CHAPTER IV

THERMODYNAMIC METAL-LIGAND STABILITY CONSTANTS
OF HETEROCYCLIC HYDROXAMIC ACIDS
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SUMMARY

The hydroxamic acids are versatile organic complexing reagents and have remarkable versatility in organic and inorganic analysis. The knowledge of the metal-ligand stability constants offers a means of obtaining fundamental knowledge of the structure of the chelates. It helps in correlating the equilibrium data with electronegativity of metal ions, the steric requirement of chelating agents and the size of the chelating rings. With this view it is desirable to determine the stabilities of heterocyclic hydroxamic acids with some divalent metal ions.

In the present investigation the thermodynamic metal-ligand stability constants of heterocyclic hydroxamic acids with Be$^{2+}$, Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ have been determined in 70% (v/v) dioxan-water media at 25°C.
METHOD USED

The titration method of Bjerrum (1) was modified by Calvin and Wilson (2) for determining the stability constants of metal complexes in mixed-aqueous solution. The procedure used here for determination of the thermodynamic stability constants is an extension of Bjerrum-Calvin pH titration method (1,2), essentially it combines the method of Van Uitert and Hass (3), Block and McIntyre (4) and Goldberg (5). The desired stability constants have been obtained by solving the simultaneous equations (4,5). These data were also fed to computer to obtain the stepwise formation constants, the importance of this method is that it provides greater statistical accuracy and yields true thermodynamic constants at all points for each constant to be determined (5,6). The final concentration of various solutions in the titre was generally as follows:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal ion</td>
<td>0.001 M</td>
</tr>
<tr>
<td>Ligand</td>
<td>0.01 M</td>
</tr>
<tr>
<td>Titrant</td>
<td>0.1 M</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

CHEMICALS

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

METAL SALT SOLUTIONS

Metal perchlorate solutions were prepared in order to avoid complexing of metal ions by anions. Since pure perchlorate of metals are not available, these were prepared by treating excess of pure oxides or carbonates of metal with perchloric acid of requisite strength. The solutions were filtered, boiled to remove any dissolved carbon dioxide and then suitably diluted. The concentrations of metal ions, $\text{Be}^{2+}$, was determined spectrophotometrically (7), while $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ were determined volumetrically with EDTA (8).

DETAILS OF TITRATION TECHNIQUE

In the present study metal ion (0.001 M) and hydroxamic acid (0.01 M) were taken in volume per cent aqueous dioxan and titrated with standard potassium hydroxide (0.1 M).
PROCEDURE

Transferred weighed quantity of hydroxamic acid, corresponding to 0.01 M solution in a final volume of 50 ml, to a dry titration vessel and added 35 ml of freshly distilled dioxan. Then 5 ml of metal solution and 10 ml water were added. Due allowance for the concentration in volume of mixing of the two solvents was made (9, 10).

Next the titration vessel with its contents was thermostated \((25\pm0.1^\circ\text{C})\) and nitrogen, presaturated with the 70\% dioxan-water mixture was bubbled through the solution, placed the glass and calomel electrodes in the titration vessel. The solution was titrated with 0.1 M potassium hydroxide, adding the same in small aliquots and noting the pH meter reading, \(B\), each time.
CALCULATION OF STEPWISE METAL-LIGAND STABILITY CONSTANTS

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

\[ M^{2+} + A^- \rightleftharpoons MA^+, \quad K_1 = \frac{[MA^+]}{[M^{2+}][A^-]} \]  

\[ MA^+ + A^- \rightleftharpoons MA_2, \quad K_2 = \frac{[MA_2]}{[MA^+][A^-]} \]  

\[ MA_{n-1}^+ + A^- \rightleftharpoons MA_n, \quad K_n = \frac{[MA_n]}{[MA_{n-1}][A^-]} \]  

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

\[ \bar{n} = \frac{\text{Total Bound Ligand}}{\text{Total Metal Ion}} = \frac{[MA^+] + 2[MA_2] + 3[MA_3] + ... + n[MA_n]}{[M^{2+}] + [MA^+] + [MA_2] + [MA_3] + ... + [MA_n]} \]  

Equation (iv) may be obtained in terms of $[A^-]$ and various formation constants $K_1, K_2, ... K_n$ by substitution of equations (i), (ii) and (iii) into equation (iv).
or for simplicity, equilibrium constants for the above coordination products may be represented by equation as follows:

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

\[K_1 = q_1 \cdot \frac{y_{MA^+}}{y_{M^{2+}}y_{A^-}}; \quad q_1 = \frac{[MA^+]}{[M^{2+}][A^-]}\]

or

\[K_1 = \frac{q_1}{y_+} \quad \text{(vi)}\]

Similarly,

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

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

or

\[K_2 = \frac{q_2}{y_+} \quad \text{(vii)}\]
Here $q_1$ and $q_2$ are molarity quotients for the equilibrium reactions represented by equation (i) and (ii). Rest of the terms have their usual significance. Equations (vi) and (vii) 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-Hückel 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.

