

Mixed chelates containing charged ions of amino acids, histidine, iminodiacetic acid, nitrilotriacetic acid and ethylenediaminetetraacetic acid as primary ligands have been studied earlier. The 1:1 complexes of these multidentate ligands are formed at low pH and remain stable upto high pH. In the 1:1 complex of these ligands with metal ion, the remaining coordination positions of the metal ion are occupied by water molecules. On the addition of a secondary ligand, water molecules are displaced resulting in the formation of the mixed ligand complex MAL where A = histidine (Hist.), iminodiacetic acid (IMDA) or nitrilotriacetic acid (NTA) and L = secondary ligand. The mixed ligand formation constant K_{MAL}^{MA} is represented by the following equation :

$$K_{MAL}^{MA} = \frac{[MAL]}{[MA][L]}$$

Histidine exhibits bi or tridentate¹ character, coordination taking place from COO⁻ and from nitrogen of the imidazole group or two nitrogens from both imidazole and amino groups. The system Zn.Hist. cyanide was studied potentiometrically by Martin and coworkers² and is of biological interest. They also studied the system Cu.Hist.Threonine both potentiometrically and by X-ray crystallographic analysis.

IMDA behaves as a tridentate³ ligand coordination taking place from the nitrogen atom and two carboxylate

groups. Sharma and Tondon⁴ studied the mixed ligand complexes of Cu(II) and Ni(II) with IMDA as a primary ligand and hydroxy acids as secondary ligand. The mixed ligand complexes of the type Ni.IMDA.L where L = pyridine, ammonia or H₂O have also been studied by Fridman and coworkers. Various mixed ligand complexes with IMDA^{5,6} as the primary ligand have been studied. Isolation of oxovanadium (IV) heterochelates of type VO.L.H₂O.X, where L = IMDA, X = pyridine, α -picoline and α -alanine have been reported⁷.

NTA behaves as a tri⁸ or tetradentate⁹ ligand, coordination taking place from nitrogen atom and two or three COO⁻ groups, respectively. Israeli and coworkers¹⁰⁻¹⁴ studied the mixed ligand complexes of Cu(II) and Ni(II) with NTA and amino acids by using spectrophotometric method. The systems M.NTA.L where M = Cu(II) and Ni(II), L = number of amino acids have been studied pH metrically by Chidambaram and Bhattacharya¹⁵. The systems M.NTA.L where L = picoline, oxine, serine, arginine, glycylglycine and ammonia have also been studied.¹⁰⁻¹⁴ Martell and coworkers¹⁶ determined the formation constant of the ternary complex U⁶⁺-NTA-hydroxyquinoline sulphonic acid. The formation constants of the mixed ligand complexes M.NTA.L where M = Cu(II), Ni(II), Zn(II) or Cd(II), and L = polyhydroxy phenol or phenolic acid have also been reported from this laboratory¹⁷. Various mixed ligand complexes with NTA¹⁸ as the primary ligand have been studied. The mixed ligand complexes of various transition metal ions containing NTA

and several secondary ligands have been synthesised.¹⁹⁻²³ Solution equilibrium of the reaction between Eriochrome Black-T and Zn(II) NTA has been studied spectrophotometrically.²⁴ The ternary system of Be(II) NTA and tiron has also been investigated by pH metric method.⁸ Co(II) complexes with amino polycarboxylic acids and nitrite ion have also been reported.²⁵

Athavale and coworkers²⁶ worked out the systems MAL where M = Th(IV), A = EDTA and L = secondary ligands, catechol and tiron. Mixed ligand complexes of the type Ni.L.X, where L = IMDA or EDTA and X = pyridine, ammonia or water have also been studied in solution by Fridman and coworkers.²⁷ Tananaeva and coworkers²⁸ have reported mixed ligand complexes of neodymium with NTA and EDTA. Various mixed ligand complexes with EDTA as the primary ligand have been studied.^{26,29} Various other systems have also been reported where dyes³⁰ and Schiff bases³¹ are primary ligands and the amino acids or hydroxy acids are the secondary ligands.

The systems MAL where M = Co(II), Ni(II), Zn(II) and Cd(II), A = histidine or IMDA and L = polyhydroxy phenols have been investigated by Bhattacharya and coworkers.³² Panchal and Bhattacharya³³ have also studied the systems Zn.NTA.thio acids. In the present chapter an account of the systems Ni.A.L where A = Hist., IMDA or NTA and L = amino acids and thio acids is being presented.

Experimental :

Determination of the mixed ligand constants :

The reagents and instruments used were same as detailed in previous chapters. Histidine, iminodiacetic acid and nitrilotriacetic acid used were of A.R. quality.

For studying the ternary systems following solutions were prepared.

For histidine systems :

1. Perchloric acid (0.2M, 5.0 ml.) + histidine (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (31.1 ml.).
2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (31.1 ml.).
3. Perchloric acid (0.2M, 5.0 ml.) + histidine (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (26.2 ml.).
4. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (26.2 ml.).
5. Perchloric acid (0.2M, 5.0 ml.) + histidine (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (21.3 ml.).

For IMDA systems :

1. Perchloric acid (0.2M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (31.1 ml.).

2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 10.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (26.2 ml.).
3. Perchloric acid (0.2M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (26.2 ml.).
4. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 10.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (21.3 ml.).
5. Perchloric acid (0.2M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (21.3 ml.).

For NTA systems :

1. Perchloric acid (0.2M, 5.0 ml.) + NTA (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (31.1 ml.).
2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 15.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (21.3 ml.).
3. Perchloric acid (0.2M, 5.0 ml.) + NTA (0.2M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (25.2 ml.).
4. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 15.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.6 ml.) + conductivity water (16.4 ml.).
5. Perchloric acid (0.2M, 5.0 ml.) + NTA (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity

water (21.3 ml.).

Total volume was made upto 50.0 ml. and ionic strength was maintained 0.2M. Each of the sample was titrated against 0.2M sodium hydroxide solution. The plots of pH against volume of alkali have been presented in figs. V-1 to V-14.

The nature of the curves in case of Ni(II) Hist., IMDA or NTA and amino acids or thio acids have been shown in figs. V-1 to V-14. As is evident from curves(1) and (3) Ni(II) Hist., IMDA or NTA 1:1 complex is formed at low pH and it is stable upto high pH. This is because the horizontal distance between the two curves remain constants upto pH ~ 7.5, 8.5 and 8.5 in case of Hist., IMDA or NTA respectively. Above this, the curves start converging indicating absence of hydrolysis or hydroxo complex formation. Amino acids and mercapto acids combine with MA at higher pH as observed from reagent curve(4) and mixed ligand curve(5). In case of secondary ligand curve(4), one, two or three equivalents of extra perchloric acid have been added to account for the hydrogen ions liberated as a result of complexation of Hist., IMDA or NTA with Ni^{2+} ion in curve(5). In the lower pH range curves (4) and (5) overlap in case of Ni.NTA.L systems showing that Ni.NTA 1:1 is formed at very low pH. However, in case of ternary systems Ni.HIST. or IMDA and secondary ligand the curve (5) is above the curve(4) upto pH ~ 6.5 and 6.0 indicating that the M.A, 1:1 complex formation is completed at that pH. Complexation of the secondary ligand (L) with MA results

in the liberation of extra hydrogen ions. In MAL where L = glycine or α -alanine systems figs. V-1, V-2, V-6, V-7 curve (5) overlaps M + A curve (3) in the lower pH range indicating that the complexation of the L does not take place in the lower pH range. Since the \bar{n}_H for the uncoordinated amino acids is one, curves (3) and (5) overlap in M.A amino acid systems. However, in case of aspartic acid and mercapto acid curve (5) is separated from the curve (3) in the lower pH range also because the self dissociation of the ligand takes place even without coordination. \bar{n} and pL values were calculated at different pH in the same manner as done in the chapter III and have been presented in tables V 2.1A to V 2.5A, V 2.1B to V 2.6B and V 2.3C to V 2.5C. The values of pL, at $\bar{n} = 0.5$ gives the values of $\log K_{MAL}^{MA}$. More precise values were obtained by plotting pL at each points against the corresponding value of $\log (1-\bar{n})/\bar{n}$ and getting a straight line (figs. V-15 to V-28). The values of $pL - \log (1-\bar{n})/\bar{n}$ at each point on the straight line is equal to the $\log K_{MAL}^{MA}$. The average values of $\log K_{MAL}^{MA}$, thus obtained, have been presented with mean deviation in table V 3.0.

Discussion :

It is observed that ⁱⁿ the ternary systems M.A.amino acids, where A = Hist. IMDA or NTA, the order of the formation constants of the reaction MA + L is same as in the binary M + L system. This can be explained in terms of the basicities of the secondary ligand as done earlier (p.34-35). However, the values of K_{MAL}^{MA} are significantly lower than

the values of K_{ML}^M . This can be explained to be due to the repulsion between the already existing charged ion Hist.(-1), IMDA (-2) or NTA (-3) and the secondary ligand L^{n-} . Thus the tendency of the secondary ligand to combine with $[NiA]$ will be less than to combine with $[Ni(H_2O)_n]^{2+}$, and this results in the lowering of values of K_{NiAL}^{NiA} . The values of K_{MAL}^{MA} are nearly equal to $K_{ML_2}^{ML}$ in the binary complexes. The values of $\log K_{ML}^M - \log K_{MAL}^{MA}$ where L = aspartic acid is higher because aspartic acid has two negative charges and hence the repulsion between the primary charged ion and the secondary ligand ion is still more. In case of aspartic acid complexes the order of the mixed ligand formation constants is

$$K_{M.Hist.L} > K_{M.IMDA.L} > K_{M.NTA.L..}$$

This can be explained by considering that the electrostatic repulsion between the primary ligand and the secondary ligand goes on increasing with the increase in the charge on the primary ligand. The values of the formation constants of the complexes $[Ni.Hist.L]$ are nearer to that of $[Ni.IMDA.L]$ though histidine has one negative charge and IMDA has two negative charges. However, histidine is a bigger molecule and will cause more steric hindrance to the incoming secondary ligand. Thus besides, charge repulsion, other factors may also affect the mixed ligand formation constants.

In cases of mercapto acids also it is observed that the values of mixed ligand formation constants K_{MAL}^{MA} are

lower than K_{ML}^M , and are in the order

$$K_{M.Hist.L} > K_{M.IMDA.L} > K_{M.NTA.L}$$

as expected from charged repulsion. In case of thiomalic acid the difference between K_{NiL}^{Ni} and K_{NiAL}^{NiA} is expected to be more because thiomalate ion has three negative charges and has a bigger size resulting in greater electrostatic repulsion. The formation of the complex, therefore, takes place in the higher pH range. Consequently, studies in case of $[Ni.Hist.TMA]$ and $[Ni.NTA.TMA]$ were not possible. In case of the system $[Ni.IMDA.TMA]$ calculations have been done. It is observed that though TMA has greater tendency to combine with Ni^{2+} ion than TGA or TLA but it has less tendency to combine with $Ni.IMDA$. Thus the values of $K_{Ni.IMDA.TMA}^{Ni.IMDA}$ are lesser than $K_{Ni.IMDA.L}^{Ni.IMDA}$ where L = thioglycollic acid or thiolactic acid.

The studies in case of system $[Ni.A.L]$ where L = hydroxy acid was not possible because the formation of ternary complex takes place in the same range where $Ni.A$ hydroxy complex formation starts.

It is thus observed that in the $[Ni.A.mercapto\ acid]$ systems, where A = Hist., IMDA or NTA, the behaviour of mercapto acids is similar to that of the σ -bonding amino acids. The $\log K_{ML}^M - \log K_{MAL}^{MA}$ values are nearly same for the pairs glycine-thioglycollic acid, α -alanine-thiolactic acid and aspartic acid-thiomalic acid. This indicates that in both the cases the factor responsible for the lowering of the values of K_{NiAL}^{Ni} is electrostatic repulsion. The situation should have ^{been} different if there would have been

significant $M \rightarrow S$ π -interaction in the mercapto acid complexes. The coordination of strong σ -bonding ligand Hist., IMDA or NTA should result^{ed} in an increase in the electron density around the $Ni.A^{n-}$. The tendency of $Ni.A^{n-}$ to donate back π -electron to a secondary ligand L should be more than that of $[Ni(H_2O)_n]^{2+}$. This should increase the strength of the Ni-S bond in $Ni.A.L$ than in $NiL..$ Thus as a result of favourable back donation in ternary complexes, the lowering in the value of K_{NiAL}^{Ni} with respect to K_{NiL}^{Ni} should not be governed by the electrostatic repulsion alone. The lowering should have been less than in case of only σ -bonding ligand. However, this expectation is not met with in the systems $Ni.A.L$, where $L =$ mercapto acids. This shows that $Ni \rightarrow S$ π -interaction, if present, is not very significant. The strengthening of Ni-S bond in the mercapto acid complexes is due to σ -interaction as explained by Jorgenson³⁴ and Klopman³⁵.

Comparison between mercapto acid and corresponding hydroxy acid would have been more relevant, because the coordinating ions in both cases have two negative charges. Amino acid ion has only one negative charge. The choice of polycarboxylic amino acid as σ -bonding primary ligand is also not ideal. In these cases the coordination from carboxylate ions is more electrostatic in nature than covalent. Significant covalent σ -bonds are formed only with the nitrogen. Thus the concentration of electrons on the metal ion will not be significant in $[MA]^{n-}$. Hence the increase in the back donating capacity of MA may be negligible. This may be the reason why the mercapto acids behave as other σ -bonding ligands. Thus the $M \rightarrow S$ π -interaction cannot be completely ruled out on the basis of the above study.

Fig. V 1 Ni(II). Hist. glycine system-30°C.

- (1) Histidine
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), glycine
- (4) Glycine
- (5) 1:1:1 Molar ratio of Ni(II), Hist and glycine.

