INTERNATIONAL JOURNAL OF PHARMACEUTICS & DRUG ANALYSIS

VOL.6, ISSUE 12, 2018; 621 - 632; http://ijpda.com; ISSN: 2348-8948

Research Article

Potentiometric Studies On The Formation Equilibria Of Ternary Complexes Of Lead (Ii), Cadmium (Ii), And Mercury (Ii) With Maleic Acid And L-Phenylalanine In Dimethylformamide-Water Mixture

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Date Received: 8th November 2018; Date accepted: 24th December 2018; Date Published: 31st December 2018

Abstract

The stability constants of ternary complexes of Pb(II), Cd(II) and Hg(II) ions with Maleic Acid (MA) and L Phenylalanine (F) were determined pH metrically in the concentration range of 0–50 % v/v in Dimethylformamide-Water Mixtures maintaining an ionic strength of 0.16 mol l^{-1} using $NaNO_3$ as an electrolyte at 303.0 K. The Value of Δ log K that is responsible for the extra stability of ternary complexes was discussedbased on statistical parameters and the nature of the species formed. The formation of various ternary species was established by modeling studies using the computer program MINIQUAD75. The best-fit chemical models were selected based on statistical parameters and residual analysis. The species detected are $MLXH_2$, ML_2X and $HML_2XH_2$for Pb (II), ML_2XH, ML_2XH_2 and $MLX_2H_3$for Cd (II) and ML_2XH, $ML_2XH_2$and MLX_2 for Hg (II). The relative stabilities of the mixed ligand complexes were compared with those of the binary complexes. The enhanced stability associated with the ternary complex is attributed to chelate effect, stacking interactions and hydrogen bonding.Influence of the solvent on the speciation was discussed based on the dielectric constant of the medium. The stability of the mixed ligand complexesis discussed in terms of the molecular structure of Maleic acid and L- Phenylalanine as well as the nature of the metal ion.

Keywords: Ternary complexes, Speciation, pH-metric study, Maleic Acid and L Phenylalanine

Introduction

Heavy metals are common in our environment and diet and many of them are essential to living organisms but some of them are highly toxic or become toxic given sufficient exposure and accumulation in the body. Metals such as Hg, Cd, Pb, Sn, Cr and As are generally not required for metabolic activity and are toxic to living organisms even at low concentrations [1]. The mechanism of the toxicity of metals is very complicated. Generally, toxicity of metals results from blocking the essential biological functional groups (-OH, -SH, and –N) or modifying the active conformation of biomolecules (enzyme, DNA, etc.,) through binding and displacing the essential metal ions from their natural binding sites of the bio-molecules with a foreign metal ion. Lead, cadmium, and mercury are among the various toxic metals especially prevalent in nature due to their high industrial use. These metals serve no biological function and their presence in tissues reflects contact of the organism with its environment [2]. The main sources of lead pollution from the battery industry, leaded petrol and gasoline exhaust which affects every organ of the body, specially the bones and teeth, the kidneys, and the nervous, cardiovascular, immune and reproductive systems [3, 4]. Lead also interferes with the normal metabolism of calcium in cells and causes it to build up within them [5].

The sources of Cd pollution in urban areas are metallurgical plants, Cd plating and battery fabricators. It can also enter the environment through natural causes, such as volcanic activity and forest fires [6]. Human exposure to cadmium mainly occurs through cigarette smoking [7]. However, exposure can also occur through contaminated food [8], water or air [9]. Cadmium is a known carcinogen to mammals [10]. Cadmium

interacts with calcium in the skeletal system to produce osteodystropies [11]. Mercury exposure is related to the release of mercury forms (Hg (0), inorganic Hg (II), and organic Hg into the environment by both natural and man -made activities [12]. Mercury is a highly toxic element because of its accumulative and persistent character in the environment and living organisms [13]. It affects the immune system, alters genetics and enzyme systems, and damages the nervous affinity for the protonated forms of thiol ligands such as cysteine [14].Therefore, Hg (II) binds strongly with the thiol group of proteins, enzymes and other bio-molecules in which this binding changes the conformation of bio-molecules in their active site [15].

Speciation studies of toxic and essential 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. The possible ligand groups in proteins are the amino acid side chains, the terminal amino, carboxyl and thiol groups and, in some cases, the amide group is the peptide backbone [16]. Chemical speciation of metals is important for understanding of their distribution, mobility, toxicity, and for setting environmental quality standards [17]. Bioavailability of a particular metal depends on its complex chemical reactions of dissolution, binding and complexation with the constituents of the environmental aquatic media [18]. To reveal the solvent effects on equilibrium processes involving charged species, we have studied the complex formation of L-phenylalanine and maleic acid with Pb (II), Cd (II) and Hg (II) as a good example in modelling of the bonding modes of peptides to toxic metal ions in mixtures containing Dimethyl form amide (DMF) and water.

