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Short Communication

Study of Stability Constants of Cu (II), Co (II), Ni (II), Mn (II) Complexes with Substituted Δ^2 Pyrazole in DMF Solvent using pH-Meter

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Abstract

The stability constant of substituted 2pyrazole (P1) with Cu(II), Co(II), Ni(II), Mn(II) complexes using pH metric titration technique in 90% DMF-water mixture at an ionic strength of 0.1M KNO3 were studied. The data obtained showed that Cu (II) has highest stability while Mn(II) has lowest stability.

Keywords: Stability constants, Pyrazole, DMF, pH-meter study.

Introduction

A pH meter is used to find out the stability constant which is useful as equilibrium constant for the formation of a complex in solution. In recent years, most of the co-workers have focused their studies on the pH-meter for stability constants in order to obtain accurate results.

R.K. Tada *et al* have investigated Evaluation of stability constant of Thiosemicarbazide (TRM-1) with copper (II), cobalt (II) and nickel (II) complexes using pH-meter[1]. A.B. Naik *et al* have investigated pH-meteric studies on the substituted pyrozoles with some lanthanides metal ions and the influence of ionic strength on complex equillibria in a 70% dioxane-water mixture[2]. G.H. Murhekar *et al* have investigated formation constants of lanthanides metal ion chelates with some substituted pyrozoles in different solvent compositions[3]. K.T. Kiranpure *et al* have studied proton ligand and metal ligand stability constant by effect of dielectric constants of methanol-water and acetone-water mixtures on Cu (II)-salicyclic acid complex[4]. M. M. Rathore *et al* have investigated the effect of dielectric constants of 1, 3 diphenyl thiazines with Cu (II) complexes in dioxane-water mixtureusing pH-meter at 0.1 M ionic strength[5]. Y.K. Meshram *et al* have reported the stability constants of transition metal complexes with substituted ketones and simple ketones at 0.1 M ionic strength using pH-meter[6]. A. Ramteke *et al* have studied stability constants of the complexes of chlorosubtituted pyrazoles and pyrazolines with Cu (II), Ni (II), Co (II) and Nd (II) metal ions in 70 % dioxane-water mixture at 0.1 M ionic strength[7].

The present work described interaction of Cu (II),Co(II), Ni(II), Mn(II) complexes with 3-(2-hydroxyl-3,5-dicholorphenyl)-4-benzoyl-5-(2'-furyl)-1-phenylpyrazole (P_1) as ligand in DMF (N, N-dimethyl formamide) solvent. The ligands are insoluble in water hence 90 % DMF-water mixture is used as a solvent.

Materials and Methods

The lignads were synthesized by known literature method .The stock solutions of the lignads (0.01 M) were prepared by dissolving the requisite quantity of the lignad in a 90% DMF-water solvent and diluted to the final volume. The solution of sodium hydroxide (0.2 N) was prepared by making it free from carbonate and standardized by titration against standard oxalic acid. 0.1M HNO_3 acid was used for the preparation of a stok solution. Its exact normality was calculated by titrating against standard sodium hydroxide. 0.1M KNO_3 solution which was prepared from carbonates free double distilled water.

Metal Chlorides: Present investigation focused on the study of transition elements: (1) Copper chlorides ($CuCl_2.2H_2O$), (2) Cobalt chlorides ($CoCl_2.6H_2O$), (3) Nickel chlorides ($NiCl_2$) and (4) Magnese chlorides ($MnCl_2.4H_2O$). Double distilled water was used for the preparation of 0.02M metal solutions.

Instruments: All the pH measurements and titrations were carried out on ELICO-L1-10 pH meter with accuracy 0.01by using a glass and calomel electrode assembly. The instrument could read the pH in 0.0 to 14 in a step of 0.005. Firstly the electrodes were washed with distilled water and dried with filter paper for any pH measurement. The pH meter was standardized before each titration with a buffer solution of pH 4.00, 7.00 and 9.20. The qualigens buffer tablets used for standardization of pH meter at pH 4.00, 7.00 and 9.20.

The determination of metal-ligand stability constants carried from three kinds of titrations: i. Acid titration: - 5ml 0.1M

(HNO_3) +5ml (0.1M) KNO_3+ 35 ml DMF+5ml water. .ii. Acid + Ligand titration: 5 ml HNO_3 (o.1M) + 5 ml KNO_3 (0.1M) + 10 ml ligand (in DMF) + 25 ml DMF + 5 ml water. iii. Acid+ Ligand+ Metal titration:- 5 ml HNO_3 (0.1M) + 5 ml KNO_3 (o.1M) + 10 ml ligand (in DMF) + 25 ml DMF 2 ml metal ion solution + 3 ml water.

0.2 N NaOH (alkali) solution used for all titrations and titration data used to draw the curves between volume of NaOH added and pH values. Readings related to estimate the value of pH and volume of alkali added presented in Table-1. Metal-ligand formation curves and acid-ligand formation curve represented in Figure-1.

Results and Discussion

The dissociation of OH^- clearly indicated by the titrations (acid + ligand) curves deviated from acid curves at pH 4.60 and continued up to pH 12.58.

