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Voltammetric study of the boric acid-salicylaldehyde-H-acid ternary system and its application to the voltammetric determination of boron[†]

Mari Kajiwara,[a] Yoshio N. Ito,[a] Yoshinobu Miyazaki,[b] Takao Fujimori,[c] Kô Takehara[a] and Kazuhisa Yoshimura[a]*

[a] Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan. E-mail: kazz@chem.kyushu-univ.jp

[b] Department of Chemistry, Fukuoka University of Education, Akamabunkyo-machi, Munakata, Fukuoka 811-4192, Japan

[c] Department of Chemical Science and Engineering, National Institute of Technology, Miyakonojo College, Yoshio-cho, Miyakonojo, Miyazaki 885-8567, Japan

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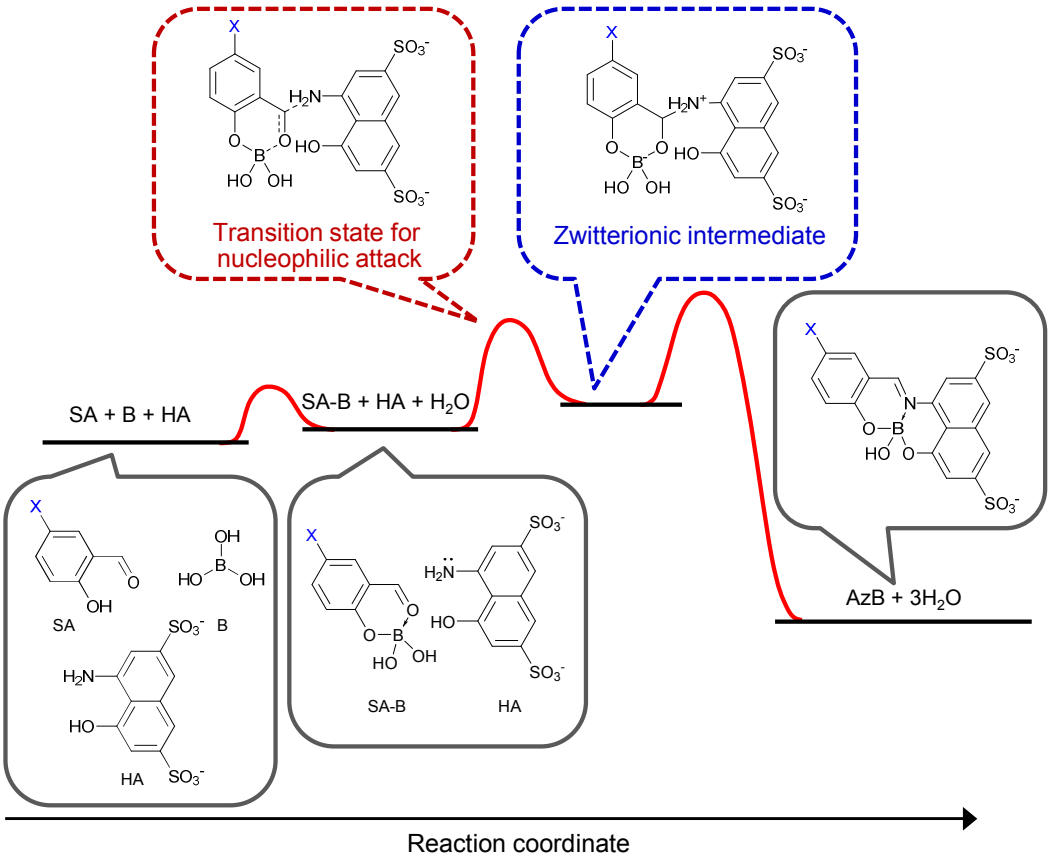
We fully elucidated the three-component reaction kinetics and thermodynamics of a boric acid complex with H-acid and salicylaldehydes by voltammetry and NMR spectroscopy.



Abstract

The ternary system of boric acid, salicylaldehyde (SA) and H-acid (HA) was voltammetrically studied from kinetic and equilibrium points of view. The effect of the SA substituents was also studied by using two analogs, 5-fluorosalicylaldehyde (F-SA) and 5-methylsalicylaldehyde (Me-SA). The three cathodic peaks of Azomethine H (AzH), Azomethine H-boric acid complex (AzB), and free SA were observed in the solution containing boric acid, SA and HA. The peak potentials of AzH and SA were shifted negative with the increasing pH, while that of AzB was pH-independent. This difference indicates that a proton participates in the charge-transfer steps of the AzH and SA reductions, but not in that of the AzB reduction. The formation constants for the AzB complexation were similar among all the examined analogs. In the kinetic study, the reaction rate was higher in an acidic condition for the AzH formation, whereas in a neutral condition for the AzB formation. The rate constants for the AzB complexes were in the order of F-SA > SA ≈ Me-SA, indicating that the fluoro group accelerates the F-AzB complexation. The AzB complexation mechanism is considered to consist of more than three steps; *i.e.*, the pre-equilibrium of the salicylaldehyde-boric acid complex (SA-B) formation, the nucleophilic attack of HA on SA-B, and remaining some steps to form AzB. Based on these results, the voltammetric determination method of boron using F-SA was optimized, which allowed the boron concentration to be determined only within 5 min with a 0.03 mg B dm^{-3} detection limit.

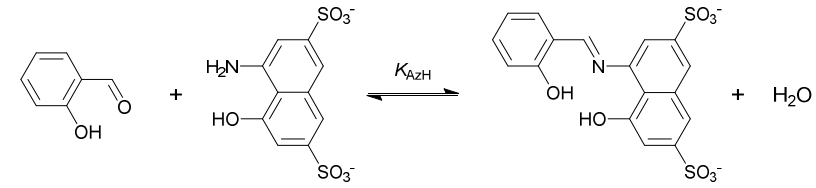
Introduction

Boron mainly exists as boric acid or the borate anion. Boric acid acts as a Lewis acid to produce the borate anion, accepting the electron pair of a hydroxide ion [1]. It is well-known that boron produces chelate complexes by interactions between the borate and polyol compounds [2-6]. The complexation reaction of borate with polyol is characterized by the dehydration condensation reaction between the alcoholic hydroxyl groups of polyol and the hydroxyl groups of borate to give

mono and bischelate complexes. In the case of the acidic polyol, boric acid accepts an electron pair through the nucleophilic attack of the dissociated ligand, followed by a condensation reaction to form the 1:1 monochelate complex. The monochelate complex then reacts with the ligand through the condensation reaction to give the 1:2 bischelate complex [7-9]. For the development of adsorbents selective to boron and analytical methods of boron, reactions between the borate and various polyol compounds have been studied [10-16].

