

Study of Chelation Behavior of Mixed-ligand Ternary and Mixed Metal-Mixed ligand Quaternary Complexes of Toxic Metal Hg (II) and Cd (II) Ions Involving 2-Aminosuccinic acid and 5-methyluracil

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Abstract

The ternary and quaternary chelates formed by metal – ligand interaction of Hg (II) and Cd (II) ions with 2-Aminosuccinic acid and 5-methyluracil have been studied at silver-silver chloride electrode by the potentiometric technique. The stability constants of Hg (II)- 2-Aminosuccinic acid- 5-methyluracil, Cd (II)- 2-Aminosuccinic acid - 5-methyluracil and Hg (II) – Cd (II)- 2-Aminosuccinic acid - 5-methyluracil were determined using SCOGS computer programme and the complex formation were elucidated with the aid of species distribution curves. The molar ratios of ternary and quaternary chelates were kept as 1:1:1 and 1:1:1:1 respectively.

Keywords- Stability Constant, SCOGS, Chelation, Complexes.

I. INTRODUCTION

Metal are widely used by human beings direct or indirect way. Some metals are toxic in nature. These toxic metals cause various types of diseases and disorder. When two or

more donor atoms of a ligand bind single metal ion and form a heterocyclic ring structure, it is said to be a chelating ligand and the complex compound itself is termed as metal chelate. The metal chelates play an important role in various field of biological [1]analytical[2] industrial [3-4]and medicinal[5] importance. 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 human body contains many chelating agents such as amino acids, globins, proteins, enzymes, carboxylic acids and nucleic acid-bases, which form chelate compounds [6]with the metal ion present in the living organism. 2-Aminosuccinic acid combines with other amino acids to form molecules that

absorb toxins and remove them from the blood stream[7,8]. Metal ion complex formations are among the prominent interaction in nature [9]. Mixed metal–mixed ligand complexes studies gives clues to the roles of metal ions in many enzymic reactions [10, 11].

II. EXPERIMENTAL

The potentiometry is an important method to study the electrochemical [12] behavior of equilibria of interaction of metal ions and ligands, where there is release of hydrogen ions accompanying the complexation reaction. In such cases, a glass electrode furnishes information on the H^+ ion concentration and thereby on the extent of complex formation.

In the present paper a study has been done on mixed- ligand MAB (ternary) and mixed metal–mixed ligand M_1M_2AB (quaternary) systems of Hg (II) and Cd (II) with amino acid and nucleobase by pH-metry using Bjerrum's[13] method modified by Irving and Rossotti[14].

In this experiment amino acid was taken as primary ligand (A) and nucleobase was taken as secondary ligand (B). 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. Potentiometric titrations of each ligand with standard carbonate free sodium hydroxide were carried out at

$37 \pm 1^\circ C$ 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 [15] in presence of suitable indicators.

PROCEDURE:

For study of all binary, ternary and quaternary system following solution mixtures were prepared in double distilled water keeping the total volume 50 ml in each case:

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

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

Solution C: 5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 5ml A (0.01M) + 5 ml M (II) (0.01M) + 30 ml water.

Mixed ligand ternary system (1: 1: 1): (M: A: B)

Solution D: 5 ml $NaNO_3$ (1.0 M) + 5ml HNO_3 (0.02M) + 5ml A (0.01M) + 5 ml M (II) (0.01M) + 5 ml B (0.01M) + 25 ml water

Mixed metal mixed ligand quaternary system: (1: 1:1: 1) (M_1 : M_2 : A: B)

Solution E : 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) + 20 ml water

Overall strength of the acid = 0.002 M HNO₃

Overall strength of the ligand=0.001 M

Overall strength of M (II) = 0.001 M

Over all Ionic strength = 0.1 M (NaNO₃)

Strength of alkali = 0.1 M

Where M₁ (II) and M₂ (II) were Hg and Cd.

A=Primary ligand (2-Aminosuccinic acid) 2-ASA

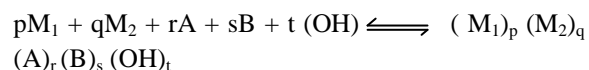
B = Secondary ligand (5-methyluracil) 5-MU

Each set of solution was then titrated against alkali (NaOH). The pH meter reading with progressive addition of alkali to the titration mixtures were noted, when the reading of pH meter stabilized.

III. RESULTS AND DISCUSSION

The metal ligand formation constant of binary, ternary and quaternary complexes were evaluated by using SCOGS [16] (Stability constant of generalized species) computer programme developed by Sayce.

The overall stability constants (β_{pqrst}) of binary, ternary and quaternary complexes are expressed by the general equation in aqueous solutions as follows:



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

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.

