Bayero Journal of Pure and Applied Sciences, 2(2): 191 - 193
Received: August, 2009
Accepted: November, 2009

DETERMINATION OF STABILITY CONSTANTS OF MANGANESE (II) AMINO ACID COMPLEXES

H. N. Aliyu and J. Na'aliya
Department of Chemistry Bayero University, P. M. B. 3011, Kano, Nigeria
Correspondence author: hnuhu2000@yahoo.com

ABSTRACT
The stepwise and the overall stability constants of the complexes formed by manganese (II) ion and twelve (12) amino acids have been determined. The dissociation constants, pKa, 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 (10.54), threonine (10.31), tryptophan (9.77), and valine (9.99). The average number of amino acids coordinated to manganese (II) ion determined is 3. The Stepwise Stability Constants of manganese (II) amino acid complexes determined were 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.

Keywords: Amino acids, dissociation constant, potentiometry, stability constant

INTRODUCTION

Acids – base titration involves the gradual addition or removal of protons for example using the deprotic form of glycine. The plot has two distinct stages corresponding to the deprotonation of the two different groups on glycine. Each of the stage resembles in shape the titration curve of a monoprotic acid. At very low pH, the predominant ionic species of glycine is $H_3N^+CH_2COOH$, the fully protonated form. At the midpoint of the titration, the - COOH group loses its proton and the pH is equal to pKa of the protonated group being titrated. The pH at midpoint is 2.34, thus its – COOH group has a pKa labeled pK_1. The pKa is a measure of the tendency of a group to give up a proton (David and Michael, 2000). Amino acids are known to produce complexes with transition metals repeatedly in the literature (Meyer and Bauman*,* 1970; Sigel and Cormik*,* 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). Manganese appears to be essential in trace amount to virtually all forms of life (Cotton and Wilkinson, 1980). It is essential for the activities of various enzymes (Hill and Holman, 1980). The concentration in human plasma has been reported as 9.37 – 11.36μg/g (Yalwa, 2002). It is an essential trace mineral in human nutrition. Manganese also is known to be an essential component in chlorophyll, which is a green pigment that assists in photosynthesis (Cotton and Wilkinson, 1980). Manganese is also the preferred metal co-factor in glycosyltransferases and deficiency in manganese result in Vitamin K deficiency which causes loss of body weight, changes in hair and beard (Ayodele and Madu, 2006), fatigue, lack of physical endurance, slow growth of finger nails and hair, impaired metabolism of bone and cartilage, weight loss, reduced fertility and change hair colour. The sources of manganese include whole grain, leafy vegetables, and nuts.

This paper reports the determination of stability constants of manganese (II) amino acid complexes using potentiometer.

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 pKa of the Amino Acids

The determination was carried by first measuring the pH of the reaction mixture prepared by adding into $400cm^3$ beaker containing magnetic stirring bar $90cm^3$ of distilled water, $100cm^3$ of $0.04moldm^{-3}$ potassium trioxonitrate (V) and $10cm^3$ of 0.08 mol/dm^3 of glycine respectively. The electrodes of the standardized pH meter were then introduced into the reaction mixture and with stirring aliquots ($0.5cm^3$) of standardized 0.1 $moldm^{-3}$ sodium hydroxide were added from a burette into the reaction mixture.

After each addition of the aliquot the corresponding stable pH reading was recorded. The same procedure was repeated for each of the remaining amino acids (Angelici, 1977).

Determination of Stability Constants of Manganese (II) Amino Acids Complexes

Into a 400cm^3 beaker 100 cm^3 of 0.04M, KNO_3 10cm^3 of 0.02M HNO_3, 90 cm^3 of distilled water and 1 millimole (0.001 mole) of manganese (II) chloride tetrahydrate were added respectively. 0.5 cm^3 of 0.1M 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. The same procedure was repeated for each of the remaining amino acids (Angelici, 1977).

