# CHAPTER V

A. Ternary Systems - Metal ion, NTA and Polyhydroxy phenol or Phenolic acid.

B. Ternary Systems - Metal ion, Histidine, IMDA or EDTA and Polyhydroxy phenol or Phenolic acid.

## SECTION A

Since 1956, an extensive amount of research work has been done on the ternary systems involving the combination of a secondary ligand with a metal ion already bound to a charged ligand ion i.e. of nitrilotriacetic acid or ethylenediamine-tetraacetic acid. The mixed ligand complex formed by the combination of a secondary ligand with a metal ion already bound to a charged ligand ion was studied by Intorre and coworkers[1]. Mori and coworkers[2] synthesised the nitrilotriaceto ethylenediamine cobalt (II) $H_2O$ complex. The mixed ligand complexes of various transition metal ions containing NTA and several secondary ligands have been synthesised[3,4]. Various other systems have also been studied where dyes[5] are primary ligands and the amino acids or hydroxy acids are the secondary ligands. The formation constants of mixed ligand complexes of Cu(II) and Ni(II) with NTA and glycine and other mixed ligand systems were studied by Israeli[6]. Thomson and coworkers[7] studied the various mixed ligand complexes involving nitrilotriacetic acid as the primary ligand. The mixed complex of Cu(II) with picolinate and NTA ions have also been reported[8]. Kirson and coworkers[9] reported the triple complex Cu-en-NTA and determined its instability constant. Formation constants of some mixed complexes resulting from the reaction of disodium nitrilotriacetic acid with versenates (EDTA) were studied[10]. Mixed ligand chelates of Th(IV) were reported by Martell and coworkers[11]. A pH metric method has been employed to measure the solution stabilities of the ternary systems of Be(II) containing NTA and tiron[12]. The mixed

ligand complexes of various transition metal ions with NTA have been reported by Steinhaus and coworkers.[13] Daytlova and coworkers[14] studied the behaviour of aqueous solution of Be(II) in the presence of amino poly carboxylic acid. Martell and coworkers[15] have determined the stability of the 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[16] reported the chromium(III) complexes with NTA as a tridentate or tetradentate ligand. Solution equilibrium between Eriochrome Black T and Zn(II).NTA has been studied spectrophotometrically.[17] The mixed ligand complexes of Cr(III) with NTA have also been reported[18]. Equilibrium and stereochemical studies of the interactions of amino acids and their esters with bivalent metal nitrilotriacetic acid complex have been carried out[19]. Kodama and coworkers[20] reported the kinetic and solution equilibrium of metal NTA complexes. A pH metric study of the ternary systems M.NTA.glycine where M = Cu(II), Ni(II), Zn(II) has been reported.[21] Israeli and coworkers[22] studied the mixed complexes of metallic nitrilotriacetates with glutamic acid and aspartic acid. Mixed complexes of serine and arginine with Cu-NTA, Ni-NTA, Co-NTA, Zn-NTA, Mn-NTA, Pb-NTA have also been reported.[23] Israeli[24] has also carried out the potentiometric study of the reactions of glycine with metal NTA. Mixed complexes of imidazole[25] and histidine[26] with various metal.NTA have also been studied. Freeberg[27] employed thermometric titrations to study nitrilotriacetate complexation reaction with bivalent

metal ions. Malinina and coworkers[28] observed the interaction of Ce(IV) with NTA. Stability in solution of mixed compounds of copper(II) with ammonia and complexone was also reported.[29] Potentiometric studies on stepwise formation of complexes containing Cu(II), Ni(II), Zn(II), NTA and hydroxy acid, were also reported by Tondon and coworkers.[30] Co(II) complexes with amino poly carboxylic acid and nitrite ion have been reported.[31] Mixed complexes of neodymium with NTA and EDTA were studied by Tananaeva and coworkers.[32] Reaction of metal NTA with prolinee was studied by Israeli and coworkers.[33] Chidambaram and Bhattacharya[34] have carried out the pH metric study of ternary system [M.NTA.L] where M = $Cu^{2+}$ and L = various amino acids. Panchal and Bhattacharya[35] recently reported the formation constants of the ternary system [M.NTA.L] where M = $Zn^{2+}$ and L = thio acids. But no attempt has been made to study the ternary system [M.NTA.L] where L = polyhydroxy phenols or phenolic acid. In the present investigation, the study of the ternary system [M.NTA.L] where M = $Zn^{2+}$ or $Cd^{2+}$ and L = catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid has been carried out. The reaction can be represented as follows :

$$M^{2+} + NTA^{3-} \rightleftharpoons [M.NTA]^{-}$$

$$[M.NTA]^{-} + L^{2-} \rightleftharpoons [M.NTA.L]^{3-}$$

$$K^{M.NTA}_{M.NTA.L} = \frac{[M.NTA.L]^{3-}}{[M.NTA]^{-}\,[L]^{2-}}$$

For the determination of the mixed ligand formation constant $K^{M.NTA}_{M.NTA.L}$ corresponding to the association of the polyhydroxy

phenols or phenolic acid with $[M.NTA]^-$, a modified form of Irving-Rossotti titration technique, as suggested by earlier workers[36,37], has been used.

It is necessary for such study that $[M.NTA]^-$ complex, formed at low pH, should not undergo hydrolysis or dissociation in the higher pH range. Secondary ligand (L) should combine in the higher pH range where the formation of $[M.NTA]^-$ is complete.

The following experiments were carried out in case of $M^{2+}$.NTA.polyhydroxy phenols or phenolic acid systems. The reagents and the instrument used are same as detailed in chapter II (p. 38-41). Nitrilotriacetic acid (A.R.) used was supplied by Eastman Chemical Company, Inc.New York.

For studying the ternary systems, following solutions were prepared in 50.0 ml. volume for titration :

1. Perchloric acid (0.2M, 5.0 ml.) + nitrilotriacetic acid (19.1 mg.) + sodium perchlorate (1.0M, 8.9 ml.) + conductivity water (36.1 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 15.0 ml.) + sodium perchlorate (1.0M, 8.7 ml.) + conductivity water (21.3 ml.) ; total volume = 50.0 ml., $\mu$ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + nitrilotriacetic acid (19.1 mg.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + conductivity water (31.2 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.

4. perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 15.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.6 ml.) + conductivity water (16.4 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + nitrilotriacetic acid (19.1 mg.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.7 ml.) + conductivity water (26.3 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.

The ionic strength of each solution was thus initially raised to 0.2M. Each of the above samples was titrated against 0.2M sodium hydroxide solution. Nitrogen gas was passed throughout the titration to avoid oxidation of ligands. The plots of pH against volume of alkali have been presented in figs. V A 1 to V A 8.

Observation of the titration graphs gives the following information.

It has been shown earlier that 1:1 complex of NTA and $Zn^{2+}$ or $Cd^{2+}$ are formed at lower pH.[38,39] The horizontal distance between the curves (1) and (3) in the figures is maintained almost constant at high pH showing that M.NTA 1:1 complex does not dissociate at higher pH. M.NTA.secondary ligand (i.e. L = catechol, pyrogallol or 2,3-dihydroxynaphthalene) curve (5) is not below the M.NTA curve (3) in the lower pH range. This is an evidence that in this range where $M^{2+}$.NTA 1:1 complexation takes place, the polyhydroxy phenols do not combine with metal ion. In case of protocatechuic acid, M.NTA.L curve (5) shows separation from M.NTA curve (3) at

lower pH due to the self dissociation of carboxylic group even though ligand coordinates with metal at higher pH. After pH 6.5 curve (5) goes below curve (4).(secondary ligand + 3 equivalents of extra acid). This confirms that in this range coordination of polyhydroxy phenols and phenolic acid with M.NTA takes place resulting in the liberation of extra $H^+$ ions. The reaction can be represented as follows :

$$M^{2+} + NTA^{3-} \rightleftharpoons [M.NTA]^- + 3H^+$$

$$[M.NTA]^- + [C_6H_4(OH)_2] \rightleftharpoons [M.NTA.(C_6H_4O_2)]^{3-} + 2H^+$$

In the polyhydroxy phenols and phenolic acid (curve (4)), three equivalents of extra perchloric acid have been added to compensate for the hydrogen ions liberated by the combination of $M^{2+}$ with NTA in the metal + NTA + secondary ligand solution, (curve (5)).

The additional hydrogen ions liberated as a result of coordination of polyhydroxy phenols or phenolic acid with $[M.NTA]^-$ ion can be determined from the horizontal distance (V"'-V") between curves (5) and (4). The distance can be used for the calculation of $\bar{n}$ value , where $\bar{n}$ is the average number of polyhydroxy phenols or phenolic acid molecules associated with a single $[M.NTA]^-$ ion. The following Irving-Rossotti equation is applicable in calculating $\bar{n}$ values.

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

where $T^{\circ}_{M}$ is the concentration of $[M.NTA]^{-}$, which is equal to the concentration of metal perchlorate used. The pL values were also calculated by using equation as in the previous chapter (p.49 ). The $\bar{n}$ and pL values calculated at different pH are reported in the tables V A 3.1b to V A 3.4c. pL at $\bar{n} = 0.5$ gives the values of log $K^{MA}_{MAL}$. This however, will mean using only one point and the values may be erroneous. More precise values were obtained by using the method of linear plot.[40] The values have been presented in table V A 4.0.

It is observed from tables that the order of formation constants, corresponding to the association of polyhydroxy phenols and phenolic acid with M.NTA , is same as in the binary metal and catechol, pyrogallol, 2,3-dihydroxy-naphthalene or protocatechuic acid systems (chapter II, p. 79 ). This can be explained in terms of the basicities of the ligands. However, $K^{MA}_{MAL}$ corresponding to the association of the secondary ligand with M.NTA is much less (2.5 log to 3.3 log units) than the first formation constant $K^{M}_{ML}$, corresponding to the association of the polyhydroxy secondary ligands with metal ions. $K^{MA}_{MAL}$ is even less than the second formation constant $K^{ML}_{ML_2}$. This can be explained to be due to the fact that $NTA^{3-}$ (nitrilotriacetate anion) and $L^{2-}$ (polyhydroxy phenolate anion) are negatively charged ions and hence during the coordination of polyhydroxy phenolic ligand (L) with $[M.NTA]^{-}$, there will be an electrostatic repulsion due to already existing $NTA^{3-}$. Thus the tendency of polyhydroxy phenol or phenolic acid to combine with $[M.NTA]^{-}$ ion, will be less than its tendency to combine with

$[M(H_2O)_n]^{2+}$ ion. This explains why the value of $K^{MA}_{MAL}$ is less than $K^{M}_{ML_1}$. During the formation of $[ML_2]^{2-}$ also, the incoming $L^{2-}$ has to face the electrostatic repulsion due to already existing $L^{2-}$. This will, however, be less than the electrostatic repulsion between $NTA^{3-}$ and $L^{2-}$. Further $NTA^{3-}$ occupies more space around the metal ion and hence imposes steric hinderence on the incoming $L^{2-}$. As a result of it, $K^{MA}_{MAL}$ is even less than $K^{ML}_{ML_2}$.

It is observed that $K^{Cd}_{Cd.L} - K^{Cd.NTA}_{Cd.NTA.L}$ is less than $K^{Zn}_{Zn.L} - K^{Zn.NTA}_{Zn.NTA.L}$. This is because cadmium ion with bigger size has greater space and hence electrostatic repulsion and steric hinderence on the secondary ligand due to NTA is less.

## Table VA 1.0

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{NTA}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.026M

*Perchloric acid

| NTA | | Zn.NTA | | Cd.NTA | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.58 | 1.00 | 1.60 | 1.00 | 1.60 |
| 2.00 | 1.60 | 2.00 | 1.70 | 2.00 | 1.65 |
| 3.00 | 1.75 | 2.50 | 1.75 | 3.00 | 1.80 |
| 4.00 | 1.85 | 3.00 | 1.85 | 4.00 | 2.00 |
| 5.00 | 2.10 | 3.50 | 1.95 | 5.00 | 2.25 |
| 5.50 | 2.35 | 4.00 | 2.10 | 5.50 | 2.50 |
| 5.80 | 2.50 | 4.50 | 2.25 | 5.80 | 2.70 |
| 5.90 | 2.60 | 5.00 | 2.45 | 5.90 | 2.75 |
| 6.00 | 2.70 | 5.50 | 2.85 | 6.00 | 2.90 |
| 6.10 | 2.85 | 5.60 | 3.00 | 6.10 | 3.05 |
| 6.20 | 3.05 | 5.70 | 3.25 | 6.15 | 3.20 |
| 6.30 | 3.45 | 5.80 | 3.75 | 6.20 | 3.40 |
| 6.40 | 4.00 | 5.90 | 4.05 | 6.25 | 3.60 |
| 6.44 | 4.35 | 5.94 | 4.25 | 6.30 | 3.98 |
| 6.48 | 4.75 | 5.98 | 4.55 | 6.35 | 4.30 |
| 6.49 | 4.90 | 6.00 | 7.90 | 6.40 | 4.60 |
| 6.50 | 9.50 | 6.04 | 8.50 | 6.44 | 4.95 |
| 6.54 | 9.80 | 6.08 | 8.85 | 6.48 | 5.20 |
| 6.58 | 10.00 | 6.10 | 8.95 | 6.50 | 8.70 |
| 6.65 | 10.30 | 6.15 | 9.20 | 6.54 | 9.05 |
| 6.70 | 10.45 | 6.20 | 9.35 | 6.58 | 9.30 |
| 6.80 | 10.65 | 6.25 | 9.50 | 6.62 | 9.48 |
| 6.90 | 10.72 | 6.30 | 9.65 | 6.66 | 9.60 |
| 7.00 | 10.86 | 6.35 | 9.75 | 6.70 | 9.72 |
| 7.10 | 10.95 | 6.40 | 9.90 | 6.80 | 9.98 |
| 7.14 | 11.00 | 6.50 | 10.10 | 6.90 | 10.20 |
| | | 6.60 | 10.30 | 7.00 | 10.35 |
| | | 6.70 | 10.45 | 7.10 | 10.52 |
| | | 6.80 | 10.65 | 7.20 | 10.65 |
| | | 6.90 | 10.72 | 7.30 | 10.75 |
| | | 7.00 | 10.86 | 7.40 | 10.80 |
| | | 7.10 | 10.95 | 7.50 | 10.90 |
| | | 7.14 | 11.00 | 7.60 | 10.95 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | 0.00 | 1.55 |
| | | | | | | 1.00 | 1.60 |
| | | | | | | 2.00 | 1.65 |
| | | | | | | 3.00 | 1.80 |
| | | | | | | 4.00 | 2.00 |
| | | | | | | 5.00 | 2.30 |
| | | | | | | 5.50 | 2.60 |
| | | | | | | 5.80 | 2.80 |
| | | | | | | 5.90 | 2.88 |
| | | | | | | 6.00 | 3.05 |
| | | | | | | 6.10 | 3.25 |
| | | | | | | 6.15 | 3.38 |
| | | | | | | 6.20 | 3.52 |
| | | | | | | 6.25 | 3.70 |
| | | | | | | 6.30 | 3.95 |
| | | | | | | 6.35 | 4.25 |
| | | | | | | 6.40 | 4.60 |
| | | | | | | 6.44 | 4.90 |
| | | | | | | 6.48 | 5.25 |
| | | | | | | 6.50 | 8.50 |
| | | | | | | 6.54 | 9.05 |
| | | | | | | 6.58 | 9.45 |
| | | | | | | 6.62 | 9.70 |
| | | | | | | 6.66 | 9.90 |
| | | | | | | 6.70 | 10.10 |
| | | | | | | 6.80 | 10.38 |
| | | | | | | 6.90 | 10.52 |
| | | | | | | 7.00 | 10.65 |
| | | | | | | 7.10 | 10.75 |
| | | | | | | 7.20 | 10.82 |
| | | | | | | 7.30 | 10.90 |
| | | | | | | 7.40 | 10.95 |
| | | | | | | 7.50 | 11.00 |

## Table VA 2.1

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{NTA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.026M

| *Catechol | | Zn.NTA.Catechol | | Cd.NTA.Catechol | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.58 | 1.00 | 1.60 | 1.00 | 1.60 |
| 2.00 | 1.60 | 2.00 | 1.65 | 2.00 | 1.65 |
| 3.00 | 1.75 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 1.85 | 4.00 | 2.00 | 4.00 | 2.00 |
| 5.00 | 2.10 | 5.00 | 2.25 | 5.00 | 2.30 |
| 5.50 | 2.35 | 5.50 | 2.50 | 5.50 | 2.60 |
| 5.80 | 2.50 | 5.80 | 2.70 | 5.80 | 2.80 |
| 5.90 | 2.60 | 5.90 | 2.75 | 5.90 | 2.88 |
| 6.00 | 2.70 | 6.00 | 2.90 | 6.00 | 3.05 |
| 6.10 | 2.85 | 6.10 | 3.05 | 6.10 | 3.25 |
| 6.20 | 3.05 | 6.20 | 3.40 | 6.20 | 3.52 |
| 6.30 | 3.45 | 6.25 | 3.60 | 6.25 | 3.70 |
| 6.40 | 4.00 | 6.30 | 3.98 | 6.30 | 3.95 |
| 6.44 | 4.35 | 6.35 | 4.30 | 6.35 | 4.25 |
| 6.48 | 4.75 | 6.40 | 4.60 | 6.40 | 4.60 |
| 6.50 | 7.90 | 6.44 | 4.95 | 6.44 | 4.90 |
| 6.54 | 8.32 | 6.48 | 5.20 | 6.48 | 5.25 |
| 6.58 | 8.65 | 6.50 | 7.25 | 6.50 | 7.75 |
| 6.62 | 8.80 | 6.54 | 7.70 | 6.54 | 8.10 |
| 6.66 | 8.95 | 6.58 | 8.10 | 6.58 | 8.35 |
| 6.70 | 9.10 | 6.62 | 8.28 | 6.62 | 8.52 |
| 6.74 | 9.22 | 6.66 | 8.38 | 6.66 | 8.70 |
| 6.78 | 9.35 | 6.70 | 8.52 | 6.70 | 8.80 |
| 6.82 | 9.48 | 6.80 | 8.78 | 6.80 | 9.10 |
| 6.90 | 9.65 | 6.90 | 8.94 | 6.90 | 9.40 |
| 7.00 | 9.96 | 7.00 | 9.05 | 7.00 | 9.60 |
| 7.10 | 10.25 | 7.10 | 9.20 | 7.10 | 9.78 |
| 7.20 | 10.48 | 7.20 | 9.38 | 7.20 | 10.00 |
| 7.30 | 10.65 | 7.40 | 9.80 | 7.30 | 10.18 |
| 7.40 | 10.75 | 7.50 | 10.00 | 7.40 | 10.35 |
| 7.50 | 10.85 | 7.60 | 10.20 | 7.50 | 10.52 |
| 7.60 | 10.95 | 7.80 | 10.60 | 7.60 | 10.65 |
| | | 8.00 | 10.90 | 7.80 | 10.88 |
| | | 8.10 | 11.00 | 8.00 | 11.00 |

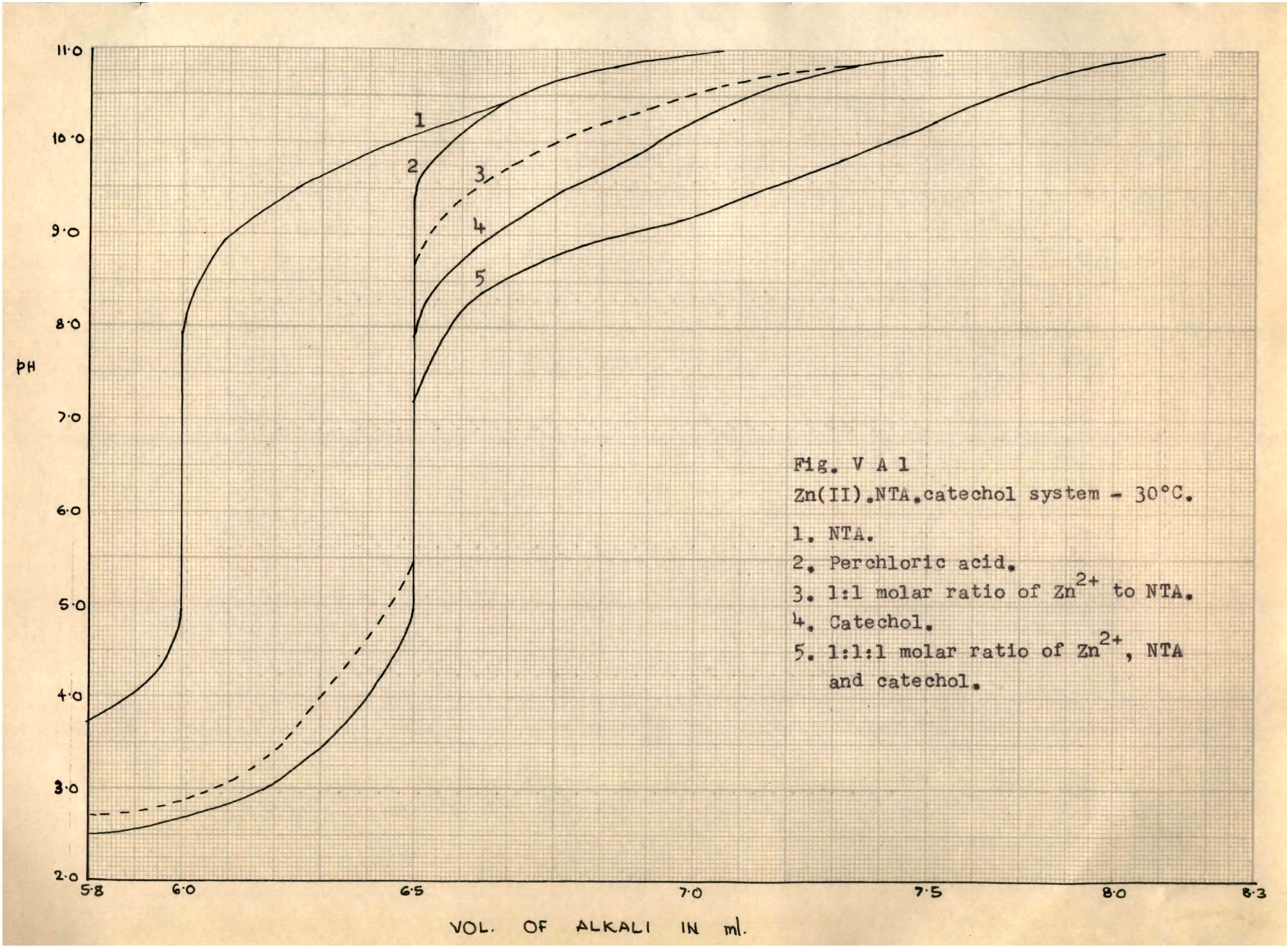


Fig. V A 1

Zn(II).NTA.catechol system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to NTA.
4. Catechol.
5. 1:1:1 molar ratio of $Zn^{2+}$, NTA and catechol.

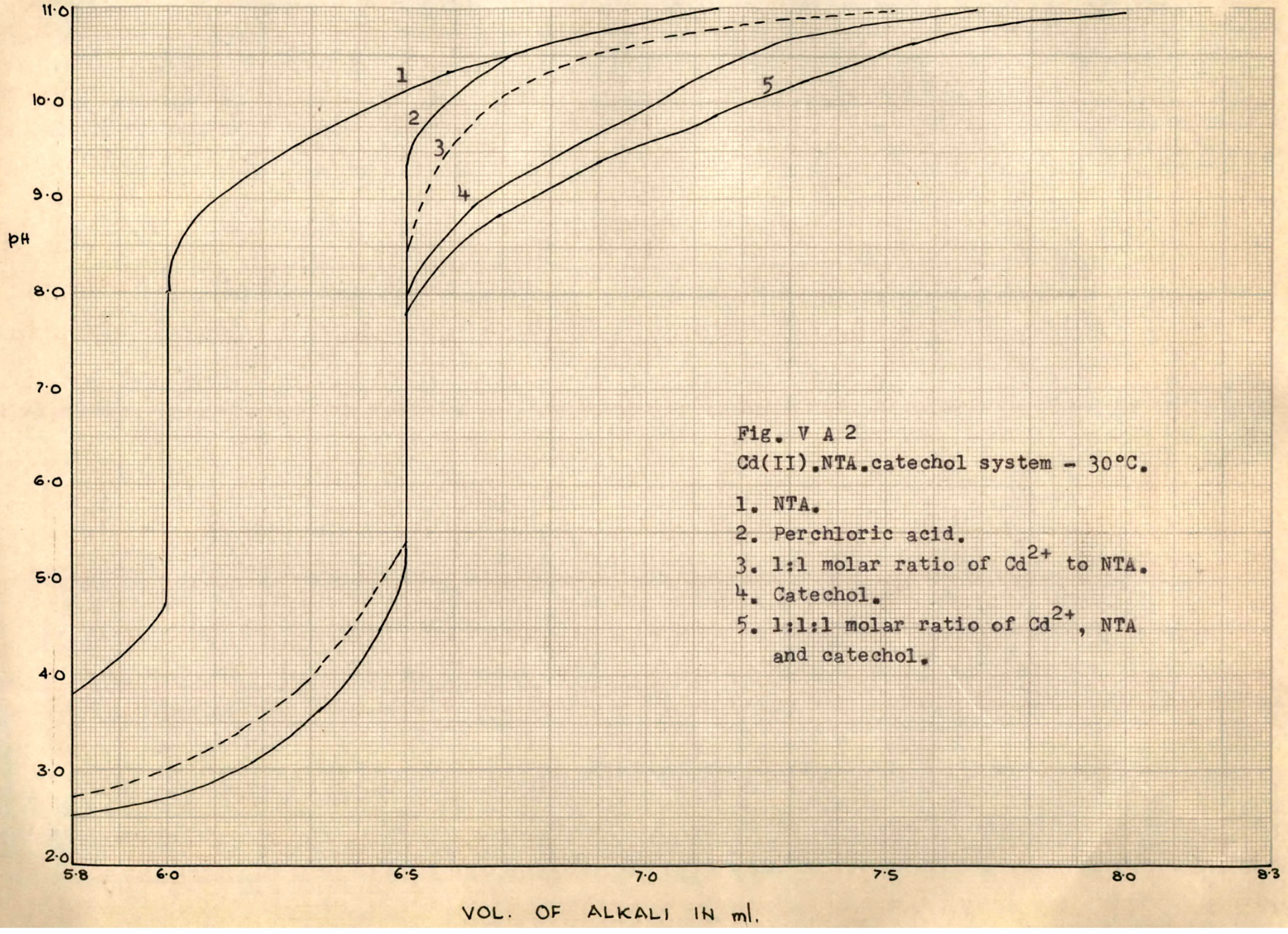


Fig. V A 2
Cd(II).NTA.catechol system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to NTA.
4. Catechol.
5. 1:1:1 molar ratio of $Cd^{2+}$, NTA and catechol.

## Table VA 2.2

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{NTA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.026M

| *Pyrogallol | | Zn.NTA.Pyrogallol | | Cd.NTA.Pyrogallol | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.58 | 1.00 | 1.60 | 1.00 | 1.60 |
| 2.00 | 1.62 | 2.00 | 1.65 | 2.00 | 1.65 |
| 3.00 | 1.75 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 1.85 | 4.00 | 2.00 | 4.00 | 2.00 |
| 5.00 | 2.15 | 5.00 | 2.25 | 5.00 | 2.30 |
| 5.50 | 2.35 | 5.50 | 2.50 | 5.50 | 2.60 |
| 5.80 | 2.50 | 5.80 | 2.70 | 5.80 | 2.80 |
| 5.90 | 2.58 | 5.90 | 2.75 | 5.90 | 2.88 |
| 6.00 | 2.68 | 6.00 | 2.90 | 6.00 | 3.05 |
| 6.10 | 2.84 | 6.10 | 3.05 | 6.10 | 3.25 |
| 6.20 | 3.10 | 6.20 | 3.40 | 6.20 | 3.52 |
| 6.30 | 3.45 | 6.25 | 3.60 | 6.25 | 3.70 |
| 6.40 | 4.05 | 6.30 | 3.98 | 6.30 | 3.95 |
| 6.44 | 4.35 | 6.35 | 4.30 | 6.35 | 4.25 |
| 6.48 | 4.75 | 6.40 | 4.60 | 6.40 | 4.60 |
| 6.50 | 7.45 | 6.44 | 4.95 | 6.44 | 4.90 |
| 6.54 | 7.70 | 6.48 | 5.20 | 6.48 | 5.25 |
| 6.58 | 7.95 | 6.50 | 7.25 | 6.50 | 7.35 |
| 6.62 | 8.20 | 6.54 | 7.48 | 6.54 | 7.60 |
| 6.68 | 8.45 | 6.58 | 7.70 | 6.58 | 7.80 |
| 6.70 | 8.55 | 6.62 | 7.90 | 6.62 | 8.00 |
| 6.75 | 8.75 | 6.66 | 8.12 | 6.66 | 8.18 |
| 6.80 | 8.95 | 6.70 | 8.30 | 6.70 | 8.35 |
| 6.90 | 9.25 | 6.75 | 8.40 | 6.75 | 8.55 |
| 7.00 | 9.60 | 6.80 | 8.50 | 6.80 | 8.70 |
| 7.10 | 9.80 | 6.90 | 8.80 | 6.90 | 9.00 |
| 7.20 | 10.15 | 7.00 | 9.00 | 7.00 | 9.30 |
| 7.30 | 10.30 | 7.10 | 9.22 | 7.10 | 9.55 |
| 7.40 | 10.40 | 7.20 | 9.38 | 7.20 | 9.80 |
| 7.60 | 10.68 | 7.30 | 9.55 | 7.30 | 10.00 |
| 7.80 | 10.80 | 7.40 | 9.70 | 7.40 | 10.20 |
| 8.00 | 10.90 | 7.50 | 9.80 | 7.50 | 10.32 |
| 8.10 | 11.00 | 7.60 | 10.10 | 7.60 | 10.42 |
| | | 7.80 | 10.35 | 7.80 | 10.55 |
| | | 8.00 | 10.55 | 8.00 | 10.75 |
| | | 8.20 | 10.75 | 8.20 | 10.88 |
| | | 8.30 | 10.90 | 8.30 | 11.00 |
| | | 8.40 | 11.05 | | |

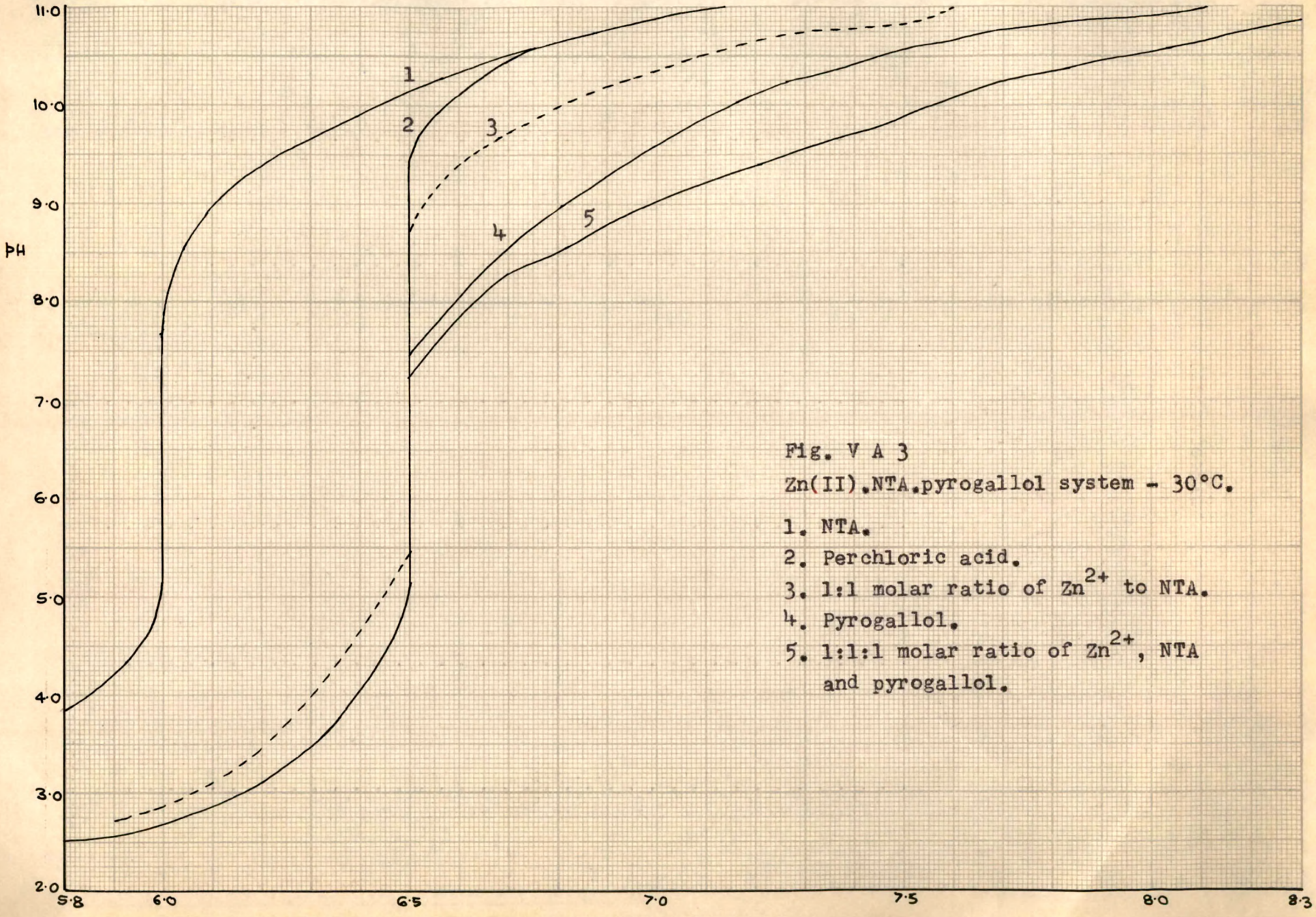


Fig. V A 3
Zn(II).NTA.pyrogallol system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to NTA.
4. Pyrogallol.
5. 1:1:1 molar ratio of $Zn^{2+}$, NTA and pyrogallol.

