

A Chemometric Speciation Study of Binary Complexes of L-Histidine and L-Glutamic Acid with Pb (II), Cd (II) and Hg (II) In Organic Media- Water Mixture

Meti Mengistu, Rajalakshmanan Eswaramoorthy and Hadgu Hailekiros Belay*

Department of Applied Chemistry, Adama Science and Technology University, Adama, Oromia, Ethiopia
Corresponding Author: Meti Mengistu

Abstract: Chemical speciation of Pb (II), Cd(II) and Hg(II) complexes of L-Histidine and L-Glutamic acid in 0.0-50 % v/v Dimethylformamide-water mixtures maintaining an ionic strength of 0.16mol dm^{-3} at 310 K has been studied pH metrically. The present investigation the dominant species detected L-Histidine with metal were ML_2H_4 , ML_2H_3 , ML_2H_2 , ML_2H and ML_2 for Pb(II) and Cd(II) and Hg(II) forms ML_2H_4 , ML_2H_3 , ML_2 and ML . for L-Glutamic acid MX_2H_4 , MX_2H_3 , MX_2H_2 , MX and MX_2 for Pb(II), Cd(II) and Hg(II) in DMF-water mixtures. Models containing different numbers of species were refined by using the computer program MINIQUAD75. Selection of the best-fit chemical models were arrived at based on statistical parameters. The appropriateness of the experimental conditions was verified by introducing errors deliberately. The trend in variation of stability constant of the complexes with dielectric constant of the medium was attributed for the formation and possible structures of the complex species presented. Distributions of species, formation equilibria and effect of influential parameters on the stability constants have been presented. Possible structures of the various species present in solution are also indicated based on the analysis of the pH metric data.

Key Words: Complex equilibria, Chemical speciation, L-Histidine, L-Glutamic acid and DMF

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I. Introduction

Lead (Pb) is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Lead and other heavy metals create reactive radicals, which damage cell structures including DNA and membranes. Lead also interferes with DNA transcription, enzymes that help in the synthesis of vitamin D, and enzymes that maintain the integrity of the cell membrane [1]. Lead affects every organ of the body, specially the bones and teeth, the kidneys, and the nervous, cardiovascular, immune and reproductive systems [2]. Lead, even in Pico molar concentration, can replace calcium, thereby affecting key neurotransmitters like protein kinase C, which regulates long-term neural excitation and memory storage.

Cadmium (Cd) is one of the most toxic metal ions of our environment and is found in air, food and water. Cd ions are absorbed by most tissues of the body and become concentrated mainly in liver and kidney and it has a long biological half-life of 11 to 20 years in humans [3]. On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, brain, lung, heart, fragile bones and lung damage [4]. Cadmium-induced oxidative damage has been demonstrated by the increased lipid peroxidation and inhibition of enzymes required to prevent such oxidative damage.

Mercury (Hg) has no known essential functions to the body but elemental mercury and its metabolites have biochemical damage to tissues and genes through diverse mechanisms, such as interrupting intracellular calcium homeostasis, disrupting membrane potential, denaturing and altering protein synthesis, inhibiting enzymes and interrupting excitatory amino acid pathways in the central nervous system [5]. Mitochondrial damage, lipid peroxidation, microtubule destruction, and the neurotoxic accumulation of serotonin, aspartate, and glutamate are all mechanisms of methyl mercury neurotoxicity [6].

Chemical species is specific form of an element defined as to isotopic composition, electronic or oxidation state, or complex or molecular structure. Speciation studies of toxic metal ion complexes are useful in order to understand the role played by the active site cavities in biological molecules and the bonding behavior of their residues with metal ions [7]. To reduce the toxicity and to figure out the complete mechanism of hepatocellular

damage induced by toxic metals in order to set up proper therapeutics approaches for chronic and acute metal-protein detoxification speciation study have the a key role.

Most of the speciation studies are performed in aqueous medium and other solvent under the conditions comparable to those existing in the biological systems. Hence, Dimethylformamide-water mixtures are chosen to study the acido-basic and complexation equilibria to mimic the physiological conditions where the concept of equivalent solution dielectric constant for protein cavities is applicable

N, N-Dimethylformamide (DMF) used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides. So far, no systematic report has appeared on studies speciation of L-Histidine (H) and L-Glutamic acid (E) with toxic heavy metal in DMF-water mixtures of various concentrations. Hence, stability constants and chemical speciation studies of H and E with some toxic metals like Pb, Cd and Hg in DMF-water mixtures are reported in this paper.

II. Materials and Methods

Chemicals and Standard Solution

Chemicals

All the chemicals used in this experiment were of analytical reagent grade purity. Triple distilled deionized water was used for the preparation of all the solutions. Solutions of 0.1 mol dm⁻³ of Pb(II), Cd(II), Hg(II) nitrates (E-Merck, Germany) were prepared maintaining 0.05 mol dm⁻³ nitric acid to suppress the hydrolysis of metal salts. A solution (0.05 mol dm⁻³) of L-Histidine and L-Glutamic acid (Kerala, India) was prepared by maintaining a 0.05 mol dm⁻³ nitric acid concentration to increase its solubility. Dimethylformamide (Qualigens, India) was used as received. Solutions of 0.2 mol dm⁻³ nitric acid and 0.4 mol dm⁻³ sodium hydroxide (Merck, India) were prepared. A solution of 2.0 mol dm⁻³ sodium nitrate (Merck, India) was prepared to maintain the ionic strength in the titrand. All the solutions were standardized by the usual oxalic acid and potassium hydrogen phthalate solutions, while the normality of nitric acid was determined by using the standardized sodium hydroxide and the primary borax solutions [8]. The concentration of the metal ions were determined complexometrically by titrating against a standard solution of EDTA using Xylenol orange indicator and hexamine powder as buffer to maintain the pH at 5-6 [9]. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to one-way analysis of variance (ANOVA) by using the computer program COSWT [10]. The acid-base titrations were analyzed by using the Gran plot method [11].

Apparatus

The titrimetric data were obtained with a calibrated Elico (Ad8000, India) pH meter (readability -2.00-16.00) which can monitor changes in the H⁺ ion activity. The electrode of the cell was calibrated with 0.05 mol dm⁻³ potassium hydrogen phthalate solution in the acidic region and with 0.01 mol dm⁻³ borax solution in the alkaline region to measure the response in the pH range. The glass electrode was equilibrated in a well-stirred DMF-water mixture containing an inert electrolyte. Mechanical stirring of the solution was carried out by means of a magnetic stirrer. The effects of variations in the asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of the glass electrode were accounted for in the form of correction factors (log F) [12].

