glyoxal complex was obtained. This was crystallised by 40 parts acetonitrile.

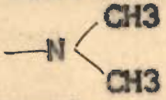
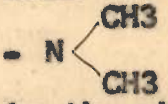
Decomposition point = 208°C.

The zinc content was estimated by the method given earlier.

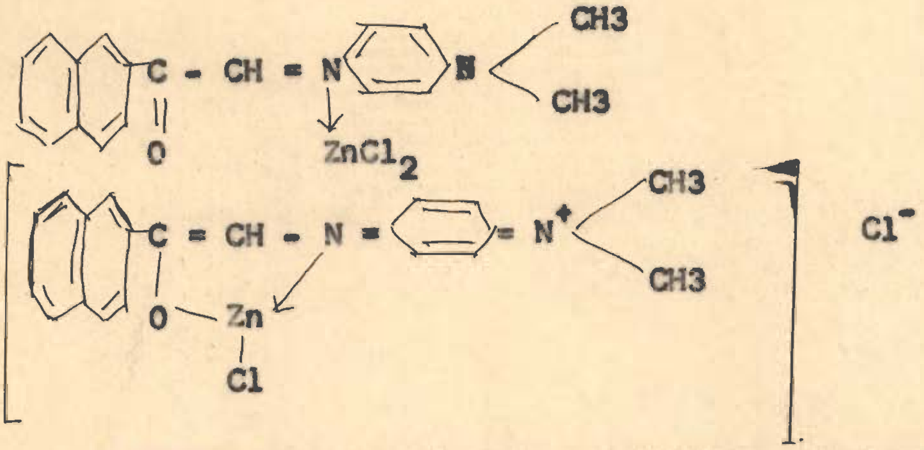
The results of chemical analysis were as follows :-

Calculated	Found
Zn-14.92; Cl-16.20;	Zn-14.53; Cl-16.01;
C-54.77; H-4.10;	C-54.06; H-3.98;
N-6.39 and	N-5.89 and
0-3.62 (By difference)	0-5.53 (By difference)

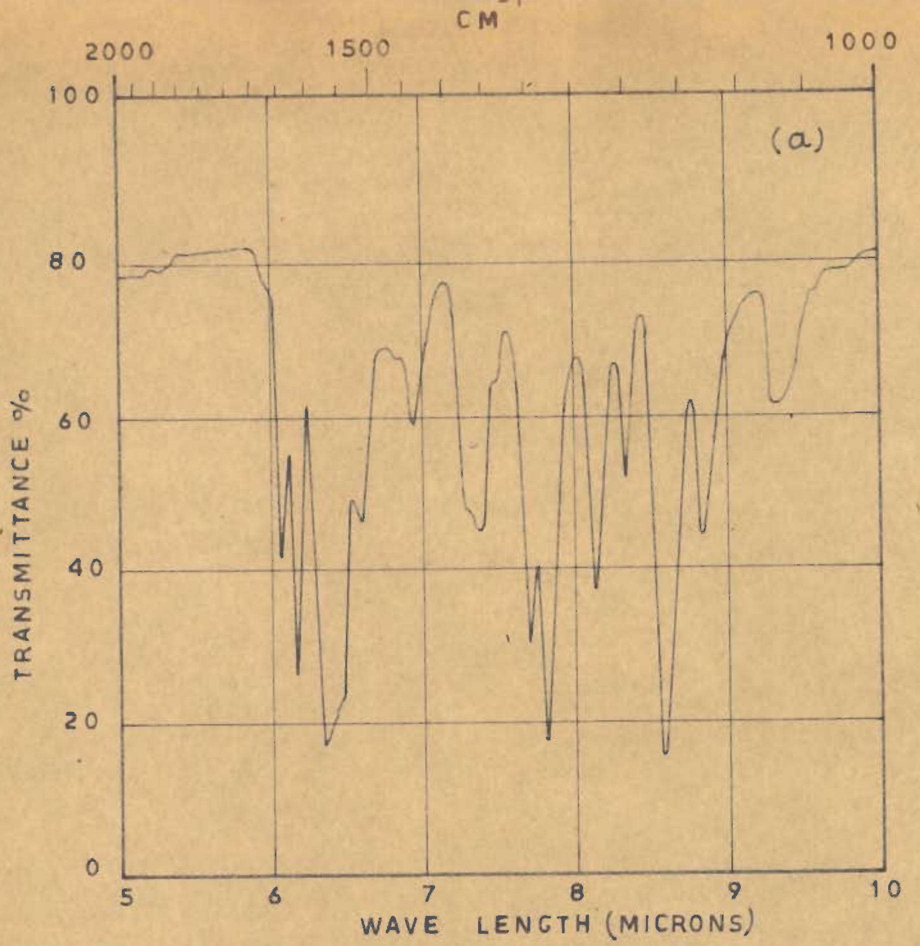
Structureof the complex -

In the ligand p-dimethyl amino anil of -naphthyl glyoxal, there are two N atoms containing a free pair of electrons each for coordination  $—N\Big\langle\begin{matrix}CH3\\CH3\end{matrix}$, grouping becomes more electron dense due to + inductive effect of two methyl grouping attached to para-anilino group. When zinc chloride as a Lewis acid interacts with p-p-dimethyl amino anil of β-naphthyl glyoxal, a Zwitter ion is created at  $- N\Big\langle\begin{matrix}CH3\\CH3\end{matrix}$ auxochromic grouping. This causes quinonoism in the whole molecule (responsible for bathochromic effect). Consequently one of the seats of interaction e.g. $\rangle C = 0$ becomes more negative and hence labile for interaction.

I.R.of Zn (II) - p - dimethyl amino anil of β-napthyl glyoxal complex shows lowering of stretching frequencies of keto group from 1640 to 1600 cm^{-1} and - CH=N from 1600 to 1580 cm^{-1} (fig.22). This shows that there are two sites responsible for interaction. The following structure can, therefore, be assigned to the chelate



A white ppt. was formed on addition of ethanolic solution of $AgNO_3$ to the isolated complex in ethanolic media. This provides evidence for the presence of Cl^- ions outside the coordination sphere.



p-DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL

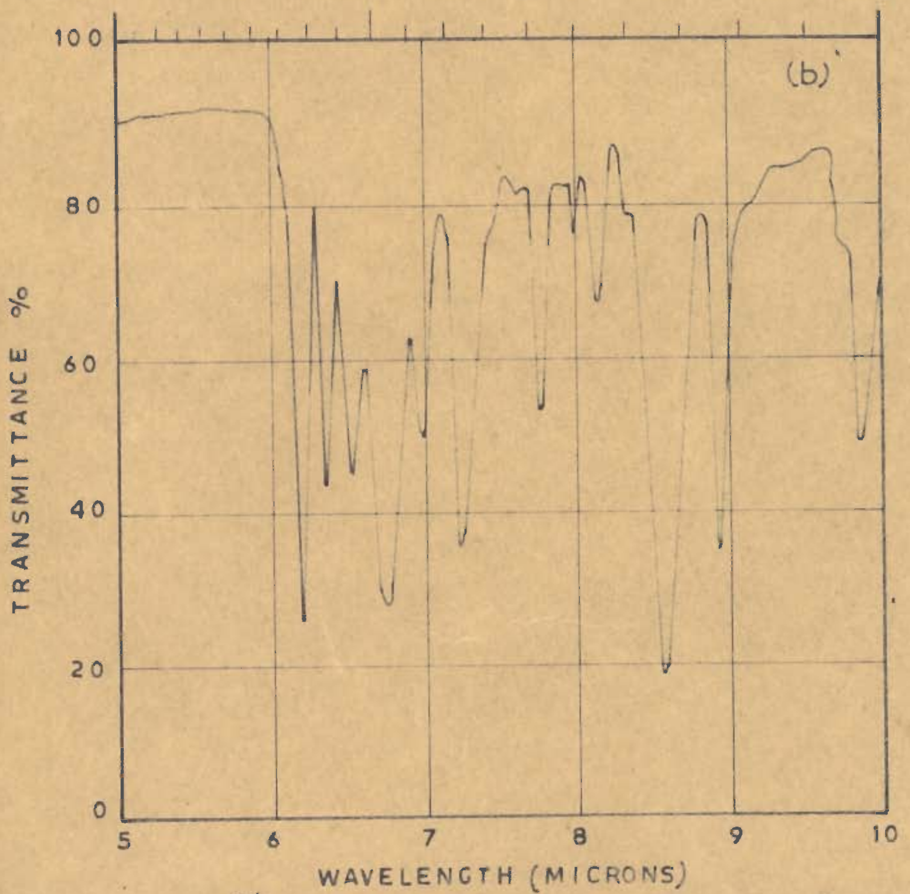


FIG.22 _ Zn^{++}-p-DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL COMPLEX

Composition of Cd(II)-p-dimethyl amino anil of β-naphthyl glyoxal complex in Acetonic medium :-

Vosburgh and Cooper's method was employed for determining the number of complexes formed in the interaction and also to select a suitable wave-length to determine the stoichiometry of the components. Mixtures of solutions having different proportion (1:1, 2:3, 2:1, 1:2 and 3:2) of equinolar concentration of (0.66×10^{-3}M) cadmium iodide and the reagent were prepared. Optical density measurement were made by Bausch and Lomb 'spectronic 20' after warming up for a sufficient period. Absorbance were measured from wave-length 325 mu to 625 mu.

The absorbance curves show two maxima at 435 mu and 550 mu (Fig.23.). The maxima of the ligand as a blank appears at 435 mu. Therefore the max. at 435 mu is only due to the excess of the ligand present in different ratios of the mixtures. Hence the wave length 550 mu was considered as a suitable one for absorption measurements.

Table No. 19

Vosburgh and Cooper method

concentration of CdI_2 = $0.66\times10^{-3}M$
concentration of ligand = $0.66\times10^{-3}M$

Fig. 23

wave length mu	Ratio of cadmium iodide to ligand 1:1	2:3	2:1	1:2	3:2
325	0.80	0.35	0.28	0.20	0.19
350	0.75	0.19	0.15	0.10	0.10
375	0.70	0.18	0.15	0.11	0.06
405	0.65	0.57	0.32	0.20	0.14
415	0.60	0.66	0.50	0.35	0.22
425	0.60	0.725	0.65	0.45	0.28
435	0.60	0.75	0.68	0.48	0.30
450	0.57	0.675	0.62	0.375	0.225
475	0.475	0.42	0.25	0.18	0.11
500	0.27	0.26	0.13	0.12	0.08
525	0.175	0.175	0.12	0.08	0.08
540	0.25	0.225	0.15	0.20	0.11
550	0.31	0.30	0.26	0.225	0.16
560	0.26	0.28	0.24	0.20	0.10
575	0.25	0.25	0.17	0.125	0.14
600	0.14	0.15	0.08	0.08	0.08
625	0.03	0.07	0.05	0.07	-

Job's method of continued variation was followed for determining the composition of the complex. Equimolar solutions of cadmium Iodide and p-dimethyl amino anil of β-naphthyl glyoxal were mixed according to the method of continuous variation and optical densities measurements were carried out at three different wave lengths as well as at three concentrations of the reactants (0.90×10^{-3}M , 0.83×10^{-3}M and 0.769×10^{-3}M). The difference of optical densities of the mixtures and ligand was plotted against

$$\frac{cd^{++}}{cd^{++} + \text{Reagent}}$$

Job's method - Set No. 1

concentration of cadmium iodide = 0.90×10^{-3}M
concentration of ligand = 0.90×10^{-3}M
wave length - 540 mu

Table No. 20

Wave length -540 mu					Wave length - 550 mu		
Vol. of CdI_2 cc	Vol. of ligand cc	O.D. Mixture c	O.D. ligand a	Difference (c-a)	O.D. Mixt. c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.465	0.43	0.035	0.52	0.45	0.070
2.0	8.0	0.39	0.33	0.06	0.50	0.35	0.150
3.0	7.0	0.35	0.25	0.10	0.485	0.27	0.215
4.0	6.0	0.38	0.18	0.20	0.450	0.20	0.250
5.0	5.0	0.36	0.11	0.25	0.420	0.15	0.275
6.0	4.0	0.30	0.10	0.20	0.40	0.14	0.260
7.0	3.0	0.22	0.09	0.13	0.335	0.12	0.215
8.0	2.0	0.135	0.07	0.065	0.265	0.11	0.155
9.0	1.0	0.075	0.05	0.025	0.175	0.10	0.075

Fig. 24 curve 1 Fig. 25 curve 1

Table No. 21

Wave length - 560 mu

Vol. of CdI_2 cc	Vol. of ligand cc	O.D. mixture c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.475	0.40	0.075
2.0	8.0	0.44	0 .30	0.14
3.0	7.0	0.41	0.23	0.180
4.0	6.0	0.378	0.16	0.218
5.0	5.0	0.330	0.10	0.230
6.0	4.0	0.30	0.08	0.220
7.0	3.0	0.250	0.07	0.180
8.0	2.0	0.190	0.06	0.130
9.0	1.0	0.130	0.04	0.09

Fig. 26 curve 1

Set No. 2 - concentration of cadmium iodide = 0.83×10^{-3}M

concentration of ligand = 0.83×10^{-3}M

(Fig. 24,25,26 curve 2)

Set No. 3 - concentration of CdI_2 = 0.769×10^{-3}M

concentration of ligand= 0.769×10^{-3}M

(Fig. 24,25,26 curve 3)

Slope ratio method :-

In order to confirm the composition arrived at by Job's method slope ratio was employed. In one set of mixtures one of the component was kept constant while the other was varied. In the second set the reactants were mixed in the reverse manner. The total volume in both the sets was kept constant at 10 cc. The optical densities of all the solutions were measured at 540 mu. These were plotted against the variant. The ratio of the two linear curves determine the composition of the chelate as 1:1. The experiments were also repeated at 550 mu and 560 mu and the same combining ratio was found to exist.

Slope ratio method - Set No. 1

concentration of ligand = 1×10^{-3}M
concentration of CdI_2 = 2×10^{-3}M
Total volume = 10 cc

Table No. 22

Volume of ligand cc	Volume of CdI_2 cc	O.D. at 540 mu	O.D. at 550 mu	O.D. at 560 mu
5.0	0.20	0.13	0.16	0.08
5.0	0.40	0.26	0.30	0.20
5.0	0.60	0.38	0.42	0.32
5.0	0.80	0.50	0.53	0.44
5.0	1.0	0.64	0.66	0.53
5.0	1.2	0.76	0.78	0.67
5.0	1.4	0.86	0.90	0.78
	Fig. 27 curve	1	2	3

Set No. 2 -

concentration of ligand = 2×10^{-3}M
concentration of CdI_2 = 1×10^{-3}M
Total volume = 10.0 cc

Fig. 27 curve (4) (5) (6)

Table No. 23

Volume of ligand cc	Volume of CdI_2 cc	O.D. at 540 mu	O.D. at 550 mu	O.D. at 560 mu
0.20	5.0	0.10	0.20	0.12
0.40	5.0	0.22	0.32	0.24
0.60	5.0	0.34	0.44	0.37
0.80	5.0	0.44	0.55	0.47
1.0	5.0	0.57	0.67	0.60
1.2	5.0	0.68	0.80	0.70
1.4	5.0	0.78	0.84	0.80

Mono-variation method :-

Molar ratio method (loc.cit.) was tried to confirm the results of Job's and slope ratio methods. Along with it the stability constant of the complex was determined. Solutions were mixed in the usual manner (keeping cadmium iodide constant and varying the concentration of the ligand). Experiments were carried out at two different concentrations of cadmium iodide. The optical density was measured at 550 mu and 560 mu.

Molar ratio method -

Set No. 1 - concentration of ligand = 1.66×10^{-3}M
concentration of cadmium iodide = 1.66×10^{-3}M
Total volume = 15.0 cc

Set No. 2 - concentration of ligand = 0.83×10^{-3}M
concentration of cadmium iodide = 0.83×10^{-3}M
Total volume = 15.0 cc

Table No. 24

		Set No. 1		Set No. 2	
Vol. of CdI_2 cc	Vol. of ligand cc	O.D. at 550 mu	O.D. at 560 mu	O.D. at 550 mu	O.D. at 560 mu
5.0	1.0	0.18	0.14	0.04	0.03
5.0	2.0	0.34	0.26	0.17	0.15
5.0	3.0	0.50	0.40	0.28	0.25
5.0	4.0	0.63	0.53	0.42	0.34
5.0	5.0	0.72	0.64	0.54	0.47
5.0	6.0	0.73	0.65	0.56	0.50
5.0	7.0	0.73	0.65	0.57	0.51
5.0	8.0	0.73	0.65	0.57	0.51
5.0	9.0	0.73	0.66	0.57	0.51
		Fig.28 curve 1	Fig.29 curve 1	Fig.28 curve 2	Fig.29 curve 2

For stability constant, the equation used were,

$$K = \frac{(1-\alpha)}{C\alpha 2} \quad \text{and}$$

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

where α, E_m, E_s and C have their usual meanings.

JOB'S METHOD

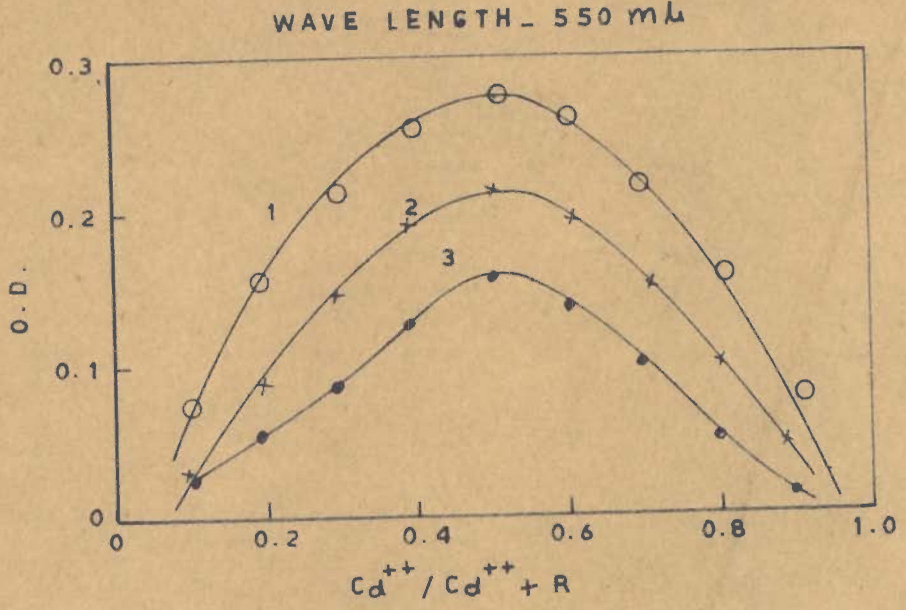


FIG. 25

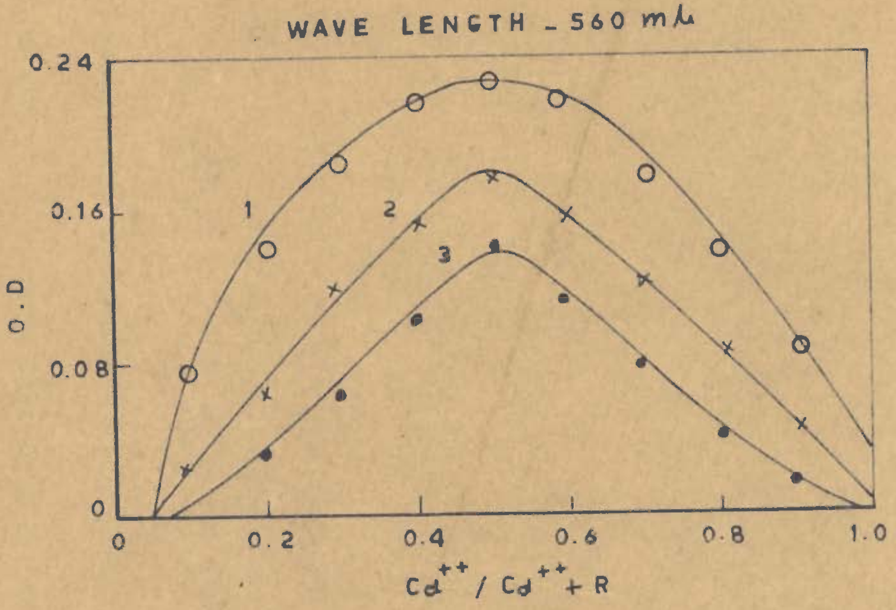


FIG. 26

SLOPE RATIO METHOD

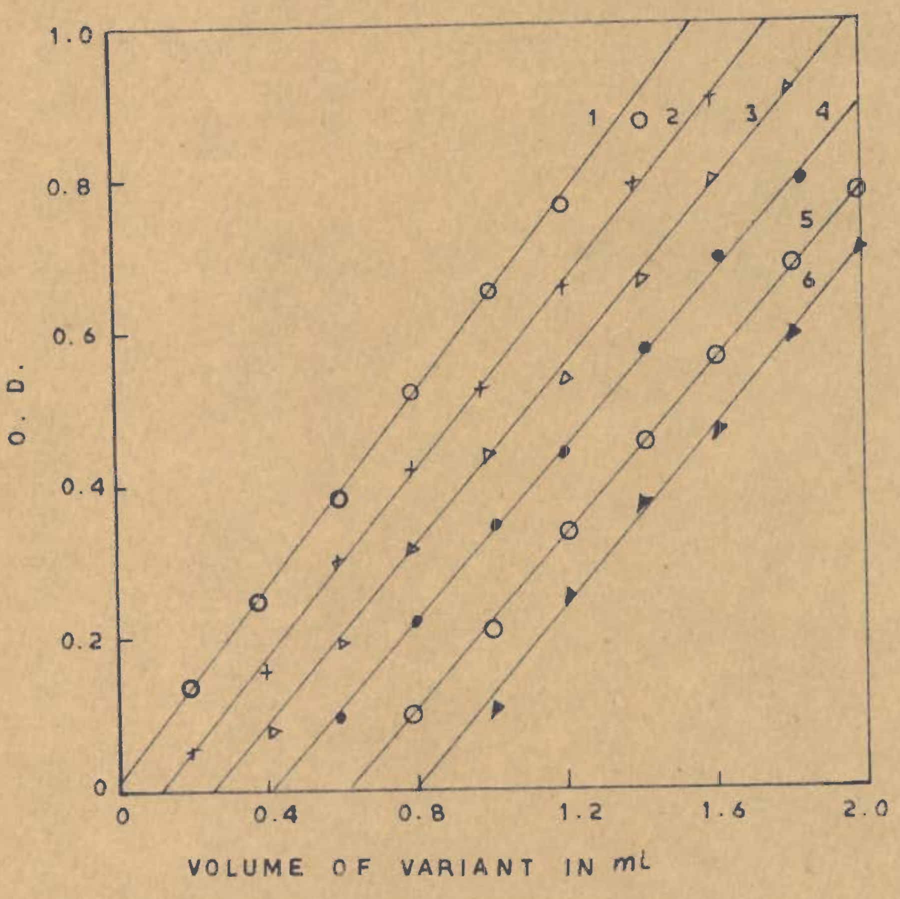


FIG. 27

MOLAR RATIO METHOD

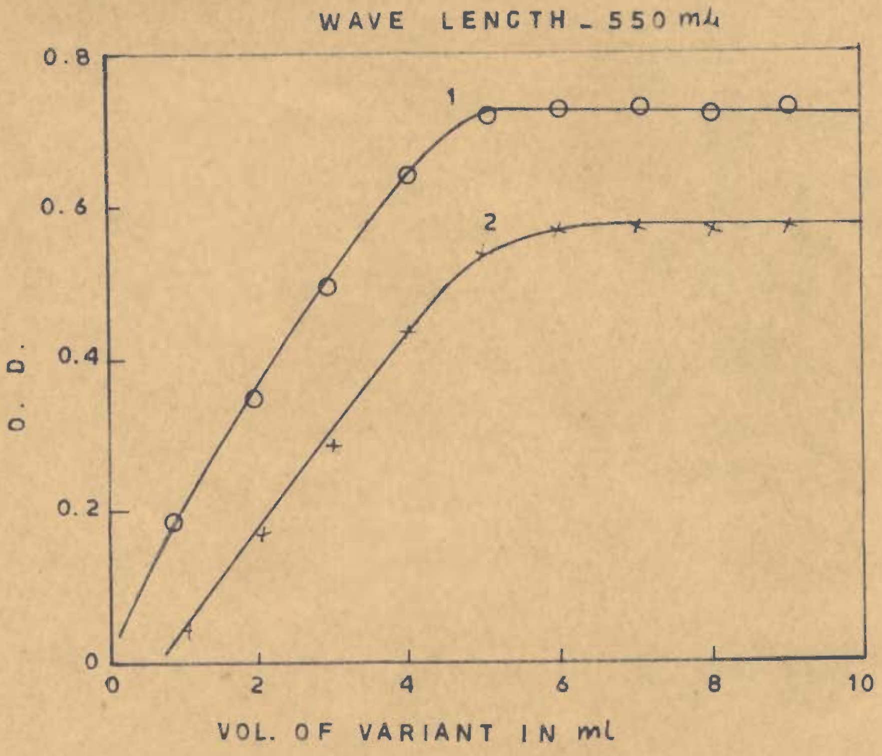


FIG. 28

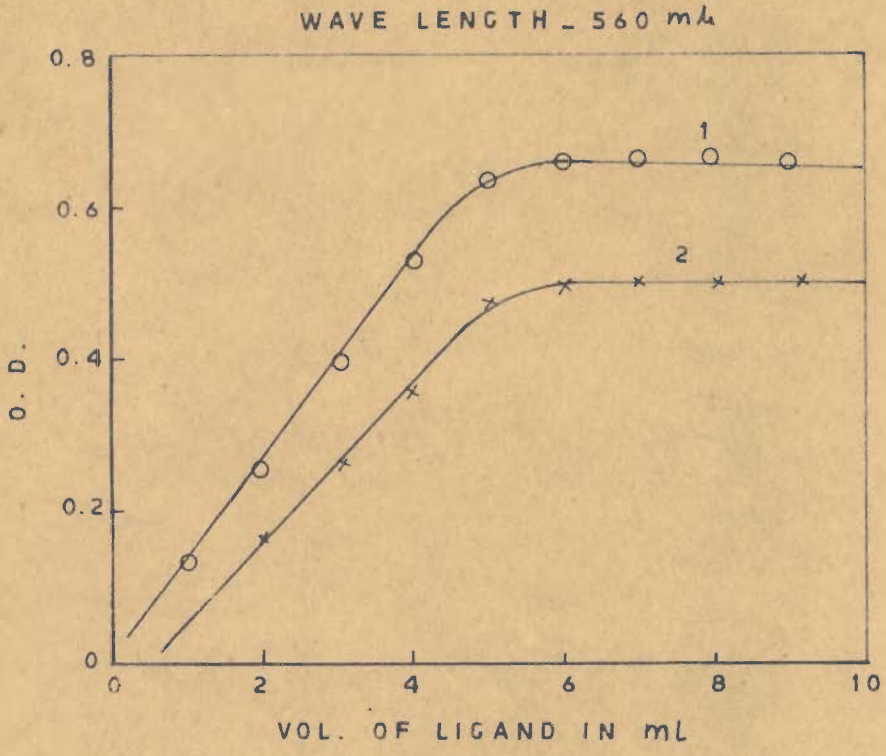


FIG. 29

By putting the value of $E_m = 0.53$; $E_s = 0.58$

(Table No.24 curve 2)

$\alpha = 0.08$ and $C = 0.276 \times 10^{-3}M$

the value of K_s come out to $K_s = 5.2 \times 10^5$.

By knowing the value of stability constant, the change in free energy was calculated by the relationship at 25°C

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

$$= - 7.8 \text{ K Cals/mole at } 25^\circ C.$$

Isolation and chemical analysis of the bluish green cadmium p-dimethyl amino anil of β-naphthyl glyoxal complex :-

Concentrated equimolar solutions of cadmium iodide and the reagent were mixed. The resulting precipitate was thoroughly washed with acetonitrile. It was then dried in a vacuum dessicator over calcium chloride.

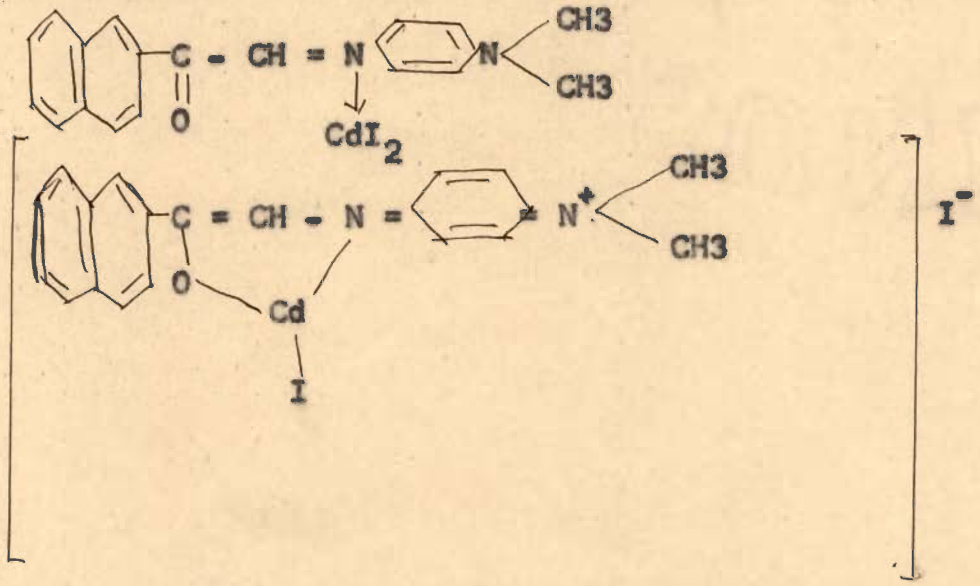
Decomposition point = 235°C.

Cadmium was estimated by the usual method. The results of chemical analysis are as follows :-

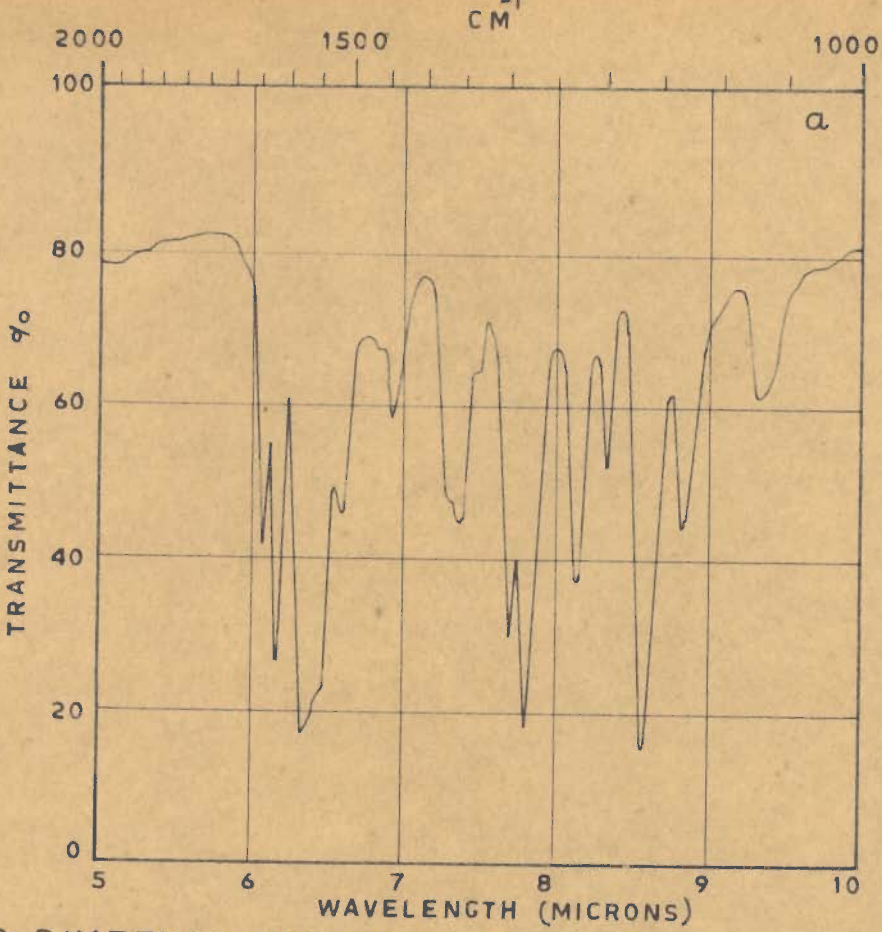
Calculated	Found
Cd - 16.81; I - 37.97	Cd - 16.02; I - 37.08
C - 35.91; H - 2.69;	C - 35.01; H - 2.63;
N - 4.18 and	N - 4.20 and
O - 2.44 (By difference)	O - 5.06 (By difference)

Structure of the complex -

Cd (II) chelate was isolated as a solid nonhygroscopic product and its I.R. recorded in KBr pallets. The interaction of the metal ion with the ligand is quite evident from the lowering of frequencies at the centres of $>C = 0$ and - $CH=N$ (1600 to 1570 cm^{-1}) (1640 to 1600 cm^{-1}) Fig. 30. On the basis of the absorption and chemical analysis data as well as from IR studies the following structure for the chelate may be put forward,



The ionic iodine outside the coordination sphere of the chelate was confirmed by the appearance of a yellowish precipitate of AgI by mixing ethanolic solution of $AgNO_3$ and the isolated complex.



p-DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL

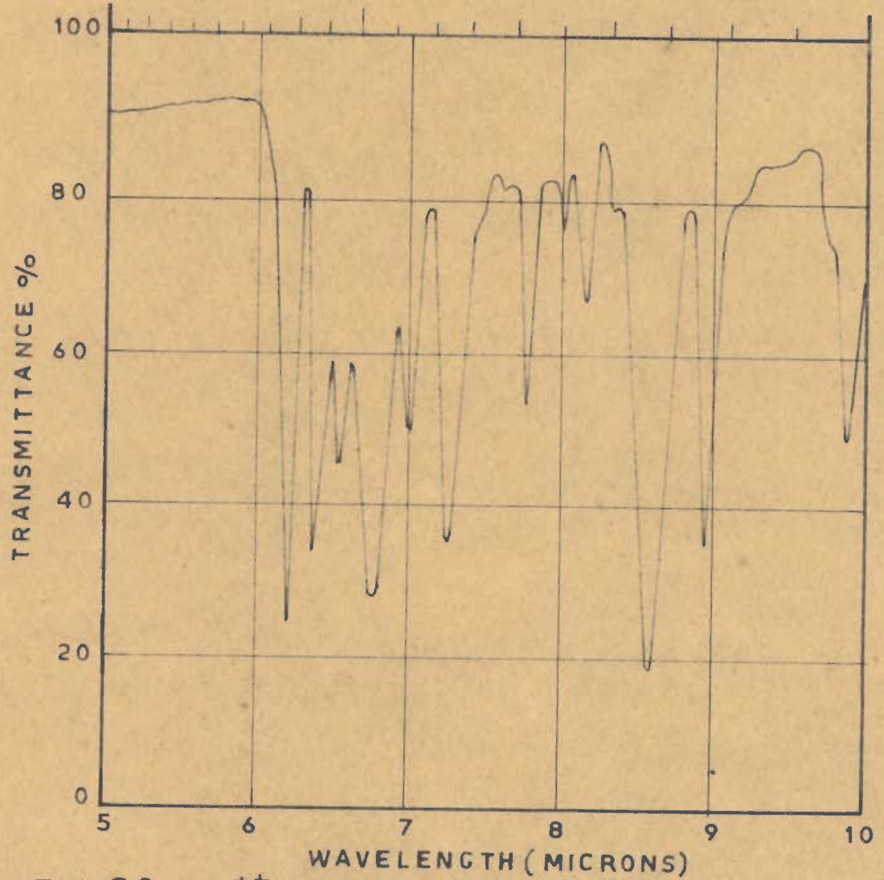


FIG. 30 – Cd^{++} – p-DIMETHYL AMINO ANIL OF β-NAPHTHYL GLYOXAL COMPLEX

Studies on Hg(II) - p - dimethyl amino anil of methyl glyoxal complex :-

In order to determine the number of complexes formed by the interaction of $HgCl_2$ with p-dimethyl amino anil of methyl glyoxal, Vosburgh and Cooper's method was followed.

Equimolar solutions ($1.0 \times 10^{-3}M$) of mercuric chloride and p-dimethyl amino anil of methyl glyoxal were mixed in the ratios 2:1, 3:1, 3:2, 1:1, 2:3 and 1:2 respectively. Their optical densities at different wave lengths were measured with the help of Bausch and Lomb 'spectronic 20'. The change in λmax. of the chelate ffom either of the reactant was taken as an indication for chelation. Similar behaviour was found when the acetonic solutions of ligand and metal irons were mixed. In some of the mixtures prepared above two λmax. were observed at 400 mu and 520 mu. The λmax. of the ligand itself is at 400 mu. Hence it was assumed that 400 mu maxima was due to the excess of the ligand present in the mixtures. Hence 520 mu was choosen as the proper wave-length to study the composition and other thermodynamic data of the complex.

Job's method of continuous variation was employed to determine the composition of reddish violet complex. The following sets of mixtures were prepared :-

9.0, 8.0, 7.0   2.0, 1.0 cc $1 \times 10^{-3}M$, ligand

1.0, 2.0, 3.0   8.0, 9.0 cc $1 \times 10^{-3}M$ Hg (II)

Table No. 25

concentration of $HgCl_2$ = $1.0\times10^{-3}M$

concentration of ligand = $1.0\times10^{-3}M$

OPTICAL DENSITY - Fig. 31

wave length mu	Ratio of ligand to $HgCl_2$					
	2:1	3:1	3:2	1:1	2:3	1:2
325	0.98	0.80	0.60	0.40	0.25	-
350	0.36	0.20	0.15	0.09	0.06	-
375	0.45	0.30	0.18	0.14	0.07	-
380	0.70	0.40	0.30	0.20	0.10	-
400	1.7	1.45	1.1	0.65	0.78	-
410	1.65	1.40	1.0	0.50	0.65	1.7
425	1.40	1.1	0.62	0.30	0.45	1.4
450	0.70	0.50	0.24	0.13	0.16	0.90
475	0.22	0.16	0.12	0.07	0.04	0.30
500	0.26	0.17	0.11	0.07	0.04	0.35
510	0.37	0.20	0.15	0.12	0.05	0.43
520	0.50	0.39	0.25	0.20	0.12	0.58
530	0.45	0.30	0.20	0.14	0.08	0.51
550	0.31	0.20	0.19	0.07	0.04	0.40
575	0.19	0.09	0.05	0.03	0.02	0.28
600	0.09	0.03	0.03	0.01	0.01	0.17
625	0.02	-	-	-	0	0.10

Similar volume of the ligand in each case was taken and diluted by the solvent to 10 cc as constant volume. The absorbances of all these solutions were deter-

-mined and the difference in O.D. of the complementary mixture and the ligand was plotted against the molar fraction of the metal (Fig. 32-33).

The curve shows almost a parabolic locus whose maximum corresponds to the composition 1:1.

Similar results were obtained when the method was studied at 1.428×10^{-3}M concentration each.

Table No. 26

Job's method - Set No. 1

concentration of mercuric chloride = 1.0×10^{-3}M
concentration of ligand = 1.0×10^{-3}M
wave length - 510 mu
Wave length - 520 mu

Vol. of mercuric chloride cc	Vol. of ligand cc	O.D. of mixture c	O.D. of ligand a	Difference (c-a)	O.D. of ligand a	O.D. of mixture c	Difference (c-a)
1.0	9.0	0.56	0.54	0.02	0.60	0.62	0.02
2.0	8.0	0.46	0.42	0.04	0.50	0.53	0.03
3.0	7.0	0.41	0.35	0.06	0.40	0.45	0.05
4.0	6.0	0.35	0.27	0.08	0.32	0.374	0.054
5.0	5.0	0.32	0.22	0.10	0.27	0.352	0.082
6.0	4.0	0.28	0.20	0.08	0.25	0.316	0.066
7.0	3.0	0.254	0.20	0.054	0.22	0.26	0.04
8.0	2.0	0.182	0.16	0.022	0.20	0.22	0.02
9.0	1.0	0.16	0.15	0.01	0.18	0.19	0.01

Fig. 32 curve 1

Fig. 32 curve 2

Table No. 27

Wave length - 530 mu

Volume of HgCl$_2$ cc	Volume of ligand cc	O.D. of ligand a	O.D. of mixture c	Difference (c-a)
1.0	9.0	0.62	0.63	0.01
2.0	8.0	0.52	0.54	0.02
3.0	7.0	0.44	0.472	0.032
4.0	6.0	0.34	0.394	0.054
5.0	5.0	0.29	0.360	0.070
6.0	4.0	0.29	0.35	0.06
7.0	3.0	0.25	0.282	0.032
8.0	2.0	0.22	0.24	0.02
9.0	1.0	0.20	0.21	0.01

Set No. 2 concentration of the reactants = 1.428×10^{-3}M

(Fig. 33 curve 1,2,3)

Stability constant of the chelate :-

Slope and molar ratio methods were employed to determine the stability as well as the composition of the chelate. Moore and Anderson (loc. cit.) method could not be employed to determine the stability constant since one of the constituents was coloured. Modification of this method in which one of the component is coloured was also not found suitable, because the plots of O.D. did not fall at the stoichiometric ratio of the complex (△ O.D plots, however, behave so). Job's equation for non-equilibrium concentration was employed. (Table No. 28 Fig. 34 curve 1 and Table No. 29 Fig. 34, curve 2).

The value of K was calculated by the formula

$$K = \frac{c\left[(p+1)x-1\right]^2}{(p-1)(1-2x)}$$

where C = molar concentration of the metal solution

p = molar concentration of ligand/molar concentration of metal and

x = value of maxima

Table No. 28

Set No. 1 - concentration of ligand = 1.42×10^{-3}M
concentration of $HgCl_2$ = 0.66×10^{-3}M
total volume = 22 cc

Set No. 2 - concentration of ligand = 1.25×10^{-3}M
concentration of $HgCl_2$ = 0.625×10^{-3}M
total volume = 20 cc

------

wave length - 520 mu

volume of ligand cc	volume of $HgCl_2$ cc	O.D. of ligand c	O.D. of mixture a	Difference (c-a)
1	19.26	0.082	0.07	0.012
2	17.12	0.122	0.090	0.032
3	14.98	0.166	0.10	0.066
4	12.84	0.230	0.11	0.120
5	10.70	0.260	0.12	0.140
6	8.56	0.282	0.160	0.122
7	6.42	0.31	0.20	0.10
8	4.28	0.322	0.25	0.072
9	2.14	0.344	0.32	0.024

x = 0.30 Fig. 34 curve 1

Table No. 29

Wave length - 520 mu

volume of ligand cc	volume of $HgCl_2$ cc	O.D. of ligand c	O.D. of mixture a	Difference (c-a)
1	18	0.008	0	0.008
2	16	0.03	0.01	0.020
3	14	0.070	0.03	0.044
4	12	0.11	0.04	0.070
5	10	0.15	0.05	0.10
6	8	0.174	0.10	0.074
7	6	0.190	0.140	0.050
8	4	0.202	0.20	0.022
9	2	0.262	0.260	0.002

$x = 0.31$ Fig. 34 curve 2

Set No. 1 $p = 2.15$; $x = 0.30$

By substituting the value, in the above formula

K comes out tobe $= 8.50\times10^{-7}$

Set No. 2 $K_1 = 8.05\times10^{-7}$; $x = 0.31$, $p = 2.0$

$$\text{Stability constant} = \frac{1}{\text{Instability constant.}}$$

$$= 1.2\times10^{6}$$

Change in free energy

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

Where R, T and ΔF have their usual significance. By putting $T = 298$; $R = 2$ and $K = 1.2\times10^{6}$

ΔF comes out to $= -$ 8.3 K cals/mole at 25°C.

