Spectrophotometric Study of W(VI)-G Lycinamide Complex Formation

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The formation constants of W(VI)-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 ℃) using UV-visible spectrophotometric method. The optical absorption spectra of W(VI)-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 biological importance of tungsten has been fully proved in the last decade due to the isolation of a number of tungsten containing enzymes from hyperthermophilic archaea. Tungsten was previously considered only as an antagonist of molybdenum, because the replacement of molybdenum by tungsten(due to their chemical similarity) leads to inactivation of molybdenum containing enzymes. In addition to the "true W enzymes" in which tungsten cannot be replaced by molybdenum, recently some enzymes have been isolated which can use either molybdenum or tungsten in the catalytic process[1-8]. Metal complexes with amino acids are used as model compounds in the study of the interactions of proteins with metal cations[9-17]. In most complexes, amino acids behave as bidentate ligands through NH$_2$ and COO$^-$ ends[18-30]. Mixed metal complexes play an important role in various biological systems[31-36] and in different field of chemistry[37-40].

This paper reports the interaction of Na$_2$WO$_4$ 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[41]. In particular, we determined the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the binding of tungsten complexes of glycinamide. Comparison of thermodynamic data leads us to understand the mechanism of interaction.

EXPERIMENTAL

Sodium tungstnate dihydrate (Merck), hydrochloric acid (Merck), potassium hydrogen phthalate, (Merck), sodium perchlorate (Merck), glycinamide hydrochloride, H$_2$N-CH$_2$-CONH$_2$·HCl (Fluka) 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 ℃.

Methods: All experiments were carried out in double distilled water at pH = 4.0 potassium hydrogen phthalate, hydrochloric acid buffer and 0.1M NaClO$_4$. In all exreriments, the complex solutions were freshly prepared before spectral analysis. In typical experiment, 2 mL of Na$_2$WO$_4$ solution 0.0003 M in 0.1M NaClO$_4$ (ionic strength) was titrated by glycinamide 0.0024 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 additions 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 show typical titration spectra of Na$_2$WO$_4$ upon increasing addition of glycinamide at 25 ℃. The observed spectral changes were used for determining the combining constants 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[42,43]. The input data consist of (a) the absorbance values (b) the total

glycinamide and Na_2WO_4 concentrations. The Gauss-Newton non-linear least-squares algorithmis is used for making minimum total residual squares by eqn. 1.

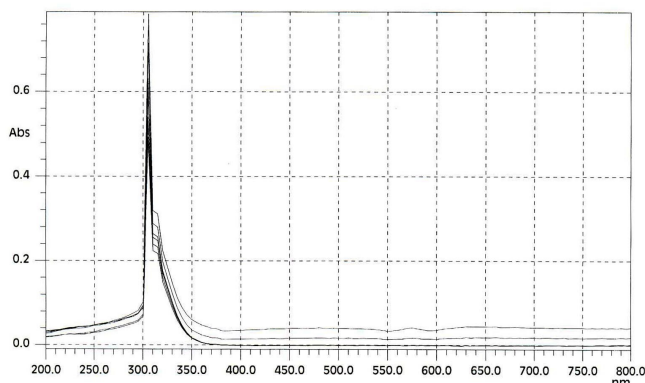Fig. 1.   Titration absorption spectra of Na_2WO_4 (0.0003 M) by Ga (0.0024 M) in $NaClO_4$ 0.1 M at 298 K

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

where $A_{i,k}$ is the absorbance value of ith solution at kth wavelength, give 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 W_iGa_j, where W is Na_2WO_4 and Ga is glycinamide corresponds to the following equilibrium.

$$iW = jGa \leftrightarrow W_iGa_j \qquad (2)$$
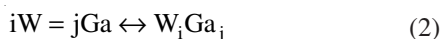
The values of U and per cent of error represent uncertainty for log K_{ij} calculating of program. The absorption data were analyzed by assuming 1:1 or 2:1 and/or simultaneous 1:1 and 2:1 molar ratios of Na_2WO_4 to glycinamide. Fitting of the experimental data (15 points), to the propsed stoichiometric 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 W^{6+}-glycinamide binding process: A prerequisite for a deeper insight in to the molecular basis of Na_2WO_4-glycinamide interactions is thorough characterization of the energetic governing complex formation. The energetic of Na_2WO_4-glycinamide equilibrium can be conveniently characterized by thermodynamic parameters such as standard Gibbs energy ($\Delta G°$), standard molar enthalpy change ($\Delta H°$) and standard molar entropy change ($\Delta S°$). The standard Gibbs energy change is usually calculated due to equilibrium constant (K) of the reaction, by the following relationship

$$\Delta G° = -RT \ln K \qquad (3)$$

TABLE-1
THERMODYNAMIC PARAMETERS AND BINDING
CONSTANTS FOR BINDING OF Na_2WO_4 TO GLYCINAMIDE

T (K)	log K_1 (M^{-1})	$\Delta G°_1$ (kJ mol^{-1})	$\Delta H°_1$ (kJ mol^{-1})	$\Delta S°_1$ (J mol^{-1} K^{-1})
283	1.95	-10.6	219.4	812.7
288	2.59 ± 0.11	-14.3	219.4	811.5
293	3.46 ± 0.21	-19.4	219.4	815.0
298	4.14 ± 0.32	-23.6	219.4	815.4
303	4.53 ± 0.21	-26.3	219.4	810.9

