CHAPTER –IV

RESULT & DISCUSSION

"Determination of Stability Constant of Metal Ligand Complexes Poetentiometrically"

FINAL REPORT
OF
MINOR RESEARCH PROJECT (CHEMISTRY)

UGC SANCTION NO FILE NO. 47-340/12 (WRO)

DATE: 08 MARCH 2013

Submitted TO

UNIVERSITY GRANT COMMISSION
WESTERN REGIONAL OFFICE,PUNE

Submitted By

Dr. Sayyed H.S.
Asst. Professor,
Dept. Of Chemistry,
Sir Sayyed College,
Aurangabad - 431001 (M.S.)

2013-2015

Date: 28/10/2015

CERTIFICATE

This is to certify that a copy of the final report of Minor Research Project entitled as "Determination of Stability Constant of Metal Ligand Complexes Poetentiometrically" completed by ***Dr. Sayyed H.S File No. 47-340/12 (WRO)*** Assistant Professor, Department of Chemistry has been kept in the library of Chemistry Department and an executive summary of the report has beenPosted on the website of the Sir SayyedCollege, Aurangabad.

Principal
Sir Sayyed College
Aurangabad.

UNIVERSITY GRANTS COMMISSION
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Phones: (020) 25696897,
25691477, 25691178,
Fax: (020) 25691477
Web site: www.ugc.ac.in

...o: 47-340/12(WRO)

...ccounts Officer
...sity Grants Commission
...khind, Pune-411007.

8 MAR 2013

26 FEB 2013

...: *Financial assistance to college teachers for undertaking Minor Research Projects – Release of first installment during XII[th] Plan.*

...dam,

The UGC on the recommendations of the Expert Committee has approved the Minor ...ch Project in the subject of **Chemistry** entitled "Determination of Stability Constants of Ligand Complexes Poetentiometrically" to be undertaken by **Dr. Mr. Sayyed H. S.**, of **SIR ...ED COLLEGE OF ARTS, COMMERCE AND SCIENCE, POST. BOX NO. 89, ...NGABAD, AURANGABAD-431 001.** The financial assistance of the UGC would be ... to Rs. 85000/-(Rupees Only) for a period of two years. An amount of Rs. **62500/-** (Rupees ... is presently being sanctioned as the first installment.

...Recurring ...t for Two	Amount (Rs)	Recurring grant	1[st] Year Amount	2[nd] Year Amount	Head of a/c
...s & Journals	10000	Contingency	5000	5000	4(iv)b (For General) 1.B(i)h(i)b (For SC) 1.B(i)h(i)b (For ST)
...ment	30000	Special Need	0	0	
		Travel/Field work	2500	2500	
		Chemicals & Glassware	15000	15000	
		Others	0	0	
...(Rs.)	40000		22500	22500	

...amount for the project: Rs. 85000/-

...ant is subject to the terms and conditions as mentioned below.

A Certificate of Acceptance of the conditions governing the research project should be sent immediately to this office.

The amount of the grant shall be drawn by the Accounts Officer (D.D.O), University Grants Commission on the grant-in-aid bill and shall be disbursed to and credited to the above-mentioned institute through D.D./ RTGS Confirmation No/ NEFT/ Transfer No.

The sanctioned amount is debatable to the Major Head 4(iv)b(For General), 1.B(i)h(i)b (For SC), 1.B(i)h(i)b (For ST) and is valid for payment during the financial year 2012 -2013 only.

The grant is subject to adjustment on the basis of Utilization Certificate in prescribed proforma submitted by University/College/Institute.

...OTE:

1. **The grant shall not be used self-financial/ non-grant/unaided courses & teachers.**
2. **Date of implementation will be the date of sanction of first installment.**
3. **The researcher is required to submit an Acceptance Certificate of the project in the enclosed format to the affiliating university, which would then be sent to UGC (WRO) in a bunch by the University.**

विश्वविद्यालय अनुदान आयोग
University Grants Commission
मानव संसाधन विकास मंत्रालय, भारत सरकार
Ministry of Human Resource Development, Govt. of India
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Western Regional Office, Ganeshkhind, Pune – 411007

Ph: 020 – 25696896, Fax: 020 – 25691477
Website- www.ugc.ac.in
Email: wrougc@gmail.com

No. F. 47-340/12(WRO)

Date: [illegible] 2015

THE PRINCIPAL,
SIR SAYYED COLLEGE OF ARTS COMMERCE & SCIENCE,
POST BOX NO. 89,,
ROSHAN GATE,
AURANGABAD - 431 001.

Subject: Submission of documents for Minor Research Project awarded to Dr. Mr. Sayyed H. S. in the Subject -Chemistry - Finalization of account.

Sir/Madam,

With reference to your letter No. SSC/ 2013-14 / 8201 dated 15 / 3 / 2014 you are requested to submit the following documents as marked tick below for settlement of accounts.

1. Audited Consolidated Utilisation Certificate for the amount actually incurred, duly signed by the Principal & C. A. with stamp.
2. Audited Consolidated Statement of Expenditure with item wise details under 'non-recurring & 'recurring' heads for the amount actually incurred duly signed by the Principal & C. A. with stamp & Registration No.
3. ~~Annual~~ / Final Report of the Project.
4. Assets Certificate.
5. Accession Certificate
6. Acceptance Certificate.
7. A copy of the proof about uploading of Executive summary of the report, Research documents, monograph, academic papers published under Minor Research Project on the website of the University/College.
8. Date of Starting ___________ Date of completion of the project__________
9. Refund of Rs. _________________ due to unspent balance

Yours faithfully,

(L. N. Sahu)
Section Officer

Copy to: -

DR. MR. SAYYED H. S.,
SIR SAYYED COLLEGE OF ARTS COMMERCE
& SCIENCE, POST BOX NO. 89,,
ROSHAN GATE,
AURANGABAD - 431 001

P.T.O.

Submit above documents early
10-06-2015

INDEX

Complexation is very important as far as bioinorganic chemistry is concerned. In nature there are various metal complexes present such as chlorophyll, hemoglobin etc. which are of vital importance. Porphyrin and corrin form chelate with metals. Several metal ions are used over centuries for treatment of different diseases for example Hg^{2+} for syphilis, Mg^{2+} for intestinal disorders and Fe^{2+} for anemia. Arsenic is a well known poison, but arsenic based compounds are used as antiprotozoal agents. The Literature survey reveals that metal complexes play important role in the biological activity of drugs. Antimicrobial agents have chelation tendency. The transition metal complexes of pyrimidine work as catalysts for drug interactions. The metal complexes of 5-carboxy-2-thiouracil have antitumour and antimicrobial activity. The magnesium complexes of 5-carboxy uracil have been reported as a potentially useful for Magnesium supplementation while its lithium complexes have been used in lithium therapies [1].

