CHAPTER TWO

Proton-ligand and metal-ligand formation constant studies in Ni(II) or Cu(II)-polyhydroxy aromatic ligand systems.

The formation constants of Cu(II) and Ni(II) complexes with catechol, pyrogallol, 2,3-dihydroxynaphthalene, protocatechuic and gallic acid were determined using Irving-Rossotti titration technique.

A. Preparation of solutions :

(1) Water :

Distilled water was redistilled over alkaline potassium permanganate. The resulting distillate was boiled to expel the carbondioxide and was cooled in well stoppered pyrex flask. The pH of this water was about 6.8. This water was used for preparing all the solutions.

(2) Oxalic acid solution :

Standard A.R. oxalic acid of strength 0.5N was prepared by dissolving the required amount of the sample in double distilled water.

(3) Sodium hydroxide solution :

Sodium hydroxide solution free from carbonate was prepared according to the method of Allen and Low[1]. 20.0 g. of sodium hydroxide were dissolved in 500 ml. of double distilled water in a pyrex flask. The flask was corked and left over for 48 hrs. The clear supernatant liquid was filtered rapidly through sintered bed Jena glass crucible of porosity G4 using vacuum pump. A suitable volume of the filtrate was diluted to obtain approximately 0.5N solution which was preserved out of contact with carbondioxide. The stock solution was standardised against a standard oxalic acid solution and 0.2N solution was prepared by suitable dilution of the stock solution.

(4) Sodium perchlorate solution :

A weighed quantity of A.R. sodium perchlorate was dissolved in double distilled water to get a solution of 1.0M concentration and stored in well stoppered pyrex flask.

(5) Perchloric acid solution :

The 60 % acid (A.R.) was diluted with double distilled water to obtained 500 ml. of approximately 0.2M perchloric acid solution and standardised by titration against standard sodium hydroxide solution. It was diluted to get 0.1M concentration.

(6) Metal salt solutions :

(i) Nickel perchlorate solution : Nickel sulphate (A.R.) solution was treated with a solution of sodium carbonate (A.R.). The precipitate of basic carbonate was digested, washed with water until free from sulphate ion and dried. The solid was refluxed with 50 ml. (~ 1.0M) of perchloric acid solution in a pyrex flask fitted with air condenser for about one hour. Addition of nickel carbonate was continued till an excess of a solid was left. The metal perchlorate thus obtained had pH 6.7 i.e. below the pH of hydrolysis of nickel ions. Filtrate was diluted to 250 ml. and metal content was estimated by the precipitation of nickel dimethylglyoxime complex[2].

(ii) Copper perchlorate solution : Copper carbonate (A.R.) was refluxed with 50 ml. (~ 1.0M) perchloric acid in a pyrex flask fitted with air condenser for about one hour. Addition of copper carbonate was continued till an excess of a solid was left. To avoid the hydrolysis of cupric salt, it was filtered in a known amount of perchloric acid solution. This was diluted to 250 ml.. The metal content was estimated by precipitation of $Cu_2(CNS)_2$[3]. It was used as a stock solution. The stock solution was diluted by adding requisite amount of perchloric acid solution to get a concentration of 0.01M with respect to the metal and 0.1M with respect to the perchloric acid. 5.0 ml. of this solution was used for the titration.

(7) Solutions of complexing agents :

Catechol, pyrogallol, 2,3-dihydroxynaphthalene, perchloric and gallic acid of A.R. quality were used. All the ligands used are soluble in water. The required amount was weighed accurately in stoppered weighing bottle and dissolved in double distilled water. The solutions were diluted to get 0.05M concentrations. In case of protocatechuic and gallic acid, the solubility is less in cold water and hence requisite amount was dissolved in hot water and diluted to 100 ml. to get 0.05M concentration. Due to lesser solubility of 2,3-dihydroxynaphthalene in water, requisite amount of the solid was directly added to the reaction mixture. Care was taken to avoid excess contact with air during the preparation and dilution of the ligand solution, because the compounds have a tendency to get oxidised in air. Fresh solutions were prepared and used every time. The surface of the stock solution was kept covered with toluene to avoid oxidation by air.

B. Apparata :

The glassware used were all pyrex. The micro burette which was graduated upto 0.01 of a ml. was calibrated in accordance with the method described by Vogel[4]. Similarly other apparata such as pipettes, measuring flasks etc. were calibrated with the help of the standard burette.

C. pH Meter and Accessories :

A pH meter with the following specifications was used throughout the course of the investigation.

Model	Metrohm E 350A
Number	16/1423
Mains voltage	220-240 volts; 40-60 c.p.s.
Range	0 --- 14 pH
Accuracy	± 0.05 pH
Scale graduation	0.1 pH
Temp. range	0° - 100°C.
Equipment	1 EA 120X combined glass electrode
Supplier	Metrohm, Switzerland.

The instrument required 15 minutes for heating and to be ready for work. The instrument was operated through a voltage stabilizer to avoid the effect of voltage fluctuation.

D. Calibration of the pH meter :

The pH meter was calibrated with the standard buffer solutions of pH 4.0 and 7.0. After completion of pH measurement for a set, the calibration was checked again.

E. Bubbling of Nitrogen :

The experiment in the present investigation were carried out in an inert atmosphere. This was achieved by bubbling 'Oxygen free' nitrogen through the solution in which the electrode was dipping. The nitrogen gas served to prevent oxidation due to atmospheric air and also kept the solution stirring.

Details of the Irving-Rossotti titrations :

All the titrations were carried out in a lipless pyrex beaker, fitted with perspex cover through which were admitted the electrode, gas inlet, burette tip and glass stirrer. The beakers were kept in a thermostat maintained at 25 ± 0.1°C. Three solution mixtures were prepared as detailed below. The total volume (50 ml.) and the ionic strength of solutions (0.2M) were kept constant in all the cases by the addition of double distilled water and neutral salt i.e. sodium perchlorate respectively.

(i) Acid titration :

Perchloric acid (0.05M, 10 ml.) + sodium perchlorate (1M, 9.5 ml.) + double distilled water (30.5 ml.) ; total volume 50 ml., $\mu = 0.2M$.

(ii) Reagent titration :

Perchloric acid (0.05M, 10 ml.) + sodium perchlorate (1M, 9.0 ml.) + reagent (0.05M, 10 ml.) + double distilled water (21.0 ml.); total volume 50 ml., $\mu = 0.2M$.

(iii) Metal titration :

Perchloric acid (0.05M, 10 ml.) + sodium perchlorate (1M, 8.95 ml.) + reagent (0.05M, 10 ml.) + metal solution (0.01M; 5 ml.) + double distilled water (16.05 ml.); total volume 50 ml., $\mu = 0.2M$.

In case of copper, metal solution was prepared in requisite amount of perchloric acid and hence perchloric acid was not added.

These solutions were titrated against standard sodium hydroxide solution. pH was noted after the addition of each 0.02 ml. of alkali. The pH was checked each time. The volume of alkali added and the pH measured have been recorded in tables 1.1 to 1.5. The plots of pH against the volume of alkali have been presented in figs. II 1-5..

Calculation of $\bar{n}_H$ and $\bar{n}$:

The stoichiometric hydrogen ion concentration $[H]'$ at any point of the acid titration curve is given by :

$$[H]' = [E]' + [OH]' - [Na]' \quad ..... \qquad (2.1)$$

where E' = concentration of mineral acid in solution and Na' = concentration of Na^+ ions from the NaOH added. The latter term does not include the Na^+ ions present due to the neutral salt $NaClO_4$ added to maintain a constant ionic strength at the beginning of the titration. The term OH' results from hydrolysis which neutralizes the effect of the addition of alkali and hence is positive.

For the reagent titration the corresponding equation is

$$[H]'' = [E]' + [OH]'' - [Na]'' + YT_L'' - \bar{n}_H''.T_L'' \quad ... \qquad (2.2)$$

The term YT_L'' represents the number of titratable hydrogen ions (replaceable hydrogen ions) in gram ion per litre, arising from the acidic complexing agent H_YL. But when the complexing agent is a base Y will be zero. The last term $\bar{n}_H'' . T_L''$ gives the number of hydrogen ions removed as a result of the formation of proton ligand complexes and results from the definition of $\bar{n}_H$ given previously (page 21).

If two solutions have the same ionic strength, it follows from the equation[5-7]

$$- \log [H] = B + \log f + \log U_H^{o} \;.... \qquad (2.3)$$

In the case of aqueous solutions f (activity coefficient of the hydrogen ions in the solution) and U_H^o (correction at zero ionic strength) are both equal to one and hence B (the pH-meter reading) is equal to pH.

The points on the corresponding titration curve where the B values are identical :

$$[H]' = [H]'' \;..... \qquad (2.4)$$

Since $[H]$ and $[OH]$ are related by the ionic product of water which is constant at constant ionic strength and temperature so

$$[OH]' = [OH]'' \;..... \qquad (2.5)$$

Thus from (2.1) and (2.2) the following relationship is obtained.

$$\bar{n}_H'' = \frac{\left\{ (E'' - E') - ([Na]'' - [Na]') + YT_L'' \right\}}{T_L''} \qquad (2.6)$$

Further, if for two titrations the initial volumes of solutions V°, the initial mineral acid concentration E°, and the concentration of alkali N, are the same and T_L^o is the initial total ligand concentration, the following equations can be obtained if V' and V'' are the volumes of alkali needed for reaching the same pH value in both the titrations.

$$E'' = V^{\circ}E^{\circ} / (V^{\circ} + V'') \quad ..... \qquad (2.7)$$

$$[Na]'' = V''N / (V^{\circ} + V'') \quad .... \qquad (2.8)$$

and $$T_L'' = V^{\circ}T_L^{\circ} / (V^{\circ} + V'') \quad ...... \qquad (2.9)$$

Similar equations would represent the values for E', Na', T_L' and V'.

Then from (2.1)

$$\bar{n}_H = \left\{ YT_L^{\circ} + \frac{(V' - V'')\ (N + E^{\circ})}{(V^{\circ} + V')} \right\} \Big/ T_L^{\circ} \quad .... \qquad (2.10)$$

The metal titration curve gives the relation

$$[H]''' = E''' + YT_L''' + [OH]''' - [Na]''' - \bar{n}_H''' \left\{ T_L''' - \bar{n}'''.T_M''' \right\} \quad (2.11)$$

in which the last term has the same significance as the last term in (2.2) with the difference that the former takes into account the decrease in the concentration of the uncomplexed ligand after the formation of necessary amount of metal ligand complex. The term $\bar{n}''' . T_M'''$ arises from the definition of $\bar{n}$ on page 20.

For those points on the reagent and metal titration curves where B values are same, the following relation must hold under similar conditions of ionic strength and temperature.

$$[H]'' = [H]''' \quad \text{and} \quad [OH]'' = [OH]'''$$

and in addition

$$\bar{n}_H'' = \bar{n}_H'''$$

The following equation is, therefore, obtained.

$$\bar{n}''' = \frac{(E'' - E''') + (T_L'' - T_L''')\ (Y - \bar{n}_H''') - ([Na]'' - [Na]''')}{\bar{n}_H'' . T_M'''} \qquad (2.11)$$

From the above expression and equations similar to (2.7) to (2.9), the expression

$$\bar{n}''' = \frac{(V''' - V'')\left\{N + E^{\circ} + T_{L}^{\circ}(Y - \bar{n}_{H}'')\right\}}{(V^{\circ} + V'')\ \bar{n}_{H}''.T_{M}^{\circ}} \qquad .... \quad (2.12)$$

would result under considerations given below :

(a) V°, E°, T_{L}° and N, the normality of alkali are the same as for the reagent,

(b) V''' is the volume of alkali required to reach the same B value in metal titration, and

(c) T_{M}° is the initial concentration of the metal.

The values of $\bar{n}_H$ and $\bar{n}$ obtained have been recorded in tables 2.1 to 2.5 and 4.1 to 4.10 respectively.

Calculation of proton ligand formation constants :

The advantage of Irving-Rossotti method of determination of formation constants is that proton ligand stability constants can also be determined simulteneously under the experimental condition from the values of $\bar{n}_H$ calculated. For this it is necessary to ascertain the stages which lead to formation of the acid from its conjugate base. Catechol and 2,3-dihydroxy-naphthalene being dibasic the formation can be represented by following equilibria .

$$L^{2-} + H^{+} \rightleftharpoons LH^{-}$$

$$LH^{-} + H^{+} \rightleftharpoons LH_2$$

The equilibrium constants governing each step of formation are known as proton ligand stability constants and are represented as ${}^{P}K_{1}{}^{H}$ and ${}^{P}K_{2}{}^{H}$. In case of pyrogallol, the third OH group dissociates at a much higher pH, and it does not take part in the formation of the complex, because three OH groups at 1, 2, 3 positions in the benzene ring can not bend to occupy three spacial positions around the metal ion. In the equation (2.10) for the calculation of $\bar{n}_H$, in the case of above three ligands, therefore, Y (replaceable hydrogen) has been considered to be two . ${}^{P}K_1{}^{H}$ and ${}^{P}K_2{}^{H}$ calculated correspond to the association of two OH protons in case of catechol and 2,3-dihydroxynaphthalene and to the association of second and third OH protons in case of pyrogallol.

In case of protocatechuic and gallic acids, two OH groups at ortho position are supposed to take part in coordination. Carboxylic group dissociates in the region of complexation even though it does not take part in coordination. The proton ligand stability constants corresponding to these three groups are, therefore, essential. Gallic acid has an additional OH group. Since the dissociation of this OH group takes place at high pH, and it does not take part in coordination, for both protocatechuic acid and gallic acid Y has been considered to be three. Proton ligand formation constants ${}^{P}K_1{}^{H}$, ${}^{P}K_2{}^{H}$ and ${}^{P}K_3{}^{H}$ calculated correspond to the association of two hydroxy groups and the carboxylic hydrogen in case of protocatechuic acid and to the association of second and third OH and the carboxylic hydrogen in case of gallic acid.

For the determination of proton ligand stability constants, formation curves can be drawn by plotting $\bar{n}_H$ against pH as in figs. II.6-10. pH at $\bar{n}_H$ 0.5 and 1.5 correspond to log $K_1{}^{H}$ and log $K_2{}^{H}$. However, to get precise values of $K_1{}^{H}$ and

K_2^H, an equation corresponding to the formation function of metal ligand complexes (page 21 , eq.No. 14) can be derived for the proton ligand complexes.

$$\bar{n}_H + (\bar{n}_H - 1)\, K_1^H[H] + (\bar{n}_H - 2)(K_1^H K_2^H)^2\, [H]^2 + \ldots\ldots$$

$$(\bar{n}_H - N)\,(K_1^H K_2^H \ldots\ldots K_N^H)^N\, [H]^N = 0 \qquad (2.13)$$

In case of acids where K_1^H and K_2^H differ significantly, the formation of the species LH is not overlaped by LH_2 and hence the formation equation for the two stages are separate and get reduced to the following forms :

$$\bar{n}_H + (\bar{n}_H - 1)\, {}^{P}K_1^{H}\, [H] = 0 \qquad \text{and}$$

$$\bar{n}_H + (\bar{n}_H - 2)\, {}^{P}K_2^{H}\, [H]^2 = 0 \qquad (2.14)$$

This relation suggests that the plots of log $\bar{n}_H / (1 - \bar{n}_H)$ against pH should be straight line. These plots are important since they indicate the validity of $\bar{n}_H$ and pH data. The values of log $\bar{n}_H / (1 - \bar{n}_H)$ were plotted against pH in the region where $\bar{n}_H > 0 < 1$ and $\bar{n}_H > 1 < 2$. Two separate straight lines were obtained (figs. II 11-15). At all the points in the straight line, the following relationship tends to hold good

$$\log {}^{P}K_n^{H} = pH + \log \bar{n}_H / (1 - \bar{n}_H) \quad \ldots \qquad (2.15)$$

The average values obtained from the points on a straight line in the region $\bar{n}_H > 0 < 1$ corresponds to ${}^{P}K_1^{H}$ and that in the region $\bar{n}_H > 1 < 2$ corresponds to ${}^{P}K_2^{H}$. ${}^{P}K_1^{H}$ and ${}^{P}K_2^{H}$ obtained by this method have been reported in the Table 3.0. In the case of catechol, pyrogallol and 2,3-dihydroxynaphthalene since the values of $\bar{n}_H$ does not go very much below one even at high pH, the number of points for drawing the straight line in the region where $\bar{n}_H > 0 < 1$ are few. The values of $^P{K_1}^H$ have, therefore, been further verified by using the following relationship :

$$\log {}^P{K_1}^H \, {}^P{K_2}^H = 2\text{pH} \ (\text{ at } \bar{n}_H = 1 \ ) \ .... \quad (2.16)$$

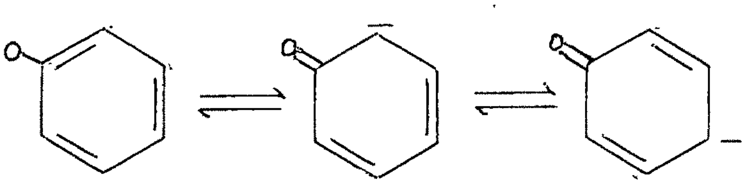
From the values of overall constant thus obtained, the values of $^P{K_2}^H$ calculated from the linear plot in the region $\bar{n}_H > 1 < 2$ was substracted and the values of $^P{K_1}^H$ was obtained. The values obtained by two methods, (presented in table 3.0) almost agree with one another.

In the case of protocatechuic acid and gallic acid, where Y = 3, three straight lines are obtained (figs. II 16-21) corresponding to the region $\bar{n}_H > 0 < 1$, $\bar{n}_H > 1 < 2$ and $\bar{n}_H > 2 < 3$ and these yielded the values of $^P{K_1}^H$, $^P{K_2}^H$ and $^P{K_3}^H$ respectively. In these cases also values of $\bar{n}_H$ very much less than one, could not be obtained and hence values of $^P{K_1}^H$ were further varified by using the above equation (2.16). The values thus obtained have been reported in the table 3.0. In all cases values of $^P{K_1}^H$ obtained by the second method have been used in the calculations.

It is observed that in all these compounds, even the dissociation of second OH group is much less in the pH region of the study. Thus the consideration, that the third OH group in pyrogallol and gallic acid, which do not take part in coordination, remains undissociated, finds experimental support.

The values of $^{P}K_{1}^{H}$ and $\bar{n}_H$ calculated have an accuracy of ± 0.05 and ± 0.02 depending on the accuracy of the pH meter and the burette reading respectively.

Proton ligand stability constant values indicate that the polyhydroxy derivatives of benzene are more acidic than the alcohols. This is because of the electron attracting nature of the phenyl group. Another factor boosting the acidity is the existence of following resonating structures of the phenolate ion.



(1) (2) (3)

In the structures 2 and 3 the negative charge is spread over the whole benzene nucleus, while in case of alcohol it ramains localized on the oxygen atom of the alkoxy ion. Protons can, therefore, be released more readily from a phenol. This accounts for its higher acidity. Further introduction of hydroxy groups with negative inductive effect will increase the acidity. Thus catechol is more acidic than phenol. Pyrogallol with third OH group is more acidic than catechol. 2,3-dihydroxynaphthalene is more acidic than catechol due to the presence of another benzene ring.

It is interesting to observe that $^{P}K_{1}^{H}$ and $^{P}K_{2}^{H}$ values (i.e. association constants for OH protons) of protocatechuic and gallic acids bear an interesting relationship with that of catechol and pyrogallol respectively.