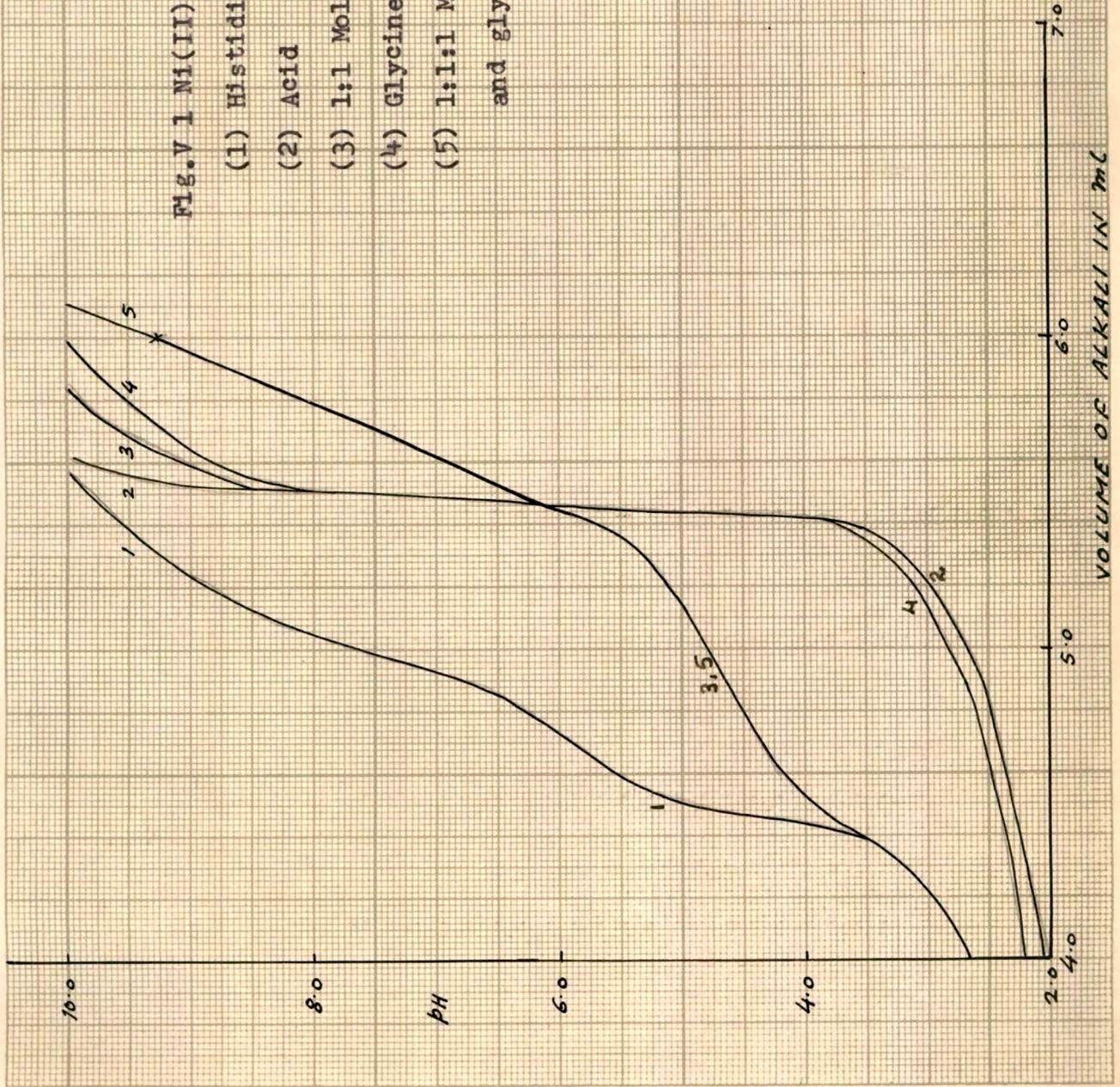


Table V 1.2A

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{Hist}}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.022M$ $T_L^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

α -Alanine		Ni.Hist. α -Alanine	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60
1.00	1.65	1.00	1.70
2.00	1.75	2.00	1.80
3.00	1.95	3.00	2.00
4.00	2.20	4.00	2.65
4.20	2.25	4.20	3.00
4.40	2.30	4.40	3.50
4.60	2.20	4.60	4.20
4.80	2.55	4.80	4.50
5.00	2.75	4.90	4.60
5.10	2.90	5.00	4.75
5.20	3.05	5.10	4.90
5.30	3.30	5.20	5.10
5.35	3.55	5.30	5.30
5.40	3.85	5.35	5.45
5.44	4.20	5.40	5.60
5.46	5.00	5.45	6.00
5.48	6.75	5.50	6.40
5.50	7.50	5.54	6.80
5.52	8.00	5.58	7.10
5.55	8.50	5.62	7.35
5.60	8.90	5.66	7.60
5.65	9.15	5.70	7.80
5.70	9.35	5.75	8.05
5.75	9.50	5.80	8.25
5.80	9.65	5.85	8.50
5.90	9.85	5.90	8.75
5.96	10.00	6.00	9.30

(ppts.)

Fig. V 2 Ni(II), Hist. α -Alanine system-

30°C.

(1) Histidine

(2) Acid

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

(4) α -Alanine

(5) 1:1:1 Molar ratio of Ni(II),
Hist. and α -Alanine.

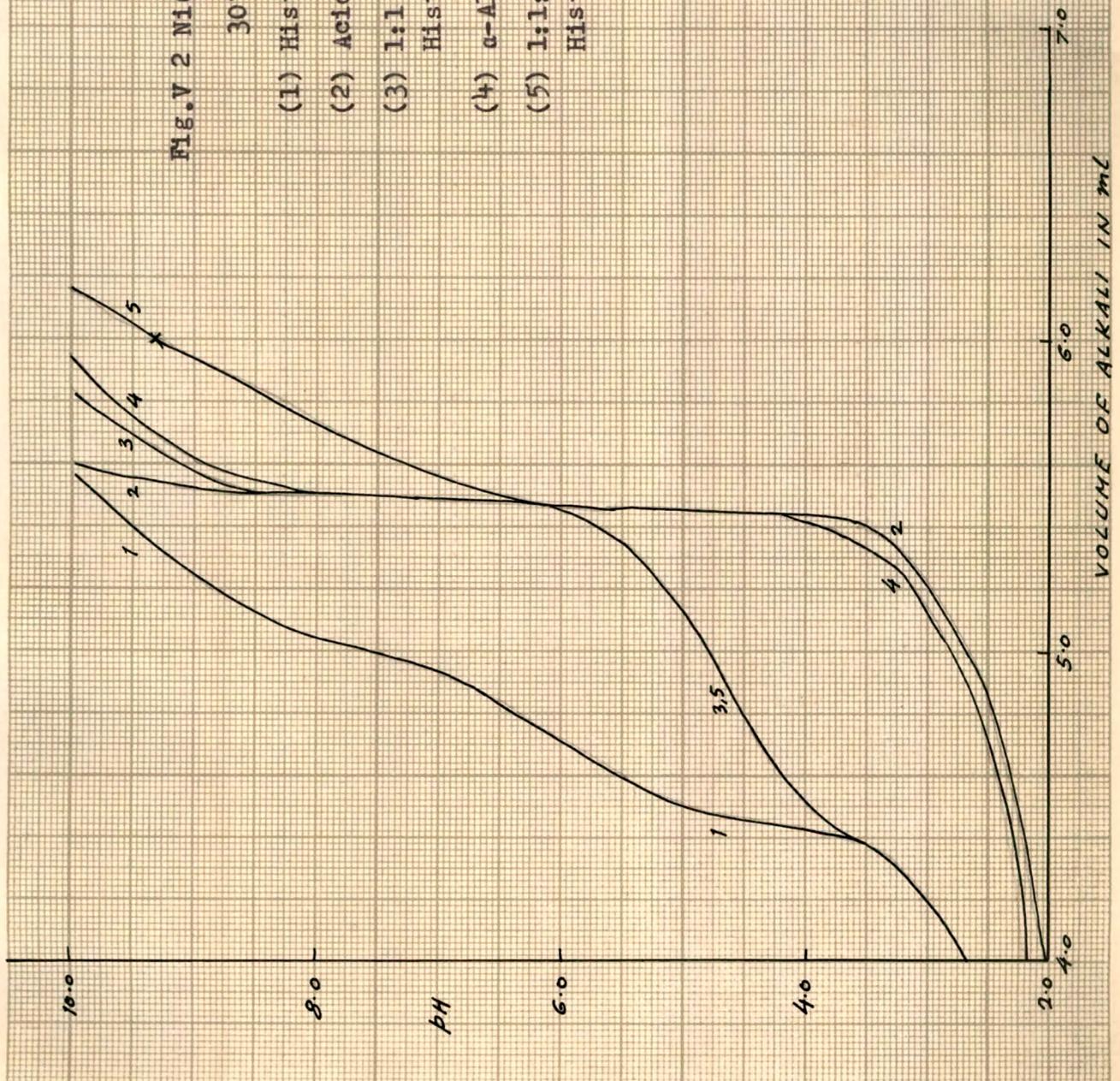


Table V 1.3A

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{Hist}}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.022M$ $T_L^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

Aspartic acid		Ni.Hist.Aspartic acid	
Vol. of alkali (in ml.)	B	Vol. of alkali (in ml.)	B
0.00	1.50	0.00	1.60
1.00	1.65	1.00	1.80
2.00	1.75	2.00	1.90
3.00	1.85	3.00	2.15
4.00	2.10	4.00	2.70
4.40	2.25	4.20	2.90
4.80	2.40	4.40	3.15
5.00	2.60	4.60	3.55
5.10	2.70	4.70	3.75
5.20	2.85	4.80	3.95
5.30	3.00	4.90	4.10
5.40	3.15	5.00	4.25
5.50	3.35	5.20	4.50
5.60	3.55	5.40	4.65
5.70	3.85	5.60	5.00
5.75	4.05	5.70	5.20
5.80	4.25	5.80	5.45
5.85	4.70	5.90	5.80
5.90	5.25	6.00	6.20
5.95	6.25	6.05	6.50
6.00	8.30	6.10	6.80
6.04	8.75	6.15	7.15
6.08	8.95	6.20	7.45
6.10	9.00	6.25	7.90
6.20	9.25	6.30	8.35
6.30	9.50	6.40	9.10
6.50	9.95	6.50	9.55

Fig. V 3 Ni(II).Hist.Aspartic acid system - 30°C.

- (1) Histidine
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), Histidine
- (4) Aspartic acid
- (5) 1:1:1 Molar ratio of Ni(II), Histidine and Aspartic acid.



Table V 1.4A

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{Hist}}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.022M$ $T_L^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

Thioglycollic acid		Ni.Hist.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	1.65
2.00	1.65	2.00	1.75
3.00	1.75	3.00	1.90
4.00	2.05	3.40	2.20
4.20	2.05	3.80	2.40
4.40	2.10	4.00	2.50
4.60	2.15	4.10	2.55
4.80	2.30	4.20	2.65
4.90	2.35	4.30	2.75
5.00	2.45	4.40	2.90
5.10	2.50	4.50	3.05
5.20	2.60	4.60	3.20
5.30	2.70	4.70	3.40
5.40	2.85	4.80	3.55
5.50	3.00	4.90	3.80
5.60	3.15	5.00	4.05
5.70	3.40	5.10	4.20
5.75	3.55	5.20	4.35
5.80	3.70	5.30	4.45
5.85	3.95	5.40	4.60
5.90	4.25	5.50	4.70
5.94	4.65	5.60	4.80
5.98	6.00	5.80	5.15
6.00	7.00	5.90	5.40
6.04	8.25	6.00	5.65
6.08	8.75	6.04	6.05
6.10	9.00	6.08	6.30
6.15	9.40	6.12	6.55
6.20	9.60	6.16	6.80
6.30	10.00	6.20	7.10
		6.24	7.50
		6.28	8.00
		6.30	8.50
		6.35	9.30
		6.40	9.70
		6.48	10.00

Fig V 4 Ni(II), Hist. thioglycollic acid system - 30°C.

- (1) Histidine
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), Histidine
- (4) Thioglycollic acid
- (5) 1:1:1 Molar ratio of Ni(II), Histidine and thioglycollic acid.

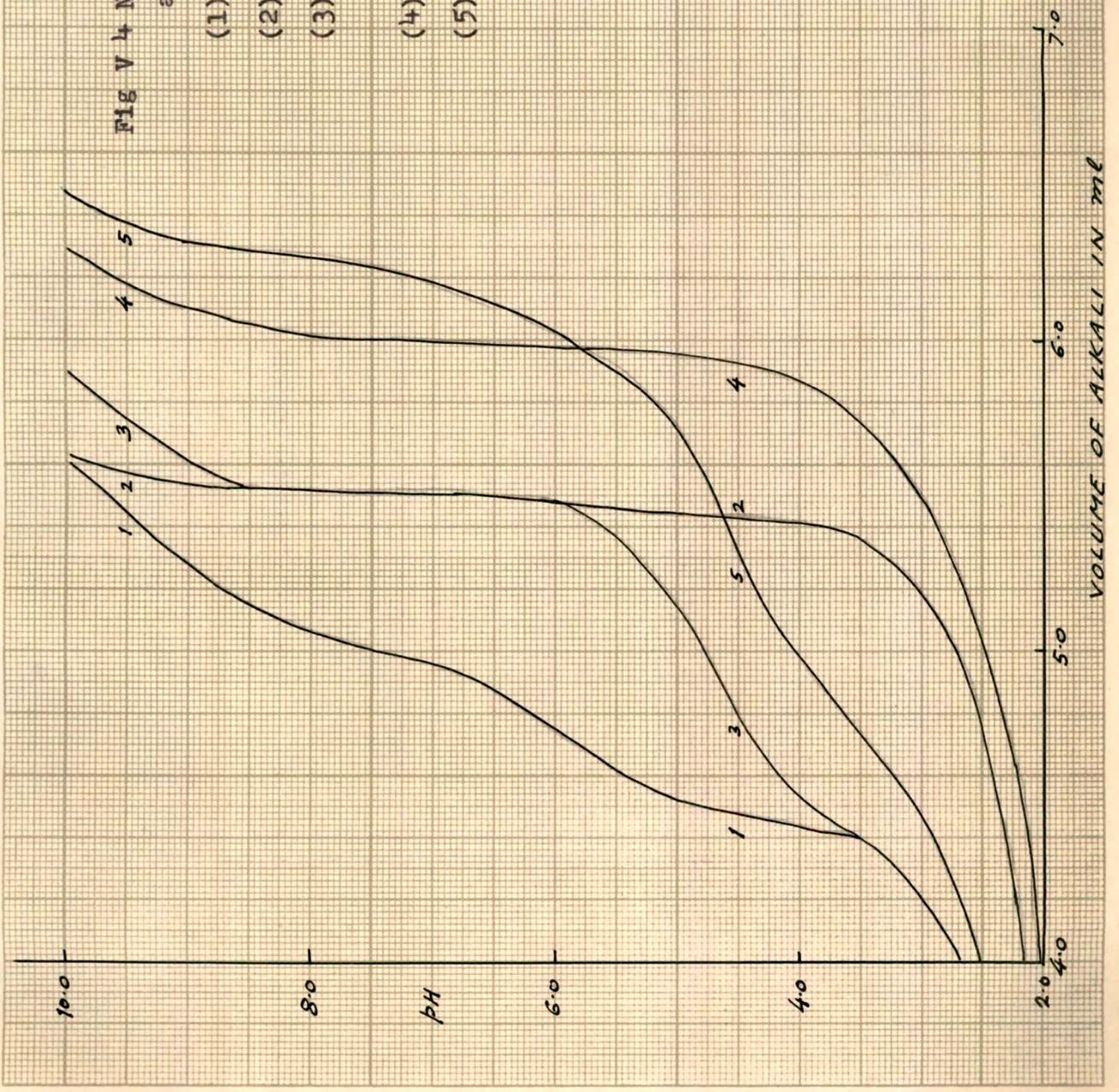


Table V 1.5A

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{Hist}}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.022M$ $T_L^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

Thiolactic acid		Ni.Hist.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	1.70
2.00	1.75	2.00	1.85
3.00	1.80	3.00	2.00
4.00	2.10	4.00	2.55
4.20	2.15	4.20	2.70
4.40	2.20	4.40	2.90
4.60	2.30	4.60	3.20
4.80	2.40	4.80	3.60
4.90	2.45	5.00	4.00
5.00	2.55	5.10	4.15
5.10	2.65	5.20	4.30
5.20	2.75	5.30	4.45
5.30	2.85	5.40	4.55
5.40	3.00	5.50	4.65
5.50	3.15	5.60	4.80
5.60	3.30	5.70	4.95
5.70	3.55	5.88	5.05
5.80	3.85	5.90	5.30
5.85	4.05	6.00	5.60
5.90	4.25	6.04	5.85
5.95	4.60	6.08	6.00
5.98	5.00	6.12	6.20
6.00	5.50	6.16	6.35
6.02	7.40	6.20	6.55
6.05	8.00	6.25	6.80
6.08	8.50	6.30	7.05
6.12	8.90	6.35	7.40
6.16	9.25	6.40	7.75
6.20	9.45	6.44	8.25
6.32	10.00	6.46	8.50
		6.48	9.15
		6.50	9.50
		6.58	10.00

Fig. V 5 Ni(II).Hist.Thioloactic acid system - 30°C.