Now a days much interest has been paid to the transitional metal-ligand complexes, because they are very useful in various consumer products and processes, such as pulp and paper, textile, cosmetic, pharmaceuticals, food and detergent industry to remove metal ions [2]. Important reason for studying transitional metal-chelators is to prevent some diseases caused by excessive metal ions in the body. Metal ions found in our environment in a low concentration and our body needs it in small amounts. However due to increasing industrial use of metal, such as Copper, Cadmium, Lead, Mercury, Nickel, Iron, etc. people may be exposed to high metal ion concentration thus accumulate too much such metal ions in their body. In order to prevent some disease caused by metal poisoning and to reduce the concentration of metal ions in blood and urine in the body, chelating agent of metal or ligand therapy has been studied extensively. At present chelating agents such as ethylenediaminetetraacetate (EDTA), 2,3-dimercaptopropanol (BAL), D-penicillamine (D-PA), *mes*-2,3 dimercapto succinic acid (DMSA), Sodium 2,3-dimercapto-1-propanesulfonate (DMPS) and sodium 4,5-dihydroxybenzene- 1,3-disulfonate (Tiron) have been used for metal intoxication. These chelating agents are well known for their stable complex with some metal ions.[3]. Several studies have been reported on the interaction between chelating agent from certain phenolic acids e. g. gallic acid, pyridine carboxylic acid and non protein amino acids. Phenolic acids are complex groups of substances from secondary plant metabolites and naturally present in almost all plant materials. Recently, a lot of attention has been focused on phenolic acids because of their ecological role, physiological effects and natural anti-oxidant capacity. There are many phenolic acid compounds, such as vanillic acid, gallic acid, syringic acid, caffeic acid, ferulic acid, etc. [4]

Pyridine carboxylic acid is a group of organic compound which possesses both pyridine ring and carboxylic acid. The nitrogen center of pyridine provides a basic lone pair of electrons. Since this lone pair of electrons are not a part of the aromatic ring, they make pyridine behaves like a base with chemical properties similar to tertiary amines and acts as a Lewis base by donating this electron pair to Lewis acid, Pyridine is a weak ligand in forming complex with transitional metal ion. There are a few studies reporting the complex formation between some transitional metal ions with pyridine carboxylic acids such as picolinic acid, nicotinic acid, dipicolinic acid and isonicotinic acid. Non protein amino acids are amino acids which are not involved in primary metabolism. More than 700 such amino acids have been reported and 300 of them are found in plant. Several studies on non protein amino acids have been conducted, such as 4-*N*-oxalyl-2,4-diaminobutyric acid, diaminobutyric acid, 2,3-diaminopropionic acid, 3-*N*-oxalyl-2,3-diaminopropionic acid, 2-amino-6,*N*-oxalylureidopropionic, norleucine, etc .[5]

Hence the aim of present study is to determine the stability constant values of the complexes that are formed between transition metal ions (Cu^{2+}, Ni^{2+} ,Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}) with Nicotinic Acid (NA), Mandelic Acid (MA) , Gallic acid (GA) 3,5 Dinitro-Salicylic acid (DNS), 4-amino benzoic acid (PABA), 3-aminophenol (AMP),Quinol (Qu) ,2,2-bipyridyl¸ (BPD) in aqueous solution using pH-potentiometric titration technique. All these studies are conducted at constant ionic strength (Sodium nitrate 1 M) at 27^{0}C.

1.1 Metals -Biological Role and Toxicity

Metals occur in nature in the combined or Free State. The earth's crust is the biggest source of metals. Some soluble salts of metal are also found in sea water.
Metals are essential elements that naturally appear in the earth crust and involve in all aspects of life, e.g. the stabilization of biological structures from cell walls to protein formation. Metals have tendency to donate electrons and form basic oxides. [6] Biologically, 30 out of 112 elements known are essential for living organism and involved in cellular, physiological and structural function, cofactors of enzymes and also play important role in muscle contraction, nerve transmission, blood clotting and oxygen transport. An essential element is an element that is required in a small amount for preventing impaired function. An element is called essential elements if it meets certain criteria such as physiological deficiency appears when the element is removed from purified diet; The deficiency can be made good by addition of specific element but can't be wholly replaced. These 30 essential elements have been

CHAPTER –IV

RESULT& DISCUSSION

The results obtained during the determination of stability constant using potentiometer are analyzed by the computer programme and the stability constant values are calculated. Graph of $\overline{n_A}$ vs. pH for proton ligand system was plotted and in most of the cases found to extend between 0-2 indicates that ligand has two replaceable protons. Ligand titration curve had a lower pH value than acid titration curve. Displacement of ligand titration curve along volume axis with respect to acid titration curve is indication of proton dissociation. Values of $\overline{n_A}$ obtained are within range 0.2- 0.8 and 1.2-1.8 indicating formation of 1:1 and 1:2 complexes. Deviation of A+L curves from A+L+M curves indicates formation of complex.

The Metal-ligand stability constants of binary complexes are evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes are absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds.

1) Maximum value of $\overline{n_A}$ is 2 indicating the formation of 1:1 and 1:2 complexes only.

2) The metal ion solution used in the study are very dilute, hence there is no possibility of formation of polynuclear complexes.

3) The hydrolysis of the metal ions was suppressed due to complex formation, precipitation did not appear during the titration.

4) The metal titration curves are displaced to the right hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand.

5) The large decrease in pH for the metal titration curves relative to the ligand titration curves points to the formation metal complexes.

a) In most cases, the colour of the solution after complex formation observed to be different from the colour of the ligand at the same pH.

Higher is the pKa value, lesser is the tendency to ionize or in other words lesser acidic character. Some variations may be due to different experimental condition.The addition of metal ions to free ligand solutions lowered pH value .This shows that the complexation reactions proceed through release of protons.

Farooqui et al [1] reported that a low value of stability constant suggests that ligand is suitable for formation of complex at optimum physiological condition. This may favour the binding of ligand with nucleic acid of cell through transition metal and helps in transportation of drugs to the site of its physiological action.

In the present investigation values of $logK_1$ found to be more than $logK_2$ which is in agreement with literature. [2-7]. The results shows that the ratio of $logK_1/logK_2$ is positive in most of the cases which indicate that there is a little or no steric hinderance to the addition of secondary ligands molecules which in agreement work reported by Deosarkar and Narwade.[8]. Higher $logK_1$ may be due to weaker interaction of second ligand than first one. In few cases reported the $logK_2$ values are higher than $logK_1$, this is in agreement with some earlier researchers.[9-11]. $LogK_1$ for some ligands are higher than $logK_2$, this is due to fact that the interaction of second bulky ligand is weaker than the first ligand i.e.1:2 species is not formed until complete formation of 1:1 species. This can be ascribed to i) increase in the Lewis acidity of free metal ion as compared to 1:1 chelated ion ii) the steric hinderance caused by second bulky ligand molecule. Higher value of $logK_2$ than $logK_1$ indicates trans effect for second coordination.

Dissociation process is nonspontaneous process, endothermic and entropically unfavourable. The formation of metal complexes has been found to be spontaneous, endothermic and entropically favoured. In the following section, a detail discussion regarding potentiometric evaluation of stability constant is given. These values are represented in the table 4.1(a) & b for 1:1 and 1:2 complexes.

4.1 Complexes of Nicotinic Acid

The complexation of Nicotinic acid with transition metal ions has been studied under the experimental condition as described in Chapter II. These are presented in tabular form (table 4.1a & b) for 1:1 complexes & 1:2 complexes. The titration curves were plotted for ligand, and ligand + metal system. The values were analysed to get protonation constant and metal –ligand stability constant.