L-phenylalanine (F) is nonpolar α-amino acid because of the hydrophobic nature of the benzyl side chain with the formula $C_6H_5CH_2CH(NH_2)COOH$. This is essential amino acid, one of the 20 common amino acids used to form proteins biochemically. F actively participates in acido-basic equilibria especially in physiological pH conditions. F has two functional groups and one is protonated, amino group followed by one carboxylic group. Hence, F has bidentate behavior resulting in five membered ring structures. Nitrogen donor atoms can associate with hydrogen ions in physiological pH ranges [10].

Maleic acid (MA) is a dicarboxylic acid and acts as bidentate ligand resulting in seven membered ring structures. There is often significant competition between hydrogen and metal ion for the donor sites. To reveal the solvent effects on equilibrium processes involving charged species, we have studied the complex formation of F and MA with Pb (II), Cd (II) and Hg (II) as a good example in modelling of the bonding modes of peptides to toxic metal ions in mixtures containing Dimethylformamide (DMF) and water [11].

N, N-Dimethylformamide (DMF) is an organic compound and a common solvent for chemical reactions which is miscible with water and the majority of organic liquids.It is a polar aprotic solvent with a high boiling point, which facilitates reactions that follow polar mechanisms. It can be hydrolyzed by strong acids and bases, especially at elevated temperatures [19].

MATERIALS AND METHODS

Chemicals

DMF (Qualigens, India) was used as received. Aqueous solutions of L-Phenylalanine and Maleic acid of 0.05 mol L^{-1} (GR grade, Loba, India) and Hydrochloric acid of 0.2 mol L^{-1} (AR, E-Merck) were prepared in triple-distilled deionized water. Sodium nitrate (Qualigens, India) of 2 mol L^{-1} was prepared to maintain the ionic strength in the titrand. 0.1 mol L^{-1} solutions of Pb (II), Cd (II) and Hg (II) nitrate (E-Merck, Germany) were prepared. To increase the solubility of ligands and to suppress the hydrolysis of metal salts, the mineral acid concentration in the above solutions was maintained at 0.05 mol L^{-1}. Sodium hydroxide (Qualigens, India) of 0.4 mol L^{-1} was prepared [11]. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one-way classification (ANOVA) by using the computer program, COST [20]]. The strengths of alkali and mineral acid were determined using the Gran plot method [21].

Apparatus

The titrimetric data were obtained using ELICO (Model LI-120) pH meter (readability 0.01), which was calibrated with 0.05 mol L^{-1} potassium hydrogen phthalate in acidic region and 0.01 mol L^{-1} borax solution in basic region. The glass electrode was equilibrated in a well-stirred DMF-water mixture containing the inert electrolyte. All the titrations were carried out in the medium containing varying concentrations of DMF-water mixtures (0-50% v/v) by maintaining an ionic strength of 0.16 mol L^{-1} with sodium nitrate at 303±0.1 K. The effect of variation in asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon

dioxide on the response of glass electrode was accounted for in the form of correction factor [22].

Table .1: Parameters of best-fit chemical models of F and MA complexes of Pb (II), Cd (II) and Hg (II) in DMF-water mixtures. Temperature=303 K, Ionic strength=0.16 mol dm^{-3}.

% v/v DMF	log β(SD)					pH-Range	NP	U_{corr} ×10^8	χ^2	Skewness	Kurtosis	R-factor
	$MLXH_2$	ML_2XH	ML_2XH_2	MLX_2H_3	MLX_2							
Pb(II)												
0.0	22.33(5)	22.26(2)	28.72(3)	-	-	3.0-8.6	58	2.40	36.51	1.04	8.14	0.0831
10	22.05(6)	21.81(0)	28.36(5)	-	-	3.0-7.6	66	6.11	32.14	-0.53	5.02	0.0182
20	22.10(5)	21.22(6)	27.40(9)	-	-	3.0-7.6	55	8.34	17.50	-0.42	3.03	0.0203
30	22.36(2)	20.61(7)	27.72(4)	-	-	3.0-7.6	67	2.22	28.01	-1.02	9.83	0.0101
40	21.55(9)	20.17(9)	27.19(7)	-	-	3.0-7.6	55	9.34	20.54	0.12	4.90	0.0212
50	20.71(4)	20.04(6)	26.82(7)	-	-	3.0-7.6	45	6.32	21.37	-0.60	6.04	0.0300
Cd(II)												
0.0	-	21.93(1)	28.93(5)	30.52(0)	-	3.0-9.4	59	7.43	22.34	1.13	6.93	0.0821
10	-	22.91(5)	28.33(6)	30.71(4)	-	3.0-7.4	44	4.62	13.16	0.54	3.63	0.0162
20	-	21.61(3)	27.75(9)	30.39(6)		3.0-7.4	66	5.32	17.20	-0.23	4.11	0.0171
30	-	21.44(7)	27.91(4)	30.11(7)	-	3.0-7.4	72	1.50	21.42	-0.05	2.40	0.0381
40	-	19.55(9)	25.83(7)	29.08(8)	-	3.0-7.4	55	3.85	31.18	0.39	4.81	0.0222
50	-	19.23(8)	25.72(7)	29.35(7)	-	3.0-7.4	66	3.71	11.16	0.33	5.02	0.0142
Hg(II)												
0.0	-	22.84(4)	28.51(5)	-	13.45(1)	2.4-6.8	66	1.54	18.00	0.38	3.30	0.0031
10	-	23.81(6)	29.37(6)	-	15.46(7)	3.0-6.8	77	7.33	15.03	0.42	4.02	0.0201
20	-	23.93(9)	30.29(9)	-	14.19(9)	3.0-6.8	64	6.32	13.81	-0.05	3.06	0.0171
30		23.41(2)	29.38(7)	-	14.23(8)	3.0-6.8	53	3.50	11.90	-0.16	2.94	0.0137
40	-	23.59(4)	29.38(8)	-	14.44(7)	3.0-6.8	58	7.29	12.23	-0.19	2.81	0.0191
50	-	23.65(7)	28.89(6)	-	15.19(5)	3.0-6.8	80	6.53	11.39	0.234	2.82	0.0165

