

Potentiometric Studies on Some Binary Metal Complexes

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ABSTRACT

For the evaluation of stability constant of metal chelate, the proton ligand stability constant of the ligand is required. The values of proton ligand stability constant of Bis-(3-[-2-NITRO(phenyl)]-prop-2-enoyl)-4-hydroxy-6-methyl-2H-chromen-2-one[M(II)], have been obtained at $30 \pm 1^\circ\text{C}$ by liner plot of pH against $\log \frac{\bar{n}_A}{1 - \bar{n}_A}$. At each point on straight line $\text{pH} + \log \frac{\bar{n}_A}{1 - \bar{n}_A} = \text{pK}^H$. pK_1^H and pK_2^H values were obtained in the range \bar{n}_A 0 to 1 and 1 to 2 respectively. Irving and rossotti method has been employed for this potentiometric studies.

Keywords : Coumarin, Chalcone, Metal complexes, Stability constant, pH Metric titration.

I. INTRODUCTION

Metal complexes of chalcone have been extensively studied because chalcone possess good synthetic flexibility, selectivity and sensitivity towards the central metal atom. Chalcones of 4-hydroxy coumarin derivative is known by their antimicrobial activity[1] and also acts as a good chelating agent due to their O-O electron donor system. Many binary complexes of transition and inner transition metals have been studied potentiometrically[2,3]. Some of the coumarins show distinct physiological photodynamic and bacteriostatic activities[4] and have been used in several applications[5]. The physicochemical properties[6,7] of the coumarin with chelating group at appropriate position and their metal complexes reveal that the ligand can be used as a potential analytical reagent[8].

Chalcones are useful for the detection of Fe(II)[9] and Ca(II)[10] ions in presence of Ba and Sr as it reacts with a number of metal ions. So the present study was undertaken to determine the formation constant of binary complexes of chalcone of 4-Hydroxy coumarin with Cu(II), Ni(II), Co(II) and Mn(II) pH metrically.

II. METHODS AND MATERIAL

The ligand was prepared and purified by the method reported in the literature[11]. The solution of the ligand was prepared in AR Grade 1,4 dioxane. The metal solution were prepared by dissolving metal nitrate of AR Grade in double distilled water and standardized by EDTA[12]. The other reagents NaNO_3 , NaOH and

HNO_3 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 with 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. 60%(v/v) aqueous 1,4 dioxane were corrected by the method of Van-Uitert and Hass[13]. The $\log \text{pK}^H$, and $\log \text{K}$ values were evaluated.

The method of Bjerrum & Calvin as modified by Irving and Rossotti[14] has been used to determine \bar{n} , \bar{n}_A , pL values. The experimental procedure involved potentiometric titration of the following sets of solution.

- 1) 0.8 ml. HNO_3 (1.0 M) + 11.2 ml. water + 24.0 ml dioxane + 4.0 ml. NaNO_3 (1.0M).
- 2) 0.8 ml. HNO_3 (1.0 M) + 11.2 ml. water + 22.0 ml dioxane + 2.0 ml. ligand solution
(0.1 M) + 4.0 ml. NaNO_3 (1.0 M).

- 3) 0.8 ml. HNO₃ (1.0 M) + 10.8 ml. water + 22.0 ml dixoane + 2.0 ml. ligand solution (0.1 M) + 0.4 ml. metal solution + 4.0 ml NaNO₃ (1.0 M).

The proton-ligand formation curves is obtained on plotting \tilde{n}_A versus pH. The metal-ligand formation curves were obtained on plotting \tilde{n} versus pL.

The value of proton ligand stability has been obtained by linear plot of pH against

$\log \tilde{n}_A / 1 - \tilde{n}_A$. Metal -ligand stability constant has been obtained by extrapolating the linear plot of $\log \tilde{n} / 1 - \tilde{n}$ against pL and half \tilde{n} values.

The pK values for ligand were determined pH metrically for the first time \tilde{n} 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-I. 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.

The effects to make compounds more covalent, Cu(II) has greater lattice and solution energies, hence higher formation constant for complexes of Cu(II) ions is 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 stability shown by Mn(II) with the ligand is the lowest due to the lower charge and specific behavior of metal ion. 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 stabilities[15].

Thus the binary ML₂(H₂O)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.

Table – I : Proton ligand and binary metal ligand stability constants of metal complexes at temperature 30 ± 1° C.

Proton-Ligand Formation Constants	Metal – ligand Formation Constants			
	Cu	Ni	Co	Mn
Log pK ₁ ^H = 11.	LogK ₁ = 11.05	LogK ₁ = 11.	LogK ₁ = 11.03	LogK ₁ = 11.20
Log pK ₂ ^H = 3.10	LogK ₂ = 11.02	LogK ₂ = 10.05	LogK ₂ = 10.52	LogK ₂ = 09.61
	Logβ = 22.07	Logβ = 21.05	Logβ = 21.55	Logβ = 20.81

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IV. REFERENCES

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