CHAPTER IV

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

B. Ternary Systems - Metal ion, Dipyridyl and Salicylic acid or Thiosalicylic acid.

C. Isolation of solid mixed ligand complexes.

SECTION A

Though the formation of mixed ligand complexes is known since the times of Werner, study of mixed ligand chelates has invited special attention of chemists since 1959. A number of studies in solids and solutions have been reported for the ternary metallic complexes involving a neutral molecule i.e. dipyridyl as primary ligand and various secondary ligands.

Punger and coworkers[1] employed the high frequency titrimetry to study the complexes of Ni(II) with dipyridyl and dimethyl glyoxime. Schillt[2] carried out the potentiometric and spectrophotometric titrations of dicyano-bis(bipy) iron(II) and dicyano-bis(1,10-phenanthroline) iron(II) in acetic acid. He also reported mixed ligand complex of Fe(III) with CN- and bipyridyl or o-phenanthroline and characterised the compounds[3]. The preparation and resolution of bis (oxalato) 2,2'-bipy-chromate (III) and bis (oxalato) 1,10-phen-chromate(III) ions have been reported[4]. Grignard's method was utilized in the preparation of benzene bis(bipyridyl) Cr(III) iodide and diphenyl bis (bipyridyl) Cr(III) iodide and diphenyl bis(bipyridyl) Cr(III) iodide by Tsutsu[5]. Coates and coworkers[6] studied the formation of coloured complex of Be-dialkyl and diaryl derivatives with 2,2'-bipyridyl. Schillt[7] used the complexes, dicyano-bis (1,10-phen) Fe(II).$2H_2O$ (Ferrocy.phen) and dicyano bis(2,2'-bipy) Fe(II).$3H_2O$ (Ferrocy.bipy), as indicator in redox determination of aqueous solution of p-$C_6H_4(OH)_2$ and primary aromatic amines. Chelate compounds of organo tin halides were prepared with 2,2'-bipyridyl and 1,10-phenanthroline by Alleston and coworkers[8].

Spectrophotometric determination of titanium through the formation of mixed complex with bipyridyl and salicylate is known.[9] Octahedral Co(III) complexes containing bipyridyl and amino acids have been synthesised and characterised by Murakami and coworkers.[10] Atkinson and coworkers[11] studied the chelate effect of mixed ligand complexes of bipyridine and pyridine with Mn(II), Ni(II), Cu(II) and Zn(II) by carrying out colorimetric, potentiometric and electron spin resonance spectral studies. Chelates of the type $Mo(CO)_3(bipy)L$ where $L = Ph_3P$, Ph_2S and pyridine are known.[12] The preparation of heterochelates of the type $(bipyH_2)\,[(VO_2)_2(SO_4)_2(C_2O_4)CO(NH_2)_2]$ has been reported by Markov and coworkers.[13] The complex of chromium(II) acetate with 2,2'-bipyridine i.e. $[Cr(bipy)_2(OAC)_2]$ was also reported.[14] Bis(bipy) dicyano Rh(II) complex was synthesised by Sen and coworkers.[15] Herzog and coworkers[16] reported the formation of diacetato 2,2'-bipyridyl Cu(II) complex. The mixed ligand complexes $[Co(III)(bipy)YCl_2]X$ where Y = bidentate amino acids were examined polarographically.[17] $UCl_3.OET.bipy_2$ and $UCl_3.OET.phen_2$ were isolated by Gans and coworkers.[18] Dutta and coworkers[19] observed that cis-diamine Co(II) sulphate reacts readily with ethylenediamine, o-phenanthroline or bipyridyl liberating ammonia with the formation of mixed ligand complexes. The complexes of 2,3-dihydroxynaphthalene and bipyridyl and o-phenanthroline have been studied with a series of cation and oxycations.[20] The fluorescent properties of various Eu(II) chelates of dibenzoylmethane, benzoylacetonate, acetylacetone, β-naphthylacetonate were observed to be enhanced on coordination with bipy or o-phen.[21] Yamamoto and coworkers[22] synthesised diethyl bis(bipy) iron and ethyl (bipy) nickel. The new seleno cyanato complexes of Pd(II) or Pt(II) with bipyridyl have been worked out.[23] The compounds di(phthalimide) 2,2'-bipy.Co(II) and di(phthalimide) 1,10-phen.Co(II) have been characterised by infra-red spectral study.[24] Mixed complexes containing Co(III), paludrine and bipyridyl and o-phenanthroline have been described by Gheorghiu and coworkers.[25] The solution stabilities of mixed ligand complexes of the type [Cu(bipy)(L)] where L is polyhydroxy phenols, and acids have been reported by Martell and coworkers.[26] Potentiometric titration technique has been used in the study of binuclear diolated Cu(II) complexes of $[Cu_2(OH)_2L_2]^{2+}$ ion, where L = bipy. or o-phen. or histamine.[27] Dutta and coworkers[28] reported the synthesis of a variety of oxo.vanadium (IV) heterochelates containing bipy. and o-phen.. The precipitation and characterisation of the mixed ligand complex Cu(II) phthalimide with bipy. or o-phen. was reported by Narain.[29] Electrode potentials for a variety of mixed ligand complexes of Os(III) and Os(II) have been measured in aqueous solution.[30] Bipyridyl derivatives of nitrato pentacarbonyl Mn(I) is known.[31] Mixed Tl(III) complexes of bipyridyl involving coordinated perchlorate and nitrate ions have been listed by Faruer and Nord.[32] Ripan and Saceban[33] reported the synthesis of ternary complexes of UO_2(II) with bipy., 1,10-phen. and o-, m- and p-amino benzoic acids. Complexes of Tc(IV) with Ph_3P and Ph_3As and bipyridyl have been synthesised.[34] Paramagnetic adducts of Ni(II) chelate of mono thio β-diketones have been obtained with bipy. and o-phen.[35]. A detailed study of synthesis and spectra of cyanomethylene complexes of Fe(III) with bipyridyl and o-phenanthroline has been reported.[36] The formation of compounds $MoCl_3$(pyridine)(o-phen), $MoCl_3$(pyridine)(bipy) has also been reported.[37] Palade[38] studied the introduction of o-phen. into the internal sphere of ammonium disulphato tetramine cobaltate. Lal and Agarwal[39] determined the formation constants and synthesised the heterochelates containing oxo.vanadium(IV),o-phen. and eighteen dihydric phenolic compounds. The synthesis of heterochelates of the type $[VO(C_2O_4)(bipy)]$ has been reported by Dutta and coworkers.[40] Dutta and coworkers[41] also suggested a new synthetic procedure for the preparation of a series of vanadyl heterochelates of the type VO(AA)XYX and VO(AB)XYX where AA is bipyridyl or acetylacetone and AB is glycine or phenolic acid or 8-hydroxyquinoline and XYX is a tridentate ligand e.g. pyridine 2,6-carboxylic acid. The binuclear complex of Fe(III), $[(phen)_2Fe(OH)_2\text{-}Fe(phen)_2](SO_4)_2.7H_2O$ containing the hydroxo bridges has been isolated.[42] Dutta and coworkers[43] reported the synthesis of heterochelates of Co(II) with bipy., o-phen. and biguanide. Mixed ligand chelates of rare earth metals with propionylacetone and bipyridyl are also known to be formed.[44] Sigel and coworkers[45-48] have investigated ternary transition metal complexes with bipyridyl as the primary ligand and many monodentate or bidentate secondary ligands, coordinating through two oxygen atoms, two nitrogen atoms or one oxygen and one nitrogen atom. Octahedral complexes of Co(II) bis-ethylacetoacetate with aromatic heterocyclic amines as bipy. or o-phen. have been synthesised.[49] Komomenko and coworkers[50] prepared and characterised the ternary complex of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadiene and 1,10-phen. or bipy. with VO(II) ion. Crystalline mixed ligand chelates of Cr(III) with bipy. or o-phen. halides, acetylacetone have been prepared.[51] Broomhead and coworkers[52] synthesised and resolved the heterochelates of Cr(III) and Co(III) with the ligands bipy., o-phen., and oxalate ion. Synthesis of octahedral complexes $[Co(A)L_2]Cl_2$ where A = bipy., o-phen., acetylacetone; L = halides have been described.[53] Heterochelates of Cu(II) and 2,2'-bipyridyl and o-phenanthroline with biguanide have been prepared and characterised.[54] Syamal[55] reported the formation of $(Ni\ L\ L'_2)Cl_2$ in good yield where L = picolyl amine and L' = bipyridyl. The ternary complexes in solution where bipyridyl is used as the primary ligand and aliphatic and aromatic acids are the secondary ligands, have been reported.[56] Reactions of trimethyl (β-dioxo) Pr(IV) complexes with bipy. and o-phen. resulted in the formation of heterochelates.[57] Dutta and coworkers[58] isolated and characterised several Cu(II) complexes of empirical composition $Cu(AA)(X)_2$ where (AA) = 2,2'-dipyridyl/o-phenanthroline/5-nitro-o-phenanthroline and X = NCS, NO_2 or N_3. They also synthesised a number of mixed chelates of Cu(II) containing glycine or α-(DL)-alanine and α,α'-dipyridyl, o-phenanthroline or 5-nitro-o-phenanthroline of the type $[Cu(AA)(XY)]Z.xH_2O$ where Z = Cl, Br, I.[59] Preparation and properties of malanato bis(bipy) Co(III) salts have been described.[60] $[VO(bipy)_3(NCSe)_2]$, $[VO(phen)_3(NCSe)_2]$ have also been reported.[61] Sigel and coworkers[62] reported the stability constant of 2,2'-bipyridyl-Cu(II)-pyrocatechol complex. The ternary system phenyl bis(bipy)Ni(II)chloride is known.[63] Yashuhiro and coworkers[64] described the formation of mixed copper complexes of some β-diketones with bipyridyl. Sigel and coworkers[65] also determined the rate constant for the formation and dissociation of the mixed ligand complex $[Cu(bipy)(gly)]^{2+}$

using temperature jump technique. Structural varieties in mixed Co(III) and Co(II) chloro compounds with 1,10-phenanthroline and 2,2'-bipyridyl have been investigated.[66] The ternary transition metal complexes with bipyridyl have been reported by Griesser and Sigel.[67] Systems MAL where M = Cu(II), Ni(II); A = dipyridyl or o-phenanthroline and L = various amino acids have been studied in solution by Chidambaram and Bhattacharya.[68]

However, the study of mixed ligand systems using dipyridyl as primary ligand and the polyhydroxy phenols as the secondary ligands is not much.[26,62] An attempt has, therefore, been made in the present investigation to study the formation constants of the system MAL, where M = Zn^{2+} or Cd^{2+} ; A = dipyridyl and L = catechol, pyrogallol, 2,3-dihydroxynaphthalene and protocatechuic acid using a modified form of Irving-Rossotti titration technique.[69,65] The reaction for the mixed ligand complex formation can be represented as follows :

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

$$K_{MA} = \frac{[M(\text{bipy})]}{[M]\ [\text{bipy}]}$$

$$M(\text{bipy})^{2+} + L^{-1} \rightleftharpoons [M(\text{bipy})L]^{1+}$$

$$K_{MAL} = \frac{[M(\text{bipy})L]}{[M(\text{bipy})]^{2+}[L]^{-1}}$$

The above reaction is based on the consideration that the formation of 1:1 metal bipyridyl complex is complete at low pH. The 1:1 complex forms $[M(\text{bipy})(OH)_2]$ at higher pH. However, in the presence of a secondary ligand formation of hydroxy complex does not take place and instead ternary complex

$[M(bipy)L]^{1+}$ results. The above required conditions do not hold good in the complexes of Tl^{+}, Mg^{2+} and UO_2^{2+} and so the ternary systems could not be investigated in these cases.

For the Zn(II) and Cd(II) complexes, solutions were prepared as follows :

1. Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1.0M, 9.0 ml.) + conductivity water (36.0 ml.); total volume = 50.0 ml., μ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + bipyridyl (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + conductivity water (31.1 ml.); total volume = 50.0 ml., μ = 0.2M.
3. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + conductivity water (31.1 ml.); total volume = 50.0 ml., μ = 0.2M.
4. Perchloric acid (0.2M, 5.0 ml.) + bipyridyl (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., μ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + bipyridyl (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., μ = 0.2M.

The ionic strength of each solution was thus initially raised to 0.2M. Each of the above samples was titrated against 0.2M sodium hydroxide solution. The volume of alkali added and pH measured have been recorded in tables IV A 1.0 to IV A 2.3. The plots of pH against volume of alkali have been presented in figs. IV A 1 to IV A 5.

An observation of mixed ligand system curves (figs. IV A 1 to IV A 5) shows that metal bipyridyl curve (4) diverges from the bipyridyl curve (2) at low pH. The calculation of $\bar{n}$ shows that it continues to be one upto pH ~ 6.0 after which metal bipyridyl curve (4) diverges from the bipyridyl curve(2) showing formation of hydroxy complex $M(bipy)(OH)_2$. After pH ~ 9.5 the complex decomposes forming metal hydroxide which precipitates out indicating that metal bipyridyl complex 1:1 formed at low pH is stable upto high pH. Metal bipyridyl phenolic ligand curve (5) and metal bipyridyl curve (4) overlap each other at low pH. This indicates that in the range where bipyridyl combines with metal, combination of phenolic ligand does not take place. Since the dissociation of the ligands catechol and pyrogallol at low pH is negligible, the curves (4) and (5) overlap. In case of protocatechuic acid the metal bipyridyl protocatechuic acid curve (5) separates from metal bipyridyl curve (4) due to self dissociation of carboxylic group. In cases of all the ligands, however, curve (5) diverges from the ligand curve (3) after pH ~ 6.5 in Zn^{2+} and Cd^{2+} systems. In this range combination of secondary ligand with metal bipyridyl starts. The reaction can be represented as follows :

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

$$[M(A)]^{2+} + LH_2 \rightleftharpoons [MAL] + 2H^+$$

Since the dissociation of M-bipyridyl does not take place in the range of the association of the secondary ligand, it can be considered that the secondary ligand combines with $(M\text{-bipyridyl})^{2+}$ just as it does with $(M.aq)^{2+}$ in the simple system. In the ternary systems the secondary ligands add in the same pH range where M(bipyridyl)$(OH)_2$ formation takes place. It has been presumed that in the presence of highly complexing secondary ligand, formation of M(bipyridyl)$(OH)_2$ is suppressed. Similar consideration has been made by earlier workers[56] in the study of the formation constant of the mixed ligand system (Zn.bipyridyl.glycollic acid) where glycollic acid combines at higher pH. The horizontal distance between curve (3) and curve (5) can be measured and used for the calculation of $\bar{n}$, where $\bar{n}$ is the average number of phenolic ligands associated with one $(M.bipyridyl)^{2+}$. The equation for the calculation will be the same as in the original paper.[69]

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

Here T_M° is the concentration of $(M.bipyridyl)^{2+}$ which is equal to concentration of M^{2+}. $\bar{n}$ and pL were calculated at different pH values, and have been presented in tables IV A 2.1b to IV A 2.3c. pL at $\bar{n} = 0.5$ gives the values of log K_{MAL}. This, however, will mean using only one point and the value will be erroneous . More precise values were obtained by using the method of linear plot.[70] The values have been presented in the table IV A 3.0.