- (1) Histidine
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), Histidine
- (4) Thioloactic acid
- (5) 1:1:1 Molar ratio of Ni(II), Hist. and thioloactic acid.

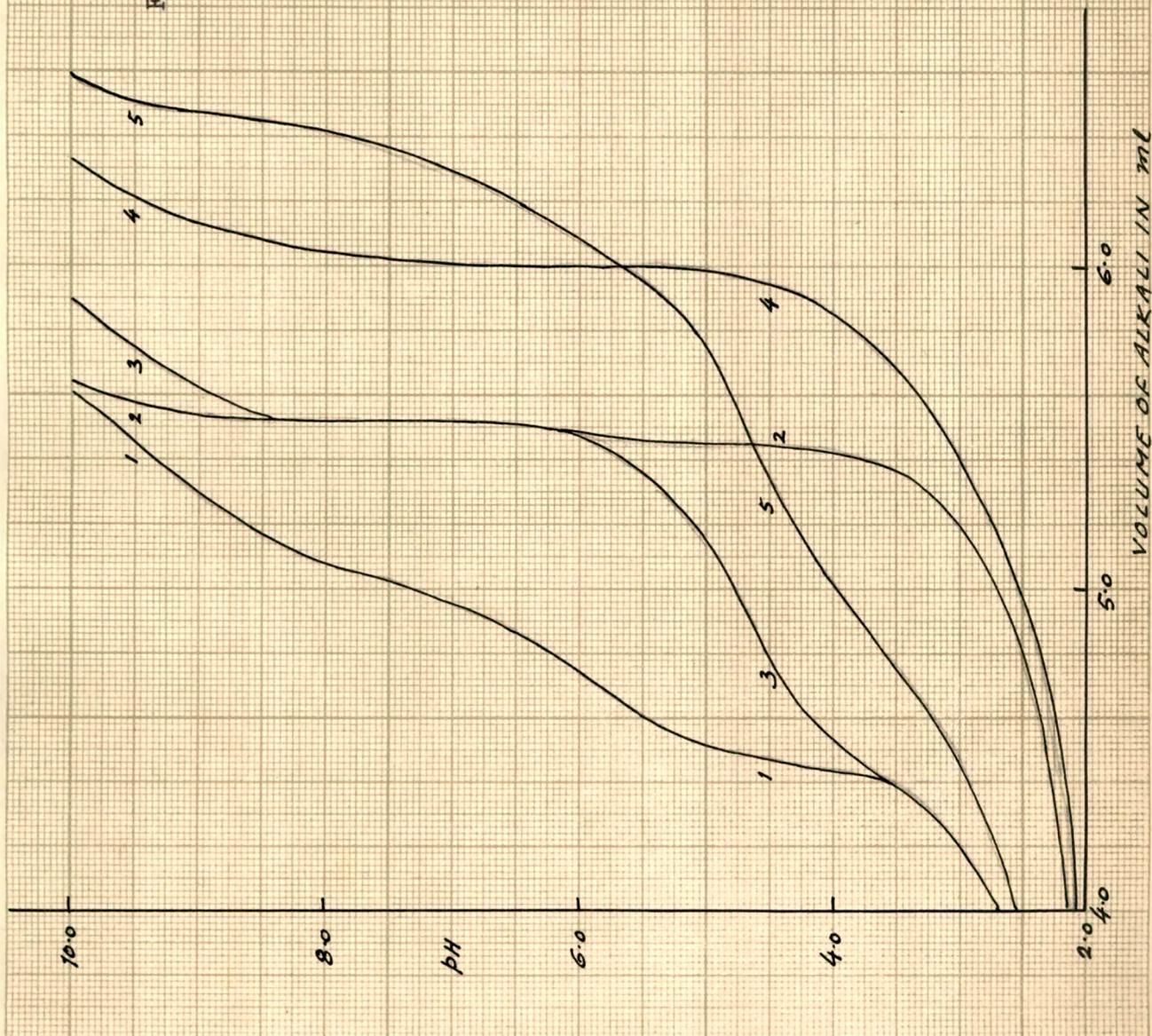


Table V 1.1B

N = 0.2M V° = 50 ml. T_M = 0.002M T_M = 0.002M
 E° = 0.02M *E° = 0.024M T_L = 30°C. t = 30°C.

* Perchloric acid I MDA NI. I MDA * Glycine NI. J MDA. Glycine

Vol. of alkali (in ml.)	B	Vol. of alkali (in ml.)	B						
0.00	1.50	0.00	1.50	0.00	1.55	0.00	1.55	0.00	1.55
1.00	1.60	1.00	1.60	1.00	1.65	1.00	1.60	1.00	1.65
2.00	1.65	2.00	1.75	2.00	1.80	2.00	1.70	2.00	1.80
3.00	1.80	3.00	1.90	3.00	1.95	3.00	1.95	3.00	1.95
4.00	2.05	4.00	2.15	4.00	2.15	4.00	2.05	4.00	2.15
4.20	2.10	4.20	2.20	4.20	2.20	4.20	2.10	4.20	2.25
4.40	2.20	4.40	2.25	4.40	2.35	4.40	2.25	4.40	2.50
4.60	2.25	4.60	2.30	4.60	2.50	4.60	2.40	4.60	2.65
4.80	2.30	4.80	2.35	4.80	2.70	4.80	2.45	4.80	2.90
5.00	2.40	5.00	2.45	5.00	2.80	5.00	2.55	5.00	3.25
5.10	2.45	5.10	2.50	5.10	2.95	5.10	2.70	5.10	3.90
5.20	2.50	5.20	2.55	5.20	3.05	5.20	2.95	5.20	4.35
5.30	2.60	5.30	2.60	5.30	3.25	5.30	3.40	5.30	5.00
5.40	2.70	5.40	2.70	5.40	3.50	5.40	3.75	5.40	5.30
5.50	2.80	5.50	2.80	5.50	3.90	5.50	4.35	5.50	5.65
5.60	2.90	5.60	2.90	5.60	4.40	5.60	5.00	5.60	6.35
5.70	3.00	5.70	3.05	5.70	4.95	5.70	5.98	5.70	6.60
5.80	3.10	5.80	3.35	5.80	5.25	5.80	6.00	5.80	6.90
5.90	3.20	5.90	3.55	5.90	5.55	5.90	6.02	5.90	7.15
6.00	3.30	6.00	3.95	6.00	6.00	6.00	6.04	6.00	7.35
6.10	3.40	6.10	4.50	6.10	6.00	6.10	6.06	6.10	7.55
6.20	3.50	6.20	4.80	6.20	7.00	6.20	6.08	6.20	7.80
6.30	3.60	6.30	5.00	6.30	7.00	6.30	6.10	6.30	8.05
6.40	3.70	6.40	5.25	6.40	8.00	6.40	6.15	6.40	8.25
6.50	3.80	6.50	5.50	6.50	8.10	6.50	6.30	6.50	8.75
6.60	3.90	6.60	5.65	6.60	9.00	6.60	6.54	6.60	9.35
6.70	4.00	6.70	5.80	6.70	9.10	6.70	10.00	6.70	(ppts.)

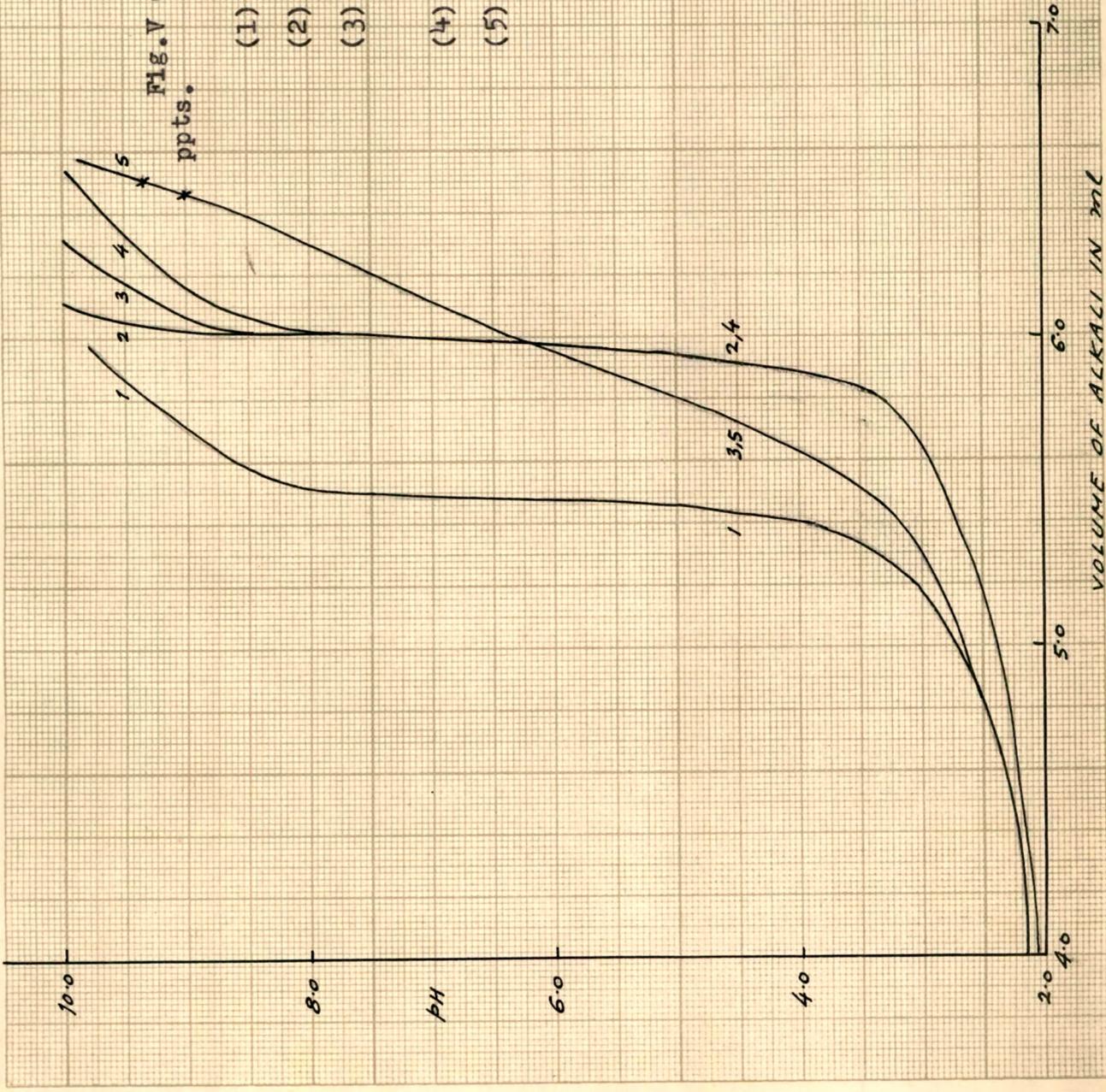


Fig. V 6 Ni(II).IMDA.glycine system-
30°C.

- (1) IMDA
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II),
IMDA
- (4) Glycine
- (5) 1:1:1 Molar ratio of Ni(II),
IMDA, glycine.

Table V 1.2B

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{I}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.024M$ $T_L^{\circ} = 0.002M$ $t = 30^{\circ}C.$

α -Alanine		Ni.IMDA. α -Alanine	
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	1.75
2.00	1.85	2.00	1.85
3.00	1.95	3.00	1.95
4.00	2.05	4.00	2.15
4.40	2.20	4.40	2.25
4.80	2.30	4.80	2.50
5.00	2.40	5.00	2.70
5.20	2.55	5.20	2.95
5.40	2.70	5.40	3.25
5.60	2.95	5.60	3.90
5.70	3.10	5.70	4.40
5.80	3.40	5.80	4.95
5.84	3.65	5.85	5.25
5.88	4.00	5.90	5.55
5.92	4.50	5.95	6.00
5.96	5.50	5.98	6.50
5.98	6.50	6.00	6.60
6.00	7.50	6.04	6.95
6.04	8.65	6.08	7.25
6.08	9.05	6.12	7.50
6.10	9.15	6.16	7.75
6.15	9.30	6.20	7.95
6.20	9.45	6.25	8.20
6.30	9.75	6.30	8.45
6.40	10.00		(ppts.)

Fig. V 7 Ni(II).IMDA. α -Alanine
system - 30°C.

turbidity

(1) IMDA

(2) Acid

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

(4) α -Alanine

(5) 1:1:1 Molar ratio of Ni(II),
IMDA and α -alanine.

