CHAPTER THREE

TERNARY METAL, α-α'-DIPYRIDYL OR o-PHENANTHROLINE AND DIAMINE SYSTEMS

In the present chapter studies of the systems MAL where M = Cu(II), Ni(II); A = dipyridyl (dipy) or o-phenanthroline (o-phen) and L = diamines have been carried out using modified form of Irving-Rossotti titration technique[1]. The formation constants K^{MA}_{MAL} have been determined using two methods, viz. (I) titration of M + A + L mixture against alkali and (II) titration of M + A mixture against concentrated solution of secondary ligand. Second method was not used where L = N-substituted ethylenediamine and 1,3-diaminopropane because a concentrated solution of the diamine is required and they are very costly.

Experimental :

Materials, purification, preparation and standardisation :

Conductivity water was used throughout the work. Solutions of oxalic acid, sodium hydroxide, perchloric acid, sodium perchlorate and diamines were prepared and standardised as discussed in chapter II. The other reagents used were as follows :

Dipyridyl and o-phenanthroline (E.M., pure), diamines (Fluka, pure). Their solutions of required molarity were prepared by diluting the standard stock solution, prepared by dissolving the exactly weighed quantity of samples in conductivity water. Nickel perchlorate was prepared as discussed in chapter II. The instruments used were same as detailed in previous chapters.

Method I :

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

1. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (31.1 ml.) total volume = 50 ml., μ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (21.3 ml.) total volume = 50.0 ml., μ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (26.2 ml.), total volume = 50.0 ml., μ = 0.2M.
4. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity 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.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (26.2 ml.), total volume = 50.0 ml. μ = 0.2M.
6. Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + conductivity water (36.0 ml.). total volume = 50.0 ml., μ = 0.2M.

Method II :

For the determination of mixed ligand formation constants by this method, following solutions were prepared :

For dipyridyl :

1. Perchloric acid (0.5M, 10.0 ml.) + sodium perchlorate (1M, 5.0 ml.) + conductivity water (35.0 ml.), total volume = 50.0 ml. μ = 0.2M.
2. Perchloric acid (0.5M, 10.0 ml.) + dipyridyl (0.02M, 10.0 ml.)+

metal perchlorate (0.02M, 10.0 ml.) + sodium perchlorate (1M, 4.6 ml.) + conductivity water (15.4 ml.), total volume = 50.0 ml. μ = 0.2M.

For o-phenanthroline :

1. Perchloric acid (0.5M, 5.0 ml.) + sodium perchlorate (1M, 7.5 ml.) + conductivity water (37.5 ml.), total volume = 50.0 ml. μ = 0.2M.
2. Perchloric acid (0.5M, 5.0 ml.) + o-phenanthroline (0.01M, 5.0 ml.) + metal perchlorate (0.01M, 5.0 ml.) + sodium perchlorate (1M, 7.4 ml.) + conductivity water (27.6 ml.), total volume = 50.0 ml., μ = 0.2M.

For the mixed ligand systems with o-phenanthroline the same number of sets as in case of dipyridyl were prepared but the concentrations of metal ion solution, o-phenanthroline, and secondary ligand were kept half that of corresponding solutions for dipyridyl in method I and concentration of metal ion and o-phenanthroline solutions were kept one fourth in the method II. This is because in concentrated solution precipitation of metal o-phenanthroline complex takes place.

The ionic strength of each solution was initially raised to 0.2M in both the methods. In method I the solutions (1-6) were titrated against 0.2M sodium hydroxide. In method II, where dipyridyl was the primary ligand, the samples were titrated against 1.0M secondary ligand. However, where o-phenanthroline was the primary ligand, solutions were titrated against 0.5M secondary ligand.

The plots of pH against volume of alkali in method I have been shown in fig. III 1 - III 4 and III 7 - III 15 and

plots of pH against volume of secondary ligand in method II have been shown in figs. III 5, III 6, III 16 and III 17.

Discussion :

The formation of mixed ligand complex can be represented in following two steps :

$$M^{2+} + dipy \rightleftharpoons [M.dipy]^{2+}$$

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

Mixed ligand formation constant

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

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

In method I, M.dipyridyl curve(5) diverges from the dipyridyl curve(IV) at lower pH indicating that the $[M(dipy)]^{2+}$ is formed at lower pH by the dissociation of protons attached with the tertiary nitrogens of dipyridyl molecules. The M.dipyridyl curve(5) diverges from acid curve(6) at higher pH, indicating that the formation of hydroxy complex $[M(dipy)(OH)_2]$ starts in this pH range. The curve(2) remains merged with curve(1) at low pH showing that complexation of the diamine does not take place at low pH. The curve(2) diverges from curve(1) at higher pH showing that Metal + dipyridyl + diamine combination takes place where M + dipyridyl 1:1 complex formation is complete. In this range hydroxo complex formation also does not occur.

In method II curve(2) lies slightly above curve(1) at low pH because the coordination of dipyridyl is not complete and it absorbs protons from solution. At pH between 3 and 4 both the curves overlap showing that M.dipyridyl 1:1 complex formation is complete at low pH. Curve(2) diverges from curve(1) after pH ~ 3.5 showing that the complexation with secondary ligand starts at that pH.

Since o-phenanthroline is structurally similar to dipyridyl, it can be expected to behave in a similar way. The nature of the o-phenanthroline curve(4) and Ni.o-phenanthroline curve(5), fig.III 14 are also similar to that of dipyridyl and Ni.dipyridyl curves indicating that $\left[Ni(o\text{-}phen)(H_2O)_2\right]^{2+}$ formed at low pH is stable at higher pH range.

The horizontal distance between curve(1) and curve(2) can be measured and used for the calculation of $\bar{n}$ where $\bar{n}$ is the average number of secondary ligand molecules associated with one $\left[M(dipy)\right]^{2+}$. Equation used for the calculation of $\bar{n}$ for method I would be same as given in the original paper[2].

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

For method II, $\bar{n}$ can be calculated using equation

$$\bar{n} = \frac{(V'' - V').\,L}{V^\circ.\,T_M^\circ}$$

Here T_M° is the concentration of $\left[M(dipy)\right]^{2+}$ which is equal to the concentration of the metal taken. The other terms have the usual meaning as detailed in the chapter II. The calculation of $\bar{n}$ was carried out below the pH where $\left[M(dipy)(OH)_2\right]$ formation starts, i.e. where $\left[M(dipy)\right]^{2+}$. curve(5) diverges

from the dipyridyl curve(4). $\bar{n}$ and pL were calculated at different pH values and have been presented in tables III 2.1Aa to III 2.5Aa, III 2.1Ab to III 2.6Ab and III 2.1B to III 2.2'B.

The value of pL at $\bar{n} = 0.5$ is equal to $\log K^{MA}_{MAL}$. However, this will be only one point and may involve experimental error. More precise values were obtained by plotting pL at each point against $\log (1-\bar{n})/\bar{n}$ and getting a straight line (figs. III 18 to III 36). At each point on the straight line $\log K^{MA}_{MAL} = pL - \log(1-\bar{n})/\bar{n}$. The average values were thus calculated and have been presented with mean deviation in table III 3.0.

The titrations could not be done in mixed ligand systems with Cu.dipy.N-N-diethyl en, Ni.dipy.N-N-diethyl en and Ni.dipy-N-N-dimethyl en as the mixed ligand complex formation takes place in the higher pH range. The study of [Cu(o-phen)L] and [Ni(o-phen)L] systems where L = N-substituted ethylenediamine or 1,3-diaminopropane was also not possible because precipitation takes place.

It is observed that the values of K^{MA}_{MAL} obtained by the two widely different methods give nearly the same values (within $\pm$ 0.1). The identity of the results indicates that the assumptions made are valid. The values are also in close agreement with the literature values obtained in some cases using other methods[3].

The values of mixed ligand formation constants K^{MA}_{MAL} where L = ethylenediamine are less than those where L = propylenediamine. This is in accordance with the basicities of the

ligands. K^{MA}_{MAL} value is still lower where L = 1,3-diamino-propane. This forms six membered ring which is less stable than five membered rings. In all the three cases, however, $K^{M}_{ML} - K^{MA}_{MAL}$ is much less than what is expected from statistical consideration. This is in accordance with the observations of earlier workers[4-7] using various other secondary ligands. In the present systems also the small difference between K^{MA}_{MAL} and K^{M}_{ML} can be attributed to the fact that dipyridyl is a π-bonding ligand and hence besides the M$\leftarrow$N σ-bonding there is significant M$\rightarrow$N $d\pi$-$p\pi$ interaction. Existence of M$\rightarrow$N π-interaction in dipyridyl complexes has been confirmed earlier.[8-11] Thus the electron density around the metal ion does not increase much as a result of complex formation. In other words the electronegativity of $\left[M.dipy\right]^{2+}$ remains almost the same as that of $\left[M(H_2O)_n\right]^{2+}$. Thus the tendency of $\left[M(dipy)\right]^{2+}$ to combine with the secondary ligand is the same as that of $\left[M(aq)\right]^{2+}$. Consequently the enthalpy changes remain same in the reaction $\left[M.dipy\right]^{2+} + L \rightleftharpoons \left[M.dipy.L\right]^{2+}$ and $M^{2+} + L \rightleftharpoons \left[ML\right]^{2+}$. Since there is no charge neutralization in either reactions, the entropy changes are also similar and hence the total free energy changes are nearly equal. This explains why K^{MA}_{MAL} is very close to K^{M}_{ML}.

In the system MAL, where L is a charged ion, K^{MA}_{MAL} is much higher than $K^{ML}_{ML_2}$ because in the formation of ML_2, the second L^{n-} has to face repulsion from the already existing charged L^{n-} ion and this lowers the value of $K^{ML}_{ML_2}$. In case of diamine, however, both primary and secondary ligands are neutral and hence there is no electrostatic repulsion in the formation

of MAL and ML_2. Since the charges on MAL and ML_2 are same the entropy changes are also same. Thus the difference $K^{MA}_{MAL} - K^{ML}_{ML_2}$ is less. The small difference is because A is a π-bonding ligand and hence does not allow the concentration of the electron to go up around the metal ion, whereas in $[ML]^{2+}$ the concentration of electrons around metal ion is more than in $[M(H_2O)_2]^{2+}$. Thus the tendency of L to combine with $[M.dipy]$ is more than to combine with ML . $K^{MA}_{MA_1}$ is, therefore, slightly higher than $K^{ML}_{ML_2}$.

$K^{M}_{ML_1} - K^{MA}_{MAL}$ is less in cases of copper complexes. It had been observed that the $K^{Cu.A}_{Cu.A.L}$ is even more than $K^{Cu}_{Cu.L}$ where L = catechol[6]. According to Sigel[8] this can be attributed to Jahn-Teller distortion. The distorted octahedral $[Cu(H_2O)_6]^{2+}$ will be some what more strongly distorted towards a square planar structure by the coordination of 2,2'-dipyridyl, thus creating the right geometry for the coordination of the secondary ligand.

However, in case of complexes of alkyl N-substituted ethylenediamine K^{MA}_{MAL} is lower than $K^{M}_{ML_1}$. This is because dipyridyl is a big molecule and may lead to steric hindrance with the alkyl group on the nitrogen atom. The lowering in the values is in the order

N-N-dimethyl en > N-N'-dimethyl en > N-ethyl en > N-methyl en > en.

This is in accordance with the increasing size of the alkyl groups on the nitrogen atom.

Table III 1.1A

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

E° = 0.02M T°_{L} = 0.002M μ = 0.2M t = 30°C.

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	1.50
1.00	1.65	1.00	1.70	1.00	1.65	1.00	1.65
2.00	1.80	2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.00	3.00	2.00	3.00	2.00	3.00	2.00
3.60	2.10	4.00	2.65	4.00	2.35	4.00	2.25
3.80	2.20	4.10	2.80	4.20	2.45	4.40	2.50
4.00	2.25	4.20	3.05	4.30	2.55	4.60	2.75
4.20	2.40	4.44	3.50	4.40	2.60	4.70	3.05
4.40	2.55	4.50	3.85	4.50	2.80	4.74	3.20
4.60	2.75	4.55	4.05	4.60	3.05	4.80	3.40
4.70	3.00	4.60	4.20	4.65	3.15	4.85	3.65
4.80	3.25	4.70	4.55	4.70	3.25	4.88	3.80
4.84	3.40	4.80	4.95	4.75	3.40	4.90	4.00
4.90	4.00	4.85	5.20	4.80	3.50	4.94	4.80
4.92	4.40	4.90	5.40	4.85	3.65	4.98	6.20
4.94	4.70	4.95	5.70	4.90	3.80	5.00	7.50
4.96	5.20	5.00	7.30	5.00	5.90	5.02	7.90
4.98	6.60	5.04	8.50	5.05	6.05	5.06	8.05
5.00	8.00	5.10	8.95	5.10	6.20	5.10	8.20
5.02	8.30	5.20	9.30		(ppts)	5.14	8.35
5.06	8.70	5.30	9.50			5.18	8.40
5.10	9.05	5.40	9.75			5.20	8.50
5.20	9.35	5.55	9.99			5.25	8.70
5.30	9.60	5.50	9.80			5.30	8.75
5.45	10.00					5.40	8.95

Table III 1.2A

N = 0.2M V° = 50 ml. $T°_{Dipy}$ = 0.002M $T°_{M}$ = 0.002M

E° = 0.02M $T°_{L}$ = 0.002M μ = 0.2M t = 30°C.

Ethylenediamine		Cu.dipy.en		Cu.en		Ni.dipy.en		Ni.en	
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	1.60	0.00	1.60	0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.70	1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.90	2.00	1.85	2.00	1.90	2.00	1.85	2.00	1.85
3.00	2.20	3.00	2.25	3.00	2.25	3.00	2.20	3.00	2.20
3.50	2.70	3.50	2.80	3.50	2.80	3.50	2.60	3.50	2.60
3.70	3.00	3.60	3.00	3.60	3.00	3.60	2.90	3.60	2.90
3.80	3.30	3.70	3.55	3.70	3.50	3.80	3.20	3.80	3.60
3.85	3.75	3.72	3.80	3.80	3.90	3.85	3.70	3.84	4.10
3.88	4.50	3.74	4.00	3.90	4.10	3.88	4.00	3.86	4.90
3.90	5.10	3.80	4.30	4.00	4.25	3.90	4.80	3.88	5.10
3.92	5.60	3.85	4.50	4.10	4.35	3.92	5.20	3.94	5.40
3.94	5.80	3.88	4.60	4.20	4.50	3.96	5.45	4.00	5.55
4.00	6.20	3.94	4.70	4.40	4.75	4.00	5.60	4.10	5.70
4.10	6.70	4.00	4.80	4.50	4.90	4.10	5.90	4.20	5.85
4.20	7.00	4.10	4.90	4.60	5.10	4.20	6.15	4.30	5.95
4.30	7.40	4.20	5.05	4.70	5.35	4.30	6.25	4.40	6.10
4.40	7.85	4.30	5.15	4.75	5.60	4.40	6.40	4.60	6.35
4.45	8.10	4.40	5.30	4.78	5.85	4.50	6.55	4.70	6.60
4.50	8.50	4.50	5.45	4.84	6.20	4.60	6.70	4.80	6.70
4.55	8.75	4.60	5.70	4.90	6.50	4.70	6.95	4.90	6.95
4.60	9.00	4.70	5.95	5.00	6.70	4.80	7.15	4.95	7.20
4.70	9.30	4.75	6.15	5.10	7.00	4.90	7.50	5.00	7.90
4.80	9.60	4.80	6.60	5.24	7.60	4.95	7.75	5.02	8.25
5.00	9.95	4.84	7.10 (ppts)	5.30	8.15 (ppts)	5.00	8.40 (ppts)	5.04	8.40 (ppts)

Fig. III 1

Ni(II)dipy.en system - 30°C.

