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## Influence Of Dielectric Constants Of Dimethyl Sulphoxide Medium On The Complex Equilibria Of Maleic Acid With Pb(II) And Cd(II)

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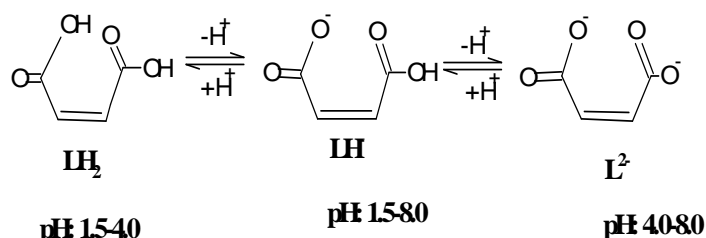
### ABSTRACT

Chemical speciation of Maleic acid complexes of Pb(II) and Cd(II) in the presence of (0-50% v/v) Dimethyl sulfoxide-water mixtures has been studied pH-metrically at 303.0K and at an ionic strength of 0.16 molL<sup>-1</sup>. The models containing different number of species were refined by using the computer program MINQUAD75. The number of species in the models is chosen based on exhaustive modeling. The predominant species detected are ML<sub>2</sub>, ML<sub>2</sub>H and ML<sub>3</sub>. The best fit chemical models were arrived at based on statistical parameters. The appropriateness of the models is ascertained by studying the effect of errors in concentrations of ingredients. The trend in variation of stability constants with change in the composition of medium is explained on the basis of electrostatic and non-electrostatic forces. Chemical speciation was discussed based on the distribution diagrams.

**Keywords:** Chemical speciation, Maleic acid, Dimethyl sulfoxide, Stability constants.

### INTRODUCTION

A number of studies have been reported on chemical speciation of carboxylic acid 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 an organic compound that 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. Maleic acid 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. The Protonation - deprotonation equilibria of Maleic acid is given below.



Lead affects every organ of the body, especially the bones and teeth, the kidneys, the nervous, cardiovascular, immune and reproductive systems (6). Lead has no known physiologically relevant role in the body (7-8). Lead may

also be harmful to the developing immune system, causing production of excessive inflammatory proteins; this mechanism may mean that lead exposure is risk factor for asthma in children (9). Cadmium, a potentially toxic metal, has been shown to accumulate in plants, where it is detoxified by binding to phytochelatin (10-11), a family of thiol-rich peptides (12). The possible effects of long term low-level exposure to cadmium are of concern because it is readily distributed to tissues of liver and kidney, which are the main target organs in acute and chronic cadmium exposure (13-14).

Dimethyl sulphoxide is a polar aprotic solvent. It is extensively used as an extractant in biochemistry and cell biology. In medicine, Dimethyl sulphoxide is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant. Dimethyl sulphoxide is finding increased use in manufacturing processes to produce microelectronic devices (15) In organic synthesis, Dimethyl sulphoxide is used as a mild oxidant (16).

## MATERIALS AND METHODS

### Materials

Maleic acid (Qualigens, India) solution ( $0.05\text{molL}^{-1}$ ) was prepared in triple-distilled water by maintaining  $0.05\text{molL}^{-1}$  nitric acid concentration to increase the solubility. Dimethyl sulphoxide (Merck, India) was used as received.  $2\text{molL}^{-1}$  sodium nitrate (Qualigens, India) was prepared to maintain the ionic strength in the titrand.  $0.05\text{molL}^{-1}$  aqueous solutions of Pb(II) and Cd(II) nitrates were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple-distilled water maintaining  $0.05\text{molL}^{-1}$  nitric acid to suppress the hydrolysis of metal salts. All the solutions were standardized by standard methods. 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 (17). The strengths of alkali and mineral acid were determined using the Gran plot method (18-19).

