

# Speciation of Nickel (II) and Cobalt (II) Quaternary Complexes of L-Aspartic acid and Uracil

N.K. TRIPATHI and V. KRISHNA

Department of Chemistry, University of Allahabad, Allahabad-211002 (INDIA)

Email: neerajktripathi@hotmail.com, Vkrishna\_alld@rediffmail.com.

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## Abstract

Mixed metal-mixed ligand complexes of Ni (II) and Co (II) has been investigated with L-aspartic acid and uracil at silver-silver chloride electrode by the potentiometric technique. The stability constants of Ni (II)–L-aspartic acid–uracil, Co (II)–L-aspartic acid–uracil and Ni (II)–Co (II)–aspartic acid–uracil were determined using SCOGS computer programme and the complex formation were elucidated with the aid of speciation curves. The molar ratio of ternary and quaternary complexes was kept as 1:1:1 and 1: 1: 1: 1: respectively.

*Key words:* Potentiometric Studies, Aspartic acid, Uracil, SCOGS.

## Introduction

Complexation of metal ions of biological importance with amino acid, small peptides and their derivatives are of great significance as these serve as models for many complex metal amino acid equilibria occurring in enzymatic processes<sup>1,2</sup>. Metal ion complex formations are among the prominent interaction in nature<sup>3</sup>. The studies of mixed-ligand complexes play an important role in biological processes<sup>4-7</sup>. Aspartic acid combines with other amino acids to form molecules that absorb toxins and remove them from the blood stream<sup>8,9</sup>. In continuation of our earlier studies<sup>10-13</sup> on metal

complexes, we report in this paper the formation of Ni (II) and Co (II) complexes with aspartic acid and uracil.

## Experimental

All the solutions were prepared in double 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 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 in presence of suitable indicators<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:

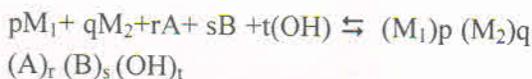
- (i) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + H<sub>2</sub>O
- (ii) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + 5ml A(0.01M) + H<sub>2</sub>O
- (iii) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + 5ml B(0.01M) + H<sub>2</sub>O
- (iv) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + 5ml A(0.01M) + 5ml M<sub>1</sub>(II)(0.01M) + H<sub>2</sub>O
- (v) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + 5ml A(0.01M) + 5ml M<sub>1</sub>(II)(0.01M) + 5ml B (0.01M) + H<sub>2</sub>O
- (vi) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + 5ml A(0.01M) + 5ml M<sub>2</sub>(II)(0.01M) + 5ml B (0.01M) + H<sub>2</sub>O
- (vii) 5ml NaNO<sub>3</sub>(1.0M) + 5ml HNO<sub>3</sub>(0.02M) + 5ml A(0.01M) + 5ml M<sub>1</sub>(II)(0.01M) + 5ml B (0.01M) + 5ml M<sub>2</sub>(II)(0.01M) + H<sub>2</sub>O

Where, M<sub>1</sub> (II) and M<sub>2</sub> (II) are Ni/Co; A is the primary ligand Aspartic acid and B is the secondary ligand *i.e.* uracil. Species distribution curves were obtained by plotting % concentration of the species obtained through SCOGS<sup>15</sup>, against pH.

## Results and Discussion

The ligand Aspartic acid behaves as a tridentate ligand, coordinating through a nitrogen and two carboxyl oxygen atoms. The secondary ligand Uracil functions as a monodentate ligand. Proton ligand stability constants obtained for both the ligand are presented in Table 1.

The formation of ternary and 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 number 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.

1:1:1 (M<sub>1</sub>:A:B), 1:1:1 (M<sub>2</sub>:A:B) ternary and 1:1:1:1 (M<sub>1</sub>:M<sub>2</sub>:A:B) quaternary mixture have been used in this study to ensure the exclusive formation of the M<sub>1</sub>AB, M<sub>2</sub>AB and M<sub>1</sub>M<sub>2</sub>AB complex, considering protonation constants of the ligand and hydrolytic constants of the M<sup>II</sup> aqueous ions, the following species have been considered to exist in the equilibria 1:1:1:1.

