

Stability of ternary complexes of Cu(II) metal ion with 2,2'-Bipyridyl and Oxalic acid, Tyrosin, Ethylenediamine, Glycine, α -Alaline, Phenylalanine, Tryptophan

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Abstract: In the present work the formation constant of ternary complexes [MAL], where M = Cu(II), A = 2,2'-Bipyridyl(2,2'-bipy) and L = Oxalic acid, Tyrosin, Ethylenediamine, Glycine, α -Alaline, Phenylalanine, Tryptophan have been determined and the values of $\Delta\log K$ have been calculated by using SCOG computer program. The analysis of the representative species distribution curves shows that in the pH range 1-3, metal ion Cu(II) is the major species. In the pH range 3-5, the species [MA] and [ML] is predominate. In the pH range 5-7, the species [MAL] exists. The value of $\Delta\log K$ of the complexes [Cu(2,2'-bipy)L] show more positive value when, L = tyr. This is due to the fact that the intramolecular interligand interaction involves in complex. The non-coordinated side group hydroxyphenyl ring of tyrosin comes over the pyridyl ring of 2,2'-bipyridyl and hence non-covalent hydrophobic interaction is possible. This intramolecular interligand interaction stabilizes the ternary complex, leading the more positive $\Delta\log K$ value. when L = Ethylenediamine (en), glycine (gly), α -alanine (α -ala), phenylalanine (ph-ala) the $\Delta\log K$ values are negative. The $\Delta\log K$ value are more negative in case of Cu(II) complexes with above ligand because of the presence of Jahn-Teller effect of the complexes.

Keywords: Stability, Ternary Complex, 2,2'-Bipyridyl, SCOG etc.

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I. Introduction

In a complex where two or more ligands of the same type are bonded with a metal ion is called a binary ligand complexes and if the different types of ligand are present, then the complexes is said to be ternary complexes or mixed ligands complex[1]. It is now generally agreed that in a solution containing metal ions and two different suitable ligands are usually combined. During the past three decades metal complexes have gained a growing interest as pharmaceuticals due to their potential therapeutic applications [2]. Metal ions displace one another in accordance with the stability constants of their coordinated compounds. It has been observed that the stability constant of the mixed ligand complexes depends on the nature of the metal ions and the nature of the ligands[3]. The transition metal complexes with nitrogen and oxygen donor ligands are applied in various activities such as anticancer, antitubercular, antibiotic, antimicrobial and antifungal agents[4-5]. Complexation behavior of metal ions with ligand has significance interest in field of coordination chemistry due to potential activity of complexes formation. In this phenomenon metal acts a central role in chelates formation with ligand [6]. The formation of mixed ligand complexes of Copper with 2,2'-Bipyridyl and some biologically important amino acids like Phenyl Alanine (Ph-ala), α - Alanine (α -ala), Glycine, L-Valine and Sarcosine (N-methyl glycine) as lignds have great socio economic importance and unique significance in the field of biochemistry[7-8]. The stability of complexes plays a major role in elucidation of mechanism of drug action. The acute action of drug and their complex formation in complex media is dependent on metal ligands selectivity and stability constants[9]. Many attempts have been made to evaluate different factors affecting the stability of the metal chelates along with their stability constants [10-11]. Therefore it is necessary to investigate the mixed ligand complexes of Cu(II) involving various types of bi- and tri- dented biologically important ligands

II. Objectives

The aim of the present works is to prepare the mixed ligand complexes [MAL], where M refers to Cu(II) and A refers to 2,2'-Bipyridyl(2,2'-bipy), L refers to Oxalic acid (ox), Tyrosin (tyro), Tryptophans (tryp), Phenyl Alanine (ph-ala), α - Alanine (α -ala), Glycine (gly), Ethyldiamine (en) etc. bi-dented biologically important ligands.

The line of approach of the present works may be summarized below:

(i) Preparation of ternary complexes.

(ii) Determination of the stability constant of the complexes.

Stability constant of complex compound is very essential for MRI, Catalysis for RNA cleavage, kinetics of reaction, Radiopharmaceuticals, Molecular recognition, Macrocyclic complexes, Host-guest interactions, Enthalpy determination, Cation and Anion selective complexation, Supramolecular complexes, Action of Drug, Environmental effects, Metallomics (including peptides) etc. For imbalance of stability constant above phenomena would be disorder. So, Studies are required to determine the stability constant. Result obtain from the present work would be helpful in the development of biological, pharmaceutical and physiological implication in the future.

III. Methodology/Experimental Design:

(a) Preparation of metal perchlorate:

Metal perchlorate will be prepared from analytically pure metal carbonate by treatment with 70% perchloric acid (A.R).The resulting solids will be vacuum filtered, washed with ethanol till free from excess acid and recrystallized several times from ethanol(metal perchlorates are partially soluble in alcohol).