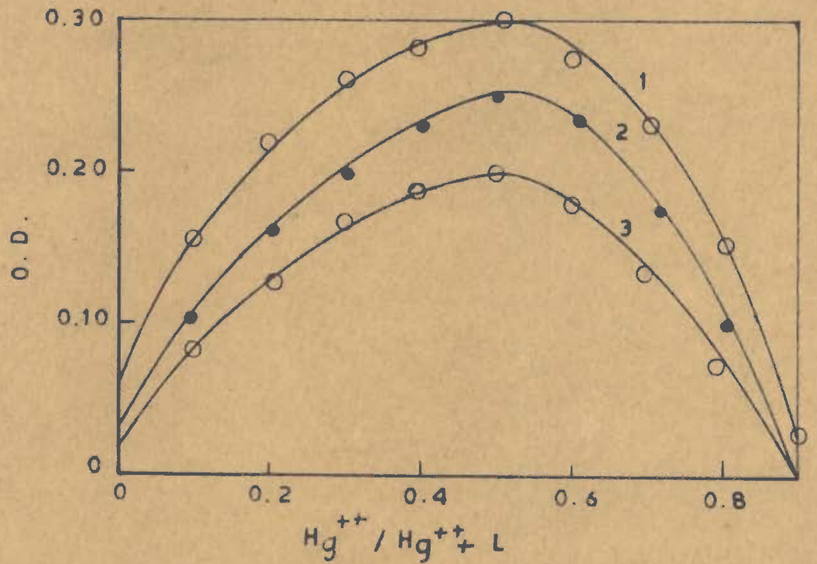

JOB'S METHOD

FIG. 33

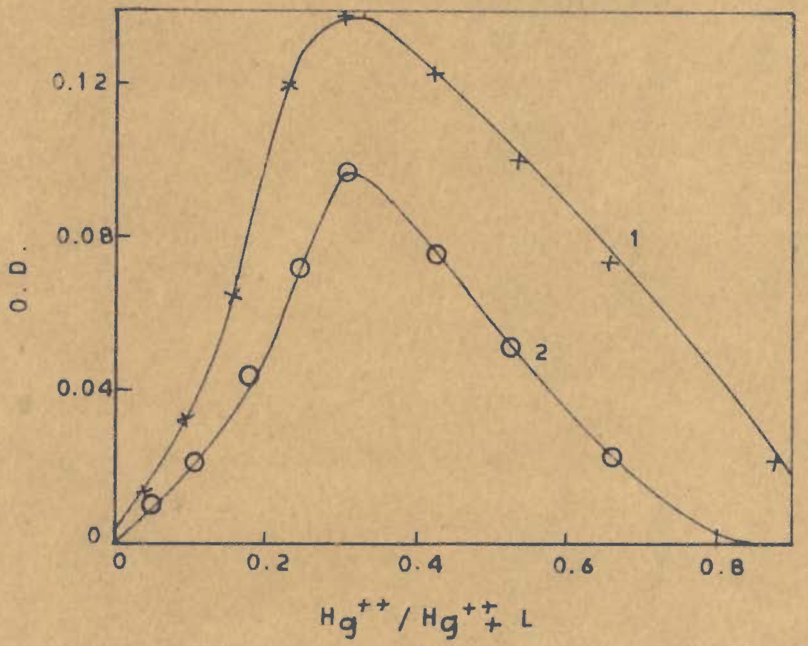

JOB'S – NON EQUIMOLAR CONC.
(STABILITY CONSTANT)

FIG. 34

Isolation and chemical analysis of Hg(II) p-dimethyl amino anil of Methyl Glyoxal complex :-

60 cc of mercuric chloride solution in acetonitrile was added to the same volume of p-dimethyl amino anil of methyl glyoxal (both 0.005M). The bluish green coloured crystalline precipitate of complex was obtained.

Decomposition point - 157°C.

Metal was estimated by the method given in the previous chapter.

The results of analysis are as follows :-

Calculated	Found
Hg-43.46; Cl-15.38	Hg-42.46; Cl-15.12;
C-28.60; H-3.03;	C-28.98; H-3.10;
N-6.06 and	N- 5.94 and
O-3.47 (By difference)	O- 4.40 (By difference)

Nature of the complex :-

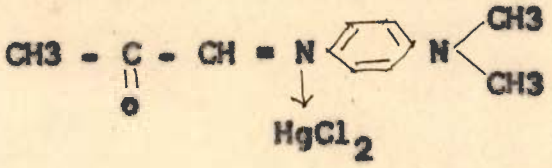
The ligand p-dimethyl amino anil of methylglyoxal possess the groups - CH_3 attached to keto group, $>C=O$, - CH=N and the auxochromic group - $N\left\langle \begin{matrix} CH3 \\ CH3 \end{matrix}\right.$ respectively. To ascertain the role of the functional groups, I.R.; spectrum of it was recorded by Perkin and Elmer infra cord, using KBr technique. There is a sharp peak at 1370 cm^{-1} which can be due to a single methyl group attached to -C atom of keto grouping. Because such frequency lies in the range of 1383-1377 cm^{-1}. The keto group of saturated aliphatic ketones falls around 1700 cm^{-1} and that of C = N at 1600 cm^{-1} respectively. In the spectrum of the ligand such frequencies are quite pronounced. The auxochromic grouping $-N\begin{matrix}CH3\\CH3\end{matrix}$ attached to phenyl skeleton causes mesomeric effect during the interaction. This is responsible for the appearance of stretching frequencies around 2829 cm^{-1}.

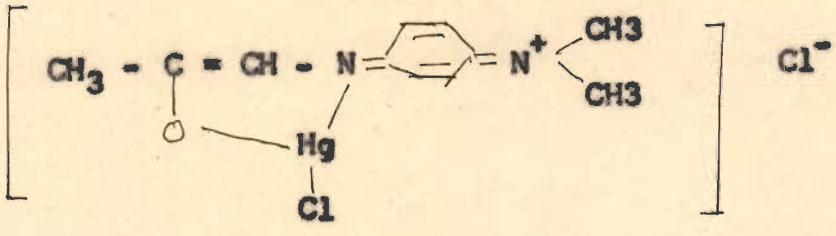
I.R. studies of the spectra of the different chelate with the above ligand has given useful information about the positions of actual interaction. On examining the spectrum of Hg (II) - p - dimethyl amino anil of methyl glyoxal, there is one stretching frequency at 1675 cm^{-1} and another at 1570 cm^{-1}. Their existence is possible when the frequencies of $>C = O$ and - CH=N got lowered in the process of chelation (Fig. 35).

C = C and C - C linkages undergo rearrangement due to quinonoism causing bathochromic effect.

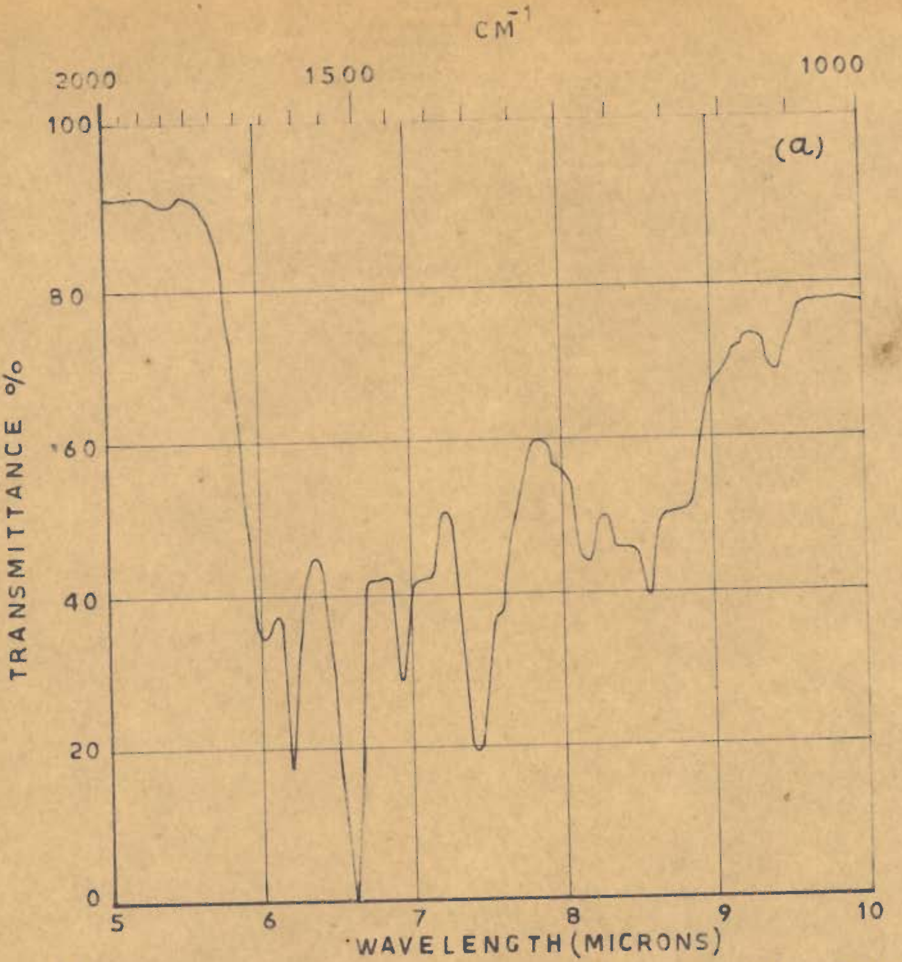
It is supported by the spectrum of the complex where some perturbation in the frequencies of aromatic unit is observed.

On the basis of I.R. studies, spectro-photometric measurements and chemical analysis the following structure may be assigned to the chelate :





The chelate in solution is ionic in character. On addition of alcoholic $AgNO_3$ to the isolated complex in the same solvent, a white ppt soluble in ammonium hydroxide and insoluble in dil. HNO_3 was obtained. This ppt. is due to the formation of AgCl, because of Cl^- ions existing in the complex outside the coordinating sphere.



p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL

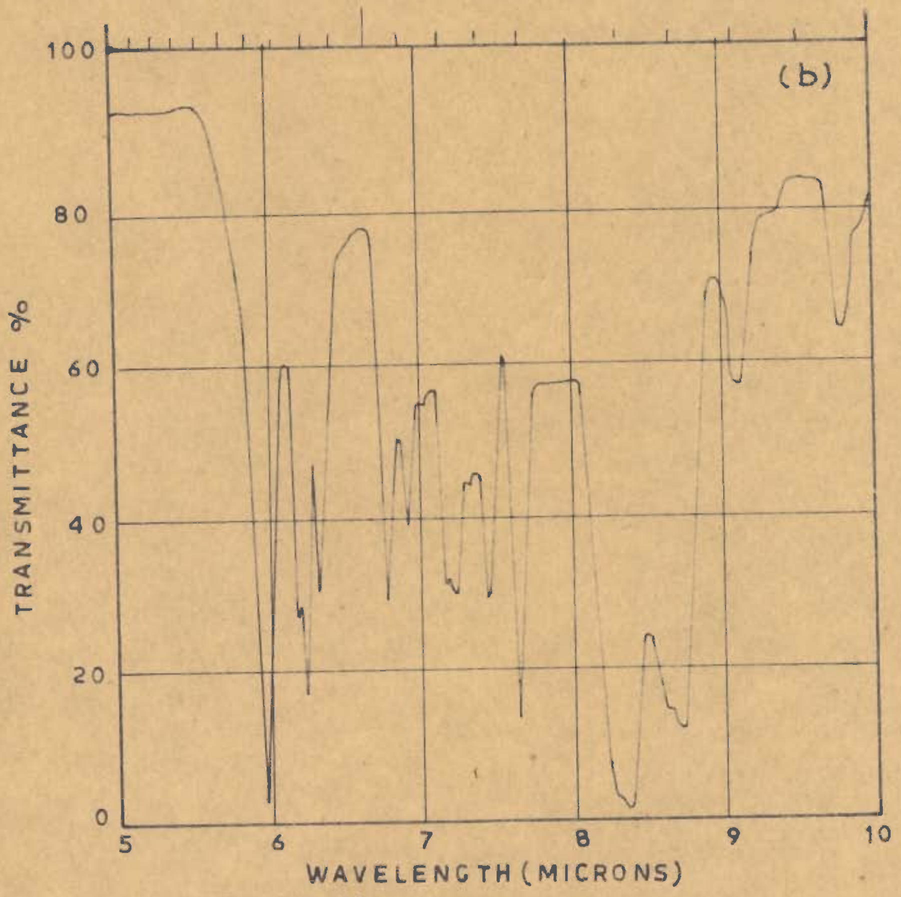


FIG. 35 _ Hg^{++} - p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL COMPLEX

Studies on Fe (III) - p- dimethyl amino anil of methyl glyoxal complex :-

Like Hg (II) - p- dimethyl amino anil of methyl glyoxal chelate Fe (III) also gives a soluble complex in the acetonic medium. The mixing of the reactants is accompanied by a marked deepening in colour. Absorption studies in the visible region could, therefore, be carried out with great accuracy.

Measurement were carried out with the help of Bausch and Lomb "spectronic 20", while I.R. spectra were recorded in solid state by Perkin-Elmer Infra Cord.

The natue of the chelate was determined by Vosburgh and Cooper's method (loc. cit.). The observations are given below :

concentration of the metal ion = 0.45×10^{-3}M

concentration of ligand = 0.45×10^{-3}M

Table No. 30

Vosburgh and Cooper's method

Concentration of ferric chloride = $0.45 \times 10^{-3}M$
Concentration of ligand = $0.45 \times 10^{-3}M$

Fig. 36

Wave length	Ratio of ligand to ferric chloride					
mu	4:1	3:2	1:1	2:1	2:3	1:2
325	0.62	0.53	0.39	0.30	0.20	-
350	0.12	0.10	0.11	0.08	0.07	-
375	0.20	0.35	0.15	0.10	0.07	-
400	1.0	1.1	0.70	0.50	0.38	1.1
410	0.90	1.0	0.55	0.30	0.30	1.05
420	0.67	0.90	0.40	0.30	0.20	0.90
425	0.60	0.75	0.38	0.27	0.17	0.87
450	0.23	0.30	0. 14	0.12	0.07	0.50
475	0.13	0.16	0.08	0.05	0.02	0.28
500	0.10	0.13	0.05	0.04	0.01	0.22
525	0.20	0.20	0.12	0.10	0.04	0.27
540	0.23	0.30	0.15	0.17	0.08	0.37
550	0.30	0.40	0.23	0.25	0.17	0.45
560	0.20	0.30	0.12	0.17	0.10	0 .40
575	0.10	0.20	0.05	0.13	0.03	0.28
600	0.05	0.05	-	0.12	0.02	0.10
625	-	-	-	0.08	-	0.03

Here one of the peak was due to excess of the ligand, while the other at 550 mu corresponded to that of the chelate.

Job's method of continuous variation was employed for determining the composition of the complex. Three sets of mixtures were prepared according to the following scheme:

Set I - Equimolar solutions of ferric chloride and p-dimethyl amino anil of methyl glyoxal of 0.625×10^{-3}M were prepared and mixed in the following order,

1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 cc of ferric chloride were mixed with 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 cc of the reagent respectively. The O.D. of the above mixtures were measured at three wave length 540, 550 and 560 mu.

The O.D. of the ferric chloride was found to be negligible at this concentration.

Set II - Equimolar solutions of ferric chloride and the reagent of concentration 0.55×10^{-3}M were mixed in the same order as in set I.

Set III -Equimolar solutions of the reactants being used of concentration 0.50×10^{-3}M.

The difference in O.D. was plotted against

$$\frac{Fe^{+++}}{Fe^{+++} + L}$$

Table No. 31

Job's method - Set No. 1

concentration of ferric chloride = 0.625×10^{-3}M
concentration of ligand = 0.65×10^{-3}M
total volume = 12.0 cc
wave length - 540 mu   wave length - 550 mu

Vol. of $FeCl_3$ cc	Vol. of ligand cc	O.D. Mixture c	O.D. ligand a	Difference (c-a)	O.D. Mixture c	O.D. Ligand a	Difference (c-a)
1.0	11.0	0.358	0.33	0.028	0.37	0.36	0.01
2.0	10.6	0.267	0.20	0.067	0.246	0.22	0.026
3.0	9.0	0.235	0.13	0.105	0.160	0.15	0.10
4.0	8.0	0.200	0.08	0.120	0.240	0.11	0.130
5.0	7.0	0.155	.05	0.105	0.215	0.10	0.115
6.0	6.0	0.10	0.02	0.08	0.170	0.07	0.10
7.0	5.0	0.064	0.00	0.064	0.114	0.03	0.084
8.0	4.0	0.050	0	0.050	0.078	0.01	0.068
9.0	3.0	0.032	0	0.030	0.052	0	0.052
10.0	2.0	0.018	0	0.018	0.037	0	0.037
11.0	1.0	0.008	0	0.008	0.025	0	0.025

Fig.39 curve 1   Fig. 38 curve 1

Table No. 32

Wave length - 560 mu

Fig. 37 curve 1

Vol. of $FeCl_3$ cc	Vol. of ligand cc	O.D. mixture c	O.D. ligand a	Difference (c-a)
1.0	11.0	0.328	0.30	0.028
2.0	10.0	0.218	0.15	0.068
3.0	9.0	0.195	0.09	0.105
4.0	8.0	0.145	0.02	0.125
5.0	7.0	0.107	0	0.107
6.0	6.0	0.09	0	0.09
7.0	5.0	0.074	0	0.074
8.0	4.0	0.066	0	0.066
9.0	3.0	0.04	0	0.04
10.0	2.0	0.027	0	0.027
11.0	1.0	0.015	0	0.015

Mole ratio and slope ratio method :-

The results of Job's method was further confirmed by molar ratio and slope ratio methods (table 33-35). From the results it was concluded that two moles of the ligand combines with one mole of the metal to give the ionic chelate.

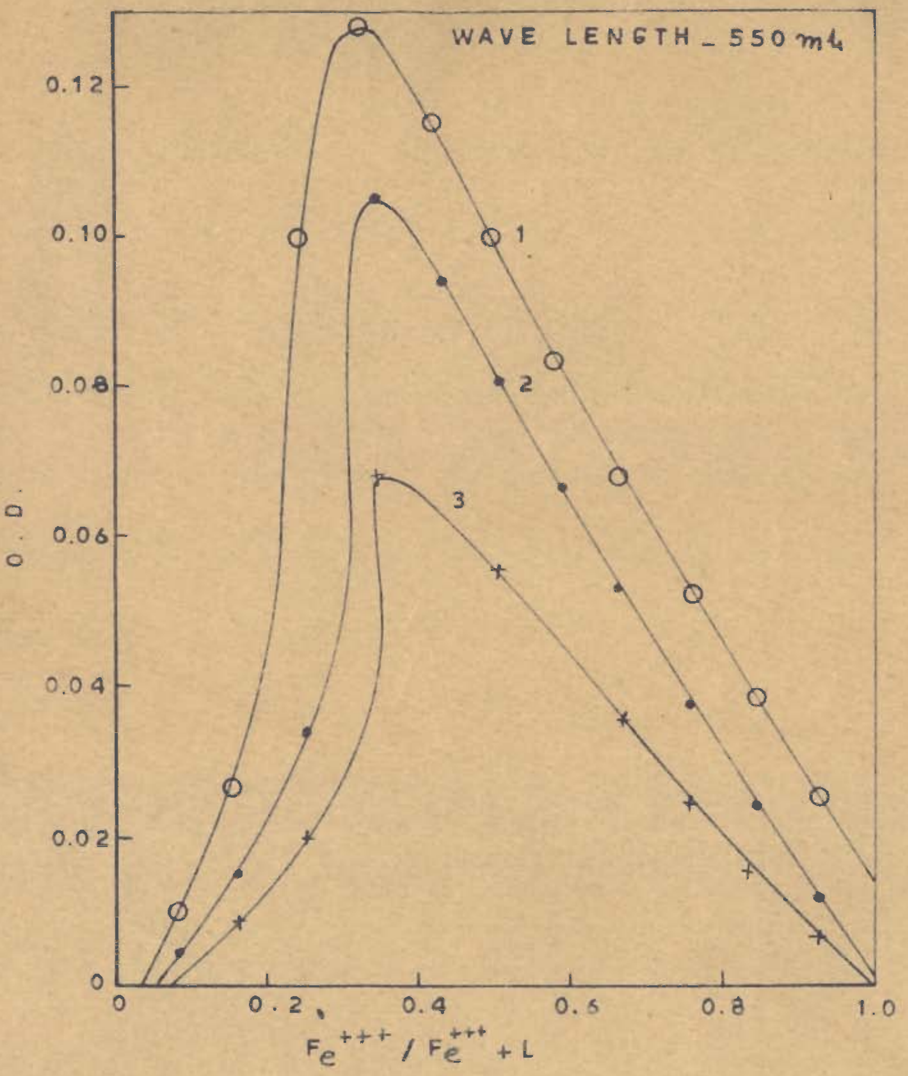
Job's method -

Set No. 2 -

Concentration of ferric chloride = 0.55×10^{-3}M
Concentration of ligand = 0.55×10^{-3}M
Total volume = 12 cc
Fig. 37,38,39 curve 2.

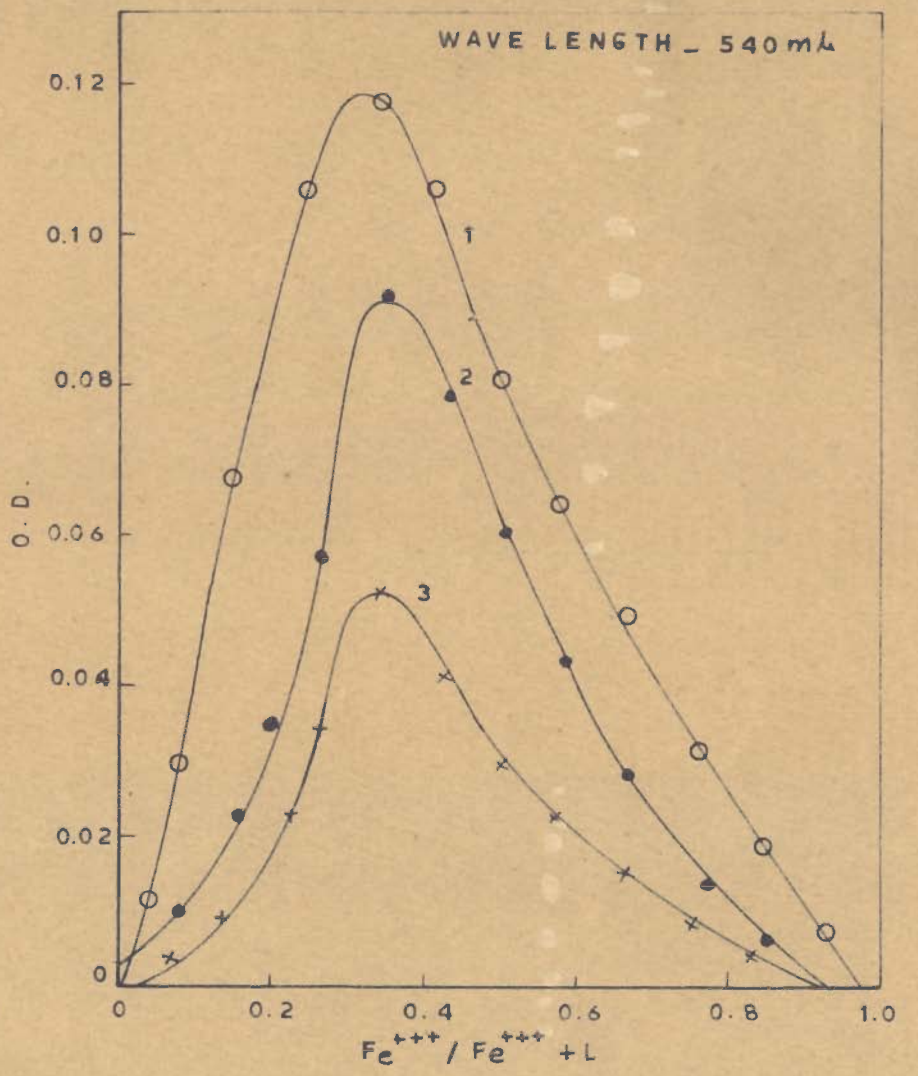
Set No. 3 -

Concentration of ferric chloride = 0.50×10^{-3}M
Concentration of ligand = 0.50×10^{-3}M
Total volume = 12.0 cc
Fig. 37,38, 39 curve 3.



WAVE LENGTH _ 550 mμ
O. D.
0.12
0.10
0.08
0.06
0.04
0.02
0
0
0.2
0.4
0.6
0.8
1.0
1
2
3
Fe+++ / Fe+++ + L

FIG. 38



WAVE LENGTH _ 540 mμ
O. D.
0.12
0.10
0.08
0.06
0.04
0.02
0
0
0.2
0.4
0.6
0.8
1.0
1
2
3
Fe+++ / Fe+++ + L

FIG. 39

Molar ratio method -

Set No. 1 - concentration of ligand = $1.25 \times 10^{-3} M$
concentration of ferric chloride = $0.625 \times 10^{-3} M$
total volume = 20.0 cc

Set No. 2 - concentration of ligand = $1.0 \times 10^{-3} M$
concentration of ferric chloride = $0.50 \times 10^{-3} M$
total volume = 20.0 cc

Set No. 1 Table No. 33

vol. of ligand cc	vol. of $FeCl_3$ cc	O.D. at 540 mu	O.D. at 550 mu	O.D. at 540 mu	O.D. at 550 mu
1.0	5.0	0.09	0.10	0.04	0.05
2.0	5.0	0.19	0.21	0.11	0.12
3.0	5.0	0.30	0.34	0.18	0.20
4.0	5.0	0.42	0.45	0.30	0.28
5.0	5.0	0.55	0.58	0.35	0.37
6.0	5.0	0.58	0.59	0.38	0.39
7.0	5.0	0.59	0.60	0.40	0.39
8.0	5.0	0.60	0.71	0.41	0.40
10.0	5.0	0.61	0.72	0.42	0.41
12.5	5.0	0.62	0.73	0.43	0.42
		Fig. 41 curve 1	Fig. 40 curve 1	Fig. 41 curve 2	Fig. 40 curve 2

Slope ratio method

Set No. 1 - concentration of ligand = 0.83×10^{-3}M

concentration of ferric chloride = 0.415×10^{-3}M

total volume = 15.0 cc

Fig. 42 curve 2

Table No. 34

Volume of $FeCl_3$ cc	Volume of ligand cc	O.D. at 550 mu
5.0	1.0	0.12
5.0	2.0	0.14
5.0	3.0	0.155
5.0	4.0	0.180
5.0	5.0	0.190
5.0	6.0	0.21

Set No. 2 - concentration of ligand = 0.415×10^{-3}M

concentration of ferric chloride = 0.83×10^{-3}M

total volume = 15 cc

Table No. 35 Fig. 42 curve 1

Volume of $FeCl_3$ cc	Volume of ligand cc	O.D. at 550 mu
1.0	5.0	0.34
2.0	5.0	0.36
3.0	5.0	0.39
4.0	5.0	0.43
5.0	5.0	0.47
6.0	5.0	0.51

MOLAR RATIO METHOD

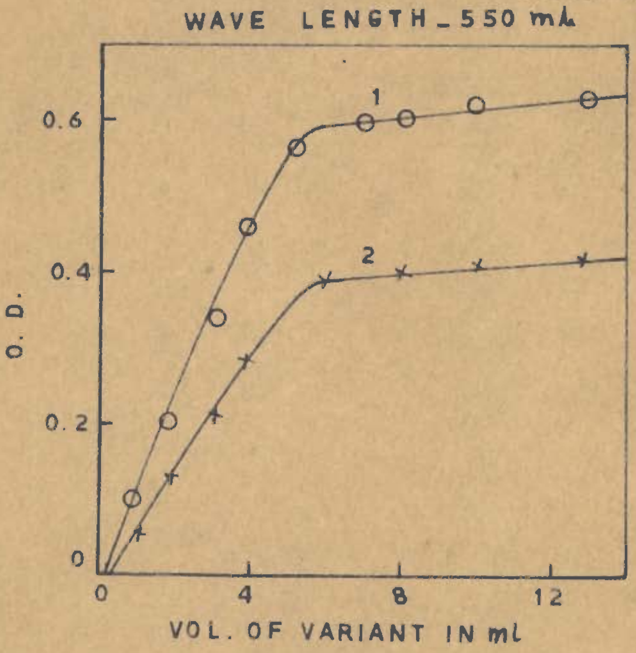

WAVE LENGTH – 550 mμ

FIG. 40

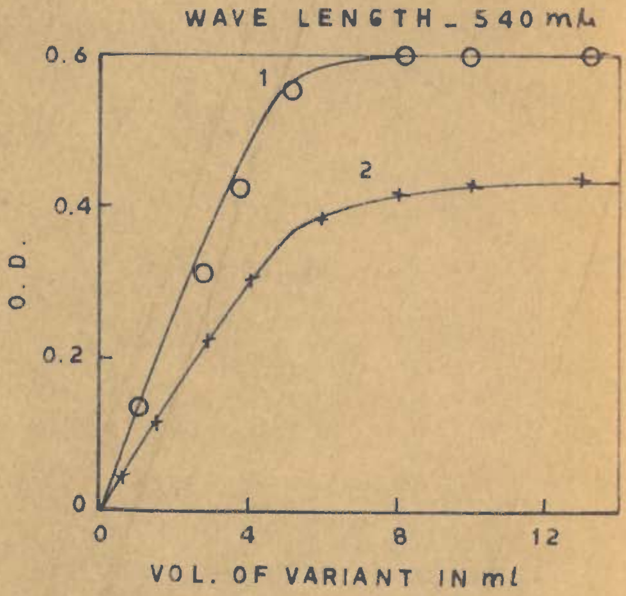

WAVE LENGTH – 540 mμ

FIG. 41

SLOPE RATIO METHOD

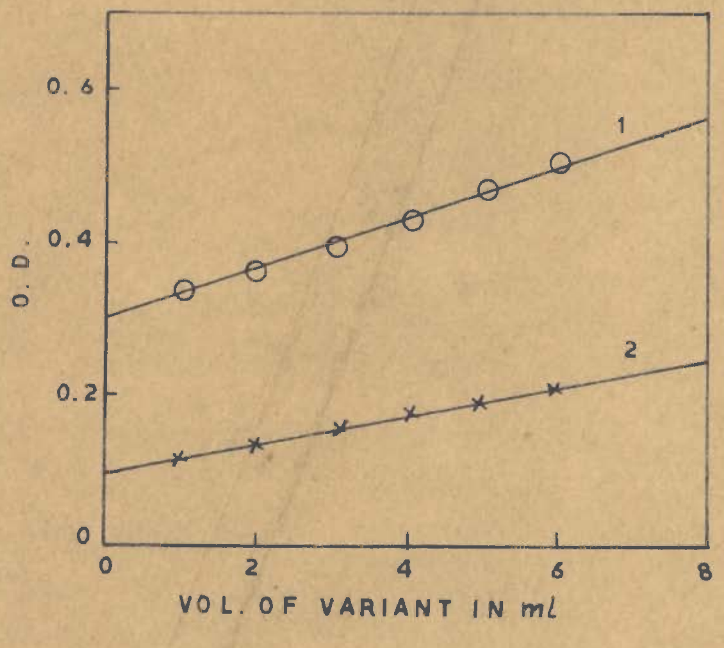


FIG. 42

Stability constant of reddish violet complex :-

Consider the dissociation of the complex as

$$FeR_2 \rightleftharpoons Fe + 2R \qquad \text{Initial concentration}$$

$$C(1-\alpha) \quad \alpha C \quad \alpha C \qquad \text{Final concentration}$$

Where C is the total concentration of the complex in moles per litre, and α is the degree of dissociation. The equilibrium constant K is given by the equation

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

The value of α ,may be obtained by the mole ratio (Fig. 40 curve 1) $\alpha = \dfrac{E_m - E_s}{E_m}$

where E_m is the maximum absorption obtained from the horizontal portion of the curve, when all the iron is present in the form of complex and E_s is the observed absorption of stoichiometric molar ratio of the reagent to iron in the complex.

K was calculated from the data of Fig. 40 curve 1 (Table No. 33).

$E_m = 0.61 \qquad C = 0.156\times10^{-3}M$

$E_s = 0.58 \qquad \therefore K_1 = 1.531\times10^{12}$

$\alpha = 0.04$

Change in free energy was calculated by the relationship,

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

$$= -\ 16.77\ \text{Kcals/mole at } 25^\circ C.$$

Isolation and chemical analysis of the Fe^{+++} - p-dimethyl amino anil of methyl glyoxal complex :-

100 cc of (0.005M) acetonic solution of ferric chloride was added to an equal volume of 0.005M reagent. The resulting mixture was concentrated by evaporation under Vacuum when the blue coloured complex was obtained. Fe (III) was estimated in the complex, gravimetrically as Fe_2O_3.

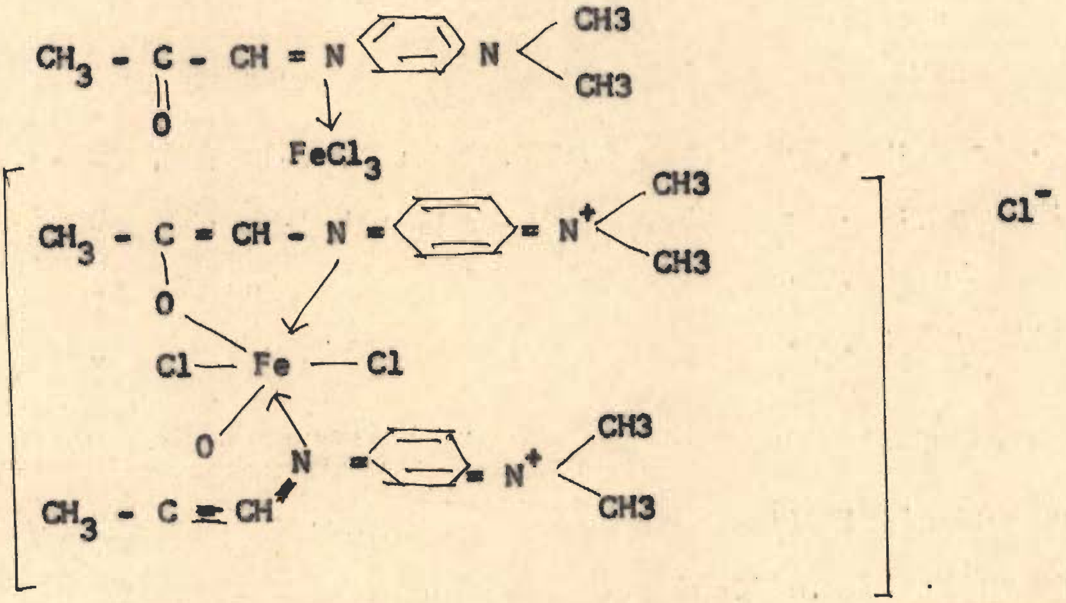
Decomposition point - 181°C.

The results of the analysis are as follows :-

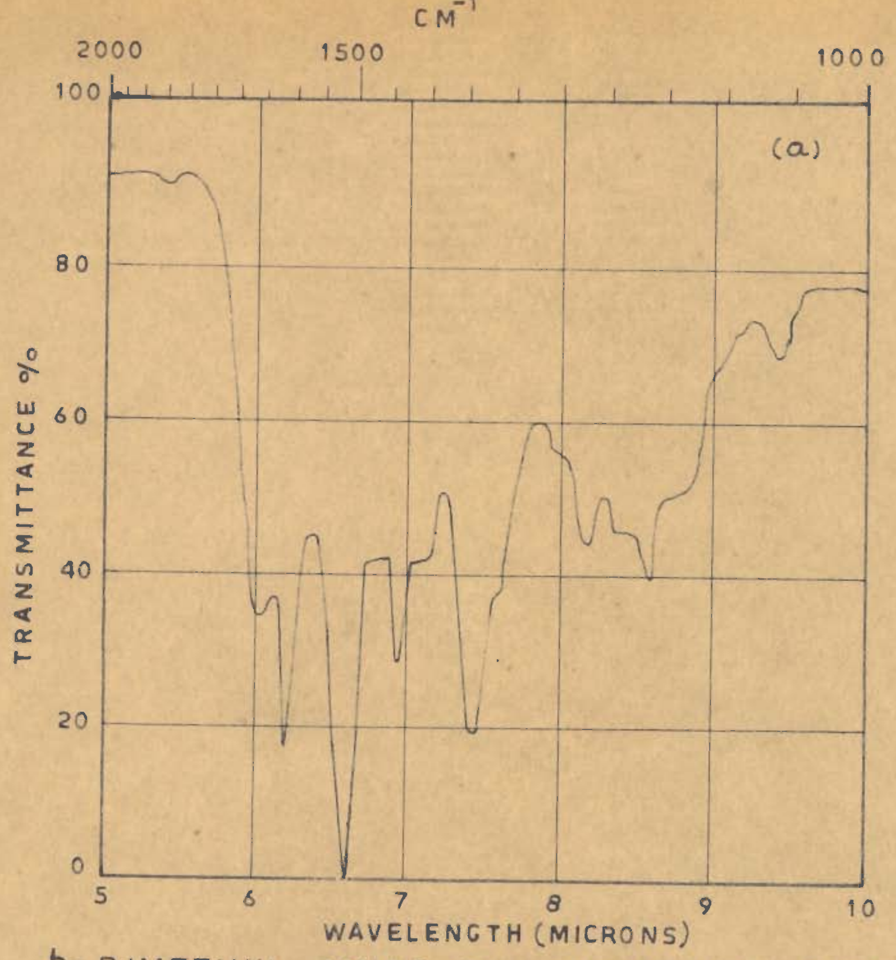
Calculated	Found
Fe -10.29; Cl-19.63;	Fe-10.00; Cl-19.42;
C -48.64; H-5.16;	C-48.34; H-5.00;
N -10.33 and	N-10.30 and
O - 5.92 (By difference)	O- 6.94 (By difference)

Nature of the complex :-

Like other Lewis acids $FeCl_3$ is in the quest of free electrons to undergo coordination. This free pair of electron provided by the N-atom of -CH=N and $-N{<}^{CH3}_{CH3}$. However, due to positive inductive effect the electron density in the auxchromic group is larger in $-N{<}^{CH3}_{CH3}$ than -CH=N on the addition of $FeCl_3$ to the ligand the electron moves from $- N{<}^{CH3}_{CH3}$ causing rearrangement in the skeleton of the whole molecule. $>C = O$ group of the anil now becomes more susceptible for interaction than $- N{<}^{CH3}_{CH3}$. In the course of chelation, therefore the only available seats for interaction in the ligand are $>C = O$ and - CH=N respectively. That these two positions are responsible for interaction was proved beyohd doubt by the I.R. studies of $FeCl_3$ - p - dimethyl amino anil of methyl glyoxal, when a marked lowering of stretching frequency (1600-1570 cm^{-1}, 1640 - 1600 cm^{-1}) takes place on chelation (Fig. 43). Keeping in view the six coordination number of Fe (III) and the chemical composition already determined, the following structure can be propounded to this type of chelate.



The chelate is not a neutral complex. Formation of white ppt. of AgCl on addition of silver nitrate as mentioned aforesaid shows that the Cl^- is outside the coordination sphere.



p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL

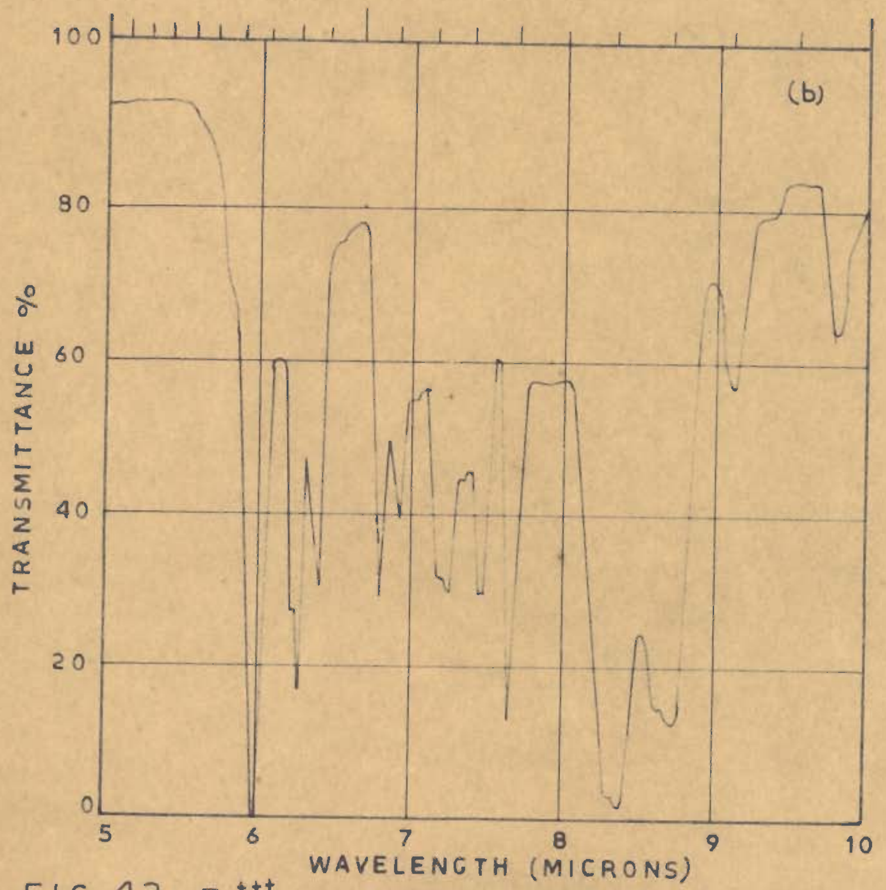


FIG. 43_ Fe^{+++}-p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL COMPLEX

Studies on Zn (II) - p - dimethyl amino anil of methyl glyoxal complex :-

Nature of the complex - Zn (II) when mixed with p-dimethyl amino anil of methyl-glyoxal in acetonic solution gave violet coloured chelate. 500 mu was choosen as the wave-length to study the stoichiometry of the complex. Since 400 mu max. was due to the excess of the ligand.

Table No. 36

Vosburgh and Cooper's method

concentration of zinc chloride = 0.55×10^{-3}M

concentration of ligand = 0.55×10^{-3}M

Wave length mu	Ratios of ligand to zinc chloride					
	3:1	2:1	3:2	4:3	3:4	1:1
325	0.68	0.78	0.42	0.26	0.18	-
350	0.13	0.20	0.08	0.04	0.01	-
375	0.50	0.30	0.24	0.15	0.11	-
400	1.6	1.25	0.94	0.60	0.74	1.60
410	1.55	1.20	0.80	0.45	0.40	1.58
420	1.44	0.90	0.57	0.30	0.25	1.40
425	1.20	0.78	0.50	0.25	0.20	1.30
450	0.40	0.32	0.15	0.09	0.05	0.50
475	0.18	0.15	0.10	0.05	0.02	0.34
490	0.30	0.22	0.12	0.20	0.07	0.50
500	0.60	0.43	0.25	0.30	0.17	0.64
510	0.43	0.33	0.18	0.20	0.08	0.55
525	0.31	0.20	0.09	0.11	0.05	0.40
550	0.18	0.09	0.05	0.08	0.02	0.25
575	0.11	0.08	0.02	0.05	0	0.115
600	0.05	0.05	-	0.03	-	0.08
625	0.02	0.02	-	0.01	-	0.02

Fig. 44

* * *

Job's continuous method -

The observations in Job's continued variation method are as follows:-

Job's method - Set No. 1

Table No. 37

Wave length - 500 mu　　　　Wave length - 510 mu

Vol.of $ZnCl_2$ cc	Vol.of ligand cc	O.D. Mixt. c	O.D. ligand a	Difference (c-a)	O.D. Mixt. c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.68	0.58	0.10	0.64	0.54	0.10
2.0	8.0	0.666	0.49	0.176	0.59	0.42	0.175
3.0	7.0	0.63	0.38	0.25	0.56	0.35	0.21
4.0	6.0	0.60	0.30	0.30	0.54	0.27	0.27
5.0	5.0	0.55	0.22	0.330	0.52	0.22	0.30
6.0	4.0	0.525	0.20	0.325	0.485	0.20	0.285
7.0	3.0	0.455	0.18	0.275	0.450	0.20	0.25
8.0	2.0	0.405	0.17	0.225	0.36	0.16	0.20
9.0	1.0	0.24	0.14	0.10	0.28	0.15	0.13

Fig. 45 curve 1　　　　Fig. 46 curve 1

From the peaks of the curves (Fig.45,46) it is quite evident that 1 mol. of $ZnCl_2$ combines with 1 mole of the ligand to form the chelate.

Slope and molar ratio method -

The results obtained by these two methods are given below. Both the methods gave 1:1 as the combining ratio:

Set No. 1 -

Concentration of ligand = 1.0×10^{-3}M

Concentration of $ZnCl_2$ = 1.0×10^{-3}M

Set No. 2 -

Concentration of reactants = 0.833×10^{-3}M

Fig. 45,46 curve 2.

Set No. 3 -

Concentration of reactants = 0.714×10^{-3}M

Fig. 45,46 curve 3.

