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Full Length Research Article

Potentiometric Study of Trismethioninato Complexes of some Essential Transition Metals

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ABSTRACT: Potentiometric study of methionine complexes of chromium, manganese, iron, cobalt and nickel was carried out in aqueous media by titrating with standard sodium hydroxide solution. The values of the stepwise and overall stability constant were obtained by new computational method, 'ORIGIN 50'. The values of the stepwise stability constants of the complexes were found in general to follow the order $K_1 > K_2 > K_3$ and that of the overall constants, logβ to be in the range 26.55 – 28.73.
Keywords: Methionine, complexes, nickel, chelate and enzymes

INTRODUCTION

Amino acids are the essential constituents of plants and animal tissues (Holmes and Hazel, 1993). Among the standard amino acids that were obtained including methionine are said to be essential and can only be supplemented with proper nutrition. Methionine helps in calcium absorption, formation of collagen, production of antibodies hormones, enzymes, chelating agent for heavy metals and as an additive in poultry feed (Stryer, 1988 and David and Micheal, 2000). As a chelating agent it forms chelates on association with metals. These chelates are of great interest because they may be used as a basis for understanding of metal – protein interaction. Many proteins within the body need metal ions to work, for example in enzymatic catalysis of most biological processes, major component of muscle – muscle contraction, differentiation of cells and control of growth (Stryer, 1988). Methionine being an amino acid is known to produce complexes with transition metals (Sigel and McCormik, 1971 and Meyer *et al.,* 1970). These complexes help in provision of mechanical support via skin, bones etc (Stryer, 1988). This paper therefore reports potentiometric study of complexes formed by methionine and the metals: zinc, copper, iron, manganese, cobalt, nickel and chromium.

MATERIALS AND METHODS

All the chemicals used in this work are of analytical grade purity and were used without further purification. All weighing were carried out using AB 54 model electronic Metler balance. The pH was measured using Jenway pH Meter model 3320.

Determination of pH of Methionine

The pH of the reaction mixture containing 90 cm^3 distilled water, 100 cm^3 0.04 $moldm^{-3}$ potassium trioxonitrate (V) and 10 cm^3 of 0.08 $moldm^{-3}$ of methionine and magnetic stirring bar respectively in a 400 cm^3 beaker was measured using the pH meter (Angelici, 1977, Aliyu and Na'aliya, 2010). The measurement was carried by addition of 0.5 cm^3 standardized 0.1 $moldm^{-3}$ sodium hydroxide from a burette into the reaction mixture and after each addition of the aliquot, the corresponding stable reading of the pH was recorded. The pH readings were used to obtain the pKa value (Figure 2) of the methionine which served as a qualitative test for its identification.

Determination of Stability Constants of Complexes

One millimole (0.001 mol) of chromium(III) nitrate was added into a 400 cm^3 beaker containing 100cm^3 of 0.04 $moldm^{-3}$ KNO_3, 10 cm^3 of 0.02 $moldm^{-3}$ HNO_3, 90 cm^3 of distilled water and. Then 0.5 cm^3 of 0.1 $moldm^{-3}$ sodium methioninate was added into the reaction mixture and after each addition with stirring, the corresponding stable pH reading was recorded. The addition of the aliquots was continued until 10cm^3 was added. The same procedure was repeated with manganese (II) sulphate, cobalt (II) sulphate, iron (II) sulphate, copper (II) sulphate, zinc (II) sulphate and nickel (II) sulphate respectively.

The stepwise and overall stability constants of the complexes were obtained by using 'ORIGIN 50' computational method (Na'aliya, 2008) from the graphs obtained by plotting the values of log $[A^-]$ versus n developed by Bjerrum (Angelici, 1977). The values of $[A^-]$ (deprotinated amino acid) and n (average number of ligand per metal ion) were calculated from the experimentally known quantities using the expressions;

$K_x = 1/ [A^-]_n$, where n = ½, 3/2,5/2 for stepwise stability constant and $Log\beta = K_1 + K_2 + \ldots K_x$ for overall stability constant

RESULTS AND DISCUSSION

The results obtained (Table 1) show the stepwise and overall stability constants to be high indicating good stability of the complexes. In general the stepwise stability constants (K_1, K_2 and K_3) follow the order K_1 >

$K_2 > K_3$ for the iron, manganese, cobalt and nickel complexes respectively while $K_1 > K_2$ for chromium, copper and zinc complexes. The steady decrease of the values with increasing number of ligands is in agreement with the prediction made by Angeleci (1977). The decrease could be attributted to the fact that as the number of the ligands (Methioninate ions) that enters the coordination zone increases the aqua molecules available for replacement by the ligands become less. Thus, the metal ions become less electron greedy with progressive intake of the methioninate ligands and this results in the decrease in the values of the constants (Satya *et al.,* 2006; Cotton and Wilkinson, 1980; Angelici, 1977). Also the stability of the complexes is influenced by the size and number of the chelate rings. All the complexes form rings in their structure as methionine, a bidentate ligand, bound the metal ions in the glycinato way (Sovago *et al*., 1993) forming chelate rings. Also from the ΔG values of the complexes (Figure 1), the stability of the complexes increases with increase in atomic number from Cr to Mn and some what the values stabilizes for Mn, Fe, Ni and Co and falls at Cu and Zn.

