Spectrophotometric Study of Ferrous(II) and Ferric(III) Metal Complexes

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Abstract

The stability constant of complexes of Fe(II) and Fe (III) metals with 8-aceto-7-hydroxy-coumarin hydrazone was determined by Job's method at Wavelength 440 and 570 nm by keeping metal:ligand ratio is 1:1. The structure elucidation have been done by elemental analysis, IR spectra, conductivity and Magnetic studies.

Key words : Coumarin, hydrazone, metal complex, spectrophometric study.
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Introduction

The usefulness of coumarins and coumarin derivatives have been shown in various areas of analysis [1]. Stability constant of metal complexes have been determined by different methods such as spectrophotometry and potentiometry. Antiallergic action of coumarin in mice has been reported [2]. Coumarins can also be used as fluorescent probes in the study of membrane and protein preparations [3]. The complex of Mn(II), Ni(II), Co(II), Cu (II), Zn(II), Cd(II) and Hg(II) with 4-oxo-4H-1-benzobenzyl pyran-3(carboxaldehyde-4-chlorobenzyl hydrazone) and 4-oxo-4H-1-benzo pyran-3(carboxaldehyde-4-methylbenzyl hydrazone) have been synthesized and characterized[4].

The conditional stability constant of the complexes were determine from Yoe and Jones mole ratio method[5] and job's continuous variation method. In continues of our earlier work[6] we thought worthwhile to synthesize Fe(II) and Fe(III) metal complexes of hydrazone of 7- hydroxy coumarin and studied their stability constant spectrophotometrically.
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Results and Discussion

All the compounds gave satisfactory elemental analysis values and are close with the calculated value (**Table-IV**)

The solids do not melt sharply and undergo decomposition above 260^0C temperature. The chelates described here are also investigated for their magnetic susceptibility. The metal chelate of Fe(II) and Fe(III) are paramagnetic in nature and having high spin tetrahedral geometry..

Most of the band appeared in the spectra of corresponding ligand are observed at similar position in the IR spectra of metal complexes. The broad band between 3600-3400 cm^{-1} in ligand is disappeared in spectra of metal complex. This shows that H, of O-H group is involved in chelate formation with metal. The peak at 1720 cm^{-1} is attributed to δ-lactone ring of coumarin. All compounds containing the C=N group show a streaching band in the 1689-1471 cm^{-1} region of spectrum. A broad band in the region 3300-3250 cm^{-1} remains unchanged after complexation, reveals that –NH$_2$ is free in metal complex.

One new band in infrared appears at 560-580 cm^{-1} which probably due to M-O, M-N band[11]. Job's method of continuous variation could be made applicable and this study revealed that the chelates of Fe(II) and Fe(III) are formed with metal ligand molar ratio 1:1.

Materials and Methods

All chemicals used in the present work were of A.R. grade, melting point of compound were determined on open capillary tubes and are uncorrected. Molecular weight is determined by Rast's method. Job's method of continuous variation has been applied for confirming metal-ligand ratio and stability constant. Molar conductivity was measured on systronics conductivity meter using DMF. The magnetic measurements were made at room temperature by the Gouy balance method[7]. Infra red spectra were measured in the range 4000-400 cm^{-1} on a Schimadzu FT IR-801 spectrophotometer with KBr pellets.

The ligand 8-aceto-7-hydroxy-coumarin hydrazone(AHCH) is prepared[8] by condensing 8-aceto-7-hydroxy-coumarin with hydrazine hydrate, which is prepared from 7-hydroxy –coumarin by Fries migration and Acetylation. Complexes were prepared by standard procedure[9].

Synthesis of 8-Aceto-7-Hydroxy- coumarin hydrazone
An ethanolic solution of 8-acetoxy -7-Hydroxy- coumarin (20.4 gm), Hydrazine hydrate(3.5 ml) and pyridine (1.0 ml) were mixed together in a round bottomed flask, fitted with reflux condenser. The mixture was refluxed on water bath at 135° C for 1 hour then it was left to cool overnight and then it was neutralized by adding dilute KOH solution. The solid hydrazone obtained was separated and washed with absolute alcohol. Reddish crystalline needles of hydrazone were obtained. Yield: 72%, m.p. : 160°C.