### Apparatus

The titrimetric data were obtained using ELICO (Model LI-120) pH meter (readability 0.01), which was calibrated with  $0.05\text{molL}^{-1}$  potassium hydrogen phthalate in acidic region and  $0.01\text{molL}^{-1}$  borax solution in basic region. The glass electrode was equilibrated in a well stirred Dimethyl sulphoxide -water mixture containing the inert electrolyte. All the titrations were carried out in the medium containing varying concentrations of Dimethyl sulphoxide - water mixtures (0-50% v/v) by maintaining an ionic strength of  $0.16\text{molL}^{-1}$  with sodium nitrate at  $303.0 \pm 0.1\text{K}$ . 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 (20-21).

### Procedure

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 Dimethyl sulphoxide - water mixture of equivalent composition as that of 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) of metal-to-ligand were carried out with  $0.4\text{molL}^{-1}$  sodium hydroxide. Other experimental details are given elsewhere (22).

### Modeling Strategy

The computer program SCPHD (23-24) was used to calculate the correction factor. The binary stability constants were calculated with the pH-metric titration data using the computer program MINQUAD75 (25-26), 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 dielectric constants of the medium was analysed on electrostatic grounds based on solute-solute and solute - solvent interactions.

## RESULTS AND DISCUSSION

The results of exhaustive modeling for the Pb(II)-MA system in 20% v/v DMS-water mixture are given Table 2. The models gave better statistics as the number of species was increased, confirming better fit. There was no further improvement in the fit on inclusion of some more species in the model containing  $\text{PbL}_2$ ,  $\text{PbL}_2\text{H}$  and  $\text{PbL}_3$ . This

indicates that the final model appropriately fit the experimental data. Such exhaustive modeling was performed for all the systems. The results of the final 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 ingredients 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 (27).

### 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 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  $\chi^2$ , Skewness, Kurtosis and R-factor. These statistical parameters show that the best-fit models portray the metal-ligand species in Dimethyl sulfoxide - water mixtures, as discussed below.

In the present study, the kurtosis values indicate that the residuals form leptokurtic pattern. The values of skewness recorded in Table 1 are between 0.18 and 3.36 for Cd(II), -0.25 and 0.76 for Pb(II). These data evince that the residuals form part of a normal distribution. Hence, least square 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 portray the metal-ligand species in Dimethyl sulfoxide media.

### 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 3). 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 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.

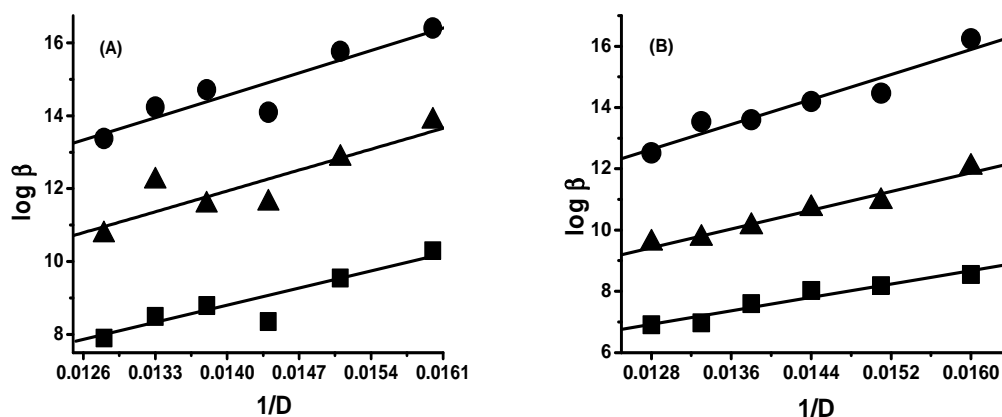


Figure 1. Variation of overall stability constant values of metal- Maleic acid complexes with Dimethyl sulfoxide - water mixtures (A) Pb(II) and (B) Cd(II); (■)  $\log \beta_{\text{ML}_2}$ ; (▲)  $\log \beta_{\text{ML}_3}$ ; and (●)  $\log \beta_{\text{ML}_2\text{H}}$

