



pH – Metric Studies in Binary and Ternary Complexes of Dicarboxylic Acids and Amino Acids with some Transition and Inner Transition Metal Ions

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ABSTRACT

The present work deals with the study of proton - ligands and metal- ligands of tartaric acid, Adipic acid , Glutaric acid and β -Amino propionic acid(APA) with Mn(II), Cu(II), Fe(III), Ni(II) and UO₂(II). More over the Binary chelates of carboxylic acids and amino acids have been studied with Lanthanides. The metal ligand stability constant of Binary and Ternary complexes were evaluated using Irving–Rossotti titration technique.

Key words : pH-metry , binary, ternary, Stability constants, Cu(II), Mn(II), Fe(III), Ni(II) and UO₂(II), complexes.

INTRODUCTION

Recently pH metric studies on formation constant of complexes of substituted pyrazoles with some lanthanide metal ions and the influence of ionic strengths on complex equilibria in 70% Dioxane-water mix.¹ There has been considerable interest in the study of binary ternary and quaternary complexes by pH – metric method²⁻⁵. The metal ligand stability constants of pr(III) and Nd(III) ion complexes with some substituted pyrazoles have been reported⁶References indicate that the metal ligand stability constants and proton ligand stability constants of Cu(II) salicylic acid complex have been studied⁷Formation constants & thermodynamic parameters of bivalent metal ion complexes with 3-amino 5-methyl isoxazole Schiff bases have been reported⁸

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 etal.⁹

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 Agrawal¹⁰

The mixed ligand complexes of transition metals are comparatively less studied than inner transition elements¹¹. Ternary complexes of Ni_(II) with glycine and glycineamide as primary ligands and imidazole, histamine and L – histidine as secondary ligands have been investigated by Nair and Neelkantan¹², Nair et al¹³.

The ternary complexes of Ni_(II) and Cu_(II) with Nicotinic acid as primary ligand and imidazole, benzimidazole, histamine and L – histidine as secondary ligands have been studied potentiometrically¹⁴.

The study of stability constant of Mn_(II), Co_(II), Ni_(II), Cu_(II) and Zn_(II) with nitrilotriacetic acid (NTA) and imino_diacetic acid (IMDA) as primary ligands and pyridoxine hydrochloride (PHC) and ethambutol hydrochloride (EHC) as secondary ligands was reported by Patil etal¹¹.

The stability constants of Mn_(II), Cu_(II), Ni_(II), Fe_(III) and UO₂ have not reported in literature. It was therefore of interest to study the stability constant of binary and ternary complexes of these metal ions with ligands have studied using Irving–Rossotti pH – metric titration technique in aqueous medium in the present work.

EXPERIMENTAL SECTION

All the ligands was obtained from AR grade. NaClO₄ was used from fluka chemical. NaOH was standardized by standard KHP from AR grade. All other Solution were 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 $30 \pm 0.5^\circ\text{C}$ 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

- 1] 2×10^{-1} M HClO₄
- 2] 2×10^{-1} M HClO₄ + 1×10^{-2} M secondary ligands.
- 3] 2×10^{-1} M HClO₄ + 1×10^{-2} M secondary ligands + 1×10^{-2} M metal ions.

Ternary System

- 1] 2×10^{-1} M HClO₄
- 2] 2×10^{-1} M HClO₄ + 1×10^{-2} M secondary ligands.
- 3] 2×10^{-1} M HClO₄ + 1×10^{-2} M primary ligands + 1×10^{-2} M metal ions.
- 4] 2×10^{-1} M HClO₄ + 1×10^{-2} M primary ligands + 1×10^{-2} M secondary ligands + 1×10^{-2} M metal ions.

The ionic strength was mentioned constant by adding of (1M) NaClO₄.

The ratio of metal (M) : Secondary ligand (L) was maintained at 1 : 5 in each of the Binary system and ratio of metal : Primary ligands (A) : Secondary ligand (L) was maintained at 1 : 5 : 5 in each of the ternary systems.

RESULTS AND DISCUSSION

Proton–Ligand stability constants.

The plots of volume of alkali (NaOH) against pH – meter readings were used to evaluate the proton–ligand stability constants of Glutaric acid and Adipic acid. The deviation between free acid titration curve & secondary ligand titration curve was used to evaluate the formation functions \bar{n}_A .

