pH-metric Investigations of Some Protonated & Nonprotonated Bivalent Metal Ion Complexes with \( \beta \)-Furan-2aldoxime in Aqueous Dioxane

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The formation constants of protonated and nonprotonated complexes of \( \text{Mn}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Co}^{2+} \), \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Cd}^{2+} \) and \( \text{UO}_{2}^{2+} \) with \( \beta \)-furan-2-aldoxime (FDH) have already been reported, and formation of both protonated as well as nonprotonated complexes with the transition metals has been established. The ligand (FDH) has been shown to function as bidentate coordinating through furan and oxime oxygens, and as monodentate coordinating through the furan oxygen atom. With iron(III), formation of protonated and nonprotonated complexes has also been observed in aqueous dioxane, ethanol and methanol media. Al-Komser and Sen reported the stability constants of 1:1 and 1:2 complexes of FDH with \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Pd}^{2+} \) and \( \text{Pt}^{2+} \) and 1:2 (metal-ligand) complexes with \( \text{Fe}^{3+} \) and \( \text{Co}^{3+} \) in 75:25 dioxane-water media but did not consider the formation of any protonated complexes, though it is well known that the titrations for a system should be repeated at different metal-ligand concentration to confirm the absence of protonated and polynuclear complexes. Subsequently, approximate stability constants of some metal-FDH complexes were reported but this study also excluded from consideration the formation of protonated complexes. In view of these, it was felt necessary to reinvestigate the stability constants of the bivalent metal complexes with FDH more accurately. The results of such a reinvestigation are reported in this paper. The stability constants were determined pH-metrically using Calvin-Wilson's technique as given by Irving and Rosotti in aqueous dioxane (containing 40%, 50% and 60% v/v dioxane, respectively) having 0.1 M sodium perchlorate as the ionic concentration at 20°C. The formation of complexes of the type MFD\(^{+}\), M(FD)\(^{−}\), and [M(FD)(FDH)]\(^{+}\) (with the exception of \( \text{Mn}^{2+} \) and \( \text{UO}_{2}^{2+} \) which form only MFD\(^{+}\); and \( \text{Ni}^{2+} \) which forms in addition \( \text{Ni} (\text{FD})_{3}^{−} \) and \( \text{Ni(FD)}_{2}^{+} \) (FDH) also) has been observed. Graphic methods are described for the evaluation of their respective formation constants; which have been used to evaluate the effective ionic radii of the species MFD\(^{+}\) using Born's equation. The stabilities of the complexes have been compared with the corresponding pyridine-2-aldoxime complexes and the trends in the formation constants discussed.

Materials and Methods

Fresh solutions of \( \beta \)-furan-2-aldoxime of appropriate concentrations were used. Stock solutions of the bivalent metal ions, viz., manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and uranyl were prepared from AR or pro-Analyse salts in approximately 0.05N perchloric acid (E. Merck pro-Analyse). These were standardized gravimetrically and the concentration of the free mineral acid (=\( E' \)) in the metal solutions was determined using Gran's titration method. Sodium perchlorate (BDH, LR) was used to maintain the constant ionic concentration (0.1M). Carbonate-free sodium hydroxide solution was prepared from BDH (AR) sample and standardized using potassium hydrogen phthalate. Dioxane was purified as described.

A Beckman Zeromatic pH-meter with suitable glass electrode and standard calomel reference electrode was used.

Titration Procedure

The concentration \( E' \) of the free perchloric acid present in the metal solutions was determined titrimetrically. The following solutions were then prepared for the titration of a metal-reagent set in 50%, v/v water-dioxane medium. (1) 5 ml of \( E \) molar perchloric acid, (4-10 \( E \)) ml of 0.50 M sodium perchlorate, and (1-10\( E \)) ml of distilled water (total...
aqueous phase 10 ml) and 10 ml dioxane; (2) aqueous phase prepared in identical manner as described in (1) and 10 ml of \( T_H \) molar organic reagent solution prepared in dioxane; (3) 5 ml of \( T_M \) molar metal solution prepared in \( E' \) molar perchloric acid (pH adjusted to 2.00), (4-10E') ml 0.5M sodium perchlorate, (1-10E') ml distilled water (total aq. phase 10 ml) (values for \( E' \) ranged from 0.044 M to 0.040 M in different metal solutions) and 10 ml of \( T_H \) molar organic reagent solution prepared in dioxan.

