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Equilibrium Studies of Binary and Ternary Complexes of M(II) Involving Dipicolonic acid, Iminodiacetic acid and some Ligands of Biological Significance.

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Submitted by:

Hania Najah Salem Khalifa

Under Supervision of:

Dr :Hassan Amroun Ewais

Chemsitry Department

Faculty of Science

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Equilibrium Studies of Binary and Ternary Complexes of Palladium (II) Involving Dipicolonic Acid, Iminodiacetic Acid and some Ligands of Biological Significance

By

Hania Najah Salem Khalifa

Approved by:

Dr.Hassan Amroun Ewais
(Supervisor) ....

Prof.Ismael S. Busheina
(External examiner) ....

DrMohamed Alaa Ezz El-Arab
(Internal examiner) ....

Countersigned by:

Dr. Ahmed Farag Mhgoub
(Dean of faculty of science)

بسم الله الرحمن الرحيم

(يرفع الله الذين أمنوا منكم والذين اوتوا العلم
درجات والله بما تعملون خبير)

صدق الله العظيم

الاية(11) من سورة المجادلة

To my family,

....Friends

And teachers

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Hania Najah Salem Khalifa.

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ABBREVIATIONS

DPA = Dipicolinic acid.

IDA = Iminodiacetic acid.

En = Ethylenediamine.

Dien = Diethylenetriamine.

Phen = 1, 10-phenanthroline.

NTA = Nitrilotriacetic acid.

Pc. = Picolinic acid.

SUMMARY

Summary

The present work comprises a study of the equilibrium constants of binary and ternary complexes of palladium(II) involving dipicolinic acid (DPA), iminodiacetic acid (IDA) as a primary ligands and amino acids, aliphatic acids and aromatic acids as secondary ligands. These studies include the following:

Chapter I:

This chapter contains two parts as following:

Part I:

Introduction, included the nature, properties and biological importance of dipicolonic acid (DPA), iminodiacetic acid (IDA), amino acids and aliphatic and aromatic acids. Also, this part included biological importance of palladium(II) and ternary complexes.

Part II:

This part included the literature survey about this study, which contains the binary and ternary complexes of palladium(II) involving biological important ligands. Also this part contains the potentiometer studies of the formation complexes of picoline acid, dipicolinic acid and iminodiacetic acid with divalent metals.

Chapter II:

Experimental, which included chemicals, methods of preparation of different solutions, instrumental and procedure of calculation which used in this study.

Chapter III:

Included the results and discussion of these studies. This chapter contains two parts as following:

Part I:

In this part, the acidity constants of the ligands used (DPA, amino acids, aliphatic and aromatic acids) were calculated at 30 °C and I = 0.5M.

The formation constants of binary complexes of palladium(II) with DPA, amino acids, aliphatic and aromatic acids were calculated.

The formation constants of the ternary complexes of palladium(II) involving DPA as a primary ligand and amino acids, aliphatic and aromatic acids as a secondary ligands were calculated potentiometrically at 30°C and I = 0.5 M.

Part II:

In this part, the protonation constants of iminodiacetic acid (IDA) were calculated.

The formation constants of binary and ternary complexes of palladium(II) involving IDA as a primary ligand and amino acids, aliphatic and aromatic acids as a secondary ligands were calculated potentiometrically at 30C° and I = 0.5M .

The formation constants of ternary complex were found to lie in the sequence:

Aromatic acids > aliphatic acids > amino acids

The conductometric studies of the ternary complexes of palladium(II) were investigated.

CHAPTER I

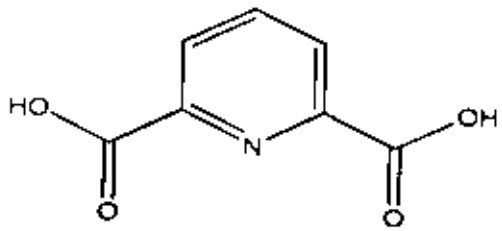
INTRODUCTION

1. INTRODUCTION

1.1. Nature and properties of dipicolinic acid, iminodiacetic acid, α-amino acids and its metal complexes.

1.1.1. Nature, chemical properties and biological importance of dipicolinic acid (DPA).

Dipicolinic acid (pyridine 2,6-dicarboxylic acid) is a dicarboxylic acid, which has two carboxyl groups in the ortho position with relation to the nitrogen atom of pyridine ring.



pyridine2,6dicarboxylic acid (DPA)

Dipicolinic acid shows various biological functions including activation/inactivation of some metalloenzymes[1,2], inhibition of electron transport system[3], acts as a strong inhibitor of LDL(low density lipoprotein) oxidation[4], and was incorporated to malaria-infected human red blood cells[5].

Dipicolinic acid which is synthesized in a large amount in the spore of genus Bacillus[6], inhibits lipid peroxidation[7], and protects glutathione reductase from the copper- dependent inactivation.[8]

Recently it was showed that dipicolinic acid acted as an antioxidant. Effect of dipicolinic acid and pyridine compounds on the copper-dependent oxidation of human low density lipoprotein was analyzed in relation to the inhibition of copper reduction.[8]

Dipicolinic acid inhibited copper-dependent LDL oxidation completely, but the LDL oxidation was slightly inhibited by pyridine compounds with one carboxyl group at 2 or 6-position.[4]

Protective effect of dipicolinic acid on the LDL oxidation was closely correlated with the copper-reducing activity. Dipicolinic acid shows an antioxidant action by the formation of a chelation complex with copper. This may have implications in understanding mechanisms of preventing LDL oxidation during the early phase of atherosclerosis. Inhibitory effects of dipicolinic acid on the iron-dependent lipid peroxidation and the copper-mediated inactivation of glutathione reductase are related to the electron deficient nature of pyridine ring.

Pyridine ring has the unshared pair of electrons on the nitrogen atom, and introduction of electron-attracting carboxylic groups to 2- and 6-positions further causes higher electron deficiency[3]. Copper binds to dipicolinic acid, which can attract electron from Cu^{+} as the prooxidant to form Cu^{2+}, resulting in the inhibition of formation of reactive oxygen species. Antioxidant effect of dipicolinic acid can be explained by the formation of the inactive chelation complex with copper.

Dipicolinic acid and pyridine carboxylates show higher chelating activity toward most metals such as copper and iron. Dipicolinic acid is a major constituent of bacterial endospores (including B.anthracis spores), comprising 5–14% of their dry weight after extraction[9]. The analysis of DPA is of importance in studies of sporulation, germination, and spore structure [10], and its presence is considered diagnostic for the bacterial endospores.

The rapid identification of Bacillus anthracis spores is of importance because of its potential use as a biological warfare agent[11].

There are several methods such as spectrophotometry[12,13], ultraviolet spectrophotometry[14], Fourier transform infrared

spectroscopy[15], liquid chromatography[16,17], luminescence[18,21], electron monochromatic mass spectrometry[22], fluorescence[23], pyrolysis–gas chromatography/ion mobility spectrometry[24] and pyrolysis mass spectrometry[25,26] have been applied for DPA detection. In consideration of emergency response plans for such an attack with biological weapons, the development of an inexpensive, rapid, and sensitive field portable sensor is extremely valuable for military and civilian use, and so a potentiometric chemosensory for selective determination of dipicolinic acid was developed.[27]

Studies on the structure of dipicolinic acid performed with the aim to explain the singular function of this compound in its biological environment have suggested that the carboxyl groups are partially polarized and neither the dilation nor the fully prorogated acid form accounts adequately for the properties of the bacterial spores[28].

Among pyridinedicarboxylic acids, dipicolinic acid (DPA) seems to have the best chelating properties because it is terdentate. Dipicolinic acid (DPA), H_2A can be further prorogated as the acidity of the medium increases forming a monopositive species, H_3A^+. However, in the pH rang utilized, this cationic form always proved negligible as checked previously using spectrophotometric technique[29].

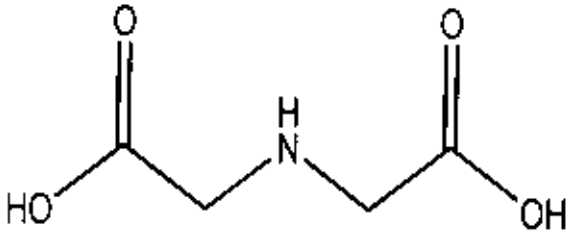
It is known from vibrational spectra that dipicolinic acid in the solid state shows a rather complex behaviour of self-association, with chains stabilized by intermolecular hydrogen bonds leading to the formation of the usual carboxylic rings[30].

Since dipicolinic acid is a dicarboxylic acid, it may be a system more favorable to possible association by hydrogen bonding of heteroaromatic molecules in aqueous solution. The nitrogen atom of the pyridine ring provides a potential hydrogen bond site. Moreover, the

presence of carboxylic groups provides other additional sites which may enhance association [31].

1.1.2. Chemical properties of iminodiacetic acid (IDA).

Iminodiacetic acid ($IDAH_2$) titrates as a biprotic acid in the pH range 2 – 4.5 due to successive deprotonation of its two carboxylic acid groups.



iminodiacetic acid (IDA)

It shows another buffer region in the pH range(8–10) due to ionisation of the iminium proton. The iminodiacetate dianion (IDA^{2-}) coordinates as a (O–, N, O–) terdentate ligand[32]. Imine is a compound containing the bivalent = NH group combined with a bivalent non acid group, as R-HC=NH. It is produced by the condensation reactions of aldehydes or ketones with ammonia (or amines). Imino is a prefix denoting the presence of the bivalent group = NH attached to nonacid radicals.

The role of technetium(98)^a Tc(98)^a (a: a value in parentheses denotes the mass number of the radioisotope of longest half-life) iminodiacetic acid (IDA) cholescintigraphy in acute acalculous cholecystitis[33]. Technetium(98)^a iminodiacetic acid(IDA) cholescintigraphy was performed in 15 patients with acute acalculous cholecystitis. Fourteen of the 15 patients with acute disease had positive findings, indicating the presence of cystic duct or common duct obstruction. One case in which the gallbladder was visualized failed to

respond to sincalide stimulation; this was classified as a suggestive finding of disease. The technetium(98)^{a}-IDA study is recommended as the imaging procedure of choice for examining patients with suspected acute a calculous cholecystitis. A chelating agent, iminodiacetic acid (IDA), was used as a protecting agent to diminish protein-polymer interactions and thus enhance the cumulative release of bovine serum albumin (BSA) from PEG hydrogels. Divalent metal ions such as copper, zinc, and nickel were also used synergistically with the IDA to evaluate the effect of ligand affinity on the degree of protein protection.

Silica particles of different porosity were functionalised with iminodiacetic acid (IDA) and loaded with Fe(III) to yield immobilised metal affinity chromatography stationary phases (Fe(III)-IDA-silica) for phosphopeptide enrichment[34]. The elution step of bound phosphopeptides was optimised with radioactive labelled peptide by a comprehensive study. Several elution systems, including phosphate buffers of different pH and concentration and ethylenediaminetetraacetic acid solutions were employed.

1.1.3. Chemistry of α-amino acids [35,36].

1.1.3.1. Structure and classification of α-amino acids.

Alpha-amino acids include amino group (-NH_2) adjacent to the (α-) carboxyl group, with the exception of proline and hydroxyproline, which have a secondary amino group. All other amino acids have a primary amino function. The solubility of amino acids in water decreases rapidly as the size of the side chain increases, glycine is quite soluble whereas tryptophan and phenylalanine have limited solubilites.

The differences in structure of the side chain serve as a convenient way for classifying α-amino acids into various categories:

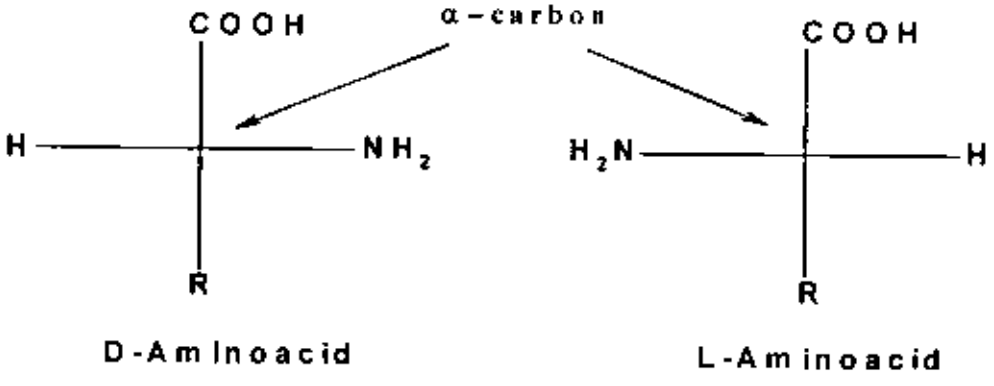
First category includes neutral amino acids which contain one acidic group and one basic amino group.

Second category includes acidic amino acids because they contain two acidic groups and only one basic amino group. The side chains of the acidic amino acids are negatively charged at the physiological pH (that is, the carboxyl group does not exist as -COOH but rather as the ion $-COO^-$) hence, acidic amino acids are very soluble in water.

Third category includes basic amino acids, because they contain two basic groups and only one acidic -COOH group. The basic amino acids are quite soluble in water because of the polar nature of the side chain (positive charged).

1.1.3.2. Stereochemistry of α-amino acids: D- and L- families.

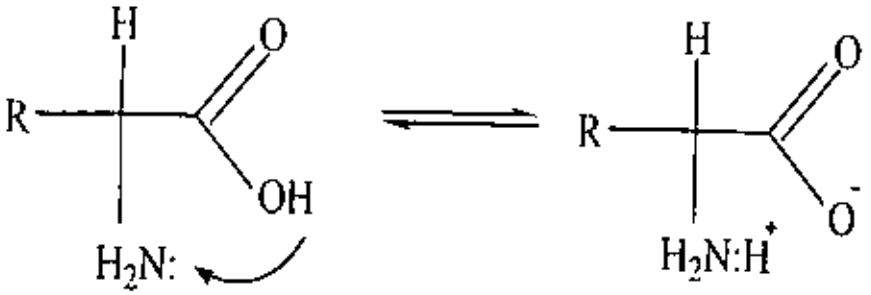
The α-amino acids have the four different groups attached to the α-carbon. This carbon is therefore a chiral center. As a result, there are two possible structures, one the mirror image of the other. By analogy with the convention adopted in carbohydrate chemistry, we divide α-amino acids into D- and L- families. D- amino acids are those in which the NH_2 group points to the right of the α-carbon in the Fisher representation of an amino acid (the -COOH is at the top and the carbon chain is at the bottom in the Fisher structure). Conversely, L- amino acids have the NH_2 pointing to the left, as shown in scheme (1).



Scheme (1) Stereochemistry of α-amino acids

1.1.3.3. Ionic properties of α-amino acids.

For simplicity, the α-amino and the α-carboxyl groups of the α-amino acids were written in their unionized forms, (R-CH(NH_2)-COOH). The acidic group (-COOH) and the basic group (-NH_2) are attached to the same α-carbon. We could expect the proton from the -COOH group to be transferred to the basic -NH_2 group in an internal acid-base reaction as follows:



Scheme (2) Internal acid-base dipolar structure of an α-amino reaction in amino acids acid (a Zwitterion).

The resulting structure, which has a positive and negative charge within the same molecule,is called a dipolar ion or zwitterion at (pH = 7). The zwitterionic structure is in agreement also with the amphoteric properties of α-amino acids[35,36].

In strongly acidic medium, the carboxylate anion (-COO^-) picks up a proton and is converted to a carboxyl group (-COOH). As a result, the dipolar ion is transformed to a cationic form, which has a net positive charge. Also, in strongly basic medium, the charged ammonium ion (-NH_3^+) gives up its proton to the hydroxide ion and is converted to a neutral amino group (-NH_2). Because of their amphoteric properties, amino acids can act as biological buffers and can thus maintain the pH of the body.

1.1.4. Biological importance of palladium(II) and palatnium(II) complexes

Palladium(II) and palatnium(II) complexes have the same structure with higher reactivates. Palladium(II) complexes are a good models for the analogous palatnium(II) complexes in solution[37].

Platinum(II) complexes were used for treatment of human solid cancers such as lung, colon and stomach carcinomas[38,39]. Cis platin, Cis–diammine dichloroplatinum(II), is one of the most effective anticancer agents that are clinically active to solid tumors, platinum(II), is a widely used second generation platinum anticancer drug. Palladium(II) complexes were used as antioxidant.

New complexes of Pd(II) with *N*-substituted thiosemicarbazone (1)–(3) have been synthesised and characterised by elemental analyses, IR, electronic, ^{1}H NMR spectroscopies. The electrochemical behaviour of the complexes has been tested by using cyclic voltammetry. The crystal structures of the complexes have been determined by single crystal X-ray diffraction technique. In all the complexes the thiosemicarbazone ligand is coordinated to palladium through ONS mode. The new complexes have been tested for their antibacterial activity against various pathogenic bacteria.[40]

A new palladium(II) complex with methionine sulfoxide was synthesized and characterized by a set of chemical and spectroscopic techniques. Elemental and mass spectrometry analyses of the solid complex fit to the composition $[Pd(C_5H_{10}NO_3S)_2]\cdot H_2O$. ^{13}C NMR, [^{1}H–^{15}N] NMR and infrared spectra indicate coordination of the amino acid to Pd(II) through the carboxylate and amino groups in a square planar geometry, biological activity was evaluated by cytotoxic analysis using HeLa cells. Determination of cell death was assessed using a tetrazolium salt colorimetric assay, which reflects the cells viability.[41]

1.1.5. Ternary complexes:

The system which consists of a metal ion and more than one type of ligand is defined as ternary complexes. Such ternary complexes are important in analytical chemistry, and in metal ion catalyzed reactions.

They might appear in biological fluids creating specific structures, most frequently manifesting themselves as enzyme-metal ion-substrate complexes. This explains why ternary system has recently received increasing attenation. This complexes have been widely studied for several decades due to their utility as model systems for metal-protein complexes observed in, for example, protein-protein interactions and present in certain proteins such as metalloenzymes[42].

Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases have attracted much interest as they can display exceptionally high stability.[43]

1.2. Literature Survey

1.2.1. Interaction between Palladium(II) complexes of the type $[Pd(amine)(H_2O)_2]^{2+}$ and amino acids, peptides and DNA constituents.

Reactions of $[Pd(en)(H_2O)_2]^{2+}$ (en = ethylenediamine) with the amino-acids (glycine, L-alanine, sarcosine, N,N-dimethylglycine, L-leucine, L-phenylalanine, L-proline, L-tryptophan, L-methionine and methylcystiene) were studied by potentiometric titration[44]. For L-methionine and S-methylcystiene, equilibria (1) and (2) held principally in solution were significant.

$$[Pd(en)(H_2O)_2]^{2+} + L^- \rightleftharpoons [Pd(en)(L)]^+ + 2H_2O \qquad (K_1).....(1)$$

$$[Pd(en)(H_2O)_2]^{2+} + HL \rightleftharpoons [Pd(en)(HL)]^{2+} + 2H_2O \qquad (K_1^H).....(2)$$

Where $L^- = MeS[CH_2]_nCH(NH_2)CO_2^-$ (n = 1 or 2). For the remaining amino acids only equilibria (1) were significant.

Mixed-ligand complexes of Palladium(II) involving diaqua-(ethylenediamine)palladium(II) and L-aspargine or L-glutamine[45] were studied in 0.5 mol.dm^{-3} KNO_3 applying a potentiometric technique. The reaction occurred in two steps; The formation of the mixed ligand complex $[Pd(en)L]^+$, followed by deprotonation of the amide group. The acid-dissociation constant of the amide group of the palladium(II) complexes, $K^{\backslash}_a$ revealed interesting biological implications. Under normal physiological conditions (pH = 7.4) the two peptides coordinated with $[Pd(en)(H_2O)_2]^{2+}$ in entirely different fashions; so that whereas asparginate would be entirely present in the deprotonated from, while glutaminate would exist solely in the prorogated form. This showed that even though $[Pd(en)(H_2O)_2]^{2+}$ could catalyse the deprotonation of the amide groups from both asparginate and glutaminate. Its catalytic action

would be very specific under physiological conditions, being merely confined to aspargine. The slight difference in the side chains of the two peptide would produce dramatic differences in their behaviour towards the palladium species.

Hay et. al [46], studied the complex formation equilibria involving $[Pd(en)(H_2O)_2]^{2+}$ and amino acid ester (L) by a potentiometric technique. The kinetics of hydrolysis of $[Pd(en)L]^{2+}$ were studied by pH-static technique and rate constants for processes (3) and (4), where A = $NH_2CH(R)CO_2^-$ and L = ethyl glycinate (Gly-OEt),

$$[Pd(en)L]^{2+} + H_2O \rightleftharpoons [Pd(en)A]^{+} + R'OH + H^{+} \quad (K_{H2O}).....(3)$$

$$[Pd(en)L]^{2+} + OH^{-} \rightleftharpoons [Pd(en)A]^{+} + R'OH \quad (K_{OH}).....(4)$$

Possible mechanisms for these reactions were considered which suggested that the reaction may involve kinetically important ion-pairing between the complex and the incoming nucleophile prior to nucleophilic attack on the ester ligand.

Lim and Martin[47], pointed out that the proton NMR spectra of a mixture of uridine and thymidine respectively with $[Pd(dien)(OH)_2]^{2+}$ (where dien = diethylenetriamine), $[Pd(en)(OH_2)_2]^{+2}$ and their platinum analogues showed variation with pH. They assumed that in dien compolex a (1:1) metal to ligand complex was formed whereas en complex both (1:1) and (1:2) metal to ligand complexes were formed. However, because of the high concentrations of nucleosides and the metallic species employed in the NMR study, it was not possible to determine with precision the species distribution in solution at various pH, as well as the stability constants. For the platinum complexes, because of the slow rate at which equilibrium was attained and the high temperature required to attain equilibrium it was not convenient to

determine the species distribution and to find out the stability constants by conventional pH titration.

For these reasons, Lim et. al[48], studied the complex formation equilibria of aqua-(diethylenetriamine)palladium(II) and diaqua-ethylenediamine)palladium(II) with uracil, uridine and thymidine. $[Pd(dien)(H_2O)_2]^{2+}$, and it was found that (1:1) complexes are formed with the mentioned ligands. Alternatively, $[Pd(en)(H_2O)_2]^{2+}$ formed (1:1) and (1:2) (metal:ligand) complexes. The formation constants were evaluated. The species distribution at different pH values and the mode of coordination were discussed based on these values.

The kinetic and thermodynamic data were reported[49] for the complex formation reactions:

$$[Pd(en)(H_2O)_2]^{2+} + Cl^- \rightleftharpoons [Pd(en)(H_2O)Cl]^+ + H_2O \quad (K_1).....(5)$$

$$[Pd(en)(H_2O)Cl]^+ + Cl^- \rightleftharpoons [Pd(en)Cl_2] + H_2O \quad (K_2).....(6)$$

These species served as models for the mechanistic behaviour of the antitumour active cis-$Pt(NH_3)_2Cl_2$ complex. Spectrophotometric and potentiometric techniques were employed to determine the equilibrium constants.

The kinetic and thermodynamic data were reported for the complex formation reactions involving N-substituted (ethylenediamine) palladium(II) complexes as a function of steric hindrance for the substituent[50]. The results were discussed in view of the corresponding data for the unsubstituted (en) system and the cis-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ species.

Haring et. al.[51], studied the complexes of (ethylenediamine) Pd(II) with inosine, guanosine, adenosine and their phosphates. In the complex formation reaction, $Pd(en)^{2+}$ was found to react in acidic solutions with

N_7 while in basic solutions with N_1. In a wide pH range region around the neutral pH both N_7 and N_1 coordination occurred leading to possible formation of polymeric complexes.

The complex-formation reactions of $Pd(Et_4en)Cl_2$ (Et_4en = N,N,N',N'-tetraethylethylenediamine) with inosine and inosine 5'-monophosphate were also studied[52] as influenced by nucleophile and chloride concentration. Two consecutive reaction steps were observed under all experimental condititions. A detailed kinetic analysis revealed that $[Pd(Et_4en)Cl(OH_2)]^+$ was the reactive species in the first complex formation step, for which a steady-state approximation could be applied.

In the case of the second step, a rapid pre-equilibrium occurred, and is followed by rate-determining substitution of aqua complex to produce the (1:2) product species.

$$[Pd(Et_4en)(Nu)Cl]^+ + H_2O \rightleftharpoons [Pd(Et_4en)(Nu)H_2O]^{2+} + Cl^- \cdots\cdots (7)$$

The complex - formation equilibria[53] of $[Pd(R_4en)Cl_2]$ (R_4en = N,N,N',N'-tetramethylethylenediamine and N,N,N',N'-tetraethylethylene-diamine) with inosine, inosine 5'-monophosphate and guanosine 5'-monophosphate were investigated at different temperatures using a potentiometric technique. The stepwise formation constants of the complexes formed in solution were calculated using the non-linear least-square program MINIQUAD-75. The mode of binding of the DNA unit to the Pd(II) complexes was discussed. Comparison of the potentiometric results with the corresponding data obtained from kinetic measurements indicated that N_7 constituted the binding site in acidic media but N_1 in basic media. The concentration distribution of the various complex species was evaluated as a function of pH.

The reactions of $[Pd(en)(H_2O)_2]^{2+}$ with ethanolamine. L-serine, L-threonine, L-homoserine and L-hydroxyproline in 0.1 M KNO_3 at 25C[o] were studied by potentiometric titration[54]. The results were explained by the following equilibria, where L = ethanolamine or anionic form of the amino acids (charges were left out for simplicity)

$$[Pd(en)(H_2O)_2]^{2+} + L \rightleftharpoons [Pd(en)L] + 2H_2O \quad (K_1).....(8)$$

$$[Pd(en)L] \rightleftharpoons [Pd(en)(LH^{-1})] + H^{+} \quad (K^{\backslash}_1).....(9)$$

The value of $\log K_1$ and $\log K^{\backslash}_1$ of those complexes suggested that, for ethanolamine, the neutral alcohol group was coordinated to palladium. For L-serine, L-thereonine and L-homoserine, group would not coordinate to the metal center, but coordination would occur upon deprotonation of the alcohol group. For L-hydroxyproline, both the neutral alcohol group and deprotonated hydroxyl group did not coordinate to the metal center.

The hydrolysis of amino acid esters in mixed ligand complexes with (bipyridyl) palladium(II) was studied[55]. The complexes were found to undergo water hydrolysis or by hydroxide ion. The use of π-acceptor ligands as bipyridyl led to an increase in the Lewis acidity of central metal center and more rapid hydrolysis rates.

1.2.2. Other Palladium (II) Complexes

Pd(II) is known to induce the ionization of peptide H near pH = 3.5 to yield tetragonal complexes with amide N donor atoms similar to Cu(II) and Ni(II) peptide complexes[56].

The formation of the Pd mixed-ligand complex, $[PdLL']$ (I) (H_2L = L-cysteic acid, HL' = L-theonine) were studied[57]. (I) was characterized by ^{1}H, ^{13}C NMR, absorption and CD spectra. The results indicate a ligand-ligand interaction between the hydroxyl H atom of the L' ligand

and SO^-_3 group of L^{2-}. PdL_2 (HL = histidine) and $[Pd(H_2L)Cl_2]Cl_2$ were prepared[58] by reaction of $PdCl_2$ with histidine in presence of NaOH or with histidine hydrochloride, respectively. Treatment of PdL_2 with excess HCl gave $[Pd(HL)_2]Cl_2$. In PdL_2, histidine is bidentate whereas in $[Pd(H_2L)_2Cl_2]$ histidine is monodentate with coordination occurring through the amino N atom.

The complexes were characterized by IR and ^1H NMR spectra. Effects of electrostatic ligand-ligand interaction on the side chain in ternary amino acid-Pd(II) complexes were studied[59] by measuring ^{13}C spin-lattice relaxation times, T_1. The NT_1 values (N = the number of H atoms bound to the C) of glutamate (Glu) in the systems containing Pd(II) and Arg. Pd(L-or D-Glu)(L-Arg), where side chain interactions existed at considerably smaller values than those for Pd(L-or D-Glu)(L-Ala) without the interaction which were close to those of $Pd(Glu)_2$. Comparison of the NT_1 values revealed that the motions of the α-carbons are strongly dependent on the ligand-ligand interactions, whereas the β- and γ-carbons can move relatively freely even in their presence. The motions of the side chain of Arg also were affected by the interaction.

Nine new Pd(II) complexes of the formula $[Pd(bipy)(AA)]^{n+}$ (where bipy is 2,2'-bipyridine and AA is an anion of L-cysteine, L-aspartic acid, L-glutei acid, L-methionine, L-histidine, L-arginine, L-phenylalanine, L-tyrosine, or L-tryptophan, and n = 0 or 1) were prepared by the reaction of $[Pd(bipy)Cl_2]$ with an sodium salt of amino acid in water[60]. The Pd(II) complexes were characterized by chemical analysis and by Visible, IR and ^1H NMR spectroscopy. The modes of binding of amino acids in these Pd(II) complexes were ascertained by IR and ^1H NMR spectroscopy. The molar conductance of these complexes in water suggested that they were either nonelectrolytes or (1:1) electrolytes. The complexes showed growth-inhibitory activity against L1210 lymphoid

leukemic, P388 lymphocytic leukemia, sarcoma 180, and Ehrlich ascots tumour cells. Some of the complexes show ID_{50} values comparable to or lower than cis-diamminedichloro platinum.

Coordination of Pd(II) with ethylenediamine, diethylenertriamine and tris (β-aminoethyl) amines was studied[61] at 25 °C and ionic strength 0.1 M using pH meter and UV measurements. Br^- and OH^- were used as auxiliary ligands. Stability constants of the complexes formed were calculated.

Kasselouri et al.[62] studied Pd(II) and Pt(II) ternary complexes with nucleosides and amino acids. cis-PtL_2Cl_2(L= inosine) and cis-PdL'_2Cl_2(L' = guanosine) reacted with the Na salts of amino acids to give cis-$[PtL_2Q]Cl$ (I) and cis-PdL'_2Cl_2(L' = guanosine) and cis-$[PdL'_2Q]Cl$(II) respectively, (HQ = glycine, L-iso-leucine, L-valine, L-proline, L-alanine, L-phenylalanine). Compounds I and II reacted with HCl to give cis-$[PtL_2(HQ)Cl]Cl$ (III) and cis-$[PtL'_2(HQ)Cl]Cl$ (IV), respectively. The complexes were characterized by IR and ^1H NMR spectra. In I and II the amino acidato ligands behaved as bidentate whereas in compounds III and IV they behaved as monodentate, (N-bonded). All the Pd complexes exhibited rotational isomerism in D_2O, but not in DMSO-d_6 solutions.

Synthesis of other nine palladium(II) complexes of the type $[Pd(Phen)(AA)]^+$ (Phen = 1, 10-phenanthroline; AA = amino acid anion) have been achieved[63]. These palladium(II) complexes have been characterized by UV-visible, IR and ^1H NMR spectroscopy. The binding studies of several complexes $[M(NN)AA]^+$ (M = Pd, Pt, NN = 2, 2'-bipyridine, 1, 10-phenanthroline; AA = amino acid anion) with calf thymus DNA were carried out using UV difference in absorption and fluorescence spectroscopy. The above complexes have also screened for cytotoxicity in P388 lymphocytic cells. Only two complexes of them, show cytotoxicity.

Spectrophotometric, paper ionophoresis and mass spectra (fast-ion-bombardment) methods were used to study complexation of Pd(II) aqua ions with the aliphatic amino acids: glycine, L-alanine, DL-valine, DL-leucine, L-proline(HL)[64]. At Pd : HL ratio (1:3) in 1M $KClO_4$, $PdHL^{2+}$ forms; in 0.1 M HCl at Pd : HL = 1 : 40, $Pd(HL)_2^{2+}$ forms. Stabilities of (1:1) complexes decreased with increasing aliphatic chain length of HL, while the stabilities of the (1:2) complexes increased as chain lengths increase.

[Pd(Phen)L]Cl (I; HL = lysine, proline, arginine, Phen = 1,10-phenanthroline) were prepared [65] from $Pd(Phen)Cl_2$ and HL and were characterized by elemental analysis and IR spectra. Their antitumour effects were tested by the vital dye exclusion assay and S_{180} in test mice. (I) have some antitumour activities in varying degrees. The toxicity of the complexes against mice was less and the solubility of (I) (HL = proline, arginine) was greater than cis-$Pt(NH_3)_2Cl_2$.

The glycine chelate ring in Pd(II)-Gly-Phe complex was planar up to pH = 10 and was only distorted from planarity when the ligand behaved as bidentate. ^1H NMR studies of Pd(II) complexes with Ala-Tyr and D-Leu-Tyr revealed the essential role of metal ion in inducing the dipeptide conformation in solution[66]. In a complex with tridentate coordination of dipeptide (pH =3-10) the most stable conformer of a tyrosine residue was that the aromatic ring existing in gauche position to carboxyl and amine groups. At high pH a dipeptide behaved as a bidentate ligand (NH_2, N-), while the tyrosine residue changed its conformation drastically, and the most stable conformer was that with the aromatic ring in trans position to the carbonyl group. The C-terminal amino acid did not have a considerable effect on the conformation of an N-terminal amino acid in both kinds of complexes with Pd(II).

Jezowska-Trzebiatowska et. al.[67], studied the dipeptide: palladium(II):purine nucleoside ternary complexes in water solutions. The effect of coordination of Pd(II)-GlyX complexes (X =Tyr, Phe) to purine nucleosides on the NMR chemical shift change of the H(2) and H(8) protons located near donor sites was related to two contrary effects. First the coordination of the Pd(II) ion to N(7) (N(1)) of purines caused a downfield shift of the H(8) (H(2)) proton signals.

Synthesis and characterization of palladium(II) and platinum(II) complex with 2-[1-(2-pyridyl) ethylidene] oxamolydragide were investigated[68]. The structure was confirmed by IR, H^1-NMR and ^{13}C-NMR spectroscopy.

1.2.3. Complexes of pyridine dicarboxylic acids:

Potentiometric and spectrophotometreic investigation on the formation of binary complexes of Al(III) with dipicolonic acid at 25 C° in aqueous 0.5 M $NaClO_4$ ionic strength is reported previously by Napoli[69].

Chromium(III) complexes of 2,2-pyridinedicarboxylic acid have been studied by Marks [70].

In 1996, Ibrahim et al[71], studied the ternary complex systems of M = (Cu(II), Ni(II), Co(II), Hg(II), Cd(II), Pb(II), UO_2(II), y(II) and Ce(III) with dipicolonic acid (primary ligand) and N-(2-acetamido) iminodiacetic acid or amino acids (secondary ligands) potentiometrically in aqueous media at ionic strength 0.1 M KNO_3 and 25.0 °C. The value of stability constants for binary and ternary complexes formed have been evaluated and discussed in terms of the nature of metal ions as well as the nature of the secondary ligand . Studies showed that, except in the case of dicarboxylic amino acids, the ternary complexes mentioned have lower

stability than those corresponding to binary ones for the secondary ligands .

The stability constants of mixed-ligand complexes of Cu(II) and Ni(II) with dipocolinic acid and iminodiacetic acid (as primary ligands) and some selected secondary ligands (alanine, phenanthrolin, tyrosine ,tryptophane, ethlenediamine, 1,3-propane-diamine, oxalic acid, catechol, catechuic acid, tiron pyrogallol,o-aminophenol, o-phenylenediamine) have been determined by Bhattacharya and co-worker[72], in 1991. The values have been determined potentiometrically using the SCOGS computer programme. Study of inter-ligand stacking interaction in Cu(II) and Ni(II) ternary complexes is performed by the same authors [73].

Sharma and co-workers[74], studied the complexation equilibrium for some ternary systems involving transition metal ions (Cu(II) , Ni(II) and Zn(II) and some dicarboxylic acids , (thiodiacetic acid , iminodiacetic acid and pyridine –2,6 – dicarboxylic acid) and furan -2- carboxylic acid . The stability constants of these systems have been evaluated potentiometrically and free energies of formation (ΔG) have also been calculated.

Konkani et al[75], determined the stability constants of ternary complexes of the type (Cu X Y) where X = dipicolonic acid (primary ligand) and Y = DL-α-alanine, β-alanine, glycine or glutamic acid as secondary ligands.The stability constants have been evaluated in aqueous solution using pH technique at 25C° and at 0.1M ionic strength. Cu(II) formed (1:1:1) ternary complexes with dipicolonic acid and the previously mentioned amino acids. The preferential formation of the mixed-ligand complexes over the binary ones have been discussed in terms of equilibrium constants.

The formation constants of the binary and ternary complexes of chromium(III) involving dipicolinic acid (DPA)[76] as a brimary ligand and DL-aspartic acid[77], DL-valine[78] and L-arginine as a secondary ligands were calculated potentiometrically as follow: 6.61± 0.04, 6.78±0.05, 6.81± 0.07 and 6.91±0.05 respectivaly at I = 0.1 M and at 30°C.

1.2.4. Complexes of iminodiacetic acid (IDA):

Acid dissociation constants of iminodiacetic acid and iminodipropionic acid, and the chelate stability constants of the corresponding anions with cupric, nickel, cobalt, zinc and cadmium ions are reported for a temperature of 30° and 0.1 M ionic strength[79]. The replacement of acetate groups by β-propionate groups in the ligand results in a considerable decrease in the stability of the chelate.

This is the first of a series of publications describing the effect of structure of the ligand on the stability of aqueous metal complexes. The chelating agents to be described are amino acids, soluble in water in the form of their salts, which have more or less ability to combine with the more basic metal ions, such as the alkaline earth metals, and having appreciable affinity for transition metals and other (heavy metal) ions. Thus all the compounds in this series may be classified as sequestering agents. By changing these basic structures with respect to variation of the number of acetic acid groups, and replacement of these by other groups, it may be possible to draw logical conclusions concerning the basic of metal ion affinity in these compounds. Thus quantitative study of the stabilities of the corresponding metal chelates may lead to a better understanding of the method of function of sequestering agents, and to the development of superior sequestering agents[80].

Potentiometric and spectrophotometric investigations on the complex formation equilibria of Cu^{II} with iminodiacetate(ida^{2-}) and hetrocyclic N-bases, viz. imidazole and benzimidazole(B), in aqueous solution in binary and ternary systems using different molar ratios of the reactants indicated the formation of complexes of the types , Cu(ida), $Cu(ida)(OH)^{-}$,$(ida)Cu(OH)Cu(ida)^{-}$,$Cu(B)^{+2}$.$Cu(H_{-1}B)^{+}$. $Cu(ida)(H_{-1}B)^{-1}$, (ida)Cu(B)Cu(ida) and $(ida)Cu(H_{-1}B)Cu(ida)^{-}$. Formation constants of the complexes at 25 ± 1° at a fixed ionic strength, I = 0.1 $mol.dm^{-3}$ ($NaNO_3$) in aqueous solution were evaluated and the complex formation equilibria were elucidated with the aid of speciation curves[81].

The formation constants of chromium(III) complexes with iminodiacetic acid(IDA) and L-aspartic acid as the tridentate ligands were determined by the pH method in the ionic strength, I = 0.1 M and at 25 °C.[82]

The formation constants of the chromium(III) complex of iminodiacetic acid(IDA)[83] as a binary ligand and chromium(III)-IDA-DL-aspartic acid[84] as a ternary complex were calculated potentiometrically 2.91±0.02 and 2.41 ± 0.04 at I =0.2 M and at 45°C.

AIM OF WORK

The work included in this thesis aimed to study the stability and formation constants of biological important ligands and its metal complexes by using potentiometric technique.

The choice of this work according to the following reasones :

1- Biological importance of the Palladium(II) and complexes as anticancer and antioxidant.

2-To study the effect of secondary ligand on the stability of metal complexes.

3-The present work reports that the formation of binary and ternary complexes by potentiometric and conductometric techniques.

4-Calculation of the stability constants of the metal complexes .

In the present work, a systematic study of the formation of binary and ternary complexes of Palladium(II) involving dipicolinic acid and iminodiacetic acid as a primary ligands and amino acids (aliphatic and aromatic acids) as a secondary ligands by potentiometric technique at 30°C and I = 0.5 M promoted us to calculated the stability and formation constants of ligands and its Palladium(II) complexes.

CHAPTER II

EXPERIMENTAL

2. Experimental

2.1. Materials:

Dipicolonic acid, iminodiacetic acid, amino acids are obtained from Fluke, Palladium(II) chloride provided by BDH, Sodium nitrate (grade A.R), KH-phthalate solution, nitric acid, aliphatic and aromatic carboxylic acids were from Merck.

2.2. Solutions:

Stock solutions of dipicolinic acid(DPA), iminodiacetic acid(IDA), amino acids, aliphatic and aromatic acids were prepared by dissolving precisely weighted amounts of the its in suitable volumes of distilled water as following :-

(1) - Dipicolinic acid (99%):

0.01 M in 100ml water:

Weight = 0.01×167.1× 100 /1000 = 0.1671gm.

(2) - Iminodiacetic acid (99.1%):

0.01 M in 100ml water:

Weight = 0.01×133.1× 100 /1000 = 0.1331gm.

(3) - Glycine (99.7%):

0.01 M in 100ml water:

Weight = 0.01×75.07 × 100 /1000 = 0.0751gm

(4) – Alanine (99%):

0.01 M in 100ml water:

Weight = 0.01×89.09× 100 /1000 = 0.0891gm.

(5) - Valine (99.1%):

0.01 M in 100ml water:

Weight = 0.01×117.15× 100 /1000 = 0.1172gm.

(6) - Phenylalanine (99.2 %): .
0.01 M in 100ml water:

Weight = 0.01×165× 100 /1000 = 0.165gm.

(7) - Tryptophan (99 %):
0.01 M in 100ml water:

Weight = 0.01×204.23× 100 /1000 = 0.2042gm.

(8) - Methionine (99 %):
0.01 M in 100ml water:

Weight = 0.01×149.21× 100 /1000 = 0.1492gm.

(9) - Leucine (99.1 %):
0.01 M in 100ml water:

Weight = 0.01×131.18× 100 /1000 = 0.1312gm.

(10) - Aspartic acid (98 %):
0.01 M in 100ml water:

Weight = 0.01×133.1 × 100 /1000 = 0.1331gm.

(11) - Glutamic acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×147.13 × 100 /1000 = 0.1471gm.

(12) - Histadiene (99 %):
0.01 M in 100ml water:

Weight = 0.01×209.63 × 100 /1000 = 0.2096gm.

(13) - Phathalic acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×166 × 100 /1000 = 0.166gm.

(14) - Salicylic acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×138.12 × 100 /1000 = 0.1381gm.

(15) - Succinic acid (99.5 %):
0.01 M in 100ml water:

Weight = 0.01×118.09 × 100 /1000 = 0.1181gm.

(16) - Malonic acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×118.09 × 100 /1000 = 0.1181gm.

(17) - Malic acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×134.09 × 100 /1000 = 0.1341gm.

(18) - Oxalic acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×134.09 × 100 /1000 = 0.1341gm.

(19) - Tartaric acid (99 %):
0.01 M in 100ml water:

Weight = 0.01×134.09 × 100 /1000 = 0.1341gm.

Palladium(II) chloride was prepared by dissolving precisely weighted amounts of the its in suitable volumes of distilled water as following :-
Pd(II) 0.01 M in 100ml water:

Weight = 0.01×171.31 × 100 /1000 = 0.1713gm.

Carbonate-free sodium hydroxide(titrant, prepared in 0.5 M $NaNO_3$ solutions) was prepared[85] and then standardized potentiometrically against KH-phthalate solution as following:

NaOH 0.1M in 250ml water:

Weight = 0.1M ×40 × 250 /1000 = 1gm.