The value of $\overline{n_A}$ lies in the range of 0-1 indicating that ligand has only one replaceable proton. The pK_H value obtained is 5.425 considering the half integral method. In case of 1:2 ratio of metal and ligand, Co(II) complexes are exceptionally more stable than Cu(II) complexes. Iztok Turel et al [12] have studied complexation of Ciprofloxacin in aqueous solution at 25^0 C; They reported two pKa values, 6.17 for 3-carboxylic group and 8.54 for nitrogen of piperazine group. They also reported formation of 1:1 complexes. The complexation of Nicotinic acid with metal ions under study gives metal ligand stability constants which are shown in the table 4.1 a and 4.1 b

Table 4.1a Proton Ligand Constant and Stability constants of Nicotinic acid (1:1 ratio)

Proton-Ligand stability constant	Metal- ligand stability constant	
	Metal	Log K_1
Half integer pK_1- 5.200 Point wise pK_1 - 5.4254	Cu (II)	3.72205
	Zn (II)	3.65391
	Ni (II)	3.61710
	Co(II)	3.6623
	Cd (II)	3.5100

Table 4.1b Metal Ligand Stability Constants for Nicotinic acid (1:2)

Metal ion	Metal Ligand Stability Constants		
	Log K_1	Log K_2	Log β
Cu (II)	3.1144	3.1032	6.2176
Zn (II)	3.1080	3.0983	6.2064
Ni (II)	3.1099	3.1491	6.2591
Fe (III)	4.1094	3.8639	7.9733
Co (II)	3.1029	3.1311	6.2341
Cd (II)	3.1057	3.1027	6.2084

Tuncer Degim et al [13] compared stabilities of naproxen and salicylic acid and reported value 6.512 and 4.325 for carboxyl group in naproxen and salicylic acid. M.Khalil et al [14] studied complexes of dipicolinic acid and amino acids with bivalent metal ions in aqueous medium, evaluated pKa 4.53 and 2.32 for dipicolinic acid. They also reported high stabilities for Copper and Nickel complexes. Patil et al [15] studied interaction of transition metal ions with Ibuprofen and Paracetamol. They assigned pKa value for –COOH group in Ibuprofen is 5.32. They also reported formation of 1:1 complexes and high value of stabilities for Copper and Zinc complexes. Sekhon et al [16] reported pKa value 5.709 (carboxyl group) and 8.044 (piperazinyl group) for Ciprofloxacin. Gamerio P. et al [17] reported pKa values 6.25, 8.44 and 6.10, 8.60 for norfloxacin and ofloxacin. Patil [18] reported two pKa values for NA as 9.05 and 4.95. He also reported high value of stability constant for complexes of Copper (II) and Zinc ion (II). Hence the order of stability is in agreement with our results. Patil et al [19] studied interaction of transition metal ions with NA and reported pKa value 4.74 for NA. They have found that the sequence of stability complexes with respect to metal ions is due to decreasing atomic radius and increasing second ionization potential. Janrao et al [20] have recently observed 4.90 pKa value for the NA and 6.4790 for metal ligand stability constant of Zinc complex. They also reported formation of 1:1 complexes. Zaid et al [21] studied stabilities of ciprofloxacin moiety and observed high values of stability for Copper complexes. Farooqui et al [22] evaluated two pKa values for picolinic acid as 10.95 and 8.83 in aqueous medium using potentiometry. They also reported high values of stability constants for Cobalt than Nickel complex. Nair et al [23] observed two stability constants for NA as 4.69 and 7.02 at 37° C. They reported formation of 1:1 and 1:2 complexes. They also reported NA as a bidentate ligand and binding of ligand to metal ion through N-pyridine and O of carboxalato atoms like that of pyridine-2-carboxylic acid.

Anita Gupta [24] studied stability of ampicillin trihydrate in water ethanol medium 50% V/V maintaining ionic strength at 0.1M KNO_3 with bivalent metal ions. She reported pKa value of 6.98 and formation of 1:1 complexes. For drugs to remain in biologically active form, the stability constants should be in the range of 3-5. The stability values are found to be in biologically active range and highest value was found for Copper (II) metal ion. These stability values may be informative for biochemist during drug design or drug discovery.

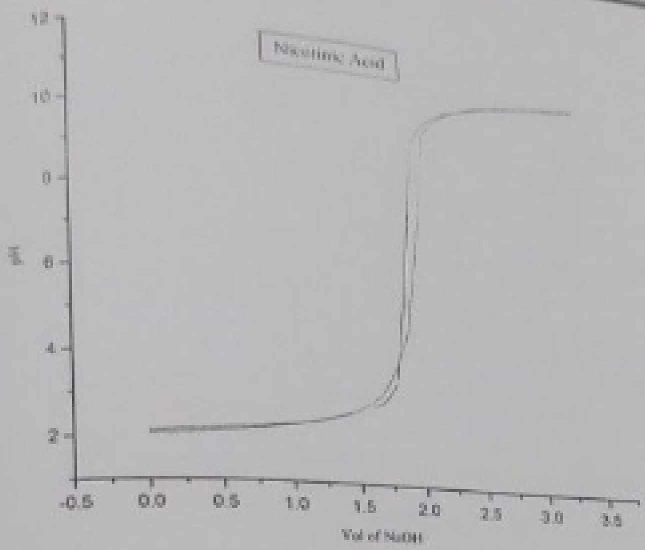
Erzalina Hernowo [25] reported two values of pKa as 2.22 and 4.59 for carboxylic acid group and pyridine nitrogen, also compared stability constant of NA with GA and proved that NA is weaker ligand.

For the present investigation, the order of stability may be assigned as follows

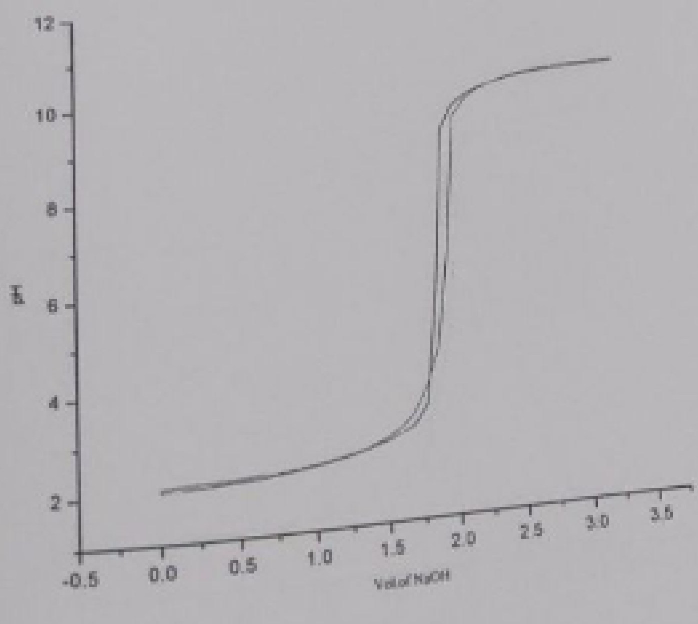
Cu(II) > Zn(II) > Ni(II) > Co(II) > Cd(II) for 1:1 complexes and

Fe(III) > Zn(II) > Co(II) > Cu(II) > Cd(II) > Zn (II) for 1:2 complexes.

