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# EQUILIBRIUM AND THERMODYNAMIC STUDY OF COMPLEXES OF THALLIUM WITH URACIL AT DIFFERENT TEMPERATURES AND CONSTANT IONIC STRENGTH

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**ABSTRACT.** In aqueous solution, the protonation equilibria of uracil and their complex formation with thallium(I) ion were investigated using a combination of potentiometric and spectrophotometric methods at different temptatures (283.15, 288.15, 293.15, 298.15, 303.15 and 308.15) K and constant ionic strength (0.1mol dm$^{-3}$ sodium perchlorate). A careful and accurate method based on chemometrical concepts was used 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. 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 were determined and it was shown that thallium(I) forms a mononuclear 1:1 species with the uracil, of the type TlL in the pH range of study (1.0-12.4), where L represents each heterocyclic base. Finally, The effect of temprature on the protonation and stability constants were studied and thermodynamic functions such as change in enthalpy ($\Delta H$), change in entropy ($\Delta S$) and change in gibbs energy ($\Delta G$) have been obtained for the complexes of thallium(I) ion with the heterocyclic bases from the stability constants values and their temperature dependence.

***Key words:*** *Equispec, Thallium(I) complexe, Uracil, Temperature, Constant ionic strengh.*

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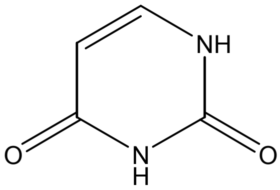
## INTRODUCTION

In our life today, the physico-chemical data of biological and organic molecules are very important due to their usages in various fields of industry such as food, pharmacy, cosmetic and detergents. Also, these data help us to better understanding of interaction between molecules in their solutions [1-8].

Uracil is one of the four nucleobases in the nucleic acid of RNA. In the body Uracil help to carry out the synthesis of many enzymes necessary for cell function through bonding with riboses and phosphates [9]. It can be used for drug delivery and as a pharmaceutical [10].



**Scheme 1.** Structures of the uracil

On the otherhand, thallium is a toxic element and acts on the central nervous system and induces inflammatory response. Since thallium(I) shows marked similarities to that of potassium cation, its interaction with nucleotides, the monomeric units of DNA and RNA, in aqueous would be of a major biochemical interest [11].

Aqueous solutions of Metal complex were studied by various techniques [12]. Also, there are several methods for the determination of acidity constants [13-18]. Spectroscopic methods are in general highly sensitive and are frequently used to analyze chemical equilibria in solution. In among of various properties of analyte, the physical property is measured (in most of these methods) as a function of the pH of the solution and the resulting data are used for the determination of the dissociation constants [19].

In the present work, the protonation and stability constants of uracil with Tl(I) were determined spectropotometrically at six different temperatures in ionic strength 0.1 mol $dm^{-3}$ $NaClO_4$.

The stability constants of the formed complexes at different tempratures were evaluted 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.

## RESULTS AND DISCUSSION

All measurements were carried out at six different temperatures (283.15, 288.15, 293.15, 298.15, 303.15 and 308.15) K. The ionic strength was maintained to 0.1 mol dm$^{-3}$ with sodium perchlorate. The pH meter was calibrated for the revalent 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 [20]. Junction potential corrections have been calculated from the bellow equation:

$$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured} \quad (1)$$

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 strength in solutions.

The species $M_pH_qL_r^{(np+q+r)+}$ formed is characterized by it stoichiometry (x:y:z), where M and L represent the metal ion and each ligand, respectively. To determine the stability constant of the complexation or protonation, eq 2 is defined by $\beta_{pqr}$ [21]:

$$pM^{n+} + qH^+ + rL^- \Leftrightarrow M_pH_qL_r^{(np+q+r)+} \quad (2)$$

$$\beta_{pqr} = \frac{[M_pH_qL_r^{(np+q+r)+}]}{[M^{+n}]^p[H^+]^q[L^-]^r} \quad (3)$$

The protonation constants of the heterocyclic bases have been used for computation of the stability constant, $\beta_{pqr}$, of the metal-ligand. For thallium (I)-uracil system a linear relation between log*β* and 1/*T* is observed in Figure 1. In addition, all these linear diagrams (log*β* vs 1/*T*) have the high $R^2$ ($R^2 \approx 0.99$).

