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## Chemical Speciation of Maleic Acid Complexes with Some Biologically Important Metal Ions in Anionic Micellar Medium.

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### ABSTRACT

The impact of anionic micelles on the speciation of maleic acid complexes with essential metal ions have been studied by monitoring hydrogen ion concentration pH-metrically at 303 K and at an ionic strength of 0.16 mol L<sup>-1</sup>. The binary stability constants have been calculated with the computer program MINIQUAD75. The predominant species detected were ML, ML<sub>2</sub> and ML<sub>2</sub>H<sub>2</sub>. The best fit chemical models are arrived at based on statistical parameters. The trend in the variation of stability constants of the complexes with mole fraction of the SLS is attributed to the compartmentalisation of complexation equilibria. Distribution of species and effect of influential parameters on chemical speciation have also been presented.

**Keywords:** Anionic micelles, speciation, maleic acid, stability constants, essential metal ions, binary complexes, SLS.

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## INTRODUCTION

Maleic acid is a dibasic unsaturated carboxylic acid, which is widely used in medicine, in the preparation of drugs, in agriculture as the plant growth regulators, in food industry and in plastic production [1]. Maleic acid is an industrial raw material for the production of glyoxylic acid by ozonolysis [2]. The maleate ion is the ionised form of maleic acid. The maleate ion is useful in biochemistry as an inhibitor of transaminase reactions.

Sodium Lauryl Sulphate (SLS) or sodium dodecyl sulphate (SDS) is an anionic surfactant used in many cleaning and hygiene products, food, pharmaceuticals and cosmetics. It tends to denature proteins and profoundly influences the bulk properties of physiological systems. It can solubilise, concentrate and compartmentalize ions and molecules [3]. Hence, the influence of anionic micellar media (SLS) on the chemical speciation of maleic acid has been investigated. Extensive attention has been paid in recent years to the study of the chemical speciation of ligands with metal ions [4-8].

Co(II), Ni(II) and Cu(II) have several significant applications in biological systems [9-13]. It seems to very interesting to study the feasibility of controlling their level by complexation. The studies carried out on these systems under the present experimental conditions are useful to understand the role played by the active site cavities in biological molecules. Hence, the speciation studies on the interaction of maleic acid with the Co(II), Ni(II) and Cu(II) in varying compositions of SLS-water mixtures have been carried out.

## EXPERIMENTAL

### Materials

0.05 mol L<sup>-1</sup> aqueous solution of Maleic acid (GR grade, E-Merck, Germany) was prepared by dissolving sample in water. To increase the solubility of ligand, 0.05 mol L<sup>-1</sup> hydrochloric acid concentration was maintained in the solution. GR samples of sodium lauryl sulfate (SLS, Qualigens, India) was used as such and its purity was checked by determining critical micellar concentration (CMC) conductometrically. The CMC value of SLS was 0.0081 mol L<sup>-1</sup> at 303K. Solutions of Co(II), Ni(II) and Cu(II) chlorides (0.1 mol L<sup>-1</sup>) were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple distilled water maintaining 0.05 mol L<sup>-1</sup> acid (HCl) to suppresses the hydrolysis of metal salts. Carbonate free sodium hydroxide (Qualigens, India) pellets were used for the preparation of 0.40 mol L<sup>-1</sup> solution. All the solutions were standardized by standard methods. Cobalt, Nickel and Copper chlorides were standardized using EDTA. 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 [14]. The strengths of alkali and mineral acid were determined using the Gran plot method [15].

### Alkalimetric titrations

Alkalimetric titrations were carried out using an ELICO (Model LI 120, India) pH meter of 0.01 readability (0-14 pH) in conjunction with a glass combination pH electrode was used to monitor changes in hydrogen ion concentration with varying composition of SLS (0.0-2.5% w/v) maintaining an ionic strength of 0.16 mol L<sup>-1</sup> with sodium chloride at 303.0±0.1 K. Potassium hydrogen phthalate (0.05 mol L<sup>-1</sup>) and borax (0.01 mol L<sup>-1</sup>) solutions were used to calibrate the pH meter. The glass electrode was equilibrated in a well stirred SLS-water mixture containing inert electrolyte for several days. At regular intervals strong acid was titrated against alkali to check the complete equilibration of the glass electrode. In each of the titrations, the titrand consisted of approximately 1m mol mineral acid in a total volume of 50 cm<sup>3</sup>. Titrations with different metal-to-ligand ratios (1:2.5, 1:3.75 and 1: 5) were carried out with 0.4 mol L<sup>-1</sup> sodium hydroxide.

