Study of Ni(II)-glycinamide complex formation by spectrophotometric method at various temperatures with pH=4.0 and I=0.2

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ABSTRACT

The formation constants of Ni(II)-glycinamide system were determined in buffer solution, pH=4.0 (I=0.2 mol 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, ΔG⁰, ΔH⁰ and ΔS⁰ related to the considered complexes.

Key words: Glycinamide, SQUAD, Optical absorption, Formation constants, Thermodynamic parameters.

INTRODUCTION

Nickel is an essential element for many archa, bacteria and plants and may yet be found to play a role in the metabolism of higher organisms¹⁶. Ni(II) crosses cell membranes via calcium channel and probably competes with Ca²⁺ for specific intracellular receptors⁷⁻¹⁶. The transition metal complexes formed with amide ligands have attracted much interest over the past decade because of their important role in various industrial and biological processes. Copper and nickel amide complexes are used in enantioselective catalysis¹⁷⁻²⁴ and metal ion therapeutics²⁵⁻³⁰. Studies of complexes with amide moieties are also of fundamental interest in order to understand the role of metalloproteins in the control of cell metabolism³¹⁻³⁴. In most complexes, amino acids behave as bidentate ligands through NH₂ and COO⁻ ends³⁵⁻³⁷. This paper reports the interaction of Ni(NO₃)₂ with glycinamide (I=0.2molL⁻¹ in NaClO₄) at various temperatures using Uv-Visible absorption technique. The binding constants were determined by analyzing optical absorption spectra of complexes at various glycinamide concentrations using SQUAD software³⁸. In particular, we determined the standard free energy (ΔG⁰), enthalpy(ΔH⁰) and entropy(ΔS⁰) for the binding of mentioned complexes to glycinamide. Comparison of thermodynamic data leads us to understand the mechanism of interaction.

EXPERIMENTAL

Materials

Ni(NO₃)₂•6H₂O, nickel nitrate hexahydrate (Merck), HCl, hydrochloric acid (Merck), C₈H₅O₄K, potassium hydrogen phthalate, (Merck), sodium perchlorate, NaClO₄, (Merck), glycinamide hydrochloride, H₂N-CH₂-CONH₂·HCl, (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 taken on a spectrophotometer special model Camspec M350 UV-Visible double beam 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, hydrochloric acid buffer and 0.2M NaClO₄. In all experiments, the complex solutions were freshly prepared before spectral analysis. In typical experiment, 2ml of Ni(NO₃)₂ solution 0.03M in 0.2M NaClO₄ (ionic strength) was titrated by glycinamide 0.24M solution. UV-Vis spectra of combinations were recorded in range of 200-800nm in 10 minutes after adding 50µl glycinamide solution. About 15 adds were taken place. About 50 wavelengths showing suitable variations by adding glycinamide solution were chosen and their absorbance rate was recorded.

**RESULTS AND DISCUSSION**

**Absorption spectroscopy and SQUAD software analysis**

The figures (1-5) show typical titration spectras of Ni(NO₃)₂ upon increasing addition of glycinamide at 10.0, 15.0, 20.0, 25.0, 30.0°C. The observed spectral changes were used for determining the combining constants due to by using SQUAD program which was developed to empower the evaluation of the best combining constants due to absorbance measurements by using a non-linear least-square method³⁹,⁴⁰. The input data consist of (a) the absorbance values (b) the total glycinamide and 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.

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

Where $A_{i,k}$ is the absorbance value of ith solution at kth wavelength, give atotal 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 ($K_{ij}$) for formation of NiGa, where Ni is Ni(NO₃)₂ and Ga is glycinamide corresponds to the following equilibrium.

$$i\text{Ni} + j\text{Ga} \leftrightarrow i\text{NiGa}_j$$  ...(3)

The values of U and percent of error represent uncertainty for logK, 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 glycinamide. 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 suitable case is corresponded to 1:1 and 2:1 combining models at range of studied temperatures with total residual squares, and range of U was between $10^{-3}$ and $10^{-4}$. The combining constants are given in table (1, 2, 3). As it can be seen in this table, the combining constants are increased by increasing temperatures. It can be described as an increase of complex stability which results in higher values of combining constants.