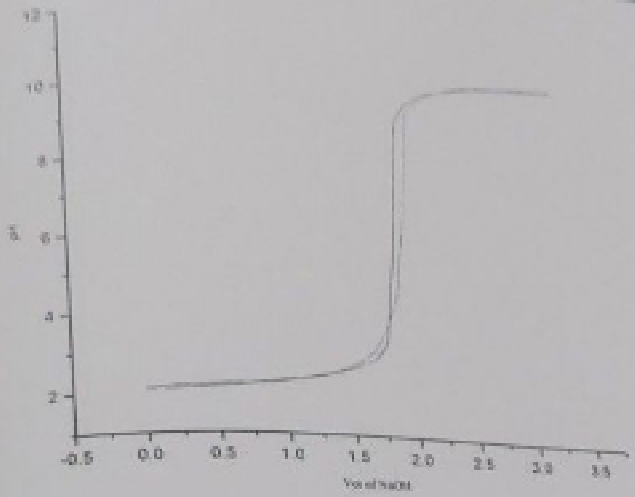
Rasheed H. A. and Maqsood Z.T. [26] studied solid state complexes of NA with Cu (II) , reported that NA complexes are water insoluble, octahedral in nature and formation of 1:1 and 1:2 complexes is detected. Cu (II) nicotinate complexes reported to exert diverse bioactivities. Monodentate nature of NA and possibility of bonding through Nitrogen was observed. Low values of stability of NA-Cu (II) complexes are due to weak nature of NA ligand. Kayande et al [27] also studied the complexation of NA with Cu (II), observed pKa 3.48. Interactions of insulin –mimetic zinc complexes of 2-picolinic acid was studied by E. Anna Ebedy et al [28], they also reported complexation through pyridine nitrogen and carboxylate oxygen for pKa 1.00 and 5.19. Solution behaviour of enrofloxacin (erf) complexes with transition metal ions in the presence of 1, 10 phenanthroline was investigated by R. Saraiva et al [29]. The results obtained show that at physiological condition only Copper form stable complexes, they reported pKa values 6.17 and 9.34 for -COOH group and piperazine in erf respectively.



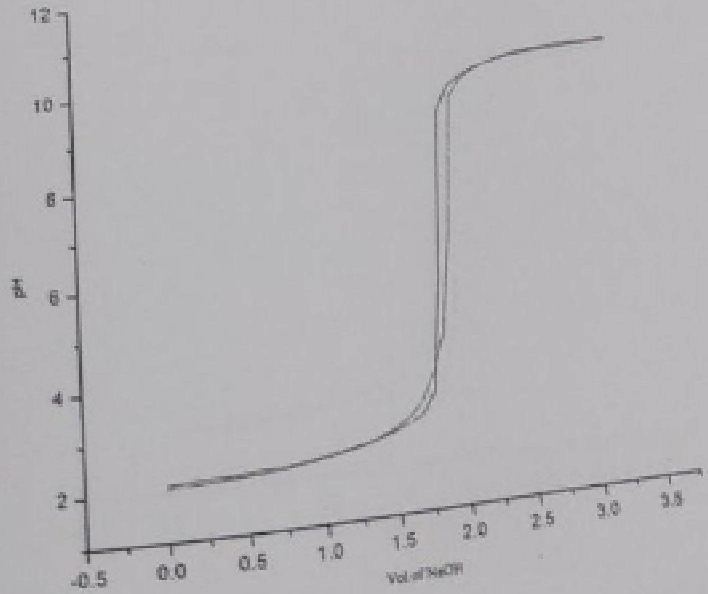
Graph 1.1 pH metric titration curve for Cu(II) + Nicotinic Acid (1:1 ratio)



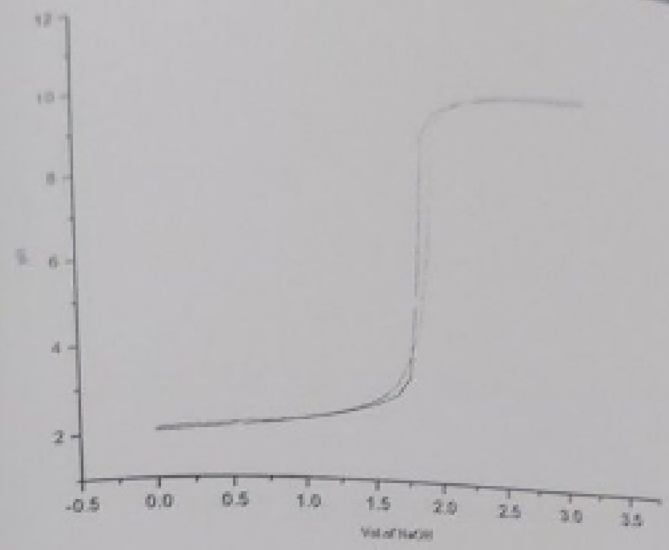
Graph1.2 pH metric titration curve for Ni (II) + Nicotinic Acid (1:1 ratio)



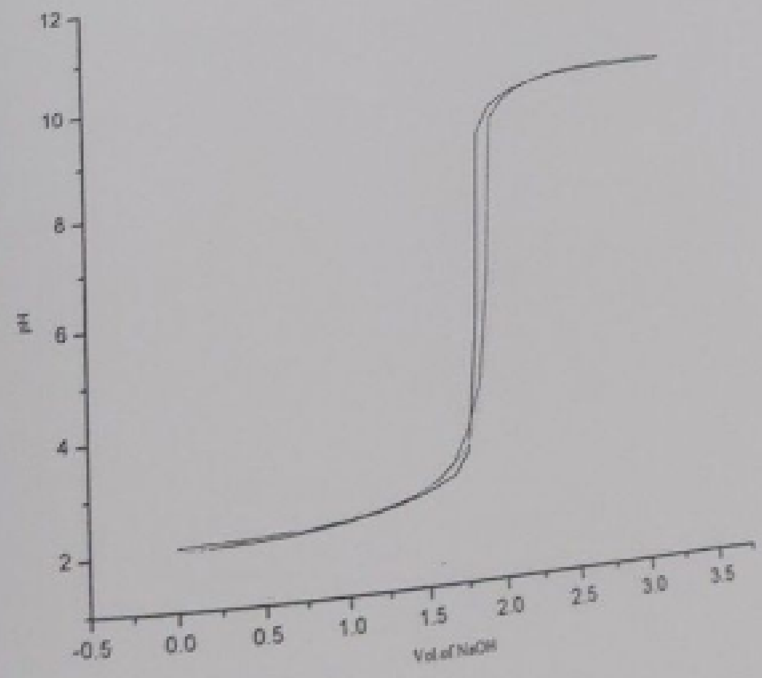
Graph1.3 pH metric titration curve for Zn (II) + Nicotinic Acid (1:1 ratio)



