CHAPTER - II

TERNARY METAL, α-α-DIPYRIDYL OR O-PHENANTHROLINE AND AROMATIC ALDEHYDE OR KETONE SYSTEMS

A number of studies have been reported on the formation of binary metal complexes of bidentate metal complexes of aromatic aldehydes and ketones. Maley and Mellor[1,2] reported the formation constants of metal salicylaldehyde complexes, containing Cu^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+} metal ions. Von Uitert and Fernelius[3] studied the formation constants of salicyldehyde complexes of Cu^{2+}, Mg^{2+}, Mn^{2+} and Ni^{2+} in 75% dioxan. Rydberg[4] studied the formation constant of thorium salicyldehyde complex in ethanol (50%) medium. Agren[5] reported metal ligand formation constants of metal salicyldehyde and metal-2-hydroxy-acetophenone complexes. Perrin[6] also investigated the metal salicylaldehyde and metal-2-hydroxy-acetophenone complexes. Williams and coworkers[7] studied the complex formation of 2-hydroxy-1-naphthaldehyde in 75% dioxan. Ingle otal carried out potentiometric studies of complex formation of Mn(II),

Co(II), Ni(II) and Zn (II) with o-hydroxy-acetophenone oxime in 75% dioxan employing Bjeerum Calvin Titration technique, as adopted by Irving-Rossotti[8]. Potentiometric studies have also been carried out of the complexes of Co(II), Cu(II), Ni(II) with Schiff bases, derived from salicylaldehyde[9]. Calvin[10] has considered the possibility of formation of conjugated six member rings analogous to benzene in the case of metal-salicylaldehyde and 2-hydroxy-1-naphthaldehyde complexes. He indicated the possibility of the donation of π electrons from oxygen to vacant metal orbitals. However, he himself has suggested that such structures raise questions concerning the availability and geometry or d orbitals of metals.

In the case of metal-β- diketonate complexes, it has been suggested that the metal $d\pi$ orbitals interact with the π molecular orbitals over the enolate ion. Although extensive $Op_{\pi} \rightarrow Mp_{\pi}$ (or d_{π}) bonding may not take place, some mixing of Op_{π} and metal $p\pi$ and (or) $d\pi$ orbitals will doubtless occur, where permitted by symmetry and is likely to have some effect on the electronic structure and spectrum. Forman, Murrel and Orgel[11] have carried out NMR studies of tris acetylacetonato (acac) vanadyl (III) complexes. The resonance frequency of the ring protons, $H\alpha$, in tris (acac) vanadyl (III) is considerably shifted from its position. This contact shift has been attributed to the delocalization of umpaired π electron density of the metal electrons over the ligand atom. The negative spin density of the electron over the third atom produces a positive spin density over the proton. This brings a shielding effect and causes shifts in the signals of ligand protons.

However, no study has been made on the possibility of M⟶Lπ interaction in salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-acetophenone and such complexes of the transition metal ions. In order to investigate the above possibility, formation constants of binary and ternary complexes of Cu-dipy-L, where L = salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy acetophenone or 2-hydroxy-propiophenone, have been studied in the present chapter using pH metric titration technique.

Various methods have been used for the determination of formation constants. J.I.Watters and coworkers carried out the study of the system Cu-pyrophosphate ethylenediamine complex using spectrophotometric method.[12,13] They used the ligand displacement technique, in which a more complexing ligand was added to a mixture of metal ion and a less complexing ligand. They, however, got the value of the equillibrium constant for the reproportionation reaction:

$$MA_2 + MB_2 \rightleftharpoons 2MAB$$

$$K_{reprop.} = \frac{(MAB)^2}{(MA_2)(MB_2)}$$

They further determined[14-16] the mixed ligand formation constants of M-ethylenediamine-oxalate systems using pH metric and spectrophotometric methods. The reaction can be shown as under

$$M + aA + bB \rightleftharpoons MAaBb$$

$$K^{M}_{MAaBb} = \frac{(MAaBb)}{(M)(A)(B)}$$

If the metal ion is tetracoordinate and the ligands are bidentate the equation is reduced to

$$M + A + B \rightleftharpoons MAB \quad \text{and} \quad K^{M}_{MAB} = \frac{(MAB)}{(M)(A)(B)}$$

Nasanen and coworkers[17] determined the formation constant K^{M}_{MAL} of Cu-diaminopropane-5-sulphosalicylic system by using pH method.

Martell[18] suggested a pH metric method, for the determination of log K^{M}_{MAB} in the system Cu-tetra-methylenediaminesalicylic acid. From the known values of K^{M}_{MA} and K^{M}_{MB}, the formation constants K^{MA}_{MAB} and K^{MB}_{MBA} could be calculated.

Punger and coworkers[19] employed the high frequency titrimetry technique, to study the complexes of Ni(II) with dimethylglyoxime and dipyridyl. Perrin and Sharma have studied the ternary systems in detail[20,21]. Perrin and coworkers[22] have devised a programme SCOUSS (stability constant of unknown single specie) for the ternary system comprising of a bivalent metal and two ligands H_2A and H_2L. They ignored the formation of hydroxo, protonated and polynuclear species.

Sigel determined the mixed-ligand formation constant by using Zajicek's iteration method[23]. They too, ignored the hydroxo, protonated and polynuclear species. Perrin & Sayce[24] worked out the equillibrium concentration of all the possible species in a multimetal-multiligand system, using a computer programme called COMICS (concentration of metal ions and complexing species). If M^a, M^b, M^c represent the different kinds of ligands, any complex that is formed can be represented by $(M^a)_\alpha$, $(M^b)_\beta$, $(M^c)_\gamma$ .... $(L^v)p$ $(L^s)_\sigma$ $(L^t)_\nu$ .... $(OH)w$, where $\alpha, \beta, \gamma \ldots\ldots\ldots\ldots$ p, σ, t may be possible integers or zero and w may be positive integer (for hydrolysed species). Zero or a negative integer (for protonated species).

The consideration of all the species in solution is essential in the calculation of formation constants of ternary complexes, if the two ligands A & L have similar coordinating tendencies and combine simultaneously with the metal ion. However, if the ligand A has much higher complexing tendency than L, formation of mixed ligand complex in solution containing M, A and L in 1:1:1 ratio takes place in two distinctly separated steps:

$$M + A \rightleftharpoons MA \qquad\qquad MA + L \rightleftharpoons MAL$$

There is only one mixed ligand constant which characterises the reaction :

$$K^{MA}_{MAL} = (MAL) / (MA)\ (L)$$

Martell and coworkers[25] carried out the study of the system CuAL, where A = dipyridyl or o- phenanthroline and L = Tiron, chromotropic salt or salicylate ion, by making use of the above consideration. The necessary condition for such a system is, that the two ligands must combine with the metal ion in different pH ranges. The formation of MA should be complete in the lower pH range and (MA) should be stable in the higher pH range, where the combination of L starts. The tendency of MA to form hydroxo complex should be negligible compared to formation of MAL.

It has been shoun earlier[25], that Cu (II) forms 1:1 chelate with bidentate polyamines such as α-α-dipyridyl, which forms hydroxo complex stable over a limited pH range in aqueous solution. Since the hydroxo complex MAOH does not disproportionate readily into $M(OH)_2$ and MA_2, it seems reasonable that mixed ligand complex MLA will be formed, if L is strongly coordinating and combines with

MA in the pH range before hydroxo complex formation starts.

Sigel and coworkers[26] determined the formation constants of some (M.dipy.L) complexes, considering the reaction to be strictly of the type M.dipy + L $\rightleftharpoons$ M.dipy.L. They also determined the formation constants K^{MA}_{MAL}, by using the computer programme and considering all the possible equilibria as in the system M + A + L $\rightleftharpoons$ MAL. The values of K^{MA}_{MAL} obtained by both methods were in close agreement showing that the assumptions in the simpler method are correct.

The above fact is also true in the cases where the first ligand is a polydentate amino acid. Martell and coworkers[27,28] and also Thompson and Loraas[29] determined the formation constants of the complexes M-aminopolycarboxylate-L systems, considering the reaction to be of MA + L $\rightleftharpoons$ MAL type.

Bhattacharya and coworkers applied the Irving-Rossotti titration technique as used for binary complexes[30], to the study of the systems M.dipy.L[31] and M-aminopolycarboxylate-L[32]. Various types of ternary complexes in solution, where dipyridyl or o-phenanthroline are primary ligands and amino acids, polyhydroxy phenols, thioacids as secondary ligand have been studied from our lab. as detailed in Chapter-I (Ref.-38-42). Studies have also been extended to systems where secondary ligand is diketone or their derivatives[33,34].

In the present chapter binary complexes containing Cu.L and ternary complexes containing Cu-dipyridyl-L, where, L = Salicylaldelyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy acetophenone or 2-hydroxypropiophenone, have been investigated using modified Irving-Rossotti titration technique[30-32]. The technique involves the measurement of

pH, which was carried out using a glass calomel electrode and pH meter combination. All the titrations have been carried out in 50% (V/V) dioxan, which was purified by the known[35] method. The formation constants have been determined by titrating a mixture of M + A + L against standard alkali.

