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Computer augmented modelling studies of Co(II), Ni(II), and Cu(II) complexes with maleic acid in non-ionic micellar medium

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ABSTRACT

Chemical speciation of binary complexes of Co(II), Ni(II), and Cu(II) ions with maleic acid have been studied pH metrically in the concentration range of 0.0-2.5% v/v nonionic surfactant(TX100) – water mixtures maintaining an ionic strength of 0.16 M at 303K. Alkalimetric titrations were carried out in different relative concentrations of metal and maleic acid. Models containing different numbers of species were refined by using the computer program MINIQUAD75. Selection of the best fit chemical models was based on statistical parameters and residual analysis. The predominant complexes formed are ML, ML_2 and ML_2H_2 for Co(II), Ni(II), and Cu(II). The trend in the variation of stability constants with change in mole fraction of the medium was explained on the basis of electrostatic and non-electrostatic forces. Distributions of species, formation equilibria and effect of influential parameters on the stability constants have been presented. The possible structures of the various species are elucidated on the basis of the analysis of the pH metric data.

Keywords: Chemical speciation, Maleic acid, Nonionic surfactant, Stability constants, Alkalimetric titrations

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INTRODUCTION

The binary complexes of Co(II), Ni(II), and Cu(II) with Maleic acid (MA) are studied in the presence of poly oxyethylene diisobutyl phenol (Triton X-100 or TX100, $R_8C_6H_4[OCH_2CH_2]_{9.5}OH$) to understand the influence of co-solvent on the speciation. A number of studies have been reported on chemical speciation of α-amino acids and dicarboxylic acids in different media in recent times [1-3]. Chemical speciation of a molecule is governed by its structure and solvent effects [4, 5]. Maleic acid is a dicarboxylic acid. It is soluble in water and moderately toxic. It is used to make artificial resins and anti-histamins, and to preserve fats and oils. MA is an industrial raw material for the production of glyoxylic acid by ozonolysis. The major industrial use of maleic acid is its conversion to fumaric acid. TritonX-100 ($C_{14}H_{22}O(C_2H_4O)_n$ is a nonionic surfactant that has a hydrophilic polyethylene oxide and an aromatic hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl) -phenyl group. Triton X-100 is a commonly used detergent in laboratories. Triton X-100 is widely used to lyse cells to extract protein or organelles, or to permeabilize the membranes of living cells [6]. Co(II), Ni(II) and Cu(II) are associated with several enzymes and any variation in their concentrations leads to metabolic disorders [7]. Hence, the speciation of Co(II), Ni(II) and Cu(II) complexes of Ma in varying compositions of TX100 – water mixtures have been studied.

MATERIALS AND METHODS

Materials

0.05 mol L^{-1} aqueous solution of MA (GR grade, E-Merck, Germany) was prepared by dissolving sample in water. To increase the solubility of ligand, 0.05 mol L^{-1} hydrochloric acid concentration was maintained in the solution.GR samples of TritonX100 (TX100, AR, Qualigens, India) was used as such and its purity was checked by determining critical micellar concentration (CMC) conductometrically. The CMC value of TX100 was 0.54 vol. % at 303K. Solutions of Co(II), Ni(II) and Cu(II) chlorides (0.1 mol L^{-1}) were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple distilled water maintaining 0.05 mol L^{-1}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^{-1} 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 [8]. The strengths of alkali and mineral acid were determined using the Gran plot method [9].

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. The pH meter was calibrated with potassium hydrogen phthalate (0.050 mol L^{-1}) in acidic region and borax (0.010 mol L^{-1}) in basic region. The glass electrode was equilibrated for several days in a well stirred TX100 -water mixture containing inert electrolyte. The effect of variations in asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of correction factor [10].

