Acceleration of Electoreduction Reaction of Water-Soluble Selenium Compounds in the Presence of Methyl Viologen

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ABSTRACT

The addition of methyl viologen (MV^{2+}) accelerates the reduction of Na_2SeO_3 not only in 0.1 mol dm^{-3} sodium phosphate buffer (PBS, pH 7) but also in 0.22 mol dm^{-3} sodium acetate buffer (pH 4). Water-insoluble red Se is dispersed in the vicinity of the electrode surface as the reduced product. Michaelis-Menten-type relationship is obtained between the reduction current and the concentration of Na_2SeO_3 , suggesting that MV^{2+} molecules mediate the electron transfer from the electrode to $HSeO_3^-$ or SeO_3^{2-} dissolved in PBS. MV^{2+} is also effective in accelerating the reduction of SeO_4^{2-} , which has already been reported to be electrochemically inactive.

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1. Introduction

The demand for various elements, especially rare metals and metalloids, is continuously rising. Se is one such element and it is important ingredient in the production of photoelectric devices, photosensitive drums used in dry copying, and semi-conductors. Se is also an important trace element from environmental and biological points of view; however its intake as a nutrient should be restricted to very narrow concentration range: its intake outside this range leads to deficiency or toxicity.¹ Se has several oxidation states in the environment, i.e., selenate (+6), selenite (+4), elemental Se (0), and selenide (−2). Human activities such as petroleum refining, mining and fossil fuel combustion result in the environmental contamination because of the formation of selenate (SeO_4^{2-}) or/and selenite (SeO_3^{2-}). These water-soluble oxyanions are the primary forms of Se in aerated environments. In Japan, it has been mandated by the government that the total Se concentration in industrial Se-contaminated wastewater should not exceed 0.1 mg of Se in 1 dm^{-3} because of the toxicity of these ions. While physicochemical methods including ion exchange, ferrihydrite adsorption/precipitation, and chemical reduction by zero valent iron, are generally applied for Se removal from wastewater,² these methods are not suitable for Se recycling, which are rather expensive for practical use in industries. Biological treatments are promising alternative techniques to detoxify the water-soluble forms of Se to less toxic and insoluble elemental form.² However, they are not applicable for industrial wastewaters containing relatively high concentrations of Se at various pH and salinity values.

The electrochemistry of Se is important in diverse contexts ranging from the chemical analysis of environmental samples³ to electrochemical co-deposition to grow compound semiconductors.⁴ In aqueous solutions, only two oxidation states of Se(−2) and Se(+4) exhibit electrochemical activity,⁵ whereas Se(+6) does not undergo reduction on mercury electrodes.⁶ In addition, the reduction of Se(+4) is accompanied by fairly high overpotential values. The present paper reports the reduction behavior of water-soluble Se oxyanions in the presence of methyl viologen (MV^{2+}). We found that the addition of MV^{2+} accelerates the electrochemical reduction of not only SeO_3^{2-} but also SeO_4^{2-} in both acidic and neutral aqueous conditions. Red precipitates or

colloids of Se are generated as the reduction products, suggesting the possibility of electrochemical treatment for Se-containing wastewater.

2. Experimental

Sodium selenite (Na_2SeO_3), sodium selenate (Na_2SeO_4), N,N' -dimethyl-4,4'-bipyridinium dichloride (MV^{2+}), and all other chemicals were of reagent grade and used as received.

All electrochemical measurements were carried out in a conventional three-electrode cell equipped with a glassy carbon working electrode (GCE, geometric area 0.071 cm^2), a Pt coil counter electrode, and a $Ag|AgCl$ (saturated KCl) reference electrode. The surface of GCE was polished with $0.05\text{-}\mu\text{m}$ alumina particle suspension on a moistened polishing cloth prior to use. Cyclic voltammograms (CVs) were measured using a potentiostat HZ5000 (Hokuto Denko) at 25°C in 0.1 ($1.0, 0.01$) mol dm^{-3} sodium phosphate buffer (PBS, pH 7) or 0.22 mol dm^{-3} acetate buffer (pH 4) deaerated by Ar bubbling.