### Effect of Solvent

The variation of protonation constant or change in free energy with co-solvent content depends upon two factors, viz., electrostatic and non-electrostatic. Born's classical treatment holds good in accounting for the electrostatic contribution to the free energy change (28). According to this treatment, the energy of electrostatic interaction is related to dielectric constant. Hence, the logarithm of overall stability constant ( $\log \beta$ ) should vary linearly as a

function of the reciprocal of the dielectric constant ( $1/D$ ) of the medium. These plots (Figure 1) in Dimethyl sulfoxide -water mixtures show that the log  $\beta$  values are linearly increasing with decreasing dielectric constant values.

### 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 1.5-3.5, 3.5-8.0, and 4.0-8.0, respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the existence of  $ML_2H$ ,  $ML_2$  and  $ML_3$  for Pb(II) and Cd(II). The  $ML_2$  species is the predominant species (Figure 2) at higher pH and  $ML_2H$  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 Dimethyl sulphoxide - water media are shown in Figure 2. The species of  $ML_2H$ ,  $ML_3$  and  $ML_2$  are formed in the pH range of 1.5-5.5 for Pb(II) and 1.5-8.0 for Cd(II) respectively.  $ML_2H$  is formed at lower pH and  $ML_2$ ,  $ML_3$  are formed with the increasing pH.  $ML_3$  and  $ML_2$  species percentage successively increases with increasing pH. Successive deprotonation of  $ML_2H_2$ ,  $MLH$  and protination of  $ML$  forms  $ML_2H$  [Equilibria (1), (2) and (3)].  $ML_2$  formed at higher pH. [Equilibria (5), (6) and (7)]. The percentage of the  $ML_2$  species increases successively with increase in pH. The concentration of  $ML_2H$  species decreased, while the concentration of  $ML_2$  and  $ML_3$  increased in the pH range.

