An Electrometric Investigation on Chemical Speciation of Binary Complexes of Biologically Essential Metal Ions with Histamine in TX100-Water Mixtures

P. Seetharam[a], M. Balakrishna[a], R. Neeraja[b], M. Ramanaiah[c*], S. Deepthi[d], S. Gouthamsri[c]

[a]Department of Chemistry, Lendi Institute of Engineering and Technology, Vizianagaram-535005, India-535005

[b]Department of Chemistry, Government College for Women (A), Srikakulam, Andhra Pradesh, India-532001

[c]Department of Chemistry, Aditya Institute of Technology and Management, Tekkali, India-532201

[d]Department of Physics, Lendi Institute of Engineering and Technology, Vizianagaram-535005, India-535005

*Corresponding Author: ramanaiahmalla4@gmail.com

Abstract

The present investigation deals with the nature the binary metal ligand complexes formed in between essential metal ions with Histamine in (0.0-2.5% v/v) TX100-water mixture. pH meter is employed for this investigation, and the data is obtained by maintaining the temperature at 303.0 K and ionic strength of the medium at 0.16 mol L^{-1}.There are number of metal ligand complexes formed and which were studied by a computer modelling known as MINIQUAD75. The titremetric data is subjected to statistical analysis and the selection of best fit chemical model is done using the statistical parameters such as R-factor, Standard deviation and U-Correction etc. In this investigation, it observed that electrostatic and non-electrostatic forces are showing noticeable effect on the stability constants of binary metal ligand complexes formed with respective to the mole fraction of the TX-100. Percentages of species and species distribution diagrams are presented.

Keywords: Formation constants, Binary metal ligand complexes, Histamine, TX100, pH.

1. Introduction

Chemical speciation is one of the emerging studies in the world, where it describes about toxicology and bioavailability of metals and their complexes. The term chemical species stands for the composition of an element or molecular structure of an element. Speciation of an element means distribution of the element in defined chemical species of a system. The author(s) has been studied the protonation constants of Histamine in different medium like SLS-water, CTAB-water and TX100-water mixtures and the protonation constant values are also reported

(Seetharam et al. 2021, Ramanaiah et al. 2019 and Seetharam et al. 2016), along with this the author(s) also studied the chemical speciation of Ca(II), Zn(II) and Mn(II) metal ions with Histamine in CTAB-water mixtures, and the results were reported (Seetharam et al. 2020). The inorganic form of some essential metal ions like Cobalt is vital for human body, the excess or deficiency of which causes adverse effects (Balakrishna et al. 2021 and Balakrishna et al. 2021). The main aim of the present electrometric investigation is understand type of species formed and their stability constants and also to present how the stability constants are affected by changing the concentration of acid, base, ligand and metal ions. In the present study the author has studied the stability constants of Ca (II), Mg (II), and Zn (II) binary metal ligand complexes in Histamine-water medium. This investigation has been carried out by using pH meter. The obtained data is very useful in understanding the biological activity of the type of complexes formed (Seetharam et al. 2017, Ramanaiah et al. 2017 and Balakrishna et al. 2017).

2. Experimental

Histamine solution was prepared with 0.05 mol L^{-1}concentration by dissolving the pure chemical substance in distilled water with little amount of 0.05 mol L-^{1}hydrochloric acid, which increases the solubility of Histamine. Sodium hydroxide solution having the concentration 0.4 mol L^{-1} is prepared by dissolving the pellets in distilled water. Sodium chloride is used to maintain ion strength of the titrand solution, which is prepared with 2.0 mol L^{-1} concentration by dissolving the substance in distilled water. Ca(II), Mg(II), and Zn(II) Chloride metal ion solutions were produced by dissolving the substances in distilled water to having the concentration at 0.05 mol L^{-1}. Hydrochloric acid solution having the concentration 0.2 mol L^{-1} is prepared by dissolving in distilled water. TX100 is used as it is obtained from the company without any further purification. Histamine is obtained from Spectrochem, India, Sodium chyloride is obtained from Qualigens, India. Triple distilled water is used for preparing all the solutions and for cleaning of glassware apparatus. Standardisation of hydrochloric acid, sodium hydroxide and metal ion solutions were done by using standard methods. The analysis of variance of one way classification is used to assess any inaccuracies in the concentration determination [Balakrishna et al. 2017]. The standard method, Gran plot is used to assess the strengths of acid and bases (Ramanaiah et al. 2017 and Gran 1952).