1. Ethylenediamine
2. 1:1:1 Molar ratio of Ni(II) or Cu(II).dipy. and en.
3. 1:1 Molar ratio of Ni(II) or Cu(II) and en.

Fig. III 2

Cu(II).dipy.en system - 30°C.

4. Dipyridyl
5. 1:1 Molar ratio of Ni(II) or Cu(II) and dipyridyl
6. Acid.

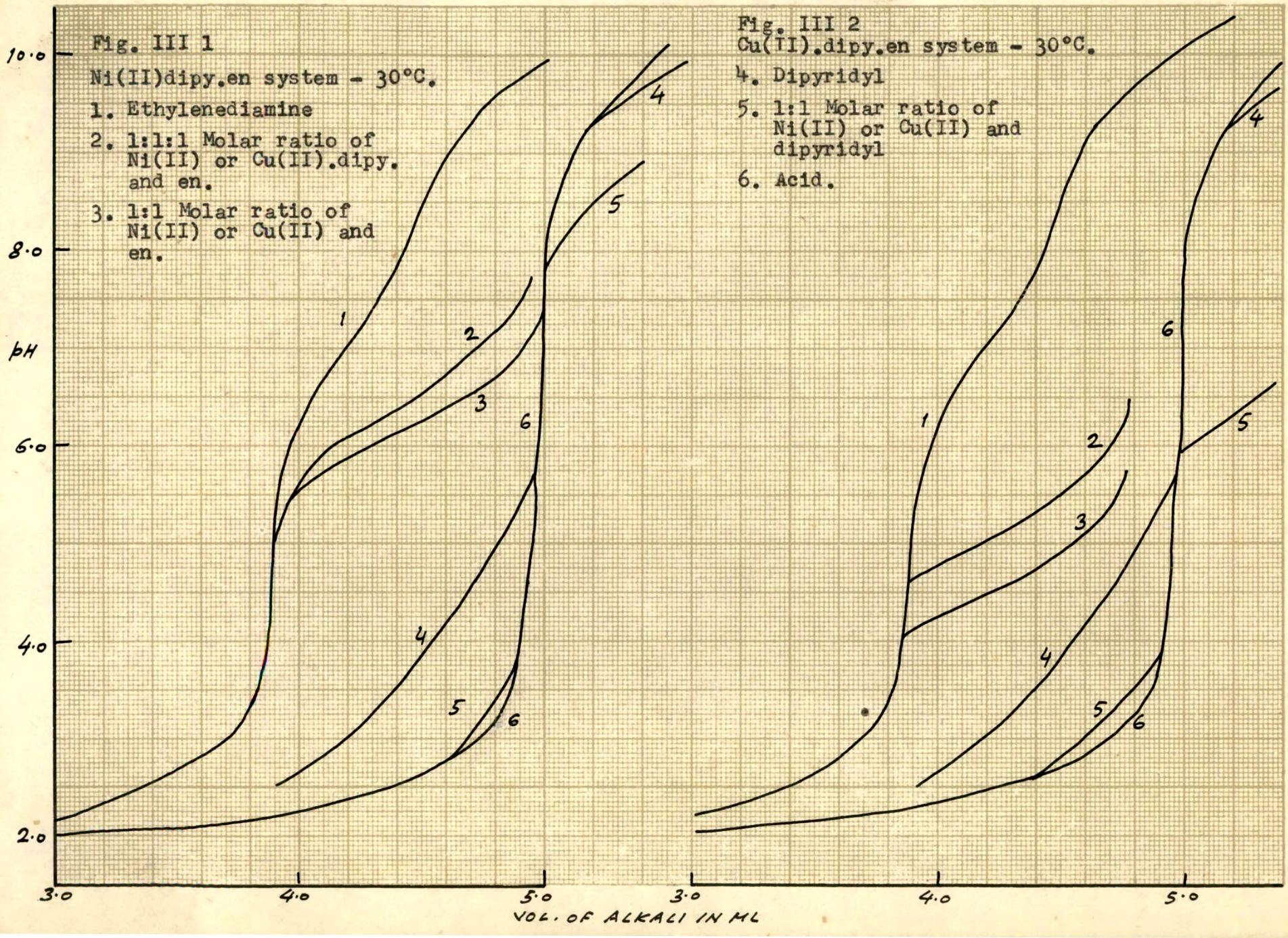


Table III 1.3A

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

E° = 0.02M T°_{L} = 0.002M μ = 0.2M t = 30°C.

Propylenediamine		Cu.dipy.pn		Cu.pn		Ni.dipy.pn		Ni.pn	
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	1.60	0.00	1.60	0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.70	1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.90	2.00	1.80	2.00	1.90	2.00	1.85	2.00	1.85
3.00	2.30	3.00	2.20	3.00	2.30	3.00	2.20	3.00	2.20
3.60	2.80	3.60	2.90	3.50	2.70	3.60	2.70	3.50	2.55
3.80	3.25	3.70	3.40	3.60	3.00	3.50	2.55	3.60	2.80
3.85	3.50	3.80	4.00	3.70	3.25	3.80	3.20	3.80	3.25
3.88	3.80	3.90	4.25	3.80	3.60	3.85	3.65	3.85	3.60
3.90	4.20	3.95	4.35	4.00	3.90	3.88	3.85	3.90	4.20
3.92	4.80	4.00	4.45	4.20	4.15	3.90	4.20	3.92	4.60
3.96	5.65	4.10	4.55	4.30	4.25	3.92	4.80	3.94	4.90
4.00	5.95	4.20	4.70	4.44	4.40	3.94	5.10	3.96	5.10
4.05	6.20	4.30	4.85	4.50	4.55	3.96	5.35	4.00	5.30
4.10	6.45	4.40	5.00	4.60	4.75	4.00	5.50	4.10	5.55
4.20	6.80	4.50	5.15	4.70	5.00	4.10	5.75	4.20	5.75
4.30	7.10	4.60	5.35	4.75	5.20	4.20	5.95	4.30	5.90
4.40	7.55	4.70	5.70	4.82	5.80	4.30	6.10	4.40	6.00
4.50	8.30	4.76	5.90	4.90	6.35	4.40	6.30	4.60	6.25
4.45	7.85	4.82	6.40	5.00	6.60	4.50	6.45	4.80	6.60
4.55	8.80	4.84	6.60	5.10	6.90	4.60	6.60	4.90	6.85
4.60	9.10	4.86	6.90	5.20	7.25	4.80	7.05	4.95	7.05
4.70	9.45	4.88	7.20	5.26	7.50	4.90	7.50	5.00	7.50
4.80	9.70	4.90	7.60	5.30	8.00	4.96	8.10	5.05	8.40
5.00	10.10		(ppts)	5.34	8.30 (ppts)	5.00	8.70 (ppts)	5.10	8.70 (ppts.)

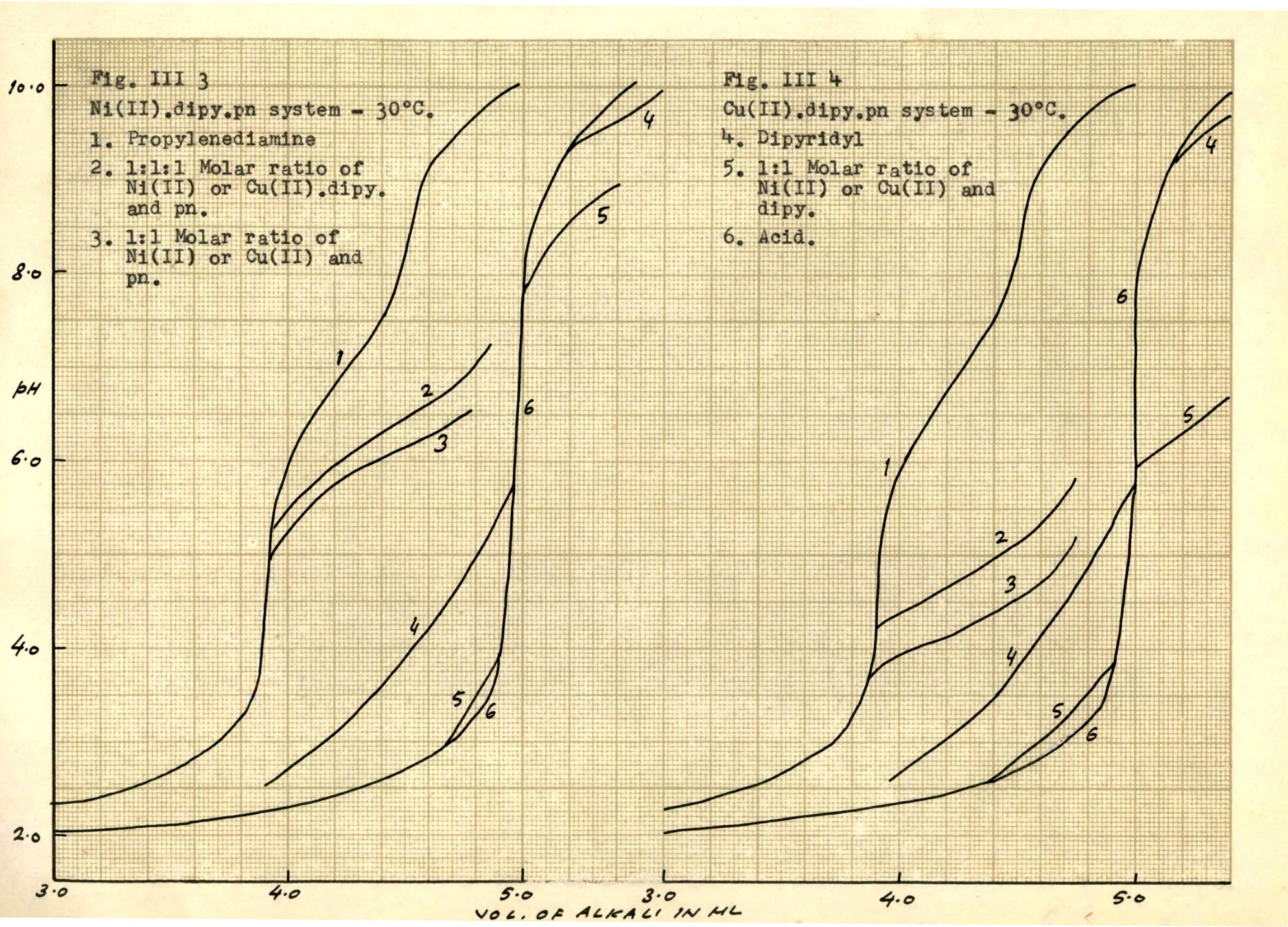


Fig. III 3
Ni(II).dipy.pn system - 30°C.
1. Propylenediamine
2. 1:1:1 Molar ratio of Ni(II) or Cu(II).dipy. and pn.
3. 1:1 Molar ratio of Ni(II) or Cu(II) and pn.
Fig. III 4
Cu(II).dipy.pn system - 30°C.
4. Dipyridyl
5. 1:1 Molar ratio of Ni(II) or Cu(II) and dipy.
6. Acid.
pH
10·0
8·0
6·0
4·0
2·0
3·0
4·0
5·0
VOL. OF ALKALI IN ML

Table III 1.2'A

N = 1.0M V° = 50 ml. T°_{dipy} = 0.004M T°_{M} = 0.004M

E° = 0.1M μ = 0.2M t = 30°C.

Perchloric acid		Cu.dipy en		Ni.dipy en	
Vol.of en (in ml.)	B	Vol.of en (in ml.)	B	Vol.of en (in ml.)	B
0.00	0.90	0.00	0.90	0.00	0.90
1.00	1.10	1.00	1.10	1.00	1.10
2.00	1.60	2.00	1.55	2.00	1.60
2.30	2.00	2.30	2.00	2.30	2.00
2.45	2.50	2.43	2.50	2.42	2.45
2.49	3.00	2.44	2.70	2.44	2.70
2.50	4.40	2.49	3.00	2.46	2.90
2.52	5.25	2.50	3.80	2.48	3.10
2.56	5.75	2.52	4.00	2.50	4.80
2.60	6.00	2.55	4.20	2.52	5.10
2.65	6.15	2.60	4.40	2.56	5.30
2.70	6.30	2.65	4.60	2.60	5.50
2.75	6.45	2.70	4.90	2.65	5.65
2.80	6.55	2.74	5.05	2.70	5.80
2.90	6.75	2.76	5.60	2.75	5.90
3.00	6.85	2.80	5.95	2.80	6.00
3.10	6.95	2.85	6.10	2.90	6.20
3.20	7.05	2.90	6.30	3.00	6.35
3.40	7.20	3.00	6.50	3.10	6.50
3.60	7.35	3.10	6.60	3.20	6.60
3.80	7.50	3.30	6.80	3.30	6.70
4.00	7.60	3.50	7.00	3.40	6.80
4.20	7.80	3.70	7.15		(ppts.)
4.50	8.00	4.00	7.35		
4.70	8.25	4.20	7.45		
		4.40	7.60		
		4.80	7.90		

Table III 1.3'A

N = 1.0M V° = 50 ml. T°_{dipy} = 0.004M T°_{M} = 0.004M

E° = 0.1M μ = 0.2M t = 30°C.