Procedure

All the titrations have been carried out in the medium containing varying concentrations of TX100 – water mixtures (0.0-2.5%v/v) maintaining an ionic strength of 0.16 mol L^{-1} with sodium chloride at 303.0 K. In each of the titrations, the titrand consisted of approximately 1 mmol mineral acid in a total volume of 50 cm^3. Titrations with different ratios (1:2.5, 1:3.5, 1:5.0) of metal to ligand were carried out with 0.4 mol L^{-1} sodium hydroxide. Other experimental details are given elsewhere [11].

Modelling Strategy

The computer program SCPHD [12] was used to calculate the correction factor. The binary stability constants were calculated with the pH-metric titration data using the computer program MINIQUAD75 [13], 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

Binary complexes formation of Co(II), Ni(II), and Cu(II) with MA were investigated in TX100 – water mixtures of different compositions. 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 Table 1. A very low standard deviation in the log β values indicates the precision of these parameters. The small values of U_{corr} (sum of the squares of the deviations in the concentrations of ligand and hydrogen ions at all experimental points corrected for degrees of freedom) indicate that the experimental data can be represented by the model. Small values of the mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean with little dispersion. For an ideal normal distribution, the values of the kurtosis and skewness should be three and zero, respectively [14]. The kurtosis values in the present study indicate that the residuals form mainly leptokurtic pattern and a few form a mesokurtic pattern. The values of the skewness given in the Tables are between -0.19 and 1.38. These data evince that the residuals form a 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 the low crystallographic *R*-value recorded. Thus, these statistical parameters show that the best fit models reveal the metal-ligand species in TX100 – water mixtures.

Table 1: Parameters of best fit chemical models of M(II) – MA complexes in TX100 – water medium

% v/v TX100	**logβ$_{mlh}$ (SD)**			**NP**	**U$_{corr}$**	**Skew-ness**	**χ^2**	**R-Factor**	**Kurtosis**
	ML	**ML$_2$**	**ML$_2$H$_2$**						
Co(II) (pH range 2.0 to 7.0)									
0.0	4.56(15)	6.88(15)	17.76(07)	160	5.06	1.38	34.57	0.0091	8.43
0.5	4.15(66)	6.21(52)	17.53(59)	60	7.68	0.16	52.09	0.0107	7.71
1.0	4.05(19)	6.22(22)	17.24(08)	80	2.05	0.18	19.54	0.0084	4.72
1.5	4.29(38)	7.87(22)	18.33(20)	72	5.43	0.38	43.70	0.0074	5.32
2.0	4.04(36)	7.62(16)	18.06(12)	83	3.26	-0.11	22.07	0.0188	3.49
2.5	4.18(26)	7.50(16)	18.18(14)	44	0.77	1.14	13.31	0.0113	6.51
Ni(II) (pH range 2.0 to 7.5)									
0.0	5.45(08)	7.42(26)	16.37(12)	104	5.06	0.54	46.26	0.0130	4.92
0.5	5.17(24)	7.36(24)	18.45(16)	112	6.25	-0.18	9.59	0.0080	3.38
1.0	6.13(07)	8.09(35)	16.58(13)	159	0.57	0.50	10.53	0.0113	5.44
1.5	4.40(33)	7.96(23)	18.51(22)	60	1.81	-0.18	11.97	0.0152	2.64
2.0	4.00(36)	7.59(20)	18.20(20)	40	15.69	0.28	6.68	0.0203	4.26
2.5	4.15(30)	7.72(15)	18.26(14)	69	4.61	-0.20	10.44	0.0229	2.72
Cu(II) (pH range 2.0 to 6.0)									
0.0	4.98 (05)	7.79(09)	15.80(14)	73	1.59	0.07	8.84	0.0088	3.43
0.5	4.36(44)	7.61(45)	16.42(29)	99	5.48	-0.19	42.56	0.0049	4.34
1.0	5.08(31)	8.39(32)	17.46(21)	95	1.59	-0.12	9.36	0.0082	2.99
1.5	6.19(26)	9.70(29)	18.96(29)	34	4.68	0.64	6.69	0.0109	5.00
2.0	5.98(16)	9.50(20)	18.35(16)	65	1.94	-0.14	12.60	0.0205	3.90
2.5	6.50(25)	10.06(28)	18.98(28)	63	2.35	0.01	4.67	0.0187	3.33

U_{corr} = U/(NP-m)X10^8, where m = number of species; NP=Number of experimental points; SD=Standard deviation

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 undertaken 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. Some species were even rejected when errors were introduced in the concentrations. 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 were done under varied experimental conditions with different accuracies.

