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Mixed LIGAND Complexes Of Copper (II) And Zinc (Ii) With L-2-Amino-3-Hydroxy PROPANOIC Acid And 2,2'-Bipyridine

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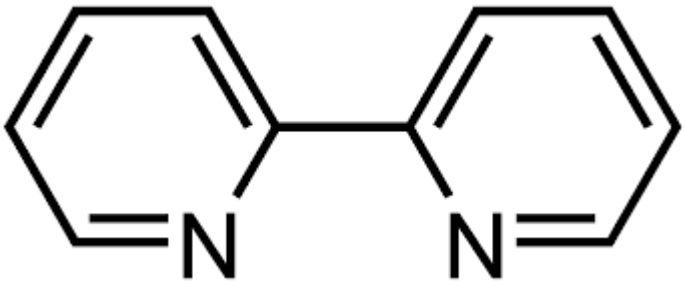
Abstract:-*Mixed ligand complexes are those in which more than one kind of ligand , other than the solvent molecule is present in the innermost coordination sphere of central metal ion.The importance of mixed ligand chelates in various fields of chemical, biological and medicinal science is manifold. The stability of mixed chelate is important in biological systems, as many metabolic and toxicological functions are to a large extent dependent on them (1).Recently the study of such complexes of different biological important ligands have been carried out (2-5, 6,7,8) Williams and others (9) illustrated the formation of an ion mixed ligand complex in enzyme inhibitor metal systems. Many analytical methods based on complex formation involve the formation of the mixed chelate (4).*

I. Introduction:-

2,2'-Bipyridine (abbr. Bipy.) is a typical bidentate chelating agent through the nitrogen atoms with the formation of five-member ring. It acts as a good donor and as well as a good acceptor (10) and stabilizes both low and high valency state (11).



Metal chelates of Bipy are formed at low pH and are stable at higher pH or forming hydroxo complexes, which do not disproportionate readily to the metal hydroxide. As such many scientists (12,13) have used it as a primary ligand in the mixed ligand complex formation.

In the present work, stability constant of ternary metal complex of Cu (II) and Zn (II) has been carried out with 2,2'-Bipyridine as a primary ligand and L-2-Amino-3-hydroxypropanoic acid as secondary ligand. The stability constants evaluated by using Irving-Rossotti technique as modified by Chidambram and Bhattacharya (8,12).

The reaction for the mixed ligand complex formation can be represented as follows:

$$(M.\ Bipy)^{+2} + L^{-} \rightleftarrows (M.\ Bipy.L^{+})$$

$$K_m.\ Bipy.L. = [M.\ Bipy.L^{+}] / [M.\ Bipy]^{+2}\ [\ L^{-}\ ]$$

The use of the above method is based on the consideration of the fact that $[M.\ Bipy]^{+2}$, 1:1 complex is formed at low pH and the complex M. Bipy $(H_2O)_2^{+2}$ is stable at higher pH. [Serine combines at higher pH replacing the water molecule resulting in mixed ligand complex $[M.\ Bipy.L]^{+}$.

II. Experimental Details

The experiments have been carried out in aqueous media.

Reagents :-

a) Stock solutions of the ligands namely l-2-Amino-3-Hydroxy Propanoic Acid (BDH Chemicals Ltd Poole England) commonly known as L-Serine, and 2,2'-bipyridine (E, Merk India Pvt. Ltd., Bombay), were prepared by dissolving accurately weighed amounts in conductivity water and organic solvents (A.R. grade) were employed for obtaining aqua-organic media

b) Metal solution – standard solutions of metals (Sarabhai, M, Johnson-Mathey Co. Ltd., London, A.R. Grade0 were prepared by dissolving the required amounts of their sulphates (Cu II) and Chlorides (Zn II) in conductivity water and were standardized by estimating the metal contents.

c) Other reagents – solution of sodium hydroxide, potassium nitrate, sodium perchlorate, hydrochloric acid, potassium chloride etc. were prepared in conductivity water using A. R grade.