- (1) Ni (II) (2) Co (II) (3) H<sub>3</sub>A (4) H<sub>2</sub>A (5) HA (6) HB (7) Ni (OH)<sub>2</sub> (8) Ni (OH)<sup>+</sup> (9) Co(OH)<sub>2</sub> (10) Co (OH)<sup>+</sup> (11) NiA (12) CoA (13) NiB (14) CoB (15) NiAB (16) CoAB (17) NiCoAB

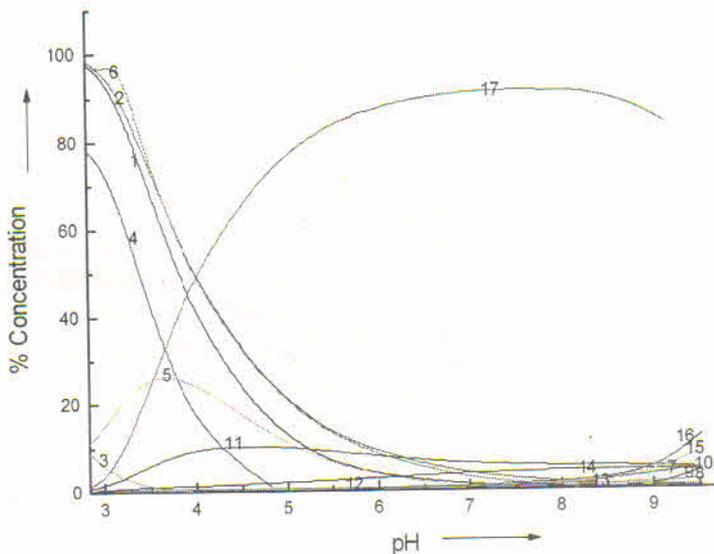


Fig. 1.0. Speciation Curves of 1:1:1:1 Ni (II)-Co (II)-Aspartic acid (A)-Uracil (B) System

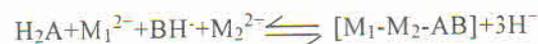
On the basis of speciation curves obtained through SCOGS, following equilibria have been proposed:



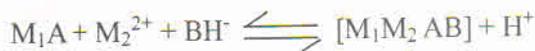
Mixed-ligand complexes may be formed as per the following equilibria:



The simultaneous formation of quaternary complex may be expressed as:



An alternative equilibrium showing step wise formation of quaternary complex may be represented as:



Formation of hydroxo species is governed as per the equilibria shown below:

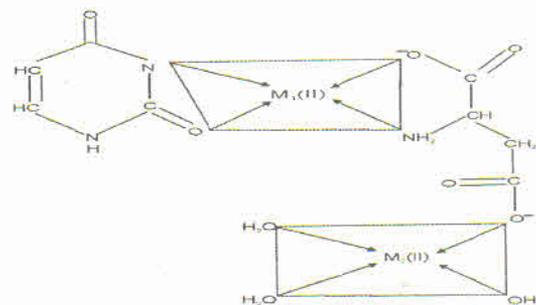
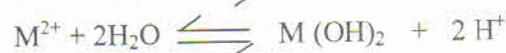


Fig. 2.0 Proposed structure of quaternary  $M_1-M_2$ -Aspartic acid-Uracil Complex

**Table-1**

Stability constants of mixed metal-mixed ligand complexes with Aspartic acid (A) and Uracil (B) in aqueous solution, at  $37 \pm 1^\circ\text{C}$  and  $I=0.1\text{m}$ ,  $\text{NaNO}_3$

(a) Proton complexes formation constant of the ( $\log \beta_{\text{oorst}}$ ) of the ligands:

Aspartic acid	H <sub>3</sub> A	H <sub>2</sub> A	HA
Log $\beta$	15.26	13.33	9.63
Uracil	-	-	HB
Log $\beta$	-	-	9.49

(b) Hydrolytic constants ( $\text{Log } \beta_{\text{poooot}}$ ) of metal ions:

	Ni	Co
M (OH) <sup>+</sup>	-8.10	-8.23
M (OH) <sub>2</sub>	-16.87	-17.83

(c) Stability constants ( $\text{Log } \beta_{\text{porst}}$ ) of binary complexes:

	Ni	Co
MA	7.65	5.99
MB	6.70	6.24

(d) Stability constant ( $\text{Log } \beta_{\text{porst}}$ ) of ternary complexes:

	Ni	Co
MAB	12.90	12.50

(e) Stability constants ( $\text{Log } \beta_{\text{pqrst}}$ ) of quaternary complexes:

	Ni -Co
M <sub>1</sub> M <sub>2</sub> AB	18.50

## Conclusions

The stability of all the analogous complexes was in order of Ni (II) > Co (II) as anticipated from the increasing charge density along the transition metal series. 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.

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