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Electrochemical Sensing of Sulfate Using Mixed Thiol-derivatized β-Cyclodextrin/Pentanethiol Monolayers

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The oxidation of ferrocene on a defect-free mixed per-6-thio-β-cyclodextrin/pentanethiol monolayer in a $NaClO_4$ solution was inhibited in the presence of sulfate. The peak current in differential pulse voltammograms linearly decreased with the logarithm of the sulfate concentration in an extremely wide range from 1 nM to 1 mM, showing the possible application as an electrochemical sensor of sulfate.

Sulfates occur in rainwater, ground water, seawater, and also drinking water over a wide concentration range from nM to mM.[1–4] Analytical methods often used for its determination are gravimetry, ion chromatography, and spectrophotometry. A gravimetry method measuring precipitated barium sulfate is suitable for sulfate concentrations above 100 μM.[1] Ion chromatography covers the concentration range from 1 μM to 1 mM.[5] The sensitivity of spectrophotometry is dependent on the type of chromophore, but the most common detection limit, for example, of the diphenylcarbazide method[6] and 1,10-phenanthroline extraction method,[7] is around 1 μM. It decreases to 1 nM for fluorescence analysis.[8] The applicable detection range in these methods is usually limited to three orders of magnitude. We now report a novel electrochemical sensor based on the inhibition effect of sulfate on the oxidation of ferrocene on a defect-free mixed per-6-thio-β-cyclodextrin (CD-SH)/pentanethiol (C_5SH) monolayer. This method covers a concentration range of over six orders of magnitude, and the detection limit is sub-nM.

CD-SH was synthesized according to a method described in a previous paper.[9,10] All other chemicals are of reagent or better grades and used as received except for reagent grade ferrocene, which was purified by sublimation. All the aqueous solutions were prepared with Milli-Q water and were sufficiently deaerated with 5-N purity argon. The substrate electrode was a thin gold film (thickness: 200 nm) on a glass slide, which was prepared by a vacuum evaporation method. After flame-annealing, the electrode showed typical characteristics of Au(111) for oxide-formation in 0.1 M H_2SO_4.

Differential pulse voltammetry (DPV) experiments were performed using a three-electrode cell and an HZ-5000 automatic polarization system (Hokuto Denko, Japan). The pulse amplitude, width, and scan rate were 100 mV, 1 ms, and 10 mV s^{-1}, respectively. The reference electrode was a Ag/AgCl (saturated KCl) electrode, and all potentials in the text are referred to this electrode. A platinized platinum foil served as the counter electrode. All measurements were carried out in an Ar-filled glovebox.

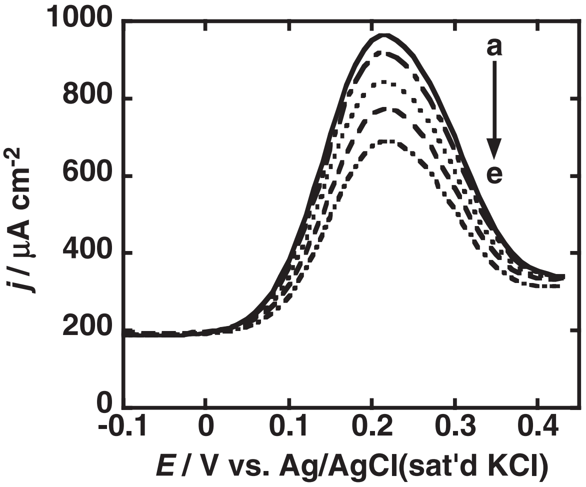

Figure 1. Differential pulse voltammograms for the oxidation of ferrocene on the mixed CD-SH/C_5SH monolayer (a) in 0.1 M $NaClO_4$ and (b)–(e) in 0.1 M $NaClO_4$ + Na_2SO_4. The sulfate concentrations are (b) 1 nM, (c) 100 nM, (d) 10 μM, and (e) 1 mM.

The mixed CD-SH/C_5SH monolayers were constructed by successively immersing the gold electrode in 1.0 mM CD-SH in DMSO/H_2O (3:2, v/v) solvent for more than 72 h, an aqueous 60 μM ferrocene (Fc) solution over 1 h, and a mixed 2.5 mM Fc + 0.5 mM C_5SH in an EtOH/H_2O (1:1, v/v) solution overnight. The characterization of the thus prepared monolayer was conducted using reductive desorption voltammetry and chronocoulometry, and the following characteristics were evaluated.[9] (1) The adsorption amount of CD-SH was 74.0 pmol cm^{-2}, which corresponds to 92% of that expected for the hexagonally close packed adlayer, (2) the intermolecular vacancies between the adsorbed CD-SH molecules were completely filled with C_5SH, and (3) the cyclodextrin (CD) cavities were not occupied with C_5SH, and hence were open to guest compounds. Thus the CD-cavities are the only accessible sites for guest compounds and any other reactants. We consider that precise control of the surface structure is very important to control reactions at electrode/solution interfaces and to finally obtain highly reproducible electrochemical response, which is required for an electrochemical sensor.