**Bound Hydrogen = Total Hydrogen - Reacted - Dissociated Hydrogen**

$$[HA] = C_{HA} - C_{OH} - \left\{ [H^+] - [OH^-] \right\} \quad (viii)$$

But for the reaction $H^+ + A^- \rightleftharpoons HA$

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

Hence,

$$[HA] = q_H [H^+] [A^-] \quad (ix)$$

Substitution of equation (ix) into (viii), gives
\[ [A^-] = \frac{C_{HA} - C_{OH} - \left\{ [H^+] - [OH^-] \right\}}{q_H [H^+]} \]  

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 for the hydroxamic acid, \( HA \), is defined as

\[ K_a = \frac{[H^+] [A^-]}{[HA]} \cdot \frac{y_{HA}^+ y_{A^-}}{y_{HA}} \]  

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

\[ K_a = \frac{1}{q_H} \cdot y_\pm^2 \]  

or

\[ \log q_H = pK_a - 2 \log \frac{1}{y_\pm} \]  

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

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

\[ = \frac{(\text{Total Ligand}) - (\text{Protonated Ligand}) - (\text{free Ligand})}{\text{Total metal}} \]  

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

\[ = \frac{C_{HA} - (q_H [H^+] + 1) [A^-]}{C_M} \]  

(xii)
where $C_M$ = mole/litre of the metal ion added.

The hydrogen ion concentration, as required in equation (xiii) and (xiv), is calculated by the general formula

$$- \log [H^+] = B + \log U_H^0 - \log \frac{1}{y_\pm}$$

where $B$ is the pH meter reading in dioxan-water mixture,

$\log U_H^0$ is the correction factor for meter reading, and $y_\pm$ is the mean activity coefficient of uni-univalent electrolyte at a particular molarity and solvent composition.

Thus from the knowledge of the values of $\bar{n}$ with corresponding value of $[A^-]$ from equations (x) and (xiii), respectively the molarity quotients $q_1$ and $q_2$ may be calculated by a linear least squares fit of the equation (xiv).

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

where values of $\bar{n}$ used were restricted to the range 0.5 and 1.5.

Calculation of thermodynamic stepwise formation constants $K_1$ and $K_2$ is easily accomplished by equation (vi) and (vii) and (viii) and (xiv) in the form

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

$$\log K_2 = \log q_2 + 2 \log \frac{1}{y_\pm}$$  (xvi)
RESULTS AND DISCUSSION

The thermodynamic metal-ligand stability constants of heterocyclic hydroxamic acids with Be(II), Mg(II), Ca(II) and Ba(II) have been determined in 70% (v/v) dioxan-water at 25°C, since the complexes were not soluble in lower dioxan concentration. The values of stability constants are given in Tables 1-4.

The titration was stopped if at any stage the system became heterogeneous from precipitation of metal as a complex or hydrolysed species, since an essential condition for the determination of the solution stability constants of the complexes is that the system must remain in a homogeneous medium. The ligand to metal ratio in some titrations was varied to observe any effect due to polynuclear complex formation. The formation function $\tilde{n}$, is independent of metal concentration if the system contains mononuclear complexes only. In all the systems investigated in the present work, no evidence for the formation of polynuclear complexes was observed. The mole ratio of metal to ligand in the experiments was generally maintained at 1:10.

