C H A P T E R III

TERNARY SYSTEMS CONTAINING METAL ION, TERTIARYAMINE AND POLYPHENOLIC LIGANDS.

It is observed from the survey of the existing literature (Chapter I), that the ternary systems Cu.dipy.L and Ni.dipy.L, where L = polyhydroxy aromatic ligands, have not been investigated. An attempt has, therefore, been made in the present investigation to study the systems MAL, where M = Cu(II), Ni(II); A = dipyridyl or orthophenanthroline and L = catechol, pyrogallol and protocatechuic acid. Mixed ligand formation constants have been determined by using modified form of Irving-Rossotti titration technique[1]. The study of the system Cu.dipy.catechol had been carried out earlier[2]. Mixed ligand formation constants could not be determined in mixed ligand system where 2,3-dihydroxynaphthalene is the secondary ligand, because the heterochelate gets precipitated at very low pH.

The reaction steps are as follows :

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

$$K_{MA} = \frac{[M.\text{dipy.}]}{[M]^{2+}.[\text{dipy.}]}$$

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

OR

$$[M(\text{dipy})]^{2+} + L^{3-} \rightleftharpoons [M.\text{dipy.}L]^{1-}$$

where L^{3-} = protocatechuate ion.

$$K_{MAL}^{MA} = \frac{[M.\text{dipy.}L]}{[M.\text{dipy.}]^{2+}[L]^{2-}} \quad \text{OR} \quad \frac{[M.\text{dipy.}L]^{1-}}{[M.\text{dipy.}]^{2+}[L]^{3-}}$$

The same type of reaction is observed in [Ni-1,10 phenanthroline L]

systems. In case of Cu(II), however, precipitation takes place on mixing with 1,10 phenanthroline and the reaction could not be studied further.

The above reaction is based on the consideration that the formation of M + dipyridyl 1:1 complex is complete at lower pH, before the combination of the secondary ligand starts. 1:1 (metal - dipyridyl) complex is stable in the higher pH range where combination of the secondary ligand takes place.

Cu.dipyridyl (1:1) formation is complete before pH $\sim$ 4. This has been established by earlier workers[3]. It is known that Ni(II) ion also behaves as Cu(II) ion in forming 1:1 complex with dipyridyl in the lower pH range[4,5] and is stable at higher pH.

In case of Be(II), Al(III) and Co(II), however, dipyridyl and polyphenol combine in the same pH range and hence mixed ligand formation constant study could not be possible.

For the Cu(II) and Ni(II) complexes solutions were prepared as follows :

1. Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + double distilled water (36.0 ml.) , total volume = 50.0 ml., μ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + double distilled water (31.1 ml.) , total volume = 50.0 ml., μ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) +

+ metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + double distilled water (26.2 ml.), total volume = 50.0 ml., μ = 0.2M.

4. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + double distilled water (31.1 ml.), total volume = 50.0 ml., μ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + double distilled water (21.3 ml.), total volume = 50.0 ml., μ = 0.2M.

The ionic strength of each solution was thus initially raised to 0.2M. Each of the above samples was titrated against 0.2M sodium hydroxide. The plots of pH against volume of alkali have been shown in figs. III 1 to III 6.

Since dipyridyl and o-phenanthroline are structurally alike, o-phenanthroline should give same type of reactions. The study in heterochelates systems $\left[M(o\text{-phen.})L\right]^{0}$, where M = Ni(II) and L = polyphenolic ligands was possible. The formation of $\left[Ni(o\text{-phen.})\right]^{2+}$ at low pH has been shown earlier[1,6-9]. This is stable at higher pH where polyphenols combine to form ternary complex. The formation constants of these ternary systems $\left[Ni(o\text{-phen.})L\right]^{0}$, where L = catechol and protocatechuic acid have been determined by the same method as above. The mixed ligand study of $\left[Ni(o\text{-phen.})\right]$ with pyrogallol and 2,3-dihydroxynaphthalene was not possible because the heterochelates get precipitated.

Since o-phenanthroline is less soluble in water, dilute

solutions were prepared as follows :

1. Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + double distilled water (36.0 ml.), total volume = 50.0 ml., μ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + o-phenanthroline (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.95 ml.) + double distilled water (31.05 ml.,), total volume = 50.0 ml., μ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + o-phenanthroline (0.01M, 5.0 ml.) + nickel perchlorate (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.85 ml.) + double distilled water (26.15 ml.), total volume = 50.0 ml., μ = 0.2M.
4. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.95 ml.) + double distilled water (31.05 ml.), total volume = 50.0 ml., μ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + o-phenanthroline (0.01M, 5.0 ml.) + secondary ligand (0.01M, 5.0 ml.) + nickel perchlorate (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + double distilled water (21.1 ml.), total volume = 50.0 ml., μ = 0.2M.

The above solutions were titrated against 0.2M alkali. The plot of volume of alkali versus pH is represented in figs. III 13 to III 14. The observation of the curves in the above figures shows that metal dipyridyl or o-phenanthroline curve (3) diverges from the dipyridyl curve (2) at low pH indicating that metal dipyridyl or o-phenanthroline complex formation takes place at low pH. The calculation of $\bar{n}$ shows that it continues to be one upto pH $\sim$ 6, after which metal dipyridyl or o-phenanthroline curve diverges from the dipyridyl

or o-phenanthroline curve showing formation of hydroxy complex $[M(dipy.)(OH)_2]$. After pH ~9.5 the complex decomposes forming metal hydroxide which precipitates out indicating that the metal dipyridyl complex 1:1 formed at low pH, is stable upto high pH. Metal dipyridyl polyphenolic ligand curve (5) and metal dipyridyl curve (3) overlap each other at low pH. This indicates that in the pH range where dipyridyl combines with metal, combination of polyphenolic ligand does not take place. Since the dissociation of the ligands catechol and pyrogallol at low pH is negligible, the curve (3) and (5) overlap. In case of protocatechuic acid, the metal + dipyridyl + protocatechuic acid curve (5) separates from metal + dipyridyl curve (3) at low pH due to self dissociation of carboxylic group. In cases of all the ligands, however, curve (5) diverges from curve (4), after pH ~4 in copper systems and at pH ~ 6.5 in nickel systems. In this range coordination of polyphenols starts. This is represented by the following reactions :

$$M^{2+} + A \rightleftharpoons [MA]^{2+}$$

$$[MA]^{2+} + LH_2 \rightleftharpoons [MAL]^{\circ} + 2H^{+}$$

Since $[M.dipy.]^{2+}$ does not dissociate in the higher pH range, it can be considered that the second ligand combines with the species $[M.dipy]^{2+}$ just as it does with $[M(aqu)]^{2+}$ in simple system. In case of Cu^{2+} system the combination of secondary ligand is completed before the pH where $[Cu(dipy.)(OH)_2]$ formation takes place. In case of Ni^{2+} system secondary ligand combines in the range of $[Ni(dipy.)(OH)_2]$ formation. However, in the presence of strongly complexing secondary

ligand the formation of $[Ni(dipy.)(OH)_2]$ is supressed.

As such the horizontal distance between curves (4) and (5) can be measured and used for calculation of $\bar{n}$, the average number of polyphenolic ligands associated with one $[M(A)]^{2+}$. The equation used for the calculation of $\bar{n}$ will be same as given in the original paper[1].

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

Here T_M° = concentration of $[M(A)]^{2+}$ which is equal to the concentration of the metal used. In the above equation V" and V"' are the volumes of alkali added to reach the same pH in the secondary ligand curve and metal + dipyridyl + secondary ligand curve, respectively. $\bar{n}_H$ values and the proton ligand stability values of the secondary ligand, for pL calculation, have been taken from earlier chapter. $\bar{n}$ and pL values have been calculated at different pH values and have been shown in tables III 5 to III 10 and III 14 to III 15. pL at $\bar{n} = 0.5$, gives the value of log K_{MAL}. More precise values were obtained by plotting pL at each point against log $(1-\bar{n})/\bar{n}$ and obtaining a straight line. At each point on the straight line log K_{MAL} = pL - log $(1-\bar{n})/\bar{n}$.

It is observed that the order of the mixed ligand formation constants in metal dipyridyl polyphenolic ligand is protocatechuic acid > catechol > pyrogallol as in the binary system.

It is observed that the difference between K_{MAL} and K_{ML}, is much less. Dipyridyl molecule has a greater coordinating

tendency with metallic ion and forms more stable σ bonds than water and hence in $[M(dipy.)(aqu.)]^{2+}$ the concentration of electrons around M^{2+} ion should be more than in simple $[M(aqu.)]^{2+}$. Hence the constant corresponding to the reaction $[M(A)]^{2+} + L^{2-}$ should be less than the constants for $M^{2+} + L^{2-}$.

Thus the values of the formation constants of $[M(dipy.)(L)]$ are much higher than what is expected from statistical considerations. K_{MAL} is much higher than K_{ML_2} and only slightly lower than K_{ML}. This can be attributed to the special behaviour of dipyridyl or o-phenanthroline.

Dipyridyl and o-phenanthroline molecules are bound to the metal by σ bonding as in the case of ethylenediamine. Besides, that there is also π bond formation by the back donation of electrons from metal to the ligand. The $d\pi$-$p\pi$ interactions have been observed in metal-dipyridyl complexes by earlier workers[10-13] using different methods of investigations. The $d\pi$-$p\pi$ interaction does not allow the concentration of electrons on the metal ion to increase significantly. In other words, positive charge on the metal ion in $[M(dipy.)]^{2+}$ is almost same as in $[M(aqu.)]^{2+}$ complexes.