JOB'S METHOD

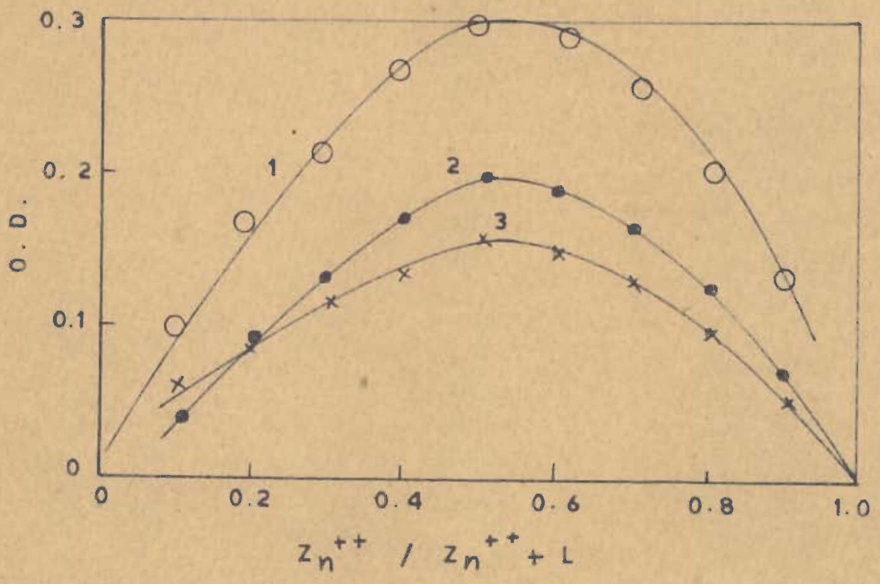


FIG. 46

MOLAR RATIO METHOD

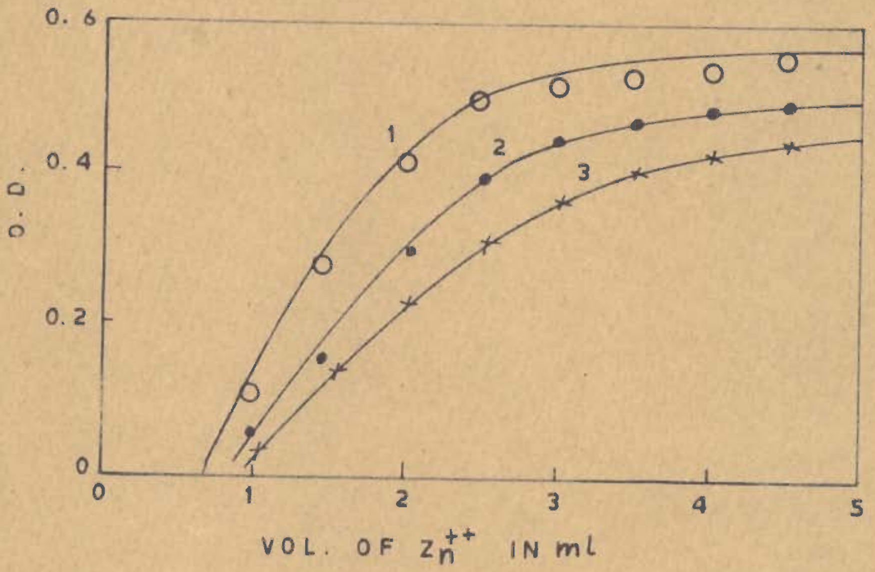


FIG. 47

Mole ratio method

Set No. 1 - concentration of ligand = 1.0×10^{-3}M
concentration of $ZnCl_2$ = 5.0×10^{-4}M

Total volume = 12 ml.

Table No. 38

Vol. of $ZnCl_2$ cc	Vol. of ligand cc	O.D. at 490 mu	O.D. at 500 mu	O.D. at 510 mu
5.0	1.0	0.06	0.10	0.03
5.0	1.5	0.15	0.27	0.14
5.0	2.0	0.30	0.40	0.23
5.0	2.5	0.40	0.50	0.30
5.0	3.0	0.45	0.52	0.37
5.0	3.5	0.47	0.53	0.40
5.0	4.0	0.48	0.54	0.43
5.0	4.5	0.50	0.57	0.45
	Fig. 47 curve	2	1	3

Set No. 2 - concentration of ligand = 2.0×10^{-3}M
concentration of zinc chloride = 2.0×10^{-3}M

Total volume = 15.0 cc

Table No. 39

Vol. of $ZnCl_2$ cc	Vol. of ligand cc	O.D. at 490 mu	O.D. at 500 mu	O.D. at 510 mu
5.0	1.0	0.10	0.20	0.12
5.0	2.0	0.24	0.37	0.23
5.0	3.0	0.37	0.47	0.32
5.0	4.0	0.45	0.55	0.37
5.0	5.0	0.51	0.60	0.46
5.0	6.0	0.54	0.62	0.47
5.0	7.0	0.56	0.63	0.50
5.0	8.0	0.57	0.66	0.51
	Fig.48curve	(2)	(1)	(3)

Slope ratio method -

Set No. 1 - concentration of ligand = $2.0\times10^{-3}M$
concentration of zinc chloride = $1.0\times10^{-3}M$
Total volume = 12.0 cc

Table No. 40

Volume of ligand cc	Volume of zinc chloride cc	O.D. at 490 mu	O.D. at 500 mu	O.D. at 510 mu
5.0	1.0	0.15	0.22	0.18
5.0	1.5	0.30	0.36	0.31
5.0	2.0	0.42	0.50	0.47
5.0	2.5	0.57	0.65	0.74
5.0	3.0	0.72	0.78	0.88
5.0	3.5	0.87	0.92	0.90
Fig. 49 curve		(1)	(3)	(2)

Set No. 2 - concentration of ligand = $1.0\times10^{-3}M$
concentration of zinc chloride = $2.0\times10^{-3}M$

Total Volume = 12.0 cc

Table No. 41

Volume of $ZnCl_2$ cc	Volume of ligand cc	O.D. at 490 mu	O.D. at 500 mu	O.D. at 510 mu
5.0	1.0	0.11	0.15	0.12
5.0	1.5	0.25	0.30	0.27
5.0	2.0	0.40	0.44	0.38
5.0	2.5	0.54	0.60	0.58
5.0	3.0	0.70	0.76	0.70
5.0	3.5	0.82	0.80	0.87
Fig. 49 curve		(4)	(6)	(5)

MOLAR RATIO METHOD

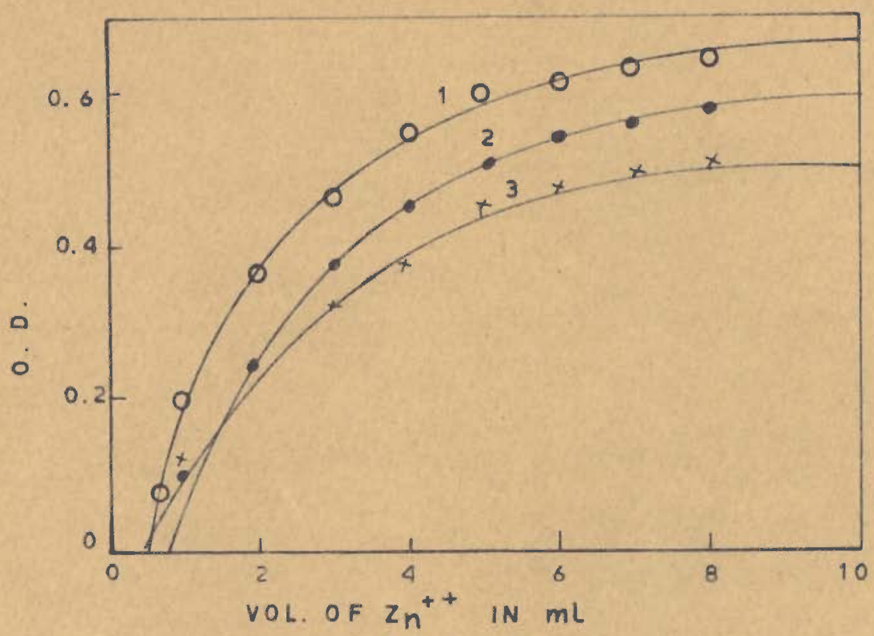


FIG. 48

SLOPE RATIO METHOD

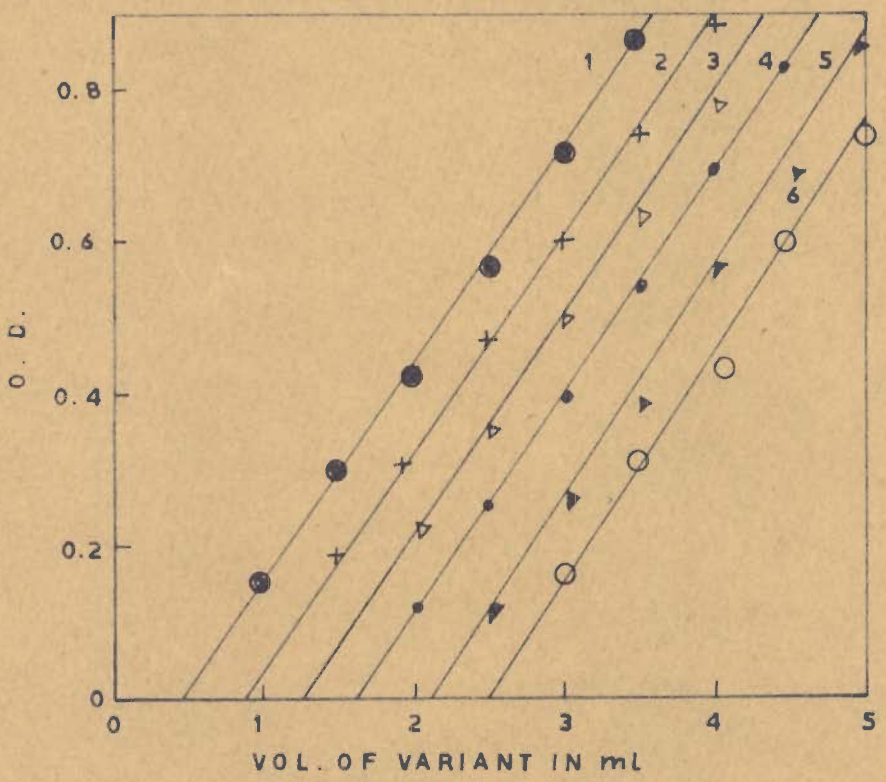


FIG. 49 _ Zn^{++} + p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL

Stability constant -

Consider the dissociation of Zn complex as

$$ZnR \rightleftharpoons Zn + R$$

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

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

where C is the total concentration of the complex in moles/litre. α is the degree of dissociation, the stability constant is given by

$$K_s = \frac{C\,(1-\alpha)}{C\alpha \times \alpha c} = \frac{1-\alpha}{C\alpha^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The value of α was obtained from the relationship,

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

where E_m - is the maximum extinction obtained from the horizontal portion of the curve. E_s is the observed absorption corresponding to the stoichiometric molar ratio of the ligand to zinc.

Data from Fig. 47 curve 1, table No.38 were used to investigate stability constant.

$$E_m = 0.57; \; E_s = 0.50; \alpha = 0.12; \; C = 2.08 \times 10^{-4} M$$

By putting the value on above equation, the value of

$$K_s = 29 \times 10^5$$

The change in free energy of the complex was calculated from the relation,

$$-\Delta F^0 = RT \ln K$$

where the terms have their usual significance. In this system the value of F works out to be -7.49 Kcals/mole at 25^{o}. The reaction is accompanied with a considerable decrease of free energy at room temperature indicating the spontaneous nature of complex formation.

Chemical analysis -

100 cc of 0.002M zinc chloride was added to an equal volume of 0.002M reagent in acetonitrile. The resulting bluish green ppt. was washed with acetonitrile and dried under vacuum over calcium chloride.

Decomposition point - $227^{o}C$.

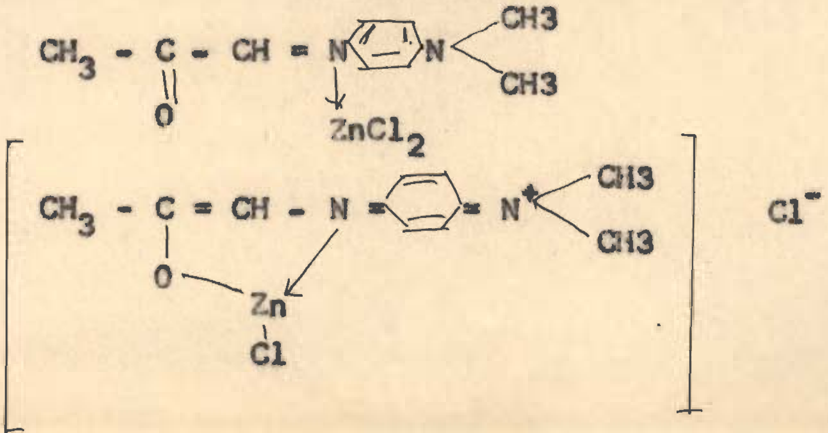
Zinc was estimated in the complex, gravimetrically as zinc Pyrophosphate.

The results of the analysis are as follows :-

Calculated	Found
Zn - 20.03; Cl-21.75;	Zn-19.98; Cl-20.87;
C - 40.05; H-4.29;	C-40.87; H-4.12;
N - 8.58 and	N- 8.34 and
O - 4.90 (By difference)	O- 5.82 (By difference)

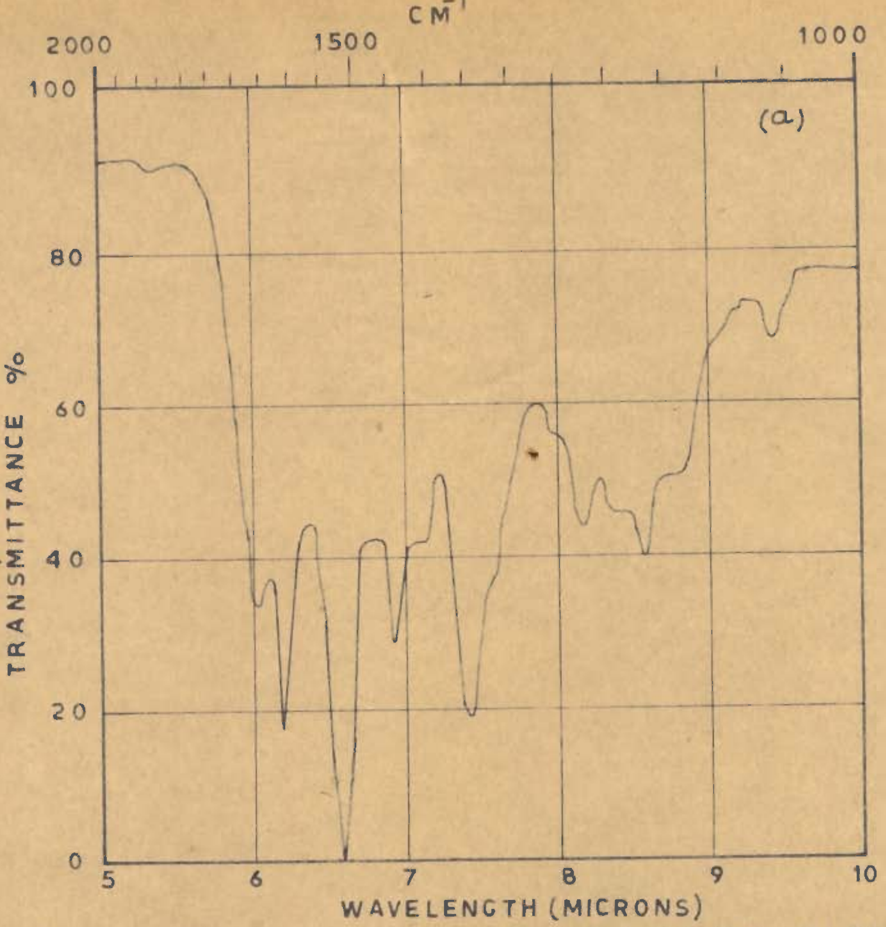
Nature of the complex -

Zinc chloride is the Lewis acid and likewise forms 1:1 chelate with the anil. The following structure for such type of coordinated complex may be assigned :



In this complex also there is a lowering of frequency of $>C=O$ and $-CH=N$ from 1700 to 1675 cm^{-1} and 1600 to 1580 cm^{-1} respectively (Fig. 50). This lowering suggest that these two groups are the centres of interaction for complex formation.

The fact that chloride ion exists outside the coordinating sphere is confirmed by the appearance of the white ppt. on adding ethanolic solution of silver nitrate to the isolated complex.



p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL

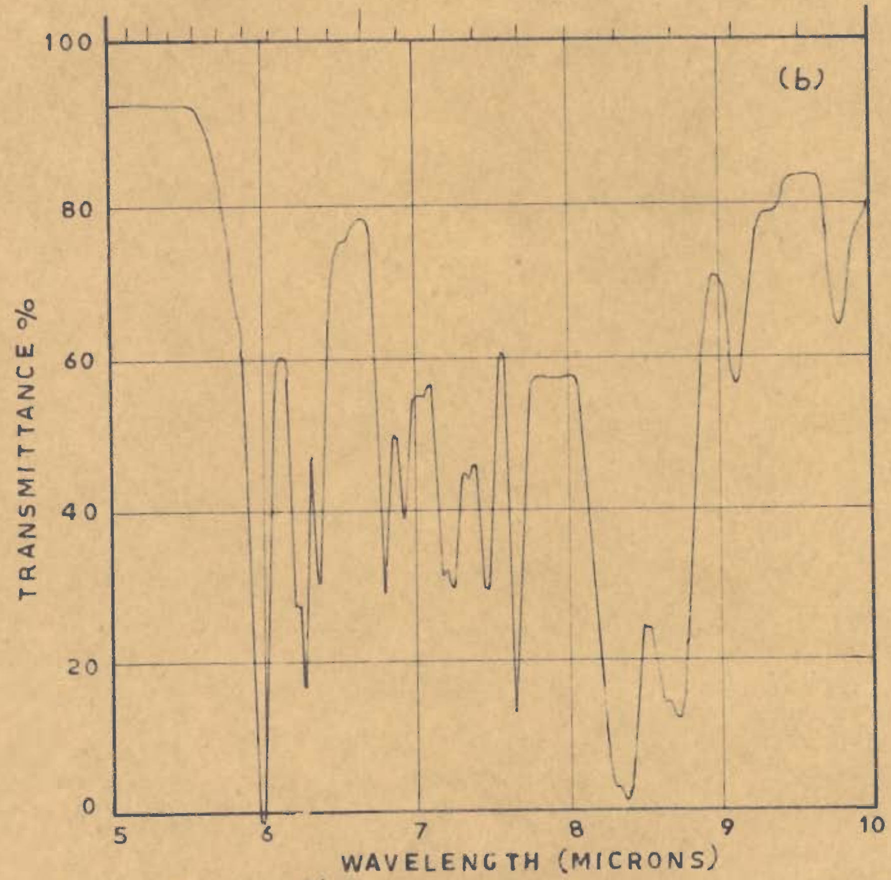


FIG. 50 _ Zn^{++}- p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL COMPLEX

Composition of cadmium Iodide - p- dimethyl amino anil of methyl glyoxal complex in Acetonic medium :-

Vosburgh and Cooper's method was employed for determining the number of complexes formed during chelation as well as to select a suitable wave-length for employing Job's and other spectrophotometric methods. Mixtures of different proportions (4:3, 3:2, 3:1, 2:1 and 1:1) of cadmium Iodide and the reagent were prepared. There was a sharp colour change in the system, showing bathochromism and hence chelation. Two maxima were obtained at 400 and 530 mu respectively. The max. of the ligand as a blank was found at 400 mu. So it may be assumed that 400 mu is the maxima due to the excess of ligand - present in certain mixtures. Hence 530 mu was choosen as the wave-length to study the composition and to calculate other thermodynamic data of the chelate. At this wave-length there was a marked difference in absorbances between the mixtures and that of the ligand.

Table No. 42

Vosburgh and Cooper's method

concentration of cadmium Iodide = 0.714×10^{-3}M
concentration of ligand = 0.714×10^{-3}M

Fig. 51

wave length mu	Ratio of ligand to cadmium iodide 4:3	3:2	3:1	2:1	1:1
325	0.30	0.24	0.14	0.05	0.90
350	0.09	0.12	0.05	0.03	0.82
375	0.27	0.22	0.11	0.06	0.78
385	0.45	0.35	0.25	0.11	0.72
400	0.62	0.55	0.45	0.28	0.65
415	0.60	0.52	0.40	0.26	0.62
425	0.58	0.50	0.40	0.23	0.60
450	0.48	0.36	0.27	0.13	0.53
475	0.20	0.15	0.10	0.03	0.30
500	0.10	0.08	0.05	0.02	0.18
520	0.25	0.27	0.17	0.10	0.35
530	0.40	0.35	0.33	0.22	0.45
540	0.38	0.32	0.30	0.20	0.40
550	0.35	0.31	0.25	0.17	0.39
575	0.20	0.15	0.12	0.01	0.23
600	0.05	0.02	0.02	0	0.20
625	0.04	0.0	-	-	0.17

Stoichiometry of the complex :-

Job's method of continued variation was employed to determine the composition of the violet complex. Equimolecular solutions of cadmium Iodide and the reagent were mixed and optical density measured at three different wave-lengths i.e. 520 mu 530 mu and 540 mu respectively. The observations are given in the following tables:

Table No. 43

Job's method Set No. 1

concentration of cadmium iodide = 1.0×10^{-3}M
concentration of ligand = 1.0×10^{-3}M
Total volume = 10.0 cc

wave length - 520 mu w ave length - 530 mu

Vol.of CdI_2 cc	Vol.of ligand cc	O.D. Mixt. c	O.D. ligand a	Difference (c-a)	O.D. Mixt. c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.68	0.60	0.08	0.72	0.62	0.10
2.0	8.0	0.66	0.50	0.16	0.70	0.52	0.18
3.0	7.0	0.635	0.40	0.235	0.69	0.44	0.25
4.0	6.0	0.60	0.32	0.28	0.64	0.34	0.30
5.0	5.0	0.59	0.27	0.325	0.62	0.29	0.33
6.0	4.0	0.55	0.25	0.30	0.59	0.29	0.30
7.0	3.0	0.47	0.22	0.25	0.50	0.25	0.25
8.0	2.0	0.375	0.20	0.175	0.37	0.22	0.15
9.0	1.0	0.255	0.18	0.075	0.25	0.20	0.05

Fig. 53 curve 1 Fig. 52 curve 1

Table No. 44

Wave length = 540 mu

Vol. of CdI_2 cc	Vol. of ligand cc	O.D. Mixture c	O.D. ligand a	Difference (c-a)
1.0	9.0	0.62	0.57	0.05
2.0	8.0	0.57	0.48	0.09
3.0	7.0	0.55	0.40	0.15
4.0	6.0	0.53	0.30	0.23
5.0	5.0	0.50	0.20	0.30
6.0	4.0	0.45	0.20	0.25
7.0	3.0	0.355	0.18	0.175
8.0	2.0	0.27	0.17	0.10
9.0	1.0	0.21	0.16	0.05

Fig.54 curve 1

Set No. 2 -

Concentration of cadmium Iodide =0.90×10^{-3}M

Concentration of ligand =0.90×10^{-3}M

Total volume =10.0 cc

Fig. 52,53,54 Curve 2

Set No. 3 -

Concentration of cadmium Iodide =0.83×10^{-3}M

Concentration of ligand =0.83×10^{-3}M

Total volume = 10.0 cc

Fig. 52,53,54 curve 3

JOB'S METHOD

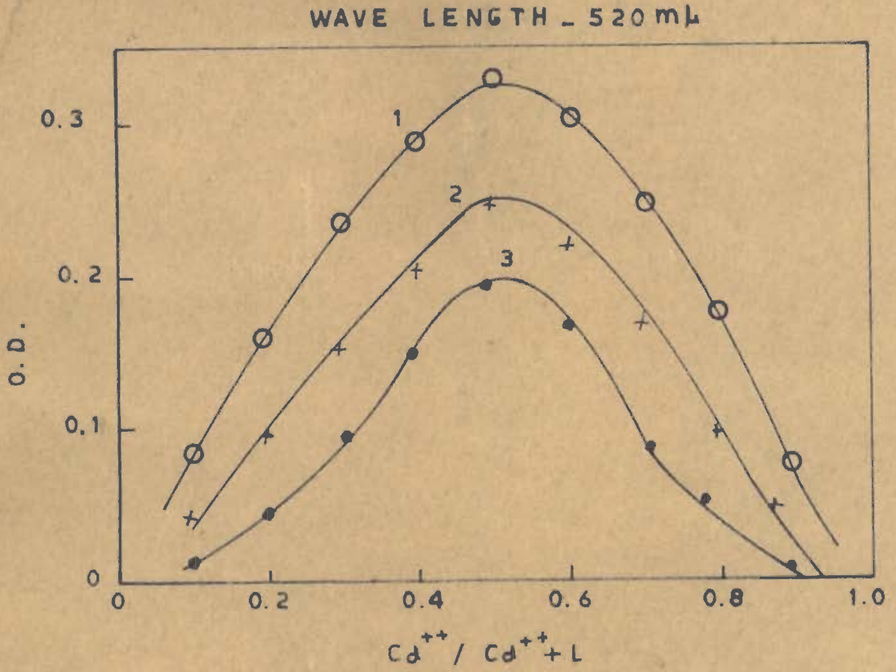


FIG. 53

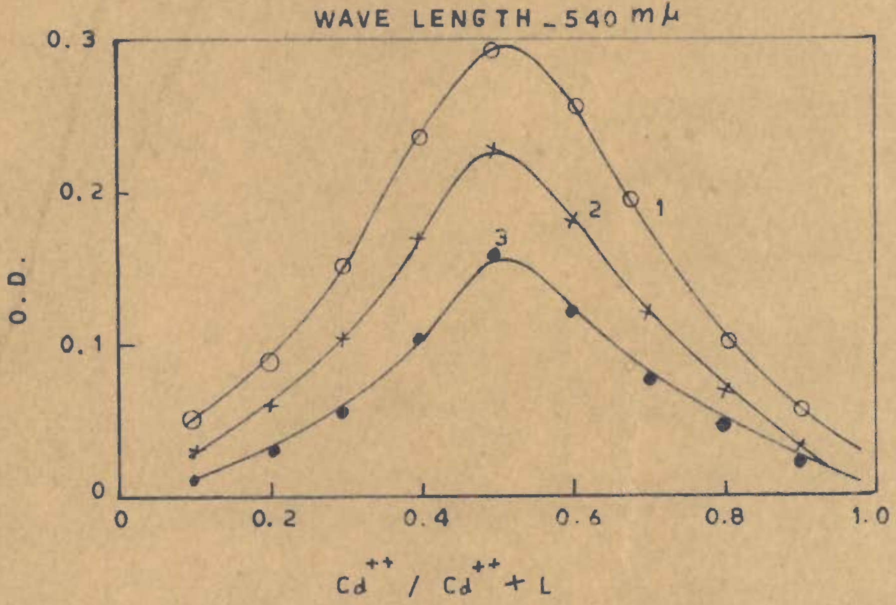


FIG. 54

Molar ratio method :-

To confirm the results of Job's method molar ratio method was performed. Two set of mixtures were prepared in which one of the components is varied while the other kept constant and vice versa. Optical densities of all the mixtures were measured and a plot was drawn between O.D. and the volume of the variant. Since there is a dissociation in the reagent itself, so the curve reached to saturation which was approximately parallel to the axis in which the volume of the component was varied. On extrapolation of the two curves point of interaction gave molar ratio of the two compound approximately.

Table No. 45

Molar ratio method

Set No. 1 - concentration of ligand = 1.0×10^{-3}M
concentration of CdI_2 = 1.0×10^{-3}M
total volume = 15.0 cc

Set No. 2 - concentration of ligand = 0.90×10^{-3}M
concentration of CdI_2 = 0.90×10^{-3}M
total volume = 15.0 cc

		Set No. 1		Set No. 2	
Volume of CdI_2 cc	Volume of ligand cc	O.D. at 530 mu	O.D. at 520 mu	O.D. at 530 mu	O.D. at 520 mu
5.0	1.0	0.15	0.12	0.05	0.05
5.0	2.0	0.26	0.26	0.16	0.12
5.0	3.0	0.36	0.36	0.28	0.20
5.0	4.0	0.45	0.43	0.36	0.30
5.0	5.0	0.50	0.46	0.42	0.36
5.0	6.0	0.53	0.48	0.45	0.39
5.0	7.0	0.54	0.49	0.45	0.40
5.0	8.0	0.56	0.50	0.47	0.40
5.0	9.0	0.56	0.51	0.48	0.42
		Fig.55 curve 1	Fig.56 curve 1	Fig.55 curve 2	Fig. 56 curve 2

Slope ratio method :-

The stoichiometry arrived at by the aforesaid methods was further confirmed by slope ratio method. The concentration of the component which was kept is constant was diluted 10 times so that the optical density might be only due to the component varied. Optical densities for the two sets were measured and plotted against the volume of the variable component. The slope of the two curves gave the composition as 1:1.

Table No. 46

concentration of ligand = 1.66×10^{-3}M
concentration of cadmium iodide = 0.83×10^{-3}M
total volume = 12 cc

Volume of CdI_2 cc	Volume of ligand cc	O.D. at 520 mu	O.D. at 530 mu	O.D. at 540 mu
1.0	2.0	0.10	0.11	0.10
2.0	2.0	0.15	0.18	0.15
3.0	2.0	0.18	0.25	0.17
4.0	2.0	0.19	0.30	0.17
6.0	2.0	0.30	0.43	0.23
8.0	2.0	0.40	0.55	0.38
10.0	2.0	0.55	0.70	0.52
	Fig. 57 curve	(3)	(1)	(5)

MOLAR RATIO METHOD

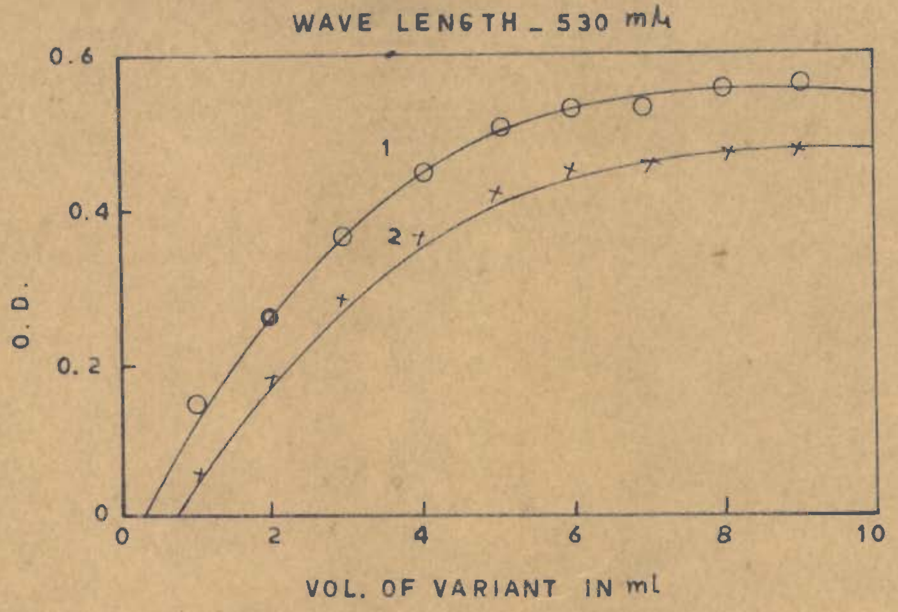


FIG. 55

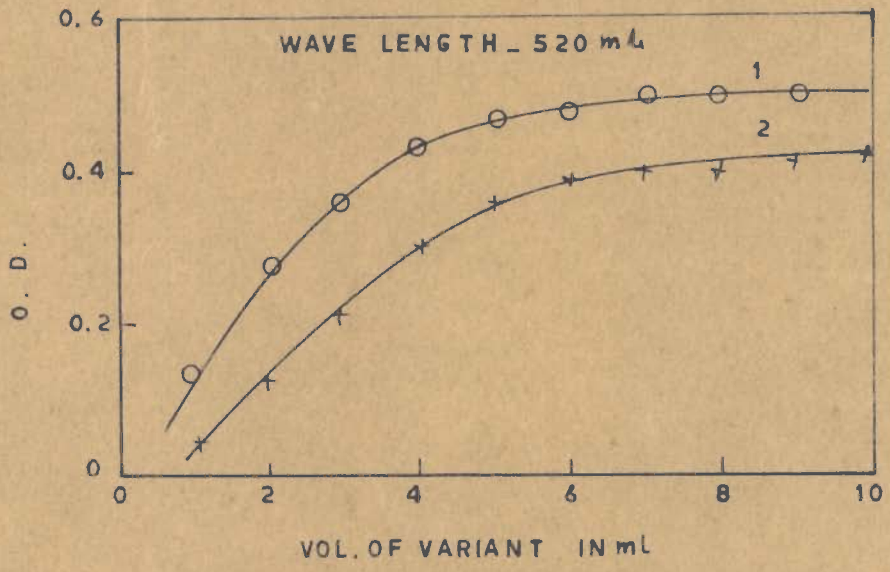


FIG. 56

SLOPE RATIO METHOD

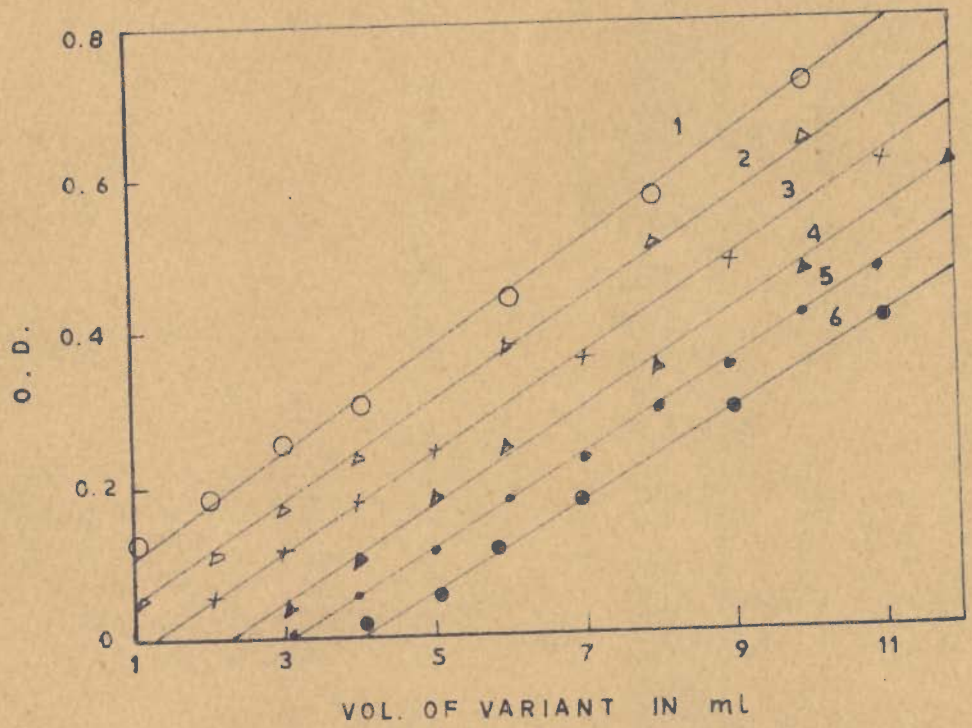


FIG. 57

Table No. 47

Set No. 2 -

concentrationof ligand = 0.83×10^{-3}M

concentration of cadmium iodide = 1.66×10^{-3}M

total volume = 12 cc

volume of CdI_2 cc	volume of ligand cc	O.D. at 520 mu	O.D. at 530 mu	O.D. at 540 mu
2.0	1.0	0.10	0.11	0.09
2.0	2.0	0.12	0.18	0.11
2.0	3.0	0.17	0.24	0.15
2.0	4.0	0.24	0.26	0.17
2.0	6.0	0.35	0.37	0.28
2.0	8.0	0.47	0.50	0.40
2.0	10.0	0.60	0.62	0.52
	Fig. 57 curve	(4)	(2)	(6)

Stability constant of cadmium -p-dimethyl amino anil of methyl glyoxal complex :-

The mixtures of the three methods were kept for about one week and still their optical densities remained same. This gave an indication that the chelate was a stable one. Stability constant of the complex was determined by mole ratio method (loc. cit.).

The equation for 1:1 complex may be written as

$$CdR \rightleftharpoons Cd + R$$

$$C \quad 0 \quad 0 \text{ (Initial concentration)}$$

$$C(1-\alpha) \quad \alpha C \quad \alpha C \text{ (Equilibrium concentration)}$$

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

$$K_s = \frac{C(1-\alpha)}{\alpha C \times \alpha C} = \frac{1-\alpha}{C\alpha^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The value of α was obtained from the 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 all the cadmium is converted to the complex. E_s is the observed extinction of the stoichiometric molar ratio of the reagent to cadmium in the complex. Data from Set I (vide Table No.45 Fig.55) were used to calculate the stability constant.

$E_m = 0.56$; $E_s = 0.50$; $\alpha = 0.10$, and

$C = 0.33 \times 10^{-3} M$

$\therefore K_s = 9 \times 10^6$

The standard free energy of formation of the complex was calculated from the following relationship:

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

where ΔF, R, and T have their usual meaning.

In this system the value of ΔF comes out to - 9.54 Kcals/mole at 25°C. The reaction is accompanied with a considerable decrease of free energy at room temp. indicating the spontaneous nature of the complex formation.

Chemical analysis :-

By mixing (0.01M each) of acetonitrilic solutions of the reactants, a bluish green ppt. was obtained. It was washed with acetonitrile and dried under vacuum over calcium chloride.

Decomposition point = 240°C.

Cadmium was estimated in the complex (loc.cit.) gravimetrically as cadmium molybdate.

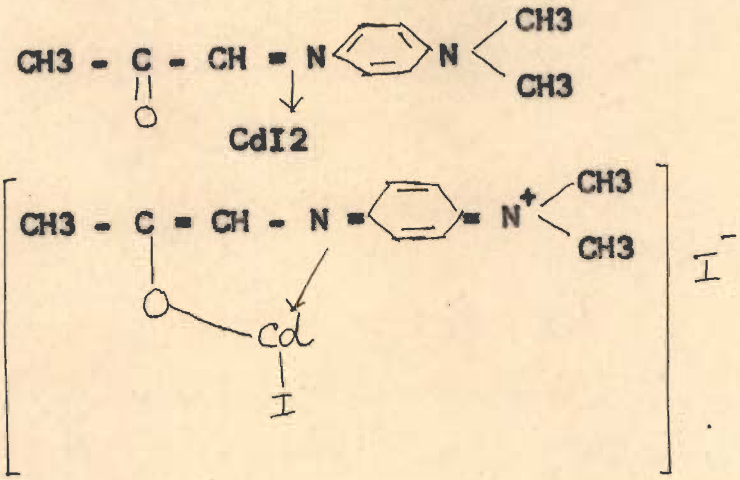
The results of chemical analysis are as follows :

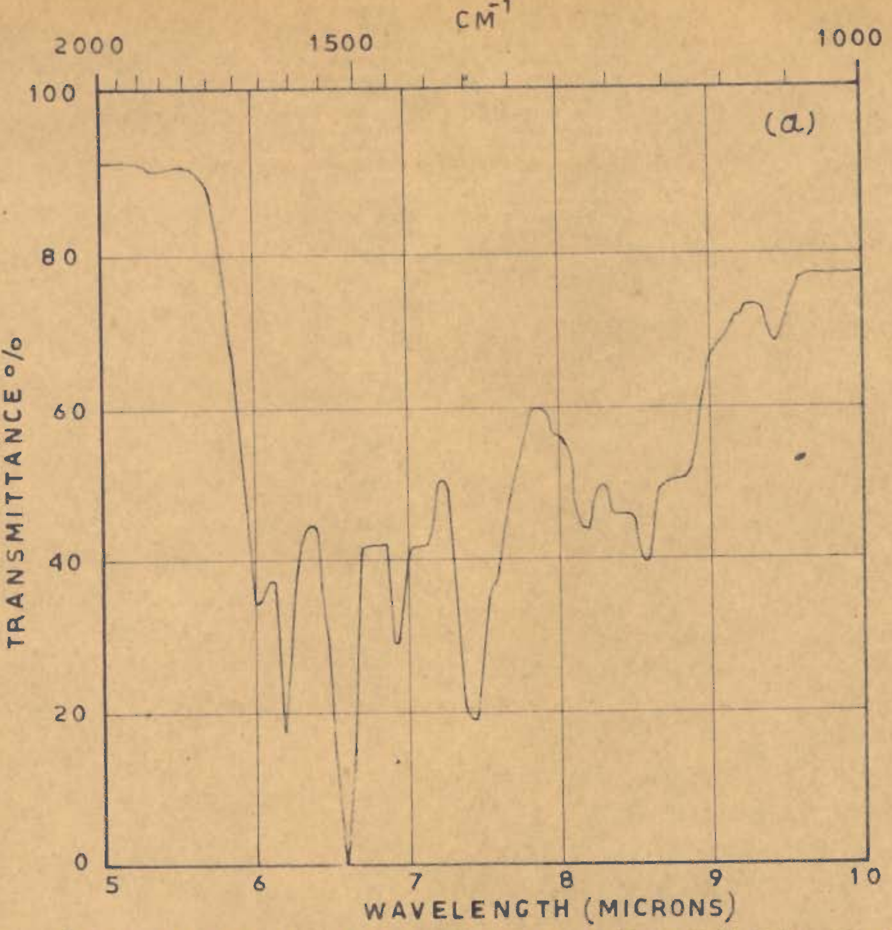
Calculated	Found
Cd - 20.20; I - 45.63;	Cd - 19.87; I - 44.78;
C - 23.73; H - 2.51;	C - 23.37; H - 2.41;
N - 5.03 and	N - 4.89 and
O - 2.90 (By difference)	O - 4.68 (By difference)

Nature of the complex :-

Two donor groups $>C = O$ and - $CH=N$ are present in the p-dimethyl amino anil of methyl-glyoxal. During the interaction of CdI_2 and the ligand, M-L bonding is created which will naturally cause a lowering of the stretching frequencies of the above groups. It is quite evident that much lowering takes place in the spectrum of the chelate Cd(II) - p-dimethyl amino anil of methyl glyoxal (1680 and 1560 Cm^{-1} respectively Fig. 58). The quinonoism in the chelate can be accounted for due to formation of a singlet from the doublet of the ligand around 830 cm^{-1} in p-disubstituted skeleton.

An alcoholic solution of the isolated complex produces a yellowish precipitate of AgI on treatment with ethanolic $AgNO_3$. This is due to ionic iodine and not the covalent one. On the basis of the above evidences the following structure may be assigned to the complex.





p-DIMETHYL AMINO ANIL OF METHYL GLYOXAL

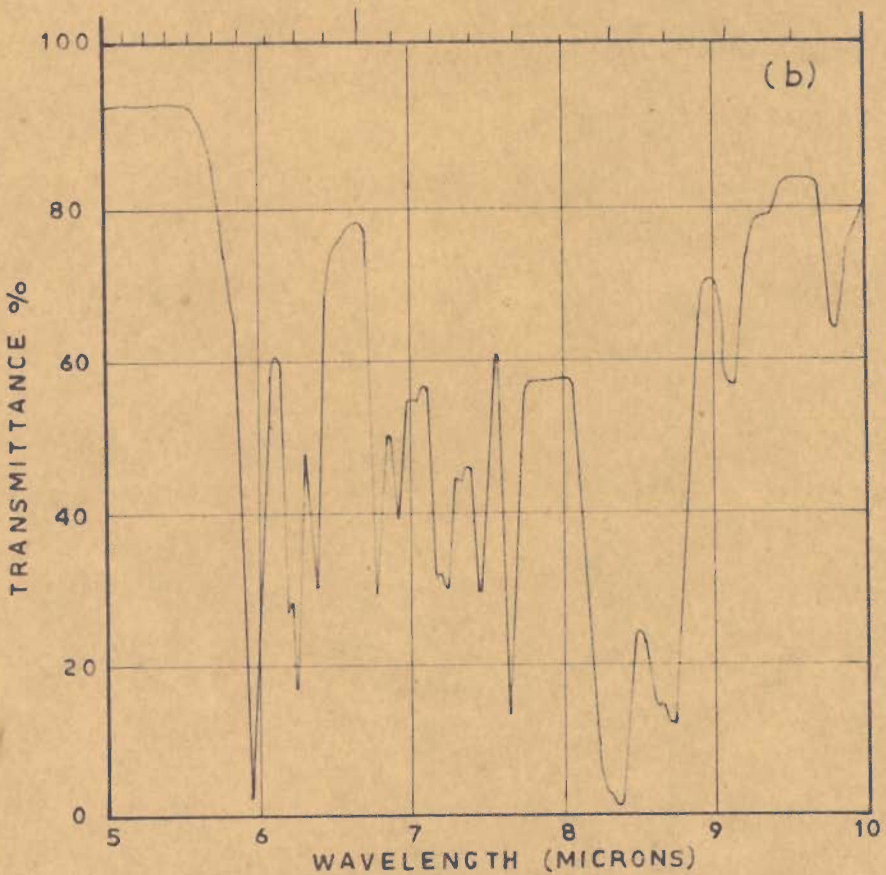


FIG. 58 _ Cd^{++}- p- DIMETHYL AMINO ANIL OF METHYL GLYOXAL COMPLEX

CHAPTER IV

(i) Spectrophotometric studies on the adsorption of anils by silica, alumina, aluminium silicate, ferric silicate and aluminium molybdate gels from non polar solvents.

(ii) Availability of pores of silica gel to the metal complexes of anils.

INTRODUCTION :-

Adsorption studies with organic compounds as absorbates are befret with many difficulties, which assume complexities of much higher magnitude when aqueous solvents are repleced by non-aqueous ones. The experimental results have, therefore, to be examined more critically before any attempt is made to fit in the experimental data in some of the well known isotherms equations.

Organic substances employed as adsorbates can be roughly divided into three heads:-

(i) fatty acids (ii) dyes and (iii) compounds whose adsorbality is dependent on their constitution. To the latter class may be added compounds which undergo structural changes, e.g. bathochromic effect, when brought in contact with the adsorbent.