The value of \( E \) in these titration sets was kept at 0.01M (to correspond to pH 2.00). For 60\%, and 40\% (v/v) dioxan-water mixtures, the volume of water and dioxan were suitably adjusted.

The solution (1), (2), or (3) was placed in the titration vessel and nitrogen gas presaturated with 40\%, 50\% or 60\% (v/v) aqueous dioxane was bubbled through it. Sodium hydroxide (0.2N) was gradually added to the solution and the equilibrium pH-meter reading (\( R \)) of the solution recorded after each addition of alkali. The titration in the case of solution (3) was stopped at the appearance of opalescence in the solutions.

The metal-reagent ratios in solution (3) were (i) 1:5, 1:2.5; (ii) 1:25, 1:12.5, 1:5 and (iii) 1:50, 1:25,1:10.

All the above titrations were repeated till the pH-meter readings were found to be within 0.02 pH units at each addition of alkali.

**Results**

**Proton-ligand system** — The proton-ligand association constants, \( \beta_i^H \) for the anion \( FD^- \) in different media were determined at 20° from the respective formation functions \( n_0(h) \) where \( n_i \) is the average number of protons attached per \( FD^- \) at equilibrium hydrogen ion concentration \( h \). The values of \( h \) were calculated from the pH-meter readings using the correction terms\(^a\). The values of \( \beta_i^H \) obtained in 40\%, 50\% and 60\% aq. dioxane are 12.9, 13.52 and 14.20 respectively, which agree well with those reported under similar conditions\(^b\).

**Metal-ligand systems** — Average number of ligands attached per metal ion \( (\bar{n}) \) was calculated from the titration curves using the equations proposed by Irving and Rossotti\(^c\). The free ligand concentration of the anion \( FD^- \) \( (=a) \) was calculated using Eq. (1), \( A^N \) being the concentration of the reagent not bound to metal ions, calculated by the method of successive approximation\(^d\).

\[
a = A^N / (1 + \beta_i^H \cdot h)
\]

(1)

As the formation curves, \( \bar{n} \) versus (log \( a \)) curves, calculated for different initial concentration sets of metal and FDH were found to be independent of the total metal taken (=\( T_M \)) but dependent on the total initial concentration of FDH (=\( T_H \)) the formation of mononuclear but protonated complexes with respect to the metal ions, i.e. \( ML_nH_i \) was inferred and the stoichiometric stability constant \( \beta_{st} \) was defined as

\[
\beta_{st} = \frac{[ML_nH_i]}{[M][L]^n[H]^i} = \frac{[ML_nH_i]}{b \cdot a^n \cdot h^i}
\]

(2)

where \( b \) is concentration of free metal ions and the square brackets denote the molar concentrations. As the hydroxo complexes can also be represented as \( ML_nH_i \) (with negative values for \( j \)), the average number of the ligands attached per metal ion (=\( \bar{n} \)) is given by the expression (3):

\[
n = \frac{1}{B} \left( \sum_{j=0}^{N} n [ML_nH_i] \right) \quad \text{(3)}
\]

Using Eq. (2), the expression (3) can be rearranged to

\[
n = \frac{\sum_{j=0}^{N} n [ML_nH_i]}{\sum_{j=0}^{N} n F_n a^n} \quad \text{(4)}
\]

where \( F_n \) is given by the expression (5) and is constant at a given \( h \)—value for a metal-ligand set

\[
F_n = \sum_{j=0}^{N} n [ML_nH_i] 
\]

(5)

Since by definition \( F_0 = \sum_{j=0}^{N} [M] = 1 \), if the formation of hydroxo complexes is ignored (an assumption which is presently made as FDH is reported to be a strong field ligand\(^d\) and also because of the work of Bryson and Dwyer\(^a\) and our own observations\(^1\) \& \(^2\) the values of the functions \( F_n \) were obtained by transforming Eq. (4) first into Eq. (7).