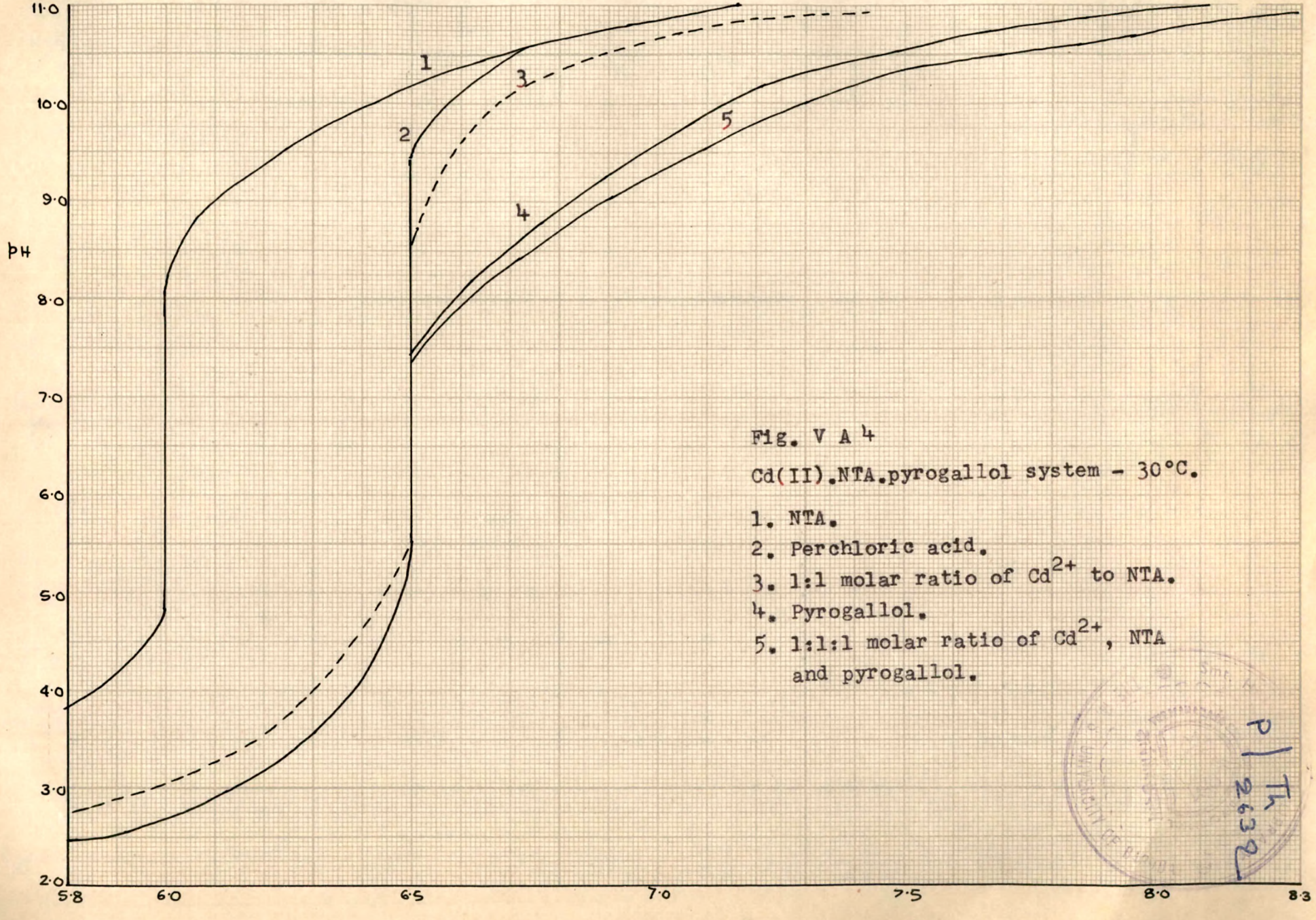


Fig. V A 4

Cd(II).NTA.pyrogallol system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to NTA.
4. Pyrogallol.
5. 1:1:1 molar ratio of $Cd^{2+}$, NTA and pyrogallol.

## Table VA 2.3

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{NTA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.026M

| *Protocatechuic acid | | Zn.NTA.Protocatechuic acid | | Cd.NTA.Protocatechuic acid | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.58 | 1.00 | 1.58 | 1.00 | 1.58 |
| 2.00 | 1.60 | 2.00 | 1.60 | 2.00 | 1.60 |
| 3.00 | 1.75 | 3.00 | 1.75 | 3.00 | 1.75 |
| 4.00 | 1.85 | 4.00 | 1.85 | 4.00 | 1.85 |
| 5.00 | 2.10 | 5.00 | 2.10 | 5.00 | 2.10 |
| 5.50 | 2.35 | 5.50 | 2.35 | 5.50 | 2.35 |
| 5.80 | 2.50 | 5.80 | 2.50 | 5.80 | 2.50 |
| 6.00 | 2.70 | 6.00 | 2.70 | 6.00 | 2.70 |
| 6.10 | 2.85 | 6.10 | 2.85 | 6.10 | 2.85 |
| 6.20 | 3.05 | 6.20 | 3.05 | 6.20 | 3.05 |
| 6.30 | 3.20 | 6.30 | 3.20 | 6.30 | 3.20 |
| 6.40 | 3.50 | 6.40 | 3.50 | 6.40 | 3.50 |
| 6.50 | 3.85 | 6.50 | 3.85 | 6.50 | 3.85 |
| 6.55 | 4.00 | 6.55 | 3.95 | 6.55 | 4.00 |
| 6.60 | 4.20 | 6.60 | 4.10 | 6.60 | 4.20 |
| 6.65 | 4.40 | 6.65 | 4.25 | 6.65 | 4.35 |
| 6.70 | 4.65 | 6.70 | 4.45 | 6.70 | 4.55 |
| 6.73 | 4.85 | 6.73 | 4.58 | 6.73 | 4.70 |
| 6.76 | 5.10 | 6.76 | 4.70 | 6.76 | 4.85 |
| 6.79 | 5.40 | 6.79 | 4.85 | 6.79 | 5.05 |
| 6.82 | 5.95 | 6.82 | 5.10 | 6.82 | 5.35 |
| 6.85 | 7.00 | 6.85 | 5.45 | 6.85 | 5.75 |
| 6.88 | 7.50 | 6.88 | 6.15 | 6.88 | 6.40 |
| 6.92 | 7.70 | 6.92 | 7.10 | 6.92 | 7.30 |
| 6.96 | 8.05 | 6.96 | 7.50 | 6.96 | 7.60 |
| 7.00 | 8.25 | 7.00 | 7.80 | 7.00 | 7.85 |
| 7.04 | 8.40 | 7.05 | 8.05 | 7.05 | 8.08 |
| 7.12 | 8.72 | 7.10 | 8.22 | 7.10 | 8.30 |
| 7.16 | 8.90 | 7.20 | 8.40 | 7.20 | 8.62 |
| 7.20 | 9.02 | 7.40 | 8.72 | 7.30 | 8.95 |
| 7.30 | 9.45 | 7.60 | 9.05 | 7.40 | 9.32 |
| 7.40 | 9.95 | 7.80 | 9.40 | 7.60 | 9.85 |
| 7.50 | 10.25 | 7.90 | 9.75 | 7.80 | 10.20 |
| 7.60 | 10.50 | 8.00 | 10.20 | 7.90 | 10.40 |
| 7.80 | 10.75 | 8.20 | 10.65 | 8.20 | 10.75 |
| 8.00 | 11.00 | 8.40 | 11.05 | 8.40 | 11.00 |

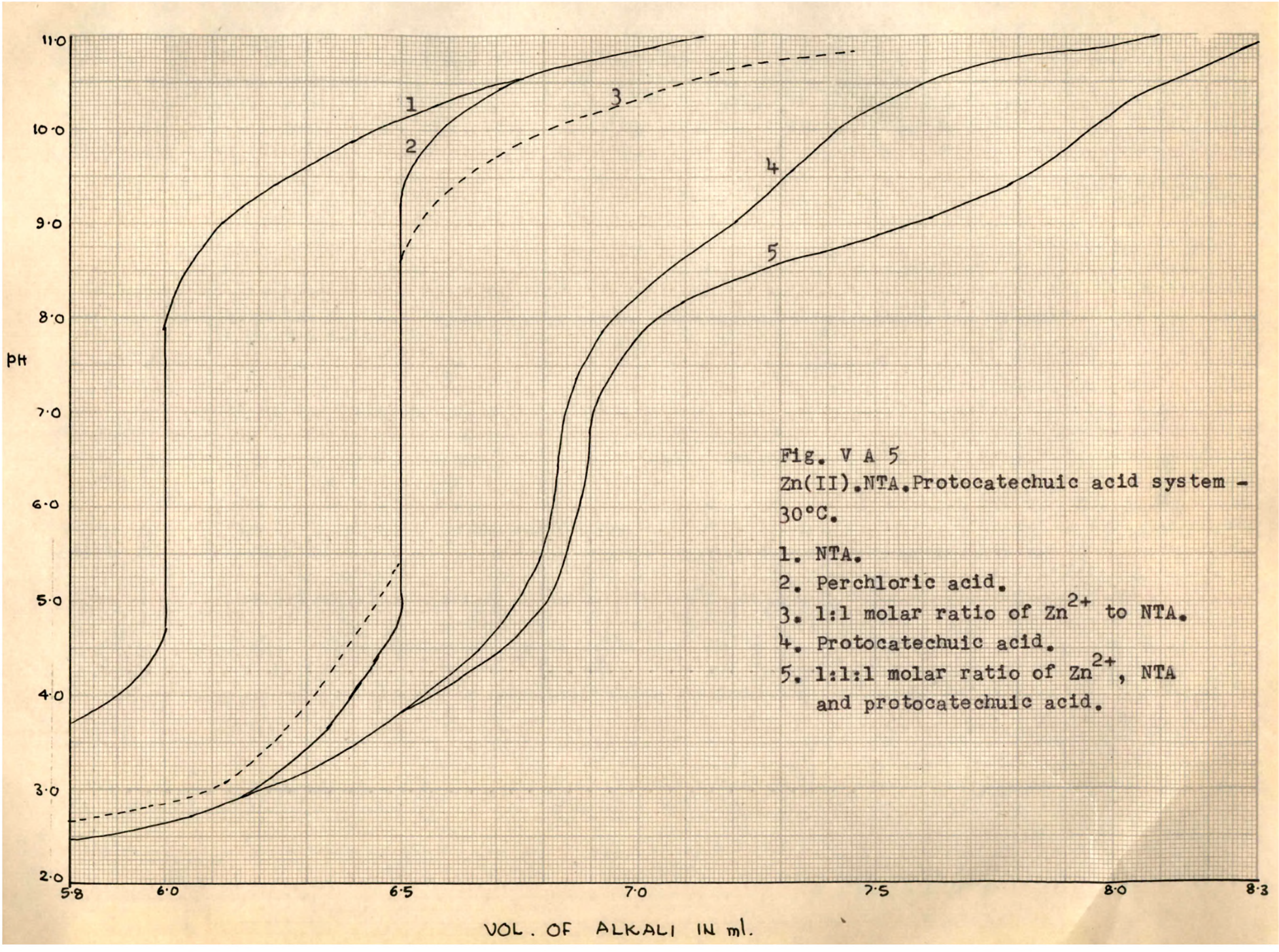


Fig. V A 5
Zn(II).NTA.Protocatechuic acid system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to NTA.
4. Protocatechuic acid.
5. 1:1:1 molar ratio of $Zn^{2+}$, NTA and protocatechuic acid.

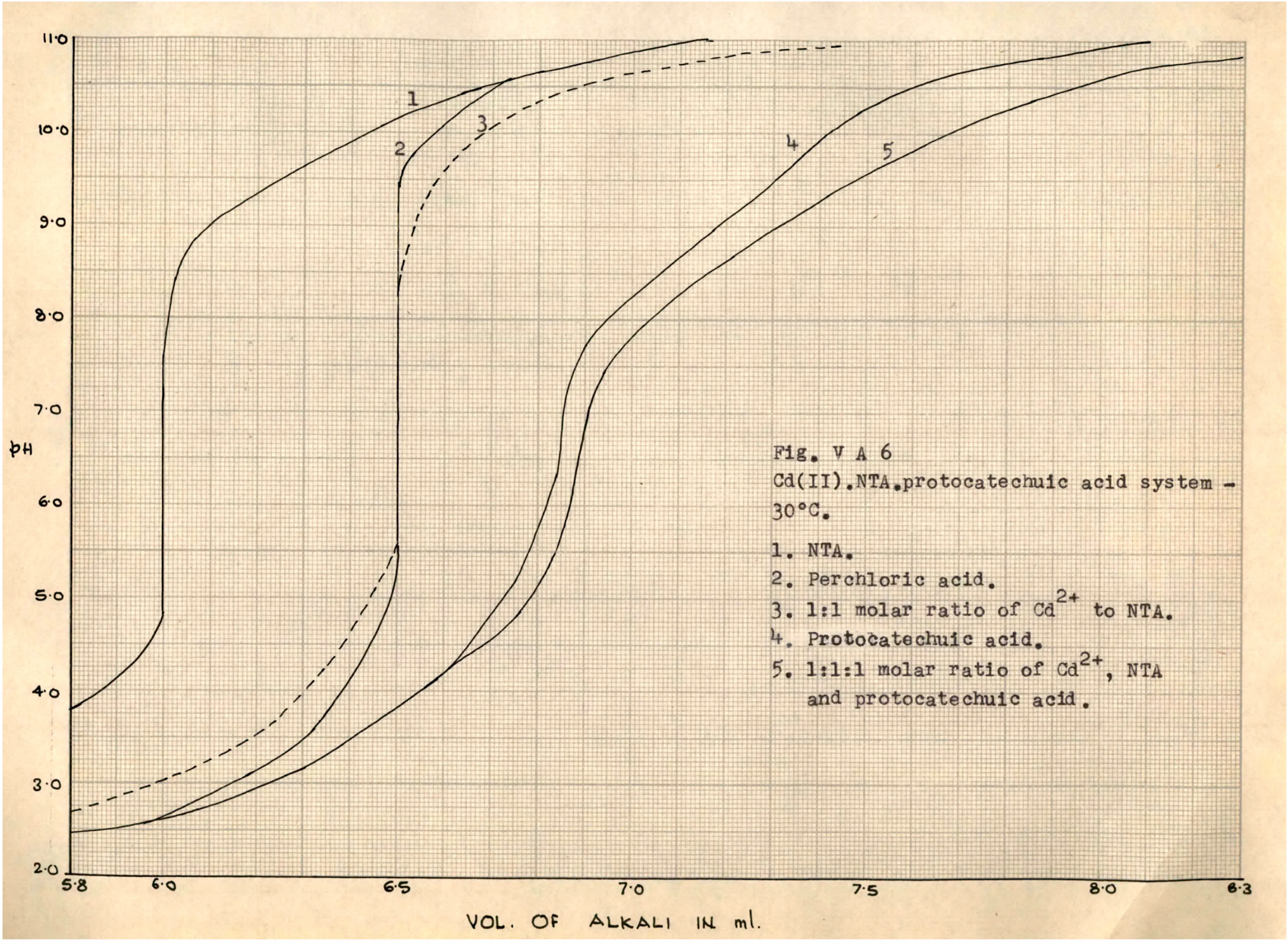


Fig. V A 6
Cd(II).NTA.protocatechuic acid system – 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to NTA.
4. Protocatechuic acid.
5. 1:1:1 molar ratio of $Cd^{2+}$, NTA and protocatechuic acid.

## Table VA 2.4

$N = 0.2M$ $V^\circ = 50$ ml. $\mu = 0.2M$ $t = 30^\circ C.$

$E^\circ = 0.02M$ $T^\circ_{NTA} = 0.002M$ $T^\circ_L = 0.002M$ $T^\circ_M = 0.002M$

$^*E^\circ = 0.026M$

| *2,3-Dihydroxy-naphthalene | | Zn.NTA.2,3-Dihydroxy-naphthalene | | Cd.NTA.2,3-Dihydroxy-naphthalene | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.58 | 1.00 | 1.60 | 1.00 | 1.60 |
| 2.00 | 1.60 | 2.00 | 1.65 | 2.00 | 1.65 |
| 3.00 | 1.75 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 1.85 | 4.00 | 2.00 | 4.00 | 2.00 |
| 5.00 | 2.10 | 5.00 | 2.25 | 5.00 | 2.30 |
| 5.50 | 2.35 | 5.50 | 2.50 | 5.50 | 2.60 |
| 5.80 | 2.50 | 5.80 | 2.70 | 5.80 | 2.80 |
| 5.90 | 2.58 | 5.90 | 2.75 | 5.90 | 2.88 |
| 6.00 | 2.68 | 6.00 | 2.90 | 6.00 | 3.05 |
| 6.10 | 2.85 | 6.10 | 3.05 | 6.10 | 3.25 |
| 6.20 | 3.10 | 6.20 | 3.40 | 6.20 | 3.52 |
| 6.30 | 3.45 | 6.25 | 3.60 | 6.25 | 3.70 |
| 6.40 | 4.02 | 6.30 | 3.98 | 6.30 | 3.95 |
| 6.43 | 4.25 | 6.35 | 4.30 | 6.35 | 4.25 |
| 6.46 | 4.50 | 6.40 | 4.60 | 6.40 | 4.60 |
| 6.48 | 4.70 | 6.44 | 4.95 | 6.44 | 4.90 |
| 6.50 | 7.70 | 6.48 | 5.20 | 6.48 | 5.25 |
| 6.54 | 7.95 | 6.50 | 7.30 | 6.50 | 7.50 |
| 6.58 | 8.10 | 6.54 | 7.55 | 6.54 | 7.66 |
| 6.62 | 8.30 | 6.58 | 7.72 | 6.58 | 7.88 |
| 6.66 | 8.45 | 6.62 | 7.82 | 6.62 | 8.05 |
| 6.70 | 8.60 | 6.66 | 8.00 | 6.66 | 8.20 |
| 6.74 | 8.76 | 6.70 | 8.08 | 6.70 | 8.30 |
| 6.78 | 8.90 | 6.80 | 8.22 | 6.80 | 8.65 |
| 6.82 | 9.15 | 6.85 | 8.30 | 6.85 | 8.85 |
| 6.86 | 9.30 | 6.90 | 8.36 | 6.90 | 9.10 |
| 6.90 | 9.50 | 6.95 | 8.45 | 6.95 | 9.30 |
| 6.95 | 9.75 | 7.00 | 8.55 | 7.00 | 9.42 |
| 7.00 | 10.00 | 7.10 | 8.75 | 7.10 | 9.65 |
| 7.10 | 10.30 | 7.20 | 9.00 | 7.20 | 9.90 |
| 7.20 | 10.50 | 7.30 | 9.50 | 7.30 | 10.15 |
| 7.40 | 10.75 | 7.40 | 9.85 | 7.40 | 10.32 |
| 7.60 | 10.95 | 7.50 | 10.20 | 7.50 | 10.45 |
| 7.65 | 11.00 | 7.60 | 10.40 | 7.60 | 10.60 |
| | | 7.70 | 10.60 | 7.70 | 10.70 |
| | | 7.90 | 10.80 | 7.90 | 10.90 |
| | | 8.00 | 11.00 | 8.00 | 11.05 |

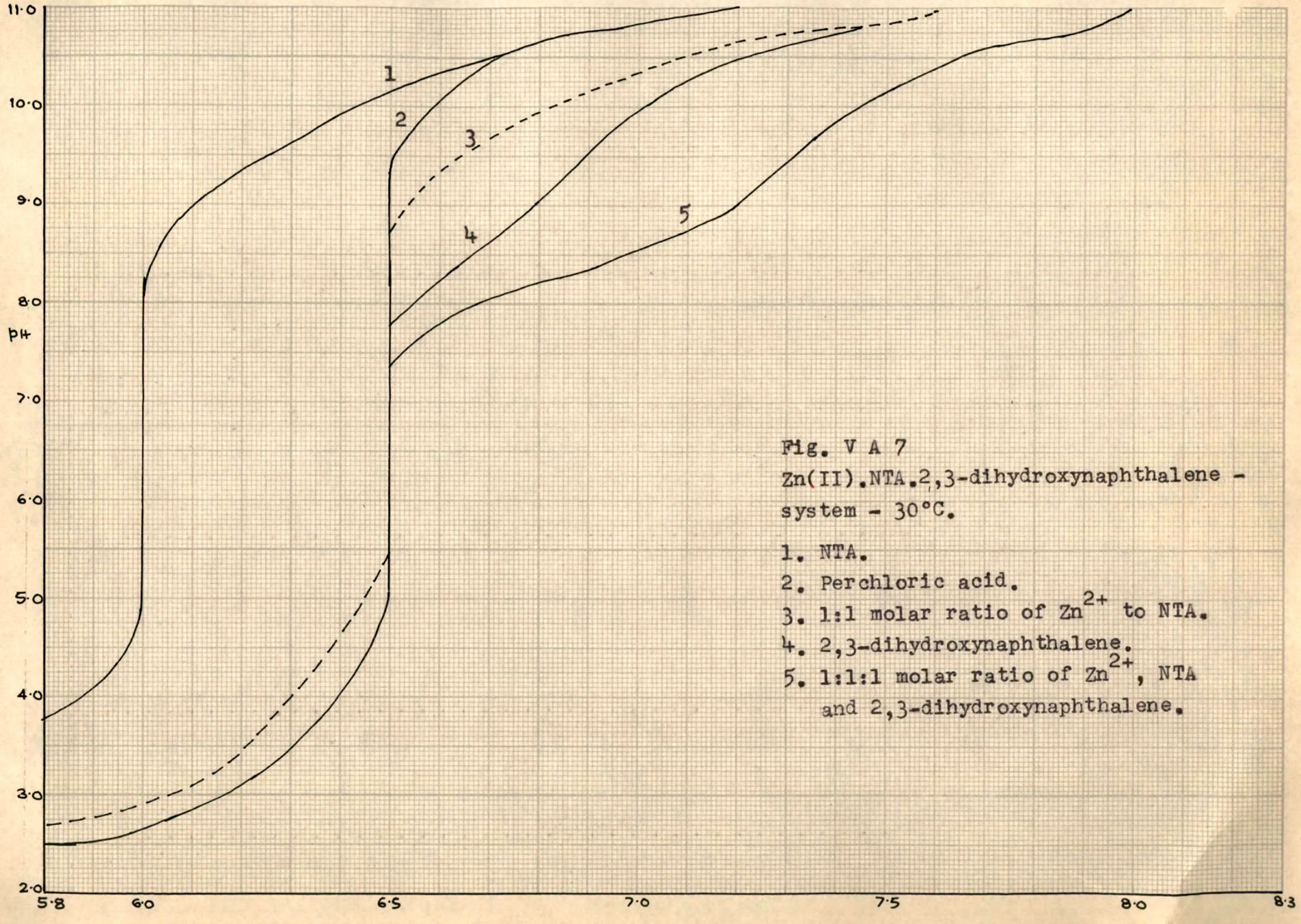


Fig. V A 7
Zn(II).NTA.2,3-dihydroxynaphthalene - system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to NTA.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Zn^{2+}$, NTA and 2,3-dihydroxynaphthalene.

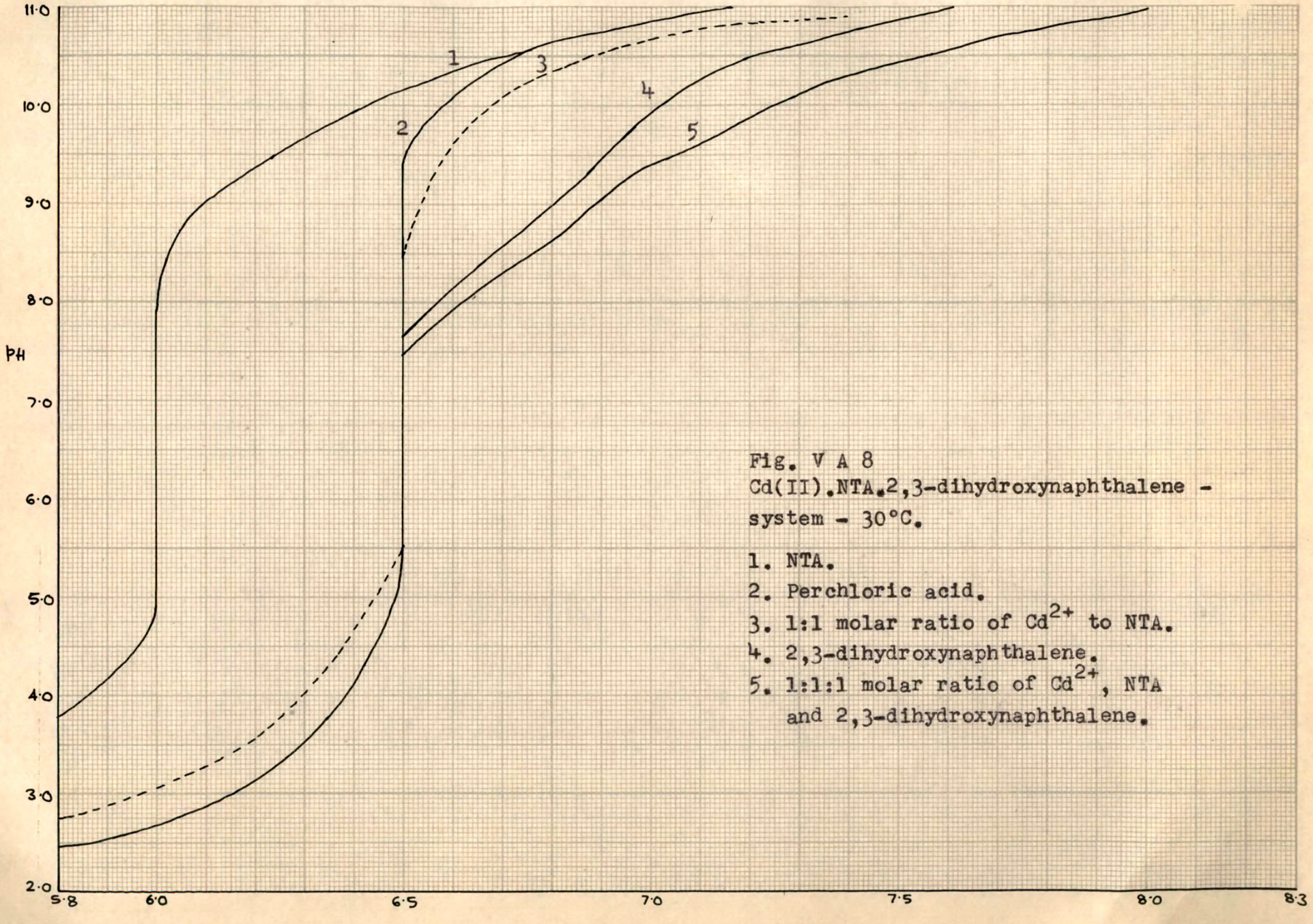


Fig. V A 8
Cd(II).NTA.2,3-dihydroxynaphthalene - system - 30°C.

1. NTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to NTA.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Cd^{2+}$, NTA and 2,3-dihydroxynaphthalene.

