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A COMPUTER BASED ANALYTICAL STUDY ON CHELATE COMPOUNDS OF HEAVY METAL IONS INTERACTING WITH AMINO ACID AND NUCLEOBASE

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ABSTRACT

The study on mixed - ligand chelation of heavy metal ions Hg (II) and Cd (II) with amino acid taken as primary ligand (A) and nucleobase taken as secondary ligand (B) at silver-silver chloride electrode by the pH - metric technique at 37 ± 1°C in two different molar ratio 1:2:1 and 1:2:2 for mixed- ligand ternary chelates. The stability constants and stability order of MA, MB and MAB complexes have been discussed with the help of SCOGS at fixed temperature and ionic strength. The species distribution curves described the formation of chelate compound play important role in biological system.

KEYWORDS: Chelation, Chelate Compound, pH-Metry, Stability Order, SCOGS, Distribution Curves

INTRODUCTION

There are a large number of toxic metals are found in nature. They are also known as heavy elements or heavy metals such as arsenic, bismuth, cadmium, chromium lead, manganese, mercury etc. The chelating agent must be of low toxicity and not metabolized so as to persist on changes in the biological system to perform their scavenging functions due to their interaction with metal ions to form metal chelates or dislodging the bound metals and excreting these as soluble chelates from the system. The metal chelates play an important role in biological[1]analytical[2] industrial[3, 4,] and medicinal[5] area. In the present paper amino acid (2-Amino succinic acid) and nucleobase (5-methyluracil) behave as a very good chelating agent which form ternary chelate compound of biological significance interacting with heavy metal ions Hg (II) and Cd (II)**.** Some essential and non - essential or potentially toxic metal ions are present in biological systems[6, 7]. In biological processes[8-10] ternary chelation plays very valuable role. Mercury is a heavy metal may be called the mad hatters mineral. It is a toxic substance which has no known function in human biochemistry or physiology. Cadmium is called the pseudo-macho or the violent element.

It is biopersistent and once absorbed by an organism remains resident for many years although it is eventually excreted. The normal and acceptable value of Hg (II) and Cd (II) metals are about 0.25 ppm and 0.08 ppm respectively. Mostly, amino acids are soluble in water which shows zwitter ion in solution. They normally coordinate to metal ions through the amino and carboxylato groups. Attractive ligand-ligand interactions favor the formation of mixed ligand complexes, giving rise to ligand selectivity or a preferred combination of ligands around a metal ion. The importance of metal ion–nucleic acid interactions in the metabolic machinery is well recognized and applied medicinal chemistry. Metal ions can interact with nucleobases and sugar moieties as well as with phosphates. Martin in an extensive review discussed the competition between the N_1 and N_7 nitrogen atoms in purines for metal ions in aqueous solutions. 2-Aminosuccinic acid play valuable role in absorption of toxins and removal from the bloodstream[11, 12] and also acts as a neurotransmitter[13]. The nucleobase, 5-methyluracil combined with deoxyribose creates the nucleoside deoxythymidine, which is synonymous with the term thymidine. Thymidine is significant because of its involvement in the biosynthesis of DNA and in the preservation and transfer of genetic information.

EXPERIMENTAL

Complex formation in solution proceeds by the stepwise addition of the ligands to the metal ion, a number of successive equilibria can be formulated according to Abegg and Bodlander[14,15].

$$M + L \rightleftharpoons ML$$

$$ML + L \rightleftharpoons ML_2$$

$$ML_{n-1} + L \rightleftharpoons ML_n \quad (1)$$

From Law of Mass Action,

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]} \quad (2)$$

Where n represents the coordination number of the metal ions, terms in bracket [ ] refers to the activities of different species and K_n are thermodynamic stepwise stability constant or formation constant.

$$\beta n = \frac{[ML_n]}{[M]\,[L]^{n}} \quad (3)$$

Where βn (overall stability constant) is the product of stepwise formation constant.