### Modelling Strategy

The computer program SCPHD [16] 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 [17], which exploits 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 maleic acid were fixed. The variation of stability constants with the mole

fraction of the medium was analysed on electrostatic grounds based on solute-solute and solute-solvent interactions.

## 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. A very low standard deviation in  $\log\beta$  values indicates the precision of these parameters. The small values of  $U_{\text{corr}}$  (the sum of squares of deviations in concentrations of reactants at all experimental points) corrected for degrees of freedom, indicate that the model can represent the experimental data. Small values of mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean with little dispersion.

### 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 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 following normal distribution in the least squares analysis, the residuals are tested for normal distribution. 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 SLS-water mixtures, as discussed below.

### $\chi^2$ Test

$\chi^2$  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. If the  $\chi^2$  calculated is less than the table value, the model is accepted.

### Crystallographic R-test

Hamilton's R-factor ratio test [18] 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  $R_{\text{limit}}$  which represents the upper boundary of R beyond which the model bears no significance. When these are different numbers of species the models whose values are 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 -0.11 and 1.38 for Co(II), -0.20 and 0.54 for Ni(II) and -0.19 and 0.64 for Cu(II). These data evince that the residuals form a part of normal distribution, hence, least-squares method can be applied to the present data.

### Kurtosis

It is a measure of the peakedness of the error distribution near a modal 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). The kurtosis values in the present study indicate that the residuals form leptokurtic pattern.

**Table 1: Parameters of best fit chemical models of M(II) – Maleic acid complexes in SLS-water medium**

% w/v SLS	log $\beta_{\text{min}}$ (SD)			NP	U <sub>corr</sub>	Skew-ness	$\chi^2$	R-Factor	kurtosis	pH-Range
	ML	ML <sub>2</sub>	ML <sub>2</sub> H <sub>2</sub>							
<b>Co(II)</b>										
0.0	4.56(15)	6.88(15)	17.76(07)	160	5.06	1.38	34.57	0.0091	8.43	1.5-8.0
0.5	4.22(33)	6.08(38)	17.88(35)	60	1.48	0.16	52.09	0.0107	7.71	2.2-8.0
1.0	3.48(09)	6.27(06)	17.47(05)	67	1.11	0.18	19.54	0.0084	4.72	2.2-8.0
1.5	3.27(08)	5.92(05)	17.03(05)	66	0.86	0.38	43.70	0.0074	5.32	2.2-8.0
2.0	4.38(23)	7.08(16)	18.22(10)	79	8.09	-0.11	22.07	0.0188	3.49	2.0-8.0
2.5	3.11(33)	6.46(10)	17.34(09)	54	2.98	1.14	13.31	0.0113	6.51	2.0-8.0
<b>Ni(II)</b>										
0.0	5.45(08)	7.42(26)	16.37(12)	104	5.06	0.54	46.26	0.0130	4.92	1.8-6.7
0.5	3.75(22)	5.69(24)	17.3(22)	46	1.16	-0.18	9.59	0.0080	3.38	2.1-6.7
1.0	4.38(16)	7.29(13)	18.35(11)	41	1.77	0.50	10.53	0.0113	5.44	2.1-6.7
1.5	4.33(28)	7.45(23)	18.35(23)	65	3.73	-0.18	11.97	0.0152	2.64	2.1-6.7
2.0	4.21(31)	6.97(21)	18.05(10)	55	9.68	0.28	6.68	0.0203	4.26	1.9-6.7
2.5	3.39(47)	6.43(22)	17.64(16)	48	10.22	-0.20	10.44	0.0229	2.72	1.9-6.7
<b>Cu(II)</b>										
0.0	4.98 (05)	7.79(09)	15.80(14)	73	1.59	0.07	8.84	0.0088	3.43	2.0-5.9
0.5	3.85(08)	6.23(08)	16.76(07)	48	0.57	-0.19	42.56	0.0049	4.34	2.0-5.9
1.0	4.77(18)	7.92(13)	18.44(12)	50	1.81	-0.12	9.36	0.0082	2.99	2.0-5.9
1.5	3.71(16)	6.96(09)	17.33(09)	39	1.68	0.64	6.69	0.0109	5.00	2.1-5.9
2.0	4.91(27)	7.84(21)	18.25(13)	38	6.58	-0.14	12.60	0.0205	3.90	2.1-5.9
2.5	3.29(56)	7.18(28)	17.38(34)	34	4.32	0.01	4.67	0.0187	3.33	2.5-5.9

U<sub>corr</sub> = U/(NP-m)X10<sup>8</sup>, where m = number of species; NP=Number of experimental points; SD=Standard deviation

### Effect of Systematic Errors on Best Fit Model

In order to obtain the best chemical 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 like concentrations of alkali, mineral acid, ligand and metal (Table 2). The order of the compounds that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > ligand > metal. Some species were even rejected when errors are introduced in the concentrations. The rejection of some species and increased standard deviations in the stability constants on introduction of errors confirm the suitability of the experimental conditions (concentrations of reactants) and choice of the best fit models.

