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# CHAPTER III

Section A Ternary metal, α-α-dipyridyl or o-phenanthroline and β-diketone systems

Section B Ternary metal, α-α-dipyridyl or o-phenanthroline and β-ketoimine systems

Section C Ternary metal, IMDA or NTA and β-diketone systems

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Section A

The complexes, in which the metal ion has two or more types of ligands in its coordination sphere, are termed mixed ligand complexes. The ligands may be unidentate or polydentate. In the latter case the complex is known as heterochelate. It is now generally agreed that in a solution containing metal ions and two different suitable ligands, mixed ligand complexes will be formed.

The catalytical action of metal chelates and enzymes often involve the intermediate formation of ternary or mixed ligand complexes in which a metal ion is bound to two or more ligands.[1-3] Watters[4,5] pointed out that the formation of mixed ligand complex, MAB, from a metal ion M in presence of equal concentrations of ligand A and B, is always more favoured, on a statistical basis, than the formation of $MA_2$ or $MB_2$. Thus the probability of bringing two different ligands together, or a small substrate molecule and enzyme via a metal ion is enhanced --- a factor having great biological implications.

In the systems containing one metal and two ligands, with significant differences in complexing tendencies, simplex complex is formed between the more complexing ligand and the metal ion, whereas, the other ligand remains unbound in solution. However, if the complexing tendencies do not differ very much, following types of reactions take place, leading to the formation of mixed ligand complexes.[6]

(i) Coordination of the metal ion with both ligands simultaneously to form a mixed ligand chelate in a single step or two overlapping steps, reflecting slight difference in the affinities of the ligands for the metal ion -

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

(ii) The formation of a mixed ligand chelate in two distinctly separated steps, reflecting a large difference in the affinities of the ligand for the metal ion -

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

In the reaction of the first type the solution consists of the species MA, ML, MAL, $MA_2$ and $ML_2$, formation of each being governed by a formation constant. The following reactions can lead to the formation of mixed ligand complex MAL and four different formation constants have to be considered -

$$MA + L \rightleftharpoons MAL \qquad K_1 = [MAL]/[MA][L]$$
$$ML + A \rightleftharpoons MAL \qquad K_2 = [MAL]/[ML][A]$$
$$M + A + L \rightleftharpoons MAL \qquad K_3 = [MAL]/[M][A][L]$$
$$MA_2 + ML_2 \rightleftharpoons 2MAL \qquad K_4 = [MAL]^2/[MA_2][ML_2]$$

The study of such systems has been carried out by Watters and coworkers[5,7,8] Nansen and coworkers[9,10] and Perrin and Sharma[11-13] have also extensively worked out such ternary complexes.

In the second type of reaction the species present in the solution can be MA and MAL. There is only one mixed ligand formation constant which characterises the reaction -

$$MA + L \rightleftharpoons MAL \qquad K^{MA}_{MAL} = [MAL] / [MA][L]$$

The necessary condition for such a system is that the two ligands must combine with the metal ion in the different pH ranges. The formation of [MA] should take place at lower pH and it should be stable upto higher pH. In 1:1 complex [MA], the remaining coordination positions of the metal ion are occupied by water molecules. On the addition of a secondary ligand L, water molecules are displaced resulting in the formation of mixed ligand complex [MAL].

Several systems of the above type have been studied. Punger and coworkers[15] employed the high frequency titrimetry technique to study the complexes of Ni(II) with dimethylglyoxime and dipyridyl. The solution stabilities of mixed ligand complexes of the type [Cu(dipy)L] where L is polyhydroxy phenols and acids have been reported by Martell and coworkers.[16] Formation constants of mixed ligand chelates of Cu(II) have been determined by Martell[17], where dipyridyl and o-phenanthroline are primary ligands. The secondary ligands being hydroxy compounds, substituted salicylic acids and oxalic acid. Sigel and coworkers[18-21] have investigated ternary transition metal complexes with dipyridyl as the primary ligand and many monodentate or bidentate secondary ligands coordinating through two oxygen atoms, two nitrogen atoms or one oxygen and one nitrogen. The ternary complexes in solution, where dipyridyl is used as primary ligand and aliphatic and aromatic acids are the secondary ligands, have been reported.[22] Sigel and coworkers[23] reported the stability constants of 2,2'-dipyridyl Cu(II) pyrocatechol complex. The ternary transition metal complexes with dipyridyl have been reported by Greiser and Sigel.[24] They[25] have also determined the rate constant for the formation and dissociation of the mixed ligand complex $[Cu(dipy)(gly)]^{2+}$ using temperature jump technique. The mixed complex studies in solution, where dipyridyl or o-phenanthroline is the primary ligand and amino acids, polyhydroxy phenols, thioacids are the secondary ligands have been reported from our laboratory.[26-33]

The experimental methods for the determination of mixed ligand complex formation constants have been discussed by Beck.[34] The stability of mixed complexes in solution have been reviewed excellently by Marcus and Eliezer.[35] Sharma has discussed about the statistical factors in the formation and stability of ternary and mixed complexes.[36] Rammorthy has suggested a method for evaluation of stability constant of mixed ligand complexes pH-metrically.[37] Recently Sigel has reported[38-41] on the stability of mixed ligand complexes of biological importance having dipyridyl as primary ligand and amino acids, diamines, dipeptides as secondary ligands.

Sigel used pH metric method for the calculation of formation constants in the reaction of the second type.[24] He calculated $K^{MA}_{MAL}$ considering the reaction to be strictly of the type $MA + L \rightleftharpoons MAL$ and also by considering it to be of the first type i.e. involving species ML and the step $ML + A \rightleftharpoons MAL$. The values worked out to be almost same.

A study of ternary complex $[M(dipy)L]$ has shown that in cases where L is a $\sigma$ bonding ligand $K^{M}_{ML}$ is nearly equal to $K^{M(dipy)}_{M(dipy)L}$ and this has been explained to be due to $M \longrightarrow N$ $\pi$ interaction in $[M(dipy)]^{2+}$ complex.[23,24,26,42-44] Values of mixed ligand formation constants in cases where L is a mercapto acid follow the same order as other charged $\sigma$ bonding ligands and on this basis it has been infered that the contribution of $\pi$ interaction in M--S bond is not significant.[30,45] In order to confirm the results further, an attempt was made to study, the system $[MAL]$ where L is an established $\pi$ bonding ligand. Acetylacetone is known to be a strongly chelating compound and the M--O $\pi$ interaction in the acetylacetone complexes has been established.[46,47] The $\pi$ interaction is also expected in benzoylacetone and dibenzoylmethane complexes.

In the present chapter studies of the system $[MAL]$ where M = Cu(II), Ni(II); A = dipyridyl(dipy) or o-phenanthroline(o-phen) and L = acetylacetone(AcAc) or benzoylacetone(BA) or dibenzoylmethand(DBM) have been carried out using modified form of Irving-Rossotti titration technique.[26,48]

The formation constants have been determined by titrating a mixture of M + A + L against standard alkali.

Experimental :

Materials, purification, preparation and standardisation.

Conductivity water was used throughout the work. All titrations were carried out in 50% dioxan medium. Dioxan was purified by the known method.[49] Solutions of oxalic acid, sodium hydroxide, perchloric acid, sodium perchlorate were prepared and standardised as discussed in chapter II.

The other reagents were Dipyridyl and o-phenanthroline (Merck,pure), Acetylacetone (BDH,pure), Benzoylacetone (Fluka,pure), Dibenzoylmethane (K.Light). Their standard solutions were prepared by dissolving the required weighed quantity in known volume of purified dioxan. Metal perchlorates and instruments used were same as detailed in previous chapter.

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

(1) Perchloric acid (0.2M,5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + conductivity water (11.0 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

(2) Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (6.1 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

(3) Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (1.2 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 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 (11.1 ml.) + dioxan (20.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

(5) Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (1.3 ml.) + dioxan (20.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

(6) 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 (6.2 ml.) + dioxan (20.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

In cases where o-phenanthroline was the primary ligand, more dilute solutions were used (0.01M concentration of metal, primary ligand and secondary ligand) because precipitates of M-o-phen are formed in concentrated solutions.

The ionic strength of each solution was initially raised to 0.2M. The solutions were titrated against 0.2M sodium hydroxide. The plots of pH against volume of alkali have been shown in figs. IIIA 1 to IIIA 8.

Discussion :

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

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

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

Mixed ligand formation constants -

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

The above equations presume that the formation of $[M(dipy)]^{2+}$ complex takes place at 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 presumptions.

M-dipy curve diverges from the dipyridyl curve at lower pH indicating that the $[M(dipy)]^{2+}$ is formed at lower pH by the dissociation of the protons attached with the tertiary nitrogen of dipyridyl molecules. The M-dipy curve diverges from acid curve at higher pH indicating that the formation of hydroxy complex $[M(dipy)(OH)_2]$ starts in this pH range. The curve(5) remains merged with curve(4) at low pH showing that complexation of β-diketone does not take place at low pH. The curve(5) diverges from curve(4) at higher pH showing that M + dipy + β-diketone combination takes place where M + dipy 1:1 complex formation is complete. In this range hydroxo complex formation also does not occur.

Since o-phenanthroline is structurally similar to dipyridyl, it can be expected to behave in a similar way. The natures of the o-phenanthroline curve and Ni-O-phen, curve are also similar to that of dipyridyl and Ni-dipy 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(4) and (5), $V''' - V''$ can be measured and used for 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 calculation of $\bar{n}$ would be same as given in original paper[50] and the terms used have the same meaning as in binary systems.

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

The calculation of $\bar{n}$ was carried out below the pH where $\left[M(dipy)(OH)_2\right]^{2+}$ formation starts, i.e. where $\left[M(dipy)\right]^{2+}$ curve diverges from the dipyridyl curve. $\bar{n}$ and pL were calculated at different pH values and have been presented in tables IIIA 2.1a - IIIA 2.8c.

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. (fig. IIIA 9 - IIIA 16). At each point on the straight line $\log K^{MA}_{MAL}$ is equal to pL - $\log(1-\bar{n})/\bar{n}$. The average values were thus calculated and have been presented with mean deviation in tables IIIA 2.1a - IIIA 2.8c.

Mixed copper complex in case of DBM was not possible due to precipitation. Studies were not possible in [Cu(o-phen)L] due to the fact that the binary complex [Cu(o-phen)] is insoluble and precipitates out.

The order of formation constants in the mixed ligand system is same as in binary complexes - DBM > BA > AcAc. This can be explained from basicity considerations. It is observed that the values of $\log K^{M(dipy)}_{M(dipy)(\beta\text{-diket})}$ are in the same order as in the binary complexes. The values of $\log K^{M(dipy)}_{M(dipy)(\beta\text{-diket})}$ also does not show much difference from the values of $\log K^{M}_{M(\beta\text{-diket})}$. In case of earlier studies also it was shown that $\log K^{M(dipy)}_{M(dipy)L} \approx \log K^{M}_{ML}$. This has been explained to be due to the special behaviour of dipyridyl.[23,24,26,42-44] Besides N⟶M $\sigma$ bonding there exists M⟶N $\pi$ interaction in dipyridyl complexes. This retains the electronegativity of the metal ion in $[M(dipy)]^{2+}$ same as in $[M(H_2O)n]^{2+}$. Thus the tendency of L to get bound with $MA^{2+}$ is same as with $M^{2+}$ and hence $K^{MA}_{MAL}$ is nearly equal to $K^{M}_{ML}$. In case of $\beta$-diketone complexes, however, there exists $\pi$ interaction between the metal $d\pi$ orbitals and the $\pi$ electron cloud on the $\beta$-diketonate ion. Thus there is back donation from metal to $\beta$-diketone. In case of mixed ligand complexes, [M(dipy)($\beta$-diketone)] both the ligands are $\pi$ bonded. The metal after having donated $\pi$ electrons to the dipyridyl molecule should have less tendency to donate the electron to the second ligand i.e. $\beta$-diketone.

Similar explanation is extended for the greater difference between $K_1$ and $K_2$ in case of binary $\pi$ bonded complexes.[51] However, it is observed that the value of $K^{M(dipy)}_{M(dipy)(\beta\text{-diket})}$ is nearly same as $K^{M}_{ML}$. Thus, it does not agree with the theoretical expectation. The reason lies in the fact that the above generalisation may not always be true. Even in $[M(dipy)_2]^{2+}$ and $[M(\beta\text{-diket})_2]$ systems, $K_1/K_2$ ratio is not high.[52,53] This may be because M→L $\pi$ interaction is balanced by L→M $\sigma$ interaction and the electronegativity of $[M(dipy)]^{2+}$ is same as in $[M(aq)]^{2+}$. If this is true the tendency of a second ligand to form both $\sigma$ and $\pi$ bonds with $[M(dipy)]^{2+}$ should be same as with $[M(aq)]^{2+}$. Thus the extent of stability of Metal - β-diketone bond will not be reduced in $[M(dipy)(\beta\text{-diket})]$ and hence $K^{M(dipy)}_{M(dipy)(\beta\text{-diket})}$ is nearly same as $K^{M}_{M(\beta\text{-diket})}$. Even if there is some lowering in $\sigma$ or $\pi$ bonding of the secondary ligand, they compensate each other. If there is some lowering in the $\pi$ interaction in M-β-diketone bond in $[M(dipy)(\beta\text{-diket})]$ the increase in $\sigma$ interaction is more and vice-versa and hence the stability of metal and β-diketone bond in $[M(dipy)(\beta\text{-diket})]$ remains same as in binary metal-β-diketone complexes even in spite of M-β-diketone $\pi$ interaction.

Table IIIA 1.1

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

E° = 0.02M   $T^{\circ}_{L}$ = 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 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.85 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.25 | 3.00 | 2.20 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.60 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.10 | 2.70 | 4.50 | 2.85 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.20 | 2.80 | 4.60 | 2.95 | 4.60 | 2.90 |
| 4.70 | 2.95 | 4.30 | 2.95 | 4.70 | 3.05 | 4.70 | 3.05 |
| 4.80 | 3.15 | 4.40 | 3.05 | 4.80 | 3.15 | 4.80 | 3.25 |
| 4.85 | 3.30 | 4.50 | 3.20 | 4.85 | 3.35 | 4.85 | 3.45 |
| 4.90 | 3.55 | 4.60 | 3.40 | 4.90 | 3.55 | 4.90 | 3.65 |
| 4.92 | 3.65 | 4.70 | 3.65 | 4.93 | 3.80 | 4.92 | 3.75 |
| 4.94 | 3.85 | 4.80 | 4.00 | 4.96 | 4.15 | 4.94 | 3.85 |
| 4.96 | 4.15 | 4.85 | 4.20 | 4.98 | 4.50 | 4.96 | 4.15 |
| 4.98 | 4.50 | 4.90 | 4.50 | 5.00 | 6.05 | 4.98 | 4.50 |
| 5.00 | 7.20 | 4.94 | 4.80 | 5.10 ppts | 6.55 | 5.00 | 6.80 |
| 5.01 | 8.50 | 4.98 | 5.55 | 5.20 | 6.80 | 5.05 | 7.60 |
| 5.05 | 9.55 | 5.00 | 7.15 | 5.30 | 7.00 | 5.10 | 7.95 |
| 5.08 | 10.20 | 5.01 | 8.50 | 5.40 | 7.40 | 5.20 | 8.35 |
| 5.10 | 10.45 | 5.05 | 9.55 | 5.50 | 8.15 | 5.30 | 8.55 |
| | | 5.10 | 10.45 | 5.60 | 9.05 | | |

## Table IIIA 1.2

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

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

| AcAc | | Cu.Dipy.AcAc | | Cu.AcAc | | Ni.Dipy.AcAc | | Ni.AcAc | |
|---|---|---|---|---|---|---|---|---|---|
| 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 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.85 | 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.95 | 4.60 | 2.85 | 4.60 | 2.90 | 4.60 | 2.85 |
| 4.70 | 2.95 | 4.70 | 3.05 | 4.70 | 2.95 | 4.70 | 3.05 | 4.70 | 2.95 |
| 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.30 | 4.80 | 3.15 |
| 4.85 | 3.30 | 4.90 | 3.25 | 4.90 | 3.25 | 4.85 | 3.50 | 4.85 | 3.30 |
| 4.90 | 3.55 | 5.00 | 3.30 | 5.00 | 3.30 | 4.90 | 3.65 | 4.90 | 3.55 |
| 4.93 | 3.80 | 5.10 | 3.45 | 5.10 | 3.45 | 4.93 | 3.80 | 4.93 | 3.80 |
| 4.96 | 4.15 | 5.20 | 3.75 | 5.20 | 3.75 | 4.96 | 4.10 | 4.96 | 4.15 |
| 4.98 | 4.50 | 5.30 | 4.35 | 5.30 | 4.35 | 4.98 | 4.50 | 4.98 | 4.40 |
| 5.00 | 7.15 | 5.40 | 5.20 | 5.40 | 5.05 | 5.00 | 4.70 | 5.00 | 4.65 |
| 5.05 | 8.45 | 5.50 | 6.35 | 5.50 | 5.70 | 5.05 | 5.25 | 5.05 | 5.10 |
| 5.10 | 8.95 | 5.60 | 7.95 | 5.60 | 6.20 | 5.10 | 5.55 | 5.10 | 5.40 |
| 5.20 | 9.40 | 5.70 | 9.65 | 5.70 | 6.50 | 5.20 | 6.05 | 5.20 | 5.90 |
| 5.30 | 9.70 | 5.80 | 10.45 | 5.80 | 6.75 | 5.40 | 7.00 | 5.40 | 6.75 |
| 5.40 | 10.00 | | | 5.90 | 7.10 | 5.60 | 8.45 | 5.60 | 7.90 |
| 5.50 | 10.25 | | | 6.00 | 7.60 | 5.80 | 9.75 | 5.80 | 8.65 |
| 5.60 | 10.55 | | | | | 5.90 | 10.10 | 6.00 | 9.40 |

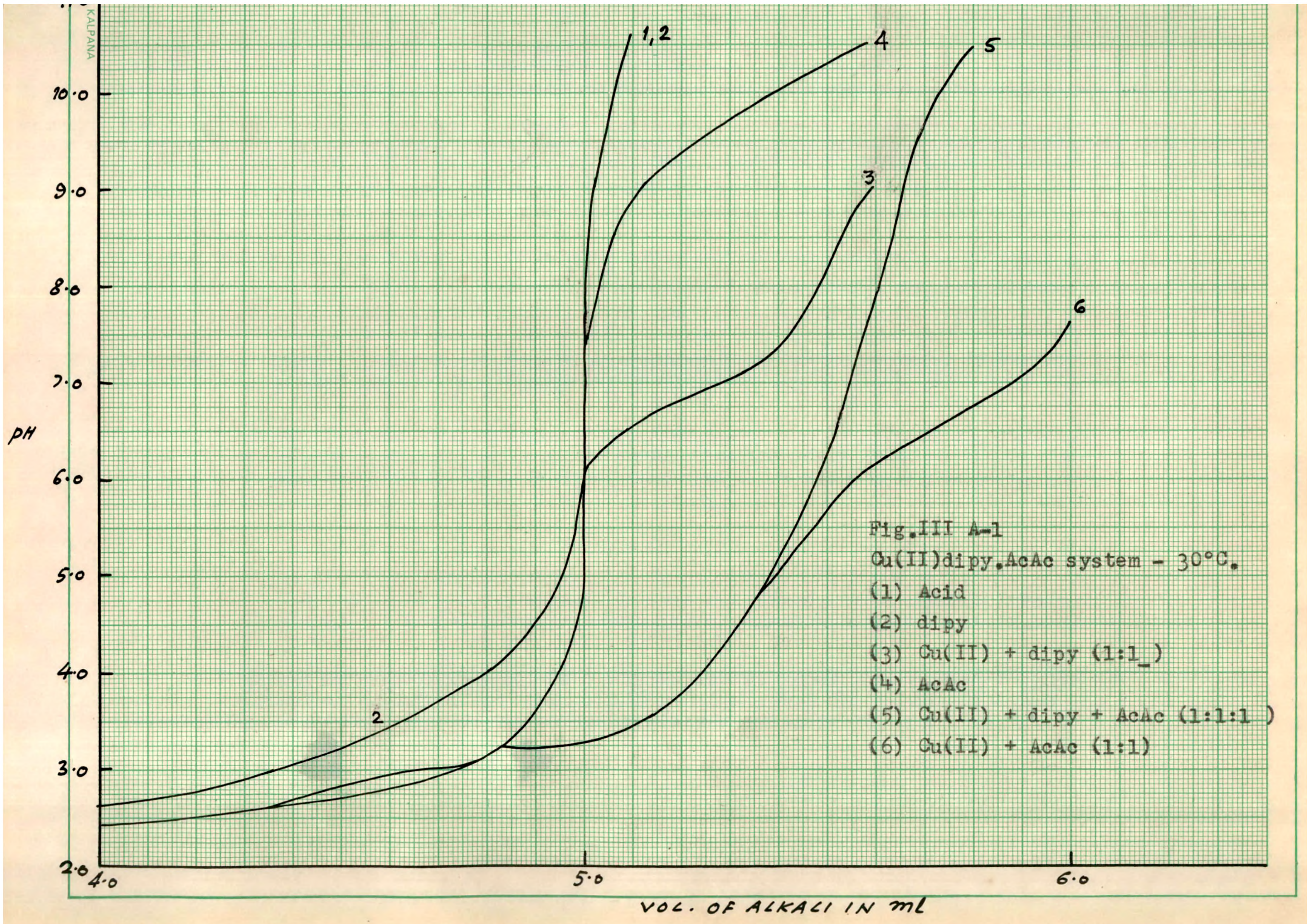



Fig.III A-1

Cu(II)dipy.AcAc system - 30°C.

(1) Acid
(2) dipy
(3) Cu(II) + dipy (1:1_)
(4) AcAc
(5) Cu(II) + dipy + AcAc (1:1:1 )
(6) Cu(II) + AcAc (1:1)

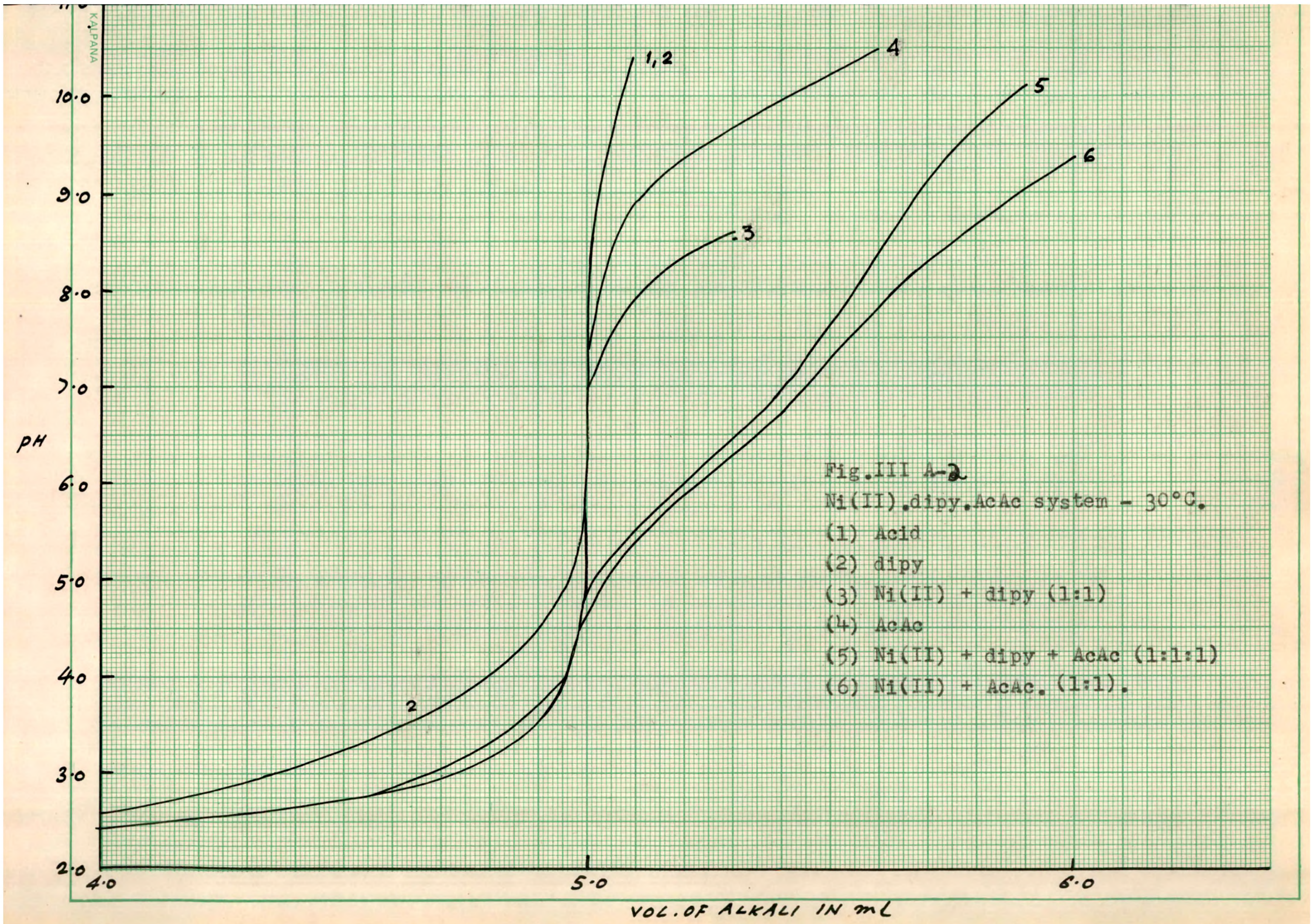



Fig.III A-2
Ni(II).dipy.AcAc system - 30°C.
(1) Acid
(2) dipy
(3) Ni(II) + dipy (1:1)
(4) AcAc
(5) Ni(II) + dipy + AcAc (1:1:1)
(6) Ni(II) + AcAc. (1:1).

Table IIIA 1.3

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

$E^\circ = 0.02M$ $T^\circ_{Dipy} = 0.002M$ $\mu = 0.2M$ $t = 30^\circ C.$

| BA | | Cu.Dipy.BA | | Cu.BA | | Ni.Dipy.BA | | Ni.BA | |
|---|---|---|---|---|---|---|---|---|---|
| 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 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.85 | 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.95 | 4.60 | 2.80 | 4.60 | 2.90 | 4.60 | 2.85 |
| 4.70 | 2.95 | 4.70 | 3.05 | 4.70 | 2.95 | 4.70 | 3.05 | 4.70 | 2.95 |
| 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.30 | 4.80 | 3.15 |
| 4.85 | 3.30 | 4.90 | 3.20 | 4.90 | 3.20 | 4.85 | 3.50 | 4.85 | 3.30 |
| 4.90 | 3.55 | 5.00 | 3.25 | 5.00 | 3.25 | 4.90 | 3.65 | 4.90 | 3.55 |
| 4.94 | 3.85 | 5.10 | 3.35 | 5.10 | 3.35 | 4.94 | 3.85 | 4.95 | 4.00 |
| 4.98 | 4.50 | 5.20 | 3.55 | 5.20 | 3.55 | 4.98 | 4.40 | 5.00 | 4.45 |
| 5.00 | 6.90 | 5.30 | 4.20 | 5.30 | 4.20 | 5.00 | 4.55 | 5.05 | 4.80 |
| 5.03 | 8.20 | 5.40 | 5.25 | 5.40 | 5.25 | 5.05 | 4.95 | 5.10 | 5.20 |
| 5.05 | 8.50 | 5.50 | 6.50 | 5.50 | 5.95 | 5.10 | 5.30 | 5.20 | 5.75 |
| 5.10 | 9.00 | 5.60 | 7.80 | 5.60 | 6.30 | 5.20 | 5.90 | 5.40 | 6.95 |
| 5.20 | 9.50 | 5.70 | 9.20 | 5.70 | 6.65 | 5.40 | 7.10 | 5.60 | 8.15 |
| 5.30 | 9.80 | 5.80 | 10.50 | 5.80 | 6.85 | 5.60 | 9.00 | 5.80 | 9.15 |
| 5.40 | 10.05 | | | 6.00 | 7.35 | 5.80 | 10.45 | 6.00 | 10.00 |
| 5.50 | 10.25 | | | | | | | | |
| 5.60 | 10.50 | | | | | | | | |

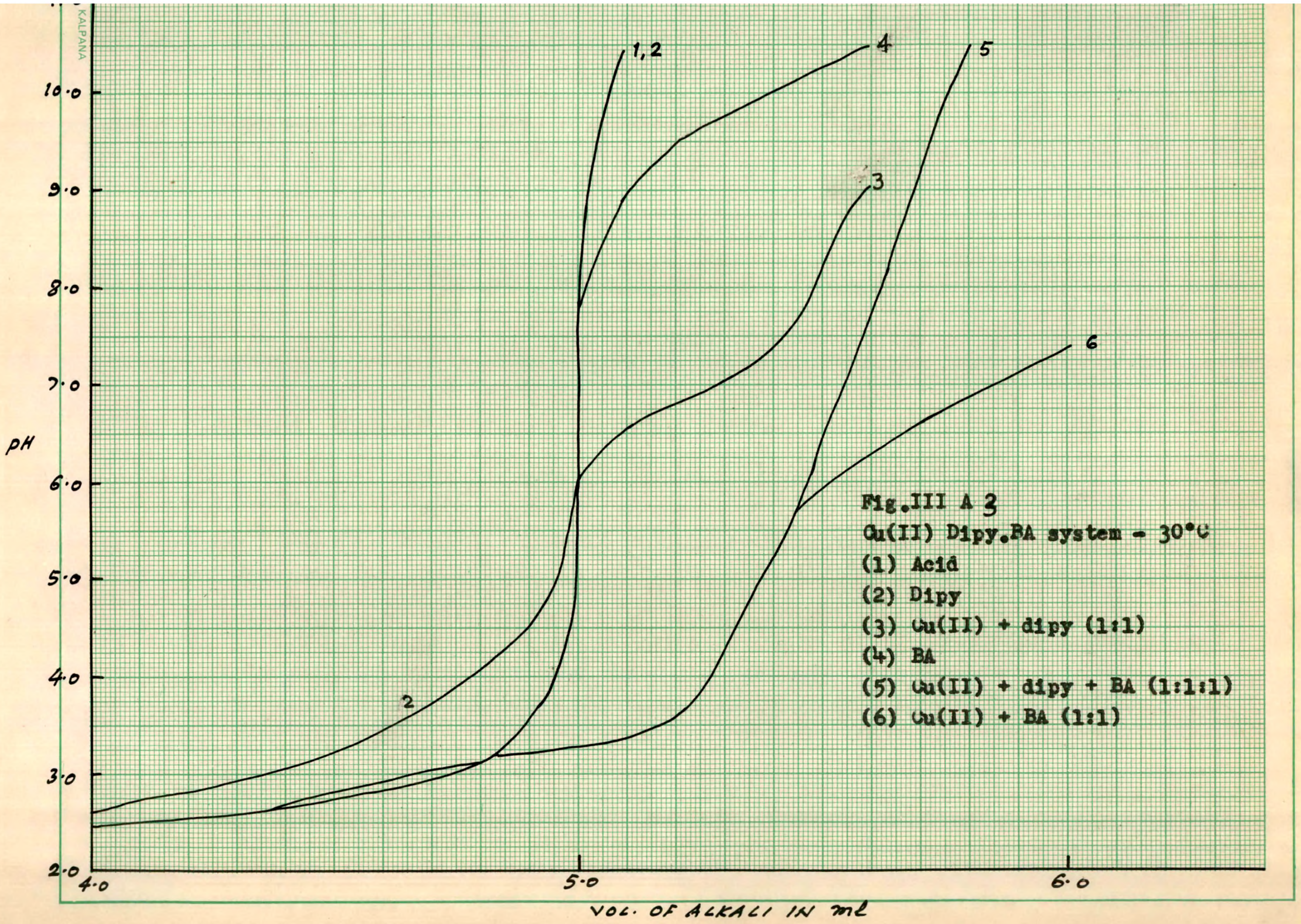



Fig.III A 3
Cu(II) Dipy.BA system - 30°C
(1) Acid
(2) Dipy
(3) Cu(II) + dipy (1:1)
(4) BA
(5) Cu(II) + dipy + BA (1:1:1)
(6) Cu(II) + BA (1:1)