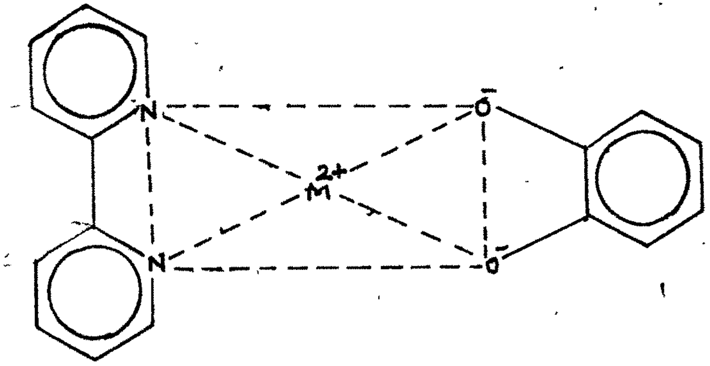
The titration could not be done in mixed ligand systems with 2,3-dihydroxynaphthalene, because the heterochelates gets precipitated. In case of Cd.bipy.pyrogallol system also $\bar{n}$ does not go beyond 0.15 and hence K_{MAL} could not be calculated.

It is interesting to observe the values of mixed ligand formation constants K_{MAL}. The order is same i.e. Zn(II) > Cd(II) as in the case of binary systems. The relative tendencies of the secondary ligands to combine with $(M.bipyridyl)^{2+}$ is in accordance with the basicities of the ligands.

It has been observed that in cases where A = ethylenediamine, log K_{MAL}[71] is significantly lower than log K_{ML_1}. This is because of the fact that the tendency of L to get bound to aquated metal ion is more than to the metal ion bound with ethylenediamine. Ethylenediamine molecule has a greater σ-bonding tendency than the water molecules and thus increases the concentration of electrons around the metal ion and hence the tendency of $[M(en)]^{2+}$ to get bound with L will be less. Bipyridyl should behave in the same way as it is a neutral compound and log K_{MAL} should have been much lower than K_{ML_1}. But it is observed that $K_{MAL} \approx K_{ML_1}$ (where M = Zn^{2+} or Cd^{2+}, A = bipyridyl and L = catechol, pyrogallol or protocatechuic acid). This can be attributed to the special behaviour of bipyridyl.

Bipyridyl is bound to a metal by a σ bond as in case of ethylenediamine. Besides that it can also form a π bond by the back donation of the electrons from the $d\pi$ orbitals of metal to the nitrogen $p\pi$ orbitals on the ligand molecules. The $d\pi$-$p\pi$ interaction has been observed in metal bipyridyl complexes by earlier workers[56,62,72,73] using different methods of investigation. The $d\pi$-$p\pi$ interaction does not allow the concentration of electrons on the metal ion to increase significantly. In other words positive charge on the metal ion in $[M(bipyridyl)]^{2+}$ is almost same as in $[M(aq)]^{2+}$ complexes.

As such the tendency of metal bipyridyl to combine with the ligands is almost same as the tendency of ligand to get bound with $[M(aq)]^{2+}$ systems. This explains why $K_{MAL} \approx K_{ML_1}$. In case of chelating ligand molecules containing two 0-0 donor atoms like catechol (and also pyrogallol and protocatechuic acid), the resulting mixed ligand system is neutral as in the structural formula :



As a result of formation of neutral molecules, the solvent molecules are no longer bound with the mixed ligand complex and hence the freedom of movement of the solvent molecule is more i.e. entropy change is positive. Thus the entropy and enthalpy factors add up and hance $K^{M}_{ML_1} - K^{MA}_{MAL}$ is still less.

Similar observation of $K_{MAL} \approx K_{ML_1}$ has been made by earlier workers[74] in the system where M = Ni(II) or Cu(II); A = bipyridyl and L = amino acids or oxygen containing ligands. In these cases the secondary ligands combine at much lower pH than where MA(OH) formation starts. Since the values in case of Zn(II) and Cd(II) complexes are in agreement with previous cases, it can be argued that the consideration that the hydroxy complex formation is suppressed in presence of strongly complexing secondary ligand, is valid.

Table IVA 1.0

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

E° = 0.02M T^{o}_{Dipy} = 0.002M T^{o}_{M} = 0.002M

Perchloric acid		Dipyridyl		Zn.Dipyridyl		Cd.Dipyridyl	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.00	3.00	2.30	3.00	2.05	3.00	2.05
4.00	2.35	3.50	2.70	3.50	2.20	3.50	2.20
4.50	2.60	4.00	3.30	4.00	2.40	4.00	2.40
4.60	2.70	4.50	3.70	4.50	2.70	4.50	2.70
4.70	2.88	4.55	3.85	4.55	2.75	4.55	2.75
4.80	3.10	4.60	4.02	4.60	2.80	4.60	2.80
4.90	3.50	4.65	4.20	4.65	2.88	4.65	2.90
4.94	3.70	4.70	4.40	4.70	3.00	4.70	3.02
4.98	3.95	4.75	4.52	4.80	3.25	4.80	3.30
5.00	8.75	4.80	4.65	4.85	3.55	4.85	3.50
5.02	9.20	4.85	4.82	4.90	3.90	4.90	3.75
5.04	9.45	4.90	5.02	4.95	4.30	4.95	4.00
5.06	9.75	4.95	5.25	4.98	4.50	4.98	4.30
5.08	9.85	4.98	5.45	5.00	6.70	5.00	7.45
5.10	10.00	5.00	9.10	5.05	6.95	5.05	7.90
5.20	10.38	5.03	9.50	5.10	7.15	5.10	8.25
5.30	10.60	5.06	9.80	5.20	7.50	5.15	8.42
5.40	10.78	5.10	10.10	5.30	7.68	5.20	8.65
5.50	11.00	5.20	10.50	5.40	7.90	5.25	8.80
		5.30	10.65	5.45	8.10	5.30	8.90
		5.40	10.78	5.50	8.40	5.35	9.05
		5.50	11.00	5.55	8.70	5.40	9.25
				5.60	9.10		(ppts)
				5.70	9.60		
				5.80	9.90		
					(ppt.)		

Table IVA 2.1

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

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Catechol		Zn.Dipy.Catechol		Cd.Dipy.Catechol	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.00	3.00	2.05	3.00	2.05
4.00	2.35	4.00	2.40	4.00	2.40
4.50	2.60	4.50	2.70	4.50	2.70
4.60	2.70	4.60	2.80	4.60	2.80
4.70	2.88	4.70	3.02	4.70	3.02
4.80	3.10	4.80	3.25	4.80	3.30
4.90	3.50	4.90	3.90	4.90	3.75
4.94	3.70	4.95	4.30	4.95	4.00
4.98	3.95	4.98	4.50	4.98	4.30
5.00	7.60	5.00	6.60	5.00	7.15
5.02	7.70	5.02	6.70	5.02	7.25
5.04	7.82	5.04	6.80	5.04	7.45
5.08	8.40	5.08	6.98	5.08	7.65
5.10	8.52	5.12	7.15	5.12	7.90
5.12	8.60	5.15	7.30	5.15	8.00
5.14	8.65	5.20	7.40	5.20	8.08
5.18	8.72	5.25	7.50	5.25	8.15
5.20	8.80	5.30	7.58	5.30	8.20
5.25	9.00	5.40	7.70	5.40	8.35
5.30	9.38	5.50	7.82	5.50	8.45
5.40	9.55	5.60	7.95	5.60	8.60
5.50	9.80	5.70	8.12	5.70	8.72
5.60	10.08	5.80	8.48	5.75	8.80
5.70	10.40	5.90	8.95	5.80	8.90
5.80	10.60	6.00	9.40	5.90	9.20
5.90	10.70	6.10	9.75	6.00	9.50
6.00	10.75	6.20	10.00	6.10	9.65
6.10	10.82	6.30	10.14		(ppt.)
6.20	10.90	6.40	10.30		
6.30	11.00	6.60	10.60		
		6.80	10.80		
		7.00	11.00		

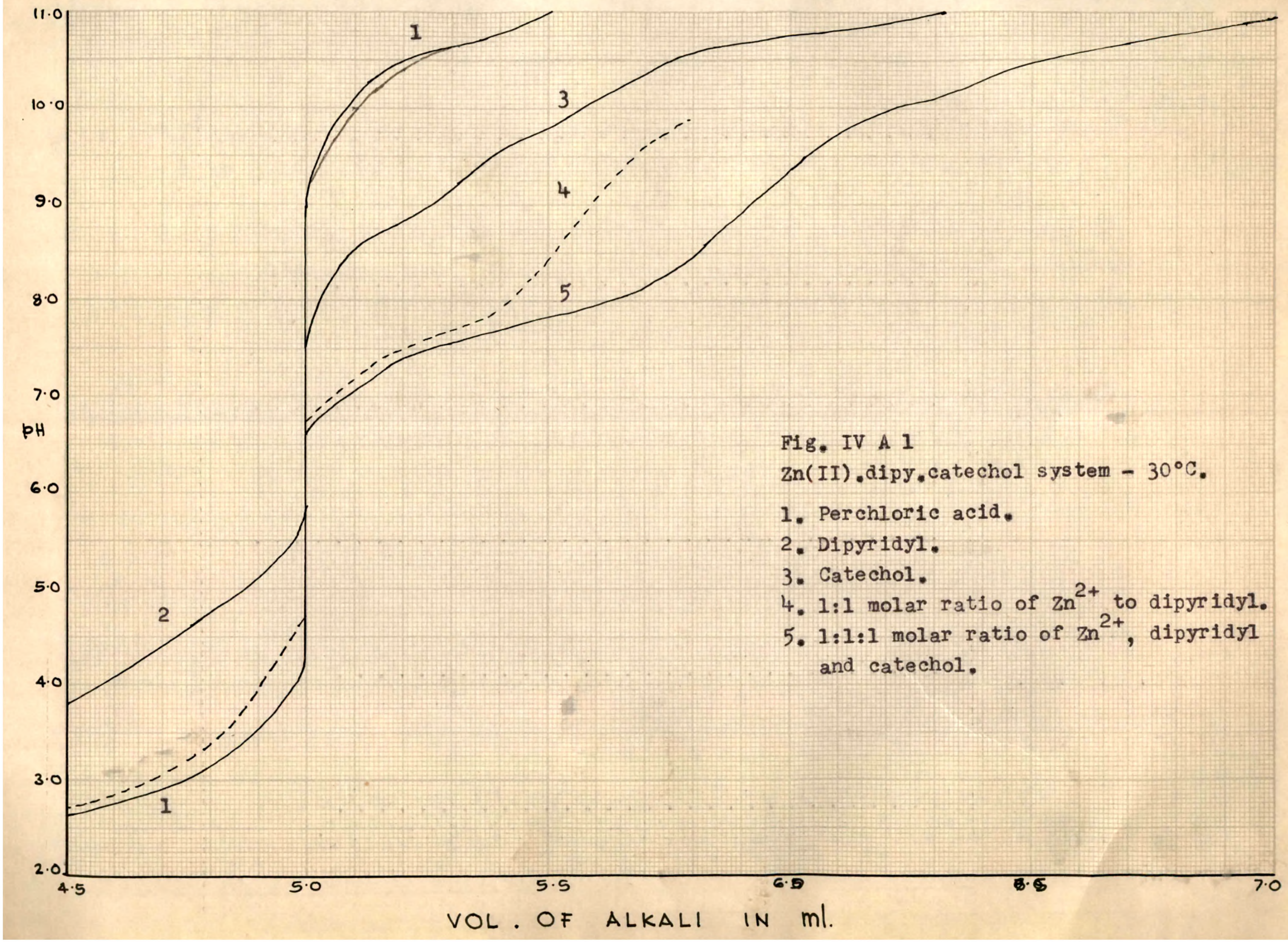


Fig. IV A 1

Zn(II).dipy.catechol system - 30°C.