Metal ion hydrolysis: The pH at which metal ion start association (hydroxylation) with OH^- group showed its co-relation with the process of complex formation with the ligand. The formation of hydroxide M (OH) is given by the equation,

$$M + H_2O \rightleftharpoons M(OH^-) + H^+$$

At the time of departure of metal complexes titration curve was observed always at lowest pH values than the pH of hydrolysis of metal ion.

Formation of Curves: The deviation of metal titration curves from ligand curve (metal+ ligand) were found in between 4.50 to and continue up to 12.58. This shows the formation of complexes with respect to change in colour.

Conclusion

From the graphical data it was conclude that the formation of strong metal complexes due to higest pH values of ligand titration curves as compare to metal titration curves. The higher co-ordination achieved by large metal ion, hence Cu (II) shows highest stability and Mn(II) shows lowest stability.

Table-1
The pH titration reading of acid, acid + Ligand, acid + Ligand 0.1M, T = 25^{0}C, solvent DMF-water (90:10) + Metal, Ionic Strength μ =

Vol. of Alkali Adade	Acid	Acid + Ligand (P_1)	Acid + Ligand (P_1) + Cu (II)	Acid + Ligand (P_1) + Co (II)	Acid + Ligand (P_1) + Ni (II)	Acid + Ligand (P_1) + Mn (II)
0.00	3.37	3.42	3.51	3.49	3.40	3.41
0.10	3.40	3.54	3.52	3.50	3.49	3.50
0.20	3.51	3.56	3.58	3.56	3.55	3.54
0.30	3.57	3.60	3.62	3.60	3.58	3.56
0.40	3.62	3.69	3.70	3.68	3.67	3.65
0.50	3.70	3.75	3.73	3.72	3.70	3.71
0.60	3.82	3.82	3.80	3.78	3.79	3.76
0.70	4.05	4.17	4.10	4.03	4.02	4.01
0.80	4.58	4.60	4.58	4.56	4.55	4.54
0.90	11.30	10.88	10.76	10.64	10.56	10.52
1.00	12.35	11.68	11.55	11.02	10.88	10.60
1.10	12.56	11.50	11.12	11.00	10.98	10.90
1.20	12.60	12.55	12.52	12.40	12.38	12.36
1.30	12.40	12.20	12.00	11.90	11.12	11.10
1.40	12.68	12.58	12.48	12.02	12.79	11.70

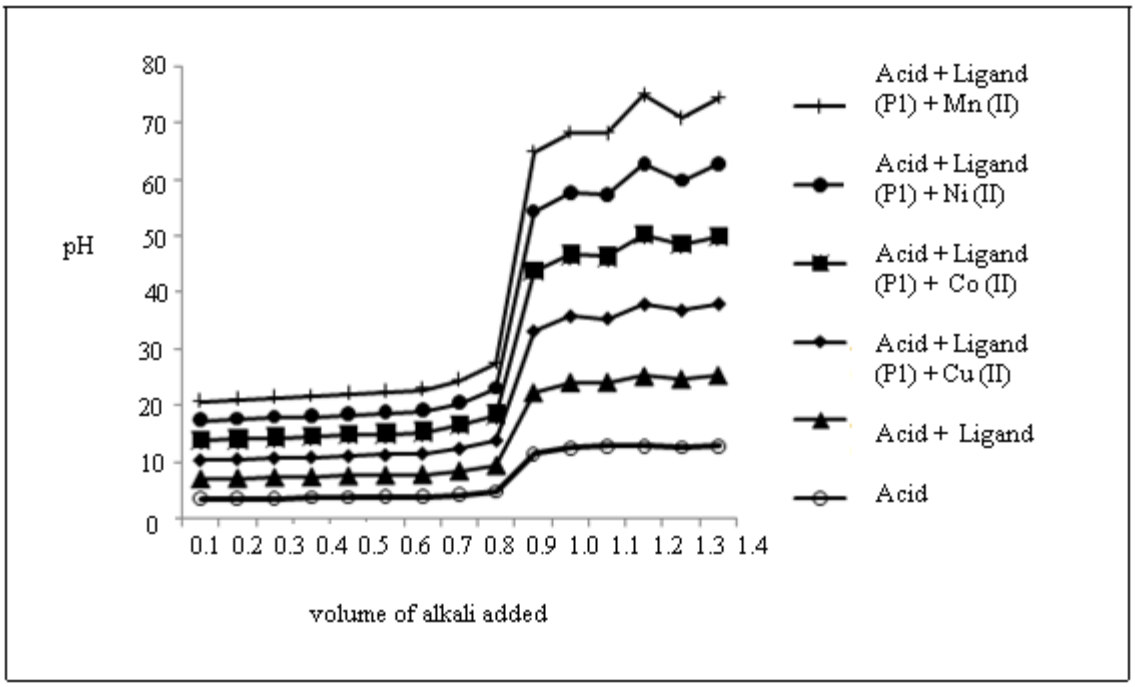

Figure-1
Experimental curve of acid, acid+ligand and acid + ligand +metal

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