3. Results and Discussion

3.1 Reduction of Se(+4) in the absence of MV^{2+}

Figure 1 shows CVs for the reduction of Se(+4) species measured at GCE in neutral and acidic aqueous solutions. In 0.1 mol dm^{-3} PBS (pH 7), the reduction current started to increase at -0.5 V for $30.1 \text{ mmol dm}^{-3}$ Na_2SeO_3 , whereas no apparent reduction current appeared for 4.0 mmol dm^{-3} Na_2SeO_3 . Compared with the CVs at pH 7, the reduction current in 0.22 mol dm^{-3} acetate buffer (pH 4) containing 4.0 mmol dm^{-3} Na_2SeO_3 increased with a shift in its onset potential to -0.3 V . Further increasing the Na_2SeO_3 concentration to $30.1 \text{ mmol dm}^{-3}$ resulted in a decrease in the reduction current due probably to the deposition of the insulating red Se on the electrode surface. According to the acid-base equilibria (1) and (2) (written below), $HSeO_3^-$ is dominant at pH 4, whereas at pH 7, a mixture of $HSeO_3^-$ and SeO_3^{2-} exists. The difference in the reduction onset potential between pH 4 and 7 can be explained by the pH dependence of redox potentials for the reactions (3) and (4). In addition, high overpotentials for these reductions are confirmed from the fact that the onset potentials at pH 4 and 7 are more

Figure 1. Cyclic voltammograms measured at glassy carbon working electrode (GCE) in (a) 0.1 mol dm⁻³ sodium phosphate buffer (PBS) (pH 7) and (b) 0.22 mol dm⁻³ acetate buffer (pH 4) containing 0 (solid line), 4.0 (dashed line), and 30.1 (dotted line) mmol dm⁻³ of Na₂SeO₃.

Figure 2. Cyclic voltammograms measured at GCE in 0.1 mol dm⁻³ PBS (pH 7) containing 1 mmol dm⁻³ methyl viologen (MV²⁺) and 0 (solid line), 4.0 (dashed line), and 30.1 (dotted line) mmol dm⁻³ of Na₂SeO₃.

negative than the redox potentials of reactions (3) and (4) at the corresponding pH values.

3.2 Reduction of Se(+4) in the presence of MV²⁺

The addition of 1 mmol dm⁻³ MV²⁺ accelerated the reduction of Se(+4) by more than 500 times at pH 7 (Fig. 2). During the reduction, water-insoluble red Se was dispersed in the vicinity of the GCE surface. The onset potential of the reduction current coincides with that of the MV²⁺ reduction. As shown in Fig. 3, Michaelis-Menten-type plots were obtained for the relationship between the magnitude of the current increment (Δi) and the concentration of

Figure 3. Magnitude of the current increase (Δi) as a function of the concentration of Na₂SeO₃ in the presence of 1.0 (○), 5.0 (□), 10 (△), and 20 (◇) mmol dm⁻³ of MV²⁺.

Figure 4. Cyclic voltammograms measured at GCE in 0.22 mol dm⁻³ acetate buffer (pH 4) containing 1 mmol dm⁻³ MV²⁺ and 0 (solid line), 4.0 (dashed line), or 30.1 (dotted line) mmol dm⁻³ of Na₂SeO₃.

Na₂SeO₃, where the Δi value increased with the concentration of Na₂SeO₃ and leveled off above 15 mmol dm⁻³. The Δi value increased by 1.4 times when the concentration of MV²⁺ was increased from 1 to 5 mmol dm⁻³; however, no further increase was observed at concentration above 5 mmol dm⁻³. Although the acceleration mechanism is not fully understood, the Michaelis-Menten-type plots suggest that MV²⁺ mediates the electron transfer from GCE to Se(+4) dissolved in PBS.

The Se(+4) reduction also accelerated in 0.22 mol dm⁻³ sodium acetate buffer (pH 4) as shown in Fig. 4. Greater Δi values and a positive shift in the onset potential of Na₂SeO₃ reduction were observed in comparison to pH 7, which is attributable to the positive shift in the redox potentials of reactions (3) and (4) on decreasing the pH. Based on the potential range where the reduction current increases, large Δi is likely to be originated from the mediation by MV²⁺. However, for 4.0 mmol dm⁻³ Na₂SeO₃, the potential at which the reduction current begins to flow is more positive than that for MV²⁺, suggesting at the coexistence of other acceleration mechanisms in addition to the mediation by MV²⁺. In contrast, the acceleration of Se(+4) reduction did not occur at pH 9 (data not shown), where SeO₃²⁻ is the main Se(+4) species. Our recent measurements⁸ suggest that the difference between the redox properties of HSeO₃⁻ and SeO₃²⁻ reflects the pH dependence of the acceleration.