Perchloric acid		Cu.dipy pn		Ni.dipy pn	
Vol.of pn (in ml.)	B	Vol.of pn (in ml.)	B	Vol.of pn (in ml.)	B
0.00	0.90	0.00	0.90	0.00	0.90
1.00	1.00	1.00	1.00	1.00	1.05
2.00	1.45	2.00	1.45	2.00	1.50
2.30	1.85	2.30	1.90	2.30	1.80
2.40	2.20	2.40	2.25	2.40	2.20
2.42	2.35	2.43	2.70	2.41	2.65
2.44	2.65	2.45	2.85	2.44	2.90
2.47	2.90	2.46	2.95	2.46	3.10
2.48	3.80	2.48	3.35	2.48	3.50
2.50	4.90	2.50	3.60	2.50	4.50
2.52	5.15	2.52	3.70	2.52	4.80
2.54	5.35	2.56	3.90	2.54	4.95
2.60	5.70	2.60	4.10	2.56	5.10
2.65	5.85	2.65	4.30	2.60	5.30
2.70	6.00	2.68	4.70	2.65	5.45
2.80	6.20	2.70	4.90	2.70	5.60
2.85	6.30	2.72	5.20	2.75	5.70
2.90	6.35	2.74	5.35	2.80	5.80
3.00	6.50	2.76	5.45	2.90	6.00
3.10	6.60	2.80	5.65	3.00	6.20
3.30	6.75	2.85	5.90	3.10	6.30
3.60	7.00	2.90	6.00	3.20	6.40
4.00	7.30	3.00	6.20	3.30	6.50
4.20	7.45	3.15	6.40	3.40	6.60
4.40	7.65	3.30	6.60	3.50	6.70
4.60	7.85	3.60	6.75		(ppts.)
4.80	8.10	4.00	7.10		
5.00	8.40				

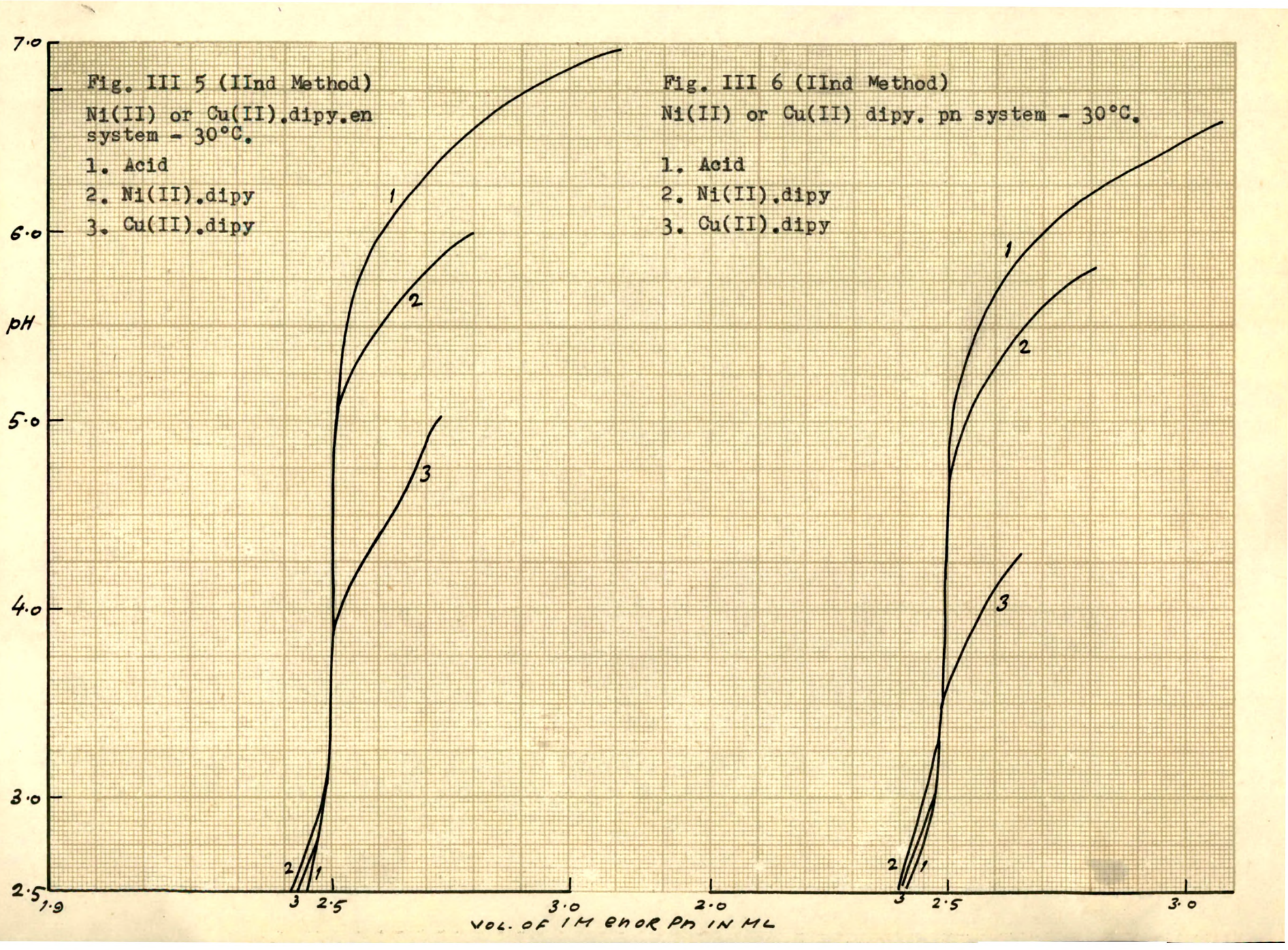


Fig. III 5 (IInd Method)
Ni(II) or Cu(II).dipy.en system - 30°C.
1. Acid
2. Ni(II).dipy
3. Cu(II).dipy
Fig. III 6 (IInd Method)
Ni(II) or Cu(II) dipy. pn system - 30°C.
1. Acid
2. Ni(II).dipy
3. Cu(II).dipy
pH
7·0
6·0
5·0
4·0
3·0
2·5
1·9
2·5
3·0
2·0
2·5
3·0
VOL. OF 1M en OR Pn IN ML

Table III 1.4A

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

E° = 0.02M T°_{L} = 0.002M μ = 0.2M t = 30°C.

N-Methyl en		Cu.dipy-N-Methyl en		Cu.N-Methyl en		Ni.dipy N-Methyl en		Ni.N-Methyl en	
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	1.60	0.00	1.60	0.00	1.60	0.00	1.65	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.70	1.00	1.75	1.00	1.70
2.00	2.00	2.00	1.95	2.00	1.90	2.00	1.90	2.00	1.90
3.00	2.30	3.00	2.30	3.00	2.30	3.00	2.30	3.00	2.20
3.40	2.60	3.50	2.70	3.40	2.55	3.30	2.50	3.60	2.80
3.70	3.05	3.70	3.10	3.60	2.85	3.60	2.80	3.70	3.05
3.80	3.45	3.80	3.65	3.70	3.10	3.70	3.05	3.80	3.60
3.84	3.80	3.82	3.90	3.78	3.55	3.80	3.45	3.86	4.65
3.88	4.50	3.84	4.15	3.82	3.80	3.86	4.10	3.88	4.90
3.90	4.90	3.86	4.40	3.86	4.00	3.88	4.55	3.90	5.20
3.92	5.50	3.90	4.60	3.90	4.10	3.90	5.00	3.94	5.45
3.94	5.90	3.95	4.80	3.95	4.20	3.92	5.30	4.00	5.65
4.00	6.35	4.00	4.95	4.00	4.30	3.96	5.70	4.10	5.90
4.05	6.65	4.10	5.20	4.10	4.45	4.00	5.90	4.20	6.10
4.10	6.85	4.20	5.35	4.20	4.55	4.10	6.15	4.30	6.25
4.20	7.20	4.30	5.55	4.30	4.70	4.20	6.40	4.40	6.35
4.30	7.55	4.40	5.70	4.40	4.80	4.30	6.55	4.50	6.50
4.40	8.00	4.50	5.80	4.60	5.10	4.40	6.75	4.60	6.65
4.50	8.60	4.60	5.95	4.70	5.35	4.50	6.90	4.70	6.80
4.60	9.05	4.70	6.15	4.80	5.70	4.60	7.10	4.80	7.00
4.70	9.35	4.80	6.40	4.90	6.20	4.70	7.40	4.90	7.40
4.80	9.60	4.85	6.65	5.00	6.55	4.80	7.70	4.95	7.70
5.00	9.90	4.88	6.90	5.10	6.80	4.90	8.20	5.00	8.10
5.20	10.15	4.92	7.30 (ppts.)	5.20	7.10 (ppts.)	5.00	8.60 (ppts.)	5.08	8.50 (ppts.)

Fig. III 7

Ni(II).dipy.N-methyl en system - 30°C.

1. N-Methyl en
2. 1:1:1 Molar ratio of Ni(II) or Cu(II) dipy and N-methyl en.
3. 1:1 Molar ratio of Ni(II) or Cu(II) and N-methyl en.

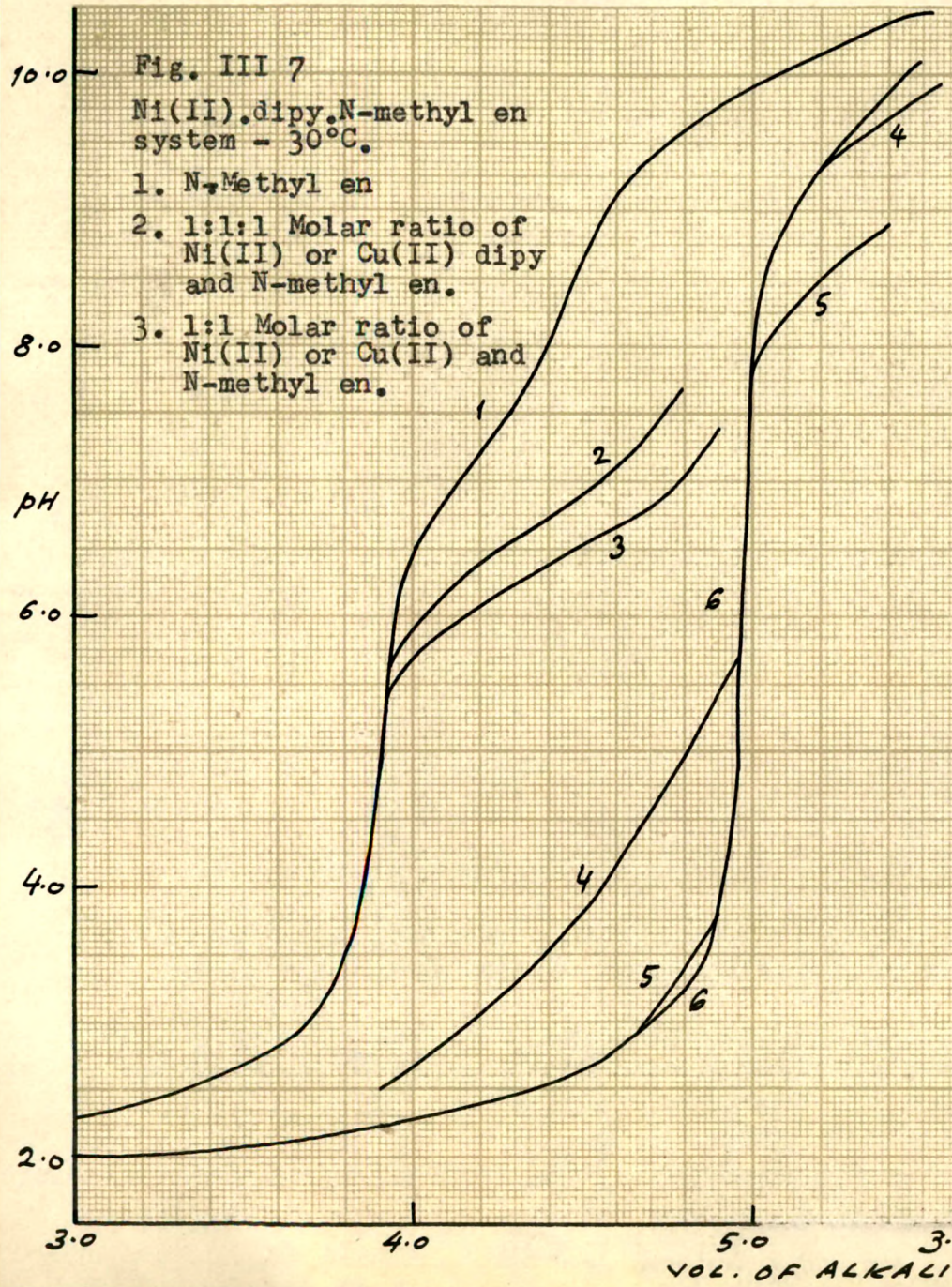


Fig. III 8

Cu(II).dipy.N-methyl en system - 30°C.

4. Dipyridyl
5. 1:1 Molar ratio of Ni(II) or Cu(II) and dipy.
6. Acid.

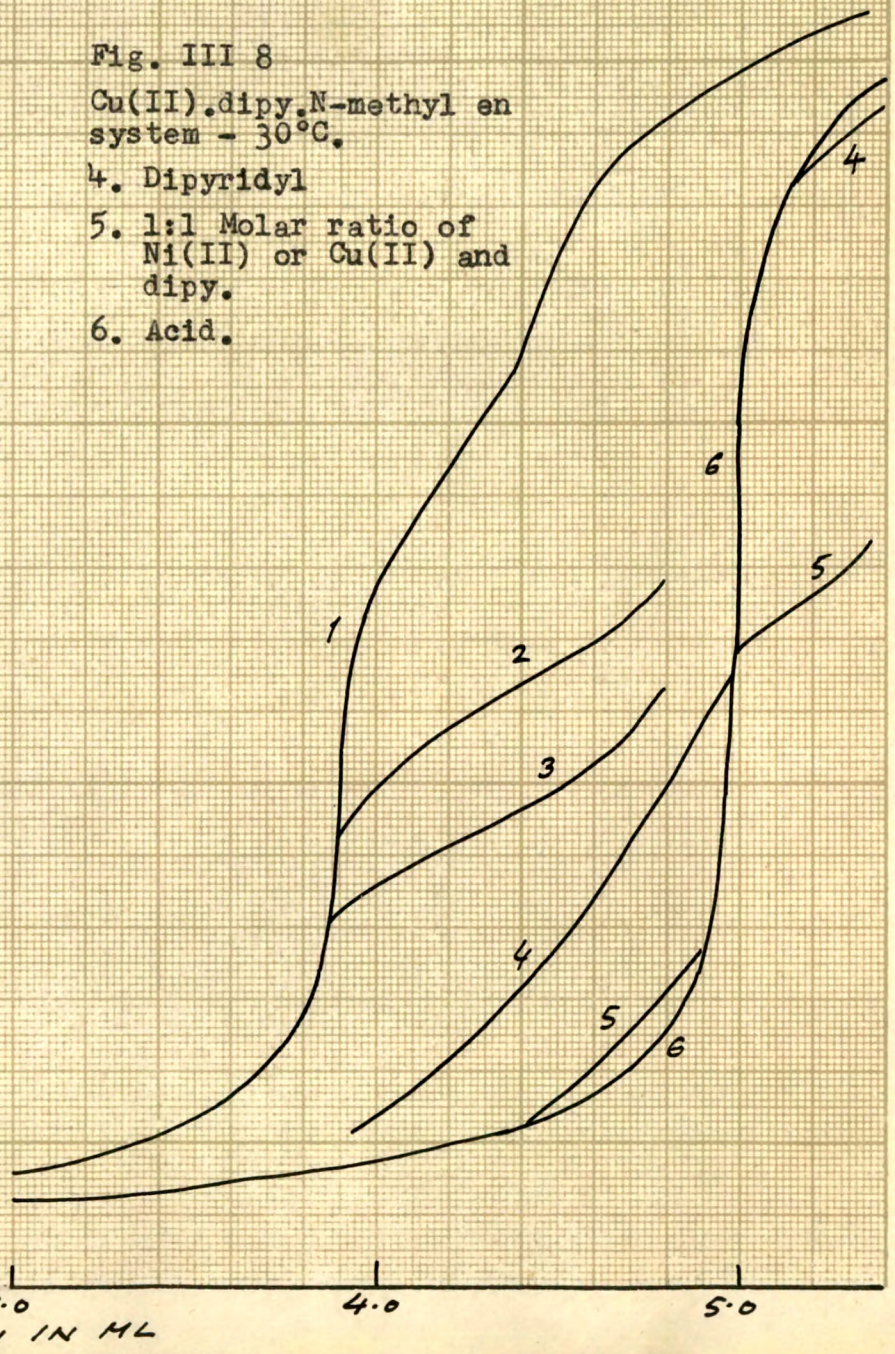


Table III 1.5A

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

E° = 0.02M T°_{L} = 0.002M μ = 0.2M t = 30°C.

