CHAPTER THREE

TERNARY METAL; α-α'-DIPYRIDYL OR o-PHENANTHROLINE AND AMINO ACID OR THIOACID SYSTEMS.

The reactions involving one metal ion and two ligands have received the attention of chemists recently, though such reactions are known since the time of Werner. Martell[1] has classified the reactions in such ternary systems. If two ligands L and A differing significantly in their complexing tendencies are added to the metal ion, there is formation of MA and the less complexing ligand L is left free in the solution. However, if the difference in the complexing tendencies of the two ligands is not high, formation of mixed ligand complex MAL takes place either in one step or in two consecutive steps as follows :

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

$$M + A \rightleftharpoons MA, \quad MA + L \rightleftharpoons MAL$$

In case the ligands A and L are multidentate the resulting ternary complexes are known as heterochelates. Mixed ligand complexes are more common among the systems which do not allow fast substitution reactions (inert). The heterochelate should be sterically stable otherwise it undergoes disproportionation $2MAL \rightleftharpoons MA_2 + ML_2$.

For the mixed ligand complex formation to take place in steps, the two ligands should combine with the metal ion in two different pH ranges. The complex formation of MA should be complete in the lower pH range and it should be stable in the region where combination of the secondary ligand takes place. In such systems the solution consists of species MA, MAL and also MAL_2, if there is an excess of the ligand L. This presumes that MA does not undergo hydrolysis of hydroxy complex formation in the range where the combination of ligand L takes place. The ligand combining first with the metal ion is known as primary ligand, whereas the one combining later is called secondary ligand. The formation constant corresponding to the combination of the secondary ligand L with MA is known as mixed ligand formation constant K_{MAL}^{MA}.

Mixed ligand systems containing neutral molecule as primary ligand have been studied potentiometrically by Watters and Dewitt[2a-2b]. They have also studied the systems of the type MAL where M = Cu(II), Ni(II), A = ethylenediamine and L = oxalate ion. The mixed ligand complex Ni(II)DMG dipyridyl was studied by applying high frequency titrimetry technique[3]. The ternary complex phenyl bis(dipy)Ni(II) has also been reported[4]. Paramagnetic adducts of Ni(II) chelates of monothio-β-diketone have been obtained with dipyridyl and orthophenanthroline[5]. The formation of $[Ni.L'L_2]Cl_2$ in good yield where L = picolylamine and L' = dipyridyl has also been reported by Syamal[6].

Narain[7] reported the preparation and cheracterisation of the mixed ligand complex Cu(II)phthalamide with dipyridyl and orthophenanthroline. Dutta and coworkers[8] isolated and characterised several Cu(II) complexes of the type $Cu(A\text{-}A)X_2$, where A-A = dipyridyl, orthophenanthroline or 5-nitro-o-phenanthroline and X = NCS^-, NO_2^- or N_3^-. Mixed complexes of the type M.dipy.pyridine were studied colorimetrically, potentiometrically and by ESR spectral studies with number of first row transition metals[9]. Co(III) complexes containing dipyridyl and amino acids have been reported by Murakami and coworkers[10]. Mixed ligand complexes of the type $[Co^{3+}(dipy.)Y]Cl_2.XH_2O$, where Y = bidentate amino acid, were studied polarographically[11]. Mixed ligand complexes of Co(III) with dipyridyl, orthophenanthroline and paludrine were also studied[12]. Broomhead and coworkers[13] synthesised and resolved the heterochelates of Co(II) and Cr(II) with the ligand dipyridyl or orthophenanthroline. Synthesis of glycine oxide Co(III) heterochelate has been reported[14]. Co(III) + dipy. + amino acid mixed ligand complexes have been studied polarographically by Maki and Itatani[11]. Formation of diaceto bis dipyridyl Cr(II) by treatment of Cr(II) acetate with dipyridyl has been described[15]. The formation of diaceto dipyridyl bis iso-propyl amine Cr(II) has also been reported[16]. Crystalline mixed ligand chelates of Cr(III) with dipyridyl or orthophenanthroline halide and acetylacetone have been reported[17]. The bis dipyridyl dicyano Rh(II) complex has been synthesised by Sen and coworkers[18]. The mixed ligand complexes of Ir(III) with orthophenanthroline were synthesised by Chisewell and coworkers[19]. Gans and coworkers[20] isolated $[UCl_3.OEt(dipy)_2]$ and $[UCl_3.OEt(phen)_2]$. The new seleno cyanato complexes of Pd(II) or Pt(II) with dipyridyl have been worked out[21]. The mixed ligand complexes [$MoCl_3$.pyridine-o-phenanthroline], [$MoCl_3$.pyridine.dipyridyl] have also been reported[22]. $[Vo(dipy)_3(NCSe)_2]$, $[Vo(o\text{-}phen)_3(NCSe)_2]$ have also been prepared[23]. The synergic extraction of Eu(III) bis-o-phenanthroline tris-salicylate complex has been described[24].

Sigel and coworkers[25-31] have investigated ternary transition metal complexes containing dipyridyl as a primary ligand and many monodentate or bidentate secondary ligands, coordinating through two oxygen atoms, two nitrogen atoms or from one oxygen and one nitrogen atom. The systems [Cu(dipy)L] where L = polyhydroxy phenol or phenolic acids have been studied by Martell and coworkers[32]. The potentiometric titration technique has been used in the study of binuclear diolated Cu(II) complexes of the type $[Cu_2(OH)_2L_2]^{2+}$ where L = dipyridyl or orthophenanthroline or histamine[33]. The mixed ligand complex studies in solution, where dipyridyl or orthophenanthroline is the primary ligand and amino acids, polyhydroxy phenols or amines are secondary ligands have been reported from our laboratory.[34,35] In all cases where the secondary ligand is a σ-bonding ligand, it is observed that K^{MA}_{MAL} is very close to K^{M}_{ML}. The reason for this has been attributed to the π-bonding character of metal dipyridyl bond.

In the present chapter studies of the systems Ni.dipy.L where L = amino acids, hydroxy acids or corresponding mercapto acids have been carried out to find out the relative tendencies of N, O and S containing ligands to combine as secondary ligand. The study was possible in the cases of the systems, NiAL where A = dipyridyl or orthophenanthroline and L = aspartic acid, thioglycollic acid, thiolactic acid or thiomalic acid. The study in the systems Ni.dipy.L where L = hydroxy acids is not possible because the hydroxy acids combine with the Ni(dipy) in the region where it undergoes hydroxo complex formation. Such systems have, therefore, not been reported.

Experimental :

Materials, purification, preparation and standardisation :

Conductivity water was used throughout the work. Solutions of oxalic acid, sodium hydroxide, perchloric acid, sodium perchlorate and amino acids were prepared and standardised as discussed in chapter two. The other reagents used are as follows : Dipyridyl, o-phenanthroline and thioglycollic acid (E.Merck, pure), thiolactic and thiomalic acid (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 two. The instruments used were same as detailed in previous chapter.

In cases of Ni(dipy).L systems solutions were prepared as follows :

1. 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.
2. 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.
3. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.)+ nickel 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.) + secondary ligand (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.) + secondary ligand (0.02M, 5.0 ml.) + nickel perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (21.3 ml.) total volume 50.0 ml.; μ = 0.2M.

For Ni(o-phen).L systems solutions were prepared as follows :

1. 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.
2. Perchloric acid (0.2M, 5.0 ml.) + o-phenanthroline (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.95ml.) + conductivity 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.) + conductivity 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.) + conductivity 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.)+ conductivity water (21.1 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 solution. The plot of pH against volume of alkali have been shown in figs.III 1 - III 8.

Discussion :

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

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

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

mixed ligand formation constant

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

The above equations presume that the formation of $[\text{M(dipy)}]^{2+}$ complex takes place at a lower pH, and it is stable at higher pH where the combination of aspartic acid or mercapto acids takes place. The observation of the titration curves supports this presumption. The Ni.dipyridyl curve(3) diverges from the dipyridyl curve(2) at lower pH indicating that the $[\text{Ni(dipy)}]^{2+}$ is formed at lower pH by the dissociation of protons attached with the tertiary nitrogens of dipyridyl molecule. The $\bar{n}$ attains value 1 at pH ~ 3.5. The $\bar{n}$ value continues to remain 1 even upto pH ~ 6.0. This indicates that $[\text{Ni(dipy)(H}_2\text{O)}_2]^{2+}$ is stable upto high pH. After pH ~3.5. The dipyridyl and metal dipyridyl curves start converging because the proton associated with dipyridyl are less at higher pH. The Ni.dipyridyl curve(3) diverges from acid curve(1) at pH ~ 8.0 indicating that the formation of hydroxy complex $[\text{Ni(dipy)(OH)}_2]$ starts in this pH range.

Since o-phenahtroline is structurally similar to dipyridyl, it can be expected to behave in a similar way. Ni(II) and o-phenanthroline mixed in 1:1 ratio form water soluble complex. The natures of the o-phenanthroline curve(2) and Ni-o-phenanthroline curve(3), fig. III·5 are also similar to that of dipyridyl and Ni.dipyridyl curves indicating that $[Ni(o\text{-}phen)(H_2O)_2]^{2+}$ formed at low pH is stable at higher pH range.

The $[Ni(dipy)L]$ curve(5) where L = aspartic acid or thio acids, overlaps the secondary ligand curve(4) in the lower pH range. Separation between curves (4) and (5) starts after pH ~ 5.0 in case of aspartic acid and after pH ~ 5.5 in case of thio acids. This shows that the secondary ligand combines with the Ni(II) after the formation of $[Ni(dipy)]^{2+}$ is complete. $[Ni(dipy)]^{2+}$ is stable in the pH range of the combination of the secondary ligand. Thus it can be considered that the secondary ligand combines with $[Ni(dipy)]^{2+}$ just as it does with $[Ni(aq)]^{2+}$ in binary systems. The application of an extended Irving-Rossotti titration technique to such systems is, therefore, valid. The horizontal distance between curves (4) and (5) 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 $[M(dipy)]^{2+}$. Equation used for the calculation of $\bar{n}$ would be same as given in the original paper[36].

