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STABILITY OF BINARY COMPLEXES OF Pb(II), Cd(II) AND Hg(II) WITH MALEIC ACID IN TX100-WATER MIXTURES

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ABSTRACT. Binary complexes of maleic acid with toxic metal ions such as Pb(II), Cd(II) and Hg(II) have been studied in 0.0-2.5% v/v tritonX-100 (TX100) - water media at 303 K at an ionic strength of 0.16 M. The active forms of the ligand are LH_2, LH^- and L^{2-}. The derived 'best fit' chemical speciation models are based on crystallographic R-factors, χ^2 and Skewness and Kurtosis factors. The predominant species formed are of the type ML_2, ML_2H and ML_3. The trend in variation of complex stability constants with change in the mole fraction of the medium is explained on the basis of prevailing electrostatic and non-electrostatic forces. The species distribution as a function of pH at different compositions of TX100-water mixtures and plausible speciation equilibria are presented and discussed.

KEY WORDS: Maleic acid, TritonX-100, Toxic metal ions, Mole fraction, Binary complexes

INTRODUCTION

The toxicity, bio-availability, bio-degradability, bio-accumulation, persistence, mobility, solubility, extractability and many other critical properties of chemical species depend on their form and nature [1-3]. Speciation analysis or simply 'speciation' is the determination and characterisation of these species. Speciation has gained wide recognition as a major characteristic of inorganic chemistry, since knowledge of the total concentration of an element in a specific medium is often inadequate to explain its properties and function. The term speciation encompasses two connotations 'functional' and 'operational'. This may overlap but are not identical. Functionally we may identify and distinguish between species that are, for example, available to plants or ecotoxic species of an element that are more easily exchangeable in mineral surfaces than others.

The International Union of Pure and Applied Chemistry (IUPAC) [4] has differentiated 'speciation' from 'functionality' by defining speciation as the process yielding evidence of the molecular form of an analyte. However, even if this is the objective of all studies, operationally speciation is determined by the physicochemical properties of the real natural entities. Speciation refers, to the determination of the concentration of various fractions, which are clusters of species having different physicochemical properties and as such are extractable or detectable under specific conditions.

The role of micelles is simple, but vital, resulting in compartmentalization of the energy transfer partners. Additionally the micro-environment created around the micelle favors dissociation of complexes. By binding the metal ions electrostatically to the negatively charged micellar surface, their effective concentration is substantially increased. The concentration of these counter cations in the micellar surface has been estimated [5] to be around 3.0 M. A literature survey [6, 7] reveals that increased concentration of micellised surfactant leads to the distribution of the reactants over a wide micelle concentration range which leads to reactants dilution in the micellar pseudo phase and decreases the observed rate constants. Micellar effects

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on reactivity are generally independent of changes in micellar size and shape. The effect of micelles on overall reaction rates and equilibria depends upon the incorporation of solutes into the micellar pseudo phase. Also, the species with lower charge or higher hydrophobicity are stabilized in the micellar pseudo phase. Thus, metal ligand combinations resulting in neutral complexes are favored. It has been demonstrated that water insoluble metal chelates can be solubilised with a micellar solution of non-ionic surfactant such as TX100. This solubilisation technique is frequently utilized in analytical procedures [8]. Since TX100 is a non-ionic surfactant, it is expected to destabilize charged species in aqueous solutions. This paper reports a speciation study of binary complexes of Pb(II), Cd(II) and Hg(II) with maleic acid using non-ionic micelles to stabilize intermediates.

EXPERIMENTAL

Materials

Maleic acid (E-Merck, Germany) solution (0.05 M) was prepared in triple-distilled deionised water by maintaining 0.05 M nitric acid concentration to increase the solubility. TX100 (Merck, India) was used as received. 2 M sodium nitrate (Qualigens, India) was prepared to maintain the ionic strength in the titrand. 0.1 M^1 aqueous solutions of Pb(II), Cd(II) and 0.05 M aqueous solution of Hg(II) nitrates were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple-distilled water maintaining 0.05 M nitric acid to suppress the hydrolysis of metal salts. All the solutions were standardized by standard methods. To assess errors in concentration determinations, the data were subjected to analysis of variance of one way classification [9]. The strengths of alkali and mineral acid were determined using the Gran plot method [10, 11].

