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## Chemical Speciation Studies of Malonic Acid Complexes of Co(II), Cu(II), Ni(II) and Zn(II) in Dioxan-Water Mixtures

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### ABSTRACT

Equilibrium study on complex formation of malonic acid with Co(II), Cu(II), Ni(II) and Zn(II) has been investigated pH-metrically in dioxan-water mixtures (0.0-60.0% v/v) at  $303 \pm 0.1$  K and  $0.16 \text{ mol L}^{-1}$  ionic strength. The predominant species detected for Co(II) and Cu(II) are  $ML$ ,  $ML_2$ ,  $ML_2H_2$  and  $ML_2H$  and those for Ni(II) and Zn(II) are  $ML_2$ ,  $ML_2H_2$ ,  $ML_2H$ . The appropriateness of experimental conditions is verified by introducing errors intentionally in the concentrations of ingredients. The models containing different numbers of species were refined by using the computer program MINQUAD75. The best-fit chemical models were arrived at based on statistical parameters. The trend in variation of stability constants of the complexes with dielectric constant of the medium is attributed to the electrostatic and non-electrostatic forces. The possible structure, species distribution and the plausible equilibria for the formation of the species are also presented.

**Keywords:** Complex equilibria, Malonic acid, Dioxan, Stability constants, Chemical speciation.

### INTRODUCTION

The toxicity, bioavailability, bioaccumulation, biodegradability, persistence, mobility, solubility, extractability and many other critical properties depend on the form and nature of the chemical species [1-3]. Bioavailability of metal ions depends on either in free state or in binding state or in complexation state with various constituents present in the requisite amounts during biological reactions. The changes in various constraints like change in pH, temperature, ionic strength cause change in complexation behavior of metals and binding state. So complexation can signify the bioavailability of the metal ions in various biosystems [4-5].

Speciation analysis, the determination of the concentrations of separate and unique atomic and molecular forms of an element instead of its total concentration in a sample is important in human biology, nutrition, toxicology and in clinical practice [6-8]. The speciation study of toxic and essential metal ion complexes is also useful to understand the role played by the active site cavities in biological molecules.

An exhaustive survey of the existing literature reveals that a very little has been done on the metal complexes of dibasic acid. Malonate complexes are known which Cu(II) metal ion have been reviewed [9]. Complexes formations between iron (II) and oxalate, malonate succinate and glutarate ion have been studied [10]. Speciation of Uranium (VI) complexes of malonic acid have been studied in micellar media [11]. Stability constants of the complexes of different stoichiometry formed by uranium(VI) with phthalic, maleic, oxalic, malonic, succinic and propane-1,2,3-tricarboxylic acids have been studied potentiometrically [12]. Recently potentiometry studies of speciation of Ni(II) complexes with oxalic and malonic acid in  $1.0 \text{ mol dm}^{-3}$  NaCl at  $25^\circ \text{C}$  has been conducted and the result has shown that nickel(II)-malonic acid system the complexes  $[\text{NiHL}]^+$ ,  $[\text{NiL}]$ ,  $[\text{Ni}(\text{OH})\text{L}]^-$ , and  $[\text{Ni}(\text{OH})_2\text{L}]^{2-}$  were investigated

[13]. The complex species formed in aqueous solution (25 °C, I = 3.0 mol.dm<sup>-3</sup> KCl ionic medium) between V<sup>3+</sup> cation and the dicarboxylic acids oxalic, malonic and succinic (H<sub>2</sub>L) have also been studied potentiometrically and complexes [VHL]<sup>2+</sup>, [VL]<sup>+</sup>, [VL<sub>2</sub>]<sup>-</sup>, [V(OH)L<sub>2</sub>]<sup>2-</sup>, [V(OH)<sub>2</sub>L<sub>2</sub>]<sup>3-</sup>, [VL<sub>3</sub>]<sup>3-</sup> and [V(OH)L<sub>3</sub>]<sup>4-</sup> with malonic acid reported [14].

The stability constants and species distributions of Co(II), Cu(II), Ni(II) and Zn(II) malonic acid in mixed solvent of dioxan-water mixture of various concentration have not reported before, as can be seen in the Stability Constants Database [15]. It was therefore of interests of study the stability constant and speciation of binary complexes of these essential metal ions using pH-metric titration technique in dioxan-water mixtures in the present work.

