Dissociation Constant of 1-(2,3-Dihydroxy-4-pyridylazo)-benzene-4-sulphonic Acid (DHP-4S) & Stability Constants of Its Complexes with Mn(II), Cd(II), Co(II), Ni(II), Zn(II), Fe(II) & UO$_2^{2+}$

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Received 11 January 1977; accepted 20 July 1977

Dissociation constant of 1-(2,3-dihydroxy-4-pyridylazo)-benzene-4-sulphonic acid (DHP-4S) and stability constants of its complexes with UO$_2^{2+}$, Ni(II), Co(II), Fe(II), Zn(II), Cd(II) and Mn(II) have been determined potentiometrically in aqueous medium at different ionic strengths and temperatures. The order of stability constants of the complexes of the various metal ions is: Mn(II) < Cd(II) < Co(II) < Zn(II) < Ni(II) < Fe(II). In the case of UO$_2^{2+}$, only log K could be determined.

Values of $\delta h$ and $E_r$ (Mn-Zn) have been calculated.

Dissociation constant of 2,3-dihydroxy pyridine (DHP) has been reported earlier$^1$. 1-(2,3-Dihydroxy - benzene-4-pyridylazo)-4-sulphonic acid (DHP-4S) has been used as an analytical reagent for the complexometric determination of Zn(II), Cd(II), Hg(II)$^2$ and Co(II), Ni(II), Cu(II)$^3$. Garg$^4$ et al. have used the reaction for the formation of DHP-4S, as a sensitive test for nitrite ion. The present note deals with the determination of dissociation constant of the DHP-4S and stability constant of its complexes with Mn(II), Cd(II), Co(II), Ni(II), Zn(II), Fe(II) and UO$_2^{2+}$, in aqueous medium and at different ionic strengths and temperatures.

1-(2,3-Dihydroxy-4-pyridylazo)-benzene-4-sulphonic acid was prepared by diazotizing sulphamic acid and subsequently coupling the diazotized product with 2,3-dihydroxy pyridine. Purity of the ligand was checked by TLC and elemental analysis.

Melting point of the purified DHP-4S is high, i.e. above 360°. Solution of the ligand was prepared in doubly distilled water. All the metal ion solutions were prepared from the corresponding nitrates or sulphates (BDH, AK) and were standardized by conventional methods wherever necessary. Chemically pure sodium perchlorate (Riedel) was used to keep the ionic strengths constant (0-005, 0-06, 0-1 and 0-2M).

A 0-05M solution of tetramethylammonium hydroxide (TMAH) (E. Merck) in doubly distilled water was used as the titrant. It was standardized with a solution of potassium hydrogen phthalate. Titrations were carried out in an inert atmosphere (by bubbling oxygen-free pre-saturated nitrogen through the solutions). A Beckman expandometric pH-meter, SS-2, with glass electrode (pH range 0-14) was used for pH measurements.

Titrations procedure — The experimental method of Bjerrum and Calvin as modified by Irving and Rossotti$^8$ was used to determine $n$ and $\bar{p}L$ values. The following mixtures (total volume 20 ml, ionic strength adjusted with 2M NaClO$_4$) were titrated potentiometrically against standard 0-05M tetramethylammonium hydroxide (TMAH).

(i) 4-00 ml HClO$_4$ (0-01M) + 1-00 ml of metal ion solution (0-01M).
(ii) 4-00 ml HClO$_4$ (0-01M) + 7-5 ml of ligand (M/150)+1-00 ml of metal ion solution (0-01M).
(iii) 4-00 ml HClO$_4$ (0-01M) + 7-5 ml of ligand (M/150)+1-00 ml of metal ion solution (0-01M).

In all the cases corrections for changes in volumes, which take place during the course of titrations due to the addition of TMAH, were made.

A tentative structure (I) has been assigned to the ligand. Its IR spectrum in KBr shows $\nu$=N=N, $\nu$S=O and $\nu$O-H at 1585, 1180 and 3250 cm$^{-1}$ respectively. The metal ions are expected to form five-membered chelates by coordination through the azo nitrogen and OH group in the ortho position to it (I). Since only one proton per ligand molecule is liberated on complexation, Y = 1 in all the cases.

From the titration curves (i) and (ii) of acid alone and in the presence of ligand, $\bar{p}H$ values of the ligand at various pH values were calculated and the $pK_a$ values of the ligand at different ionic strengths and temperatures were evaluated by plotting log $\bar{p}H/(1-\bar{p}H)$ versus $\bar{p}H$, when linear plots of intercept equal to $pK_a$ and slope equal to 1 were obtained. The values of proton-ligand stability constants are given in Table 1.