3. Procedure

In the process of determining the stability constants of metal ligand complexes, initially a titration has to be carried out between acid and alkali, which will help in checking the equilibrium attained or not. The electrode used this method has to be kept in TX100-water solution to allow the electrode a equilibrium state. The same process of keeping electrode in TX100-water mixtures for all the compositions of the mixtures, 1 mmol of mineral acid has to be added to the titrand in each titration against 0.4 mol L^{-1} of sodium hydroxide. Titrations are carried out by varying the metal-ligand ratios (1:2.5, 1:3.75, 1:5).Other experimental details are given elsewhere (Gran 1988).

Table 1: Total initial concentrations of ingredients (in mmol) for metal - ligand titrations in TX100-water mixtures. [NaOH] = 0.4 mol dm^{-3}; V_0 = 50 cm^3; Temperature = 303 K; Mineral acid = 1.0 mmol; μ = 0.16 mol dm^{-3}.

%(v/v) TX100	TM0			TL0 (Him)	TL0/TM0
	Ca(II)	Mg(II)	Zn(II)		
0.0	0.1023	0.1013	0.1002	0.2495 0.3743 0.4991	2.50 3.75 5.00
0.5	0.1023	0.1013	0.1002	0.2499 0.3749 0.4999	2.50 3.75 5.00
1.0	0.1023	0.1013	0.1002	0.2494 0.3741 0.4988	2.50 3.75 5.00
1.5	0.1023	0.1013	0.1002	0.2493 0.3740 0.4987	2.50 3.75 5.00
2.0	0.1023	0.1013	0.1002	0.2491 0.3737 0.4983	2.50 3.75 5.00
2.5	0.1023	0.1013	0.1002	0.2489 0.3733 0.4978	2.50 3.75 5.00

4. Modeling Strategy

SCPHD is a computer application, which is used in our study for calculating correction factor [Seetharam et al. 2016, Balakrishna et al. 2017 and Balakrishna et al. 2017]. The data obtained in the pH metric titrations is simulated using a computer program called MINIQUAD75 to get the stability constants of binary complexes [Seetharam et al. 2021], In order to refine the stability constants of the metal ligand complexes, the correction factor and protonation constants of Histamine have to be fixed. There will be a fluctuation in the stability constants of binary metal ligand complexes with the mole fraction of the TX100-water medium; this might be due to the solvent-solute interactions and solute-solute interactions. The affect of solute-solvent and solute-solute interactions were investigated electro statically.

5. RESULTS AND DISCUSSION

The important statistical parameters, complex species, overall formation constants and stiochiometry were used for obtaining best-fit models. The statistical data was given in the below Table 2. The low standard deviation values obtained in the present model indicates the precision

of the stability constants (Grans 1976, Ramanaiah et al. 2014 and Seetharam et al. 2020)

6. Residual Analysis

In data analysis with least squares methods, the residuals are expected to follow a Gaussian or normal distribution. The residuals are checked for normal distribution in accordance with the hypothesis that the errors are random. χ^2, Skewness, Kurtosis, and R-factor are examples of such tests. The models obtained in the present study are accepted as the χ^2 values are less than the table values. The residuals in this investigation have a leptokurtic pattern, based on the kurtosis values. The skewness values obtained in the present study are ranging from -1.19 to 3.43 for Ca (II), -1.45 to 1.46 for Mg (II) and -0.03 to 2.55 for Zn (II). The values of Ucorr,χ^2, Skewness, Kurtosis, and R-factor are shown in the below Table.2.

Table 2: Parameters of best fit chemical models of M(II) – Histamine complexes in Triton X - water medium