## MATERIALS AND METHODS

### Materials

1, 4-Dioxane (1,4-Diethyleneoxide, DOX), obtained from Merck, India, was used as received. A solution 0.050 mol dm<sup>-3</sup> of malonic acid (MA) (Himedia, India) was prepared in triple distilled water. 0.10 mol dm<sup>-3</sup> aqueous solutions of Co(II), Ni(II), Cu(II) and Zn(II) chlorides (Merck, India) were prepared. To increase the solubility of MA and to suppress the hydrolysis of metal salts, hydrochloric acid concentration was maintained at 0.050 mol dm<sup>-3</sup>. Metal ion solutions were estimated using the conventional standard method [16]. Carbonate free sodium hydroxide solution was prepared and standardized by oxalic acid and potassium hydrogen phthalate. Hydrochloric acid solution was prepared and used after standardization using borax. 0.2 mol L<sup>-1</sup> Hydrochloric acid (Qualigens, India) was prepared. 2 mol L<sup>-1</sup> Sodium chloride (Merck, India) was prepared to maintain the ionic strength in the titrand. To assess the errors that might have entered into the determinations of the concentrations, the data were subjected to analysis of variance of one way classification (ANOVA) [17]. The strength of the alkali and mineral acid were determined using the Gran plot method [18].

### Procedure

The titrimetric data were obtained with a calibrated Elico (Model L1-120) pH meter (readability 0.01), which can monitor changes in the H<sup>+</sup> concentration. The pH meter was calibrated with a 0.050 mol dm<sup>-3</sup> potassium hydrogen phthalate solution in the acidic region and a 0.010 mol dm<sup>-3</sup> borax solution in the basic region. The glass electrode was equilibrated in a well-stirred DOX-water mixtures containing an inert electrolyte. The effects of variations in the asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of the glass electrode were accounted for in the form of correction factors (log F) [19]. The emf of the cell may be expressed by the equation  $E = E^0 + (RT/F) \ln a_{H^+}$  or  $E = E^0 + 0.059 \text{ pH}$  at 25°C, where E<sup>0</sup> is a constant partly dependent upon the nature of the glass used for making the membrane. The value of E<sup>0</sup> may vary slightly with time, and it is related to the existence of an asymmetry potential [20] in a glass electrode. Owing to the asymmetry potential, if a glass electrode is inserted into a test solution, which is identical with the internal HCl solution, the electrode shall have a small potential which is found to vary with time. Hence, glass electrode was standardized frequently using a buffer of known hydrogen activity.

The titrations were performed at 303±0.1 K in media containing 0.0-60.0% v/v DOX, whereby the ionic strength was maintained constant at 0.16 mol dm<sup>-3</sup> with sodium chloride and a total volume was kept constant 50ml. The electrode was kept, usually for 2–3 days, in the required solvent system for equilibration. To verify whether the electrode was equilibrated, a strong acid was titrated with an alkali every day until no appreciable differences were observed between the pH values of two titrations at the corresponding volumes of titrant. Under the above conditions, the electrode was assumed to be equilibrated. A calomel electrode was refilled with DOX-water mixture of the equivalent composition to that of the titrand. Free acid titrations were performed before the metal–ligand titrations to calculate the correction factor. In each of the titrations, the titrand consisted of a mineral acid of approximately 1 mmol in a total volume of 50 cm<sup>3</sup>. Titrations with different ratios (1:2.5, 1:3.75 and 1:5.0) of metal–ligand were performed with 0.40 mol dm<sup>-3</sup> sodium hydroxide. During the titrations a stream of nitrogen was bubbled through for both stirring and for maintaining an inert atmosphere. The pH meter dial reading was recorded only after a constant value was displayed [21].

### Modeling strategy

The approximate complex stability constants of metal-MA complexes were calculated with the computer program SCPHD [22]. The best fit chemical model for each investigated system was arrived at using MINIQUAD75 [23], which exploit the advantage of the constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. The variation of stability constants of metal-ligand species was analyzed by electrostatic grounds and on the basis of solute-solute and solute-solvent interactions.

**Table 1: Parameters of best fit chemical models of MA complexes of Co(II), Ni(II), Cu(II) and Zn(II) in DOX-water mixtures***No of titrations in each percentage = 3, Temperature = 303K±0.1, Ionic strength = 0.16mol dm<sup>-3</sup>.*

