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Electrochemical Reduction of Selenium(+4) in Acidic Perchlorate Solutions

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The mechanism of selenium(+4) electrochemical reduction in acidic perchlorate solutions was studied. Dropping mercury and hanging mercury drop electrodes were used in direct current, alternating current, pulse and differential pulse polarographic and voltammetric measurements. Potentiostatic electrolysis experiments on mercury electrode were also performed.

Precipitates formed on the electrode surface were identified using the x-ray diffraction and x-ray fluorescence. At the mercury electrode surface, depending on selenium concentration in the solution, mercury selenide or elemental selenium was accumulated. The results were greatly influenced by the presence of Hg^{2+} ions in the perchlorate medium. The potential of the peak is pH dependent. Surface active substances supress the peak height, while the cupric ions significantly enhance it.

INTRODUCTION

During the last decades the chemistry and the physics of selenium have been studied intensively because of its semiconducting properties, its environmental and health effects. In biological processes selenium is an essential trace element[1] and a constituent of an enzyme glutathione peroxidase[2] that catalyses the reduction of peroxides, thus protecting biomembranes against oxidative damage. Furthermore, selenium is a powerful agent against mercury[3] and methyl mercury[4] toxicity (which also demonstrates its cancer protecting activity).

Epidemiological evidence indicates inverse associations between human cancer mortalities and the dietary selenium intakes.[5] However, at high concentrations selenium is also toxic.[6,7] Some acute and chronic diseases in livestock have been ascribed to selenium poisoning caused by a high intake of seleniferous plants[8] mainly of the *Astragalus* group.

Redistribution of selenium in the environment is a result of natural weathering processes and human activities, such as fossil fuel combustion, roasting of sulfide ores, uranium mining and milling,[9] *etc.* It is thus of great importance that a reliable method for the determination of selenium in water, soil, plants, and organisms be available. The knowledge of selenium concentration levels is important not only from the pollution point of view (mine residues) but also for the identification of seleniferous and deficient areas. For this purpose different analytical techniques, such as neutron activation analysis, atomic absorption spectrometry, gas-liquid chromatography, spectrophotometry, fluorimetry, and X-ray fluorescence, are usually used.[10] However, because of their simplicity, selectivity, and high sensitivity, the application of electroanalytical techniques also seems promising.

In natural waters[11] selenium appears as Se(+6) and Se(+4), only the latter being electroactive.[12] A detailed knowledge of the redox mechanism of selenium(+4) in aqueous solutions is, therefore, of prime importance for the development and application of high sensitivity voltammetric methods for measurements of environmental samples. Since 1935 many papers have been published on the polarography and voltammetry of selenium(+4) in different aqueous media.[12–20] A critical review has recently been published.[21] Unfortunately, there is still a certain confusion in the interpretation of experimental results. Depending on the solutes and the initial conditions two or three cathodic waves have been observed in acidic media. There is general agreement that in the second and the third wave, Se(+4) is reduced through a six electron reduction to a —2 valent state. The second polarographic wave is reversible. However, there is no agreement on the mechanisms and the products that correspond to the first porographic wave. The majority of researchers support the mechanism suggested by Lingane and Niedrach:[12] the primary electrode reaction is a six electron reduction:

$$H_2SeO_3 + 6\,H^+ + 6\,e = H_2Se + 3\,H_2O \qquad (1)$$

This reduction is followed by the anodic depolarization of the mercury electrode by H_2Se

$$H_2Se + Hg = HgSe + 2\,H^+ + 2\,e \qquad (2)$$

Thus, the net reaction is a four electron process

$$H_2SeO_3 + 4\,H^+ + Hg + 4\,e = HgSe + 3\,H_2O \qquad (3)$$

The alternative mechanism to be found in the literature suggests that the first polarographic wave results from a four electron reduction of Se(4+) to the elemental state.[14]

$$H_2SeO_3 + 4\,e + 4\,H^+ = Se^\circ + 3\,H_2O \qquad (4)$$

Nevertheless, in stationary electrode voltammetry, the product of the electrode reaction of the first polarographic wave is adsorbed and accumulated on the electrode surface, giving one or more sharp reduction peaks at the potential of the second polarographic wave, enabling cathodic stripping voltammetric determination of selenium under certain conditions.[22] The sensitivity of such measurements can be significantly increased by the presence of moderate concentrations of Cu^{2+} ions in the solution[23,24] and/or by the application of differential pulse (DP) stripping voltammetric techniques.[22]