## Table VA 3.1b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.50 | $1.81_6$ | 6.56 | 6.68 | 0.12 | $0.12_8$ | $0.83_3$ | $6.30_2$ | - |
| 8.60 | $1.79_2$ | 6.57 | 6.73 | 0.16 | $0.16_3$ | $0.71_0$ | $6.31_8$ | - |
| 8.70 | $1.74_4$ | 6.59 | 6.77 | 0.18 | $0.20_1$ | $0.59_9$ | $5.99_7$ | - |
| 8.80 | $1.71_9$ | 6.61 | 6.81 | 0.20 | $0.22_6$ | $0.53_4$ | $5.84_2$ | $5.30_4$ |
| 8.90 | $1.67_2$ | 6.64 | 6.91 | 0.27 | $0.31_4$ | $0.33_9$ | $5.73_2$ | $5.39_3$ |
| 9.00 | $1.64_0$ | 6.67 | 6.96 | 0.29 | $0.34_4$ | $0.28_0$ | $5.59_2$ | $5.31_2$ |
| 9.10 | $1.56_0$ | 6.70 | 7.01 | 0.31 | $0.40_6$ | $0.16_5$ | $5.48_4$ | $5.31_9$ |
| 9.20 | $1.48_0$ | 6.73 | 7.10 | 0.37 | $0.48_6$ | $0.02_4$ | $5.40_0$ | $5.37_6$ |
| 9.30 | $1.44_9$ | 6.76 | 7.15 | 0.39 | $0.52_4$ | $\bar{1}.95_8$ | $5.29_1$ | $5.33_3$ |
| 9.40 | $1.37_7$ | 6.80 | 7.21 | 0.41 | $0.59_1$ | $\bar{1}.84_0$ | $5.22_2$ | $5.38_2$ |
| 9.50 | $1.29_7$ | 6.83 | 7.25 | 0.42 | $0.63_0$ | $\bar{1}.76_8$ | $5.13_5$ | $5.36_7$ |

$\log K_{MAL} = 5.36 \pm 0.06$

## Table VA 3.2b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.70 | $1.56_0$ | 6.74 | 6.86 | 0.12 | $0.14_9$ | $0.75_6$ | $5.06_1$ | $4.30_5$ |
| 8.80 | $1.52_8$ | 6.76 | 6.90 | 0.14 | $0.17_8$ | $0.66_4$ | $4.93_1$ | $4.26_7$ |
| 8.90 | $1.41_2$ | 6.78 | 6.94 | 0.16 | $0.22_0$ | $0.54_9$ | $4.85_1$ | $4.30_2$ |
| 9.00 | $1.37_2$ | 6.82 | 7.00 | 0.18 | $0.25_5$ | $0.46_5$ | $4.70_0$ | $4.23_5$ |
| 9.10 | $1.29_2$ | 6.84 | 7.04 | 0.20 | $0.30_1$ | $0.36_5$ | $4.59_9$ | $4.23_4$ |
| 9.20 | $1.22_0$ | 6.87 | 7.09 | 0.22 | $0.35_1$ | $0.26_6$ | $4.50_6$ | $4.24_0$ |
| 9.30 | $1.16_0$ | 6.91 | 7.15 | 0.24 | $0.40_2$ | $0.17_2$ | $4.42_2$ | $4.25_0$ |
| 9.40 | $1.10_0$ | 6.95 | 7.21 | 0.26 | $0.45_9$ | $0.07_1$ | $4.34_9$ | $4.27_8$ |
| 9.50 | $1.09_3$ | 6.97 | 7.26 | 0.29 | $0.51_6$ | $\bar{1}.97_2$ | $4.27_3$ | $4.30_1$ |

$\log K_{MAL} = 4.26 \pm 0.04$

## Table VA 3.3b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.20 | $1.80_0$ | 6.99 | 7.09 | 0.10 | $0.10_8$ | $0.91_7$ | $7.49_5$ | $6.57_8$ |
| 8.30 | $1.76_0$ | 7.01 | 7.14 | 0.13 | $0.14_4$ | $0.77_4$ | $7.33_4$ | $6.56_0$ |
| 8.40 | $1.72_0$ | 7.04 | 7.20 | 0.16 | $0.18_1$ | $0.65_5$ | $7.17_8$ | $6.52_3$ |
| 8.50 | $1.68_0$ | 7.06 | 7.26 | 0.20 | $0.23_2$ | $0.51_9$ | $7.03_6$ | $6.51_7$ |
| 8.60 | $1.60_0$ | 7.09 | 7.33 | 0.24 | $0.29_2$ | $0.38_4$ | $6.90_6$ | $6.52_2$ |
| 8.70 | $1.56_0$ | 7.11 | 7.39 | 0.28 | $0.35_0$ | $0.26_8$ | $6.78_2$ | $6.51_4$ |
| 8.80 | $1.52_0$ | 7.14 | 7.46 | 0.32 | $0.41_0$ | $0.15_8$ | $6.68_0$ | $6.52_2$ |
| 8.90 | $1.48_0$ | 7.16 | 7.52 | 0.36 | $0.47_4$ | $0.04_5$ | $6.57_1$ | $6.52_6$ |
| 9.00 | $1.40_0$ | 7.19 | 7.59 | 0.40 | $0.57_1$ | $\bar{1}.87_5$ | $6.50_2$ | - |

$\log K_{MAL} = 6.54 \pm 0.03$

## Table VA 3.4b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Zn.NTA. 2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.00 | $1.77_3$ | 6.55 | 6.66 | 0.11 | $0.12_0$ | $0.86_5$ | $7.92_4$ | $7.05_9$ |
| 8.10 | $1.71_3$ | 6.58 | 6.73 | 0.15 | $0.17_0$ | $0.68_8$ | $7.78_2$ | $7.09_4$ |
| 8.20 | $1.67_3$ | 6.60 | 6.79 | 0.19 | $0.22_1$ | $0.54_7$ | $7.64_4$ | $7.09_7$ |
| 8.30 | $1.63_3$ | 6.62 | 6.85 | 0.23 | $0.27_4$ | $0.42_3$ | $7.51_4$ | $7.09_1$ |
| 8.40 | $1.55_3$ | 6.65 | 6.91 | 0.26 | $0.32_6$ | $0.31_5$ | $7.39_3$ | $7.07_8$ |
| 8.50 | $1.51_4$ | 6.67 | 6.96 | 0.29 | $0.37_3$ | $0.22_7$ | $7.27_8$ | $7.05_1$ |
| 8.60 | $1.43_4$ | 6.70 | 7.02 | 0.32 | $0.43_4$ | $0.11_5$ | $7.17_8$ | $7.06_3$ |
| 8.70 | $1.39_4$ | 6.73 | 7.08 | 0.35 | $0.48_9$ | $0.01_9$ | $7.08_8$ | $7.06_9$ |
| 8.80 | $1.35_6$ | 6.75 | 7.13 | 0.38 | $0.54_6$ | $\bar{1}.91_9$ | $7.00_3$ | $7.08_4$ |
| 8.90 | $1.31_7$ | 6.78 | 7.17 | 0.39 | $0.57_7$ | $\bar{1}.86_5$ | $6.90_7$ | $7.03_2$ |

$\log K_{MAL} = 7.07 \pm 0.03$

Fig. V A 10
Zn(II).NTA.pyrogallol system - 30°C.

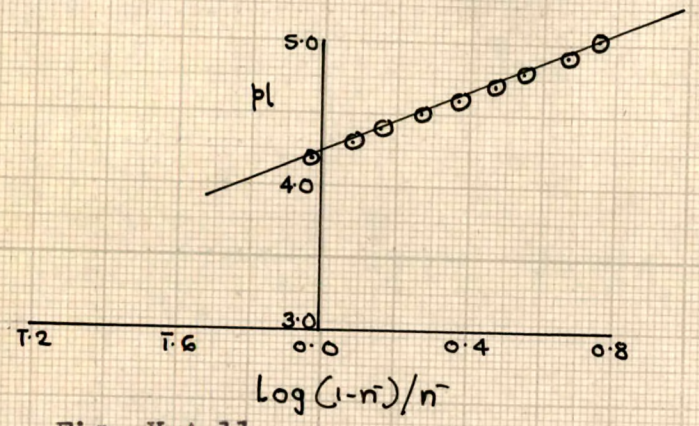


Fig. V A 11
Zn(II).NTA.protocatechuic acid system - 30°C.

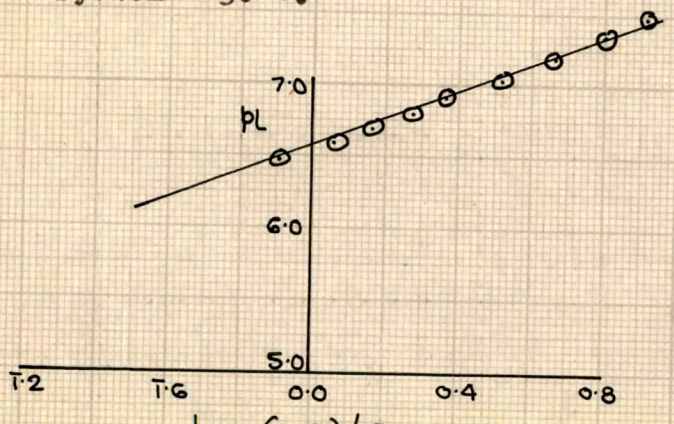


Fig. V A 9
Zn(II).NTA.catechol system - 30°C.

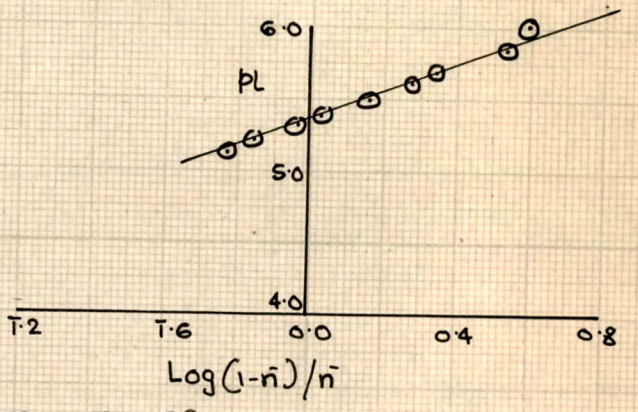


Fig. V A 12
Zn(II).NTA.2,3-dihydroxynaphthalene system - 30°C.

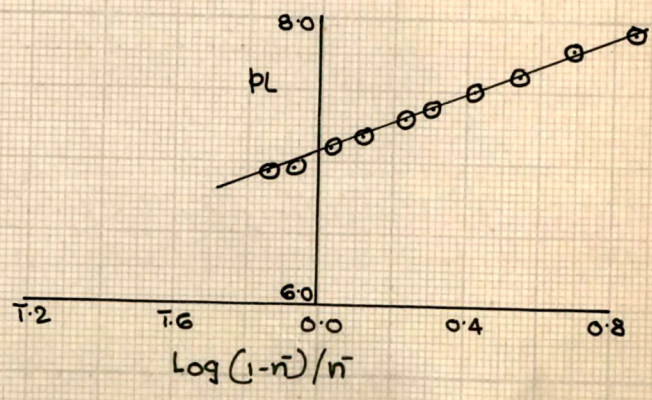

Table VA 3.1c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.40 | $1.37_7$ | 6.80 | 6.89 | 0.09 | $0.12_7$ | $0.83_7$ | $4.88_6$ | $4.04_9$ |
| 9.50 | $1.29_7$ | 6.83 | 6.94 | 0.11 | $0.16_5$ | $0.70_4$ | $4.77_9$ | $4.07_5$ |
| 9.60 | $1.26_6$ | 6.86 | 6.99 | 0.13 | $0.19_9$ | $0.60_4$ | $4.67_2$ | $4.06_8$ |
| 9.70 | $1.22_6$ | 6.90 | 7.05 | 0.15 | $0.23_8$ | $0.50_5$ | $4.57_1$ | $4.06_6$ |
| 9.80 | $1.15_4$ | 6.94 | 7.11 | 0.17 | $0.28_6$ | $0.39_6$ | $4.48_2$ | $4.08_6$ |
| 9.90 | $1.11_5$ | 6.98 | 7.16 | 0.18 | $0.31_4$ | $0.33_9$ | $4.38_4$ | $4.04_5$ |
| 10.00 | $1.08_3$ | 7.00 | 7.20 | 0.20 | $0.35_9$ | $0.25_1$ | $4.30_2$ | $4.05_1$ |
| 10.10 | $1.00_4$ | 7.05 | 7.27 | 0.22 | $0.40_9$ | $0.15_5$ | $4.22_8$ | $4.06_9$ |
| 10.20 | $1.00_7$ | 7.09 | 7.33 | 0.24 | $0.46_3$ | $0.06_4$ | $4.16_1$ | $4.09_7$ |
| 10.30 | $0.99_9$ | 7.11 | 7.37 | 0.26 | $0.50_5$ | $\bar{1}.99_1$ | $4.09_0$ | $4.09_9$ |
| 10.40 | $0.95_6$ | 7.15 | 7.43 | 0.28 | $0.56_8$ | $\bar{1}.88_1$ | $4.04_4$ | - |

$\log K_{MAL} = 4.07 \pm 0.03$

Table VA 3.2c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.50 | $1.09_3$ | 6.97 | 7.07 | 0.10 | $0.17_8$ | $0.66_4$ | $4.05_1$ | $3.38_7$ |
| 9.60 | $1.03_3$ | 7.00 | 7.11 | 0.11 | $0.20_7$ | $0.58_3$ | $3.95_6$ | $3.37_3$ |
| 9.70 | $0.99_3$ | 7.04 | 7.16 | 0.12 | $0.23_5$ | $0.51_2$ | $3.86_2$ | $3.35_0$ |
| 9.80 | $0.96_2$ | 7.07 | 7.20 | 0.13 | $0.26_2$ | $0.44_9$ | $3.77_0$ | $3.32_1$ |
| 9.90 | $0.91_8$ | 7.10 | 7.24 | 0.14 | $0.29_6$ | $0.37_6$ | $3.68_5$ | $3.30_9$ |
| 10.00 | $0.89_9$ | 7.15 | 7.30 | 0.15 | $0.32_4$ | $0.31_9$ | $3.59_8$ | - |
| 10.10 | $0.81_9$ | 7.17 | 7.33 | 0.16 | $0.37_9$ | $0.21_4$ | $3.53_3$ | $3.31_9$ |
| 10.20 | $0.81_2$ | 7.22 | 7.40 | 0.18 | $0.43_0$ | $0.12_2$ | $3.46_6$ | $3.34_4$ |
| 10.30 | $0.76_4$ | 7.30 | 7.49 | 0.19 | $0.48_2$ | $0.03_1$ | $3.40_5$ | $3.37_4$ |
| 10.40 | $0.74_2$ | 7.38 | 7.58 | 0.20 | $0.52_2$ | $\bar{1}.96_1$ | $3.33_9$ | $3.37_8$ |

$\log K_{MAL} = 3.35 \pm 0.04$

## Table VA 3.3c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.30 | $1.31_3$ | 7.26 | 7.38 | 0.12 | $0.17_8$ | $0.66_4$ | $5.83_3$ | $5.16_9$ |
| 9.40 | $1.29_7$ | 7.29 | 7.43 | 0.14 | $0.21_0$ | $0.57_5$ | $5.72_8$ | $5.15_3$ |
| 9.50 | $1.26_6$ | 7.31 | 7.47 | 0.16 | $0.24_6$ | $0.48_6$ | $5.62_8$ | $5.14_2$ |
| 9.60 | $1.23_4$ | 7.34 | 7.52 | 0.18 | $0.28_4$ | $0.40_1$ | $5.53_4$ | $5.13_3$ |
| 9.70 | $1.20_2$ | 7.35 | 7.55 | 0.20 | $0.32_4$ | $0.31_9$ | $5.44_6$ | $5.12_7$ |
| 9.80 | $1.18_3$ | 7.37 | 7.59 | 0.22 | $0.36_2$ | $0.24_6$ | $5.36_1$ | $5.11_5$ |
| 9.90 | $1.16_4$ | 7.39 | 7.64 | 0.25 | $0.41_8$ | $0.14_3$ | $5.29_2$ | $5.14_9$ |
| 10.00 | $1.14_5$ | 7.41 | 7.68 | 0.27 | $0.45_9$ | $0.07_1$ | $5.21_7$ | $5.14_6$ |
| 10.10 | $1.12_5$ | 7.45 | 7.73 | 0.28 | $0.48_4$ | $0.02_7$ | $5.13_1$ | $5.10_4$ |
| 10.20 | $1.08_6$ | 7.48 | 7.78 | 0.30 | $0.53_7$ | $\bar{1}.93_5$ | $5.07_1$ | $5.13_6$ |

$\log K_{MAL} = 5.13 \pm 0.03$

## Table VA 3.4c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Cd.NTA.2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.30 | $1.18_7$ | 6.86 | 6.95 | 0.10 | $0.16_4$ | $0.70_7$ | $6.15_1$ | $5.44_4$ |
| 9.40 | $1.14_4$ | 6.88 | 6.99 | 0.11 | $0.18_7$ | $0.63_9$ | $6.04_0$ | $5.40_1$ |
| 9.50 | $1.08_4$ | 6.90 | 7.03 | 0.13 | $0.23_3$ | $0.51_7$ | $5.95_7$ | $5.44_0$ |
| 9.60 | $1.06_4$ | 6.92 | 7.07 | 0.15 | $0.27_4$ | $0.42_3$ | $5.87_4$ | $5.45_1$ |
| 9.70 | $1.06_5$ | 6.94 | 7.11 | 0.17 | $0.31_0$ | $0.34_7$ | $5.79_1$ | $5.44_4$ |
| 9.80 | $1.04_5$ | 6.96 | 7.15 | 0.19 | $0.35_4$ | $0.26_1$ | $5.71_4$ | $5.45_3$ |
| 9.90 | $1.04_5$ | 6.98 | 7.19 | 0.21 | $0.39_1$ | $0.19_2$ | $5.63_7$ | $5.44_5$ |
| 10.00 | $1.02_5$ | 7.00 | 7.23 | 0.23 | $0.43_6$ | $0.11_8$ | $5.56_8$ | $5.45_7$ |
| 10.10 | $1.00_3$ | 7.03 | 7.28 | 0.25 | $0.48_4$ | $0.02_7$ | $5.50_5$ | $5.47_8$ |
| 10.20 | $1.00_3$ | 7.06 | 7.33 | 0.27 | $0.52_3$ | $\bar{1}.96_0$ | $5.43_7$ | $5.46_7$ |
| 10.30 | $1.00_3$ | 7.10 | 7.39 | 0.29 | $0.56_1$ | $\bar{1}.89_3$ | $5.37_2$ | $5.47_9$ |

$\log K_{MAL} = 5.45 \pm 0.05$

Fig. V A 14
Cd(II).NTA.pyrogallol system - 30°C.

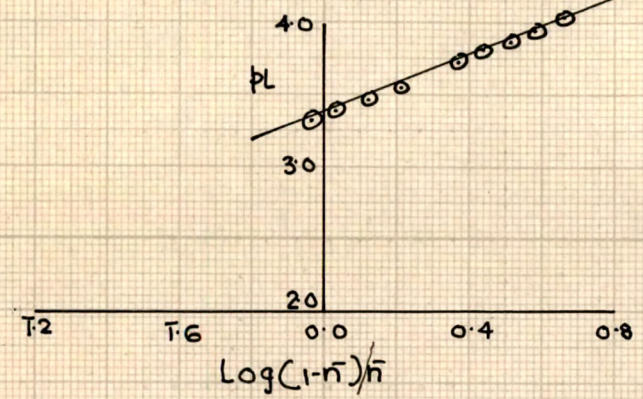


Fig. V A 13
Cd(II).NTA.catechol system - 30°C.

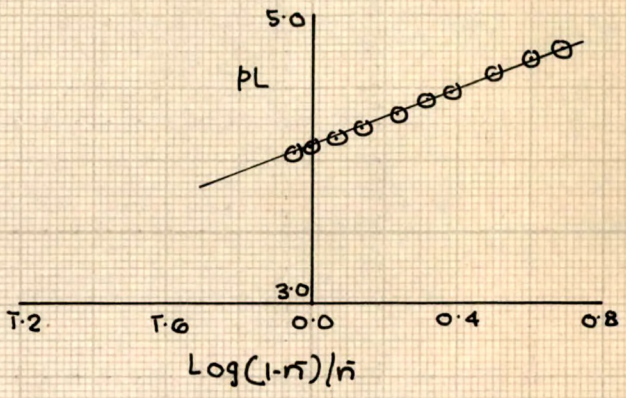


Fig. V A 15
Cd(II).NTA.protocatechuic acid
system - 30°C.

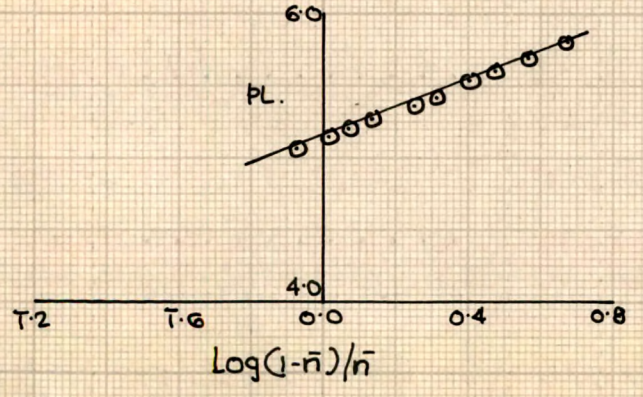


Fig. V A 16
Cd(II).NTA.2,3-dihydroxynaphthalene
system - 30°C.

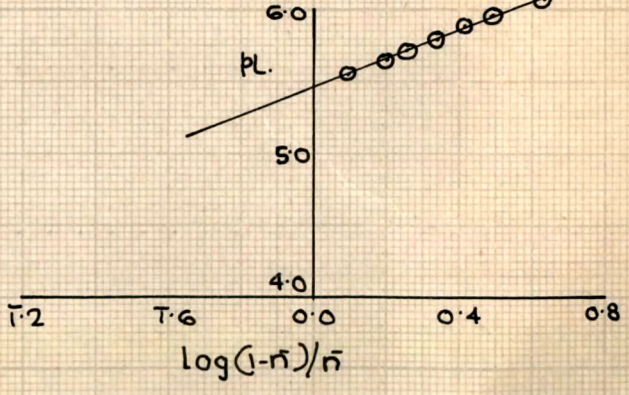

Table VA 4.0

Logarithms of stability constants of ternary NTA-$M^{2+}$-ligand complexes ( $\mu$ = 0.2M, 30°C.)

| | Ligand (L) | | | |
|---|---|---|---|---|
| | Catechol | Pyrogallol | Protocatechuic acid | 2,3-Dihydroxy-naphthalene |
| $\log K^{Zn(NTA)}_{Zn(NTA)L}$ | 5.36 ± 0.06 | 4.26 ± 0.04 | 6.54 ± 0.03 | 7.07 ± 0.03 |
| $\log K^{Cd(NTA)}_{Cd(NTA)L}$ | 4.07 ± 0.03 | 3.35 ± 0.04 | 5.13 ± 0.03 | 5.45 ± 0.05 |

Table VA 5.0

| | Ligand (L) | | | |
|---|---|---|---|---|
| | Catechol | Pyrogallol | Protocatechuic acid | 2,3-Dihydroxy-naphthalene |
| $\log K^{Zn}_{Zn.L} - \log K^{Zn.NTA.}_{Zn.NTA.L}$ | 2.88 ± 0.02 | 3.41 ± 0.00 | 2.57 ± 0.01 | 2.85 ± 0.02 |
| $\log K^{Cd}_{Cd.L} - \log K^{Cd.NTA.}_{Cd.NTA.L}$ | 2.69 ± 0.03 | 2.80 ± 0.02 | 2.93 ± 0.01 | 3.09 ± 0.02 |

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## SECTION B

Since 1958, various workers investigated the ternary systems involving histidine or iminodiacetic acid or ethylenediaminetetraacetic acid as a primary ligand. Numerous solids have also been isolated and characterised by different studies.

Histidine is known to form complexes with a large number of metal ions.[1-3] The metal histidine complexes in deuterium oxide solution were studied by infra-red and proton magnetic resonance study by Ronald and coworkers.[4] X-ray crystallographic analysis of a mixed amino acid complex of L-histidinato-L-threoninato Cu(II) hydrate, was carried out by Nickolds and coworkers.[5] Martin and coworkers[6] studied potentiometrically the mixed coordination of metallic ions with compounds of biological interest. Martin and coworkers[7] also studied potentiometrically the equilibrium of the reactions of Cu(II) ions with L or D-histidine and L-threonine in aqueous solution. Tridentate character of histidine was shown by William, & David.[8]

Iminodiacetic acid (IMDA) is known to form complexes with number of metal ions.[9-12] Thompson and coworkers[13] observed that 1:1 rare earth-N-hydroxy ethylenediaminetriacetic acid (Ln(HEDTA)) forms mixed 1:1:1 chelates with glycine, ethylenediaminediacetic acid (EDDA), iminodiacetic acid (IMDA) and N-hydroxyethyl iminodiacetic acid (HIMDA). Isolation of oxovanadium (IV) heterochelates of the type $[VO(IMDA)(H_2O)X]$ where X = pyridine, α-picoline or aniline have also been carried out.[14] Fridman and coworkers[15] reported the solution studies of

the type NiLX where L = IMDA or EDTA and X = pyridine, $NH_3$ or $H_2O$. Potentiometric studies on stepwise mixed ligand complex formation involving IMDA as the primary ligand were carried out by Sharma and Tondon.[16,17] They have also reported[18] the mixed ligand formation constants of the ternary system $[M(IMDA)L]$ where M = $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$ or $Cd^{2+}$, and L = glycine, α-alanine or dl-aspartic acid, 1,2-propylenediamine, salicylic acid, sulphosalicylic acid, chromotropic acid or tiron.

EDTA mostly exhibits quadridentate character, coordination taking place from two nitrogen atoms and two $COO^-$.[19] EDTA forms complexes with number of metal ions.[20-22] The triple complex of niobium and tantalum with catechol and EDTA was studied spectrophotometrically by Babko & Lukachina.[23] Mixed ligand derivatives of Th.EDTA with monohydroxy monocarboxylic acid were studied potentiometrically by Gupta and Agarwal.[24] Spectrophotometric determinations of the stability constants of mixed ligand complexes of Hg(II).EDTA with thiocyanate and bromide were carried out by Nomura Toshiaki.[25] Shetty and coworkers[26] studied potentiometrically the stability of some mixed ligand complexes of thorium, involving EDTA as primary ligand and tiron, catechol, chromotropic acid (CTA) or gallic acid as secondary ligand. The formation of mixed complexes $MYL^{2-}$, by the reaction of imidazole perchlorate ($LH^+$) with M.EDTA ($MY^{2-}$), was studied by Israeli and coworkers.[27] Bogdanovich and coworkers[28] studied the mixed complexes of neodymium and praseodymium with ethylenediaminetetraacetic acid and hydrogen peroxide by absorption spectral method . The stability constants of mixed complexes of general stfuctures

$ZnL(NH_3)_m$ or $ZnL(NH_3)_x X_m$ formed by a reaction of ZnL (L = iminodiacetate, (hydroxyethylimino) diacetate, nitrilotriacetate or EDTA anion) with X (X = pyridine, $H_2O$, $SCN^-$, thiourea, or $S_2O_3^{2-}$) in aqueous solution, were reported by Fridman and coworkers[29]. Cerium(IV)-EDTA-hydrogen peroxide ternary complex was studied by spectral absorption analysis by Pilipenko and Loriya.[30] The formation constants of mixed complexes $LnAT^{3-}$ where Ln = rare earth ion, A = EDTA ion, and T = tartarate ion, were determined potentiometrically by Spitsyn.[31] But the ternary systems MAL, where A = ethylene-diaminetetraacetic acid, iminodiacetic acid or histidine and L = polyhydroxy phenols or phenolic acid have not been studied. In the present investigation an attempt has been made to study the formation constants of such mixed ligand complexes. The reactions can be represented as follows :

$$[MA]^+ + L^{2-} \rightleftharpoons [MAL]^{1-}$$

$$[MB]^\circ + L^{2-} \rightleftharpoons [MBL]^{2-}$$

$$[MC]^{2-} + L^{2-} \rightleftharpoons [MCL]^{4-}$$

where M = Zn(II) or Cd(II); A = histidine, B = iminodiacetic acid (IMDA), C = ethylenediaminetetraacetic acid (EDTA) and $LH_2$ = catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid.

Histidine exhibits bi or tri-dentate character;[32]

coordination taking place from $COO^-$ and from nitrogen of the imidazole or two nitrogens from both imidazole and amino groups. IMDA exhibits tri-dentate character[33] coordination taking place from the nitrogen and two carboxylate oxygens.[34] EDTA mostly exhibits quadridentate character[19], coordination taking place from two nitrogen atoms and two $COO^-$. In case of 1:1 histidine, IMDA or EDTA complexes of metal ions with high coordination numbers, the vacant positions are occupied by water molecules or hydroxyl ions. On addition to this of a bidentate ligand coordinating with metal ion at higher pH, vacant positions around the metal ion are occupied by the secondary ligand, resulting in the formation of the mixed ligand complexes of the type M.Histidine.L or M.IMDA.L or M.EDTA.L. The reaction is characterised by the formation constant $K^{MA}_{MAL}$.

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

where A = histidine, IMDA or EDTA.

The charges have been avoided for the sake of generalisation. The formation constants $K^{MA}_{MAL}$, corresponding to the association of polyhydroxy phenols or phenolic acid with M.Histidine or M.IMDA or M.EDTA, have been determined by using the modified form of Irving-Rossotti titration technique as done earlier in the study of M.NTA.L system.

The following experiments were carried out in case of M.Histidine or IMDA or EDTA. polyhydroxy phenols or phenolic acid systems.

The reagents and instrument used are same as detailed

in chapter II (p.38-41). Histidine (Merck,Germany), IMDA (BDH, England) and disodium salt of EDTA (BDH, England) were used.

For studying the ternary systems following solutions were prepared in 50.0 ml. volume.

For Histidine systems :

1. Perchloric acid (0.2M, 5.0 ml.) + histidine (0.02M, 5.0 ml.)+ sodium perchlorate (1.0M, 8.9 ml.) + conductivity water (31.1 ml.) ; total volume = 50.0 ml., $\mu$ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + conductivity water (31.1 ml.) ; total volume = 50.0 ml., $\mu$ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + histidine (0.02M, 5.0 ml.)+ metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + conductivity water (26.2 ml.) ; total volume = 50.0 ml., $\mu$ = 0.2M.
4. Perchloric acid (0.2M, 5.0 ml.)+ perchloric acid (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + conductivity water (26.2 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + histidine (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.7 ml.) + conductivity water (21.3 ml.) ; total volume = 50.0 ml., $\mu$ = 0.2M.

For IMDA systems :

1. Perchloric acid (0.2M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + conductivity water

(31.1 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.

2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 10.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + conductivity water (26.2 ml.) ; total volume = 50.0 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 (1.0M, 8.8 ml.) + conductivity water (26.2 ml.) ; total volume = 50.0 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 (1.0M, 8.7 ml.) + conductivity water (21.3 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + IMDA (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.7 ml.) + conductivity water (21.3 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.

For EDTA systems :

1. Perchloric acid(0.2M, 5.0 ml.) + EDTA (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + conductivity water (31.1 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + perchloric acid (0.02M, 10.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + conductivity water (26.2 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + EDTA (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + conductivity water (26.2 ml.) ; total volume = 50.0 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 (1.0M, 8.7 ml.) + conductivity water (21.3 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.

5. Perchloric acid (0.2M, 5.0 ml.) + EDTA (0.02M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.7 ml.) + conductivity water (21.3 ml.); total volume = 50.0 ml., $\mu$ = 0.2M.

The ionic strength of each solution was thus initially raised to 0.2M. Each of the above samples was titrated against 0.2M sodium hydroxide solution. Nitrogen gas was passed through the solution to avoid oxidation of the aromatic ligands. The plots of pH against volume of alkali have been presented in figs. V B 1 to V B 4 in case of histidine, V B 9 to V B 15 in case of IMDA and V B 23 to V B 28 in case of EDTA.