| % v/v<br>PG | log β <sub>min</sub> (SD) |          |           |           | NP | U <sub>corr</sub> | χ <sup>2</sup> | Skewness | Kurtosis | R-factor | pH-range  |
|-------------|---------------------------|----------|-----------|-----------|----|-------------------|----------------|----------|----------|----------|-----------|
|             | 110                       | 120      | 121       | 122       |    |                   |                |          |          |          |           |
| Co(II)      |                           |          |           |           |    |                   |                |          |          |          |           |
| 0.00        | 2.59(58)                  | 4.97(52) | 10.17(69) | 14.71(22) | 53 | 3.392             | 31.54          | -0.51    | 4.02     | 0.0156   | 2.50-6.50 |
| 10.00       | 3.24(10)                  | 5.64(12) | 10.55(43) | 15.41(12) | 33 | 0.194             | 4.52           | 0.06     | 5.76     | 0.0044   | 3.30-6.40 |
| 20.00       | 3.02(16)                  | 6.00(06) | 11.38(12) | 15.75(11) | 35 | 0.153             | 8.60           | -0.69    | 5.39     | 0.0040   | 3.40-6.80 |
| 30.00       | 4.87(21)                  | 8.25(16) | 13.17(50) | 18.05(17) | 29 | 0.815             | 3.21           | 0.56     | 3.08     | 0.0086   | 3.30-6.10 |
| 40.00       | 4.30(89)                  | 7.99(19) | 13.31(78) | 18.06(16) | 39 | 6.730             | 12.98          | -0.11    | 2.09     | 0.0214   | 2.90-6.20 |
| 50.00       | 3.88(21)                  | 7.23(05) | 13.32(13) | 17.94(8)  | 36 | 0.356             | 35.26          | -0.41    | 6.28     | 0.0054   | 3.50-6.80 |
| 60.00       | 3.98(33)                  | 6.87(37) | 13.16(74) | 17.93(57) | 27 | 1.736             | 5.81           | 0.18     | 2.45     | 0.0108   | 3.80-6.30 |
| Cu(II)      |                           |          |           |           |    |                   |                |          |          |          |           |
| 0.00        | 5.33(77)                  | 8.85(11) | 12.71(11) | 15.98(8)  | 77 | 1.680             | 13.05          | -0.39    | 3.99     | 0.0088   | 2.10-6.20 |
| 10.00       | 5.73(19)                  | 9.73(9)  | 14.13(15) | 16.92(21) | 52 | 0.772             | 18.15          | 1.87     | 6.81     | 0.0077   | 2.50-6.50 |
| 20.00       | 5.71(6)                   | 9.36(3)  | 13.81(9)  | 16.75(11) | 49 | 0.155             | 10.77          | 0.64     | 5.99     | 0.0035   | 2.60-6.60 |
| 30.00       | 5.95(7)                   | 9.78(3)  | 14.46(9)  | 17.61(9)  | 50 | 0.225             | 3.60           | 0.21     | 2.73     | 0.0039   | 2.60-6.30 |
| 40.00       | 5.70(34)                  | 9.61(9)  | 15.16(14) | 18.85(7)  | 49 | 1.136             | 7.61           | -0.13    | 2.52     | 0.0081   | 2.50-6.10 |
| 50.00       | 6.45(4)                   | 10.82(3) | 15.47(8)  | 18.80(11) | 54 | 0.125             | 13.01          | -0.46    | 3.74     | 0.0027   | 2.60-6.60 |
| 60.00       | 6.71(10)                  | 11.92(4) | 16.68(7)  | 19.95(18) | 56 | 0.344             | 27.52          | -0.02    | 3.59     | 0.0042   | 2.50-6.60 |
| Ni(II)      |                           |          |           |           |    |                   |                |          |          |          |           |
| 0.00        | ---                       | 5.90(11) | 10.91(16) | 15.01(17) | 77 | 6.200             | 19.70          | -0.26    | 3.21     | 0.0171   | 2.10-6.20 |
| 10.00       | ---                       | 5.83(3)  | 11.23(4)  | 15.38(6)  | 68 | 0.520             | 19.06          | -0.51    | 3.66     | 0.0050   | 2.20-6.00 |
| 20.00       | ---                       | 5.78(5)  | 11.42(6)  | 15.11(25) | 66 | 0.838             | 50.97          | -0.92    | 5.12     | 0.0063   | 2.20-6.00 |
| 30.00       | ---                       | 5.85(25) | 11.41(48) | 16.18(72) | 30 | 23.96             | 33.47          | 0.10     | 3.78     | 0.0402   | 2.90-6.60 |
| 40.00       | ---                       | 6.29(22) | 12.39(23) | 16.64(14) | 54 | 10.53             | 28.02          | -1.35    | 6.69     | 0.0223   | 2.20-6.00 |
| 50.00       | ---                       | 7.00(7)  | 13.34(4)  | 17.10(33) | 63 | 0.618             | 68.82          | 1.25     | 4.33     | 0.0049   | 2.20-6.10 |
| 60.00       | ---                       | 7.96(13) | 14.51(7)  | 19.10(11) | 62 | 1.800             | 32.32          | 0.07     | 3.25     | 0.0085   | 2.20-6.30 |
| Zn(II)      |                           |          |           |           |    |                   |                |          |          |          |           |
| 0.00        | ---                       | 5.52(16) | 10.89(21) | 15.70(16) | 53 | 7.902             | 37.58          | -0.27    | 3.92     | 0.0235   | 2.40-6.40 |
| 10.00       | ---                       | 5.16(8)  | 10.70(12) | 14.98(23) | 60 | 2.121             | 35.29          | -0.64    | 5.44     | 0.0113   | 2.40-6.30 |
| 20.00       | ---                       | 5.63(7)  | 11.30(10) | 15.96(11) | 57 | 1.945             | 45.84          | -0.60    | 3.81     | 0.0106   | 2.40-6.30 |
| 30.00       | ---                       | 5.87(7)  | 11.67(11) | 16.37(17) | 55 | 1.962             | 22.10          | -0.86    | 5.51     | 0.0104   | 2.40-6.30 |
| 40.00       | ---                       | 6.94(14) | 12.73(22) | 17.98(14) | 52 | 7.140             | 19.90          | -0.78    | 4.40     | 0.0197   | 2.40-6.30 |
| 50.00       | ---                       | 6.40(8)  | 12.45(13) | 17.51(23) | 52 | 1.630             | 50.77          | -0.41    | 4.04     | 0.0088   | 2.40-6.30 |
| 60.00       | ---                       | 8.71(15) | 14.42(40) | 20.60(11) | 45 | 6.279             | 27.67          | -1.28    | 7.15     | 0.0179   | 2.40-6.30 |

