Short communication

STEPWISE FORMATION AND BINDING OF INDIUM TRICHLORIDE WITH SOME AMINO ACIDS IN AQUEOUS PHASE

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Introduction

Amino acids play a vital role in various biological systems and their metal complexes have been extensively studied due to the coordinating ability of amino and carboxylic groups [1—3]. In recent years a detailed study was made by the authors on the interaction of transition metals having unusual oxidation states and metals belonging to the platinum group [4—13]. From the present literature it appears that no effort has yet been made to calculate the stepwise equilibrium and overall stability constants of indium trichloride amino acid systems employing Bjerrum's [14] method modified by Albert [15] in aqueous medium. The present communication reports the stability and binding of In(III) with some amino acids. The relation $\Delta G^0 = -RT \ln K_s$ was employed to calculate the values of $\Delta G^0$ at 24°C, where $K_s$ is the overall stability constant of a particular system. All titrations were carried out in anaerobic condition.

Experimental

Amino acids such as glycine, DL-α-alanine, L-asparagine, DL-serine, DL-valine, L-proline, taurine (B.D.H., England, biologically pure products) and DL-phenylalanine, β-alanine, DL-methionine, L-leucine and DL-leucine (E. Merck, Germany), chromatographically pure, were used in these investigations and their aqueous solutions were prepared in doubly distilled air-free water. Indium trichloride (Schuchardt, Germany) was estimated gravimetrically [16]. pH-metric titrations were performed with an Elico-pH meter, model L-1 (India) in conjunction with glass and saturated calomel electrodes.

Results and discussion

For each system, pH-metric titrations in triplicate were performed in the order (a) 0.01 M amino acids, (b) 0.0033 M indium trichloride and (c) a mixture of amino acid and metal salt having overall concentration of 0.01 M and
0.0033 M, respectively. The strength 0.1 M of carbonate-free KOH was checked before employing it as a titrant. An appreciable shift was observed indicating thereby, the stepwise association of the ligand, amino acid with metal. Metal ion-amino acid (ligand) systems may be explained by considering the stepwise formation of complex species of different composition in solution phase, MA, MA₂, MA₃ ... MAₙ, where A stands for ligand and M for metal ion and n for number of amino acid (ligand) molecules bound by the metal ion. In general, at equilibrium the concentration of each species is related to that of each of the other complex species by a series of expressions.

\[ k_1 = \frac{[MA]}{[M][A]}, \ k_2 = \frac{[MA_2]}{[M][A]} \text{ and } k_n = \frac{[MA_n]}{[MA_{n-1}][A]} \]

In case of a 2+ metal ion binding two ligand groups, the values may be written as

\[ k_1 = \frac{[MA^+]}{[M^{2+}][A^-]}, \ k_2 = \frac{[MA_2^+]}{[MA^+][A^-]} \]

and

\[ K_s = \frac{[MA_2]}{[M^{2+}][A^-]^2} \]

where \( k_1 \) and \( k_2 \) are the stepwise equilibrium or association constants, and \( K_s \), the overall stability constant, is the sum of the logarithms of the equilibrium constants.

\[ \log K_s = \log k_1 + \log k_2 \]

Concentrations are used for simplicity and convenience. As the complex formation starts, \( H^+ \) ions are released, and the measurements of the concentration of these ions provide a useful way to determine the extent of complexation of metal with amino acid in solution phase.

The values of stepwise equilibrium constants may be given as

\[ k_1 = \frac{\bar{n}}{(1 - \bar{n})}[Sc], \ k_2 = \frac{(\bar{n} - 1)/(2 - \bar{n})}{[Sc]} \]

Here \( \bar{n} \) is the average number of molecules of complex forming agent attached to one atom of the metal, and [Sc] is the concentration of the coordinating species, and values may be calculated from the relation given below:

\[ \log [Sc] = (pH - pK_a) + \log([HSc^0] - [KOH]) \]

This relation holds good between pH 3 and 11 and [HSc⁰] stands for the initial concentration of the amino acid before the addition of the metal and [KOH] is the concentration of the alkali when a complex forming agent (amino acid) and metal are both absent. \( \bar{n} \) is governed by the relation

\[ \bar{n} = 2 \frac{[KOH]}{[HSc^0]} \]

The regular values of log \( k_1 \), log \( k_2 \) and log \( K_s \) are given in Table 1. The ranges are \( \log k_1 (\bar{n} = 1.00-0.80) \) and \( \log k_2 (\bar{n} = 1.26-1.80) \) respectively in all the cases reported herein. The plots, \( \bar{n} \) vs. \( \log [Sc] \) (formation curves) are given in Fig. 1 for a few amino acid-InCl₃ systems.
TABLE 1