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

Here T_M° is the concentration of $[Ni(dipy)]^{2+}$ which is equal to the concentration of the metal taken. The other terms have the usual meaning, as detailed in the chapter two. The calculation of $\bar{n}$ was carried out below the pH where

$[Ni(dipy)(OH)_2]$ formation starts, i.e. where $[Ni(dipy)]^{2+}$ curve(3) diverges from the dipyridyl curve(2). The $\bar{n}_H$ values of the secondary ligand are required in the above equation and also for the calculation of proton ligand stability constant values which are required for pL calculation. These values have been determined earlier[37-40] but to get the values under same experimental conditions, the calculations of $\bar{n}_H$ and $^{P}K^{H}$ had to be repeated by finding the horizontal distance between acid and secondary ligand curve. The values agree very well with the previous data and have been reported in the table III 3.0. pL values were calculated using the equation (3·1) given in chapter two. The values have been presented in the tables III 2.1A to III 2.4A and III 2.1B to III 2.4B. The values of $\bar{n}$ upto ~ 0.65 only were obtained, since only one molecule of the secondary ligand can combine. The values of pL at $\bar{n} = 0.5$ is equal to log K^{NiA}_{NiAL}. However, this will be only one point and may involve experimental error. Further in some cases $\bar{n}$ value upto 0.5 could not be obtained below the pH of hydroxo complex formation. 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 9 to III 16). At each point on the straight line log $K^{NiA}_{NiAL} = pL - \log(1-\bar{n})/\bar{n}$. The average values were thus calculated and have been presented with mean deviation in table III 5.0. The values of $[Ni(dipy)L]$ where L = glycine or α-alanine have been taken from the literature. The study of $[Cu(dipy)L]$ where L = thio acids was not possible because precipitation takes place at low pH.

The values of the formation constants for the binary systems ML (log K^{Ni}_{NiL}) are required for the comparison with the values of log K^{NiA}_{NiAL}. Such values are known for the cases where M = Ni(II) and L = glycine or α-alanine[41] and have been presented in the chapter two. The value of the formation constant of Ni.aspartic acid system has also been worked out in the previous chapter. The formation constants of binary complexes of Ni.thio acids[37-39] are also known and have been presented in table III 4.0.

It is observed that mixed ligand formation constant in the M.dipy.amino acid systems are in the order aspartic acid > α-alanine > glycine as in the binary systems. This is in expected order of the decreasing basicities of the ligand.

The more important aspect of the study is the observation that the values of K^{MA}_{MAL} and K^{M}_{ML}, are nearly same. Watters and Dewitt[1-2] studied the systems of the type MAL where M = Cu(II), Ni(II), A = ethylenediamine and L = oxalate ion. They observed that K^{MA}_{MAL} is much lower than K^{M}_{ML}, in these cases. It has been explained to be due to the fact that the tendency of L to get bound with aquated metal ion is more than to combine with the metal ion already bound with ethylenediamine. From statistical consideration also the driving force for the binding of the secondary ligand with $[MA]^{2+}$ should be less than for the binding of L with $[M(aq)]^{2+}$ in binary systems. Dipyridyl being a neutral molecule should behave like ethylenediamine. It has more tendency to combine with metallic ions and forms more stable σ-bonds than water. K_{MAL}^{MA} should, therefore, be less than $K_{ML_1}^{M}$ where A = dipyridyl or o-phenanthroline. However, the values of the K_{MAL}^{MA} are found to be much higher than what is expected from statistical considerations. K_{MAL}^{MA} is much higher than $K_{ML_2}^{M}$ and only slightly lower than $K_{ML_1}^{M}$. 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 dπ-pπ interaction has been observed in metal dipyridyl complexes by earlier workers[42-44] using different methods of investigations. The dπ-pπ 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 $[M(aq)]^{2+}$ complexes.

Enthalpy changes in the coordination of L^{2-} (aspartate ion) with $[M(aq)]^{2+}$ or $[M(dipy)]^{2+}$ can be expected to be same. Since the species $[ML]$ or $[MAL]$ are both neutral, the entropy changes will also be same in both the cases. Since the formation constant is dependent on the free energy changes, which in turn is related to the enthalpy and entropy changes, $K_{MAL}^{MA} \approx K_{ML_1}^{M}$. K_{MAL}^{MA} is much higher than $K_{ML_2}^{M}$ 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 the repulsion due to already existing charged ion 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 changes are thus more favourable in the formation of MAL. The favourable enthalpy and entropy changes make $K^{MA}_{MAL} > K^{ML}_{ML_2}$.

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

In cases of [Ni(dipy)L] systems (L = thioglycollate, thiolactate and thiomalate ions) K^{MA}_{MAL} is nearly equal to K^{M}_{ML}. This can also be explained by considering M → N π-interaction in M-dipy complex. Thus the behaviour of thioglycollic, thiolactic and thiomalic acids are similar to that of σ-bonding analogues glycine, α-alanine and aspartic acid, respectively. However, the possibility of M-S π-interaction has been indicated earlier. If this could have been significant, K^{MA}_{MAL} where L = TGA, TLA and TMA should have been lower than K^{M}_{ML}. This is expected because the metal ion in [M(dipy]$^{2+}$, having donated π electrons to the dipyridyl molecule, should have much less tendency to form π-bond with the secondary ligand. Thus the extent of M-S π-bonding in [M(dipy)L] should be much less than in ML. Thus the value of $K^{Ni.dipy}_{Ni.dipy.L}$ should be significantly lower. However, it has been observed that K^{Ni}_{NiL} and $K^{Ni.dipy.}_{Ni.dipy.L}$ are nearly same. This indicates that M-S π-interaction does not play a significant role in the metallic complexes. The greater stability of M-S bond than M-O bond in binary complexes can, therefore, be attributed to greater M-S σ-interaction.

It can be argued that in $[M(dipy)]^{2+}$ complex there are both $M \leftrightarrow N$ σ-bond and $M \rightarrow N$ π-bond. The contribution of both being same, the electronegativity of the metal ion is considered to be same as in $[M(aq)]^{2+}$ complex. In cases of σ-bonding ligands, it has been argued that extent of M-L σ-bonding remains same in $[M(dipy)L]$ and M.L.. Similarly it can be argued that if σ and π-interaction balance each other in M.dipy, resulting in the electronegativity of $[M(dipy)]^{2+}$ same as $[M(aq)]^{2+}$, $M \rightarrow L$ π-interaction in ML and $[M(dipy)L]$ should also be same. Even if there is some lowering in the $M \rightarrow L$ π-interaction in $[M(dipy)L]$, the increase in t$M \leftarrow L$ σ-interaction is more, and vice versa and thus M-L bond strengths in $[ML]$ and $[M(dipy)L]$ are nearly same. Thus it can be expected that $K^{Ni.dipy.}_{Ni.dipy.L}$ should be equal to $K^{Ni}_{Ni.L}$ even in the presence of $M \rightarrow S$ π-interaction.

In order to further investigate the point, the study has been extended to ternary systems MAL where A is a purely σ-bonding ligand and L is amino acid or corresponding thio acid.

Table III 1.1A

$N = 0.2M$ $V^{\circ} = 50$ ml. $T^{\circ}_{Dipy} = 0.002$ $T^{\circ}_{M} = 0.002M$

$E^{\circ} = 0.02M$ $T^{\circ}_{L} = 0.002M.$ $\mu = 0.2M$ $t = 30°C.$

Perchloric acid		Dipyridyl		Ni.Dipyridyl		Aspartic acid		Ni.Dipy.Aspartic acid	
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	1.50	0.00	1.55	0.00	1.50	0.00	1.50	0.00	1.50
1.00	1.65	1.00	1.70	1.00	1.65	1.00	1.65	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.80	2.00	1.80	2.00	1.85
2.50	1.85	3.00	2.00	3.00	2.00	3.00	2.00	3.00	2.05
3.00	2.00	4.00	2.65	4.00	2.25	4.00	2.25	4.00	2.30
3.60	2.10	4.10	2.80	4.40	2.50	4.40	2.45	4.40	2.50
3.80	2.20	4.20	3.00	4.60	2.75	4.60	2.70	4.60	2.70
4.00	2.25	4.30	3.25	4.70	2.95	4.80	3.00	4.80	3.00
4.20	2.35	4.40	3.55	4.75	3.05	4.90	3.15	4.90	3.15
4.40	2.50	4.50	3.90	4.80	3.25	5.00	3.30	5.00	3.25
4.60	2.70	4.55	4.05	4.85	3.50	5.10	3.55	5.10	3.50
4.70	2.85	4.60	4.25	4.88	3.80	5.20	3.80	5.20	3.70
4.80	3.10	4.70	4.60	4.90	4.00	5.25	4.00	5.30	4.05
4.90	3.65	4.70	4.80	4.94	5.25	5.30	4.25	5.40	4.45
4.94	5.25	4.80	5.00	4.98	5.75	5.35	4.60	5.45	4.70
4.98	5.75	4.85	5.30	5.00	7.30	5.40	5.20	5.50	4.95
5.00	7.30	4.90	5.60	5.04	7.75	5.45	6.25	5.55	5.25
5.02	9.20	4.95	5.90	5.08	8.00	5.50	7.50	5.60	5.50
5.04	9.45	5.00	7.30	5.15	8.20	5.54	8.55	5.65	5.75
5.06	9.70	5.04	9.30	5.20	8.35	5.58	8.85	5.70	6.00
5.08	9.85	5.08	9.50	5.30	8.55	5.60	8.90	5.75	6.30
5.10	10.00	5.15	9.85	5.40	8.90	5.70	9.25	5.80	6.70
					(ppts.)	5.80	9.50	5.84	7.10
						5.90	9.70	5.88	7.75
						6.00	9.90	5.90	8.00
								5.95	8.50
								6.00	8.95
								6.10	9.65
								6.20	10.10