EXPERIMENTAL

Conductivity water was used throughout the work. Ligands used were all of pure grade. Purity was checked by noting melting and boiling points. Ligands used were dipyridyl and o-phenanthroline (Merck Pure), Salicylaldehyde (Fluka), 2-hydroxy-1-naphthaldehyde (Riedel), 2-hydroxy-acetophenone (Made in Germany) and 2-hydroxy-propiophenone (Made in Germany). The standard solutions were prepared by dissolving weighed quantity in known volume of purified dioxan. Since dioxan solvent is easily oxidised, fresh solutions of ligands were prepared prior to titration.

Preparation of Sodium Hydroxide

The solution was prepared by dissolving 50 g.of Sodium hydroxide (Chemapol) in 500 ml. of double distilled water and was allowed to stand for two days. The solution was filtered through G4 sintered glass crucible. This was standardised against standard oxalic acid solution and stored out of contact with carbon-dioxide, using a sodalime guard tube. This solution was diluted to get solutions of required concentration.

Sodium perchlorate

The required quantity of sodium perchlorate (A.R.Riedel) was weighed and dissolved in 500 ml. of double distilled water to prepare 1M solution.

Perchloric Acid Solution

The perchloric acid (Riedel, analysed) supplied was of 80% concentration. A definite volume of acid was dissolved in 500 ml. of double distilled water to get a solution of approximate 0.2 M strength. The exact concentration was determined by titrating against standard sodium hydroxide solution.

Metal Salt Solution

In order to avoid the complexing tendencies of the anion, the perchlorates of Ni(II) were prepared by refluxing their respective carbonetes with perchloric acid, till an excess of metal carbonate was left. The filtrate was neutral solution of metal-perchlorate. In case of preparation of copper parchlorate, however, weighed quantity of copper carbonate was dissolved in known excess of perchloric acid. This is to avoid hydrolysis of Cu(II). The amounts of metal present were estimated. From this stock solution, required concentration of metal-perchlorates were prepared by proper dilution.

Apparata:

All glassware used were of Pyrex glass. The micro-burette was calibrated to 0.01 by the method described by Vogel.[49] The measuring vessels such as micro-pipettes, measuring flasks of various capacities, pipettes etc. were calibrated by using a standard burette.

pH Meter and Accessories:

A Metrohm pH Meter of type E 350A operating on 220-240 volts and 40-60 cycles and designed for entire pH range from 0 to 14 and having glass and calomel electrode combination was used. The pH meter

has readability of ± 0.05 unit and a reproducibility of 0.02 pH unit. It was calibrated with buffer of 4 and 7 pH. The calibration was intermittently checked.

Details of Irving-Rossotti titration technique:

All glassware used were of Pyrex glass and were calibrated. The titration was carried out in a 100 ml beaker having a cover provided with three holes. Through one was admitted the electrode, the other two were used for burette tip and glass stirrer.

In case of M(dipy)L systems solutions were prepared as follows :

(1) Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + conductivity water (11.0 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., μ = 0.2M.

(2) Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (6.1 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., μ = 0.2 M.

(3) Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (1.2 ml.) + dioxan (25.0 ml.) Total volume = 50 ml., μ = 0.2M.

(4) Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (11.1 ml.) + dioxan (20.0 ml.). Total volume = 50 ml., μ = 0.2 M.

(5) Perchloric acid (0.2 M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (1.3 ml.) + dioxan (20.0 ml.). Total volume = 50 ml., μ = 0.2M.

(6) Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) +conductivity water (6.2 ml.) dioxan (20.0 ml.) Total volume = 50 ml., μ = 0.2M.

The ionic strength of each solution was initially raised to 0.2M. The solutions were titrated against 0.2M sodium hydroxide. The plots of pH against volume of alkali have been shown in figs(1 to 4).

The titration beakers containing above solutions were allowed to stand for some time. The ratio of metal salt to ligand was maintained 1:1 in all the metal titrations in order to compare K_{MAL} with K_{ML}, under identical conditions. After addition of each portion of alkali, pH was noted. The highest reading which remains steady was recorded in all cases. pH corrections for the dioxan solvent have been made for each reading as suggested by Van Uitert and Haas[50]. In 50% V/V aqueous dioxan medium the pH correction was found to be - 0.1. 0.1 was, therefore, substracted from the pH values recorded. The titration data are given in the table II 1.1 - 1.5.

Determination of Proton Ligand and Metal-Ligand Stability Constants

It is seen in the Irving-Rossotti titration curves that in the lower pH range the acid and the ligand curves (1 & 4) overlap each other. In the higher pH range, however, the ligand curve exhibits lower valves of pH than the acid titration curve, showing presence of more number of titratable H^+ ions due to the dissociation of the H^+ of O-H. Because of the liberation of this proton of O-H, the ligand has extra titratable H^+ ions.

Calculation of $\bar{n}_H$ and proton ligand stability constants:

The $\bar{n}_H$ values can be calculated by using curves 1 and 4. The horizontal distance between these two curves is used for the calculations of $\bar{n}_H$ at different pH by using the following equation :

$$\bar{n}_H = \frac{(V' - V'')\ (N + E^o)}{(V^o + V').T_L^o} + Y \qquad (2.1)$$

Where,

$\bar{n}_H$ = mean number of protons bound per not complex bound ligand molecule.

V^o = initial volume of solutions.

V', V'' = volume of alkali required to attain the same pH in the acid and acid + ligand curves.

N = concentration of alkali.

E^o = initial concentration of mineral acid.

T_L^o = initial total ligand concentration.

Y = number of replaceable hydrogens from ligand.

The values of proton ligand stability constants have been obtained by linear plot of pH against log $\bar{n}_H/1-\bar{n}_H$. At each point on the straight line pH - log $\bar{n}_H/1-\bar{n}_H = K_H \cdot K_1^H$ values were obtained in the range $\bar{n}_H$ 0 to 1 and have been represented in table II(1.14).

Calculation of metal ligand formation constants: -

It is observed that the metal and ligand curves are separated from the acid curve at higher pH. This is due to the liberation of extra hydrogen ions on the coordination of the ligand with metal ion. The $\bar{n}$ values have been calculated by measuring the horizontal difference in the volume of alkali required to produce the same pH in the metal and ligand titration curves and substituting it in the following equation :

$$\bar{n} = \left[\frac{(V''' - V'')\{N + E^o + T_L^o (Y - \bar{n}_H)\}}{(V^o + V'') \cdot \bar{n}_H \cdot T_M^o}\right] \qquad (2.2)$$

where,

T_M^o = initial total metal ion concentration.

V''', V'' = volumes of alkali required to attain the same pH, in the acid + ligand and metal + acid + ligand curves.

Calculation of pL:

For the calculation pL i.e. negative logarithm of free ligand ion, the following equation was used:

$$-\log L = pL = \log \left[\frac{1 + {}^{P}K_1^H \left(\frac{1}{\text{antilog } B}\right) + {}^{P}K_1^H \cdot {}^{P}K_2^H \left(\frac{1}{\text{antilog } B}\right)^2}{T_L^o - \bar{n} \cdot T_M^o} \cdot \frac{V^o + V''}{V^o}\right] \qquad (2.3)$$

TL' = Total concentration of ligand

TM' = Total metal ion concentration

Hence the concentration of free ligand = $TL' - \bar{n}\ TM'$

where $\bar{n}$ = average number of ligand bound per metal ion.

The values of $\bar{n}$ have an accuracy of $\pm$ 0.01 depending on the burette precision and the values of pL are significant upto $\pm$ 0.05 depending upon the readability of the pH scale.

The value of pL at $\bar{n}$ = 0.5 corresponds to K^{M}_{KL}. This is, however, not very accurate. Precise values have been calculated by using the method of linear plot[51].

In this method the formation function in the region of formation of ML, reduces to the following form :

$$\bar{n} + (\bar{n} - 1)\ K_1\ (L) = 0$$

This means that log of $(1-\bar{n})/\bar{n}$ has a linear relationship with pL. The plots of log of $(1-\bar{n})/\bar{n}$ against pL in the range $\bar{n} > 0 < 1$ have been shown in fig. (Five) . The values of log K_1 have been calculated and represented in tables II 1.6—1.14 . Deviation of each individual value from the average value was calculated and that has also been presented in table.

Discussion:

The present ligands have only one pK^{H} value, corresponding to H of O-H. The pK_1^{H} values follow the order:

2-hydroxy-1-naphthaldehyde < Salicylaldehyde < 2-hydroxy acetophenone ≈ 2-hydroxy propiophenone.

The higher acidity of 2-hydroxy-1-naphthaldehyde than salicylaldehyde can be attributed to the additional phenyl ring in naphthaldehyde. The phenyl ring is 'e' withdrawing by nature. Further, existence of resonating structures impart stability to the naphtholate ion. These two factors added together make the H of O-H more labile, accounting for higher dissociation of 2-hydroxy-1-naphthaldehyde.