Alkalimetric Titrations

Alkalimetric titrations were carried out in media containing varying compositions of DMF (0-50% v/v) maintaining an ionic strength of 0.16 mol dm⁻³ with sodium Nitrate at 310K. In each titration, the titrand contained approximately 1 mmol of Nitric acid. While the concentration of ligand was of the order of 0.25-0.50 mmol in different experiments Solutions containing metal ions and ligands (metal to ligand ratios being in the range of 1:2.50, 1:3.75 and 1:5.0 for Pb (II), Cd (II) and Hg (II)) were titrated with 0.4 mol dm⁻³ sodium hydroxide. In these entire titrations, metal ion was the last component added to the titrand.

Modeling Strategy

The computer program SCPHD [13] was used to calculate the correction factor. The binary stability constants were calculated from with the pH-metric titration data using the computer program MINQUAD75 [14], which exploit the advantage of a constrained least-squares method in the initial refinement and reliable convergence of the Marquardt algorithm. During the refinement of the binary systems, the correction factor and the protonation constants of H and E were fixed.

III. Results and Discussion

Typical alkalimetric titration curves are given in Figure 1 from which the stability constants of binary metal-ligand complexes were determined.

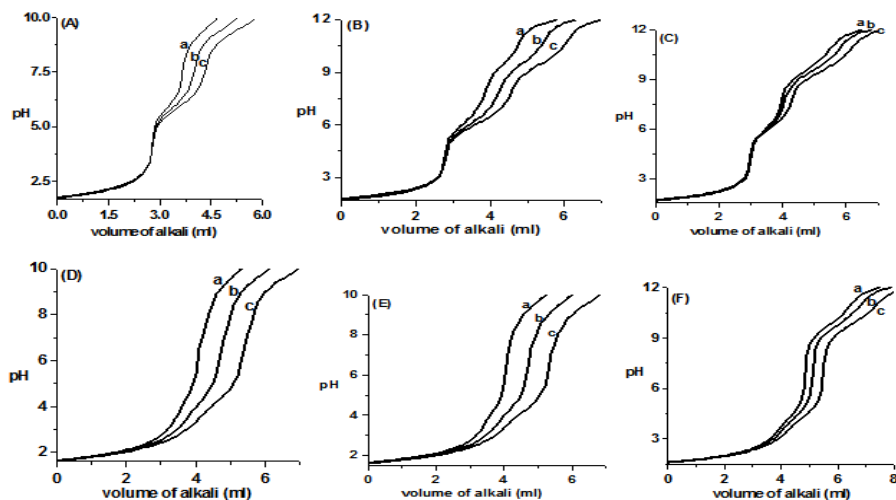


Figure 1: Alkalimetric titration curves for H complexes and E in 20% (v/v) DMF-water mixture (A) Pb(II), (B) Cd(II), (C) Hg(II) complex for H and (D) Pb(II), (E) Cd(II), (F) Hg(II) complexes for E; amount of the ligand (a) 0.250 (b) 0.375 (c) 0.500 mmol.

These curves indicate that the precipitation of the H complexes of Pb (II) in DMF-water mixtures takes place in the pH range 9.0-9.5 and Pb(II)-E system in 6.9-7.2. It suggests that Pb (II)-E complexes are hydrolyzed at lower pH when compared to Pb (II)-H system. Cd (II)-H complexes in DMF- water mixtures was observed in the pH above 11.5. Cd (II)-E system in DMF-water mixtures in the pH range 10.0-11.5. In the case of Hg(II) a different situation was observed in DMF- water mixtures for both the ligands (H and E); the precipitation was observed at very lower pH range i.e. 2.3-2.8. It indicates that the hydrolysis of mercuric ion takes place at very low pH in the presence of H and E. Some typical plots given in Figure 2 show more spread in some pH regions, indicating the presence of protonated metal complexes, but in A, B, E and F the curves are slightly overlapped with each other, indicating the absence of the protonated complexes. Little deviation from overlapping is due to the formation of hydroxyl species or due to varying concentration of mineral acid. In all these curves, the maximum observed value is less than 2 which indicates consumption of two mole of ligand per mole of metal ion during the complexation.

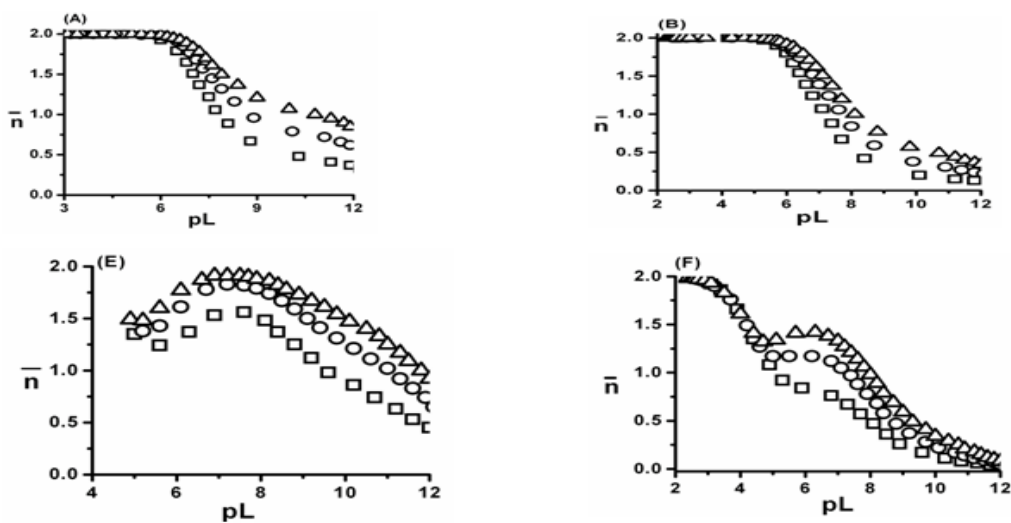


Figure 2: Formation curves H and E complexes in 50% v/v and 10% v/v DMF-water

A) Pb(II), (B) Cd(II) for H complexes in 50% v/v DMF-water mixture and (E) Pb(II), (F) Cd(II) E complexes in 10% v/v DMF-water mixture; ligand concentrations in mmols are 0.25(□-□), 0.375(○-○) and 0.5(Δ-Δ).

