Chapter-5

Stabilities of Proton and Binary Lanthanide Complexes of 4-Hydroxyquinoline 2-Carboxylic acid in Various Dioxane-Water Medium

Introduction:

In course of our work on various quinoline derivatives as ligands, we considered it proper to use 4-hydroxyquinoline 2-carboxylic acid as the ligand. The present chapter describes the research with this ligand. Literature survey indicates that no work is done with this ligand for the determination of the stability of lanthanide complexes. Pujari et al.\(^1\) have reported stabilities of some ternary complexes of \textit{Y(III)} with NTA, EDTA or \textit{H}_2DTA as primary ligand and picolinic acid as the secondary ligand. Picolinic acid can be regarded as having a structure very similar to the present ligand. The proton-ligand formation constant has been reported to be 5.29 at 25°C whereas the stability for \textit{Y-EDTA-picolinic acid} and \textit{Y-NTA-picolinic acid} to be 3.28 and 3.69 respectively. Shelke and Jahagirdar\(^2\) have used picolinic acid as the primary ligand while studying the stability of some ternary complexes of \textit{Nd(III)} with some dicarboxylic acid as the secondary ligand. The \textit{Nd-picolinic acid} stepwise formation constant in aqueous medium at 30°C were found to be 3.96 for the \textit{M-L} complex and 3.04 for \textit{ML}_2 complex. Roulet et al.\(^3\) has reported the
thermodynamic proton-ligand and complex stability of rare earths with furan 2-carboxylic acid and thiophene-2-carboxylic acid. The values of proton-ligand formation constants are 3.19 and 3.54 for furan and thiophene derivatives respectively.

Experimental:

The ligand is not soluble in water, so for every alkali titrations requisite amount of the ligand were weighed out and the titration were done in mixed aqueous solvents only. Details of the experiments are described in the chapter 'Materials and methods'. To determine the $PK_n^H$ of the ligand, the ligand concentration was maintained at 0.002(M) due to its low solubility; for determination of the stability constant of binary complexes of the ligand with lanthanide elements e.g., La(III), Gd(III) and Dy(III), the metal concentration was maintained at 0.0005(M) so as to keep the ratio of metal:ligand at 1:4. To determine the stability of the ternary complexes the concentrations of the metal ions and the primary ligands were maintained at 0.001(M) to keep the ratio of metal ion : primary ligand : secondary ligand at 1:1:2. The ligand was obtained from Fluka and used after recrystallisation. It is important to mention here that this ligand was found to have low basicity and poor chelating property, and also it did not form ternary complexes. So elaborate studies as with the three former ligands are not done with this ligand.
Fig. 19 – Alkali titration curves for La-4-hydroxy quinoline 2-carboxylic acid in aqueous medium at 30°C.
Calculation:

Same methods of calculation as discussed in Chapter-1 were also adopted for this ligand to determine the proton ligand formation function, metal-ligand formation function, proton-ligand formation constant, free ligand concentration and metal ligand formation constant.

Results and discussion:

a) Proton-ligand formation constant - As the ligand is having two dissociable proton, two values of proton-ligand formation constant is expected. The third one expected for the protonation of the quinoline nitrogen is not obtained. This may be due to presence of the carboxylic acid group in its vicinity. The carboxylic acid group can withdraw the electron density of the quinoline ring and can reduce the basicity of the nitrogen atom disfavouring the formation of NH\(^+\) group. The other reason may be that the proton from carboxylic acid can form the zwitterion with nitrogen atom as it is present in 2-position. During the alkali titrations as shown in Fig. 19 there is no initial rise in the pH of the ligand solution, indicating the absence of proton absorption from the solution. The proton dissociation from the phenolic-OH group occurs at higher pH above 11. Generally the glass electrodes become a little insensitive at this pH region so the values calculated may be a little erroneous. Keeping in mind the above fact and
also that lanthanides should prefer to form chelate complexes with the ligand with quinoline nitrogen and carboxylic oxygen as the donor atoms. The participation of phenolic-OH group in the chelate formation being sterically incompatible the constants corresponding to -OH group are not calculated and reported. The only values of proton-ligand formation constants reported are due to the carboxylic group. The reported values are nearer to the published data for the carboxylic groups. The proton ligand formation for the ligand is determined in various v/v percentage from 30% to 70% of dioxane and shown in the following table.

