Effect of Substituted Thiocarbamido-1-Naphthols on Stability Constant using Cu(II), Cd(II) and Cr(III) Metal Ions in 70% Ethanol-Water Mixture

D.T. Tayade¹, A.B. Wadekar²*

¹Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati – 444 604, Maharashtra, India.
²Department of Chemistry, S.D.M. Burungale Science and Arts College, Shegaon – 442 203, Maharashtra, India.

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Stability Constant

1. Introduction

Thiocarbamido, hydroxyl, amino and benzenoid nucleus possessing molecule create their own important in various field of pharmaceutical and medicinal sciences. These types of drugs effectively used against various diseases. Several modern theories and concept are concerning to physical as well as chemical study of benzenoid, non-benzenoid, heterocycles and heterocycles. Aminonaphthols and thiocarbamido nucleus containing heterocycles possesses pharmaceutical, medicinal agricultural industrial and biotechnological significances [1-5]. It is also well known that some medicinal drugs exhibit increased activity when administered as metal complexes. The manifold research work has been done on the study of metal and nitrogen and sulphur atoms containing ligands [6-7].

The study of substituted thioypyrimidine complexes in mixed solvents media pH-metrically had been carried out by many researchers [8]. References indicates that the metal ligand stability constants and proton ligand stability constants of Cu(II)-salicylic acid complex have been studied [9]. Stability constant of lanthanide ions with some substituted sulphonic acid spectrometrically investigated by Narwade et al [10]. Mane, et al [11] evaluated the proton - ligands and metal- ligands stability constant of maleic acid and Glycine with Mn(II), Cu(II), Fe(III), Ni(II) and UO₂(II). Stability constant and Formation constant of some metal complexes was studied [12-13]. There has been considerable interest in the study of binary ternary and quaternary complexes by pH-metric method [14-17]. Thakur et al was investigated stability study of complexation of trivalent rare earth metals with isosionizd: thermodynamic aspect. [18]. Some more authors evaluated the influence of transition metal on a stability of complex by pH metrically [19-20]. The stability constants of Cu(II), Cd(II) and Cr(III) with ligands 5-amino-1-naphthol(L₁), 5-phenylthiocarbamido-1-naphthol(L₂) and 5-p-chlorophenyliothiocarbamido-1-naphthol(L₃) have not been reported in literature. Hence this study made an interest to study the stability constant of complexes form by interaction of 5-amino-1-naphthol, 5-phenylthiocarbamido-1-naphthol and 5-p-chlorophenyliothiocarbamido-1-naphthol with Cu(II), Cd(II) and Cr(III) metal ions at 0.1 M ionic strength pH-metrically in 70% ethanol-water mixture.

2. Experimental Methods

All chemicals used were of AR grade. 5-amino-1-naphthol (L₁), 5-phenylthiocarbamido-1-naphthol (L₂) and 5-p-chlorophenyliothiocarbamido-1-naphthol (L₃) was synthesized in the laboratory. The stock solution of ligands was prepared by 70% (ethanol + water) mixture.

Titration of (i) free acid (0.01 M), (ii) free acid (0.01 M) and ligand (20 x 10^-4 M) and (iii) free acid (0.01 M), ligand (20 x 10^-4 M) and metal ion (4 x 10^-4 M) against standard 0.1 N NaOH solution. The ionic strength of all the solutions was maintained constant i.e. 1 M by adding appropriate amount of KNO₃ solution. All the titrations were carried out in 70% (ethanol-water) mixture and the reading were recorded for each 0.2 mL addition. The graph of volume of alkali added (NaOH) against pH were plotted. The ligands involved in the present work is considered as a monobasic acid having only one dissociable H⁺ ion from phenolic-OH group and it can therefore, be represented as HL. The dissociating equilibria can be shown as,

\[ HL \rightleftharpoons H^+ + L^- \]

By the law of mass action, we have,

\[ K = \frac{[H^+][L^-]}{[HL]} \]  \hspace{1cm} (1)

Where, the quantities in bracket denote the activities of the species at equilibrium.