From the titration curves of the solutions (i) and (iii), $\bar{p}H$ values of the metal complexes were determined at various pH values. From a knowledge of practical $pK_a$ values and $\bar{p}H$ at a particular $\bar{p}H$, the corresponding value of $pL$ was then calculated. The $\bar{p}H$ values are plotted against the

$\delta h$ and $E_r$ (Mn-Zn) have been calculated.
TABLE 1 — PROTON-LIGAND STABILITY CONSTANTS AND METAL-LIGAND STABILITY CONSTANTS OF Mn(II), Cd(II), Zn(II) AND Co(II) COMPLEXES AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

<table>
<thead>
<tr>
<th>H+</th>
<th>Mn(II)</th>
<th>Cd(II)</th>
<th>Zn(II)</th>
<th>Co(II)</th>
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<tr>
<td>log K1</td>
<td>log K2</td>
<td>log β2</td>
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</tr>
<tr>
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<td>3.07</td>
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<td>3.76</td>
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<tr>
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<td>5.88</td>
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<td>—</td>
<td>—</td>
<td>3.56</td>
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</tbody>
</table>

TABLE 2 — METAL-LIGAND STABILITY CONSTANTS OF Ni(II), Fe(II) AND UO22+ COMPLEXES

<table>
<thead>
<tr>
<th>Ni(II)</th>
<th>Fe(II)</th>
<th>UO22+</th>
</tr>
</thead>
<tbody>
<tr>
<td>log K1</td>
<td>log K2</td>
<td>log β2</td>
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<td>5.38</td>
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<tr>
<td>5.02</td>
<td>4.73</td>
<td>9.75</td>
</tr>
</tbody>
</table>

The corresponding pL value to give formation curve of the metal chelation equilibria.

The values of log K1 and log K2 were calculated by using the correction term method of Irving and Rossotti. Log K3 value in case of Fe(II) was read directly from the formation curves using Bjerrum's half rule method. In the case of UO22+, only log K2 was obtained.

From the results (Tables 1 and 2) it is seen that the pK4 value of the DHP-4S decreases with increase in temperature and ionic strength. The pK5a value of the ligand at zero ionic strength obtained by extrapolation is 6.43.

The order of stability of bivalent metal complexes with DHP-4S is as follows: Mn(II) < Cd(II) < Co(II) < Zn(II) < Ni(II) < Fe(II).

Except for the Fe(II) complex, this sequence is in agreement with the Irving-Williams order. An abnormally high stability of the Fe(II) complexes has been observed in many cases, particularly with aromatic ligands, e.g. riboflavin, folic acid, o-phenanthroline, etc. It has been attributed to the resonance stabilization energy of Fe(II) complexes upon coordination with a ligand having an aromatic ring system. An oxidation of Fe(II) to Fe(III) did not occur in our experiments as the potentiometric titrations were performed in inert atmosphere.

Formation curve for Cu(II) could not be drawn because the pH drop during chelation was too much. This type of behaviour has been reported for Ni(II) with 4-(2-pyridylazo)-resorcinol and 1-(2-pyridylazo)-2-phenanthrol also.
From the log $K_1$ values of the complexes formed by metals having 3$d^3$ and 3$d^{10}$ configurations, the values of thermodynamic stabilization energy ($\Delta H$) were calculated according to the method described by George and McClure. The values have been found to be 19, 25 and 35 for the Fe(II), Co(II) and Ni(II) complexes respectively.

The Er (Mn-Zn) value found to be 49, is of the same order as observed for many other ligands which coordinate to the metal ion through one nitrogen atom. The values of $\Delta H$ observed for the Co(II) and Ni(II) are also of the same order. This indicates that the metal ions are bonded through one nitrogen and one oxygen to the ligand molecule. Shift of $\nu N\rightarrow N$ to lower values in the IR spectra of some complexes, which were isolated in solid state, confirms this mode of coordination.

The fact is further supported by a slight shift to higher atomic numbers in the curve of $\Delta H$ (heat of complexation) against atomic number (Fig. 1, curve B) as compared to the curve of $\Delta H$ (heat of hydration of metal ion) against atomic number (Fig. 1, curve A). The straight lines joining Mn and Zn represent the situation in the absence of crystal field stabilization.

One of the authors (J.P.G.) is thankful to the UGC, New Delhi, for providing financial assistance.

References


