MULTIDISCIPLINARY RESEARCH

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25

Spectrophotometric Complex studies of Fe(III) with 2-hydroxy acetophenone and its Chloro substituted derivatives.

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Abstract:

The purpose of the present work was to investigate the Spectroscopic Complex studies of Fe(III) with 2-hydroxy acetophenone and its Chloro substituted derivatives in 50% (v/v) ethanol-water mixture solution, as the color of the complex formed was light pink. The minimum and maximum absorbance at two different pH values, the energy of activation and thermodynamic K were determined.

Keywords: OHA=2-hydroxy acetophenone, 3-Cl=3-Chloro,2-hydroxy acetophenone, 4-Cl=4-Chloro,2-hydroxy acetophenone, 5-Cl=5-Chloro, 2-hydroxy acetophenone, 3,5$(Cl)_2$=3,5 dichloro,2-hyroxy acetophenone.

Introduction:

Spectrophotometric methods are used to obtain equilibrium data. It is an effective analytical tool for the determination of structures, dissociation constants of indicators and many other organic compounds[1-5].

This technique is considered to be complementary to the Potentiometric measurements. They are particularly useful and employed for Fe(III)complexes. It includes a number of ligands having phenolic -OH group. Iron has been determined spectrophotometrically using various reagents[6-9]. It can used for aqueous or aqua-organic solvent systems. Its measurements are mainly confined to Ultra-violet and Visible regions.

To determine the stability constants of a given complex spectrophotometrically, it is important to know the number of ligands attached to the metal ion, and determination of composition of the complex. This problem can be solved by using the Jobs method of continuous variation[10].

Jobs method has been adopted in the present investigation. It can be used for the determination of the composition of the complex. It was further modified by Vosburgh and Gould[11]. It gives reliable and good results, only when one species is present in the solution.

Taking into consideration the information about Fe(III) attempt has been made to report the thermodynamic stability constant of Fe (III) with 2-hydroxy acetophenone and its Chloro substituted derivatives by Jobs method.

Experimental:

SD Fine (AR grade) chemicals and reagents were used in this investigation. The measurement of absorbance was made by using Chemita, 215-D Spectrophotometer. It had an accuracy of +0.01 it had an range 350nm to 700nm. The pH of solutions was measured on the Elico digital pH meter model (LI-120). The solutions were brought to a desired value of pH by the addition of HCl or NaOH as the case may be. To investigate the complex formation process between Fe(III) with 2-hydroxy acetophenone and its Chloro substituted derivatives, Jobs method was applied.

Jobs method:

Equimolar solutions of the ligand and the metal ion were prepared. Ten different mixtures of the solutions were prepared by adding 'x' ml of a metal ion solution to (10-x) ml of ligand solution. The value of 'x' ranged from 1 to 9 ml. $NaClO_4$ solution (5ml) was added to maintain a constant ionic strength. The total volume of the solution was made to 50 ml by addition of alcohol and water in a required proportion to maintain 50 %(v/v) ratio. The pH of all mixtures was adjusted to the same value by the addition of few drops of either HCl or NaOH. Fresh solutions were always used for all the measurements.

Result and discussion:

In the present investigation it was observed that the color of the complex was light pink. It changes as the pH of the solution goes on increasing. Therefore it was decided to do Spectrophotometric study of Fe(III) with 2-hydroxy acetophenone and its Chloro substituted derivatives in 50% (v/v) ethanol-water mixture solution.

An attempt was made to scan the spectra of all ligands for along range of 200-600 nm to know their maximum and minimum absorbance.

It revealed that the absorption of all ligands taken for the experimental purpose were higher and lower than 210 and 350 nm respectively.

The values of max of all ligands viz. 2-hydroxy acetophenone and its Chloro substituted derivatives are listed in Table 1.

It has been observed from this table that in 2-hydroxy acetophenone, the absorbance is minimum at 212.5 whereas maximum at 328 nm.

The absorbance of other ligands viz.3-Cl, 4-Cl, 5-Cl, and 3, 5 $(Cl)_2$.
were determined and listed in Table1.

Table1:

Sr.no	Name of the ligand	Abbreviations	Tnm	€
1.	2-hydroxy acetophenone	OHA	328	330
			253	983
			212.5	153
2.	3-Chloro,	3-Cl	332	364
	2-hydroxy acetophenone		257	965
			216	1772
3.	4-Chloro,	4-Cl	322	373
	2-hydroxy acetophenone		260	1158
			215.5	1594
4.	5-Chloro,	5-Cl	336.5	323
	2-hydroxy acetophenone		252.5	689
			219.0	2026
5.	3,5-dichloro,	3,5 $(Cl)_2$	347	333
	2-hydroxy acetophenone		256	686
			220	1987

The spectrophotometric data provided for the Jobs method are listed in Table 2.