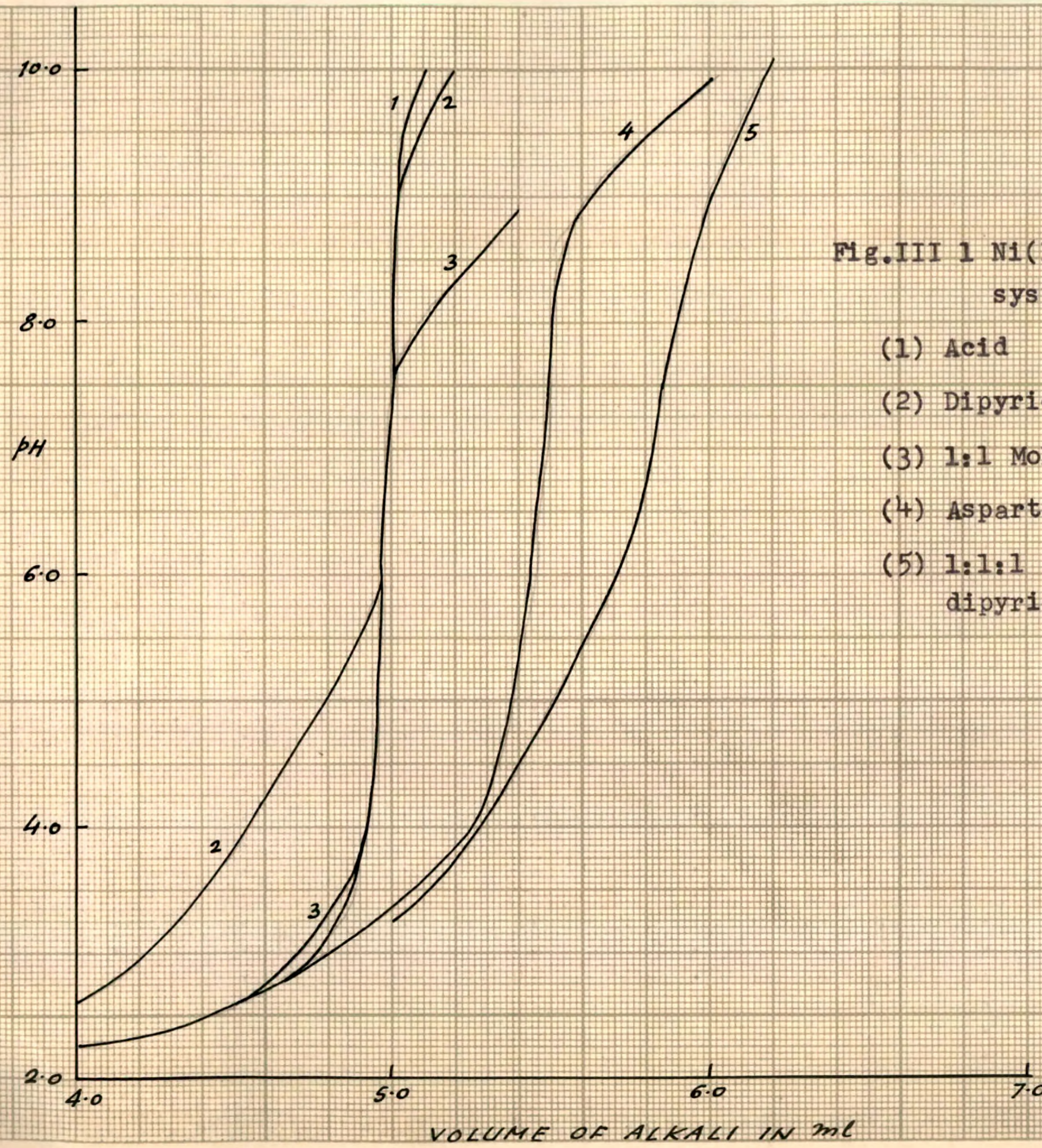

Fig.III 1 Ni(II).dipyridyl.aspartic acid system - 30°C.

(1) Acid

(2) Dipyridyl

(3) 1:1 Molar ratio of Ni(II),dipyridyl

(4) Aspartic acid

(5) 1:1:1 Molar ratio of Ni(II), dipyridyl, and aspartic acid.

Table III 1.2A

N = 0.2M V° = 50 ml. T°_L = 0.002M μ = 0.2M

E° = 0.02M T°_{Dipy} = 0.002M T°_M = 0.002M t = 30°C.

Thioglycollic acid		Ni.Dipy.Thioglycollic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.65	1.00	1.65
2.00	1.80	2.00	1.80
3.00	1.95	3.00	1.95
4.00	2.25	4.00	2.25
4.20	2.30	4.20	2.30
4.40	2.35	4.40	2.35
4.60	2.60	4.60	2.60
4.70	2.70	4.70	2.70
4.80	2.85	4.80	2.85
4.90	3.00	4.90	3.00
5.00	3.20	5.00	3.20
5.10	3.40	5.10	3.40
5.20	3.50	5.20	3.50
5.30	3.95	5.30	3.95
5.35	4.10	5.35	4.10
5.40	4.35	5.40	4.35
5.44	4.75	5.44	5.75
5.48	5.50	5.50	5.40
5.50	6.50	5.54	5.55
5.54	6.75	5.58	5.75
5.58	9.05	5.65	6.00
5.65	9.45	5.70	6.25
5.80	9.95	5.75	6.50
		5.80	7.00
		5.82	7.75
		5.84	8.25
		5.90	8.85
		6.00	9.25
		6.20	9.75
		6.30	10.00

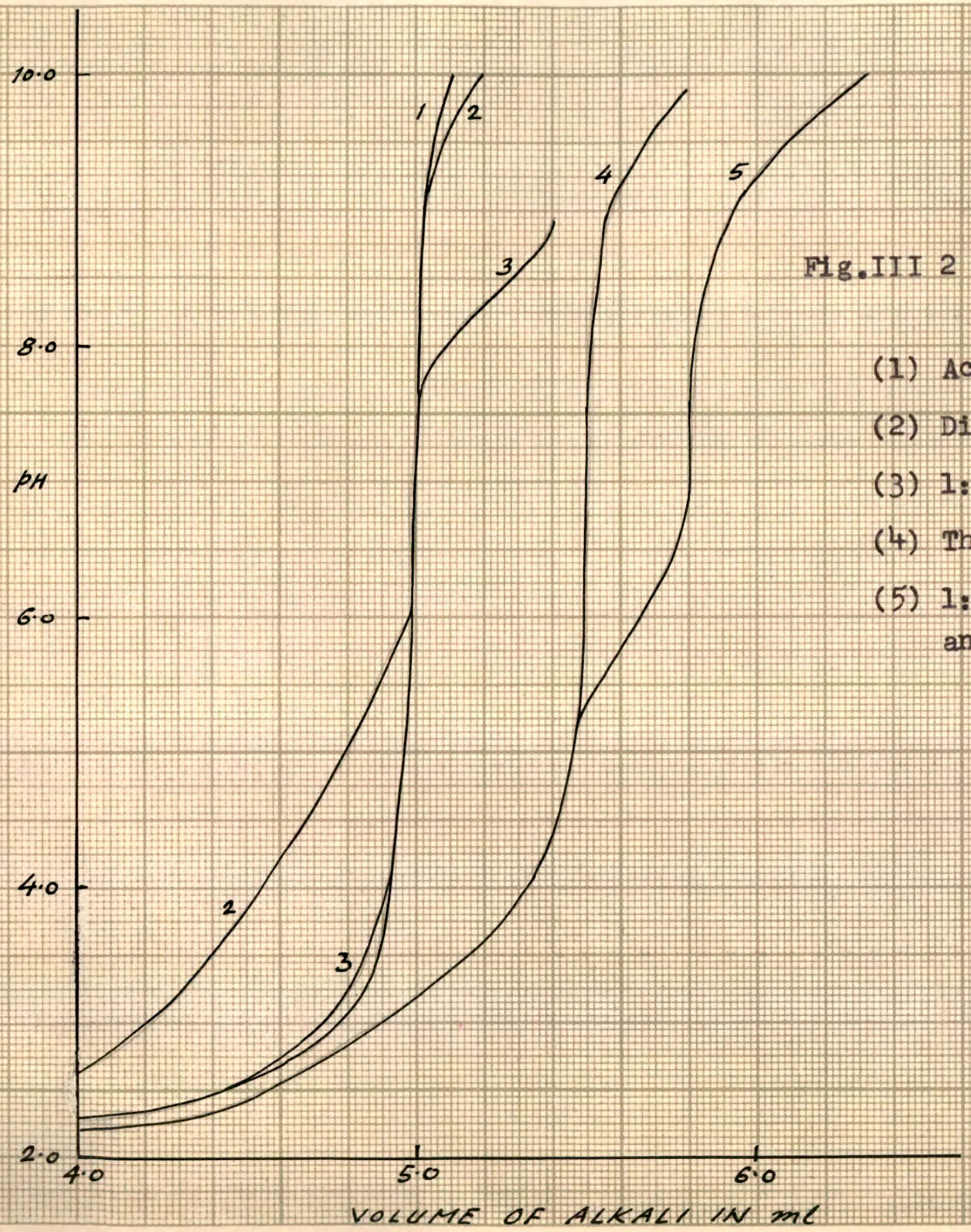

Fig.III 2 Ni(II).Dipyridyl.Thioglycollic acid system - 30°C.

(1) Acid

(2) Dipyridyl

(3) 1:1 Molar ratio of Ni(II),dipyridyl

(4) Thioglycollic acid

(5) 1:1:1 Molar ratio of Ni(II), dipyridyl and thioglycollic acid.

Table III 1.3A

N = 0.2M V° = 50 ml. T°_L = 0.002M μ = 0.2M

E° = 0.02M T°_{Dipy} = 0.002M T°_M = 0.002M t = 30°C.

Thiolactic acid		Ni.Dipy.Thiolactic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.65	1.00	1.65
2.00	1.80	2.00	1.80
3.00	1.95	3.00	1.95
4.00	2.25	4.00	2.25
4.40	2.35	4.40	2.35
4.60	2.55	4.60	2.55
4.80	2.75	4.80	2.75
5.00	3.05	5.00	3.05
5.10	3.25	5.10	3.25
5.20	3.45	5.20	3.45
5.30	3.75	5.30	3.75
5.35	4.05	5.35	4.05
5.40	4.40	5.40	4.40
5.44	4.90	5.44	4.90
5.48	6.20	5.50	5.35
5.50	7.25	5.54	5.55
5.52	8.25	5.58	5.75
5.55	8.80	5.65	6.05
5.58	9.00	5.70	6.20
5.65	9.40	5.75	6.40
5.70	9.60	5.80	6.70
5.80	9.80	5.85	7.05
5.85	10.00	5.90	7.50
		5.95	8.55
		6.00	9.10
		6.05	9.35
		6.10	9.50 (ppts.)

