Study Of Ni(II)-G Lycaminamide Complex Formation by Spectrophotometric Method in Various Temperatures and pH=4.0, I=0.5

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Abstract: The formation constants of Ni(II)-glycinamide system were determined in buffer solution, pH=4.0 (I=0.5mol L⁻¹) in NaClO₄ at 10.0, 15.0, 20.0, 25.0, 30.0°C) using UV-Visible spectrophotometric method. The optical absorption spectra of Ni(II)-glycinamide system were analyzed in order to obtain formation constants and stoichiometries based on SQUAD software. Determining the formation constants at various temperatures enabled us to calculate some thermodynamic parameters as K, ΔG°, ΔH° and ΔS° related to the considered complexes.

Key words: Glycinamide • SQUAD • Optical absorption • Formation constants • Thermodynamic parameters

INTRODUCTION

The metal coordination in metal amino acid complexes has received much attention because they are simple systems for studying the coordination of environment of metal -ions in metal oproteins [1-6]. Many 1:1or 1:2 complexes between nickel(II) and amino acids have been reported in the last two decades, most of them being either mononuclear structures [7-16]. Amide bonds or groups provide the linkage between adjacent amino acid residues in proteins [17-24]. An amide group offers two potential donor atoms, the carbonyl amide oxygen and nitrogen, for complexation of protons and metal ions [25-30]. Peptide bonds in living systems are formed by condensation of an amino group of one amino acid with an activated ester of another with elimination of an alcohol [31-34]. Nickel is an essential element for many bacteria. Although a nickel deficiency disease for nickel in humans has not been identified, there is substantial evidence for the essential status of nickel. Also, under some circumstances nickel compounds are potent human carcinogens as reported from International Agency for Research on Cancer [35-37].

This paper reports the interaction of Ni(NO₃)₂, with glycaminamide (I: ionic strength =0.5molL⁻¹ in NaClO₄) at various temperatures using spectrophotometry by UV -Visible absorption spectroscopy. The binding constants were determined by analyzing the optical absorption spectra of complexes at various glycaminamide concentrations, which were then analyzed using the SQUAD software (38). In particular, we determined the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the binding of mentioned complexes to glycaminamide. Comparison of thermodynamic data leads us to understand the mechanism of interaction between Ni(II) and glycaminamide.

MATERIALS AND METHODS

Materials: Ni(NO₃)₂. 6H₂O, nickel nitrate hexahydrate (Merk), HCl, hydrochloric acid (Merk), C₂H₃O₂K, potassium hydrogen phthalate, (Merk), sodium perchlorate, NaClO₄, (Merk), glyc glycaminamide hydrochloride, H₂N-CH₂-CO-NH₂HCl, (Fulka) were used without further purification. In all experiments double -distilled water with special conductivity has been used equal to (1.3±0.1) μs cm⁻¹.

Apparatus: Absorbance measurements were performed on a spectrophotometer special model Camspec M350 UV-Visible double beam spectrophotometer by using a 4cm optical-pathway quartz cell with a thermostat controlling the cell compartment temperature by precision of ±0.1°C.

Methods: All experiments were carried out in double distilled water at pH=4.0 potassium hydrogen phthalate (0.45M) hydrochloric acid buffer and 0.5M NaClO₄. In all experiments, the complex solutions were freshly prepared before spectral analysis. In typical experiment, 2mL of a

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Ni(NO₃)₂ solution (0.03M) in 0.5 M NaClO₄ (ionic strength) was titrated with by glycaminide (0.24M) solution. UV-Vis spectra of combinations were recorded in range of 200-800nm in 10 minutes after adding 50µL of the glycaminide solution. About 50 wavelengths showing suitable variations by adding glycaminide solution were chosen and their absorbance was recorded.

RESULTS AND DISCUSSION

Absorption Spectroscopy and SQUAD Software Analysis: Figure 1 show a typical set of spectra of Ni(NO₃)₂ upon increasing addition of glycaminide concentration at 25.0°C. The observed spectral changes were used for determining the equilibrium combining constants due to by using SQUAD program which was developed to empower the evaluation of the best equilibrium constants due to absorbance measurements by using a non-linear least-square method [39, 40]. The input data consist of L (a) the absorbance values(b) the total glycaminide and (c) Ni(NO₃)₂ concentrations. The Gauss-Newton non-linear least-squares algorithm is used for making minimum total residual squares, calculating of eq. no.1.

$$U = \sum_{i=1}^{I} \sum_{k=1}^{NW} \left( A_{i,k}^{exp} - A_{i,k}^{the}\right)^2$$