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Synthesis of Bis -[8-aceto -7-Hydroxy- coumarin hydrazone]Ferrous(II)complex

1% ethanol solution of 8-aceto-7-hydroxy- coumarin hydrazone was added dropwise to a warm Ferrous ammonium sulphate solution maintaining the pH of the mixture at pH 7.5 during the reaction. Yellowish brown precipitates thus obtained were washed with warm ethanol. The precipitates are soluble in chloroform, carbon tetrachloride and benzene. The m.p. of Bis -[8-aceto -7-Hydroxy- coumarin hydrazone]Ferrous(II)complex is 222°C.

Synthesis of Bis -[8-aceto -7-Hydroxy- coumarin hydrazone]Ferric(III)complex

1% ethanol solution of 8-aceto -7-hydroxy- coumarin hydrazone was added dropwise to a warm Ferric chloride solution maintaining the pH of the mixture at pH 6.5 to 7.0 during the reaction. Light brownish yellow precipitates thus obtained were washed with warm ethanol. The precipitates are soluble in chloroform, carbon tetrachloride and benzene. The m.p. of Bis -[8-aceto -7-Hydroxy- coumarin hydrazone]Ferric(III)complex is 254°C.

Molecular weight determination by Rast's method

The molecular weights of the metal chelates were determined by Rast's method using pure Camphor. In each case,

> Weight of complex is taken 0.2 gm.
> Weight of Camphor is taken 2.0 gm.
> K_f of Camphor is taken 39.68^{0} C/1000 ml.

The results are recorded in the **Table-I**.

Table – I : Molecular weight determination data by Rast's method

Sr. No.	Chelates with -8-aceto-7-hydroxy coumarin hydrazone	Depression in F.P.		Molecular weights	
		Theoretical (T_c)	Experimental (T_o)	Theoretical (M_c)	Experimental (M_o)
1	$Fe(C_{11}H_9O_3N_2)_2$	8.02	7.9	272.85	274.0

Spectrophotometric Study

The composition of Fe(II) and Fe(III) chelate with the reagent 8-aceto-7-hydroxy coumarin hydrazone (AHCH) has been determined on the basis of Job's continuous variation method.

Composition of Fe(II) (AHCH)₂ and Fe(III)(AHCH)₂ complexes by Job's continuous variation method

A 0.002 M solution of Fe(II)and Fe(III) was prepared by suitable dilution of the standard solution. The solution of reagent AHCH(0.002M) was prepared in absolute alcohol or DMF. The solution of metal salt and the regent were mixed in varying proportions as under:

> Metal ion solution. 1 2 3 4 5 6 7 8
> Reagent solution . 9 8 7 6 5 4 3 2

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pH of the solution was adjusted to 6.5. The precipitated complex was extracted with three 5 ml portion of chloroform and final volume of chloroform to 25 ml. The absorbance of chloroform extracts were measured at 440 and 570 nm. The results are tabulated in **Table –II** and **Table-III**.

It is evident from the graph that absorbance gradually increases up to molar composition of metal to the reagent and after that it becomes constant indicating 1:1 stoichiometry of the complex.

Evaluation of stability constant

$$MLn \quad = \quad M+nL$$
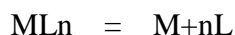
$$C(1-\alpha) \quad C\,[n.c\ \alpha]^n$$

$$Ks \ = \ c(1-\alpha)/c[n.c\ \alpha]^n$$

Taking n=2 in this case the equation reduces to

$$Ks = 1 - \alpha/4\ c^2\ \alpha^2 \quad \text{Where} \quad \alpha = (Em-Es)/Em$$

Em= Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines.
Es =Absorbance at the stoichiometry molar ratio of the metal to reagent in complex.