N-Ethyl en		Cu.dipy-N-Ethyl en.		Cu.N-Ethyl en		Ni.dipy-N-Ethyl en.		Ni.N-Ethyl en	
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	1.60	0.00	1.60	0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.75	1.00	1.75	1.00	1.70	1.00	1.70	1.00	1.75
2.00	1.95	2.00	1.95	2.00	1.90	2.00	1.90	2.00	2.00
3.00	2.25	3.00	2.25	3.00	2.30	3.00	2.20	3.00	2.25
3.50	2.70	3.40	2.60	3.40	2.55	3.60	2.80	3.40	2.60
3.70	3.00	3.60	2.90	3.60	2.85	3.80	3.30	3.60	2.80
3.80	3.30	3.70	3.15	3.70	3.15	3.85	3.60	3.80	3.30
3.85	3.60	3.80	3.70	3.76	3.45	3.88	4.00	3.86	3.75
3.88	3.90	3.82	4.10	3.78	3.60	3.90	4.60	3.88	4.10
3.90	4.50	3.84	4.40	3.80	3.80	3.92	5.20	3.90	4.60
3.92	5.10	3.86	4.65	3.82	4.00	3.94	5.55	3.92	5.20
3.94	5.60	3.90	4.95	3.84	4.15	3.96	5.80	3.96	5.70
3.98	6.15	3.95	5.15	3.88	4.30	4.00	6.10	4.00	5.95
4.00	6.30	4.00	5.30	4.00	4.55	4.05	6.30	4.05	6.10
4.10	6.70	4.05	5.40	4.10	4.75	4.10	6.45	4.10	6.25
4.20	7.05	4.15	5.65	4.20	4.90	4.15	6.60	4.20	6.40
4.30	7.50	4.20	5.70	4.30	5.00	4.20	6.70	4.30	6.60
4.40	8.10	4.30	5.90	4.40	5.10	4.30	6.90	4.40	6.75
4.45	8.50	4.40	6.05	4.60	5.35	4.40	7.05	4.50	6.90
4.50	8.85	4.50	6.15	4.70	5.55	4.50	7.30	4.60	7.05
4.60	9.40	4.60	6.35	4.80	5.80	4.60	7.50	4.70	7.25
4.70	9.75	4.70	6.55	4.90	6.20	4.70	7.80	4.80	7.55
4.90	10.10	4.80	6.80	4.95	6.40	4.80	8.25	4.92	8.00
5.20	10.40		(ppts.)	5.00	6.55	4.85	8.40	5.00	8.40
					(ppts.)		(ppts.)		(ppts.)

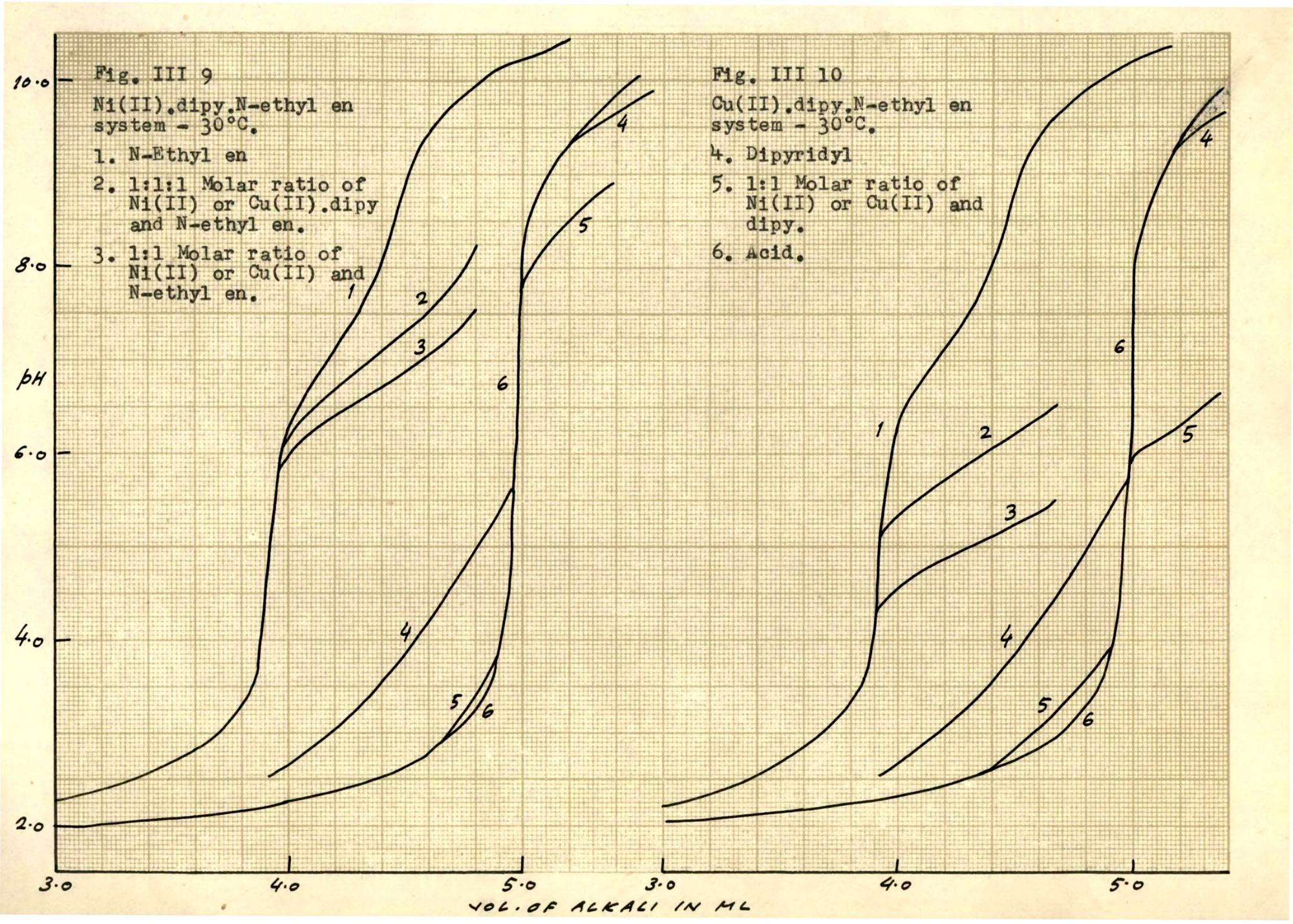


Fig. III 9
Ni(II).dipy.N-ethyl en system - 30°C.
1. N-Ethyl en
2. 1:1:1 Molar ratio of Ni(II) or Cu(II).dipy and N-ethyl en.
3. 1:1 Molar ratio of Ni(II) or Cu(II) and N-ethyl en.
Fig. III 10
Cu(II).dipy.N-ethyl en system - 30°C.
4. Dipyridyl
5. 1:1 Molar ratio of Ni(II) or Cu(II) and dipy.
6. Acid.
pH
10·0
8·0
6·0
4·0
2·0
3·0
4·0
5·0
VOL. OF ALKALI IN ML

Table III 1.6A

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

E° = 0.02M T°_{L} = 0.002M μ = 0.2M t = 30°C.

N-N'Dimethyl en		Cu.dipy N-N'Dimethyl en		Cu.N-N'Dimethyl en		Ni.dipy-N-N'Dimethyl en		Ni.N-N'Dimethyl en	
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	1.65	0.00	1.60	0.00	1.60	0.00	1.65	0.00	1.65
1.00	1.80	1.00	1.70	1.00	1.70	1.00	1.80	1.00	1.80
2.00	2.00	2.00	1.90	2.00	1.90	2.00	2.00	2.00	2.00
3.00	2.30	3.00	2.20	3.00	2.20	3.00	2.30	3.00	2.30
3.50	2.75	3.40	2.50	3.40	2.60	3.60	2.80	3.40	2.60
3.70	3.05	3.60	2.70	3.60	2.80	3.80	3.35	3.60	2.85
3.80	3.30	3.70	3.20	3.70	3.10	3.85	3.75	3.80	3.40
3.86	3.75	3.80	3.50	3.80	3.40	3.88	4.20	3.85	3.80
3.88	4.10	3.85	3.70	3.85	3.80	3.90	4.70	3.88	4.35
3.90	4.50	3.88	4.00	3.90	4.10	3.92	5.05	3.90	4.80
3.92	5.00	3.92	4.20	3.95	4.25	3.94	5.40	3.92	5.10
3.94	5.40	3.96	4.65	4.00	4.40	3.96	5.65	3.94	5.40
3.96	5.80	4.00	4.90	4.10	4.70	4.00	5.95	4.00	5.80
4.00	6.10	4.05	5.20	4.20	4.85	4.05	6.15	4.05	5.95
4.10	6.70	4.10	5.40	4.30	4.95	4.10	6.30	4.10	6.05
4.20	7.00	4.20	5.70	4.40	5.10	4.20	6.50	4.20	6.25
4.30	7.40	4.30	5.90	4.60	5.30	4.30	6.75	4.30	6.45
4.40	7.90	4.40	6.10	4.70	5.50	4.40	6.95	4.40	6.60
4.50	8.50	4.50	6.25	4.80	5.75	4.50	7.20	4.50	6.75
4.60	9.10	4.60	6.50	4.90	6.25	4.60	7.50	4.60	6.90
4.70	9.50		(ppts.)	4.95	6.55	4.70	7.80	4.70	7.20
4.80	9.80			5.00	6.70	4.80	8.25	4.80	7.50
4.90	10.00			5.10	7.00	4.75	8.05	4.90	8.10
5.00	10.15			5.20	7.30	4.85	8.30	5.00	8.70
				5.30	7.55		(ppts.)		(ppts.)
				5.40	7.90				
				5.50	8.50				
					(ppts.)				

Fig. III 11

Ni(II).dipy.N,N'-dimethyl en system - 30°C.

1. N-N'-dimethyl en
2. 1:1:1 Molar ratio of Ni(II) or Cu(II).dipy and N-N'-dimethyl en.
3. 1:1 Molar ratio of Ni(II) or Cu(II) and N-N'-dimethyl en.

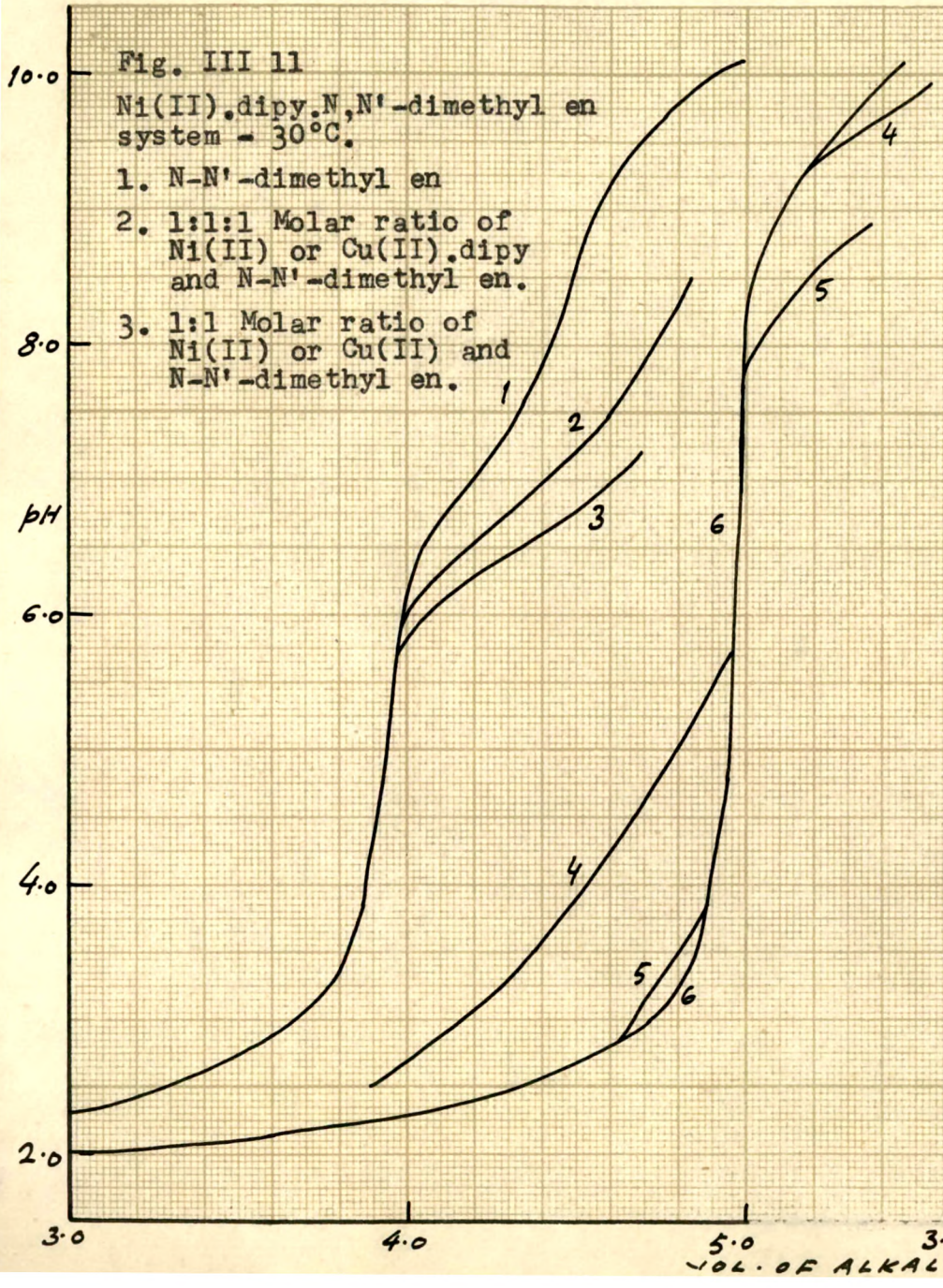
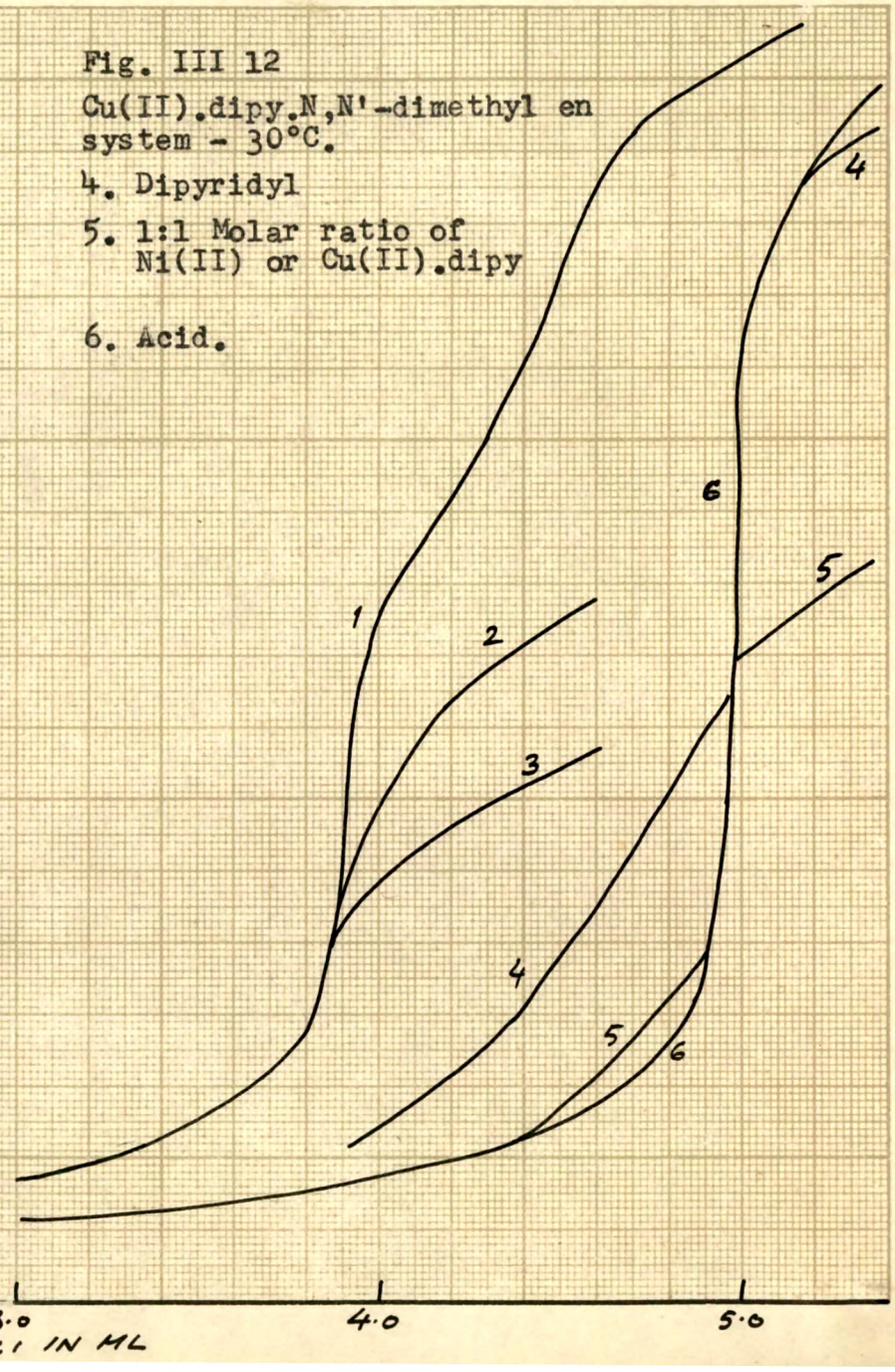


