Complexometric study of Complexes of Ni(II),Cu(II), and Co(II) with Benzothiazolyl Substitute Hydrazone Schiff's Bases in 70% Acetone–Water Mixture.

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Abstract

The Physico-chemical properties i.e proton–ligand and metal–ligand stability constants of complexes of substituted L_1→2-[1-(Benzothiazole-2-yl hydrazono)-ethyl]-5-methyl phenol.L_2→2-[1-(Benzothiazole-2-yl hydrazono)-ethyl]-5- phenol.L_3→N-Benzothiazole-2-yl-N-(1-phenyl-ethylidine)-hydrazine, L_4→N-Benzothiazole-2-yl-N-(1-2-chloro-phenyl-ethylidine]-hydrazine,L_5→2-(Benzothiazole-2-yl hydrazono)-methyl)- phenol,L_6→N-Benzothiazole-2-yl-N-(4-chloro-benzylidene)- hydrazine. with Ni(II), Cu(II),and Co(II) were determined in mixed solvents . Presence of OH/NH group(s) in these compounds was confirmed at 0.1 M ionic strength in 70% acetone-water mixture pH-metrically. It is observed that Ni(II), Cu(II), and Co(II) metal ions formed 1 : 1 and 1 : 2 complex with all the six ligands.

Keywords: Proton-ligand and metal-ligand stability constants, pH-metric study,metal ions,complexes

INTRODUCTION

In the last five decades, considerable research work had been done on the study of complexes in solution. Janik, Bjerrum desertation [1]was published in 1941 and from then the progress in this field was initiated. Calvin, Bjerrum, Rosstti,Schwarzenbach, Irving and Martel have made important contribution to the rapid progress not only in our understanding of metal-complexes in aqueous but also in mixed solvents.

Rossotti and Rossotti[2] have defined a complex as a species formed by the association of two or more simple species each capable of independent existence. When one of the simple species is a metal ion, the resulting species is called as metal complex. Some ligands are attached to the metal atom by more than one donor atom in such a manner as to form a heterocyclic ring. The species is called as chelate. This phenomenon is called as chelation. The chelates have been extensively studied in solution as well as in solid state by many workers, due to it's remarkable properties and high stability.

With the help of various experimental techniques, the extensive work in coordination complexes has been made possible and has lead in a number of empirical conclusions which have been detailed by Martell[3].

The stability of complex in solutions depends on nature of central metal ion and ligands. The most important characteristics of the central atom which influence the stability of complex compounds are the degree of oxidation, the radius and electronic structure.The stability order of metal complexes of transition metal ion was found by Irving and Williams[4] as Mn2+<Fe2+ <Ni2+ <Cu2+>Zn2+. The interaction of metal ions with biologically active compounds may enhance their activities[5].

The literature survey reveals that work has been done on heterocyclic compounds for their antibacterial activities on gram positive and gram negative bacteria also their antifungal activity on different fungi's. Benzothiazole derivatives are an important class of compounds, which is becoming increasingly important due to their broad spectrum of biological activities [6-7]. Literature survey shows that many Benzothiazole derivatives are known to exhibit pharmacological activities such as anti-bacterial [8], anti-microbial and cytotoxic[9], anti-diabetic [10], antitumor [11], anti- inflammatory [12], anthelmintic [13], antifungal [14] activities etc. Hence, synthesis of such compounds are of considerable interest.

Deosarkar[15] have studied stability constants of Al(III), Cr(III) and Fe(III) metal ion complexes with substituted sulphonic acid.

Meshram[16] have studied the association and dissociation constant of Pr(III) complexes with 3-(2-hydroxy-3-iodo-5-methyl phenyl)1,5 diphenyl pyrazoline at different ionic strength.

Swami[17] has discussed the stabilities of palladium chelates of substituted hydrazine and the effect of substituting groups CH3,OCH3, and Cl. An attempt has been made to correlate the p*Ka* values of ligand with the first step and overall stability constants.

Jamode[18-19] have been reported the physicochemical properties and the stability constant of substituted pyrazoles with Cu(II), Co(II), and Ni(II).

Some of the ligands acquired stepwise complex formation and other are simultaneously due to nitro and bromo electron-withdrawing groups, respectively.

