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Multimetal - multiligand complexes of Hg (II), Cd (II) and Pb (II) ions involving 2-aminosuccinic acid and 5 methyluracil

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Abstract

Potentiometric study of multimetal-multiligand complexes of toxic metals Hg(II), Pb(II) and Cd(II) with two different ligands amino acid acts as a neurotransmitter or neuromodulator 2- aminosuccinic acid (2-ASA) and pyramidine base 5-methyluracil (5-MU) at silver-silver chloride electrode forming the binary, ternary and quaternary complexes having great significance for living beings. The protonation constants, stability constants, titration curves and speciation curves were studied by using special computer programme SCOGS and ORIGIN which gives correct and accurate percentage information of the complex formation.

Key words: Potentiometric Studies, 2- ASA, (5-MU), SCOGS.ORIGIN.

Introduction

Metal are widely used by human beings direct or indirect way. Some metals are fruitful while some others are harmful. In these metals some are poisonous which causes various types of diseases and disorder in human body. 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. Biological system contains[1,2] various essential and non- essential or potentially toxic metal ions sodium, calcium, manganese, cobalt, copper, zinc, lead, mercury and cadmium, etc. The human body contains many chelating agents such as amino acids, globins, proteins, enzymes, carboxylic acids and nucleic acid-bases, which form chelate compounds[3] with the metal ion present in the living organism. Metal chelates include substances such as hemoglobin, haemocyanin, myoglobin, vitamin B_{12}, chlorophyll, nucleic acid and various enzymes.[4] Mixed chelation occurs commonly in biological fluids, *i.e.* as million of potential ligands are likely to compete for metal ions found in vivo. It is an important phenomenon[5] in the coordination chemistry of living organisms. This paper deals with the investigation of Hg(II) Pb(II) and Cd(II) quaternary complexes with metals M_1(II), M_2(II) with ligand 2- ASA,(A) and 5-MU (B). 2- ASA,(A) acts as a neurotransmitter[6] or neuromodulator and play a very important role in the neuroendocrine[7] system, as regulator in the synthesis and release of hormones.

Literature Review:

The metal complexes of polydentate ligands have provided both coordination chemist and biochemist with grist for their experimental mills for a long time. Polydentate ligand goes to formation of one or more rings. The resulting structures have been called chelate rings or simple chelates by Morgan and Drew[8] Cyclic polydentate ligands (Macrocyclic Compound) have attracted increasing interest owing to their role in the under-standing of molecular processes occurring in biochemistry, catalysis and coordination chemistry.[9-12] Patel and his coworkers[13,14] investigated solution equilibrium of mixed metal mixed ligand complexes of Cu (II), Ni (II) and Zn (II) with glycylalanine, L-cysteine, L-threonine and imidazole in aqueous solution by potentiometry, spectrophotometry and electron paramagnetic resonance spectroscopy. F.B.Ansari et al[15] investigated the complex formation equilibrium of Ni^{2+}, Co^{2+} and Mg^{2+} with glycine and p-aminobenzoic acid by pH-metry. P. R. Shirode[16] reported the synthesis and physicochemical studies of mixed ligand complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with acetophenone semicarbazone and acetone semicarbazone. Prachi Arya, Neha Singh, Ranu Gadi and Sulekh Chandra[17] studied thepreparation, characterization and antiulcer activity of mixed ligand complex of Zn (II) with famotidine and glycine. A.B. Patil [18] described the stability constants of ternery complexes of transition metal (II) ions with aspartic acid and glutamic acid as primary ligands and ampicillin and cephalexin as secondary ligands. Chaudhary Rakhi and Shelly[19] described the synthesis, spectral and pharmacological study of Cu (II), Ni (II) and Co (II) coordination complexes. G.V. Mane, L.P.Shinde and D.G. Kolhatkar[20] described the pH metric study of proton-ligand and metal-ligand stability constant complexes of transition and inner transition metal ions with some organic acids.

Research Methodology/ Experimental Procedure:

The potentiometry is still one of the most important methods to study the electrochemical[21] behavior of equilibria of interaction of metal ions and ligands, In the present investigations binary, ternary and quaternary systems have been studied by pH-metry using Bjerrum's[22] method modified by Irving and Rossotti.[23] Potentiometric study of each ligand with standard carbonate free sodium hydroxide were carried out with an electric digital pH meter (Century-model CP901-S) with a glass electrode at 37 ± 1^0C and I = 0.1M $NaNO_3$. Relatively low concentrations of metals and ligands are used. A stream of purified nitrogen was passed through the solutions throughout the titration. All the metal salts used were of Analar Grade and were standardized volumetrically by titration with the disodium salt of EDTA[24] is presence of suitable indicators. Volume of solution, keeping the total 50.0 ml in each case:

- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA(A) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 5-MU (B) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (A) (0.01M) + 5ml Hg(II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA(A) (0.01M) + 5ml Pb (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA(A) (0.01M) + 5ml Cd (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 5-MU (B) (0.01M) + 5ml Cd (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 5-MU (B) (0.01M) + 5ml Cd (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 5-MU (B) (0.01M) + 5ml Cd (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Hg(II)(0.01M) + 5ml 5-MU (B) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Pb(II)(0.01M) + 5ml 5-MU (B) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Cd(II)(0.01M) + 5ml 5-MU (B) (0.01M) + H_2O
- 5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 5ml A (0.01M) + 5 ml M_1(II) (0.01M) + 5ml B(0.01M)+ 5ml M_2(II) (0.01M) + H_2O

  Overall strength of the acid = 0.002 M HNO_3
  Overall strength of the ligand=0.001 M
  Overall strength of M (II) = 0.001 M
  Overall Ionic strength = 0.1 M ($NaNO_3$)
  Strength of alkali = 0.1 M

Results and Discussion

In this study different binary, ternary and quaternary complexes have been investigated. Titration curves and Species distribution curves for all complexes discussed under.

Titration Curves For 1:1:1:1 Quaternary System :

The curves were obtained by plotting pH vs. volume of alkali and finaly sketched by running the computer program ORIGIN 4.0 Each lines of the curve were denoted by alphabetic word which are A, B, C, D and E. In the curves, "A" represents the Acid, "B" represent the Ligand "C" represent the binary complex "D" represents the mixed ligand ternary complex and "E" represents the mixed metal-mixed ligand quaternary complex.

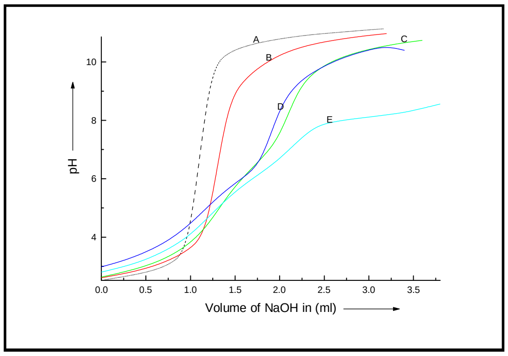


Fig. 5.4 Titration Curves of 1:1:1:1 Hg (II)-Cd(II) - 2-ASA (A) -5-MU (B)system

(A) Acid (B) Ligand (C) Hg(II)- 2-ASA(D) Hg(II)- 2-ASA- 5-MU (E)Hg(II)-Cd(II)-2-ASA - 5-MU

Species distribution curves :

Species distribution curves are obtained by plotting percent (%) concentration of the species against pH. The distribution curves are finally sketched by running the computer program ORIGIN 4.0

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

The species distribution diagram for this system is given in fig 5.16.

Species distribution diagram reveals the following types of species in the present system:Free metal ion species: Hg^{2+}(aq.), Cd^{2+}(aq.), Protonated ligand species: H_3A, H_2A, HA, BH. Hydroxo species: Hg $(OH)_2$, Cd $(OH)^+$ Cd $(OH)_2$ Binary complex species: Hg A, CdA, CdB, Ternary complex species: Hg AB, Cd AB, Quaternary complex species: Hg Cd AB. It is evident from the distribution diagram that all the protonated ligand species H_3A, H_2A, HA and BH were existed in this system. Binary complex of Hg with ligand A have the maximum existence ~20% at the very start of titration which is gradually decreases with increases in pH value. while the another binary complex Hg B is not observed in this system . Cd- A complex have maximum concentration ~5.0% at the start of titration shows decline trend with increase in pH while the Cd B complex attain the maximum concentration ~38% at the ~ 8.0 pH. Hg AB existed with low amount attaining maximum concentration ~5.0% at the ~ 8.5 pH value and ternary complex of Cd AB existed with maximum concentration ~50% at the ~ 8.5 pH. The major species which is quaternary complex of Hg Cd AB attain the maximum concentration ~77% at the ~ 5.3pH. Hydroxo species Hg $(OH)_2$, Cd $(OH)^+$ Cd $(OH)_2$ also observed.

• *Hg (II)-Pb (II) - 2-ASA (A) and 5-MU (B) System:*

Distribution diagram provide evidence for existence of following species Hg^{2+}, Pb^{2+} H_3A, H_2A HA, BH, Hg $(OH)_2$, Hg A, HgB, PbA, PbB, HgAB, PbAB and Hg Pb AB .Binary complex of Hg with ligand A have their existence very low while the another binary complex Hg B shows amount ~12% at the pH ~ 7.5. Complex PB- A attain maximum concentration ~2.0% at the start of pH titration. Pb B complex attain the maximum concentration ~17% at the ~ 7.5 pH value. Ternary complexes of Hg AB existed with maximum concentration ~10% at the ~ 4.2 pH while the PbAB existed with maximum concentration ~92% at the ~ 9.5 pH. The major species which is quaternary complex of Hg Pb AB attain the maximum concentration ~92% at the ~ 4.8 pH. Hydroxo species Hg $(OH)_2$ shows very well existence in this system.

