

# Speciation of Ternary and Quaternary Complexes of Copper (II) and Cobalt (II) ions involving L-Aspartic acid and 5-Methyluracil

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**ABSTRACT:** Ternary and quaternary complexes of Cu (II) and Co (II) ions with L-aspartic acid (A) and 5-methyluracil (B) ligands in aqueous solution have been investigated. Formation constant of ternary and quaternary metal complexes and speciation equilibria at temperature  $37 \pm 1^\circ\text{C}$  at constant ionic strength ( $I = 0.1 \text{ M NaNO}_3$ ) have been explored by potentiometrically. Complexes of the type MAB (1:1:1) and  $M_1M_2AB$  (1:1:1:1) have been discussed by using SCOGS and ORIGIN computer program.

**KEYWORDS:** Ternary complexes, Quaternary complexes, L-Aspartic acid, SCOGS.

## I. INTRODUCTION

Ternary and quaternary complexes are of great significance in the study of bio-fluids particularly when hyper accumulated metal ions are present for pathological nature<sup>1,2</sup>. Human body contains many amino acids and nucleic acid-bases, which form chelate compounds<sup>3,4</sup> with the metal ion present in the living organism. Recent research results<sup>5,6,7,8</sup> have clearly demonstrated the need for comprehensive studies of metal ions and bio-ligand interaction as model systems. Mixed metal mixed ligand complexes studies gives clues to the roles of metal ions in many enzymic reactions<sup>9,10</sup>. This paper is a comprehensive study of formation of metal complexes of L-aspartic acid and a nucleobase 5-methyluracil with Cu (II) and Co (II) ions in the biologically relevant conditions. The relevant stability constants and speciation curves have been obtained using SCOGS<sup>11,12</sup> computer program.

## II. MATERIALS AND METHODS

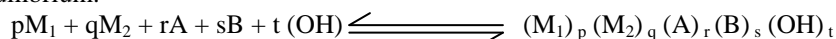
All the solutions were prepared in triple distilled water. Potentiometric titrations of each ligand with standard carbonate free sodium hydroxide were carried out with an electric digital pH meter (Eutech 501) with a glass electrode at  $37 \pm 1^\circ\text{C}$  and  $I = 0.1 \text{ M NaNO}_3$ . Relatively low concentration 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 in presence of suitable indicators, as described by Schwarzenbach<sup>13</sup>. The potentiometric study done by using Irving-Rossotti technique<sup>14</sup>. For all the binary, ternary and quaternary systems, following solution mixture have been titrated against standardized NaOH (0.01M) solution, keeping the total volume 50.0 ml in each case:

- (i) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + \text{H}_2\text{O}$
- (ii) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + 5\text{ml A}(0.01\text{M}) + \text{H}_2\text{O}$
- (iii) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + 5\text{ml B}(0.01\text{M}) + \text{H}_2\text{O}$
- (iv) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + 5\text{ml A}(0.01\text{M}) + 5\text{ml Cu/Co(II)}(0.01\text{M}) + \text{H}_2\text{O}$
- (v) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + 5\text{ml B}(0.01\text{M}) + 5\text{ml Cu/Co(II)}(0.01\text{M}) + \text{H}_2\text{O}$
- (vi) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + 5\text{ml A}(0.01\text{M}) + 5\text{ml Cu/Co(II)}(0.01\text{M}) + 5\text{ml B}(0.01\text{M}) + \text{H}_2\text{O}$
- (vii) 5ml  $\text{NaNO}_3(1.0\text{M}) + 5\text{ml HNO}_3(0.02\text{M}) + 5\text{ml A}(0.01\text{M}) + 5\text{ml Cu(II)}(0.01\text{M}) + 5\text{ml B}(0.01\text{M}) + 5\text{ml Co(II)}(0.01\text{M}) + \text{H}_2\text{O}$

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 obtained as computer output.

### III. RESULTS AND DISCUSSIONS

The ligand L- aspartic acid behaves as a tridentate ligand, coordinating through a nitrogen and two carboxyl oxygen atoms. The secondary ligand 5-methyluracil acts as a monodentate ligand as well as bidentate ligand. Proton ligand stability constants obtained for both the ligands are presented in Table 1, which are in good agreement with literature values<sup>15, 16</sup>. The formation of quaternary complexes in an aqueous solution may be conveniently expressed by the equilibrium:



The overall stability constant is given by:

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

Where the stoichiometric numbers p, q, r, 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.