Selection of Best fit Model

The models containing different number of species were tried from the primary alkalimetric titration data. a few species were refined while other species were rejected by MINQUAD75 [10]. The results of the best-fit models that contain the type of species and overall formation constants along with some of the important statistical parameters are given in Tables 1-2.

Table 1: Parameters of best-fit chemical models of H complexes of Pb(II), Cd(II) and Hg(II) in DMF-water

DMF % v/v	log β _m (SD)						NP	U _{corr} ×10 ⁸	Skewness	Kurtosis	χ ²	R-Factor	pH-Range
	110	120	121	122	123	124							
Pb(II)													
0.0	-----	09.36(0)	18.38(3)	25.09(3)	31.12(6)	36.92(6)	99	0.0001	0.64	3.11	12.10	0.006	3.4-9.1
10.0	-----	10.15(1)	18.51(1)	24.77(5)	30.36(8)	35.93(7)	67	0.0072	1.83	2.45	12.62	0.004	3.4-9.1
20.0	-----	10.39(1)	19.00(6)	25.15(6)	30.63(0)	36.00(5)	84	0.0030	0.07	2.36	12.35	0.002	3.4-9.1
30.0	-----	10.30(2)	19.63(7)	25.98(5)	31.34(3)	36.91(0)	60	0.0081	0.28	3.70	12.81	0.003	3.4-9.1
40.0	-----	11.60(1)	20.02(8)	25.26(7)	30.67(5)	35.16(9)	99	0.0034	0.07	2.50	12.13	0.007	3.4-8.9
50.0	-----	10.92(0)	19.75 (2)	25.60(5)	30.70(9)	35.83(7)	78	0.0090	0.65	4.61	12.83	0.002	3.4-9.1
Cd(II)													
0.0	-----	10.23(5)	17.83(2)	24.37(6)	30.57(9)	36.29(18)	77	0.0028	1.84	2.01	13.21	0.007	3.0-8.2
10.0	-----	10.76(6)	17.90(9)	24.13(12)	30.05(4)	35.35(14)	90	0.0078	1.13	3.26	12.51	0.006	3.0-8.2
20.0	-----	10.95(7)	18.17(7)	24.25(7)	30.05(4)	35.33(16)	70	0.0017	1.90	3.17	12.53	0.005	3.0-8.2
30.0	-----	11.12 (5)	18.25(9)	24.30(5)	29.66(4)	34.65(24)	88	0.0026	1.35	4.15	11.33	0.001	3.4-8.0
40.0	-----	12.30(4)	19.15(8)	24.95(6)	30.25(1)	34.57(33)	67	0.0044	0.27	5.43	14.17	0.007	3.0-8.0
50.0	-----	11.92(1)	18.76(7)	24.67(0)	29.60(8)	34.59(9)	87	0.0068	0.07	4.96	12.75	0.001	3.0-8.0
Hg(II)													
0.0	10.08(7)	13.19(5)	-----	-----	33.85(2)	35.23(4)	90	0.0081	-0.76	4.00	13.13	0.009	2.0-8.0
10.0	11.76(5)	15.65(9)	-----	-----	34.20(2)	35.42(5)	68	0.0043	-0.50	4.60	12.41	0.005	1.9-8.0
20.0	11.97(4)	15.93(4)	-----	-----	34.27(0)	36.03(7)	70	0.0069	-0.20	3.21	12.25	0.003	2.0-8.0
30.0	12.15(7)	15.72(5)	-----	-----	34.83(7)	36.51(6)	93	0.0057	-0.09	3.50	11.80	0.004	2.0-8.0
40.0	12.20(7)	16.65(9)	-----	-----	34.35(6)	36.15(5)	88	0.0014	-0.36	3.20	12.71	0.003	2.0-8.0
50.0	14.97(6)	20.45(6)	-----	-----	34.97(9)	37.50(8)	99	0.0043	0.23	4.41	12.70	0.003	2.0-8.0

Table 2: Parameters of the best-fit chemical models of E complexes of Pb(II), Cd(II) and Hg(II) in DMF- water mixtures

DMF % v/v	log β _m (SD)					pH-Range	NP	U _{corr} ×10 ⁸	χ ²	Skewness	Kurtosis	R-Factor
	ML	ML ₂	ML ₂ H ₂	ML ₂ H ₃	ML ₂ H ₄							
Pb(II)												
0.0	4.85(7)	8.86(8)	24.07(3)	29.16(4)	33.00(9)	3.9-8.0	55	0.0045	12.78	0.36	3.74	0.0031
10.0	5.34(1)	9.13(1)	24.26(4)	28.90(9)	32.52(0)	3.6-8.0	77	0.0077	12.36	0.44	3.94	0.0046
20.0	5.47(9)	9.67(1)	24.70(8)	29.51(8)	33.28(7)	2.7-8.0	99	0.0063	12.44	0.07	3.72	0.0047
30.0	5.48(2)	9.27(5)	24.90(6)	30.30(0)	34.23(8)	4.0-8.0	77	0.0023	12.99	0.22	3.90	0.0071
40.0	7.40(8)	12.17(1)	26.80(7)	31.36(9)	35.47(6)	3.0-8.0	88	0.0012	11.90	-0.37	7.14	0.0022
50.0	6.30(0)	10.18(5)	25.87(7)	31.17(7)	35.65(7)	4.0-8.0	90	0.0014	12.11	0.44	3.12	0.0044
Cd(II)												
0.0	3.96(6)	7.57(0)	23.77(1)	28.92(4)	33.17(7)	3.0-9.0	66	0.0055	12.90	1.07	4.24	0.0083
10.0	4.53(4)	8.63(6)	24.26(6)	29.00(6)	32.86(8)	3.4-9.0	47	0.0066	12.88	1.18	4.60	0.0089
20.0	4.90(9)	8.70(8)	24.57(1)	29.43(1)	33.38(9)	2.0-9.0	99	0.0077	12.67	0.15	4.82	0.0045
30.0	4.72(9)	8.16(7)	24.50(1)	29.87(1)	33.83(1)	2.0-9.5	107	0.0022	11.44	-0.56	4.60	0.0045
40.0	5.51(5)	9.72(5)	25.27(5)	30.06(9)	33.96(2)	2.4-9.0	88	0.0017	12.77	0.03	4.25	0.0031
50.0	5.23(5)	9.09(9)	24.77(9)	30.67(0)	35.47(5)	4.4-9.0	65	0.0010	12.80	0.18	3.26	0.0080
Hg(II)												
0.0	9.25(7)	12.26(7)	26.05(9)	30.08(5)	32.67(9)	2.0-9.0	99	0.0013	12.41	0.26	7.90	0.0034
10.0	9.67(6)	14.00(8)	26.49(7)	30.30(5)	33.25(6)	2.0-9.0	87	0.0012	12.45	1.95	5.12	0.0024
20.0	10.26(7)	13.75(4)	27.83(7)	31.95(4)	34.77(5)	2.0-9.0	66	0.0014	11.06	0.65	6.51	0.0023
30.0	12.63(0)	14.68(3)	30.35(4)	34.43(7)	37.56(8)	2.0-10.0	45	0.0019	12.13	-0.44	6.00	0.0033
40.0	11.63(5)	14.92(8)	30.36(7)	33.33(4)	36.55(3)	2.0-10.0	47	0.0111	12.73	-0.06	4.80	0.0020
50.0	12.62(6)	18.36(1)	30.44(9)	34.25(6)	37.35(4)	2.0-10.0	49	0.0213	12.44	-0.87	5.07	0.0021

