

Potentiometric Studies of Some Binary Complexes of Fe(II) with Ligands Containing Coumarin Moiety

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ABSTRACT

The present paper describes the study of the complex formation of Ferric(III) ion with the chalcones derived from 3-acetyl- 4-hydroxy-6-methyl-coumarin and cinnamaldehyde, 3,4-dimethoxybenzaldehyde and 2-nitrobenzaldehyde. The stability constant of their complexes with Ferrous(II) ions, have been studied by using Irving-Rossotti method at constant temperature $30 \pm 1^\circ\text{C}$ and ionic strength $\mu = 0.1 \text{ M dm}^{-3}$.

Keywords: Ferric(III) ions, Binary complexes, Stability constants, pH Metric titration.

I. INTRODUCTION

Chalcone plays a vital role in the synthesis of many heterocyclic compounds as well as metal complexes. 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 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 chalcones of 4-Hydroxy coumarin with Fe(III) pH metrically.

The present communication deals with synthesis of Bis-(3-[(3-(cinnamyl))-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[Fe(III)], **(Compd.2a)** Bis-(3-[(3-(3',4'-dimethoxyphenyl))-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[Fe(III)] **(Compd.2b)** and Bis-(3-[(3-(2'-nitrophenyl))-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[Fe(III)] **(Compd.2c)**, 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 ligands were 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)(ν_{\max} , 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.

Synthesis of 3-[[3-(3',4'-Di methoxy phenyl)}-prop-2-enoyl]-4-hydroxy-6methyl-2H-chromen-2-one.(Compd.1b)

A mixture of 3-Acetyl-4- hydroxy-6-methyl-2-benzopyranone (2.52 gm, 0.01M); 3', 4'-dimethoxybenzaldehyde (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 $\text{C}_{21}\text{H}_{18}\text{O}_6$ 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]iron(III)complex $[\text{Fe}(\text{C}_{21}\text{H}_{17}\text{O}_6)_2(\text{H}_2\text{O})_2]$.(Compd.2b)

A mixture of ferric Chloridesolution (10.0ml., 0.1M) diluted to 50 ml. and ammonium hydroxide followed few drops of glacial acetic acid to get the pH between 5.0-6.0. 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 3-4 hours when reddish coffee precipitates of iron complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100°C . The complex was crystallized from DMF. Yield 61%.Found : C,61.20%, H, 5.0%,Fe, 6.6 % for $[\text{Fe}(\text{C}_{21}\text{H}_{17}\text{O}_6)_2]$ required C, 61.32%, H, 5.11%, Fe, 6.79%.

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

IR Spectral analyses

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

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

- (I) All the IR spectra have identical bands at their respective positions.
- (II) Most of the bands appeared in the spectra of ligand are observed at the similar position in the IR spectra of metal complexes.
- (III) The band between $3200\text{ - }3400\text{ cm}^{-1}$ 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.
- (IV) In addition the IR spectra of complexes showed new bands between $590\text{-}500\text{ cm}^{-1}$ assigned to metal-ligand vibration (M-O).

Potentiometric Study

The solution of the ligands were prepared in AR Grade 1,4dioxane. 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 $\pm 0.1^\circ\text{C}$.**

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[14]. The $\log pK^H$, and $\log K$ values were evaluated.

The method of Bjerrum & Calvin as modified by Irving and Rossotti[15] has been used to determine \tilde{n} , \tilde{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. HNO_3 (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 NaNO_3 (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.

III. RESULTS AND DISCUSSION

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 $-\text{OH}$ group.

Thus the binary $\text{ML}_2(\text{H}_2\text{O})_2$ 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.

