

## EQUILIBRIUM STUDIES OF MERCURY (II), LEAD (II) AND CADMIUM (II) IONS INVOLVING ASPARTIC ACID AND THYMINE

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### ABSTRACT

Equilibrium studies of Hg (II), Pb (II) and Cd (II) ions with aspartic acid (X) and thymine (Y) ligands in aqueous solution have been investigated. Stability constants of the complexes and the complex formation equilibria at temperature  $37 \pm 1^\circ\text{C}$  at the ionic strength  $I = 0.1 \text{ M}$  ( $\text{NaNO}_3$ ) have been determined by potentiometric method. Complexes of the type  $\text{MXY}$  (1:1:1) and  $\text{M}_1\text{M}_2\text{XY}$  (1:1:1:1) have been discussed.

**Keywords:** SCOGS, Aspartic acid, Thymine and Quaternary complexes.

### INTRODUCTION

Human body contains many chelating agents such as amino acids, globins, proteins, enzymes, carboxylic acids and nucleic acid-bases, which form chelate compounds<sup>1, 2</sup> with the metal ion present in the living organism. Recent research results<sup>3, 4, 5, 6, 7</sup> have clearly demonstrated the need for comprehensive studies of metal ions and bio-ligand interaction as model systems. Multi metal-multiligand complexes studied gives clues to the roles of metal ions in many enzymic reactions<sup>8, 9</sup>. This paper deals with the investigation of Hg (II), Pb (II) and Cd (II) complexes with aspartic acid and thymine. The relevant stability constants have been calculated using SCOGS<sup>10</sup> computer program.

### MATERIALS AND METHODS

All the reagents were of A.R. grade and their solution were prepared in double distilled  $\text{CO}_2$ -free water. Metal nitrate solutions were standardized by EDTA titration methods<sup>11</sup> combined with ion exchange and acid base titration<sup>12</sup>. For all the binary, ternary and quaternary systems, following solution mixture have been titrated against standardized  $\text{NaOH}$  (0.01M) solution, keeping the total volume 50.0 ml in each case:

- (i) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) +  $\text{H}_2\text{O}$

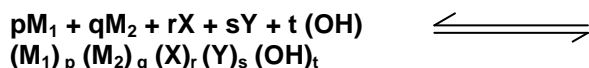
- (ii) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) + 5ml X(0.01M) +  $\text{H}_2\text{O}$   
 (iii) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) + 5ml Y(0.01M) +  $\text{H}_2\text{O}$   
 (iv) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) + 5ml X(0.01M) + 5ml  $\text{M}_1$ (II)(0.01M) +  $\text{H}_2\text{O}$   
 (v) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) + 5ml X(0.01M) + 5ml  $\text{M}_1$ (II)(0.01M) + 5ml Y (0.01M) +  $\text{H}_2\text{O}$   
 (vi) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) + 5ml X(0.01M) + 5ml  $\text{M}_2$ (II)(0.01M) + 5ml Y (0.01M) +  $\text{H}_2\text{O}$   
 (vii) 5ml  $\text{NaNO}_3$ (1.0M) + 5ml  $\text{HNO}_3$ (0.02M) + 5ml X(0.01M) + 5ml  $\text{M}_1$ (II)(0.01M) + 5ml Y (0.01M) + 5ml  $\text{M}_2$ (II)(0.01M) +  $\text{H}_2\text{O}$

Where,  $\text{M}_1$  (II) and  $\text{M}_2$  (II) are Hg (II)/Pb (II) / Cd (II). X = Aspartic acid and Y =Thymine  
Species distribution curves were obtained by plotting % concentration of the species obtained through SCOGS against pH. Complex formation equilibria were elucidated with the aid of the species distribution curve.