% v/v TX1OO	log β_{mlh} (SD) MXH	MX_2	MX_2H	pH-Range	NP	U_{corr} $\times 10^8$	χ^2	Skewness	Kurtosis	R-factor
				Ca(II)						
0.0	10.16(25)	7.73(14)	15.06(20)	2.0-9.0	57	18.93	29.94	2.59	14.95	0.0220
0.5	10.12(35)	8.04(26)	15.58(32)	2.0-9.0	99	7.262	18.99	0.48	5.37	0.0456
1.0	10.72(28)	8.36(34)	16.23(28)	2.8-10.0	41	14.23	23.92	3.43	16.26	0.0529
1.5	9.85(21)	8.71(33)	16.88(30)	2.4-8.8	40	10.31	23.42	1.20	6.94	0.0390
2.0	9.61(22)	8.55(35)	16.61(31)	2.6-8.9	20	11.06	18.00	-0.67	4.42	0.0444
2.5	9.77(36)	8.53(32)	16.97(31)	2.6-8.9	19	30.19	17.00	-1.19	5.38	0.0428
				Mg(II)						
0.0	10.05(22)	08.67(28)	17.30(31)	2.4-9.9	52	13.28	7.52	-0.01	8.04	0.0388
0.5	9.58(26)	7.84(30)	15.95(35)	2.4-9.9	57	9.072	16.39	-0.79	8.81	0.0457
1.0	9.60(34)	08.26(31)	16.00(29)	2.4-8.2	34	19.14	35.10	-0.90	7.28	0.0328
1.5	10.13(23)	8.35(28)	15.86(41)	2.4-9.9	32	17.24	23.13	1.46	9.78	0.0403
2.0	9.55(31)	8.65(21)	15.53(37)	2.4-8.9	20	13.98	21.33	0.24	7.96	0.0442
2.5	9.37(19)	8.34(26)	15.29(24)	2.4-8.9	49	16.33	35.60	-1.45	12.66	0.0363
				Zn(II)						
0.0	10.54(24)	9.86(32)	16.30(27)	2.5-8.0	48	19.17	11.33	0.49	6.83	0.0336
0.5	10.65(22)	9.56(25)	15.81(31)	2.7-7.9	45	35.15	15.61	-0.03	5.92	0.0286
1.0	10.26(27)	9.41(29)	16.12(29)	2.8-8.0	46	26.39	23.45	0.70	6.65	0.0237
1.5	10.04(32)	9.40(34)	15.85(29)	2.4-8.6	21	9.412	10.33	2.55	10.39	0.0525
2.0	9.85(26)	9.19(28)	16.04(36)	2.4-8.0	36	9.739	10.05	2.29	9.06	0.0351
2.5	9.93(25)	8.84(32)	15.59(27)	2.4-8.0	37	15.9	24.4	0.34	6.03	0.0254

7. Consequences of Best-Fit Model Errors

The effect of concentrations of alkali, acid, metal, ligand,volumeand log F values on the stability constants of binary metal ligand complexes are presented in the below Table 3. The high standard deviation values of stability constants indicates the inadequacy of the model and will clearly shows the effect of strengthsof alkali, acid, metal, ligand, volume and log F values.

Table 3: Effect of errors in influential parameters on the stability constants of Zn(II)-Him complexes in 2.5% v/v TX100-water medium.

Ingredient	% Error	Log β_{mlh}(SD)		
		111	120	121
Acid	0	9.37(19)	8.34(26)	15.29(24)
	-5	Rejected	9.25(53)	16.18(60)
	-2	9.55(52)	8.97(46)	16.07(37)
	+2	9.52(49)	8.58(32)	15.52(40)
	+5	9.72(57)	7.99(54)	Rejected
Alkali	-5	9.62(35)	8.57(52)	Rejected
	-2	9.50(44)	8.12(34)	15.63(37)
	+2	9.51(41)	8.78(43)	15.85(30)
	+5	Rejected	Rejected	15.08(44)
Ligand	-5	9.46 (34)	8.16(32)	15.30(29)
	-2	9.47(24)	8.37(28)	14.74(29)
	+2	8.95(33)	8.68(38)	15.92(37)
	+5	8.75(56)	8.52(35)	15.89(55)
Metal	-5	9.33(22)	8.41(29)	15.66(25)
	-2	9.46(26)	8.39(30)	15.65(26)
	+2	9.47(12)	8.38(31)	15.52(29)
	+5	9.52(22)	8.33(33)	15.50(32)
Volume	-5	9.33(21)	8.28(30)	15.45(25)
	-2	9.37(19)	8.35(27)	15.50(25)
	+2	9.44(18)	8.45(28)	15.57(29)
	+5	9.50(17)	8.56(39)	15.62(30)
Log F	-5	9.46(22)	8.46(29)	15.70(27)
	-2	9.43(23)	8.40(29)	15.76(26)
	+2	9.40(21)	8.39(30)	15.71(26)
	+5	9.41(22)	8.36(27)	15.66(27)

8. Effect of Surfactant

The effect of electrostatic and non-electrostatic forces has to be considered as they may dominate one on another, which is due to the nature of solute and solvent (Ramanaiah et al. 2019 and Feakins 1983). The increase in the concentration of surfactant increases number of micelles (Bunton 1979). The protonation-deprotonation equilibria are directly influenced by the medium's dielectric constant (Ramanaiah et al. 2022, Balakrishna et al. 2022, Nageswara rao et al. 2016 and Gowri Kumari et al. 2015). According to Born equation, the energy to electrostatic interaction is related to dielectric constant of medium (Ramanaiah et al. 2014, Nageswara rao et al. 2014 and Ramanaiah et al. 2014). It is observed that the variation in the log β values of binary metal ligand complexes of Glycylglycine with respective to the mole fraction of TX100-water mixtures are given in Figure.1. There is a linear trend in the logβ values with respective to mole fraction indicates the interaction between metal and ligand, which is electrostatic in nature.