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

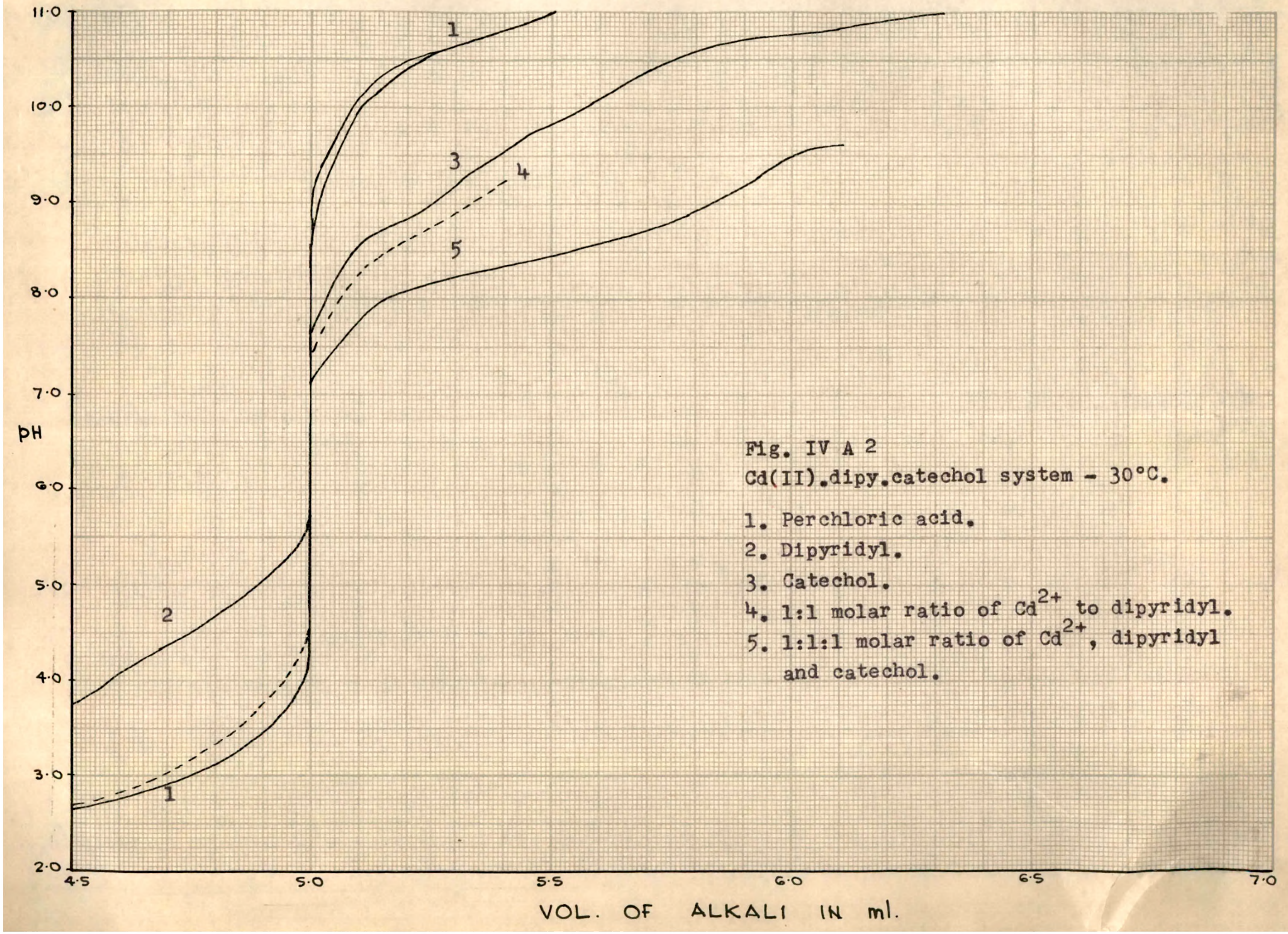


Fig. IV A 2

Cd(II).dipy.catechol system - 30°C.

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

Table IVA 2.2

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

E° = 0.02M T°_{Dipy} = 0.002M T°_L = 0.002M T°_M = 0.002M

Pyrogallol		Zn.Dipy.Pyrogallol	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80
3.00	2.00	3.00	2.05
4.00	2.35	4.00	2.40
4.50	2.60	4.50	2.70
4.60	2.75	4.60	2.80
4.70	2.88	4.70	3.02
4.80	3.10	4.80	3.25
4.90	3.55	4.90	3.90
4.94	3.75	4.95	4.30
4.98	4.00	4.98	4.50
5.00	6.75	5.00	6.45
5.02	6.95	5.02	6.60
5.04	7.20	5.04	6.70
5.08	7.75	5.08	6.82
5.10	7.95	5.10	6.88
5.12	8.10	5.12	6.92
5.14	8.25	5.14	6.98
5.20	8.60	5.16	7.02
5.25	8.80	5.18	7.05
5.30	8.90	5.26	7.15
5.40	9.30	5.36	7.25
5.50	9.65	5.40	7.32
5.60	9.90	5.44	7.40
5.70	10.20	5.48	7.48
5.80	10.32	5.50	7.50 (ppt.)
5.90	10.50		
6.00	10.68		
6.10	10.82		
6.20	11.00		

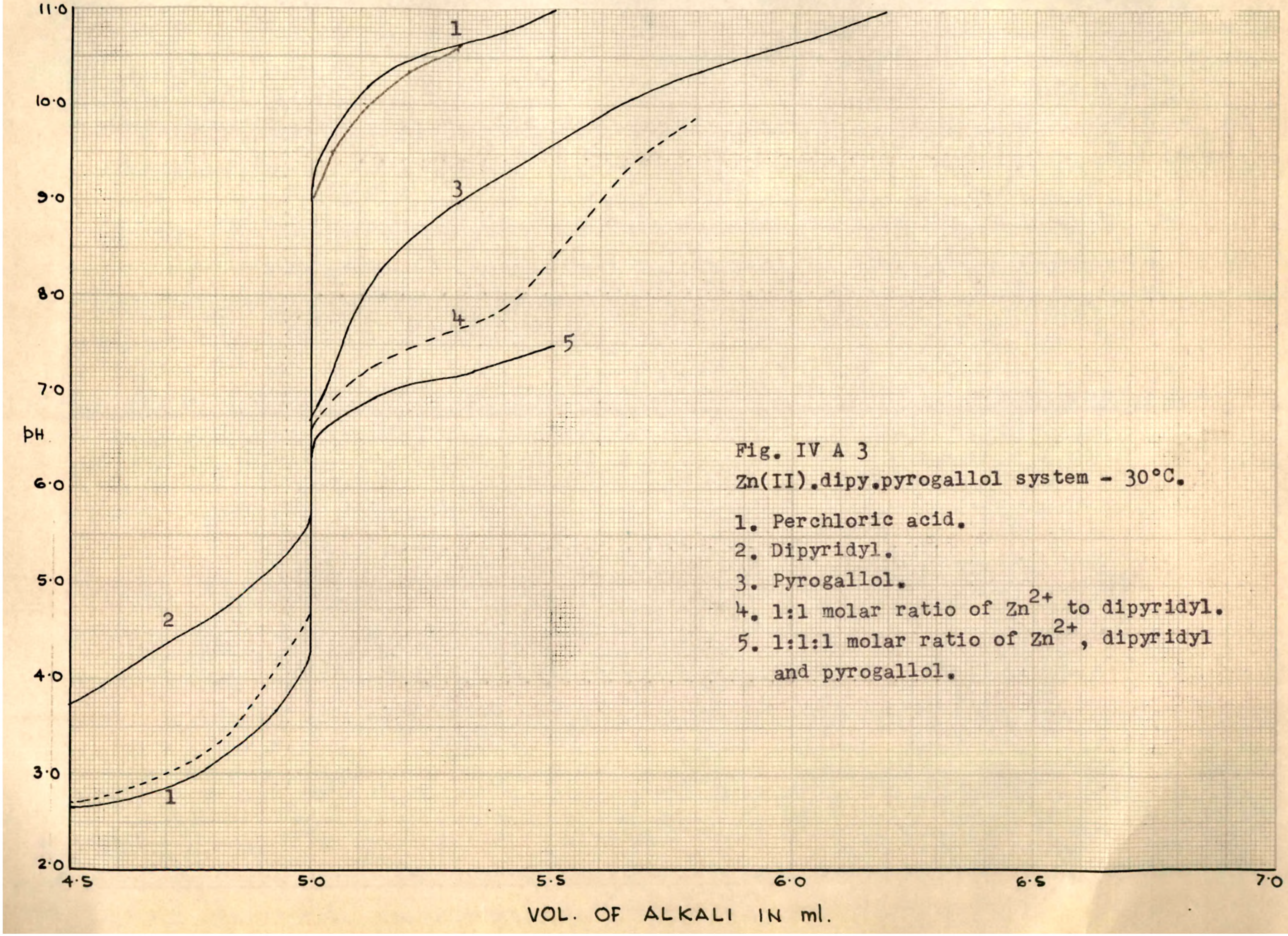


Fig. IV A 3

Zn(II).dipy.pyrogallol system - 30°C.

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

Table IVA 2.3

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

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

Protocatechuic acid		Zn.Dipy.Protocatechuic acid		Cd.Dipy.Protocatechuic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.00	3.00	2.00	3.00	2.00
4.00	2.35	4.00	2.35	4.00	2.35
4.50	2.60	4.50	2.60	4.50	2.60
4.60	2.74	4.60	2.74	4.60	2.74
4.70	2.86	4.70	2.86	4.70	2.86
4.80	3.10	4.80	3.10	4.80	3.10
4.85	3.30	4.90	3.45	4.90	3.45
4.90	3.45	5.00	3.80	5.00	3.80
4.95	3.60	5.05	3.95	5.05	3.95
5.00	3.80	5.10	4.20	5.10	4.20
5.05	3.95	5.15	4.32	5.15	4.32
5.10	4.20	5.20	4.50	5.20	4.50
5.15	4.32	5.25	4.75	5.25	4.75
5.20	4.50	5.30	5.00	5.30	5.00
5.25	4.75	5.34	5.35	5.34	5.35
5.30	5.00	5.38	5.90	5.38	5.90
5.34	5.35	5.40	6.25	5.40	6.25
5.38	5.90	5.44	6.50	5.44	6.75
5.40	6.25	5.48	6.72	5.48	7.05
5.42	6.65	5.52	6.90	5.52	7.25
5.44	7.00	5.60	7.15	5.60	7.60
5.46	7.30	5.65	7.24	5.65	7.78
5.50	7.70	5.70	7.30	5.70	7.88
5.54	8.00	5.75	7.35	5.75	7.95
5.58	8.25	5.80	7.40	5.80	8.00
5.62	8.45	5.90	7.55	5.90	8.15
5.66	8.60	6.00	7.70	6.00	8.30
5.70	8.70	6.10	7.80	6.10	8.40
5.80	9.20	6.15	7.95	6.15	8.45
5.90	9.60	6.20	8.10	6.20	8.55
6.00	10.00	6.30	8.60	6.30	8.75
6.10	10.25	6.40	9.10	6.40	9.10
6.20	10.50	6.50	9.60	6.50	9.40
6.30	10.70	6.60	9.90	6.60	9.75
6.40	10.90	6.80	10.40	6.80	10.30
6.50	11.00	7.00	10.65	7.00	10.80
		7.20	10.90	7.20	11.00
		7.30	11.05		

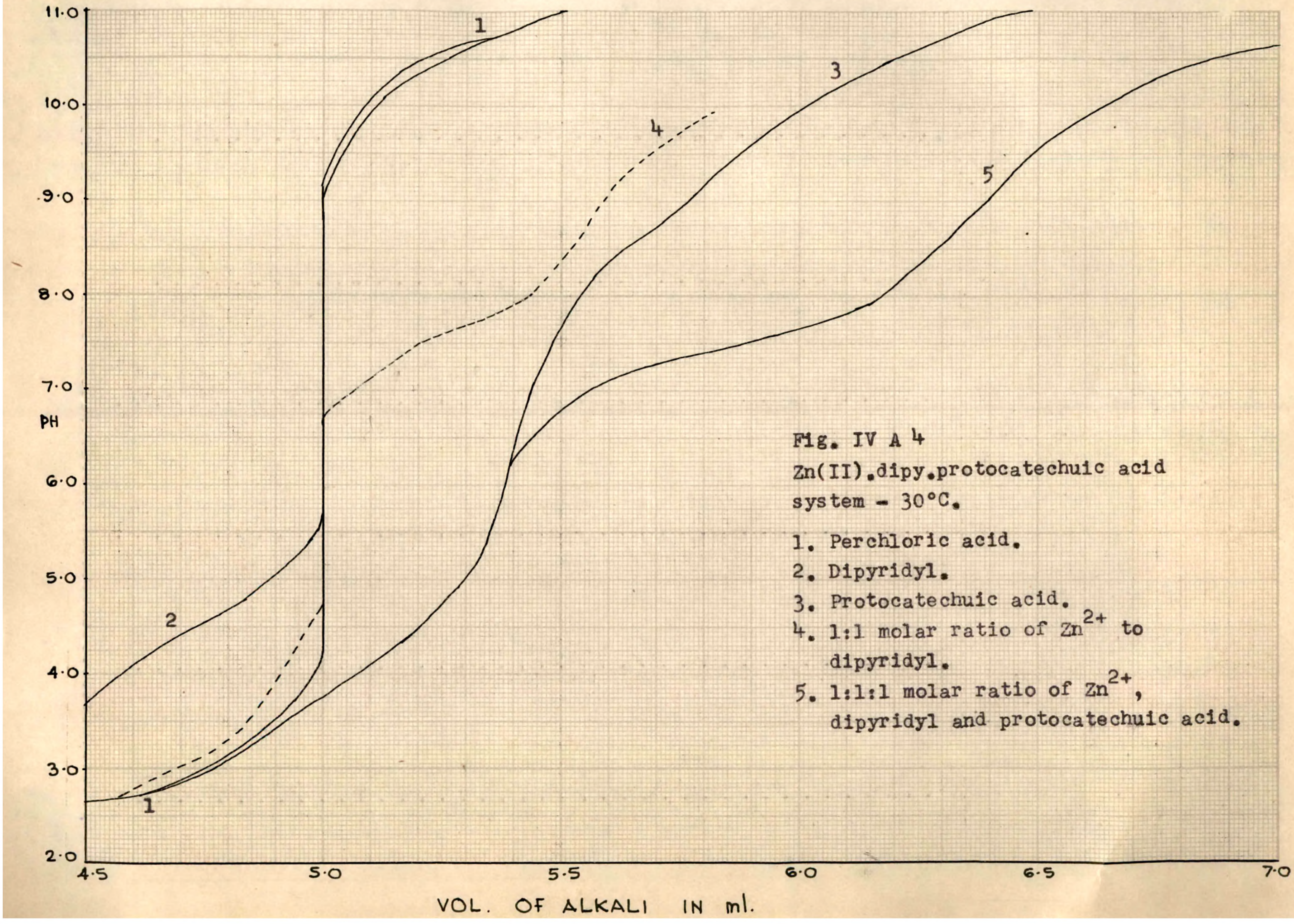


Fig. IV A 4
Zn(II).dipy.protocatechuic acid
system - 30°C.