**Table 2 : Effect of errors in influential parameters on the stability constants of Cu(II)-Ma complexes in 1.5% w/v SLS-water medium.**

Reactant	% Error	log $\beta$ (SD)		
		ML	ML <sub>2</sub>	ML <sub>2</sub> H <sub>2</sub>
	0	3.71(16)	6.96(09)	17.34(09)
Alkali	-5	Rejected	Rejected	Rejected
	-2	Rejected	5.81(12)	16.12(24)
	+2	5.55(38)	9.02(37)	18.78(36)
	+5	7.04(33)	11.14(45)	17.90(63)
Acid	-5	Rejected	Rejected	Rejected
	-2	5.41(34)	8.80(32)	18.81(32)
	+2	2.32(79)	6.01(09)	16.19(18)
	+5	Rejected	5.06(26)	Rejected
Ligand	-5	4.29(20)	7.76(14)	17.84(13)
	-2	3.93(17)	7.26(10)	17.53(10)
	+2	3.50(17)	6.67(09)	17.15(09)
	+5	3.20(22)	6.27(10)	16.87(10)
Metal	-5	3.73(18)	7.07(09)	17.39(09)
	-2	3.72(17)	7.00(09)	17.06(09)
	+2	3.70(16)	6.92(09)	17.31(09)
	+5	3.69(15)	6.86(09)	17.08(09)

### Effect of surfactant

Many workers were of the opinion that both electrostatic and non-electrostatic effects should be considered even in the case of simple acido-basic equilibria; one dominates the other, depending upon the nature of solute and solvent [19-22]. Born's classical treatment [23] holds good in accounting for the electrostatic contribution to the free energy change.

The variations of stability constants ( $\log \beta$ ) with mole fraction of different micellar media are shown in Figure 1. The stabilities of binary complexes varied almost linearly with the mole fraction of the surfactant. This linear variation, due to the dielectric constant of the medium, decreases with increasing concentration of the surfactant [24, 25]. The non-linear variation depends upon the polarity of the medium, charge on the micellar surface and on the non-electrostatic forces/hydrophobic interactions operating between the complex species and micellar surface. The species should be stabilized in the micellar medium with opposite charges due to electrostatic interactions but these charged species should be destabilized due to the decreased dielectric constant of the medium. The stabilities of these species in SLS – water medium do not show a particular trend because of the accumulation of metal ions and ligands on the surface of micelles with an increased concentration of surfactant and species with lower charge or high hydrophobicity are stabilized in the micellar pseudophase. This trend reflects in all M(II)-maleic acid complexes (Figure 1).

