CHAPTER IV

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF RARE EARTHS

ABSTRACT

The thermodynamic metal ligand stability constants of rare earths, La, Pr, Nd, Sm, Eu, Gd, Tb, with N-p-chlorophenyl-m-substituted benzohydroxamic acids in different dioxan-water media (60-70%) at 25±0.1°C, have been determined by potentiometric method.

The effect of basicity of the ligand, central metal ion, order of the stability constants is discussed.

The order of stability constants of the rare earths with the hydroxamic acid has been found as

La < Pr < Nd < Sm < Eu > Gd < Tb.

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF RARE EARTHS

The term stability denotes the amount of association that occurs in solutions containing two or more species in equilibrium. Hence it follows that greater the association, more stable the complex is. The term equilibrium constant, which is general one, now assumes a new name and is referred to as stability constant.

Many workers turned their attention to the quantitative characterisation of complex compounds by determining their stability constants. Just a knowledge of ionization constants of acids and bases has helped to systematise our understanding of the behaviour of these substances in all kinds of systems, so a knowledge of stability constants will be helpful to rationalise our understanding of the behaviour of metal complexes in solutions. In addition, qualitative measurements of the equilibria involved in chelate formation offers a means of obtaining fundamental knowledge of the structure of chelates. It has now become to correlate equilibrium data with such important factors as the (i) basicity of ligand (ii) electronegativity of metal ions, (iii) steric requirements of chelating agents and (iv) the size and number of the chelate rings. The results of such studies find application in a systematic and rational search for new analytical reagents showing better "specific and selective" reaction with metal ions.

Hydroxamic acids are the versatile analytical reagents and form stable chelates with several metal ions (1-6). However, little work has been done on the rare earth complexes, except their stability constants with benzo-, N-phenylbenzo-, N-o-, m- and p-tolyl-m-nitrobenzo-hydroxamic acids which have been studied by Agrawal et al. (7). In the present investigation the metal ligand stability constants of La, Pr, Nd, Sm, Eu, Gd and Tb have been determined with N-p-chlorophenyl-m-substituted benzohydroxamic acids at 60 and 70% (v/v) dioxan-water media at 25±0.1°C, with a view to have more selective and sensitive reagent from the family of hydroxamic acids for their analytical applications for rare earths.

METHOD USED IN THE PRESENT WORK

Bjerrum's (8) original titration method was modified by Calvin and Wilson (9) for determining the stability constants of metal complexes in mixed-aqueous medium. The procedure used for determining the thermodynamic stability constants in the present investigation, is an extension of Bjerrum-Calvin pH titration method (8,9), essentially it combines the method of Van Uitert and Hass (10), Block and McIntyre (11) and Goldberg (12) and Agrawal and his co-workers (13-15). Instead of evaluating the desired stability constants by the less precise graphical method, these have been obtained by solving the simultaneous equations (11-13).

N-aryl hydroxamic acids and also their metal complexes have insufficient solubility in water and at lower percent of dioxan-water. Hence it was impossible to determine the stepwise stability constants below 60% dioxan-water media due to the same reason. Hence the stepwise solution stability constants were determined at 60% and 70% (v/v) dioxan-water media.

The final concentration of the various solutions in the titre was as follows :

Metal ion	0.001 M
Ligand	0.005 M
Titrant	0.1 M

Inert salts were generally not added to the titre and hence the activity coefficient at low ionic strengths of experiments were readily computed by Agrawal data ([illegible]6).

CALCULATION OF STEPWISE SOLUTION STABILITY CONSTANTS

The stepwise formation of a series of metal chelates (of hydroxamic acids) of the type MA_1, MA_2, ... MA_n are defined by equations (i) to (iii)

$$M + A = MA \quad ; \; K_1 = \frac{[MA]}{[M]\,[A]} \tag{i}$$

$$M A + A = MA_2 \quad ; \; K_2 = \frac{[MA_2]}{[MA]\,[A]} \tag{ii}$$

$$\vdots \qquad\qquad\qquad\qquad \vdots$$

$$M A_{n-1} + A = MA_n \quad ; \; K_n = \frac{[MA_n]}{[MA_{n-1}]\,[A]} \tag{iii}$$

The formation function, $\bar{n}$, which is defined as the average number of ligands bound per metal ion, in case of 1:1, 1:2,... 1:n complexes is obtained as under

$$\bar{n} = \frac{\text{Total Bound Ligand}}{\text{Total Metal Ion}}$$

$$= \frac{[MA] + 2\,[MA_2] + 3\,[MA_3] + \ldots + n\,[MA_n]}{[M] + [MA] + [MA_2] + [MA_3] + \ldots + [MA_n]} \tag{iv}$$

Equation (iv) may be obtained in terms of $[A]$ and various formation constants K_1, K_2, ... K_n by substitution of equation (i), (ii) and (iii) into equation (iv).