Instruments: -

a) Potentiometer: - the pH measurementswere carried out by the Elico microprocessor based pH analyzer L1612 (accuracy ± .001 pH). Standard buffers of different pH values calibrated the instrument before and after each series of measurements.

b) Thermostat: - $U7^0$ type German thermostat having an accuracy ± 0.1 ^{0}C was employed to maintain temperature constant in all the experimental work.

Procedure: -

All experiments were carried out in inert atmosphere of nitrogen at a constant temperature, maintaining ionic strength constant by adding required amounts of sodium perchlorate or potassium nitrate.

The experimental procedure for determining soichiometry, stability constants and related thermodynamic parameters involves a series of titration of the ligand in the absence and presence of metal ions at different metal to ligand ratio with standard NaOH, keeping the total volume 25 ml.

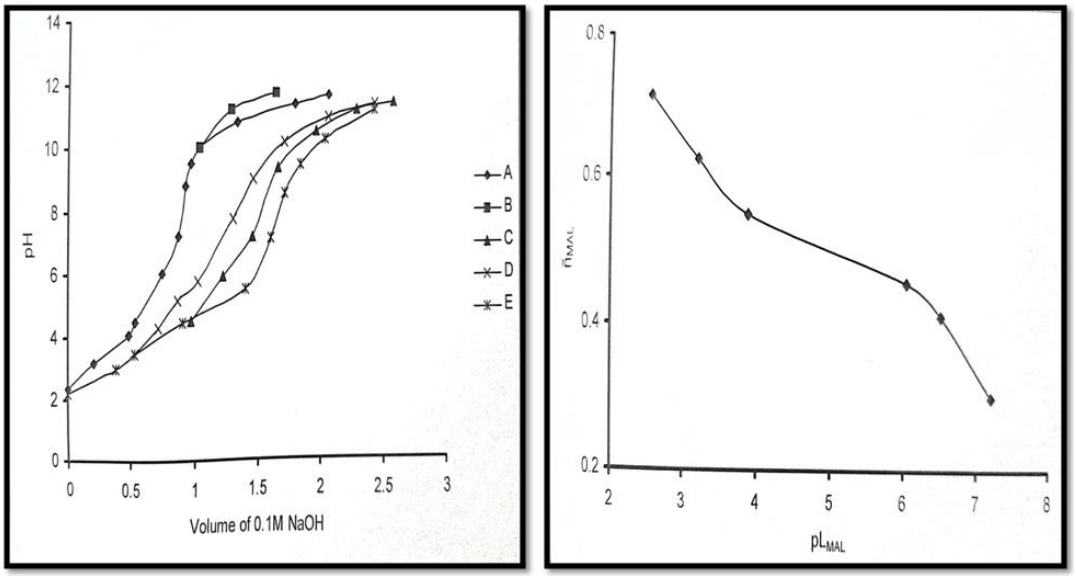
Table 1. Values of $\bar{n}_{MAL}$ and pL_{MAL} for Cu^{+2}-L-Serne system at 20^0C (μ=0.1M) $T_C{}^0{}_L$ = 2mM (L- Serine), N^0 = 0.1M NaOH, $T_C{}^0M$ = 2mM (Cu^{+2}) V^0 = 25 ml, E^0 =8mM, 2,2- Bipyridine= 2mM

pH	V'''-V'	V"	$\bar{n}_{MAL}$	pL_{MAL}
4.5	0.19	0.725	0.25	11.05
5.4	0.23	0.92	0.465	9.75
6.0	0.26	1.055	0.561	8.7
6.8	0.29	1.19	0.8	7.6
7.2	0.35	1.203	1.06	6.95
7.45	0.375	1.211	1.13	6.3