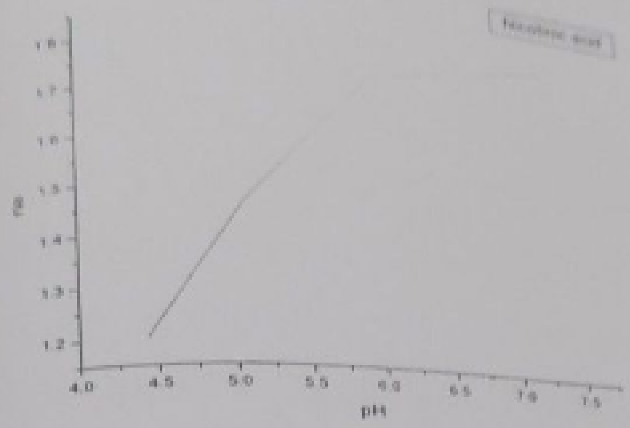
Graph 1.4 pH metric titration curve for Fe (III) + Nicotinic Acid (1:1 ratio)



Graph 1.5 pH metric titration curve for Co (II) + Nicotinic Acid (1:1 ratio)



Graph 1.6 pH metric titration curve for Cd (II) + Nicotinic Acid (1:1 ratio)



Graph 1.7 n_A vs pH for Nicotinic Acid

...plexes of 4-Amino-Benzoic Acid

...gand 4-Amino Benzoic acid has two ionisable groups -COOH and $-NH_2$. In the ... investigation the observed value of pK_H for PABA are 9.1654 & 4.6449. The ... of protonation constant 4.6449 may be due to ionization of -COOH group ...ved in many acids benzoic acid salicylic acid and the protonation constant ...54 may be due to ionisation of $-NH_2$ group observed in case of amines.

...observed value of pKa for PABA are in agreement with literature. [30].

...order of stability towards complexation with PABA is

Fe(III) > Ni(II) > Cu(II) > Cd(II) > Zn(II) > Co(II) for 1:1 complexes and

Co(II) > Cu(II) > Fe(III) > Ni(II) > Zn(II) > Cd (II) for 1:2 complexes.

...e order is in agreement with Irving Williams natural order. The metal ligand ...ability constants of PABA with metal ions are given in the table 4.5a & 4.5b.

Table 4.5a Proton Ligand Constant and Metal Ligand Stability Constants for 4-Amino Benzoic Acid (1:1)

Proton Ligand Constant	Metal Ligand Stability Constants			
	Metal ion	Log K_1	Log K_2	Log β
Half integer pK_1 = 4.6485 pK_2 = 9.1620 Point wise pK_1 = 4.776 pK_2 = 8.880	Cu (II)	6.7243	6.4397	13.2129
	Zn (II)	5.9446	5.5661	11.5107
	Ni (II)	13.0085	4.3775	17.3166
	Fe (III)	11.4881	10.5396	22.0277
	Co (II)	4.5264	4.3369	8.8634
	Cd (II)	6.8998	4.9594	11.8811

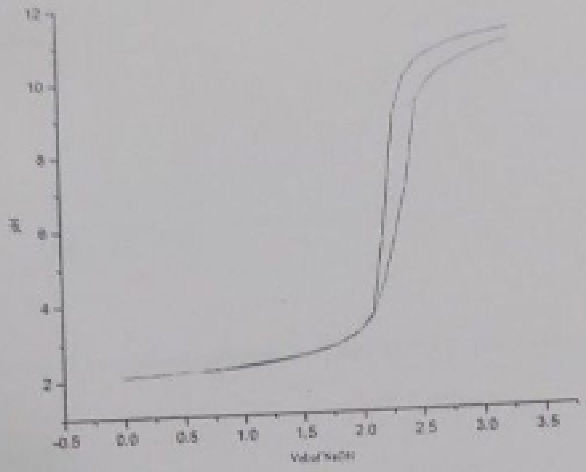
Table 4.5b Stability constants of 4-aminobenzoic acid (1:2)

Metal ion	Log K_1	Log K_2	Log β
Cu (II)	3.7159	3.2199	6.9359
Zn (II)	3.1246	3.1213	6.2460
Ni (II)	3.0666	3.1184	6.2690
Fe (III)	3.1574	3.1443	6.3017
Co (II)	3.2331	3.8327	7.0658
Cd (II)	3.1201	3.1121	6.2323

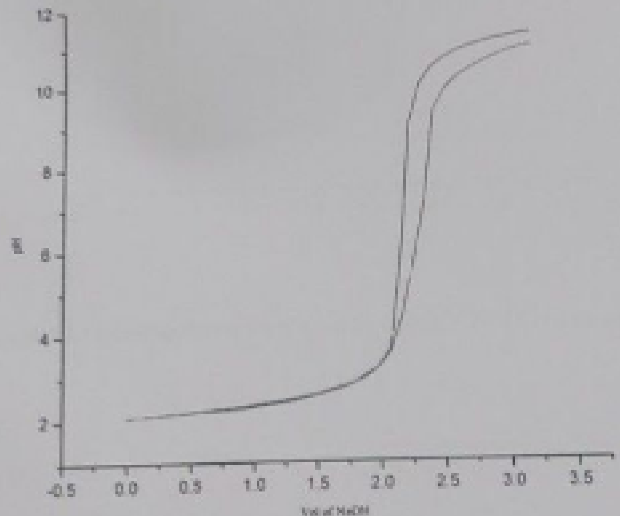
Ansari et al [31] studied stability complexes of PABA with transition metals and reported only one value of pKa 5.913 and they observed high value of stability for Cobalt complexes than Nickel complexes, more stability for 1:2 complexes of Nickel was observed. Abd-El Wahed et al [32] studied thermodynamic and electrical properties of aminophenol and anthranillic acid (ANA), the complexes of ANA more stable than aminophenol. The order of stability towards ANA is Mn(II) < Fe(II) < Ni(II) < Cu(II). The two pKa values for ANA as 8.37 and 4.45.

Endang Hernowo reported two values of pKa for norleucine having two protonation sites i.e.-COOH and $-NH_2$ as 2.35 and 9.35. H. N. Aliyu and J. Naaliya [33] studied stability constants of eleven amino acids with manganese ions. The high values of stability constants indicating formation of stable complexes. The values of stepwise stability constants decrease in the order as $\log K_1 > \log K_2 > \log K_3$.

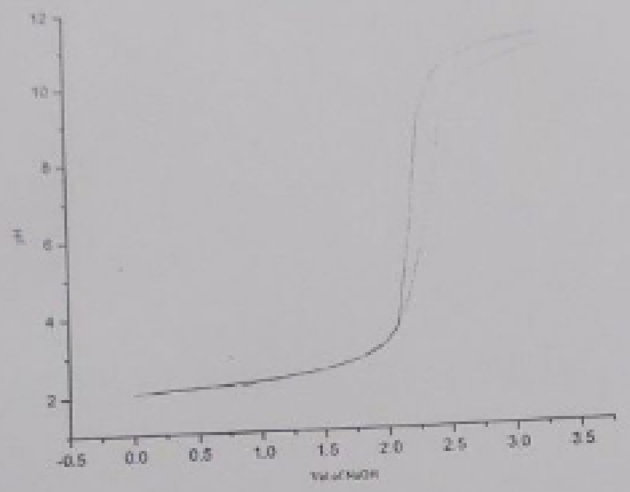
Thakur S.V. et al [34] worked on complexes of adenosine (AD), determined protonation constant as 3.292 for –OH group and 11.659 for $-NH_2$ group. They found the formation of 1:1 and 1:2 complexes. Shashi Agrawal and Satyendra singh [35] studied metal complexes of glycil glycine, reported pKa as 3.1 and 8.1. Kayande et al [36] studied complexation of amino acids and reported two pKa for glycine (2.34, 9.60) and penicillamine (1.8, 10.7) and valine (2.32, 9.62), lower value may be due to dissociation of –COOH group and higher due to $-NH_2$ group.Vighe et al [37] studied effect of ionic strength on stability constant of Co (II) prolyl alanine complexes, pKa found to be 6.80 and 10.67. They observed formation of 1:1, 1:2 complexes with high value of stabilities. Fatma Hassan [38] studied mixed ligand complexes of metals with Schiffs bases and cysteine and determined the two pKa values for cysteine as 7.7 (-COOH) and 8.8 ($-NH_2$ group). Highest value of stability observed for iron (III) complexes which in agreement with literature. [39].The transition metal ions because of availability of d-orbital give rise to a large number of stable complexes.