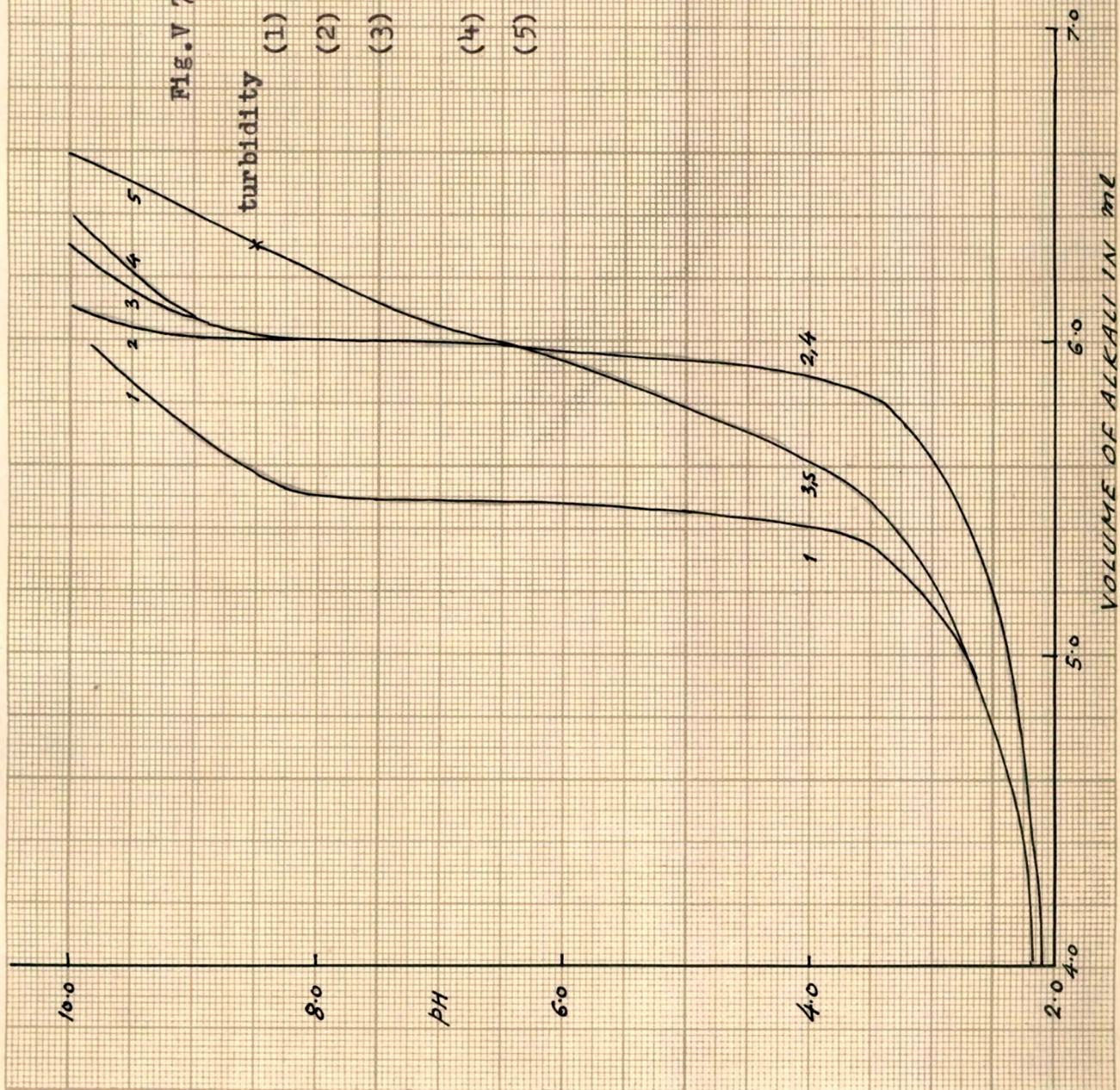


Table V 1.3B

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{IMDA}}^{\circ} = 0.002M$ $T_{\text{M}}^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.024M$ $T_{\text{L}}^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

Aspartic acid		Ni.IMDA.Aspartic acid	
Vol. of alkali. (in ml.)	B	Vol. of alkali (in ml.)	B
0.00	1.50	0.00	1.60
1.00	1.65	1.00	1.75
2.00	1.75	2.00	1.85
3.00	1.80	3.00	2.05
4.00	2.10	4.00	2.30
4.40	2.15	4.40	2.45
4.80	2.25	4.80	2.60
5.00	2.30	5.00	2.75
5.20	2.35	5.20	2.90
5.40	2.45	5.40	3.10
5.60	2.70	5.60	3.35
5.70	2.85	5.80	3.70
5.80	3.00	6.00	4.15
5.90	3.20	6.10	4.45
6.00	3.35	6.20	4.80
6.10	3.55	6.25	5.00
6.20	3.85	6.30	5.15
6.30	4.25	6.35	5.35
6.35	4.65	6.40	5.60
6.40	5.10	6.45	5.80
6.45	6.00	6.50	6.10
6.50	8.40	6.55	6.35
6.55	8.75	6.60	6.65
6.60	8.95	6.65	6.95
6.65	9.15	6.70	7.20
6.70	9.25	6.75	7.55
6.80	9.50	6.80	7.90
6.90	9.75	6.85	8.35
		6.90	8.70
		6.95	9.10
		7.00	9.40

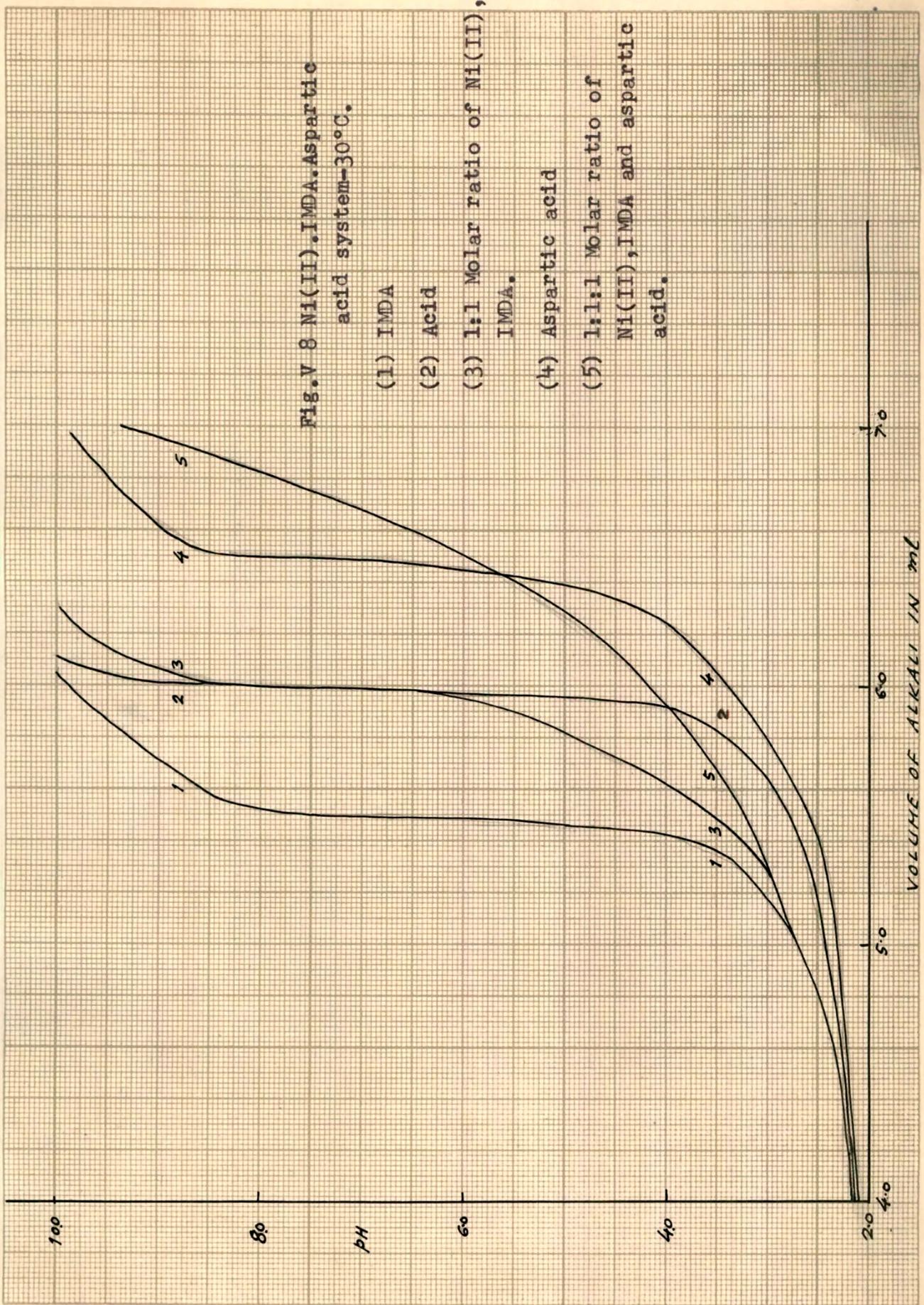


Fig. V 8 Ni(II).IMDA.Aspartic acid system-30°C.

- (1) IMDA
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), IMDA.
- (4) Aspartic acid
- (5) 1:1:1 Molar ratio of Ni(II),IMDA and aspartic acid.

Table V 1.4B

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{IMDA}}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.024M$ $T_L^{\circ} = 0.002M$ $t = 30^{\circ}C.$

Thioglycollic acid		Ni,IMDA,Thioglycollic acid	
Vol. of alkali (in ml.)	B	Vol. of alkali (in ml.)	B
0.00	1.60	0.00	1.60
1.00	1.65	1.00	1.65
2.00	1.70	2.00	1.75
3.00	1.80	3.00	1.85
4.00	2.10	4.00	2.15
4.40	2.20	4.40	2.25
4.60	2.25	4.80	2.50
4.80	2.30	5.00	2.75
5.00	2.40	5.20	2.90
5.20	2.55	5.40	3.10
5.40	2.65	5.60	3.35
5.60	2.85	5.70	3.50
5.70	2.95	5.80	3.70
5.80	3.05	5.90	3.85
5.85	3.10	6.00	4.05
5.90	3.15	6.10	4.35
6.00	3.25	6.20	4.70
6.10	3.45	6.30	5.10
6.20	3.65	6.40	5.50
6.30	3.95	6.46	6.00
6.35	4.15	6.50	6.10
6.40	4.40	6.54	6.40
6.44	5.00	6.58	6.65
6.48	6.25	6.62	6.95
6.50	7.00	6.66	7.15
6.52	8.00	6.70	7.45
6.54	9.50	6.75	7.75
6.58	9.00	6.78	8.00
6.60	9.25	6.80	8.30
6.65	9.50	6.84	9.00
6.70	9.70	6.88	9.50
6.80	10.00	6.98	10.00

Fig. V 9 Ni(II), IMDA, Thio-
glycollic acid system-
30°C.

- (1) IMDA
- (2) Acid
- (3) 1:1 Molar ratio of
Ni(II), IMDA
- (4) Thioglycollic acid
- (5) 1:1:1 Molar ratio of
Ni(II), IMDA and thio-
glycollic acid.

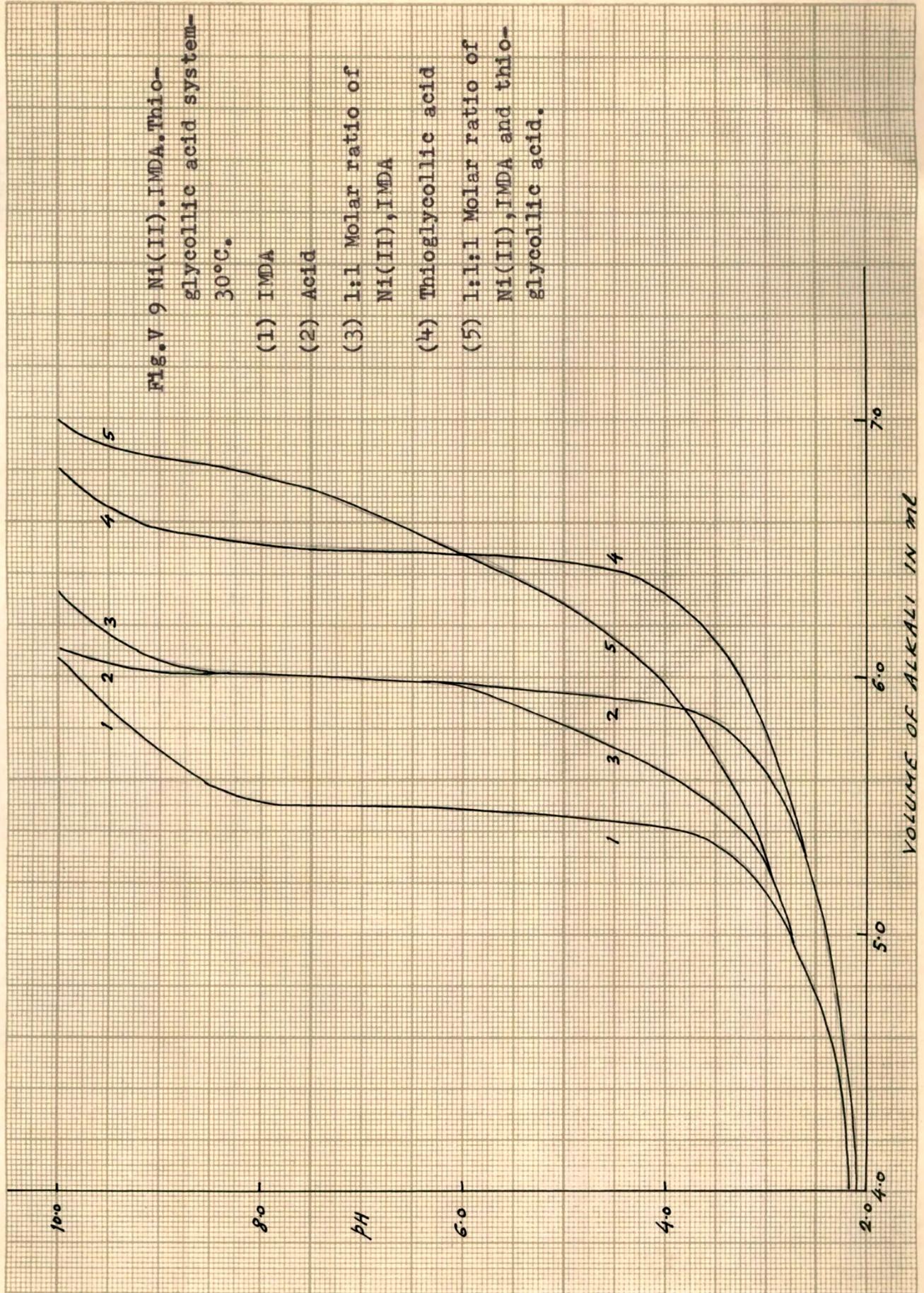


Table V 1.5B

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{IMDA}}^{\circ} = 0.002M$ $T_{\text{M}}^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.024M$ $T_{\text{L}}^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

Thiolactic acid		Ni.IMDA.Thiolactic acid	
Vol. of alkali (in ml.)	B	Vol. of alkali (in ml.)	B
0.00	1.55	0.00	1.60
1.00	1.65	1.00	1.70
2.00	1.75	2.00	1.85
3.00	1.85	3.00	1.95
4.00	2.00	4.00	2.20
4.20	2.05	4.40	2.25
4.40	2.10	4.80	2.50
4.80	2.20	5.00	2.65
5.00	2.30	5.20	2.80
5.20	2.40	5.40	2.95
5.40	2.50	5.60	3.20
5.50	2.55	5.70	3.30
5.60	2.65	5.80	3.45
5.70	2.75	5.90	3.65
5.80	2.85	6.00	3.95
5.90	3.00	6.10	4.30
6.00	3.15	6.20	4.70
6.10	3.35	6.25	4.95
6.20	3.60	6.30	5.15
6.25	3.75	6.35	5.35
6.30	3.95	6.40	5.55
6.35	4.15	6.45	5.80
6.40	4.55	6.50	6.05
6.45	5.50	6.54	6.30
6.48	6.50	6.58	6.45
6.50	7.50	6.62	6.65
6.52	8.50	6.66	6.80
6.55	9.00	6.70	7.00
6.60	9.35	6.75	7.40
6.65	9.60	6.80	7.70
6.70	9.75	6.90	8.55
6.78	10.00	6.95	9.50
		7.00	10.00

Fig. V 10 Ni(II), IMDA, Thio-
lactic acid system-
30°C.

- (1) IMDA
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), IMDA.
- (4) Thiolactic acid
- (5) 1:1:1 Molar ratio of Ni(II), IMDA and thiolactic acid.

