EFFECT OF IONIC STRENGTH ON STABILITY CONSTANT OF GLYCYL-GLYCINE-RARE EARTH COMPLEXES.

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Stability constants of La(III), Pr(III), Nd(III), Sm(III), Tb(III), Dy(III), Yb(III) with glycyl-glycine has been determined by pH metric technique at different ionic strengths i.e. from 0.075 to 1 M KNO_3 at 27°C.

The metal complexes of amino acids have interested both co-ordination chemists and biochemists for a long time. A literature survey revealed that extensive studies[1] have been made on the complexation of glycyl-glycine with few metal ions of rare earth metals. The present communication describes the determination of successive stability constants of the complexes of glycyl-glycine with various rare earth metal ions at different ionic strengths (0.075, 0.1, 0.25, 0.5, 0.7 and 1.1 M KNO_3) using pH metry [2].

EXPERIMENTAL

N-Glycyl-glycine was obtained from Fluka AG, and all other chemicals used were of AR grade. Solution of N-glycyl-glycine was prepared in hot double distilled water. All other solutions were prepared in double-distilled water. The carbonate free NaOH solution was prepared and standardised [4]. Fresh metal nitrate solutions were prepared from AR grade metal salts and were standardised complexometrically by EDTA titrations. The entire study was carried out in an inert atmosphere of nitrogen and the fresh solutions were used to avoid any effect of ageing and oxidations.

pH measurements were carried out on a digital pH meter model Li-120 (Elico Pvt. Ltd), with glass-calomel assembly in nitrogen atmosphere. The temperature of the cell was maintained by thermostat having accuracy of 29 ± 0.1°C.

Requisite quantity of KNO_3 were added to the solution mixture for maintaining a constant ionic strength. The final volume in all the mixture was made upto 50 ml with double distilled water. For determination of stability constants at 27°C the ratio of metal to ligand was always (1:4). For quantitative determination of complex formation, stoichiometric titrations were performed by solution containing N-glycyl-glycine and metal ion against carbonate free 0.1N sodium hydroxide at different ionic strengths. The experimental method of Irving and Rossotti was applied to determine the values of $\bar{n}$ and pL.

RESULTS AND DISCUSSION

Stoichiometry

The addition of equimolar concentration of metal ion greatly alters the shape of free ligand titration curve (Fig.1) indicating the complex formation, which results in the lowering buffer region

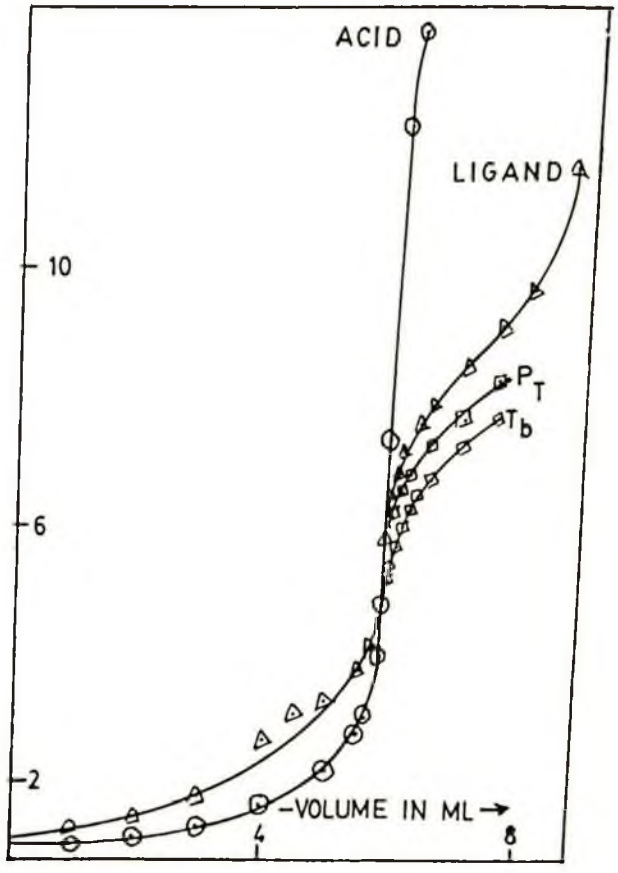


Fig. 1 Titration Curve Glycyl-Glycine

due to proton displacement. Since extent of proton displacement depends upon relative affinity of the ligand for H ions and metal ions, it is obvious from curve that the affinity of M^{3+} ions