Adsorption of dyes has been most hotly pursued by surface chemist because of their practical utility in the dyeing industry. In most cases adsorption of dyes has been corelated to their basicity. For example, Birutovich(1) found that the adsorption in the case of dyes is a function of their basicity. It has thus been observed that adsorption is decreased by lower pH for methylene blue and bismarck brown, but increases for picric acid and water blue. Yajnik et al(2) studied the effect on adsorption from solution and during their investigation found that adsorption of various acids and basic dyes was greatest for alumina and less on silica gel.

The adsorbents usually employed are silica and the hydrousoxides gels. The latter owe their importance to their use as mordants or as materials in chromatographic analysis. Pelet and Jolivet(3) Bancroft(4); Liechti and suids(5-6) made quantitative observations on the adsorption of dyes in presence of anions and cations by the hydrous oxides and demonstrated that readily adsorbed anions such as sulphate and phosphate cut down the adsorption of acid dyes and readily adsorbed cations such as magnesium and calcium increase their adsorption.

Giles, Ealson and McKay(7) studied the mechanism of adsorption of cationic dyes by alumina. In this study a range of cationic dyes was applied to alkaline chromatographic alumina powder and the nature of adsorption was interpreted from the shape of the adsorption isotherms. Mashai and Koizumi(8) studied the isotherms of Rhodamine 6G(I) and Rhodamine B(II) by silica gel. in darkness and under the irradiation of light. They found that the amount of adsorption decreases with irradiation only in the case of Rhodamine 6G(I).

Brooks(9) studied the mechanism of methylene blue dye adsorption on silicieous minerals found in the petroleum reservoir formations. According to him in the case of clays the saturation dye adsorption capacity may be attributed to two mechanisms: (i) cation exchange resulting from isomorphous substitution in the aluminosilicate lattice and (ii) an adsorption mechanism which might be either physical (vander Weals) adsorption or chemisorp-

-tion (hydrogen bonding with the surface Si-OH and Al-OH of the alumino silicate lattice). On the other hand the dye adsorption on silica may be due to either physical or chemisorption mechanism.

Adsorption of fatty acids was studied at length by Holmes and McKelvey(10) using toluenic solution of fatty acids on silica. They found that the adsorption was greater in shorter chain than in longer chain compounds. Bartell obtained the similar results with solution in carbontetrachloride(11-28). These results do not follow Traube's rule which states that the adsorption in homologous series increases rapidly as the hydrocarbon chains are lengthened. It appears that the rule is very well obeyed in aqueous solution but is reversed in organic solvents.

Organic compounds such as amines hydroxy acids, alkaloids etc. have given interesting results on the basis of adsorption studies. Bhatnagar et al(29); Gyani(30) Malquori(31) and Tsai(32-34) studied the adsorption of various alkaloids and picric acid on silica gel and found that the adsorption of alkaloids followed Freundlich while the picric acid Langmuir isotherms. Dobay(35), Gyani(36), Bartell(37), Brown(38), Stober(39) and Aktavova(40-45) studied the adsorption of aliphatic and aromatic amines on silica and alumina gel, and found that in some cases Langmuir isotherms were obtained while others where best explained by B.E.T. equation. A study of the adsorption of eighteen organic compounds of various kinds by silica gel was undertaken by Grette(46). From this study it was concluded that adsorption was proportional to the basic strength of this compound. pH of the solution was also found to influence the adsorption of acids and bases(47-52). Blank, Rosingston and Weinland(53) studied the adsorption of organic compounds on portland cement and found that in some cases Langmuir while in others Freundlich isotherms are followed.

Numerous examples of constitutive influences in adsorption have been pointed out by various workers. Amongst them may be mentioned Freundlich(54), Miller(55), Bartell(56), Linner and Gortner(57-59). From Miller's (loc. cit.) data it was concluded that the position of the hydroxyl and amino groups in hydroxy and amino benzoic acids had a marked effect on adsorption. The adsorption values were greatest when these groups were in the ortho position, smallest in the meta position and intermediate in the para position. This implies that the adsorption depends largely on the nature and arrangement of the atoms or groups in the molecule, certain groups favouring and others opposing to the adsorption phenomenon. These facts may be indicative of the molecular orientation during adsorption.

From the point of view of constitutive influences, the class of compounds known as anils have not so far been studied. It has been reported that these compounds due to the existence of bathochromic effect in them, undergo complex ion formation with Lewis acids. They also develop blue violet colour on silica gel from their solutions in benzene. As to how this change takes place is yet to be investigated. Investigation in this direction can prove to be fruitful.

The present chapter deals with the adsorption of phenacylidene aniline, p-dimethyl amino anil of phenylglyoxal and p-dimethyl amino anil of phenylglyoxal nitrile in the solvents (benzene, xylene, toluene, carbon tetrachloride and dioxane) on a number of inorganic gels namely silica, Alumina, aluminium silicate, ferric silicate and Al-molybdate.

EXPERIMENTAL

MATERIALS -

(a) Adsorbents :-

(i) Silica (ii) Alumina (iii) Aluminium silicate (iv) Ferric silicate and Aluminium molybdate gels.

(b) Solvents :-

All chemicals used were from B.D.H. The solvents (Benzene, xylene, toluene, carbontetrachloride and Dioxane) were purified by standard methods(60) and obtained free from moisture.

(c) Adsorbates :-

Stock solutions of different anils, viz. phenacylidene aniline, p-dimethyl amino anil of phenyl glyoxal and p-dimethyl amino anil of phenylglyoxal nitrile were prepared as described previously (Chapter II) in different solvents.

In order to study Beer's Law, solutions of different concentration of anils were prepared. It will be seen from the Table -1 that the optical density (O.D) is directly proportional to the concentration.

Table No. -1

Verification of Beer's Law.

O.D. at different dilutions of the anils

concn. of phenacylidene aniline	O.D. at 350 mu of phen. aniline	concn. of p-dimethyl amino anil of phenylglyoxal	O.D. at 425 mu of p-dimethyl amino anil of phenylglyoxal	concn. of p-dimethyl amino anil of phenylglyoxal nitrile	O.D. at 525 mu of p-dimethyl amino anil of phenyl glyoxal nitrile
1.6×10^{-3}M	1.0	1.0×10^{-3}M	0.80	4×10^{-4}M	0.54
1.6×10^{-4}M	0.80	2.5×10^{-4}M	0.72	1.9×10^{-5}M	0.30
6×10^{-5}M	0.50	4.0×10^{-5}M	0.52	5.0×10^{-5}M	0.37
7×10^{-5}M	0.55	9.02×10^{-5}M	0.57	7.0×10^{-5}M	0.40
10×10^{-5}M	0.60	10×10^{-5}M	0.59	9.0×10^{-5}M	0.45

2. Apparatus and technique -

Bausch and Lomb 'spectronic 20' was used for absorption measurements.

Procedure -

To study the adsorption of anils 25.0 ml. solution of the known concn. of anils were taken in several 100 ml. flasks containing 1.0 g. of gel. The flasks were shaken well and kept at room temperature for several hours. The supernatant liquids were taken out, centrifuged to allow the gel settle and concentration of anils in the supernatant liquid determined spectro photometrically. The wave length used were 350, 425 and 525 mu respectively for phenacylidene aniline, p-dimethyl amino anil of phenylglyoxal and p-dimethyl amino anil of phenylglyoxal nitrile. By substracting the values of equilibrium concentration from the values of the original concentration, adsorption was calculated.

The results are summarised in the following tables. Curves were plotted between equilibrium concentration (c_s) and the millimoles of anil adsorbed per gm. (x/m) of the adsorbent.

Table No. 2

Maxima of anils.

O.D. of the anils at different wave lengths

Wave length mu	Absorption for $5.0x10^{-4}$M phenacylidene anilene	Wave length mu	O.D. of $5.0x10^{-4}$M p-dimethyl amino anil of phenylglyoxal	Wave length mu	O.D.of ($5.0x10^{-4}$M) p-dimethyl amino anil of phenylglyoxal nitrile
325	0.91	325	0.78	325	0.70
350	1.90	350	0.96	350	0.72
375	1.26	375	1.0	375	0.76
400	0.90	400	1.20	400	0.80
425	0.85	425	1.50	425	0.84
450	0.70	450	1.20	450	0.92
475	0.65	475	1.00	475	0.96
500	0.60	500	0.90	500	1.0
525	0.52	525	0.83	525	1.20
550	0.45	550	0.73	550	1.0
575	0.40	575	0.61	575	0.90
600	0.38	600	0.54	600	0.74
625	0.32	625	0.43	625	0.60
650	0.27	650	0.37	650	0.52
675	0.24	675	0.31	675	0.47
700	0.21	700	0.27	700	0.39

Table No. 3

Solute - phenacylidene aniline
Gel - Al-molybdate
Solvent- carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq. concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.23	0.74	0.83	1.35
2.00	1.05	0.72	1.0	1.38
1.66	0.90	0.70	1.1	1.42
1.42	0.80	0.70	1.2	1.42
1.25	0.60	0.66	1.6	1.50
1.00	0.40	0.62	2.5	1.61
0.83	0.30	0.56	3.3	1.78
0.71	0.20	0.40	5.0	2.50

a = 5.93
b = 0.87 Fig. 1(1)

Table No. 4

Solute -phenacylidene aniline
gel -ferric silicate
solvent -carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq. concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.50	2.30	2.0	0.43
1.42	0.40	2.05	2.5	0.48
1.25	0.30	1.90	3.33	0.52
1.00	0.20	1.60	5.0	0.62
0.83	0.10	1.48	10.0	0.67
0.71	0.10	1.22	10.0	0.81
0.62	0.10	1.05	10.0	0.95

a = 4.50
b = 3.33 Fig. 2 (1)

Table No. 5

Solute - phenacylidene aniline
Gel - Al-silicate
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.50	2.32	2.0	0.43
1.42	0.40	2.02	2.50	0.50
1.25	0.30	1.95	3.33	0.51
1.00	0.25	1.52	4.0	0.65
0.83	0.20	1.25	5.0	0.80
0.71	0.20	1.00	5.0	1.0

a = 1.66
b = 5.00 Fig. 3(1)

Table No. 6

Solute - phenacylidene aniline
Gel - silica
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.40	2.52	2.50	0.39
1.42	0.30	2.25	3.33	0.44
1.25	0.25	1.99	4.0	0.50
1.00	0.20	1 .61	5.0	0.61
0.833	0.15	1.38	6.66	0.72
0.71	0.10	1.22	10.0	0.81
0.62	0.08	1.04	12.50	0.96

a = 7.13
b = 2.56 Fig. 4(1)

○ 1. PHENACYLIDENE ANILINE.

× 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL

● 3. p DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE

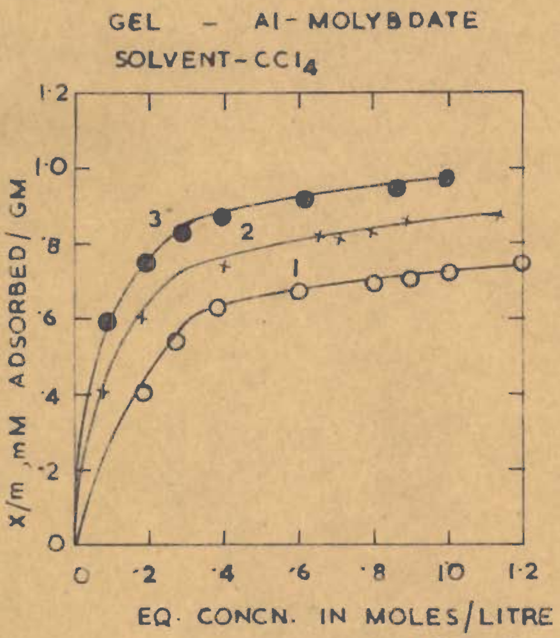

GEL – Al-MOLYBDATE
SOLVENT-CCl_4

FIG. 1

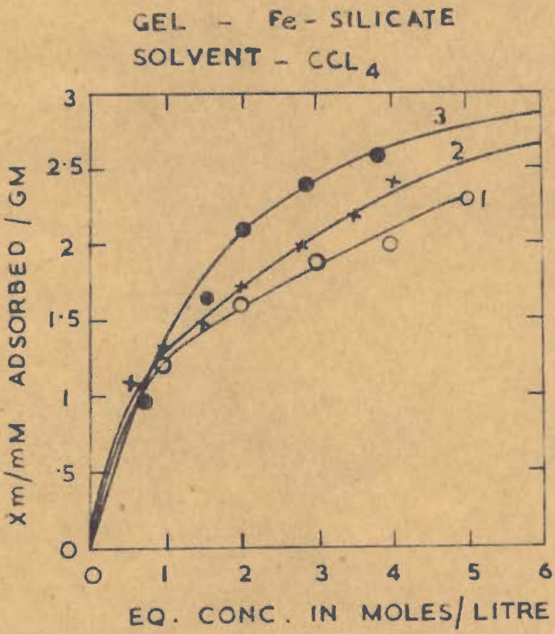

GEL – Fe-SILICATE
SOLVENT – CCL_4

FIG. 2

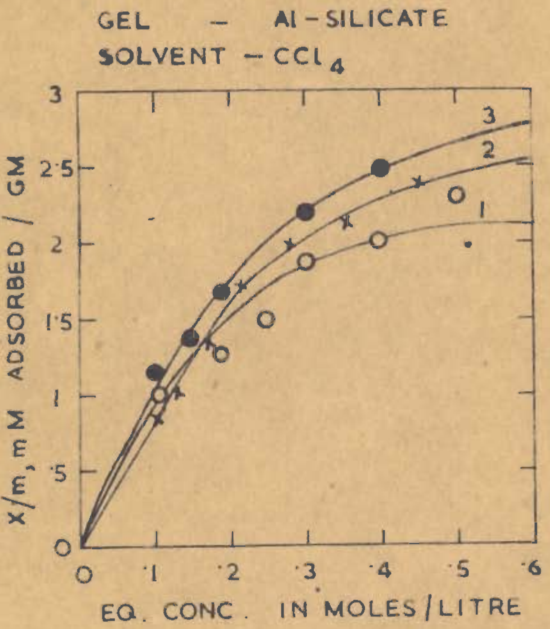

GEL – Al-SILICATE
SOLVENT – CCL_4

FIG. 3

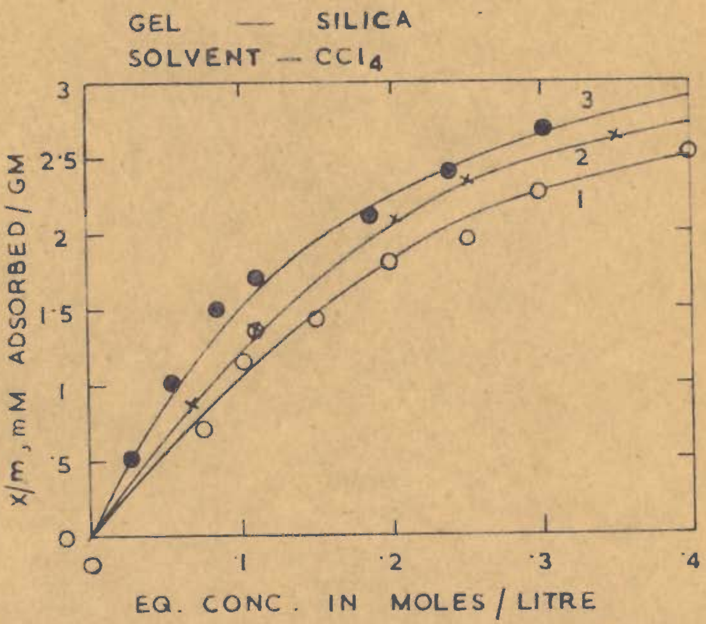

GEL — SILICA
SOLVENT — CCl_4

FIG. 4

Table No. 7

Solute - phenacylidene aniline
Gel - alumina
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$ M	Eq.concn. c_s in moles per litre	x/m millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.50	2.32	2.0	0.42
1.42	0.30	2.22	3.33	0.45
1.25	0.25	2.00	4.0	0.50
1.00	0.20	1.64	5.0	0.60
0.833	0.11	1.38	9.01	0.72
0.71	0.08	1.22	12.50	0.81
0.62	0.07	1.02	14.22	0.98

a = 12.78
b = 2.38 Fig. 5(1)

Table No. 8

Solute - phenacylidene aniline
Gel - silica
Solvent - benzene

Initial concn. $\times 10^{-4}$ M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	m/x
2.50	1.0	3.02	1.0	0.33
2.00	0.70	2.65	1.42	0.37
1.66	0.50	2.34	2.0	0.42
1.42	0.40	2.06	2.50	0.48
1.25	0.30	1.92	3.33	0.52
1.00	0.25	1.50	4.0	0.66
0.83	0.23	1.37	4.34	0.72

a = 2.02
b = 4.54 Fig. 6(1)

Table No. 9

Solute - phenacylidene aniline
Gel - Alumina
Solvent - Benzene

Initial concn. $x10^{-4}M$	Eq.concn. c_s in moles per litre	x/m, milli - moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.34	2.32	0.74	0.43
2.00	0.96	2.08	1.03	0 .48
1.60	0.77	1.85	1.29	0.54
1.42	0.71	1.43	1.40	0.69
1.25	0.64	1.24	1.56	0.80
1.00	0.64	0.90	1.56	1.11
0.83	0.20	0.30	5.0	3.33

a = 4.40
b = 2.50 Fig.7(1)

Table No. 10

Solute - phenacylidene aniline
Gel - Al-molybdate
Solvent - Benzene

Initial concn. $x10^{-4}M$	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	2.0	0.90	0.50	1.11
2.00	1.56	0.87	0.64	1.15
1.66	1.21	0.83	0.82	1.20
1.42	1.05	0.74	1.0	1.35
1.25	0.90	0.75	1.11	1.33
1.00	0.80	0.72	1.25	1.38
0.83	0.70	0.68	1.42	1.47
0.71	0.60	0.60	1.66	1.66

a = 4.40
b = 0.90 Fig. 8(1)

1. PHENACYLIDENE ANILINE.
2. þ-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
3. þ-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

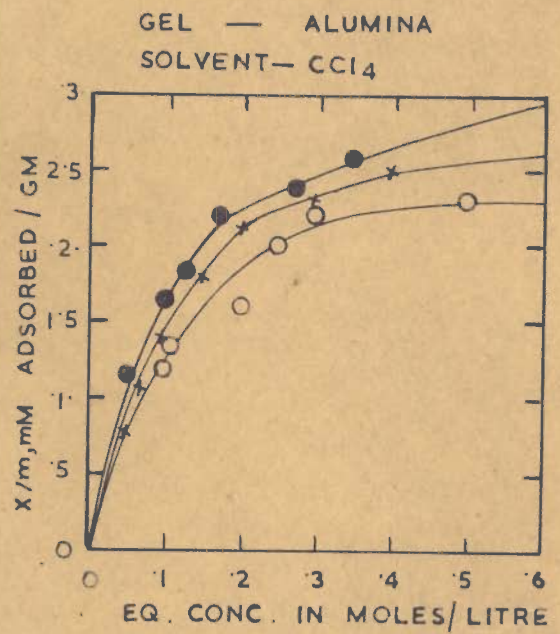

GEL — ALUMINA
SOLVENT— CCl_4

FIG. 5

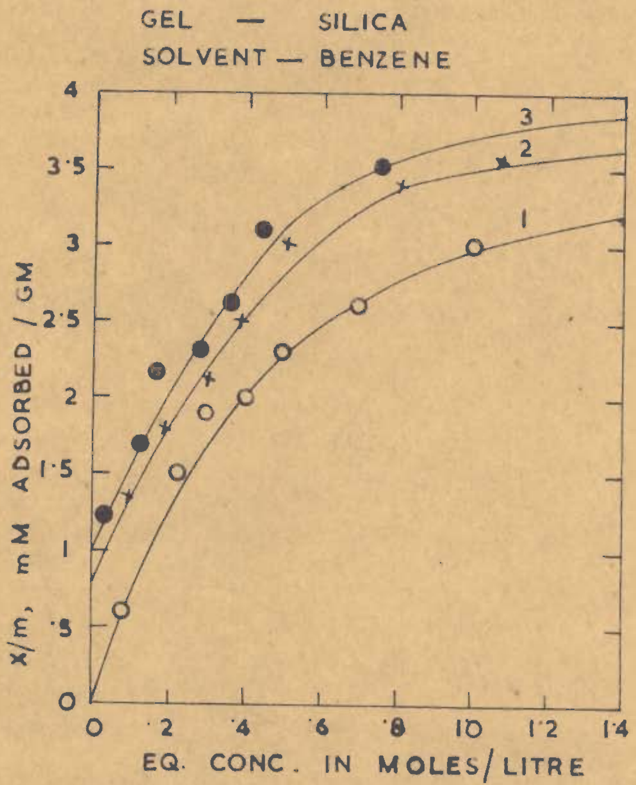

GEL — SILICA
SOLVENT — BENZENE

FIG. 6

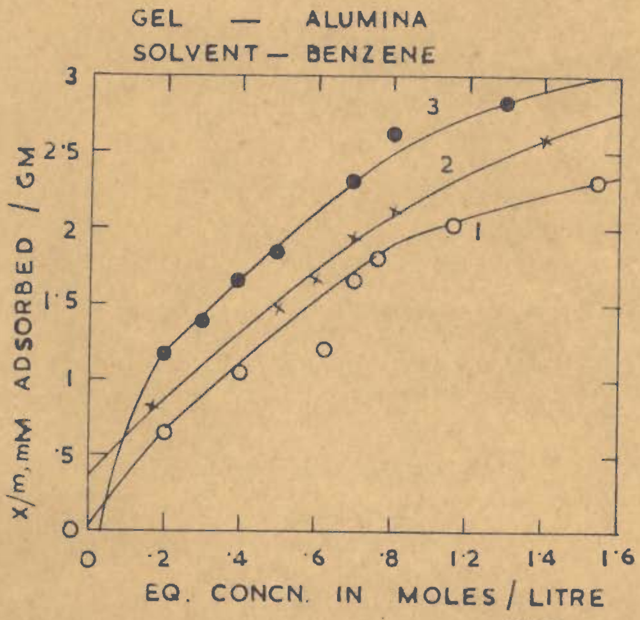

GEL — ALUMINA
SOLVENT — BENZENE

FIG. 7

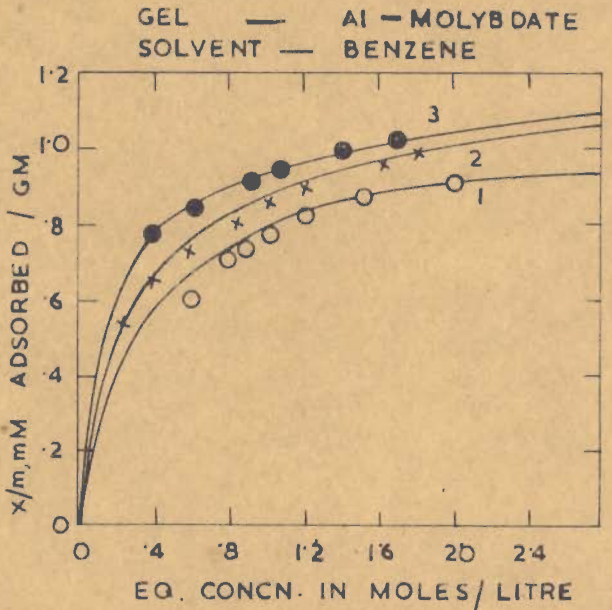

GEL — Al – MOLYBDATE
SOLVENT — BENZENE

FIG. 8

Table No. 11

Solute - phenacylidene aniline
Gel - Fe-silicate
Solvent - Benzene

Initial concn. $\times 10^{-4}$ M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.63	1.80	0.61	0.55
2.00	1.24	1.68	0.80	0.59
1.66	0.85	1.60	1.17	0.62
1.42	0.80	1.22	1.25	0.81
1.25	0.70	1.10	1.42	0.90
1.00	0.60	0.80	1.62	1.25
0.83	0.54	0.70	1.85	1.42

a = 2.35
b = 1.88 Fig. 9(1)

Table No. 12

Solute - phenacylidene aniline
Gel - Al-silicate
Solvent - Benzene

Initial concn. $\times 10^{-4}$ M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.54	2.0	0.64	0.50
2.00	1.24	1.63	0.80	0.61
1.66	0.90	1.54	1.11	0.64
1.42	0.80	1.30	1.25	0.70
1.25	0.60	1.24	1.62	0.80
1.00	0.50	1.02	2.0	0.98
0.83	0.40	0.80	2.50	1.25

a = 1.91
b = 2.04 Fig. 10(1)

Table No. 13

Solute - phenacylidene aniline
Gel - ferric silicate
Solvent - toluene

Initial concn. $x10^{-4}M$	Eq.concn. in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	2.10	0.74	0.47	1.35
2.00	1.80	0.70	0.55	1.42
1.66	1.50	0.68	0.66	1.47
1.42	1.20	0.60	0.83	1.66
1.25	0.90	0.50	1.11	2.0
1.00	0.60	0.40	1.66	2.50
0.83	0.30	0.26	3.33	3.61

a = 8.37
b = 1.17 Fig. 11(1)

Table No. 14

Solute - phenacylidene aniline
Gel - alumina
Solvent - toluene

Initial concn. $x10^{-4}M$	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.50	2.0	0.66	0.50
2.00	1.0	2.0	1.0	0.50
1.66	0.70	1.95	1.42	0.51
1.42	0.60	1.64	1.66	0.60
1.25	0.50	1.53	2.0	0.64
1.00	0.40	1.21	2.50	0.82
0.83	0.28	1.00	3.57	1.0

a = 1.91
b = 2.94 Fig. 12(1)

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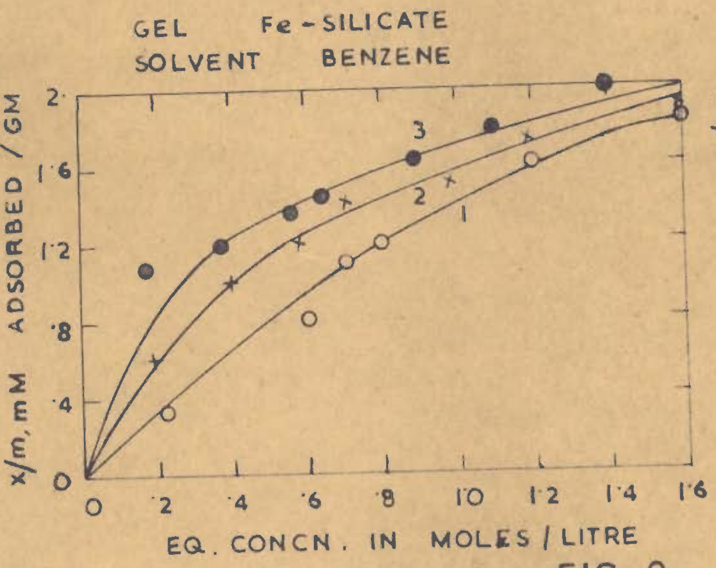

FIG. 9

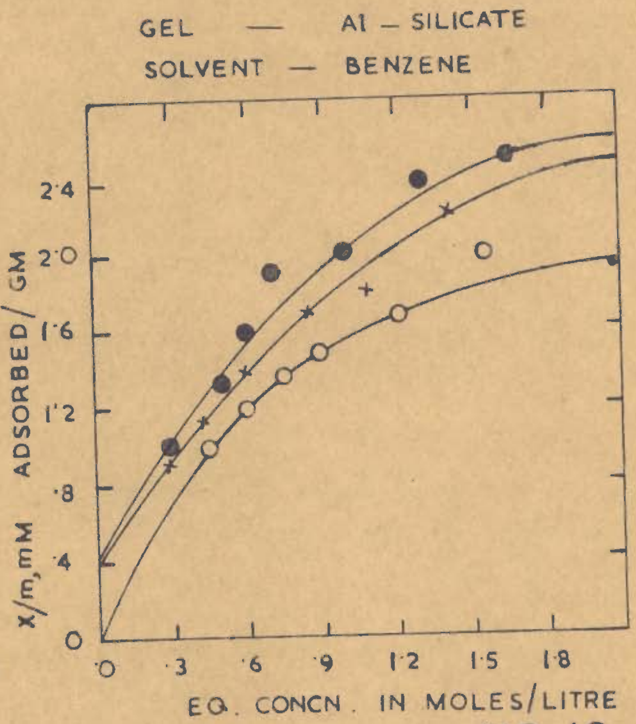

FIG. 10

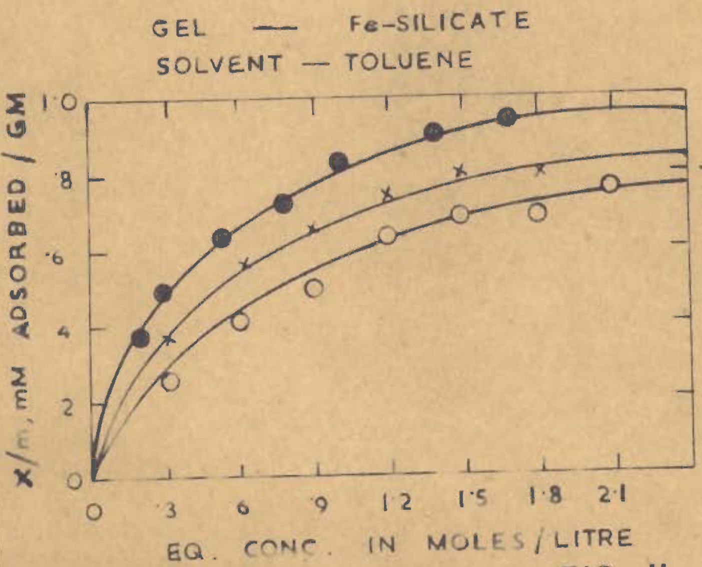

FIG. 11

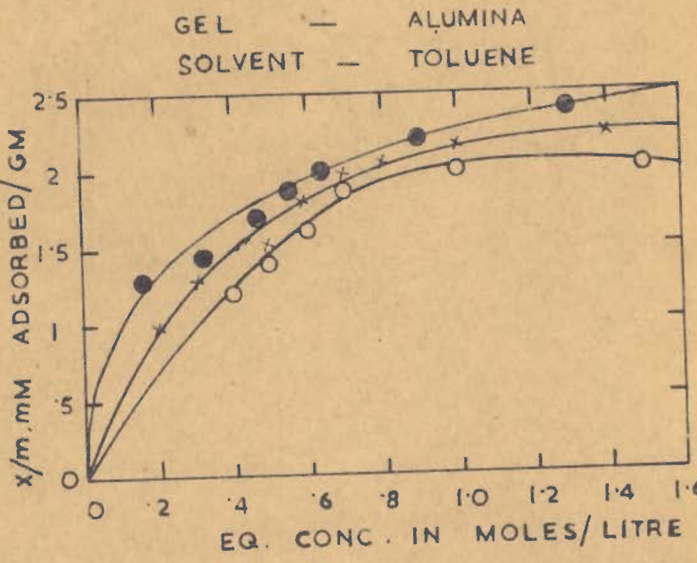

FIG. 12

Table No. 15

Solute - phenacylidene aniline
Gel - Al-molybdate
Solvent - toluene

Initial concn. $\times 10^4$ M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.64	1.82	0.60	0.54
2.00	1.20	1.71	0.83	0.58
1.66	0.80	1.66	1.25	0.60
1.42	0.70	1.42	1.42	0.70
1.25	0.60	1.30	1.66	0.76
1.00	0.40	1.20	2.50	0.83
0.83	0.30	1.08	3.33	0.92

a = 2.78
b = 2.22 Fig. 13(1)

Table No. 16

Solute - phenacylidene aniline
Gel - silica
Solvent - toluene

Initial concn. $\times 10^4$ M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	0.50	4.04	2.0	0.24
2.00	0.40	3.25	2.5	0.30
1.66	0.30	2.74	3.33	0.36
1.42	0.20	2.43	5.0	0.41
1.20	0.10	2.32	10.0	0.43
1.00	0.10	1.80	10.0	0.55
0.83	0.10	1.41	10.0	0.70

a = 2.90
b = 6.25 Fig. 14(1)

Table No. 17

Solute - phenacylidene aniline
Gel - Ferric silicate
Solvent - toluene

Initial concn. $\times 10^{-4}$ M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.60	2.10	1.66	0.47
1.42	0.55	1.75	1 .81	0.57
1.25	0.35	1.80	2.85	0.55
1.00	0.20	1.62	5.0	0.61
0.83	0.10	1.43	10.0	0.69
0.71	0.08	1.25	12.5	0.80

a = 2.0
b = 1.81 Fig. 15(1)

Table No. 18

Solute - phenacylidene aniline
Gel - silica
Solvent - xylene

Initial concn. $\times 10^{-4}$ M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.20	2.60	0.83	0.38
2.00	0.85	2.30	1.17	0.43
1.66	0.60	2.12	1.66	0.47
1.42	0.55	1.74	1.80	0.57
1.25	0.40	1.53	2.50	0.65
1.00	0.35	1.35	2.85	0.74
0.83	0.20	1.14	5.0	0.87

a = 2.11
b = 3.12 Fig. 16(1)

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1. PHENACYLIDENE ANILINE.
2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

GEL — Al-MOLYBDATE
SOLVENT — TOLUENE

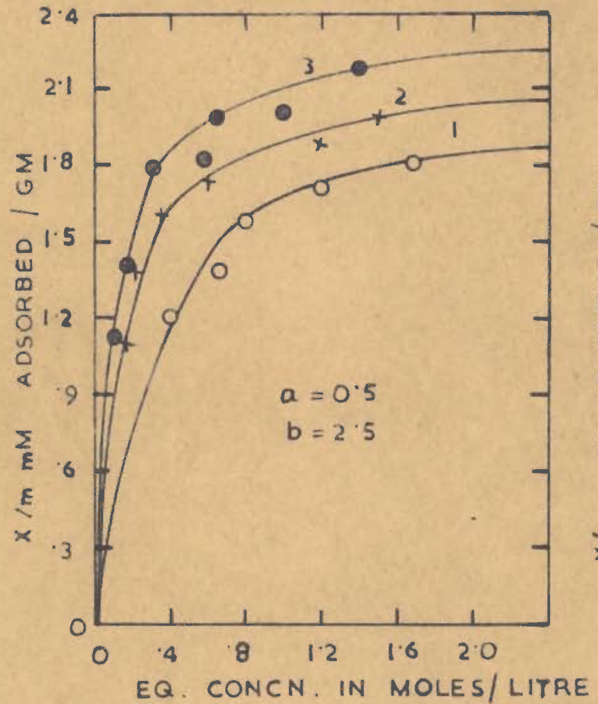

FIG.13

GEL — SILICA
SOLVENT—TOLUENE

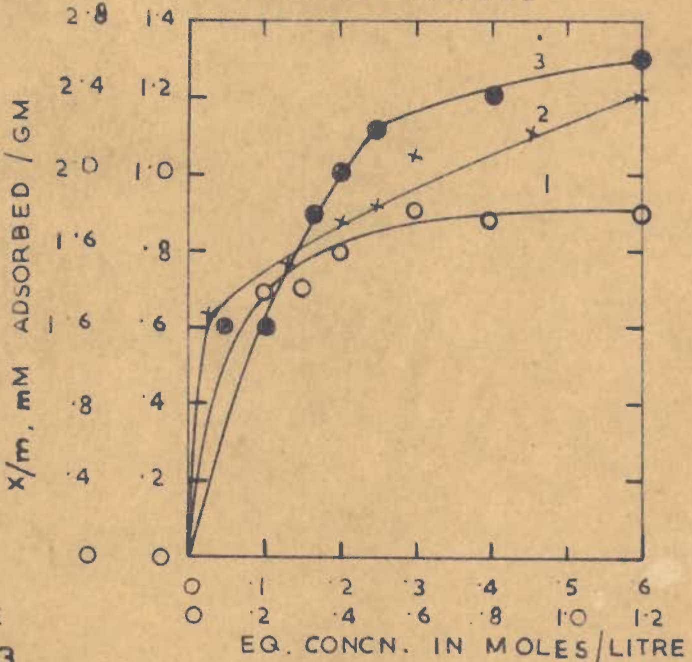

FIG. 14

GEL — Al-SILICATE
SOLVENT — TOLUENE

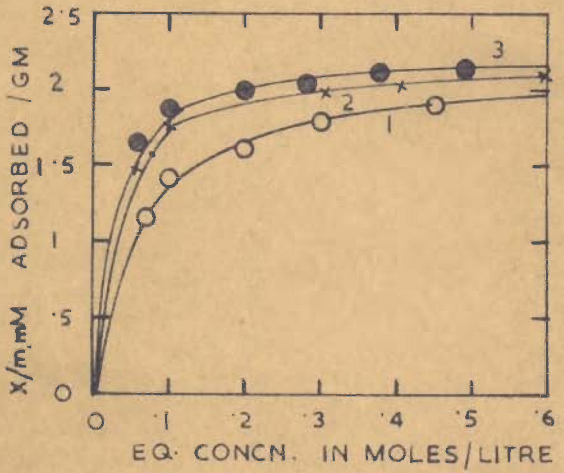

FIG. 15

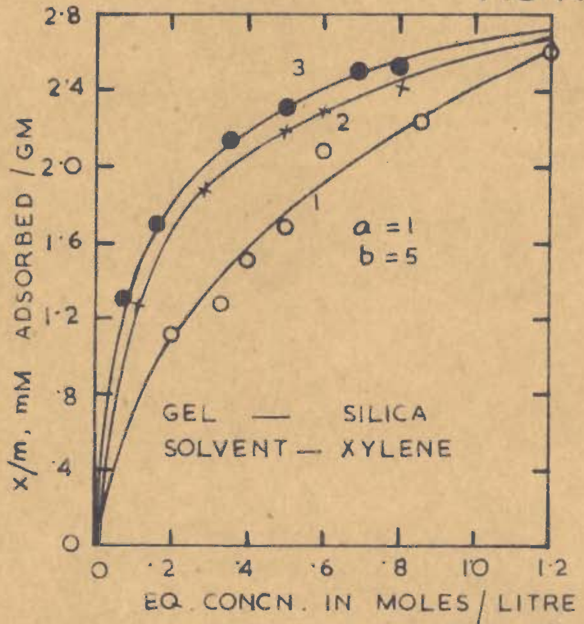

FIG. 16

Table No. 19

Solute - phenacylideneaniline
Gel - ferric silicate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.70	1.60	0.58	0.62
2.0	1.22	1.54	0.81	0.64
1.66	1.0	1.28	1.0	0.77
1.42	1.0	1.12	1.0	0.89
1.25	0.80	1.04	1.25	0.96
1.00	0.70	0.60	1.42	1.66
0.83	0.60	0.20	1.66	5.0

a = 2.97
b = 1.63 Fig. 17(1)

Table No. 20

Solute - phenacylidene aniline
Gel - alumina
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre.	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.5	2.01	0.66	0.50
2.00	1.0	2.00	1.00	0.50
1.66	0.70	1.93	1.40	0.51
1.42	0.60	1.64	1.66	0.60
1.25	0.50	1.52	2.0	0.65
1.00	0.40	1.27	2.50	0.78
0.83	0.30	1.04	3.33	0.96

a = 0.91
b = 4.76 Fig. 18(1)

Table No. 21

Solute - phenacylidene aniline
Gel - Al-silicate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.500	1.54	1.93	0.64	0.51
2.00	1.14	1.72	0.86	0.58
1.66	0.80	1.60	1.25	0.62
1.42	0.70	1.44	1.42	0.69
1.25	0.52	1.35	1.92	0.74
1.00	0.40	1.26	2.50	0.79
0.83	0.37	1.02	2.70	0.98

a = 3.0
b = 2.0 Fig. 19(1)

Table No. 22

Solute - phenacylidene aniline
Gel - Al-molybdate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.50	0.92	0.66	1.08
2.0	1.20	0.84	0.83	1.19
1.66	0.90	0.75	1.11	1.33
1.42	0.80	0.64	1.25	1.56
1.25	0.70	0.63	1.42	1.58
1.00	0.58	0.54	1.72	1.85
0.83	0.50	0.50	2.00	2.0

a = 3.03
b = 0.93 Fig. 20(1)

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3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

GEL — Fe-SILICATE
SOLVENT — XYLENE

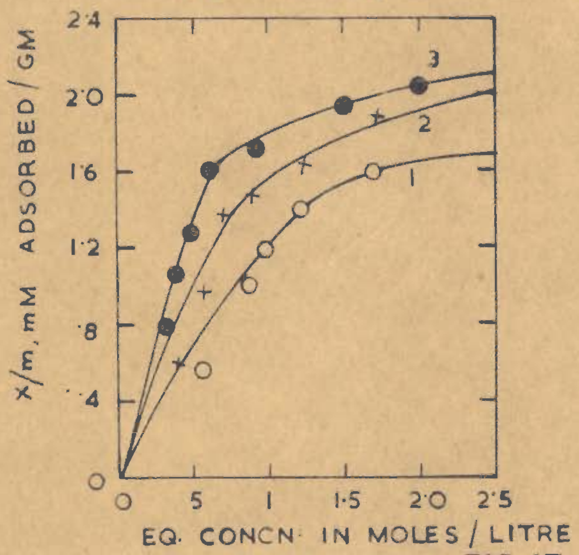


FIG.17

GEL — ALUMINA
SOLVENT — XYLENE

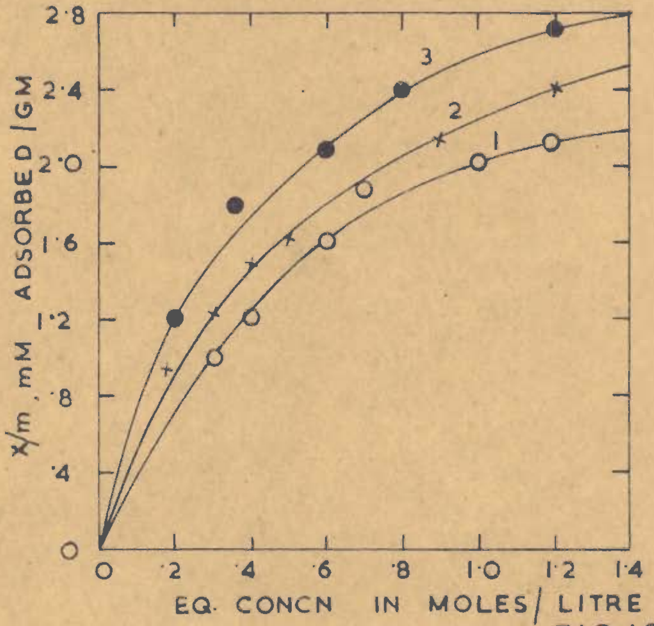


FIG.18

GEL — Al-SILICATE
SOLVENT-XYLENE

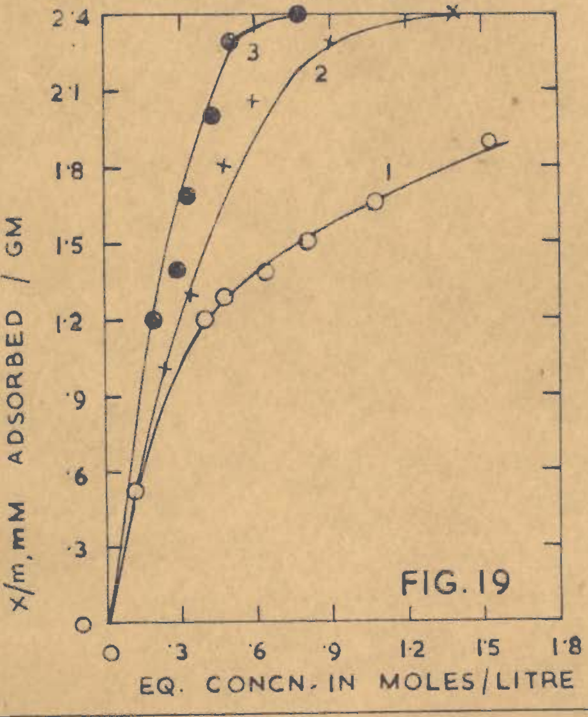


FIG. 19

GEL — Al-MOLYBDATE
SOLVENT— XYLENE

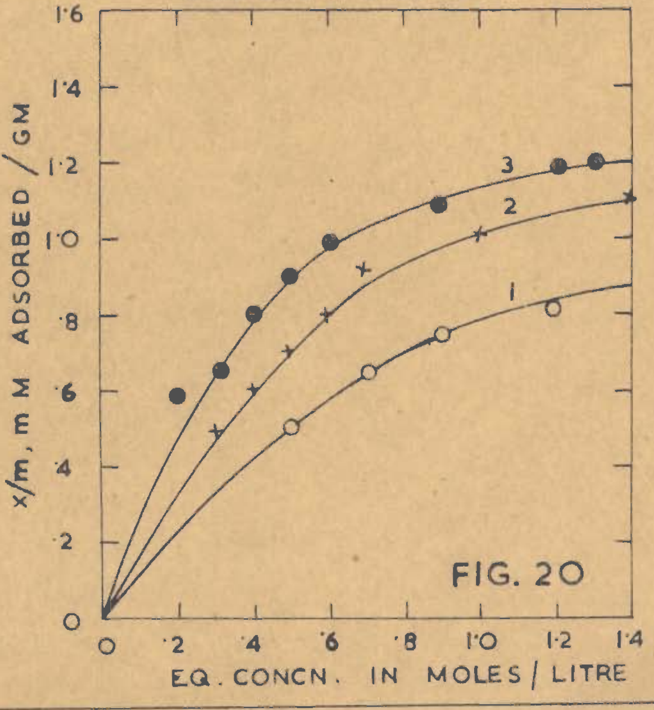


FIG. 20

Table No. 23

Solute - Phenacylidene aniline
Gel - Ferric silicate
Solvent - Dioxane

Initial concn. $\times 10^{-4}$M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed pergm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.70	0.80	0.58	1.25
2.00	1.30	0.75	0.76	1.33
1.66	0.80	0.72	1.25	1.37
1.42	0.70	0.70	1.42	1.42
1.25	0.40	0.60	2.50	1.66
1.00	0.30	0.50	3.33	2.0
0.833	0.16	0.34	6.25	2.94

a = 6.24
b = 0.83 Fig. 21(1)

