CHAPTER II

Binary systems containing metal ion and polyhydroxy phenol or phenolic acid.

Solution Stability in Binary Systems :

For the determination of proton-ligand formation constants of the ligands and metal ligand formation constants of UO_2^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+} and Tl^{+} complexes with catechol, pyrogallol, 2,3-dihydroxynaphthalene and protocatechuic acid, Irving-Rossotti titration technique[1] was employed. This technique involves the measurement of pH which was carried out using pH meter with glass electrodes. As all the metals and ligands are soluble in water, water was used as a solvent throughout.

A. Materials and Purifications :

(i) Water :

The double distilled conductivity water was used in all experimental work. 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 the water, thus obtained, was found to be $\sim$ 6.8. This water was used for preparing all the solutions.

(ii) Ligands and other chemicals :

The ligands used were A.R. pure. They were obtained from different chemical companies, and their purities were checked by noting the melting points. The chemicals used are as follows :

Pyrocatechol (E.Merck, Germany), Pyrogallol (BDH, England), Protocatechuic acid (Fluka, Switzerland), 2,3-Dihydroxy-naphthalene (Fluka, Switzerland), Perchloric acid (Baker,analysed

Reagent N.J.), Sodium perchlorate (Fluka, Switzerland), Sodium hydroxide (Chemapol, Czechoslovakia), Zinc carbonate (BDH, England), Cadmium carbonate (BDH, England), Magnesium carbonate (BDH, England), Thallium carbonate (BDH, England), Uranyl nitrate (BDH, England), and Oxalic acid (BDH, England).

B. Preparation of solutions :

(i) 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.

(ii) Sodium hydroxide :

Sodium hydroxide solution free from carbonate was prepared according to the method of Allen and Low.[2] 50.0 gms. of sodium hydroxide were dissolved in 500 ml. of conductivity water in a well corked flask and kept for 48 hrs.. The clear supernatant liquid was filtered rapidly through sintered bed Jena Glass crucible of porosity G_4 using vaccum pump. A convenient volume of the filtrate was diluted to obtain an approximately 0.5M solution. It was preserved out of contact with carbondioxide by connecting to a soda lime guard tube. The stock solution was standardised against a standard oxalic acid solution and 0.2M solution was prepared by suitable dilution of the stock solution.

(iii) Sodium perchlorate solution:

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

(iv) Perchloric acid :

A definite volume of 80% acid was diluted with conductivity water to obtain approximately 0.5M solution of perchloric acid in 500 ml.. It was standardised by titration against standard sodium hydroxide solution. It was diluted to get 0.1M concentration.

(v) Metal salt solutions:

Zinc perchlorate solution, cadmium perchlorate solution, magnesium perchlorate solution, thallium perchlorate solution :

In order to avoid the complexing tendencies of the anions, metal perchlorates were prepared by refluxing the respective metal carbonates with perchloric acid till an excess of metal carbonate was left. The filtrate was a neutral solution of metal perchlorate. The amounts of metal present were estimated. By proper dilution 0.01M and 0.02M metal perchlorate solutions were prepared from the above estimated stock solution.

Uranyl nitrate :

Due to non-availability of uranyl carbonate, uranyl nitrate had to be used. An exactly weighed quantity of uranyl nitrate was dissolved in conductivity water to get a solution of 0.01M concentration. The concentration was confirmed by estimating uranium content[3].

(vi) Solutions of complexing agents :

Since the ligands catechol, pyrogallol and 2,3-dihydroxy-naphthalene were of A.R. quality, their standard solutions were prepared by dissolving the required quantity in double distilled water. The solutions were diluted upto 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. In case of protocatechuic 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. As the compounds have tendency to get oxidised in air, care was taken to avoid excess contact with air during the preparation and dilution of the ligand solutions. Fresh solutions were prepared and used every time. To avoid aerial oxidation stock solution was kept covered with toluene.

C. Apparata :

All glasswares used were of pyrex glass. The micro-burette was calibrated to 0.01 ml. by the method described by Vogel.[4] The other apparata such as micro-pipettes, pipettes, measuring flasks of various capacities were calibrated with the help of the standard burette.

D. pH Meter and Accessories :

For measuring the pH throughout the investigations, a pH meter with the following specifications was used :

Model	Metrohm E 350 A
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
Temperature range	0° - 100°C.
Equipment	1 EA 120X combined glass electrode
Supplier	Metrohm, Switzerland.

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

E. Calibration of the pH meter :

Before using the pH meter, it was calibrated with different buffer solutions of pH 4.0 and 7.0. The calibration was checked again after completion of pH measurement for a set.

F. Bubbling of Nitrogen :

In the present investigation, the experiments 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 bubbling of nitrogen serves two purposes : (a) prevention of oxidation due to atmospheric oxygen, (b) stirring of solution.

Details of Irving-Rossotti titration technique :

The solutions to be titrated were taken in a lipless pyrex beaker, fitted with perspex cover having four holes to insert the electrode, gas inlet, glass stirrer and the burette tip. The beakers were kept at a constant temp. 30°C. (± 0.1°C.) in a thermostatic bath. Three solution mixtures were prepared as detailed below. The total volume of 50.0 ml. was maintained by the addition of conductivity water and the initial ionic strength of the solution was raised to 0.2M in all the cases by the addition of the required amount of neutral salt i.e. sodium perchlorate.

(i) Acid titration :

Perchloric acid (0.05M, 10.0 ml.) + sodium perchlorate

(1.0M, 9.5 ml.) + conductivity water (30.5 ml.) ; total volume 50.0 ml., μ = 0.2M.

(ii) Reagent titration :

Perchloric acid (0.05M, 10.0 ml.) + sodium perchlorate (1.0M, 9.0 ml.) + reagent (0.05M, 10.0 ml.) + conductivity water (21.0 ml.) ; total volume 50.0 ml., μ = 0.2M.

(iii) Metal titration :

Perchloric acid (0.05M, 10.0 ml.) + sodium perchlorate (1.0M, 8.95 ml.)+ reagent (0.05M, 10.0 ml.) + metal solution (0.01M, 5.0 ml.) + conductivity water (16.05 ml.).; total volume 50.0 ml., μ = 0.2M.

All the above solutions were titrated against 0.2M sodium hydroxide solution. After addition of each portion of alkali, pH was noted. The highest reading which remained steady was recorded in all cases. The volume of alkali added and pH measured have been recorded in tables II 1.1 to II 2.4 and the plots of pH against volume of alkali added have been presented in figures II 1 to II 7.

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

The values of $\bar{n}_H$, average number of hydrogen ions bound per free ligand, and $\bar{n}$, average number of ligands bound per metal ion, were calculated by using following well known equations[1].

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

And

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

where Y = replacable hydrogen ions, V° = total volume, V' = volume of alkali required by acid, V'' = volume of alkali required by ligand, V''' = volume of alkali required by metal + ligand, N = the concentration of alkali, E° = total strength of acid, T_L° = total concentration of ligand and T_M° = total concentration of metal.

The values of $\bar{n}_H$ and $\bar{n}$ obtained have been reported in table II 4.1a to II 4.4e.

Calculation of proton ligand formation constants :

Irving-Rossotti method has the advantage that the simultaneous determination of proton ligand stability constants is possible from the values of $\bar{n}_H$ calculated. For this it is necessary to ascertain the stages which lead to the formation of the acid from its conjugate base. The steps in cases of catechol and 2,3-dihydroxynaphthalene which are dibasic, can be represented by the 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 formation constants and are represented as $^{P}K_1^H$ and $^{P}K_2^H$. The third OH group in case of pyrogallol, 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 coordination positions around the metal ion. As such, for the calculation of $\bar{n}_H$, Y (number of replacable hydrogen ions) has been considered to be 2, in case

of pyrogallol also, $^{P}K_{1}^{H}$ and $^{P}K_{2}^{H}$ calculated correspond to the association of the 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.

The two OH groups at ortho position in protocatechuic acid are supposed to take part in coordination.[5,6] 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 groups are, therefore essential. And hence Y has been considered to be three in protocatechuic acid. Proton ligand formation constants $^{P}K_{1}^{H}$, $^{P}K_{2}^{H}$ and $^{P}K_{3}^{H}$ calculated correspond to the association of two OH groups and the carboxylic hydrogen in case of protocatechuic acid.

For the determination of proton ligand stability constants, formation curves have been drawn by plotting $\bar{n}_H$ against pH. pH at $\bar{n}_H = 0.5$ and $\bar{n}_H = 1.5$ correspond to $\log K_1^H$ and $\log K_2^H$. However, to get precise values of K_1^H and K_2^H the method of linear plot[7] was applied. In case of acids where K_1^H and K_2^H differ significantly, the formation of the species LH is not overlapped by LH_2 and hence the formation equations for the two stages are separate and get reduced to the following forms :

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

and

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

From these equations, it can be said 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. If values of $\log \bar{n}_H / (1-\bar{n}_H)$ are plotted against pH in the region where $\bar{n}_H > 0 < 1$ and $\bar{n}_H > 1 < 2$, two separate straight lines are obtained. The following relationship tends to hold good at all the points in the straight line.

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

The average values obtained from the points on a straight line in the region $\bar{n}_H > 0 < 1$ and $\bar{n}_H > 1 < 2$ correspond to ${}^{P}K_1^H$ and ${}^{P}K_2^H$, respectively. In case of catechol, pyrogallol and 2,3-dihydroxynaphthalene, since the values of $\bar{n}_H$ do 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 varified by using the following relationship :

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

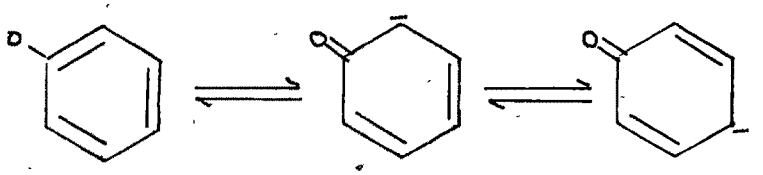
In cases of catechol, pyrogallol, 2,3-dihydroxy-naphthalene and protocatechuic acid, even the dissociation of second OH group is much less in the pH region of the study. Thus the consideration, that the third OH group in pyrogallol, which does not take part in coordination, remains undissociated finds experimental support. Only the values of proton ligand stability constants for the different ligands have been presented in the table II 3.0. The details of intermediate stages of calculation and graph have not been given because such data have been incorporated in the thesis submitted earlier.[8]

Calculations had to be repeated to get log K^H values under experimental conditions.

It is observed from the proton ligand stability constants that the basicities of the ligands are in the order pyrogallol < catechol < 2,3-dihydroxynaphthalene. The poly-hydroxy derivatives of benzene are more acidic than the alcohols. This is because of the two factors.

(i) Electron attracting nature of phenyl group,

(ii) The existence of following resonating structures of the phenolate ion.



(1) (2) (3)

The negative charge in case of alcohol remains localized on the oxygen atom of the alkoxy ion, while the negative charge in the structures (2) and (3) spreads over the whole benzene molecule. Therefore, proton can be replaced more rapidly 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 and 2,3-dihydroxy-naphthalene is more basic than catechol due to the presence of another benzene ring.

The OH proton ligand stability constant values of

protocatechuic acid are higher than that of catechol and pyrogallol. This can be accounted for by the fact that the -COOH group in the protocatechuic acid dissociates first and the resulting carboxylate ion has a positive rather than negative inductive effect.

Calculation of metal ligand formation constants :

It is necessary for the calculation of metal ligand formation constants that metal should be present in solution 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. The possibility of the presence of first two species has been eliminated because (i) the metal perchlorates have been used, (ii) the titrations have been carried out using dilute solutions.

The smooth increase in the horizontal distance between the metal curve and the ligand curve indicates the absence of metal hydroxide or the hydroxyl complexes. The sudden change in the distance between the two curves, on the addition of more alkali, indicates the formation of hydroxide or hydroxyl complex. The pH readings become unstable if the formation of the insoluble hydroxide takes place. No such effect has been observed in the pH range of this study.

The calculations of metal ligand stability constants in cases of UO_2^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+} and Tl^{+} complexes with catechol, pyrogallol, 2,3-dihydroxynaphthalene and protocatechuic

acid were carried out upto pH ~ 9.4. The separation between the two curves i.e. ligand and metal + ligand is very small in Tl-pyrogallolate system and hence the calculation of $\bar{n}$ was not possible.

For the pL calculation in cases of catechol, pyrogallol, 2,3-dihydroxynaphthalene the following equation was used[1].

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

As three proton ligand formation constants have been considered in case of protocatechuic acid, the following equation was used for pL calculation :

$$pL=\log\left[\frac{1+{}^{P}K_1^{H}\left(\frac{1}{\text{antilog } B}\right)+{}^{P}K_1^{H}\,{}^{P}K_2^{H}\left(\frac{1}{\text{antilog } B}\right)^2+{}^{P}K_1^{H}\,{}^{P}K_2^{H}\,{}^{P}K_3^{H}\left(\frac{1}{\text{antilog } B}\right)^3}{T_L^{\circ}-\bar{n}\cdot T_M^{\circ}}\cdot\frac{V^{\circ}+V'''}{V^{\circ}}\right]$$

In case of Zn^{2+} and UO_2^{2+} complexes of protocatechuic acid complexation is at low pH where $\bar{n}_H > 2$. Here self dissociation of -COOH group is incomplete. Since -COOH group does not take part in coordination, the carboxylic -H will remain bound even after complex formation. Therefore, it will be wrong to consider the number of replacable hydrogen Y equal to 3. In case of protocatechuic acid complex, therefore, for calculation of $\bar{n}$, Y has been considered to be equal to 2. In other words $\bar{n}$ has been calculated by using Calvin-Melchior method[9]. For the calculation of pL, however, Y has been considered to be 3 in order to account for the extent of -COOH group dissociation.

The pL values at different pH have been presented in table II 4.1a to II 4.4e. pL at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ correspond to log K_1 and log K_2. In case of Mg^{2+} and Tl^{+} complexes of catechol, 2,3-dihydroxynaphthalene and protocatechuic acid, the $\bar{n}$ values do not go beyond $\bar{n} = 1.0$ and hence the calculation of log K_2 values was not possible. The same situation occurs in Mg^{2+}-pyrogallol, Zn^{2+}-pyrogallol, Cd^{2+}-pyrogallol and Cd^{2+}-protocatechuic acid systems. Since in case of the complexes studied, the spreading factor is high i.e. $K_1/K_2 > 10^{2.5}$, the values of formation constant obtained by interpolation at half integral values of $\bar{n}$ can be considered to be correct. In this method, however, the formation constant values depend on the accuracy of readings at a single point and hence, can involve error.