Hydroxamic acids are known to act as bidentate ligands and form chelates with metal ions (6,11,12). The maximum $\tilde{n}$ values for all the cases obtained are almost 2 showing the formation of 1:1 and 1:2 complexes.
The metal to ligand ratio in the complexes examined here is 1:2 showing a coordination number 4 for the metal ion. The titration data and the formation curves indicate that in solutions too the maximum complexation involves the four coordinated species, and no penta or hexa coordinated species are formed. The two complex species which are formed stepwise can be explained by the following reactions.

\[
\begin{align*}
R_1 - N - OH + M^{2+} & \rightleftharpoons R_1 - N - O + M^{+} + H^+ \\
R - C = O & \quad \quad R - C = O
\end{align*}
\]

\[
\begin{align*}
R_1 - N - O + M^{+} & \rightleftharpoons M^{2+} + H^+ \\
R - C = O & \quad \quad R - C = O
\end{align*}
\]

Where, \(K_1\) and \(K_2\) are the first and second stepwise metal chelate stability constants.

\(M^{2+}\) is \(Be^{2+}, Mg^{2+}, Ca^{2+}\) and \(Ba^{2+}\).
CORRELATION BETWEEN IONISATION CONSTANTS AND STABILITY
OF THE COMPLEX

It has been shown by several workers (13-22) that an approximately linear relationship exists between the logarithms of the stability constants, \( \log K_1 \) (or \( \log K_2 \) or \( \log B_2 \)) of a series of metal complexes derived from same metal ion with a set of closely related ligands. On this basis it is expected that more basic ligand should form more stable complexes.

\[
\log K_{MA} = BpK + \log K_{MA} - BpKo \quad (xvii)
\]
\[
\log K_{MA} = C \log K_{MAo} + \text{pK} - C_{pKo} \quad (xviii)
\]

Equation (xvii) holds good for the stability constant of the complexes of one metal with set of some substituted ligands. Equation (xviii) compares the stability constants of the closely related ligands with a series of metal ions.

In Figs. 1-3 the stability constants of divalent metal ions are plotted against \( \text{pK}_a \) of corresponding heterocyclic hydroxamic acids. It is clear from these plots that an almost linear relationship for \( \log K_1 \), \( \log K_2 \) and \( \log B_2 \) is obtained for heterocyclic hydroxamic acids. The equations for empirical relationship are given in Table 5, where 'c' and 'm' are constants and the slopes of the straight lines, respectively. Therefore, if there is a linear relationship for a series of
FIG. 1 VARIATION OF $\log K_1$ WITH $pK_a$ OF HYDROXAMIC ACIDS IN 70% DIOXAN WATER AT 25°C
FIG. 2 VARIATION OF $\log K_2$ WITH $P_{ka}$ OF HYDROXAMIC ACIDS IN 70% DIOXAN-WATER AT 25°C
FIG. 3 VARIATION OF log $\beta_2$ WITH $P^k_\alpha$ OF HYDROXAMIC ACIDS IN 70% DIOXAN-WATER AT 25°C
ligands, three cases should be distinguished (6).

(i) slope = 1; substitution affects the stability of the metal complexes to the same extent as that of the corresponding proton complexes.

(ii) slope < 1; substitution affects the stability of the metal complexes to a lesser extent than that of the corresponding proton complexes.

(iii) slope > 1; substitution affects the stability of the metal complexes to a greater extent than that of the corresponding proton complexes.

In the present work, the slope 'm' is always found more than one. This shows that the nuclear substitution brings about the greater change in the stability of the metal complexes than the corresponding proton complexes.

The magnitude of the slope depends on many factors such as ionisation potential of the metal ion (24), polarisation of the ligand by the metal ion (25), nuclear repulsion between the metal ion and donor atoms (23), tendency of the metal ion to form \( \pi \) bonds (18) and the ligand field stabilization (26). It is difficult to say what extent of each of these factors affects the magnitude of the slopes of the linear relationships.

From the pK\(_a\) values of hydroxamic acids and logarithm of the successive stability constants of the corresponding metal
ligand complexes given in Tables 1-4. It is evident that the introduction of substituent have parallel effect on proton-ligand and metal-ligand stability constants as

\[
\begin{align*}
pK_a & \quad \text{CH}_3\text{-Theno} > \text{CH}_3\text{-Furo} > \text{p-Cl-Theno} > \text{p-Cl-Furo} > \text{m-Cl-Theno} > \text{m-Cl-Furo} > \text{H-Theno} > \text{H-Furo} \\
\log K_1 & \quad \text{CH}_3\text{-Theno} > \text{CH}_3\text{-Furo} > \text{p-Cl-Theno} > \text{p-Cl-Furo} > \text{m-Cl-Theno} > \text{m-Cl-Furo} > \text{H-Theno} > \text{H-Furo} \\
\log K_2 & \quad \text{CH}_3\text{-Theno} > \text{CH}_3\text{-Furo} > \text{p-Cl-Theno} > \text{p-Cl-Furo} > \text{m-Cl-Theno} > \text{m-Cl-Furo} > \text{H-Theno} > \text{H-Furo} \\
\log B_2 & \quad \text{CH}_3\text{-Theno} > \text{CH}_3\text{-Furo} > \text{p-Cl-Theno} > \text{p-Cl-Furo} > \text{m-Cl-Theno} > \text{m-Cl-Furo} > \text{H-Theno} > \text{H-Furo}
\end{align*}
\]