Study of formation and stability constants of thorium (IV)complexes with substituted pyrazolines was done by Narwade[20-21].

The present paper reports pH-metric studies on the interaction of L_1→2-[1-(Benzothiazole-2-yl hydrazono)-ethyl]-5-methyl phenol.L_2→2-[1-(Benzothiazole-2-yl hydrazono)-ethyl]-5- phenol.L_3→N-Benzothiazole-2-yl-N-(1-phenyl-ethylidine)-hydrazine, L_4→N-Benzothiazole-2-yl-N-(1-2-chloro-phenyl-ethylidine]-hydrazine,L_5→2-(Benzothiazole-2-yl hydrazono)-methyl)- phenol,L_6→N-Benzothiazole-2-yl-N-(4-chloro-benzylidene)- hydrazine in the 1 : 1 ratio at30+0.1K.The70% acetone-water mixture was used as solvent.The ionic strength was maintained constant at 0.1 M.The proton ligand and metal ligand stability constant were calculated by pointwise calculation method and half integral method.

Materials and solutions.

The ligands and their derivatives were synthesized by a known literature method[22]. Purity of these compounds exceeds 99.5% and was verified by TLC, and the structures were confirmed by NMR, IR, and melting points. The stock solutions of the ligands (4.0×10–2mol dm–3) were prepared by dissolving the required amount of the ligands in a minimum volume of acetone subsequently diluted to the final volume. Nitrates of rare-earth metal ions (from Sigma and Aldrich) were used to prepare metal solutions (1.0×10–2mol dm–3) and standardized by the EDTA titration method as discussed in literature[23] .The stock solution of perchloric acid was prepared and used after standardization[24].

The ionic strength(0.1 mol dm–3) was maintained constant by using 1M KNO3 solutions. The standard NaOH solution was preparedby Vogel’s method[25].

Apparatus and procedure.

Chemicals used were of AR grade. Distilled water used was free from carbon dioxide and pH of this water was about 7.80. pH-Measurements were carried out with Digital pH-meter model EQ-610 with accuracy 0.005 unit using glass electrode and saturated calomel electrode at 27°C. It was calibrated by buffer solution of pH 4.00, 7.00, and 9.20 at 27°C before processing the titrations. Digital analytical balance (model no. CA224) was used for measurement. Oxalic acid was used and its solution of 0.01 M was prepared in distilled water. Sodium hydroxide pellets was used and its solution of 0.1 M was prepared in distilled water.Sodium perchlorate was used and its solution of 1 M was prepared in distilled water. Perchloric acid was used and its solution of 0.1 M was prepared in distilled water.

The pH-metric titrations were carried out by following ways :

1) Acid titrations : HNO3(0.1M)

2) Acid + ligand titrations : HNO3(0.1M) + ligand(0.01M) + metal ion (0.01M).

The ionic strength of all the solution was maintained constant by adding appropriate amount of KNO3 solution. All the titrations were carried out in 70% acetone-water mixture & the reading were recorded for each 0.5ml addition by using Calvin-Bjerrum pH-metric titration technique[25-26]. The graph of volume of alkali (NaOH) against pH were plotted. From the pH values, proton-ligand stability constants were calculated by using Irving-Rossetti method[27]. The values of proton-ligand stability constants are given in table-1

RESULTS AND DISCUSSION

The evaluated proton-ligand dissociation constants for various ligands in the present study are in good concordance with reported values. The pH-metric titration curve shows only one inflection point indicated that there is only one acidic group, and the proton dissociation constants for HL have been calculated by using the following equations.

The extent of deviation may be the dissociation of OH group completely. The proton-ligand formation number $\tilde{n}_A$ was calculated by the Irving-Rossotti expression.

The p*K* values of the ligands and formation constants of the complexes were calculated by the algebraic method pointwise calculation and also estimated from formation curves $\tilde{n}_A$vs pH (half-integral method)by noting pH at which $\tilde{n}_A = 0.5$ (Bjerrum, 1957). The accurate values of pK were determined by pointwise calculation. The pK values were calculated from the following equation.

$$\overline{n_A} = \gamma - \frac{(V_2 - V_1) \text{ x } (N + E^0)}{(V^0 + V_1) \text{ x } T_L{}^0} \qquad \text{....1}$$

$$\overline{n} = \frac{(V_3 - V_2) \ (N + E^0)}{(V^0 + V_2) \overline{n_A} \ T_M{}^0} \qquad \text{.....2}$$

Where γ-denotes the number of dissociable protons,*N* is the concentration of NaOH(0.1071 mol dm–3),E is resultant Concentration of ligand,V is initial volume of the reaction mixture V_1 and v_2 are volume of alkali added in acid,ligand titration and metal titration T^0 m is concentration of the metal ion in the reaction mixture. Similarly, the metal-ligand stability constants were determined by the half-integral method by plotting $\tilde{n}$. The experimental values are determined using the expression.

