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POTENTIOMETRIC STUDIES OF THE COMPLEXES FORMED BY COPPER (II) AND ZINC (II) WITH SOME POLAR UNCHARGED AMINO ACIDS

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ABSTRACT

The overall stability constants of copper (II) and zinc (II) ions with some polar uncharged amino acids including proline, threonine and asparagines were determined by potentiometric titration in aqueous solution. The values of the constants were found using ORIGIN 50 program computational method of analysis to be 19.56, 20.32, and 17.87 for copper (II) prolinate, copper (II) threoninate and copper (II) asparaginate respectively, that of zinc (II) prolinate, zinc (II) threoninate and zinc (II) asparaginate were found to be 18.51, 18.69 and 16.98 respectively. The average number of coordinated amino acids to the copper (II) and zinc (II) ions were found to be two in all the complexes.

Keywords: Copper(II) ion, Potentiometric, Stability constant, Zinc(II) ion.

INTRODUCTION

Stability constants of amino acids metal complexes and dissociation constants of the amino acids have been determined by many researchers (Na'aliya, 2008). However despite the numerous work carried out in the area of stability constants it is still desirable to carry out more of such determinations owing to the various roles being played by the amino acids and their corresponding metal complexes in biological systems. Such determinations are being repeated by many researchers due to varying enviromental conditions and to be able to have suffiently large values for resonable comparison. Copper which occur in plants in the form of Cu^{2+} or Cu^{1+} in smaller quantity is found in diets such as cereals, meat and vegetables. Zinc is important in metabolic functions and for healthy growth in man (Yalwa, 2002) and serve as a cofactor to several enzymes like copper which is also a constituent of various enzymes and proteins both functions in the brain and liver. Copper and zinc are very essential to enzyme structure (Ayodele and Madu, 2004).

Sovago *et al* (1993) reported the values of stability constants of Cu(II), Ni(II), Co(II) and Zn(II) with aliphatic amino acids such as alanine, valine, 2-aminopentanoic acid. Also Berthon (1995) reported the stability constants of non-transition metals such as Al(III), Be(II) e.t.c. and transition metals such as Co(II), Cr(II), Cr(III),Fe(II) and Fe(III) with amino acids having polar side chains including cystine, methionine, asparagines and serine. Similarly Gergely *et al* (1972) reported the values of stability constants of Cu(II) complexes with threonine and glycine. However despite the work reported by various researchers it is still desirable to carry out more determination of stability constants owing to the various roles being played by amino acids and the corresponding complexes formed by them. Thus because of the importance of copper and zinc in biological systems and their ability to form complexes, this paper therefore reports the determination of stability constants of complexes formed by copper and zinc with amino acids that have polar uncharged groups. The constants obtained will help in the understanding of the function and efficiency of copper and zinc in biological systems.

MATERIALS AND METHODS

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

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pH Determination of Amino acids with Polar Uncharged Groups

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 threonine ($C_5H_{12}N_2O_3$) and magnetic stirring bar in a 400 cm^3 beaker was measured using a pH meter with continuous stirring (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 same procedure was repeated for proline ($C_5H_8N_2O_2$) and asparagines ($C_5H_8N_2O_3$). The pH readings were used to obtain the pKa values (Figures 1 – 3) of the amino acids which served as a qualitative test for their identification.

Stability constants of Copper (II) and Zinc (II) Amino acids Complexes

1 millimole (0.001 mol) of copper (II) sulphate 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. Then 0.5 cm^3 aliquot of 0.1mol dm^{-3} sodium threoninate ($C_5H_{11}N_2O_3Na$) was added into the reaction mixture, after each addition with stirring using a magnetic bar, the corresponding stable pH reading was measured and recorded. The addition of the aliquots was continued until all 10cm^3 of a 0.1 $moldm^{-3}$ sodium threoninate was added. The same procedure was repeated using sodium prolinate and sodium asparaginate. The procedure was repeated with zinc (II) sulphate to obtain zinc (II) complexes of the amino acids.