Whereas pK_1^H value of protocatechuic acid and gallic acid are higher than that of catechol and pyrogallol respectively, pK_2^H values are lower. This can be explained by considering that -COOH group in the phenolic acid dissociates first and the resulting carboxylate ion has a positive rather than negative inductive effect. o-p orienting effect of COO^- makes the hydrogen of the p-hydroxy group less labile and that of m-hydroxy group more labile[8]. This accounts for proton ligand stability constant values of the phenolic acids.

Calculation of metal ligand formation constants :

The calculation of metal ligand formation constants involved two steps. The formation curves were obtained by plotting $\bar{n}$ against pL. These were next analysed to derive the formation constants. The values of V'' and V''' obtained from the curves corresponding to the titration of ligand and ligand + metal solution against alkali (figs. II 1- 5), were substituted in the equation (2.12) for the calculation of $\bar{n}$. The necessary condition for the calculation is that metal should be present in solution only as a free metal ion and/or in the form of complex ion with different number of ligand molecules attached. The absence of the species such as undissociated metal salt, polynuclear complex, hydroxy complex or the hydroxide of the metal should be ensured. Since the perchlorates of the metal have been used and the titrations have been carried out using dilute solutions, the likelihood of the presence of first two species has been eliminated.

The absence of the hydroxyl complexes or the metal hydroxide has been ascertained by using only that part of the titration curves where there is a smooth increase in the horizontal distance between the metal curve and the ligand curve. As the volume of alkali is increased, the formation of hydroxy complex or the hydroxyl causes a sudden change in the distance between the two curves. Further the formation of insoluble hydroxide makes the pH readings unstable. In case of complexes of catechol, 2,3-dihydroxynaphthalene and protocatechuic acid the calculations were carried out upto pH ~ 8.5 in case of Ni(II) and upto pH ~ 6.75 in case of Cu(II). The limit of the pH in case of complexes of pyrogallol and gallic acid (Ni-complex ~ 7.5 and Cu-complex ~ 5.0) was, however, kept lower because these complexes are less soluble and tend to get precipitated at higher pH.

The portions of the titration curves at very low pH, where there is very small separation between the two curves, were also avoided. This is because the readings in this range may involve considerable error.

For the calculation of pL in case of catechol, pyrogallol and 2,3-dihydroxynaphthalene the following equation was used :

$$\mathrm{pL}=\log\left[\frac{\left\{1+{}^{P}K_{1}{}^{H}\left(\frac{1}{\text{antilog } B}\right)+{}^{P}K_{1}{}^{H}\cdot{}^{P}K_{2}{}^{H}\left(\frac{1}{\text{antilog } B}\right)^{2}\right\}}{T_L^{\circ}-\bar{n}\cdot T_M^{\circ}}\cdot\frac{V^{\circ}+V''}{V^{\circ}}\right] \qquad (2.17).$$

In case of protocatechuic acid and gallic acid, where three proton ligand formation constants have been considered, the following equation was used for the calculation of pL.

$$pL = \log\left[\frac{1 + PK_1^H\left[\frac{1}{\text{antilog } B}\right] + PK_1^H PK_2^H\left[\frac{1}{\text{antilog } B}\right]^2 + PK_1^H PK_2^H PK_3^H\left[\frac{1}{\text{antilog } B}\right]^3}{T_L^0 - \bar{n}T_M^0} \cdot \frac{V^0 + V'''}{V^0}\right] \quad \ldots\ldots(2.18)$$

In the case of copper complexes of protocatechuic acid and gallic acid since complexation is at low pH where $\bar{n}_H > 2$, incomplete self dissociation of -COOH is indicated. Since -COOH group does not take part in coordination, the carboxylic -H will remain as such even after complex formation. It will therefore be wrong to consider Y = 3. In these two cases Y has been considered to be 2 for $\bar{n}$ calculation. In other words $\bar{n}$ has been calculated by using Calvin-Melchior method[9]. In pL calculation, however, three proton ligand formation constants have been considered, in order to account for the extent of the dissociation of -COOH group.

In the case of all the complexes $\bar{n}$ values at different pH have been plotted against pL values. The formation curves thus obtained have been presented in figs. II 22-31. pL at $\bar{n}$ 0.5 and 1.5 correspond to log K_1 and log K_2. In case of nickel complexes with pyrogallol, protocatechuic acid and gallic acid and copper complexes with pyrogallol and gallic acid, the $\bar{n}$ values do not go beyond 1.0 and hence log K_2 values could not be calculated. Since in case of complexes studied $K_1 / K_2 > 10^{2.5}$, the spreading factor is high and hence the values of formation constant obtained by interpolation at half integral values of $\bar{n}$ can be considered to be correct. However, in this method formation constant value depends on the accuracy of readings at a single point and hence can involve error.

Since the formation constants differ significantly, there will not be simultaneous formation of the species ML_1 and ML_2. The methods based on the use of the formation function, such as solution of simultaneous equation or the method of least square cannot, therefore, be applied to calculate the precise values of the formation constants. The formation functions in the two regions of formation of ML_1 and ML_2 reduce to the following form in such cases

$$\bar{n} + (\bar{n} - 1) K_1 [L] = 0 \quad \text{and}$$

$$\bar{n} + (\bar{n} - 2) K_2 [L]^2 = 0$$

This in other words means that $\log (1 - \bar{n}) / \bar{n}$ has a linear relationship with pL in the two regions where $\bar{n} > 0 < 1$ and $\bar{n} > 1 < 2$. The $\bar{n}$ values used in the calculation in each region were such as obtained by deducting the whole number from the values reported in tables (4.1 to 4.10). The plots of $\log 1 - \bar{n} / \bar{n}$ against pL have been shown in figs. III 32-46. The value of $\log K_1$ and $\log K_2$ can be calculated at each point on straight lines corresponding to the two region $\bar{n} > 0 < 1$ and $\bar{n} > 1 < 2$ by using the relationship

$$\log K_n = pL - \log (1 - \bar{n}) / \bar{n}$$

The average of all these values was obtained and the deviation of each individual value from the average value was calculated. The mean deviation could thus be calculated. The average values of $\log K_1$ and $\log K_2$ with mean deviation have been presented in the table 5.0.

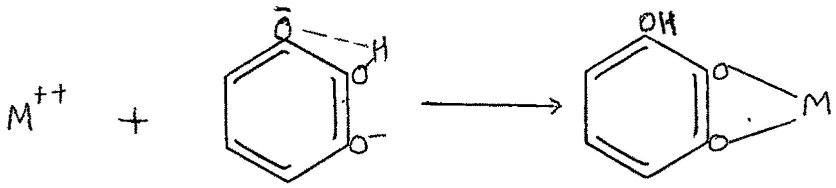
It is observed that copper complexes are more stable than nickel complexes. This is in accordance with the Irving-Willams order[10].

In the case of both Cu(II) and Ni(II) complexes the order of stabilities is 2,3-dihydroxynaphthalene complex > catechol complex > pyrogallol complex. This is in accordance with their basicities.

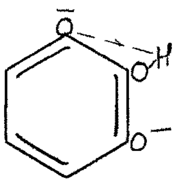
Protocatechuic acid and gallic acid though more acidic form complexes more stable than catechol and pyrogallol respectively. The titration curves indicate that the region of complex formation in case of catechol, pyrogallol, protocatechuic acid and gallic acid are same. This indicate that the site of coordination in protocatechuic acid and gallic acid are same as in catechol and pyrogallol i.e. the two hydroxy groups in ortho position. If the -COOH group would have been involved in the complexation, the separation of metal and ligand curve should have started at lower pH. The coordination of -COOH group from the meta position is also less likely. Similar consideration of the coordination of adjacent -OH group in the protocatechuic acid and gallic acid complexes has been made by earlier workers[11,12] also. The formation constants of protocatechuate and gallate complexes should, therefore, depend on proton ligand stability complexes of the two hydroxy groups and not that of the carboxylic group. Since $P_{K_1}{}^{H}$. $P_{K_2}{}^{H}$, in case of protocatechuic acid and gallic acid, is more than in case of catechol and pyrogallol, respectively, the protocatechuate and gallate complexes are naturally expected to be more stable than the corresponding catecholate and pyrogallolate respectively. High value of protocatechuate complexes was also obtained by Murakami and coworkers[13]. They have explained the reversal in the order of formation constants and basicities by considering that besides L→M σ bond, there is a π overlap involving the metal $d\pi$ orbitals, lone pair orbitals of the ligand oxygen atom and π orbitals of the benzene ring. Higher the basicity of the ligand, lesser the M→L π interaction. Since protocatechuic acid and gallic acid are more acidic, π interaction is more and hence the greater stability of the complexes. This also supports the consideration of coordination from the two ortho -OH groups in all ligands.

In the case of pyrogallol and gallic acid there are three -OH groups at 1, 2 and 3 positions. It can be argued that the middle -OH is more hydrogen bonded than those at 1 and 3 positions and hence the OH group remaining undissociated should be the central one. As such the $^{P}K_{1}{}^{H}$ and $^{P}K_{2}{}^{H}$ values calculated will not correspond to the association of the protons of two ortho hydroxyl groups which take part in coordination. However, as revealed by the later solid state studies, it is evident that the behaviour of pyrogallol is similar to that of catechol. Pyrogallol also contributes two negative charges indicating that only the protons of the two coordinated -OH are liberated and the third -OH group retains its hydrogen.

Reaction in the case of pyrogallol can, therefore, be considered to be taking place as follows :



The ligand ion being



thus the consideration of K_1^H and K_2^H in the calculation of pL is valid. Same agrument stands true in case of gallic acid. This reaction mechanism suggested is, however, only presumption and needs further evidence.

The greater stability of Cu(II) complexes than Ni(II) complexes has been observed by earlier workers and this has been attributed to Jahn-Teller distortion in Cu(II) complexes with d^9 configuration. This has been discussed in chapter I, page 12.

Table 1.1

N = 0.2 M V° = 50 ml. μ = 0.2M t = 25°C.

E°= 0.01M T°_{L} = 0.01M T°_{M} = 0.001M

Perchloric acid		Catechol		Nickel (II)		Copper (II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.95	0.00	1.95	0.00	1.95	0.00	1.95
1.00	2.18	1.00	2.18	1.00	2.17	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.32
2.00	2.68	2.00	2.68	2.00	2.65	2.00	2.60
2.10	2.78	2.10	2.78	2.10	2.75	2.10	2.70
2.20	2.88	2.20	2.88	2.20	2.85	2.20	2.80
2.30	3.10	2.30	3.10	2.30	3.00	2.30	2.93
2.40	3.42	2.40	3.40	2.40	3.25	2.40	3.15
2.45	3.68	2.45	3.65	2.45	3.48	2.45	3.30
2.48	4.85	2.48	4.05	2.48	3.70	2.48	3.45
2.50	7.75	2.50	4.75	2.50	3.90	2.50	3.55
2.52	9.15	2.52	6.62	2.52	4.35	2.52	3.70
2.54	9.65	2.54	7.15	2.54	5.60	2.54	3.90
2.56	9.95	2.56	7.45	2.56	6.60	2.56	4.20
2.58	10.10	2.58	7.68	2.58	6.90	2.58	4.45
2.60	10.25	2.60	7.82	2.60	7.10	2.60	4.65
2.64	10.40	2.64	8.00	2.64	7.30	2.64	4.75
2.68	10.50	2.68	8.18	2.68	7.40	2.68	4.90
2.72	10.60	2.72	8.28	2.72	7.50	2.80	5.15
2.80	10.70	2.80	8.42	2.80	7.65	2.90	5.30
2.90	10.80	2.90	8.60	2.85	7.72	3.00	5.60
3.00	10.88	3.00	8.72	2.90	7.80	3.10	6.05
3.20	10.98	3.20	8.90	3.00	7.95	3.20	6.35
3.40	11.05	3.40	9.10	3.10	8.10	3.30	6.55
		3.60	9.20	3.20	8.25	3.41	6.75
		3.80	9.35	3.30	8.40	3.50	6.95

Table 1.1 (contd.)

4.00	9.50	3.40	8.55	3.60	7.40
4.20	9.65	3.50	8.65	3.70	8.00
4.40	9.78	3.70	8.90	3.80	8.30
4.60	9.90	3.90	9.05	3.90	8.50
4.80	10.10	4.10	9.18	4.00	8.65
5.00	10.28	4.30	9.30	4.20	8.90
5.20	10.48	4.50	9.45	4.40	9.05
5.40	10.70	4.70	9.57	4.60	9.25
5.60	10.85	4.90	9.70	4.80	9.40
5.80	10.95	5.20	9.95	5.00	9.55
6.00	11.02	5.50	10.25	5.20	9.75
		5.80	10.55	5.40	9.95
		6.10	10.80	5.60	10.20
		6.40	10.95	5.80	10.45
				6.00	10.60
				6.20	10.80
				6.40	10.95

Table 1.2

$N = 0.2M$ $V^\circ = 50$ ml. $\mu = 0.2M$ t = 25°C.

$E^\circ = 0.01M$ $T^\circ_L = 0.01M$ $T^\circ_M = 0.001M$

Perchloric acid		2,3-dihydroxy naphthalene		Nickel (II)		Copper (II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.95	0.00	1.95	0.00	1.95	0.00	1.95
1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35
2.00	2.65	2.00	2.65	2.00	2.65	2.00	2.65
2.10	2.75	2.10	2.75	2.10	2.75	2.20	2.85
2.20	2.85	2.20	2.85	2.20	2.85	2.40	3.30
2.30	3.05	2.30	3.05	2.30	3.05	2.45	3.50
2.40	3.35	2.40	3.35	2.40	3.35	2.52	4.00
2.45	3.65	2.45	3.65	2.45	3.60	2.56	4.20
2.48	4.55	2.48	4.50	2.50	4.00	2.60	4.30
2.50	6.00	2.50	6.10	2.55	6.45	2.70	4.50
2.52	7.75	2.52	6.60	2.60	6.60	2.80	4.70
2.54	9.05	2.54	6.85	2.70	6.75	2.90	4.90
2.56	9.60	2.58	7.10	2.80	6.90	3.00	5.20
2.58	9.80	2.64	7.35	2.90	7.10	3.05	5.45
2.60	10.15	2.70	7.55	3.00	7.20	3.10	5.60
2.64	10.35	2.82	7.75	3.10	7.38	3.15	5.75
2.68	10.45	2.90	7.85	3.18	7.54	3.20	5.82
2.76	10.60	3.00	8.00	3.30	7.66	3.30	6.00
2.85	10.80	3.20	8.20	3.40	7.82	3.40	6.20
3.00	10.90	3.40	8.35	3.50	7.92	3.50	6.45
3.20	11.00	3.60	8.50	3.58	8.04	3.60	7.00
		3.80	8.65	3.70	8.14	3.66	7.30

Table 1.2 (contd.)

4.00	8.80	3.82	8.22	3.70	7.45
4.20	8.95	3.90	8.30	3.80	7.70
4.40	9.17	4.00	8.36	3.90	7.90
4.60	9.33	4.25	8.50	4.00	8.05
4.80	9.60	4.40	8.65	4.10	8.20
5.00	10.05	4.60	8.80	4.30	8.35
5.10	10.30	4.80	8.95	4.50	8.55
5.20	10.50	5.00	9.12	4.70	8.70
5.30	10.70	5.20	9.30	4.90	8.95
5.40	10.85	5.40	9.58	5.10	9.15
5.50	11.00	5.60	9.95	5.30	9.40
		5.80	10.40	5.50	9.80
		6.00	10.75	5.60	10.10
		6.20	10.90	5.70	10.35
				5.80	10.55
				6.00	10.90

Table 1.3

N = 0.2M
V° = 50 ml.
μ = 0.2M
t = 25°C.

E° = 0.01M
T°_{L} = 0.01M
T°_{M} = 0.001M

Perchloric acid		Protocatechuic acid		Nickel (II)		Copper (II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.95	0.00	1.95	0,00	1.95	0.00	1.95
1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35
2.00	2.65	2.00	2.65	2.00	2.65	2.00	2.60
2.10	2.75	2.20	2.80	2.20	2.80	2.20	2.75
2.20	2.85	2.40	3.00	2.40	3.00	2.40	2.92
2.30	3.05	2.60	3.30	2.60	3.25	2.60	3.18
2.40	3.40	2.80	3.55	2.80	3.50	2.80	3.45
2.45	3.65	3.00	3.75	3.00	3.70	3.00	3.62
2.48	4.15	3.20	3.90	3.20	3.85	3.20	3.80
2.50	4.75	3.40	4.05	3.40	4.00	3.40	3.95
2.52	8.00	3.60	4.20	3.60	4.15	3.60	4.10
2.54	9.10	3.80	4.35	3.80	4.30	3.80	4.25
2.56	9.60	4.00	4.50	4.00	4.45	4.00	4.35
2.58	9.95	4.20	4.65	4.20	4.60	4.20	4.45
2.60	10.10	4.40	4.80	4.40	4.75	4.40	4.60
2.64	10.30	4.60	5.02	4.60	4.97	4.60	4.75
2.68	10.45	4.80	5.40	4.80	5.30	4.80	4.90
2.72	10.52	4.85	5.55	4.85	5.40	5.00	5.00
2.80	10.65	4.90	5.75	4.90	5.55	5.10	5.10
2.90	10.75	4.95	5.95	4.95	5.75	5.20	5.20
3.00	10.85	5.00	6.55	5.00	6.10	5.30	5.35
3.20	10.95	5.05	7.10	5.05	6.80	5.40	5.50
3.40	11.05	5.10	7.40	5.15	6.90	5.50	5.70

Table 1.3 (contd.)

5.15	7.55	5.20	7.00	5.60	5.95
5.20	7.70	5.25	7.15	5.70	6.15
5.30	7.90	5.30	7.25	5.80	6.30
5.40	8.05	5.40	7.35	5.90	6.50
5.50	8.15	5.50	7.50	6.00	6.65
5.60	8.25	5.60	7.65	6.10	6.90
5.80	8.45	5.80	7.90	6.20	7.30
6.00	8.60	6.00	8.15	6.30	7.65
6.20	8.70	6.20	8.35	6.40	7.90
6.40	8.90	6.40	8.50	6.50	8.05
6.60	9.02	6.60	8.65	6.60	8.20
6.80	9.20	6.80	8.80	6.70	8.30
7.00	9.35	7.00	8.95	6.80	8.42
7.20	9.55	7.20	9.10	7.00	8.60
7.40	9.90	7.40	9.25	7.20	8.80
7.60	10.30	7.60	9.50	7.40	8.95
7.80	10.60	7.80	9.70	7.70	9.25
8.00	10.75	8.00	10.05	7.90	9.55
8.20	10.83	8.20	10.35	8.10	9.85
8.40	10.95	8.40	10.65	8.30	10.30
8.60	11.05	8.60	10.80	8.50	10.60
		8.80	10.90	8.70	10.75
				9.00	10.90

Table 1.4

N = 0.2M V° = 50 ml. μ = 0.2M t = 25°C.