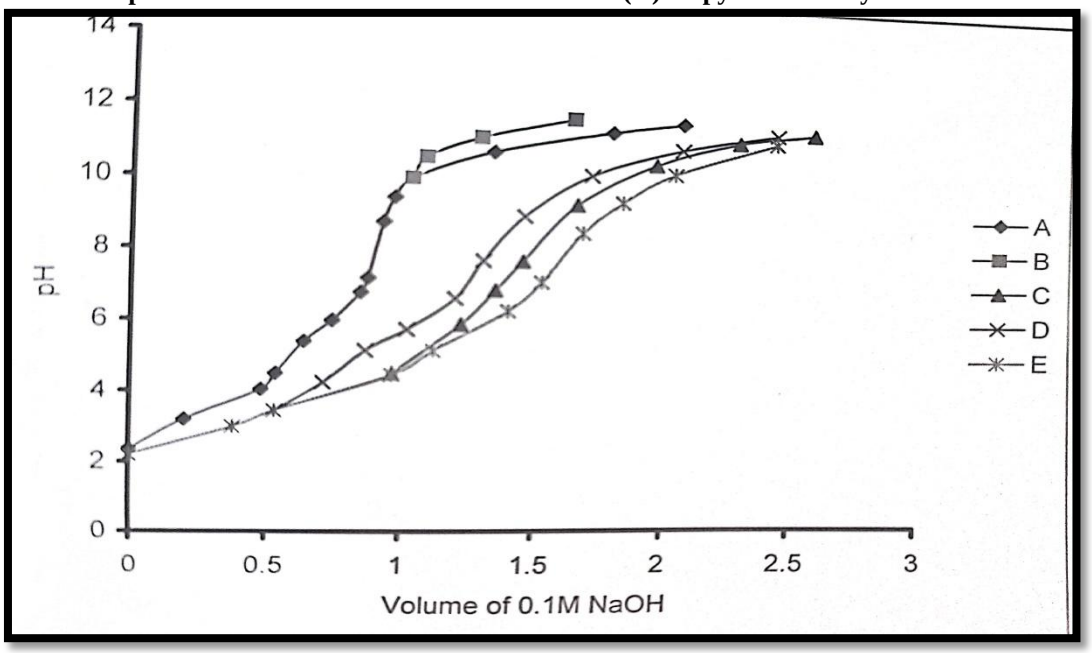
Table 2. Values of $\bar{n}_{MAL}$ and pL_{MAL} for Zn^{+2}-L-Serne system at 20^0C (μ=0.1M) $T_C{}^0{}_L$ = 2mM (L- Serine), N^0 = 0.1M NaOH, $T_C{}^0M$ = 2mM (Zn^{+2}) V^0 = 25 ml, E^0 =8mM, 2,2- Bipyridine= 2mM

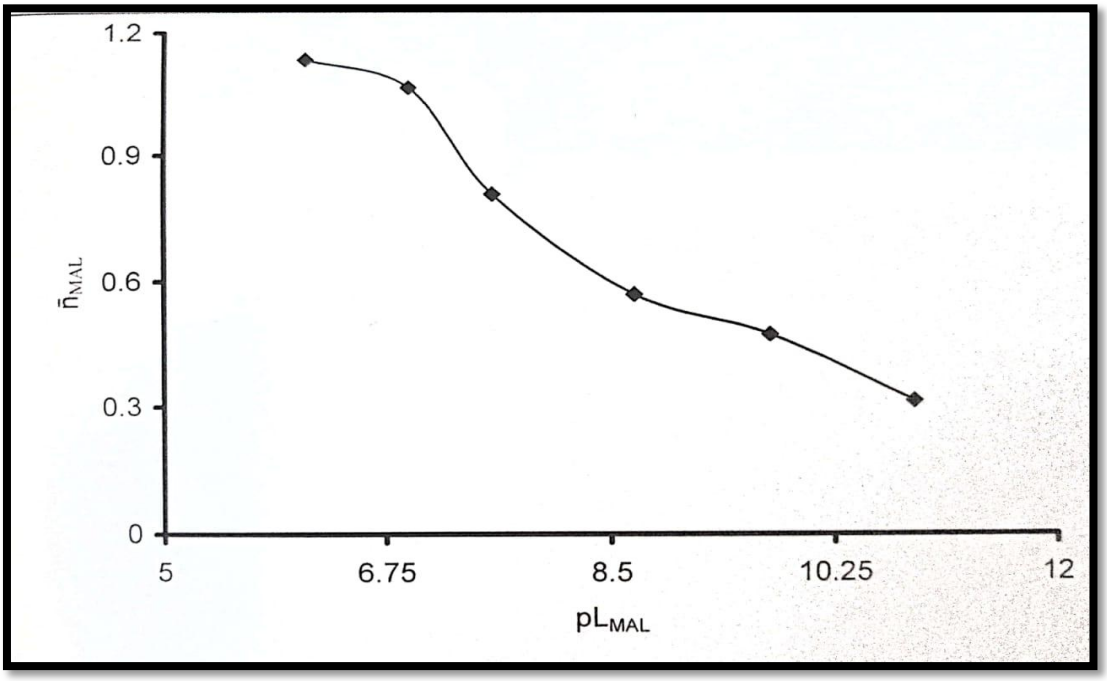
pH	V'''-V'	V"	$\bar{n}_{MAL}$	pL_{MAL}
5.1	0.14	0.815	0.301	7.1
5.521	0.19	1.01	0.41	6.5
6.28	0.21	1.11	.455	6.05
7.05	0.32	1.25	0.546	3.8
7.35	0.335	1.29	0.621	3.3
7.5	0.339	1.32	0.711	2.55