As the values of log K_1 and log K_2 differ significantly the possibility of simultaneous formation of the species ML_1 and ML_2 does not exist. 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 formations of ML_1 and ML_2 reduce to the following forms in such cases.

$$\bar{n} + (\bar{n} - 1) K_1 [L] = 0$$
$$\bar{n} + (\bar{n} - 2) K_2 [L]^2 = 0$$

In other words, 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 II 4.1a to II 4.4e. The plots of log$(1-\bar{n})/\bar{n}$

against pL have been shown in figs. II 8 to II 35. The values of log K_1 and log K_2 can be calculated at each point on straight lines corresponding to the regions $\bar{n} > 0 < 1$ and $\bar{n} > 1 < 2$ by using the relationship

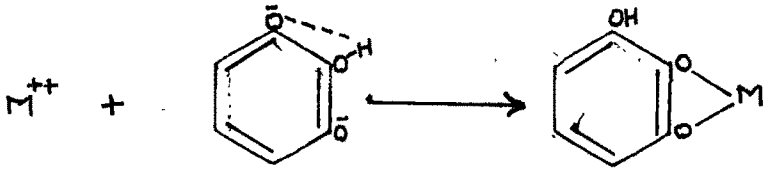
$$\log K_n = pL - \log (1 - \bar{n})/ \bar{n}$$

The average of all these values was obtained and the deviation of each individual value from the average value was calculated and from that the mean diviation was also calculated. The average values of log K_1 and log K_2 with mean diviation have been presented in table II 5.0.

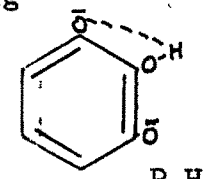
It is observed that in UO_2^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+} and Tl^{+} complexes the order of stability is 2,3-dihydroxynaphthalene complex > catechol complex > pyrogallol complex. This is in accordance with the basicities of the ligands.

In case of pyrogallol 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. The reaction in case of pyrogallol can be considered to be probably taking

place as follows :



The ligand ion being



thus the consideration of $^{P}K_{1}^{H}$ and $^{P}K_{2}^{H}$ in the calculation of pL is valid.

It is observed that protocatechuic acid complexes are more stable than catechol and pyrogallol complexes. In view of the fact that the overall acidity of protocatechuic acid is more, Murakami and coworkers[10] explained the reversal in the order of formation constant by considering that besides $L \longrightarrow M$ σ bond , there is a π overlap involving the metal $d\pi$ orbitals, lone pair orbitals of the oxygen atom and π orbitals of the benzene ring. The $M \longrightarrow L$ π interaction will be lesser, if the basicity of the ligand is high. As protocatechuic acid is more acidic than catechol and pyrogallol, the π interaction is more and hence forms more stable complexes than catechol and pyrogallol. An alternative explanation can also be extended. In protocatechuic acid the hydrogen ions liberated during coordination are from the -OH groups. Since the complex is formed beyond the range of -COOH dissociation and the resulting COO^{-} produces a positive inductive effect, $^{P}K_{1}^{H}$ and $^{P}K_{2}^{H}$ corresponding to -OH protons are more in protocatechuate ion than in catechol. Thus the -OH groups in protocatechuate ion are more basic and hence it is more

complex forming.

The values of formation constants indicate that the order of the stability constants is

$$UO_2^{2+} > Zn^{2+} > Cd^{2+} > Mg^{2+} > Tl^{+}.$$

Tl^{+} and Mg^{2+} form less stable complexes because they being non transition metal ions, possess no capture levels and have low ionic potential. The tendency of these metal ions to accept the electron pair from the ligand is less and M - L bond is less covalent in character. Tl^{+} with a still bigger size and one positive charge forms least stable complexes.

It is observed that the stabilities of Zn(II) complexes are higher than those of corresponding Ni(II) complexes, as reported by Patel and Bhattacharya.[11,12] This indicates that Metal-Ligand interaction is electrostatic in nature with small contribution due to CFSE. However, M-L bond in polyphenol complexes is expected to be sufficiently covalent in nature with significant ligand field splitting. The greater stability of Zn(II) complexes has been explained by Murakami[10] to be due to the fact that Zn(II) with d^{10} configuration contributes more to M $\rightarrow$ L π bond between metal dπ orbitals and π orbitals over the ligand. Cd(II) with bigger ionic radius has less electronegativity with greater possibility of M $\rightarrow$ L π bonding. However, there is decrease in L $\rightarrow$ M σ bonding and hence Cd(II) complexes are less stable than Zn(II) complexes.

Uranyl ion has U^{6+} bound to two oxides. Further, as revealed by the MO diagram of UO_2^{2+}, O $\rightarrow$ U π interaction is less and hence electronegativity of uranium ion is high. Consequently, UO_2^{2+} forms the most stable complexes.

Table II 1.1

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.01M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		Catechol		Uranyl UO_2^{2+}		Zinc(II)		Magnesium(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	Vol.of alkali (in ml.)	B
0.00	1.95	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	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35
2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70
2.10	2.90	2.10	2.90	2.10	2.90	2.10	2.90	2.10	2.90
2.20	3.02	2.20	3.02	2.20	3.05	2.20	3.02	2.20	3.02
2.30	3.25	2.30	3.25	2.30	3.20	2.40	3.52	2.40	3.52
2.40	3.52	2.40	3.52	2.40	3.35	2.45	3.60	2.45	3.60
2.45	3.60	2.45	3.60	2.50	3.50	2.48	3.70	2.48	3.70
2.48	3.70	2.48	3.70	2.52	3.55	2.50	5.10	2.50	5.10
2.50	9.00	2.50	5.10	2.54	3.58	2.52	6.25	2.52	6.50
2.52	9.15	2.52	6.50	2.58	3.65	2.54	6.40	2.54	6.75
2.54	9.32	2.54	7.00	2.60	3.70	2.58	6.60	2.58	7.25
2.56	9.50	2.56	7.35	2.64	3.80	2.62	6.75	2.60	7.40
2.58	9.60	2.58	7.50	2.68	3.85	2.64	6.80	2.66	7.67
2.60	9.70	2.60	7.58	2.72	3.94	2.68	6.86	2.76	8.00
2.64	9.97	2.64	7.78	2.76	4.04	2.72	6.95	2.80	8.12
2.68	10.18	2.68	7.95	2.80	4.15	2.76	7.05	2.86	8.27
2.72	10.35	2.72	8.07	2.84	4.38	2.80	7.10	2.90	8.35
2.80	10.60	2.80	8.30	2.88	4.75	2.88	7.25	2.96	8.40
2.90	10.87	2.90	8.45	2.90	4.95	2.92	7.30	3.06	8.55
3.00	11.00	3.00	8.57	2.92	5.30	3.04	7.55	3.14	8.62
		3.20	8.75	2.94	5.55	3.16	7.80	3.26	8.69
		3.40	8.90	2.96	5.84	3.20	7.90	3.32	8.73
		3.60	9.05	3.00	6.07	3.30	8.05	3.50	8.90

Table II 1.1 (contd.)

3.80	9.18	3.02	6.20	3.40	8.20	3.57	8.95
4.00	9.28	3.06	6.37	3.50	8.30	3.72	9.05
4.20	9.37	3.10	6.45	3.80	8.60	3.86	9.10
4.40	9.50	3.14	6.55	4.00	8.75	3.97	9.15
4.60	9.65	4.18	6.64	4.40	9.12	4.30	9.31
4.80	9.82	3.30	6.82	4.60	9.27	4.60	9.50
5.00	10.00	3.60	7.45	4.80	9.42	4.80	9.70
5.20	10.22	3.80	8.00	5.00	9.60	5.00	9.98
5.40	10.52	4.00	8.50	5.20	9.80	5.20	10.22
5.60	10.85	4.20	8.77	5.40	10.00	5.40	10.52
5.70	11.00	4.40	8.95	5.60	10.25	5.60	10.85
		4.60	9.20	5.80	10.50	5.75	11.00
		5.00	9.40	6.00	10.75		
		5.20	9.60	6.12	11.00		
		5.40	9.84				
		5.60	10.05				
		5.80	10.30				
		6.00	10.65				
		6.18	11.00				

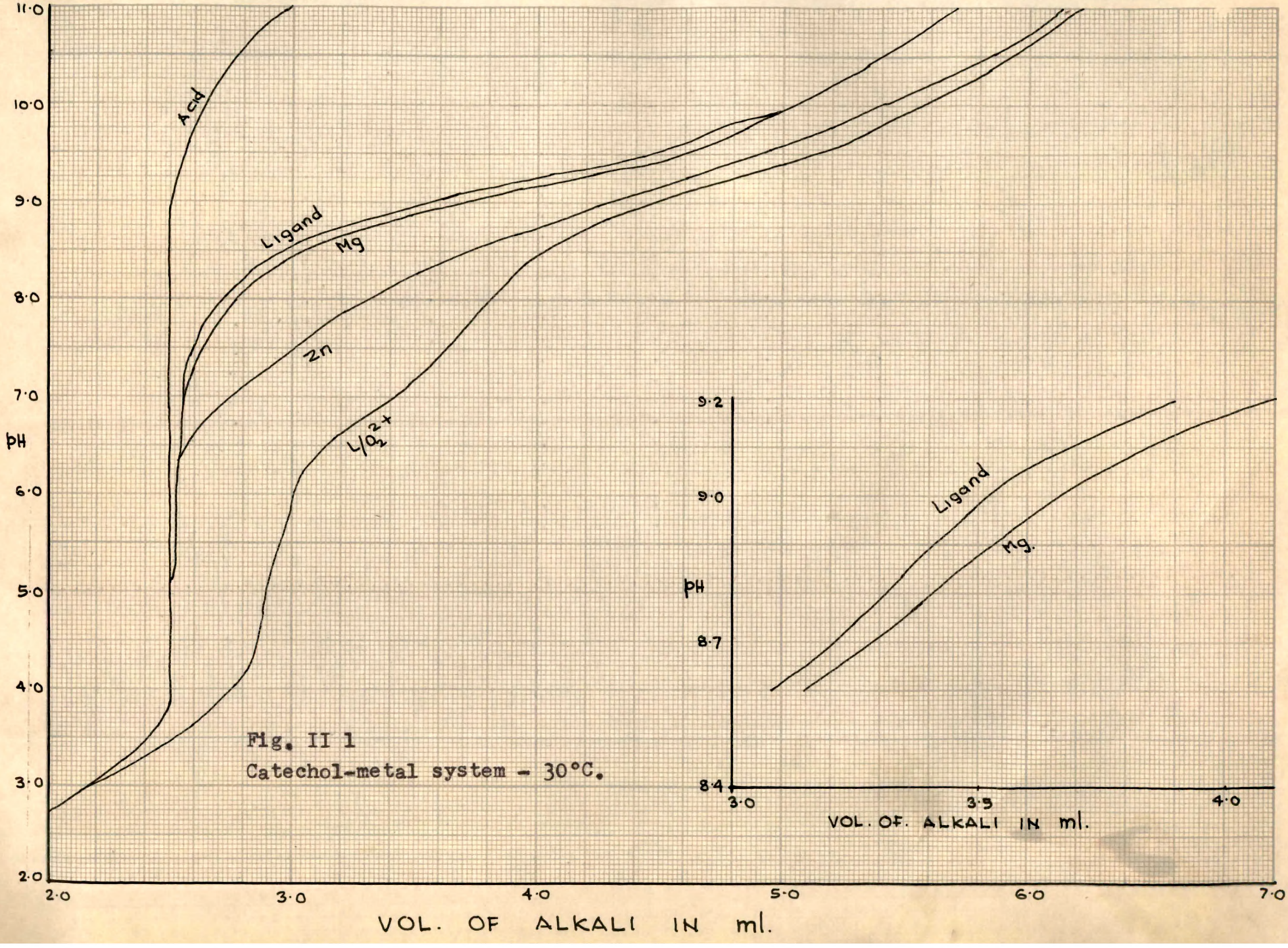


Fig. II 1
Catechol-metal system - 30°C.

Table II 1.2

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.01M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		Pyrogallol		Uranyl UO_2^{2+}		Zinc(II)		Cadmium(II)		Magnesium(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	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	0.00	1.95	0.00	1.95
1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35
2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70
2.10	2.72	2.10	2.72	2.10	2.72	2.10	2.72	2.10	2.72	2.10	2.72
2.20	2.90	2.20	2.92	2.20	2.92	2.20	2.92	2.20	2.92	2.20	2.92
2.30	3.12	2.30	3.12	2.30	3.05	2.30	3.12	2.30	3.12	2.30	3.12
2.40	3.46	2.40	3.46	2.34	3.10	2.40	3.46	2.40	3.46	2.40	3.46
2.46	3.75	2.46	3.75	2.38	3.14	2.46	3.75	2.46	3.75	2.46	3.75
2.48	3.84	2.48	3.84	2.42	3.20	2.48	3.84	2.48	3.84	2.48	3.84
2.50	9.00	2.50	5.95	2.46	3.32	2.50	5.95	2.50	5.95	2.50	5.95
2.52	9.15	2.52	6.05	2.50	3.37	2.52	6.05	2.52	6.05	2.52	6.05
2.54	9.32	2.54	6.40	2.54	3.45	2.54	6.10	2.54	6.40	2.54	6.40
2.56	9.50	2.56	6.50	2.58	3.50	2.56	6.20	2.56	6.50	2.56	6.50
2.58	9.60	2.58	6.90	2.62	3.55	2.58	6.30	2.58	6.65	2.58	6.90
2.60	9.70	2.60	7.20	2.66	3.58	2.60	6.40	2.60	6.85	2.60	7.05
2.64	9.97	2.64	7.30	2.70	3.67	2.62	6.44	2.62	7.00	2.64	7.25
2.68	10.18	2.68	7.50	2.74	3.78	2.65	6.50	2.64	7.10	2.68	7.35
2.72	10.35	2.72	7.65	2.78	3.90	2.68	6.54	2.66	7.20	2.72	7.55
2.80	10.60	2.80	7.80	2.82	4.08	2.70	6.62	2.71	7.30	2.78	7.65
2.90	10.87	2.90	8.00	2.86	4.30	2.75	6.74	2.74	7.34	2.86	7.82
3.00	11.00	3.00	8.15	2.90	4.50	2.80	6.84	2.78	7.40	2.94	7.98
		3.20	8.38	2.94	4.65	2.84	6.90 (ppt.)	2.83	7.46	3.04	8.10

Table II 1.2 (contd.)