E° = 0.01M T°_L = 0.01M T°_M = 0.001M

Perchloric acid		Pyrogallol		Nickel (II)		Copper (II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.95	0.00	1.95	0.00	1.95	0.00	1.95
1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.33
2.00	2.65	2.00	2.65	2.00	2.65	2.00	2.62
2.10	2.75	2.10	2.75	2.10	2.75	2.10	2.70
2.20	2.85	2.20	2.85	2.20	2.85	2.20	2.80
2.30	3.05	2.30	3.05	2.30	3.00	2.30	2.95
2.40	3.40	2.40	3.35	2.40	3.25	2.40	3.15
2.45	3.68	2.45	3.58	2.45	3.45	2.45	3.30
2.48	4.25	2.48	3.82	2.48	3.70	2.48	3.40
2.50	4.90	2.50	4.25	2.50	3.85	2.50	3.50
2.52	8.20	2.52	5.05	2.52	4.25	2.52	3.60
2.54	9.10	2.54	6.30	2.54	5.25	2.54	3.75
2.56	9.62	2.56	6.80	2.56	6.10	2.56	3.90
2.58	9.90	2.58	7.15	2.58	6.50	2.58	4.15
2.60	10.10	2.60	7.30	2.60	6.70	2.60	4.25
2.64	10.30	2.64	7.55	2.64	6.95	2.62	4.35
2.68	10.40	2.68	7.70	2.68	7.05	2.64	4.40
2.72	10.50	2.72	7.85	2.72	7.15	2.66	4.45
2.80	10.65	2.80	8.05	2.76	7.22	2.70	ppt.appears
2.90	10.75	2.90	8.25	2.80	7.28		
3.00	10.85	3.00	8.38	2.84	7.35		
3.20	10.98	3.20	8.60	2.88	7.40		

Table 1.4 (contd.)

3.40	8.75	2.92	7.45
3.60	8.90	2.95	7.50
3.80	9.05	3.00	ppt.appears
4.00	9.18		
4.20	9.33		
4.40	9.45		
4.60	9.55		
4.80	9.72		
5.00	9.92		
5.20	10.12		
5.40	10.28		
5.60	10.42		
5.80	10.55		
6.00	10.65		
6.20	10.72		
6.40	10.80		
6.60	10.85		
6.80	10.90		
7.00	10.95		

Table 1.5

N = 0.2M

V° = 50 ml.

μ = 0.2M

t = 25°C.

E° = 0.01M

T°_{L} = 0.01M

T°_{M} = 0.001M

Perchloric acid		Gallic acid		Nickel (II)		Copper (II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.95	0.00	1.95	0.00	1.95	0.00	1.95
1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15
1.50	2.35	1.50	2.32	1.50	2.32	1.50	2.28
2.00	2.65	2.00	2.60	2.00	2.60	2.00	2.52
2.10	2.78	2.20	2.78	2.20	2.78	2.20	2.65
2.20	2.85	2.40	3.00	2.40	3.00	2.40	2.82
2.30	3.05	2.60	3.20	2.60	3.20	2.60	3.00
2.40	3.35	2.80	3.45	2.80	3.45	2.80	3.25
2.45	3.65	3.02	3.65	3.00	3.65	3.00	3.45
2.48	4.00	3.18	3.78	3.20	3.78	3.08	3.55
2.50	4.85	3.40	3.95	3.40	3.95	3.16	3.65
2.52	7.20	3.60	4.10	3.60	4.10	3.31	3.75
2.54	9.30	3.80	4.25	3.80	4.22	3.37	3.80
2.56	9.70	4.00	4.35	4.00	4.35	3.42	3.85
2.58	9.90	4.20	4.50	4.20	4.50	3.55	3.95
2.60	10.10	4.40	4.75	4.40	4.70	3.62	4.00
2.64	10.30	4.60	4.95	4.60	4.90	3.69	4.05
2.68	10.40	4.80	5.30	4.80	5.25	3.76	4.10
2.72	10.50	4.85	5.50	4.85	5.40	3.86	4.15
2.80	10.65	4.90	5.70	4.90	5.60	3.97	4.20
2.90	10.75	4.95	6.10	4.95	5.85	4.08	4.25
3.00	10.83	5.00	6.55	5.00	6.20	4.18	4.30
3.20	10.95	5.04	6.90	5.05	6.45	4.30	ppt.appears.
3.40	11.02	5.08	7.15	5.10	6.60		

Table 1.5 (contd.)

5.12	7.30	5.13	6.75
5.20	7.55	5.20	6.90
5.25	7.65	5.25	7.00
5.35	7.80	5.30	7.08
5.40	7.90	5.35	7.15
5.50	8.00	5.41	7.20
5.60	8.10	5.45	7.25
5.80	8.30	5.50	ppt.appears.
6.00	8.45		
6.20	8.60		
6.40	8.72		
6.60	8.88		
6.80	9.02		
7.00	9.22		
7.20	9.42		
7.40	9.65		
7.60	9.93		
7.80	10.20		
8.00	10.38		
8.30	10.58		
8.60	10.70		
8.90	10.80		
9.20	10.90		
9.50	10.95		
9.70	11.00		

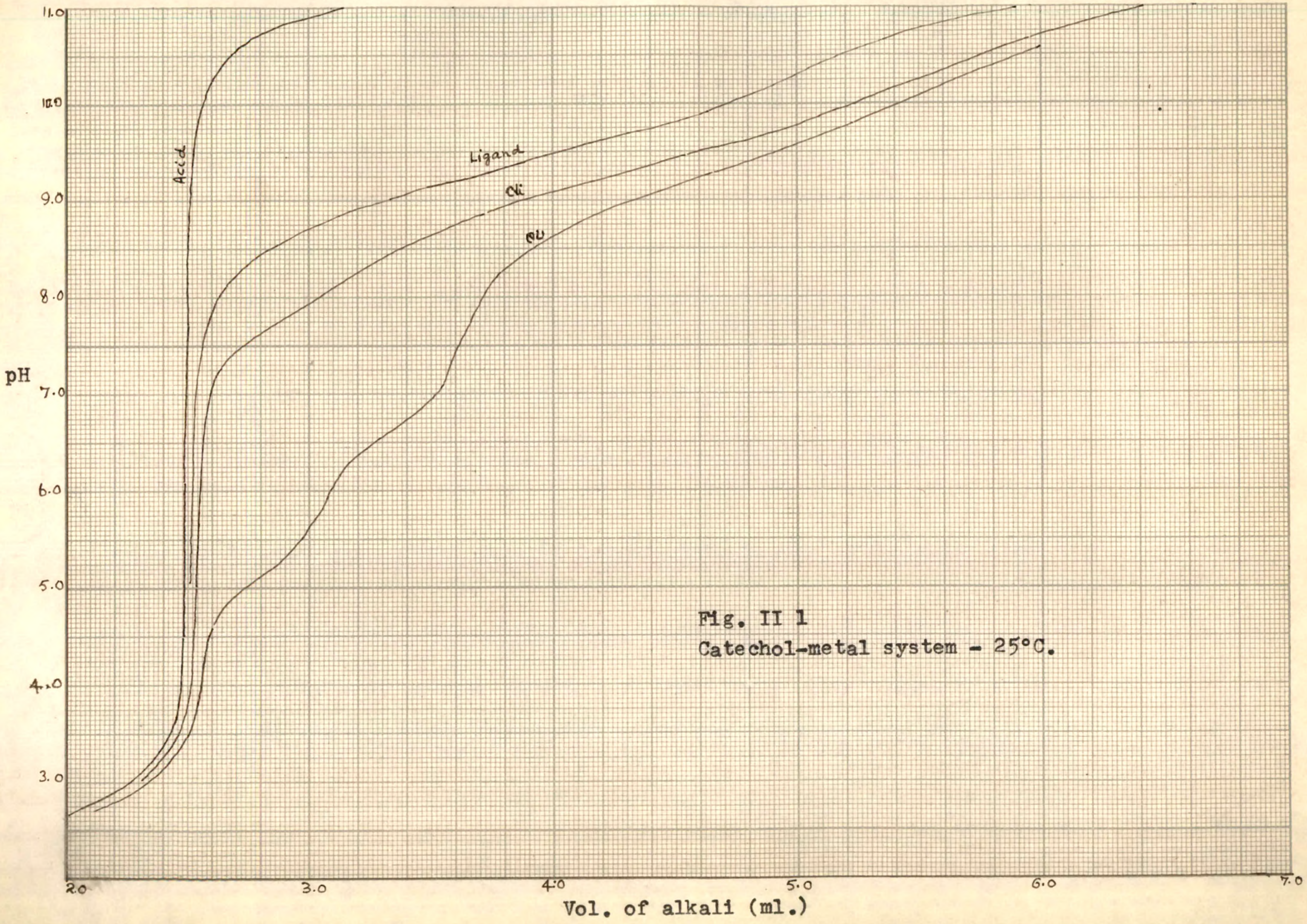


Fig. II 1
Catechol-metal system - 25°C.

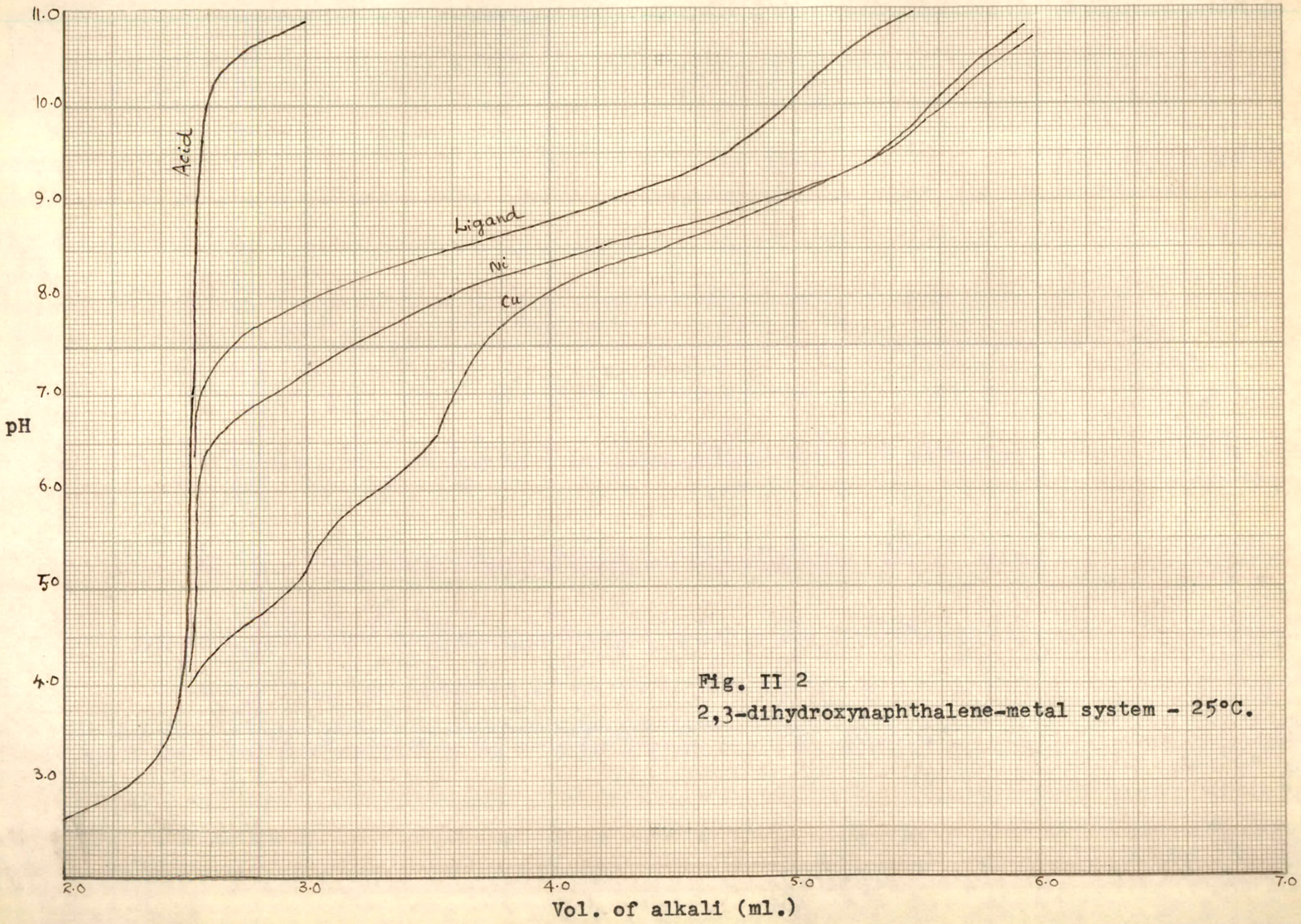


Fig. II 2
2,3-dihydroxynaphthalene-metal system - 25°C.

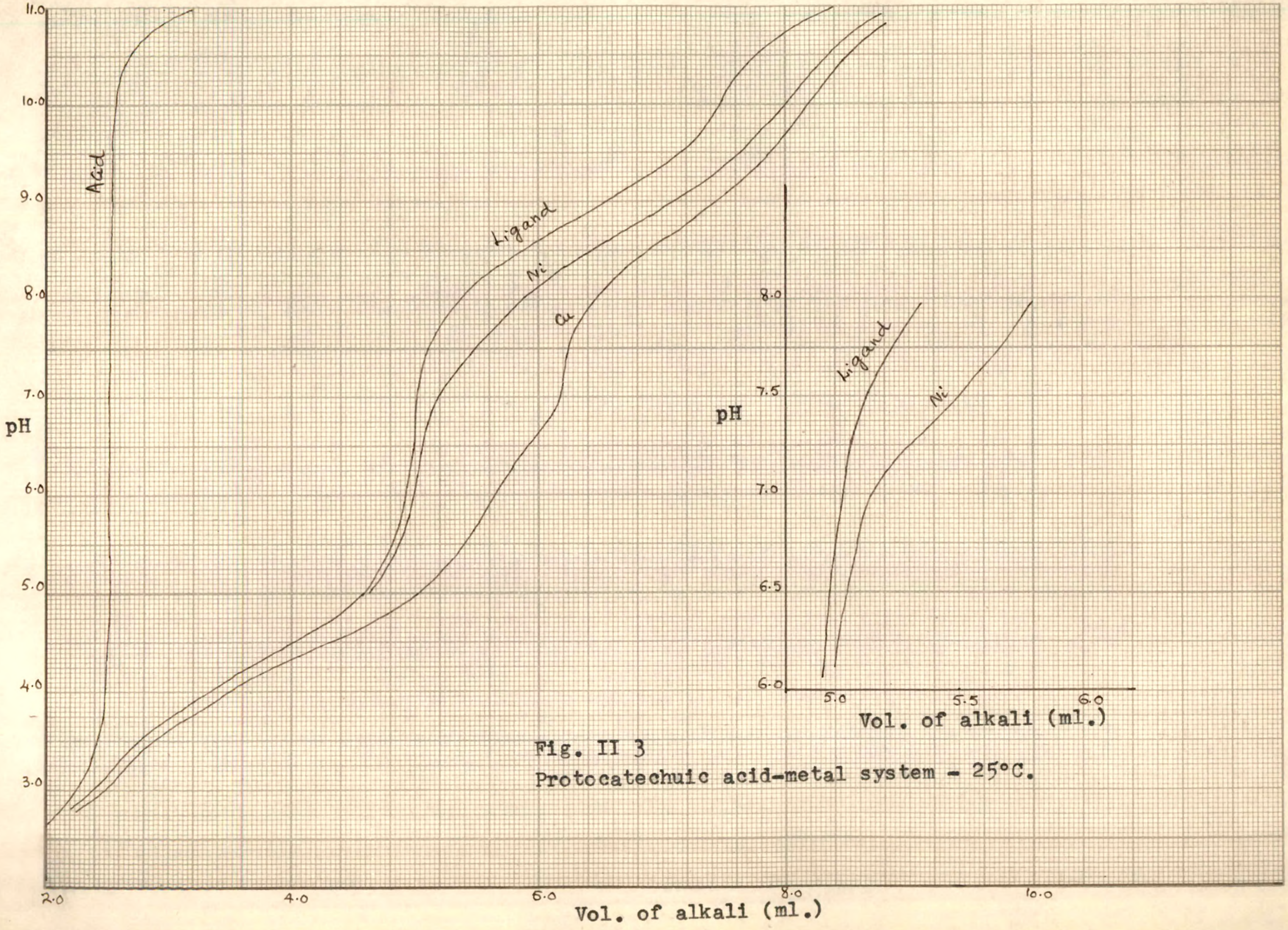


Fig. II 3
Protocatechuic acid-metal system - 25°C.

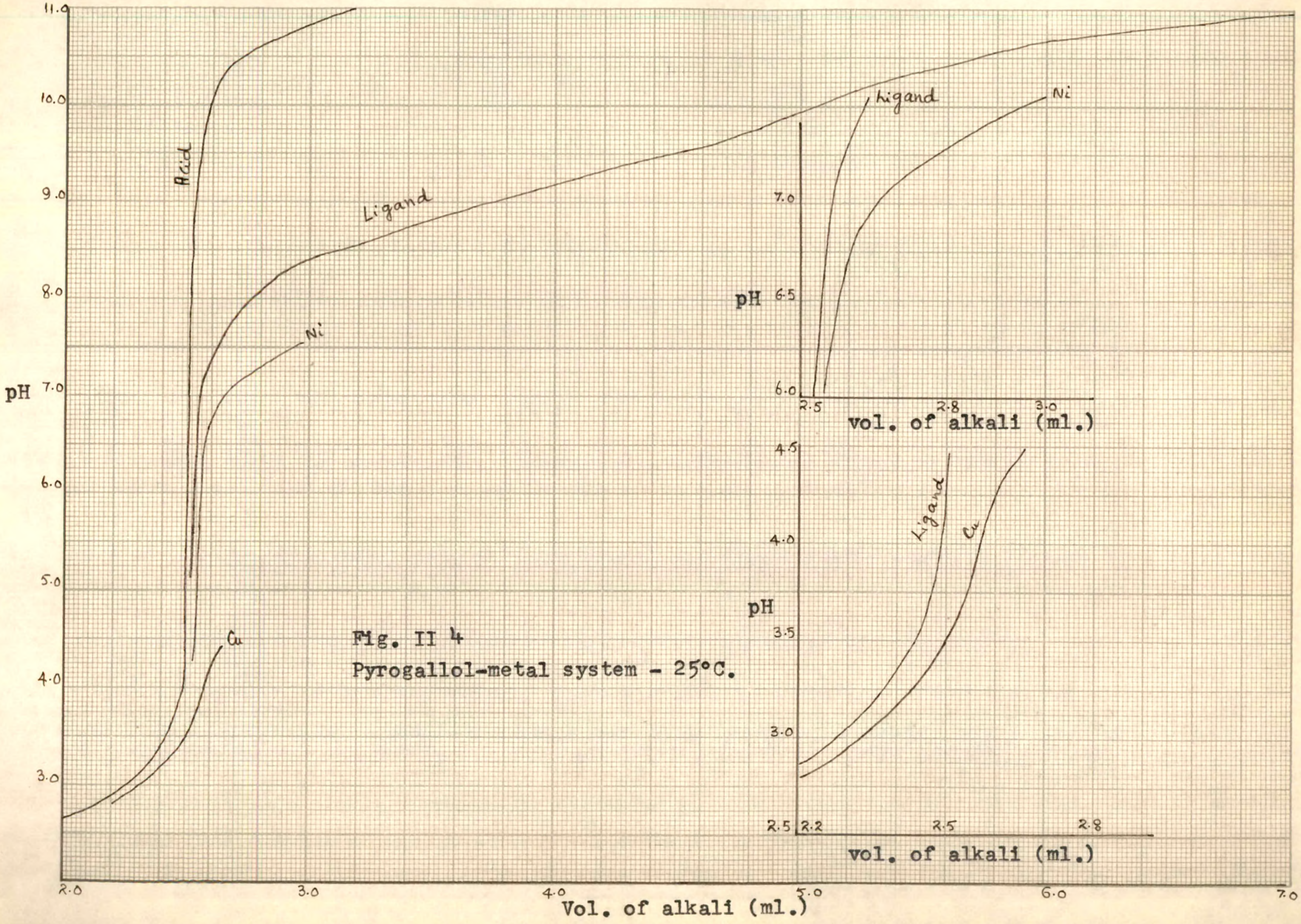


Fig. II 4

Pyrogallol-metal system - 25°C.