Enthalpy changes in the coordination of L^{2-} with $[M(aqu.)]^{2+}$ or $[M(dipy.)]^{2+}$ can be expected to be same. Since the species $[ML]$ or $[MAL]$ are both neutral, the entropy change will also be same in both the cases. Since the formation constant is dependent on the free energy, which in turn is related to the enthalpy and entropy changes, $K^{MA}_{MAL} \approx K^{M}_{ML}$. K^{MA}_{MAL} is much higher than $K^{ML}_{ML_2}$ because dipyridyl is a neutral ligand and hence L^{2-} has not to face any repulsion while getting bound

with MA. However, during the formation of ML_2, the incoming L^{2-} has to face a repulsion due to already existing charged ion in L^{2-}. Further MAL is a neutral species while $[ML_2]^{2-}$ has two negative charges. The former will not get solvated and hence the solvent molecules are free to move. The entropy change is thus more favourable in the formation of MAL. The favourable enthalpy and entropy changes make $K^{MA}_{MAL} > K^{ML}_{ML_2}$.

It is observed that in case of Cu(II) complexes K_{MAL} is higher than K_{ML}. Such observation has been made in case of [Cu(dipy.)(cat)] earlier[2]. This can be attributed to dynamic Jahn-Tellor distortion. Dipyridyl being a neutral ligand produces stronger electrical field around the Cu(II) ion, during formation of $[Cu(dipy.)(H_2O)_2]^{2+}$. The distorted octahedron $[Cu(H_2O)_6]^{2+}$ will be somewhat more strongly distorted towards the square planar coordination by the coordination of α-α'-dipyridyl, thus creating the right geometry for the coordination of the secondary ligand and resulting in the increase in the value of K_{MAL}[14].

In case of [Ni(dipy.)+secondary ligand] systems, the formation constants are higher than corresponding [Ni(o-phen.)+secondary ligand] system. This can be expected to be due to the bigger size of o-phenanthroline molecule which produces more steric hinderance. Besides this the metal to ligand π interaction is less in $[Ni(o\text{-}phen.)]^{2+}$ and hence its tendency to combine with secondary ligand will be less than that of $[Ni(dipy.)]^{2+}$.

Table III 1

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

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Perchloric acid		Dipyridyl		Cu.Dipyridyl		Ni.Dipyridyl	
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	1.50	0.00	1.55	0.00	1.50	0.00	1.60
1.00	1.60	1.00	1.70	1.00	1.60	1.00	1.70
1.50	1.65	1.50	1.75	1.50	1.65	1.50	1.75
2.00	1.70	2.00	1.80	2.00	1.70	2.00	1.80
2.50	1.80	2.50	1.90	3.00	1.90	2.50	1.90
3.00	1.90	4.00	2.60	3.50	2.00	3.00	2.00
3.50	2.00	4.20	2.90	4.00	2.20	3.50	2.20
4.00	2.20	4.40	3.30	4.50	2.60	4.40	2.55
4.50	2.60	4.50	3.70	4.60	2.70	4.50	2.60
4.60	2.70	4.60	4.00	4.70	2.75	4.60	2.75
4.70	2.85	4.70	4.40	4.80	3.00	4.70	2.90
4.80	3.00	4.76	4.60	4.90	3.30	4.80	3.10
4.90	3.15	4.80	4.80	4.95	3.50	4.90	3.30
5.00	3.80	4.85	5.00	5.00	3.90	4.95	3.50
5.01	9.20	4.90	5.30	5.05	6.20 (ppt.)	4.98	4.00
5.04	9.50	4.95	5.60			5.00	4.50
5.06	9.70	5.00	6.00			5.02	7.60
5.08	9.85	5.02	9.50			5.04	7.80
5.10	10.00	5.04	9.70			5.06	7.90
5.14	10.20	5.06	9.85			5.10	8.20
5.16	10.30	5.10	10.10			5.14	8.55
5.20	10.50	5.14	10.25			5.20	8.80
5.25	10.70	5.20	10.50			5.25	8.85
5.30	10.80	5.25	10.70			5.30	9.00
5.40	10.90	5.30	10.80			5.35	9.20
5.50	11.00	5.35	10.85			5.40	9.35
		5.40	10.90			5.45	9.50
		5.50	11.00			5.50	9.60
						5.55	9.80
						5.60	9.95
						5.65	10.05
						5.70	10.20
						5.80	10.40
						5.90	10.60
						6.00	10.65
						6.10	10.75
						6.20	10.90
						6.30	11.00

Table III 2

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

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Catechol		Cu.Dipy.Catechol		Ni.Dipy.Catechol	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.55	0.00	1.50	0.00	1.60
1.00	1.60	1.00	1.60	1.00	1.70
1.50	1.65	1.50	1.65	1.50	1.75
2.00	1.70	2.00	1.70	2.00	1.80
2.50	1.80	3.00	1.90	2.50	1.90
3.00	1.90	3.50	2.00	3.00	2.00
3.50	2.00	4.00	2.20	3.50	2.20
4.00	2.20	4.50	2.60	4.00	2.45
4.50	2.60	4.70	2.85	4.50	2.60
4.60	2.75	4.80	3.05	4.60	2.75
4.70	2.85	4.90	3.30	4.70	2.90
4.80	3.00	4.95	3.50	4.80	3.10
4.90	3.15	5.00	3.90	4.90	3.30
5.00	3.80	5.05	4.30	4.95	3.50
5.04	7.70	5.15	4.60	4.98	4.00
5.08	8.10	5.25	4.80	5.00	4.50
5.12	8.40	5.40	5.00	5.04	7.05
5.16	8.65	5.50	5.10	5.08	7.15
5.20	8.80	5.60	5.25	5.12	7.30
5.25	9.00	5.70	5.50	5.16	7.35
5.30	9.20	5.80	5.80	5.20	7.45
5.35	9.40	5.90	6.35	5.25	7.50
5.40	9.55	5.95	6.90	5.30	7.60
5.50	9.80	6.00	7.75	5.40	7.70
5.60	10.10	6.02	8.50	5.50	7.80
5.70	10.40	6.10	9.00	5.60	7.90
5.80	10.55	6.15	9.25	5.70	8.15
6.00	10.80	6.22	9.50	5.75	8.30
6.10	10.85	6.30	9.75	5.80	8.60
6.20	10.90	6.40	10.00	5.90	8.90
6.30	11.00	6.50	10.20	5.96	9.10 (ppt.)
		6.65	10.50		
		6.75	10.75		
		6.83	11.00		

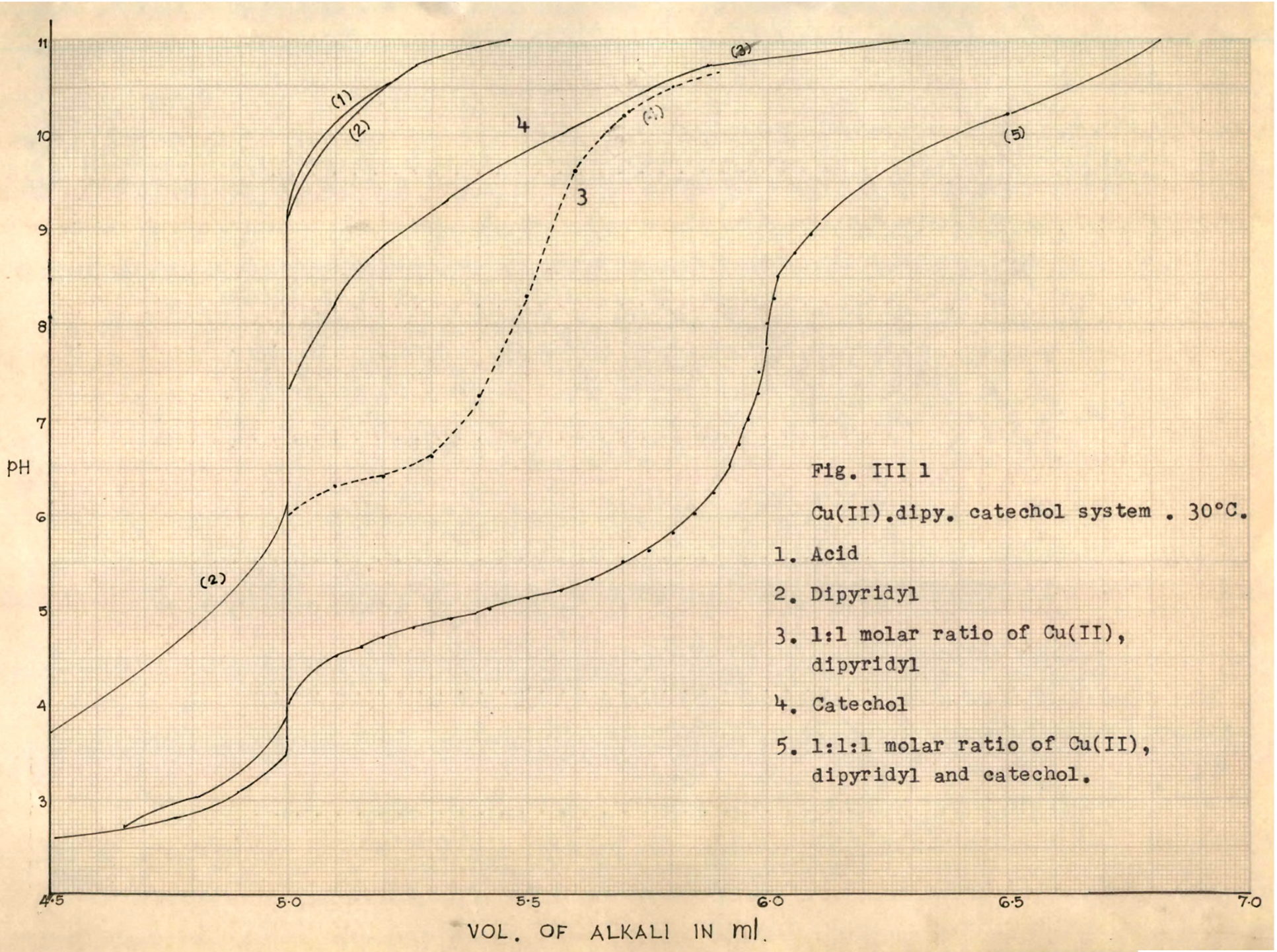

Fig. III 1

Cu(II).dipy. catechol system . 30°C.