In the present study, the formation of complex was confirmed by the color changes from colorless to yellow or green at the time of titration. During titration, the color changes were due to the simultaneous formation of 1:1 and 1:2 complex by the ligand with metal ion.Metal ion and size of metal ion are very important factors because the chelation properties can be related to the properties of metal ion. Mellor and Malley[28] have obtained the following order of relative stabilities of complexes of bivalent metal ions –

Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg

Gupta and Mehta[29] have obtained the following order of relative stability of trivalent metal ions –La(III) < Nd(III) < Sm(IIl) < Gd(IlI) < Tb(IIl) which is in agreement with lanthanide contraction.

In the present study the stability trend obtained mey be given as Ni(II)<Cu(II) <Co(II).

Table 1 : Proton-ligand stability constants (pK) of ligand L1to L3at 0.1 M ionic strength and at (30±0.1oC) temperature in 70% acetone-water medium.

S.N.	Ligands	Half integral method (pK)
1	L1	7.5
2	L2	6.8
3	L3	8.08
4	L4	8.05
5	L5	7.04
6	L6	7.02

In the result of proton-ligand stability constants, variations are obtained in the values. This may be due to the intermolecular interactions like solute-solvent and solvent-solvent interactions as the solvents are polar in nature.

S.N	System	Constants	Half integral method	Pointwise calculation method
1	Co^{II}-L^{I}	Log K_1	5.12	5.11
		Log K_2	3.65	3.60
2	Ni^{II}-L^{1}	Log K_1	4.92	4.96
		Log K_2	4.05	4.01
3	Cu^{II}-L^{1I}	Log K_1	5.12	4.66
		Log K_2	2.55	2.59
4	Co^{II}-L^{II}	Log K_1	4.94	5.40
		Log K_2	3.35	3.30
5	Ni^{II}-L^{1I}	Log K_1	4.49	4.51
		Log K_2	2.95	3.01
6	Cu^{II}-L^{1I}	Log K_1	4.40	4.80
		Log K_2	2.20	2.25
7	Co^{II}-L^{3}	Log K_1	5.16	4.92
		Log K_2	3.60	2.89
8	Ni^{II}-L^{3}	Log K_1	5.50	5.62
		Log K_2	4.08	3.98
9	Cu^{II}-L^{3}	Log K_1	4.90	5.18
		Log K_2	2.44	2.20
10	Co^{II}-L^{4}	Log K_1	4.80	5.10
		Log K_2	3.45	3.40
11	Ni^{II}-L^{4}	Log K_1	5.09	5.04
		Log K_2	3.85	3.70
12	Cu^{II}-L^{4}	Log K_1	4.70	5.08
		Log K_2	2.15	2.13

13	Co^{II}-L^5	Log K$_1$	5.20	5.50
		Log K$_2$	2.45	2.52
14	Ni^{II}-L^5	Log K$_1$	5.80	5.40
		Log K$_2$	4.35	4.25
15	Cu^{II}-L^5	Log K$_1$	5.30	5.28
		Log K$_2$	3.13	3.10
16	Co^{II}-L^6	Log K$_1$	4.15	4.10
		Log K$_2$	3.42	3.40
17	Ni^{II}-L^6	Log K$_1$	4.45	4.40
		Log K$_2$	3.06	2.99
18	Cu^{II}-L^6	Log K$_1$	4.05	4.02
		Log K$_2$	3.01	2.95

Table 2 : Metal-ligand stability constants of complexes Co(II), Ni(II), Cu(II) with ligand L1 to L6 in 70% acetone-water medium.

