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Study of Metal-Ligand and Proton Ligand Stability Constants of Ba(Ii), Sr(Ii) Ni(Ii) & Cu(Ii) With A, B Unsaturated Ketimines by Ph Metrically

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Abstract:
Complex formation between Ba(II), Sr(II), Ni(II) and Cu(II) metal ions with α, β Unsaturated Ketimines have been investigated by employing Bjerrum-Calvin pH metric techniques at 35 ºC in 70 % dioxane-water medium. The data obtained can be used for the determination of proton-ligand forma- tion numbers (η_A). From the formation curve, proton-ligand stability constant pK values have been evaluated using half integral method. The metal-ligand formation numbers (η) are estimated by using Irving- Rossotti's expression. Metal-ligand stability constants for 1:1 and 1:2 complexes have been calculated which are designated by letters log K1 and log K2, respectively.
KEYWORDS: Stability constant, ketimines etc.

INTRODUCTION:

Stability constant is well known tool for solution chemist, biochemist, and chemist. In general to help for determination the properties of metal-ligand reactions in water and biological system [1]. Biological properties of some rare earth complexes have been reported by Sharma [2, 3]. The pharmaceutical use of metal complexes has been reported by many workers [4,5].The α, β Unsaturated Ketimines having imine group could be easily found in most of the plants naturally and is an intermediate precursor of flavonoids and isoflavonoids. The presence of a reactive α-β unsaturated keto function in Chalcones and their imine analogues is found to be responsible for their antimicrobial activity. The synthesis and assaying of biological activity of imines have considerable interest in recent decades [6]. α, β-Unsaturated ketimines are chalcone Schiff's bases posses various pharmacological properties [7-9]. The class of α, β Unsaturated Ketimines is one of the most versatile chelating agents having many analytical applications. Chalcone of substituted imine have wide range of applications in the field of biology and biochemistry. The chalcone of substituted imines have been reported to possess various biological activities such as antimicrobial, anti-inflammatory, anti- malarial, antileishmanial, antioxidant, anti tubercular [10]. In the present work we report 2-Hydroxy chalcone imines prepared by reported methods[10]. In view of the analytical application of α, β Unsaturated Ketimines and confirmation of dissociable hydroxy group (-OH), it is necessary to know the physico-chemical properties such as proton-ligand and metal-ligand stability constant by pH-metrically.

EXPERIMENTAL

- Distilled water: Carbon dioxide free, doubly distilled water was used. Distilled water so obtained was again distilled over alkaline permanganate in a glass quick-fit set up and was always used fresh one. Nitrogen gas was bubbled through it, before using it. The pH of this water was found to be 6.98
- 1,4 Dioxane: 1,4 dioxane is a widely used solvent for many recently developed synthetic procedures because of its powerful solvating properties and its chemical stability in the absence of acidic or basic catalysts.
- Sodium Hydroxide: The solution of sodium hydroxide (A.R grade) was prepared free from carbonate by allowing the solution to stand for a long period till any carbonate if present precipitated. The solution was filtered through a sintered Pyrex glass crucible and kept in a Pyrex vessel free from carbon dioxide and was used as the titrant for the pH titration. The solution was standardized by titrating it with standard oxalic acid (AR grade) before use.
- Nitric Acid: Nitric acid is used for preparation of stock solution. Stock solution of 0.1M was prepared by diluting a suitable quantity of original commercial acid. Its exact molarity was calculated by titrating against sodium hydroxide solution.
- Potassium Nitrate: The potassium nitrate was used of AR grade. The stock solution was prepared by dissolving the requisite amount in distilled water.
- Metal Salts: All the metal ions Ba(II), Sr(II), Ni(II)and Cu(II)) used were in the form of their nitrates in order to avoid the possibility of complex formation of the metal ion with anions. Stock solution of 0.01M of each metal salt was prepared by dissolving the requisite quantities in distilled water. The concentrations of metal in solutions are estimated by titrating against standard EDTA solution.
- Ligands: The substituted ketimine will be synthesized by standard method[10]. The ligand

used in the present investigation is 2-Hydroxy-5-bromo-4-chloro-N-(p-methyl phenyl)-ketimine (L_A)

pH meter (accuracy ± 0.01 unit) along with saturated calomel electrode and glass electrode calibrated with buffer solution of pH 4, 7 and 9.2 at 35 ºC was used for the pH measurements. The titration were carried out in 100 mL pyrex glass beaker kept in water bath maintained at constant temperature (35 ± 0.1 ºC). The pH meter readings were taken for each addition of 0.2 mL.

