

Ph-Metric Study of Binary and Ternary Complexes of Innertransition Metals With Carboxylic Acids and Amino Acids

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Abstract: The present work deals with the study of proton - ligands and metal- ligands Constant of Binary and ternary complexes. Where M= Innertransition metals, L= Primary ligands(malic acid, maleic acid and Malonic acid) and secondary ligands B = Glycine have been studied Potentiometrically in biologically relevant conditions. At ionic strength $\mu= 0.1M NaClO_4$. All the ligands forms 1:1:1 ternary complexes, the relative stability of ternary complexes expressed in terms of statistical parameter $\Delta \log k$ and $-\Delta \log k$ values suggest that the formation of ternary complexes are favorable and variation of $\Delta \log k$ has been explained in terms of metal-ligand-n interaction, size of chelate ring, and steric factor.

Key words: pH-metric study, formation constants, binary, ternary complexes.

I. Introduction

The lanthanides are given unique position in the periodic table due to their various chemical and physical characteristics¹. Therefore the study of coordination chemistry of lanthanides has attracted the attention of several workers during last two to three decades. There fore it is considerable interest in the study of binary and ternary complexes of lanthanides by pH- metric methods²⁻⁵.

The study of Kinetic parameter and formation constants of (Mn- antibiotics cefoperazone) complexes Vis-à-vis Kinetics of electrode reaction have been investigated by Farid Khan & Rakhi Agrawal⁶ The study of formation constants of metal-methionine and metal-methionine NTA (Nitrilotriacetic acid) (binary and mixed) Complexes have been investigated by Praveen P.Singh et al.⁷

Siddiqui et al⁸⁻⁹ studied the complexes of lanthanide ion with drug molecule like barbituric acid derivatives and suggested the ionic character of metal ligand bonds in the complexes. Nahendram et al¹⁰. Also suggest that the ionic nature of metal ligand bond in complexes of lanthanides with 2-hydroxy methyl benzimidazole, among the numerous selective and specific complexing agents, the biologically active ligands like drug molecules have special importance in the formation of lanthanidecomplexes.

A search through the literature has revealed that there is no systematic study on stability constant of binary and ternary complexes of these metal ions with ligands have studied using Irving Rossotti pH- metric titration techniques in aqueous medium in the present work.

II. Experimental

All the ligands was obtained from AR grade. $NaClO_4$ was used from fluka chemical. NaOH was standardized by standard KHP from AR grade¹². All other Solution was prepared in doubly distilled water. The pH-metry measurement work carried out by using ELICO digital model LI – 120 pH-meter with glass calomel electrode with an accuracy of ± 0.01 of pH unit at $25\pm 0.1^\circ C$ was standardized against 0.05M KHP (4 pH) 0.01M borax solution (9.18 pH) for the determination of proton–ligand stability constant of the secondary ligands and metal-ligands stability constants of the binary and ternary complexes the following sets of solution were prepared and titrated against stand. Alkali solution.

Binary System

- $2 \times 10^{-1} M HClO_4$
- $a + 1 \times 10^{-2} M$ primary ligands.
- $a+b + 1 \times 10^{-2} M$ metal ions.
- $a + 1 \times 10^{-2} M$ secondary ligands.
- $d + 1 \times 10^{-2} M$ metal ions.
- $b + 1 \times 10^{-2} M$ secondary ligands + $1 \times 10^{-2} M$ metal ions.

The ionic strength of above solution was mentioned at 0.1 M constant by adding of (1M) $NaClO_4$.and total volume of solution was made 50ml.

III. Results And Discussion

Stability constants of these ligands are determined by Irving- Rossotti techniques¹¹ at constant temperature 25±0.1°C in 60% ethanol-water medium.

Proton ligand and metal ligand stability constant of primary ligands with lanthanides are calculated by Irving-Rossotti titration method and represented in table-1. Primary ligand forms 1:1 and 1:2 complexes with lanthanides in the pH range. Stability constant of bivalent metal complexes derived from similar type of ligands. The deviations of (acid +ligand) curve from (acid +ligand +metal ion) curve along volume axis indicate the formation of complex species shown in fig.1. and it lies in the pH- region, where hydrolysis is not expected. Metal ligand stability constant of primary and secondary ligand are given in table -2.