Where $A_{i,k}$ is the absorbance value of ith solution at kth wavelength, given a total of I solutions and a grand total of NW wavelength (in our experiments I=15 and NW=50). The output data are the logarithm of macroscopic binding constant ($K_{eq}$) for formation of Ni₃Ga₃, where Ni is Ni(NO₃)₂, and Ga is glycaminide corresponds to the following equilibrium:

$$iNi + jGa \leftrightarrow Ni_{i}Ga_{j}$$

The values of U and percent error represent uncertainty for log$K_{eq}$ calculating of program. The absorption data were analyzed by assuming 1:1 or 2:1 and/or simultaneous 1:1 and 2:1 molar ratios of Ni(NO₃)₂ to glycaminide. Fitting of the experimental data (15 points), to the proposed stoichiometric models was evaluated by the sum of squares of the calculated points by the model. The results show that the most significant solution corresponded to 1:1 and 2:1 complexation models for the range of studied temperatures with a total residual squares and range of U between 10-3and 10-4.

![Fig. 1: The titration absorption spectra of Ni(NO₃)₂ (0.03M) by Ga (0.24M) in NaClO₄ 0.5M at 298K](image)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>log $K_1$ (M⁻¹)</th>
<th>ΔGᵢ¹ (kJ mol⁻¹)</th>
<th>ΔHᵢ¹ (kJ mol⁻¹)</th>
<th>ΔSᵢ¹ (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
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<td>0.44</td>
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<td>410.1</td>
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<tr>
<td>288</td>
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<td>1462.2</td>
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<tr>
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<tr>
<td>303</td>
<td>5.43</td>
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<tr>
<th>T (K)</th>
<th>log $K_2$ (M⁻¹)</th>
<th>ΔGᵢ² (kJ mol⁻¹)</th>
<th>ΔHᵢ² (kJ mol⁻¹)</th>
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Table 3: Thermodynamic parameters and binding constants for binding of Ni(NO₃)₂ to Glycinamide

<table>
<thead>
<tr>
<th>T (K)</th>
<th>log β (M⁻¹)</th>
<th>ΔGᵦ (kJ mol⁻¹)</th>
<th>ΔHᵦ (kJ mol⁻¹)</th>
<th>ΔSᵦ (J mol⁻¹ K⁻¹)</th>
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<td>326.8</td>
<td>1241.3</td>
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</table>

Fig. 2: The vant’ Hoff plot of Ga to Ni(NO₃)₂

The combining constants are given in Table (1-3). As it can be seen in this table, The equilibrium constants increase with increasing temperatures.

**Thermodynamics of Ni²⁺-Glycinamide Binding Process:**

A prerequisite for a deeper insight of the molecular basis of Ni(NO₃)₂-glycinamide interactions is the characterization of the energetic governing complex formation. The energetic of Ni(NO₃)₂-glycinamide equilibrium can be conveniently characterized by thermodynamic parameters such as standard Gibbs energy, ΔGᵦ, standard molar enthalpy change, (ΔHᵦ) and standard molar entropy change, ΔSᵦ. The standard Gibbs energy change is usually calculated due to equilibrium constant (K) of the reaction, by the following relationship.

\[ ΔGᵦ = -RT \ln K \]  \hspace{1cm} (3)

Where R and T are the gas constant and the absolute temperature, respectively. Since the activity coefficients of the reactions are not known, the usual procedure is to assume them to be unity and use the equilibrium concentrations instead of the activity. Therefore, it will be appropriate to adjust the terminology of apparent equilibrium constant K' and Gibbs energy ΔG'ᵦ. Apparent standard molar enthalpies can be obtained from the temperature dependence of K' using the vant Hoff equation.

\[ d \ln K' = -\left( \frac{ΔH'ᵦ}{R} \right) d(1/T) \] \hspace{1cm} (4)

This is the so-called vant Hoff enthalpy. The apparent standard entropy change, ΔS'ᵦ, can be derived from the Eq. (5).

\[ ΔS'ᵦ = \left( ΔH'ᵦ - ΔG'ᵦ \right) / T \] \hspace{1cm} (5)

The vant Hoff plot for interaction of Ni(NO₃)₂ complexes with glycinamide are shown in Figures 2, 3. The calculated thermodynamic parameters for binding of Ni(NO₃)₂ to glycinamide are listed in Tables 1-3.

**CONCLUSION**

Our results have demonstrated that the stoichiometry of glycinamide-Ni(NO₃)₂ complexes are 1:1 and 2:1. Shaping these combinations in our results is increased entropy (ΔSₒ>0). Shaping constants are as magnitude in a satisfactory way concluding relative stability of studied complexes (ΔGₒ<0).

**ACKNOWLEDGEMENTS**

We are grateful to Islamic Azad University, Varamin (Pishva) branch and Islamic Azad University Science and Research branch, for their financial support.
REFERENCES