Notes

Adsorptive Stripping Voltammetry of Selenium(IV) in the Presence of Thioglycolic Acid

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The physiological effects of selenium have only recently been understood. Although it is an essential nutrient at trace levels¹, it becomes toxic when in excess.^{2,3} The determination of selenium(IV) has usually been carried out by spectrophotometry using Bismuthiol II⁴, ferrous ion⁵, 3,3'-diaminobenzidine⁶, thioglycolic acid (TGA)⁷ and by fluorometry using 3,3'-diaminobenzidine⁸ and 2,3-diaminonaphthalene⁹ as reagents.

For the determination of Se(IV) many electrochemical methods have been used.¹⁰⁻¹² Of these methods, anodic stripping voltammetry¹¹ and cathodic stripping voltammetry¹², in which elementary selenium or its amalgam with mercury is accumulated on the surface of an electrode are the more sensitive. The recently developed adsorptive stripping voltammetry is capable of measuring lower levels of selenium by using mainly aromatic diamines¹³⁻¹⁶ as ligands. In this work, the adsorptive stripping voltammetry of Se(IV) in the presence of TGA was first investigated. A soluble complex of selenium thioglycolate⁷ between Se(IV) and TGA was formed in 4 M HCl. The complex was adsorbed onto a mercury drop *via* a preconcentration or adsorption step. In the deposition step, voltammetric responses were produced which showed marked gains in sensitivity, higher specificity and lower limits of detection compared to the conventional anodic or cathodic stripping voltammetry.

Experimental

Apparatus

A polarographic analyzer (PAR 174A) and Linseis LY 1600 model X-Y recorder were used to record all of the voltammograms. The pH values were measured with a Hanna HI 8521 pH meter. A home-made capillary hanging mercury drop electrode (HMDE) was used as the working electrode. For the HMDE, a glass stopcock was sealed to glass tubing. The lower end of the tubing was extended as a capillary, and a platinum wire was sealed into the capillary below the stopcock. The upper section of the stopcock was used as a mercury reservoir. By turning the stopcock, a drop could be suspended prior to each experiment. A platinum wire

was used as the counter electrode and SCE as the reference electrode. All potentials were measured against the SCE.

Reagents

All of the chemicals used were prepared from analytical-grade chemicals (Merck), and triply distilled water was used throughout. The stock solution of Se(IV) (0.1 M) was prepared by dissolving SeO₂ in hot water. The stock solution of TGA (0.224 M) was freshly prepared from a concentrated TGA (1 l=1.33 kg, M=92.12 g mol⁻¹, 97%) solution.

Working standard solutions of Se(IV) and TGA were prepared by diluting the stock solutions to appropriate volumes.

Procedure

The solution was deaerated for 10 min with pure nitrogen (99.999%). Then, a mercury drop was suspended and deposition was carried out for 2 min at -0.1 V while stirring the solution by passing nitrogen at a flow rate of 100 ml min⁻¹. After a rest period of 15 s, the response curve was recorded by scanning the potential from -0.1 to -0.7 V at a scan rate of 50 mV s⁻¹.

Results and Discussion

Polarographic behavior of TGA and the Se(IV)-TGA complex

The electrochemical behavior of TGA and the Se(IV)-TGA complex had not been yet studied. Thus, normal polarographic waves of the TGA molecule were studied over a wide range of pH. Thioglycolic acid gave a single pH-dependent reduction wave. The half-wave potential in 2 M HCl was -0.05 V, and shifted to -0.57 V in 0.1 M NaOH. The reduction of TGA became easier in an acidic solution, and the diffusion current was lower in basic solution compared to that in an acidic solution. The change in the half-wave potentials and diffusion currents of TGA with the pH are given in Table I. Polarographic waves of the Se(IV)-TGA complex were well defined, and the half-wave potentials of the complex shifted from -0.53 to -0.48 V in the concentration range of 1.0 - 4.0 M HCl. Thioglycolic acid polarograms could not be obtained in 3.0 - 4.0 M HCl solution, since its half-

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Table 1 Effect of the pH on the half-wave potential and diffusion current for 3.35×10^{-4} M TGA

pH	$E_{1/2}/V$	$i_d/\mu A$
2 M HCl	-0.05	105
0.1 M HCl	-0.12	97.5
2.56	-0.15	84.0
4.82	-0.26	70.5
8.35	-0.46	55.5
11.35	-0.51	54.0
0.1 M NaOH	-0.57	49.5

Britton–Robinson (B–R buffer solution) was used between pH 2.56–11.35. Potential scan rate = 5 mV s^{-1} , and drop time = 2.7 s.

wave potential is so positive that the reduction of mercury chloride on the electrode was observed.