U_{corr} = U/(NP-m)X10⁸, where m = number of species; NP=Number of experimental points; SD=Standard deviation

Residuals Analysis

The SD and confidence intervals in β are meaningful only when unweighted residuals follow χ^2 distribution, which measures the possibility of residuals forming a plot of standard normal distribution with zero mean and unit standard deviation.

Higher χ^2 values than expected are due to 1) the inadequacy of the model although the experimental data are of high quality, 2) use of poor data even though the model is appropriate, and 3) invoking optimistic estimates of errors in primary data.

A persual of Tables 1-2 indicates that the χ^2 values range between 11.33-14.17 for DMF-water mixtures. The values of kurtosis and skewness range from 2.01-7.90 and -0.87-1.95 for DMF-water mixtures respectively. Most of the residuals form leptokurtic patterns and remaining form platykurtic patterns. Skewness values are very nearer to zero. This indicates the residuals form normal distribution. Deviation of the values of kurtosis and skewness from three and zero, respectively, show the tendency of these residuals to concentrate more to the left or right of the mean and broadening of the peak. However, the values of U_{corr} in all the three mass-balance equations, are very low confirming the adequacy of the chemical model to represent the experimental data.

Effect of systematic errors on best-fit model:-

In order to rely upon the best chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was made by introducing pessimistic errors in the concentrations of alkali, mineral acid, ligand, metal and volume (Table 3). The data show that the order of affecting the magnitudes of stability constant is alkali > acid > ligand > metal. The increased standard deviation in stability constants and even rejection of some species on the introduction of errors confirms the correctness of the proposed models. This type of investigation is significant as the data acquisition was done under varied experimental conditions with different accuracies.

Table 3: Effect of errors in influential parameters on Pb(II)-E complex stability constants in 20% v/v DMF-water mixture

Ingredient	% of error	log β_{mlh} (SD)				
		ML	ML ₂	ML ₂ H ₂	ML ₂ H ₃	ML ₂ H ₄
	0	4.47(9)	9.67(1)	24.70(8)	29.51(8)	33.28(7)
Alkali	-5	3.18(44)	Rejected	Rejected	Rejected	33.27(45)
	-2	3.95(70)	7.36(55)	Rejected	28.97(55)	32.95(33)
	+2	6.95(22)	11.19(33)	25.85(27)	30.22(33)	34.00(26)
	+5	9.74(24)	Rejected	26.95(26)	31.34(21)	34.48(19)
Acid	-5	9.82(22)	14.57(23)	27.55(11)	31.75(19)	35.04(83)
	-2	6.67(23)	10.83(18)	26.00(17)	30.39(29)	34.25(51)
	+2	4.07(23)	7.63(12)	Rejected	28.57(42)	30.78(99)
	+5	3.17(96)	6.65(38)	Rejected	Rejected	Rejected
Ligand	-5	5.33(10)	9.38(29)	24.64(9)	29.86(25)	33.67(31)
	-2	5.09(19)	9.99(28)	24.58(9)	29.22(14)	33.16(12)
	+2	4.77(29)	9.49(29)	24.46(11)	29.56(10)	33.54(7)
	+5	4.52(10)	8.07(10)	24.28(14)	29.76(9)	33.77(6)
Metal	-5	4.44(10)	8.62(29)	24.77(10)	29.43(11)	33.20(19)
	-2	4.43(9)	8.68(28)	24.75(10)	29.41(11)	33.28(19)
	+2	4.41(9)	8.68(28)	24.72(19)	29.39(11)	33.26(19)
	+5	5.44(8)	8.66(38)	24.75(19)	29.19(13)	33.13(12)

** Standard deviation is very high

Effect of Solvent on Metal-ligand Equilibria

The variation of overall stability constant values with co-solvent content depends upon two factors, viz., electrostatic and non-electrostatic. The trends of stability constant ($\log \beta$) values of complexes of H and E with 1/D of DMF-water mixture are given in Figure 3. The almost linear trend indicates that the dielectric constant or long-range interactions are responsible for the stability trend. This linear increase indicates the dominance of the structure-forming nature of DMF over the complexing ability. The non-linearity observed in E complexes of Hg(II) in Figure 24F may be due to considerable contribution from non-electrostatic forces.