$$\frac{K_1[A] + 2K_1K_2[A]^2 + 3K_1K_2K_3[A]^3 + \ldots + nK_1K_2\ldots K_n[A]^n}{1+K_1[A] + 2K_1K_2[A]^2 + 3K_1K_2K_3[A]^3 + \ldots + nK_1K_2\ldots K_n[A]^n} \qquad \text{(v)}$$

or for simplicity, equilibrium constants for the above coordination products may be represented by

$$K_1 = \frac{[MA^+]}{[M^{2+}]\,[A^-]} \cdot \frac{y_{MA^+}}{y_{M^{2+}}\ y_{A^-}}$$

$$= q_1 \frac{y_{MA^+}}{y_{M^{2+}}\ y_{A^-}} \qquad ; \ q_1 = \frac{[MA^+]}{[M^{2+}]\ [A^-]}$$

or $$K_1 = \frac{q_1}{y_\pm^4} \qquad \text{(vi)}$$

Similarly,

$$K_2 = \frac{[MA_2]}{[MA^+]\ [A^-]} \cdot \frac{y_{MA_2}}{y_{MA^+} \cdot y_{A^-}}$$

$$= q_2 \frac{y_{MA_2}}{y_{MA^+}\ y_{A^-}} \qquad ; \ q_2 = \frac{[MA_2]}{[MA^+]\ [A^-]}$$

or $$K_2 = \frac{q_2}{y_\pm^2} \qquad \text{(vii)}$$

and similarly

$$K_3 = q_3 \qquad \text{(viii)}$$

Here q_1, q_2 and q_3 are molarity quotients for the equilibrium reactions represented by equation (i), (ii) and (iii). Rest of the terms have their usual significance. Equations (vi), (vii) and (viii) have been derived on the simple assumption that the activity coefficient of the neutral species is unity and that of unipositive and uninegative ions is approximately equal to the mean activity coefficient $y_{\pm}$ of hydrochloric acid. Further, in the limiting case in which the Debye-Huckel limiting law applies, it is assumed that $\log y_{M^{2+}} = 4 \log y_{\pm}$.

The concentration of free ligand $[A^-]$ is obtained as shown below

$$\text{Bound Hydrogen} = \begin{matrix}\text{Total}\\ \text{hydrogen}\end{matrix} - \begin{matrix}\text{Reacted}\\ \text{hydrogen}\end{matrix} - \begin{matrix}\text{Dissociated}\\ \text{hydrogen}\end{matrix}$$

$$[HA] = C_{HA} - C_{OH} - [H^+] - [OH^-] \qquad \text{(ix)}$$

But for the reaction $H^+ + A^- = HA$

$$q_H = \frac{[HA]}{[H^+][A^-]}$$

Hence,

$$[HA] = q_H\ [H^+]\ [A^-] \qquad \text{(x)}$$

Substitution for $[HA]$ from equation (x) into (ix) gives

$$[A^-] = \frac{C_{HA} - C_{OH^-} - [H^+] - [OH^-]}{q_H\ [H^+]} \qquad \text{(xi)}$$

where C_{HA} = moles/litre of hydroxamic acid added. Each of the quantities except q_H on the right hand side of the above equation is easily available from the titration data. The value of q_H is readily obtained from a knowledge of the thermodynamic ionisation constant of the ligand.

The thermodynamic ionization constant for the hydroxamic acid HA, is defined as

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \quad \frac{y_{H^+}\;y_{A^-}}{y_{HA}}$$

Assuming y_{HA} to be unity and $y_{H^+} = y_{A^-} = y_{\pm}$

$$K_a = \frac{1}{q_H} \quad y_{\pm}^2 \qquad \text{(xii)}$$

$$\text{or} \quad \log q_H = pK_a - 2 \log \frac{1}{y_{\pm}} \qquad \text{(xiii)}$$

The formation function $\bar{n}$ is obtained as under,

$$\bar{n} = \frac{\text{Total Bound Ligand}}{\text{Total Metal Ion}}$$

$$= \frac{\text{total ligand - protonated ligand - free ligand}}{\text{total metal}}$$

$$= \frac{C_{HA} - [HA] - [A^-]}{C_M}$$

$$= \frac{C_{HA} - q_H\,[H^+]\,[A^-] - [A^-]}{C_M} \qquad \text{(xiv)}$$

where, C_M = mole/litre of the metal ion added. The hydrogen ion concentration, as required in equation (xi) and (xiv) is calculated by the general formula (6)

$$-\log[H^+] = B + \log U_H^\circ - \log\frac{1}{y_\pm}$$

where B is the pH meter reading in dioxan-water mixture, $\log U_H^\circ$ is the correction factor for pH meter reading, and $y_\pm$ is the mean activity coefficient of univalent electrolyte at a particular molarity and solvent composition.

Thus from the knowledge of the values of $\bar{n}$ with corresponding values of $[A^-]$ from equation (xi) and (xiv), respectively the molarity quotients q_1, q_2 and q_3 may be calculated by a linear least square fit of the equation (xv)

$$\frac{\bar{n}}{(1-\bar{n})\,[A^-]} = \frac{q_1 \cdot q_2 \cdot (2-\bar{n})\,[A^-]}{(1-\bar{n})} + q_1 \qquad \text{(xv)}$$

where values of $\bar{n}$ used were restricted to the range 0.15-0.85 and 1.15-1.85.

The formation constants for these chelates were calculated by the solution of simultaneous linear equations derived from (xvi),

$$\frac{\bar{n}}{(1-\bar{n})\,[A^-]} = q_1 q_2 \frac{(2-\bar{n})\,[A^-]}{(1-\bar{n})} + \frac{q_1 q_2 q_3\,(3-\bar{n})\,[A^-]^2}{(1-\bar{n})} + q_1 \qquad \text{(xvi)}$$

The values of $\bar{n}$ used were restricted to the ranges 0.15-0.85, 1.15-1.85 and 2.15-2.85.

