STUDY OF THE COMPLEX EQUILIBRIUM BETWEEN TITANIUM (IV) AND TANNIC ACID

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ABSTRACT

Titanium-tannin (Ti-TA) complex is used in the modern leather technology as an alternative of chromium tannage and as an effective modification of vegetable tanning. The ratio between metal and tanning reagent is a key factor for minimizing the unused quantities of tannic acid that could reach the environment by waste waters and cause damages on aqueous ecosystems. However, a lack of reliable data about Ti-TA complexation limits the possibility for fine tuning of the composition of tanning solutions. This study is aimed at characterization of titanyl-tannin complex: its structure, stoichiometry and stability constant. The data of alpha-coefficient of titanyl-hydroxocomplexation at different pH values were also presented. The results obtained showed that in the concentration interval 5x10^-6 – 2x10^-4 M and pH 4, the main titanium IV species in titanyl/tannin/formate solutions is titanyl-hydroxo-tannin complex TiO(OH)TA. It was proved by UV-Vis and IR spectrometry that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen of tannin are involved in the coordination of titanyl ion. The stability constant of TiO(OH)TA was estimated: lgβ = 16.53. The obtained molar ratio curves and the calculated values of the equilibrium constants could be used in leather technology for selecting an appropriate composition of tanning solutions.

Keywords: tannin, titanium, titanyl, stability constant, complexation, leather tanning.

INTRODUCTION

The titanium-tannin (Ti-TA) complex is a modern tanning-coloring agent used in leather technology research in attempts to replace the synthetic dyes with natural ones and to decrease the level of allergic impact of produced leather. Moreover, the leather treated with tannic acid, is supposed to possess at a certain level the antimicrobial and antifungal properties of the used metal-tannin complexes [1, 2]. The leather treated by titanium (IV) - tannin solution is very soft, flexible and possess good thermal stability [3]. The leather technology calls for proper data about the Ti-TA complex composition and stability so that to achieve a fine tuning of the composition of tanning solutions. The ratio between metal and tanning reagent is a key factor for minimizing the unused quantities of tannic acid in wastewaters. On the one hand, high levels of tannic acid in water provoke an intensive grow of algae, on the other hand, tannin decomposition rapidly increases water COD and causes damages on aqueous ecosystems. A detailed study of the Ti (III) – tannic acid mixture in a combined tanning procedure was reported by Bo Teng et al. [3]. Tannins with different origin and different content of gallic acid were studied. The results presented showed that the quality of the treated leather depends on the structure and origin of the used tannins.

The data about Ti-TA complexes found in the literature are very scarce. Tannic acid was reported as an effective precipitating reagent for titanium determination in chloride solutions [4]. Spectrophotometric determination based on titanium complexation by tannin and thioglycolic acid was described [5], however the structure and the origin of studied tannin, as well as the
absorption spectra of the formed compound were not presented. The strong complexation of Ti (IV) by tannin was used for photosensitization of nanocrystalline TiO$_2$ films [6]. The force of induced photoelectricity depends on the structure and origin of the used tannin. Electrospray mass spectrometry was applied to study copper complexation by ligands derived from tannic acid [7]. Although the proposed method is important for characterization of different classes of ligands found in natural waters, quantitative data about their stability constants are not presented.

The chemistry of Ti (IV) salts tanning is reported to be dominated by the titanyl ion TiO$^{2+}$ [1, 9]. The complexes formed in water-sulphuric acid are described as chains of titanium ions bridged by hydroxy and sulphato ligands [10]. An advantage of tanning with titanium (IV) is the resulting white leather. However, Ti (IV) salts tend to hydrolyse and precipitate in dilute solution [1]. The hydrolysis of such titanium complexes proceeded through the coordination of hydroxo groups and formation of oxo bridges. The higher the concentration of Ti (IV) and sulphuric acid is the more extensive the degree of polymerization is [9]. It was proposed that mixtures of the metal sulphates could be stabilised against hydrolysis at pH 4 by complexing (masking) with gluconate [1].

