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Thermodynamic Study on the Interaction Between Tl(I) Ion and L-Alanine

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The formation constant of interaction of Tl(I) ion with L-alanine was experimentally studied at pH = 4.1 ± 0.01 (50 mM of potassium hydrogen phthalate buffer), ionic strength of 0.1 M potassium nitrate at 5 different temperatures 15, 20, 25, 30 and 35 °C by UV-Vis spectrophotometric method. The optical absorption spectra of mixtures containing considered cation and L-alanine were analyzed by using SQUAD software, in order to obtain the formation constant and the stoichiometry of respect complex. The best fitting of present results showed that the 1:1 complex in respect to the studied system (Tl^+(aq) + L-alanine) is formed. Regarding the values of formation constant at different temperatures and using Van't Hoff equation, it is possible to calculate the respective thermodynamic functions of formation such as ΔG°, ΔH°, ΔS° of the studied complex.

Key Words: L-Alanine, Tl(I) complex, Thermodynamic parameters.

INTRODUCTION

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 physico-chemical properties of amino acids in order to explain the behaviour 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 studied. The explanation of these constants, which are the measure of amino acids phenomena in the biological systems can be possible almost by the determination of metal ions tendency to make several complexes[1,2]. Metal complexes of amino acids and peptides are the subject of active research although there are many publications related to the coordination chemistry of both groups of ligands.

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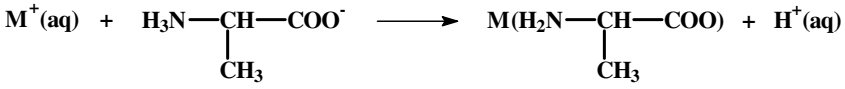
In addition to the naturally occurring amino acids, some synthetic, analogues and derivatives of amino acids and peptides have also been considered due to their biological or theoretical significance as well as important application in chemistry or medicine[3]. The number of papers dealing with the synthetic, analytical or bio-medical application of amino acids complexes has significantly increased in the past few years[4].

The formation of metal ion complexes is often highly dependent on the pH of the solution. This is because there is a competition for the ligand between the metal ion and the proton as they both bind to the same sites of the ligand. For L-alanine at low pH, the metal ion has to displace a proton from the amine in order to form a stable complex

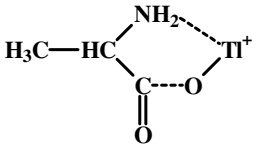


(1)

The number of protons displaced through chelate formation can be determined from a titration of ligand and metal ion, in this instance a 1:1 mixture of L-alanine and Tl^+(aq) is used[5,6].

Thallium(I) compounds have high aqueous solubility and readily absorbed through the skin. Thallium is a suspected human carcinogen. Part of the reason for thallium high toxicity is that, when present in aqueous solution as the univalent thallium(I) ion, it exhibits some similarities with essential alkali metal cations, particularly potassium (as the atomic radius is almost identical). It can thus enter the body *via* potassium uptake pathways[7-9].

The coordination of amino acids to the metal ions is well nearly known with strong binding to the ions *via* a chelate binding mode involving both carboxylate and amine groups[10] as shown in **Scheme-I**.



Scheme-I

The formation reaction of 'L-alanine + Tl^+(aq)' may be represented as:

$$L^- + M^+ \rightarrow ML \quad (2)$$

where L^- ion stands for the anionic form of L-alanine and M^+ is the Tl^+. Amino acids are symbolized by the HL formula. It was observed the ML complex related to the Tl^+(aq)ion disproportionate at pH higher than 8 to give thallium(I) hydroxide precipitates. Therefore, the measurements and calculation of formation constants were carried out upon the spectrophotometric data concerning to the pH range 4 to 8[5,6].

EXPERIMENTAL

L-Alanine and thallium(I) 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 0.1 M potassium nitrate was supplied. All of the work solutions were made by dissolving the solid compounds in buffer solution. The metal ion $Tl^+(aq)$ solution was freshly prepared before spectral analysis and their concentration range was 4.00×10^{-2}–8.00×10^{-2} M. L-Alanine solution was prepared at room temperature and the concentration range was 0.6-1.0 M. The titration of considered metal ion solution as a function of L-alanine concentration was performed at 15, 20, 25, 30 and 35 ºC. Spectrophotometric measurements were performed on a UV-Vis spectrophotometer (Camspec M350) and a 1 cm quartz cuvette in the spectral range of 200-800 nm with a thermostat cell compartment that controls the temperature around the cell within ± 0.1 ºC were used.

