

Supporting information

1. Peak analysis

The parameters of the baseline, SA, AzH, and AzB peaks were optimized by using eq (1):

$$f(E) = \gamma \cdot f_L(E) + (1 - \gamma) \cdot f_G(E) \quad (1)$$

where $f_L(E)$ and $f_G(E)$ are the Lorentz and Gauss functions, respectively. The $f_L(E)$ and $f_G(E)$ are expressed by the following respective eqs (2) and (3),

$$f_L(E) = \frac{h}{1 + (E - E_p)^2 / \omega^2} \quad (2)$$

$$f_G(E) = h \cdot \exp\left\{-\frac{(E - E_p)^2}{\omega^2}\right\} \quad (3)$$

where h is the peak height, E_p the peak potential, ω the half width of the peak, and γ the contribution degree of Lorentz function.

As a result, all the peaks could be separated, as shown in Fig. S1.

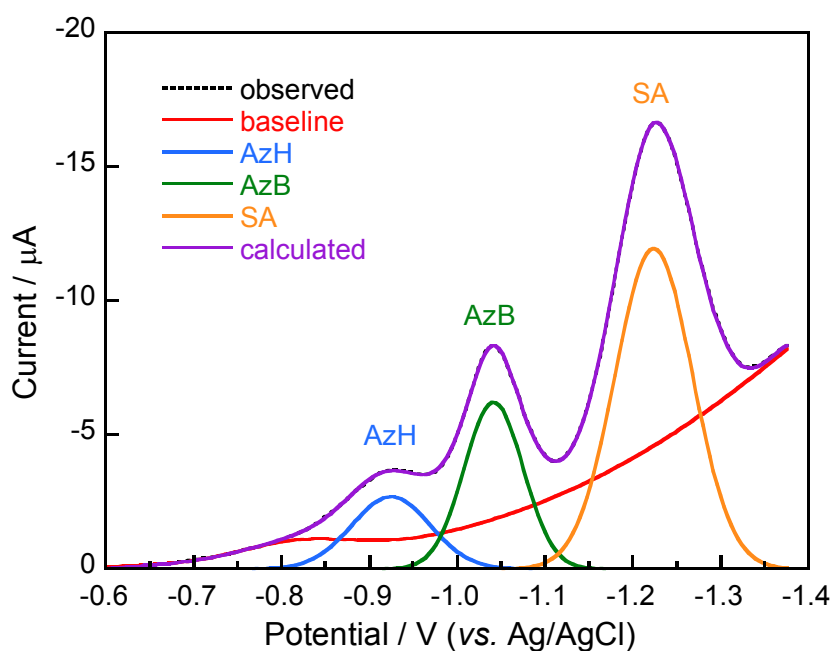


Fig. S1. SWV of AzH solution containing 10 mg B dm⁻³.

2. Equilibria study

Tables S1 and S2 shows the respective results obtained by repeated measurements of K_{AzH} and K_{AzB} .

Table S1. Formation constants for AzH formation

| Aldehyde | S_{AzH} | S_{SA} | C_{HA} / mol dm ⁻³ | K_{AzH} / mol ⁻¹ dm ³ |
|----------|-----------|----------|------------------------------------|--|
| SA | 0.50 | 2.18 | 0.025 | 9.74 |
| | 0.50 | 2.15 | 0.025 | 9.88 |
| | 0.50 | 2.13 | 0.025 | 9.97 |
| F-SA | 0.35 | 1.37 | 0.025 | 11.0 |
| | 0.34 | 1.32 | 0.025 | 10.9 |
| | 0.34 | 1.31 | 0.025 | 11.1 |
| Me-SA | 0.29 | 2.49 | 0.025 | 4.93 |
| | 0.27 | 2.23 | 0.025 | 5.15 |
| | 0.27 | 2.34 | 0.025 | 5.01 |