\[
f_1 = \frac{n}{(1-n) a}
\]

\[
f_1 = \frac{\sum_{j=0}^{N} n [ML_nH_i]}{\sum_{j=0}^{N} n F_n a^n} \quad \text{(7)}
\]

![Fig. 1 — Plot of \( f_1 \) against \( (1-n) a \) for \( Co^{3+} \) in \( 60\% \) dioxane containing 0.1 M NaClO₄ at \( h = 3.98 \times 10^{-4} \) (1), \( 2.52 \times 10^{-4} \) (2) and \( 1.00 \times 10^{-4} \) (3).](image-url)
The plot of $f_2 = \frac{(n-\bar{n})a^{n-1}}{(1-n)}$ against $2(1-n)a$ should give a curve with intercept $= F_2$ and limiting slope $= F_2$ as $a \rightarrow 0$. It is observed that in all the cases studied (except that of Ni$^{2+}$-FDH), a linear plot was obtained (see Fig. 1) indicating that the second term

$$
\sum_{\bar{n}}^N \frac{(n-\bar{n})a^{n-1}}{(1-n)}, \quad F_2 = 0
$$

and the maximum value of $n$, i.e. $N = 2$. In the case of Ni(II) system, the plots had curvature, so that after the determination of $F_3$ from Eq. (7), the values of $F_2$ and $F_3$ were determined graphically by further rearrangement of Eq. (4) into Eq. (8):

$$
f_2 = \frac{n}{(2-n)a^2} + \frac{n-1}{2-n} \cdot \frac{F_1}{a}
$$

$$
= F_4 + \frac{3-n}{2-n} \cdot aF_3 + \frac{n-\bar{n}}{2-n} \cdot F_3a^{2n-2} \ldots (8)
$$

The plots of $f_2$ against $3(1-n)$ $a/(2-n)$ were linear with intercept $F_2$ and slope $F_3$, indicating that in the case of Ni(II)-FDH system, the highest complex formed is having Ni(II) : FD$^-$ in the ratio 1:3.

After determining the functions $F_n$ at different $h$ values, the respective stability constants were found from $F_n(h)$ as follows:

$$
F_n = \beta_{10} + \beta_{11}h + \beta_{12}h^2 + \ldots \ldots \ldots (9)
$$

The functions $F_n$ for all the complexes studied was found to be constant, so that $F_1 = \beta_{10}$ and the absence of the protonated 1:1 (M:L) complex is indicated. This is to be expected as the formation of the protonated complex MLH$^+$ will not result in the change of pH, so that the pH-metric method is not suitable for the determination of the stability constants for the "addition complexes".

The plots of $F_2$ against $h$ were, however, linear (Fig. 2) so that for $F_2$, Eq. (9) took the form:

$$
F_2 = \beta_{20} + \beta_{21}h + \beta_{22}h^2 + \ldots \ldots \ldots \ldots (10)
$$

The plots of $F_3$ against $h$ for Co$^{3+}$-FDH system [Y=11(1)] and Zn$^{2+}$-FDH system [Y=12 (2)] in 60% dioxane.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\log_{10} \beta_{10}$ in Dioxane</th>
<th>$\log_{10} K_{20}$ in Dioxane</th>
<th>$\log_{10} \beta_{20}$ in Dioxane</th>
<th>$\log_{10} \beta_{30}$ in Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$</td>
<td>4.24 3.27 2.72</td>
<td>60% 50% 40%</td>
<td>5.20 4.22 3.68</td>
<td>11.37</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>5.68 4.89 4.35</td>
<td>60% 50% 40%</td>
<td>7.79 7.59 7.37</td>
<td>7.00 6.10 5.14 4.40 12.40 10.63 9.07 22.12 20.20 18.63</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>6.30 5.49 4.67</td>
<td>60% 50% 40%</td>
<td>6.87 6.02 5.48</td>
<td>7.79 7.16 6.33 16.90 15.05 13.97</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>8.86 7.89 7.34</td>
<td>60% 50% 40%</td>
<td>8.47a 10.25 9.99b 7.23a</td>
<td>8.04 7.16 6.63 16.90 15.05 13.97</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>6.06 5.17 4.67</td>
<td>60% 50% 40%</td>
<td>8.10b 7.45b</td>
<td>12.96 11.09 10.06</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>6.90 5.92 5.39</td>
<td>60% 50% 40%</td>
<td>6.46a 12.20b</td>
<td>6.06 5.17 4.67 12.96 11.09 10.06</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>4.37 3.89 3.52</td>
<td>60% 50% 40%</td>
<td>11.23 10.45 10.00</td>
<td>21.46 19.40 18.72</td>
</tr>
</tbody>
</table>