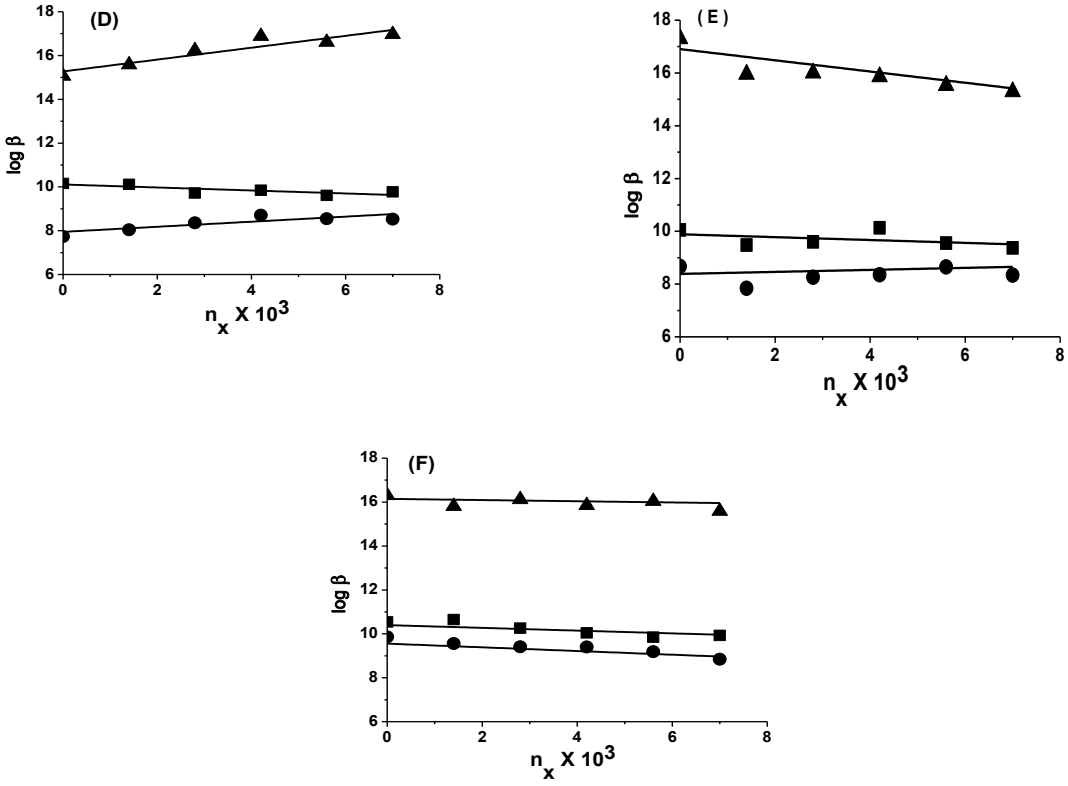

Fig. 1: Variation of stability constants of Him complexes of (D) Ca(II), (E) Mg(II) and (F) Zn(II) with mole fraction of TX100-water mixtures: (■) logβMXH, (●)logβ$MX_2$and (▲)logβMX_2H.

9. Distribution Diagrams

The different forms of Histamine forms metal ligand complexes, which are XH_2^{2+}, $XH^+$and X in the pH-range of 3.0 – 7.0, 4.5 – 10.5 and 8.0 – 11.0. The present study confirms that the formation of metal ligand complexes with Ca(II), Mg(II) and Zn(II) are MXH, MX_2, MX_2H. Some typical distribution diagrams of TX100 – water media are shown in Figure 2.