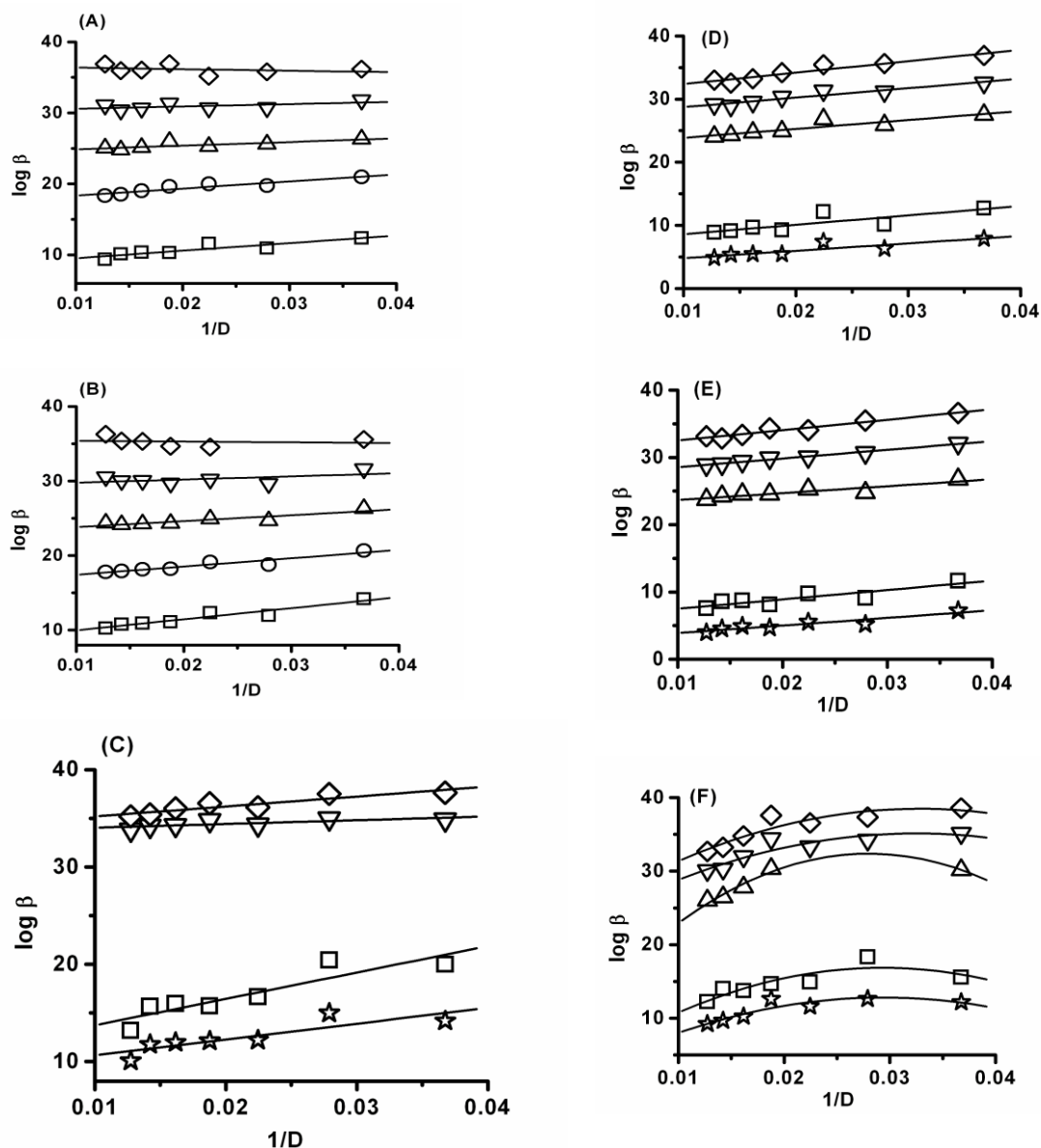


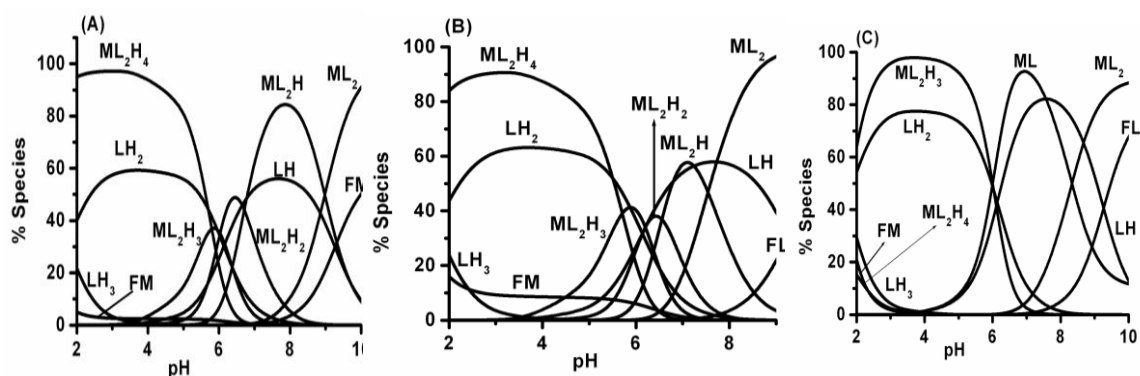
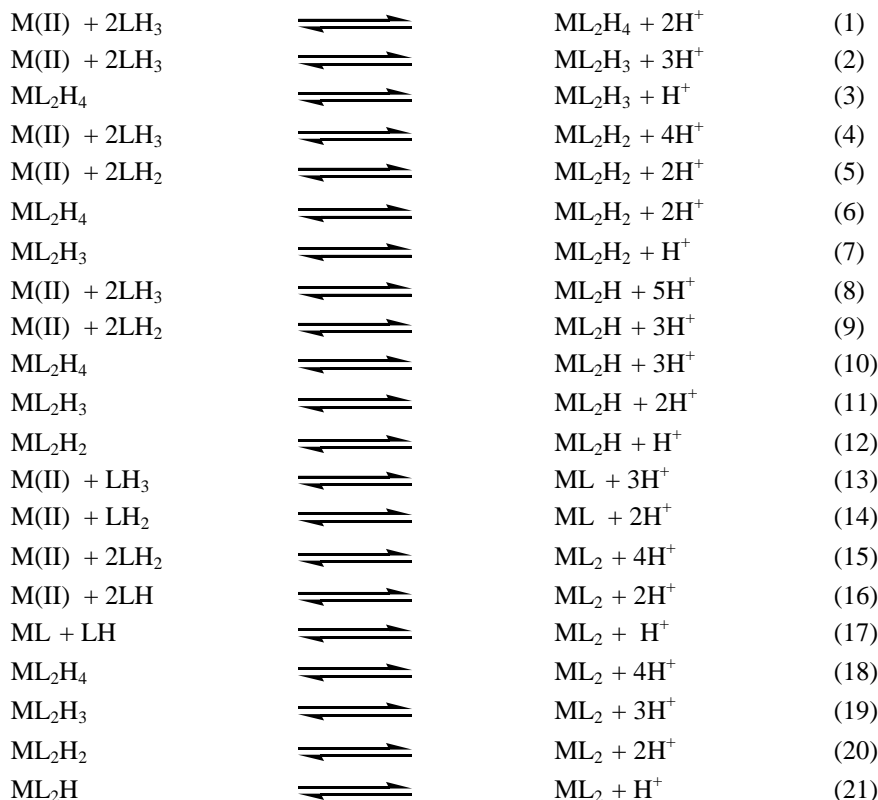
Figure 3: Variation of stability constant values of (A-C) H and (D-F) E complexes with reciprocal of dielectric constant ($1/D$) of DMF-water mixtures:

(A and D) Pb(II); (B and E) Cd(II); (C and F) Hg(II); (\star) $\log \beta_{ML}$; (\square) $\log \beta_{ML2}$; (\circ) $\log \beta_{ML2H}$; (Δ) $\log \beta_{ML2H2}$; (∇) $\log \beta_{ML2H3}$; (\diamond) $\log \beta_{ML2H4}$.