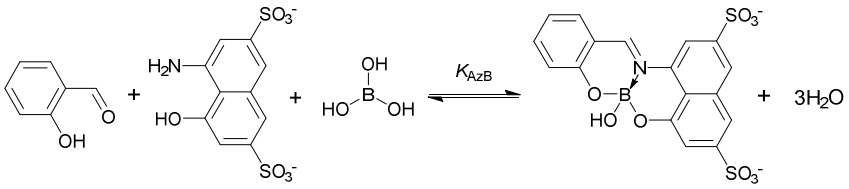
On the other hand, in the field of boron analysis, the boron concentration in water is determined by various methods as reviewed by Sah and Brown [17] and by Yoshimura *et al.* [18]. Among them, a significant number of spectrophotometric studies have focused on the development of methods which enable one to determine the concentration of boric acid in an aqueous solution under moderate conditions. The Azomethine H method, proposed by Capelle in 1964 [19], has been employed for the boron analyses of natural and waste waters, soils and plants [20-22]. Azomethine H (AzH, 8-hydroxy-1-(salicylideneamino)-3,6-naphthalenedisulfonic acid) is a Schiff base of salicylaldehyde (SA) and H-acid (HA, 1-amino-8-naphthol-3,6-disulfonic acid), and its solution exhibits an absorption maximum at 412 nm in the presence of boric acid. Different from polyols and acidic polyols, the interaction between boric acid and AzH has not been well understood, although a number of studies have been performed for the optimization of conditions for boron determination using AzH as a coloring agent. It has been pointed out in some papers that AzH reacts with boric acid to form chelate complexes in solution, and then the complexes exhibit an absorption maximum in the visible region. Some possible complexes were a 1:1 monochelate complex of trigonal boric acid, a 1:1 bischelate complex with tetrahedral boron, a 1:1 monochelate complex with tetrahedral boron, and its corresponding 1:2 complex [23]. On the contrary, Harp had suggested that the absorption maximum is due only to the AzH species [24]. Direct evidence regarding the coloring processes and the structure of the borate complex has not been provided until our ^{11}B NMR study [23]; ^{11}B NMR spectroscopy provided direct evidence that boric acid

reacts with AzH to form a 1:1 bischelate complex (AzB) with a new peak due to the chelate complex containing tetrahedral boron. It has been quantitatively confirmed that the reaction includes two chemical equilibria; one is related to the ligand formation and the other to the complex formation, as shown by the following equations.



Salicylaldehyde (SA) H acid (HA) Azomethine H (AzH)

(1)



Boric acid (B) Boric acid-Azomethine H complex (AzB)

(2)

The formation constant for the ligand is low, whereas that for the complex is relatively high. AzH is hydrolyzed in an aqueous solution due to its low stability, and the ligand formation is responsible for the nature of its complexation with boric acid.

The electrochemical determination is an easy and simple method, however, it cannot be applied to the direct determination of boron because boron usually exists as an electrochemically inactive form in solutions. Alternatively, the complexation of boric acid with an electroactive ligand can be applied to the electrochemical determination of inert boric acid by voltammetry through the change in the redox potentials of the ligand by complexation with boric acid [25]. We recently reported the voltammetric determination of boron using the boric acid-AzH system [26]. The cathodic peak of the SA, dissociated from the AzH reagent, affects the peak current of the target complex in the voltammograms, and therefore, the concentration of SA was carefully chosen as low as possible unless it affects the formation of AzB; *i.e.*, the complexation degree could be kept constant if the product of the concentrations of SA and HA was maintained constant, and the free

SA concentration was reduced by increasing the electrochemically inactive HA concentration. The unique dissociation-formation characteristics of AzH should provide a novel approach to design a voltammetric method optimized for the determination of boric acid using AzH.

Elucidation of the complexation mechanism is important to improve the condition for boron determination using AzH by not only voltammetry, but also by spectrophotometry. The AzB complexation between AzH and boric acid is not very fast for practical use. One of the purposes of this study was to clarify the boric acid-SA-HA system from kinetic and equilibrium points of view by combination of the voltammetric and ^{11}B NMR studies. We also clarified the effect of the substituent groups of salicylaldehyde on the AzB complexation using 5-fluorosalicylaldehyde (F-SA) and 5-methylsalicylaldehyde (Me-SA) instead of SA. Based on the determined properties, the voltammetric determination of boron using the boric acid-SA-HA system could be done within 5 min.

Experimental

Chemicals

All chemicals, except for boric acid, F-SA, Me-SA, and HA, were of analytical reagent grade and used without further purification. Deionized water prepared by a Milli-Q system (Millipore, USA) was used throughout the study. A boric acid solution was prepared by diluting the 1000 mg B dm^{-3} boron standard solution (Wako, Japan). A 0.05 mol dm^{-3} aldehyde solution was prepared by dissolving SA (Wako, Japan), F-SA (purity > 98.0%, Tokyo Chemical Industry, Japan) or Me-SA (purity > 98.0%, Tokyo Chemical Industry, Japan) in ethanol. The HA (8-amino-1-naphthol-3,6-disulfonic acid) was a reagent grade monosodium salt (Wako, Japan) and was used without further purification. The purity of HA was determined by acid-base titration of the amino group of HA to be 87.8 ± 1.6 % (n = 4). The rest is reported to be mainly water. The pH of the solution was adjusted using acetate (pH 4 – 6), phosphate (pH 6 – 8), and carbonate (pH 9)

buffer reagents. An excess of sodium hydroxide (Wako, Japan) was added to the buffer solution in order to neutralize HA. Sodium chloride (Wako, Japan) was added to adjust the ionic strength at 0.5 mol dm^{-3}.

Determination of acid dissociation constants of salicylaldehyde derivatives and HA

The acid dissociation constants were calculated according to the absorption spectra of the 3.7 × 10^{-4} mol dm^{-3} respective aldehyde derivative solutions measured at pH 1.76 – 8.99 and of 3.5 × 10^{-4} mol dm^{-3} HA solutions at pH 0.49 – 8.62. A U-3500s spectrophotometer (Hitachi, Tokyo) was used for the measurements. All the solutions were prepared under a nitrogen gas for avoiding the oxidation of reagents by oxygen. The ionic strength of the solutions was adjusted to 0.5 mol dm^{-3} using NaCl. The pH measurements were done using a Horiba pH meter, F-22 (Kyoto, Japan) with a glass electrode. The dissociation constants of the salicylaldehyde derivatives and HA were evaluated from their absorption spectra at different pHs using the non-linear least-square Solver program of Excel.

Voltammetric measurements

Square wave voltammetry (SWV) was performed by a BD-101 (Satoda Science, Japan). A conventional three-electrode system was used with a glassy carbon (3-mm diameter, BAS, Japan), Ag/AgCl (3 mol dm^{-3} NaCl, BAS, Japan), and platinum wire as the working, reference, and counter electrodes, respectively. The SWV parameters were as follows: the frequency was 100 Hz, the amplitude was 25 mV, and the step potential was 4 mV. The potential was scanned from -0.2 to -1.6 V (*vs*. Ag/AgCl).

For the kinetic study of the complexation, the time variation of the SWV signals was observed. The 20 cm^3 sample with or without 10 mg B dm^{-3} boric acid was used to investigate the processes for the AzH and AzB formations. The reaction was started after adding the aldehyde

solution to the mixture containing the buffer solution and HA with or without boric acid. The measurements were performed until the reaction reached equilibrium. The temperature was usually set at 298 K. For the measurement to estimate the activation parameters, the temperature was changed between 283 K and 303 K at 5 K intervals using a thermostated bath.

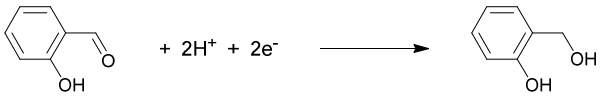
The concentration condition optimized in a previous study was employed for the determination of boron in this study [26]. The solution was prepared by adding a 5 cm^3 buffer solution, 0.25 g HA, and 1 cm^3 aldehyde solution to a 20 cm^3 sample solution. The solution was allowed to stand for 5 min before the SWV measurement after mixing these reagents. A calibration curve was prepared in the range between 0 and 10 mg B dm^{-3} boric acid.

A curve fitting program was used to separate the peak of the AzB complex from the other peaks for the SWV measurements. Allowing for an appropriate baseline, the shape of each peak was symmetric with respect to the applied potential. Therefore, the pseudo-Voigt function, which is a linear combination of the Lorentz and Gauss functions, was applied to the curve fitting (Fig. S1 in the ESI).