Table S2. Formation constants for AzB complexation

| Aldehyde | S_{AzH} | S_{AzB} | S_{SA} | S_T | C_{SA} / mol dm ⁻³ | C_{HA} / mol dm ⁻³ | C_B / mol dm ⁻³ | K_{AzB} / 10 ³ mol ⁻² dm ⁶ |
|----------|-----------|-----------|----------|-------|------------------------------------|------------------------------------|---------------------------------|--|
| SA | 0.44 | 0.73 | 1.32 | 2.49 | 0.0019 | 0.025 | 0.00071 | 165 |
| | 0.48 | 0.71 | 1.30 | 2.49 | 0.0019 | 0.025 | 0.00071 | 144 |
| | 0.43 | 0.72 | 1.29 | 2.43 | 0.0019 | 0.025 | 0.00071 | 163 |
| F-SA | 0.33 | 0.59 | 0.97 | 1.89 | 0.0019 | 0.025 | 0.00071 | 223 |
| | 0.30 | 0.56 | 0.93 | 1.79 | 0.0019 | 0.025 | 0.00071 | 238 |
| | 0.34 | 0.53 | 0.87 | 1.74 | 0.0019 | 0.025 | 0.00071 | 206 |
| Me-SA | 0.29 | 0.67 | 1.59 | 2.56 | 0.0020 | 0.025 | 0.00071 | 92 |
| | 0.28 | 0.64 | 1.47 | 2.39 | 0.0020 | 0.025 | 0.00071 | 100 |
| | 0.29 | 0.65 | 1.53 | 2.46 | 0.0020 | 0.025 | 0.00071 | 90 |

3. Kinetic study for AzH formation

Fig. S2 shows the time dependence of SWVs for AzH formation of the SA derivatives.