The protonation of the ligand L occurs in steps exactly in the same way as complexation reaction consequently following proton ligand equilibria may be considered:

$$L + H \rightleftharpoons HL$$

$$H_{n-1}L + H \rightleftharpoons H_nL \quad (4)$$

The proton ligand stability constants thus are given by,

$$K_n^{H} = \frac{[H_nL]}{[H_{n-1}L]\,[H]} \quad (5)$$

Hence βn^H, the overall proton ligand stability constant is determined by,

$$\beta_n^{H} = \frac{[H_nL]}{[H]^n\,[H_{n-1}L]} \quad (6)$$

The formation of mixed - ligand ternary systems can be considered to take place as follows:

$$M + L_1 + L_2 \rightleftharpoons ML_1L_2$$

$$\beta_{ML1L2} = \frac{[ML_1L_2]}{[M]\,[L_1]\,[L_2]} \quad (7)$$

pH- Metric Titration

This paper contains analytical study of mixed - ligand ternary chelates of Hg (II) and Cd (II) with 2-Aminosuccinic acid (A) and 5-methyluracil (B) by potentiometry in aqueous medium using Bjerrum's[16] method modified by Irving and Rossotti.[17] in two different molar ratio 1:2:1 and 1:2:2. All the solutions were prepared in double distilled water. The pH measurements were done by an electric digital pH meter (Eutech 501) with a glass electrode supplied with the instrument and working on 220V/50 cycles stabilized by A.C. mains. The pH meter has a reproducibility of ±0.01 pH. The pH meter calibrated with buffer solutions of pH (4.0) and pH (9.2) respectively which were prepared by dissolving buffer tablets (BDH) in double distilled water in appropriate concentrations. A carbonate free sodium hydroxide solution[18] was prepared for completion of this work. All the metal salts used were of Analar Grade and were standardized volumetrically by titration with the disodium salt of EDTA [19] is presence of suitable indicators. Each set of solution was then titrated against above carbonate free alkali (NaOH).

Following set of solution mixtures were prepared for analytical study:

Acid Solution

5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 40 ml water

Ligand - Solution

5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 5ml A (0.01M) + 35 ml. water

Binary System (1: 1) (M: A) / (M: B)

5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 5ml A (2-ASA) / B (5- MU) (0.01M) + 5 ml M (II) (0.01M) + 30 ml water.

Mixed Ligand Ternary System (1:2: 1) (M:A: B)

5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 10ml A (2-ASA) (0.01M) + 5 ml Hg (II) / Cd (II) (0.01M) + 5 ml B (5- MU) (0.01M) + 20 ml water

Mixed Ligand Ternary System (1:2: 2) (M: A: B)

5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 10ml A (2-ASA) (0.01M) +5 ml Hg (II) / Cd (II) (0.01M) + 10 ml B (5- MU) (0.01M) + 15 ml water

Calculation of Stability Constant

I.G.Sayce[20-22] developed a computer program named as SCOGS (Stability constant of generalized species) which employs the conventional non linear least square approach. The program is written in FORTRAN IV. It is capable of calculating simultaneously or individually, association constants for any of the species formed in the system containing up to two metals and two ligands, provided that the degree of complex formation is pH-dependent. Thus, SCOGS may be utilized to analyse appropriate pH titration data to yield metal-ion hydrolytic constants, stability constants of simple complexes (MA, MB and MA_2 etc.). SCOGS may also be used to calculate constants for "mixed" complexes containing two different metals and two different ligands resulting the formation of MAB and M_1M_2 AB types of complexes.

RESULTS AND DISCUSSIONS

The present paper concerned with the formation of metal chelates and evaluation of stability constant of mixed - ligand ternary system in rational study that means single metal and two ligands interacting in different ratios. For the evaluation of overall stability constant (β_{pqrst}) of mixed - ligand ternary complexes of biological significances we apply a special computer programme SCOGS according to which:-

$$pM_1 / qM_2 + rA + sB + t(OH) \rightleftharpoons (M_1)_p / (M_2)_q (A)_r (B)_s (OH)_t$$

$$\beta_{pqrst} = \frac{[(M_1)_p / (M_2)_q (A)_r (B)_s (OH)_t]}{[M_1]^p / [M_2]^q [A]^r [B]^s [OH]^t} \quad (8)$$

In above equation the p, q, r and s are either the zero or positive integer and t is a negative integer for a protonated species like H_3A, H_2A, HA and BH, positive integer for a hydroxo or a deprotonated species like $[M(OH)^+]$, $[M(OH)_2^+]$ and zero for a neutral or normal species like [M A] [M B] and [M A B] etc.

Species Distribution Curves

The species distribution curves are obtained by plotting percent (%) concentration of the species obtained through SCOGS computer programme against pH. The species distribution curves of studied systems were finally sketched by running the computer program ORIGIN 4.0.