1. Acid
2. Dipyridyl
3. 1:1 molar ratio of Cu(II), dipyridyl
4. Catechol
5. 1:1:1 molar ratio of Cu(II), dipyridyl and catechol.

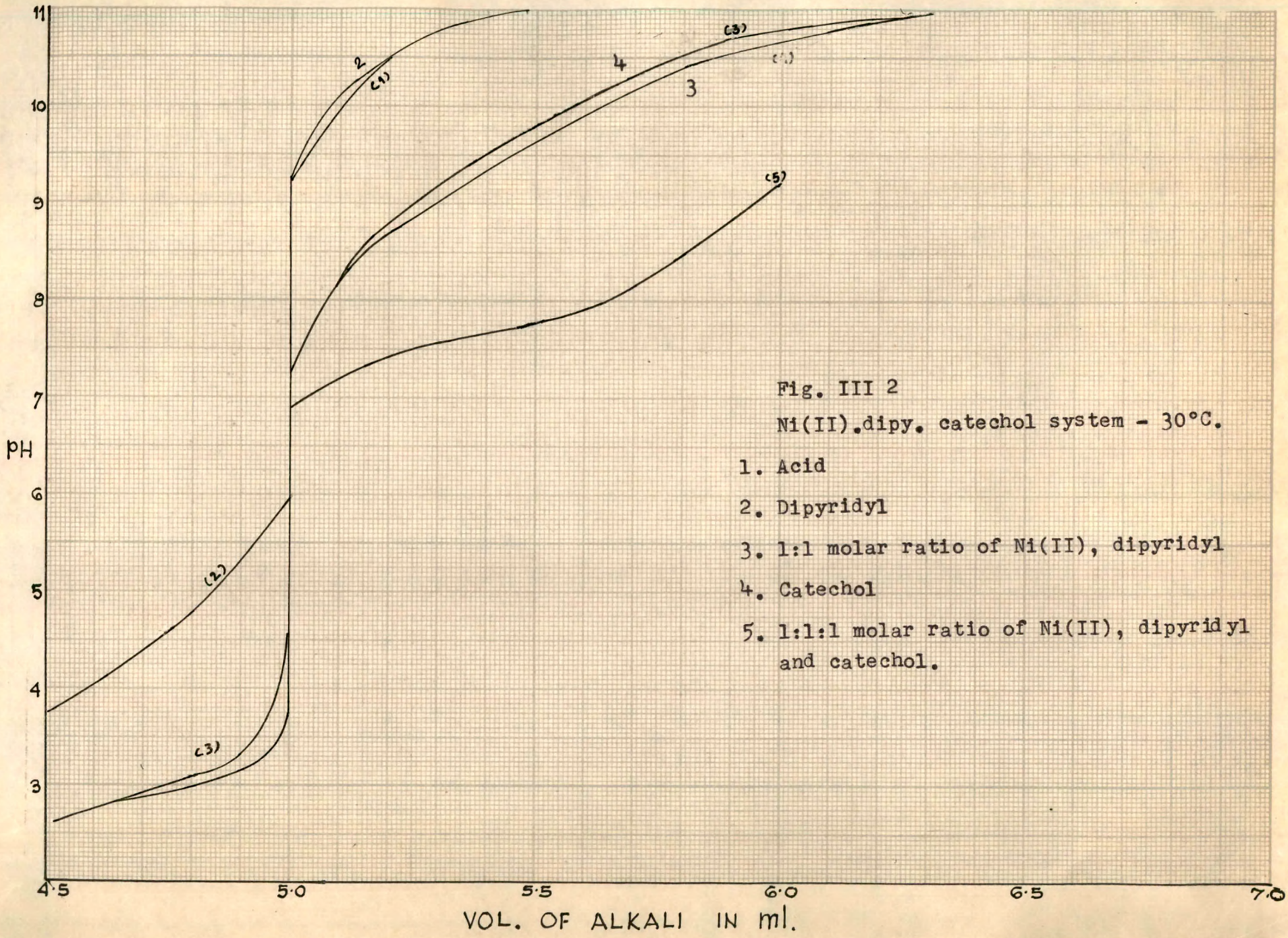

Fig. III 2

Ni(II).dipy. catechol system - 30°C.

1. Acid
2. Dipyridyl
3. 1:1 molar ratio of Ni(II), dipyridyl
4. Catechol
5. 1:1:1 molar ratio of Ni(II), dipyridyl and catechol.

Table III 3

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

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Pyrogallol		Cu.Dipy.Pyrogallol		Ni.Dipy.Pyrogallol	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50	0.00	1.55
1.00	1.60	1.00	1.60	1.00	1.70
2.00	1.70	1.50	1.65	2.00	1.80
3.00	1.90	2.00	1.70	3.00	2.00
4.00	2.20	3.00	1.90	4.00	2.45
4.50	2.55	3.50	2.00	4.50	2.60
4.60	2.70	4.00	2.20	4.60	2.75
4.70	2.80	4.50	2.60	4.70	2.90
4.80	3.00	4.65	2.75	4.80	3.10
4.90	3.25	4.70	2.85	4.90	3.30
5.00	3.70	4.80	3.05	4.95	3.50
5.05	8.00	4.90	3.30	4.98	4.00
5.10	8.30	4.95	3.50	5.00	4.50
5.15	8.60	5.00	3.90	5.05	6.70
5.20	8.80	5.12	4.05	5.10	7.05
5.25	9.00	5.20	4.25	5.15	7.20
5.30	9.20	5.35	4.50	5.20	7.30
5.35	9.35	5.40	4.60	5.25	7.40
5.40	9.50		(ppt.)	5.30	7.45
5.50	9.90			5.40	7.50
5.60	10.20			5.50	7.60
5.65	10.40			5.60	7.70
5.70	10.50			5.70	7.80
5.80	10.60			5.80	8.00
5.90	10.80			5.90	8.10
6.00	10.90			5.95	8.20
6.05	11.00			6.00	8.40 (ppt.)