Graph 1. Titration & Formation Curve for Cu (II) -Bipy-L-Serine System at 20^0C



Graph 2. Titration & Formation Curve for Zn (II) -Bipy-L-Serine System at 20^0C





III. Result and Discussion

For the determination of formation constants of the mixed ligand system, the following solutions were prepared in 25ml volume for titration as follows:

1) 0.008 M $HClO_4$ + 0.1 M $NaClO_4$
2) 0.008 M $HClO_4$ + 0.1 M $NaClO_4$ + 0.002M Bipy
3) 0.008 M $HClO_4$ + 0.1 M $NaClO_4$ + 0.002M Bipy + 0.002M (M^{+2}) solution
4) 0.008 M $HClO_4$ + 0.1 M $NaClO_4$ + 0.002M L- Serine
5) 0.008 M $HClO_4$ + 0.1 M $NaClO_4$ + 0.002M Bipy + 0.002M (M^{+2}) solution + 0.002M L- Serine

Each of the above samples was titrated against 0.1M NaOH.

The values of the stability constants for the mixed ligand complex of Cu(II)/Zn(II) -2,2' Bipyridine and L-Serine at 20^0C (μ=0.1M) have been recorded in Table 1 and Table 2. the values of stability constant of their binary complexed also are given for comparison of two.

It can be observed from the plots of pH values against values of alkali (Graph 1 and Graph 2) that L-Serine does not combine with metal ion below pH ~ 2.9 where primary combination takes place with 2,2'-bipyridine but above pH ~2.9 suggesting the coordination of L-Serine. Dissociation of primary complex does not take place in the pH range of 2.9-8. It may be considered that L-Serine combines with M (aq)+2 in simple system.

It is interesting to observe from Table 3 that the stability of ternary complex is lower than that of the corresponding binary complex. The behavior is expected and can be explained on the basis that there are fewer number of sites available for bonding on the [M (Bipy)] binary complex than that on aquated M (II) ions. Thus the secondary ligand (amino acid) expected to bind the [M (Bipy)] complex with a smaller formation constant than that with the aquated metal ion (13,1) or it can be say that the primary ligand molecules like Bipy. May put a barrier to the approach of the secondary ligand and this might lead to a decrease in the stability of ternary complex

Table 3. log k_{MAL} value for Cu (II)/ Zn (II) – 2,2 Bipyridne- L-Serine system in aqueous media at 20^0C (μ=0.1M)

Metal Complex	Stability Constants		
	log k_1	log k_2	log k_{MAL}
Cu (II)	9.35	5.44	9.112
Zn (II)	5.35	4.25	4.875

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