Ucorr= U/ (NP-m) x 108; NP = Number of points; m = number of constants; SD = Standard deviation

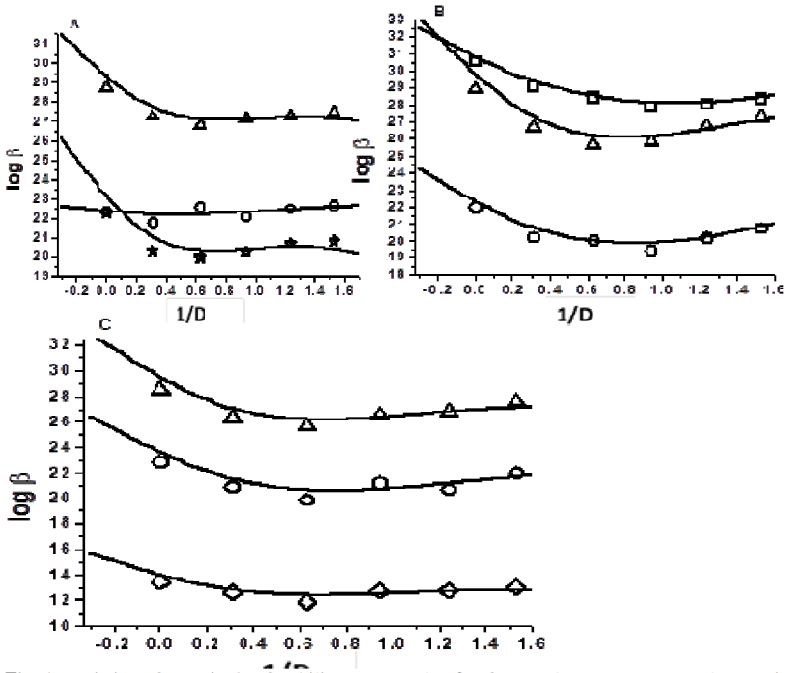

Fig. 1: Variation of magnitude of stability constant (log β) of F-metal-MA ternary complex species in DMF-water mixtures: (A) Pb(II) (B) Cd(II) (C) Hg(II): (○) $\log\beta_{ML2XH}$, (Δ) $\log\beta_{ML2XH2}$, (☆) $\log\beta_{MLXH2}$, (□)$\log\beta_{MLX2H3}$,(◊) $\log\beta_{MLX2}$, respectively