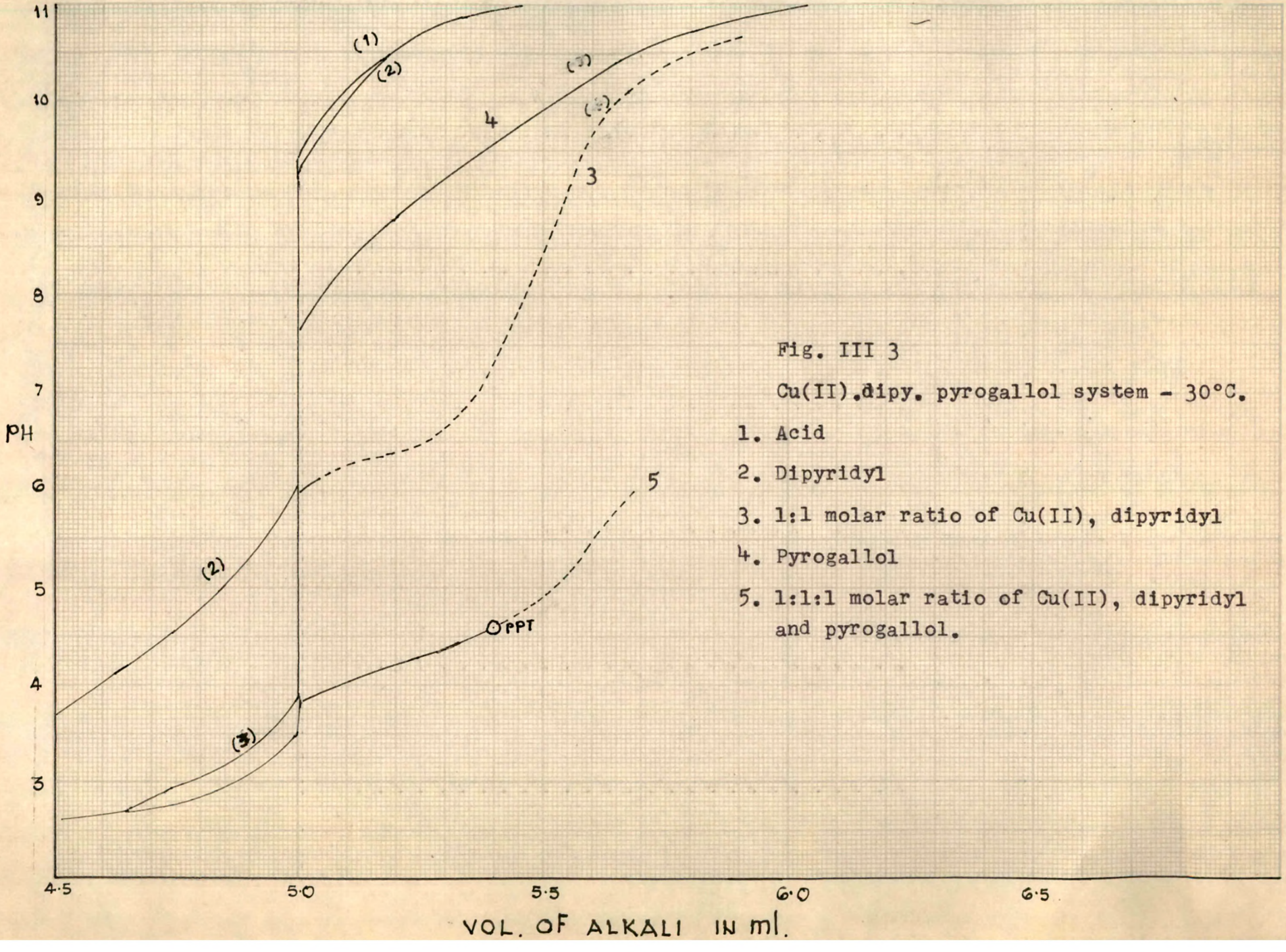

Fig. III 3

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

1. Acid
2. Dipyridyl
3. 1:1 molar ratio of Cu(II), dipyridyl
4. Pyrogallol
5. 1:1:1 molar ratio of Cu(II), dipyridyl and pyrogallol.

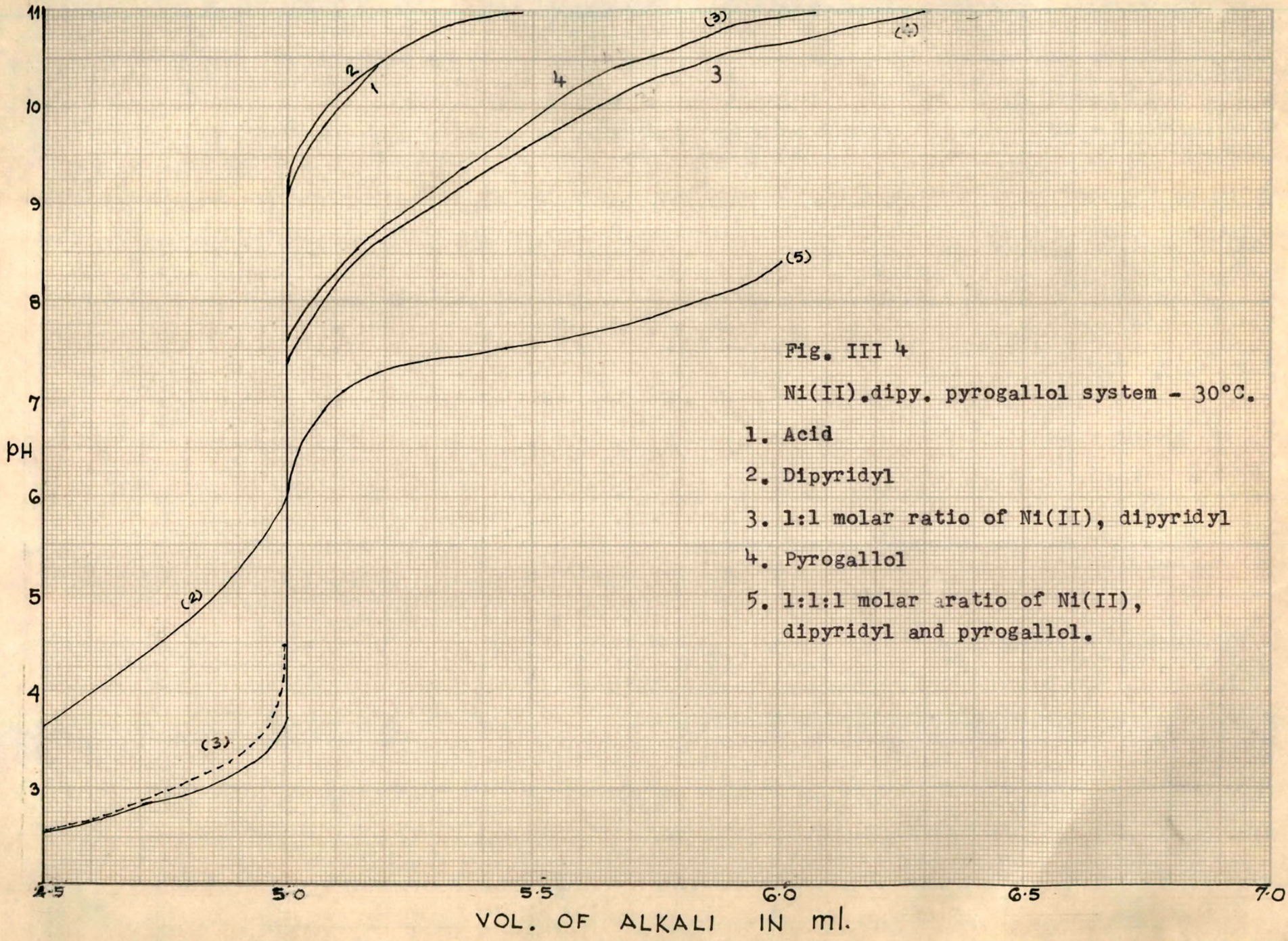

Fig. III 4

Ni(II).dipy. pyrogallol system - 30°C.

1. Acid
2. Dipyridyl
3. 1:1 molar ratio of Ni(II), dipyridyl
4. Pyrogallol
5. 1:1:1 molar aratio of Ni(II), dipyridyl and pyrogallol.

Table III 4

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

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Protocatechuic acid		Cu.Dipy Protocatechuic acid		Ni.Dipy Protocatechuic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.85
2.50	1.90	2.50	1.90	2.50	1.90
3.00	2.00	3.00	2.00	3.00	2.00
3.50	2.15	3.50	2.15	3.50	2.20
4.00	2.30	4.00	2.30	4.00	2.40
4.50	2.60	4.50	2.60	4.60	2.65
4.70	2.80	4.60	2.70	4.70	2.80
4.80	3.00	4.70	2.80	4.80	3.00
4.90	3.20	4.80	3.00	4.90	3.20
4.95	3.45	4.90	3.10	4.95	3.45
5.00	3.65	4.95	3.25	5.00	3.65
5.05	3.90	5.00	3.50	5.05	3.90
5.10	4.05	5.05	3.75	5.10	4.05
5.15	4.30	5.10	3.90	5.15	4.30
5.20	4.50	5.30	4.00	5.20	4.50
5.26	4.70	5.55	4.25	5.25	4.70
5.30	5.00	5.85	4.50	5.30	5.00
5.35	5.35	6.02	5.00	5.35	5.35
5.40	6.00	6.05	5.15	5.40	6.00
5.44	7.40	6.12	5.50	5.45	6.70
5.50	7.90	6.24	6.00	5.50	7.00
5.55	8.10	6.32	6.50	5.65	7.30
5.60	8.40	6.35	6.75	5.80	7.50
5.70	8.70	6.40	7.00	6.00	7.70
5.75	8.95	6.45	7.25	6.10	7.95
5.80	9.20	6.50	7.50	6.20	8.25
5.85	9.40	6.55	7.75	6.30	8.50
5.90	9.60	6.63	8.00	6.40	8.80
5.95	9.80	6.70	8.25	6.50	9.20
6.00	10.00	6.80	8.50	6.60	9.60
6.10	10.30	6.87	8.75	6.70	9.85
6.20	10.55	7.00	9.00	6.80	10.10
6.30	10.70	7.05	9.25	6.90	10.40
6.50	10.90	7.08	9.50	7.00	10.50
6.60	11.00	7.15	10.00		
		7.25	10.25		
		7.35	10.50		