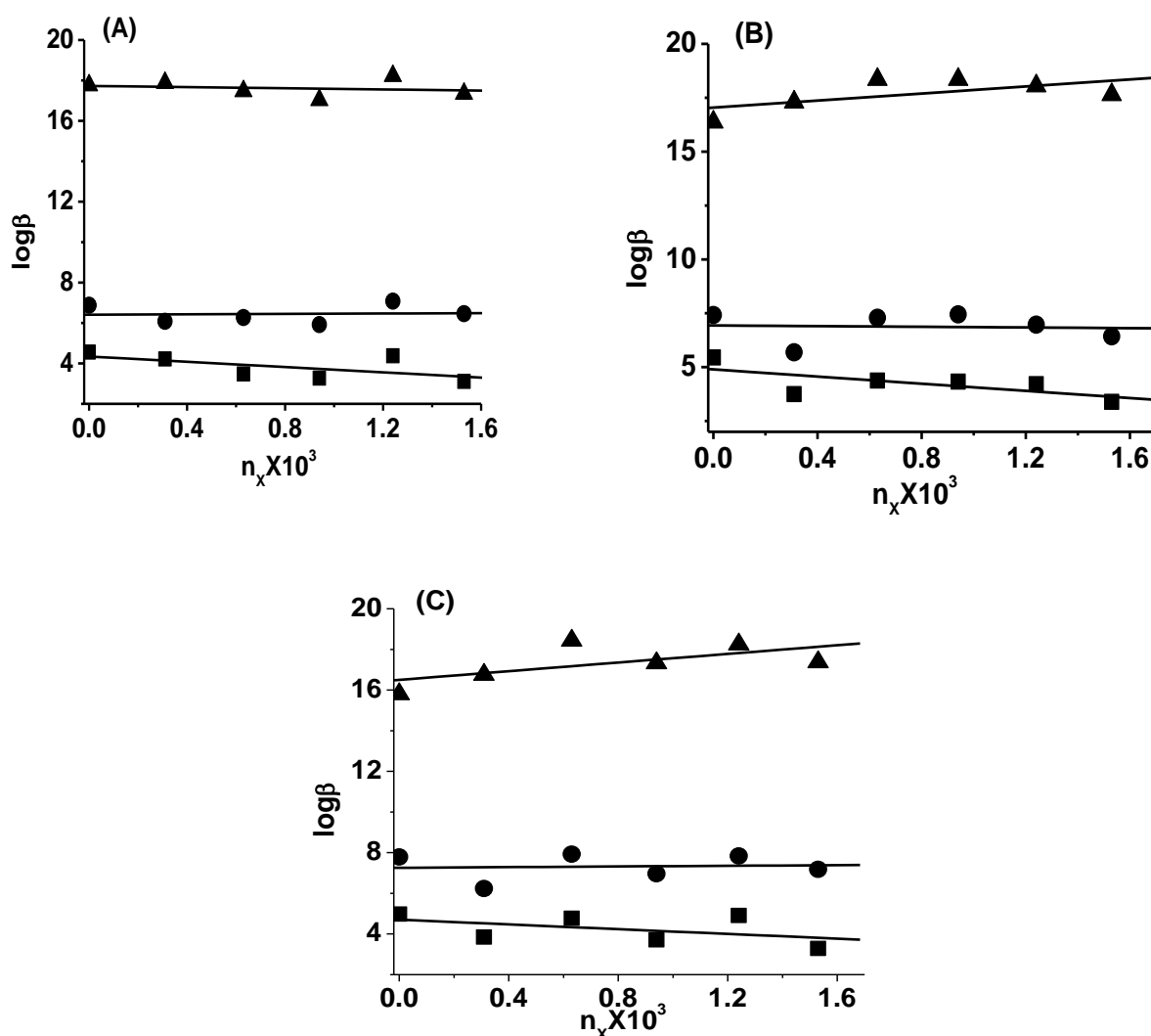


Figure. 1 : Variation of stability constant values of metal-maleic acid complexes with mole fraction of SLS-water medium Here (A) (■)  $\log \beta_{ML}$ , (●)  $\log \beta_{ML_2}$ , (▲)  $\log \beta_{ML_2H_2}$  for Co(II), (B) (■)  $\log \beta_{ML}$ , (●)  $\log \beta_{ML_2}$ , (▲)  $\log \beta_{ML_2H_2}$  for Ni(II) and (C) (■)  $\log \beta_{ML}$ , (●)  $\log \beta_{ML_2}$ , (▲)  $\log \beta_{ML_2H_2}$  For Cu(II) .

## Distribution Diagrams

Some typical distribution diagrams of M(II)-maleic acid in SLS-water medium are shown in the Figure. 2. The different forms of maleic acid are  $LH_2$ ,  $LH^-$  and  $L^{2-}$  in the pH-range of 1.7 – 4.0, 1.7 – 6.5 and 4.5 – 6.5 respectively. The plausible binary metal-ligand species in different systems can be predicted from these data. The present investigation reveals the existence of  $ML$ ,  $ML_2$  and  $ML_2H_2$  for  $Co(II)$ ,  $Ni(II)$  and  $Cu(II)$ . The  $ML_2$  species is the predominant species (Figure. 2) at higher pH and  $ML_2H_2$  is the predominant species at lower pH among all the binary complexes. Low concentration of free metal ion (FM) indicates the strong complexing nature of maleic acid. The formation of various binary complex species is shown in the following equilibria. Some typical distribution diagrams of SLS-water media are shown in Figure. 2. Equilibria (1), (2) and (3) represent the formation of complexes from metal ion and the ligand. In alkalimetric titrations, protons are removed successively from the complexes by the addition of aliquots of the alkali. Equilibrium (4) represents the successive deprotonation of the complexes with increasing pH of the solution during alkalimetric titrations. Formation of  $ML_2$  through the equilibria (4), (5) and (6) is proved by the increase in concentration of  $ML_2$  by the decrease in concentration of  $ML$  and  $ML_2H_2$ . The formation of various binary complex species is shown in the following equilibria.