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

## 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 ( $\log \beta$ ) signifies the precision of these constants. The small values of  $U_{\text{corr}}$  (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 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 depict the metal-ligand species in DOX-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 [25] 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 -0.69 and 0.56 for Co(II), -0.46 and 1.87 for Cu(II), -1.35 and 1.25 for Ni(II) and -1.28 and -0.27 for Zn(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 mostly leptokurtic pattern.

### *Effect of systematic errors on best fit model*

In order to rely upon the best fit chemical model for critical evolution of stability constants in present set of experimental conditions, an investigation is made by introducing pessimistic error in concentrations of alkali, acid, ligand and metal content in calculation. MINIQUAD75 does not have direct option for calculation of systematic error on stability constants but pessimistic small changes in various components used can be explained as changes in stability constants are presented as percentage error in Table 2. The order is alkali > acid > ligand > metal. When the error is more, percentage of species ML,  $ML_2$ ,  $ML_2H$  and  $ML_2H_2$  get changed. 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 conform the suitability of the chosen best-fit models. This study also indicates the relative sensitivities of model parameters.

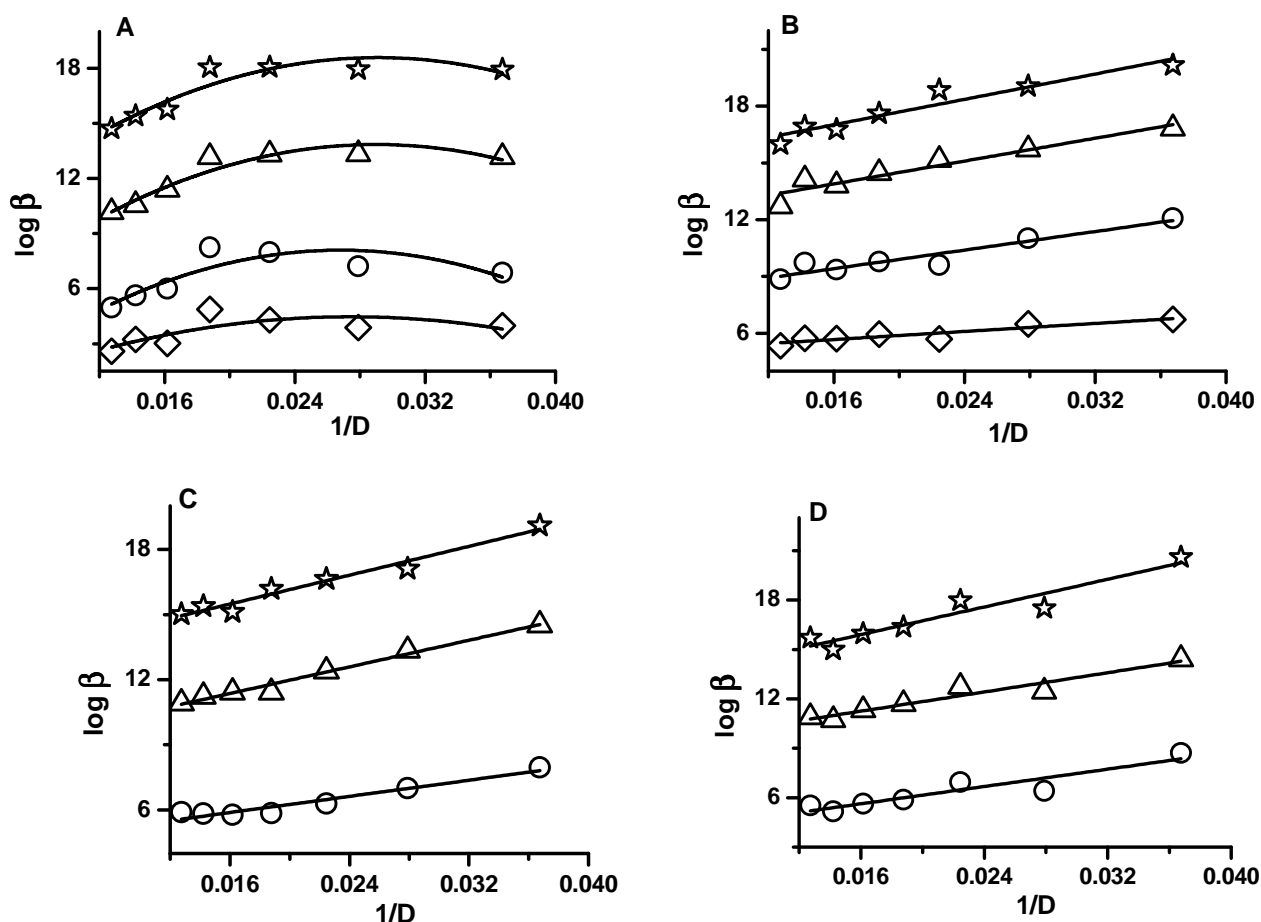
### *Effect of solvent*

The addition of DOX to water decreases the dielectric constant of medium. The dielectric constant values for DOX-water mixture are taken from literature [26]. The change in overall stability constants or change in free energy with change in cosolvent depends on two factors (1) Electrostatic effect (2) Non electrostatic effect.

Table 2: Effect of errors in influential parameters on Cu(II)-MA complex stability constants in 30% v/v DOX-water mixtures.

| Ingredient | % Error | $\log \beta_{mlh}$ (SD) |           |           |           |
|------------|---------|-------------------------|-----------|-----------|-----------|