In the present work, the mechanism of selenium(+4) electrochemical reduction in acidic perchlorate solutions was studied. Dropping mercury (DME) and hanging mercury drop (HMDE) electrodes were used in direct current (DC), alternating current (AC), pulse (PP) and differential pulse (DPP) polarographic and voltammetric measurements. Potentiostatic electrolysis experiments on a mercury electrode were also performed. Attempts were made to explain the mechanism of the electrode reactions. At the same time, the coloured precipitates formed during the potentiostatic electrolysis on the mercury surface were analysed using x-ray diffraction and x-ray fluorescence.

EXPERIMENTAL

The polarographic and voltammetric measurements were made by means of the PAR 174 A (Princeton Applied Research Corp., Princeton, N. Y., USA) and a Hewlett Packard 7004B x—y recorder. The AC polarographic measurements and constant potential electrolysis were performed using the PAR 170 electrochemistry system.

The universal electrochemical cell Model EA 875-50 (»Metrohm«), provided with a Model EA 290 HMDE (»Metrohm«) or an ordinary DME with a drop timer, platinum wire as counter electrode and Ag/AgCl or saturated calomel (SCE) as reference electrode, was used. The solution was stirred with a magnetic stirring bar during the accumulation step. The potentiostatic electrolysis experiments were performed in a glass cell with a stirred mercury pool electrode of 44 cm^2 surface area, a SCE reference electrode and a platinum counter electrode separated from the investigated solution with a cation exchange membrane (Water Softeners Ltd.), as described earlier.[25] The volume of the electrolysed solution was usually 50 cm^3.

A standard solution of selenium(+4), approximately 0.01 mol dm^{-3}, was prepared by dissolving sodium selenite (Kemika, Zagreb, or Hopkin and Williams, Chadwell Heath), and standardized iodometrically.[26] It was acidified with perchloric acid to pH 1 to prevent adsorption on the container walls. This solution was daily diluted to lower concentrations required to avoid the ageing process of solution.

All chemicals used were of reagent grade. High purity nitrogen was used for deaeration of the solutions. Triply distilled water and doubly distilled mercury were used throughout the experiment.

Each measurement with the HMDE was made on a fresh mercury drop and several drops were discarded before starting a new measurement.

RESULTS

The DC and Pulse Polarography of Se(+4)

The DC and pulse polarographic measurements of Se(+4) in acidic perchlorate solutions in the pH range 0—2.8 were carried out at the constant ionic strength $\mu = 1$ mol dm^{-3} and selenium concentrations of 1×10^{-4} mol dm^{-3}. Typical curves are presented in Figure 1.

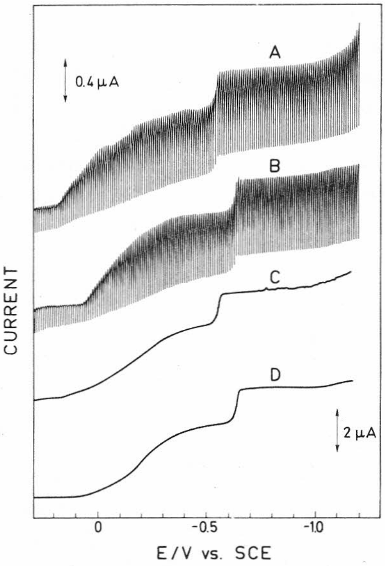

Figure 1. D. C. and pulse polarograms obtained for selenium(+4) 10^{-4} mol dm^{-3} solutions of the constant ionic strength (NaClO$_4$ + HClO$_4$ = 1 mol dm^{-3}). Perchloric acid concentration: (A) and (C) 1 mol dm^{-3} (B) and (D) 5×10^{-3} mol dm^{-3}.