Observation of the titration graphs gives the following informations :

It is evident from curve (1) and (3) that 1:1 complexes of histidine, IMDA and EDTA with $Zn^{2+}$ and $Cd^{2+}$ are formed at lower pH and are stable at higher pH. The separation between two curves starts at low pH and reaches maximum at pH $\sim$ 6.5 in histidine, at pH $\sim$ 6.5 in IMDA and at pH $\sim$ 4.2 in EDTA. This shows that 1:1 complex formation is complete at lower pH. At higher pH the curves converge showing absence of hydrolysis or hydroxy complex formation. M.Histidine or EDTA.secondary ligand (catechol, pyrogallol or 2,3-dihydroxynaphthalene) curve (5) is not below M.Histidine or EDTA curve (3) in the lower pH range. This is an evidence that in this range where

$M^{2+}$ and histidine or EDTA 1:1 complexation takes place, the polyhydroxy phenols do not combine with metal ion. In the polyhydroxy phenols (curve(4)) one and two equivalents of extra perchloric acid (where primary ligand is histidine or IMDA, EDTA respectively) have been added to compensate for hydrogen ions liberated by the combination of $M^{2+}$ with histidine, IMDA or EDTA, in the M.Histidine, IMDA or EDTA. secondary ligand solution (curve(5)). Below pH $\sim$ 6.8 in histidine, pH $\sim$ 6.5 in IMDA and pH $\sim$ 4.2 in EDTA, the curve (5) is not overlapping curve (4) but it is slightly above it. This is due to the fact that in the lower pH range amino acids take up hydrogen ion from the solution and exist as a mixture of species $CH_2NH_3^+.COOH$ and $CH_2NH_3^+.COO^-$. After pH $\sim$ 6.0 curve (5) goes below curve (4). This confirms that in this range coordination of secondary ligand with M.Histidine or M.EDTA takes place resulting in the liberation of extra hydrogen ions. In case of M.IMDA.L system combination of secondary ligand starts before the completion of 1:1 M.IMDA complex. However, above pH $\sim$ 6.5 formation of 1:1 M.IMDA complex is complete and the horizontal distance between curves(4) and (5) is due to the liberation of extra hydrogen ions as result of coordination of secondary ligand with M.IMDA.. Reactions can be represented as follows :

$$M^{2+} + [\text{Histidine}]^- \rightleftharpoons [\text{M.Hist}]^+ + H^+$$

$$[\text{M.Hist}]^+ + [C_6H_4(OH)_2] \rightleftharpoons [\text{M.Hist}(C_6H_4O_2)]^- + 2H^+$$

In case of IMDA:

$$M^{2+} + \text{IMDA}^{2-} \rightleftharpoons [\text{M.IMDA}]^\circ + 2H^+$$

$$[\text{M.IMDA}]^\circ + [C_6H_4(OH)_2] \rightleftharpoons [\text{M.IMDA}(C_6H_4O_2)]^{2-} + 2H^+$$

In case of EDTA (disodium salt) :

$$M^{2+} + [Na_2EDTA] \rightleftharpoons [M.EDTA]^{2-} + 2Na^{+} + 2H^{+}$$

$$[M.EDTA]^{2-} + [C_6H_4(OH)_2] \rightleftharpoons [M.EDTA(C_6H_4O_2)]^{4-} + 2H^{+}.$$

$\bar{n}$ values were calculated from the horizontal distance between curves (4) and (5), and pL values were calculated using the equations given in chapter II (p. 49 ). The values have been presented in the tables V B 3.1b to V B 3.4c, V B 5.1b to V B 5.4c and V B 7.1b to V B 7.4c. Precise values of mixed ligand formation constants were determined by using the method of linear plot.[35] The values of $\log K^{MA}_{MAL}$ have been presented in table V B 8.0.

In case of Zn.Histidine.2,3-dihydroxynaphthalene, Zn.Histidine.protocatechuic acid and Cd.Histidine.protocatechuic acid, the method could not be applied because the coordination of secondary ligand starts before the formation of M.Histidine 1:1 complex is complete. In the system Cd.Histidine.pyrogallol, there is precipitation after pH $\sim$ 6.0 onwards and hence calculation was not carried out. In the system Cd.IMDA.pyrogallol also $\bar{n}$ does not go beyond 0.2 and hence $K^{MA}_{MAL}$ could not be calculated. In the system M.EDTA.pyrogallol (where M = $Zn^{2+}$ or $Cd^{2+}$) calculation could not be possible because the separation between curves (4) and (5) is very small.

It is observed that in all cases $K^{MA}_{MAL}$ has lower values than $K^{M}_{ML_1}$. The values of $K^{M.Hist.}_{M.Hist.L}$ is less than $K^{M}_{ML_1}$ by about 1.0 to 1.2 log unit, $K^{M.IMDA}_{M.IMDA.L}$ is less than $K^{M}_{ML_1}$ by about 1.2 to 1.7 log unit and $K^{M.EDTA}_{M.EDTA.L}$ is less

than $K^{M}_{ML}$, (where M = $Zn^{2+}$ or $Cd^{2+}$, L = polyhydroxy aromatic ligands) by about 3.5 to 4.7 log units. This can be explained to be due to electrostatic repulsion between the incoming ligand and already existing charged ion histidine or IMDA or EDTA. The values are in the order $K^{M.Hist.}_{M.Hist.L} > K^{M.IMDA}_{M.IMDA.L} > K^{M.NTA}_{M.NTA.L} > K^{M.EDTA}_{M.EDTA.L}$. The values of $K^{MA}_{MAL}$ are higher where A = histidine. This is because histidine has one negative charge and exerts lesser repulsion on the incoming ligand than IMDA, NTA and EDTA with two, three and four negative charges, respectively.

The difference in case of $K^{M.Hist.}_{M.Hist.L}$ and $K^{M.IMDA}_{M.IMDA.L}$ is less because histidine is a bigger molecule and hence there may be some steric hinderence to the incoming ligand.

Table VB 1.0

N = 0.2M V° = 50 ml. $\mu$ = 0.2M t = 30°C.

E° = 0.02M $T^{\circ}_{Hist.}$ = 0.002M $T^{\circ}_{M}$ = 0.002M

*E° = 0.022M

| *Perchloric acid | | Histidine | | Zn.Histidine | | Cd.Histidine | |
|---|---|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.80 | 1.00 | 1.80 | 1.00 | 1.80 | 1.00 | 1.80 |
| 2.00 | 1.85 | 2.00 | 1.90 | 2.00 | 1.85 | 2.00 | 1.85 |
| 3.00 | 1.90 | 3.00 | 2.15 | 3.00 | 2.10 | 3.00 | 2.10 |
| 4.00 | 2.20 | 3.50 | 2.40 | 3.50 | 2.32 | 4.00 | 2.40 |
| 4.50 | 2.35 | 4.00 | 2.70 | 4.00 | 2.55 | 4.10 | 2.95 |
| 4.70 | 2.42 | 4.10 | 3.18 | 4.10 | 2.75 | 4.20 | 3.42 |
| 4.90 | 2.50 | 4.20 | 3.60 | 4.20 | 3.02 | 4.30 | 3.80 |
| 5.00 | 2.60 | 4.30 | 4.05 | 4.30 | 3.32 | 4.40 | 4.26 |
| 5.10 | 2.70 | 4.40 | 4.50 | 4.40 | 3.78 | 4.50 | 4.50 |
| 5.20 | 2.90 | 4.50 | 4.95 | 4.50 | 4.05 | 4.60 | 4.55 |
| 5.30 | 3.20 | 4.54 | 5.15 | 4.60 | 4.10 | 4.70 | 4.70 |
| 5.35 | 3.45 | 4.58 | 5.35 | 4.80 | 4.20 | 4.80 | 4.85 |
| 5.40 | 3.70 | 4.62 | 5.60 | 4.90 | 4.30 | 4.90 | 5.02 |
| 5.43 | 3.90 | 4.66 | 5.82 | 5.00 | 4.45 | 5.00 | 5.20 |
| 5.46 | 4.15 | 4.70 | 6.10 | 5.10 | 4.70 | 5.10 | 5.35 |
| 5.49 | 4.45 | 4.74 | 6.30 | 5.20 | 4.95 | 5.20 | 5.57 |
| 5.50 | 8.65 | 4.78 | 6.55 | 5.25 | 5.12 | 5.25 | 5.70 |
| 5.53 | 9.00 | 4.82 | 6.80 | 5.30 | 5.30 | 5.30 | 5.85 |
| 5.56 | 9.25 | 4.86 | 7.00 | 5.38 | 5.65 | 5.38 | 6.12 |
| 5.59 | 9.45 | 4.90 | 7.25 | 5.42 | 5.90 | 5.43 | 6.35 |
| 5.64 | 9.65 | 5.02 | 7.95 | 5.46 | 6.20 | 5.46 | 6.50 |
| 5.70 | 9.90 | 5.10 | 8.40 | 5.49 | 6.50 | 5.49 | 6.75 |
| 5.75 | 10.05 | 5.18 | 8.75 | 5.50 | 7.25 | 5.50 | 8.05 |
| 5.80 | 10.28 | 5.30 | 9.12 | 5.54 | 7.42 | 5.58 | 8.65 |
| 5.85 | 10.35 | 5.40 | 9.40 | 5.64 | 7.75 | 5.68 | 9.15 |
| 5.90 | 10.45 | 5.50 | 9.64 | 5.68 | 7.90 | 5.80 | 9.55 |
| 6.00 | 10.65 | 5.60 | 9.85 | 5.76 | 8.22 | 5.90 | 9.85 |
| 6.10 | 10.80 | 5.70 | 10.10 | 5.86 | 8.75 | 6.00 | 10.20 |
| 6.20 | 11.00 | 5.80 | 10.30 | 5.90 | 9.00 | | (ppt.) |
| | | 6.00 | 10.65 | 5.94 | 9.30 | | |
| | | 6.20 | 11.00 | 6.05 | 9.90 | | |
| | | | | 6.25 | 10.40 | | |
| | | | | 6.33 | 10.50 (ppt.) | | |

## Table VB 2.1

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{Hist.}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.022M

| *Catechol | | Zn.Hist.Catechol | | Cd.Hist.Catechol | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.80 | 1.00 | 1.80 | 1.00 | 1.80 |
| 2.00 | 1.85 | 2.00 | 1.85 | 2.00 | 1.85 |
| 3.00 | 1.90 | 3.00 | 2.10 | 3.00 | 2.10 |
| 4.00 | 2.20 | 3.50 | 2.32 | 4.00 | 2.40 |
| 4.50 | 2.35 | 4.00 | 2.55 | 4.10 | 2.95 |
| 4.80 | 2.48 | 4.10 | 2.75 | 4.20 | 3.42 |
| 5.00 | 2.60 | 4.20 | 3.02 | 4.30 | 3.80 |
| 5.10 | 2.70 | 4.30 | 3.32 | 4.40 | 4.26 |
| 5.20 | 2.90 | 4.35 | 3.54 | 4.50 | 4.50 |
| 5.30 | 3.20 | 4.40 | 3.78 | 4.60 | 4.55 |
| 5.35 | 3.45 | 4.45 | 4.00 | 4.70 | 4.70 |
| 5.40 | 3.70 | 4.50 | 4.05 | 4.90 | 5.02 |
| 5.43 | 3.90 | 4.60 | 4.10 | 5.10 | 5.35 |
| 5.46 | 4.15 | 4.70 | 4.15 | 5.20 | 5.57 |
| 5.49 | 4.40 | 4.80 | 4.20 | 5.25 | 5.70 |
| 5.50 | 7.85 | 4.90 | 4.30 | 5.30 | 5.85 |
| 5.54 | 8.20 | 5.00 | 4.45 | 5.34 | 5.95 |
| 5.58 | 8.50 | 5.10 | 4.70 | 5.38 | 6.12 |
| 5.62 | 8.70 | 5.20 | 4.95 | 5.43 | 6.35 |
| 5.66 | 8.90 | 5.30 | 5.30 | 5.46 | 6.50 |
| 5.70 | 9.08 | 5.38 | 5.65 | 5.49 | 6.75 |
| 5.74 | 9.25 | 5.43 | 6.00 | 5.50 | 7.85 |
| 5.78 | 9.38 | 5.46 | 6.20 | 5.60 | 8.10 |
| 5.82 | 9.50 | 5.49 | 6.50 | 5.70 | 8.32 |
| 5.86 | 9.65 | 5.50 | 7.20 | 5.80 | 8.50 |
| 5.90 | 9.75 | 5.60 | 7.50 | 5.90 | 8.65 |
| 6.00 | 10.08 | 5.70 | 7.70 | 6.00 | 8.80 |
| 6.10 | 10.30 | 5.90 | 8.00 | 6.10 | 9.00 |
| 6.20 | 10.50 | 6.10 | 8.25 | 6.20 | 9.20 |
| 6.30 | 10.65 | 6.20 | 8.40 | 6.25 | 9.35 |
| 6.40 | 10.78 | 6.30 | 8.68 | 6.30 | 9.50 |
| 6.50 | 10.90 | 6.35 | 8.92 | 6.40 | 9.75 |
| 6.60 | 11.00 | 6.40 | 9.18 | 6.50 | 10.00 |
| | | 6.45 | 9.45 | | (ppt.) |
| | | 6.50 | 9.75 | | |
| | | 6.60 | 10.15 | | |
| | | 6.80 | 10.50 | | |
| | | 7.00 | 10.85 | | |
| | | 7.20 | 11.10 | | |

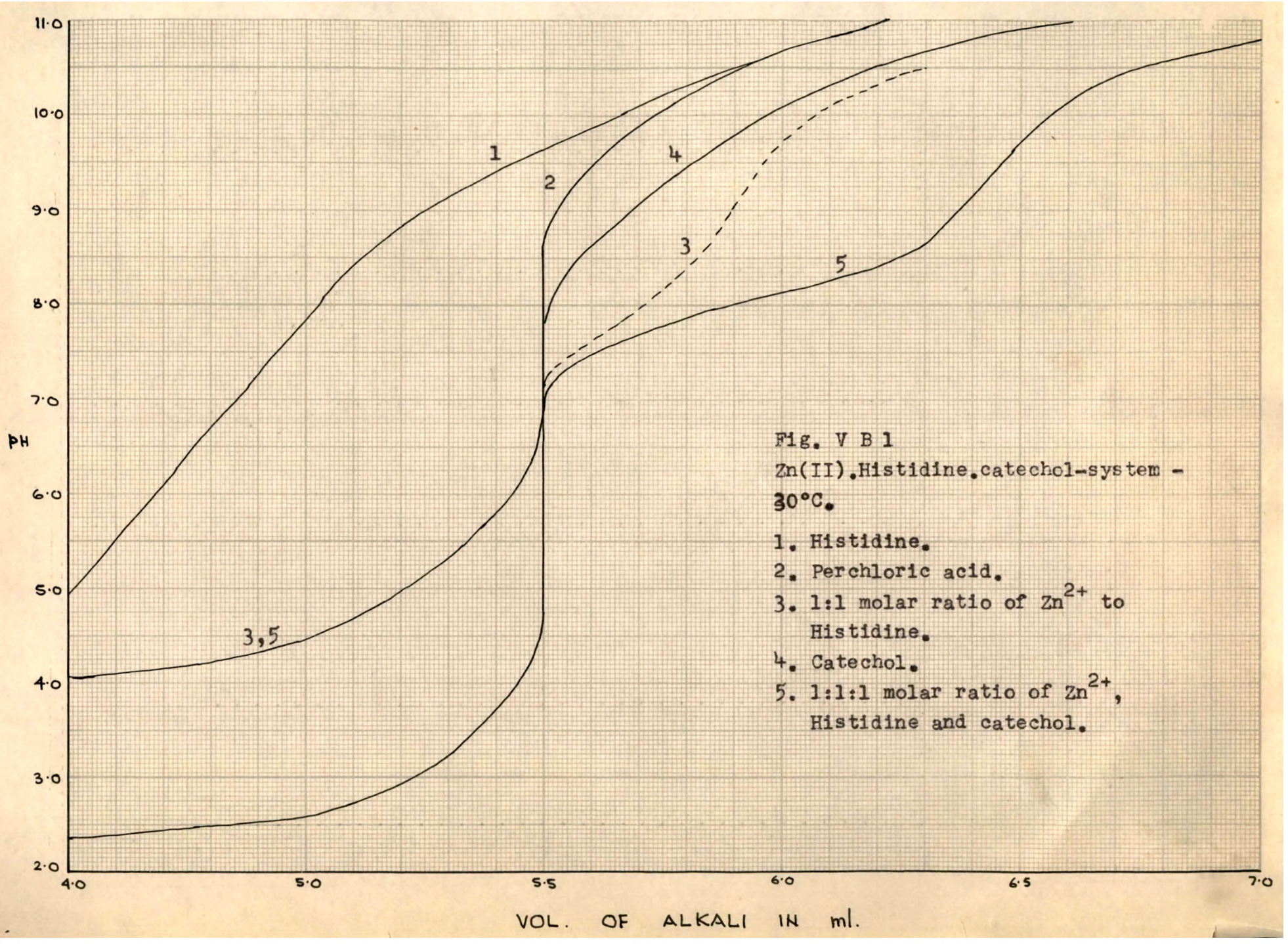



Fig. V B 1
Zn(II).Histidine.catechol-system - 30°C.

1. Histidine.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to Histidine.
4. Catechol.
5. 1:1:1 molar ratio of $Zn^{2+}$, Histidine and catechol.

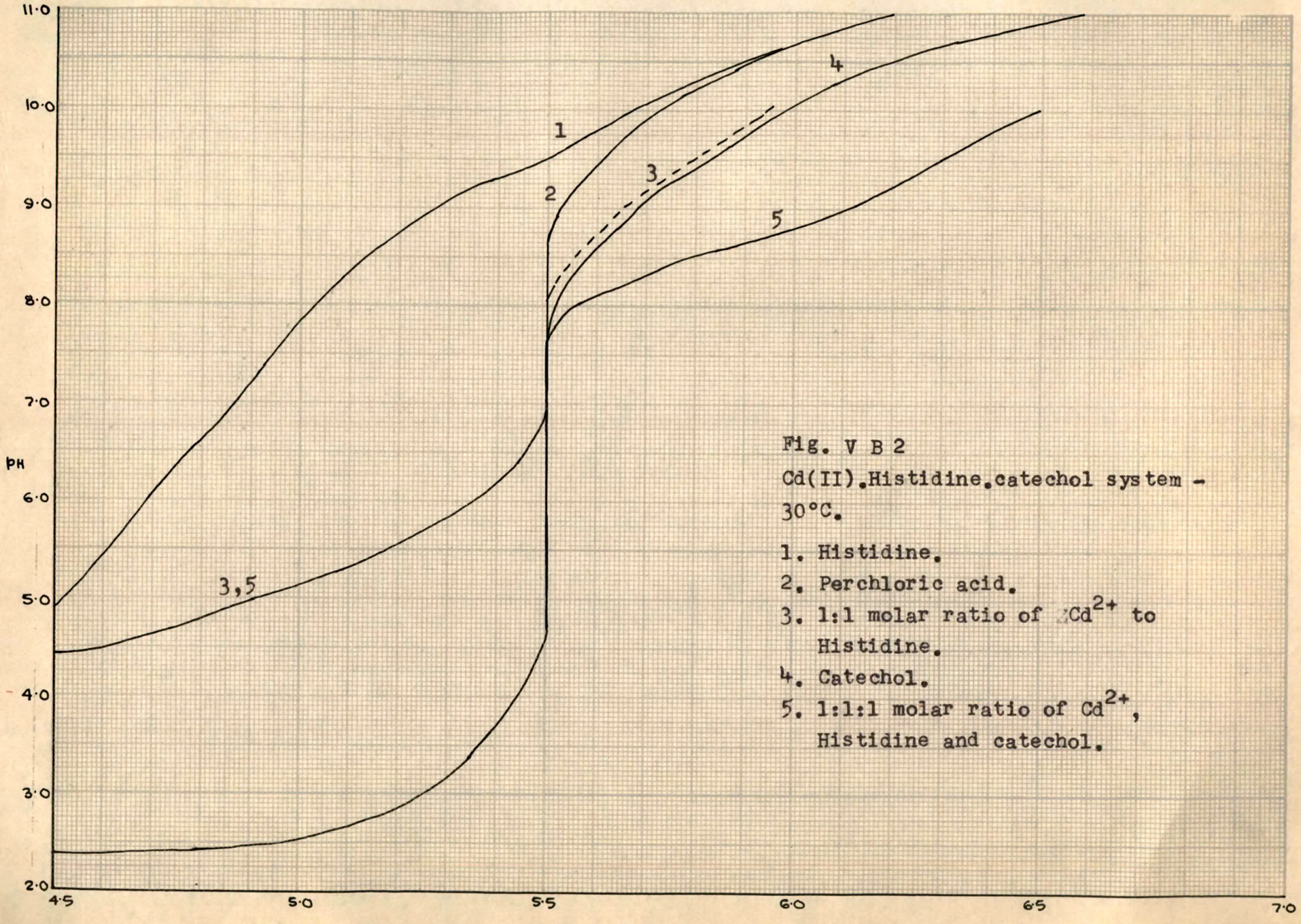



Fig. V B 2

Cd(II).Histidine.catechol system - 30°C.

1. Histidine.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to Histidine.
4. Catechol.
5. 1:1:1 molar ratio of $Cd^{2+}$, Histidine and catechol.

## Table VB 2.2

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{Hist.}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.022M

| *Pyrogallol | | Zn.Hist.Pyrogallol | |
|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.80 | 1.00 | 1.80 |
| 2.00 | 1.85 | 2.00 | 1.85 |
| 3.00 | 1.90 | 3.00 | 2.10 |
| 4.00 | 2.20 | 3.50 | 2.32 |
| 4.50 | 2.35 | 4.00 | 2.55 |
| 4.80 | 2.48 | 4.10 | 2.75 |
| 5.00 | 2.60 | 4.20 | 3.02 |
| 5.10 | 2.70 | 4.30 | 3.32 |
| 5.20 | 2.90 | 4.40 | 3.78 |
| 5.30 | 3.20 | 4.50 | 4.05 |
| 5.35 | 3.45 | 4.60 | 4.10 |
| 5.40 | 3.70 | 4.70 | 4.15 |
| 5.43 | 3.90 | 4.80 | 4.20 |
| 5.46 | 4.15 | 4.90 | 4.30 |
| 5.49 | 4.45 | 5.00 | 4.45 |
| 5.50 | 7.15 | 5.10 | 4.70 |
| 5.53 | 7.55 | 5.20 | 4.95 |
| 5.56 | 8.00 | 5.30 | 5.30 |
| 5.59 | 8.25 | 5.34 | 5.45 |
| 5.62 | 8.45 | 5.38 | 5.65 |
| 5.66 | 8.68 | 5.43 | 5.92 |
| 5.70 | 8.82 | 5.46 | 6.20 |
| 5.75 | 9.02 | 5.49 | 6.50 |
| 5.80 | 9.24 | 5.50 | 6.95 |
| 5.90 | 9.60 | 5.60 | 7.25 |
| 6.00 | 9.90 | 5.80 | 7.48 |
| 6.10 | 10.20 | 5.90 | 7.65 |
| 6.20 | 10.35 | 6.00 | 7.72 |
| 6.40 | 10.65 | 6.20 | 8.05 |
| 6.60 | 10.80 | 6.30 | 8.40 |
| 6.80 | 10.90 | 6.40 | 9.00 |
| 7.00 | 11.00 | 6.50 | 9.40 |
| | | 6.60 | 9.70 |
| | | 6.80 | 10.20 |
| | | 7.00 | 10.60 |
| | | 7.20 | 11.00 |

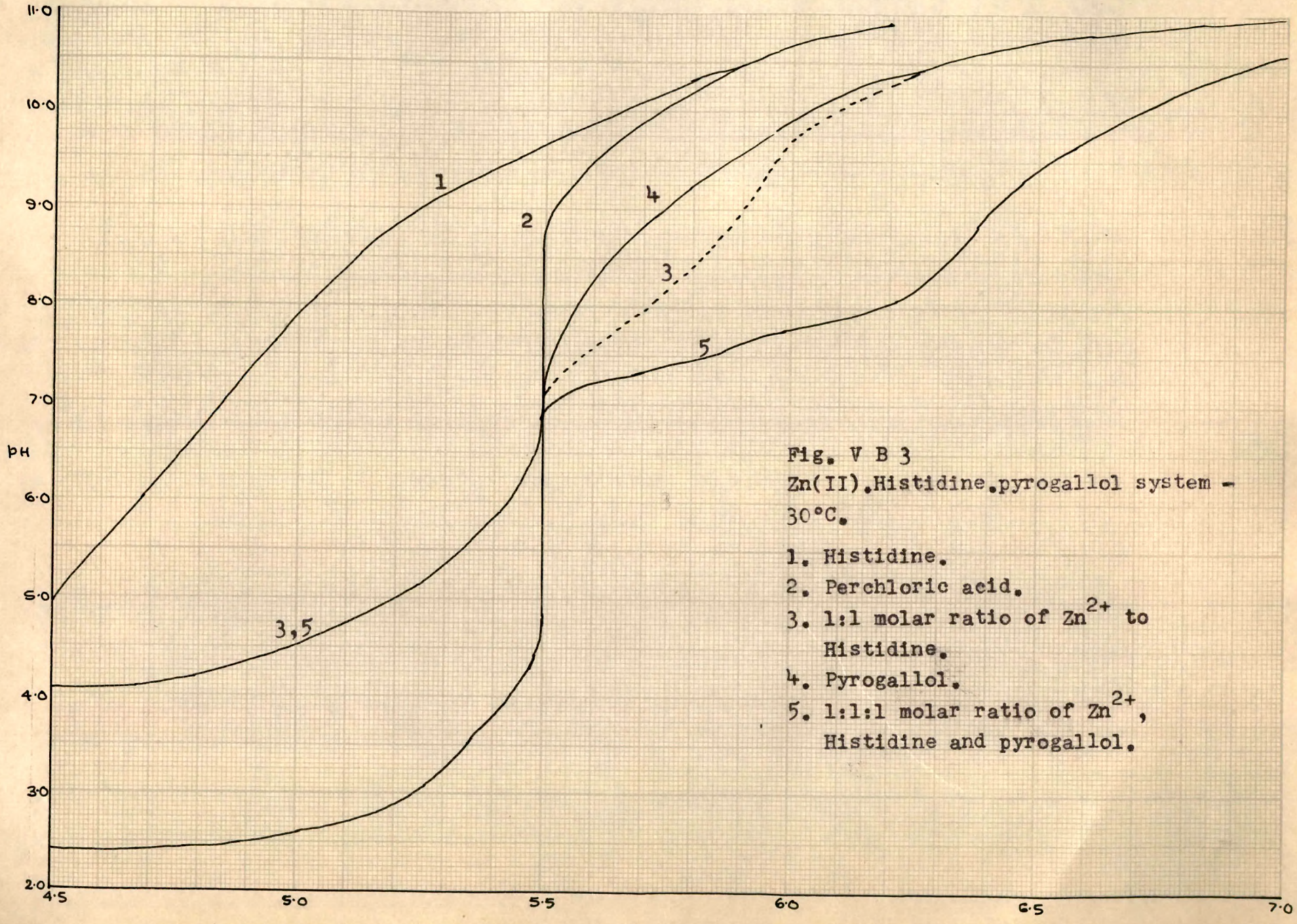



Fig. V B 3
Zn(II).Histidine.pyrogallol system - 30°C.

1. Histidine.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to Histidine.
4. Pyrogallol.
5. 1:1:1 molar ratio of $Zn^{2+}$, Histidine and pyrogallol.

## Table VB 2.4

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{Hist.}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.022M

| *2,3-Dihydroxy-naphthalene | | Cd.Hist.2,3-Dihydroxy-naphthalene | |
|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.80 | 1.00 | 1.80 |
| 2.00 | 1.85 | 2.00 | 1.85 |
| 3.00 | 1.90 | 3.00 | 2.10 |
| 4.00 | 2.20 | 4.00 | 2.40 |
| 4.50 | 2.35 | 4.10 | 2.95 |
| 4.80 | 2.48 | 4.20 | 3.42 |
| 5.00 | 2.60 | 4.30 | 3.80 |
| 5.10 | 2.70 | 4.40 | 4.26 |
| 5.20 | 2.90 | 4.50 | 4.50 |
| 5.30 | 3.25 | 4.60 | 4.55 |
| 5.35 | 3.45 | 4.70 | 4.70 |
| 5.40 | 3.70 | 4.90 | 5.02 |
| 5.43 | 3.90 | 5.10 | 5.35 |
| 5.46 | 4.15 | 5.20 | 5.57 |
| 5.49 | 4.40 | 5.25 | 5.70 |
| 5.50 | 7.85 | 5.30 | 5.85 |
| 5.52 | 8.10 | 5.34 | 5.95 |
| 5.56 | 8.45 | 5.38 | 6.12 |
| 5.60 | 8.75 | 5.43 | 6.35 |
| 5.63 | 8.85 | 5.46 | 6.50 |
| 5.70 | 9.10 | 5.49 | 6.75 |
| 5.80 | 9.48 | 5.50 | 7.40 |
| 5.90 | 9.80 | 5.60 | 7.58 |
| 6.00 | 10.15 | 5.70 | 7.70 |
| 6.10 | 10.35 | 5.80 | 7.85 |
| 6.20 | 10.50 | 5.90 | 8.04 |
| 6.30 | 10.60 | 6.00 | 8.20 |
| 6.40 | 10.70 | 6.05 | 8.28 |
| 6.50 | 10.82 | 6.10 | 8.35 |
| 6.60 | 10.90 | 6.15 | 8.45 |
| 6.70 | 11.00 | 6.21 | 8.60 (ppt.) |

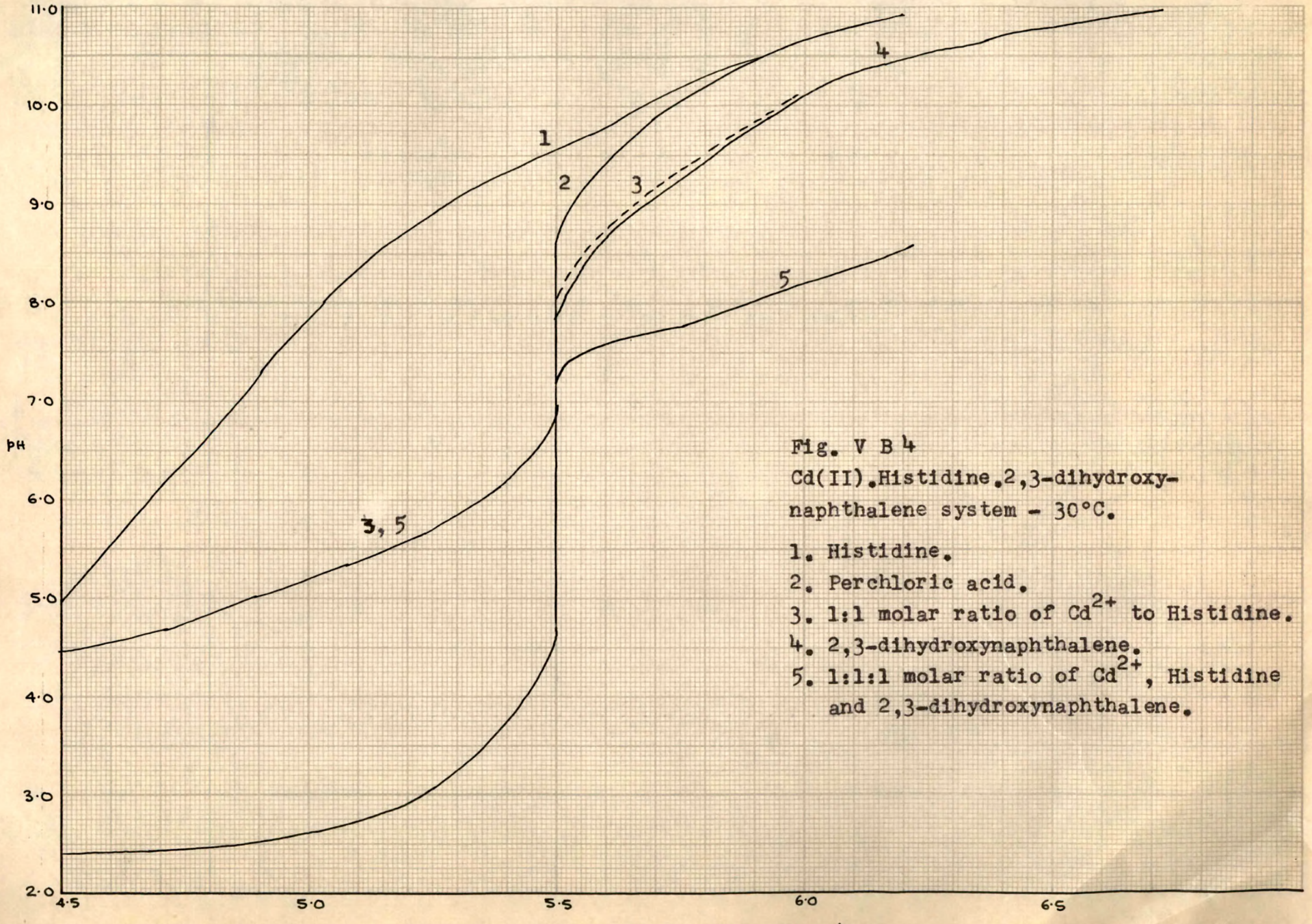



Fig. V B 4
Cd(II).Histidine.2,3-dihydroxy-naphthalene system - 30°C.