Fig. III 12

Cu(II).dipy.N,N'-dimethyl en system - 30°C.

4. Dipyridyl
5. 1:1 Molar ratio of Ni(II) or Cu(II).dipy
6. Acid.



VOL. OF ALKALI IN ML

Table III 1.7A

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

N-N Dimethyl en		Ni.dipy N-N Dimethyl en		Ni N-N Dimethyl en	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.65	0.00	1.65
1.00	1.70	1.00	1.75	1.00	1.80
2.00	1.90	2.00	2.00	2.00	2.00
3.00	2.25	3.00	2.35	3.00	2.30
3.60	2.75	3.40	2.60	3.40	2.60
3.80	3.20	3.70	2.95	3.70	2.95
3.85	3.45	3.80	3.30	3.80	3.50
3.88	3.80	3.86	3.70	3.86	4.00
3.90	4.20	3.88	4.00	3.88	4.40
3.92	4.70	3.90	4.50	3.90	4.60
3.94	5.10	3.92	4.95	3.95	5.30
3.98	5.60	3.94	5.25	4.00	5.50
4.05	6.00	3.96	5.45	4.10	5.80
4.10	6.20	4.00	5.70	4.20	6.00
4.20	6.50	4.10	6.10	4.30	6.20
4.30	6.90	4.20	6.35	4.40	6.40
4.40	7.50	4.30	6.60	4.50	6.55
4.45	8.05	4.40	6.80	4.60	6.70
4.50	8.55	4.50	7.05	4.70	6.95
4.55	8.85	4.60	7.35	4.80	7.20
4.60	9.05	4.70	7.70	4.85	7.40
4.70	9.40	4.75	7.90	4.92	7.90
4.80	9.60	4.80	8.05	5.00	8.30
5.00	10.05	4.90	8.50 (ppts.)	5.05	8.50 (ppts.)

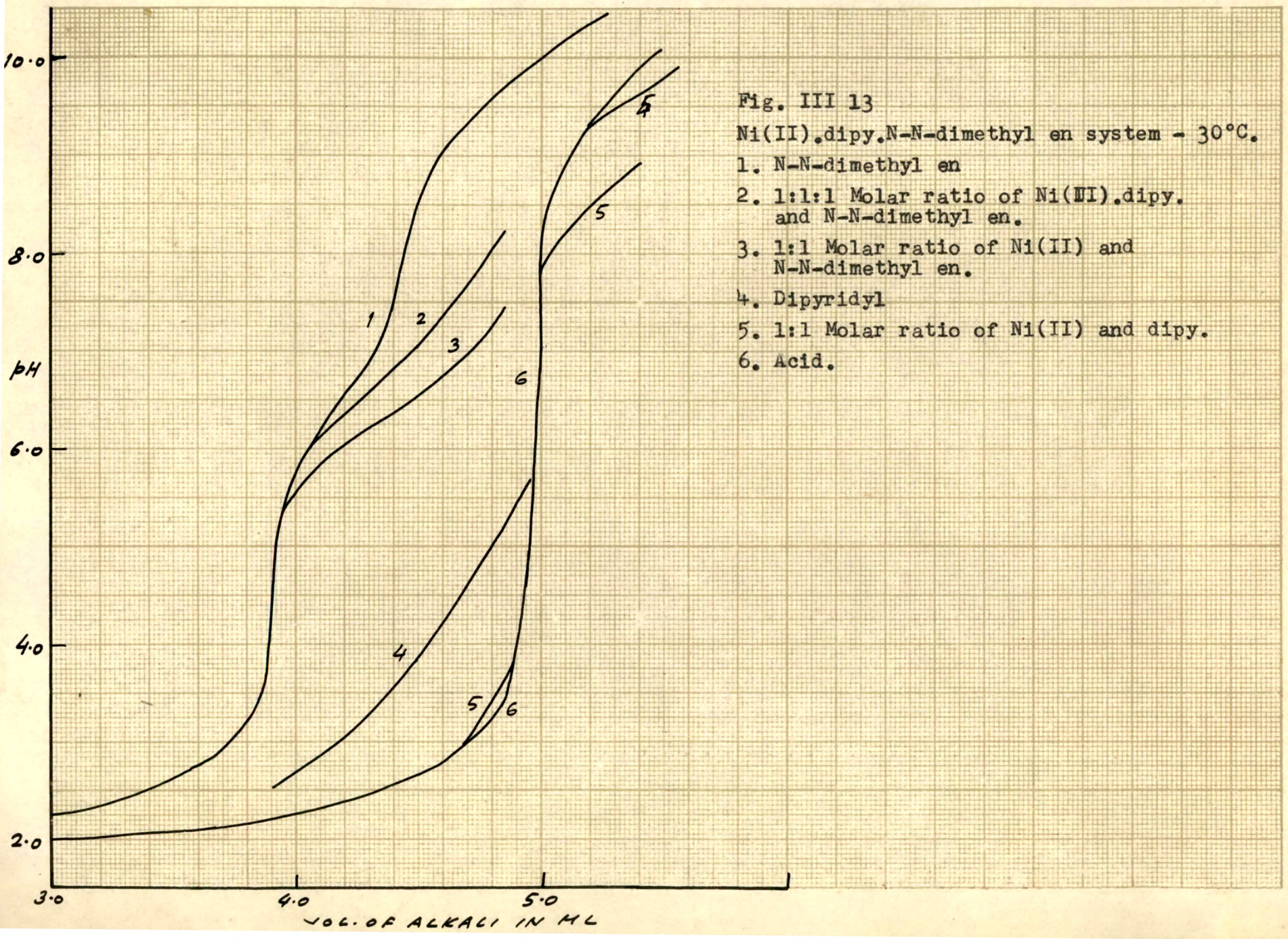


Fig. III 13

Ni(II).dipy.N-N-dimethyl en system - 30°C.

1. N-N-dimethyl en
2. 1:1:1 Molar ratio of Ni(II).dipy. and N-N-dimethyl en.
3. 1:1 Molar ratio of Ni(II) and N-N-dimethyl en.
4. Dipyridyl
5. 1:1 Molar ratio of Ni(II) and dipy.
6. Acid.

Table III 1.1B

N = 0.2M V° = 50 ml. T°_{L} = 0.001M t = 30°C.

E° = 0.02M $T^{\circ}_{o\text{-phen}}$ = 0.001M T°_{M} = 0.001M μ = 0.2M

Perchloric acid		o-phen		Ni-o-phen		Ethylenediamine		Ni-o-phen en	
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	1.55	0.00	1.55	0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.65	1.00	1.65	1.00	1.65	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.85	2.00	1.80	2.00	1.80	2.00	1.80
3.00	1.90	3.00	2.05	2.50	1.85	3.00	2.10	3.00	2.05
4.00	2.20	4.00	2.40	3.00	2.00	3.50	2.30	4.00	2.60
4.40	2.50	4.10	2.50	3.60	2.10	3.80	2.45	4.20	3.00
4.60	2.70	4.20	2.60	3.80	2.20	4.00	2.65	4.30	3.15
4.80	3.10	4.30	2.75	4.00	2.25	4.20	2.95	4.35	3.50
4.85	3.40	4.40	2.90	4.30	2.50	4.30	3.20	4.38	3.70
4.88	3.65	4.50	3.10	4.50	2.75	4.36	3.50	4.40	3.90
4.90	4.00	4.60	3.45	4.60	2.90	4.38	3.80	4.42	5.00
4.92	4.50	4.65	3.85	4.70	3.10	4.40	4.60	4.46	5.50
4.94	5.20	4.70	4.20	4.80	3.40	4.42	5.20	4.50	5.80
4.96	5.80	4.75	4.60	4.85	3.80	4.44	5.60	4.54	6.00
4.98	6.80	4.80	5.00	4.88	4.10	4.46	5.90	4.60	6.25
5.00	8.20	4.85	5.40	4.90	4.40	4.50	6.20	4.68	6.50
5.02	8.70	4.90	5.70	4.94	5.30	4.55	6.60	4.75	6.70
5.04	9.00	4.95	5.90	4.96	6.00	4.60	7.00	4.80	6.85
5.06	9.20	4.98	6.50	4.98	6.60	4.64	7.30	4.85	7.05
5.10	9.50	5.00	8.30	5.00	8.30	4.68	7.60	4.90	7.30
5.15	9.80	5.02	8.70	5.05	8.60	4.70	7.95	4.94	7.55
5.20	10.05	5.04	9.10	5.10	8.95	4.74	8.50	4.96	7.75
5.30	10.35	5.10	9.50	5.15	9.15	4.80	9.00	4.98	8.30
5.40	10.60	5.20	9.85	5.20	9.30	4.90	9.50	5.00	8.70
5.60	11.00	5.25	10.00	5.30	9.55	5.00	9.90		(ppts.)

Table III 1.2B

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

Propylenediamine		Ni.o-Phen pn	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80
3.00	2.10	3.00	2.05
4.00	2.60	4.00	2.60
4.20	2.95	4.30	3.10
4.34	3.40	4.36	3.50
4.38	3.90	4.38	3.75
4.40	4.50	4.40	4.20
4.42	5.10	4.42	4.80
4.44	5.60	4.44	5.20
4.46	5.85	4.46	5.45
4.50	6.20	4.50	5.75
4.55	6.50	4.55	5.95
4.60	6.80	4.60	6.10
4.65	7.15	4.70	6.40
4.68	7.40	4.80	6.70
4.70	7.60	4.85	6.95
4.72	7.90	4.90	7.25
4.74	8.25	4.92	7.50
4.78	8.70	4.94	7.65
4.82	9.10	4.96	7.95
4.86	9.25	4.98	8.30
4.90	9.45	5.00	8.60
5.00	9.80		(ppts.)
5.10	10.05		

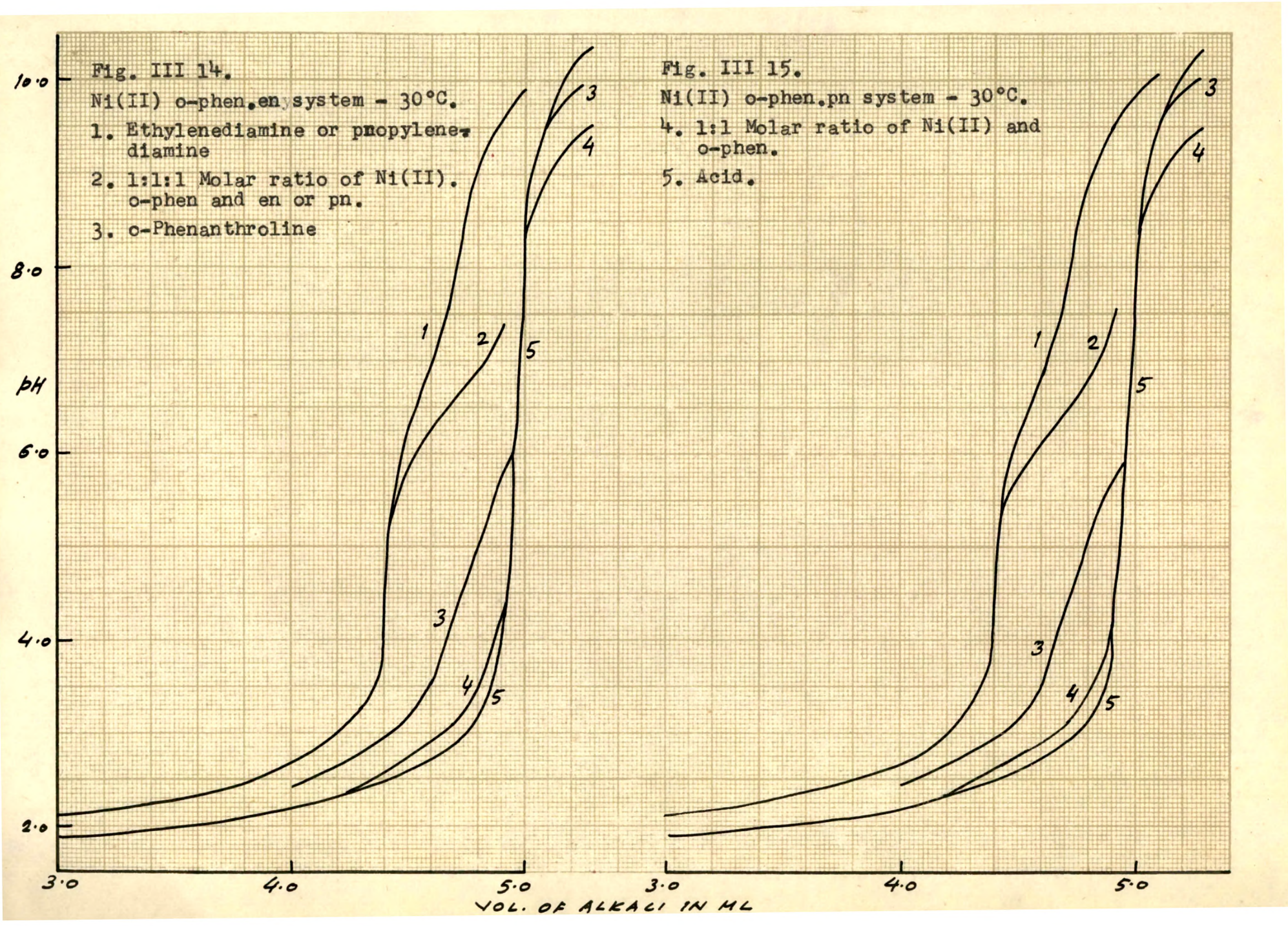


Fig. III 14.
Ni(II) o-phen.en system - 30°C.
1. Ethylenediamine or propylene-diamine
2. 1:1:1 Molar ratio of Ni(II). o-phen and en or pn.
3. o-Phenanthroline
10·0
8·0
6·0
4·0
2·0
pH
3·0
4·0
5·0
VOL. OF ALKALI IN ML
Fig. III 15.
Ni(II) o-phen.pn system - 30°C.
4. 1:1 Molar ratio of Ni(II) and o-phen.
5. Acid.
3·0
4·0
5·0