Calculation of thermodynamic stepwise formation constants K_1, K_2 and K_3 is easily accomplished by equations (vi), (vii), (viii), (xiv) and (xvi) in the form

$$\log K_1 = \log q_1 + 4 \log \frac{1}{y_{\pm}}$$

$$\log K_2 = \log q_2 + 2 \log \frac{1}{y_{\pm}}$$

$$\log K_3 = \log q_3$$

EXPERIMENTAL

CHEMICALS

All the chemicals used were of G.R. or AnalaR grades of E. Merck and B.D.H., respectively unless otherwise stated.

SOLVENTS

Distilled water : Described in Chapter II.

Dioxan : Described in Chapter III.

REAGENTS

Potassium hydroxide : Described in Chapter III.

Hydroxamic acids : Described in Chapter II.

Metal perchlorate solutions : Solutions of metal perchlorates were prepared in order to minimise interference of anions. Since pure perchlorates were not available, these were prepared by treating an excess of pure oxide of metal with requisite strength of perchloric acid. The solutions were filtered, boiled to remove any dissolved carbon dioxide and suitably diluted. The concentration of metal ions were determined volumetrically by titration against EDTA (16).

APPARATUS

A radiometer pH meter PHM 85 equipped with a combined electrode was used for pH meter titrations. The pH meter was standardised at the desired temperature (25±0.1°C) with aqueous buffer solutions such as 0.05 M potassium acid phthalate (pH - 4.005 at 25°C) and 0.01 M borax (pH - 9.18 at 25°C). Standardisation was checked both before and after each titration.

TITRATION VESSEL

A titration vessel, with a capacity of 75 ml was specially fabricated for the pH titrations. Besides an inlet from the side for nitrogen gas, it had three necks, which accomodated the combined electrode and the microburette.

NITROGEN

Nitrogen was passed through a series of bubblers containing a saturated alkaline solution of pyrogallol, 2 N sulphuric acid, distilled water and finally the required solvent.

PROCEDURE

Into the 75-ml three necked titration vessel having an inlet for nitrogen, the weighed amount of hydroxamic acid (corresponding to 0.005 M in a final volume of 50 ml) was transferred along with freshly distilled dioxan 'x' ml (corresponding to 60 or 70% dioxan). Metal perchlorate (5 ml of 0.01 M), and water $[50-(x + 5)]$ ml were then added. The titration vessel was thermostated at 25±0.1°C. The solution was titrated against 0.1 M KOH solution which was prepared so as to contain the requisite percent dioxan by adding in small aliquots and recording the pH.

RESULTS AND DISCUSSION

A large number of pH titrations were performed at different concentrations of reactants and by varying the metal to ligand ratio. Experimental observations for a few representative titrations and formation curves (Figs. I-III) are recorded in Appendix II.

N-p-chlorophenyl-m-substituted benzohydroxamic acid complexes were so insoluble that they precipitated immediately on mixing dioxan with water (50% dioxan-water) and hence their stability constants were determined by increasing the dioxan content to 60 and 70 percent (v/v). The average values of stability constants are given in Tables 1-8.

Hydroxamic acids are the bidentate ligands and form chelate with metal ions. Trivalent metal ions examined here form solid inner complexes with N-p-chlorophenyl-m-substituted benzohydroxamic acids (Chapter V). The metal to ligand ratio in these complexes is 1:3, showing a coordination number 6 for the metal ion. The titration data and formation curves indicate that in solutions too the maximum complexation involves the six coordinated species, and no hepta or octa coordinated species is formed. The three species which are formed stepwise can be explained by the undernoted reactions.

TABLE 1

THERMODYNAMIC METAL LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN 60% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	log K_1	log K_2	log K_3	log β_3	log $\frac{K_1}{K_2}$
			Compd. I; X = H		
H^+	11.47				
La^{3+}	11.0	9.6	8.3	28.9	1.4
Pr^{3+}	11.7	10.3	9.1	31.1	1.4
Nd^{3+}	12.0	10.5	9.2	31.7	1.5
Sm^{3+}	12.3	10.8	9.3	32.4	1.5
Eu^{3+}	12.7	11.3	10.0	34.0	1.4
Gd^{3+}	12.5	11.1	9.8	33.4	1.4
Tb^{3+}	13.0	11.5	10.2	34.7	1.5
			Compd. II; X = CH_3		
H^+	11.54				
La^{3+}	11.5	10.1	8.8	30.4	1.4
Pr^{3+}	12.1	10.6	9.3	32.0	1.5
Nd^{3+}	12.3	10.9	9.7	32.9	1.4
Sm^{3+}	12.6	11.2	9.9	33.7	1.4
Eu^{3+}	12.9	11.4	10.2	34.5	1.5
Gd^{3+}	12.7	11.2	10.0	33.9	1.5
Tb^{3+}	13.2	11.8	10.5	35.5	1.4