**ORDER OF STABILITY CONSTANTS**

The sequence for complexes of Be(II), Mg(II), Ca(II) and Ba(II) can be explained by (i) ionic radii (ii) electronegativity and (iii) ionization potential. It can be seen from the data given in Tables 1-4 that the \( \log K_1 \), \( \log K_2 \) and \( \log B_2 \) (\( \log K_1K_2 \)) have the following order

\[
\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}
\]

The same order of the stabilities of these metal chelates have been observed with amino barbituric acid - N, N-diacetic acid, B-alanine-N,N-diacetic acid and others (26,27-29).
**TABLE 1**

Thermodynamic metal ligand stability constants of Beryllium(II) with heterocyclic hydroxamic acids in 70% (v/v) dioxan-water media at 25°C.

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Substituent</th>
<th>$H^+$</th>
<th>log $K_1$</th>
<th>log $K_2$</th>
<th>log $K_1K_2$</th>
<th>log $K_1/K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>N-phenyl-2-Furo</td>
<td>12.53</td>
<td>9.98</td>
<td>8.72</td>
<td>18.70</td>
<td>1.16</td>
</tr>
<tr>
<td>II.</td>
<td>N-p-Tolyl-2-Furo</td>
<td>12.81</td>
<td>10.40</td>
<td>9.20</td>
<td>19.60</td>
<td>1.20</td>
</tr>
<tr>
<td>III.</td>
<td>N-p-cl-ph-2-Furo</td>
<td>12.70</td>
<td>10.25</td>
<td>9.00</td>
<td>19.25</td>
<td>1.25</td>
</tr>
<tr>
<td>IV.</td>
<td>N-m-cl-ph-2-Furo</td>
<td>12.60</td>
<td>10.09</td>
<td>8.86</td>
<td>18.91</td>
<td>1.21</td>
</tr>
<tr>
<td>V.</td>
<td>N-ph-2-Theno</td>
<td>12.60</td>
<td>10.11</td>
<td>8.90</td>
<td>19.11</td>
<td>1.21</td>
</tr>
<tr>
<td>VI.</td>
<td>N-p-Tolyl-2-Theno</td>
<td>12.92</td>
<td>10.62</td>
<td>9.40</td>
<td>20.02</td>
<td>1.22</td>
</tr>
<tr>
<td>VII.</td>
<td>N-p-cl-ph-2-Theno</td>
<td>12.75</td>
<td>10.40</td>
<td>9.21</td>
<td>19.61</td>
<td>1.19</td>
</tr>
<tr>
<td>VIII.</td>
<td>N-m-cl-ph-2-Theno</td>
<td>12.68</td>
<td>10.20</td>
<td>8.97</td>
<td>19.25</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Thermodynamic metal ligand stability constants of Magnesium(II) with heterocyclic hydroxamic acids in 70% (v/v) dioxan-water media at 25°C.