The higher value of 2-hydroxy acetophenone and 2-hydroxy propiophenone, than salicylaldehyde can be attributed to the presence of methyl and ethyl groups, respectively, which increase the concentration of 'e' on - C = O. This inturn increases the magnitude of H bonding as compared to salicyleldehyde & 2-hydroxy-1-naphthaldehyde[36]. This renders H of O-H in 2-hydroxy acetophenone and 2-hydroxy propiophenone, less labile, resulting in higher values of pK_1H for these ligands. The pK_1H value for 2-hydroxy-propiophenone is slightly higher than 2-hydroxy acetophenone. This is because of the $-C_2H_5$ group which is more 'e' releasing than - CH_3 group. Since the difference in 'e' releasing effects of - CH_3 and C_2H_5 is not marked, the pK_1H values of the two ligands are also quite close.

The formation constants of the binary complexes K^M_{ML} have been determined for the Cu.complexes of salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-acetophenone and 2-hydroxy propiophenone (even though such values are available in literature) in order to have these values under similar conditions, as used for the determination of the formation constants of the corresponding ternary complexes Cu.dipy.L.

The values of the formation constants of binary and ternary complexes indicate the possibility of π interaction in M⟶L bond of the present complexes studied. In the case of Cu-salicylaldehyde complex, the log K^{M}_{ML} value is significantly larger than expected from the basicity of this ligand. The pK_1H value for the salicylaldehyde is lower than that of 2-hydroxy-acetophenone, yet the difference between the log K^{M}_{ML} values of salicylaldehyde and 2-hydroxy acetophenone or 2-hydroxy-propiophenone is not much. Another striking feature is that the log K^{M}_{ML} values of Cu-2-hydroxy-1-naphthaldehyde complex is almost same as that of Cu-salicylaldehyde complex, though 2-hydroxy-1-naphthaldehyde is more acidic than salicylaldehyde. The formation constant values of these metal complexes indicate a possibility of π interaction between the metal $d\pi$ orbitals and the $p\pi$ of - C= O and phenolate O^-. This results in the formation of delocalized π electron ring over the metal and ligand bond. This imparts a double bond character and makes the complex more stable. The additional phenyl ring, in the case of naphthaldehyde, helps in the back donation because of the possibility of π electrons being delocalized over two rings. Since the extent of back donation in 2-hydroxy-1-naphthaldehyde is more, the log K^{M}_{ML} value is higher than expected from its basicity alone.

In 2-hydroxy acetophenone and 2-hydroxy-propiophenone, the CH_3 and C_2H_5 groups, respectively, are 'e' releasing by nature. This increases the density of 'e' over - C = O and thus makes it less 'e' accepting. Hence the possibility of M-L back donation is less in these complexes than M-salicylaldehyde or M-2-hydroxy-1-naphthaldehyde.

This explains, why 2-hydroxy acetophenone and 2-hydroxy-propiophenone, though more basic, do not show much higher values of log K^{M}_{ML} than salicylaldehyde or 2-hydroxy-1-naphthaldehyde complexes. Since there is not much disparity in the electron releasing tendencies of the $-CH_3$ and $-C_2H_5$ groups, the log K^{M}_{ML} values can be expected to be almost same in 2-hydroxy acetophenone and 2-hydroxy propiophenone complexes.

In the ternary systems the formation of mixed ligand complex can be represented in the following two steps :

$$M^{2+} + \text{dipy} \rightleftharpoons [M(\text{dipy})]^{2+}$$

$$[M(\text{dipy})^{2+}] + L \rightleftharpoons [M(\text{dipy})\,L]^{2+}$$

Mixed ligand formation constant

$$K^{M(\text{dipy})}_{M(\text{dipy}).L} \rightleftharpoons \frac{[M(\text{dipy})\,L]^{2+}}{[M(\text{dipy})^{2+}]\,[L]}$$

The above equations presume that the formation of $[M(\text{dipy})]^{2+}$ complex takes place at lower pH and it is stable at higher pH, where the combination of the secondary ligand commences. The observation of the titration curve (fig.1) supports this presumption.

M-dipy curve diverges from the dipyridyl curve at lower pH, indicating that $[M(\text{dipy})]^{2+}$ is formed at lower pH by the dissociation of protons attached with the tertiary nitrogens of dipyridyl monecules. The M-dipy curve diverges from acid curve at pH 6.1, indicating that the formation of hydroxy complex $[M(\text{dipy})(OH)_2]$ starts only at high pH. The curve 5 (M + A + L) remains almost merged in the beginning with 4 (L), indicating that the complexation with secondary ligand does not take place at low pH. The curve 5 diverges

from 4 at higher pH, showing that M + dipy.+ L combination takes place where M + dipy. 1:1 complex formation is complete. In this range hydroxo complex formation also does not take place.

The horizontal distance between curves 4 and 5 (V"' - V") can be measured and used for calculation of $\bar{n}$, where $\bar{n}$ is the average number of secondary ligand molecules associated with one $\left[M(dipy)\right]^{2+}$. Equation used for calculation of $\bar{n}$ would be the same as given in the Irving-Rossotti's original paper[31] and the terms have the same meaning as elaborated earlier(equation 2.2).

The calculation of $\bar{n}$ was carried out below the pH 6.0,where $\left[M(dipy)(OH)_2\right]^{2+}$ formation starts. $\bar{n}$ and pL were calculated at different pH values and have been presented in table II 1.6-1.13 .

The value of pL at $\bar{n}$ = 0.5 is equal to log K^{MA}_{MAL}. However, this will be only one point and may involve experimental error. More precise values were obtained by plotting pL at each point against log $(1-\bar{n})/\bar{n}$ and getting a straight line. At each point on the straight line log K^{MA}_{MAL} is equal to pL - log $(1-\bar{n})/\bar{n}$. The average values, were,thus calculated and have been presented with mean deviation in tables II 1.6-1.13.

Complexes of the type Ni-dipy (or O-phen.)-L could not be studied as the ligand L combines with Ni-dipy. at higher pH where formation of Ni.dipy.$(OH)_2$ starts. Studies were also not possible for Cu.(O-Phen.) L complexes due to the fact that binary complex (Cu-ophen.) is insoluble and precipitates out of solution.

The order of formation constants of the mixed-ligand complexes is found to be the same as in the case of binary complexes i.e. $K^{Cu.dipy.}_{Cu.dipy.salicylaldehyde} \lessapprox K^{Cu.dipy}_{Cu.dipy.2\text{-hydroxy-1-naphthaldehyde}} > K^{Cu.dipy.}_{Cu.dipy.2\text{-hydroxy acetophenone}} \lessapprox K^{Cu.dipy}_{Cu.dipy.2\text{-hydroxy-propiophenone}}$,

However, the mixed-ligand formation constant values of all these complexes are higher than the corresponding binary complex formation constants. This is in keeping with the behaviour of oxygen binding secondary ligands.[25]

The higher values of log K^{MA}_{MAL} can be attributed to three factors. First is the special behaviour of dipyridyl.[25,31,37 - 39] Besides N $\longrightarrow$ M σ bonding, there exists M $\longrightarrow$ N π interaction in dipyridyl complexes. This retains the electronegativity of metal ion in $\left[M(dipy)\right]^{2+}$ same as in $\left[M(H_2O)_n\right]^{2+}$. Thus, the tendency of L to get bound with MA^{2+} is same, as with M^{2+} and hence log $K^{MA}_{MAL} \lessapprox$ log K^{M}_{ML}, where M = Cu (II), L = dipy. or O-Phen.

Secondly the distorted octahedron $\left[Cu\ (H_2O)_6\right]^{2+}$ will be some what more strongly distorted towards the square-planar coordination, by the coordination of α-α-dipyridyl, thus orienting the right geometry for coordination of the secondary ligand resulting in the increased value of log K^{MA}_{MAL}.[26]

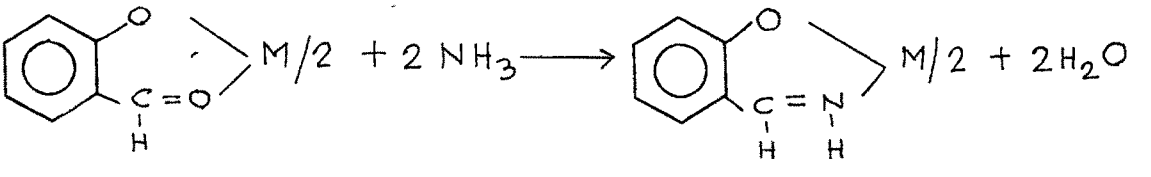
Besides the above two factors, another plausible operative factor could be the existence of π bonding in secondary ligands i.e. between copper and aromatic aldehyde or ketone. The π interactions between M - A and M - L, mutually stabilize each other

and thus contributes to higher value of log K^{MA}_{MAL}. This effect is expected to be high in Cu-dipy-2-hydroxy-1-naphthaldehyde and Cu-dipy-salicylaldehyde complexes, because of greater M $\rightarrow$L π interaction than in Cu-dipy - L, where L = 2-hydroxy-acetophenone and 2-hydroxy-propiophenone. It is observed that log K^{MA}_{MAL} - log K^{M}_{ML}, is more, where L = salicylaldehyde and 2-hydroxy-1-naphthaldehyde.