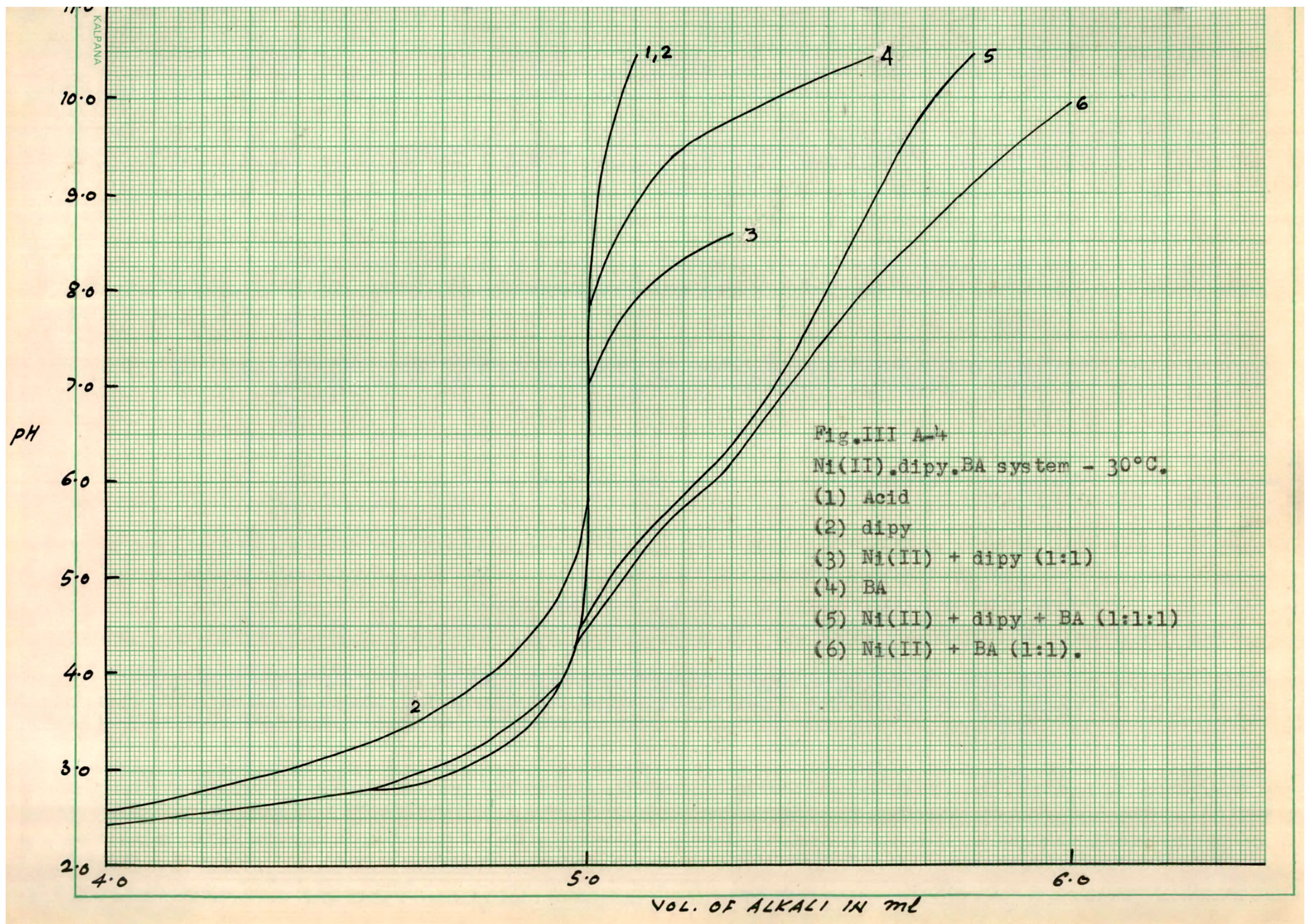


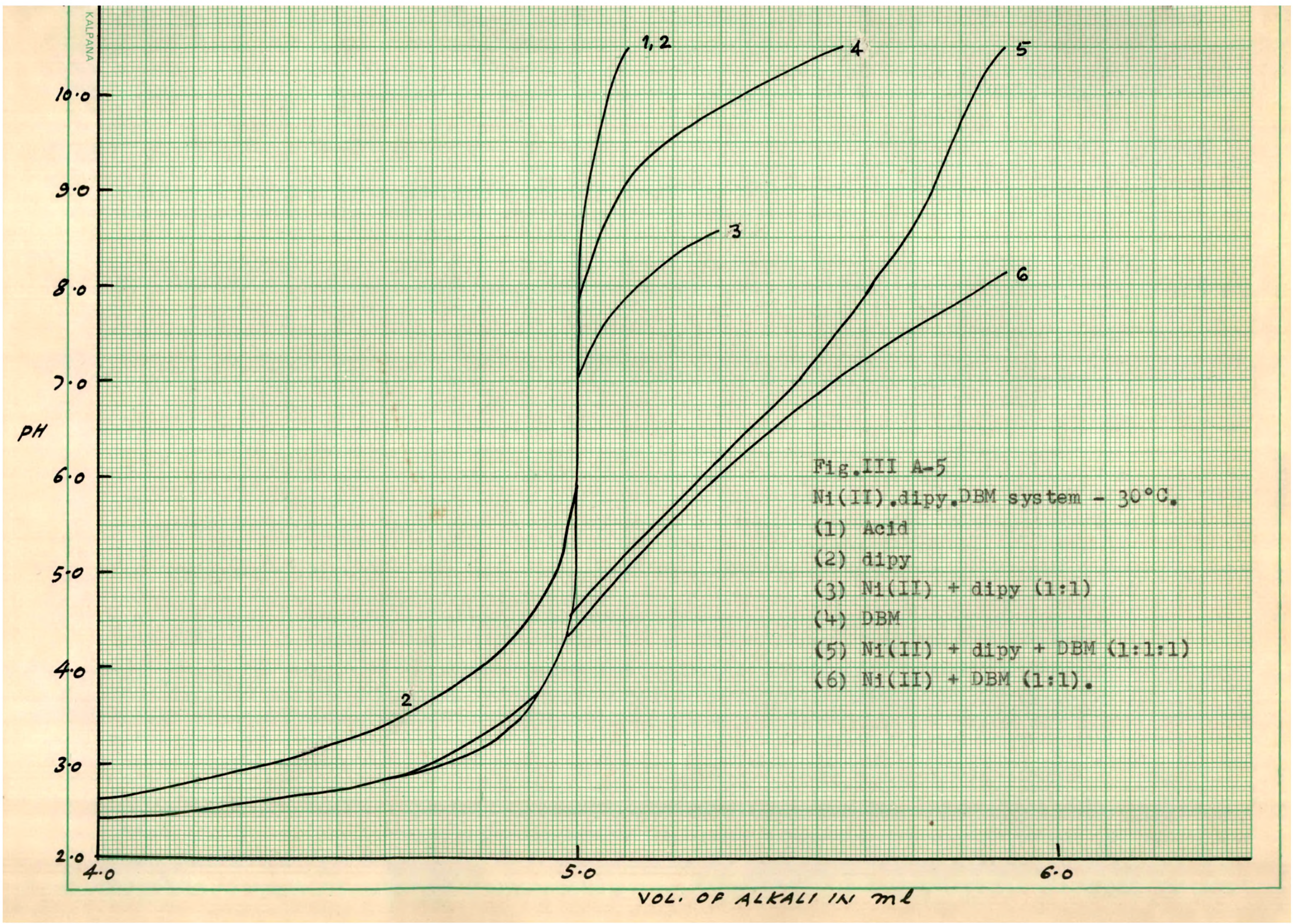
Fig. III A-4
Ni(II).dipy.BA system - 30°C.
(1) Acid
(2) dipy
(3) Ni(II) + dipy (1:1)
(4) BA
(5) Ni(II) + dipy + BA (1:1:1)
(6) Ni(II) + BA (1:1).
pH
VOL. OF ALKALI IN ml
1,2
2
3
4
5
6
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
4.0
5.0
6.0

Table IIIA 1.4

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

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

| DBM | | Ni.Dipy.DBM | | Ni.DBM | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.90 | 4.60 | 2.85 |
| 4.70 | 2.95 | 4.70 | 3.05 | 4.70 | 2.95 |
| 4.80 | 3.15 | 4.80 | 3.30 | 4.80 | 3.15 |
| 4.85 | 3.30 | 4.85 | 3.50 | 4.85 | 3.35 |
| 4.90 | 3.55 | 4.90 | 3.65 | 4.90 | 3.55 |
| 4.93 | 3.80 | 4.94 | 3.85 | 4.94 | 3.85 |
| 4.96 | 4.10 | 4.98 | 4.40 | 4.98 | 4.35 |
| 4.98 | 4.60 | 5.00 | 4.65 | 5.00 | 4.50 |
| 5.00 | 7.35 | 5.05 | 4.90 | 5.05 | 4.75 |
| 5.03 | 8.15 | 5.10 | 5.20 | 5.10 | 5.05 |
| 5.05 | 8.55 | 5.20 | 5.70 | 5.20 | 5.60 |
| 5.10 | 9.10 | 5.30 | 6.25 | 5.30 | 6.10 |
| 5.20 | 9.60 | 5.40 | 6.70 | 5.40 | 6.50 |
| 5.30 | 9.85 | 5.60 | 7.90 | 5.60 | 7.25 |
| 5.40 | 10.15 | 5.80 | 9.80 | 5.80 | 7.85 |
| 5.50 | 10.35 | 5.90 | 10.55 | 5.90 | 8.15 |



KALPANA
10·0
9·0
8·0
7·0
pH
6·0
5·0
4·0
3·0
2·0
4·0
5·0
6·0
VOL. OF ALKALI IN ml
1,2
4
5
3
6
2
Fig.III A-5
Ni(II).dipy.DBM system - 30°C.
(1) Acid
(2) dipy
(3) Ni(II) + dipy (1:1)
(4) DBM
(5) Ni(II) + dipy + DBM (1:1:1)
(6) Ni(II) + DBM (1:1).

## Table IIIA 1.5

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

$E^\circ$ = 0.02M  $T^\circ_{o\text{-}phen}$ = 0.001M  $\mu$ = 0.2M  t = 30°C.

| Perchloric acid | | o-phen | | Ni.o-phen | | AcAc | | Ni.o-phen.AcAc | |
|---|---|---|---|---|---|---|---|---|---|
| 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 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.95 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.05 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.25 | 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.65 | 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.10 | 2.70 | 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.20 | 2.75 | 4.60 | 2.85 | 4.60 | 2.85 | 4.60 | 2.85 |
| 4.70 | 2.95 | 4.30 | 2.85 | 4.70 | 2.95 | 4.70 | 2.95 | 4.70 | 2.95 |
| 4.80 | 3.15 | 4.40 | 2.95 | 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.15 |
| 4.85 | 3.30 | 4.50 | 3.10 | 4.85 | 3.30 | 4.85 | 3.30 | 4.85 | 3.30 |
| 4.90 | 3.55 | 4.60 | 3.30 | 4.90 | 3.55 | 4.90 | 3.55 | 4.90 | 3.55 |
| 4.92 | 3.65 | 4.70 | 3.70 | 4.92 | 3.65 | 4.94 | 3.80 | 4.94 | 3.80 |
| 4.94 | 3.85 | 4.80 | 4.25 | 4.94 | 3.85 | 4.98 | 4.50 | 4.98 | 4.50 |
| 4.96 | 4.15 | 4.85 | 4.60 | 4.96 | 4.15 | 5.00 | 6.95 | 5.00 | 5.30 |
| 4.98 | 4.50 | 4.90 | 4.95 | 4.98 | 4.50 | 5.02 | 7.75 | 5.05 | 5.95 |
| 5.00 | 7.20 | 4.94 | 5.55 | 5.00 | 6.45 | 5.05 | 8.15 | 5.10 | 6.35 |
| 5.01 | 8.50 | 4.98 | 6.20 | 5.02 | 7.50 | 5.10 | 8.65 | 5.20 | 6.85 |
| 5.05 | 9.55 | 5.00 | 7.95 | 5.05 | 7.80 | 5.20 | 9.45 | 5.30 | 7.50 |
| 5.08 | 10.20 | 5.01 | 8.50 | 5.10 | 8.35 | 5.30 | 9.90 | 5.40 | 9.00 |
| 5.10 | 10.45 | 5.05 | 9.55 | 5.20 | 9.10 | 5.40 | 10.30 | 5.60 | 10.45 |
| | | 5.10 | 10.45 | | | 5.50 | 10.60 | | |

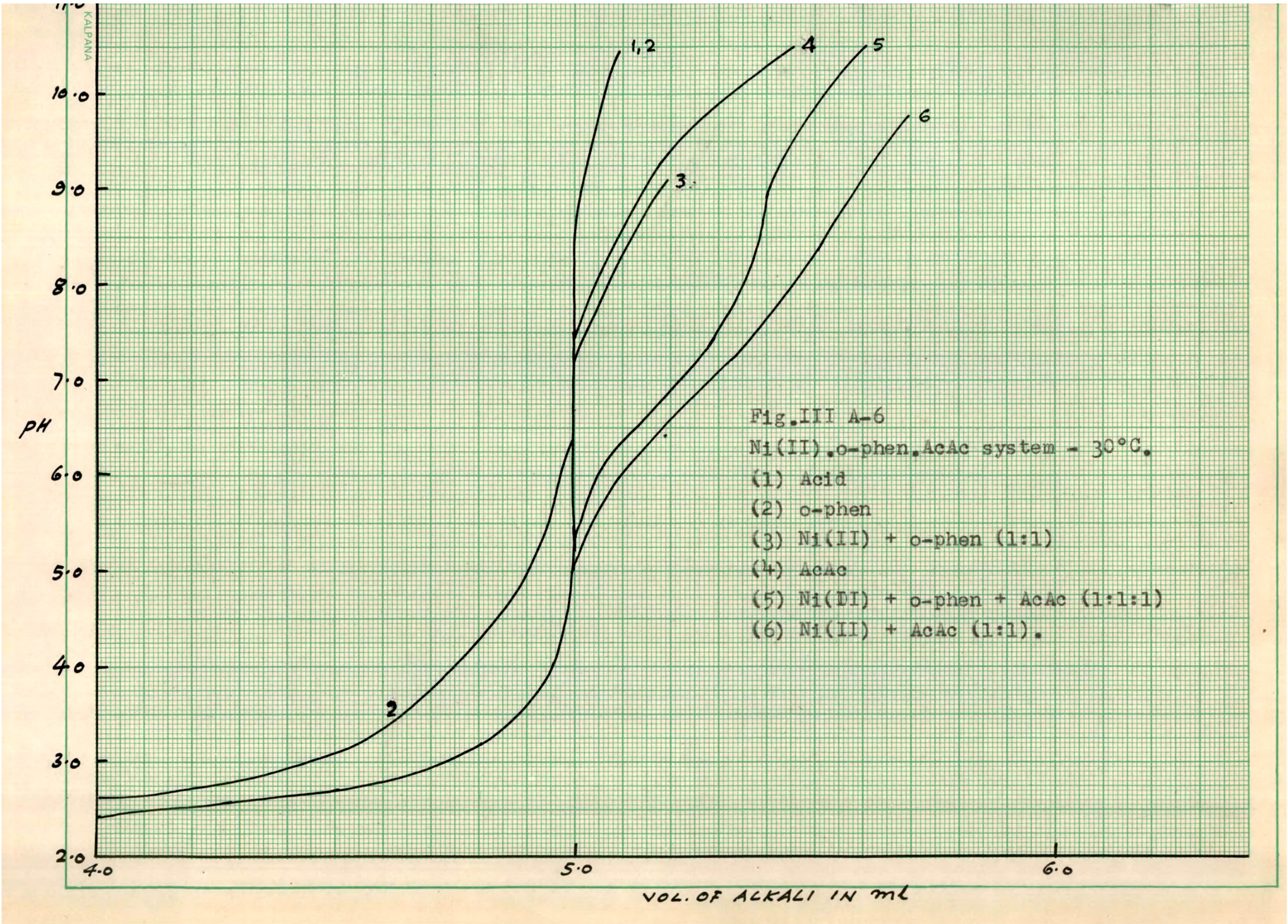



Fig.III A-6

Ni(II).o-phen.AcAc system - 30°C.

(1) Acid

(2) o-phen

(3) Ni(II) + o-phen (1:1)

(4) AcAc

(5) Ni(II) + o-phen + AcAc (1:1:1)

(6) Ni(II) + AcAc (1:1).

## Table IIIA 1.6

N = 0.2M V° = 50 ml. $T^{\circ}_{o\text{-phen}}$ = 0.001M $T^{\circ}_{M}$ = 0.001M

E° = 0.02M $T^{\circ}_{L}$ = 0.001M $\mu$ = 0.2M t = 30°C.

| BA | | Ni.o-phen BA | | DBM | | Ni.o-phen DBM | |
|---|---|---|---|---|---|---|---|
| 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 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.85 | 4.60 | 2.85 | 4.60 | 2.85 |
| 4.70 | 2.95 | 4.70 | 2.95 | 4.70 | 2.95 | 4.70 | 2.95 |
| 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.15 | 4.80 | 3.15 |
| 4.85 | 3.30 | 4.85 | 3.30 | 4.85 | 3.30 | 4.85 | 3.30 |
| 4.90 | 3.55 | 4.90 | 3.55 | 4.90 | 3.55 | 4.90 | 3.55 |
| 4.94 | 3.80 | 4.94 | 3.80 | 4.94 | 3.80 | 4.94 | 3.80 |
| 4.98 | 4.50 | 4.98 | 4.50 | 4.98 | 4.50 | 4.98 | 4.50 |
| 5.00 | 7.05 | 5.00 | 4.75 | 5.00 | 7.00 | 5.00 | 5.30 |
| 5.02 | 8.30 | 5.05 | 5.75 | 5.02 | 8.40 | 5.05 | 5.95 |
| 5.05 | 8.80 | 5.10 | 6.30 | 5.05 | 8.90 | 5.10 | 6.20 |
| 5.10 | 9.25 | 5.20 | 7.25 | 5.10 | 9.40 | 5.20 | 6.70 |
| 5.20 | 9.85 | 5.30 | 8.55 | 5.20 | 9.95 | 5.30 | 7.50 |
| 5.30 | 10.35 | 5.40 | 9.95 | 5.30 | 10.45 | 5.40 | 8.65 |
| 5.40 | 10.75 | 5.50 | 10.45 | 5.40 | 10.90 | 5.50 | 9.95 |

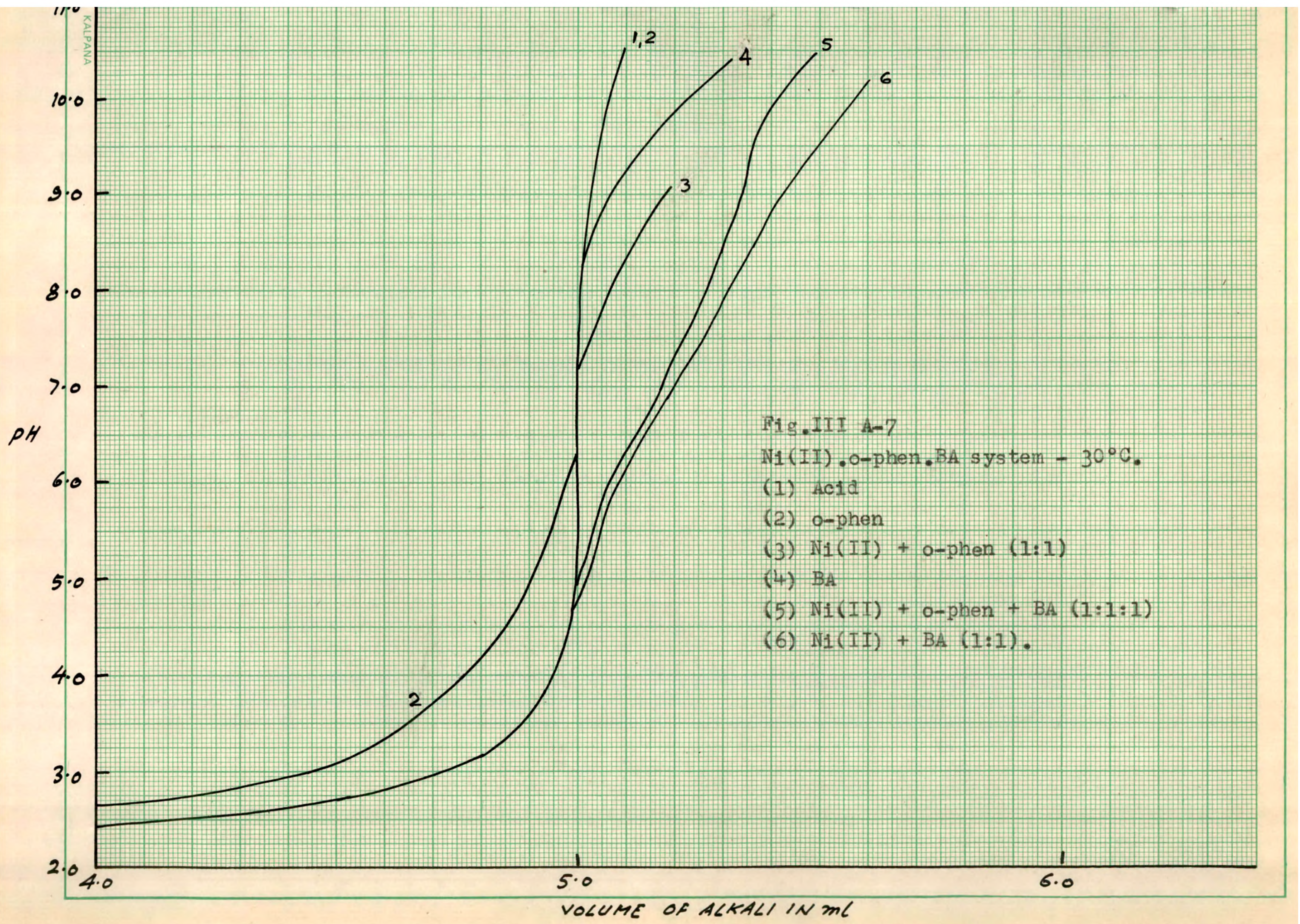



Fig.III A-7

Ni(II).o-phen.BA system - 30°C.

(1) Acid

(2) o-phen

(3) Ni(II) + o-phen (1:1)

(4) BA

(5) Ni(II) + o-phen + BA (1:1:1)

(6) Ni(II) + BA (1:1).

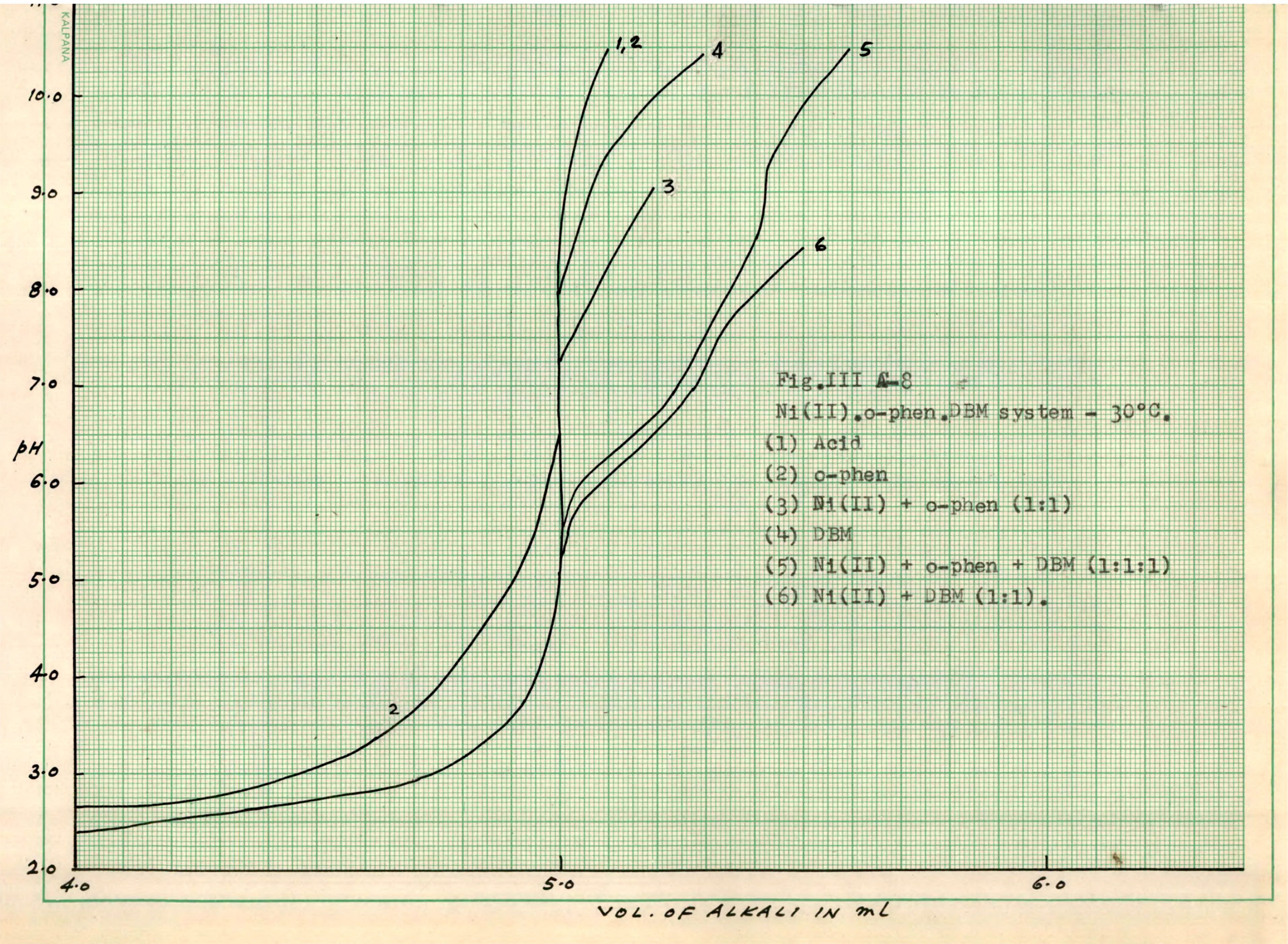



Fig. III A-8

Ni(II).o-phen.DBM system - 30°C.

(1) Acid

(2) o-phen

(3) Ni(II) + o-phen (1:1)

(4) DBM

(5) Ni(II) + o-phen + DBM (1:1:1)

(6) Ni(II) + DBM (1:1).

## Table IIIA 2.1a

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 acetylacetone system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 3.50 | $1.00_0$ | 4.89 | 5.12 | 0.23 | $0.46_1$ | $0.06_9$ | $9.21_9$ | $9.15_0$ |
| 3.55 | $1.00_0$ | 4.90 | 5.14 | 0.24 | $0.48_0$ | $0.03_5$ | $9.18_6$ | $9.15_1$ |
| 3.60 | $1.00_0$ | 4.91 | 5.16 | 0.25 | $0.50_0$ | - | $9.15_3$ | $9.15_3$ |
| 3.65 | $1.00_0$ | 4.92 | 5.17 | 0.25 | $0.50_0$ | - | $9.10_3$ | $9.10_3$ |
| 3.70 | $1.00_0$ | 4.93 | 5.19 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $9.07_1$ | $9.10_6$ |

$\log K_{MAL} = 9.13 \pm 0.01$

## Table IIIA 2.2a

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 benzoylacetone system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 3.35 | $1.00_0$ | 4.86 | 5.07 | 0.21 | $0.42_1$ | $0.13_8$ | $9.47_8$ | $9.34_0$ |
| 3.40 | $1.00_0$ | 4.88 | 5.12 | 0.24 | $0.48_1$ | $0.03_3$ | $9.47_6$ | $9.44_3$ |
| 3.45 | $1.00_0$ | 4.89 | 5.16 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $9.47_9$ | $9.55_0$ |
| 3.50 | $1.00_0$ | 4.90 | 5.19 | 0.29 | $0.58_1$ | $\bar{1}.85_6$ | $9.46_9$ | $9.61_3$ |
| 3.55 | $1.00_0$ | 4.91 | 5.20 | 0.29 | $0.58_1$ | $\bar{1}.85_6$ | $9.41_9$ | $9.56_3$ |

$\log K_{MAL} = 9.50 \pm 0.06$

Fig.III A-9 : Cu(II).dipy.AcAc system - 30°C.

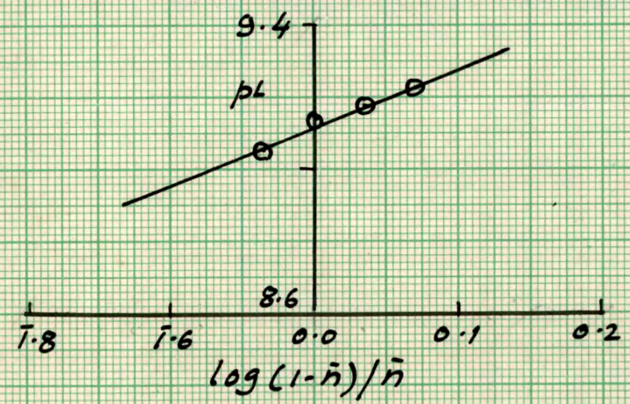
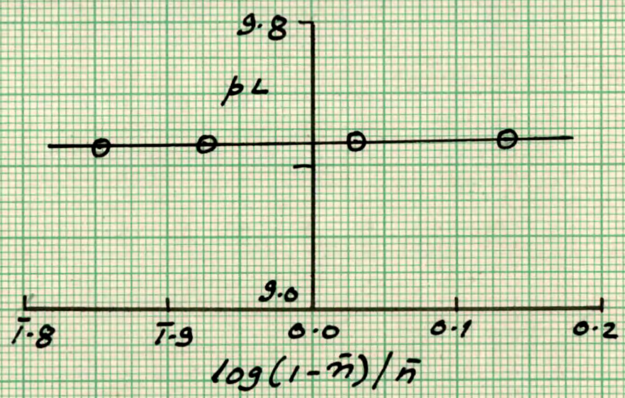



Fig.III A-10 : Cu(II).dipy.BA system - 30°C.



## Table IIIA 2.3b

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 acetylacetone 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 | $1.00_0$ | 5.00 | 5.19 | 0.19 | $0.38_0$ | $0.21_3$ | $6.65_9$ | $6.44_6$ |
| 6.10 | $1.00_0$ | 5.00 | 5.21 | 0.21 | $0.42_0$ | $0.14_0$ | $6.58_9$ | $6.44_9$ |
| 6.20 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.07_0$ | $6.51_9$ | $6.44_9$ |
| 6.25 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $6.50_3$ | $6.50_3$ |
| 6.30 | $1.00_0$ | 5.00 | 5.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $6.47_1$ | $6.50_6$ |
| 6.40 | $1.00_0$ | 5.00 | 5.29 | 0.29 | $0.58_0$ | $\bar{1}.86_0$ | $6.42_9$ | $6.56_9$ |
| 6.50 | $1.00_0$ | 5.00 | 5.31 | 0.31 | $0.62_0$ | $\bar{1}.78_7$ | $6.37_3$ | $6.58_6$ |

$\log K_{MAL} = 6.50 \pm 0.02$

## Table IIIA 2.4b

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 benzoylacetone 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 | $1.00_0$ | 5.00 | 5.20 | 0.20 | $0.40_0$ | $0.17_6$ | $6.91_4$ | $6.73_8$ |
| 6.00 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.06_9$ | $6.85_9$ | $6.79_0$ |
| 6.10 | $1.00_0$ | 5.00 | 5.24 | 0.24 | $0.48_0$ | $0.03_5$ | $6.77_6$ | $6.74_1$ |
| 6.15 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $6.74_3$ | $6.74_3$ |
| 6.20 | $1.00_0$ | 5.00 | 5.27 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $6.72_9$ | $6.79_4$ |
| 6.30 | $1.00_0$ | 5.00 | 5.28 | 0.28 | $0.56_0$ | $\bar{1}.89_5$ | $6.64_9$ | $6.75_4$ |
| 6.40 | $1.00_0$ | 5.00 | 5.29 | 0.29 | $0.58_0$ | $\bar{1}.85_9$ | $6.56_9$ | $6.71_0$ |

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

## Table IIIA 2.5b

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 dibenzoylmethane 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 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.06_9$ | $7.17_9$ | $7.11_0$ |
| 5.95 | $1.00_0$ | 5.00 | 5.24 | 0.24 | $0.48_0$ | $0.03_5$ | $7.14_6$ | $7.11_1$ |
| 6.00 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $7.11_3$ | $7.11_3$ |
| 6.05 | $1.00_0$ | 5.00 | 5.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $7.08_1$ | $7.11_6$ |
| 6.10 | $1.00_0$ | 5.00 | 5.27 | 0.27 | $0.54_0$ | $\bar{1}.93_6$ | $7.04_9$ | $7.11_3$ |
| 6.15 | $1.00_0$ | 5.00 | 5.28 | 0.28 | $0.56_0$ | $\bar{1}.89_5$ | $7.01_9$ | $7.12_4$ |
| 6.20 | $1.00_0$ | 5.00 | 5.29 | 0.29 | $0.58_0$ | $\bar{1}.85_9$ | $6.98_9$ | $7.13_0$ |

$\log K_{MAL} = 7.11 \pm 0.01$

Fig.III A-11 : Ni(II).dipy.AcAc system - 30°C.