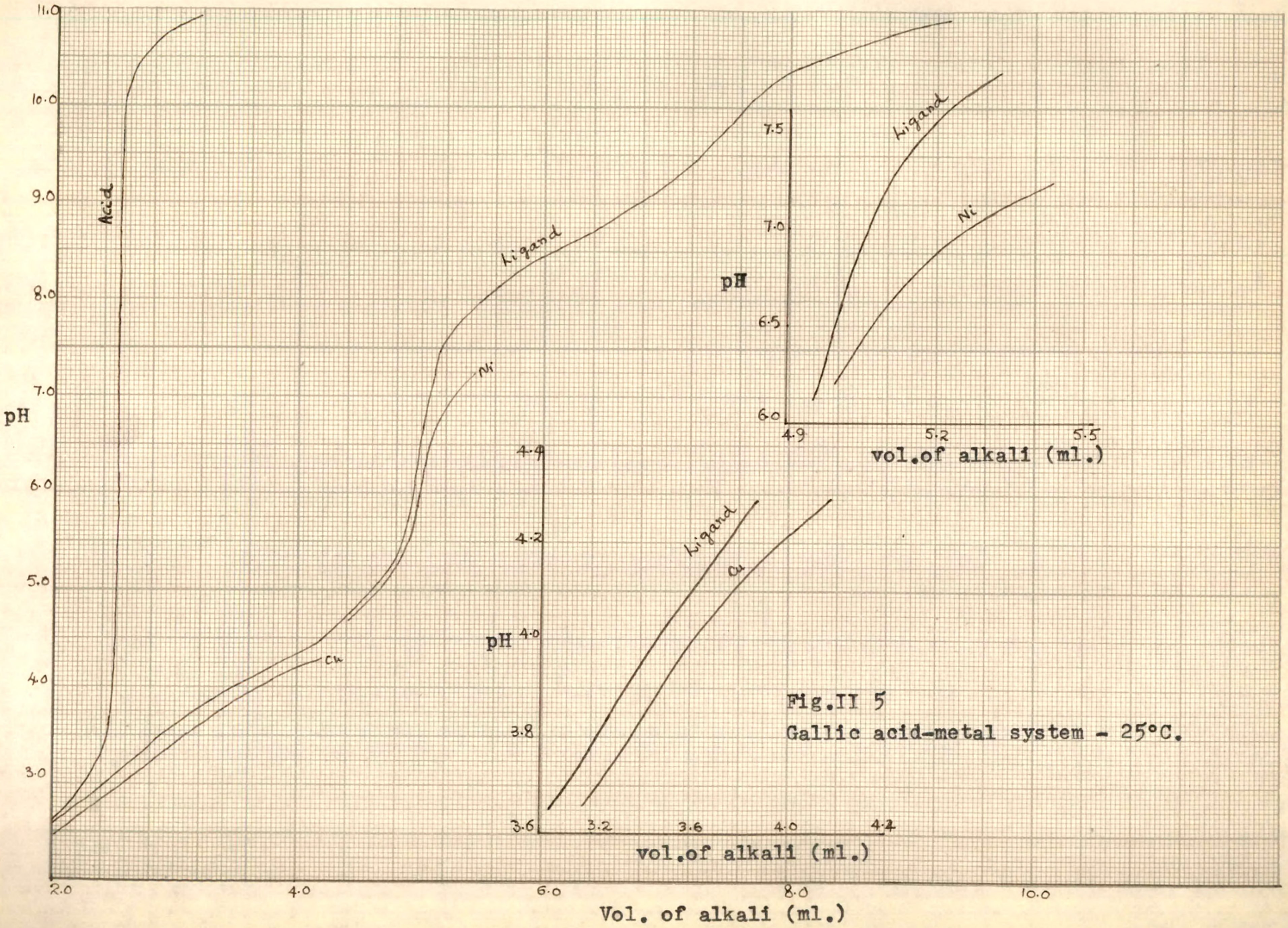


Fig.II 5

Gallic acid-metal system - 25°C.

Table 2.1

B, $\bar{n}_H$, log $\bar{n}_H/(1-\bar{n}_H)$ data for catechol at 25°C.

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
4.00	2.47	2.49	0.02	1.99_2	-
4.50	2.48	2.50	0.02	1.99_2	-
4.75	2.48	2.50	0.02	1.99_2	-
5.00	2.48	2.50	0.02	1.99_2	-
5.25	2.48	2.50	0.02	1.99_2	-
5.50	2.48	2.50	0.02	1.99_2	-
5.75	2.48	2.50	0.02	1.99_2	-
6.00	2.49	2.51	0.02	1.99_2	-
6.25	2.49	2.51	0.02	1.99_2	-
6.50	2.49	2.51	0.02	1.99_2	-
6.75	2.49	2.51	0.02	1.99_2	2.09_3
7.00	2.50	2.53	0.03	1.98_8	1.91_6
7.25	2.50	2.54	0.04	1.98_4	1.78_9
7.40	2.50	2.55	0.05	1.98_0	1.69_0
7.50	2.50	2.56	0.06	1.97_6	1.60_9
7.60	2.50	2.57	0.07	1.97_2	1.54_0
7.70	2.50	2.58	0.08	1.96_8	1.48_1
7.80	2.50	2.59	0.09	1.96_4	1.42_8
7.90	2.50	2.61	0.11	1.95_6	1.33_7
8.00	2.51	2.64	0.13	1.94_8	1.26_1
8.10	2.51	2.66	0.15	1.94_0	1.19_5
8.20	2.51	2.69	0.18	1.92_8	1.11_0
8.30	2.51	2.73	0.22	1.91_2	1.01_5
8.40	2.51	2.77	0.26	1.89_6	0.93_5
8.60	2.52	2.90	0.38	1.84_8	0.74_7
8.80	2.52	3.06	0.54	1.78_4	0.56_0
9.00	2.52	3.29	0.77	1.69_2	0.35_2
9.20	2.52	3.60	1.08	1.56_8	0.11_9
9.40	2.53	3.87	1.34	1.46_5	$\bar{1}.94_0$
9.60	2.54	4.14	1.60	1.36_0	$\bar{1}.75_1$
9.80	2.55	4.44	1.89	1.24_3	$\bar{1}.50_6$

Table 2.1 (contd.)

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
10.00	2.56	4.71	2.15	1.14_1	$\bar{1}.21_5$
10.20	2.59	4.92	2.33	1.07_0	$\bar{2}.87_7$
10.40	2.64	5.06	2.44	1.03_5	$\bar{2}.56_0$
10.50	2.67	5.20	2.53	0.99_1	2.04_2
10.60	2.72	5.31	2.59	0.96_9	1.49_5
10.70	2.78	5.41	2.63	0.95_3	1.30_7
10.80	2.90	5.56	2.66	0.94_5	1.23_5
10.90	3.04	5.74	2.70	0.93_1	1.13_0
11.00	3.06	5.80	2.74	0.91_6	1.03_7

Table 2.2

B, $\bar{n}_H$, log $\bar{n}_H/(1-\bar{n}_H)$ data for 2,3-dihydroxynaphthalene at 25°C.

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
4.00	2.48	2.48	0.00	2.00_0	-
4.25	2.48	2.48	0.00	2.00_0	-
4.35	2.48	2.48	0.00	2.00_0	-
4.50	2.48	2.48	0.00	2.00_0	-
4.60	2.48	2.48	0.00	2.00_0	-
4.75	2.49	2.49	0.00	2.00_0	-
4.85	2.49	2.49	0.00	2.00_0	-
5.00	2.50	2.50	0.00	2.00_0	-
5.25	2.50	2.50	0.00	2.00_0	-
5.50	2.50	2.50	0.00	2.00_0	-
5.75	2.51	2.51	0.00	2.00_0	-
5.85	2.51	2.51	0.00	2.00_0	-
6.00	2.51	2.51	0.00	2.00_0	-
6.10	2.51	2.51	0.00	2.00_0	-
6.25	2.51	2.52	0.01	1.99_6	2.39_6
6.35	2.51	2.52	0.01	1.99_6	2.39_6
6.50	2.51	2.53	0.02	1.99_2	2.09_3
6.75	2.52	2.54	0.02	1.99_2	2.09_3
7.00	2.52	2.56	0.04	1.98_4	1.78_9
7.15	2.52	2.59	0.07	1.97_2	1.54_0
7.25	2.52	2.61	0.09	1.96_4	1.42_8
7.50	2.52	2.69	0.17	1.93_2	1.13_7
7.75	2.53	2.82	0.29	1.88_4	0.86_2
8.00	2.53	3.00	0.47	1.81_2	0.63_5
8.25	2.54	3.26	0.72	1.71_2	0.39_3
8.50	2.54	3.60	1.06	1.57_6	0.13_3
8.75	2.54	3.95	1.41	1.43_6	$\bar{1}.88_8$
9.00	2.55	4.23	1.68	1.32_9	$\bar{1}.69_0$
9.25	2.56	4.53	1.97	1.21_4	$\bar{1}.43_5$
9.50	2.57	4.75	2.18	1.13_0	$\bar{1}.17_4$

Table 2.2 (contd.)

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
9.75	2.60	4.88	2.28	1.09_0	$\bar{2}.99_5$
10.00	2.63	4.99	2.36	1.05_8	$\bar{2}.78_9$
10.25	2.67	5.09	2.42	1.03_5	$\bar{2}.55_9$
10.50	2.73	5.20	2.47	1.01_6	$\bar{2}.31_1$
10.75	2.82	5.33	2.51	1.00_2	$\bar{3}.30_2$

Table 2.3

B, $\bar{n}_H$, log $\bar{n}_H/(1-\bar{n}_H)$ data for protocatechuic acid at 25°C.

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
3.00	2.26	2.40	0.14	2.94_3	1.21_9
3.25	2.37	2.57	0.20	2.91_9	1.05_5
3.50	2.43	2.77	0.34	2.86_3	0.80_0
3.75	2.47	3.00	0.53	2.78_7	0.56_8
4.00	2.48	3.32	0.84	2.66_3	0.29_4
4.25	2.49	3.65	1.16	2.53_6	0.06_2
4.50	2.50	4.00	1.50	2.40_0	$\bar{1}.82_3$
4.60	2.50	4.16	1.66	2.33_6	$\bar{1}.70_4$
4.75	2.50	4.36	1.86	2.25_6	$\bar{1}.63_6$
4.85	2.50	4.46	1.96	2.25_9	$\bar{1}.54_3$
5.00	2.50	4.58	2.08	2.16_8	$\bar{1}.30_5$
5.10	2.50	4.64	2.14	2.14_4	$\bar{1}.22_6$
5.25	2.50	4.73	2.23	2.10_8	$\bar{1}.08_3$
5.50	2.51	4.83	2.32	2.07_2	$\bar{2}.89_0$
5.75	2.51	4.90	2.39	2.04_5	$\bar{2}.67_3$
6.00	2.52	4.95	2.43	2.02_8	$\bar{2}.46_0$
6.10	2.52	4.96	2.44	2.02_5	$\bar{2}.40_8$
6.25	2.52	4.97	2.45	2.02_1	$\bar{2}.33_1$
6.35	2.52	4.98	2.46	2.01_7	$\bar{2}.23_8$
6.50	2.52	4.99	2.47	2.01_2	$\bar{2}.08_5$
6.75	2.52	5.01	2.49	2.00_4	$\bar{3}.60_4$
7.00	2.52	5.04	2.52	1.99_3	2.15_1
7.15	2.52	5.05	2.53	1.98_9	1.95_3
7.25	2.52	5.07	2.55	1.98_0	1.69_0
7.35	2.53	5.09	2.56	1.97_7	1.62_8
7.50	2.53	5.13	2.60	1.96_0	1.38_0
7.60	2.53	5.17	2.64	1.94_5	1.23_5
7.75	2.53	5.23	2.70	1.92_1	1.02_6
8.00	2.53	5.37	2.84	1.86_5	0.77_5
8.25	2.53	5.60	3.07	1.77_2	0.53_9

Table 2.3 (contd.)

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
8.50	2.54	5.87	3.33	1.67_0	0.30_7
8.75	2.54	6.25	3.71	1.51_7	0.02_9
9.00	2.54	6.56	4.02	1.39_4	$\bar{1}.81_3$
9.25	2.54	6.87	4.33	1.26_9	$\bar{1}.56_5$
9.50	2.55	7.17	4.62	1.15_4	$\bar{1}.26_0$
9.75	2.56	7.33	4.77	1.09_2	$\bar{1}.00_5$
10.00	2.59	7.45	4.86	1.06_0	$\bar{2}.80_5$
10.25	2.63	7.58	4.95	1.02_6	$\bar{2}.42_6$
10.35	2.66	7.64	4.98	1.01_4	$\bar{2}.15_3$
10.50	2.70	7.73	5.03	0.99_6	2.39_6
10.60	2.73	7.80	5.07	0.98_1	1.71_3
10.75	2.89	7.98	5.09	0.97_9	1.66_8
10.85	3.00	8.14	5.14	0.96_4	1.42_8
11.00	3.30	8.50	5.20	0.95_2	1.29_7

Table 2.4

B, $\bar{n}_H$, log $\bar{n}_H/(1-\bar{n}_H)$ data for pyrogallol at 25°C.

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
3.50	2.42	2.44	0.02	1.99_2	-
3.75	2.45	2.47	0.02	1.99_2	-
4.00	2.47	2.49	0.02	1.99_2	-
4.10	2.48	2.50	0.02	1.99_2	-
4.20	2.48	2.50	0.02	1.99_2	-
4.30	2.49	2.51	0.02	1.99_2	-
4.40	2.49	2.51	0.02	1.99_2	-
4.50	2.49	2.51	0.02	1.99_2	-
5.00	2.50	2.52	0.02	1.99_2	2.09_3
6.00	2.51	2.54	0.03	1.98_8	1.91_5
6.50	2.51	2.55	0.04	1.98_4	1.78_8
6.75	2.51	2.56	0.05	1.98_0	1.69_0
7.00	2.51	2.57	0.06	1.97_6	1.69_0
7.10	2.51	2.58	0.07	1.97_2	1.54_0
7.20	2.52	2.59	0.07	1.97_2	1.54_0
7.30	2.52	2.60	0.08	1.96_8	1.48_0
7.40	2.52	2.61	0.09	1.96_4	1.42_7
7.50	2.52	2.63	0.11	1.95_6	1.33_7
7.75	2.52	2.69	0.17	1.93_2	1.13_7
8.00	2.52	2.78	0.26	1.89_6	0.93_5
8.25	2.52	2.91	0.39	1.84_4	0.73_3
8.50	2.53	3.11	0.58	1.76_8	0.52_0
8.75	2.54	3.37	0.83	1.66_8	0.30_4
9.00	2.54	3.72	1.18	1.52_8	0.04_9
9.25	2.55	4.09	1.54	1.38_4	$\bar{1}.79_6$
9.50	2.55	4.52	1.97	1.21_4	$\bar{1}.43_5$

Table 2.4 (contd.)

B	V'	V''	V''-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
9.75	2.57	4.85	2.28	1.08_9	$\bar{2}.99_0$
10.00	2.59	5.11	2.52	0.99_3	$\bar{2}.15_1$
10.15	2.60	5.26	2.66	0.93_8	1.18_0
10.25	2.62	5.38	2.76	0.89_9	0.94_9
10.35	2.65	5.50	2.85	0.86_3	0.80_0
10.50	2.72	5.73	3.01	0.80_1	0.60_2
10.65	2.81	6.00	3.19	0.73_1	0.43_4
10.75	2.89	6.24	3.35	0.67_0	0.30_7

Table 2.5

B, $\bar{n}_H$, log $\bar{n}_H/(1-\bar{n}_H)$ data for gallic acid at 25°C.

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
3.00	2.29	2.40	0.11	2.95_5	1.32_7
3.15	2.35	2.56	0.21	2.91_6	1.03_7
3.25	2.39	2.63	0.24	2.90_3	0.96_9
3.35	2.41	2.71	0.30	2.88_0	0.86_5
3.50	2.44	2.87	0.43	2.82_8	0.68_4
3.65	2.45	3.02	0.57	2.77_2	0.52_9
3.75	2.47	3.16	0.69	2.72_3	0.41_8
3.85	2.47	3.27	0.80	2.68_0	0.32_7
4.00	2.49	3.46	0.97	2.61_2	0.19_8
4.10	2.49	3.60	1.11	2.55_6	0.09_7
4.15	2.49	3.67	1.18	2.52_8	0.04_8
4.20	2.49	3.74	1.25	2.50_2	0.01_3
4.25	2.49	3.80	1.31	2.47_6	$\bar{1}.95_8$
4.30	2.49	3.88	1.39	2.44_4	$\bar{1}.90_3$
4.50	2.50	4.20	1.70	2.32_6	$\bar{1}.67_3$
4.75	2.50	4.40	1.90	2.24_0	$\bar{1}.49_9$
5.00	2.50	4.63	2.13	2.14_8	$\bar{1}.25_0$
5.50	2.51	4.85	2.34	2.06_4	$\bar{2}.83_5$
6.00	2.51	4.94	2.43	2.02_8	$\bar{2}.46_0$
6.25	2.52	4.97	2.45	2.02_0	$\bar{2}.32_0$
6.40	2.52	4.98	2.46	2.01_6	$\bar{2}.23_0$
6.50	2.52	5.00	2.48	2.01_0	$\bar{2}.13_4$
6.65	2.52	5.01	2.49	2.00_4	$\bar{3}.60_4$
6.85	2.52	5.03	2.51	1.99_7	2.52_1
6.95	2.52	5.04	2.52	1.99_3	2.15_1
7.00	2.52	5.05	2.53	1.98_9	1.95_3
7.10	2.52	5.07	2.55	1.98_0	1.69_0
7.20	2.52	5.09	2.57	1.97_2	1.54_0
7.50	2.53	5.18	2.65	1.94_1	1.20_2
7.75	2.53	5.31	2.78	1.88_9	0.90_3

Table 2.5 (contd.)