• *Cd (II) - Pb (II) - 2-ASA (A)- 5-MU (B) System :*

In the species distribution diagram following species are identified:

Cd^{2+},Pb^{2+},H_3A, H_2A, HA, BH, $Cd(OH)_2$, $Cd(OH)^+$, $Pb(OH)_2$ Cd B, Pb A Pb B, Cd AB, Pb AB and Cd Pb AB. From the distribution diagram it is evident that all the protonated ligand species H_3A, H_2A, HA and BH were existed in this system. H_3A existed with very low value but H_2A exist with higher value having maximum concentration ~73% at very start of the titration showing gradual decline trend with the raise in pH. HA first increases till ~ 3.8 pH ~26% maximum concentration after that gradually decreases. Free metal ion Cd^{2+} (aq.) have the maximum concentration ~92% at the start of titration shows decline trend with increase in pH while free metal ion Pb^{2+} (aq.) have low existence.

Binary complex of Cd with ligand A not observed in this system while the another binary complex Cd-B shows maximum amount 19.5% at the pH ~ 9.0. Pb- A complex have maximum concentration ~87% at the start of titration shows decline trend with increase in pH while the Pb B complex is found in very low amount. Ternary complex of Cd AB existed with maximum concentration ~22% at the ~ 9.5 pH value and ternary complex of Pb AB existed with maximum concentration ~10% at the ~9.7pH. Quaternary complex of Cd Pb AB attain the maximum concentration ~82% at the ~ 7.8 pH. Metal hydroxo complexes viz. $Cd(OH)_2$, Cd $(OH)^+$ and $Pb(OH)_2$ are observed with remarkable presence.

Equilibria of complex formation:

The binary, ternary, quaternary and general hydrolytic equilibria have been derived on the basis of distribution curves of the complexes occurring at different pH.

$$M^{2+} + H_2A \rightleftharpoons [MA] + 2H^+$$

$$M^{2+} + BH^- \rightleftharpoons [MB] + H^+$$

$MA + BH^- \rightleftharpoons [MAB] + H^+$

$M^{2+} + H_2A + BH^- \rightleftharpoons [MAB] + 3H^+$

$H_2A + M_1^{2+} + BH^- + M_2^{2+} \rightleftharpoons [M_1\text{-}M2\text{-}A\text{-}B] + 3H^+$

$M_1A + M_2^{2+} + BH^- \rightleftharpoons [M_1\text{-}M_2\text{-}A\text{-}B] + H^+$

$M^{2+} + H_2O \rightleftharpoons M_2(OH)^+ + H^+$

$M^{2+} + 2H_2O \rightleftharpoons M_2(OH)_2 + 2H^+$

Evaluation of Stability Constant:

The metal ligand formation constant of binary, ternary and quaternary complexes were evaluated by using SCOGS[25] computer programme (Stability constant of generalized species) developed by Sayce. The overall stability constants ($ß_{pqrst}$) of ternary and quaternary complexes are expressed by the general equation in aqueous solutions as follows:

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

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

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

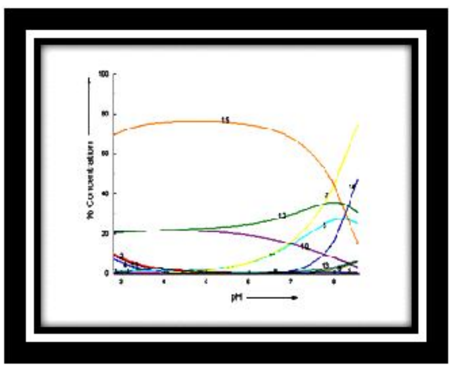


Fig 5.16- Distribution Curves of 1:1:1:1 Hg(II)–Cd(II)–2-ASA(A)- 5-MU (B) System

(1) Hg^{2+}(II) (2) Cd^{2+}(II) (3) H_3A (4) H_2A (5) HA (6)BH (7) Hg $(OH)_2$ (8) Cd $(OH)_2$ (9) Cd $(OH)^+$ (10)Hg A (11)Cd A (12)Cd B (13)Hg AB (14)Cd A B(15)Hg Cd AB