Calculation of stability constant

The stability constant is calculated from the above relation. The standard free energy change ΔG^0 for the formation reaction of complex has been calculated at 25 C^0 using the formula:

$$\Delta G^0 \ = \ - RTLnK$$

Job's Method	Em	Es	α	Ks	ΔG^0
Fe(II)λ=440	0.174	0.170	0.022	9.78×10^8	-12.259kcal/mole
Fe(III) λ=440	0.092	0.090	0.021	9.79×10^8	-12.266kcal/mole
Fe(II) λ=570	0.118	0.115	0.026	9.74×10^8	-12.256kcal/mole
Fe(III) λ=570	0.065	0.063	0.030	9.70×10^8	-12.253kcal/mole

Fe(II)(AHCH)$_2$
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Metal solution	: 0.002M
Ligand solution	: 0.002M
Final volume of Chloroform extract	: 25ml
Wavelength	: 440nm, 570nm.
pH	: 6.5

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Table-II : Job's method for Bis[8-aceto -7-hydroxy- coumarin hydrazone] Ferrous (II) complex

Ferrous Solution Taken ml	Reagent Solution ml	Optical Density	
		λ=440 nm	λ=570 nm
1	9	0.050	0.030
2	8	0.083	0.053
3	7	0.115	0.078
4	6	0.143	0.098
5	5	0.170	0.115
6	4	0.153	0.097
7	3	0.127	0.073
8	2	0.094	0.050

Reagent 0.002 M in C_2H_5OH
$FeSO_4 (NH_4)_2 6H_2O = 0.002$ M
Wavelength used   λ= ○ 440 nm
                               λ= □ 570 nm

Reagent
8-aceto-7-hydroxy-coumarin hydrazone
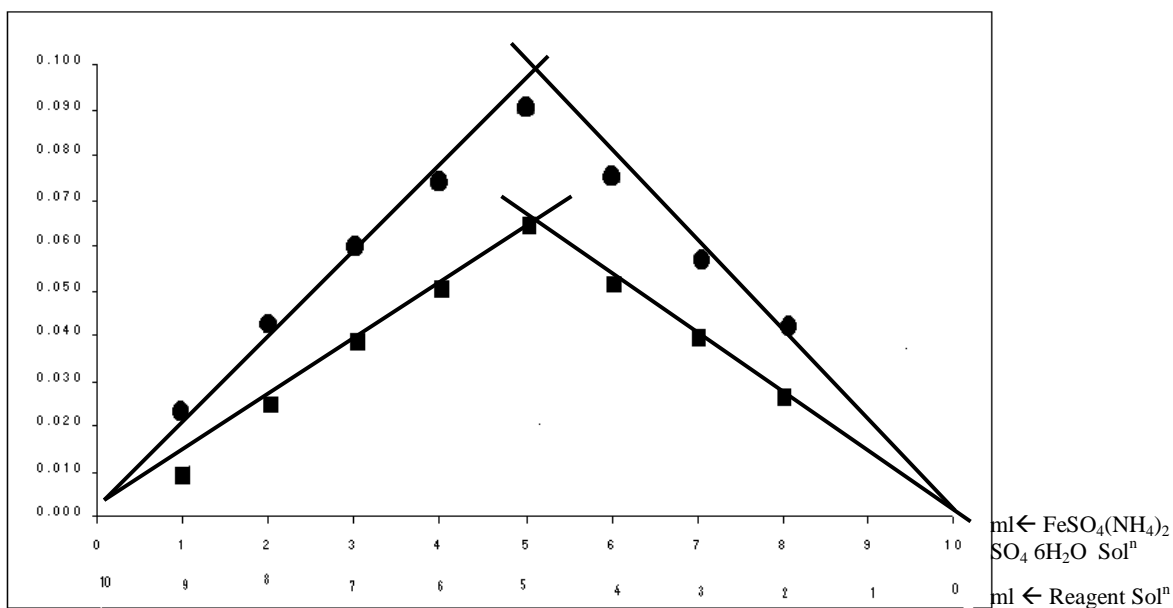
Metal: Ligand ratio 1:1

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Reagent 0.002 M in C_2H_5OH
Ferric chloride Solution = 0.002 M
Wavelength used λ= ○ 440 nm
                     λ= □ 570 nm