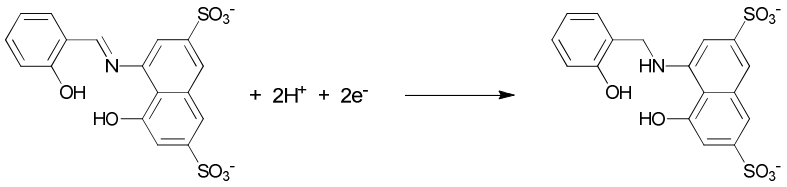
NMR measurements

^{11}B NMR measurements were performed using a JEOL JNM-ECX400 spectrometer at a resonance frequency of 128.3 MHz with 10-mm multinuclear probe at 296 K. The field frequency lock was achieved with the deuterium resonance of D_2O in a concentric capillary tube. The chemical shifts were referenced with respect to an external BF_3-OEt_2 standard at 0.0 ppm. On this scale, the signal of boric acid occurs at 19.4 ppm. The standard NMR parameters were as follows: the flip angle was *ca*. 90° (28 μs), the pulse repetition time was 1s, and the spectral width was 22 kHz. The sample solutions (the ionic strength was 0.5 mol dm^{-3}, NaCl) containing known amounts of boric acid/borate and ligands were prepared, and the pHs were adjusted with the buffer solutions. After being allowed to stand for about 100 min, the solutions were used for the NMR

177 measurements. A Lorenzian curve-fitting method was used to evaluate the individual signal
178 intensities.
179
180 **Results and discussion**
181 **SWV peak potentials**
182 The following three solutions were prepared for the assignment of the SWV peaks: a 2.0
183 mmol dm^{-3} SA solution (pH 4.3), a 2.0 mmol dm^{-3} SA and 25 mmol dm^{-3} HA solution (pH 4.3) with
184 or without 10 mg B dm^{-3} boric acid. Figure 1 shows the voltammograms of the SWV measurements
185 for these solutions. Only one peak was observed at -1.22 V in the solution containing only SA.
186 Thus, this peak can be assigned to the reduction of the free SA. For the solution containing SA and
187 HA without boric acid, another peak was observed at -0.92 V in addition to the SA peak. There
188 should be SA, HA, and AzH in the solution. Because HA is an electro-inactive species, the peak
189 can be assigned to the reduction of AzH. For the solution containing SA and HA with boric acid, a
190 third peak different from the SA and AzH peaks was observed at -1.04 V, and therefore, the peak at
191 -1.04 V was assigned to the reduction of AzB. In the same way, all peaks were assigned for each
192 system using F-SA or Me-SA.
193 Because protonation might be involved in the reduction process of SA, AzH, and AzB,
194 the effect of the solution pH on the SWV was examined (Fig. 2). The cathodic peak potentials of
195 both SA and AzH shifted to more negative potentials with the increasing pH. On the other hand, the
196 peak potential of AzB was scarcely affected by the pH change. Similar results were also obtained
197 for the F-SA and Me-SA systems. These results indicated that a proton participates in the case of
198 the SA and AzH reductions, which are shown in eqs (3) and (4). SA would be reduced to form the
199 salicylalcohol, and AzH would be reduced *via* the protonation of the C=N unit.
200

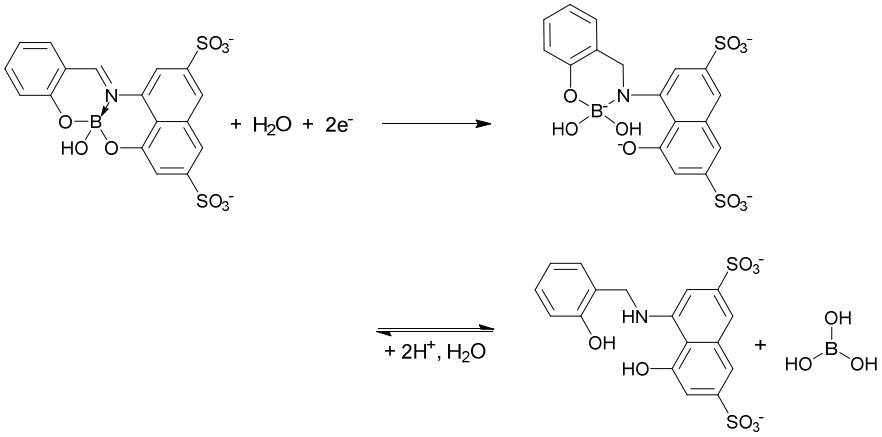


(3)



(4)

In contrast, because the peak potential of AzB is independent of the pH, the possible reaction may be given in the first step of eq (5).



(5)

The effect of the substituent on the peak potentials was also examined (Fig. 2). The cathodic peak potentials of the analogs differed depending on the aldehyde used at the same pH. The fluoro group is known as an electron-withdrawing group and expected to decrease the electron density of the reduction site. In fact, the peak potentials of the fluoro species became more positive than the other analogs. On the other hand, the methyl group is a weak electron-donating group, and the peak potentials of Me-SA were observed at a slightly more negative potential than SA. Because the shift was small, the methyl group did not have a great influence on the peak potentials.

The peak area of the cathodic current was used to determine each concentration of the electroactive species, that is, SA, AzH and AzB, because the charge transfer steps of these compounds include the same number of electrons as shown by eqs (3), (4) and (5).

Complexation equilibria of the boric acid-SA-HA system

The formation constants for the AzH and AzB formations (K_{AzH} and K_{AzB}) are defined by the following equations:

$$K_{AzH} = \frac{[AzH]}{[SA][HA]} \quad (6)$$

$$K_{AzH} = \frac{[AzB]}{[SA][HA][B]} \quad (7)$$

where [SA], [HA], [AzH], [AzB], and [B] are the concentrations of the respective species. The K_{AzH} and K_{AzB} values affect the observed reduction peak intensity of each corresponding species. The higher the formation constant, the higher the peaks of AzH and AzB would be obtained.

The K_{AzH} and K_{AzB} were estimated by analyzing the reduction peaks obtained by the SWV measurements for the solutions with or without 10 mg B dm^{-3}. The reactions were completed in about 60 min. To estimate the K_{AzH} and K_{AzB} values, the peak area (S) of each species obtained by separating the peaks was used. Because a large excess amount of HA was added relative to those of SA and boric acid, the concentration of free HA can be assumed to be constant. Thus, K_{AzH} can be calculated by eq (8).

$$K_{AzH} = \frac{S_{AzH}}{S_{SA} C_{HA}} \left(1 + \frac{K_a^{SA}}{a_{H^+}}\right)\left(\frac{a_{H^+}}{K_{a1}^{HA}} + 1 + \frac{K_{a2}^{HA}}{a_{H^+}}\right) \quad (8)$$

K_a^{SA} is the dissociation constant of SA defined by $K_a^{SA} = a_{H^+}[SA^-]/[SA]$, and K_{a1}^{HA} and K_{a2}^{HA} are the first and second dissociation constants of HA defined by $K_{a1}^{HA} = a_{H^+}[HA]/[HA^+]$ and $K_{a2}^{HA} = a_{H^+}[HA^-]/[HA]$, where a_{H^+} is the hydrogen ion activity. All the equilibrium constants

involved in the AzH formation are presented in Fig. 3.

For the estimation of K_{AzB}, the mass balance equation for the concentrations of the boron species is expressed as eq (9) in a pH range lower than the boric acid pK_a^B.

$$[B] = C_B - [AzB] \quad (9)$$

By using the total peak area $S_T = S_{SA} + S_{AzH} + S_{AzB}$ and the total concentration of SA (C_{SA}), K_{AzB} can be calculated by eq (10), because the charge transfer steps of these compounds include the same number of electrons (See eqs (3) – (5)).

$$K_{AzB} = \frac{S_{AzB}}{S_{SA} C_{HA} (C_B - (S_{AzB}/S_T) C_{SA})} \left(1 + \frac{K_a^{SA}}{a_{H^+}}\right)\left(\frac{a_{H^+}}{K_{a1}^{HA}} + 1 + \frac{K_{a2}^{HA}}{a_{H^+}}\right) \quad (10)$$

The K_{AzH} values determined by voltammetry and the K_{AzB} values determined by voltammetry (Tables S1 and S2 in the ESI) and ^{11}B NMR measurementsare shown in Table 1. In the case of SA as the aldehyde, Matsuo *et al*. reported that K_{AzH} is lower than 10 and K_{AzB} is $10^{5.91}$ (I = 0.1) [23]. These values are in fairly good agreement between the two methods. Among the examined analogs of salicylaldehyde, Me-SA was found to produce the lowest K_{AzH} value. The K_{AzB} values were similar among SA analogs, even though the value for Me-SA was a little lower than the others and the formation constants of the reaction, AzH + B ⇌ AzB, corresponding to K_{AzB}/K_{AzH}, were almost the same, which suggested that there are no differences in the free energy changes between AzB and AzH for the three aldehyde analogs.