**Cu (II)-L-Aspartic acid-5-Methyluracil (1:1:1) System:**

pH titration curves and speciation curves of [Cu (II)-L-Aspartic acid-B] system are represented in fig.(1) and fig.(2) respectively. The free metal ion  $Cu^{2+}$  (aq.) is 84% in concentration and shows its gradual decline with the increasing pH. The protonated ligand species;  $H_3A$ ,  $H_2A$ ,  $HA$  and  $HB$  are present in the system having their maximum concentration to be  $\approx 8\%$ ,  $70\%$ ,  $39\%$  and  $95\%$  at pH  $\sim 2.5$  respectively. The binary species [Cu (II)-L-Aspartic acid] gradually increases to attain maximum concentration of  $\approx 60\%$  at pH  $\sim 5.1$ . Other binary complex i.e. [Cu (II)-B] shows its presence at entire pH range. The ternary complex [Cu (II)-L-Aspartic acid-B] is the predominant species at pH  $\sim 8.5$  to be  $\approx 76\%$  in concentration. Considering the decline in the concentration of binary species as well as ligands and formation of the ternary species within the pH range  $\sim 4.6 - 8.5$ , it is a step wise complexation.

**Co (II)-L-Aspartic acid-5-Methyluracil (1:1:1) System:**

Titration curves and speciation curves of [Co (II)-L-Aspartic acid-B] are presented in fig. (3) and fig. (4) respectively. Species  $H_3A$ ,  $H_2A$ ,  $HA$ ,  $HB$  binary and ternary complex species all exist in their usual trend of complexation. The free metal ion and protonated ligand species of both the ligands have been found to follow a pattern of decreasing concentration with rise in pH. It's clear from speciation curve that concentration of binary complexes [Co (II)-L-Aspartic acid] and [Co(II)-B] are maximum in the pH range  $\approx 4.0 - 9.0$ , whereas concentration of [Co(II)-L-Aspartic acid-B] is maximum in the pH range  $\sim 7.0 - 10.0$ . The ternary complex starts appearing from the pH  $\approx 6.9$ . It is clear evident for the step wise complexation, which is the trend in all [Co (II)-L-Aspartic acid-B] complexes. Hydroxo species is found in higher pH range.

**Cu (II)-Co (II)-L-Aspartic acid-5-Methyluracil (1:1:1:1) System:**

Fig. (5) Shows the following complex species-

Binary complex species:  $CuA$ ,  $CuB$ ,  $CoA$  and  $CoB$

Ternary complex species:  $CuAB$  and  $CoAB$

Quaternary complex:  $CuCoAB$

Hydroxo species:  $Cu(OH)^+$ ,  $Cu(OH)_2$ ,  $Co(OH)^+$  and  $Co(OH)_2$

Among binary complexes existing in the present system,  $CuA$  is present in maximum ( $\approx 37\%$ ) at pH  $\sim 3.8$ , which gradually decreases reaching up to negligible amount at pH  $> 8.5$ . The other binary species  $CoA$ ,  $CoB$  are showing their presence at relatively higher pH region. The maximum concentration of  $CuAB$  is  $\approx 22\%$  at pH  $\sim 9.5$  while that of  $CoAB$  is  $\approx 8.6\%$  at the same pH. There is a simultaneous process of quaternary complexation as it is formed right from the beginning of the titration. Its concentration, after a gradual incline attains maxima at pH  $\sim 6.5$  ( $\approx 80\%$ ) and thereafter follows a declining trend. Formation of hydroxo species have also been taken into considerations as the buffer region corresponding to the metal ligand formation equilibria has been found to be overlapping with the hydrolytic equilibria of  $M^{2+}$  (aq) metal ions.