1. Histidine.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to Histidine.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Cd^{2+}$, Histidine and 2,3-dihydroxynaphthalene.

## Table VB 3.1b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.60 | $1.95_2$ | 5.50 | 5.64 | 0.14 | $0.14_2$ | $0.78_1$ | $8.02_5$ | $7.24_4$ |
| 7.70 | $1.94_8$ | 5.50 | 5.69 | 0.19 | $0.19_3$ | $0.62_1$ | $7.85_6$ | $7.23_5$ |
| 7.80 | $1.94_4$ | 5.50 | 5.75 | 0.25 | $0.25_4$ | $0.46_7$ | $7.69_5$ | $7.22_8$ |
| 7.90 | $1.93_6$ | 5.51 | 5.83 | 0.32 | $0.32_7$ | $0.31_3$ | $7.54_5$ | $7.23_2$ |
| 8.00 | $1.92_4$ | 5.51 | 5.91 | 0.40 | $0.41_2$ | $0.15_4$ | $7.41_1$ | $7.25_7$ |
| 8.10 | $1.90_8$ | 5.53 | 6.00 | 0.47 | $0.48_8$ | $0.02_0$ | $7.25_7$ | $7.23_7$ |
| 8.20 | $1.88_8$ | 5.54 | 6.06 | 0.52 | $0.54_6$ | $\bar{1}.91_9$ | $7.14_3$ | $7.22_4$ |
| 8.30 | $1.86_8$ | 5.55 | 6.14 | 0.59 | $0.62_6$ | $\bar{1}.77_6$ | $7.04_0$ | $7.26_4$ |
| 8.40 | $1.84_8$ | 5.57 | 6.22 | 0.65 | $0.69_7$ | $\bar{1}.63_8$ | $6.94_7$ | - |

$\log K_{MAL} = 7.24 \pm 0.02$

## Table VB 3.2b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.40 | $1.94_4$ | 5.52 | 5.73 | 0.21 | $0.21_4$ | $0.56_4$ | $7.39_3$ | $6.82_8$ |
| 7.50 | $1.92_8$ | 5.53 | 5.82 | 0.29 | $0.29_7$ | $0.37_4$ | $7.24_9$ | - |
| 7.60 | $1.92_0$ | 5.53 | 5.88 | 0.35 | $0.36_1$ | $0.24_8$ | $7.09_6$ | - |
| 7.70 | $1.90_4$ | 5.54 | 5.95 | 0.41 | $0.42_6$ | $0.12_9$ | $6.95_3$ | $6.82_4$ |
| 7.80 | $1.88_0$ | 5.55 | 6.02 | 0.47 | $0.49_5$ | $0.00_8$ | $6.82_0$ | $6.81_2$ |
| 7.90 | $1.85_6$ | 5.55 | 6.09 | 0.54 | $0.57_6$ | $\bar{1}.86_7$ | $6.71_0$ | $6.84_3$ |
| 8.00 | $1.84_0$ | 5.56 | 6.16 | 0.60 | $0.64_7$ | $\bar{1}.73_6$ | $6.60_5$ | $6.86_9$ |
| 8.10 | $1.80_0$ | 5.57 | 6.23 | 0.64 | $0.70_5$ | $\bar{1}.62_1$ | $6.50_2$ | $6.88_1$ |

$\log K_{MAL} = 6.84 \pm 0.04$

Fig. V B 6

Zn(II).Histidine.pyrogallol system - 30°C.

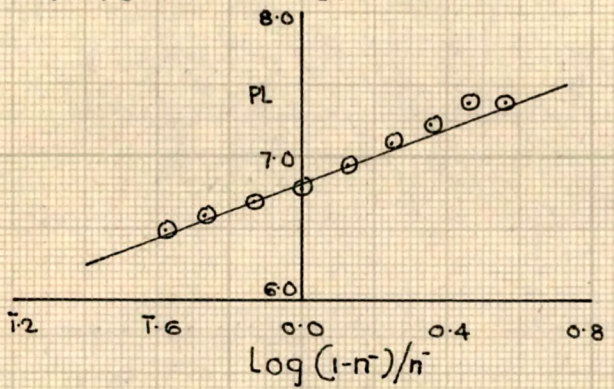
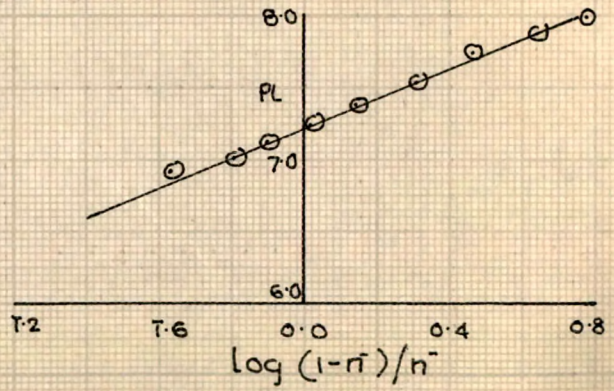



Fig. V B 5

Zn(II).Histidine.catechol system - 30°C.



## Table VB 3.1c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.40 | $1.84_8$ | 5.57 | 5.71 | 0.14 | $0.15_0$ | $0.74_8$ | $6.49_5$ | $5.74_7$ |
| 8.50 | $1.81_6$ | 5.58 | 5.78 | 0.20 | $0.21_8$ | $0.55_6$ | $6.35_0$ | $5.79_4$ |
| 8.60 | $1.79_2$ | 5.60 | 5.85 | 0.25 | $0.27_6$ | $0.41_8$ | $6.20_6$ | $5.78_8$ |
| 8.70 | $1.74_4$ | 5.62 | 5.92 | 0.30 | $0.34_0$ | $0.28_8$ | $6.07_5$ | $5.78_7$ |
| 8.80 | $1.71_9$ | 5.63 | 5.98 | 0.35 | $0.40_3$ | $0.17_0$ | $5.94_9$ | $5.77_9$ |
| 8.90 | $1.67_2$ | 5.66 | 6.05 | 0.39 | $0.46_0$ | $0.06_9$ | $5.83_0$ | $5.76_1$ |
| 9.00 | $1.64_0$ | 5.68 | 6.11 | 0.43 | $0.51_9$ | $\bar{1}.96_6$ | $5.72_1$ | $5.75_5$ |
| 9.10 | $1.56_0$ | 5.70 | 6.15 | 0.45 | $0.57_1$ | $\bar{1}.87_5$ | $5.69_8$ | - |
| 9.20 | $1.48_0$ | 5.72 | 6.19 | 0.47 | $0.62_9$ | $\bar{1}.77_0$ | $5.53_4$ | $5.76_4$ |

$\log K_{MAL} = 5.76 \pm 0.03$

## Table VB 3.4c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Cd.histidine. 2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.70 | $1.85_2$ | 5.53 | 5.68 | 0.15 | $0.16_0$ | $0.72_0$ | $8.47_5$ | $7.75_5$ |
| 7.80 | $1.82_4$ | 5.55 | 5.75 | 0.20 | $0.21_7$ | $0.55_7$ | $8.32_3$ | $7.76_6$ |
| 7.90 | $1.79_2$ | 5.57 | 5.82 | 0.25 | $0.27_6$ | $0.41_8$ | $8.17_9$ | $7.76_1$ |
| 8.00 | $1.77_3$ | 5.58 | 5.88 | 0.30 | $0.33_5$ | $0.29_7$ | $8.04_1$ | $7.74_4$ |
| 8.10 | $1.71_3$ | 5.60 | 5.94 | 0.34 | $0.39_3$ | $0.18_8$ | $7.91_2$ | $7.72_4$ |
| 8.20 | $1.67_3$ | 5.62 | 6.00 | 0.38 | $0.45_0$ | $0.08_7$ | $7.78_9$ | $7.70_2$ |
| 8.30 | $1.63_3$ | 5.65 | 6.06 | 0.42 | $0.50_9$ | $\bar{1}.98_4$ | $7.68_8$ | $7.70_4$ |
| 8.40 | $1.55_3$ | 5.66 | 6.12 | 0.46 | $0.58_7$ | $\bar{1}.84_7$ | $7.60_0$ | $7.75_3$ |
| 8.50 | $1.51_4$ | 5.68 | 6.16 | 0.48 | $0.62_9$ | $\bar{1}.77_0$ | $7.49_7$ | $7.72_7$ |
| 8.60 | $1.43_4$ | 5.71 | 6.21 | 0.50 | $0.69_1$ | $\bar{1}.65_0$ | $7.43_6$ | $7.78_6$ |

$\log K_{MAL} = 7.74 \pm 0.04$

Fig. V B 7
Cd(II).Histidine.catechol
system - 30°C.

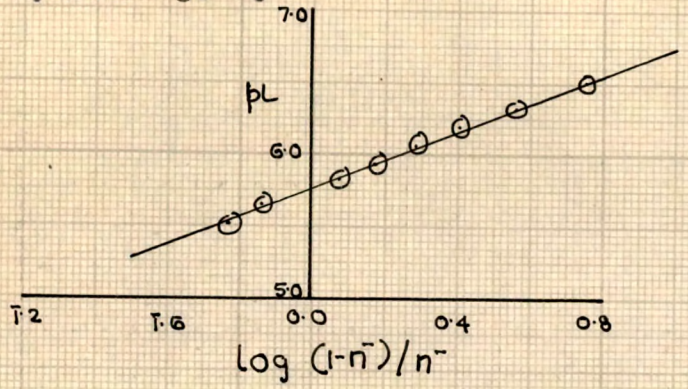



Fig. V B 8
Cd(II).Histidine.2,3-dihydroxy-
naphthalene system - 30°C.

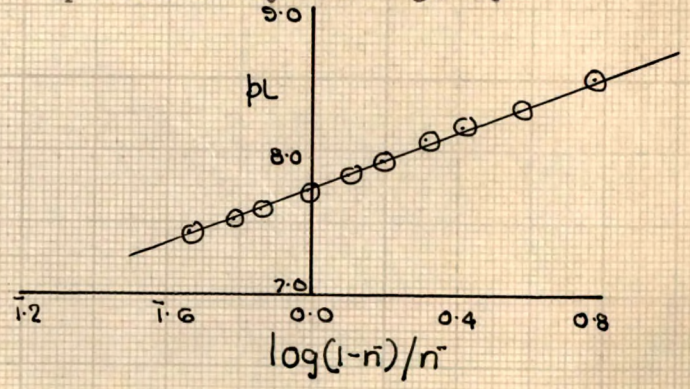


Table VB 4.0

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{IMDA}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *Perchloric acid | | IMDA | | Zn.IMDA | | Cd.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 | 1.50 | 0.00 | 1.55 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.60 | 1.00 | 1.75 | 1.00 | 1.70 | 1.00 | 1.70 |
| 1.50 | 1.65 | 2.00 | 1.85 | 2.00 | 1.80 | 2.00 | 1.80 |
| 2.00 | 1.70 | 3.00 | 2.00 | 3.00 | 1.90 | 3.00 | 2.00 |
| 2.50 | 1.80 | 4.00 | 2.30 | 4.00 | 2.20 | 4.00 | 2.20 |
| 3.00 | 1.85 | 5.00 | 2.80 | 5.00 | 2.80 | 5.00 | 2.70 |
| 4.00 | 2.00 | 5.10 | 3.00 | 5.50 | 3.75 | 5.50 | 4.20 |
| 5.00 | 2.30 | 5.20 | 3.20 | 5.60 | 4.28 | 5.55 | 4.75 |
| 5.50 | 2.70 | 5.30 | 3.50 | 5.70 | 4.75 | 5.60 | 5.30 |
| 5.60 | 2.80 | 5.36 | 3.75 | 5.80 | 5.25 | 5.70 | 5.90 |
| 5.70 | 2.95 | 5.42 | 4.00 | 5.90 | 5.75 | 5.80 | 6.30 |
| 5.80 | 3.15 | 5.46 | 4.25 | 5.95 | 6.05 | 5.90 | 6.80 |
| 5.90 | 3.45 | 5.49 | 4.50 | 5.97 | 6.20 | 5.95 | 7.00 |
| 5.94 | 3.65 | 5.50 | 4.75 | 6.00 | 6.55 | 6.00 | 7.22 |
| 5.98 | 4.00 | 5.52 | 7.00 | 6.02 | 6.75 | 6.02 | 7.30 |
| 6.00 | 8.80 | 5.53 | 7.25 | 6.05 | 7.05 | 6.05 | 7.60 |
| 6.02 | 9.10 | 5.55 | 7.50 | 6.07 | 7.22 | 6.07 | 7.75 |
| 6.04 | 9.25 | 5.58 | 7.75 | 6.10 | 7.40 | 6.10 | 8.00 |
| 6.07 | 9.50 | 5.60 | 8.00 | 6.15 | 7.68 | 6.15 | 8.30 |
| 6.10 | 9.70 | 5.64 | 8.25 | 6.20 | 7.85 | 6.20 | 8.52 |
| 6.15 | 9.95 | 5.67 | 8.50 | 6.25 | 8.00 | 6.25 | 8.75 |
| 6.20 | 10.10 | 5.70 | 8.70 | 6.30 | 8.20 | 6.30 | 8.90 |
| 6.30 | 10.35 | 5.78 | 9.00 | 6.40 | 8.55 | 6.35 | 9.05 |
| 6.40 | 10.50 | 5.85 | 9.20 | 6.45 | 8.70 | 6.40 | 9.25 |
| 6.60 | 10.70 | 5.90 | 9.40 | 6.50 | 8.95 | | (ppt.) |
| 6.80 | 10.90 | 6.00 | 9.60 | 6.55 | 9.20 | | |
| 6.90 | 11.00 | 6.05 | 9.75 | 6.60 | 9.45 | | |
| | | 6.15 | 10.00 | | (ppt.) | | |
| | | 6.25 | 10.25 | | | | |
| | | 6.40 | 10.50 | | | | |
| | | 6.65 | 10.75 | | | | |
| | | 6.90 | 11.00 | | | | |

## Table VB 4.1

$N = 0.2M$ $V° = 50$ ml. $\mu = 0.2M$ $t = 30°C.$

$E° = 0.02M$ $T°_{IMDA} = 0.002M$ $T°_{L} = 0.002M$ $T°_{M} = 0.002M$

$^{*}E° = 0.024M$

| *Catechol | | Zn.IMDA.Catechol | | Cd.IMDA.Catechol | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.50 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.60 | 1.00 | 1.70 | 1.00 | 1.70 |
| 1.50 | 1.65 | 2.00 | 1.80 | 2.00 | 1.80 |
| 2.00 | 1.70 | 3.00 | 1.90 | 3.00 | 2.00 |
| 2.50 | 1.80 | 4.00 | 2.20 | 4.00 | 2.20 |
| 3.00 | 1.85 | 5.00 | 2.80 | 5.00 | 2.70 |
| 3.50 | 1.90 | 5.50 | 3.75 | 5.50 | 4.20 |
| 4.00 | 2.00 | 5.60 | 4.28 | 5.55 | 4.75 |
| 4.50 | 2.10 | 5.70 | 4.75 | 5.60 | 5.30 |
| 5.00 | 2.30 | 5.80 | 5.25 | 5.70 | 5.90 |
| 5.50 | 2.70 | 5.90 | 5.75 | 5.80 | 6.30 |
| 5.60 | 2.80 | 5.95 | 6.05 | 5.90 | 6.80 |
| 5.70 | 2.95 | 5.97 | 6.30 | 5.95 | 7.00 |
| 5.80 | 3.15 | 6.00 | 6.50 | 6.00 | 7.20 |
| 5.90 | 3.45 | 6.02 | 6.62 | 6.02 | 7.32 |
| 5.94 | 3.65 | 6.05 | 6.95 | 6.05 | 7.45 |
| 5.98 | 4.00 | 6.08 | 7.20 | 6.08 | 7.70 |
| 6.00 | 7.25 | 6.10 | 7.30 | 6.10 | 7.80 |
| 6.02 | 7.40 | 6.15 | 7.55 | 6.15 | 8.00 |
| 6.05 | 7.75 | 6.20 | 7.72 | 6.20 | 8.20 |
| 6.10 | 8.15 | 6.30 | 7.95 | 6.30 | 8.50 |
| 6.15 | 8.50 | 6.40 | 8.07 | 6.40 | 8.70 |
| 6.20 | 8.75 | 6.50 | 8.20 | 6.50 | 8.82 |
| 6.30 | 9.05 | 6.60 | 8.35 | 6.60 | 9.00 |
| 6.40 | 9.40 | 6.70 | 8.50 | 6.70 | 9.15 |
| 6.50 | 9.65 | 6.80 | 8.62 | 6.80 | 9.30 |
| 6.60 | 9.80 | 7.00 | 9.20 | 6.90 | 9.55 |
| 6.70 | 10.05 | 7.20 | 9.80 | 7.00 | 9.70 |
| 6.80 | 10.30 | 7.40 | 10.30 | 7.20 | 10.10 |
| 7.00 | 10.50 | 7.60 | 10.55 | 7.40 | 10.55 |
| 7.20 | 10.65 | 7.80 | 10.85 | 7.60 | 10.95 |
| 7.40 | 10.85 | 8.00 | 11.00 | | |
| 7.60 | 11.00 | | | | |

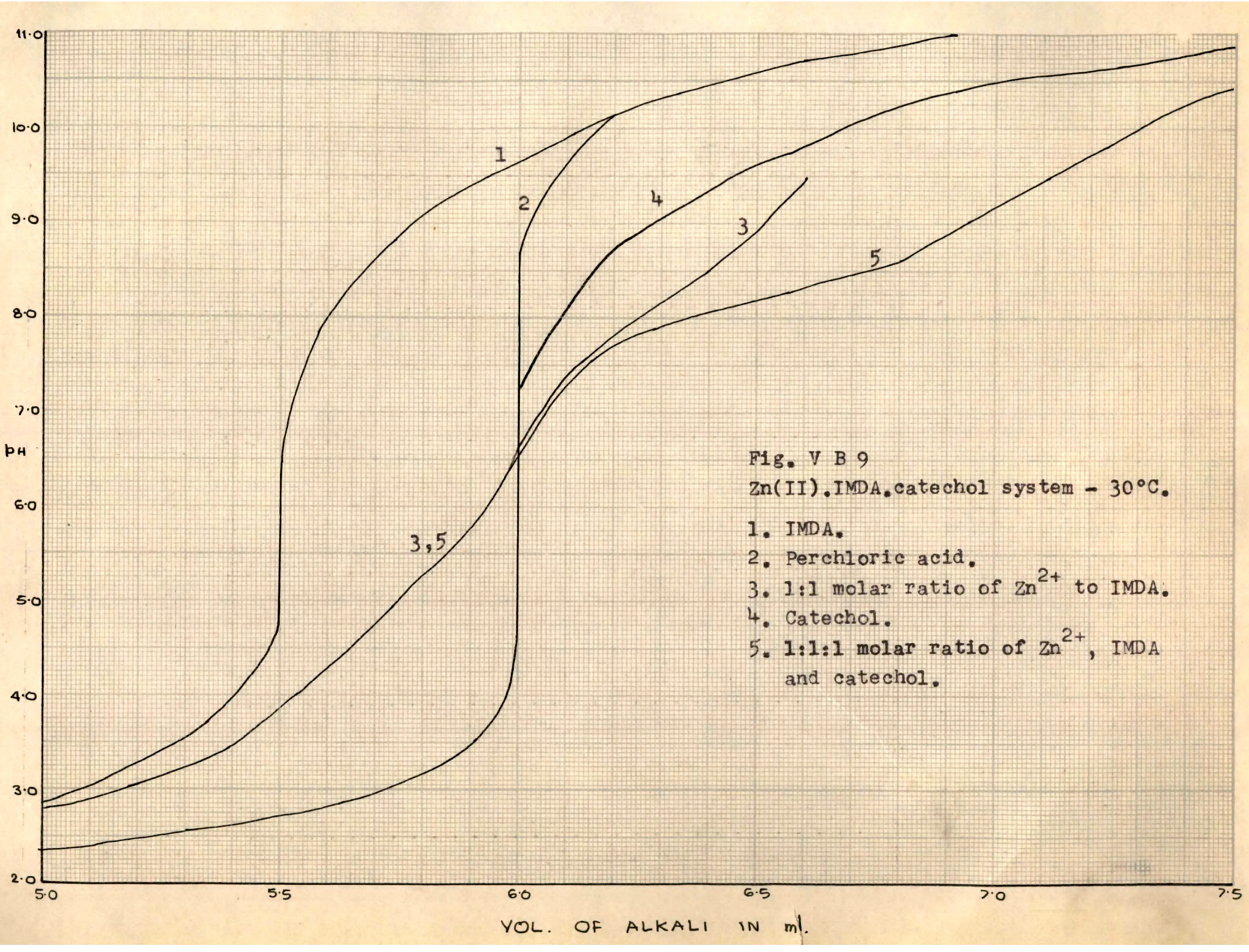



Fig. V B 9
Zn(II).IMDA.catechol system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to IMDA.
4. Catechol.
5. 1:1:1 molar ratio of $Zn^{2+}$, IMDA and catechol.

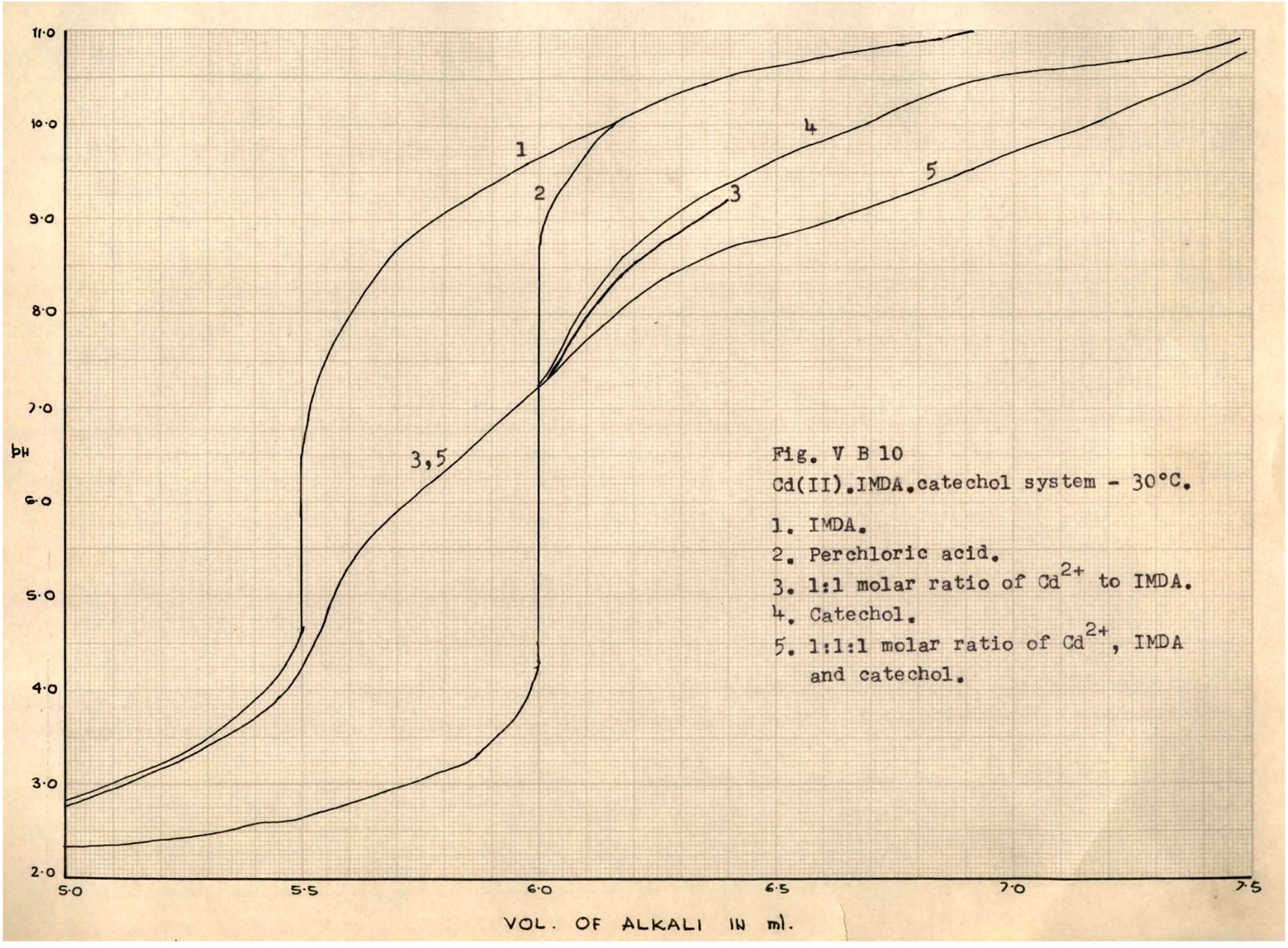



Fig. V B 10
Cd(II).IMDA.catechol system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to IMDA.
4. Catechol.
5. 1:1:1 molar ratio of $Cd^{2+}$, IMDA and catechol.

Table VB 4.2

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

E° = 0.02M  $T°_{IMDA.}$ = 0.002M  $T°_{L}$ = 0.002M  $T°_{M}$ = 0.002M

*E° = 0.024M

*Pyrogallol

| Vol.of alkali (in ml.) | B |
|---|---|
| 0.00 | 1.50 |
| 1.00 | 1.60 |
| 1.50 | 1.65 |
| 2.00 | 1.70 |
| 3.00 | 1.85 |
| 4.00 | 2.00 |
| 5.00 | 2.30 |
| 5.60 | 2.80 |
| 5.70 | 2.95 |
| 5.80 | 3.15 |
| 5.90 | 3.45 |
| 5.94 | 3.65 |
| 5.98 | 4.00 |
| 6.00 | 6.85 |
| 6.02 | 7.05 |
| 6.05 | 7.35 |
| 6.10 | 7.70 |
| 6.15 | 8.00 |
| 6.20 | 8.30 |
| 6.30 | 8.75 |
| 6.40 | 9.12 |
| 6.50 | 9.40 |
| 6.60 | 9.75 |
| 6.70 | 10.05 |
| 6.80 | 10.35 |
| 7.00 | 10.70 |
| 7.20 | 10.95 |

Zn.IMDA.Pyrogallol

| Vol.of alkali (in ml.) | B |
|---|---|
| 0.00 | 1.55 |
| 1.00 | 1.70 |
| 2.00 | 1.80 |
| 3.00 | 1.90 |
| 4.00 | 2.20 |
| 5.00 | 2.80 |
| 5.50 | 3.75 |
| 5.60 | 4.75 |
| 5.80 | 5.25 |
| 5.90 | 5.75 |
| 5.95 | 6.05 |
| 5.97 | 6.20 |
| 6.00 | 6.45 |
| 6.05 | 6.75 |
| 6.10 | 6.95 |
| 6.15 | 7.20 |
| 6.20 | 7.40 |
| 6.25 | 7.60 |
| 6.30 | 7.70 |
| 6.40 | 7.85 |
| 6.50 | 7.95 |
| 6.60 | 8.05 |
| 6.70 | 8.22 |
| 6.80 | 8.40 |
| 6.90 | 8.65 |
| 7.00 | 8.90 |
| 7.10 | 9.20 |
| 7.30 | 9.80 |
| 7.50 | 10.40 |
| 7.70 | 11.00 |

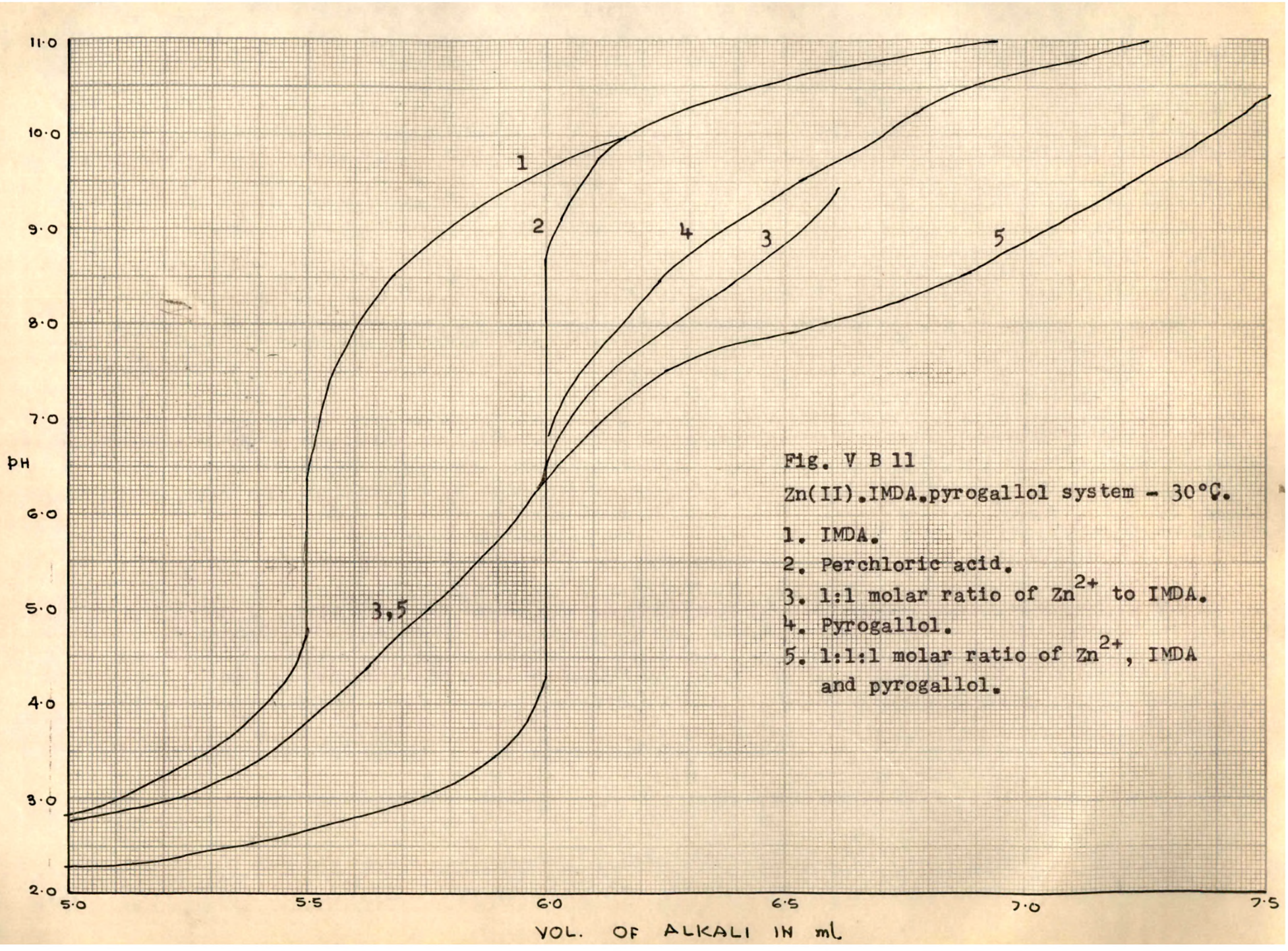



Fig. V B 11

Zn(II).IMDA.pyrogallol system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to IMDA.
4. Pyrogallol.
5. 1:1:1 molar ratio of $Zn^{2+}$, IMDA and pyrogallol.