Kinetic study on the boric acid-SA-HA system

The time variation of the SWV signals was observed using the solutions with or without 10 mg B dm^{-3} boric acid. The AzH and AzB formation processes were observed at pH 4.3 and 7.5 – 7.7. Figure 4 shows the voltammograms of the SWV measurements for the solutions containing SA and HA without boric acid. The peak intensity of AzH became constant within 10 min at pH 4.3, whereas it took about 30 min at pH 7.5. For this reason, the formation rate of AzH depended on the

pH and that the rate was higher at the low pH. Similar SWV peak trends were also observed at the SWVs of the F-SA and Me-SA species (Fig. S2 in the ESI). Generally, it is known that Schiff-base formation is catalyzed by protons. The pH dependence of the formation rates for various Schiff-bases was reported. For example, the formation reaction of *N*-*p*-chlorobenzylidene aniline became faster with the decreasing pH in the range of pH 4 to 6 [27], which is similar to the results obtained in this study.

Figure 5 shows the voltammograms of the SWV measurements for the solutions containing SA, HA and 10 mg B dm^{-3} boric acid. In this case, the pH dependence of the AzB formation rate was also observed. The peak intensities of AzB and its analogs increased for 40 min at pH 4.3, while they became constant within 10 min at pH 7.5 – 7.7. Contrary to the AzH formation, the rate of AzB was higher under a neutral condition than under an acidic condition.

In order to quantitatively discuss the substituent effect for the AzB complexation reaction, we estimated the rate constants for the reaction by analyzing in detail the voltammograms of the solution containing 10 mg B dm^{-3} boric acid. Equation (11) is the third-order rate equation of the overall reaction of the formation of AzB from SA, HA, and boric acid.

$$v = \frac{d[\mathrm{AzB}]}{dt} = k_{\mathrm{app}}[\mathrm{B}][\mathrm{SA}][\mathrm{HA}] \qquad (11)$$

This rate constant is defined as the apparent rate constant (k_{app}), and was experimentally obtained here (Table 2). Because a large excess amount of HA was added, eq (11) can be approximated by the pseudo-second order equation. At pH 4.3, the AzH formation is fast, so it was considered that the reaction had already reached equilibrium in the measured time period. Equation (11) can then be converted to eq (12) using the mass balance equations.

$$\frac{d[\mathrm{AzB}]}{dt} = k_{\mathrm{app}} \cdot \frac{C_{\mathrm{HA}}(C_{\mathrm{SA}} - [\mathrm{AzB}])(C_{\mathrm{B}} - [\mathrm{AzB}])}{\left(a_{\mathrm{H}^+}/K_{\mathrm{a1}}^{\mathrm{HA}} + 1\right)\left(1 + K_{\mathrm{AzH}}C_{\mathrm{HA}}/\left(a_{\mathrm{H}^+}/K_{\mathrm{a1}}^{\mathrm{HA}} + 1\right)\right)} \qquad (12)$$

Equation (13) is obtained by solving eq (12). The apparent rate constants were calculated from the

slope of the plot of eq (13) (Fig. S3 in the ESI).

$$\ln\frac{C_{\mathrm{B}}(C_{\mathrm{SA}}-[\mathrm{AzB}])}{C_{\mathrm{SA}}(C_{\mathrm{B}}-[\mathrm{AzB}])}=k_{\mathrm{app}}\cdot\frac{C_{\mathrm{HA}}(C_{\mathrm{SA}}-C_{\mathrm{B}})}{\left(a_{\mathrm{H}^+}/K_{\mathrm{a1}}^{\mathrm{HA}}+1\right)\left(1+K_{\mathrm{AzH}}C_{\mathrm{HA}}/\left(a_{\mathrm{H}^+}/K_{\mathrm{a1}}^{\mathrm{HA}}+1\right)\right)}\cdot t \tag{13}$$

At pH 7.6, in contrast, the rate constant could not be calculated in the way as stated above, because the AzH formation reaction became slower under this pH condition. Although the best approach is to consider two parallel reactions of the AzH and AzB formations, the rate equation is too complicated to solve in this case. Thus, we approximately estimated k_{app} at pH 7.6 as follows. The [SA] and [HA] were approximated with their initial concentrations using only the results during the initial reaction time of 150 s, in which the consumption of SA and HA was only 15%. Thus, Equation 12 can be converted as follows:

$$\frac{d[\mathrm{AzB}]}{dt}=\frac{k_{\mathrm{app}}C_{\mathrm{HA}}C_{\mathrm{SA}}(C_{\mathrm{B}}-[\mathrm{AzB}])}{\left(1+K_{\mathrm{a2}}^{\mathrm{HA}}/a_{\mathrm{H}^+}\right)\left(1+K_{\mathrm{a}}^{\mathrm{SA}}/a_{\mathrm{H}^+}\right)} \tag{14}$$

$$\ln(C_{\mathrm{B}}-[\mathrm{AzB}])=-\frac{k_{\mathrm{app}}C_{\mathrm{HA}}C_{\mathrm{SA}}}{\left(1+K_{\mathrm{a2}}^{\mathrm{HA}}/a_{\mathrm{H}^+}\right)\left(1+K_{\mathrm{a}}^{\mathrm{SA}}/a_{\mathrm{H}^+}\right)}\cdot t+\ln C_{\mathrm{B}} \tag{15}$$

The apparent rate constants were calculated from the slope of the plot of eq (15) (Fig. S4 in the ESI). As shown in Table 2, the rate constants at pH 7.6 were somewhat higher than those at pH 4.3. However, if HA and HA^- are assumed to have the same reactivity, they were almost the same for each analog. The k_{app} values varied with the aldehydes used in the order of F-SA > SA ≈ Me-SA. Therefore, it is indicated that the fluoro group is kinetically-favored for the AzB complexation.

The effect of the temperature on the apparent rate constant was investigated in the range of 283 – 303 K. The activation parameters were calculated by the Eyring equation (eq (16)).

$$\ln\frac{k_{\mathrm{app}}}{T}=-\frac{\Delta H^{\ddagger}}{RT}+\ln\frac{k_{\mathrm{B}}}{h}+\frac{\Delta S^{\ddagger}}{R} \tag{16}$$

where R is the gas constant, T the absolute temperature, k_{B} the Boltzmann constant, and h Planck's constant (Fig. S5 in the ESI). The obtained data are summarized in Table 3. The lowest activation

enthalpy change was found for F-SA as the aldehyde. The activation entropy changes were negative in all the investigated analogs. A slightly lower activation free energy change was observed for F-AzB than for the other analogs. For the contribution to the activation free energy, it was found that the contribution of the activation entropy changes is much higher than that of the activation enthalpy changes.

Boric acid-SA-HA complexation mechanism

Summarizing the above information, we now propose the reaction mechanisms of the AzB formation. The formation reactions of AzH were faster at a lower pH in the cases using any aldehydes. The conditions at pH 4.3 and 7.5 – 7.7 used in this study are sensitive to the acid dissociation of SA and HA, as shown in Fig. 3. AzH originates by nucleophilic attack of the nitrogen atom of the amino group in HA on the formyl group in SA. This reaction would be accelerated using an aldehyde with a higher electrophilicity. SA is stabilized by the intramolecular hydrogen bond, which should contribute to the decrease in the electron density of the carbon atom. It is expected that the dissociated SA (SA^-) and protonated HA (HA^+) are not involved in the AzH formation [28].