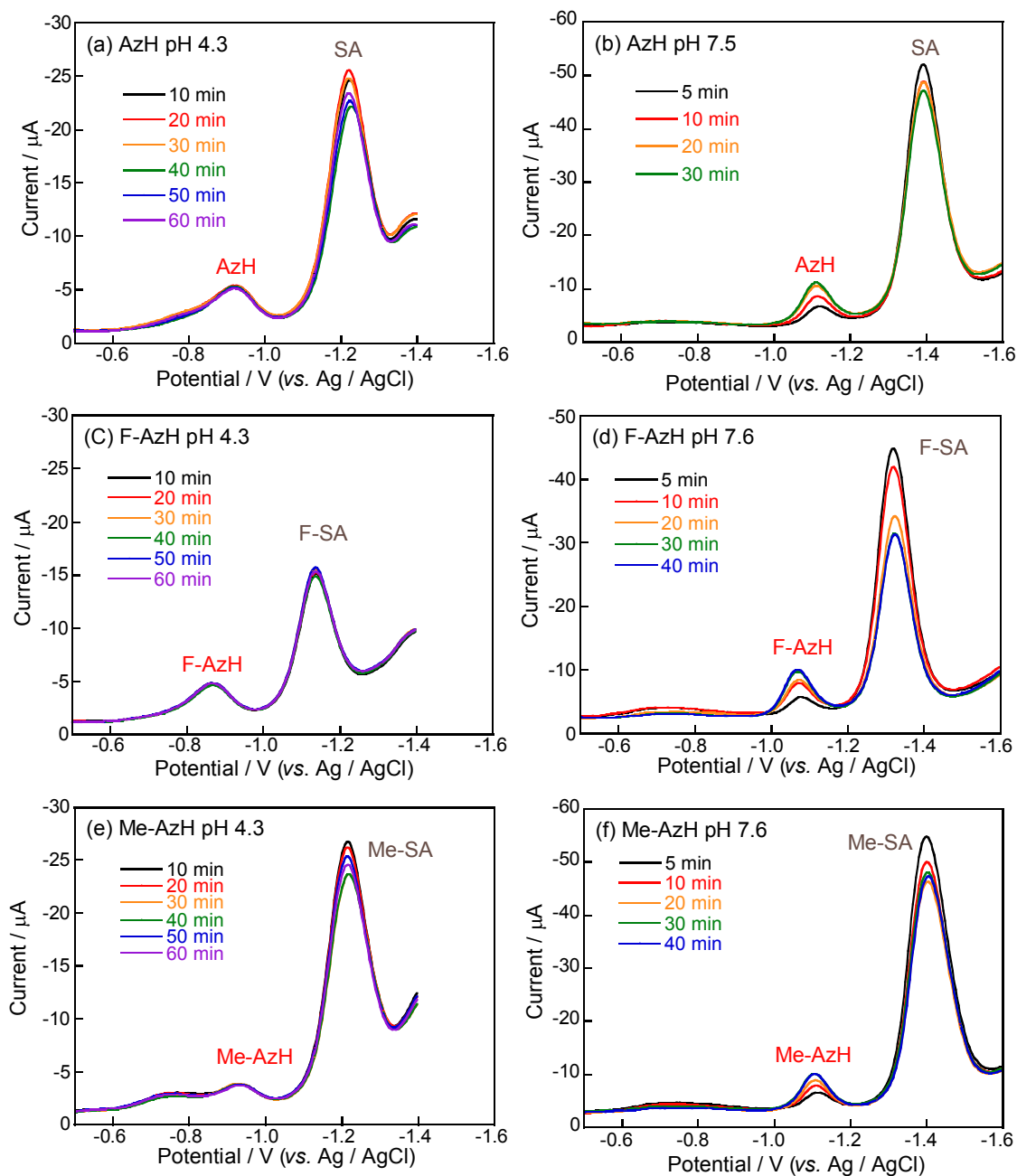


Fig. S2. Dependence of SWVs on reaction time for AzH formation. SA: (a) pH 4.3, (b) pH 7.5; F-SA: (c) pH 4.3, (d) pH 7.6; Me-SA: (e) pH 4.3, (f) pH 7.6.

4. Kinetic study for AzB formation

Figs. S3 and S4 are the plots using eqs (4) and (5), respectively. The rate constants were calculated by using respective slope values.

$$\ln \frac{C_B (C_{SA} - [AzB])}{C_{SA} (C_B - [AzB])} = k_{app} \cdot \frac{C_{HA} (C_{SA} - C_B)}{(a_{H^+} / K_{a1}^{HA} + 1) (1 + K_{AzH} C_{HA} / (a_{H^+} / K_{a1}^{HA} + 1))} \cdot t \quad (4)$$

$$\ln(C_B - [AzB]) = -\frac{k_{app} C_{HA} C_{SA}}{(1 + K_{a2}^{HA} / a_{H^+}) (1 + K_a^{SA} / a_{H^+})} \cdot t + \ln C_B \quad (5)$$

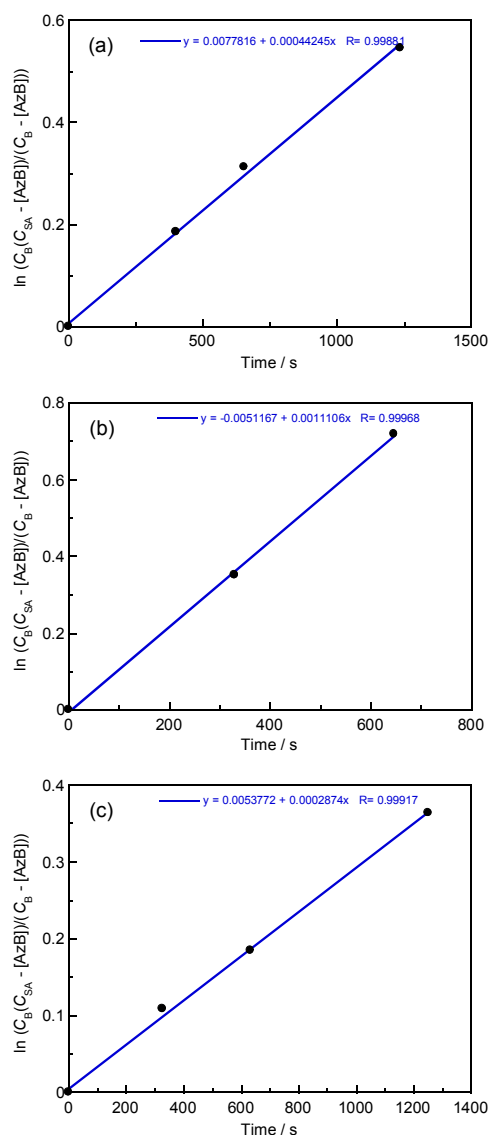


Fig. S3. Plots for estimation of rate constants at pH 4.3. (a) SA, (b) F-SA, (c) Me-SA.