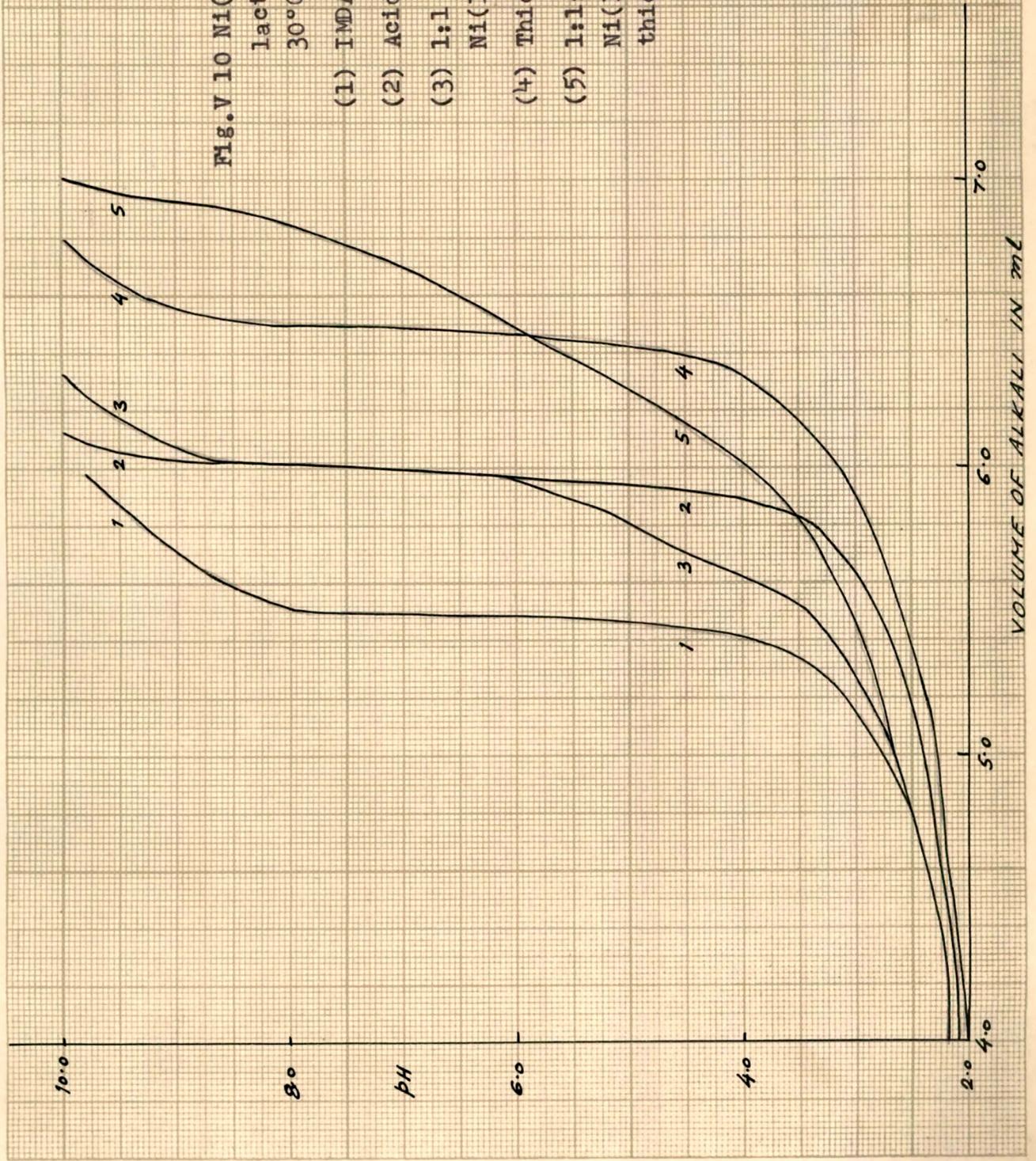


Table V 1.6B

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{\text{IMDA}}^{\circ} = 0.002M$ $T_{\text{M}}^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.024M$ $T_{\text{L}}^{\circ} = 0.002M$ $t = 30^{\circ}\text{C.}$

Thiomalic acid		Ni.IMDA.Thiomalic acid	
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	1.90	2.00	1.85
3.00	1.90	3.00	1.95
4.00	2.00	4.00	2.20
4.40	2.10	4.40	2.25
4.80	2.20	4.80	2.45
5.00	2.25	5.00	2.55
5.20	2.35	5.20	2.65
5.40	2.50	5.40	2.80
5.60	2.65	5.60	3.05
5.80	2.90	5.70	3.15
6.00	3.00	5.80	3.30
6.10	3.10	5.90	3.40
6.20	3.25	6.00	3.55
6.30	3.45	6.10	3.70
6.40	3.70	6.20	3.90
6.50	3.90	6.30	4.10
6.60	4.15	6.40	4.30
6.70	4.45	6.50	4.50
6.75	4.60	6.60	4.80
6.80	4.80	6.70	5.05
6.85	5.00	6.80	5.35
6.90	5.30	6.90	5.65
6.94	5.65	7.00	6.05
6.98	6.25	7.04	6.30
7.00	6.30	7.08	6.50
7.02	7.75	7.12	6.75
7.04	8.50	7.16	7.00
7.06	8.75	7.20	7.25
7.10	9.20	7.25	7.50
7.15	9.55	7.30	7.90
7.20	9.75	7.38	8.50
7.30	10.00	7.42	9.05
		7.46	9.65
		7.50	10.00

Fig V 1:1 Ni(II).IMDA.
Thiomalic acid
system-30°C.

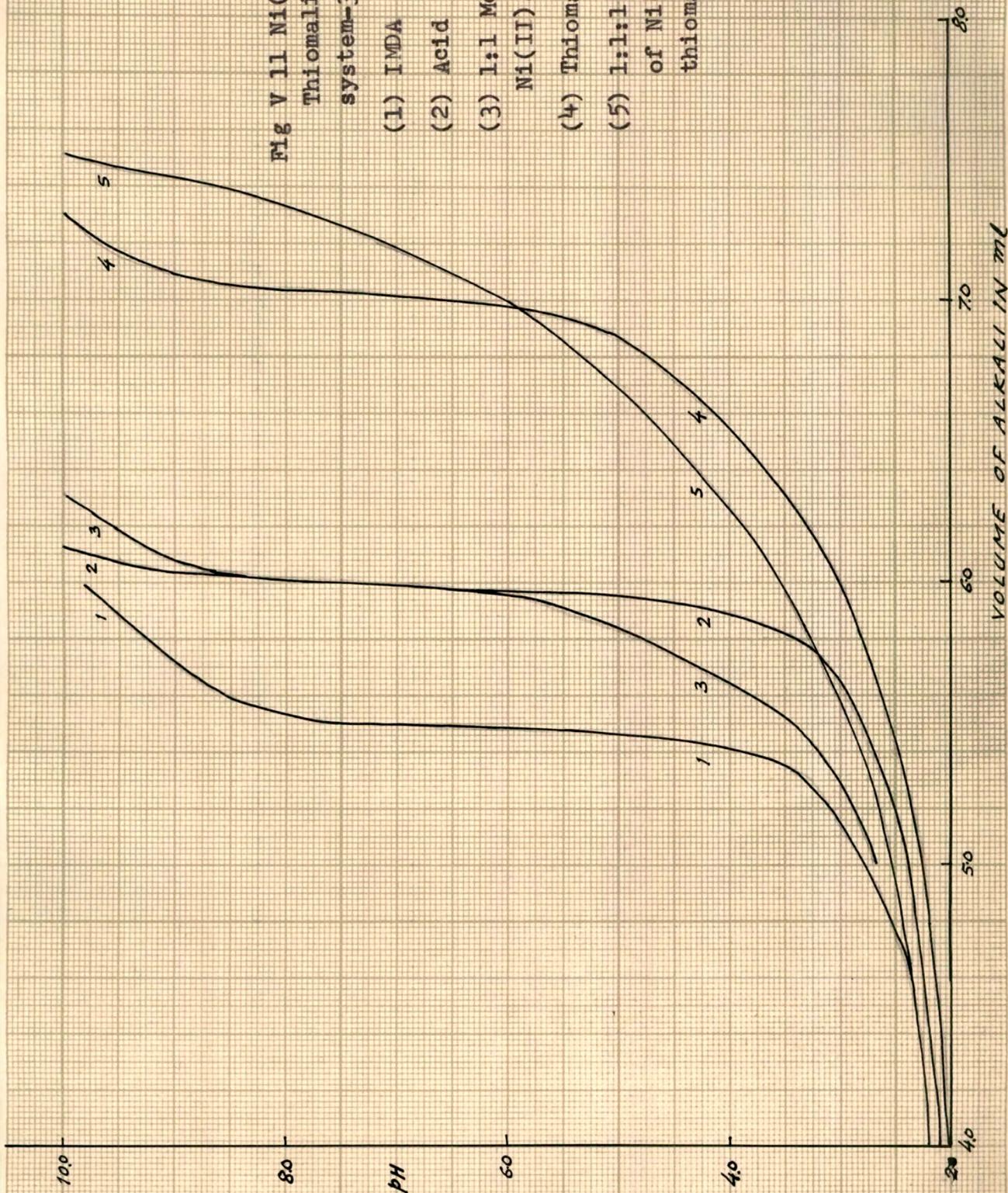
(1) IMDA

(2) Acid

(3) 1:1 Molar ratio of
Ni(II), IMDA.

(4) Thiomalic acid

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



VOLUME OF ALKALI IN ml

Table V 1.3C

N = 0.2M		V° = 50 ml.		H = 0.2M		T _{NTA} = 0.002M		T _M = 0.002M	
E° = 0.02M		*E° = 0.026M				T _L = 0.002M		t = 30°C.	
* Perchloric acid		NTA		Ni.NTA		Aspartic acid		Ni.NTA.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	1.50	0.00	1.50	0.00	1.50	0.00	1.50
1.00	1.55	1.00	1.60	1.00	1.60	1.00	1.60	1.00	1.65
2.00	1.65	2.00	1.70	2.00	1.70	2.00	1.65	2.00	1.75
3.00	1.70	3.00	1.85	3.00	1.85	3.00	1.75	3.00	1.95
4.00	1.85	4.00	2.05	4.00	2.05	4.00	1.90	4.00	2.00
4.40	1.95	4.40	2.15	5.00	2.15	4.40	2.00	4.40	2.10
4.80	2.05	4.80	2.30	5.20	2.30	4.80	2.10	4.80	2.20
5.00	2.10	5.00	2.40	5.40	2.40	5.00	2.15	5.00	2.25
5.20	2.20	5.20	2.55	5.60	2.55	5.20	2.20	5.20	2.30
5.40	2.25	5.40	2.60	5.80	2.60	5.40	2.25	5.40	2.35
5.60	2.35	5.60	2.70	6.00	2.70	5.60	2.30	5.60	2.45
5.70	2.40	5.70	2.80	6.10	2.80	5.80	2.40	5.80	2.55
5.80	2.45	5.80	2.95	6.20	2.95	6.00	2.60	6.00	2.70
5.90	2.50	5.90	3.15	6.30	3.15	6.20	2.85	6.20	2.90
6.00	2.60	6.00	3.45	6.35	3.35	6.40	3.15	6.40	3.15
6.10	2.65	6.10	3.25	6.40	3.65	6.50	3.35	6.50	3.35
6.20	2.85	6.20	4.65	6.44	4.00	6.60	3.55	6.60	3.55
6.30	3.05	6.30	4.75	6.48	4.55	6.70	3.80	6.70	3.80
6.35	3.20	6.35	6.15	6.50	4.80	6.80	4.30	6.80	4.30
6.40	3.35	6.40	7.75	6.52	8.00	6.85	4.65	6.85	4.65
6.44	3.55	6.44	8.15	6.55	8.45	6.90	5.30	6.90	5.30
6.48	4.00	6.48	8.40	6.58	8.70	6.95	6.30	6.95	6.30
6.50	4.50	6.50	8.70	6.60	8.90	7.00	6.35	7.00	6.35
6.52	7.00	6.52	8.90	6.65	9.35	7.04	8.70	7.05	7.55

Table V 1.3C (contd.)

6.54	8.50	6.20	9.10	6.70	9.75	7.08	8.90	7.08	7.75
6.56	9.25	6.30	9.50	6.74	10.00	7.10	8.95	7.10	7.85
6.58	9.60	6.40	9.85			7.15	9.10	7.15	8.05
6.60	10.00	6.44	10.00			7.20	9.25	7.20	8.25
						7.30	9.50	7.25	8.50
						7.40	9.75	7.30	8.70
								7.40	9.05
								7.50	9.45
								7.60	9.80

Fig. V 12 Ni(II).NTA.Aspartic acid system - 30°C.

- (1) NTA
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), NTA
- (4) Aspartic acid
- (5) 1:1:1 Molar ratio of Ni(II), NTA, Aspartic acid.