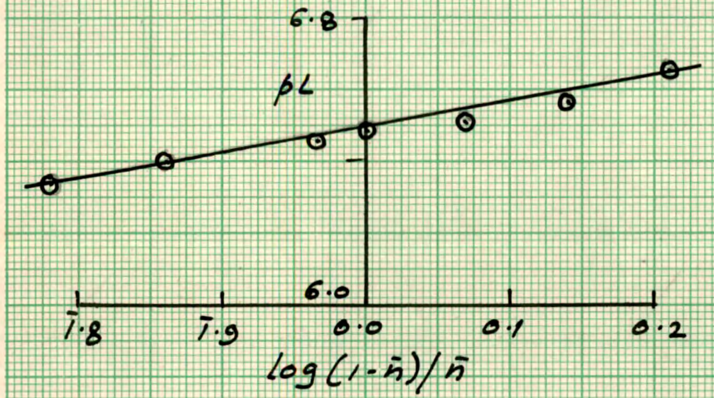



Fig.III A-12 : Ni(II).dipy.BA system - 30°C.

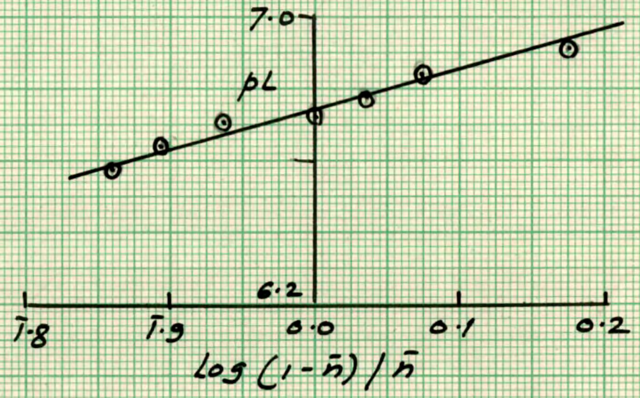



Fig.III A-13 : Ni(II).dipy.DBM system - 30°C.

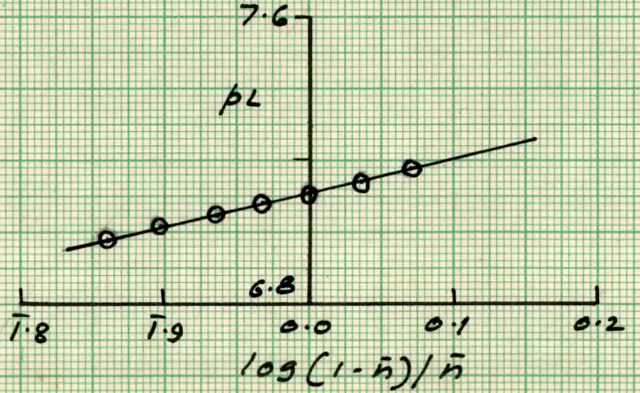


Table IIIA 2.6c

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-phenanthroline acetylacetone system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL$-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 6.15 | $1.00_0$ | 5.00 | 5.07 | 0.07 | $0.28_0$ | $0.41_0$ | $6.74_5$ | $6.33_5$ |
| 6.20 | $1.00_0$ | 5.00 | 5.08 | 0.08 | $0.32_0$ | $0.32_7$ | $6.71_9$ | $6.39_2$ |
| 6.25 | $1.00_0$ | 5.00 | 5.08 | 0.08 | $0.32_0$ | $0.32_7$ | $6.66_9$ | $6.34_2$ |
| 6.30 | $1.00_0$ | 5.00 | 5.09 | 0.09 | $0.36_0$ | $0.24_9$ | $6.64_6$ | $6.39_7$ |
| 6.35 | $1.00_0$ | 5.00 | 5.10 | 0.10 | $0.40_0$ | $0.17_6$ | $6.62_4$ | $6.44_8$ |

$\log K_{MAL} = 6.38 \pm 0.04$

Table IIIA 2.7c

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-phenanthroline benzoylacetone 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 | $1.00_0$ | 5.00 | 5.09 | 0.09 | $0.36_0$ | $0.24_9$ | $6.88_6$ | $6.63_7$ |
| 6.30 | $1.00_0$ | 5.00 | 5.10 | 0.10 | $0.40_0$ | $0.17_6$ | $6.81_4$ | $6.63_8$ |
| 6.40 | $1.00_0$ | 5.00 | 5.11 | 0.11 | $0.44_0$ | $0.10_5$ | $6.74_4$ | $6.63_9$ |
| 6.50 | $1.00_0$ | 5.00 | 5.12 | 0.12 | $0.48_0$ | $0.03_5$ | $6.67_6$ | $6.64_1$ |
| 6.60 | $1.00_0$ | 5.00 | 5.13 | 0.13 | $0.52_0$ | $\bar{1}.96_5$ | $6.61_1$ | $6.64_6$ |

$\log K_{MAL} = 6.64 \pm 0.01$

Table IIIA 2.8c

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-phenanthroline dibenzoylmethane 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 | $1.00_0$ | 5.00 | 5.10 | 0.10 | $0.40_0$ | $0.17_6$ | $7.13_4$ | $6.95_8$ |
| 6.25 | $1.00_0$ | 5.00 | 5.11 | 0.11 | $0.44_0$ | $0.10_5$ | $7.11_4$ | $7.00_9$ |
| 6.30 | $1.00_0$ | 5.00 | 5.12 | 0.12 | $0.48_0$ | $0.03_5$ | $7.09_6$ | $7.06_1$ |
| 6.35 | $1.00_0$ | 5.00 | 5.13 | 0.13 | $0.52_0$ | $\bar{1}.96_5$ | $7.08_1$ | $7.11_6$ |

$\log K_{MAL} = 7.04 \pm 0.04$

Fig.III A-14 : Ni(II).o-phen.AcAc system - 30°C.

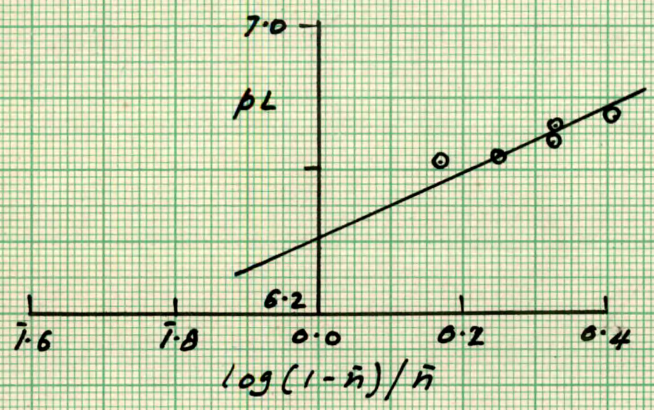



Fig.III A-15 : Ni(II).o-phen.BA system - 30°C.

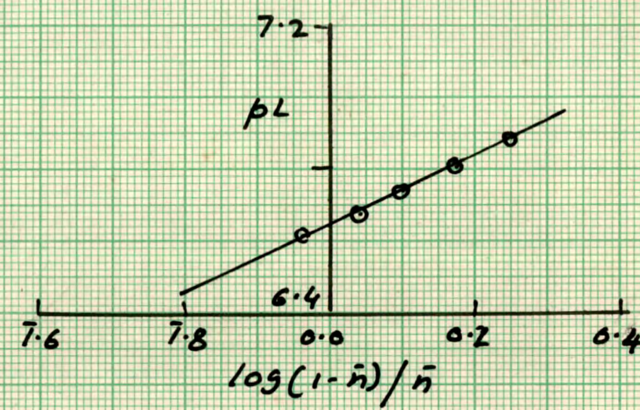



Fig.III A-16 : Ni(II).o.phen.DBM system - 30°C.

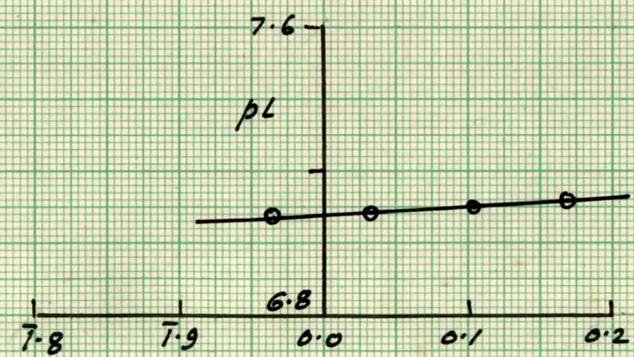


Table III A-3.0 : Stability constants of ternary dipyridyl-$M^{2+}$-complexes and o-phenanthroline $M^{2+}$-ligand complexes - 30°C.

| Ligand | $\log K^{Cu.dipy}_{Cu.dipy.L}$ | $\log K^{Ni.dipy}_{Ni.dipy.L}$ | $\log K^{Ni.o-phen}_{Ni.o-phen.L}$ |
|---|---|---|---|
| Acetylacetone | $9.13 \pm 0.01$ | $6.50 \pm 0.02$ | $6.38 \pm 0.04$ |
| Benzoylacetone | $9.50 \pm 0.06$ | $6.75 \pm 0.04$ | $6.64 \pm 0.01$ |
| Dibenzoylmethane | - | $7.12 \pm 0.01$ | $7.04 \pm 0.04$ |

## Section B

A survey of the literature shows that not much work has been done on mixed ligand complexes containing dipyridyl or o-phenanthroline and tridentate Schiff base ligands.

As seen in previous chapter in cases of ligands HEA, HEBA, HPA and HPBA it could not be confirmed whether the ligand is tridentate or bidentate in binary complexes. The ternary complexes [MAL] were therefore studied where M = Cu(II) or Ni(II); A = dipyridyl or o-phenanthroline and L = HEA or HEBA or HPA or HPBA. An extension of Irving-Rossotti titration technique[26,48] has been used as in previous Section III-A.

## Experimental :

The tridentate Schiff bases, used as secondary ligands, were prepared as detailed in chapter II- Section II-c. Other chemicals used were same as detailed in previous Section III-A. All solutions were prepared in 50% dioxan medium. The solutions were prepared as follows :

1. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.05M, 10.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (11.1 ml.) + dioxan (15.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.05M, 10.0 ml.) + metal perchlorate (0.01M, 5.0 ml.) + dipyridyl (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (1.3 ml.) + dioxan (15.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

3. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.05M, 10.0 ml.) + metal perchlorate (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (6.2 ml.) + dioxan (15.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.
4. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.01M, 5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + conductivity water (6.0 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl (0.01M, 5.0 ml.) + metal perchlorate (0.01M, 5.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (1.2 ml.)+ dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.
6. Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1M, 9.0 ml.) + conductivity water (11.0 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

It is seen that in $[M(dipy)L]$ solutions the ligands are in the ratio 1:1:1. An excess of the secondary ligand has been taken unlike in the cases of mixed ligand systems described in the previous section. This is because the tridentate Schiff base undergoes hydrolysis in dilute solutions.

Discussion :

$[M(dipy)]^{2+}$ formation is complete at low pH and stable upto high pH as seen in previous section. The combination of the secondary ligands (tridentate Schiff bases) with $[M(dipy)]^{2+}$ takes place below the pH where $[M(dipy)(OH)_2]$ is formed. $\bar{n}$ and pL values were calculated by using the equation suggested in previous section. Average value of $\log K^{M(dipy)}_{M(dipy)L}$ was found out by using the method of linear plots.[54] The figs. and tables have been presented in fig. IIIB 1 to IIIB 12 and tables IIIB 2.1a to IIIB 2.4c.

It is observed that the values of formation constants $K^{M}_{M(S.B.)} \approx K^{M(dipy)}_{M(dipy)(S.B.)}$. Earlier studies of the ternary systems $[M(dipy)(\beta\text{-diket})]$ also has shown that $K^{M}_{M(\beta\text{-diket})}$ is nearly equal to $K^{M(dipy)}_{M(dipy)(\beta\text{-diket})}$. This has been attributed to the special behaviour of dipyridyl as explained in section IIIA.[23,24,26,42-44]

The study of the tridentate ligand in ternary complexes in solutions will show whether the coordination from alkylamine -OH is possible or not.

It is observed that in Cu(II) complexes $K^{MA}_{MAL}$ is slightly higher than $K^{M}_{ML}$. Such observation has been made earlier[16] in case of $[Cu(dipy)(polyphenols)]$. This can be attributed to dynamic Jahn-Tellor distortion. Dipyridyl being a strongly coordinating neutral ligand produces stronger electrical field around the Cu(II) ion during formation of $[Cu(dipy)(H_2O)_2]^{2+}$. The distorted octahedron $[Cu(H_2O)_6]^{2+}$ gets somewhat more strongly distorted towards the square planar structure on coordination of dipyridyl, thus creating the right geometry for coordination of secondary ligand and resulting in increase in the value of $K^{MA}_{MAL}$.[24]

In case of Ni(II) mixed ligand complexes with dipyridyl, the formation constants $K^{M(dipy)}_{M(dipy)L}$ are higher than corresponding mixed ligand complexes with o-phenanthroline,

$K^{M(o\text{-}phen)}_{M(o\text{-}phen)L}$. This can be expected to be due to the bigger size of o-phenanthroline molecule; which produces more steric hindrance. Besides, the metal ligand $\pi$ interaction is less in $[Ni(o\text{-}phen)]^{2+}$ and hence its tendency to bind with the secondary ligand will be less than that of $[Ni(dipy)]^{2+}$.

Thus the present ligands behave similarly as earlier bidentate ligands. If the ligand would have been tridentate, a lowering in the value of $K^{Cu}_{Cu.A.L}$ would have been observed. In case of Cu(II) mixed ligand complex, dipyridyl already occupies two positions in the equatorial plane. The tridentate ligand with a double bond cannot occupy two positions in equatorial and one in the axial direction.[55,56] A large amount of strain will be felt if the tridentate ligand occupies one position in the equatorial and two in the axial direction forming a trigonal bipyramidal structure. Due to Jahn-Tellor effect in Cu(II) complexes, the ligand will be put to strain in occupying the two axial positions.[57] The strain would cause $K^{Cu.A}_{Cu.A.L}$ to go down considerably compared to $K^{Cu}_{Cu.L}$. However, $K^{Cu.A}_{Cu.A.L}$ is nearly equal to $K^{Cu}_{Cu.L}$. Hence it can be concluded that the -OH end of the alkylamine part of the ligand does not get coordinated and the Schiff base behaves as a bidentate ligand; in the binary as well as the ternary complexes. It has been shown by various workers that other tridentate Schiff bases, though having three coordination sites, behave as bidentate in solution.[57a]

## Table IIIB 1.1

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

$E^{\circ} = 0.02M$  $T^{\circ}_{L} = 0.01M$  $\mu = 0.2M$  $t = 30^{\circ}C.$

| 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 | 1.85 | 0.00 | 1.85 | 0.00 | 1.85 | 0.00 | 1.85 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.20 | 3.00 | 2.20 | 3.00 | 2.20 | 3.00 | 2.25 |
| 4.00 | 2.40 | 3.50 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.00 | 2.75 | 4.50 | 2.85 | 4.50 | 2.90 |
| 4.60 | 2.85 | 4.50 | 3.20 | 4.60 | 2.95 | 4.60 | 3.05 |
| 4.70 | 3.00 | 4.60 | 3.35 | 4.70 | 3.05 | 4.70 | 3.20 |
| 4.80 | 3.25 | 4.70 | 3.60 | 4.80 | 3.25 | 4.80 | 3.45 |
| 4.85 | 3.45 | 4.80 | 4.00 | 4.85 | 3.45 | 4.85 | 3.60 |
| 4.90 | 3.75 | 4.85 | 4.40 | 4.90 | 3.75 | 4.90 | 3.80 |
| 4.93 | 4.00 | 4.90 | 4.90 | 5.00 | 5.50 | 4.95 | 4.45 |
| 4.96 | 4.75 | 4.93 | 5.20 | 5.10 | 6.30 | 5.00 | 5.40 |
| 4.98 | 5.25 | 4.96 | 5.65 | 5.20 | 6.50 | 5.10 | 6.85 |
| 5.00 | 7.85 | 5.00 | 7.50 | 5.30 | 6.85 | 5.20 | 7.00 |
| 5.02 | 8.60 | 5.05 | 9.30 | 5.40 | 7.50 | 5.30 | 7.75 (ppts) |
| 5.05 | 9.20 | 5.10 | 10.05 | 5.50 | 8.65 (ppts) | | |
| 5.08 | 9.75 | 5.15 | 10.50 | | | | |
| 5.10 | 10.00 | | | | | | |
| 5.15 | 10.50 | | | | | | |

Table IIIB 1.2

N = 0.2M  V° = 50 ml.  $T^{\circ}_{L}$ = 0.01M  $T^{\circ}_{M}$ = 0.001M

E° = 0.02M  $T^{\circ}_{Dipy}$ = 0.001M  $\mu$ = 0.2M  t = 30°C.

| HEA | | Cu.Dipy.HEA | | Ni.Dipy.HEA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 |
| 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 |
| 1.00 | 2.25 | 1.00 | 2.25 | 1.00 | 2.20 |
| 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 |
| 2.00 | 2.80 | 2.00 | 2.80 | 2.00 | 2.80 |
| 2.10 | 2.90 | 2.20 | 3.05 | 2.20 | 3.05 |
| 2.20 | 3.05 | 2.40 | 3.10 | 2.40 | 4.00 |
| 2.30 | 3.30 | 2.50 | 3.15 | 2.50 | 4.50 |
| 2.35 | 3.45 | 2.60 | 3.25 | 2.60 | 5.15 |
| 2.40 | 4.05 | 2.70 | 3.45 | 2.70 | 5.80 |
| 2.43 | 6.00 | 2.80 | 3.95 | 2.80 | 6.35 |
| 2.47 | 6.90 | 2.90 | 5.45 | 2.90 | 7.00 |
| 2.50 | 7.25 | 3.00 | 6.45 | 3.00 | 7.50 |
| 2.60 | 7.75 | 3.10 | 7.45 | 3.10 | 7.85 |
| 2.70 | 8.00 | 3.20 | 8.10 | 3.20 | 8.10 |
| 2.80 | 8.20 | 3.30 | 8.40 | 3.30 | 8.30 |
| 2.90 | 8.35 | 3.40 | 8.60 | 3.40 | 8.50 |
| 3.00 | 8.45 | | | | |
| 3.50 | 8.70 | | | | |
| 4.00 | 8.90 | | | | |
| 4.50 | 9.20 | | | | |
| 5.00 | 9.50 | | | | |
| 5.50 | 9.65 | | | | |
| 6.00 | 9.85 | | | | |

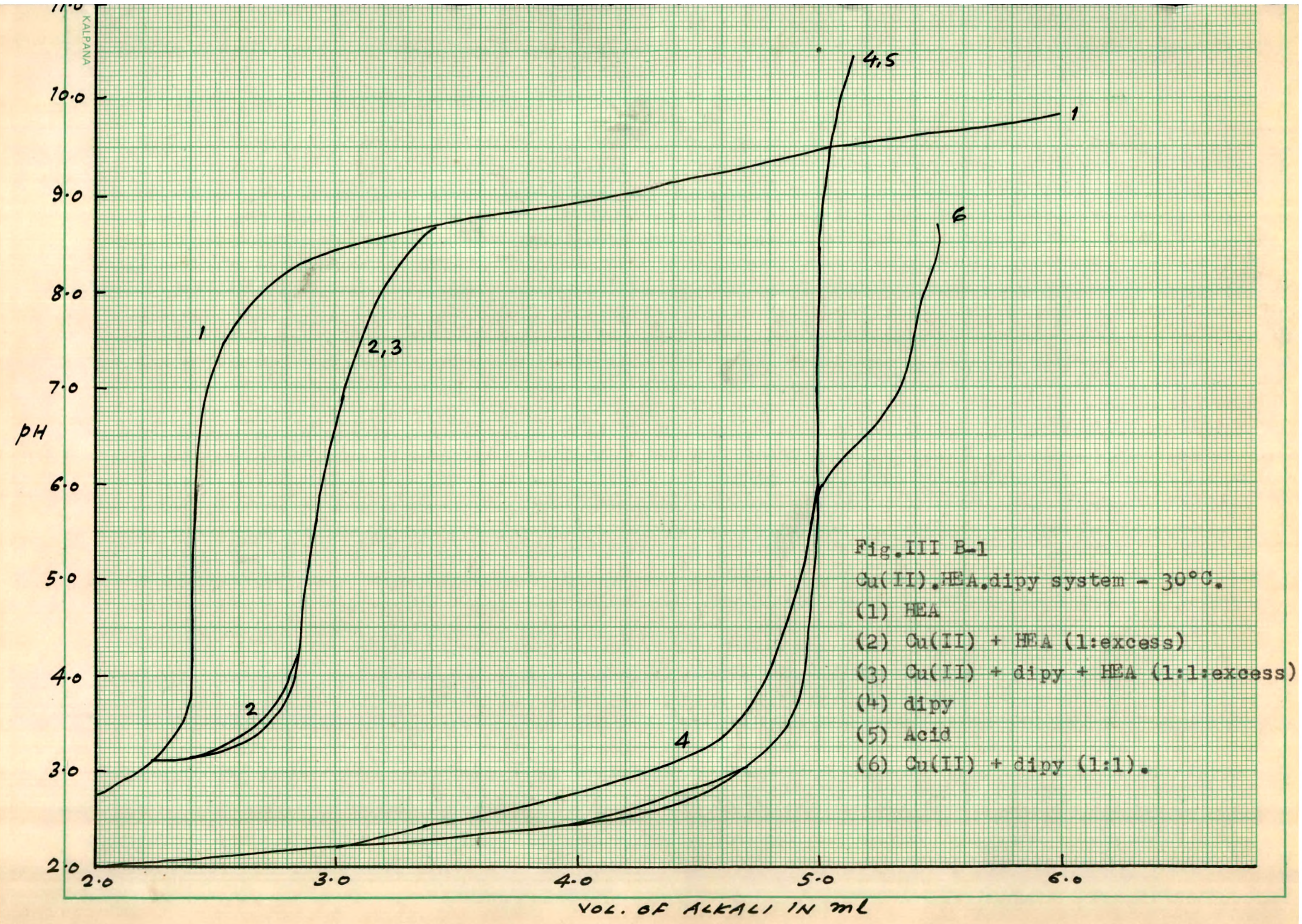



Fig. III B-1
Cu(II).HEA.dipy system - 30°C.
(1) HEA
(2) Cu(II) + HEA (1:excess)
(3) Cu(II) + dipy + HEA (1:1:excess)
(4) dipy
(5) Acid
(6) Cu(II) + dipy (1:1).

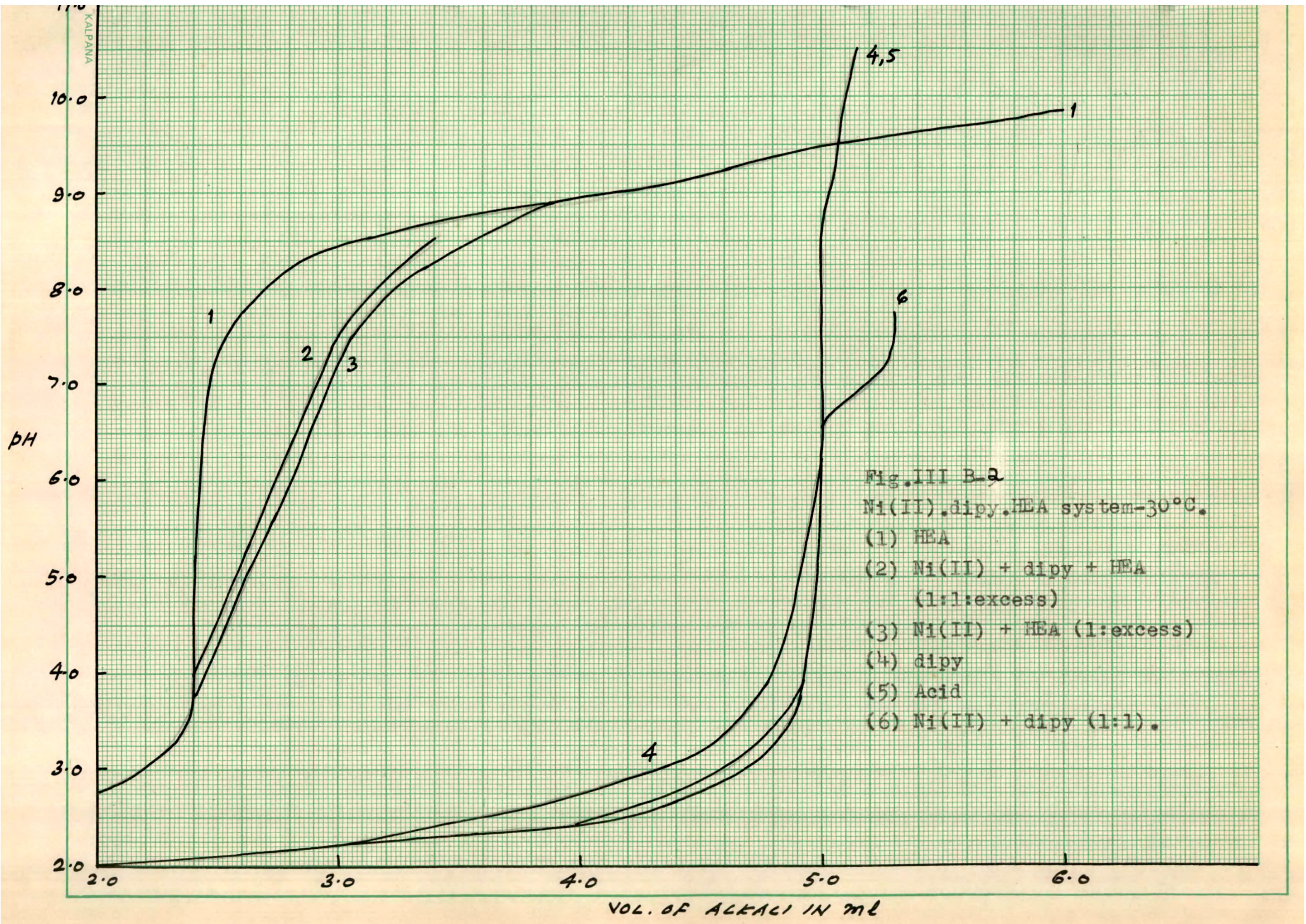



Fig.III B-2

Ni(II).dipy.HEA system-30°C.

(1) HEA

(2) Ni(II) + dipy + HEA
(1:1:excess)

(3) Ni(II) + HEA (1:excess)

(4) dipy

(5) Acid

(6) Ni(II) + dipy (1:1).

## Table IIIB 1.3

N = 0.2M  $V^{\circ}$ = 50 ml.  $T_L^{\circ}$ = 0.01M  $T_M^{\circ}$ = 0.001M

$E^{\circ}$ = 0.02M  $T_{Dipy}^{\circ}$ = 0.001M  $\mu$ = 0.2M  t = 30°C.

| HEBA | | Cu.Dipy.HEBA | | Ni.Dipy.HEBA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 |
| 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 |
| 1.00 | 2.25 | 1.00 | 2.25 | 1.00 | 2.25 |
| 1.50 | 2.50 | 1.50 | 2.50 | 2.00 | 2.85 |
| 2.00 | 2.85 | 2.00 | 2.85 | 2.20 | 3.10 |
| 2.10 | 2.95 | 2.10 | 2.95 | 2.40 | 3.75 |
| 2.20 | 3.10 | 2.20 | 3.10 | 2.50 | 4.70 |
| 2.30 | 3.35 | 2.40 | 3.15 | 2.60 | 5.30 |
| 2.35 | 3.55 | 2.50 | 3.20 | 2.70 | 5.75 |
| 2.40 | 3.80 | 2.60 | 3.30 | 2.80 | 6.35 |
| 2.43 | 5.25 | 2.70 | 3.50 | 2.90 | 6.90 |
| 2.45 | 6.60 | 2.80 | 3.80 | 3.00 | 7.45 |
| 2.50 | 7.45 | 2.90 | 4.30 | 3.10 | 7.85 |
| 2.60 | 7.85 | 3.00 | 5.75 | 3.20 | 8.10 |
| 2.70 | 8.05 | 3.10 | 8.00 | 3.30 | 8.25 |
| 2.80 | 8.25 | 3.20 | 8.50 | 3.40 | 8.40 |
| 2.90 | 8.40 | 3.30 | 8.75 | 3.50 | 8.55 |
| 3.00 | 8.50 | 3.40 | 8.80 | 3.60 | 8.65 |
| 3.50 | 8.80 | | | 3.70 | 8.75 |
| 4.00 | 9.05 | | | 3.80 | 8.80 |
| 4.50 | 9.20 | | | | |
| 5.00 | 9.45 | | | | |
| 5.50 | 9.80 | | | | |
| 6.00 | 10.15 | | | | |

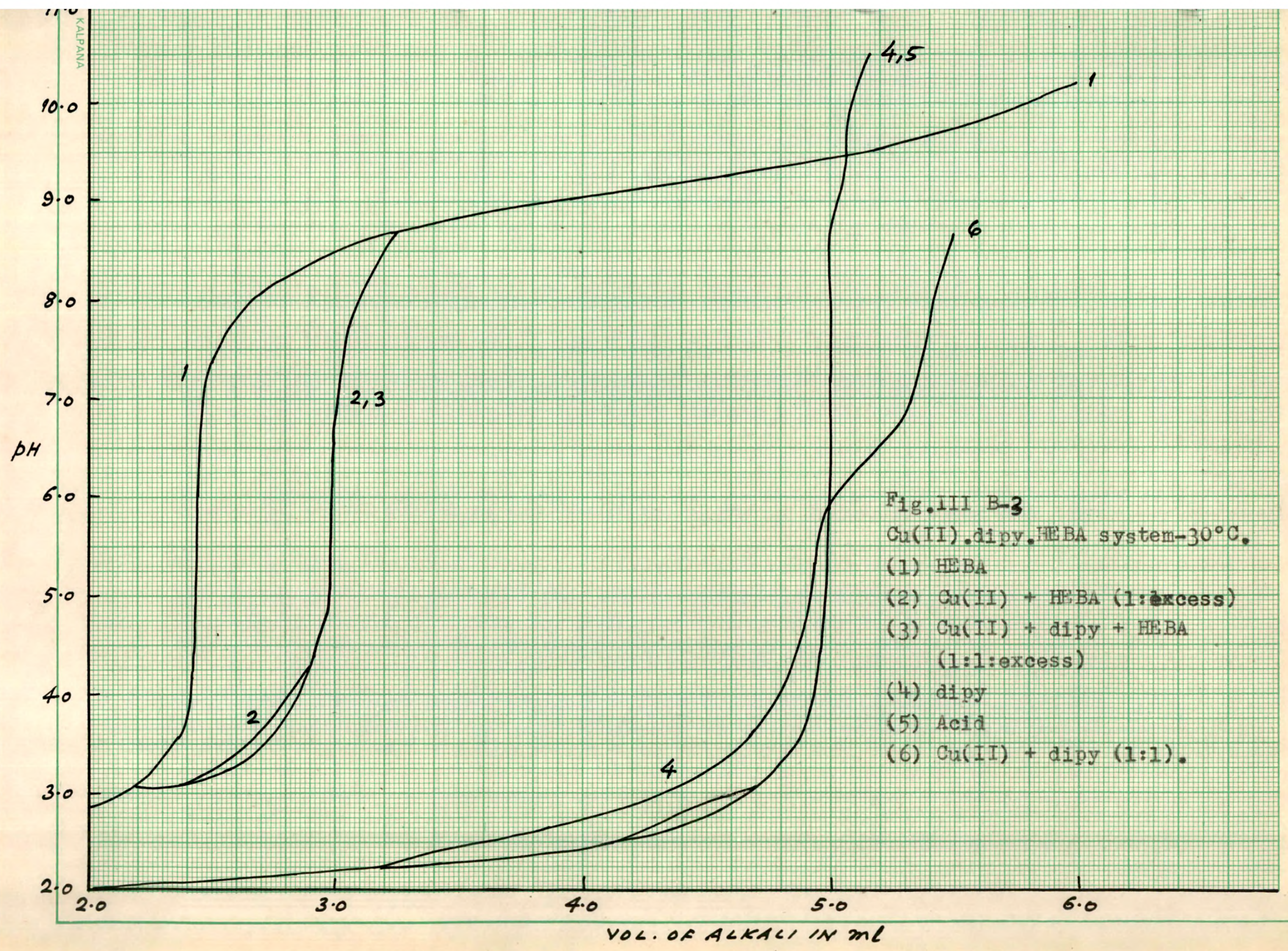



Fig.III B-3

Cu(II).dipy.HEBA system-30°C.