Instrumentation

The titrimetric data were obtained using an ELICO (Model LI-120) pH meter (readability 0.01), which was calibrated with 0.05 M potassium hydrogen phthalate in acidic region and 0.01 M borax solution in basic region. The glass electrode was equilibrated in a well-stirred TX100-water mixture containing the inert electrolyte. All the titrations were carried out in a medium containing varying concentrations of TX100-water mixtures (0.0-2.5% v/v) by maintaining an ionic strength of 0.16 M with sodium nitrate at 303.0 ± 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 the glass electrode was accounted for by a correction factor [12, 13].

Analytical procedures

For the determination of stability constants of metal-ligand binary species, initially titrations of strong acid with alkali were carried out at regular intervals to check whether complete equilibration was achieved. Then the calomel electrode was refilled with TX-water mixture of equivalent composition as that of the titrand. In each of the titrations, the titrand consisted of approximately 1 mmol mineral acid in a total volume of 50 mL. Titrations with different ratios (1:2.5, 1:3.75 and 1:5.0 in the case of Pb(II) and Cd(II) and 1:7.5, 1:8.5 and 1:10.0 in the case of Hg(II)) of metal-to-ligand were carried out with 0.4 M sodium hydroxide. Other experimental details are as reported previously [14, 15].

Modeling strategy

The computer program SCPHD [16] was used to calculate the correction factor. By using the pH-metric titration data, the binary stability constants were calculated with the computer

program MINIQUAD75 [17], which exploit the advantage of the constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of binary systems, the correction factor and the protonation constants of maleic acid were fixed. The variation of stability constants with the mole fraction of the medium was investigated on electrostatic and non-electrostatic forces on the basis of solute-solute and solute-solvent interactions.

RESULTS AND DISCUSSION

The results of the final 'best-fit' models that reveal the stoichiometry of the complex species and their overall formation constants along with some of the associated statistical parameters are given in Table 1. Very low-standard deviation in overall stability constants (log β) signifies the precision of these data. The small values of U_{corr} (sum of squares of deviations in concentrations of ingredients at all experimental points) corrected for degrees of freedom, small values of mean, standard deviation and mean deviation for the systems studied are validated by the residual analysis [18, 19].

Table 1. Parameters of 'best fit' models of Pb(II), Cd(II) and Hg(II) - maleic acid complexes in TX100-water mixtures.

% v/v TX100	log β_{mlh} (SD)			pH-range	NP	U_{corr}	χ^2	Skewness	Kurtosis	R-factor
	ML_2	ML_2H	ML_3							
Pb (II)										
0.0	6.65(25)	11.61(27)	10.15(23)	2.8-7.7	41	22.11	116.41	4.11	20.90	0.0498
0.5	7.49(20)	12.29(24)	10.60(24)	2.8-6.6	19	1.25	20.33	3.59	19.23	0.0466
1.0	7.40(25)	12.68(24)	10.26(25)	3.8-6.2	19	28.12	22.02	-1.54	5.28	0.0592
1.5	7.29(13)	12.56(14)	10.63(13)	3.8-6.2	26	0.43	3.23	0.52	2.98	0.0174
2.0	7.47(22)	12.31(25)	10.56(24)	3.8-6.2	28	18.80	3.62	0.49	4.16	0.0466
2.5	7.65 (13)	12.43(26)	10.75(29)	4.0-6.0	20	4.71	12.00	0.31	4.40	0.0244
Cd (II)										
0.0	6.76(18)	11.73(24)	10.32(12)	4.0-7.2	24	3.18	5.11	0.26	3.14	0.0152
0.5	6.90(23)	12.26(26)	10.25(25)	4.6-6.8	20	7.06	2.93	-0.38	2.89	0.0303
1.0	6.46(23)	12.19(22)	9.80(20)	4.0-7.2	26	4.78	19.23	1.39	4.38	0.0235
1.5	6.68(09)	11.92(15)	9.81(11)	4.1-7.2	28	1.20	14.29	0.95	4.54	0.0130
2.0	6.61(14)	11.99(19)	9.80(14)	4.1-7.2	28	2.00	8.76	0.93	3.90	0.0169
2.5	6.64(14)	11.86(17)	10.20(08)	4.1-7.0	26	0.87	6.10	1.55	3.32	0.0112
Hg (II)										
0.0	6.93(26)	12.75(25)	9.35(29)	4.2-6.4	21	7.22	3.92	1.14	5.11	0.0291
0.5	6.64(23)	12.11(25)	9.32(25)	3.6-5.8	19	11.87	4.05	0.33	3.95	0.0343
1.0	6.55(05)	12.65(03)	9.37(14)	2.2-5.8	23	1.50	9.49	0.29	4.17	0.0138
1.5	6.62(20)	12.31(19)	9.45(26)	3.6-6.4	26	3.91	4.67	0.48	2.91	0.0234
2.0	6.60(17)	12.32(18)	9.53(21)	3.6-6.4	24	2.38	2.89	0.30	3.21	0.0196
2.5	6.56(22)	12.58(14)	9.50(27)	3.4-7.0	14	0.91	7.14	-0.04	2.20	0.0162

