



THE STABILITY CONSTANTS OF NICKEL (II) COMPLEXES OF AMINO ACIDS WITH POLAR UNCHARGED R – GROUPS

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ABSTRACT

The dissociation constant, pK_a of proline, threonine and asparagines were determined by potentiometric titration in aqueous solution. The pK_a of proline, threonine and asparagines were found graphically by extrapolations to be 10.54, 10.31 and 9.39 respectively. The overall stability constant of the corresponding nickel (II) complexes were also determined by potentiometric titration in aqueous solution. The values of the constant were found using ORIGIN 50 program to be 28.75, 2743 and 25.64 for nickel (II) proline, nickel (II) threonine, and nickel (II) asparaginate respectively. The number of coordinated amino acids to the nickel (II) ion in all the complexes was found to be three.

Key words: polar, stability constant, complexation, asparaginate and enzymes.

INTRODUCTION

Nickel is a constituent of urban air possibly due to fossil fuel combustion. If not of quite recent, nickel is among the first row transition elements lacking any inherent biochemical role (Cotton and Wilkinson, 1980). However, it functions in kidney, lung, skin and adrenal ovary have been reported (Bala, 2005). Nickel being an essential part of some enzymes therefore functions in association with some molecules in the biological systems. Thus like other transition metals it form complexes of the type ML , ML_2 and ML_3 respectively especially with amino acids which are themselves bidentate ligands (Sovago *et al.*, 1993). Polar amino acids such as proline, threonine and asparagine are components in proteins and are thus essential (David and Micheal, 2000; Stryer, 1988). Also from the Chemical point of view, all are optically active and include side chain groups likely to form chelate rings with nickel ion bound to α – nitrogen. Thus, from structural characteristics, if these amino acids are to behave as didentate ligands, then they will form 5 – membered and 6- membered chelate rings respectively with polar amino acids. Stability constants are important parameters in determination of stability of complexes which in turn influence the function of metals and amino acids. From the available literature not much have been reported about the stability constants of polar amino acids metal complexes, but the few reported values for threonine are too different to allow for any meaningful comparison (Berthon, 1995). With the discovery of biological importance of nickel, it is desirable to study its complexation with amino acids in order to understand more about function of its complexes. In this article, the determination of stability constant of nickel complexes with non – polar amino acids is reported using a new approach of interpolation technique by incorporating ORIGIN '50' program of data analysis.

MATERIALS AND METHODS

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

Determination of dissociation constants

The determination of the pK_a of polar amino acids including proline, threonine and asparagine carried out by first measuring the pH of the reaction mixture prepared by adding into 400cm³ beaker containing magnetic stirring bar, 90cm³ distilled water, 100cm³ of 0.04 mol dm⁻³ potassium trioxonitrate (V) and 10cm³ of 0.08 moldm⁻³ of threonine respectively (Angelici, 1977). An aliquot of standardized 0.1mol dm⁻³ sodium hydroxide from a burette was added into the reaction mixture and after each addition of the aliquot, the corresponding stable reading of pH was recorded after the appearance of stable linear graph sign using Jenway pH meter model 3320.

The same procedure was repeated for proline and asparagine respectively. The results obtained are shown in Figures 1 to 3.

Determination of stability constants of copper (II) amino acids complexes

Into a 400cm³ beaker, 100cm³ of 0.04mol dm⁻³ KNO₃, 10 cm³ of 0.02 mol dm⁻³ HNO₃, 90 cm³ of distilled water and 1 milimole (0.0001 mole) of nickel(II) chloride were added respectively 0.5cm³ of 0.1mol dm⁻³ sodium threoninate was added and after each addition with stirring the corresponding pH reading was recorded. The addition of the aliquot was continued until the full 10cm³ was added. The same procedure was repeated with sodium proline and asparaginate respectively. The results obtained are shown in Table 1.

RESULTS AND DISCUSSION

The dissociation constant of polar amino acids, pKa studied were obtained at the intercept of the graph of pH versus $\log [HA]/[A^-]$, which is a new approach developed in the course of the study. This is in accordance to the equation, $K_a = [H^+][A^-] / [HA]$ used by Csaba *et al.*, (1999) for the calculation of pKa. The equation was modified to conform with the equation,

$pH = - \log [HA]/[A^-] + pK_a$ which was used for the determination. This is the first time from the available literature it was put on plot as many researchers had used different equations for the calculation of pKa. The pKa values (values at the intercepts) for threonine, asparagine and proline obtained are shown in Figures 1 to 3 respectively.

