Boric Acid Detection in Water by Gallacetophenone

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Abstract

The detection of boron down to ppt order in ultrapure water is required to ensure high-quality and stable semiconductor manufacturing. To realize a simple yet sensitive method for the detection of boron (boric acid), we designed a ruthenium complex possessing a stable ligand with boric acid sensing function. Gallacetophenone (2’,3’,4’-trihydroxyacetophenone) ligand has a β-diketone moiety that can coordinate to a metal and a cis-diol moiety that shows reactivity with boric acid. Comparison of UV-vis absorption spectra measured in the presence and absence of boric acid at various pH revealed that gallacetophenone showed the greatest response to boric acid at pH 8.58. From the spectral changes in the absorbance of gallacetophenone aqueous solution in various concentrations of boric acid at pH 8.58, decreases in the absorbance at the wavelength of 330 nm were observed with increasing boric acid concentration. On the basis of the relationship between the absorption spectra and the boric acid concentration, the binding constant (assuming a 1:1 binding model) for the interaction between gallacetophenone and boric acid was estimated to be 420.7 ± 28.0 mol⁻¹ dm³. The electrochemical detection of boric acid was also conducted.

Keywords: Gallacetophenone, Boric acid, Absorptiometry, Voltammetry

1. Introduction

Boron is an essential nutrient in humans, but excessive intake of this element has produced deleterious effects on the human body[1-4]. Therefore, boron detection is particularly important from the perspective of water quality conservation. In countries that lack water resources, drinking water is derived from seawater treated in seawater desalination facilities using reverse osmosis (RO) membranes[5,6]. However, there have been cases of boron leakage from RO membranes[7,8]. Seawater contains approximately 4 mg/L of boron[3,4], and this concentration exceeds Japanese tap water quality standards[4]. It is necessary to treat boron and monitor its concentration in seawater desalination facilities.

Semiconductors are indispensable components of electronic devices used in today’s society. In the semiconductor manufacturing process, large volumes of ultrapure water used as rinsing water for semiconductors are re-processed mainly through RO membranes. To maintain the quality and stability of semiconductors, the ultra-sensitive detection of boron down to ppt order in ultrapure water is required[6-7].

The present circumstances call for the development of a simple yet sensitive boron detection method. Current methods for boron quantification, such as methylene blue absorptiometry[8-9] and azomethine-H absorptiometry[4,10,11], are complicated and the detection sensitivity is of ppm order. Alternatively, expensive equipment that has high sensitivity and enables rapid measurement is available, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES)[11-13] and inductively coupled plasma-mass spectrometry (ICP-MS)[5,13,14]. The development of a new boron quantification method that can overcome these problems is anticipated.

Many colorimetric reagents for boron detection have been proposed[15-19]. These reagents possess a cis-diol moiety or a β-
diketone moiety that reacts with boric acid\textsuperscript{16-20}. In this study, we look into the use of a ligand that has a cis-diol moiety for the detection of boron in ultrapure water.

We attempt to detect boron using a (β-diketonato)ruthenium complex possessing a gallacetophenone ligand. We focus on gallacetophenone (2′,3′,4′-trihydroxyacetophenone, Fig. 1), which is the simplest organic compound having a β-diketone moiety and a cis-diol moiety. Gallacetophenone has relatively high solubility in water, and the bond between the cis-diol moiety and boronic acid is expected to have a large electronic effect on the metal coordination moiety. The reactivity with boronic acid of gallacetophenone when used as a ligand of the (β-diketonato)ruthenium complex is investigated by UV-vis absorption measurement and voltammetry.

2. Materials and Methods

2.1 Apparatus

All pH values were recorded with a Horiba F-52 or F-72 pH meter (HORIBA, Ltd., Kyoto, Japan). UV-vis absorption spectra were measured with a Jasco V-570 (Jasco, Inc., Tokyo, Japan) using a 1.0-cm quartz cell. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were conducted by using ALS600D (BAS, Inc., Tokyo, Japan) as the potentiotstat, 3-mm-diameter GCDE (BAS, Inc., Tokyo, Japan) as the working electrode, Ag/AgCl \( 3 \text{ M NaCl} \) (BAS, Inc., Tokyo, Japan) as the reference electrode, and a 23-cm platinum wire electrode (BAS, Inc., Tokyo, Japan) as the counter electrode.