3.40	8.57	2.98	4.85	2.86	7.50	3.12	8.20
3.60	8.70	3.06	5.18	2.90	7.56	3.20	8.30
3.80	8.90	3.10	5.28	2.92	7.60	3.30	8.40
4.00	8.94	3.18	5.45		(ppt.)	3.50	8.54
4.26	9.10	3.24	5.58			3.60	8.60
4.50	9.20	3.28	5.65			3.80	8.72
4.70	9.35	3.40	5.95			4.00	8.81
4.90	9.50	3.50	6.30			4.10	8.86
5.10	9.70	3.60	6.62			4.20	8.90
5.30	9.90	3.70	6.95			4.40	9.00
5.50	10.07	3.80	7.20			4.60	9.14
5.70	10.12	4.00	7.62			4.80	9.30
5.90	10.40	4.10	7.80			5.10	9.70
6.10	10.55	4.30	8.05			5.30	9.90
6.30	10.80	4.60	8.45			5.50	10.07
6.40	11.00	4.80	8.65			5.70	10.12
		5.00	8.85			5.80	10.30
		5.20	9.05			6.00	10.45
		5.40	9.27			6.20	10.65
		5.60	9.50			6.40	11.00
		5.80	9.75				
		6.00	10.05				
		6.20	10.28				
		6.40	10.55				
		6.60	10.90				
		6.70	11.05				

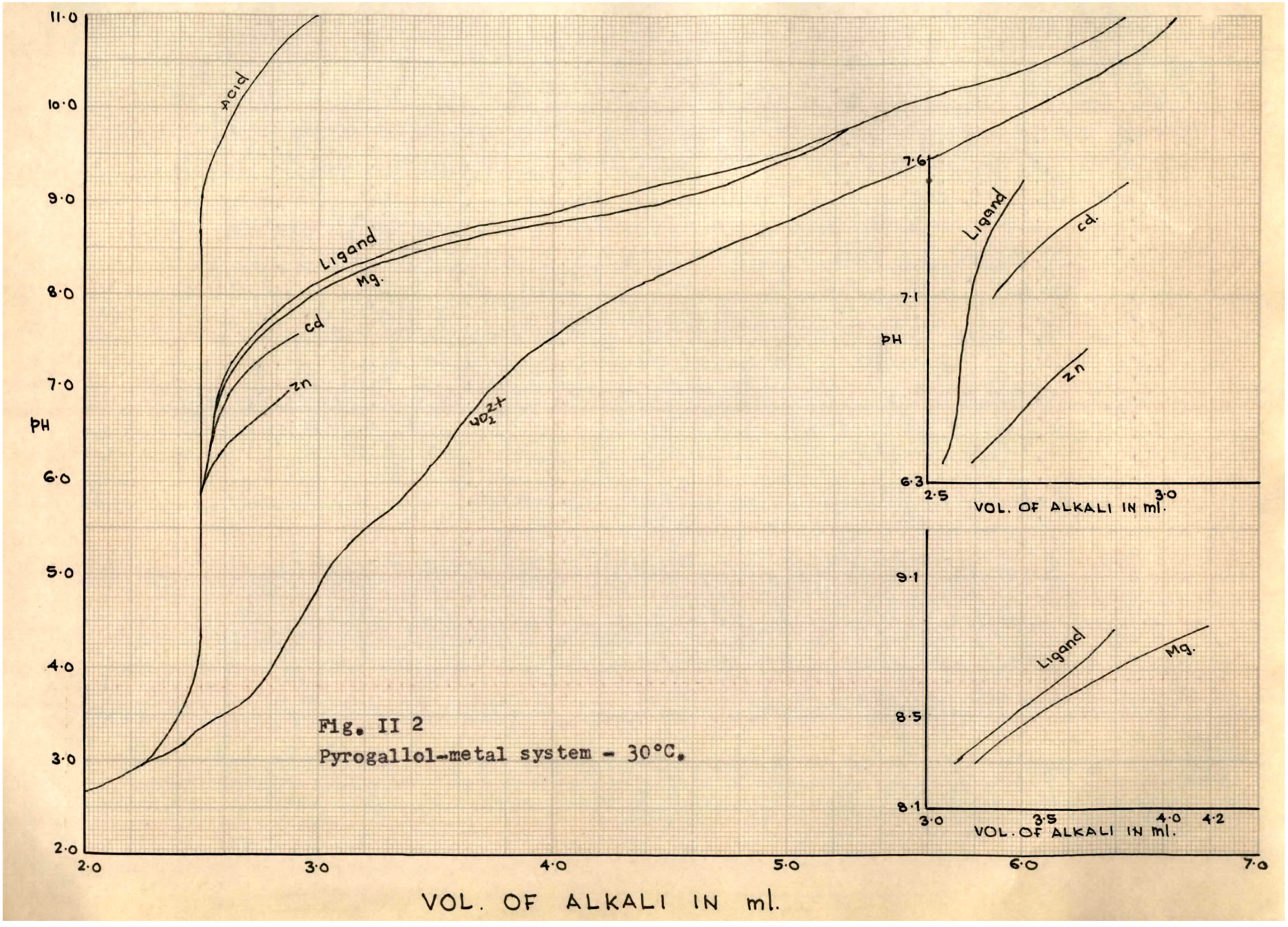


Fig. II 2
Pyrogallol-metal system - 30°C.

Table II 1.3

$N = 0.2M$ $V^\circ = 50$ ml. $\mu = 0.2M$ $t = 30^\circ C.$

$E^\circ = 0.01M$ $T_L^\circ = 0.01M$ $T_M^\circ = 0.001M$

Perchloric acid		Protocatechuic acid		Uranyl UO_2^{2+}		Zinc(II)		Magnesium(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	Vol.of alkali (in ml.)	B
0.00	1.95	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	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	2.00	2.75	2.00	2.75
2.00	2.75	2.00	2.75	2.00	2.75	2.20	2.90	2.20	2.90
2.10	2.80	2.20	2.90	2.20	2.80	2.40	3.00	2.40	3.00
2.20	2.90	2.40	3.00	2.40	3.00	2.60	3.30	2.60	3.30
2.30	3.00	2.60	3.30	2.60	3.25	2.80	3.60	2.80	3.60
2.40	3.27	2.80	3.60	2.80	3.50	3.00	3.80	3.00	3.80
2.45	3.40	3.00	3.80	3.00	3.72	3.20	4.00	3.20	4.00
2.48	3.65	3.20	4.00	3.20	3.93	3.40	4.10	3.40	4.10
2.50	9.00	3.40	4.10	3.40	4.04	3.60	4.20	3.60	4.20
2.52	9.15	3.60	4.20	3.60	4.12	3.80	4.30	3.80	4.30
2.54	9.32	3.80	4.30	4.00	4.26	4.20	4.60	4.20	4.60
2.56	9.50	4.00	4.40	4.43	4.50	4.40	4.80	4.40	4.80
2.58	9.60	4.20	4.60	4.60	4.75	4.60	5.30	4.60	5.30
2.60	9.70	4.40	4.80	4.80	5.05	4.80	6.25	4.80	6.80
2.64	9.97	4.60	5.30	4.90	5.30	4.90	6.71	5.00	7.55
2.68	10.18	4.80	6.80	5.00	5.55	5.10	7.00	5.40	8.00
2.72	10.35	4.85	7.20	5.10	5.75	5.30	7.35	5.60	8.20
2.80	10.60	4.90	7.40	5.20	6.00	5.50	7.60	5.80	8.40
2.90	10.87	5.00	7.60	5.40	6.32	5.70	7.81	5.92	8.50
3.00	11.00	5.10	7.75	5.50	6.50	5.80	7.92	6.00	8.54
		5.20	7.90	5.60	6.60	5.90	8.02	6.10	8.59

Table II 1.3 (contd.)

5.30	8.00	5.70	6.68	6.00	8.10	6.20	8.64
5.50	8.20	5.80	6.75	6.20	8.25	6.40	8.79
5.60	8.30	6.00	6.95	6.40	8.40	6.60	8.94
5.80	8.50	6.40	7.37	6.60	8.52	6.80	9.10
6.00	8.60	6.60	7.60	6.80	8.70	7.00	9.30
6.20	8.80	6.80	7.90	7.00	8.85	7.20	9.55
6.40	8.95	7.00	8.15	7.20	9.07	7.40	9.85
6.60	9.10	7.20	8.45	7.40	9.35	7.60	10.10
6.80	9.35	7.40	8.75	7.60	9.60	7.80	10.32
7.00	9.60	7.60	8.95	7.80	9.85	8.00	10.55
7.20	9.80	7.80	9.20	8.00	10.10	8.20	10.75
7.40	10.10	8.00	9.50	8.20	10.25	8.40	10.95
7.60	10.30	8.20	9.75	8.40	10.45		
7.80	10.48	8.40	10.00	8.60	10.55		
8.00	10.62	8.60	10.20	8.80	10.70		
8.20	10.75	9.00	10.50	9.00	10.80		
8.40	10.95	9.20	10.75	9.20	10.90		
		9.40	10.85	9.40	11.00		
		9.60	10.95				

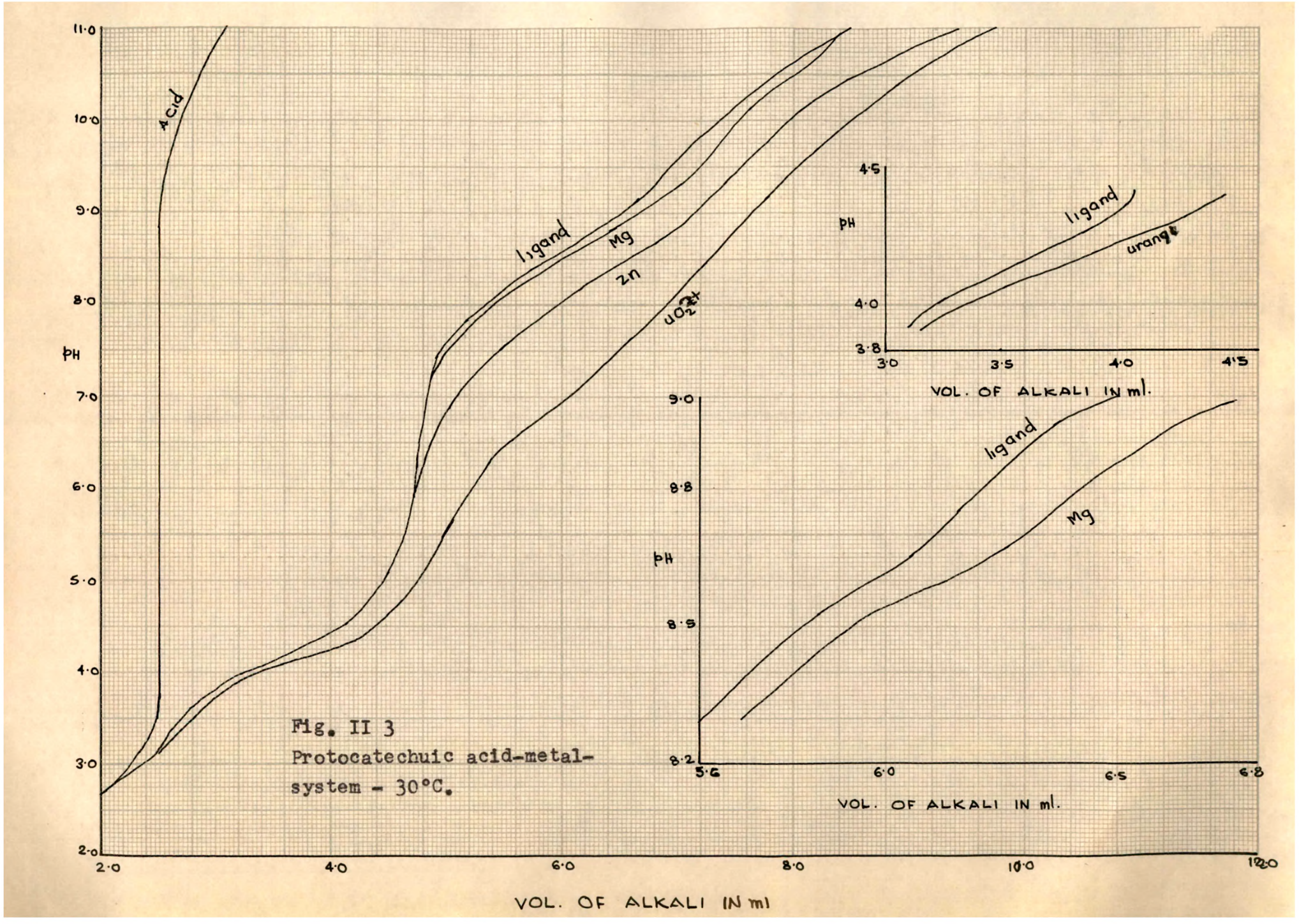


Fig. II 3
Protocatechuic acid-metal-system - 30°C.

Table II 1.4

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.01M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		2,3-dihydroxy naphthalene		Uranyl UO_2^{2+}		Zinc(II)		Magnesium(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	Vol.of alkali (in ml.)	B
0.00	1.95	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	1.00	2.15
1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35	1.50	2.35
2.00	2.75	2.00	2.75	2.00	2.75	2.00	2.75	2.00	2.75
2.10	2.82	2.10	2.82	2.10	2.82	2.10	2.82	2.10	2.82
2.20	2.95	2.20	2.95	2.20	2.95	2.20	2.95	2.20	2.95
2.30	3.10	2.30	3.10	2.30	3.10	2.30	3.10	2.30	3.10
2.40	3.27	2.40	3.27	2.40	3.20	2.40	3.27	2.40	3.27
2.45	3.50	2.45	3.50	2.50	3.32	2.48	3.85	2.48	3.85
2.48	3.85	2.50	6.00	2.54	3.40	2.50	5.75	2.50	6.00
2.50	9.00	2.52	6.25	2.62	3.55	2.52	5.85	2.52	6.15
2.52	9.15	2.54	6.50	2.68	3.65	2.56	6.07	2.56	6.50
2.54	9.32	2.58	6.90	2.76	3.81	2.60	6.25	2.60	6.72
2.56	9.50	2.64	7.15	2.84	4.05	2.66	6.35	2.66	7.00
2.58	9.60	2.70	7.32	2.88	4.25	2.72	6.45	2.72	7.20
2.60	9.70	2.82	7.60	2.92	4.55	2.84	6.62	2.84	7.50
2.64	9.97	2.90	7.75	2.98	5.00	3.06	7.05	3.02	7.80
2.68	10.18	3.00	7.90	3.06	5.50	3.12	7.16	3.12	7.90
2.72	10.35	3.20	8.12	3.18	5.85	3.24	7.38	3.20	7.96
2.80	10.60	3.40	8.27	3.30	6.02	3.30	7.45	3.32	8.05
2.90	10.87	3.60	8.40	3.50	6.45	3.40	7.55	3.40	8.10
3.00	11.00	3.80	8.55	3.70	6.82	3.60	7.78	3.54	8.20

Table II 1.4 (contd.)

