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Potentiometric Determination of Stability Constant of Transition and Inner Transition Metals Complexes of Some Acids

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The present work deals with the study of proton-ligands and metal ligands of oxalic acid, malonic acid, malic acid, maleic acid, glycine and alanine with Mn(II), Cu(II), Fe(III), Ni(II), La(III), Ce(III) and UO_2(II). The metal ligands stability constant of binary and ternary complexes were evaluated using Irving-Rossotti titration technique.

Key Words: Potentiometric, Determination, Binary, Ternary, Formation constants, Cu(II), Mn(II), Fe(III), Ni(II), La(III), Ce(III) and UO_2(II), Complexes.

INTRODUCTION

Recently, there has been considerable interest in the study of binary, ternary and quaternary complexes by pH-metric method[1-4]. The mixed ligand complexes of transition metals are comparatively less studied than inner transition elements[5]. Ternary complexes of Ni(II) with glycine and glycinamide as primary ligands and imidazole, histamine and L-histidine as secondary ligands have been investigated by Nair and Neelkantan[6-8]. 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 potentiometrically[8].

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 al.*[5].

The stability constants of Mn(II), Cu(II), Ni(II), Fe(III), La(III), Ce(III) and UO_2(II) complexes of some amino acid and carboxylic acid 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 some amino acid and carboxylic acid have studied using Irving-Rossotti pH-metric titration technique in aqueous medium in the present work.

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EXPERIMENTAL

All the ligands were obtained from AR grade. $NaClO_4$ was used from fluka chemical. Sodium hydroxide was standardized by standard potassium hydrogen phosphate from AR grade[10]. 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 ºC was standardized against 0.05 M potassium hydrogen phosphate. Borax solution (0.01 M, pH 9.18) 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 solutions were prepared and titrated against standard alkali solution.

Binary system:

(1) 2×10^{-1} M $HClO_4$

(2) 2×10^{-1} M $HClO_4$ + 1×10^{-2} M secondary ligands.

(3) 2×10^{-1} M $HClO_4$ + 1×10^{-2} M secondary ligands + 1×10^{-2} M metal ions.

Ternary system:

(1) 2×10^{-1} M $HClO_4$

(2) 2×10^{-1} M $HClO_4$ + 1×10^{-2} M secondary ligands.

(3) 2×10^{-1} M $HClO_4$ + 1×10^{-2} M primary ligands + 1×10^{-2} M metal ions.

(4) 2×10^{-1} M $HClO_4$ + 1×10^{-2} M primary ligands + 1×10^{-2} M secondary ligands + 1×10^{-2} M metal ions.

The ionic strength was maintained constant by adding of (1 M) $NaClO_4$.

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 (Fig. 1) were used to evaluate the proton-ligand stability constants of malic acid and maleic acid. The deviation between free acid titration curve and 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 (Fig. 1) 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-1
PROTON-LIGAND STABILITY CONSTANTS
TEMPERATURE = 30 ± 0.5 ºC

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

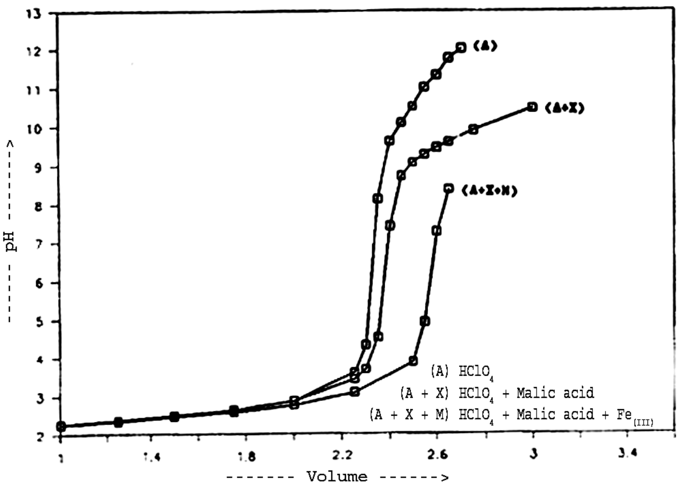

Fig. 1. Plots of alkali (NaOH) against pH-meter readings

Metal-ligand stability constants of binary complexes: The metal ligand stability constants of binary complexes were evaluated by considering that the formation of hydrolyzed 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 P_L were obtained. The formation curves obtained were used to evaluate the metal. Ligand stability constants by methods are presented in Table-2.

TABLE-2
METAL-LIGAND STABILITY CONSTANTS OF BINARY COMPLEXES

Ligands	Stability constant $\log K_1^M$				
	Fe(III)	UO_2(II)	Ni(II)	Cu(II)	Mn(II)
Malic acid	8.083	4.200	8.099	4.628	6.472
Maleic acid	5.151	5.264	6.081	4.892	6.386

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-2, it is obvious that the metal-ligand stability constants of malic acid were greater than with repect to maleic acid in every metal. The Irving-Williams order[11,12] of stability constants was followed by both ligands.

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 $\log_{\text{Malic}}^{\text{Glycine}}$ and $\log_{\text{Maleic}}^{\text{Glycine}}$ have been evaluated from the formation curves ($\bar{n}$ *vs.* PL). At $\bar{n}$ = 0.5 in the formation curve, P_L = log K. The log K values were also evaluated by pointwise calculation method. The metal-ligand stability constant of malic acid and maleic acid as secondary ligands and glycine as primary ligands are presented in Table-3.

TABLE-3
METAL-LIGAND STABILITY CONSTANTS OF TERNARY COMPLEXES

Metal	Stability constant	Ligands		
		Glycine	Malic acid	Maleic acid
La(III)	$\log K_1^M$	5.32	5.47	6.30
Ce(III)	$\log K_1^M$	5.40	5.78	6.61

The Irving Williams-natural order[11,12] was observed in case of binary as well as ternary complexes which is:

$$Mn(II) < Fe(III) < Ni(II) < Cu(II) < UO_2(II)$$

The aim of the study was to know the effects of binary and ternary ligands on metal complexes. Malic acid has been shown to be useful as analytical reagent because of its reducing and complexing properties. The higher protonation values ($\log K_1^H$) were assigned to the - OH group.

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 study the stability constants of mixed ligand complexes of the present ligand with transition and inner transition metal ion by maintaining metal:primary ligand:secondary ligand ratio as 1:5:5 (M ≠ X = Y). The stability constants of the mixed ligand complexes have been computed by adopting an appropriate method proposed for such a condition.

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