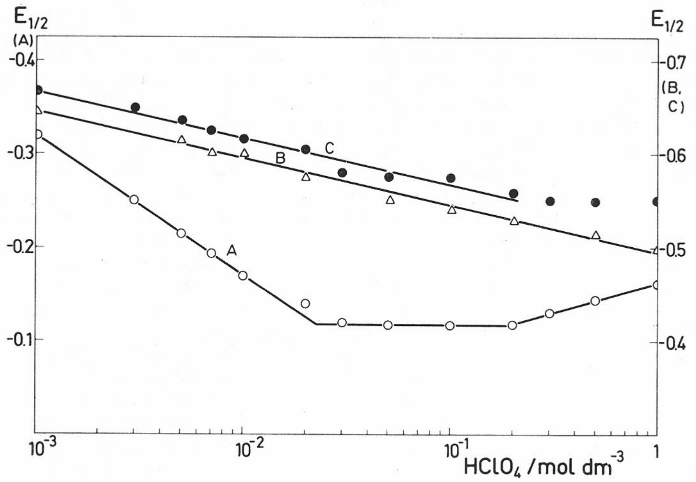

Figure 2. Dependence of selenium(+4) (10^{-4} mol dm^{-3}) half-wave and peak potentials on perchloric acid concentration in solutions of the constant 1 mol dm^{-3} ionic strength ($NaClO_4$ + $HClO_4$). Symbols: (○) the first and (●) the second cathodic wave of pulse polarography;(△) the first anodic peak in cyclic voltametry.

Two consecutive reduction polarographic waves are observed. The first one appears at about —0.1 V and the second at about —0.6 V (vs. SCE). These polarograms are ill-defined and unsuiatble for quantitative analysis.

The pulse polarographic waves are, however, well defined. The slope of the first one is about 200 mV, corresponding to a very irreversible process. This slope is acidity independent in the investigated $HClO_4$ concentration range, *i. e.,* 0.001—1 mol dm^{-3}. The $E_{1/2}$ of this wave, however, depends upon acidity of the solution, as shown in Figure 2. In the $HClO_4$ concentration range 0.2—1.0 mol dm^{-3} the half-wave potential is shifted positive by 55 mV/pH. In less acidic solutions, 0.03—0.2 mol $HClO_4$ dm^{-3}, it is pH independent. In the third range, from 0.001 to 0.02 mol $HClO_4$ dm^{-3}, there is a shift of —150 mV/pH. According to these results, one proton seems to be involved in the rate determining step of the irreversible reduction of Se(+4) if pH is higher than 1.5.

The half-wave potential of the second pulse polarographic wave is also acidity dependent, —55 mV/pH. The slope of this wave is about 20 mV, too steep for a two electron reversible wave.

The Voltammetry and Cathodic Stripping Voltammetry of Se(+4)

Voltammetric and cathodic stripping voltammetric measurements of selenium(+4) on HMDE in the concentration range of 10^{-4} — 10^{-7} Se(+4) mol dm^{-3} were carried out using dilute $HClO_4$ (pH 1—1.4) or acidic perchlorate solutions (μ = 1 mol dm^{-3}) as basic electrolytes. Typical curves for the latter case are shown in Figure 3. Two cathodic peaks (c_1, c_2) and one anodic peak (a_2) are usually observed. c_1 is a broad, ill-defined peak and its potential cannot be

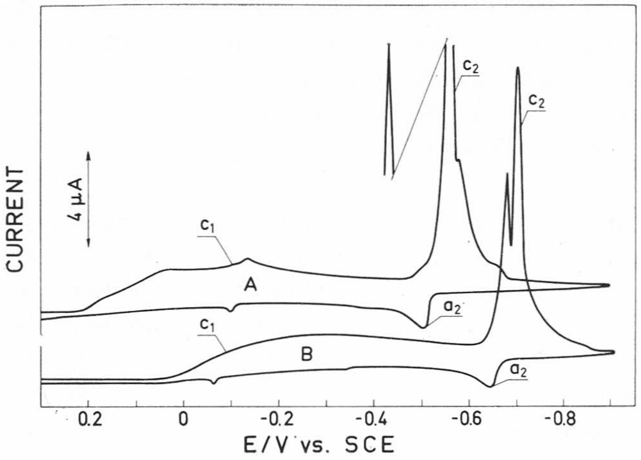

Figure 3. Cyclic voltammetric curves obtained for selenium(+4) 10^{-4} mol dm^{-3} solutions of the constant 1 mol dm^{-3} ionic strength ($NaClO_4 + HClO_4$). Perchloric acid concentration: (A) 1 mol dm^{-3}; (B) 1×10^{-3} mol dm^{-3}.

measured precisely. Depending on the pH value, its appearance potential varies from about +0.200 to +0.050 V. This peak corresponds to the first polarographic wave.