|            |         | 110                     | 120       | 121       | 122       |
|            | 0       | 5.95(7)                 | 9.78(3)   | 14.46(9)  | 17.61(9)  |
| Acid       | -5      | 6.76(36)                | 12.17(23) | 15.27(56) | Rejected  |
|            | -2      | 6.36(17)                | 10.84(10) | 14.82(28) | 16.28(**) |
|            | +2      | 5.69(3)                 | 8.37(6)   | Rejected  | 17.50(6)  |
|            | +5      | 4.40(7)                 | Rejected  | Rejected  | 17.21(7)  |
| Alkali     | -5      | Rejected                | Rejected  | 12.19(6)  | 17.03(6)  |
|            | -2      | 5.56(3)                 | 7.64(11)  | Rejected  | 17.62(5)  |
|            | +2      | 6.35(15)                | 11.08(11) | 14.86(22) | Rejected  |
|            | +5      | Rejected                | 12.23(21) | 15.65(21) | Rejected  |
| Ligand     | -5      | 6.06(20)                | 10.44(10) | 14.63(26) | 17.46(46) |
|            | -2      | 6.00(11)                | 10.08(6)  | 14.53(15) | 17.54(19) |
|            | +2      | 5.89(7)                 | 9.47(3)   | 14.40(9)  | 17.69(7)  |
|            | +5      | 5.77(12)                | 8.92(7)   | 14.29(15) | 17.79(9)  |
| Metal      | -5      | 6.01(8)                 | 10.00(4)  | 14.55(11) | 17.53(15) |
|            | -2      | 5.98(7)                 | 9.87(4)   | 14.49(10) | 17.58(11) |
|            | +2      | 5.93(6)                 | 9.70(3)   | 14.42(9)  | 17.64(8)  |
|            | +5      | 5.57(2)                 | 7.93(7)   | Rejected  | 17.76(4)  |
| Volume     | -5      | 5.92(7)                 | 9.76(4)   | 14.44(9)  | 17.59(9)  |
|            | -2      | 5.94(7)                 | 9.77(4)   | 14.45(9)  | 17.60(9)  |
|            | +2      | 5.97(7)                 | 9.80(4)   | 14.46(10) | 17.62(9)  |
|            | +5      | 5.99(7)                 | 9.82(4)   | 14.47(10) | 17.64(10) |

\*\* Indicates high standard deviation.

Figure 1: Variation of stability constants of metal-MA complexes with reciprocal of dielectric constant ( $1/D$ ) in DOX-water mixtures. (A) Co(II); (B) Cu(II); (C) Ni(II) and (D) Zn(II): (☆)  $\log \beta_{ML2H2}$ , (△)  $\log \beta_{ML2H}$ , (○)  $\log \beta_{ML2}$ , (◇)  $\log \beta_{ML}$ .