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

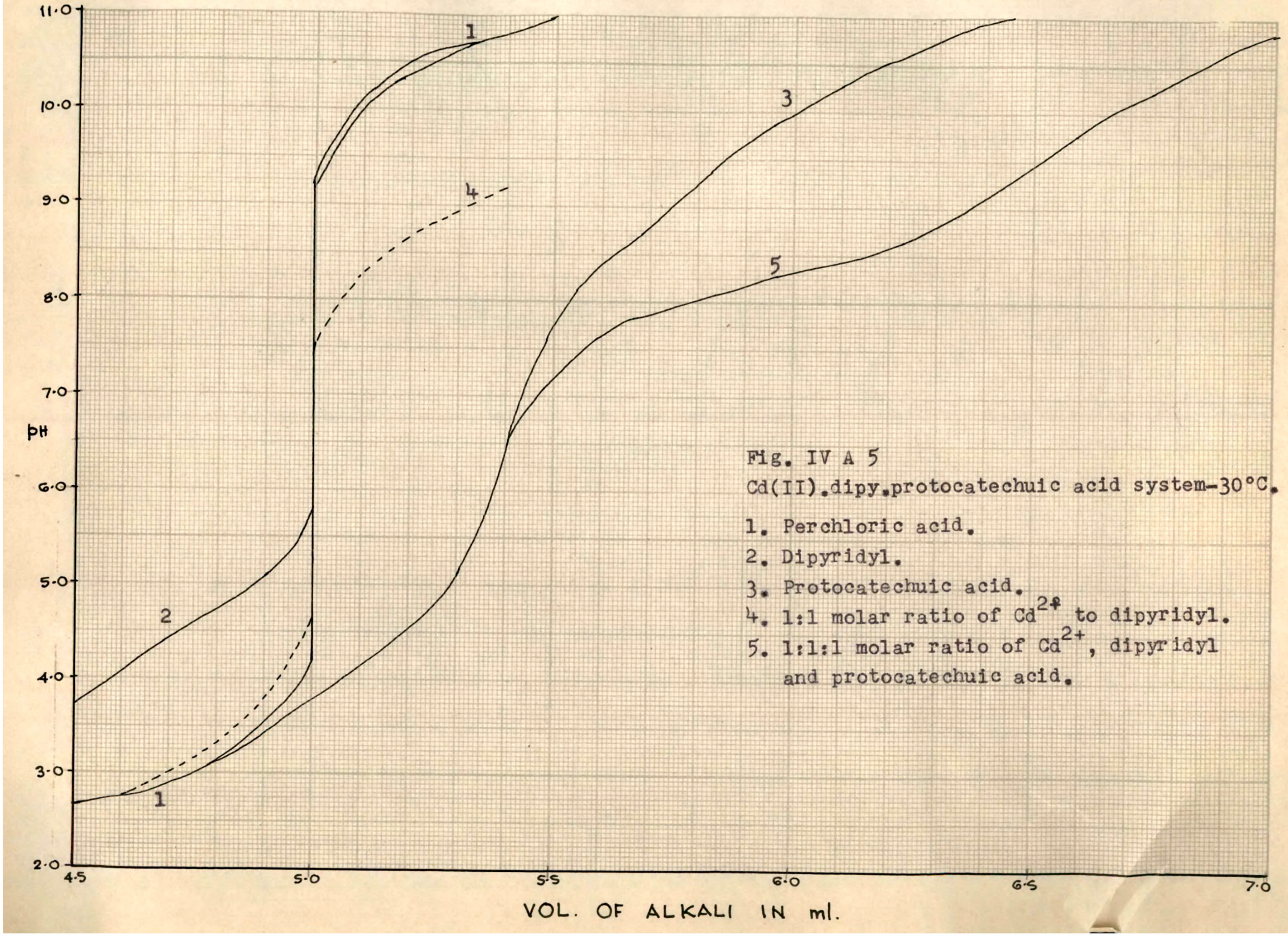


Fig. IV A 5

Cd(II).dipy.protocatechuic acid system-30°C.

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

Table IVA 2.1b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL$-\log(1-\bar{n})/\bar{n}$
7.30	1.97_2	5.00	5.15	0.15	0.15_2	0.74_6	8.62_0	7.87_4
7.40	1.96_2	5.00	5.20	0.20	0.20_3	0.59_4	8.44_9	7.85_5
7.50	1.96_0	5.00	5.27	0.27	0.27_5	0.42_1	8.29_3	7.87_2
7.60	1.95_2	5.00	5.34	0.34	0.34_8	0.27_2	8.14_2	7.87_0
7.70	1.94_8	5.01	5.42	0.41	0.42_1	0.13_8	7.99_8	7.86_0
7.80	1.94_4	5.02	5.50	0.48	0.49_3	0.12_2	7.85_0	7.83_8
7.90	1.93_6	5.02	5.56	0.54	0.55_7	$\bar{1}.90_0$	7.72_5	7.82_5
8.00	1.92_4	5.03	5.63	0.60	0.62_3	$\bar{1}.78_1$	7.60_2	7.82_1
8.10	1.90_8	5.04	5.69	0.65	0.68_1	$\bar{1}.67_0$	7.48_3	7.81_3

$\log K_{MAL} = 7.84 \pm 0.03$

Table IVA 2.2b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL$-\log(1-\bar{n})/\bar{n}$
6.90	1.97_2	5.02	5.11	0.09	0.09_1	0.99_9	8.30_9	7.31_0
7.00	1.96_8	5.03	5.15	0.14	0.14_2	0.78_1	8.13_7	7.35_6
7.10	1.96_4	5.04	5.24	0.20	0.20_3	0.59_4	7.97_2	7.37_8
7.20	1.96_0	5.04	5.31	0.27	0.27_5	0.42_1	7.81_7	7.39_6
7.30	1.95_2	5.05	5.37	0.32	0.32_7	0.31_3	7.65_0	7.33_7
7.40	1.94_4	5.05	5.43	0.38	0.39_0	0.19_2	7.50_1	7.30_9
7.50	1.92_8	5.05	5.50	0.45	0.46_6	0.05_9	7.36_5	7.30_4

$\log K_{MAL} = 7.34 \pm 0.05$

Table IVA 2.3b

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

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.10	2.00_0	5.45	5.55	0.10	0.09_9	0.95_9	9.59_7	-
7.20	2.00_0	5.46	5.63	0.17	0.16_8	0.69_4	9.43_5	8.74_1
7.30	2.00_0	5.46	5.70	0.24	0.23_8	0.50_5	9.30_5	-
7.40	2.00_0	5.47	5.78	0.31	0.30_7	0.35_3	9.12_1	8.76_8
7.50	2.00_0	5.48	5.86	0.38	0.37_6	0.22_0	8.96_8	8.74_8
7.60	1.94_9	5.49	5.93	0.44	0.45_5	0.07_8	8.83_4	8.75_6
7.70	1.93_5	5.50	6.00	0.50	0.52_1	$\bar{1}.96_3$	8.69_8	8.73_5
7.80	1.93_5	5.51	6.07	0.56	0.58_4	$\bar{1}.85_2$	8.57_6	8.72_4
7.90	1.92_0	5.52	6.14	0.62	0.65_1	$\bar{1}.72_9$	8.45_6	8.72_7

$\log K_{MAL} = 8.75 \pm 0.03$

Fig. IV A 7

Zn(II).dipy.pyrogallol system - 30°C.

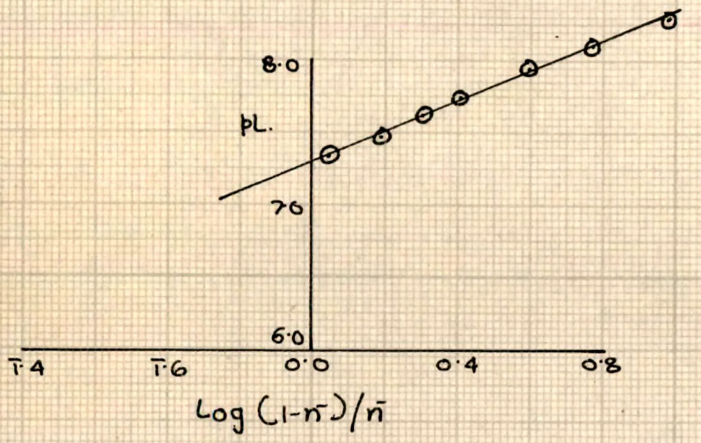


Fig. IV A 6

Zn(II).dipy.catechol system - 30°C.

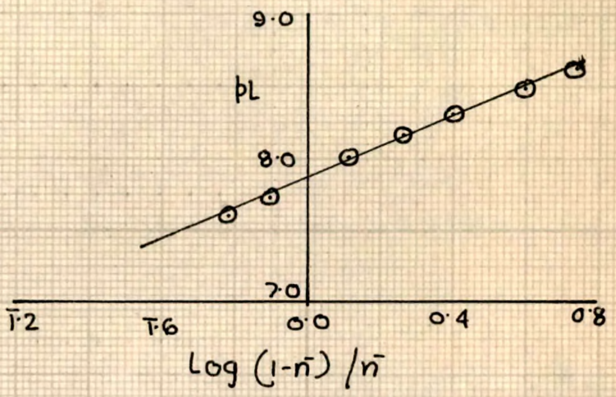


Fig. IV A 8

Zn(II).dipy.protocatechuic acid

system - 30°C.

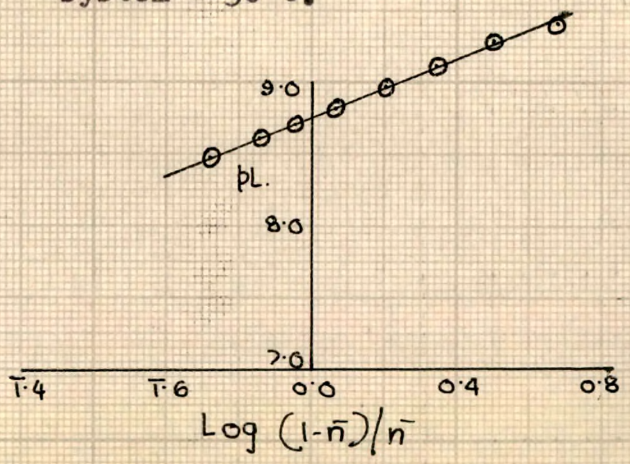


Table IVA 2.1c

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.90	1.93_6	5.02	5.12	0.10	0.10_3	0.94_0	7.41_5	-
8.00	1.92_4	5.03	5.17	0.14	0.14_5	0.77_0	7.23_6	6.46_6
8.10	1.90_8	5.04	5.22	0.18	0.18_8	0.73_5	7.07_4	6.43_9
8.20	1.88_8	5.05	5.30	0.25	0.26_4	0.44_5	6.92_7	6.48_2
8.30	1.86_8	5.06	5.37	0.31	0.33_1	0.30_5	6.78_2	-
8.40	1.84_8	5.08	5.45	0.37	0.40_0	0.17_6	6.63_5	6.45_9
8.50	1.81_6	5.09	5.52	0.43	0.47_1	0.05_0	6.51_8	6.46_8
8.60	1.79_2	5.12	5.60	0.48	0.53_0	$\bar{1}.94_7$	6.39_2	6.44_4
8.70	1.74_4	5.16	5.68	0.52	0.59_5	$\bar{1}.83_3$	6.28_4	6.45_1
8.80	1.71_9	5.20	5.75	0.55	0.63_9	$\bar{1}.75_2$	6.16_5	6.41_3
8.90	1.67_2	5.23	5.80	0.57	0.68_0	$\bar{1}.65_8$	6.05_4	-

$\log K_{MAL} = 6.44 \pm 0.04$

Table IVA 2.3c

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.80	1.93_5	5.51	5.66	0.15	0.15_3	0.74_3	8.25_6	7.51_3
7.90	1.92_6	5.52	5.73	0.21	0.22_0	0.54_9	8.10_1	7.55_2
8.00	1.88_0	5.53	5.80	0.27	0.28_9	0.39_1	7.95_4	7.56_3
8.10	1.84_0	5.55	5.87	0.32	0.35_1	0.26_6	7.80_7	7.54_1
8.20	1.80_0	5.57	5.94	0.37	0.41_5	0.14_9	7.67_0	7.52_1
8.30	1.76_0	5.58	6.01	0.43	0.49_3	0.01_2	7.55_4	7.54_2
8.40	1.72_0	5.60	6.09	0.49	0.57_6	$\bar{1}.86_7$	7.45_5	7.58_8
8.50	1.680	5.62	6.15	0.53	0.63_7	$\bar{1}.75_5$	7.35_2	7.59_7

$\log K_{MAL} = 7.55 \pm 0.04$

Fig. IV A 9

Cd(II).dipy.catechol system - 30°C.

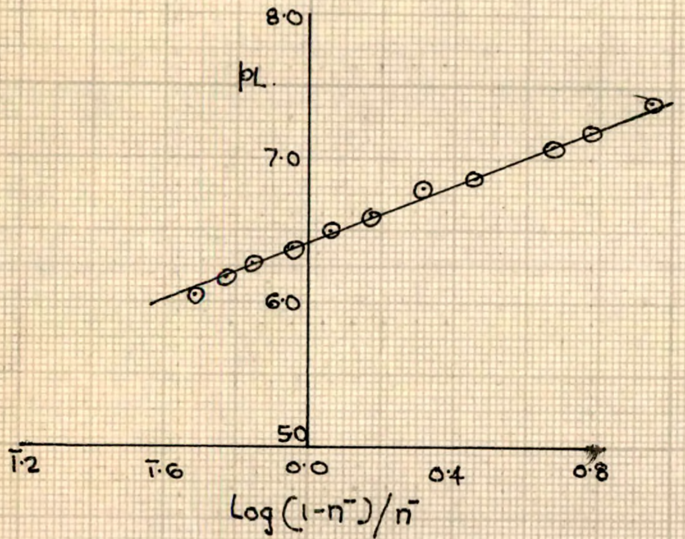


Fig. IV A 10

Cd(II).dipy.protocatechuic acid
system - 30°C.

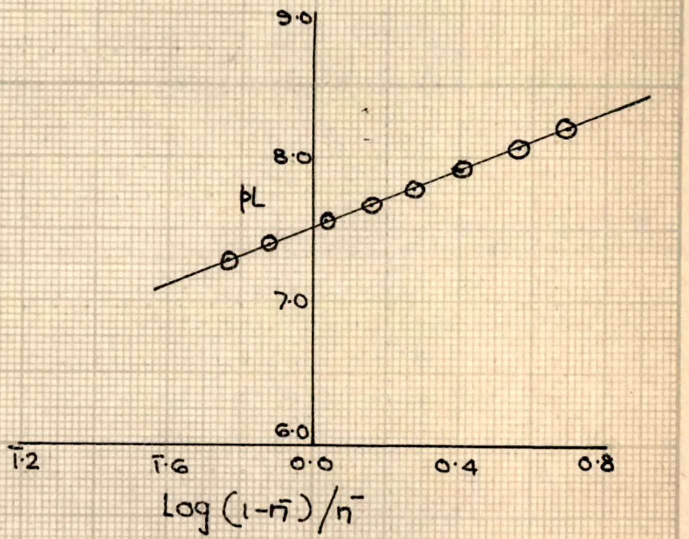


Table IVA 3.0

Logarithms of stability constants of ternary 2,2'-Dipyridyl-M^{2+}-ligand complexes (μ = 0.2M, 30°C.)

