

Spectrophotometric Study of Ni(II)-Glycinamide Complex Formation

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The formation constants of Ni(II)-glycinamide system were determined in buffer solution, pH 4.0 ($I = 0.1 \text{ mol L}^{-1}$ in NaClO_4 at 5, 10, 15, 20, 25, 30 °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. Determination of the formation constants at various temperatures enabled us to calculate some thermodynamic parameters as K , ΔG° , ΔH° and ΔS° related to Ni(II)-glycinamide complex.

Key Words: Nickel(II), Glycinamide, SQUAD, Optical absorption, Formation constants, Thermodynamic parameters.

INTRODUCTION

Nickel is an essential element for many archea, bacteria and plants and may yet be found to play a role in the metabolism of higher organisms¹⁻⁶. Ni(II) crosses cell membranes *via* calcium channel and probably competes with Ca^{2+} for specific intracellular receptors⁷⁻¹⁵. 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 catalysis¹⁶⁻²³ and metal ion therapeutics²⁴⁻²⁹. Studies of complexes with amide moieties are also of fundamental interest in order to understand the role of metalloproteins in the control of cell metabolism³⁰⁻³³. In most complexes, amino acids behave as bidentate ligands coordinated through NH_2 and COO^- ends³⁴⁻³⁶. This paper reports the interaction of $\text{Ni}(\text{NO}_3)_2$ with glycinamide ($I = 0.1 \text{ mol L}^{-1}$ in NaClO_4) 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 software³⁷. In particular, we determined the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the binding of mentioned complexes to glycinamide. Comparison of thermodynamic data leads us to understand the mechanism of interaction.

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EXPERIMENTAL

Nickel nitrate hexahydrate (Merck), hydrochloric acid (Merck), potassium hydrogen phthalate (Merck), sodium perchlorate (Merck), glycineamide hydrochloride, $\text{H}_2\text{N}-\text{CH}_2-\text{CONH}_2\cdot\text{HCl}$ (Fluka) were used without further purification.

In all experiments, double distilled water with special conductivity has been used equal to $(1.3 \pm 0.1) \mu\text{s cm}^{-1}$.

Absorbance measurements were taken on a spectrophotometer special model CamSpec M350 UV-visible double beam by using a 4 cm optical-pathway quartz cell with a thermostat controlling the cell compartment temperature by precision of $\pm 0.1 \text{ }^\circ\text{C}$.

Methods: All experiments were carried out in double distilled water at pH 4 potassium hydrogen phthalate, hydrochloric acid buffer and 0.1 M NaClO_4 . In all experiments, the complex solutions were freshly prepared before spectral analysis. In typical experiment, 2 mL of $\text{Ni}(\text{NO}_3)_2$ solution 0.03 M in 0.1 M NaClO_4 (ionic strength) was titrated by glycineamide 0.24 M solution. UV-Vis spectra of combinations were recorded in range of 200-800 nm in 10 min after adding 50 μL glycineamide hydrochloride solution were taken place *ca.* 50 nm wavelengths showing suitable variations by adding glycineamide solution were chosen and their absorbance rate was recorded.

RESULTS AND DISCUSSION

Absorption spectroscopy and SQUAD software analysis: Fig. 1 shows typical titration spectra of $\text{Ni}(\text{NO}_3)_2$ upon increasing addition of glycineamide at 25 $^\circ\text{C}$. 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 method^{34,35}. The input data consist of (a) the absorbance values (b) the total glycineamide and $\text{Ni}(\text{NO}_3)_2$ concentrations. The Gauss-Newton non-linear least-squares algorithm is used for making minimum total residual squares, calculating of eqn. 1.

$$U = \sum_{i=1}^I \sum_{k=1}^{NW} (A_{i,k}^{\text{cal}} - A_{i,k}^{\text{obs}})^2 \quad (1)$$

where $A_{i,k}$ is the absorbance value of *i*th solution at *k*th wavelength, give 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 ($K_{i,j}$) for formation of Ni_iGa_j , where *Ni* is $\text{Ni}(\text{NO}_3)_2$ and *Ga* is glycineamide corresponds to the following equilibrium.



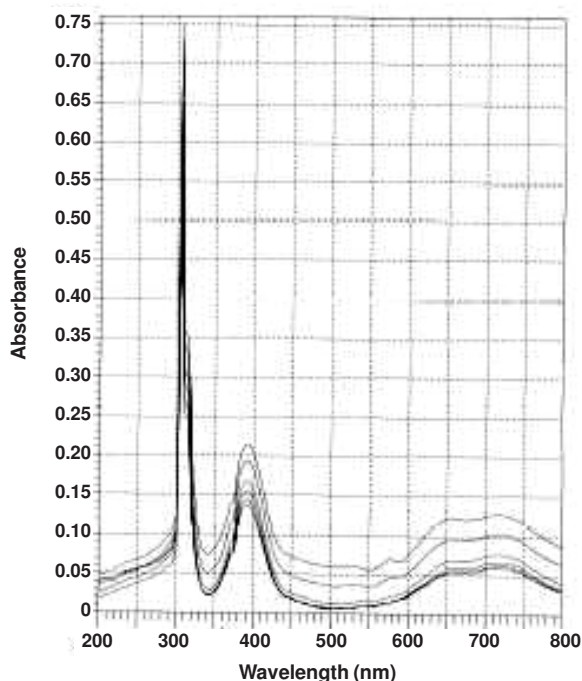


Fig. 1. Titration absorption spectra of Ni(NO₃)₂ (0.03 M) by glycinamide (0.24 M) in NaClO₄ 0.1 M at 298 K

The values of U and per cent of error represent uncertainty for $\log K_{ij}$ 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 Tables 1-3. 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.

