

Metal-Ligand Stability Constants of Lanthanide(III) Chelates with some Substituted Drugs

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Abstract:

The interaction of Ce(III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb (III) and Lu (III) metal ions with 7-chloro-5-(o- chloro phenyl)-1, 3-dihydro-3-hydroxy-2H-1, 4-benzodi Drug (ligand-1) and 7-chloro-5-phenyl -1, 3-dihydro-3-hydroxy -2H-1, 4-benzodi Drug (ligand-2) have been investigated by pH-metric technique at 0.1 M ionic strength at ± 0.1 °C in 70% dioxane– water mixture. The data obtained were used to estimate the value of proton-ligand stability constant (pK) and metal- ligand stability constant (log K). It is observed that Ce(III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb (III) and Lu (III) metal ions formed 1:1 and 1:2 complexes with all the ligands.

Key-Words: stability constant, Substituted Drugs, Lanthanides (III)

Introduction:

Several workers have investigated the metal-ligand stability constants of the several metal ions with organic compounds viz., substituted sulphonic acids^{1,2}, substituted isoxazoline^{3,4}, substituted pyrazolines⁵, aromatic ketones and alkyl-monomines⁶, substituted coumarines⁷ and substituted benzothiazoles⁸.

In this paper, stability constant of some substituted drugs [viz., 7-chloro-5-(o- chloro phenyl)-1, 3-dihydro-3-hydroxy-2H-1, 4-benzodi Drug (ligand - 1) and 7-chloro-5-phenyl -1, 3-dihydro-3-hydroxy -2H-1, 4-benzodi Drug (ligand-2)] with Ce(III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb (III) and Lu (III) metal ions by pH-metric method are reported.

Experimental work:

The ligands- 7-chloro-5-(o- chloro phenyl)-1, 3-dihydro-3-hydroxy-2H-1, 4-benzodi Drug (ligand 1) and 7-chloro-5-phenyl -1, 3-dihydro-3-hydroxy -2H-1, 4-benzodi Drug (ligand-2) have been synthesized according to the reported method⁹.

The ligands made soluble in 70% dioxane – water (v/v) and used as solvent. Metal nitrates (BDH) were dissolved in perchloric acid and their concentration were estimated by standard method¹⁰. The nitrates of rare earths were used and their solutions were prepared in double distilled water. The solution of sodium perchlorate were prepared (0.1M) and used for 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 ± 0.01 pH unit. The instrument was calibrated by using 0.05M potassium hydrogenphthalate solution (pH=4) and standard buffer tablet (pH=9). All titrations carried out at constant temperature to keep ionic strength $\mu=0.1$ M NaClO₄, total volume (50ml) and concentration of Ce(III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb (III) and Lu (III) metal ions and ligand constant at the beginning of each titration. Each titration was repeated at least twice.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (0.2M)

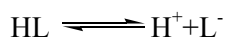
- 1) 5ml NaClO₄ solution + 5 ml HClO₄ solution + 35 ml dioxane solvent + 5 ml distilled water (free acid)
- 2) 5 ml NaClO₄ solution + 5 ml HClO₄ solution + 35 ml dioxane solvent + 3 ml distilled water + 2 ml ligand (free acid+ligand)
- 3) 5 ml NaClO₄ solution + 5 ml HClO₄ solution + 35 ml dioxane solvent + 1 ml distilled water + 2 ml ligand + 2 ml metal solution (free acid+ligand+metal).

The method of Irving and Rossotti¹¹ was applied to evaluate the value of \bar{n} and pL. The overall 0.1M ionic strength of solution was calculated by expression $\mu = \frac{1}{2} \sum C_i Z_i^2$. The contribution of other ions in addition to Na⁺ and ClO₄⁻ were also taken into consideration.

Results And Discussion:

Proton-ligand stability constant:

Substituted drugs may be considered as a monobasic acids having only one replaceable H⁺ ion from -OH group dissociate completely above pH 9 and can there fore be represented as HL.



The titration data is used to construct the curves between volume of NaOH vs. pH. Free acid, acid-ligand and acid-ligand-metal 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 and deviated continuously upto pH 12. The deviation shows that dissociation of -OH group in substituted drugs.

The value of \bar{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 Rossotti¹¹.

Proton -ligand stability constants were calculated from the plot \bar{n}_A vs. pH, the values of pK were determined. (half integral method). By noting the pH at which $\bar{n}_A=0.5$. The accurate value of pK were estimated by pointwise calculation method (Table-1).