U_{corr} = U/ (NP-m) X 10^8; NP = number of points; m = number of protonation constants; SD = standard deviation.

Residual analysis

In data analysis involving 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 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, the residuals are tested for normal distribution. Such tests are χ^2, skewness, kurtosis and R-factor. These statistical parameters show that the 'best-fit' models reveal the metal-ligand species in TX100-water mixtures.

χ^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. The kurtosis values in this study indicate that the residuals form a leptokurtic pattern. The values of skewness recorded in Table 1 are between -1.54 and 4.11 for Pb(II), -0.38 and 1.55 for Cd(II) and -0.04 and 1.14 for Hg(II). These data show that the residuals form part of a normal distribution. Hence, the least squares method can be applied to the present data. The sufficiency of the model is further evident from crystallographic *R*-values. These statistical parameters thus show that the 'best-fit' models characterise the metal-ligand species in TX100 media.

Effect of systematic errors on 'best fit' model

In order to rely upon the 'best-fit' model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was undertaken by introducing pessimistic errors in the influential parameters such as concentrations of alkali, mineral acid, ligand, metal, log F and volume (Table 2).

Table 2. Effect of errors in influential parameters on Hg(II)-maleic acid complex stability constants in 2% v/v TX100-water mixture.

Ingredient	% Error	Log β_{mlh}(SD)		
		ML_2	ML_2H	ML_3
Acid	0	6.60(17)	12.32(18)	9.53(21)
	-5	10.05(43)	15.56(35)	13.96(34)
	-2	7.53(28)	13.38(27)	11.00(29)
	+2	6.08(05)	11.02(32)	Rejected
	+5	5.06(11)	Rejected	Rejected
Alkali	-5	Rejected	Rejected	Rejected
	-2	5.83(05)	10.89(35)	Rejected
	+2	7.79(39)	13.68(36)	11.51(37)
	+5	11.89(74)	17.40(45)	16.44(41)
Ligand	-5	6.94(44)	13.00(22)	10.69(23)
	-2	6.73(24)	12.60(18)	10.02(20)
	+2	6.46(13)	12.00(20)	8.95(29)
	+5	6.21(07)	11.50(21)	Rejected
Metal	-5	6.62(20)	12.39(18)	9.68(20)
	-2	6.61(18)	12.34(18)	9.59(21)
	+2	6.59(16)	12.29(18)	9.47(22)
	+5	6.57(15)	12.25(18)	9.38(23)
Volume	-5	6.71(24)	12.57(18)	9.98(20)
	-2	6.72(24)	12.59(18)	10.00(20)
	+2	6.75(24)	12.62(18)	10.04(20)
	+5	6.76(24)	12.63(180	10.06(20)
Log F	-5	6.71(23)	12.56(19)	9.92(21)
	-2	6.72(24)	12.59(18)	9.99(20)
	+2	6.73(25)	12.61(18)	10.05(20)
	+5	6.74(26)	12.64(18)	10.11(19)

The order of the components that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > metal > ligand > total volume > log F. Some species

were even rejected when errors were introduced in the concentrations. The rejection of some binary species and increased standard deviations in the stability constants on introduction of errors confirm the suitability of the experimental conditions (concentrations of components) and choice of the best-fit models.