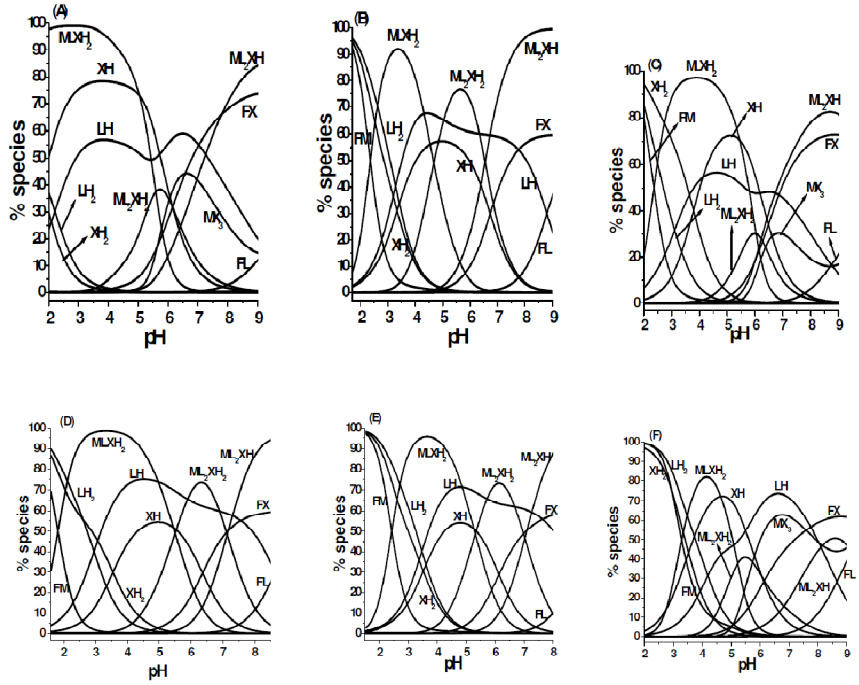

Fig.2: Distribution diagrams of F-Pb (II)-MA complexes in DMF-water mixtures % v/v (A) 0.0, (B) 10, (C) 20, (D) 30, (E) 40 and (F) 50.

Procedure

Initially strong acid was titrated against alkali at regular intervals to check the complete equilibration of the glass electrode. Then the calomel electrode was refilled with DMF-water mixture of equivalent composition as that of the titrand. In each of the titrations, the titrand consisted of approximately 1 m mol mineral acid in a total volume of 50 ml. Titrations with different ratios (1:2.5, 1:3.75 and 1:5) of metal-to-ligand were carried with 0.4 mol L^{-1} sodium hydroxide [23].

Modeling Strategy

The computer program SCPHD [24] was used to calculate the correction factor. By using pH metric titration data, the ternary stability constants were calculated with the computer program MINIQUAD75 [23]. Which exploit the advantage of constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of ternary systems, the correction factor and stability constants of MA and F and their ternary complexes with Pb (II), Cd (II) and Hg (II) in DMF-water mixtures were fixed.

RESULTS AND DISCUSSION

The results of the best-fit models that contain the stoichiometry of the complex species and their overall formation constants along with some of the important statistical parameters are given in Table 1. Very low standard deviation in overall stability constants (log β) signifies the precision of these constants. The small values of Ucorr (sum of squares of deviations in concentrations of ligand and hydrogen ion at all experimental points corrected for degrees of freedom), small values of mean, standard deviation and mean deviation for the systems are validated by the residual analysis [24].

Residual Analysis

In data analysis with least squares methods, the residuals (the differences between the experimental data and the data simulated based on model parameters) are assumed to follow Gaussian or normal distribution. When the data are fit into the models, the residuals should ideally be equal to zero. If statistical measures of the residuals and the errors are assumed in the models are not significantly different from each other, the model is said to be adequate. Further, a model is considered adequate only if the residuals do not show any trend. Respecting the hypothesis that the errors are random following normal distribution in the least squares analysis, the residuals are tested for normal distribution [25]. Such tests are $\chi 2$, skewness, kurtosis and R factor. These statistical parameters show that the best-fit models portray the metal-ligand species in DMF-water mixtures, as discussed below.

χ^2 Test

$X^2$is a special case of gamma distribution whose probability density function is an asymmetrical function. This distribution measures the probability of residuals forming a part of standard normal distribution with zero mean and unit standard deviation [26]. If the calculated $\chi 2$ is less than the table value, the model is accepted.

Crystallographic R-test

Hamilton's R factor ratio test is applied in complex equilibria to decide whether inclusion of more species in the model is necessary or not. In pH-metric method, the readability of pH meter is taken as the Rlimit, which represents the upper boundary of R beyond which the model bears no significance [27]. When there are different numbers of species the models with values greater than R-table are rejected. The low crystallographic R-values given in Table 1 indicate the sufficiency of the model.

Skewness

It is a dimensionless quantity indicating the shape of the error distribution profile. A value of zero for skewness indicates that the underlying distribution is symmetrical. If the skewness is greater than zero, the peak of the error distribution curve is to the left of the mean and the peak is to the right of the mean if skewness is less than zero. The values of skewness recorded in Table. 1.are between -1.02 and 1.04 for Pb (II), -0.23 and 1.13 for Cd (II) -0.19, and 0.42 for Hg (II). These data evince that the residuals form a part of normal distribution; hence, least-squares method can be applied to the present data.

