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Equilibrium studies on ternary chelates of trivalent chromium metal ion with dipeptides Glycyl –DL-Alanine and Glycyl-γ-Aminobutyric acid as primary ligands and amino acids, leucine and DL-alanine as secondary ligands.

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Abstract: pH-metric equilibrium studies of (1:1:1) ternary chelates of trivalent chromium metal with some dipeptides such as Glycyl –DL-Alanine and Glycyl-γ-Aminobutyric acid as primary ligands and amino acids, such as Leucine and DL-Alanine as secondary ligands have been carried out in 80% (v/v) ethanol water medium at 30^0C and 0.1 M ($NaClO_4$) ionic strength. The formation constants of binary complexes (ML and ML_2) are also determined under similar experimental conditions. The formation constants of ternary complexes MLR are evaluated and their relative stabilities compared to the corresponding binary complexes are expressed in terms of statistical parameters β_{111}, $\beta_{20,}$ β_{02}, K_L, K_R, K_r and ΔlogK. Formation of complex species with respect to pH have been discussed by Irving-Rossotti technique and evaluated by SCOGS computer program.

Keywords- Ternary chelates, formation constants, ΔlogK.,SCOGS.

Introduction

Many of the human body's important hormones are dipeptide[1-5], they have good coordination sites for metal complexation. Although research work on dipeptides have been carried out by many workers[6-8] but no sigficant quantitative studies were made on ternary chelates of dipeptides selected for this study in solution. The present paper reports the pH metric study of the formation and stability of trivalent metal ion ternary chelates, MLR where $M=Cr^{III}$, L_1=Glycyl-DL-Alanine and L_2=Glycyl-γ-aminobutyric acid and R_1=Leucine, R_2 = DL-alanine in 80% (v/v) ethanol-water mixture at 30 ± 0.1^0C and 0.1M ($NaClO_4$) ionic strength.

Experimental

All the reagents used were of A.R. Grade, solutions were prepared in 80% ethanol-water mixture. Dry and distilled ethanol and double distilled water was used for solution preparations. The solutions were standardized by known procedures[13,14]. The pH metric titration of 50ml of acidified solutions were carried out against 0.4 N NaOH solution at 0.1 M ($NaCLO_4$) ionic strength. The proton-ligand and metal-ligand binary formation constants were determined by Irving-Rossotti method[9]. The formation constants and various statistical parameters of ternary complexes were evaluated by using computer program SCOGS[15,16].

Results and discussions

1.1:Binary systems –

The pK values of all the ligands have been determined and are presented in Table No.1. The pK_1 and pK_2 values obtained in both the primary ligands used were assigned to carboxylic and amino groups respectively.

The formation constants of (1:1) ML and (1:2) ML_2[9] binary chelates are determined by analyzing titration curves and experimental data given in Table 1. The stabilities of binary complexes are found to be $ML>ML_2$ as expected on statistical grounds[10]. In Gly-γ-aminobutyric acid, the higher values of metal ligand equilibrium constants are due to the carboxylic and amino groups which binds the metal ions during the course of titration, so two logK values are observed. In case of Glycyl-DL-Alanine only one metal ligand interaction is observed due to carboxylic group but the second metal ligand formation takes place at much higher pH, which cannot be determined by this technique.

1.2:Ternary Systems-

In all the ternary systems, distinct inflections were observed in the titration curves, indicating the formation of chelates. Formation of ternary complexes was further confirmed from the non-superimposible nature of theoretical composite curves on the experimental curve in the region of ternary complex formation. The species distribution curves, as a function of pH were generated using the computer program SCOGS, also supports the formation of ternary chelates. In case of $Cr^{III}L_1R_2$ system. Fig.1. shows that concentration of ternary complex increases from pH 3.8 to 6.0 which confirms the formation of ternary complex. The maximum percentage of formation of ternary chelate is less than formation of $Cr^{III}R_2$ binary complex and greater than $Cr^{III}L_1$ binary complex, this indicates that, the ternary complex is less stable than binary complex of secondary ligand and more stable than binary complex of primary ligand.

Table No. 1: Proton-ligand and metal-ligand stability constants in binary system.