TABLE 2

THERMODYNAMIC METAL LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED-BENZOHYDROXAMIC ACIDS IN 60% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_3$	$\log \frac{K_1}{K_2}$
			Compd. III; $X = OCH_3$		
H^+	11.36				
La^{3+}	10.9	9.4	8.2	28.5	1.5
Pr^{3+}	11.5	10.0	8.8	30.3	1.5
Nd^{3+}	11.8	10.4	9.1	31.3	1.4
Sm^{3+}	12.1	10.7	9.4	32.2	1.4
Eu^{3+}	12.4	10.9	9.7	33.0	1.5
Gd^{3+}	12.2	10.8	9.5	32.5	1.4
Tb^{3+}	12.6	11.2	10.0	33.8	1.4
			Compd. IV; $X = F$		
H^+	11.12				
La^{3+}	10.8	9.3	8.0	28.1	1.4
Pr^{3+}	11.2	9.7	8.4	29.3	1.5
Nd^{3+}	11.6	10.2	9.0	30.8	1.4
Sm^{3+}	11.9	10.5	9.3	31.7	1.4
Eu^{3+}	12.1	10.7	9.5	32.3	1.4
Gd^{3+}	12.0	10.6	9.4	32.0	1.4
Tb^{3+}	12.4	10.9	9.6	32.9	1.5

TABLE 3

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED-BENZOHYDROXAMIC ACIDS IN 60% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	log K_1	log K_2	log K_3	log β_3	log $\frac{K_1}{K_2}$
		Compd. V; X = Cl			
H^+	11.07				
La^{3+}	9.9	8.5	7.2	25.6	1.4
Pr^{3+}	10.7	9.3	8.0	28.0	1.4
Nd^{3+}	11.0	9.6	8.4	29.0	1.4
Sm^{3+}	11.3	9.8	8.7	29.8	1.5
Eu^{3+}	11.6	10.2	9.0	30.8	1.4
Gd^{3+}	11.4	9.9	8.7	30.0	1.5
Tb^{3+}	11.8	10.4	9.2	31.4	1.4
		Compd. VI; X = Br			
H^+	11.04				
La^{3+}	9.8	8.4	7.1	25.3	1.4
Pr^{3+}	10.6	9.1	7.9	27.6	1.5
Nd^{3+}	10.9	9.4	8.2	28.5	1.5
Sm^{3+}	11.1	9.6	8.4	29.1	1.5
Eu^{3+}	11.4	9.9	8.6	29.9	1.5
Gd^{3+}	11.2	9.8	8.5	29.5	1.4
Tb^{3+}	11.6	10.2	9.0	30.8	1.4

TABLE 4

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED-BENZOHYDROXAMIC ACIDS IN 60% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C

Complexing ion	log K_1	log K_2	log K_3	log β_3	log $\frac{K_1}{K_2}$
			Compd. VII; X = I		
H^+	11.10				
La^{3+}	10.3	8.8	7.5	26.6	1.5
Pr^{3+}	11.0	9.5	8.3	28.8	1.5
Nd^{3+}	11.3	9.9	8.6	29.8	1.4
Sm^{3+}	11.7	10.3	9.0	31.0	1.4
Eu^{3+}	11.9	10.4	9.2	31.5	1.5
Gd^{3+}	11.8	10.3	9.0	31.1	1.5
Tb^{3+}	12.1	10.7	9.4	32.1	1.4
			Compd. VIII; X= NO_2		
H^+	10.65				
La^{3+}	9.0	7.5	6.2	22.7	1.5
Pr^{3+}	9.6	8.2	7.0	24.8	1.4
Nd^{3+}	9.9	8.5	7.3	25.7	1.4
Sm^{3+}	10.2	8.8	7.5	26.5	1.4
Eu^{3+}	10.7	9.2	8.0	27.9	1.5
Gd^{3+}	10.4	8.9	7.6	26.9	1.5
Tb^{3+}	10.9	9.4	8.2	28.5	1.5

TABLE 5

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED-BENZOHYDROXAMIC ACIDS IN 70% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	log K_1	log K_2	log K_3	log β_3	$\log \frac{K_1}{K_2}$
		Compd. I; X = H			
H^+	12.43				
La^{3+}	12.0	10.5	9.2	31.7	1.5
Pr^{3+}	12.6	11.1	10.0	33.7	1.5
Nd^{3+}	13.2	11.7	10.5	35.4	1.5
Sm^{3+}	13.5	12.0	10.8	36.3	1.5
Eu^{3+}	13.7	12.3	11.1	37.1	1.4
Gd^{3+}	13.6	12.1	10.9	36.6	1.5
Tb^{3+}	14.1	13.5	11.3	37.9	1.4
		Compd. II; X = CH_3			
H^+	12.45				
La^{3+}	12.4	11.0	9.7	33.1	1.4
Pr^{3+}	13.0	11.5	10.4	34.9	1.5
Nd^{3+}	13.4	11.9	10.6	35.9	1.5
Sm^{3+}	13.7	12.3	11.1	37.1	1.4
Eu^{3+}	13.9	12.5	11.5	37.9	1.4
Gd^{3+}	13.8	12.3	11.2	37.3	1.5
Tb^{3+}	14.3	12.9	11.6	38.8	1.5