Voltammetric behavior of TGA and the Se(IV)-TGA complex

Cathodic stripping voltammograms of Se(IV) and the Se(IV)-TGA complex on a capillary HMDE in 4 M HCl is shown in Fig. 1. When there was only 2.0×10^{-7} M Se(IV) in a basal solution of 4 M HCl, a deposition potential of -0.1 V was applied for 2 min by passing nitrogen through the solution at a flow rate of 100 ml min^{-1} . After a rest period of 15 s, a potential scan of 50 mV s^{-1} was applied toward the negative potential, and a reduction peak of Se(IV) at -0.44 V was observed. Then, a TGA solution was added to the cell, so that the TGA concentration would be $2.24 \times 10^{-3} \text{ M}$. The solution was stirred for 1 min without applying any potential in order to allow a reaction between Se(IV) and TGA to form the complex. The same deposition and stripping procedure was applied for the Se(IV)-TGA complex, and a new reduction peak at -0.46 V was observed. As can be seen from Fig. 1, this peak was 2–3 times larger than the corresponding selenite peak, and the peak height was proportional to the concentration of Se(IV). Since Se(IV) was deposited as the adsorbed complex on the electrode, the peak current was large enough to have better sensitivities than the ordinary stripping of selenium. This peak could therefore be used for the determination of Se(IV). Thioglycolic acid alone did not give a cathodic stripping peak in 4 M HCl.

Adsorptivity

The adsorptivity of TGA and the Se(IV)-TGA complex was examined using several techniques. Normal polarographic waves of TGA and the Se(IV)-TGA complex in acidic solution showed a linear dependence between the column height of the mercury reservoir with limiting current. This is a fundamental criterion for the adsorption control of the polarographic wave height. In the linear-scan voltammetry of TGA in acidic solutions, the linear relationship between the logarithm of the peak current and the logarithm of the scan rate with a slope of 0.97 indicates that the molecule was adsorbed on the electrode.¹⁷

Fig. 1 Cathodic stripping voltammogram of Se(IV) with and without TGA in a 4 M HCl solution. 1) 4 M HCl; 2) 2.0×10^{-7} M Se(IV); 3) 2.0×10^{-7} M Se(IV) and 2.24×10^{-3} M TGA. Deposition potential, -0.1 V ; deposition time, 2 min; scan rate, 50 mV s^{-1} .

To consider the adsorptive behavior of TGA and the Se(IV)-TGA complex on the electrode, the drop times of a dropping mercury electrode were measured at different potentials. The drop time in a solution containing TGA or the Se(IV)-TGA complex was investigated in 4 M HCl compared to an electrolyte solution over a wide range (-0.1 V to -1.0 V) of potential. The electrocapillary curves for TGA and the complex were obtained as it was expected based on the adsorption phenomenon. The curve for the complex and supporting electrolyte are given in Fig. 2. This suggested that TGA, itself, and the Se(IV)-TGA complex were adsorbed on the electrode surface.¹⁸ This complex was produced from the reaction of the adsorbed TGA and the adsorbed selenium, which had been formed by the reduction of selenite on HMDE. The adsorption of selenium on the HMDE was proven in our former cyclic voltammetric studies.¹⁹

Effect of HCl concentration on the peak height of the Se(IV)-TGA complex

Selenium(IV)-TGA complex was studied in a 1–4 M HCl solution spectrophotometrically.⁷ For this reason, an HCl solution was selected as the supporting electrolyte. The effect of the HCl concentration on the Se(IV)-TGA voltammograms was studied using CSV techniques to determine the optimum HCl concentration. In a solution containing 2.0×10^{-7} M Se(IV) and 2.2×10^{-3} M TGA, the peak heights initially increased along with increasing HCl concentration up to 4 M, whereas it was diminished at higher HCl concentrations.

Effect of the deposition potential

The relationship between the peak current and the deposition potential is shown in Fig. 3. In 4 M HCl, which contained 1.0×10^{-7} M Se(IV) and 1.12×10^{-3} M TGA, the Se(IV)-TGA complex was deposited on the HMDE for 2 min at several deposition potentials. The

Fig. 2 Effect of applied potentials on the drop time for Se(IV)-TGA complex. (a) supporting electrolyte (4 M HCl); (b) Se(IV)-TGA complex.