The second cathodic peak c_2 appears at about —0.6 V and usually consists of several peaks placed close together (Figure 3). It corresponds to the second polarographic wave and depends upon acidity in a similar manner.

The anodic peak (a_2) appears at about —0.6 V (vs. SCE) and represents the reversible oxidation of the product of the c_2 peak. In acidic prechlorate solutions of constant ionic strength, $\mu = 1$ mol dm^{-3}, the a_2 peak potential is shifted by —50 mV/pH (Figure 2). According to this result, two protons are involved in the reversible oxidation process.

A small oxidation peak indicated in Figure 3 near 0 V (*vs.* SCE) could not be undoubtedly ascribed to a selenium oxidation process.

If cathodic stripping voltammetry is applied, the number of peaks and their shape depend on the potential and time of accumulation, the selenium concentration, the rate of stirring and the scan rate. The deposition potential defines the size and appearance of the peaks. In dilute $HClO_4$ (0.06 mol dm^{-3}) three potential regions could be distinguished. The first from +0.05 to —0.15 V, the second between —0.15 and —0.40 V, and the third from —0.40 to —0.50 V (*vs.* SCE). By accumulation in the first or third potential range (at low selenium concentrations and relatively short deposition times) a single well-defined cathodic stripping peak is obtained, being slightly heigher ofter deposition in the first region. With increasing selenium concentration it becomes less defined and double or triple cathodic peaks appear. Concentrations of 10^{-5} — 10^{-4} Se(+4) mol dm^{-3} and deposition times of 60 seconds are usually too high to obtain a single cathodic stripping peak. After deposition in the second potential range, ill-defined multiple waves generally appear. This effect is very pronounced at high selenium concentrations and/or after long periods of accumulation.

At increased concentrations of selenium and at longer deposition times, a new cathodic peak c_3 appears at approximately —0.80 V (*vs. SCE*). Typical voltammetric curves illustrating the effect of accumulation time on the appearance of c_3 are given in Figure 4. Curve A represents the experimental conditions under which the third cathodic stripping peak appears. By decreasing the deposition time to half of its previous value and by doubling the concentration of selenium(+4) in the solution, c_3 disappears almost completely. This indicates the predominant influence of accumulation time on the appearance of this peak.

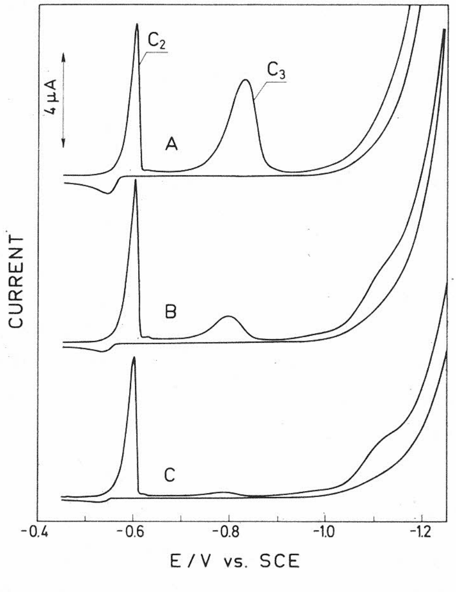

Figure 4. Influence of selenium(+4) concentration and accumulation time on the second (c_2) and third (c_3) cathodic peak measured by cathodic stripping voltammetry: (A) 2.4 × 10^{-6} mol Se(+4) dm^{-3}, 480 seconds; (B) 4.8 × 10^{-6} mol Se(+4) dm^{-3}, 240 seconds; (C) 9.6 × 10^{-6} mol Se(+4) dm^{-3}, 120 seconds. Deposition potential: —0.45 V *vs.* SCE. Scan rate: 50 mV s^{-1}.

