



STABILITY CONSTANTS OF Ce (III), Tb (III), Nd (III), Gd (III), & Dy (III), CHELATES WITH SOME SUBSTITUTED HETEROCYCLIC DRUGS

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ABSTRACT The interaction of Ce (III), Tb (III), Nd (III), Gd (III), & Dy (III), metal ions with Idoquinol 5,7-di-iodo-8-quinolinol (ligand - 1) And Chlorothalidon 2-chloro-5-(1-hydroxy-3-oxo-1,2-dihydroisindol-1-yl)-benzenesulfonamide (ligand - 2) have been investigated by pH – metric technique at 0.1 M ionic strength at $27 \pm 0.10^\circ\text{C}$ in 70% dioxane – water mixture. The data obtained were used to estimate the values of proton-ligand stability constant (pK) and metal- ligand stability constant log K. It is observed that Ce (III), Tb (III), Nd (III), Gd (III), & Dy (III), metal ions formed 1:1 and 1:2 complexes with all the ligands.

KEYWORDS :

INTRODUCTION

Substituted drugs are good complexing agents due to presence of electron donor oxygen. They form coloured complexes with metal ions.

Khobragade et al¹ have investigated the metal- ligand stability constants of Uo₂ (II) and Cu(II) complexes with some substituted sulphonic acids Tekade et al² have studied the complex formation of Co (II) and Cu (II) metal ion complexes with substituted Isoxazoline. Meshram Y.K. et al³ have investigated metal ligand stability constants of Pr (III), Nd (III) and Sm (III) Chelates with some substituted Pyrazolines. The interaction between Cu (II) – Chelates with 2-Hydroxy aromatic ketones and alkyl-monomines is studied by Rabindranath⁴ Metal Chelates of 3 (2-Hydroxy.Phenyl) -5-Phenyl isoxazoline with Be (II), Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Uo₂ (II), have been investigated by khadikar et al⁵

Mahajan et al⁶ have studied Cu (II), complex with sulphonic acid potentiometrically.

Mandakmare et al⁷ have studied the stability constants of Uo₂ (II) complexes with some substituted coumarines at 0.1 M ionic strength pH-metrically and spectrophotometrically. P.J. Parmar et al⁸ have studied the proton- ligand stability constants of some substituted pyrazoles, isoxazoles, thiosixazoles, Pyrazolines, isoxazolines and thio-oxazolines by pH – metrically at 0.1 M ionic strength. Pawar et al⁹ have studied proton- ligand stability and metal- ligand stability constants of transition metal ions with some substituted pyrazolines pH – metrically. Formation constants of chelates of 2- hydroxyl – benzilidene-o-Aminobenzothiazole with Co (II), Ni (II), Cu (II), Zn (II) and Cd (II), ions have been studied by Pulkeshi Desai and et al¹⁰.

pH-metric and thermodynamic studies on metal chelates of the lanthanon (III) ions with tridentate biprotic ligands have been carried by Anu Sharma et al.¹¹

Pratibha B. Agrawal and et al¹² have been studied the metal-ligand stability constant at 0.1 M ionic strength of 2[3(2-Hydroxy 5-Methyl anyl) pyrazol 5I-7I] -5-amino 1,3,4 thiazololes [HMAPAT] in 70% ethanol – water mixture.

After review of literature survey it was thought of interest to study the chelating properties of some drugs with Ce (III), Tb (III), Nd (III), Gd (III), & Dy (III), metal ions by pH metric method.

EXPERIMENTAL

All the chelating agents have been synthesized in the laboratory and the compounds were crystallized before use.

The substituted drugs are made soluble in 70% dioxane-water (v/v) was used as a solvent. Metal nitrates (BDH) were dissolved in perchloric acid and their concentration were estimated by standard method¹³. The metal ligand stability constants of some drugs were determined pH metrically. The nitrates of rare earths were used and their solutions were prepared in double distilled water. The solution of

sodium perchlorate was prepared (0.1M) and used for maintaining ionic strength constant.

pH metric titration were carried out with ELICO [L1-613] pH meter using combined glass and calomel electrode assembly having accuracy of $\pm 0.01\text{pH}$ unit. The instrument was calibrated by using (0.05M) potassium hydrogenphthalate solution (pH=4) and standard buffer tablets (pH=9) all titration were carried out at constant temperature 27^oC keeping ionic strength $\mu = 0.1\text{M}$ NaClO₄, total volume (50ml) and concentration of Ce (III), Tb (III), Nd (III), Gd (III), & Dy (III), metals ions and ligand constant at the beginning of each titration. Each titration was repeated at least twice to gain the reproducibility of the result.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (0.2M). Solution keeping the total volume (50ml).

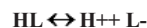
- 1) 5 ml NaClO₄ Solution + 5 ml HClO₄ solution + 35 ml Dioxane solvent + 5 ml distilled water. (Free Acid)
- 2) 5 ml NaClO₄ Solution + 5 ml HClO₄ solution + 35 ml Dioxane solvent + 3 ml distilled water + 2 ml ligand. (Free Acid + ligand)
- 3) 5 ml NaClO₄ Solution + 5 ml HClO₄ solution + 35 ml Dioxane solvent + 1 ml distilled water + 2 ml ligand + 2 ml metal solution. (Free Acid + ligand + metal)

The method of Irving and Rossotti¹⁴ was applied to find out the value of n and PL. The overall 0.1M ionic strength of solution was calculated by the expression $\mu = \frac{1}{2} \sum C_i Z_i^2$. The contribution of the other ions in addition to Na⁺ and ClO₄⁻ were also taken in to consideration.