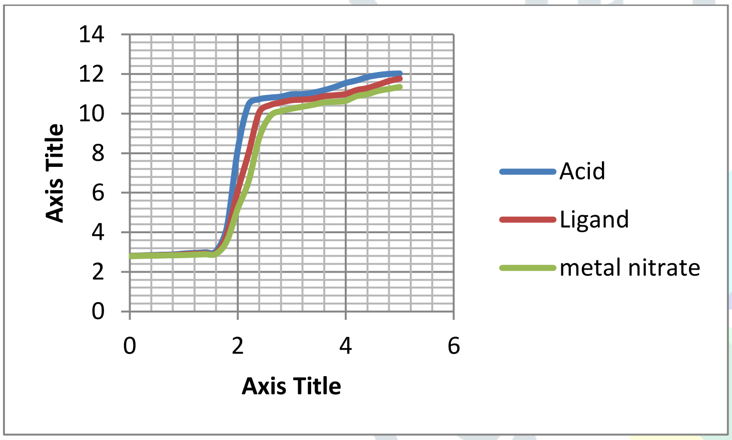

Figure 1 : pH-Metric titration curve

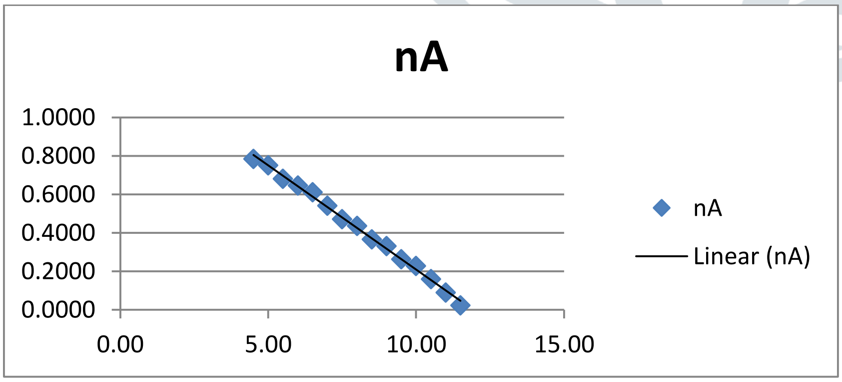

Figure 2 : Proton- ligand stability constant

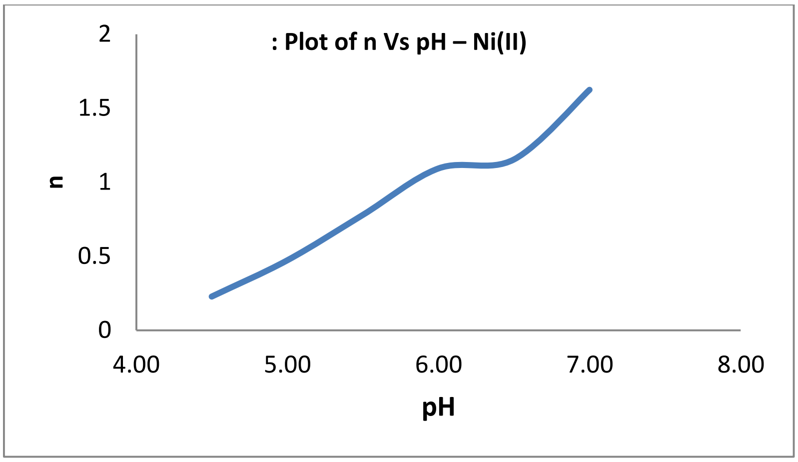

Figure 3 : Metal-ligand stability constant

conclusion

Present research work reveals the 1:1 complex formation between Ni(II), Cu(II), and Co(II) metal ions formed with respect to all the six ligands of L_1→2-[1-(Benzothiazole-2-yl hydrazono)-ethyl]-5-methyl phenol.L_2→2-[1-(Benzothiazole-2-yl hydrazono)-ethyl]-5- phenol.L_3→N-Benzothiazole-2-yl-N-(1-phenyl-ethylidine)-hydrazine, L_4→N-Benzothiazole-2-yl-N-(1-2-chloro-phenyl-ethylidine]-hydrazine,L_5→2-(Benzothiazole-2-yl hydrazono)-methyl)- phenol,L_6→N-Benzothiazole-2-yl-N-(4-chloro-benzylidene)-hydrazine.

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