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PH- Metric Study of Mixed Ligand Complexes of Vanadium with Catechol as Primary and Amino Acids as Secondary Ligands.

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ABSTRACT

The solution equilibrium of mixed ligand complexes of vanadium with catechol (L_1) and amino acids such as serine (L_2) and threonine (L_3) have been studied at 0.1 M ionic strength in 70% ethanol-water medium using pH-metric method. It was observed that vanadium form mixed ligand complex with catechol (L_1) and amino acids (L_2 & L_3) in 1:1:1 proportion. Proton-ligand and metal- ligand stability constants were estimated using Irving-Rossotti titration method. The effects of amino acids bonded to central metal atom were studied from estimated data.

Keywords: Catechol, amino acids, Vanadium, metal ligand stability constant, pH-metry.

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INTRODUCTION

The mixed ligand complexes of vanadium metal ion have received considerable attention owing to available reports indicating they possess insulin enhancing effects and can prevent the symptoms of diabetes in a variety of animal models [1]. Amino acids with one or more than one coordination site along with different functional groups have a significant role in metal chelation as detoxification remediation of metal pollutants [2].

The importance of complex formation between metal ions of biological importance with drugs, amino acid and their derivatives is already emphasized by authors [3].

The studies in metal ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in biological kingdom. Metal complexation not only brings the reacting molecules together to give activated complex but also polarized electrons from the ligand towards the metal [4]. The formation constant and free energy change value helps to know the relation between stability and basicity of ligands, bulkier group increases the basicity of ligands as well as stability.

Tayade and Wadekar [5] have reported pH metric study of complexes of substituted Thiocarbamidonapthols with different transition metal ions in 70% mixed solvent media.

Spectroscopic and pH metric studies on Pb(II), Cd(II), Al(III) and Cu(II) complexes of paracetamol and ascorbic acids were reported by Chandrathilaka et al. [6].

Nilesh Jadhao have investigated the stability constant of Fluorophenyl amino and chlorophenyl amino substituted isoxazole with lanthanide series metal ions in 70% ethanol-water mixture [7].

In another paper Tayade and Wadekar [8] have reported the interactions of Cu(II), Cd(II) and Cr(III) metal ions with 5-phenylthiocarbamido-1-naphthol (L2) and 5-p-tolylthiocarbamido-1-naphthol (L4) at 0.1 M ionic strength in 70% ethanol-water mixture by Bjerrum method as adopted by Calcin and Wilson.

Vyas et al. [9] selectively pH metric study of Fe (II) ion complexes of substituted derivatives of cumarin.

In continuation to their work on same topic Tayade and Wadekar have [10] have reported pH-metric study on interaction of 5-chlorophenyl-thiocarbamido-1-naphthol and Cu(II), Cd(II) and Cr(III) complexes in 70% ethanol-water medium. Jadhao and Naik [11] have investigated stability constant of complexes of lanthanide metals with bromophenyl amino and iodophenyl amino substituted isoxazole in 70% ethanol water mixture at 0.1 M ionic strength.

The present work deals with pH metric studies on proton ligand stability constant and metal ligand stability constant of mixed ligand complexes of vanadium metal Ion with catechol as primary and amino acids as secondary ligands in 70% ethanol water mixture.

MATERIALS AND METHODS

All the chemicals used were of AR grade. Catechol and amino acids serine and threonine purchased from S. D. Fine Chemicals private limited. The stock solutions of the ligands and metal ions were prepared by dissolving required amount of compounds in 70% ethanol-water mixture.

PH metric measurements

The pH metric titration of prepared solution was measured with Coslab pH meter instrument with combined glass electrode assembly with accuracy +/- 0.005 units. The instrument was calibrated before starting the titration with standard buffer solution of pH 4.00, 7.00 and 9.00.