3. Results and Discussion

3.1 Calculation of Proton-Ligand Stability Constant (b₃)

The plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H⁺ ions from functional group of ligand with respect to pH value). The horizontal difference (V₁-V₂) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number b₃ at various pH values and fixed ionic strength \( \mu = 0.1 \) M using Irving and Rossof's Eq. (2) and (3).
\[ \bar{n} = \gamma - \left( \frac{(V_2 - V_1)(N + E^0)}{(V^0 + V_1)E^0} \right) \]  

where, \( V^0 \) is the initial volume of the solution. \( E^0 \) and \( T^0 \) are initial concentrations of the mineral acid and ligand respectively. \( V_1 \) and \( V_2 \) are the volumes of alkali of normality \( N \) during the acid and ligand titration at given \( pH \). \( \gamma \) is the replaceable proton from the ligand. The data of \( \bar{n} \) obtained at various \( pH \) along with the horizontal difference for some representative systems are presented in Table 1. The metal-ligand formation number (\( \bar{n} \)) is estimated by Irving-Rossotti’s equation,

\[ \bar{n} = \left( \frac{V_1 - V_2}{V^0 + V_2} \right) \times (N + E^0) \]  

where, the notations have the same meaning as given in earlier equation.

The horizontal difference (\( V_1 - V_2 \)) between the metal complex (\( A+M+L \)) and reagent (\( A+L \)) curve is used to evaluate the value of \( n \) using Irving-Rossotti’s equation (Figs. 1-9).

<table>
<thead>
<tr>
<th>Ligand System</th>
<th>pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 5-amino-1-naphthol</td>
<td>9.20 7.76</td>
</tr>
<tr>
<td>L2 5-phenylthiocarbamido-1-naphthol</td>
<td>10.55 10.62</td>
</tr>
<tr>
<td>L3 5-p-chlorophenylthiocarbamido-1-naphthol</td>
<td>9.80 8.98</td>
</tr>
</tbody>
</table>

Table 2 Metal-ligand stability constant (log K)

<table>
<thead>
<tr>
<th>System</th>
<th>Log ( K_1 )</th>
<th>Log ( K_2 )</th>
<th>( \Delta \log K )</th>
<th>Log ( K_1/\log K_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1+Cu(II)</td>
<td>5.48</td>
<td>5.75</td>
<td>0.27</td>
<td>0.9530</td>
</tr>
<tr>
<td>L1+Cr(III)</td>
<td>5.42</td>
<td>6.22</td>
<td>0.8</td>
<td>0.8713</td>
</tr>
<tr>
<td>L2+Cu(II)</td>
<td>5.22</td>
<td>5.58</td>
<td>0.36</td>
<td>0.9354</td>
</tr>
<tr>
<td>L2+Cr(III)</td>
<td>5.39</td>
<td>6.05</td>
<td>0.66</td>
<td>0.8909</td>
</tr>
<tr>
<td>L2+GD(II)</td>
<td>5.72</td>
<td>6.45</td>
<td>0.73</td>
<td>0.8868</td>
</tr>
<tr>
<td>L1+Cu(II)</td>
<td>5.36</td>
<td>6.15</td>
<td>0.79</td>
<td>0.8715</td>
</tr>
<tr>
<td>L1+Cr(III)</td>
<td>5.35</td>
<td>6.15</td>
<td>0.8</td>
<td>0.8699</td>
</tr>
<tr>
<td>L3+GD(II)</td>
<td>5.81</td>
<td>6.52</td>
<td>0.71</td>
<td>0.8911</td>
</tr>
<tr>
<td>L3+Cu(II)</td>
<td>5.43</td>
<td>6.41</td>
<td>0.98</td>
<td>0.8471</td>
</tr>
</tbody>
</table>

Fig. 1 Plot between \( \bar{n} \) vs pH System-L1+Cu(II)

Fig. 2 Plot between \( \bar{n} \) vs pH System-L1+Cr(III)

Fig. 3 Plot between \( \bar{n} \) vs pH System-L1+Cd(II)

Fig. 4 Plot between \( \bar{n} \) vs pH System-L2+Cu(II)

Fig. 5 Plot between \( \bar{n} \) vs pH System-L2+Cr(III)

Fig. 6 Plot between \( \bar{n} \) vs pH System-L3+Cd(II)

Fig. 7 Plot between \( \bar{n} \) vs pH System-L3+Cu(II)
indicates that Cu(II) forms more stable complex with ligand-2 than Cu(II) and Cr(III). While for 5-chloro-phenylthiocarbamido-1-naphthol (L₃) difference between the values of log K₂ and log K₃ is higher with Cr (III) complex than Cu(II) and Cd(II) complexes. Cr (III) forms more stable complex with L₃ than Cu (II) and Cd (II) metal ions.

References