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Substituent</th>
<th>H⁺</th>
<th>Magnesium(II)</th>
<th>log K₁</th>
<th>log K₂</th>
<th>log K₁K₂</th>
<th>log K₁/K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>N-phenyl-2-Furo</td>
<td>12.53</td>
<td></td>
<td>7.00</td>
<td>5.87</td>
<td>12.87</td>
<td>1.13</td>
</tr>
<tr>
<td>II.</td>
<td>N-p-Tolyl-2-Furo</td>
<td>12.81</td>
<td></td>
<td>7.80</td>
<td>6.62</td>
<td>14.42</td>
<td>1.18</td>
</tr>
<tr>
<td>III.</td>
<td>N-p-cl-ph-2-Furo</td>
<td>12.70</td>
<td></td>
<td>7.46</td>
<td>6.34</td>
<td>13.80</td>
<td>1.12</td>
</tr>
<tr>
<td>IV.</td>
<td>N-m-cl-ph-2-Furo</td>
<td>12.60</td>
<td></td>
<td>7.18</td>
<td>6.03</td>
<td>13.21</td>
<td>1.15</td>
</tr>
<tr>
<td>V.</td>
<td>N-ph-2-Theno-</td>
<td>12.60</td>
<td></td>
<td>7.21</td>
<td>6.16</td>
<td>13.43</td>
<td>1.11</td>
</tr>
<tr>
<td>VI.</td>
<td>N-p-Tolyl-2-Theno-</td>
<td>12.92</td>
<td></td>
<td>8.02</td>
<td>6.86</td>
<td>14.88</td>
<td>1.16</td>
</tr>
<tr>
<td>VII.</td>
<td>N-p-cl-ph-2-Theno-</td>
<td>12.75</td>
<td></td>
<td>7.64</td>
<td>6.44</td>
<td>14.08</td>
<td>1.20</td>
</tr>
<tr>
<td>VIII.</td>
<td>N-m-cl-ph-2-Theno-</td>
<td>12.68</td>
<td></td>
<td>7.34</td>
<td>6.20</td>
<td>13.54</td>
<td>1.14</td>
</tr>
</tbody>
</table>
TABLE 3
Thermodynamic metal ligand stability constants of Calcium(II) with heterocyclic hydroxamic acids in 70% (v/v) dioxan-water media at 25°C.

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Substituent</th>
<th>H⁺</th>
<th>Calcium(II)</th>
<th>log K₁</th>
<th>log K₂</th>
<th>log K₁K₂</th>
<th>log K₁/K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>N-phenyl-2-Furo</td>
<td>12.53</td>
<td></td>
<td>6.70</td>
<td>5.54</td>
<td>12.24</td>
<td>1.16</td>
</tr>
<tr>
<td>II</td>
<td>N-p-Tolyl-2-Furo</td>
<td>12.81</td>
<td></td>
<td>7.40</td>
<td>6.20</td>
<td>13.60</td>
<td>1.20</td>
</tr>
<tr>
<td>III</td>
<td>N-p-cl-ph-2-Furo</td>
<td>12.70</td>
<td></td>
<td>7.10</td>
<td>5.89</td>
<td>12.99</td>
<td>1.21</td>
</tr>
<tr>
<td>IV</td>
<td>N-m-cl-ph-2-Furo</td>
<td>12.60</td>
<td></td>
<td>6.84</td>
<td>5.68</td>
<td>12.52</td>
<td>1.16</td>
</tr>
<tr>
<td>V</td>
<td>N-ph-2-Theno</td>
<td>12.60</td>
<td></td>
<td>6.92</td>
<td>5.77</td>
<td>12.69</td>
<td>1.15</td>
</tr>
<tr>
<td>VI</td>
<td>N-p-Tolyl±2-Theno</td>
<td>12.92</td>
<td></td>
<td>7.62</td>
<td>6.46</td>
<td>14.08</td>
<td>1.16</td>
</tr>
<tr>
<td>VII</td>
<td>N-p-cl-ph-2-Theno</td>
<td>12.75</td>
<td></td>
<td>7.25</td>
<td>6.05</td>
<td>13.30</td>
<td>1.20</td>
</tr>
<tr>
<td>VIII</td>
<td>N-m-cl-ph-2-Theno</td>
<td>12.68</td>
<td></td>
<td>7.02</td>
<td>5.87</td>
<td>12.89</td>
<td>1.15</td>
</tr>
</tbody>
</table>
TABLE 4
Thermodynamic metal ligand stability constants of Barium(II) with heterocyclic hydroxamic acids in 70% (v/v) dioxan-water media at 25°C.