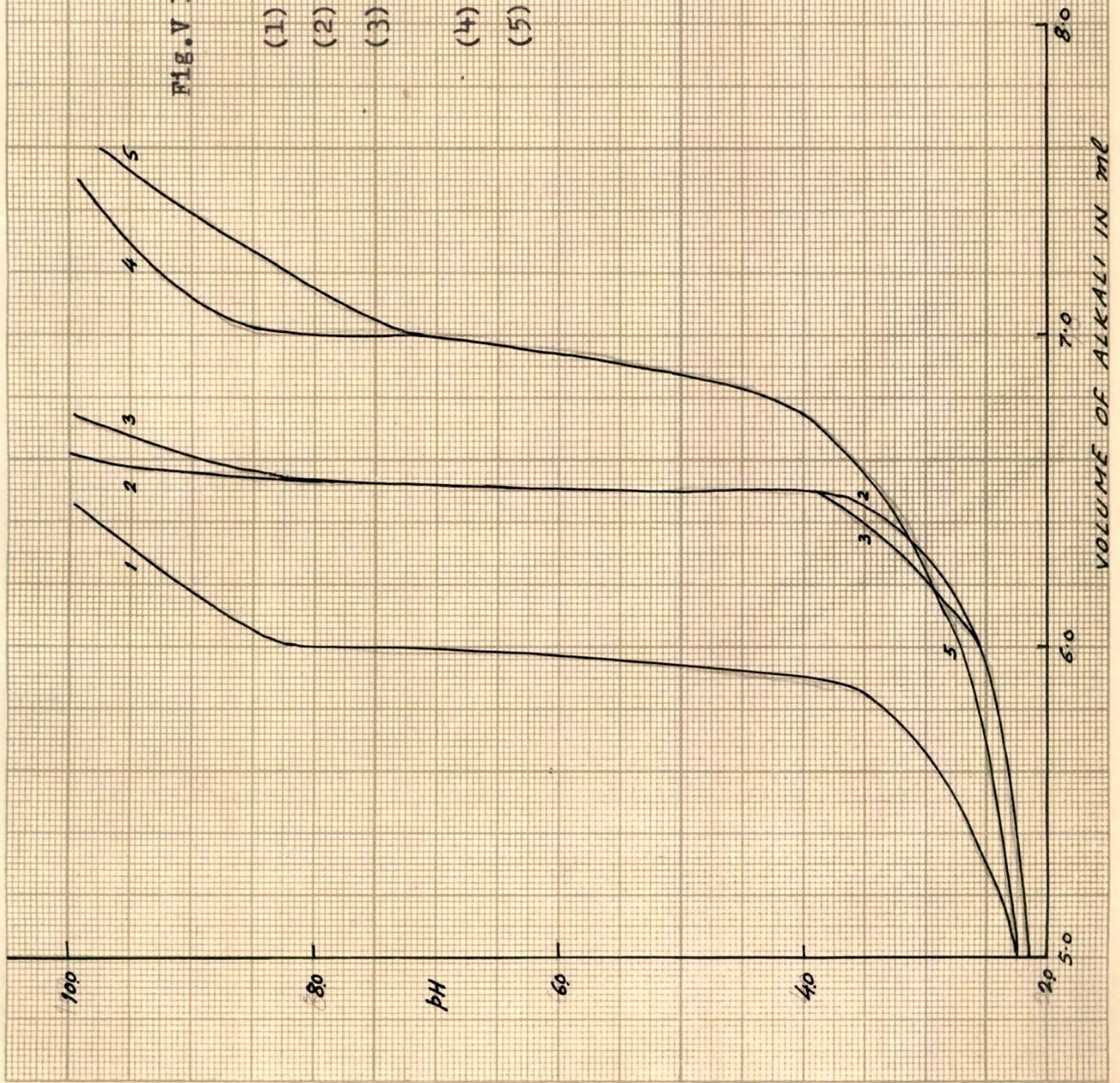


Table V 1.4C

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{NTA}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.026M$ $T_I^{\circ} = 0.002M$ $t = 30^{\circ}C.$

Thioglycollic acid		Ni.NTA.Thioglycollic acid	
Vol. of alkali (in ml.)	B	Vol. of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.55	1.00	1.55
2.00	1.60	2.00	1.60
3.00	1.70	3.00	1.70
4.00	1.85	4.00	1.85
5.00	2.05	5.00	2.05
5.20	2.25	5.40	2.25
5.60	2.35	5.60	2.35
5.70	2.40	5.70	2.40
5.90	2.45	5.90	2.45
6.00	2.50	6.00	2.50
6.10	2.60	6.10	2.60
6.20	2.70	6.20	2.70
6.30	2.80	6.30	2.80
6.40	2.85	6.40	2.85
6.50	3.05	6.50	3.05
6.60	3.20	6.60	3.20
6.70	3.40	6.70	3.40
6.80	3.70	6.80	3.70
6.85	3.90	6.85	3.90
6.90	4.15	6.90	4.15
6.94	4.40	6.94	4.40
6.98	5.50	6.98	5.50
7.00	6.50	7.00	5.75
7.02	8.00	7.04	6.10
7.04	8.40	7.08	6.50
7.06	8.70	7.12	6.85
7.08	9.00	7.16	7.25
7.10	9.20	7.20	7.70
7.20	9.70	7.24	8.10
7.28	10.00	7.28	8.50
		7.32	8.85
		7.36	9.20
		7.40	9.45
		7.46	10.00

Fig. V 13 Ni(II), NTA, Thioglycollic acid system - 30°C.

- (1) NTA
- (2) Acid
- (3) 1:1 Molar ratio of Ni(II), NTA
- (4) Thioglycollic acid
- (5) 1:1:1 Molar ratio of Ni(II), NTA and Thioglycollic acid.

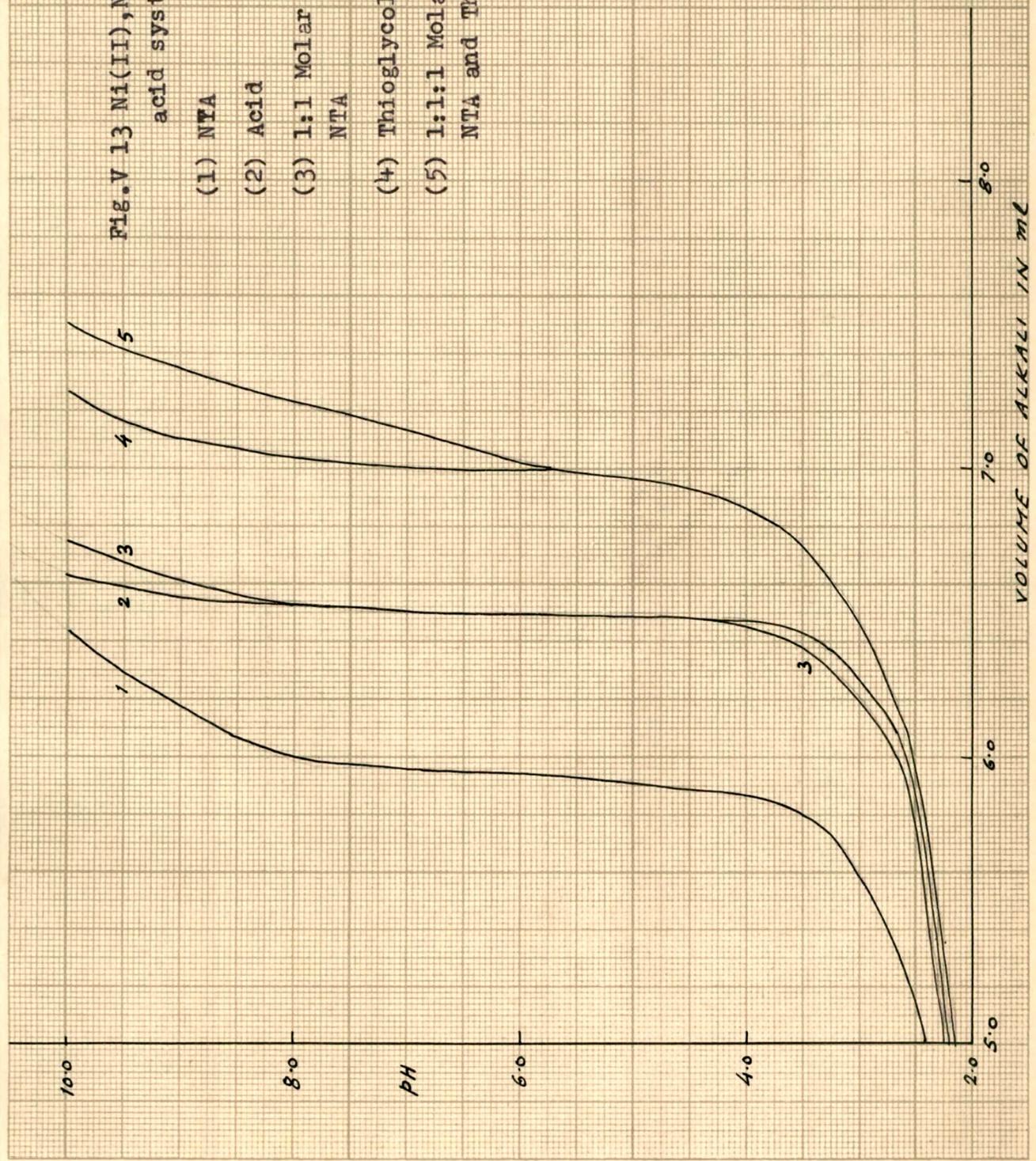


Table V 1.5C

$N = 0.2M$ $V^{\circ} = 50 \text{ ml.}$ $\mu = 0.2M$ $T_{NTA}^{\circ} = 0.002M$ $T_M^{\circ} = 0.002M$
 $E^{\circ} = 0.02M$ $*E^{\circ} = 0.026M$ $T_I^{\circ} = 0.002M$ $t = 30^{\circ}C.$

Thiolactic acid		Ni.NTA.Thiolactic acid	
Vol. of alkali (in ml.)	B	Vol. of alkali (in ml.)	B
0.00	1.50	0.00	1.50
1.00	1.55	1.00	1.55
2.00	1.60	2.00	1.60
3.00	1.70	3.00	1.70
4.00	1.85	4.00	1.95
5.00	2.10	5.00	2.10
5.20	2.15	5.20	2.15
5.40	2.20	5.40	2.20
5.60	2.25	5.60	2.25
5.80	2.35	5.80	2.35
6.00	2.50	6.00	2.50
6.10	2.55	6.10	2.55
6.20	2.65	6.20	2.65
6.30	2.80	6.30	2.80
6.40	2.90	6.40	2.90
6.50	3.10	6.50	3.10
6.60	3.25	6.60	3.25
6.70	3.50	6.70	3.50
6.80	3.75	6.80	3.75
6.85	3.95	6.85	3.95
6.90	4.25	6.90	4.25
6.94	4.50	6.94	4.50
6.98	5.25	6.98	5.25
7.00	6.00	7.00	5.50
7.02	7.50	7.04	5.75
7.04	8.25	7.08	6.15
7.08	9.00	7.10	6.30
7.10	9.20	7.14	6.60
7.15	9.55	7.18	7.00
7.20	9.75	7.20	7.20
7.30	10.00	7.24	8.00
		7.28	8.50
		7.32	8.80
		7.36	9.00
		7.40	9.25
		7.52	10.00

Fig V 14 Ni(II).NTA.Thioloactic acid system - 30°C.

(1) NTA

(2) Acid

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

(4) Thioloactic acid

(5) 1:1:1 Molar ratio of Ni(II), NTA and Thioloactic acid.

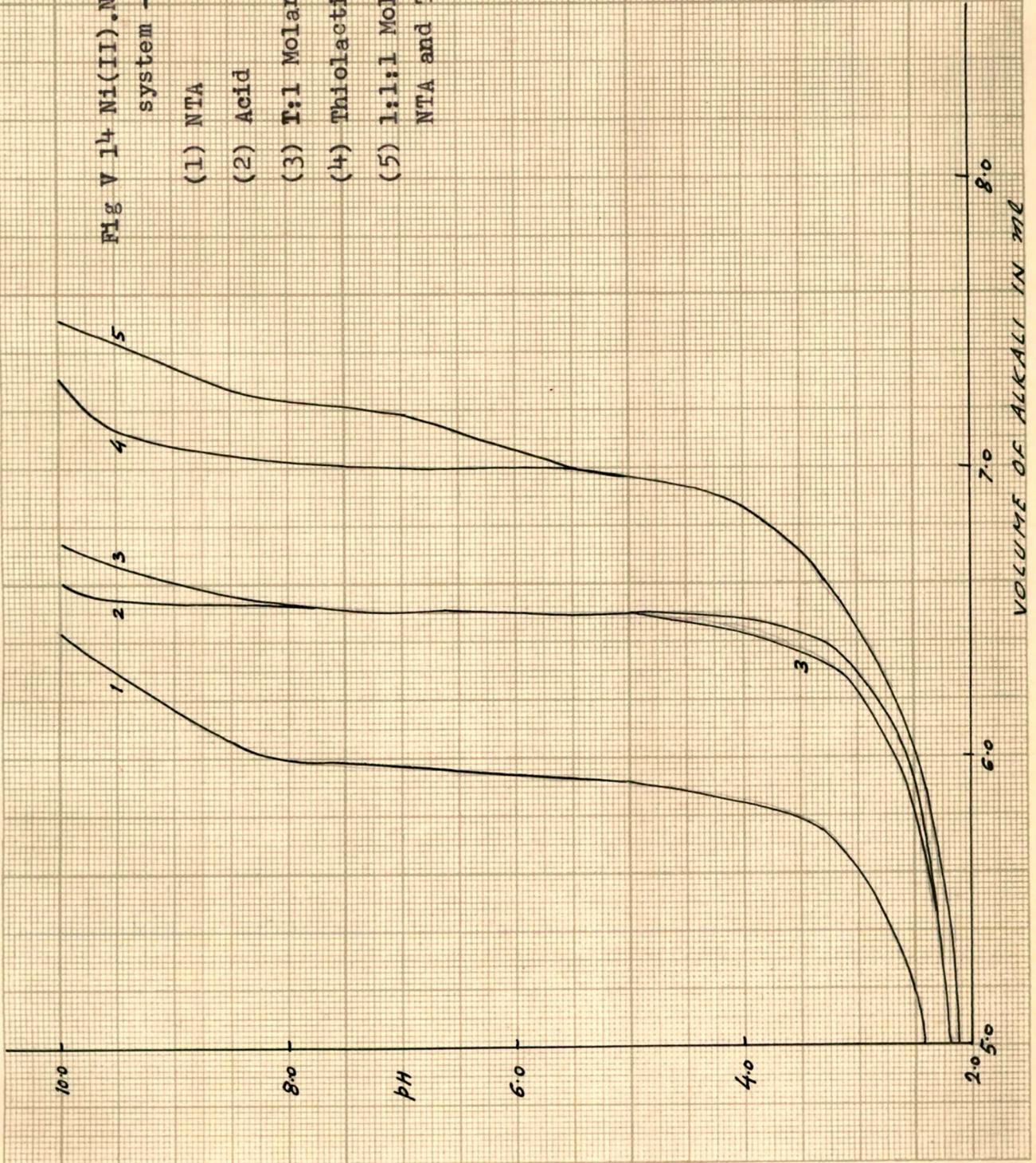


Table V 2.1A

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

R	\bar{n}_H	V''	V'''	V'''-V''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
7.25	1.00 ₀	5.50	5.66	0.16	0.32 ₀	0.32 ₇	5.24 ₃	4.91 ₆
7.30	1.00 ₀	5.50	5.67	0.17	0.34 ₀	0.28 ₈	5.20 ₆	4.91 ₈
7.35	1.00 ₀	5.50	5.68	0.18	0.36 ₀	0.25 ₀	5.17 ₀	4.92 ₀
7.40	1.00 ₀	5.50	5.69	0.19	0.38 ₀	0.21 ₃	5.13 ₃	4.92 ₀
7.45	1.00 ₀	5.50	5.70	0.20	0.40 ₀	0.17 ₆	5.09 ₈	4.92 ₂
7.55	1.00 ₀	5.50	5.71	0.21	0.42 ₀	0.14 ₀	5.01 ₃	4.87 ₃
7.60	1.00 ₀	5.50	5.72	0.22	0.44 ₀	0.10 ₅	4.97 ₈	4.87 ₃
7.65	1.00 ₀	5.50	5.73	0.23	0.46 ₀	0.07 ₀	4.94 ₄	4.87 ₄
7.70	1.00 ₀	5.50	5.74	0.24	0.48 ₀	0.03 ₅	4.83 ₀	4.87 ₅
7.75	0.99 ₆	5.50	5.75	0.25	0.50 ₀	0.00 ₀	4.87 ₇	4.87 ₇

$$\log K_{MAL} = 4.89 \pm 0.02$$

Table V 2.2A

R, \bar{n}_H , \bar{n} , $\log(1-\bar{n})/\bar{n}$, pL and pL- $\log(1-\bar{n})/\bar{n}$ data of Ni.Histidine.
 α -Alanine system - 30°C.

