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PH- Metric Study of Mixed Ligand Complexes of Vanadium Metal Ion with 8-Hydroxyquinoline and L-Amino Acids in 50% Methanol-Water System

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KEYWORDS
8-hydroxyquinoline, amino acids, Vanadium, metal ligand stability constant (log k), pH-metry.

ABSTRACT:
The interaction between vanadium metal ions with 8-hydroxyquinoline (L1) and amino acids such as Cysteine (L2), Methionine (L3) etc. have been studied at 0.2 M ionic strength in 50% Methanol-water medium. Experimental works have been done through simple pH metrically and calculation parts have been done by Bjerrum method. It is observed that metal vanadium ion form a complexes with (L1) 8-hydroxyquinoline and (L2) amino acids in 1:1:1 proportion. The values of metal ligand stability constant (log k) during formation of complex were estimate and compare with literature data. The effects of various amino acids bonded to central metal atom were studied from estimated data.

Introduction:

The stability of mixed ligand metal complexes means in a most general sense, the complex exist under suitable conditions may be stored for a long period of time. However when the formation of complexes in solution is studied, they are having two types of stabilities, thermodynamic stability and kinetic stability [1, 2].

In the language of thermal stability of complexes, the equilibrium constant of complex formation reaction are the measures of the heat released in the reaction and entropy change during complex formation reaction. The greater amount of heat evolved in the reaction most stable are the complexes. Secondly the increase in entropy during complex formation reaction, greater is the stability of product of complexes. Here we are mainly concerned with the thermodynamic stability of the complex compound [3, 4].

Stability constant of mixed ligand alkaline earth metal complexes with metal ion was studied [5] many workers study the effect of transition metal on stability of complexes in pH metrically [6, 7] the studies of metal ligand complexes in solution having number of metal ions with ligands carboxylic acids, oximes, phenols etc. would be interesting which through a light on mode of storage and transport of metal ions in biological kingdom [8] metal complexation not only brings reacting molecules together to give activated complexes but also polarized electrons from the ligands towards the metal [9] [10] carried out pH metric studies on formation constant of complexes of substituted pyrazoles with some lanthanide metal ions and the influence of ionic strength of on complex equilibria in 50% dioxane-water mixture [11] has reported the potentiometric studies on Ni (II), Co (II) and Zn (II) with Schiff base in 60% dioxane-water mixture [12] reported pH metric studies on stability constant of bromophenyl amino and iodophenyl amino substituted isoxazole with lanthanide metal ions in 50% Methanol-water mixture.

The present work deals with pH-metric studies on stability constant of 8-hydroxyquinoline (L1) and amino acid (L2) with vanadium metal ions in 50% Methanol-water mixture.

Materials and methods:

All chemicals used are of AR grade. The ligands (L1) and (L2 were) purchased from Atmaja Chemicals Chhtrapati Sambhajinagar, recrystallize it before use. The stock solutions of the ligands and metal ions were

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prepared by dissolving required amount of compounds in 50% Methanol-water mixture.

General Procedure:

Types of Titrations: (Total volume 25 ml)

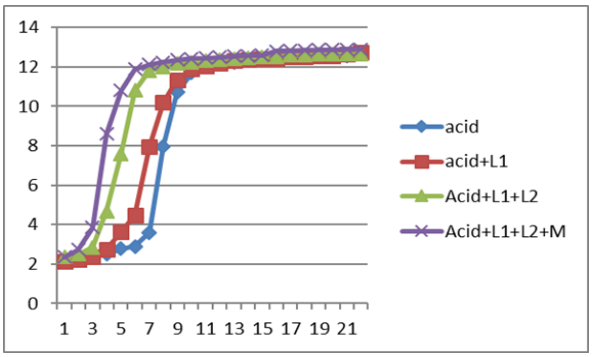
i) Free acid HNO_3 (0.02M)
ii) Free acid HNO_3 (0.02M) + ligands (0.002M)
iii) Free acid HNO_3 (0.02M) + ligands (0.002M) + Metal ion (0.0004M) against standard 0.1N NaOH solution. All the titrations were carried out in 50% Methanol-water mixture and readings were noted down for each 1.0 ml addition of NaOH. The graph of alkali added against pH values was plotted. The ligands involved in the present work may be considered as a monobasic acid having only one dissociable proton ion from acidic group of amino acids and it can therefore, be represented as HL. The dissociating equilibriua can be shown as.