Peak heights c_2 and c_3 are linearly proportional to the scan rate, indicating that both peaks are brought about by adsorption and/or precipitation (Figure 5),[27] which agrees with the strong influence shown by surfactants in Figure 6.

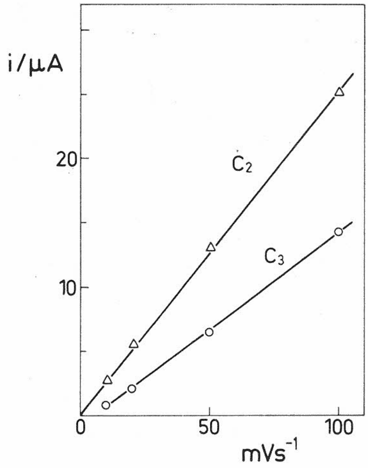

Figure 5. Selenium(+4) (10^{-4} mol dm^{-3}) peak height as a function of applied scan rate in CSV. Perchloric acid concentration: 7×10^{-2} mol dm^{-3}. Accumulation period: 60 seconds at —0.45 V *vs.* Ag/AgCl, without mixing.

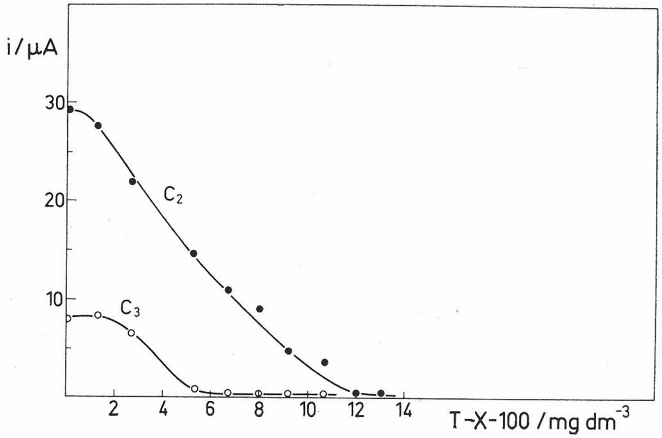

Figure 6. Influence of the surface active substance Triton-X-100 on the selenium(+4) (1×10^{-4} mol dm^{-3}) peak height. Perchloric acid concentration: 7×10^{-2} mol dm^{-3} Accumulation period: 60 seconds at —0.50 V *vs.* Ag/AgCl.

AC Voltammetric Measurement

To elucidate the nature of the Se(+4) electro-reduction product, phase sensitive AC voltammetric curves were recorded in the presence and absence of Hg^{2+} and Cu^{2+} ions. From the typical experimental results, shown in Figure 7, it is evident that in the presence of Hg^{2+}, the AC current decreases in the potential range between the first and second selenium cathodic peak. At potentials more negative than the second peak, no difference in AC current could be detected between the supporting electrolyte and solutions with selenium. This result indicates that Hg^{2+} ions play an important role in the

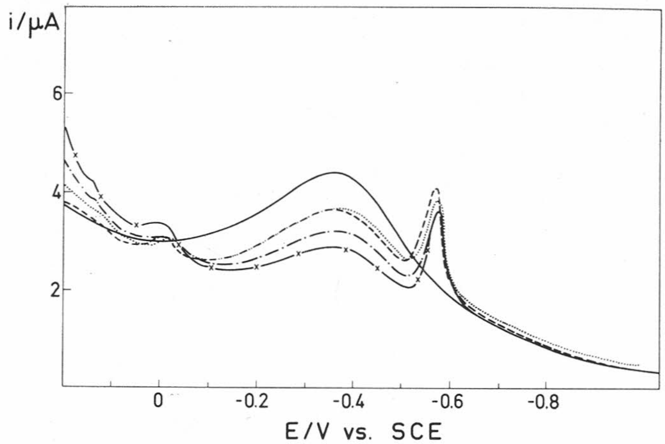

Figure 7. AC polarographic curves of Se(+4) for solutions of (—) 0.1 mol dm^{-3} $HClO_4$ (- - -) 3×10^{-5} mol dm^{-3} Se(+4) in the perchloric acid solution and in the presence of (· · ·) 1×10^{-5}, (—·—·—·—) 3×10^{-5}, (— × —) 6×10^{-5} mol dm^{-3} Hg^{2+}.

electrode process in the first wave. However, it is difficult to conclude whether they are incorporated in the product in the first polarographic wave.