Table VB 4.3

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{IMDA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *Protocatechuic acid | | Zn.IMDA.Protocatechuic acid | | Cd.IMDA.Protocatechuic acid | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.50 | 0.00 | 1.50 | 0.00 | 1.50 |
| 1.00 | 1.60 | 1.00 | 1.60 | 1.00 | 1.60 |
| 2.00 | 1.70 | 2.00 | 1.70 | 2.00 | 1.70 |
| 3.00 | 1.80 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 2.00 | 4.00 | 2.00 | 4.00 | 2.00 |
| 5.00 | 2.30 | 5.00 | 2.30 | 5.00 | 2.30 |
| 5.40 | 2.55 | 5.40 | 2.55 | 5.40 | 2.55 |
| 5.50 | 2.60 | 5.50 | 2.60 | 5.50 | 2.60 |
| 5.60 | 2.70 | 5.60 | 2.70 | 5.60 | 2.70 |
| 5.70 | 2.80 | 5.70 | 2.80 | 5.70 | 2.80 |
| 5.80 | 3.00 | 5.80 | 3.00 | 5.80 | 3.00 |
| 5.90 | 3.20 | 5.90 | 3.20 | 5.90 | 3.20 |
| 6.00 | 3.50 | 6.00 | 3.50 | 6.00 | 3.50 |
| 6.10 | 3.80 | 6.10 | 3.80 | 6.10 | 3.80 |
| 6.15 | 4.00 | 6.15 | 4.00 | 6.15 | 4.00 |
| 6.20 | 4.20 | 6.20 | 4.20 | 6.20 | 4.20 |
| 6.30 | 4.50 | 6.30 | 4.50 | 6.30 | 4.50 |
| 6.35 | 4.75 | 6.35 | 4.75 | 6.35 | 4.75 |
| 6.40 | 5.00 | 6.40 | 5.00 | 6.40 | 5.00 |
| 6.42 | 5.15 | 6.42 | 5.15 | 6.42 | 5.15 |
| 6.45 | 5.45 | 6.45 | 5.45 | 6.45 | 5.45 |
| 6.48 | 6.00 | 6.48 | 6.00 | 6.48 | 6.00 |
| 6.50 | 7.20 | 6.50 | 6.80 | 6.50 | 7.20 |
| 6.55 | 7.80 | 6.55 | 7.10 | 6.55 | 7.60 |
| 6.60 | 8.10 | 6.60 | 7.36 | 6.60 | 7.85 |
| 6.70 | 8.60 | 6.70 | 7.65 | 6.70 | 8.24 |
| 6.80 | 9.00 | 6.80 | 7.80 | 6.80 | 8.45 |
| 6.90 | 9.35 | 6.90 | 7.92 | 6.90 | 8.60 |
| 7.00 | 9.75 | 7.00 | 8.05 | 7.00 | 8.80 |
| 7.10 | 10.10 | 7.10 | 8.22 | 7.10 | 8.95 |
| 7.20 | 10.40 | 7.20 | 8.35 | 7.20 | 9.08 |
| 7.40 | 10.80 | 7.30 | 8.60 | 7.30 | 9.30 |
| 7.55 | 11.00 | 7.40 | 8.95 | 7.40 | 9.55 |
| | | 7.50 | 9.60 | 7.50 | 9.85 |
| | | 7.60 | 10.10 | 7.60 | 10.12 |
| | | 7.80 | 10.45 | 7.80 | 10.50 |
| | | 8.00 | 11.00 | 8.00 | 10.95 |

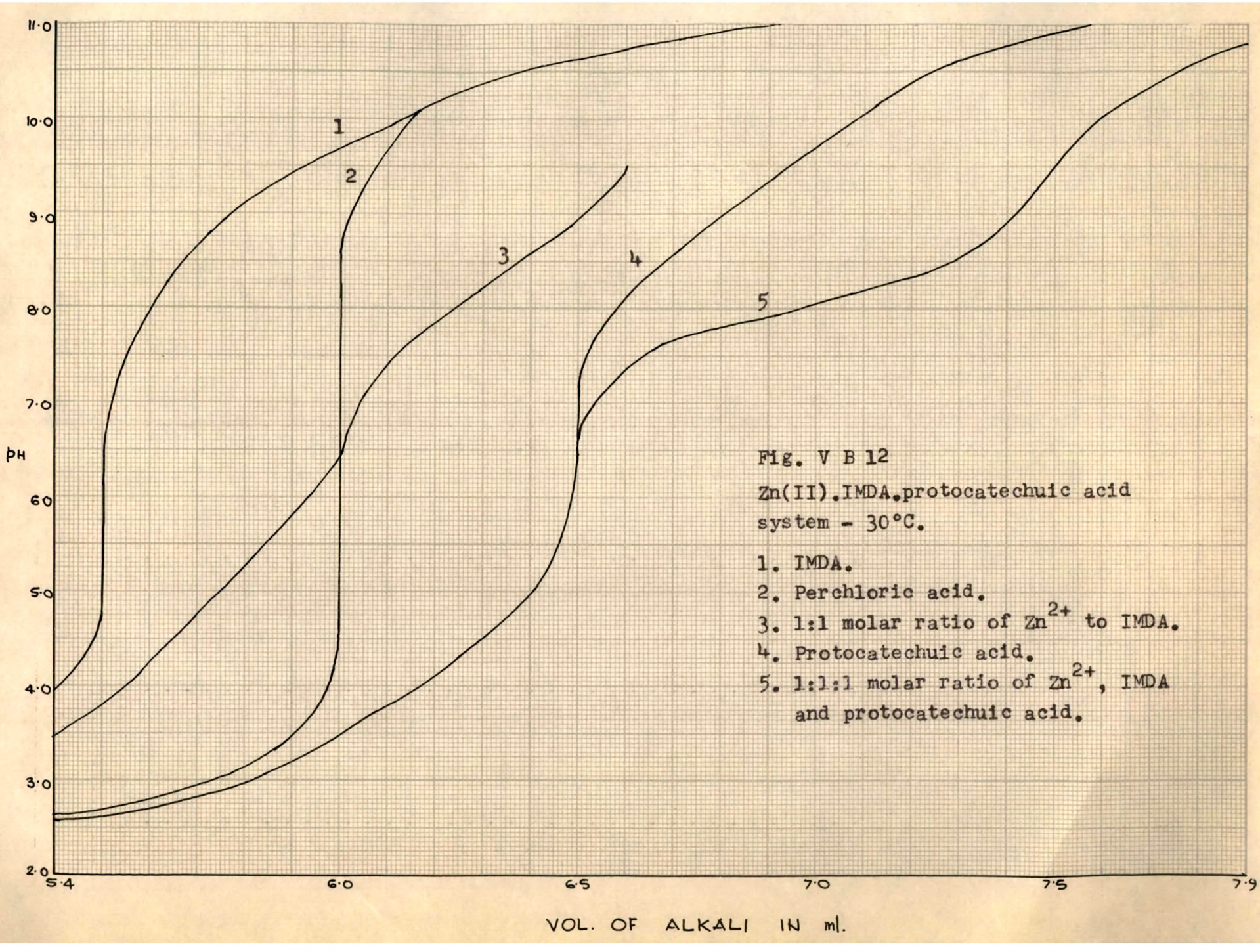



Fig. V B 12

Zn(II).IMDA.protocatechuic acid system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to IMDA.
4. Protocatechuic acid.
5. 1:1:1 molar ratio of $Zn^{2+}$, IMDA and protocatechuic acid.

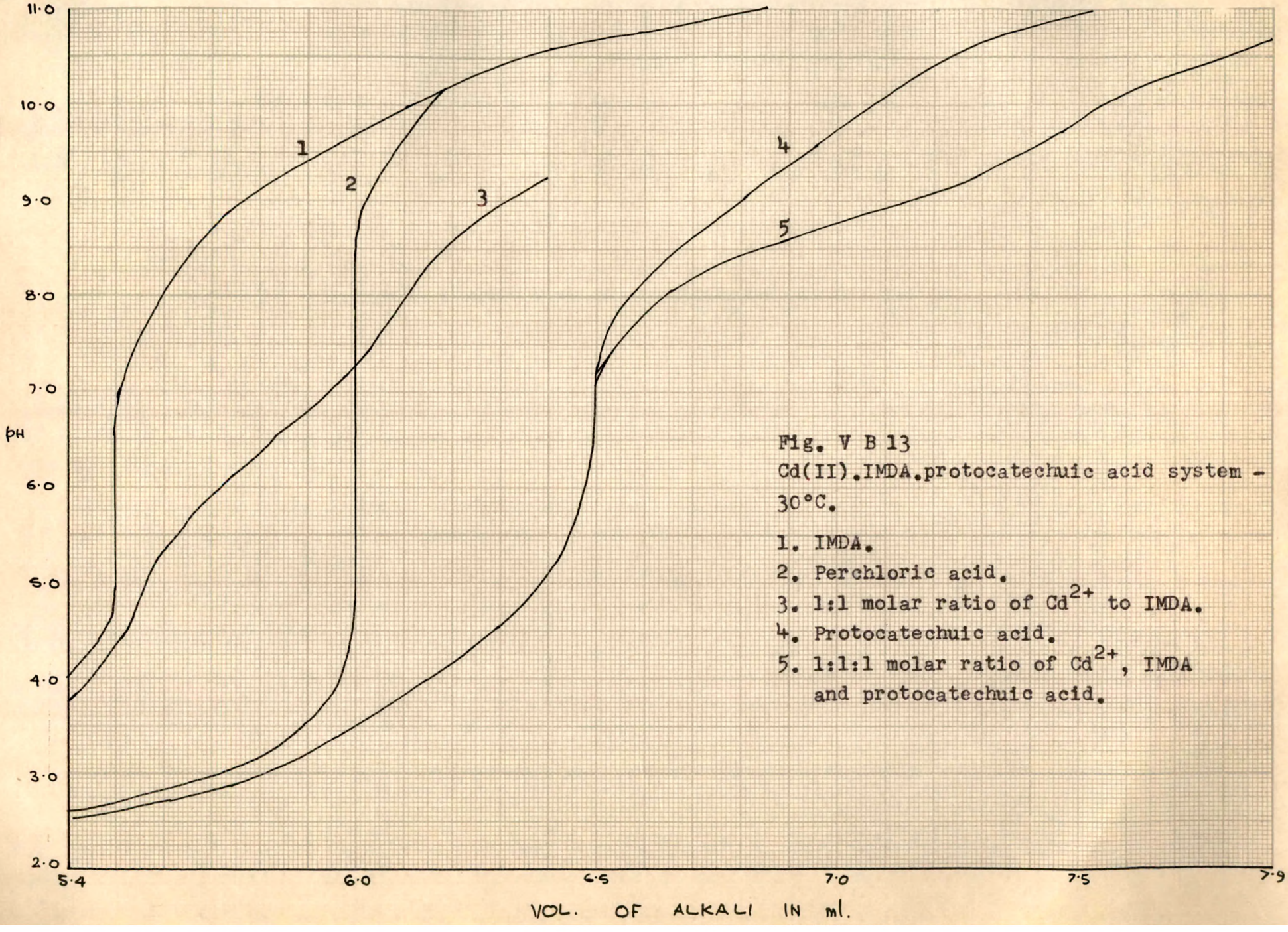



Fig. V B 13
Cd(II).IMDA.protocatechuic acid system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to IMDA.
4. Protocatechuic acid.
5. 1:1:1 molar ratio of $Cd^{2+}$, IMDA and protocatechuic acid.

## Table VB 4.4

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{IMDA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *2,3-Dihydroxy-naphthalene | | Zn.IMDA.2,3-Dihydroxy-naphthalene | | Cd.IMDA.2,3-Dihydroxy-naphthalene | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.50 | 0.00 | 1.55 | 0.00 | 1.55 |
| 1.00 | 1.60 | 1.00 | 1.70 | 1.00 | 1.70 |
| 1.50 | 1.65 | 2.00 | 1.80 | 2.00 | 1.80 |
| 2.00 | 1.70 | 3.00 | 1.90 | 3.00 | 2.00 |
| 2.50 | 1.80 | 4.00 | 2.20 | 4.00 | 2.20 |
| 3.00 | 1.85 | 5.00 | 2.80 | 5.00 | 2.70 |
| 3.50 | 1.90 | 5.50 | 3.75 | 5.55 | 4.20 |
| 4.00 | 2.00 | 5.60 | 4.28 | 5.60 | 5.30 |
| 4.50 | 2.10 | 5.70 | 4.75 | 5.70 | 5.90 |
| 5.00 | 2.30 | 5.80 | 5.25 | 5.80 | 6.30 |
| 5.50 | 2.70 | 5.90 | 5.75 | 5.90 | 6.68 |
| 5.60 | 2.80 | 5.95 | 6.05 | 5.95 | 6.80 |
| 5.70 | 2.95 | 5.97 | 6.20 | 5.98 | 6.90 |
| 5.80 | 3.15 | 6.00 | 6.40 | 6.00 | 6.95 |
| 5.90 | 3.45 | 6.02 | 6.50 | 6.02 | 7.04 |
| 5.94 | 3.65 | 6.05 | 6.65 | 6.05 | 7.15 |
| 5.98 | 4.00 | 6.10 | 6.90 | 6.10 | 7.32 |
| 6.00 | 6.60 | 6.15 | 7.15 | 6.15 | 7.50 |
| 6.02 | 6.90 | 6.20 | 7.30 | 6.20 | 7.65 |
| 6.05 | 7.20 | 6.30 | 7.45 | 6.25 | 7.80 |
| 6.10 | 7.55 | 6.40 | 7.57 | 6.30 | 7.90 |
| 6.15 | 7.85 | 6.50 | 7.70 | 6.40 | 8.07 |
| 6.20 | 8.10 | 6.60 | 7.85 | 6.50 | 8.24 |
| 6.30 | 8.50 | 6.70 | 7.98 | 6.60 | 8.38 |
| 6.40 | 8.90 | 6.80 | 8.20 | 6.68 | 8.50 |
| 6.50 | 9.40 | 6.90 | 8.58 | | (ppt.) |
| 6.60 | 9.95 | 7.00 | 9.15 | | |
| 6.70 | 10.30 | 7.10 | 9.60 | | |
| 6.80 | 10.55 | 7.20 | 9.90 | | |
| 6.90 | 10.75 | 7.30 | 10.20 | | |
| 7.00 | 10.92 | 7.40 | 10.60 | | |
| | | 7.45 | 11.00 | | |

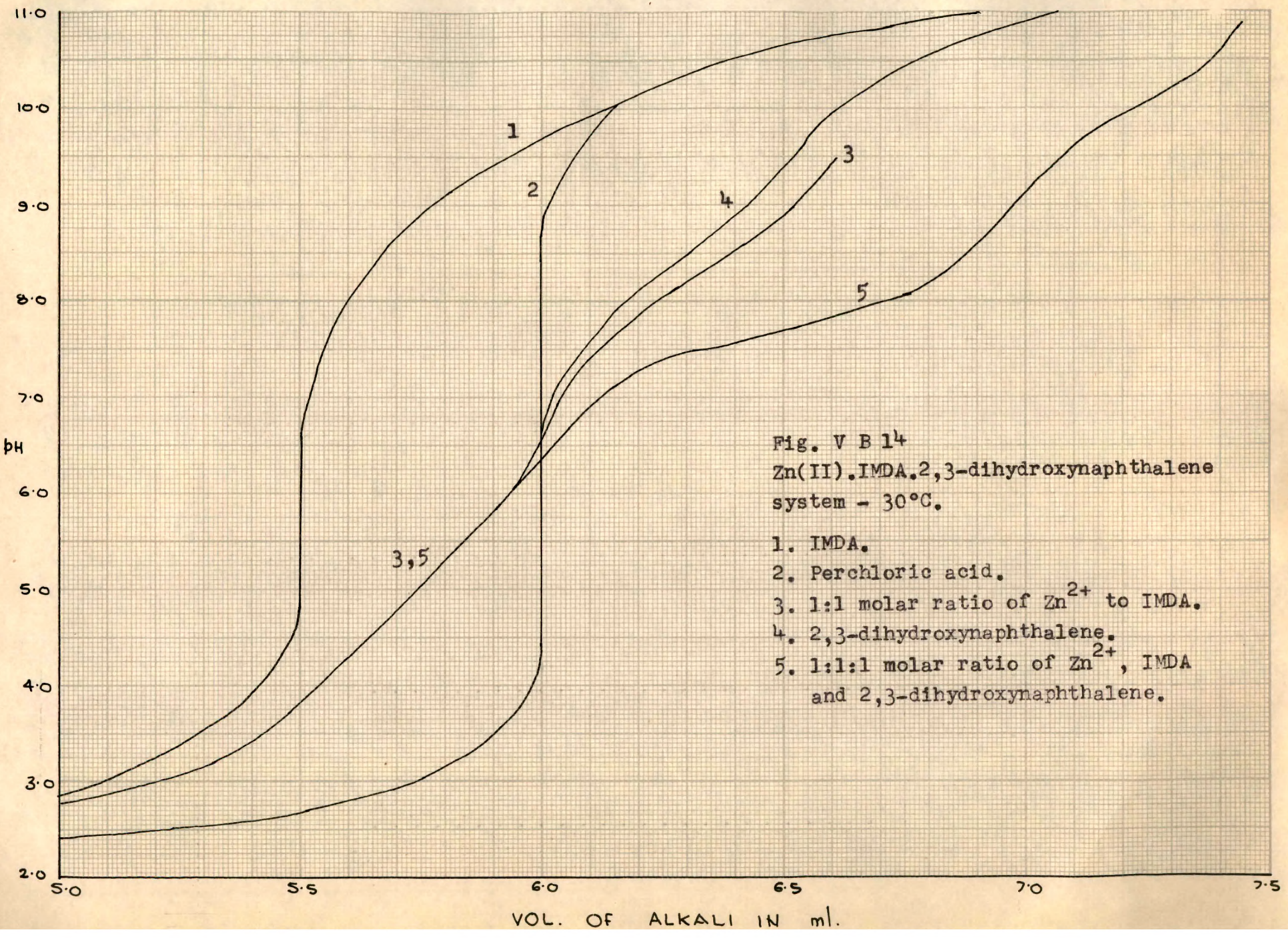



Fig. V B 14
Zn(II).IMDA.2,3-dihydroxynaphthalene system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to IMDA.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Zn^{2+}$, IMDA and 2,3-dihydroxynaphthalene.

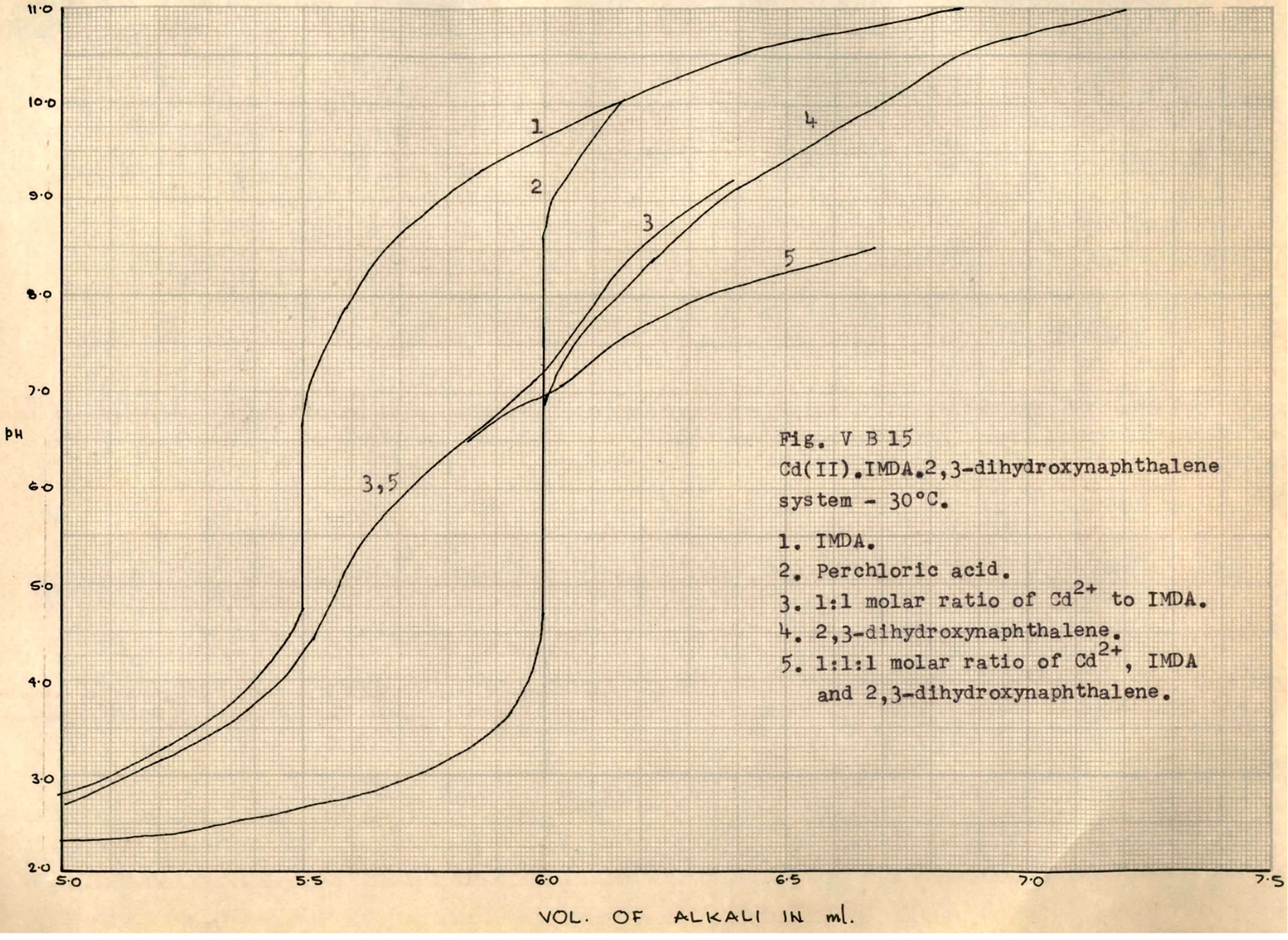



Fig. V B 15
Cd(II).IMDA.2,3-dihydroxynaphthalene system - 30°C.

1. IMDA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to IMDA.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Cd^{2+}$, IMDA and 2,3-dihydroxynaphthalene.

## Table VB 5.1b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.80 | $1.9^4_4$ | 6.06 | 6.19 | 0.13 | $0.13_3$ | $0.81_4$ | $7.63_3$ | $6.81_9$ |
| 7.90 | $1.93_6$ | 6.07 | 6.26 | 0.19 | $0.19_6$ | $0.61_3$ | $7.47_1$ | $6.85_8$ |
| 8.00 | $1.92_4$ | 6.08 | 6.33 | 0.25 | $0.25_9$ | $0.45_6$ | $7.32_3$ | $6.86_7$ |
| 8.10 | $1.90_8$ | 6.09 | 6.41 | 0.32 | $0.33_4$ | $0.29_9$ | $7.14_5$ | $6.84_6$ |
| 8.20 | $1.88_8$ | 6.10 | 6.50 | 0.40 | $0.41_8$ | $0.14_3$ | $7.03_5$ | $6.89_2$ |
| 8.30 | $1.86_8$ | 6.12 | 6.56 | 0.44 | $0.47_0$ | $0.05_2$ | $6.89_2$ | $6.84_0$ |
| 8.40 | $1.8^4_8$ | 6.14 | 6.64 | 0.50 | $0.53_9$ | $\bar{1}.93_2$ | $6.81_9$ | $6.88_7$ |
| 8.50 | $1.81_6$ | 6.15 | 6.70 | 0.55 | $0.60_4$ | $\bar{1}.81_6$ | $6.62_6$ | $6.81_0$ |
| 8.60 | $1.79_2$ | 6.18 | 6.78 | 0.60 | $0.66_7$ | $\bar{1}.69_8$ | $6.55_1$ | $6.85_3$ |

$\log K_{MAL} = 6.84 \pm 0.05$

## Table VB 5.2b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.70 | $1.90_4$ | 6.10 | 6.30 | 0.20 | $0.20_9$ | $0.57_8$ | $6.80_1$ | $6.22_3$ |
| 7.80 | $1.88_0$ | 6.11 | 6.36 | 0.25 | $0.28_9$ | $0.39_1$ | $6.68_0$ | $6.28_9$ |
| 7.90 | $1.85_6$ | 6.13 | 6.47 | 0.34 | $0.36_5$ | $0.24_0$ | $6.53_7$ | $6.29_7$ |
| 8.00 | $1.8^4_0$ | 6.15 | 6.55 | 0.40 | $0.4^4_4$ | $0.10_5$ | $6.41_1$ | - |
| 8.10 | $1.80_0$ | 6.16 | 6.61 | 0.45 | $0.49_8$ | $0.00_3$ | $6.28_6$ | $6.28_3$ |
| 8.20 | $1.78_4$ | 6.18 | 6.68 | 0.50 | $0.55_8$ | $\bar{1}.89_8$ | $6.12_3$ | $6.22_5$ |
| 8.30 | $1.75_2$ | 6.20 | 6.73 | 0.53 | $0.60_2$ | $\bar{1}.82_0$ | $6.02_9$ | $6.20_9$ |
| 8.40 | $1.71_2$ | 6.22 | 6.79 | 0.57 | $0.66_3$ | $\bar{1}.70_6$ | $5.91_8$ | $6.21_2$ |

$\log K_{MAL} = 6.25 \pm 0.04$

## Table VB 5.3b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.60 | $1.94_9$ | 6.52 | 6.65 | 0.13 | $0.13_2$ | $0.81_7$ | $8.63_7$ | - |
| 7.70 | $1.93_5$ | 6.53 | 6.71 | 0.18 | $0.18_4$ | $0.64_6$ | $8.47_2$ | $7.82_6$ |
| 7.80 | $1.93_5$ | 6.54 | 6.80 | 0.26 | $0.26_6$ | $0.44_0$ | $8.32_6$ | $7.88_6$ |
| 7.90 | $1.92_0$ | 6.56 | 6.89 | 0.33 | $0.34_0$ | $0.28_8$ | $8.18_3$ | - |
| 8.00 | $1.88_0$ | 6.58 | 6.96 | 0.38 | $0.40_0$ | $0.17_6$ | $8.03_6$ | $7.84_0$ |
| 8.10 | $1.84_0$ | 6.60 | 7.02 | 0.42 | $0.45_1$ | $0.08_5$ | $7.88_9$ | $7.80_4$ |
| 8.20 | $1.80_0$ | 6.61 | 7.09 | 0.48 | $0.52_7$ | $\bar{1}.95_3$ | $7.76_1$ | $7.80_8$ |
| 8.30 | $1.76_0$ | 6.63 | 7.81 | 0.55 | $0.61_8$ | $\bar{1}.79_1$ | $7.67_9$ | $7.87_8$ |

$\log K_{MAL} = 7.83 \pm 0.04$

## Table VB 5.4b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Zn.IMDA.2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.30 | $1.93_2$ | 6.06 | 6.20 | 0.14 | $0.14_4$ | $0.77_4$ | $9.21_3$ | $8.43_9$ |
| 7.40 | $1.91_2$ | 6.07 | 6.26 | 0.19 | $0.19_8$ | $0.60_7$ | $9.06_4$ | $8.45_7$ |
| 7.50 | $1.89_2$ | 6.09 | 6.35 | 0.26 | $0.27_4$ | $0.42_3$ | $8.91_8$ | $8.49_5$ |
| 7.60 | $1.87_2$ | 6.11 | 6.43 | 0.32 | $0.34_1$ | $0.28_6$ | $8.77_2$ | $8.48_6$ |
| 7.70 | $1.85_2$ | 6.12 | 6.49 | 0.37 | $0.39_8$ | $0.17_9$ | $8.62_6$ | $8.44_7$ |
| 7.80 | $1.82_4$ | 6.14 | 6.56 | 0.42 | $0.45_9$ | $0.07_1$ | $8.49_1$ | $8.42_0$ |
| 7.90 | $1.79_2$ | 6.16 | 6.63 | 0.47 | $0.52_3$ | $\bar{1}.96_0$ | $8.36_6$ | $8.40_6$ |
| 8.00 | $1.77_3$ | 6.18 | 6.71 | 0.53 | $0.59_5$ | $\bar{1}.83_3$ | $8.26_3$ | $8.43_0$ |
| 8.10 | $1.71_3$ | 6.20 | 6.76 | 0.56 | $0.65_1$ | $\bar{1}.72_9$ | $8.15_8$ | $8.42_9$ |

$\log K_{MAL} = 8.44 \pm 0.05$

Fig. V B 17
Zn(II).IMDA.pyrogallol system - 30°C.

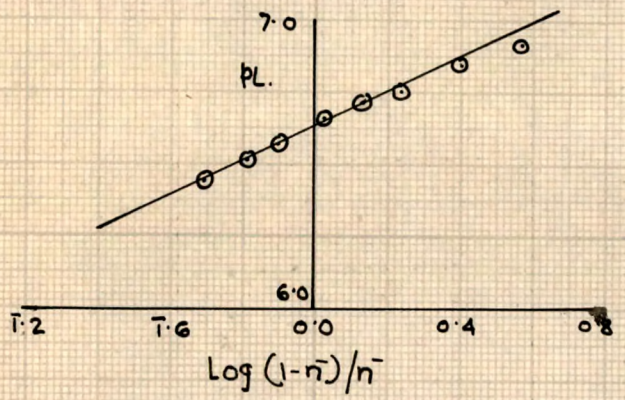



Fig. V B 16
Zn(II).IMDA.catechol system - 30°C.

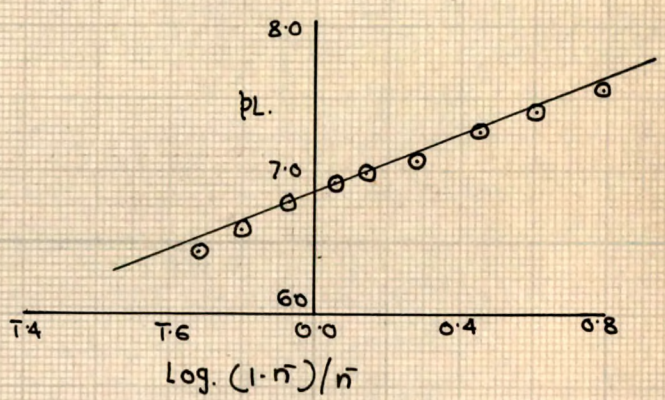



Fig. V B 18
Zn(II).IMDA.protocatechuic acid system - 30°C.

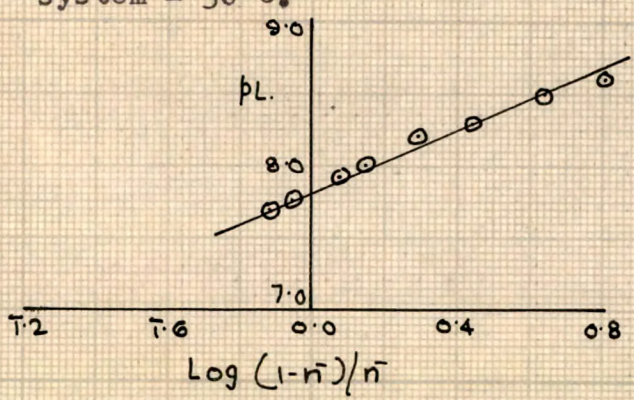
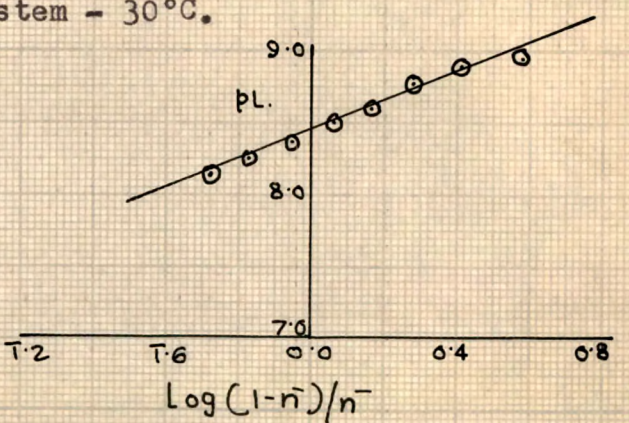



Fig. V B 19
Zn(II).IMDA.2,3-dihydroxynaphthalene system - 30°C.



