African Scientist Vol. 11, No. 2, June 30, 2010
Printed in Nigeria

1595-6881/2010 $12.00 + 0.00

http://www.klobex.org/afs

AFS 2009118/11207

Potentiometric Investigations of Chromium (III) Amino Acid Complexes

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(Received October 13, 2009)

ABSTRACT: Potentiometric investigations of complexes formed by chromium (III) ion and amino acids have been carried out. The dissociation constants of the amino acids, the stepwise formation constants and the overall stability constants of the metal ions and amino acids complexes were determined. The dissociation constants of the amino acids determined are; alanine (10.29), arginine (12.02), asparagine (9.39), glycine (9.87), histidine (7.01), lysine (9.28), methionine (9.68), phenyalanine (9.61), proline (10.53), threonine (10.31), tryptophan (9.77), and valine (10.28). The average number of coordinated amino acids to chromium (II) ion determined is 3. The Stepwise Stability Constants of chromium (III) ion and amino acid complexes determined have been found to decrease in the order $K_1 > K_2 > K_3$ for all the complexes. The values of the overall stability constants of the complexes obtained are relatively high indicating good stability for the complexes.

Key Words: Amino acids, dissociation constant, potentiometry, stability constant

Introduction

Amino acids are organic molecules containing amino group, - NH_2 and carboxylic acid group, - COOH both attached to the same carbon atom called α – carbon. Such amino acids are also known as α – amino acids. Thus an α – amino acid consists of an amino group (- NH_2), a carboxylic group (- COOH), a hydrogen atom (H) and a distinctive R – group bonded to the α – amino carbon atom. The carbon atom to which these groups are attached is called α – amino because it is adjacent to the carbonyl acidic group. Amino acids were earlier discovered as constituents of natural products even before they were recognized as components of proteins; asparagine was discovered in 1806 in juice of asparagus plant and cystine in 1810 in urinary stones. In deed their names are based on the sources from which they were isolated (Akpurieme, 2001). The first amino acid isolated from hydrolysis of protein was glycine, obtained in 1820 from gelatin by Braconnot as reported by Lehninger (2000).He also reported threonine as the most recently discovered amino acid isolated from hydrolyzates of fibrin by Rose in 1935 (Lehninger, 2000).

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Amino acids are known to produce complexes with transition metals repeatedly in the literature (Meyer *et al.,* 1970; Sigel *et al.,* 1971; Tsangaris *et al.,* 1969 and Takaji *et al.,* 1965) All the naturally occurring α-amino acids bind in what is known as glycinato way which means that a five – membered ring is formed with metal, amine nitrogen and the carboxylic oxygen (Takaji *et al.,* 1965). This arrangement is always present for the natural human amino acids.

The metal complexes of N – protected α-amino acids are of great interest because they may be used as a basis for understanding metal – protein interaction. Many proteins within the body need metal ions to work and also the proteins can be activated or deactivated by metal ions. The metals that have been used in the complexation with amino acids include copper, silver, cadmium, palladium and zinc (Andreoli *et al.,* 1980; Antolini *et al.,* 1980; Battaglia *et al.,* 1981).

Amino acids are the building blocks of proteins and also many other biologically occurring amino acids serve other functions in cells. In addition, the amino acids ions serve as bidentate ligand in complex formation with transition metal ions. Generally the biological function of proteins depends on their amino acids constituents or contents and proteins play crucial roles in virtually all the biological processes (Stryer, 1988).

Chromium has been recognized to be an essential element only recently (Cotton and Wilkinson 1980). Chromium in the trivalent and hexavalent states are the forms that are of biological significance even though the trivalent state is the most common. It occurs in the earth crust as chromates, dichromate's etc. chromium is applied in tanning, wood preservation, pigments and dyes for plastic (Kennish, 1992). Trace amount of chromium can be obtained from meat, liver, grains, nuts and cheese (Robert *et al*., 1993). It is also important in the functioning of hormone insulin for glucose uptake (Yalwa, 2002) and that. It controls the removal of glucose from blood (Cotton and Wilkinson, 1980) together with the insulin. Deficiency of chromium in humans may occur in infants suffering from protein malnutrition and elderly people with impaired glucose tolerance. Also exposure to chromium especially in chrome production and chrome pigment industries is associated with Cancer of respiratory tract (Bala, 2005).

This paper reports the potentiometric investigation of chromium (III) amino acid complexes as exhaustive literature search revealed limited information.

Material and Method

The chemicals and solvents used in this work were of Analar grade. All the glass wares used were washed thoroughly with distilled water and dried in an oven. Weighing was carried out on electric metler balance, model AB 54. The pH measurements were carried out using Jenway pH meter model 3320.

