Complexes of thallium (I) ion with adenine and adenosine at different temperatures and constant ionic strength

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Abstract

The protonation equilibria of Adenine, Adenosine and their complex formation with thallium(I) ion in aqueous solution were studied using a combination of potentiometric and spectrophotometric methods at different temperatures (10, 15, 20, 25, 30 and 35 °C) and constant ionic strength (0.1 mol dm⁻³ sodium perchlorate). An accurate and sophisticated method based on chemometrical concepts was applied in order to determine stability constants. For this purpose, spectral titration data were used and the spectra were recorded in the range (200-500 nm). The stability constants of thallium (I) ion with all the heterocyclic bases were calculated at various temperatures by means of computer fitting of the pH-absorbance data with appropriate mass balance equations according to mono- and di- acids. The computer program equispec was used to extract the desired information from the spectral data. The outputs of the fitting processes were protonation and stability constants, spectral profiles of pure forms, distribution diagrams, and other factor analysis data. The composition of the formed complexes was determined and it was shown that thallium(I) forms two mononuclear 1:1 species with the ligands, of the type Tl(HL) and TlL in the pH range of study (1.0 – 12.4), where L represents each heterocyclic base. Finally, The effect of temperature on the protonation and stability constants were studied and thermodynamic functions have been obtained for the complexes of thallium(I) ion with the heterocyclic bases from the stability constants values and their temperature dependence.

Keywords: Thallium(I) complexes, adenine, adenosine, equispec, distribution diagrams.

1. Introduction

Of all fields of chemistry, the study of the nucleic acids is perhaps the most exciting, taking into account that these compounds control heredity on the molecular level. The backbone of the nucleic ribonucleic acid molecule is a polyester chain (called a polynucleotide chain) derived from phosphoric acid and a sugar (1).

![Adenine](image1)

![Adenosine](image2)

Scheme 1. Structures of the heterocyclic bases
Acid dissociation constants (i.e. pK_a values) can be a key parameter for understanding and quantifying chemical phenomena such as reaction rates, biological activity, biological uptake, biological transport and environmental fate (2). They are useful physico-chemical parameters describing the extent of ionization of functional groups with respect to pH. These parameters are important in research areas such as pharmaceutical drug development, where knowledge of the ionization state of a particular functional group often is crucial in order to understand its pharmacokinetics and pharmacodynamics (3).

On the other hand, research results have clearly demonstrated that certain transition metal ions play a basic role in directing a number of biochemical processes. Many biological processes involve hydrolysis of proteins. Metal ions can promote the hydrolysis of proteins in both homogeneous and heterogeneous systems. Hydrolysis of proteins has been studied more from a biochemical than from chemical point of view, and since certain proteolytic enzymes require metal ions for activity, hydrolysis reactions with metal ions have attracted the attention of chemists (4).

Thallium has been recognized as a toxic element for many years. It produces a variety of adverse effects in human being. This element acts on the central nervous system and induces inflammatory response. However, the metabolic mechanism and fate of thallium toxicity is still not well understood. Since thallium (I) shows marked similarities to that of potassium action, its interaction with nucleotides, the monomeric units of DNA and RNA, in aqueous would be of a major biochemical interest (5).

The increasing rate of the environment pollution has stimulated worldwide research concerning new materials capable to remove metal of thallium from contaminated soils and wastes. This revealed the need for comprehensive studies of metal ion-bioligand interactions, as model systems. Metal complexes in aqueous solution were studied by various techniques (4). Also, there have been several methods of the determination of acidity constants, including the use of potentiometric titration, spectrophotometry, capillary electrophoresis, liquid chromatography and so on (2, 6, 7-14). In most of these methods a physical property of the analyte is measured as a function of the pH of the solution and the resulting data are used for the determination of the dissociation constants (15).

Spectroscopic methods are in general highly sensitive and are frequently used to analyze chemical equilibria in solution. If the components involved can be obtained in pure form, or if their spectral responses do not overlap, such analysis is, in general, trivial. For many systems, particularly those with similar components, this is not the case, and these have been difficult to analyze (13). In 1971 Lawton and Sylvestre introduced chemometric methods for spectral analysis (16). The methods are today commonly used in spectral analysis of test samples. In general, such an analysis is made in two steps: first, the number of components is determined, and then the spectral responses and concentrations of the components are calculated. Several methods have been devised for the second step; and they widely depend on auxiliary information and experimental design (17-20). The first step, determining the number of components, is pertinent to all forms of spectral analysis (21-23). There are several approaches to determine the number of components that contribute.