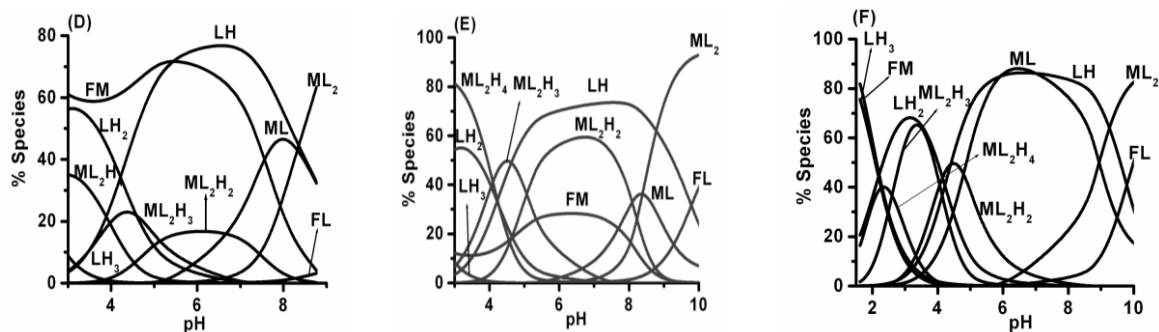
IV. Distribution Diagrams

L-Histidine Complexes

The present investigation reveals the existence of ML_2H_4 , ML_2H_3 , ML_2H_2 , ML_2H and ML_2 for Pb(II) and Cd(II) and Hg(II) forms ML_2H_4 , ML_2H_3 , ML_2 and ML . The formation of various L-histidine complex species is shown in the following equilibria.



The species distribution diagrams are shown in Figures 4 and 5. They indicate that H complexes of Pb(II), Cd(II) and Hg(II) are formed in the pH range 2.0-9.0. At lower pH, ML_2H_4 species is formed by the interaction of free metal ion with LH_3 form of the ligand (Equi.1). The species ML_2H_3 may be formed from $M(II)$ and LH_3 or by the deprotonation of ML_2H_4 (Equi 2 and 3). In the same manner, the species ML_2H_2 may be formed either from free metal ion and LH_3/LH_2 (Equi. 4 and 5) or deprotonation of ML_2H_4 and ML_2H_3 (Equi.6 and 7). At lower pH, the interaction of free metal ion with LH_3 or LH_2 (Equi 4 and 5) and at higher pH, deprotonation of ML_2H_4 and ML_2H_3 (Equi 6 and 7) result in the formation of ML_2H_2 species. ML_2H is formed from $M(II)$ and LH_3 or LH_2 at lower pH or deprotonation of ML_2H_4 , ML_2H_3 and ML_2H_2 species at higher pH (Equilibria 8-12). The ML_2 species is formed from the interaction of free metal ion with LH_2 or LH (Equi. 15 and 16) or ML and LH (Equi. 17) or deprotonation of ML_2H_4 , ML_2H_3 , ML_2H_2 and ML_2H species (Equi. 18-21).



(A) Pb(II), (B) Cd(II), (C) Hg(II) with H and (D) Pb(II), (E) Cd(II), (F) Hg(II) with E. Ratio of Pb(II) (or Cd(II)) and H (or E) is 1.0:5.0 and that of Hg(II) is 1.0:5.0.

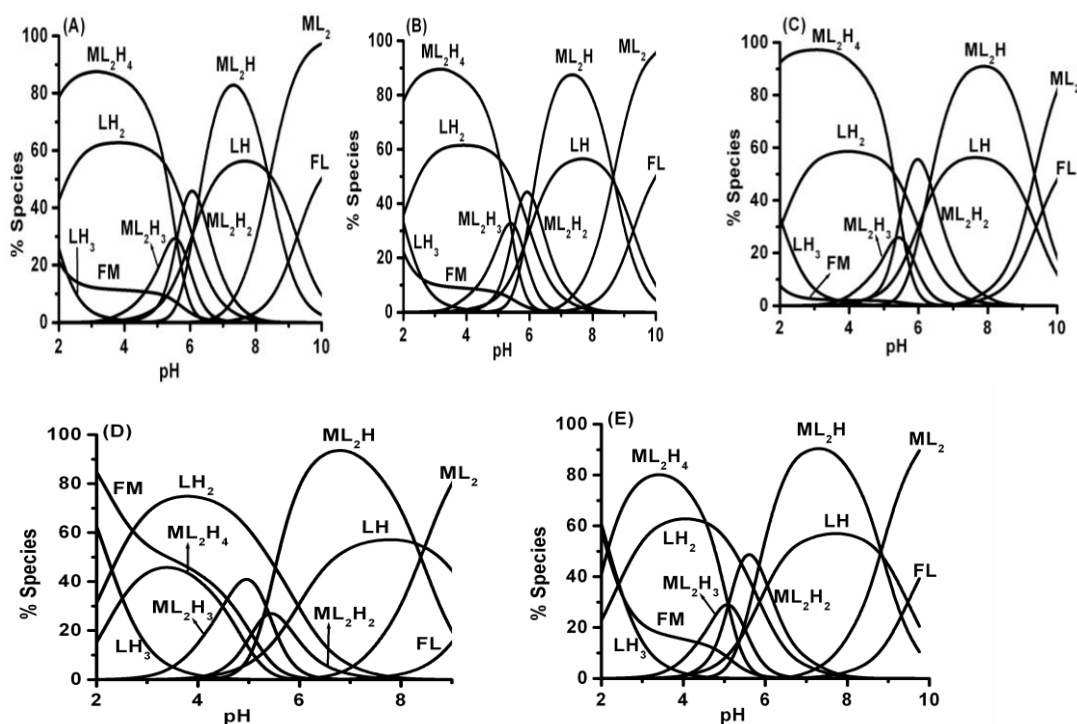
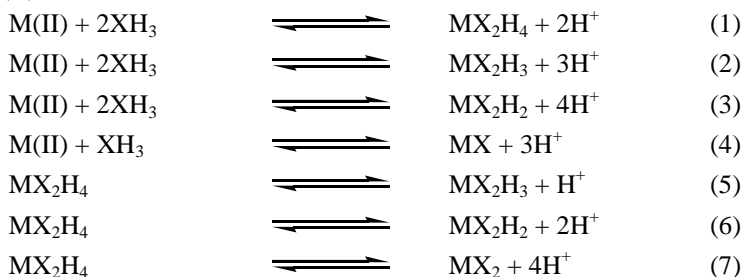
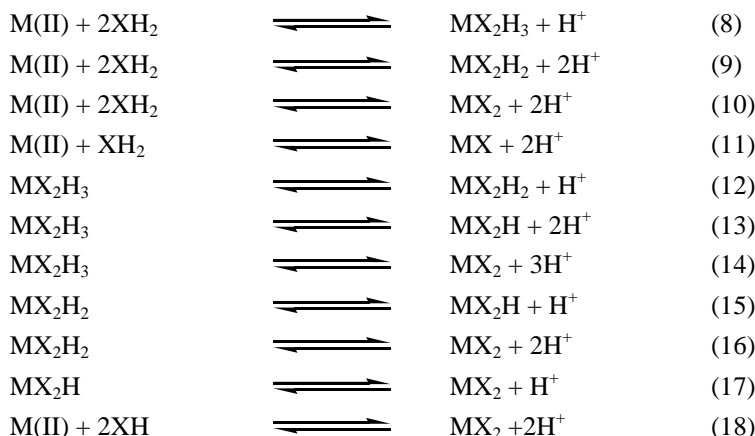