R	\bar{n}_H	V''	V'''	V'''-V''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
7.65	0.96 ₆	5.50	5.66	0.16	0.32 ₁	0.32 ₅	4.97 ₃	4.64 ₈
7.70	0.99 ₂	5.50	5.67	0.17	0.34 ₂	0.28 ₄	4.94 ₆	4.65 ₂
7.75	0.99 ₂	5.51	5.69	0.18	0.36 ₃	0.24 ₄	4.90 ₂	4.65 ₈
7.80	0.98 ₈	5.51	5.70	0.19	0.38 ₅	0.20 ₃	4.86 ₇	4.66 ₄
7.85	0.98 ₈	5.51	5.71	0.20	0.40 ₅	0.17 ₂	4.83 ₂	4.66 ₀
7.90	0.98 ₈	5.51	5.72	0.21	0.42 ₅	0.13 ₁	4.79 ₆	4.66 ₅
7.95	0.98 ₄	5.51	5.73	0.22	0.44 ₇	0.09 ₃	4.76 ₃	4.67 ₁
8.00	0.98 ₄	5.51	5.74	0.23	0.46 ₇	0.05 ₇	4.72 ₉	4.67 ₂
8.05	0.98 ₀	5.52	5.75	0.23	0.46 ₇	0.05 ₇	4.67 ₉	4.62 ₂
8.10	0.98 ₀	5.52	5.76	0.24	0.49 ₀	0.01 ₇	4.64 ₉	4.63 ₂

$$\log K_{MAL} = 4.64 \pm 0.02$$

Table V.2.3A

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

R	\bar{n}_H	v''	v'''	$v''' - v''$	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pI	$pI - \log(1-\bar{n})/\bar{n}$
7.60	1.00 ₀	6.00	6.21	0.21	0.42 ₃	0.13 ₅	4.98 ₉	4.85 ₄
7.70	1.00 ₀	6.00	6.22	0.22	0.44 ₃	0.10 ₀	4.91 ₄	4.81 ₄
7.90	0.99 ₆	6.00	6.24	0.24	0.48 ₅	0.02 ₆	4.83 ₈	4.81 ₂
7.90	0.99 ₂	6.00	6.25	0.25	0.50 ₈	1.98 ₆	4.75 ₈	4.77 ₂
8.00	0.98 ₀	6.00	6.26	0.26	0.53 ₄	1.94 ₁	4.68 ₂	4.74 ₁
8.10	0.98 ₀	6.00	6.27	0.27	0.55 ₅	1.90 ₄	4.60 ₂	4.69 ₈

$$\log K_{MAL} = 4.78 \pm 0.05$$

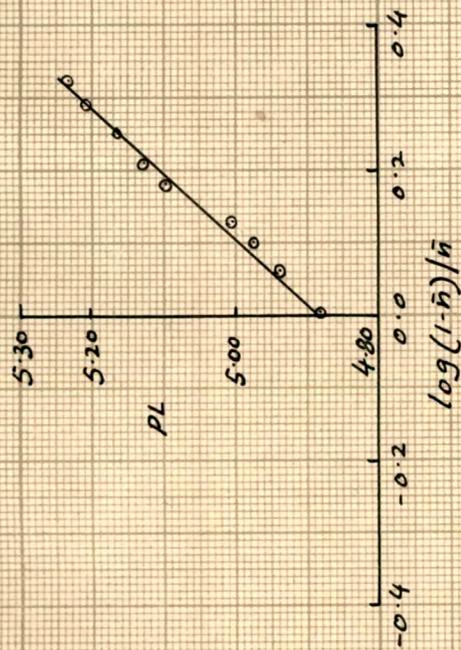


Fig V 15 Ni(II).Hist.Glycine system-30°C.

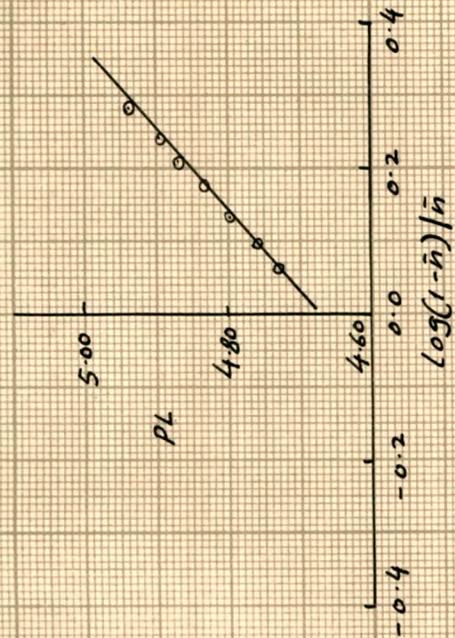


Fig.V 16 Ni(II).Hist. α -Alanine system - 30°C.

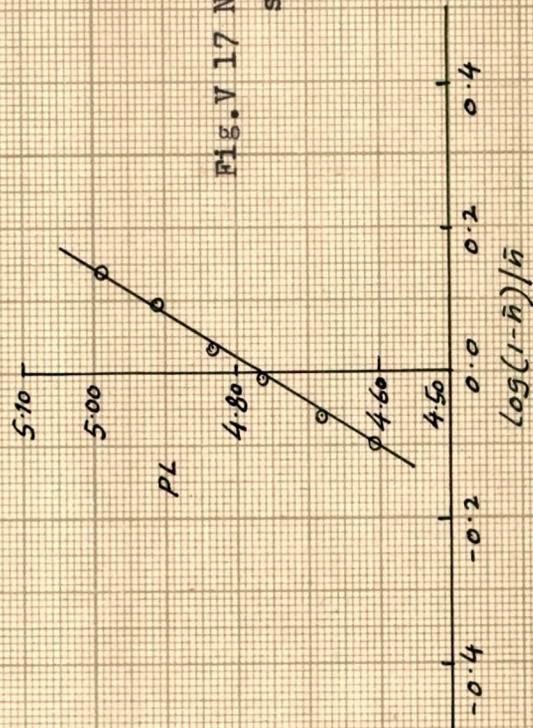


Fig.V 17 Ni(II).Hist.Aspartic acid system - 30°C.

Table V 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.Histidine.
thioglycollic acid system - 30°C.

B	\bar{n}_H	V''	V'''	V'''-V''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
6.70	1.00 ₄	6.00	6.14	0.14	0.27 ₇	0.41 ₇	6.34 ₅	5.92 ₈
6.80	1.00 ₄	6.00	6.16	0.16	0.31 ₇	0.33 ₃	6.27 ₅	5.94 ₂
6.90	1.00 ₄	6.00	6.17	0.17	0.33 ₇	0.29 ₄	6.18 ₈	5.89 ₄
7.00	1.00 ₄	6.00	6.19	0.19	0.37 ₇	0.21 ₈	6.11 ₅	5.89 ₇
7.10	1.00 ₄	6.00	6.20	0.20	0.39 ₆	0.18 ₃	6.02 ₉	5.94 ₆
7.20	1.00 ₀	6.00	6.21	0.21	0.41 ₆	0.14 ₇	5.94 ₃	5.79 ₆
7.25	1.00 ₀	6.00	6.22	0.22	0.43 ₆	0.11 ₂	5.90 ₉	5.79 ₇

$$\log K_{MAL} = 5.87 \pm 0.05$$

Table V 2.5A

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

B	\bar{n}_H	V''	V'''	V'''-V''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
6.30	1.00 ₇	6.00	6.14	0.14	0.27 ₈	0.41 ₄	6.78 ₁	6.36 ₇
6.40	1.00 ₇	6.00	6.16	0.16	0.31 ₇	0.33 ₃	6.70 ₅	6.37 ₂
6.50	1.00 ₄	6.00	6.19	0.19	0.37 ₈	0.21 ₆	6.64 ₆	6.43 ₀
6.60	1.00 ₄	6.00	6.21	0.21	0.41 ₈	0.14 ₄	6.57 ₅	6.43 ₁
6.70	1.00 ₄	6.00	6.23	0.23	0.45 ₈	0.07 ₃	6.50 ₆	6.43 ₃
6.80	1.00 ₄	6.00	6.25	0.25	0.49 ₈	0.00 ₃	6.43 ₉	6.43 ₆
6.90	1.00 ₄	6.01	6.27	0.26	0.51 ₇	1.97 ₀	6.35 ₆	6.38 ₆
7.00	1.00 ₄	6.01	6.29	0.28	0.55 ₇	1.90 ₀	6.29 ₄	6.39 ₄
7.10	1.00 ₄	6.01	6.31	0.30	0.59 ₇	1.82 ₉	6.23 ₅	6.40 ₆

$$\log K_{MAL} = 6.41 \pm 0.03$$

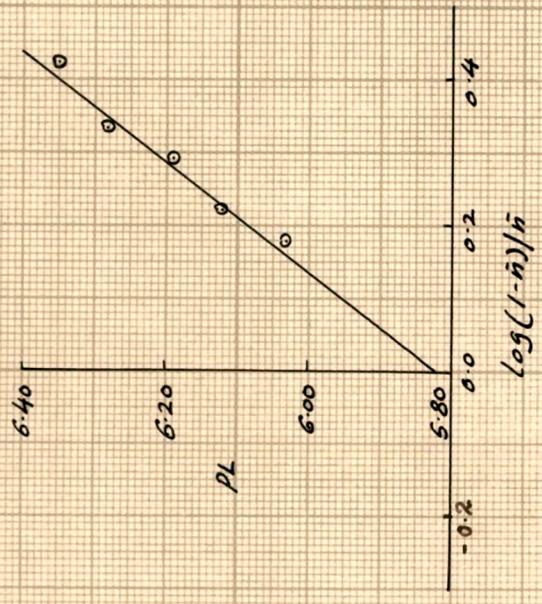


Fig. V 18 Ni(II).Hist. Thioglycollic acid system - 30°C.

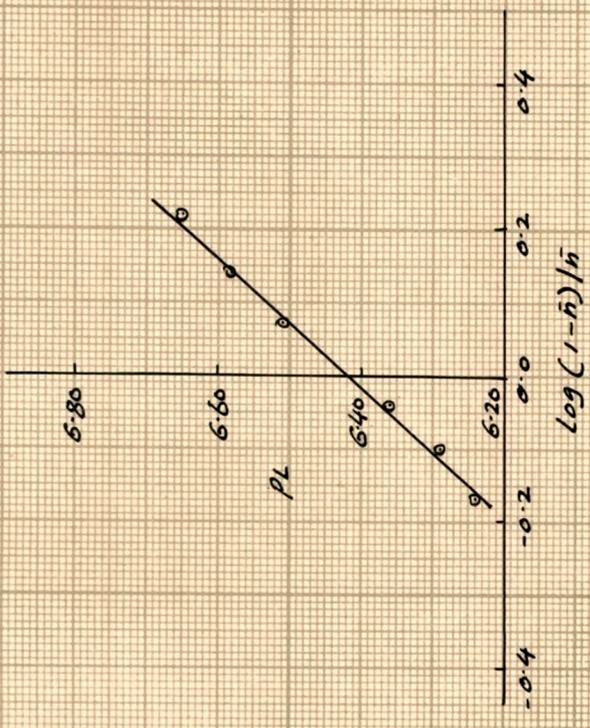


Fig. V 19 Ni(II).Hist. Thiolactic acid system - 30°C.

Table V 2.3B.

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

B	\bar{n}_H	v''	v'''	$v'''-v''$	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pI	pI- $\log(1-\bar{n})/\bar{n}$
7.00	1.00 ₀	6.47	6.66	0.17	0.33 ₇	0.22 ₄	5.53 ₂	5.23 ₈
7.10	1.00 ₈	6.49	6.68	0.19	0.37 ₇	0.21 ₈	5.45 ₉	5.24 ₁
7.20	1.00 ₄	6.49	6.69	0.20	0.39 ₉	0.17 ₈	5.37 ₅	5.19 ₇
7.30	1.00 ₄	6.49	6.71	0.22	0.43 ₈	0.11 ₈	5.30 ₄	5.18 ₆
7.40	1.00 ₄	6.49	6.73	0.24	0.47 ₈	0.03 ₈	5.23 ₆	5.19 ₈
7.50	1.00 ₀	6.49	6.74	0.25	0.50 ₀	0.00 ₀	5.15 ₅	5.15 ₅
7.60	1.00 ₀	6.49	6.75	0.26	0.52 ₀	1.96 ₅	5.07 ₃	5.10 ₈
7.70	1.00 ₀	6.49	6.77	0.28	0.56 ₀	1.89 ₅	5.01 ₁	5.11 ₆

$$\log K_{MAL} = 5.18 \pm 0.04$$

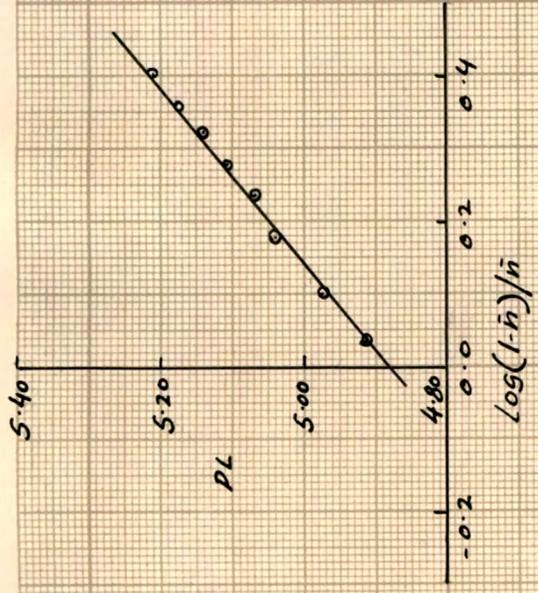


Fig. V 20 Ni(II).IMDA.Glycine system - 30°C.

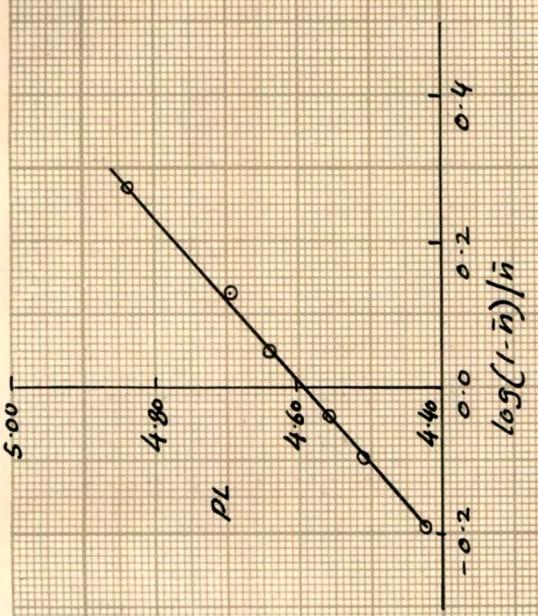


Fig. V 21 Ni(II).IMDA.alpha-Alanine system 30°C.