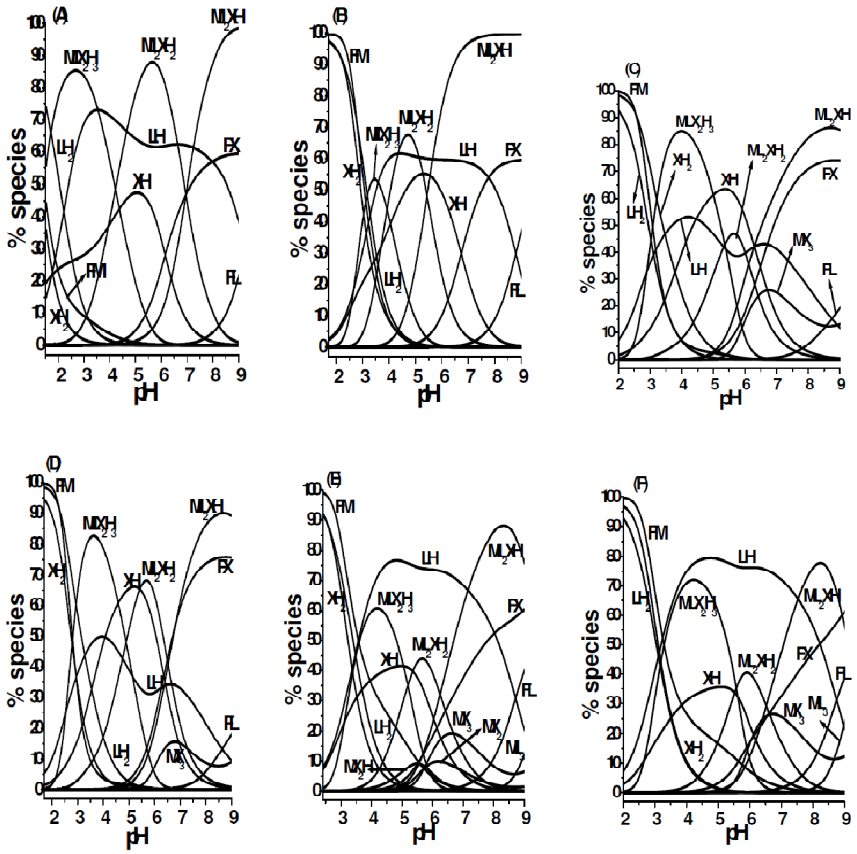

Fig. 3: Distribution diagrams of F-Cd (II)-MA complexes in DMF-water mixtures % v/v (A) 0.0, (B) 10, (C) 20, (D) 30, (E) 40 and (F) 50.

Kurtosis

It is a measure of the peakedness of the error distribution near a model value. For an ideal normal distribution, kurtosis value should be three (mesokurtic). If the calculated kurtosis is less than three, the peak of the error distribution curve is flat (platykurtic) and if the kurtosis is greater than three, the distribution shall have sharp peak (leptokurtic) [27]. The kurtosis values in the present study indicate that the residuals form leptokurtic pattern.

Effect of systematic errors on best-fit model

In order to rely upon the best fit 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 influential parameters like concentrations of alkali, mineral acid, ligand and metal (Table 2). The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > metal > ligand > volume > log F. Some species were even rejected and the standard deviation is high in few cases when errors are introduced in the concentrations. The rejection of some species and increased standard deviations in the stability constants on introduction of errors conform the appropriateness of the chosen best-fit models. This study also indicates the relative sensitivities of model parameters.

Effect of Solvent

DMF is a polar aprotic solvent. The dielectric constant of DMF-water mixture decreases with increasing concentration of DMF and these solutions are expected to mimic physiological conditions where the concept of the equivalent solution dielectric constant for protein cavities is applicable [28]. The increase in organic solvent content decreases the dielectric constant of the medium. The change in log β values of Pb(II), Cd(II) and Hg(II) complexes of F and MA with 1/D (Fig. 1 is almost linear which indicates that the dielectric constant or long range interactions are responsible for the stability trend in both DMF-

water media. The deviation from linearity may be due to some contributions from non- electrostatic forces.

Table 2: Effect of errors in influential parameters on the stability constants of ternary complexes of Cd (II) with F-MA in 20% (v/v) DMF-water mixture

Ingredient	% Error	Log β_{mlxh}(SD)		
		1211	1212	1123
Alkali	0	21.61(3)	27.75(9)	30.39(6)
	-5	Rejected	26.84(55)	31.58(43)
	-2	19.46(39)	26.37(44)	30.33(48)
	+2	Rejected	26.14(66)	Rejected
	+5	Rejected	Rejected	Rejected
Acid	-5	Rejected	Rejected	Rejected
	-2	23.76(93)	29.42(95)	Rejected
	+2	19.21(19)	26.11(19)	30.29(26)
	+5	16.95(93)	25.84(48)	30.76(31)
Ligand(L)	-5	21.68(44)	27.81(49)	30.36(45)
	-2	21.65(46)	27.76(49)	30.33(33)
	+2	21.58(52)	27.69(58)	30.32(33)
	+5	21.54(52)	27.66(48)	30.29(37)
Ligand(X)	-5	23.03(93)	28.76(93)	30.71(94)
	-2	22.19(54)	28.17(52)	30.45(53)
	+2	21.14(33)	27.42(29)	30.26(29)
	+5	20.59(25)	27.12(22)	30.29(14)
Metal	-5	21.84(52)	27.84(45)	30.37(46)
	-2	21.68(46)	27.77(42)	30.34(39)
	+2	21.51(41)	27.67(37)	30.30(34)
	+5	21.37(37)	27.61(34)	30.29(29)
Log F	-5	21.56(43)	27.68(39)	30.34(34)
	-2	21.58(43)	27.74(37)	30.33(35)
	+2	21.63(44)	27.77(38)	30.35(36)
	+5	21.69(44)	27.75(37)	30.34(37)
Volume	-5	21.63(45)	27.76(41)	30.36(39)
	-2	21.62(44)	27.75(37)	30.35(36)
	+2	21.58(43)	27.73(39)	30.35(36)
	+5	21.57(45)	27.72(44)	30.36(37)

