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Investigation of Stability Constants of Selected Lanthanide(III)–Substituted Chalcone Complexes

G.D.Tambatkar

Department of Chemistry,Shri.D.M.Burungale Science And Arts College,Shegaon.Dist-Buldana pin-444203.(India)

Abstract

The complexation behaviour of Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III), and Lu(III) metal ions with two substituted chalcone ligands, namely **2′-hydroxy-(3,4-dioxymethylene)-5′-methylchalcone (Ligand-I)** and **2′-hydroxy-5′-methyl-4-methoxychalcone (Ligand-II)**, has been investigated using the pH-metric technique. The studies were carried out at an ionic strength of **0.1 M** and a temperature of **27 ± 0.1 °C** in a **70% dioxane–water medium**.

The experimental data were analysed to determine the **proton–ligand stability constants (pK)** and **metal–ligand stability constants (log K)**. The results indicate that all the investigated lanthanide(III) ions—Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III), and Lu(III)—form stable **1:1 and 1:2 metal-to-ligand complexes** with both substituted chalcone ligands under the experimental conditions. The stability constants provide useful information regarding the complexation behavior and relative binding affinities of these lanthanide(III) ions toward the selected chalcone ligands.

INTRODUCTION

Substituted chalcones constitute an important class of organic compounds possessing versatile coordination properties. The presence of electron-donating oxygen atoms, particularly phenolic and carbonyl oxygen, enables these ligands to interact effectively with a variety of metal ions through chelation. Such interactions frequently result in the formation of stable and intensely coloured metal complexes. Consequently, substituted chalcones have attracted considerable attention in equilibrium and coordination chemistry.

Several investigations have been reported on the determination of proton–ligand and metal–ligand stability constants of organic ligands and their metal complexes. **Khobragade et al.**[1] investigated the metal–ligand stability constants of UO_2(II) and Cu(II) complexes with selected substituted sulphonic acids. **Tekade et al.**[2] studied the complex formation equilibria of Co(II) and Cu(II) with substituted isoxazolines. **Meshram et al.**[3] investigated the metal–ligand stability constants of Pr(III), Nd(III), and Sm(III) chelates with substituted pyrazolines.

The complexation behavior of transition-metal ions with hydroxy-containing ligands has also been extensively investigated. **Rabindranath**[4] studied Cu(II) chelates with 2-hydroxy aromatic ketones and alkyl monoamines. **Khadikar et al.**[5] investigated metal chelates of 3-(2-hydroxyphenyl)-5-phenylisoxazoline with Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and UO_2(II) ions.

Mahajan et al.[6] investigated Cu(II) complexes with substituted sulphonic acids using potentiometric methods. **Mandakmare et al.**[7] studied the stability constants of UO_2(II) complexes with selected substituted coumarins at

an ionic strength of 0.1 M using pH-metric and spectrophotometric techniques. **P. J. Parmar et al.**[8] reported proton–ligand stability constants of several substituted heterocyclic ligands, including pyrazoles, isoxazoles, thioisoxazoles, pyrazolines, isoxazolines, and thiooxazolines, using pH-metric methods at an ionic strength of 0.1 M.

Pawar et al.[9] investigated proton–ligand and metal–ligand stability constants of transition-metal complexes with substituted pyrazolines by pH-metric methods. **Pulkeshi Desai et al.**[10] studied the formation constants of chelates of 2-hydroxybenzylidene-o-aminobenzothiazole with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions.

Studies involving lanthanide ions have also contributed significantly to the understanding of their solution-phase coordination chemistry. **Anu Sharma et al.**[11] reported pH-metric and thermodynamic investigations of metal chelates of lanthanide(III) ions with tridentate biprotic ligands. **Pratibha B. Agrawal et al.**[12] investigated the metal–ligand stability constant of HMAPAT, namely 2-[3′-(2″-hydroxy-5″-methylphenyl)pyrazol-5′-yl]-5-amino-1,3,4-thiadiazole, at an ionic strength of 0.1 M in a 70% ethanol–water medium.