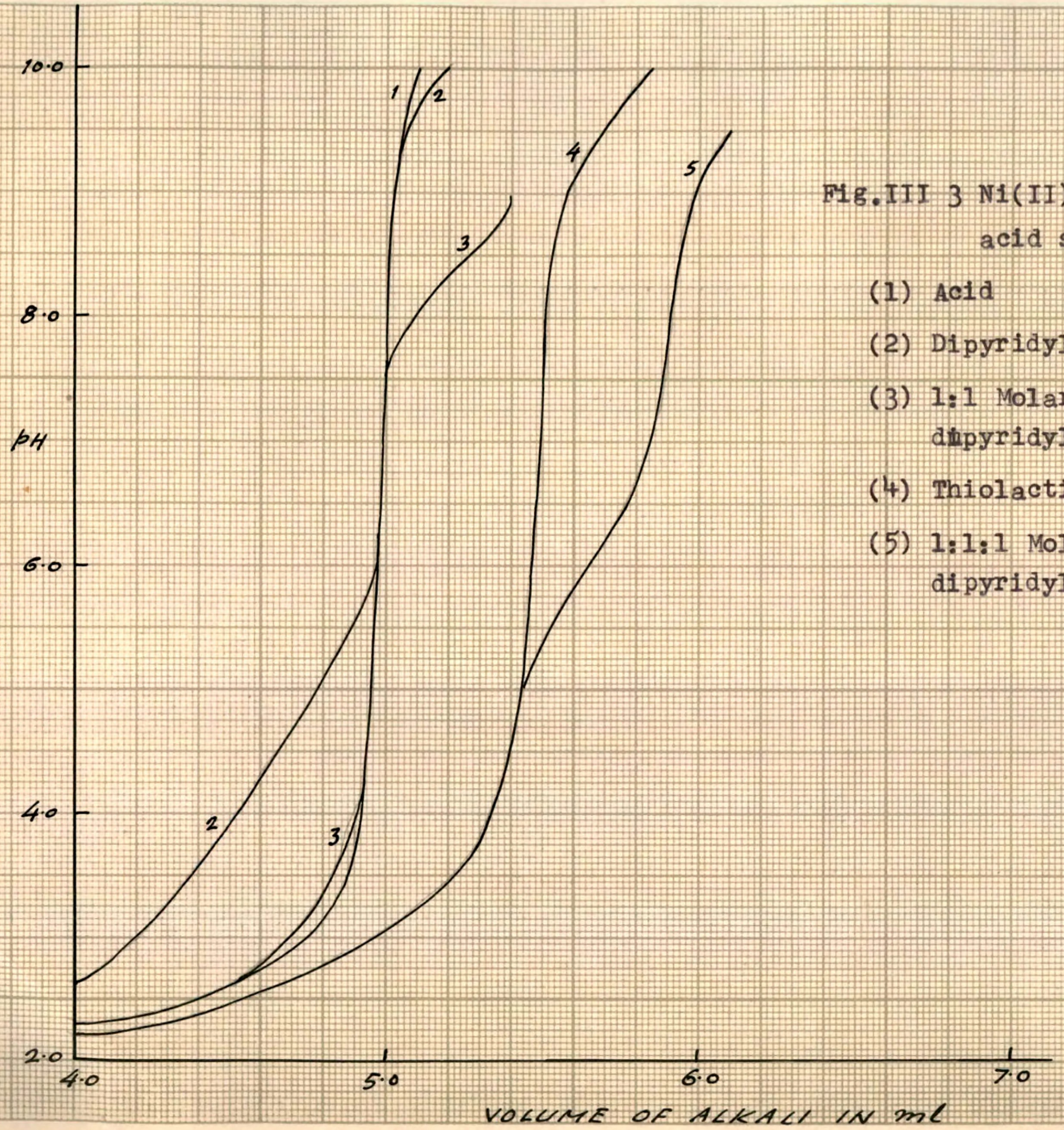

Fig.III 3 Ni(II).Dipyridyl.Thiolactic acid system - 30°C.

(1) Acid

(2) Dipyridyl

(3) 1:1 Molar ratio of Ni(II), dipyridyl

(4) Thiolactic acid

(5) 1:1:1 Molar ratio of Ni(II), dipyridyl and thiolactic acid.

Table III 1.4A

$N = 0.2M$ $V^\circ = 50$ ml. $T^\circ_L = 0.002M$ $\mu = 0.2M$

$E^\circ = 0.02M$ $T^\circ_{Dipy} = 0.002M$ $T^\circ_M = 0.002M$ $t = 30^\circ C$.

Thiomalic acid		Ni.Dipy.Thiomalic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80
3.00	1.95	3.00	1.95
4.00	2.25	4.00	2.25
4.20	2.35	4.20	2.35
4.40	2.45	4.40	2.45
4.60	2.60	4.60	2.60
4.80	2.75	4.80	2.75
5.00	3.00	5.00	3.00
5.10	3.10	5.10	3.10
5.20	3.30	5.20	3.30
5.30	3.50	5.30	3.50
5.40	3.70	5.40	3.70
5.50	3.95	5.50	3.95
5.60	4.25	5.60	4.20
5.70	4.60	5.70	4.50
5.80	5.00	5.80	4.80
5.90	5.60	5.90	5.10
5.95	6.10	5.95	5.25
6.00	7.10	6.00	5.40
6.02	8.50	6.05	5.60
6.04	9.00	6.10	5.85
6.08	9.30	6.15	6.15
6.10	9.50	6.20	6.75
6.18	10.00	6.24	8.15
		6.28	8.50
		6.35	8.85
		6.40	9.05 (ppts.)

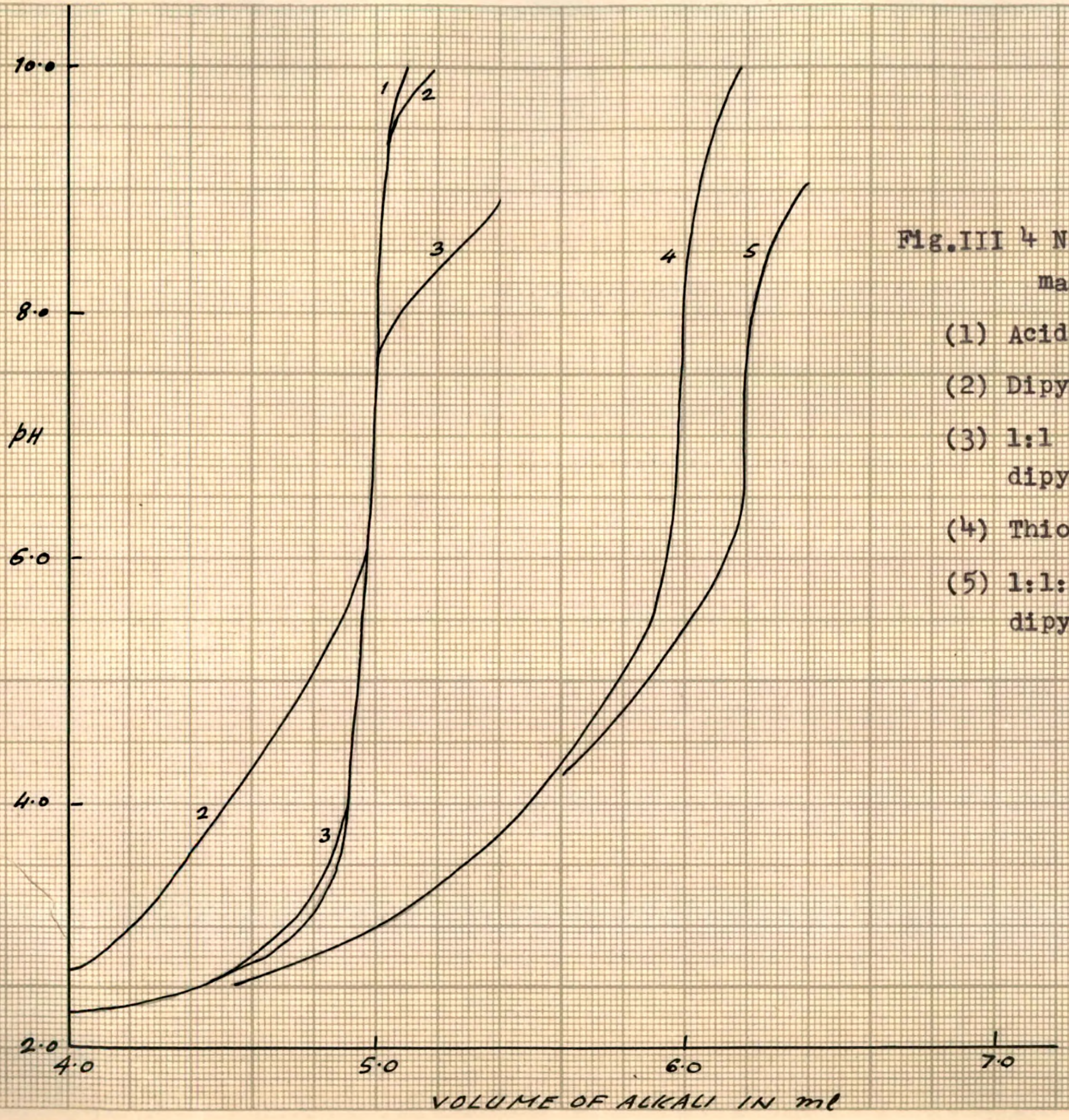

Fig.III 4 Ni(II).Dipyridyl.Thiomalic acid system - 30°C.

(1) Acid

(2) Dipyridyl

(3) 1:1 Molar ratio of Ni(II), dipyridyl

(4) Thiomalic acid

(5) 1:1:1 Molar ratio of Ni(II), dipyridyl and thiomalic acid.

Table III 1.1B

N = 0.2M
E° = 0.02M
V° = 50 ml.
$T^{\circ}_{\text{o-phen}}$ = 0.001M
T°_{L} = 0.001M
T°_{M} = 0.001M
t = 30°C.
μ = 0.2M

Perchloric acid		o-Phen		Ni-o-Phen		Aspartic acid		Ni-o-Phen-Aspartic acid	
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	1.55	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	1.65	1.00	1.65
2.00	1.80	2.00	1.85	2.00	1.80	2.00	1.80	2.00	1.85
2.50	1.85	3.00	2.05	2.50	1.85	2.50	1.85	2.50	1.90
3.00	2.00	4.00	2.35	3.00	2.00	3.00	2.00	3.00	2.05
3.60	2.10	4.10	2.40	3.60	2.10	3.60	2.10	3.60	2.15
3.80	2.20	4.20	2.50	3.80	2.20	3.80	2.20	3.80	2.25
4.00	2.25	4.30	2.65	4.00	2.25	4.00	2.25	4.00	2.30
4.20	2.35	4.40	2.80	4.20	2.35	4.20	2.35	4.20	2.35
4.40	2.50	4.50	3.05	4.40	2.50	4.40	2.45	4.40	2.55
4.60	2.70	4.60	3.40	4.60	2.70	4.60	2.70	4.60	2.75
4.70	2.85	4.70	3.95	4.70	2.85	4.80	3.05	4.80	3.05
4.80	3.10	4.75	4.35	4.80	3.10	4.90	3.30	4.90	3.30
4.90	3.65	4.80	4.75	4.90	3.65	5.00	3.60	5.00	3.60
4.94	5.25	4.85	5.10	4.94	5.25	5.05	3.85	5.05	3.85
4.96	5.75	4.90	5.50	4.96	5.75	5.10	4.10	5.10	4.10
5.00	8.30	4.95	5.85	5.00	8.00	5.15	4.75	5.15	4.60
5.02	9.00	4.98	6.05	5.05	8.50	5.20	6.00	5.20	5.15
5.04	9.45	5.00	8.30	5.10	8.80	5.25	8.30	5.24	5.60
5.06	9.70	5.02	9.00	5.15	9.10	5.28	8.75	5.28	6.00
5.08	9.85	5.04	9.45	5.20	9.30	5.30	8.95	5.30	6.20
5.10	10.00	5.10	9.75	5.30	9.80	5.40	9.35	5.35	6.65
		5.15	10.00			5.50	9.65	5.38	7.50
						5.60	10.00	5.40	7.80
								5.44	8.50
								5.50	9.10
								5.60	9.70