Stability of Ternary Complexes

The change in the stability of the ternary complexes as compared to their binary analogues was quantified [29] based on the disproportion constant (log X) given by Equation 1 which corresponds to the equilibrium as shown Eq. 2.

$$\log X = 2\log K^{M}_{MLX} - \log K^{M}_{ML} - \log K^{M}_{MX} \quad \text{.....1}$$

$$ML_2 + MX_2 \rightleftharpoons 2\,MLX \quad \text{.....2}$$

Under the equilibrium conditions one can expect the formation of 50% ternary complexes and 25%

each of the binary complexes statistically and the value of log X shall be 0.6 [30]. A value greater than this, accounts for the extra stability of MLX. Another approach to quantify the stability of ternary complexes was based on the difference in stability (Δlog K) for the reactions ML with X and M (aq) with L and X, where L is the primary ligand (MA) and X is the secondary ligand (F). It is compared with that calculated purely on the statistical grounds as given in Eq. 3.

$$\Delta \log K = \log K^{M}_{MLX} - \log K^{M}_{ML} - \log K^{M}_{MX} \quad \text{.....3}$$

Various possible log K values obtained from these equations are given in Table 3. In the present study, the log K values range from 1.301 to 1.458 for Pb (II), 1.283 to 1.461 for Cd (II) and 1.128 to 1.469 for Hg (II) and all values are found to be higher than those expected on statistical bases (0.6). These higher values account for the extra stability of the ternary complexes. The reason for the extra stability of these ternary complexes may be due to interactions outside the coordination sphere such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect and stacking interactions [31].

Distribution Diagrams

Distribution diagrams were drawn using the formation constants of the best fit models and are shown in Figs.2 and 4. The patterns of the distribution of species with pH show that the concentration of species is affected by solvent. This trend depends on the relative solvation of DMF. The distribution diagrams are givenin Figs. 2 to 4 for DMF-water media, which contain protonated and un-protonated species like $MLXH_2$, ML_2XH_2 and ML_2XH for Pb (II) and MLX_2H_3, ML_2XH_2 and ML_2XH for Cd (II) and ML_2XH_2, ML_2XH and MLX_2 for Hg (II). Where M=Pb (II), Cd (II) and Hg (II). The distribution diagrams indicate the relative abundance of various forms of metal ions (chemical speciation) at different pH and dielectric conditions. A stable ternary complex shall be responsible for metal ion transportation in bio-systems and the weak binary metal complexes make the essential metal ions bioavailable. The increased concentrations of complexing agents make the essential metal ions unavailable due to the formation of stable complexes. The formation of the possible complex species can be represented by the following equilibria.

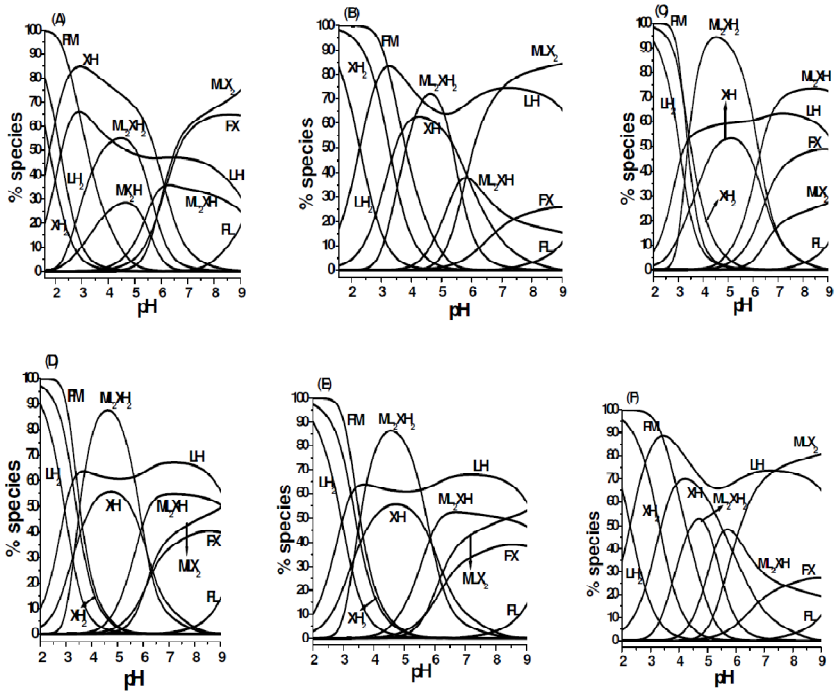

Fig. 4: Distribution diagrams of F-Hg (II)-MA complexes in DMF-water mixtures % v/v (A) 0.0, (B) 10, (C) 20, (D) 30, (E) 40 and (F) 50.