### RESULTS AND DISCUSSIONS

The ligand aspartic acid is potentially a tridentate ligand towards metal ions coordinating through a nitrogen and two carboxyl oxygen atoms. The secondary ligand thymine is chemically 2, 4-dioxo-5-methylpyrimidine. It has been concluded that in general, thymine acts as a bidentate ligand.<sup>13</sup>

Proton ligand stability constants obtained for both the ligands and other related stability constants are presented in table 1-5. Which are in good agreement with literature values<sup>14</sup>. The formation of quaternary complexes in an aqueous solution may be conveniently expressed by the equilibrium

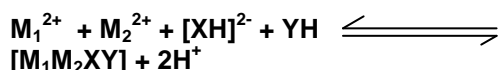


The overall stability constant is given by

$$\beta_{parst} = \frac{[(M_1)_p (M_2)_q (X)_r (Y)_s (OH)_t]}{[M_1]^p [M_2]^q [X]^r [Y]^s [OH]^t}$$

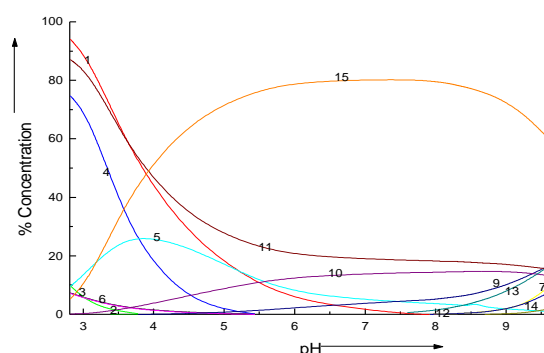
Where the stoichiometric numbers p, q, r, s are either zero or positive integer and t is a negative integer for a protonated species, positive for a hydroxo or a deprotonated species and zero for a neutral species.

The speciation curves indicate the formation of heterobinuclear complex species  $M_1M_2XY$  in the pH range -2.6-9.5, according to the following equilibria



It is clear from the speciation curves that formation of heterobimetallic complexes is preferred over the homometallic complexes.

the following species have been considered to exist in the equilibria  $Pb(II)-Cd(II)-X-Y$  (1:1:1:1)



**Fig. 1: Distribution Curves of 1:1:1:1 Pb(II)-Cd(II)-X-Y System**  
 (1)  $Cd^{2+}(II)$  (2)  $Pb^{2+}(II)$  (3)  $H_3X$  (4)  $H_2X$  (5)  $HX$  (6)  $YH$  (7)  $Cd(OH)_2$  (8)  $Cd(OH)^+$  (9)  $Pb(OH)_2$  (10)  $CdY$  (11)  $PbX$  (12)  $PbY$  (13)  $CdXY$  (14)  $PbXY$  (15)  $PbCdXY$

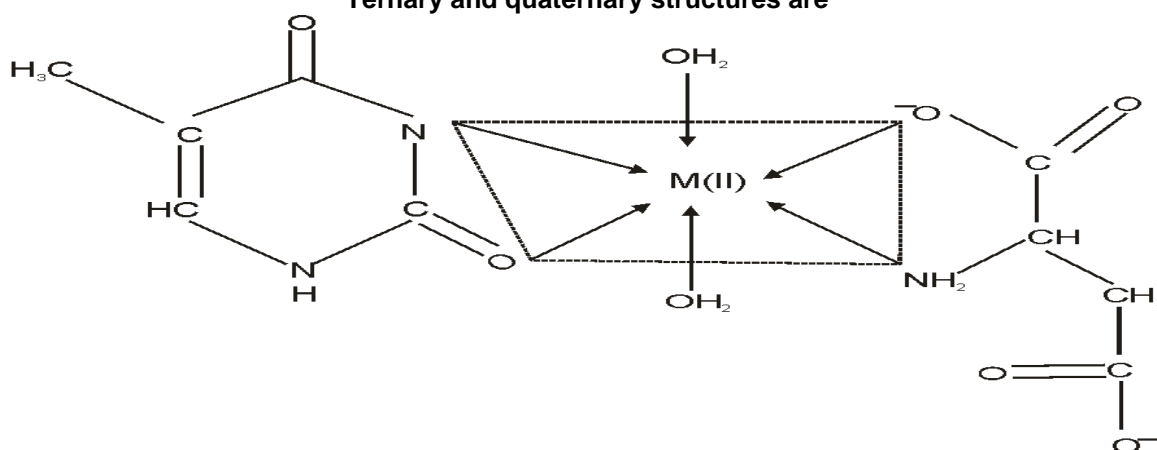
## CONCLUSIONS

On the basis of experimental results we have to say that, ternary and quaternary complexes of mercury are more stable in comparison of lead and cadmium. The overall stability constants of ternary ( $MX_2Y$ ) and quaternary systems ( $M_1M_2XY$ ) have been found to follow the following order:

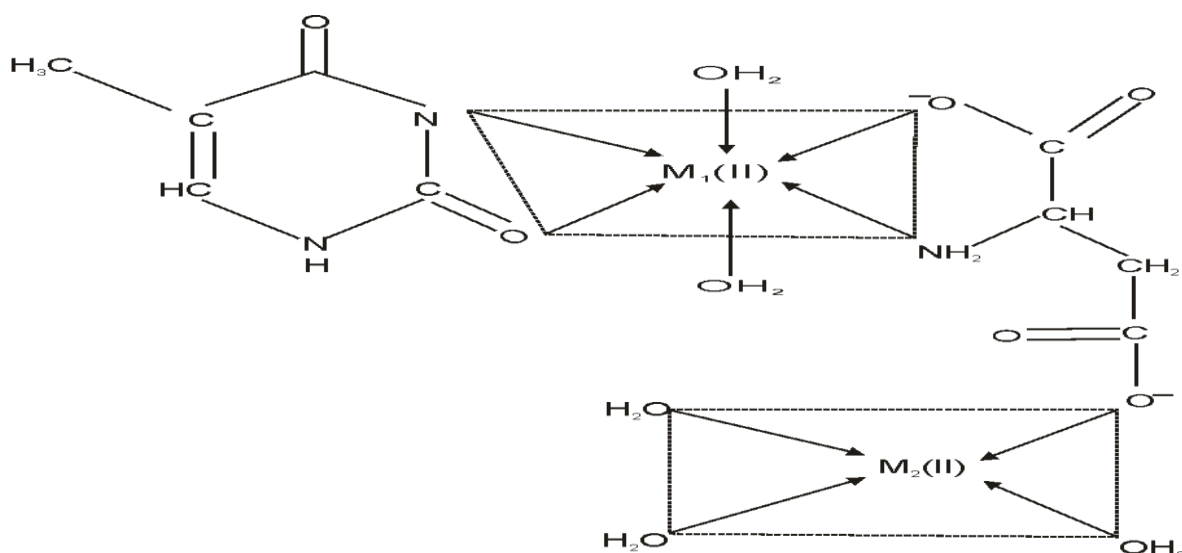
Ternary System:  $HgXY > PbXY > CdXY$

Quaternary System:  $Hg-Pb-XY > Hg-Cd-XY > Cd-Pb-XY$

Ternary and quaternary structures are



**Structure 1: Ternary ( $MX_2Y$ )**

Structure 2: Quaternary ( $M_1M_2XY$ )Table 1: Proton-ligand formation constant ( $\log \beta_{00r0t} / \log \beta_{000st}$ ) of Aspartic acid and Thymine at  $37 \pm 1^\circ\text{C}$ ,  $I = 0.1 \text{ NaNO}_3$ 

Complex	$\log \beta_{00r0t} / \log \beta_{000st}$
$H_3X$	15.26
$H_2X$	13.33
$HX$	9.63
$YH$	9.94

Table 2: Hydrolytic constants ( $\log \beta_{p000t} / \log \beta_{0q00t}$ )  $M^{2+}$  (aq.) ions

Complex	Hg	Pb	Cd
$M(OH)^+$	-3.84	-9.84	-6.89
$M(OH)_2$	-6.38	-15.54	-14.35

Table 3: Metal-Ligand constants ( $\log \beta_{p0r00} / \log \beta_{0qr00} / \log \beta_{p00s0} / \log \beta_{0q0s0}$ ) Binary System

Complex	Hg	Pb	Cd
$MX$	13.08	11.60	4.38
$MY$	13.42	12.77	11.45

Table 4: Metal-Ligand constants ( $\log \beta_{p0rs0} / \log \beta_{0qrs0}$ ): Ternary System (1:1:1)

Complex	Hg	Pb	Cd
$MXY$	21.11	18.08	14.15

Table 5: Metal-Ligand constants ( $\log \beta_{pqrst}$ ): Quaternary System (1:1:1:1)

Complex	Hg-Pb	Hg-Cd	Cd-Pb
$M_1M_2XY$	28.81	27.80	26.82

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