A Spectrophotometric Study of the Association of Nickel with Taurine

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With 4 Figures

Summary

Interaction of nickel with taurine was investigated by different spectrophotometric methods. The results, thus obtained were interpreted in terms of complex formation between nickel and taurine in the ration 1:2. Further evidence to this effect was provided by conductometric studies. Moreover, the effect of pH on the nature of nickel ion binding to taurine was also studied spectrophotometrically.

In view of the importance of nickel-ion in biological systems[1]) its interaction with naturally occuring substances such as proteins[2])[3]), peptides[4])[5]) and amino acids [5])[6])[7]) was extensively investigated, and a lot of useful quantitative informations regarding the composition and stability of the metal complex of simple peptides and amino acids could be obtained, mostly by (Bjerrum)[8]) potentiometric method. But the elucidation of the real nature of nickel-ligand bond by this method was not always possible. Spectrophotometry can, however, be advantageously used for this purpose. It was, therefore, thought worthwhile to carry out systematic studies in this direction.

The present communication presents a detailed spectrophotometric studies as of quite a new system, viz; nickel-taurine system, taurine being an analogue of β-alanine. Conductometric results supporting the absorption studies have also been included. Moreover polarographic method could not be used due to the irreversible nature of the reduction of nickel complex at the dropping mercury electrode.

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[1]) W. J. Crewther, Australien J. biol. Chem. 6, 597 (1953); see also L. Hellerman and C. C. Stock, J. Amer. chem. Soc. 58, 2654 (1936).

[2]) Salahuddin and Wahid Uddin Malik, J. Indian. Chem. Soc. 40, 703 (1963).

[3]) M. S. N. Rao, J. Amer. chem. Soc. 84, 1788 (1962).

[4]) R. B. Martin, M. Chemberlin and J. T. Edsall, ibid 82, 495 (1960).

[5]) A. Albert, Biochem. J. 47, 531 (1950); ibid. 50, 690 (1952).

[6]) C. B. Monk, Trans. Faraday Soc. 47, 297 (1951).

[7]) A. R. Mannyak, C. B. Murphy and A. E. Martall, Arch. Biochem. 59, 373 (1955).

[8]) N. Bjerrum, Metal Ammine Formation in Aqueous Solution, P. Haase and Son, 1957.

Experimental

Preparation of Solution: Potassium nitrate (A. R.) and nickel nitrate (B. D. H.) were dissolved in all glass double distilled water to prepare their respective stock solutions. The nickel content was determined gravimetrically[9]) by precipitating the metal with alcoholic solution of dimethylglyoxime. Stock solution of 2-Aminoethane sulfonic acid (taurine) was prepared by dissolving the pure and dry [dried for 1 hour at 120 °C before weighing] sample obtained from Eastman Organic Chemicals, U.S.A., in conductivity water. Corbonate-free sodium hydroxide solution was made from A. R. quality of the salt. Nitric acid was. c. p. grade.

pH measurements were carried out by means of Beckman pH meter Model G, using glass electrodes.

Measurement of Conductances: The conductivity of the solutions was measured by the help of Cambridge conductivity bridge with Visual indicator employing platinised cambridge electrodes at 30°C,

Light absorption measurement: Optical density of the solution was determined by means of Bausch and Lomb Spectronic 20, Colorimeter using matched test tubes having internal diameter, 11.7 mm.

Results and Discussion

Experiments performed at different wave-lengths with nickel nitrate solution of varying concentrations show that (i) nickel ion absorbs maximum light in the vicinity of 700 mμ and (ii) that LAMBERT-BEER's Law holds good throughout the entire range of metal ion concentration (0.02 M. to 0.1 M) used in these investigations. Mixtures containing nickel nitrate and taurine were prepared in accordance with "JOBS Method of continous variations"[10]) at four different concentration ranging from 0.02 M to 0.1 M keeping the total volume 10 ml in each case and their optical densities measured between 600—850 mμ following VOSBURGH and COOPER[11]), in order to know whether one or more than one complex was formed during the interaction of nickel ion with taurine. These results indicated the formation of only one complex. Similar set of nickel nitrate solution without taurine was also studied. The optical density of the mixture was greater than that of the corresponding nickel nitrate solution in each case. The difference in optical densities of the mixture and metal ion solution was plotted against the increasing concentration of the metal ion as shown in Fig. 1 which, however, shows the observation only at two concentrations viz; 0.05 M and 0.1 M (results at other concentration lead to the same conclusion and were, therefore, omitted) and at two wave lengths, 675 mμ and 700 mμ. Since the nickel complex absorps light near 700 mμ the choice of this wave length was

[9]) W. W. SCOTT, "Standard Methods of Chemical Analysis" Ed. H. Furman, D. van Noxtraned So., Inc. New York, 1945, Vol. 1, p 619.