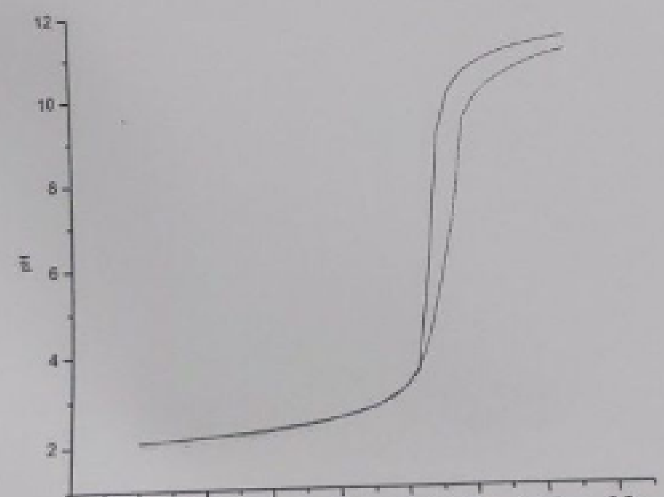
Graph 3.9 Potentiometric titration curve for Zn (II) + PABA (1:1 ratio)



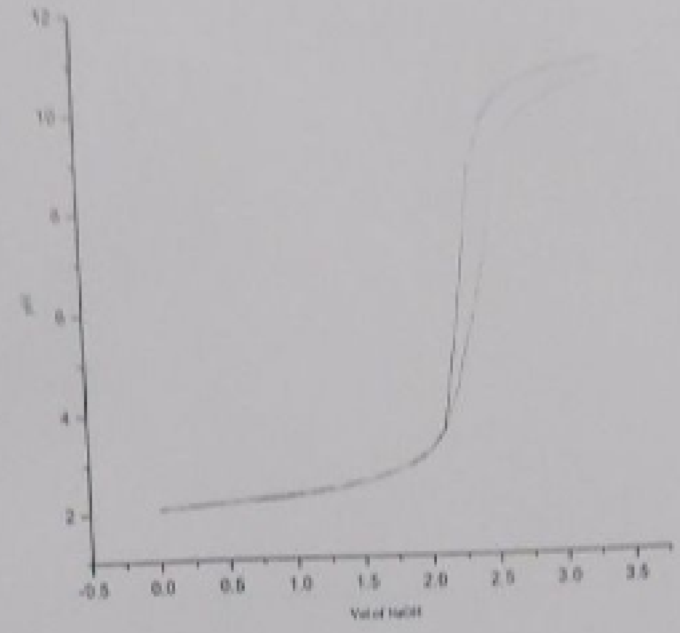
Graph 4.0 Potentiometric titration curve for Cd (II) + PABA (1:1 ratio)



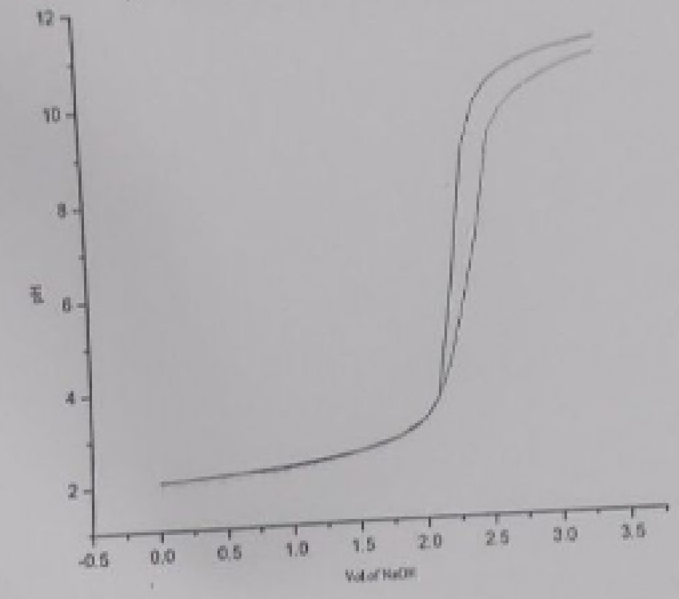
Graph 4.1 Potentiometric titration curve for Cu (II) + PABA (1:1 ratio)



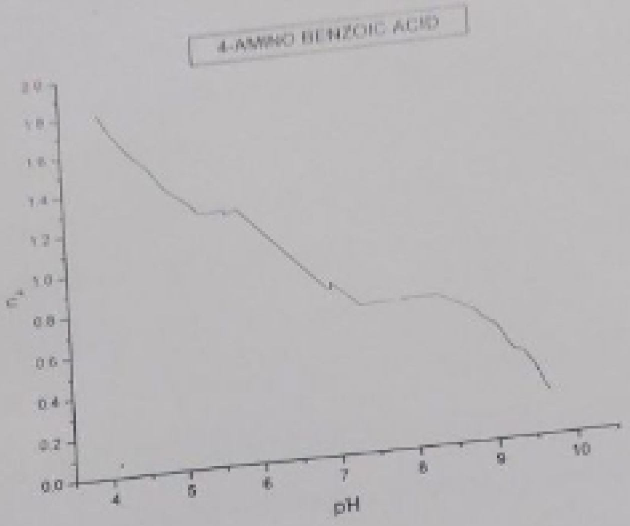
Graph 4.2 Potentiometric titration curve for Fe (III) + PABA (1:1 ratio)



Graph 4.3 Potentiometric titration curve for Co (II) + PABA (1:1 ratio)



Graph 4.4 Potentiometric titration curve for Ni (II) + PABA (1:1 ratio)



Graph 4.5 n_A vs. pH for PABA

4.8 Complexes of 2, 2 Bipyridyl

2,2 Bipyridyl is used as ligand for the present study. The protonation constant for bpd observed are 4.300 and 9.264. The ligand used is a bidentate. It provides two aromatic nitrogen whose unshared electron pairs are properly placed to act cooperatively in binding metal ions. This ligand is electron defficient they are excellent electron acceptors. Order of stability constant for present study is

Co (II) > Fe (III) > Cu(II) > Ni(II) > Zn(II) > Cd(II) for 1:1 complexes and

Ni(II) > Cu(II) > Zn(II) > Co(II) > Cd(II) > Fe(III) for 1:2 complexes.