TITRATION AND SPECIES DISTRIBUTION CURVES:

The pH titration curves for the ternary and quaternary complexes were drawn by plotting pH Vs volume of alkali given in fig. 1 and fig 3. The species distribution curves were obtained by plotting percent (%) concentration of the species obtained through SCOGS computer programme against pH given in fig. 2. and fig 4. The pH titration curves and species distribution curves are finally sketched by running the computer program ORIGIN 4.0. A detailed study of species distribution curves for ternary (Cd AB) and quaternary (Hg Cd AB) complexes are given here.

• Cd(II)- 2-ASA(A)- 5-MU (B) System:

The distribution curves of Cd AB are represented in fig.2. In the present system following 9 species were identified:

Protonated ligand species: H₃A, H₂A, HA, BH.

Hydroxo species: Cd (OH)₂.

Free metal ion Cd²⁺ (aq.).

Binary species: CdA, CdB

Ternary species: Cd AB

Cd²⁺ (aq.) species shows higher value at very starting of titration which shows decline trend with increasing pH. H₂A species shows maximum concentration ~ 78% at the very initial stage which decreases with the increase in pH range. HA has maximum

concentration ~ 64% at the pH~ 4.4 in this system binary complex of metal and ligand A is existed with maximum concentration ~ 5.0% at the pH range ~4.8. Another binary complex CdB is found to be maximum concentration ~ 86% at the pH ~4.0. In this system major complex which is ternary complex Cd AB is attained maximum concentration ~ 98% at the very high pH ~ 9.8.

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

The species distribution diagram for this system is given in fig. 4.

Species distribution diagram reveals the following types of species in the present system:

Free metal ion species: $\text{Hg}^{2+}(\text{aq.}), \text{Cd}^{2+}(\text{aq.})$

Protonated ligand species: $\text{H}_3\text{A}, \text{H}_2\text{A}, \text{HA}, \text{BH}$

Hydroxo species: $\text{Hg}(\text{OH})_2, \text{Cd}(\text{OH})^+, \text{Cd}(\text{OH})_2$

Binary complex species: $\text{Hg A}, \text{CdA}, \text{CdB}$

Ternary complex species: $\text{HgAB}, \text{Cd AB}$

Quaternary complex species: Hg Cd AB

It is evident from the distribution diagram that all the protonated ligand species $\text{H}_3\text{A}, \text{H}_2\text{A}, \text{HA}$ 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.

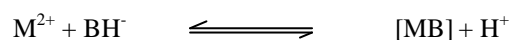
The major species which is quaternary complex of Hg Cd AB attain the maximum concentration ~77% at the ~ 5.3pH. Hydroxo species $\text{Hg}(\text{OH})_2, \text{Cd}(\text{OH})^+, \text{Cd}(\text{OH})_2$ also observed.

EQUILIBRIA OF COMPLEX FORMATION

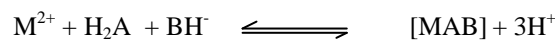
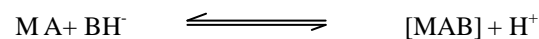
Complex formation equilibria have been derived on the basis of distribution curves of the complexes (obtained through SCOGS) occurring at different pH.

Following equilibria have been proposed for all the systems:

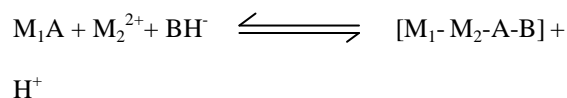
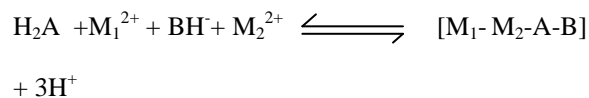
BINARY SYSTEM:



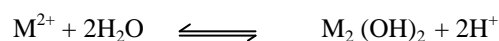
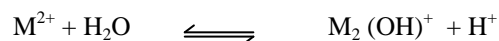
TERNARY SYSTEM:



QUATERNARY SYSTEM:



GENERAL HYDROLYTIC EQUILIBRIA:



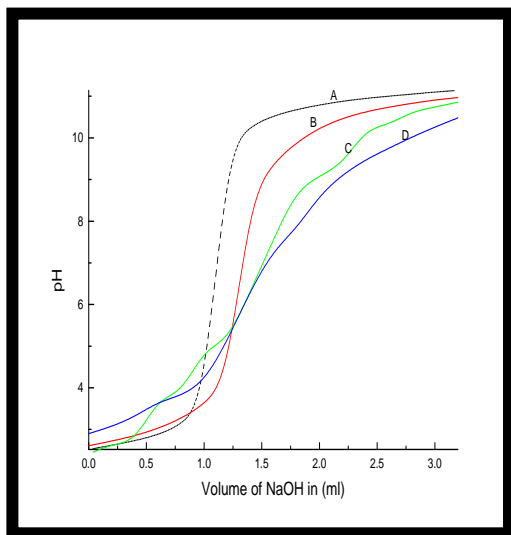


Fig.1. Titration Curves of 1:1:1 Cd (II)- 2-ASA (A) - 5-MU (B) System
(A) Acid (B) Ligand (C) Cd(II)- 2-ASA (D) Cd(II)-2-ASA - 5-MU