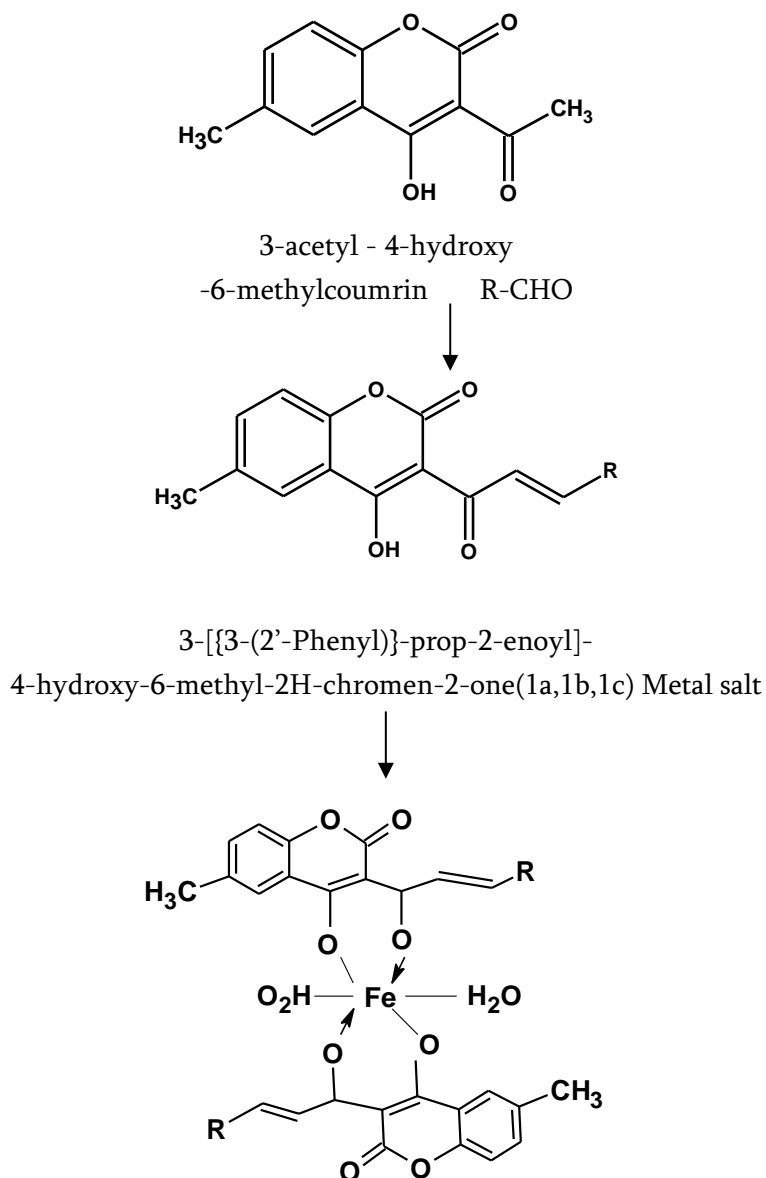
Table – I : Proton ligand and binary metal ligand stability constants of metal complexes at temperature $30 \pm 1^\circ \text{C}$.

Metal-ligand Formation Constants		
2(a)	2(b)	2(c)
LogK ₁ = 11.21	LogK ₁ = 11.25	LogK ₁ = 11.02
LogK ₂ =11.60	LogK ₂ =10.25	LogK ₂ =09.96
Logβ = 22.81	Logβ = 21.50	Logβ = 20.98
Proton-Ligand Formation Constants		
Log pK ₁ ^H = 11.21	Log pK ₁ ^H = 11.25	Log pK ₁ ^H = 11.02
Log pK ₂ ^H = 3.62	Log pK ₂ ^H = 3.40	Log pK ₂ ^H = 3.58

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Scheme



Bis-(3-[[3-(Aryl)]-prop-2-enoyl]
-4-hydroxy-6-methyl-2H-chromen-2-one) Fe (III)Complex (2a,2b,2c)

Where,

R= Cinnamyl, 3'4'-dimethoxy phenyl and 2'-nitro phenyl

V. REFERENCES

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