The stepwise and overall stability constants of the copper (II) and zinc (II) complexes were separately obtained by using 'ORIGIN 50' graphical/computational method (Na'aliya, 2008). From the graphs obtained by plotting the values of log $[A^-]$ versus n developed by Bjerrum as reported by Angelici (Angelici, 1977), the values of $[A^-]$ (deprotinated amino acid) and n (average number of ligands 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

$Log\beta = Logk_1 + Logk_2 + \ldots logk_x$ for overall stability constant

$$\boldsymbol{n} = \frac{\boldsymbol{A_{tot}} - \left(\boldsymbol{1} + \frac{\boldsymbol{Ka}}{[\boldsymbol{H^+}]}\right)(\boldsymbol{C_H} - [\boldsymbol{OH^-}] - [\boldsymbol{H^+}])}{\boldsymbol{M_{tot}}}$$

Where Ka = dissociation constant of the amino acid

$[H^+]$ = concentration of the H^+ after each aliquot addition

M_{tot} = total metal ion concentration

A_{tot} = total amino acid concentration

n = number of coordinated ligands

C_H = concentration of nitric acid

$[A^-]$ = concentration of dissociated amino acid

$Log\beta$ = overall stability constant

RESULTS AND DISCUSSION

The values of pKa of the amino acids with uncharged polar groups were obtained from Figures 1 – 3 as intercepts of the graphs and were found to be 9.39, 10.53 and 10.30 for asparagine, proline and threonine respectively. The values were found to be in agreement with reported values in the literature (Berthon, 1995; Robert and Melvin, 1982-83; David and Micheal, 2000). The values of the pKa served as a qualitative test for the amino acids used in the work.

The complexation of amino acids ligands with metal ion often result in the formation of complexes of the type ML_n (n = 1, 2 or 3) (Sovago *et al.*, 1993) and the type of linkage that take place is glycinato type which also results in the formation of chelated rings (Yamuchi and Odani, 1996). The size and number of rings contribute to the stability of the complexes formed (Satya *et al.*, 2006, Cotton and Wilkinson, 1980). The values of the stepwise constants obtained using the graphs of log $[A^-]$ versus n and above expressions for K_x and $Log\beta$ (Tables 1 and 2) follows the pattern $K_1 > K_2$ and were higher than the values reported within the range of 13 – 18 for alanine, valine, threonine, methionine and aspargine copper(II) complexes (Sovago *et al*., 1993; Berthon, 1995; Sovago and Gergely, 1973; Gergely *et al*., 1972) The overall stability constants indicates that threoninate complexes are the most stable followed by the prolinate complexes while the asparaginate complexes are the least stable for the copper complexes. The same trend occurs for zinc complexes but the values of the constants are generally lower than those of the copper complexes. The stability of the complexes might be associated with chelation which depends on the size of amino acids (Satya *et al.*, 2006; Cotton and Wilkinson, 1980). The greater stability of the copper complexes compared to corresponding zinc complexes could be explained interms of Irvin William rule (Sovago *et al.,* 1993 ; *Satya et al.,* 2006) as Cu^{2+} is larger than Zn^{2+} and the larger the size of the ion the greater the ability to form stable complexes. The average number of ligand per metal ion, n of two were found for both copper(II) and zinc(II) complexes (Tables 1 and 2) and this could be due Jahn Teller effect (Cotton and Wilkinson, 1980).