Stock solutions of nitric acid were prepared by suitable dilutions of the concentrated stock solutions(14.0M), was used for maintaining constant ionic strength.

HNO_3(65%) 0.04M in 250ml water:

Strength = % × d × 10
= 65× 1.4 × 10
= 910

Strength = M × Maw

M = 910/63 = 14

N × V = N' × V'

14 × V = 0.04 × 250

V = 0.04 × 250 / 14

V = 0.7ml.

Where put 0.7ml of nitric acid in measuring flask 250 ml and dilute by distilled water.

Stock solution (0.5M) of sodium nitrate was prepared by dissolving the exact weight of it in the required volume of distilled water and then certain volumes were used to maintain constant ionic strength.

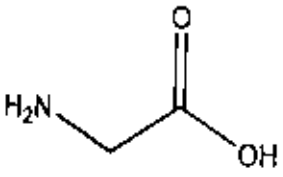
$NaNO_3$(99.5%) 0.5M in 250ml water:

Weight = 0.5M ×84.99 × 250 /1000 = 10.62gm.

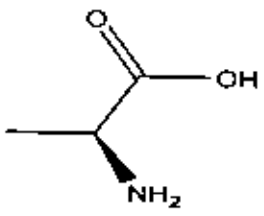
KH-phthalate was prepared and used to calibrate electrode system before and after each titration at 30 ± 0.1C°.

A frech sample was weighted and solution was prepared for each titration to exclude loss by hydrolysis or photochemical decomposition.

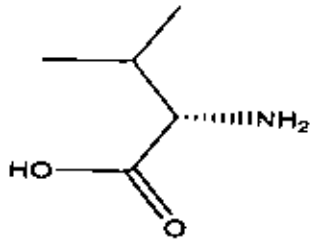
The geometrical structure of the ligands used in this work are represented in scheme (3):



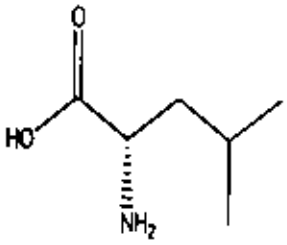
glycine



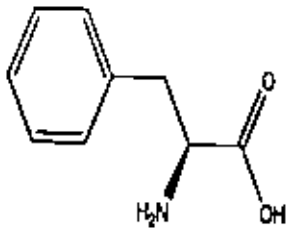
alanine



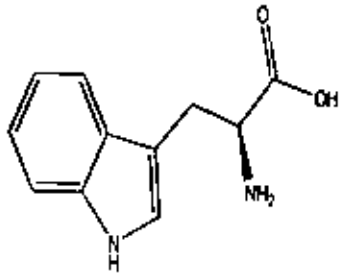
valine



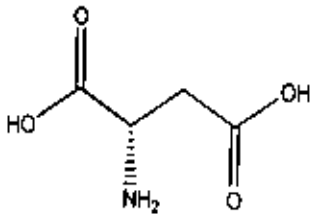
leucine



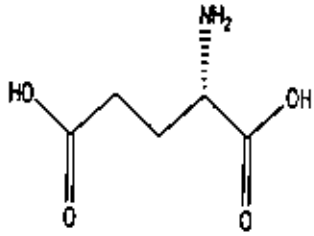
phenylalanine



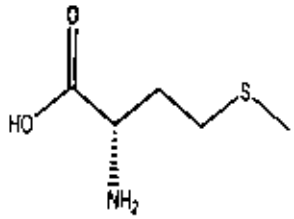
tryptophane



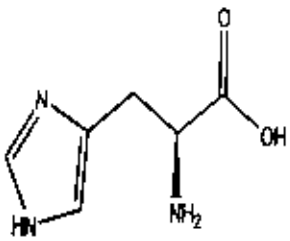
aspartic acid



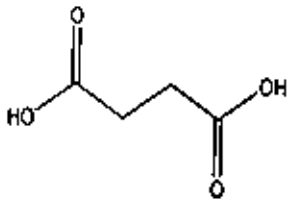
glutamic acid



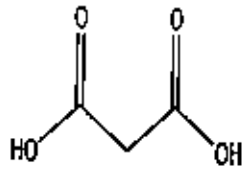
methionine



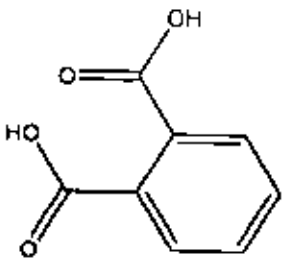
histidine



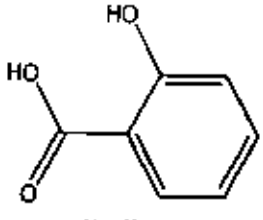
succinic acid



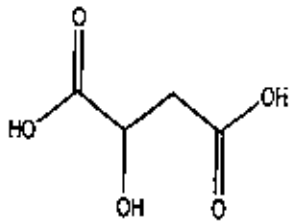
malonic acid



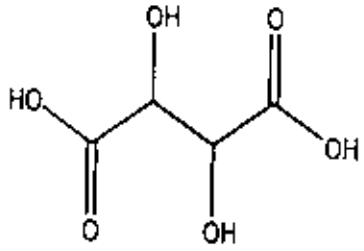
phthalic acid



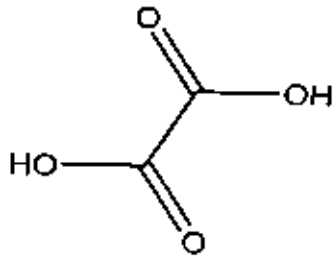
salicylic acid



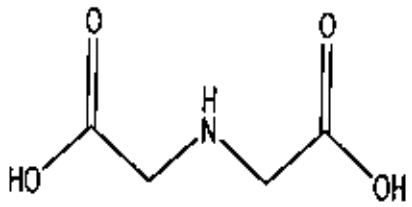
malic acid



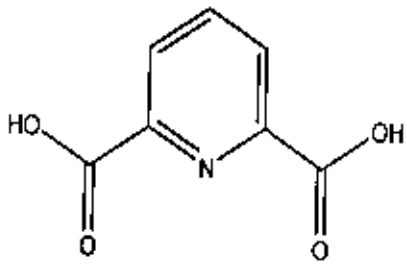
tartaric acid



oxalic acid



iminodiacetic acid (IDA)



pyridine2,6dicarboxylic acid (DPA)

Scheme (3) : Geometrical structure of the ligands.

2.3. Experimental techniques:-

Potentiometry using glass electrode was discovered upon observing an electric potential difference set when a then glass membrane was placed between two solutions, many cations, especially protons, may be detected.

Haber and Klemenswicz[86] showed that the response was strict and number of tests was concerned with the electrode properties[87,88] Jacques[90] first suggested that the glass electrode potentiometry could be used for determining formation constants and concentrations.

It was only after the work of Bjerrum[91] that the field was widely extended in the 1950's and 1960's, becoming then standard tool utilized for the determination of formation constants[92, 94].

The method as applied for measurement of metal-complex stability constants, has been briefly based on pH-metric titration of the ligand in absence and presence of metal ions.

The main advantages of potentiometry are:

(i) Very little chemical reaction takes place at the electrode solutions interface during each measurement .

(ii) Concentration of metal ions as low as 10^{-7}mol/dm^3 for H_3O^+, even less for S^{2-}, can be measured at as low as a precision as 0.05%.

(iii) The method produces formation constants with greater degree of precision as reflected by considerably small standard deviations.

2.4. Apparatus :

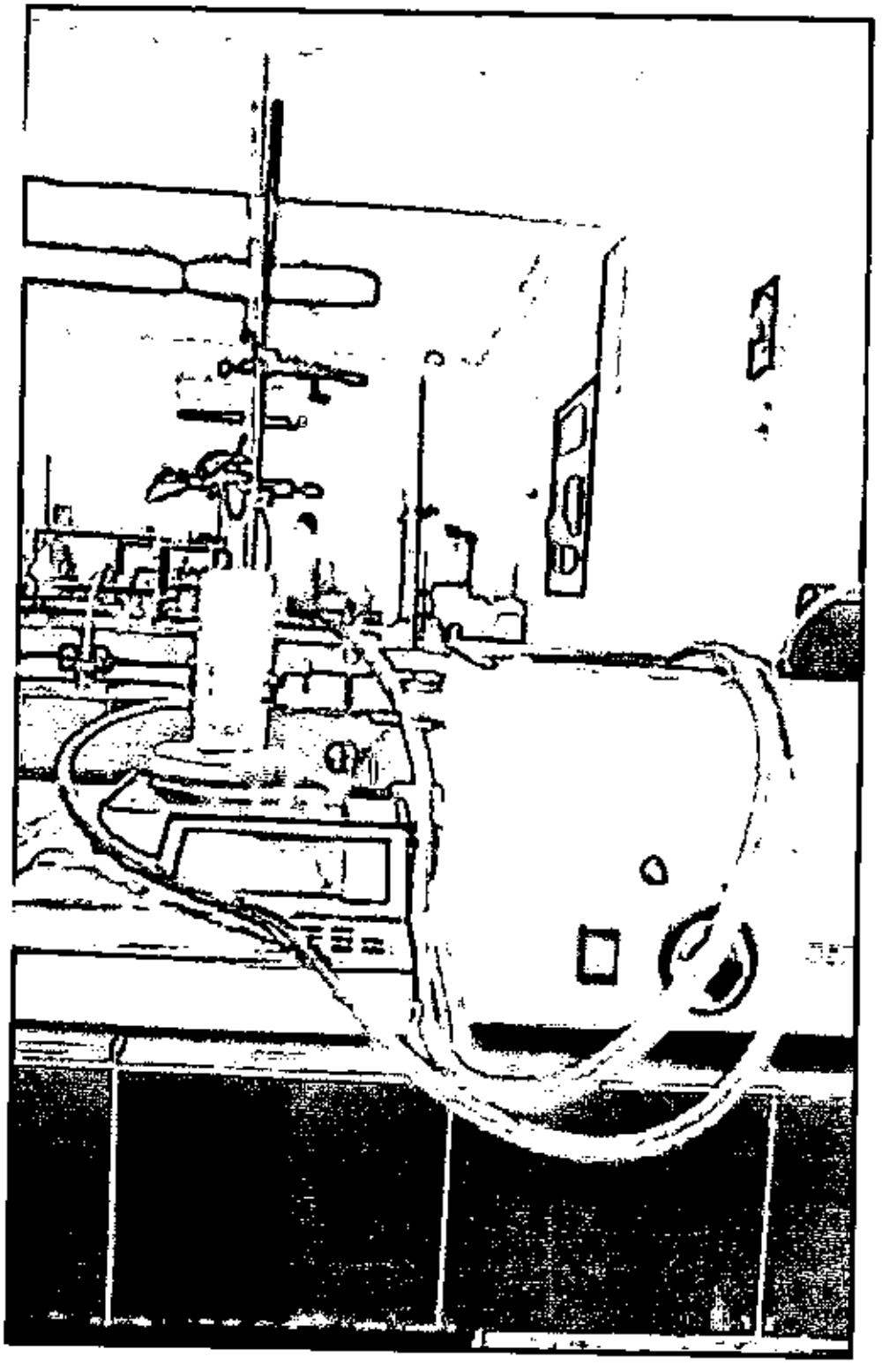
All glass-ware used were pyrex and checked with the standard burette[95]. Potentiometric pH measurement were carried out on solutions in a double-walled glass vessel at 30 ± 0.1°C using a pH-meter CG 825 pH-meter.

The temperature was controlled by circulating water through the jacket, from a constant temperature bath. The titration cell was equipped with magnetic stirrer and a tightly fitting rubber stopper, and electrode system were inserted.

The electrode system is a combined glass electrode(2-12 pH) which was calibrated with a standrad 0.05M KH- phthalate solution (pH = 4.01) before and after each titration.

The electrode system was calibrated in terms of hydrogen ion concentration instead of activities. Thus, all constants determined in our work are concentration constants. Conductance of solutions were measured with HANNA HI 9835, Microprocessor conductivity / TDS Meter.

The conductance measurements were performed at 30°C ± 0.01°C where the temperature was controlled by circulating water through the cell jacket, from a constant temperature bath.



2.5. Procedure and measuring techniques:-

The following mixtures are prepared to investigate the equilibria involved in proton /or metal– ligand complexes. Mixture(a-f) was prepared and titrate potentiometrically with standradized carbonate–free sodium hydroxide solution (0.1 M in 0.5M $NaNO_3$ solution).

(a) 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$(10ml).

(b) 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$(10ml)+ 0.01M DPA or IDA(5ml)

(c) 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$(10ml) + 0.01M DPA or IDA(5ml) + 0.01M Pd(II) ion (2ml).

(d) 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$(10ml) + 0.01M amino acid or carboxylic acid (5ml).

(e) 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$(10ml) + 0.01M amino acid or carboxylic acid (5ml) + 0.01 M Pd(II) ion (2ml).

(f) 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$(10ml) + 0.01 M Pd(II) ion (5ml) + 0.01M DPA or IDA (5ml) + 0.01M amino acid or carboxylic acid (5ml)

(g) 0.01M Pd(II) ion (10ml) + 0.01M DPA or IDA (10ml) + 0.01M amino acid or carboxylic acid (10ml).

Mixture(g) was titrated conductometrically against 0.1M NaOH solution.

Where :-

DPA = Dipicolonic acid .

IDA = Iminodiacetic acid .

Amino acids = (glycine, alanine, histidine, leucine, aspartic, glutamic, valine, tryptophane, methionine and phenylalanine).

Aliphatic or aromatic acids = (malic, malonic, phthalic, oxalic, tartaric, succinic and salicylic).

In all systems, the total volume in each case was adjusted to 50 ml by adding distilled water. All pH-metric titration were performed

at 30 °C and I = 0.5 M ($NaNO_3$). An irving and Rossotti pH titration technique with modifications[96,99] was used to determine the protonation constants of the ligands and formation constants of the metal complexes. Multiple titrations have been performed for each system. The equilibrium constants were calculated from six indepenedent titration curves. All our calculations of stability constants have been determined successfully at the optimum pH region (usually low pH region). Thus, the formation of hydroxy complexes or mixed-ligand complexes with hydroxy groups could be neglected .

2.6. Calculation of the formation constnts:

An Irving and Rossotti pH titration technique with modifications[96,99] was used to determine the protonation constants of the ligands and formation constants of the different binary and ternary metal ion complexes.

2.6.1. Proton –ligand and Palladium(II)– ligand formation constant:

The protonation constants of the ligands were determined from the titration curves (Fig.7) of solutions **(a+b)** and **(a+d)** by plotting the parameter n'_H (n'_H = average number of mole protons associated with the ligands) with pH (Figs. 2 & 3). The stability constants pKa_1 and pKa_2 of the ligands (DPA, IDA, aliphatic and aromatic acids) were obtained from the relationship as shown in Fig.(2) at n'_H equal to 1.5 and 0.5 we have pH which equal to pKa_1 and pKa_2 respectively. The stability constant pKa_2 of the amino acid ligands was determined from the relationship in Fig.(3) at $n'_H = 0.5$.

The metal ligand formation constants were determined from the titration curves of the solutions **(a + b + c)** and **(a + d + e)** by plotting the parameter n' (n' = average number of moles of ligand coordinated to

metal ions) versus pL (pL = free ligand exponent at several pH values) as shown in Figs. (4) & (5).

The formation constant of the binary complexes ($\log K_{ML}^{M}$) was determined from the relationship as shown in Figs. (4) & (5) at n' = 0.5, we have pL is equal to ($\log K_{ML}^{M}$) where K_{ML}^{M} is the formation constant values of the (1:1) binary complexes

An Irving and Rossotti program contains the following equations (10-16) which were used for the calculation of stability and formation constants of ligangs and it is metal complexes. First, using the pH – metric titration curves **(a+b)** and **(a+d)** the average number of moles of protons per mole of ligand, n'_H, at several pH values for the above mentioned ligands was calculated using the following equations :

$$\bar{n}_H = Y - \frac{(V_b or V_d - V_a)(E^0 + N^0)}{(V_0 + V_a)T_L^0} \quad \text{.....(10)}$$

The average number of moles of ligand coordinated to metal ion is calculated from the relationship:

$$\bar{n} = \frac{(V_e - V_b) or (V_e - V_d)\left[(E^0 + N^0) + T_L^0 (Y - \bar{n}_H)\right]}{(V_0 + V_b) or (V_0 + V_d)\bar{n}_H T_M^0} \quad \text{.....(11)}$$

And since , $(E^o + N^o) >>> T_L^o$, thus:

$$\bar{n} = \frac{(V_e - V_b) or (V_e - V_d)(E^0 + N^0)}{(V_0 + V_b) or (V_0 + V_d)\bar{n}_H T_M^0} \quad \text{.....(12)}$$

Generally we obtain ,

$$pL = \log\left\{ \sum_{y=0}^{y=1or2} \frac{B_y (1/10^B)^y}{T_L^0 - n\bar{T}_M^0} \times \frac{(V_0 + V_e or V_e)}{V_0} \right\} \quad \text{.....(13)}$$

Thus , for binary metal complexes, equation (13) was simplified to become as follows:

$$pL = \log\left\{ \frac{1+10^{pk_{a2}}(1/10^B)}{T_L^0 - n\bar{T}_M^0} \times \frac{(V_e + V_0)}{V_0} \right\} \quad \text{.....(14)}$$

For the binary metal complexes of dipicolonic acid, succinic, oxalic, malic, malonic, tartaric, salicylic, and phthalic acids, equation (13), was used in the following form:

$$pL = \log\left\{ \frac{1+10^{pk_{a2}}(1/10^B)+10^{pk_{a2}+pk_{a1}}(1/10^B)^2}{T_L^0 - n\bar{T}_M^0} \times \frac{(V_0 + V_c)}{V_0} \right\} \quad \text{....(15)}$$

where :

Y = no. of dissociable protons of the investigated ligands (y=1 in case of amino acids, and y = 2 in case of dipicolonic acid, iminodiacetic acid,aromatic and aliphatic acid).

T_L° = initial total molar concentration of all primary and secondary ligands studied in the titrated solution $=1\times 10^{-3}$ mol,dm^{-3}.

$V_\circ$ = Original volume of titrated solution = 50 cm^3.

V_a, V_b, V_c, V_d and V_e are the volumes of NaOH consumed volumes to reach at the same pH value for solutions a, b, c, d and e , respectively.

B_y = The proton – formation constant values of all the ligands studies .

$E_\circ$ = Concentration of HNO_3 acid in the titrated solution in mol.dm^{-3}.

$N_\circ$ = Concentration of NaOH in mol.dm^{-3}.

T_{M° = initial total molar concentration of metal ions used in the titrated solution in mol.dm^{-3}.

pK_{a2} = the second acid dissociation constant of the secondary ligands .

pK_{a1} & pK_{a2} = the first and the second acid dissociation constant value of primary ligands.

B = the pH – meter reading.

Experimental formation curves corresponding to the various ligands and their (1:1), binary metal complexes were obtained by plotting n'_H against pH and n' against pL, respectively. The corresponding acid formation constant values of the ligands and the stability constant values of their complexes were determined from the constructed n'_H - pH and pL curves, respectively.

2.7. Ternary palladium(II) complexes :

From the titration curves of the solutions (e) and (f) (Fig. 7), $n'_{mix.}$, the average number of moles of the secondary ligands (amino acids, aliphatic acids and aromatic acids) coordinated to the (1:1) binary complexes, [Pd(DPA)] or [Pd(IDA)].

Formation curves corresponding to the different ternary complexes under investigation were constructed by plotting $n'_{mix.}$ versus pL_{mix} (Fig. 6), the corresponding formation constant for the formed (1:1:1) mixed –ligand complexes were obtained by applying the average value method where at n'_{mix} equal 0.5, we have $pL_{mix.}$ is equal to $\log K^{MA}_{MAL}$ where, K^{MA}_{MAL} is the formation constant values of (1:1:1) mixed-ligand complexes formed.

$n'_{mix.}$ is the average number of moles of the secondary ligands is calculated from the following equations.

$$\bar{n}_{mix} = \frac{(V_f - V_c)\left[E^0 + N^0 + T_b^0(Y - \bar{n}_H)\right]}{(V_0 + V_c)\left[T^0_{M(DPA)or(CA)}\right]\bar{n}_H} \qquad \text{.....(16)}$$

and since $E^\circ + N^\circ >> T_L^\circ$

$$\bar{n}_{mix} = \frac{(V_f - V_c)\left[E^0 + N^0\right]}{(V_0 + V_c)\left[T^0_{M(DPA)or(CA)}\right]\bar{n}_H} \qquad \text{.....(17)}$$

Where V_f and V_c are the volumes of NaOH consumed to reach same pH value in the curves (f) and (c), respectively.

$[T^\circ_M$ (DPA) or (IDA) $|$ is the concentration of the binary metal-dipicolonic acid or metal–iminodiacetic acid complex which is equivalent to the initial metal ion concentration T°_M , $\bar{n}_H$ is the average number of protons associated with the secondary ligand , (these values are available

at different pH values from the binary complexing system). T°_{L} is the initial concentration of the secondary ligand and y is equal 1 in case of amino acid and y = 2 in case of dicarboxylic acid. $V_{\circ}$, E° and N° have the same meaning as mentioned before .

From the values of n'_{mix} so obtained, free secondary ligand exponent , pL'_{mix} was calculated using the equation :

$$pL_{mix} = \log\left\{ \sum_{y=0}^{y=1or2} \frac{B_y (\frac{1}{10^B})^y}{T_L^0 - \bar{n}_{mix} T_M^0} \times \frac{(V_0 + V_f)}{V_0} \right\} \quad \text{.....(18)}$$

By = the acid formation constant value for the secondary ligand .

T°_{L} = the initial total molar concentration of secondary ligands.

B = the pH – meter reading.

Thus on applying amino acids and carboxylic acids as secondary ligand , we obtain :

$$pl_{mix} = \log\left\{ \frac{1 + 10^{pk_{a2}} (\frac{1}{10^B})}{T_L^0 - \bar{n}_{mix} T_M^0} \times \frac{(V_0 + V_f)}{V_0} \right\} \quad \text{.....(19)}$$

Formation curves corresponding to the different ternary complexes under investigation were constructed by plotting $n_{mix.}$ Versus $pL_{mix.}$, the corresponding formation constant for the formed (1:1:1) mixed –ligand complexes were obtained by applying the verage value method where at

$\bar{n}_{mix}$ equal 0.5 , we have pL_{mix}. is equal to log K^{MA}_{MAL} where , K^{MA}_{MAL} is the formation constant values of (1:1:1) mixed- ligand complexes formed.

The stability constants of the palladium(II) complexes under infistigation can not be determined spectrophotometerically.It was found that there is no change in the absorbance of these complexes with the change of pH from 2 to 12. This mean that the colour of the palladium(II) complexes can not effected by the change of pH.

Table(1): Potintiometric titration values of glycine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$) as example for calculation.

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.55	2.71	2.55
0.25	2.71	2.75	2.44	2.57	2.81	2.61
0.5	2.77	2.80	2.49	2.59	2.88	2.66
0.75	2.88	2.89	2.56	2.61	2.98	2.73
1	3.02	2.96	2.62	2.62	3.06	2.79
1.25	3.23	3.10	2.70	2.64	3.17	2.88
1.5	3.65	3.23	2.78	3.00	3.29	2.96
1.75	5.13	3.46	2.90	4.08	3.61	3.10
2	8.30	3.60	3.00	7.40	4.20	3.22
2.25	10.39	3.80	3.18	9.64	8.17	3.44
2.5	10.81	4.40	3.35	10.45	9.29	3.78
2.75	11.11	5.25	3.74	10.66	9.89	4.33
3	11.27	6.85	4.68	10.80	10.39	6.37
3.25	11.41	9.61	8.44	11.02	10.81	7.73
3.5	11.49	10.61	9.90	11.21	10.99	9.38
3.75	11.59	10.88	10.40	11.34	11.14	10.22
4	11.65	11.11	10.74	11.45	11.30	10.58
4.25	11.69	11.26	10.91	11.55	11.42	10.94
4.5	11.73	11.37	11.06	11.63	11.50	11.10
4.75	11.80	11.46	11.22	11.69	11.60	11.26
5	11.83	11.54	11.38	11.73	11.65	11.35

Where:

(a) : 0.04M HNO_3(5ml) + 0.5M $NaNO_3$ (10ml) + 35ml water.

(b) : 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$ (10ml) + 30ml water.

(C) : 0.04M HNO_3(5ml)+ 0.5M $NaNO_3$ (10ml) + 0.01M DPA(5ml) + 0.01M Metal ion(2ml) +28 ml water.

(d) : 0.04 M HNO_3(5ml) + 0.5M $NaNO_3$(10ml) + 0.01M glycine (5ml)+ 30ml water.

(e) : 0.04 M $HN0_3$ (5ml) + 0.5M $NaNO_3$ (10ml) + 0.01 M glycine (5ml) + 0.01 M Pd(II) ion (2ml) + 28ml water.

(f) : 0.04M HNO_3 (5ml) + 0.5M $NaNO_3$ (10ml) +0.01M metal ion (5ml) +0.01M DPA (5ml) + 0.01M glycine (5ml) + 20ml water.

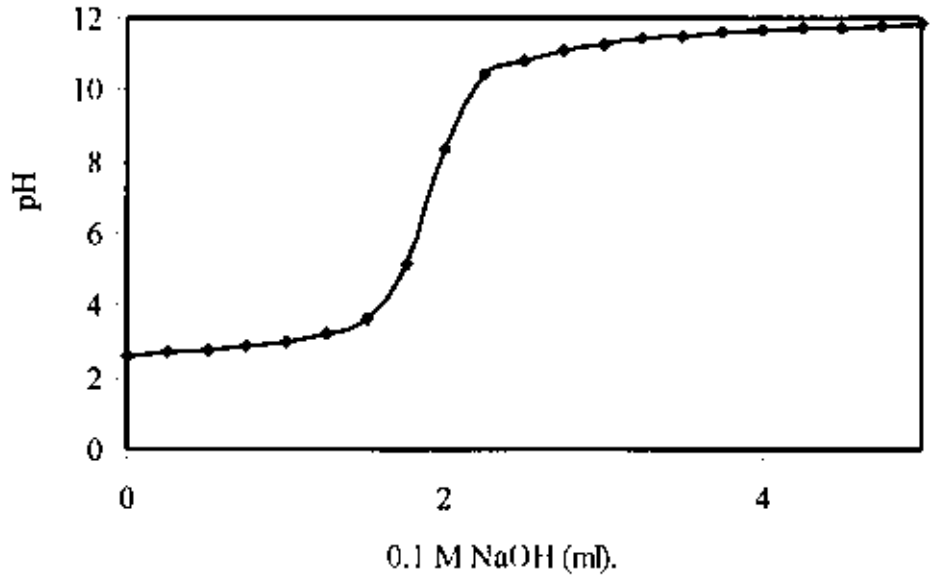


Fig.(1-a):Potintiometric titration curve for nitric acid system.

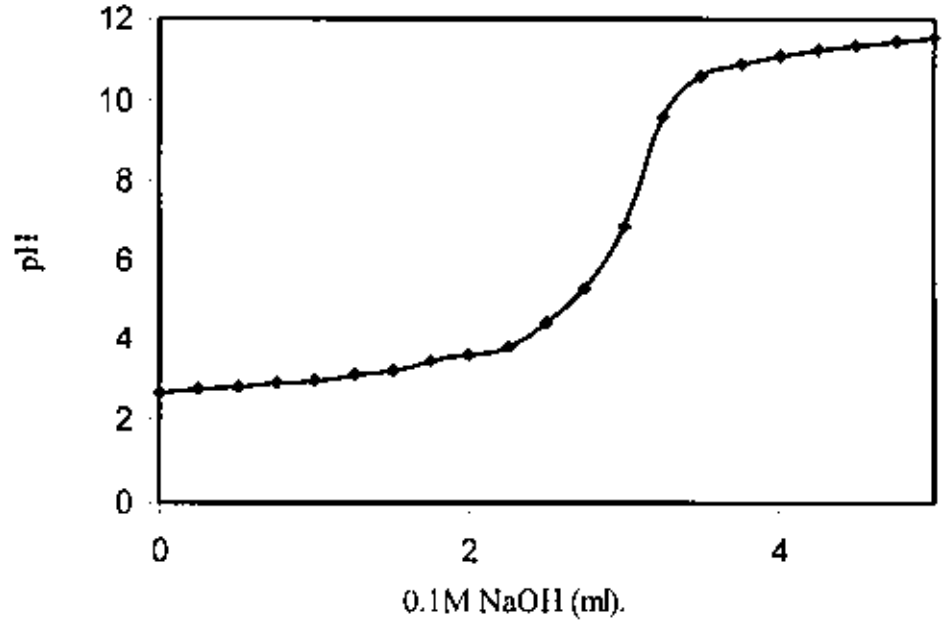


Fig.(1-b):Potintiometric titration curve for brimary ligand(DPA) system.

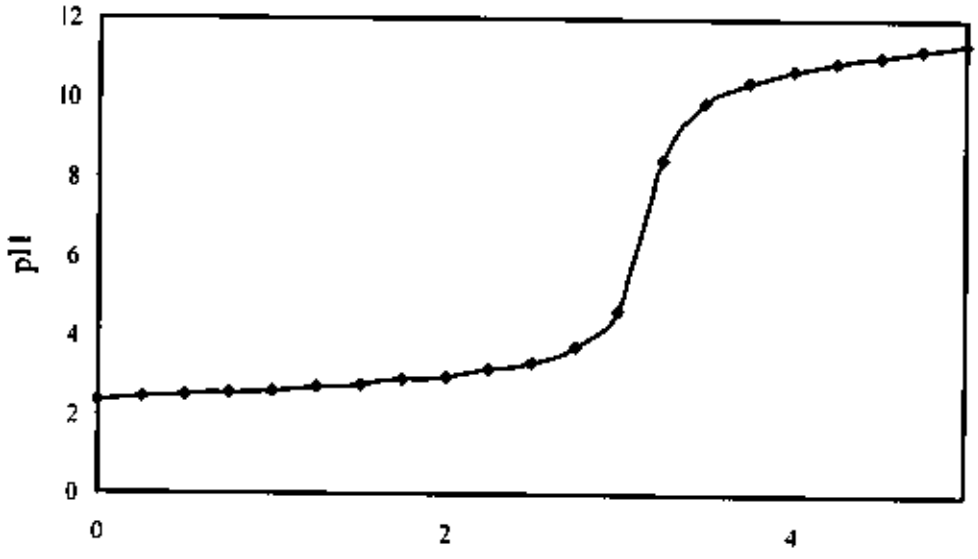


Fig.(1-c):Potintiometric titration curve for binary complex (DPA-Pd(II)) system.

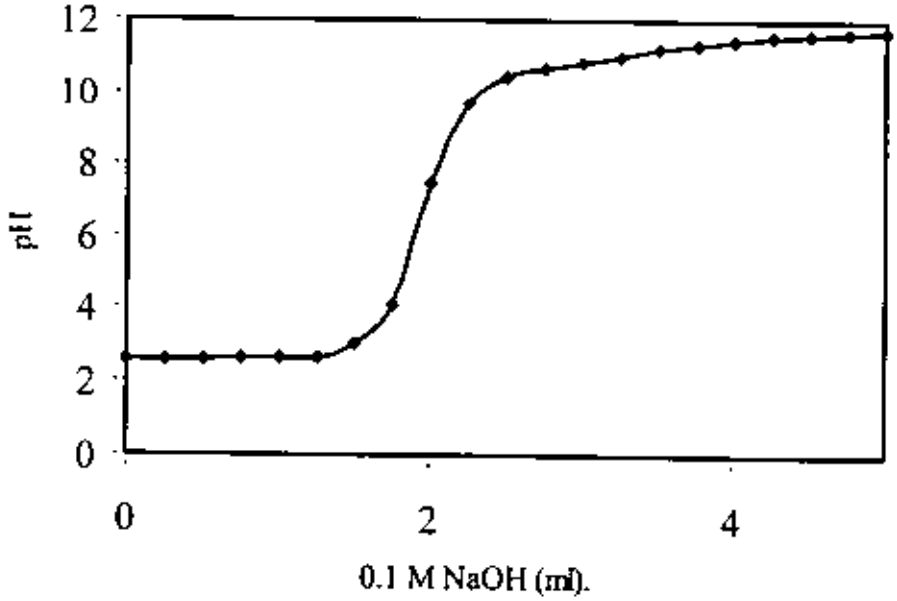


Fig.(1-d):Potentiometric titration curve for secondary ligand system(glycine).

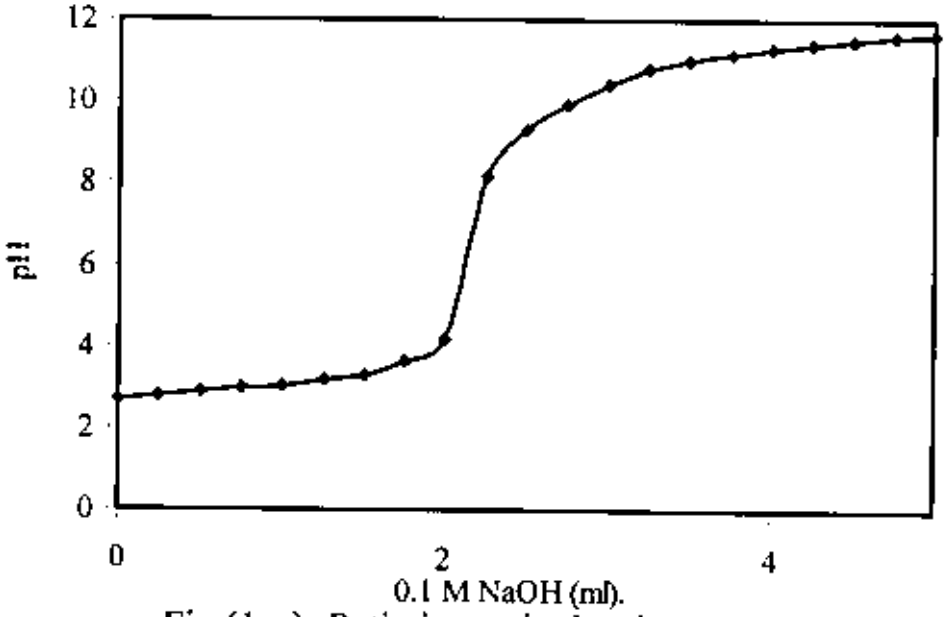


Fig.(1-e): Potintiometric titration curve for binary complex(glycine-Pd(II)) system.

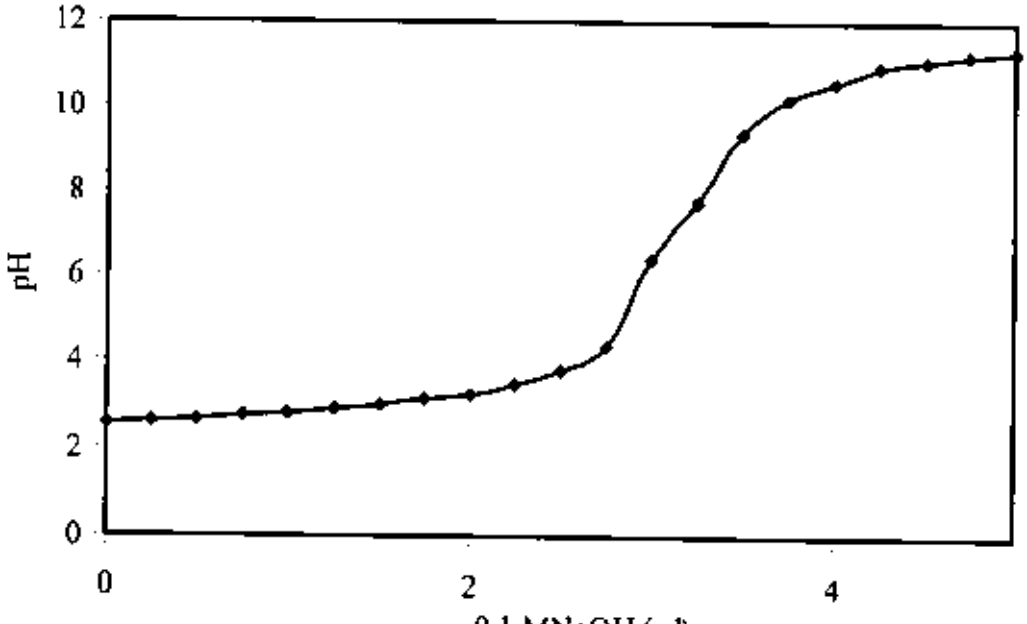


Fig.(1-f):Potentiometric titration curve for ternary complex(glycine-Pd(II)-DPA) system.

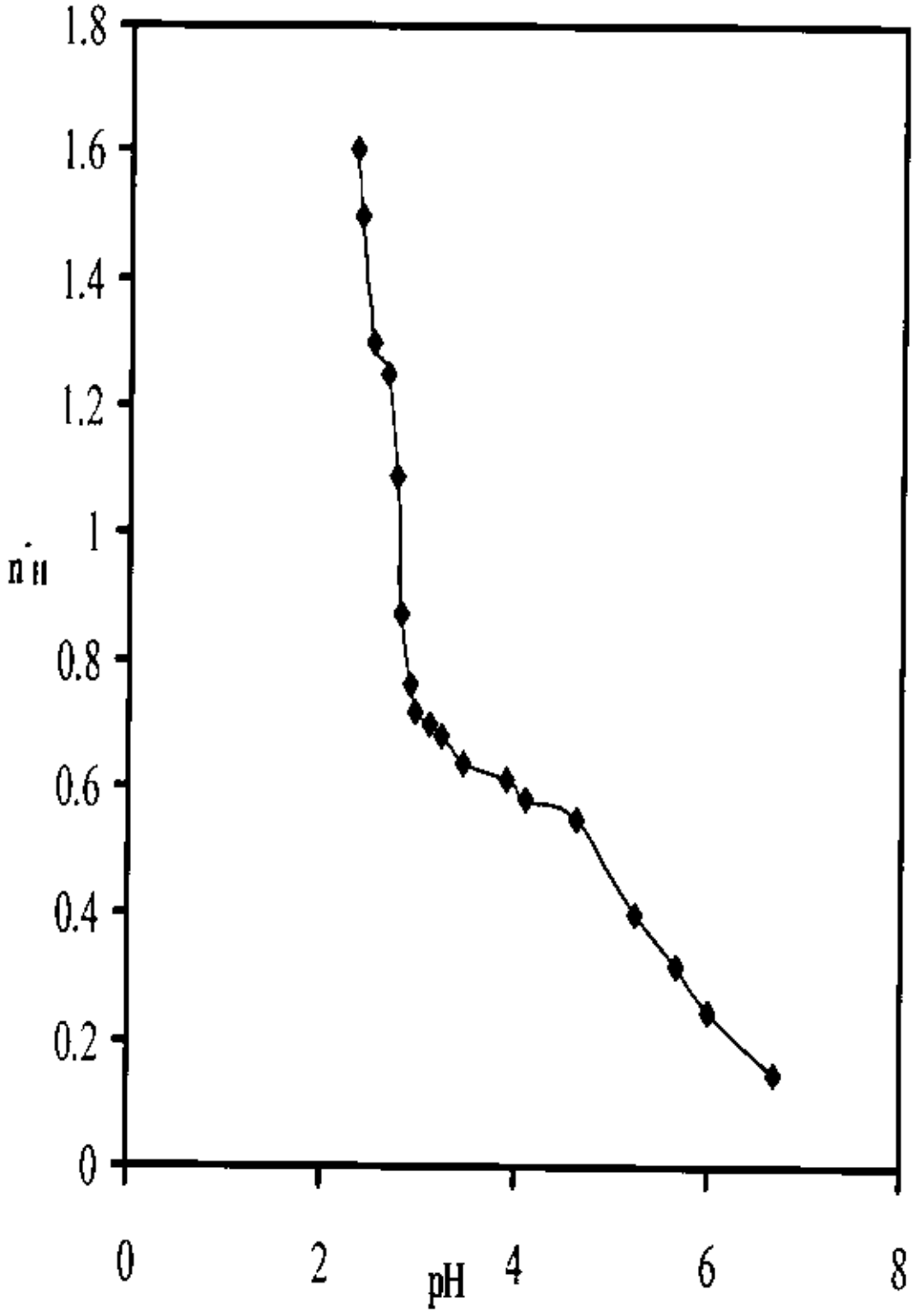


Fig.(2) Formatoin curve for proton-dipicolinic acid system.

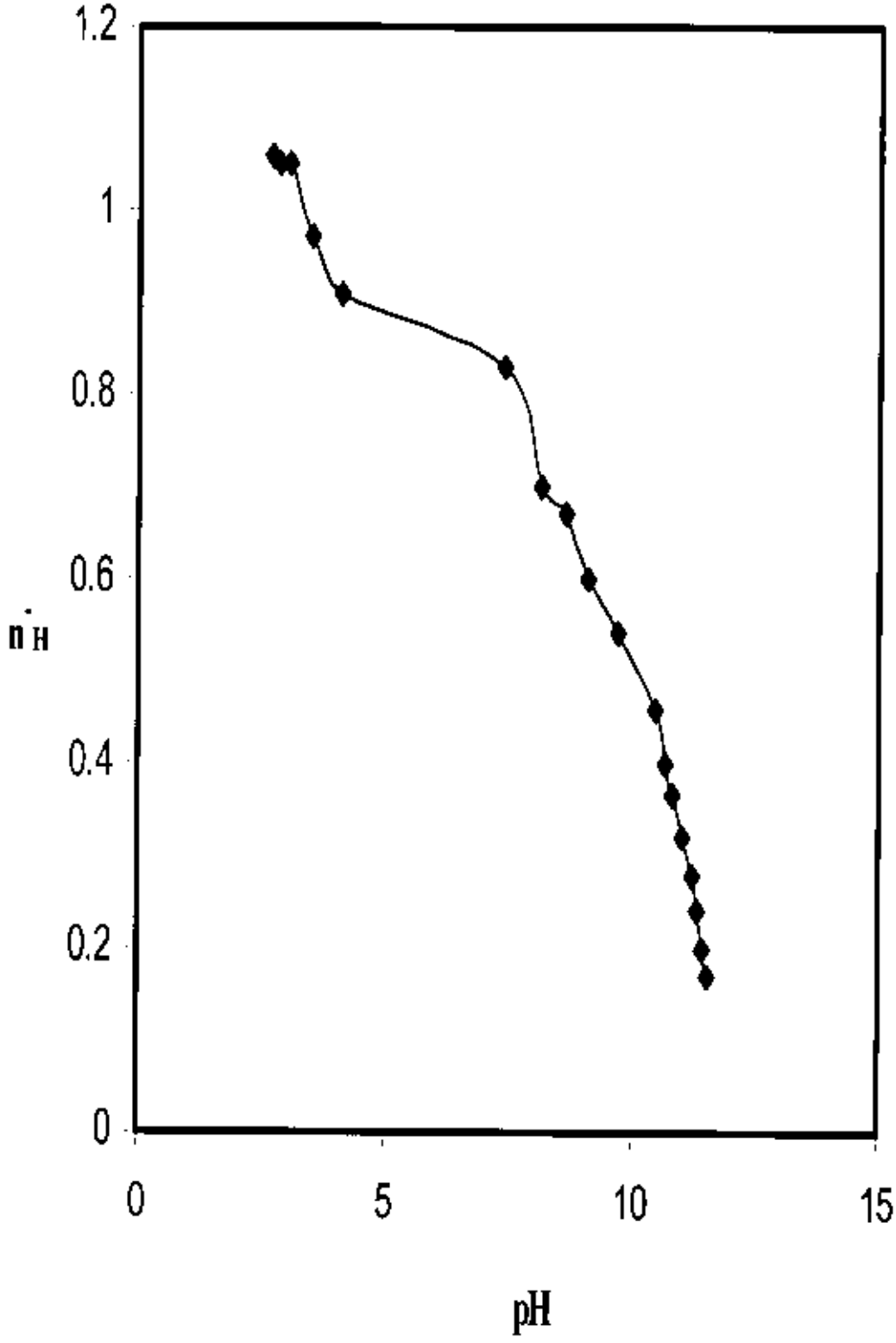


Fig.(3) Formatoin curve for proton-glycine system.