Table 2: **Spectrophotometric data of Job's method of continuous variation**
Fe (III) = 2 hydroxy acetophenone, pH = 2.10, Color = Pink.
λmax = 530nm. Solvent: Ethanol- Water mixture solution (50%)
Fe (III) = OHA $=1\times10^{-2}\mathrm{M}$

Fe (III)solution (ml)	OHA Solution	O.D. (absorbance)
1	9	0.194
2	8	0.295
3	7	0.360
4	6	0.395
5	5	0.412
6	4	0.374
7	3	0.291
8	2	0.210
9	1	0.101

The verification of the Beers law has been represented in Table 3 and in the figure given below:

Table: 3

Verification of Beers Law:

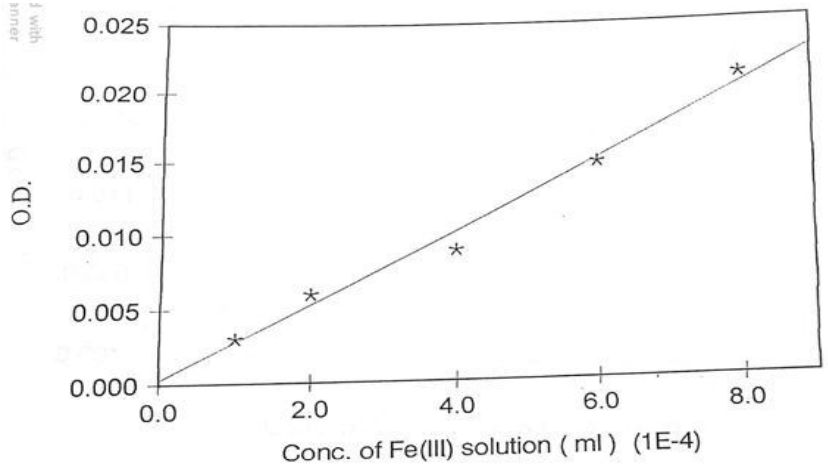
Fe (III) = 2 hydroxy acetophenone, pH = 2.10, Color = Pink.

max = 530nm.

Solvent: Ethanol- Water mixture solution (50%)

Fe (III) = OHA $=1\times10^{-2}\mathrm{M}$

Conc. of Fe (III)solution(ml)	O.D. (absorbance)
1	0.003
2	0.006
4	0.009
6	0.015
8	0.021



The stability constant of a complex can be determined by Jobs method . It can by changing concentrations of either ligand or metal ion , then optical density can be measured at suitable pH and wavelength. By knowing the optical density the extinction coefficient values can be determined. After it the stability constant values can be obtained. The values of Conditional stability constant(K_c) can be obtained.The values of it does not take into account the dissociation of the ligand.

A relationship between conditional stability constant (K_C) and Thermodynamic stability constant (K_{th}) have been given by Banks and Singh[12].

The purpose of selecting 2-hydroxy acetophenone is that the pK value it was reported by Naikwade.[13]Therefore it was convenient to report the thermodynamic 'K' of them which are listed in Table(4), which are on the lines of Jahagirdar[14].

Table 4: Values of λ_{max} , K_C, pK_{th}, K_{th}:

Name of the ligand	λ_{max}	**pK_{th}**	**K_C**	**K_{th}**
2-hydroxy acetophenone	530	10.70*	2.97	9.07

Similarly the value of energy of transition (ΔE) was determined .

It was determined by using the formula $\Delta E = h/c\ \lambda$. The value of 2-hydroxy acetophenone was considered as E_0(2.7283) obtained from literature[13] and that of others as E_1, thus values of ΔE were determined.

The values of λ_{max} were determined at two different pH values one ranging from pH =2.00 to 3.00 and second pH =3.00 to 4.00. Therefore the values of ΔE were expressed as ΔE_1 and ΔE_2.

The values of them are listed in Tables 6 :

Table 6: Values of λ Δ E_1 and ΔE_2 of 1:1 Fe(III) complex:

Fe (III) complex with ligands	λmax nm	pH = 2 -3 Δ E X 10^{-8}eV	Δ E1	λmax	pH = 3-3.5 X 10^{-8}eV	Δ E2
OHA	535	2.7283	-	530	2.7201	-
3-Cl	525	2.7201	10	490	2.6901	35
4-Cl	505	2.7032	30	500	2.6989	25
5-Cl	515	2.7118	20	490	2.6901	35
3,5 (Cl)2	500	2.6989	35	495	2.9460	30

Thus in the present work, an attempt was made determine and report the above data, as references of them were not available.

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