

To Compare Formation And Stability Of complexes Of Some Transition Metal Ions With Amino Acids With Stability Constant.

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Abstract: Chemistry of Proteins which are the most complex substances known to man is one of the great challenges in modern science. In the present work peptides of amino acid were used to study metal-ligand stability constants. Various chelates of metal ions like Al(III), Cr(III), Fe(III), Pt(IV) etc. with various chalcones and amino acids were studied for their stability determination.

In the present work complexes of transition metal ions like Cu(II) and Ni(II) with peptide; DL-Alanyl-DL-Alanine were prepared and progress of their formation and metal-ligand stability constants at 0.1M ionic strength were studied potentiometrically. It was found that for Cu(II) the colourless solution changed to blue at about pH 5.0 and for Ni(II) at pH 5.25 the colourless solution changed to orange. The stability was studied from β (ligand number) values and logK values. It is concluded from results that complex of Cu(II) with DL-Alanyl-DL-Alanine is more stable than that for Ni(II).

Key Words: Complex, Peptides, Stability constant, pH etc.

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I. Introduction

The chemistry of proteins was one of the great challenges in modern science, since the centuries. It has been proposed that crucial step in origin of life was the formation of important biopolymers from the simple organic molecules contained in the primitive atmosphere.

The amino acids are formed by hydrolysis of protein and a certain structural features in common. Each has an acidic carbonyl group (-COOH) and a basic amino group (-NH₂) or imino group (-NH-). Both acidic and basic group are attached to the same carbon atom, called α -carbon. This

carbon atom has two other units linked; one is invariably H-atom. In 1820, French chemist, Henry Braconnot isolated the simplest amino acid, glycine. In every protein, amino acid, except glycine can exist in two geometrical forms, L and D, mirror images of each other.

Rossotti and Rossotti have defined a complex as a species formed by the association of two or more simple species, each capable of independent existence, when one of the simple species is a metal ion, the resultant entity is known as 'metal complex'. Some ligands are attached to metal atom by more than one donor atom in such a manner as to form heterocyclic ring, known as Chelation.

The stability of transition metal amino acid complexes in solution has been extensively studied. The thermodynamic stability constants of a species are measures of the extent to which this species will be formed from or be transferred into other species under certain conditions which the system has reached equilibrium. The kinetic stability of species refers to the speed with which transformation leads to the attainment of equilibrium. The complex formation is favoured by negative enthalpy and positive entropy changes. The metal ligand complex formation may be considered due to the displacement of proton from the ligand, causing a change in pH-value of solution. Irving and Rossotti have given a method for calculation of stability constant of complexes by potentiometry.

II. Material And Method

Irving and Rossotti made use of the potentiometric technique first used by Calvin and Melchior and now generally known as Calvin-Bjerrum titration technique. The method of Irving and Rossotti has been employed in this present investigation.

In method solutions of nitrates of Cu(II) and Ni(II) in distilled water, solution of KNO₃ in distilled water, 0.01M solution of HNO₃ in distilled water as free acid, solution of NaOH in water, solution of peptide; DL-Alanyl-DL-Alanine in water were used. pH-meter (ELICO-model) with glass-electrode and a saturated

calomel electrode was used. For the calibration of pH-meter the standard buffer solutions of pH 4.01, 7.00 and 9.15 were used. Following equations 1 and 2 were used to calculate $\tilde{\eta}_A$ and $\tilde{\eta}$.

$$\tilde{\eta}_A = \frac{Y}{(V_0 + V_1) \times T_L^0} - \frac{(V_2 - V_1)(N + E^0)}{(V_0 + V_1) \times T_L^0} \quad \text{-----} \quad 1$$

$$\tilde{\eta} = \frac{(V_3 - V_2)(N + E^0)}{(V_0 + V_2) \times T_L^0 \times \tilde{\eta}_A} \quad \text{-----} \quad 2$$

III. Result And Discussion

The data obtained by titration for systems of Cu(II) and Ni(II) metal ions was used to plot Graphs, constructed between the volume of NaOH and pH of solution for all systems as shown in figures 1 and 2.

Proton – ligand stability constants of the ligand were calculated from acid titration curve and acid+ ligand titration curve. The deviation in the curves for both the systems started at about pH 3.0. These deviations increased continuously upto pH 11.0. This may be due to fact of dissociation of functional groups (-COOH and -NH₃⁺) of ligands.

The values of $\tilde{\eta}_A$ along with the differences (V₂-V₁) were determined. The formation curve ($\tilde{\eta}_A$ vs pH) was plotted and from it pK₁(4.5) corresponding to $\tilde{\eta}_A = 1.5$ and pK₂(10.1) corresponding to $\tilde{\eta}_A = 0.5$ for ligand were estimated. This is called half integral method.