<table>
<thead>
<tr>
<th>System</th>
<th>( \log k_1 )</th>
<th>( \log k_2 )</th>
<th>( \log K_a )</th>
<th>( -\Delta G^0 / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL-( \alpha )-Alanine-( \text{InCl}_3 ) system</td>
<td>8.40</td>
<td>8.25</td>
<td>16.65</td>
<td>94.63</td>
</tr>
<tr>
<td>( \beta )-Alanine-( \text{InCl}_3 ) system</td>
<td>8.30</td>
<td>8.22</td>
<td>16.52</td>
<td>93.94</td>
</tr>
<tr>
<td>L-Asparagine-( \text{InCl}_3 ) system</td>
<td>7.17</td>
<td>7.21</td>
<td>14.38</td>
<td>81.83</td>
</tr>
<tr>
<td>Glycine-( \text{InCl}_3 ) system</td>
<td>8.22</td>
<td>8.02</td>
<td>16.23</td>
<td>92.34</td>
</tr>
<tr>
<td>DL-Leucine-( \text{InCl}_3 ) system</td>
<td>7.76</td>
<td>7.65</td>
<td>15.41</td>
<td>87.64</td>
</tr>
<tr>
<td>L-Leucine-( \text{InCl}_3 ) system</td>
<td>8.26</td>
<td>7.48</td>
<td>15.74</td>
<td>89.51</td>
</tr>
<tr>
<td>DL-Methionine-( \text{InCl}_3 ) system</td>
<td>7.75</td>
<td>7.42</td>
<td>15.17</td>
<td>86.29</td>
</tr>
<tr>
<td>DL-Phenylalanine-( \text{InCl}_3 ) system</td>
<td>7.36</td>
<td>7.22</td>
<td>14.58</td>
<td>82.95</td>
</tr>
<tr>
<td>L-Proline-( \text{InCl}_3 ) system</td>
<td>9.04</td>
<td>8.64</td>
<td>17.68</td>
<td>100.64</td>
</tr>
<tr>
<td>DL-Serine-( \text{InCl}_3 ) system</td>
<td>7.53</td>
<td>7.05</td>
<td>14.58</td>
<td>82.90</td>
</tr>
<tr>
<td>DL-Taurine-( \text{InCl}_3 ) system</td>
<td>7.44</td>
<td>7.13</td>
<td>14.57</td>
<td>88.55</td>
</tr>
<tr>
<td>DL-Valine-( \text{InCl}_3 ) system</td>
<td>8.28</td>
<td>7.52</td>
<td>15.80</td>
<td>89.85</td>
</tr>
</tbody>
</table>

Fig. 1. Plots of \( \bar{n} \) vs. \( \log [\text{Sc}] \) for several amino acid-\( \text{InCl}_3 \) systems. (\( \bullet \)) \( \text{InCl}_3 \)-DL-phenylalanine system; (\( \Delta \)) \( \text{InCl}_3 \)-DL-leucine system; (\( \circ \)) \( \text{InCl}_3 \)-glycine system.
The stability constants of the systems vary from 17.68 (log $K_s$ for L-proline) to 14.39 (log $K_s$ for L-asparagine) and the order of the stability may be written as: L-proline > DL-$\alpha$-alanine > $\beta$-alanine > glycine > DL-valine > L-leucine > DL-leucine > DL-methionine > phenylalanine > DL-serine > taurine > L-asparagine. Deviation is observed in a few cases perhaps due to the formation of polynuclear compounds [17]. In the majority of cases the values of $-2 \log[Sc]$ at $\bar{n} = 1$ correspond to the value of the log $K_s$.

The sulphur containing amino acids, methionine and taurine did not show any abnormality and appeared to behave like other simple amino acids. It may be said that thioether type sulphur in methionine, CH$_3$SCH$_2$CH$_2$(NH$_2$)COOH, contributes almost nothing to the stability of the complex [7—12]. In general, the value of log $K_s$ decreases as the distance between the amino and carboxylic groups increases (between NH$_2$ and SO$_2$OH in the case of taurine [11]. The present study does not throw light on the part played by sulphur atom and the real mode of binding is only a matter of speculation.

The conductometric titrations revealed a ratio of 1 : 1 (metal : amino acid) in aqueous solution at 24°C. These observations could not be substantiated by other data due to the fact that the complexes could not be isolated in the solid state.

Acknowledgements

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