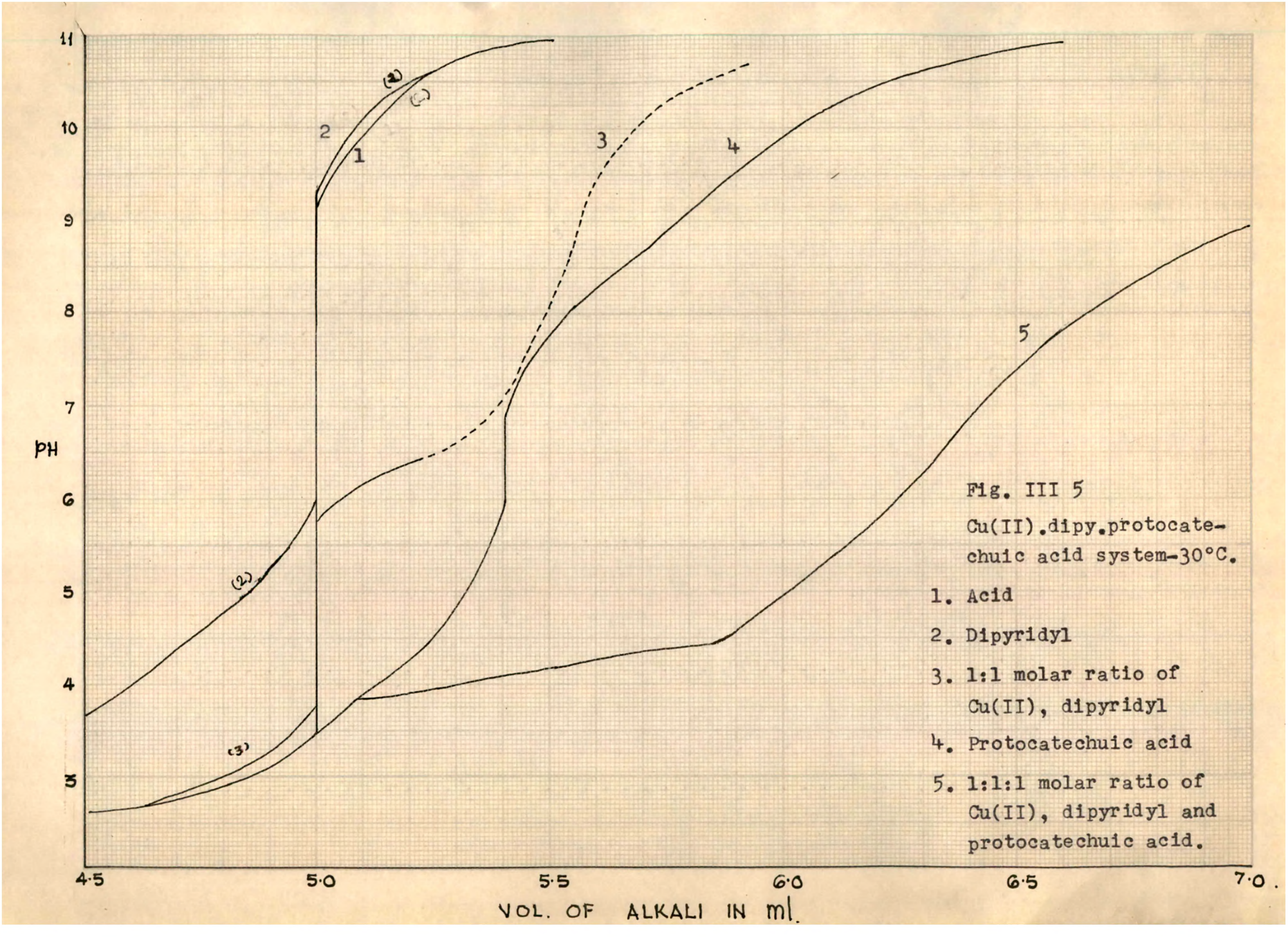

Fig. III 5

Cu(II).dipy.protocatechuic acid system-30°C.

1. Acid
2. Dipyridyl
3. 1:1 molar ratio of Cu(II), dipyridyl
4. Protocatechuic acid
5. 1:1:1 molar ratio of Cu(II), dipyridyl and protocatechuic acid.

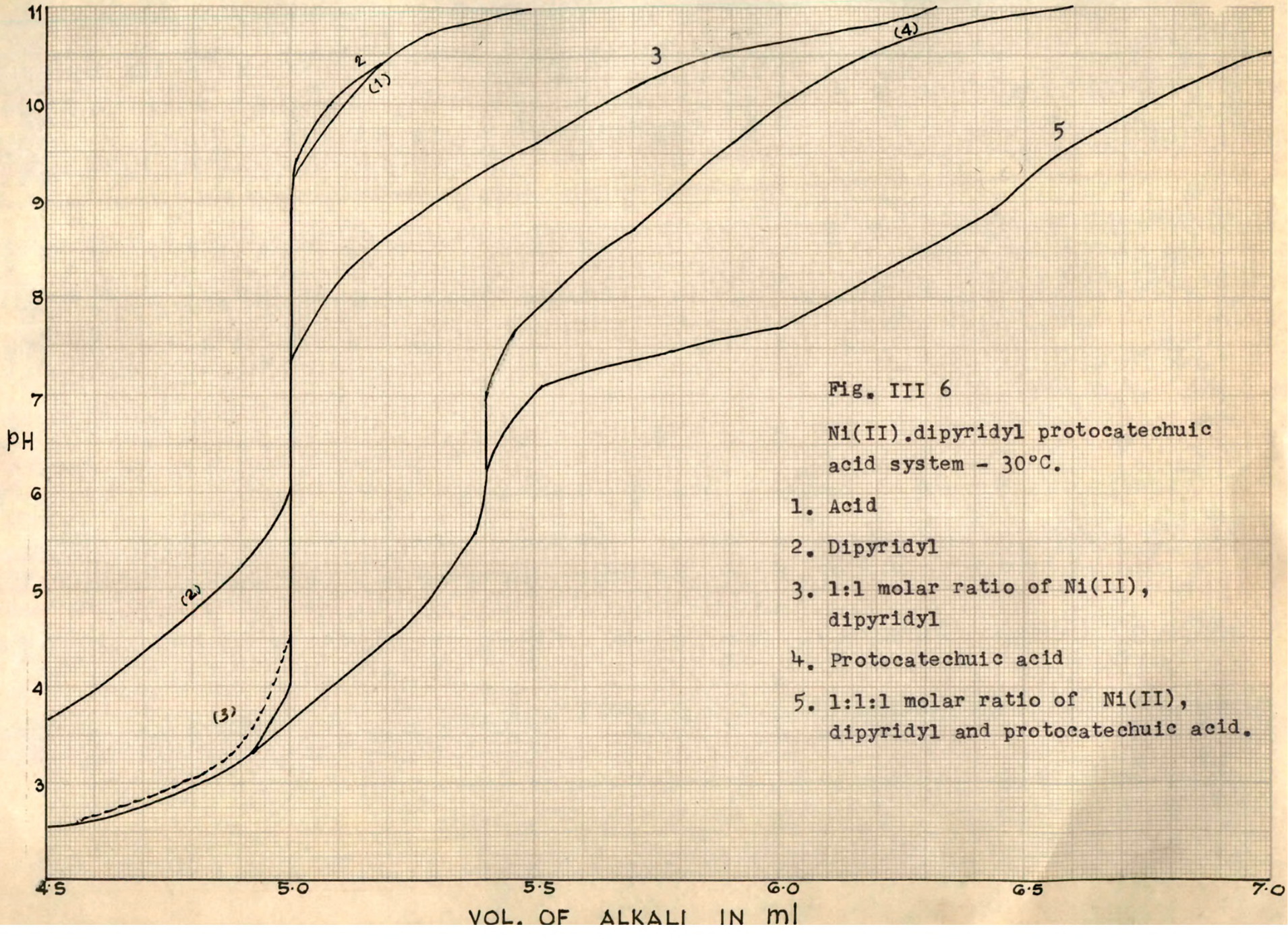

Fig. III 6

Ni(II).dipyridyl protocatechuic acid system - 30°C.

1. Acid
2. Dipyridyl
3. 1:1 molar ratio of Ni(II), dipyridyl
4. Protocatechuic acid
5. 1:1:1 molar ratio of Ni(II), dipyridyl and protocatechuic acid.

Table III 5

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cu.dipy. catechol system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
4.50	2.00_0	5.00	5.10	0.10	0.10_0	0.95_4	14.18_6	13.23_2
4.60	2.00_0	5.00	5.15	0.15	0.15_0	0.75_3	14.01_2	13.25_9
4.70	2.00_0	5.00	5.20	0.20	0.20_0	0.60_2	13.83_8	13.23_6
4.80	2.00_0	5.00	5.26	0.26	0.26_0	0.45_4	13.67_3	13.21_9
4.90	2.00_0	5.00	5.34	0.34	0.34_0	0.28_8	13.52_3	13.23_5
5.00	2.00_0	5.00	5.42	0.42	0.42_0	0.14_0	13.38_0	13.24_0
5.10	2.00_0	5.00	5.50	0.50	0.50_0	0.00_0	13.24_5	13.24_5
5.20	2.00_0	5.00	5.57	0.57	0.57_0	$\bar{1}.97_7$	13.11_1	13.13_4

$\log K_{MAL} = 13.22 \pm 0.09$

Table III 6

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cu.dipy. pyrogallol system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
4.10	2.00_0	5.00	5.12	0.12	0.12_0	0.86_5	13.91_6	13.05_1
4.20	2.00_0	5.00	5.17	0.17	0.17_0	0.68_8	13.74_2	13.05_4
4.30	2.00_0	5.00	5.24	0.24	0.24_0	0.50_0	13.58_1	13.08_1
4.40	2.00_0	5.00	5.30	0.30	0.30_0	0.36_8	13.41_7	13.04_9
4.50	2.00_0	5.00	5.36	0.36	0.36_0	0.24_9	13.25_6	13.00_7

$\log K_{MAL} = 13.04 \pm 0.04$

Table III 7

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cu.dipy. protocatechuic acid system - 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	5.10	5.20	0.10	0.09_9	0.95_9	16.42_5	15.46_6
4.00	2.00_0	5.12	5.28	0.16	0.15_9	0.72_3	16.26_6	15.54_3
4.10	2.00_0	5.15	5.36	0.21	0.20_9	0.57_8	16.01_9	15.54_1
4.20	2.00_0	5.18	5.50	0.32	0.31_8	0.33_1	15.78_2	15.45_1
4.30	2.00_0	5.20	5.64	0.44	0.43_8	0.10_8	15.56_1	15.45_3
4.40	2.00_0	5.23	5.77	0.54	0.51_7	$\bar{1}.97_0$	15.44_2	15.47_2
4.50	2.00_0	5.25	5.85	0.60	0.59_7	$\bar{1}.82_9$	15.29_8	15.46_9