Table 3: Δ log K of ternary complexes of F and MA in DMF-water mixtures

% v/v DMF	Δlog $KMLXH_2$	Δlog KML_2XH	Δlog KML_2XH_2	Δlog $KMLX_2$
Pb(II)				
0.0	1.348	1.347	1.458	-
10	1.343	1.338	1.452	-
20	1.344	1.326	1.437	-
30	1.349	1.314	1.442	-
40	1.333	1.304	1.434	-
50	1.316	1.301	1.428	-
Cd(II)				
0.0	-	1.341	1.461	-
10	-	1.360	1.452	-
20	-	1.334	1.443	-
30	-	1.331	1.445	-
40	-	1.291	1.412	-
50	-	1.283	1.410	-
Hg(II)				
0.0	-	1.358	1.454	1.128
10	-	1.376	1.464	1.189
20	-	1.378	1.481	1.151
30	-	1.369	1.468	1.153
40	-	1.372	1.468	1.159
50	-	1.373	1.469	1.181

$M(II) + LH_2^+ + XH_2$	$\rightleftharpoons$	$MLXH_2^+ + 2H^+$ (1)
$M(II) + 2LH_2^+ + XH_2$	$\rightleftharpoons$	$ML_2XH_2 + 4H^+$ (2)
$M(II) + 2LH_2^+ + XH^-$	$\rightleftharpoons$	$ML_2XH_2 + 3H^+$ (3)
$ML_2H^+ + XH_2$	$\rightleftharpoons$	$ML_2XH_2 + H^+$ (4)
ML_2XH_2	$\rightleftharpoons$	$ML_2XH^- + H^+$ (5)
$M(II) + 2LH_2^+ + XH_2$	$\rightleftharpoons$	$ML_2XH^- + 5H^+$ (6)
$M(II) + 2LH + XH_2$	$\rightleftharpoons$	$ML_2XH^- + 3H^+$ (7)
$M(II) + 2LH_2^+ + XH^-$	$\rightleftharpoons$	$ML_2XH^- + 4H^+$ (8)
$ML_2 + XH_2$	$\rightleftharpoons$	$ML_2XH^- + H^+$ (9)
$ML_2H^+ + XH_2$	$\rightleftharpoons$	$ML_2XH^- + 2H^+$ (10)
$ML_2H^+ + XH^-$	$\rightleftharpoons$	$ML_2XH^- + H^+$ (11)
$M(II) + LH_2^+ + 2XH_2$	$\rightleftharpoons$	$MLX_2H_3 + 3H^+$ (12)
MLX_2H_3	$\rightleftharpoons$	$MLX_2^{3-} + 3H^+$ (13)
$M(II) + LH_2^+ + 2XH_2$	$\rightleftharpoons$	$MLX_2^{3-} + 6H^+$ (14)
$M(II) + LH + 2XH^-$	$\rightleftharpoons$	$MLX_2^{3-} + 3H^+$ (15)
$MX_2^{2-} + LH_2^+$	$\rightleftharpoons$	$MLX_2^{3-} + 2H^+$ (16)
$MX_2^{2-} + LH$	$\rightleftharpoons$	$MLX_2^{3-} + H^+$ (17)

Figs. 2, 3 and 4 show the formation of F-Pb (II)-MA complexes, $MLXH_2$, ML_2XH_2 and ML_2XH in DMF- water mixtures in the pH range 3.0-8.6. In this range total metal ion, participate in bonding. At lower pH the species $MLXH_2$ has high concentration and it is formed by the reaction of FM with LH_2 and XH_2 (Equilibria 1). As the pH, increases the concentration of $MLXH_2$, $LH_2^+$and XH_2 decreased and the concentration of ML_2XH_2 and ML_2XH were increased (Equilibria 2, 3, 6, 7 and 10). Above pH value 6.2, the concentration of ML_2XH_2 species decreases with increasing ML_2XH species indicates that ML_2XH forms through the Equilibria 5, 9, 10 and 11.Figs. 2, 3 and 4show the formation of F-Cd (II)-MA complexes, MLX_2H_3, ML_2XH_2 and ML_2XH in DMF-water mixtures in the pH range3.0-9.4.At lower pH value, the concentration of MLX_2H_3 is high (Equilibria 12). As the pH, value increases the concentration of MLX_2H_3 decreases with increasing the concentration of ML_2XH_2 species (Equilibria 2 and 3). Above 5.2 pH value ML_2XH complex formed while the XH_2 and MX_2H species decreased (Equilibria 10 and 11).Figs. 3, and 4show the formation of F-Hg(II)-MA complexes, MLX_2H_3, ML_2XH_2 and ML_2XH in DMF- water mixtures in the pH range2.4-6.8. At lower pH, the species ML_2XH_2 had high concentration (Equilibria 2 and 3). As the pH increases the concentration of $MLXH_2$, $LH_2^+$and XH_2 decreased and the concentration of ML_2XH is increases (Equilibria 5, 6 and 7). Above pH value 5.4, MLX_2 species has high concentration (Equilibria 13 and 14).