In the case of the AzB formation reaction, the main process of the AzB complexation from SA, HA, and boric acid is considered to consist of more than three steps [29]: (1) the pre-equilibrium of the boric acid-salicylaldehyde complex (SA-B) formation, (2) the nucleophilic attack of HA to SA-B affording the zwitterionic intermediate, and (3) some remaining steps to form AzB including proton transfers, the elimination of a water and intramolecular dehydration between the hydroxy group in the boric acid moiety and the phenolic hydroxyl group in the HA moiety (Fig. 6). Although it is likely that AzH directly reacts with boric acid, this reaction path should not be the main process because the kinetics of the AzH and AzB formations exhibited the opposite characteristics to the pH. It is expected that the electron density of the formyl group is decreased by

the SA-B formation in a way similar to the intramolecular hydrogen bond of SA. The subsequent nucleophilic attack of HA on SA-B easily takes place, and the reaction affords the thermodynamically stable AzB complex even under the conditions of a higher pH at which the activation by protonation is not expected.

By considering the proposed mechanism, eq (11) can also be converted to the intrinsic rate equation as follows:

$$v = \frac{d[\mathrm{AzB}]}{dt} = k_{\mathrm{app}}[\mathrm{B}][\mathrm{SA}][\mathrm{HA}] = k[\mathrm{SA\text{-}B}][\mathrm{HA}] \quad (17)$$

where k is the intrinsic rate constant of the reaction between SA-B and HA. Therefore, the apparent rate constant obtained in this study can be expressed using $K_{\mathrm{SA\text{-}B}}$, *i.e.*, $k_{\mathrm{app}} = k \cdot K_{\mathrm{SA\text{-}B}}$. However, it was difficult to determine $K_{\mathrm{SA\text{-}B}}$; the interaction between SAs and boric acid could not be confirmed by the ^{11}B NMR measurements because of very low solubilities of SAs in water and low $K_{\mathrm{SA\text{-}B}}$ nor by absorption spectra measurements in a UV region because of their similar absorption spectra of the free SAs and SA-B and low $K_{\mathrm{SA\text{-}B}}$.

The initial aldehyde concentration might affect the observed results from the kinetic experiments. Because C_{SA} was limited to about one-tenth of C_{HA} to reduce the overlap of the reduction peaks [26], the AzH and SA-B formation reactions are considered to have competitively proceeded. At pH 4.3, SA would be consumed by the AzH formation because the reaction was faster at this pH. Due to the slow reaction between AzH and boric acid, it took a longer time to attain the equilibrium for the AzB formation from them. On the other hand, because the AzH formation was slower at pH 7.5 – 7.7, SA might be scarcely consumed by the AzH formation during the initial stage of the reaction. From the viewpoint of the AzB formation, it is expected that the concentration of SA, which can be used for the reaction, was different depending on the pH.

Analytical application to voltammetric determination of boron

From a practical point of view, the formation constants and rate constants are related to the peak intensities of the target complex and measurement time, respectively. As already mentioned, the AzB complexation rate, which alters in accordance with the pH, is faster around the neutral region. For this reason, it is better to measure the boron concentration in the neutral region. The K_{AzB} values are similar among the SA analogs, which produces no difference in the sensitivity among the three kinds of SAs. It is also better for practical use that the AzB peak is separated from the other peaks, in particular, from SA, because its peak has the highest intensity. The cathodic peaks of AzB, AzH, and SA were observed in a close potential range, while the peak potentials of AzH and SA were affected by both the pH and the substituents. It was found that the peaks of SA and AzH shifted to negative potentials with the increasing pH, whereas the peak potential of AzB scarcely changed with the pH (Fig. 2). With the increasing pH, the separation of peaks would be better, however, the AzB complexation degree should decrease over pH 8 due to the acid dissociation of SA. Thus, it is reasonable to determine the boron concentration under a neutral condition. In this study, the determination of boron was performed at pH 7.5 ± 0.1. Under this pH condition, F-SA showed the best separation between the AzB and AzH peaks (Fig. 5), and was chosen as the aldehyde.

The effect of foreign ions is shown in Table 4. In the case of the phosphate buffer, insoluble salts were formed with the calcium and magnesium ions. Thus, the HEPES buffer was used instead of the phosphate buffer. The HEPES buffer exhibited no influence in the scanned potential range. Copper interfered with the boron determination by the proposed method if present in 2 times higher concentrations than that of boric acid (Fig. S6 in the ESI). For the other examined ions, it was confirmed that the amounts of coexisting ions normally present in seawater and desalinated water are tolerable. In addition, the proposed method can be sufficiently applied to industrial effluents. If samples contain more than 1 mg dm^{-3} copper, pretreatment using a chelate resin column, such as InertSep ME-1 (GL Science, Tokyo, Japan), was effective in order to remove the copper.

Under the optimized conditions, the AzB peak could be observed within 5 min and was proportional to the boron concentration (Fig. 7). In order to make a calibration curve for practical use, the following parameters were defined: E_{peak} is the peak potential of AzB; E_{base} is the baseline potential outside the peak; I_{peak} and I_{base} are the respective currents at E_{peak} and E_{base}. A calibration curve was made for the difference between I_{peak} and I_{base} versus the boron concentration: ΔI / μA = I_{peak} / μA – I_{base} / μA = –1.075 C_B / mg dm^{-3} – 0.400 (R^2 = 0.999), where C_B is the boric acid concentration. In this study, E_{peak} was observed at -0.96 V, and E_{base} was set to -0.50 V. The limit of detection, which is defined as the concentration that gives a current corresponding to 3σ for the standard deviation of the fluctuation of the blank, was 0.03 mg B dm^{-3} (n = 5). This limit of detection is better than the value (0.1 mg B dm^{-3}) obtained in a previous study [26].

The recovery test was also made using the standard addition method. This test was applied to the samples of seawater and the water from a desalination plant using reverse osmosis (RO). All the samples were 5 times diluted. The recoveries were nearly 100% for all the examined water samples (Table 5).

The proposed SWV method was used to determine the boron concentration in seawater, RO water from a desalination plant, and industrial effluent samples. The results are summarized in Table 6. For all the water samples measured, the boron concentrations determined by the SWV method were in good agreement with those determined by the conventional spectroscopic methods having differences of less than 10%. These results prove the validity of the proposed method. In the case of the samples with a high ionic strength over 1, direct measurements without dilution resulted in about -20% differences. However, the problem was solved by measuring after a 5 times dilution.

Conclusion

The reaction of the AzB complexation has been practically applied to the determination of boron concentrations in solution using absorption spectrophotometry and voltammetry. Nevertheless, its

406 reaction mechanism has not been studied in detail for a long time as it is a ternary complex system.
407 In this study, the AzB complexation mechanism was completely clarified from kinetic and
408 equilibrium points of view using SWV and ^{11}B NMR measurements. F-SA and Me-SA were helpful
409 to clarify the effect of the substituent groups.

410 Based on the full knowledge of this system, the boron determination system using SWV,
411 which has been proposed in our laboratory, was optimized. The peak potentials of AzH and SA
412 were shifted negative with the increasing pH, while that of AzB was pH-independent. Because a
413 neutral condition is favorable from the viewpoints of the AzB formation rate and peak potentials,
414 the measurements were performed at pH 7.5 ± 0.1. In addition, F-SA was chosen because it showed
415 a better peak separation. The proposed method enabled the determination of a lower boron
416 concentration in a shorter time than the previous method. This method is simple, rapid and easy to
417 operate, and can be applied to samples, such as seawater, RO water, and some industrial effluents.
418 The information obtained in this study is also expected to be applied to the boron determination
419 using absorption spectrophotometry, which will be reported elsewhere [30].