(b) Stability Constant determination:

Potentiometric titration will be carried out in aqueous media using pH meter with accuracy 0.01 pH unit using 0.2 M NaOH solution. The solutions of reagents will be prepared in double distilled and deionized water. The freshly prepared NaOH solution will be used as a titrant for pH metric titrations. It will be standardized with oxalic acid according to the literature method [12]. The 1.0 M NaClO₄ solutions were prepared to maintain the 0.2 M ionic strength of the titration solutions by taking required amount of sodium perchlorate. The metal solutions also will be standardized according to literature method[13]. The pH electrode will be calibrated in aqueous solution using buffer solution of pH 4.01 and 6.86. As usual pH metric titration method [14] will be used for solution works. The stability constant of metal complexes will be determined potentiometrically by using SCOGS[15] computer program..

IV. Experimental

Determination Stability Constant:

Irving Rossotti titration technique has been used to determine the formation constants of the ternary complexes using SCOGS (Stability Constant of Generalized Species) computer program[16].The activity coefficient of H⁺ under experimental condition has been considered to be equal to unity and the value of the ionic product of water 14.167 has been used. For the determination of formation constants all solutions were titrated potentiometrically against standard (0.02M) sodium hydroxide solution. In all the cases acid concentration was kept 2.00 ×10⁻² M and the total ionic strength (I) of the solution was maintained at 0.2M.

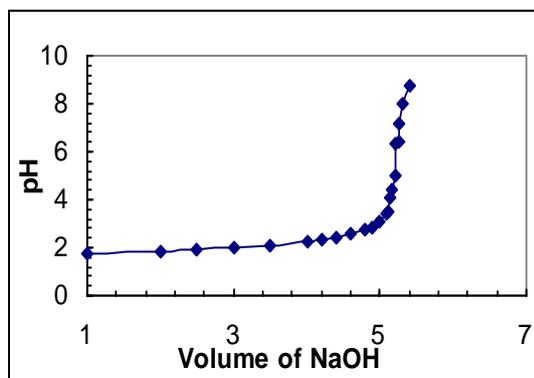
For the determination of the formation constants of the ternary complexes [MAL], the following solution (50cm³) having M:A:L in the ratio 1:1:1 were prepared. 0.02M HClO₄, 0.002M metal perchlorate, 0.002M ligand (A), 0.002M ligand (L) and 0.174M NaClO₄ set was titrated against standard alkali. All the titrations were carried out in aqueous medium and the temperature was maintained at 25°C±1°C during the progress of titration. Titrations were carried out by using TOA pH-METER HM- 20S, having an accuracy of ±0.01 pH unit. The glass electrode was calibrated using buffer solutions of pH 6.86 and 4.01. Hence the stability constants calculated are stoichiometric constants. The calculations were carried out by computer, Dell, Optiplex, GX 280.

Table – 1: Proton ligand formation constant of ligands and formation constant of their Cu(II) binary complexes in aqueous medium with I = 0.2 M (NaClO₄) at 25°C ± 1°C.

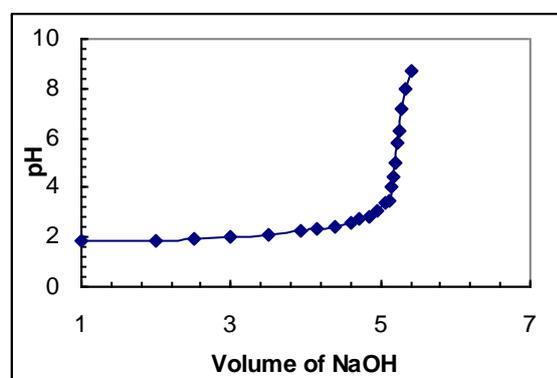
Ligands	$\log K_1^H$	$\log K_2^H$	$\log K_{CuL}^{Cu}$	$\log K_{CuL_2}^{Cu}$
Oxalic acid	3.88	2.33	4.90	8.42
Ethylenediamine	10.43	7.12	10.05	18.88
Glycine	9.58	2.42	7.00	14.37
α-alanine	9.65	2.18	7.63	14.68
Phenylalanine	9.22	1.96	7.49	14.11
Tyrosine	9.33	1.72	7.39	14.02
Tryptophan	9.43	2.03	7.97	15.33
2,2'-Bipyridyl(2,2'-bipy)	4.43	1.61	6.30	7.96

Table – 2: Stability constant of mixed ligand complexes [Cu(2,2'-bipy)(L)] in aqueous medium with I = 0.2 M (NaClO₄) at 25°C ± 1°C.