Table I: PROTON – LIGAND STABILITY CONSTANTS.
Temperature = 25±0.1°C. (μ=0.1M NaClO₄)

Ligand	log K ₁ ^H	log K ₂ ^H
Malonic acid	9.519	11.360
Malic acid	8.828	11.873
Maleic acid	8.550	11.934

The stability constant of bivalent metal complexes derived from similar type of ligands generally follow Irving-Rossotti techniques and present complexes follow the order of stability as.



Tb > Eu > Sm > Nd > Gd > Pr > Ce > La.

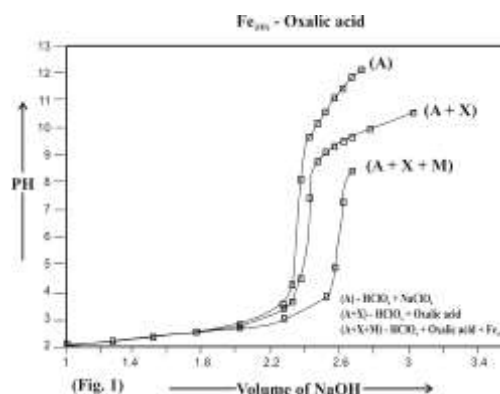
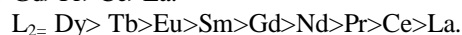


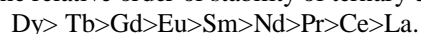
TABLE – 2: METAL – LIGAND STABILITY CONSTANTS:

Metal	Stability Constant	Ligands				
		Glycine	Alanine	Malic acid	Maleic acid	Malonic acid
La _(III)	log K ₁ ^M	5.32	5.30	5.47	6.30	5.34
Ce _(III)	log K ₁ ^M	5.40	5.42	5.76	6.61	5.72
Pr _(III)	log K ₁ ^M	5.54	5.56	6.18	6.62	5.92
Nd _(III)	log K ₁ ^M	5.64	5.66	6.75	6.78	6.01
Sm _(III)	log K ₁ ^M	5.75	5.76	6.77	6.84	6.12
Eu _(III)	log K ₁ ^M	5.80	5.82	6.82	6.98	6.10
Gd _(III)	log K ₁ ^M	5.72	5.70	6.72	6.80	5.94
Tb _(III)	log K ₁ ^M	5.92	5.93	6.92	7.10	6.26
Dy _(III)	log K ₁ ^M	6.10	6.08	7.20	7.22	6.32

Formation of Ternary Complexes:-

The formation equilibria of mixed ligand complexes with the ligands and lanthanides are 1:1:1 ternary complexes and these are formed by simultaneous equilibrium. The preferential formation of ternary complexes over binary complexes has been discussed in terms of equilibrium constants and on the basis of speciation curves and percentage concentration species F_M, F_L and F_B, and stability constant of ternary complexes are calculated by using SCOG computer program and values are given in table -3.

The relative order of stability of ternary complexes in terms of the metal ions as found in this work are



Which may be attributed to decreasing size and increasing charge / radius ratio of metal ions.

Formation constant of the complexes were calculated by using the SCOGS computer programme¹². Estimate of some of the binary constant were obtained by the method of Irving and Rossotti's. overall constant B₀₂, B₂₀, B₁₁

were obtained as computer out puts, from which the other constants were calculated using the appropriate reactions.

TABLE – 3: STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES:

Metal ion	Mixed ligand system	$\log K_{MXY}$	$\Delta \log K$
La _(III)	Glycine – Malic acid	9.226	1.564
	Glycine – Maleic acid	13.942	-2.322
	Glycine – Malonic acid	13.017	-2.357
Ce _(III)	Glycine – Malic acid	9.463	1.697
	Glycine – Maleic acid	14.181	-2.171
	Glycine – Malonic acid	15.585	-2.690
Pr _(III)	Glycine – Malic acid	10.030	1.690
	Glycine – Maleic acid	14.245	-2.085
	Glycine – Malonic acid	14.155	-2.695
Nd _(III)	Glycine – Malic acid	09.084	3.306
	Glycine – Maleic acid	15.175	-2.755
	Glycine – Malonic acid	14.816	-2.505
Sm _(III)	Glycine – Malic acid	9.848	2.672
	Glycine – Maleic acid	15.530	-4.465
	Glycine – Malonic acid	14.937	-3.067

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