## Table VB 5.1c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.60 | $1.79_2$ | 6.18 | 6.33 | 0.15 | $0.16_6$ | $0.70_1$ | $6.15_0$ | $5.44_9$ |
| 8.70 | $1.74_4$ | 6.20 | 6.40 | 0.20 | $0.22_8$ | $0.52_9$ | $6.00_9$ | $5.48_0$ |
| 8.80 | $1.71_9$ | 6.22 | 6.46 | 0.24 | $0.27_8$ | $0.41_4$ | $5.87_0$ | $5.45_6$ |
| 8.90 | $1.67_2$ | 6.25 | 6.53 | 0.28 | $0.33_3$ | $0.30_1$ | $5.74_0$ | $5.43_9$ |
| 9.00 | $1.64_0$ | 6.27 | 6.59 | 0.32 | $0.38_8$ | $0.19_8$ | $5.61_9$ | $5.42_1$ |
| 9.10 | $1.56_0$ | 6.31 | 6.66 | 0.35 | $0.44_6$ | $\underline{0}.09_4$ | $5.50_6$ | $5.41_2$ |
| 9.20 | $1.48_0$ | 6.34 | 6.73 | 0.39 | $0.52_3$ | $\underline{1}.98_0$ | $5.42_9$ | $5.43_9$ |
| 9.30 | $1.44_9$ | 6.37 | 6.79 | 0.42 | $0.57_5$ | $\underline{1}.86_8$ | $5.33_5$ | $5.46_7$ |

$\log K_{MAL} = 5.44 \pm 0.04$

## Table VB 5.3c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 8.30 | $1.76_0$ | 6.63 | 6.72 | 0.09 | $0.10_1$ | $0.94_9$ | $7.31_0$ | $6.36_1$ |
| 8.40 | $1.72_0$ | 6.65 | 6.77 | 0.12 | $0.13_7$ | $0.79_9$ | $7.15_2$ | $6.35_3$ |
| 8.50 | $1.68_0$ | 6.68 | 6.83 | 0.15 | $0.17_6$ | $0.67_0$ | $7.00_2$ | $6.33_2$ |
| 8.60 | $1.60_0$ | 6.70 | 6.88 | 0.18 | $0.22_2$ | $0.54_4$ | $6.86_1$ | $6.31_7$ |
| 8.70 | $1.56_0$ | 6.72 | 6.94 | 0.22 | $0.27_8$ | $0.41_4$ | $6.73_4$ | $6.32_0$ |
| 8.80 | $1.52_0$ | 6.75 | 7.01 | 0.26 | $0.33_7$ | $0.29_3$ | $6.61_5$ | $6.32_2$ |
| 8.90 | $1.48_0$ | 6.78 | 7.08 | 0.30 | $0.39_9$ | $0.17_7$ | $6.51_0$ | $6.33_3$ |
| 9.00 | $1.40_0$ | 6.80 | 7.14 | 0.34 | $0.47_8$ | $\underline{0}.03_8$ | $6.42_8$ | $6.39_0$ |
| 9.10 | $1.36_8$ | 6.82 | 7.22 | 0.40 | $0.57_6$ | $\underline{1}.86_7$ | $6.36_5$ | - |

$\log K_{MAL} = 6.34 \pm 0.05$

## Table VB 5.4c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cd.IMDA.2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 7.80 | $1.82_4$ | 6.14 | 6.24 | 0.10 | $0.10_9$ | $0.91_2$ | $8.27_1$ | $7.35_9$ |
| 7.90 | $1.79_2$ | 6.16 | 6.30 | 0.14 | $0.15_5$ | $0.73_6$ | $8.11_5$ | $7.37_9$ |
| 8.00 | $1.77_3$ | 6.18 | 6.36 | 0.18 | $0.20_2$ | $0.59_6$ | $7.96_6$ | $7.37_0$ |
| 8.10 | $1.71_3$ | 6.20 | 6.41 | 0.21 | $0.24_4$ | $0.49_1$ | $7.81_9$ | $7.32_8$ |
| 8.20 | $1.67_3$ | 6.22 | 6.46 | 0.25 | $0.29_7$ | $0.37_4$ | $7.68_6$ | $7.31_2$ |
| 8.30 | $1.63_3$ | 6.25 | 6.55 | 0.30 | $0.36_5$ | $0.24_0$ | $7.57_1$ | $7.33_1$ |
| 8.40 | $1.55_3$ | 6.27 | 6.61 | 0.34 | $0.43_5$ | $0.11_3$ | $7.46_7$ | $7.35_4$ |
| 8.50 | $1.51_4$ | 6.30 | 6.68 | 0.38 | $0.49_9$ | $0.00_1$ | $7.37_1$ | $7.37_0$ |

$\log K_{MAL} = 7.3^4 \pm 0.03$

Fig. V B 20
Cd(II).IMDA.catechol system - 30°C.

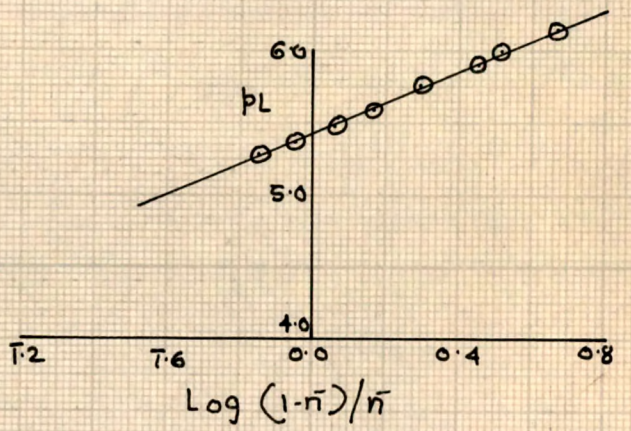



Fig. V B 21
Cd(II).IMDA.protocatechuic acid
system - 30°C.

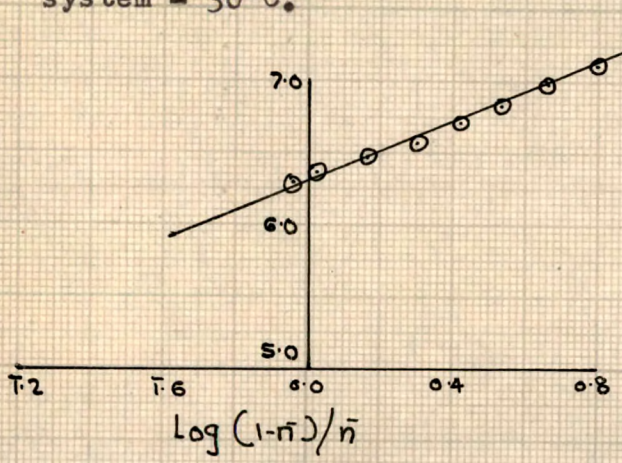
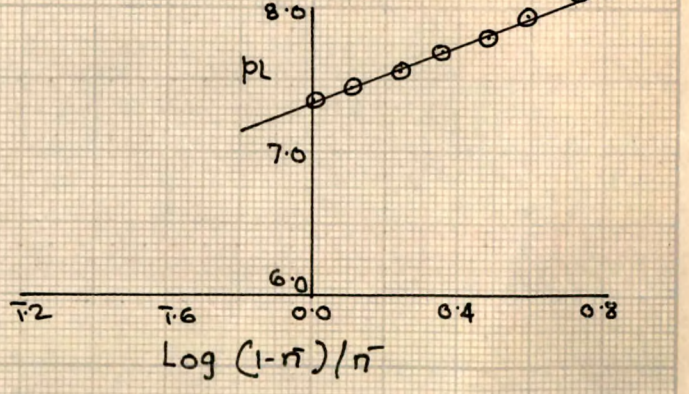



Fig. V B 22
Cd(II).IMDA.2,3-dihydroxy-
naphthalene system - 30°C.



## Table VB 6.0

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{EDTA}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *Perchloric acid | | EDTA | | Zn.EDTA | | Cd.EDTA | |
|---|---|---|---|---|---|---|---|
| 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 | 1.45 | 0.00 | 1.45 | 0.00 | 1.45 | 0.00 | 1.45 |
| 1.00 | 1.50 | 1.00 | 1.60 | 1.00 | 1.50 | 1.00 | 1.50 |
| 2.00 | 1.60 | 2.00 | 1.70 | 2.00 | 1.60 | 2.00 | 1.60 |
| 3.00 | 1.70 | 2.50 | 1.80 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 1.90 | 3.00 | 1.90 | 4.00 | 2.10 | 4.00 | 2.10 |
| 5.00 | 2.15 | 3.50 | 2.05 | 5.00 | 2.50 | 5.00 | 2.45 |
| 5.25 | 2.25 | 4.00 | 2.30 | 5.25 | 2.60 | 5.25 | 2.60 |
| 5.50 | 2.36 | 4.20 | 2.60 | 5.50 | 2.82 | 5.50 | 2.75 |
| 5.60 | 2.50 | 4.40 | 2.90 | 5.60 | 2.95 | 5.60 | 2.88 |
| 5.65 | 2.62 | 4.60 | 3.30 | 5.70 | 3.15 | 5.70 | 3.05 |
| 5.70 | 2.70 | 4.80 | 3.70 | 5.75 | 3.25 | 5.75 | 3.15 |
| 5.75 | 2.80 | 5.00 | 4.10 | 5.80 | 3.40 | 5.80 | 3.30 |
| 5.80 | 2.92 | 5.10 | 4.55 | 5.85 | 3.52 | 5.85 | 3.45 |
| 5.85 | 3.05 | 5.15 | 4.80 | 5.90 | 3.65 | 5.90 | 3.62 |
| 5.90 | 3.25 | 5.20 | 5.05 | 5.96 | 3.90 | 5.93 | 3.75 |
| 5.93 | 3.40 | 5.25 | 5.30 | 5.98 | 4.00 | 5.96 | 3.95 |
| 5.96 | 3.60 | 5.30 | 5.56 | 6.00 | 7.50 | 5.98 | 4.00 |
| 5.98 | 3.80 | 5.35 | 5.88 | 6.03 | 8.38 | 6.00 | 7.65 |
| 6.00 | 7.25 | 5.40 | 6.25 | 6.06 | 8.75 | 6.03 | 8.05 |
| 6.02 | 9.00 | 5.45 | 6.60 | 6.10 | 9.10 | 6.06 | 8.40 |
| 6.04 | 9.25 | 5.50 | 7.05 | 6.14 | 9.40 | 6.10 | 8.75 |
| 6.06 | 9.40 | 5.54 | 7.50 | 6.18 | 9.75 | 6.14 | 9.10 |
| 6.08 | 9.55 | 5.58 | 7.90 | 6.22 | 9.95 | 6.22 | 9.60 |
| 6.12 | 9.80 | 5.62 | 8.30 | 6.30 | 10.25 | 6.30 | 10.00 |
| 6.20 | 10.20 | 5.66 | 8.55 | 6.40 | 10.50 | 6.40 | 10.30 |
| 6.30 | 10.50 | 5.70 | 8.78 | 6.50 | 10.65 | 6.50 | 10.50 |
| 6.40 | 10.85 | 5.80 | 9.20 | 6.60 | 10.75 | 6.60 | 10.70 |
| 6.45 | 11.00 | 5.90 | 9.55 | 6.80 | 10.85 | 6.80 | 10.94 |
| | | 6.00 | 9.88 | 6.90 | 10.92 | | |
| | | 6.10 | 10.18 | 6.96 | 11.00 | | |
| | | 6.20 | 10.42 | | | | |
| | | 6.30 | 10.68 | | | | |
| | | 6.40 | 10.92 | | | | |

## Table VB 6.1

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{EDTA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *Catechol | | Zn.EDTA.Catechol | | Cd.EDTA.Catechol | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.45 | 0.00 | 1.45 | 0.00 | 1.45 |
| 1.00 | 1.50 | 1.00 | 1.50 | 1.00 | 1.50 |
| 2.00 | 1.60 | 2.00 | 1.60 | 2.00 | 1.60 |
| 3.00 | 1.70 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 1.90 | 4.00 | 2.10 | 4.00 | 2.10 |
| 5.00 | 2.15 | 5.00 | 2.50 | 5.00 | 2.45 |
| 5.50 | 2.36 | 5.50 | 2.82 | 5.50 | 2.75 |
| 5.60 | 2.50 | 5.60 | 2.95 | 5.60 | 2.88 |
| 5.70 | 2.70 | 5.70 | 3.15 | 5.70 | 3.05 |
| 5.80 | 2.92 | 5.80 | 3.40 | 5.80 | 3.30 |
| 5.85 | 3.05 | 5.85 | 3.52 | 5.85 | 3.45 |
| 5.90 | 3.25 | 5.90 | 3.65 | 5.90 | 3.62 |
| 5.93 | 3.40 | 5.93 | 3.75 | 5.93 | 3.75 |
| 5.96 | 3.60 | 5.96 | 3.90 | 5.96 | 3.95 |
| 5.98 | 3.80 | 5.98 | 4.00 | 5.98 | 4.00 |
| 6.00 | 7.25 | 6.00 | 6.80 | 6.00 | 6.85 |
| 6.04 | 7.65 | 6.04 | 7.20 | 6.04 | 7.25 |
| 6.08 | 7.90 | 6.08 | 7.50 | 6.08 | 7.52 |
| 6.12 | 8.10 | 6.12 | 7.80 | 6.12 | 7.85 |
| 6.16 | 8.30 | 6.16 | 7.90 | 6.16 | 8.08 |
| 6.20 | 8.48 | 6.20 | 8.08 | 6.20 | 8.26 |
| 6.25 | 8.75 | 6.25 | 8.32 | 6.25 | 8.50 |
| 6.30 | 9.00 | 6.30 | 8.55 | 6.30 | 8.70 |
| 6.40 | 9.40 | 6.40 | 8.95 | 6.40 | 9.10 |
| 6.50 | 9.80 | 6.50 | 9.32 | 6.50 | 9.50 |
| 6.60 | 10.05 | 6.60 | 9.68 | 6.60 | 9.80 |
| 6.70 | 10.30 | 6.70 | 9.95 | 6.70 | 10.02 |
| 6.80 | 10.50 | 6.80 | 10.15 | 6.80 | 10.22 |
| 6.90 | 10.70 | 6.90 | 10.35 | 6.90 | 10.40 |
| 7.00 | 10.90 | 7.00 | 10.50 | 7.00 | 10.50 |
| 7.10 | 11.00 | 7.10 | 10.68 | 7.10 | 10.68 |
| | | 7.20 | 10.82 | 7.20 | 10.88 |
| | | 7.30 | 10.95 | 7.30 | 11.08 |

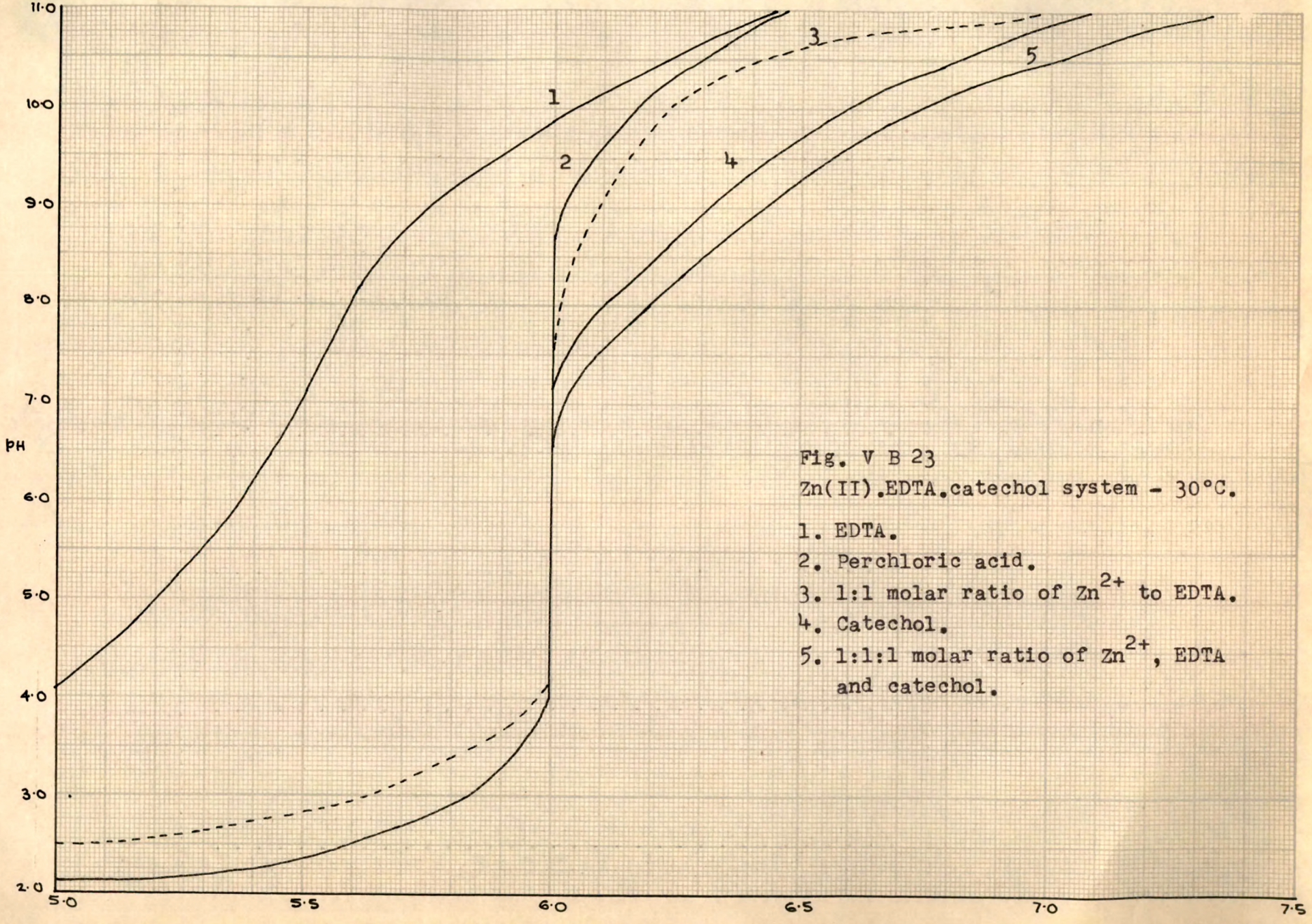



Fig. V B 23
Zn(II).EDTA.catechol system - 30°C.

1. EDTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to EDTA.
4. Catechol.
5. 1:1:1 molar ratio of $Zn^{2+}$, EDTA and catechol.

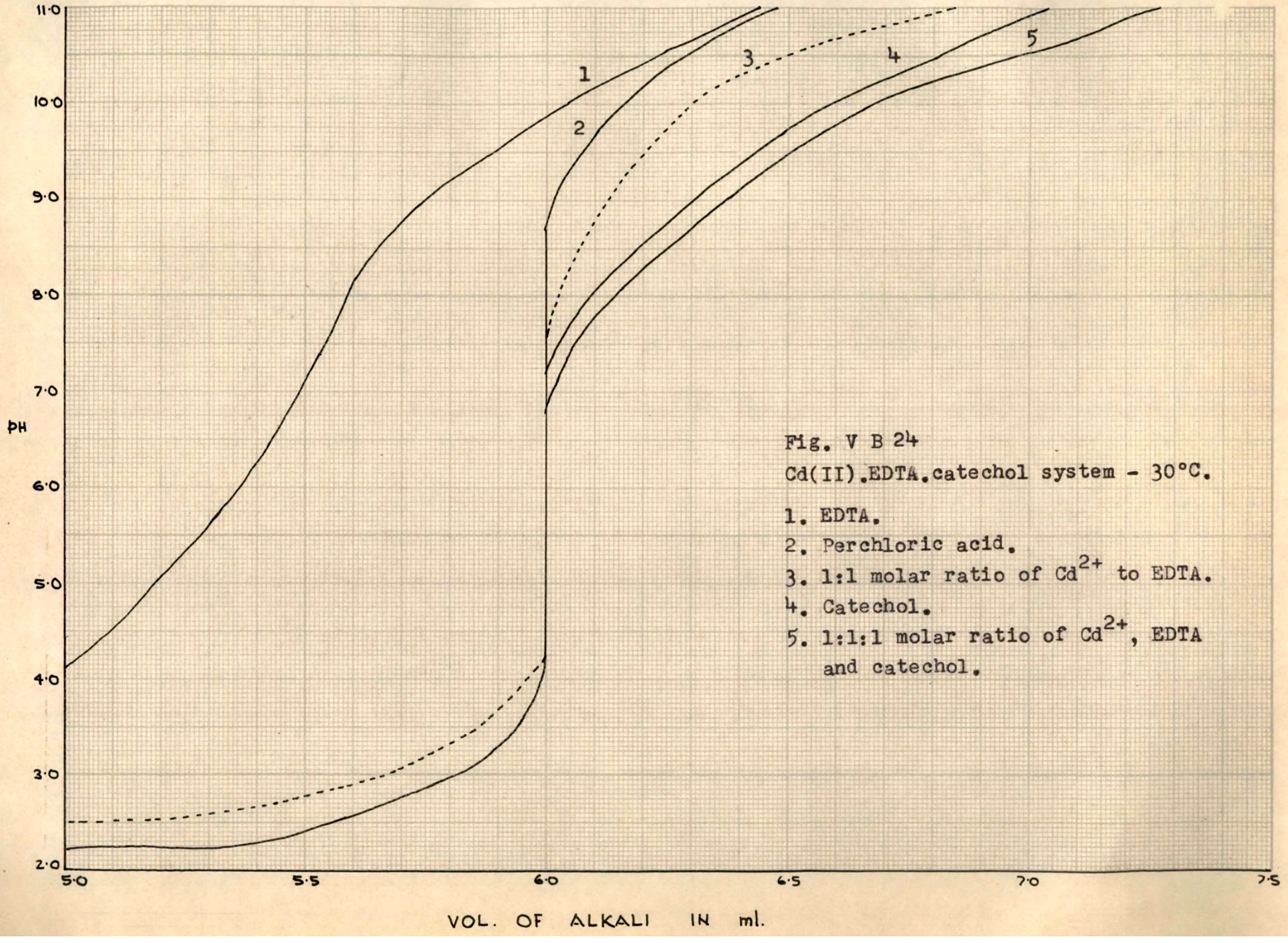



Fig. V B 24

Cd(II).EDTA.catechol system - 30°C.

1. EDTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to EDTA.
4. Catechol.
5. 1:1:1 molar ratio of $Cd^{2+}$, EDTA and catechol.

## Table VB 6.3

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{EDTA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *Protocatechuic acid | | Zn.EDTA.Protocatechuic acid | | Cd.EDTA.Protocatechuic acid | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.45 | 0.00 | 1.45 | 0.00 | 1.45 |
| 1.00 | 1.50 | 1.00 | 1.50 | 1.00 | 1.50 |
| 2.00 | 1.70 | 2.00 | 1.70 | 2.00 | 1.70 |
| 3.00 | 1.75 | 3.00 | 1.75 | 3.00 | 1.75 |
| 4.00 | 1.85 | 4.00 | 1.85 | 4.00 | 1.85 |
| 5.00 | 2.15 | 5.00 | 2.15 | 5.00 | 2.15 |
| 5.50 | 2.36 | 5.50 | 2.36 | 5.50 | 2.36 |
| 5.60 | 2.50 | 5.60 | 2.50 | 5.60 | 2.50 |
| 5.70 | 2.70 | 5.70 | 2.70 | 5.70 | 2.70 |
| 5.80 | 2.92 | 5.80 | 2.92 | 5.80 | 2.92 |
| 5.90 | 3.25 | 5.90 | 3.25 | 5.90 | 3.25 |
| 5.95 | 3.55 | 5.95 | 3.55 | 5.95 | 3.55 |
| 6.00 | 3.85 | 6.00 | 3.85 | 6.00 | 3.85 |
| 6.10 | 4.25 | 6.10 | 4.15 | 6.10 | 4.25 |
| 6.15 | 4.50 | 6.15 | 4.30 | 6.15 | 4.40 |
| 6.20 | 4.75 | 6.20 | 4.50 | 6.20 | 4.62 |
| 6.23 | 5.00 | 6.23 | 4.65 | 6.23 | 4.80 |
| 6.26 | 5.35 | 6.26 | 4.80 | 6.26 | 5.00 |
| 6.29 | 5.85 | 6.29 | 4.95 | 6.29 | 5.25 |
| 6.33 | 6.70 | 6.33 | 5.35 | 6.33 | 5.75 |
| 6.36 | 7.25 | 6.36 | 5.90 | 6.36 | 6.25 |
| 6.39 | 7.60 | 6.39 | 6.40 | 6.39 | 6.80 |
| 6.42 | 7.85 | 6.42 | 6.95 | 6.42 | 7.30 |
| 6.45 | 8.05 | 6.45 | 7.32 | 6.45 | 7.60 |
| 6.50 | 8.32 | 6.50 | 7.80 | 6.50 | 7.95 |
| 6.55 | 8.52 | 6.55 | 8.08 | 6.55 | 8.20 |
| 6.60 | 8.72 | 6.60 | 8.30 | 6.60 | 8.45 |
| 6.70 | 9.10 | 6.70 | 8.75 | 6.70 | 8.80 |
| 6.80 | 9.50 | 6.80 | 9.15 | 6.80 | 9.18 |
| 6.90 | 9.98 | 6.90 | 9.50 | 6.90 | 9.55 |
| 7.00 | 10.35 | 7.00 | 9.80 | 7.00 | 9.92 |
| 7.10 | 10.55 | 7.10 | 10.08 | 7.10 | 10.15 |
| 7.20 | 10.70 | 7.30 | 10.45 | 7.30 | 10.50 |
| 7.30 | 10.80 | 7.50 | 10.70 | 7.50 | 10.70 |
| 7.40 | 10.90 | 7.70 | 10.90 | 7.70 | 10.95 |
| 7.50 | 11.00 | 7.90 | 11.05 | | |

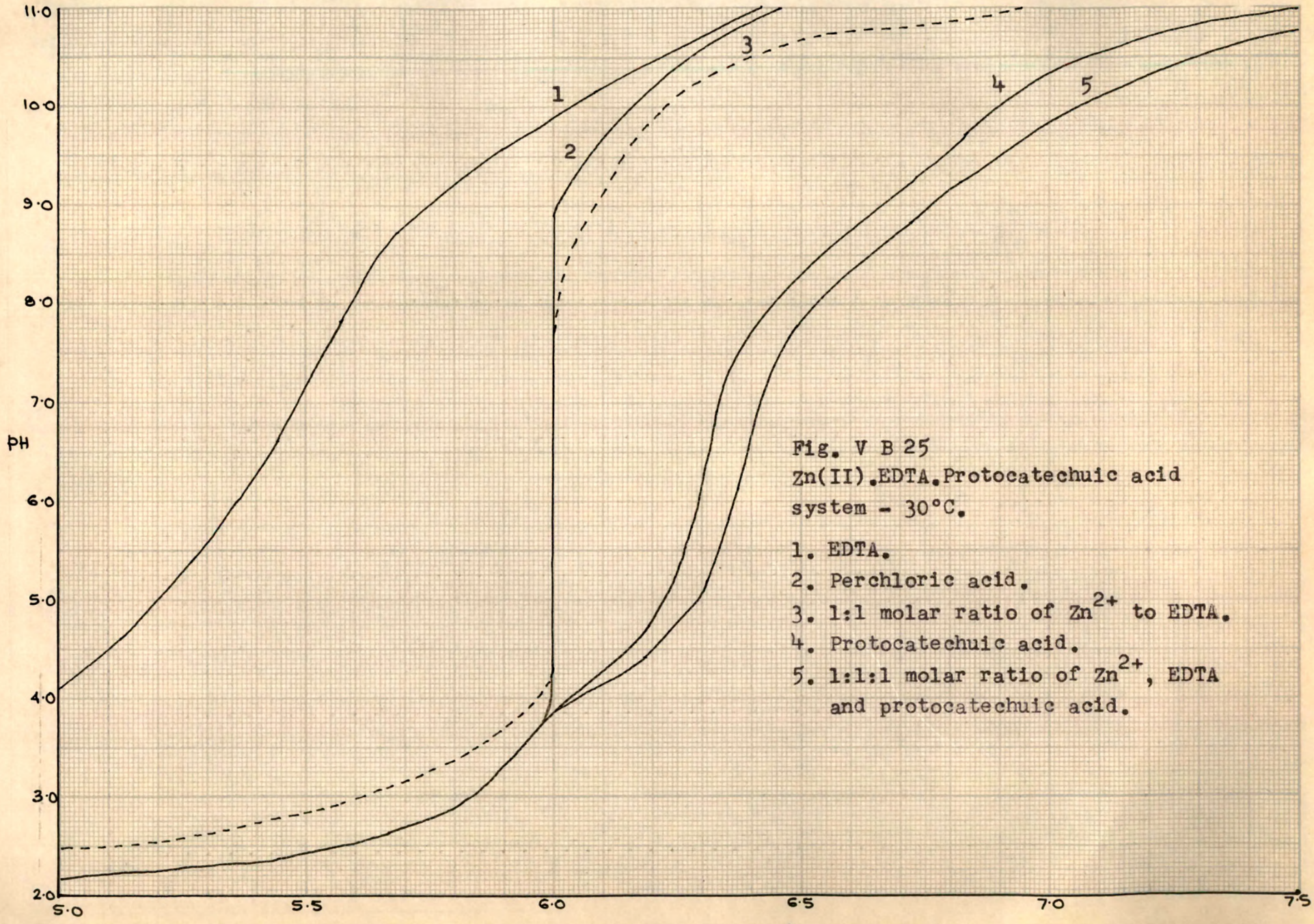



Fig. V B 25
Zn(II).EDTA.Protocatechuic acid system - 30°C.

1. EDTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to EDTA.
4. Protocatechuic acid.
5. 1:1:1 molar ratio of $Zn^{2+}$, EDTA and protocatechuic acid.