Figure 5 represents the effect of the concentration of PBS (pH 7) on the Δi value in the presence of 1 mmol dm⁻³ MV²⁺. The greater magnitude of acceleration was obtained at higher concentrations of PBS. At 0.01 mol dm⁻³ PBS, the Δi -[Na₂SeO₃] plot revealed a maximum Δi value of approximately 4.0 mmol dm⁻³, in contrast to the plots at 0.1 and 1.0 mol dm⁻³ PBS. When Na₂SeO₃ is added into PBS, the concentration of H⁺ (pH) changes through the acid-base equilibrium (2) and the reductions (3) and (4). Because of the lower

Figure 5. Magnitude of the current increase (Δi) as a function of the concentration of Na_2SeO_3 in the presence of 1.0 mmol dm^{-3} of MV^{2+} in 0.01 ($\ominus$), 0.1 ($\bullet$), and 1.0 ($\circ$) mol dm^{-3} PBS (pH 7). To examine the effect of ionic strength on the reduction current, the ionic strength of 0.01 mol dm^{-3} PBS was increased to 0.22 ($\square$) and 2.2 ($\blacksquare$) mol dm^{-3} by adding an appropriate amount of NaCl.

buffer capacity of 0.01 mol dm^{-3} PBS, the pH value increases with the addition of Na_2SeO_3 . This is the reason for the formation of the convex plot, because the magnitude of acceleration becomes lower with increasing pH, as mentioned above. The ionic strength of PBS changes concomitantly with its concentration. In order to examine the effect of ionic strength on the acceleration of reduction, the ionic strength of 0.01 mol dm^{-3} PBS ($0.022 \text{ mol dm}^{-3}$) was raised to 0.22 or 2.2 mol dm^{-3} by adding appropriate amount of NaCl. The shapes of the resulting Δi - $[\text{Na}_2\text{SeO}_3]$ plots were similar to that obtained with the original 0.01 mol dm^{-3} PBS and independent of the ionic strength. The electrochemical reduction of Na_2SeO_3 mediated by MV^{2+} consists of two steps: (1) the reduction of MV^{2+} to MV^+ at the electrode surface, and (2) the reduction of $\text{Se}(+4)$ to $\text{Se}(0)$ by MV^+ in the buffer solution. The shape and magnitude of CV for the $\text{MV}^{2+}/+$ redox couple were independent of the PBS concentration, showing that the PBS concentration is likely to affect the latter step. Since protons are included in the reductions (3) and (4), the higher buffer capacity (higher buffer concentration) seems to be decisive in achieving greater acceleration.

3.3 Reduction of $\text{Se}(+6)$ in the presence of MV^{2+}

The addition of MV^{2+} is also effective in accelerating the reduction of $\text{Se}(+6)$, which has been reported to be electrochemically inactive,⁶ under both neutral and acidic conditions (Fig. 6). According to the $\text{p}K$ values for the acid-base equilibria of H_2SeO_4 ,⁵ SeO_4^{2-} is the main redox component at pH 4 and 7. In spite of the fact that the redox potentials for the reduction reactions of SeO_4^{2-} , (5) and (6), are more positive than those for the reduction of $\text{Se}(+4)$, the magnitude of acceleration is lower for SeO_4^{2-} than for $\text{Se}(+4)$, suggesting more sluggish nature of the MV^{2+} -mediated reduction of SeO_4^{2-} .

Figure 6. Cyclic voltammograms (CVs) measured at GCE in (a) 0.1 mol dm^{-3} PBS (pH 7) and (b) 0.22 mol dm^{-3} acetate buffer (pH 4) containing 1 mmol dm^{-3} MV^{2+} and 0 (solid line), 30 (dashed line), or 117 (dotted line) mmol dm^{-3} of Na_2SeO_4 . CVs measured for 117 mmol dm^{-3} of Na_2SeO_4 in the same buffer solutions in the absence of MV^{2+} are also shown (dashed-dotted line).

4. Conclusions

MV^{2+} is able to accelerate the reduction of water-soluble $\text{Se}(+4)$ and $\text{Se}(+6)$ species. The greatest magnitude of acceleration (more than 500 times) was obtained for the reduction of Na_2SeO_3 in 0.1 mol dm^{-3} PBS (pH 7) in the presence of 5 mmol dm^{-3} MV^{2+} . The Michaelis-Menten-type relationships between the reduction current and the concentration of Na_2SeO_3 indicate that MV^{2+} molecules mediate the electron transfer from the electrode to $\text{Se}(+4)$ dissolved in buffer solutions. Benzyl viologen, heptyl viologen, and alizarin red S (data not shown) are also effective in accelerating the reduction of Na_2SeO_3 , although the magnitude of acceleration is the highest for MV^{2+} . The properties of the mediator required for effective acceleration are yet to be clarified. It is suggested that high buffer capacity is important to achieve greater acceleration. Red precipitates or colloids of Se are generated as the reduction products, which will be useful for recycling of Se from Se-containing wastewaters. Detailed analysis of the acceleration mechanism is still under investigation.

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