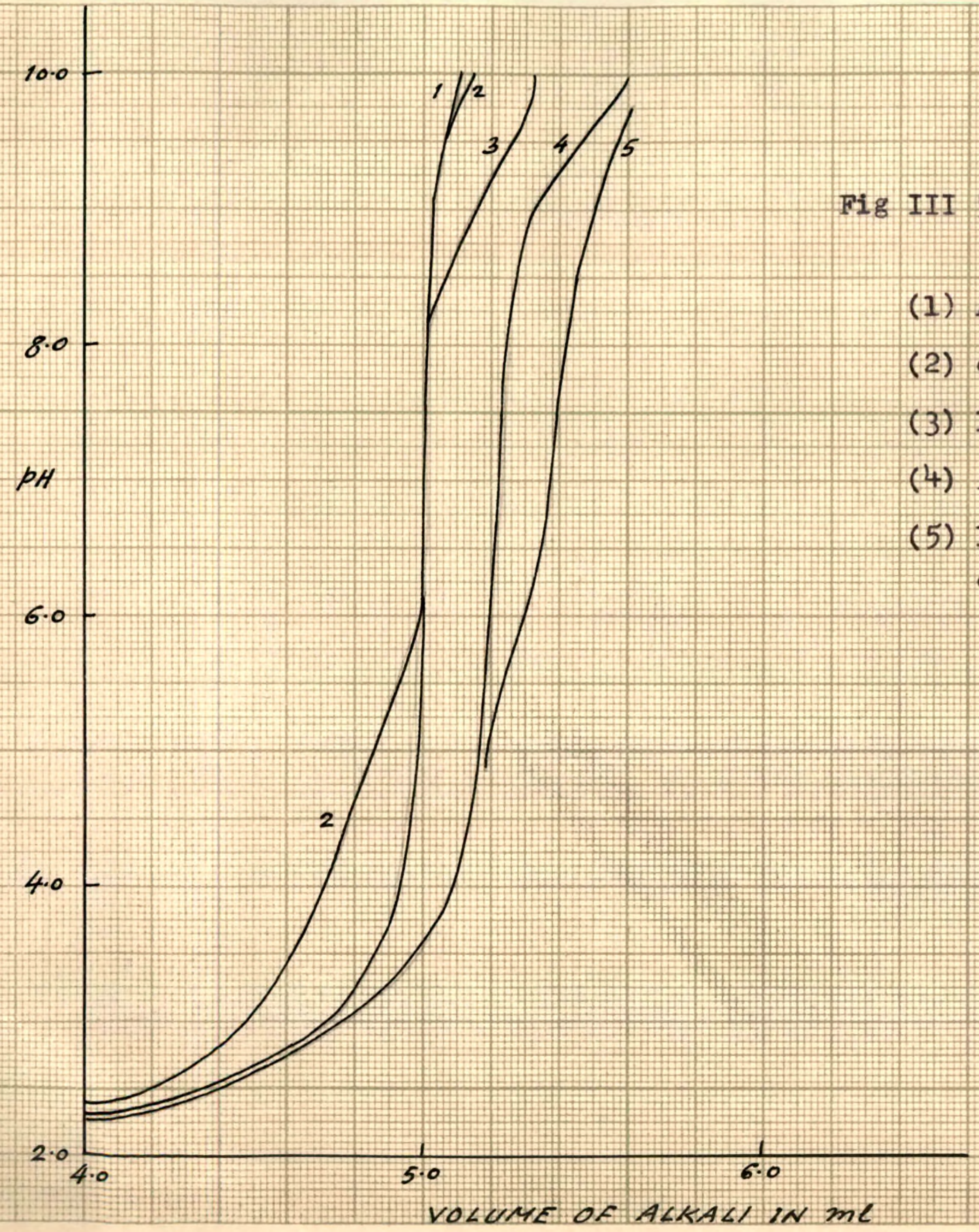

Fig III 5 Ni(II).o-phen.Aspartic acid
system - 30°C.

(1) Acid

(2) o-phenanthroline

(3) 1:1 Molar ratio of Ni(II), o-phen.

(4) Aspartic acid

(5) 1:1:1 Molar ratio of Ni(II), o-phen. and aspartic acid.

Table III 1.2B

$N = 0.2M$ $V° = 50$ ml. $T^{\circ}_{L} = 0.001M$ $\mu = 0.2M$

$E° = 0.02M$ $T^{\circ}_{o\text{-}phen} = 0.001M$ $T^{\circ}_{M} = 0.001M$ $t = 30°C$.

Thioglycollic acid		Ni.o-phen.Thioglycollic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.55	0.00	1.55
1.00	1.60	1.00	1.60
2.00	1.70	2.00	1.70
3.00	1.90	3.00	1.90
4.00	2.20	4.00	2.20
4.20	2.30	4.20	2.30
4.40	2.40	4.40	2.40
4.60	2.55	4.60	2.55
4.80	2.85	4.80	2.85
4.90	3.05	4.95	3.15
4.95	3.15	5.00	3.30
5.00	3.30	5.05	3.45
5.05	3.45	5.10	3.70
5.10	3.70	5.15	4.00
5.15	4.00	5.20	4.50
5.20	4.50	5.24	5.50
5.24	6.25	5.28	5.90
5.28	8.55	5.32	6.20
5.32	9.10	5.36	6.60
5.36	9.35	5.40	7.15
5.40	9.55	5.44	7.75
5.50	10.00	5.46	8.50
		5.50	9.00
		5.60	9.65 (ppts.)

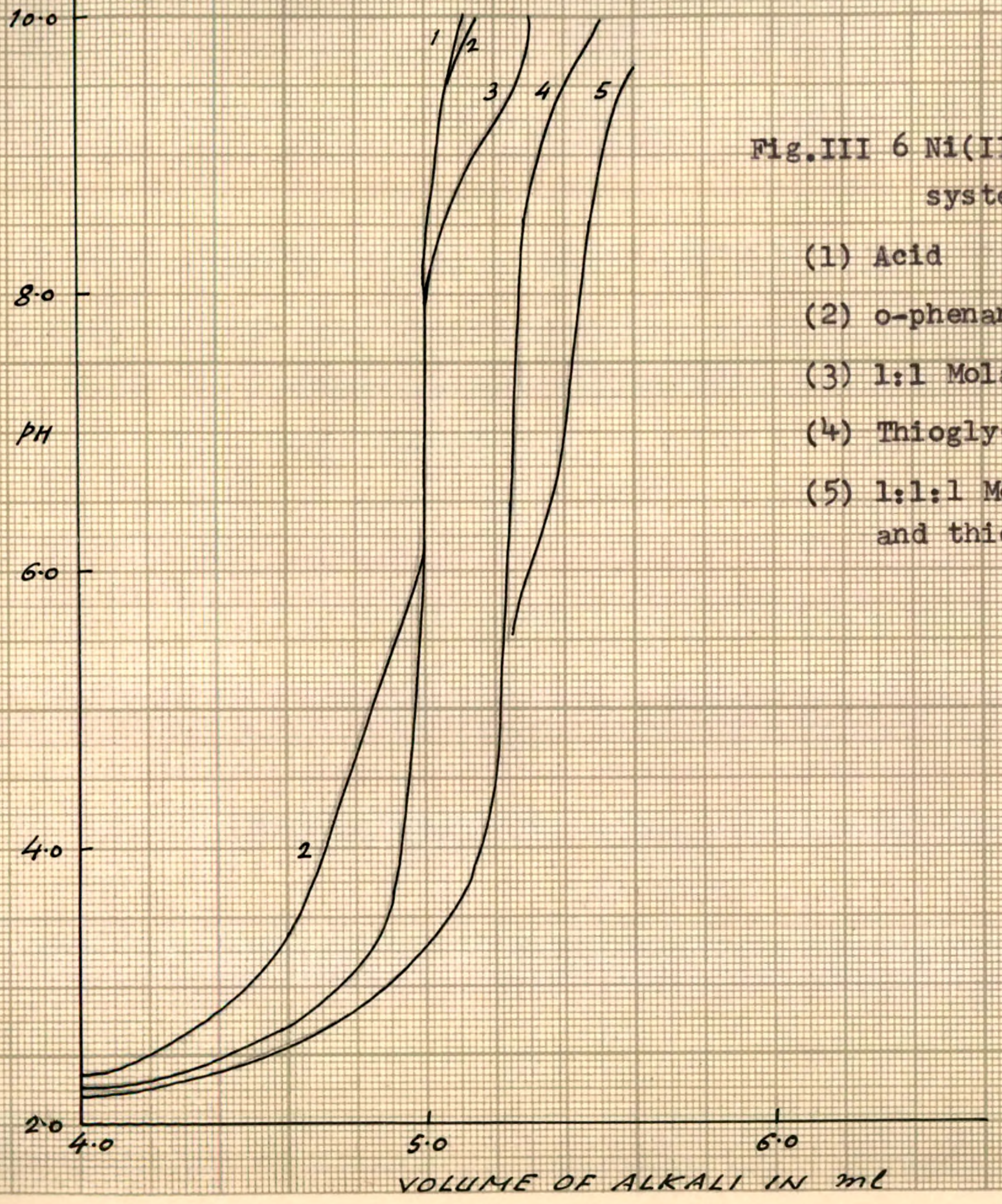

Fig.III 6 Ni(II).o-phen.Thioglycollic acid system - 30°C.

(1) Acid

(2) o-phenanthroline

(3) 1:1 Molar ratio of Ni(II),o-phen.

(4) Thioglycollic acid

(5) 1:1:1 Molar ratio of Ni(II), o-phen. and thioglycollic acid.

Table III 1.3B

$N = 0.2M$ $V^\circ = 50$ ml. $T^\circ_L = 0.001M$ $\mu = 0.2M$

$E^\circ = 0.02M$ $T^\circ_{o\text{-}phen} = 0.001M$ $T^\circ_M = 0.001M$ $t = 30°C.$

Thiolactic acid		Ni.o-phen.Thiolactic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.55	0.00	1.55
1.00	1.65	1.00	1.65
2.00	1.80	2.00	1.80
3.00	1.95	3.00	1.95
4.00	2.25	4.00	2.25
4.20	2.30	4.20	2.30
4.40	2.45	4.40	2.45
4.60	2.65	4.60	2.65
4.70	2.80	4.70	2.80
4.80	2.95	4.80	2.95
4.90	3.15	4.90	3.15
4.95	3.20	4.95	3.20
5.00	3.30	5.00	3.30
5.10	3.65	5.10	3.65
5.15	4.00	5.15	4.00
5.20	4.75	5.20	4.75
5.24	5.75	5.24	5.50
5.26	7.50	5.28	6.00
5.28	8.25	5.32	6.30
5.30	8.90	5.36	6.65
5.35	9.45	5.40	6.90
5.40	9.70	5.45	7.50
5.48	10.00	5.48	8.00
		5.52	8.90 (ppts.)