Hg (II) - 2-ASA (A)- 5-MU(B) Ternary (1:2:1) System

From the species distribution curves given in (figure. 1) it is clear that the binary complex of Hg B exist in good concentration ~ 73% at start of the titration and gradually decreases with increase in pH range. Another binary complex shows its value~ 37% concentration at the pH ~3.3. H_2A have the maximum concentration ~ 57% at the start of titration. Ternary complex of Hg AB exist with higher value having maximum concentration ~ 93% at higher pH ~ 9.5.

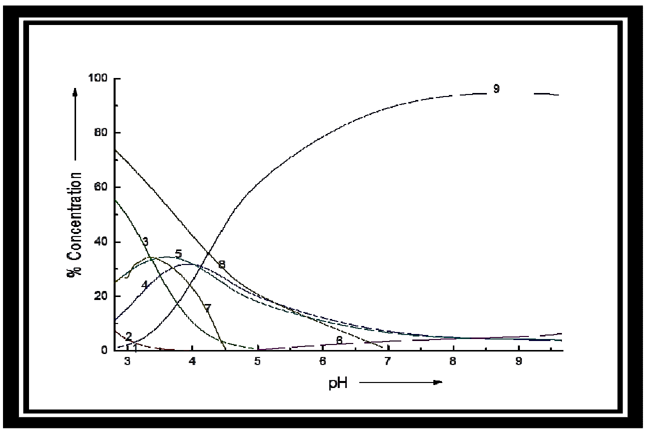

Figure 1: Species Distribution Curves of 1:2:1 Hg (II)-2-ASA (A) - 5-M U (B) System (1)Hg^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6) $Hg(OH)_2$ (7)Hg A (8)HgB (9) HgAB

Cd(II)- 2-ASA(A) - 5-MU(B) Ternary (1:2:1) System

For this system the distribution curves are represented in figure. 2.In the present system H_2A species shows maximum concentration ~ 70% at the very initial stage which decreases with the increase in pH range. HA have maximum concentration ~ 90% at the pH ~ 4.8. In this system binary complex of metal and ligand B is existed maximum concentration ~ 96% at the pH range 4.5. Major complex which is ternary complex of Cd AB is attained maximum concentration ~ 98% at the very high pH ~ 9.9.

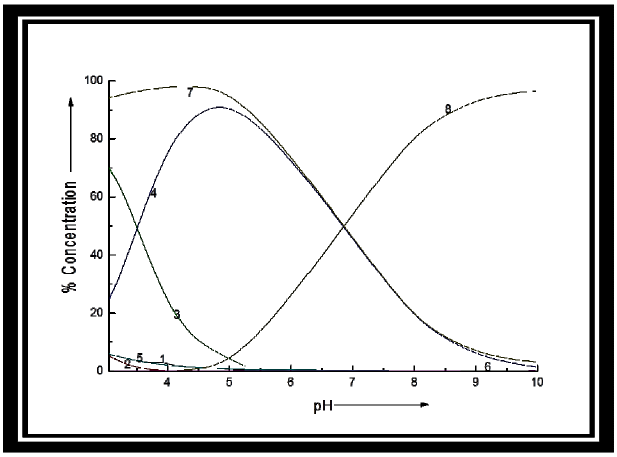

Figure 2: Distribution Curves of 1:2:1 Cd (II)-2-ASA (A) - 5-MU (B) System
(1)Cd^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6)$Cd(OH)_2$ (7) CdB (8) CdAB

Hg (II)-2-ASA (A) and 5-M U (B) Ternary (1:2:2) System

From the species distribution curves given in (figure 3) it is clear that the binary complex of Hg A exist in concentration ~ 39.5% at pH ~4.2. Another binary complex Hg B shows its maximum concentration ~ 76% at the start of titration. Ternary complex of Hg AB exist with higher value having maximum concentration ~ 90% at higher pH ~ 9.0. Protonated ligand species H_3A, H_2A, HA and BH shows their remarkable presence. Hydroxo species also existed in this system. H_2A attain maximum concentration ~ 57% at the start of titration. HA attain maximum concentration ~ 48% at pH ~ 9.0.The gradual decline in the concentration of binary complexes there is concomitant incline in concentration of ternary complexes species attaining maximum concentration shows the step wise formation of ternary complex.