In the presence of Cu^{2+} ions the AC curves were greatly complicated by the appearance of the copper reduction peak in the same potential region as Se. Possibly the influence of Cu^{2+} is similar to that of Hg^{2+} but the AC polarographic results are inconclusive.

Potentiostatic Electrolysis

The electrolysis was performed at 5×10^{-4} mol dm^{-3} and 6×10^{-3} mol dm^{-3} selenium concentrations. The product of potentiostatic electrolysis at —0.1 V (*vs.* SCE) at lower concentration of Se(+4) was always the same black precipitate which stuck to the mercury pool surface, irrespective of the rate of stirring. The precipitate was separated from the solution by filtration through a 0.45 µm Millipore membrane filter. After elimination of visible mercury drops, an x-ray diffraction spectrum was recorded. The spectrum indicated the presence of hexagonal HgSe in the precipitate.

The electrolysis time was 5 to 6 minutes and the number of coulombs consumed in the electrode process corresponded to a four electron reaction. At the end of electrolysis, if the potential was slowly changed to —0.8 V, the black precipitate disappeared and small gas bubbles were formed on the electrode surface. The characteristic smell of H_2Se was detected. By changing the potential back to —0.1 V the black precipitate was formed again.

In solutions containing selenium(+4) at a concentration of 6×10^{-3} mol dm^{-3}, the composition of the electrolysis product depended upon the rate of stirring of the mercury pool. At low stirring rates, a black precipitate, similar to that described above, was formed and the solution remained clear all the time. If the electrolysis was carried out by vigorous stirring of the solution and the mercury pool cathode, a red voluminous precipitate was obtained. The precipitate partly coagulated after 1 or 2 minutes of electrolysis. According to the x-ray diffraction spectra the product was amorphous. As the Se/Hg ratio was greater than 30, as determined by x-ray fluorescence spectroscopy, one can conclude that it was composed of amorphous elemental selenium. In the presence of Hg^{2+} ions, black-brownish precipitates were formed with Se/Hg ratios from 0.3 to 0.7 and x-ray diffraction spectra that corresponded to the crystalline HgSe. Too high a mercury content of the product could be ascribed to the elemental mercury which remained after separation.

Differential Pulse Cathodic Stripping Voltammetry

For analytical purposes, the results obtained using differential pulse cathodic stripping voltammetry on HMDE are very important. The height and shape of the peak located at about —0.450 V *vs.* Ag/AgCl depend also on the applied pulse modulation amplitude. After a short accumulation time, *e. g.* 60 seconds at —0.050 V *vs.* Ag/AgCl, a rounded peak always results in the concentration range $1 \times 10^{-8} - 1 \times 10^{-7}$ Se(+4) dm^{-3} with a modulation amplitude of 100 mV. In more concentrated solutions the peak becomes disproportionately high and very sharp. The »jump« appears at [Se] $\approx 3 \times 10^{-7}$ mol dm^{-3}. There is, however, a linear relationship between selenium concentration and peak height. The results obtained with the rounded peaks lie on one straight line while those obtained with sharp peaks are situated on another (Figure 8). If the initial selenium concentration is of a lower order of magnitude, *i. e.*, 1×10^{-9} mol dm^{-3} with ten times longer deposition period, the results are different. Under such conditions it seems that a modulation amplitude of 25 mV is optimal. If it is higher or lower, the peak is not well-developed, being too broad or too low, respectively. The current-concentration plot is linear from $1 \times 10^{-9} - 4 \times 10^{-8}$ mol dm^{-3} without any sudden jumps in peak height. With a further increase of selenium concentration, the peak becomes more and more deformed and is composed of two or three peaks placed close together. At concentrations higher than [Se] $= 2 \times 10^{-7}$ mol dm^{-3} a modulation amplitude of 25 mV is inappropriate, because only a badly shaped peak is formed, irrespective of the