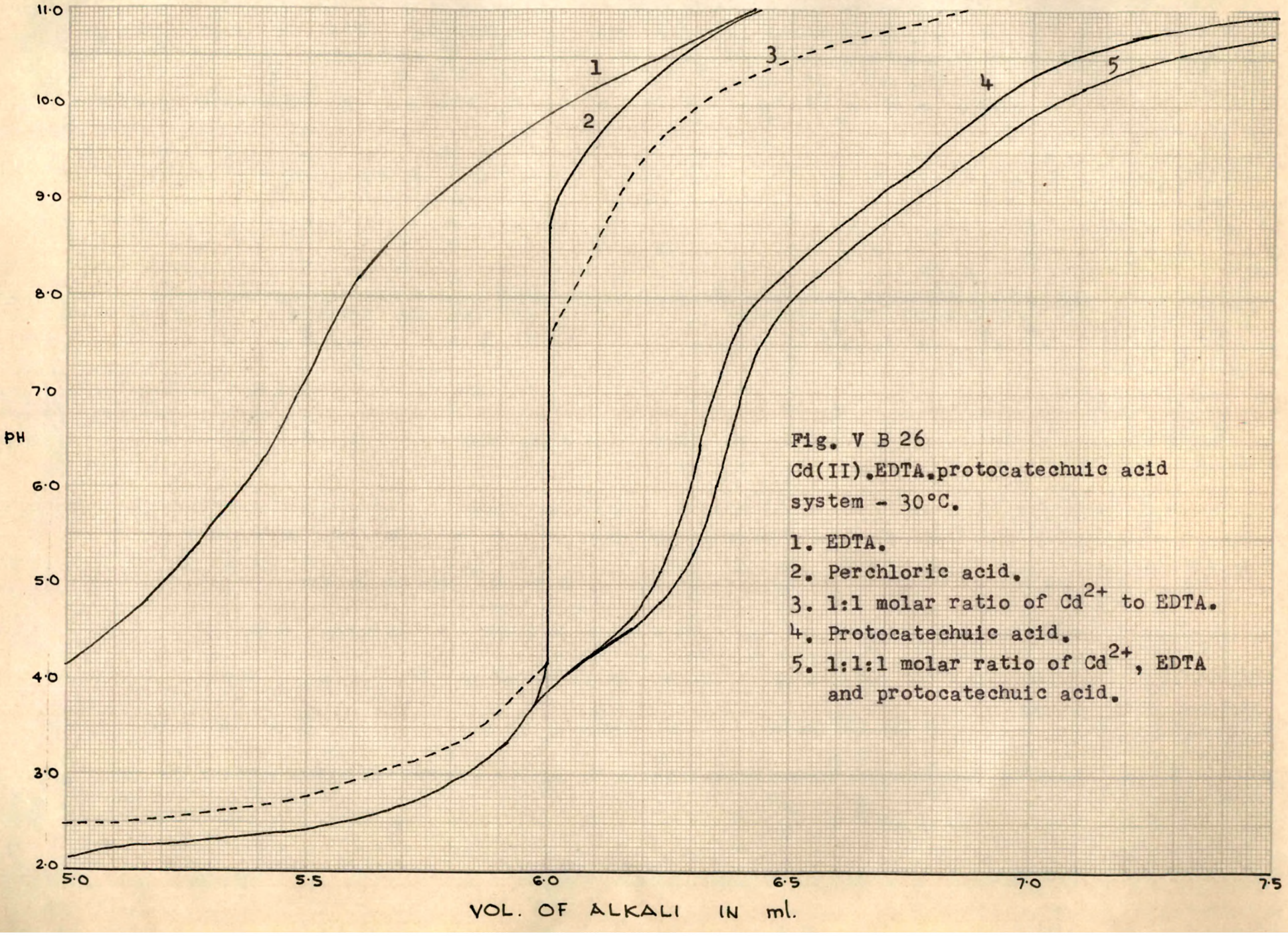



Fig. V B 26
Cd(II).EDTA.protocatechuic acid system - 30°C.

1. EDTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to EDTA.
4. Protocatechuic acid.
5. 1:1:1 molar ratio of $Cd^{2+}$, EDTA and protocatechuic acid.

## Table VB 6.4

N = 0.2M  V° = 50 ml.  $\mu$ = 0.2M  t = 30°C.

E° = 0.02M  $T^{\circ}_{EDTA}$ = 0.002M  $T^{\circ}_{L}$ = 0.002M  $T^{\circ}_{M}$ = 0.002M

*E° = 0.024M

| *2,3-Dihydroxy-naphthalene | | Zn.EDTA.2,3-Dihydroxy-naphthalene | | Cd.EDTA.2,3-Dihydroxy-naphthalene | |
|---|---|---|---|---|---|
| Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B | Vol.of alkali (in ml.) | B |
| 0.00 | 1.45 | 0.00 | 1.45 | 0.00 | 1.45 |
| 1.00 | 1.50 | 1.00 | 1.50 | 1.00 | 1.50 |
| 2.00 | 1.60 | 2.00 | 1.60 | 2.00 | 1.60 |
| 3.00 | 1.70 | 3.00 | 1.80 | 3.00 | 1.80 |
| 4.00 | 1.90 | 4.00 | 2.10 | 4.00 | 2.10 |
| 5.00 | 2.15 | 5.00 | 2.50 | 5.00 | 2.45 |
| 5.50 | 2.36 | 5.50 | 2.82 | 5.50 | 2.75 |
| 5.60 | 2.50 | 5.60 | 2.95 | 5.60 | 2.88 |
| 5.70 | 2.70 | 5.70 | 3.15 | 5.70 | 3.05 |
| 5.80 | 2.92 | 5.80 | 3.40 | 5.80 | 3.30 |
| 5.85 | 3.05 | 5.85 | 3.52 | 5.85 | 3.45 |
| 5.90 | 3.25 | 5.90 | 3.65 | 5.90 | 3.62 |
| 5.93 | 3.40 | 5.93 | 3.75 | 5.93 | 3.75 |
| 5.96 | 3.60 | 5.96 | 3.90 | 5.96 | 3.95 |
| 5.98 | 3.80 | 5.98 | 4.00 | 5.98 | 4.00 |
| 6.00 | 6.90 | 6.00 | 6.20 | 6.00 | 6.60 |
| 6.04 | 7.15 | 6.04 | 6.60 | 6.04 | 6.95 |
| 6.08 | 7.45 | 6.08 | 6.95 | 6.08 | 7.25 |
| 6.12 | 7.72 | 6.12 | 7.25 | 6.12 | 7.50 |
| 6.16 | 8.00 | 6.16 | 7.50 | 6.16 | 7.72 |
| 6.20 | 8.20 | 6.20 | 7.75 | 6.20 | 7.94 |
| 6.24 | 8.45 | 6.24 | 8.00 | 6.24 | 8.18 |
| 6.28 | 8.70 | 6.28 | 8.20 | 6.28 | 8.38 |
| 6.32 | 8.92 | 6.32 | 8.42 | 6.32 | 8.60 |
| 6.36 | 9.15 | 6.36 | 8.65 | 6.36 | 8.82 |
| 6.40 | 9.35 | 6.40 | 8.85 | 6.40 | 9.00 |
| 6.44 | 9.60 | 6.48 | 9.25 | 6.48 | 9.40 |
| 6.48 | 9.85 | 6.54 | 9.55 | 6.54 | 9.68 |
| 6.52 | 10.10 | 6.62 | 9.80 | 6.62 | 9.95 |
| 6.58 | 10.45 | 6.70 | 10.05 | 6.70 | 10.22 |
| 6.66 | 10.75 | 6.80 | 10.32 | 6.80 | 10.55 |
| 6.70 | 10.85 | 6.90 | 10.55 | 6.90 | 10.82 |
| 6.80 | 11.00 | 7.00 | 10.78 | 7.00 | 11.00 |
| | | 7.10 | 10.95 | | |

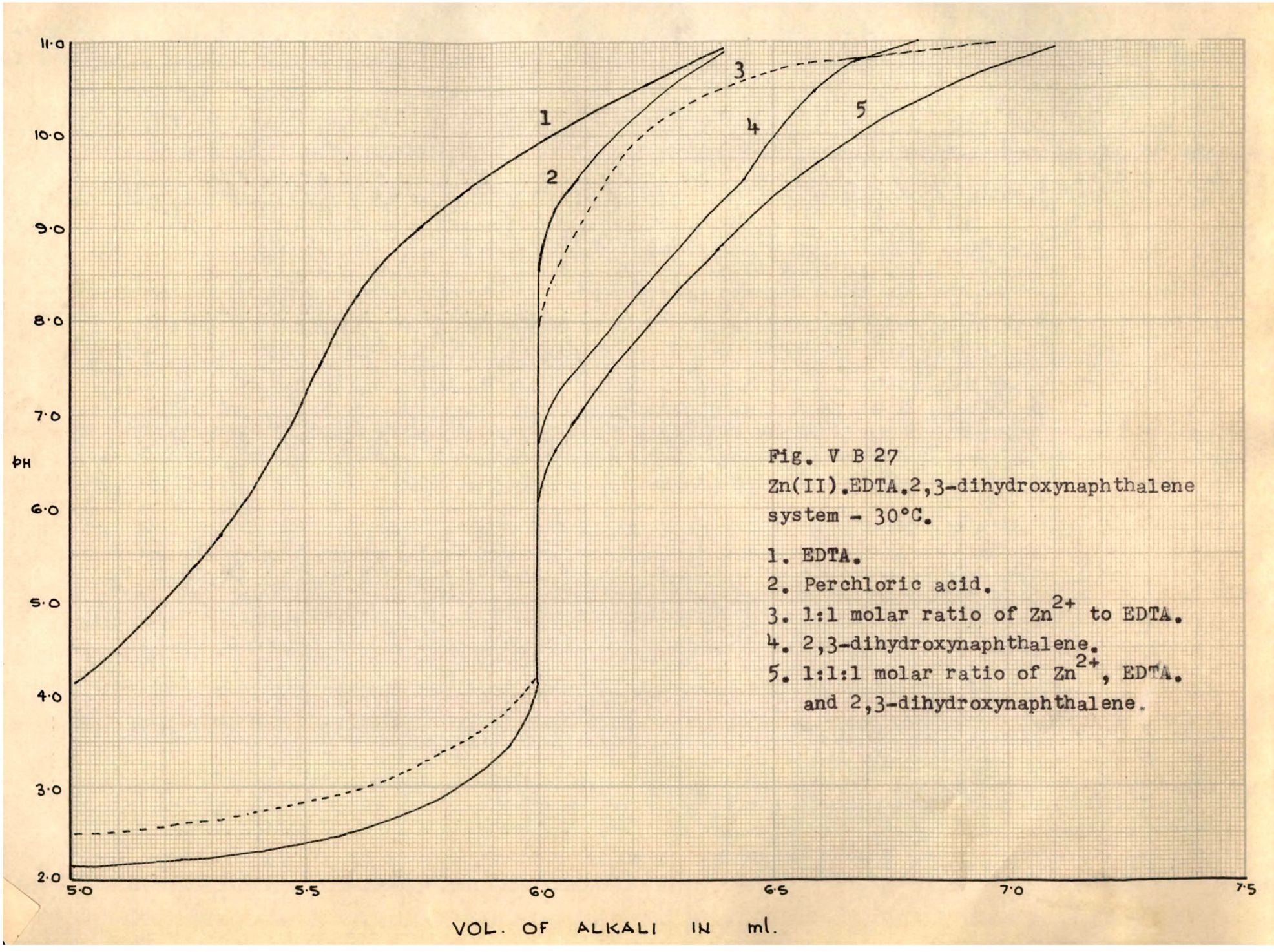



Fig. V B 27
Zn(II).EDTA.2,3-dihydroxynaphthalene system - 30°C.

1. EDTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Zn^{2+}$ to EDTA.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Zn^{2+}$, EDTA. and 2,3-dihydroxynaphthalene.

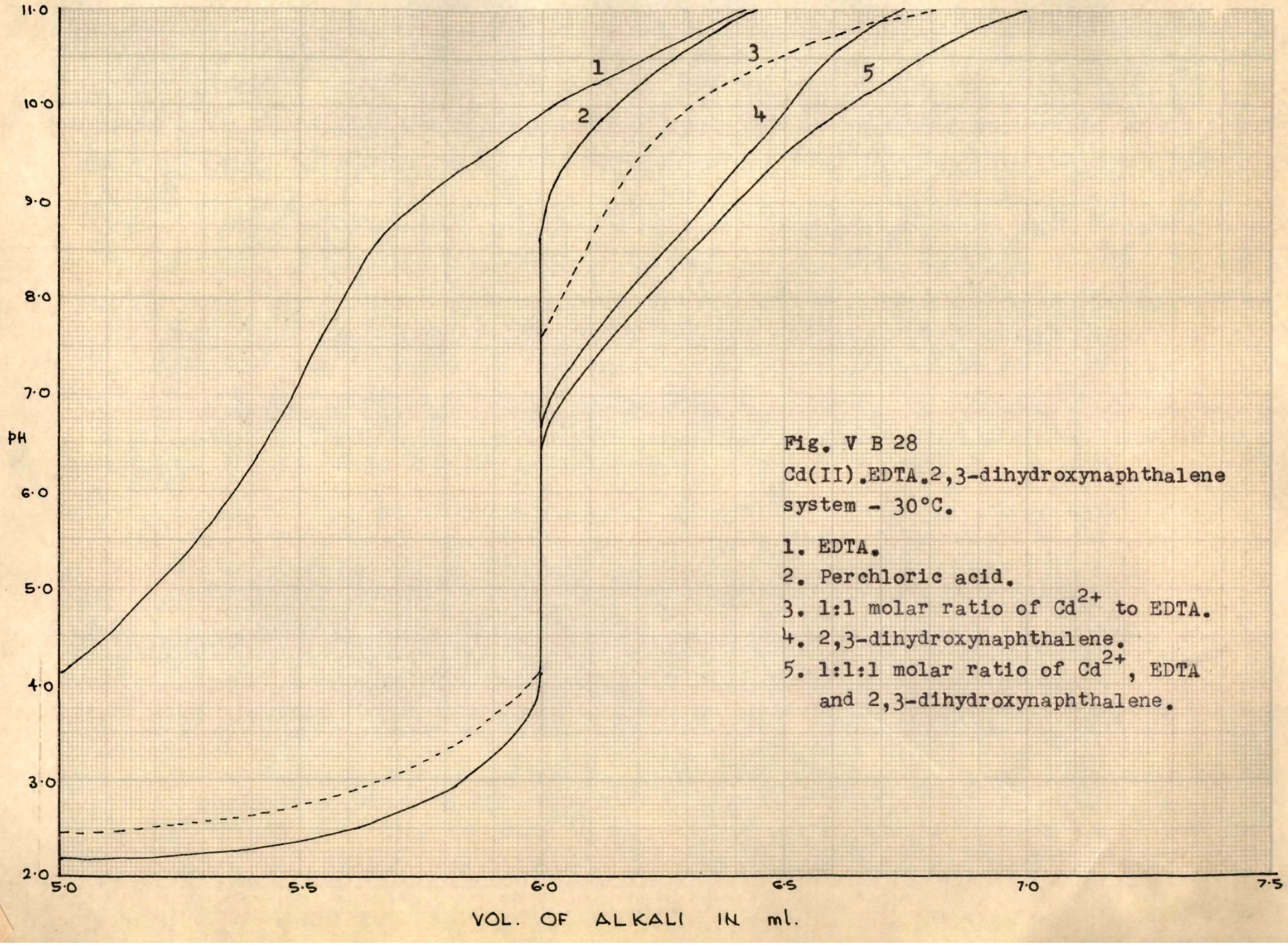



Fig. V B 28
Cd(II).EDTA.2,3-dihydroxynaphthalene system - 30°C.

1. EDTA.
2. Perchloric acid.
3. 1:1 molar ratio of $Cd^{2+}$ to EDTA.
4. 2,3-dihydroxynaphthalene.
5. 1:1:1 molar ratio of $Cd^{2+}$, EDTA and 2,3-dihydroxynaphthalene.

## Table VB 7.1b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.80 | $1.15_4$ | 6.50 | 6.60 | 0.10 | $0.16_9$ | $0.69_1$ | $4.41_2$ | - |
| 9.90 | $1.11_5$ | 6.56 | 6.68 | 0.12 | $0.21_0$ | $0.57_5$ | $4.31_9$ | $3.74_4$ |
| 10.00 | $1.08_3$ | 6.58 | 6.71 | 0.13 | $0.25_3$ | $0.47_0$ | $4.23_1$ | $3.76_1$ |
| 10.10 | $1.04_3$ | 6.61 | 6.76 | 0.15 | $0.28_1$ | $0.40_8$ | $4.11_9$ | $3.71_1$ |
| 10.20 | $1.00_7$ | 6.65 | 6.81 | 0.16 | $0.31_1$ | $0.34_5$ | $4.04_9$ | $3.70_4$ |
| 10.30 | $0.99_7$ | 6.69 | 6.87 | 0.18 | $0.35_3$ | $0.26_3$ | $3.97_0$ | $3.70_7$ |
| 10.40 | $0.95_6$ | 6.75 | 6.95 | 0.20 | $0.40_9$ | $0.15_9$ | $3.90_4$ | $3.74_5$ |
| 10.50 | $0.94_1$ | 6.80 | 7.01 | 0.21 | $0.43_6$ | $0.11_1$ | $3.86_2$ | $3.75_1$ |

$\log K_{MAL} = 3.73 \pm 0.03$

## Table VB 7.3b

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | pL-$\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.70 | $1.20_2$ | 6.84 | 6.96 | 0.12 | $0.19_6$ | $0.61_3$ | $5.36_6$ | $4.75_3$ |
| 9.80 | $1.18_3$ | 6.86 | 7.00 | 0.14 | $0.23_2$ | $0.51_9$ | $5.27_6$ | $4.75_7$ |
| 9.90 | $1.16_4$ | 6.87 | 7.03 | 0.16 | $0.27_0$ | $0.43_1$ | $5.19_1$ | $4.76_0$ |
| 10.00 | $1.14_5$ | 6.88 | 7.06 | 0.18 | $0.30_9$ | $0.34_9$ | $5.10_5$ | $4.75_6$ |
| 10.10 | $1.12_5$ | 6.93 | 7.12 | 0.19 | $0.33_1$ | $0.30_5$ | $5.01_5$ | $4.71_0$ |
| 10.20 | $1.08_6$ | 6.96 | 7.17 | 0.21 | $0.37_8$ | $0.21_6$ | $4.94_2$ | $4.72_6$ |
| 10.30 | $1.04_7$ | 6.98 | 7.21 | 0.23 | $0.43_1$ | $0.12_0$ | $4.87_2$ | $4.75_2$ |

$\log K_{MAL} = 4.74 \pm 0.03$

Table VB 7.4b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Zn.EDTA.2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.50 | $1.08_4$ | 6.42 | 6.52 | 0.10 | $0.18_1$ | $0.59_9$ | $5.92_4$ | - |
| 9.60 | $1.06_4$ | 6.44 | 6.56 | 0.12 | $0.22_1$ | $0.54_7$ | $5.83_9$ | $5.29_2$ |
| 9.70 | $1.06_5$ | 6.45 | 6.59 | 0.14 | $0.25_8$ | $0.45_8$ | $5.75_4$ | $5.29_6$ |
| 9.80 | $1.04_5$ | 6.47 | 6.62 | 0.15 | $0.28_1$ | $0.40_8$ | $5.66_5$ | $5.25_7$ |
| 9.90 | $1.04_5$ | 6.49 | 6.65 | 0.16 | $0.30_0$ | $0.36_8$ | $5.57_2$ | - |
| 10.00 | $1.02_5$ | 6.50 | 6.68 | 0.18 | $0.34_4$ | $0.28_0$ | $5.49_8$ | $5.21_8$ |
| 10.10 | $1.00_3$ | 6.51 | 6.71 | 0.20 | $0.39_1$ | $0.19_2$ | $5.42_7$ | $5.23_5$ |
| 10.20 | $1.00_3$ | 6.52 | 6.74 | 0.22 | $0.43_0$ | $0.12_2$ | $5.35_5$ | $5.23_3$ |

$\log K_{MAL} = 5.25 \pm 0.04$

Fig. V B 29
Zn(II).EDTA.catechol system - 30°C.

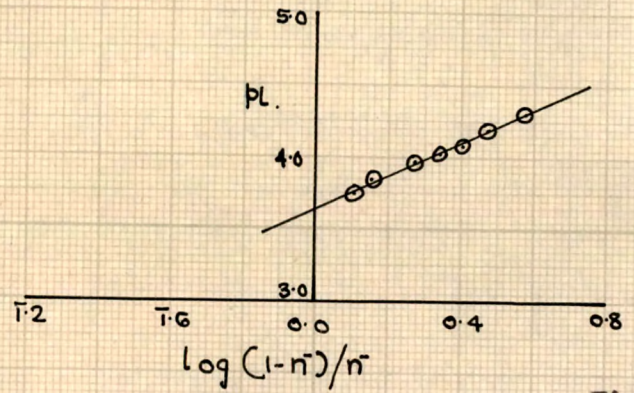



Fig. V B 30
Zn(II).EDTA.protocatechuic acid system - 30°C.

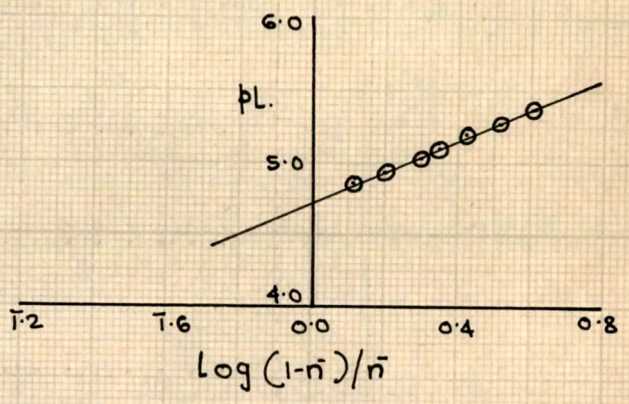
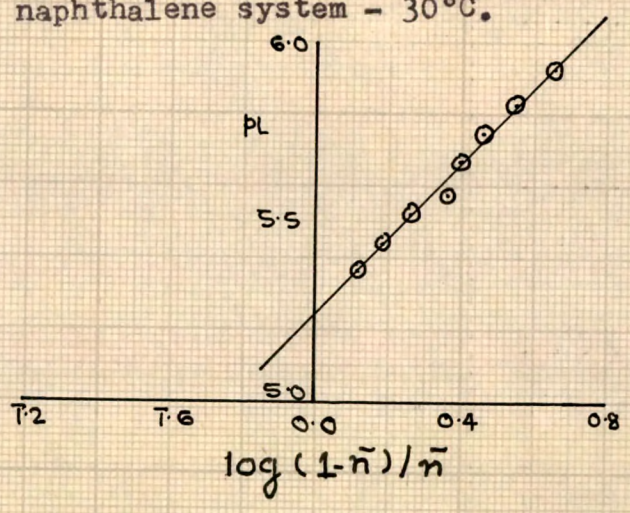



Fig. V B 31
Zn(II).EDTA.2,3-dihydroxy-naphthalene system - 30°C.



## Table VB 7.1c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 10.00 | $1.08_3$ | 6.58 | 6.68 | 0.10 | $0.18_0$ | $0.65_8$ | $4.19_1$ | $3.53_3$ |
| 10.10 | $1.04_3$ | 6.61 | 6.73 | 0.12 | $0.22_5$ | $0.53_7$ | $4.10_6$ | $3.56_9$ |
| 10.20 | $1.00_7$ | 6.65 | 6.78 | 0.13 | $0.25_2$ | $0.47_2$ | $4.01_3$ | $3.54_1$ |
| 10.30 | $0.99_9$ | 6.69 | 6.83 | 0.14 | $0.27_4$ | $0.42_3$ | $3.91_9$ | $3.49_6$ |
| 10.40 | $0.95_6$ | 6.75 | 6.91 | 0.16 | $0.32_7$ | $0.31_3$ | $3.84_3$ | $3.53_0$ |
| 10.50 | $0.94_1$ | 6.80 | 6.98 | 0.18 | $0.37_3$ | $0.22_5$ | $3.77_6$ | $3.55_1$ |

$\log K_{MAL} = 3.53 \pm 0.04$

## Table VB 7.3c

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

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.90 | $1.16_4$ | 6.87 | 6.99 | 0.12 | $0.20_2$ | $0.59_6$ | $5.11_8$ | $4.52_2$ |
| 10.00 | $1.14_5$ | 6.88 | 7.02 | 0.14 | $0.24_0$ | $0.50_9$ | $5.06_4$ | $4.55_5$ |
| 10.10 | $1.12_5$ | 6.93 | 7.08 | 0.15 | $0.26_2$ | $0.44_9$ | $4.97_1$ | $4.52_2$ |
| 10.20 | $1.08_6$ | 6.96 | 7.13 | 0.17 | $0.30_7$ | $0.35_3$ | $4.89_4$ | $4.54_1$ |
| 10.30 | $1.04_7$ | 6.98 | 7.17 | 0.19 | $0.35_6$ | $0.25_7$ | $4.82_1$ | $4.56_4$ |
| 10.40 | $1.01_7$ | 7.03 | 7.23 | 0.20 | $0.38_6$ | $0.19_1$ | $4.74_0$ | $4.54_9$ |
| 10.50 | $1.00_3$ | 7.08 | 7.30 | 0.22 | $0.43_3$ | $0.11_7$ | $4.67_3$ | $4.55_6$ |

$\log K_{MAL} = 4.54 \pm 0.02$

Table VB 7.4c

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and $pL-\log(1-\bar{n})/\bar{n}$ data of Cd.EDTA.2,3-dihydroxynaphthalene system - 30°C.

| B | $\bar{n}_H$ | V" | V"' | V"'-V" | $\bar{n}$ | $\log(1-\bar{n})/\bar{n}$ | pL | $pL-\log(1-\bar{n})/\bar{n}$ |
|---|---|---|---|---|---|---|---|---|
| 9.80 | $1.04_5$ | 6.47 | 6.56 | 0.09 | $0.16_9$ | $0.69_1$ | $5.60_1$ | $4.91_0$ |
| 9.90 | $1.04_5$ | 6.49 | 6.60 | 0.11 | $0.20_6$ | $0.58_5$ | $5.51_7$ | $4.93_2$ |
| 10.00 | $1.02_5$ | 6.50 | 6.63 | 0.13 | $0.24_9$ | $0.47_9$ | $5.43_8$ | $4.95_9$ |
| 10.10 | $1.00_3$ | 6.51 | 6.66 | 0.15 | $0.29_3$ | $0.38_2$ | $5.36_2$ | $4.98_0$ |
| 10.20 | $1.00_3$ | 6.52 | 6.69 | 0.17 | $0.33_2$ | $0.30_3$ | $5.28_6$ | $4.98_3$ |
| 10.30 | $1.00_3$ | 6.53 | 6.72 | 0.19 | $0.37_1$ | $0.28_9$ | $5.21_1$ | $4.92_2$ |
| 10.40 | $1.00_5$ | 6.54 | 6.75 | 0.21 | $0.41_0$ | $0.15_8$ | $5.13_7$ | $4.97_9$ |

$\log K_{MAL} = 4.95 \pm 0.04$

Fig. V B 32
Cd(II).EDTA.catechol system - 30°C.

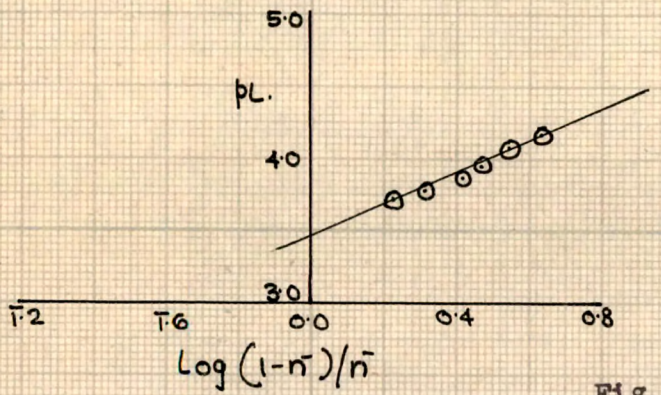



Fig. V B 33
Cd(II).EDTA.protocatechuic acid system - 30°C.

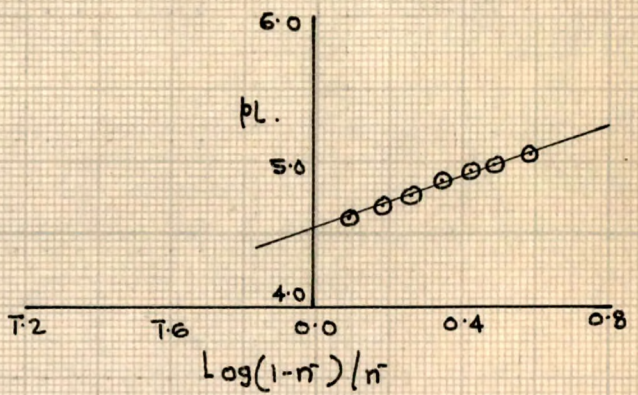



Fig. V B 34
Cd(II).EDTA.2,3-dihydroxy-naphthalene system - 30°C.

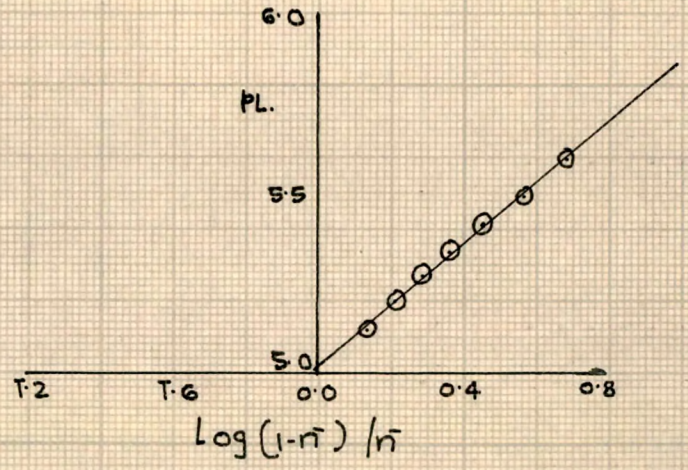


Table VB 8.0

Logarithms of stability constants of ternary Histidine-$M^{2+}$-ligand complexes, IMDA-$M^{2+}$-ligand complexes and EDTA-$M^{2+}$-ligand complexes. ( $\mu$ = 0.2M, 30°C.).

| | Ligand (L) | | | |
|---|---|---|---|---|
| | Catechol | Pyrogallol | Protocatechuic acid | 2,3-Dihydroxy-naphthalene |
| $\log K^{Zn(Histidine)}_{Zn(Histidine)L}$ | 7.24 ± 0.02 | 6.84 ± 0.04 | - | - |
| $\log K^{Cd(Histidine)}_{Cd(Histidine)L}$ | 5.76 ± 0.03 | - | - | 7.74 ± 0.03 |
| $\log K^{Zn(IMDA)}_{Zn(IMDA)L}$ | 6.84 ± 0.05 | 6.25 ± 0.04 | 7.83 ± 0.04 | 8.44 ± 0.05 |
| $\log K^{Cd(IMDA)}_{Cd(IMDA)L}$ | 5.44 ± 0.04 | - | 6.34 ± 0.05 | 7.34 ± 0.03 |
| $\log K^{Zn(EDTA)}_{Zn(EDTA)L}$ | 3.73 ± 0.03 | - | 4.74 ± 0.03 | 5.24 ± 0.04 |
| $\log K^{Cd(EDTA)}_{Cd(EDTA)L}$ | 3.53 ± 0.04 | - | 4.54 ± 0.02 | 4.95 ± 0.04 |

Table VB 9.0

| | Ligand (L) | | | |
|---|---|---|---|---|
| | Catechol | Pyrogallol | Protocatechuic acid | 2,3-Dihydroxy-naphthalene |
| $\log K^{Zn}_{Zn.L} - \log K^{Zn.Hist.}_{Zn.Hist.L}$ | 1.00 ± 0.02 | 0.83 ± 0.00 | - | - |
| $\log K^{Cd}_{Cd.L} - \log K^{Cd.Hist.}_{Cd.Hist.L}$ | 1.00 ± 0.03 | - | - | 0.80 ± 0.00 |
| $\log K^{Zn}_{Zn.L} - \log K^{Zn.IMDA.}_{Zn.IMDA.L}$ | 1.40 ± 0.01 | 1.42 ± 0.00 | 1.28 ± 0.02 | 1.48 ± 0.04 |
| $\log K^{Cd.}_{Cd.L} - \log K^{Cd.IMDA.}_{Cd.IMDA.L}$ | 1.32 ± 0.02 | - | 1.72 ± 0.01 | 1.20 ± 0.00 |
| $\log K^{Zn}_{Zn.L} - \log K^{Zn.EDTA.}_{Zn.EDTA.L}$ | 4.51 ± 0.01 | - | 4.37 ± 0.01 | 4.68 ± 0.03 |
| $\log K^{Cd}_{Cd.L} - \log K^{Cd.EDTA.}_{Cd.EDTA.L}$ | 3.23 ± 0.02 | - | 3.52 ± 0.02 | 3.59 ± 0.01 |

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