



SYNTHESIS, CHARACTERIZATION AND pH METRIC STUDY OF SOME NOVEL METAL COMPLEXES

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ABSTRACT

The novel metal complexes of first transition metal ions with chromene derivative as ligands have been synthesized and characterized by elemental analysis. Formation of ML_2 type metal complexes have been established from pH measurements on the interaction of M (II) ions [M = Mn, Cu, Ni, Co] with ligand 3-[3-(9'-anthryl)-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one in the presence of an electrolyte (0.2M) at constant temperature $30^\circ \pm 1^\circ$ C by Irving –Rossotti titration technique. Various factors influencing the formation and stability of metal complexes have been discussed..

Key words : Coumarin, Metal complexes, Stability constant, pH Metric titration.

INTRODUCTION

The transition metals have tendency to form coordination compounds with Lewis bases with groups, which are able to donate an electron pair. Some of the coumarins show distinct physiological photodynamic and bacteriostatic activities¹ and has been used in several application². Their chelating characteristics have long been observed and the bacteriostatic activity seems to be due to chelation. The physicochemical properties^{3, 4} of the coumarins with chelating group at appropriate position and their metal complexes reveal that the ligand can be used as potential analytical reagents⁵. Many binary complexes of transition and inner transition metals have been studied potentiometrically^{6, 7}.

Chalcones are useful for the detection of Fe (II)⁸ and Ca (II)⁹ ions in presence of Ba and Sr as it reacts with a number of metal ions. Chalcones of 4-hydroxy coumarin derivative is known by their antimicrobial activity¹⁰ and also acts as a good chelating agent due to their O-O electron donor system. In the present work, the formation constants of binary chalcone of 4-hydroxy coumarin with Cu (II), Ni (II), Co (II) and Mn (II) have been

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determined pH metrically.

EXPERIMENTAL

The ligand (I) was prepared and purified by the method reported in the literature¹¹. The solution of the compound (I) was prepared in AR Grade 44 dioxane. The metal solution was prepared by dissolving metal nitrate of AR Grade in double distilled water and standardized by EDTA¹². The other reagents NaNO₃, NaOH and HNO₃ of AR Grade were used and their solutions were prepared in double distilled water and standardized by the usual methods.

pH-metric titration was carried out with systronic- μ pH meter 361 having combined glass electrode and temperature probe maintained with readability $\pm 0.1^\circ\text{C}$.

The metal ligand ratio was maintained at 1 : 5. The ligand concentration was maintained at 2.00×10^{-3} M and the metal ion concentration was maintained at 4.00×10^{-4} M. The total volume was maintained at 50 mL. The ionic strength was maintained at 0.1 M by adding requisite amount of sodium nitrate in binary titrations. All the solutions were titrated against 0.1 M sodium hydroxide solution. 60% of aqueous 1, 4-dioxane medium is maintained in all the titrations. pH meter reading in 60% (v/v) aqueous 1, 4-dioxane were corrected by the method of Van-Uitert and Hass¹³. The log K values were evaluated.

The method of Bjerrum and Calvin as modified by Irving and Rossotti¹⁴ has been used to determine \tilde{n} , \tilde{n}_A , pL values. The experimental procedure involved potentiometric titration of the following sets of solution.

The following three sets were prepared for titration :

- (i) 0.8 mL. HNO₃ (1.0 M) + 11.2 mL. water + 24.0 mL dioxane + 4.0 mL. NaNO₃ (1.0M).
- (ii) 0.8 mL. HNO₃ (1.0 M) + 11.2 mL. water + 22.0 mL dioxane + 2.0 mL. ligand solution (0.1 M) + 4.0 mL. NaNO₃ (1.0 M).
- (iii) 0.8 mL. HNO₃ (1.0 M) + 10.8 mL. water + 22.0 mL dioxane + 2.0 mL. ligand solution (0.1 M) + 0.4 mL. metal solution + 4.0 mL NaNO₃ (1.0 M).

The value of proton ligand stability has been obtained by linear plot of pH against $\log \tilde{n}_A / 1 - \tilde{n}_A$.

RESULTS AND DISCUSSION

The solution chemistry of first transition series is very interesting. The following factors explain satisfactorily the overall characteristics of stability and other aspects; ionization enthalpies of metal atoms, ionic radius, electronic structure of metal ions, nature of ligands involved in $d\pi$ - $p\pi$ interactions, nature of solvent etc.

The effects to make compounds more covalent, Cu (II) has greater lattice and solution energies and hence, higher formation constant for complexes of Cu (II) ions was observed. Amongst three, Cu (II) shows higher stability as expected. Co (II) complexes with ligand is more stable than corresponding Ni (II) complexes. This is attributed to the size of the metal ions.

The order of stability constants of the metal chelates under investigation are Mn (II) < Co (II) < Ni (II) < Cu (II), which is in conformity with the Irving Williams natural order of stabilities¹⁵.

Table 1 : Proton ligand and binary metal ligand stability constants of metal complexes at temperature $30 \pm 0.2^\circ \text{C}$

Ligand pK Values	Metal – ligand formation constants			
	Cu	Ni	Co	Mn
$\text{Log pK}_1^{\text{H}} = 10.98$	$\text{LogK}_1 = 10.98$	$\text{LogK}_1 = 10.98$	$\text{LogK}_1 = 10.98$	$\text{LogK}_1 = 10.98$
$\text{Log pK}_2^{\text{H}} = 3.27$	$\text{LogK}_2 = 10.37$	$\text{LogK}_2 = 10.11$	$\text{LogK}_2 = 09.62$	$\text{LogK}_2 = 09.35$
	$\text{Log}\beta = 21.35$	$\text{Log}\beta = 21.09$	$\text{Log}\beta = 20.60$	$\text{Log}\beta = 20.33$

The pK values for ligand were determined pH metrically. β Values (0.1 – 1.0) obtained for ligand system indicate the formation of 1 : 2 complexes in solution. The acid dissociation constants and the binary formation constants so obtained are presented in

Table 1. It was established that the association of proton is affected by strength of hydrogen bonding between oxygen of hydroxy group and carbonyl group. Stronger the hydrogen bond, lesser will be the dissociation and hence, less is the acid character of –OH group.

In all the systems under investigation, the metal titration curves were depressed below the ligand titration curves. This was expected in the complex formation of the metal ion with the ligand during the metal titration in presence of excess of the ligand (nearly five times more).

Thus, the binary $ML_2(H_2O)_2$ complexes have been studied to determine their stability. It is interesting because these data are useful to understand the role of metal ions in various biochemical reactions and their role as an analytical reagent.

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