The above literature indicates that considerable work has been carried out on the complexation behavior of substituted heterocyclic ligands, aromatic ligands, and selected transition and lanthanide metal ions. However, comparatively systematic equilibrium studies involving a series of **Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III), and Lu(III)** ions with structurally related substituted chalcone ligands remain of particular interest.

Therefore, in continuation of these investigations, the present study is undertaken to examine the **chelating and complex-forming properties of selected substituted chalcones with Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III), and Lu(III) ions** by the **pH-metric method**. The study aims to determine the proton–ligand and metal–ligand stability constants and to establish the stoichiometry and comparative stability of the resulting lanthanide(III)–chalcone complexes under controlled experimental conditions

EXPERIMENTAL

Materials and Reagents

The substituted chalcone ligands employed in the present investigation were synthesized in the laboratory by established procedures. The synthesized compounds were purified by crystallization and used for the equilibrium studies after obtaining satisfactory purity.

A **70% dioxane–water mixture (v/v)** was employed as the solvent medium for dissolving the substituted chalcones. Analytical-grade rare-earth metal nitrates (BDH) were used for the preparation of the metal-ion solutions. The metal salts were dissolved appropriately, and their concentrations were determined by standard analytical procedures. [13] The metal-ion solutions were prepared using double-distilled water.

A **0.1 M sodium perchlorate ($NaClO_4$)** solution was used as the supporting electrolyte to maintain a constant ionic strength throughout the potentiometric measurements.

Potentiometric Measurements

The protonation and metal–ligand complexation equilibria of the substituted chalcones were investigated by the **pH-metric technique**. Potentiometric measurements were performed using an **ELICO L1-613 pH meter** fitted with a combined glass–calomel electrode assembly. The instrument had a precision of approximately **±0.01 pH unit**.

Prior to the measurements, the pH meter was calibrated using a **0.05 M potassium hydrogen phthalate buffer (pH ≈ 4)** and a standard alkaline buffer of **pH ≈ 9**.

All titrations were performed at a constant temperature of **27 °C**, maintaining the ionic strength at **μ = 0.1 M using $NaClO_4$**. The total volume of each titration mixture was maintained at **50 mL**. The initial concentrations of the respective metal ions and ligands were kept constant for the corresponding series of experiments. Each potentiometric titration was repeated at least twice to ensure satisfactory reproducibility.

Titration Procedure

Three different solution systems were investigated potentiometrically. Each system was titrated against a standardized **0.2 M carbonate-free sodium hydroxide solution**. The final volume of each titration mixture was maintained at **50 mL**.

System I – Free Acid

The free-acid solution consisted of:

- 5 mL of $NaClO_4$ solution +5 mL of $HClO_4$ solution + 35 mL of dioxane + 5 mL of distilled water

This solution was titrated to establish the acid titration curve under the experimental conditions.

System II – Acid–Ligand System

The acid–ligand solution was prepared by mixing:

- 5 mL of $NaClO_4$ solution + 5 mL of $HClO_4$ solution + 35 mL of dioxane + 3 mL of distilled water + 2 mL of the appropriate ligand solution.

The resulting solution was titrated potentiometrically to obtain the ligand protonation data.

System III – Acid–Ligand–Metal System

For the metal–ligand studies, the following composition was employed:

- 5 mL of $NaClO_4$ solution +5 mL of $HClO_4$ solution + 35 mL of dioxane +1 mL of distilled water + 2 mL of ligand solution + 2 mL of the corresponding metal-ion solution

The metal–ligand solution was titrated under identical experimental conditions using 0.2 M carbonate-free NaOH.

The investigated lanthanide(III) ions were **Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III), and Lu(III)**.

Evaluation of Equilibrium Data

The potentiometric titration data were analyzed according to the **Irving–Rossotti method**[14]. The average number of ligand molecules attached to each metal ion, **(\bar n)**, and the corresponding free-ligand parameter, **pL**, were evaluated from the experimental titration data.

The overall ionic strength of the reaction medium was maintained at approximately **0.1 M** and calculated using the relationship:

$$\mu = 1/2 \ \ CiZi^2$$

where (Ci) represents the concentration of the individual ionic species and (Z_i) denotes its corresponding charge.