Structures of Ternary Complexes

Depending upon the nature of the ligands and the metal ions and based on the basic chemical knowledge the structures of the ternary complexes were proposed as shown in Figure 5 These structures indicate that F and MA act as monodentate or bidentate ligands depending upon the pH conditions. In highly acidic medium the amino group of L-phenylalanine is protonated and do not participate in coordination as shown in the structure of MLX_2H_3, $MLXH_2$ and ML_2XH_2. In ML_2XH_2 species, phenylalanine act as monodentate and maleic acid acts as bidentate. In mono protonated ternary complexes like ML_2XH, phenylalanine acts as mono and bidentate ligand and maleic acid act as only bidentate and the proton is on phenylalanine but not on maleic acid. Therefore, the species is M (L_2H) X but not M (L_2) (XH).

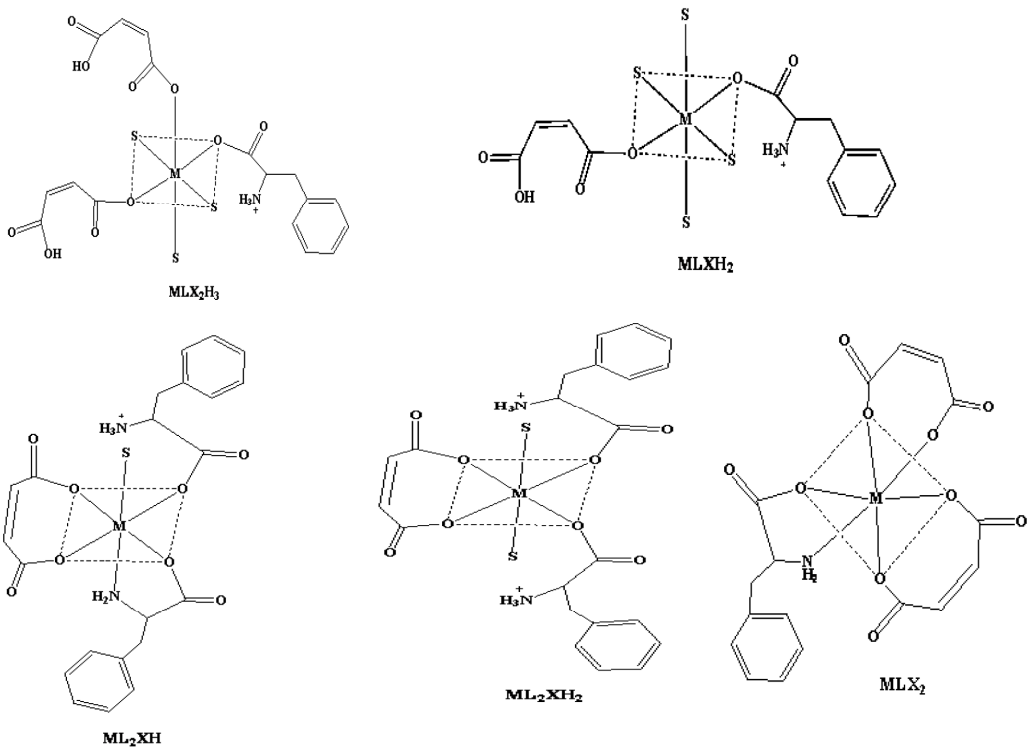

Fig. 5: structures of ternary complexes of F and MA with Pb (II), Cd (II) and Hg (II)

CONCLUSION

A study of the speciation of ternary complexes of Pb (II), Cd (II) and Hg (II) with F and MA in DMF-water media reveals the compartmentalization of metabolic reactions. The following conclusions have been drawn from the modeling studies: The ternary metal complex species detected are $MLXH_2$, ML_2XH and ML_2XH_2 for Pb(II), ML_2XH, ML_2XH_2,and MLX_2H_3 for Cd(II) and ML_2XH, ML_2XH_2 and MLX_2 for Hg(II) where L = MA and X = F. The values of Δ log K indicate that the ternary species have extra stability compared to their binary species, may be due to the interactions outside the coordination sphere, such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect, stacking interactions and the electrostatic interaction between non-coordinated charge groups of the ligands. The magnitudes of the stability constants for ternary complexes are affected by the errors in the influential parameters like the concentrations of the ingredients. The order of influence is alkali > acid > metal > ligand > volume > log F. The study also gives an insight into the metal availability metal transport in bio fluids. The ternary complexes are more amenable for "metal transport" because of their extra stability.

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