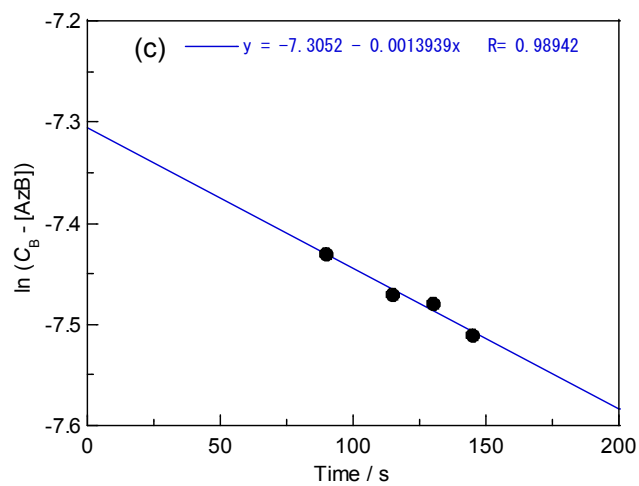
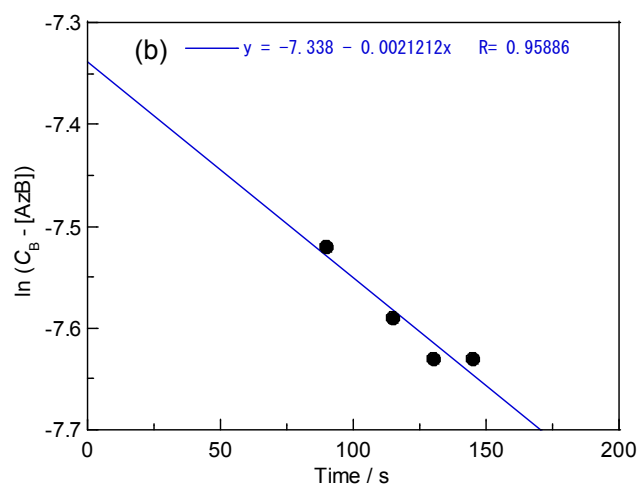
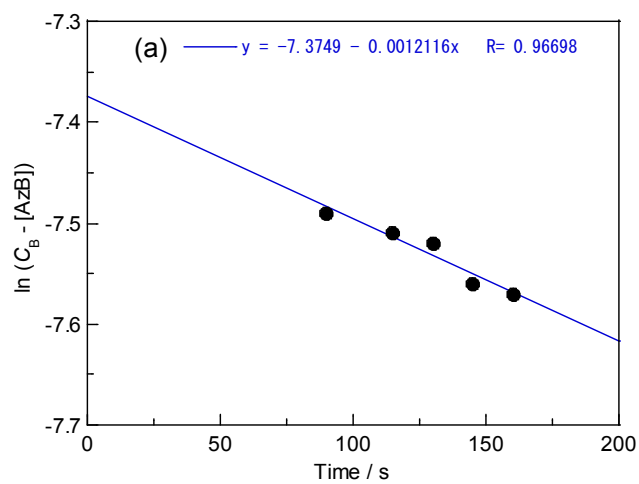


Fig. S4. Plots for estimation of rate constants at pH 7.6. (a) SA, (b) F-SA, (c) Me-SA.

5. Activation parameters

The activation parameters for the AzB complexation reaction were obtained by the Eyring plots using eq (6) and summarized in Fig. S5.

$$\ln \frac{k_{\text{app}}}{T} = -\frac{\Delta H^\ddagger}{RT} + \ln \frac{k_{\text{B}}}{h} + \frac{\Delta S^\ddagger}{R} \quad (6)$$