4.00	8.70	3.80	7.00	3.70	7.88	3.60	8.25
4.20	8.85	3.90	7.10	3.80	7.95	3.70	8.32
4.40	9.05	4.00	7.22	3.90	8.02	3.80	8.36
4.60	9.25	4.20	7.45	4.00	8.10	3.90	8.45
4.80	9.45	4.40	7.72	4.20	8.25	4.40	8.52
5.00	9.80	4.60	8.05	4.40	8.42	4.20	8.68
5.10	10.05	4.80	8.40	4.60	8.65	4.40	8.85
5.20	10.30	5.00	8.77	4.80	8.85	4.60	9.05
5.30	10.50	5.20	9.15	5.00	9.15	4.80	9.30
5.40	10.70	5.40	9.50	5.20	9.48	5.00	9.65
5.50	10.90	5.60	9.95	5.40	9.90	5.20	10.25
5.60	11.00	5.80	10.30	5.60	10.35	5.40	10.70
		6.00	10.62	5.80	10.70	5.60	11.00
		6.20	10.85	6.00	11.00		
		6.30	11.00				

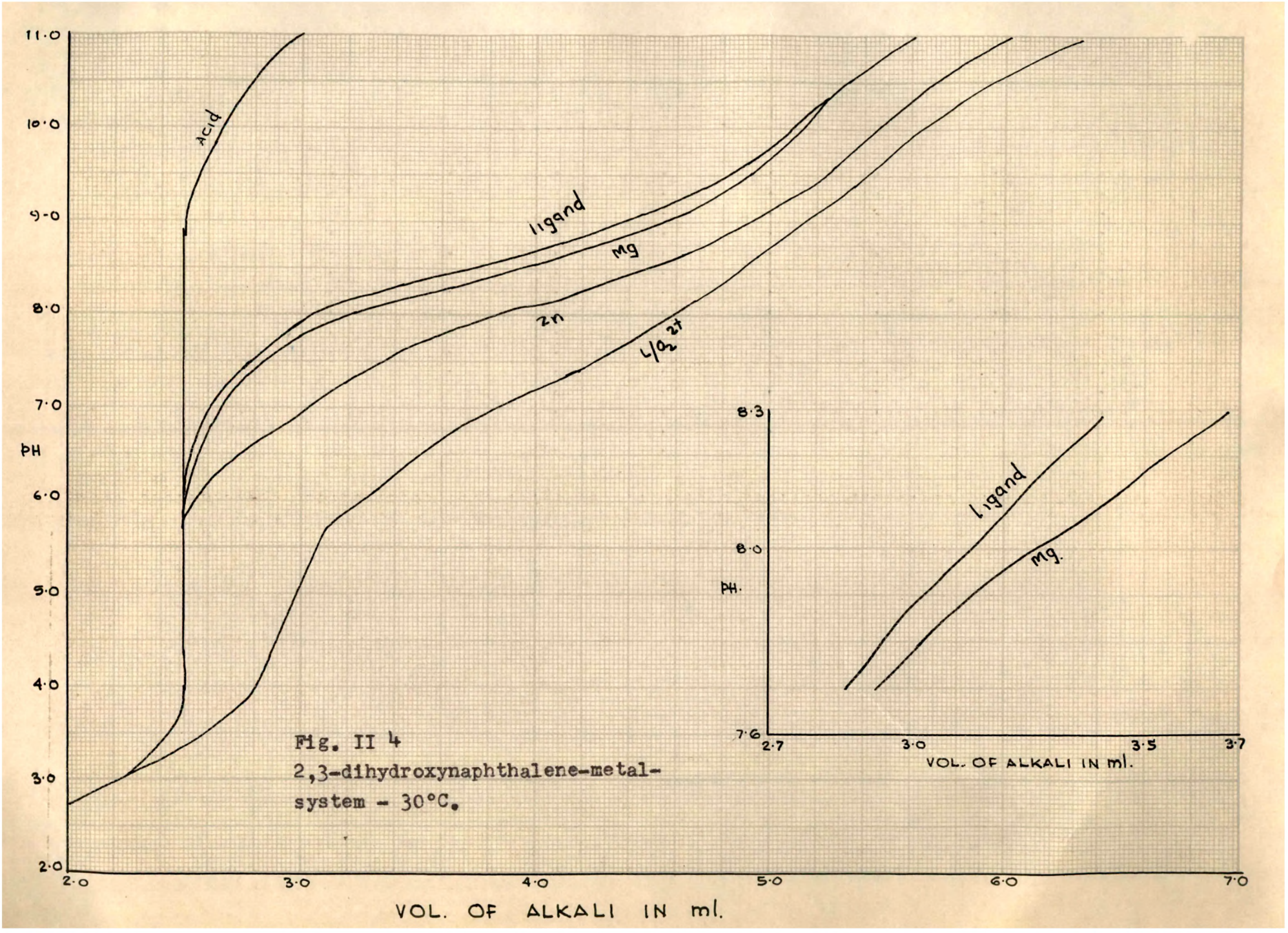


Fig. II 4
2,3-dihydroxynaphthalene-metal-system - 30°C.

Table II 2.1

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.01M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		Catechol		Cadmium(II)		Thallium(I)	
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	2.70	2.00	2.70	2.00	2.70	2.00	2.70
2.10	2.90	2.10	2.90	2.10	2.90	2.10	2.90
2.20	3.02	2.20	3.02	2.20	3.02	2.20	3.02
2.30	3.25	2.30	3.25	2.30	3.25	2.30	3.25
2.40	3.52	2.40	3.52	2.40	3.52	2.40	3.52
2.45	3.60	2.45	3.60	2.45	3.60	2.45	3.60
2.48	3.70	2.48	3.70	2.48	3.70	2.48	3.70
2.50	9.00	2.50	5.10	2.50	5.10	2.50	5.10
2.52	9.15	2.52	6.50	2.52	6.50	2.52	6.50
2.54	9.32	2.54	7.00	2.54	6.75	2.56	7.00
2.56	9.50	2.56	7.35	2.56	6.90	2.60	7.45
2.58	9.60	2.58	7.50	2.58	7.04	2.66	7.75
2.60	9.70	2.60	7.58	2.60	7.15	2.72	8.00
2.64	9.97	2.64	7.78	2.62	7.25	2.80	8.20
2.68	10.18	2.68	7.95	2.66	7.40	2.90	8.35
2.72	10.35	2.72	8.07	2.70	7.50	2.98	8.45
2.80	10.60	2.80	8.30	2.74	7.52	3.12	8.60
2.90	10.87	2.90	8.45	2.78	7.60	3.26	8.70
3.00	11.00	3.00	8.57	2.82	7.72	3.38	8.80
		3.20	8.75	2.92	7.87	3.45	8.85
		3.40	8.90	3.00	8.00	3.57	8.95
		3.60	9.05	3.10	8.10	3.62	9.00
		3.80	9.18	3.20	8.25	3.85	9.10

Table II 2.1 (contd.)

4.00	9.28	3.30	8.35	3.97	9.15
4.20	9.37	3.40	8.45	4.10	9.20
4.40	9.50	3.50	8.55	4.30	9.32
4.60	9.65	3.62	8.65	4.50	9.45
4.80	9.82	3.74	8.75	4.70	9.60
5.00	10.00	3.84	8.82	5.00	9.87
5.20	10.22	4.00	8.95	5.20	10.18
5.40	10.52	4.20	9.05	5.40	10.52
5.60	10.85	4.40	9.18	5.60	10.85
5.70	11.00	4.60	9.30	5.70	11.00
		4.80	9.45		
		5.00	9.60		
		5.20	9.82		
		5.40	10.12		
		5.60	10.40		
		5.80	10.75		
		5.90	11.00		

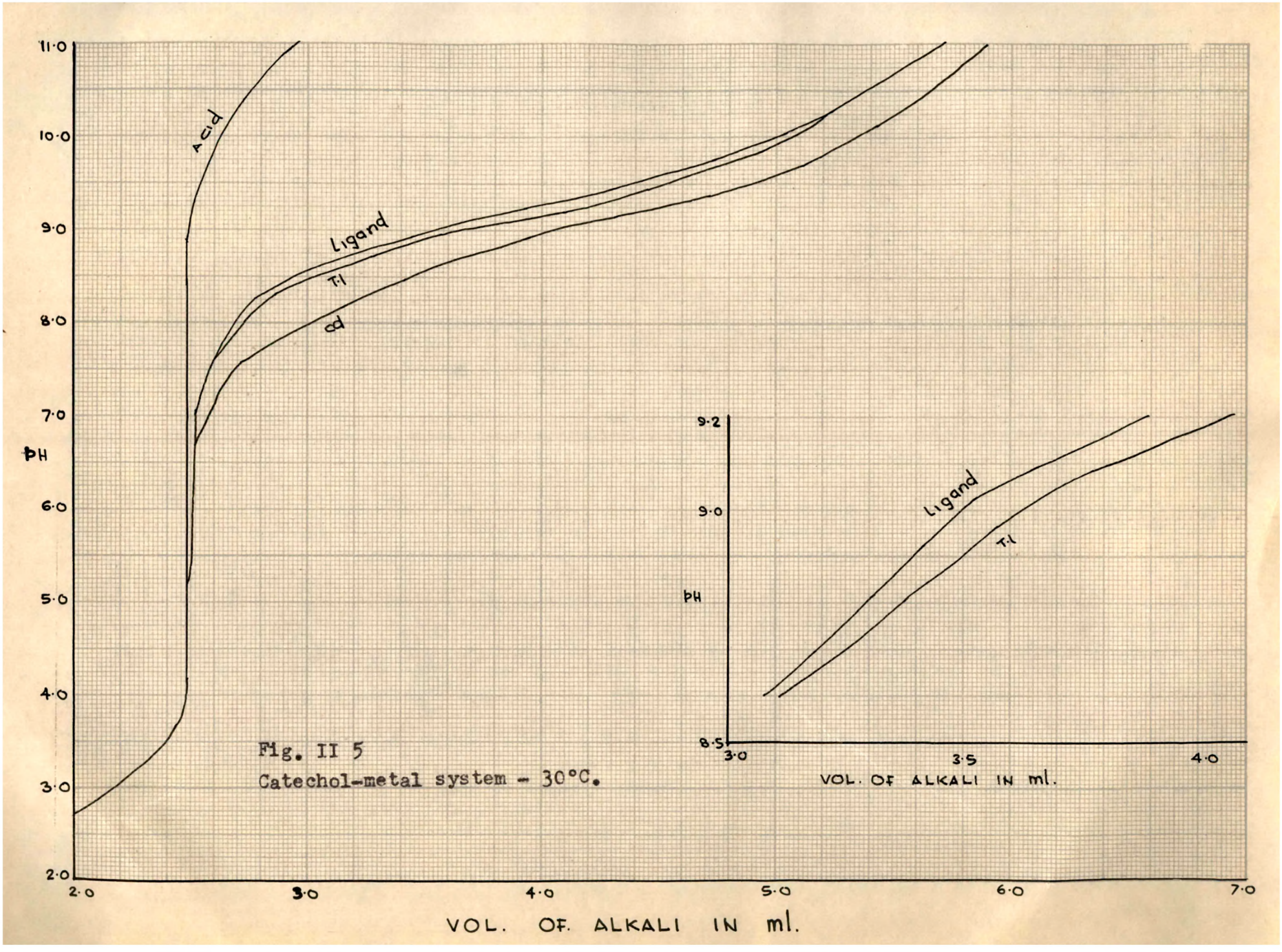


Fig. II 5
Catechol-metal system - 30°C.

Table II 2.3

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.01M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		Protocatechuic acid		Cadmium(II)		Thallium(I)	
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	2.00	2.75	2.00	2.75
2.00	2.75	2.00	2.75	2.20	2.90	2.20	2.90
2.10	2.80	2.20	2.90	2.40	3.00	2.40	3.10
2.20	2.90	2.40	3.00	2.60	3.30	2.60	3.30
2.30	3.00	2.60	3.30	2.80	3.60	2.80	3.60
2.40	3.27	2.80	3.60	3.00	3.80	3.00	3.80
2.45	3.40	3.00	3.80	3.20	4.00	3.20	4.00
2.48	3.65	3.20	4.00	3.40	4.10	3.40	4.10
2.50	9.00	3.40	4.10	3.60	4.20	3.60	4.20
2.52	9.15	3.60	4.20	3.80	4.30	3.80	4.30
2.54	9.32	3.80	4.30	4.00	4.40	4.00	4.40
2.56	9.50	4.00	4.40	4.20	4.60	4.20	4.60
2.58	9.60	4.20	4.60	4.40	4.80	4.40	4.80
2.60	9.70	4.40	4.80	4.60	5.30	4.60	5.30
2.64	9.97	4.60	5.30	4.80	6.70	4.80	6.80
2.68	10.18	4.80	6.80	4.90	7.10	5.00	7.55
2.76	10.35	4.85	7.25	5.00	7.22	5.20	7.82
2.80	10.60	4.90	7.40	5.10	7.40	5.40	8.05
2.90	10.87	5.00	7.60	5.20	7.52	5.60	8.20
3.00	11.00	5.05	7.65	5.28	7.60	5.78	8.40
		5.10	7.75	5.50	7.80	5.90	8.50
		5.20	7.90	5.60	7.85	6.00	8.55

Table II 2.3 (contd.)

5.30	8.00	5.80	8.05	6.10	8.60
5.40	8.10	6.00	8.25	6.20	8.66
5.60	8.30	6.20	8.40	6.30	8.74
5.80	8.50	6.40	8.60	6.40	8.81
6.00	8.60	6.60	8.75	6.51	9.00
6.20	8.80	6.80	8.95	6.80	9.20
6.40	8.95	7.00	9.15	7.00	9.50
6.60	9.10	7.20	9.45	7.20	9.75
6.80	9.35	7.40	9.70	7.40	10.10
7.00	9.60	7.60	9.95	7.60	10.30
7.20	9.80	7.80	10.12	7.80	10.48
7.40	10.10	8.00	10.30	8.00	10.62
7.60	10.30	8.20	10.45	8.20	10.75
7.80	10.48	8.40	10.60	8.40	10.95
8.00	10.62	8.60	10.75		
8.20	10.75	8.80	10.85		
8.40	10.95	8.90	10.95		

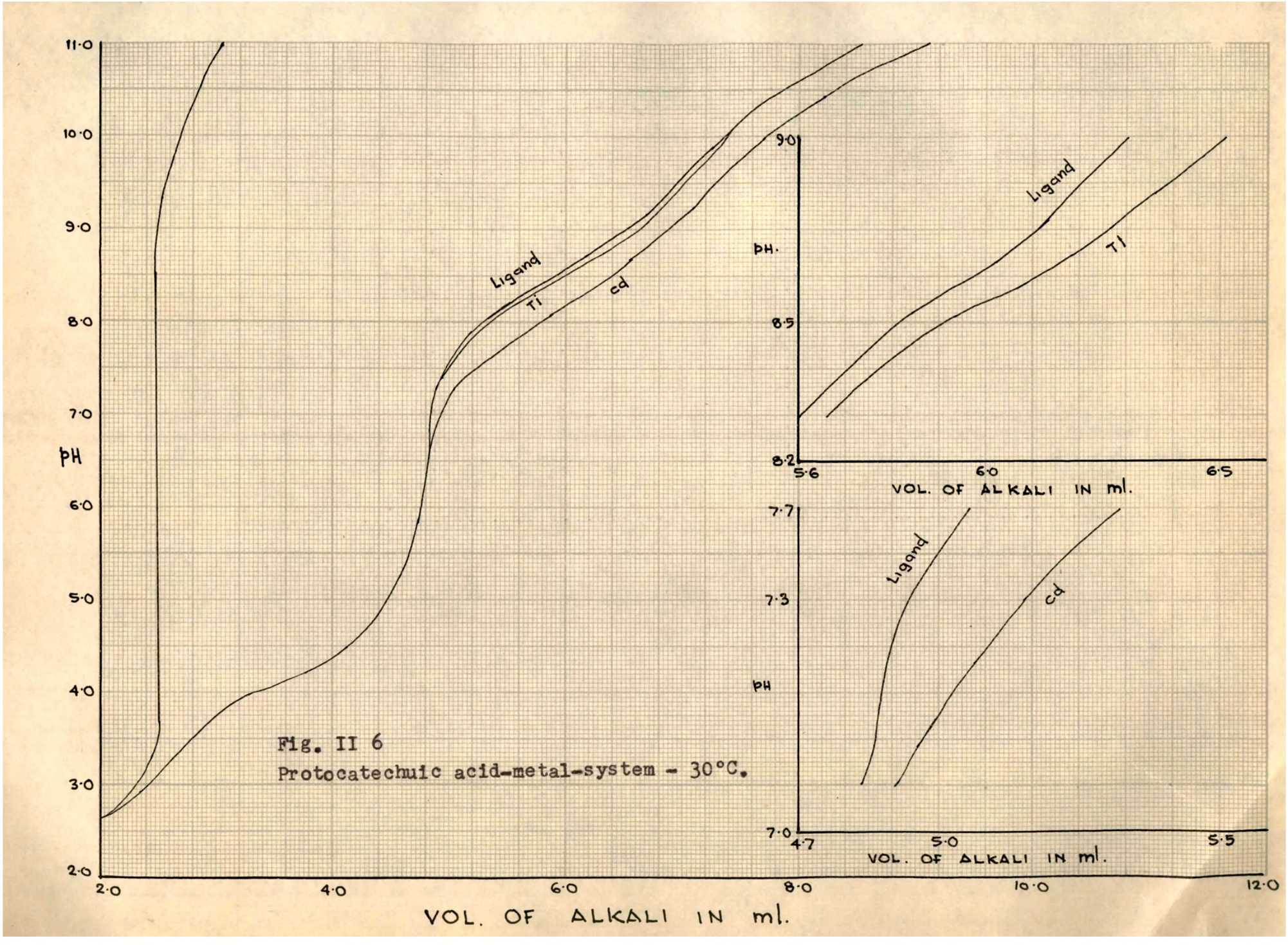


Fig. II 6
Protocatechuic acid-metal-system - 30°C.