TABLE 1

Stability constant values in various media

	0.075 M			0.1 M			0.25 M		0.5 M				0.75 M			1.0 M		
	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K	log K
La	3.42	3.05	3.01	3.31	3.04	-	3.17	2.995	2.97	3.12	3.02	3.02	3.03	2.92	-	2.99	-	-
Pr	3.75	3.23	3.16	3.44	3.16	-	3.42	3.112	3.09	3.37	3.03	3.025	3.32	2.95	-	3.11	-	-
Nd	4.13	3.28	-	3.82	3.32	3.23	3.48	3.22	3.19	3.53	3.14	-	3.48	3.08	-	3.39	-	-
Sm	4.33	3.52	-	4.04	3.36	-	3.92	3.47	3.36	3.81	3.33	3.066	3.52	3.11	-	3.51	3.08	-
Tb	4.58	3.82	-	4.51	3.71	3.51	4.12	3.51	3.47	3.87	3.4	3.35	3.74	3.27	-	3.57	3.12	-
Dy	5.55	4.27	-	5.48	4.12	4.02	4.48	3.725	3.64	4.24	3.51	-	4.14	-	-	3.72	3.17	-
Yb	5.77	4.45	-	5.54	4.23	-	5.45	4.18	4.16	4.69	3.79	-	4.28	3.39	-	4.04	3.49	-

is not great enough to compete with the relatively high concentration of hydrogen ions, upto pH≃ 6 but beyond this pH, the interaction of M^{3+} ions with NGGH is sufficient to compete with a relatively low concentration of hydrogen ions.

When metal ions and ligands are mixed in the ratio 1:2 and 1:1, the inflexion is obtained at M≃2 and 3 respectively. These influences suggests the formation of 1:2 and 1:3 complexes with considerable overlapping.

Stability Constants

Calvin and Melchiors extension of Bjerrums method has been employed for the determination of stability constants of the complexes. The pH titrations of NGGH solutions at ionic strengths of 0.075, 0.1, 0.25, 0.5, 0.75 and 1 M KNO_3 in presence of metal ions are carried out at 27°C against 0.1 N NaOH. The values of log K were determined by the formation curve generally obtained by Bjerrum-Calvin pH titrations techniques. The values of log K_1^H = 8.2 and log K_2^H = 3.0 which are in good agreement with the values reported earlier.

The values of formation constants of the metals reported in the present investigation (Table 1.) have been determined for the first time at 0.075μ, 0.1μ, 0.25μ, 0.5μ, 0.75μ and 1μ. However formation constants for La,Pr, Sm at μ = 0.1 M ($NaClO_4$) have been reported by Saxena et al[1]. It is found that stability increase with decrease in ionic strength. In case of rare earth complexes, the absence of extensive covalent bonding is indicated by the electronic configuration of the cations and also by their large crystal radii ranging from 0.86 to 1.06 A°. The 4f electrons are not available for band formation due to their shielding by 5S and 5P electrons.

REFERENCES

1. R.S. Saxena and S.P. Bansal., *Electrochim. Acta*, 25(12)(1980) 1577-79 (Eng.)

2. H.M. Irving and H.S. Rossotti *J. Chem. Soc.* (1954), 2904.

3. A.I. Vogel, 'Text Book of Quantitative Inorganic Analysis' Third Edition, *Longmans (1961)*.

4. *H.A. Flaschka 'EDTA Titrations' Pergamon Press Inc.*, N.Y. (1959)p. 78.