Thus these studies indicate a probable π interaction in M$\longrightarrow$L bond in complexes of transition metal ions with aromatic aldehydes and ketones.

The above observations throw light on the Schiff base formation from coordinated aldehydes or ketones and also on the stability of the coordinated Schiff bases to hydrolysis.

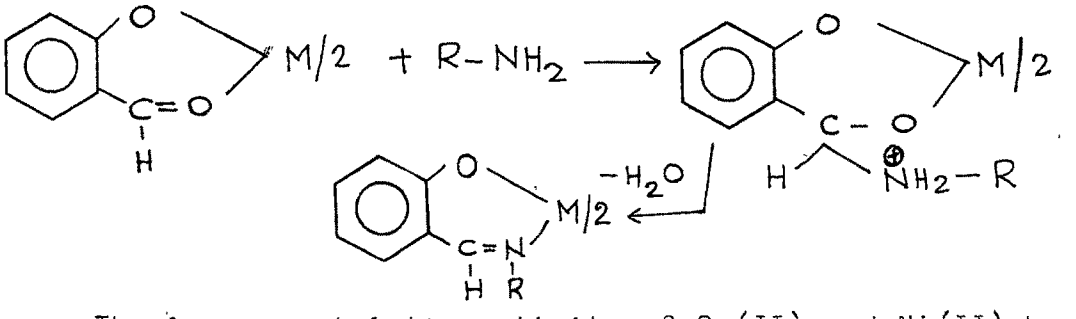
The method of preparation of Schiff base complexes by the reaction of primary amines and ammonia on metal complexes of aldehydes and ketones was suggested by Schiff[40] and later developed by Pfeiffer[41,42]. It can be shown as under :



In this method, the coordination of the carbonyl group to the positive metal ion is supposed to result in polarization of the C = O bond. The oxygen atom becomes more electro-negative and pulls the 'e' of the carbon atom, thus making it more positive. Thus the carbon atom becomes more susceptible to nucleophilic attack by the amine. It can, therefore, be expected that the Schiff base formation

should be facilitated by strongly coordinating metal ions, because there is formation of a stronger metal-ligand bond which should cause an increase in the polarization of the carbonyl group.

A quantitative study of kinetic activity associated with metal ions in Schiff base formation was first reported in 1966 and 1967 by Leussing and coworkers[43,44] Leussing and McQuate[45] did the kinetic and equilibrium studies on the formation of Zn(II) complexes of salicylaldehyde Schiff bases derived from ethylenediamine and 1:3 diamino-propane, to explain the catalytic activity of metal ions. These workers have established that Pb(II), Cd(II), Mn(II), Mg(II) and Zn(II) are kinetically active, while Co(II),Ni(Il) and Cu(II) with partially filled d orbitals are inactive in bringing Schiff base formation reactions. Hopgood and Leussing[46] established the function of metal ion in forming a mixed-ligand complex with the amine donar and carbonyl compound in a pre-equilibrium step. This leads to the formation of a carbinol-amine complex by the attack of the ammine on the - C = O. This is followed by the dehydration, resulting in Schiff base complex formation:



The lesser catalytic activity of Cu(II) and Ni(II) has been considered by these workers, to be due to,the rigid metal-ligand geometries imposed by the ligand field splitting of the 3d orbitals in the case of transition metal complexes. This does not allow Cu(II) and Ni(II) to catalyse the path forming a mixed ligand

complex leading to the Schiff base formation. However, in the case of Zn(II) C.F.S.E. being zero, the metal-ligand bonds formed are more flexible and hence the formation of the Schiff base complex through a mixed-ligand complex is facilitated. Thus the requirement of the catalysing metal ion is that it should form a ternary complex with two reactants, but should impose a minimum steric requirement on them. Leussing and coworkers[46,48] thus preferred to term the role of the metal ion as promnastic effect (match-maker) rather than template.

Leussing's observation can also be viewed from the point of view of $M \longrightarrow L\ \pi$ interaction in metal-salicylaldehyde complexes. The reason why transition metal ions like Cu(II) and Ni(II) do not catalyse the mixed-ligand formation leading to Schiff base complex, can be understood by considering the probability that 'e' from partially filled d orbitals are donated back to salicylaldehyde. Because of the back donation the 'e' density over - C = O does not go down and the attack of the amine is not facilitated and hence Cu(II) and Ni(II) fail to catalyse the Schiff base formation reaction. Since Zinc(II) has completely filled orbitals, obviously the $M \longrightarrow L\pi$ interaction is restricted. In the absence of back donation the expected increase of positive charge density over carbon atom of - C = O occurs on coordination of salicylaldehyde to Zn(II), Cd(II) and Pb(II) and hence they act as better catalysts for Schiff base formation.

The stability of Schiff base complexes to hydrolysis can also be explained in terms of π interaction. It can be expected that the hydrolysis through nucleophilic attack of water on the carbon of

- C = N should be more on coordination of the Schiff base with the metal ion through - C = N. However, the coordinated bidentate Schiff bases in transition metal complexes are found to be stable to hydrolysis. This has been explained[47] to be due to the formation of stable chelate. It is presumed that the over all stability is more than sufficient to counter-act the susceptibility of the metal coordinated - C = N group to undergo hydrolysis.

The above explanation, however, seems to be inadequate. It is not clear how the chelation can restrict the ease of nucleophilic attack over the C = N.

As in metal-salycylaldehyde complexes, there can be $M \longrightarrow L\pi$ interaction in metal Schiff base complexes also, by the interaction of metal $d\pi$ orbitals with the delocalized ligand $p\pi$ orbitals. π interaction in Schiff base complexes has been indicated by Holm and coworkers on the basis of N.M.R.studies of Schiff base complexes[48]. If the metal ion has filled $d\pi$ orbitals suitable for back donation to π occeptor orbitals on imine, then this will help to reduce the effective positive charge on the imine carbon and hence weak nucleophiles like water cannot attack at the carbon of C = N. The coordinated Schiff bases, therefore, are not hydrolysed easily. Back bonding and delocalization are more in cases of chelated Schiff bases. This explains the stability of transition metal Schiff base complexes.

Table II 1.1

N = 0.2M V^{o} = 50 ml. T^{o}Dipy = 0.002M T^{o}_{M} = 0.002M

E^{o} = 0.02M μ = 0.2M t = 30°C.

Perchloric Acid		Dipyridyl		Cu.Dipyridyl	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.75
2.00	1.90	2.00	1.90	2.00	1.90
3.00	2.10	3.00	2.20	3.00	2.10
4.00	2.30	4.00	2.60	4.00	2.30
4.20	2.50	4.10	2.70	4.20	2.50
4.40	2.60	4.20	2.80	4.40	2.65
4.60	2.80	4.30	2.95	4.50	2.80
4.70	3.00	4.40	3.05	4.60	2.95
4.80	3.30	4.50	3.20	4.70	3.10
4.86	3.50	4.60	3.40	4.75	3.15
4.90	4.10	4.70	3.65	4.80	3.40
4.93	4.70	4.80	4.00	4.90	4.10
4.96	5.60	4.85	4.40	4.93	4.70
4.99	6.20	4.88	4.50	4.96	5.60
5.00	7.80	4.90	5.00	4.99	6.00
5.02	8.60	4.95	5.80	5.00	6.05
5.07	9.50	4.95	5.80	5.10 ppts	6.30
5.11	10.00	5.00	7.15	5.20	6.80
5.15	10.10	5.01	8.50	5.30	7.10
		5.05	9.50	5.40	7.40
				5.50	8.15
				5.60	9.10

Table II 1.2

N = 0.2M V^o = 50 ml. T_M^o = 0.002M

E^o = 0.02M T_L^o = 0.002M t = 30°C

Salicyl.		Cu.dipy.salicyl.		Cu.Salicyl.	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.75
2.00	1.90	2.00	1.90	2.00	1.90
3.00	2.10	3.00	2.10	3.00	2.10
4.00	2.30	4.00	2.30	4.00	2.30
4.20	2.50	4.20	2.50	4.20	2.50
4.40	2.60	4.40	2.65	4.40	2.60
4.60	2.80	4.50	2.80	4.60	2.80
4.70	3.00	4.60	2.95	4.70	3.10
4.80	3.30	4.70	3.05	4.80	3.20
4.86	3.50	4.80	3.15	4.90	3.60
4.90	4.10	4.85	3.20	4.94	3.80
4.93	4.70	4.90	3.25	4.98	4.00
4.96	5.60	4.94	3.35	5.00	4.20
4.99	6.20	4.96	3.50	5.05	4.40
5.00	7.80	5.00	3.70	5.10	4.60
5.02	8.10	5.05	3.80	5.15	4.90
5.10	8.65	5.10	4.10	5.20	5.10
5.20	8.95	5.15	4.30	5.25	5.30
5.25	9.10	5.20	4.50	5.30	5.50
5.30	9.20	5.25	4.70	5.35	5.70
5.35	9.40	5.30	4.90	5.40	5.90
5.40	9.55	5.40	5.30	5.50	6.05
5.45	9.70	5.50	5.70	5.60	6.10
5.50	10.00	5.60	6.25	5.70	6.30
		5.70	6.90	5.90	6.60
		5.80	7.50	6.00	7.00
		5.90	8.30		

