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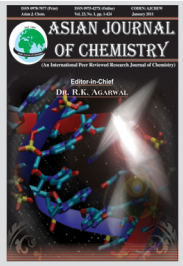

Thermodynamic Study of Zn(II)-Glycinamide Complex Formation by Spectrophotometric Method in Various Temperatures and pH = 4, Ionic Strength = 0.1 mol L^{-1}

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The formation constants of Zn(II)-glycinamide system were determined in buffer solution, pH = 4.0 (I = 0.1 mol L^{-1} in $NaClO_4$ at 10, 15, 20, 25, 30 ºC) using UV-Visible spectrophotometric method. The optical absorption spectra of Zn(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, ΔGº, ΔHº and ΔSº related to the considered complexes.

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

INTRODUCTION

Zinc is a constituent of proteins, peptide and amino acid complexes. The rich structural information on zinc enzymes is unique[1-3]. It has long been known that certain naturally occurring substances (namely amino acids, proteins and porphyrins) form stable complexes with the ions of heavy metals[4-6]. In most combinations, amino acids have a behaviour such as bidentate ligands *via* NH_2 and COO^- ends[7-9]. The metal ions binding by proteins and peptides have basic interests due to the importance of metal ions in biological systems. Metals function probably as a part of active sites of enzymes and while stabilizing macromolecular structure of proteins and affecting enzymes or membranes to control cell metabolism[10]. This paper reports the interaction of $Zn(NO_3)_2$ with glycinamide (I = 0.1 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 software[11]. In particular, we determined the standard free energy (ΔGº), enthalpy (ΔHº) and entropy (ΔSº) of the Zn(II)-glycinamide complex.

EXPERIMENTAL

Zinc nitrate hexahydrate (Merck), hydrochloric acid (Merck), potassium hydrogen phthalate, (Merck), sodium perchlorate, (Merck), glycinamide hydrochloride (H_2N-CH_2-$CONH_2$·HCl) (Fulka) were used without further purification.In all experiments double-distillated water with special conductivity has been used equal to (1.3 ± 0.1) μs 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 ± 0.1 ºC.

Methods: All experiments were carried out in double distillated water at pH = 4.0 in presence of 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 $Zn(NO_3)_2$ solution (0.03 M) in 0.1 M $NaClO_4$ (ionic strength) was titrated by glycinamide 0.24 M solution. UV-Vis spectra of combinations were recorded in range of 200-800 nm in 10 min after adding 50 μL 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: Fig. 1 shows typical titration spectra of $Zn(NO_3)_2$ upon increasing addition of glycinamide at 25 ºC. The observed spectral changes were used for determining the combining constants by 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[12]. The input data consist of (a) the absorbance values (b) the total glycinamide and $Zn(NO_3)_2$ concentrations. The Gauss-Newton

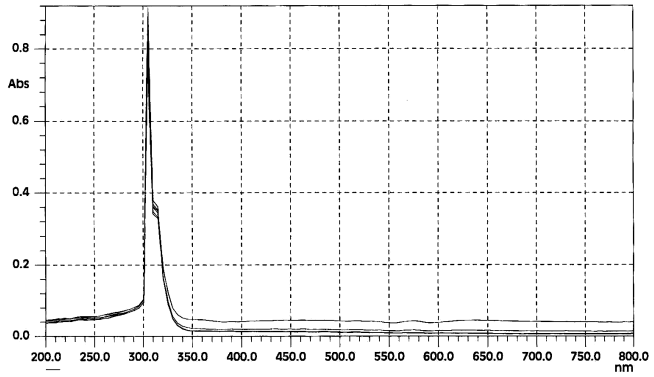

Fig. 1. Titration absorption spectra of $(ZnNO_3)_2$ (0.03 M) by glycinamide (0.24 M) in $NaClO_4$ 0.1 M at 25 ºC

non-linear least-squares algorithmis is used for making minimum total residual squares, calculating of eqn. 1.

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

where $A_{i,k}$ is the absorbance value of ith solution at kth wavelength, give a total of I solutions and a grand total of NW wavelength (in present experiments I = 15 and NW = 50). The output data are the logarithm of macroscopic binding constant ($K_{i,j}$) for formation of Zn_iGa_j, where Zn is $Zn(NO_3)_2$ and Ga is glycinamide corresponds to the following equilibrium.

$$iZn + jGa \leftrightarrow Zn_iGa_j$$

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 $Zn(NO_3)_2$ to glycinamide. Fitting of the experimental data (15 points), to the propsed 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.

Thermodynamics of Zn^{2+}-glycinamide binding process: A prerequisite for a deeper insight in to the molecular basis of $Zn(NO_3)_2$-glycinamide interactions is thorough characterization of the energetic governing complex formation. The energetic of $Zn(NO_3)_2$-glycinamide equilibrium can be conveniently characterized by thermodynamic parameters such as standard Gibbs energy (ΔGº), standard molar enthalpy change (ΔHº) and standard molar entropy change (ΔSº). The standard Gibbs energy change is usually calculated due to equilibrium constant (K) of the reaction, by the following relationship.

$$\Delta G^o = -RT\ln K \quad (3)$$

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.