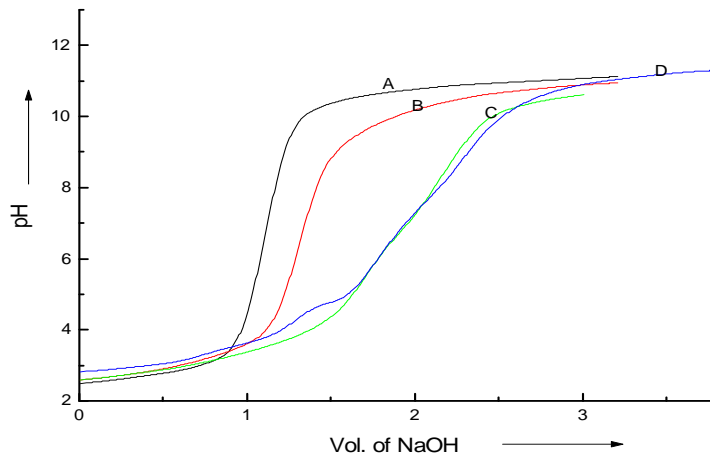


Fig. 1-Potentiometric titration Curves of 1:1:1 Cu (II)-L-Aspartic acid-5-Methyluracil-System (A) Acid (B) L-Aspartic acid (C) Cu(II)-L-Aspartic acid (D) Cu(II)-L-Asp-5-MU

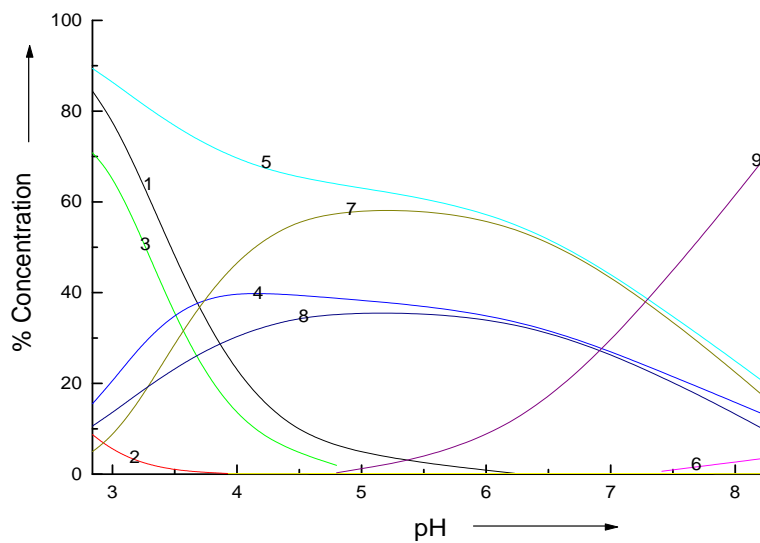


Fig. 2-Distribution Curves of 1:1:1 Cu (II)-L-Asp-5-MU System: (1) Cu (II)(2) H<sub>3</sub>A (3) H<sub>2</sub>A (4) HA (5) HB (6) Cu(OH)<sub>2</sub> (7) CuA (8) CuB (9) CuAB

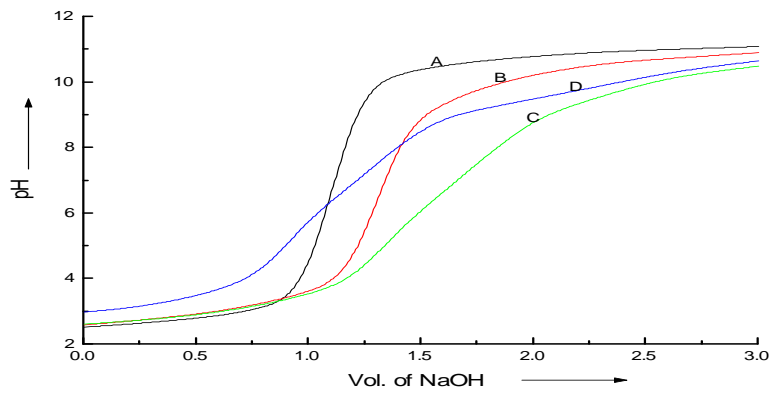


Fig. 3- Potentiometric titration Curves of 1:1:1 Co (II)-L-Aspartic acid-5-MU-System  
(A) Acid (B)L- Aspartic acid (C) Co(II)-L-Asp (D) Co(II)-L-Asp-5-MU