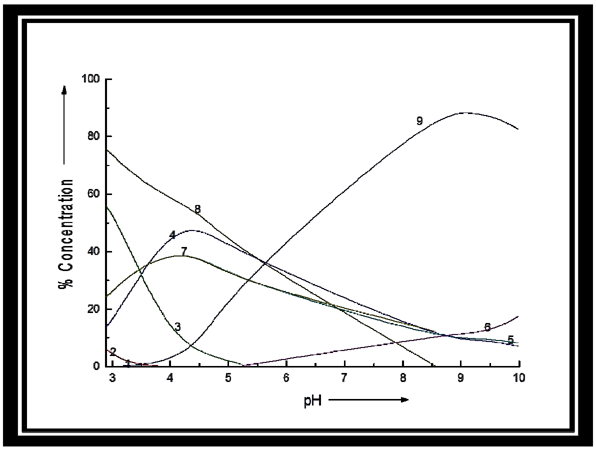

Figure 3: Distribution Curves of 1:2:2 Hg (II)-2-ASA (A) -5-MU (B) System
(1)Hg^{2+}(2) H_3A (3) H_2A (4) HA (5) BH (6)$Hg(OH)_2$ (7)Hg A (8)HgB (9) HgAB

Cd (II) - 2-ASA (A) and 5-M U (B) Ternary (1:2:2) System

The distribution curves for present system represented in (figure.4) in which it is clear that the binary complex Cd B attains maximum concentration ~ 95% at the very initial stage of titration which gradually decreases with the increase in pH range. H_2A species shows maximum concentration ~ 72% at the very initial stage which decreases with the increase in pH range. HA species shows maximum concentration ~ 83% at the pH ~ 4.6. Ternary complex of Cd AB attain maximum concentration ~ 98.5% at the very high pH ~ 9.8. Hydroxo species also existed in some extent in this system.

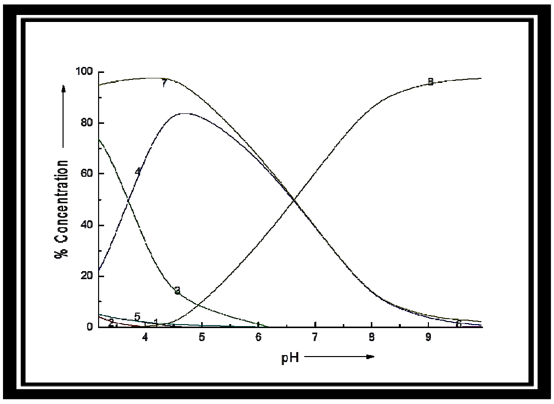

Figure 4: Distribution Curves of 1:2:2 Cd (II)-2-ASA (A) - 5-MU (B) System (1) Cd^{2+}(2) H_3A (3) H_2A (4) HA (5) BH (6) $Cd(OH)_2$ (7) Cd B (8) Cd AB

Overall Stability Constants and Other Related Constants of Binary and Ternary Complexes for M (II) 2-ASA (A) - 5-MU (B) (1:2:1), (1:2:2)) System at 37 $\pm$ 1^{0}C, I = 0.1 $NaNO_3$.

Table 1: Proton-Ligand Formation Constant (Log β_{00r0t}/ log β_{000st}) of 2-ASA-5-MU at 37 $\pm$ 1^{0}C, I = 0.1 $NaNO_3$

Complex	log β_{00r0t}/ log β_{000st}
H_3A	15.26
H_2A	13.33
HA	9.63
BH	9.94

Table 2: Hydrolytic Constants (log β_{p000t}/ log β_{0q00t}) M^{2+} (aq.) Ions

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

Table 3: Metal-Ligand Constants (Log β_{p0r00}/ log β_{0qr00}/ log β_{po0s0}/ log β_{0q0s0}) Binary System

Complex	Hg	Cd
MA	13.09	4.39
MB	13.45	11.33

Table 4: Metal-Ligand Constants (log β_{p0rs0}/ log β_{0qrs0}/): Ternary System (1:2:1)

Complex	Hg	Cd
MAB	21.45	16.54

Table 5: Metal-Ligand Constants (log β_{p0rs0}/ log β_{0qrs0}/): Ternary System (1:2:2)

