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pH metric studies of Ferrous (II) complexes of substituted derivative of Coumarin

KB Vyas[1], KS Nimavat[1], GR Jani[2*], RP Patel[3], JA Chaudhary[4] and MV Hathi

[1]Department of Chemistry, Government Science College, Gandhinagar, Gujarat, India.
[2]Department of Chemistry, M. N. College, Visanagar, Gujarat, India.
[3]C.U.Shah Science College, Ahmedabad, Gujarat, India.
[4]Science College Petlad, Gujarat, India.

ABSTRACT

The Present work is undertaken to make a systematic solution study of the complex formation of Ferrous (II)ions with the chalcones derived from 4-hydroxy-6-methyl-3-acetyl-coumarin and 9- Anthryl benzaldehyde,3-choloro benzaldehyde,3-Bromo benzaldehyde. The stability constants of their complexes with Ferrous (II) ions, have been studied by using Irving-Rossotti method at constant temperature $30 \pm 1^\circ$ C and ionic strength μ=0.1 M dM$^{-3.}$

Key words: Ferrous (II)ions, Binary Complexes, Stability Constants, Ligand, pH metric titration.

Corresponding author

INTRODUCTION

Many binary complexes of transition and inner transition metals have been studied potentiometrically [1,2]. Metal complexes of chalcone have been extensively studied because chalcone possess good synthetic flexibility, selectivity and sensitivity towards the central metal atom. Some coumarin derivatives are reported as an anti-HIV agent [3].

The literature survey reveals a wealth of data on the transition metal complexes but complexes of chalcone have been less investigated as ligands. So in continuation of our earlier work [4,5] we thought to synthesize some chalcones of hydroxy coumarin as a ligand and their Fe(II) complexes, Bis –(3-[{3-(substituted phenyl)}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[Fe(II)](H_2O)$_2$. The stability constants of synthesized compounds have been studied pH-metrically by Irving and Rossotti method [6].

EXPERIMENTAL

The ligand compounds 3-[{3-(9'-Anthryl) }-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromene-2-one (2a), 3-[{3-(3'Bromo phenyl) }-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromene-2-one 2(b) and 3-[{3-(3'Chloro phenyl) }-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromene-2-one 2(c) are prepared and purified by the method reported in the literature [7]. The solution of the ligand compounds were prepared in A R Grade 1,4 dioxane. The metal solution was prepared by dissolving ferrous ammonium sulphate of A R Grade in double distilled water and standardized by $KMnO_4$ [8]. The other reagents $NaNO_3$ (BDH), NaOH (BDH) and HNO_3 (BDH) of A R Grade were used and their solutions were prepared in double distilled water and standardized by the usual methods.

Proton ligand formation constants of the ligand and metal ligand formation constant of binary system were determined pH metrically by the method of Bjerrum and Calvin as modified by Irving and Rosootti [9] titration technique. pH-metric titration was carried out with systronic-µ pH meter 361 having combined glass electronic and temperature probe with maintained with readability $\pm$ 0.1^{o}C. The metal ligand ratio was maintained at 1:5. The total volume was maintained at 50 ml. All the solutions were titrated against 0.1 M Sodium hydroxide solution.

The titration curves are obtained by plotting pH versus volume of alkali. The logpK^H and logK values were evaluated.

The proton-ligand formation curves are 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.

RESULT AND DISCUSSION

The pK values of chalcones, which represent the deprotonation of phenolic –OH group were determined. 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 displacement of metal titration curve from ligand titration curve is in between 3.0-7.2 pH. The highest values of ñ obtained were about 2.0 indicating the formation of both 1:1 and1:2 complexes in solution. Metal-ligand complex formation occurred at pH lower than that of metal ion hydrolysis [10].

Table-I: Proton ligand and binary metal ligand stability constants of metal complexes at temperature 30 $\pm$ 0.2° C.

Metal – ligand Formation Constants		
2(a)	**2(b)**	**2(c)**
$LogK_1$ = 10.98	$LogK_1$ = 11.10	$LogK_1$ = 11.00
$LogK_2$ =09.36	$LogK_2$ = 09.33	$LogK_2$ = 09.91
$Log\beta$ = 20.34	$Log\beta$ = 21.03	$Log\beta$ = 20.91
Ligand PK^H Values		
Log pK_1^H = 10.98	Log pK_1^H = 11.10	Log pK_1^H = 11.00
Log pK_2^H = 3.27	Log pK_2^H = 3.45	Log pK_2^H = 3.76

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