TABLE 6

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED-BENZOHYDROXAMIC ACIDS IN 70% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	log K_1	log K_2	log K_3	log β_3	log $\frac{K_1}{K_2}$
		Compd. III; X =OCH$_3$			
H^+	12.32				
La^{3+}	11.8	10.3	9.0	31.1	1.5
Pr^{3+}	12.4	10.9	9.8	33.1	1.5
Nd^{3+}	13.0	11.5	10.3	34.8	1.5
Sm^{3+}	13.3	11.8	10.6	35.7	1.5
Eu^{3+}	13.5	12.0	10.9	36.4	1.5
Gd^{3+}	13.4	11.9	10.7	36.0	1.5
Tb^{3+}	13.9	12.5	11.3	37.7	1.4
		Compd. IV; X = F			
H^+	12.11				
La^{3+}	11.4	9.9	8.6	29.9	1.5
Pr^{3+}	12.0	10.5	9.4	31.9	1.5
Nd^{3+}	12.6	11.1	9.9	33.6	1.5
Sm^{3+}	12.9	11.4	10.2	34.5	1.5
Eu^{3+}	13.2	11.7	10.5	35.4	1.5
Gd^{3+}	13.0	11.5	10.3	34.8	1.5
Tb^{3+}	13.5	11.9	10.7	36.1	1.4

TABLE 7

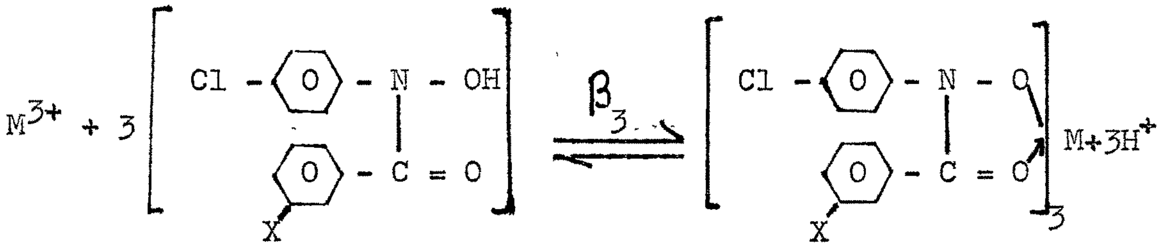
THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN 70% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	log K_1	log K_2	log K_3	log β_3	$\log \frac{K_1}{K_2}$
Compd. V; X = Cl					
H^+	12.08				
La^{3+}	10.8	9.3	8.1	28.2	1.5
Pr^{3+}	11.4	9.9	8.8	30.1	1.5
Nd^{3+}	12.0	10.5	9.3	31.8	1.5
Sm^{3+}	12.3	10.8	9.6	32.9	1.5
Eu^{3+}	12.5	11.1	9.9	33.5	1.4
Gd^{3+}	12.4	10.9	9.7	33.0	1.5
Tb^{3+}	13.0	11.5	10.3	34.8	1.5
Compd. VI, X = Br					
H^+	12.06				
La^{3+}	10.6	9.1	7.9	27.6	1.5
Pr^{3+}	11.2	9.7	8.6	29.5	1.5
Nd^{3+}	11.8	10.3	9.1	31.2	1.5
Sm^{3+}	12.1	10.6	9.4	32.1	1.5
Eu^{3+}	12.3	10.9	9.7	32.9	1.4
Gd^{3+}	12.2	10.7	9.5	32.4	1.5
Tb^{3+}	12.7	11.2	9.9	33.8	1.5

TABLE 8

THERMODYNAMIC METAL LIGAND STABILITY CONSTANTS OF N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACIDS IN 70% (v/v) DIOXAN-WATER MEDIA AT 25±0.1°C.

Complexing ion	log K_1	log K_2	log K_3	log β_3	log $\frac{K_1}{K_2}$
		Compd. VII, X = I			
H^+	12.10				
La^{3+}	11.1	9.6	8.3	29.0	1.5
Pr^{3+}	11.7	10.2	9.1	31.1	1.5
Nd^{3+}	12.3	10.8	9.6	32.7	1.5
Sm^{3+}	12.6	11.1	9.9	33.6	1.5
Eu^{3+}	12.8	11.4	10.2	34.4	1.4
Gd^{3+}	12.7	11.2	10.0	33.9	1.5
Tb^{3+}	13.3	11.8	10.6	35.7	1.5
		Compd. VIII, X = NO_2			
H^+	11.69				
La^{3+}	9.8	8.3	7.1	25.2	1.5
Pr^{3+}	10.4	8.9	7.6	26.9	1.5
Nd^{3+}	11.0	9.5	8.3	28.8	1.5
Sm^{3+}	11.3	9.9	8.7	29.9	1.4
Eu^{3+}	11.5	10.1	8.8	30.4	1.5
Gd^{3+}	11.4	10.0	8.7	30.1	1.4
Tb^{3+}	12.0	10.5	9.2	31.7	1.5

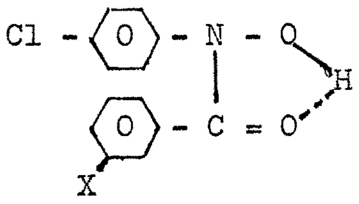


Where, β_3 = the first, second and third stepwise metal chelate stability constants (e.g. $K_1 + K_2 + K_3$)

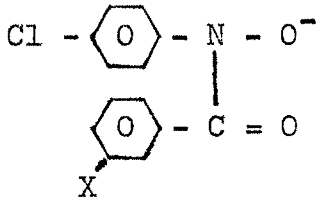
M^{3+} = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} or Tb^{3+}

X = H, CH_3, OCH_3, F, Cl, Br, I or NO_2

The unionised and ionised forms of the N-p-chlorophenyl-m-substituted benzohydroxamic acid can be represented as under.



HA



A^-

The dotted line in the formula for molecular species shows the intramolecular hydrogen bonding (Chapters II and III) between the hydroxylamino hydrogen and oxygen of the carbonyl.