	Ligand (L)			
	Catechol	Pyrogallol	Protocatechuic acid	2,3-Dihydroxy-naphthalene
$\log K^{Zn(Dipyridyl)}_{Zn(Dipyridyl)L}$	7.84 ± 0.03	7.34 ± 0.05	8.75 ± 0.03	-
$\log K^{Cd(Dipyridyl)}_{Cd(Dipyridyl)L}$	6.44 ± 0.04	-	7.55 ± 0.04	-

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SECTION B

Since 1925, various scientists have carried out work on binary or ternary systems[1-3] in solution with salicylic acid or thiosalicylic acid as the primary or secondary ligand . The isolation of the solids involving salicylic or thiosalicylic acid as the coordinating ligands have also been reported.[4,5]

Bhattacharya and coworkers[6] studied the salicylic and thiosalicylic acid complexes with class A and class B type of metal ions and have interpreted the relative tendencies of M-O and M-S bonds. The greater stability of M-S bond compared to that of M-O bond has been indicated in various complexes.[7] The stability constants of metal complexes with several sulphur containing ligands have been measured and results have been explained in terms of M-S π interaction. The stability constants of the metal complexes of thioglycollic and β-mercaptopropionic acid, 2-aminoethane dithiol, cysteine and mercapto succinic acid have been determined.[8] It is noteworthy that cysteine forms quite stable complexes with Hg(II) and Fe(III). Stabilities of uranyl chelates of hydroxy, mercapto and amino derivatives of acetic, propionic and salicylic acids fall in the order $NH_2 > OH > SH$[9]. Uranyl ion forms a stronger complex with glycollate ion than with thioglycollate ion. This indicates class A behaviour of uranyl ion. The formation constants of Ni(II), Mn(II) and Tl(I) complexes with thioglycollic, thiolactic, thiomalic and thiosalicylic acids and with their corresponding hydroxy acids have been studied by Reddy and Bhattacharya.[6,10-12] The data exhibit class B character of Ni(II), border line character of Mn(II) and class A character of Tl(I). This has been explained in terms of M-S π interaction. Li and Manning[13] observed the greater stability of cysteine complexes of Zn(II) and attributed this to the coordination from sulphur to Zn(II), i.e. class B character of Zn(II). Schwarzenbach[14] has also observed the greater chelating tendency of β-mercapto ethyl amino diacetic acid than nitrilotriacetic acid. Recently Gerlach and Holm[15] have carried out NMR studies of β-aminethione and the corresponding oxygen containing compound and indicated π interaction in the Ni-S bond. ESR studies[16] of the Cu(II) diethyl dithiocarbamate complex also indicated the presence of Cu-S π bond. Possibility of M-S π interaction has also been discussed in a recent review article by Pettit.[17] Rickards and Johnson[18] have also shown the possibility of M-S π interaction on the basis of Mossbauer studies. Bonamico and Dessy[19] carried out X-ray studies of complexes involving M-S and M-Se bonds and have confirmed the back donation of electrons from metal orbitals to vacant π orbitals of sulphur and selenium ligand atoms. However, the nature of M-S bond is still not resolved. According to Pauling M-S dπ-pπ interaction stabilizes the bond. Jorgenson[20] and Klopman,[21] however, believe that M-S bond stability is due to greater σ interaction in M-S bond and contribution due to M-S π interaction is not very significant. Pettit[22,23] has also arrived at similar conclusion. Recently Bhattacharya and coworkers[24] have determined the stabilities of Ni^{2+} and Zn^{2+} complexes in the system [MAL] where A = dipyridyl and L = thioglycollic, thiomalic and thiolactic acids and have shown that M-S π interaction has not much contribution. However, the study of the system [MAL] where L = salicylic or thiosalicylic acid has not been attempted. So in the present study, an investigation of the ternary complex [MAL] where M = Zn^{2+} or Cd^{2+}; A = dipyridyl; L = salicylic or thiosalicylic acid has been carried out. The comparison of the formation constants of mixed ligand complexes with the formation constants of 1:1 complexes i.e. metal : secondary ligand, has also been made in the present investigation.

The formation constants of binary and mixed ligand complexes have been determined by using the extension of Irving-Rossotti titration technique as used in the chapter II & IVA. The reaction for the mixed ligand formation can be represented as follows :

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

$$K^{\mathrm{M.dipy.}}_{\mathrm{M.dipy.L}} = \frac{[\mathrm{M.dipy.L}]}{[\mathrm{M.dipy}]^{2+}\,[L]^{2-}}$$

The use of the above method is based on the consideration of the fact that M.dipy $^{2+}$, (where M = Zn^{2+} or Cd^{2+}) 1:1 complex is formed at low pH and it is stable at higher pH. The salicylic acid or thiosalicylic acid (L) combines at higher pH resulting in the formation of mixed ligand complex [M.dipy.L].

Following titrations were carried out to determine the formation constants of the binary and ternary complexes :

1. Perchloric acid (0.2M, 5.0 ml.) + sodium perchlorate (1.0M, 9.0 ml.) + ethyl alcohol (25.0 ml.) + conductivity water (11.0 ml.), total volume = 50.0 ml., μ = 0.2M.
2. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl in ethyl

alcohol (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + ethyl alcohol (20.0 ml.) + conductivity water (11.1 ml.), total volume = 50.0 ml., μ = 0.2M.

3. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand in ethyl alcohol (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.9 ml.) + ethyl alcohol (20.0 ml.) + conductivity water (11.1 ml.), total volume = 50.0 ml., μ = 0.2M.
4. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl in ethyl alcohol (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + ethyl alcohol (20.0 ml.) + conductivity water (11.2 ml.), total volume = 50.0 ml., μ = 0.2M.
5. Perchloric acid (0.2M, 5.0 ml.) + dipyridyl in ethyl alcohol (0.02M, 5.0 ml.) + secondary ligand in ethyl alcohol (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.7 ml.) + ethyl alcohol (15.0 ml.) + conductivity water (6.3 ml.), total volume = 50.0 ml., μ = 0.2M.
6. Perchloric acid (0.2M, 5.0 ml.) + secondary ligand in ethyl alcohol (0.02M, 5.0 ml.) + metal perchlorate (0.02M, 5.0 ml.) + sodium perchlorate (1.0M, 8.8 ml.) + ethyl alcohol (20.0 ml.) + conductivity water (11.2 ml.), total volume = 50.0 ml., μ = 0.2M.

The ionic strength of each solution was thus initially raised to 0.2M. Each of the above samples was titrated against 0.2M sodium hydroxide solution at 17°C. in 50 % alcoholic solution. 17°C. was the lowest temperature attainable and at this temperature evaporation of alcohol is negligible. The titration data have been reported in tables IV B 1.0 to IV B 5.0.

The plots of pH against volume of alkali have been presented in figs. IV B 1 to IV B 3.

Observation of the titration graphs provides the following informations :

As detailed in last chapter, $[Zn.dipy]^{2+}$ and $[Cd.dipy]^{2+}$ 1:1 complexes are formed at low pH and remain stable at higher pH where secondary ligands (L) get bound with them. M.dipy.SA curve (5) diverges from the salicylic acid curve (3) after pH ~ 5.0 and Zn.dipy.TSA curve (5) diverges from the thiosalicylic acid curve (3) after pH ~ 3.2 indicating that beyond this pH range the coordination of salicylic or thiosalicylic acid with $[M.dipy]^{2+}$ takes place.

The M.SA (1:1) curve (6) diverges from the salicylic acid curve (3) after the pH ~ 4.8 in the Zn(II) case and after pH ~ 5.5 in Cd(II) case, while Zn.TSA (1:1) curve (6) diverges from the thiosalicylic acid curve (3) after pH ~ 3.2. The horizontal distance must be due to the liberation of hydroxyl protons. In the lower pH range, however, there exists the possibility of the formation of complexes with protonated ligands.

Study could not be possible in Cd.dipy.TSA system because precipitation occurs at low pH.

Successive steps for the reaction in the mixed ligand system may be represented by the following equations :

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

$$[M.\text{dipyridyl}]^{2+} + L^{2-} \rightleftharpoons [M.\text{dipyridyl}.L]$$

The value of $\bar{n}$ were determined by substituting the horizontal distance $(V'''-V'')$ between the curve (5) and curve (3) in the mixed ligand system, and between the curve (6) and curve (3) in the 1:1 complex formation system, in the following equation :

$$\bar{n} = \frac{(V'''-V'')\left[N + E^{\circ} + T_{L}^{\circ}\,(Y - \bar{n}_{H})\right]}{(V^{\circ} + V'').\bar{n}_{H}.T_{M}^{\circ}}$$

where T_{M}° is the concentration of $[M.\text{dipyridyl}]^{2+}$ ion which id equal to the concentration of metal perchlorate used. The pL were calculated by using equation given in the chapter II (page 49). The values of $\bar{n}_{H}$ obtained were same as reported in the earlier thesis.[25] The values of proton ligand stability constants of salicylic acid and thiosalicylic acid were calculated and have been recorded in table IV B 6.0. Values of $\bar{n}$ and pL for the mixed ligand and 1:1 complex systems have been presented in table IV B 7.0 to IV B 12.0. Precise values of $\log K_{MAL}^{MA}$ and $\log K_{ML}^{M}$, were obtained by the method of linear plot[26] and have been presented in table IV B 13.0.

It is interesting to observe from the tables that the value of $K_{M.dipy.L}^{M.dipy}$ is nearly equal to K_{ML}^{M}, where $M = Zn^{2+}$ or Cd^{2+}, L = salicylic acid. The reason for this can be sought in the special behaviour of dipyridyl molecule as explained in the previous chapter. In case of Zn(II) complexes, behaviours of both salicylic and thiosalicylic acids as secondary ligands are alike. In case of thiosalicylic acid complexes also the formation constant in the ternary system, K^{MA}_{MAL} is not sufficiently lower than K^{M}_{ML}. However, it is expected that the metal ion having already donated π electrons to dipyridyl should have less tendency to donate π electrons to the secondary ligand. Hence there should have been significant difference in the values of K^{M}_{ML} and $K^{M.dipy}_{M.dipy.L}$ in case $M \rightarrow S$ π interaction is significant. The fact that $K^{Zn}_{Zn.TSA}$ is nearly equal to $K^{Zn.dipy}_{Zn.dipy.TSA}$ shows that the stability of M-S bond in binary system is due to greater σ interaction and contribution due to M-S π interaction is not very significant.

Table IVB 1.0

N = 0.2M V° = 50 ml. μ = 0.2M t = 17°C.

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} T°_{M} = 0.002M

Perchloric acid		Dipyridyl		Zn.Dipyridyl	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.80	1.00	1.70
2.00	1.80	2.00	2.00	2.00	1.80
3.00	2.00	2.50	2.10	3.00	2.00
4.00	2.30	3.00	2.20	4.00	2.30
4.10	2.35	3.50	2.40	4.20	2.42
4.20	2.42	4.00	2.65	4.30	2.52
4.30	2.52	4.20	2.80	4.40	2.55
4.40	2.55	4.30	2.95	4.50	2.70
4.50	2.70	4.40	3.12	4.60	2.90
4.60	2.85	4.50	3.35	4.70	3.10
4.70	3.00	4.55	3.45	4.75	3.25
4.75	3.12	4.60	3.55	4.80	3.40
4.80	3.30	4.65	3.70	4.85	3.65
4.85	3.52	4.70	3.82	4.90	3.95
4.90	3.80	4.75	4.00	4.93	4.10
4.93	4.00	4.80	4.20	4.96	4.35
4.96	4.25	4.83	4.40	4.99	4.55
4.99	4.55	4.86	4.60	5.00	5.50
5.00	8.70	4.89	4.90	5.04	5.88
5.02	9.10	4.90	5.00	5.08	6.05
5.04	9.50	4.93	5.30	5.12	6.20
5.06	9.95	4.96	5.65	5.16	6.32
5.08	10.25	4.99	5.95	5.20	6.45
5.10	10.50	5.00	9.75	5.25	6.55
5.12	10.75	5.02	10.12	5.30	6.68
5.15	11.00	5.04	10.50	5.35	6.80
		5.06	10.75	5.40	6.92
		5.09	11.00	5.45	7.10
				5.50	7.20
				5.55	7.40
				5.60	7.62
				5.64	7.85
				5.68	8.15
				5.72	8.45
				5.76	8.72
				5.78	8.85
				5.80	9.00 (ppt.)

Table IVB 2.0

N = 0.2M V° = 50 ml. μ = 0.2M t = 17°C.

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Salicylic acid		Zn.Salicylic acid		Zn.Dipy.Salicylic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.10	3.00	2.10	3.00	2.10
4.00	2.30	4.00	2.30	4.00	2.30
4.50	2.55	4.50	2.55	4.50	2.55
4.60	2.62	4.60	2.62	4.70	2.70
4.70	2.70	4.80	2.85	4.80	2.85
4.80	2.85	4.90	2.95	4.90	2.95
4.90	2.95	5.00	3.14	5.00	3.14
5.00	3.14	5.10	3.35	5.10	3.35
5.05	3.25	5.15	3.50	5.20	3.65
5.10	3.35	5.25	3.82	5.25	3.82
5.15	3.50	5.30	4.00	5.30	4.00
5.20	3.65	5.33	4.15	5.35	4.25
5.25	3.82	5.36	4.30	5.40	4.50
5.30	4.00	5.40	4.50	5.44	4.80
5.33	4.15	5.44	4.75	5.48	5.15
5.36	4.30	5.48	4.90	5.52	5.30
5.39	4.48	5.52	5.02	5.60	5.62
5.43	4.75	5.56	5.15	5.65	5.86
5.46	5.00	5.60	5.25	5.70	6.05
5.49	5.30	5.65	5.40	5.75	6.25
5.50	9.50	5.70	5.58	5.80	6.42
5.52	9.88	5.74	5.82	5.85	6.56
5.54	10.15	5.78	6.00	5.90	6.75
5.56	10.30	5.86	6.26	5.95	6.95
5.58	10.42	5.90	6.40	6.00	7.15
5.60	10.55	6.00	6.70	6.05	7.36
5.63	10.70	6.05	6.85	6.10	7.60
5.66	10.85	6.10	7.05	6.15	7.82
5.70	11.00	5.15	7.20	6.20	8.10
		5.20	7.40	6.24	8.40
		6.25	7.62	6.28	8.75
		6.30	7.82	6.32	9.05
		6.35	8.04	6.36	9.35
		6.43	8.45	6.40	9.60
			(ppt.)		(ppt.)