Determination of Stability Constants of Chromium (III) Amino Acid Complexes

Into a 400cm^3 beaker 100 cm^3 of 0.04 mol dm^{-3}, KNO_3 10cm^{3}l of 0.02mol dm^{-3} HNO_3, 90 cm^3 of distilled water and 1 millimole (0.001 mole) of chromium (II) chloride hexahydrate were added respectively. 0.5 cm^3 of 0.1mol dm^{-3} Sodium glycinate was added and after each addition with stirring the corresponding pH reading was recorded. The addition of the sodium glycinate solution was continued until the full 10 cm^3 was added. The sodium glycinate was prepared by exactly neutralizing a weighed solid glycine with a calculated amount of standardized 0.1mol dm^{-3} NaOH and diluting the solution with distilled water to a total volume of 20 cm^3 out of which 10ml was put into a cleaned and rinsed burette (Angelici, 1977).

Results and Discussion

The dissociation constants of amino acids have been determined, the values (Table 1) are comparable to the values in literature. The stepwise stability constants ($K_1,\ K_2\ and\ K_3$) of the chromium (II) amino acid complex compounds been determined are high, and are found to decrease in the

order $K_1 > K_2 > K_3$. This observation was made by Satya (2006), Cotton and Wilkinson (1980) on the basis of electrostatic concept, that affinity of the amino acid anions for the complex ion decreases as the charge on the complex ion becomes less positive (Angelici, 1977; Cotton and Wilkinson, 1980; Satya 2006). The overall stability constant (which is the product of stepwise stability constants) of each chromium (III) amino acid complex compound is high, indicating good stability. These high values (Table 2) are comparable to most values in literature (Cotton and Wilkinson, 1980; Satya 2006). Even though, the overall stability constant values reported by Sovago *et al* (1993) of 25.87 for $[Cr(ala)_3]$, *and of* 20.10 *for* $[Cr(val)_3]$ and also those reported by Berthon (1995) of 21.80 for $[Cr(met)_3]^-$, and of 18.30 for $[Cr(asn)_3]$ are slightly lower than the values obtained in this work. This is probably due to the slow formation kinetics of chromium (III) complexes (Sovago *et al*., 1993).
The mean number of amino anions per chromium (III) ion determined is three for all the complexes, and this agrees with earlier reports with respect to alamine, valine, methionine, and asparagines chromium (III) complexes, respectively (Sovago *et al.,* 1993; Berthon, 1995).
The stability constants of the chromium (III) amino acid complexes determined follow the sequence;

$$[Cr(Arg)_3] > [Cr(\mathrm{Pr}\,o)_3] > [Cr(Thr)_3] < Cr(Ala)_3 > [Cr(Lys)_3] > [Cr(Gly)_3]$$
$$> [Cr(Val)_3] > [Cr(Try)_3] > [CrMet_3] > [Cr(Phe)_3] > [Cr(Asn)_3] > [Cr(His)_3]$$

This means the complex $[Cr(Arg)_3]$ is the most stable while $[Cr(His)_3]$ is least stable.

Conclusion

The potentiometric investigations of chromium (III) amino acid complexes has been carried out. The amino acids dissociation constants determined tallied with literature. The stepwise stability and the overall stability constants determined are very high, indicating stable complex compounds.

Table 1 : Dissociation Constants (pKa) of Amino Acids.

Amino Acid	Disssociation Constant (pKa)	Literature Value
Glycine	9.87	9.60
Arginine	12.02	12.48
Asparagine	9.39	9.30
Histidine	7.01	7.59
Lysine	10.28	10.51
Methionine	9.68	9.69
Phenyalanine	9.61	9.24
Threonine	10.31	10.43
Tryptophan	9.77	9.40
Valine	9.99	9.72
Alanine	10.29	9.90
Proline	10.54	10.60

Table 2 : Stepwise and Overall Stability Constants of Chromium (II) Amino Acid Complexes.

Complex	LogK1	LogK2	LogK3	Log β
$[Cr(Gly)_3]^-$	9.87	9.89	9.78	29.54
$[Cr(Ala)_3]^-$	10.13	10.05	10.05	30.23
$[Cr(Arg)_3]^-$	11.88	11.71	11.70	35.29
$[Cr(Asn)_3]^-$	9.23	9.15	9.14	27.52
$[Cr(His)_3]^-$	7.28	7.30	7.20	21.78
$[Cr(Lys)_3]^-$	10.09	10.00	9.99	30.08
$[Cr(Met)_3]^-$	9.63	9.56	9.56	28.75
$[Cr(Phe)_3]^-$	9.44	9.36	9.35	28.15
$[Cr(Pro)_3]^-$	10.63	10.63	10.60	31.86
$[Cr(Thr)_3]^-$	10.31	10.33	10.22	30.86
$[Cr(Try)_3]^-$	9.75	9.67	9.66	29.08
$[Cr(Val)_3]^-$	9.78	9.70	9.70	29.18

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