The simple picture of complex formation shows the similarity between HA and first metal ligand complex formed MA. In other words, HA can be considered as the complex formed between proton and the ligand ion A^-. This can be further explained by the order in which the stability of metal complexes and pK_a of the ligand vary. The pK_a values give a measure of the stabilities of the ligand proton complexes.

Variation of stability constants with the nature of ligands

Since the reaction leading to the formation of proton-ligand and metal-ligand complexes are similar, the constants pK_a and $\log K_1$ (or $K_1 K_2$ or β_n) should be related linearly. It has been pointed out by several workers (17-21) that an approximately linear relationship exists between the logarithms of stability constants of a series of metal complexes derived from one metal ion with a set of closely related ligands. On this basis it is expected that more basic ligand should form stabler complexes. In the case of present studies with the hydroxamic acids examined here, a linear relationship between pK_a and $\log K_1$ is observed for all the rare earths. Typical plots for a few rare earths are given in Fig. 1 which show a linear relationship. It is indicating that the increase in free energy of the first step in complex formation with ligand basicity is smaller than the corresponding increase in the proton ligand affinity. Although $\overset{\circ}{G}_{HA}$ (partial molar free energy of HA) and $\overset{\circ}{G}_{MA}$ (partial molar free energy of MA) depend similarly

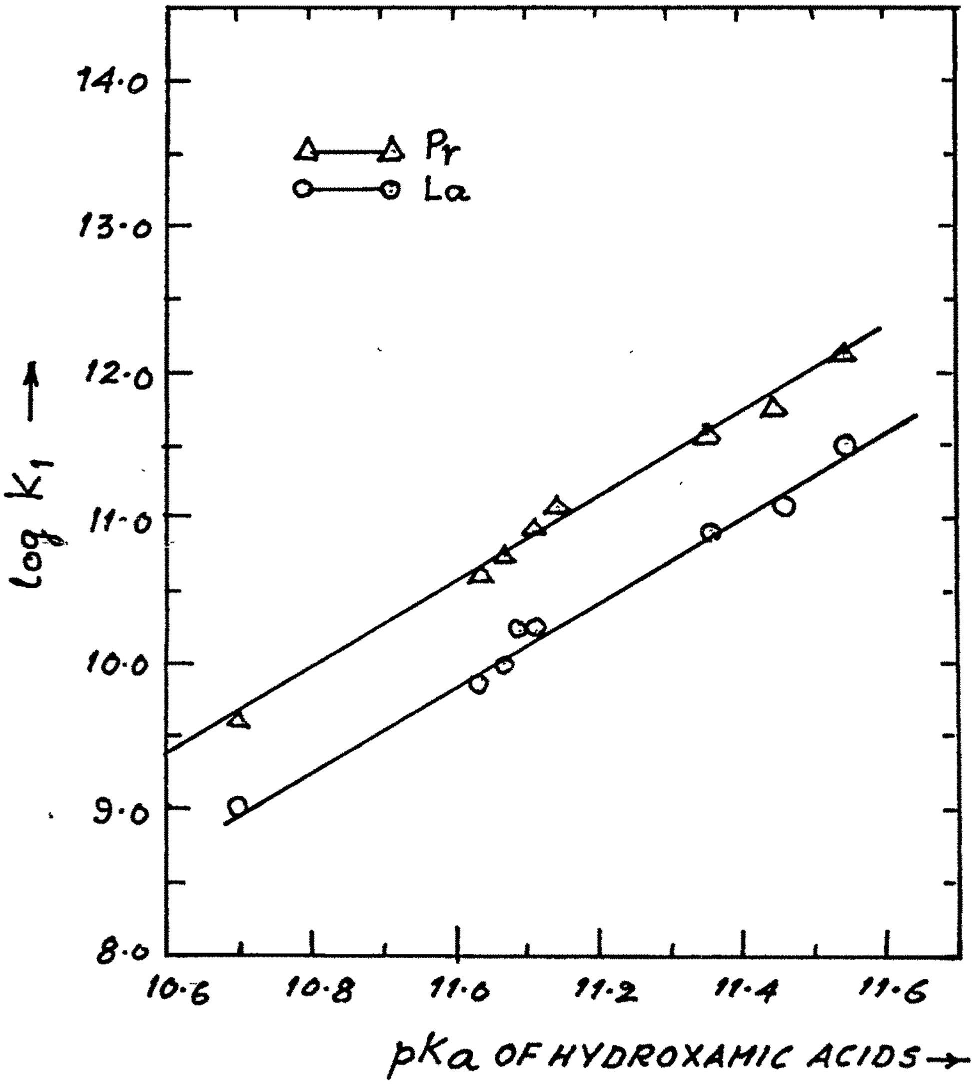


Fig. 1. Variation of stability constants with the pK_a of the N-p-chlorophenyl-m-substituted benzohydroxamic acids.

upon one property of the ligand, viz. the π donor power, they must differ in their dependence of its π donor (or acceptor) character.