In calculating the ionic strength, the contribution of the various ionic species present in the reaction mixture was taken into account, including the contributions from **Na^+ and ClO_4^- ions** and other relevant ionic species.

The resulting potentiometric data were subsequently utilized for the evaluation of the **proton–ligand stability constants** and **overall metal–ligand stability constants** of the investigated substituted chalcone systems.

RESULT AND DISCUSSION

Proton-Ligand Stability Constant

The substituted chalcones employed in the present investigation can be treated as **monobasic ligands**, since they contain one ionisable proton associated with the phenolic –OH group. The ligand may therefore be represented as **HL**. The dissociation of the proton from the phenolic group can be expressed by the following equilibrium:

$$\mathbf{HL \rightleftharpoons H^{+} + L^{-}}$$

The proton-ligand stability constants were evaluated from the potentiometric titration data. The titration curves were constructed by plotting the **volume of NaOH added against the corresponding pH values** for the free acid and ligand-containing systems. These curves provide useful information regarding the ionization behaviour of the substituted chalcones.

A comparative examination of the titration curves revealed a distinct deviation of the ligand curves from the corresponding free acid ($HClO_4$) curve at approximately **pH 7.0**. The deviation continued progressively up to about **pH 12.0**. This systematic displacement of the ligand titration curves indicates the gradual deprotonation of the phenolic –OH group of the substituted chalcones.

The observed deviation between the free-acid and ligand titration curves thus confirms the participation of the phenolic proton in the acid–base equilibrium. The extent of this deviation provides the basis for evaluating the **proton-ligand stability constant (pK)** of the investigated substituted chalcones under the experimental conditions employed.

The value of n_A at various pH values were calculated from the acid titration curves (A) and ligand titration curves (B) by using formula of Irving and Rossotti[14]

Proton ligands stability constants were calculated from the plot of n_A Vs pH (fig-1 & fig-2). From this graph the values of pK were determined (half -integral method). By noting the pH at which $n_A = 0.5$. The accurate value of pK were estimated by pointwise calculation method which are presented in table one.

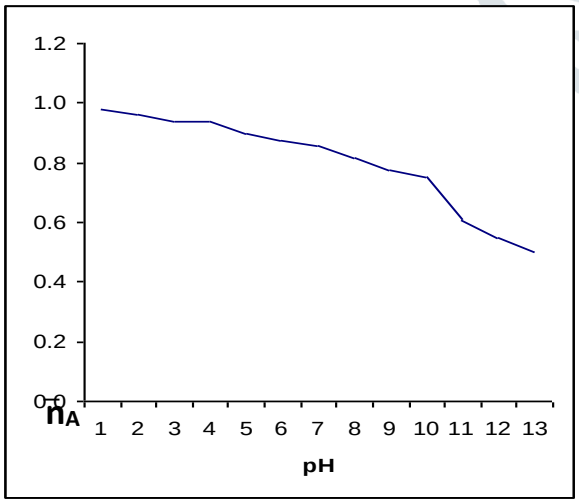

Fig – 1 [ligand -1]

(2^1 – Hydroxy (3,4 Dioxymethylene)

5^1 – Methyl Chalcone)

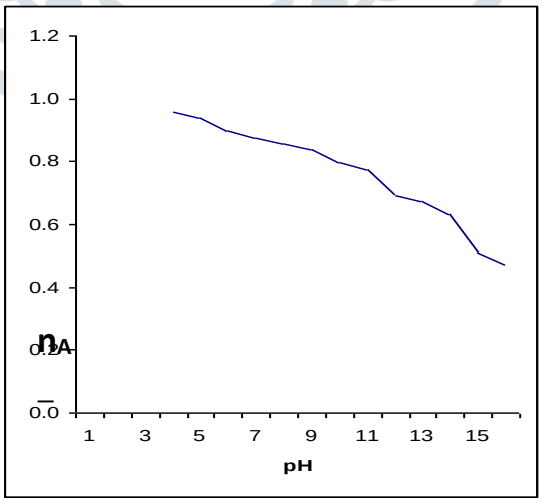

fig-2 [ligand-2]

(2^1 – Hydroxy 5^1-Methyl-

4 – Methoxy Chalcone)

TABLE – 1 :

DETERMINATION OF PROTON LIGAND STABILITY CONSTANT (pK) OF SOME SUBSTITUTED CHALCONES AT 0.1M IONIC STRENGTH.