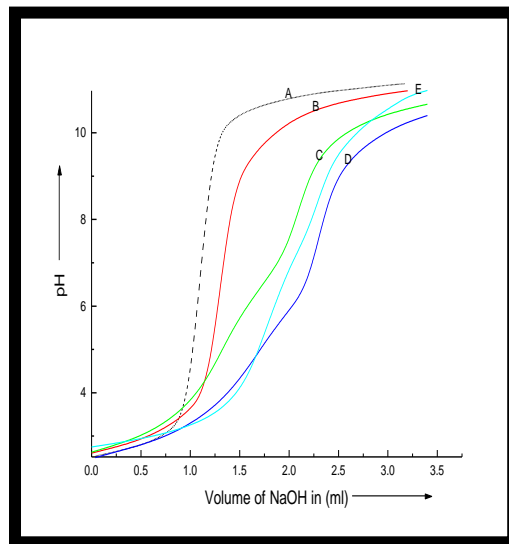


Fig. 3 Titration Curves of 1:1:1:1 Hg (II)-Cd(II) - 2-ASA (A) -5-MU (B) system
(A))Acid (B) Ligand (C) Hg(II)- 2-ASA(D)Hg(II)- 2-ASA - 5-MU (E)Hg(II)-Cd(II)-2-ASA - 5-MU

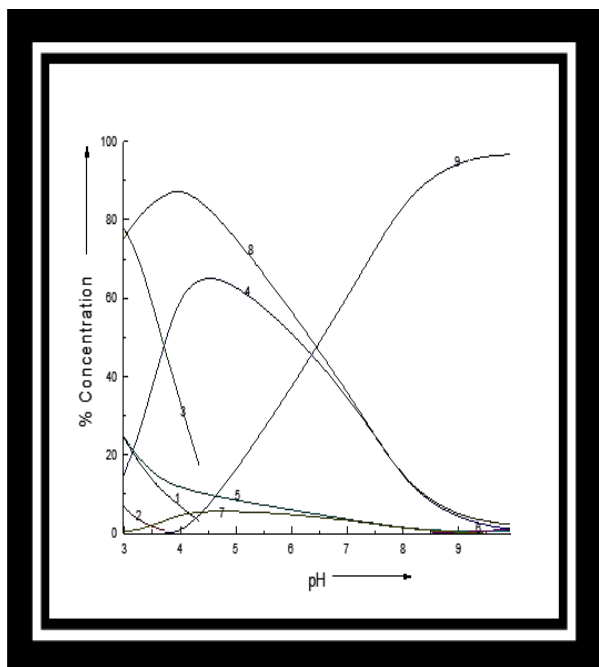


Fig .2. Distribution Curves of 1:1:1 Cd (II)-2-ASA (A) 5-MU (B) Systems
(1) Cd^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6) $Cd(OH)_2$ (7) $Cd A$ (8) CdB (9) $CdAB$

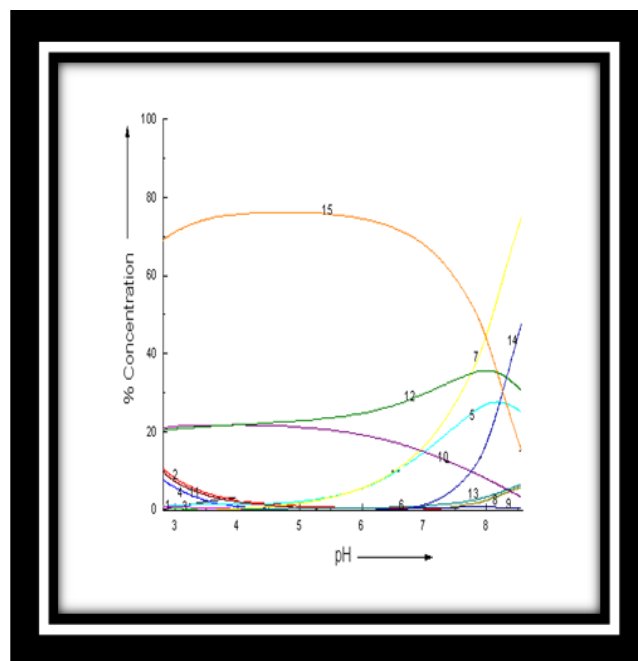


Fig 4- Distribution Curves of 1:1:1:1 Hg(II)-Cd(II)-2-ASA(A)- 5-MU (B) System
(1) $Hg^{2+}(II)$ (2) $Cd^{2+}(II)$ (3) H_3A (4) H_2A (5) HA (6) BH (7) $Hg(OH)_2$ (8) $Cd(OH)_2$ (9) $Cd(OH)^+$ (10) $Hg A$ (11) $Cd A$ (12) $Cd B$ (13) $Hg AB$ (14) $Cd A B$ (15) $Hg Cd AB$