RESULTS AND DISCUSSION

The dissociation constants, pKa, of the amino acids have been determined. The observed values are in agreement with the literature values indicated in Table 1. Histidine has the least dissociation constant (7.01) while proline has the highest value (10.54). The histidine dissociates better, yielding more hydrogen ions compared to proline with limited liberated hydrogen ions. The stepwise and the overall stability constants for each manganese (II) amino acid complex compound have been determined potentiometrically. The mean number of amino acid anions per manganese (II) determined is 3 for all the complexes in this work. The stepwise stability constants of each manganese (II) amino acid complex compound determined are high and are observed to decrease in the order $K_1 > K_2 > K_3$, which is in agreement with literature (Angelici, 1977; Cotton and Wilinson, 1980; Satya *et al*., 2006). However, Sovago *et al* (1993) and Berthon (1995), reported K_1 and K_2 values for manganese (II) complex compounds with alanine, valine, threonine, asparagine and methionine, respectively, which are found to vary slightly. This slight variation in the values of stepwise stability constants could be attributed to the use of ion-exchange and electrophoretic techniques by those workers instead of the more reliable potentiometry used in this work. The overall stability constants of the manganese (II) amino acid complex compounds are quite high and are comparable with literature (Cotton and Wilkinson, 1980; Satya *et al*., 2006). For the overall stability constants obtained, the stability of the complex ions follows the order;

$$[Mn(Thr)_3]^- > [Mn(\Pr o)_3]^- > [Mn(Lys)_3]^- > [Mn(Ala)_3]^- > [Mn(Gly)_3]^-$$
$$> [Mn(Valr)_3] > [Mn(Thr)_3]^- > [Mn(Phe)_3]^- > [Mn(Met)_3]^- > [Mn(Asn)_3]^- > [Mn(His)_3]^-$$

Thus from Table 2, the stability constant value of $[Mn(Thr)_3]^-$ complex ion is the highest, implying the most stable while $[Mn(His)_3]^-$ is the least stable, as it has the least overall stability constant value.

CONCLUSION

The dissociation constants, pKa, of amino acids have been determined. The values obtained are in agreement with literature. The stepwise and overall stability constants of manganese (II) amino acid complex compounds have been determined. The stability constants values determined are very high, which revealed that the complex compounds studied are stable.

Table 1: Dissociation constants (pKa) of amino acids

Amino acid	Dissociation constant (pKa)	Literature value	Reference
Glycine	9.87	9.60	Sovago et al, 1993
Arginine	12.02	12.48	Robert and Melvin, 1982-83
Asparagine	9.39	9.30	Berthon, 1995
Histidine	7.01	7.59	David and Michael, 2000
Lysine	10.28	10.51	Robert and Melvin, 1982-83
Methionine	9.68	9.69	Berthon, 1995
Phenyalanine	9.61	9.24	David and Michael, 2000
Threonine	10.31	10.43	David and Michael, 2000
Tryptophan	9.77	9.40	David and Michael, 2000
Valine	9.99	9.72	David and Michael, 2000
Alanine	10.29	9.90	Robert and Melvin 1982-83
Proline	10.54	10.60	David and Michael, 2000

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

Complexes	$LogK_1$	$LogK_2$	$LogK_3$	Logß
$[Mn(Gly)_3]$	9.14	9.12	8.99	27.25
$[Mn(Ala)_3]^-$	9.49	9.47	9.32	28.28
$[Mn(Arg)_{)3}]^-$	10.72	10.58	10.20	31.50
$[Mn(Asn)_3]^-$	8.57	8.56	8.32	25.45
$[Mn(His)_3]^-$	7.11	7.12	7.04	21.27
$[Mn(Lys)_3]^-$	9.66	9.64	9.60	28.90
$[Mn(Met)_3]^-$	8.9	8.93	8.77	26.65
$[Mn(Phe)_3]^-$	9.01	8.99	8.88	26.88
$[Mn(Pro)_3]^-$	9.73	9.72	9.62	29.07
$[Mn(Thr)_3]^-$	10.00	9.77	9.68	29.45
$[Mn(Try)_3]^-$	9.07	9.05	8.85	26.97
$[Mn(Val)_3]^-$	9.08	9.06	8.90	27.04