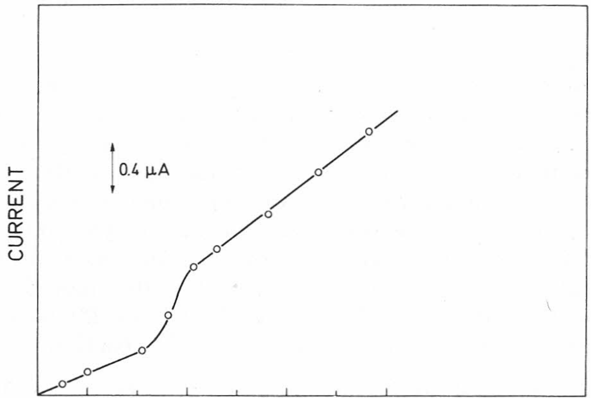

Figure 8. DPCSV current — concentration plot for selenium(+4) in acidic perchlorate solution. Accumulation time: 60 seconds at —0.050 V *vs.* Ag/AgCl. Pulse frequency: 2 Hz. Modulation amplitude: 100 mV. Scan rate: 5 mV s^{-1}.

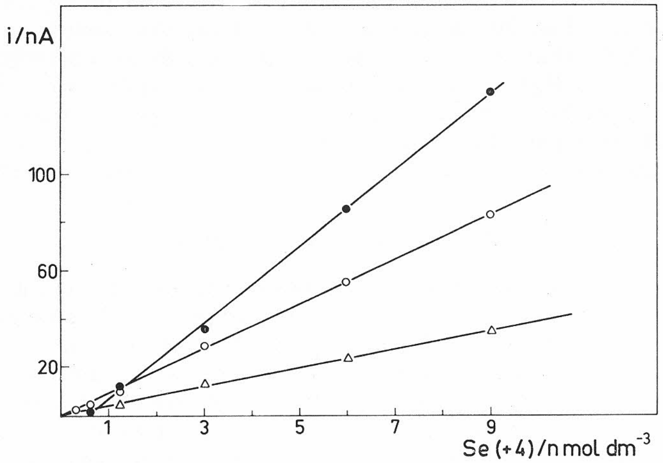

Figure 9. DPCSV current — concentration plot for selenium(+4) in acidic perchlorate solution in the presence of 2.4×10^{-5} mol dm^{-3} of copper(+2). Accumulation time: 300 seconds at —0.40 V *vs.* SCE. Modulation amplitude: (△) 25; (○) 50; (●) 100 mV. Scan rate: 5 mV s^{-1}.

accumulation period. If the amplitude of 100 mV is applied, its form changes again to the »normal« shape. However, at concentrations higher than 6×10^{-7} mol dm^{-3} a deformation of the wave appears again, irrespective of amplitude and/or accumulation times. In the presence of 10^{-5} and 10^{-4} mol dm^{-3} of ionic copper(+2) the DPCSV reduction peak of selenium(+4) is significantly higher and is situated at a more negative potential, with shifts of 60 and 120 mV, respectively. The peak is sharp, well-developed and can easily be distinguished from the background current, even at very low selenium(+4) concentrations. There is a linear relationship between the selenium concentration and the peak height from 3×10^{-10} to 10^{-8} mol dm^{-3} (at 300 second deposition time and with 25, 50 and 100 mV modulation amplitudes) (Figure 9).

DISCUSSION

According to our results, hydrogen selenide seems to be the first product of the selenium(+4) electro-reduction in acidic perchlorate solutions. In agreement with the reaction mechanism suggested by Lingane and Niedrach,[12] this product reacts with the mercury electrode, giving HgSe which remains attached to the electrode surface. In our experiments mercury selenide was identified as a product of the potentiostatic electrolysis but only when the selenium concentration was relatively low (5×10^{-4} mol dm^{-3}). However, at higher concentrations (6×10^{-3} mol dm^{-3}) and with vigorous stirring of the solution and the mercury pool, the effect of reaction (2) was negligible, and elemental selenium was formed by the following reaction:

$$H_2SeO_3 + 2\,H_2Se = 3\,Se + 3\,H_2O \qquad (5)$$

This reaction mechanism seems to be in agreement with literature data.[21] However, in the presence of Hg^{2+} ions, as the potentiostatic experiments show, the final product of the electrode reaction is HgSe. This indicates that the primary electrode process is still the formation of H_2Se, which probably reacts more easily with Hg^{2+} ions than with H_2SeO_3 present in the diffusion layer in the vicinity of the electrode surface.

