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## Complex formation equilibria of zinc (II) ion with schiff bases as primary ligands and amino acids as secondary ligand

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### ABSTRACT

The formation constant of mixed ligand complexes of zinc (II) with Schiff bases (1-(2-hydroxy benzamido)-2-(fur-2-yl)-azomethine)  $L_1$ , (1-2-hydroxyhexamido)-2-(thien-2-yl)-azomethine)  $L_2$  as primary ligands and Glycine ( $R_1$ ), DL-Valine ( $R_2$ ) as secondary ligands have been determined potentiometrically in 40% (v/v) THF-water mixture at 30<sup>o</sup> C and ionic strength of 0.1 M NaClO<sub>4</sub>. The proton ligand stability constants of free ligands and stability constant for ternary systems involving Schiff bases and amino acids were also determined under identical conditions. The  $P^H$  titration data were analysed using the computer SCOGS programme. The relative stability of ternary complexes as compared to that of corresponding binary complexes has been quantitatively explained in terms of  $\Delta \log K$ ,  $K_R$ , and  $K_L$  values. The concentration distribution of various complex species as a function of  $P^H$  was evaluated.

**Keywords:** formation constants, transition metals, Schiff bases, Amino acids, ternary complexes.

### INTRODUCTION

The Schiff bases achieved a special status amongst organic compounds because of their Co-ordinating capability, industrial, analytical, catalytic and biological activities[1-5]. The chelating ligands containing oxygen and nitrogen atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ion [6]. In biological fluids where several metal ions are present in trace quantities. Some ligand show a marked tendency to compete for metal ions. Studies on metal-ligand formation at room temperature are therefore very important. Many of the Schiff bases are reported to be physiologically active and they show fungicidal, bactericidal, antitumor, antitubercular, and anticancer activities.[7-10]. It is well known that Zn(II) ions is an integral component of many proteins and is indispensable for their catalytic function and structural stability. The biological role of Zn(II) have been well reviewed [11-13]. and seem dominated by its ability to assume distorted four or five Co-ordinated structure in enzymes. The literature survey reveals that no systematic study has been reported on the binary and ternary complexes of Zn(II) with present schiff bases. In view of this fact and the continuation of our earlier studies on binary and ternary complexes of Schiff bases[14-18]. We have under taken the study of complexes equilibrium of Zn(II) complexes of some newly synthesized Schiff bases and also the ternary complexes of these Schiff bases as primary ligands and amino acids as secondary ligands.

**MATERIALS AND METHODS**

All the reagents used were of AR grade and all the solutions were prepared in doubly distilled water and standardized by usual procedure [19]. The Schiff bases (1-(2-hydroxy benzamido)-2-(fur-2-yl)-azomethine) L<sub>1</sub>, (1-2-hydroxyhexamido)-2-(thien-2-yl)-azomethine) L<sub>2</sub> were synthesized by refluxing equimolar quantities of salicylhydrazine and respective aldehyde in ethanol for six hours. The products obtained were filtered, washed with ethanol and dried over calcium chloride. The purity was tested by elemental analysis, melting point, TLC and IR spectra. The melting point of L<sub>1</sub> is 227<sup>o</sup>C(found:C,62.05%;H,4.08%;N,12.05% calculated for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub>:C,62.60%; H,4.38%; N,12.17%). The melting point of L<sub>2</sub> is 246<sup>o</sup>C (found: C,58.81%; H,4.27 %; N,11.16% calculated for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>S C,58.52%; H,4.09; N,11.38%) The two IR bands appearing at 1600-1630 cm<sup>-1</sup> and 1190-1205 cm<sup>-1</sup>were assigned to stretching vibration modes  $\nu_{C=O}$ ,  $\nu_{C-OH}$  deformation. The phenolic. -OH stretching was found to be absent due to strong intramolecular hydrogen bonding with orthocarbonyl group. The observed lowering in normal carbonyl group frequency may be due to the effect of intramolecular hydrogen bonding.[20]. The titrations were carried out using a digital pH meter (Elico model L1-120) in conjugation with combined electrode. All titrations were carried out at 30±0.1<sup>o</sup>C. For the determination of formation constants of ternary complexes, following solutions were prepared.,0.02M perchloric acid, 0.01M metal solutions and for ionic strength, 0.1M sodiumperchlorate. The titrations were plotted by using experimental data, which were utilized to analyze the proton ligand formation constants of primary and secondary ligands and stability constants of their metal complexes. Concentration of total metal, total ligand, free metal, free ligand and various possible species that are formed during the complexation are calculated using SCOGS programme[21-22] Complex formation equilibria were elucidated with the help of species distribution curves obtained.