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Substituent</th>
<th>H⁺</th>
<th>Barium(II)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>log K₁</td>
<td>log K₂</td>
<td>log K₁K₂</td>
<td>log K₁/K₂</td>
<td></td>
</tr>
<tr>
<td>I.</td>
<td>N-phenyl-2-Furo</td>
<td>12.53</td>
<td>6.46</td>
<td>5.26</td>
<td>11.72</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>II.</td>
<td>N-p-Tolyl-2-Furo</td>
<td>12.81</td>
<td>7.12</td>
<td>5.94</td>
<td>13.06</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>III.</td>
<td>N-p-cl-ph-2-Furo</td>
<td>12.70</td>
<td>6.86</td>
<td>5.66</td>
<td>12.52</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>IV.</td>
<td>N-m-cl-ph-2-Furo</td>
<td>12.60</td>
<td>6.60</td>
<td>5.40</td>
<td>12.00</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>V.</td>
<td>N-ph-2-Theno-</td>
<td>12.60</td>
<td>6.70</td>
<td>5.52</td>
<td>12.22</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>VI.</td>
<td>N-p-Tolyl-2-Theno-</td>
<td>12.92</td>
<td>7.36</td>
<td>6.18</td>
<td>13.54</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>VII.</td>
<td>N-p-cl-ph-2-Theno-</td>
<td>12.75</td>
<td>7.00</td>
<td>5.82</td>
<td>12.82</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>VIII.</td>
<td>N-m-cl-ph-2-Theno-</td>
<td>12.68</td>
<td>6.80</td>
<td>5.64</td>
<td>12.44</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>


**TABLE 5**

Empirical correlation between \( p\text{K}_a \) and \( \log K_1 \) of heterocyclic hydroxamic acids metal complexes in 70% (v/v) dioxan-water media at 25°C

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( \log K_1 = m p\text{K}_a + c )</th>
<th>( m )</th>
<th>( c )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(^{2+})</td>
<td>1.60</td>
<td>-10.181</td>
<td>0.997</td>
<td></td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>2.64</td>
<td>-26.147</td>
<td>0.990</td>
<td></td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>2.39</td>
<td>-23.276</td>
<td>0.995</td>
<td></td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>2.28</td>
<td>-22.179</td>
<td>0.994</td>
<td></td>
</tr>
</tbody>
</table>

\( r \) = Correlation coefficient
As the atomic number increases the stability constant decreases which may be due to the increase in the atomic radii of the metal ions. In all the systems the values of \( \log K_1 > \log K_2 \).

**IONIC CHARGE AND RADIUS**

It is shown by Born (30) that if ions are assumed to be spherical, the energy of solution of gaseous ions should be expressed by equation

\[
\Delta E = \frac{e^2}{2r} (1 - \frac{1}{D})
\]

where \( D \) = dielectric constant, \( \Delta E \) = energy change, \( r \) = radius of ion and \( e \) = charge of the ion.

It has been observed that the stability constant increases with increasing the ratio of the charge to ionic radii (charge/radius) (31).

In the present investigation a linear relationship is observed between the stability constants of Mg\(^{2+}\), Ca\(^{2+}\), and Ba\(^{2+}\) heterocyclic hydroxamate complexes with \( e^2/r \) and \( 1/r \) (Figs. 4-5).
FIG. 4 PLOT OF log K₁ vs. e²/r FOR DIFFERENT HYDROXAMIC ACIDS IN 70% DIOXAN-WATER AT 25°C.
FIG. 5 VARIATION OF $\log K_1$ WITH $1/r$ OF METAL IONS
IONIZATION POTENTIAL

The strength of coordinate bond between a metal ion and a ligand is governed by two factors as pointed out by Irving and Williams.

The ionic radius of metal ions with a definite charge, controls the purely electrostatic interaction between the metal and the ligand, and the overall ionization potential of the metal for the process,

$$M \text{(gas)} \rightleftharpoons M^{2+} \text{(gas)} + 2 \text{e}.$$ 

decides the affinity of central ion to accept electrons from the ligand in the formation of covalent bond (32).

In the present work all the alkali earth metal ions are in the $2^+$ oxidation state so the electrostatic contribution to metal-ligand bond in the first complex formed with the same ligand is assumed to be almost the same. The plot of the log $K_1$ of the complexes versus the overall ionization potential of the alkali earth ions, $\text{Be}^{2+}$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ is linear (Fig. 6) (33).

In each case a straight line is obtained however, the point corresponding to $\text{Be}^{2+}$ is much higher, may be due to it's small size, lower atomic number and higher ionic radius.
FIG. 6 VARIATION OF $\log K_1$ WITH IONIZATION POTENTIAL OF METAL IONS
The ratio of successive stability constants:

As the tendency of the metal ion to take up ligand is proportional to the number of vacant site, the ratio between consecutive constants, to a certain extent, is statistically determined (1). For anionic ligands the coulombic attraction is more for $M^{2+}$ as compared to $MA^+$. As such $\log K_1 - \log K_2$ is usually positive (34). Tables 1-4 show that for all the systems studied here $\log K_1 - \log K_2$ is positive and lies within 1.0 to 1.3.
REFERENCES