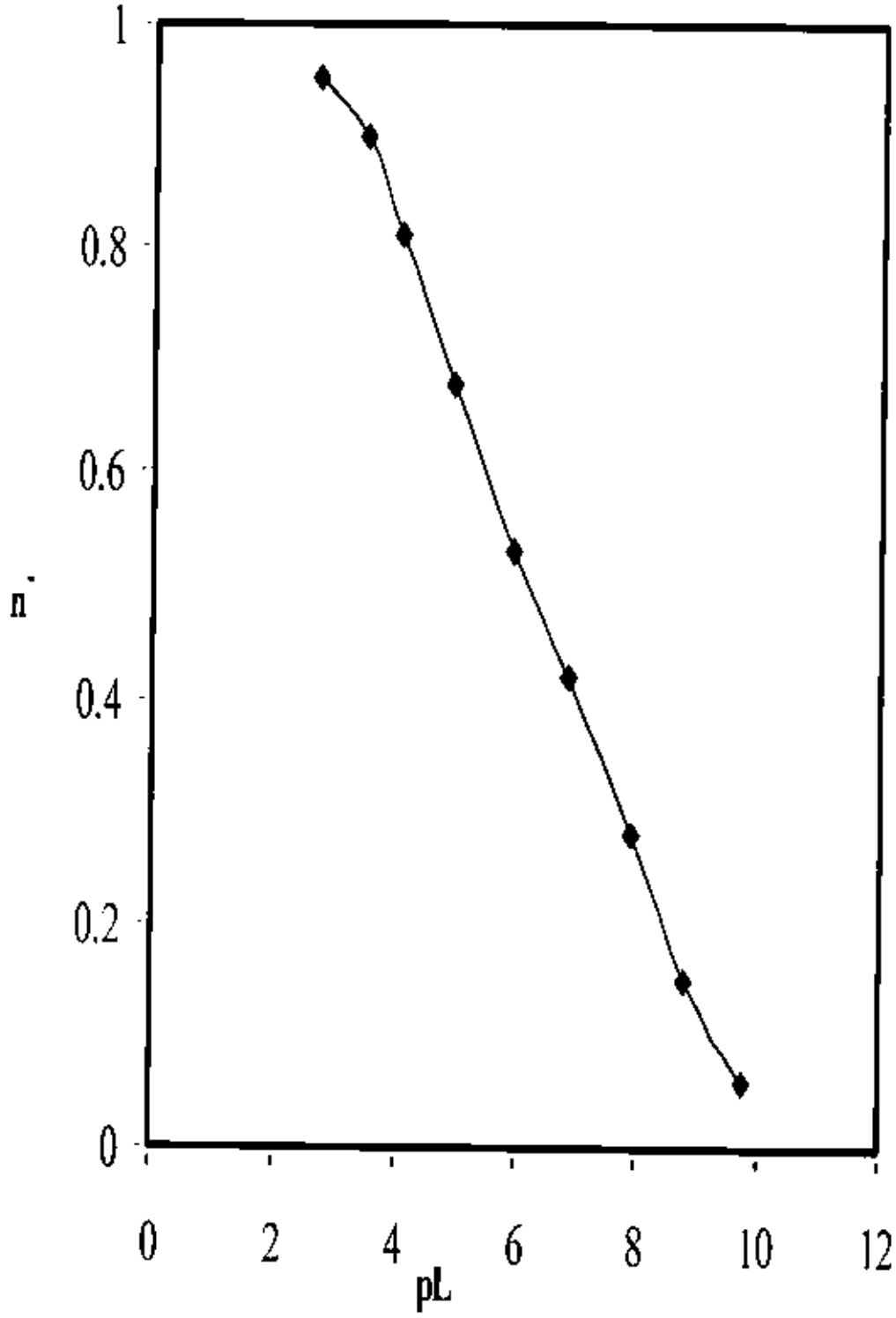


Fig.(4) Formatoin curve for pd(II)-glycine system.

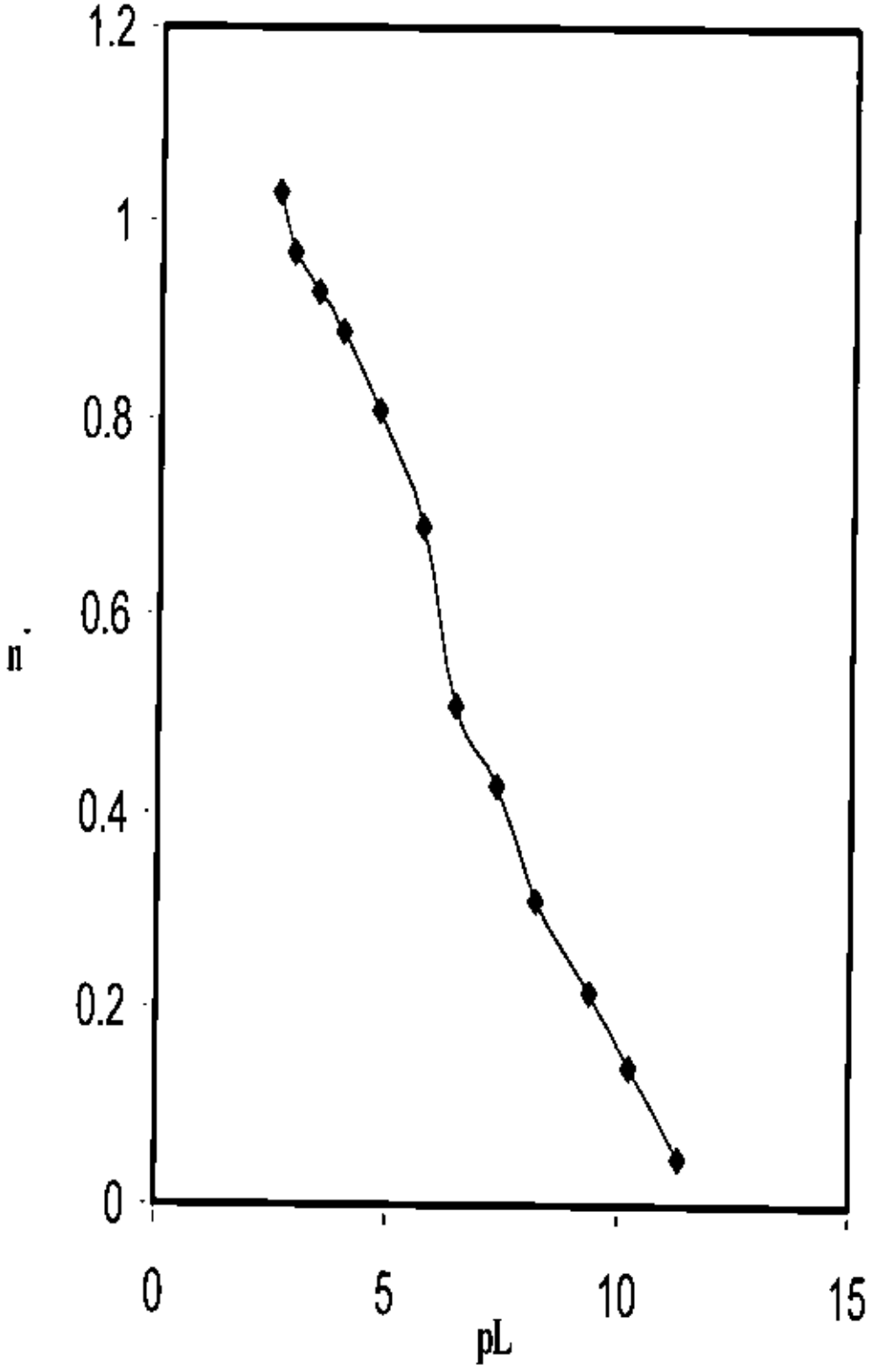


Fig.(5) Formatoin curve for pd(II)-dipicolinic acid system.

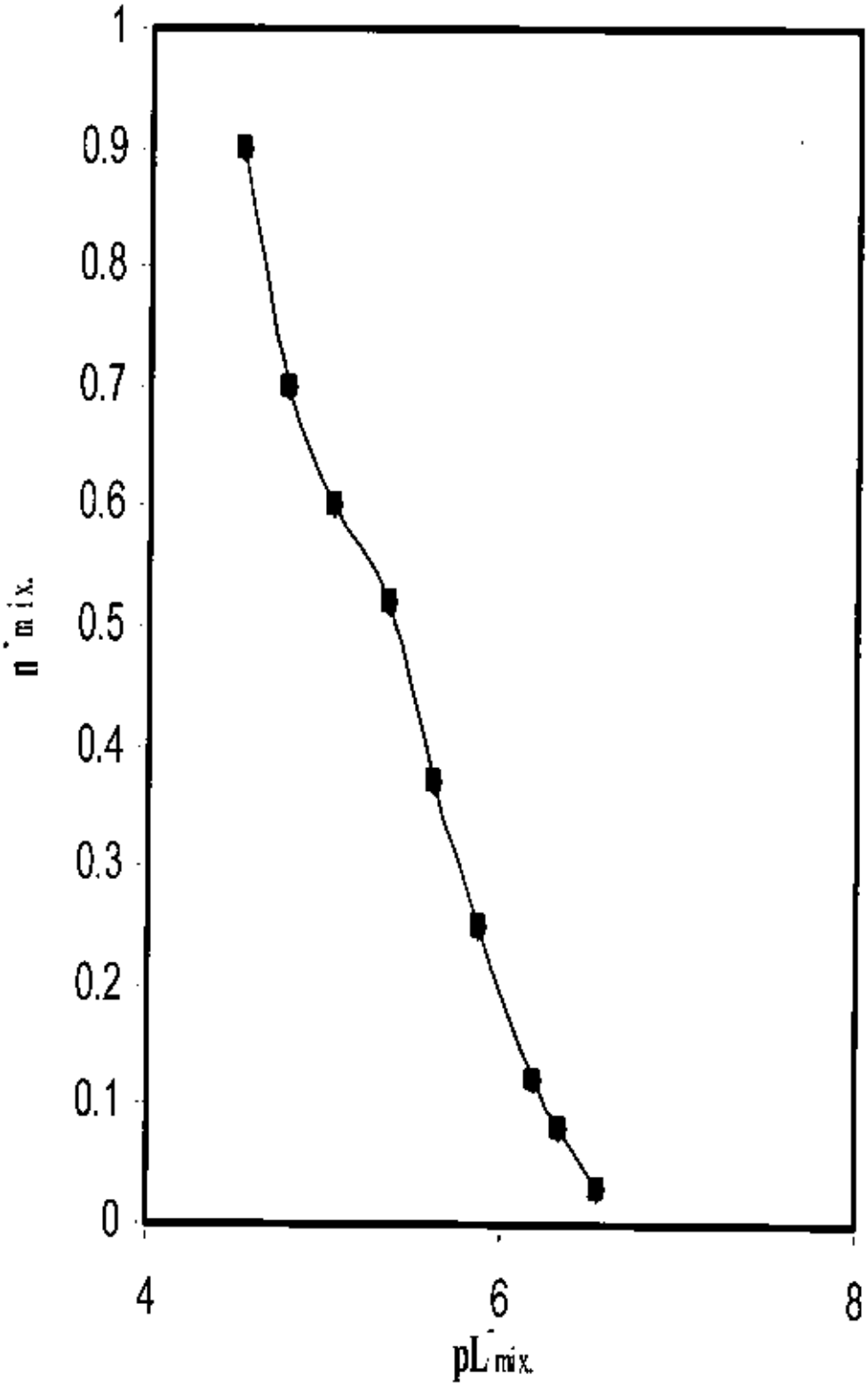


Fig.(6) Formatoin curve for pd(II)-dipicolinic acid- glycine system.

CHAPTER III

Results and discussion

3. Results and discussion

3.1. Palladium(II) complexes of dipicolinic acid (DPA) in solution :

The formation and stability of chelates of the palladium(II) with the biologically important ligands, dipicolinic acid, amino acids, aliphatic acids and aromatic acids have been studied potentiometrically. The results obtained on titration the solution mixtures (prepared as described in the experimental part) with NaOH solution are represented graphically in Figs.(7-23) as plots of pH versus ml added of NaOH. Calculations of dissociation constants of ligands and stability constants of binary and ternary complexes were obtained from the titration curves using Irving and Rossotti pH technique with modifications [96,99] are collected in Tables (19-23). Δ log K values have been evaluated and discussed .

The chelation mode of ternary complexes formed was ascertained by conductivity measurements in solution.

3.1.1. Proton – ligand equilibria :

The protonation constants of the ligands used (DPA, amino acids aliphatic and aromatic acids) could be calculated from the potentiometric titration curves **a, b** in case of primary ligand (DPA) and curves **a, d** in case of secondary ligands (amino acids, aliphatic and aromatic acids). In all protonation reactions were observed to take place within the potentiometrically measureable pH range (2-11). An Irving and Rossotti pH technique with modifications[96,99] was used to calculate the protonation constants of the ligands.

Protonated dipicolinic acid, H_2D (D = dipicolinate dianion) can be further protonated as the acidity of the medium increases forming a monopositive species, H_3D^+. However, in the pH range utilized, this cationic form always proved negligible as checked previously using spectrophotometreic technique[29]. The first and second proton

association constants of neutral DPA were determined potentiometrically in aqueous solutions, under the experimental conditions (30 °C, I = 0.5 M $NaNO_3$). The values obtained are in a good agreement with the literature values[100].

The dissociation constant values of the amino acids, aliphatic and aromatic acids were determined under identical conditions using the Irving-Rossotti method described in the previous experimental section (Table 19).

3.1.2. Formation constants of binary palladium(II) complexes:

The formation constant values of normal 1:1 binary complexes of DPA with palladium (II) ion have been determined from the titration curves **b** and **c** in all systems (HNO_3 + DPA and HNO_3 + DPA + Pd(II), respectively), using the formula of Irving and Rossotti as explained in the experimental section. Generally, it is evident that curve **c** clearly departs from curve **b** denoting strong interaction between palladium(II) and DPA (Fig.7). The n'-pL experimental formation curves of (1:1) complexes of DPA with palladium(II) (n' = average number of DPA molecules attached per palladium(II) ion and pL = free DPA exponent) as calculated from the equations reported in the experimental part. In all systems no precipitation occurred at pH lower that at which n' = 0.5, indicating that hydrolysis of binary (1:1) Pd(II) : DPA is not likely to interfere in the determination of the stability constants of these systems (Table 20).

The stability constants of (1:1) binary complexes of secondary ligands (amino acids, aliphatic and aromatic acids) with palladium(II) ion are determined from the titration curves **d** and **e** in all systems (HNO_3+ secondary ligand and HNO_3 + secondary ligand + Pd(II),

respectively) using the same equations as in experimental part. It is worthy to note that curve **e** clearly departs from curve **d**, denoting the formation of a binary complex of secondary ligands in all systems investigated. The formation constants of the different(1:1) binary Pd(II):secondary ligands complexes were calculated from the relationship between n' (n' = average number of secondary ligand molecules bound to Pd(II)) and pL (free secondary ligand exponent) (Table 20). In all cases, no precipitation occurred at pH lower than at which n' = 0.5, indicate that hydrolysis of the Pd(II) is not likely to interfere in the determination of the stability constant values of the different(1:1) Pd(II) : secondary ligand binary complexes.

3.1.3. Ternary palladium(II) complexes:

The potentiometric titration curves of Pd(II)-DPA in presence of secondary ligands (L = amino acids, aliphatic and aromatic acids) showed strong overlap with the titration curves of Pd(II)-DPA in absence of secondary ligand (1:1) binary complexes) at lower pH as shown by curve **f** and curve **e**, respectively. This suggests that secondary ligand dose not combine with the binary Pd(II)-DPA complex at lower pH. Generally, above certain pH values which is largely dependent on the nature of the secondary ligand used, one observes a deviation of the ternary titration curves from that of the corresponding binary Pd(II)-DPA ones. This shows the coordination of secondary ligand with the binary Pd(II)-DPA complex in stepwise manner, i.e., the secondary ligand glycine starts complexation after the complete formation of the binary (1:1) complex of DPA .

Thus, it may be assumed that secondary ligand would combine with [Pd(DPA)] binary complex species in ternary systems similarly as it dose with $[Pd(H_2O)_n]^{2+}$ binary system. In this respect it is

worthy to indicate that in all cases of binary [Pd(DPA)] systems, binary complexes are quite stable up to the pH range where the attachment of secondary ligand takes place forming the ternary [Pd(DPA)(L)] systems. Thus one can easily deduce that the different ternary complexes under investigation are formed before hydrolyzing pH of the corresponding binary complexes. Generally no precipitation had occurred for ternary systems, indicating that hydrolysis of the formed complexes is not likely to interfere in the determination of the stability constants of these ternary complexes.

n'_{mix} and pL'_{mix} values for the (1:1:1) Pd(II) : DPA : L ternary complex system were calculated from the titration curves as shown in Fig.(6), using the equations reported in the experimental section, (n'_{mix} = average number of the secondary ligand molecules attached per [Pd(II)-DPA] complex and pL'_{mix} = free secondary ligand exponent, respectively). The formation constant values for the ternary metal complexes were obtained from the relation between n'_{mix} and pL'_{mix} are listed in Table (21).

For the formation of the ternary complexes of the palladium(II) (M) in presence of DPA (DPA = X) and secondary ligand (L = amino acids, aliphatic and aromatic acids), the following equilibria may be considered :

$$M + X \rightleftharpoons MX \quad \text{.....(20)}$$

$$MX + L \rightleftharpoons MXL \quad \text{.....(21)}$$

$$K_{MXL}^{MX} = \frac{[MXL]}{[MX]\,[L]} \quad \text{.....(22)}$$

The relative stability of the ternary complexes as compared with that of the corresponding binary complexes can be quantitatively expressed in different ways. The most suitable comparison is in terms of ΔlogK , which represents the difference in stabilities for the addition of ligand L to the (1:1) M(DPA) complexes and to the aquated metal ion $[M(H_2O)_n]^{2+}$ as shown by equation (23)[101] .

$$\Delta \log K = \log K^{MX}_{MXL} - \log K^{M}_{ML}$$

$$= \log K^{ML}_{MXL} - \log K^{M}_{MX} \quad \text{.....(23)}$$

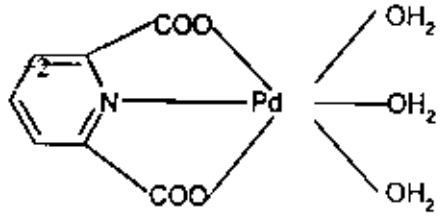
The overall stability constant, which must be determined experimentally, is connected to by equation (24) as shown below :

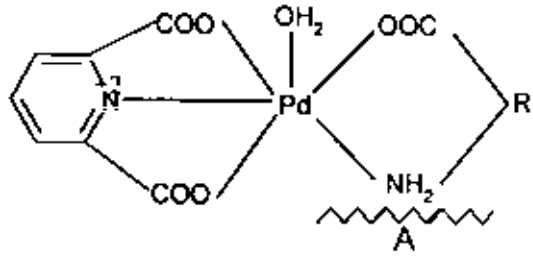
$$\log K^{MX}_{MXL} = \log \beta^{M}_{MXl} - \log K^{M}_{MX} \quad \text{.....(24)}$$

It is observed. that in general, ΔlogK for the investigated ternary complexes is negative as expected from the statistical considerations as shown table(21). Since the primary ligand is coordinated to the palladium(II) as bivalent anion, the formed binary (1:1) Pd(DPA) complexes are electrically neutral i.e., do not carry charge. Therefore, one can deduce that the coulombic attraction forces do not have a significant role in the reacation of (1:1) binary Pd(DPA) complexes with the secondary ligand to yield the (1:1:1) Pd(DPA)(L) ternary complexes . Accordingly the lower stability observed for (1:1:1) ternary complexes of most systems studied compared to the (1:1) binary complexes of the secondary ligand can be mainly interprete on the principle that there are fewer number of sites available for bonding on the neutral complex of the

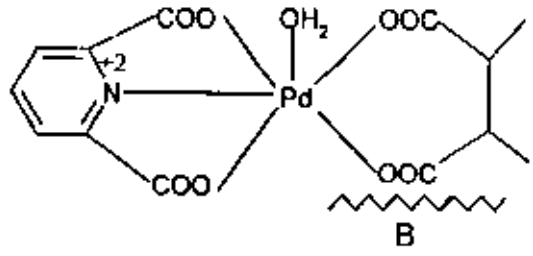
primary ligand than on the aquated palladium(II) ion. Thus, the secondary ligand is expected to bind the (1:1) complex of DPA with a smaller formation constant than that with the aquated palladium(II) ion i.e., negative value for ΔlogK.

The proposed structures of the complexes[Pd(II))- DPA- glycine] as shown in the following scheme:





Where A= (Amino acids listed in scheme(3)).



Where B = dibasic acid(aliphatic and aromatic acids listed in scheme (3)).

Scheme (4) : The proposed structures of the complexes

In this respect, it is worthy to note that the coulombic attraction forces play important role only in the formation of (1:1) Pd(II) : L complexes as it facilities the attraction of the negative secondary ligand anion to the dipositive aquated palladium(II) ions i.e., high formation constants.

There is π acidic character in the primary ligand (DPA), due to the possibility of M $\longrightarrow$N π bond formation. This behaviour is similar to that observed previously in [M-dipyridyl-L] complexes.[98,101]

In the ternary systems studied, the values of K^{MX}_{MXL} were found to lie in sequence (Table21):

Aromatic acids > aliphatic acids > amino acids

The higher stability of phathalic acid complex than salicylic acid may be explained[102] as follows : since the carboxylate oxygen is not directly bound to the benzene nucleus, it therefore adjusts stereochemically more easily than the phenolate oxygen which is directly attached to the benzene nucleus. The repulsion coulombic forces between the end oxygen will be more when both O,O donor atoms are phenolic oxygens than when they are carboxylic oxygens. Thus ΔlogK should be higher when the ligand coordinates through the two carboxylate oxygens (phathalic acid) than when it is salicylic acid, which contains one carboxylate and one phenolate oxygen.

The higher values of ΔlogK with aromatic acids than aliphatic acids may be attributed to the presence of an aromatic ring[103-104] which alters the bonding properties of these carboxylic acids.

3.1.4. Conductomertic titration

The conductometeic titration curve of the ternary complexes containing palladium(II)), DPA and secondary ligands (amino acids, aromatic and aliphatic acids) as showen in Figs.(24-29) as plots of conductance versus mole of NaOH added per mole of ligand. The studies show that there is an inflection at a = 2 for all systems, probably corresponding to the neutralization of two protons of the primary ligand (DPA), resulting from the formation of Pd(DPA) binary complex. Between $2 < a < 3$, there is a slight increase of conductance due to the formation of the ternary complex associated with the release of a proton from the secondary ligand to give the [Pd(DPA)(L)] complex. Beyond a = 3, the conductance increases more uniformly due to the presence of excess sodium hydroxide.

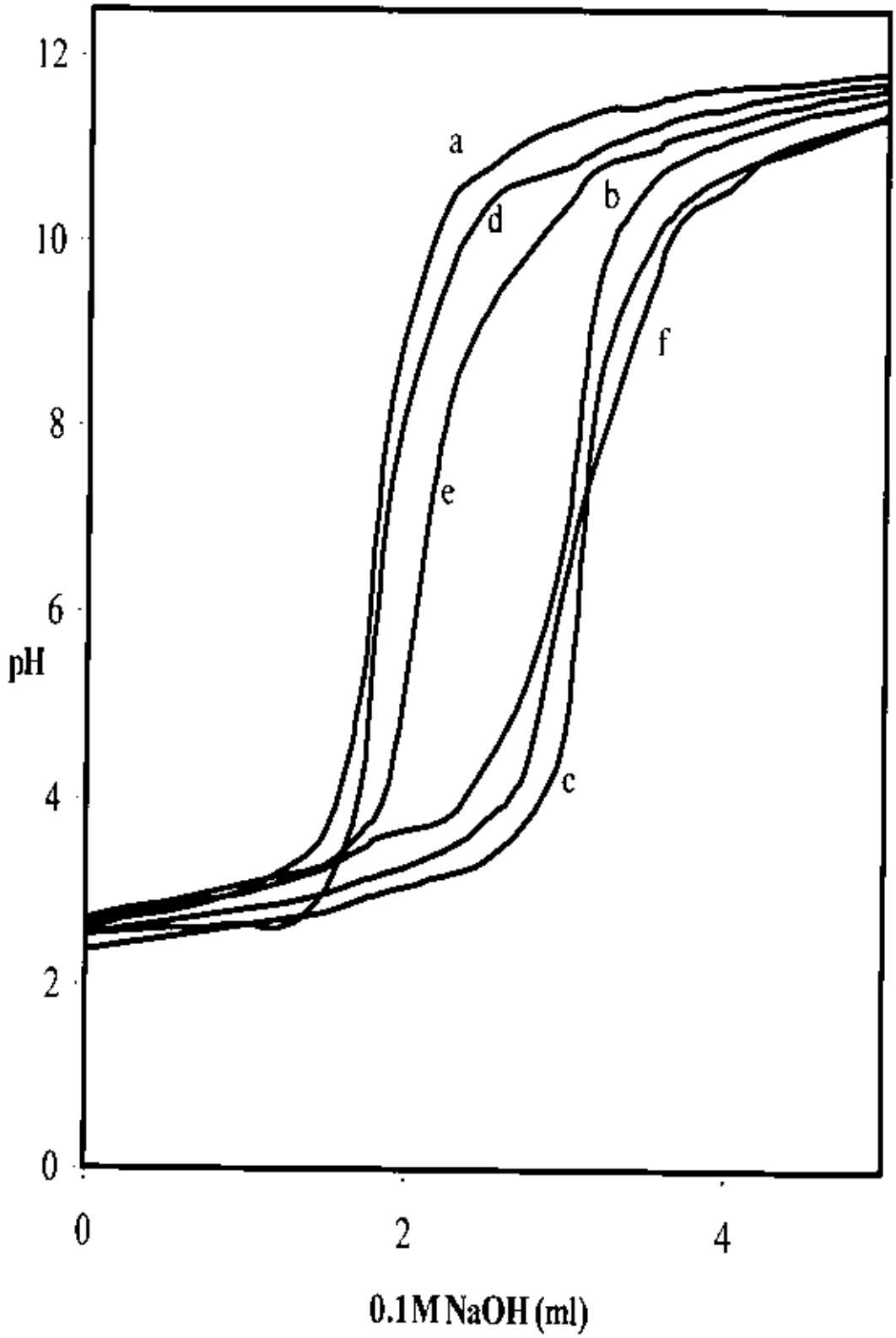


Fig.(7) Potentiometric titration curves for Pd(II)-DPA-glyine system.

Table(2): Potintiometric titration values of alanine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.55	2.89	2.56
0.25	2.71	2.75	2.44	2.57	2.97	2.65
0.5	2.77	2.80	2.49	2.59	3.03	2.68
0.75	2.88	2.89	2.56	2.61	3.19	2.74
1	3.02	2.96	2.62	2.62	3.29	2.80
1.25	3.23	3.10	2.70	2.64	3.51	2.88
1.5	3.65	3.23	2.78	3.00	3.77	2.95
1.75	5.13	3.46	2.90	4.08	4.01	3.03
2	8.30	3.77	3.00	7.40	4.34	3.13
2.25	10.39	4.00	3.18	9.64	5.20	3.30
2.5	10.81	4.33	3.35	10.45	6.47	3.44
2.75	11.11	5.25	3.74	10.66	9.48	3.74
3	11.27	6.85	4.68	10.80	10.28	4.03
3.25	11.41	9.61	8.44	11.02	10.68	4.60
3.5	11.49	10.61	9.45	11.21	10.97	5.38
3.75	11.59	10.88	10.40	11.34	11.13	7.12
3.87	11.65	11.11	10.74	11.45	11.27	8.06
4.25	11.69	11.26	10.91	11.55	11.40	9.85
4.5	11.73	11.37	11.06	11.63	11.50	10.28
4.75	11.80	11.46	11.22	11.69	11.57	10.50
5	11.83	11.54	11.38	11.73	11.63	10.79

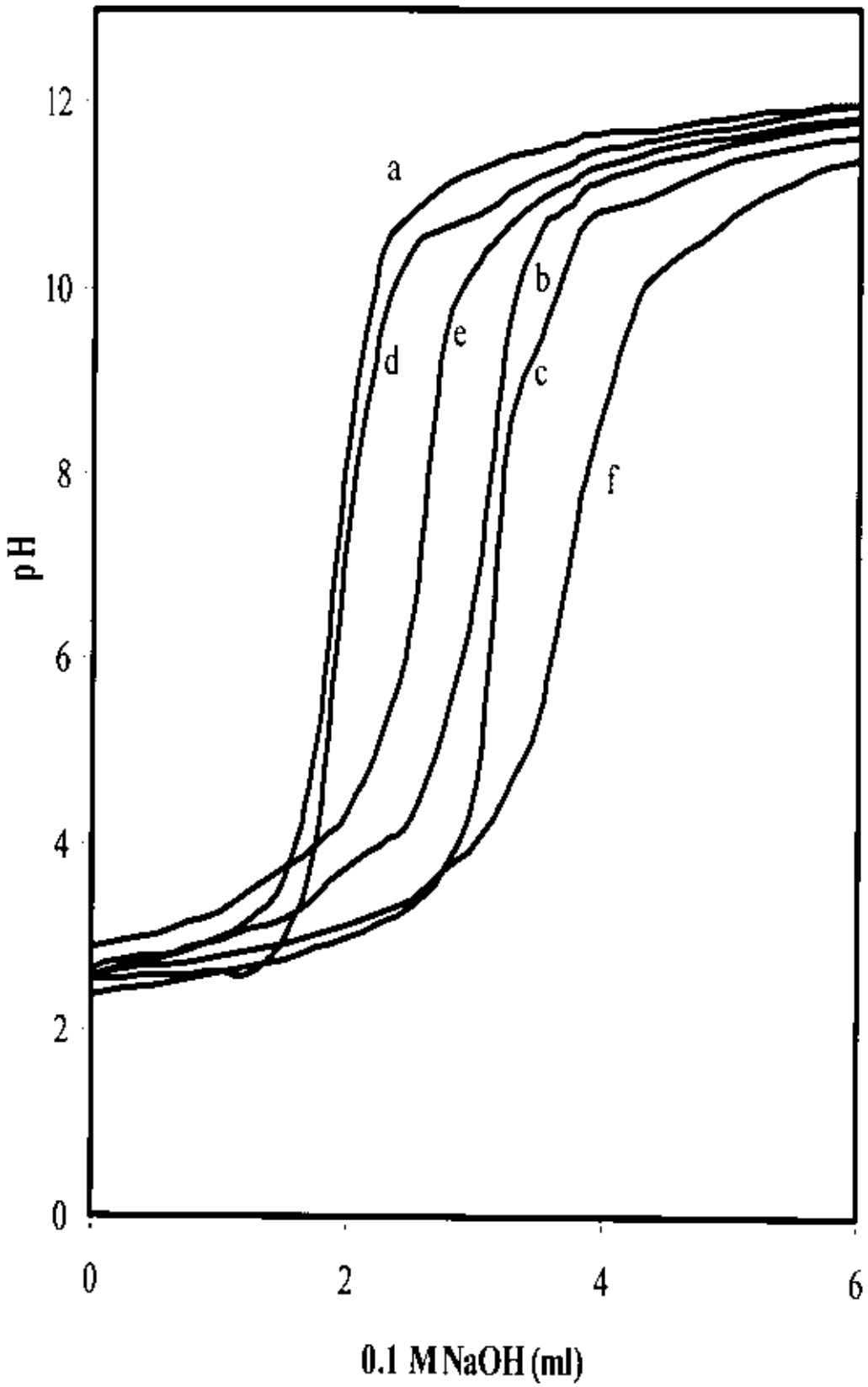


Fig.(8) Potentiometric titration curves for Pd(II) -DPA-alanine system.

Table(3): Potintiometric titration values of valine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.62	2.81	2.41
0.25	2.71	2.75	2.44	2.72	2.86	2.48
0.5	2.77	2.80	2.49	2.79	2.91	2.52
0.75	2.88	2.89	2.56	2.94	2.98	2.57
1	3.02	2.96	2.62	3.05	3.08	2.63
1.25	3.23	3.10	2.70	3.20	3.19	2.71
1.5	3.65	3.23	2.78	3.35	3.30	2.78
1.75	5.13	3.46	2.90	4.02	3.51	2.85
2	8.30	3.90	3.00	7.36	3.83	2.91
2.25	10.39	4.12	3.18	9.68	4.30	3.01
2.5	10.81	4.59	3.35	10.33	5.50	3.08
2.75	11.11	5.25	3.74	10.7	9.44	3.22
3	11.27	6.85	4.68	10.98	10.25	3.34
3.25	11.41	9.61	8.44	11.17	10.91	3.56
3.5	11.49	10.61	9.45	11.32	11.17	3.79
3.75	11.59	10.88	10.40	11.45	11.32	4.49
4	11.65	11.11	10.74	11.52	11.43	6.61
4.25	11.69	11.26	10.91	11.61	11.53	8.55
4.43	11.73	11.37	11.06	11.66	11.60	9.51
4.75	11.80	11.46	11.22	11.73	11.66	10.91
5	11.83	11.54	11.38	11.78	11.72	11.12

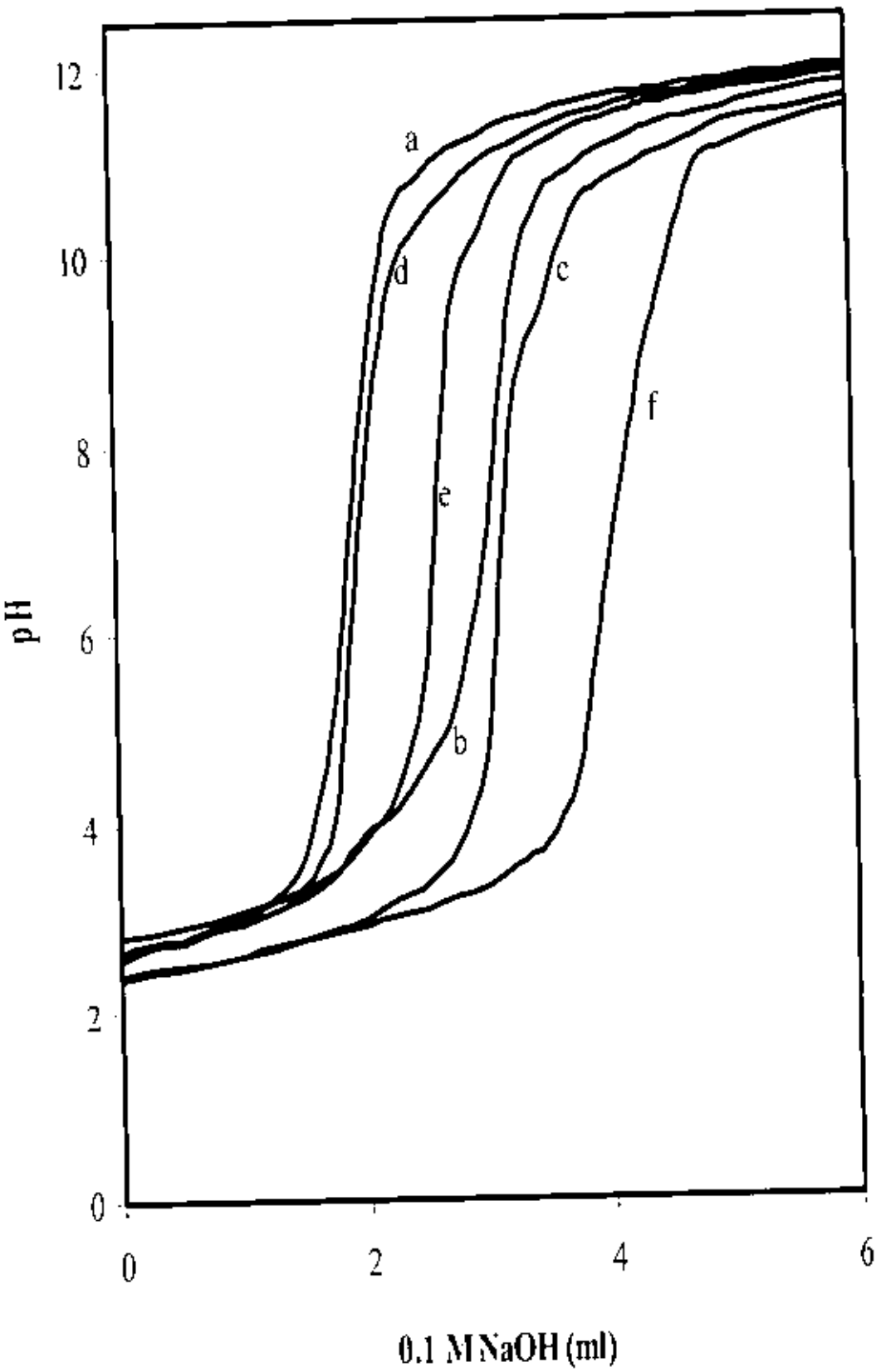


Fig.(9) Potentiometric titration curves for Pd(II)-DPA-valine system.

Table(4): Potintiometric titration values of phenylalanine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.92	2.80	2.77
0.25	2.71	2.75	2.44	3.01	2.89	2.80
0.5	2.77	2.80	2.49	3.07	2.93	2.82
0.75	2.88	2.89	2.56	3.19	3.03	2.87
1	3.02	2.96	2.62	3.37	3.10	2.90
1.25	3.23	3.10	2.70	3.54	3.25	2.95
1.5	3.65	3.23	2.78	3.95	3.36	2.99
1.75	5.13	3.46	2.90	6.39	3.45	3.05
2	8.30	3.90	3.00	8.50	3.73	3.12
2.25	10.39	4.12	3.18	9.38	4.34	3.20
2.5	10.81	4.33	3.35	9.98	6.38	3.26
2.75	11.11	5.25	3.74	10.54	9.85	3.37
3	11.27	6.85	4.68	10.87	10.40	3.52
3.25	11.41	9.61	8.44	11.05	10.94	3.69
3.5	11.49	10.61	9.74	11.32	11.10	3.98
3.75	11.59	10.88	10.40	11.46	11.32	4.64
4	11.65	11.11	10.74	11.56	11.46	7.32
4.25	11.69	11.26	10.91	11.66	11.54	8.74
4.5	11.73	11.37	11.06	11.71	11.64	10.35
4.75	11.80	11.46	11.22	11.78	11.72	10.79
5	11.83	11.54	11.38	11.84	11.77	10.99

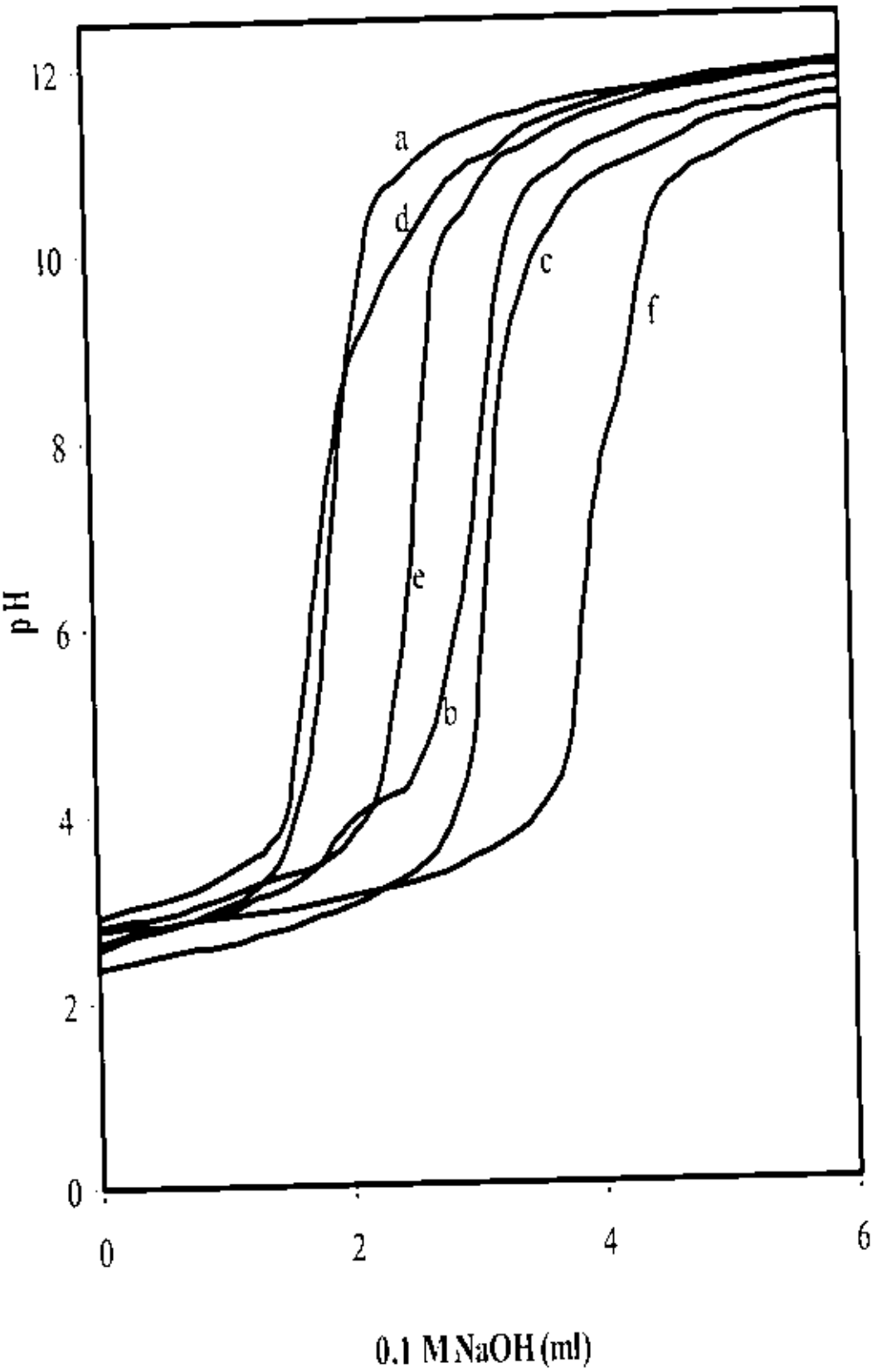


Fig.(10) Potntiometric titration curves for Pd(II) - DPA - phenylalanine system.