TABLE-2
THERMODYNAMIC PARAMETERS AND BINDING
CONSTANTS FOR BINDING OF Na_2WO_4 TO GLYCINAMIDE

T (K)	log K_2 (M^{-1})	$\Delta G°_2$ (kJ mol^{-1})	$\Delta H°_2$ (kJ mol^{-1})	$\Delta S°_2$ (J mol^{-1} K^{-1})
283	5.58	-30.2	-48.7	-65.4
288	5.49	-30.3	-48.7	-63.9
293	4.96	-27.8	-48.7	-71.3
298	5.06	-28.9	-48.7	-66.4
303	5.02	-29.1	-48.7	-64.7

TABLE-3
THERMODYNAMIC PARAMETERS AND BINDING
CONSTANTS FOR BINDING OF Na_2WO_4 TO GLYCINAMIDE

T (K)	log β (M^{-1})	$\Delta G°_T$ (kJ mol^{-1})	$\Delta H°_T$ (kJ mol^{-1})	$\Delta S°_T$ (J mol^{-1} K^{-1})
283	7.53 ± 0.37	-40.8	170.7	747.3
288	8.08 ± 0.10	-44.6	170.7	747.6
293	8.42 ± 0.66	-47.2	170.7	743.7
298	9.20 ± 0.94	-52.5	170.7	749.0
303	9.55	-55.4	170.7	746.2

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 $\Delta G°'$. Apparent standard enthalpies per mole in unique unit can be obtained on temperature of the apparent combining constant K', by vant Hoff's equation.

$$d \ln K' = -\left(\frac{\Delta H°'}{R}\right) d\left(\frac{1}{T}\right) \qquad (4)$$

This is the so-called vant Hoff enthalpy. The apparent standard entropy chang, $\Delta S°'$, can be derived from the eqn. 5.

$$\Delta S°' = \frac{(\Delta H°' - \Delta G°')}{T} \qquad (5)$$

The vant Hoff plot for interaction of Na_2WO_4 complexes with glycinamide are shown in Figs. 2 and 3. The calculated thermodynamic parameters for binding of Na_2WO_4 to glycinamide are listed in Tables 1-3.

Conclusion

In respect to present results, the stoichiometry of glycinamide-Na_2WO_4 combining are as 1:1 and 2:1. Shaping these combinations in these results is increased entropy ($\Delta S° > 0$). Shaping constants are as magnitude in a satisfactory way concluding relative stability of studied complexes ($\Delta G° < 0$).

W2

$$y = -8916.7x + 38.981$$
$$R^2 = 0.9766$$
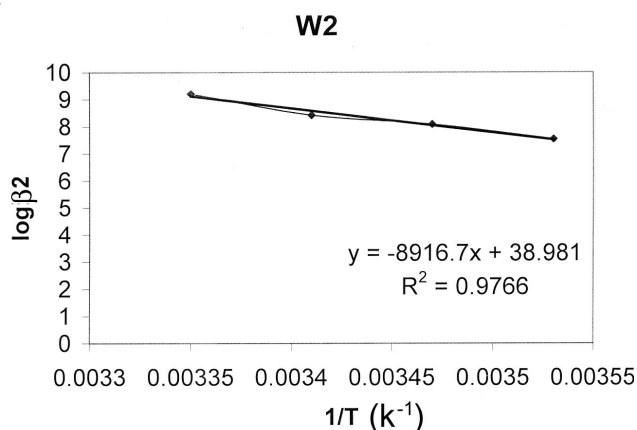
Figs. 2. Vant't Hoff plot of Ga

W1

$$y = -11459x + 42.441$$
$$R^2 = 0.9846$$
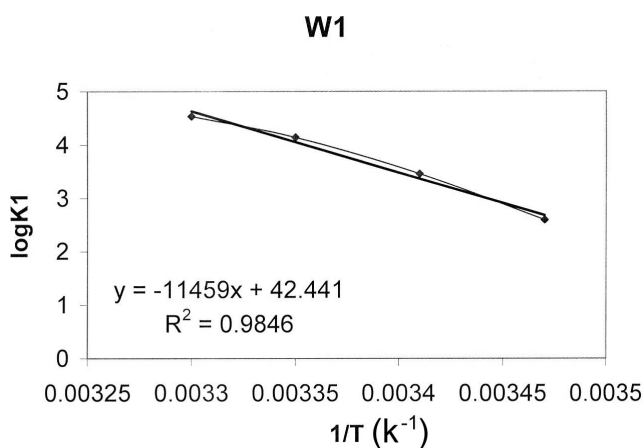
Fig. 3. Vant't Hoff plot of Na_2WO_4

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