Potentiometric Studies of Some Binary Complexes of Cu(II), Ni(II), Co(II), and Mn(II) With Ligands Containing O-O Donar Atoms

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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-[{3-(3',4'-dimethoxyphenyl)}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[M(II)], have been obtained at $30^0 \pm 1^0$ C by liner plot of pH against log $\tilde{n}_A / 1 - \tilde{n}_A$. At each point on straight line pH + log $\tilde{n}_A / 1 - \tilde{n}_A = pK^H$. pK_1^H and pK_2^H values were obtained in the range $\tilde{n}_A$ 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 potentiometric ally as well as spectrophotometrically[2,3]. Some of the coumarins show distinct physiological, photodynamic, antibacterial activities[4] and have been reported as an anti-HIV agent[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[8,9]. 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.

The present communication deals with synthesis of *Bis – (3-[{3-(3',4'-dimethoxyphenyl)}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[M(II)]*, which may be used as an analytical reagent. It belongs to chalcone series[10]. Chalcones are the compounds which are obtained by the condensation of aromatic ketone with an aldehydes; which is chelated with transition metals. The composition of complex was determined by finding their stability constant by the pH metric titration study of these complexes.

II. METHODS AND MATERIAL

The ligand was prepared and purified by the method reported in the literature[11]. All the reagents were of AR grade. All the melting points were determined in open capillary tubes and are uncorrected. Infrared spectra (KBr)(νmax, cm^{-1}) were recorded on a Shimadzu 435 –IR Spectrophotometer. Elemental analyses are quite comparable with their structure. Elemental analyses of metal complexes indicates that the metal: ligand (M:L) ratio is 1:2 for all the divalent metal ions. The conductivity of metal complexes were determined using Thoshniwal Conductivity Bridge.

Synthesis of 3-[{3-(3',4'-Di methoxy phenyl)}-prop-2-enoyl]-4-hydroxy-6 methyl-2H-chromen-2-one.

A mixture of 3-Acetyl-4- hydroxy-6-methyl-2-benzopyranone (2.52 gm, 0.01M); 3', 4'-di methoxy benzaldehyde (0.025 M) and piperidine (1 ml) were added into ethanol (50 ml). The reaction mixture was

refluxed on water bath for 4 hrs., cooled and solid was separated. Then it was crystallised from suitable solvent, reddish yellow coloured compound was obtained. Yield 70%, M.P. 217°C. Found: C, 68.85%, H, 4.91%, O, 26.23% for $C_{21}H_{18}O_6$ required C, 68.80%, H, 4.85%, O, 26.15%.

Synthesis of Bis [3-[{3-(3', 4'-Di methoxy phenyl)}prop-2-enoyl] 4-hydroxy-6- methyl-2H-chromen-2-one]copper(II)complex [$Cu(C_{21}H_{17}O_6)_2(H_2O)_2$].

Copper chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide was added to get the pH between 10.5-11.0. It was refluxed with excess of alcoholic solution of 3-[{3-(3', 4'-Di methoxy phenyl)} prop-2-enoyl] 4-hydroxy-6-methyl-2H-chromen-2-one (a) (0.1M) on a water bath for half an hour when *light green* precipitates of copper complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100° C. The complex was crystallized from DMF. Yield 62%. Found : C, 60.90%, H, 4.59%, Cu, 7.67 % for [$Cu(C_{21}H_{17}O_6)_2$]required C, 60.80%, H, 4.45%, Cu, 7.50%.

Similarly other metal complexes were prepared. The complexes did not show clear melting point. They charred at temperature above 290° C.

Conductivity

The conductivity of metal complexes was determined using Thoshniwal Conductivity Bridge. It was dissolved in DMF and conductivity was measured.

Conductivity of the DMF along was measured and solution of the complexes in DMF with different concentration was measured.

The molar conductivity was calculated using the formula.

Molecular conductivity = $\dfrac{1000 \times K}{C}$

Where, K=Conductivity of the sol. of the complexes in DMF. C = Concentration of the complexes(10^{-3} M). The conductivity data are in (Table-I) and the data indicates that the complexes are non- electrolyte in nature[12].

IR Spectral analyses

The Infrared spectra of the metal complexes were recorded on Shimadzu 435-IR Spectrophotometer between 4000-400 cm^{-1}.

The examination of the IR spectra of all the complexes reveals that

1) All the IR spectra have identical bands at their respective positions.
2) Most of the bands appeared in the spectra of ligand are observed at the similiar position in the IR spectra of metal complexes.
3) Only the discernible difference in the IR spectra of metal complexes has been appeared. The band between 3200 - 3400 cm^{-1} due to - OH group in the spectra of ligands is less broader in the spectra of all the metal complexes. This might be due to complexation of metal ion. The less broadness might be due to water molecules associated with complex formation.
4) In addition the IR spectra of complexes showed new bands between 590-500 cm^{-1} assigned to metal-ligand vibration (M-O).

Potentiometric study

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*[13]*. 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 ±0.1°c.

The metal ligand ratio was maintained at 1:5. The ligand concentration was maintained at 2.00 x 10^{-3} M and the metal ion concentration was maintained at 4.00 x 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 maintaed in all the titrations .60%(v/v) aqueous 1,4 dioxane were corrected by the method of Van-Uitert and Hass[14]. The log pK^H, and log_sK values were evaluated.

The method of Bjerrum & Calvin as modified by Irving and Rossotti[15] has been used to determine ñ, $ñ_A$, 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 dixoane + 4.0 ml. $NaNO_3$ (1.0M).
(2)   0.8 ml. HNO_3 (1.0 M) + 11.2 ml. water + 22.0 ml dixoane + 2.0 ml. ligand solution (0.1 M) + 4.0 ml. $NaNO_3$ (1.0 M).
(3)   0.8 ml. HNO_3 (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 $NaNO_3$ (1.0 M).

The proton-ligand formation curves is obtained on plotting $ñ_A$ versus pH. The metal-ligand formation curves were obtained on plotting ñ versus pL.

The value of proton ligand stability has been obtained by linear plot of pH against log $ñ_A/ 1 – ñ_A$. Metal -ligand stability constant has been obtained by extrapolating the linear plot of log ñ / 1 – ñ against pL and half ñ values.

The pK values for ligand were determined pH metrically for the first time ñ 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[16].

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.

III. RESULTS AND DISCUSSION

Table 1 : Proton ligand and binary metal ligand stability constants of metal complexes at temperature 30 $\pm 1°$ C

Proton-Ligand Formation Constants	Metal – ligand Formation Constants			
	Cu copmplex	Ni complex	Co complex	Mn complex
Log pK_1^H = 11.25	$LogK_1$= 11.25	$LogK_1$ = 11.25	$LogK_1$ = 11.25	$LogK_1$ = 11.25
Log pK_2^H = 3.40	$LogK_2$ =11.29	$LogK_2$ = 10.78	$LogK_2$ = 10.52	$LogK_2$ = 09.71
	Logβ = 22.54	Logβ = 22.03	Logβ = 21.77	Logβ = 20.96

IV. ACKNOWLEDGEMENT

V. REFERENCES

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