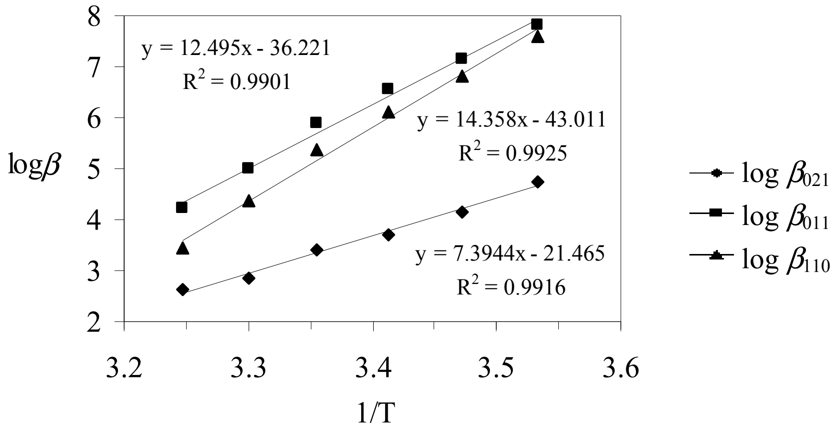


**Figure 1.** Cureve log*β* versus 1/T for Tl(I)-uracil system in ionic strength 0.1 mol dm$^{-3}$ $NaClO_4$.

In this work, the electronic absorption spectra of uracil were recorded in different tempratures and at various pH values. The protonation constants of the uracil were determined using a potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method (Microsoft Excel Solver) [22, 23]. These values are listed in Table 1 (the values reported in the literature are, $pK_1 = 0.6$ and $pK_2 = 9.46$) [24].

Determination of the formation constant was employed 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 (every 5 nm) obtained during the titrations, as a function of $H^+$ concentration, was conducted with the computer program Equispec (by using the matrix based in the Matlab environment) [25].

**Table 1.** Average values of the protonation constants of the uracil at different tempratures and constant ionic strength, I, (0.1 mol $dm^{-3}$ $NaClO_4$)

| $T$(°K) | log$\beta_{021}$ | $\Delta H$ (Kj.mol$^{-1}$) | $\Delta S$ (j.mol$^{-1}$) | $\Delta G$ (Kj.mol$^{-1}$) | log $\beta_{011}$ | $\Delta H$ (Kj.mol$^{-1}$) | $\Delta S$ (j.mol$^{-1}$) | $\Delta$G *(Kj.mol$^{-1}$)* |
|---|---|---|---|---|---|---|---|---|
| 283.15 | 4.74 ± 0.44 | | | | 7.80 ± 0.53 | | | |
| 288.15 | 4.16 ± 0.39 | | | | 7.15 ± 0.50 | | | |
| 293.15 | 3.71 ± 0.32 | | | | 6.55 ± 0.45 | | | |
| 298.15 | 3.40 ± 0.22 | -142.10 | -412.43 | -19.12 | 5.90 ± 0.12 | -248.53 | -724.91 | *-32.40* |
| 303.15 | 2.86 ± 0.23 | | | | 4.98 ± 0.41 | | | |
| *308.15* | *2.61 ± 0.34* | | | | *4.20 ± 0.21* | | | |

The stoichiometric formation 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. It is most convenient to arrange a series of the measured absorption spectra at different wavelengths and various pH values as the rows of a matrix Y. According to Beer-Lambert's law, **Y** can be decomposed into the product of a concentration matrix **C** and a matrix **A** of molar absorptivities. The concentration profiles of the absorbing species form the columns of **C** and the molar absorption spectra form the corresponding rows of **A**. Due to the instrumental and experimental errors, this decomposition is not perfect, the difference being the matrix E of residuals. A matrix equation can be written as:

$$Y = CA + E \tag{4}$$

Data fitting consists of determining those unknown parameters for which the sum of the squares over all the elements of the matrix **E** of residuals is minimal. Initially, the unknown parameters including the equilibrium constants, a vector p of nonlinear parameters, overall formation constants, and all the molar absorptivities of all the components, i.e., the complete matrix **A** of linear parameters, were determined. **C** is defined by the model and the appropriate equilibrium constants and is calculated numerically using the law of mass action and the analytical (total) concentration of each componentin solution [26, 27]. If the spectra are measured at many wavelengths, the total number of parameters could be very high, and it is crucial to reduce this number by separation of the linear and nonlinear parameters. For any set off nonlinear parameters, **p**, which defines the concentration matrix C, the best set of linear parameters, the matrix **A**, is an explicit least-squares calculation

$$A = C^{+}Y \qquad (5)$$

**$C^{+}$** is the pseudoinverse which can be calculated as **$C^{+} = (C^{t}C)^{-1}C^{t}$** or preferably using a numerically more stable algorithm (i.e., an algorithm which guarantees to reach physically meaningful final results) [28]. **A** is now defined as a function of **p** and consequently **E,** and sums of the squares (ssq) are defined as a function of the nonlinear parameters only

$$\mathrm{ssq} = \sum\sum E(i,j)^{2} = f(Y, \mathrm{model}, \mathrm{parameters}) = f(P) \qquad (6)$$

In the equilibrium condition, the model is a collection of equilibria between the component species, and the parameters are the equilibrium constants. The computation of the pseudo-seems to be a trivial task. In equilibrium studies, inverse **$C^{+}$** generally the concentration matrix **C** has, at least theoretically, full rank; i.e., the chemical and mathematical ranks are equal, and the concentration profiles for all species are linearly independent. **$C^{+}$** can be computed, and **A** is determined by eq 5. This is, however, not always the case, and near linear dependency (i.e., when the distribution diagram of some species can be expressed as a linear combination of some other species) and (or) species with only very low concentrations result in deficiencies in the equilibrium model. In this status, **C**, then, does not have full rank, and the pseudoinverse, **$C^{+}$**, is not or is only poorly defined, which can render its computation difficult to impossible and thus corrupt the resulting **A** as well as the residuals, **E,** and the sum of squares. There are powerful algorithms such as the Newton-Gauss-Levenberg/Marquardt algorithm available for this task [29].