B	V'	V"	V"-V'	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$
8.00	2.53	5.49	2.96	1.81_6	0.64_6
8.25	2.53	5.74	3.21	1.71_7	0.40_3
8.50	2.53	6.07	3.54	1.58_5	0.14_9
8.75	2.54	6.45	3.91	1.43_7	$\bar{1}.89_0$
9.00	2.54	6.74	4.20	1.32_2	$\bar{1}.67_6$
9.25	2.54	7.02	4.48	1.20_8	$\bar{1}.41_9$
9.50	2.55	7.28	4.73	1.11_0	$\bar{1}.09_2$
9.75	2.57	7.48	4.91	1.03_9	$\bar{2}.60_8$
10.00	2.59	7.65	5.06	0.98_0	1.69_0
10.15	2.60	7.75	5.15	0.94_4	1.22_7
10.25	2.62	7.85	5.23	0.91_4	1.02_6
10.35	2.65	7.96	5.31	0.88_3	0.87_8
10.50	2.71	8.75	5.44	0.83_3	0.69_7
10.60	2.76	8.36	5.60	0.77_1	0.52_8
10.75	2.89	8.73	5.84	0.68_1	0.32_9

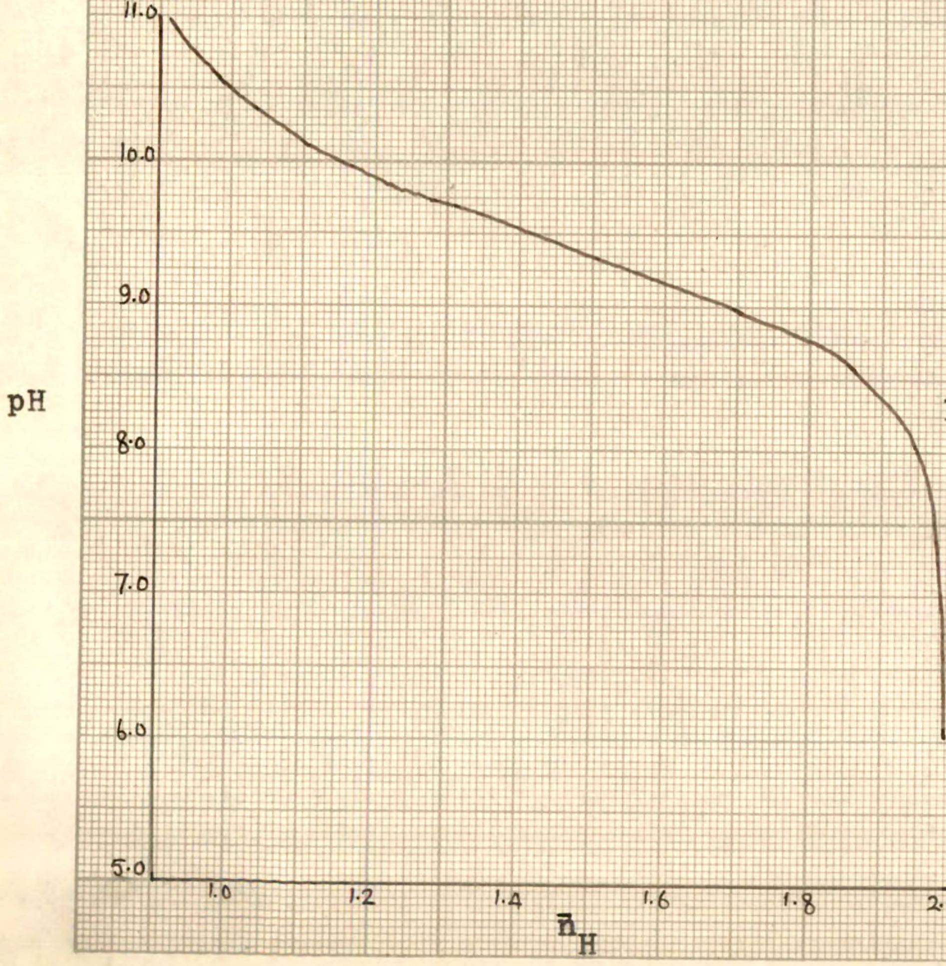


Fig. II 6.
Catechol- 25°C.

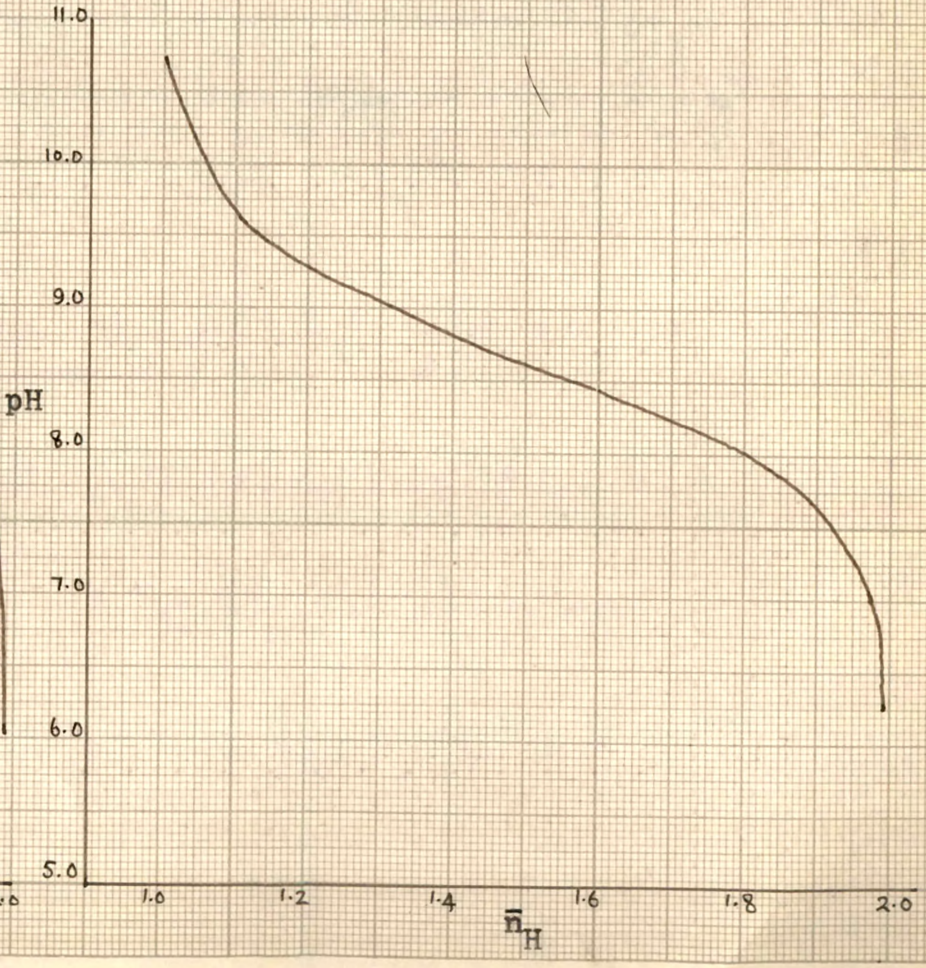
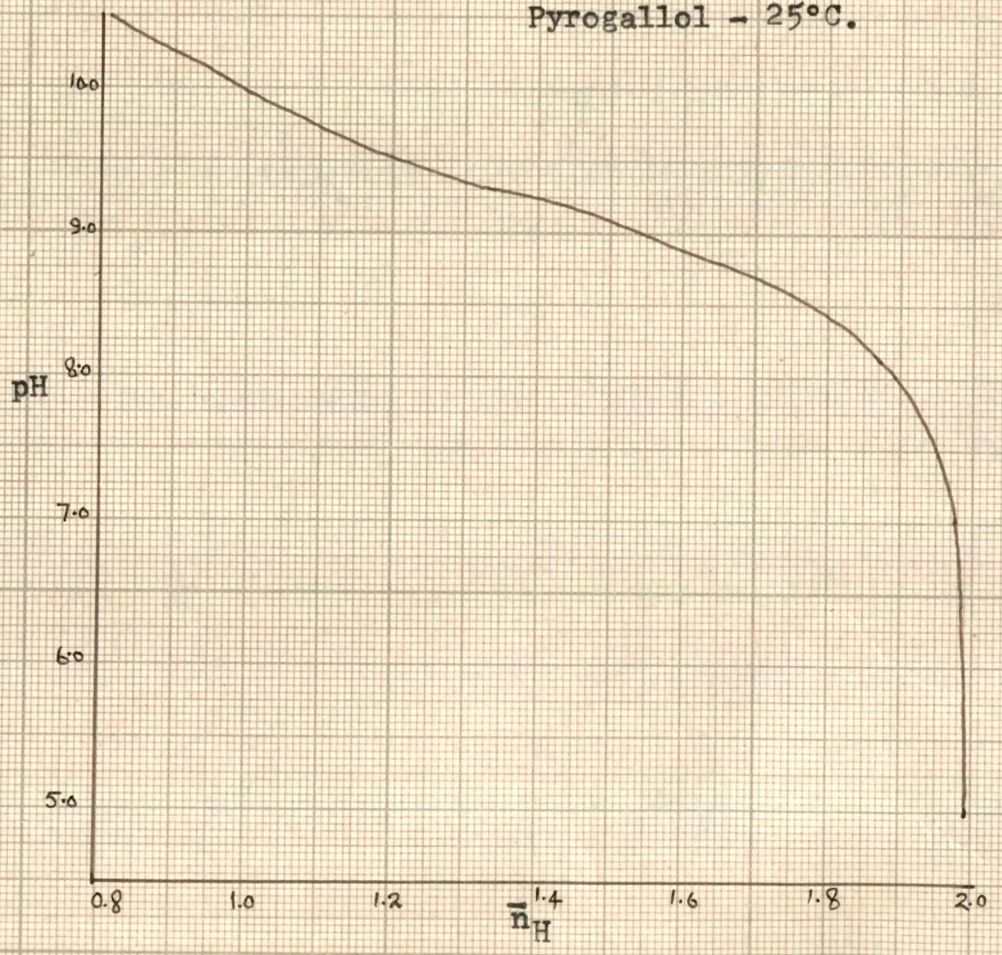


Fig. II 7
2,3-dihydroxynaphthalene - 25°C.

Fig. II 8

Pyrogallol - 25°C.



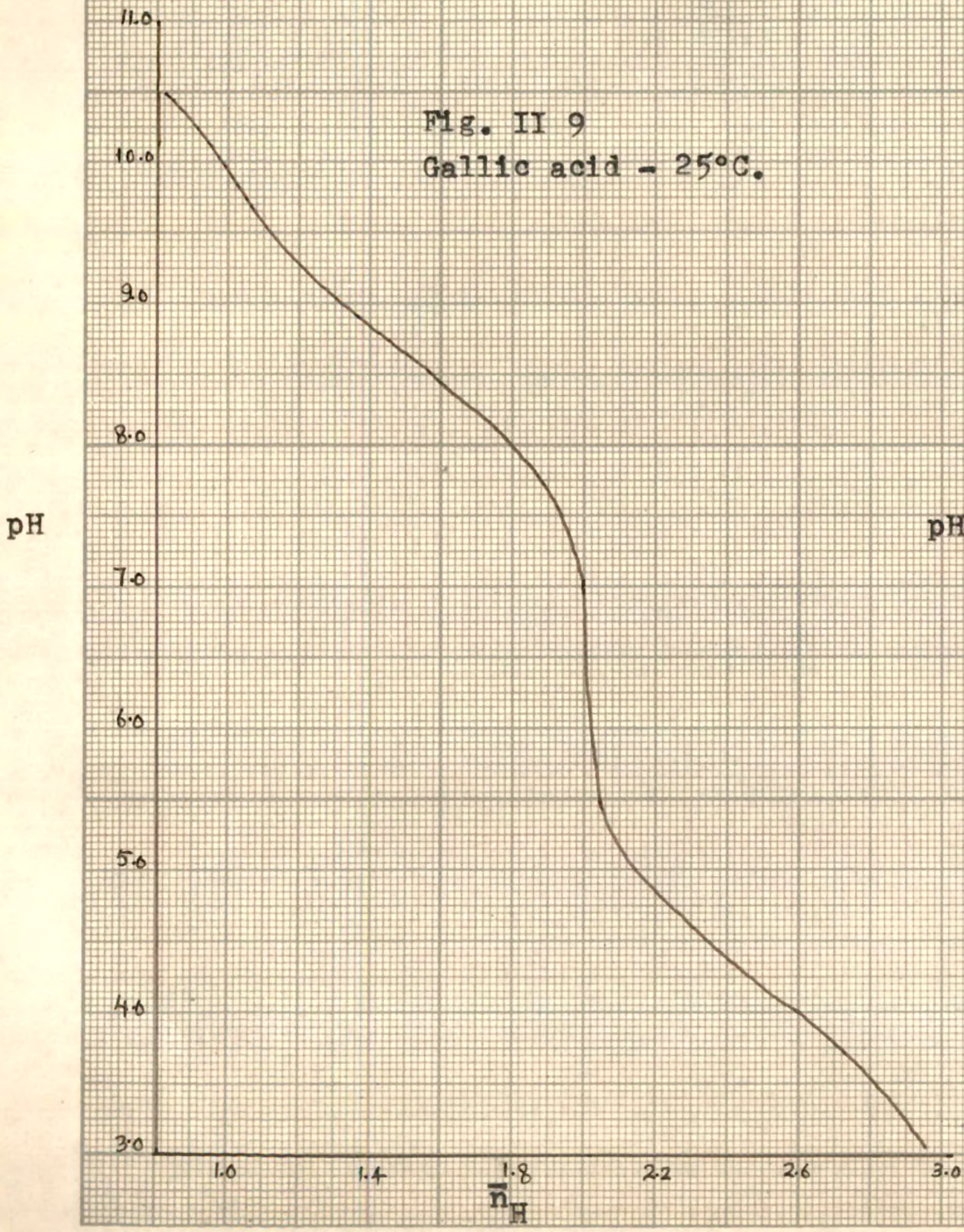


Fig. II 9
Gallic acid - 25°C.

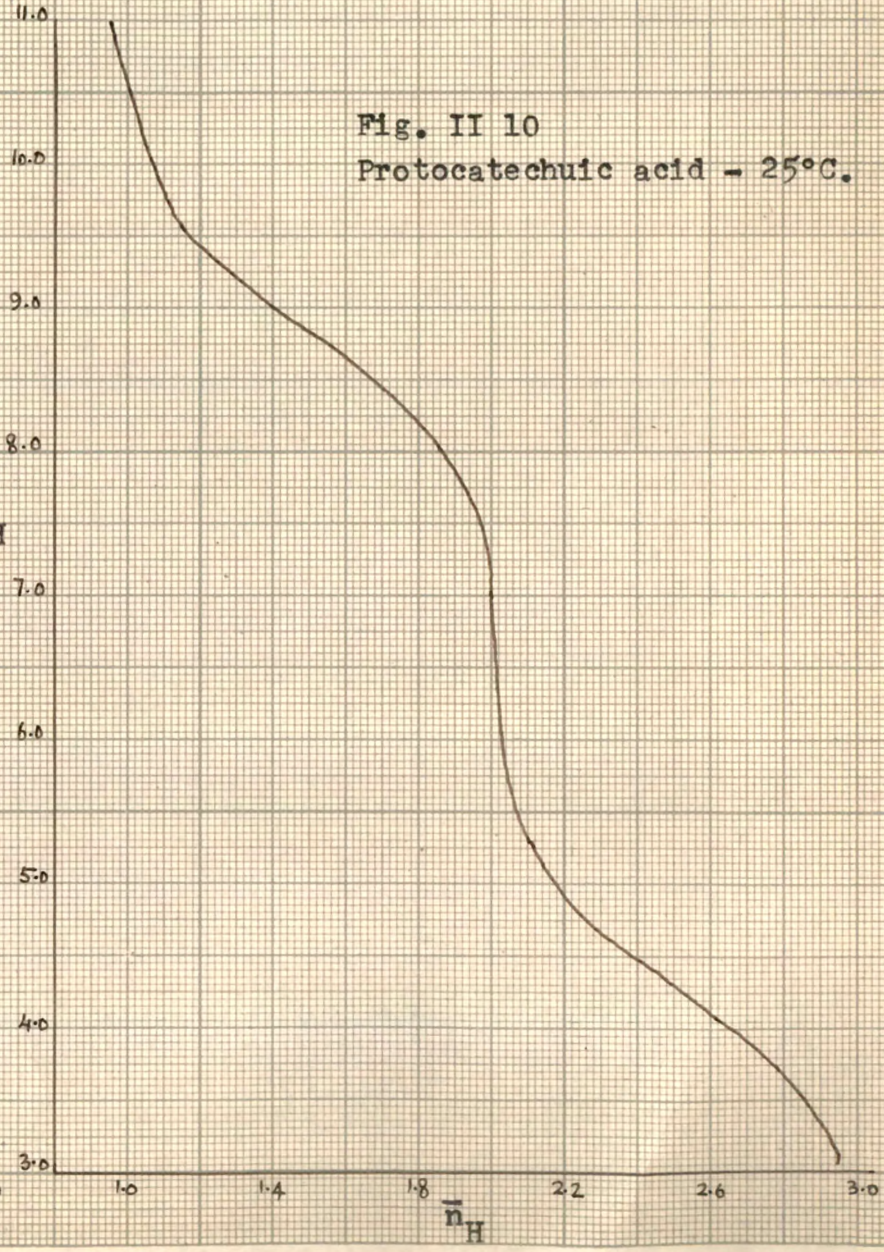


Fig. II 10
Protocatechuic acid - 25°C.

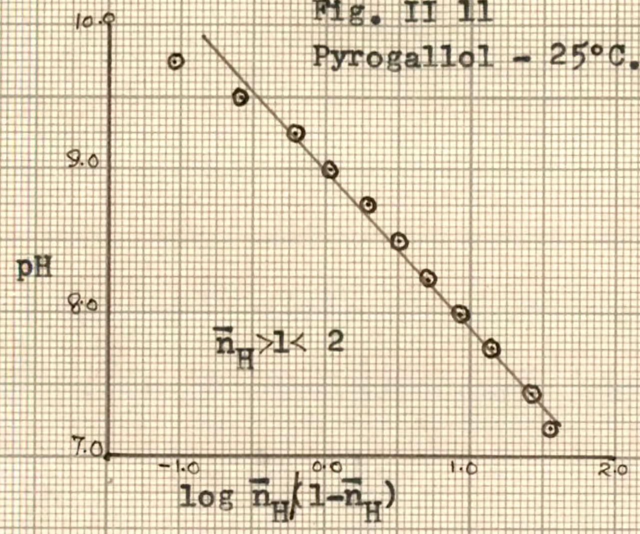


Fig. II 11
Pyrogallol - 25°C.

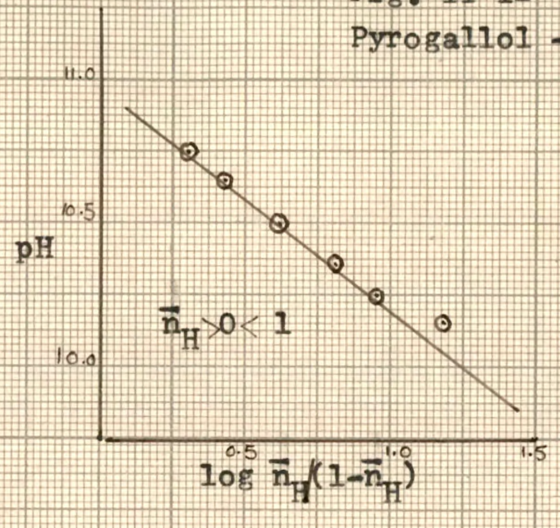


Fig. II 12
Pyrogallol - 25°C.

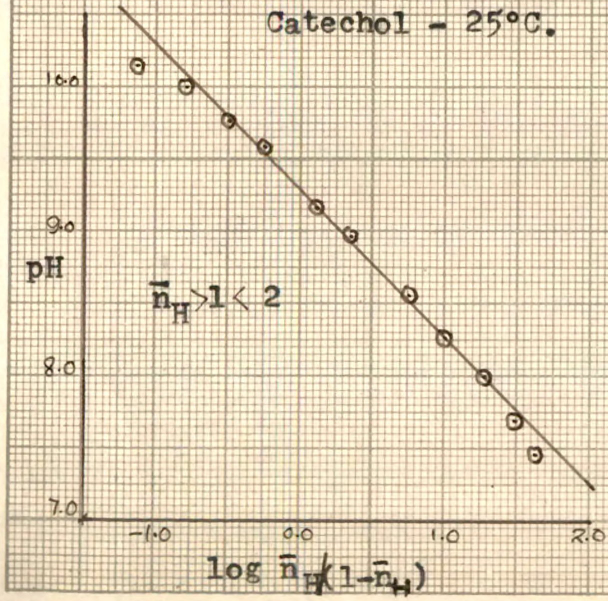


Fig. II 13
Catechol - 25°C.