RESULT AND DISCUSSION

PROTON LIGAND STABILITY CONSTANT:

Substituted drugs may be considered as a monobasic acids having only one replaceable H⁺ ions from -OH group and that -OH group generally dissociates completely above pH 9.00 and can therefore be represented as HL.



The titration data were used to construct the curves between volume of NaOH Vs pH. They are called acid, ligand metal titration curve.

It is observed from titration curves for all the systems that ligand curves start deviating from free acid (HClO₄) curves at about pH -7.00 and deviated continuously upto pH-12.0 The deviation shows that dissociation of -OH group in substituted chalcones.

The value of nA at various pH values were calculated from the acid titration curves (A) and ligand titration curves (B) by using formula of Irving and Rossotti¹⁴

Proton ligands stability constants were calculated from the plot of nA

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

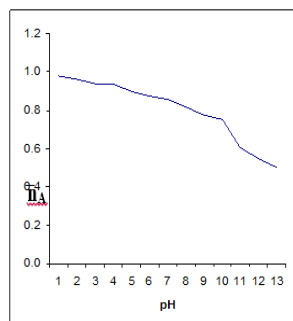


Fig – 1 [ligand -1]

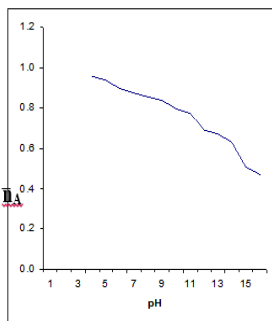


Fig-2 [ligand-2]

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	Ildoquinol-5,7-di-iodo-8-quinolinol (ligand - 1)	11.50	11.54 0.05
2	Chlorothalidon 2-chloro-5-(1-hydroxy-3-oxo-1,2-dihydroisoindol-1-yl)-benzenesulfonamide. (ligand - 2)	11.40	11.43 0.04

pK value of ligand -1 is greater than ligand-2 this may be due to the effect of strong e donating -CH₃ 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), Tb (III), Nd (III), Gd (III), & Dy (III), complexes with some substituted drugs were determined by employing Bjerrum-Calvin pH -titration technique as adopted by Irving and Rossotti.

The formation of chelates between Ce (III), Tb (III), Nd (III), Gd (III), & Dy (III), and substituted drugs was indicated by

- The significant departure starting from pH 3.00 for Ce(III), Gd(III), Dy(III).
- And deviation of Nd(III), metal titration curve from ligand curve was observed from pH 4.50.
- And deviation of Dy(III) metal titration curve from ligand curve was observed from pH 5.00.
- 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), Tb (III), Nd (III), Gd (III), & Dy (III), COMPLEXES WITH SUBSTITUTED DRUGS AT 0.1M IONIC STRENGTH.

log K₁ and log K₂ Value for ligand – 1

Sr. No.	Metal ions	log K ₁	log K ₂
1.	Ce (III) - L ₁	6.25	8.35
2.	Tb (III) - L ₁	5.75	8.20
3.	Dy (III) - L ₁	6.45	8.35
4.	Nd (III) - L ₁	4.80	8.02
5.	Gd (III) - L ₁	5.35	7.75

log K₁ and log K₂ Value for ligand – 2

Sr. No.	Metal ions	log K ₁	log K ₂
1.	Ce (III) - L ₂	6.40	8.70
2.	Tb (III) - L ₂	5.90	8.35
3.	Dy (III) - L ₂	6.60	8.75
4.	Nd (III) - L ₂	5.00	8.50
5.	Gd (III) - L ₂	5.50	8.00

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 K₁ and log K₂ 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 e releasing -CH₃ group.

The value of log K (log K₂ - log K₁) and log K₂/log K₁ 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 K₂/log K₁ 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.)

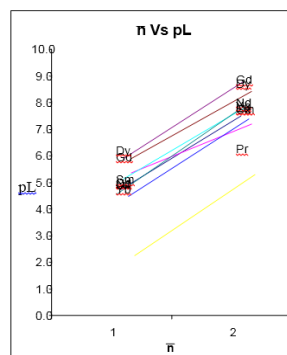


Fig –3[ligand -1]

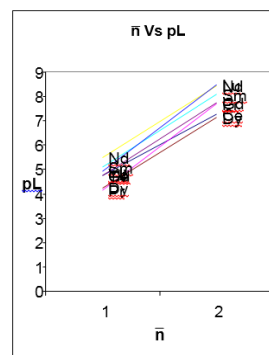


Fig –4[ligand -2]

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	Nd(III)-ligand No.1	3.00	1.61
	Nd(III)-ligand No.2	2.97	1.54
III	Gd (III)-ligand No.1	1.90	1.31
	Gd (III)-ligand No.2	2.00	1.63
IV	Dy (III)-ligand No.1	2.50	1.40
	Dy (III)-ligand No.2	2.90	1.68
V	Tb(III)-ligand No.1	3.10	1.65
	Tb(III)-ligand No.2	0.95	1.17

ACKNOWLEDGEMENT

The authors are thankful to Principal and Head of Department of Chemistry. Shri.D.M.Burungale Science & Arts College Shegaon – 444 203,(India).. For providing all the facilities.

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