A prerequisite for a deeper insight in to the molecular basis of Ni(NO₃)₂-glycinamide interactions is thorough 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, $\Delta G^\circ$, standard molar enthalpy change, $\Delta H^\circ$ and standard molar entropy change, $\Delta S^\circ$. The standard Gibbs energy change is usually calculated due to equilibrium constant (K) of the reaction, by the following relationship

$$\Delta G^\circ = -RT\ln K$$  ...(2)

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 unity and to 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 $\Delta G'^\circ$. Apparent standard enthalpies per mole in unique unit can be obtained due to depending on temperature of the apparent combining constant $K'$, by vant Hoff equation.
Fig. 1: The titration absorption spectra of Ni(NO$_3$)$_2$ (0.03M) by Ga (0.24M) in NaClO$_4$ 0.2M at 283K

Fig. 2: The titration absorption spectra of Ni(NO$_3$)$_2$ (0.03M) by Ga (0.24M) in NaClO$_4$ 0.2M at 288K

Fig. 3: The titration absorption spectra of Ni(NO$_3$)$_2$ (0.03M) by Ga (0.24M) in NaClO$_4$ 0.2M at 293K
Fig. 4: The titration absorption spectra of Ni(NO$_3$)$_2$ (0.03M) by Ga (0.24M) in NaClO$_4$ 0.2M at 298K

Fig. 5: The titration absorption spectra of Ni(NO$_3$)$_2$ (0.03M) by Ga (0.24M) in NaClO$_4$ 0.2M at 303K

Fig. 6: The vant’t Hoff plot of Ga to Ni(NO$_3$)$_2$

$$y = -10700x + 39.363$$

$$R^2 = 0.9999$$

Fig. 7: The vant’t Hoff plot of Ga to Ni(NO$_3$)$_2$

$$y = -16683x + 62.453$$

$$R^2 = 0.9915$$
Table 1: Thermodynamic parameters and binding constants for binding of Ni(NO$_3$)$_2$ to Glycinamide

<table>
<thead>
<tr>
<th>T (K)</th>
<th>log $K_1$ (M$^{-1}$)</th>
<th>$\Delta G_1^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_1^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_1^0$ (J mol$^{-1}$ K$^{-1}$)</th>
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<tbody>
<tr>
<td>283</td>
<td>1.60±0.27</td>
<td>-8.7</td>
<td>204.9</td>
<td>754.8</td>
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<tr>
<td>288</td>
<td>2.22±0.39</td>
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<td>204.9</td>
<td>753.8</td>
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<tr>
<td>293</td>
<td>2.88±0.69</td>
<td>-16.2</td>
<td>204.9</td>
<td>754.6</td>
</tr>
<tr>
<td>298</td>
<td>3.52±0.88</td>
<td>-20.1</td>
<td>204.9</td>
<td>755.0</td>
</tr>
<tr>
<td>303</td>
<td>4.05</td>
<td>-23.5</td>
<td>204.9</td>
<td>753.8</td>
</tr>
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Table 2: Thermodynamic parameters and binding constants for binding of Ni(NO$_3$)$_2$ to Glycinamide

<table>
<thead>
<tr>
<th>T (K)</th>
<th>log $K_2$ (M$^{-1}$)</th>
<th>$\Delta G_2^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_2^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_2^0$ (J mol$^{-1}$ K$^{-1}$)</th>
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<tr>
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<td>303</td>
<td>3.34</td>
<td>-19.4</td>
<td>114.5</td>
<td>441.9</td>
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</table>

Table 3: Thermodynamic parameters and binding constants for binding of Ni(NO$_3$)$_2$ to Glycinamide

<table>
<thead>
<tr>
<th>T (K)</th>
<th>log $\beta$ (M$^{-1}$)</th>
<th>$\Delta G_1^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_1^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_1^0$ (J mol$^{-1}$ K$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>283</td>
<td>3.38±0.5</td>
<td>-18.3</td>
<td>319.4</td>
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<td>4.68±0.41</td>
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<td>-32.9</td>
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<tr>
<td>298</td>
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<td>-36.1</td>
<td>319.4</td>
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<td>303</td>
<td>7.39</td>
<td>-42.9</td>
<td>319.4</td>
<td>1195.7</td>
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\[
d \ln K' = -\left(\frac{\Delta H^0}{R}\right)d\left(\frac{1}{T}\right)\] \tag{4}

This is the so-called vant Hoff enthalpy. The apparent standard entropy change, $\Delta S^0$, can be derived from the Eq(5).

\[
\Delta S^0 = \left(\frac{\Delta H^0}{T} - \Delta C^p^0\right)/T \] \tag{5}

The vant Hoff plot for interaction of Ni(NO$_3$)$_2$ complexes with glycinamide are shown in Fig. (6, 7). The calculated thermodynamic parameters for binding of Ni(NO$_3$)$_2$ to glycinamide are listed in table (1, 2, 3).

CONCLUSION

In respect to our results, the stoichiometry of glycinamide-Ni(NO$_3$)$_2$ combining are as 1:1 and 2:1. Shaping these combinations in our results is increased entropy ($\Delta S^0$>0). Shaping constants are as magnitude in a satisfactory way concluding relative stability of studied complexes ($\Delta G^0$<0).
ACKNOWLEDGEMENTS

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REFERENCES