The experimental procedure involved the following titrations:

Free acid titration: A solution containing nitric acid (1.0×10^{-2} M) in 70 % dioxane-water mixture was titrated with standard NaOH solution (0.1 M).

Free acid-ligand titration: A solution containing nitric acid and ligand (20×10^{-4} M) in 70 % dioxane-water mixture was titrated against standard 0.1 M NaOH solution.

Free acid-metal-ligand titration: A solution containing nitric acid, ligand and metal ion (4×10^{-4} M) in 70 % dioxane-water mixture was titrated against 0.1 M NaOH solution. Data obtained from the titrations was used to plot a graph between volume of NaOH and pH values.

- **Calculation of n_A, n and pK**

The values of proton-ligand formation number from ligand molecule and metal-ligand formation number are calculated by using experimental data obtained form titration curve. The titration curve is made by plotting pH Vs volume (ml.) of alkali added. From the curve, the values of V1, V2 andV3 is determined. By using value of V1, V2 andV3, the values of nA, n is determined at different pH.

$$\overline{n}_A = \gamma - \frac{(V_2-V_1)(E^0+N)}{(V_0+V_1)\,T^0L}$$

V0 = Initial volume of solution

V1 =Volume of alkali required during free acid titration.

V2 = Volume of alkali required during free acid +ligand titration.

N = Normality of sodium hydroxide.

E^0= Concentration of mineral acid (HClO4)

γ= Number of replaceable hydrogen ion.

- The value of metal-ligand formation number is calculated by using Irving and Rossotti expression.

$$\overline{n} = \frac{(V_3-V_2)(N + E^0)}{(V_0+ V_2)(T^0M \times n_A)}$$

V_3 = Volume of alkali required during free acid +ligand + metal ion titration.

T^0M = Total concentration of metal ion in solution.

n_A= Proton-ligand formation number.

pK values for different ligands are determined by using following expression.

$$pK = \log \frac{\overline{n}_A}{1-\overline{n}_A} + pH$$

Results and Discussion

- Proton -Ligand Stability Constant (Pk) Values

It could be seen from Table 1 that there is good agreement of proton ligand stability constants between half integral method and pointwise calculation method.

- Metal -Ligand Stability Constant (Log_k)

Determinations of metal-ligand stability constants require the accurate values of proton-ligand stability constants. Higher values of logK1 and logK2 showed that ligands are stronger chelating agents and vice versa. Metal–ligand stability constants of complexes have played an important role in thermochemistry for determining thermodynamic parameters (ΔH, ΔG, ΔS).

Metal-ligand stability constant of Ba(II), Sr(II), Ni(II), Cu(II) complex with some substituted ketimines were determined by employing Bjerrum Calvin pH metric titration method as adopted by Irving and Rossotti. The significant separation starting from pH = 3.95 for Ba(II), Sr(II), Ni(II), Cu(II) with ligand -L_A.

Deviation between (Acid + Ligand + Metal) titration curves from (Acid + Ligand) titration curve started from pH =3.95 which shows the commencement of complex formation.

The values of logK1/logK2 are presented in table-3. The values of log K1and log K2 determines from metal-ligand formation curve at formation number 0.5 and 1.5. The values of logK1and logK2are determined from point wise calculation .The result shows the ratio of Logk1 / Logk2 is positive and greater than one in all cases .This implies that there is little or no steric hindrance to the addition of secondary ligand molecule. It has

been observed that the difference between $LogK_1$and $LogK_2$ is different for different metal ligand complex, and difference between LogK1and $LogK_2$ has less than 2.5 this indicating the simultaneous formation of 1:1 and 1:2 complexes when the difference is more than 2.5 then in such a case there is a stepwise complex formation takes place.

Table-1 Proton-Ligand stability constants (pK)

Ligand	pK	
	Half Integral method	**Pointwise Calculation**
L_A	7.23	7.27

Table-2 Metal-ligand stability constants (log K)

Ligand	Metal	$logK_1$	$logK_2$
L_A	**Ba(II)**	5.14	3.65
	Sr (II)	4.94	4.05
	Ni(II)	5.14	2.55
	Cu(II)	4.84	2.95

Table-3 Metal-ligand stability constants (log K)

Ligand	Metal	Metal Ligand Stability Constants	
		$logK_1/logK_2$	$logk_1$-$logk_2$
L_A	**Ba(II)**	1.40	1.49
	Sr(II)	1.21	0.89
	Ni(II)	2.01	2.59
	Cu(II)	1.64	1.89

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