TABLE-1
THERMODYNAMIC PARAMETERS AND BINDING
CONSTANTS FOR BINDING OF Ni(NO₃)₂ TO GLYCINAMIDE

Temp. (K)	$\log K_1 (M^{-1})$	$\Delta G_1^\circ (kJ mol^{-1})$	$\Delta H_1^\circ (kJ mol^{-1})$	$\Delta S_1^\circ (J mol^{-1} K^{-1})$
278	0.52 ± 0.29	-2.8	263.9	959.4
283	1.25 ± 0.17	-6.8	263.9	956.5
288	1.95 ± 0.18	-10.8	263.9	953.8
293	2.62 ± 0.15	-14.7	263.9	950.9
298	3.63	-20.7	263.9	955.0
303	4.58 ± 0.04	-26.6	263.9	958.7

TABLE-2
THERMODYNAMIC PARAMETERS AND BINDING
CONSTANTS FOR BINDING OF Ni(NO₃)₂ TO GLYCINAMIDE

Temp. (K)	log β (M ⁻¹)	ΔG _T ^o (kJ mol ⁻¹)	ΔH _T ^o (kJ mol ⁻¹)	ΔS _T ^o (J mol ⁻¹ K ⁻¹)
278	2.42	-12.9	353.8	1319.0
283	4.24 ± 0.49	-23.0	353.8	1331.4
288	4.55 ± 0.98	-25.1	353.8	1315.6
293	5.03 ± 0.76	-28.2	353.8	1303.8
298	6.9	-39.4	353.8	1319.5
303	8.42 ± 0.10	-48.8	353.8	1328.7

TABLE-3
THERMODYNAMIC PARAMETERS AND BINDING
CONSTANTS FOR BINDING OF Ni(NO₃)₂ TO GLYCINAMIDE

Temp. (K)	log K ₂ (M ⁻¹)	ΔG ₂ ^o (kJ mol ⁻¹)	ΔH ₂ ^o (kJ mol ⁻¹)	ΔS ₂ ^o (J mol ⁻¹ K ⁻¹)
278	1.9	-10.1	90.0	360.0
283	3.0	-16.3	90.0	375.6
288	2.6	-14.3	90.0	362.2
293	2.4	-13.5	90.0	353.2
298	3.3	-18.8	90.0	365.1
303	3.8	-22.0	90.0	369.6

Thermodynamics of Ni²⁺-glycinamide binding process: A prerequisite for a deeper insight into 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 (ΔG^o), standard molar enthalpy change, (ΔH^o) and standard molar entropy change (ΔS^o). The standard Gibbs energy change is usually calculated due to equilibrium constant (K) of the reaction, by the following relationship:

$$\Delta G^{\circ} = -RT \ln K \quad (3)$$

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 unity and to use the equilibrium concentrations instead of the activity.

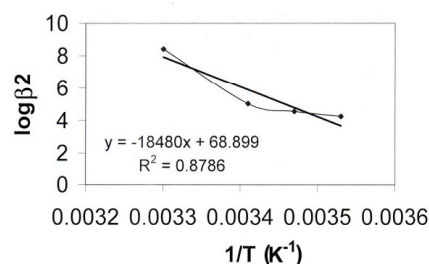
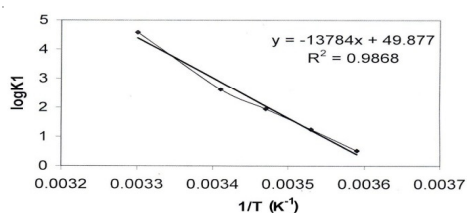
Therefore, it will be appropriate to adjust the terminology of apparent equilibrium constant K' and Gibbs energy ΔG^o. Apparent standard enthalpies per mole in unique unit can be obtained due to depending on temperature of the apparent combining constant K', by vant Hoff equation.

$$d \ln K' = - \left(\frac{\Delta H^{\circ}}{R} \right) d(1/T) \quad (4)$$

This is the so-called vant Hoff enthalpy. The apparent standard entropy change, ΔS^o, can be derived from the eqn. 5.

$$\Delta S^{\circ} = \left(\Delta H^{\circ} - \Delta G^{\circ} \right) / T \quad (5)$$

The vant Hoff plots for interaction of Ni(NO₃)₂ complexes with glycinamide are shown in Figs. 2 and 3. The calculated thermodynamic parameters for binding of Ni(NO₃)₂ to glycinamide are given in Tables 1-3.

Fig. 2. Vant' Hoff plot of Ga to Ni(NO₃)₂Fig. 3. Vant' Hoff plot of Ga to Ni(NO₃)₂

Conclusion

In respect to present results, the stoichiometry of glycinamide-Ni(NO₃)₂ combining are as 1:1 and 2:1. shaping these combinations in present results is increased entropy ($\Delta S^{\circ} > 0$). shaping constants are as magnitude in a satisfactory way concluding relative stability of studied complexes ($\Delta G^{\circ} < 0$).

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