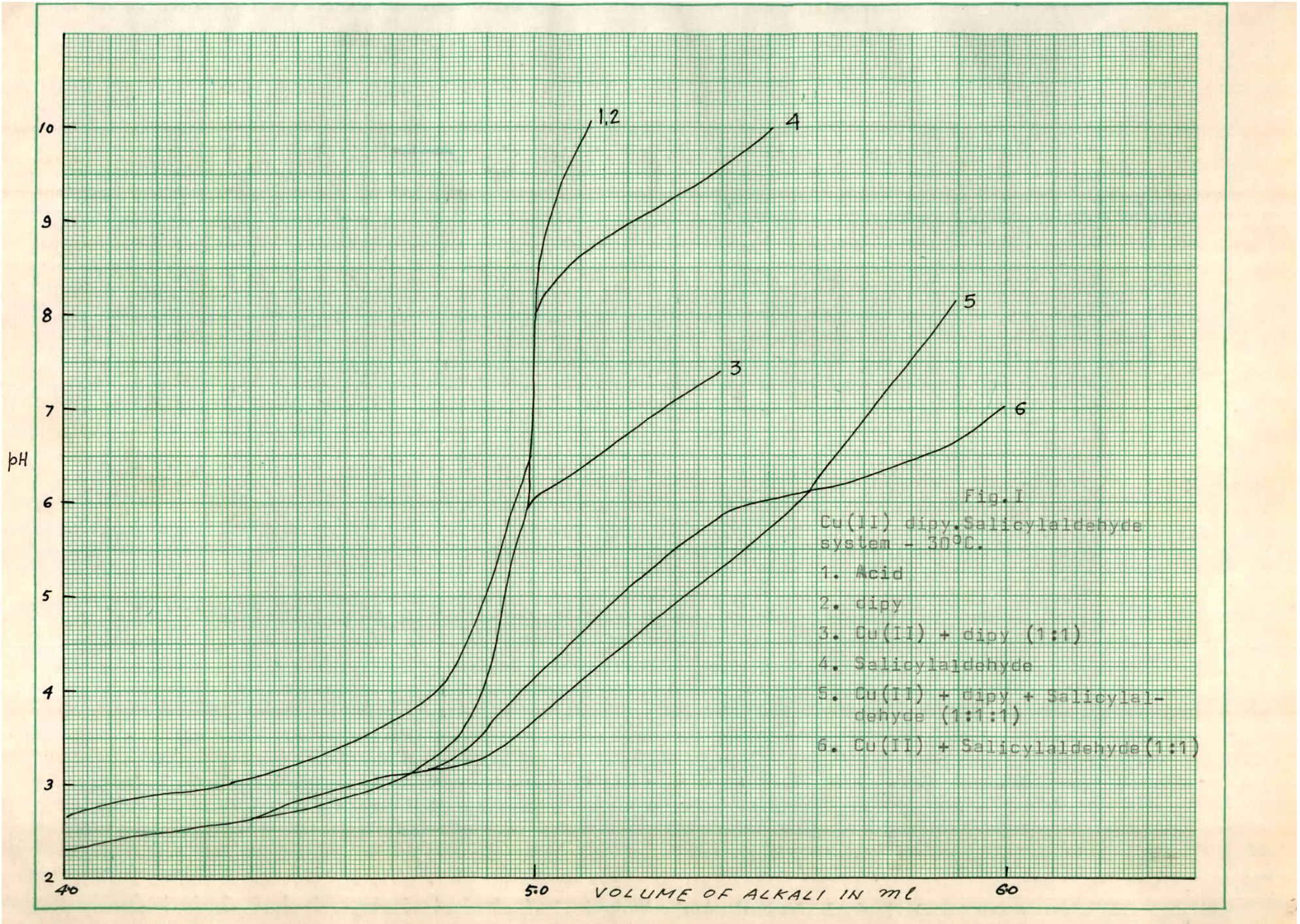


Fig. I

Cu(II) dipy.Salicylaldehyde system - 30°C.

1. Acid
2. dipy
3. Cu(II) + dipy (1:1)
4. Salicylaldehyde
5. Cu(II) + dipy + Salicylaldehyde (1:1:1)
6. Cu(II) + Salicylaldehyde (1:1)

Table II 1.3

N = 0.2M V^o = 50 ml. T_M^o = 0.002M

E^o = 0.02M T_L^o = 0.002M t = 30°C.

Naphthal.		Cu.dipy.naphthal.		Cu.naphthal.	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.75
2.00	1.90	2.00	1.90	2.00	1.90
3.00	2.10	3.00	2.10	3.00	2.10
4.00	2.30	4.00	2.30	4.00	2.30
4.20	2.50	4.20	2.50	4.20	2.50
4.40	2.60	4.40	2.65	4.40	2.60
4.60	2.80	4.50	2.80	4.50	2.80
4.70	3.00	4.50	2.95	4.70	3.10
4.80	3.30	4.70	3.05	4.80	3.20
4.86	3.50	4.80	3.15	4.90	3.30
4.90	4.10	4.90	3.20	4.94	3.50
4.93	4.70	4.94	3.25	4.98	3.60
4.96	5.60	4.98	3.30	5.00	3.65
4.99	6.20	5.00	3.40	5.05	3.80
5.00	7.40	5.05	3.40	5.10	3.90
5.05	7.70	5.10	3.50	5.15	4.10
5.10	7.90	5.15	3.60	5.20	4.30
5.15	8.00	5.20	3.80	5.25	4.60
5.20	8.15	5.25	3.90	5.30	4.80
5.30	8.40	5.30	4.00	5.35	5.10
5.45	9.10	5.40	4.40	5.40	5.30
5.50	9.40	5.45	4.80	5.45	5.60
5.55	9.65	5.50	5.30	5.50	5.80
5.60	10.00	5.55	5.90	5.55	5.90
		5.60	6.50	5.60	6.10
		5.70	7.00	5.65	6.10
		5.80	8.00	5.70	6.30
		5.90	8.60	5.80	6.80