Table III 1.2' B

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.
E° = 0.05M $T^{\circ}_{o\text{-Phen}}$ = 0.001M T°_{M} = 0.001M

Perchloric acid		Ni.o-Phen en	
Vol.of en (in ml.)	B	Vol.of en (in ml.)	B
0.00	1.10	0.00	1.15
1.00	1.35	1.00	1.35
2.00	1.80	2.00	1.80
2.34	2.40	2.30	2.25
2.40	2.60	2.40	2.60
2.44	2.90	2.44	3.20
2.46	3.20	2.46	3.40
2.48	3.90	2.48	4.00
2.50	4.90	2.50	5.10
2.52	5.40	2.52	5.30
2.54	5.60	2.54	5.45
2.56	5.75	2.56	5.55
2.60	5.95	2.60	5.75
2.65	6.20	2.65	5.90
2.70	6.35	2.70	6.05
2.75	6.45	2.80	6.25
2.80	6.60	2.90	6.45
3.00	6.85	3.00	6.55
3.10	7.00	3.10	6.65
3.30	7.15	3.20	6.75
3.50	7.30	3.30	6.85
3.60	7.40	3.40	6.95
3.80	7.50	3.60	7.10
4.00	7.70	3.80	7.25
4.20	7.80	4.00	7.40
4.40	8.00	4.20	7.55
4.60	8.15		(ppts.)
5.00	8.55		

Table III 1.2' B

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M $T^{\circ}_{o\text{-Phen}}$ = 0.001M T°_{M} = 0.001M

Perchloric acid		Ni.o-Phen pn	
Vol.of pn (in ml.)	B	Vol.of pn (in ml.)	B
0.00	1.10	0.00	1.15
1.00	1.35	1.00	1.40
2.00	1.90	2.00	1.90
2.30	2.25	2.30	2.25
2.40	2.50	2.40	2.65
2.44	2.75	2.42	2.80
2.46	3.10	2.42	3.10
2.48	3.60	2.44	3.25
2.50	4.50	2.46	3.40
2.52	5.00	2.48	3.90
2.54	5.30	2.50	4.75
2.56	5.45	2.52	5.05
2.60	5.70	2.55	5.25
2.65	5.90	2.60	5.50
2.70	6.05	2.65	5.65
2.80	6.25	2.70	5.80
2.90	6.40	2.75	5.95
3.00	6.50	2.80	6.05
3.10	6.60	2.90	6.20
3.20	6.70	3.00	6.30
3.40	6.90	3.10	6.45
3.60	7.10	3.20	6.55
3.80	7.20	3.30	6.65
4.00	7.35	3.40	6.70
4.20	7.50	3.50	6.80
4.40	7.65	3.60	6.90
4.60	7.90	3.80	7.05
4.80	8.15	4.00	7.20
5.00	8.40		(ppts.)

Fig. III 16 (IInd Method)
Ni(II) o-phen.en system - 30°C.
1. Acid
2. Ni(II).o-phen.

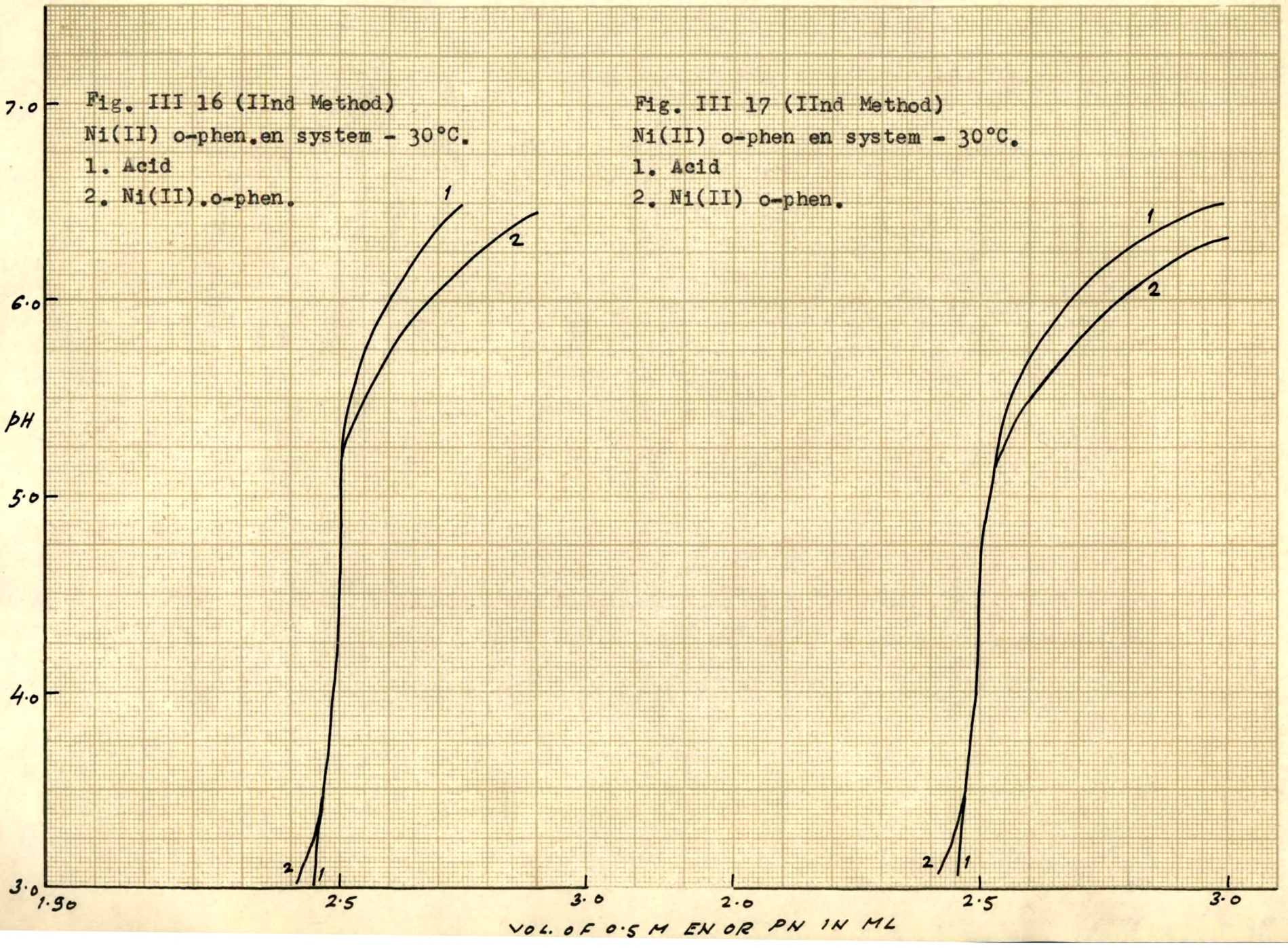


Fig. III 17 (IInd Method)
Ni(II) o-phen en system - 30°C.
1. Acid
2. Ni(II) o-phen.

Table III 2.1Aa

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
4.90	2.00_0	3.89	4.10	0.21	0.20_8	0.58_1	10.13_7	9.55_6
4.95	2.00_0	3.89	4.14	0.25	0.25_0	0.47_7	10.06_1	9.58_4
5.00	2.00_0	3.90	4.18	0.28	0.28_0	0.41_0	9.97_9	9.56_9
5.05	2.00_0	3.90	4.22	0.32	0.32_0	0.32_7	9.90_6	9.57_9
5.10	2.00_0	3.90	4.26	0.36	0.36_0	0.25_0	9.84_2	9.59_2
5.15	2.00_0	3.90	4.30	0.40	0.40_0	0.17_6	9.76_2	9.58_6
5.20	2.00_0	3.90	4.34	0.44	0.44_1	0.10_5	9.69_2	9.58_7
5.25	2.00_0	3.90	4.37	0.47	0.47_1	0.05_0	9.61_9	9.56_9
5.30	2.00_0	3.91	4.43	0.52	0.52_1	$\bar{1}.96_5$	9.56_1	9.59_6

$\log K_{MAL} = 9.58 \pm 0.02$

Table III 2.1'Aa

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

B	T_L°	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
4.10	0.04_8	2.50_0	2.53_5	0.03_5	0.17_5	0.67_3	10.24_5	9.57_2
4.15	0.04_8	2.50_0	2.54_5	0.04_5	0.22_5	0.53_7	10.14_5	9.60_8
4.20	0.04_8	2.50_0	2.55_0	0.05_0	0.25_0	0.47_7	10.04_5	9.56_8
4.25	0.04_8	2.50_0	2.56_5	0.06_5	0.32_5	0.31_7	9.94_6	9.62_9
4.30	0.04_9	2.50_0	2.58_0	0.08_0	0.40_0	0.17_6	9.74_6	9.57_0
4.35	0.04_9	2.50_0	2.59_0	0.09_0	0.45_0	0.08_7	9.74_7	9.66_0
4.40	0.04_9	2.50_0	2.60_0	0.10_0	0.50_0	0.00_0	9.64_5	9.64_5
4.45	0.04_9	2.50_0	2.61_5	0.11_5	0.57_5	$\bar{1}.86_9$	9.54_7	9.67_8

$\log K_{MAL} = 9.61 \pm 0.04$

Table III 2.2Aa

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
4.40	2.00_0	3.88	4.00	0.12	0.12_0	0.86_5	11.18_9	10.32_4
4.50	2.00_0	3.88	4.07	0.19	0.18_8	0.63_5	11.04_4	10.40_9
4.60	2.00_0	3.88	4.13	0.25	0.24_7	0.48_2	10.85_9	10.37_7
4.70	2.00_0	3.89	4.20	0.31	0.30_7	0.35_3	10.69_6	10.34_3
4.80	2.00_0	3.89	4.28	0.39	0.39_6	0.18_3	10.55_8	10.37_8
4.90	2.00_0	3.89	4.35	0.44	0.44_1	0.10_3	10.39_3	10.29_0
5.00	2.00_0	3.90	4.43	0.53	0.53_1	$\bar{1}.94_6$	10.27_2	10.32_6

$\log K_{MAL} = 10.35 \pm 0.03$

Table III 2.2'Aa

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

B	T_L°	V'	V"	V"-V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
3.80	0.04_8	2.48_5	2.53_5	0.05_0	0.25_0	0.47_7	10.94_7	10.47_0
3.90	0.04_8	2.48_5	2.55_0	0.06_5	0.32_5	0.31_7	10.74_8	10.43_1
3.95	0.04_8	2.49_0	2.56_0	0.00_7	0.35_0	0.26_9	10.64_7	10.37_8
4.00	0.04_9	2.49_0	2.57_5	0.08_5	0.42_5	0.13_1	10.54_8	10.41_7
4.05	0.04_9	2.49_0	2.58_5	0.09_5	0.47_5	0.04_3	10.44_8	10.40_5
4.10	0.04_9	2.49_0	2.60_0	0.11_0	0.55_0	$\bar{1}.91_3$	10.34_8	10.43_5
4.20	0.04_9	2.49_0	2.62_5	0.13_5	0.67_5	$\bar{1}.68_3$	10.14_9	10.46_6

$\log K_{MAL} = 10.42 \pm 0.03$

Fig. III 18 Cu(II) dipy.en system - 30°C.

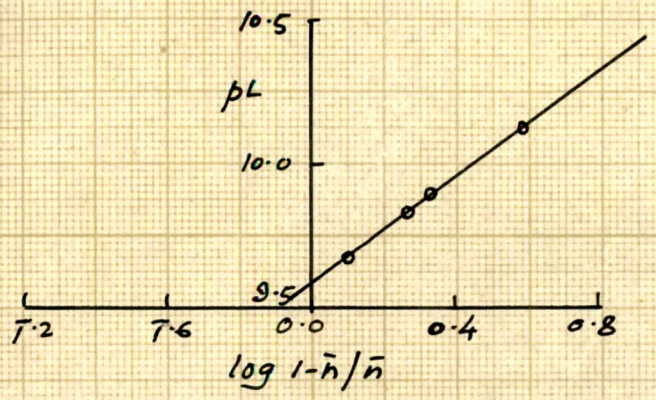


Fig. III 19 (IInd Method) Cu(II).dipy en system-30°C.

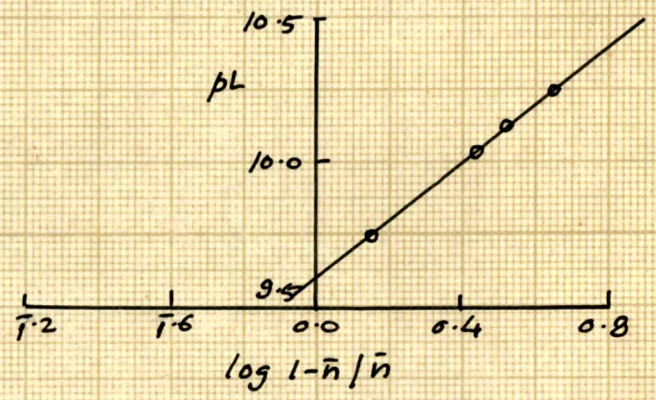


Fig. III 20 Cu(II) dipy pn system - 30°C.

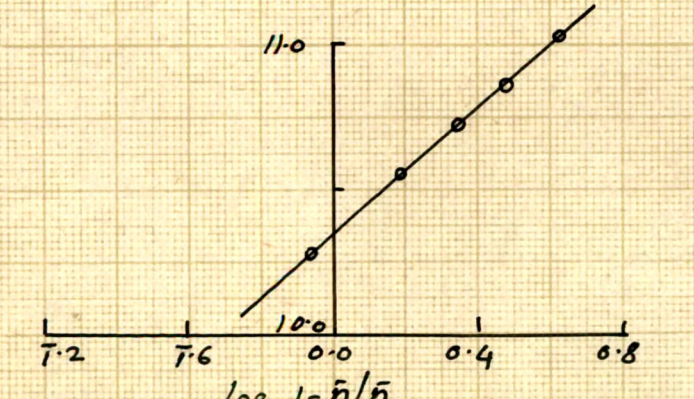


Fig.III 21 (IInd Method) Cu(II) dipy pn system-30°C.