Complex	Hg	Cd
MAB	21.85	17.00

Proposed Binary and Mixed – Ligand Ternary Structure of Complexes

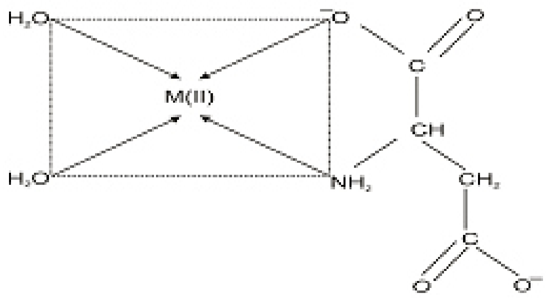

Figure 5: M (II)-ASA 4- Coordinated

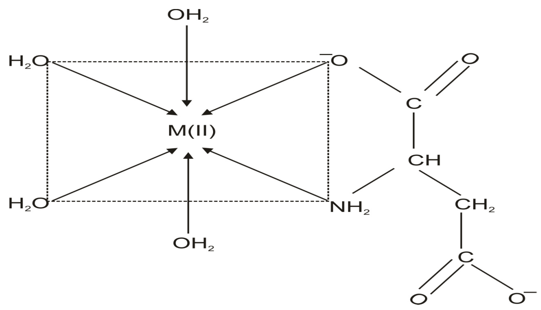

Figure 6

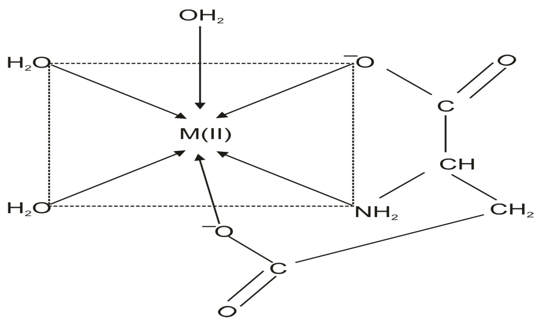

Figure 7: M (II)-ASA 6- Coordinated

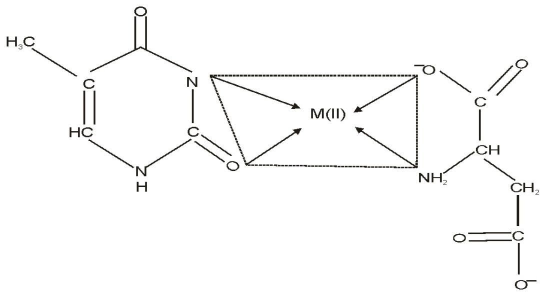

Figure 8: M (II)-ASA-5-MU 4- Coordinated

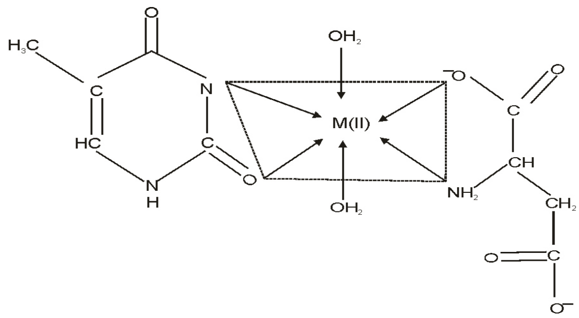

Figure 9: M (II)-ASA-5-MU 6- Coordinated

CONCLUSIONS

From the above study it is well clear that the amino acid and nucleobase used in this study have strong ability to interact with heavy metal ions and form metal chelates. We know that amino acid shows zwitter ion in solution so they normally coordinate to metal ions through the amino and carboxylato groups. Metal ions can interact with nucleobases and sugar moieties as well as with phosphates. Attractive ligand-ligand interactions favor the formation of mixed - ligand complexes of biological significance having the good ability to removal of heavy metal toxicity.

Individual Stability Order

- Mixed ligand ternary (1: 2: 1) System Hg/Cd (II)-2-ASA (A) - 5- MU (B) Hg AB > Cd AB
- Mixed ligand ternary (1: 2: 2) System: Hg/Cd (II)-2-ASA (A) - 5- MU (B) Hg AB > Cd AB

Overall Stability Order of Investigated Complex Species

Hg AB (1: 2: 2) > Hg AB (1: 2: 1) > CD AB (1: 2: 2) > Cd AB (1: 2: 1) > Hg B > Hg A > Cd B > Cd A

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