Table No. 24

Solute - phenacylidene aniline
Gel - Al-silicate
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.70	1.60	0.58	0.62
2.00	1.30	1.40	0.76	0.71
1.66	1.00	1.33	1.0	0.75
1.42	0.90	1.04	1.11	0.96
1.25	0.50	0.80	2.00	1.25
1.00	0.50	0.60	2.0	1.66
0.833	0.43	0.40	2.32	2.50

a = 1.33
b = 1.95 Fig. 22(1)

Table No.25

Solute - phenacylidene aniline
Gel - Al-molybdate
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	2.01	0.52	0.49	1.92
2.00	1.35	0.62	0.74	1.61
1.66	1.20	0.40	0.83	2.50
1.42	1.00	0.35	1.0	2.85
1.25	0.90	0.30	1.11	3.33
1.00	0.80	0.20	1.25	5.00
0.833	0.60	0.20	1.66	5.00

a = 0.40
b = 1.05 Fig. 23(1)

Table No. 26

Solute - phenacylidene aniline
Gel - alumina
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.25	2.50	0.80	0.40
2.00	1.0	2.00	1.0	0.50
1.66	0.80	1.75	1.25	0.57
1.42	0.60	1.64	1.66	0.60
1.25	0.50	1.52	2.0	0.65
1.00	0.40	1.24	2.50	0.80
0.83	0.30	1.05	3.33	0.95

a = 2.89
b = 2.32 Fig. 24(1)

Table No. 27

Solute - phenacylidene aniline
Gel - silica
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.22	2.60	0.81	0.38
2.00	0.80	2.44	1.25	0.40
1.66	0.60	2.12	1.66	0.47
1.42	0.50	1.84	2.0	0.55
1.25	0.45	1.60	2.22	0.62
1.00	0.40	1.25	2.50	0.80
0.83	0.30	1.02	3.33	0.98

a = 0.85
b = 5.0 Fig. 25(1)

Table No. 28

Solute - p-dimethyl amino anil of phenyl glyoxal
Gel - Al-molybdate
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.12	0.88	0.89	1.13
2.00	0.90	0.86	1.11	1.16
1.66	0.80	0.84	1.25	1.19
1.42	0.70	0.81	1.42	1.23
1.25	0.64	0.80	1.56	1.25
1.00	0.40	0.76	2.50	1.31
0.83	0.20	0.60	5.0	1.66
0.71	0.10	0.40	10.0	2.50

a = 8.0
b = 0.90 Fig. 1(2)

1. PHENACYLIDENE ANILINE.
2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL
3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE

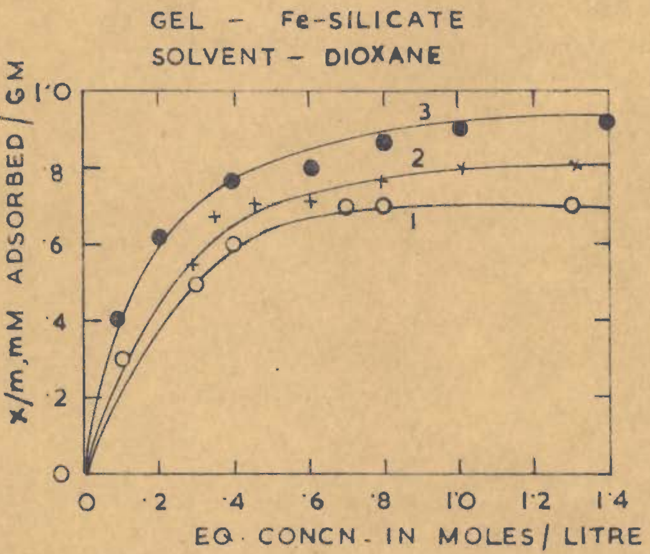


FIG. 21

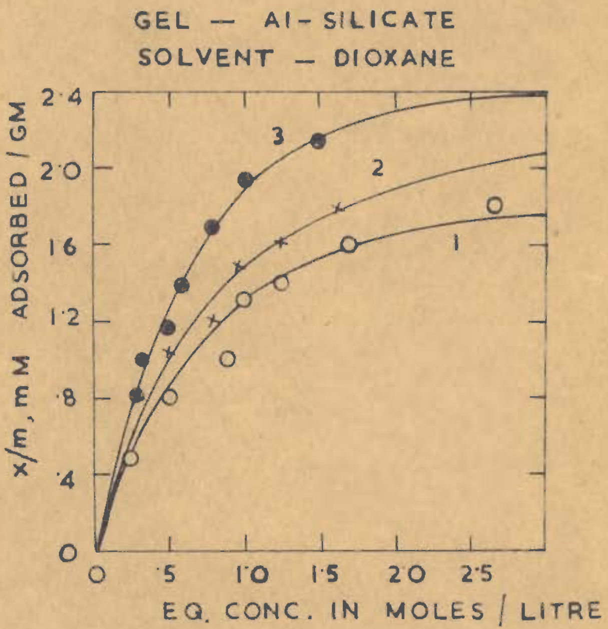


FIG. 22

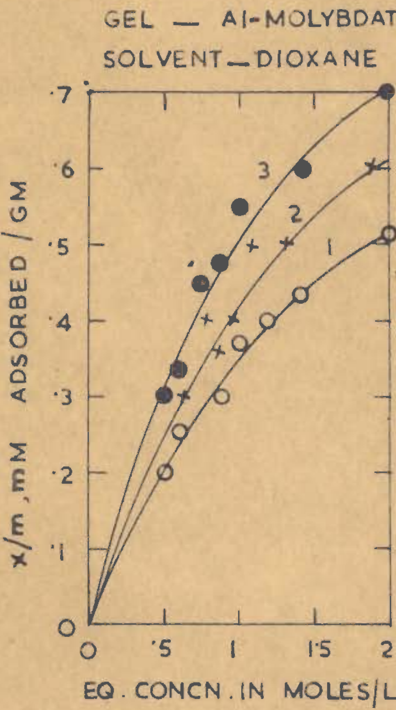


FIG. 23

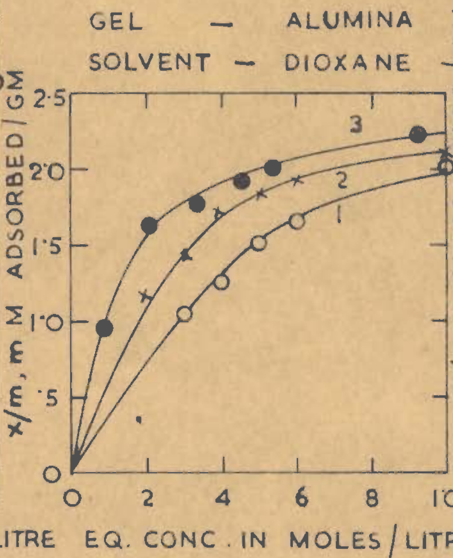


FIG. 24

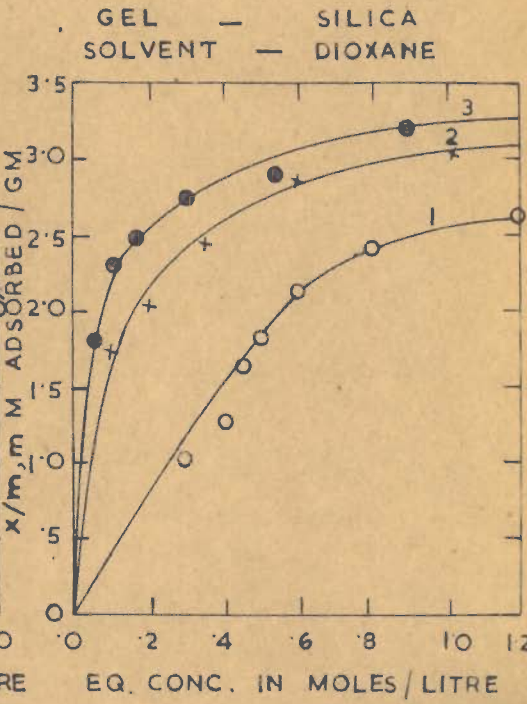


FIG. 25

Table No.29

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Fe-silicate
Solvent - carbon tetrachloride

Initial concn. $\times10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.40	2.45	2.50	0.40
1.42	0.35	2.18	2.85	0.45
1.25	0.28	2.00	3.57	0.50
1.00	0.20	1.64	5.0	0.60
0.83	0.15	1.39	6.66	0.71
0.71	0.10	1.08	10.0	0.92

a = 4.09
b = 3.70 Fig. 2(2)

Table No. 30

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-silicate
Solvent - carbon tetrachloride

Initial concn. $\times10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.45	2.42	2.22	0.41
1.42	0.35	2.15	2.85	0.46
1.25	0.28	2.00	3.57	0.50
1.00	0.18	1.33	5.55	0.75
0.83	0.12	1.00	8.33	1.0
0.71	0.10	0.08	10.00	12.50

a = 0.20
b = 5.0 Fig. 3(2)

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

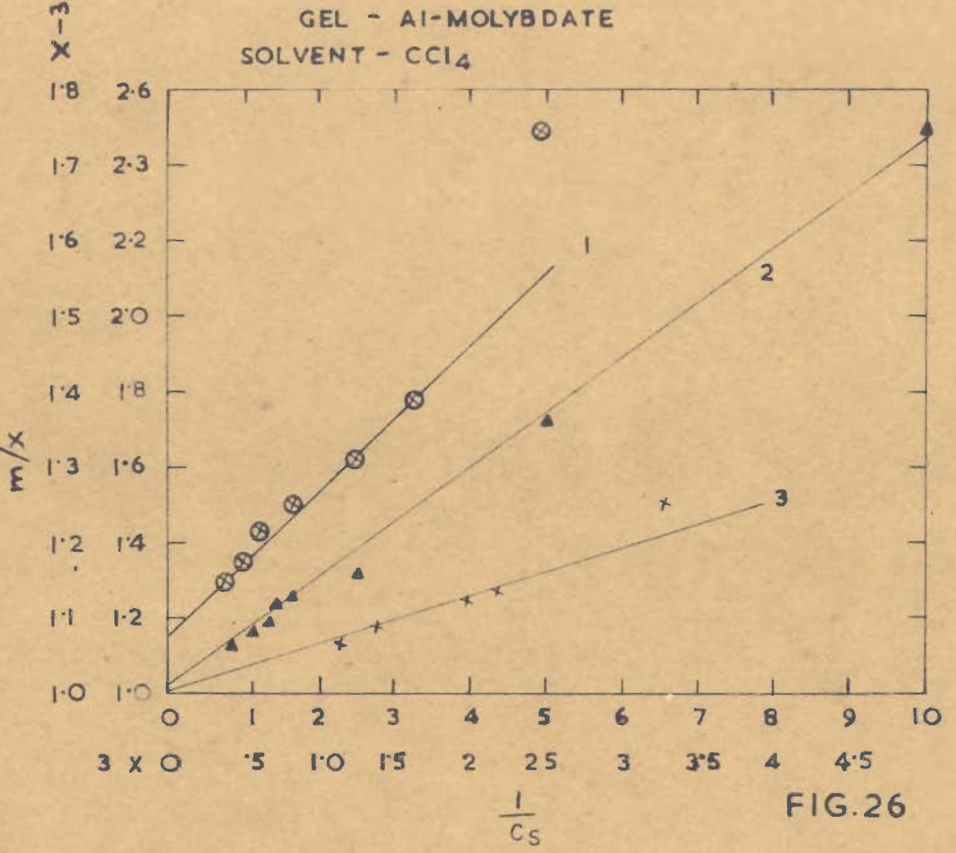


FIG.26

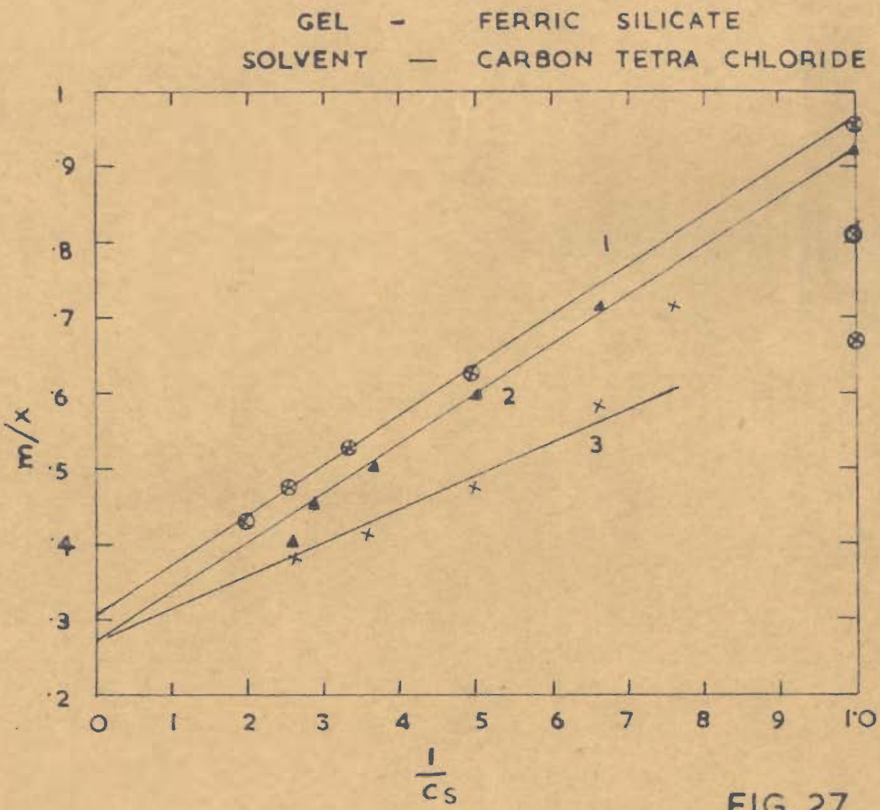


FIG. 27

Table No. 31

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - silica
Solvent - carbon tetrachloride

Initial concn. $x10^{-4}M$	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.35	2.64	2.85	0.37
1.42	0.25	2.32	4.00	0.43
1.25	0.20	2.12	5.00	0.47
1.00	.11	2.04	9.09	0.49
0.833	0.10	1.45	10.0	0.68
0.71	0.10	1.24	10.0	0.80
0.62	0.08	1.03	12.50	0.97

a = 7.73
b = 2.32 Fig. 4(2)

Table No. 32

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - alumina
Solvent - carbon tetrachloride

Initial concn. $x10^{-4}M$	Eq.concn. cs in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.40	2.58	2.50	0.38
1.42	0.30	2.25	3.33	0.44
1.25	0.20	2.10	5.0	0.47
1.00	0.15	1.78	6.66	0.56
0.833	0.10	1.40	10.0	0.71
0.71	0.08	1.22	12.50	0.82
0.62	0.07	1.05	14.28	0.95

a = 9.54
b = 2.85 Fig. 5(2)

⊗ 1. PHENACYLIDENE. ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

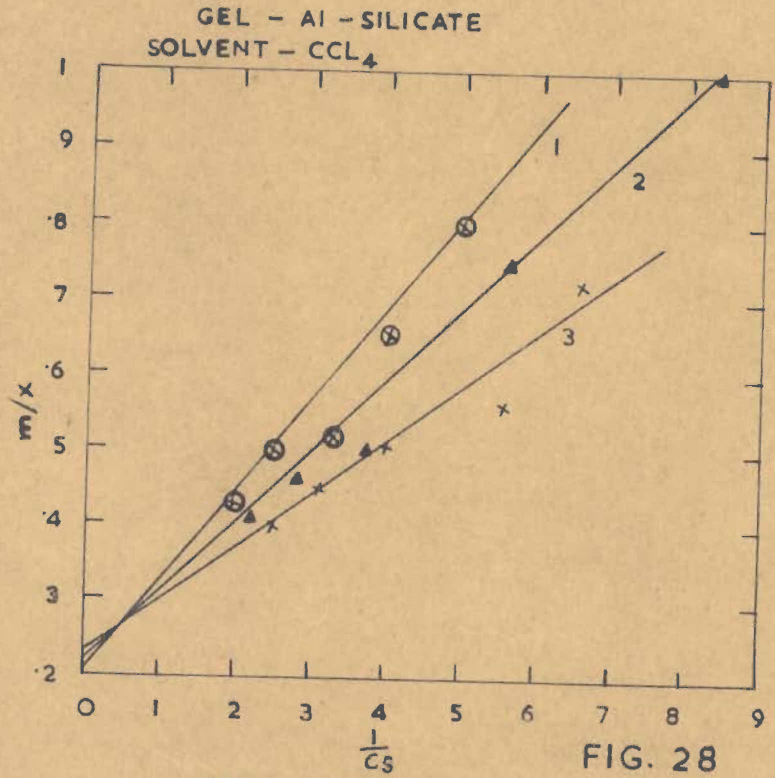


FIG. 28

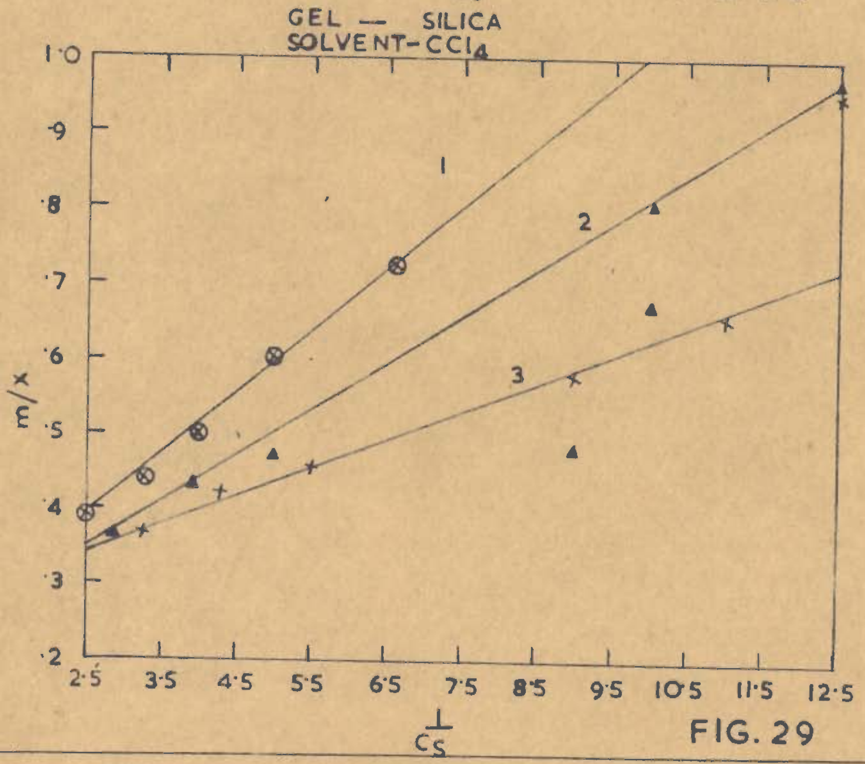


FIG. 29

Table No. 33

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - silica
Solvent - benzene

Initial concn. $\times 10^{-4}$ M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	0.80	3.4	1.25	0.29
2.00	0.50	3.0	2.0	0.33
1.66	0.40	2.51	2.50	0.39
1.42	0.30	2.24	3.33	0.44
1.25	0.20	2.06	5.0	0.48
1.00	0.10	1.80	10.0	0.55
0.83	0.08	1.50	12.50	0.66

$a = 2.33$
$b = 5.26$ Fig. 6(2)

Table No. 34

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - alumina
Solvent - benzene

Initial concn. $\times 10^{-4}$ M	Eq. conc. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.20	2.60	0.83	0.38
2.00	0.80	2.09	1.25	0.48
1.66	0.70	1.92	1.42	0.52
1.42	0.60	1.64	1.66	0.60
1.25	0.58	1.46	1.72	0.70
1.00	0.55	0.90	1.81	1.11
0.83	0.50	0.60	2.00	1.66

$a = 1.79$
$b = 3.22$ Fig. 7(2)

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

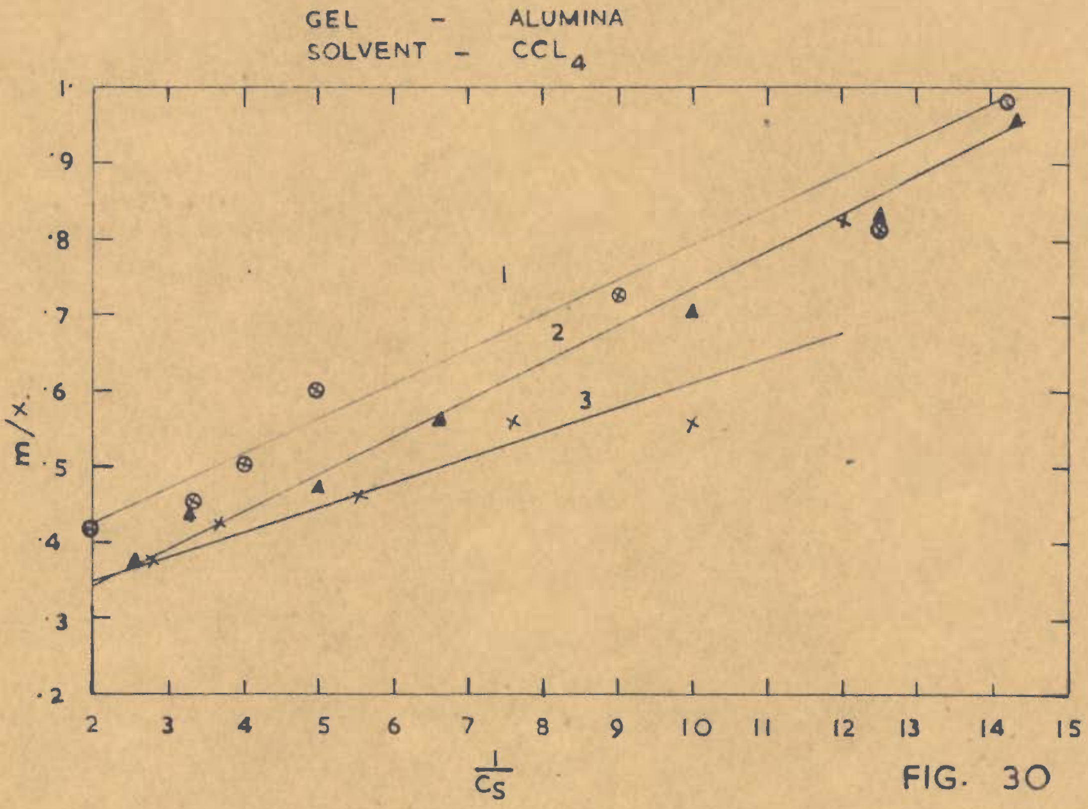


FIG. 30

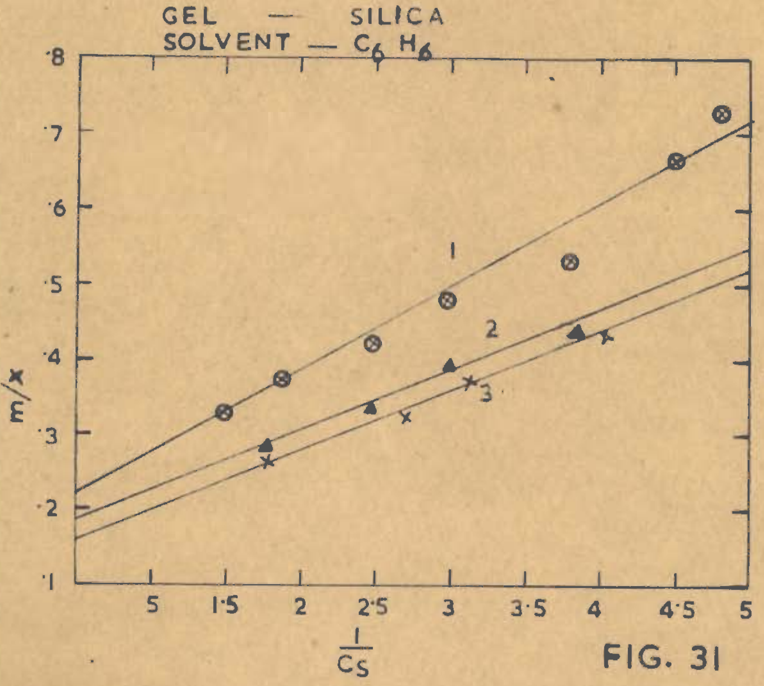


FIG. 31

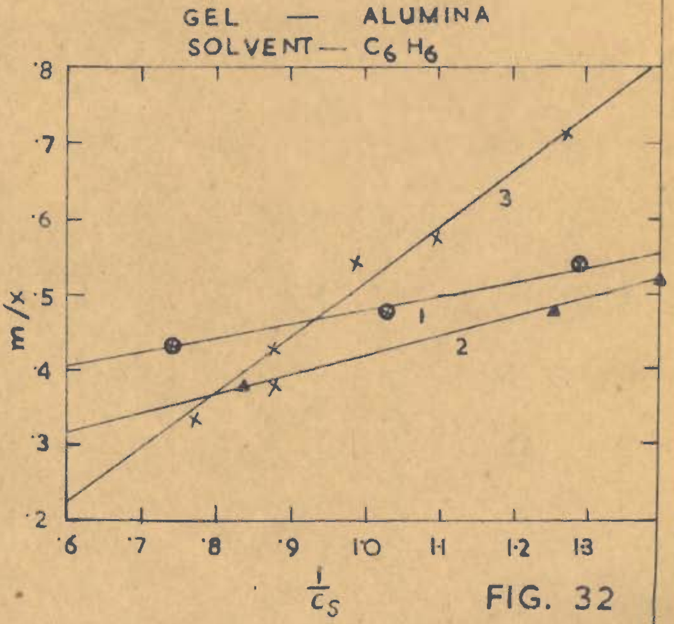


FIG. 32

Table No.35

Solute -p-dimethyl amino anil of phenylglyoxal
Gel -Al-molybdate
Solvent -benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.80	1.0	0.55	1.0
2.00	1.60	0.94	0.62	1.06
1.66	1.20	0.90	0.83	1.11
1.42	1.0	0.86	1.0	1.16
1.25	0.80	0.80	1.25	1.25
1.00	0.60	0.70	1.66	1.42
0.83	0.40	0.66	2.5	1.51

a = 6.66
b = 0.97 Fig.8(2)

Table No.36

Solute -p-dimethyl amino anil of phenylglyoxal
Gel -ferric silicate
Solvent -benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.60	1.80	0.62	0.55
2.0	1.20	1.73	0.83	0.57
1.66	1.0	1.40	1.0	0.71
1.42	0.72	1.40	1.38	0.71
1.25	0.63	1.20	1.58	0.83
1.0	0.40	1.03	2.50	0.97
0.83	0.20	0.50	5.00	2.0

a = 4.68
b = 1.85 Fig. 9(2)

⊗ 1. PHENACYLIDENE ANILINE.

▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.

× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

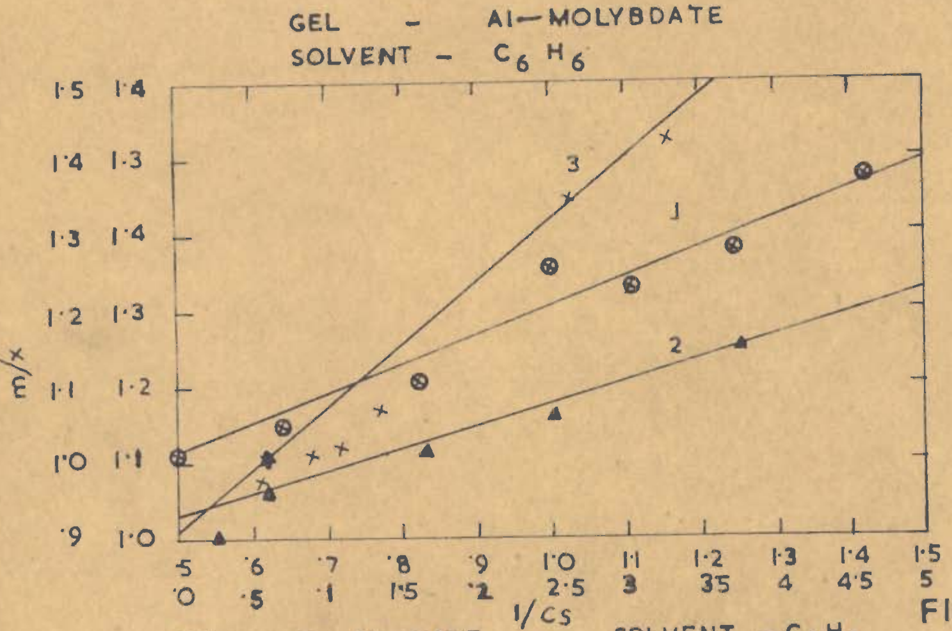


FIG. 33

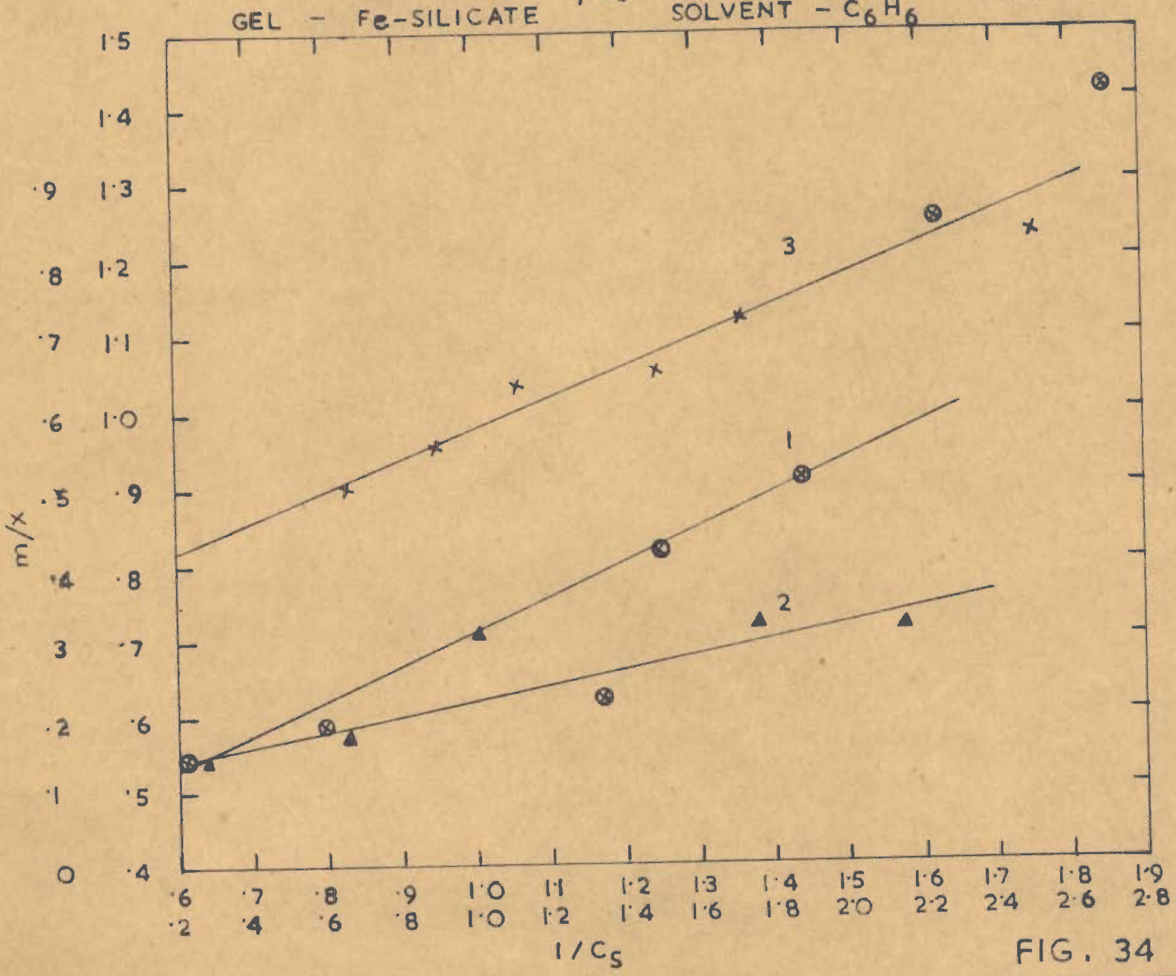


FIG. 34

Table No.37

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-silicate
Solvent - benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre.	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	2.20	0.71	0.45
2.0	1.10	1.80	0.90	0.55
1.66	0.80	1.71	1.25	0.58
1.42	0.70	1.40	1.42	0.71
1.25	0.60	1.38	1.66	0.72
1.00	0.50	1.03	2.0	0.97
0.83	0.30	0.90	3.33	1.11

a = 3.60
b = 2.22 Fig. 10(2)

Table No.38

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Fe-silicate
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.80	0.80	0.55	1.25
2.00	1.50	0.78	0.66	1.28
1.66	1.20	0.74	0.83	1.35
1.42	0.90	0.64	1.11	1.56
1.25	0.60	0.54	1.66	1.85
1.00	0.50	0.50	2.0	2.0
0.83	0.30	0.26	3.33	3.84

a = 4.01
b = 1.88 Fig. 11(2)

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE

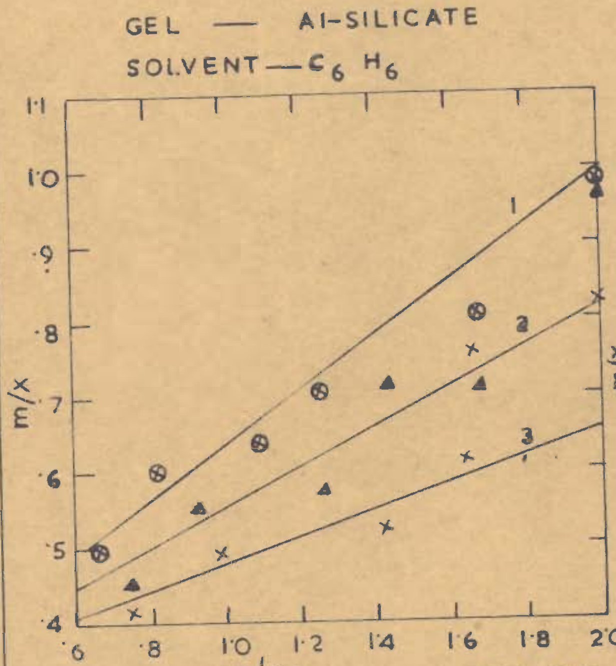


FIG. 35

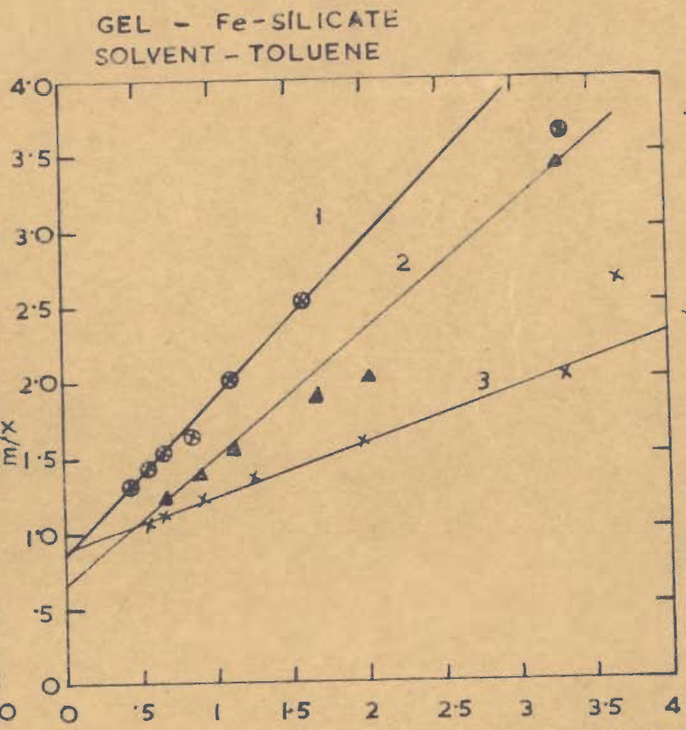


FIG. 36

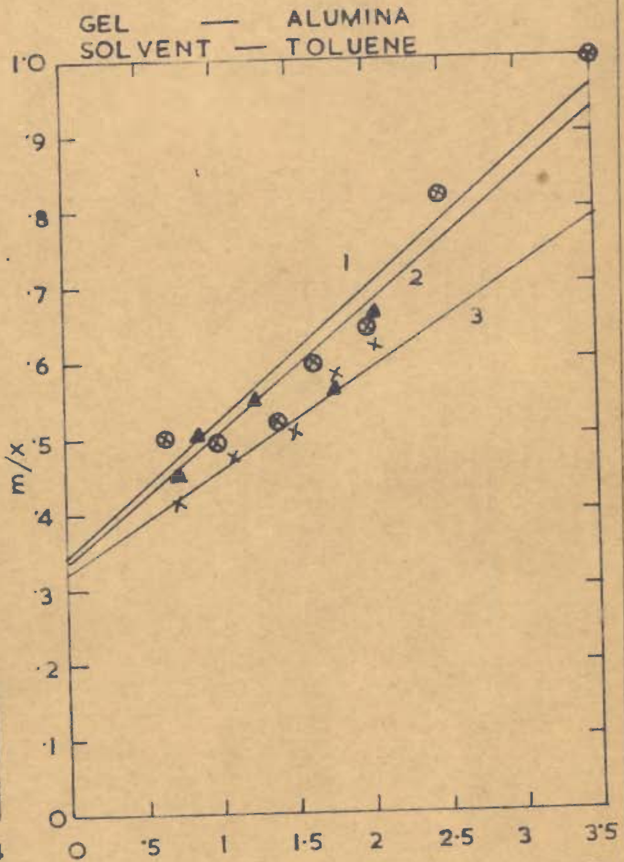


FIG. 37

Table No.39

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - alumina
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	1.40	2.2	0.71	0.45
1.42	1.20	2.0	0.83	0.50
1.25	1.00	2.0	1.0	0.50
1.00	0.81	1.8	1.23	0.55
0.83	0.63	1.75	1.58	0.56
0.71	0.50	1.5	2.0	0.66

a = 2.12
b = 2.94 Fig. 12(2)

Table No. 40

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-molybdate
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.50	2.02	0.66	0.49
2.0	1.22	1.93	0.81	0.51
1.66	0.70	1.89	1.42	0.52
1.42	0.50	1.71	2.0	0.58
1.25	0.40	1.64	2.50	0.60
1.00	0.30	1.40	3.33	0.71
0.83	0.30	1.06	3.33	0.94

a = 6.05
b = 2.27 Fig. 13(2)

⊗ 1. PHENACYLIDENE ANILINE
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

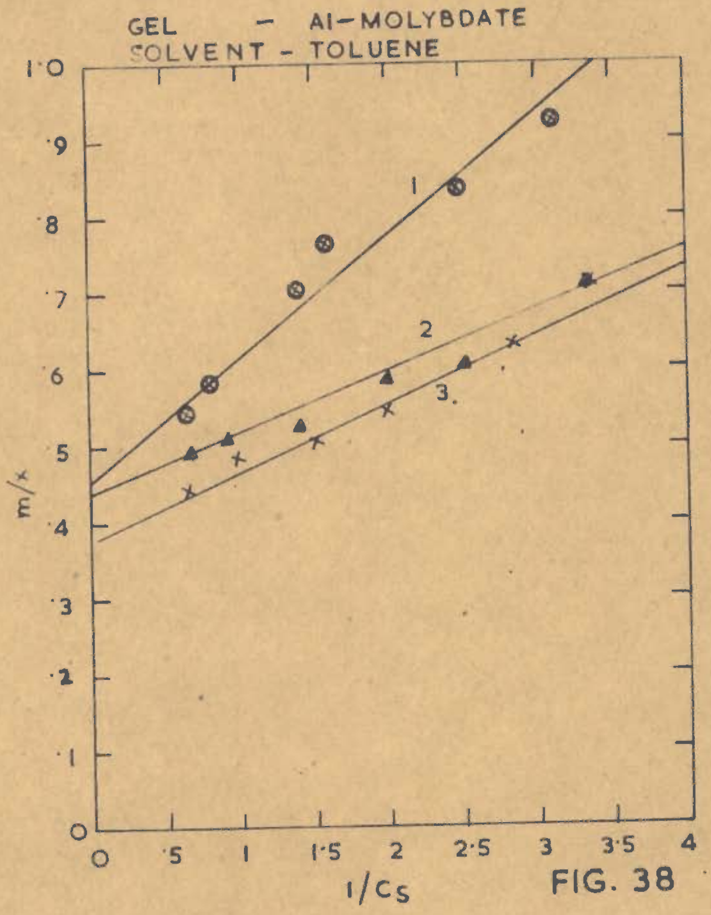


FIG. 38

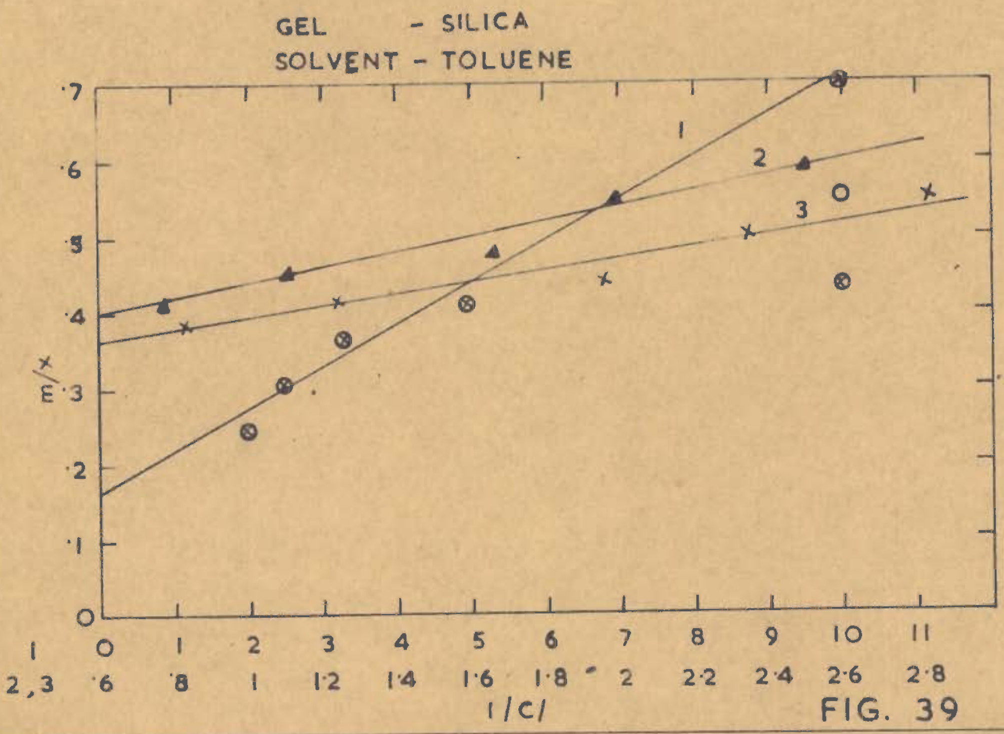


FIG. 39

Table No.41

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - silica
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	2.40	0.76	0.41
2.0	0.90	2.20	1.11	0.45
1.66	0.60	2.12	1.66	0.47
1.42	0.50	1.80	2.0	0.55
1.25	0.40	1.71	2.5	0.58
1.00	0.30	1.42	3.33	0.71
0.83	0.20	1.21	5.0	0.82

$a = 2.00$
$b = 2.50$ Fig.14(2)

Table No.42

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-silicate
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	2.21	0.71	0.45
2.00	1.03	2.02	0.97	0.49
1.66	0.70	1.80	1.42	0.55
1.42	0.60	1.66	1.66	0.60
1.25	0.50	1.50	2.0	0.66
1.00	0.35	1.28	2.85	0.78
0.83	0.20	1.00	5.0	1.0

$a = 1.78$
$b = 2.27$ Fig.15(2)

