Stability Constants of Lanthanides(III) Chelates with Substituted Chalcones

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The interaction of Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and Lu(III) metal ions with 2′-hydroxy-(3,4-dioxymethylene)-5′-methyl chalcone (ligand-1) and 2′-hydroxy-5′-methyl-4-methoxy chalcone (ligand-2) have been investigated by pH-metric technique at 0.1 M ionic strength at 27 ± 0.1 ºC 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), 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 constants, Substituted chalcones, 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 pyrazolines[5], aromatic ketones and alkyl-monomines[6], substituted coumarines[7] and substituted benzothiazoles[8].

In this paper, the stability constant of some chalcones (*viz.*, 2′-hydroxy-(3,4-dioxymethylene)-5′-methyl chalcone (ligand-1) and 2′-hydroxy-5′-methyl-4-methoxy chalcone (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

The ligands, 2′-hydroxy-(3,4-dioxymethylene)-5′-methyl chalcone (ligand-1) and 2′-hydroxy-5′-methyl-4-methoxy chalcone (ligand-2) have been synthesized according to the reported method[9].

The ligands were made soluble in 70 % dioxane-water (v/v) and used as solvent. Metal nitrates (BDH) were dissolved in percholoric acid and

there concentration were estimated by standard method[10]. The nitrates of rare earths were used and their solutions were prepared in double distilled water. The solution of sodium perchlorate was prepared (0.1 M) 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 ± 0.01 pH unit. The instrument was calibrated by using (0.05 M) potassium hydrogenphthalate solution (pH = 4) and standard buffer tablets (pH = 9) all titration were carried out at constant temperature 27 ºC keeping ionic strength μ = 0.1 M $NaClO_4$, total volume (50 mL) and concentration of Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and Lu(III) metals 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 (0.2 M). (1) 5 mL $NaClO_4$ solution + 5 mL $HClO_4$ solution + 35 mL dioxane solvent + 5 mL distilled water (free acid), (2) 5 mL $NaClO_4$ solution + 5 mL $HClO_4$ solution + 35 mL dioxane solvent + 3 mL distilled water + 2 mL ligand. (free acid + ligand), (3) 5 mL $NaClO_4$ solution + 5 mL $HClO_4$ 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 Rossotti[11] was applied to evaluate the value of $\bar{n}$ and PL. The overall 0.1 M ionic strength of solution was calculated by the expression $\mu = \frac{1}{2}\Sigma C_i Z_i^2$. The contribution of the other ions in addition to Na^+ and ClO_4^- were also taken in to consideration.

RESULTS AND DISCUSSION

Proton ligand stability constant: Substituted chalcones 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 and can therefore be represented as HL.

$$HL \rightleftharpoons H^+ + L^-$$
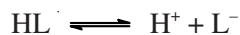
The titration data were used to construct the curves between volume of NaOH *vs.* pH. They are called acid, ligand metal titration curve.

It is observe form titration curves for all the systems that ligand curves start deviating from free acid ($HClO_4$) curves at about pH 7 and deviated continuously upto pH 12. The deviation shows that dissociation of -OH group in substituated chalcones.

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 Rossotti[11].

Proton ligands stability constants were calculated from the plot of $\overline{n}_A$ *vs.* pH, 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 (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
2'-Hydroxy-(3,4-dioxymethylene)-5'-methyl chalcone (ligand-1)	11.50	11.54 ± 0.05
2'-Hydroxy-5'-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 electron 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) and Lu(III) complexes with some substituted chalcones were determined by employing Bjerrum-Calvin pH-titration technique as adopted by Irving and Rossotti[11].

The formation of complexes between Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and Lu(III) and substituted chalcones was indicated by (i) the significant departure starting from pH 3 for Ce(III), Gd(III), 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 light yellow to light brown and then dark brown as the pH was raised from 2.5 to 8.5.

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 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 (Table-2).

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 which implied no steric hindrance to the addition of secondary ligand molecules.

TABLE-2
DETERMINATION OF METAL LIGAND STABILITY CONSTANTS
(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	5.00	7.75
Pr(III)-ligand-1	4.40	6.25
Nd(III)-ligand-1	4.95	8.00
Sm(III)-ligand-1	5.10	7.75
Gd (III)-ligand-1	5.95	7.85
Dy (III)-ligand-1	6.20	8.70
Yb(III)-ligand-1	4.75	7.85
Lu(III)-ligand-1	4.90	7.80
Ce(III)-ligand-2	4.75	7.25
Pr(III)-ligand-2	4.15	7.70
Nd(III)-ligand-2	5.48	8.45
Sm(III)-ligand-2	5.10	8.10
Gd(III)-ligand-2	4.75	7.75
Dy(III)-ligand-2	4.25	7.15
Yb(III)-ligand-2	4.80	5.65
Lu(III)-ligand-2	4.95	8.50

TABLE-3
METAL- LIGAND STABILITY CONSTANTS
AT 0.01 M IONIC STRENGTH

System	log K_2–log K_1	log K_2/log K_1
Ce(III)-ligand-1	2.75	1.55
Ce(III)-ligand-2	2.50	1.52
Pr(III)-ligand-1	1.85	1.42
Pr(III)-ligand-2	3.55	1.85
Nd(III)-ligand-1	3.00	1.61
Nd(III)-ligand-2	2.97	1.54
Sm(III)-ligand-1	2.65	1.51
Sm(III)-ligand-2	3.00	1.58
Gd(III)-ligand-1	1.90	1.31
Gd(III)-ligand-2	2.00	1.63
Dy(III)-ligand-1	2.50	1.40
Dy(III)-ligand-2	2.90	1.68
Yb(III)-ligand-1	3.10	1.65
Yb(III)-ligand-2	0.95	1.17
Lu(III)-ligand-1	2.90	1.59
Lu(III)-ligand-2	3.55	1.71

REFERENCES

1. B.G. Khobragade and M.L. Narwade, *Acta Cien. Indica*, **9c**, 32 (1983).
2. D.T. Mahajan and M.L. Narwade, *Acta Cien. Indica*, **14c**, 1 (1988).
3. P.V. Tekade, K.N. Patil, M.L. Narwade, P.S. Bodkhe and Y.K. Meshram, *Asian J. Chem.*, **18**, 2657 (2006).
4. P.Y. Khadikar, S.N. Kakkar and D.K. Burge, *Indian J. Chem.*, **13**, 844 (1975).
5. Y.K. Meshram, A.U. Mandakmare and M.L. Narwade, *Asian J. Chem.*, **12**, 1027 (2000).
6. R. Nath and R.P. Bhatnagar, *J. Indian Chem. Soc.*, **63**, 463 (1986).
7. A.U. Mandakmare and M.L. Narwade, *Acta Cien. Indica*, **20c**, 30 (1994).
8. P. Desai, B. Agrwal and P. Parmeshwaran, *Asian J. Chem.*, **15**, 53 (2003).
9. P.B. Agrwal, etal, *Acta Cien. Indica*, **29C**, 121 (2003).
10. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Logmans Green, London, p. 589 (1975).
11. H.M. Irving and H.S. Rossotti, *J. Chem Soc.*, 2904 (1954).