Figure 1 shows the differential pulse voltammograms for the oxidation of ferrocene on the mixed CD-SH/C_5SH monolayer in 0.1 M $NaClO_4$ in the absence and presence of various concentrations of sulfate. All voltammograms gave a single peak at 0.21 V

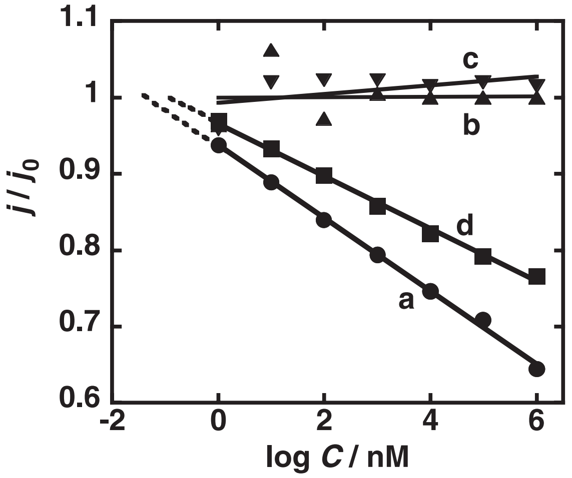

Figure 2. Concentration dependence of the relative peak current obtained by differential pulse voltammetry to that in a pure electrolyte solution (0.1 M $NaClO_4$). Coexisting anions: (a) sulfate, (b) chloride, (c) bromide, and (d) nitrate.

vs. Ag/AgCl. The peak intensity decreased with increasing $SO_4{}^{2-}$ concentration in solution. A linear relationship between the peak intensity and the logarithm of the concentration of sulfate occurs in the concentration range from 1 nM to 1 mM as shown in Figure 2, in which the relative peak current to that in a pure electrolyte solution was plotted. The total current decrease in this range was 300 μA cm^{-2} (Figure 1), which is much higher than the 10 μA cm^{-2} observed by cyclic voltammetry (300 mV s^{-1}) under similar conditions as expected. The peak intensity in 0.1 M $NaClO_4$ corresponds to that at less than 0.1 nM $SO_4{}^{2-}$ as demonstrated by the extrapolation of the linear relationship in Figure 2. Therefore, the detection limit for $SO_4{}^{2-}$ decreases to the sub-nanomolar range. This is extremely low compared with those for the other commonly used methods and is comparable to that in the most sensitive fluorescence analysis. After a series of experiments from 1 nM to 1 mM, the electrode was sufficiently washed with water and then tested in 60 μM ferrocene + 0.1 M $NaClO_4$. The peak current was almost the same as that of the virgin electrode within experimental error. Therefore, the electrode is reusable. These results show that the mixed CD-SH/C_5SH monolayer with ferrocene as a marker can be a strong candidate as a sulfate sensor for a wide range of sulfate concentrations.

The inhibition of the oxidation reaction is most likely due to the association of sulfate with the monolayer. To confirm this, the X-ray photoelectron spectra were measured. When the mixed monolayer was immersed in 0.1 M $NaClO_4$, the S 2p band due to the thiols was observed at 163 eV. After immersion in a mixed solution of 1 mM Na_2SO_4 and 0.1 M $NaClO_4$, an additional band appeared at 169 eV, which is assigned to sulfate according to the literature.[11,12] The sulfate-to-thiol ratio was 0.15:1 from the band intensities. This ratio is close to that of the CD to total Au–S bonds (0.12:1.0). Therefore, approximately a 1:1 association between the sulfate and CD was demonstrated.

The association of sulfate affects the inclusion of ferrocene into the CD cavities. The amount of the CD cavities was estimated using chronocoulometry for the oxidation of ferrecene at various potentials and concentrations of Fc according to well-known and previously reported procedures.[9] The concentration dependence of the inclusion amount was of the Langmuir type. In 0.2 M $NaClO_4$, the maximum inclusion amount of ferrocene was 66.3 ± 5.0 pmol cm^{-2}, which was almost the same as the number of surface-confined CD-SH molecules (69.0 ± 5.4 pmol cm^{-2}). These results indicate that perchlorate does not affect the inclusion of Fc into the CD cavities. In 0.2 M Na_2SO_4, on the other hand, the maximum inclusion amount of ferrocene was 3.81 ± 2.4 pmol cm^{-2}. These results indicate that the sulfate inhibits the inclusion of ferrocene into the CD cavities. The fact that the oxidation current decreased even at an extremely low concentration suggests that the association constant for sulfate is very high. Assuming that the current decrease is proportional to the association amount of sulfate, in addition, the linear dependence of the current on the logarithm of the concentration indicates that the sulfate association with the mixed monolayer obeys the Frumkin isotherm.

Differential pulse voltammetry (DPV) experiments were also conducted in 0.1 M $NaClO_4$ in the presence of other anions. Figure 2 shows the concentration dependence of the relative peak current for nitrate, chloride, and bromide. For the halide ions, no decrease in the current was observed even at 1 mM, showing no inhibition by the halides. In case of $NO_3{}^-$, however, the current decreased in the concentration range from 1 nM to 1 mM. The slope in the current vs. logarithm of the concentration plot was smaller than that for the sulfate, showing a lower sensitivity compared to sulfate.

In summary, the mixed CD-SH/C_5SH monolayer electrode can serve as a sulfate sensor using ferrocene as a marker. The detection limit is extremely low, and the linearity of the current vs. logarithm of the concentration holds over a very wide range of more than six orders of magnitude. These properties are quite superior to those of the other analytical methods for sulfate. In addition, this monolayer was not sensitive to halides, which are present at a considerably high concentration in environmental waters. Unfortunately, it also responds to nitrate. Although the nitrate concentration in natural water systems is almost always lower than that of sulfate, improvement in the selectivity to sulfate in the presence of nitrate is required to create a better sulfate sensor.

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