The complexation of 2,2 Bipyridyl with metal under study gives metal ligand stability constants which are shown in table 4.8a and 4.8b. Kapinos and Sigel [40] studied properties of substituted pyridine molecules with metal ions in aqueous solution potentiometrically, they have got high stabilities for Copper and Zinc complexes, they have reported pKa value 3.91 for 4-Bromo pyridine and 6.24 for 2, 3-dimethyl pyridine. The pKa values obtained in agreement with reported values. Pyridine and 2-methyl pyridine has pKa values of 5.17 and 5.97 due to presence of basic nitrogen. High stabilities have been reported for binary complexes of 2, 2 bipyridyl which is in agreement with literature. [41]. High values of stability for Iron (III) and Cu (II) complexes reported in our results in agreement with Guillermo et al.[42]. The stability values for binary complex of iron are in agreement with the value determined by Mukherjee and Das. [43]. They have reported two pKa values for bipyridyl and 1, 10 phenanthroline as 4.23, 1.32 and 4.86, 1.90. The reported value for stability constant of Iron complex as 9.13 which in agreement with our results.

Usha Nakara and Gupta O.D [44] have studied polarographically complexes of Cadmium (II) and Lead (II) with bpd in aqueous medium and reported high stability for Cadmium (II) complexes. Ranjana et al [45] studied complexation of

Copper (II) with purines in the aqueous system, observed formation of coloured complexes, reported pKa values for adenine as 4.45 , 9.4 and 6.77 ($logK_1$) and 5.022 ($logK_2$) for Copper complexes .

Table 4.8a Proton Ligand Constant and Metal Ligand Stability Constants For 2.2 Bipyridyl (1:1)

Proton Ligand Constant	Metal Ligand Stability Constants			
	Metal	Log K_1	Log K_2	Log β
Half integer pK_1 = 4.3001 pK_2 = 9.2643 Point wise pK_1 = 4.265 pK_2 = 9.2312	Cu (II)	5.6942	3.9872	9.6849
	Zn (II)	3.4258	3.4168	6.8426
	Ni (II)	4.2895	3.3521	7.6417
	Fe (III)	-	9.6659	9.6659
	Co (II)	11.3245	3.4273	14.7518
	Cd (II)	-	3.4150	3.4150

Table 4.8b Metal Ligand Stability Constants for 2,2 Biprydyl (1:2)

Metal ion	Log K_1	Log K_2	Log β
Cu (II)	3.2510	3.7118	6.9629
Zn (II)	3.2411	3.7059	6.9471
Ni (II)	3.2270	3.7605	6.9876
Fe (III)	3.7164	-	3.7164
Co (II)	3.1029	3.1311	6.2341
Cd (II)	3.1057	3.1027	6.2084

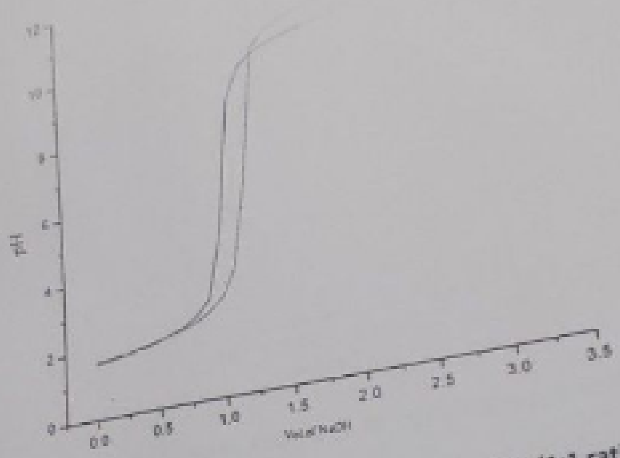
Balraj Reddy et al studied complexation of quinolinol and various ligands with **Nickel** (II) in dioxane water medium at 30^{0}C, they reported two pKa values for **bpd 2.98 and** 9.82 and formation of stable complexes with bpd.

The ligand may bound to metal ion by N-M sigma bond, beside there is also M-N pi bond formation by back donation of electrons from metal dπ orbitals to vacant delocalized pπ orbitals over the ligands. This dπ –pπ interaction does not allow the concentration of the electrons on the metal ions to increase significantly the positive charges on the metal ions is almost same as in M^{2+}. This leads to formation of more stable complexes. Kumar et al [98] prepared mixed ligand chelates of Fe (III) and Co (III) diphenates with 5-methyl -1, 10-phenanthroline (Ph) and 4-methyl -2,2^1-Dipridyl

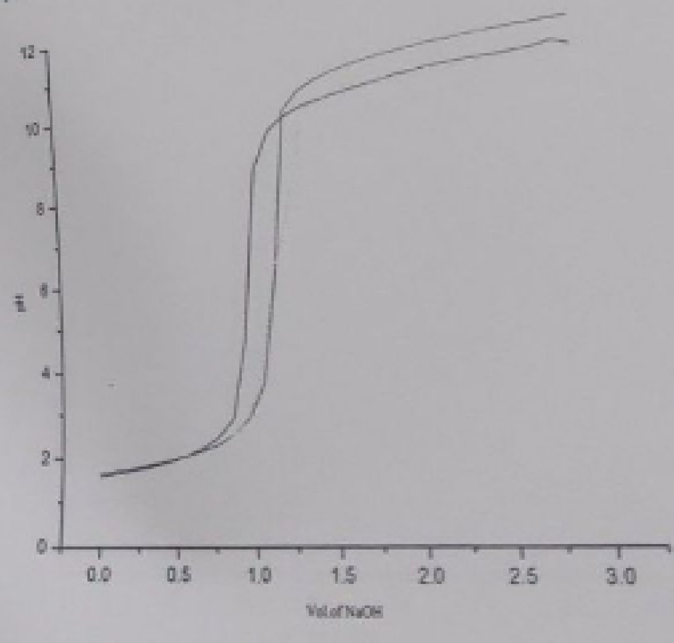
(4BDP), reported octahedral geometry. They also reported neutral nature of Ph, 4BDP and the co-ordination through tertiary nitrogen. Better chelation tendancy of the ligand was mentioned. Thakur et al studied interaction of the isoniazid with alkaline earth metals, reported two pKa values as 3.192 due to dissociation of nitrogen of pyridine ring and 10.66 due to dissociation of primary amino group and reported formation of 1:1 and 1:2 complexes.