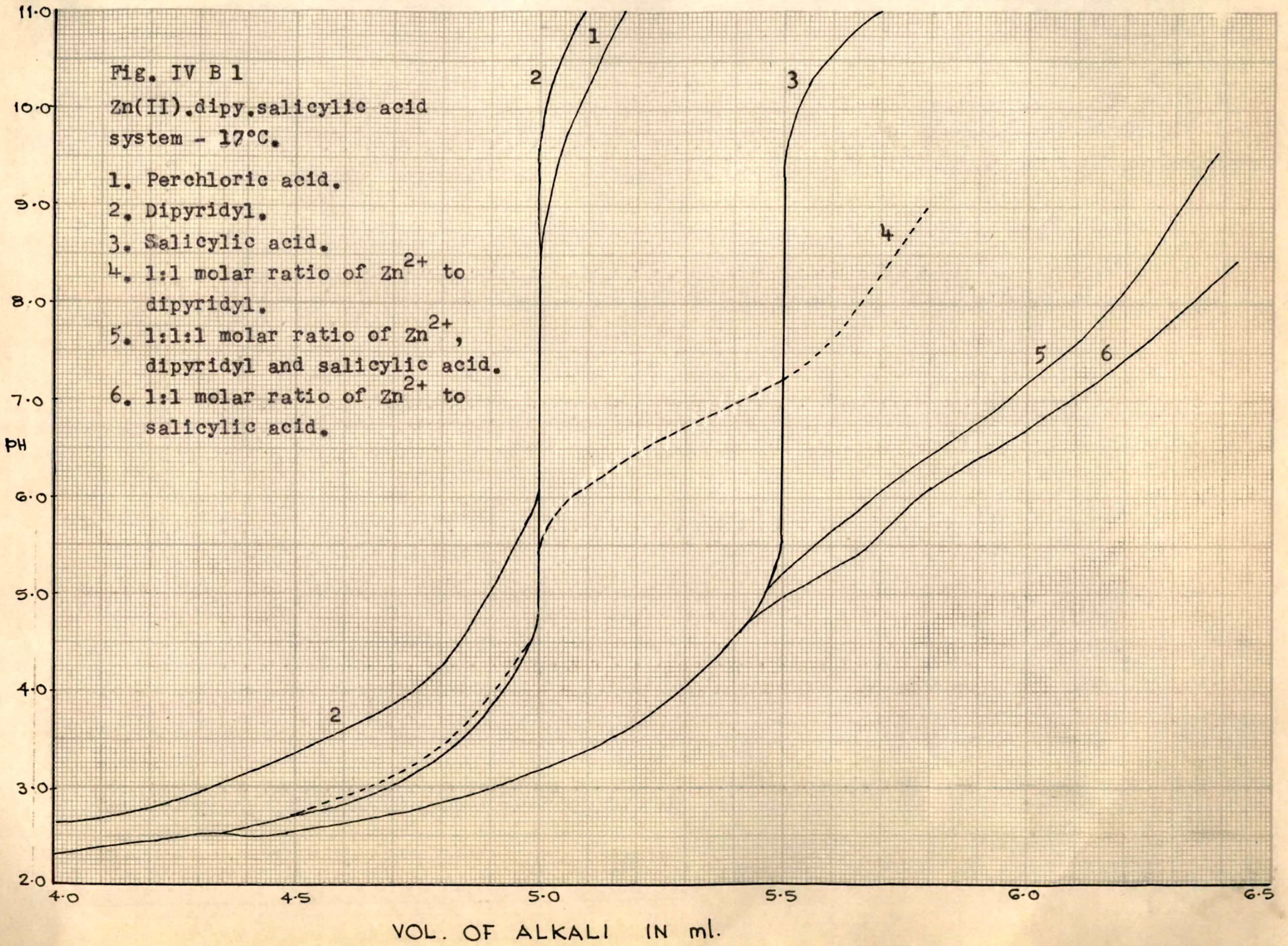

Fig. IV B 1
Zn(II).dipy.salicylic acid
system - 17°C.

1. Perchloric acid.
2. Dipyridyl.
3. Salicylic acid.
4. 1:1 molar ratio of Zn^{2+} to dipyridyl.
5. 1:1:1 molar ratio of Zn^{2+}, dipyridyl and salicylic acid.
6. 1:1 molar ratio of Zn^{2+} to salicylic acid.

Table IVB 3.0

$N = 0.2M$ $V^\circ = 50$ ml. $\mu = 0.2M$ t = 17°C.

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

Thiosalicylic acid		Zn.Thiosalicylic acid		Zn.Dipy.Thiosalicylic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.65	1.00	1.65	1.00	1.65
2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.00	3.00	2.00	3.00	2.00
4.00	2.30	4.00	2.30	4.00	2.30
4.50	2.52	4.50	2.52	4.50	2.52
4.60	2.62	4.60	2.62	4.60	2.62
4.70	2.76	4.70	2.76	4.70	2.76
4.80	2.95	4.80	2.95	4.80	2.95
4.90	3.20	4.90	3.20	4.90	3.20
5.00	3.48	5.00	3.35	5.00	3.35
5.05	3.62	5.10	3.55	5.10	3.55
5.10	3.80	5.20	3.70	5.20	3.70
5.15	3.98	5.30	3.85	5.30	3.85
5.20	4.15	5.40	3.98	5.40	3.98
5.25	4.32	5.50	4.10	5.50	4.10
5.30	4.50	5.60	4.25	5.55	4.20
5.35	4.75	5.70	4.38	5.60	4.30
5.40	5.00	5.75	4.48	5.65	4.40
5.45	5.30	5.80	4.60	5.70	4.50
5.47	5.55	5.85	4.75	5.73	4.65
5.49	6.05	5.90	5.05		(ppt.)
5.50	6.50	5.95	5.35		
5.52	7.05	6.00	5.65		
5.54	7.45	6.05	5.85		
5.56	7.70	6.10	6.05		
5.58	7.95	6.15	6.25		
5.60	8.10	6.20	6.40		
5.64	8.45	6.25	6.50		
5.72	9.00	6.30	6.60		
5.76	9.20	6.35	6.70		
5.80	9.45	6.40	6.90		
5.90	9.85	6.45	7.20		
6.00	10.20	6.50	7.55		
6.10	10.40		(ppt.)		
6.20	10.60				
6.30	10.75				
6.40	10.90				
6.50	11.00				

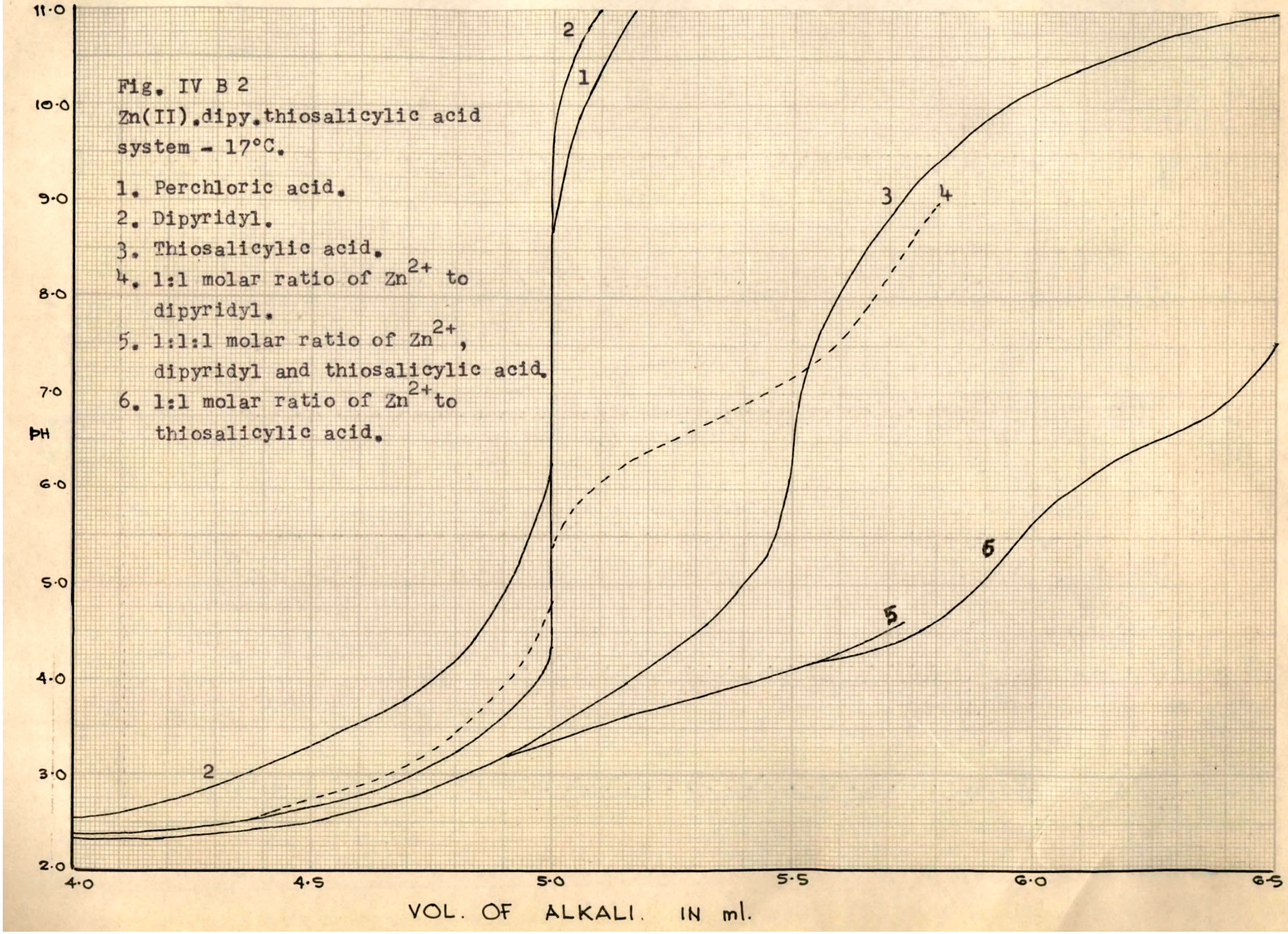

Fig. IV B 2
Zn(II).dipy.thiosalicylic acid
system - 17°C.

1. Perchloric acid.
2. Dipyridyl.
3. Thiosalicylic acid.
4. 1:1 molar ratio of Zn^{2+} to dipyridyl.
5. 1:1:1 molar ratio of Zn^{2+}, dipyridyl and thiosalicylic acid.
6. 1:1 molar ratio of Zn^{2+} to thiosalicylic acid.

Table IVB 4.0

N = 0.2M V° = 50 ml. μ = 0.2M t = 17°C.

E° = 0.02M T°_{Dipy} = 0.002M T°_M = 0.002M

Perchloric acid		Dipyridyl		Cd.Dipyridyl	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.80	1.00	1.70
2.00	1.80	2.00	2.00	2.00	1.80
3.00	2.00	2.50	2.10	3.00	2.00
4.00	2.30	3.00	2.20	4.00	2.30
4.10	2.35	3.50	2.40	4.20	2.42
4.20	2.42	4.00	2.65	4.30	2.52
4.30	2.52	4.20	2.80	4.40	2.62
4.40	2.55	4.30	2.95	4.50	2.75
4.50	2.70	4.40	3.12	4.60	2.95
4.60	2.85	4.50	3.35	4.70	3.20
4.70	3.00	4.55	3.45	4.75	3.30
4.75	3.12	4.60	3.55	4.80	3.50
4.80	3.30	4.65	3.70	4.85	3.70
4.85	3.52	4.75	4.00	4.90	4.00
4.90	3.80	4.80	4.20	4.93	4.20
4.93	4.00	4.83	4.40	4.96	4.45
4.96	4.25	4.86	4.60	4.99	4.85
4.99	4.55	4.89	4.90	5.00	5.90
5.00	8.70	4.90	5.00	5.04	6.35
5.02	9.10	4.93	5.30	5.08	6.60
5.04	9.50	4.96	5.65	5.12	6.80
5.06	9.95	4.99	5.95	5.20	7.15
5.08	10.25	5.00	9.75	5.25	7.35
5.10	10.50	5.02	10.12	5.30	7.60
5.12	10.75	5.04	10.50	5.35	7.80
5.15	11.00	5.06	10.75	5.40	8.02
		5.09	11.00	5.50	8.40
				5.60	8.75
				5.64	8.85
				5.68	9.00
				5.72	9.15
				5.76	9.35
				5.80	9.60 (ppt.)

Table IVB 5.0

N = 0.2M V° = 50 ml. μ = 0.2M t = 17°C.

E° = 0.02M T°_{Dipy} = 0.002M T°_{L} = 0.002M T°_{M} = 0.002M

Salicylic acid		Cd.Salicylic acid		Cd.Dipy.Salicylic acid	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.60	0.00	1.60
1.00	1.70	1.00	1.70	1.00	1.70
2.00	1.80	2.00	1.80	2.00	1.80
3.00	2.10	3.00	2.10	3.00	2.10
4.00	2.30	4.00	2.30	4.00	2.30
4.25	2.40	4.50	2.55	4.50	2.55
4.50	2.55	4.70	2.70	4.70	2.70
4.60	2.62	4.80	2.85	4.80	2.85
4.70	2.70	4.90	2.95	4.90	2.95
4.80	2.85	5.00	3.14	5.00	3.14
4.90	2.95	5.05	3.25	5.05	3.25
5.00	3.14	5.10	3.35	5.10	3.35
5.05	3.25	5.15	3.50	5.15	3.50
5.10	3.35	5.20	3.65	5.20	3.65
5.15	3.50	5.25	3.82	5.25	3.82
5.20	3.65	5.30	4.00	5.30	4.00
5.25	3.82	5.35	4.30	5.35	4.30
5.30	4.00	5.40	4.60	5.40	4.60
5.33	4.15	5.43	4.75	5.43	4.75
5.36	4.30	5.46	5.00	5.46	5.00
5.39	4.48	5.49	5.30	5.49	5.30
5.43	4.75	5.50	5.55	5.50	5.95
5.46	5.00	5.53	5.85	5.53	6.40
5.49	5.30	5.56	6.15	5.56	6.70
5.50	9.50	5.59	6.42	5.59	6.95
5.52	9.88	5.62	6.65	5.62	7.12
5.54	10.15	5.65	6.85	5.65	7.32
5.56	10.30	5.68	7.00	5.68	7.50
5.58	10.44	5.75	7.25	5.74	7.80
5.60	10.55	5.80	7.38	5.80	8.10
5.63	10.70	5.90	7.60	5.90	8.45
5.66	10.85	6.00	7.78	6.00	8.75
5.70	11.00	6.10	7.98		(ppt.)
		6.20	8.15		
		6.30	8.30		
		6.40	8.62		
		6.50	9.10		
			(ppt.)		