Ligands	**pK_1**	**pK_2**	**$logK_1$**	**$logK_2$**
Glycyl-DL-Alanine	4.31 (3.07)*	8.50 (8.12)*	6.74	-
Glycyl-γ-aminobutyic acid	5.89 (4.22)*	8.50 (8.12)*	12.55	9.51
Leucine	3.79 (2.33)*	10.32 (9.74)*	7.78	4.35
DL-Alanine	3.77 (2.34)*	10.21 (9.87)*	11.74	8.78

(*Indicates literature values)

Fig:1

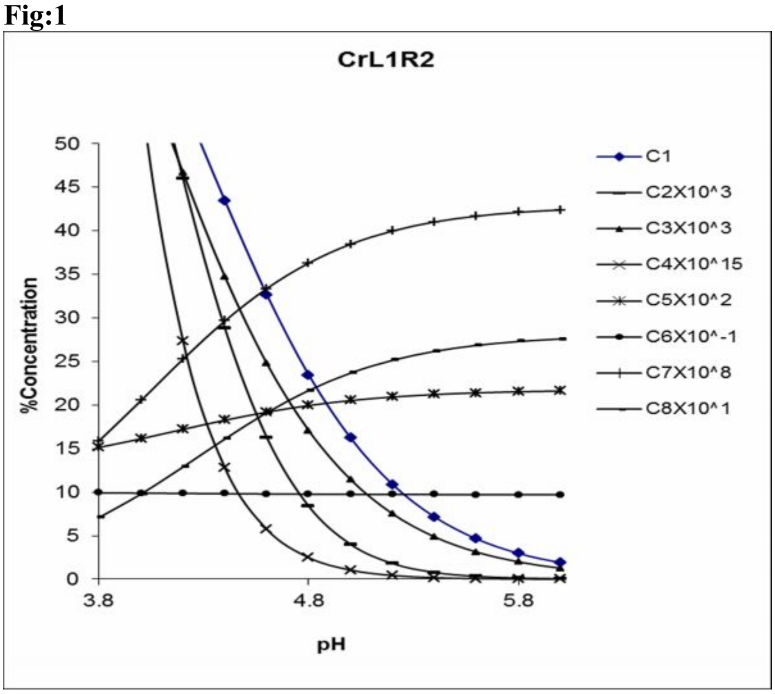
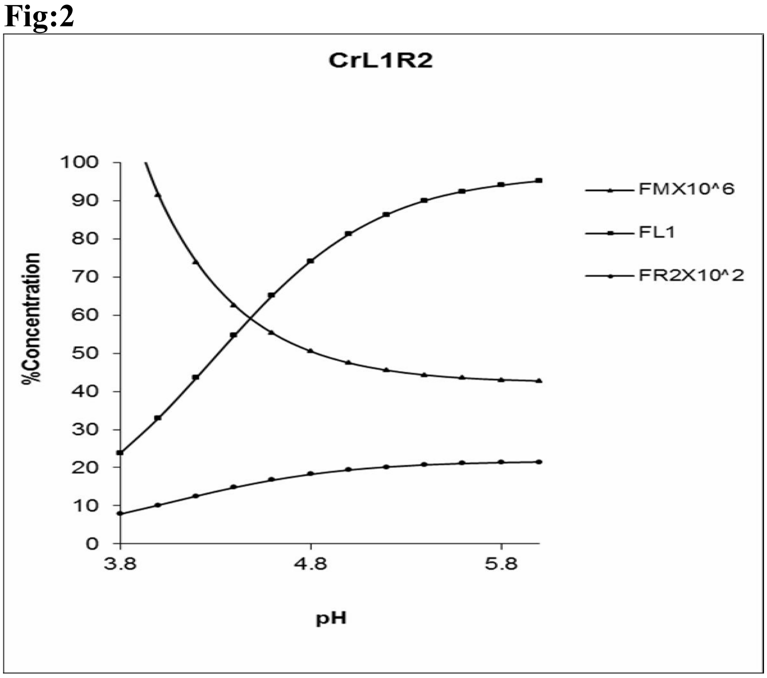


Fig.2. shows that, percentage distribution curve of free metal decreases sharply with increasing pH. This indicate involvement of metal ion in the complex formation process, where as percentage distribution of free ligands FL_1 and FR_2 increases is due to the dissociation of ligands present in the system, as a function of pH.

Fig:2



In case of $Cr^{III}L_2R_1$ system, Fig.3 indicates that, the concentration of ternary complex species continuously increases in the pH range 3.4 to 6.0, which confirms formation of ternary complex. As 1:1 binary complexes are more stable than 1:2 binary complexes, observations proves that ternary complex is less stable than 1:1 binary complex of secondary ligand.