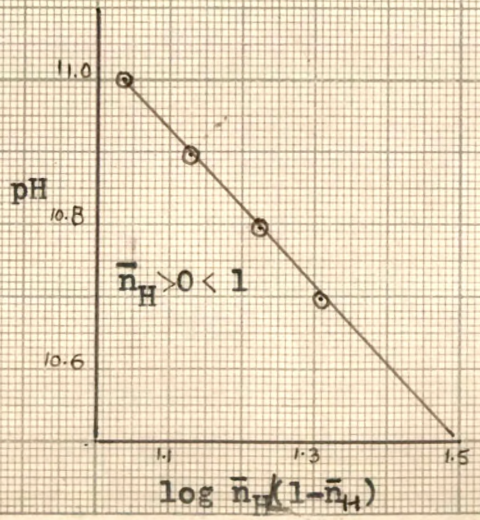


Fig. II 14
Catechol - 25°C.

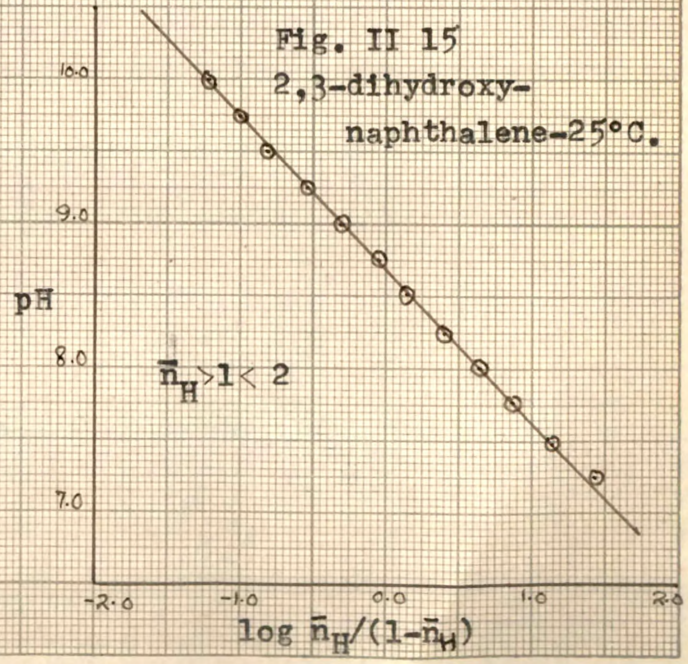


Fig. II 15
2,3-dihydroxy-
naphthalene-25°C.

Fig. II 16
Protocatechuic acid - 25°C.

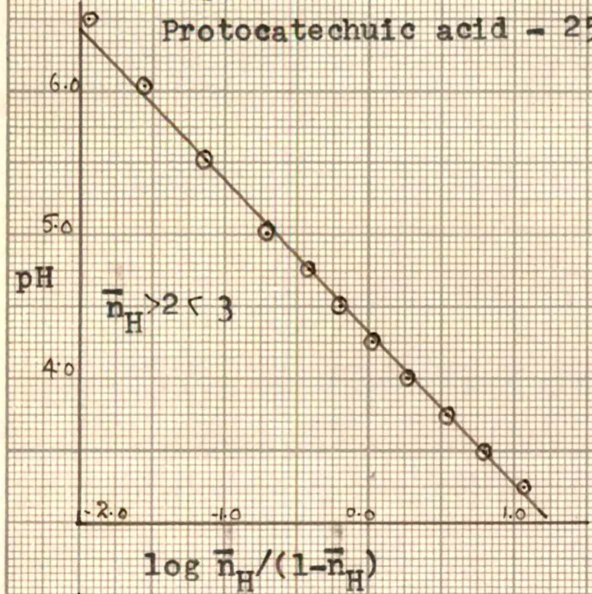


Fig. II 17
Protocatechuic acid - 25°C.

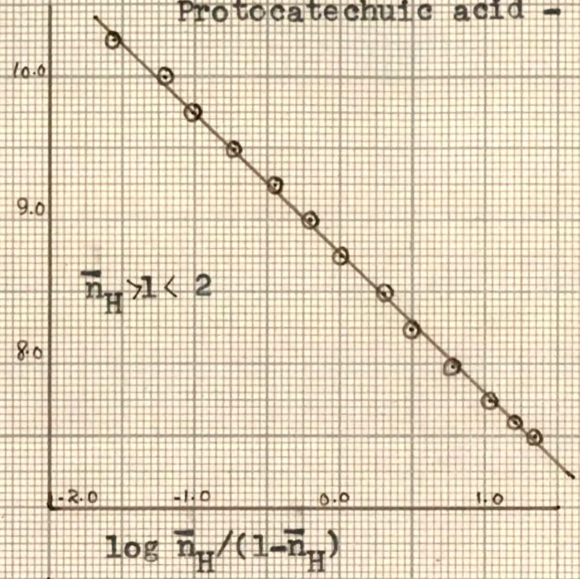


Fig. II 18
Protocatechuic acid-
25°C.

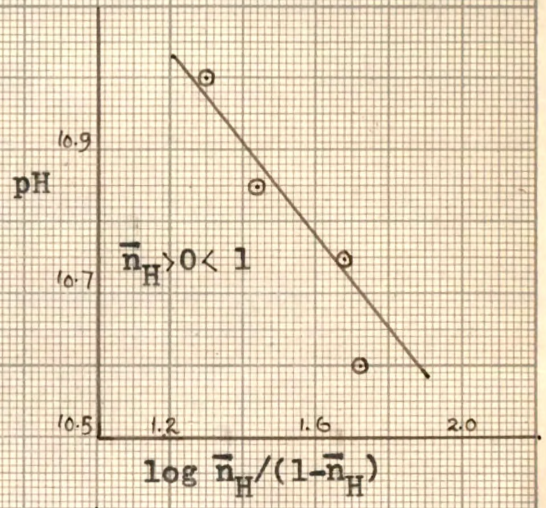


Fig. II 19
Gallic acid - 25°C.

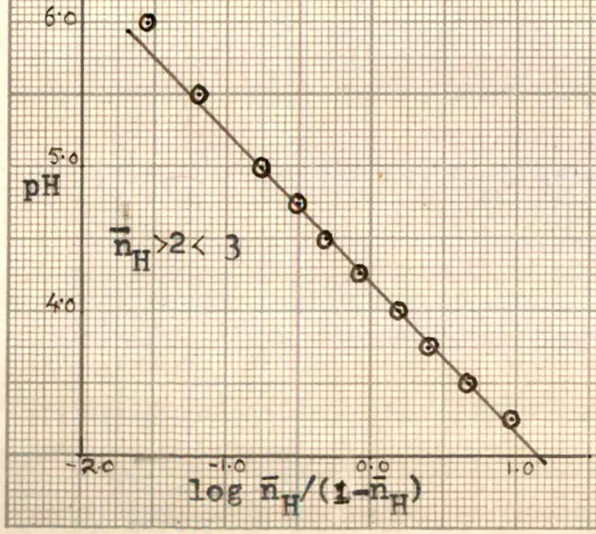


Fig. II 20
Gallic acid - 25°C.

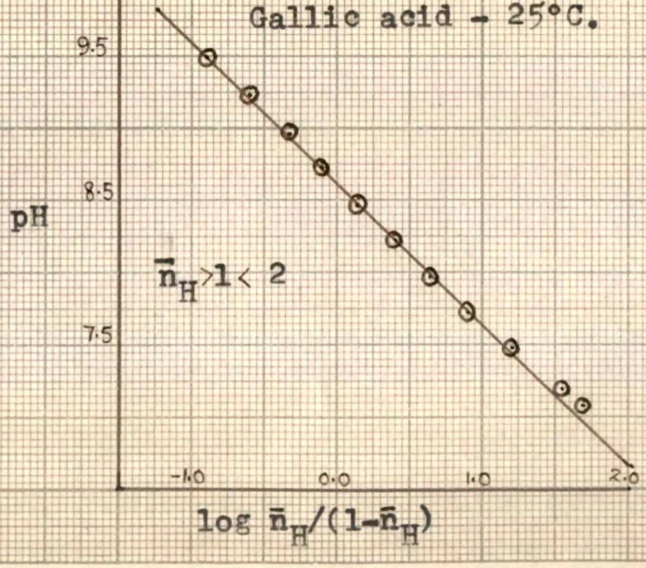


Fig. II 21
Gallic acid - 25°C.

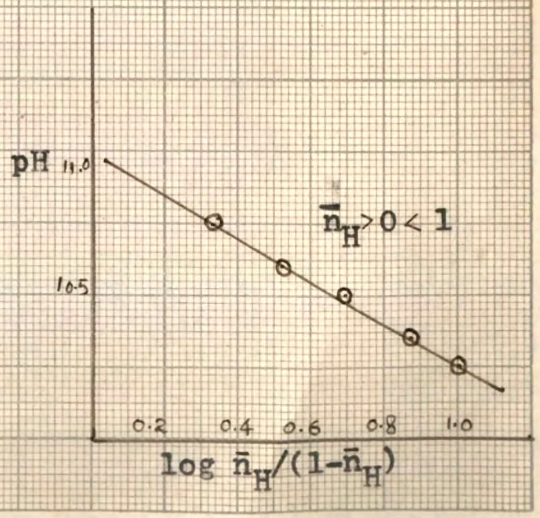


Table 3.0

Proton ligand stability constants of the ligands at 25°C.

Ligand	$P_{K_1}^{H}$		$P_{K_2}^{H}$	$P_{K_3}^{H}$
	(A)	(B)		
1. Catechol	12.03	11.72	9.22	-
2. 2,3-dihydroxynaphthalene	-	12.85	8.65	-
3. Pyrogallol	11.05	10.97	8.92	-
4. Protocatechuic acid	12.30	12.36	8.80	4.35
5. Gallic acid	11.20	11.19	8.69	4.22
6. Ethylenediamine[14]	-	10.97	7.49	-
7. Propylenediamine[14]	-	9.97	7.10	-

(A) = Values obtained using relationship $\log P_{K_n}^{H} = pH + \log \bar{n}_H/(1 - \bar{n}_H)$

(B) = Values obtained using relationship $\log P_{K_1}^{H} P_{K_2}^{H} = 2pH$ (at $\bar{n}_H = 1$).

Table 4.1

B, $\bar{n}$, log $(1-\bar{n})/\bar{n}$, pL and pL - log$(1-\bar{n})/\bar{n}$ data for Ni-catecholate at 25°C.

B	V''	V'''	$V''' - V''$	$\bar{n}$	log $(1-\bar{n})/\bar{n}$	pL	pL-log $(1-\bar{n})/\bar{n}$
7.00	2.53	2.58	0.05	0.10_0	0.95_4	8.96_9	-
7.25	2.54	2.63	0.09	0.18_1	0.65_5	8.47_5	-
7.40	2.55	2.68	0.13	0.26_2	0.45_0	8.18_1	-
7.50	2.56	2.72	0.16	0.32_4	0.32_1	7.98_5	7.66_4
7.60	2.57	2.77	0.20	0.40_5	0.16_7	7.79_1	7.62_4
7.70	2.58	2.84	0.26	0.52_8	$\bar{1}.95_1$	7.60_0	7.64_9
7.80	2.59	2.90	0.31	0.63_1	$\bar{1}.76_7$	7.40_9	7.64_2
7.90	2.61	2.96	0.35	0.71_5	$\bar{1}.60_0$	7.21_2	7.61_2
8.00	2.64	3.03	0.39	0.80_0	$\bar{1}.39_8$	7.02_7	7.62_9
8.10	2.66	3.10	0.44	0.90_7	$\bar{1}.01_1$	6.83_9	-
8.20	2.69	3.17	0.48	0.99_5	$\bar{3}.70_1$	6.65_2	-
8.30	2.73	3.24	0.51	1.06_6	1.15_1	6.46_4	5.31_3
8.40	2.77	3.30	0.53	1.11_8	0.87_3	6.18_0	5.30_7
8.60	2.90	3.46	0.56	1.21_2	0.57_0	5.91_8	5.34_8

log K_1 = 7.63 ± 0.02

log K_2 = 5.32 ± 0.02

Table 4.2

B, $\bar{n}$, log (1-$\bar{n}$)/ $\bar{n}$, pL and pL - log (1-$\bar{n}$)/ $\bar{n}$ data for Ni-2,3-dihydroxynaphthalene at 25°C.

B	V"	V"'	V"' - V"	$\bar{n}$	log(1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/ $\bar{n}$
6.25	2.51	2.56	0.05	0.10_0	0.95_4	11.12_6	-
6.50	2.53	2.60	0.07	0.14_1	0.78_5	10.53_1	9.74_6
6.65	2.54	2.66	0.12	0.24_2	0.49_6	10.25_2	9.75_6
6.75	2.54	2.70	0.16	0.32_2	0.32_4	10.04_2	9.71_8
6.85	2.54	2.76	0.22	0.44_2	0.10_1	9.85_0	9.74_9
7.00	2.56	2.85	0.29	0.58_4	$\bar{1}.85_3$	9.55_5	9.70_2
7.15	2.59	2.95	0.36	0.73_0	$\bar{1}.56_8$	9.26_1	9.69_9
7.25	2.61	3.01	0.40	0.81_4	$\bar{1}.35_9$	9.07_3	9.71_4
7.50	2.69	3.14	0.45	0.12_4	1.91_5	8.58_7	-
7.75	2.82	3.35	0.51	1.07_2	1.08_5	8.10_8	-
8.00	3.00	3.54	0.54	1.18_0	0.65_9	7.63_0	6.97_1
8.25	3.26	3.86	0.60	1.38_1	0.21_0	7.16_6	6.95_6
8.50	3.60	4.25	0.65	1.61_9	$\bar{1}.78_9$	6.72_6	6.93_7

$\log K_1 = 9.72 \pm 0.02$

$\log K_2 = 6.95 \pm 0.02$

Table 4.3

B, $\bar{n}$, log (1-$\bar{n}$)/ $\bar{n}$, pL and pL - log (1-$\bar{n}$)/ $\bar{n}$ data for Ni-protocatechuate at 25°C.

B	V"	V"'	V"' - V"	$\bar{n}$	log (1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/ $\bar{n}$
6.75	5.01	5.09	0.08	0.16_0	0.72_0	9.71_6	-
6.90	5.02	5.12	0.10	0.20_0	0.60_2	9.42_1	-
7.00	5.04	5.17	0.13	0.26_0	0.45_4	9.22_6	8.77_2
7.15	5.05	5.25	0.20	0.40_1	0.17_1	8.93_3	8.76_2
7.25	5.07	5.32	0.25	0.50_4	$\bar{1}.99_3$	8.74_1	8.74_8
7.35	5.09	5.40	0.31	0.62_6	$\bar{1}.77_7$	8.54_9	8.77_2
7.50	5.13	5.50	0.37	0.75_4	$\bar{1}.51_4$	8.27_1	8.75_7
7.60	5.17	5.57	0.40	0.82_2	$\bar{1}.33_5$	8.07_1	8.73_6
7.75	5.23	5.66	0.43	0.89_3	$\bar{1}.07_9$	7.78_8	8.70_9

$\log K_1 = 8.75 \pm 0.02$

Table 4.4

B, $\bar{n}$, log $(1-\bar{n})/\bar{n}$, pL and pL − log$(1-\bar{n})/\bar{n}$ data for Ni-pyrogallolate at 25°C.

B	V''	V'''	$V''' - V''$	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$\text{pL}-\log(1-\bar{n})/\bar{n}$
6.75	2.56	2.61	0.05	0.10_0	0.94_9	8.42_9	-
7.00	2.57	2.65	0.08	0.16_1	0.71_7	7.93_5	7.21_8
7.10	2.58	2.70	0.12	0.24_3	0.49_4	7.73_9	7.24_5
7.20	2.59	2.75	0.16	0.32_4	0.31_9	7.54_5	7.22_6
7.30	2.60	2.81	0.21	0.42_6	0.12_9	7.35_2	7.22_3
7.40	2.61	2.88	0.27	0.54_9	$\bar{1}.91_4$	7.16_1	7.24_7
7.50	2.63	2.95	0.34	0.65_5	$\bar{1}.72_1$	6.97_2	7.25_1

$\log K_1 = 7.23 \pm 0.01$

Table 4.5

B, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL$-\log(1-\bar{n})/\bar{n}$ data for Ni-gallate at 25°C.

B	V''	V'''	$V''' - V''$	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL$-\log(1-\bar{n})/\bar{n}$
6.25	4.97	5.01	0.04	0.07_9	1.06_6	9.42_7	-
6.40	4.98	5.03	0.05	0.09_8	0.96_4	9.13_0	-
6.50	5.00	5.07	0.07	0.13_9	0.79_2	8.92_6	-
6.65	5.01	5.11	0.10	0.19_9	0.60_4	8.63_4	-
6.75	5.02	5.13	0.11	0.22_0	0.55_0	8.43_7	7.88_7
6.85	5.03	5.18	0.15	0.30_6	0.36_8	8.24_1	7.87_3
6.95	5.04	5.24	0.20	0.40_1	0.17_4	8.04_6	7.87_2
7.00	5.05	5.28	0.23	0.46_2	0.08_2	7.94_8	7.86_6
7.10	5.07	5.34	0.27	0.54_5	$\bar{1}.92_2$	7.75_6	7.83_4
7.20	5.09	5.41	0.32	0.64_8	$\bar{1}.73_5$	7.56_4	7.82_9

$\log K_1 = 7.86 \pm 0.02$

Table 4.6

B, $\bar{n}$ log(1-$\bar{n}$)/ $\bar{n}$, pL and pL-log(1-$\bar{n}$)/ $\bar{n}$ data for Cu-catecholate at 25°C.

B	V"	V"'	V"' - V"	$\bar{n}$	log(1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/ $\bar{n}$
4.00	2.48	2.55	0.07	0.14_0	0.78_8	14.96_7	-
4.50	2.49	2.58	0.09	0.18_0	0.65_8	13.97_0	-
4.75	2.50	2.61	0.11	0.22_1	0.54_7	13.47_3	12.92_6
5.00	2.50	2.72	0.22	0.46_2	0.06_6	12.98_2	12.91_6
5.25	2.50	2.87	0.37	0.74_3	$\bar{1}.53_8$	12.49_8	12.96_0
5.50	2.51	2.96	0.45	0.90_4	$\bar{1}.02_6$	12.00_7	12.98_1
5.75	2.51	3.03	0.52	1.04_4	1.33_7	11.51_4	-
6.00	2.51	3.07	0.56	1.12_5	0.84_6	11.02_0	10.17_4
6.25	2.51	3.16	0.65	1.30_5	0.35_8	10.52_7	10.16_9
6.50	2.52	3.29	0.77	1.54_6	$\bar{1}.920$	10.03_9	10.11_9
6.75	2.52	3.41	0.89	1.78_5	$\bar{1}.43_8$	9.56_7	10.12_9

$\log K_1 = 12.94 \pm 0.03$

$\log K_2 = 10.16 \pm 0.02$

Table 4.7

B, $\bar{n}$, log(1-$\bar{n}$)/ $\bar{n}$, pL and pL-log(1-$\bar{m}$)/ $\bar{n}$ data for Cu-2,3-dihydroxynaphthalene at 25°C.