In the research literature tannic acid (tannin, gallo-tannin, TA) is used to designate a large group of naturally occurring polymers with different structure and molecular mass. This fact illustrates the main difficulty of using the available in the literature data: the lack of specified information about the molecular mass and the origin or structure of studied tannins limits the application of available data and the comparability of the results. This study is focused on tannin (C$_{76}$H$_{122}$O$_{66}$) with molecular mass 1 701.20 g/mol and structure described in [11], often named as “Chinese tannin” as it is found in a pure form in Chinese gals (Rhus semilata) and Sumac (Rhus typhina) [12]. Our interest to Sumac is determined on the one hand, by the fact that Sumac is a plant largely available in Europe traditionally used for vegetable leather tanning [13], and on the other hand, it could be isolated in enough pure form so that comparable quantitative data to be reported.

The aim of this study is to characterize the TiO$^{2+}$-TA complex: its structure, stoichiometry and stability constant. The study was performed at formate buffer solution. The chosen experimental conditions are supposed to correspond more closely to the combined tanning conditions than the acetate buffer experiments often found in the literature [5]. Additionally, our recent study reported that tannic acid (Chinese tannin) is a monoprotic acid with pK = 4.2 and could be regarded as a moderately strong acid [11]. The results showed that the proton of the phenolic group in the next-to-last galloyl residue in the tannin chain is more likely to govern the protolytic reaction.

**EXPERIMENTAL**

**Reagents**

The stock solution of TiO$^{2+}$ (2.087x10$^{-2}$ M) was prepared from TiO$_2$ (p.a.; Merck 99.99 %) fused with K$_2$SO$_4$ at 780°C (p.a.; Merck). The obtained melt was dissolved in 25 mL 33 % v/v H$_2$SO$_4$ at heating, after cooling the solution was diluted up to 100.0 mL with d. H$_2$O. Working standard solutions were daily prepared from the stock solution by appropriate dilution. The tannin stock solution (1.000 x 10$^{-3}$ M) was daily prepared from dried at 105°C for 1h tannin reagent (p.a. Fluka, 403040) and dissolving in d.H$_2$O. The formate buffer (0.2 M, pH = 4.00 ± 0.02) was prepared from formic acid and potassium hydroxide (p.a.; Merck). The pH was potentiometrically controlled by Boeco (Germany) combined pH electrode. Distilled water was used throughout the experiments.

**Procedures**

Molar ratio method. Working solutions at different tannin/TiO$^{2+}$ molar ratios were prepared by mixing 25 mL formate buffer (pH 4.00) with calculated volumes of the tannin stock solution (10$^{-3}$ M) and finally adding the appropriate aliquots of 1.070 x 10$^{-3}$ M solution of TiO$^{2+}$. The final volume of 50.00 mL was obtained by dilution with d. H$_2$O. After 20 min reaction time, the absorbance was measured at 322 nm in 1 cm cuvette. A blank containing the same quantity of tannin solution in formate buffer was used as a reference. The measurements were made at 25±1°C. The spectra were acquired at Cary 100 Varian spectrophotometer (Agilent).

IR spectrometry. Titanyl-tannin (TiO-TA) complex was obtained by mixing TiO$^{2+}$ and tannin solution at molar ratio 1:2 at pH 4.00 (formate buffer). The obtained yellow solution was stable during one hour. After 24 h the precipitate was formed. The obtained precipitate was dried at room temperature. The IR spectra were registered on KBr by Alfa Aesar spectrometer.
RESULTS AND DISCUSSION

NMR study of the tannin

The NMR spectra of the studied tannin is presented on Fig. 1. As can be seen, the number of the protons from the galoylic part of the molecule is 10 times higher than the number of the protons in the glucose part. This fact proves the assumed number of galoylic residues in tannin molecule. Additionally, a large signal at 7 ppm showed that some tannin monomers combined to form oligomers. The carbon NMR spectra of the tannin couldn’t be registered due to the low solubility of tannin in denatured solvents. The structure of studied tannin is presented on the Fig. 1B [11].