Table No.43

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - silica
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.20	2.60	0.83	0.38
2.0	0.80	2.40	1.25	0.41
1.66	0.60	2.28	1.66	0.43
1.42	0.50	2.20	2.0	0.45
1.25	0.32	1.86	3.12	0.53
1.00	0.10	1.26	10.0	0.79
0.83	0.08	0.84	12.50	1.19

a = 5.60
b = 2.85 Fig. 16(2)

Table No. 44

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - ferric silicate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.75	1.75	0.57	0.57
2.00	1.20	1.60	0.83	0.62
1.66	0.92	1.50	1.08	0.66
1.42	0.85	1.16	1.17	0.86
1.25	0.75	1.09	1.33	0.91
1.00	0.65	0.88	1.53	1.13
0.83	0.48	0.57	2.08	1.76

a = 3.38
b = 1.53 Fig.17(2)

Table No.45

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - alumina
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	2.40	0.76	0.41
2.0	0.90	2.21	1.11	0.45
1.66	0.60	2.08	1.66	0.48
1.42	0.50	1.85	2.0	0.54
1.25	0.45	1.48	2.22	0.67
1.0	0.35	1.30	2.85	0.76
0.83	0.28	1.08	3.57	0.92

a = 3.05
b = 3.33 Fig. 18(2)

Table No.46

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-silicate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	2.40	0.76	0.41
2.00	0.85	2.19	1.17	0.45
1.66	0.60	1.88	1.66	0.55
1.42	0.55	1.62	1.81	0.61
1.25	0.40	1.30	2.50	0.76
1.00	0.35	1.25	2.85	0.80
0.83	0.20	0.90	5.0	1.11

a = 2.61
b = 2.63 Fig.19(2)

Table No.47

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-molybdate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	1.10	0.71	0.90
2.00	1.00	1.02	1.0	0.98
1.66	0.70	0.90	1.42	1.11
1.42	0.60	0.84	1.66	1.17
1.25	0.50	0.70	2.0	1.42
1.00	0.40	0.60	2.5	1.66
0.83	0.30	0.48	3.33	2.08

a = 0.21
b = 0.94 Fig. 20(2)

Table No.48

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - ferric silicate
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.6	0.85	0.62	1.17
2.0	1.2	0.80	0.83	1.25
1.66	1.0	0.77	1.0	1.29
1.42	0.80	0.74	1.25	1.35
1.25	0.65	0.70	1.50	1.42
1.00	0.45	0.70	2.20	1.42
0.83	0.35	0.60	2.80	1.66
0.71	0.30	0.53	3.33	1.88

a = 2.20
b = 0.90 Fig. 21(2)

Table No. 49

Solute - p- dimethyl amino anil of phenylglyoxal
Gel - aluminium silicate
Solvent- dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.60	1.84	0.62	0.54
2.00	1.20	1.60	0.83	0.62
1.66	0.91	1.50	1.09	0.66
1.42	0.81	1.22	1.23	0.81
1.25	0.65	1.20	1.53	0.83
1.00	0.60	1.08	1.66	0.92
0.83	0.55	0.80	1.80	1.25

a = 3.40
b = 1.63 Fig. 22(2)

Table No. 50

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - Al-molybdate
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.90	0.60	0.52	1.66
2.00	1.31	0.50	0.75	2.0
1.66	1.10	0.45	0.90	2.22
1.42	1.00	0.40	1.0	2.50
1.25	0.82	0.38	1.20	2.64
1.00	0.70	0.30	1.42	3.33

a = 1.07
b = 0.76 Fig.23(2)

Table No.51

Solute - p- dimethyl amino anil of phenylglyoxal
Gel - alumina date
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	2.20	0.71	0.45
2.00	1.0	2.02	1.0	0.49
1.66	0.60	1.90	1.66	0.52
1.42	0.51	1.83	1.96	0.54
1.25	0.40	1.70	2.50	0.58
1.00	0.30	1 .40	3.33	0.71
0.83	0.22	1.20	4.54	0.83

a = 9.00
b = 2.22 Fig. 24(2)

Table No. 52

Solute - p-dimethyl amino anil of phenylglyoxal
Gel - silica
Solvent- dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.00	3.0	1.0	0.33
2.00	0.60	2.84	1.66	0.35
1.66	0.30	2.48	3.33	0.40
1.42	0.20	2.08	5.0	0.48
1.25	0.10	1.80	10.0	0.55
1.00	0.09	1.65	11.11	0.61
0.83	0.07	1.47	14.28	0.68

a = 5.60
b = 2.85 Fig. 25(2)

● 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

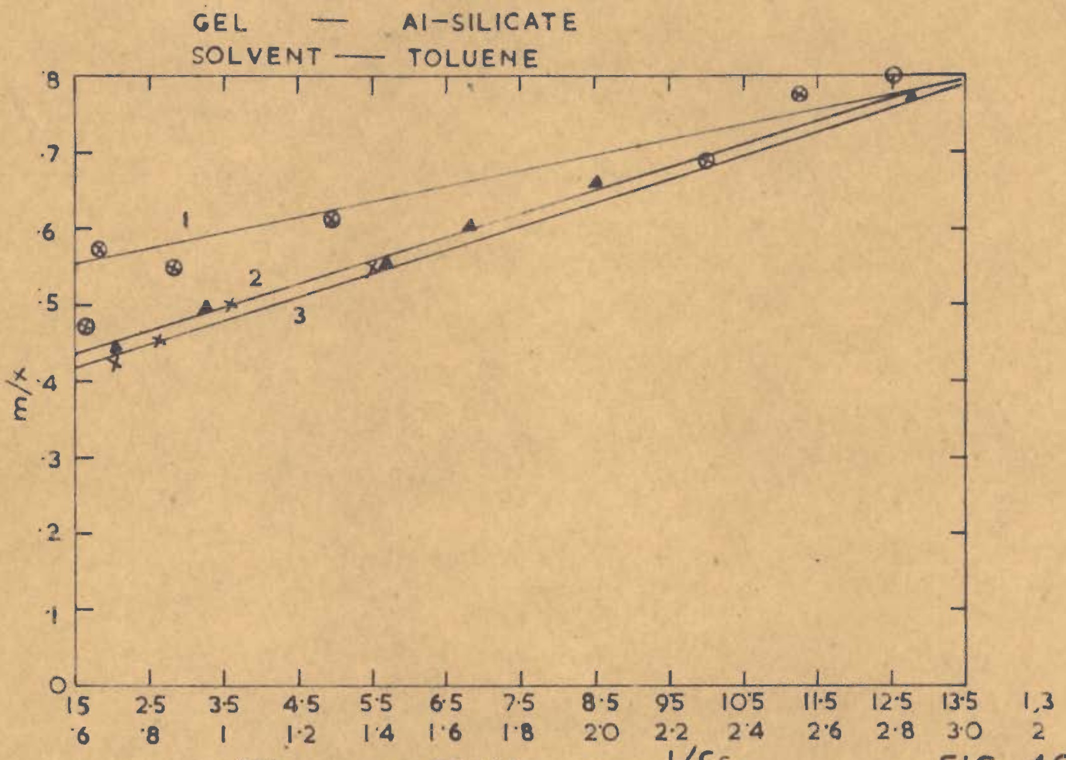


FIG. 40

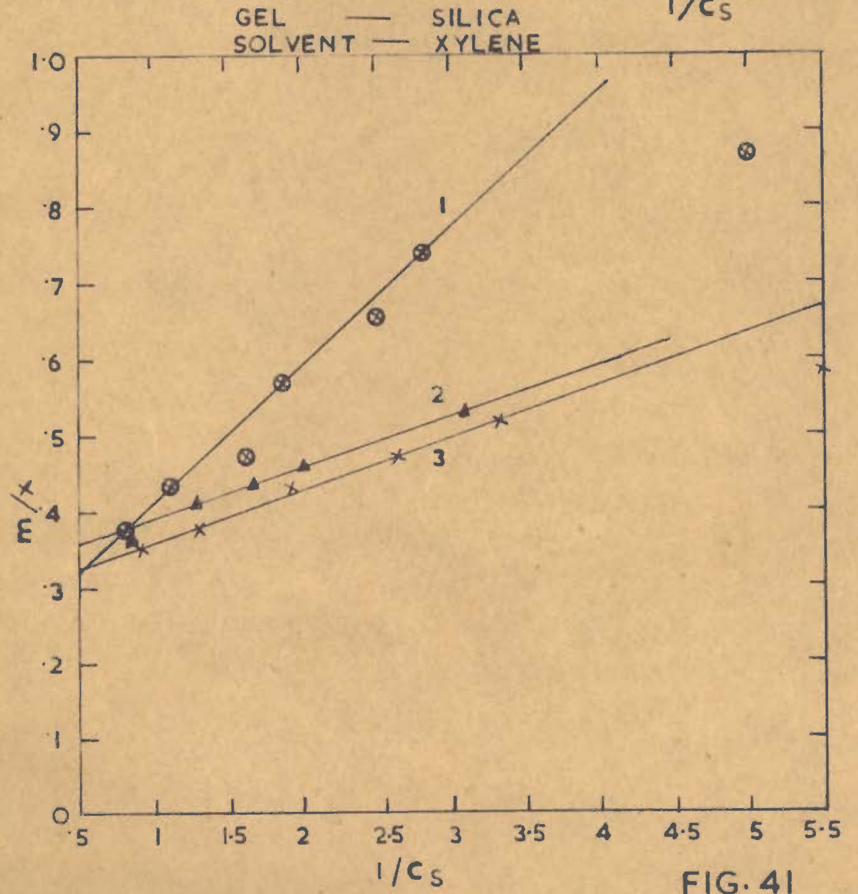


FIG. 41

Table No.53

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-molybdate
Solvent - carbon tetrachloride

Initial concn. x10^{-4}M	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.01	0.98	0.99	1.02
2.00	0.85	0.94	1.17	1.06
1.66	0.70	0.92	1.42	1.08
1.42	0.60	0.90	1.66	1.11
1.25	0.50	0.90	2.0	1.11
1.00	0.45	0.86	2.22	1.13
0.83	0.30	0. 80	3.33	1.25
0.71	0 .20	0.60	5.00	1.66

a = 0.40
b = 1.00 Fig. 1(3)

Table No.54

Solute - p- dimethyl amino anil of phenylglyoxal nitrile
Gel - Fe-silicate
Solvent - carbon tetra chloride

Initial concn. x10^{-4}M	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.38	2.60	2.63	0.38
1.42	0.28	2.40	3.57	0.41
1.25	0.20	2.12	5.00	0.47
1.00	0.15	1.71	6.66	0.58
0.83	0.13	1.43	7.68	0.71
0.71	0.08	1.00	12.50	1.00

a = 6.00
b = 3.70 Fig. 2(3)

Table No. 55

Solute - p-dimethyl amino anil of phenylglyoxal
gel - Al-silicate
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.40	2.50	2.50	0.40
1.42	0.32	2.20	3.12	0.45
1.25	0.25	2.00	4.00	0.50
1.00	0.18	1.74	5.55	0.57
0.83	0.15	1.38	6.66	0.73
0.71	0.10	1.25	10.0	0.80

a = 3.14
b = 4.54 Fig. 3(3)

Table No.56

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - silica
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.30	2.70	3.33	0.37
1.42	0.23	2.30	4.34	0.43
1.25	0.18	2.15	5.55	0.46
1.00	0.11	1.72	9.09	0.58
0.83	0.09	1.50	11.11	0.66
0.71	0.08	1.04	12.50	0.96
0.62	0.06	0.80	16.66	1.25

a = 1.15
b = 2.94 Fig. 4(3)

Table No.57

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - alumina
Solvent - carbon tetrachloride

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.36	2.60	2.77	0.38
1.42	0.28	2.32	3.57	0.43
1.25	0.18	2.20	5.55	0.45
1.00	0.13	1.80	7.68	0.55
0.83	0.10	1.77	10.0	0.56
0.71	0.08	1.20	12.50	0.83

a = 1.30
b = 2.86 Fig. 5(3)

Table No.58

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - silica
Solvent - benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	0.75	3.52	1.33	0.28
2.00	0.45	3.11	2.22	0.32
1.66	0.38	2.60	2.63	0.38
1.42	0.28	2.31	3.57	0.43
1.25	0.18	2.20	5.55	0.45
1.00	0.10	1.73	10.00	0.57
0.83	0.09	1.25	11.11	0.80

a = 2.00
b = 6.25 Fig. 6(3)

Table No. 59

Solute -p-dimethyl amino anil of phenylglyoxal nitrile
Gel -alumina
Solvent -benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.10	2.80	0.90	0 34
2.00	0.70	2.68	1.42	0.38
1.66	0.70	2.34	1.42	0.43
1.42	0.51	1.81	1.96	0.55
1.25	0.40	1.72	2.50	0.58
1.00	0.30	1.40	3.33	0.71
0.83	0.20	1.25	5.0	0.80

a = 0.55
b = 4.54 Fig. 7(3)

Table No. 60

Solute - p - dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-molybdate
Solvent - benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.74	1.02	0.57	0.98
2.00	1.42	0.98	0.71	1.02
1.66	1.12	0.94	0.89	1.06
1.42	0.90	0.90	1.11	1.11
1.25	0.70	0.86	1.42	1.16
1.00	0.60	0.80	1.66	1.20
0.83	0.38	0.74	2.63	1.35
0.71	0.30	0.70	3.30	1.42

a = 6.75
b = 1.11 Fig. 8(3)

⊗ 1. PHENACYLIDENE ANILINE.

▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.

× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

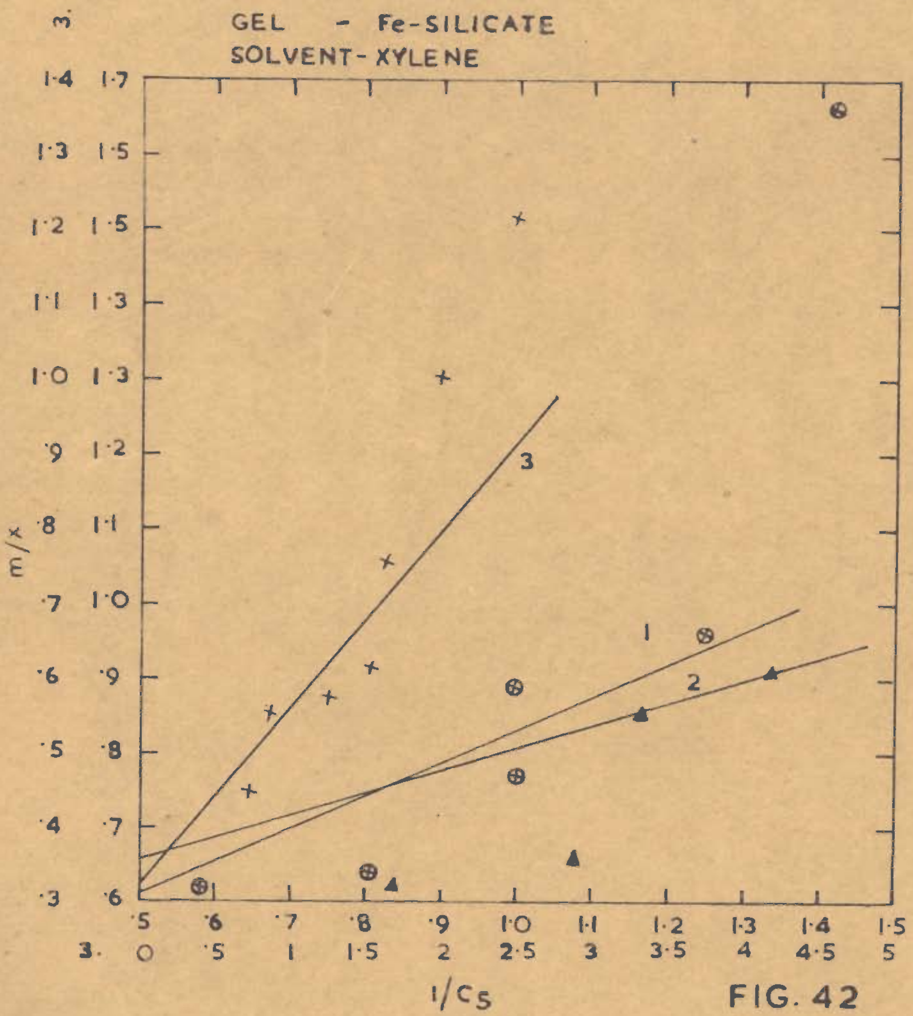


FIG. 42

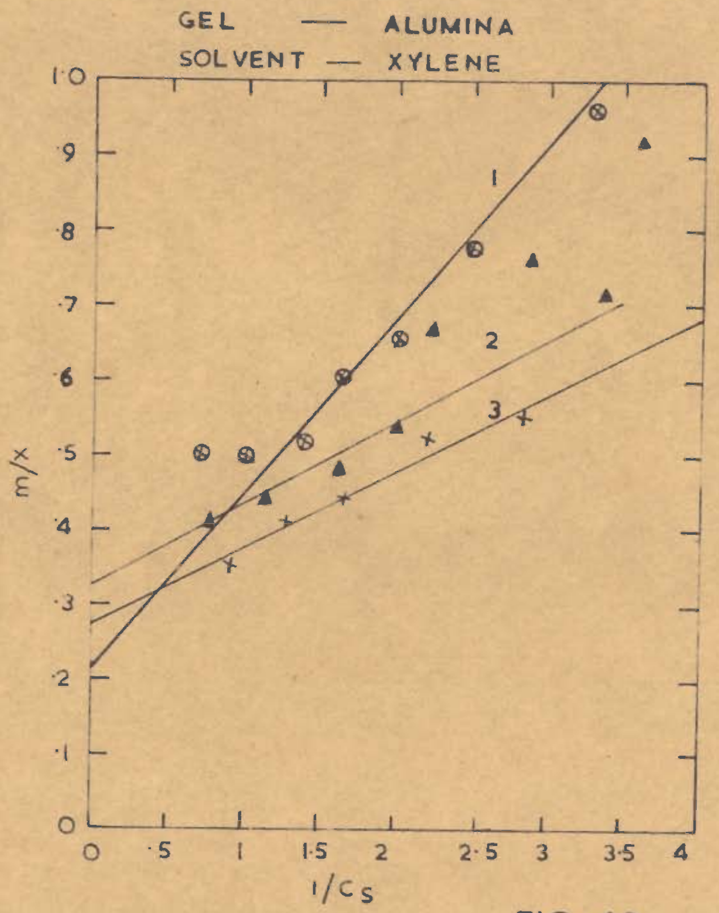


FIG. 43

Table No.61

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel -Fe-silicate
Solvent - benzene

Initial concn. $\times 10^{-4}$M	Eq.conc. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.50	2.00	0.66	0.50
2.00	1.10	1.80	0.90	0.55
1.66	0.90	1.54	1.11	0.64
1.42	0.67	1.50	1.49	0.66
1.25	0.58	1.41	1.72	0.71
1.00	0.40	1.20	2.50	0.83
0.83	0.18	1.12	5.55	0.89

a = 2.40
b = 2.38 Fig. 9(3)

Table No. 62

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-silicate
Solvent - benzene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m, milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	2.40	0.76	0.41
2.00	1.02	2.01	0.98	0.49
1.66	0.70	1.92	1.42	0.52
1.42	0.61	1.62	1.63	0.61
1.25	0.60	1.31	1.66	0.76
1.00	0.50	1.20	2.00	0.83
0.83	0.30	1.00	3.33	1.00

a = 3.46
b = 2.43 Fig. 10(3)

Table No. 63

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - ferric silicate
Solvent - toluene

Initial conc. $\times 10^{-4}$M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.76	0.92	0.56	1.08
2.00	1.48	0.90	0.67	1.11
1.66	1.02	0.82	0.98	1.21
1.42	0.80	0.74	1.25	1.35
1.25	0.50	0.64	2.0	1.56
1.00	0.30	0.50	3.33	2.00
0.83	0.27	0.38	3.70	2.63

$a = 1.08$
$b = 1.25$ Fig. 11(3)

Table No. 64

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - alumina
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq. concn. c_s in moles per litre	x/m, millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	2.40	0.76	0.41
2.00	0.90	2.10	1.11	0.47
1.66	0.66	2.00	1.51	0.50
1.42	0.58	1.74	1.72	0.57
1.25	0.48	1.60	2.08	0.62
1.0	0.33	1.40	3.03	0.71
0.83	0.18	1.30	5.55	0.76

$a = 2.40$
$b = 3.12$ Fig. 12(3)

Table No. 65

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-molybdate
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.48	2.23	0.67	0.44
2.00	1.00	2.06	1.00	0.48
1.66	0.65	2.00	1.53	0.50
1.42	0.50	1.84	2.00	0.54
1.25	0.35	1.61	2.85	0.62
1.00	0.30	1.40	3.33	0.71
0.83	0.25	1.14	4.00	0.87

a = 4.31
b = 2.70 Fig. 13(3)

Table No. 66

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - silica
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.20	2.6	0.83	0.38
2.00	0.80	2.40	1.25	0.41
1.66	0.51	2.31	1.96	0.43
1.42	0.42	2.00	2.38	0.50
1.25	0.35	1.80	2.85	0.55
1.00	0.30	1.40	3.33	0.71
0.83	0.23	1.20	4.34	0.83

a = 6.22
b = 2.77 Fig. 14(3)

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

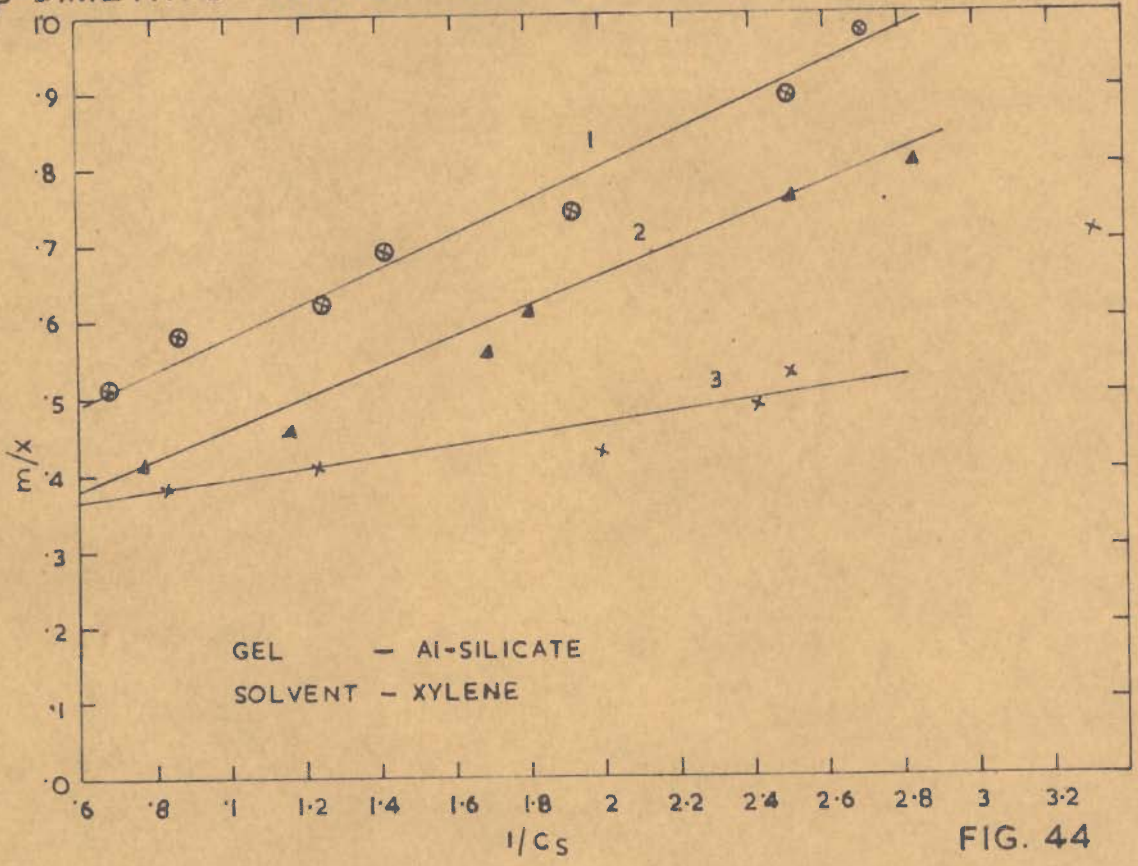


FIG. 44

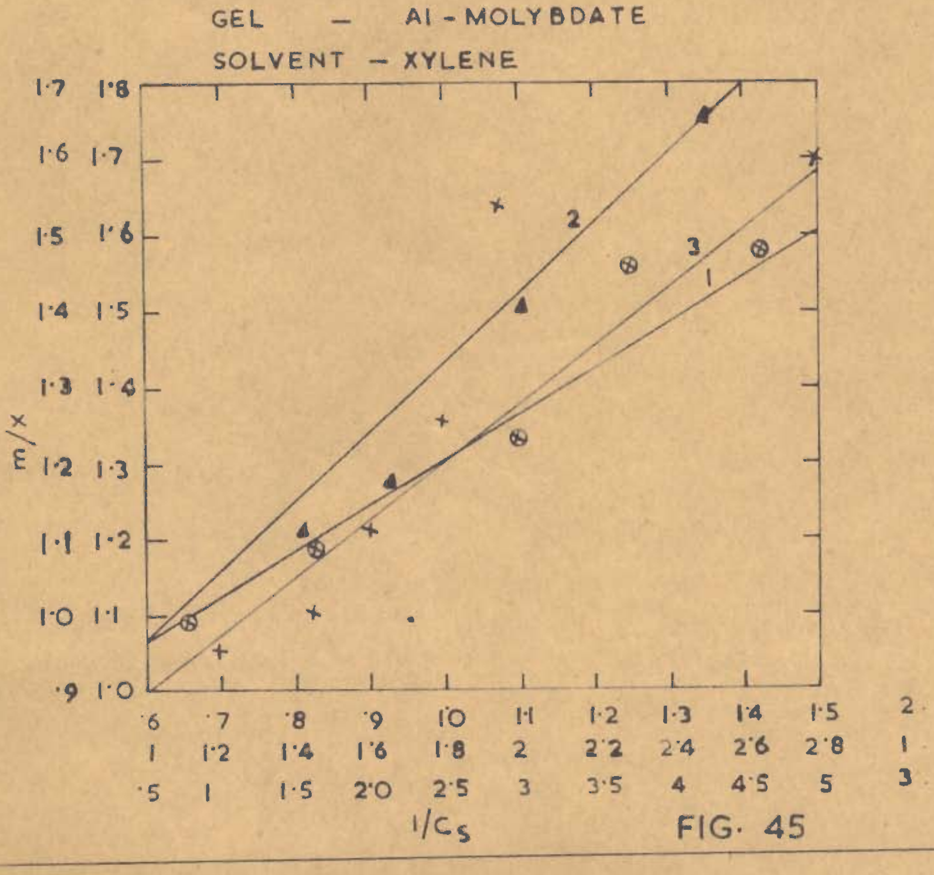


FIG. 45

Table No.67

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-silicate
Solvent - toluene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
1.66	0.48	2.35	2.08	0.42
1.42	0.38	2.18	2.63	0.45
1.25	0.28	2.00	3.57	0.50
1.00	0.18	1.82	5.55	0.55
0.83	0.09	1.80	11.11	0.55
0.71	0.07	1.70	14.28	0.58

a = 1.52
b = 2.38 Fig. 15(3)

Table No. 68

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - silica
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.10	2.80	0.90	0.35
2.00	0.76	2.48	1.31	0.40
1.66	0.52	2.29	1.92	0.43
1.42	0.38	2.14	2.63	0.46
1.25	0.30	1.90	3.33	0.52
1.00	0.18	1.70	5.55	0.58
0.83	0.10	1.29	10.0	0.77

a = 4.82
b = 3.03 Fig. 16(3)

Table No.69

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - ferric silicate
Solvent - xylene

Initial concn. $x10^{-4}M$	Eq.concn. c_s in moles per litre	x/m milli-moles per ab. gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	2.20	0.71	0.45
2.00	1.10	1.80	0.90	0.55
1.66	0.80	1.74	1.25	0.57
1.42	0.64	1.60	1.56	0.62
1.25	0.60	1.32	1.66	0.75
1.00	0.50	1.00	2.00	1.0
0.83	0.40	0.82	2.50	1.21

a = 1.33
b = 3.12

Fig. 17(3)

Table No. 70

Solute - p- dimethyl amino anil of phenylglyoxal nitrile
Gel - ~~al-silicate~~ alumina
Solvent - xylene

Initial concn. $x10^{-4}M$	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.10	2.80	0.90	0.35
2.00	0.80	2.40	1.25	0.41
1.66	0.60	2.14	1.66	0.46
1.42	0.45	1.92	2.22	0.52
1.25	0.35	1.80	2.85	0.55
1.00	0.30	1.40	3.33	0.71
0.83	0.18	1.34	5.55	0.74

a = 2.62
b = 3.70

Fig. 18(3)

Table No. 71

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-silicate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.56	1.20	2.60	0.83	0.38
2.00	0.80	2.40	1.25	0.41
1.66	0.50	2.32	2.00	0.43
1.42	0.41	2.01	2.43	0.49
1.25	0.40	1.76	2.50	0.56
1.00	0.30	1.40	3.33	0.71
0.83	0.20	1.23	5.00	0.81

a = 6.17
b = 2.77 Fig. 19(3)

Table No. 72

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-molybdate
Solvent - xylene

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m millimoles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	1.20	0.76	0.83
2.00	1.02	1.05	0.98	0.95
1.66	0.60	1.00	1.66	1.00
1.42	0.50	0.90	2.00	1.11
1.25	0.40	0.80	2.50	1.25
1.00	0.35	0.65	2.85	1.53
0.83	0.20	0.60	5.00	1.66

a = 6.75
b = 1.11 Fig. 20(3)

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p- DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

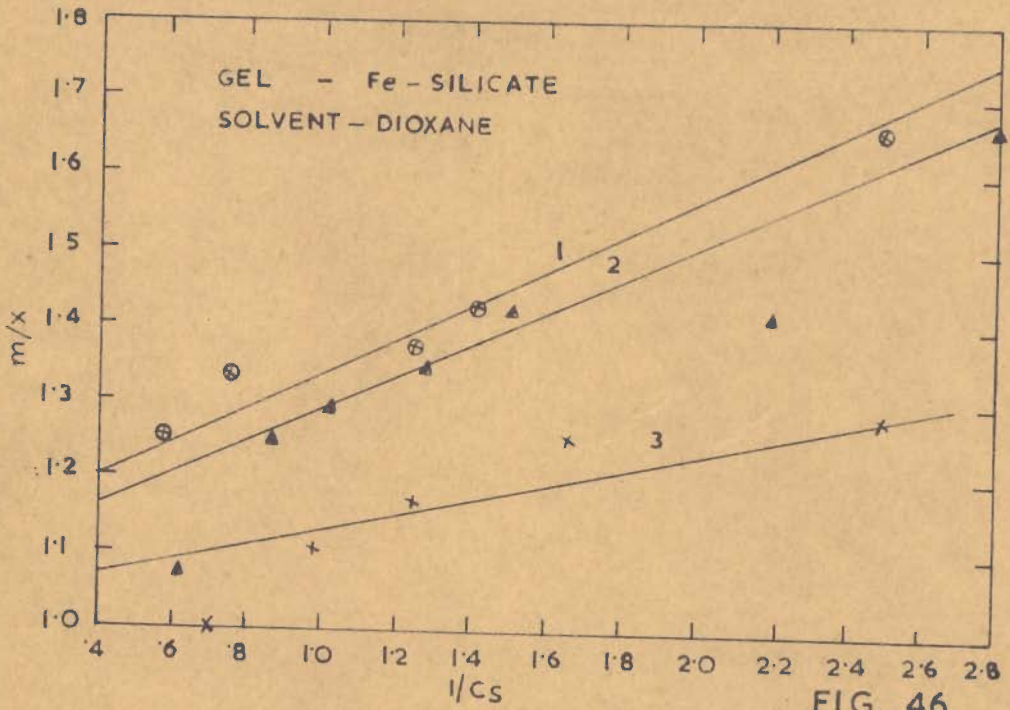


FIG. 46

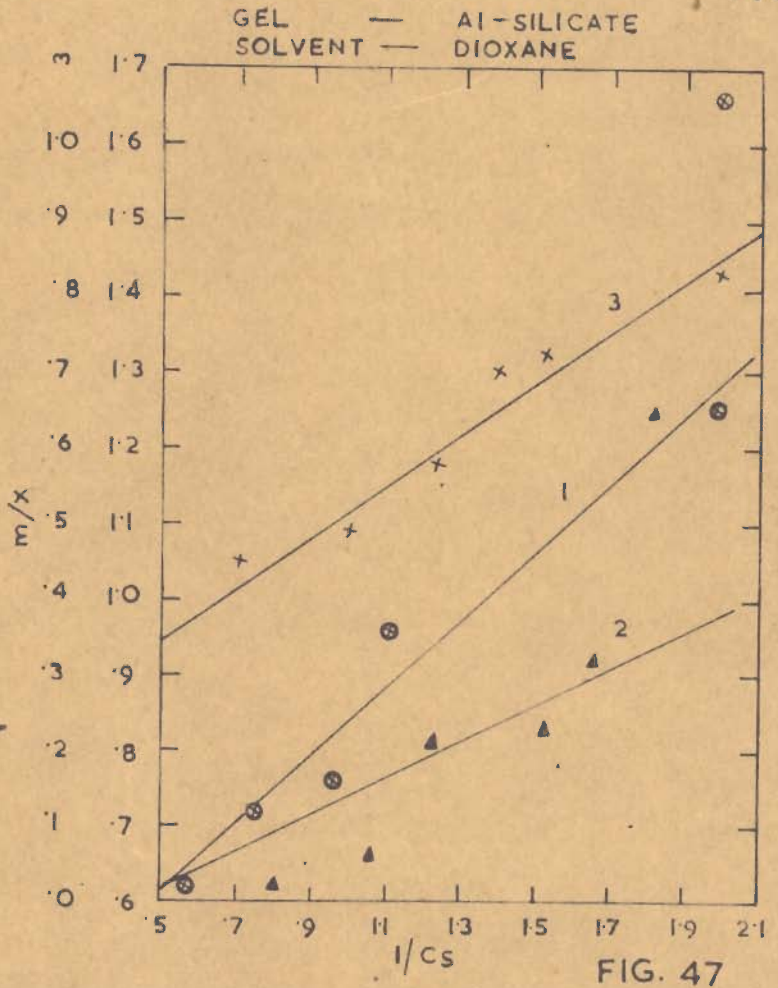


FIG. 47

Table No. 73

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Fe-silicate
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	1.0	0.71	1.00
2.00	1.01	0.90	0.99	1.11
1.66	0.80	0.86	1.25	1.16
1.42	0.60	0.80	1.66	1.25
1.25	0.40	0.78	2.50	1.28
1.00	0.30	0.70	3.33	1.42
0.83	0.20	0.60	5.00	1.66

a = 1.30
b = 0.93 Fig. 21(3)

Table No. 74

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-silicate
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.40	2.20	0.71	0.45
2.00	1.00	2.03	1.00	0.49
1.66	0.80	1.73	1.25	0.57
1.42	0.71	1.42	1.40	0.70
1.25	0.65	1.38	1.53	0.72
1.00	0.50	1.20	2.00	0.83
0.83	0.25	1.00	4.00	1.0

a = 1.13
b = 2.94
Fig. 22(3)

Table No.75

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - Al-molybdate
Solvent - dioxane

Initial concn. x10^{-4}M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.82	0.70	0.54	1.42
2.00	1.45	0.60	0.68	1.66
1.66	1.05	0.55	0.95	1.81
1.42	0.92	0.48	1.08	2 .08
1.25	0.75	0.45	1.33	2.22
1.00	0.68	0.32	1.47	3.12
0.83	0.50	0.30	2.00	3.33

a = 1.28
b = 0.90 Fig. 23(3)

Table No.76

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - alumina
Solvent - dioxane

Initial concn. x10^{-4}M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	1.30	2.40	0.76	0.41
2.00	0.90	2.20	1.11	0.45
1.66	0.55	2.05	1.88	0.48
1.42	0.48	1.92	2.08	0.52
1.25	0.38	1.82	2.63	0.55
1.00	0.20	1.64	5.0	0.60
0.83	0.10	1.06	10.00	0.94

a = 7.00
b = 2.50 Fig. 24(3)

Table No. 77

Solute - p-dimethyl amino anil of phenylglyoxal nitrile
Gel - silica
Solvent - dioxane

Initial concn. $\times 10^{-4}$M	Eq.concn. c_s in moles per litre	x/m milli-moles adsorbed per gm.	$\frac{1}{c_s}$	$\frac{m}{x}$
2.50	0.90	3.20	1.11	0.31
2.00	0.55	2.95	1.81	0.33
1.66	0.28	2.80	3.57	0.35
1.42	0.18	2.50	5.55	0.40
1.25	0.10	2.32	10.0	0.43
1.00	0.08	1.86	12.50	0.53
0.83	0.06	1.52	16.66	0 .65

a = 2.06

b = 3.22

Fig. 25(3)

* * *

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.

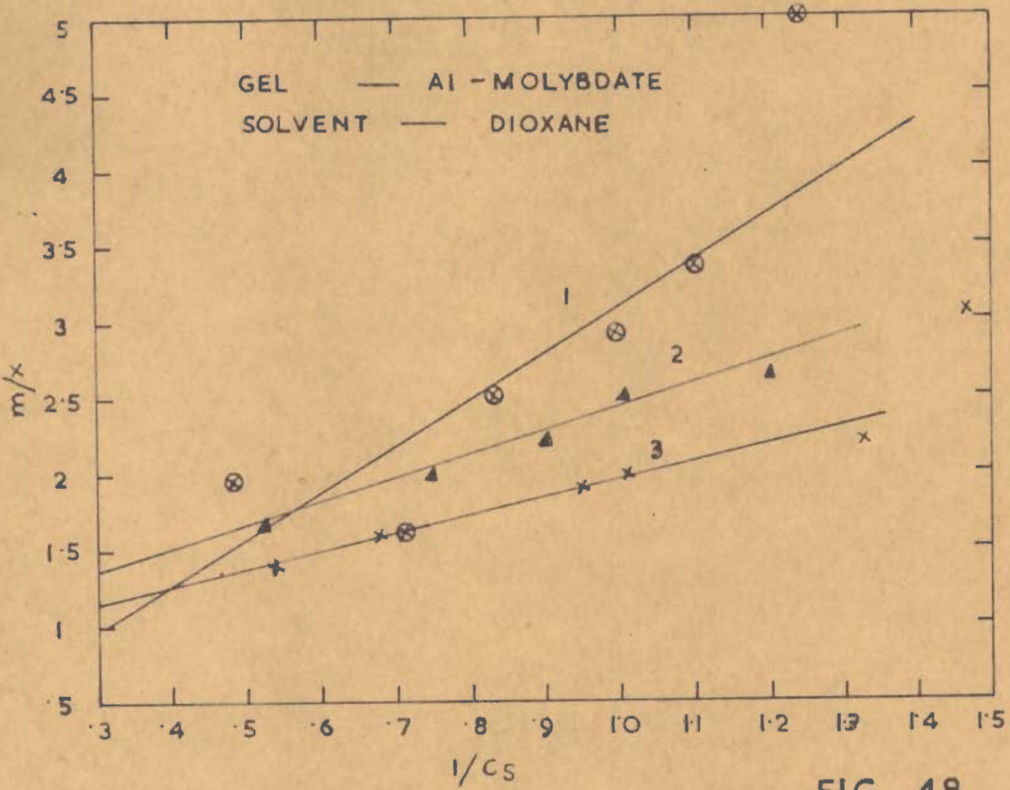


FIG. 48

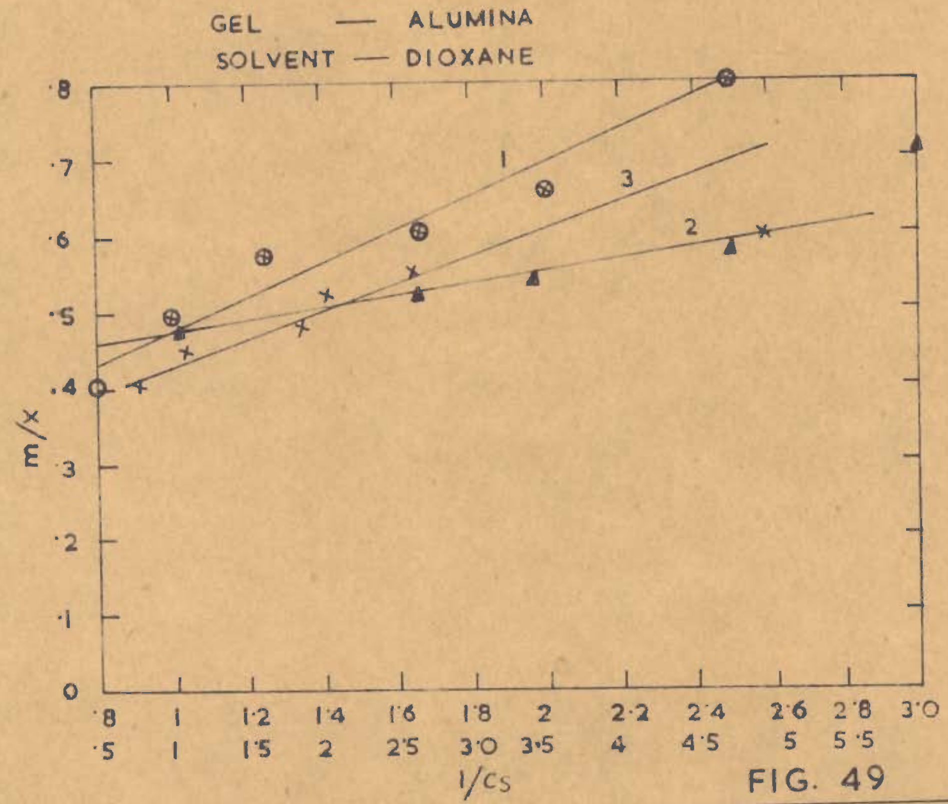


FIG. 49

3.

Preparation of adsorbents -

The behaviour of the hydrous oxides as adsorbents depends largely on the method of their preparation. Impurities on the adsorbent and heat treatment affect greatly the extent of adsorption on them. The adsorbent used in the work reported here were prepared according to methods given below :

(i) Activated silica gel(61-63):- Sodium silicate (E.Merck) solution was prepared in tripled distilled water. The sp.gravity of the solution was adjusted to 1.16 by diluting the solution and was kept in a bottle closed by a rubber stopper.

To prepare the Sol, 40 cc of conc. HCl (A.R) sp. gr. 1.2 was diluted with 125 cc of tripled distilled water, and 75 cc of the sodium silicate, solution was poured into dilute acid. The mixture was dialysed in a parchment bag against repeated changes of distilled water till the gel was formed, which usually requires 48 hours. It was broken into pieces and the salt and excess acid were washed with hot water. The rate at which the gel was dried determined the type of pore as well as the degree of porosity. Slow drying was usually practised as the first step. Air drying at 75°-120°C was first employed and then the temperature was gradually increased to 300°C. Silica gel prepared by this method was hard and glassy although by other methods it might be soft and opaque white. The gel was activated for about 4 hours and then stored in a well closed bottles. The activated gel had a water content of 3.32 % as determined by the ignition to a constant weight in a silica crucible.

(ii) Activated Alumina gel(68-70).

10 g. of aluminium sulphate in 100 ml. of water was boiled and mixedwith 50 ml. of strong ammonium hydroxide, with 20 ml. of 10 % acetic acid and put on the water - bath. A beautiful transparent raw gel appeared after five minutes. It was then transferred in air oven and dried at about 70 - 80° for 24 hours.

As regards the suitable temperature of roasting there is, however, no unaminity, Perry(64) used a temp. of 200°C. Mero et. al(65) activated alumina gel at 400°C, Wood and others(66) activated at a temperature of 1000° and Dunstant(67) recommend 600-700° for bauxite.

The gel used in the following experiments was activated at 280-290°C. Hard grains were obtained which were transparent though small in size. They did not crumble in contact with water, probably by slower drying it might have been possible to obtain larger grains(Alumina which is active as an adsorbent, always contain some water). It should not be reactivated on too high a temperature because if all the water is driven off structural changes occur(sintering) and the alumina loses activity. The adsorbent dried at this temperature still contained some moisture (8%).

(iii) Activated globular Aluminium silicate gel -

A solution of 250 ml. of 10 % sodium silicate

(E.merck) was added to a 60 ml. of 27 % sulphuric acid (A.R) for formation of silica sol (I) of pH 2.60 (I) and 15 ml. of basic aluminium sulphate(71) were mixed and aged by standing for 10 hours. The solution was sprayed through a nozzle into a chamber filled with dil. ammonium hydroxide on the bottom and allowed to stand for aging. It was cut into small pieces and washed repeatedly with distilled water till it free from foreign ions. It was dried at 200° C (water content 2.58%.).