Reagent
8-aceto-7-hydroxy-coumarin
hydrazone

Metal:Ligand ratio 1:1
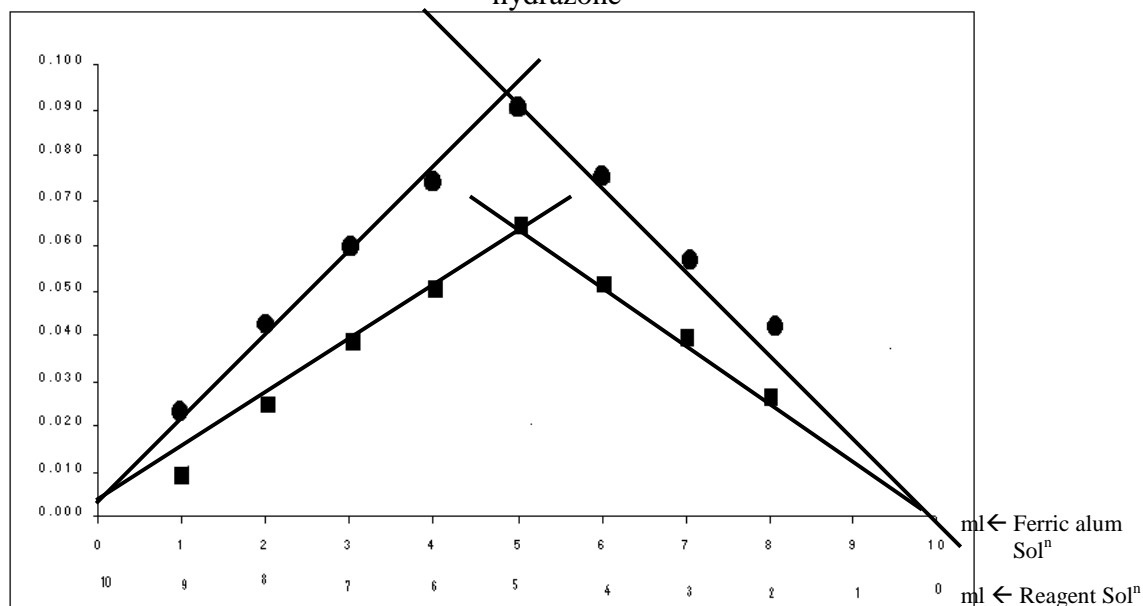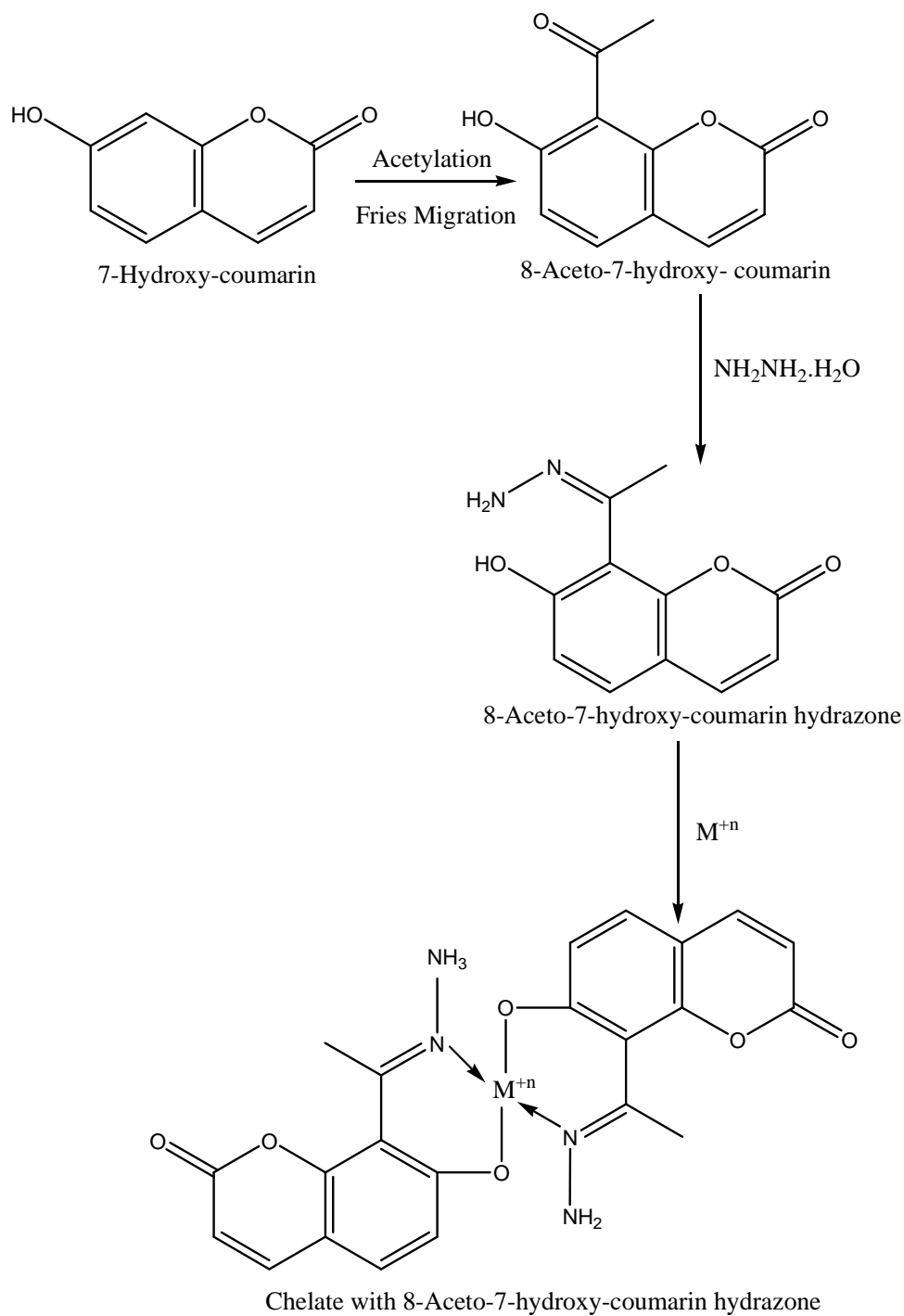
Table-III: Job's method for Bis[8-aceto -7-hydroxy- coumarin hydrazone] Ferric (III) complex