**RESULTS AND DISCUSSION**

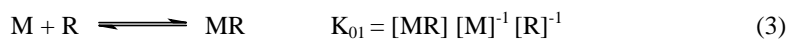
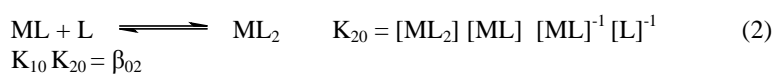
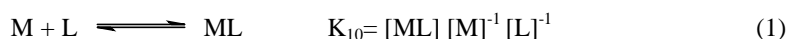
*a) Binary metal complexes:-*

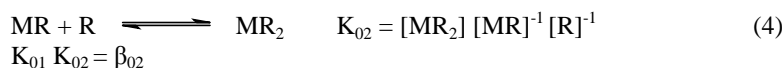
The proton ligand and metal ligand stability constants of primary ligands (1-(2-hydroxy benzamido)-2-(fur-2-yl)-azomethine) L<sub>1</sub>, (1-2-hydroxyhexamido)-2-(thien-2-yl)-azomethine) L<sub>2</sub> and secondary ligands (R<sub>1</sub>),DL- Glycine and DL- Valine (R<sub>2</sub>) with Zn (II) ions determined in 40% (v/v) THF:water medium at 30 <sup>o</sup>C and ionic strength 0.1M NaClO<sub>4</sub> have been determined by Irying-Rossoti technique after appropriate pH corrections determined by using the method suggested by Van Uitert. Their stepwise metal-ligand formation constants were also determined for the comparison with those of the ternary systems under identical conditions. The values are presented in Table1. The primary ligands both forms 1:1 and 1:2 complexes where as secondary ligands form 1:1 complexes with Zn(II) ions. The complexing tendency of Zn(II) is found to be more with L<sub>2</sub> than L<sub>1</sub>.

*Ternary metal complexes:-*

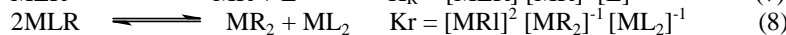
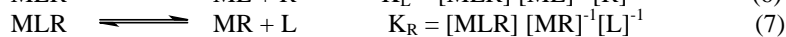
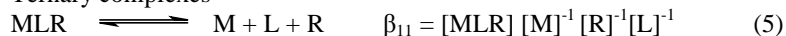
In the ternary system, The pH titration curves corresponding to mixed chelation always run below the titration curves of the pure ligand as well as their binary metal ligand curves indicating the formation of ternary complexes. Since the mixed ligand curve coincide with individual metal complexe titration curves, The formation of 1:1:1 complex by simultanius equilibria was interred. Form pH of precipitation, the mixed ligand curve deviate towards x-axis due to the formation of hydroxide species. The formation constant of ternary complexes were determined by computational programme “SCOGS” [22] to minimize the standard deviation.

The formation of 1:1:1 ternary complex have been used in this study to ensure the exclusive formation of the simplest ternary complex MLR considering the pk values of the ligands and hydrolytic constant of M<sup>2+</sup> ions the following species have been considered to exist in the complexation equilibira. M<sup>2+</sup> LH<sub>2</sub>, LH, L<sup>2-</sup> M(OH), ML, LR<sup>2+</sup>, MR(OH), R<sup>2-</sup> and MLR(OH). The relative stability of the binary and ternary complexes are quantitatively expressed in terms of  $\beta_{11}$ ,  $\beta_{20}$ ,  $\beta_{02}$ ,  $K_L$ ,  $K_R$ , and  $\Delta\log K$  values which are represented in table (2). The simplest cause of the mixed ligand complex formation is the co-ordination of two ligands with central metal ion. The two different ligands are symbolized as L and R the following equilibiria and equilibrium constant must be considered.





Ternary complexes



The relationship between equilibrium constants of the binary complexes are.