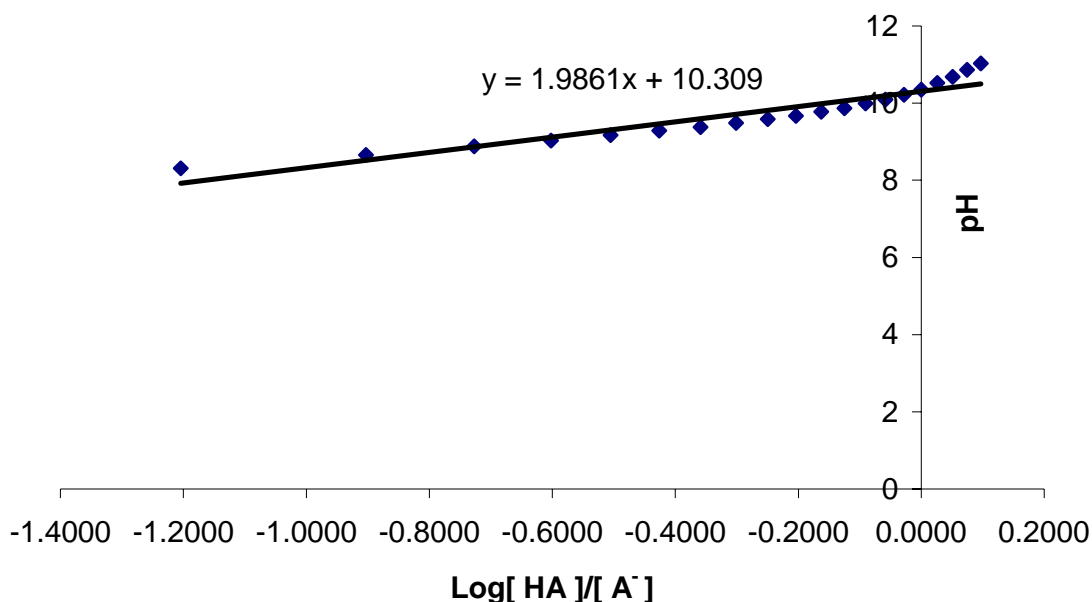


Figure 1: Plot of pH Versus $\log [HA]/[A^-]$ for pKa of Threonine

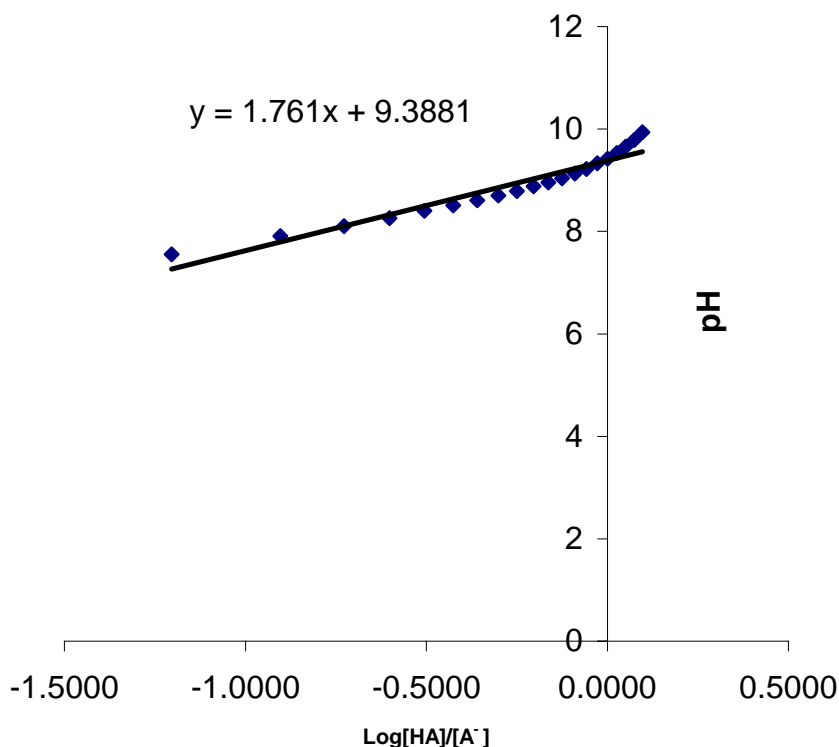


Figure 2: Plot of pH Versus $\log [HA]/[A^-]$ for pKa of Asparagine

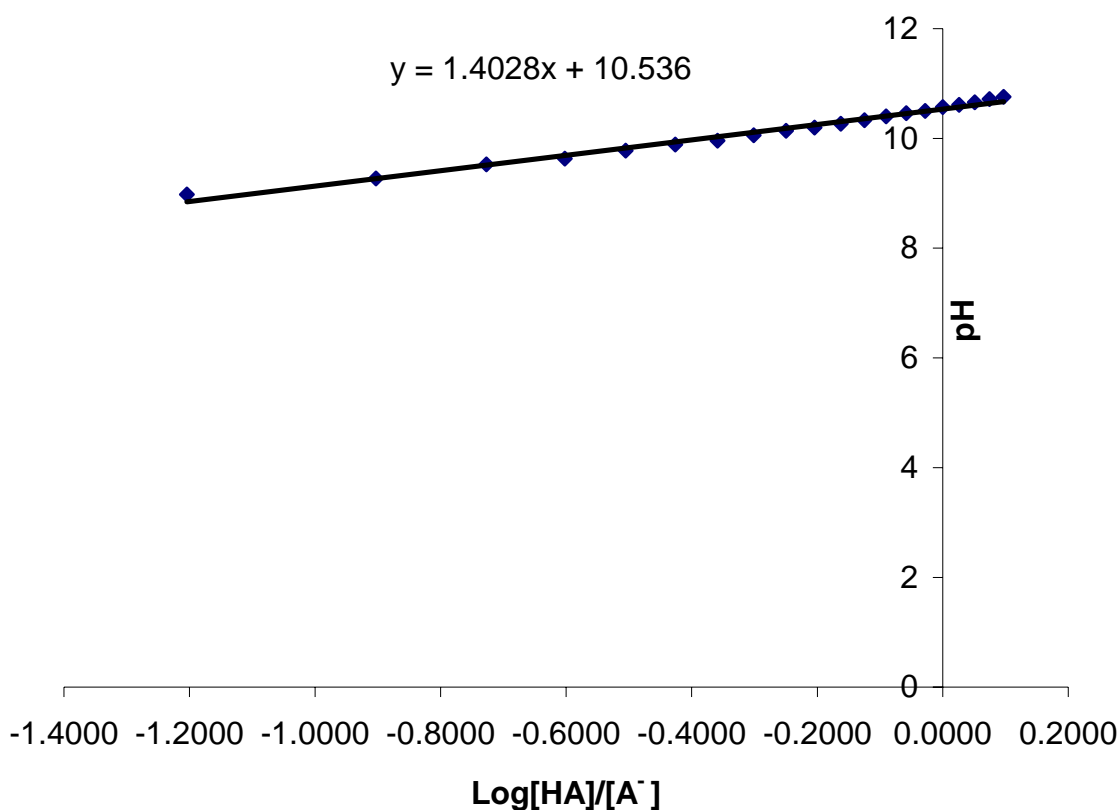


Figure 3: Plot of pH Versus Log [HA]/[A⁻] for pKa of Proline

Figure 1 gives the pKa value of 10.31 for threonine. This is similar to the 10.43 value reported by David and Micheal (2000) and also by Robert and Melvin, (1982 – 1983) but higher than the tentative value of 8.97 ± 0.06 reported by Berthon (1995) and 8.98 reported by Gergely *et al* (1972). Berthon (1995) also reported values of 10.08, 10.73 in organic medium. The pKa value of 9.39 for asparagine, from Fig. 2 is similar to the tentative value of 9.30 reported by Berthon, (1995). The value of 10.54 obtained for proline dissociation constant from Fig. 3 is similar to 10.6 reported by David and Macheal (2000), Lehninger (1975) and also by Robert and Melvin (1982 – 1983).