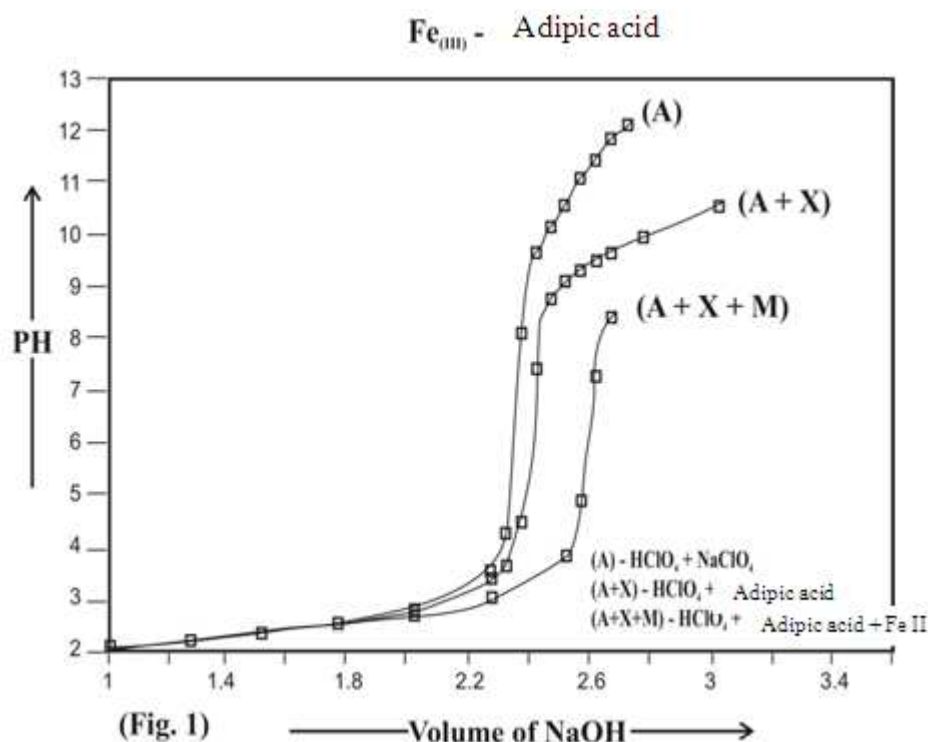
The proton–ligand formation curves were then obtained by plotting the values of \bar{n}_A Vs pH-meter readings. From the graphs the values of $\log K_1^H$ and $\log K_2^H$ were evaluated by half-integral method and pointwise calculation method and presented in Table – 1.

Table I Proton – ligand stability constants
Temperature = $30 \pm 0.5^\circ\text{C}$. ($\mu=0.1\text{M NaClO}_4$)

Ligands	$\log K_1^H$	$\log K_2^H$
Glutaric acid	9.220	11.232
Adipic acid	8.523	11.464
Tartaric acid	8.400	11.743

Metal – Ligand stability constants of Binary complexes.

The metal ligand stability constants of binary complexes were evaluated assuming that the formation of hydrolysed products, polynuclear complexes, hydrogen and hydroxyl bearing complexes were absent. An examination of titration curves indicated that ternary complex formation has taken place in solution on the following grounds.



1]The metal titration curves showed displacement with respect to the ligand titration curves along the volume axis. This indicated the affinity of ligand with metal ions which released Protons and produced the volume difference ($V_3 - V_2$).

2]The colour change of the ligand was in presence of metal ions appeared showing the formation of new species.

3]The hydrolysis of metal ions was suppressed due to complex formation and the precipitation did not appear during the titrations.

From the ligand and metal titration curves the values of \bar{n} and from that the values of PL were obtained. The formation curves obtained were used to evaluate the metal. Ligand stability constants by methods are presented in Table-II.

The variation of \bar{n} was found to be 0 to 2 which indicated that the composition of complexes was 1:5 in solution from table - II, it is obvious that the metal – ligand stability constants of Glutaric acid were greater than with respect to Adipic acid in every metal. The Irving – Williams order of stability constants was followed by both ligands.

Table – II Metal – ligand stability constants of binary complexes.

Ligand	Stability constant $\log K_1^M$				
	$\text{Fe}_{(III)}$	$\text{UO}_{2(II)}$	$\text{Ni}_{(II)}$	$\text{Cu}_{(II)}$	$\text{Mn}_{(II)}$
Glutaric acid	7.325	7.482	11.432	3.320	9.121
Adipic acid	7.229	7.424	11.430	3.325	9.129
Tartaric acid	7.924	4.212	7.922	4.534	6.362

Metal – ligand stability constants of ternary complexes.

The metal ligand stability constants of the ternary complexes were evaluated assuming that the formation of hydroxyl products, Poly nuclear complexes hydrogen and hydroxyl bearing complexes was absent. An examination of the titration curves indicated that ternary complex formation has taken place in solution on the following grounds.

1]The ternary complex titration curves show displacement with primary complex titration curves. The horizontal distance was measured between acid curves and the secondary ligand curves ($V_2 - V_1$) and subtracted through the horizontal distance between ternary complex curves and primary complex titration curves ($V_3 - V_2$) show a positive difference which proves the earlier release of protons in the formation of ternary complexes.

2]The hydrolysis of metal ions was suppressed and precipitation did not occur.

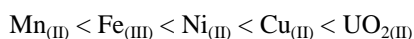
The values of \bar{n} vary from 0 to 1, thus confirming the formation of 1 : 5 : 5 mixed ligand complexes.

The values of $\log K_{Tartaric\ Acid}^{APA}$ and $\log K_{Adipic\ Acid}^{APA}$ (\bar{n} Vs PL). At $\bar{n} = 0.5$ in the formation curve, $PL = \log K$. The $\log K$ values were also evaluated by pointwise calculation method. The metal – ligand stability constant of Tartaric acid and Adipic acid as secondary ligands and β – Aminopropionic acid as primary ligands are presented in Table – 3.