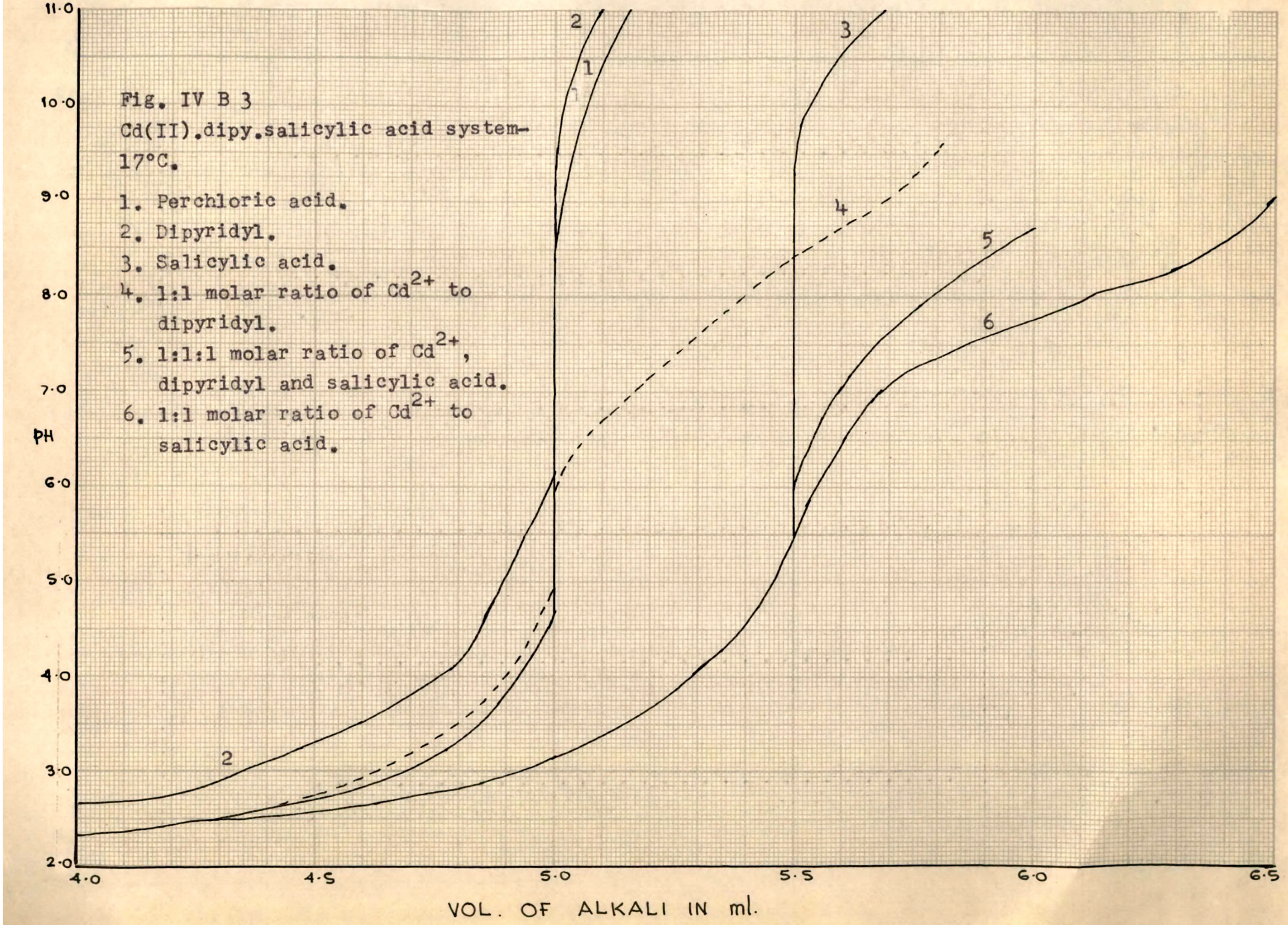

Fig. IV B 3
Cd(II).dipy.salicylic acid system-
17°C.

1. Perchloric acid.
2. Dipyridyl.
3. Salicylic acid.
4. 1:1 molar ratio of Cd^{2+} to dipyridyl.
5. 1:1:1 molar ratio of Cd^{2+}, dipyridyl and salicylic acid.
6. 1:1 molar ratio of Cd^{2+} to salicylic acid.

Table IVB 6.0

Proton ligand stability constants of various ligands (μ = 0.2M, 17°C.).

	Ligand (L)	
	Salicylic acid	Thiosalicylic acid
$\log {}^{P}K_{1}^{H}$	10.75	10.55
$\log {}^{P}K_{2}^{H}$	3.25	4.45
$\log {}^{P}K_{3}^{H}$	-	-

Table IVB 7.0

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Zn.Salicylic acid (1:1) system - 17°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
5.30	1.02_8	5.49	5.63	0.14	0.27_2	0.42_7	8.33_3	7.90_6
5.40	1.02_4	5.50	5.66	0.16	0.31_2	0.34_3	8.25_8	7.91_5
5.50	1.02_0	5.50	5.68	0.18	0.35_2	0.26_5	8.18_4	7.91_9
5.60	1.01_6	5.50	5.70	0.20	0.39_3	0.18_8	8.11_5	7.92_7
5.70	1.01_6	5.50	5.72	0.22	0.43_3	0.11_7	8.04_2	7.92_5
5.80	1.01_6	5.50	5.74	0.24	0.47_2	$\underline{0}.04_8$	7.97_5	7.92_7
5.90	1.01_2	5.50	5.76	0.26	0.51_3	$\bar{1}.97_7$	7.91_0	7.93_3
6.00	1.00_8	5.50	5.78	0.28	0.55_5	$\bar{1}.90_4$	7.84_9	7.94_5
6.10	1.00_8	5.50	5.82	0.32	0.63_4	$\bar{1}.76_1$	7.83_4	-

$\log K_1 = 7.94 \pm 0.04$

Table IVB 8.0

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Zn.dipyridyl. salicylic acid system - 17°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
5.70	1.01_6	5.50	5.62	0.12	0.23_6	0.51_0	7.91_1	7.40_1
5.80	1.01_6	5.50	5.64	0.14	0.27_5	0.42_1	7.83_6	7.41_5
5.90	1.01_2	5.50	5.66	0.16	0.31_6	0.33_5	7.76_2	7.42_7
6.00	1.00_8	5.50	5.68	0.18	0.35_7	0.25_5	7.68_8	7.43_3
6.10	1.00_8	5.50	5.70	0.20	0.39_6	0.18_3	7.61_6	7.43_3
6.20	1.00_4	5.50	5.73	0.23	0.45_8	0.07_3	7.56_2	7.48_9
6.30	1.00_4	5.50	5.75	0.25	0.49_7	$\underline{0}.05_2$	7.49_5	7.44_3
6.40	1.00_4	5.50	5.77	0.27	0.53_7	$\bar{1}.93_5$	7.43_1	7.49_6

$\log K_{MAL} = 7.43 \pm 0.06$

Fig. IV B 4
Zn(II).Salicylic acid (1:1)
system - 17°C.

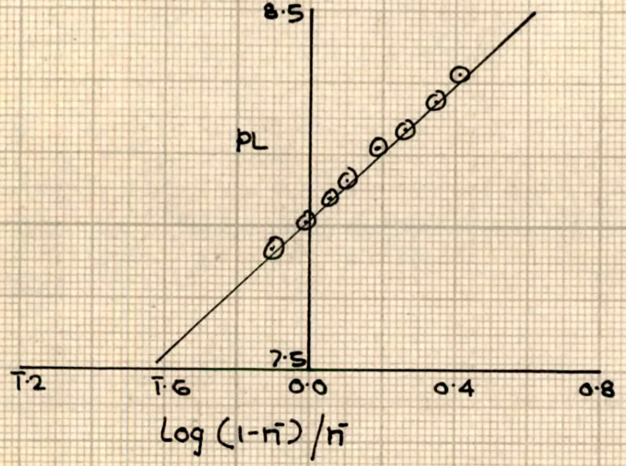

Fig. IV B 5
Zn(II).dipy.salicylic acid
system - 17°C.

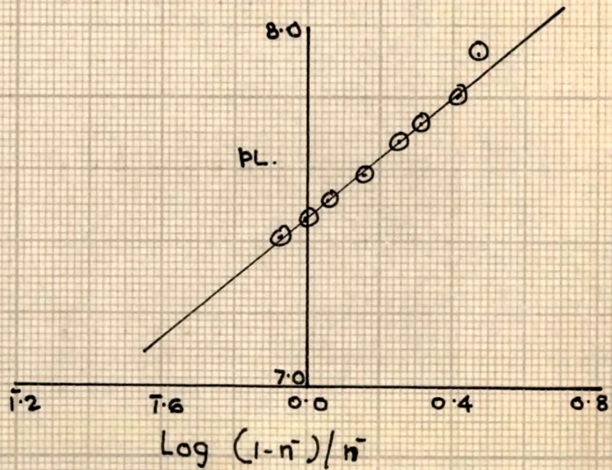

Table IVB 9.0

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Zn.Thiosalicylic acid (1:1) system - 17°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.60	1.83_1	5.04	5.11	0.07	0.07_6	1.08_4	10.63_3	-
3.70	1.79_9	5.07	5.16	0.09	0.10_0	0.95_4	10.45_8	-
3.80	1.78_3	5.10	5.25	0.15	0.16_8	0.69_4	10.31_0	9.61_6
3.90	1.74_3	5.13	5.32	0.19	0.21_7	0.55_7	10.15_6	9.59_9
4.00	1.71_1	5.16	5.40	0.24	0.28_0	0.41_0	10.01_8	9.60_8
4.10	1.65_5	5.19	5.48	0.29	0.35_0	0.26_8	9.89_1	9.62_3
4.20	1.62_3	5.22	5.54	0.32	0.39_3	0.18_8	9.75_5	9.56_7
4.30	1.58_7	5.25	5.63	0.38	0.47_8	$\underline{0}.03_8$	9.66_0	9.62_2
4.40	1.51_1	5.28	5.71	0.42	0.55_5	$\underline{1}.90_4$	9.57_4	9.67_0
4.50	1.46_3	5.30	5.76	0.46	0.62_8	$\bar{1}.77_2$	9.49_1	-

$\log K_1 = 9.61 \pm 0.06$

Table IVB 10.0

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Zn.dipyridyl. thiosalicylic acid system - 17°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.60	1.81_3	5.04	5.11	0.07	0.07_6	1.08_4	10.63_3	9.54_9
3.70	1.79_9	5.07	5.16	0.09	0.10_0	0.95_4	10.45_8	9.50_4
3.80	1.78_3	5.10	5.25	0.15	0.16_8	0.69_4	10.31_0	-
3.90	1.74_3	5.13	5.32	0.19	0.21_7	0.55_7	10.15_6	-
4.00	1.71_1	5.16	5.40	0.24	0.28_0	0.41_0	10.01_8	-
4.10	1.65_5	5.19	5.48	0.29	0.35_0	0.26_8	9.89_1	-
4.20	1.62_3	5.22	5.54	0.32	0.39_3	0.18_8	9.75_5	9.56_7
4.30	1.58_7	5.25	5.59	0.34	0.42_7	0.12_7	9.62_0	9.49_3
4.40	1.51_1	5.28	5.64	0.36	0.47_5	$\underline{0}.04_3$	9.50_3	9.46_0
4.50	1.46_3	5.30	5.70	0.40	0.54_6	$\bar{1}.91_9$	9.47_2	9.55_3

$\log K_{MAL} = 9.52 \pm 0.06$

Fig. IV B 6
Zn(II).Thiosalicylic acid (1:1)
system - 17°C.

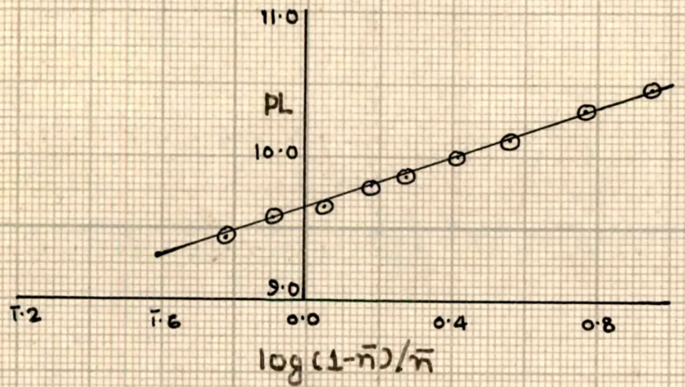

Fig. IV B 7
Zn(II).dipy.thiosalicylic acid
system - 17°C.