Spectroscopic study of the reaction between TiO$_2^{+}$ and tannin

Electronic spectra of titanyl, tannin and titanyl-tannin mixture in formate buffer at pH 4 are presented on Fig. 2. The formed complex is clearly manifested by a red shift of wave length of maximum absorption from 275 nm (tannin solution) to 300 nm (solution of TiO-TA complex) ($\Delta \lambda = 25$ nm) and by a new shoulder appearing at 400 nm. The color of the complex aqueous solution was bright yellow and the spectra profile was independent of the chemical composition of used buffers: acetate and formate. The buffer compositions at pH around 4 were chosen based on literature data [5]. However, the concentration of acetate buffer should be very high (4 M) to maintain a sufficient buffer capacity which was related to severe inconveniences in routine laboratory work. Moreover, a slight increase of the absorbance at 320 nm was noticed in formate buffer (pH 4.00) compared to the absorbance of the complex obtained in acetate buffer (pH 3.40). As regarding the application of titanyl-tannin complex in leather technology, additional advantage of formate buffer as a medium for complex study is the fact that the procedure of leather pickling is performed in HCOOH solutions. Thus the study of titanyl-tannin complex was further performed in a formate buffer. The spectra of the formed complex measured against an analytical blank containing tannin and formate buffer are presented on Fig. 3. The absorbance of pure tannin was extracted from the spectra of the titanyl-tannin complex to obtain the pure complex spectra. The differential absorbance at 270 nm due to the absorption by C=O groups in tannin molecule [14] had negative values indicating that the C=O groups did not absorb UV- light at this spectral region. The formation of titanyl-tannin complex by coordination via C=O could be supposed. The absorbance of the complex depended on the concentration of titanyl ions in the solution (Fig. 3). The maximum differential absorbance of the obtained complex was measured at 322 nm. It is worth to be

![Fig. 1. NMR spectra (A) and proposed structure (B) of the studied tannin.](image1)

![Fig. 2. UV-Vis spectra of: (1) TiO$_2^{+}$ (C = 8.35x10$^{-6}$M); (2) tannin (C = 8.54x10$^{-6}$ M) and (3) TiO$_2^{+}$-tannin mixture at pH 4 (0.1 M formate buffer). Blank: d. H$_2$O.](image2)
mentioned that at this wave length the complex TiO(OH)$_2$, formed in formate buffer solution of TiO$^{2+}$ at pH 4.00 did not absorb photons (Fig. 2, curve 1).

The complex formation was verified by IR spectroscopy on KBr. For IR study the complex was obtained at molar ratio of TiO$^{2+}$ to tannin equal to 1:2. The obtained solution of the complex was stable for an hour. The yellow colored complex was obtained by precipitation for 24 h. IR spectra of TiO$_2$, tannin and the complex are presented on Fig. 4. In the region of hydrogen bonded OH groups (3500-3200 cm$^{-1}$) a strong wide band at 3289-3228 cm$^{-1}$ was observed in the tannin spectrum (Fig. 4A). The band was assigned to the stretching vibrations of hydrogen bonded phenolic hydroxyl groups ($\nu$(OH)) and the formation of associates between tannin molecules and also intramolecular hydrogen bonds were supposed. The corresponding band wasn’t observed in TiO$_2$ spectrum. The moderately strong band at 3424 cm$^{-1}$ in the IR spectra of the complex could be also assigned to O-H stretching vibration of coordinated OH groups or of lattice water molecules [15]. The reduced intensity of the band in the region 3500-3200 cm$^{-1}$ showed the decrease in the number of H-bonded OH groups. The positive shift of the band ($\nu$(OH)= 3424 cm$^{-1}$; $\Delta \nu$(OH) = 135 cm$^{-1}$) suggested the coordination of tannin molecules with the metal ions via deprotonation [16]. The band due to C=O stretching vibration that appeared at 1715 cm$^{-1}$ in the aromatic carboxylic acids (Fig. 4A) [17] was almost vanished in the complex. The decrease in the band intensity confirmed the participation of oxygen in the C=O---M bond. The changes in the spectra profile in the region 1300-1000 cm$^{-1}$ prove that phenolic oxygen was also involved in the coordination of metal ion. The IR data suggest that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen are involved in the coordination of titanyl ion. Hence in the studied complex tannin acts as a polydentate ligand coordinating through the oxygen of C=O and OH groups. The changes of the number and the intensity of the bands in the region 1700-700 cm$^{-1}$ might be due to chelate rings formation in the complex. The coordination of OH ions or H$_2$O was also supposed based on bands at 3424 cm$^{-1}$ and 787 cm$^{-1}$ [18]. As can be seen from Fig. 4A and 4C, the large peak at 598-533 cm$^{-1}$ in TiO$_2$ spectrum disappeared in the spectrum of the complex and a new peak could be found at 455 cm$^{-1}$. The absorption band at 455 cm$^{-1}$ was attributed to Metal---O stretching vibrations. Based on the presented data, the following composition of the complex in a solid form, obtained after precipitation and drying, could be supposed [Ti(OH)$_2$TA]$^+$ [21, 22].
Spectrophotometric study of the titanyl-hydroxo-tannin complex