Table II 2.4

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.01M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		2,3-dihydroxy naphthalene		Cadmium(II)		Thallium(I)	
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	2.75	2.00	2.75	2.00	2.75	2.00	2.75
2.10	2.82	2.10	2.82	2.10	2.82	2.10	2.82
2.20	2.95	2.20	2.95	2.20	2.95	2.20	2.95
2.30	3.10	2.30	3.10	2.30	3.10	2.30	3.10
2.40	3.27	2.40	3.27	2.40	3.27	2.40	3.27
2.45	3.50	2.45	3.50	2.48	3.85	2.48	3.85
2.48	3.85	2.48	3.85	2.50	5.90	2.50	6.00
2.50	9.00	2.50	6.00	2.52	6.05	2.52	6.25
2.52	9.15	2.52	6.25	2.56	6.55	2.58	6.90
2.54	9.32	2.54	6.50	2.60	6.70	2.60	7.00
2.56	9.50	2.58	6.90	2.66	6.88	2.66	7.10
2.58	9.60	2.64	7.15	2.72	7.00	2.70	7.30
2.60	9.70	2.70	7.32	2.78	7.08	2.82	7.55
2.64	9.97	2.82	7.60	2.84	7.20	2.90	7.70
2.68	10.18	3.00	7.90	2.98	7.30	3.00	7.80
2.72	10.35	3.20	8.12	3.06	7.55	3.05	7.85
2.80	10.60	3.40	8.27	3.12	7.65	3.10	7.90
2.90	10.87	3.60	8.40	3.18	7.72	3.20	7.98
3.00	11.00	3.80	8.55	3.24	7.80	3.28	8.04
		4.00	8.70	3.30	7.85	3.36	8.10
		4.20	8.85	3.40	7.95	3.43	8.15

Table II 2.4 (contd.)

4.40	9.05	3.50	8.02	3.50	8.21
4.60	9.25	3.60	8.10	3.58	8.27
4.80	9.45	3.70	8.15	3.65	8.32
5.00	9.80	3.80	8.22	3.70	8.35
5.10	10.05	3.90	8.30	3.80	8.39
5.20	10.30	4.00	8.38	4.00	8.55
5.30	10.50	4.20	8.50	4.20	8.75
5.40	10.70	4.40	8.62	4.40	9.00
5.50	10.90	4.60	8.75	4.60	9.25
5.60	11.00	4.80	9.00	4.80	9.45
		5.00	9.30	5.00	9.80
		5.20	9.65	5.20	10.30
		5.40	10.10	5.40	10.70
		5.60	10.40	5.60	11.00
		5.80	10.70		
		6.00	11.00		

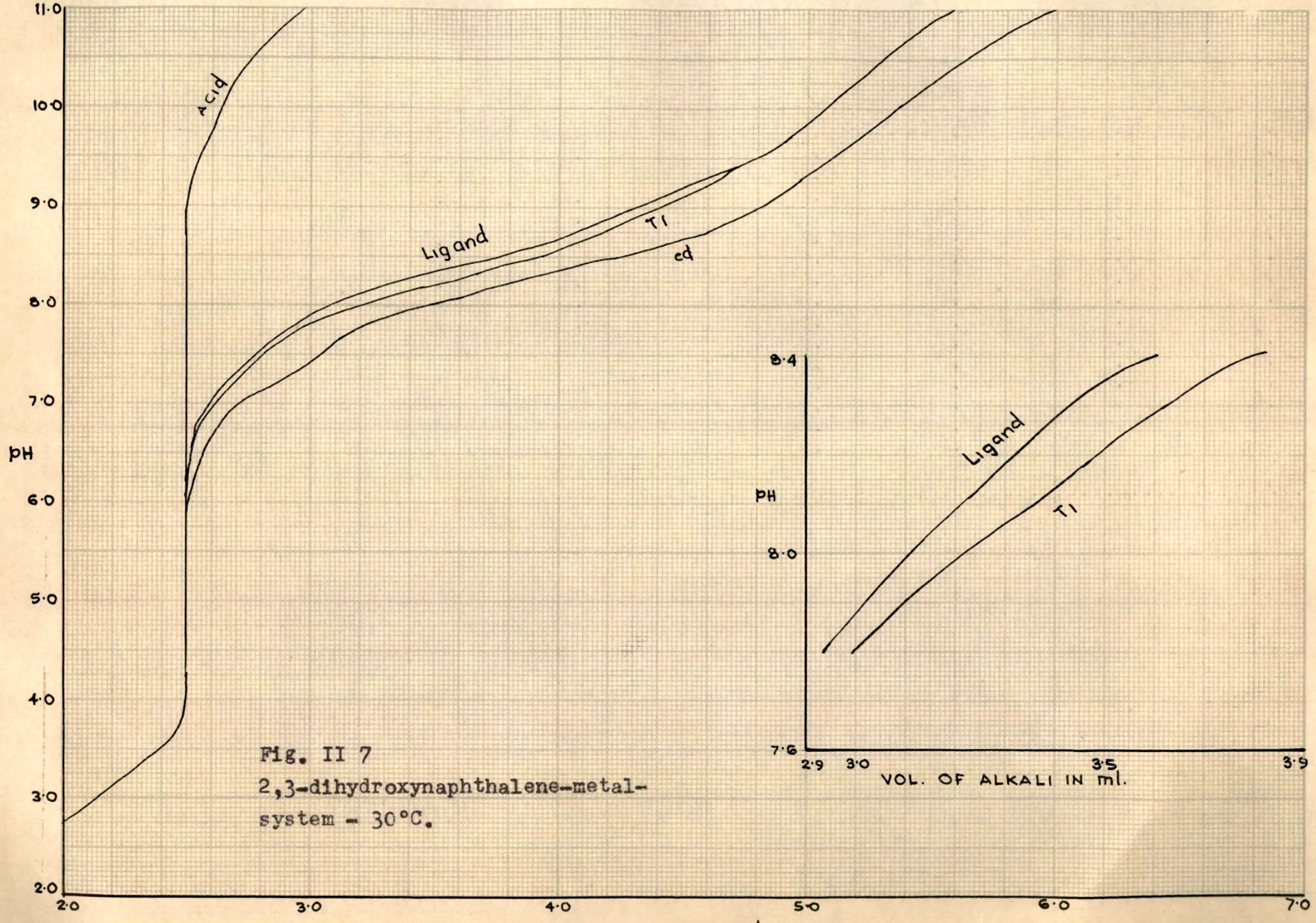


Fig. II 7
2,3-dihydroxynaphthalene-metal-system - 30°C.

Table II 3.0

Proton ligand stability constants of various ligands (μ = 0.2M, 30°C.).

		Ligand (L)			
		Catechol	Pyrogallol	Protocatechuic acid	2,3-Dihydroxy-naphthalene
$\log {}^{P}K_1^H$	(A)	11.71	10.85	12.24	12.41
$\log {}^{P}K_1^H$	(B)	11.30	10.65	12.16	12.55
$\log {}^{P}K_2^H$		9.10	8.67	8.84	8.43
$\log {}^{P}K_3^H$		-	-	4.32	-

(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 II 4.1a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of UO_2^{2+} - catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
3.50	2.00_0	2.43	2.47	0.04	0.08_0	1.06_0	15.42_4	14.36_4
3.60	2.00_0	2.46	2.53	0.06	0.12_0	0.86_5	15.22_6	14.36_1
3.70	2.00_0	2.48	2.57	0.09	0.18_0	0.65_8	15.02_9	14.37_1
3.80	2.00_0	2.49	2.64	0.14	0.28_0	0.45_4	14.83_3	14.37_9
3.90	2.00_0	2.50	2.70	0.20	0.40_0	0.17_6	14.53_9	14.36_3
4.00	2.00_0	2.50	2.74	0.24	0.48_0	$\bar{0}.03_4$	14.34_3	14.30_9
4.10	2.00_0	2.50	2.78	0.28	0.56_0	$\bar{1}.89_5$	14.24_7	14.35_2
6.50	1.99_2	2.52	3.11	0.59	1.18_4	0.63_6	9.48_1	8.84_5
6.60	1.99_2	2.52	3.16	0.64	1.28_5	0.39_9	9.28_6	8.88_7
6.70	1.99_2	2.52	3.20	0.68	1.36_5	0.24_0	9.09_0	8.85_0
6.80	1.98_4	2.54	3.28	0.74	1.49_1	$\bar{0}.01_5$	8.89_7	8.88_2
6.90	1.98_4	2.54	3.30	0.79	1.59_2	$\bar{1}.83_8$	8.70_3	8.86_5

$\log K_1 = 14.35 \pm 0.05$

$\log K_2 = 8.86 \pm 0.05$

Table II 4.2a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of UO_2^{2+} - pyrogallolate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
3.20	2.00_0	2.37	2.43	0.06	0.12_0	0.86_5	14.94_5	14.08_0
3.30	2.00_0	2.39	2.47	0.08	0.16_0	0.72_0	14.74_8	14.02_6
3.40	2.00_0	2.40	2.51	0.11	0.22_0	0.54_9	14.55_1	14.00_2
3.50	2.00_0	2.41	2.58	0.17	0.34_0	0.28_8	14.35_6	14.06_8
3.60	2.00_0	2.42	2.67	0.25	0.50_0	$\bar{0}.00_0$	14.06_4	14.06_4
3.70	2.00_0	2.43	2.71	0.28	0.56_0	$\bar{1}.89_5$	13.96_7	14.07_2
3.80	2.00_0	2.44	2.75	0.31	0.62_0	$\bar{1}.78_7$	13.77_1	13.98_4
5.20	2.00_0	2.50	3.07	0.57	1.14_0	0.78_8	10.99_7	10.20_9
5.30	2.00_0	2.50	3.11	0.61	1.22_0	0.54_9	10.79_2	10.24_3
5.40	2.00_0	2.50	3.16	0.66	1.32_0	0.33_7	10.60_8	10.27_1
5.50	2.00_0	2.50	3.20	0.70	1.40_0	0.17_6	10.41_2	10.23_6
5.60	2.00_0	2.50	3.25	0.75	1.50_0	0.00_0	10.21_7	10.21_7
5.70	2.00_0	2.50	3.31	0.81	1.62_0	$\bar{1}.78_7$	10.02_4	10.23_7

$\log K_1 = 14.05 \pm 0.04$

$\log K_2 = 10.23 \pm 0.04$

Fig. II 10

UO_2^{2+}-Pyrogallol system - 30°C.

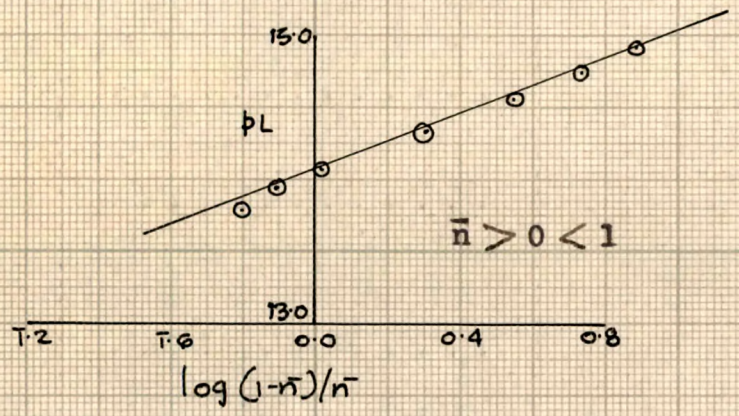


Fig. II 11

UO_2^{2+}-Pyrogallol system - 30°C.

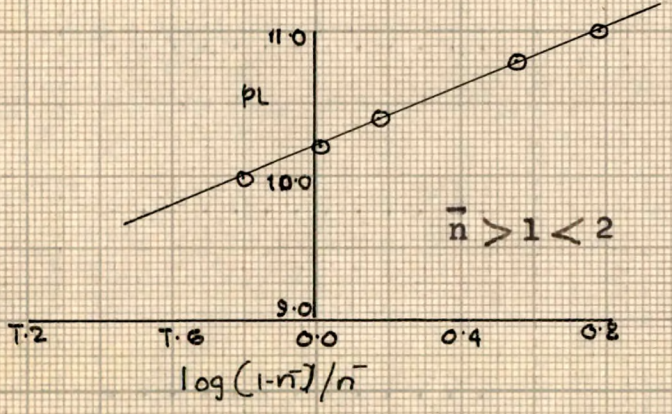


Fig. II 8

UO_2^{2+}-Catechol system - 30°C.

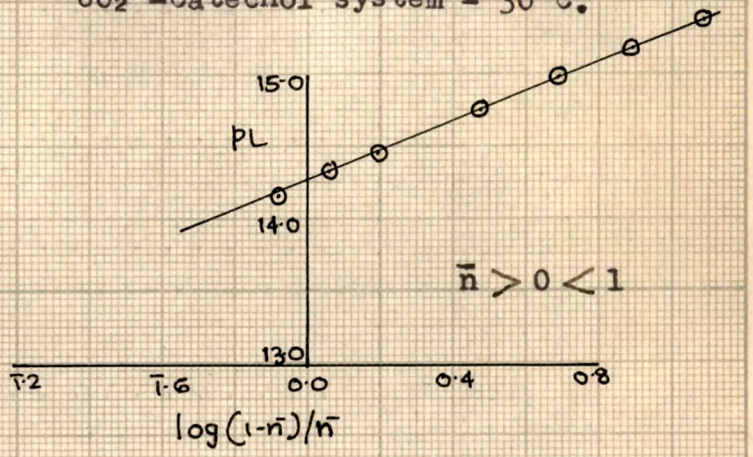


Fig. II 9

UO_2^{2+}-Catechol system - 30°C.