(1) HEBA

(2) Cu(II) + HEBA (1:excess)

(3) Cu(II) + dipy + HEBA (1:1:excess)

(4) dipy

(5) Acid

(6) Cu(II) + dipy (1:1).

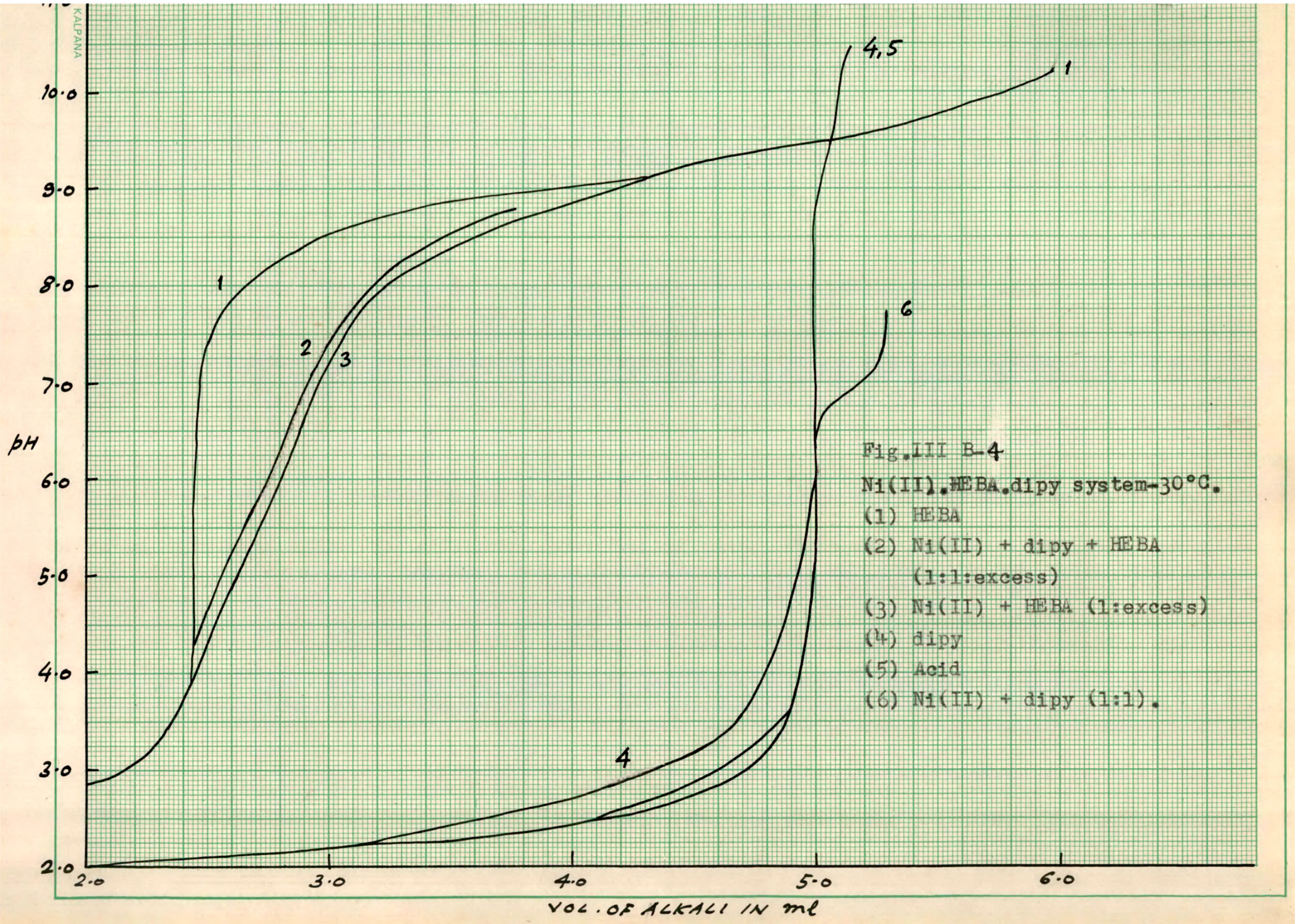



Fig. III B-4

Ni(II).HEBA.dipy system-30°C.

(1) HEBA

(2) Ni(II) + dipy + HEBA (1:1:excess)

(3) Ni(II) + HEBA (1:excess)

(4) dipy

(5) Acid

(6) Ni(II) + dipy (1:1).

Table IIIB 1.4

N = 0.2M  $V^{\circ}$ = 50 ml.  $T^{\circ}_{L}$ = 0.01M  $T^{\circ}_{M}$ = 0.001M

E° = 0.02M  $T^{\circ}_{Dipy}$ = 0.001M  $\mu$ = 0.2M  t = 30°C.

| HPA | | Cu.Dipy.HPA | | Ni.Dipy.HPA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 |
| 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 |
| 1.00 | 2.25 | 1.00 | 2.25 | 1.00 | 2.25 |
| 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 |
| 2.00 | 2.80 | 2.00 | 2.80 | 2.00 | 2.80 |
| 2.10 | 2.95 | 2.20 | 3.10 | 2.20 | 3.10 |
| 2.20 | 3.10 | 2.40 | 3.15 | 2.40 | 4.10 |
| 2.30 | 3.40 | 2.50 | 3.20 | 2.50 | 4.65 |
| 2.35 | 3.60 | 2.60 | 3.25 | 2.60 | 5.20 |
| 2.40 | 3.90 | 2.70 | 3.50 | 2.70 | 5.70 |
| 2.42 | 5.75 | 2.80 | 3.95 | 2.80 | 6.25 |
| 2.44 | 6.45 | 2.90 | 4.50 | 2.90 | 6.80 |
| 2.46 | 6.85 | 3.00 | 6.50 | 3.00 | 7.25 |
| 2.48 | 7.25 | 3.10 | 8.00 | 3.10 | 7.60 |
| 2.50 | 7.50 | 3.20 | 8.50 | 3.20 | 7.95 |
| 2.60 | 7.95 | 3.30 | 8.75 | 3.30 | 8.10 |
| 2.70 | 8.15 | 3.40 | 8.80 | 3.40 | 8.30 |
| 2.80 | 8.30 | 3.50 | 8.85 | 3.60 | 8.55 |
| 3.00 | 8.55 | 3.60 | 8.90 | 3.80 | 8.75 |
| 3.50 | 8.85 | | | 4.00 | 8.95 |
| 4.00 | 9.05 | | | | |
| 4.50 | 9.35 | | | | |
| 5.00 | 9.60 | | | | |
| 5.50 | 9.90 | | | | |
| 6.00 | 10.20 | | | | |

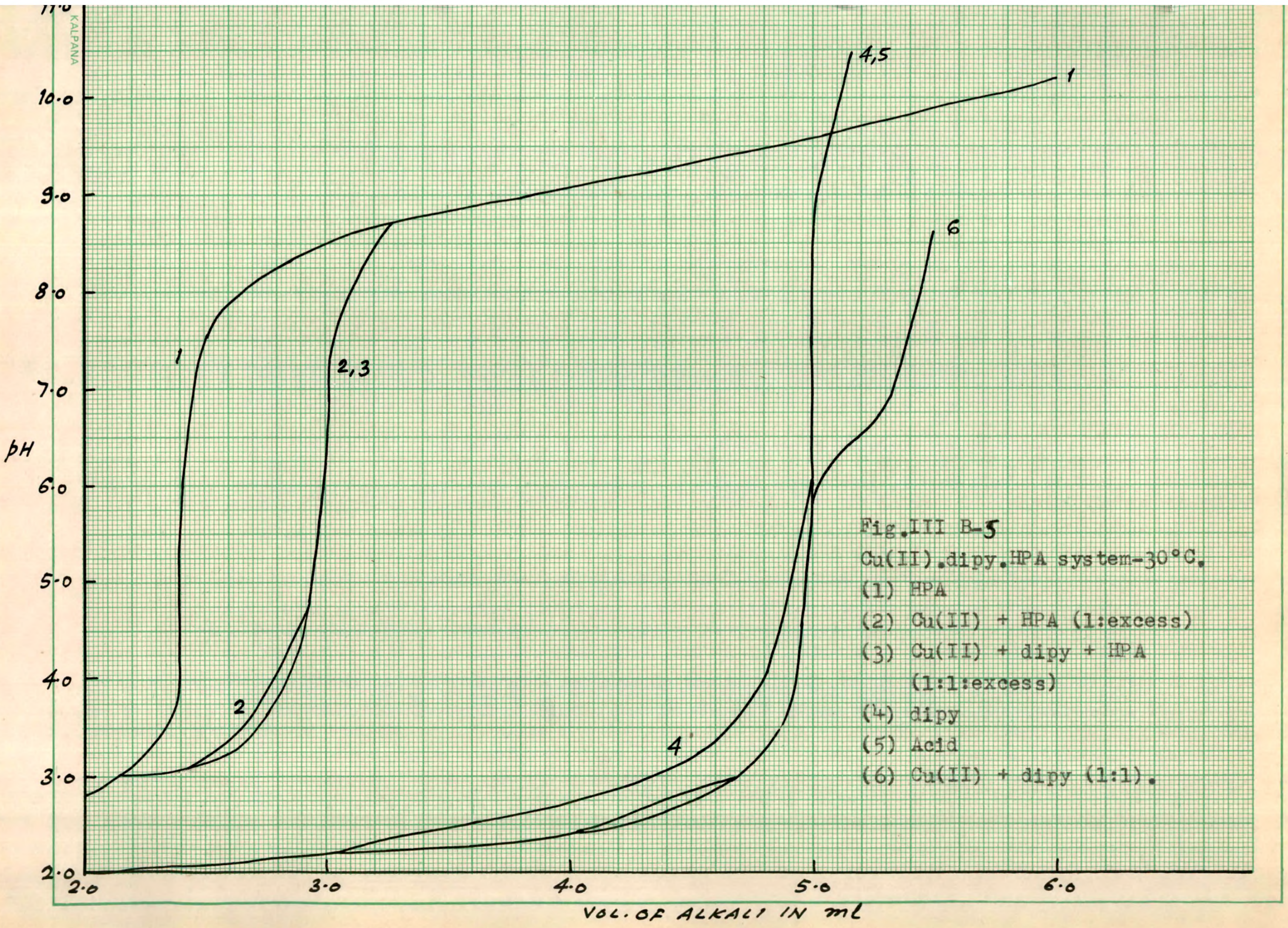



Fig. III B-5
Cu(II).dipy.HPA system-30°C.
(1) HPA
(2) Cu(II) + HPA (1:excess)
(3) Cu(II) + dipy + HPA (1:1:excess)
(4) dipy
(5) Acid
(6) Cu(II) + dipy (1:1).

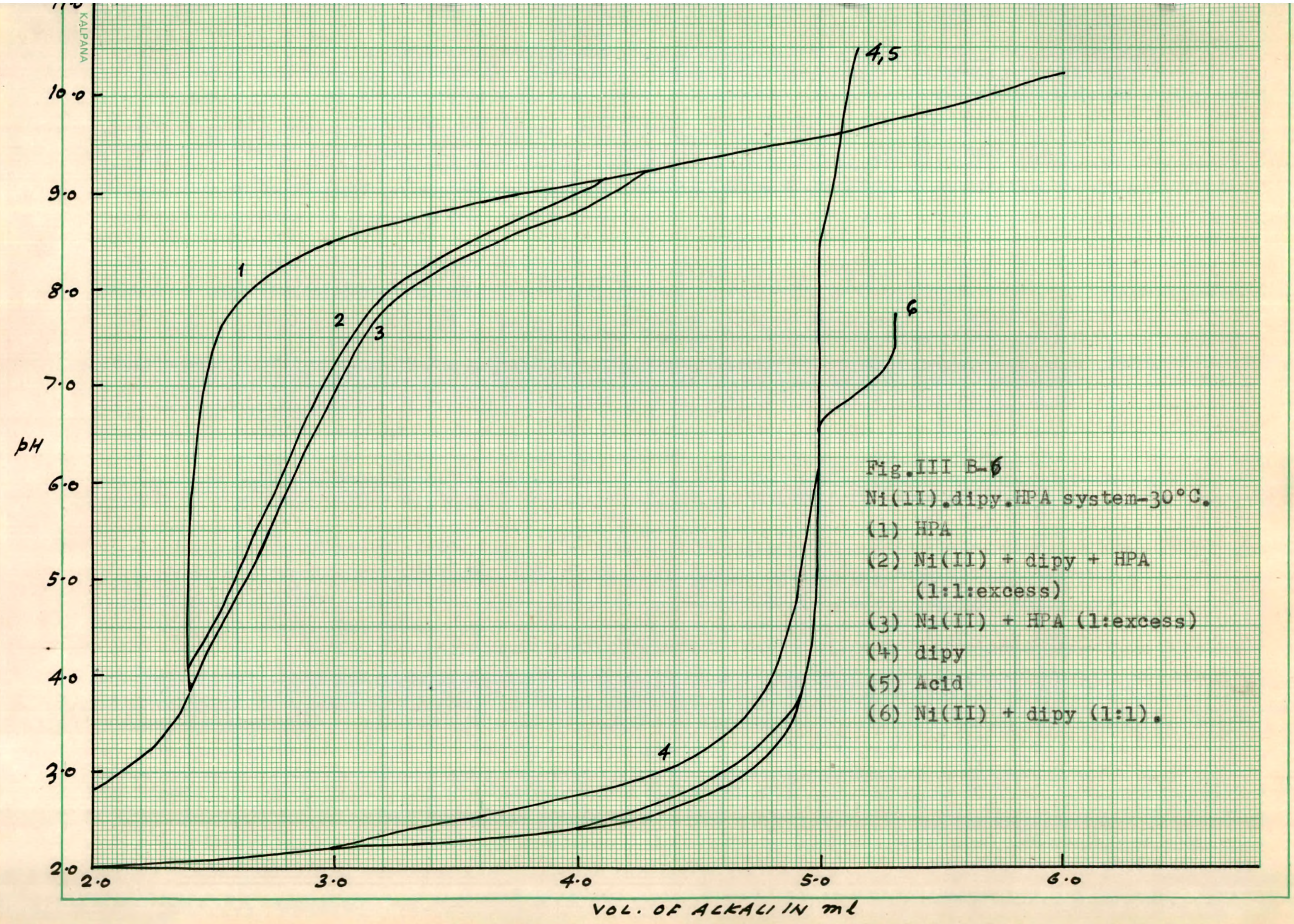


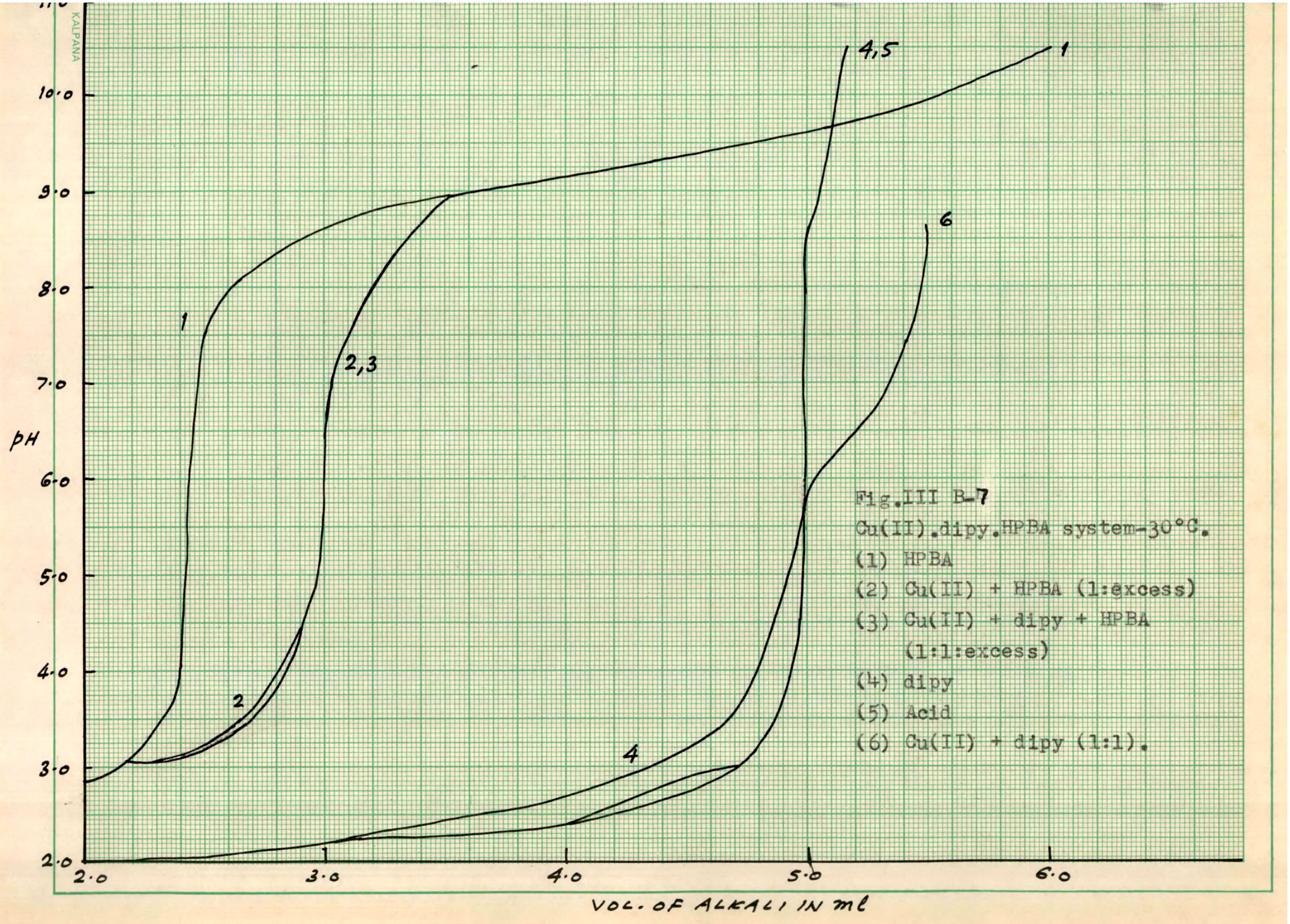
Fig.III B-6
Ni(II).dipy.HPA system-30°C.
(1) HPA
(2) Ni(II) + dipy + HPA (1:1:excess)
(3) Ni(II) + HPA (1:excess)
(4) dipy
(5) Acid
(6) Ni(II) + dipy (1:1).
pH
VOL. OF ALKALI IN ml
1
2
3
4
4,5
6
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
KALPANA

Table IIIB 1.5

N = 0.2M  V° = 50 ml.  $T_L^o$ = 0.01M  $T_M^o$ = 0.001M

E° = 0.02M  $T_{Dipy}^o$ = 0.001M  $\mu$ = 0.2M  t = 30°C.

| HPBA | | Cu.Dipy.HPBA | | Ni.Dipy.HPBA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 |
| 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 |
| 1.00 | 2.25 | 1.00 | 2.25 | 1.00 | 2.25 |
| 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 |
| 2.00 | 2.85 | 2.00 | 2.85 | 2.00 | 2.85 |
| 2.10 | 2.95 | 2.20 | 3.05 | 2.20 | 3.15 |
| 2.20 | 3.15 | 2.40 | 3.10 | 2.40 | 4.10 |
| 2.30 | 3.40 | 2.50 | 3.15 | 2.50 | 4.50 |
| 2.35 | 3.65 | 2.60 | 3.30 | 2.60 | 5.00 |
| 2.40 | 4.00 | 2.70 | 3.55 | 2.70 | 5.55 |
| 2.43 | 5.45 | 2.80 | 3.90 | 2.80 | 6.05 |
| 2.46 | 6.50 | 2.90 | 4.40 | 2.90 | 6.70 |
| 2.48 | 7.00 | 3.00 | 6.00 | 3.00 | 7.25 |
| 2.50 | 7.50 | 3.10 | 7.60 | 3.10 | 7.60 |
| 2.60 | 7.95 | 3.20 | 8.05 | 3.20 | 7.90 |
| 2.70 | 8.25 | 3.30 | 8.35 | 3.40 | 8.35 |
| 2.80 | 8.40 | 3.40 | 8.65 | 3.60 | 8.60 |
| 2.90 | 8.55 | 3.50 | 8.90 | 3.80 | 8.80 |
| 3.00 | 8.65 | 3.60 | 9.00 | 4.00 | 9.00 |
| 3.50 | 8.95 | | | | |
| 4.00 | 9.15 | | | | |
| 4.50 | 9.40 | | | | |
| 5.00 | 9.65 | | | | |
| 5.50 | 9.95 | | | | |
| 6.00 | 10.50 | | | | |



pH
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
2·0
3·0
4·0
5·0
6·0
VOL. OF ALKALI IN ml
1
2,3
2
4
4,5
6
KALPANA
Cu(II).dipy.HPBA system-30°C.
(1) HPBA
(2) Cu(II) + HPBA (1:excess)
(3) Cu(II) + dipy + HPBA
(1:1:excess)
(4) dipy
(5) Acid
(6) Cu(II) + dipy (1:1).


Fig.III B-7

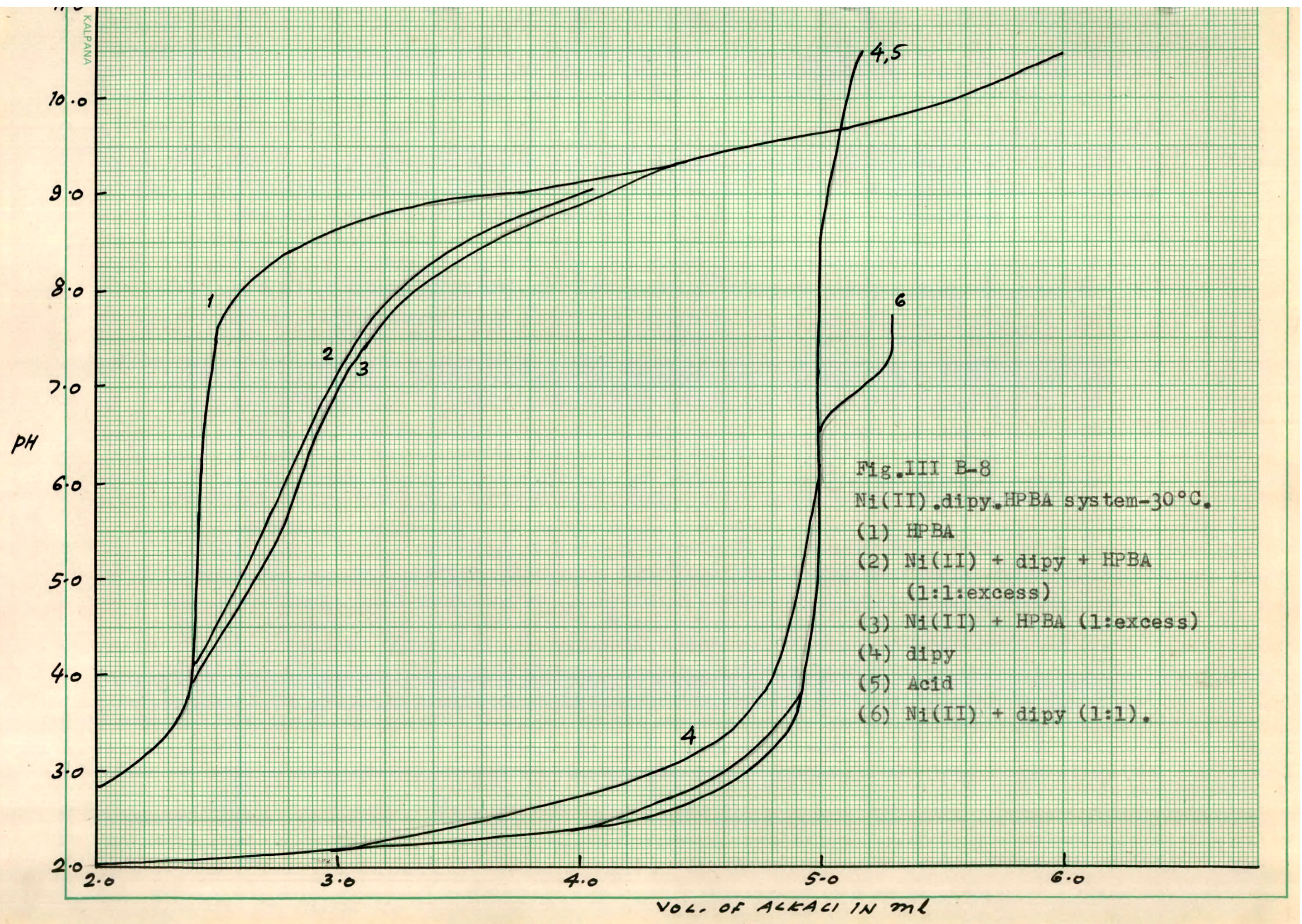



Fig.III B-8

Ni(II).dipy.HPBA system-30°C.

(1) HPBA

(2) Ni(II) + dipy + HPBA
(1:1:excess)

(3) Ni(II) + HPBA (1:excess)

(4) dipy

(5) Acid

(6) Ni(II) + dipy (1:1).

## Table IIIB 1.6

$N = 0.2M$ $V^{\circ} = 50$ ml. $T^{\circ}_{o\text{-}phen} = 0.001M$ $T^{\circ}_{M} = 0.001M$

$E^{\circ} = 0.02M$ $\mu = 0.2M$ $t = 30^{\circ}C.$

| Perchloric acid | | o-phen | | Ni.o-phen | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.85 | 0.00 | 1.85 | 0.00 | 1.85 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.20 | 3.00 | 2.20 | 3.00 | 2.20 |
| 4.00 | 2.40 | 4.00 | 2.65 | 4.00 | 2.40 |
| 4.50 | 2.75 | 4.10 | 2.70 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.20 | 2.75 | 4.60 | 2.85 |
| 4.70 | 3.00 | 4.30 | 2.85 | 4.70 | 3.00 |
| 4.80 | 3.25 | 4.40 | 2.95 | 4.80 | 3.25 |
| 4.85 | 3.35 | 4.50 | 3.15 | 4.85 | 3.35 |
| 4.90 | 3.65 | 4.60 | 3.35 | 4.90 | 3.65 |
| 4.93 | 4.00 | 4.70 | 3.65 | 4.94 | 4.35 |
| 4.96 | 4.75 | 4.80 | 4.15 | 4.98 | 5.25 |
| 4.98 | 5.25 | 4.85 | 4.45 | 5.00 | 7.00 |
| 5.00 | 7.85 | 4.90 | 4.90 | 5.05 | 7.90 |
| 5.02 | 8.60 | 4.94 | 5.25 | 5.10 | 8.35 |
| 5.05 | 9.20 | 4.98 | 5.75 | 5.20 | 9.10 |
| 5.08 | 9.75 | 5.00 | 8.50 | | |
| 5.10 | 10.00 | 5.05 | 9.20 | | |
| 5.15 | 10.50 | 5.10 | 10.00 | | |
| | | 5.15 | 10.50 | | |

## Table IIIB 1.7

N = 0.2M $V^{\circ}$ = 50 ml. $T^{\circ}_{o\text{-}phen}$ = 0.001M $T^{\circ}_{M}$ = 0.001M

$E^{\circ}$ = 0.02M $T^{\circ}_{L}$ = 0.01M $\mu$ = 0.2M t = 30°C.

| HEA | | Ni.o-phen.HEA | | HEBA | | Ni.o-phen.HEBA | |
|---|---|---|---|---|---|---|---|
| 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 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 |
| 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 |
| 1.00 | 2.25 | 1.00 | 2.20 | 1.00 | 2.25 | 1.00 | 2.25 |
| 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 |
| 2.00 | 2.80 | 2.00 | 2.80 | 2.00 | 2.85 | 2.00 | 2.85 |
| 2.10 | 2.90 | 2.20 | 3.05 | 2.10 | 2.95 | 2.20 | 3.05 |
| 2.20 | 3.05 | 2.40 | 4.00 | 2.20 | 3.10 | 2.40 | 3.75 |
| 2.30 | 3.30 | 2.50 | 4.65 | 2.30 | 3.35 | 2.50 | 4.75 |
| 2.35 | 3.45 | 2.60 | 5.30 | 2.35 | 3.55 | 2.60 | 5.30 |
| 2.40 | 4.05 | 2.70 | 5.95 | 2.40 | 3.80 | 2.70 | 5.80 |
| 2.43 | 6.00 | 2.80 | 6.45 | 2.43 | 5.25 | 2.80 | 6.50 |
| 2.47 | 6.90 | 2.90 | 7.00 | 2.45 | 6.60 | 2.90 | 7.05 |
| 2.50 | 7.25 | 3.00 | 7.50 | 2.50 | 7.45 | 3.00 | 7.50 |
| 2.60 | 7.75 | 3.10 | 7.90 | 2.60 | 7.85 | 3.10 | 7.85 |
| 2.70 | 8.00 | 3.20 | 8.20 | 2.70 | 8.05 | 3.20 | 8.10 |
| 2.80 | 8.20 | 3.30 | 8.40 | 2.80 | 8.25 | 3.30 | 8.30 |
| 2.90 | 8.35 | 3.40 | 8.50 | 2.90 | 8.40 | 3.40 | 8.40 |
| 3.00 | 8.45 | | | 3.00 | 8.50 | 3.50 | 8.55 |
| 3.50 | 8.70 | | | 3.50 | 8.80 | 3.60 | 8.65 |
| 4.00 | 8.90 | | | 4.00 | 9.05 | | |
| 4.50 | 9.20 | | | 4.50 | 9.20 | | |
| 5.00 | 9.50 | | | 5.00 | 9.45 | | |
| 5.50 | 9.65 | | | 5.50 | 9.80 | | |
| 6.00 | 9.85 | | | 6.00 | 10.15 | | |

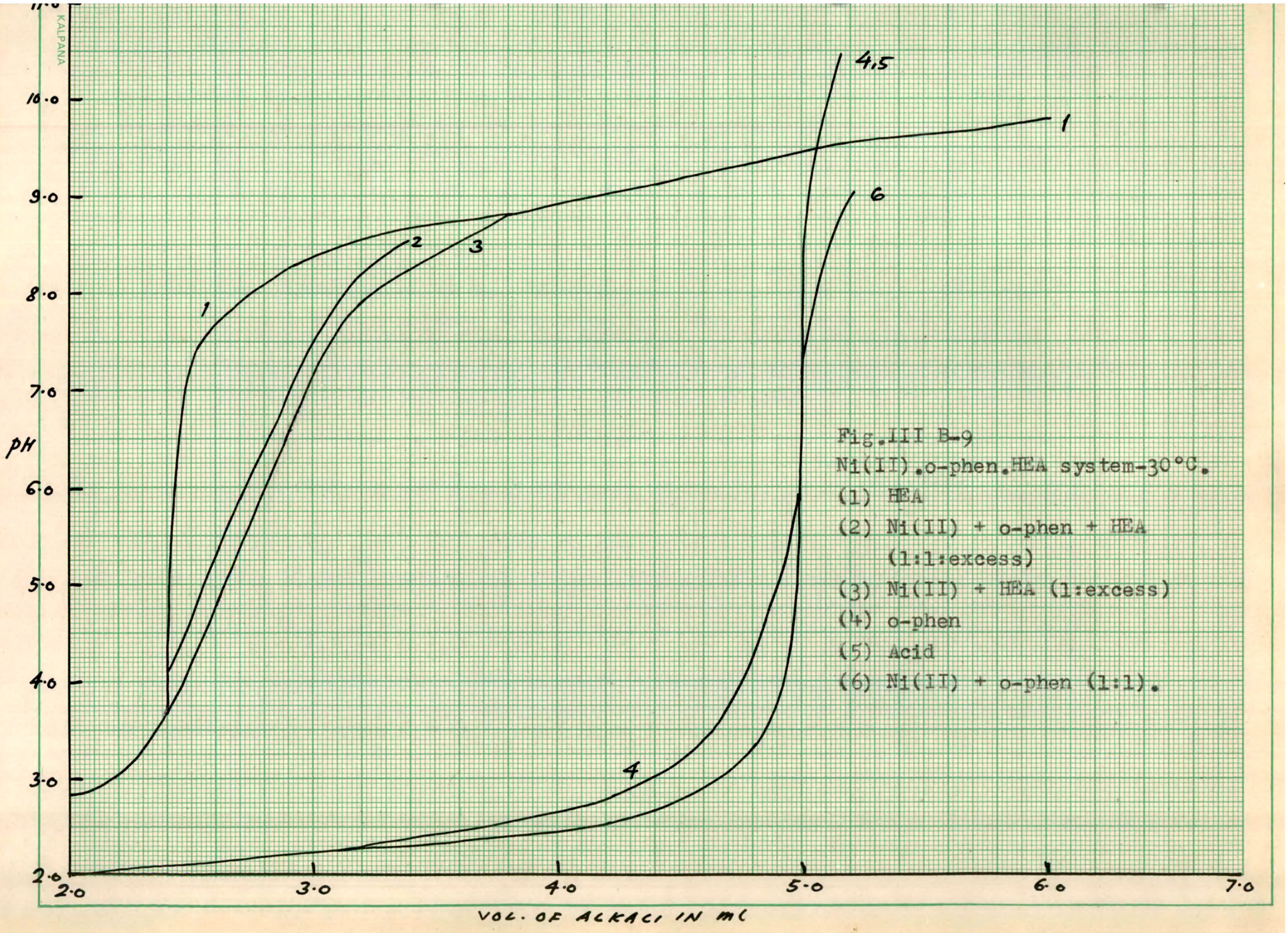



Fig.III B-9

Ni(II).o-phen.HEA system-30°C.