Effect of solvent

Variations in the magnitudes of formation constants of the complex species formed due to the interaction between metal ions and maleic acid with mole fraction of the surfactants present are shown in Figure 1, which indicates that the stabilities of the complexes varied linearly with mole fraction of the TX100 media. The linearly increased/decreased stability of the complexes with increased surfactant concentration may be due to the increased number of micelles and decreased dielectric constant of the medium. The dielectric constant of the medium has a direct influence on the protonation-deprotonation equilibria [20, 21]. According to Born's equation [22] the energy of electrostatic interactions is related to dielectric constant of the medium and log β versus $n_x \times 10^3$ (mole fraction of the medium) should be linear.

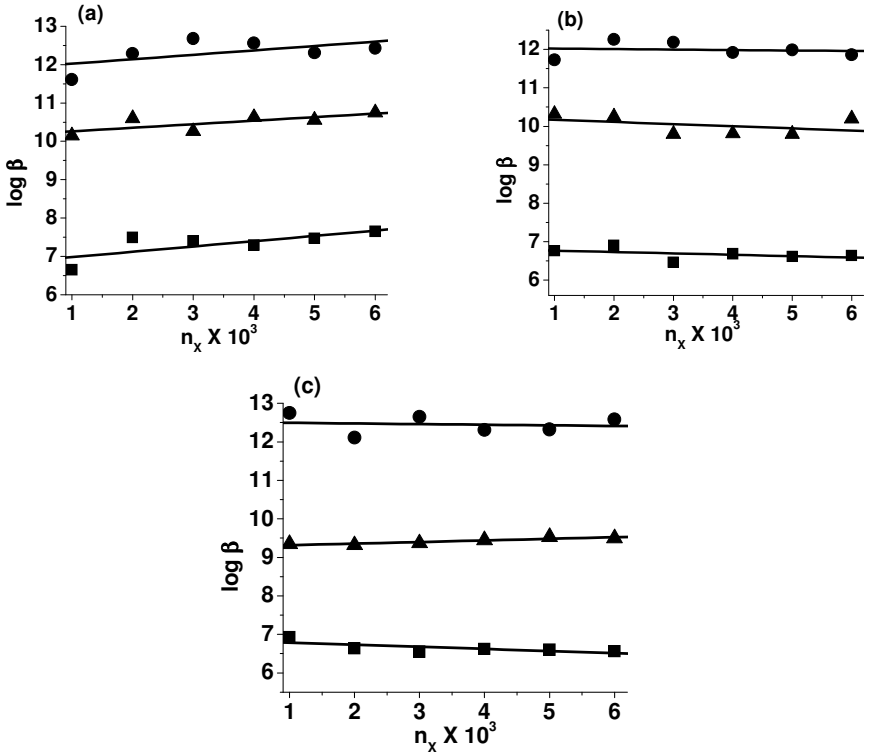

Figure 1. Variation of overall stability constant values of metal-maleic acid complexes with mole fraction ($n_x \times 10^3$) of TX100-water mixtures (a) Pb(II); (b) Cd(II); (c) Hg(II); (■)log β_{ML2}; (▲) log β_{ML3}; (●) log β_{ML2H}.

The linear variation of log β values of maleic acid complexes of Pb(II), Cd(II) and Hg(II) with mole fraction shows in Figure 1 indicates that the dominance of electrostatic solute-solvent interactions. The anion stabilizing nature of co-solvent, specific solvent-water interactions, charge dispersion and specific interactions of co-solvent with the solute may be responsible for the observed small deviations from a linear relationship. This study is helpful in understanding the co-solvent effect at the molecular level [23-25] and provides useful information in drug design.