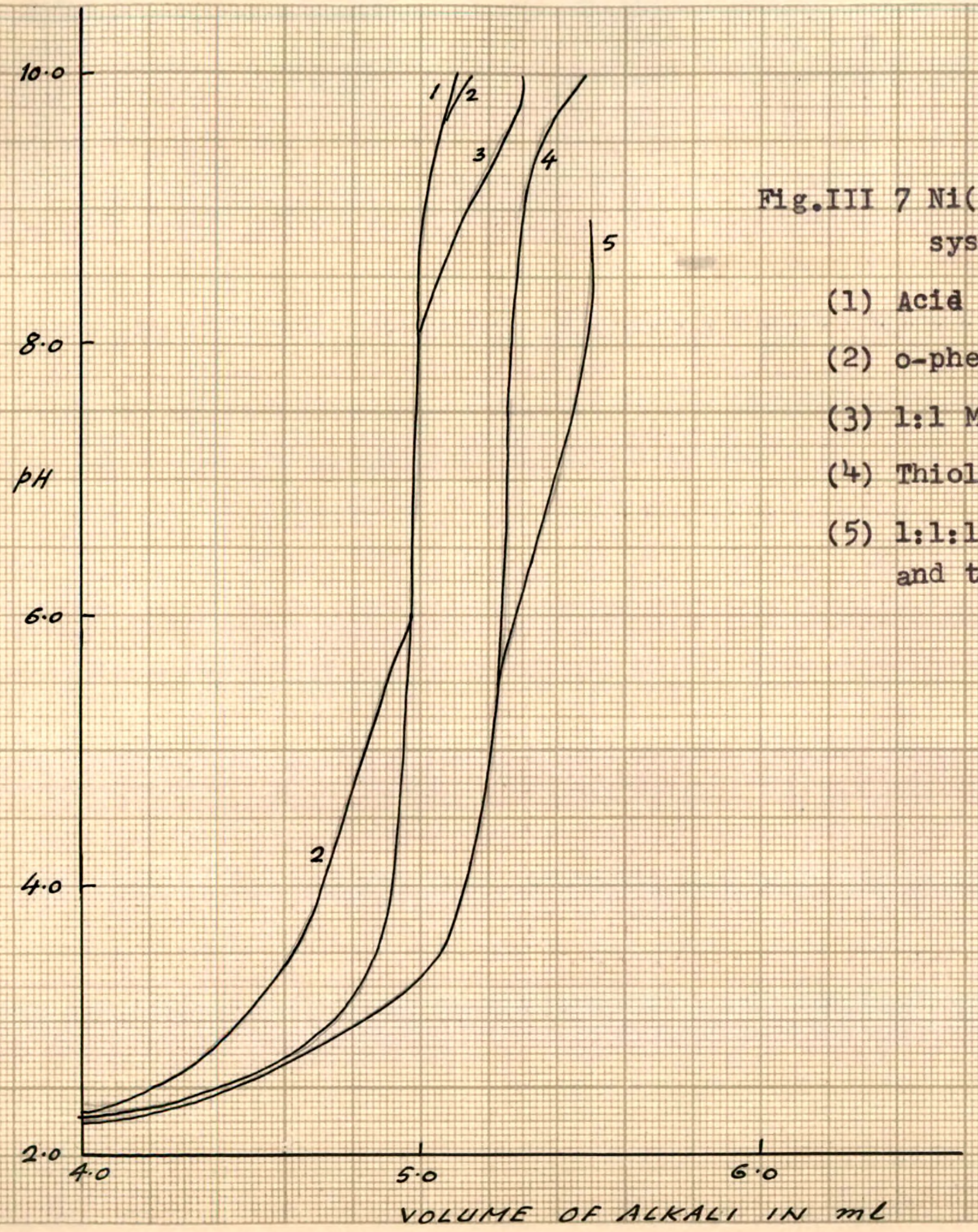

Fig.III 7 Ni(II).o-phen.Thiolactic acid
system - 30°C.

(1) Acid

(2) o-phenanthroline

(3) 1:1 Molar ratio of Ni(II),o-phen.

(4) Thiolactic acid.

(5) 1:1:1 Molar ratio of Ni(II),o-phen.
and thiolactic acid.

Table III 1.4B

$N = 0.2M$ $V^{\circ} = 50$ ml. $T^{\circ}_{L} = 0.001M$ $\mu = 0.2M$

$E^{\circ} = 0.02M$ $T^{\circ}_{o\text{-}phen} = 0.001M$ $T^{\circ}_{M} = 0.001M$ $t = 30^{\circ}C.$

Thiomalic acid		Ni.o-phen.Thiomalic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.55	0.00	1.55
1.00	1.65	1.00	1.65
2.00	1.75	2.00	1.75
3.00	1.90	3.00	1.90
4.00	2.25	4.00	2.25
4.20	2.30	4.20	2.30
4.40	2.40	4.40	2.40
4.60	2.55	4.60	2.55
4.80	2.80	4.80	2.80
4.90	2.90	4.90	2.90
5.00	3.10	5.00	3.10
5.50	3.35	5.10	3.35
5.15	3.50	5.75	3.50
5.20	3.60	5.20	3.60
5.25	3.85	5.25	3.85
5.30	4.10	5.30	4.10
5.35	4.30	5.35	4.30
5.40	4.60	5.40	4.60
5.45	5.00	5.45	4.95
5.50	5.75	5.50	5.20
5.54	7.00	5.54	5.50
5.58	9.00	5.58	5.85
5.65	9.55	5.62	6.25
5.70	9.80	5.66	6.70
5.74	10.00	5.70	7.40
		5.74	8.50
		5.78	9.10
		5.80	9.30
			(ppts.)

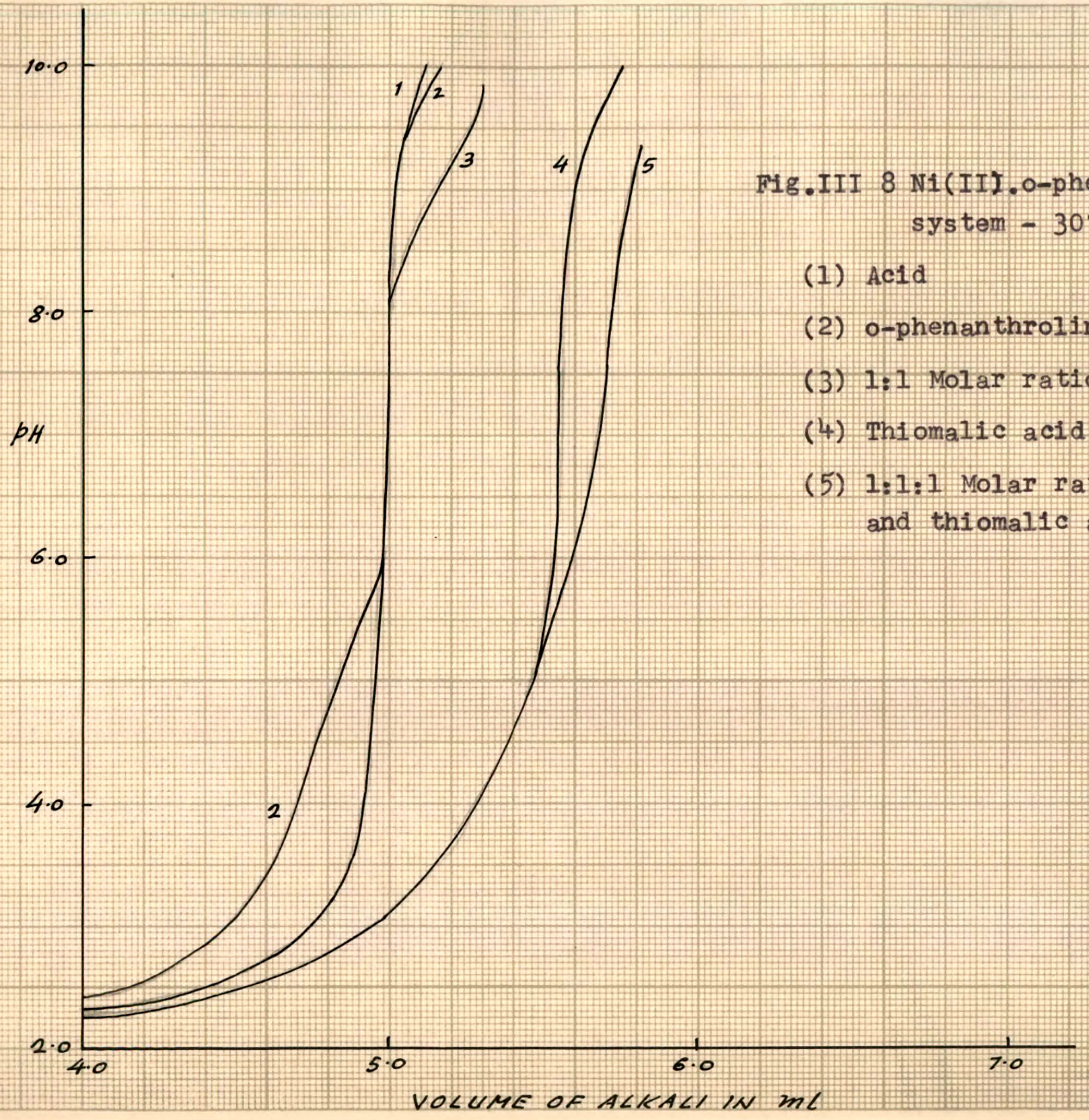

Fig.III 8 Ni(II).o-phen.Thiomalic acid
system - 30°C.

(1) Acid

(2) o-phenanthroline

(3) 1:1 Molar ratio of Ni(II),o-phen.

(4) Thiomalic acid

(5) 1:1:1 Molar ratio of Ni(II),o-phen.
and thiomalic acid.