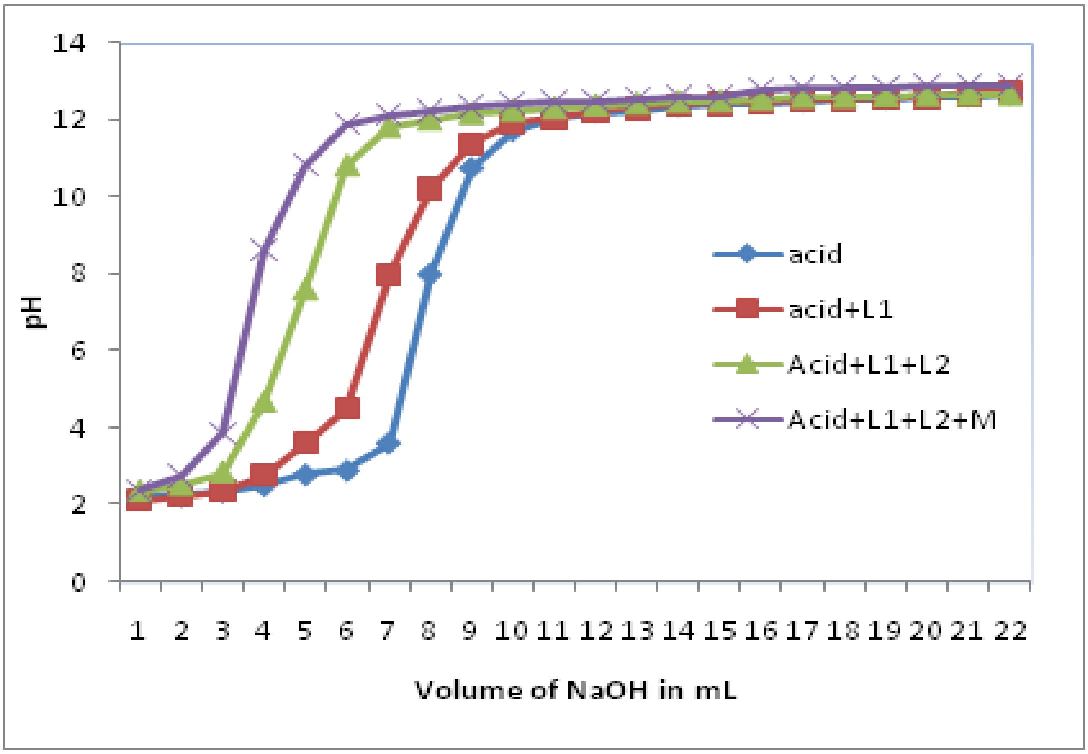
Following solutions were prepared in a total volume of 25 ml by adding required amount of double distilled deionized water at a constant ionic strength of 0.1 M.

i) Free acid HNO_3 (0.01M)
ii) Free acid HNO_3 (0.01M) + ligands (0.002M)
iii) Free acid HNO_3 (0.01M) + ligands (0.002M) + Metal ion (0.0004M)

Each solution was titrated against already standardized sodium hydroxide (NaOH) solution (0.1 N). All the titrations were carried out in 70% ethanol-water mixture and readings were noted down for each 0.5 ml addition of NaOH. The graph of volume of NaOH added against pH values was plotted.

RESULTS AND DISCUSSION

The graphs 1 and 2 (shown below) indicates titration curves of pH measurements for acid, acid + ligands Catechol (L_1), Amino acids serine (L_2) and threonine (L3), and acid + ligands (L_1+L_2) & (L_1+L_3) + metal respectively.



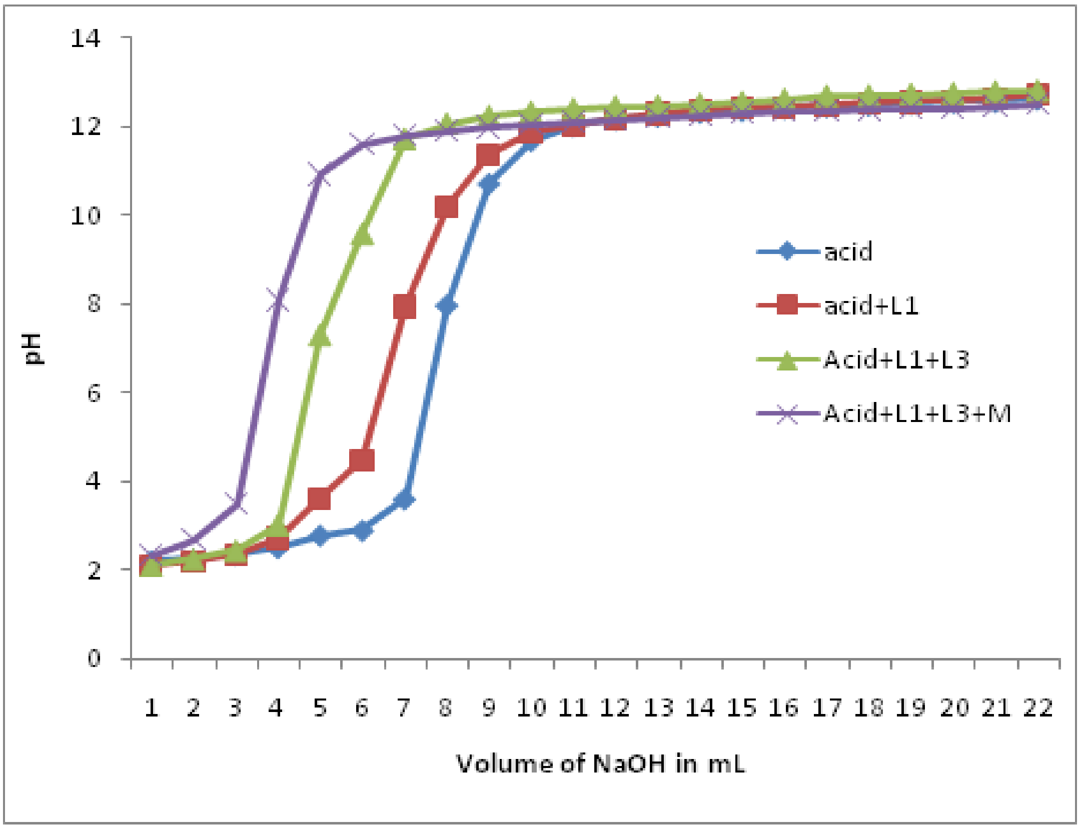
Graph 1: Acid curve, acid with ligands Catechol (L_1) and amino acid serine (L_2) curve and acid+ ligands (L_1+L_2) + metal curves