Therefore has been decided to carry out an equilibrium study of the interaction of heterocyclic bases with thallium (I) to determine stability of species formed. These complexes may serve to determine the interactions leading to metal promoted hydrolysis and the investigation of influence temperature on the acid-base behavior of simple organic compounds may contribute to a better understanding of the properties of complex substances such as natural organic matters. Also, the knowledge of the distribution of species with pH is a prerequisite for further kinetic studies (4). In the present work, the stability constants of Tl(I)
with adenine and adenosine were determined spectrophotometrically at six different temperatures in ionic strength 0.1 mol dm\(^{-3}\) NaClO\(_4\). The stability constants of the formed complexes at different temperatures were evaluated by the Equispec program using the corresponding spectral absorption-pH data and these values have been compared with similar systems and interpreted. Then, thermodynamic functions have been obtained from the stability constants values and their temperature dependence.

2. Experimental

2.1. Chemicals: Thallium (I) nitrate, Adenine (C\(_5\)H\(_5\)N\(_5\)) and adenosine (C\(_{10}\)H\(_{13}\)N\(_5\)O\(_4\)) were obtained from Fluka and Merck, respectively, as reagent grade materials. The aqueous stock solutions of the heterocyclics were freshly prepared daily. NaOH solution was prepared from a titrisol solution (Merck), and its concentration was determined by several titrations with standard HCl solution. Dilute perchloric acid (Fluka) solutions were standardized against standard NaOH solution. Sodium perchlorate (Merck) was kept in a vacuum at least 72 h before use. All The reagents were used without further purification and dilute solutions were prepared from double-distilled water with conductance equal to (1.8 ± 0.1) \(\mu\)S.

2.2. Apparatus and software: The pH values were measured with a HORIBA M-12 pH-meter using a combined glass electrode. The glass electrode was calibrated on the basis of the proton concentration at constant ionic strength (0.1 mol dm\(^{-3}\)) according to the procedure described elsewhere (24). The calibration was repeated at each specific temperature (t ± 0.1) °C by circulation of thermostated water through the jacket. Nitrogen purge gas was used to remove CO\(_2\). An Eppendorf micropipette (±0.6%) was used for the addition of a standard base to the solution. The calibration procedure was as recommended by the IUPAC for glass electrodes (25).

A HP-8453 spectrophotometer controlled by a computer and equipped with a 1 cm path length quartz cell was used for UV-Vis spectra acquisition. Spectra were acquired between 200 and 500 nm (5 nm resolution). The measurement cell was of a flow type. A Masterflex pump allowed circulation of the solution under study from the potentiometer cell to the spectrophotometer cell, so the absorbance and the pH of the solution could be measured simultaneously.

The data were preprocessed using MATLAB software, version 6.5 (Mathworks, Natick, U.S.A) and the deconvolution of the obtained data matrix was performed using Equispec version 3.1.

2.3. Measurements: All measurements were carried out at six different temperatures (10, 15, 20, 25, 30 and 35)°C. The ionic strength was maintained to 0.1 mol dm\(^{-3}\) with sodium perchlorate. The pH meter was calibrated for the relevant H\(^+\) concentration with a solution of 0.01 mol dm\(^{-3}\) perchloric acid solution containing 0.09 mol dm\(^{-3}\) sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm\(^{-3}\)). For this standard solution, we set \(-\log[H^+] = 2.00\) (26). Junction potential corrections have been calculated from eq 1:

\[
-\log[H^+\text{real}] = -\log[H^+\text{measured}] + a + b[H^+]\text{measured}
\]  

Where (a) and (b) were determined by measuring hydrogen ion concentration for two different solutions of HClO\(_4\) or NaOH with sufficient NaClO\(_4\) to adjust the ionic media.