The values of the overall stability constants (logβ) obtained for methionine-copper complex is the range values (13–18.28) of similar copper complexes reported by Sovago *et al*. Also the K_2 values reported for Mn-met complexes of 6.70 - 7.70 is lower than the value of 8.93 obtained in the present study. Similarly K_2 value for Co – met complex of 8.91obtained in this study is closer to the value of 7.91 reported by Berthon (1995). The value of K_2 for the Ni – met complex of 8.90 is lower than 9.60 also reported by Berthon (1995) even though both values indicate good stability. The difference between the reported values and the values obtained in this study might be probably as a result of temperature difference, nature and concentration of the medium and computational method.

Table 1: Stepwise and Overall Stability constants of the complexes

Complex	K_1	K_2	K_3	Logβ	ΔG ($kJmol^{-1}$)
$[Cr(met)_2]^+$	9.63	9.56	-	19.91	-113.60
$[Cu(met)_2]$	9.34	9.22	-	18.56	-105.90
$[Zn(met)_2]$	8.88	8.85	-	17.73	-101.16
$[Mn(met)_3]^-$	8.90	8.93	8.77	26.65	-152.60
$[Fe(met)_3]^-$	8.90	8.93	8.77	26.65	-152.06
$[Co(met)_3]^-$	8.94	8.91	8.73	26.58	-151.66
$[Ni(met)_3]^-$	8.92	8.90	8.73	26.55	-151.49

Key: met = methioninate ion; K: stepwise stability constant Logβ: overall stability constant; ΔG: free energy change

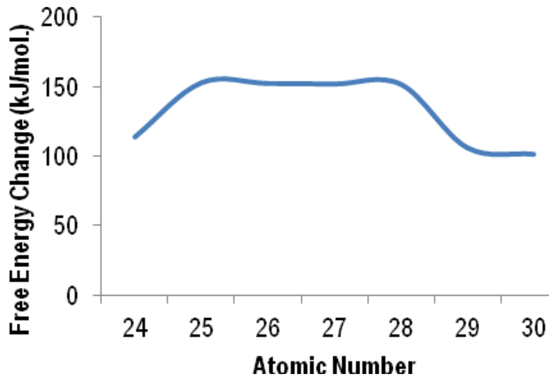

Figure 1: Plot of free energy change versus atomic number

The pKa value of 9.68 obtained for methionine (Figure 2) is slightly higher than 9.21 reported by David and Micheal (2000). However, the pKa value is similar to value of 9.69 reported by Berthon (1995) in $NaClO_4$ medium.

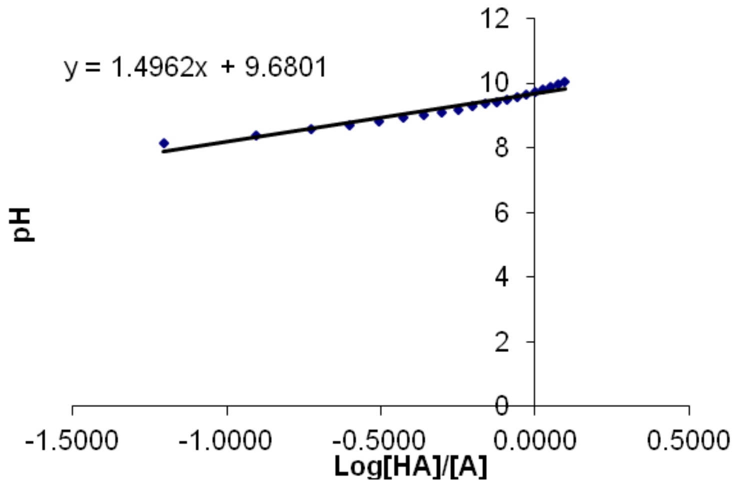

Figure 2: Plot of pH Versus Log [HA]/[A] for pKa of Methionine

CONCLUSION

The higher values of the overall stability constants of the methionine metal complexes indicates good stability of the complexes thus providing additional information for the use of methionine in poultry feed as an additive because its complexation will enhance the better efficiency of both the metals and the methionine in the body of the animals.

REFERENCES

Aliyu, H. N. and Na'aliya, J. (2010). Determination of Dissociation Constants of Amino acids using 'ORIGIN 50' Program. *African Scientist*, **11(1):** 5-19.

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

Berthon, G. (1995). The Stability constants of metal complexes of Amino Acids with polar side chains. *Pure and Appl.ied Chemistry*, **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.

David L., Micheal M.C. (2000). *Lehninger Principles of Biochemistry*, Third Edition, worth publishers, 41 Madison Avenue New York, Pp 113 – 158.

Holmes, D.J. and Hazel, P. (1993). *Analytical Biochemistry*, 2nd Ed. Longman, Sci. technical, Burnt Mill, Essex. England Pp 70 – 460.

Meyer, J.L. and Bauman Jr, J.E. (1970). Copper(II) Histidine complexes. *Journal American Chemical Society*, **92:** 4210 - 4222.

Na'aliya, J. (2008). Potentiometric studies of some essential metal amino acid complexes. PhD thesis, Department of pure and Industrial Chemistry, Bayero University, Kano (Unpublished)

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.

Sigel, H. and McCormick, D. d. |(1971). The structure of the copper (II) –L-Histidine 1.2 complex in solution. *Journal American Chemical Society*, 93: 2041 - 2044.

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

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