Table(5): Potintiometric titration values of tryptophane system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.86	2.67	2.42
0.25	2.71	2.75	2.44	2.95	2.73	2.47
0.5	2.77	2.80	2.49	3.06	2.79	2.50
0.75	2.88	2.89	2.56	3.17	2.85	2.55
1	3.02	2.96	2.62	3.30	2.93	2.64
1.25	3.23	3.10	2.70	3.52	3.02	2.69
1.5	3.65	3.23	2.78	3.85	3.13	2.74
1.75	5.13	3.46	2.90	6.34	3.30	2.80
2	8.30	3.83	3.00	9.03	3.51	2.90
2.25	10.39	4.12	3.18	9.92	4.33	2.98
2.5	10.81	4.40	3.35	10.48	7.47	3.05
2.75	11.11	5.25	3.74	10.93	10.29	3.16
3	11.27	6.85	4.68	11.16	10.79	3.32
3.25	11.41	9.61	8.44	11.36	11.15	3.57
3.5	11.49	10.61	9.45	11.59	11.29	4.20
3.75	11.59	10.88	10.40	11.65	11.40	6.01
4	11.65	11.11	10.74	11.72	11.49	8.51
4.25	11.69	11.26	10.91	11.77	11.60	9.50
4.5	11.73	11.37	11.06	11.79	11.67	10.35
4.75	11.80	11.46	11.22	11.83	11.75	10.80
5	11.83	11.54	11.38	11.87	11.81	11.02

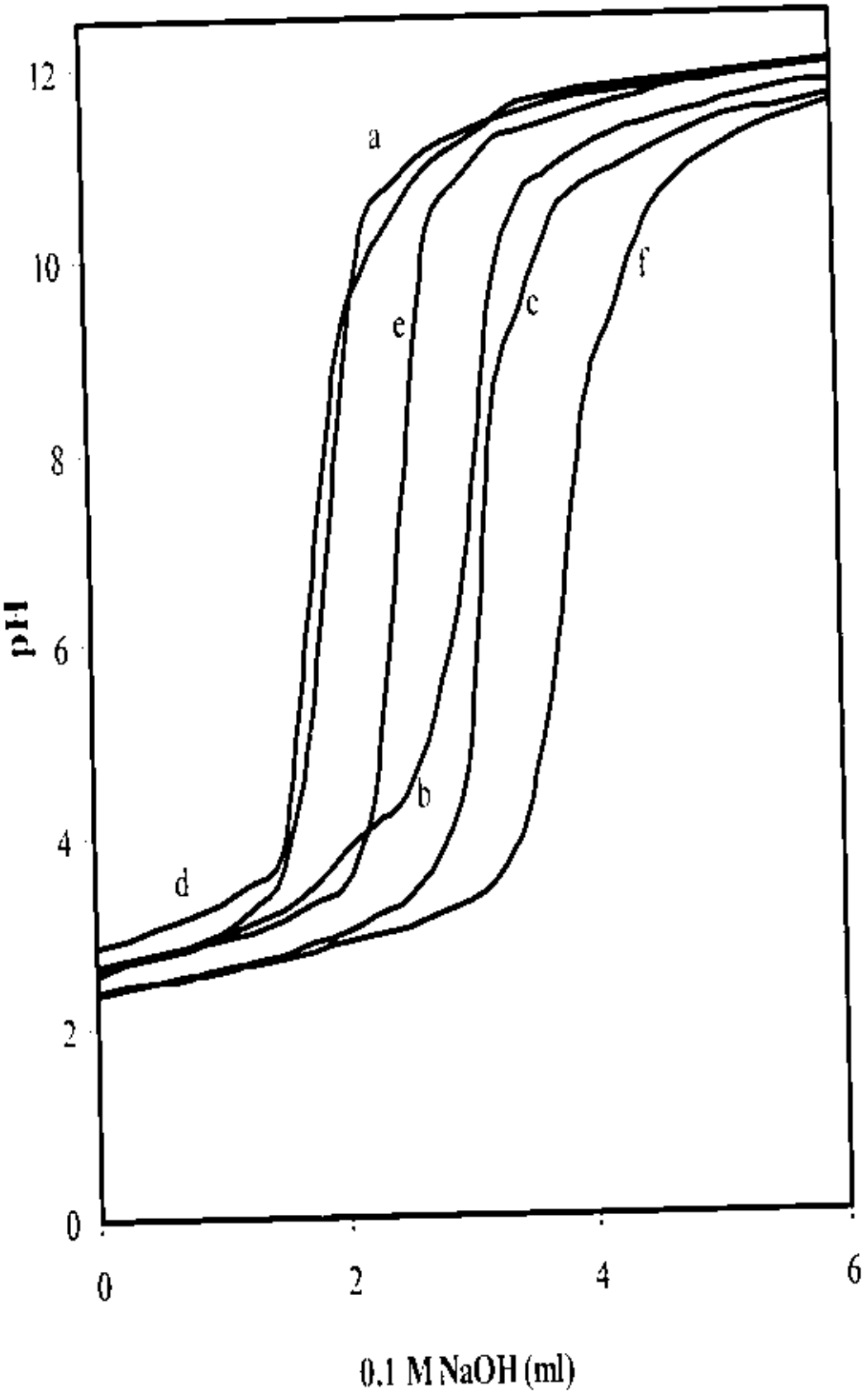


Fig.(11) Potintiometric titration curves for Pd(II) -DPA-tryptophane system.

Table(6): Potintiometric titration values of methionine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.87	2.67	2.45
0.25	2.71	2.75	2.44	2.93	2.74	2.50
0.5	2.77	2.80	2.49	3.00	2.81	2.53
0.75	2.88	2.89	2.56	3.08	2.88	2.58
1	3.02	2.96	2.62	3.20	2.94	2.62
1.25	3.23	3.10	2.70	3.33	3.04	2.67
1.5	3.65	3.23	2.78	3.52	3.13	2.72
1.75	5.13	3.46	2.90	3.89	3.26	2.77
2	8.30	3.71	3.00	6.70	3.43	2.84
2.25	10.39	3.96	3.18	9.05	3.70	2.91
2.5	10.81	4.33	3.35	9.75	4.10	2.98
2.75	11.11	5.25	3.74	10.40	9.78	3.12
3	11.27	6.85	4.68	10.70	10.66	3.21
3.25	11.41	9.61	8.44	10.97	10.95	3.38
3.5	11.49	10.61	9.45	11.16	11.19	3.55
3.75	11.59	10.88	10.40	11.33	11.36	3.99
4	11.65	11.11	10.74	11.47	11.46	6.31
4.25	11.69	11.26	10.91	11.59	11.54	8.75
4.5	11.73	11.37	11.06	11.67	11.63	9.50
4.75	11.80	11.46	11.22	11.79	11.69	10.09
5	11.83	11.54	11.38	11.83	11.73	10.45

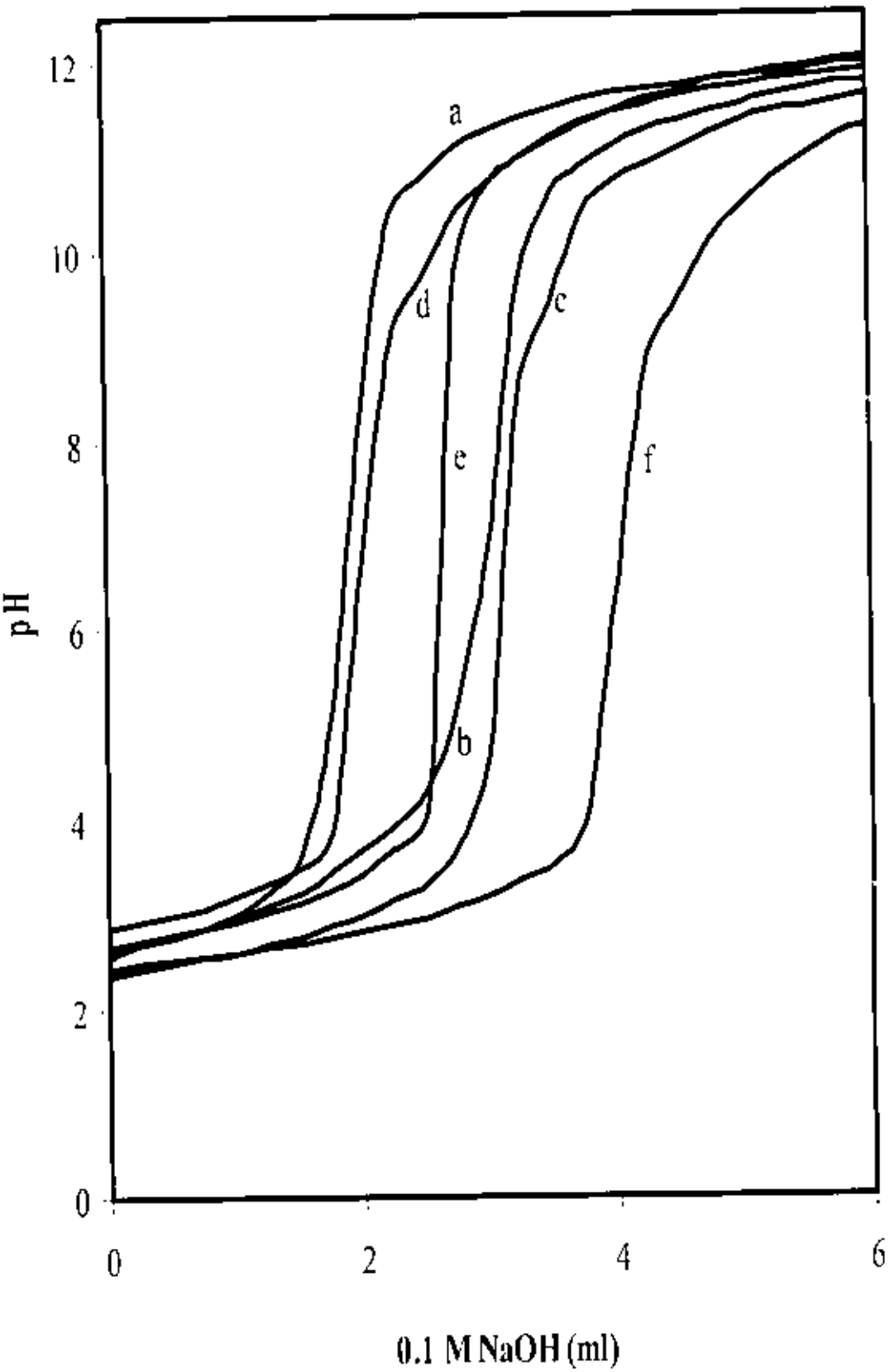


Fig.(12) Potentiometric titration curves for Pd(II)-DPA-methionine system.

Table(7): Potintiometric titration values of leucine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.81	2.62	2.62
0.25	2.71	2.75	2.44	2.91	2.69	2.66
0.5	2.77	2.80	2.49	3.01	2.76	2.69
0.75	2.88	2.89	2.56	3.09	2.83	2.73
1	3.02	2.96	2.62	3.21	2.93	2.77
1.25	3.23	3.10	2.70	3.39	3.06	2.83
1.5	3.65	3.23	2.78	3.67	3.18	2.86
1.75	5.13	3.46	2.90	5.85	3.48	2.91
2	8.30	3.90	3.00	9.39	3.86	2.98
2.25	10.39	4.12	3.18	10.12	4.55	3.07
2.5	10.81	4.53	3.35	10.56	8.89	3.14
2.75	11.11	5.25	3.74	10.97	10.34	3.26
3	11.27	6.85	4.68	11.15	10.76	3.39
3.25	11.41	9.61	8.44	11.33	11.05	3.60
3.5	11.49	10.61	9.45	11.45	11.23	3.94
3.75	11.59	10.88	10.40	11.53	11.36	4.70
4	11.65	11.11	10.74	11.61	11.45	7.24
4.07	11.69	11.26	10.91	11.67	11.56	8.27
4.5	11.73	11.37	11.06	11.73	11.61	10.68
4.75	11.80	11.46	11.22	11.78	11.66	10.95
5	11.83	11.54	11.38	11.83	11.72	11.13

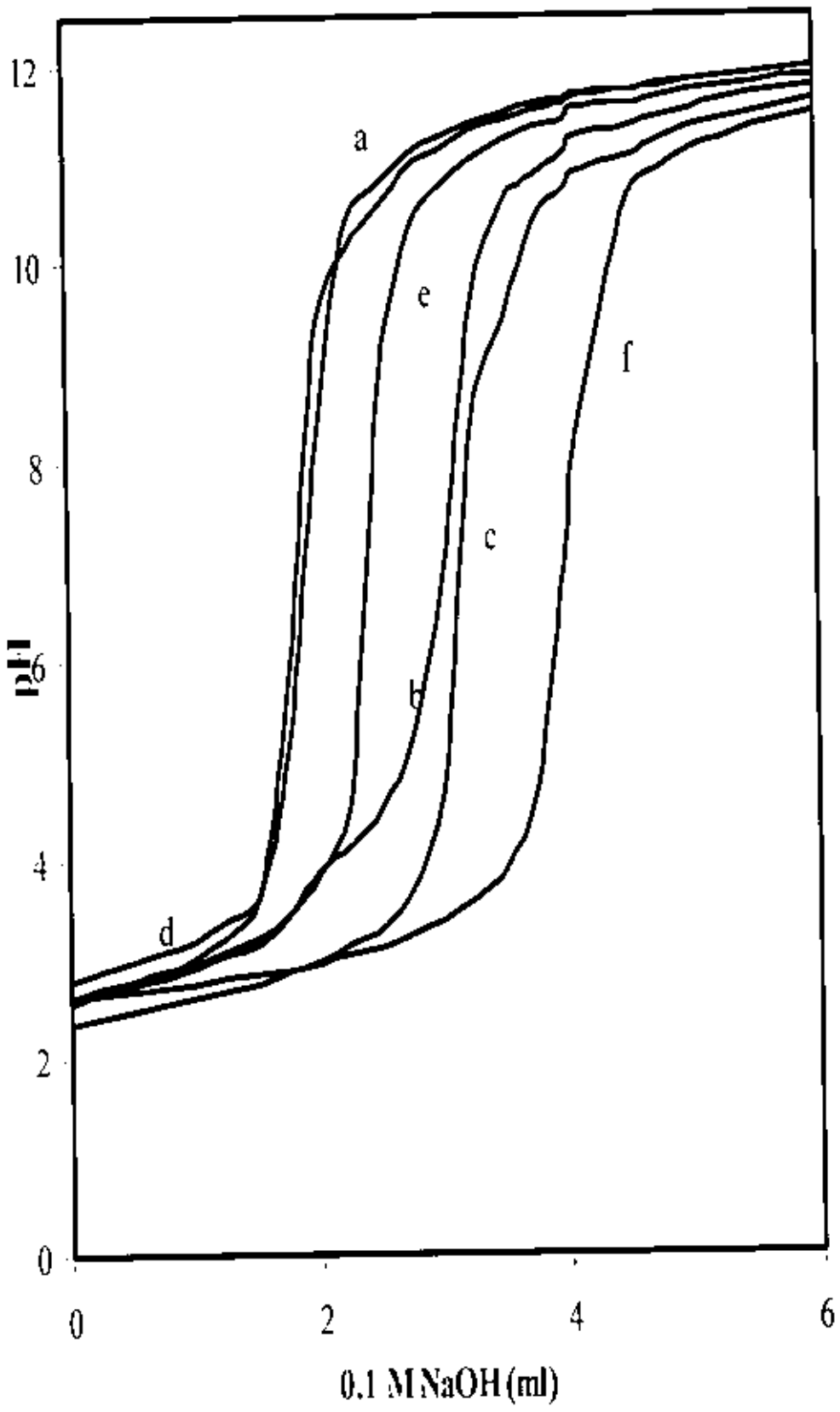


Fig.(13)Potentiometric titration curves for Pd(II)-DPA-luecine system

Table(8): Potintiometric titration values of aspartic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.56	2.68	2.55
0.25	2.71	2.75	2.44	2.72	2.72	2.58
0.5	2.77	2.80	2.49	2.78	2.77	2.62
0.75	2.88	2.89	2.56	2.90	2.83	2.66
1	3.02	2.96	2.62	3.01	2.91	2.70
1.25	3.23	3.10	2.70	3.16	3.01	2.75
1.5	3.65	3.23	2.78	3.35	3.07	2.79
1.75	5.13	3.46	2.90	3.61	3.17	2.85
2	8.30	3.90	3.00	4.06	3.27	2.92
2.25	10.39	4.12	3.18	4.78	3.47	2.98
2.5	10.81	4.69	3.35	7.75	3.71	3.08
2.75	11.11	5.25	3.74	9.73	4.07	3.19
3	11.27	6.85	4.68	10.16	4.65	3.29
3.25	11.41	9.61	8.44	10.64	6.60	3.43
3.5	11.49	10.61	9.45	10.95	9.95	3.64
3.75	11.59	10.88	10.40	11.12	10.66	3.93
4	11.65	11.11	10.74	11.25	10.96	4.26
4.25	11.69	11.26	10.91	11.37	11.17	4.83
4.5	11.73	11.37	11.06	11.47	11.31	6.41
4.75	11.80	11.46	11.22	11.55	11.41	9.94
5	11.83	11.54	11.38	11.62	11.50	10.46

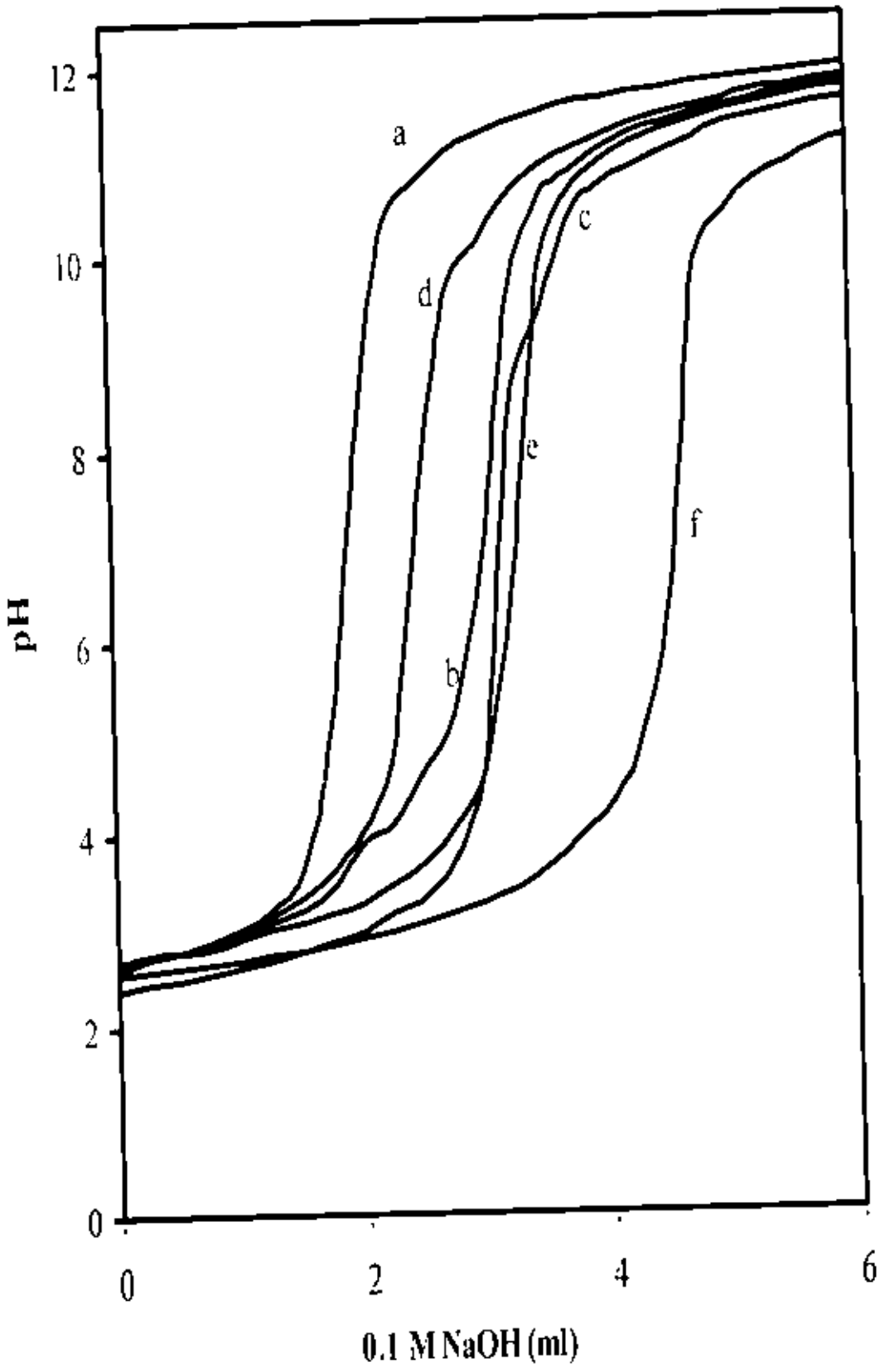


Fig.(14) Potentiometric titration curves for Pd(II) - DPA-aspartic acid system.

Table(9): Potintiometric titration values of glutamic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.84	2.73	2.58
0.25	2.71	2.75	2.44	2.94	2.83	2.62
0.5	2.77	2.80	2.49	3.01	2.90	2.66
0.75	2.88	2.89	2.56	3.09	2.97	2.70
1	3.02	2.96	2.62	3.18	3.05	2.74
1.25	3.23	3.10	2.70	3.33	3.16	2.79
1.5	3.65	3.23	2.78	3.48	3.27	2.83
1.75	5.13	3.46	2.90	3.78	3.45	2.88
2	8.30	3.90	3.00	4.30	3.60	2.94
2.25	10.39	4.12	3.18	5.16	3.95	3.03
2.5	10.81	4.33	3.35	8.77	4.36	3.12
2.75	11.11	5.25	3.74	9.87	5.03	3.21
3	11.27	6.85	4.68	10.40	6.46	3.33
3.25	11.41	9.61	8.44	10.81	9.85	3.51
3.5	11.49	10.61	9.45	11.08	10.35	3.68
3.75	11.59	10.88	10.40	11.26	10.99	4.01
4	11.65	11.11	10.74	11.36	11.19	4.46
4.25	11.69	11.26	10.91	11.48	11.36	5.26
4.5	11.73	11.37	11.06	11.56	11.45	6.36
4.75	11.80	11.46	11.22	11.66	11.55	9.27
5	11.83	11.54	11.38	11.71	11.61	10.50

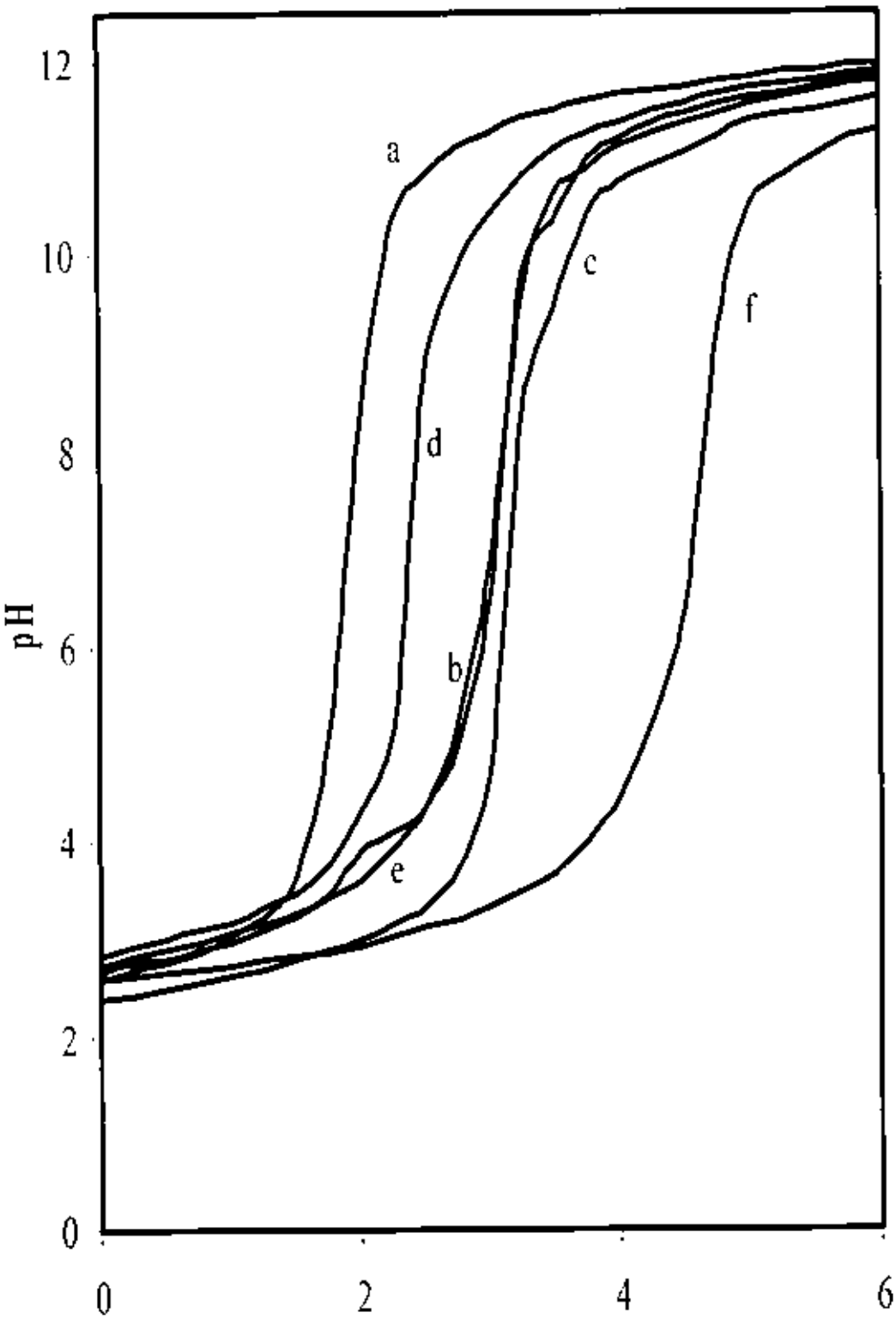


Fig.(15) Potentiometric titration curves for Pd(II)- DPA - glutamic acid system.

Table(10): Potintiometric titration values of histidine system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.67	2.53	2.46
0.25	2.71	2.75	2.44	2.74	2.61	2.50
0.5	2.77	2.80	2.49	2.82	2.66	2.53
0.75	2.88	2.89	2.56	2.91	2.72	2.57
1	3.02	2.96	2.62	3.01	2.78	2.60
1.25	3.23	3.10	2.70	3.15	2.85	2.65
1.5	3.65	3.23	2.78	3.31	2.93	2.69
1.75	5.13	3.46	2.90	3.78	3.05	2.74
2	8.30	3.80	3.00	5.25	3.14	2.78
2.25	10.39	4.12	3.18	6.25	3.26	2.85
2.5	10.81	4.54	3.35	7.50	3.46	2.90
2.75	11.11	5.25	3.74	8.73	3.96	2.99
3	11.27	6.85	4.68	9.43	6.33	3.08
3.25	11.41	9.61	8.44	10.18	9.00	3.17
3.5	11.49	10.61	9.45	10.66	10.59	3.30
3.75	11.59	10.88	10.40	10.95	10.90	3.51
4	11.65	11.11	10.74	11.13	11.12	3.73
4.25	11.69	11.26	10.91	11.31	11.23	4.25
4.5	11.73	11.37	11.06	11.41	11.36	6.17
4.75	11.80	11.46	11.22	11.50	11.45	8.40
5	11.83	11.54	11.38	11.56	11.50	9.35

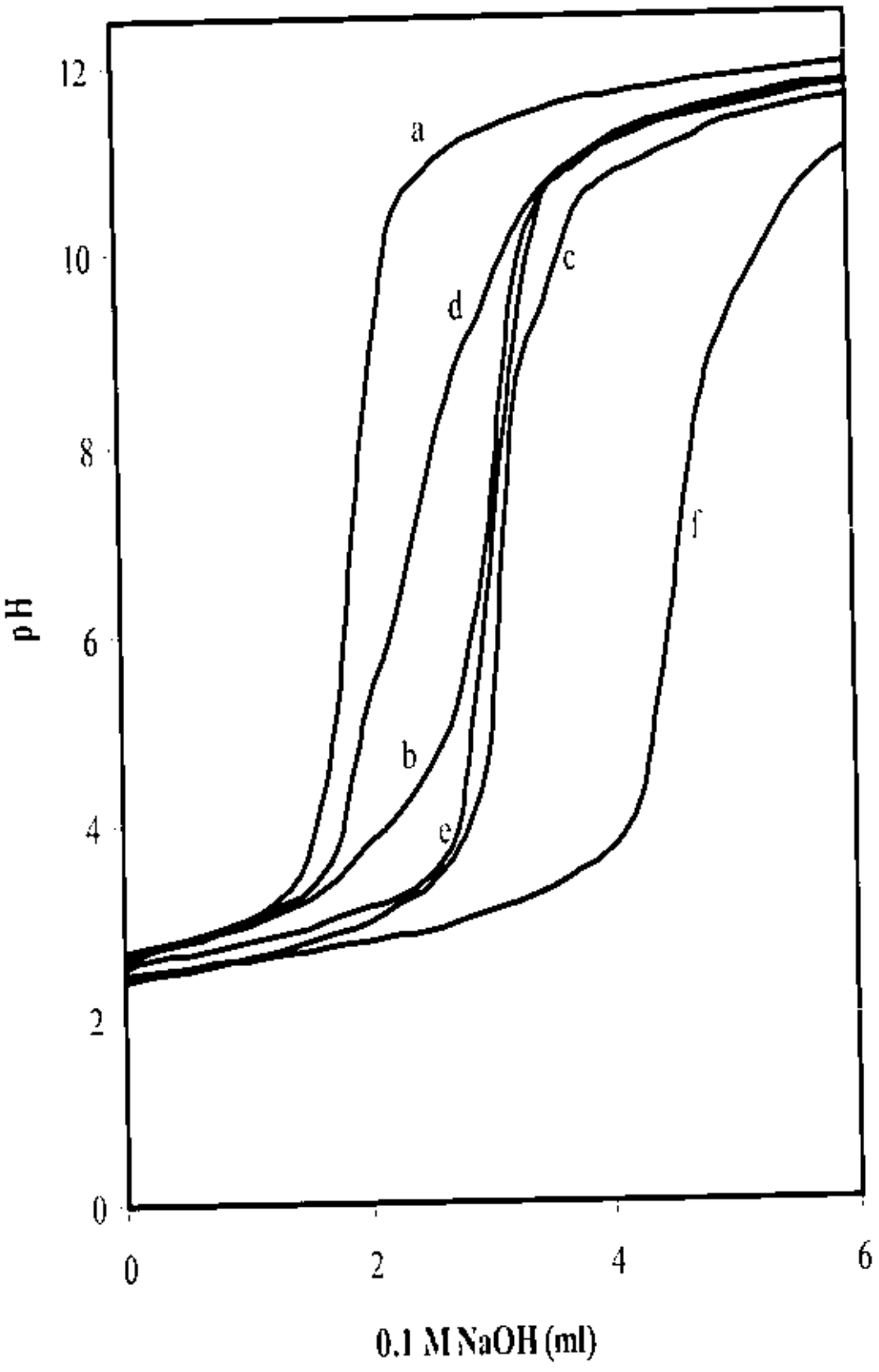
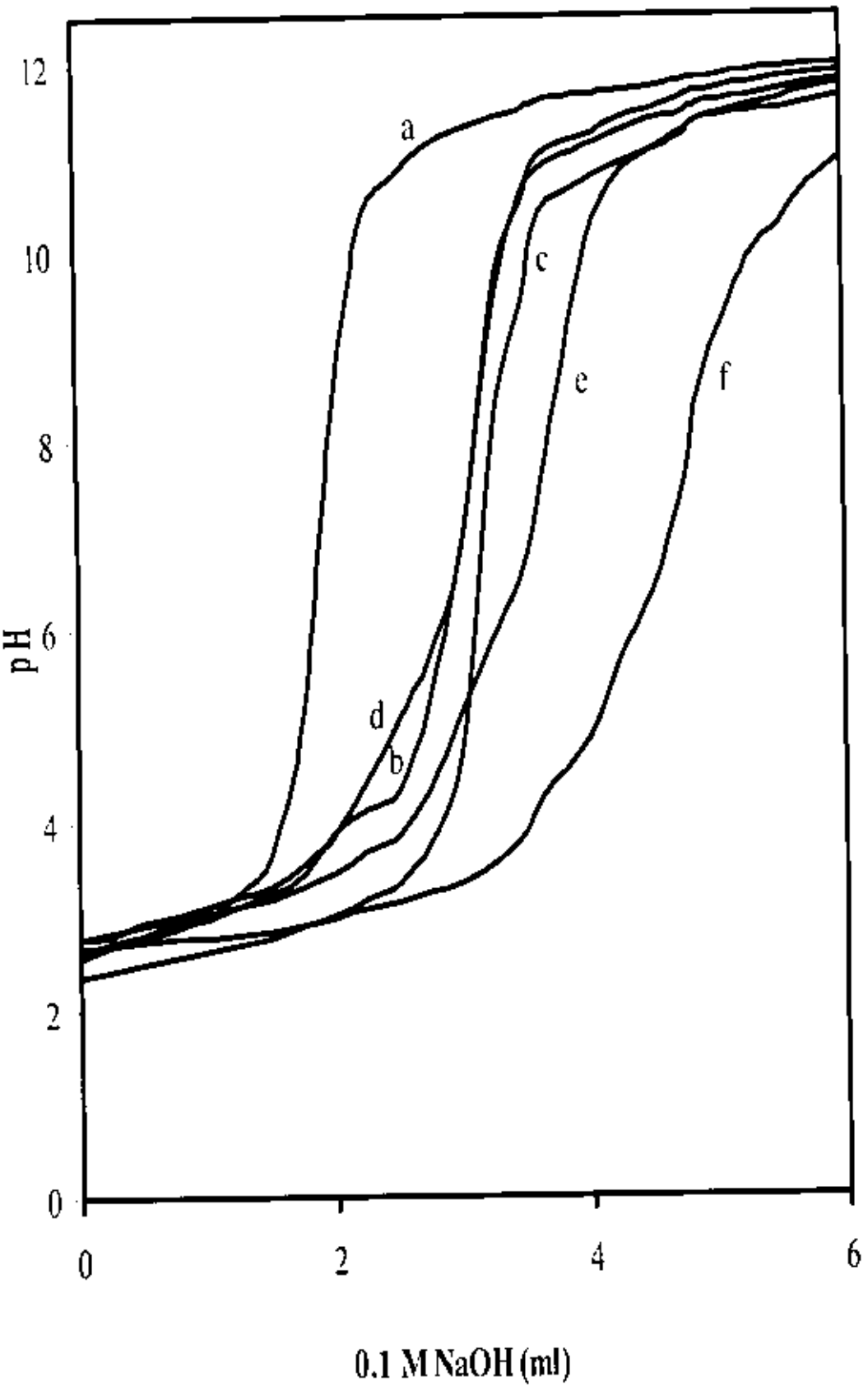


Fig.(16) Potintiometric titration curves for Pd(II) DPA-histadine system .

Table(11): Potintiometric titration values of phthalic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.77	2.78	2.67
0.25	2.71	2.75	2.44	2.82	2.84	2.70
0.5	2.77	2.80	2.49	2.93	2.89	2.72
0.75	2.88	2.89	2.56	3.02	2.98	2.76
1	3.02	2.96	2.62	3.11	3.03	2.78
1.25	3.23	3.10	2.70	3.22	3.11	2.82
1.5	3.65	3.23	2.78	3.30	3.19	2.85
1.75	5.13	3.46	2.90	3.56	3.31	2.91
2	8.30	3.90	3.00	3.84	3.43	2.97
2.25	10.39	4.12	3.18	4.42	3.67	3.06
2.5	10.81	4.33	3.35	5.08	3.84	3.14
2.75	11.11	5.25	3.74	5.72	4.32	3.25
3	11.27	6.85	4.68	6.84	5.12	3.36
3.3	11.41	9.61	8.44	9.80	6.00	3.58
3.5	11.49	10.61	9.45	10.52	6.67	3.86
3.64	11.59	10.88	10.40	11.02	7.59	4.26
4	11.65	11.11	10.74	11.23	10.09	4.86
4.25	11.69	11.26	10.91	11.40	10.78	5.66
4.5	11.73	11.37	11.06	11.50	11.05	6.40
4.75	11.80	11.46	11.22	11.63	11.26	7.61
5	11.83	11.54	11.38	11.69	11.40	8.61



Fig(17) Potntiometric titration curves for Pd(II)- DPA-phthalic acid system.

Table(12): Potintiometric titration values of salicylic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.8	2.62	2.58
0.25	2.71	2.75	2.44	2.87	2.69	2.61
0.5	2.77	2.80	2.49	2.93	2.75	2.63
0.75	2.88	2.89	2.56	3.01	2.80	2.67
1	3.02	2.96	2.62	3.10	2.86	2.71
1.25	3.23	3.10	2.70	3.23	2.98	2.76
1.5	3.65	3.23	2.78	3.39	3.08	2.80
1.75	5.13	3.46	2.90	3.51	3.20	2.86
2	8.30	3.90	3.00	3.82	3.35	2.92
2.25	10.39	4.12	3.18	4.32	3.59	3.01
2.5	10.81	4.33	3.35	7.49	3.88	3.08
2.75	11.11	5.25	3.74	10.53	5.04	3.17
3	11.27	6.85	4.68	10.89	6.67	3.30
3.25	11.41	9.61	8.44	11.09	9.75	3.50
3.5	11.49	10.61	9.45	11.25	10.30	4.13
3.75	11.59	10.88	10.40	11.43	11.03	5.67
4	11.65	11.11	10.74	11.54	11.18	6.63
4.25	11.69	11.26	10.91	11.61	11.41	7.67
4.5	11.73	11.37	11.06	11.71	11.51	8.55
4.75	11.80	11.46	11.22	11.79	11.60	10.02
5	11.83	11.54	11.38	11.81	11.67	10.52

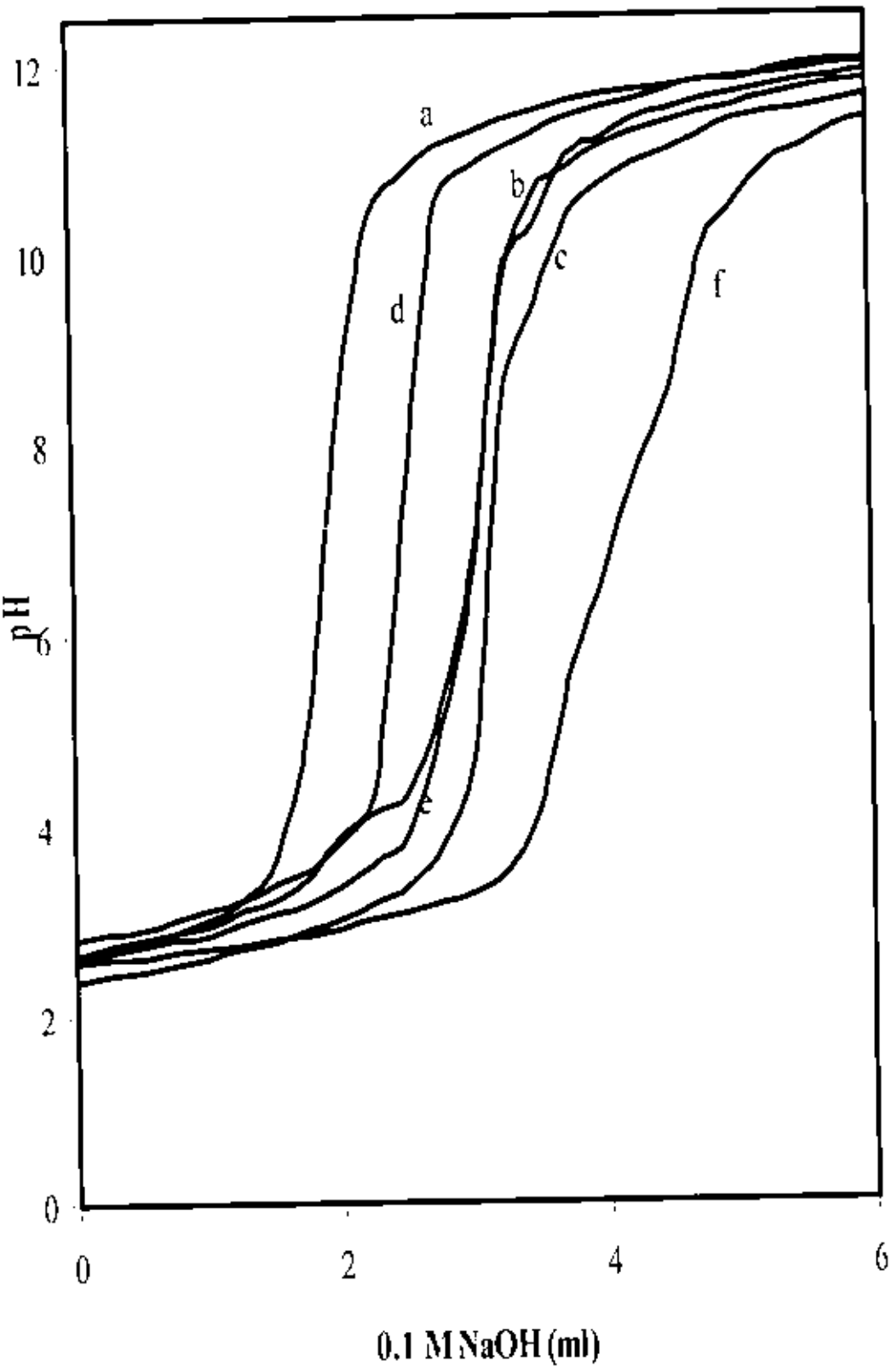


Fig.(18)Potintiometric titration curves for Pd(II)-DPA-salicylic acid system.