Fig. 3 Effect of the deposition potential on the CSV peak current obtained using CSV for 1.0×10^{-7} M Se(IV) and 1.12×10^{-3} M TGA in 4 M HCl. All other conditions were as in Fig. 1.

selenium complex could be accumulated efficiently on the electrode at -0.1 V, and a well-defined reduction peak was observed. At a more negative potential than -0.1 V the peak current decreased sharply, probably because of the reduction of selenite into selenide. When the deposition was carried out at a more positive potential than -0.1 V, the base current increased and interfered with any measurement of the reduction current of the Se(IV)-TGA complex. This was probably due to the formation of mercury chloride on the electrode. The deposition at -0.1 V was suitable for obtaining a

Fig. 4 Effect of the deposition time on the CSV peak current in 4 M HCl. (a) 5.4×10^{-8} M Se(IV); (b) 2.24×10^{-3} M TGA and 5.4×10^{-8} M Se(IV). Deposition potential, -0.1 V; scan rate, 50 mV s^{-1} .

reproducible peak current.

Effect of the deposition time

Figure 4a shows the effect of the deposition time on peak current for the reduction of Se(IV) under optimized conditions. When the deposition time was increased, a linear increment in the peak current was also observed. When the reduction current for the Se(IV)-TGA complex was measured as a function of the deposition time, there was a steady increase in the peak height from 2 to 8 min, whereas the peak height became nearly constant after 8 min (Fig. 4b). This means that the adsorption of the complex on the electrode surface approached equilibrium. As can be seen in Fig. 4b, the peak current strongly depended on the deposition time (the longer the deposition time, the larger the peak current), suggesting an effective adsorption of selenium complex on to the HMDE electrode surface.

Effect of the temperature

The influence of the reaction temperature on the CSV peak current was examined at various temperatures (Fig. 5). The reaction between Se(IV) and TGA was found to be influenced by the temperature. The peak current for the complex decreased along with increasing the temperature, as expected, because the adsorption of the complex decreased along with increasing the temperature (Fig. 5a). In the absence of TGA, the reduction peak current of Se(IV) increased between 22 – 28°C and remained constant until 35°C ; a decrease in the peak current was observed at between 35 – 40°C (Fig. 5b). For the adsorptive cathodic stripping procedure of the complex, 22°C was found to be the optimum temperature.

Fig. 5 Effect of the temperature on the peak current of the Se(IV)-TGA complex and Se(IV). (a) 2.24×10^{-3} M TGA and 6.0×10^{-7} M Se(IV); (b) 6.0×10^{-7} M Se(IV). All other conditions were as in Fig. 1.

Influences of co-existing ions

The effect of possible interferences from some metals, such as Ni(II), Cu(II), Cr(III), Pb(II), Sb(III) and Cd(II), was investigated at a concentration of 2.24×10^{-3} M Se(IV) in the presence of 2.24×10^{-3} M TGA. The co-existing ions were taken at twenty-five, fifty and hundred times the amount of Se(IV). The results are summarized in Table 2. The values in the table show the ratio of the peak currents in the presence of the co-existing ions to that in their absence (by percentage). Ni(II), Pb(II), Sb(III) and Cr(III) had little effect on the determination of Se(IV) within the range of their concentrations. Cadmium steadily increased the peak current, since the reduction potential of Cd(II) is close to that of the selenium(IV)-TGA complex. Copper decreased the peak current. This may have been due to the formation of an intermetallic compound between the copper and selenium.¹⁹

Calibration curve

When the deposition was carried out for 2 min at -0.1 V in 4 M HCl containing 2.24×10^{-3} M TGA, followed by a potential scan of 50 mV s^{-1} , the calibration curve was linear over the range 6.0×10^{-8} – 8.5×10^{-7} M Se(IV) with a correlation coefficient of 0.9953. The detection limit was 2.0×10^{-8} M at a deposition time of 2 min, and lower at larger deposition times. The relative standard deviation for five determinations of 9.3×10^{-8} M Se(IV) was 5.4%. This method can be applied for the determination of selenium in biological and environmental samples.

Table 2 Influence of co-existing ions for the peak current of Se(IV)-TGA

Ion	Concentration of co-existing ions/ μM	Signal ratio, %
Ni(II)	6	106
	12	106
	24	112
Cu(II)	6	70
	12	65
	24	55
Cr(III)	6	114
	12	117
	24	117
Pb(II)	6	95
	12	95
	24	90
Sb(III)	6	91
	12	95
	24	104
Cd(II)	6	113
	12	148
	24	160

The standard analytical procedure was applied. Selenium(IV)-thioglycolic acid (2.42×10^{-7} M Se(IV) and 2.24×10^{-3} M TGA in 4 M HCl).

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