Results and Discussion:

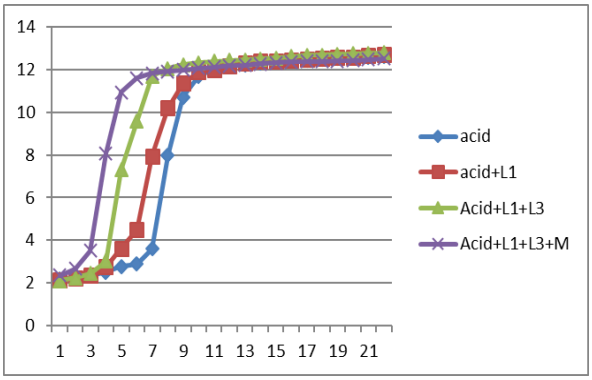
The graphs 1 and 2 indicates acid curve, acid with ligands 8-hydroxyquinoline (L1) and Amino acids (L2&L3) curve and acid+ ligands+ metal curves between pH Vs volume of NaOH added for L2 and L3 Ligands respectively. The titration curves indicate pH values of acid curve is lower than pH values of ligand 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 8-hydroxyquinoline has two dissociable protons from –OH group and amino acids have only one dissociable proton from –OH group of side chain of amino acids. The proton dissociation constant for HL have been calculated by using following equation.

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

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



Volume of NaoH



Volume of NaoH

1.1 Proton-Ligand Stability Constant:

The 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 (V2-V1) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number $\tilde{n}_A$ at various pH values[8].

$$\tilde{n}_A = \gamma - \frac{(V2-V1)(N+E^0)}{(V^0+V^1)TL^0}$$

Where, V^0 is the initial volume of the solution. E^0 and TL^0 are initial concentrations of the mineral acid and ligand respectively. V1 and V2 are the volumes of alkali of normality N during the acid and ligand titration at given pH. γ is the replaceable proton from the ligand. The data of $\tilde{n}_A$ obtained at various pH along with the horizontal difference for some representative systems are represented in Table 1.

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Table-1: Proton ligand Stability constant

Ligand	System	pK	
		Half integral method	**Point Wise Method**
L2	Cysteine	4.068	4.658
L3	Methionine	3.072	3.654

The pK values of ligand was calculated by the algebraic method point wise calculation and also estimated from formation curves by noting pH values of titrations of ligands [12]. The values of L2 (Cysteine) is higher than L3 (methionine). This difference of pK values is due to the electron donating methyl group present in L3 it is decreases the rate of proton displacement than ligand L2.

1.2 Metal ligand Stability constant:

Metal ligand stability constant were determined by the half integer method by plotting graph between ñ vs pH. The experimental values ñ are calculated by using following equation [12].

$$\tilde{N} = \frac{(E^{o} + N)(V3 - V2)}{(V^{o} + V2)\,T^{o}_{m}}$$

Where E^{o} and T^{o}_{m} denotes concentration of free acid and concentration of metal ion in reaction mixture, V2 is the volume of alkali added to reach the same pH reading,V3 is volume of alkali added in the metal titration to attain the given pH reading, V^{o} is the initial volume of reaction mixture and N is the concentration of sodium hydroxide solution. The metal ligand stability constant is shown in table-2 as follow.

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

System	Metal ligand stability constant			
	Log K1	Log K2	Δ Log K	K1/K2
V(IV) + L1	5.6253	3.8495	2.1563	2.3644
V (IV)+L1+L2	4.5216	3.1256	2.3514	2.6845
V (IV)+L1+L3	4.3654	3.4586	1.6584	2.1563

Conclusion:

It is observed that the pH metric curves of vanadium metal ion with 8-hydroxyquinoline (L1), cysteine (L2) and methionine (L3). The curves (A+L1), (A+L1+L2), (A+L1+L2+M) and (A+L1+L3+M) are started from the pH 3.00 to 3.68. The color of reaction mixture is change from colorless to faint brown in the pH range from 6.90 to 8.95 during titration it indicates complex formation between metal and ligand. The logK1 and logK2 values of L1 And L1+L2 with vanadium metal is greater than L1+L3 due to in methionine (L3) has electron releasing methyl group which decrease the activity of ligand to form more stable complex also the difference between logK1 and logK2 is less in (L1+L3) system than (L1+L2) & (L1) it indicates vanadium metal form stable complex with cysteine amino acid (L1+L2) system than methionine (L1+L3) ligands.

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