[10]) P. JOB, Ann. Chim. 9 (10), 113 (1928).

[11]) W. C. VOSBURGH and G. R. COOPER, J. Amer. chem. Soc. 63, 437 (1941).

made for further absorption studies. In order to apply modified Molar ratio method[12]), solutions containing nickel and taurine in the ratios, 1:0.25, 1:0.4, 1:0,8, 1:1 etc. were taken at two metal ion concentrations ($1 \cdot 10^{-1}$M $2 \cdot 10^{-2}$ M) and at a fixed ionic strength, μ of 0.1 (potassium nitrate was used to get the desired ionic strength), and their optical densities measured (Fig. 2). Conductivities of these solutions were also measured and the results are depicted in Fig. 3. Furthermore an attempt was also made to investigate nickel-taurine interaction by means of slope Ratio Method of HARVEY and MANNING[12]), which, however, failed to provide any definite information.

Fig. 1. Xml Ni^{++} added to (lo—x) ml of equimolar taurine → Nickel complex with taurine; Curves I and II for O-IM and Curves III and IV for 0.05 M solutions of the reactants, pH 5-6

Since the nickel ion binding to taurine was to be studied at different pHs and in unbuffered medium varrying concentrations of CO_2 free sodium hydroxide or nitric acid were added to change the pH of the solution ($0 \cdot 015$ M Ni^{++} and 0.03 M taurine at $\mu = 0.10$) in the pH range 2.7—8. The optical densities of these solutions were measured at different wave-lengths 600 to 900 mμ) as given in the Fig. 4. The pH at which the precipitation of nickel hydroxide took place was determined under the experimental condition ($\mu = 0.1$) and it was interesting to note that this pH viz; 6.4 was modified to pH 7 in presence of taurine.

The marked increase in absorbance of nickel nitrate solution in presence of taurine can only be ascribed to the uptake of the metal ion by the acid. Furthermore, this also accounts the observed increase in the pH of the onset of precipitation of metal ion (0.015 M) from 6.4 to 7.0 (taurine competes with OH^- in interacting with nickel ion).

Light absorption measurements carried out according to JOB's method at different metal ion concentrations (0.1 M and 0.05 M) and at two wave-lengths, viz; 675 mμ and 700 mμ, show, invariably distinct maxima in the curves A, B, C and D (Fig. 1) at points where the metal: acid ratio is almost 1:2 (1:2.3 in most of the cases). Spectrophotometric as well as conductrometric results obtained with the mixture of the reactants at different molar ratios
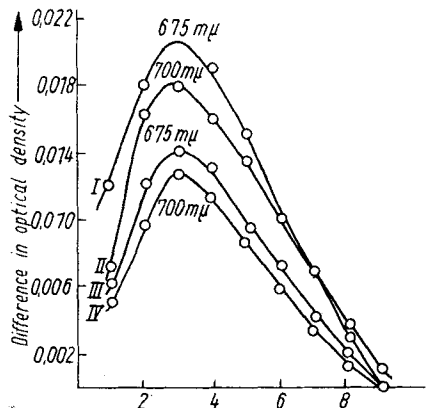
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12) A. E. HARVAY and D. L. MANNING, ibid. 72, 4488 (1950).

also supports this viewpoint. From Figs. 2 and 3 it is evident that well defined breaks in the curves occur in each case only where nickel taurine ratio is nearly 1:2. However, experimental results depicted in Fig. 2 could
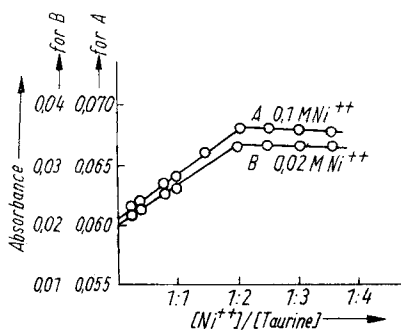