It is evident from the pK_a values of the hydroxamic acids and the logarithms of the successive stability constants of the corresponding metal ligand complexes given in Tables 1-8 that hydroxamic acid molecules have a parallel effect on the proton-ligand and metal-ligand stability constants as

pK_a order $CH_3 > H > OCH_3 > F > I > Cl > Br > NO_2$

and

$\log K_1$ order $CH_3 > H > OCH_3 > F > I > Cl > Br > NO_2$

The hydrogen ion is never π donor or acceptor and only electron density around the donor atoms affects the proton ligand bond. Further, as the metal ions are capable of accepting π electrons in their vacant orbitals or donating π electrons to the vacant orbitals of donor atoms, the electron density around the donor atoms can also affect the metal ligand bond. In the absence of the steric effects, since the methyl group is located so far from coordination centre that it causes no steric hinderance to coordination, the contribution of bonding to the metal-ligand bond can be assessed from a systematic comparison between the pK_a of closely related ligand and log K_1 of the corresponding 1:1 complexes of the ligands with the same metal ion. Irving and Rossotti (17) gave thermodynamic interpretations to the possible correlations existing between stability constants of similar types of complex species in aqueous as well as mixed solvent media.

Correlation of chelate stability with nature of metal ion

A number of empirical correlations of metal chelate stability with properties of metal ion have been employed by recent investigations. The properties selected for correlation are (i) the reciprocal of the ionic radius and (ii) the total (first, second and third) ionisation potentials of rare earths.

A plot of the stability of various rare earth chelates (log K_1) versus reciprocal of the ionic radius (Fig. 2) is linear for all the hydroxamic acids studied here. The similar relationship was obtained with EDTA chelates of rare earths (22,23).

Irving and Williams pointed out that the strength of coordinated bond between a metal ion and a ligand is governed by two factors. For metal ions of a definite charge, the ionic radius controls the contribution of purely

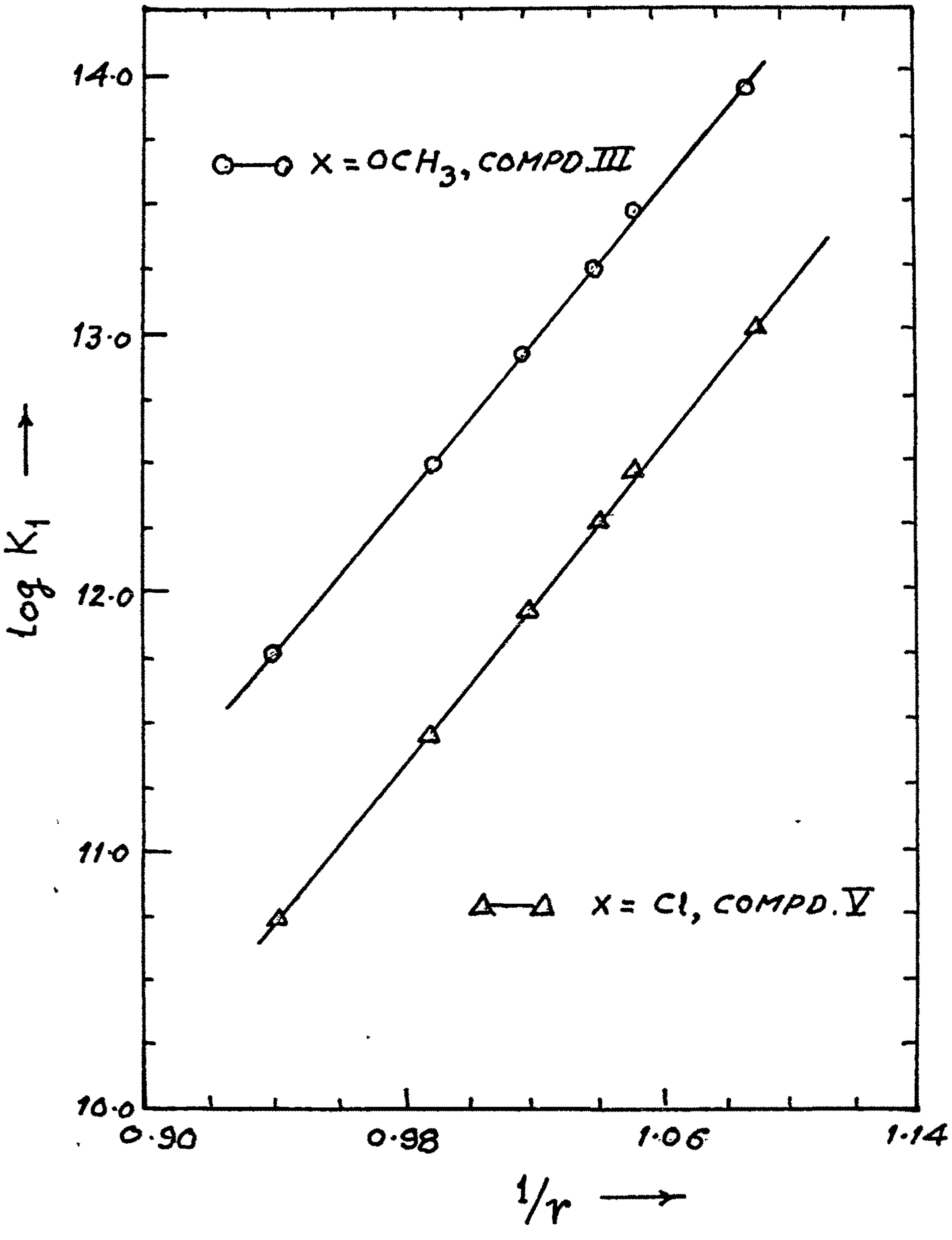


Fig. 2. Correlation between stability constants of rare earth chelates and reciprocal of ionic radius.