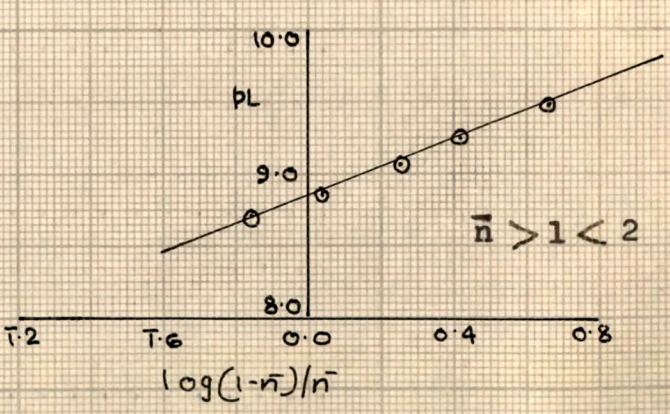


Table II 4.3a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of UO_2^{2+} - protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.90	2.00_0	3.10	3.15	0.05	0.10_0	0.99_5	15.79_0	14.79_5
4.00	2.00_0	3.20	3.28	0.08	0.16_0	0.72_0	15.52_5	14.80_5
4.10	2.00_0	3.40	3.53	0.13	0.26_0	0.45_4	15.26_5	14.81_1
4.20	2.00_0	3.60	3.80	0.20	0.40_0	0.17_6	15.01_9	14.84_3
4.30	2.00_0	3.80	4.08	0.28	0.56_0	$\bar{1}.89_5$	14.77_0	14.87_5
4.40	2.00_0	4.00	4.33	0.33	0.66_0	$\bar{1}.71_2$	14.52_8	14.81_6
4.50	2.00_0	4.06	4.45	0.39	0.78_0	$\bar{1}.45_0$	14.29_1	14.84_1
6.20	2.00_0	4.74	5.35	0.61	1.22_0	0.54_9	10.70_6	10.15_7
6.30	2.00_0	4.74	5.39	0.65	1.28_0	0.36_8	10.50_4	10.13_6
6.40	2.00_0	4.76	5.45	0.69	1.38_0	0.21_4	10.31_3	10.10_1
6.50	2.00_0	4.76	5.51	0.75	1.50_0	0.00_0	10.12_0	10.12_0
6.60	2.00_0	4.78	5.59	0.81	1.62_0	$\bar{1}.78_7$	9.92_9	10.14_2
6.70	2.00_0	4.78	5.65	0.87	1.74_0	$\bar{1}.54_6$	9.73_4	10.18_8

$\log K_1 = 14.82 \pm 0.03$

$\log K_2 = 10.13 \pm 0.05$

Table II 4.4a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of UO_2^{2+} - 2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.30	2.00_0	2.42	2.49	0.07	0.14_0	0.78_8	16.37_6	15.58_8
3.40	2.00_0	2.44	2.53	0.09	0.18_0	0.65_0	16.20_8	15.55_0
3.50	2.00_0	2.44	2.57	0.13	0.26_0	0.45_4	16.01_3	15.55_9
3.60	2.00_0	2.46	2.64	0.18	0.36_0	0.24_9	15.81_7	15.56_8
3.70	2.00_0	2.47	2.71	0.24	0.48_0	0.03_4	15.62_3	15.58_9
3.80	2.00_0	2.47	2.76	0.29	0.58_0	$\bar{1}.85_9$	15.42_8	15.56_9
3.90	2.00_0	2.48	2.81	0.33	0.66_0	$\bar{1}.71_2$	15.23_2	15.52_0
5.50	2.00_0	2.48	3.06	0.56	1.12_0	0.86_5	12.05_7	11.19_2
5.60	2.00_0	2.50	3.08	0.58	1.16_0	0.72_0	11.85_9	11.13_9
5.70	2.00_0	2.50	3.11	0.61	1.22_0	0.54_9	11.66_2	11.11_3
5.80	2.00_0	2.50	3.16	0.66	1.32_0	0.32_7	11.46_8	11.14_1
5.90	2.00_0	2.50	3.22	0.72	1.44_0	0.10_4	11.27_5	11.17_1
6.00	1.98_8	2.51	3.28	0.77	1.54_9	$\bar{1}.91_3$	11.08_0	11.16_7
6.10	1.98_8	2.51	3.32	0.81	1.63_0	$\bar{1}.76_8$	10.88_5	11.11_7

$\log K_1 = 15.56 \pm 0.04$

$\log K_2 = 11.14 \pm 0.03$

Fig. II 12

UO_2^{2+}-Protocatechuic acid system - 30°C.

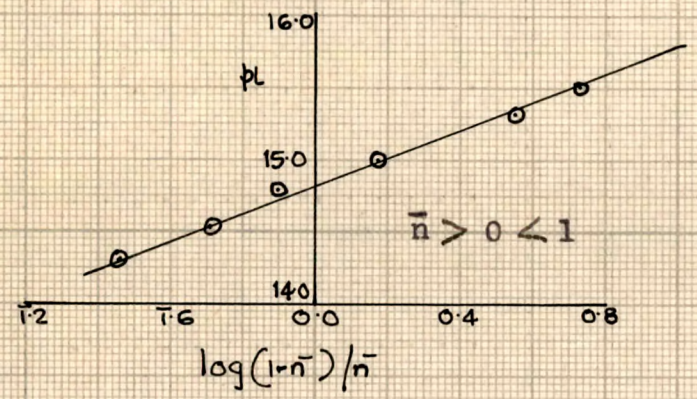


Fig. II 13

UO_2^{2+}-Protocatechuic acid system - 30°C.

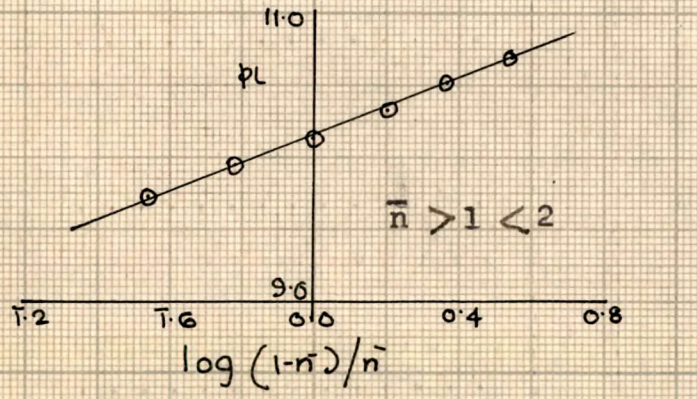


Fig. II 14

UO_2^{2+}-2,3-dihydroxynaphthalene system - 30°C.

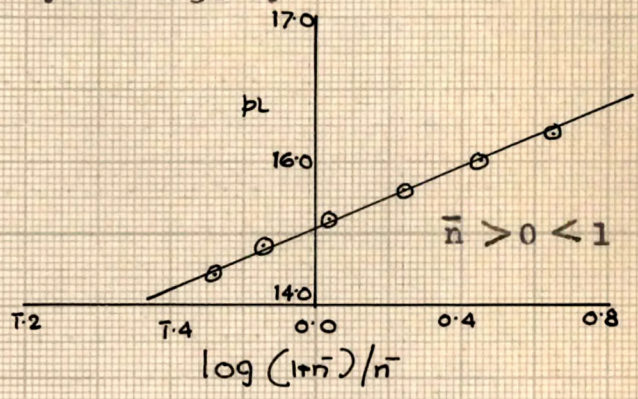


Fig. II 15

UO_2^{2+}-2,3-dihydroxynaphthalene system - 30°C.

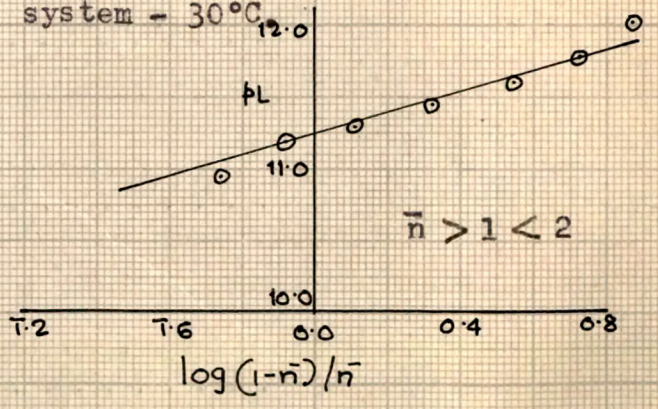


Table II 4.1b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Zn - catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.80	1.98_4	2.54	2.64	0.10	0.20_1	0.59_9	8.83_3	-
6.90	1.98_4	2.54	2.69	0.15	0.30_2	0.36_3	8.63_8	8.27_5
7.00	1.98_2	2.54	2.74	0.20	0.40_3	0.17_0	8.44_4	8.27_4
7.10	1.98_0	2.55	2.79	0.24	0.48_4	0.02_7	8.24_9	8.22_2
7.20	1.97_6	2.56	2.85	0.29	0.58_6	$\bar{1}.84_9$	8.05_4	8.20_5
7.30	1.97_2	2.57	2.92	0.35	0.70_9	$\bar{1}.61_3$	7.87_8	8.26_5
7.40	1.96_2	2.59	2.97	0.38	0.77_3	$\bar{1}.46_7$	7.66_8	8.20_0
7.90	1.93_6	2.66	3.20	0.56	1.15_6	0.73_3	6.70_7	6.02_4
8.00	1.92_4	2.69	3.28	0.59	1.22_8	0.52_9	6.51_7	5.98_8
8.10	1.90_8	2.73	3.36	0.63	1.32_0	0.32_7	6.32_9	6.00_2
8.20	1.88_8	2.78	3.44	0.66	1.37_7	0.21_8	6.13_9	5.92_1
8.30	1.86_8	2.83	3.52	0.69	1.47_7	0.04_0	5.95_1	5.91_1
8.40	1.84_8	2.88	3.60	0.72	1.57_9	$\bar{1}.86_1$	5.78_3	-

$\log K_1 = 8.24 \pm 0.04$

$\log K_2 = 5.96 \pm 0.06$

Table II 4.2b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Zn - pyrogallolate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.40	1.97_6	2.54	2.60	0.06	0.12_1	0.86_1	8.54_9	7.68_8
6.50	1.97_6	2.56	2.65	0.09	0.18_2	0.65_2	8.35_3	7.70_1
6.60	1.97_6	2.56	2.69	0.13	0.26_3	0.44_7	8.15_7	7.71_0
6.70	1.97_6	2.56	2.73	0.17	0.34_4	0.28_0	7.96_2	7.68_2
6.80	1.97_2	2.57	2.78	0.21	0.42_5	0.13_1	7.76_8	7.63_7
6.90	1.97_2	2.57	2.84	0.27	0.54_7	$\bar{1}.91_8$	7.57_5	7.65_7

$\log K_1 = 7.67 \pm 0.04$

Fig. II 16

Zn(II)-Catechol system - 30°C.

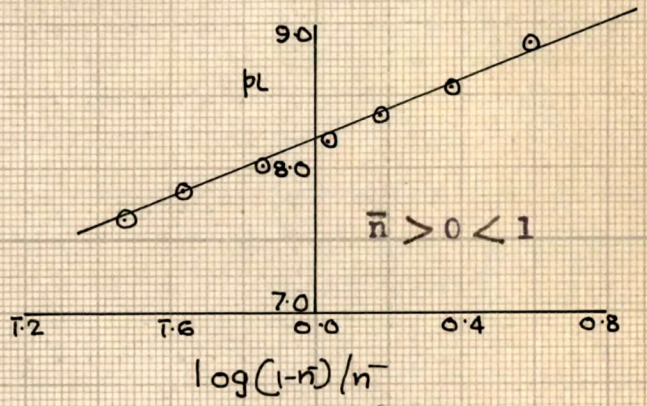


Fig. II 17

Zn(II)-Catechol system - 30°C.

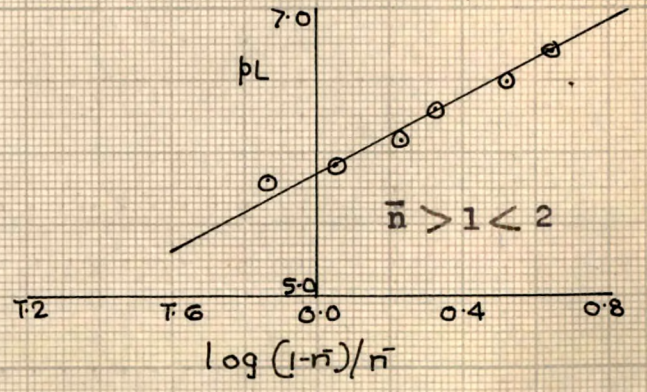


Fig. II 18

Zn(II)-Pyrogallol system - 30°C.

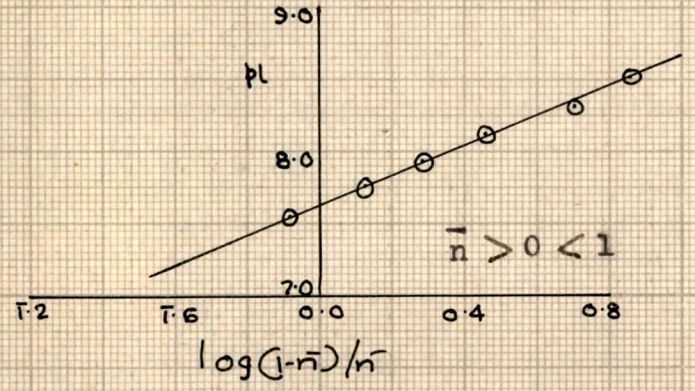


Table II 4.3b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Zn-protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.60	2.00_0	4.78	4.84	0.06	0.12_0	0.85_6	9.84_7	-
6.70	2.00_0	4.78	4.89	0.11	0.22_0	0.54_9	9.65_3	9.10_4
6.80	2.00_0	4.80	4.96	0.16	0.32_0	0.32_7	9.45_9	9.13_2
6.90	2.00_0	4.82	5.03	0.21	0.42_0	0.14_0	9.26_5	9.12_5
7.00	2.00_0	4.83	5.09	0.26	0.52_0	$\bar{1}.96_5$	9.07_1	9.10_6
7.10	2.00_0	4.84	5.13	0.29	0.58_0	$\bar{1}.85_9$	8.97_6	9.11_7
7.20	2.00_0	4.86	5.18	0.32	0.64_0	$\bar{1}.75_0$	8.68_0	-
7.80	1.93_5	5.16	5.71	0.54	1.11_5	0.88_6	7.53_7	6.65_1
7.90	1.92_0	5.20	5.76	0.56	1.16_6	0.70_1	7.34_8	6.64_7
8.00	1.88_0	5.30	5.88	0.58	1.23_4	0.51_5	7.16_4	6.64_9
8.10	1.84_0	5.40	6.01	0.61	1.32_6	0.31_5	6.98_3	6.66_8
8.20	1.80_0	5.50	6.14	0.64	1.42_2	0.13_6	6.80_6	6.67_0
8.30	1.76_0	5.60	6.28	0.67	1.52_2	$\bar{1}.96_1$	6.63_3	6.67_2
8.40	1.72_0	5.70	6.40	0.70	1.62_7	$\bar{1}.77_4$	6.46_7	6.69_3

$\log K_1 = 9.11 \pm 0.02$

$\log K_2 = 6.65 \pm 0.04$

Table II 4.4b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Zn - 2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.20	1.98_8	2.51	2.58	0.07	0.14_0	0.78_8	10.61_0	-
6.30	1.98_8	2.51	2.63	0.12	0.24_1	0.49_8	10.41_6	9.91_8
6.40	1.98_0	2.53	2.70	0.17	0.34_3	0.28_2	10.22_1	9.93_9
6.50	1.98_0	2.53	2.75	0.22	0.44_4	0.09_7	10.02_7	9.93_0
6.60	1.97_8	2.56	2.83	0.27	0.54_5	$\bar{1}.92_1$	9.83_4	9.91_3
6.70	1.97_8	2.56	2.88	0.32	0.62_6	$\bar{1}.77_6$	9.64_1	-
6.80	1.97_2	2.57	2.94	0.37	0.75_4	$\bar{1}.51_3$	9.44_7	9.93_4
6.90	1.96_8	2.58	3.00	0.42	0.85_3	$\bar{1}.23_6$	9.25_6	-
7.40	1.91_2	2.72	3.27	0.55	1.15_0	0.75_3	8.32_0	7.56_7
7.50	1.89_2	2.77	3.34	0.57	1.20_4	0.60_1	8.11_1	7.51_0
7.60	1.87_2	2.82	3.42	0.60	1.29_2	0.38_4	7.92_8	7.54_4
7.70	1.85_2	2.87	3.52	0.65	1.40_3	0.17_0	7.74_9	7.57_9
7.80	1.82_4	2.94	3.62	0.68	1.49_0	0.01_7	7.57_1	7.55_4
7.90	1.79_2	3.02	3.73	0.71	1.58_4	$\bar{1}.85_2$	7.39_8	7.54_6

$\log K_1 = 9.92 \pm 0.01$

$\log K_2 = 7.55 \pm 0.04$

Fig. II 19

Zn(II)-Protocatechuic acid system - 30°C.