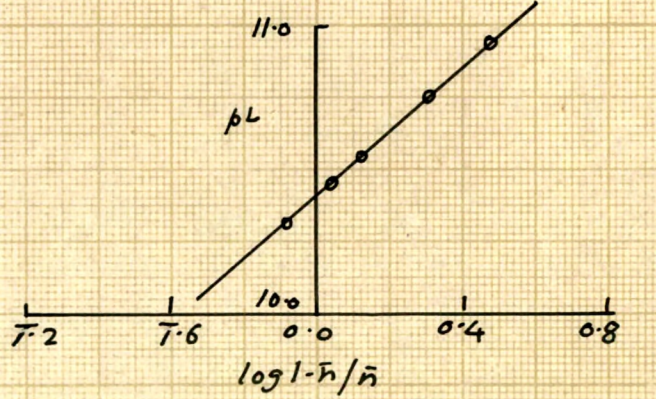


Table III 2.3Aa

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.40	2.00_0	3.92	4.21	0.29	0.29_0	0.38_9	9.49_1	9.10_2
5.50	2.00_0	3.92	4.27	0.35	0.35_0	0.26_9	9.33_2	9.06_3
5.60	2.00_0	3.92	4.34	0.42	0.42_0	0.14_0	9.18_5	9.04_5
5.70	2.00_0	3.93	4.41	0.48	0.48_0	0.03_5	9.03_7	9.00_2
5.75	2.00_0	3.93	4.46	0.53	0.53_0	$\bar{1}.94_8$	9.98_3	9.03_5
5.80	1.99_5	3.94	4.50	0.56	0.56_0	$\bar{1}.89_2$	8.91_6	9.02_4
5.85	1.98_5	3.94	4.54	0.60	0.60_5	$\bar{1}.81_5$	8.86_4	9.04_9
5.90	1.98_0	3.95	4.59	0.64	0.64_0	$\bar{1}.73_7$	8.81_6	9.07_9

$\log K_{MAL} = 9.05 \pm 0.03$

Table III 2.4Aa

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.80	2.00_0	3.96	4.23	0.27	0.27_0	0.43_2	9.28_6	8.85_4
5.90	2.00_0	3.97	4.30	0.33	0.33_0	0.30_7	9.12_7	8.82_0
6.00	1.98_5	3.98	4.39	0.41	0.41_3	0.15_2	8.99_0	8.83_8
6.10	1.96_5	3.99	4.45	0.46	0.46_8	0.05_5	8.83_9	8.78_4
6.20	1.94_0	4.00	4.50	0.50	0.51_5	$\bar{1}.97_4$	8.68_7	8.71_3
6.30	1.91_5	4.01	4.57	0.56	0.58_5	$\bar{1}.85_1$	8.56_5	8.71_3

$\log K_{MAL} = 8.78 \pm 0.04$

Table III 2.5Aa

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.90	1.93_6	3.98	4.31	0.33	0.34_1	0.28_6	8.24_5	7.95_9
5.95	1.92_6	3.99	4.34	0.35	0.36_1	0.24_8	8.07_1	7.82_3
6.00	1.91_6	3.99	4.36	0.37	0.38_6	0.20_1	8.08_3	7.88_2
6.10	1.89_6	4.00	4.42	0.42	0.44_3	0.09_9	7.93_6	7.83_7
6.20	1.87_5	4.01	4.48	0.47	0.50_2	$\bar{1}.99_6$	7.79_6	7.80_0
6.30	1.84_5	4.02	4.54	0.52	0.56_4	$\bar{1}.88_8$	7.66_8	7.78_0
6.35	1.83_0	4.03	4.59	0.56	0.61_2	$\bar{1}.80_2$	7.62_7	7.82_5

$\log K_{MAL} = 7.84 \pm 0.04$

Fig. III 22 Cu(II) dipy.N-Methyl en system - 30°C.

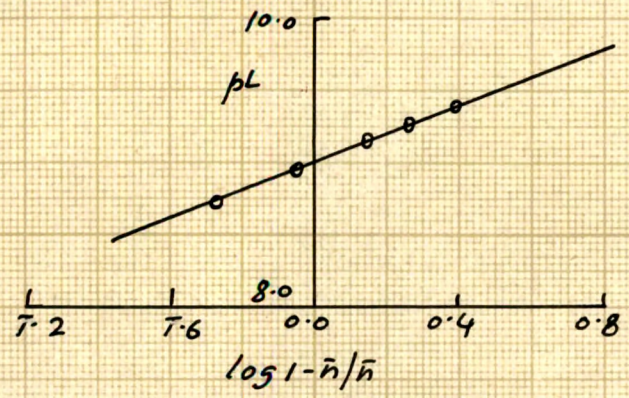


Fig. III 23 Cu(II) dipy.N-ethyl en system - 30°C.

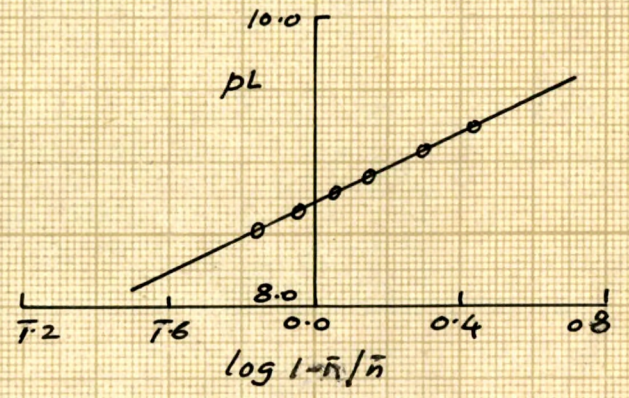


Fig. III 24 Cu(II) dipy. N-N'-dimethyl en system - 30°C.

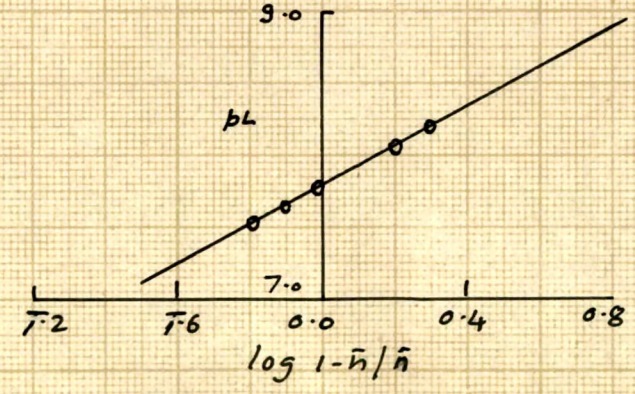


Table III 2.1Ab

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.00	1.92_2	3.96	4.14	0.18	0.18_7	0.63_8	7.96_4	7.32_6
6.10	1.90_2	3.98	4.21	0.23	0.24_2	0.49_5	7.80_6	7.31_0
6.20	1.90_0	3.99	4.28	0.29	0.30_5	0.35_7	7.65_6	7.29_8
6.30	1.84_1	4.01	4.36	0.35	0.38_0	0.21_2	7.53_0	7.31_8
6.40	1.84_1	4.04	4.45	0.41	0.44_6	0.09_4	7.40_0	7.30_6
6.50	1.80_1	4.06	4.50	0.44	0.48_9	0.01_9	7.32_0	7.30_1

$\log K_{MAL} = 7.31 \pm 0.02$

Table III 2.1'Ab

B, T°_L, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data for Ni.dipyridyl ethylenediamine system - 30°C.

B	T°_L	V'	V"	V"-V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.25	0.04_8	2.52_0	2.55_0	0.03_0	0.15_0	0.75_3	7.94_9	7.19_6
5.30	0.04_8	2.52_0	2.56_0	0.04_0	0.20_0	0.60_2	7.85_0	7.24_8
5.35	0.04_9	2.52_5	2.57_5	0.05_0	0.25_0	0.47_7	7.75_0	7.27_3
5.40	0.04_9	2.53_0	2.58_0	0.06_0	0.30_0	0.36_8	7.65_0	7.28_2
5.45	0.04_9	2.53_0	2.59_5	0.06_5	0.32_5	0.31_7	7.53_0	7.21_3
5.50	0.04_9	2.53_0	2.60_5	0.07_5	0.37_5	0.22_2	7.45_0	7.22_8
5.60	0.05_0	2.54_0	2.63_0	0.09_0	0.45_0	0.08_7	7.26_0	7.17_3
5.70	0.05_0	2.55_0	2.66_0	0.11_0	0.55_0	$\bar{1}.91_3$	7.13_0	7.21_7

$\log K_{MAL} = 7.23 \pm 0.05$

Table III 2.2Ab

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
6.20	1.82_1	4.05	4.35	0.30	0.32_9	0.30_9	7.80_6	7.49_7
6.25	1.80_1	4.06	4.39	0.33	0.36_7	0.23_6	7.7^4_2	7.50_6
6.30	1.78_1	4.07	4.41	0.3^4	0.38_0	0.21_2	7.66_3	7.45_1
6.35	1.76_1	4.08	4.46	0.38	0.43_2	0.11_9	7.61_3	7.49_4
6.40	1.72_1	4.09	4.48	0.39	0.45_3	0.08_2	7.5^4_3	7.46_1
6.45	1.70_1	4.11	4.52	0.41	0.48_2	0.02_5	7.48_3	7.45_7
6.50	1.66_1	4.13	4.56	0.43	0.51_8	$\bar{1}.96_8$	7.43_0	7.46_2

$\log K_{MAL} = 7.47 \pm 0.02$

Table III 2.2'Ab

B, T°_L, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni.dipyridyl propylenediamine system - 30°C.

B	T°_L	V'	V"	V"-V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.30	0.04_9	2.53_5	2.60_0	0.06_5	0.32_5	0.31_7	7.95_0	7.63_3
5.35	0.04_9	2.5^4_0	2.61_0	0.07_0	0.35_0	0.26_9	7.85_1	7.58_2
5.40	0.05_0	2.55_0	2.63_0	0.08_0	0.40_0	0.17_6	7.75_5	7.57_9
5.45	0.05_0	2.55_5	2.65_0	0.09_5	0.47_5	0.04_3	7.65_0	7.60_7
5.50	0.05_0	2.56_0	2.66_0	0.10_0	0.50_0	0.00_0	7.56_4	7.56_4
5.55	0.05_1	2.57_0	2.68_0	0.11_0	0.55_0	$\bar{1}.91_2$	7.46_2	7.55_0
5.60	0.05_1	2.57_5	2.70_0	0.12_5	0.62_5	$\bar{1}.77_8$	7.36_3	7.58_5

$\log K_{MAL} = 7.58 \pm 0.02$

Fig.III 25 Ni(II) dipy.en system - 30°C.

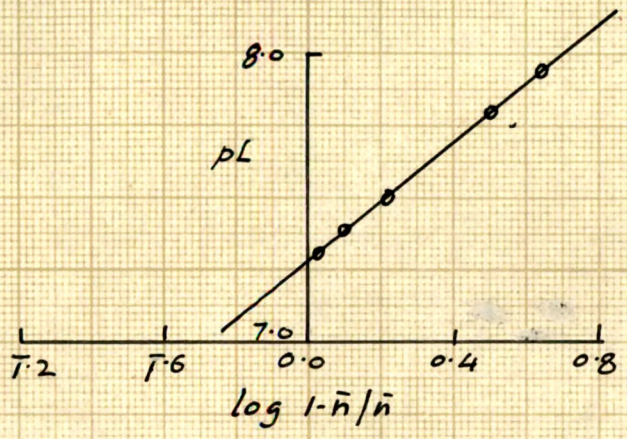


Fig.III 26 (IInd Method) Ni(II).dipy en system - 30°C.

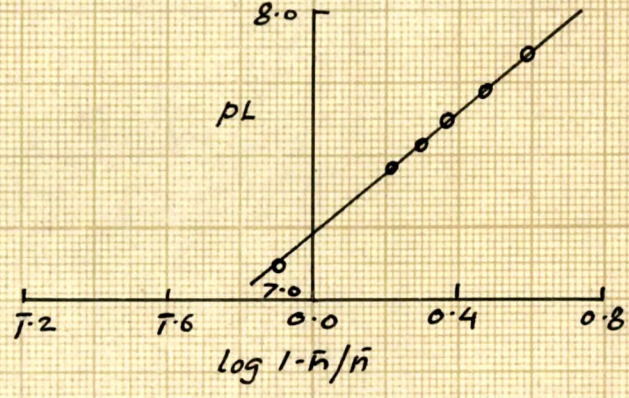


Fig.III 27 Ni(II).dipy pn system - 30°C.

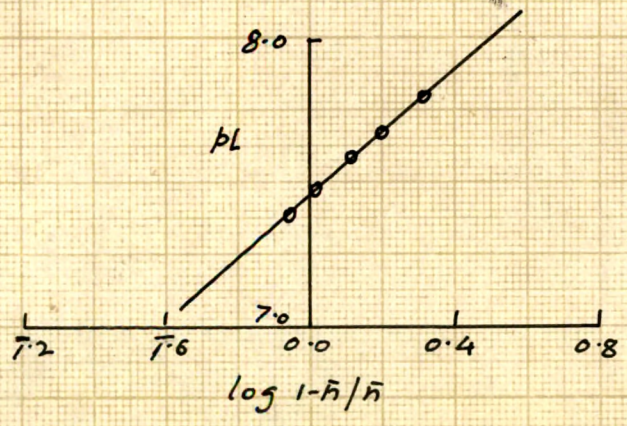


Fig.III 28 (IInd Method) Ni(II).dipy pn system - 30°C.