TABLE I

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 ($\log \beta_{00r0t} / \log \beta_{000st}$) of 2-ASA - 5-MU at $37 \pm 1^\circ\text{C}$ $I = 0.1$ NaNO_3

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

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

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

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

Complex	Hg	Cd
MA	13.09	4.39
MB	13.45	11.33

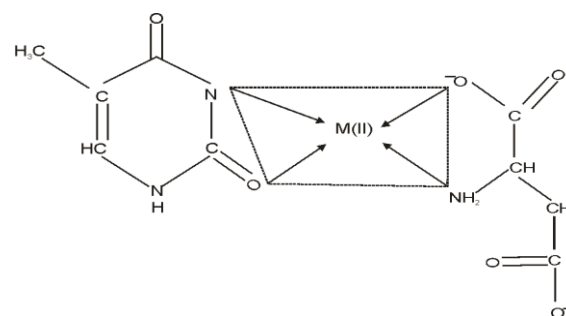
- Metal-Ligand constants ($\log \beta_{p0rs0} / \log \beta_{0qrs0}$): Ternary System(1:1:1)

Complex	Hg	Cd
MAB	21.18	15.35

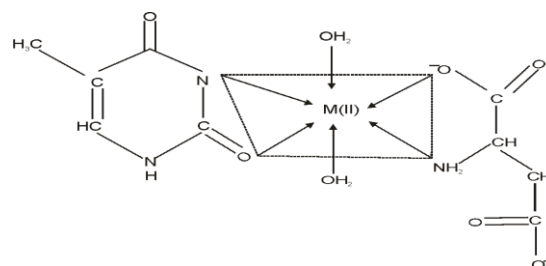
- Metal-Ligand constants ($\log \beta_{pqrst}$): Quaternary System (1:1:1:1)

Complex	Hg-Cd
$M_1, M_2\text{-A-B}$	27.75

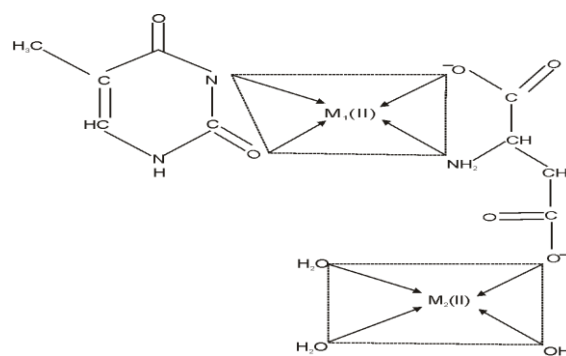
PROPOSED TERNARY AND QUATERNARY STRUCTURES:



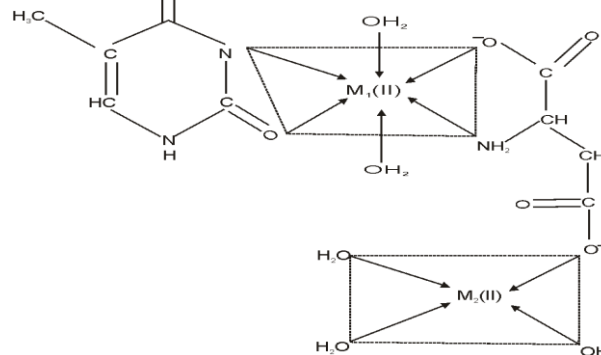
$M(II)$ -2-ASA-5-MU 4- Coordinated



$M(II)$ -2-ASA-5-MU 6- Coordinated



$M_1(II)$ - $M_2(II)$ -2- ASA-5-MU 4- Coordinated



$M_1(II)$ - $M_2(II)$ -2- ASA-5-MU 6- Coordinated

CONCLUSION:

Ternary and quaternary mixture have been used in this study to ensure the exclusive formation of the M_1AB , M_2AB and M_1M_2AB complexes, considering protonation constants of the ligand and hydrolytic constants of the $M(II)$ aqueous ions. The stability of all the analogous complexes was in order of $Hg(II) > Cd(II)$.

In term of complex species, the order was quaternary > ternary > binary, which can be explained based on the increased number of fused rings and the extra stabilization caused by ligand-ligand interactions. Formation of ternary and quaternary complexes in higher percentage proves the mixed-ligand and mixed metal-mixed ligand chelation behavior.

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