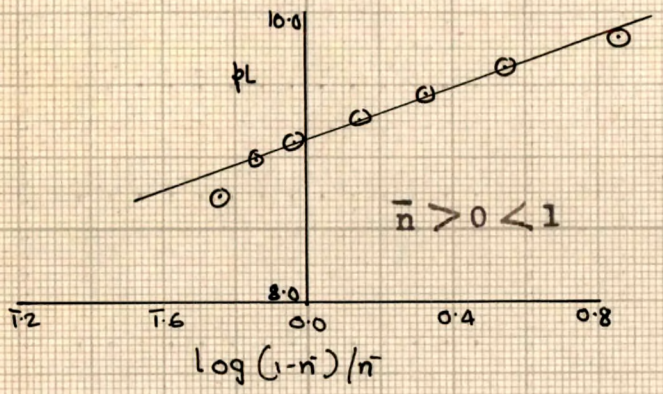


Fig. II 20

Zn(II)-Protocatechuic acid system - 30°C.

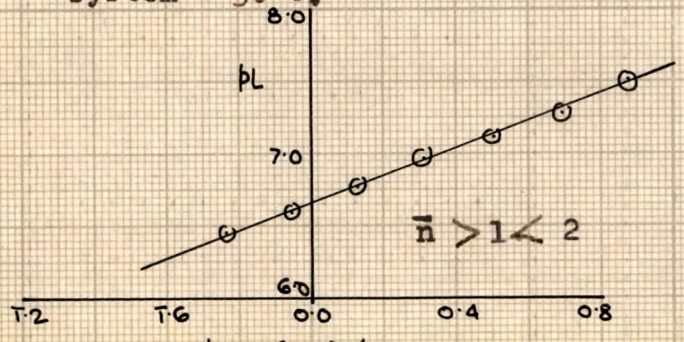


Fig. II 21

Zn(II)-2,3-dihydroxynaphthalene system - 30°C.

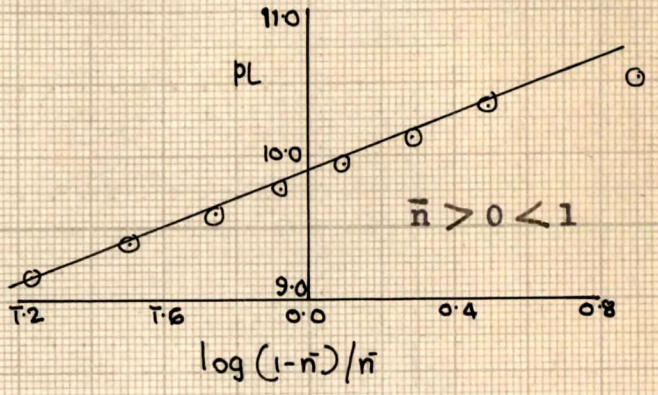


Fig. II 22

Zn(II)-2,3-dihydroxynaphthalene system - 30°C.

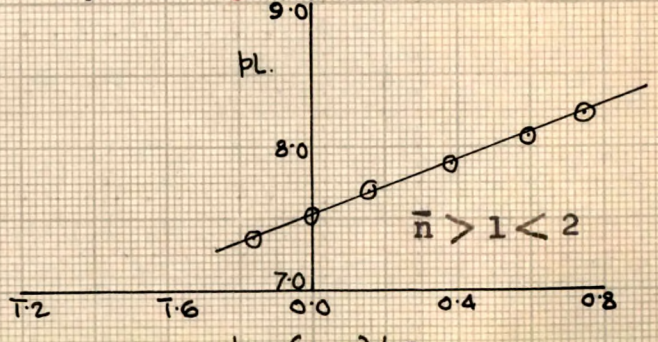


Table II 4.1c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cd - catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.40	1.96_2	2.59	2.65	0.06	0.12_2	0.85_7	7.63_5	6.77_8
7.50	1.96_0	2.60	2.70	0.10	0.20_4	0.59_9	7.44_1	-
7.60	1.95_2	2.62	2.75	0.13	0.26_6	0.44_0	7.24_7	6.80_7
7.70	1.94_8	2.64	2.80	0.16	0.32_8	0.31_5	7.05_2	6.74_1
7.80	1.94_4	2.65	2.86	0.21	0.43_2	0.11_8	6.86_2	6.74_4
7.90	1.93_6	2.67	2.93	0.26	0.53_7	$\bar{1}.93_5$	6.67_0	6.73_5
8.00	1.92_4	2.70	3.00	0.30	0.62_3	$\bar{1}.78_1$	6.48_2	6.70_1
8.70	1.74_4	3.20	3.69	0.49	1.12_2	0.85_7	5.22_8	4.37_1
8.80	1.71_9	3.30	3.80	0.50	1.16_1	0.71_7	5.06_1	4.34_4
8.90	1.67_2	3.40	3.91	0.51	1.21_7	0.55_7	4.90_1	4.34_4
9.00	1.64_0	3.50	4.02	0.52	1.26_5	0.44_3	4.74_6	4.30_3
9.10	1.56_0	3.70	4.24	0.54	1.38_1	0.21_0	4.60_0	4.39_0
9.20	1.48_0	3.90	4.44	0.54	1.45_6	0.07_6	4.45_9	4.38_3
9.30	1.44_9	4.00	4.55	0.55	1.51_4	$\bar{1}.97_5$	4.32_1	4.34_6

$\log K_1 = 6.76 \pm 0.06$

$\log K_2 = 4.35 \pm 0.05$

Table II 4.2c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cd - pyrogallolate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.10	1.96_4	2.59	2.64	0.05	0.10_1	0.94_9	7.15_7	6.20_8
7.20	1.96_0	2.60	2.67	0.07	0.14_2	0.78_1	6.96_2	6.18_1
7.30	1.95_2	2.62	2.71	0.09	0.18_4	0.64_6	6.76_9	6.12_3
7.40	1.94_4	2.64	2.78	0.14	0.28_8	0.39_3	6.57_8	6.18_5
7.50	1.92_8	2.68	2.86	0.18	0.37_3	0.22_5	6.38_9	6.16_4
7.60	1.92_0	2.70	2.92	0.22	0.45_8	0.07_3	6.20_0	6.12_7

$\log K_1 = 6.15 \pm 0.06$

Fig. II 23

Cd(II)-Catechol system - 30°C.

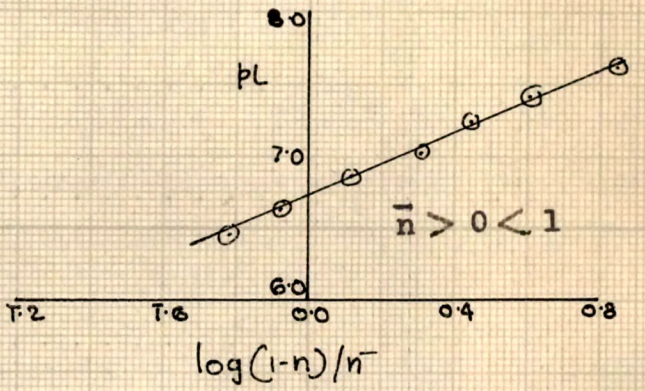


Fig. II 25

Cd(II)-Pyrogallol system - 30°C.

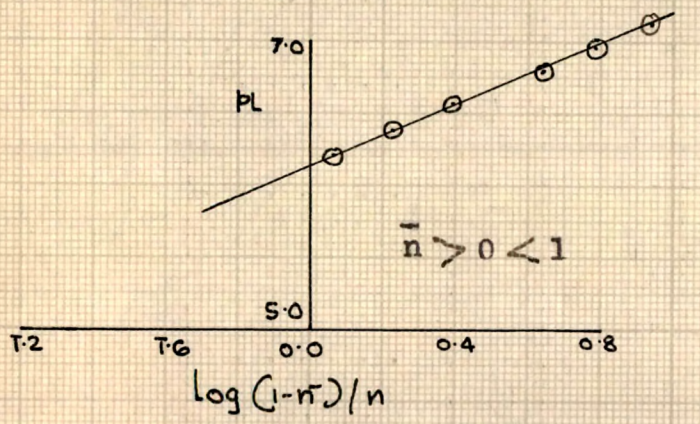


Fig. II 24

Cd(II)-Catechol system - 30°C.

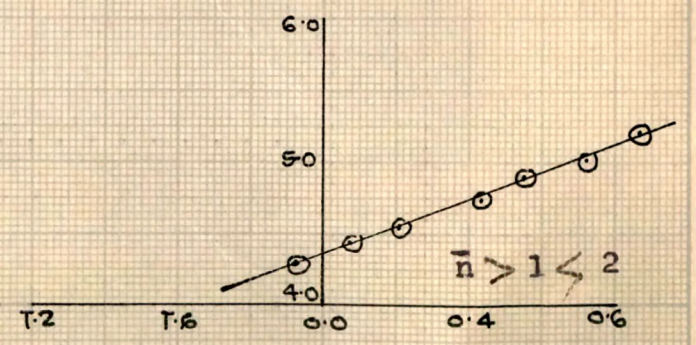


Table II 4.3c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cd - protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.10	2.00_0	4.84	4.91	0.07	0.14_0	0.78_8	8.85_4	8.06_6
7.20	2.00_0	4.86	4.96	0.10	0.20_0	0.60_2	8.65_9	8.05_7
7.30	2.00_0	4.88	5.03	0.15	0.30_0	0.36_8	8.46_6	8.09_8
7.40	2.00_0	4.90	5.10	0.20	0.40_0	0.17_6	8.27_5	8.09_9
7.50	2.00_0	4.94	5.18	0.24	0.48_0	0.03_4	8.08_3	8.04_9
7.60	1.94_9	5.00	5.28	0.28	0.57_6	$\bar{1}.86_7$	7.89_3	8.02_6
7.70	1.93_5	5.06	5.38	0.32	0.66_2	$\bar{1}.70_8$	7.68_5	-

$\log K_1 = 8.06 \pm 0.04$

Table II 4.4c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cd - 2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.80	1.97_2	2.57	2.63	0.06	0.12_1	0.86_1	9.41_7	8.55_6
6.90	1.96_8	2.58	2.67	0.09	0.18_2	0.65_2	9.22_3	8.57_1
7.00	1.96_4	2.59	2.71	0.12	0.24_4	0.49_1	9.02_8	8.53_7
7.10	1.94_8	2.63	2.79	0.16	0.32_8	0.31_1	8.83_7	8.52_6
7.20	1.93_6	2.66	2.87	0.21	0.43_3	0.11_7	8.64_6	8.52_9
7.30	1.93_2	2.67	2.93	0.26	0.53_8	$\bar{1}.93_3$	8.45_9	8.52_6
8.40	1.55_3	3.62	4.08	0.46	1.18_4	0.65_2	6.54_5	5.89_3
8.50	1.51_4	3.72	4.19	0.47	1.24_1	0.49_8	6.40_9	5.91_1
8.60	1.43_4	3.92	4.39	0.47	1.31_0	0.34_7	6.27_1	5.92_4
8.70	1.39_4	4.02	4.50	0.48	1.37_6	0.22_0	6.13_8	5.91_8
8.80	1.35_6	4.14	4.63	0.49	1.44_3	0.09_9	6.01_0	5.91_1
8.90	1.31_7	4.25	4.75	0.50	1.51_7	$\bar{1}.97_0$	5.88_7	5.91_7

$\log K_1 = 8.54 \pm 0.03$

$\log K_2 = 5.91 \pm 0.01$

Fig. II 26

Cd(II)-Protocatechuic acid system - 30°C.

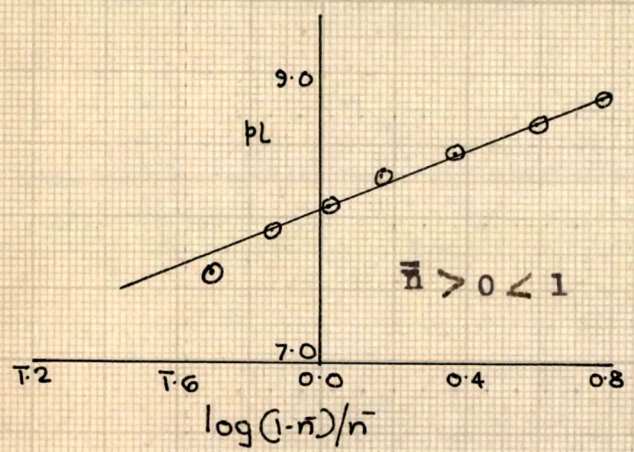


Fig. II 27

Cd(II)-2,3-dihydroxynaphthalene system - 30°C.

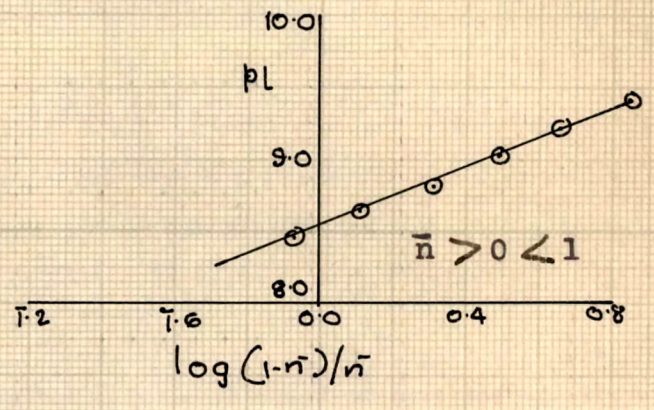


Fig. II 28

Cd(II)-2,3-dihydroxynaphthalene system - 30°C.