Table III 2.1A

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$/$\bar{n}$
5.40	1.02_7	5.42	5.58	0.16	0.31_2	0.34_3	7.11_4	6.77_1
5.50	1.02_7	5.42	5.60	0.18	0.35_1	0.26_7	7.03_8	6.77_1
5.60	1.02_3	5.43	5.62	0.19	0.37_2	0.22_8	6.96_2	6.73_4
5.70	1.01_9	5.43	5.64	0.21	0.41_3	0.15_3	6.88_0	6.72_7
5.80	1.01_9	5.43	5.66	0.23	0.45_2	0.08_4	6.80_9	6.72_5
5.90	1.01_9	5.44	5.68	0.24	0.47_2	0.04_9	6.72_5	6.67_6
6.00	1.01_9	5.44	5.70	0.26	0.51_1	$\bar{1}.98_1$	6.65_8	6.67_7
6.10	1.01_9	5.44	5.72	0.28	0.55_0	$\bar{1}.91_3$	6.59_9	6.68_6

log K_{MAL} = 6.72 ± 0.03

Table III 2.2A

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
5.80	1.01_6	5.47	5.59	0.12	0.23_6	0.51_0	7.22_3	6.71_3
5.90	1.01_6	5.48	5.61	0.13	0.25_6	0.46_3	7.13_4	6.67_1
6.00	1.01_2	5.48	5.64	0.16	0.31_6	0.33_5	7.07_0	6.73_5
6.10	1.00_8	5.49	5.67	0.18	0.35_7	0.25_6	6.96_5	6.70_9
6.20	1.00_8	5.49	5.69	0.20	0.39_7	0.18_2	6.92_5	6.74_3
6.30	1.00_8	5.49	5.71	0.22	0.43_7	0.11_0	6.85_6	6.74_6
6.40	1.00_4	5.49	5.75	0.24	0.47_8	0.03_8	6.78_8	6.74_0
6.50	1.00_4	5.49	5.74	0.25	0.49_8	0.00_9	6.70_5	6.70_1
6.60	1.00_4	5.49	5.76	0.27	0.53_8	$\bar{1}.93_4$	6.64_1	6.70_7
6.70	1.00_4	5.49	5.77	0.28	0.55_8	$\bar{1}.89_9$	6.56_9	6.67_0

log K_{MAL} = 6.71 ± 0.03

Table III 2.3A

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
6.00	1.01_2	5.46	5.64	0.18	0.35_6	0.25_7	7.12_7	6.87_0
6.10	1.01_2	5.47	5.67	0.20	0.39_5	0.18_5	7.05_5	6.87_0
6.20	1.00_7	5.47	5.69	0.22	0.43_5	0.11_4	6.98_4	6.87_0
6.30	1.00_7	5.48	5.72	0.24	0.47_7	0.04_0	6.91_8	6.87_8
6.40	1.00_7	5.48	5.74	0.26	0.51_7	$\bar{1}.97_0$	6.88_5	6.91_5
6.50	1.00_4	5.48	5.76	0.28	0.55_8	$\bar{1}.89_9$	6.78_9	6.89_0
6.60	1.00_4	5.48	5.78	0.30	0.59_8	$\bar{1}.82_7$	6.69_3	6.86_6
6.70	1.00_4	5.48	5.80	0.32	0.63_8	$\bar{1}.75_4$	6.59_7	6.84_3

$\log K_{MAL} = 6.87 \pm 0.01$

Table III 2.4A

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.70	0.96_6	5.96	6.07	0.11	0.22_4	0.54_0	7.46_6	6.92_6
5.80	0.95_5	5.96	6.09	0.13	0.26_8	0.43_6	7.38_6	6.85_0
5.90	0.94_8	5.97	6.11	0.14	0.29_0	0.38_9	7.29_9	6.91_0
6.00	0.96_7	5.97	6.13	0.16	0.33_2	0.30_4	7.23_3	6.92_9
6.10	0.93_7	5.98	6.15	0.17	0.35_7	0.25_6	7.13_8	6.88_2
6.20	0.91_3	5.98	6.16	0.18	0.38_7	0.20_0	7.05_7	6.85_7
6.30	0.91_3	5.98	6.17	0.19	0.40_9	0.16_0	6.97_3	6.81_3

$\log K_{MAL} = 7.88 \pm 0.04$

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 of Ni.o-phen. aspartic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
6.00	1.01_9	5.21	5.28	0.07	0.27_5	0.42_1	6.78_5	6.36_4
6.10	1.01_9	5.21	5.29	0.08	0.31_4	0.33_8	6.70_9	6.36_1
6.20	1.01_6	5.21	5.30	0.09	0.35_5	0.25_9	6.63_5	6.37_6
6.30	1.01_2	5.21	5.31	0.10	0.39_6	0.18_3	6.56_4	6.38_1
6.40	1.01_2	5.21	5.32	0.11	0.43_5	0.11_4	6.49_3	6.37_9
6.50	1.00_8	5.22	5.34	0.12	0.47_6	0.04_2	6.42_8	6.38_6

$\log K_{MAL} = 6.38 \pm 0.01$

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 of Ni.o-phen. thioglycollic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
6.40	1.00_4	5.25	5.34	0.09	0.35_7	0.25_5	6.99_6	6.74_1
6.50	1.00_4	5.25	5.35	0.10	0.39_6	0.18_5	6.92_3	6.74_0
6.60	1.00_4	5.25	5.36	0.11	0.43_6	0.11_3	6.85_3	6.74_0
6.70	1.00_4	5.25	5.37	0.12	0.47_6	0.04_2	6.78_5	6.74_3
6.80	1.00_4	5.25	5.38	0.13	0.51_5	$\bar{1}.97_4$	6.71_8	6.74_4
6.90	1.00_4	5.25	5.39	0.14	0.55_5	$\bar{1}.90_4$	6.65_6	6.75_2
7.00	1.00_4	5.25	5.40	0.15	0.59_5	$\bar{1}.83_3$	6.59_7	6.76_4

$\log K_{MAL} = 6.74 \pm 0.01$

Table III 2.3B

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. thiolactic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
6.00	1.01_2	5.23	5.28	0.05	0.19_7	0.61_0	7.32_9	6.71_9
6.10	1.01_2	5.24	5.30	0.06	0.23_6	0.51_0	7.25_1	6.74_1
6.30	1.00_7	5.24	5.32	0.08	0.31_6	0.33_5	7.09_9	6.76_4
6.40	1.00_7	5.24	5.33	0.09	0.35_9	0.25_2	7.02_7	6.77_5
6.50	1.00_4	5.24	5.34	0.10	0.39_7	0.18_1	6.95_4	6.77_3
6.60	1.00_4	5.24	5.355	0.11	0.43_6	0.12_2	6.88_3	6.76_1
6.80	1.00_4	5.25	5.38	0.13	0.51_6	$\bar{1}.97_2$	6.74_9	6.77_7
6.90	1.00_4	5.25	5.39	0.14	0.55_5	$\bar{1}.90_4$	6.68_6	6.78_2
7.00	1.00_4	5.25	5.40	0.15	0.59_5	$\bar{1}.83_3$	6.52_7	6.79_4

$\log K_{MAL} = 6.77 \pm 0.01$

Table III 2.4B

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. thiomalic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.80	0.95_5	5.51	5.57	0.06	0.25_1	0.47_5	7.67_5	7.20_0
5.90	0.94_8	5.51	5.58	0.07	0.29_5	0.37_8	7.59_9	7.22_1
6.10	0.93_7	5.52	5.61	0.09	0.38_4	0.20_5	7.45_3	7.24_8
6.20	0.91_9	5.52	5.62	0.10	0.43_5	0.11_3	7.39_0	7.27_7
6.30	0.91_3	5.52	5.62	0.10	0.43_8	0.10_7	7.29_1	7.18_4
6.40	0.91_3	5.52	5.63	0.11	0.48_2	0.03_9	7.22_5	7.18_6
6.50	0.91_3	5.52	5.64	0.12	0.52_5	$\bar{1}.95_6$	7.16_2	7.20_6
6.60	0.91_3	5.52	5.65	0.13	0.56_9	$\bar{1}.87_9$	7.10_4	7.22_5

$\log K_{MAL} = 7.22 \pm 0.02$

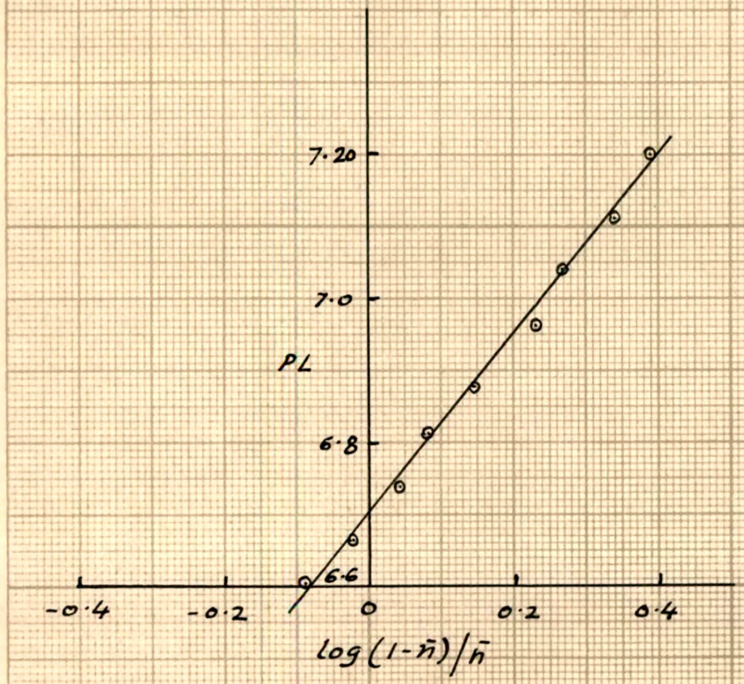

Fig.III 9 Ni(II).dipyridyl.Aspartic
acid system - 30°C.

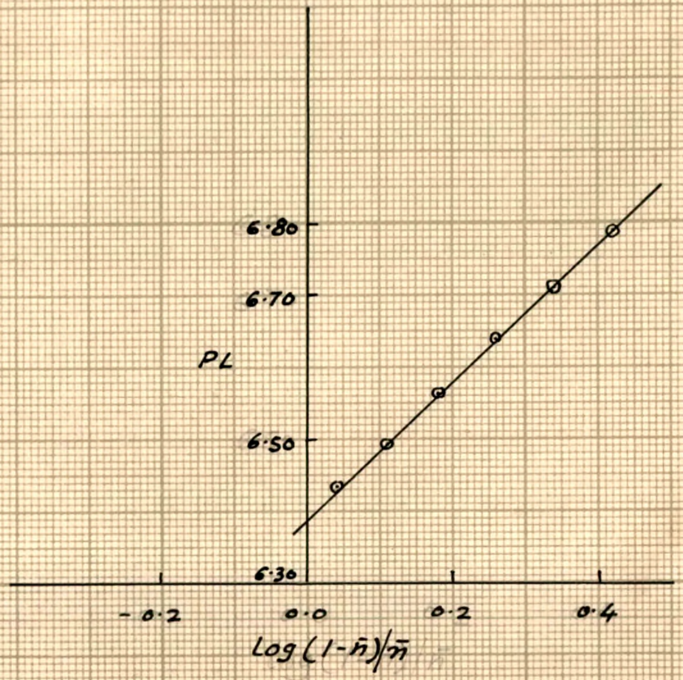

Fig.III 10 Ni(II).o-phen.Aspartic
acid system - 30°C.