$\log K_{MAL} = 15.48 \pm 0.06$

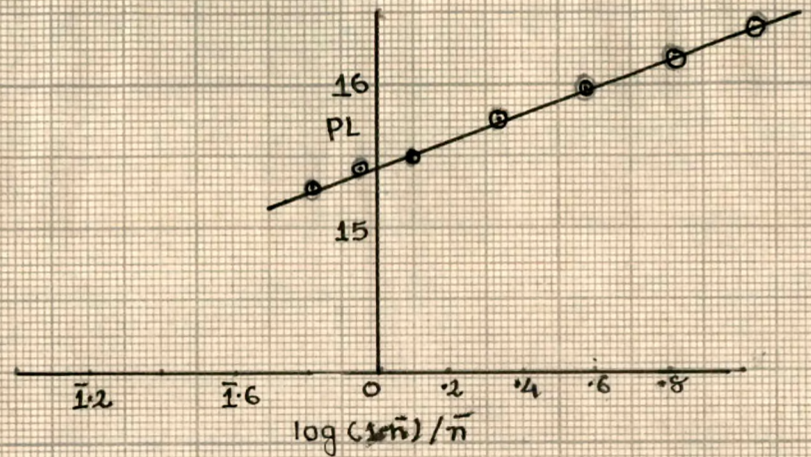

Fig.III 9
Cu(II).dipy.proto.acid system - 30°C.

Fig. III 7
Cu(II).dipy.catechol
system - 30°C.

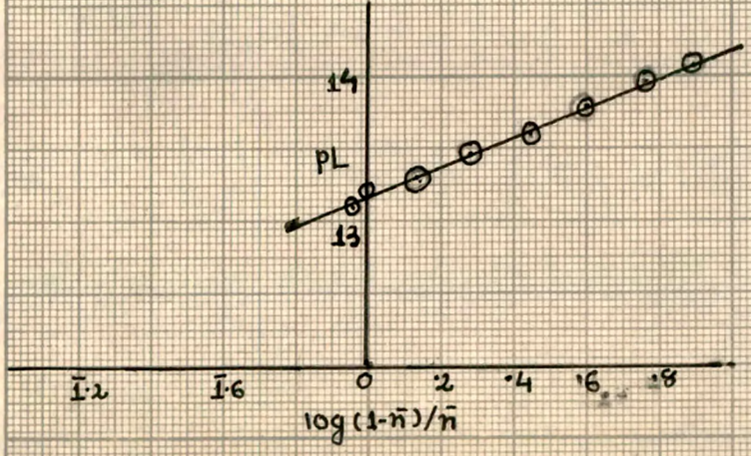

Fig. III 8
Cu(II).dipy.pyrogallol
system - 30°C.

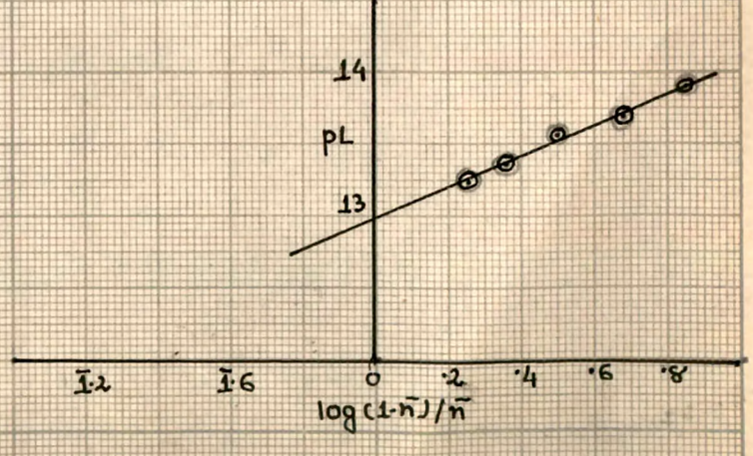

Table III 8

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Ni.dipy. catechol system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.30	1.97_2	5.00	5.14	0.14	0.14_1	0.78_4	8.57_3	7.78_9
7.40	1.96_2	5.00	5.18	0.18	0.18_3	0.64_9	8.38_2	7.73_3
7.50	1.96_0	5.01	5.24	0.23	0.23_4	0.51_5	8.19_5	7.68_0
7.60	1.95_5	5.03	5.33	0.30	0.30_7	0.35_3	8.01_3	7.66_0
7.70	1.94_8	5.04	5.42	0.38	0.38_9	0.19_6	7.83_5	7.63_9
7.80	1.94_4	5.05	5.51	0.46	0.47_2	0.04_8	7.66_0	7.61_2
7.90	1.93_6	5.06	5.60	0.54	0.55_2	$\bar{1}.90_9$	7.48_5	7.57_6

$\log K_{MAL} = 7.66 \pm 0.09$

Table III 9

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Ni.dipy. pyrogallol system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.00	1.96_8	5.00	5.09	0.09	0.09_1	0.95_9	8.11_0	7.15_1
7.10	1.96_4	5.00	5.12	0.12	0.12_1	0.86_1	7.88_8	7.01_7
7.20	1.96_0	5.00	5.16	0.16	0.16_2	0.71_3	7.70_7	6.99_4
7.30	1.95_2	5.00	5.19	0.19	0.19_3	0.62_1	7.50_5	6.88_4
7.40	1.94_4	5.00	5.35	0.35	0.36_0	0.24_9	7.34_9	7.10_0
7.50	1.92_8	5.00	5.42	0.42	0.43_5	0.11_3	7.16_8	7.05_5
7.60	1.92_0	5.00	5.45	0.45	0.46_8	0.05_5	7.15_7	7.10_2

$\log K_{MAL} = 7.01 \pm 0.09$

Table III 10

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Ni.dipy. protocatechuic acid system - 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	5.41	5.51	0.10	0.09_9	0.95_9	9.56_4	8.60_5
7.20	2.00_0	5.42	5.57	0.15	0.14_8	0.76_0	9.37_6	8.61_6
7.30	2.00_0	5.43	5.65	0.22	0.21_9	0.55_4	9.19_3	8.63_9
7.40	2.00_0	5.44	5.72	0.28	0.27_7	0.41_6	9.00_1	8.58_5
7.50	2.00_0	5.44	5.80	0.36	0.35_7	0.25_5	8.82_9	8.57_4
7.60	1.94_9	5.45	5.89	0.44	0.43_6	0.11_1	8.64_8	8.53_7
7.70	1.93_5	5.46	6.00	0.54	0.53_5	$\bar{1}.93_9$	8.48_4	8.54_5

$\log K_{MAL} = 8.58 \pm 0.05$

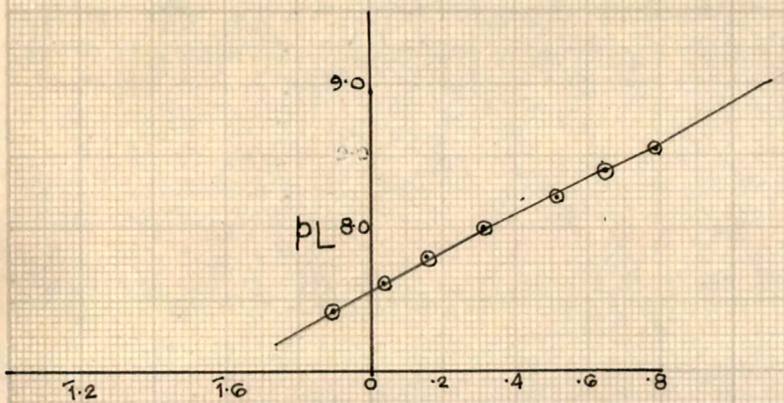

Fig. III 10
Ni(II).dipy. catechol system - 30°C.

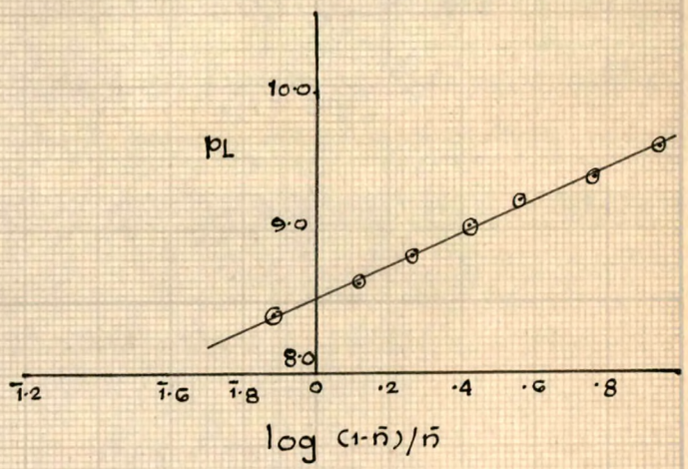

Fig. III 12
Ni(II).dipy. protocatechuic acid system - 30°C.

Fig. III 11
Ni(II).dipy.pyrogallol system - 30°C.