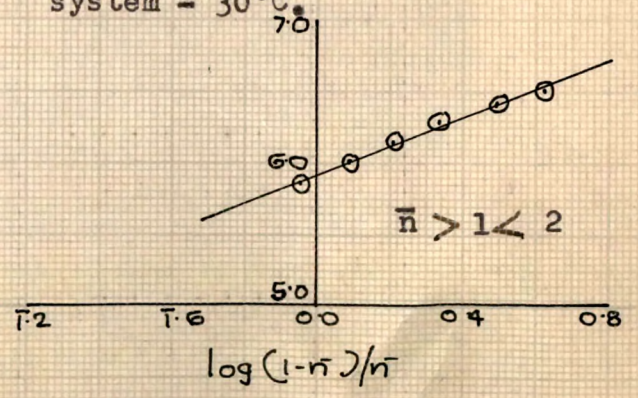


Table II 4.1d

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Mg - catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
8.50	1.81_6	2.96	3.01	0.05	0.11_0	0.90_8	5.52_8	-
8.60	1.79_2	3.08	3.14	0.06	0.13_9	0.79_2	5.35_1	-
8.70	1.74_4	3.20	3.27	0.07	0.16_0	0.72_0	5.17_9	4.45_9
8.80	1.71_9	3.30	3.40	0.10	0.23_2	0.51_9	5.01_4	4.49_5
8.90	1.67_2	3.40	3.53	0.13	0.31_0	0.34_7	4.85_5	4.50_8
9.00	1.64_0	3.50	3.65	0.15	0.36_5	0.24_0	4.74_7	4.50_7
9.10	1.56_0	3.70	3.87	0.17	0.43_5	0.11_3	4.55_1	4.43_8
9.20	1.48_0	3.90	4.10	0.20	0.53_9	1.93_2	4.41_1	4.47_9

$\log K_1 = 4.48 \pm 0.05$

Table II 4.2d

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Mg - pyrogallolate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
8.30	1.75_2	3.12	3.20	0.08	0.16_2	0.71_3	4.91_1	-
8.40	1.71_2	3.22	3.31	0.09	0.21_0	0.57_5	4.37_9	4.16_4
8.50	1.68_0	3.30	3.42	0.12	0.28_5	0.39_9	4.58_5	4.18_6
8.60	1.61_6	3.46	3.60	0.14	0.34_6	0.27_6	4.43_3	4.15_7
8.70	1.56_0	3.60	3.76	0.16	0.41_0	0.15_8	4.28_5	4.12_7
8.80	1.52_8	3.70	3.89	0.19	0.49_7	0.00_4	4.14_5	4.14_1
8.90	1.41_4	4.00	4.20	0.20	0.56_6	1.88_4	4.01_1	4.12_7

$\log K_1 = 4.15 \pm 0.05$

Table II 4.3d

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Mg - protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
8.30	1.76_0	5.60	5.68	0.08	0.18_1	0.65_5	6.56_4	5.90_9
8.40	1.72_0	5.70	5.80	0.10	0.23_2	0.51_9	6.39_2	5.87_3
8.50	1.68_0	5.80	5.92	0.12	0.28_5	0.39_9	6.22_4	5.82_5
8.60	1.60_0	5.98	6.13	0.15	0.37_5	0.22_1	6.06_4	5.84_3
8.70	1.56_0	6.10	6.28	0.18	0.46_1	0.06_7	5.90_8	5.84_1
8.80	1.52_0	6.20	6.41	0.21	0.55_2	$\bar{1}.90_9$	5.77_9	5.87_0
8.90	1.48_0	6.30	6.54	0.24	0.64_8	$\bar{1}.73_4$	5.61_4	5.88_0
9.00	1.40_0	6.50	6.76	0.26	0.74_2	$\bar{1}.54_1$	5.47_6	-

$\log K_1 = 5.86 \pm 0.04$

Table II 4.4d

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Mg - 2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.70	1.85_2	2.87	2.93	0.06	0.12_9	0.82_9	7.68_4	6.85_5
7.80	1.82_4	2.94	3.02	0.08	0.17_8	0.66_4	7.50_2	6.83_8
7.90	1.79_2	3.02	3.13	0.11	0.24_5	0.48_8	7.32_9	-
8.00	1.77_3	3.12	3.25	0.13	0.33_8	0.29_2	7.15_9	6.86_7
8.10	1.71_3	3.22	3.41	0.19	0.44_3	0.09_9	6.99_4	6.89_5
8.20	1.67_3	3.32	3.54	0.22	0.52_5	$\bar{1}.95_6$	6.83_4	6.87_8
8.30	1.63_3	3.42	3.67	0.25	0.61_2	$\bar{1}.80_2$	6.67_9	6.87_7

$\log K_1 = 6.86 \pm 0.03$

Fig. II 30

Mg(II)-Pyrogallol system - 30°C.

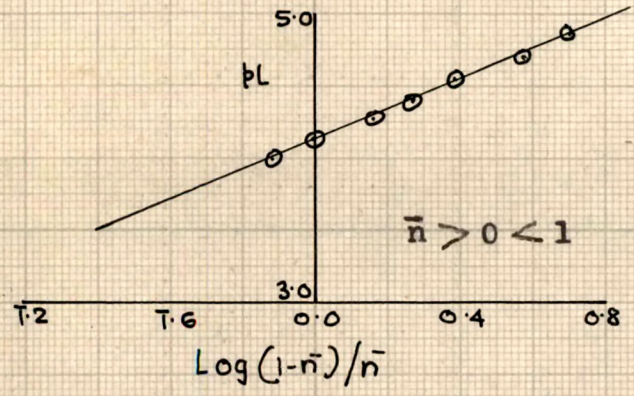


Fig. II 29

Mg(II)-Catechol system - 30°C.

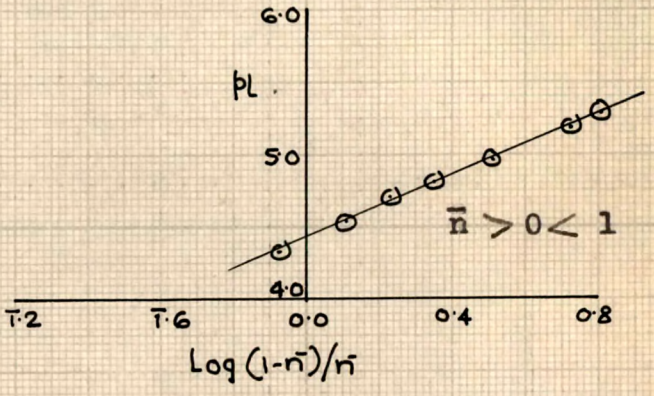


Fig. II 31

Mg(II)-Protocatechuic acid system - 30°C.

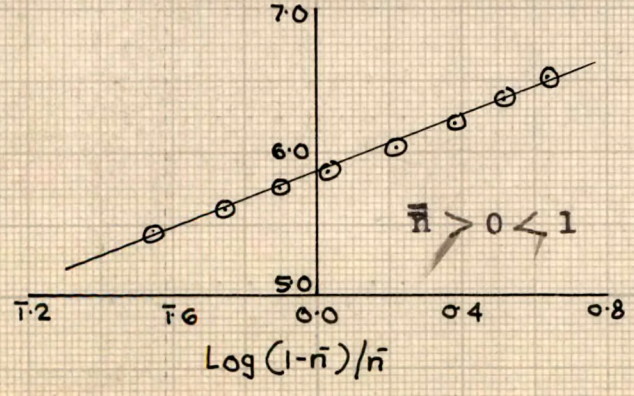


Fig. II 32

Mg(II)-2,3-dihydroxynaphthalene system - 30°C.

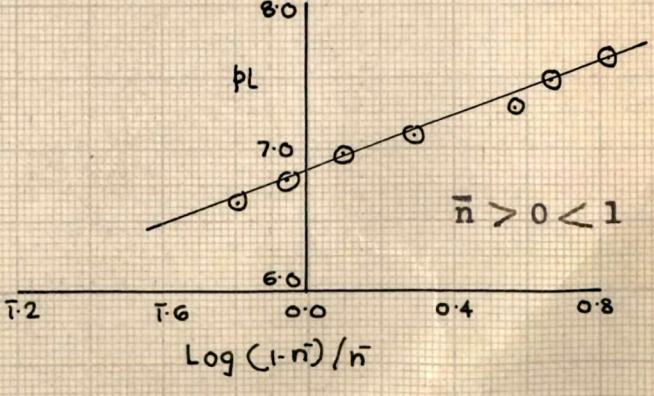


Table II 4.1e

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Tl-catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
8.60	1.79_2	3.08	3.12	0.04	0.08_9	1.01_0	5.34_8	4.33_8
8.70	1.74_4	3.20	3.26	0.06	0.13_7	0.79_9	5.17_7	4.37_8
8.80	1.71_9	3.30	3.38	0.08	0.18_6	0.58_4	5.01_1	4.42_7
8.90	1.67_2	3.40	3.50	0.10	0.23_9	0.50_3	4.89_4	4.39_1
9.00	1.64_0	3.50	3.63	0.13	0.31_6	0.33_5	4.69_7	4.36_2
9.10	1.56_0	3.70	3.86	0.16	0.40_9	0.15_9	4.54_9	4.39_0
9.20	1.48_0	3.90	4.09	0.19	0.51_0	$\bar{1}.98_2$	4.41_0	4.42_8

$\log K_1 = 4.38 \pm 0.05$

Table II 4.3e

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Tl-protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
8.30	1.76_0	5.60	5.66	0.06	0.13_6	0.80_3	6.56_2	5.75_9
8.40	1.72_0	5.70	5.78	0.08	0.18_6	0.64_1	6.38_9	5.74_8
8.50	1.68_0	5.80	5.90	0.10	0.23_8	0.50_5	6.22_1	5.71_6
8.60	1.60_0	5.98	6.10	0.12	0.30_0	0.36_8	6.06_0	5.69_2
8.70	1.56_0	6.10	6.25	0.15	0.38_4	0.20_5	5.90_5	5.69_9
8.80	1.52_0	6.20	6.38	0.18	0.47_3	0.04_6	5.75_4	5.70_8
8.90	1.48_0	6.30	6.51	0.21	0.56_7	$\bar{1}.88_1$	5.61_0	5.72_9

$\log K_1 = 5.72 \pm 0.03$

Table II 4.4e

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Tl-2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.80	1.82_4	2.9^4	3.00	0.06	0.12_4	$0.8^4{}_9$	7.50_2	6.65_3
7.90	1.79_2	3.02	3.10	0.08	0.17_8	0.66_4	7.32_6	6.65_2
8.00	1.77_3	3.12	3.23	0.11	0.24_8	0.48_1	7.15_4	6.67_3
8.10	1.71_3	3.22	3.36	0.1^4	0.32_6	0.31_5	6.98_5	6.67_0
8.20	1.67_3	3.32	$3.^49$	0.17	0.40_6	0.16_5	6.82_8	6.66_3
8.30	1.63_3	3.42	3.62	0.20	0.48_9	0.01_9	6.67_3	6.65_4
8.40	1.55_3	3.62	3.83	0.23	0.59_2	$\bar{1}.83_8$	6.52_5	6.68_7

$\log K_1 = 6.66 \pm 0.02$

Fig. II 34

T1(I)-Protocatechuic acid system - 30°C.

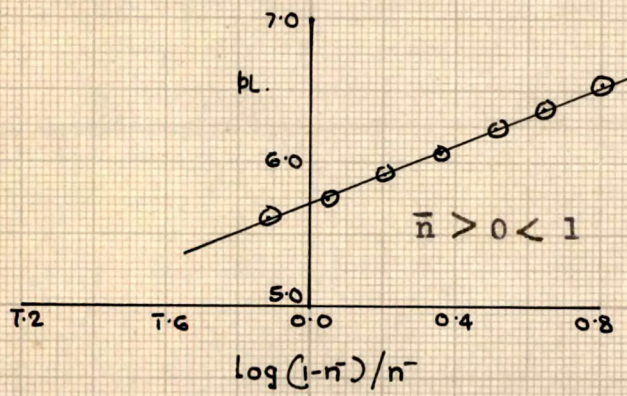


Fig. II 33

T1(I)-Catechol system - 30°C.

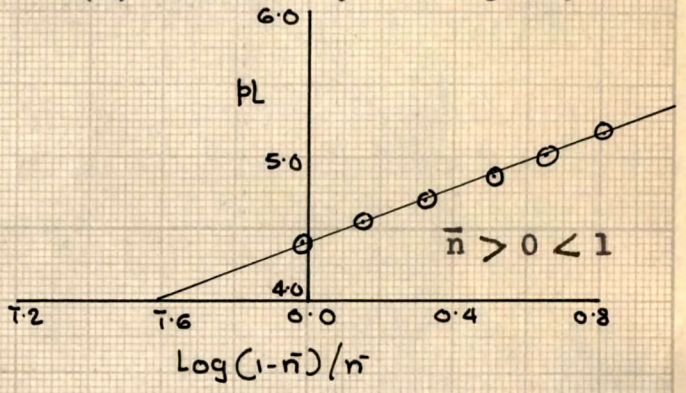


Fig. II 35

T1(I)-2,3-dihydroxynaphthalene system - 30°C.

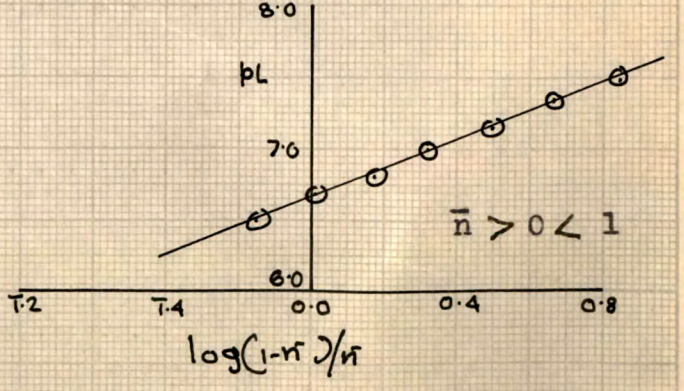


Table II 5.0

Formation constants of various metal ligand complexes (μ = 0.2M, 30°C.).

Ligand (L)		Uranyl UO_2^{2+}	Zn(II)	Cd(II)	Mg(II)	Tl(I)
Catechol	$\log K_1$	14.35 ± 0.05	8.24 ± 0.04	6.76 ± 0.06	4.48 ± 0.05	4.38 ± 0.05
	$\log K_2$	8.86 ± 0.05	5.96 ± 0.06	4.35 ± 0.05	-	-
Pyrogallol	$\log K_1$	14.05 ± 0.04	7.67 ± 0.04	6.15 ± 0.06	4.15 ± 0.05	-
	$\log K_2$	10.23 ± 0.04	-	-	-	-
Protocatechuic-acid	$\log K_1$	14.82 ± 0.03	9.11 ± 0.02	8.06 ± 0.04	5.86 ± 0.04	5.72 ± 0.03
	$\log K_2$	10.13 ± 0.05	6.65 ± 0.04	-	-	-
2,3-Dihydroxy-naphthalene	$\log K_1$	15.56 ± 0.04	9.92 ± 0.01	8.54 ± 0.03	6.86 ± 0.03	6.66 ± 0.02
	$\log K_2$	11.14 ± 0.03	7.55 ± 0.04	5.91 ± 0.01	-	-

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