Distribution diagrams

Maleic acid is a bidentate ligand that has two dissociable (carboxyl groups) protons. The different forms of maleic acid are LH_2, LH^-, and L^{2-} in the pH range < 4.0, 2.0–7.0 and > 6.0 respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the existence of ML_2, ML_2H, ML_3 for Pb(II), Cd(II) and Hg(II). The formation of various maleic acid complex species is shown in the following equilibria.

$$M(II) + LH_2 \rightleftharpoons MLH^+ + H^+ \quad (1)$$
$$MLH^+ \rightleftharpoons ML + H^+ \quad (2)$$
$$M(II) + LH_2 \rightleftharpoons ML + 2H^+ \quad (3)$$
$$M(II) + 2LH_2 \rightleftharpoons ML_2H_2 + 2H^+ \quad (4)$$
$$MLH^+ + LH_2 \rightleftharpoons ML_2H_2 + H^+ \quad (5)$$
$$ML_2H_2 \rightleftharpoons ML_2H^- + H^+ \quad (6)$$
$$MLH^+ + LH^- \rightleftharpoons ML_2H^- + H^+ \quad (7)$$
$$ML + LH_2 \rightleftharpoons ML_2H^- + H^+ \quad (8)$$
$$ML_2H^- \rightleftharpoons ML_2^{2-} + H^+ \quad (9)$$
$$ML + LH^- \rightleftharpoons ML_2^{2-} + H^+ \quad (10)$$
$$ML_2^{2-} + LH^- \rightleftharpoons ML_3^{4-} + H^+ \quad (11)$$
$$M(II) + 3LH_2 \rightleftharpoons ML_3H_3^- + 3H^+ \quad (12)$$
$$MLH^+ + 2LH_2 \rightleftharpoons ML_3H_3^- + 2H^+ \quad (13)$$
$$ML_3H_3^- \rightleftharpoons ML_3H_2^{2-} + H^+ \quad (14)$$
$$ML + 2LH_2 \rightleftharpoons ML_3H_2^{2-} + 2H^+ \quad (15)$$
$$ML_3H_2^{2-} \rightleftharpoons ML_3H^{3-} + H^+ \quad (16)$$
$$ML_3H^{3-} \rightleftharpoons ML_3^{4-} + H^+ \quad (17)$$
$$M(II) + 2LH_2 \rightleftharpoons ML_2H^- + 3H^+ \quad (18)$$
$$M(II) + 2LH_2 \rightleftharpoons ML_2^{2-} + 4H^+ \quad (19)$$
$$M(II) + 3LH_2 \rightleftharpoons ML_3H_2^{2-} + 4H^+ \quad (20)$$
$$M(II) + 3LH_2 \rightleftharpoons ML_3H^{3-} + 5H^+ \quad (21)$$
$$M(II) + 3LH_2 \rightleftharpoons ML_3^{4-} + 6H^+ \quad (22)$$
$$ML_2H_2 \rightleftharpoons ML_2^{2-} + 2H^+ \quad (23)$$
$$ML_3H_3^- \rightleftharpoons ML_3H^{3-} + 2H^+ \quad (24)$$
$$ML_3H_3^- \rightleftharpoons ML_3^{4-} + 3H^+ \quad (25)$$

The species ML_2H_2, $ML_3H_3^-$, $ML_3H_2^{2-}$ could not be detected in the present study probably because they are formed at very low pH. Some typical distribution diagrams in TX100-water mixtures are shown in Figure 2. They indicate that the binary complexes of Pb(II), Cd(II) and Hg(II) are formed in the pH range 3.0-7.0. The species ML_2H, ML_2, ML_3 are formed in the pH range of 3.0-6.5. ML_2H is formed at lower pH with higher percentage [Equilibria (6), (7), (8) and (18)]. ML_2, ML_3 are simultaneously formed with the increasing pH. Successive deprotonation of ML_2H forms ML_2 beyond a pH 6.0. The percentage of the ML_3 species increases with increasing pH up to 7. The concentration of ML_2H species decreased, while the

concentration of ML_2 and ML_3 increased in the pH range 4.5-6.5 [Equilibria (9), (10) and (11)]. ML_3 formed at higher pH with high percentage [Equilibria (11), (17), (22) and (25)].