Figure 5: distribution diagrams of Pb(II)-H in DMF-water mixtures %v/v) (A) 10.0, (B) 20.0, (C) 30.0, (D) 40.0 and (E) 50.0. Ratio of Pb (II) and H is 1.0:5.0

L-Glutamic Acid Complexes

L- Glutamic Acid has two dissociable carboxyl protons and an amino group that can associate with a proton. The different forms of E that exist in the pH regions 2.0-4.0, 2.0-5.0, 4.0-9.0 and 8.0-10.0 are XH_3^+ , XH_2 , XH^- and X^{2-} , respectively. The probable species were predicted from these data. The species formed in the present study for different metals as given in Tables 2 are MX_2H_4 , MX_2H_3 , MX_2H_2 , MX and MX_2 for Pb(II), Cd(II) and Hg(II) in DMF-water mixtures.





Distribution diagrams were drawn for various complex species using the formation constants of the best fit models shows at a pH below 4.0 MX_2H_4 species is formed for Pb(II), Cd(II) and Hg(II). With increasing pH deprotonation of MX_2H_4 takes place and gives MX_2H_3 , MX_2H_2 , MX_2H , and MX_2 . Figure 6 represent the Hg-E binary complexes. MX species is formed from free metal and XH_3 form of ligand (Equi. 4). MX_2 is formed by the deprotonation of MX_2H_4 , MX_2H_3 and MX_2H_2 .

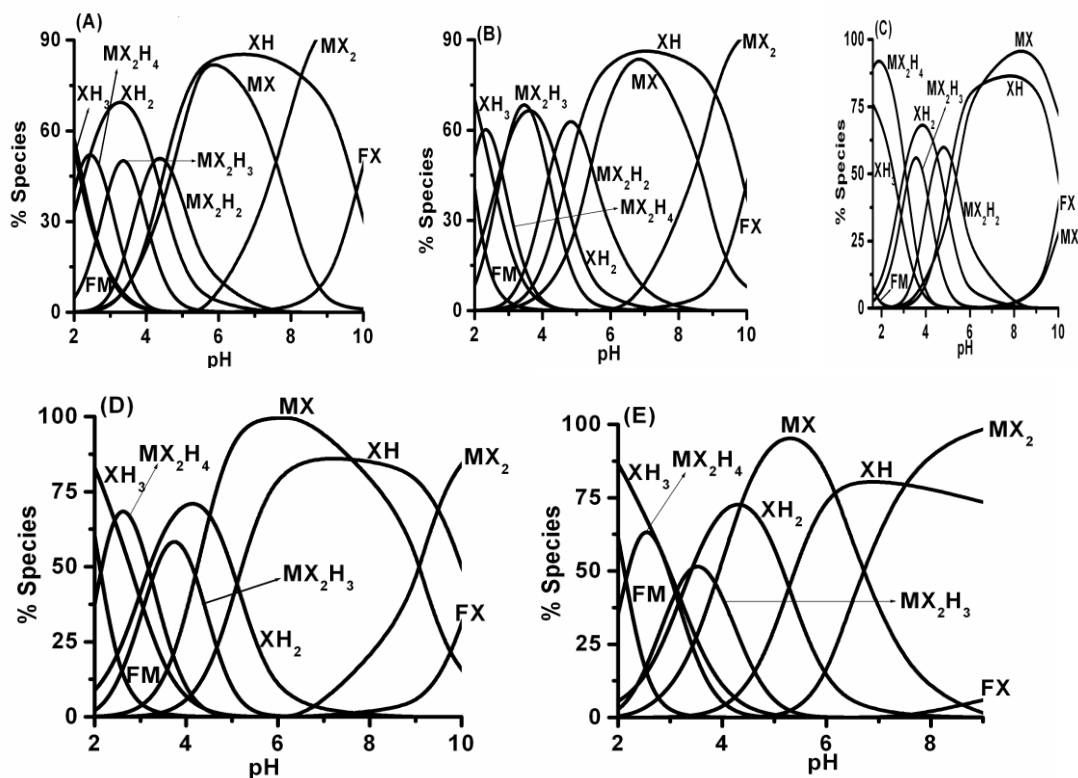


Figure 63: Distribution diagrams of Hg(II)-E in DMF-water mixtures (%v/v) (A) 10.0, (B) 20.0, (C) 30.0, (D) 40.0 and (E) 50.0. Ratio of Hg(II) and E is 1.0:5.0.

Structures of Binary Complexes

When the third donor site of the amino acid is a nitrogen atom, marked tridentate behavior is frequently found, more so when the additional chelation results in a five or six membered ring. Octahedral structures are proposed to the complexes of all the metal ions. The VSEPR theory suggests that Pb(II), Cd(II) and Hg(II) complexes shall be octahedral because there are six outer electron pairs. This argument supports the structures of complexes proposed in Figures 7 and 8.