$$\Delta \log K = \log \beta_{11} - \log K_{10} - \log K_{01}$$

$$K_r = \beta_{11}^2 / K_{20} K_{02}$$

$$K_R = \beta_{11} / K_{01}$$

$$K_L = \beta_{11} / K_{10}$$

The comparison of  $\beta_{11}$  values with  $\beta_{20}$  of these systems reveals the preferential formation of ternary complexes over binary ones. The low values of  $K_R$  and  $K_L$  show more stability of ternary complexes with respect to binary complexes of primary and secondary ligands. The negative values of  $\Delta \log K$  reveals that the stability of mixed ligand complex is comparable with 1:2 complex of binary species. The stability of 1:2 complex is less than the stability of 1:1 complex. Hence the stability of mixed ligand complex is less than the stability of 1:1 complex. In  $ZnR_1L_1$  systems, the primary ligand from 1:1 and 1:2 complexes where as secondary ligand from only 1:1 complex with Zn(II). It has been observed from table (2) that the stability of mixed ligand complexes of L, are found to be higher than that of the mixed ligand complexes L. The positive values of,  $K_R$  and  $K_L$ , show the stability of mixed ligand complexes but these complexes are less stable than the 1:1 binary complexes of primary and secondary ligands and hence we get negative values of  $\Delta \log K$ . It is however, observed that the  $\Delta \log K$  values for Zn(II) complexes are less negative than those for the corresponding Cu(II) complexes. This may be attributed to the fact that intermolecular ligand-ligand interaction is enhance in tetrahedral Zn(II) complexes, leading to a larger shift of the equilibrium to the right and therefore resulting in less negative and positive  $\Delta \log K$ .

The species distribution curve of  $Zn L_1R_1$  system indicates the formation of ternary complex are represented in fig (2). The initial concentration of ternary complexes is 1.08% which increases with increasing pH. The maximum concentration is found to be 18.60% which indicates the lower tendency of primary as well secondary ligands towards the formation of ternary complex. From the nature of curves it can be observed that there is a sharp decrease in concentration of HR ( $C_3$ ) up to pH 4.9, which is the pH range of sharp increase of concentration of ZnR. From this observation it is clear that, the major part of HR concentration is utilized in the formation of ZnR and relatively very small amount of it may be used in the formation of ternary complex. Formation of  $ZnL_1R_1$  to small extent is also possible by reaction (7).

In  $ZnL_1R_2$  system, the maximum concentration of ternary complex is 42.2% at 5.4 pH. The concentration of HR( $C_3$ ) is 76.4% at 3.7 pH and then decrease continuously to attain minimum value of 2.6% at 5.2 pH. Concentration of L ( $C_1$ ) also found to decrease with increasing pH. This decreasing nature of the curves  $C_1$  and  $C_3$  confirms the formation of ternary complexes by reaction (5) similar to the  $ZnL_1R_1$  system the strong involvement of HR species in the formation ZnR is indicated by the nature of  $C_3$  curve. Formation of ternary complexes is also possible to same extent by reaction(7). The species distribution diagram of  $ZnL_2R_1$  system, shows the similar trend as that of  $ZnL_1R_1$  system other systems  $ZnL_1R_2$  and  $ZnL_2R_2$  also shows similar behavior.

**Table 1: Proton – ligand and metal –ligand stability constants in binary system**

Ligand	$K_1^H$	$K_2^H$	Log $K_{ML}^M$
$L_1(C_{12}H_{10}O_3N_2)$	4.63	-	2.81
$L_2(C_{12}H_{10}O_2N_2S)$	8.26	-	3.69
$R_1$	3.13	9.75	3.98
$R_2$	3.27	9.81	3.51

**Table2: Stability constants of ternary complexes**

L	R	$\beta_{111}$	$\beta_{20}$	$\beta_{02}$	$K_R$	$K_L$	$\Delta\log K$
L <sub>1</sub>	Glycine	6.64	2.81	3.98	2.66	3.83	-0.75
L <sub>1</sub>	DL-Valine	7.79	2.81	3.51	4.28	4.97	-1.16
L <sub>2</sub>	Glycine	8.78	3.69	3.98	4.80	5.09	-1.39
L <sub>2</sub>	DL-Valine	8.12	3.69	3.51	4.61	4.43	-1.49