Table 2: Effect of errors in influential parameters on the stability constants of Co(II)-Ma complexes in 1.0% v/v Triton X - water medium

Ingredient	% Error	log β (SD)		
		ML	ML$_2$	ML$_2$H$_2$
	0	4.05(19)	6.22(22)	17.24(08)
Alkali	-5	Rejected	Rejected	16.43(15)
	-2	2.84(08)	Rejected	16.78(05)
	+2	5.47(48)	9.43(27)	16.70(31)
	+5	Rejected	Rejected	Rejected
Acid	-5	7.23(11)	11.03(39)	Rejected
	-2	6.52(68)	9.15(25)	17.15(19)
	+2	3.04(15)	Rejected	16.61(06)
	+5	Rejected	Rejected	15.17(66)
Ligand	-5	6.11(41)	8.85(76)	17.15(13)
	-2	4.34(25)	6.83(22)	17.35(10)
	+2	3.85(14)	5.34(53)	17.13(06)
	+5	3.31(08)	Rejected	16.96(05)
Metal	-5	4.15(21)	6.36(22)	17.28(09)
	-2	4.09(20)	6.28(22)	17.25(08)
	+2	4.02(19)	6.17(22)	17.22(08)
	+5	3.97(18)	6.09(25)	17.20(07)

Effect of Surfactant

The variations of stability constants (log β) with mole fraction of different micellar media are shown in Figure1. 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 [15, 16]. 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. This trend reflects in all M(II)-MA complexes (Figure 1).

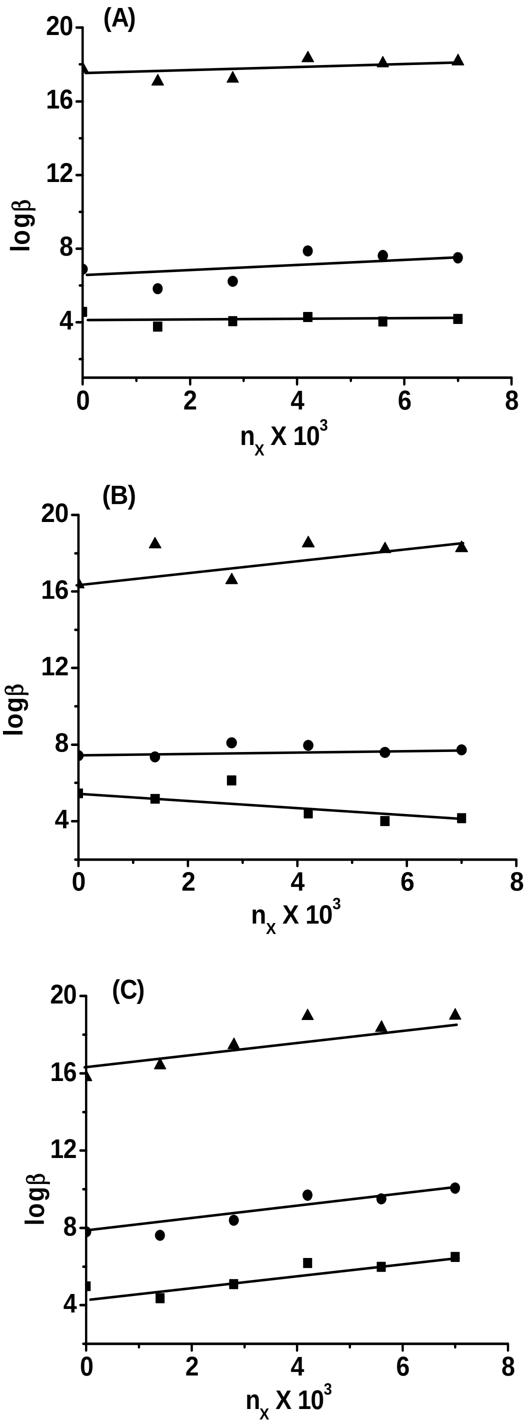
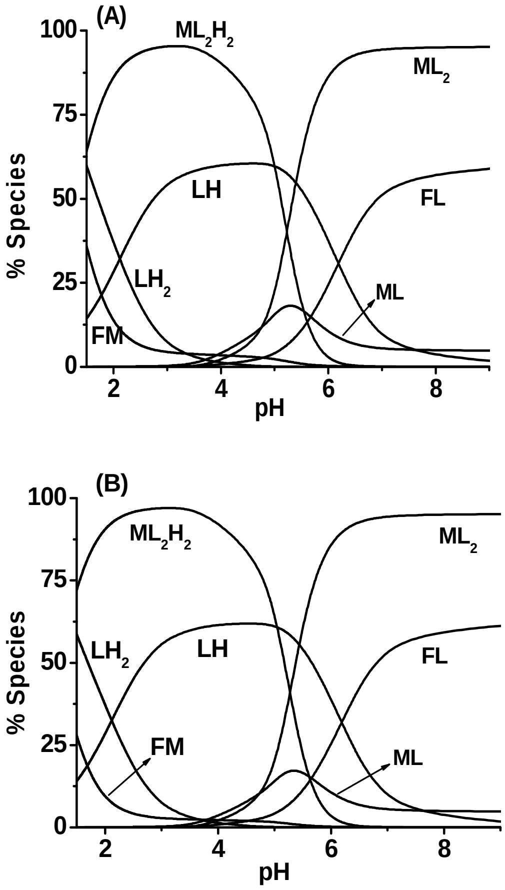