<table>
<thead>
<tr>
<th>Composition (v/v)</th>
<th>30%</th>
<th>40%</th>
<th>50%</th>
<th>60%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{E} )</td>
<td>0.0195</td>
<td>0.0234</td>
<td>0.0293</td>
<td>0.0388</td>
<td>0.0561</td>
</tr>
<tr>
<td>( PK_H^1 )</td>
<td>3.52</td>
<td>3.65</td>
<td>3.70</td>
<td>3.79</td>
<td>3.85</td>
</tr>
</tbody>
</table>

From the table it is obvious that the values of \( PK_H^1 \) increases with the increase in the values of \( \frac{1}{E} \). The values of \( PK_H^1 \) is found to be quite low compared to the \( PK_H^1 \) values of picolinic acid, may be due to the presence of -OH group at 4-position and also the presence of a fused benzene ring.

b) Binary complexes - Owing to the solubility problem, the stability constant of the binary complexes of La(III), Gd(III), and Dy(III) only were determined in 50% (v/v) dioxane-water
medium at $30^\circ$C. The values are shown in the following table.

<table>
<thead>
<tr>
<th></th>
<th>log $\beta_1$</th>
<th>log $\beta_2$</th>
<th>log $\beta_3$</th>
<th>log $K_1$</th>
<th>log $K_2$</th>
<th>log $K_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(III)</td>
<td>3.27</td>
<td>6.45</td>
<td>9.64</td>
<td>3.27</td>
<td>3.18</td>
<td>3.19</td>
</tr>
<tr>
<td>Gd(III)</td>
<td>3.33</td>
<td>6.58</td>
<td>9.80</td>
<td>3.33</td>
<td>3.25</td>
<td>3.22</td>
</tr>
<tr>
<td>Dy(III)</td>
<td>3.36</td>
<td>6.65</td>
<td>9.94</td>
<td>3.36</td>
<td>3.29</td>
<td>3.29</td>
</tr>
</tbody>
</table>

From the table it is evident that the overall formation constants and also the stepwise formation constants for the ligand increases from La to Gd and Gd to Dy. This is expected as the ionic radii decreases in the above sequence. Similar observations were made previously with the other ligands. The other trend observed was, log $K_1 >$ log $K_2 >$ log $K_3$. This can be explained by statistical factor, steric hindrance etc. as discussed in previous chapters. The low values of the formation constant of lanthanide complexes are expected as the values of proton-ligand formation constants are low or the basicity of the ligand is less compared to other ligands under the present investigation. All these values are calculated from the titration curves at lower pH region where the phenolic -OH group remain undissociated. The values of the formation constants of the binary complexes of the ligand is less compared to that of picolinic acid$^2$ is due to the low basicity of the ligand.
c) **Ternary complexes** - All attempt made to determine the ternary step constants using EDTA or NTA as primary ligand and 4-hydroxyquinoline 2-carboxylic acid as the secondary ligand at three different temperatures in 50% (v/v) D-W medium, was frustrated. The theoretical composite curve superimposes on the metal titration curve in the range of pH 3-10 showing absence of ternary complex formation. However Pujari and Munshi\(^1\) has reported the stability of ternary complexes of Y(III) with EDTA, NTA as primary ligand and picolinic acid as the secondary ligand. \(PK_1^H\) of picolinic acid was found to be 5.29 and \(\log K\) was evaluated to be 3.28 and 3.69 for EDTA and NTA as primary ligand respectively. Although picolinic acid has a similar type of structure to the present ligand (HQCA), basicity of the former is substantially higher. This may be one of the reasons that picolinic acid can form a ternary complex whereas HQCA can't. The ligand is also not expected to coordinate through the phenolic hydroxyl group due to structural incompatibility as was said earlier.

d) **Thermodynamic parameters** - The thermodynamic parameters for the ternary complexation reactions were not calculated because ternary complexes formation does not take place with this secondary ligand as discussed earlier in this chapter.
References:


