Thermodynamic study of interaction between some transition metal ions and L-Alanine

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ABSTRACT
Using UV-vis spectrophotometric method, the formation constants for interaction of Cd\(^{2+}\)\(_{aq}\) and Co\(^{2+}\)\(_{aq}\) ions with L-Alanine were experimentally studied at pH = 4.1 ± 0.01 (50mM of potassium hydrogen phthalate buffer), ionic strength of 0.1M potassium nitrate and at 5 different temperatures 15, 20, 25, 30 and 35 °C. The optical absorption spectra of mixtures containing considered cations and L-Alanine were analyzed by using SQUAD software, in order to obtain the formation constants and the stoichiometry of respect complexes. The best fitting of our results showed that the 2:1 complex respect to each studied system (Cd\(^{2+}\)\(_{aq}\) + L-Alanine) and (Co\(^{2+}\)\(_{aq}\) + L-Alanine) is formed. Regarding the values of formation constants at different temperatures and using Van't Hoff equation, enable us to calculate the respect thermodynamic functions of formation such as \(\Delta H\), \(\Delta S\), \(\Delta G\), … of studied complexes.

Keywords: Amino acid; Transition metal ions; Interaction; SQUAD

INTRODUCTION
The amino acids have special importance among the other chemical groups, since they are the foundation stone of the living organisms. It is obvious that one has to know the physicochemical properties of amino acids in order to explain the behaviors and the synthesis of peptides, proteins, and enzymes in the organisms. Among these properties the formation constants of the complexes which are formed with various metal ions are very interesting. It is known that the reactions of peptides, proteins, and enzymes with metal ions are of biochemical importance, but they are yet to be fully elucidated. The explanation of these phenomena in the biological systems can be possible almost by the determination of formation constants, which are the measure of amino acids-metal ions tendency to make several complexes [1,4]. Metal complexes of amino acids and peptides are of active research although there are many publications dealing with the coordination chemistry of both groups of ligands. In addition to the naturally occurring amino acids some synthetic, analogues, and derivatives of amino acids and peptides have been also considered due to their biological or theoretical significance or important application in
chemistry or medicine [2]. The number of papers dealing with the synthetic, analytical, or biomedical application of amino acids complexes has significantly increased in the past few years[3].

Cadmium (II) compounds and cobalt (II) compounds are known as human carcinogens [7], teratogenic [8], caused sterility [9], hephatoxic [10], pancreatic activity changes [12], genotoxic and apoptotic [13,14]. Toxic effects of cadmium compounds, and cobalt compounds have also been demonstrated on the bone formation and immune system [15,16].

That is why we studied the formation constants of the complexes formed by L-Alanine with Cd^{2+}(aq) and Co^{2+}(aq).

The coordination of amino acids to the transition metal ions is well nearly known with strong binding to the ions via a chelate binding mode involving both carboxylate and amine groups [17] as shown in scheme(1)

![Scheme 1](image)

The formation reaction of L-Alanine + Cd^{2+}(aq) and L-Alanine + Co^{2+}(aq) may be represented as:

\[ 2L^- + M^{2+} \rightarrow ML_2 \]

where L^- ion stands for the anionic form of considered amino acid and M^{2+} is the Cd^{2+}(aq) or Co^{2+}(aq). Amino acids are symbolized by the HL formula. It was observed the ML2 complex related to the Cd^{2+}(aq) or Co^{2+}(aq)ion disproportionate at pH higher than 8 to give cadmium (II) hydroxide or cobalt (II) hydroxide precipitates. Therefore, the measurements and calculation of formation constants were carried out upon the spectrophotometric data concerning to the pH range of 4-8 [5,6].

**MATERIALS AND METHODS**

L-Alanine, cadmium (II) nitrate and cobalt (II) nitrate with high purities were purchased from Merck Company and were used without further purification.

All considered solutions were prepared using double distilled water. Potassium hydrogen phthalate 50 mM, (pH = 4.1 ± 0.01) was used as buffer and the ionic strength of 0.1M potassium nitrate was supplied. All of the work solutions were made by dissolving the solid compounds in buffer solution. The transition metal ions (Cd^{2+}(aq), Co^{2+}(aq)) solutions were freshly prepared before spectral analysis and their concentration range were \(4.00 \times 10^{-5} - 5.00 \times 10^{-2}\) M. L-Alanine solutions were prepared at room temperature and the concentration range were 0.6-1 M. The titration of considered metal ion solutions as a function of L-Alanine concentration was performed at 15, 20, 25, 30 and 35°C. Spectrophotometric measurements were performed on a UV-Vis spectrophotometer (Camspace 350 M) and a 1.00cm quartz cavetto in the spectral range of 200-800nm with a thermostat cell compartment that control the temperature around the cell within ±0.1°C were used.

The stoichiometry of the complexes and the formation constants were determined by analyzing the optical absorption of considered mixtures (the transition metal ion +L-Alanine) at various L-Alanine concentrations using SQUAD software.

**RESULTS AND DISCUSSION**

The Absorbance of Cd^{2+}(aq) and Co^{2+}(aq)

Figure 1 shows that the maximum absorption band respect to the solutions of Cd^{2+} or Co^{2+} obey the Beer’s law over the concentration range of \(1 \times 10^{-5} - 5 \times 10^{-5}\) M. Figure 2 shows absorption spectra of considered transition metal ions. The band of Cd^{2+}(aq) consists 285-335nm and the band.
of Co$^{2+}$ (aq) is 275-335nm. All of the considered transition metal ions solutions were titrated at ionic strength of 0.1M potassium nitrate and in potassium hydrogen phthalate buffer 50mM, (pH = 4.1 ± 0.01).

Interaction of Cd$^{2+}$ (aq) and Co$^{2+}$ (aq) ions with L-Alanine

The two considered transition metal ions were titrated with a stock solution of L-Alanine. It can be assumed that the concentration change due to adding the titrant is negligible because the total volume change during the titration is less than 6%. Maximum bands respect to Cd$^{2+}$ (aq) were shifted hypochromicity of 15-35% while in Co$^{2+}$ (aq) maximum bands were shifted hypochromicity of 25-45%. The representative UV-Vis spectra are shown in figures 5 and 6.

The standard Gibbs free energy, ΔG$^\circ$, related to each complex formation is calculated according to equation (1)

$$\Delta G^\circ = -RT \ln K$$

where K is the equilibrium formation constant of the reaction, T is temperature in Kelvin and R is gas constant. According to the Van't Hoff equation

$$\frac{d \ln K}{dT} = -\frac{\Delta H}{R}$$

a linear plot of lnK versus 1/T is observed, if the heat capacity change for the reaction is essentially negligible.

$$\ln K = \left(-\frac{\Delta H^\circ}{R}\right) \left(\frac{1}{T}\right) + \text{constant}$$

The considered standard entropy change, ΔS$^\circ$, of the reaction is calculated from equation (4):

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

The formation constants for the considered reactions “2L$^-$+M$^{2+}$→ML$^2$” at different temperatures and their thermodynamic parameters such as ΔG$^\circ$, ΔH$^\circ$ and ΔS$^\circ$ were calculated (table 1).

SQUAD program

In order to analyze the spectral data at various concentrations of L-Alanine in titration experiments, 50 wavelengths were selected. The values of absorbances of these selected wavelengths at various L-Alanine concentrations were analyzed in order to calculate equilibrium formation constants, using SQUAD program. Input data were absorbances at 50 different wavelengths of 15 solution spectra. These 15 spectra are corresponding to 15 various concentrations of L-Alanine. The outputs were the logarithm of equilibrium formation constants, log K$_{ij}$ for the following reaction:

$$i \text{L}^- + j \text{M}^{2+} \rightleftharpoons (\text{L}^-)_i (\text{M}^{2+})_j$$

K$_{ij}$=$\frac{[(\text{L}^-)_i (\text{M}^{2+})_j] ([\text{L}^-])^i ([\text{M}^{2+}])^j}$

The estimated formation constants for the formation of 2:1 complexes respect to (2L$^-$+ Cd$^{2+}$ (aq)) and (2L$^-$+ Co$^{2+}$ (aq)) system at various temperatures are listed in table 1.

CONCLUSION

Using SQUAD program, the absorbance data obtained from the titration of (Cd$^{2+}$ (aq) + L-Alanine) system and (Co$^{2+}$ (aq) + L-Alanine) system were analyzed in order to calculate the respect formation constants. SQUAD program refines the formation constants by employing a non-linear least square approach. The results represent the formation of 2:1 complex model between considered transition ions and L-Alanine. In figure 7, a linear plot of lnK versus 1/T is observed respect to each (Cd$^{2+}$ (aq)+L-Alanine) and (Co$^{2+}$ (aq)+L-Alanine) system. The positive slopes in the plots represent the exothermicity of (Cd$^{2+}$ (aq)+L-Alanine) and (Co$^{2+}$ (aq)+L-Alanine) reactions and the high correlation coefficient of the lines indicate that the heat capacities of the components are temperature independent.
ACKNOWLEDGMENT

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Table 1. Thermodynamic parameters of binding of Cd\(^{2+}\)\(_{(aq)}\) and Co\(^{2+}\)\(_{(aq)}\) to L-Alanine in 50mM potassium hydrogen phthalate buffer, pH=4.1 ± 0.01, and ionic strength of 0.1M potassium nitrate at various temperatures

<table>
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<th>Transition metal ion</th>
<th>(\theta/\degree C)</th>
<th>(K \times 10^{-5})</th>
<th>(\Delta G^0/\text{kJmol}^{-1})</th>
<th>(\Delta H^0/\text{kJmol}^{-1})</th>
<th>(\Delta S^0/\text{Jmol}^{-1}\text{K}^{-1})</th>
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<tr>
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Fig. 1. Absorbance, Abs, as a function of concentration of Co\(^{2+}\)\(_{(aq)}\) and Cd\(^{2+}\)\(_{(aq)}\) at 25\(^\circ\)C.

Fig. 2. Absorption spectra of Co\(^{2+}\)\(_{(aq)}\), Blue line, and Cd\(^{2+}\)\(_{(aq)}\), Red line, and their maximum bands.

Fig. 3. Absorption spectra of Co\(^{2+}\)\(_{(aq)}\) upon titration with L-Alanine in potassium hydrogen phthalate buffer, pH 4.1, and ionic strength of 0.1M KNO\(_3\) at 25\(^\circ\)C.

Fig. 4. Absorption spectra of Cd\(^{2+}\)\(_{(aq)}\) upon titration with L-Alanine in potassium hydrogen phthalate buffer, pH 4.1, and ionic strength of 0.1M KNO\(_3\) at 25\(^\circ\)C.
Fig. 5. Absorption spectra of Co$^{2+}$\textsubscript{(aq)} upon titration with L-Alanine in potassium hydrogen phthalate buffer, pH 4.1, and ionic strength of 0.1M KNO$_3$ at 15, 20, 25, 30 and 35°C.

Fig. 6. Absorption spectra of Cd$^{2+}$\textsubscript{(aq)} upon titration with L-Alanine in potassium hydrogen phthalate buffer, pH 4.1, and ionic strength of 0.1M KNO$_3$ at 15, 20, 25, 30 and 35°C.

REFERENCES