Figure 1: Variation of overall stability constant values of metal – Maleic acid complexes in TX100 – water mixtures (A) Co(II), (B) Ni(II), and (C) Cu(II); (■)log β_{ML};(●)log β_{ML2}; and (▲)log β_{ML2H2}

Distribution Diagrams

Some typical distribution diagrams of M(II) – MA in TX100 – water medium are shown in the Fig. 2. The different forms of MA are LH_2, LH^- and L^{2-} in the pH-range of 3.0 – 5.0, 3.0 – 10.0 and 8.0 – 10.0 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 (Fig. 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 MA. The formation of various binary complex species is shown in the following equilibria. Some typical distribution diagrams of TX100 – water media are shown in Fig. 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.

$$\mathbf{M(II) + LH_2 \rightleftharpoons ML + 2H^+} \quad \mathbf{(1)}$$
$$\mathbf{M(II) + LH \rightleftharpoons ML + H^+} \quad \mathbf{(2)}$$
$$\mathbf{M(II) + 2LH_2 \rightleftharpoons ML_2H_2 + 2H^+} \quad \mathbf{(3)}$$
$$\mathbf{ML_2H_2 \rightleftharpoons ML_2 + 2H^+} \quad \mathbf{(4)}$$
$$\mathbf{ML + LH_2 \rightleftharpoons ML_2 + 2H^+} \quad \mathbf{(5)}$$
$$\mathbf{ML + LH \rightleftharpoons ML_2 + H^+} \quad \mathbf{(6)}$$