2.2 Reagents

Gallacetophenone was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Sodium hydroxide, HEPES, and sodium perchlorate monohydrate were purchased from FUJIFILM Wako Pure Chemical, Ltd. (Osaka, Japan). Boric acid was purchased from Kanto Chemical, Co., Inc. (Tokyo, Japan). \( N \)-Cyclohexyl-2-aminoethanesulfonic acid (CHES) was purchased from Chemical Dojindo Co., Ltd. (Kumamoto, Japan). Acetonitrile (HPLC grade) and acetonitrile (dehydration grade) were purchased from Sigma-Aldrich Japan, Co., LLC. (Tokyo, Japan) and Kanto Chemical, Co., Inc. (Tokyo, Japan), respectively. All reagents were used as received. Ultrapure water was doubly distilled and deionized by a Milli-Q water system (WG222, Yamato Scientific Co., Ltd., Tokyo, Japan; and Milli-Q Advantage, Merck Millipore, MA, USA) before use.

2.3 Preparation of measurement solutions with/without boric acid at various pH

Two solutions of HEPES (71.50 mg, 0.30 mmol) and gallacetophenone (0.50 mg, 2.97 μmol) in Milli-Q water (60 mL) were prepared, and boric acid (3.71 mg, 60 μmol) was added to one of these solutions. The absorption spectra of gallacetophenone aqueous solutions with/without boric acid at various pH were measured. The pH of each solution was adjusted by adding sodium hydroxide aqueous solution.

2.4 Preparation of UV-Vis measurement solutions having various boric acid concentrations

Gallacetophenone (10.17 mg, 60 μmol) was added to 10 mL of acetonitrile. After 2 min stirring, a 100 μL portion of this solution was added to 12 mL portion of 10 mM CHES buffer solution containing various concentration of boric acid and adjusted to pH 8.58 by adding NaOH\textsubscript{aq} solution. The solution was mixed using a stirrer and UV-Vis spectral measurement was started at 3 min later from the addition. The same procedure was used to prepare solutions having different boric acid concentrations.

2.5 Electrochemical setup and measurement conditions for gallacetophenone aqueous solutions with/without boric acid

Gallacetophenone (5.0 mg, 30 μmol) and sodium perchlorate monohydrate (735 mg, 5.23 mmol) were dissolved in Milli-Q water (60 mL). The solution was adjusted to pH 8.58 by adding NaOH\textsubscript{aq} solution. A 3 mL aliquot of this solution was used for CV and DPV measurements. Boric acid (176 mg, 2.85 mmol) was added to the remaining 57 mL portion, and this solution was used for CV and DPV measurements.

CV measurement was conducted with the potential window between -1.0 and 1.0 V, the scan rate of 0.1 V/s, and the quiet time of 10 s at room temperature. DPV measurement was performed at room temperature with the potential window between 0 and 1.0 V, the pulse amplitude of 50 mV, the pulse width of 60 ms, the sample width of 20 ms, and the pulse period of 0.2 s. All solutions were bubbled with argon gas for 2 min before measurement.

3. Results and Discussion

3.1 Determination of pH for reaction of gallacetophenone with boric acid

The absorption spectra of gallacetophenone in 100% aqueous solution without boric acid were measured at various pH values, and the results are shown in Figs. 2A and 2B. The peaks at wavelengths of 233 nm and 288 nm disappeared as the solution became basic with the addition of sodium hydroxide. On the other hand, the peaks at wavelengths of 248.5 nm and 330 nm appeared and reached a maximum at pH 9.75 as the solution became basic. At this time, isosbestic points were
observed at 240 nm, 260 nm, and 303.5 nm. When the pH was increased further, the peaks at 248.5 nm and 330 nm disappeared and the peak at 392 nm appeared. In an analogous manner, the disappearance and appearance of peaks were observed for the solutions with boric acid, but no isosbestic point at 240 nm was apparent (Figs. 2C and 2D).

The absorbance at the wavelength of 237.5 nm for the gallacetophenone aqueous solutions with/without boric acid was plotted against pH (Fig. 3). The difference was maximum at pH 8.58. This result indicated that gallacetophenone and boric acid react at pH 8.58 in water.