System	log K _{CuAL} ^{Cu}	log K _{CuA} ^{Cu}	log K _{CuAL} ^{CuA}	log K _{CuL} ^{Cu}	ΔlogK
[Cu(2,2'-bipy)(Ox)]	11.92	6.30	5.62	4.90	+0.72
[Cu(2,2'-bipy)(en)]	15.02	6.30	8.72	10.05	-1.33
[Cu(2,2'-bipy)(gly)]	12.83	6.30	6.53	7.00	-0.47
[Cu(2,2'-bipy)(α-ala)]	13.32	6.30	7.02	7.63	-0.61
[Cu(2,2'-bipy)(Ph-ala)]	13.27	6.30	6.97	7.49	-0.52
[Cu(2,2'-bipy)(Tyr)]	13.92	6.30	7.62	7.39	+0.23



Curve-1



Curve-2

Fig-1: Potentiometric titration curves of aqueous solutions containing Cu²⁺ metal ion, 2,2'-Bipyridyl and L. (each 0.001M).

Curve (1) : Cu²⁺ + 2,2'-Bipyridyl+ Oxalic Acid

Curve (2) :Cu²⁺ +2,2'-Bipyridyl + Ethylenediamine

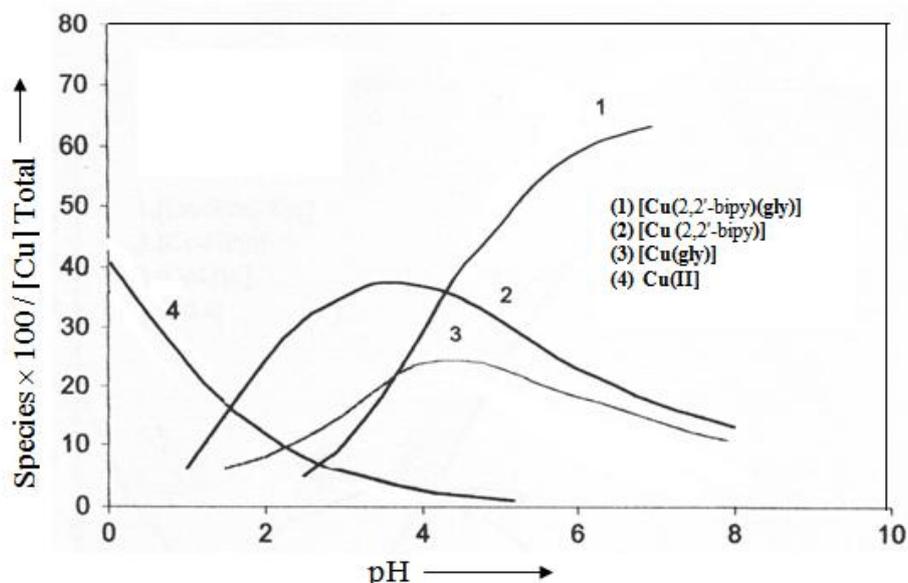


Fig –2: Species distribution diagram for the [Cu(2,2'-Bipyridyl)(gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

V. Result and Discussion

The analysis of the representative species distribution curves (Fig-2) shows that in the pH range 1-3, metal ion Cu(II) is the major species. In the pH range 3-5, the species [MA]and [ML] is predominate. In the pH range 5-7, the species [MAL] exists. where M =Cu(II) and L= Oxalic acid (ox), Tyrosin (tyro), Tryptophans (tryp), Phenyl Alanine (ph-ala), α- Alanine (α-ala), Glycine (gly), Ethyldiamine (en).

It is interesting fact that for the complexes of [Cu(2,2'-bipy)(L)] when, L= Ox and tryo the $\Delta\log K$ value is positive. In this type of complexes M→A interaction of $d\pi-p\pi$ occurs. In the formation of binary complexes, there is repulsion between the metal $d\pi$ electrons and the additional lone pairs of electrons present over the $\text{O}=\text{O}$ coordinating ligands. In the ternary complexes M→A, π -bonding reduce the electron density over the metal ion and hence the lone pair of electrons over L has to face less repulsion while combining with [MA] than with the free metal ion. It is observed that $\Delta\log K$ values for the complexes of [Cu(2,2'-bipy)L] increases. The complex [Cu (2,2'-bipy)L] show more positive value when, L=tyr because of the fact that the intramolecular interligand interaction involves in complex. The non-coordinated side group hydroxyphenyl ring of tyrosin comes over the pyridyl ring of 2,2'-bipyridyal and hence non-covalent hydrophobic interaction is possible. This intramolecular interligand interaction stabilizes the ternary complex, leading the more positive $\Delta\log K$ value. It is investigated that for the complexes of [Cu(2,2'-bipy)(L)] type the $\Delta\log K$ values are negative where L= Ethylenediamine(en), glycine(gly), α -alanine (α -ala), phenylalanine (ph-ala) because of the presence of Jahn-Teller effect of Cu(II) complexes. When a bulky group either attached to or present near the donor atom of a ligand, mutual repulsion among the ligands occurs and consequently the metal-ligand bond is weaker. Thus large bulky ligands form less stable complexes than do analogous smaller ligands. This effect is commonly referred to as steric hindrance (steric effect or steric strain). The increase in size of the metal atom the ligand will coordinate more easily to the central metal ion and form stable ternary complex.

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