Note: In order to maintain uniformity the values of the stability constants reported by (a) Sen and Al-Komser, (b) Bark and Griffin have also been given in terms of $\beta_{10}$, $K_{20}$, and $\beta_{20}$, e.g. $K_1$ (as it refers to the nonprotonated complex ML$_2$H$^+$, $j=0$) of the earlier work is reported as $K_{20}$.

(a) These values are reported at 25°C in 75% (v/v) aq dioxan containing 0.096M NaClO$_4$.

(b) These values are reported in 75% (v/v) aqueous dioxan.

For Ni(II), $\log_{10} \beta_{20} = 16.80, 14.70, 13.10$; $\log_{10} \beta_{21} = 27.80, 25.40, 23.90$ for 60%, 50% and 40% dioxane respectively.

Fig. 2 - Plot of $F_2$ against $h$ for Co$^{3+}$-FDH system [Y=11(1)] and Zn$^{2+}$-FDH system [Y=12 (2)] in 60% dioxane.
could be calculated because of precipitation around \( n = 0.40, 0.60 \) and 0.70 respectively.

In order to check the significance of these formation constants, the degree of the formation of various complexes was calculated from the stability constants given in Table 1, using the Eqs. (10)-(13).

\[
\alpha_{\text{CoL}} = \frac{\beta_{10}}{1 + \beta_{10}a + \beta_{20}a^2 + \beta_{21}a^2h} \quad \ldots \ (10)
\]

\[
\alpha_{\text{CoL}^2} = \frac{\beta_{20}}{1 + \beta_{10}a + \beta_{20}a^2 + \beta_{21}a^2h} \quad \ldots \ (11)
\]

\[
\alpha_{\text{CoL}^2H} = \frac{\beta_{21}}{1 + \beta_{10}a + \beta_{20}a^2 + \beta_{21}a^2h} \quad \ldots \ (12)
\]

\[
a = \frac{T_{\text{H}_0}^\alpha}{\rho H h} \quad \ldots \ (13)
\]

The representative plots of \( \alpha \) vs \( pH \) are given in Fig. 4 showing that the maximum number of different complexes are formed in significant proportions in solution.

**Determination of the effective ionic radii of the complexes** — From the values of the stability constants obtained in different media having different dielectric constants (\( \varepsilon \)), an attempt was made to calculate the effective ionic radii (\( r_{\text{eff}} \)) of the complexes in solutions, using Born’s equation. For this purpose, first \( \beta_{10} \) the stability constant in water, was determined by graphical extrapolation of log \( \beta_{10} \) values in different media and then log \( (\beta_{10}/\beta_{10}) \) was plotted against \( 100/\varepsilon \) (Fig. 5). The values of \( r_{\text{eff}} \) were then calculated from the interception on the \( 100/\varepsilon \)-axis; and are given in Table 2 for the complex \( \text{MFD}^+ \). The values for other complexes were not calculated because of accumulated errors in the successive stability constants inherent in any procedure adopted for the calculations.