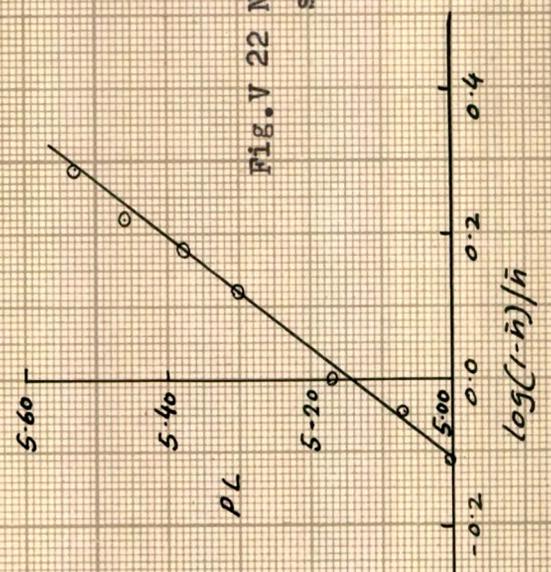


Fig. V 22 Ni(II).IMDA.Aspartic acid system - 30°C.

Table V.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.IMDA.
thioglycollic acid system - 30°C.

B	\bar{n}_H	v''	v'''	v'''-v''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
7.55	1.00 ₀	6.52	6.71	0.19	0.37 ₇	0.21 ₈	5.56 ₉	5.35 ₁
7.60	1.00 ₀	6.52	6.72	0.20	0.39 ₆	0.18 ₃	5.53 ₃	5.35 ₀
7.65	1.00 ₀	6.52	6.73	0.21	0.41 ₆	0.14 ₇	5.49 ₇	5.35 ₀
7.70	1.00 ₀	6.52	6.74	0.22	0.43 ₆	0.11 ₂	5.46 ₃	5.35 ₁
7.75	1.00 ₀	6.52	6.75	0.23	0.45 ₆	0.07 ₇	5.42 ₈	5.35 ₁
7.80	0.99 ₂	6.52	6.75	0.23	0.45 ₆	0.07 ₇	5.37 ₈	5.30 ₁
7.85	0.99 ₂	6.52	6.76	0.24	0.47 ₉	0.03 ₇	5.34 ₇	5.31 ₀

$$\log K_{MAT} = 5.34 \pm 0.02$$

Table V.2.5B

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

B	\bar{n}_H	v''	v'''	v'''-v''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
7.10	1.00 ₄	6.49	6.70	0.21	0.41 ₅	0.14 ₉	6.07 ₆	5.92 ₇
7.15	1.00 ₄	6.49	6.71	0.22	0.43 ₄	0.11 ₅	6.04 ₁	5.92 ₆
7.20	1.00 ₀	6.49	6.72	0.23	0.45 ₄	0.08 ₀	6.00 ₇	5.92 ₇
7.25	1.00 ₀	6.49	6.73	0.24	0.47 ₆	0.04 ₂	5.97 ₅	5.93 ₃
7.30	1.00 ₀	6.49	6.74	0.25	0.49 ₆	0.00 ₇	5.94 ₂	5.93 ₅
7.35	1.00 ₀	6.49	6.75	0.26	0.51 ₆	1.97 ₂	5.90 ₉	5.93 ₇
7.40	1.00 ₀	6.49	6.76	0.27	0.53 ₅	1.93 ₉	5.87 ₇	5.93 ₈

$$\log K_{MAT} = 5.94 \pm 0.01$$

Table V 2.6B

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

B	\bar{n}_H	v''	v'''	v'''-v''	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
7.10	0.90 ₁	7.00	7.17	0.17	0.37 ₁	0.22 ₉	6.13 ₈	5.90 ₉
7.15	0.90 ₁	7.00	7.18	0.18	0.39 ₃	0.18 ₉	6.11 ₄	5.92 ₄
7.25	0.89 ₅	7.00	7.19	0.19	0.41 ₇	0.14 ₆	6.03 ₂	5.88 ₆
7.30	0.89 ₅	7.00	7.20	0.20	0.43 ₉	0.10 ₇	5.99 ₉	5.89 ₂
7.35	0.89 ₅	7.00	7.21	0.21	0.46 ₁	0.06 ₈	5.96 ₆	5.89 ₈
7.40	0.89 ₅	7.00	7.22	0.22	0.48 ₃	0.03 ₀	5.93 ₄	5.90 ₄
7.45	0.89 ₅	7.00	7.23	0.23	0.50 ₅	1.99 ₁	5.90 ₃	5.91 ₂
7.50	0.89 ₅	7.00	7.24	0.24	0.52 ₇	1.95 ₃	5.87 ₃	5.92 ₀

$$\log K_{MAI} = 5.91 \pm 0.01$$

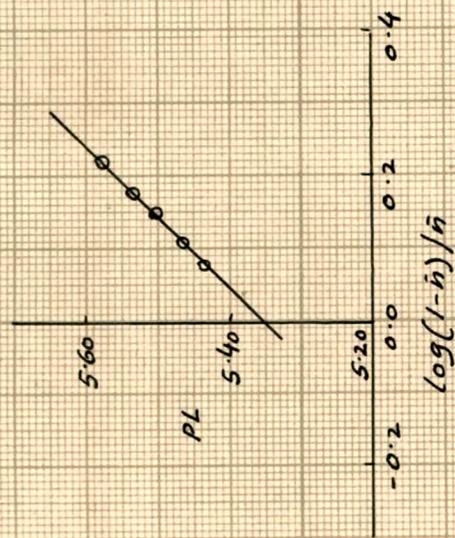


Fig. V 23 Ni(II).IMDA.Thioglycolic acid system - 30°C.

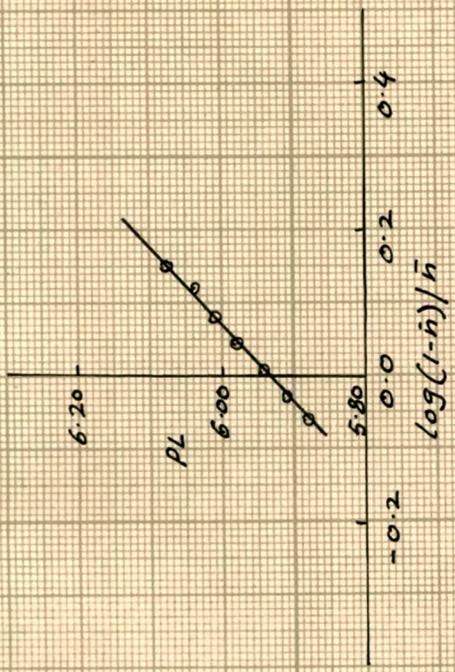


Fig. V 24 Ni(II).IMDA.Thioloactic acid system - 30°C.

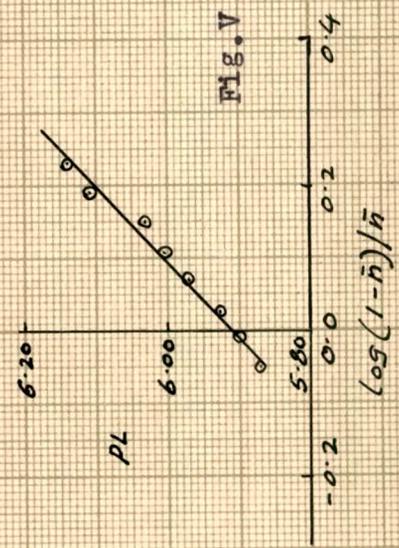


Fig. V 25 Ni(II).IMDA.Thiomalic acid system - 30°C.

Table V 2.3C

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

B	\bar{n}_H	v''	v'''	$v''' - v''$	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
8.10	0.98 ₀	7.00	7.16	0.16	0.32 ₇	0.31 ₄	4.42 ₉	4.11 ₅
8.20	0.97 ₂	7.00	7.18	0.18	0.37 ₀	0.23 ₁	4.32 ₅	4.09 ₄
8.30	0.96 ₀	7.00	7.21	0.21	0.43 ₈	0.10 ₈	4.30 ₈	4.20 ₀
8.40	0.94 ₄	7.01	7.23	0.22	0.46 ₆	0.05 ₉	4.23 ₀	4.17 ₁
8.50	0.92 ₈	7.01	7.26	0.25	0.53 ₉	1.93 ₂	4.19 ₄	4.26 ₀
8.60	0.91 ₂	7.02	7.28	0.26	0.57 ₀	1.87 ₈	4.11 ₅	4.23 ₇
8.70	0.89 ₂	7.04	7.31	0.27	0.60 ₅	1.81 ₅	4.06 ₂	4.24 ₇

$$\log K_{MAL} = 4.19 \pm 0.06$$

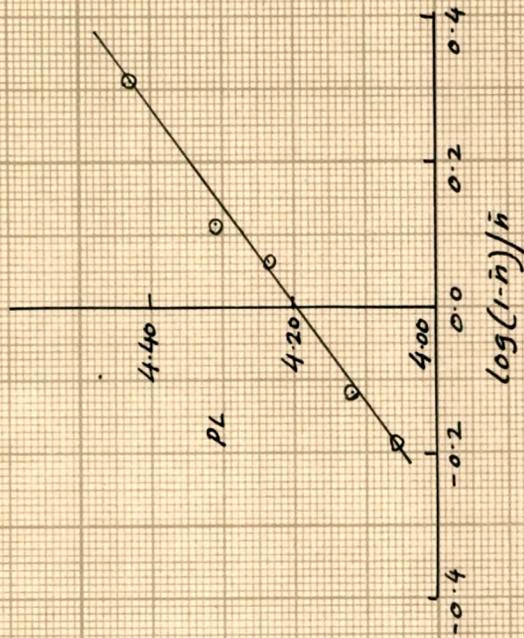


Fig. V 26 Ni(II).NTA. Aspartic acid system-30°C.

Table V 2.4C

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

B	\bar{n}_H	v''	v'''	$v''' - v''$	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
7.80	1.00 ₀	7.02	7.20	0.18	0.35 ₇	0.25 ₆	5.30 ₆	5.05 ₀
7.90	1.00 ₀	7.02	7.21	0.19	0.37 ₇	0.21 ₈	5.22 ₃	5.00 ₅
8.00	0.99 ₂	7.02	7.22	0.20	0.39 ₆	0.18 ₃	5.13 ₇	4.95 ₄
8.10	0.99 ₂	7.02	7.23	0.21	0.41 ₆	0.14 ₇	5.05 ₁	4.90 ₄
8.20	0.99 ₅	7.02	7.24	0.22	0.43 ₆	0.11 ₂	4.96 ₆	4.85 ₄
8.30	0.98 ₁	7.03	7.26	0.23	0.45 ₆	0.07 ₇	4.88 ₂	4.80 ₅

$$\log K_{MAL} = 4.93 \pm 0.08$$

Table V 2.5C

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

B	\bar{n}_H	v''	v'''	$v''' - v''$	\bar{n}	$\log(1-\bar{n})/\bar{n}$	pL	pL- $\log(1-\bar{n})/\bar{n}$
8.50	0.97 ₄	7.05	7.28	0.23	0.46 ₈	0.05 ₆	4.72 ₂	4.66 ₆
8.60	0.95 ₇	7.05	7.29	0.24	0.49 ₇	0.00 ₅	4.64 ₈	4.64 ₃
8.70	0.95 ₅	7.06	7.31	0.25	0.51 ₉	1.96 ₇	4.56 ₆	4.59 ₉
8.80	0.94 ₄	7.06	7.32	0.26	0.54 ₅	1.92 ₂	4.50 ₀	4.57 ₈
8.90	0.93 ₁	7.07	7.34	0.27	0.57 ₄	1.87 ₁	4.40 ₃	4.53 ₂
9.00	0.91 ₄	7.08	7.36	0.28	0.60 ₆	1.81 ₃	4.35 ₃	4.54 ₀

$$\log K_{MAL} = 4.59 \pm 0.04$$

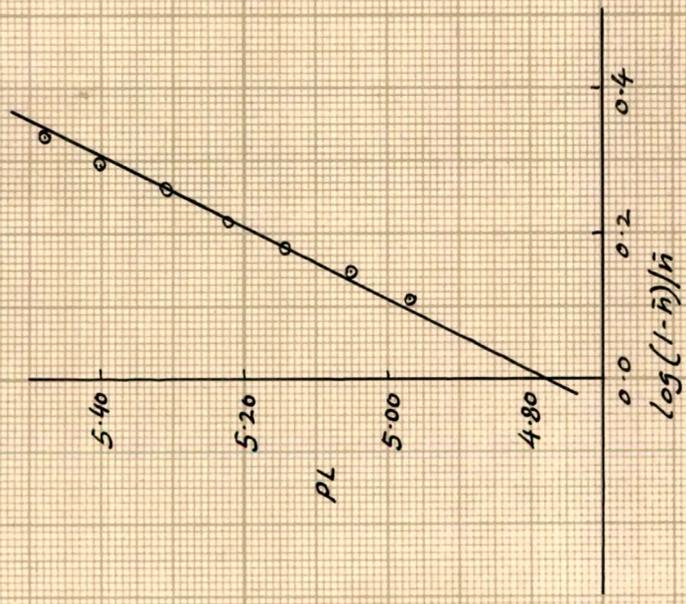


Fig. V 27 Ni(II).NTA.Thioglycollic acid system - 30°C.

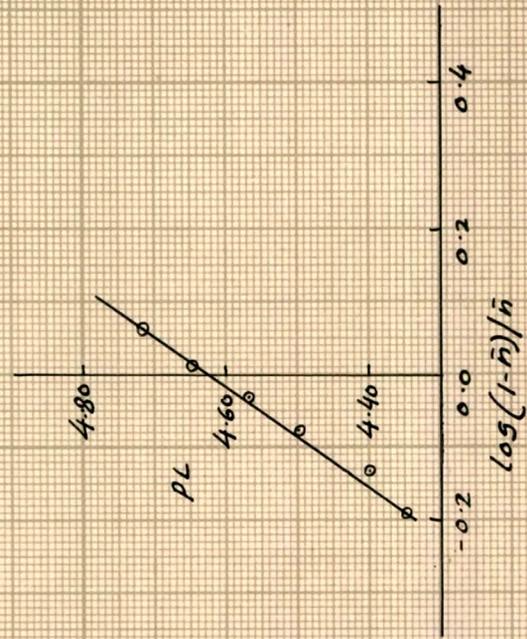


Fig. V 28 Ni(II).NTA.Thiolactic acid system - 30°C.

Table V 3.0

Logarithms of stability constants of ternary Histidine-Ni²⁺ ligand complexes, IMDA-Ni²⁺-ligand complexes and NTA-Ni²⁺-ligand complexes.

Ligand(L)	$\log K_{\text{Ni.Hist.L}}^{\text{Ni.Hist.}}$	$\log K_{\text{Ni.IMDA.L}}^{\text{Ni.IMDA}}$	$\log K_{\text{Ni.NTA.L}}^{\text{Ni.NTA}}$
Glycine	4.89 ± 0.02	4.85 ± 0.03	4.88 ± 0.04*
α-Alanine	4.64 ± 0.02	4.59 ± 0.02	4.72 ± 0.04*
Aspartic acid	4.78 ± 0.05	5.18 ± 0.04	4.19 ± 0.06
Thioglycollic acid	5.87 ± 0.05	5.34 ± 0.02	4.93 ± 0.08
Thiolactic acid	6.41 ± 0.03	5.94 ± 0.01	4.59 ± 0.04
Thiomalic acid	-	5.91 ± 0.01	-

* Values are taken from literature.

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