$M(II) + XH_2^{2+} \rightleftharpoons MXH^{3+} + H^+$ (1)

$MXH^{3+} \rightleftharpoons MX^{2+} + H^+$ (2)

$M(II) + XH_2^{2+} \rightleftharpoons MX^{2+} + 2H^+$ (3)

$M(II) + 2XH_2^{2+} \rightleftharpoons MX_2H_2^{4+} + 2H^+$ (4)

$MX_2H_2^{4+} \rightleftharpoons MX_2H^{3+} + H^+$ (5)

$M(II) + 2XH_2^{2+} \rightleftharpoons MX_2H^{3+} + 3H^+$ (6)

$MX^{2+} + LH_2^{2+} \rightleftharpoons MX_2H^{3+} + H^+$ (7)

$MX_2H^{3+} \rightleftharpoons MX_2^{2+} + 2H^+$ (8)

$MX^{2+} + XH_2^{2+} \rightleftharpoons MX_2^{2+} + 2H^+$ (9)

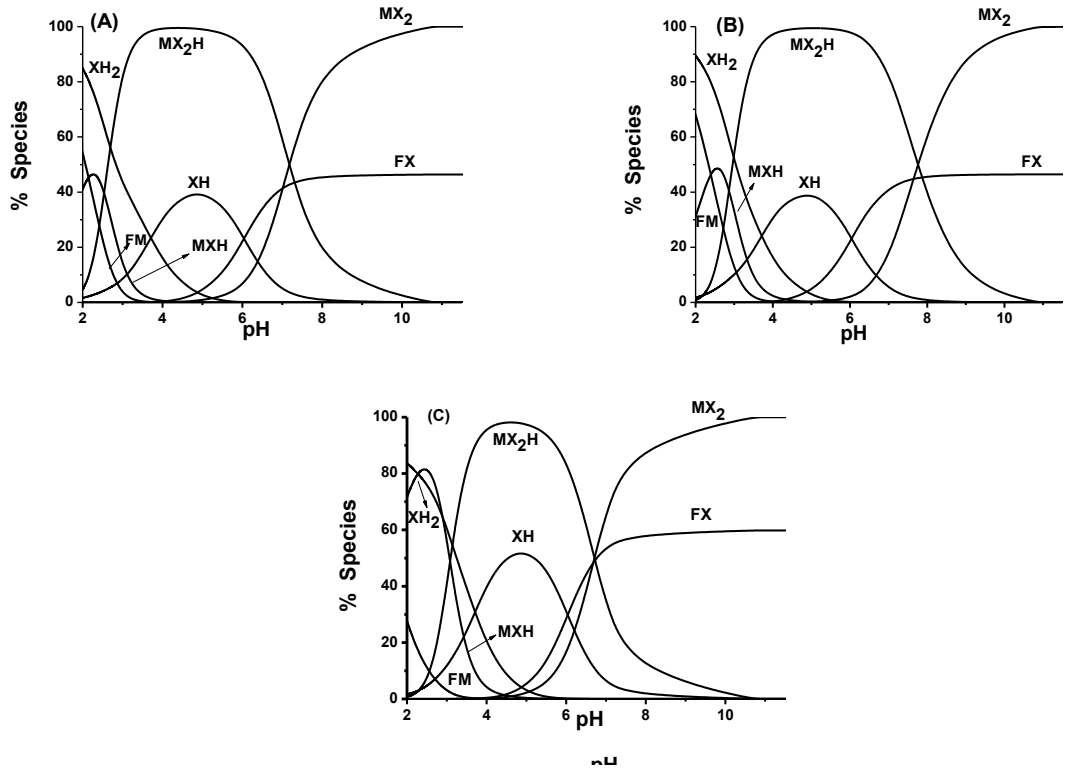

Fig. 2: Distribution schematics of metal ligand complexes of Him in 1.5% v/v TX100concentration: (A) Ca(II), (B) Mg(II), and (C) Zn(II) Distribution schematics of [A] L-leucine [B] Isoleucine 1.5% w/v SLS concentration.

10. Structures of Complexes

The proposed structures of metal ligand complexes are shown in Fig. 3. Because there are six outer electron pairs, the VSEPR theory predicts that Ca(II), Mg(II), and Zn(II) complexes will be octahedral. This additional chelation results in a six-membered ring, which is proved from the X-ray diffraction analysis of Histamine complexes of transition metal ions (Co, Cu, Zn and Cd) (Ramanaiah et al. 2014, Ramanaiah et al. 2014, Ramanaiah et al. 2014 and Ramanaiah et al. 2014). In physiological pH levels, amino nitrogen atom histamines can bind with hydrogen ions.