Sr. No.	System	Constant pK	
		Half Integral	Point wise calculation
1	2^1- Hydroxy (3,4 Dioxymethylene) 5^1- Methyl Chalcone (ligand - 1)	11.50	11.54∀ 0.05
2	2^1- Hydroxy 5^1-Methyl - 4 – Methoxy Chalcone. (ligand - 2)	11.40	11.43∀ 0.04

pK value of ligand -1 is grater than ligand-2 this may be due to the effect of strong eΓ donating $–CH_3$ group that increase the pK values but decreases the dissociation in the following orders.

Ligand-1 > ligand-2

METAL LIGAND STABILITY CONSTANTS :

The metal ligand stability constants of Ce (III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb(III) & Lu(III) complexes with some substituted chalcones were determined by employing Bjerrum-Calvin pH –titration technique as adopted by Irving and Rossotti .

The formation of chelates between Ce (III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb(III) & Lu(III) and substituted chalcones was indicated by

i) The significant departure starting from pH 3.00 for Ce(III), Gd(III), Pr(III).

ii) And deviation of Nd(III), Yb(III), Sm(III), Lu(III) metal titration curve from ligand curve was observed from pH 4.50.

iii) And deviation of Dy(III) metal titration curve from ligand curve was observed from pH 5.00.

iv) The change in colour from light yellow to light brown and then dark brown as the pH was raised from 2.5 to 8.5.

TABLE -2 :

DETERMINATION OF METAL LIGAND STABILITY CONSTANTS

(LOG K) OF Ce (III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb(III) & Lu (III) COMPLEXES WITH SUBSTITUTED CHALCONES AT 0.1M IONIC STRENGTH.

Sr. No.	System	Constant	
		Log K_1 ie. pL_1	Log K_2 ie. pL_2
1	Ce(III)-ligand No.1	5.0	7.75
2	Pr(III)-ligand No.1	4.40	6.25
3	Nd(III)-ligand No.1	4.95	8.00
4	Sm(III)-ligand No.1	5.10	7.75
5	Gd (III)-ligand No.1	5.95	7.85
6	Dy (III)-ligand No.1	6.20	8.70
7	Yb(III)-ligand No.1	4.75	7.85
8	Lu(III)-ligand No.1	4.90	7.80

Sr. No.	System	Constant	
		Log K_1 ie. pL_1	Log K_2 ie. pL_2
1	Ce(III)-ligand No.2	4.75	7.25
2	Pr(III)-ligand No.2	4.15	7.70
3	Nd(III)-ligand No.2	5.48	8.45
4	Sm(III)-ligand No.2	5.10	8.10
5	Gd (III)-ligand No.2	4.75	7.75
6	Dy (III)-ligand No.2	4.25	7.15
7	Yb(III)-ligand No.2	4.80	5.65
8	Lu(III)-ligand No.2	4.95	8.50

It is observed that the metal ligand curve is well separated from the ligand titration curves suggesting thereby that the liberation of proton is due to chelation.

From the formation on curves the value of stability constant log K_1 and log K_2 were determined which corresponds to the PL values at n = 0.5 and 1.5 respectively. The most representative values are recorded in table 2. It could be seen from table 2 that log K values follows decreasing trend and increasing trend that is neither decreasing nor increasing trend is seen. This is due to eΓ releasing – CH_3 group.

The value of log K (log K_2 – log K_1) and log K_2/ log K_1 are presented in table 3. It is observed that the smaller difference may be due to trans-structure. The results shows that the ratio log K_2/log K_1 is positive in all cases this implies that there is little or no steric hindrance to the addition of secondary ligand molecules. From the three titration curves, n values were determined at various pH values. From the data the corresponding pL values were calculated. The n values were then plotted against the corresponding pL values to get formation curve of the metal complex equilibria (fig -3 and fig -4.)