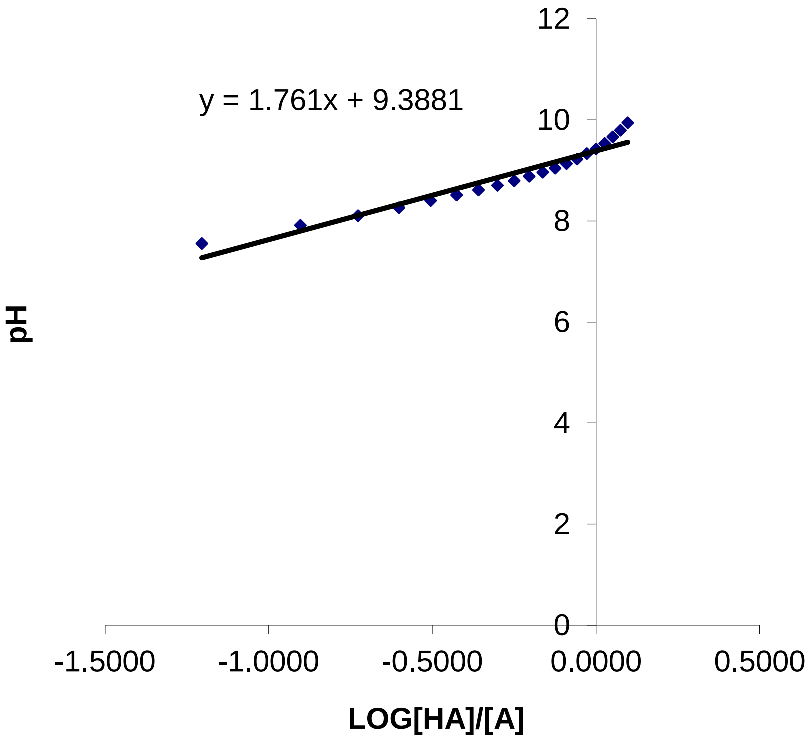

Fig.1: Acid dissociation constant (pKa) of asparagine

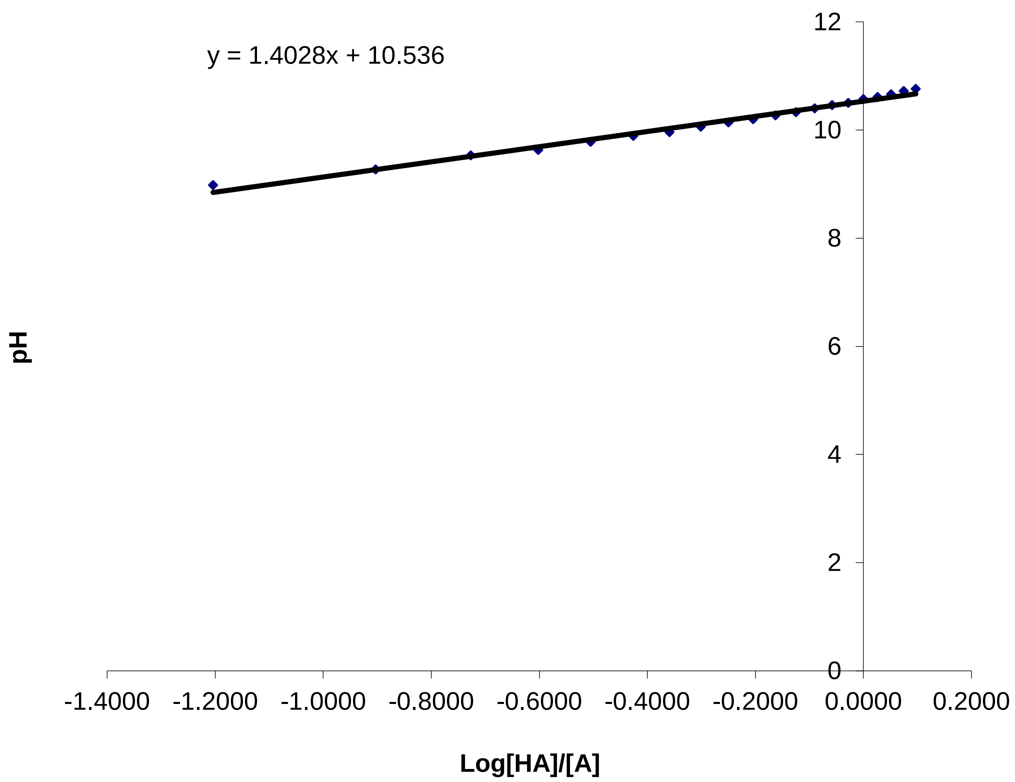

Fig.2: Acid dissociation constant (pKa) of proline

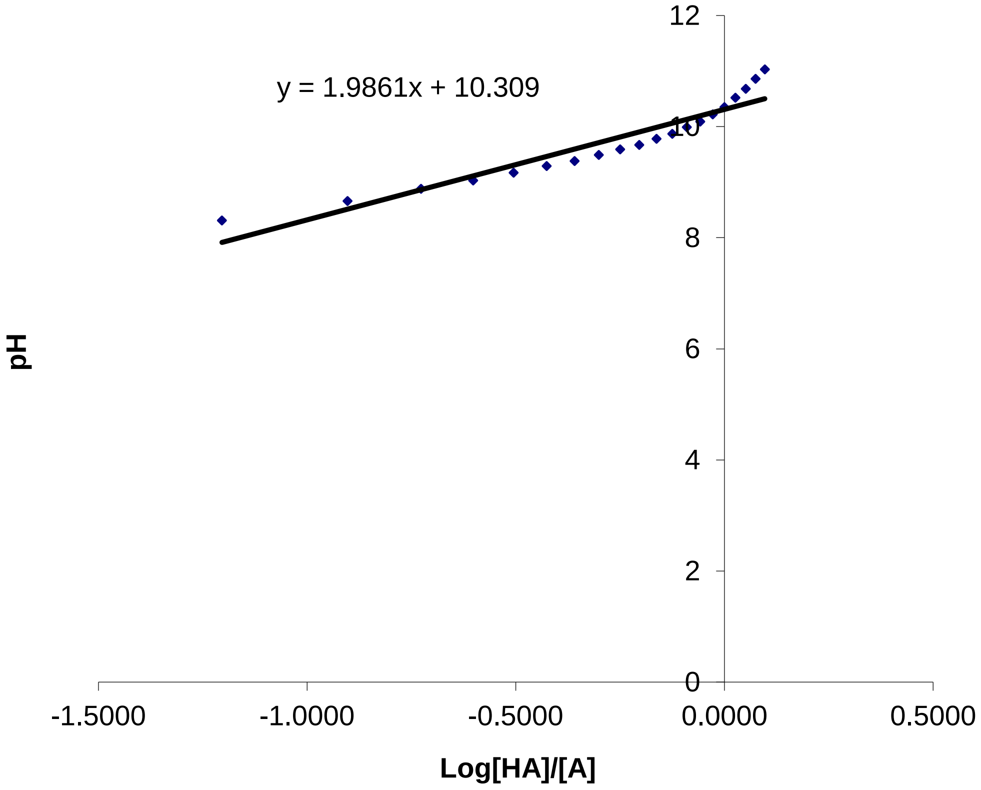

Fig.3: Acid dissociation constant (pKa) of Threonine

Table 1: Stepwise and Overall Stability Constants of Amino acids Copper Complexes

Complexes	$Logk_1$	$Logk_2$	$Log\beta$
$Cu(Asn)_2$	8.94	8.93	17.87
$Cu(Pro)_2$	9.79	9.77	19.56
$Cu(Thr)_2$	10.20	10.12	20.32

Table 2: Stepwise and Overall Stability Constants of Zinc Amino acids Complexes

Complexes	$Logk_1$	$Logk_2$	$Log\beta$
$Zn(Asn)_2$	8.50	8.48	16.98
$Zn(Pro)_2$	9.27	9.24	18.51
$Zn(Thr)_2$	9.37	9.32	18.69

CONCLUSION

It can be concluded that the high stability of the complexes of copper and zinc could be used to offer part of the reasons why copper and zinc are used as cofactors to many enzymes since metals function more efficiently in form of stable complexes. The stability will prevent the dissociation of the complex before the process catalysed by the metal is completed.

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