**Discussion**

**Stability constants** — Al-Komser and Sen have reported the stability constants of 1:3 complexes also in case of iron(II) (log \( K_{10} = 7.31 \)) and cobalt(II) (log \( K_{10} = 5.60 \)). In the case of iron(II) we observed precipitation around \( n = 0.7-0.8 \) so that only the values of \( \beta_{10} \) (and \( \beta_{21} \)) only could be calculated. In the case of cobalt-FDH system, the corresponding formation functions approached \( n = 2 \) with a dec-
increase in the slope at \( n > 1.5 \), indicating that the highest cobalt(II) : FDH ratio in this complex is 1 : 2. This is further confirmed from the analysis of the corresponding formation functions as the plots of the function \( f \) against \((2 - n) a (1 - n)\) at different values of \( a \) are linear lines. In order to explain the abnormal value in case of iron(II) and cobalt(II) complexes, the authors postulated the oxidation of the metal ions in these complexes to the tervalent state.

The earlier work on the stability constants of FDH complexes is based upon a single concentration of metal-ligand set, which is insufficient to even consider the formation of protonated complexes. The log \( K_{19} \) values for the FDH complexes are in the order

\[
\text{UO}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}
\]

whereas log \( K_{29} \) values follow the order

\[
\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}
\]

The log \( K_1 \) and log \( K_2 \) for the FDH complexes follow the Irving-William's order of stability constants (Fe\(^{2+}\) < Co\(^{2+}\) < Ni\(^{2+}\) < Cu\(^{2+}\) > Zn\(^{2+}\)). This order is, however, different from the one reported by Al-Komser and Sen, who found that the stability constants decrease in the order Fe\(^{2+}\) > Co\(^{2+}\) > Ni\(^{2+}\) > Cu\(^{2+}\) > Zn\(^{2+}\). This was attributed to the possible oxidation of Fe\(^{2+}\) and Co\(^{2+}\) under \( N_2 \) atmosphere; we, however, found that these systems do not get oxidised even up to pH 10 so readily under \( N_2 \) atmosphere, and the stability constants for Fe\(^{2+}\) and Co\(^{2+}\) complexes can be determined.

As expected log \( K \) for Co\(^{2+}\)-FDH complexes, is lower than the corresponding values for Zn\(^{2+}\)-FDH complexes, ions having similar structure tend to give weaker complexes, with increasing sizes.

In case of pyridine-2-aldoxine (PDH) complexes, the Irving-William's order is not followed which has been attributed to hydrogen bridges between the oxygen and that of phenolic hydroxyl stabilizing the ML\(_2\) complexes (M = Mn, Co, Ni and Zn).

The log \( K_{10} \) as well as log \( K_{20} \) values for Ni\(^{2+}\)-FDH complexes are much lower (by 2.55 and 1.94 respectively in 60\% aq. dioxan) than the corresponding values of Cu\(^{2+}\)-FDH complexes whereas in the case of PDH complexes, they are higher (by 0.50 and 1.4 units respectively). The difference is due to the fact that FDH is coordinating through two oxygen atoms, whereas PDH coordinates through both the nitrogen atoms; and Ni\(^{2+}\) forms weaker complexes with oxygen donors.

The stability constants for Zn\(^{2+}\)-complexes with FDH are higher than those for the corresponding Ni\(^{2+}\)-complexes and this may be due to the fact that the ions with complete \( d \)-orbitals tend to form stronger complexes with O-donor. FDH has O-donor atoms. In the case of FDH complexes (N + N donor ligand) this order is, however, reversed.

The stability constant for UO\(^{2+}\) complex is greater than that for Cu\(^{2+}\) complex; and this may also be due to the fact that in the case of FDH chelation through two oxygens resembles peri-dihydroxy compounds, which are reported to favour chelate formation, with high stability constants, with ions having a complete octet.

For a metal in different oxidation states, it has been found that the stability constants (log \( K_{19} \) as well as log \( K_{39} \) for Fe\(^{2+}\) — complexes are lower than the corresponding values for Fe\(^{3+}\) — complexes (log \( K_{10} \) = 11.87 and log \( K_{20} \) = 2.02).

Effective ionic radii — As expected, the effective ionic radii for the different FDH complexes (Table 2) follow the same order as that of their crystal radii.

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References