TABLE – 3 Metal – ligand stability constants

Metal	Stability Constant	Ligands			
		β - Amino propionic acid(APA)	Tartaric acid	Adipic acid	Glutaric acid
La _(III)	$\log K_1^M$	5.30	5.47	5.26	5.22
Ce _(III)	$\log K_1^M$	5.45	5.76	5.38	5.28
Pr _(III)	$\log K_1^M$	5.48	6.18	5.49	5.34
Nd _(III)	$\log K_1^M$	5.56	6.72	5.57	5.49
Sm _(III)	$\log K_1^M$	5.68	6.77	5.68	5.57
Eu _(III)	$\log K_1^M$	5.72	6.80	5.79	5.68
Gd _(III)	$\log K_1^M$	5.80	6.90	5.67	5.76
Tb _(III)	$\log K_1^M$	5.88	6.96	5.88	5.90
Dy _(III)	$\log K_1^M$	5.98	7.02	5.99	6.22

The Irving Williams – natural order was observed in case of binary as well as ternary complexes which is.



The aim of the study was to know the effects of binary and ternary ligands on metal complexes. Glutaric acid and Adipic acid are the efficient chelating agents for heavy metals & β - Aminopropionic acid(APA) is functions as antidote against heavy metals ions by forming stable co-ordination compounds. The higher protonation values ($\log K_1^H$) was assigned to the –OH group.

β - Aminopropionic acid(APA) are ligands of novel type bearing –NH₂ and –COOH groups. However, pH titration curves of this ligand show two well separated steps of neutralisation and hence two protonation constants are calculated. The ionization of β - Aminopropionic acid(APA) may be represented by the following equations :

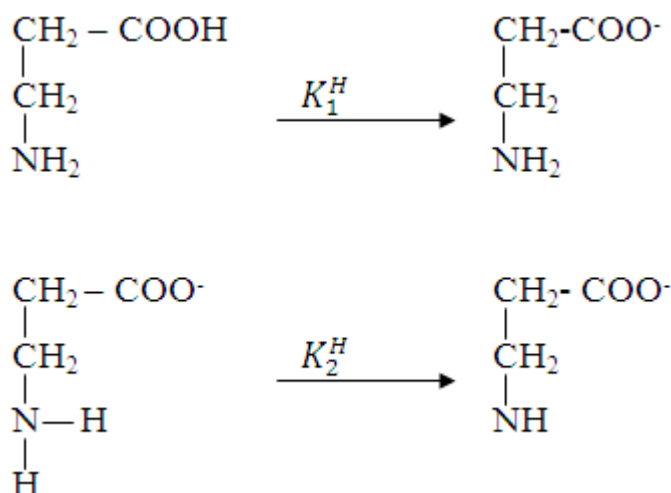


TABLE – 4 Stability constants of mixed ligand complexes

Metal ion	Mixed ligand system	$\log K_{MXY}$	$\Delta \log K$
La _(III)	APA – Tartaric acid	8.876	1.423
	APA – Adipic acid	12.828	-2.200
	APA – Glutaric acid	12.210	-2.261
Ce _(III)	APA – Tartaric acid	9.121	1.582
	APA – Adipic acid	13.892	-2.022
	APA – Glutaric acid	14.492	-2.498
Pr _(III)	APA – Tartaric acid	9.828	1.594
	APA – Adipic acid	13.834	-2.020
	APA – Glutaric acid	13.988	-2.568
Nd _(III)	APA – Tartaric acid	8.980	3.126
	APA – Adipic acid	14.100	-2.642
	APA – Glutaric acid	13.889	-2.424
Sm _(III)	APA – Tartaric acid	8.879	2.584
	APA – Adipic acid	14.430	-4.388
	APA – Glutaric acid	14.464	-3.092
Eu _(III)	APA – Tartaric acid	8.108	3.468
	APA – Adipic acid	14.134	-2.288
	APA – Glutaric acid	14.982	-3.112

The proton Ligand stability constants determined in this work were used through out the calculations of Metal – ligand stability constants as the latter were determined in an identical experimental conditions to those for the former ones. The $\log K_1^M$ values are discussed at the appropriate place.

The present investigation was undertaken with a view to studying the stability constants of mixed ligand complexes of the present ligand with rare earth metal ion by maintaining Metal : Primary ligand : Secondary ligand ratio as 1 : 5 : 5 ($M \neq X = Y$). The stability constants of the mixed ligand Complexes have been computed by adopting an appropriate method proposed for such a condition.

The relative order of stability of ternary chelates in terms of the metal ions as found in this work is



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

It is an important observation in the present work that the calculation of $\log K_{MXY}$

- in the slightly lower pH range ($= \log K'_{MXY}$)
- in the slightly higher pH range ($= \log K''_{MXY}$)
- in the middle (chosen) pH range ($= \log K_{MXY}$) that

$$\log K_{\text{MXY}} = \frac{\log K'_{\text{MXY}} + \log K''_{\text{MXY}}}{2}$$

This method proved to be an additional check on the selection of the pH range chosen for calculating an accurate stability constant of a mixed ligand complex species.

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