Fig:3

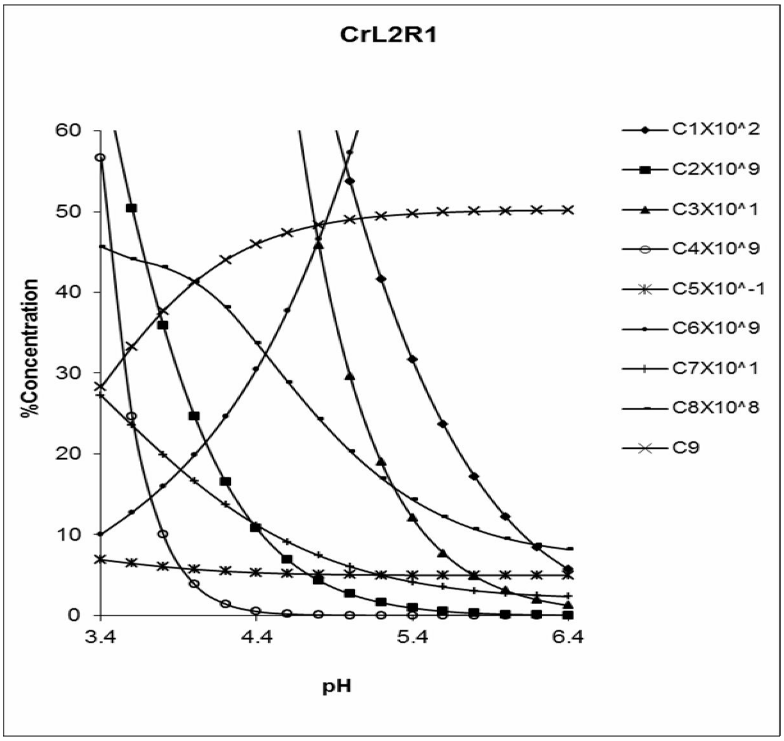


Fig:4

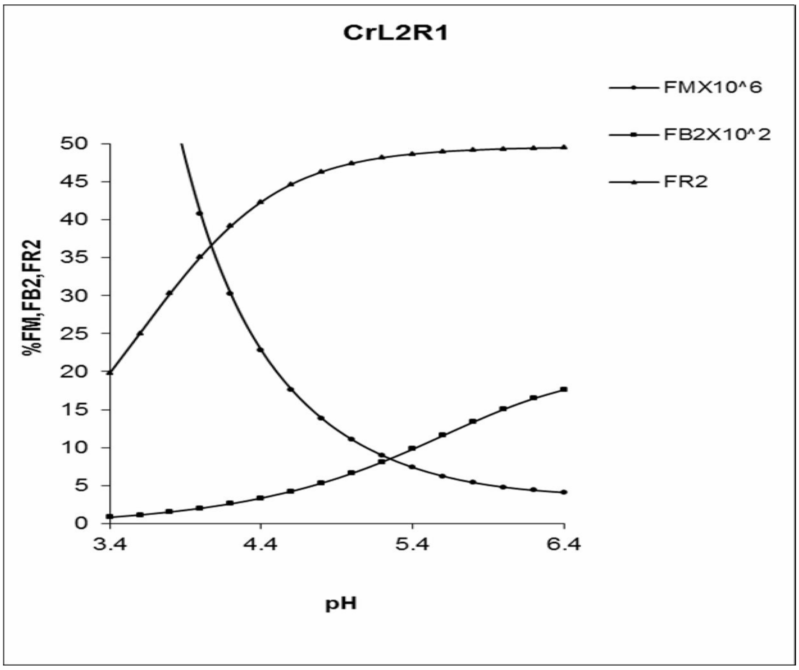


Table No.2: Stability constants of ternary complexes

Ligand	**Amino acids**	β_{111}	β_{20}	β_{02},	K_R,	K_L	K_r	**ΔlogK**
Gly-DL-Alanine	Leucine	13.23	6.74	12.14	6.49	5.45	1.40	-1.29
	Alanine	20.63	6.74	20.52	13.90	8.89	1.51	2.15
Glycyl-γ-aminobutyric acid	Leucine	17.84	22.07	12.14	5.28	10.06	1.04	-2.49
	Alanine	25.34	22.07	20.52	8.68	9.50	0.99	1.05

Percentage distribution curve of free metal (Fig. 4) decreases sharply with increasing pH, whereas free ligand curves increases indicating the dissociation of ligands and involvement of metal ion in the complex formation process. The relative stabilities of the ternary complexes compared to the corresponding binary complexes were characterized in terms of statistical parameter β_{111}, β_{20}, β_{02}, K_L, K_R, K_r and ΔlogK values which are presented in Table No.2. The results shows that ternary complex formation is less favoured over corresponding binary 1:1 complexes. It is possible due to availability of less number of coordination sties for secondary ligands on primary complex ML than on free metal ion[11,12].

Conclusion:

It is observed that, stability constants of ternary complexes are positive in some cases which indicate higher stability of ternary complexes, whereas, negative values indicates that ,the ternary complexes are less stable as compared to binary complexes of the corresponding systems. Various constants like K_L,K_R,K_r and ΔlogK from ternary stability constants are used to explain stability of mixed ligand complexes. Species distribution curves are useful in understanding the exact region of pH in which different

complexation processes takes place. After studying all the systems, it can be concluded that, the correlation between different parameters observed is rather difficult due to diverse nature of ligands used in the present investigations. **ΔlogK** values for maximum systems are negative, this is expected because ternary chelate in a way is similar to 1:2 complex and stability of 1:2 chelate is always less than 1:1 chelate.

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