TABLE-1
THERMODYNAMIC PARAMETERS AND BINDING CONSTANTS FOR BINDING OF $Zn(NO_3)_2$ TO GLYCINAMIDE

T (K)	log K_1 (M^{-1})	ΔG°_1 (kJ mol^{-1})	ΔH°_1 (kJ mol^{-1})	ΔS°_1 (J mol^{-1} K^{-1})
283	1.07 ± 0.25	-5.8	270.1	974.9
288	1.58 ± 0.21	-8.7	270.1	968.1
293	2.24 ± 0.40	-12.6	270.1	964.8
298	3.10 ± 0.38	-17.7	270.1	965.8
303	4.36 ± 0.00	-25.3	270.1	974.9

TABLE-2
THERMODYNAMIC PARAMETERS AND BINDING CONSTANTS FOR BINDING OF $Zn(NO_3)_2$ TO GLYCINAMIDE

T (K)	log β (M^{-1})	ΔG°_T (kJ mol^{-1})	ΔH°_T (kJ mol^{-1})	ΔS°_T (J mol^{-1} K^{-1})
283	3.37 ± 0.15	-18.3	459.0	1686.6
288	4.13 ± 0.79	-22.8	459.0	1672.9
293	6.18 ± 0.42	-34.7	459.0	1685.0
298	7.01 ± 0.39	-40.0	459.0	1674.5
303	8.88 ± 0.00	-51.5	459.0	1684.8

TABLE-3
THERMODYNAMIC PARAMETERS AND BINDING CONSTANTS FOR BINDING OF $Zn(NO_3)_2$ TO GLYCINAMIDE

T (K)	log K_2 (M^{-1})	ΔG°_2 (kJ mol^{-1})	ΔH°_2 (kJ mol^{-1})	ΔS°_2 (J mol^{-1} K^{-1})
283	3.28	-17.8	188.9	730.4
288	3.11	-17.1	188.9	715.3
293	2.75	-15.4	188.9	697.3
298	2.26	-12.9	188.9	677.2
303	2.03	-11.8	188.9	662.4

Therefore, it will be appropriate to adjust the terminology of apparent equilibrium constant K' and Gibbs energy ΔGº'. Apparent standard enthalpies per mole in unique unit can be obtained due to depending on temperature of the apparent combining constant K', by van't Hoff equation.

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

This is the so-called vant Hoff enthalpy. The apparent standard entropy chang, ΔSº', can be derived from the eqn. 5.

$$\Delta S^{o'} = (\Delta H^{o'} - \Delta G^{o'})/T \quad (5)$$

The van't Hoff plots for interaction of $Zn(NO_3)_2$ complexes with glycinamide are shown in Figs. 2 and 3. The calculated thermodynamic parameters for binding of $Zn(NO_3)_2$ to glycinamide are presented in Tables 1-3.

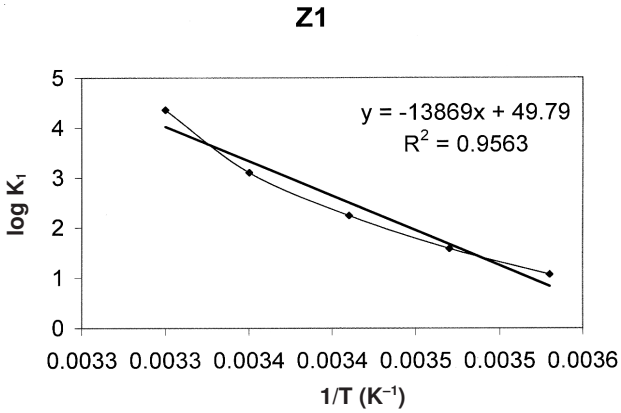

Fig. 2. vant't Hoff plot of glycinamide to $Zn(NO_3)_2$

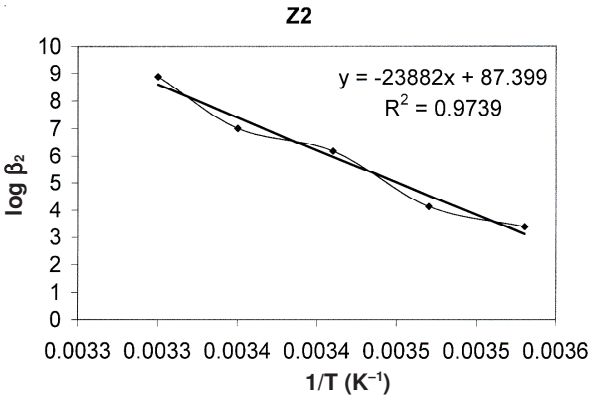

Fig. 3. vant't Hoff plot of glycinamide to $Zn(NO_3)_2$

Conclusion

In respect to present results,the stoichiometry of glycinamide-$Zn(NO_3)_2$ combining are as 1:1 and 2:1. shaping these combinations in our results is increased entropy ($\Delta S^o > 0$). shaping constants are as magnitude in a satisfactory way concluding relative stability of studied complexes ($\Delta G^o < 0$).

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