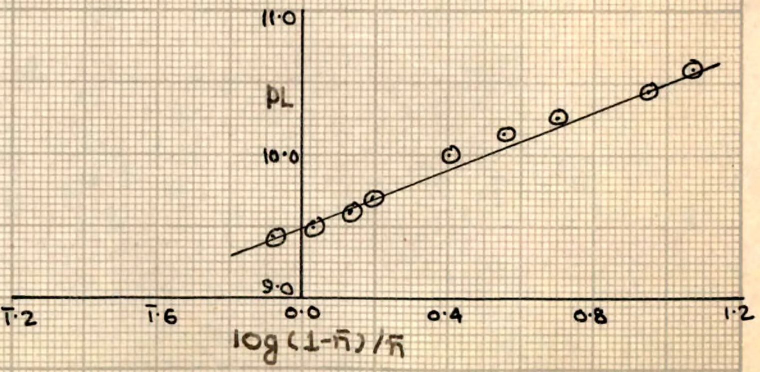

Table IVB 11.0

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Cd.Salicylic acid (1:1) system - 17°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
6.20	1.00_4	5.50	5.56	0.06	0.11_6	0.88_2	7.34_8	6.44_6
6.30	1.00_4	5.50	5.57	0.07	0.13_9	0.79_2	7.26_0	6.46_8
6.40	1.00_4	5.50	5.58	0.08	0.15_9	0.72_3	7.17_0	6.44_7
6.50	1.00_0	5.50	5.60	0.10	0.20_0	0.60_2	7.09_2	6.49_0
6.60	1.00_0	5.50	5.61	0.11	0.22_0	0.54_9	7.00_3	6.45_4
6.70	1.00_0	5.50	5.62	0.12	0.24_0	0.50_0	6.91_4	6.41_4
6.80	1.00_0	5.50	5.64	0.14	0.28_0	0.41_0	6.83_8	6.42_8
6.90	1.00_0	5.50	5.66	0.16	0.32_0	0.32_7	6.76_3	6.43_6
7.00	1.00_0	5.50	5.67	0.17	0.34_0	0.28_8	6.67_6	6.38_8
7.10	1.00_0	5.50	5.69	0.19	0.38_0	0.21_2	6.60_3	6.39_1
7.20	1.00_0	5.50	5.72	0.22	0.44_0	0.10_4	6.54_7	6.44_3

$\log K_1 = 6.44 \pm 0.05$

Table IVB 12.0

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Cd.dipyridyl. salicylic acid system - 17°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
6.70	1.00_0	5.50	5.56	0.06	0.12_0	0.86_5	6.85_0	5.98_5
6.80	1.00_0	5.50	5.57	0.07	0.14_0	0.78_8	6.76_0	5.97_2
6.90	1.00_0	5.50	5.58	0.08	0.16_0	0.72_0	6.67_0	-
7.00	1.00_0	5.50	5.60	0.10	0.20_0	0.60_2	6.59_2	5.99_0
7.10	1.00_0	5.50	5.61	0.11	0.22_0	0.54_9	6.50_3	5.95_4
7.20	1.00_0	5.50	5.63	0.13	0.26_0	0.45_4	6.42_6	5.97_2
7.30	1.00_0	5.50	5.65	0.15	0.30_0	0.36_8	6.35_0	-
7.40	1.00_0	5.50	5.67	0.17	0.34_0	0.28_8	6.27_6	-
7.50	1.00_0	5.50	5.68	0.18	0.36_0	0.24_9	6.18_9	5.94_0
7.60	1.00_0	5.50	5.70	0.20	0.40_0	0.17_6	6.11_7	5.94_1
7.70	1.00_0	5.50	5.72	0.22	0.44_0	0.10_4	6.04_7	5.94_3
7.80	0.99_2	5.50	5.74	0.24	0.48_3	0.02_9	5.98_3	-
7.90	0.99_2	5.50	5.75	0.25	0.50_4	$\bar{1}.99_3$	5.90_0	5.90_7
8.00	0.99_2	5.50	5.78	0.28	0.54_4	$\bar{1}.92_3$	5.83_7	5.90_4

$\log K_{MAL} = 5.96 \pm 0.06$

Fig. IV B 8
Cd(II).Salicylic acid (1:1)
system - 17°C.

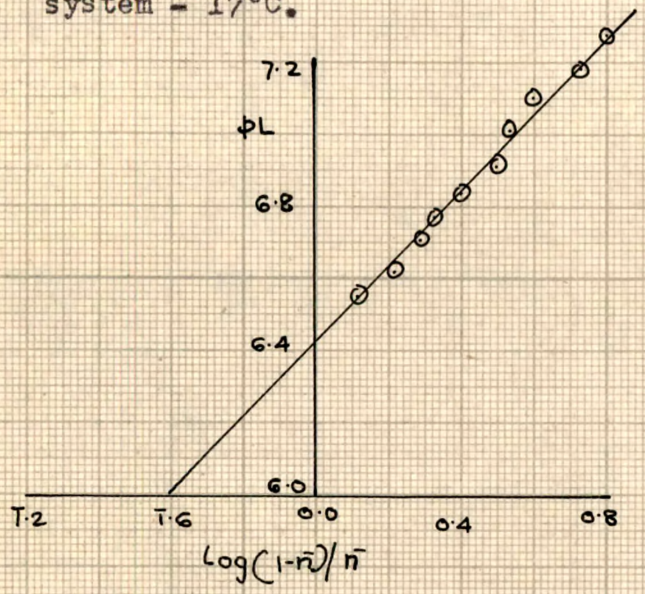

Fig. IV B 9
Cd(II).dipy.salicylic acid
system - 17°C.

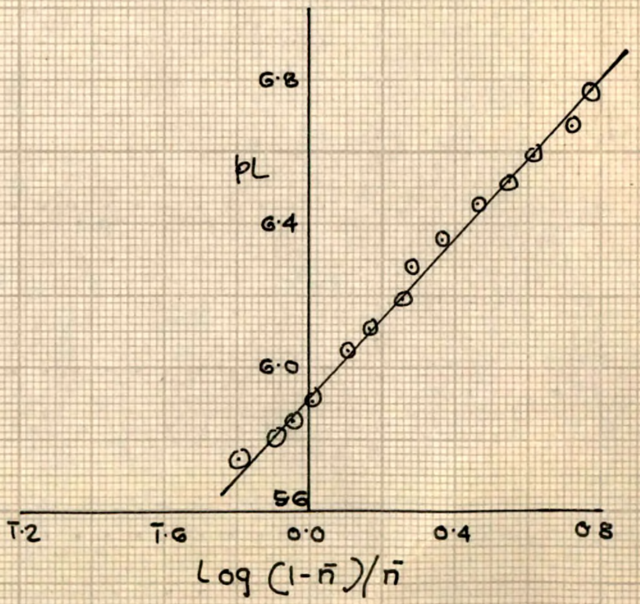

Table IVB 13.0

Logarithms of stability constants of binary M^{2+}-ligand (1:1) complexes and 2,2'-Dipyridyl-M^{2+}-ligand complexes (μ = 0.2M, 17°C.).

	Ligand (L)	
	Salicylic acid	Thiosalicylic acid
$\log K^{Zn}_{Zn.L}$	7.94 ± 0.04	9.61 ± 0.06
$\log K^{Zn(Dipyridyl)}_{Zn(Dipyridyl)L}$	7.43 ± 0.06	9.52 ± 0.06
$\log K^{Cd}_{Cd.L}$	6.44 ± 0.05	-
$\log K^{Cd(Dipyridyl)}_{Cd(Dipyridyl)L}$	5.96 ± 0.06	-

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SECTION C

The study of the formation of mixed ligand complexes in solution prompted the scientists to attempt their isolation in solid state. Various studies have been mentioned in the beginning of the section A of this chapter. Narain[1] reported the preparation and characterisation of the mixed ligand complex Cu(II) phthalamide with dipyridyl or o-phenanthroline. Condorelli and coworkers[2] synthesised the cyanomethylene complexes of Fe(II) with dipyridyl and o-phenanthroline and characterised them by spectral studies. Chidambaram and Bhattacharya[3] isolated some of the heterochelates of Cu(II) dipyridyl with amino acids. However, the mixed ligand complexes of Zn.dipyridyl or Cd.dipyridyl with polyhydroxy aromatic ligands have not been prepared. So an attempt has been made in the present investigation to isolate these compounds and to study their properties.

Method of preparation :

1. To 25 ml. of $ZnCl_2$ solution was added an equimolar solution of dipyridyl (25 ml.) dissolved in 50 % ethyl alcohol. No precipitation was observed. It was followed by the addition of equivalent catechol solution. The mixture was refluxed for five minutes. Yellowish grey coloured solid separated out. It was cooled and washed with water and then with 50 % ethyl alcohol to remove excess of dipyridyl. It was dried and analysed for the metal and nitrogen contents.

[Zn.dipy.cat].$4H_2O$ requires Zn = 16.20; N = 6.90 %,
found Zn = 16.50; N = 6.47 %.

2. To the 1:1 mixture of $ZnCl_2$ and dipyridyl solutions was added an equivalent quantity of pyrogallol solution. The mixture was refluxed for five minutes. Yellowish white coloured solid separated out. It was cooled, washed with water and 50 % ethyl alcohol and then dried and analysed for the metal and nitrogen contents.

[Zn.dipy.pyro] requires Zn = 18.73; N = 8.06 %,
found Zn = 18.45; N = 8.05 %.

3. To the 1:1 mixture of $ZnCl_2$ and dipyridyl solutions was added an equivalent quantity of 2,3-dihydroxynaphthalene dissolved in 50 % ethyl alcohol. The white coloured solid got separated. It was filtered and washed with water and 50 % ethyl alcohol to remove excess of dipyridyl and 2,3-dihydroxynaphthalene. It was dried and analysed for metal and nitrogen contents.

[Zn.dipy.2,3-di-naph] requires Zn = 14.40; N = 7.50 %,
found Zn = 14.50; N = 7.63 %.

4. To 25 ml. of $CdCl_2$ solution was added an equimolar solution of dipyridyl (25 ml.) dissolved in 50 % ethyl alcohol. No precipitation was observed. It was followed by the addition of equivalent quantity of catechol solution. The mixture was refluxed for five minutes. The yellowish grey coloured complex separated out. It was cooled, filtered and washed with water and 50 % ethyl alcohol. It was dried and analysed for the metal and nitrogen contents.

[Cd.dipy.cat].$2H_2O$ requires Cd = 27.00; N = 6.76 %,
found Cd = 27.50; N = 6.77 %.

Compounds were obtained in other cases also, but the analysis did not correspond to any definite composition.

Conductance measurements :

Solids are only partially soluble in alcohol and insoluble in water and other organic solvents. The conductivity of the alcoholic solutions were measured using Toshniwal Conductivity Bridge of the type CL01/01A. They were found to be non conducting.

Infrared spectral studies :

The infrared spectra of the complexes have been obtained in the range 4000 cm^{-1} to 400 cm^{-1} by KBr pellet technique. The bands obtained in different complexes have been shown below :

Complex	Characteristic bands cm^{-1}
1. [Zn.dipy.cat].4H_2O	~3600(w), ~3100(w), ~1590(m), ~1490(s), ~1450(w), ~1400(m), ~1320(w), ~1255(s), ~1190(m), ~1105(m), ~1030(m), ~850(m), ~790(m), ~770(m), ~740(w), ~600(w), ~410(w).
2. [Zn.dipy.pyro]	~3600(w), ~3100(w), ~2100(w), ~1950(w), ~1750(w), ~1650(s), ~1590(w), ~1510(s), ~1500(s), ~1450(s), ~1390(s), ~1310(s), ~1290(w), ~1250(w), ~1240(s), ~1170(s), ~1120(s), ~1080(w), ~1070(s), ~1040(s), ~900(s), ~780(m), ~740(s), ~600(m), ~410(w).
3. [Zn.dipy.2,3-di-naph]	~3600(w), ~3100(m), ~2100(w), ~1750(w), ~1600(s), ~1580(m),

∼1500(s), ∼1480(s), ∼1450(s),
∼1400(w), ∼1390(s), ∼1300(s),
∼1280(w), ∼1250(s), ∼1180(m),
∼1100(m), ∼1070(m), ∼1040(m),
∼ 900(m), ∼ 880(w), ∼ 780(m),
∼ 740(s), ∼ 600(m), ∼ 410(w).

4. [Cd.dipy.cat].$2H_2O$ ∼3600(w), ∼3070(w), ∼1590(m),
∼1570(m), ∼1490(s), ∼1440(s),
∼1390(m), ∼1320(w), ∼1270(s),
∼1190(m), ∼1170(m), ∼1110(m),
∼1070(m), ∼1050(m), ∼1020(m),
∼ 880(s), ∼ 790(s), ∼ 770(s),
∼ 740(w), ∼ 650(m), ∼ 630(w),
∼ 600(m), ∼ 470(w), ∼ 410(w).

Discussion :

The analytical data clearly indicate that the compounds have the composition [M.dipy.L].xH_2O (where M = Zn^{2+} or Cd^{2+}; L = catechol, pyrogallol or 2,3-dihydroxynaphthalene). This formula indicates that they are mixed ligand complexes. This can naturally be expected because dipyridyl combines with metal ions at low pH and $(M.dipy)^{2+}$ complex does not dissociate in the pH range of the combination of above polyhydroxy aromatic ligands. The water molecules are lost on heating the compounds upto 110°C. indicating that they are water of crystallisation.

The conductance measurement shows that they are non-conducting in nature. This indicates that they are non electrolyte i.e. neutral mixed ligand complexes.

The I.R. spectral studies of the complexes exhibit the bands corresponding to dipyridyl, catechol, pyrogallol or 2,3-dihydroxynaphthalene. The I.R. spectra of Zn(II) and Cd(II) compounds show band at ~ 3120-3000 cm^{-1} corresponding to C-H stretching frequency. The C=C and C=N stretching vibrations of the dipyridyl ring occurs in the range of ~ 1600-1300 cm^{-1}. Bands at ~ 1590 cm^{-1}, ~ 1490 cm^{-1}, ~ 1450 cm^{-1}, ~ 1320 cm^{-1} correspond to the ring stretching modes. The bands at ~ 1400 cm^{-1} and ~ 1250 cm^{-1} correspond to wagging and deformation of $-CH_2$ group. The C-C stretching band also occurs in the region ~ 1190 cm^{-1}. The band at ~ 1170 cm^{-1} may be due to ring -CH in plane deformation. The band at ~ 1070 cm^{-1} corresponds to C-N stretching frequency. The band at ~ 880 cm^{-1} is due to -CH out of plane deformation. M-N bond between metal and dipyridyl is expected to have partially double bond character due to π interaction and hence the band corresponding to M-N stretching is expected to have higher value than 500 cm^{-1}. Nakamoto[4] has shown that M-N stretching frequency undergoes coupling with other stretching vibrations resulting in number of bands. The bands at ~ 770 cm^{-1}, ~ 740 cm^{-1}, ~ 600 cm^{-1} may correspond to M-N vibration. The bands in the region ~ 410 cm^{-1} may be corresponding to M-O stretching.

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