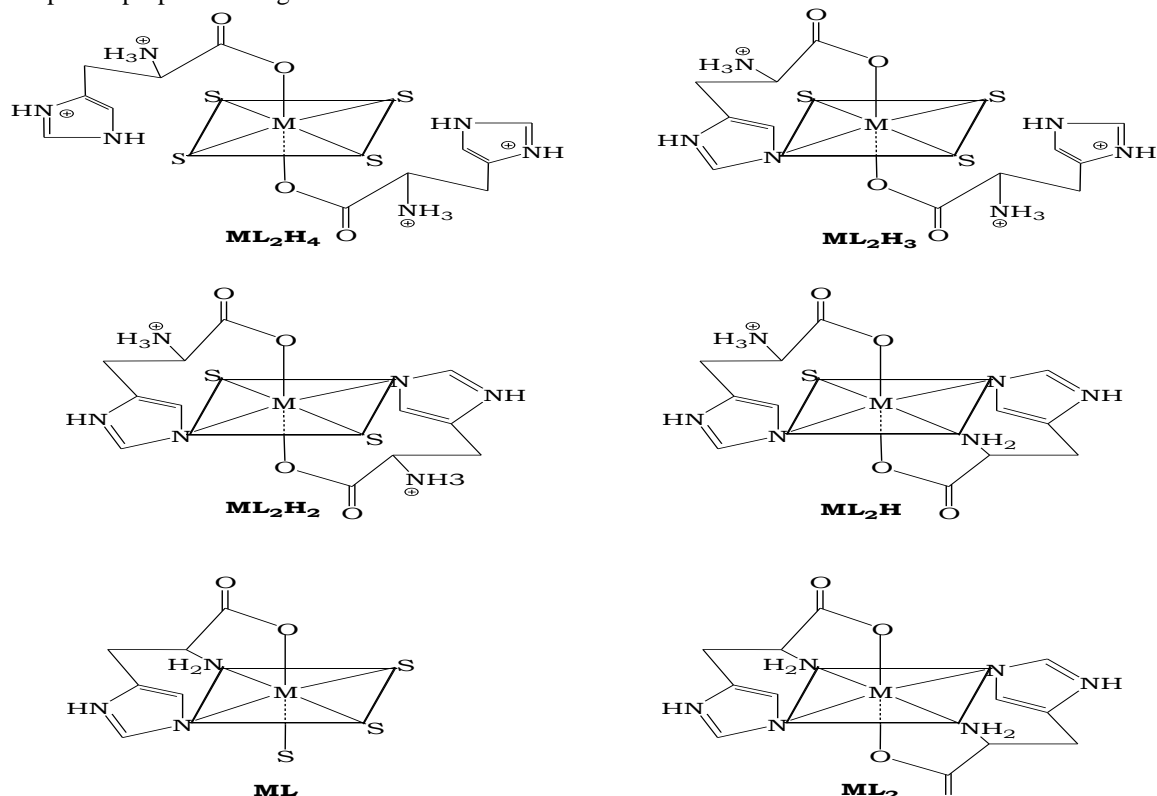


Figure 74 Speculated structures of Histidine complexes with Pb(II) and Hg(II)
Where S is either solvent or water molecules.

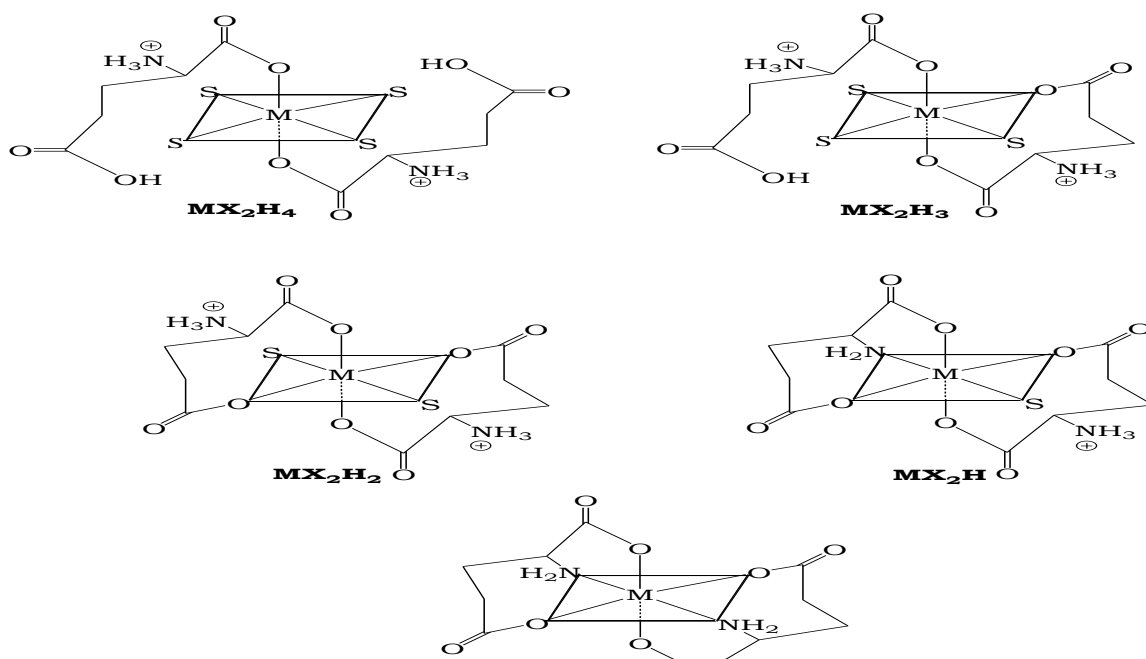


Figure 8: Speculated structures of Glutamic acid complexes with Pb(II), Cd(II) and Hg(II),
Where S is either solvent or water molecules.

V. Conclusion

In the present work, pH-metric study was performed to determine stability constants and to assess binary species for L-Histidine and L-Glutamic acid with toxic metal ions in 0.0-50.0% DMF-water mixtures in pH range of 2.0-9.0 and 2-10 respectively. The following conclusion have been drawn: The binary species formed due to the interaction of H with metals are ML_2H_4 , ML_2H_3 , ML_2H_2 , ML_2H and ML_2 for Pb(II) and Cd(II) and Hg(II) forms ML_2H_4 , ML_2H_3 , ML_2 and ML . For E MX_2H_4 , MX_2H_3 , MX_2H_2 , MX and MX_2 for Pb(II), Cd(II) and Hg(II). These models are validated by statistical treatment of data. The linear variation of stability constants as a function of $1/D$ of the medium indicates the dominance of electrostatic forces over non-electrostatic forces and the dominance of structure forming nature of the co-solvents over its coordinating power. The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal

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