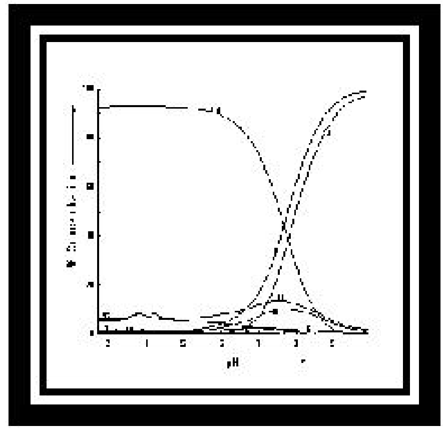


Fig 5.17- Distribution Curves of 1:1:1:1 Hg(II)–Pb (II) –2-ASA(A) - 5-MU (B) System

(1) Hg^{2+}(II) (2) Pb^{2+}(II) (3) H_3A (4) H_2A (5) HA (6)BH (7)$Hg(OH)_2$(8)Hg A (9)Hg B (10)Pb A (11)Pb B (12)Hg AB (13)Pb A B(14)Hg Pb AB

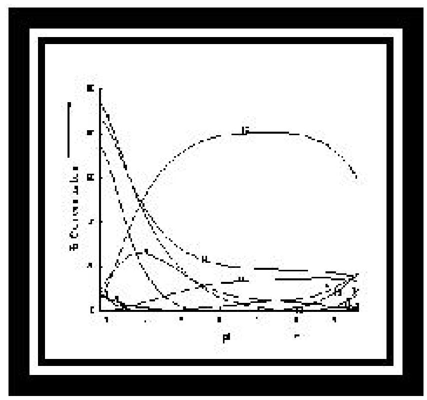


Fig 5.18- Distribution Curves of1:1:1:1 Cd (II)–Pb (II) –2-ASA (A) - 5-MU (B) System

(1)Cd^{2+}(II) (2) Pb^{2+}(II) (3) H_3A (4) H_2A (5) HA (6)BH (7)$Cd(OH)_2$ (8)$Cd(OH)^+$ (9)$Pb(OH)_2$ (10)Cd B (11)Pb A (12)Pb B (13)Cd AB (14) Pb AB(15)Cd Pb AB

Overall stability constants and other related constants of binary, ternary and quaternary complexes for M_1(II)-M_2(II) 2-ASA(A) -5-MU(B) system.

● Proton-ligand formation constant (log β_{00r0t}/ log β_{000st}) of 2-ASA - 5-MU at 37 ±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

- Hydrolytic constants (log β_{p000t}/ log β_{0q00t}) M^{2+} (aq.) ions.

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

- Metal-Ligand constants (log β_{p0r00}/ log β_{0qr00}/ log β_{po0s0}/ log β_{0q0s0}) Binary System

Complex	Hg	Cd	Pb
M A	13.09	4.39	11.61
MB	13.45	11.33	13.33

- Metal-Ligand constants (log β_{p0rs0}/ log β_{0qrs0}): Ternary System (1:1:1)

Complex	Hg	Cd	Pb
MAB	21.18	15.35	19.25

- Metal-Ligand constants (Log β_{pqrst}) : Quaternary System (1:1:1:1)

Complex	Hg-Cd	Hg-Pb	Cd-Pb
M_1 M_2-A-B	27.75	28.85	26.95

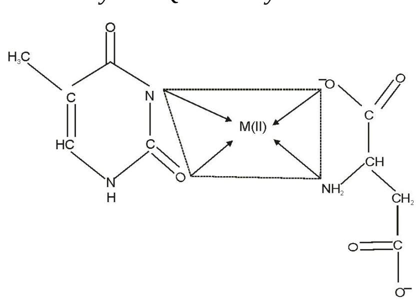
CONCLUSIONS

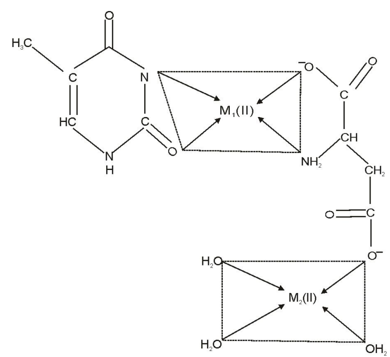
Most of the medicines are acting as chelating agent to remove excess concentration of toxic metals from the organisms. So this study is a qualitative attempt to remove toxicity of metals by using suitable chelating ligands. This clue of structural relation will throw some lights on the mechanistic paths and will help to predict structural reactivity relation, a way as milestone for the researchers in the coming generations. The stability constant and order of all binary, ternary and quaternary complexes were given under according to their experimental value as in table.

Overall stability order of investigated complexes:

- **M (II)-2-ASA (A)**
  Hg A > Pb A > Cd A
- **M (II)-5-MU (B)**
  Hg B > Pb B > Cd B
- **M (II)-2-ASA (A) - 5-MU (B)**
  Hg A B > Pb AB > Cd A B
- M_1 (II)-M_2 (II) -2-ASA (A) - 5-MU (B)
  Hg Pb A B > Hg Cd A B > Cd Pb A B

Proposed Ternary and Quaternary Structure:





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