Ferric Solution Taken ml	Reagent Solution ml	Optical Density	
		λ=440 nm	λ=570 nm
1	9	0.035	0.021
2	8	0.051	0.034
3	7	0.066	0.046
4	6	0.080	0.057
5	5	0.090	0.063
6	4	0.075	0.052
7	3	0.062	0.040
8	2	0.045	0.027

Conductivity measurements
Molar conductance data of the complexes were measured in the solvent DMF and the complexes were found to be non electrolytic[10-11]in nature. Conductivity value of the complexes are lie in the range 8.1-10.8 $Ohm^{-1}cm^2 mol^{-1}$.

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Scheme-1: Stepwise preparation of hydrazone and their chelates

7-Hydroxy-coumarin

8-Aceto-7-hydroxy- coumarin

8-Aceto-7-hydroxy-coumarin hydrazone

Chelate with 8-Aceto-7-hydroxy-coumarin hydrazone

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Conclusion

The spectral study, Spectrophotometric study and magnetic study of these metal complexes of hydrazone reveals that all the metal complexes are having high spin tetrahedral geometry and the metal ligand Ratio is 1:1. The ligand can be good analytical reagent for some metal ions.

Table – IV : Elemental data of compounds

Chelate with 8-aceto-7-hydroxy coumarin hydrazone							
Mol. Formula	Mol. Wt.	% of Elements					μ_{eff} in B.M.	
		M	C	H	(O)	N	I= 6 Amp.	I= 4 Amp.
$Fe(C_{11}H_9O_3N_2)_2$	472.94	20.51 (20.53)	48.34 (48.33)	3.28 (3.29)	17.55 (17.57)	10.27 (10.25)	4.62	5.09
$Fe(C_{11}H_9O_3N_2)_2$	472.94	20.51 (20.53)	48.34 (48.33)	3.28 (3.29)	17.55 (17.57)	10.27 (10.25)	5.69	6.10

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