**Fig-1 Potentiometric titration curve in L<sub>1</sub>R<sub>1</sub>Zn system**

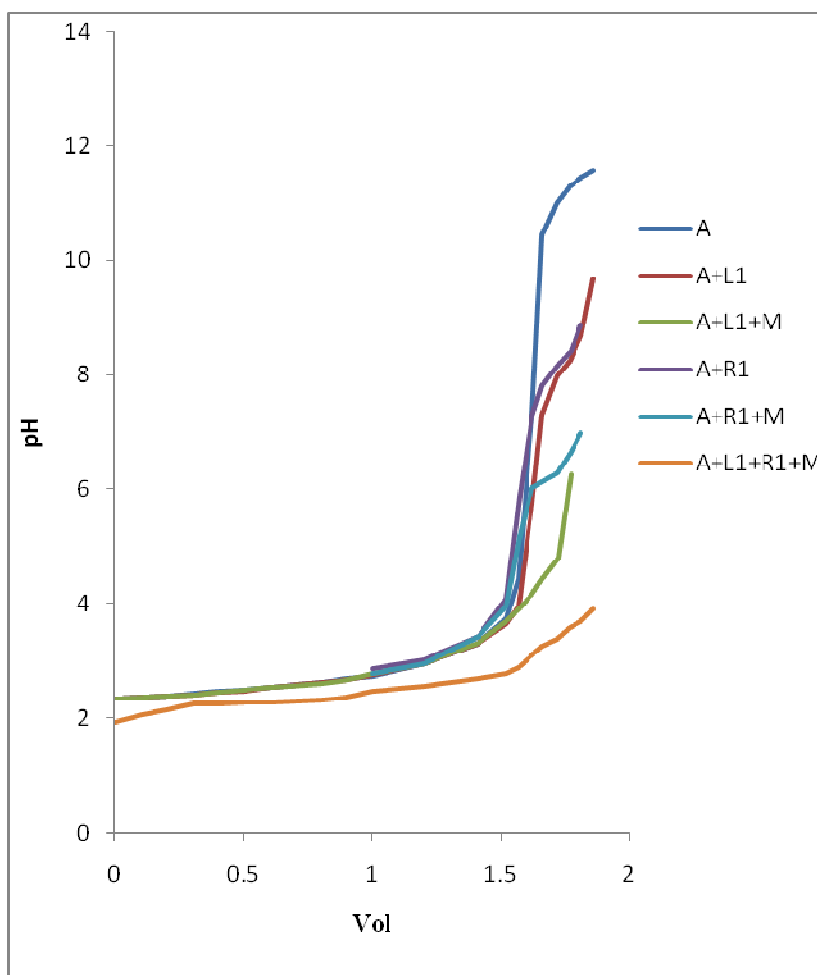
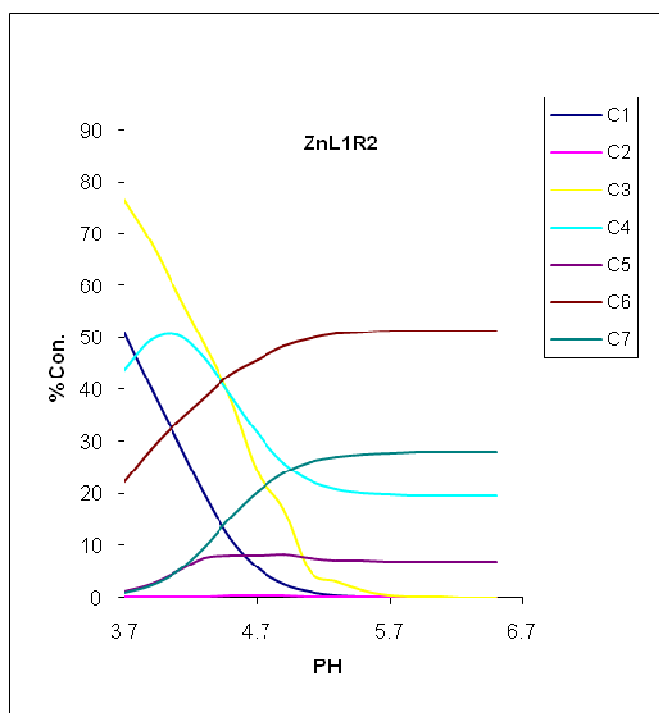
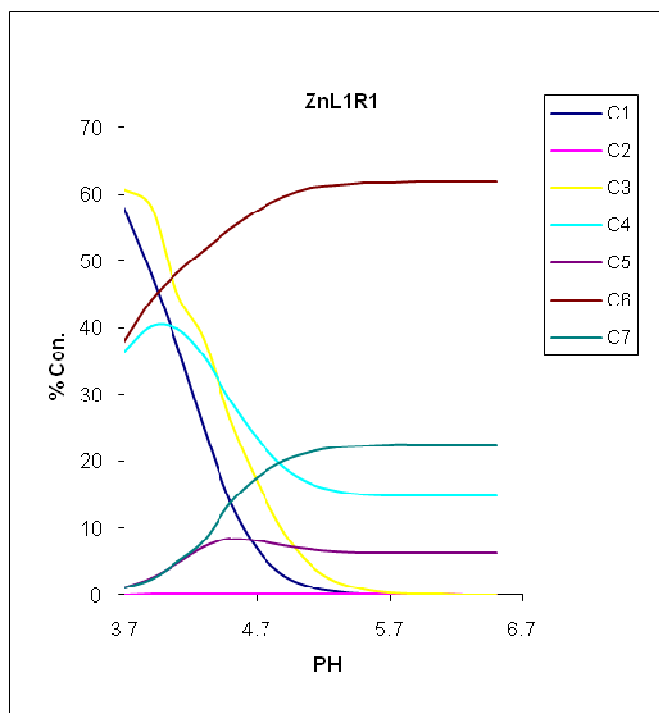


Fig-2 Species distribution diagram for  $L_1R_1Zn$  and  $L_1R_2Zn$



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