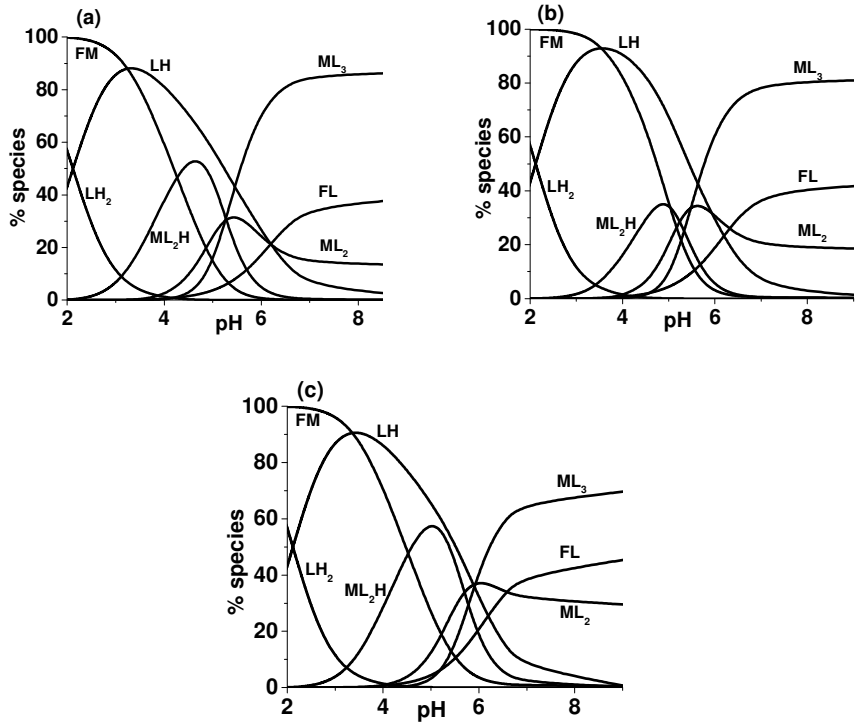

Figure 2. Distribution diagrams of binary complexes of maleic acid in 1.5% v/v TX100-water mixture: (a) Pb(II), (b) Cd(II) and (c) Hg(II).

Structures of complexes

Maleic acid acts as a bidentate ligand by using its two oxygen donor sites and the chelation results in highly stable seven membered rings (Figure 3). Octahedral structures are proposed for the complexes of all the metal ions studied. The VSEPR theory suggests that Pb(II), Cd(II) and Hg(II) complexes should be octahedral because there are six donor electron pairs, which is consistent with the structures proposed in Figure 3.

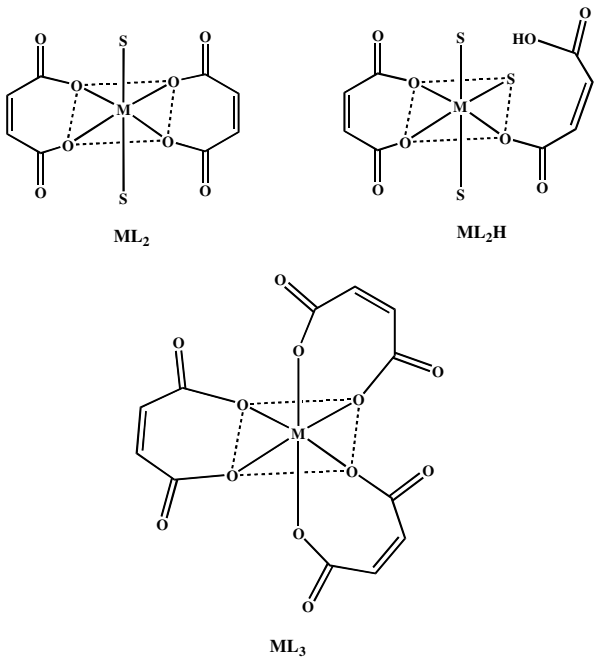

Figure 3. Structure of maleic acid complexes (S is either solvent or water molecules).

CONCLUSION

The following conclusions have been drawn from the modeling studies of the speciation of binary complexes of Pb(II), Cd(II) and Hg(II) with maleic acid in TX100-water mixtures. Maleic acid forms both protonated and unprotonated complexes over a pH range of 3.0-7.0. The binary species formed by the interaction of maleic acid with metals are PbL_2, PbL_2H, PbL_3, CdL_2, CdL_2H, CdL_3, HgL_2, HgL_2H and HgL_3. The linear variation of stability constants as a function of mole fraction of the medium indicates the dominance of electrostatic forces over non-electrostatic forces. Some species are stabilized due to electrostatic interactions and some are destabilized due to a decreased dielectric constant. The order of components influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal > total volume > log F.

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