The stoichiometry of the complex and the formation constant was determined by analyzing the optical absorption of considered mixture (the metal ion +L-alanine) at various L-alanine concentrations using SQUAD software.

RESULTS AND DISCUSSION

Absorbance of $Tl^+(aq)$: Fig. 1 shows that the maximum absorption band in respect to the solution of Tl^+ obey the Beer's law over the concentration range of 1×10^{-5}–6×10^{-5} M. Fig. 2 shows absorption spectra of considered metal ion. The band of $Tl^+(aq)$ is 285-335 nm. All of the considered metal ion solutions were titrated at ionic strength 0.1 M of potassium nitrate and in potassium hydrogen phthalate buffer 50 mM, (pH = 4.1± 0.01).

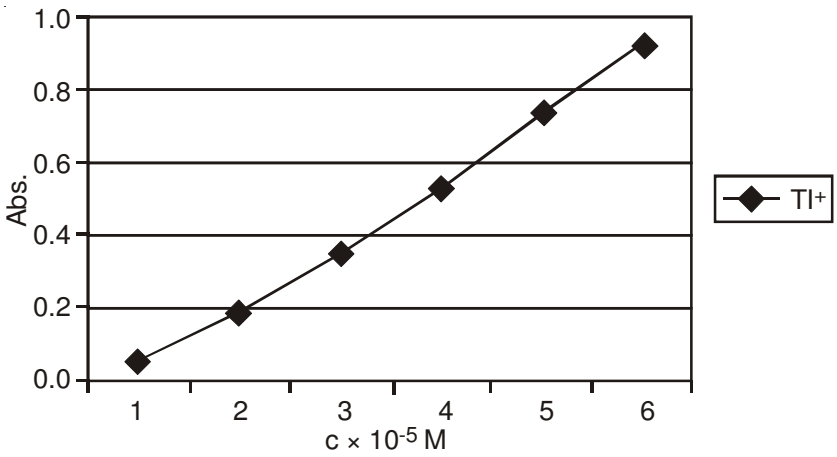


Fig. 1. Absorbance as a function of concentration of $Tl^+(aq)$ at 25 °C

Interaction of Tl^+(aq) ion with L-alanine: The solution containing Tl^+ was titrated with a stock solution of L-alanine. It can be assumed that the concentration change due to the adding the titrant is negligible because the total volume change during the titration is less than 6 %. Maximum bands respect to Tl^+(aq) were shifted hypochromicity of 15-35 %. The representative UV-Vis spectra of Tl^+(aq) with L-alanine is shown in Fig. 2.

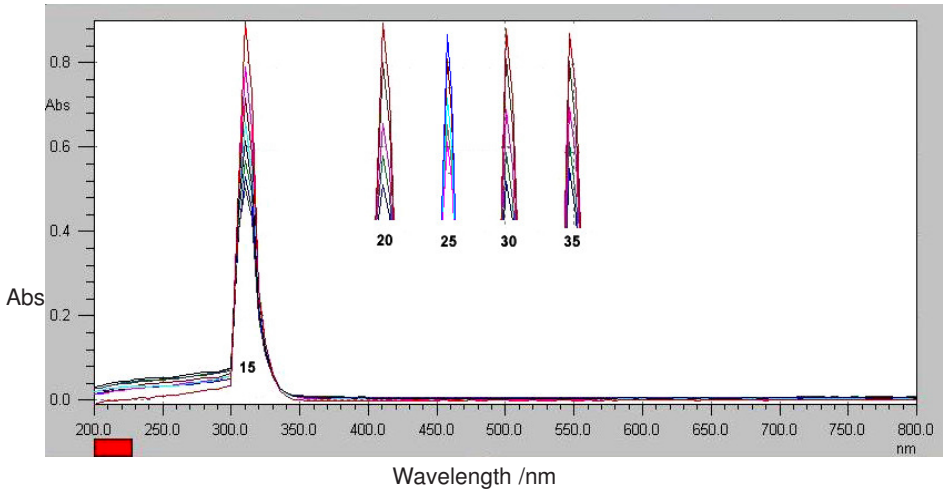


Fig. 2. Absorption spectra of Tl^+(aq) upon titration with L-alanine in potassium hydrogen phthalate buffer, pH 4.1 and ionic strength of 0.1 M KNO_3 at 15, 20, 25, 30 and 35 ºC