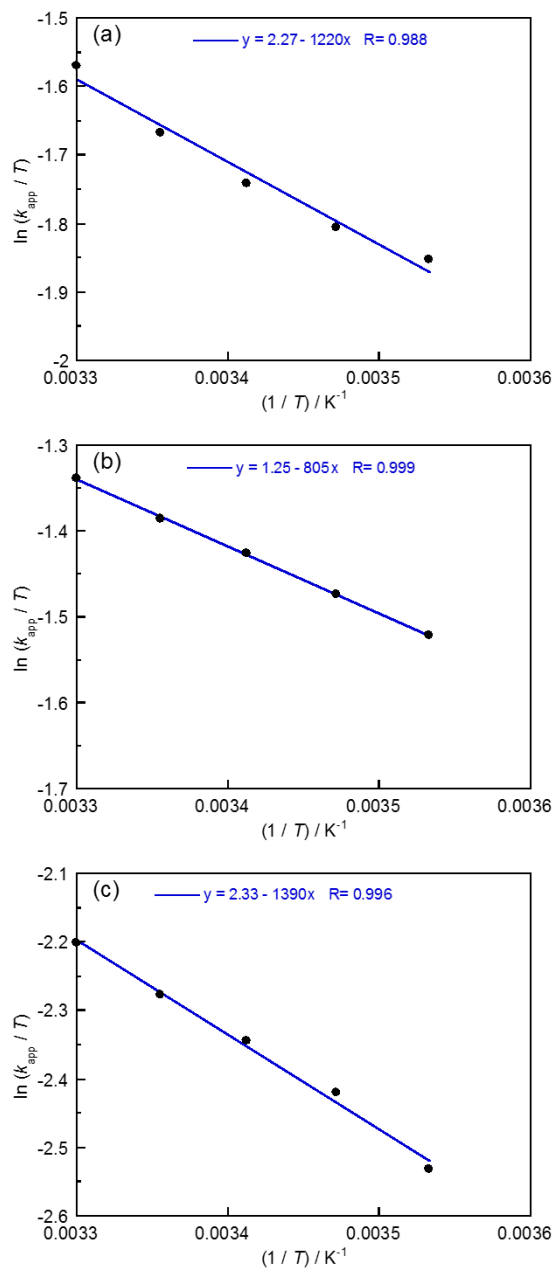


Fig. S5. Eyring plots for estimation of activation parameters.

(a) SA, (b) F-SA, (c) Me-SA.

6. Interference by copper for the SWV determination of boric acid

It was found that copper ions interfere if present in 2 times higher concentration than that of boric acid. As shown in Fig. S6, the currents around -1.5 V in the case of the solution containing 10 mg Cu dm⁻³ were not detected accurately because of high currents over the limit of the detector. There may be a peak derived from copper around -1.5 V, resulting in the positive error by overlapping on a target peak.

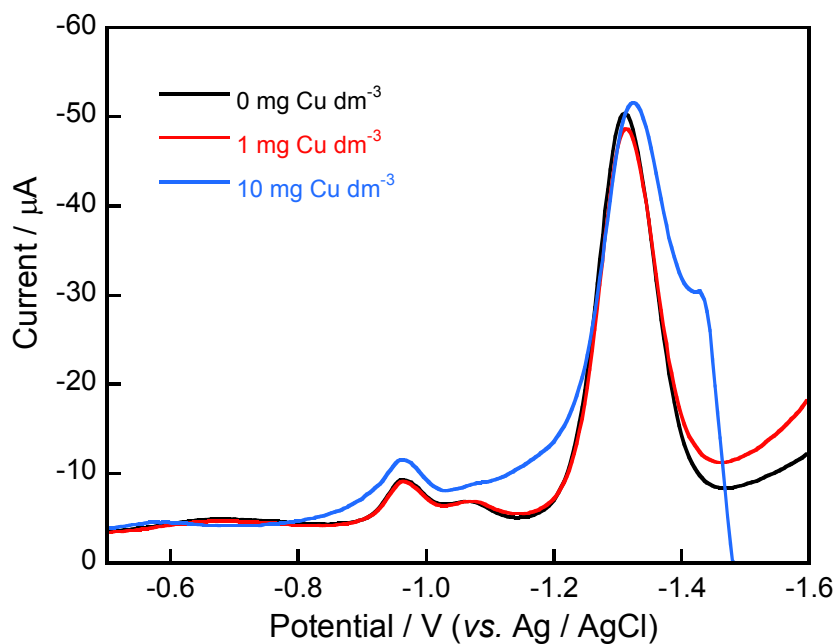


Fig. S6. SWVs of the AzB solution containing 5 mg B dm⁻³ with 0 - 10 mg Cu dm⁻³.