(iv) Ferric silicate -

First of all a colloidal solution of ferric silicate was prepared as described below(73);

Ferric chloride solution (100cc) having 4.3 gm. atoms of chlorine per litre diluted to 400 cc with distilled water, was taken to prepare the colloid. Sodium silicate solution (193.9 cc) having a 11.092 moles of Na_2O and 12.4 moles of SiO_2 per litre was taken which had Na_2O content equivalent to the total chloride content of the 100 cc of the ferric chloride solution and diluted to 1550 cc with distilled water. This diluted sodium-silicate solution was gradually added to ferric chloride solution with constant stirring. The precipitate of iron silicate formed was peptised by ferric or hydrogen ions. A yellowish red sol. of iron silicate was obtained.

The gel was prepared by the dialysis of the above sol against distilled water. The gel thus obtained was cut into small pieces and was washed repeatedly with distilled water and dried at 200°C (water content 2.0 %).

(v) Aluminium Molybdate Gels(74) -

This gel was prepared by mixing equal volume of 12 % solution of aluminium chloride (A.R) with 20 % solution of sodium molybdate (A.R). A precipitate was thrown off immediately on mixing the two gel forming solutions which got peptised in a few minutes and a clear sol was obtained, which finally settled to a translucent gel. It was washed and dried at 200°C (moisture content 4.0 %).

Surface area of adsorbents -

The surface areas of the gel powders were determined by adsorbing-p-nitrophenol (PNP) from water(75) at pH 10.0. The quantity of p-nitrophenol adsorbed was determined by measuring the difference between the p-nitrophenol concentration in the solution before and after adsorption (for details vide Chapter V). The concentration of the dye was determined by measuring the O.D. of PNP at 400 mu.

Surface area and pore volume of different gels are tabulated below :

Table - 78

Gel	Surface area m^2/g	Pore volume(Detail is given in Chapter V)
Silica	700	0.70
Alumina	614	0.50
Aluminium silicate	560	0.90
Ferric silicate	500	0.43
Aluminium molybdate	480	0.60

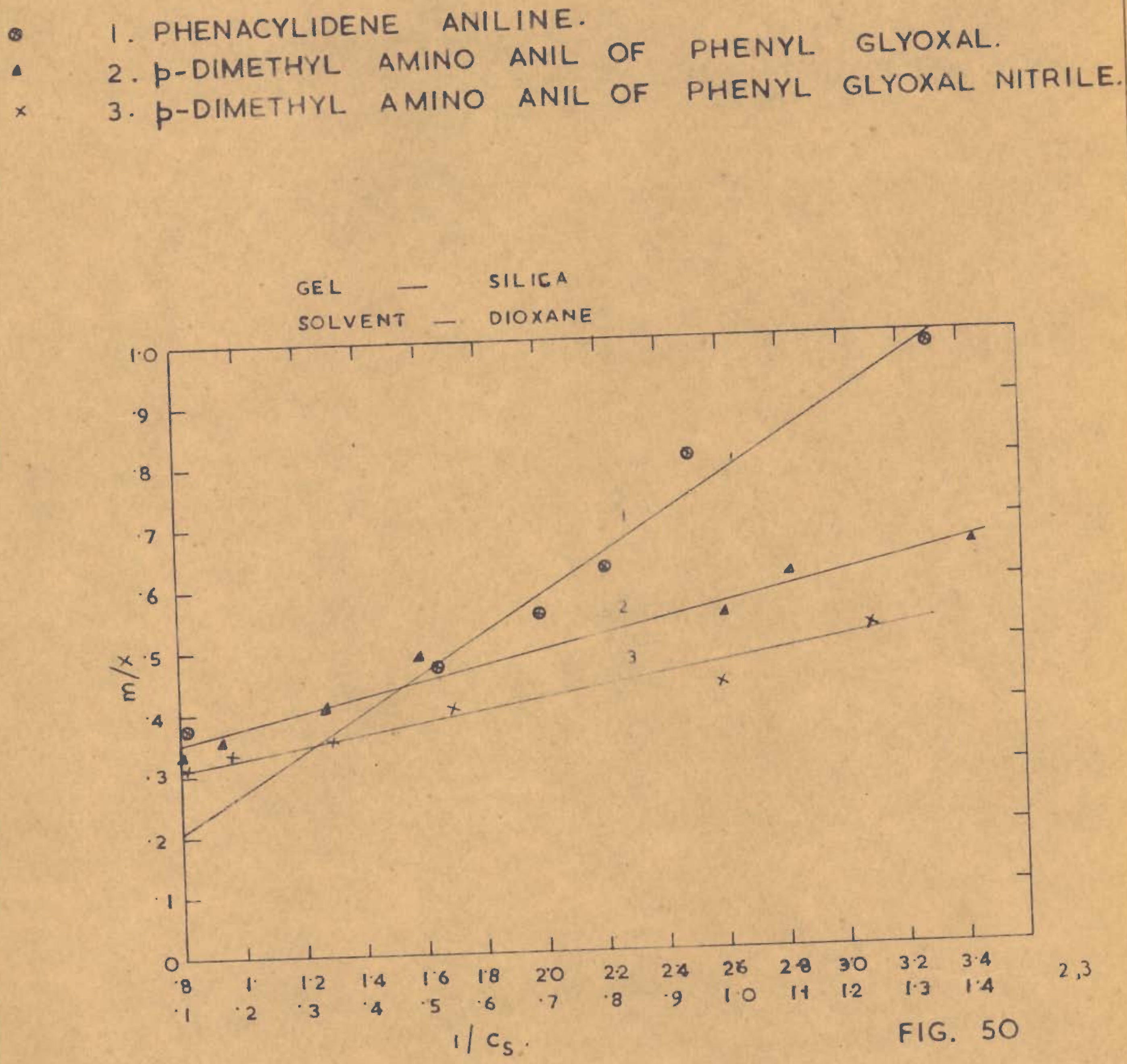

⊗ 1. PHENACYLIDENE ANILINE.
▲ 2. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL.
× 3. p-DIMETHYL AMINO ANIL OF PHENYL GLYOXAL NITRILE.
GEL — SILICA
SOLVENT — DIOXANE
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
m/x
1
2
3
·8 1· 1·2 1·4 1·6 1·8 2·0 2·2 2·4 2·6 2·8 3·0 3·2 3·4
·1 ·2 ·3 ·4 ·5 ·6 ·7 ·8 ·9 1·0 1·1 1·2 1·3 1·4
2,3
1/Cs.

FIG. 50

Desorption and reversibility -

A set of experiments was designed to see if the anils adsorption process was truly reversible. It consisted of adsorbing anils solution in benzene, xylene, toluene, carbon tetrachloride and dioxane, on to silica, alumina, Al-silicate, ferric silicate and Al-molybdate gels at room temperature, decanting as much of the excess solution as possible, adding some pure solvent, and desorbing by agitating the gel and solvent slurry. The desorbing solvents used were benzene, xylene toluene, carbon tetrachloride, dioxane, chloroform, ethyl alchol, methyl alcohol, acetone, ethyl-acetate and acetonitrile. In nonpolar solvent desorption was slow and complete in few hours (8-9). Desorption with polar solvent was complete in one to two hours. This shows the physical adsorption of the anils.

The assumption of a spherical shape of the particles was used as a basis for calculating the average particle diameters. The values obtained for these diameters are not at all arbitrary. A few simple calculations demonstrate the fact that exactly the same numerical results are obtained in each of the following cases:

The average pore diameters were calculated in a strictly comparable manner. Here, however, in the formula

$$d = 6\ (V/A),$$

the volume specified is the pore volume(76-78), which is numerically equal to the $(\text{particle density})^{-1} - (\text{real density})^{-1}$.

(i) If the particles are spherical with diameter = d, volume, $V = \pi d^3/6$, and Area, $A = \pi d^2$, then $d = 6\ (V/A)$.

(ii) If the particles are cubes with length of side = d, volume = d^3, Area = $6d^2$, then $d = 6\ (V/A)$.

(iii) If the particles are cylinders with height = diameter = d, volume = $\pi d^3/4$, and Area = $3\pi d^2/2$, then $d = 6\ (V/A)$.

Table - 79

Gels	Surface area m^2/g	Real density g/cc	Particle density g/cc	Pore volume cc/g	Particle diameter A.U.	Av.Pore diameter A.U
Silica	700	2.24	0.87	0.70	38	60
Alumina	614	2.16	1.03	0.50	45	48
Al-silicate	560	2.20	0.73	0.90	48	96
Fe-silicate	500	2.80	1.01	0.43	66	51
Al-molybdate	480	2.00	0.90	0.60	62	75

Thus, it is evident that so long as the particles approximate any of these simple geometrical shapes, the values reported in the accompanying tables as average particles diameters are actually significant figures. They should give close approximations to the true average dimensions of the particles. These values are calculated from the surface area (A) and the reciprocal of the real density of the gel. The method which has been used to determine the real density of such gels is pycnometric$^{(79)}$ (given in Chapter V).

Results and Discussion

Adsorption isotherms of phenacylidene aniline, p-dimethyl amino anil of phenyl glyoxal and p-dimethyl amino anil of phenyl glyoxal nitrile in a non polar solvents samples of different gels are shown in (table 3-77). It will be seen that the isotherms are practically of the same nature in all gels. Positive adsorption is detected with all the solutes and the rapidity of adsorption shows that it occurs only on the external surface of the particles(80). The adsorption isotherms given in (fig 1-25) shows that the adsorption increases with increasing concentration of the anils. The adsorption isotherms are however regular and concave to the concentration axis. This suggest that this adsorption is possibly of uni-molecular layer.

Much of the data in the literature in which a solute is adsorbed from solution on a solid adsorbent can be satisfactorily fitted to a Langmuir type equation indicating that the adsorption is mono-molecular in nature. In the present experiments the adsorption of anils from nonpolar solvents on different inorganic gels appear to be essential Langmuir in character and the order of adsorption is p-dimethyl - amino anil of phenyl glyoxal nitrile > p-dimethyl amino anil of phenyl glyoxal > phenacylidene aniline. The adsorption affinities of the gels are in the order silica gel > alumina > al-silicate > fe-silicate > al-molybdate. The presence of -CN and double bonds raises the adsorbability in the solute(82). The experimental results further suggest that adsorption increases as the mol. wt. increases.

The Langmuir equation can be expressed in the form

$$x/m = abc\ (1 + ac)$$

$$\text{or}\quad \frac{c}{(x/m)} = \frac{1}{ab} + \frac{c}{b}$$

Inthe above equation x, is the amount adsorbed in moles per gm. and C is the eq. concentration.

A plot of m/x against $\frac{1}{c_s}$ (fig.26-50) was linear for the anils in nonpolar solvents on different gels indicating that the Langmuir equation provides a reasonable fit for these data. From such isotherms the values of the constant a and b were determined. The values of the constants a, and b, provided the following information.

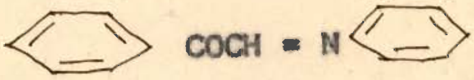
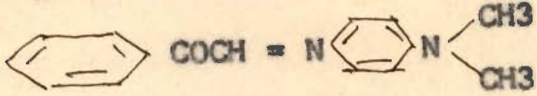
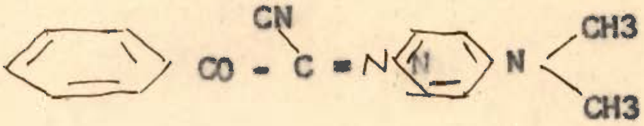
The adsorption affinities of the gels as inferred from the constant a, for different nonpolar solvents are in the following order :

Silica > Alumina > Al-silicate > Fe-silicate > Al-molybdate. The values of b, are also in the same order i.e. Silica > Alumina > Al-silicate > Fe-silicate > Al-molybdate, which shows that the surface area of the gels available for adsorption of anils from nonpolar solvents decreases in the following order :

Silica gel > Alumina > Al-silicate > Fe-silicate > Al-molybdate.

The extent of adsorption however clearly varies considerably with the nature of the solvent. A possible interpretation would be that the orientation of the anils molecules at the surface; varies according to the solvent from which it was adsorbed.

It is also possible to say something regarding the orientation of the solute molecules at the gel surface from the formation of the purple violet coloured complex on the adsorbent surface. There are two adsorption sites in the solute molecules, one = O, and the other = N -. Free rotation is possible of the phenyl group attached to - C = O, according to the model made for

	cross sectional Area
	$110\ \text{A}^{o^{2}}$
	$123.5\ \text{A}^{o^{2}}$
	$132.3\ \text{A}^{o^{2}}$

(cross sectional area of solutes were determined from geometry without considering orientation even when a two site surface interaction is assumed). Due to - OH groups present on the surface of the adsorbent, the structure of the anils might be changing from benzenoid to quinonoid form, thereby developing colour.

Two observations support this :-

(a) Coloured complexes are formed in the decreasing strength in the order silica, alumina, Al-silicate, Fe-silicate and Al-molybdate (no colour). The first two gels are having a high density of surface - OH groups(83) and the other which have these groups to a much lesser extent (silica 8-OH/$100A^{o2}$, Alumina 6-OH/$100A^{o2}$, Al-silicate 3-OH/$100A^{o2}$, Fe-silicate 2-OH/$100A^{o2}$ and Al-molybdate - Nil).

(b) The solvents (acetone, chloroform, acetonitrile, ethyl alcohol) which easily elute the complex are those which form strong bonds with surface - OH groups.

(ii) INTRODUCTION:

Silica gel possess enough pores which can act as centres for the adsorption of ions or solvents or both. With pure solvent it may be a purely physical phenomenon but when solutions are used then the mechanism of adsorption is quite complicated and several factors have to be taken into account to explain it. Dalton(1) reached the following conclusion on the exclusion of ions (nitrate) in aqueous solution from the pores of high surface area silica gel :

(1) Exclusion of nitrates is due to the cation, not the nitrate ion.

(2) Water adsorbed on the gel surface does not play a role in the exclusion phenomenon.

(3) Cation exchange is usually slight enough to be negligible; in doubtful cases addition of excess acid represses exchange.

(4) Exclusion can be related to ion hydrate size, with the greater size (and greater exclusion) it is associated with ions of higher charge and smaller ionic radius.

McConnell and Maatman(2) extended the studies to nitrates of complex cobalt amines. According to them the pore volume available to anion can be an index of the size of its hydrate. Hydrophilic ligands like CO(III) amines, would show lesser pore availability than hydrophobic tris-bidendate complex of cobalt of smaller size. Furthermore the less stable complexes in which exchange of the ligand with water is possible, reaction with the silica is enhanced as can be seen from the following example of the interaction of cobalt 1,2 propylene diamine, co $(pn)3^{+3}$ with silica gel:

$$\left[CO(pn)2\right]^{+3} + 2H_2O \xrightleftharpoons{K_1} \left[CO(pn)_2\,(H_2O)_2\right]^{+3} + pn \text{ ....(i)}$$

$$pn + H_2O \xrightleftharpoons{K_2} \left[Hpn\right]^{+} + OH^{-} \text{ ....(ii)}$$

$$\left[CO(pn)_2\,(H_2O)_2\right]^{+3} + 2\ SiOH \xrightleftharpoons{K_3} \left[CO(pn)_2(OSi)_2\right]^{+1}$$
$$+ 2H + 2H_2O \text{ ....(iii)}$$

$$pn + SiOH \xrightleftharpoons{K_4} \left[SiOH\ pn\right] \text{ .... (iv)}$$

$$\left[CO(pn)_3\right]^{+3} + 2.SiOH \xrightleftharpoons{K_5} \left[CO\ (pn)_2\ (OSi)_2\right]^{+1} + 2H^{+} + pn\text{..(v)}$$

(1) K_2 was determined by measuring Ph in pn-H_2O solutions.

(2) K_1 was determined by measuring pH in $\left[CO\ (pn)_3\right]$ - $(NO_3)_3$ - H_2O solutions; to make the calculation reaction II was taken into account.

(3) K_4 was determined by measuring pH in gel - water - pn mixtures, taking into account reaction (II).

(4) Since reaction V is redundant K_3 could be calculated by measuring the pH of gel-water - $CO(pn)_3^{+3}$ mixtures, taking into account reactions, I,II and IV.

(5) With K_3 known, the extent of $(CO\ (pn)_2\ (OSi)_2\ )$ formation as a function of salt concentration and pH could be predicted.

In the light of the above discussion, another interesting aspect for further study can be whether the consideration involved in the above interactions can be applied to systems comprising of non-aqueous solution of complexes and silica gel. To investigate this Zn^{++}, Cd^{++}, Hg^{++} complexes of p-dimethyl-amino anil of phenyl-glyoxal and p-dimethyl amino anil of β-naphthyl glyoxal were chosen employing the polar compound acetone as the solvent.

EXPERIMENTAL

Materials :-

Stock solutions of 1.0×10^{-3}M concentration of Zn^{++}, Cd^{++}, Hg^{++} complexes of p-dimethyl amino anil of phenylglyoxal and p-dimethyl amino anil of β-naphthyl glyoxal (isolation of the complexes are given in Chapter II and III) were prepared in double distilled acetone(3).

Silica gel was prepared as described in previous Chapter. The pore volume and surface area of the gel were 0.50 ml/g and 700 m^2/g respectively (vide Chapter V).

Procedure :-

25 ml. (brownish yellow coloured complex) solutions of different concentration (5.0×10^{-4}; 3.33×10^{-4}, 2.50×10^{-4}, 2.0×10^{-4}, 1.66×10^{-4}, 1.42×10^{-4}, 1.25×10^{-4}, 1.11×10^{-4}, 1.0×10^{-4}M) were mixed with 12.0 g. silica gel in a number of pyrex tubes. The mixtures were shaken for about four hours and kept overnight to attain the equilibrium. The contents of the test tubes were then centrifuged

for about 10 minutes and the concentration of the centrifugate was estimated from absorbance measurements (carried out at λmax. 540-580 mu vide Chapters II and III) using unicam SP-500 spectrophotometer.

Some solutions were acidified with hydrochloric acid (1.0×10^{-3}M) in order to repress the possible cationic exchange with hydrogen of the surface silanol groups.

Formula used - "Percent availability" A is the percentage of the pore volume of the gel available to a solute, using as 100 % reference the pore volume available to the solvent. Thus, when A is less than 100 %, the solute does not see as much pore volume as the solvent. To measure A, a solution of known volume and concentration is mixed with a known weight of gel and the mixture is held at the desired temperature. After a steady state is achieved, the concentration of the solution external to the gel particle is measured. The amount of solute (in moles) within the pores of 1 g. of gel is

$$\frac{C_i\ V - C_f\ (V - WP)}{W}$$

where C_i and V are the concentration(moles/ml.) and volume (ml) of the solution added to Wgm. gel of pore volume P(ml)/gm. and C_f is the concentration of the solution external to the gel particles when a steady state is achieved. The amount of solute there would be in the pores of one gram of gel if the percent availability were 100% is C_fP. Therefore, A is given by dividing the actual amount by C_fP and multiplying by 100

$$A = \frac{C_i - C_f\,(V-WP)}{W} \times \frac{1}{C_f P} \times 100$$

$$A = \frac{V}{WP}\left(\frac{C_i}{C_f} - 1\right) + 1 \qquad \times 100$$

Table No. 1

Apparent pore availability of silica to Zn^{++}-p-dimethyl amino anil of phenyl-glyoxal complex.

Initial concn. $x10^{-4}M$	Eq.concn. $x10^{-4}M$	o/o Availabilities A	Average A,value
5.0	4.464	150.01	
3.33	2.973	150.02	
2.50	2.241	148.10	
2.00	1.805	145.00	145.91
1.66	1.494	146.29	
1.42	1.287	143.51	
1.25	1.135	142.21	
1.00	0.908	142.21	

$$\frac{V}{PW} = 4.166$$

Fig. 1 - Curve 1

Table No. 2

Apparent pore availability of silica to Zn^{++}-p-dimethyl amino anil of phenyl glyoxal complex. conc.HCl(1.0×10^{-3}M)

Initial concn. $\times10^{-4}$M	Eq.concn. $\times10^{-4}$M	% Availabilities A	Average A,value
5.0	4.325	165.01	
3.33	2.898	162.38	
2.50	2.185	160.06	
2.00	1.748	160.63	158.39
1.66	1.457	158.04	
1.42	1.254	155.14	
1.25	1.108	153.39	
1.00	0.888	152.54	

Table No. 3

Apparent pore availability of silica to Cd^{++}- p - dimethyl amino anil of phenylglyoxal complex.

Initial concn. $\times10^{-4}$M	Eq.conc. $\times10^{-4}$M	% Availabilities A	Average A,value
5.00	4.612	135.04	
3.33	3.094	131.90	
2.50	2.347	127.11	
2.00	1.887	125.00	124.74
1.66	1.576	122.20	
1.42	1.351	121.27	
1.25	1.198	118.08	
1.00	0.960	117.35	

Table No. 4

Apparent pore availability of silica to Cd^{++}-p-dimethyl amino anil of phenyl-glyoxal complex.
Concn. Hcl (1.0×10^{-3}M)

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A,value
5.00	4.471	149.29	
3.33	3.025	142.00	
2.50	2.301	136.02	134.45
2.00	1.853	133.04	
1.66	1.541	132.17	
1.42	1.325	129.86	
1.25	1.171	128.10	
1.00	0.943	125.18	

Table No. 5

Apparent pore availability of silica to Hg^{++} - p - dimethyl amino anil of phenylglyoxal complex.

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A,value
5.00	4.716	125.08	
3.33	3.170	121.65	
2.50	2.390	119.17	
2.00	1.949	116.60	115.57
1.66	1.606	114.00	
1.42	1.381	111.76	
1.25	1.223	109.11	
1.00	0.983	107.20	

Table No.6

Apparent pore availability of silica to Hg^{++}-p-dimethyl amino anil of phenyl-glyoxal complex.
Concn. Hcl(1.0×10^{-3}M)

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.562	139.99	
3.33	3.085	133.08	
2.50	2.331	130.20	
2.00	1.881	126.35	128.09
1.66	1.558	127.27	
1.42	1.341	124.54	
1.25	1.184	123.22	
1.00	0.954	120.08	

Table No. 7

Apparent pore availability of silica to Zn^{++} - p - dimethyl amino anil of β-naphthyl glyoxal complex.

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.280	170.08	
3.33	2.856	169.19	
2.50	2.158	166.02	
2.00	1.730	165.01	164.15
1.66	1.441	163.31	
1.42	1.241	160.90	
1.25	1.092	160.28	
1.00	0.877	158.42	

Table No. 8

Apparent pore availability of silica to Zn^{++} - p - dimethyl amino anil of β-naphthyl glyoxal complex. Concn. Hcl (1.0×10^{-3}M)

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.180	181.79	176.11
3.33	2.782	182.06	
2.50	2.093	181.01	
2.00	1.683	178.46	
1.66	1.403	176.31	
1.42	1.208	173.11	
1.25	1.070	170.08	
1.00	0.863	166.13	

Table No. 9

Apparent pore availability of silica to Cd^{++} - p - dimethyl amino anil of β-naphthyl glyoxal complex.

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.36	161.15	152.60
3.33	2.929	157.03	
2.50	2.208	155.09	
2.00	1.770	154.13	
1.66	1.475	152.00	
1.42	1.267	150.30	
1.25	1.123	147.11	
1.00	0.90	144.0	

Table No.10

Apparent pore availability of silica to Cd^{++} - p - dimethyl amino anil of β -naphthyl glyoxal complex. Concn. Hcl (1.0×10^{-3}M)

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.286	170.00	
3.33	2.862	168.12	
2.50	2.162	165.10	
2.00	1.737	163.00	162.08
1.66	1.447	161.32	
1.42	1.246	158.17	
1.25	1.10	156.80	
1.00	0.885	154.13	

Table No. 11

Apparent pore availability of silica to Hg^{++} - p - dimethyl amino anil of β -naphthylglyoxal complex.

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.561	140.09	
3.33	3.051	138.0	
2.50	2.296	137.01	
2.00	1.848	134.26	132.97
1.66	1.545	131.00	
1.42	1.327	129.19	
1.25	1.171	128.10	
1.00	0.941	126.12	

Table No. 12

Apparent pore availability of silica to Hg^{++} - p - dimethyl amino anil of β-naphthyl glyoxal complex. Concn. Hcl (1.0×10^{-3}M)

Initial concn. $\times 10^{-4}$M	Eq.concn. $\times 10^{-4}$M	% Availabilities A	Average A, value
5.00	4.473	149.10	
3.33	2.992	147.3	
2.50	2.261	144.03	
2.00	1.824	140.19	139.55
1.66	1.529	138.0	
1.42	1.27	134.31	
1.25	1.158	133.09	
1.00	0.932	130.39	

RESULTS AND DISCUSSION

The pore availability values, A, for allthe three complexes are higher than hundred (Table 1-12). Values smaller than hundred can be obtained under two conditions :-

(i) the silica pores would exclude the complex cation in preference to the solvent;

(ii) the cation increases in size through solvation.

Higher values of A rule out either of the two possibilities. Since adsorption is intimately connected with pore availability (greater the pore availability, - larger the adsorption of the solute), it may be safely concluded that the silica gel does not make its pore available to the solvent for adsorption. This is quite a normal behaviour, because, unlike water, acetone will exhibit very little tendency to interact with the polar silica gel.

The large availability of silica pores to the cations go to show that the complex ion does not become large through solvation. It appears that the ligands p-dimethyl amino anil of phenyl-glyoxal and p-dimethyl amino anil of β-naphthyl-glyoxal are lyophobic in character and hence there is little tendency of the solvent either to solvate itself or diffuse into the coordinating sphere to make the complex ion large enough for exclusion from the silica pores.

Further confirmation to the fact that ion size largely influences the pore availability (and consequently adsorption) is forthcoming on comparing the average A values with the ionic radii of the cations. Assuming that the simple metal ions and the complex ion does not differ very much in size due to non solvation (or hydration if the medium is aqueous, the comparative values would be:

Table No. 13

Cation	Ionic radii	Pore availability A (p-dimethyl amino anil of phenylglyoxal complexes)	Pore availability A (p-dimethyl amino anil of β-naphthyl glyoxal complexes)
Zn^{++}	0.74 A°	145.91	164.15
Cd^{++}	0.97 A°	124.74	152.60
Hg^{++}	1.10 A°	115.57	132.97

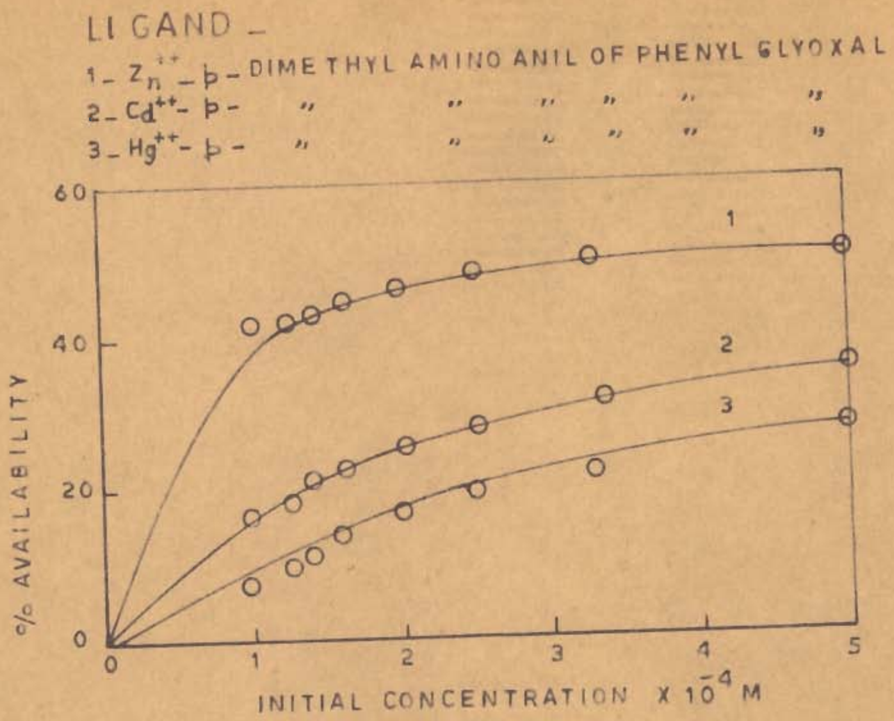

LIGAND –
1 – Zn^{++} – p – DIMETHYL AMINO ANIL OF PHENYL GLYOXAL
2 – Cd^{++} – p – " " " " " "
3 – Hg^{++} – p – " " " " " "
60
40
20
0
1
2
3
0
1
2
3
4
5
% AVAILABILITY
INITIAL CONCENTRATION X 10^{-4} M

FIG. 1

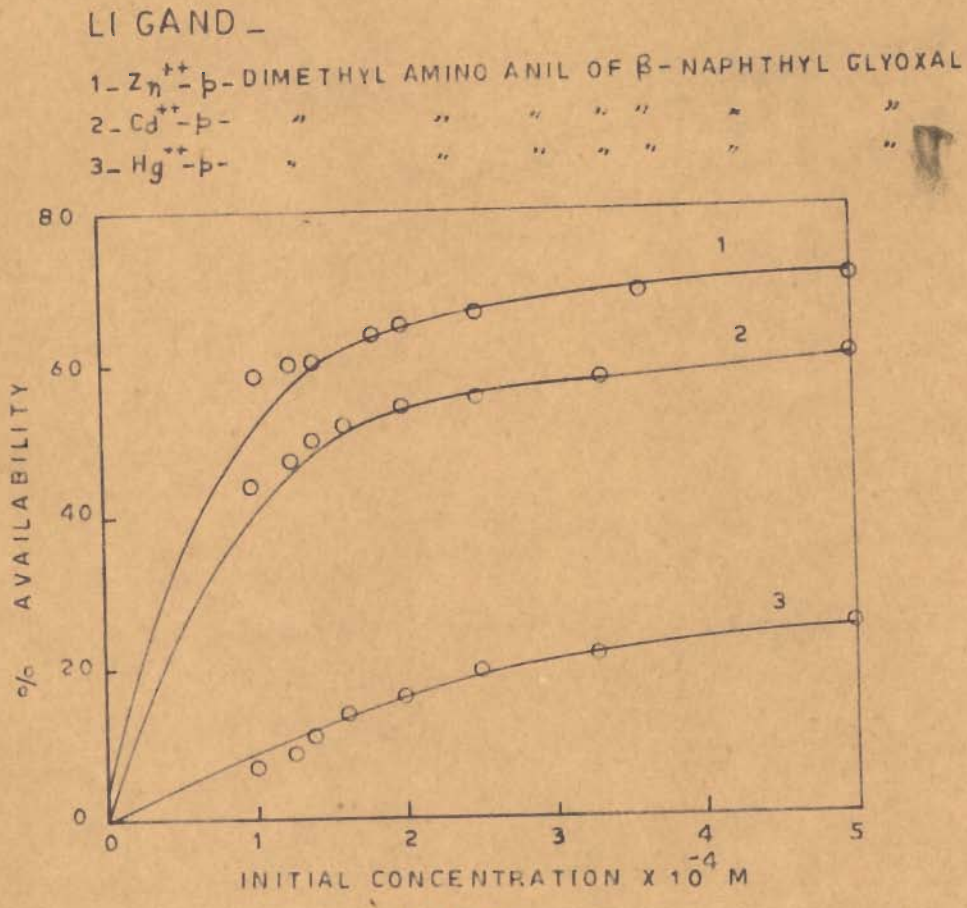

LIGAND –
1 – Zn^{++} – p – DIMETHYL AMINO ANIL OF β – NAPHTHYL GLYOXAL
2 – Cd^{++} – p – " " " " " " "
3 – Hg^{++} – p – " " " " " " "
80
60
40
20
0
1
2
3
0
1
2
3
4
5
% AVAILABILITY
INITIAL CONCENTRATION X 10^{-4} M

FIG. 2

From the above table it is quite evident that the pore availability increases with decrease in the size of the ion.

The contention that pore availability is closely related to adsorption is borne out by the fact that the plots between A and the initial concentration of the complex give curves similar to adsorption isotherm curves (vide typical curves) - (Fig.1-2).

Addition of acid to the adsorbate would normally bring about a decrease in the value of A due to exchange adsorption of hydrogen ions on silica gel. But here the values become higher on addition of even 1.0×10^{-3}M Hcl. This would only be possible if the complex is unstable in presence of acid, decomposing either into simple metal ions or changing into a species which will readily react with the silica gel.

CHAPTER V

Determination of surface area and pore volume of gels.

INTRODUCTION :

A precise knowledge of surface area of materials may be clays or pigments, metals or their hydrous oxides, colloidal dispersions or macromolecules, is of great importance to the chemist, chemical engineer or technologist. Many properties like chemical reactivity in the hetrogeneous system, rate of solution, adsorptive properties, permeability,various type of electrical potentials existing on the particles as such or on the membranes obtained from them, electrical conductivity etc. are greatly influenced by particle size and hence the surface area.

This property is also inter-related to another important characteristic of the solid material, viz., crystallinity. For example, it has been found that the well crystallised material possesses a much lower surface area than the poorly crystallised one. Fripiat(1) reviewing the surface properties of aluminosilicate, drew attention to the influence of such relative characteristics as constitution hydroxyls and surface hydroxyls on surface properties. The development of hydrated surface area in electrically charged clay minerals may be cited as a typical example in support of this view point.

With clays one comes across two more terms viz. internal surface area and external surface. There are clays which have 'internal' surfaces like montmorillonite. The ability of certain molecules to penetrate the montmorillonite layer structure and settle at the interior layer surface, causes a tremendous increase of total surface area covered by the solute molecules. Certain area in a particle, between cracks and splits and in pores can be regarded as internal surface too(1).

Highly porous solids having larger internal area are, therefore, the best adsorbent. On the contrary one speaks about 'external' surfaces of a soil, measuring the entire surface which is surrounding the separate grains as such.

Methods of determination of surface area :-

Many methods primarily based on the use of adsorbed molecules of different phases and properties as gas or liquid phases, polar or nonpolar molecules, and utilising different mechanisms, such as monomolecular adsorption on powders or permeability of the adsorbent for air flow(1) are in vouge. Those based on different principle are the microscopic examination, x-ray and optical scattering, eledtrolytic, interference, radioactive tracer, electron emission, radioactive exchange methods are the methods requiring knowledge of sedimentation rate, rate of dissolution, heat of immersion or heat of solution, heat of conductance and heat of wetting. But these are, however, in limited use. For example, the electrolytic method developed by Bowden and Rideal(2) although quite accurate, is applicable only to metals, while the heat conductance method (based on the retardation of heat transfer by the fine fibres of the gel)(3) is applicable to gels with very open pores. Similarly the heat of wetting method based on the principle that major part of adsorption is due to capillary condensation(4) is applicable only to porous solids like silica although some progress has been made in its use for non-porous substances(5) like titanium dioxide powder.

Determination of surface area by methods based on the adsorption of either gases, liquids or the solutes from the solution have found a more universal use than the methods mentioned briefly in the preceeding paragraph. These methods are the B.E.T. method (gases as adsorbate) fatty acid adsorption method, dye adsorption method and p-nitrophenol (PNP) adsorption method. Before discussing the latter method, which has been successfully employed in the present investigation, it will be worthwhile to review briefly the other methods.

B.E.T. method :-

The most versatile method based on adsorption from gases is the BET method abbreviated after the names of Bruanuer, Emmett and Teller.

Theory - The B.E.T. multilayer adsorption isotherm can be written in the form:

$$\frac{p}{v(po-p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{p}{po} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where po is the saturation pressure of the gas.

v is the volume at S.T.P. of the gas adsorbed at a pressure p of the system, and

V_m is the volume at S.T.P. of the gas adsorbed when the surface of the adsorbent is completely covered with a monolayer of the adsorbate.

C   is a constant for a given system and it is approximately equal to $e^{(E_1-E_2/RT)}$ where E_1 is the heat of adsorption of the first layer and E_2 is the heat of liquefaction.

It follows from the equation (1) that the plot of the left hand side of the equation against $p/_{po}$ is a straight line, the intercept of which on the vertical axis and the slope are equal to 1/mc and V_m, can thus be evaluated. Further more, by combining the above relations,

$$V_m = \frac{1}{\text{intercept + slope}}$$

In practice, the plot is often linear at values of $p/_{po}$ smaller than about$^{(6)}$0.3. In order to determine the surface area of the adsorbent, it is necessary to find the cross section of the gas molecule, i.e, the area of the surface covered by each adsorbed molecule. This area is given by the relation,

$$A = 4(0.866)\left(\frac{M}{4\sqrt{2Nd}}\right)^{2/3}$$

where   M   is the molecular wt. of the gas

d   is the density of the liquefied or solidified adsorbent, and N is the Avogadro's number. For nitrogen at liquid introgen temperature A is 16.24.

A typical example would illustrate the method of calculating surface area by this method.

First calculate the values of $p/V \times (p_o - p)$ and p/po where p_o is 764 mm.

Table (1)

Sample I	p(mm)	38	52	74	90	116	150
	V(ml.)	4.9	5.4	5.9	6.1	6.6	7.0

Table (2)

Sample I	p(mm)	38	52	74	90	116	150
	$p/po \times 10^2$	5	6.8	9.7	11.8	15.2	19.6
	$p/V(po-p) \times 10^3$	10.7	13.5	18.2	21.9	27.1	34.9

The values of $p/V(p_o - p)$ versus p/po for the sample are plotted from the intercepts and slopes of the resulting straight line.

Intercept $= 2.6 \times 10^{-3}$ and

Slope $= 16.4 \times 10^{-2}$

Hence $\frac{(C-1)}{V_m c} = 16.4 \times 10^{-2}$

$C = 64 \quad V_m = 6.0$ ml.

The surface area of the adsorbent is now found by multiplying the number of molecules in V_m ml. by 16.2

(since 10^{20} $A^{o^2} = 1m^2$)

$\therefore$ Surface area of the sample per 100g

$$= \frac{6.6 \times 6.023 \times 10^{23} \times 16.2}{10^{20} \times 22414.6}$$

$$= 26.12 \text{ m}^2$$

The gas adsorption method has several advantages over the other methods. The method is fairly accurate and compares favourably with the electron microscopic and other visual methods. It can be applied equally well to both porous and non-porous material but is not suitable enough for soils since the non-polar gases do not measure the internal surface of extra-ordinary clay minerals of the soil(7-13). Besides the method is economical since the adsorbate can be easily recovered after the completion of the experiment.

Fatty acid adsorption method :-

The method employing the adsorption of straight chain fatty acids from non-aqueous solution is based on studies with insoluble monolayers. It has been shown that properly compressed films of these straight chain fatty acids on a water surface are mono-molecular and occupy the same area of the interface per molecule regardless of the number of carbon atoms in the molecules.

According to Adam(14) each molecule occupies an area of 20.5A^{o^2}. Harkins and Gans(15) found that oleic acid adsorbed as a monomolecular layer on titanium-dioxide and calculated a surface area for the solid which was in good agreement with results obtained by measurement under the microscope.

Although irreversible chemisorption of fatty acids has been observed on such active metals as Adams - platinum and Raney-nickel catalysts, the fatty acid are usually physically adsorbed. The curves obtained are of the Langmuir or L type with the horizontal portion of the curve corresponding to the formation of monomolecular layer. The acid should be free from traces of water(16) (otherwise water initiates chemisorption with reactive materials such as Cu, Cu_2O, CuO, Zn and ZnO etc.). In certain cases (water as the solvent, when the water molecules compete the solute in adsorption) multilayer adsorption is observed, e.g. in the adsorption of fatty acids by graphite(17). Here characteristic of a BET type isotherms are obtained.

Measurement of the surface area of solids by fatty acids adsorption is very simple in principle. A sample of the solid is placed in contact with a fatty acid solution of known concentrations. After adsorption the concentration of fatty acid is again determined by analysis. The difference between initial and final concentration of fatty acid in solution is equal to the amount adsorbed. If the area occupied by each molecule of fatty acid is known, the total area of the solid can be calculated by the expression,

$$S = \left(\frac{x^{1}}{M} \right) N A_m$$

where S - is the surface area of the adsorbent.

x' - gms of solute per gram of solid.

M - the molecular weight of the solute

A_m - the area occupied by one molecule of solute on the surface of solid

N - Avogadro's number.

Dye adsorption method :-

Perhaps the most convenient method for measuring surface area is by the adsorption of dye from aqueous solution. Dye(18-19) concentrations can be determined readily by spectrophotometric methods. Since aqueous solutions are used exhaustive drying of solid and solution is unnecessary unfortunately, the method is not of general validity at present and can only be used in the case of gels. The dye molecules are frequently adsorbed as an ionic micelles(20) and the true cross-sectional area of the adsorbed species is then indeterminate, although even so the method can be used for relative areas of different samples of the same solid.

p-nitrophenol adsorption method (P.N.P) :-

In a recent survey of the forms and significance of solution adsorption isotherms(21), the following requirements for a solute to give reliable specific surface area measurements were listed. These are :

(i) highly polar to ensure strong attachment to the whole surface of polar solids,

(ii) partly hydrophobic to ensure adsorption by nonpolar solids,

(iii) of small molecular size preferably with a planer molecule and likely to be adsorbed with its molecule stacked close together end-on to the surface, to ensure accurate estimates of the area covered per molecule,

(iv) not surface active to avoid the formation of three dimensional molecules at the surface,

(v) coloured, for ease of analysis,

(vi) readily soluble both in water and in non-polar solvents.

It was suggested that p-nitrophenol (PNP) satisfied these requirements best.

EXPERIMENTAL

p-nitrophenol was crystallised from water. Distilled water was used since our material was water insoluble. A stock solution of material was prepared, and diluted as needed.

The adsorptions of aqueous solutions were measured on the spectrophotometer (unicam SP 500) at 400 mu after buffering with a drop of alkali (pH-10 to 11). Sets comprising of eight test tubes containing a weighed sample of powder (1 gm) were arranged, Into each tube were then placed 10 ml. of the solution, varying over a wide range of concentrations, in order to get adsorption values for plotting a suitable adsorption isotherm. The tubes were securely stoppered and then shaken mechanically at room temperature until adsorption equilibrium was reached (generally 4-6 hours).

After agitation the tubes were set aside for 15 min. when most powders had completely settled and the supernatant liquid could be decanted, the samples were subjected to analysis as such or after dilution. Some powders like that of silica and alumina required centfifugation for separating the layers. In cases where a little powder remained floating on the surface of the solution, a drop of ethanol was added to reduce surface tension thereby allowing the powder to sink. On knowing the final concentration of the solution a graph was plotted between equilibrium concentration and amount adsorbed per gm. The monolayer capacity was calculated from the plateau of the isotherm.

Calculation of specific surface area (S.S.a) :-

The monolayer capacity Xm of an adsorbent is the quantity of adsorbate which can be adsorbed by one gram of the adsorbent in a full up monolayer. Its units are the same as those of adsorption x, itself, and may be expressed as moles grams or cubic centimetres (N.T.P); all per gm of adsorbent, according to convenience. If X_m is expressed in gms, then

$$S = \frac{X_m}{M} . N . Am \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where M is the molecular weight of the adsorbats, and N is the Avogadro's number.

A_m the area of surface occupied by each solute molecule in sq.cm.

Here $A_m = 25\ A^{o^2} = 25 \times 10^{-16}$ Sq.cm g^{-1} if X_m - the monolayer capacity is expressed in moles per g then the above relation (1) changes to

ADSORPTION ISOTHERMS OF

1 _ SILICA ... ... PNP
2 _ ALUMINA ... ... PNP
3 _ AL _ SILICATE ... ... PNP
4 _ Fe^{+++} _ SILICATE ... ... PNP
5 _ AL - MOLYBDATE ... ... PNP

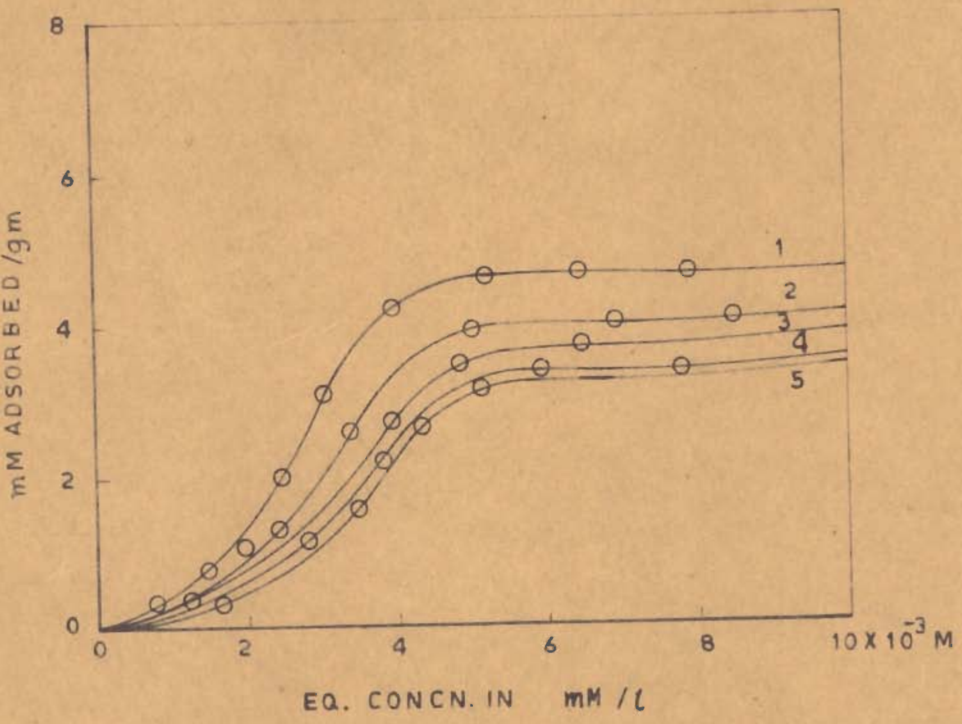


FIGURE _ 1

$S = X_m NA_m$ -(2) with the same usual notation.

