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Spectroscopic Study of the Interaction of Amino Acids with Copper(II) Ions in Aqueous Solution

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The interactions of copper(II) ions with some essential amino acids *viz.*, L-leucine(Leu), L-glycylglycine (Gly.gly), L-methionine (meth), L-lysine (Lys) have been studied in aqueous solution at different temperatures by visible spectrophotometric method. The equilibrium constants of the process.

$$[Cu(H_2O)_4]^{2+} + L = [Cu(H_2O)_3L]^{2+} + H_2O$$

(where L stands for the monodentate amino acid) have been determined and the thermodynamic parameters *i.e.*, ΔG^o, ΔH^o and ΔS^o have been calculated.

Key Words: Equilibrium constant, Amino acids, Cu(II), Visible spectrophotometry.

INTRODUCTION

Amino acids are well known chelating agents and play an important role in biochemical process[1]. The amino acid compounds are biologically active, creating considerable interest in their metal complexes[2]. The study of thermodynamic parameters will help towards understanding the driving forces that lead to the formation of amino acid metal complexes in biological systems. Therefore the study of their complexes has great significance specially when they form complexes with amino acid. Many workers[3-7] tried to resolve the nature of coordination of α-amino acids in complexes of the first series of transition metal ions and concluded that in the complexes the amino acids exist as zwitterion being coordinated through the carboxylate group at pH > 7.

When an amino acid is added to an aqueous solution of the metal ion, the water molecule from the coordination sphere of the metal ion is replaced by the amino acid molecule. Though the stepwise formation of the complex predicts the formation of several complexes of the type $[M(H_2O)_{6-n}L_n]^{2+}$ (where n = 1, 2, 3 *etc.*) yet the presence of mono-, *bis*- and *tris*- complexes have only been reported[4,8]. Oztsumi and Ohtaki[8] showed that the *bis*- and *tris*-glycinato complexes of copper(II) are formed only when the ratio of $[gly]/[Cu^{2+}] > 13.7$. In aqueous solution Cu(II) ion forms $[Cu(H_2O)_4]^{2+}$ ions[9].

Diffrent methods have been used to study such interactions, but the interaction of copper(II) ion with amino acids in aqueous solutions to find out thermodynamic parameters, have not yet been studied by visible spectrophotometric method. In this work, the interactions of Cu(II) ion with selecterd amino acids in aqueous solutions have been studied by visible spectrophotometric method. We have studied the interaction at constant ionic strength (0.01 M KCl) and in the temperature range from 20 to 40 ºC. The equilibrium constants of the replacement process along with ΔG^o, ΔH^o and ΔS^o have been reported.

EXPERIMENTAL

Copper(II) sulphate (AnalaR) used for the experiment has been repeatedly recrystallized from double distilled water. Aqueous solutions of the salt were prepared in triple distilled water and standarized[10]. L-leucine (LOBA), L-glycylglycine (LOBA), L-methionine (Merck) and L-lysine (LOBA) have been used as such.

The amino acids were heated at 110-120 ºC for 5 h just before preparing the solution with triple distilled water. Spectra were recorded using a Shimadzu UV-24 spectrophotometer equipped with a thermostate. pH of the solutions were measured with a Elico Li-120 pH meter.

The concentrations of the amino acids were kept as low as possible. Based on the report of Ozutsumi and Ohtaki[8], it was assumed that only one molecule of water from the coordination sphere of the metal ion has been replaced by the amino acid molecule. The replacement process can be represented as:

$$[Cu(H_2O)_4]^{2+} + L = [Cu(H_2O)_3L]^{2+} + H_2O$$

where L stands for the monodentate amino acid. The equlibrium constants were evaluated from the linearized equation[5,16].

$$\frac{1}{(\varepsilon-\varepsilon_0)} = \frac{1}{(\varepsilon_1-\varepsilon_0)}\frac{[H_2O]}{K_1[L]} + \frac{1}{(\varepsilon_1-\varepsilon_0)}$$

where ε is the apparent extinction coefficients of the sample solution and ε_0 and ε_1 are those of $[Cu(H_2O)_4]^{2+}$ and $[Cu(H_2O)_3L]^{2+}$, respectively, $[H_2O]$ and [L] are the concentrations of free solvent and free amino acid. A plot of $1/(\varepsilon-\varepsilon_0)$ *vs.* $[H_2O]/[L]$ gives the intercept $1/(\varepsilon_1-\varepsilon_0)$ and the slops $1/[K_1(\varepsilon_1-\varepsilon_0)]$. The equilibrium constant (K_1) and the molar extinction coefficients of the Cu^{2+} and amino acid solutions have been calculated from the slopes and the intercepts.

RESULTS AND DISCUSSION

The absorption peak for $[Cu(H_2O)_4]^{2+}$ ion have been observed at 819 nm. When amino acids are added, the peaks suffer blue shift to 774 nm. The shift is due to the replacement of water molecule by the amino acid molecule. Molar concentrations have been used to calculate the equilibrium constants of the replacement process.

There are evidences[3-7] that in solution amino acids exist mainly as zwitter ion especially at pH 4 to 7. The values of the equilibrium constants found in the present experiment will be neither of ML^{2+} nor ML^{+}, but may be the average of both the complexes, as reported earlier[11].