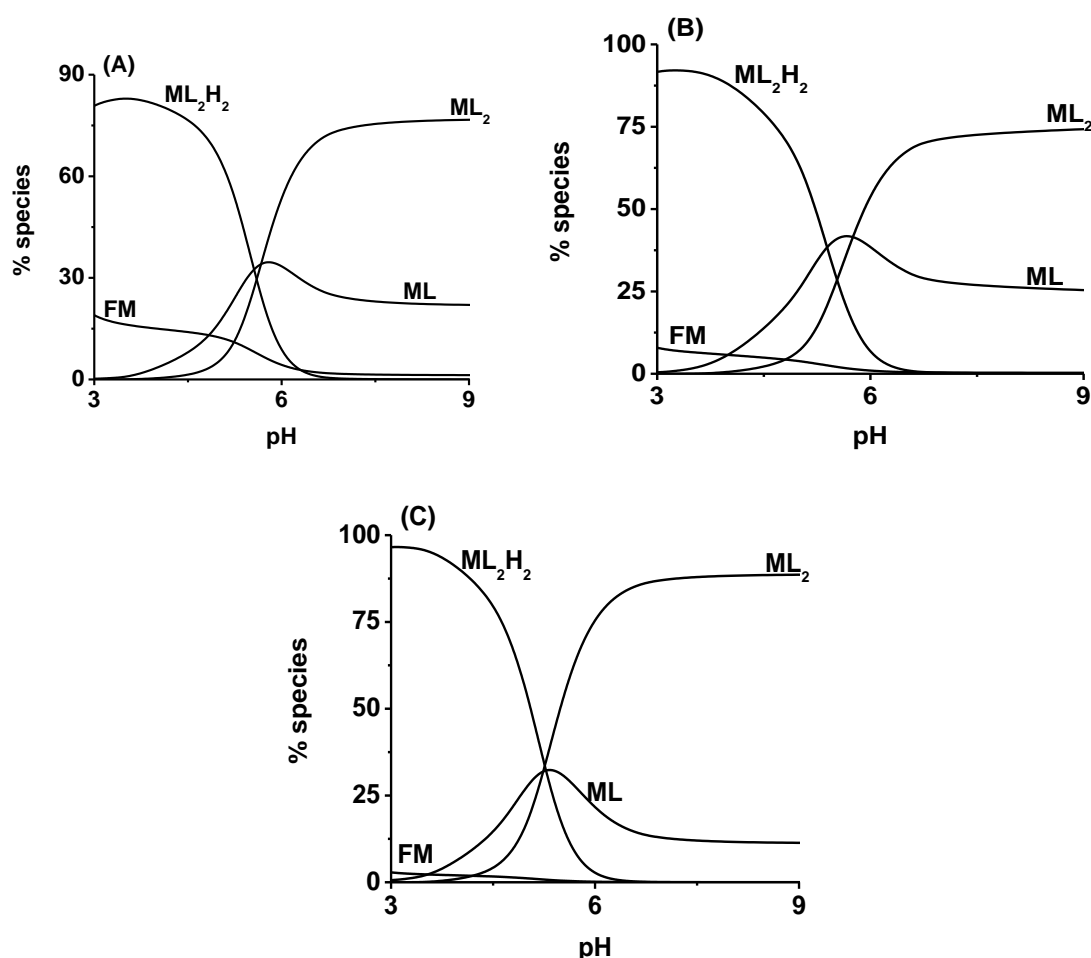
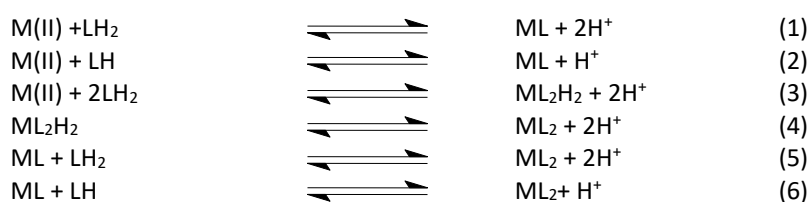


Figure.2: Distribution diagrams of Ma complexes in 1.0 % w/v SLS - water medium. (A)  $Co(II)$  (B)  $Ni(II)$  and (C)  $Cu(II)$ .