420

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Figure captions

Fig. 1 SWVs of a 2.0 mmol dm^{-3} SA solution, and 2.0 mmol dm^{-3} SA and 25 mmol dm^{-3} HA solutions with or without 10 mg B dm^{-3} (pH 4.3).

Fig. 2 pH dependence of peak potentials for 25 mmol dm^{-3} HA solutions containing 2.0 mmol dm^{-3} (a) SA, (b) F-SA or (c) Me-SA with or without 10 mg B dm^{-3}.

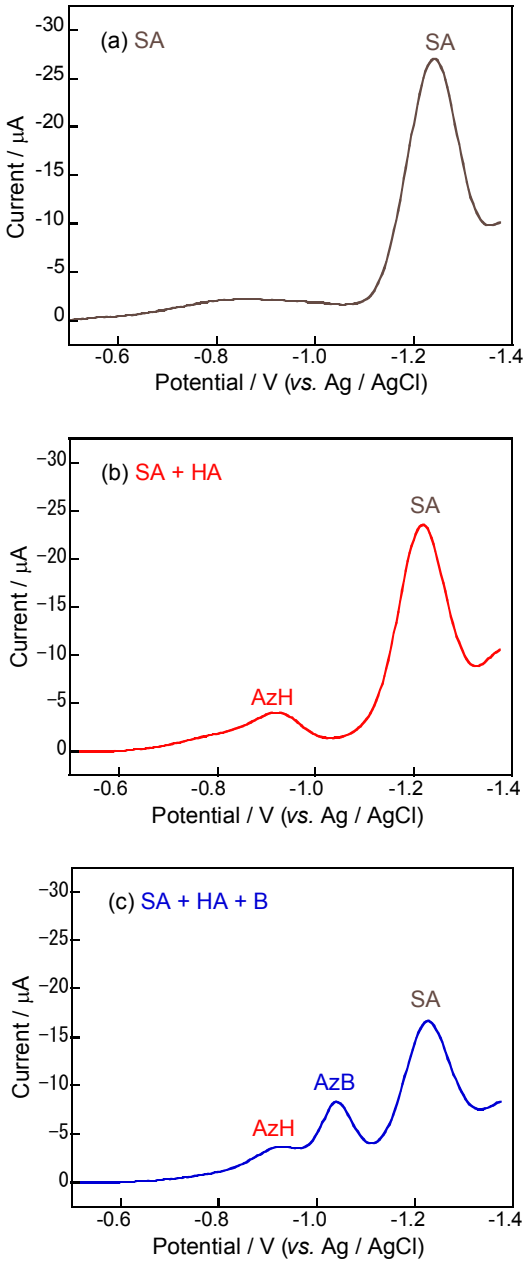
Fig. 3 AzH formation equilibrium and the acid dissociation of the starting materials.

Fig. 4 Dependence of SWVs on reaction time for AzH formation in solutions containing 2.0 mmol dm^{-3} SA and 25 mmol dm^{-3} HA at (a) pH 4.3 and (b) pH 7.5.

Fig. 5 Dependence of SWVs on reaction time for AzB formation in solutions containing 2.0 mmol dm^{-3} SA analog, 25 mmol dm^{-3} HA and 10 mg B dm^{-3}. AzB: (a) pH 4.3, (b) pH 7.5; F-AzB: (c) pH 4.3, (d) pH 7.7; Me-AzB: (e) pH 4.3, (f) pH 7.7.

Fig. 6 Plausible energy diagram for AzB formation from SA, B and HA. The energy diagram for subsequent reactions of zwitterionic intermediate formation was simplified.

Fig. 7 Dependence of SWVs on the boron concentration for the F-AzB formation system at pH 7.5 ± 0.1. Concentrations of SA and HA are 2.0 mmol dm^{-3} and 25 mmol dm^{-3}.



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511 Fig. 1.