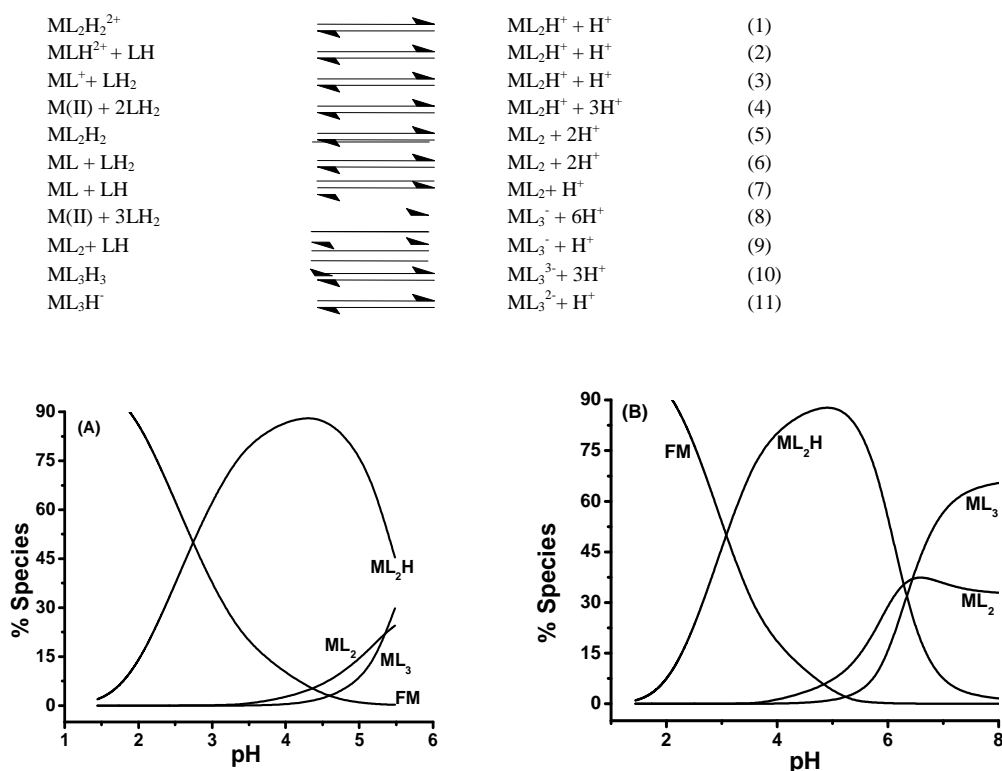


Figure 2: Distribution diagrams of binary complexes of Maleic acid in 40% v/v Dimethyl sulfoxide - water mixture: (A) Pb(II) and (B) Cd(II)

### 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 Pb(II) and Cd(II) complexes shall be octahedral because there are six outer electron pairs.

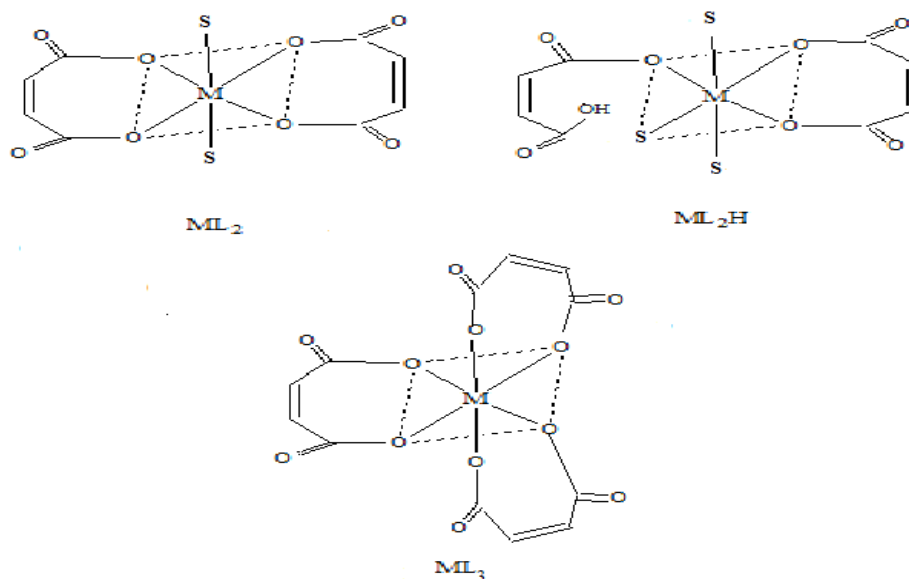


Figure 3. Structures of binary complexes of Maleic acid with M(II). Where S is either solvent or water molecule

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

%v/v DMSO	log $\beta_{mih}$ (SD)			NP	U <sub>corr</sub>	Skew-ness	$\chi^2$	R-Factor	Kurtosis	pH-Range
	ML <sub>2</sub>	ML <sub>3</sub>	ML <sub>2</sub> H							
<b>Pb(II)</b>										
0	7.90(19)	10.73(15)	13.38(05)	75	4.88	0.04	12.02	0.0166	2.35	2.0-6.0
10	8.49(39)	12.21(14)	14.24(08)	71	13.89	0.52	7.21	0.0295	4.08	2.0-6.0
20	8.79(30)	11.55(26)	14.72(10)	61	9.91	-0.25	15.25	0.0246	5.60	2.0-6.0
30	8.35(21)	11.60(41)	14.10(15)	20	26.61	0.76	20.00	0.0565	4.35	2.8-7.4
40	9.55(37)	12.83(24)	15.77(05)	55	3.62	-0.07	9.79	0.0140	3.55	2.0-6.0
50	10.30(34)	13.85(22)	16.41(07)	61	6.39	-0.08	19.10	0.0186	3.25	2.0-7.5
<b>Cd(II)</b>										
0	6.91(19)	9.57(86)	12.52(61)	41	87.07	3.36	114.33	0.1086	13.37	3.0-8.5
10	6.97(72)	9.73(50)	13.54(20)	74	79.63	0.18	24.99	0.0733	3.39	2.0-8.0
20	7.60(40)	10.11(42)	13.60(14)	80	32.88	2.50	60.67	0.0446	13.42	2.0-8.0
30	8.03(35)	10.70(37)	14.20(16)	87	46.92	4.31	205.97	0.0523	24.61	2.0-8.0
40	8.19(69)	10.93(65)	14.47(30)	89	91.26	2.67	84.85	0.0701	14.00	2.0-8.0
50	8.55(45)	12.05(17)	16.25(10)	71	17.78	1.69	44.84	0.0332	10.19	2.0-8.0