Table(13): Potintiometric titration values of succinic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.79	2.75	2.57
0.25	2.71	2.75	2.44	2.88	2.83	2.62
0.5	2.77	2.80	2.49	2.93	2.91	2.63
0.75	2.88	2.89	2.56	3.04	3.01	2.68
1	3.02	2.96	2.62	3.14	3.07	2.71
1.25	3.23	3.10	2.70	3.30	3.24	2.75
1.5	3.65	3.23	2.78	3.50	3.38	2.81
1.75	5.13	3.34	2.90	3.88	3.70	2.88
2	8.30	3.51	3.00	4.33	3.93	2.94
2.25	10.39	3.93	3.18	4.93	4.32	3.01
2.5	10.81	4.33	3.35	5.48	4.65	3.11
2.75	11.11	5.25	3.74	6.10	5.09	3.28
3	11.27	6.85	4.68	6.76	5.41	3.46
3.25	11.41	9.61	8.44	10.04	6.08	3.78
3.42	11.49	10.61	9.45	10.67	6.83	4.16
3.75	11.59	10.88	10.40	11.03	9.59	4.57
4	11.65	11.11	10.74	11.19	10.39	5.10
4.25	11.69	11.26	10.91	11.35	10.84	5.69
4.5	11.73	11.37	11.06	11.49	11.09	6.50
4.75	11.80	11.46	11.22	11.57	11.33	7.37
5	11.83	11.54	11.38	11.65	11.41	8.35

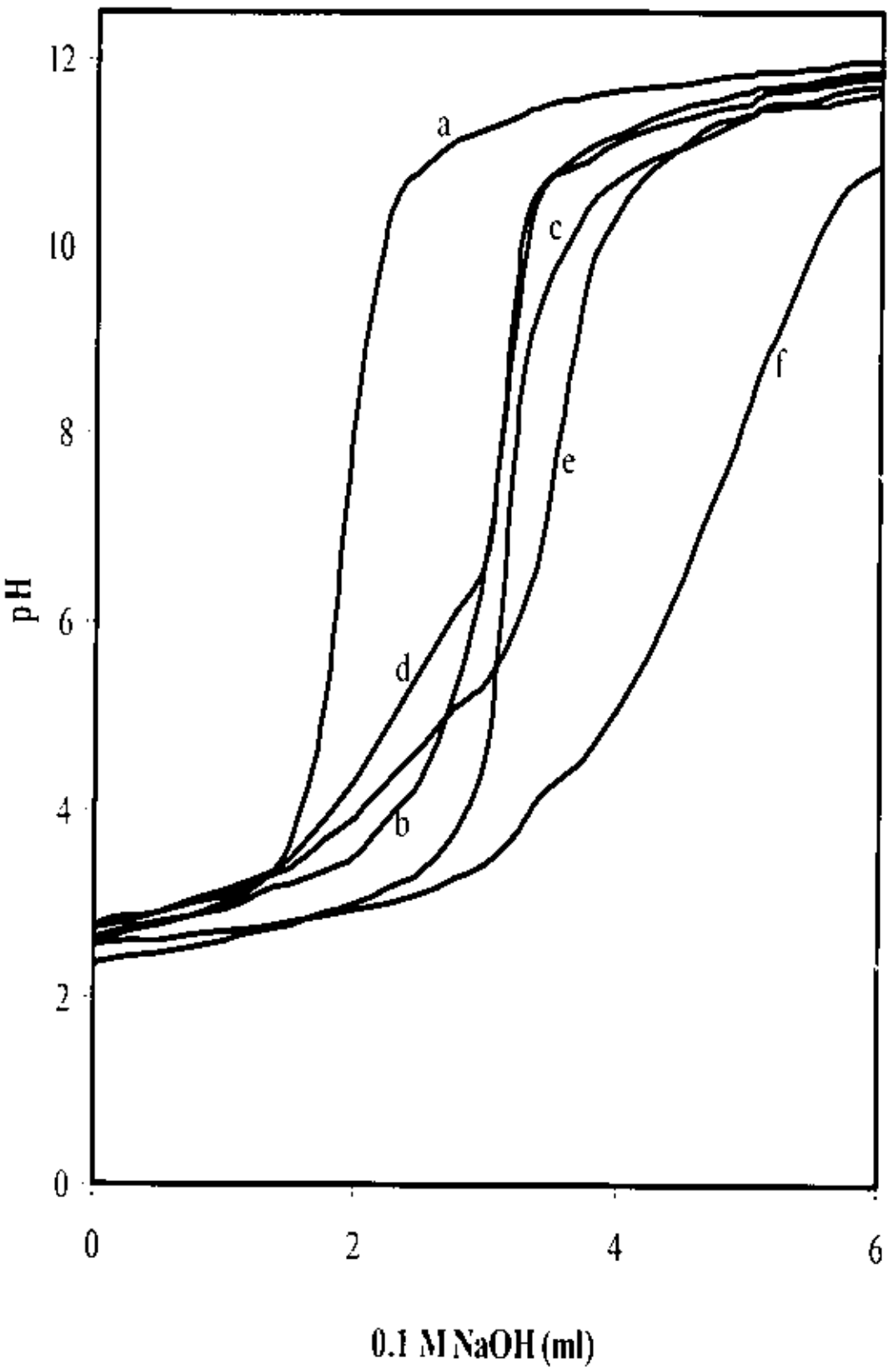


Fig.(19) Potntiometric titration curves for Pd(II) -DPA-succinic acid system.

Table(14): Potintiometric titration values of malonic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.83	2.75	2.61
0.25	2.71	2.75	2.44	2.89	2.83	2.65
0.5	2.77	2.80	2.49	2.95	2.87	2.69
0.75	2.88	2.89	2.56	3.02	2.93	2.73
1	3.02	2.96	2.62	3.09	2.99	2.76
1.25	3.23	3.10	2.70	3.22	3.07	2.80
1.5	3.65	3.23	2.78	3.30	3.13	2.85
1.75	5.13	3.46	2.90	3.44	3.23	2.89
2	8.30	3.90	3.00	3.75	3.30	2.96
2.4	10.39	4.12	3.18	4.80	3.50	3.04
2.55	10.81	4.33	3.35	5.36	3.70	3.10
2.75	11.11	5.25	3.74	6.10	4.23	3.21
3	11.27	6.85	4.68	6.98	4.94	3.31
3.25	11.41	9.61	8.44	10.15	6.90	3.52
3.5	11.49	10.61	9.45	10.73	7.85	3.70
3.75	11.59	10.88	10.40	11.06	9.44	4.20
4	11.65	11.11	10.74	11.24	10.24	4.97
4.25	11.69	11.26	10.91	11.41	10.77	5.83
4.5	11.73	11.37	11.06	11.54	11.02	6.78
4.75	11.80	11.46	11.22	11.62	11.25	7.93
5	11.83	11.54	11.38	11.71	11.38	8.25

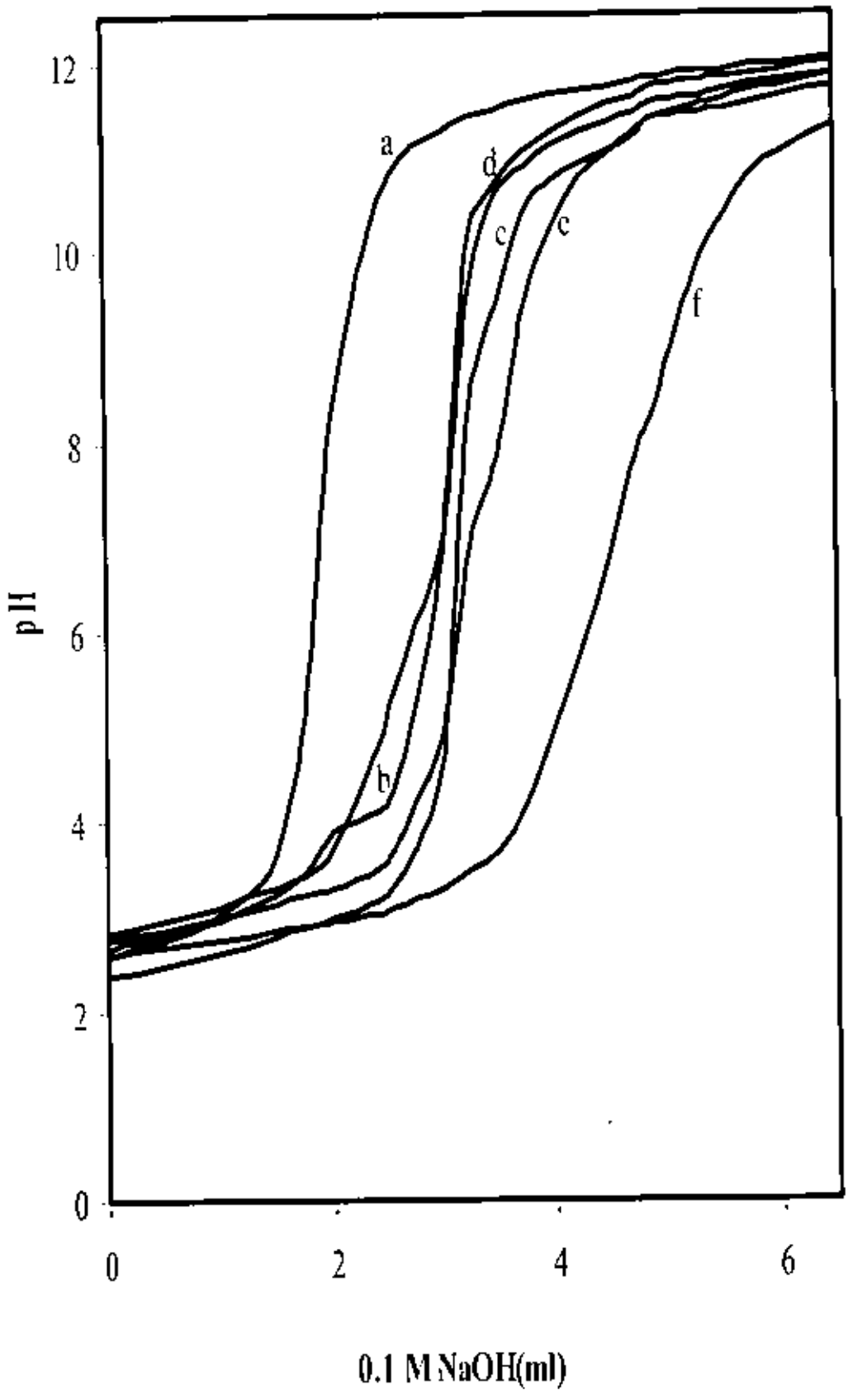
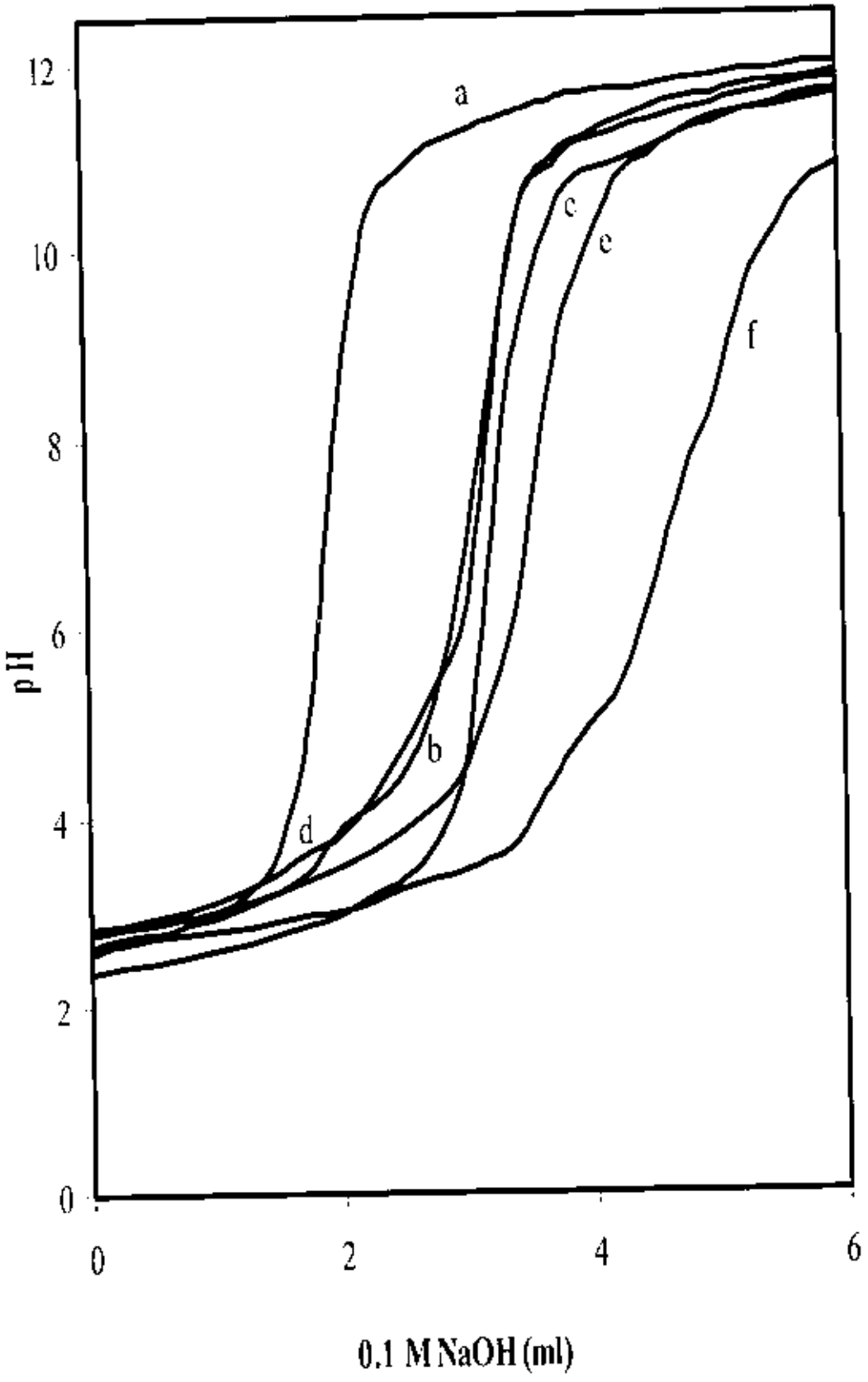


Fig.(20) Potntiometric titration curves for Pd(II)-DPA-malonic acid system.

Table(15): Potintiometric titration values of malic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.84	2.79	2.67
0.25	2.71	2.75	2.44	2.90	2.84	2.7
0.5	2.77	2.8	2.49	2.96	2.89	2.74
0.75	2.88	2.89	2.56	3.04	2.96	2.79
1	3.02	2.96	2.62	3.13	3.01	2.83
1.25	3.23	3.10	2.70	3.26	3.14	2.87
1.5	3.65	3.23	2.78	3.42	3.24	2.91
1.75	5.13	3.46	2.90	3.65	3.36	2.98
2	8.30	3.90	3.00	3.84	3.48	3.04
2.25	10.39	4.12	3.18	4.23	3.66	3.13
2.5	10.81	4.46	3.35	4.74	3.87	3.25
2.75	11.11	5.25	3.74	5.39	4.14	3.36
3	11.27	6.85	4.68	6.20	4.56	3.46
3.34	11.41	9.61	8.44	9.60	5.83	3.65
3.5	11.49	10.61	9.45	10.60	7.02	3.98
3.75	11.59	10.88	10.40	10.99	8.96	4.51
4	11.65	11.11	10.74	11.17	9.67	4.84
4.25	11.69	11.26	10.91	11.36	10.76	5.44
4.5	11.73	11.37	11.06	11.48	10.99	6.46
4.75	11.80	11.46	11.22	11.58	11.23	7.56
5	11.83	11.54	11.38	11.64	11.33	8.44



Fig(21) Potntiometric titration curves for Pd(II) -DPA - malic acid system.

Table(16): Potintiometric titration values of oxalic acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	1.99	1.86	1.90
0.25	2.71	2.75	2.44	2.01	1.91	1.93
0.5	2.77	2.80	2.49	2.03	1.98	1.95
0.75	2.88	2.89	2.56	2.05	2.01	1.97
1	3.02	2.96	2.62	2.08	2.03	2.00
1.25	3.23	3.10	2.70	2.10	2.06	2.02
1.5	3.65	3.23	2.78	2.12	2.08	2.04
1.75	5.13	3.46	2.90	2.17	2.12	2.07
2	8.30	3.60	3.00	2.21	2.17	2.10
2.25	10.39	3.90	3.18	2.28	2.23	2.14
2.5	11.00	4.33	3.35	2.30	2.27	2.17
2.75	11.11	4.60	3.74	2.40	2.35	2.20
3	11.27	5.25	4.68	2.45	2.42	2.26
3.25	11.41	9.61	8.44	2.60	2.55	2.32
3.5	11.49	10.61	9.67	2.80	2.66	2.37
3.75	11.59	10.88	10.40	3.26	2.91	2.45
4	11.65	11.11	10.74	4.00	3.18	2.53
4.25	11.69	11.26	10.91	5.47	4.16	2.64
4.5	11.73	11.37	11.06	7.00	7.28	2.75
4.75	11.80	11.46	11.22	9.98	8.66	2.92
5	11.83	11.54	11.38	10.36	9.53	3.20
5.25	11.88	11.62	11.45	10.55	10.11	3.57
5.5	11.91	11.69	11.5	10.71	10.32	4.01
5.75	11.95	11.75	11.57	10.83	10.48	5.31
6	11.97	11.78	11.62	10.88	10.63	7.43
6.25	12.01	11.83	11.68	10.94	10.76	8.70
6.5	12.03	11.86	11.71	11.02	10.82	9.30
6.75	12.06	11.89	11.76	11.08	10.89	10.03
7	12.08	11.92	11.81	11.13	10.95	10.24
7.25	12.10	11.96	11.85	11.18	11.04	10.40
7.5	12.12	11.98	11.88	11.21	11.09	10.58
7.75	12.13	12.01	11.90	11.24	11.12	10.69
8	12.16	12.03	11.93	11.26	11.16	10.80

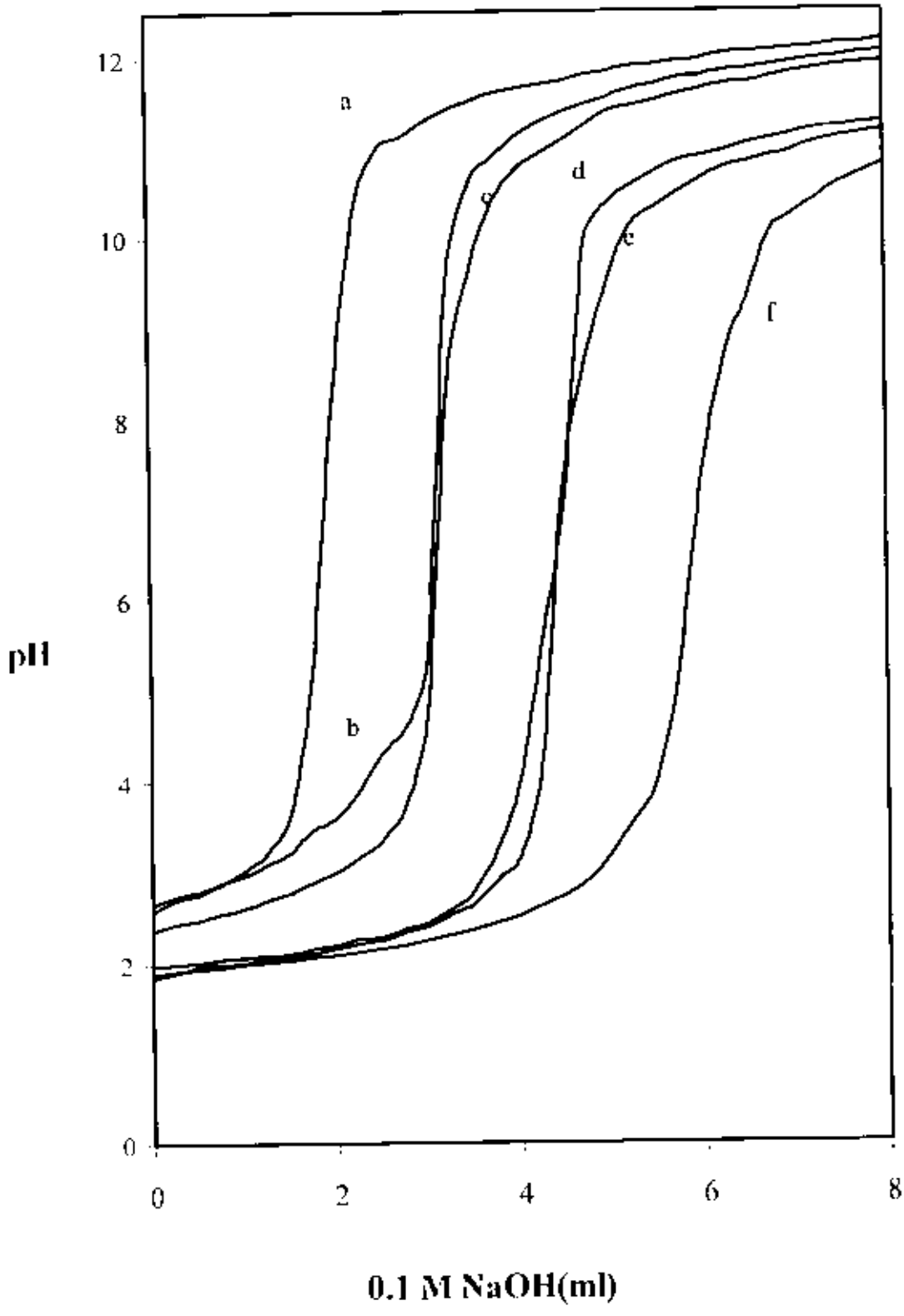


Fig.(22)Potentiometric titration curves for Pd(II)-DPA-oxalic acid system.

Table(17): Potintiometric titration values of tartaric acid system in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.65	2.38	2.14	2.07	1.89
0.25	2.71	2.75	2.44	2.17	2.11	2.01
0.5	2.77	2.80	2.49	2.19	2.13	2.02
0.75	2.88	2.89	2.56	2.22	2.18	2.04
1	3.02	2.96	2.62	2.25	2.20	2.05
1.25	3.23	3.10	2.70	2.32	2.27	2.07
1.5	3.65	3.20	2.78	2.35	2.31	2.10
1.75	5.13	3.29	2.90	2.41	2.35	2.14
2	8.30	3.46	3.00	2.47	2.40	2.16
2.25	10.39	3.57	3.18	2.58	2.49	2.18
2.6	10.81	3.96	3.35	2.84	2.55	2.24
2.75	11.11	4.46	3.74	3.02	2.65	2.30
3	11.27	5.25	4.68	3.28	2.76	2.32
3.25	11.41	9.61	8.44	3.45	2.89	2.39
3.5	11.55	10.61	9.67	3.55	3.01	2.47
3.75	11.59	11.05	10.49	3.87	3.20	2.54
4	11.65	11.16	10.74	4.50	3.38	2.65
4.25	11.69	11.26	10.91	5.42	3.66	2.74
4.5	11.73	11.37	11.06	6.80	3.98	2.89
4.75	11.8	11.46	11.22	9.83	4.69	3.04
5	11.83	11.54	11.38	10.20	6.05	3.28
5.25	11.88	11.62	11.45	10.43	7.13	3.49
5.5	11.91	11.69	11.5	10.57	9.23	3.76
5.75	11.95	11.75	11.57	10.71	10.43	4.25
6	11.97	11.78	11.62	10.79	10.56	5.39
6.25	12.01	11.83	11.68	10.89	10.70	7.30
6.5	12.03	11.86	11.71	10.94	10.77	8.26
6.75	12.06	11.89	11.76	11.01	10.89	9.61
7	12.08	11.92	11.81	11.05	10.95	10.01
7.25	12.10	11.96	11.85	11.09	11.01	10.28
7.5	12.12	11.98	11.88	11.13	11.07	10.49
7.75	12.13	12.01	11.90	11.17	11.11	10.64
8	12.16	12.03	11.93	11.19	11.14	10.70

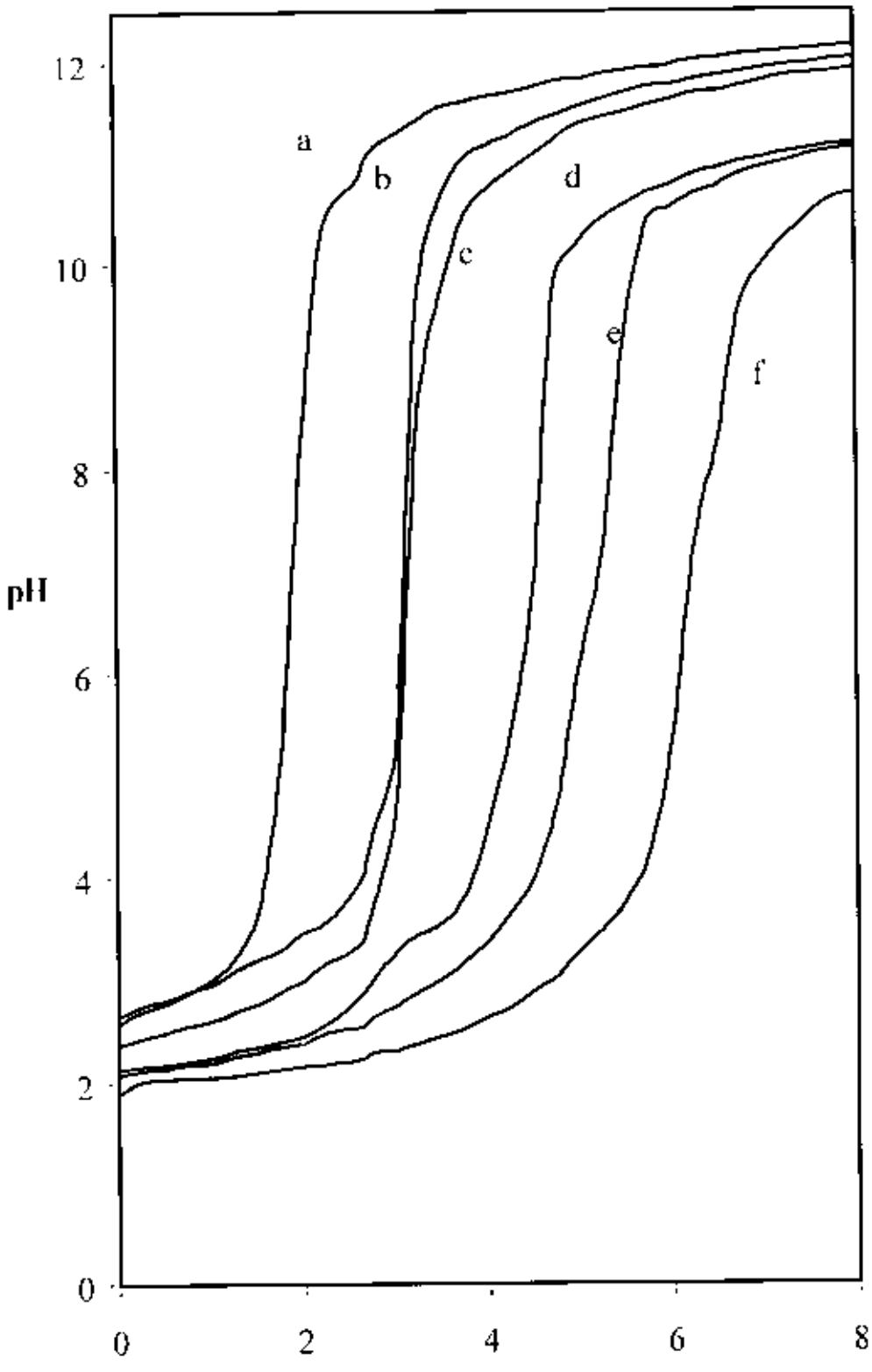


Fig.(23)Potentiometric titration curves for Pd(II)-DPA-tartaric acid system.

Table(18): Conductometric titration values for some ternary complexes with DPA in aqueous solution at 30°C and I = 0.5 M (NaNO3).

	glycine	alanine	aspartic	histadine	succinic	phthalic
ml	C	C	C	C	C	C
0	8.45	9.02	11.48	14.67	16.76	14.81
0.25	8.12	8.32	10.64	13.69	15.95	14.08
0.5	7.70	7.74	9.85	13.04	15.11	13.53
0.75	7.22	7.09	9.34	12.39	14.44	12.66
1	6.91	6.68	8.86	11.83	13.81	12.05
1.25	6.42	6.03	8.37	11.33	13.03	11.38
1.5	6.03	5.47	7.98	10.82	12.31	10.89
1.75	5.57	4.99	7.46	10.16	11.29	10.39
2	5.10	4.62	7.12	9.75	10.60	9.78
2.25	4.73	4.34	7.01	9.22	9.95	9.22
2.5	4.38	4.10	6.23	8.73	9.35	8.90
2.75	4.10	4.03	5.77	8.22	8.47	8.12
3	3.86	3.99	5.44	7.70	8.06	7.66
3.25	3.95	4.05	5.07	7.38	7.31	7.18
3.5	4.00	4.16	4.84	7.21	6.77	6.77
3.75	4.06	4.38	4.72	6.53	6.21	6.27
4	4.24	4.51	4.71	6.12	5.85	5.91
4.25	4.47	4.78	4.80	5.93	5.52	5.55
4.5	4.80	5.02	4.93	5.66	5.46	5.29
4.75	5.17	5.29	5.14	5.46	5.65	4.96
5	5.36	5.52	5.32	5.53	5.73	4.90
5.25	5.78	5.88	5.61	5.74	5.98	5.04
5.5	6.05	6.07	5.98	5.98	6.11	5.17
5.75	6.35	6.48	6.34	6.19	6.40	5.41

6	6.55	6.87	6.69	6.37	6.55	5.58
6.25	6.88	7.15	7.02	6.58	6.82	5.76
6.5	7.19	7.31	7.25	6.94	6.97	5.96
6.75	7.65	7.93	7.57	7.18	7.23	6.19
7	7.92	8.34	7.86	7.41	7.51	6.27
7.25	8.44	8.73	8.27	7.85	7.90	6.69
7.5	8.66	9.11	8.55	8.18	8.17	6.98
7.75	8.95	9.52	8.82	8.54	8.55	7.37
8	9.23	9.91	9.08	8.90	8.99	7.60
8.25	9.72	10.32	9.48	9.37	9.45	7.98
8.5	10.05	10.74	9.85	9.81	9.81	8.32
8.75	10.36	11.12	10.29	10.25	10.29	8.85
9	10.77	11.35	10.56	10.63	10.77	9.03
9.25	11.33	11.98	11.04	10.79	11.11	9.50
9.5	11.49	12.40	11.46	11.32	11.60	9.83
9.75	12.06	12.65	11.90	11.89	12.05	10.28
10	12.41	12.99	12.28	12.30	12.59	10.65

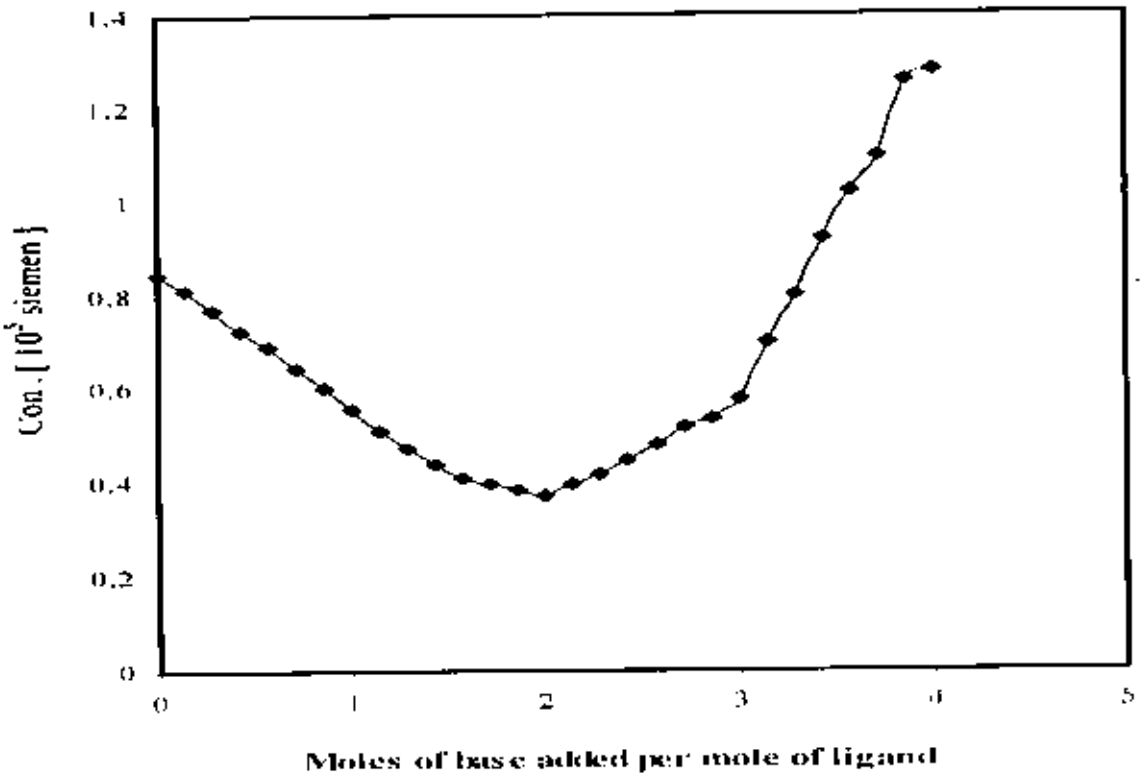


Fig.(24)Conductometric titration curves for Pd(II)-DPA-glycine system.

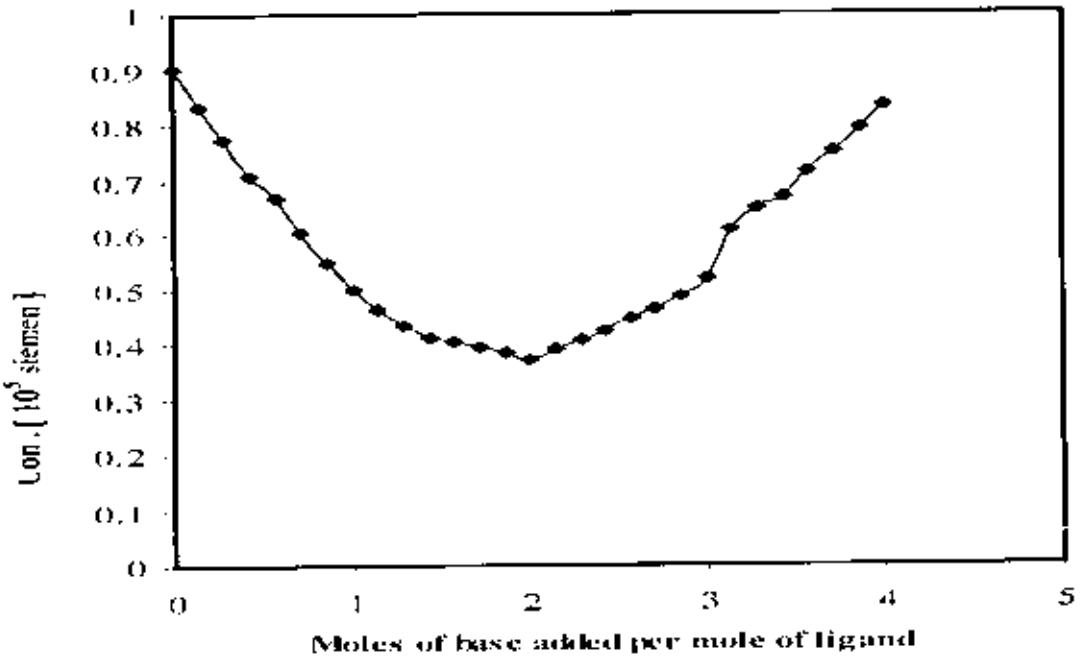


Fig.(25)Conductometric titration curves for Pd(II)-DPA-alanine system.

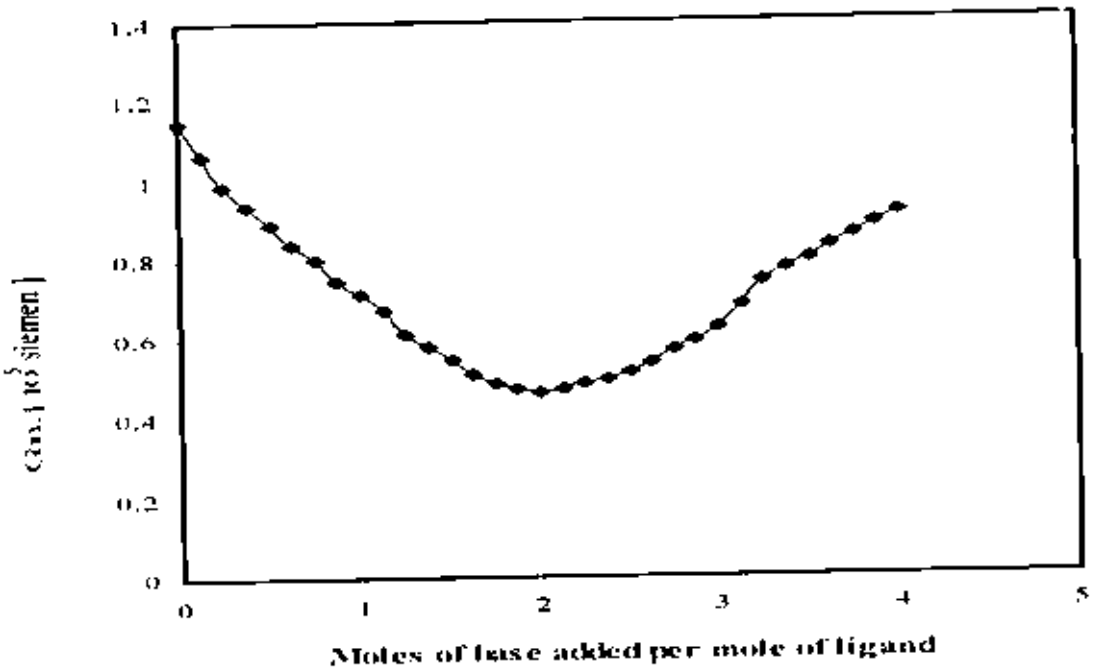


Fig.(26)Conductometric titration curves for Pd(II)-DPA-aspartic acid system.

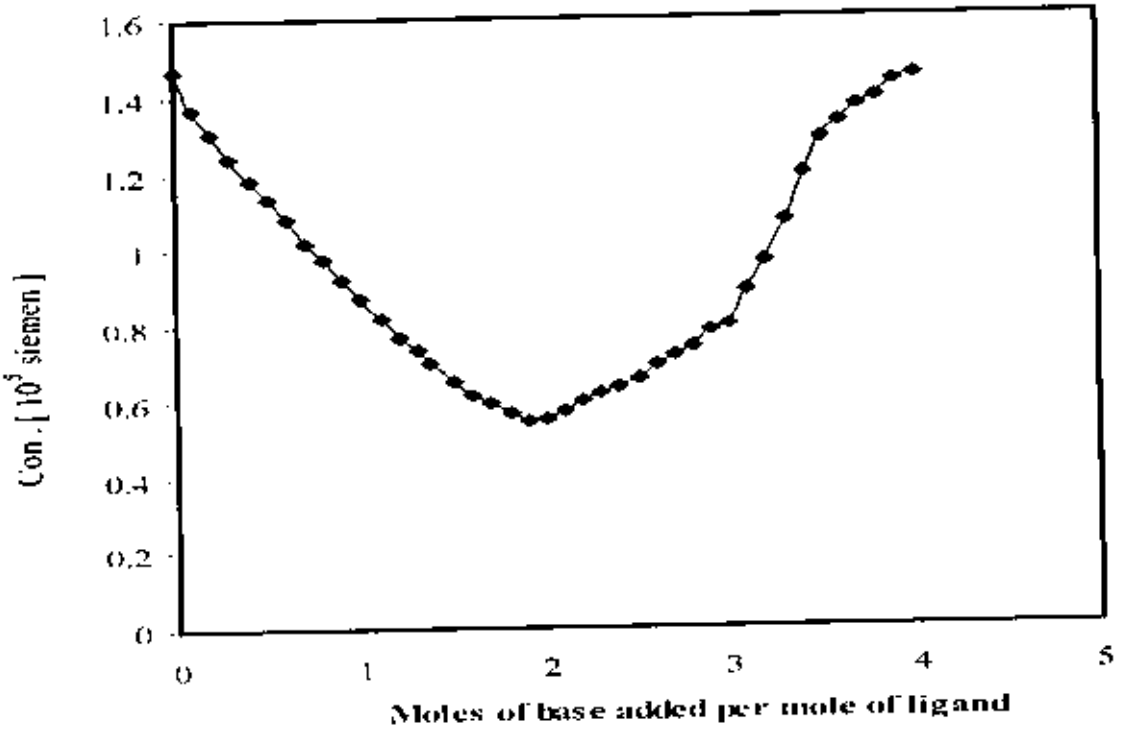


Fig.(27)Conductometric titration curves for Pd(II)-DPA-histadine system.

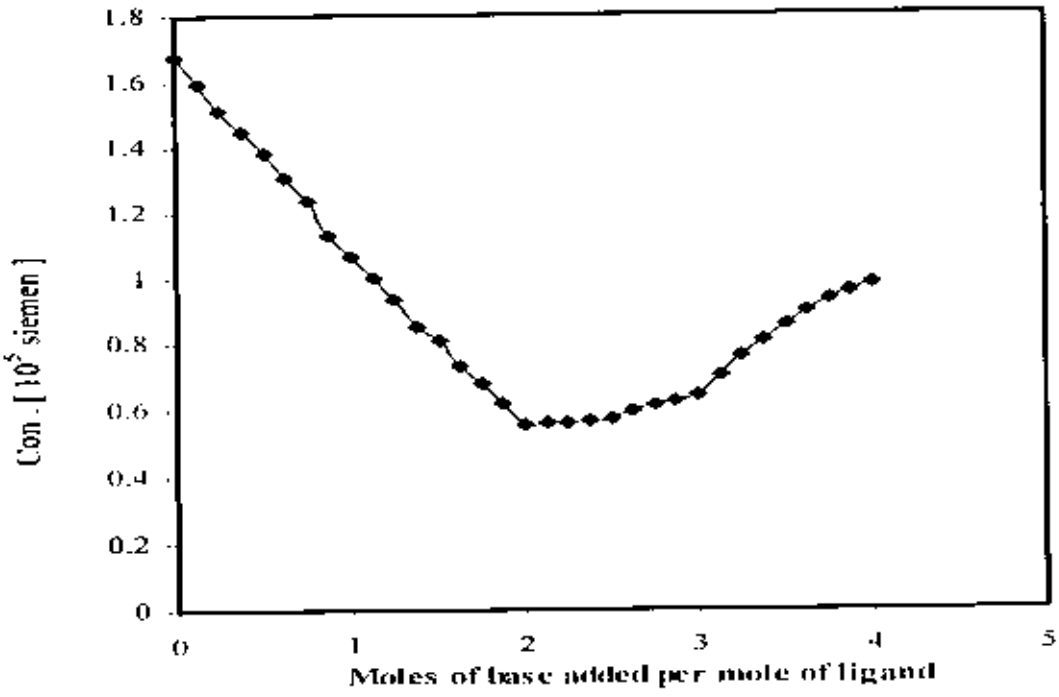


Fig.(28)Conductometric titration curves for Pd(II)-DPA-succinic system.

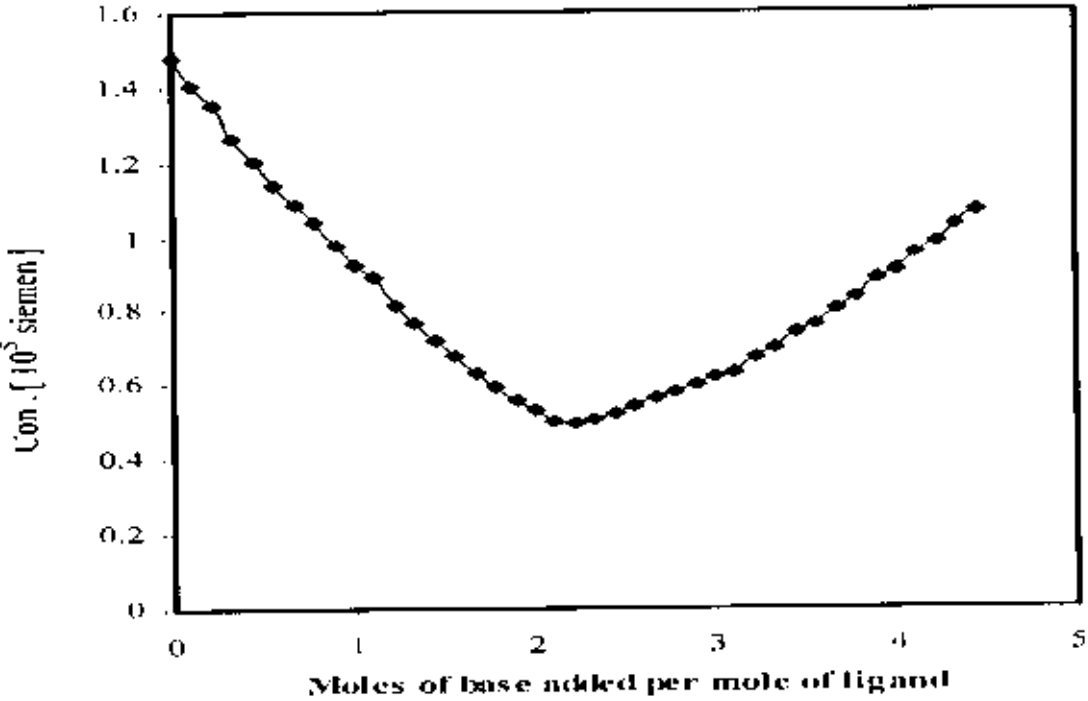


Fig.(29)Conductometric titration curves for Pd(II)-DPA-phthalic acid system.