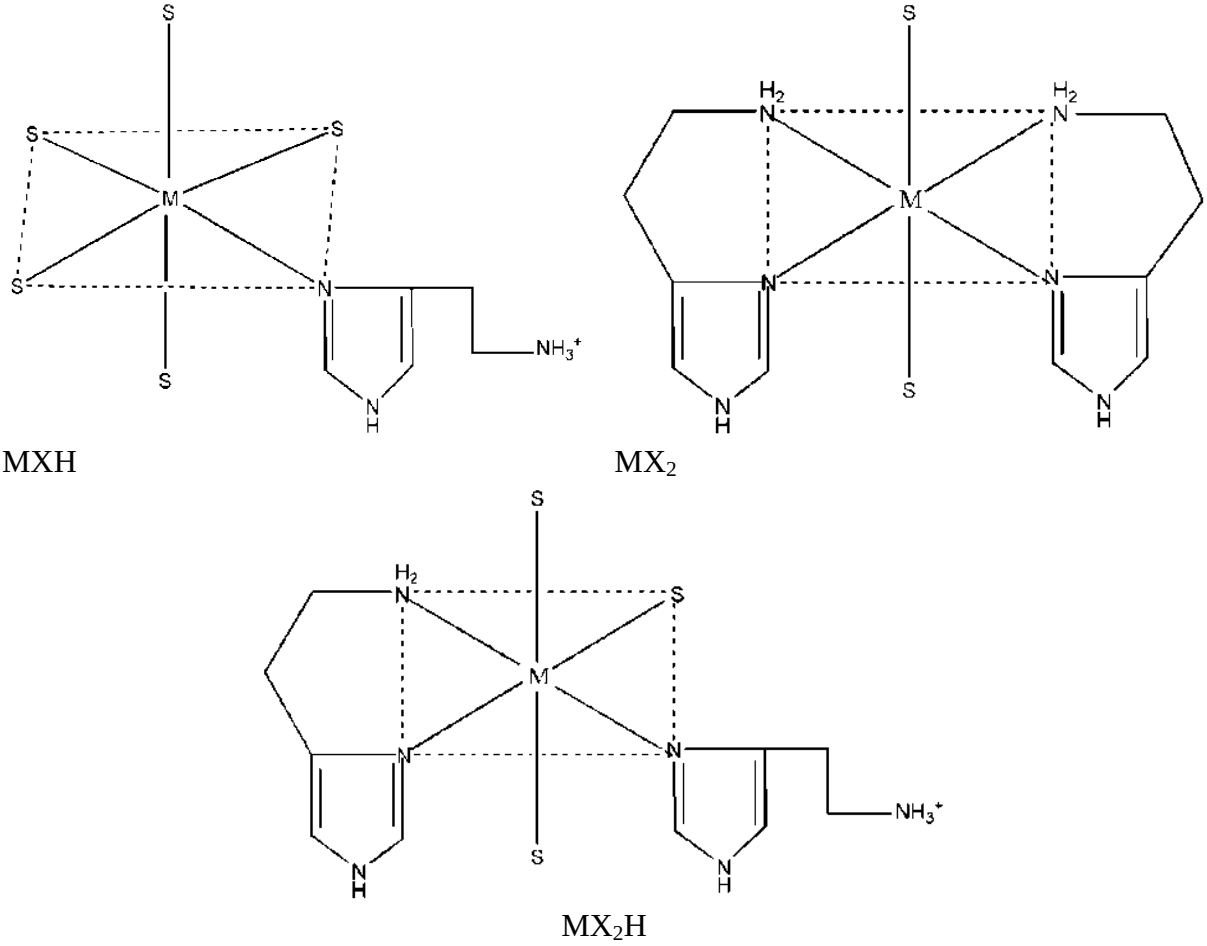

Fig. 3: Him-M(II) metal ligand complexes, S is solvent or water.

11. Conclusion

Histamine forms complexes with Ca(II), Mg(II) and Zn(II) TX100-watermixture are described below, the complexes are formed in the pH range 2.0-10.0. The dominance of electrostatic forces over non-electrostatic forces is indicated by the linear fluctuation of stability constants as a function of the medium's dielectric constant. The formed complexes in the present investigation between metal and ligand are MXH, $MX_2$and MX_2H. The statistical parameters obtained in the present study indicate the best-fit of the present model. The effect of errors on the stability can be understood in the following way, the concentration of alkali shows major effect on the stability constants of metal ligand complexes and log F values shows very less effect, which is represented as alkali > acid > ligand.> metal > total volume >LogF.

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