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Analysis of metal-ligand stability constants at 0.1m ionic strength

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Abstract
pK values of Methyl-1-phenyl-3-(2'-hydroxy aryl) pyrazole-5-carboxylate. [MPHAPC] in 70% ethanol-water mixtures and log K values of alkaline earth metal (Sr) and rare earth metals (Pr, Nd, Tb) chelates has been investigated pH metrically. It showed the formation of 1:1 and 1:2 complexes in the pH range 2.5 to 5.5.

Keywords: metal-ligand

Introduction
Yamuna *et al*. [1–5] have studied the vital complexes of dithiocarbamates and determined the proton-ligand stability constants below pH 11.00. Kabadi *et al*, [1] Jahagirdar [3] have determined the pK values of salicylaldehyde, salicyclic acid, sulphonic acid and coumarins respectively. Hiremath *et al*. [6] have investigated the metal ligand stability constants of Co(II), Ni(II) and Cu(II) metal ions with substituted amino 1, 3, 4-thiadiazoles. Synthesis and characterization study of lanthanide complexes with 2-acetyl amino thiazoline have been done spectro-photometrically by Singh *et al*. [7]. Complex study of transition metal ions with Schiff bases has been done by Pokhariyal and Singh [8]. Athappan *et al*., has synthesized the complexes of transition metal ions with substituted triazine and determined their physical properties. Sawalakhe [7] have studied the metal-ligand stability constants with some substituted pyrazoles, pyrazolines and diketones. Similar type of work have been done by Kadu [8]. But the study of complexes between Sr(II), Pr(III), Nd(II), Tb(III) and MPHAPC was still lacking. So the following work has been undertaken to determine metal-ligand stability constants at 0.1 m ionic strength.

Material and Methods
Potentiometric measurement involved potentiometric titrations of solution of:
a) Nitric acid (1.00×10^{-2}M)
b) Nitric acid (1.00×10^{-2}M) and the ligand (20.002×10^{-4} M)
c) Nitric acid (1.00×10^{-2}M), the ligand (20.00×10^{-4} M) and the metal salt (4.00×10^{-4} M).

Against standard carbonate free sodium hydroxide solution (0.193 to 0.201 N) carried out in 70% ethanol-water mixture. Titrations were carried out in inert atmosphere by bubbling nitrogen gas. Ionic strength of solution was maintained constant at 0.1 M by adding an appropriate amount of 1 M KNO_3 solution. All the pH measurement and titrations were carried out with ELICO-LI-10 pH meter (accuracy ± 0.05 units) with a glass and calomel electrode assembly. The instrument could read pH in the range 0-14.0 in the steps of 0.01. This pH meter has a built in internal electronic voltage stabilizer for ± 10% fluctuations in voltage supply with temperature compensator covering the range 0-100°C. The pH meter was switched on half an: before-starting the titrations for the initial warm up, of the instrument. [Before taking any reading from the. pH meter, the electrodes were washed with distilled water and dried with filter er,'the readings were recorded only when the instrument registered a steady value for at one Minutes]. The pH meter was standardized before each titration by a buffer solution oassiurn hydrogen phthalate in acidic range (N/20 with a pH value of 4.01 at 30°C)

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Results and Discussion

The acid + ligand titration curves (A + L) and acid titration curves (A) for MPHAPC were found to be coinciding up to pH 2.40. The deviation of acid + ligand curve (A + L) from acid curve (A) was continued up to pH 12.00. This indicated the dissociation of –OH group of the ligand. The increase in deviation is due to the dissociation of –OH group of the ligands.

The ligands involved in the present work may be considered as a monobasic acid having only one dissociable H^+ ion from phenolic –OH group and it can therefore, be represented as a HL. The dissociating equilibria can be shown as:

$$HL \rightleftharpoons H^+ + L^-$$

By the law of mass action, we have

$$k = \frac{[H^+][L^-]}{[HL]} \tag{1}$$

Where, the quantities in brackets denote the activities of the species at equilibrium. The plots between volume of NaOH and pH of the solution were used to determine the proton-ligand formation numbers (representing the replacement of from functional group of ligand with respect to pH value) and evaluate the proton-ligand stability constants of the ligands.

Metal Ion Hydrolysis: The pH at which metal ion starts hydrolyzing should be known to ascertain the complex formation with the ligand. The formation of hydroxide M $(OH)^-$ is given by the equation,

$$M + H_2O \rightleftharpoons M(OH)^- + H^+$$
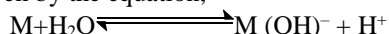
It may cause displacement of metal titration curve even in absence of the reagent. The pH of hydrolysis of a metal ion was found from the departure of the metal curve from that of acid curve. The departure of the metal complex titration curve was observed always at lower pH value than the pH of hydrolysis. This would indicate that complex formation has taken place.

Polynuclear Complexes: Since the solutions were very dilute, the probability of existence of polynuclear species under present experimental conditions was not expected to be high. The values of n are calculated by Irving-Rossotti's expression. It is also observed that there is no appreciable difference between log K_1 and log K_2 values. This clearly showed the formation of 1:1 and 1:2 complexes simultaneously.

Sr(III) and Rare Earths: The colour of complexes with Sr(III) and rare earths was observed in the pH range of 2.0 to 9.5. The formation of colours showed the commencement of the complex formation. The horizontal difference between ligand curve and metal curves was very small.

For each system the pH values at which metal complex formation started and hydrolysis commenced have been tabulated and data are presented in Table.

Table 1: pK values of MPHAPC

Temp. = 27±0.1⁰C   μ = 0.1M

Name of the Ligand	pK (Half Integral)	Pk (Pointwise)
MPHAPC	3.144	3.261±0.13

Table 2: Metal–Ligand Stability Constants at 0.1 M Ionic Strength

System	log K_1	log K_2
Sr(II) – MPHAPC	3.36	2.92
Pr(III) – MPHAPC	3.42	3.01
Nd(II) – MPHAPC	3.45	3.12
Tb(III) – MPHAPC	3.28	3.81

Table 3: pH Values at the commencement of Hydrolysis and Complex Formation

System	pH at the commencement of Hydrolysis	MPHAPC
Sr(II)	5.2	2.3
Pr(III)	7.0	2.4
Nd(II)	7.0	2.5
Tb(III)	6.9	2.6

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