Table (19): Acidity constant of ligands in aqueous solution at 30 °C and I = 0.5M ($NaNO_3$).

Ligands	pK_{a1}	pK_{a2}	pK_{a3}
DPA	2.38 ± 0.06	4.65 ± 0.05	-
Glycine	-	9.72 ± 0.04	-
Alanine	-	9.81 ± 0.06	-
Valine	-	9.67 ± 0.03	-
Phenylalanine	-	9.23 ± 0.05	-
Tryptophan	-	9.55 ± 0.07	-
Methionine	-	9.34 ± 0.06	-
Leucine	-	9.18 ± 0.06	-
Aspartic acid	-	9.87 ± 0.05	3.90 ± 0.03
Glutamic acid	-	9.76 ± 0.04	4.21 ± 0.05
Histadiene	-	9.28 ± 0.07	6.32 ± 0.07
Phathalic acid	2.82 ± 0.04	5.47 ± 0.05	-
Salicylic acid	2.78 ± 0.06	13.60*	-
Succinic acid	4.12 ± 0.03	5.72 ± 0.05	-
Malonic acid	2.84 ± 0.06	5.68 ± 0.05	-
Malic acid	3.32 ± 0.04	5.28 ± 0.07	-
Oxalic acid	1.40*	4.35 ± 0.05	-
Tartaric acid	3.10 ± 0.03	4.42 ± 0.06	-

*ref.[105]

Table (20): Stability constants of binary complexes involving Pd(II) and dipicolonic acid or some amino acid or some aliphatic and aromatic acid at 30 °C and I = 0.5 M ($NaNO_3$).

Ligands	$\log K_{ML}^{M}$
DPA	6.45 ± 0.06
Glycine	5.93 ± 0.05
Alanine	5.42 ± 0.04
Valine	6.95 ± 0.05
Phenylalanine	5.24 ± 0.04
Tryptophan	6.32 ± 0.06
Methionine	6.25 ± 0.07
Leucine	5.84 ± 0.05
Aspartic acid	5.84 ± 0.04
Glutamic acid	6.14 ± 0.06
Histadiene	6.47 ± 0.05
Phathalic acid	5.94 ± 0.07
Salicylic acid	6.39 ± 0.05
Succinic acid	6.33 ± 0.04
Malonic acid	5.97 ± 0.05
Malic acid	5.07 ± 0.08
Oxalic acid	5.79 ± 0.04
Tartaric acid	5.07 ± 0.06

Table (21): Formation constant of the ternary complexes of Pd(II) involving DPA as a primary ligand and amino acid or aliphatic and aromatic acid as a secondary ligand at 30 °C and $I = 0.5$ M ($NaNO_3$).

Ligands	$\log K_{MXL}^{MX}$	$\log \beta_{MXL}^{M}$	$\Delta \log K$
Glycine	5.35 ± 0.06	11.80	-0.58
Alanine	5.30 ± 0.05	11.75	0.12
Valine	5.93 ± 0.06	12.37	-1.02
Phenylalanine	5.49 ± 0.07	11.94	0.25
Tryptophan	6.02 ± 0.05	12.47	-0.3
Methionine	6.16 ± 0.04	12.61	-0.09
Leucine	6.09 ± 0.05	12.54	0.25
Aspartic acid	6.20 ± 0.07	12.65	0.36
Glutamic acid	6.18 ± 0.04	12.63	0.12
Histadiene	6.33 ± 0.06	12.78	-0.14
Phathalic acid	6.83 ± 0.04	13.28	0.87
Salicylic acid	6.89 ± 0.03	13.34	0.50
Succinic acid	6.70 ± 0.05	13.15	0.37
Malonic acid	6.23 ± 0.04	12.68	0.26
Malic acid	5.41 ± 0.06	11.86	0.34
Oxalic acid	5.92 ± 0.05	12.37	0.13
Tartaric acid	5.18 ± 0.07	11.63	0.11

3.2. Palladium(II) complexes of iminodiacetic acid (IDA) in aqueous medium:

The formation and stability of binary and ternary complexes of palladium(II) with iminodiacetic acid (IDA) as a primary ligand and biologically important ligands (amino acids, aliphatic acids and aromatic acids as a secondary ligand were studied by potentiometric technique at 30 °C and I = 0.5 M in aqueous solutions. The results obtained on titration the solution mixtures (prepared as described in the experimental part) with NaOH solution are represented graphically in Figs.(30-46) as plots of pH versus ml added of NaOH. Calculations of dissociation constants of ligands and stability constants of binary and ternary complexes were obtained from the titration curves using Irving and Rossotti pH technique with modifications[96,99] are collected in Tables (20, 40and 41). ΔlogK values have been evaluated and discussed .

The mode chelation of ternary complexes formed was carried out by conductivity measurements in solution.

3.2.1. Proton – ligand equilibria :

The protonation constants of the iminodiacetic acid (IDA) could be calculated from the potentiometric titration curves (a+b). Protonated iminodiacetic acid (H_2IDA^+) titrated as a biprotic acid in the pH range 2-4 due to to successive deprotonation of its two carboxylic acid groups. The ionization of the iminium proton occurred at the pH range (8-10). The iminodiacetate dianion coordinates as a (O^-, N, O^-) terdented ligand. The formation constant of the binary pd(IDA) complex was calculated from the poteniometric titration curve c. An Irving and Rossotti pH technique with modifications [96,99] was used to determine the dissociation constants of IDA and formation constant of pd(IDA) (Table 4). The acidity constants of the secondary ligands (amino acids, aliphatic and aromatic

acids) and formation constants of its binary complexes were calculated in Tables (19 & 20).

3.2.2. Mixed –ligand complexes of iminodiacetic acid:

The potentiometric titration curves of [Pd(II)-IDA] in presence of secondary ligands (L = amino acids, aliphatic and aromatic acids) showed, strong overlap with the titration curves of [Pd(II)-IDA] in absence of secondary ligand (1:1) binary complexes at lower pH (as shown by curve **f** and curve **e** , respectively) .This suggests that the secondary ligand dose not combine with the binary [Pd(II)–IDA] complex at lower pH. Generally, above certain pH values which is largely dependent on the nature of the secondary ligand used, one observes a divergence of the ternary titration curves from that of the corresponding binary [Pd(II)-IDA] ones. This shows the coordination of secondary ligand with the binary [Pd(II)-IDA] complex in stepwise manner, i.e., the secondary ligand starts complexation after the complete formation of the binary (1:1) complex of IDA to form the ternary [Pd(IDA)(L)] systems.

The formation constant values of the mixed–ligand systems were calculated from the experimental titration curves Figs.(30-46), using the equations reported in the experimental by Irving and Rossotti. It was found that, in all systems, the mixed–ligand complex curve **f** is deviated considerably from the binary complex curve **e** of the iminodiacetic acid indicating the formation of ternary complex. The formation constant values for the mixed–ligand systems were obtained from the relation between n'_{mix} and pL'_{mix} (n'_{mix} = average number of the secondary ligand molecules attached per [Pd(II)-DPA] complex and pL'_{mix} = free secondary ligand exponent, respectively) are listed in Table(41).

Therefore, it is assumed that in the presence of both ligands (primary, IDA, and secondary ligand, amino acids, aliphatic and aromatic acids) the IDA is ligated to the metal ion, then followed by ligation of secondary ligand, i.e., the ternary complex formation could be considered in stepwise equilibria Eqs. (25 & 26):

$$M + A \rightleftharpoons MA \quad \text{.....(25)}$$

$$MA + L \rightleftharpoons MAL \quad \text{.....(26)}$$

$$K_{MAL}^{MA} = \frac{[MAL]}{[MA][L]} \quad \text{.....(27)}$$

The overall stability constant, which must be determined experimentally is connected to by equation (28) as shown below :

$$\log K_{MAL}^{MA} = \log \beta_{MAL}^{M} - \log K_{MA}^{M} \quad \text{.....(28)}$$

where A = IDA, L = amino acids or aliphatic acids or aromatic acids, M = palladium(II).

Table (41) demonstrates the difference in stabilities of the binary and ternary complexes in terms ΔlogK as defined by equation (29):

$$\Delta \log K = \log K_{MXL}^{MX} - \log K_{ML}^{M}$$

$$= \log K_{MXL}^{ML} - \log K_{MX}^{M} \quad \text{.....(29)}$$

In the ternary systems studied, the values of K_{MAL}^{MA} were found to lie in sequence (Table 41) :

Aromatic acids > aliphatic acids > amino acids

The relative stabilities of the ternary complexes with respect to aliphatic acids and amino acids are in accord with the basicities (pK_{a1} + pK_{a2}) of the ligands. It is well known that the increase in basicity of a ligand increases the stability of its metal complexes. The higher values of ΔlogK with aromatic acids than aliphatic acids may be attributed to the presence of an aromatic ring[103,104] which alters the bonding properties of these carboxylic acids.

3.2.3. Conductomertic titration

The conductometeic titration curve of the ternary complexes containing palladium(II), IDA as a primary ligand and secondary ligands (amino acids, aromatic and aliphatic acids) as showen in Figs. (47-52) as plots of conductance versus mole of base added per mole of ligand. The studies show that there is an inflection at a = 2 for all systems, probably corresponding to the neutralization of two protons of the primary ligand (IDA), resulting from the formation of [Pd(IDA)] binary complex. Between $2 < a < 3$, there is a slight increase of conductance due to the formation of the ternary complex associated with the release of a proton from the secondary ligand to give the [Pd(IDA)(L)] complex . Beyond a = 3 , the conductance increases more uniformly due to the presence of excess sodium hydroxide.

Table(22): Potintiometric titration values of glycine system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.14	2.07	1.93
0.25	2.71	2.91	2.72	2.17	2.11	1.95
0.5	2.77	2.96	2.76	2.19	2.13	1.96
0.75	2.88	3.02	2.83	2.22	2.18	1.98
1	3.02	3.07	2.89	2.25	2.20	2.01
1.25	3.23	3.16	2.99	2.32	2.27	2.04
1.5	3.65	3.23	3.08	2.35	2.31	2.06
1.75	5.13	3.35	3.17	2.41	2.35	2.09
2	8.30	3.46	3.32	2.47	2.40	2.14
2.25	10.39	3.67	3.54	2.58	2.49	2.18
2.5	10.81	3.91	3.81	3.00	2.55	2.22
2.75	11.11	4.77	4.72	3.02	2.65	2.27
3	11.27	7.59	7.44	3.28	2.76	2.33
3.32	11.41	8.65	10.47	3.45	2.89	2.42
3.5	11.49	10.24	10.80	3.55	3.01	2.48
3.75	11.59	10.68	11.13	3.70	3.20	2.56
4	11.65	10.84	11.29	4.50	3.38	2.65
4.25	11.69	11.05	11.43	5.42	3.66	2.81
4.5	11.73	11.25	11.53	6.80	3.98	2.92
4.75	11.80	11.30	11.63	9.83	4.69	3.20
5	11.83	11.38	11.72	10.20	6.05	3.29
5.25	11.88	11.50	11.78	10.43	7.13	3.65
5.5	11.91	11.56	11.82	10.57	9.23	3.82
5.75	11.95	11.67	11.88	10.71	10.43	4.73
6	11.97	11.72	11.90	10.79	10.56	6.32
6.25	12.01	11.78	11.94	10.89	10.70	6.95
6.5	12.03	11.82	11.97	10.94	10.77	9.53
6.75	12.06	11.87	12.01	11.01	10.89	9.98
7	12.08	11.90	12.04	11.05	10.95	10.21
7.25	12.10	11.95	12.07	11.09	11.01	10.45
7.5	12.12	11.98	12.08	11.13	11.07	10.56
7.75	12.13	12.01	12.10	11.17	11.11	10.69
8	12.16	12.03	12.11	11.19	11.14	10.77

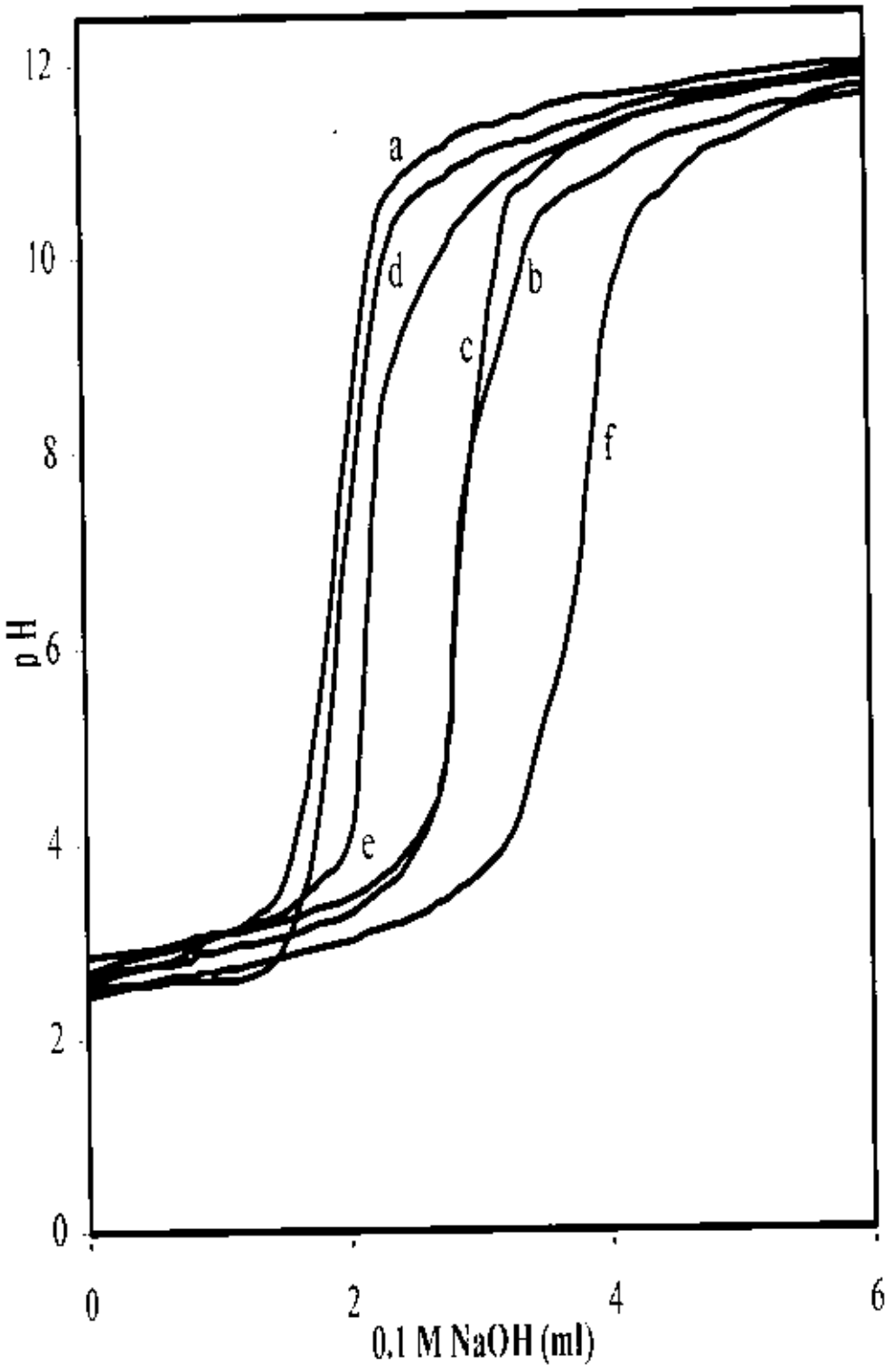


Fig.(30)Potentiometric titration curves for Pd(II)-IDA-glycine system.

Table(23): Potintiometric titration values of alanine system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.55	2.89	2.69
0.25	2.71	2.91	2.72	2.57	2.97	2.74
0.5	2.77	2.96	2.76	2.59	3.03	2.78
0.75	2.88	3.02	2.83	2.61	3.19	2.82
1	3.02	3.07	2.89	2.62	3.27	2.89
1.3	3.23	3.16	2.99	2.71	3.43	2.96
1.5	3.65	3.23	3.08	3.00	3.76	3.05
1.75	5.13	3.35	3.17	4.08	4.01	3.14
2	8.30	3.46	3.32	7.40	4.34	3.25
2.25	10.39	3.67	3.54	9.64	5.20	3.46
2.5	10.81	3.91	3.81	10.45	6.47	3.60
2.75	11.11	4.77	4.72	10.66	9.48	3.82
2.96	11.27	7.59	7.44	10.80	10.28	4.36
3.25	11.41	8.86	10.47	11.02	10.68	5.10
3.5	11.49	10.24	10.80	11.21	10.97	5.80
3.75	11.59	10.68	11.13	11.34	11.13	6.55
4	11.65	10.84	11.29	11.45	11.27	8.20
4.25	11.69	11.05	11.43	11.55	11.40	9.93
4.5	11.73	11.25	11.53	11.63	11.50	10.41
4.75	11.80	11.30	11.63	11.69	11.57	10.81
5	11.83	11.38	11.72	11.73	11.63	11.03
5.25	11.88	11.50	11.78	11.79	11.70	11.27
5.5	11.91	11.56	11.82	11.86	11.74	11.34
5.75	11.95	11.67	11.88	11.92	11.79	11.46
6	11.97	11.72	11.90	11.95	11.83	11.54

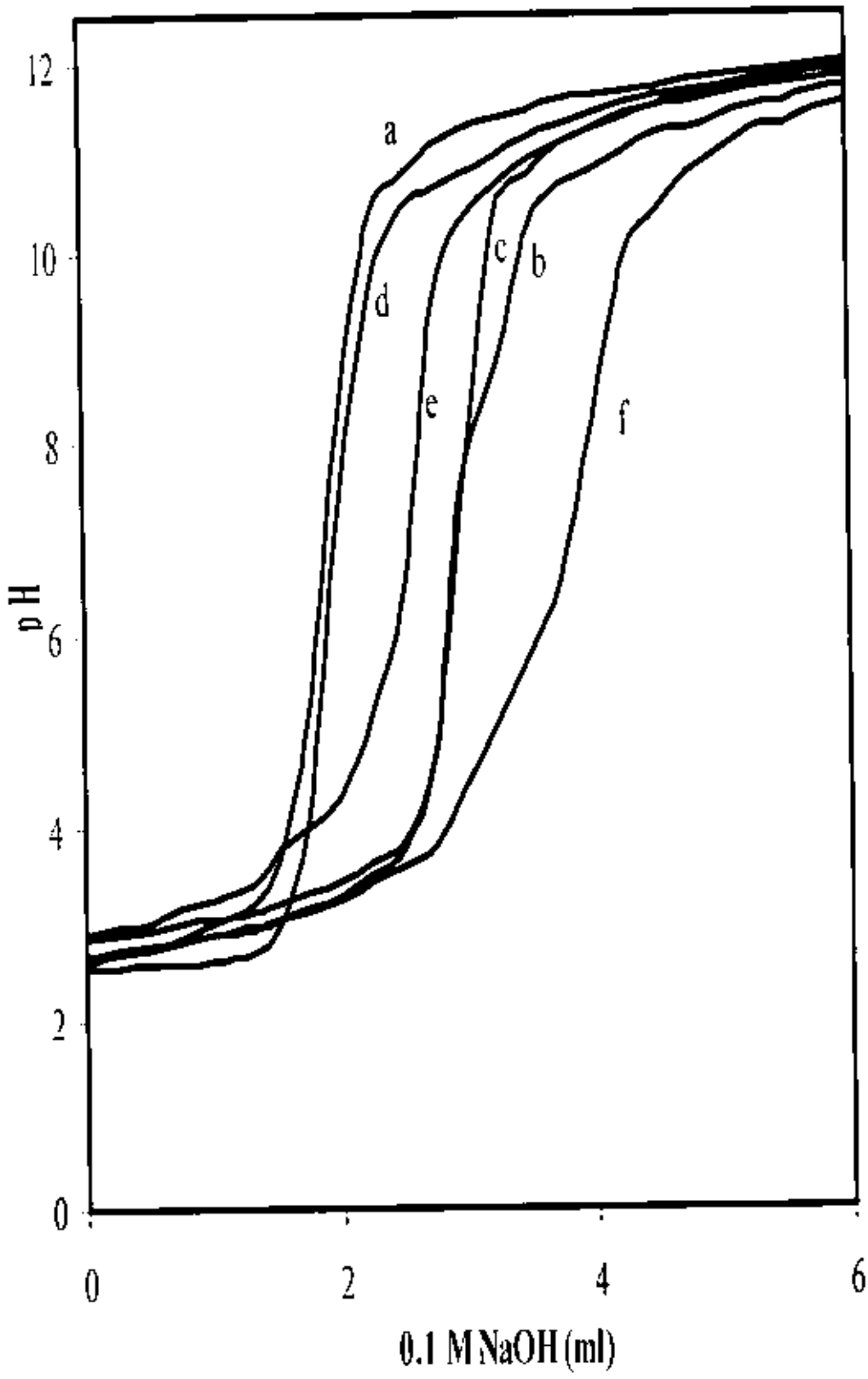


Fig.(31) Potentiometric titration curves for Pd(II) -IDA-alanine system.

Table(24): Potintiometric titration values of valine system with IDA in aqueous solution at 30 °C and $I = 0.5$ M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.62	2.81	2.82
0.25	2.71	2.91	2.72	2.72	2.86	2.86
0.5	2.77	2.96	2.76	2.79	2.91	2.9
0.75	2.88	3.02	2.83	2.94	2.98	2.95
1	3.02	3.07	2.89	3.05	3.08	3.01
1.25	3.23	3.16	2.99	3.20	3.19	3.06
1.5	3.65	3.23	3.08	3.35	3.30	3.12
1.75	5.13	3.35	3.17	4.02	3.51	3.19
2	8.30	3.46	3.32	7.36	3.83	3.29
2.25	10.39	3.67	3.54	9.68	4.30	3.40
2.5	10.81	3.91	3.81	10.18	5.50	3.54
2.75	11.11	4.77	4.72	10.70	9.44	3.65
3	11.27	7.59	7.44	10.98	10.27	3.86
3.25	11.41	8.65	10.47	11.17	10.91	4.25
3.5	11.49	10.24	10.80	11.32	11.17	5.00
3.75	11.59	10.68	11.13	11.45	11.32	6.38
3.93	11.65	10.84	11.29	11.52	11.43	7.32
4.25	11.69	11.05	11.43	11.61	11.53	9.98
4.5	11.73	11.25	11.53	11.66	11.60	10.66
4.75	11.80	11.30	11.63	11.73	11.66	11.02
5	11.83	11.38	11.72	11.78	11.72	11.25
5.25	11.88	11.50	11.78	11.83	11.76	11.41
5.5	11.91	11.56	11.82	11.86	11.81	11.50
5.75	11.95	11.67	11.88	11.90	11.85	11.60
6	11.97	11.72	11.90	11.92	11.88	11.65

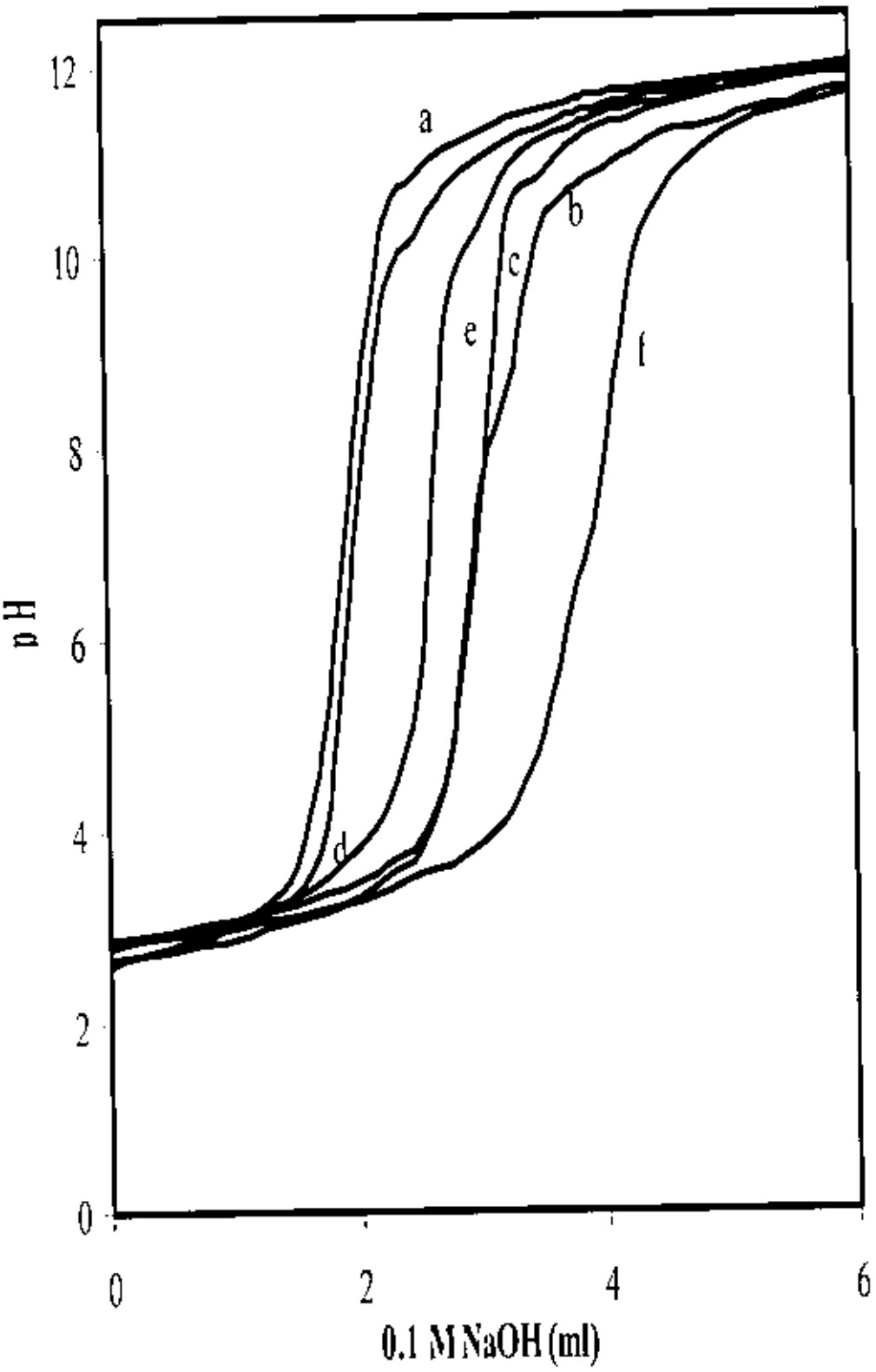


Fig.(32) Potentiometric titration curves for Pd(II) -IDA-valine system.

Table(25): Potintiometric titration values of phenylalanine system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.92	2.80	2.86
0.25	2.71	2.91	2.72	3.01	2.89	2.89
0.5	2.77	2.96	2.76	3.07	2.93	2.93
0.75	2.88	3.02	2.83	3.19	3.03	2.98
1	3.02	3.07	2.89	3.37	3.10	3.01
1.25	3.23	3.16	2.99	3.54	3.25	3.07
1.5	3.65	3.23	3.08	3.95	3.36	3.11
1.75	5.13	3.35	3.17	6.39	3.45	3.18
2	8.30	3.46	3.32	8.50	3.73	3.25
2.25	10.39	3.67	3.54	9.38	4.34	3.34
2.5	10.81	3.91	3.81	9.98	6.38	3.43
2.75	11.11	4.77	4.72	10.54	9.85	3.59
3	11.27	7.59	7.44	10.87	10.40	3.75
3.25	11.41	8.65	10.47	11.05	10.94	4.05
3.5	11.49	10.24	10.80	11.32	11.10	4.33
3.75	11.59	10.68	11.13	11.46	11.32	5.40
4	11.65	10.84	11.29	11.56	11.46	7.90
4.25	11.69	11.05	11.43	11.66	11.54	9.90
4.5	11.73	11.25	11.53	11.71	11.64	10.53
4.75	11.80	11.30	11.63	11.78	11.72	10.95
5	11.83	11.38	11.72	11.84	11.77	11.16
5.25	11.88	11.50	11.78	11.87	11.83	11.33
5.5	11.91	11.56	11.82	11.91	11.87	11.42
5.75	11.95	11.67	11.88	11.96	11.91	11.56
6	11.97	11.72	11.90	11.98	11.94	11.63

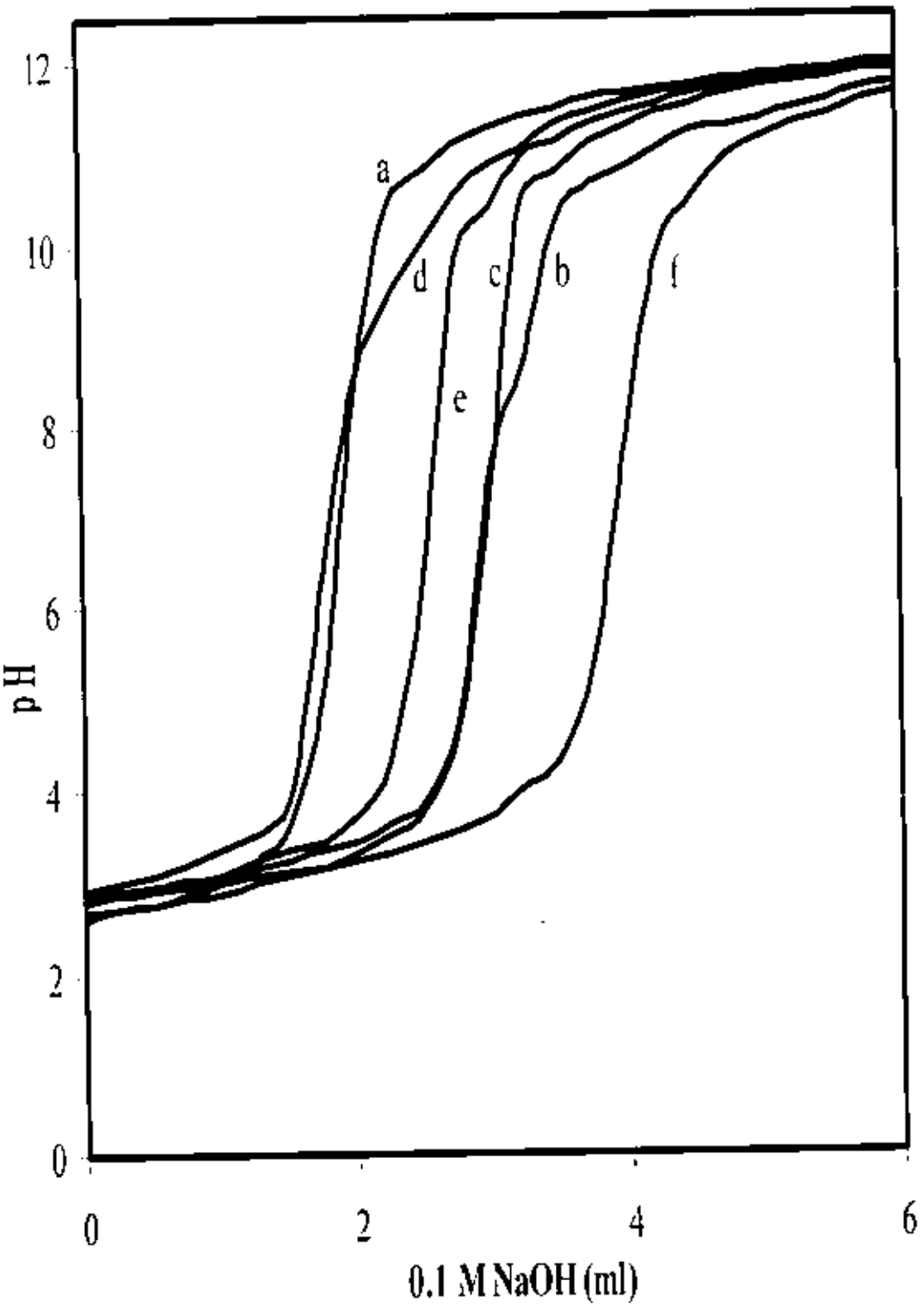


Fig.(33) Potentiometric titration curves for Pd(II) - IDA-phenylalanine system.

Table(26): Potintiometric titration values of tryptophane system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.86	2.67	2.83
0.25	2.71	2.91	2.72	2.95	2.73	2.87
0.5	2.77	2.96	2.76	3.06	2.79	2.90
0.75	2.88	3.02	2.83	3.17	2.85	2.93
1	3.02	3.07	2.89	3.30	2.93	2.98
1.25	3.23	3.16	2.99	3.52	3.02	3.04
1.5	3.65	3.23	3.08	3.85	3.13	3.08
1.75	5.13	3.35	3.17	6.34	3.30	3.14
2	8.30	3.46	3.32	9.03	3.51	3.19
2.25	10.39	3.67	3.54	9.92	4.33	3.28
2.5	10.81	3.91	3.81	10.48	7.47	3.37
2.75	11.11	4.77	4.72	10.93	10.29	3.51
3	11.27	7.59	7.44	11.16	10.79	3.65
3.25	11.41	8.65	10.47	11.36	11.15	3.85
3.5	11.49	10.24	10.80	11.59	11.29	4.22
3.75	11.59	10.68	11.13	11.65	11.40	5.26
4	11.65	10.92	11.29	11.72	11.49	7.70
4.25	11.69	11.05	11.43	11.77	11.60	8.58
4.5	11.73	11.25	11.53	11.79	11.67	10.38
4.75	11.80	11.30	11.63	11.83	11.75	10.80
5	11.83	11.38	11.72	11.87	11.81	10.92
5.25	11.88	11.50	11.78	11.90	11.86	11.18
5.5	11.91	11.56	11.82	11.93	11.90	11.33
5.75	11.95	11.67	11.88	11.96	11.94	11.49
6	11.97	11.72	11.90	11.99	11.98	11.56

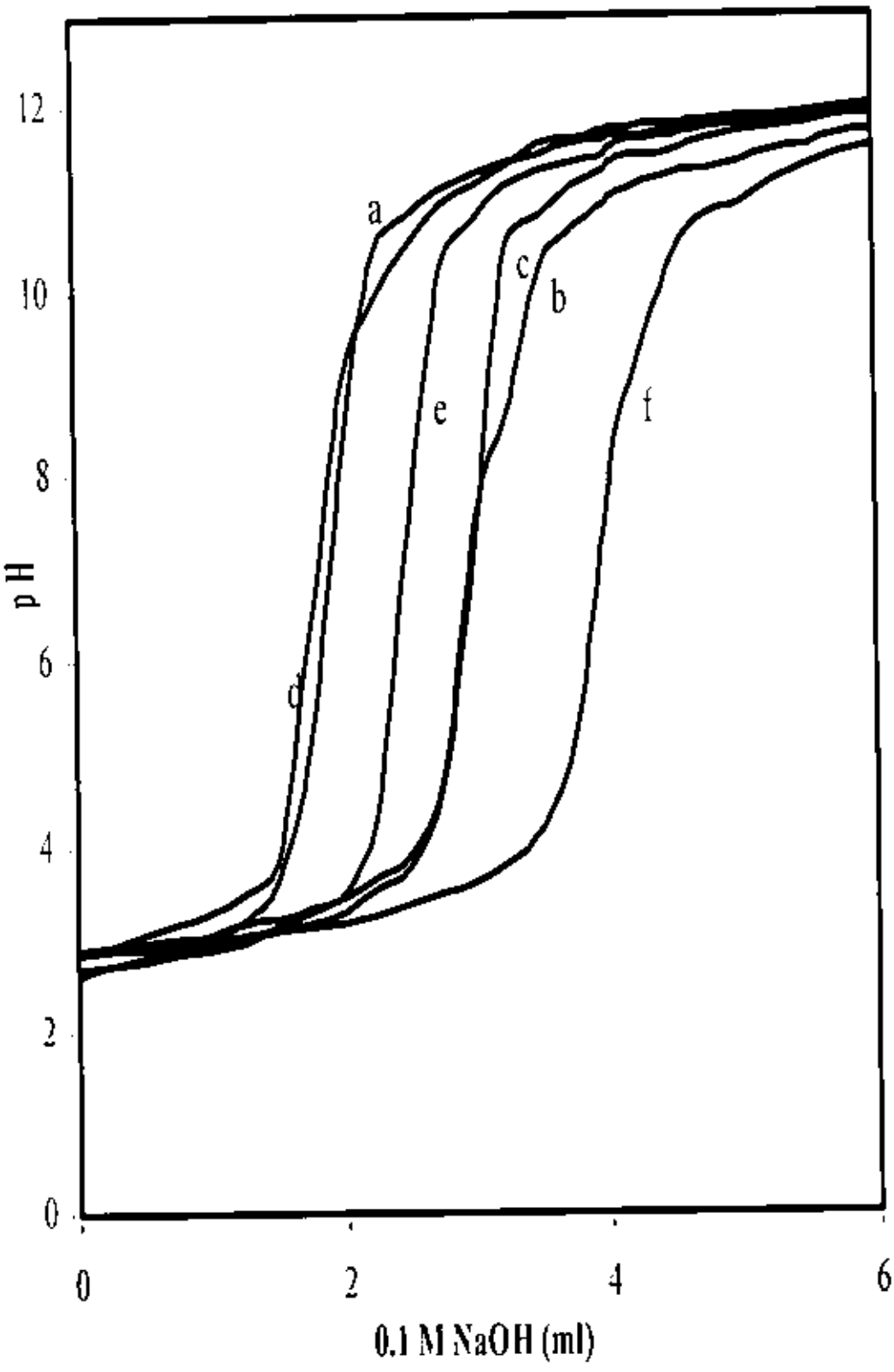


Fig.(34)Potentiometric titration curves for Pd(II)- IDA-tryptophane system.

Table(27): Potintiometric titration values of methionine system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.87	2.67	2.84
0.25	2.71	2.91	2.72	2.93	2.74	2.88
0.5	2.77	2.96	2.76	3.00	2.81	2.92
0.75	2.88	3.02	2.83	3.08	2.88	2.95
1	3.02	3.07	2.89	3.20	2.94	2.99
1.25	3.23	3.16	2.99	3.33	3.04	3.04
1.5	3.65	3.23	3.08	3.52	3.13	3.10
1.75	5.13	3.35	3.17	3.89	3.26	3.16
2	8.30	3.46	3.32	6.70	3.43	3.21
2.25	10.39	3.67	3.54	9.05	3.70	3.30
2.5	10.81	3.91	3.81	9.75	4.10	3.37
2.75	11.11	4.77	4.72	10.40	9.78	3.50
3	11.27	7.59	7.44	10.70	10.66	3.59
3.25	11.41	8.65	10.47	10.97	10.95	3.79
3.5	11.49	10.24	10.80	11.16	11.19	4.03
3.69	11.59	10.68	11.13	11.33	11.36	4.50
4	11.65	10.84	11.29	11.47	11.46	7.40
4.2	11.69	11.05	11.43	11.59	11.54	8.45
4.5	11.73	11.25	11.53	11.67	11.63	10.24
4.75	11.80	11.30	11.63	11.79	11.69	10.82
5	11.83	11.38	11.72	11.83	11.73	11.03
5.25	11.88	11.50	11.78	11.90	11.79	11.25
5.5	11.91	11.56	11.82	11.94	11.83	11.33
5.75	11.95	11.67	11.88	12.00	11.87	11.45
6	11.97	11.72	11.90	12.03	11.91	11.55

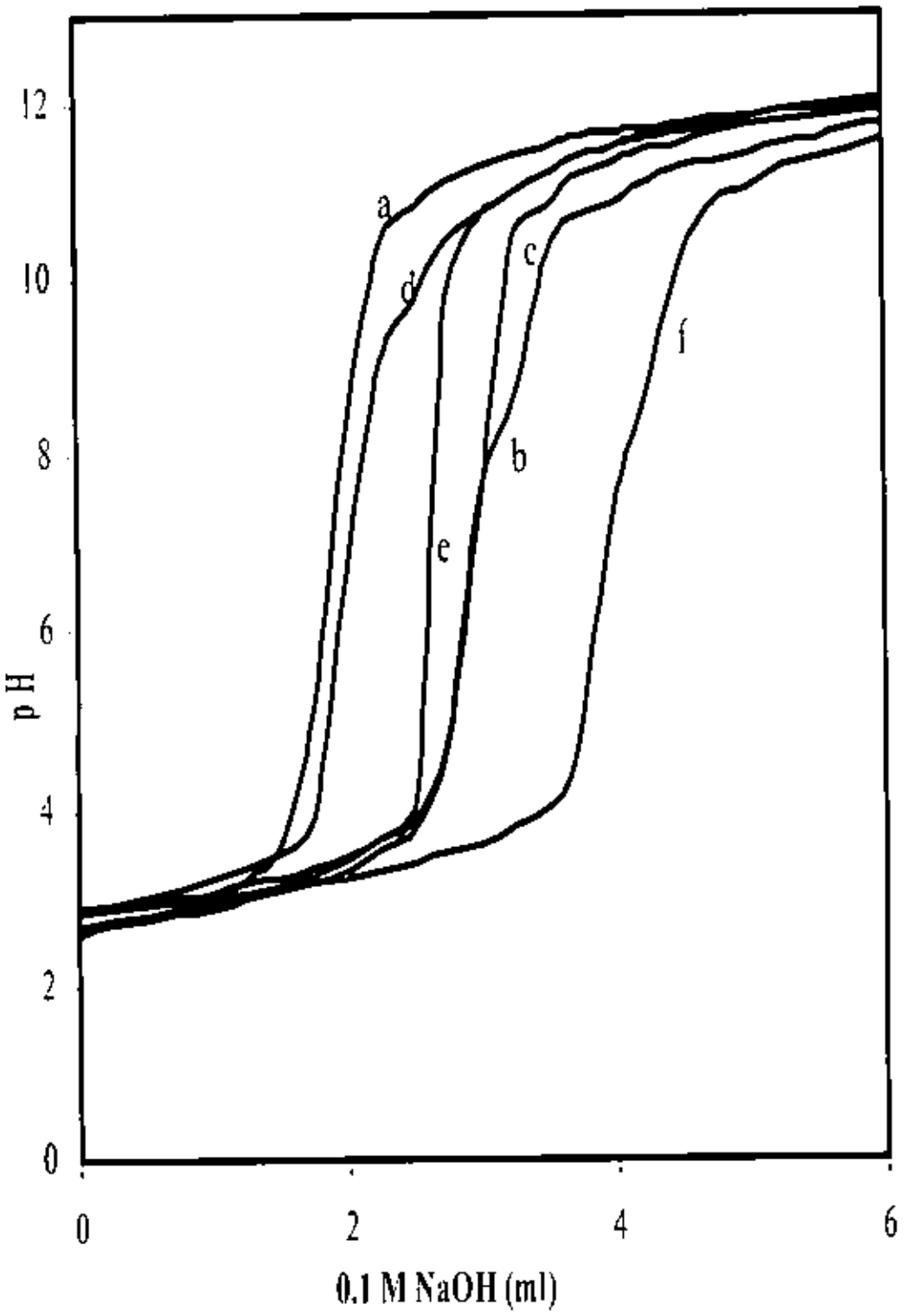


Fig.(35) Potentiometric titration curves for Pd(II) -IDA-methionine system.