Fig: 1 (Graph for Cu(II) - DL-Alanyl-DL-Alanine System)

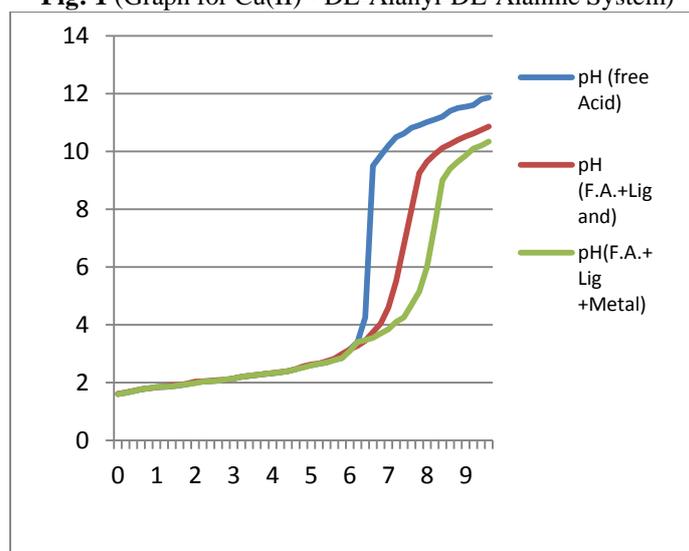


Fig: 2 (Graph for Ni(II) - DL-Alanyl-DL-Alanine System)

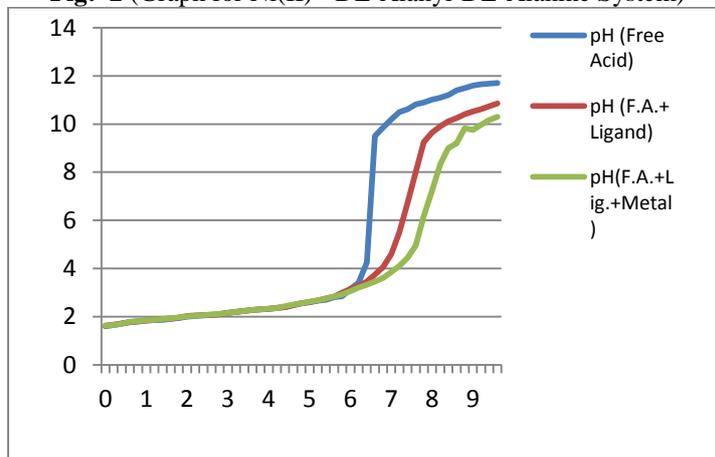
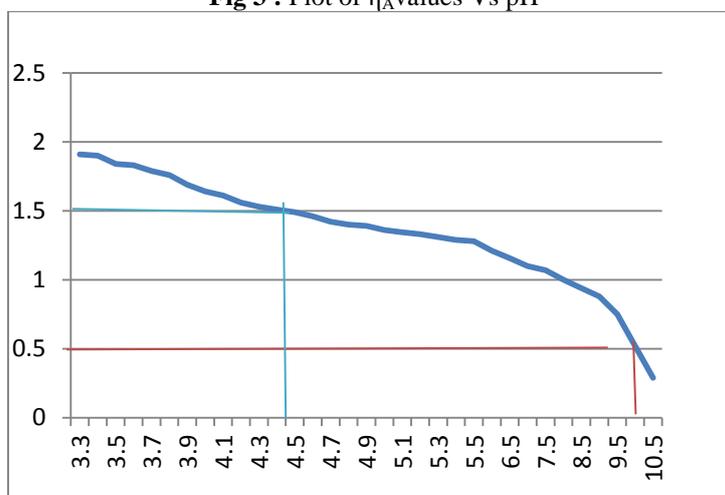


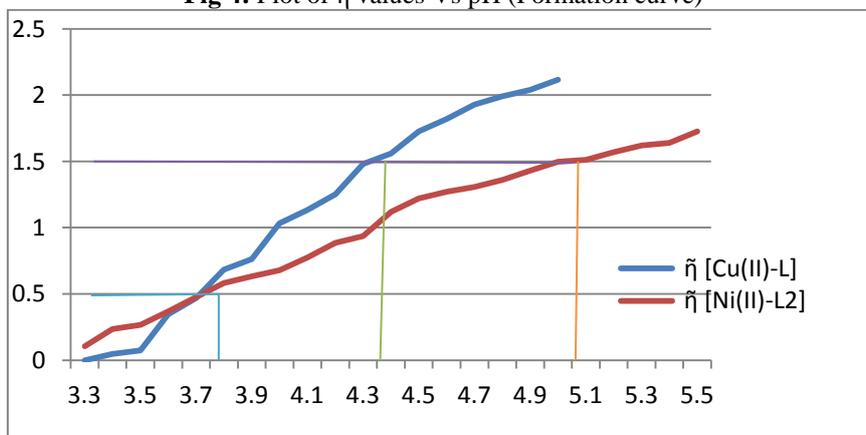
Fig 3 : Plot of $\bar{\eta}_A$ values Vs pH



The formation of chelate of DL-Alanyl-DL-Alanine with Cu(II) and Ni(II) is indicated by –
 i) The significant departure starting at pH 2.75 of metal complex titration curve from the ligand curve and
 ii) The change in colour from colourless to blue at about pH 5.0 for Cu(II) and from colourless to orange at pH 5.25 for Ni(II).

The formation constant $\bar{\eta}$ was calculated using equation 2. The values of $\bar{\eta}$ were plotted against pH to construct formation curve for metal – ligand complexes.

Fig 4: Plot of $\bar{\eta}$ values Vs pH (Formation curve)



The stability constants were calculated by half integral method.

Log K_1 (9.9447) at $\bar{\eta}=0.5$ log K_2 (8.6958) at $\bar{\eta}=1.5$ for Cu(II) – L and Log K_1 (9.7447) at $\bar{\eta}=0.5$ log K_2 (7.1959) at $\bar{\eta}=1.5$ for Ni(II) – L were obtained.

IV. Conclusion

It is concluded from results that complex of Cu(II) with DL- Alanyl-DL- Alanine is more stable than that for Ni(II).

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