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STABILITY CONSTANTS OF Cu (II) Ni (II) AND Mn (II) METAL COMPLEXES WITH CETRIZINE AND BENZOIC ACID

B. R. AGRAWAL[a], B. K. MAGARE[b], M. N. FAROOQUI[c], D. M. JANRAO[a] and M. B. UBALE[*]

Vasantrao Naik Mahavidhyalaya, AURANGABAD – 431001 (M. S.) INDIA
[a]J. E. S. College JALNA – 431203 (M. S.) INDIA
[b] Shivaji Art's Commerce and Science College KANNAD – 431103 (M. S.) INDIA
[c]Aurangabad College for Women, Navkhanda, AURANGABAD – 431001 (M. S.) INDIA

ABSTRACT

Stability constants of binary and ternary complexes of Cu (II), Ni (II) and Mn (II) transition metal ions with cetrizine and benzoic acid have been determined at fixed ionic strength in aqueous solution at 25ºC pH metrically. Formation constants has been calculated by using Calvin Bjerrum method as modified by Irving and Rossoti. Stability constants were discussed in terms of order of stability and correlated with atomic number, ionization potential, electro negativity and reciprocal of ionic radii.

Key words : Stability Constant, Complex, Benzoic acid, Cetrizine

INTRODUCTION

The coordination chemistry of metal complexes play a vital role in biological system of organism. Various researchers have studied the mixed ligand complexes of transition metal ions with simple and substituted organic acids[1]. Magare et. al[2] studied the stability constant of Mg (II) and Ca (II) metal ions. Investigations on the stability constants of transition metal ions with medicinal drugs are increasingly becoming more important and will give an idea about the role of metal ions in the biological systems[3]. The cetrizine {2-[4-[(4-chlorophenyl)]-1-piperazinyl] ethoxy] acetic acid} is used in the treatment of allergies, hay fever angioederma and urticaria[4] as a H^1 receptor antagonists, antihistamine, antiallergiec drugs. Benzoic acid is used as a preservative in food stuff and in soft drinks to inhibits growth of bacteria at low pH value[5].

[*] Author for correspondence

Present communication deals with the systematic study of stability constants of binary and ternary complexes of Cu (II), Ni (II) and Mn (II) transition metal ions with cetrizine and benzoic acid

EXPERIMENTAL

All the chemicals used in the experiments were Analar grade quality. The ligand cetrizine (M. P. 110ºC-115ºC) and benzoic acid (M. P. 122ºC) are crystallized from ethanol and their purity were checked by melting point. The solution of metal ions salt, free acid, ligands and NaOH were prepared in triply glass distilled water and standardised by known procedures [6].

pH measurement were made with Elico pH meter (Model L1-120, Elico Pvt. Ltd. Hyderabad) with combined glass electrode by using Calvin Bjerrum method as modified by Irving and Rossoti titration technique[7].

RESULTS AND DISCUSSION

Proton ligand stability constant (pK^H)

Proton ligand stability constant of both ligands were determined by pointwise calculation method as well as half integral method as suggested by Irving and Rossoti. pK^H value of cetrizine drugs was; $pK^H = 9.55$, which is higher than acetic acid i $pK^H = 4.2$ as the ethoxy group increases the basicity of drugs as shown in the structure.

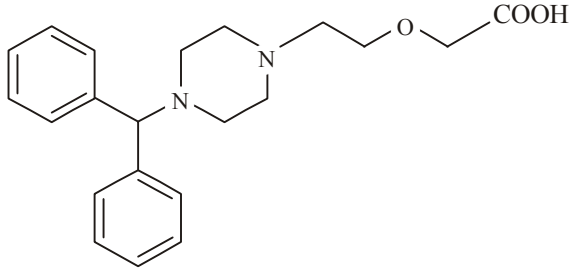

Fig. 1 : Structure of cetrizine

Proton ligand stability constant of cetrizing indicates that it has less pK^H value than histamine ($pK^H = 10$) to inhibit the stimulated secretion of gastric acid. pK^H value of benzoic acid has good agreement with literature valu ($pK^H = 4.19$).

Metal ligand stability constant (Log K)

The displacement of metal titration curves from ligand titration curves along volume axis indicates the formation of metal complex species and lies in the pH range, where hydrolysis is not possible. Metal ligand stability constant (LogK) of Cu (II), Ni (II) and Mn (II) metal ions with ligand were calculated by point wise and half integral method as suggested by Irving and Rossoti (Table 1).

Table 1 : Metal ligand stability constant (Log K) and mixed metal ligand stability constant (Log K_{MRL}) of Cu (II), Ni (II) and Mn (II) metal ions with ligands

Metal ions	Log K for cetrizine	Log K for Benzoic acid	Log K_{MRL}
Cu (II)	9.12	8.40	9.81
Ni (II)	8.32	7.32	10.24
Mn (II)	7.87	6.12	7.83

Highest value of $\bar{n}$ is around one, which indicates the formation of 1 : 1 complexes only. Higher value of Log K indicates the possibility of covalent interaction as the low value gives idea about ionic interaction[8]. Observed trend in the order of stability constant was Cu (II) > Ni (II) > Mn (II), which are in accordance with the William- Irving series[9]. The graphs of log K vs atomic number, atomic radii, electro negativity etc. were plotted and found in good agreement with earlier studies.

Mixed ligand stability constant (Log K_{MRL}) : - Mixed ligand titration curve does not coincide with either of individual titration curve and therefore, 1 : 1 : 1 ternary complex is formed. The formation of mixed ligand complexes can be represented by following equilibria –

$$M\,(aq) + R \rightleftharpoons MR$$

$$MR + L \rightleftharpoons MRL$$

$$M + R + L \rightleftharpoons MRL$$

$$\therefore \text{Log } K_{MRL} = \frac{[MRL]}{[M]\,[R]\,[L]}$$

The stability of mixed ligand complex shows following trend Mn (II) < Cu (II) < Ni (II). The deviation from general trend i. e. is low value of Cu (II) may be due to the

tendency of Cu (II) (d^9) to have distorted octahedral or square planar structure, which is inhesent to John – Teller distortion[10], particularly in the presence of strongly coordinating ligands.

The relative stability of ternary complexes has been compared with the corresponding binary complexes of metal ions in terms of Δ Log K.

$$\Delta \text{ LogK} = \text{Log K}_{\text{MRL}} - \text{Log K}_{\text{ML}}$$

It is found that stability constant of ternary complexes are higher than the corresponding stability constant of binary complexes, which indicates that ternary complexes are more stable than binary complexes.

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