Table(28): Potintiometric titration values of leucine system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.81	2.57	2.81
0.25	2.71	2.91	2.72	2.91	2.69	2.84
0.5	2.77	2.96	2.76	3.01	2.76	2.88
0.75	2.88	3.02	2.83	3.09	2.83	2.93
1	3.02	3.07	2.89	3.21	2.93	2.98
1.25	3.23	3.16	2.99	3.39	3.06	3.05
1.5	3.65	3.23	3.08	3.67	3.18	3.10
1.75	5.13	3.35	3.17	5.85	3.48	3.15
2	8.30	3.46	3.32	9.39	3.86	3.23
2.25	10.39	3.67	3.54	10.12	4.55	3.32
2.5	10.81	3.91	3.81	10.56	8.89	3.42
2.75	11.11	4.77	4.72	10.97	10.34	3.58
3	11.27	7.59	7.44	11.15	10.76	3.77
3.25	11.41	8.65	10.47	11.33	11.05	4.06
3.5	11.49	10.24	10.80	11.45	11.23	4.59
3.75	11.59	10.68	11.13	11.53	11.36	5.90
4	11.65	10.84	11.29	11.61	11.45	7.60
4.25	11.69	11.05	11.43	11.67	11.56	8.97
4.5	11.73	11.25	11.53	11.73	11.61	10.45
4.75	11.80	11.30	11.63	11.78	11.66	10.88
5	11.83	11.38	11.72	11.83	11.72	11.11
5.25	11.88	11.50	11.78	11.86	11.78	11.33
5.5	11.91	11.56	11.82	11.90	11.81	11.44
5.75	11.95	11.67	11.88	11.94	11.86	11.55
6	11.97	11.72	11.90	11.96	11.88	11.63

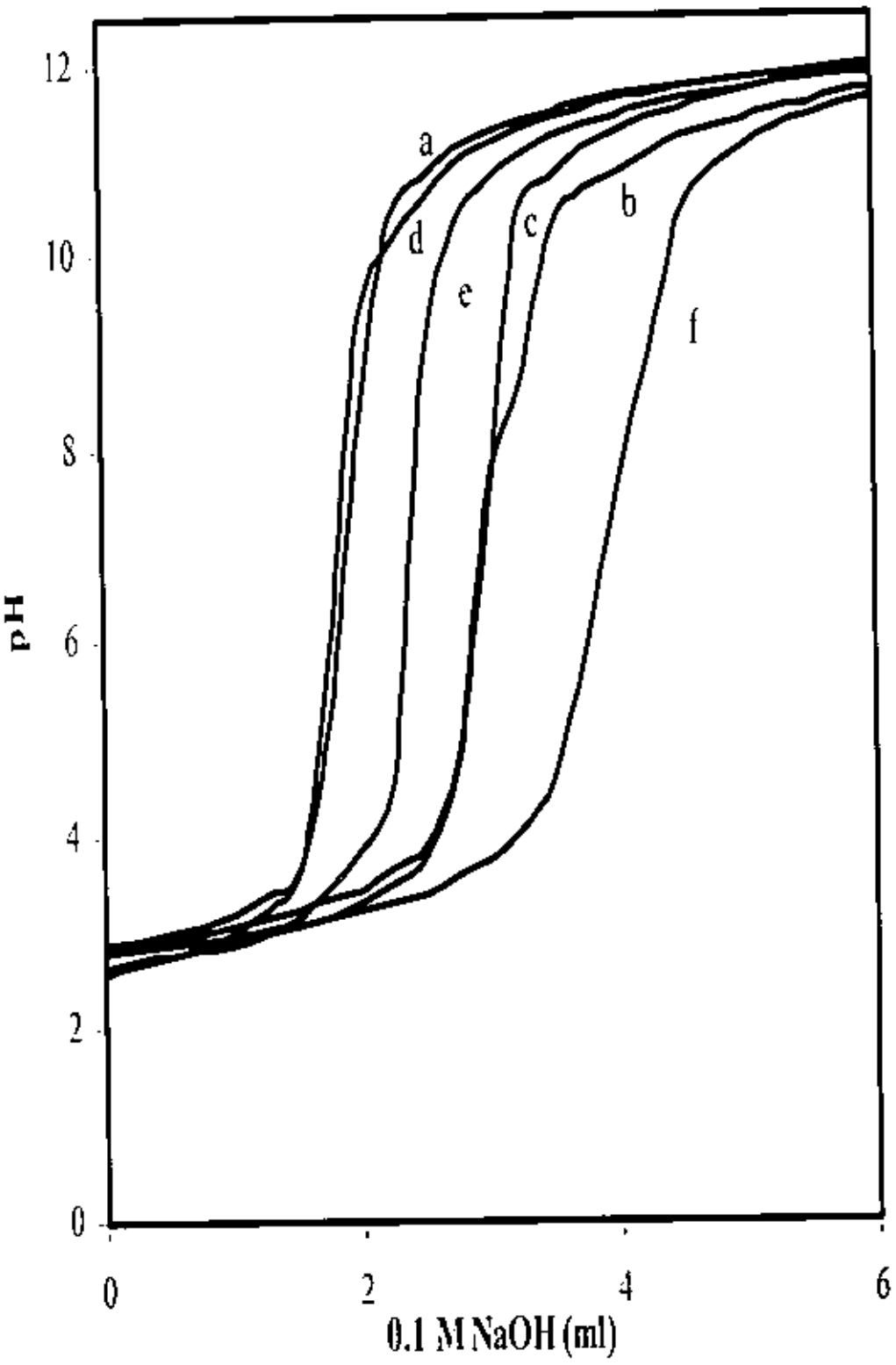


Fig.(36) Potentiometric titration curves for Pd(II)-IDA-leucine system

Table(29): Potintiometric titration values of aspartic acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.56	2.68	2.41
0.25	2.71	2.91	2.72	2.72	2.72	2.45
0.5	2.77	2.96	2.76	2.78	2.77	2.50
0.75	2.88	3.02	2.83	2.90	2.83	2.52
1	3.02	3.07	2.89	3.01	2.91	2.57
1.25	3.23	3.16	2.99	3.16	3.01	2.59
1.5	3.65	3.23	3.08	3.35	3.07	2.65
1.75	5.13	3.35	3.17	3.61	3.17	2.69
2	8.30	3.46	3.32	4.06	3.27	2.72
2.25	10.39	3.67	3.54	4.78	3.47	2.81
2.5	10.81	3.91	3.81	7.75	3.71	2.86
2.75	11.11	4.77	4.72	9.73	4.07	2.98
3	11.27	7.59	7.44	10.16	4.65	3.08
3.25	11.41	8.65	10.47	10.64	6.60	3.29
3.5	11.49	10.24	10.80	10.95	9.95	3.50
3.75	11.59	10.68	11.13	11.12	10.66	3.76
4	11.65	10.84	11.29	11.25	10.96	4.20
4.25	11.69	11.05	11.43	11.37	11.17	5.26
4.5	11.73	11.25	11.53	11.47	11.31	7.13
4.75	11.8	11.30	11.63	11.55	11.41	8.55
5	11.83	11.38	11.72	11.62	11.50	9.72
5.25	11.88	11.50	11.78	11.69	11.58	10.97
5.5	11.91	11.56	11.82	11.74	11.64	11.17
5.75	11.95	11.67	11.88	11.80	11.71	11.37
6	11.97	11.72	11.90	11.83	11.75	11.48

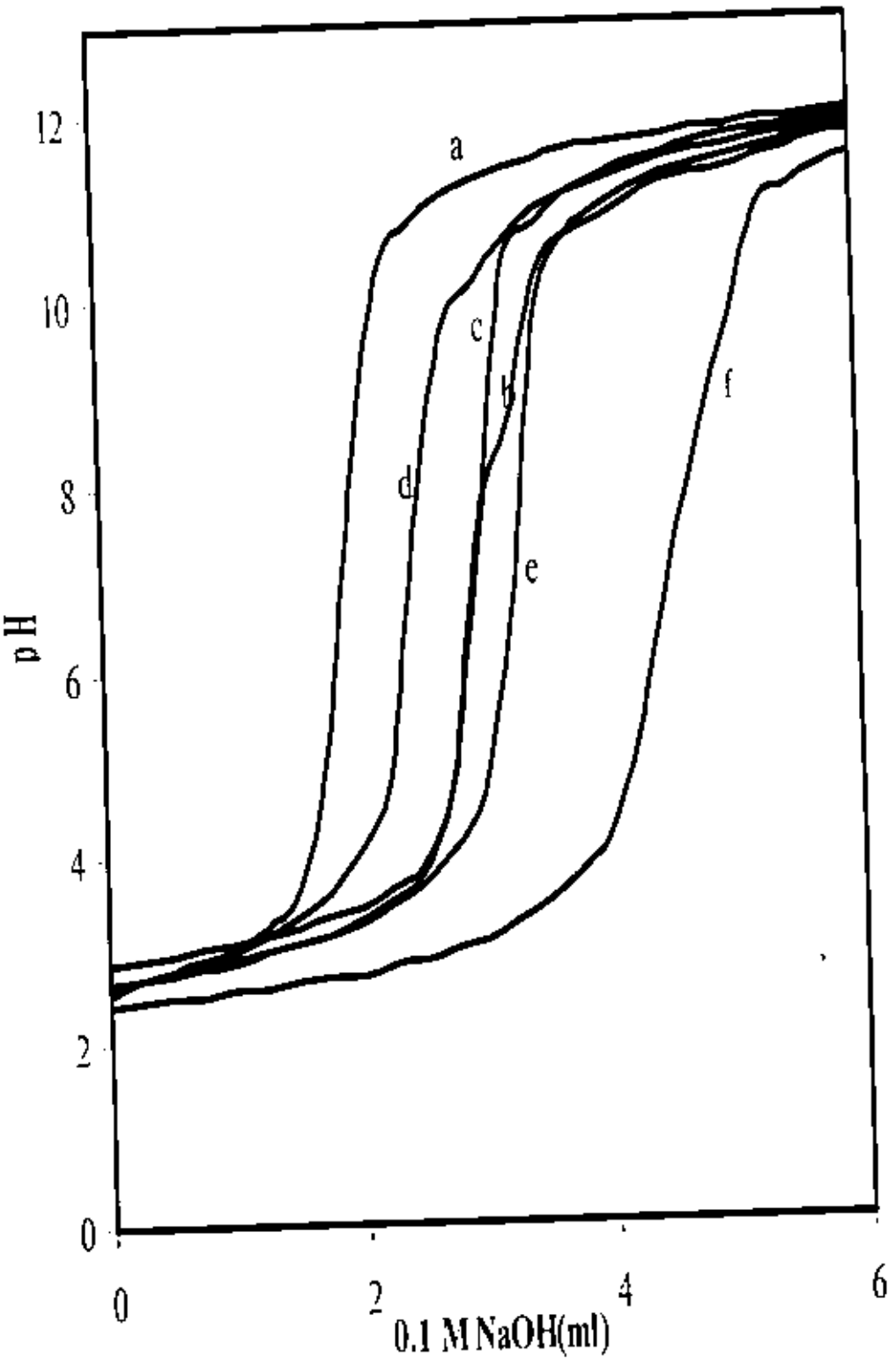


Fig.(37) Potentiomeric titration curves for Pd(II) -IDA-aspartic acid system

Table(30): Potintiometric titration values of glutamic acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.84	2.73	2.87
0.25	2.71	2.91	2.72	2.94	2.83	2.91
0.5	2.77	2.96	2.76	3.01	2.90	2.95
0.75	2.88	3.02	2.83	3.09	2.97	2.98
1	3.02	3.07	2.89	3.18	3.05	3.01
1.25	3.23	3.16	2.99	3.33	3.16	3.05
1.5	3.65	3.23	3.08	3.48	3.27	3.14
1.75	5.13	3.35	3.17	3.78	3.45	3.18
2	8.30	3.46	3.32	4.30	3.60	3.24
2.25	10.39	3.67	3.54	5.16	3.95	3.32
2.5	10.81	3.91	3.81	8.77	4.36	3.41
2.75	11.11	4.77	4.72	9.87	5.03	3.58
3	11.27	7.59	7.44	10.40	6.46	3.72
3.25	11.41	8.65	10.47	10.81	9.85	3.96
3.5	11.49	10.24	10.80	11.08	10.35	4.20
3.75	11.59	10.68	11.13	11.26	10.99	4.45
4	11.65	10.84	11.29	11.36	11.19	5.15
4.25	11.69	11.05	11.43	11.48	11.36	6.33
4.5	11.73	11.25	11.53	11.56	11.45	7.56
4.75	11.80	11.30	11.63	11.66	11.55	9.78
5	11.83	11.38	11.72	11.71	11.61	10.53
5.25	11.88	11.50	11.78	11.76	11.67	10.93
5.5	11.91	11.56	11.82	11.80	11.73	11.12
5.75	11.95	11.67	11.88	11.85	11.79	11.30
6	11.97	11.72	11.90	11.88	11.83	11.43

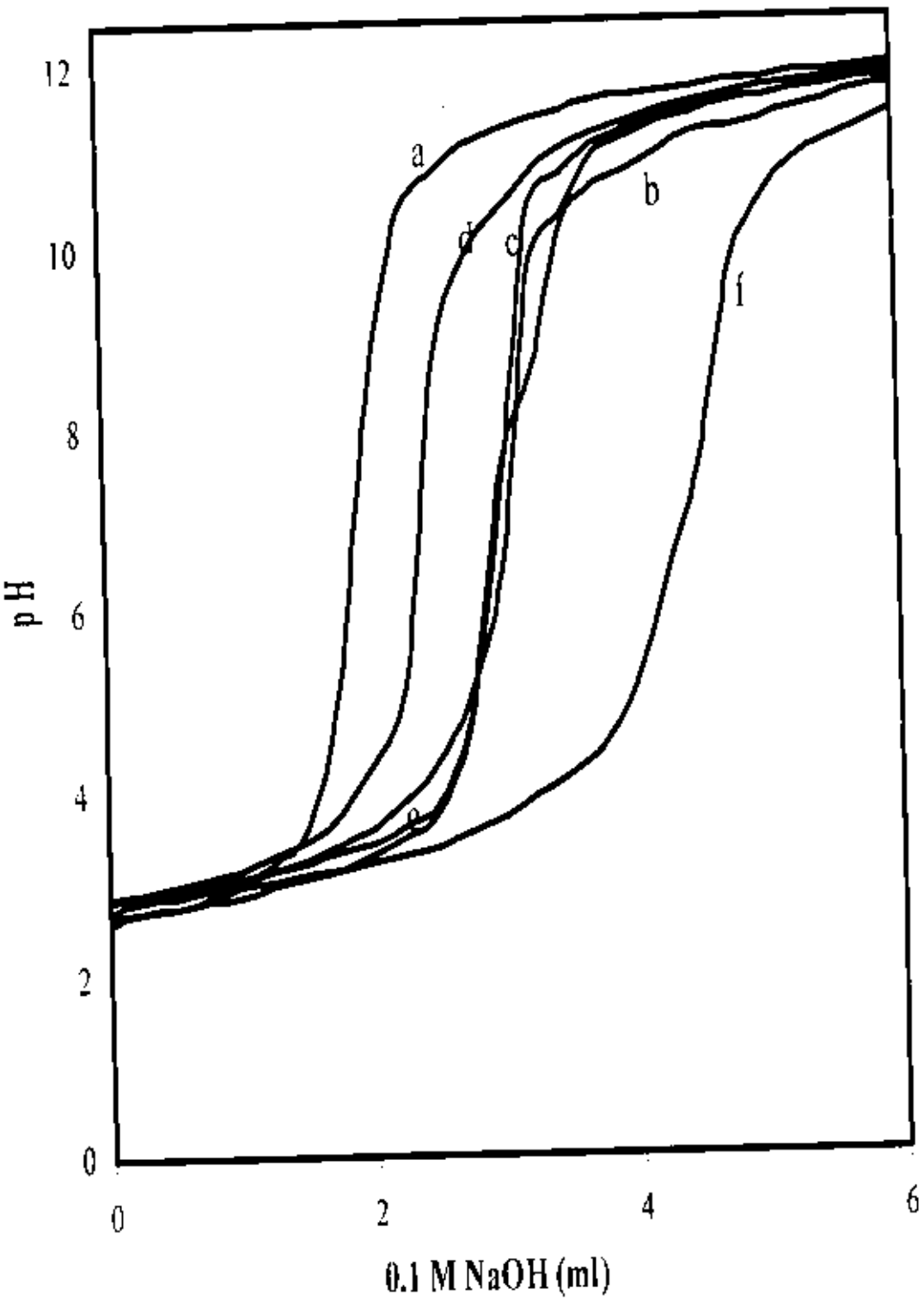


Fig.(38) Potentiometric titration curves for Pd(II) -IDA-glutamic acid system.

Table(31): Potintiometric titration values of histadine system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.67	2.53	2.81
0.25	2.71	2.91	2.72	2.74	2.61	2.83
0.5	2.77	2.96	2.76	2.82	2.66	2.85
0.75	2.88	3.02	2.83	2.91	2.72	2.88
1	3.02	3.07	2.89	3.01	2.78	2.91
1.25	3.23	3.16	2.99	3.15	2.85	2.95
1.5	3.65	3.23	3.08	3.31	2.93	2.99
1.75	5.13	3.35	3.17	3.78	3.05	3.05
2	8.30	3.46	3.32	5.25	3.14	3.11
2.25	10.22	3.67	3.54	6.25	3.26	3.17
2.5	10.81	3.91	3.81	7.50	3.46	3.23
2.75	11.11	4.77	4.72	8.73	3.96	3.30
3	11.27	7.59	7.44	9.43	6.33	3.41
3.25	11.41	8.65	10.47	10.18	9.00	3.52
3.5	11.49	10.24	10.80	10.66	10.59	3.64
3.75	11.59	10.68	11.13	10.95	10.90	3.83
4	11.65	10.84	11.29	11.13	11.12	4.04
4.25	11.69	11.05	11.43	11.31	11.23	4.80
4.5	11.73	11.25	11.53	11.41	11.36	6.90
4.75	11.80	11.30	11.63	11.50	11.45	8.85
5	11.83	11.38	11.72	11.56	11.50	10.06
5.25	11.88	11.50	11.78	11.65	11.58	10.65
5.5	11.91	11.56	11.82	11.68	11.63	10.95
5.75	11.95	11.67	11.88	11.74	11.70	11.16
6	11.97	11.72	11.90	11.78	11.74	11.30

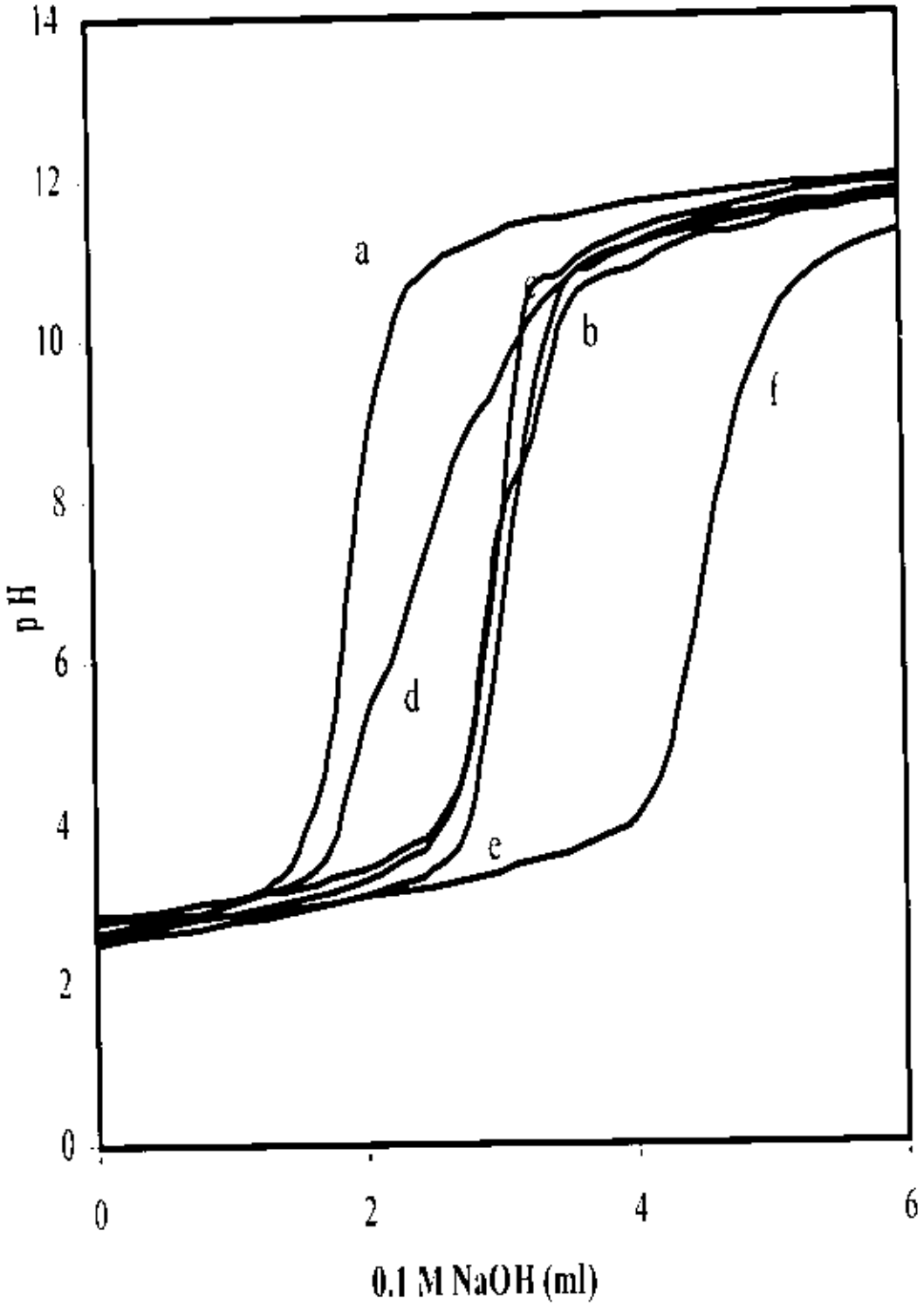


Fig.(39)Potentiometric titration curves for Pd(II)-IDA - histadine system.

Table(32): Potintiometric titration values of phthalic acid system with IDA in aqueous solution at 30 °C and $I = 0.5$ M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.77	2.78	2.79
0.25	2.71	2.91	2.72	2.82	2.84	2.83
0.5	2.77	2.96	2.76	2.93	2.89	2.85
0.75	2.88	3.02	2.83	3.02	2.98	2.89
1	3.02	3.07	2.89	3.11	3.03	2.97
1.25	3.23	3.16	2.99	3.22	3.11	3.02
1.5	3.65	3.23	3.08	3.30	3.19	3.06
1.75	5.13	3.35	3.17	3.56	3.31	3.13
2	8.30	3.46	3.32	3.84	3.43	3.21
2.25	10.39	3.67	3.54	4.42	3.67	3.28
2.5	10.81	3.91	3.81	5.08	3.84	3.41
2.75	11.11	4.77	4.72	5.72	4.32	3.52
3	11.27	7.59	7.44	6.84	5.12	3.69
3.25	11.41	8.65	10.47	9.80	6.12	3.84
3.5	11.49	10.24	10.80	10.52	6.89	4.28
3.68	11.59	10.68	11.13	11.02	7.74	4.72
4	11.65	10.84	11.29	11.23	10.09	5.79
4.25	11.69	11.05	11.43	11.40	10.78	6.65
4.5	11.73	11.25	11.53	11.50	11.05	7.50
4.75	11.80	11.30	11.63	11.63	11.26	8.40
5	11.83	11.38	11.72	11.69	11.40	9.60
5.25	11.88	11.50	11.78	11.76	11.52	10.08
5.5	11.91	11.56	11.82	11.81	11.60	10.70
5.75	11.95	11.67	11.88	11.86	11.68	10.94
6	11.97	11.72	11.90	11.90	11.75	11.16

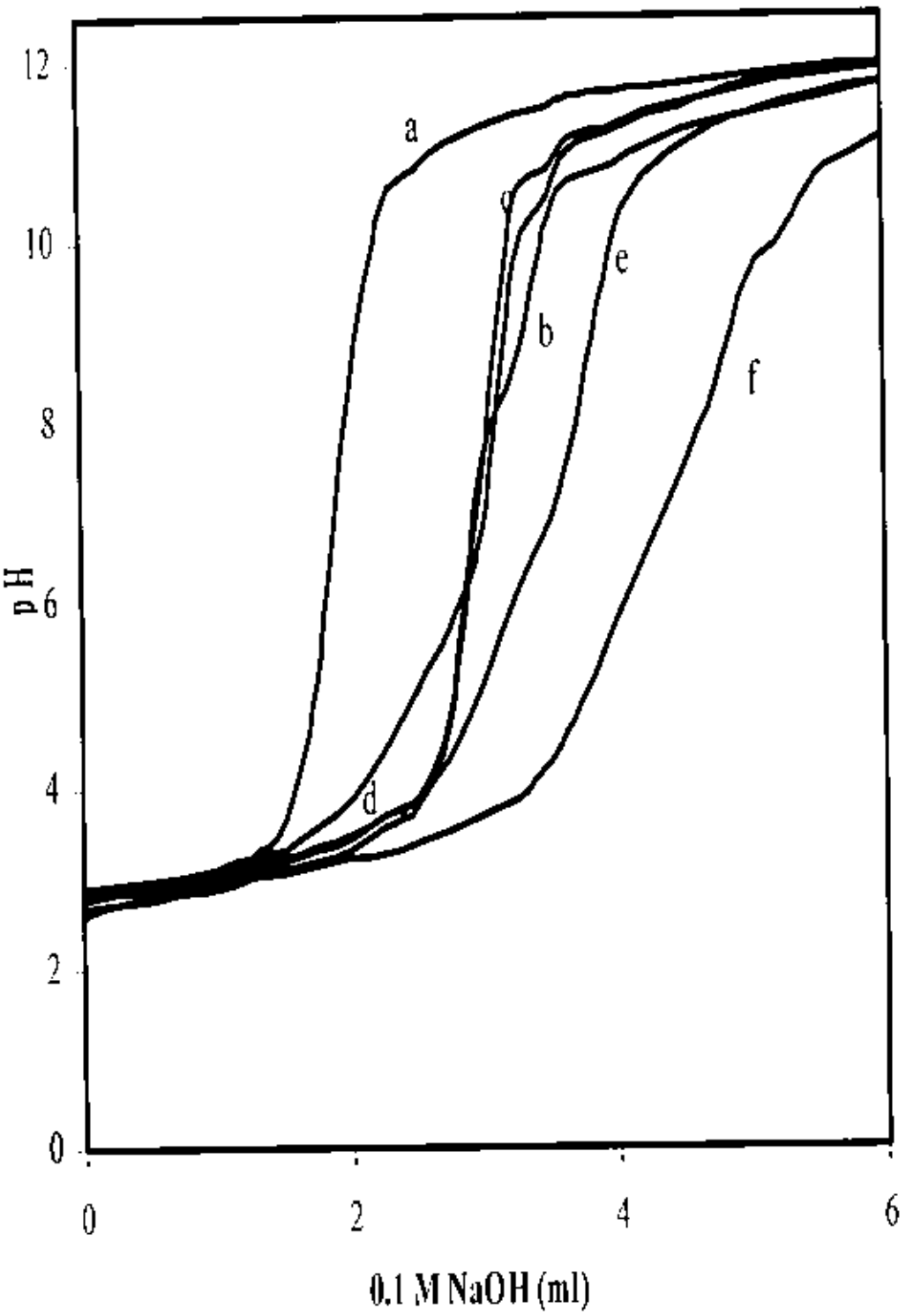
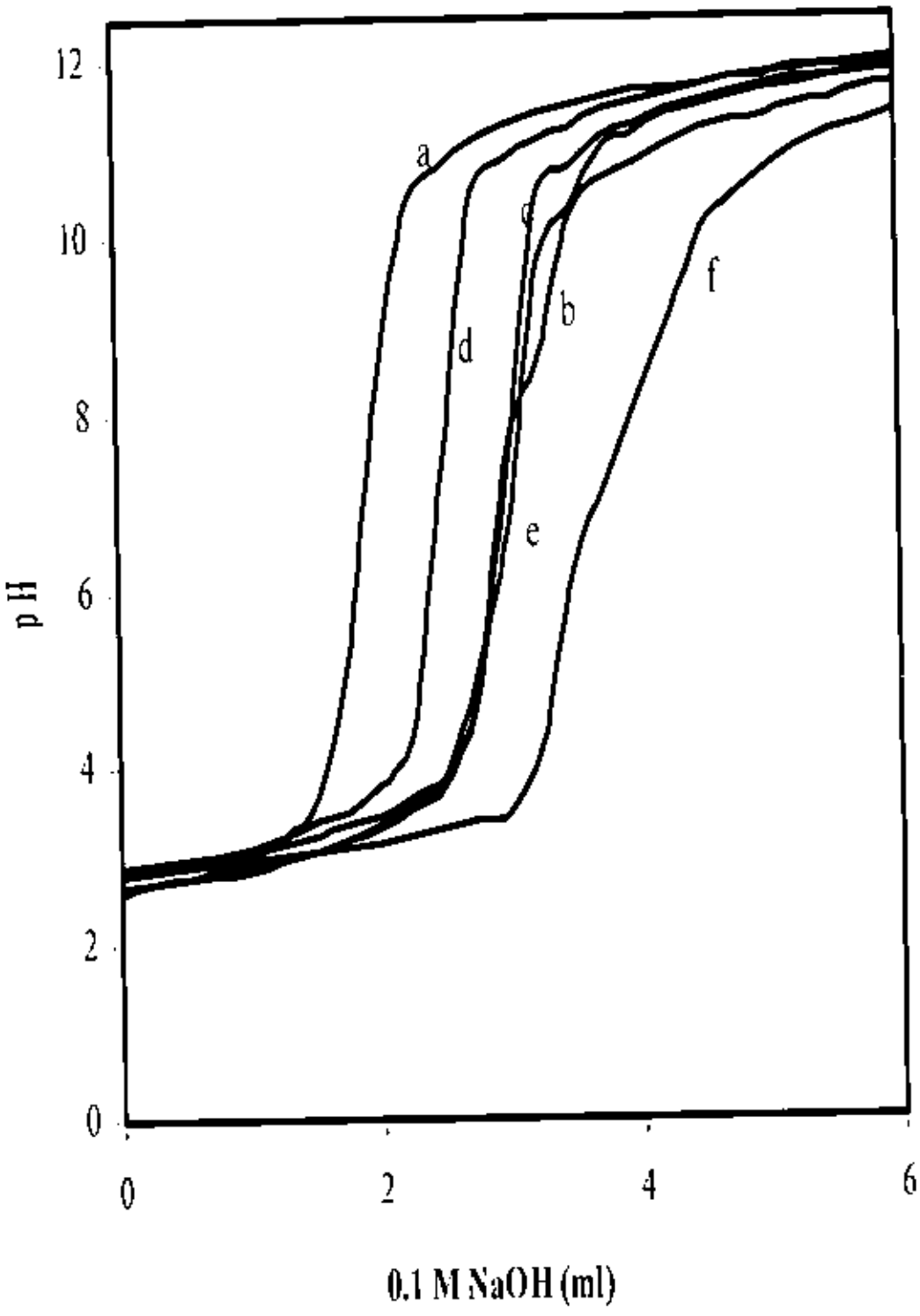


Fig.(40)Potentiometric titration curves for Pd(II)-IDA-phthalic acid system

Table(33): Potintiometric titration values of salicylic acid system with IDA in aqueous solution at 30 °C and $I = 0.5$ M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.80	2.62	2.78
0.25	2.71	2.91	2.72	2.87	2.69	2.83
0.5	2.77	2.96	2.76	2.93	2.75	2.87
0.75	2.88	3.02	2.83	3.01	2.80	2.91
1	3.02	3.07	2.89	3.10	2.86	2.96
1.25	3.23	3.16	2.99	3.23	2.98	3.01
1.5	3.65	3.23	3.08	3.39	3.08	3.05
1.75	5.13	3.35	3.17	3.51	3.20	3.12
2	8.30	3.46	3.32	3.82	3.35	3.16
2.25	10.39	3.67	3.54	4.32	3.59	3.24
2.5	10.81	3.91	3.81	7.49	3.88	3.33
2.75	11.11	4.77	4.72	10.53	5.04	3.40
3	11.27	7.59	7.44	10.89	6.67	3.51
3.25	11.41	8.65	10.47	11.09	9.75	4.23
3.5	11.49	10.24	10.80	11.25	10.30	6.22
3.75	11.59	10.68	11.13	11.43	11.03	7.22
4	11.65	10.84	11.29	11.54	11.18	8.18
4.25	11.69	11.05	11.43	11.61	11.41	9.09
4.5	11.73	11.25	11.53	11.71	11.51	10.11
4.75	11.80	11.30	11.63	11.79	11.60	10.44
5	11.83	11.38	11.72	11.81	11.67	10.77
5.25	11.88	11.50	11.78	11.91	11.73	11.00
5.5	11.91	11.56	11.82	11.95	11.79	11.19
5.75	11.95	11.67	11.88	11.99	11.84	11.29
6	11.97	11.72	11.90	12.01	11.89	11.41



Fig(41)Potentiometric titration curves for Pd(II)-IDA-salicylic acid system.

Table(34): Potintiometric titration values of succinic acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.79	2.75	2.81
0.25	2.71	2.91	2.72	2.88	2.83	2.84
0.5	2.77	2.96	2.76	2.93	2.91	2.86
0.75	2.88	3.02	2.83	3.04	3.01	2.91
1	3.02	3.07	2.89	3.14	3.07	2.94
1.25	3.23	3.16	2.99	3.30	3.24	2.99
1.5	3.65	3.23	3.08	3.50	3.38	3.03
1.75	5.13	3.35	3.17	3.88	3.70	3.10
2	8.30	3.46	3.32	4.33	3.99	3.15
2.25	10.39	3.67	3.54	4.93	4.32	3.26
2.5	10.81	3.91	3.81	5.43	4.65	3.38
2.75	11.11	4.77	4.72	6.10	5.09	3.52
3	11.27	7.59	7.44	6.76	5.41	3.68
3.25	11.41	8.65	10.47	10.04	6.08	4.03
3.5	11.49	10.24	10.8	10.67	7.06	4.34
3.75	11.59	10.68	11.13	11.03	9.59	4.77
4	11.65	10.84	11.29	11.19	10.39	5.24
4.25	11.69	11.05	11.43	11.35	10.84	6.00
4.45	11.73	11.25	11.53	11.49	11.09	6.83
4.62	11.80	11.30	11.63	11.57	11.33	7.45
4.92	11.83	11.38	11.72	11.65	11.41	8.46
5.25	11.88	11.50	11.78	11.71	11.51	9.23
5.5	11.91	11.56	11.82	11.76	11.56	10.07
5.75	11.95	11.67	11.88	11.82	11.66	10.56
6	11.97	11.72	11.90	11.86	11.71	10.69

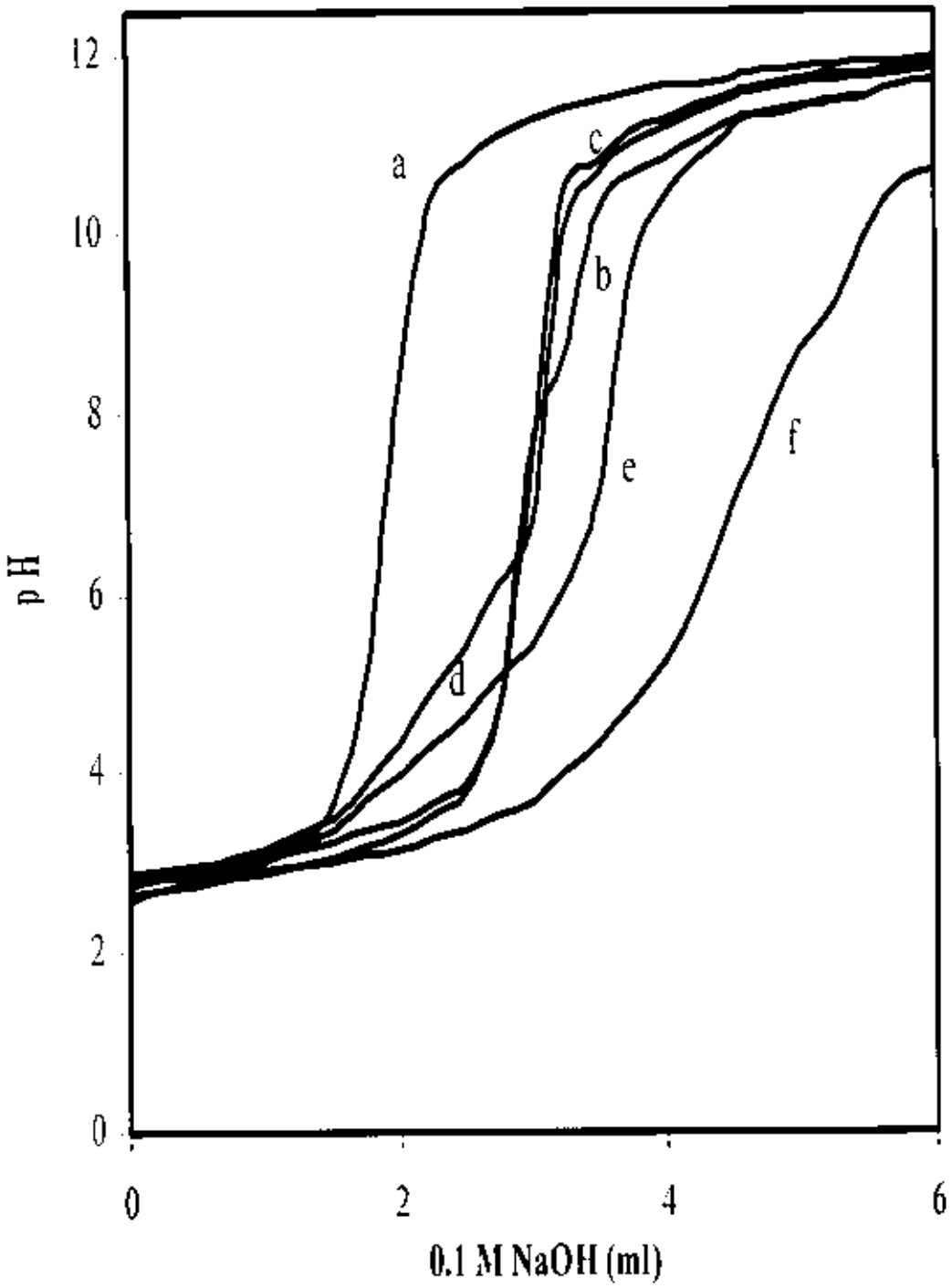


Fig.(42)Potentiometric titration curves for Pd(II)- IDA-succinic acid system.

Table(35): Potintiometric titration values of malonic acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.83	2.75	2.72
0.25	2.71	2.91	2.72	2.89	2.83	2.73
0.5	2.77	2.96	2.76	2.95	2.87	2.76
0.75	2.88	3.02	2.83	3.02	2.93	2.79
1	3.02	3.07	2.89	3.09	2.99	2.81
1.25	3.23	3.16	2.99	3.22	3.07	2.86
1.5	3.65	3.23	3.08	3.30	3.13	2.91
1.75	5.13	3.35	3.17	3.44	3.23	2.95
2	8.30	3.46	3.32	3.75	3.30	2.98
2.31	10.39	3.67	3.54	4.98	3.50	3.05
2.5	10.81	3.91	3.81	5.36	3.70	3.11
2.75	11.11	4.77	4.72	6.10	4.23	3.23
3	11.27	7.59	7.44	6.98	4.94	3.30
3.34	11.41	9.06	10.47	10.15	6.90	3.50
3.5	11.49	10.24	10.80	10.73	7.70	3.60
3.75	11.59	10.68	11.13	11.06	9.44	3.88
4	11.65	10.84	11.29	11.24	10.24	4.12
4.25	11.69	11.05	11.43	11.41	10.77	4.75
4.5	11.73	11.25	11.53	11.54	11.02	5.74
4.75	11.80	11.30	11.63	11.62	11.25	7.55
5	11.83	11.38	11.72	11.71	11.38	8.33
5.25	11.88	11.50	11.78	11.78	11.52	8.85
5.5	11.91	11.56	11.82	11.83	11.60	9.40
5.75	11.95	11.67	11.88	11.87	11.68	9.95
6	11.97	11.72	11.90	11.91	11.72	10.55

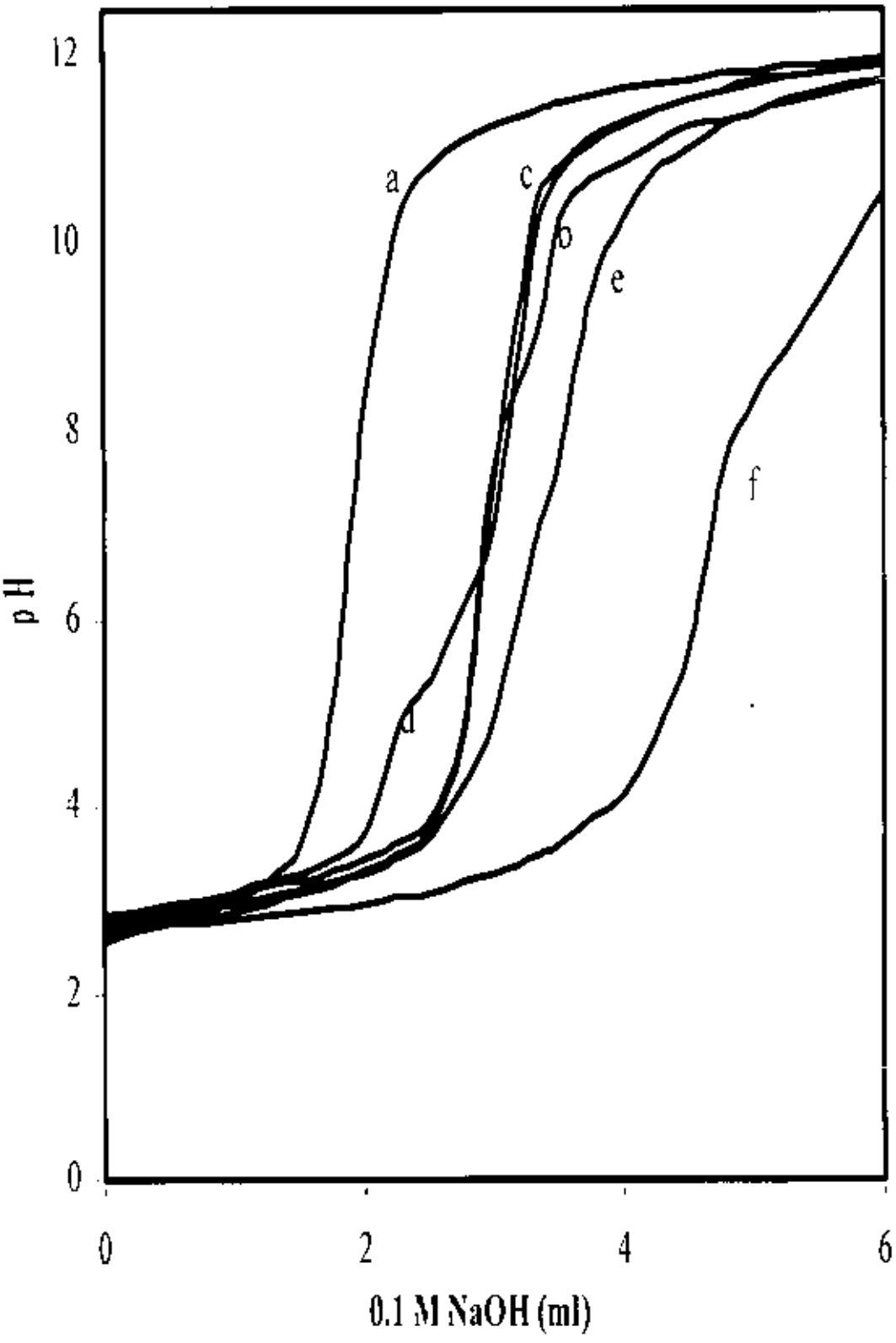


Fig.(43)Potentiometric titration curves for Pd(II)-IDA-malonic acid system.