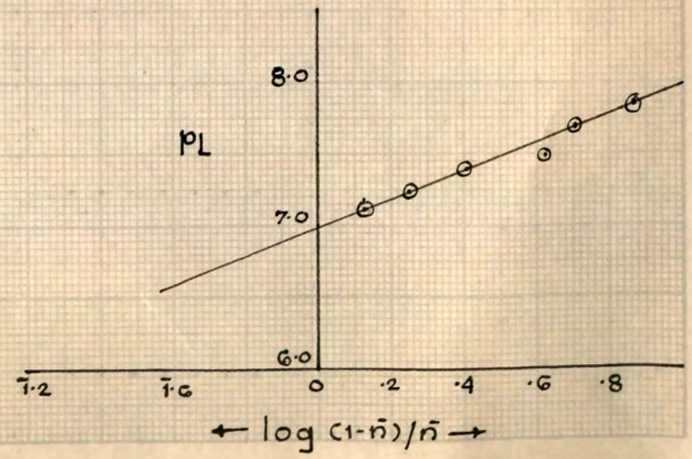

Table III 11

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

E° = 0.02M $T^{\circ}_{o\text{-phen}}$ = 0.001M T°_{M} = 0.001M

Perchloric acid		o-Phenanthroline		Ni-o-Phenanthroline	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50	0.00	1.50
1.00	1.60	1.00	1.60	1.00	1.60
2.00	1.70	1.50	1.65	1.50	1.65
2.50	1.80	2.00	1.70	2.00	1.70
3.00	1.90	2.50	1.80	2.50	1.80
3.50	2.05	3.00	1.90	3.00	1.90
4.00	2.20	3.50	2.15	3.40	2.10
4.50	2.70	4.00	2.30	4.00	2.20
4.60	2.80	4.50	2.90	4.50	2.75
4.70	3.00	4.60	3.30	4.60	2.80
4.80	3.20	4.70	3.60	4.70	3.10
4.90	3.70	4.80	4.05	4.80	3.40
4.95	4.00	4.85	4.45	4.85	3.65
5.00	4.55	4.90	5.00	4.90	3.95
5.04	8.95	4.94	5.50	4.95	4.35
5.10	9.40	4.96	5.90	5.00	4.70
5.14	9.65	4.98	6.50	5.04	7.70
5.18	9.90	4.99	8.70	5.08	8.40
5.22	10.10	5.00	9.00	5.12	8.80
5.26	10.25	5.04	9.30	5.16	9.10
5.30	10.40	5.08	9.60	5.20	9.30
5.34	10.60	5.12	9.85	5.24	9.50
5.38	10.70	5.16	10.10	5.28	9.65
5.46	10.90	5.20	10.30	5.30	9.70
5.50	11.00	5.24	10.45	5.35	9.90
		5.28	10.60	5.40	10.10
		5.32	10.65	5.45	10.25
		5.35	10.70	5.50	10.40
		5.40	10.80	5.60	10.70
		5.45	10.90	5.70	10.90
		5.50	11.00	5.80	11.00

Table III 12

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

E° = 0.02M $T^{\circ}_{o\text{-phen}}$ = 0.001M T°_{L} = 0.001M T°_{M} = 0.001M

Catechol		Ni.o-Phen.Catechol	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.60	1.00	1.60
1.50	1.65	1.50	1.65
2.00	1.70	2.00	1.70
2.50	1.80	2.50	1.80
3.00	1.90	3.00	1.90
3.50	2.05	3.50	2.05
4.00	2.20	4.00	2.20
4.50	2.70	4.50	2.70
4.60	2.80	4.60	2.80
4.70	3.00	4.70	3.10
4.80	3.20	4.80	3.45
4.90	3.70	4.85	3.65
4.95	4.00	4.90	3.95
5.00	4.55	4.94	4.25
5.03	8.30	4.96	4.50
5.05	8.45	5.00	4.70
5.08	8.70	5.04	7.35
5.10	8.90	5.08	7.70
5.14	9.10	5.12	7.90
5.18	9.35	5.16	8.05
5.22	9.45	5.20	8.15
5.26	9.55	5.24	8.20
5.30	9.70	5.28	8.30
5.35	9.90	5.32	8.40
5.40	10.05	5.36	8.55
5.45	10.15	5.40	8.65
5.50	10.30	5.44	8.85
5.55	10.40	5.48	9.00
5.58	10.50	5.56	9.30
5.66	10.60	5.60	9.45
5.70	10.70	5.65	9.70
5.75	10.80	5.70	10.00
5.80	10.90	5.80	10.30
5.85	10.95	5.90	10.50
5.90	11.00	6.00	10.65

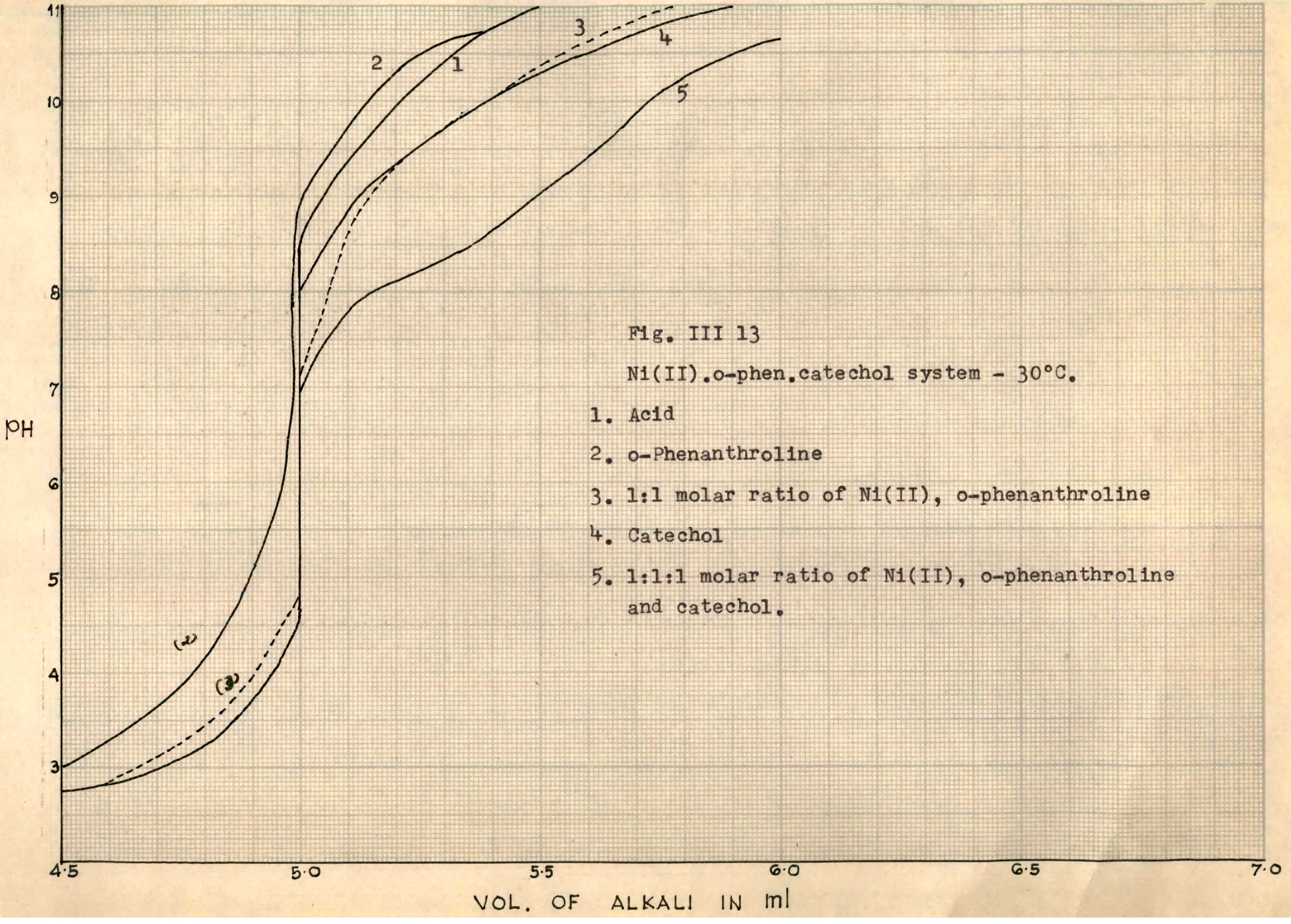

Fig. III 13

Ni(II).o-phen.catechol system - 30°C.

1. Acid
2. o-Phenanthroline
3. 1:1 molar ratio of Ni(II), o-phenanthroline
4. Catechol
5. 1:1:1 molar ratio of Ni(II), o-phenanthroline and catechol.