(1) HEA

(2) Ni(II) + o-phen + HEA (1:1:excess)

(3) Ni(II) + HEA (1:excess)

(4) o-phen

(5) Acid

(6) Ni(II) + o-phen (1:1).

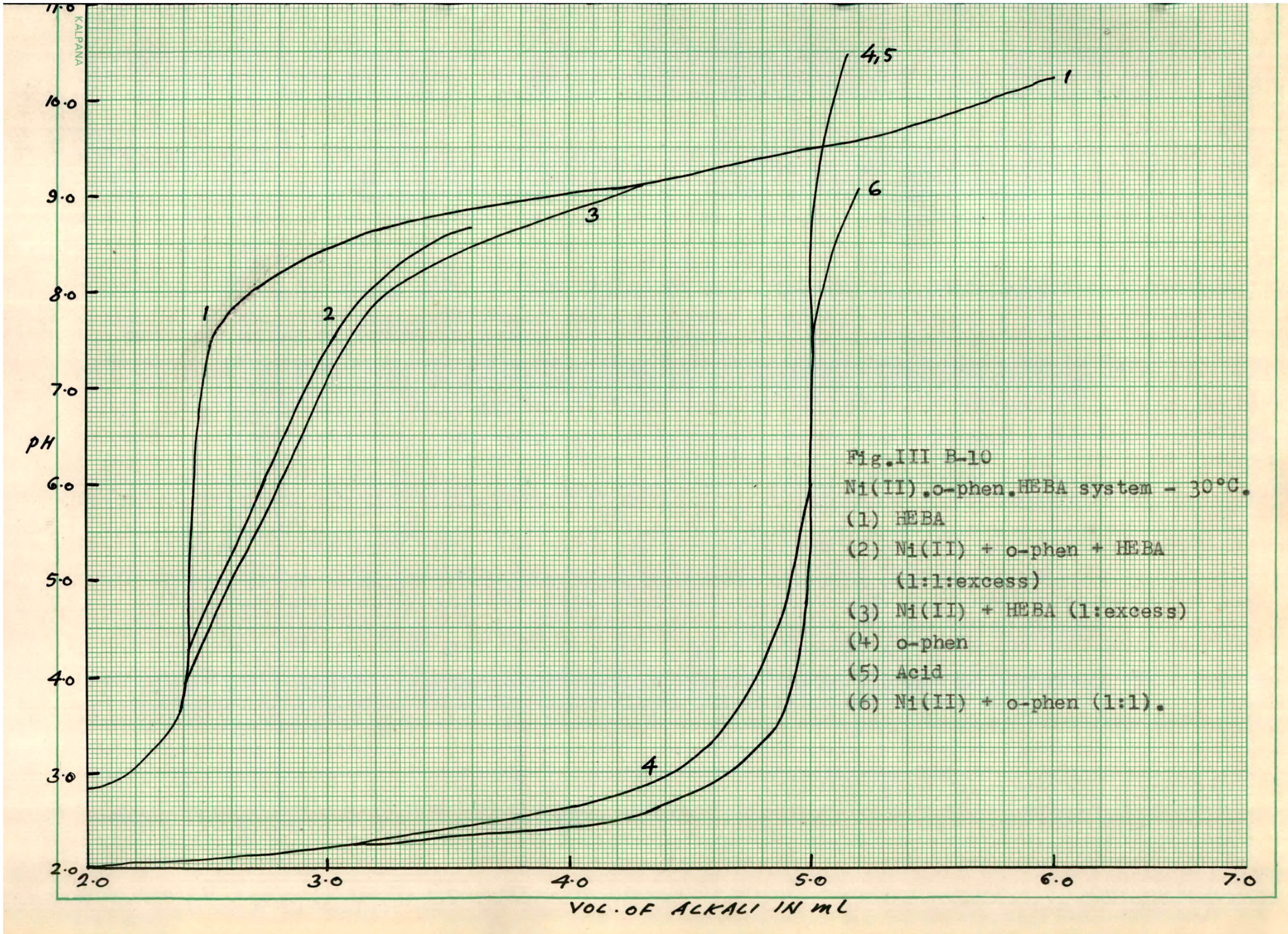


Fig.III B-10
Ni(II).o-phen.HEBA system - 30°C.
(1) HEBA
(2) Ni(II) + o-phen + HEBA
(1:1:excess)
(3) Ni(II) + HEBA (1:excess)
(4) o-phen
(5) Acid
(6) Ni(II) + o-phen (1:1).
pH
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
2.0
3.0
4.0
5.0
6.0
7.0
VOL. OF ALKALI IN ml
1
2
3
4
4,5
6
KALPANA

Table IIIB 1.8

N = 0.2M  V° = 50 ml.  $T^{\circ}_{o-phen}$ = 0.001M  $T^{\circ}_{M}$ = 0.001M

E° = 0.02M  $T^{\circ}_{L}$ = 0.01M  $\mu$ = 0.2M  t = 30°C.

| HPA | | Ni.o-phen.HPA | | HPBA | | Ni.o-phen.HPBA | |
|---|---|---|---|---|---|---|---|
| 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 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 | 0.00 | 2.05 |
| 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 | 0.50 | 2.15 |
| 1.00 | 2.25 | 1.00 | 2.25 | 1.00 | 2.25 | 1.00 | 2.25 |
| 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 | 1.50 | 2.50 |
| 2.00 | 2.80 | 2.00 | 2.80 | 2.00 | 2.85 | 2.00 | 2.85 |
| 2.10 | 2.95 | 2.20 | 3.10 | 2.10 | 2.95 | 2.20 | 3.15 |
| 2.20 | 3.10 | 2.40 | 4.25 | 2.20 | 3.15 | 2.40 | 4.05 |
| 2.30 | 3.40 | 2.50 | 4.75 | 2.30 | 3.40 | 2.50 | 4.55 |
| 2.35 | 3.60 | 2.60 | 5.20 | 2.35 | 3.65 | 2.60 | 5.05 |
| 2.40 | 3.90 | 2.70 | 5.75 | 2.40 | 4.00 | 2.70 | 5.60 |
| 2.42 | 5.75 | 2.80 | 6.25 | 2.43 | 5.45 | 2.80 | 6.15 |
| 2.44 | 6.45 | 2.90 | 6.80 | 2.46 | 6.50 | 2.90 | 6.75 |
| 2.46 | 6.85 | 3.00 | 7.30 | 2.48 | 7.00 | 3.00 | 7.25 |
| 2.48 | 7.25 | 3.10 | 7.70 | 2.50 | 7.50 | 3.10 | 7.75 |
| 2.50 | 7.50 | 3.20 | 7.95 | 2.60 | 7.95 | 3.20 | 8.00 |
| 2.60 | 7.95 | 3.30 | 8.20 | 2.70 | 8.25 | 3.30 | 8.20 |
| 2.70 | 8.15 | 3.40 | 8.40 | 2.80 | 8.40 | 3.40 | 8.35 |
| 2.80 | 8.30 | 3.50 | 8.55 | 2.90 | 8.55 | 3.50 | 8.50 |
| 3.00 | 8.55 | 3.60 | 8.70 | 3.00 | 8.65 | 3.60 | 8.65 |
| 3.50 | 8.85 | | | 3.50 | 8.95 | 3.80 | 8.95 |
| 4.00 | 9.05 | | | 4.00 | 9.15 | | |
| 4.50 | 9.35 | | | 4.50 | 9.40 | | |
| 5.00 | 9.60 | | | 5.00 | 9.65 | | |
| 5.50 | 9.90 | | | 5.50 | 9.95 | | |
| 6.00 | 10.20 | | | 6.00 | 10.50 | | |

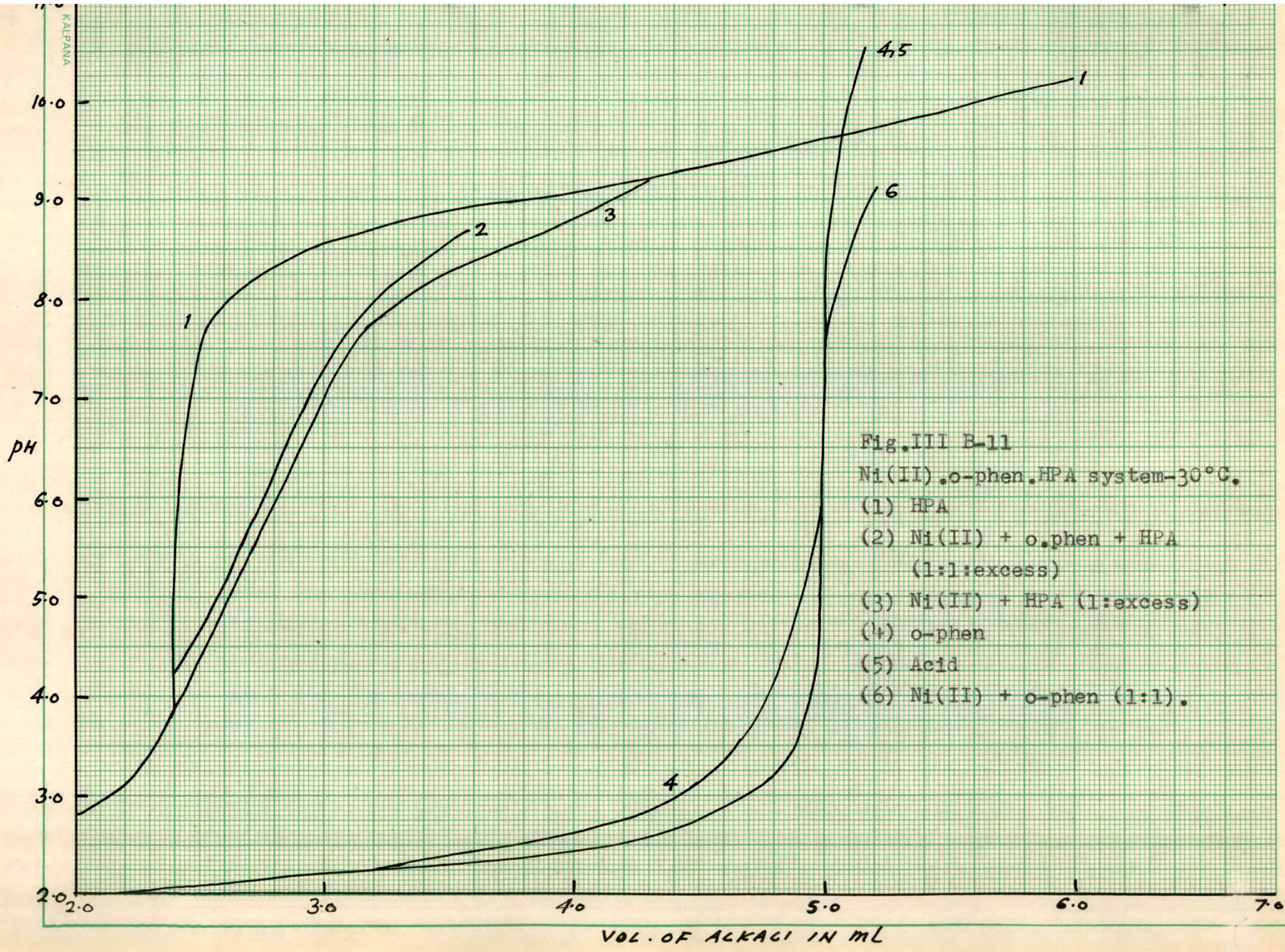



Fig.III B-11

Ni(II).o-phen.HPA system-30°C.

(1) HPA

(2) Ni(II) + o.phen + HPA (1:1:excess)

(3) Ni(II) + HPA (1:excess)

(4) o-phen

(5) Acid

(6) Ni(II) + o-phen (1:1).

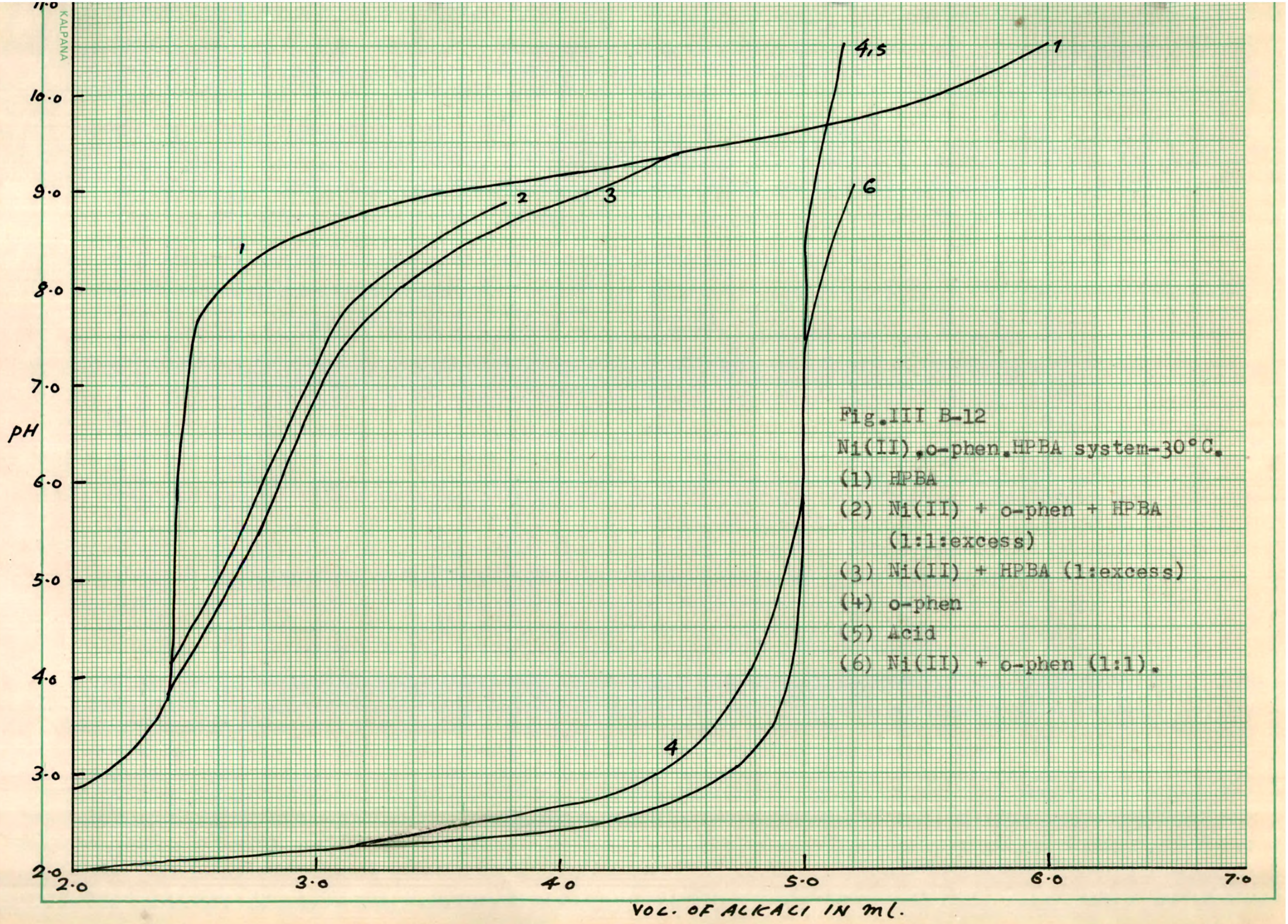



Fig.III B-12

Ni(II),o-phen.HPBA system-30°C.

(1) HPBA

(2) Ni(II) + o-phen + HPBA (1:1:excess)

(3) Ni(II) + HPBA (1:excess)

(4) o-phen

(5) Acid

(6) Ni(II) + o-phen (1:1).

## Table IIIB 2.1a

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 HEA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 3.10 | $2.00_0$ | 2.24 | 2.44 | 0.20 | $0.40_2$ | $0.17_3$ | $14.71_8$ | $14.54_5$ |
| 3.15 | $2.00_0$ | 2.26 | 2.48 | 0.22 | $0.44_2$ | $0.10_1$ | $14.62_1$ | $14.52_0$ |
| 3.20 | $2.00_0$ | 2.28 | 2.52 | 0.24 | $0.48_2$ | $0.03_1$ | $14.52_3$ | $14.49_2$ |
| 3.25 | $2.00_0$ | 2.30 | 2.58 | 0.28 | $0.56_2$ | $\bar{1}.89_0$ | $14.42_7$ | $14.53_7$ |
| 3.30 | $2.00_0$ | 2.31 | 2.62 | 0.31 | $0.62_2$ | $\bar{1}.78_4$ | $14.33_0$ | $14.54_6$ |

$\log K_{MAL} = 14.53 \pm 0.02$

## Table IIIB 2.2a

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 HEBA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 3.15 | $2.00_0$ | 2.24 | 2.44 | 0.20 | $0.40_2$ | $0.17_3$ | $15.07_8$ | $14.90_5$ |
| 3.20 | $2.00_0$ | 2.26 | 2.50 | 0.24 | $0.48_2$ | $0.03_1$ | $14.98_3$ | $14.95_2$ |
| 3.25 | $2.00_0$ | 2.28 | 2.54 | 0.26 | $0.52_2$ | $\bar{1}.96_2$ | $14.88_5$ | $14.92_3$ |
| 3.30 | $2.00_0$ | 2.29 | 2.58 | 0.29 | $0.58_2$ | $\bar{1}.85_6$ | $14.78_8$ | $14.93_2$ |
| 3.35 | $2.00_0$ | 2.30 | 2.60 | 0.30 | $0.60_2$ | $\bar{1}.81_8$ | $14.68_9$ | $14.87_1$ |

$\log K_{MAL} = 14.92 \pm 0.03$

Table IIIB 2.3a

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 HPA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 3.10 | $2.00_0$ | 2.20 | 2.44 | 0.24 | $0.48_3$ | $0.02_9$ | $15.26_2$ | $15.23_3$ |
| 3.15 | $2.00_0$ | 2.22 | 2.50 | 0.28 | $0.56_3$ | $\bar{1}.89_0$ | $15.16_6$ | $15.27_6$ |
| 3.20 | $2.00_0$ | 2.24 | 2.56 | 0.32 | $0.64_3$ | $\bar{1}.74_5$ | $15.07_1$ | $15.32_6$ |
| 3.25 | $2.00_0$ | 2.26 | 2.60 | 0.34 | $0.68_3$ | $\bar{1}.66_8$ | $14.97_3$ | $15.30_5$ |
| 3.30 | $2.00_0$ | 2.28 | 2.63 | 0.35 | $0.70_3$ | $\bar{1}.52_6$ | $14.87_4$ | $15.34_8$ |

$\log K_{MAL} = 15.30 \pm 0.03$

Table IIIB 2.4a

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 HPBA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 3.10 | $2.00_0$ | 2.19 | 2.42 | 0.23 | $0.46_3$ | $0.06_4$ | $15.57_1$ | $15.50_7$ |
| 3.15 | $2.00_0$ | 2.21 | 2.48 | 0.27 | $0.54_3$ | $\bar{1}.92_5$ | $15.47_5$ | $15.55_0$ |
| 3.20 | $2.00_0$ | 2.23 | 2.52 | 0.29 | $0.58_3$ | $\bar{1}.85_4$ | $15.37_8$ | $15.52_4$ |
| 3.25 | $2.00_0$ | 2.25 | 2.55 | 0.30 | $0.60_3$ | $\bar{1}.81_9$ | $15.27_9$ | $15.46_0$ |
| 3.30 | $2.00_0$ | 2.26 | 2.58 | 0.32 | $0.64_3$ | $\bar{1}.74_5$ | $15.18_1$ | $15.43_6$ |

$\log K_{MAL} = 15.50 \pm 0.03$

Fig.III B-13 : Cu(II).dipy.HEA system - 30°C.

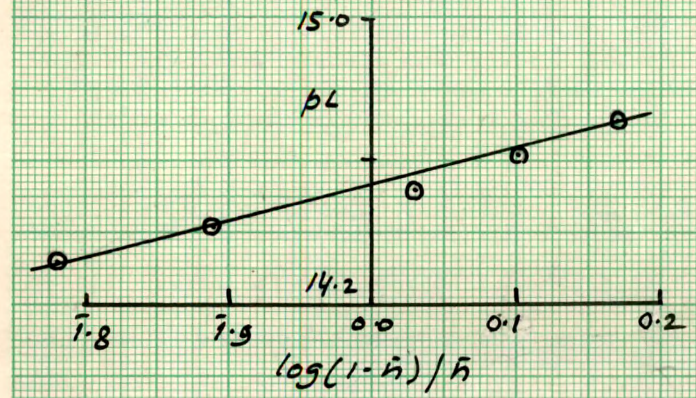



Fig.III B-14 : Cu(II).dipy.HEBA system - 30°C.

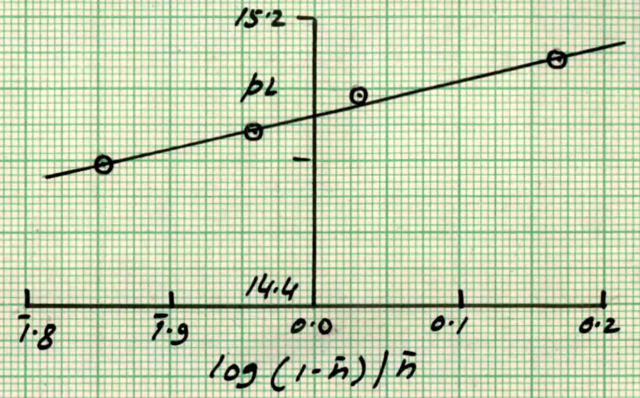



Fig.III B-15 : Cu(II).dipy.HPA system - 30°C.

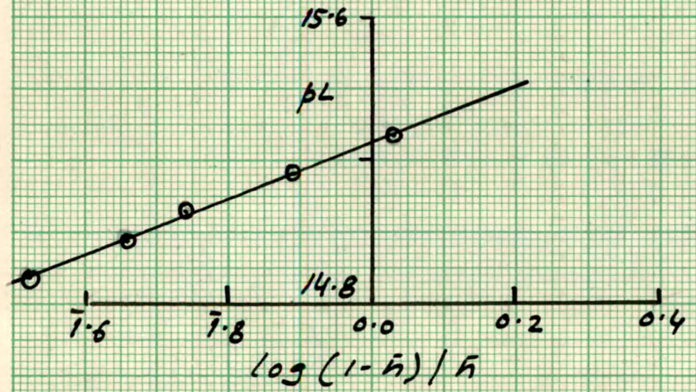
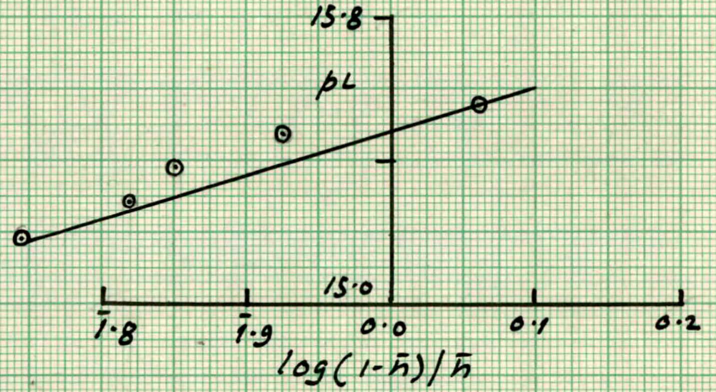



Fig.III B-16 : Cu(II).dipy.HPBA system - 30°C.



## Table IIIB 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.dipyridyl HEA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 5.55 | $2.00_0$ | 2.42 | 2.66 | 0.24 | $0.48_0$ | $0.03_5$ | $9.82_4$ | $9.78_9$ |
| 5.60 | $2.00_0$ | 2.42 | 2.67 | 0.25 | $0.50_0$ | - | $9.72_5$ | $9.72_5$ |
| 5.65 | $2.00_0$ | 2.42 | 2.68 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $9.62_6$ | $9.66_1$ |
| 5.70 | $2.00_0$ | 2.42 | 2.69 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $9.52_7$ | $9.59_8$ |
| 5.75 | $2.00_0$ | 2.42 | 2.70 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $9.42_8$ | $9.53_5$ |

$\log K_{MAL} = 9.66 \pm 0.05$

## Table IIIB 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.dipyridyl HEBA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 5.65 | $2.00_0$ | 2.44 | 2.68 | 0.24 | $0.48_0$ | $0.03_5$ | $9.98_4$ | $9.94_9$ |
| 5.70 | $2.00_0$ | 2.44 | 2.69 | 0.25 | $0.50_0$ | - | $9.88_5$ | $9.88_5$ |
| 5.75 | $2.00_0$ | 2.44 | 2.70 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $9.78_6$ | $9.82_1$ |
| 5.80 | $2.00_0$ | 2.44 | 2.71 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $9.68_7$ | $9.75_8$ |
| 5.85 | $2.00_0$ | 2.44 | 2.72 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $9.58_9$ | $9.69_6$ |

$\log K_{MAL} = 9.82 \pm 0.05$

## Table IIIB 2.3b

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 HPA 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 | $2.00_0$ | 2.40 | 2.64 | 0.24 | $0.48_1$ | $0.03_3$ | $10.66_4$ | $10.63_1$ |
| 5.45 | $2.00_0$ | 2.40 | 2.65 | 0.25 | $0.50_1$ | $\bar{1}.99_8$ | $10.56_5$ | $10.56_7$ |
| 5.50 | $2.00_0$ | 2.40 | 2.66 | 0.26 | $0.52_1$ | $\bar{1}.96_4$ | $10.46_6$ | $10.50_2$ |
| 5.55 | $2.00_0$ | 2.40 | 2.67 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $10.36_7$ | $10.43_8$ |
| 5.60 | $2.00_0$ | 2.40 | 2.68 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $10.26_8$ | $10.37_5$ |

$\log K_{MAL} = 10.50 \pm 0.05$

## Table IIIB 2.4b

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 HPBA 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 | $2.00_0$ | 2.44 | 2.68 | 0.24 | $0.48_0$ | $0.03_5$ | $10.97_4$ | $10.93_9$ |
| 5.45 | $2.00_0$ | 2.44 | 2.69 | 0.25 | $0.50_0$ | - | $10.87_5$ | $10.87_5$ |
| 5.50 | $2.00_0$ | 2.44 | 2.70 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $10.77_6$ | $10.81_1$ |
| 5.55 | $2.00_0$ | 2.44 | 2.71 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $10.68_7$ | $10.75_8$ |
| 5.60 | $2.00_0$ | 2.44 | 2.72 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $10.57_8$ | $10.68_5$ |

$\log K_{MAL} = 10.81 \pm 0.05$

Fig.III B-17 : Ni(II).dipy.HEA system - 30°C.

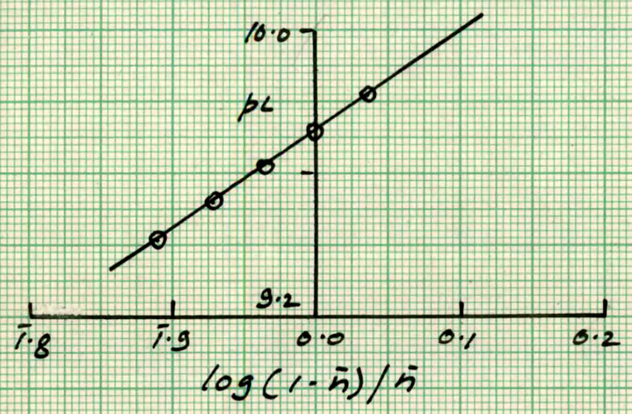



Fig.III B-18 : Ni(II).dipy.HEBA system - 30°C.

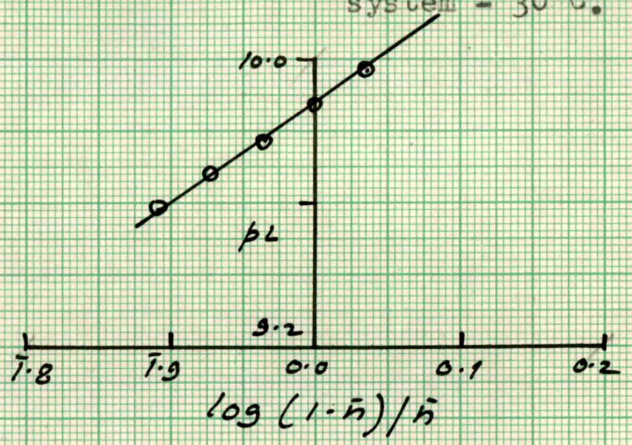



Fig.III B-19 : Ni(II).dipy.HPA system - 30°C.

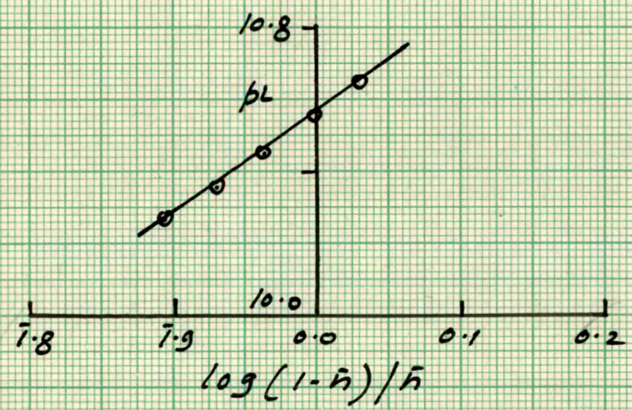



Fig.III B-20 : Ni(II).dipy.HPBA system - 30°C.