It has also been observed[12,13] that the equilibrium constant for Cu^{2+} ion complexed with amino acid is of the order: Leu > Meth. > Lys > gly.gly (Table-1). Similar variation in the equilibrium constant has also been reported earlier[12,13], for bivalent metal ion. The variation of equilibrium constants with temperature are shown in the Fig. 1. The figure shows that the values of equilibrium constants decrease with the rise in temperature, indicating exothemic nature of the reactions.

TABLE-1
EQUILIBRIUM CONSTANTS AND THERMODYNAMIC PARAMETERS

S. No.	Metal ion	Amino acids	pH	Temp. (K)	log K	$-\Delta G^o$ (kJ mol^{-1})	$-\Delta H^o$ (kJ mol^{-1})	$-\Delta S^o$ (kJK^{-1} mol^{-1})
1	Cu(II)	L-glycylglycine	4.80	293	3.875	21.386	43.521	0.743
				298	3.748			
				303	3.644			
				308	3.532			
				313	3.413			
2	Cu(II)	L-lysine	5.20	293	4.505	25.009	44.670	0.660
				298	4.383			
				303	4.261			
				308	4.125			
				313	4.005			
3	Cu(II)	L-methionine	5.14	293	5.658	31.485	57.441	0.871
				298	5.518			
				303	5.348			
				308	5.211			
				313	5.086			
4	Cu(II)	L-leucine	5.28	293	5.989	32.883	76.589	1.467
				298	5.763			
				303	5.558			
				308	5.327			
				313	5.163			

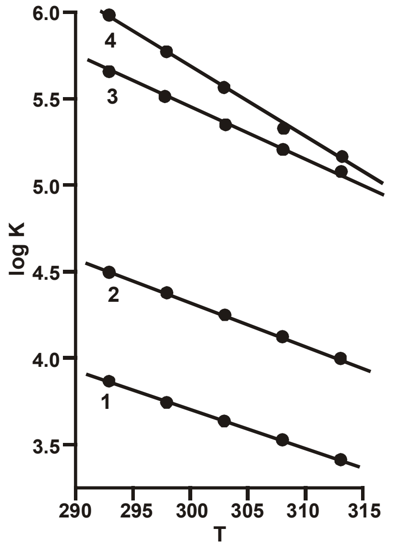

Fig. 1. Variation of log K with T

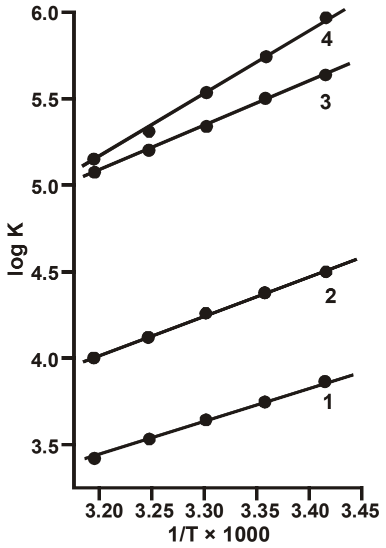

Fig. 2. Variation of log K with 1/T

The lowest value of equilibrium constant of L-glycylglycine complex over L-lysinate, L-methionine and L-leucine complexes of copper, is due to the fact that L-glycylglycine molecule is folded in such a way that its positive charge -NH_3^+ group comes adjacent to its α-amino group and therefore, metal cation is repelled by the adjacent positive charge resulting in lesser stability of its complex than the other complexes[14]. The lower value of L-lysine complex over L-methionine and L-leucine can be attributed to the fact that, if the bulky substituents are introduced into the ligand molecule, steric hindrance may result in additional decrease in the stability of complexes[15]. It has also been reported that L-lysine form an 8 membered ring with Cu(II) ion[13]; as the ring size increases stability of the complexes decreases[15].

The highest value of equilibrium constant of L-leucine copper complex among four amino acid complexes is perhaps due to the presence of electron repelling alkyl group in [$>CH(CH_3)_2$] L-leucine which increases the basicity of the amino acid molecule[13,16]. The thermodynamic functions were calculated by using the equations[17],

$$\Delta G^o = -RT \ln K = \Delta H^o - T\Delta S^o$$

$$\Delta S^o = \frac{\Delta H^o - T\Delta G^o}{T} \qquad (1)$$

where ΔG° is the change of Gibbs free energy, ΔH° is the change of enthalpy and ΔS° is the change of entropy.

The value of ΔHº is calculated by plotting log K *vs.* the reciprocal of absolute temperature (1/T), the slope of the straight line is equal to ΔHº/ 2.303 R. Then ΔSº can be calculated by eqn. 1. The plot of log K *vs.* 1/T gives good straight line (Fig. 2) which reflects the high temperature sensitivity for the carboxylate group[17].

For Cu(II) ions, the variation of the change of free energy follows the sequences:

L-leucine > L-methionine > L-lysine > -glycylglycine.

As the size of carbon chain attached to the amino group is increased, the change of Gibbs free energy of the amino acid metal complexes increases. L-leucine can most easily replace water molecule from the coordination sphere of the metal ion. Similar explainations can be given for the other amino acid molecules L-methionine, L-lysine and L-glycylglycine. The negative values of ΔGº reflect spontaneity of the reaction.

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