Table(36): Potintiometric titration values of malic acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.84	2.79	2.74
0.25	2.71	2.91	2.72	2.90	2.84	2.78
0.5	2.77	2.96	2.76	2.96	2.89	2.82
0.75	2.88	3.02	2.83	3.04	2.96	2.86
1	3.02	3.07	2.89	3.13	3.01	2.90
1.25	3.23	3.16	2.99	3.26	3.14	2.95
1.5	3.65	3.23	3.08	3.42	3.24	2.99
1.75	5.13	3.35	3.17	3.65	3.36	3.07
2	8.30	3.46	3.32	3.84	3.48	3.14
2.25	10.39	3.67	3.54	4.23	3.66	3.22
2.5	10.81	3.91	3.81	4.74	3.87	3.30
2.75	11.11	4.77	4.72	5.39	4.14	3.43
3	11.27	7.59	7.44	6.20	4.56	3.56
3.22	11.41	8.98	10.47	9.60	6.01	3.68
3.36	11.49	10.24	10.80	10.60	6.80	3.82
3.75	11.59	10.68	11.13	10.99	8.96	4.40
4	11.65	10.84	11.29	11.17	9.82	4.77
4.25	11.69	11.05	11.43	11.36	10.76	5.41
4.5	11.73	11.25	11.53	11.48	10.99	6.38
4.75	11.80	11.30	11.63	11.58	11.23	7.25
5	11.83	11.38	11.72	11.64	11.33	8.50
5.25	11.88	11.50	11.78	11.74	11.46	9.78
5.5	11.91	11.56	11.82	11.77	11.54	10.20
5.75	11.95	11.67	11.88	11.81	11.63	10.68
6	11.97	11.72	11.90	11.86	11.66	10.87

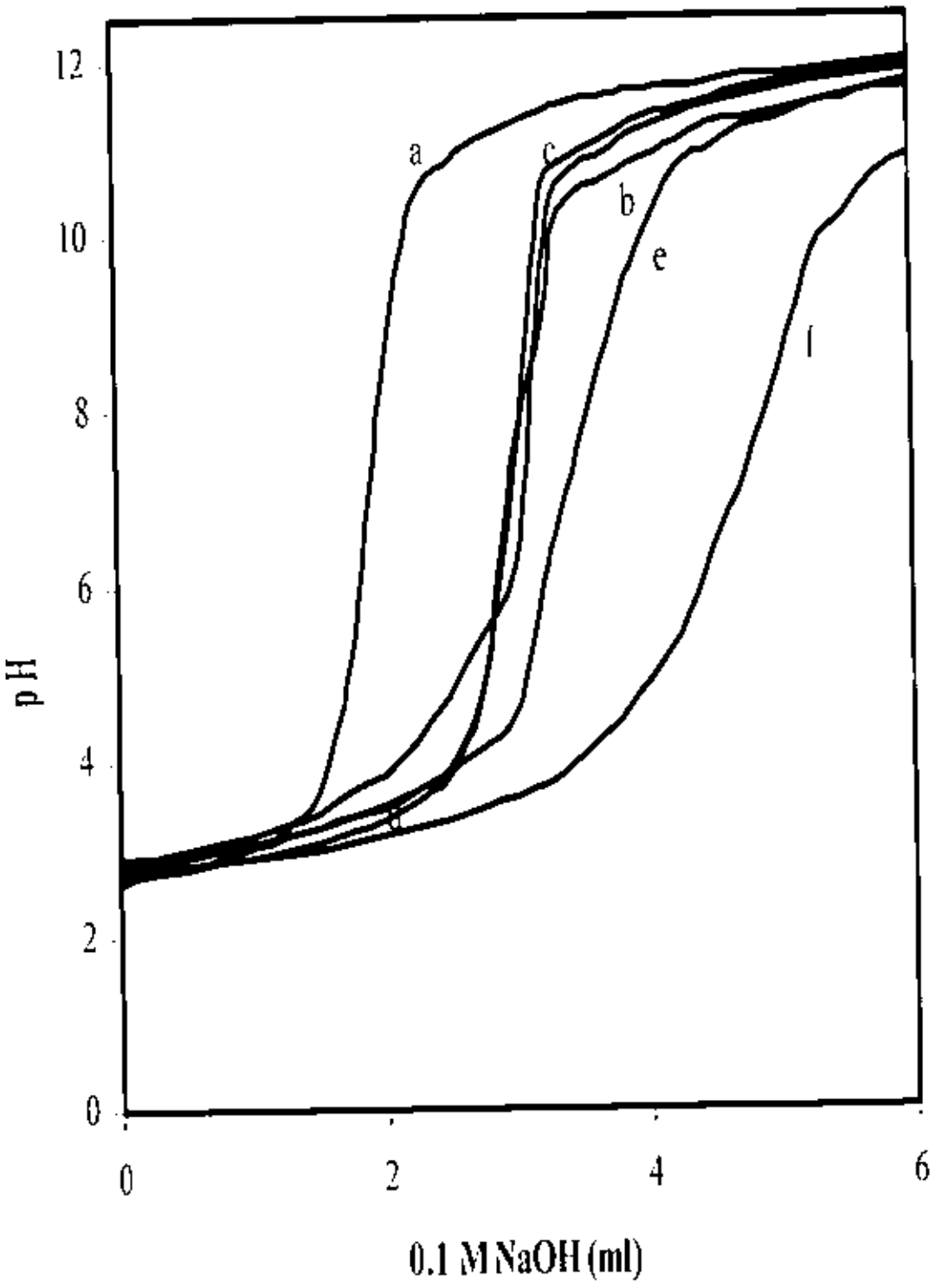


Fig.(44)Potentiometric titration curves for Pd(II)-IDA-malic acid system.

Table(37): Potintiometric titration values of oxalic acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	1.99	1.86	1.88
0.25	2.71	2.91	2.72	2.01	1.91	1.93
0.5	2.77	2.96	2.76	2.03	1.98	1.95
0.75	2.88	3.02	2.83	2.05	2.01	1.97
1	3.02	3.07	2.89	2.08	2.03	2.00
1.25	3.23	3.16	2.99	2.10	2.06	2.02
1.5	3.65	3.23	3.08	2.12	2.08	2.04
1.75	5.13	3.35	3.17	2.17	2.12	2.07
2	8.30	3.46	3.32	2.21	2.17	2.10
2.25	10.39	3.67	3.54	2.28	2.23	2.14
2.5	10.81	3.91	3.81	2.30	2.27	2.17
2.75	11.11	4.77	4.72	2.40	2.35	2.20
3	11.27	7.59	7.44	2.45	2.42	2.26
3.25	11.41	8.65	10.47	2.60	2.55	2.32
3.5	11.49	10.24	10.80	2.80	2.66	2.37
3.75	11.59	10.68	11.13	3.26	2.91	2.45
4	11.65	10.84	11.29	4.00	3.18	2.53
4.25	11.69	11.05	11.43	5.47	4.16	2.64
4.5	11.73	11.25	11.53	7.00	7.28	2.75
4.75	11.80	11.30	11.63	9.98	8.66	2.92
5	11.83	11.38	11.72	10.36	9.53	3.20
5.25	11.88	11.50	11.78	10.55	10.11	3.57
5.5	11.91	11.56	11.82	10.71	10.32	4.01
5.75	11.95	11.67	11.88	10.83	10.48	5.31
6	11.97	11.72	11.90	10.88	10.63	7.43
6.25	12.01	11.78	11.94	10.94	10.76	8.05
6.5	12.03	11.82	11.97	11.02	10.82	9.30
6.75	12.06	11.87	12.01	11.08	10.89	10.03
7	12.08	11.90	12.04	11.13	10.95	10.24
7.25	12.10	11.95	12.07	11.18	11.04	10.40
7.5	12.12	11.98	12.08	11.21	11.09	10.58
7.75	12.13	12.01	12.10	11.24	11.12	10.69
8	12.16	12.03	12.11	11.26	11.16	10.80

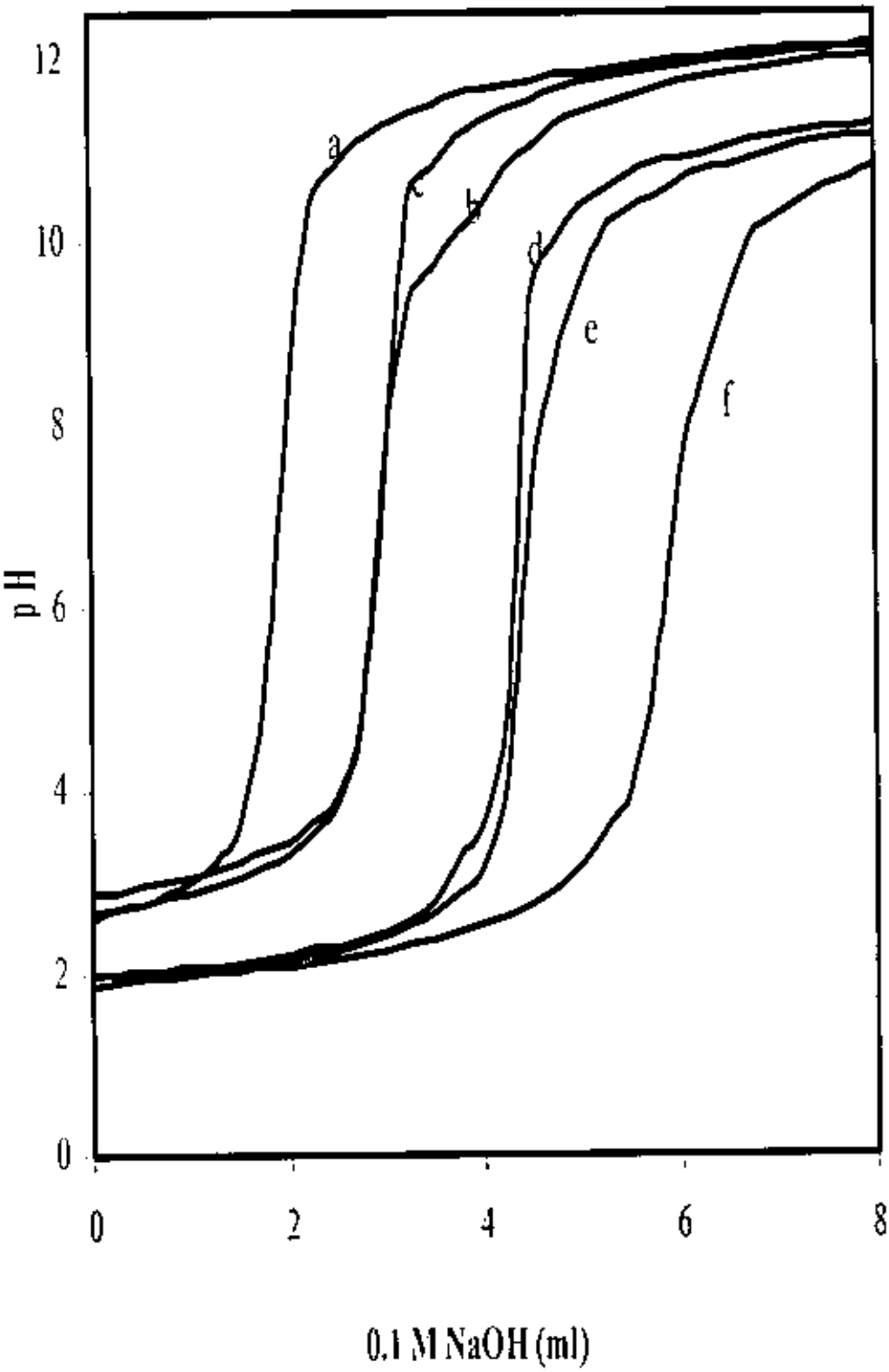


Fig.(45)Potentiometric titration curves for Pd(II)-IDA-oxalic acid system.

Table(38): Potintiometric titration values of tartaric acid system with IDA in aqueous solution at 30 °C and I = 0.5 M ($NaNO_3$).

ml	a	b	c	d	e	f
0	2.58	2.87	2.66	2.14	2.07	1.93
0.25	2.71	2.91	2.72	2.17	2.11	1.95
0.5	2.77	2.96	2.76	2.19	2.13	1.96
0.75	2.88	3.02	2.83	2.22	2.18	1.98
1	3.02	3.07	2.89	2.25	2.20	2.01
1.25	3.23	3.16	2.99	2.32	2.27	2.04
1.5	3.65	3.23	3.08	2.35	2.31	2.06
1.75	5.13	3.35	3.17	2.41	2.35	2.09
2	8.30	3.46	3.32	2.47	2.40	2.14
2.25	10.39	3.67	3.54	2.58	2.49	2.18
2.5	10.81	3.91	3.81	3.00	2.55	2.22
2.75	11.11	4.77	4.72	3.02	2.65	2.27
3	11.27	7.59	7.44	3.28	2.76	2.33
3.32	11.41	8.65	10.47	3.45	2.89	2.42
3.5	11.49	10.24	10.80	3.55	3.01	2.48
3.75	11.59	10.68	11.13	3.70	3.20	2.56
3.97	11.65	10.84	11.29	4.50	3.38	2.65
4.25	11.69	11.05	11.43	5.42	3.66	2.81
4.5	11.73	11.25	11.53	6.80	3.98	2.92
4.75	11.80	11.30	11.63	9.83	4.69	3.20
5	11.83	11.38	11.72	10.20	6.05	3.29
5.25	11.88	11.50	11.78	10.43	7.13	3.65
5.5	11.91	11.56	11.82	10.57	9.23	3.82
5.75	11.95	11.67	11.88	10.71	10.43	4.73
6	11.97	11.72	11.90	10.79	10.56	6.32
6.25	12.01	11.78	11.94	10.89	10.70	6.95
6.5	12.03	11.82	11.97	10.94	10.77	9.53
6.75	12.06	11.87	12.01	11.01	10.89	9.98
7	12.08	11.90	12.04	11.05	10.95	10.21
7.25	12.10	11.95	12.07	11.09	11.01	10.45
7.5	12.12	11.98	12.08	11.13	11.07	10.56
7.75	12.13	12.01	12.10	11.17	11.11	10.69
8	12.16	12.03	12.11	11.19	11.14	10.77

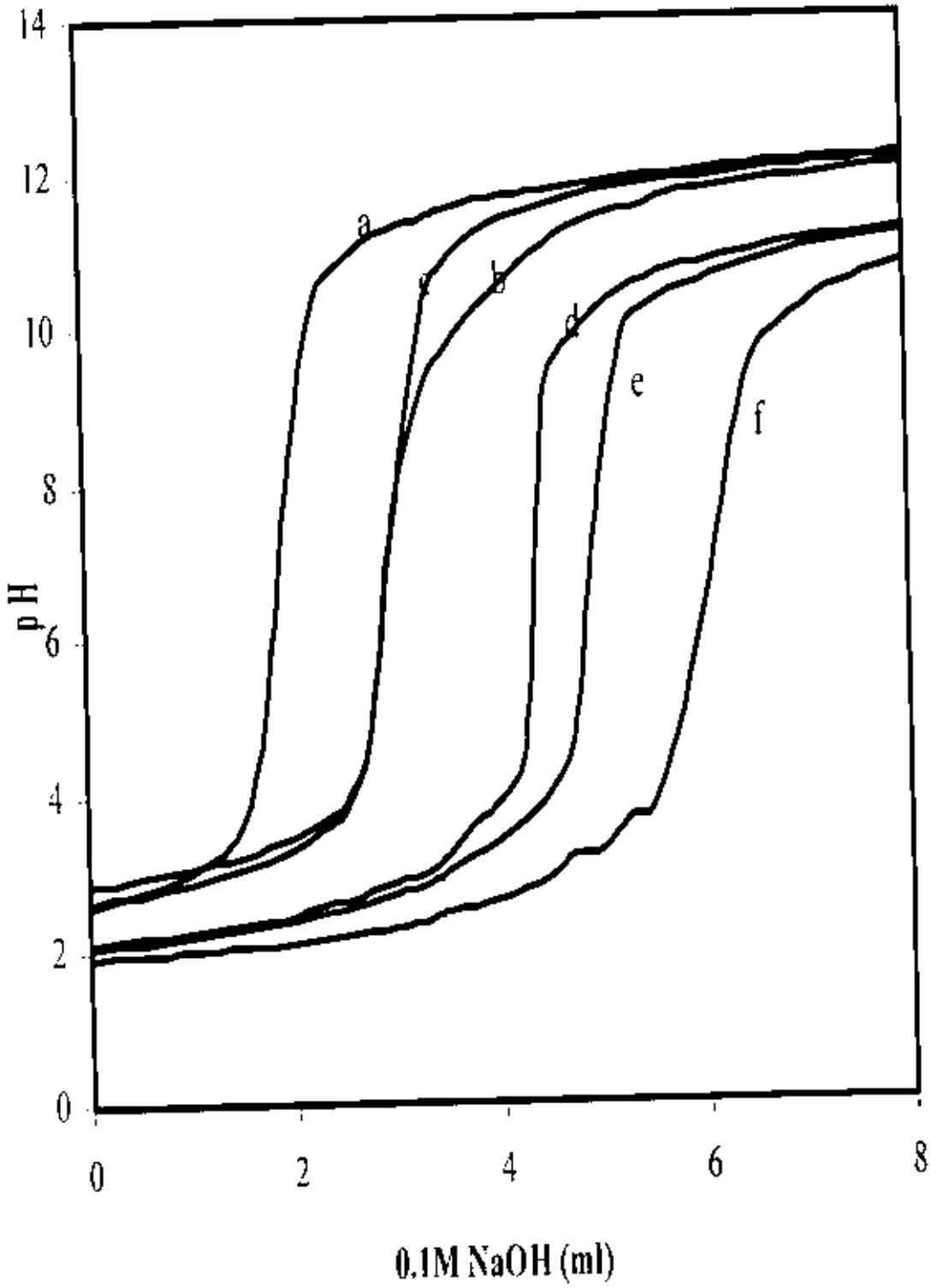


Fig.(46)Potentiometric titration curves for Pd(II)-IDA-tartaric acid system.

Table(39): Conductometric titration values for some ternary complexes with IDA in aqueous solution at 30°C and I = 0.5 M (NaNO3).

	glycine	alanine	aspartic	histadine	succinic	phthalic
ml	C	C	C	C	C	C
0	7.34	8.06	10.89	12.86	12.92	13.66
0.25	7.14	7.40	10.06	12.28	12.08	13.05
0.5	6.76	6.90	9.47	11.61	11.59	12.61
0.75	6.24	6.35	8.84	10.95	11.01	11.93
1	5.93	5.91	8.15	10.51	10.54	11.38
1.25	5.63	5.28	7.78	10.05	9.80	10.90
1.5	5.25	4.92	7.31	9.52	9.36	10.46
1.75	4.86	4.74	6.83	9.11	8.83	9.92
2	4.56	4.21	6.66	8.67	8.48	9.38
2.25	4.35	3.89	5.91	8.14	7.65	8.85
2.5	4.08	3.78	5.62	7.85	7.31	8.42
2.75	3.80	3.69	5.18	7.32	6.61	7.89
3	3.73	3.65	5.00	7.02	6.32	7.47
3.25	3.67	3.83	4.78	6.64	5.66	6.96
3.5	3.57	4.01	4.66	6.37	5.41	7.00
3.75	3.70	4.19	4.69	6.04	5.01	6.13
4	3.89	4.36	4.71	5.81	4.73	5.86
4.25	4.19	4.64	4.81	5.58	4.65	5.52
4.5	4.51	4.93	4.86	5.43	4.67	5.29
4.75	4.93	5.30	5.13	5.38	4.78	5.13
5	5.23	5.63	5.24	5.45	4.96	5.16
5.25	5.68	6.04	5.66	5.73	5.16	5.37
5.5	6.00	6.46	5.77	5.92	5.33	5.59
5.75	6.51	6.83	6.38	6.38	5.61	5.95

6	6.87	7.22	6.87	6.62	5.76	6.08
6.25	7.17	7.71	7.04	6.93	5.94	6.34
6.5	7.63	8.06	7.68	7.25	6.17	6.73
6.75	8.09	8.56	8.03	7.72	6.39	6.90
7	8.30	8.93	8.45	7.98	6.63	6.98
7.25	8.84	9.37	8.70	8.43	6.89	7.30
7.5	9.26	9.78	9.40	8.85	7.19	7.63
7.75	9.69	10.32	9.64	9.24	7.49	7.90
8	10.08	10.63	10.21	9.79	8.15	8.36
8.25	10.67	11.19	10.35	9.98	8.36	8.95
8.5	10.89	11.44	11.17	10.51	8.69	9.27
8.75	11.36	11.88	11.57	10.86	9.26	9.82
9	11.72	12.32	11.94	11.22	9.60	10.29
9.25	12.01	12.64	12.47	11.65	9.97	10.85
9.5	12.46	13.11	12.88	12.13	10.44	11.12
9.75	12.8	13.49	13.23	12.61	10.78	11.75
10	13.24	13.80	13.57	12.88	11.38	12.21

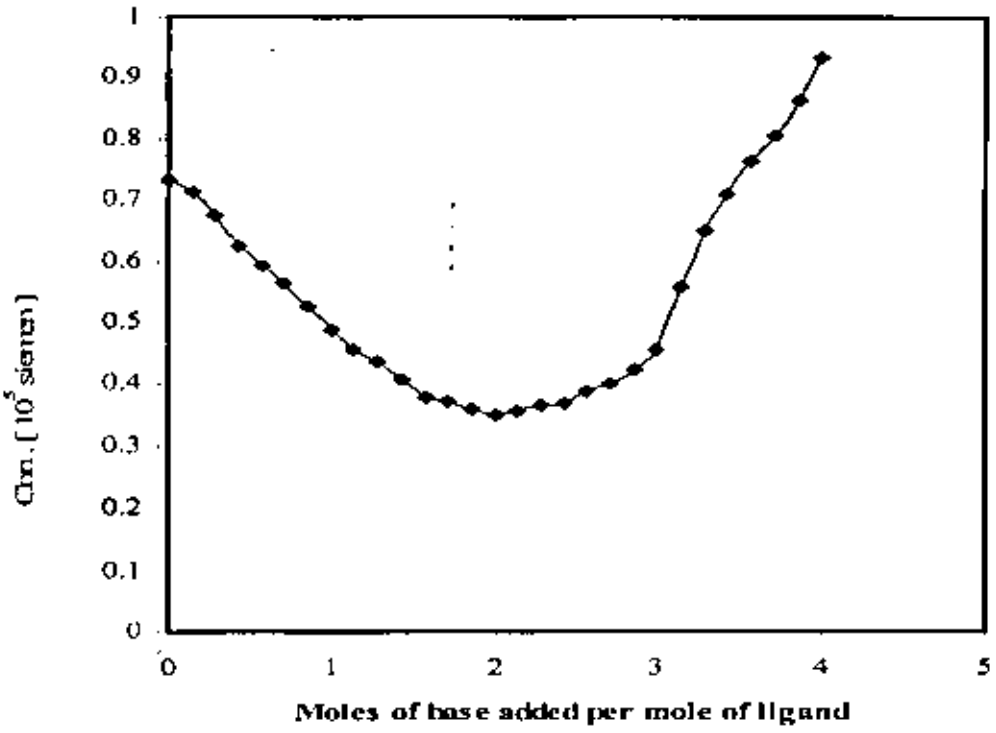


Fig.(47)Conductometric titration curves for Pd(II)-IDA-glycine system.

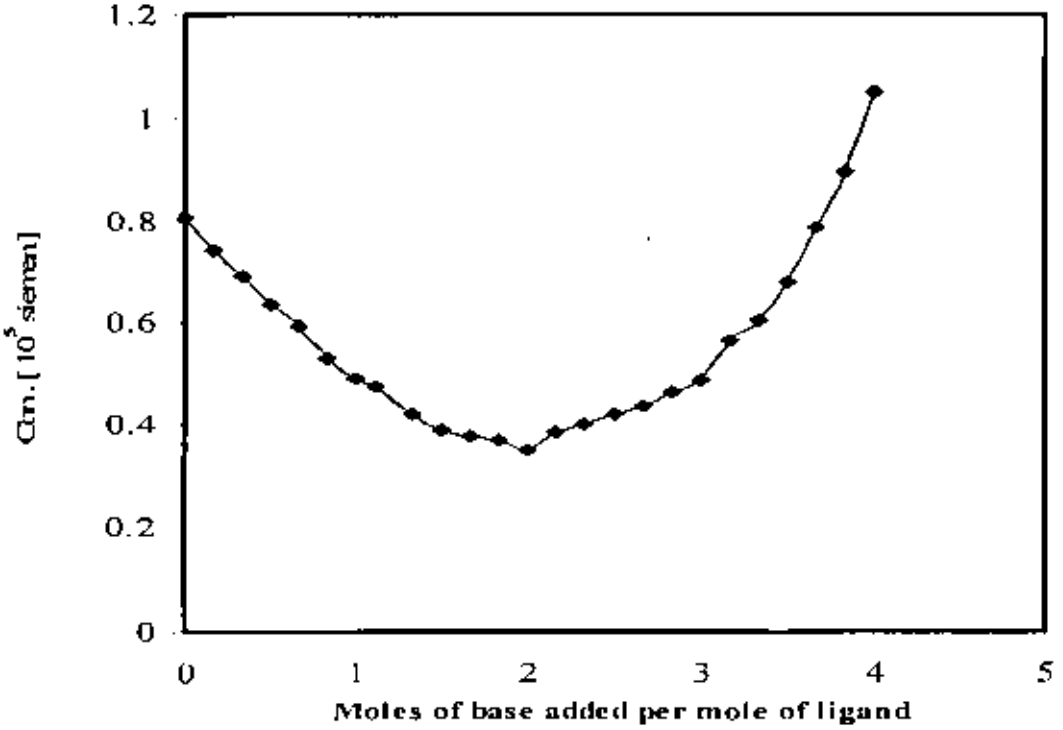


Fig.(48)Conductometric titration curves for Pd(II)-IDA-alanine system.

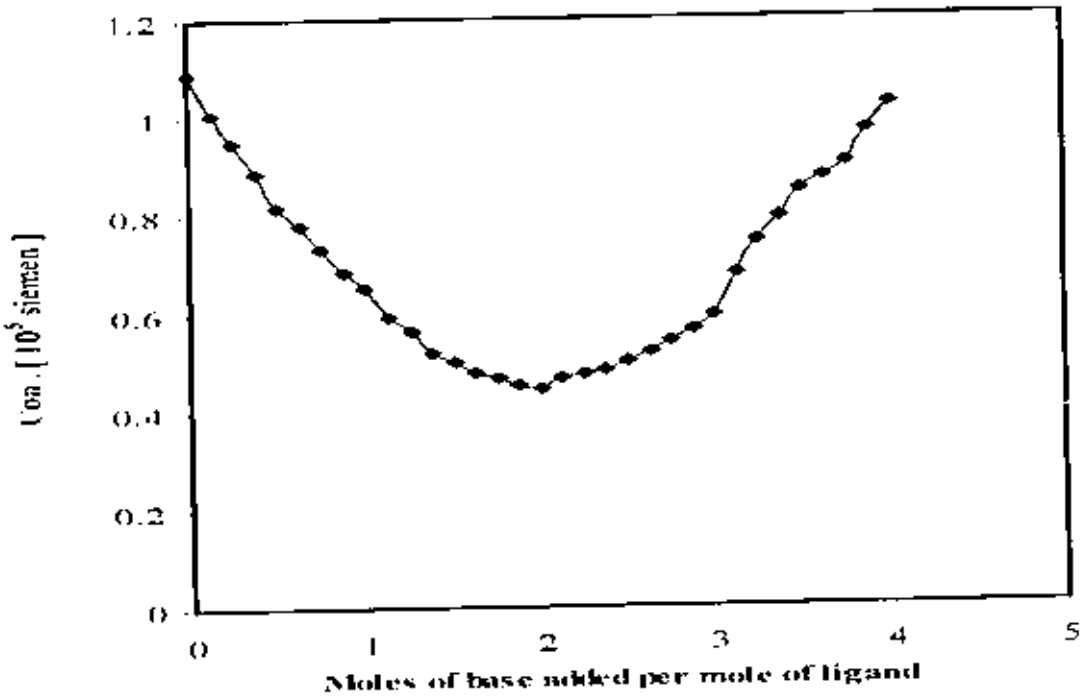


Fig.(49)Conductometric titration curves for Pd(II)-IDA-aspartic acid system.

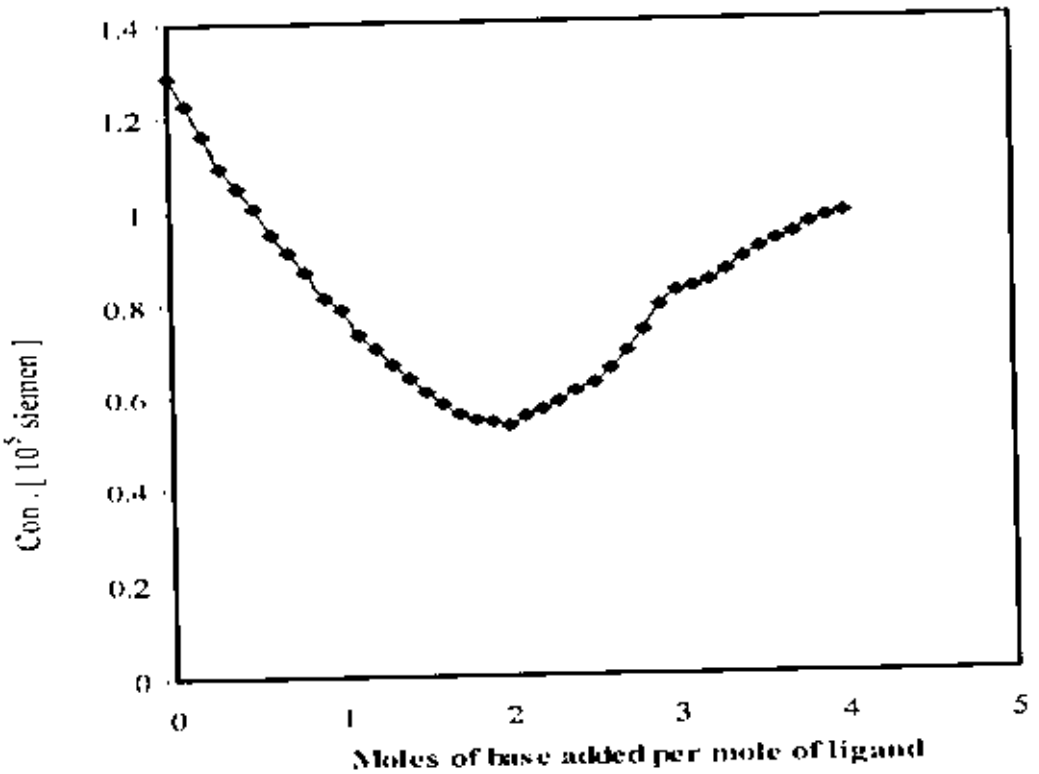


Fig.(50)Conductometric titration curves for Pd(II)-IDA-histadine system.

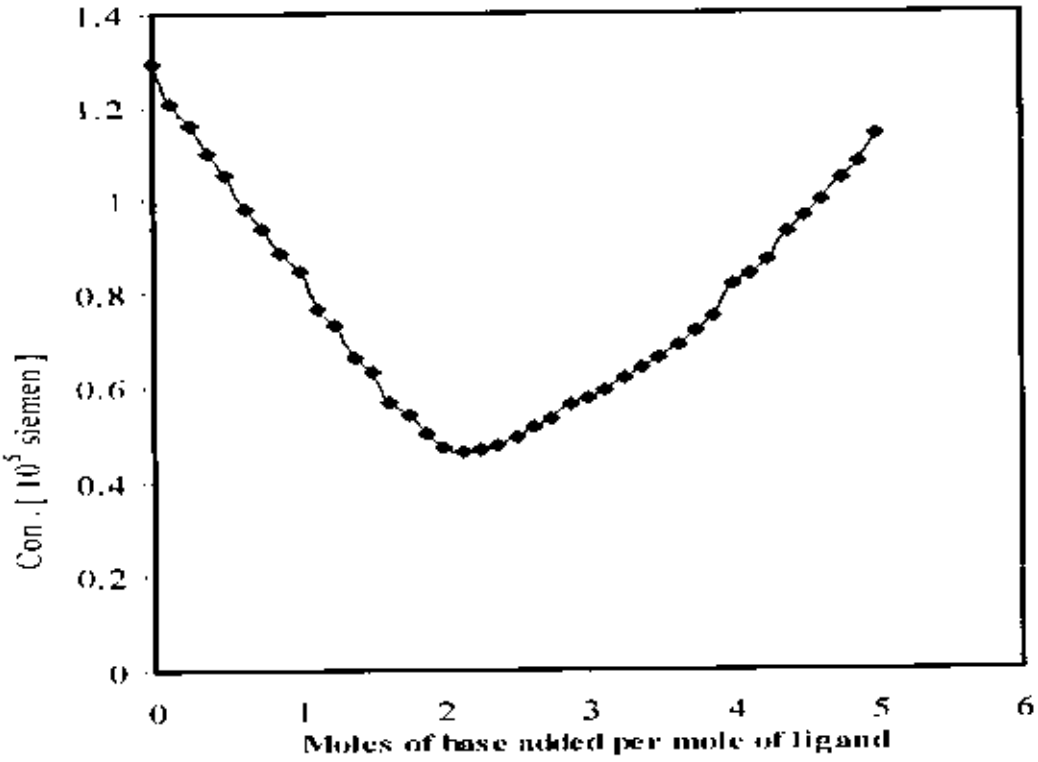


Fig.(51)Conductometric titration curves for Pd(II)-IDA-succinic system.

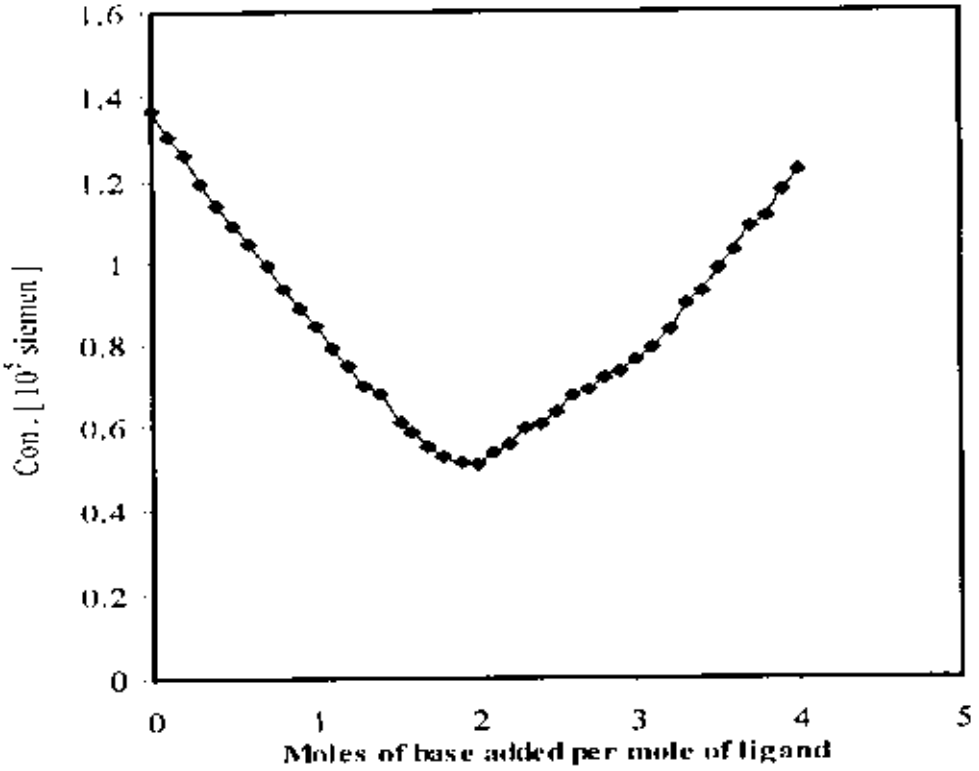


Fig.(52)Conductometric titration curves for Pd(II)-IDA-phthalic acid system.

Table (40): Stability constants and formation constant of IDA and its binary complex in aqueous solution at 30 °C and I = 0.1 M.

Ligand	pK_{a1}	pK_{a2}	pK_{a3}	$\log K^{M}_{ML}$
IDA	1.80*	2.59	9.44	6.08

*From ref. (81)

Table(41): Formation constant of the ternary complexes of pd(II) involving IDA as a primary ligand and amino acid or aliphatic and aromatic acid as a secondary ligand at 30 °C and I = 0.1 M.

Ligands	$\log K^{MN}_{MXL}$	$\log \beta^{M}_{MXL}$	$\Delta \log K$
Glycine	5.24 ± 0.04	11.32	-0.69
Alanine	5.17 ± 0.07	11.25	-0.25
Valine	6.31 ± 0.05	12.39	-0.64
Phenylalanine	5.20 ± 0.05	11.28	-0.04
Tryptophan	5.96 ± 0.06	12.04	-0.36
Methionine	5.72 ± 0.05	11.80	-0.53
Leucine	5.92 ± 0.06	12.00	0.08
Aspartic acid	5.64 ± 0.05	11.72	0.07
Glutamic acid	6.23 ± 0.06	12.31	0.09
Histadiene	6.31 ± 0.05	12.39	-0.16
Phathalic acid	6.62 ± 0.06	12.70	0.68
Salicylic acid	6.54 ± 0.04	12.62	0.15
Succinic acid	6.42 ± 0.04	12.50	0.09
Malonic acid	6.03 ± 0.06	12.11	0.06
Malic acid	5.10 ± 0.05	11.18	0.03
Oxalic acid	5.80 ± 0.03	11.88	0.03
Tartaric acid	5.09 ± 0.05	11.17	0.02

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ARABIC SUMMARY

ملخـــص الـرسـالة

تتضمن الرسالة دراسة اتزان المتراكبات الثنائية و الثلاثية للعناصر الثنائية المحتوية على حامض ثنائي البيكولنيك و حامض أمينو ثنائي الاسيتات مع بعض الليجندات ذات الاهمية البيولوجية .

وتتكون الرسالة من ثلاثة فصول :-

الفصل الاول:

ويتكون من جزئين :

الجزء الاول:

وهو عبارة عن مقدمة الرسالة ويتضمن الطبيعة والخواص والاهمية البيولوجية لليجندات موضوع الدراسة ايضا يشتمل على الاهمية البيولوجية للبلاديوم الثنائي و المتراكبات الثلاثية .

الجزء الثاني:

ويشتمل ملخصا للدراسات السابقة التي اجريت من قبل على بعض المتراكبات الثنائية و الثلاثية للبلاديوم الثنائي المحتوية على ليجندات ذات اهمية بيولوجية ايضا يحتوي هذا الجزء على الدراسات الجهدية لتكوين متراكبات لبعض الليجندات مثل حامض البيكولينك و حامض ثنائي البيكولينك وحامض أمينو ثنائي الاسيتات مع بعض العناصر الثنائية.

الفصل الثاني:

يتضمن هذا الفصل الجزء التجريبي الخاص بالرسالة ويشتمل على طرق تحضير المواد و المحاليل المستخدمة في الدراسة، طرق اجراء القياسات المطلوبة، اجهزة القياس المختلفة، الظروف المعملية الخاصة بتكوين المتراكبات مع شرح مبسط لطريقة حساب ثوابت التفكك لليجندات المستخدمة و ثوابت الاستقرار للمتراكبات الثنائية والثلاثية .

الفصل الثالث:

ويشتمل على النتائج التي تم الحصول عليها بالاضافة الى شرح و تفسير هذه النتائج ويمكن ذكر ما يتضمنه هذا الفصل على النحو التالي:

الجزء الاول:

دراسة البلاديوم الثنائي ، حامض البيكولونيك ، الاحماض الامينية، الاحماض الاليفاتية والاروماتية كنظام ثلاثي.

تم دراسة اتزانات الحامضية و القاعدية لليجندات المتضمنة في هذا النظام(حامض البيكولينك، الاحماض الامينية ، الاحماض الاليفاتية و الاروماتية) عند درجة حرارة 30م° وقوة ايونية 0.5 مولر, تم ايضا دراسة المتراكبات الثنائية لعنصر البلاديوم الثنائي مع كل من حامض البيكولينك ، الاحماض الامينية ، والاحماض الاليفاتية والاروماتية.

تم دراسة المتراكبات الثلاثية لهذه الليجندات على النحو التالي:

حامض البيكولينك كليجند أولي، الاحماض الامينية، الاليفاتية و الاروماتية كليجند ثانوي عند درجة حرارة 30م° وقوة ايونية 0.5 مولر.

الجزء الثاني:

دراسة المتراكبات الثنائية والثلاثية للبلاديوم الثنائي مع امينو ثنائي حمض الاسيتات مع بعض الاحماض الامينية، الاليفاتية والاروماتية.

اولا تم تعيين ثابت التفكك الهيدروجيني للامينو ثنائي حمض الخليك ، وكذلك حساب ثابت التكوين للمتراكبات الثنائية و الثلاثية للامينو ثنائي حامض الخليك كمرتبط اولي و الاحماض الامينية، الاليفاتية والاروماتية كمرتبط ثانوي عند درجة حرارة 30م° وقوة ايونية 0.5 مولر.

وقد وجد ان استقرارية المتراكبات الثلاثية تزداد على هذا النحو:

الاحماض الاروماتية > الاحماض الاليفاتية > الاحماض الامينية.

ايضا تم دراسة التوصيلية للمتراكبات الثلاثية للبلاديوم الثنائي .

الملخص باللغة العربية

الاهـــــــــداء

الي عائلتي,

.....اساتذتي,

واصدقائي.

والي كل من يهمه امري خالصا لوجهه تعالي .....

بسم الله الرحمن الرحيم

(يرفع الله الذين أمنوا منكم والذين اوتوا العلم
درجات والله بما تعملون خبير)

صدق الله العظيم

الاية(11) من سورة المجادلة

التاريخ / 12-5-2008
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كلية العلوم

قسم الكيمياء

عنوان البحث

دراسات اتزان التراكبات الثنائية و الثلاثية للبلاديوم الثنائي المحتوية على حامض ثنائي البيكلونيك، حامض أمينو ثنائي الأسيتات مع بعض الليجندات ذات الأهمية البيولوجية

مقدمة من الطالبة
هنية نجام سالم

* * لجنة المناقشة :

1 – د.حسن عمرون عوين ..... (مشرفاً)

2 – أ.د.إسماعيل صالح ابشينة ..... (ممتحناً خارجياً)

3 – د.محمد علاء محمد فتحي ..... (ممتحناً داخلياً)

يعتمد
د.أحمد فرج الشريف
أمين اللجنة الشعبية لكلية العلوم