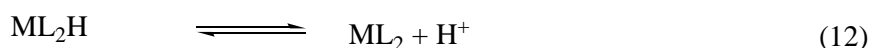
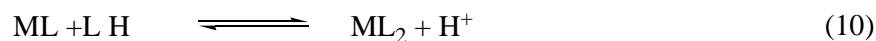
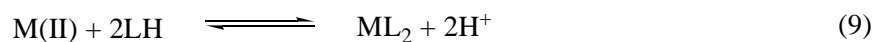
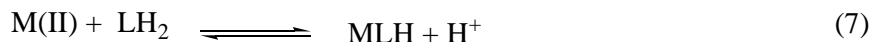
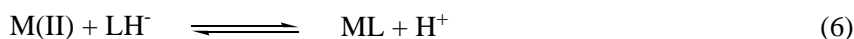
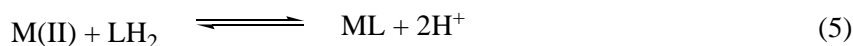
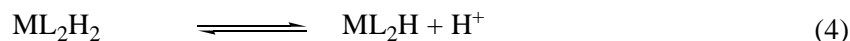
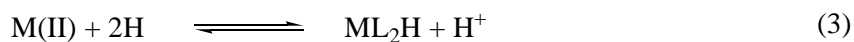
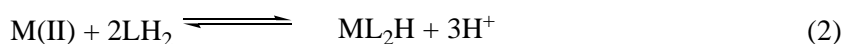
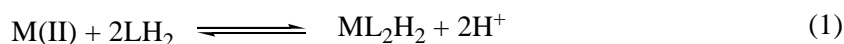
As basicity of DOX is lower than that of water, the non-electrostatic effect seems to decrease proton accepting property of ligand in mixed solvents equilibrium. Addition of more DOX removes water molecules from coordination sphere of metal ion making it more susceptible to react with MA. According to Born equation, the energy to electrostatic interaction is related to dielectric constant of medium [27, 28]. So  $\log \beta$  should increase linearly (Figure 1) with decrease in dielectric constant of medium (with increase in DOX content). So  $\log \beta$  values increase with increase in DOX content in mixtures.

Also interaction between metal ion and ligand is electrostatic in nature, variation of stability constant is linear up to 50% after that deviations are observed which may due to nonelectrostatic effects. The cation solvating nature of cosolvent, specific solvent-water interaction, charge dispersion and in some system interaction of cosolvent with solute also accounts for small deviation from a linear relationship. So complex formation is considered as competition between pure and solvated form of ligand and metal ion, solvent-solvent interaction, relative thermodynamic stability and kinetic lability [29].

#### *Distribution diagrams*

MA contains two ionizable carboxyl protons. The different forms of MA are  $LH_2$ ,  $LH^-$  and  $L^{2-}$  in the pH range 1.6 - 4.30, 1.6.0 - 7.10 and 4.30 - 7.10, respectively.  $LH_2$  species is predominant at  $pH < 2$ . As the pH increases its concentration decreases exponentially and become almost zero around 5. The  $LH^-$  species has the maximum concentration at  $pH \approx 4.5$ . The free ligand ( $L^{2-}$ ) concentration progressively increases at higher pH value. The concentration of  $LH_2$  species is almost insignificant compared to that of  $LH^-$ . Hence, from the above data plausible binary metal-ligand complexes can be predicted. The present investigation reveals the existence of  $ML$ ,  $ML_2$ ,  $ML_2H$  and  $ML_2H_2$  for Co(II) and Cu(II) and  $ML_2$ ,  $ML_2H$  and  $ML_2H_2$  for Ni(II) and Zn(II).

The formation of binary complex species is presented in the following equilibria.



The species MLH (equilibria 7 and 8) could not be identified in the present study probably because it will be formed at very low pH or might be quickly deprotonated. The species distribution diagram in Dox-water mixtures also presented in Figure 2. From the figures the formation of binary complexes of Co(II), Cu(II) and Ni(II) and Zn(II) range from 2.0 to 7.0 pH.  $ML_2H_2$ ,  $ML_2H$  and ML are predominant species in narrow pH range (3.0-5.0) but  $ML_2$  is predominant above pH of 6 and the highest percentage traced at neutral pH (7.50). At low pH,  $ML_2H_2$  species is formed from free metal ions interact with  $LH_2$  form of the ligand (equilibrium 1). The interaction of free metal ions with  $LH_2$  or  $LH^-$  at lower pH (equilibria 2 and 3) and deprotonation of  $ML_2H_2$  at higher pH (equilibrium 4) result the formation of  $ML_2H$  species. Higher concentration of  $ML_2H$  than that of  $ML_2H_2$  signifies the  $ML_2H$  is formed from equilibria 2, 3 and 4. The  $ML_2$  species is formed from interaction of free metal ion with  $LH^-$  (equilibrium 9) or from ML and  $LH^-$  (equilibrium 10) or deprotonation of  $ML_2H$  and  $ML_2H_2$  (equilibria 11 and 12).

In the case of Co(II) and Cu(II) ( Figure 2A and 2B) the ML species may be formed from the interaction of free metal ion with  $LH_2$  or  $LH^-$  (equilibria 5 and 6) or deprotonation of MLH (equilibrium 8). However, equilibrium 8 was not detected in the present study hence, ML only formed from the interaction of  $LH_2$  and  $LH^-$  with free metal ions.