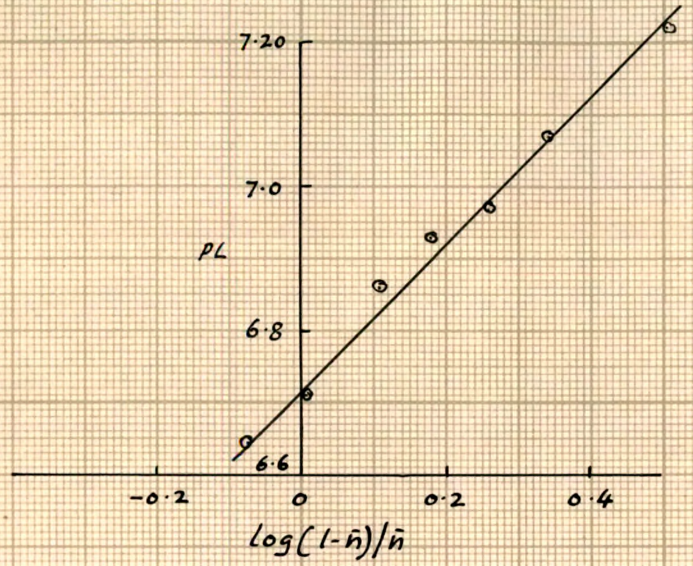

Fig.III 11 Ni(II).dipy.thioglycollic acid system-30°C.

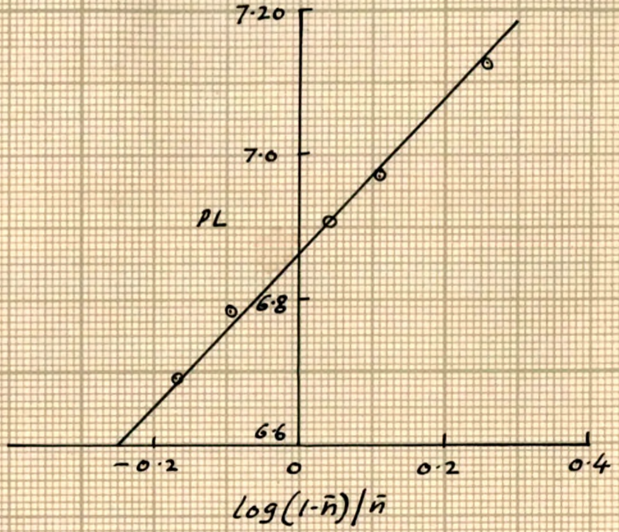

Fig.III 12 Ni(II).dipy.thiolactic acid system-30°C.

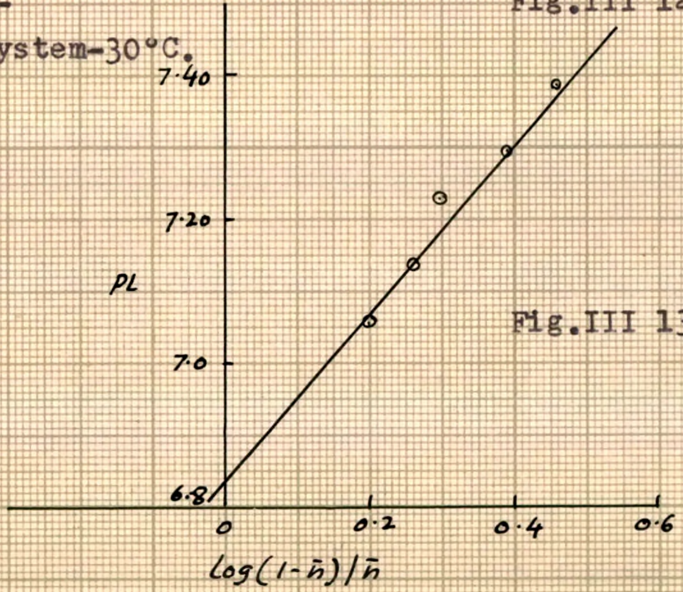

Fig.III 13 Ni(II).dipy.thiomalic acid system-30°C.

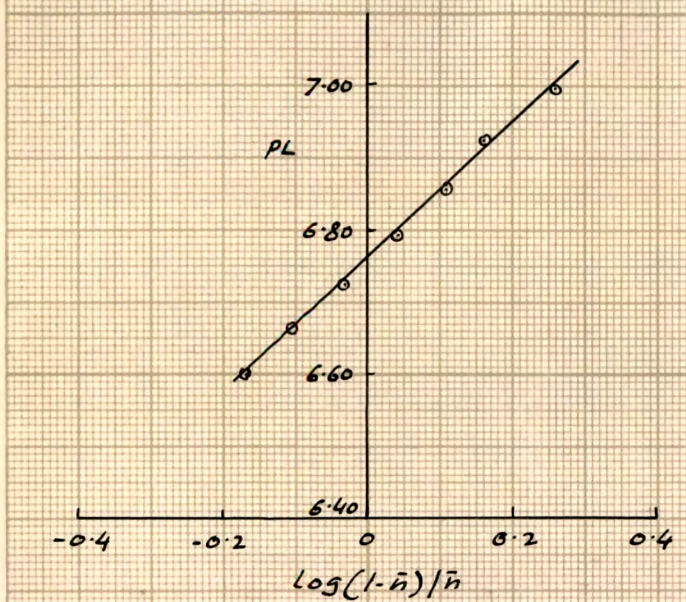

Fig.III 14 Ni(II).o-phen.
thioglycollic acid
system - 30°C.

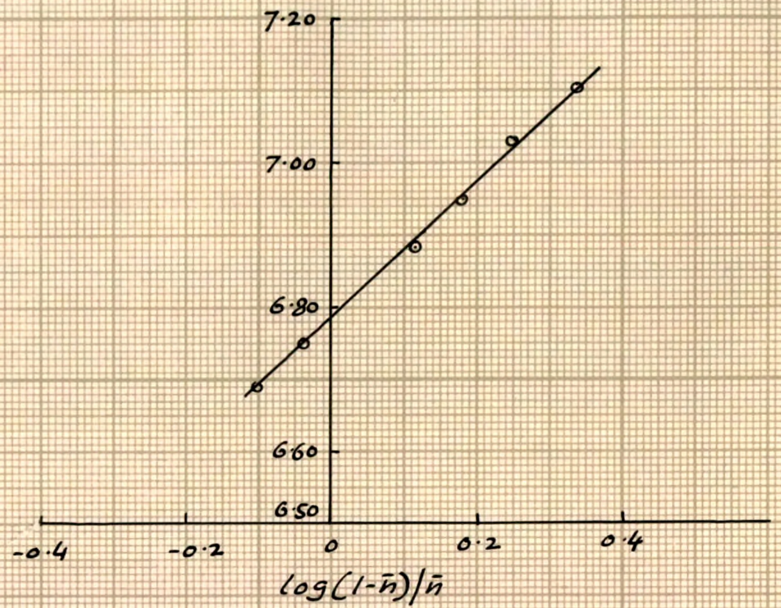

Fig.III 15 Ni(II).o-phen.thiolactic
acid system - 30°C.

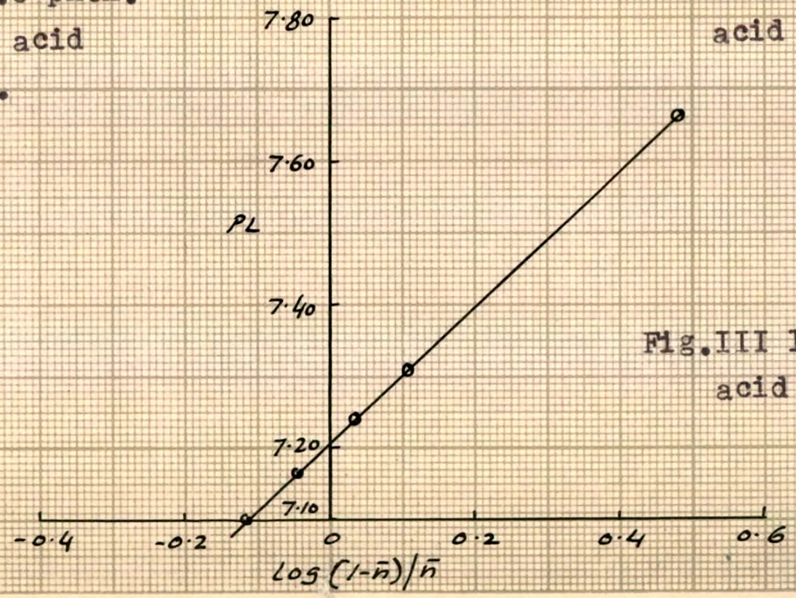

Fig.III 16 Ni(II).o-phen.thiomalic
acid system - 30°C.

Table III 3.0

Proton ligand stability constants of various mercapto acids-30°C.

Ligand (L)	$P_{K_3}^{H}$	$P_{K_2}^{H}$	$P_{K_1}^{H}$
Thioglycollic acid	-	3.27 ± 0.02	10.16 ± 0.03
Thiolactic acid	-	3.39 ± 0.01	10.19 ± 0.01
Thiomalic acid	2.91 ± 0.01	4.31 ± 0.02	10.29 ± 0.03

Table III 4.0

Formation constants of various thioacid chelates - 30°C.

	Ni(II) *	
Ligand (L)	log K_1	log K_2
Thioglycollic acid	6.78 ± 0.02	6.63 ± 0.02
Thiolactic acid	7.31 ± 0.05	6.98 ± 0.04
Thiomalic acid	7.68 ± 0.07	6.62 ± 0.09

* Values are taken from literature for comparison.

Table III 5.0

Logarithms of stability constants of ternary dipyridyl Ni^{2+} ligand complexes and o-phenanthroline-Ni^{2+} ligand complexes.

Ligand (L)	$\log K^{Ni.dipy.}_{Ni.dipy.L}$	$\log K^{Ni.o\text{-}phen.}_{Ni.o\text{-}phen.L.}$
Glycine	5.50 ± 0.02*	5.28 ± 0.02*
α-Alanine	5.14 ± 0.05*	5.18 ± 0.02*
Aspartic acid	6.72 ± 0.03	6.38 ± 0.01
Thioglycollic acid	6.71 ± 0.03	6.74 ± 0.01
Thiolactic acid	6.87 ± 0.01	6.77 ± 0.01
Thiomalic acid	7.88 ± 0.04	7.22 ± 0.02

* Values are taken from literature

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