Table III 13

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

E° = 0.02M $T^{\circ}_{o\text{-}phen}$ = 0.001M T°_{L} = 0.001M T°_{M} = 0.001M

Protocatechuic acid		Ni.o-Phen.Protocatechuic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.60	1.00	1.60
1.50	1.65	1.50	1.65
2.00	1.70	2.00	1.70
2.50	1.80	2.50	1.80
3.00	1.90	3.00	1.90
3.50	2.10	3.50	2.10
4.00	2.20	4.00	2.20
4.50	2.75	4.50	2.75
4.60	2.80	4.70	3.00
4.70	3.00	4.80	3.20
4.80	3.20	4.85	3.30
4.90	3.50	4.90	3.50
5.00	4.05	5.00	3.90
5.05	4.55	5.05	4.20
5.10	5.00	5.10	4.45
5.14	5.60	5.14	4.80
5.16	5.95	5.18	5.20
5.18	6.75	5.22	5.60
5.20	7.30	5.26	6.35
5.22	7.70	5.30	6.95
5.24	8.00	5.33	7.30
5.28	8.40	5.36	7.55
5.30	8.60	5.40	7.70
5.32	8.75	5.44	7.90
5.36	9.05	5.50	8.15
5.40	9.30	5.58	8.55
5.42	9.40	5.62	8.70
5.46	9.60	5.66	8.90
5.50	9.90	5.70	9.05
5.54	10.05	5.74	9.30
5.60	10.30	5.78	9.50
5.64	10.40	5.84	9.85
5.68	10.45	5.88	10.10
5.72	10.55	5.96	10.40
5.76	10.60	6.05	10.70
5.90	10.85	6.20	10.90
6.00	11.00	6.30	11.00

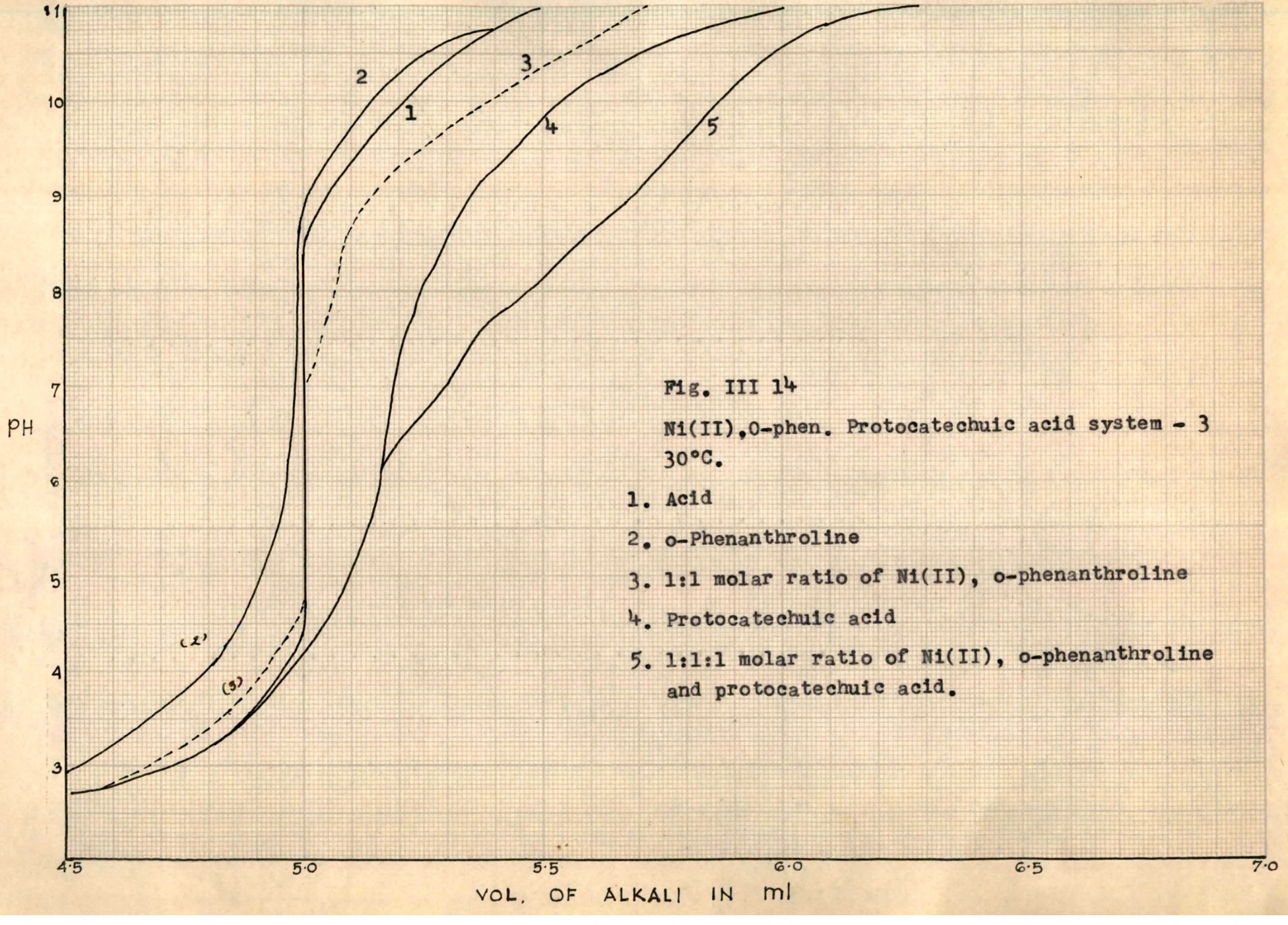

Fig. III 14

Ni(II),O-phen. Protocatechuic acid system - 3
30°C.

1. Acid
2. o-Phenanthroline
3. 1:1 molar ratio of Ni(II), o-phenanthroline
4. Protocatechuic acid
5. 1:1:1 molar ratio of Ni(II), o-phenanthroline and protocatechuic acid.

Table III 14

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Ni.o-phen. catechol system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.90	1.93_6	5.00	5.11	0.11	0.22_7	0.53_2	7.41_8	6.88_6
8.00	1.92_4	5.00	5.15	0.15	0.31_1	0.33_5	7.24_7	6.91_2
8.10	1.90_8	5.01	5.19	0.18	0.37_7	0.21_8	7.08_4	6.86_6
8.20	1.88_8	5.02	5.23	0.21	0.44_5	0.09_5	6.95_1	6.85_6
8.30	1.86_8	5.03	5.27	0.24	0.51_3	$\bar{1}.97_7$	6.83_4	6.85_7
8.40	1.84_8	5.04	5.32	0.28	0.60_5	$\bar{1}.81_4$	6.67_6	6.86_2
8.50	1.81_6	5.05	5.35	0.32	0.70_4	$\bar{1}.62_3$	6.32_7	6.70_4

$\log K_{MAL} = 6.84 \pm 0.07$

Table III 15

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Ni.o-phen. protocatechuic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.60	1.94_9	5.21	5.34	0.13	0.26_5	0.44_3	8.52_8	8.08_5
7.70	1.93_5	5.22	5.39	0.17	0.35_0	0.26_8	8.35_7	8.08_9
7.80	1.93_5	5.23	5.43	0.20	0.41_1	0.15_4	8.17_6	8.02_0
7.90	1.92_0	5.23	5.44	0.21	0.43_5	0.11_3	8.09_6	7.98_3
8.00	1.88_0	5.24	5.47	0.23	0.48_7	0.02_2	8.01_2	7.99_0
8.10	1.84_0	5.25	5.49	0.24	0.51_9	$\bar{1}.96_6$	7.94_4	7.97_8
8.20	1.80_0	5.26	5.51	0.25	0.55_2	$\bar{1}.90_9$	7.89_2	7.98_3

$\log K_{MAL} = 8.01 \pm 0.07$

Fig. III 15

Ni(II).o-phen. catechol system - 30°C.

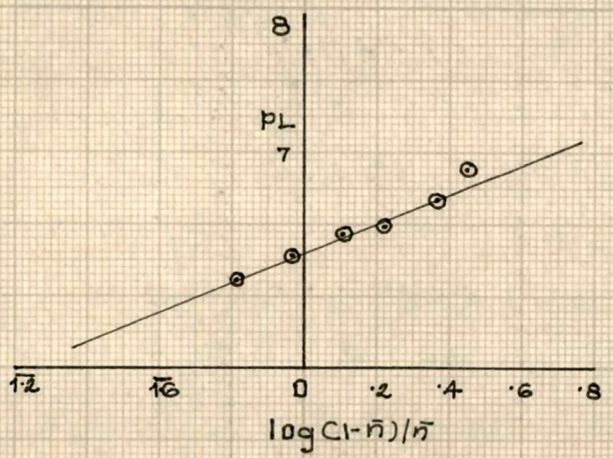

Fig. III 16

Ni(II).o-phen. protocatechuic acid system - 30°C.

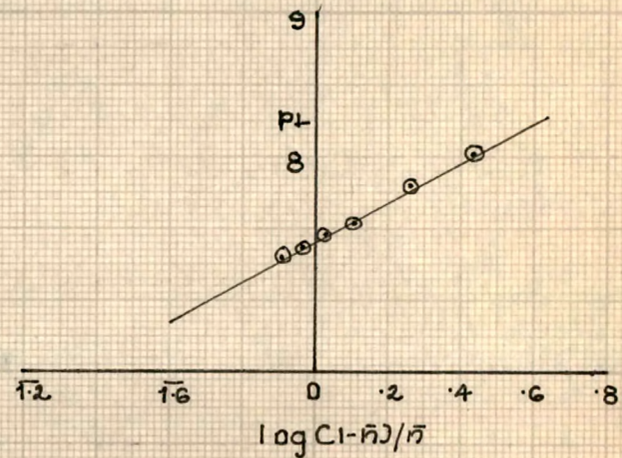

Table III 16

Logarithms of stability constants of ternary Dipyridyl-M^{2+}-ligand complexes and o-Phenanthroline-Ni^{2+}-ligand complexes.

	Ligand (L)			
	Catechol	Pyrogallol	2,3-Dihydroxy-naphthalene	Protocatechuic acid
$\log K^{Cu.Dipy.}_{Cu.Dipy.L}$	13.22 ± 0.09	13.04 ± 0.04	-	15.48 ± 0.06
$\log K^{Ni.Dipy.}_{Ni.Dipy.L}$	7.66 ± 0.09	7.01 ± 0.09	-	8.58 ± 0.05
$\log K^{Ni.o-Phen.}_{Ni.o-Phen.L}$	6.84 ± 0.07	-	-	8.01 ± 0.07

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