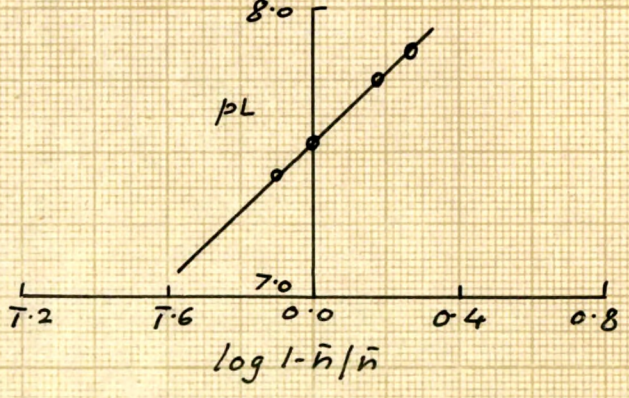


Table III 2.3Ab

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data for Ni.dipyridyl N-methylethylenediamine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.60	1.76_5	4.05	4.31	0.26	0.29_5	0.37_8	7.20_6	6.82_8
6.70	1.72_0	4.07	4.38	0.31	0.36_1	0.24_8	7.07_5	6.82_7
6.80	1.67_0	4.10	4.43	0.33	0.39_5	0.18_5	6.93_0	6.74_5
6.90	1.60_0	4.13	4.50	0.37	0.46_3	0.06_4	6.81_9	6.75_4
7.00	1.55_0	4.15	4.55	0.40	0.51_7	$\bar{1}.97_0$	6.70_6	6.73_6
7.10	1.50_0	4.18	4.60	0.42	0.56_0	$\bar{1}.89_5$	6.59_4	6.69_9
7.20	1.43_5	4.20	4.63	0.43	0.60_0	$\bar{1}.82_4$	6.48_9	6.66_5

$\log K_{MAL} = 6.75 \pm 0.04$

Table III 2.4Ab

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data for Ni.dipyridyl N-ethylethylenediamine 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	1.46_5	4.26	4.50	0.24	0.32_7	0.31_3	6.63_5	6.32_1
7.40	1.40_5	4.28	4.54	0.26	0.37_0	0.23_1	6.52_0	6.28_9
7.50	1.36_0	4.31	4.60	0.29	0.42_6	0.12_9	6.42_2	6.29_3
7.60	1.32_5	4.32	4.63	0.31	0.46_8	0.05_5	6.32_2	6.26_7
7.70	1.29_0	4.35	4.67	0.32	0.49_6	0.00_7	6.21_7	6.21_0
7.80	1.25_5	4.36	4.70	0.34	0.54_2	$\bar{1}.92_7$	6.13_5	6.20_8
7.90	1.22_0	4.38	4.73	0.35	0.57_4	$\bar{1}.87_0$	6.04_6	6.17_6

$\log K_{MAL} = 6.25 \pm 0.05$

Table III 2.5Ab

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data for Ni.dipyridyl N.N'-dimethylethylenediamine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.20	1.42_5	4.26	4.50	0.24	0.33_7	0.29_4	5.99_7	5.70_3
7.30	1.37_5	4.28	4.54	0.26	0.37_8	0.21_6	5.88_6	5.67_0
7.40	1.32_5	4.30	4.58	0.28	0.42_3	0.13_5	5.78_6	5.65_1
7.50	1.27_5	4.31	4.60	0.29	0.45_5	0.07_8	5.68_2	5.60_4
7.60	1.23_5	4.33	4.63	0.30	0.48_6	0.02_5	5.58_4	5.55_9
7.70	1.20_0	4.35	4.67	0.32	0.53_4	$\bar{1}.94_1$	5.50_7	5.56_6

$\log K_{MAL} = 5.62 \pm 0.05$

Table III 2.6Ab

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data for Ni.dipyridyl N-N-dimethylethylenediamine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
7.20	1.21_5	4.35	4.55	0.20	0.32_9	0.30_9	5.70_9	5.40_0
7.30	1.19_5	4.37	4.59	0.22	0.36_8	0.23_5	5.62_0	5.38_5
7.40	1.17_0	4.38	4.62	0.24	0.41_0	0.15_8	5.53_8	5.38_0
7.50	1.14_5	4.40	4.65	0.25	0.43_7	0.11_0	5.44_8	5.33_8
7.60	1.12_5	4.41	4.67	0.26	0.46_2	0.06_6	5.36_0	5.29_4
7.70	1.11_0	4.42	4.70	0.28	0.50_4	$\bar{1}.99_3$	5.28_9	5.29_6
7.80	1.09_5	4.43	4.73	0.30	0.54_8	$\bar{1}.91_6$	5.22_4	5.30_8

$\log K_{MAL} = 5.34 \pm 0.05$

Fig. III 29 Ni(II).dipy N-methyl
en system - 30°C.

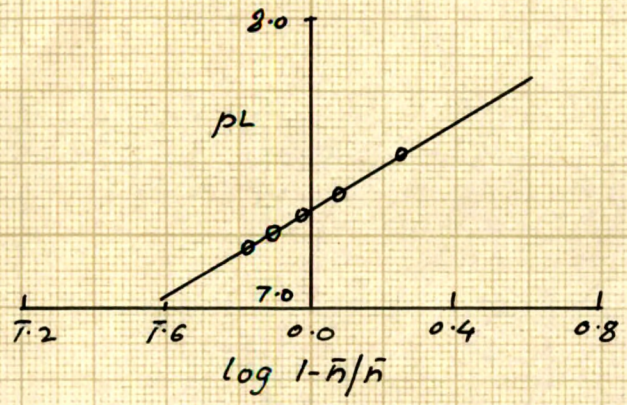


Fig. III 30 Ni(II).dipy N-ethyl
en system - 30°C.

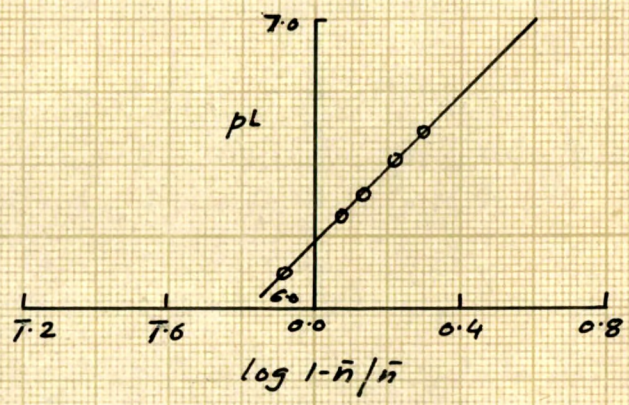


Fig. III 31 Ni(II) dipy N-N'-dimethyl
en system - 30°C.

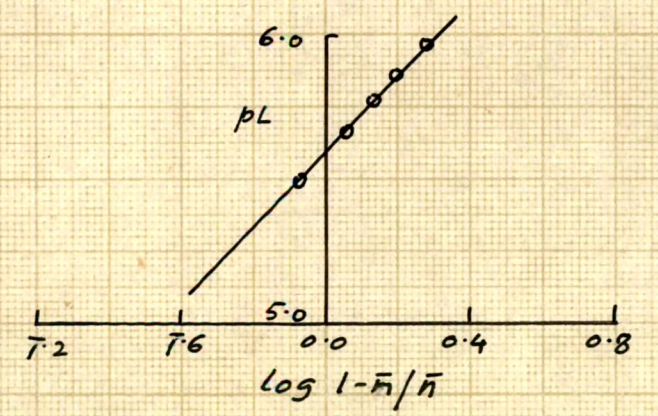


Fig. III 32 Ni(II) dipy N-N-dimethyl
en system - 30°C.

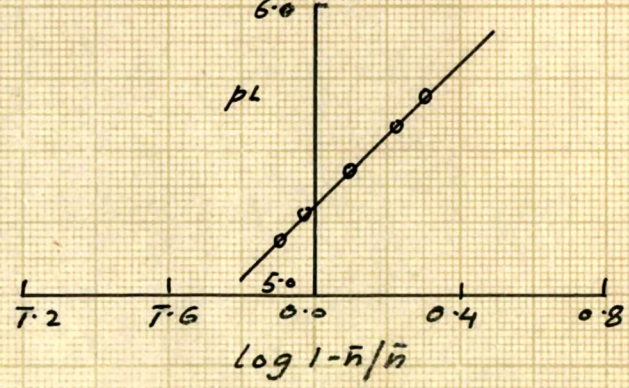


Table III 2.1B

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.40	1.80_0	4.52	4.64	0.12	0.26_7	0.43_9	7.57_0	7.13_1
6.50	1.76_0	4.54	4.68	0.14	0.31_8	0.33_1	7.42_0	7.08_9
6.60	1.72_0	4.55	4.71	0.16	0.37_2	0.22_7	7.28_7	7.06_0
6.70	1.68_0	4.56	4.75	0.19	0.45_2	0.08_4	7.17_6	7.09_2
6.80	1.64_0	4.57	4.78	0.21	0.51_2	$\bar{1}.97_9$	7.06_3	7.08_4
6.90	1.60_0	4.58	4.81	0.23	0.57_5	$\bar{1}.86_8$	6.96_5	7.09_7
7.00	1.53_0	4.60	4.84	0.24	0.63_1	$\bar{1}.76_5$	6.87_5	7.11_0

$\log K_{MAL} = 7.09 \pm 0.02$

Table III 2.1'B

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

B	T_L°	V'	V"	V"-V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.50	0.02_4	2.53_0	2.55_0	0.02_0	0.20_0	0.60_2	7.75_4	7.15_2
5.60	0.02_4	2.54_0	2.57_0	0.03_0	0.30_0	0.36_8	7.55_0	7.18_2
5.70	0.02_4	2.55_5	2.59_0	0.03_5	0.35_0	0.26_9	7.35_8	7.08_9
5.80	0.02_4	2.57_0	2.62_0	0.05_0	0.50_0	0.00_0	7.16_0	7.16_0
5.90	0.02_5	2.58_0	2.64_0	0.06_0	0.60_0	$\bar{1}.82_4$	6.96_6	7.14_2
6.00	0.02_5	2.61_0	2.68_0	0.07_0	0.70_0	$\bar{1}.63_2$	6.77_1	7.13_9

$\log K_{MAL} = 7.14 \pm 0.02$

Table III 2.2B

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
6.10	1.92_0	4.50	4.60	0.10	0.20_8	0.58_0	8.21_8	7.63_8
6.20	1.88_0	4.51	4.64	0.13	0.27_6	0.41_7	8.07_6	7.65_9
6.30	1.80_0	4.53	4.67	0.14	0.31_2	0.34_3	7.92_0	7.57_7
6.40	1.76_0	4.54	4.70	0.16	0.36_3	0.24_3	7.78_1	7.53_8
6.50	1.68_0	4.56	4.74	0.18	0.42_8	0.12_4	7.65_9	7.53_5
6.60	1.68_0	4.56	4.76	0.20	0.47_6	0.04_1	7.53_3	7.49_2
6.70	1.60_0	4.58	4.80	0.22	0.55_0	$\bar{1}.91_3$	7.44_0	7.52_7

$\log K_{MAL} = 7.57 \pm 0.05$

Table III 2.2'B

B, T_L^v, $\bar{n}$, $\log(1-\bar{n})\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data for Ni.o-phen. propylenediamine system - 30°C.

B	T_L^v	V'	V"	V"-V'	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	$pL-\log(1-\bar{n})/\bar{n}$
5.30	0.02_4	2.54_0	2.56_0	0.02_0	0.20_0	0.60_2	8.25_2	7.65_0
5.40	0.02_4	2.55_0	2.58_0	0.03_0	0.30_0	0.36_8	8.05_4	7.68_6
5.50	0.02_4	2.56_0	2.60_0	0.04_0	0.40_0	0.17_6	7.85_6	7.68_0
5.60	0.02_5	2.58_0	2.63_0	0.05_0	0.50_0	0.00_0	7.66_0	7.66_0
5.70	0.02_5	2.60_0	2.66_0	0.06_0	0.60_0	$\bar{1}.82_4$	7.46_4	7.64_0
5.80	0.02_5	2.63_0	2.70_0	0.07_0	0.70_0	$\bar{1}.63_2$	7.16_5	7.63_3

$\log K_{MAL} = 7.66 \pm 0.02$

Fig. III 33 Ni(II)o-phen.en system - 30°C.

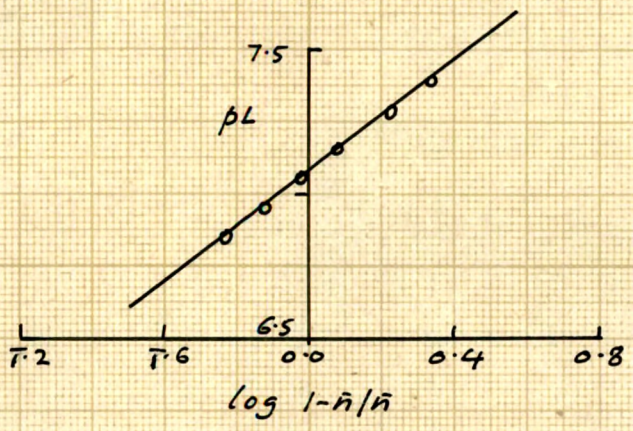


Fig. III 34 (IInd Method) Ni(II)o-phen.en system-30°C.

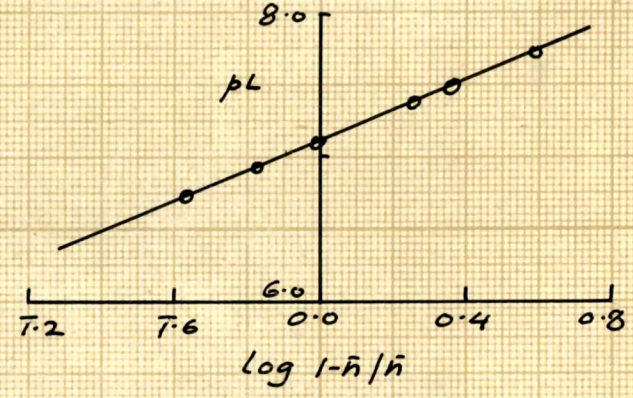


Fig. III 35 Ni(II)o-phen.pn system - 30°C.

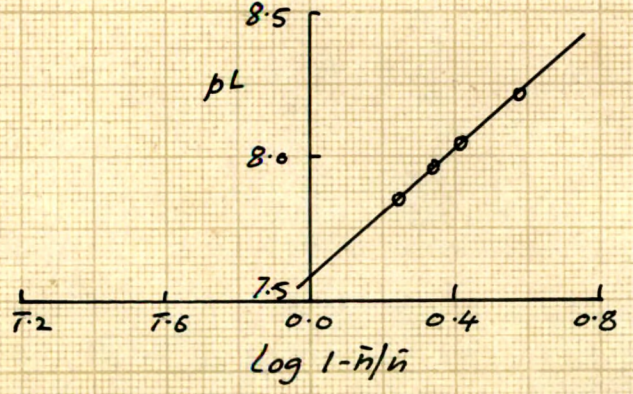


Fig. III 36 (IInd Method) Ni(II)o-phen-pn system-30°C.

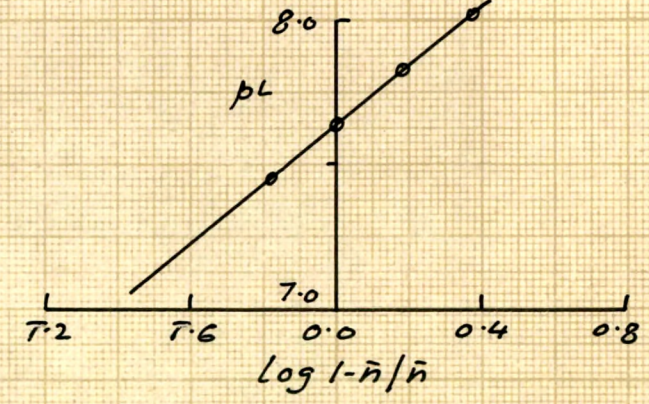


Table III 3.0

Logarithms of stability constants of ternary dipyridyl -M^{2+}-ligand complexes and o-phen-M^{2+} - ligand complexes by method I and II.

Ligand(L)	$\log K^{Cu.dipy}_{Cu.dipy.L}$		$\log K^{Ni.dipy}_{Ni.dipy.L}$		$\log K^{Ni.o\text{-}phen}_{Ni.o\text{-}phen.L}$	
	I	II	I	II	I	II
Ethylenediamine(en)	9.58±0.02	9.61±0.04	7.31±0.02	7.23±0.05	7.09±0.02	7.14±0.02
Propylenediamine(pn)	10.35±0.03	10.42±0.03	7.47±0.02	7.58±0.02	7.57±0.05	7.66±0.02
N-Methyl en	9.05±0.03	-	6.75±0.04	-	-	-
N-Ethyl en	8.78±0.04	-	6.25±0.05	-	-	-
N-N'-dimethyl en	7.84±0.04	-	5.62±0.05	-	-	-
N-N-dimethyl en	-	-	5.34±0.05	-	-	-

References :

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