### Structures of complexes

Co(II), Ni(II) and Cu(II) form octahedral complexes. Hence the plausible structures for the above complexes are proposed in Figure 3. These structures support the existence of protonated and deprotonated complexes shown in Equilibria 1-6.

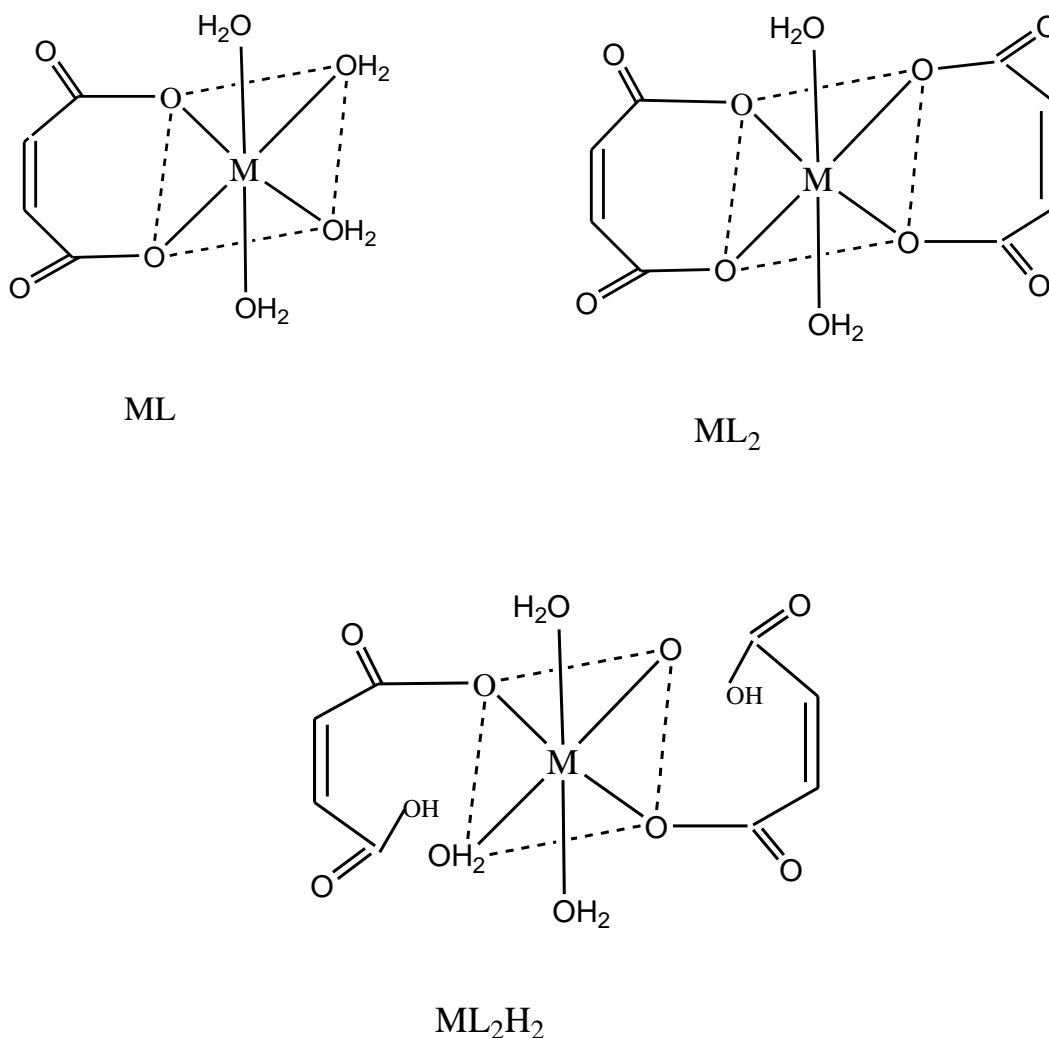


Figure.3: Structures of binary complexes of Ma with M(II)

### CONCLUSIONS

- The binary species detected are CoL, CoL<sub>2</sub>, CoL<sub>2</sub>H<sub>2</sub>, NiL, NiL<sub>2</sub>, NiL<sub>2</sub>H<sub>2</sub>, CuL, CuL<sub>2</sub>, CuL<sub>2</sub>H<sub>2</sub>. These models are validated by statistical treatment of data.
- The linear or almost linear variation of log β values with the 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 the decreased dielectric constant.
- The order of reactants influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali>acid>ligand>metal.

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