The number of coordinating amino acid ligands to nickel (II) was found to be three potentiometrically (Angelici, 1977). This is in agreement with the report of Sovago *et al* (1993) as nickel is among the metal ions that form complexes of the type ML, ML₂ and ML₃ respectively. The overall stability constant, $\log \beta$ for the complexes were obtained from the values of stepwise stability $\log K_1$, $\log K_2$ and $\log K_3$ for stepwise formation of the ML, ML₂ and ML₃ for nickel (II) complexes using the expression $\log \beta = \log K_1 + \log K_2 + \log K_3$ (Angelici, 1977). The stepwise stability constants also decrease from $K_1 - K_3$ as expected (Angelici, 1997; Cotton and Wilkinson, 1980; Satya, *et al.*, 2006).

The steady decrease in the values K_1 , K_2 and K_3 with increase in the number of ligands is due to the fact that as more and more ligands move into the coordination zone, less and less aqua molecules are available to fresh ligands for replacement. Thus the Ni(II) ion becomes less electron greedy with progressive intake of the ligands (amino acids) and thus results in decrease in the values of the constants (Satya *et al.*, 2006).

The values of the overall stability constants, $\log \beta$ (Table 1) are high indicating good stability for the complexes due to chelation effect (Cotton and Wilkinson, 1980; Satya *et al.*, 2006). The values of the overall stability constants, $\log \beta$ for nickel complexes determined were found to decrease in the order $[\text{Ni}(\text{Pro})_3]^- > [\text{Ni}(\text{Thr})_3]^- > [\text{Ni}(\text{Asn})_3]^-$. The decrease could be due to chelation effect. All the complexes form rings in their structure on coordination of the Ni(II) ion with the amino acids being bidentate ligands and this result in the complexes being more stable. The decrease in the stability could be attributed to the larger number of rings formed in $[\text{Ni}(\text{Pro})_3]^-$ as proline itself is cyclic on coordination. However $[\text{Ni}(\text{Thr})_3]^-$ and $[\text{Ni}(\text{Asn})_3]^-$ are having almost the same number of rings in their structure but the greater stability of $[\text{Ni}(\text{Thr})_3]^-$ compared to $[\text{Ni}(\text{Asn})_3]^-$ might be due to the formation of intramolecular H-bonding in threonine complex due to the presence of -NH and -OH polar groups (Cotton and Wilkinson, 1980; Satya *et al.*, 2006).

Table 1: Values of stepwise and overall stability constants of the Ni(II) complexes

Complexes	Log K ₁	Log K ₂	Log K ₃	Log β
[Ni(Pro) ₃] ⁻	9.62	9.61	9.52	28.75
[Ni(Thr) ₃] ⁻	9.37	9.22	8.84	27.43
[Ni(Asn) ₃] ⁻	8.64	8.62	8.38	25.64

CONCLUSION

The stability of the complexes could be associated to the nature of the chelation taking place in the complexes. The high stability of the complexes also is

one of the determinants of the other factors that enhances the functioning of the complexes in the relevant biological processes taking place in the body.

REFERENCES

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

Bala, M. (2005). Determination of some mineral Elements and Heavy metals in soils, water and lettuce collected from two pollution prone Irrigation Areas around Kano metropolis. Unpublished Usmanu Danfodio University, M.Sc., Dissertation, Sokoto.

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.

Csaba, V. Janos, Z, Gyorgy, L., Andras, D., Attila, K and Liliana, F. (1999). On the Oximine complexes of Transition metals, part CXIV. New mixed sulfite – cobalt (III) – complexes with Alicyclic α - Dioximes. *Periodica Polytechnica Ser. Chem.* 43, (1): 51 – 64.

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

Lehninger, A. L. (1975). *Biochemistry* Second Edition, Johns Hopkins University School of Medicine, worth publishers, Pp71 – 91.

Robert C. W. and Melvin J. A. (1982 – 1983) *Hand book of chemistry and physics* 63rd ed CRC Press. Pp. C756 – 759.

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.

Satya, P; Tuli G. D.; Basu S. K. and Madan R. D. (2006). *Advanced Inorganic Chemistry* Vol. II S. chand and Company India Pp 30 – 52.

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.

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