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NOTE

Micronutrient Complexation with Amino Acid: Electrochemical, Bioanalytical and Thermodynamic Data

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Electrochemical behaviour of several amino acids *viz.*, glycine, lysine, valine, alanine etc. and their complexation with micronutrients *viz.*, Cu^{2+}, Co^{2+}, Zn^{2+} and Fe^{3+} in binary and mixed system could be estimated alongwith thermodynamic parameters ΔG, ΔH, ΔS. Dissociation constants were determined employing Albert and Serjeant, Noyes and Irving-Rossotti techniques. Free amino acids take part in numerous metabolic reactions. Mechanistic studies in amino acids are an effort to correlate the data obtained from electrochemical, bioanalytical and thermodynamic studies. The validity of the mechanism is tested on the basis of recalculation, TLC, formation constant, higher sensitive polarographic methods and available bioanalytical procedures.

Amino acids, containing —NH_2 and —COOH groups, have great significance in the pharmaceutical and biological fields because of their direct involvement in metabolic and enzymatic activities of trace elements, the so-called micronutrients or oligoelements.[1, 2] These elements catalyse and control biochemical reactions within the body. Every trace element is potentially toxic when the range of safety is exceeded as per Bertrand's plateau. Looking at the activities of amino acids as well as trace elements in the biosystem, the authors proposed to undertake this study. Due to close association with life and related activities, attention has been paid to the coordination studies of such potential ligands with trace elements.

All the chemicals used were of AnalaR grade. Glycine, lysine, alanine, valine etc. were of Hi-media, Bombay. The divalent metal ion solution such as Fe^{3+}, Co^{2+}, Zn^{2+} and Cu^{2+} were prepared from their salts of BDH grade. The ionic strengths were maintained using $NaClO_4$ for the sets prepared for observation. The dissociation constants were determined using Albert and Serjeant technique[3] and by Irving-Rossotti technique[4]. pH measurements were made on Systronics pH-meter model No. 335 (digital type). Spectral observations were taken on Systronics photoelectric colorimeter model No. 112. Thermodynamic parameters at 25 ± 1°C *i.e.*, ΔG, ΔH, ΔS have also been evaluated at $\mu = 0$, 1 M $NaClO_4$ in some cases along with their complexation nature using Elico-pen recording polarograph model LR-21. Thin layer chromatography on silica gel G plate could be successfully performed for characterization and complexation studies in suitable cases. All the studies have been done in bidistilled water.

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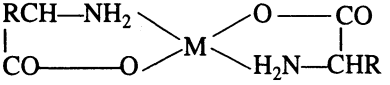
In an amino acid NH_2—A—COOH, which contains both the basic and an acidic group, complex formation can take place between two groups. Crystal structure of amino acids shows that in solid state they exist as internal salt or zwitter ions H_3N^+—A—COO^-. Divalent trace metals (micronutrients) *viz.*, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} show that possible coordination of the following structure and the data have been computed.



Complexation studies and observations of dissociation have been carried out using spectral and electrometric methods.[5] Cu-valinate system revealed log $\beta_1 = 8.02$ and $\log \beta_2 = 14.90$. Howevers Cu-alanine reported $\log \beta = 7.80$ at 25 ± 1°C. The dissociation constants are found to vary with temperature and have a maximum value at 25°C. On examining the data revealed that pK_q^1 and pK_q^2 values of the acids slightly decrease with rise in temperature[6]. The ligational tendency of amino acids revealed that they form the most stable complex with Zn^{2+}. These observations are of tremendous biological significance as out of many divalent ions nature preferentially selects Zn^{2+} ions as the cofactor in certain enzymatic processes. ΔH, ΔS and ΔG values have been calculated with the help of Gibbs-Helmholtz equations[7], $\Delta G = -RT \ln K_a$ and $T\Delta S = \Delta H - \Delta G$ etc. for each of the pK_q values. Significantly lower values were obtained at pK_q for ΔG and ΔH in kcal $mole^{-1}$. However, predominant change was observed in the value of ΔS cal deg^{-1} $mole^{-1}$ in the polarographic and pH-metric measurements. Observations on trivalent metal ions with special reference to Fe^{3+} are also under study. Tentative explanations, mechanistic studies, Co-TLC dissociation constants and mode of binary and ternary complex formation along with ΔH, ΔS and ΔG values will attract the attention of research workers in many more aspects. The work is in progress in our laboratory.

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