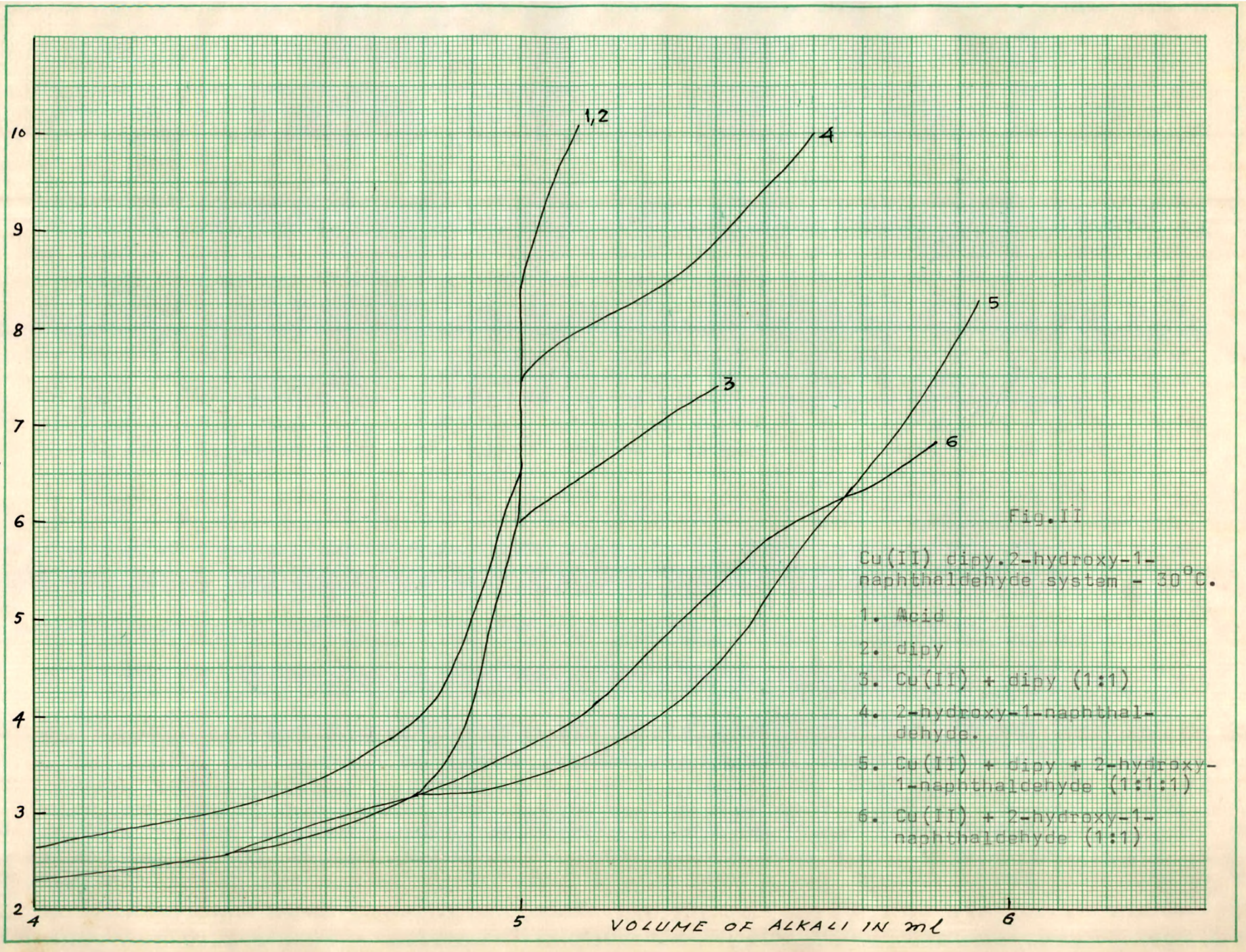


Fig.II

Cu(II) dipy.2-hydroxy-1-naphthaldehyde system - 30°C.

1. Acid
2. dipy
3. Cu(II) + dipy (1:1)
4. 2-hydroxy-1-naphthaldehyde.
5. Cu(II) + dipy + 2-hydroxy-1-naphthaldehyde (1:1:1)
6. Cu(II) + 2-hydroxy-1-naphthaldehyde (1:1)

Table II 1.4

N = 0.2M V^{o} = 50 ml. T_{M}^{o} = 0.002M

E^{o} = 0.02M T_{L}^{o} = 0.002M t = 30^{o}C

Acph.		Cu.dipy.Acph.		Cu.Acph.	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.75
2.00	1.90	2.00	1.90	2.00	1.90
3.00	2.10	3.00	2.10	3.00	2.10
4.00	2.30	4.00	2.30	4.00	2.30
4.20	2.50	4.20	2.50	4.20	2.50
4.40	2.60	4.40	2.65	4.40	2.65
4.50	2.80	4.50	2.80	4.50	2.80
4.70	3.00	4.60	2.95	4.70	3.10
4.80	3.30	4.70	3.05	4.80	3.20
4.86	3.50	4.80	3.15	4.90	4.25
4.90	4.10	4.85	3.30	4.94	4.80
4.93	4.70	4.90	4.20	4.98	5.15
4.96	5.60	4.94	4.50	5.00	5.25
4.99	6.20	4.98	4.85	5.05	5.45
5.00	7.60	5.00	5.00	5.10	5.65
5.05	8.25	5.05	5.20	5.18	5.75
5.10	8.90	5.11	5.50	5.20	5.80
5.15	9.40	5.15	5.70	5.30	5.85
5.20	9.70	5.20	5.80	5.40	6.00
5.25	10.00	5.25	6.00	5.50	6.00
5.35	10.30	5.30	6.10	5.60	6.30
		5.40	6.30	5.70	6.50
		5.50	6.50	5.80	6.60
		5.60	6.70	6.00	7.30
		5.70	7.20		

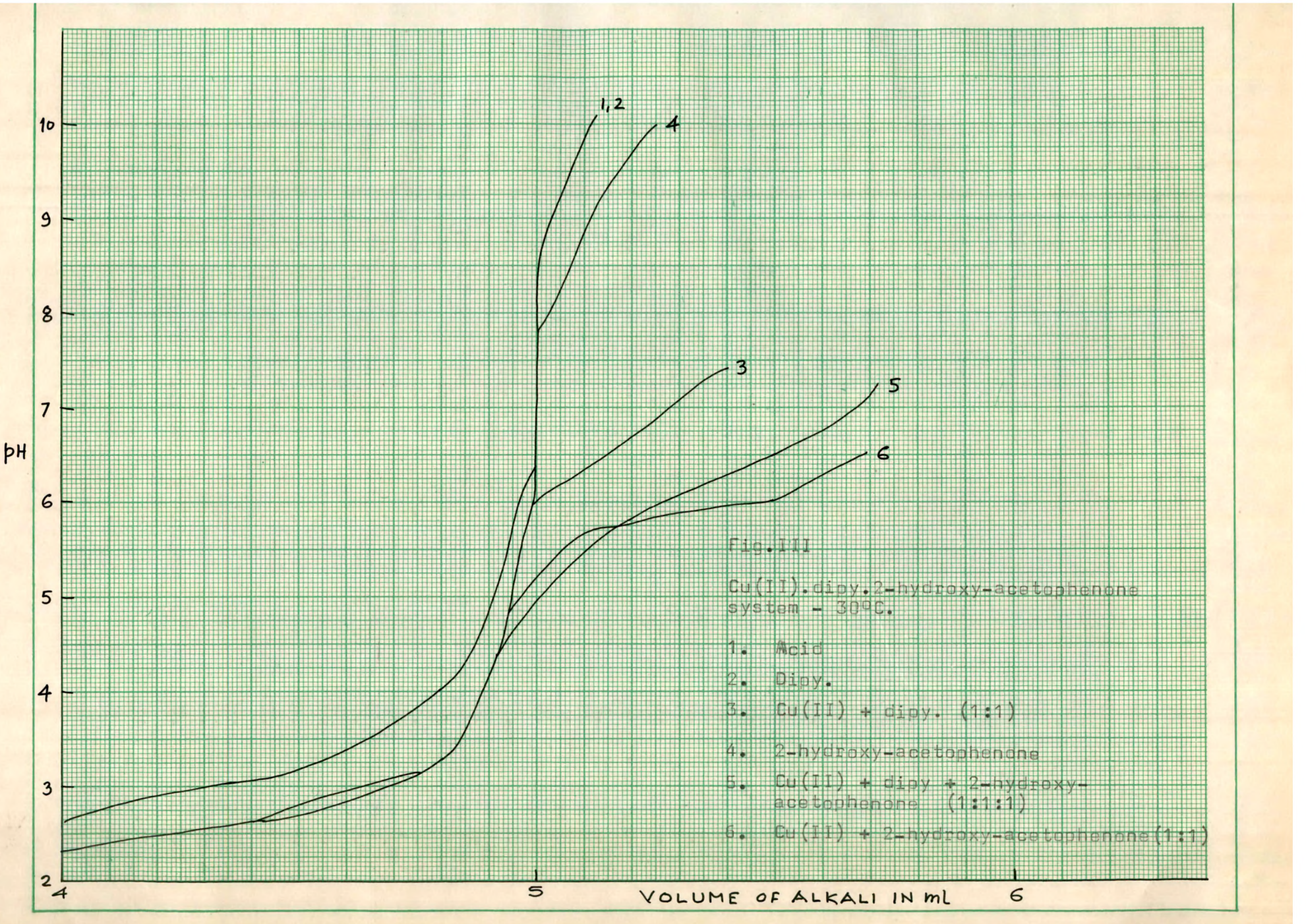


Fig. III

Cu(II).dipy.2-hydroxy-acetophenone system - 30°C.

1. Acid
2. Dipy.
3. Cu(II) + dipy. (1:1)
4. 2-hydroxy-acetophenone
5. Cu(II) + dipy + 2-hydroxy-acetophenone (1:1:1)
6. Cu(II) + 2-hydroxy-acetophenone (1:1)

Table II 1.5

N = 0.2M V^{o} = 50 ml. T_{M}^{o} = 0.002 M

E^{o} = 0.02M T_{L}^{o} = 0.002M. t = 30°C.