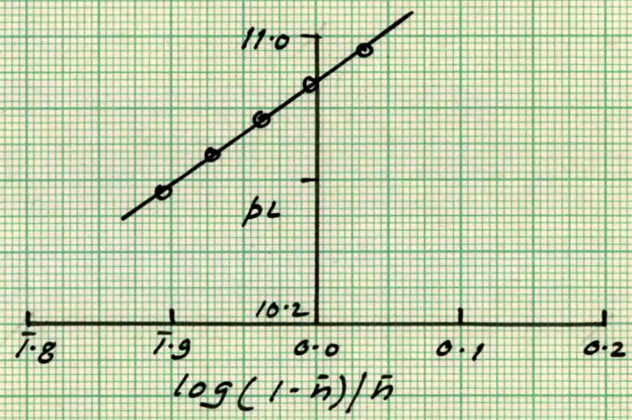


Table IIIB 2.1c

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-phenanthroline HEA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 5.75 | $2.00_0$ | 2.43 | 2.67 | 0.24 | $0.48_0$ | $0.03_5$ | $9.42_4$ | $9.38_9$ |
| 5.80 | $2.00_0$ | 2.43 | 2.68 | 0.25 | $0.50_0$ | - | $9.32_5$ | $9.32_5$ |
| 5.90 | $2.00_0$ | 2.43 | 2.69 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $9.13_4$ | $9.16_9$ |
| 5.95 | $2.00_0$ | 2.43 | 2.70 | 0.27 | $0.54_0$ | $\bar{1}.92_9$ | $9.02_7$ | $9.09_8$ |
| 6.00 | $2.00_0$ | 2.43 | 2.72 | 0.28 | $0.56_0$ | $\bar{1}.89_3$ | $8.92_8$ | $9.03_5$ |

$\log K_{MAL} = 9.20 \pm 0.07$

Table IIIB 2.2c

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-phenanthroline HEBA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 5.75 | $2.00_0$ | 2.44 | 2.68 | 0.24 | $0.48_0$ | $0.03_5$ | $9.78_4$ | $9.74_9$ |
| 5.80 | $2.00_0$ | 2.44 | 2.69 | 0.25 | $0.50_0$ | - | $9.68_5$ | $9.68_5$ |
| 5.85 | $2.00_0$ | 2.44 | 2.70 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $9.58_7$ | $9.62_2$ |
| 5.95 | $2.00_0$ | 2.44 | 2.71 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $9.38_8$ | $9.45_9$ |
| 6.00 | $2.00_0$ | 2.44 | 2.72 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $9.28_9$ | $9.39_6$ |

$\log K_{MAL} = 9.58 \pm 0.07$

Table IIIB 2.3c

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-phenanthroline HPA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 5.50 | $2.00_0$ | 2.42 | 2.66 | 0.24 | $0.48_0$ | $0.03_5$ | $10.46_4$ | $10.42_9$ |
| 5.55 | $2.00_0$ | 2.42 | 2.67 | 0.25 | $0.50_0$ | - | $10.36_5$ | $10.36_5$ |
| 5.60 | $2.00_0$ | 2.42 | 2.68 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $10.26_6$ | $10.30_1$ |
| 5.65 | $2.00_0$ | 2.42 | 2.69 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $10.16_7$ | $10.24_8$ |
| 5.70 | $2.00_0$ | 2.42 | 2.70 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $10.06_8$ | $10.17_5$ |

$\log K_{MAL} = 10.30 \pm 0.07$

Table IIIB 2.4c

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-phenanthroline HPBA system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 5.50 | $2.00_0$ | 2.44 | 2.68 | 0.24 | $0.48_0$ | $0.03_5$ | $10.77_4$ | $10.73_9$ |
| 5.55 | $2.00_0$ | 2.44 | 2.69 | 0.25 | $0.50_0$ | - | $10.67_5$ | $10.67_5$ |
| 5.60 | $2.00_0$ | 2.44 | 2.70 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $10.57_6$ | $10.61_1$ |
| 5.65 | $2.00_0$ | 2.44 | 2.71 | 0.27 | $0.54_1$ | $\bar{1}.92_9$ | $10.47_7$ | $10.54_8$ |
| 5.70 | $2.00_0$ | 2.44 | 2.72 | 0.28 | $0.56_1$ | $\bar{1}.89_3$ | $10.37_8$ | $10.48_5$ |

$\log K_{MAL} = 10.61 \pm 0.05$

Fig.III B-21 : Ni(II).o-phen.HEA system - 30°C.

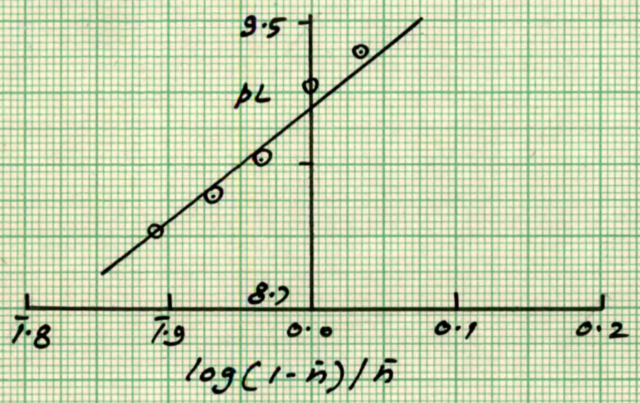



Fig.III B-22 : Ni(II).o-phen.HEBA system - 30°C.

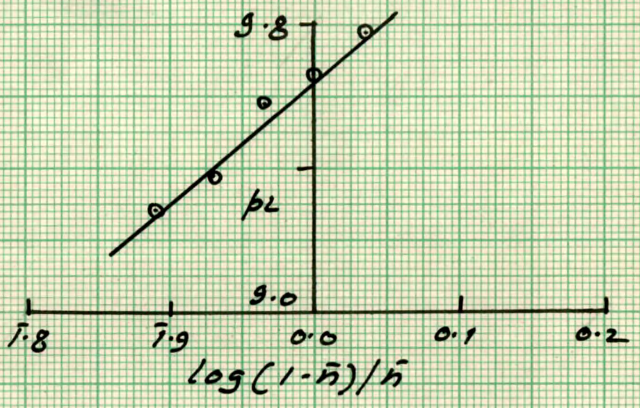



Fig.III B-23 : Ni(II).o-phen.HPA system - 30°C.

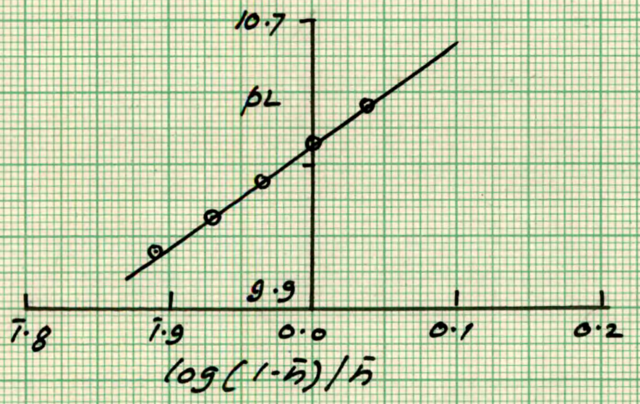



Fig.III B-24 : Ni(II).o-phen.HPBA system - 30°C.

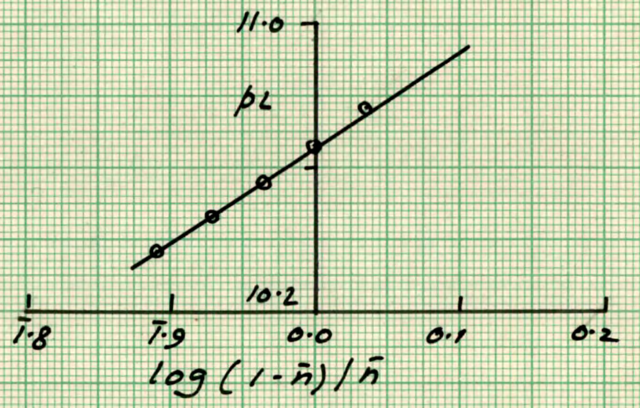


Table III B-3.0 : Stability constants of ternary dipyridyl-$M^{2+}$-ligand complexes and o-phenanthroline-$M^{2+}$-ligand complexes - 30°C.

| Ligand | $\log K^{Cu.dipy}_{Cu.dipy.L}$ | $\log K^{Ni.dipy}_{Ni.dipy.L}$ | $\log K^{Ni.o\text{-}phen}_{Ni.o\text{-}phen.L}$ |
|---|---|---|---|
| HEA | $14.53 \pm 0.02$ | $9.66 \pm 0.05$ | $9.20 \pm 0.07$ |
| HEBA | $14.92 \pm 0.03$ | $9.82 \pm 0.05$ | $9.58 \pm 0.07$ |
| HPA | $15.30 \pm 0.03$ | $10.50 \pm 0.05$ | $10.30 \pm 0.07$ |
| HPBA | $15.50 \pm 0.03$ | $10.81 \pm 0.05$ | $10.61 \pm 0.05$ |

Section C

Mixed ligand complexes containing charged ligand ions as primary ligand have been studied earlier.[58-61] Various mixed ligand complexes with iminodiacetic acid as the primary ligand have been studied.[62,63] The mixed ligand complexes of the type [Ni.IMDA.L] where L = pyridine, ammonia or water have been studied by Fridman and coworkers.[64] Potentiometric studies on stepwise mixed ligand complex formation involving IMDA as the primary ligand were carried out by Sharma and Tandon.[65,66] They also reported[67] the mixed ligand formation constants of the ternary system [M.IMDA.L] where M = Cu(II), Ni(II), Zn(II) or Cd(II) and L = glycine, α-alanine, dextro rotatory aspartic acid, 1,2-propylenediamine, salicylic acid, sulphosalicylic acid, chromotropic acid or tyron. The formation constants of the complexes of the type [Cu.A.L.] where A = IMDA and L = pyridine or N-butylamine were studied by potentiometric method.[68] Israeli[69] studied the formation constants of mixed ligand complexes of Cu(II) and Ni(II) with NTA and glycine and other mixed ligand systems. Kirson and coworkers[70] reported the ternary complex [Cu.en.NTA] and determined its instability constant. A pH metric method has been employed to measure the solution stabilities of the ternary systems of Be(II) containing NTA and tyron.[71] Martell and coworkers[72] have determined the stability of ternary complexes containing U(VI), NTA and hydroxy quinoline sulphonic acid, using their own method based on the consideration that U(VI) NTA complex formed at lower pH combines with the secondary ligand at higher pH. Vehava and coworkers[73] reported the Cr(III) complexes with NTA as a tridentate or tetradentate ligand. A pH metric study of the ternary systems, [M.NTA.glycine] where M = Cu(II) or Ni(II) or Zn(II) has been reported.[14] Israeli and coworkers[74-77] studied the mixed ligand complexes of Cu(II) and Ni(II) with NTA and amino acid by using spectrophotometric method. Potentiometric studies of stepwise formation of complexes containing Cu(II), Ni(II), NTA and hydroxy acid were also reported by Tandon and coworkers.[78] The system [M(NTA)L] where L = picoline, oxime, serine, arginine and ammonia have also been studied.[79,80] Complexation of rare earth metal ions with DBM, AcAc or BA and EDTA or hydroxyethylenetriacetic acid have been studied in aqueous acetone solutions.[81,82] Hetero ligand complexes of Neodymium, Holmium and Erbium have been studied spectrophotometrically[83] with EDTA and BA. Formation constants of lanthanones, with EDTA or NTA and citric acid were determined pH metrically.[84,85] Complexes of the type [M.NTA.L] where M = Cu(II), Ni(II), Zn(II) and Cd(II) and L = amino acids, polyhydroxy phenols and mercapto acids have been reported from our laboratory.[46,51,57,86,87]

In all the above 1:1 complexes of the multidentate amino polycarboxylate ions the remaining, coordination positions of the metal ions are occupied by water molecules.

On the addition of a secondary ligand the water molecules are displaced resulting in the formation of the mixed ligand complex $[MAL]^{n-}$.

The present section consists of the study of ternary systems, [MAL] where M = Cu(II) or Ni(II); A = iminodiacetic acid(IMDA) or nitrilotriacetic acid(NTA) and L = AcAc or BA or DBM.

IMDA behaves as a tridentate[88] ligand, coordination taking place from the nitrogen atom and the two carboxylate groups. NTA behaves as tri[71] or tetradentate[89] ligand coordination taking place from nitrogen atom and two or three $COO^-$ groups, respectively.

Experimental :

The reagents and instruments used were same as detailed in previous chapter.II. IMDA and NTA used were of A.R. quality. All titrations were carried out in 50% dioxan medium. An extension of Irving-Rossotti titration technique has been used as in earlier cases.

For studying the ternary systems the following solutions were prepared :

For IMDA :

1. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 10.0 ml.) + sodium perchlorate (1M, 8.8 ml.) + conductivity water (1.2 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.9 ml.) + conductivity water (6.1 ml.) + dioxan (25.0 ml.) Total volume = 50 ml., $\mu$=0.2M.

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 (1.2 ml.) + dioxan (25.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

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 (1.3 ml.)+ dioxan (20.0 ml.). Total volume = 50 ml., $\mu$ = 0.2M.

5. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.)+ metal perchlorate (0.02M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + sodium perchlorate (1M, 8.7 ml.) + conductivity water (1.3 ml.) + dioxan (20.0 ml.). Total volume = 50.0 ml., $\mu$ = 0.2M.

In case of NTA, the trisodium salt of NTA, was used and, therefore, the addition of extra acid was not required. The sets were prepared as in case of dipyridyl systems in previous section III-A.

Total volume was made 50 ml. and ionic strength was raised to 0.2M. The solutions were titrated against 0.2M sodium hydroxide. The plots of pH against volume of alkali have been represented in figs. IIIC 1 to 5 and IIIC 11 to 15.

For the curve (1) and curve (4) in the IMDA systems two equivalents of extra acid have been added in order to account for the extra hydrogen ions liberated due to the combination of the primary ligands with the metal ion. In NTA the extra acid is not added, because, trisodium salt of NTA is used.

It is observed from curve (3) and (1) that MA is formed at low pH. It undergoes hydroxo complex formation at high pH. The curve (5) remains merged with curve (4), at low pH showing that complexation of β-diketone does not take place at low pH. Curve (5) diverges from curve (4) at higher pH showing that [MAL] formation takes place where MA 1:1 complex formation is complete. In this range hydroxo complex formation also does not start. The horizontal distance between curve (4) and (5) corresponds to the amount of secondary ligand which gets bound with MA.

The $\bar{n}$ and pL values were calculated at different pH in the same manner, as done in Chapter III A and have been presented in tables IIIC 2.1a to IIIC 2.5b and IIIC 4.1a to IIIC 4.5b.

The values of pL at $\bar{n} = 0.5$ gives the values of $\log K^{MA}_{MAL}$. More precise values were obtained by plotting pL at each point against the corresponding value of $\log(1-\bar{n})/\bar{n}$ and getting a straight line. The values of $pL - \log(1-\bar{n})/\bar{n}$ at each point on the straight line is equal to $\log K^{MA}_{MAL}$. The average values of $\log K^{MA}_{MAL}$, thus obtained have been presented with mean deviation in table IIIC 2.1a to IIIC 2.5b and IIIC 4.1a to IIIC 4.5b.

In systems of the type [MAL] where A is a charged primary ligand such as IMDA or NTA; it is to be expected that $K_{MAL}$ is less than $K_{ML}$ by nearly one log unit. In NTA it is even higher. This may be explained to be due to the coulombic repulsion between the charged primary ligands, $IMDA^{2-}$ or $NTA^{3-}$ and the incoming secondary ligand $L^{2-}$.

This repulsion is greater than the repulsion between the first diketonate ion and the second diketonate ion during the formation of $[ML_2]$ in the binary system. $K_{MAL}$ is, therefore, even less than $K_{ML_2}$. Also as the charge on the primary ligand goes on increasing the repulsion on the incoming secondary ligand is more and hence the value of $K^{MA}_{MAL}$ goes down.

In M-A-β-diketone system where A = IMDA or NTA, it is expected that the lowering in the value of $K^{MA}_{MA(\beta\text{-diket})}$ should not be as much as in uninegative charged σ bonding ligand. The π interaction in M-β-diketone bond is expected to increase in the M-A-(β-diketone) system. The expectation is based on the consideration that the σ bonding primary ligand should increase the concentration of electrons around the metal ions and hence the tendency to donate π electrons must be more in MA than in $[M(aq)]^{2+}$. On the basis of this argument it was indicated that the M--S π interaction is not significant[30,45]. However, in [M--A-(β-diketone)] system also $K^{M}_{M(\beta\text{-diket})} - K^{MA}_{MA(\beta\text{-diket})}$ is of the same order rather higher than M-A-glycine system. Two possible explanations can be put forth. In IMDA and NTA there is coordination from one nitrogen and rest carboxylate ions. Since the M-carboxylate bond is more ionic in nature, the concentration of electrons around the metal ion in MA is not significantly higher than in $[M(aq)]^{2+}$. Therefore the tendency to form π bond also does not show an increase. Further in β-diketone the charge is delocalised over the whole molecule and may affect the extent of repulsion, between the β-diketonate ion, and the already existing IMDA or NTA ion.

It is observed that the difference $\log K^{M}_{M(\beta\text{-diket})}$ - $\log K^{MA}_{MAL}$ is more in case of Cu(II) complexes. This observation can be explained in terms of Jahn-Tellor distortion.[90]

In case of Cu(II) complexes Jahn-Tellor distortion brings in additional stability. Ligand along the Z axis are at a greater distance than those in the equatorial plane. It can be naturally expected that in this elongation distortion, the incoming ligand occupying position along Z axis, will be loosely held by the metal ion. The formation constants corresponding to association of that ligand will have a lower value. NTA acts as tridentate[71] ligand occupying three positions around the Cu(II) ion in the XY plane. The secondary ligand has to occupy the remaining positions, one necessarily along the Z axis. In distorted Cu(II) complex the secondary ligand has to span more. This is the reason why the difference $\log K^{M}_{M(\beta\text{-diket})}$ - $\log K^{MA}_{MAL}$ is more in case of Cu(II) complexes.

In case of [Cu.IMDA.L] the values of $K^{Cu}_{Cu.A.L}$ are not very much lowered. This is because in [Cu.IMDA.L] the primary ligand occupies only two equatorial positions and hence leaves the other two equatorial positions to be occupied by the secondary ligand.

Thus the secondary ligand has not to occupy positions along the distorted axial direction.

## Table IIIC 1.1

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

E° = 0.02M    *E° = 0.024M    $\mu$ = 0.2M    t = 30°C.

$T^{\circ}_{L}$ = 0.002M

| Perchloric acid | | IMDA | | Cu.IMDA | | Ni.IMDA | |
|---|---|---|---|---|---|---|---|
| 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 | 1.75 | 0.00 | 1.75 | 0.00 | 1.75 |
| 1.00 | 1.70 | 1.00 | 1.85 | 1.00 | 1.85 | 1.00 | 1.85 |
| 2.00 | 1.80 | 2.00 | 1.95 | 2.00 | 1.95 | 2.00 | 1.95 |
| 3.00 | 1.90 | 3.00 | 2.20 | 3.00 | 2.10 | 3.00 | 2.20 |
| 4.00 | 2.05 | 4.00 | 2.50 | 4.00 | 2.25 | 4.00 | 2.50 |
| 5.00 | 2.40 | 5.00 | 3.20 | 5.00 | 2.55 | 5.00 | 2.90 |
| 5.50 | 2.75 | 5.10 | 3.35 | 5.50 | 2.85 | 5.50 | 3.35 |
| 5.60 | 2.85 | 5.20 | 3.50 | 5.60 | 3.05 | 5.60 | 3.50 |
| 5.70 | 3.05 | 5.30 | 3.75 | 5.70 | 3.25 | 5.70 | 3.70 |
| 5.80 | 3.30 | 5.35 | 3.95 | 5.80 | 3.55 | 5.80 | 3.95 |
| 5.85 | 3.50 | 5.40 | 4.20 | 5.85 | 3.75 | 5.85 | 4.20 |
| 5.90 | 3.75 | 5.43 | 4.35 | 5.90 | 4.15 | 5.90 | 4.50 |
| 5.93 | 4.10 | 5.46 | 4.65 | 5.94 | 4.35 | 5.94 | 4.90 |
| 5.96 | 4.60 | 5.48 | 5.00 | 5.98 | 5.05 | 5.98 | 5.40 |
| 5.98 | 5.20 | 5.50 | 6.85 | 6.00 | 6.85 | 6.00 | 6.80 |
| 6.00 | 7.25 | 5.52 | 7.50 | 6.05 | 7.45 | 6.05 | 7.70 |
| 6.02 | 8.30 | 5.55 | 8.20 | 6.10 | 7.80 | 6.10 | 8.05 |
| 6.05 | 8.80 | 5.60 | 8.70 | 6.20 | 8.25 | 6.20 | 8.65 |
| 6.10 | 9.45 | 5.70 | 9.25 | 6.30 | 8.65 | 6.30 | 9.15 |
| 6.15 | 10.05 | 5.80 | 9.60 | 6.40 | 8.95 | 6.40 | 9.55 |
| 6.20 | 10.40 | 6.00 | 10.10 | 6.50 | 9.30 | 6.50 | 9.85 |
| | | 6.20 | 10.45 | | | | |

## Table IIIC 1.2

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

$E^\circ$ = 0.02M  *$E^\circ$ = 0.024M  $\mu$ = 0.2M  t = 30°C.

$T^\circ_{IMDA}$ = 0.002M

| *AcAc | | Cu.IMDA.AcAc | | Ni.IMDA.AcAc | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.65 | 0.00 | 1.75 | 0.00 | 1.75 |
| 1.00 | 1.75 | 1.00 | 1.85 | 1.00 | 1.85 |
| 2.00 | 1.80 | 2.00 | 1.95 | 2.00 | 2.00 |
| 3.00 | 1.90 | 3.00 | 2.10 | 3.00 | 2.20 |
| 4.00 | 2.05 | 4.00 | 2.25 | 4.00 | 2.50 |
| 5.00 | 2.40 | 5.00 | 2.55 | 5.00 | 2.90 |
| 5.50 | 2.75 | 5.50 | 2.85 | 5.50 | 3.35 |
| 5.60 | 2.85 | 5.60 | 3.05 | 5.60 | 3.50 |
| 5.70 | 3.05 | 5.70 | 3.25 | 5.70 | 3.70 |
| 5.80 | 3.30 | 5.80 | 3.55 | 5.80 | 3.95 |
| 5.85 | 3.50 | 5.85 | 3.75 | 5.85 | 4.20 |
| 5.90 | 3.75 | 5.90 | 4.15 | 5.90 | 4.50 |
| 5.93 | 4.10 | 5.94 | 4.35 | 5.94 | 4.90 |
| 5.96 | 4.60 | 5.98 | 5.05 | 5.98 | 5.40 |
| 5.98 | 5.20 | 6.00 | 5.30 | 6.00 | 5.80 |
| 6.00 | 6.85 | 6.05 | 5.65 | 6.05 | 6.35 |
| 6.02 | 7.60 | 6.10 | 5.90 | 6.10 | 6.65 |
| 6.05 | 8.00 | 6.20 | 6.30 | 6.20 | 7.10 |
| 6.10 | 8.55 | 6.30 | 6.80 | 6.30 | 7.60 |
| 6.20 | 9.15 | 6.40 | 7.40 | 6.40 | 8.15 |
| 6.30 | 9.60 | 6.50 | 8.15 | 6.50 | 9.20 |
| 6.40 | 9.95 | 6.60 | 9.20 | 6.60 | 10.00 |
| 6.50 | 10.15 | 6.70 | 9.95 | 6.70 | 10.50 |
| 6.60 | 10.35 | 6.80 | 10.50 | | |

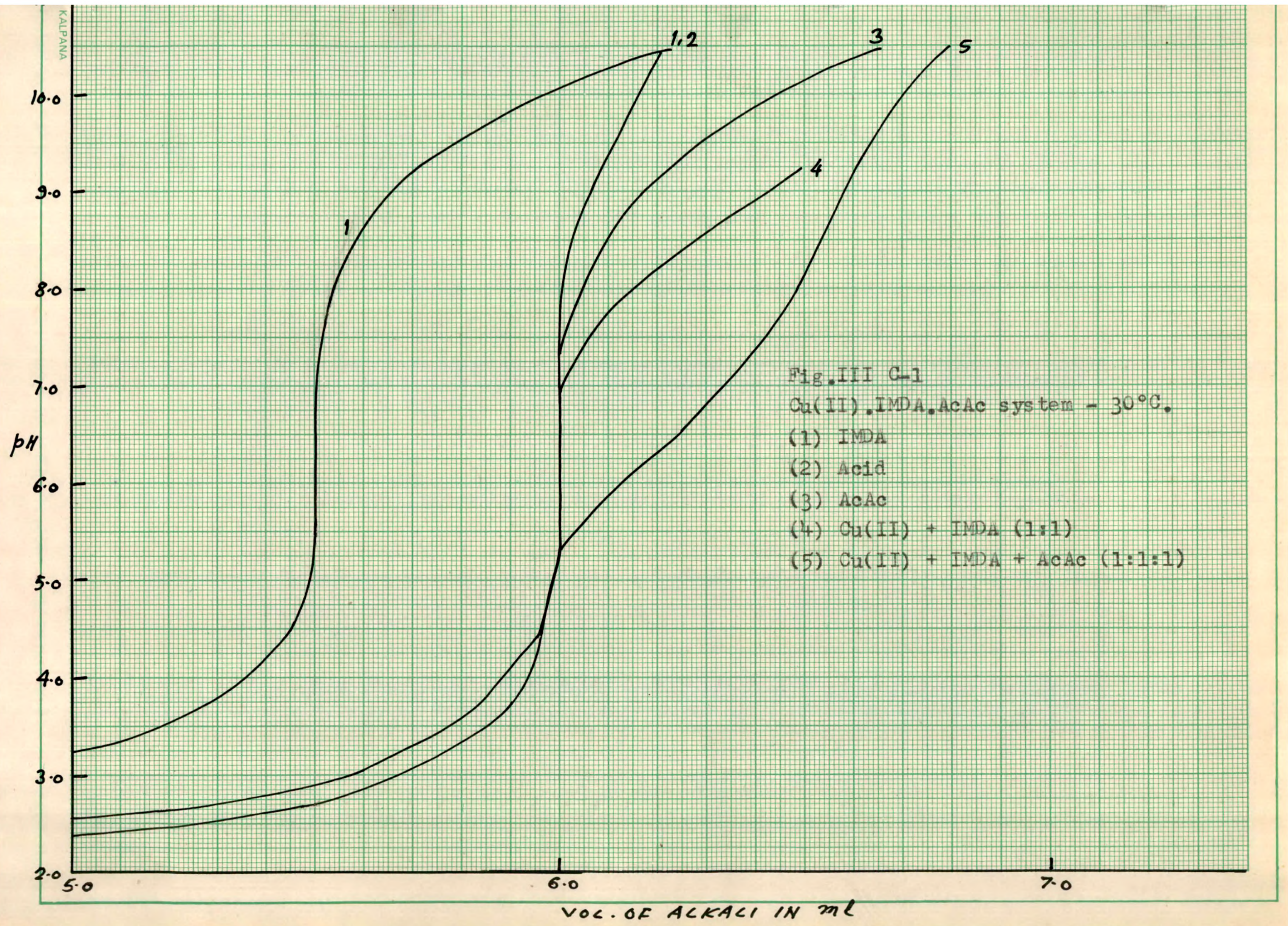


Fig.III C-1
Cu(II).IMDA.AcAc system - 30°C.
(1) IMDA
(2) Acid
(3) AcAc
(4) Cu(II) + IMDA (1:1)
(5) Cu(II) + IMDA + AcAc (1:1:1)
pH
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
5.0
6.0
7.0
VOL. OF ALKALI IN ml
1
1,2
3
4
5

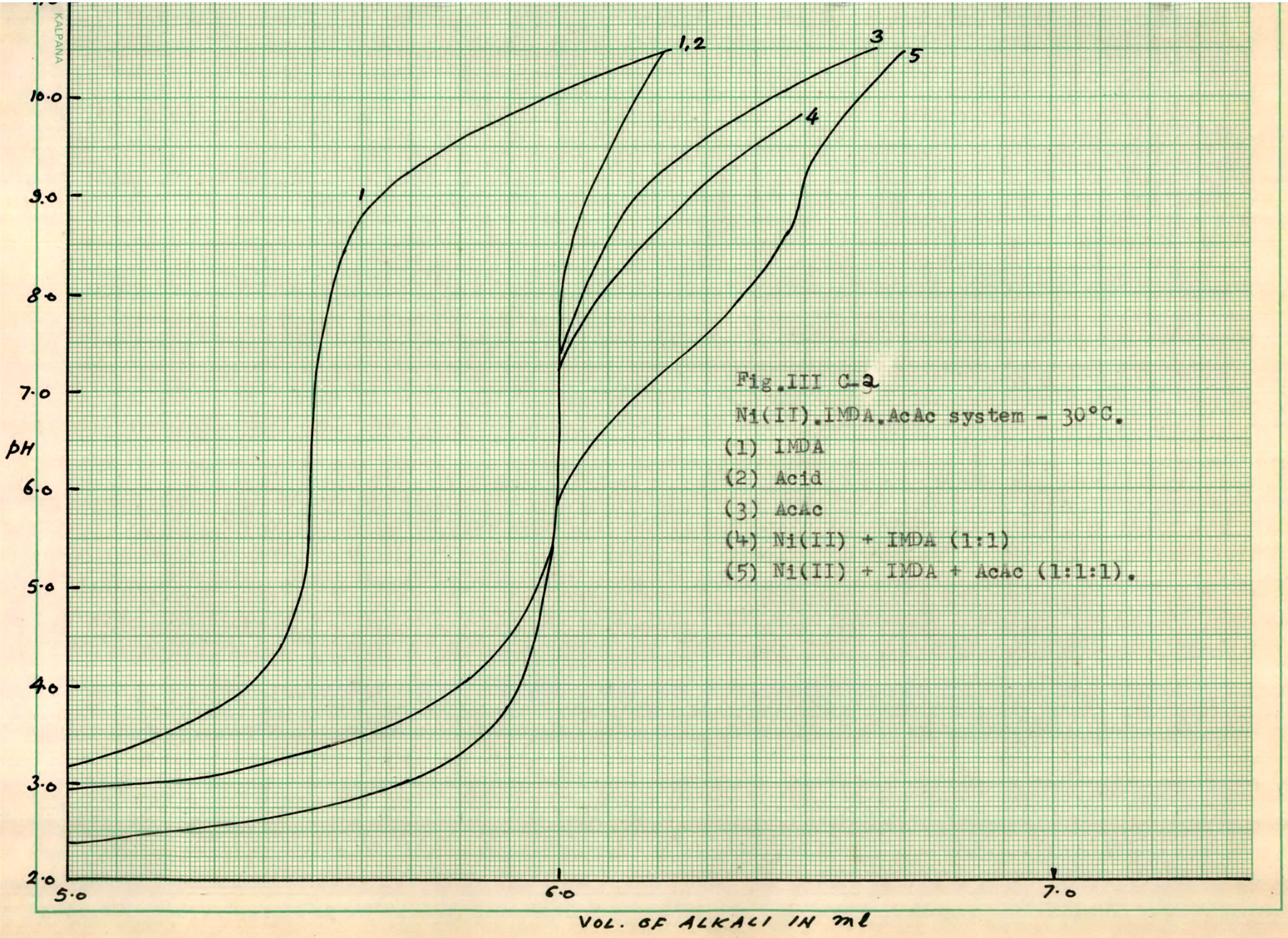

1,2
3
4
5
1
10.0
9.0
8.0
7.0
pH
6.0
5.0
4.0
3.0
2.0
5.0
6.0
7.0
VOL. OF ALKALI IN ml
Fig.III C.2
Ni(II).IMDA.AcAc system - 30°C.
(1) IMDA
(2) Acid
(3) AcAc
(4) Ni(II) + IMDA (1:1)
(5) Ni(II) + IMDA + AcAc (1:1:1).