Shrama et al studied interaction of lanthanones with 2-amino pyridine and 4-amino pyridine. They reported two protonation constant as 6.91, 11.32 and 9.25, 11.47 respectively. Mohan et al studied binary and mixed ligand complexes of various ligands with phosphonoformic acid, observed two pKa values for bpd and one for phen as 1.52, 5.88 and 4.87, they also reported formation of 1:1 and 1:2 complexes. Beda and Helmut studied ternary complexes of pyr and bpd like ligands with transition metal ions, in aqueous solution, high stability values were found. They reported that the stability of the ternary complexes depends on the π –accepting qualities of the heteroaromatic N base, enhanced stability is lost if heteroaromatic N base replaced by an aliphatic amine. The pKa values determined by them are 7.14(2,2 bipyridyl amine), 2.69,5.18 (2,2'dipyridyl methane), 3.06 (2,2' dipyridyl ketone). They observed high stability for Copper complexes. The Order stability found by them was Cu (II) > Ni (II) > Co (II) > Zn (II)

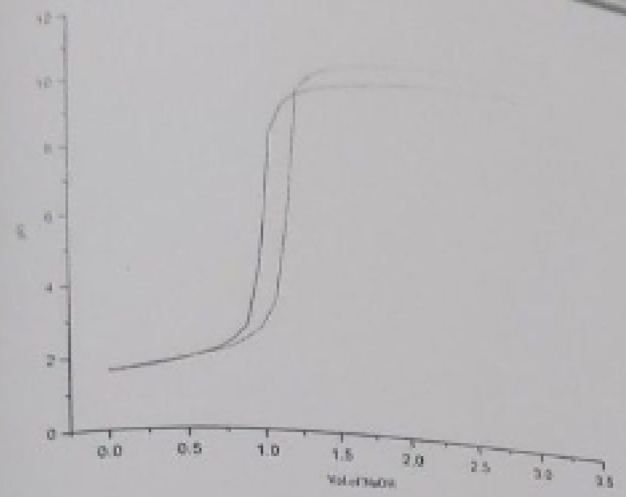
M.M.Khalil et al studied complexation of divalent metal ions with some Zwitter ionic buffers and triazoles at room temperature in aqueous medium, they reported complex formation occurred in stepwise manner and formation of 1:1 and 1:2 complexes. They observed two pKa values for 3-amino-1,2,4 triazole (TRZAM) 4.17 and 10.82 and observed that the stability constants of different 1:2 metal ligand complexes are lower than corresponding 1:1 system. The sequence of stability for bdp



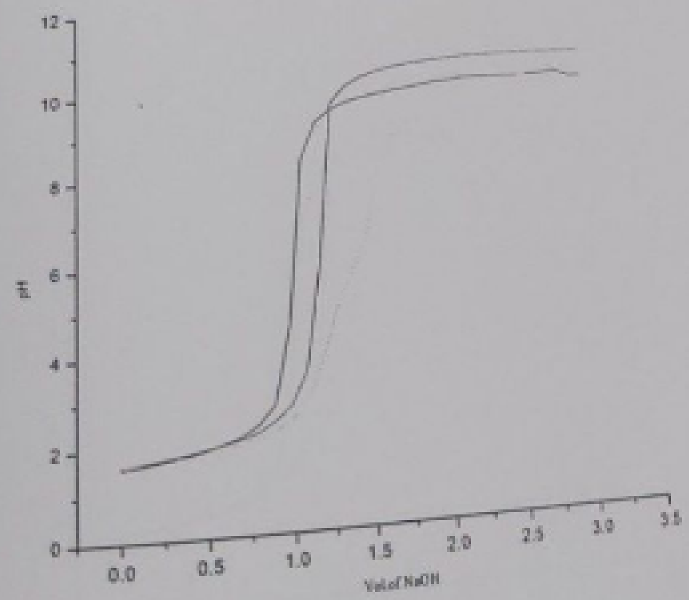
Graph 6.0 Potentiometric titration curve for Co (II) + BPD (1:1 ratio)



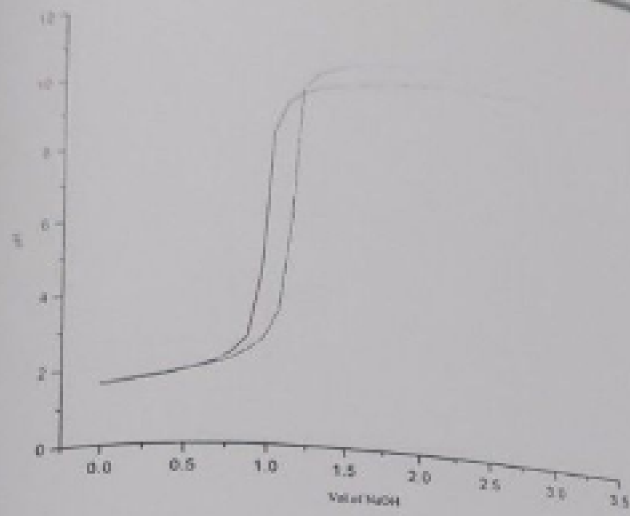
Graph 6.1 Potentiometric titration curve for Ni (II) +BPD (1:1 ratio)



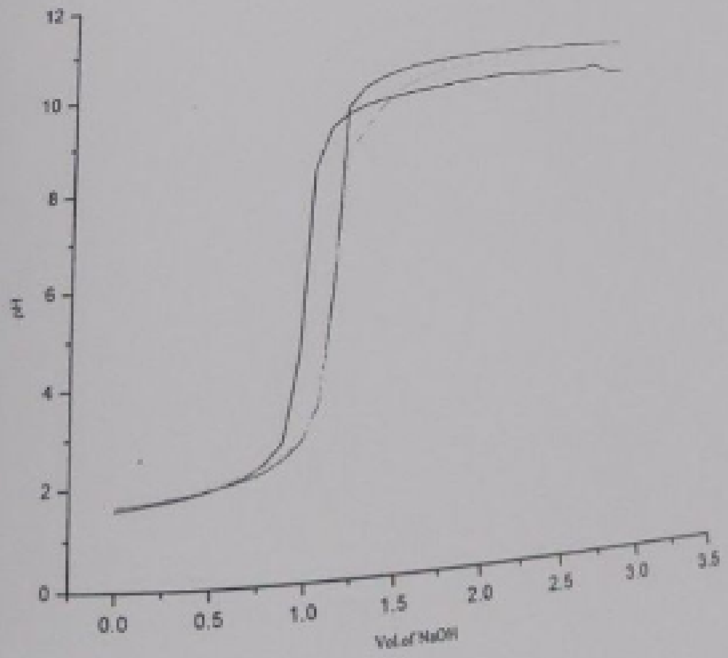
Graph 6.2 Potentiometric titration curve for Cu (II) + BPD (1:1 ratio)



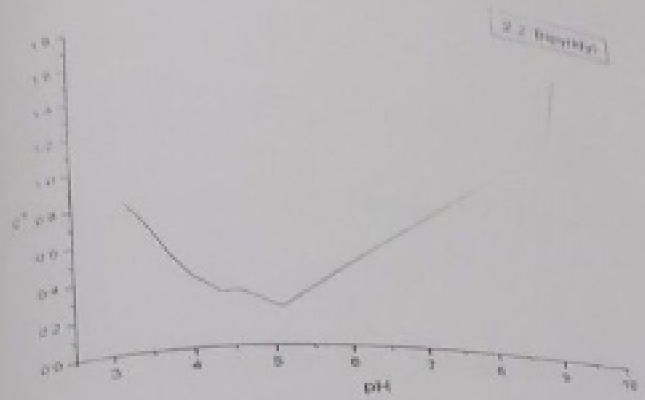
Graph 6.3 Potentiometric titration curve for Fe (III) +BPD (1:1 ratio)



Graph 6.4 Potentiometric titration curve for Zn (II) + BPD (1:1 ratio)



Graph 6.5 Potentiometric titration curve for Cd (II) + BPD (1:1 ratio)



Graph 6.6 n_A vs. pH for BPD