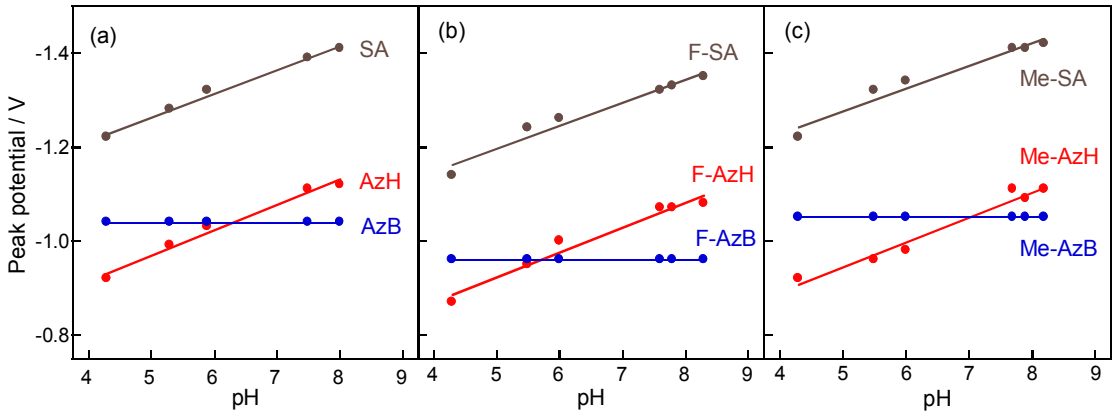

Fig. 2

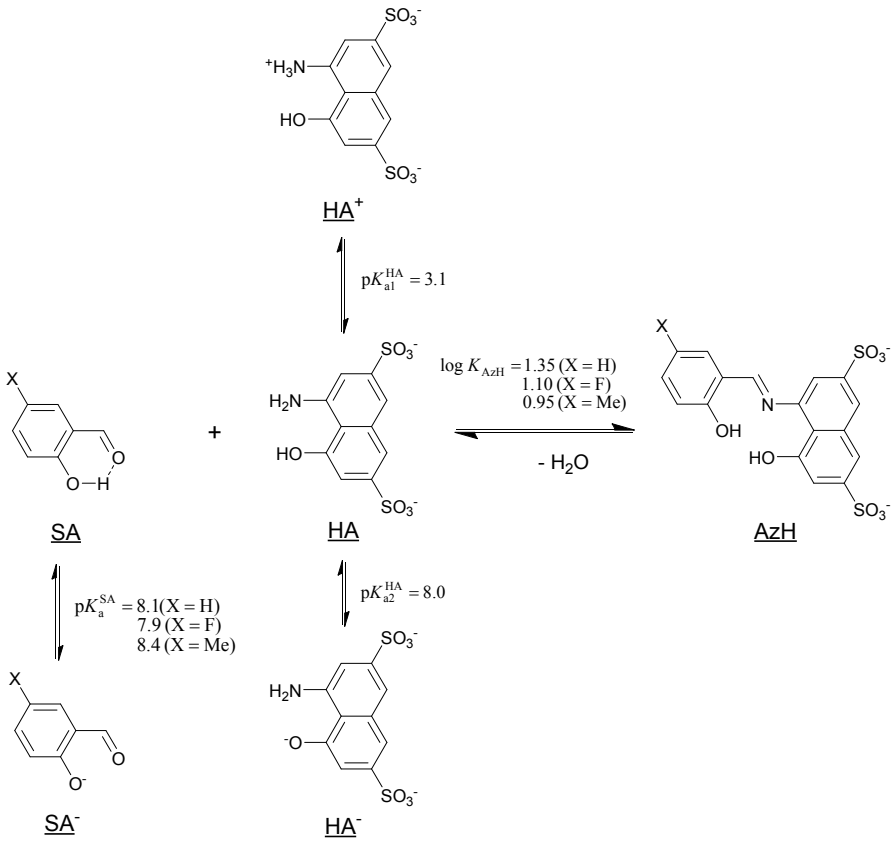

Fig. 3

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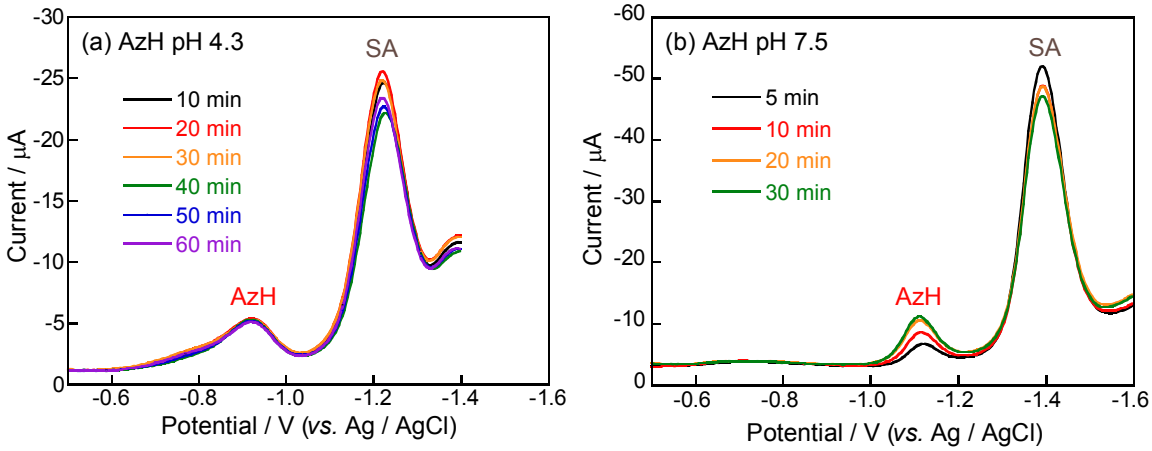

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547 Fig. 4

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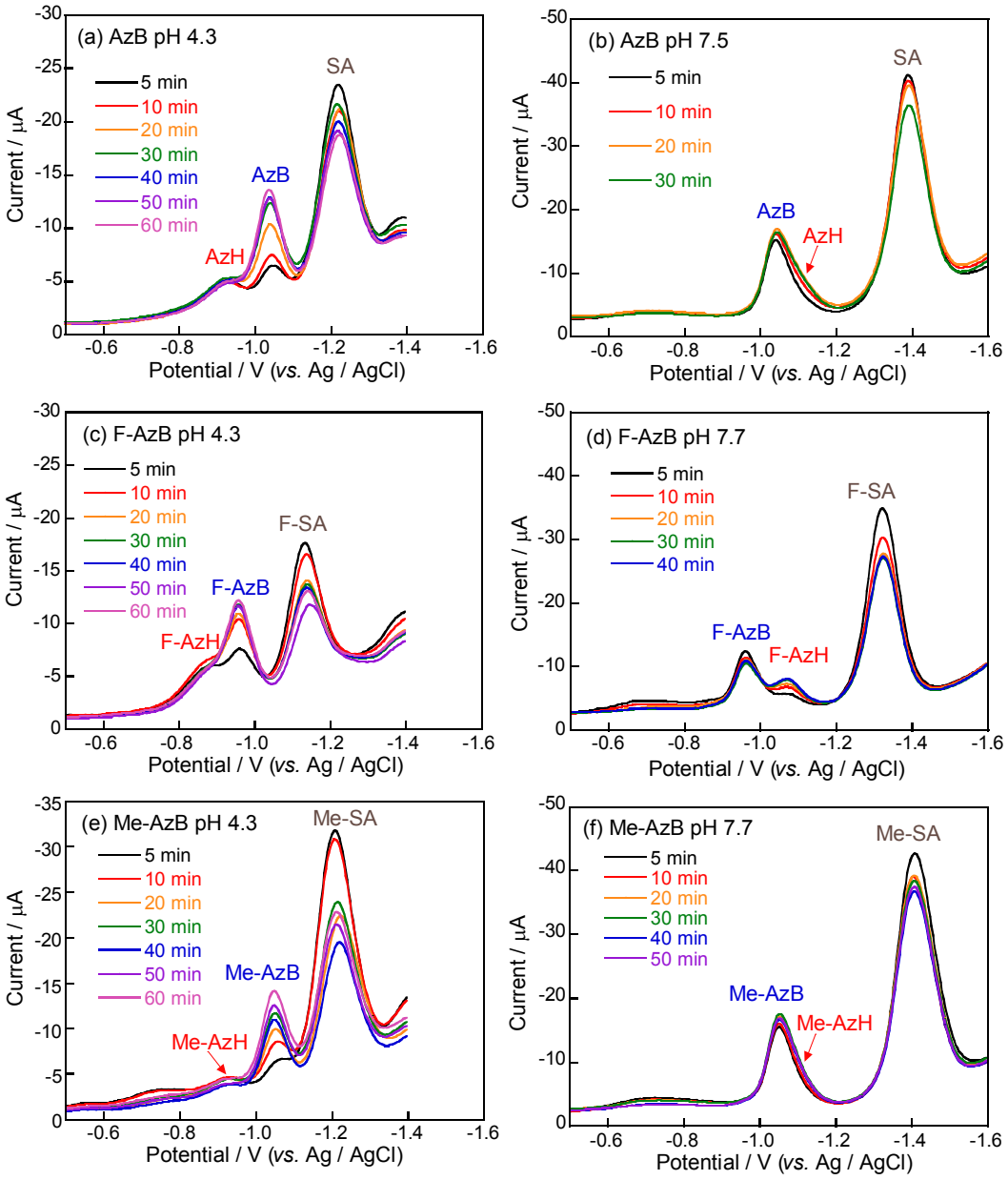