Fig. 2. Modified Molar Ratio Method: Absorption spectra of Nickelt-taurine complex at 700 mu, pH 5.6, ionic strength = 0.10
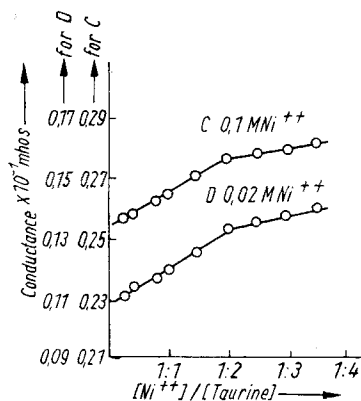

Fig. 3. Conductometric titration of nickel taurine co mixtures at pH = 5.6

not be used in determining the instability constant of the complex since the value of maximum absorbance with increase in taurine concentration did not exhibit constancy. In fact an increase 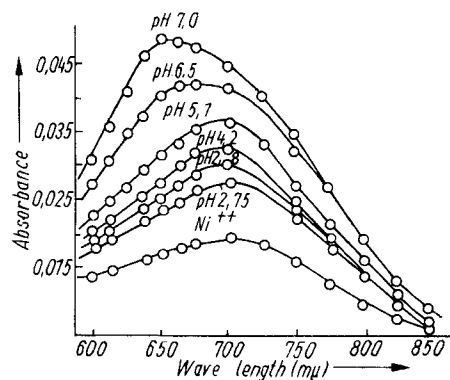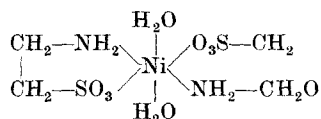in optical density followed by a detectable decrease was noticed (Fig. 2) and the curves were not parallel to the molar ratio-axis as found by HARVEY and MANNING during their studies on iron-tiron complex [12]. Furthermore, a three fold increase in the total ionic strength could not greatly modify the shapes of these curves.

Fig 4. Absorption spectra of Nickel-taurine complex at different pH values; Ni(No₃)₂ 0.015M, taurine 0.03M; total ionic strengh = 0.10

Effect of pH: Although extensive studies regarding the electrochemical properties of taurine showing conclusively its zwitterionic character ($NH_3^+CH_2CH_2SO_3^-$) have been described by KING [13], considerable uncertainty axists about the pK value of its sulphonic group. However, KING [12], found that the pK value was greater than unity and that the value of the second disso-

[13] E. J. KING, ibid. **75**, 2204 (1953).

ciation constant was $8{,}69 \cdot 10^{-10}$ at 25°C. During the present spectro-
photometric investigation it was observed that the optical density of the
mixture containing 0.015 M $Ni^{+\cdot}$ and 0.03 M taurine at u $= 0.1$, was very
slightly increased (0.007 units of optical density) even with nearly two fold
increase in pH (from 2.7 to 5.1) and that the position of the absorption
maxima remains unaltered (near 700 mμ Fig. 4). This was due to the fact
that almost all sulphonic groups would undergo deprotonation in the
neighbourhood of pH 2 making themselves available for binding nickel ions
and increase in pH from 2.7 to 5.1 would, therefore, have no influence. But
when pH exceeded 6 the maxima shifted to shorter wave lengths till at pH 7
it occured near 650 mμ characteristic of the interaction of nickel with both
the oxygen and nitrogen atoms of taurine simaltaneously as found by sepa-
rate absorption experiment on nickel glycine-complex in which it has been
suggested that nickel enters into combination with two oxygen atoms (of
COOH groups and two nitrogen atoms (of aminogroups)[14]. Hence the pos-
sible structure may be as follows:

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\begin{array}{ccc}
 & H_2O & \\
CH_2\!-\!NH_2\!\diagdown & | & \diagup O_3S\!-\!CH_2 \\
 & \!\!Ni\!\!\diagup\diagdown & \\
CH_2\!-\!SO_3\diagup & | & \diagdown NH_2\!-\!CH_2O \\
 & H_2O & \\
\end{array}
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[14] J. B. NEILANDS and P. K. STUMPHS, "Outlines of Enzyme Chemistry". John Wiley
and Sons Inc., New York, 1958, p 34.

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