B	V''	V'''	V'''-V''	$\bar{n}$	log(1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/ $\bar{n}$
4.25	2.48	2.58	0.10	0.20_0	0.60_2	15.03_1	-
4.35	2.48	2.64	0.16	0.32_0	0.32_7	14.83_7	-
4.50	2.48	2.70	0.22	0.44_0	0.10_5	14.54_3	14.43_8
4.60	2.48	2.75	0.27	0.54_0	$\bar{1}.93_1$	14.34_7	14.41_6
4.75	2.49	2.83	0.34	0.68_0	$\bar{1}.67_3$	14.05_5	14.38_2
4.85	2.49	2.88	0.39	0.78_0	$\bar{1}.45_0$	13.86_0	14.41_0
5.00	2.50	2.94	0.44	0.88_0	$\bar{1}.13_5$	13.56_7	14.43_2
5.25	2.50	3.01	0.51	1.02_0	1.69_0	13.07_3	-
5.50	2.50	3.07	0.57	1.14_0	0.78_8	12.58_0	11.79_2
5.75	2.51	3.17	0.66	1.32_0	0.22_7	12.08_7	11.76_0
5.85	2.51	3.22	0.71	1.42_6	0.14_0	11.89_4	11.75_4
6.00	2.51	3.30	0.79	1.58_1	$\bar{1}.86_0$	11.60_3	11.74_3
6.10	2.51	3.35	0.84	1.68_0	$\bar{1}.67_3$	11.40_8	11.73_5
6.25	2.52	3.42	0.90	1.80_2	$\bar{1}.39_2$	11.11_4	11.72_2

$\log K_1 = 14.41 \pm 0.02$

$\log K_2 = 11.75 \pm 0.02$

Table 4.8

B, $\bar{n}$ log(1-$\bar{n}$)/ $\bar{n}$, pL and pL-log(1-$\bar{n}$)/ $\bar{n}$ data for Cu-protocatechuate at 25°C.

B	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/ $\bar{n}$
4.25	3.65	3.75	0.10	0.20_0	0.60_2	15.05_8	-
4.50	4.00	4.19	0.19	0.38_0	0.25_0	14.44_5	14.19_5
4.60	4.16	4.41	0.25	0.50_0	0.00_0	14.18_2	14.18_2
4.75	4.36	4.69	0.33	0.66_0	$\bar{1}.71_2$	13.86_9	14.15_7
4.85	4.46	4.84	0.38	0.76_0	$\bar{1}.50_0$	13.64_7	14.14_7
5.00	4.58	5.02	0.44	0.88_0	$\bar{1}.13_5$	13.30_7	14.17_2
5.10	4.64	5.10	0.46	0.92_0	$\bar{2}.94_5$	13.10_9	14.16_4
5.25	4.73	5.24	0.51	1.02_0	1.69_1	12.79_6	-
5.50	4.83	5.40	0.57	1.14_0	0.78_8	12.28_2	-
5.75	4.90	5.52	0.62	1.24_0	0.50_0	11.77_4	-
6.00	4.95	5.60	0.65	1.30_0	0.36_8	11.27_5	10.90_7
6.10	4.96	5.66	0.70	1.40_0	0.17_6	11.07_8	10.90_2
6.25	4.97	5.76	0.79	1.58_0	$\bar{1}.86_0$	10.78_9	10.92_9
6.35	4.98	5.82	0.84	1.68_0	$\bar{1}.67_3$	10.59_4	10.92_1
6.50	4.99	5.89	0.90	1.80_0	$\bar{1}.39_7$	10.30_3	10.90_6

$\log K_1 = 14.17 \pm 0.02$

$\log K_2 = 10.91 \pm 0.01$

Table 4.9

B, $\bar{n}$, log (1-$\bar{n}$) / $\bar{n}$, pL and pL - log(1-$\bar{n}$) / $\bar{n}$ data for Cu-pyrogallolate at 25°C.

B	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
3.50	2.44	2.50	0.06	0.12_0	0.86_5	14.92_6	-
3.75	2.47	2.54	0.07	0.14_0	0.78_8	14.42_7	-
4.00	2.49	2.56	0.07	0.14_0	0.78_8	13.92_8	-
4.10	2.50	2.58	0.08	0.16_0	0.72_0	13.73_0	-
4.20	2.50	2.59	0.09	0.18_0	0.66_0	13.53_0	-
4.30	2.51	2.60	0.09	0.18_0	0.66_0	13.33_0	12.67_0
4.40	2.51	2.64	0.13	0.26_0	0.45_4	13.13_3	12.67_9
4.50	2.51	2.68	0.17	0.34_0	0.28_8	12.93_7	12.64_9

$\log K_1 = 12.66 \pm 0.01$

Table 4.10

B, $\bar{n}$, log (1-$\bar{n}$)/ $\bar{n}$, pL and pL - log (1-$\bar{n}$)/ $\bar{n}$ data for Cu-gallate at 25°C.

B	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/ $\bar{n}$	pL	pL-log(1-$\bar{n}$)/ $\bar{n}$
3.65	3.02	3.16	0.14	0.28_6	0.41_6	15.29_2	-
3.75	3.16	3.31	0.15	0.30_0	0.36_8	15.01_6	-
3.85	3.27	3.42	0.15	0.30_0	0.36_8	14.74_8	-
4.00	3.46	3.62	0.16	0.32_0	0.32_7	14.35_0	-
4.10	3.60	3.76	0.16	0.32_0	0.32_7	14.09_2	13.76_5
4.15	3.67	3.86	0.19	0.38_6	0.21_3	13.97_1	13.75_8
4.20	3.74	3.97	0.23	0.46_0	0.06_9	13.84_3	13.77_4
4.25	3.81	4.08	0.27	0.54_0	$\bar{1}.93_0$	13.72_1	13.79_1
4.30	3.88	4.18	0.30	0.60_0	$\bar{1}.82_4$	13.60_0	13.77_6

log K_1 = 13.11 ± 0.01

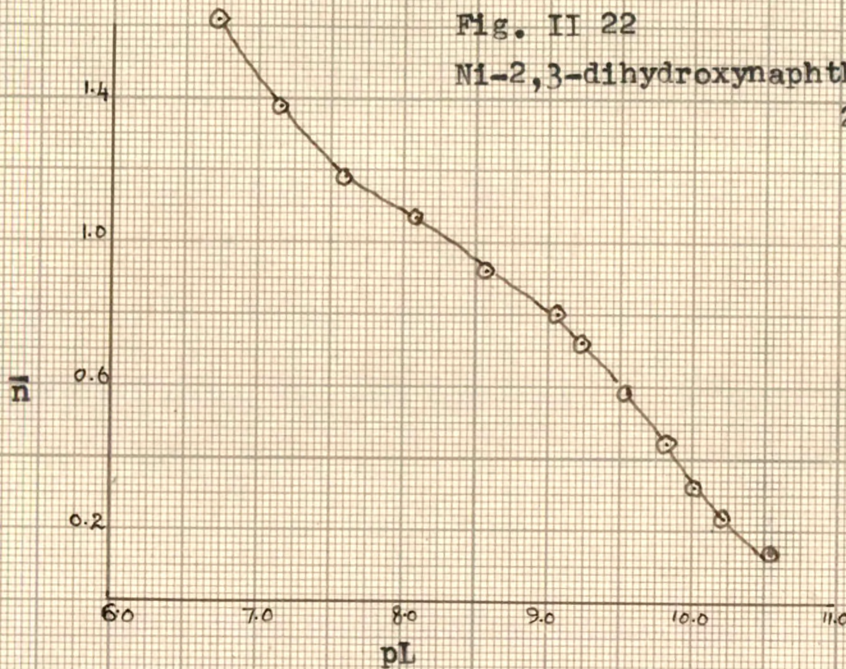


Fig. II 22
Ni-2,3-dihydroxynaphthalene-
25°C.

Fig. II 23
Ni-Protocatechuic acid-25°C.

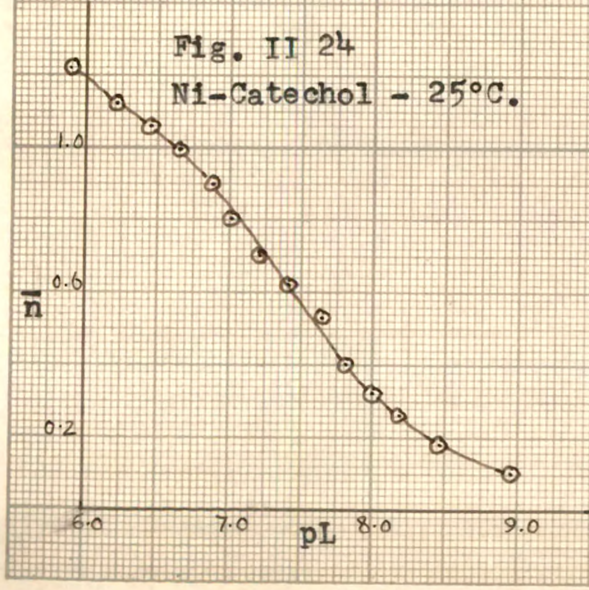


Fig. II 24
Ni-Catechol - 25°C.

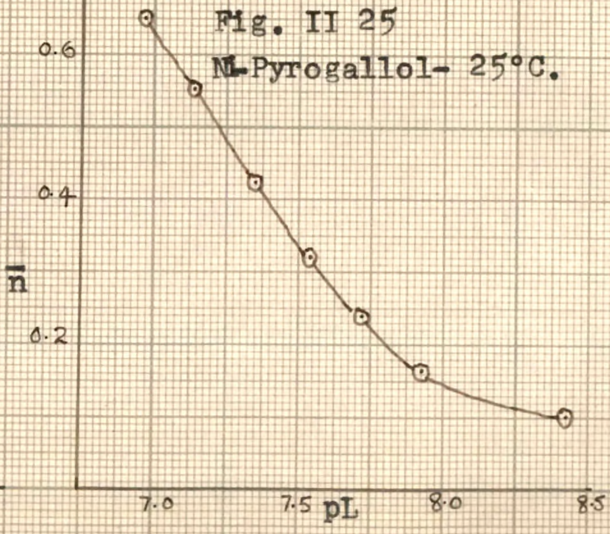


Fig. II 25
Ni-Pyrogallol- 25°C.

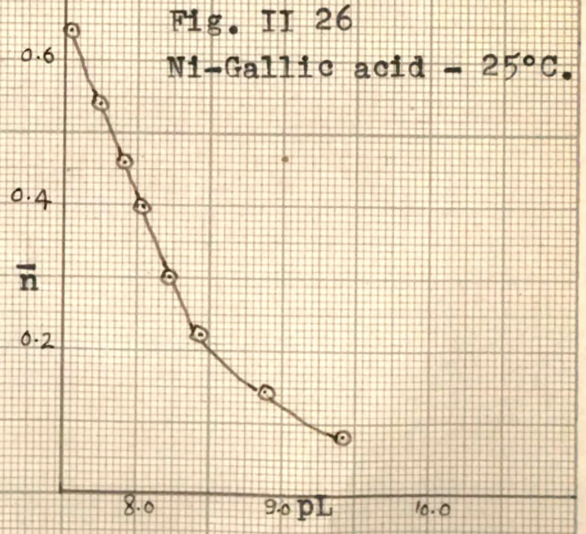


Fig. II 26
Ni-Gallic acid - 25°C.

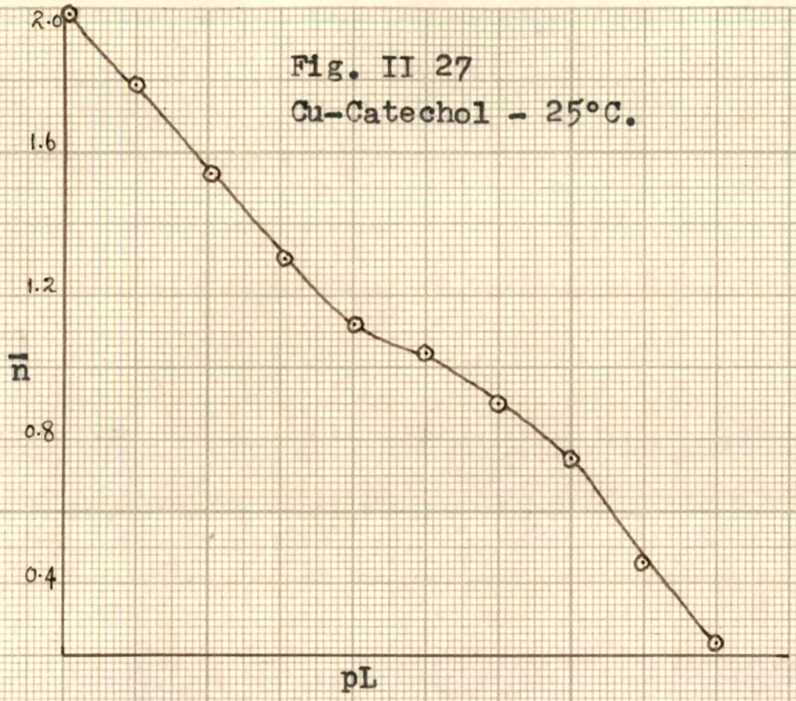


Fig. II 27
Cu-Catechol - 25°C.

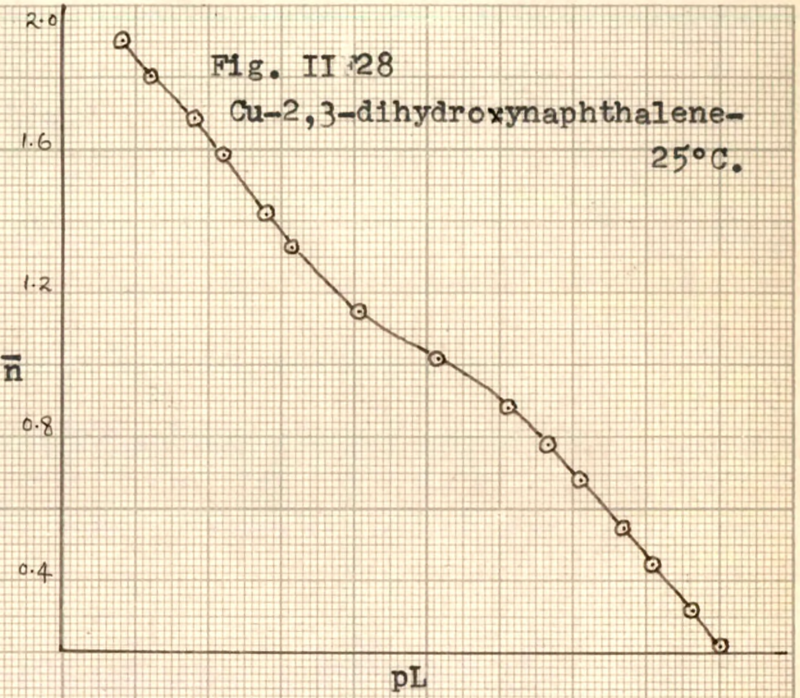


Fig. II 28
Cu-2,3-dihydroxynaphthalene-
25°C.

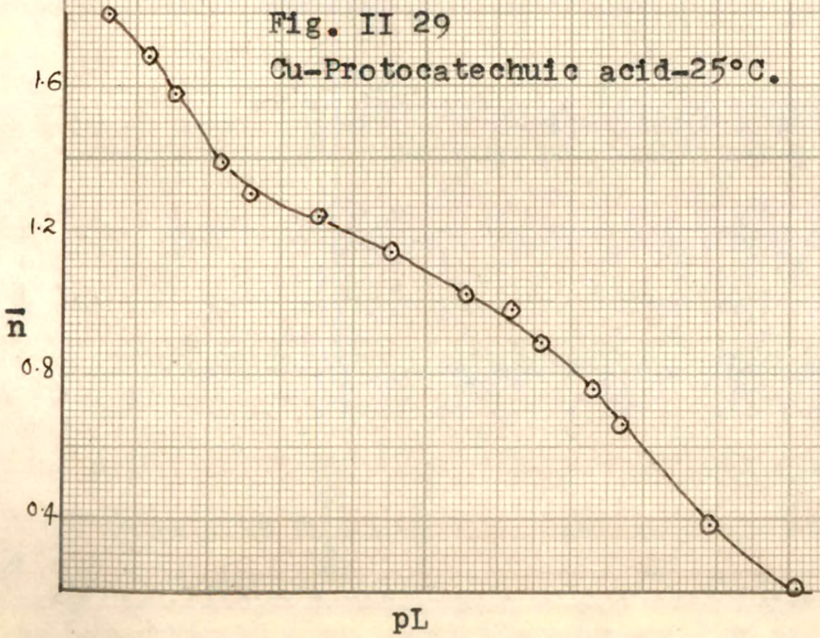


Fig. II 29
Cu-Protocatechuic acid-25°C.

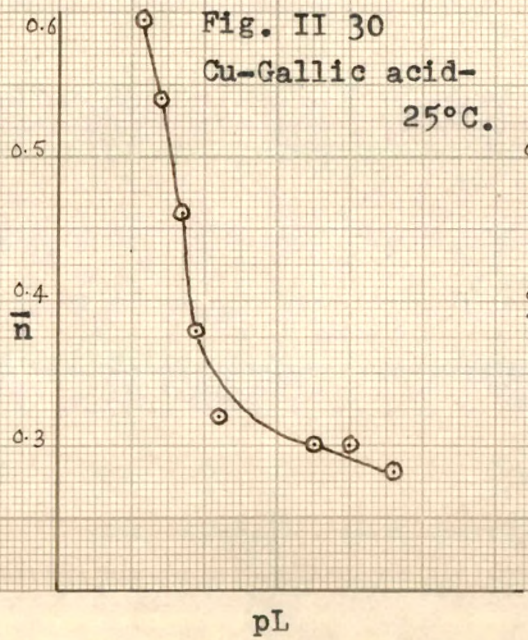


Fig. II 30
Cu-Gallic acid-
25°C.

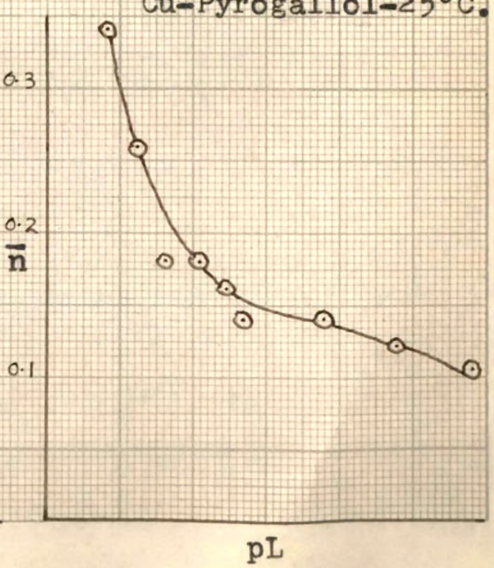


Fig. II 31
Cu-Pyrogallol-25°C.

Fig. II 32

Ni-2,3-dihydroxynaphthalene- 25°C.

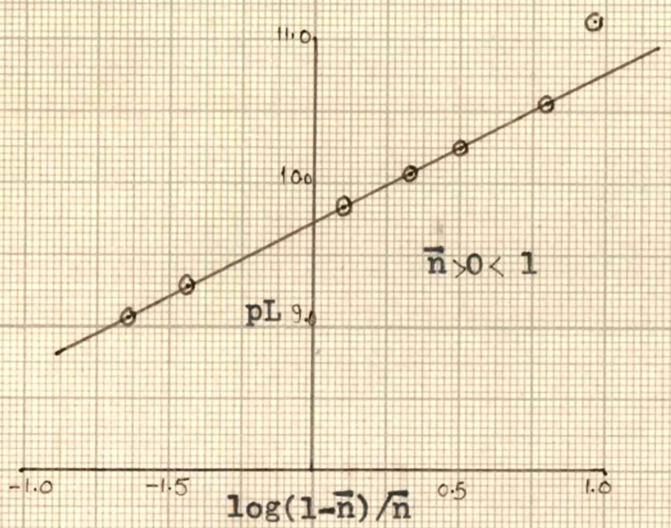


Fig. II 33

Ni-2,3-dihydroxynaphthalene-25°C.