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553 Fig. 5

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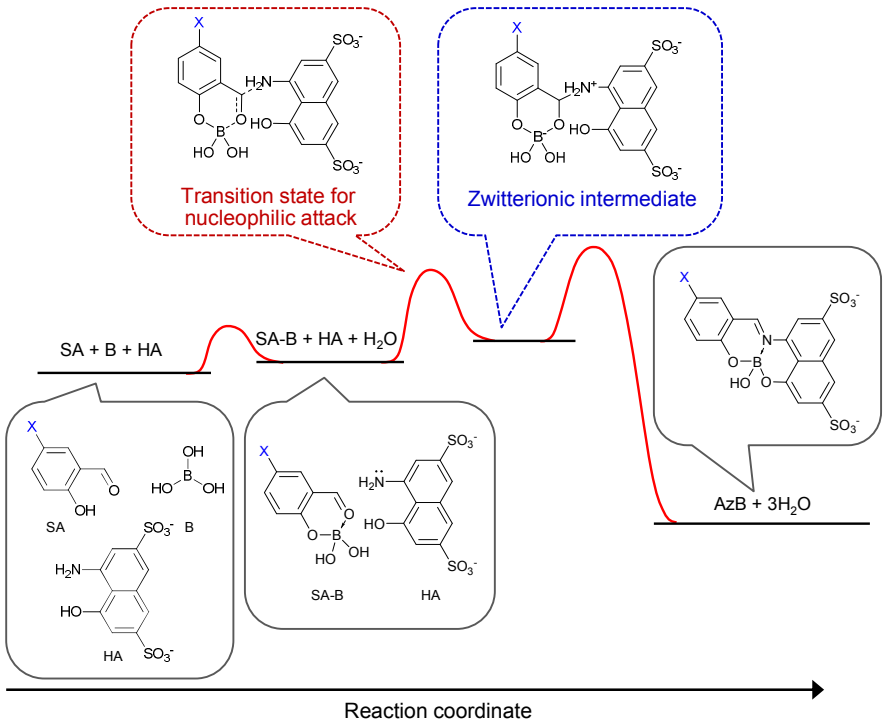
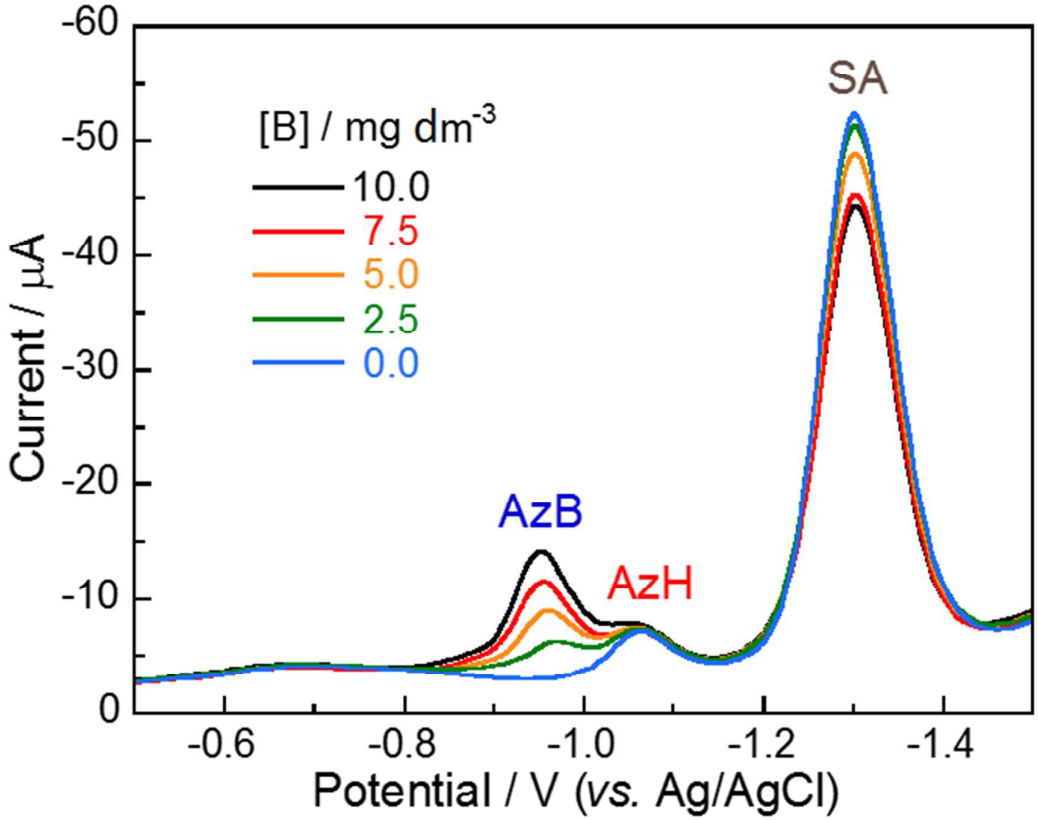


Fig. 6



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576 Fig. 7

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579 Table 1. Formation constants of AzH and AzB for SA and its analogs (I = 0.5)

Aldehyde	Voltammetry			^{11}B NMR		
	pH	log (K_{AzH} / mol^{-1} dm^3)	log (K_{AzB} / mol^{-2} dm^6)	pH	log (K_{AzB} / mol^{-2} dm^6)	
SA	4.3	0.99 ± 0.01	5.20 ± 0.03	4.5	5.38	
				5.3	5.16	5.24 ± 0.14 [a]
				6.0	5.14	
F-SA	4.3	1.04 ± 0.00	5.35 ± 0.03	4.5	5.03	
				5.3	4.97	5.01 ± 0.03
				6.3	5.02	
Me-SA	4.3	0.70 ± 0.01	4.97 ± 0.02	4.4	5.36	
				5.2	5.15	5.22 ± 0.14
				6.1	5.11	

580 [a] 5.91 ± 0.07 (I = 0.1) [23]

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583 Table 2. Rate constants for the AzB complexation among B, HA, and SA or its analogs at 298 K

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Aldehyde	pH	k_{app} / mol^{-2} dm^6 s^{-1}
SA	4.3	22 ± 0
	7.6	38 ± 4 [a]
		30 ± 3 [b]
F-SA	4.3	62 ± 2
	7.6	76 ± 3 [a]
		59 ± 3 [b]
Me-SA	4.3	14 ± 0
	7.6	43 ± 2 [a]
		34 ± 2 [b]

585 [a] HA is assumed to be the only active species.

586 [b] HA and HA^- are assumed to be the active species.

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590 Table 3. Activation parameters for the AzB complexation from B, HA, and SA or its analogs at

591 pH 4.3

	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / 10 J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
SA	10.2 ± 0.9	-18 ± 3	63 ± 9 [a]
F-SA	6.7 ± 0.1	-19 ± 1	62 ± 2 [a]
Me-SA	11.6 ± 0.6	-18 ± 2	65 ± 5 [a]

[a] Calculated as $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ at $T = 298$ K.

592

593 Table 4. Effects of foreign ions on the determination of boron

	Coexisting ion / mg dm^{-3}	Found B / mg dm^{-3}	Relative error, %
Ca^{2+}	1000	5.09	+1.8
Mg^{2+}	1000	5.30	+5.9
Al^{3+}	100	5.06	+2.8
Fe^{3+}	100	5.04	+2.1
Pb^{2+}	100	4.90	-1.8
Zn^{2+}	100	5.29	+5.4
F^-	100	4.80	-3.2
Cu^{2+}	10	7.12	+42.9
	1	5.22	+4.7

(5 mg B dm^{-3})

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596 Table 5. Recovery test of boron using standard addition

Sample	B added / mg dm^{-3}	B found / mg dm^{-3}	Recovery, %
ISW	0.00	0.86 ± 0.01 (n = 3)	–
	2.51	3.32	98
	5.00	5.88	100
REW	0.00	1.50 ± 0.02 (n = 3)	–
	2.50	3.93	97
	4.97	6.28	96
BHRO	0.00	1.68 ± 0.02 (n = 3)	–
	2.50	4.15	99
	5.00	6.54	97

ISW: Intake seawater; REW: RO effluent water; BHRO: Brine from high pressure RO.

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600 Table 6. Boron concentrations of waters from a RO desalination plant and an industrial
601 wastewater treatment plant

Sample	Ionic strength	SWV [a] / mg dm^{-3}	ABS [b] / mg dm^{-3}
RO desalination			
PLRO	4.1×10^{-3}	0.82 ± 0.01	0.77
PW	1.7×10^{-3}	1.23 ± 0.08	1.33
PHRO	2.0×10^{-3}	1.61 ± 0.03	1.59
FLRO	4.6×10^{-3}	2.99 ± 0.03	2.85
UFF	0.59	4.74 ± 0.08	4.68
ISW	0.59	4.64 ± 0.05	4.46
REW	1.1	5.94 [c]	7.19
		7.14 ± 0.08 [d]	
BHRO	1.3	6.62 [c]	8.05
		7.98 ± 0.07 [d]	
Industrial wastewater treatment			
After	< 0.1	0.09 ± 0.03	0.08[f]
Before	< 0.1	13.0 ± 0.4[e]	13[f]

PLRO: Permeate low pressure RO; PW: Product water; PHRO: Permeate high pressure RO; FLRO: Feed for low pressure RO; UFF: UF filtrate; ISW: Intake seawater; REW: RO effluent water; BHRO: Brine from high pressure RO.

[a] Proposed SWV method (n = 3);

[b] Conventional Azomethine H absorption spectrophotometry;

[c] No dilution; [d] 5 times dilution; [e] 2 times dilution; [f] ICP-AES.

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