Table-1 Determination of proton ligand stability constant (pK) of some substituted chalcones at 0.1 m ionic strength

| System | Constant pK | |
|---|---------------|------------------------|
| | Half integral | Point wise calculation |
| 7-chloro-5-(o-chloro phenyl)-1, 3-dihydro-3-hydroxy-2H-1, 4-benzodi Drug (ligand-1) | 11.60 | 11.63 ± 0.05 |
| 7-chloro-5-phenyl -1, 3-dihydro-3-hydroxy -2H-1, 4-benzodi Drug (ligand-2) | 11.80 | 11.82 ± 0.03 |

pK value of ligand-2 is greater than ligand-1 this may be due to the effect of strong electron withdrawing -Cl group that decreases the pK values but increases the dissociation in the following orders: ligand-2 > ligand-1.

Metal-Ligand Stability Constants:

The metal ligand stability constants of Ce(III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb (III) and Lu (III) complexes with some substituted drugs were determined by employing Berrum-Calvin pH – titration technique as adopted by Irving and Rossotti¹¹.

The formation of complexes between Ce(III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III), Yb (III) and Lu (III) and substituted drugs was indicated by (i) the significant departure starting from pH 3 for Ce(III), Gd(III) and Pr (III), (ii) deviation of Nd(III), Yb (III), Sm (III), Lu (III) metal titration curve from ligand curve observed from pH 4.5, (iii) while deviation of Dy(III) metal titration curve from ligand curve observed from pH 5, (iv) the change in colour from yellowishwhite to light brown and then dark brown as the pH was raised from 2.5 to 8.5.

It was 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 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 (Table-2).

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 is due to trans-structure. The results show that the ratio log K₂/log K₁ is positive in all cases which implied no steric hindrance to the addition of secondary ligand molecules.

Table-2 Determination of metal ligand stability constant (log k) of Ln(III) complexes with substituted chalcones at 0.1 m ionic strength

| SYSTEM | CONSTANT | |
|--------------------|---|---|
| | log K ₁ i.e. pL ₁ | log K ₂ i.e. pL ₂ |
| Ce(III)-LIGAND-1 | 7.65 | 9.75 |
| Pr (III) -LIGAND-1 | 8.50 | 10.15 |
| Nd (III) -LIGAND-1 | 8.90 | 9.95 |
| Sm (III) -LIGAND-1 | 7.60 | 10.25 |
| Gd (III) -LIGAND-1 | 9.95 | 10.98 |
| Dy (III) -LIGAND-1 | 8.15 | 10.35 |
| Yb (III) -LIGAND-1 | 7.15 | 9.97 |

| | | |
|--------------------|------|-------|
| Lu (III) -LIGAND-1 | 8.05 | 10.55 |
| Ce(III)-LIGAND-2 | 7.95 | 10.21 |
| Pr (III) -LIGAND-2 | 7.34 | 10.84 |
| Nd (III) -LIGAND-2 | 9.04 | 10.34 |
| Sm (III) -LIGAND-2 | 7.23 | 9.78 |
| Gd (III) -LIGAND-2 | 9.74 | 11.74 |
| Dy (III) -LIGAND-2 | 7.37 | 9.97 |
| Yb (III) -LIGAND-2 | 8.57 | 10.27 |
| Lu (III) -LIGAND-2 | 9.26 | 10.66 |

The relation of $\log K = a \text{ pK} + b$ was also studied . The order of stability of complex is as follows

(I) $\log K_1$ for Ligand - 1

Gd > Nd > Pr > Dy > Lu > Ce > Sm > Yb

(II) $\log K_1$ for Ligand -2

Gd > Lu > Nd > Yb > Ce > Dy > Pr > Sm

These vlues are also observed by Tambatkar etal¹² and Y.K.Meshram etal⁵.

Table-3 Metal ligand stability constant at 0.1 m ionic strength

| SYSTEM | $\log K_2 - \log K_1$ | $\log K_2 / \log K_1$ |
|------------------|-----------------------|-----------------------|
| Ce(III)-Ligand-1 | 2.10 | 1.27 |
| Ce(III)-Ligand-2 | 2.26 | 1.28 |
| Pr(III)-Ligand-1 | 1.65 | 1.19 |
| Pr(III)-Ligand-2 | 3.5 | 1.47 |
| Nd(III)-Ligand-1 | 1.05 | 1.11 |
| Nd(III)-Ligand-2 | 1.30 | 1.14 |
| Sm(III)-Ligand-1 | 2.65 | 1.35 |
| Sm(III)-Ligand-2 | 2.55 | 1.35 |
| Gd(III)-Ligand-1 | 1.43 | 1.15 |
| Gd(III)-Ligand-2 | 2.00 | 1.21 |
| Dy(III)-Ligand-1 | 2.20 | 1.27 |
| Dy(III)-Ligand-2 | 2.60 | 1.35 |
| Yb(III)-Ligand-1 | 2.82 | 1.39 |
| Yb(III)-Ligand-2 | 1.70 | 1.20 |
| Lu(III)-Ligand-1 | 2.50 | 1.31 |
| LU(III)-Ligand-2 | 1.40 | 1.15 |

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