3.2 Absorption spectral changes at various boric acid concentrations at pH 8.58

From the results of section 3.1, the UV-vis absorption spectra of gallacetophenone aqueous solutions with different boric acid concentrations at pH 8.58 were measured, and the results are shown in Fig. 4. The absorbance at the wavelengths of 237.5 nm and 305 nm increased and that at the wavelength of 330 nm decreased as boric acid concentration increased. The intensity at 240 nm was measured at various boric acid concentrations. Binding constant \( (K') \) was calculated from the plot of intensity at 240 nm against boric acid concentration (Fig. 4B). The data were analyzed by using the KaleidaGraph program according to a theoretical equation derived from the 1:1 binding model (Eq. 1):

\[
I - I_0 = \frac{I_{lim} - I_0}{2c_B} \left[ \frac{c_g + c_B + 1}{K'} - \left( \frac{c_g + c_B + 1}{K'} \right)^2 - 4c_g c_B \right]^{1/2} \tag{1}
\]

where \( c_g \) and \( c_B \) are the total concentration of gallacetophenone and boric acid; \( I \) and \( I_0 \) represent the absorbance intensity at 240 nm in the presence and absence of boric acid, respectively; \( I_{lim} \) is the absorbance at 240 nm when the change of \( I \) reaches saturation; and \( K' \) is the conditional equilibrium constant for the reaction of gallacetophenone with boric acid. The binding
constant for the interaction between gallacetophenone and boric acid was estimated to be $420.7 \pm 28.0 \text{ mol}^{-1} \text{ dm}^{3}$.

3.3 Electrochemical measurement of gallacetophenone with/without boric acid at pH 8.58

CV and DPV measurements of gallacetophenone without boric acid in water at pH 8.58 yielded current peaks at 0.10 V, 0.32 V, 0.70 V, and 0.82 V. In the case of gallacetophenone aqueous solution with boric acid, the current peak at 0.10 V disappeared and the current peaks at 0.32 V, 0.70 V, and 0.82 V became smaller. These changes were caused by the reaction of gallacetophenone and boric acid and suggested the possibility of electrochemical detection of boric acid in water.

3.2 Absorption spectral changes at various boric acid concentration

Fig. 4 (A) UV-vis absorption spectral changes of gallacetophenone aqueous solution with the addition of boric acid, 10 mM CHES/NaOH buffer in 0.8% AN in water (B) without boric acid at (A) acidic pH and (B) basic pH, and (C) acidic pH and (D) basic pH.

The absorbance at the wavelengths of 240 nm and 305 nm increased and that at the wavelength of 330 nm decreased with increasing boric acid concentration. Electrochemical measurements were performed on gallacetophenone aqueous solutions with/without boric acid at pH 8.58. In the case of gallacetophenone aqueous solution with boric acid, the current peak at 0.10 V disappeared and the current peaks at 0.32 V, 0.70 V, and 0.82 V became smaller. Our gallacetophenone-based boron detection method is rapid, simple, and economical, but lacking in sensitivity. We are investigating more sensitivity boron detection method that employs a ($\beta$-diketonato)ruthenium complex with gallacetophenone as the ligand.

4. Conclusion

Aiming to develop a simple yet sensitive boron detection method, we investigated the reactivity of gallacetophenone with boric acid by UV-vis absorption and voltammetry measurements. The absorption spectra of gallacetophenone aqueous solution with/without boric acid at various pH were investigated. Gallacetophenone showed the best response to boric acid at pH 8.58 in water. The absorbance changes of gallacetophenone aqueous solution with various concentrations of boric acid at pH 8.58 were measured. The absorbance at the wavelengths of 240 nm and 305 nm increased and that at the wavelength of 330 nm decreased with increasing boric acid concentration. Electrochemical measurements were performed on gallacetophenone aqueous solutions with/without boric acid at pH 8.58. In the case of gallacetophenone aqueous solution with boric acid, the current peak at 0.10 V disappeared and the current peaks at 0.32 V, 0.70 V, and 0.82 V became smaller. Our gallacetophenone-based boron detection method is rapid, simple, and economical, but lacking in sensitivity. We are investigating more sensitivity boron detection method that employs a ($\beta$-diketonato)ruthenium complex with gallacetophenone as the ligand.

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