

DETERMINATION OF FORMATION CONSTANT OF ACIDS AND AMINO ACIDS WITH TRANSITION AND INNER TRANSITION METALS BY PH-METRY

Suresh D. Dhage

Department of Chemistry, SSJES, Arts, Commerce & Science College,

Gangakhed-431514 Dist. Parbhani. (M.S.)

E-mail: dhage137@gmail.com

Abstract : The present work deals with the study of proton - ligands and metal- ligands of malic acid, maleic acid and Glycine with Mn(II), Cu(II), Fe(III), Ni(II) and UO₂(II). More over the Binary chelate of carboxylic acids and amino acids have been studied with Lanthanides. The metal ligands stability constant of Binary and ternary complexes were evaluated using Irving–Rossotti titration technique.

Keywords : pH-metry, determination, binary, ternary, formation constants, Cu(II), Mn(II), Fe(III), Ni(II) and UO₂(II), complexes.

I. INTRODUCTION

Recently there has been considerable interest in the study of binary ternary and quaternary complexes by pH – metric method¹⁻⁴. 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.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 mixed ligand complexes of transition metals are comparatively less studied than inner transition elements⁷. 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 Neelkantan⁹, Nair et al¹⁰. 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 potentiometrically⁸. The study of stability constants of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with nitrilotriacetic acid (NTA) and iminodiacetic acid (IMDA) as primary ligands and pyridoxine hydrochloride (PHC) and ethambutol hydrochloride (EHC) as secondary ligands was reported by Patil et al⁷ 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.

II. EXPERIMENTAL

All the ligands was obtained from AR grade. NaClO₄ was used from fluka chemical. NaOH was standardized by standard KHP from AR grade¹². 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 ± 0.5°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.

III. RESULT 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 malonic acid and oxalic 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.

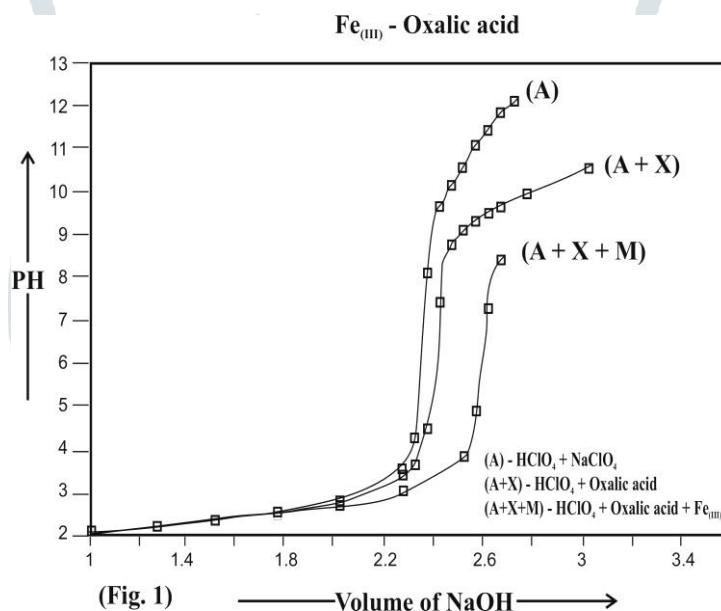
From the graphs the values of $\log K_1^H$ and $\log K_2^H$ were evaluated by half-integral method and pointwise calculation method and presented in Table – 1.

Table I
PROTON – LIGAND STABILITY CONSTANTS.
Temperature = $30 \pm 0.5^\circ\text{C}$. ($\mu=0.1\text{M NaClO}_4$)

Ligands	$\log K_1^H$	$\log K_2^H$
Malonic acid	9.519	11.360
Malic acid	8.828	11.873
Maleic acid	8.550	11.934

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 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 Malonic acid were greater than with respect to oxalic acid in every metal. The Irving – Williams order^{13,14} of stability constants was followed by both ligands.

Table – II
METAL – LIGAND STABILITY CONSTANTS OF BINARY COMPLEXES.

Ligand	Stability constant $\log K_1^M$				
	Fe(III)	UO ₂ (II)	Ni(II)	Cu(II)	Mn(II)
Malonic acid	7.455	7.589	12.552	3.361	9.250
Malic acid	8.083	4.200	8.099	4.628	6.472
Maleic acid	5.151	5.264	6.081	4.892	6.386

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, Polynuclear 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 \bar{n} and $\log K$ have been evaluated from the formation curves (\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 maleic acid and Malic acid as secondary ligands and Glycine as primary ligands are presented in Table – 3.

TABLE – 4
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

The Irving Williams – natural order^{13, 14} was observed in case of binary as well as ternary complexes which is.
Mn(II) < Fe(III) < Ni(II) < Cu(II) < UO₂(II)

The aim of the study was to know the effects of binary and ternary ligands on metal complexes. Malonic acid and oxalic acid are the efficient chelating agents for heavy metals & Glycine 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.

Glycine and Alanine 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 Glycine and Alanine may be represented by the following equations:

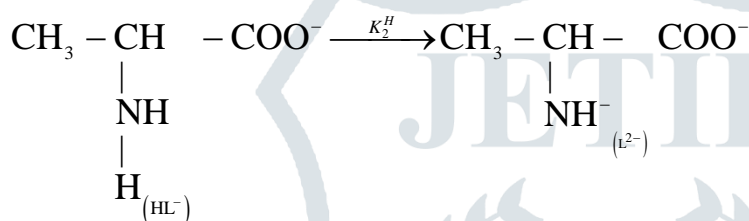
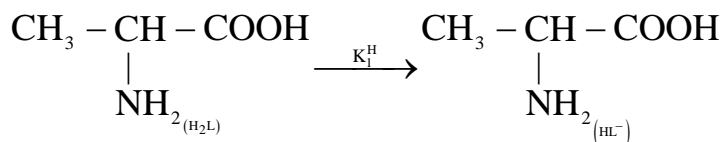
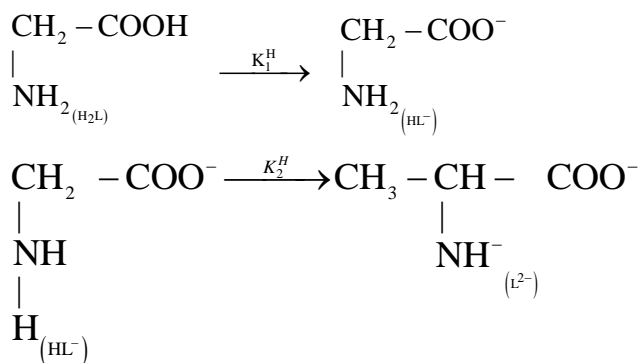


Table 4
STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES

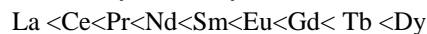
Metal ion	Mixed ligand system	$\log K_{\text{MXY}}$	$\Delta \log K$
La(III)	Glycine – Malic acid	9.226	1.564
	Glycine – Maleic acid	13.942	-2.322
	Glycine – Malonic acid	13.017	-2.357
Ce(III)	Glycine – Malic acid	9.463	1.697
	Glycine – Maleic acid	14.181	-2.171
	Glycine – Malonic acid	15.585	-2.690
Pr(III)	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

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

$\log K_{\text{MXY}}$

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

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

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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