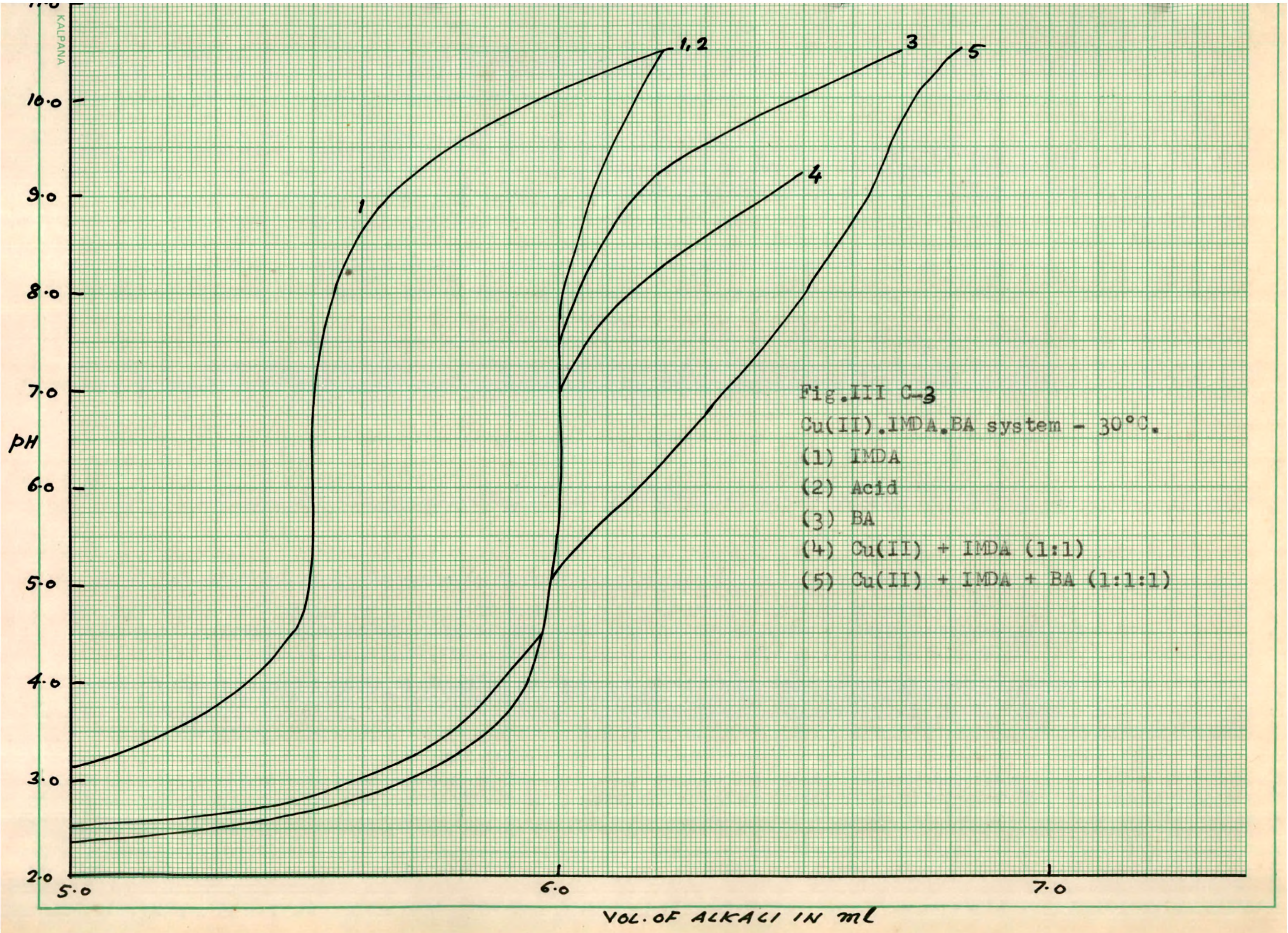
Table IIIC 1.3

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

$E^{\circ} = 0.02M$  $^{*}E^{\circ} = 0.024M$  $\mu = 0.2M$  $t = 30°C.$

$T^{\circ}_{IMDA} = 0.002M$

| *BA | | Cu.IMDA.BA | | Ni.IMDA.BA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.65 | 0.00 | 1.75 | 0.00 | 1.75 |
| 1.00 | 1.70 | 1.00 | 1.85 | 1.00 | 1.85 |
| 2.00 | 1.80 | 2.00 | 1.95 | 2.00 | 1.95 |
| 3.00 | 1.90 | 3.00 | 2.10 | 3.00 | 2.20 |
| 4.00 | 2.05 | 4.00 | 2.25 | 4.00 | 2.50 |
| 5.00 | 2.40 | 5.00 | 2.55 | 5.00 | 2.90 |
| 5.50 | 2.75 | 5.50 | 2.85 | 5.50 | 2.35 |
| 5.60 | 2.85 | 5.60 | 3.05 | 5.60 | 3.50 |
| 5.70 | 3.05 | 5.70 | 3.25 | 5.70 | 3.70 |
| 5.80 | 3.30 | 5.80 | 3.55 | 5.80 | 3.95 |
| 5.85 | 3.50 | 5.85 | 3.75 | 5.85 | 4.20 |
| 5.90 | 3.75 | 5.90 | 4.15 | 5.90 | 4.50 |
| 5.93 | 4.10 | 5.94 | 4.35 | 5.94 | 4.90 |
| 5.96 | 4.60 | 5.98 | 4.95 | 5.98 | 5.40 |
| 5.98 | 5.20 | 6.00 | 5.15 | 6.00 | 5.70 |
| 6.00 | 7.20 | 6.05 | 5.45 | 6.05 | 6.25 |
| 6.05 | 8.10 | 6.10 | 5.70 | 6.10 | 6.55 |
| 6.10 | 8.60 | 6.20 | 6.25 | 6.20 | 7.00 |
| 6.15 | 9.00 | 6.30 | 6.75 | 6.30 | 7.50 |
| 6.20 | 9.20 | 6.40 | 7.35 | 6.40 | 8.15 |
| 6.30 | 9.55 | 6.50 | 8.05 | 6.50 | 8.75 |
| 6.40 | 9.80 | 6.60 | 8.85 | 6.60 | 9.60 |
| 6.50 | 10.05 | 6.70 | 9.80 | 6.70 | 10.20 |
| 6.60 | 10.25 | 6.80 | 10.45 | 6.80 | 10.85 |
| 6.70 | 10.50 | | | | |


KALPANA
1, 2
3
5
4
1
10.0
9.0
8.0
7.0
pH
6.0
5.0
4.0
3.0
2.0
5.0
6.0
7.0
VOL. OF ALKALI IN ml
Fig.III C-3
Cu(II).IMDA.BA system - 30°C.
(1) IMDA
(2) Acid
(3) BA
(4) Cu(II) + IMDA (1:1)
(5) Cu(II) + IMDA + BA (1:1:1)

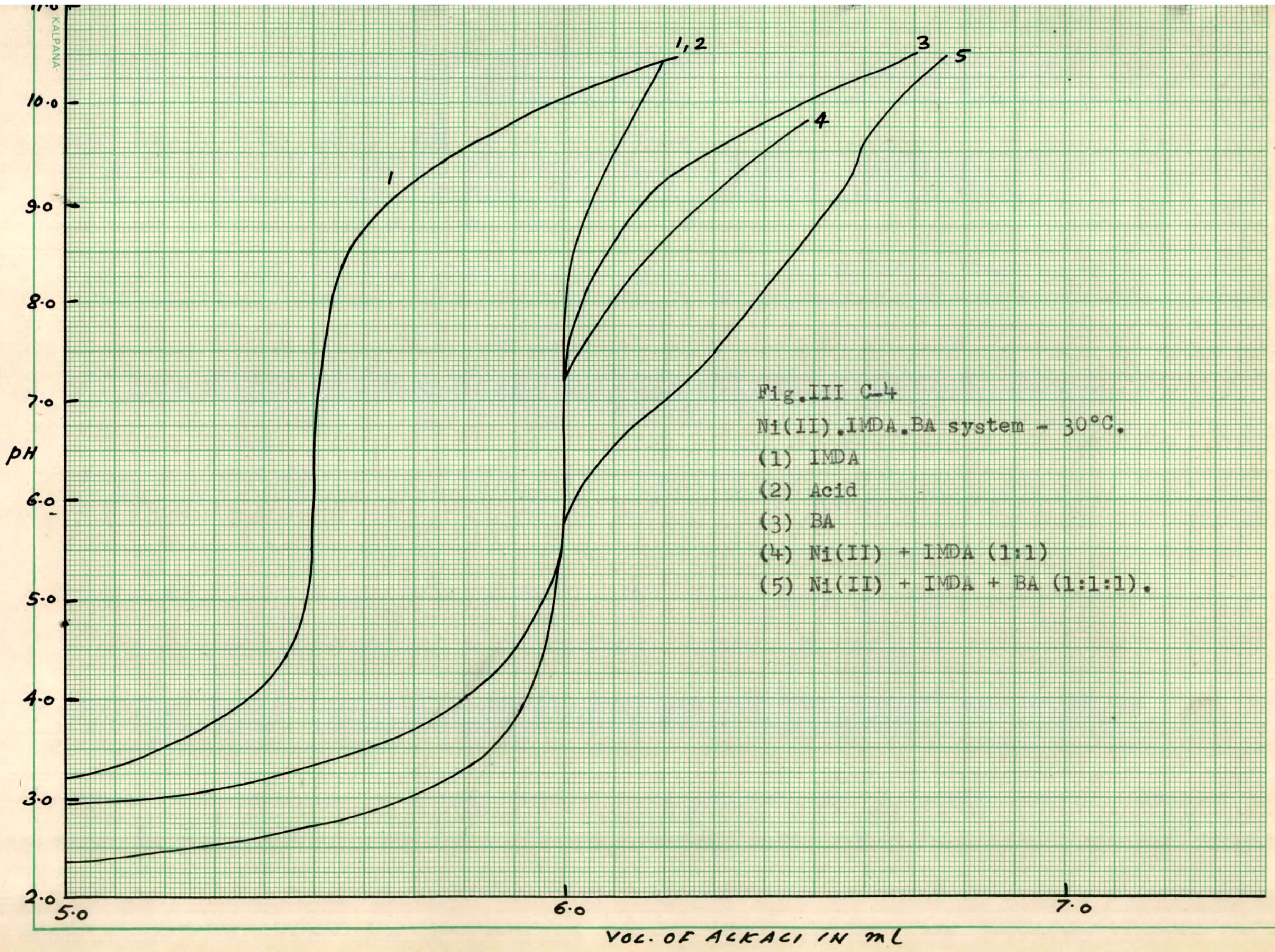



Fig.III C-4

Ni(II).IMDA.BA system - 30°C.

(1) IMDA

(2) Acid

(3) BA

(4) Ni(II) + IMDA (1:1)

(5) Ni(II) + IMDA + BA (1:1:1).

Table IIIC 1.4

N = 0.2M  $V^{o}$ = 50 ml.  $T^{o}_{L}$ = 0.002M  $T^{o}_{M}$ = 0.002M

$E^{o}$ = 0.02M  $^{*}E^{o}$ = 0.024M  $\mu$ = 0.2M  t = 30°C.

$T^{o}_{IMDA}$ = 0.002M

| *DBM | | Ni.IMDA.DBM | |
|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.65 | 0.00 | 1.75 |
| 1.00 | 1.70 | 1.00 | 1.85 |
| 2.00 | 1.80 | 2.00 | 1.95 |
| 3.00 | 1.90 | 3.00 | 2.20 |
| 4.00 | 2.05 | 4.00 | 2.50 |
| 5.00 | 2.40 | 5.00 | 2.90 |
| 5.50 | 2.75 | 5.50 | 3.35 |
| 5.60 | 2.85 | 5.60 | 3.50 |
| 5.70 | 3.05 | 5.70 | 3.70 |
| 5.80 | 3.30 | 5.80 | 3.95 |
| 5.85 | 3.50 | 5.85 | 4.20 |
| 5.90 | 3.75 | 5.90 | 4.50 |
| 5.93 | 4.10 | 5.94 | 4.90 |
| 5.96 | 4.60 | 5.98 | 5.40 |
| 5.98 | 5.20 | 6.00 | 5.60 |
| 6.00 | 7.20 | 6.05 | 6.00 |
| 6.05 | 8.05 | 6.10 | 6.30 |
| 6.10 | 8.65 | 6.20 | 6.75 |
| 6.15 | 9.05 | 6.30 | 7.10 |
| 6.20 | 9.35 | 6.40 | 7.55 |
| 6.30 | 9.80 | 6.50 | 8.15 |
| 6.40 | 10.05 | 6.60 | 9.15 |
| 6.50 | 10.30 | 6.70 | 10.10 |
| 6.60 | 10.50 | 6.80 | 10.65 |

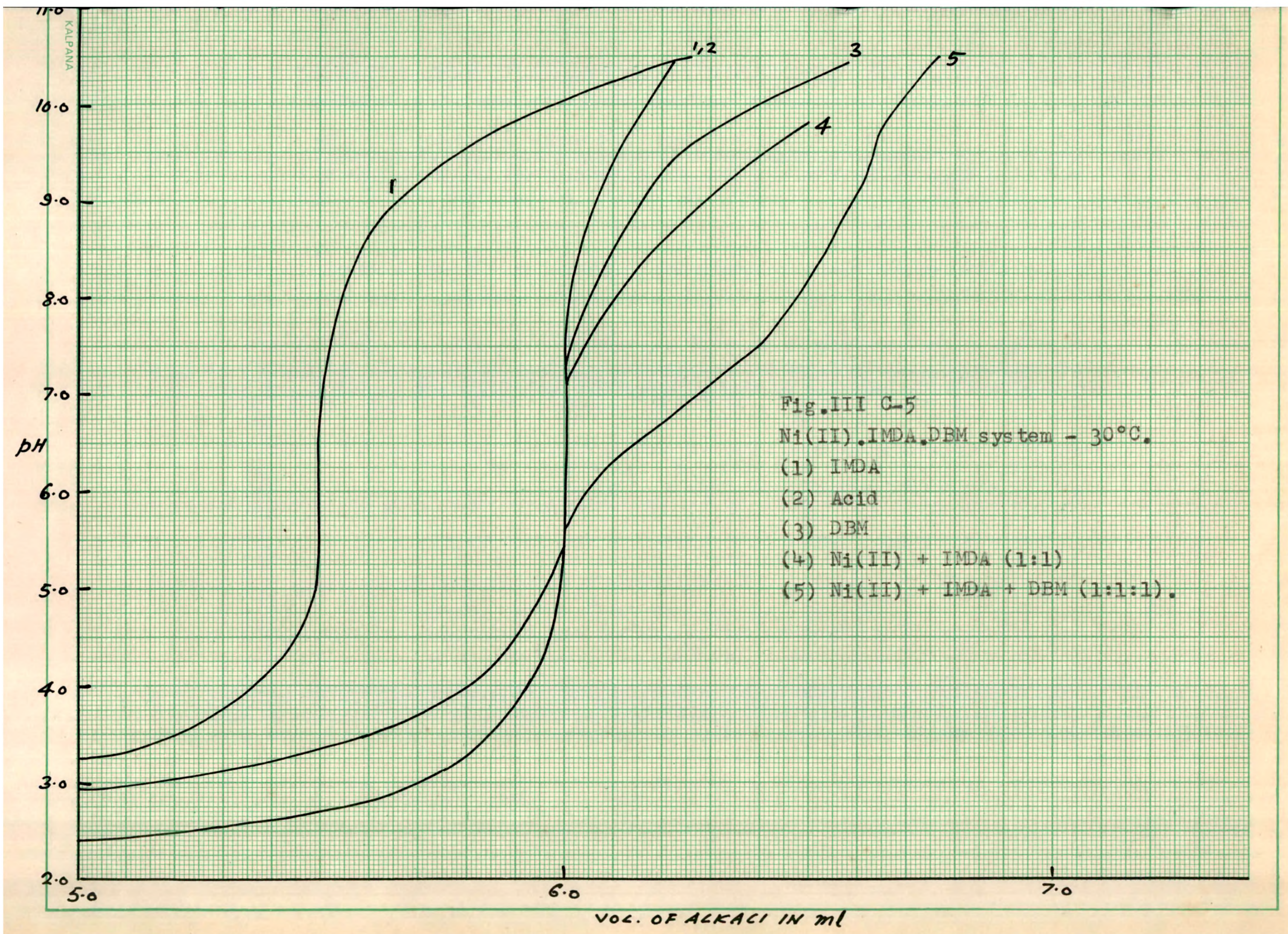



Fig.III C-5

Ni(II).IMDA.DBM system - 30°C.

(1) IMDA

(2) Acid

(3) DBM

(4) Ni(II) + IMDA (1:1)

(5) Ni(II) + IMDA + DBM (1:1:1).

Table IIIC 3.1

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

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

| Perchloric acid | | NTA | | Cu.NTA | | Ni.NTA | |
|---|---|---|---|---|---|---|---|
| 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 | 1.80 | 0.00 | 1.90 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 2.05 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.25 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.55 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 3.25 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.10 | 3.35 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.20 | 3.45 | 4.60 | 2.95 | 4.60 | 2.90 |
| 4.70 | 2.95 | 4.30 | 3.75 | 4.70 | 3.10 | 4.70 | 3.10 |
| 4.80 | 3.15 | 4.35 | 3.90 | 4.80 | 3.35 | 4.80 | 3.35 |
| 4.85 | 3.35 | 4.40 | 4.15 | 4.85 | 3.55 | 4.85 | 3.60 |
| 4.90 | 3.55 | 4.44 | 4.50 | 4.90 | 3.75 | 4.90 | 3.95 |
| 4.92 | 3.65 | 4.48 | 5.00 | 4.93 | 4.00 | 4.93 | 4.20 |
| 4.94 | 3.85 | 4.50 | 7.10 | 4.96 | 4.20 | 4.96 | 4.55 |
| 4.96 | 4.15 | 4.52 | 7.50 | 5.00 | 6.90 | 5.00 | 7.50 |
| 4.98 | 4.50 | 4.55 | 7.90 | 5.05 | 7.90 | 5.02 | 8.45 |
| 5.00 | 7.20 | 4.60 | 8.35 | 5.10 | 8.25 | 5.05 | 8.80 |
| 5.01 | 8.50 | 4.70 | 8.95 | 5.20 | 8.75 | 5.10 | 9.25 |
| 5.05 | 9.55 | 4.80 | 9.35 | 5.30 | 9.25 | 5.20 | 9.95 |
| 5.08 | 10.20 | 4.90 | 9.70 | 5.40 | 9.70 | 5.30 | 10.50 |
| 5.10 | 10.45 | 5.00 | 10.05 | 5.50 | 10.00 | | |
| | | 5.10 | 10.40 | 5.60 | 10.20 | | |

Table IIIC 3.2

N = 0.2M  $V^{\circ}$ = 50 ml.  $T_L^{\circ}$ = 0.002M  $T_M^{\circ}$ = 0.002M

$E^{\circ}$ = 0.02M  $T_{NTA}^{\circ}$ = 0.002M  $\mu$ = 0.2M  t = 30°C.

| AcAc | | Cu.NTA.AcAc | | Ni.NTA.AcAc | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.95 | 4.60 | 2.90 |
| 4.70 | 2.95 | 4.70 | 3.10 | 4.70 | 3.10 |
| 4.80 | 3.15 | 4.80 | 3.35 | 4.80 | 3.35 |
| 4.85 | 3.30 | 4.85 | 3.55 | 4.85 | 3.60 |
| 4.90 | 3.55 | 4.90 | 3.75 | 4.90 | 3.95 |
| 4.93 | 3.80 | 4.93 | 4.00 | 4.93 | 4.20 |
| 4.96 | 4.15 | 4.96 | 4.20 | 4.96 | 4.55 |
| 4.98 | 4.50 | 5.00 | 5.80 | 5.00 | 6.00 |
| 5.00 | 7.15 | 5.05 | 6.35 | 5.05 | 6.70 |
| 5.05 | 8.45 | 5.10 | 6.70 | 5.10 | 7.05 |
| 5.10 | 8.95 | 5.20 | 7.20 | 5.20 | 7.50 |
| 5.20 | 9.40 | 5.30 | 7.65 | 5.30 | 8.10 |
| 5.30 | 9.70 | 5.40 | 8.05 | 5.40 | 8.75 |
| 5.40 | 10.00 | 5.50 | 8.55 | 5.50 | 9.30 |
| 5.50 | 10.25 | 5.60 | 9.35 | 5.60 | 9.85 |
| 5.60 | 10.55 | 5.70 | 9.90 | 5.70 | 10.35 |
| | | 5.80 | 10.30 | | |

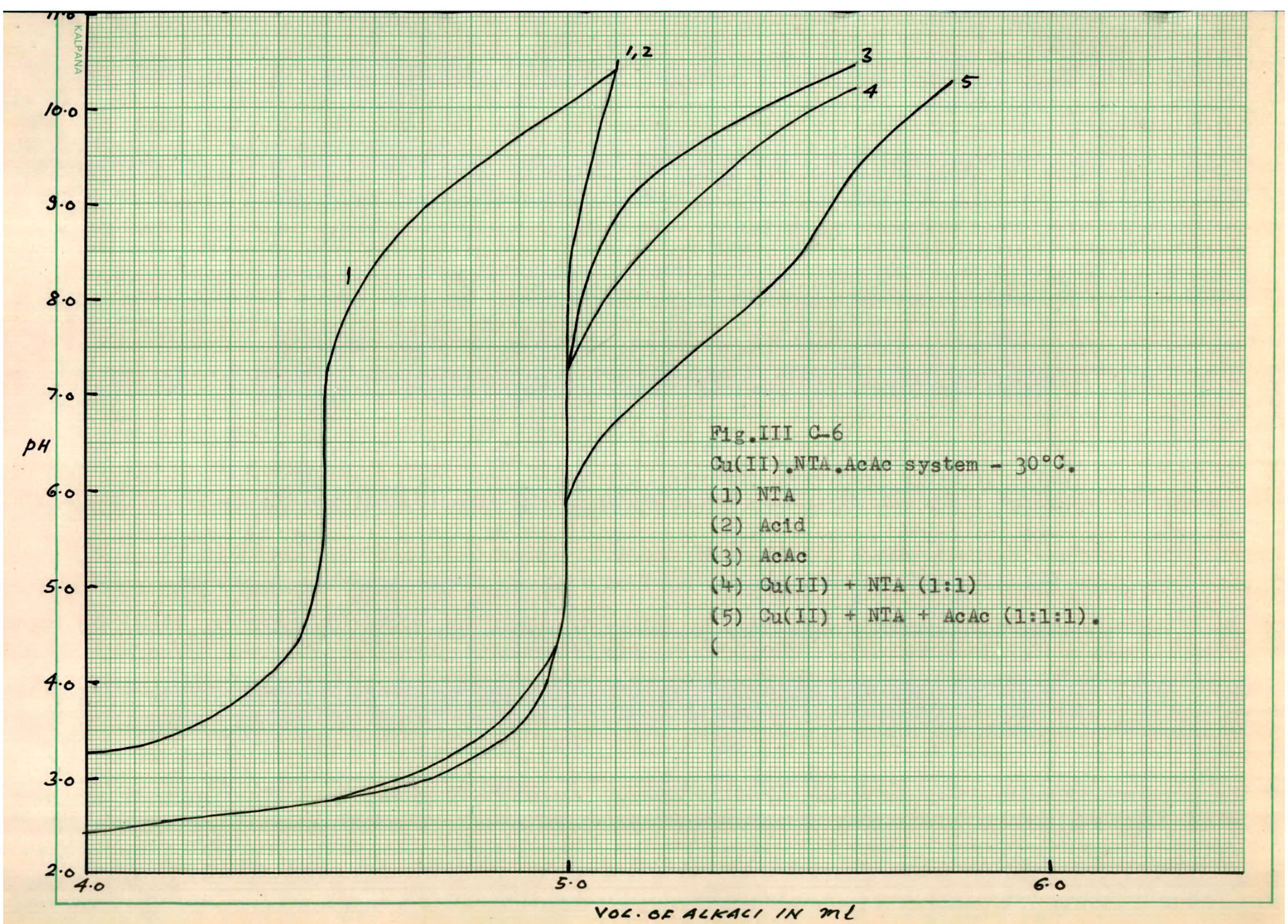



Fig.III C-6

Cu(II).NTA.AcAc system - 30°C.

(1) NTA

(2) Acid

(3) AcAc

(4) Cu(II) + NTA (1:1)

(5) Cu(II) + NTA + AcAc (1:1:1).

(

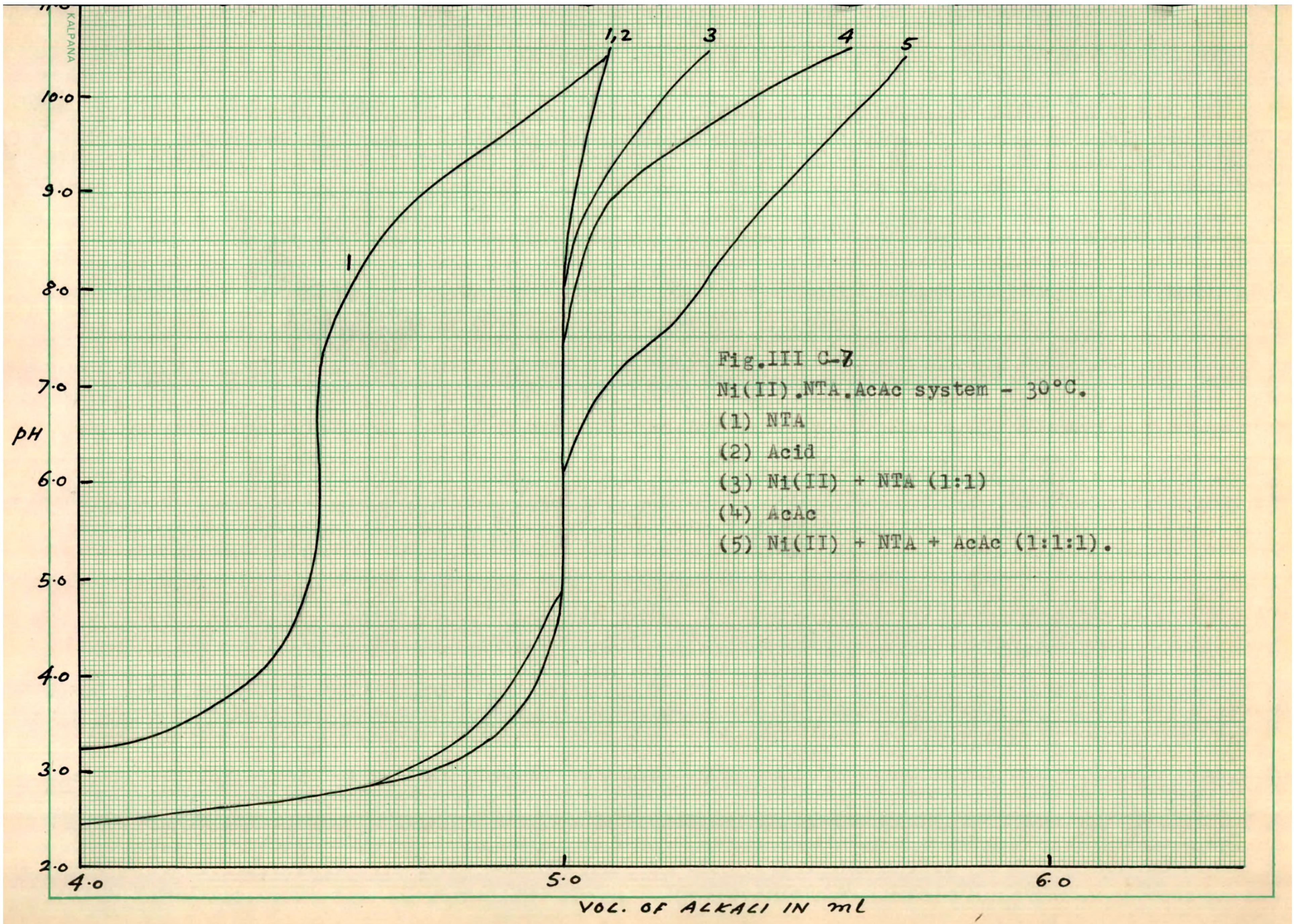


Fig.III C-7
Ni(II).NTA.AcAc system - 30°C.
(1) NTA
(2) Acid
(3) Ni(II) + NTA (1:1)
(4) AcAc
(5) Ni(II) + NTA + AcAc (1:1:1).
pH
VOL. OF ALKALI IN ml
1,2
3
4
5
1
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
4.0
5.0
6.0
KALPANA

## Table IIIC 3.3

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

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

| BA | | Cu.NTA.BA | | Ni.NTA.BA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.80 | 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.95 | 4.60 | 2.90 |
| 4.70 | 2.95 | 4.70 | 3.10 | 4.70 | 3.10 |
| 4.80 | 3.15 | 4.80 | 3.35 | 4.80 | 3.35 |
| 4.85 | 3.35 | 4.90 | 3.75 | 4.90 | 3.95 |
| 4.90 | 3.55 | 4.93 | 4.00 | 4.93 | 4.20 |
| 4.94 | 3.85 | 4.96 | 4.20 | 4.96 | 4.55 |
| 4.98 | 4.50 | 5.00 | 5.55 | 5.00 | 6.00 |
| 5.00 | 6.90 | 5.95 | 6.35 | 5.05 | 6.60 |
| 5.03 | 8.20 | 5.10 | 6.70 | 5.10 | 6.95 |
| 5.05 | 8.50 | 5.20 | 7.20 | 5.20 | 7.50 |
| 5.10 | 9.00 | 5.30 | 7.60 | 5.30 | 8.00 |
| 5.20 | 9.50 | 5.40 | 8.15 | 5.40 | 8.55 |
| 5.30 | 9.80 | 5.50 | 8.65 | 5.50 | 9.15 |
| 5.40 | 10.05 | 5.60 | 9.30 | 5.60 | 9.70 |
| 5.50 | 10.25 | 5.70 | 9.95 | 5.70 | 10.20 |
| 5.60 | 10.50 | 5.80 | 10.30 | 5.80 | 10.60 |

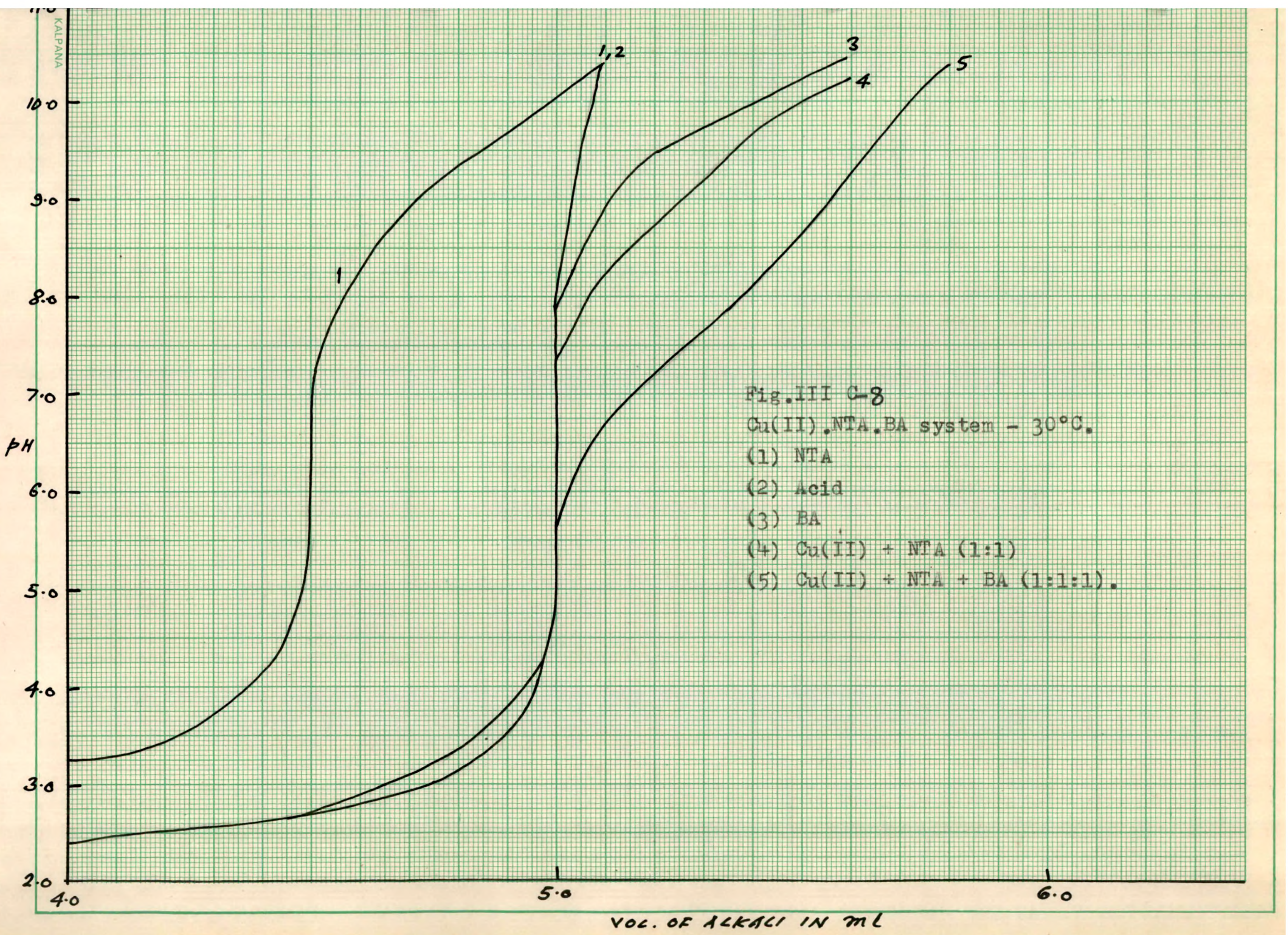


Fig.III C-8
Cu(II).NTA.BA system - 30°C.
(1) NTA
(2) Acid
(3) BA
(4) Cu(II) + NTA (1:1)
(5) Cu(II) + NTA + BA (1:1:1).
pH
VOL. OF ALKALI IN ml
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
4.0
5.0
6.0
1,2
3
4
5
1