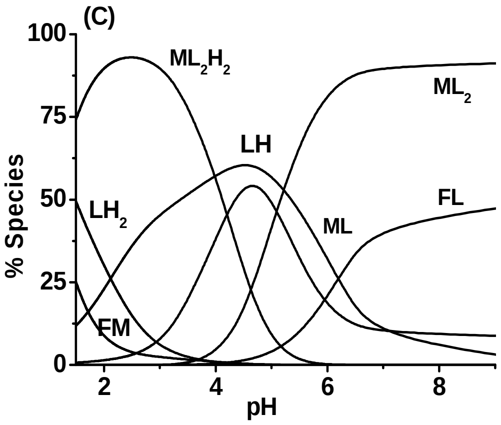
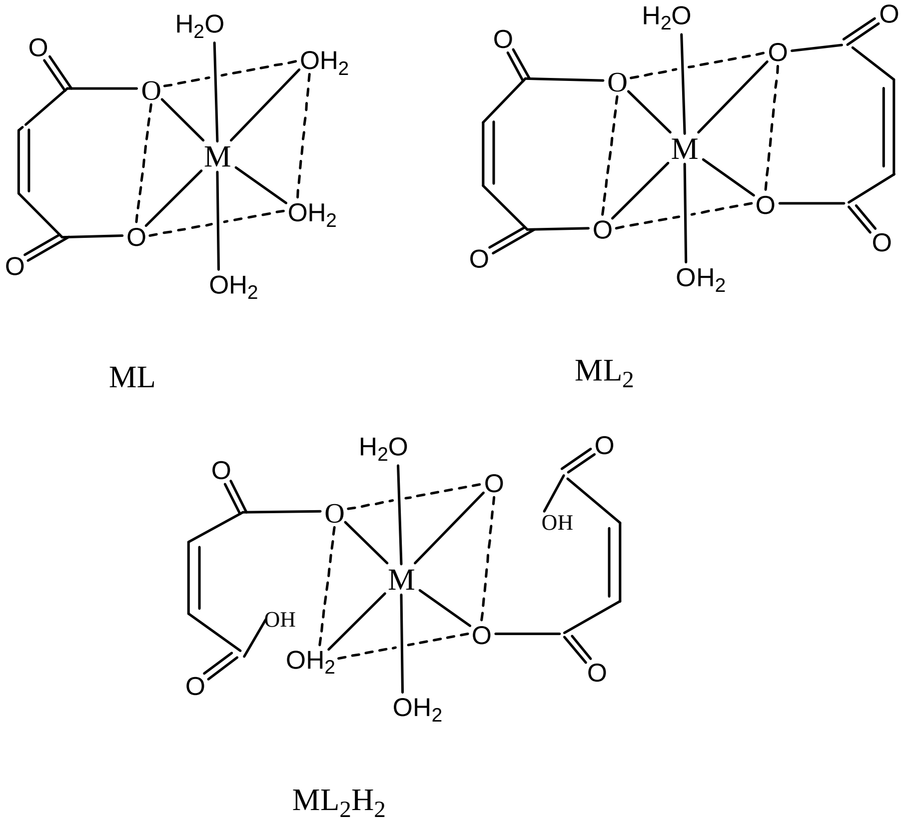


Figure 2: Distribution diagrams of binary complexes of Maleic acid in 1.5% v/v TX100 – water mixtures: (A) Co(II), (B) Ni(II), and (C) Cu(II)

Structures of complexes

Depending upon the nature of the ligands and the metal ions and based on the basic chemical knowledge the structures of the binary complexes were proposed as shown in Figure 3. These structures indicate that maleic acid acts as bidentate ligand depending upon the pH conditions. Octahedral structures are proposed to the complexes of all the metal ions. The VSEPR theory suggests that Co(II), Ni(II), and Cu(II) complexes shall be octahedral because there are six outer electron pairs.



ML

ML_2

ML_2H_2

Figure 3: Structures of binary complexes of Maleic acid with M(II)

CONCLUSION

1. The present biomimetic studies of metal ion complexes with Maleic acid in TX100 – water mixtures indicate that all the complexes were protonated in acidic pH values.
2. The predominant species detected were ML, ML_2 and ML_2H_2.
3. The log β values linearly or almost linear vary with mole fraction of the medium, indicating the dominance of electrostatic forces over non-electrostatic forces.
4. The order of the compounds influencing the magnitudes of the stability constants due to the incorporation of errors was alkali > acid > ligand > metal.
5. The higher concentrations of complex chemical species indicate that the metals are more amenable for transportation at biological pH.

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