Propio.		Cu.dipy.Propio.		Cu.Propio.	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.75
2.00	1.90	2.00	1.90	2.00	1.90
3.00	2.10	3.00	2.10	3.00	2.10
4.00	2.30	4.00	2.30	4.00	2.30
4.20	2.50	4.20	2.50	4.20	2.50
4.40	2.60	4.40	2.65	4.40	2.60
4.60	2.80	4.50	2.80	4.60	2.80
4.70	3.00	4.60	2.95	4.70	3.10
4.80	3.30	4.70	3.05	4.80	3.20
4.86	3.50	4.80	3.15	4.85	3.50
4.90	4.10	4.85	3.50	4.90	4.15
4.93	4.70	4.90	4.15	4.92	4.60
4.96	5.60	4.92	4.50	4.94	4.95
4.99	6.20	4.94	4.80	4.98	5.20
5.00	8.00	4.96	4.90	5.00	5.30
5.05	8.40	5.00	5.10	5.10	5.80
5.10	9.15	5.04	5.60	5.15	5.90
5.15	9.70	5.10	5.70	5.25	5.90
5.20	9.80	5.15	5.90	5.30	5.90
5.25	10.05	5.20	6.10	5.35	5.90
5.30	10.25	5.40	6.80	5.40	6.00
		5.50	7.50	5.50	6.10
				5.80	6.50
				5.90	6.90
				6.00	7.20

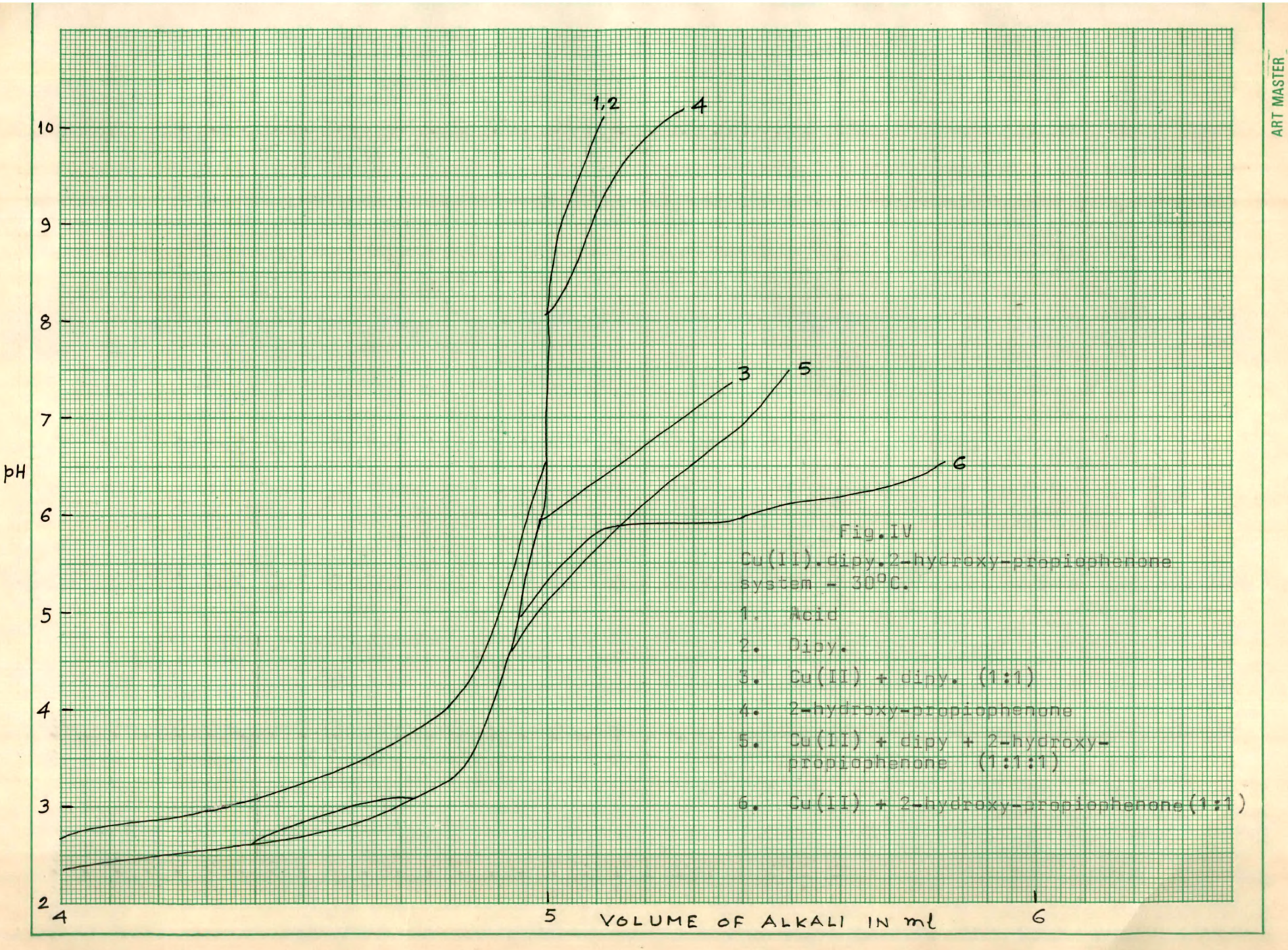


Fig. IV

Cu(II).dipy.2-hydroxy-propiophenone system - 30°C.

1. Acid
2. Dipy.
3. Cu(II) + dipy. (1:1)
4. 2-hydroxy-propiophenone
5. Cu(II) + dipy + 2-hydroxy-propiophenone (1:1:1)
6. Cu(II) + 2-hydroxy-propiophenone (1:1)

Table II 1.6

B, $\bar{n}$, log $(1-\bar{n})/\bar{n}$, pL and pL-log$(1-\bar{n})/\bar{n}$ data for Cu(II) Salicylaldehyde system - 30°C.

B	V'''	V''	V''' - V''	$\bar{n}$	log$(1-\bar{n})/\bar{n}$	pL	pL-log$(1-\bar{n})/\bar{n}$
5.00	5.18	4.95	0.23	0.46	0.09	7.30_9	7.21_9
5.10	5.20	4.96	0.24	0.48	0.034	7.22_5	7.19_1
5.20	5.23	4.97	0.26	0.52	$\bar{1}.964$	7.16_1	7.19_7
5.30	5.25	4.97	0.28	0.56	$\bar{1}.895$	7.06_4	7.16_9
5.40	5.28	4.98	0.30	0.60	$\bar{1}.823$	6.99_9	7.17_6
5.50	5.30	4.98	0.32	0.64	$\bar{1}.750$	6.98_6	7.23_6

log $K_1 = 7.18 \pm 0.0$

Table II 1.7

B, $\bar{n}$, log $(1-\bar{n})/\bar{n}$, pL and pL-log $(1-\bar{n})/\bar{n}$ data for Cu(II) dipyridyl Salicyladehyde system - 30°C.

B	V'''	V''	V''' - V''	$\bar{n}$	log$(1-\bar{n})/\bar{n}$	pL	pL-log$(1-\bar{n})/\bar{n}$
4.10	5.10	4.90	0.20	0.40	0.176	8.16_3	7.98_7
4.20	5.12	4.91	0.21	0.42	0.139	8.17_8	7.93_9
4.30	5.15	4.92	0.23	0.46	0.09	8.00_9	7.91_9
4.40	5.17	4.93	0.24	0.48	0.034	7.92_5	7.89_1
4.50	5.20	4.93	0.27	0.54	$\bar{1}.930$	7.87_9	7.94_9
4.60	5.22	4.94	0.28	0.56	$\bar{1}.895$	7.79_9	7.90_4
4.70	5.25	4.94	0.31	0.62	$\bar{1}.787$	7.76_3	7.97_6
4.80	5.27	4.95	0.32	0.64	$\bar{1}.750$	7.68_6	7.93_6

log $K_{MAL} = 7.93 \pm 0.02$.

Table II 1.8

B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL - $\log(1-\bar{n})/\bar{n}$ data for Cu(II) 2-hydroxy-1- naphthaldehyde system - 30°C.

B	V'''	V''	V''' - V''	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
4.00	5.12	4.91	0.21	0.42	0.139	7.35_8	7.21_9
4.10	5.14	4.91	0.23	0.46	0.069	7.28_9	7.22_0
4.20	5.16	4.92	0.24	0.48	0.034	7.20_5	7.17_1
4.30	5.19	4.92	0.27	0.54	$\bar{1}$.963	7.15_9	7.19_6
4.40	5.21	4.93	0.28	0.56	$\bar{1}$.895	7.07_9	7.18_4
4.50	5.23	4.93	0.30	0.60	$\bar{1}$.823	7.02_9	7.20_6
4.60	5.25	4.93	0.32	0.64	$\bar{1}$.750	6.96_6	7.21_6

$\log K_1 = 7.19 \pm 0.01$

Table II 1.9

B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL - $\log(1-\bar{n})/\bar{n}$ data for Cu (II) Dipyridyl.2-hydroxy-1-naphthaldehyde system - 30°C.

B	V'''	V''	V''' - V''	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.45	5.06	4.84	0.22	0.44	0.104	7.92_2	7.81_8
3.50	5.10	4.85	0.25	0.50	0.00	7.92_2	7.92_2
3.55	5.12	4.85	0.27	0.54	$\bar{1}$.963	7.90_9	7.94_6
3.60	5.14	4.86	0.28	0.56	$\bar{1}$.895	7.87_8	7.98_3
3.65	5.16	4.87	0.29	0.58	$\bar{1}$.860	7.84_8	7.98_8
3.70	5.18	4.87	0.31	0.62	$\bar{1}$.787	7.84_2	8.05_5

$\log K_{MAL} = 7.94 \pm 0.05$.