$U_{corr} = U/(NP-m) \times 10^8$ , where  $m$  = number of species; NP=Number of experimental points; SD=Standard deviation

Table 2: Results of exhaustive modeling studies of Pb(II)-MA in 20% v/v DMS-water mixture, pH 2.0-6.0, NP =61								
Model No.	log $\beta_{mih}$ (SD)			U <sub>corr</sub>	$\chi^2$	Skewness	Kurtosis	R-factor
	120	121	130					
1	Rejected	--	--	--	--	--	--	--
2	--	15.78(11)	--	15.65	52.85	-0.48	3.90	0.0309
3	--	--	11.59(10)	10.76	16.56	0.05	5.30	0.0256
4	Rejected	15.78(11)	--	15.66	52.85	-0.48	3.90	0.0309
5	8.62(29)	--	11.38(24)	10.25	19.97	-0.12	5.35	0.0250
6	--	14.70(11)	11.75(15)	10.48	22.42	-0.04	5.52	0.0253
7	8.79(30)	14.72(10)	11.55(26)	9.91	15.25	-0.25	5.60	0.0246

**Table 3: Effect of errors in influential parameters on Cd(II) - Maleic acid complex stability constants in 40% v/v Dimethyl sulfoxide - water mixture**

Ingredient	% Error	Log $\beta_{min}(SD)$		
		120	130	121
Acid	0	8.19(69)	14.47(30)	10.93(65)
	-5	Rejected	15.92(32)	14.80(80)
	-2	8.51(98)	14.60(31)	11.39(82)
	+2	8.29(97)	14.67(27)	11.67(64)
	+5	10.27(47)	Rejected	Rejected
Alkali	-5	Rejected	Rejected	Rejected
	-2	10.62(35)	Rejected	Rejected
	+2	Rejected	15.15(27)	13.65(67)
	+5	Rejected	Rejected	Rejected
Ligand	-5	Rejected	14.89(29)	13.00(72)
	-2	7.88(**)	14.64(29)	11.99(62)
	+2	11.27(26)	Rejected	Rejected
	+5	10.98(28)	Rejected	Rejected
Metal	-5	11.51(26)	Rejected	13.87(**)
	-2	8.21(80)	14.48(30)	11.01(69)
	+2	8.17(84)	14.46(31)	10.87(74)
	+5	8.13(60)	14.44(29)	10.74(66)

\*\* means high standard deviation

### CONCLUSION

1. The present biomimetic studies of metal ion complexes with Maleic acid in Dimethyl sulphoxide - water mixtures indicate that all the complexes were protonated in acidic pH values.
2. The predominant species detected were  $ML_2H$ ,  $ML_2$  and  $ML_3$ .
3. The log  $\beta$  values linearly vary with reciprocal of dielectric constant values 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 concentration of free metal in low pH values make the metal more bioavailable, more so in the case of toxic metals. At higher pH values, the higher concentrations of complex chemical species indicate that the metals are more amenable for transportation at higher pH values.

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