electrostatic interaction between the metal and the ligand, and the overall ionisation potential of the metal for the process,

$$M \text{ (gas)} \rightleftharpoons M^{2+} \text{ (gas)} + Ze,$$

decides the affinity of central ion to accept electrons from the ligand in covalent bond formation (24). In the present study, since all the rare earth ions were in 3^+ oxidation state and are more or less of the same size, the electrostatic contribution to metal-ligand bond in the first complexes formed with the same ligand is assumed to be very nearly the same. Therefore, log K_1 values for the metal complexes with different ligands were plotted against the respective overall ionisation potential of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+} (23) to see the effect of the electron affinity of the rare earth ions on the stability of the complexes they formed. In each case a straight line was obtained. This indicates that in each ligand system, the stability of first complex formed was directly proportional to the total ionisation potential of the central atom.

Order of stability constants

The log K_1, log K_2 and log K_3 values (Tables 1-8) for rare earths metal complexes examined here on comparison show the following order irrespective of the substituent in hydroxamic acid :

$La^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+} < Eu^{3+} > Gd^{3+} < Tb^{3+}$

The trend noticed here is, a regular increase in the stability constants from La^{3+} to Tb^{3+} which can be attributed to the electrostatic force of attraction between the rare earth ion and the ligand along the series. As the cationic radius of the rare earths decreases or atomic number increases the coulombic attraction for the ligand towards the rare earths increases and the stability constants (log K_1, log K_2, log K_3 or β_n) increase form La^{3+} to Tb^{3+} with all the N-p-chlorophenyl-m-substituted benzohydroxamic acids. The only exception in this finding is noticed in the case of the stability constants of Gd^{3+}, where the stability constants are less than that of Eu^{3+}. This may be due to the change in crystal radii centering at the Gd^{3+}. Further variation in the enthalpy and entropy contribution to energy is also responsible for this change.

The log K_1 values for rare earth complexes with N-p-chlorophenyl-m-substituted benzohydroxamic acid plotted against the atomic number, shown in Fig, 3, exhibit more or less regularly increasing stability with increasing atomic number upto the Eu^{3+}, there is a sudden decrease at Gd^{3+} and then further increase to Tb^{3+}. Similar trends have been observed in other instances also (25,26).

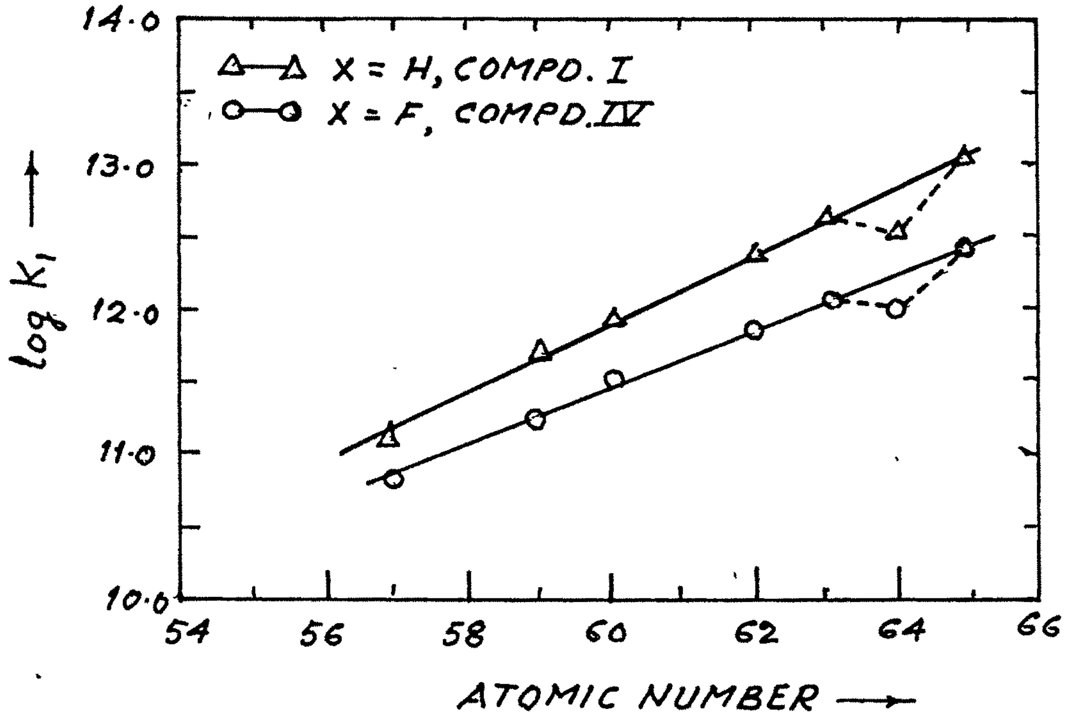


Fig. 3. Plot of log K_1 values of rare earth complexes vs atomic number.

The ratio of successive stability constants

As the tendency of a metal ion to take up ligand is proportional to the number of vacant sites, the ratio between consecutive constants, to a certain extent, is statistically determined (8). For anionic ligands the coulombic attraction is more for M^{3+} as compared to MA^{+}. As such log K_1-log K_2 is usually positive (27). Tables 1-8 show that for all systems studied here, log K_1-log K_2 is positive and lies within 1.4-1.5 log units.

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