REFERENCES

Andreoli, R., Gavioli, G. B., Benedetti, L., Grandi, G., Marcotrigiano, G., Menabue, L. and Pellacani, G. C. (1980). Complex formation of zinc (II) ion with glycine, N-acetyl – and N – benzoyl – glycine anions in aqueous and ethanolic solution by polarographic method. *Inorganica Chemica Acta*, 46: 215 - 219.

Angelici, R. J. (1977). *Synthesis and techniques in inorganic chemistry* W. B. Saunders campany, 2nd Edition Philadelphia, Pp 115 – 127.

Antolini, L., Menabue, M. Saladini, M., and Morini, P. (1980). Silver (I) complexes with N – protected amino acids. *Inorg. Chimica Acta*, 46: L77 - L78.

Ayodele, J. T. and Madu, F. M. (2006). Manganese in human milk. *Scientia Africana*, 2: 133 – 142.

Battaglia, L. P., Corradi, A. B., Marcotriglano, G.; Menabue, L. and Pellacani, G. C. (1981) copper (II) complexes of N-protected Amino acids: Synthesis, spectroscopic, magnetic and structural properties of Bis (N-acetyl-β-alaninato) diaqua copper (II) and tetrakis $\mu-(N-acetyll-\beta-ala\min ato)$ diaquadicopper (II) dihydrate. A case of structural isomerism. *Inorg. Chem.*, 20: 1075 - 1080.

Berthon, G. (1995). The Stability constants of metal complexes of Amino Acids with polar side chains. *Pure and Appl. Chem*.., 67 (7): 1117 – 1240.

Cotton**,** F. A. and Wilkinson, G. (1980). *Advanced inorganic chemistry*, A comprehensive Text, fourth Edition, John Wiley and Sons, New York, Pp 1310 – 1344.

Hill, G. C and Holman, J. S. (1980), *Chemistry in Context*: 1st ed. ELBS, Pp 273.

David, L. and Michael, M.C. (2000). *Lehninger Principles of Biochemistry* Third Edition, Worth publishers, 41 Madison Avenue, New York Pp113 – 158.

Meyer, J. L. and Bauman Jr, J. E (1970). Copper (II) Histidine complexes. *J. Amer Chem.Soc.*, 92: 4210 - 4222.

Satya, P; Tuli G. D.; Basu S. K. and Madan R. D. (2006). *Advanced Inorganic Chemistry* Vol. I S. chand and Company India Pp 705 - 706.

Sovago, I., Kiss, T. and Gergely, A. (1993). Critical survey of the stability constants of complexes of Aliphatic Amino Acids. *Pure and Appl. Chem*.., 65 (5): 1029 – 1080.

Sigel, H. and Mc Cormik, D. D. |(1971). The structure of the copper (II) –L-Histidine 1.2 complex in solution. *J. Amer. Chem.. Soc*. 93: 2041 - 2044.

Stryer, L. (1988). *International student Edition Biochemistry*, Third Edition W. H. Freeman and Company, NewYork Pp 15 – 42.

Takaji,Y., Hidaka, J. and Shimura, Y. (1965).Circular dichroism of Copper(II) Complexes with optically active amino acids. *J. Amer. Chem.*, 87: 2762 - 2763.

Tsangaris, J. M., Chang, T. W. and Martin, R. B. (1969). Ultraviolet Circular Dichroism of Cupric and Nickel ion Complexes of Amino acids and peptides. *J. Amer. Chem. Soc.*,91: 726 - 731.

Yalwa, I. R. (2002). Proximate and Amino acid composition of Vigna dekindtiana, Un published Bayero University M.Sc. Dissertation, Kano