The distribution of the species over the entire pH range is useful to understand the pH where a particular species is likely to form. By using these data, the bioavailability of a metal can be predicted. For instance, in Figure 2 the concentration of free metal ion (FM) is very high in acidic pH values. Hence, in these pH ranges the metals are more bioavailable than in higher pH ranges. Hence, the concentrations of the complex chemical species have more significance than the total concentrations for the bioavailability and toxicity of essential metals in soils and water.

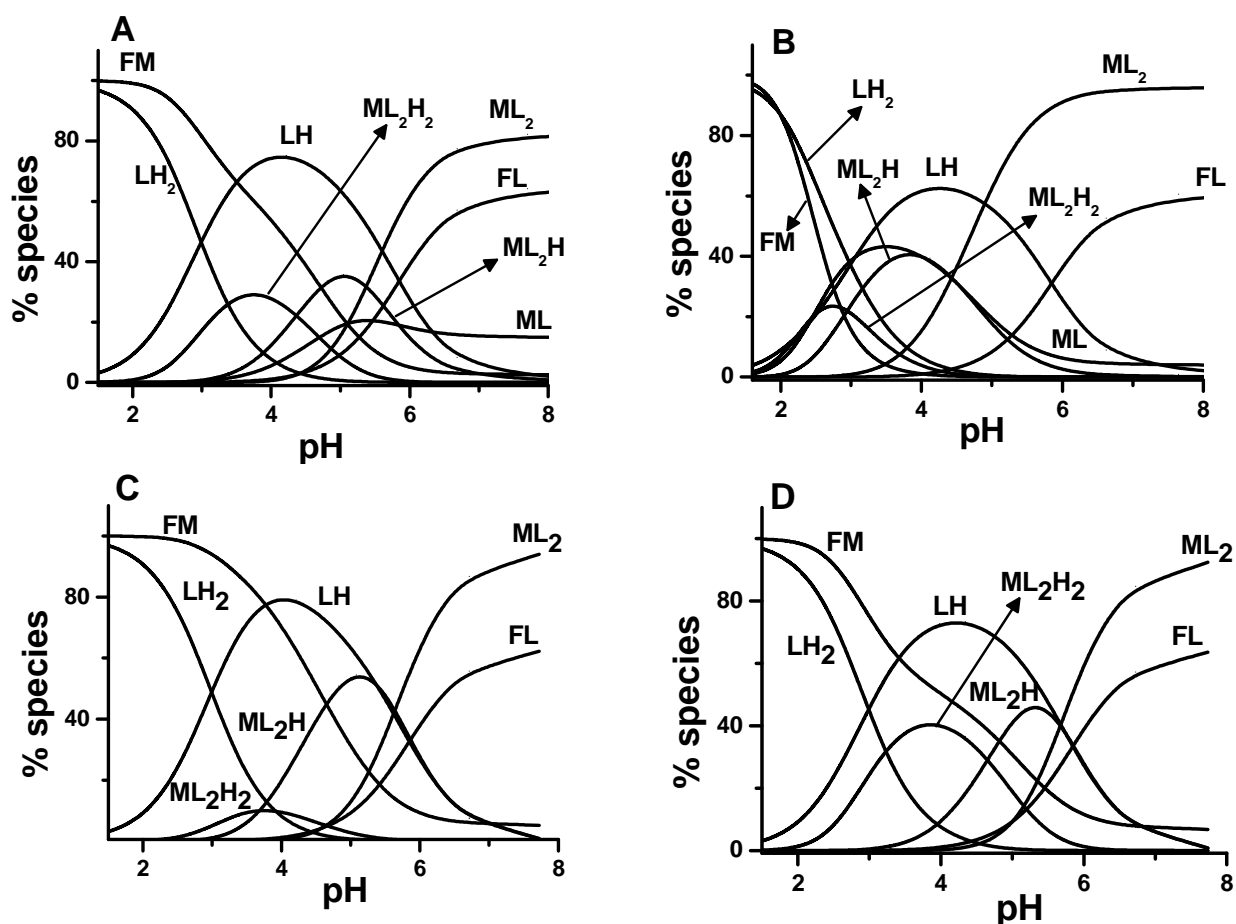


Figure 2: Distribution diagrams of MA-Metal complexes in 20 % DOX- water mixtures. (A) Co(II), (B) Cu(II), (C) Ni(II) and (D) Zn(II).

#### Structures of complexes

MA possesses two carboxylic acid groups that can form complexes with metal ions. The complexation ability of the acid type ligand depends on the pH of the media, due to the different degree of dissociation [30]. Generally, from table 1 the final model containing ML,  $ML_2$ ,  $ML_2H$  and  $ML_2H_2$  appropriately fits the experimental data. Octahedral

structures (Figure 3) are proposed to the complexes of all the metal ions. The VSEPR theory suggests that (Cu(II), Ni(II), Cu(II) and Zn(II) complexes shall be octahedral because there are six outer electron pairs.