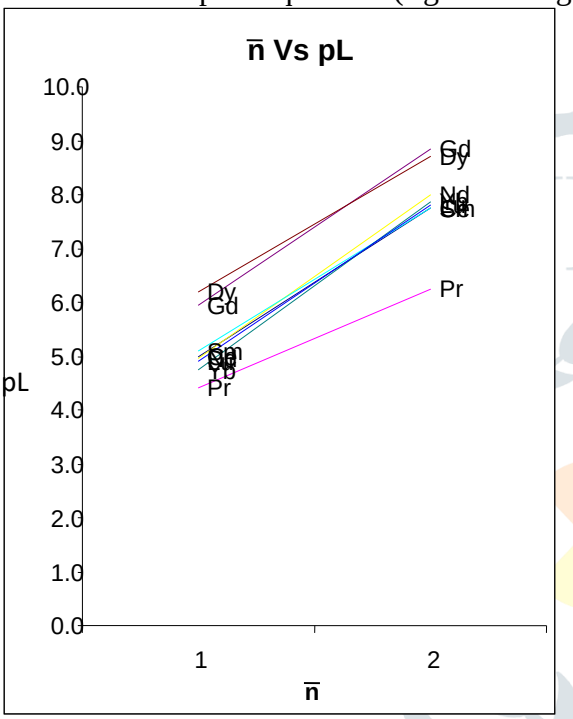

Fig –3[ligand -1]

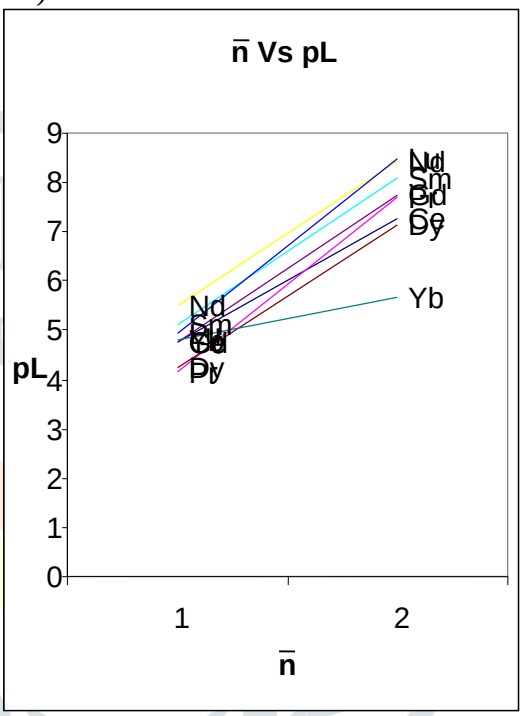

Fig –4[ligand -2]

TABLE -3 :

METAL- LIGAND STABILITY CONSTANTS AT 0.01M IONIC STRENGTH.

Sr. No.	System	log K_2- logK_1	log K_2/ log k_1
I	Ce(III)-ligand No.1	2.75	1.55
	Ce(III)-ligand No.2	2.50	1.52
II	Pr(III)-ligand No.1	1.85	1.42
	Pr(III)-ligand No.2	3.55	1.85
III	Nd(III)-ligand No.1	3.00	1.61
	Nd(III)-ligand No.2	2.97	1.54

IV	Sm(III)-ligand No.1 Sm(III)-ligand No.2	2.65 3.00	1.51 1.58
V	Gd (III)-ligand No.1 Gd (III)-ligand No.2	1.90 2.00	1.31 1.63
VI	Dy (III)-ligand No.1 Dy (III)-ligand No.2	2.50 2.90	1.40 1.68
VII	Yb(III)-ligand No.1 Yb(III)-ligand No.2	3.10 0.95	1.65 1.17
VIII	Lu(III)-ligand No.1 Lu(III)-ligand No.2	2.90 3.55	1.59 1.71

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