To exclude carbon dioxide and oxygen from the system, a stream of purified nitrogen was passed through a sodium hydroxide solution and then bubbled slowly through the reaction vessel.
2.4. Procedure: Volumes of 10 cm$^3$ acidic solution of Tl$^+$ [(3.85×10$^{-5}$ to 2.8×10$^{-4}$ mol dm$^{-3}$)] was titrated with an alkali solution (0.1 mol dm$^{-3}$ NaOH) of the heterocyclic bases [(8.05×10$^{-5}$ to 1.6×10$^{-4}$ mol dm$^{-3}$)]. Titration of each the heterocyclic base was carried out at 6 temperatures (10, 15, 20, 25, 30 and 35) ºC in ionic strength 0.1 mol dm$^{-3}$. Ionic strength fixed with NaClO$_4$ solution. The starting points of pH titrations were pH 1.0, which were set using concentrated solutions of HCl and NaOH. The concentrated NaOH solution was also used for titrations, to avoid dilution of the working solutions. The $-\log[H^+]$ and absorbance were measured after addition of a few drops of titrant, and the procedure was extended up to required $-\log[H^+]$. A purified nitrogen atmosphere was maintained in the vessel during the titrations. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations from the average are shown in the Tables 1 and 2.

### Table 1. Average values of the protonation constants of the ligands at different temperatures and constant ionic strength, I, (0.1 mol dm$^{-3}$ NaClO$_4$)

<table>
<thead>
<tr>
<th>T(ºC)</th>
<th>$\log \beta_{011}$</th>
<th>$\Delta H$ (Kj.mol$^{-1}$)</th>
<th>$\Delta S$ (j.mol$^{-1}$)</th>
<th>$\Delta G$ (Kj.mol$^{-1}$)</th>
<th>$\log \beta_{011}$</th>
<th>$\Delta H$ (Kj.mol$^{-1}$)</th>
<th>$\Delta S$ (j.mol$^{-1}$)</th>
<th>$\Delta G$ (Kj.mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>13.78±0.46</td>
<td>-74.13</td>
<td>1.302</td>
<td>-74.53</td>
<td>16.99±0.42</td>
<td>-109.62</td>
<td>-62.86</td>
<td>-90.88</td>
</tr>
<tr>
<td>15</td>
<td>13.46±0.49</td>
<td>16.52±0.45</td>
<td></td>
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<td>20</td>
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<td>-90.88</td>
</tr>
<tr>
<td>25</td>
<td>13.47±0.27</td>
<td>15.91±0.24</td>
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</tr>
<tr>
<td>30</td>
<td>12.87±0.23</td>
<td>15.61±0.21</td>
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<tr>
<td>35</td>
<td>3.04±0.9</td>
<td>8.68±0.53</td>
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<table>
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<th>Adenosine</th>
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<tr>
<td>25</td>
<td>13.47±0.27</td>
<td>15.91±0.24</td>
<td>12.34±0.23</td>
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<th>Adenosine</th>
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<tr>
<td>25</td>
<td>12.34±0.23</td>
<td>10.49±0.23</td>
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</table>

* The values are at zero ionic strength
Table 2. Average values of the formation constants of Tl(I) with heterocyclic bases at different temperature and constant ionic strength (0.1 mol dm$^{-3}$ NaClO$_4$) some thermodynamic parameters at different temperatures.

<table>
<thead>
<tr>
<th>T(ºC)</th>
<th>log$\beta_{101}$</th>
<th>$\Delta H$ (KJ.mol$^{-1}$)</th>
<th>$\Delta S$ (J.mol$^{-1}$)</th>
<th>$\Delta G$ (KJ.mol$^{-1}$)</th>
<th>log $\beta_{111}$</th>
<th>$\Delta H$ (KJ.mol$^{-1}$)</th>
<th>$\Delta S$ (J.mol$^{-1}$)</th>
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</tr>
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<tr>
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<td>13.26±0.46</td>
<td>-190.65</td>
<td>-347.52</td>
<td>-87.03</td>
<td>16.25±0.42</td>
<td>-218.99</td>
<td>-456.47</td>
<td>-82.89</td>
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<tr>
<td>25</td>
<td>13.07±0.27</td>
<td>-190.65</td>
<td>-347.52</td>
<td>-87.03</td>
<td>15.91±0.24</td>
<td>-218.99</td>
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<td>35</td>
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<td>-190.65</td>
<td>-347.52</td>
<td>-87.03</td>
<td>15.31±0.19</td>
<td>-218.99</td>
<td>-456.47</td>
<td>-82.89</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The stoichiometry of each complex species is expressed by means of indexes (p:q:r), coherently with the general reaction:

$$pM^{n+} + qH^+ + rL^- \rightleftharpoons M_pH_qL_r^{(np+q+r)^+}$$

Where M and L represent the metal ion and adenine or adenosine, respectively. To determine the stability constant of the complexation, eq 2 is defined by $\beta_{pqr}$ (27):

$$\beta_{pqr} = \frac{[M_pH_qL_r^{(np+q+r)^+}]}{[M^{n+}]^p[H^+]^q[L^-]^r}$$

The protonation constants of the heterocyclic bases have been used for computation of the stability constant, $\beta_{pqr}$, of the metal-ligand.

In this work, the electronic absorption spectra of adenine and adenosine were recorded in different temperatures and at various pH values. The protonation constants of the adenine and adenosine were determined using a potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method (Microsoft Excel Solver) (28).

These values are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported earlier (29).

The stability constants were calculated using the method mentioned before. Absorbance, A, and -log [H$^+$] were measured by successive addition of an alkali solution of the ligand to the acidic metal ion solution in the UV range (200 to 500) nm; see Experimental Section. Treatment of the spectrophotometric data (each 5 nm) obtained during the titrations, as a function of the hydrogen ion concentration was submitted with the computer program Equispec (by using the matrix based in the Matlab environment). The stoichiometric forma-
Complexes of thallium(i) ion with adenine and adenosine at different temperatures and constant ionic strength

The protonation constants were computed from the data using the computer program. The number of experimental points (absorbance vs pH) was more than 30 for each titration.

The output of Equispec comprises the spectrum, pKₐ values and diagrams of the concentration distribution of each assumed species. From inspection of the experimental spectra, it is hard to guess even the number of protolytic species involved (30-35).

Considering eq 2, different models including ML, MHL and several protonated and poly-nuclear species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were, MH₂L, and MHL₂, ML₂ and MH₂L₂ (the charges were omitted for simplicity). Values for some species were calculated by the program, but the species were not considered further because the estimated error in its formation constant was unacceptable, and its inclusion does not improve the goodness of the fit. The chosen models, formed by ML and MHL for the studied system, resulted in satisfactory fit.

In similar investigations, the stability constants values of Tl(I) with adenine and adenosine were determined by the potentiometric titration method at (10, 15, 20, 25, 30 and 35) °C in aqueous solution. Also, the thermodynamic functions for the heterocyclic bases have been obtained from the protonation and stability constants values and their temperature dependence. The calculated average values of the protonation and stability constants for different experiments are listed in Table 2 and figure 2.

In figure 3 the equilibrium distributions of various species of Tl(I) with adenine and adenosine systems are shown as a function of –log [H⁺], respectively. The most important features of the distribution diagrams are the pH limits of the evolving and disappearing of components. The calculations shown are based on the stability constant values given in Tables 1 and 2. The curves clearly demonstrate that an increase of the pH is accompanied by an increase in the formation of deprotonated complex species.

As it can be seen from Tables 1 and 2 the higher temperature the smaller logβ values. The results show apparent acid dissociation and stability constants are corresponding to thermodynamic constants.

**Figure 1.** Curve of logβ versus 1/T for (a) Tl(I)-Adenine, (b) Tl(I)-Adenosine systems in ionic strength 0.1 mol dm⁻³ NaClO₄. (♦: 021, ■: 011, ▲: 101, ●: 111)
4. Conclusion

The stability constants of thallium (I) complexes of the heterocyclic bases adenine and adenosine were determined by spectrophotometric titrations using a chemometric technique in aqueous medium. The striking advantage of the proposed method is using of the whole spectral information in the computation process which enable us to have more accurate thermodynamic constants in comparison to the classical methods such as single wavelength approach. The effect of the temperature on the protonation and stability constants was calculated. The results show the logarithm of protonation and stability constants are a linear function of the reciprocal of the absolute temperature. The results show suitable consistency with the previous reported results. Of course, there are differences and these may be explained by the fact that the results depending on the conditions such as various temperatures, different ionic strengths with distinctive background electrolytes, and special methods that were used in the experiments.

Acknowledgments

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