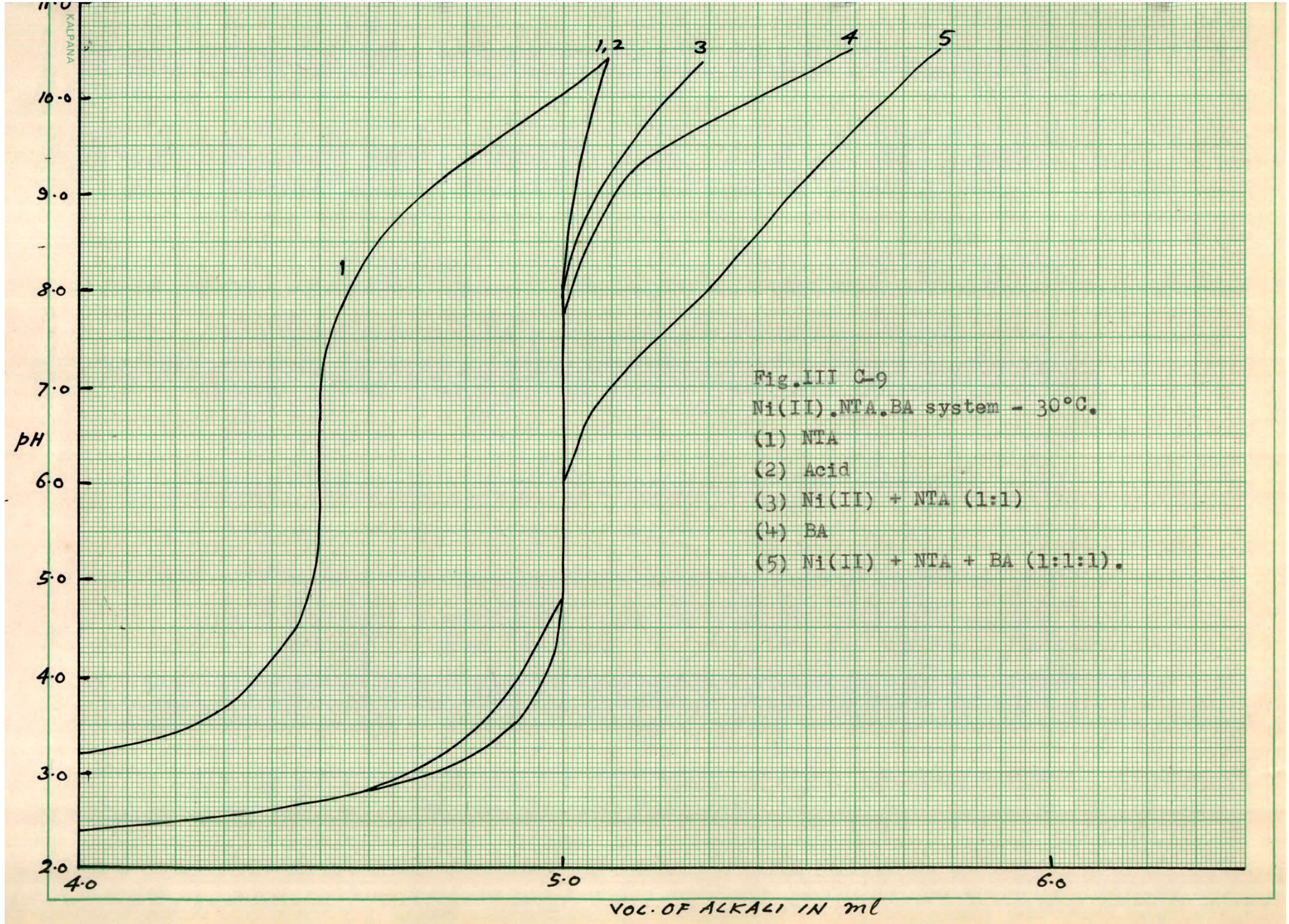


Fig.III C-9
Ni(II).NTA.BA system - 30°C.
(1) NTA
(2) Acid
(3) Ni(II) + NTA (1:1)
(4) BA
(5) Ni(II) + NTA + BA (1:1:1).
pH
VOL. OF ALKALI IN ml
1,2
3
4
5
1
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
4.0
5.0
6.0

## Table IIIC 3.4

$N = 0.2M$   $V^{\circ} = 50$ ml.   $T_L^{\circ} = 0.002M$   $T_M^{\circ} = 0.002M$

$E^{\circ} = 0.02M$   $T_{NTA}^{\circ} = 0.002M$   $\mu = 0.2M$   $t = 30°C$.

| DBM | | Ni.NTA.DBM | |
|---|---|---|---|
| Vol. of alkali (in ml.) | B | Vol. of alkali (in ml.) | B |
| 0.00 | 1.80 | 0.00 | 1.80 |
| 1.00 | 1.90 | 1.00 | 1.90 |
| 2.00 | 2.00 | 2.00 | 2.00 |
| 3.00 | 2.15 | 3.00 | 2.15 |
| 4.00 | 2.45 | 4.00 | 2.45 |
| 4.50 | 2.75 | 4.50 | 2.75 |
| 4.60 | 2.85 | 4.60 | 2.90 |
| 4.70 | 2.95 | 4.70 | 3.10 |
| 4.80 | 3.15 | 4.80 | 3.35 |
| 4.85 | 3.30 | 4.85 | 3.60 |
| 4.90 | 3.55 | 4.90 | 3.95 |
| 4.93 | 3.80 | 4.93 | 4.20 |
| 4.96 | 4.10 | 4.96 | 4.55 |
| 4.98 | 4.60 | 5.00 | 5.85 |
| 5.00 | 7.35 | 5.05 | 6.55 |
| 5.03 | 8.15 | 5.10 | 6.95 |
| 5.05 | 8.55 | 5.20 | 7.45 |
| 5.10 | 9.10 | 5.30 | 7.90 |
| 5.20 | 9.60 | 5.40 | 8.40 |
| 5.30 | 9.85 | 5.50 | 9.10 |
| 5.40 | 10.15 | 5.60 | 9.80 |
| 5.50 | 10.35 | 5.70 | 10.35 |

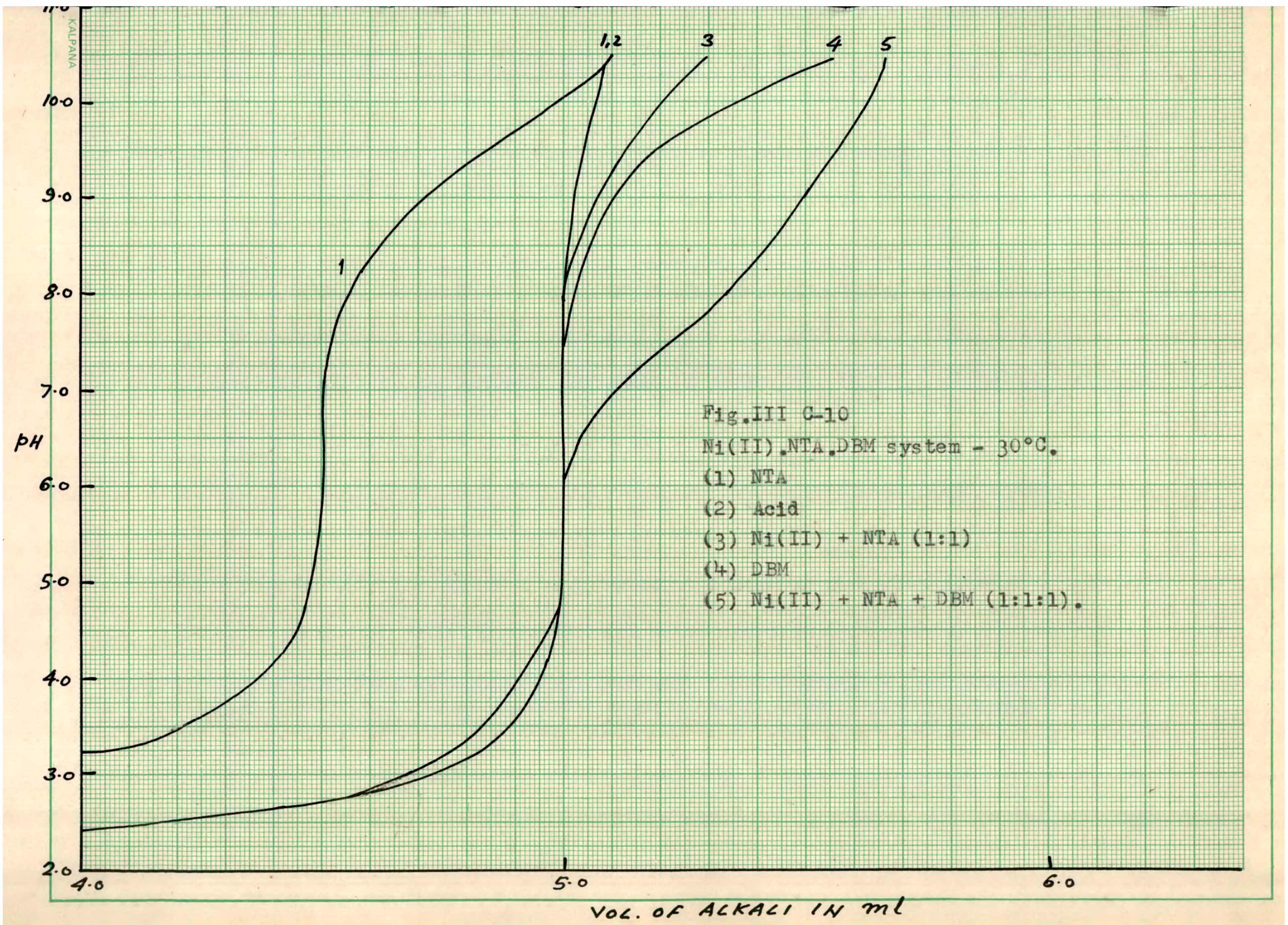


Fig.III C-10
Ni(II).NTA.DBM system - 30°C.
(1) NTA
(2) Acid
(3) Ni(II) + NTA (1:1)
(4) DBM
(5) Ni(II) + NTA + DBM (1:1:1).
1,2
3
4
5
1
pH
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
4.0
5.0
6.0
VOL. OF ALKALI IN ml
KALPANA

## Table IIIC 2.1a

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 6.45 | $1.00_0$ | 6.00 | 6.23 | 0.23 | $0.46_0$ | $0.06_9$ | $6.27_7$ | $6.20_8$ |
| 6.50 | $1.00_0$ | 6.00 | 6.24 | 0.24 | $0.48_0$ | $0.03_5$ | $6.24_4$ | $6.20_9$ |
| 6.55 | $1.00_0$ | 6.00 | 6.25 | 0.25 | $0.50_0$ | - | $6.21_1$ | $6.21_1$ |
| 6.60 | $1.00_0$ | 6.00 | 6.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $6.17_9$ | $6.21_4$ |
| 6.65 | $1.00_0$ | 6.00 | 6.27 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $6.14_7$ | $6.21_2$ |
| 6.70 | $1.00_0$ | 6.00 | 6.28 | 0.28 | $0.56_0$ | $\bar{1}.89_5$ | $6.11_7$ | $6.22_2$ |

$\log K_{MAL}$ = 6.21 $\pm$ 0.01

## Table IIIC 2.2a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Cu.IMDA-benzoylacetone 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 | $1.00_0$ | 6.00 | 6.23 | 0.23 | $0.46_0$ | $0.06_9$ | $6.46_7$ | $6.39_8$ |
| 6.45 | $1.00_0$ | 6.00 | 6.24 | 0.24 | $0.48_0$ | $0.03_5$ | $6.43_4$ | $6.39_9$ |
| 6.50 | $1.00_0$ | 6.00 | 6.25 | 0.25 | $0.50_0$ | - | $6.40_1$ | $6.40_1$ |
| 6.55 | $1.00_0$ | 6.00 | 6.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $6.36_9$ | $6.40_4$ |
| 6.60 | $1.00_0$ | 6.00 | 6.27 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $6.33_7$ | $6.40_2$ |
| 6.65 | $1.00_0$ | 6.00 | 6.28 | 0.28 | $0.56_0$ | $\bar{1}.89_5$ | $6.30_7$ | $6.41_2$ |

$\log K_{MAL}$ = 6.40 $\pm$ 0.01

Fig.III C-11 : Cu(II).IMDA.AcAc
syatem - 30°C.

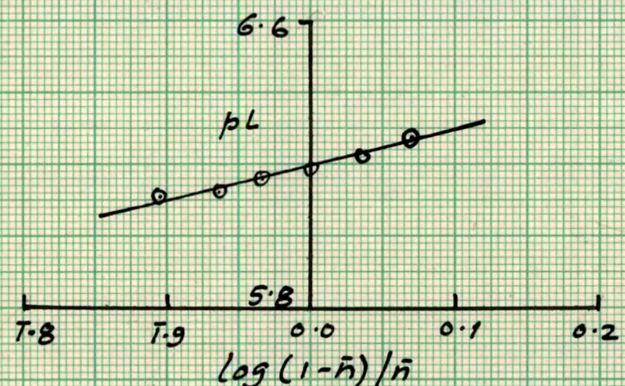
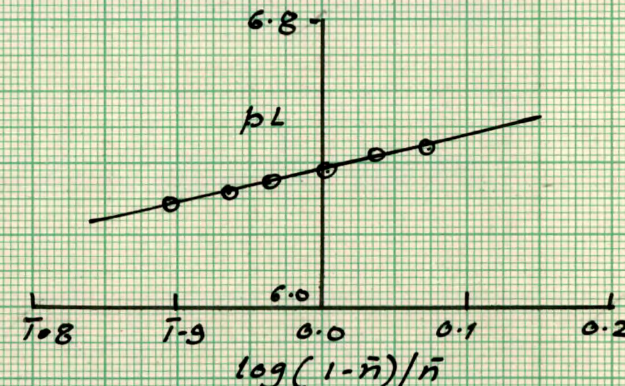



Fig.III C-12 : Cu(II).IMDA.BA
system - 30°C.

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## Table IIIC 2.3b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.25 | $1.00_0$ | 6.00 | 6.23 | 0.23 | $0.46_0$ | $0.06_9$ | $5.47_7$ | $5.40_8$ |
| 7.30 | $1.00_0$ | 6.00 | 6.24 | 0.24 | $0.48_0$ | $0.03_5$ | $5.44_4$ | $5.40_9$ |
| 7.35 | $1.00_0$ | 6.00 | 6.25 | 0.25 | $0.50_0$ | - | $5.41_1$ | $5.41_1$ |
| 7.40 | $1.00_0$ | 6.01 | 6.26 | 0.25 | $0.50_0$ | - | $5.36_1$ | $5.36_1$ |
| 7.45 | $1.00_0$ | 6.01 | 6.27 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $5.22_9$ | $5.26_4$ |
| 7.50 | $1.00_0$ | 6.01 | 6.28 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $5.29_7$ | $5.36_2$ |

$\log K_{MAL} = 5.37 \pm 0.04$

## Table IIIC 2.4b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni.IMDA-benzoylacetone 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 | $1.00_0$ | 6.00 | 6.22 | 0.22 | $0.44_0$ | $0.10_5$ | $5.75_2$ | $5.64_7$ |
| 7.15 | $1.00_0$ | 6.00 | 6.23 | 0.23 | $0.46_0$ | $0.06_9$ | $5.71_7$ | $5.64_8$ |
| 7.20 | $1.00_0$ | 6.00 | 6.24 | 0.24 | $0.48_0$ | $0.03_5$ | $5.68_4$ | $5.64_9$ |
| 7.25 | $1.00_0$ | 6.00 | 6.25 | 0.25 | $0.50_0$ | - | $5.65_1$ | $5.65_1$ |
| 7.30 | $1.00_0$ | 6.00 | 6.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $5.61_9$ | $5.65_4$ |
| 7.35 | $1.00_0$ | 6.00 | 6.27 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $5.62_7$ | $5.69_2$ |

$\log K_{MAL} = 5.66 \pm 0.01$

## Table IIIC 2.5b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 6.75 | $1.00_0$ | 6.00 | 6.20 | 0.20 | $0.48_0$ | $0.17_6$ | $6.29_2$ | $6.11_6$ |
| 6.85 | $1.00_0$ | 6.00 | 6.23 | 0.23 | $0.46_0$ | $0.06_9$ | $6.23_7$ | $6.16_8$ |
| 6.90 | $1.00_0$ | 6.00 | 6.24 | 0.24 | $0.48_0$ | $0.03_5$ | $6.20_4$ | $6.16_9$ |
| 6.95 | $1.00_0$ | 6.00 | 6.25 | 0.25 | $0.50_0$ | - | $6.17_1$ | $6.17_1$ |
| 7.00 | $1.00_0$ | 6.00 | 6.27 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $6.15_7$ | $6.22_2$ |
| 7.10 | $1.00_0$ | 6.00 | 6.29 | 0.29 | $0.58_0$ | $\bar{1}.85_9$ | $6.09_7$ | $6.23_8$ |

$\log K_{MAL} = 6.18 \pm 0.01$

Fig.III C-13 : Ni(II).IMDA.AcAc system - 30°C.

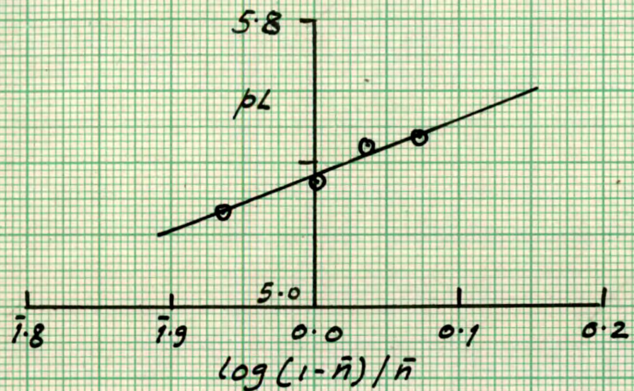



Fig.III C-14 : Ni(II).IMDA.BA system - 30°C.

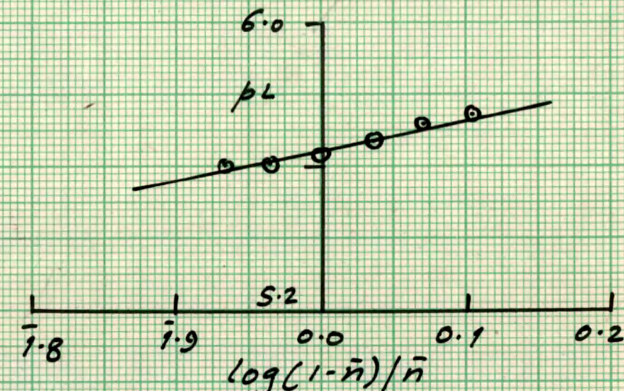
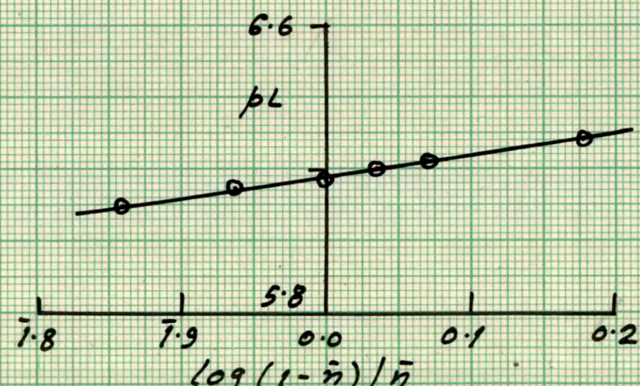



Fig.III C-15 : Ni(II).IMDA.DBM System - 30°C.



## Table IIIC 4.1a

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.35 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.06_9$ | $5.36_9$ | $5.30_0$ |
| 7.40 | $1.00_0$ | 5.00 | 5.24 | 0.24 | $0.48_0$ | $0.03_5$ | $5.33_6$ | $5.30_1$ |
| 7.45 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $5.30_3$ | $5.30_3$ |
| 7.50 | $1.00_0$ | 5.01 | 5.27 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $5.27_1$ | $5.30_6$ |
| 7.55 | $1.00_0$ | 5.01 | 5.28 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $5.23_9$ | $5.30_4$ |
| 7.60 | $1.00_0$ | 5.01 | 5.29 | 0.28 | $0.56_0$ | $\bar{1}.89_5$ | $5.20_9$ | $5.31_4$ |

$\log K_{MAL} = 5.30 \pm 0.01$

## Table IIIC 4.2a

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.35 | $1.00_0$ | 5.00 | 5.22 | 0.22 | $0.44_0$ | $0.10_5$ | $5.49_4$ | $5.38_9$ |
| 7.40 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.06_9$ | $5.45_9$ | $5.39_0$ |
| 7.45 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $5.44_3$ | $5.44_3$ |
| 7.50 | $1.00_0$ | 5.00 | 5.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $5.41_1$ | $5.44_6$ |
| 7.55 | $1.00_0$ | 5.00 | 5.27 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $5.37_9$ | $5.44_4$ |
| 7.60 | $1.00_0$ | 5.00 | 5.28 | 0.28 | $0.56_0$ | $\bar{1}.89_5$ | $5.34_9$ | $5.45_4$ |

$\log K_{MAL} = 5.43 \pm 0.01$

Fig.III C-16 : Cu(II).NTA.AcAc system - 30°C.

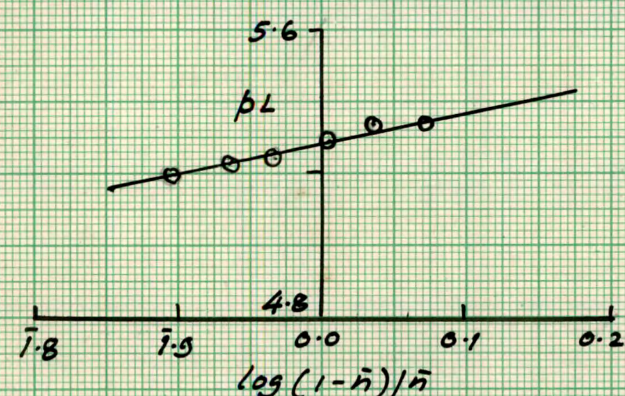
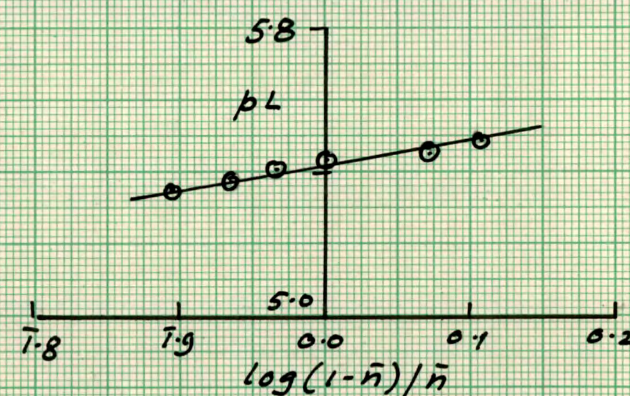



Fig.III C-17 : Cu(II).NTA.BA System - 30°C.



## Table IIIC 4.3b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.60 | $1.00_0$ | 5.01 | 5.21 | 0.20 | $0.40_0$ | $0.17_6$ | $5.07_4$ | $4.89_8$ |
| 7.65 | $1.00_0$ | 5.01 | 5.22 | 0.21 | $0.42_0$ | $0.14_0$ | $5.03_9$ | $4.89_9$ |
| 7.70 | $1.00_0$ | 5.01 | 5.23 | 0.22 | $0.44_0$ | $0.10_5$ | $5.00_4$ | $4.89_9$ |
| 7.80 | $1.00_0$ | 5.02 | 5.25 | 0.23 | $0.46_0$ | $0.06_9$ | $4.91_9$ | $4.85_0$ |
| 7.90 | $1.00_0$ | 5.02 | 5.27 | 0.25 | $0.50_0$ | - | $4.85_3$ | $4.85_3$ |
| 8.00 | $1.00_0$ | 5.03 | 5.29 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $4.77_1$ | $4.80_6$ |
| 8.10 | $1.00_0$ | 5.03 | 5.30 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $4.68_9$ | $4.75_4$ |

$\log K_{MAL} = 4.85 \pm 0.02$

## Table IIIC 4.4b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.50 | $1.00_0$ | 5.00 | 5.20 | 0.20 | $0.40_0$ | $0.17_6$ | $5.31_4$ | $5.13_8$ |
| 7.55 | $1.00_0$ | 5.00 | 5.21 | 0.21 | $0.42_0$ | $0.14_0$ | $5.27_8$ | $5.13_8$ |
| 7.60 | $1.00_0$ | 5.00 | 5.22 | 0.22 | $0.44_0$ | $0.10_5$ | $5.24_4$ | $5.13_9$ |
| 7.65 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.06_9$ | $5.21_9$ | $5.14_0$ |
| 7.70 | $1.00_0$ | 5.00 | 5.24 | 0.24 | $0.48_0$ | $0.03_5$ | $5.17_6$ | $5.14_1$ |
| 7.75 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $5.14_3$ | $5.14_3$ |
| 7.80 | $1.00_0$ | 5.00 | 5.26 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $5.11_1$ | $5.14_6$ |

$\log K_{MAL} = 5.14 \pm 0.01$

## Table IIIC 4.5b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | log(1-$\bar{n}$)/$\bar{n}$ | pL | pL-log(1-$\bar{n}$)/$\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.50 | $1.00_0$ | 5.00 | 5.21 | 0.21 | $0.42_0$ | $0.14_0$ | $5.54_8$ | $5.40_8$ |
| 7.55 | $1.00_0$ | 5.00 | 5.22 | 0.22 | $0.44_0$ | $0.10_5$ | $5.51_4$ | $5.40_9$ |
| 7.60 | $1.00_0$ | 5.00 | 5.23 | 0.23 | $0.46_0$ | $0.06_9$ | $5.47_9$ | $5.41_0$ |
| 7.65 | $1.00_0$ | 5.00 | 5.24 | 0.24 | $0.48_0$ | $0.03_5$ | $5.44_6$ | $5.41_1$ |
| 7.70 | $1.00_0$ | 5.00 | 5.25 | 0.25 | $0.50_0$ | - | $5.41_3$ | $5.41_3$ |
| 7.75 | $1.00_0$ | 5.01 | 5.27 | 0.26 | $0.52_0$ | $\bar{1}.96_5$ | $5.38_1$ | $5.41_6$ |
| 7.80 | $1.00_0$ | 5.01 | 5.28 | 0.27 | $0.54_0$ | $\bar{1}.93_5$ | $5.34_9$ | $5.41_4$ |

$\log K_{MAL} = 5.41 \pm 0.01$

Fig. III C-18 : Ni(II).NTA.AcAc
system - 30°C.

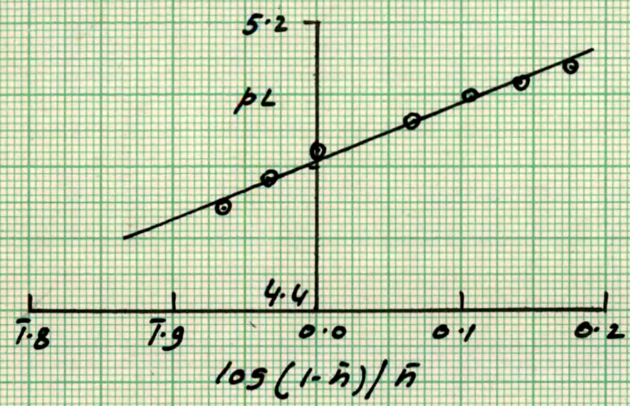



Fig. III C-19 : Ni(II).NTA.BA
system - 30°C.

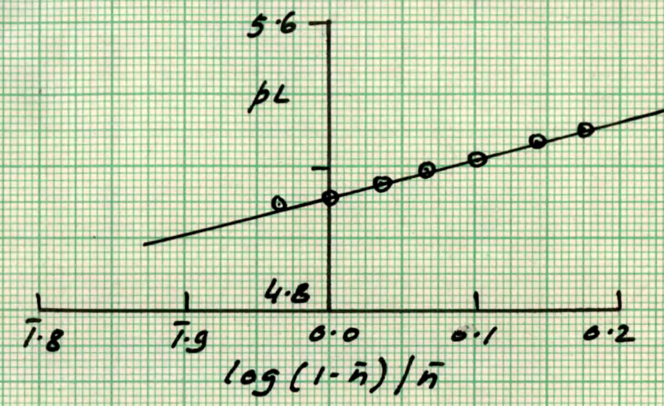



Fig. III C-20 : Ni(II).NTA.DBM
system - 30°C.

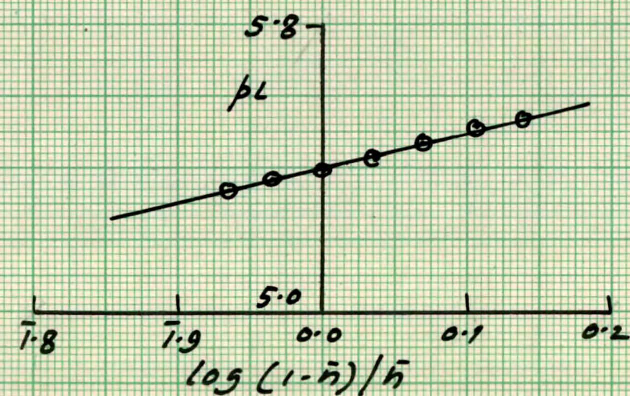


Table III C-5.0 : Stability constants of ternary IMDA-$M^{2+}$-ligand complexes, NTA-$M^{2+}$ ligand complexes - 30°C.

| Ligand | $\log K^{Cu.IMDA}_{Cu.IMDA.L}$ | $\log K^{Ni.IMDA}_{Ni.IMDA.L}$ | $\log K^{Cu.NTA}_{Cu.NTA.L}$ | $\log K^{Ni.NTA}_{Ni.NTA.L}$ |
|---|---|---|---|---|
| Acetylacetone | 6.21 ± 0.01 | 5.37 ± 0.04 | 5.30 ± 0.01 | 4.85 ± 0.02 |
| Benzoylacetone | 6.40 ± 0.01 | 5.66 ± 0.01 | 5.43 ± 0.01 | 5.14 ± 0.01 |
| Dibenzoylmethane | - | 6.18 ± 0.01 | - | 5.41 ± 0.01 |

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