DISCUSSION

In the case of the adsorption of PNP the nature of the adsorption isotherms gives an idea of the orientation of the molecule on the surface of the adsorbent.

Two types of orientations, viz. end-on at polar surfaces, and flat-on surfaces, composed of aromatic nuclei have been proposed. End-on adsorption from water gives S-2 type isotherm (initially convex to the solution concentration axis and with a plateau), while flat adsorption gives the normal L-2 type, isotherms or sometimes the H-2 type (starting at a positive value on the vertical axis).

The end-on adsorption is also represented by L4 type of curves possessing a plateau about twice the height of the first.

The adsorption isotherms for the adsorption of PNP on various gels (Fig.1) give S-2 type of curves indicating thereby end-on orientation of the molecule on the surface of the adsorbent. The effective cross sectional area of the adsorbed molecule at room temperature for water as the solvent may therefore be taken as 25 A^{o^2} approximately(22). This value was therefore be chosen to calculate the surface area of the gels from the different adsorption isotherms.

Further confirmation would have been possible if experiments were carried out at different temperature.

In view of the fact that the adsorption of PNP like all other solution adsorptions is exothermic, the amount adsorbed consequently would increase with fall in temperature.

Pore volume :-

To determine the weight of the water content a known weight of the substance was weighed (x) and after this the substance was allowed to stand in water for few hours and reweighed (y). The difference (y-x) gives the amount of water adsorbed by substance, knowing the specific density of the water, the pore volume was calculated:

$$P_v = \frac{(y - x)}{\rho}$$

P_v - Pore volume

Table 3

Observations

		Silica	Al-	Al-Silicate	Fe-Silicate	Al-molybdate
wt. of sample (gm.)	x	3.7810	3.5273	3.3303	3.9573	3.4713
wt.of sample + adsorbed water	y	6.4277	5.2910	6.3276	5.6589	5.5541
pore volume cc	P_v	2.6467	1.7637	2.9973	1.7016	2.0828
pore volume cc/g.	P_v	0.70	0.50	0.90	0.43	0.60

Specific gravity or real density :-

Dried pycnometer was weighed empty, then the pycnometer and capillary stopper were filled with water and weighed. The pycnometer was next emptied and dried, using alcohol and finally an ether or acetone rinse to facilitate the drying operation. A convenient quantity (W) of gel is now carefully introduced into the dry pycnometer, the stopper replaced, and the weight of the pycnometer plus gel was obtained. The pycnometer with gel in it was then filled with water, and stopper replaced, observing that water overflows the capillary. The outside of the pycnometer was wiped dry and the weight of the pycnometer, gel and sufficient water to fill the pycnometer was obtained.

Sp. gr. was determined by the following way :

Wt. of sample in air = W gm.

Wt. of pycnometer filled with water = W_1 gm.

Wt. of pycnometer + sample + enough water to fill it = W_2 gm.

weight of water displaced
or
loss of weight in water = $(W_1 + W - W_2)$ gm.

$$\text{Sp. gr.} = \frac{\text{weight of solid}}{\text{loss of weight in water}}$$

$$= \frac{W}{(W_1 + W - W_2)}$$

Table 4

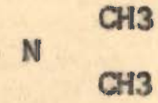
Observations

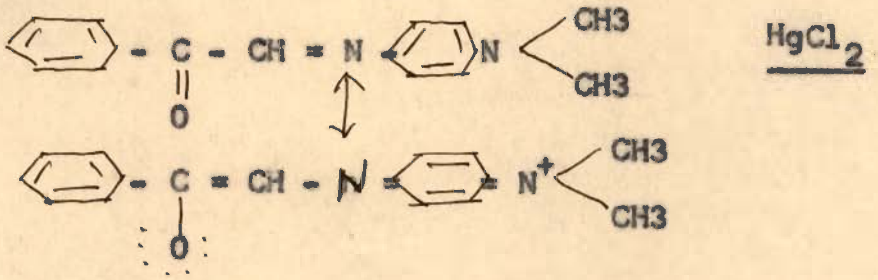
		Silica	Alumina	Al-Silicate	Fe-Silicate	Al-molybdate
wt.of gel in air gm.	W	5.000	5.3200	5.3721	4.8012	5.2750
wt.of Pycnometer + water gm.	W_1	67.458	67.458	67.458	67.458	67.458
wt.of Pycnometer + water + gel gm	W_2	70.226	70.315	70.3881	70.5392	70.0955
Sp.gravity of gel	ρ	2.24	2.16	2.20	2.80	2.00

APPENDIX

Magnetic measurements of Zn(II), Cd(II), Hg(II) complexes of p-dimethyl amino anil of phenyl glyoxal, p-dimethyl amino anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal.

INTRODUCTION :-

Anils having auxochromic group such as  $- N \begin{matrix} CH3 \\ CH3 \end{matrix}$ when brought in contact with Lewis acids experience a resonance throughout the molecule. Due to this effect the seats of interaction become more electron dense and hence more susceptible for chelation.



Ordinarily the above compound should exhibit a diamagnetic behaviour due to the presence of a pair of electrons. But contrary to this, the ligands under investigation show paramagnetic nature (vide infrared). Magnetic susceptibility measurements of the ligand and the metal complexes formed were therefore undertaken to know the structural behaviour of the anils under investigation.

Determination of the expression of magnetic susceptibility -

The magnetic susceptibility measurements, were carried out in this laboratory with the help of Gouy's magnetic balance having a semimicro Mettlar balance and an electro magnetic field of 8.5×10^3 Gauss. The field in the magnet was created by passing an A.C.current via rectifier and stabiliser (universal scientific CO Bombay). Before determining the magnetic susceptibility the constant of the tube was found employing copper sulphate (A.R) as the standard.

(i) wt. of empty tube without magnetic field = W_1 gm.

(ii) wt. of empty tube with magnetic field = W_2 gm.

(iii) wt. of $CuSO_4$. 5H20 without magnetic field = W_3 gm.

(iv) wt. of $CuSO_4 . 5H_2O$ with magnetic field = W_4 gm.

$$W = (W_3 - W_1)$$

$$= \Delta W = (W_4 - W_3) - (W_2 - W_1)$$

$$F = \Delta W \quad g$$

We know

$$\psi = C \frac{\Delta W}{W}$$

where ψ = Sp. susceptibility

C = tube constant

ΔW = change in wt. of the substance under the influence of magnetic field to be measured in mg.

W = wt. of sample.

$$\therefore \text{Sp. susceptibility } \psi = \frac{\text{molar susceptibility}}{\text{mol. wt}}$$

$$= \frac{1460 \times 10^{-6}}{249.69} \text{ for } CuSO_4\ 5H_2O$$

$$\therefore C = \frac{1460 \times 10^{-6}}{249.69} \times \frac{W}{\Delta W}$$

Similar observations were repeated with the complexes to be studied and the effective magnetic moment was determined as follows :-

(i) wt. of empty tube without magnetic field = W_1

(ii) wt. of empty tube with magnetic field $= W_2$

(iii) wt. of complex or substance without magnetic field $= W_3$

(iv) wt. of complex or substance with magnetic field $= W_4$

$$\therefore W = (W_3 - W_1)$$

$$\Delta W = (W_4 - W_3) - (W_2 - W_1) \text{ gm.}$$

Convert ΔW in mg.

$$F = \Delta W \text{ g.}$$

We know that $\psi = C. \frac{\Delta W}{W}$ (with usual notation).

Molar susceptibility $\psi_m = \psi \times$ Mol. wt. of the substance,

$\psi'_M = \psi_M -$ (Diamagnetic correction of the organic molecule under interaction).

$$\mu_{eff} = 2.84 \sqrt{Q'_M \times T}$$

where

μ_{eff} - Effective magnetic moment

$T = 273^{o}$

Diamagnetic correction of :-

p-dimethyl amino anil of methyl glyoxal	p-dimethyl amino anil of phenyl glyoxal	p-dimethyl amino anil of β-naphthyl glyoxal	Cl	I_2
-111.71×10^{-6}	-150.46×10^{-6}	-188.66×10^{-6}	-20.1×10^{-6}	-89.20×10^{-6}

Observations : -

For finding out the value of C, the tube constant :

(i) wt. of empty tube without magnetic field (W_1) = 12.80740 gm.

(ii) wt.of empty tube with magnetic field (W_2) = 12.80732 gm.

$\therefore W_2 - W_1 = - 0.00008$ gm.

Length of the tube upto which it was filled with substance

= 12.0 cm.

(iii) wt. of tube + $CuSO_4 . 5H_2O$ without magnetic field (W_3) = 13.01990 gm.

wt. of tube + $CuSO_4 . 5H_2O$ with magnetic field (W_4) = 13.02592 gm.

$W = W_3 - W_1 = 0.21250$ gm.

$W_4 - W_3 = 0.00602$ gm.

$\Delta W = (W_4 - W_3) - (W_2 - W_1)$

$= 0.00602 + 0.00008 = 0.00610$ gm.

$= 6.1$ mg.

$T = 295^0$

$\psi = C \frac{\Delta W}{W}$

$$\therefore C = \frac{1460 \times 10^{-6}}{249.69} \times \frac{0.21250}{6.1} = 0.2042 \times 10^{-6}$$

Table - 1

Substance:- p-dimethyl amino anil of phenylglyoxal.

wt. of Substance	I	II	III
without magnetic field	13.07910 gm.	13.07910 gm.	13.07910 gm.
In magnetic field	13.07963 gm.	13.07963 gm.	13.07963 gm.

Table - 2

Substance:- p- dimethyl amino anil of phenylglyoxal Cd^{++}- complex

Wt. of Substance	I	II	III
without magnetic field	13.51750 gm.	13.51750 gm.	13.51750 gm.
In magnetic field	13.52428 gm.	13.52428 gm.	13.52428 gm.

Table - 3

Substance:- p- dimethyl amino anil of phenylglyoxal Zn^{++}- complex

Wt. of Substance	I	II	III
without magnetic field	13.07585 gm.	13.07585 gm.	13.07585 gm.
In magnetic field	13.07620 gm.	13.07620 gm.	13.07620 gm.

Table - 4

Substance:- p-dimethyl amino anil of phenylglyoxal Hg^{++}- complex.

Wt. of Substance	I	II	III
without magnetic field	13.27835 gm.	13.27835 gm.	13.27835 gm.
In magnetic field	13.28022 gm.	13.28022 gm.	13.28022 gm.

Table - 5

Substance :- p-dimethyl amino anil of β -naphthylglyoxal

Wt.of Substance	I	II	III
without magnetic field	13.09265 gm.	13.09265 gm.	13.09265 gm.
with magnetic field	13.09622 gm.	13.09622 gm.	13.09622 gm.

Table - 6

Substance :- p-dimethyl amino anil of β -naphthylglyoxal
Cd^{++} - complex.

Wt. of Substance	I	II	III
without magnetic field	13.21180 gm.	13.21180 gm.	13.21180 gm.
with magnetic field	13.21277 gm.	13.21277 gm.	13.21277 gm.

Table - 7

Substance :- p- dimethyl amino anil of β-naphthylglyoxal
Zn^{++} complex.

Wt. of Substance	I	II	III
without magnetic field	13.23395 gm.	13.23395 gm.	13.23395 gm.
with magnetic field	13.23672 gm.	13.23672 gm.	13.23672 gm.

Table - 8

Substance :- p-dimethyl amino anil of β-naphthyl-glyoxal
Hg^{++} complex.

Wt. of Substance	I	II	III
without magnetic field	13.27540 gm.	13.27540 gm.	13.27540 gm.
with magnetic field	13.27799 gm.	13.27799 gm.	13.27799 gm.

Table - 9

Substance :- p-dimethyl amino anil of methylglyoxal

Wt. of substance	I	II	III
without magnetic field	13.07753 gm.	13.07753 gm.	13.07753 gm.
with magnetic field	13.07781 gm.	13.07781 gm.	13.07781 gm.

Table - 10

Substance : - p-dimethyl amino anil of methylglyoxal
Cd^{++} complex.

Wt. of substance	I	II	III
without magnetic field	13.11420 gm.	13.11420 gm.	13.11420 gm.
with magnetic field	13.11437 gm.	13.11437 gm.	13.11437 gm.

Table - 11

Substance :- p-dimethyl amino anil of methylglyoxal
Zn^{++} complex

Wt. of substance	I	II	III
without magnetic field	13.21232 gm.	13.21232 gm.	13.21232 gm.
with magnetic field	13.21276 gm.	13.21276 gm.	13.21276 gm.

Table - 12

Substance :- p-dimethyl amino anil of methylglyoxal
Hg^{++} - complex

Wt. of substance	I	II	III
without magnetic field	13.27538 gm.	13.27538 gm.	13.27538 gm.
with magnetic field	13.27668 gm.	13.27668 gm.	13.27668 gm.

Table - 13

Magnetic measurements of Zn^{++}, Cd^{++}, Hg^{++} complexes of p-dimethyl amino anil of phenylglyoxal

Sl. no.	Name of compd.or complex	W_4-W_3 gm.	Cx	ψ	M ϕ_M	M ρ_M	B.M μ_{eff}
1.	p-dimethyl amino anil of phenyl-glyoxal	0.00053	0.2042×10^{-6}	0.437×10^{-6}	1.1×10^{-4}	1.1×10^{-4}	0.511
2.	p-dimethyl amino anil of phenyl-glyoxal Cd^{++} complex.	0.00678	"	0.218×10^{-6}	1.3484×10^{-4}	3.745×10^{-5}	0.945
3.	p-dimethyl amino anil of phenyl-glyoxal Zn^{++} complex.	0.00035	"	0.3275×10^{-6}	1.272×10^{-4}	3.182×10^{-4}	0.8693
4.	p-dimethyl amino anil of phenyl-glyoxal Hg^{++} complex.	0.00187	"	0.848×10^{-6}	4.4334×10^{-4}	6.44×10^{-4}	1.235

Table - 14

Magnetic measurements of Zn^{++}, Cd^{++}, Hg^{++} complexes of p-dimethyl amino anil of β - naphthyl glyoxal

Sl no.	Name of Compd.or complex.	W_4-W_3 gm.	Cx	ψ	ψM	ψ M	B.M μeff
1.	p-dimethyl amino anil of β-naphthyl glyoxal.	0.00357	0.2042×10^{-6}	2.615×10^{-6}	7.9×10^{-4}	7.9×10^{-4}	1.37
2.	p-dimethyl amino anil of β-naphthyl glyoxal Cd^{++} complex	0.00097	"	0.49×10^{-6}	3.2714×10^{-4}	6.05×10^{-4}	1.20
3.	p-dimethyl amino anil of β-naphthyl glyoxal Zn^{++} complex	0.00277	"	1.364×10^{-6}	5.9814×10^{-4}	8.27×10^{-4}	1.40
4.	p-dimethyl amino anil of β-naphthyl glyoxal Hg^{++} complex	0.00249	"	1.12×10^{-6}	6.4316×10^{-4}	8.72×10^{-4}	1.44

Table 15

Magnetic measurements of Zn^{++}, Cd^{++}, Hg^{++} complexes of p-dimethyl amino anil of methyl-glyoxal

Sl. no.	Name of Compd. or complex	(W_4-W_3) gm	C	ψ	ψ_M	ψ'_M	μ_{eff} B.M
1.	p-dimethyl amino anil of methyl-glyoxal	0.00028	0.2042×10^{-6}	0.2705×10^{-6}	0.5149×10^{-4}	1.632×10^{-4}	0.623
2.	p-dimethyl amino anil of methyl-glyoxal Zn^{++} complex	0.00044	"	0.261×10^{-6}	0.8529×10^{-4}	2.732×10^{-4}	0.751
3.	p-dimethyl amino anil of methyl glyoxal Cd^{++} complex	0.00017	"	0.1638×10^{-6}	0.9109×10^{-4}	2.92×10^{-4}	0.834
4.	p-dimethyl amino anil of methyl-glyoxal Hg^{++} complex	0.00130	"	0.605×10^{-6}	2.7909×10^{-4}	4.31×10^{-4}	1.012

Conclusion :-

The most interesting feature in this study is the paramagnetic behaviour shown by these reagents. All the three reagents, viz. p-dimethyl amino anil of phenyl glyoxal, p-dimethyl amino anil of β- naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal show the effective moment of 0.511, 1.37 and .623 B.M. respectively, although from electronic consideration they should normally have a zero moment. This abnormal behaviour may arise if there is some partial charge transfer rendering the ligand paramagnetic.

This paramagnetic behaviour is well manifested in the various metal complexes studied. Here the magnetic moment values are higher than the ligand, and the following order exists in their value :-

Ligand	Complexes
1. p-dimethyl amino anil of phenyl-glyoxal	$Hg^{++} > Cd^{++} > Zn^{++}$
2. p-dimethyl amino anil of β-naphthyl-glyoxal	$Hg^{++} > Zn^{++}$
3. p-dimethyl amino anil of methyl-glyoxal	$Hg^{++} > Zn^{++} > Cd^{++}$

The higher magnetic moment values of the complexes as against the corresponding ligands may be attributed to the appearance of a new metal - ligand bond on chelation. The high values in the Hg(II) complex may be accounted in terms of angular moments existing in the metal itself.

SUMMARY

A resume on the preparation of new anils and the physico-chemical aspects of a few of them is given in the following pages:

1. New anils and their derivatives :-

Anils of β-naphthyl glyoxal were obtained by condensing with aniline, p-toluidene, p-chloroaniline, m-nitroaniline, p-nitroaniline, α-naphthyl amine, β-naphthyl amine and p-dimethyl amino aniline.

Anil of methyl glyoxal was obtained by condensing with p-dimethyl amino aniline.

In both cases the products were crystallised from either methanolic or ethanolic solutions, and dried under vacuum dessicator over sulphuric acid. Derivatives prepared for characterising them were 2:4 DNP, semicarbazones and oximes (p-8).

β- naphthyl glyoxal and methyl glyoxal were prepared by the usual SeO_2 oxidation (β-naphthyl methyl Ketone and acetone respectively) method.

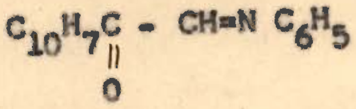
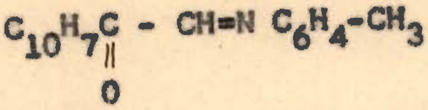
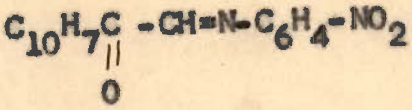
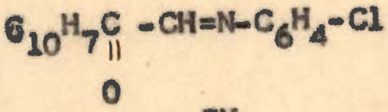
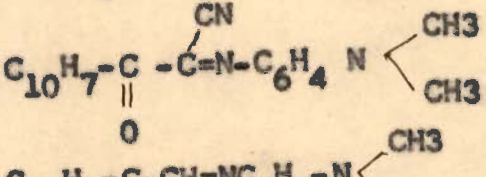
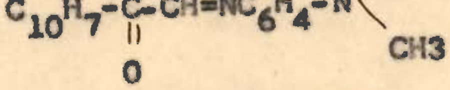
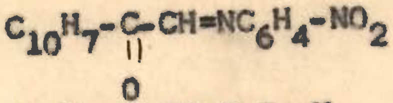
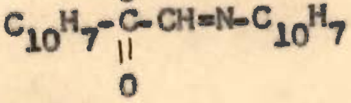
p-dimethyl amino anil of β-naphthyl glyoxal nitrile was prepared as follows:

β-naphthyl Ketone was iodinated to give β-naphthyl iodide. It was further reacted with pyridine to form β-naphthacyl pyridinium iodide. The quaternary base iodide was then reacted with p-nitroso dimethyl aniline in presence of sodium cyanide to get the required product. Recrystallisation was done either with glacial acetic acid or ethyl acetate solution.

2:4 DNP, semicarbazone and oxime derivatives were prepared for characterisation (p-8).

2. Structure :-

The structure of the anils was found by running the IR spectra of a few typical cases by KBr technique. From the stretching frequencies of $>C = O$ and azomethine group - CH=N, (p9) as well as from the nature of the derivatives obtained, the following structures were proposed (p-9)

	Name of anils	Structure of anils
1.	R- aniline	 $C_{10}H_7\underset{\underset{O}{\|}}{C} - CH{=}N\ C_6H_5$
2.	R-p-toluidene	 $C_{10}H_7\underset{\underset{O}{\|}}{C} - CH{=}N\ C_6H_4-CH_3$
3.	R-p-nitroaniline	 $C_{10}H_7\underset{\underset{O}{\|}}{C} -CH{=}N-C_6H_4-NO_2$
4.	R-p-chloroaniline	 $C_{10}H_7\underset{\underset{O}{\|}}{C} -CH{=}N-C_6H_4-Cl$
5.	p-dimethyl amino anil of β-naphthyl glyoxal nitribe	 $C_{10}H_7-\underset{\underset{O}{\|}}{C} -\overset{CN}{C}{=}N-C_6H_4\ N\begin{smallmatrix}CH3\\CH3\end{smallmatrix}$
6.	p-dimethyl amino anil of β-naphthyl glyoxal	 $C_{10}H_7-\underset{\underset{O}{\|}}{C}-CH{=}NC_6H_4-N\begin{smallmatrix}CH3\\CH3\end{smallmatrix}$
7.	R-m-nitroaniline	 $C_{10}H_7-\underset{\underset{O}{\|}}{C}-CH{=}NC_6H_4-NO_2$
8.	R-α-naphthyl amine	 $C_{10}H_7-\underset{\underset{O}{\|}}{C}-CH{=}N-C_{10}H_7$

* β-naphthacylidene aniline.

3. Zn(II), cd(II), Hg(II) and Fe(III) complexes of p-dimethyl amino anil of phenyl glyoxal :-

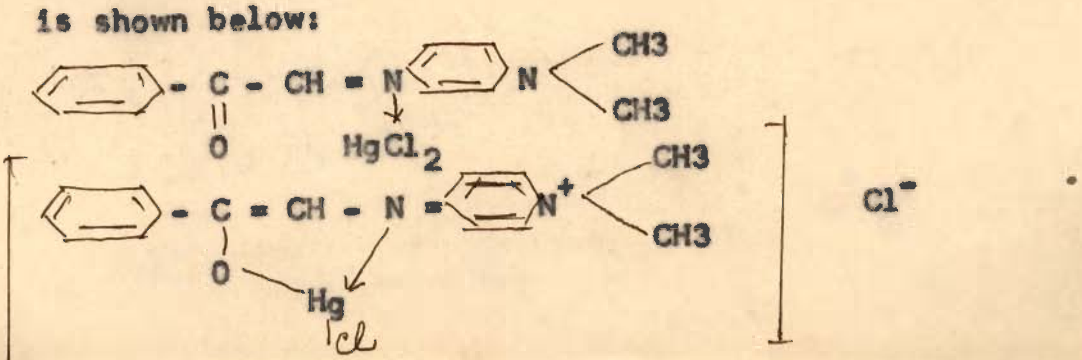
p-dimethyl amino anil of phenyl glyoxal was obtained by the method recommended by Krohnke and Gross(1). The interaction of this anil with various Lewis acid was studied. A sharp change in colour yellow to blue, green, etc; as summarised in the following table, was observed:

Table 1

Colour reaction of p-dimethyl amino anil of phenyl glyoxal with Lewis acids.

Name of anil	Own colour	colouring with			
		$Zncl_2$	CdI_2	$HgCl_2$	$FeCl_3$
p-dimethyl amino anil of phenyl glyoxal	yellow	olive green	bluish	reddish violet	yellow green

The change in colour was taken as an indication of chelation accompanied by bathochromic effect. The composition, stability and other thermodynamic data were studied spectrophotometrically employing Job's, slope and molar ratio methods. The position of linkages to cause complexation was studied by I.R. spectroscopy in solid state using KBr disc technique (p-31). Further confirmation was obtained by chemical analysis (p-28). A typical structure is shown below:



The various thermodynamic data are tabulated below:-

Table 2

Stability constant and ΔF values of Lewis acid complexes of p-dimethyl amino anil of phenyl glyoxal

No.	Name of chelate	Ratio	Stability constant	Change in free energy Kcal/mole
1.	$Zn^{++} - L^{*}$	1:1	1.1×10^{5}	-6.8
2.	$Cd^{++} - L$	1:1	3.5×10^{5}	-7.6
3.	$Hg^{++} - L$	1:1	6.4×10^{3}	-5.2
4.	$Fe^{+++} - L$	1:2	1.012×10^{12}	-16.50

* p-dimethyl amino anil of phenyl glyoxal

---

4. Zn(II), Cd(II), Hg(II), Fe(III) complexes of p-dimethyl amino anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal :-

p-dimethyl amino anil of β-naphthyl glyoxal and p-dimethyl amino anil of methyl glyoxal also undergo chelation accompanied by bathochromic effect, when interacted by different Lewis acids. The nature of the chelates formed was studied by absorption measurements using the technique mentioned in the preceeding paragraph. Various thermodynamical data arrived at for these chelate ard given below:-

Table 3

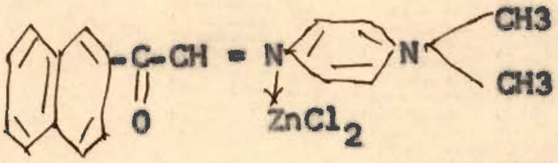
No.	Name of chelate	Colour change	Ratio	Stability constant	Change in free energy Kcals/mole at 25°C
1.	$Zn^{++} - L^{*}$	Dark violet	1:1	6.6×10^{4}	-6.61
2.	$Cd^{++} - L$	bluish green	1:1	5.2×10^{5}	-7.8
3.	$Hg^{++} - L$	violet	1:1	3.9×10^{5}	-7.6
4.	$Fe^{+++} - L$	yellowish green	1:2	1.2×10^{12}	-16.6
5.	$Zn^{++} - L'$	green	1:1	2.9×10^{5}	-7.49
6.	$Cd^{++} - L'$	bluish	1:1	9.0×10^{6}	-9.54
7.	$Hg^{++} - L'$	reddish violet	1:1	1.2×10^{6}	-8.3
8.	$Fe^{+++} - L'$	reddish	1:2	1.531×10^{12}	-16.77

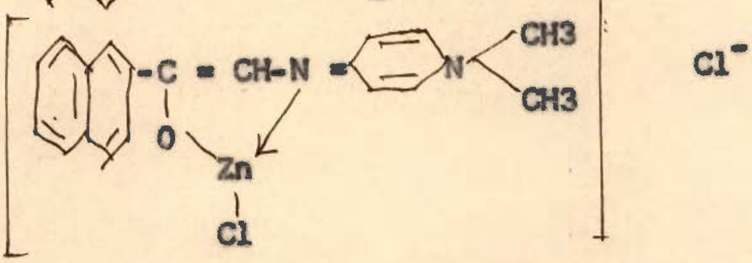
L^{*} - p-dimethyl amino anil of β-naphthyl glyoxal

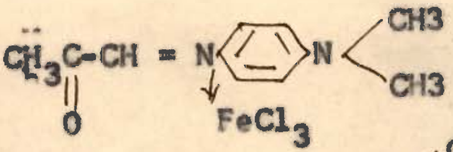
L' - p-dimethyl amino anil of methyl glyoxal.

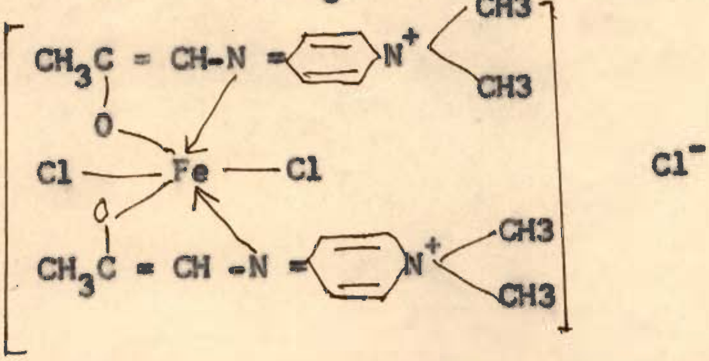
Here too IR spectra was considered as a useful technique to locate the seats of interaction to cause chelation. The spectra of the above ligands showed stretching frequencies around 1700 cm^{-1} and 1600 cm^{-1} characteristic of $>C=O$ and $-CH=N$ groupings. Lowering of stretching frequencies were found in the spectra of the corresponding chelate. This lowering was attributed to interlocking at the above two centres in presence of the metalions (pp 69,79,88,98,106,118, 126, 135). Further confirmation was obtained by chemical analysis.

Typical structure of the metal complexes shown below:-









5. Adsorption of anils on various inorganic gels:-

Adsorption of organic compounds on surfaces in influenced by many factors. Of these two are most important, viz; the structural one and the solvent effect. These were investigated by observing the interaction of phenacylidene aniline, p-dimethyl amino anil of phenyl glyoxal and p-dimethyl amino anil of phenyl glyoxal nitrile in non - polar solvents using silica, alumina, aluminium silicate, ferric silicate and aluminium molybdate as adsorbents.

The surface area of the gel was determined by PNP (p-nitrophenol) adsorption technique. This method was found to be quite reliable and convenient for the present studies (vide Chapter V).

Colour changes at the surfaces of the gels were observed in most of the cases. The results are tabulated below:-

Table 4

Colour changes on the gel surface in presence of anils

No.	Anil	Own colour	Solvent	Colouring with gel				
				Silica	Alumina	Al-silicate	Fe-silicate	Al-molybdate
1.	p-dimethyl amino anil of phenyl glyoxal	Yellowish	S*	Violet	Red-violet	Red-violet	Red-violet	
2.	p-dimethyl amino anil of phenyl glyoxal nitrile	Dark red	S*	Violet	Red-violet	Red-violet	Red violet	

* (benzene, xylene, toluene and carbon tetrachloride

From the above table it was concluded that bathochromic effect is observed with p-dimethyl amino anil of phenyl glyoxal and p-dimethyl amino anil of phenyl glyoxal nitrile anils when brought in contact with silica, alumina, aluminium silicate and ferric silicate gels.

Adsorption studies carried out spectrophotometrically, show that the data fit well in Langmuir's isotherm (pp 145-182). The order of adsorption is:

p-dimethyl amino anil of phenyl glyoxal nitrile $>$ p-dimethyl amino anil of phenyl glyoxal $>$ phenacylidene aniline.

The values of a and b are summarised in the following tables :

Table 5

Solute - p- phenacylidene aniline

Solvents	Silica		Alumina		Al-silicate		Fe-silicate		Al-molybdate	
	a	b	a	b	a	b	a	b	a	b
Benzene	2.02	4.54	4.40	2.50	1.91	2.04	2.35	1.88	4.40	0.90
Xylene	2.11	3.12	0.91	4.76	3.0	2.0	2.97	1.63	3.03	0.93
Toluene	2.90	6.25	1.91	2.94	2.0	1.81	8.37	1.17	2.78	2.22
Carbon tetrachloride	7.13	2.56	12.78	2.38	1.66	5.00	4.50	3.33	5.93	0.87
Dioxane	0.85	5.0	2.89	2.32	1.33	1.95	6.24	0.83	0.40	1.05

Table 6

Solute - p-dimethyl amino anil of phenyl glyoxal

Benzene	2.33	5.26	1.79	3.22	3.60	2.22	4.68	1.85	6.66	0.97
Xylene	5.60	2.85	3.05	3.33	2.61	2.63	3.38	1.53	0.21	0.94
Toluene	2.0	2.50	2.12	2.94	1.78	2.27	4.01	1.88	6.05	2.27
Carbon tetrachloride	7.73	2.32	9.54	2.85	0.20	5.0	4.09	3.70	8.0	0.90
Dioxane	5.60	2.85	9.0	2.22	3.43	1.63	2.20	0.90	1.07	0.76

Table 7

Solute - p-dimethyl amino anil of phenyl glyoxal nitrile

Solvents	Silica		Alumina		Al-silicate		Fe-silicate		Al-molybdate	
	a	b	a	b	a	b	a	b	a	b
Benzene	2.0	6.25	0.55	4.54	3.46	2.43	2.40	2.38	6.75	1.11
Xylene	4.82	3.03	2.62	3.70	6.17	2.77	1.33	3.12	6.75	1.11
Toluene	6.22	2.77	2.40	3.12	1.52	2.38	1.08	1.25	4.31	2.70
Carbon tetrachloride	1.15	2.94	1.30	2.86	3.14	4.54	6.00	3.70	0.40	1.00
Dioxane	2.06	3.22	7.00	2.50	1.13	2.94	1.30	0.93	1.28	0.90

The values of the constants a and b provided the following information.

The adsorption affinities of the gels as inferred from the values of a are in the order:-

Silica > Alumina > Al-silicate > Fe-silicate > Al-molybdate.

The values of b are also in the same order. From these data it may be concluded that the surface area of the gels available for adsorption of anils is highest for silica and lowest for Al-molybdate.

6. Pore availability and adsorption :-

Exclusion of ions from the pore of the adsorbent results in the decrease in the factor A, pore availability. This phenomenon occurs when the solvent is preferentially adsorbed or the solute interacts with the surface of the adsorbent. A few study of water soluble complexes of cobalt with hydrophobic and hydrophilic ligands have thrown some light on this view point.

The behaviour in non-aqueous solvent, acetone, with Zn(II), Cd(II), Hg(II) complexes of p-dimethyl amino anil of phenyl glyoxal and p-dimethyl amino anil of β-naphthyl glyoxal as adsorbates was studied using silica gel of known porosity.

The values of A were always found to be greater than 100. The following order of pore availability was observed :-

$$Zn^{++} > Cd^{++} > Hg^{++}$$

A comparison of the ionic radii (p-204) (assuming that the solute does not extend its ionic radii in non aqueous medium) has shown that the pore availability increases with decrease in the size of the ion.

Experiments performed in slightly acidic medium give higher values of A. It may be attributed to the dissociation of the complex.

7. Magnetic susceptibility :-

The chelates of the above anils with Zn(II), Cd(II) and Hg(II) were isolated as pure crystalline products. Gouy's method was employed for calculating the μeff of the chelates and the chelating agents (anils). The following relation was used to calculate the moment

$$\mu_{eff} = 2.84 \sqrt{CM \times T} \quad B.M$$

Unlike the usual behaviour of showing diamagnetism the chelating agents showed paramagnetism. Except for free radicals which contain an odd electron, all the organic reagents are diamagnetic in character. This has been explained in terms of charge transfer in the anil molecules. Higher values (pp 227-230) in the chelates can be accounted for either in terms of angular orbital moment of the metal ion e.g. mercury complex, which enhanced charge transfer experienced during the formation of M - L bond. Both the influences may work simultaneously.

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SUMMARY (Reference)

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LIST OF PUBLICATIONS

1. Condensation of β-naphthyl glyoxal hydrate with aromatic amines (Journal of Indian Chemical Society - In press).
2. Spectrophotometric studies of Zn^{++}, Cd^{++}, Hg^{++}, Fe^{+++} -p- dimethyl amino anil of phenyl glyoxal complexes (communicated).
3. Composition and stability of Zn(II), Cd(II), Hg(II), Fe(III) -p-dimethyl amino anil of methyl glyoxal chelates (communicated).
4. Spectrophotometric studies on complexes of Zn(II), Cd(II), Hg(II) and Fe(III) with p-dimethyl amino anil of β-naphthyl glyoxal (communicated).
5. Adsorption of phenacylidene aniline, p-dimethyl amino anil of phenyl glyoxal, and p-dimethyl amino anil of phenyl glyoxal nitrile from non polar solvents on different inorganic gels (communicated).
6. Availability of pores of silica gel to the complexes of anils (communicated).

Condensation of β -naphthyl-glyoxal hydrate with aromatic amines -

" Wahid U. Malik and R .C. Saxena "

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Anils derived from glyoxal and aromatic amines have not been investigated comprehensively. Few references are available on the anils derived from glyoxals and aromatic amines. The only reference worth mentioning is that of Krohnke and Gross(1) who synthesised p-dimethyl amino anil of phenyl-glyoxal to investigate bathochromic effect in the compound in presence of Lewis acids and silica gel.

Recently anils derived from phenylglyoxal hydrate and primary aromatic amines have been reported(2). In the present communication investigation on the synthesis of anils obtained from β-naphthyl-glyoxal hydrate are reported. The methods recommended by the authors are employed in their preparation except in the case of the anil, p-dimethyl amino anil of β-naphthyl-glyoxal nitrile where a different route(3) has to be used. These anils have been characterised from their 2:4, - Dinitrophenyl hydrazones, semicarbazones and oximes.

Preparation of anils :-

The anils listed in table (I) were prepared by refluxing on water bath equimolar quantities of β-naphthyl-glyoxal hydrate(4) and corresponding amines in a mixture of glacial acetic acid and ethanol (1:6 $\frac{v}{v}$) except in the case of p-dimethyl(5) amino anil of β-naphthyl-glyoxal in which condensation was carried out in 70 % ethanol at room temperature on cooling a yellow oil was obtained which was difficult to crystallise. The following procedure was, therefore, adopted. The oily mass was dissolved in a minimum quantity of benzene and chromatographed over Brockmann Alumina. Petroleum ether (60-80°), benzene, chloroform and their mixtures were used as the eluants. Most of the fractions were found to be greasy except that from chloroform which afforded a solid mass on evaporating the solvent. The left over was charcolised and rechromatographed but even then solid could not be obtained. The fraction obtained from chloroform was crystallised from hot methanol.

The anils reported above are soluble in benzene, xylene, toluene, acetone, chloroform and acetonitrile but are practically insoluble in water.

Preparation of p-dimethyl amino anil of β -naphthyl - glyoxal nitrile :-

Pyridinium iodide of β-naphthyl methyl Ketone was synthesised by the interaction of iodine with β-naphthyl methyl Ketone in presence of Pyridine(6). 0.80 gm. of Pyridinium iodide of β-naphthyl methyl Ketone was dissolved in 10 cc of 50 % ethanol and treated with 0.33 g. of p-nitrosodimethyl amiline(7) in 10.0 cc ethanol. This was followed by the addition of 1.50 g. of sodium cyanide in 4.0 cc water, maintaining a temperature of 0-10° throughout the course of reaction. On addition of more water with subsequent chilling, scarlet red crystals of the anil were obtained which could be crystallised from glacial acetic acid - mp. 140°C (Table I).

TABLE (I)

Anils derived from β-naphthyl glyoxal hydrate and aromatic amines.

Anil	Colour	M.P 0^{c}	Yield	Formula	Nitrogen c/o	
					Calculated	Found
R - Aniline	Yellow	96-97	90 %	$C_{18}H_{13}NO$	5.40	5.36
R - p-toluidene	brick red	90-92	92-93%	$C_{19}H_{15}NO$	5.12	5.00
R - p-chloroaniline.	yellow	140-141	80 %	$C_{18}H_{12}NOCl$	4.77	4.65
R - m-nitroaniline	yellow	98°	70 %	$C_{18}H_{12}N_2O_3$	9.21	9.16
R - p-nitroaniline	yellow	123-124°	72 %	$C_{18}H_{12}N_2O_3$	9.21	9.12
R* - α-naphthyl amine	yellow	144-145	70 %	$C_{22}H_{15}NO$	4.53	4.35
R* - β-naphthyl amine	gummy mass	-	-	$C_{22}H_{15}NO$	-	-
R -p- dimethyl amino aniline	Reddish orange	112-113	80 %	$C_{20}H_{18}N_2O$	9.27	9.21
R - nitrile p-dimethyl amino aniline	Dark red	140-141	90 %	$C_{21}H_{17}N_3O$	12.84	12.78

R - $C_{10}H_7COCH$ = (β-naphthacyl)

* - slight warming was necessary.

TABLE (II)

Characteristics of the Derivative of anils

Anil	2:4-Dinitrophenyl hydrazones			Semicarbazones			Oximes		
	M.P.	Calcd. N %	Found	M.P.	Calcd. N%	Found	M.P.	Calcd. N %	Found
	o^{c}			o^{c}			o^{c}		
R - aniline	167d	15.94	15.90	130-131	17.72	17.70	105-106	10.21	10.20
R - p-toluidine	172-173	15.45	15.42	150-152	16.96	16.89	123-124	9.72	9.59
R - p-chloroaniline	130-131	14.78	14.71	110-111	15.97	15.93	117-118	9.07	9.00
R - m-nitroaniline	120-121	17.35	17.30	150-151	19.39	19.40	170-171	13.16	13.10
R - p-nitroaniline	150-151	17.35	17.32	135-136	19.39	19.36	190-192	13.16	13.13
R - α-naphthylamine	235d	14.31	14.29	210-212	15.30	15.19	153-155	8.64	8.61
R - β-naphthylamine	218-220	14.31	14.34	200-201	15.30	15.25	186-187	8.64	8.60
R^{x}- p-dimethyl amino aniline	150-151	17.42	17.40	180-182	19.49	19.44	181-182	13.24	13.21
R - p-dimethyl amino aniline acid nitrile	250-252	19.32	19.30	131-	21.87	21.82	145-146	16.37	16.34

R - $C_{10}H_7COCH$ (β - naphthacyl)

d - decompose

x - No warming was necessary.

Derivative of anils :-

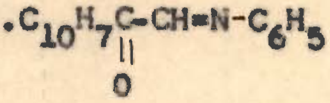
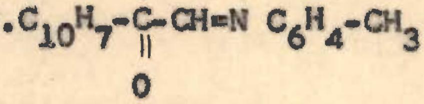
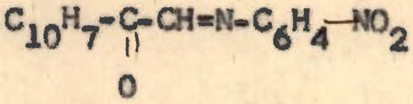
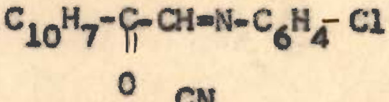
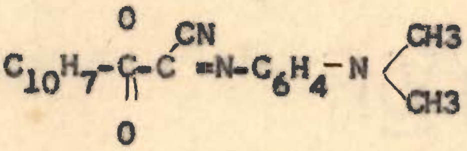
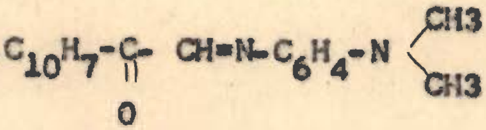
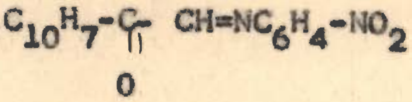
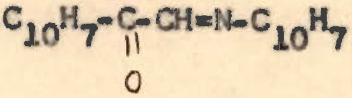
2:4 Dinitro phenyl-hydrazones, semicarbazones and the oximes of the anils were prepared by the usual methods and were obtained almost in theoretical yields. They were crystallised from hot alcohol. Characteristics of the derivatives are recorded in Table II.

Infra red spectra of anils :-

In order to ascertain the functional groups of anils listed in table (I) their Infra red spectra were recorded in Potassium bromide medium by Perkin-Elmer Infracord. The stretching frequencies of the groups are listed in table (III).

TABLE (III)

Stretching frequencies of the functional groups of the anils

Structure of Anils	CH=N cm^{-1}	$\rangle$C=O Cm^{-1}	p-disubstituted groups Cm^{-1}
1.  $C_{10}H_7\underset{\overset{\Vert}{O}}{C}-CH=N-C_6H_5$	1580	1660	-
2.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-CH=N\ C_6H_4-CH_3$	1600	1660	820
3.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-CH=N-C_6H_4-NO_2$	1600	1640	840
4.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-CH=N-C_6H_4-Cl$	1600	1650	830
5.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-\overset{CN}{C}=N-C_6H_4-N\Big\langle\begin{matrix}CH3\\CH3\end{matrix}$	1575	1680	825
6.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-CH=N-C_6H_4-N\Big\langle\begin{matrix}CH3\\CH3\end{matrix}$	1625	1660	830
7.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-CH=NC_6H_4-NO_2$	1540	1640	827
8.  $C_{10}H_7-\underset{\overset{\Vert}{O}}{C}-CH=N-C_{10}H_7$	1610	1680	-

The stretching frequency of an aryl or a naphthyl Ketone lies between 1695-1715 cm^{-1} (8). Conjugation with respect to $C = O$, phenyl or naphthyl group generally decreases this frequency. Since the frequencies of the anils reported here are around the above range, it may be concluded that the anils possess a $C = O$ group in the vicinity of β-naphthyl skeleton. Moreover, the stretching frequency of $C{=}N$ (8) (unconjugated) lies between 1610-1700 cm^{-1} The stretching frequencies of the anils range from 1540 to 1625 cm^{-1}. Evidence for the presence of $C{=}N$ is therefore available. The lower value may again be due to conjugation. The frequency around 820-840 cm^{-1} may be due to paradisubstituted derivatives.

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Chemical Laboratories,
University of Roorkee,
ROORKEE.

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