The output of Equispec comprises the spectrum, $pk_a$ values and diagrams of the concentration distribution of each assumed species. From inspection of the experimantal spectra, it is hard to guess even the number of protolytic species involved.

Considering eq 2, different models including ML, MHL and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were, $MH_2L$, and $MHL_2$, $ML_2$ and $MH_2L_2$. 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 models finally chosen, formed by ML for the studied system, resulted in a satisfactory fitting.

Also, the thermodynamic functions for the heterocyclic base 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 Tables 1, 2. In Figure 2 the equilibrium distributions of various species of Tl(I) with uracil system 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.

**Table 2.** Avrage values of the formation constants of Tl(I) with uracil at different temperature and constant ionic strength (0.1 mol $dm^{-3}$ $NaClO_4$) some thermodynmic Parameters at Different Temperatures

| T (ºK) | $\log\beta_{101}$ | $\Delta H$ (Kj.mol$^{-1}$) | $\Delta S$ (j.mol$^{-1}$) | $\Delta G$ (Kj.mol$^{-1}$) |
|---|---|---|---|---|
| 283.15 | 7.60±0.65 | -275 | -823.52 | -29.52 |
| 288.15 | 6.82±0.65 | | | |
| 293.15 | 6.10±0.65 | | | |
| 298.15 | 5.36±0.65 | | | |
| 303.15 | 4.38±0.65 | | | |
| 308.15 | 3.44±0.72 | | | |

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.

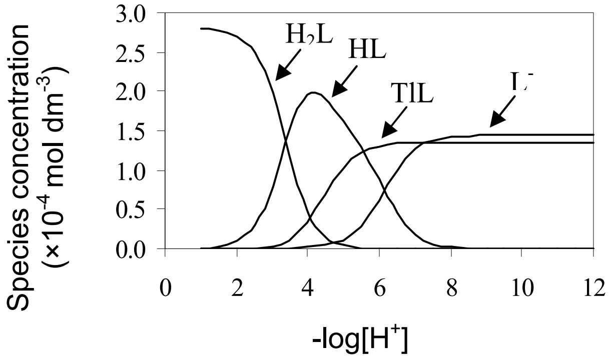


**Figure 2.** The equilibrium distribution of the species for the system Tl(I)-uracil as a function of log[$H^+$] at 298.15 K and constant ionic strength 0.1 mol $dm^{-3}$ $NaClO_4$.

## CONCLUSION

The stability constants of thallium(I) with uracil were calculated with spectrophotometric titrations using a chemometric method. The striking advantage of the proposed method is using of the whole spectral information in the computation process which enable us to have more precise and accurate thermodynamic constants in comparison to the classical methods such as single wavelength approach. The effect of the temprature on the acid dissociation and stability constants is investigated and it reveals the complex relations of the acid dissociation and stability constants to temprature. The results show good consistency with the previous reported results. However, the differences are mostly due to the different techniques, various ionic strengths with different background electrolytes, and different temperatures that were used.

## EXPERIMENTAL

### Chemicals

All the chemicals used were of analytical reagent grade. Uracil ($C_4H_4N_2O_2$) was obtained from Merck. The aqueous stock solutions of the uracil were freshly prepared daily. The NaOH solution was prepared from a titrisol solution (Merck), and its concentration was determined by several titrations with standard HCl. Perchloric acid and thallium (I) nitrate were from Fluka and were used without further purification. Dilute perchloric acid solutions were standardized against standard NaOH solution. Sodium perchlorate was purchased from Merck and was kept in a vacuum at least 72 h before use.

All The reagents were used without furthere purification and dilute solutions were prepared from double-distilled water with specific conductance equal to (1.8 ± 0.1) $\mu\Omega^{-1}$ $cm^{-1}$.

### 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 [30]. 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 [31].

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.

### Procedure

Volumes of 10 $cm^3$ acidic solution of $Tl^+$ [($3.85\times10^{-5}$ to $2.8\times10^{-4}$ mol $dm^{-3}$)] was titrated with an alkali solution (0.1 mol $dm^{-3}$ NaOH) of the uracil [($8.05\times10^{-5}$ to $1.6\times10^{-4}$ mol $dm^{-3}$). Titration of each the heterocyclic base was carried out at 6 temperatures (283.15, 288.15, 293.15, 298.15, 303.15 and 308.15) K in ionic strength 0.1mol $dm^{-3}$. 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.

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