The titration curves indicate pH values of acid curve is lower than pH values of ligand curve and metal curves at the same volume of NaOH added. This is due to the amino acids dose not form cation easily of free acid resulting in the decrease in the H^+ ion concentration.

The ligand catechol has two dissociable protons from –OH group and amino acids have only one dissociable proton from carboxylic group of amino acids. The proton dissociation constant for HL have been calculated by using following equation.

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

$$K = \frac{[H^+][L^-]}{[HL]}$$



Graph 2: Acid curve, acid with ligands Catechol (L_1) and amino acid threonine (L_3) curve and acid+ ligands (L_1+L_3) + metal curves

Proton-Ligand Stability Constant

The graph plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H^+ ions from functional group of ligand with respect to pH value). The horizontal difference (V_2-V_1) was measured accurately between the titration curves of free acid and acid + ligands. It was used to calculate the formation number, n_A, at various pH values [8] using Irving & Rossotti equation.

$$n_A = \gamma - \frac{(V_2-V_1)(N+E)}{(V^0+V^1)TL^0}$$

Where,
V^0 = Initial volume of the solution
E^0 = Initial concentration of the mineral acid
TL^0 = Initial concentration of ligands
V_1 & V_2 = Volumes of NaOH added
γ = Replaceable proton from the ligand.

The proton ligand stability constant values n_A is calculated and it is represented in Table 1.

Table 1: Proton ligand Stability constant

Ligand	System	pKa	
		Half integral method	Point Wise Method
L_2	Serine	3.055	3.166
L_3	Threonine	2.037	2.254

The pK_a values of ligands were calculated by algebraic methods such as half intergral and point wise method and also estimated from formation curves by noting pH values of titrations of ligands [11]. It was observed that the values of serine (L_2) were higher than those of threonine (L_3). This difference of pK_a values is due to the electron donating methyl group present in threonine (L_3); it decreases the rate of proton displacement than that in case of L_2.

Metal ligand Stability constants

Metal ligand stability constants were determined by the half integer method by plotting graph between n versus pH. The experimental values ñ are calculated by using following equation [11].

$$\tilde{n} = \frac{(E_0 + N)(V_3 - V_2)}{(V_0 + V_2)T^0 m}$$

Where,
E^o = Concentration of free acid in reaction mixture
T^o_m = Concentration of metal ion in reaction mixture,
V_2 = Volume of alkali added to reach the same pH reading,
V_3 = Volume of alkali added in the metal titration to attain the given pH reading,
V^o = Initial volume of reaction mixture
N = Concentration of sodium hydroxide solution.

The metal ligand stability constants calculated is shown in Table 2 as follows.

Table 2: Metal ligand stability constant at room temp at 0.1 M ionic strength

System	Metal ligand stability constant			
	Log K_1	Log K_2	Δ Log K	K_1/K_2
V(IV) + L_1	4.9107	2.9464	1.9643	1.6666
V (IV) + L_1 + L_2	3.9285	2.4553	1.4732	1.6000
V (IV) + L_1 + L_3	3.4070	2.2482	0.5588	1.1961

CONCLUSION

In present investigation pH metric study for determination of proton ligand and metal ligand stability constants of mixed ligand complexes of vanadium with catechol (L_1) as primary ligand and serine (L_2) and threonine (L_3) as secondary ligands is presented. The titration curves ($A+L_1$), ($A+L_1+L_2$), ($A+L_1+L_2+M$) and ($A+L_1+L_3+M$) were started from pH value 2.00 to 2.50. The color of reaction mixture was changed from colorless to faint brown in the pH range 7.00 to 8.70 during titration which indicates complex formation between metal and ligand. The metal ligand stability constant values for serine system are found to be greater than that of threonine system. This is due to the presence of electron releasing methyl group in threonine which decrease the activity of ligand.

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