The standard Gibbs free energy change, $\Delta G°$, related to complex formation is calculated according to eqn. 3:

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

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 eqn. 4:

$$d \ln K/d (1/T) = -\Delta H°/R \quad (4)$$

a linear plot of ln K *versus* 1/T is observed (Fig. 3), if the heat capacity change for the reaction is essentially negligible

$$\ln K = (-\Delta H°/R)(1/T) + \text{constant} \quad (5)$$

The standard entropy change, ΔS^o, of the reaction is calculated from eqn. 6:

$$\Delta S° = (\Delta H° - \Delta G°)/T \quad (6)$$

The formation constants for the reaction (2)

$$L^- + M^+ \rightarrow ML \quad (2)$$

at different temperatures and their thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated (Table-1).

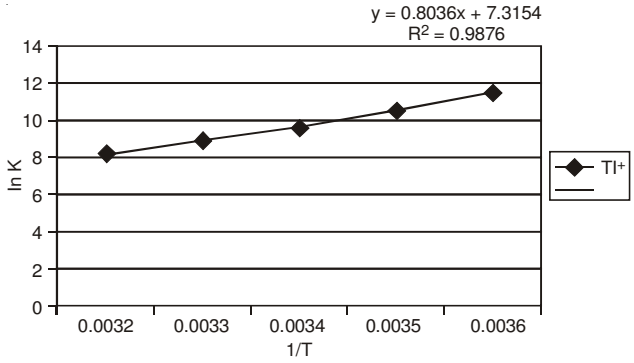


Fig. 3. Linear plot of ln K *versus* 1/T for binding of Tl^+(aq) to L-Alanine in the potassium hydrogen phthalate buffer, pH 4.1 and ionic strength of 0.1 M KNO_3

TABLE-1
THERMODYNAMIC PARAMETERS FOR BINDING OF Tl^+(aq) TO L-ALANINE IN 50 mM POTASSIUM HYDROGEN PHTHALATE BUFFER, pH = 4.1 ± 0.01 AND IONIC STRENGTH OF 0.1 M POTASSIUM NITRATE AT VARIOUS TEMPERATURES

θ (º)	(K ± ΔK) × 10^{-4}	ΔGº ± ΔΔGº (kJ mol^{-1})	ΔHº ± ΔΔHº (kJ mol^{-1})	ΔSº ± ΔΔSº (J mol^{-1} K^{-1})
15	9.5499 ± 1.034	-27.470 ± 0.080	-66.524 ± 0.136	-135.5383 ± 0.194
20	3.6307 ± 1.025	-25.590 ± 0.061	-66.524 ± 0.136	-139.6398 ± 0.255
25	1.3803 ± 1.033	-23.629 ± 0.079	-66.524 ± 0.136	-143.8754 ± 0.191
30	0.7079 ± 1.028	-22.342 ± 0.071	-66.524 ± 0.136	-145.7478 ± 0.214
35	0.3890 ± 1.039	-21.177 ± 0.073	-66.524 ± 0.136	-147.1639 ± 0.204

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 correspond to 15 various concentrations of L-alanine. The outputs were the logarithm of equilibrium formation constants, log K_{ij} for the following reaction:

$$i\,L^- + j\,M^+ \rightleftharpoons (M^+)_j(L^-)_i \quad (7)$$

$$K_{ij} = [(M^+)_j\,(L^-)_i]/[(L^-)_i][(M^+)_j] \quad (8)$$

The estimated formation constants for the formation of 1:1 complex between (L^- + Tl^+(aq)) at various temperatures are listed in Table-1.

Conclusion

Using SQUAD program, the absorbance data obtained from the titration of (Tl^+(aq) + L-alanine) system was analyzed in order to calculate the respective formation constants. SQUAD program refines the formation constants by employing a non-linear least square approach. The results represent the formation of 1:1 complex

model between considered metal ion and L-alanine. In Fig. 5, a linear plot of ln K *versus* 1/T is observed respect to (Tl^+(aq) + L-alanine) system. The positive slopes in the plots represent the exothermicity of (Tl^+(aq) + L-alanine) reaction and the high correlation coefficient of the line indicate that the heat capacities of the component is temperature independent.

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