The molar ratio method was chosen for this study as the exact concentrations of metal and ligand for practically complete complex formation process could be easily obtained from the curves \( A = f(C_{\text{tannin}}/C_{\text{titanyl}}) \). The obtained results are presented on Fig. 5. Each curve was constructed from a large number of experiments in order to obtain reliable results; each point was obtained as a mean of six values of absorbance of two solutions at the same concentrations. The formation of a complex at 1:1 molar ratio between \( \text{TiO}^{2+} \) – tannin was proved by the intercept of two linear parts of the curves. The obtained results have showed that the absorbance increased linearly with the concentration of titanyl ions at titanyl/tannin ratios more than 2 (Fig. 5B). The following equation was obtained: \( A = 0.002 + 37.453xC_{\text{TiO}^{2+}} \) with correlation coefficient of 0.999 (Fig. 5B). As it was described above, the only absorbing species at 322 nm was the titanyl-tannin complex (Fig. 2, curve 3). Hence, the concentration of the formed complex TiO-TA increased linearly with the concentration of TiO\(^{2+}\) and the molar absorptivity of TiO-TA complex could be calculated from the slope of the curve presented on Fig. 5B: \( \varepsilon = 3.75 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1} \). The results showed also that the Beer’s law was obeyed in the studied concentration interval of the complex.

At the conditions of the present study (pH 4, formate buffer), a formation of TiO(OH)\(^-\) complex could also proceed in a considerable extent. The calculated values of alpha coefficients, based on the previously reported stability constant of titanyl-hydroxo complex TiO(OH)\(^-\):

\[
\lg \beta = 13.7 \quad [19]
\]

are presented on Fig. 6. The logarithmic value of \( \alpha_{\text{TiO(OH)}} \) at pH 4 was 3.7 or \( \left[ \frac{[\text{TiO(OH)}]}{[\text{TiO}^{2+}]} \right] = 10^{3.7} \). As it could be seen from the Fig. 2, curve 1, the species TiO(OH)\(^-\) did not absorb photons at the wave length chosen for the absorbance measurement in the mole ratio method (322 nm).

Based on the above mentioned results, the formation of a mixed ligand titanyl-hydroxo-tannin TiO(OH)TA complex was supposed at the studied conditions. The coordination of OH- as a second ligand has been already reported for some Ti (IV) or titanyl complexes [21, 22]. The following mechanism of the complex formation and corresponding equilibrium constants were proposed:

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\text{Fig. 5. Molar ratio plots at different concentrations of TiO}^{2+} \text{ at pH 4: (1) 6.04x10^{-6}M; (2) 8.35x10^{-6}M; (3) 1.15 \times 10^{-5}M and (4) 2.00x10^{-5}M. The absorbance was measured at 322 nm against an analytical blank.}
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\text{Fig. 6. Logarithmic values of } \alpha_{\text{TiO(OH)}} \text{ at different pH.}
\]
The overall equilibrium constants could be described as:

\[ K_1 = \frac{[TiO(OH)]^+ [H^+]}{[TiO^{2+}]} ; \beta_1 = \frac{[TiO(OH)]}{[TiO^{2+}][OH^-]} \]  

(1)

\[ [TiO(OH)]^+ + TA^- \leftrightarrow [TiO(OH)TA] \]

(2)

\[ TiO^{2+} + TA^- + H_2O \equiv [TiO(OH)TA] + H^+ \]  

(3)

The results obtained in this study warrant the conclusion that at concentrations in the interval 5x10^{-6} – 2x10^{-5} M and at pH 4 the main titanium (IV) species in titanyl tannin formate solutions is titanyl-hydroxo-tannin complex [TiO(OH)TA]. It was proved by UV-Vis and IR spectrometry that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen of tannin are involved in the coordination of titanyl ion. It was supposed that in a solid form the complex composition is [Ti(OH)TA]^+. The stability constant of TiO(OH)TA was estimated: \( lgK' = 16.53 \). The obtained molar ratio curves and calculated values of the derived constants could be used by leather technologists for selecting an appropriate composition of tanning solutions.

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