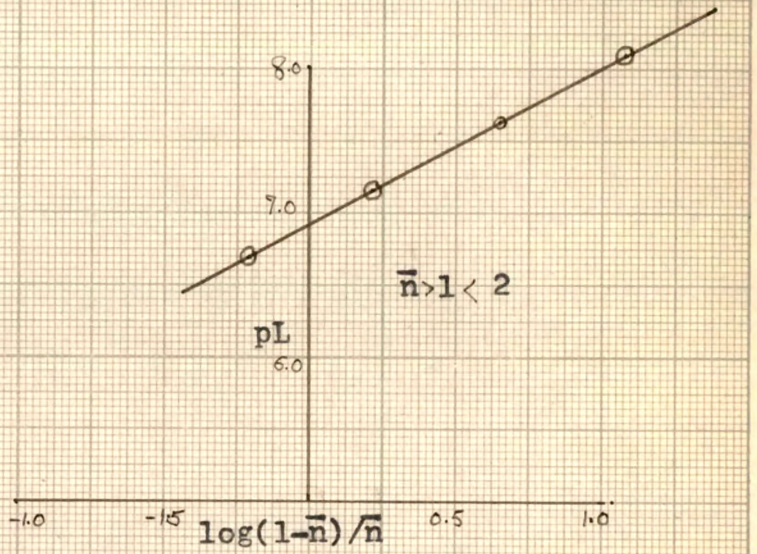


Fig. II 34

Ni-Catechol - 25°C.

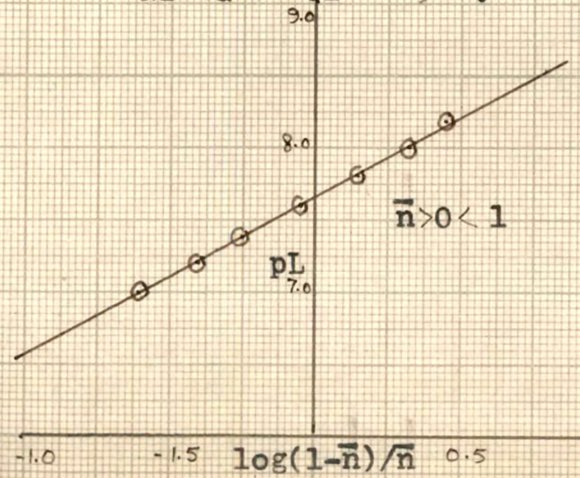


Fig. II 35

Ni-Catechol - 25°C.

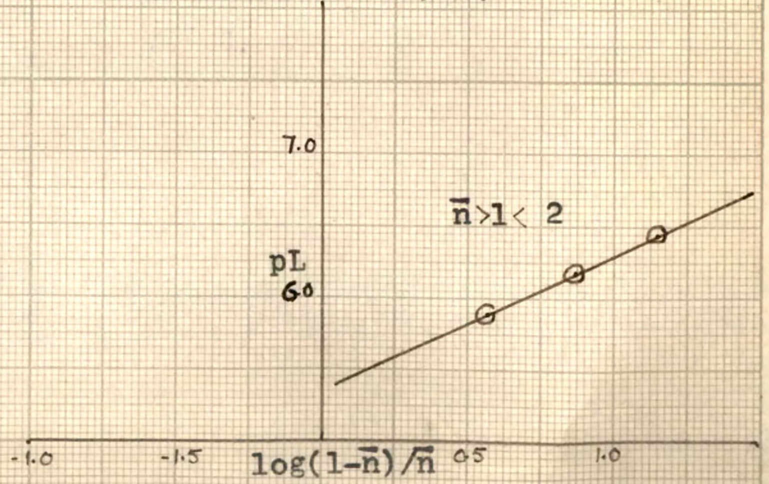


Fig. II 36

Ni-Protocatechuic acid - 25°C.

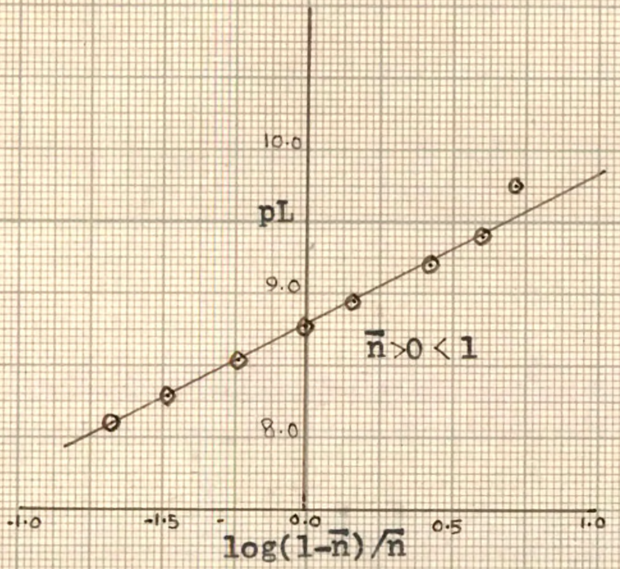


Fig. II 37

Ni-Gallic acid - 25°C.

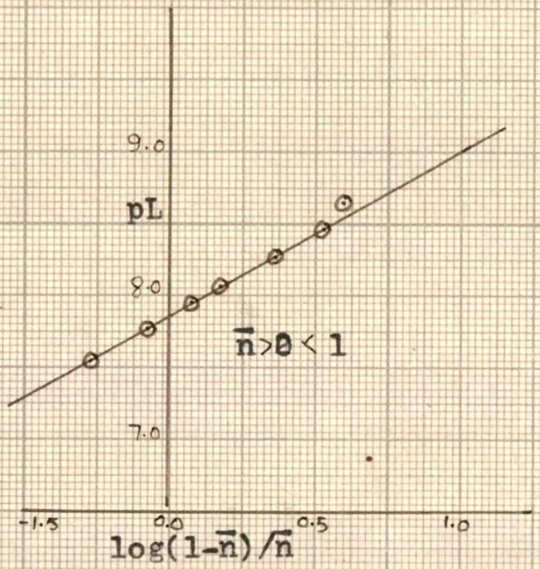


Fig. II 38

Ni-Pyrogallol - 25°C.

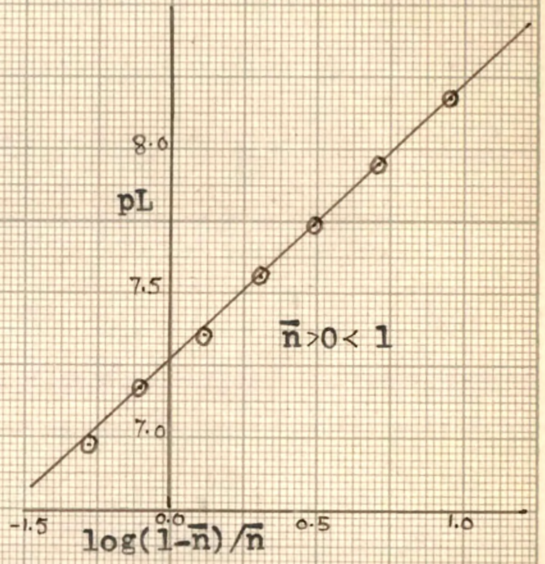


Fig. II 39

Cu-2,3-dihydroxynaphthalene - 25°C.

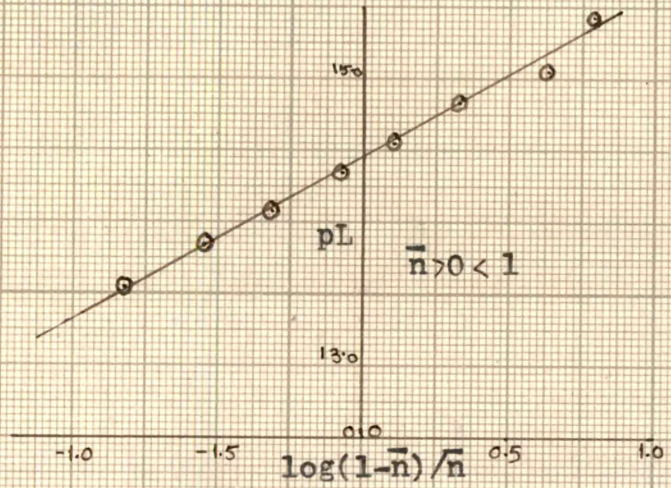


Fig. II 40

Cu-2,3-dihydroxynaphthalene - 25°C.

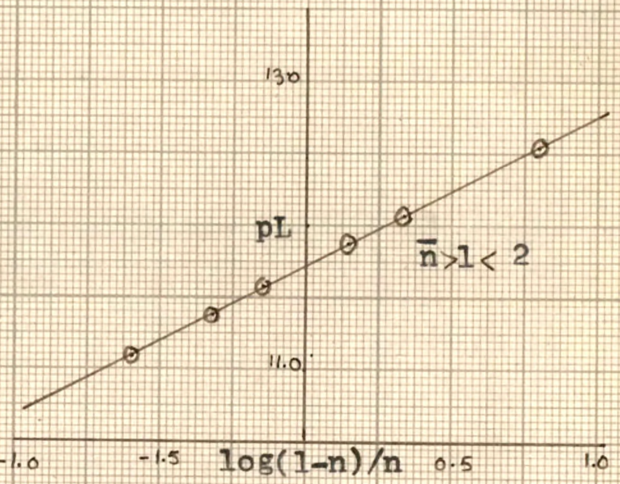


Fig. II 41

Cu-Catechol - 25°C.

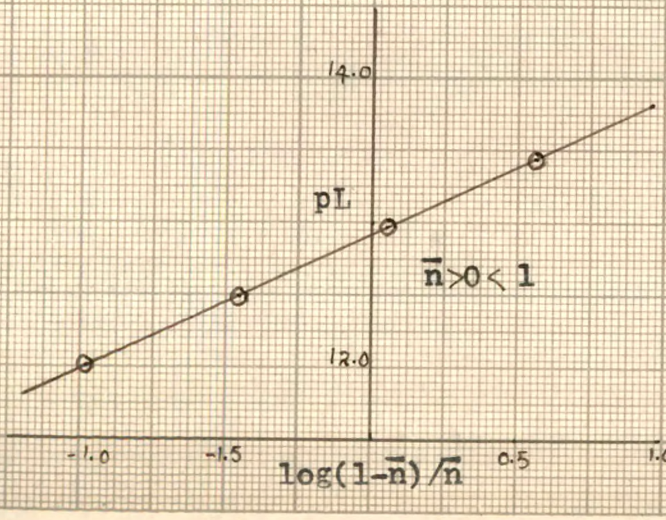


Fig. II 42

Cu-Catechol - 25°C.

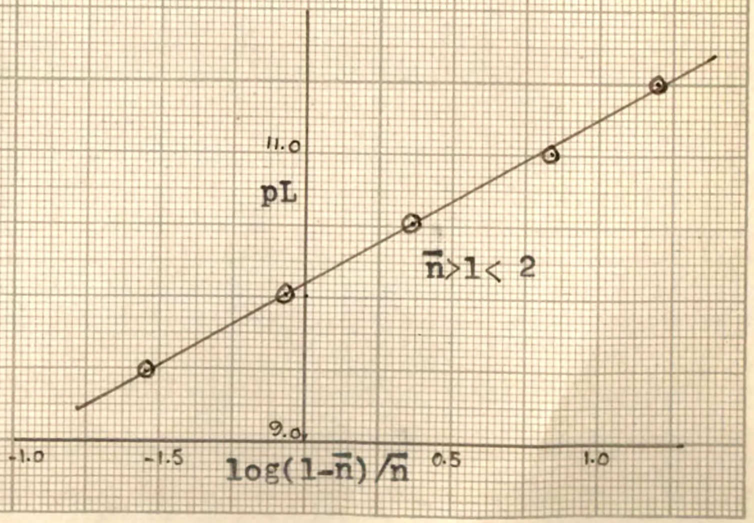


Fig. II 43

Cu-Gallic acid - 25°C.

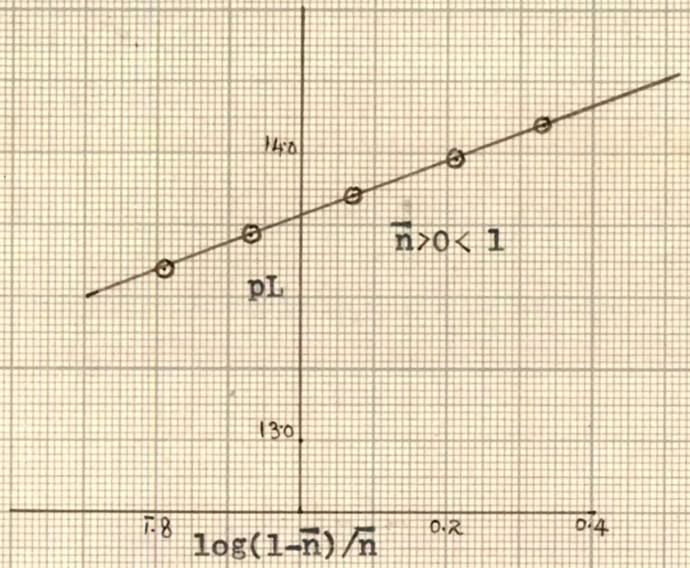


Fig. II 44

Cu-Pyrogallol - 25°C.

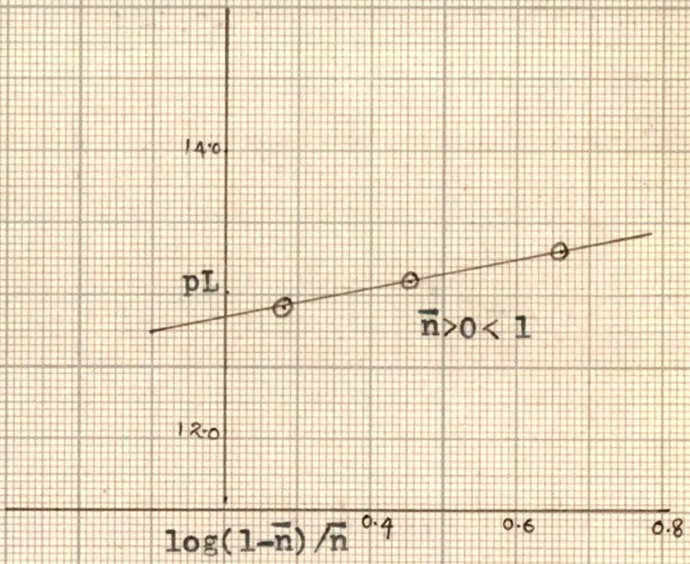


Fig. II 45

Cu-Protocatechuic acid - 25°C.

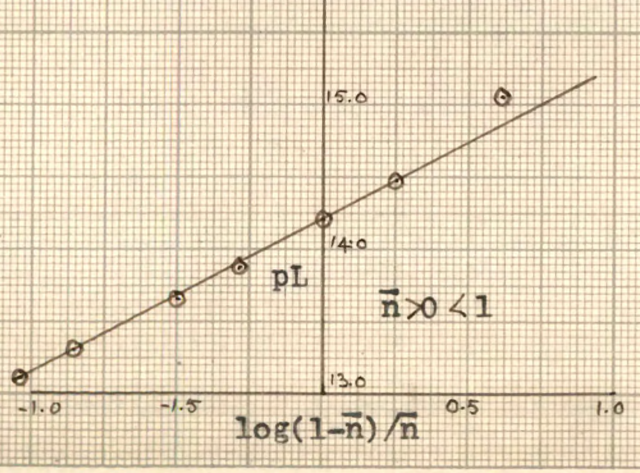


Fig. II 46

Cu-Protocatechuic acid - 25°C.

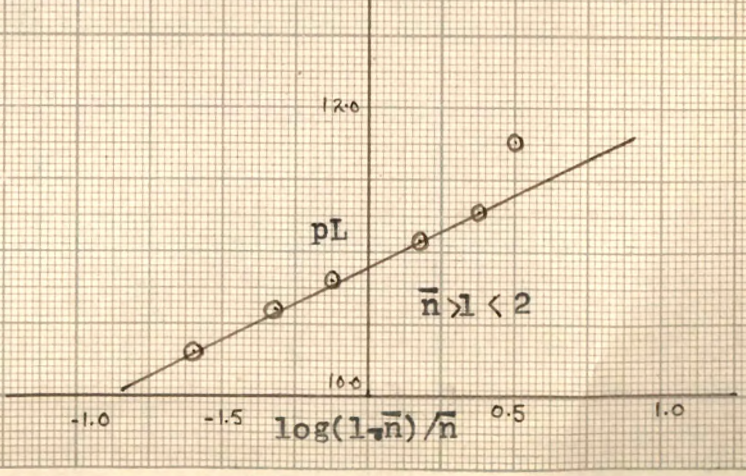


Table 5.0

Formation constants of Ni(II) and Cu(II) chelates at 25°C.

Ligand	Ni(II)		Cu(II)	
	log K_1	log K_2	log K_1	log K_2
1. Catechol	7.63 ± 0.02	5.32 ± 0.02	12.94 ± 0.03	10.16 ± 0.02
2. 2,3-dihydroxynaphthalene	9.72 ± 0.02	6.95 ± 0.02	14.41 ± 0.02	11.75 ± 0.02
3. Pyrogallol	7.23 ± 0.01	-	12.66 ± 0.01	-
4. Protocatechuic acid	8.75 ± 0.02	-	14.17 ± 0.02	10.91 ± 0.01
5. Gallic acid	7.86 ± 0.02	-	13.77 ± 0.01	-
6. Ethylenediamine [14]	7.52	6.28	10.72	9.31
7. Propylenediamine [14]	7.43	6.19	10.78	9.28

References :

1. Allen,N., and Low,C.W., " Industrial and Engg.Chem." Anal.Ed., 5, 192, (1933).
2. Vogel,A.I., " A Text Book of Quantitative Inorganic Analysis." The English Language Book Society and Longmans Green and Co., Ltd. London, p.479, (1964).
3. ibid., p. 497.
4. ibid., p. 204.
5. Van Uitert,L.G., and Haas,C.G., J.Amer.Chem.Soc., 75, 451, (1953).
6. Van Uitert,L.G., Fernelius,W.C., and Douglas,B.E., J.Amer.Chem.Soc., 75, 3577, (1953).
7. Harned,H.S., and Owen,B.B., " The Physical Chemistry of Electrolytic Solutions", 2nd Ed.Reinhold Publishing Corporation, New York, N.Y., p.548, (1950).
8. Finar,I.L., " Organic Chemistry", Vol. One., p.495, (1964).
9. Calvin and Melchior, J.Amer.Chem.Soc., 70, 3270, (1948).
10. Irving,H., and Williams,R.J.P., Nature, 162, 746, (1948).
11. Tserkvnitskaya,I.A., and Epimakhov,V.N., Vop.Anal.Khim. Miner, Veschchestv, Leningrad, Gos.Univ., 5, (1966).
12. Athavale,V.T., Krishnan,C.V., Ramnathan,P.S., and Venkateswarlu,CH., Ind.J.Chem., 7, 1040-3, (1969).
13. Yukito Murakami, Katsuyuki Nakamura and Masasuke Tokunaga, Bull.Chem.Soc., Japan, 36(6), 669, (1963).
14. "Stability Constants" Special Publication No. 17, London: The Chemical Society, Burlington House, W.1, (1964), p. 370-2 and 393-4.