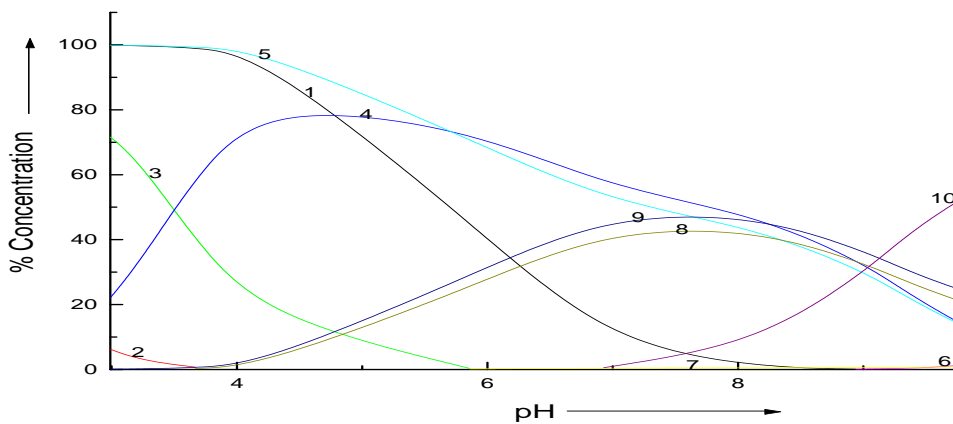


Fig.4-Speciation Curves of 1:1:1 Co (II)-L-Asp-5-Methyluracil System  
(1) Co (II) (2) H<sub>3</sub>A (3) H<sub>2</sub>A (4) HA (5) HB (6) Co (OH)<sub>2</sub> (7) Co (OH)<sup>+</sup> (8) Co A (9) CoB (10) Co AB

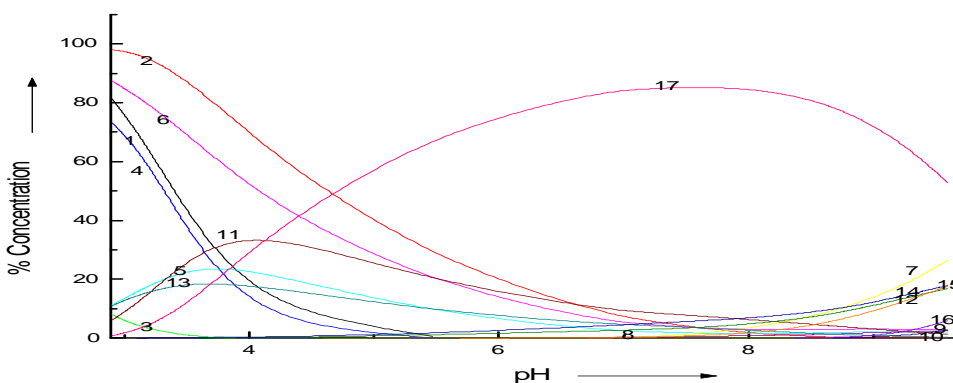


Fig. 5- Speciation Curves of 1:1:1:1 Cu (II)-Co (II)-L-Asp (A)-5-Methyluracil (B) System  
(1) Cu (II) (2) Co (II) (3) H<sub>3</sub>A (4) H<sub>2</sub>A (5) HA (6) HB (7) Cu (OH)<sub>2</sub> (8) Cu (OH)<sup>+</sup> (9) Co (OH)<sub>2</sub> (10) Co (OH)<sup>+</sup> (11) CuA (12) CoA (13) CuB (14) CoB (15) CuAB (16) CoAB (17) Cu CoAB



**TABLE-1**

Proton-ligand formation constant ( $\log \beta_{00rot} / \log \beta_{000st}$ ) of L-Aspartic acid and 5-Methyluracil at  $37 \pm 1^{\circ}\text{C}$   $I = 0.1$   $\text{NaNO}_3$

Complex	$\log \beta_{00rot} / \log \beta_{000st}$
H <sub>3</sub> A	15.26
H <sub>2</sub> A	13.33
HA	9.63
BH	9.94

**TABLE-2**

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

Complex	Cu	Co
$\text{M}(\text{OH})^+$	-6.29	-8.23
$\text{M}(\text{OH})_2$	-13.10	-17.83

**TABLE-3**

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

Complex	Cu	Co
MA	8.57	5.85
MB	8.25	6.28

**TABLE-4**

Metal-Ligand constants ( $\log \beta_{p0r50} / \log \beta_{0qr50}$ ): Ternary System (1:1:1)

Complex	Cu	Co
MAB	13.62	9.28

**TABLE-5**

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

Complex	Cu-Co
$\text{M}_1 \text{M}_2 \text{AB}$	18.91



#### IV. CONCLUSION

Quaternary complexes are more stable in comparison of ternary and binary complexes. In ternary complexes stability order is:

$CuAB > CoAB$

In binary system stability order is:

$CuA > CuB > CoB > CoA$

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