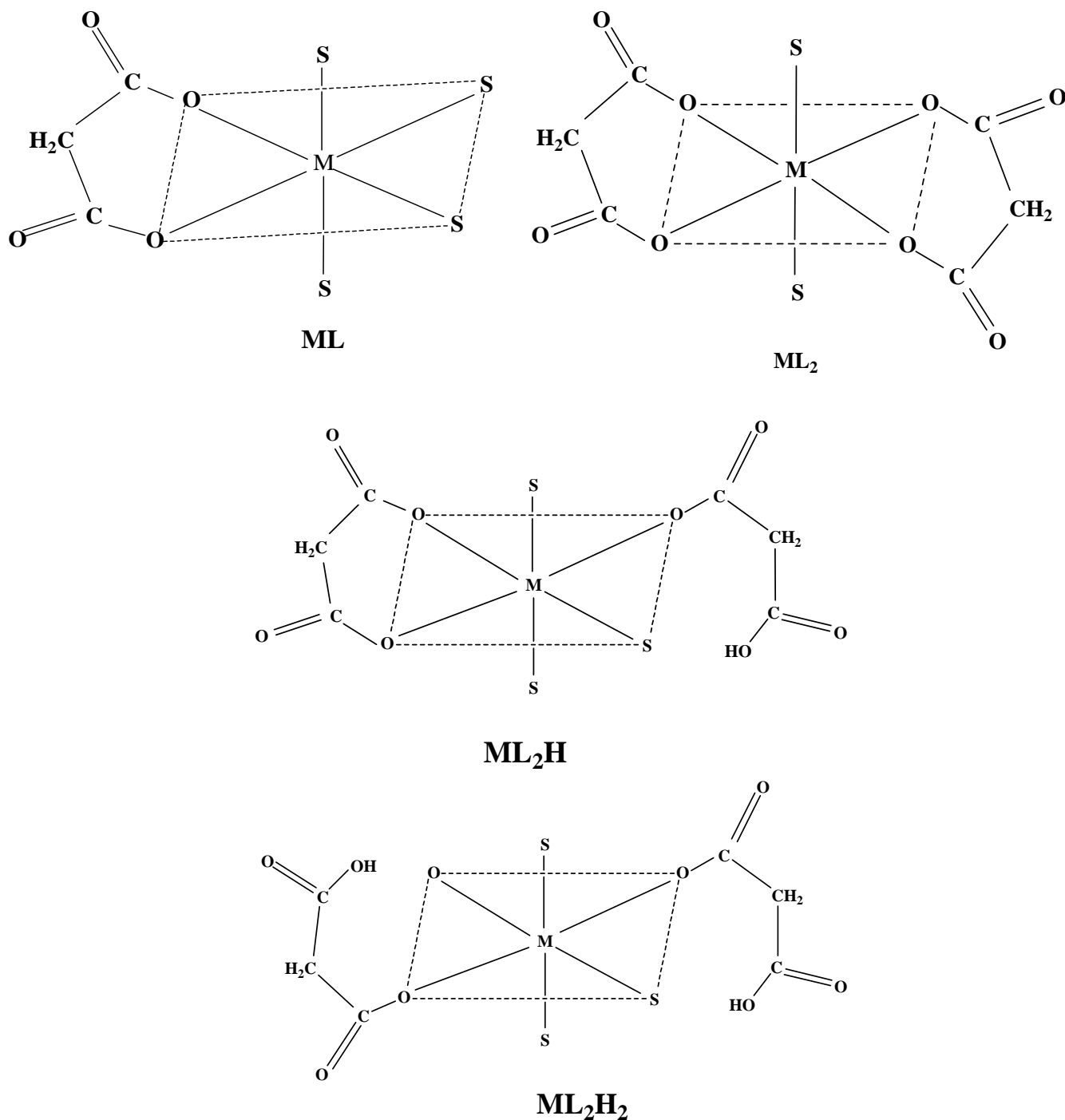


Figure 3: Structure of MA complexes of Co(II), Cu(II), Ni(II) and Zn(II). S is either solvent or water molecule.

### CONCLUSION

In the present work, pH-metric study was performed to determine stability constants and to assess binary species for MA with essential metal ions in 0.0-60.0% DOX-water mixture in pH range of 2.0-7.0. The following conclusions have been drawn:

1. The binary species formed due to the interaction of MA with metals are  $ML_2H_2$ ,  $ML_2H$ ,  $ML_2$  and  $ML$  for Co(II) and Cu(II) and  $ML_2H_2$ ,  $ML_2H$ ,  $ML_2$ . For Ni(II) and Zn(II). These models are validated by statistical treatment of data.



2. The linear variation of stability constants as a function of 1/D of the medium indicates the dominance of electrostatic forces over non-electrostatic forces and the dominance of structure forming nature of the co-solvents over its coordinating power.
3. Systematic errors strongly affect complexation equilibria. The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal > volume.

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