Table II 1.10

B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL - \log(1-\bar{n})/\bar{n}$ data for Cu(II) 2-hydroxy Acetophenone - 30°C.

B	V''	V'	V'' - V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.45	5.04	4.96	0.08	0.16	0.720	8.16_8	7.44_5
5.55	5.07	4.96	0.11	0.22	0.549	8.09_8	7.54_5
5.65	5.10	4.97	0.14	0.28	0.410	8.03_4	7.62_4
5.75	5.13	4.97	0.16	0.32	0.327	7.95_9	7.63_2
5.80	5.19	4.97	0.22	0.44	0.104	7.98_5	7.88_1

$\log K_1 = 7.61 \pm 0.09$

Table II 1.11

B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL - \log(1-\bar{n})/\bar{n}$ data for Cu (II) Dipyridyl. 2-hydroxy Acetophenone - 30°C.

B	V''	V'	V'' - V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.30	5.07	4.96	0.11	0.22	0.549	8.34_7	7.79_9
5.40	5.09	4.96	0.12	0.24	0.500	8.26_1	7.76_1
5.50	5.11	4.96	0.13	0.26	0.454	8.17_2	7.71_8
5.60	5.13	4.97	0.16	0.32	0.327	8.10_9	7.78_2
5.70	5.15	4.97	0.18	0.36	0.249	8.10_3	7.95_4
5.80	5.19	4.97	0.22	0.44	0.104	7.99_3	7.88_9
5.90	5.21	4.98	0.23	0.46	0.069	7.91_0	7.74_1
6.00	5.24	5.98	0.26	0.52	$\bar{1}.865$	7.86_1	7.99_6

$\log K_{MAL} = 7.88 \pm 0.08$

Table II 1.12

B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL- $\log(1-\bar{n})/\bar{n}$ data for Cu (II) 2-hydroxy Propiophenone system - 30°C.

B	V''	V'	V'' - V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.60	5.04	4.97	0.07	0.14	0.788	8.20_6	7.41_8
5.65	5.05	4.97	0.08	0.16	0.720	8.18_0	7.46_0
5.70	5.07	4.97	0.10	0.20	0.602	8.14_3	7.54_1
5.75	5.09	4.97	0.12	0.24	0.500	8.09_8	7.59_8
5.80	5.10	4.97	0.13	0.26	0.454	8.07_2	7.61_8
5.85	5.125	4.97	0.155	0.31	0.347	0.06_2	7.71_5
5.90	5.15	4.97	0.18	0.36	0.249	8.03_7	7.78_8

$\log K_1 = 7.52 \pm 0.07$

Table II 1.13.

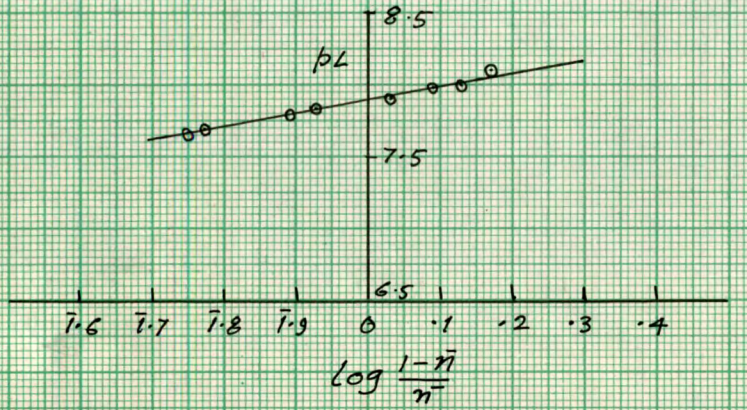
B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL - log $(1-\bar{n})/\bar{n}$ data for Cu (II) Dipyridyl.2-hydroxy-Propiophenone system - 30°C.

B	V''	V'	V'' - V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.50	5.07	4.96	0.11	0.22	0.549	8.39_8	7.84_9
5.55	5.08	4.96	0.12	0.24	0.500	8.31_0	7.81_0
5.60	5.09	4.96	0.13	0.26	0.454	8.27_1	7.81_7
5.65	5.10	4.96	0.14	0.28	0.410	8.22_3	7.81_7
5.70	5.11	4.96	0.15	0.30	0.366	8.18_6	7.82_0
5.75	5.12	4.97	0.15	0.30	0.366	8.13_6	7.77_0
5.80	5.13	4.97	0.16	0.32	0.326	8.09_8	7.77_2
5.85	5.15	4.97	0.18	0.36	0.249	8.07_5	7.82_6

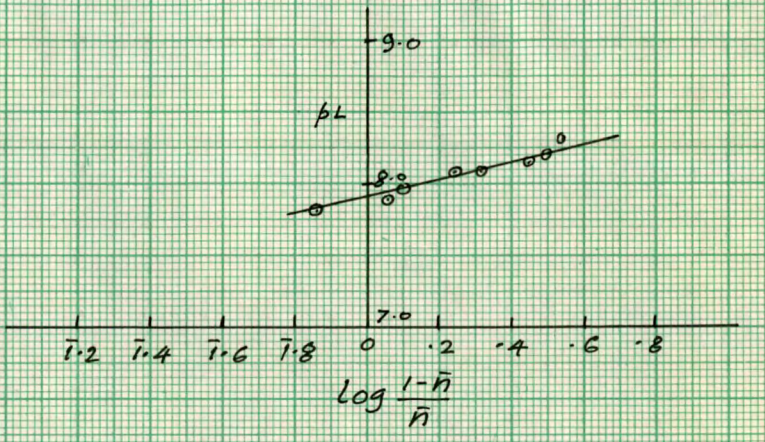
$\log K_{MAL} = 7.80 \pm 0.02$

Fig. V

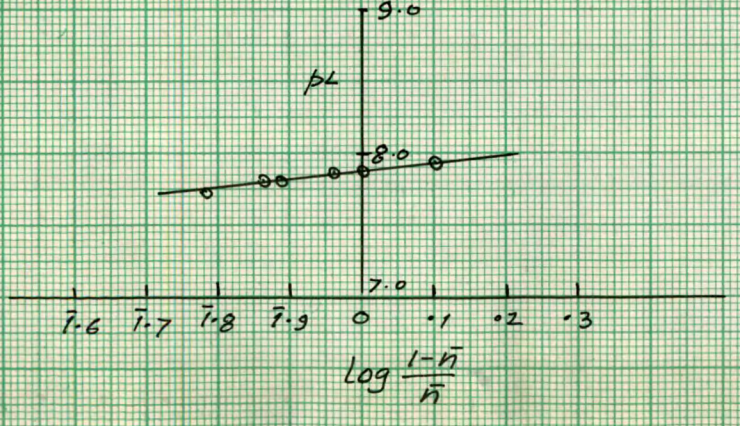
Cu.dipy.Salicylaldehyde system - 30°C



Cu.dipy.2-hydroxyacetophenone system-30°C.



Cu.dipy.2-hydroxy-1-naphthaldehyde system - 30°C.



Cu.dipy.2-hydroxypropiophenone system - 30°C.

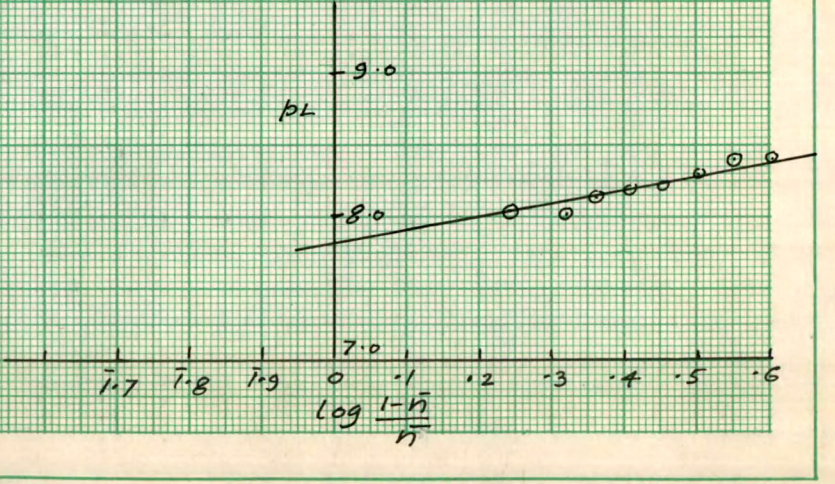


Table II 1.14

Proton and metal ligand stability constants of aromatic aldehydes and ketones - 30°C.

Ligand	$P_{K1}H$	log $K^{Cu}_{Cu.L}$	log $K^{Cu.dipy}_{Cu.dipy.L}$
Salicyladehyde	9.30	7.18± 0.02	7.93± 0.02
2-hydroxy- 1 - naphthaldehyde.	8.38	7.19± 0.01	7.94± 0.05
2-hydroxy - Acetophenone.	10.80	7.61± 0.09	7.83± 0.08
2-hydroxy - Propiophenone.	11.00	7.52± 0.07	7.80± 0.02

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