$$Hg^{2+} + H_2Se = HgSe + 2\,H^+ \tag{6}$$

Such a reaction is indicated not only by the composition of the electrolysis product, but also by the AC voltammetric measurements. With an increase of Hg^{2+} concentration, there is a simultaneous decrease of the AC current at the potentials of the first polarographic wave. This indicates the formation of a product, incorporating Hg^{2+} ions, deposited or adsorbed on the electrode surface (Figure 7). In a recently published paper, Jarzabek and Kublik[28] also suggested that mercury selenide is the product that accumulates on the mercury surface during voltammetric measurements. However, a mercury electrode covered with several monolayers of HgSe behaves as an inert electrode, *i. e.*, on such an electrode elemental selenium is formed instead of mercury selenide. At the low concentrations normally encountered in analytical determinations of Se, the accumulated product on the HMDE will only be mercury selenide.

The slope of the first pulse polarographic wave (200 mV) of selenium(+4) suggests an irreversible proces in the 10^{-3} to 1 mol dm^{-3} $HClO_4$ concentration range. The slope of the wave is acidity independent and shows that there is no significant change in the character of the electrode process. However, as the half-wave potential is dependent on pH, this indicates that protons are involved in the rate determining step, preceding the electrode reaction. The shift of —150 mV/pH, observed in the pH range from 2 to 3, suggests that in the rate determining step, 0.85, *i. e.*, one proton, is consumed. This data was calculated on the basis of the well-known relation[29]

$$\frac{d \log \dfrac{i}{i_d - i}}{d \log [X]} = -n + k$$

in which n and k denote the number of »ligands«, *i. e.*, hydrogen atoms in the selenium(+4) »complex« before and after the chemical reaction, respectively. Observing that half-wave potential shift appears at acidities where the dissociation of H_2SeO_3 to $HSeO_3^-$ is significant,[30] one can conclude that the rate determining step of the electrode reaction is the protonation of the $HSeO_3^-$ ions. However, in the net electrochemical reduction of $HSeO_3^-$ according to the reaction:

$$HSeO_3^- + 7\,H^+ + 6\,e = H_2Se + 3\,H_2O \tag{7}$$

seven H^+ ions should be consumed. Thus, it seems likely that there are several other rate determining steps in this process. The fact that in the solution where H_2SeO_3 is the predominant species ($pH < 2$) there is no half-wave potential shift of the first wave, leads us to the conclusion that the most probable rate determining step is still the protonation reaction of $HSeO_3^-$.

The half-wave potential shift of the second pulse polarographic wave, 55 mV, and the peak potential shift of the corresponding anodic peak a_2, 50 mV, indicates that two protons are involved in the two electron reversible redox process. The shift of $E_{1/2}$ to more regative values, on increasing the pH, shows that in the reduction process two protons are consumed, while in the corresponding oxidation reaction two protons are released. This is most probably in accordance with reaction (2), the reaction mechanism in acidic media suggested by Lingane and Niedrach.[12]

Although nanogram quantitites of selenium(+4) can be measured using DPCSV, such methods are not used in the routine analyses of environmental samples. In natural waters direct measurements are complicated by the presence of surface active substances and interfering foreign ions. However, one is usually interested not only in the selenium(+4) concentration but also in the speciation problem and total selenium content. Such measurements cannot be performed directly because selenium-(+6) is electroinactive. Perhaps, the only well-known case of successful water analyses using DPCSV without any pretreatment of the sample is described by Nguyen *et al.*[22] However, rain water, which they studied, is relatively free from foreign substances and does not contain selenium(+6).[31] Lowry[32] described the voltammetric determination of total selenium in environmental samples after the destruction of organic matter, reduction of selenium(+6) to selenium(+4) and coelectrodeposition of the latter with copper on HMDE. Our results also confirm the literature data that the sensitivity of DPCSV measurements is significantly increased in the presence of Cu^{2+} ions. However, for a successful application of the method, further investigations of selenium chemistry and electrochemistry, especially at the trace level, are necessary.

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SAŽETAK

Elektrokemijska redukcija selena(+4) u kiselim otopinama perklorata

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Ispitan je mehanizam elektrokemijske redukcije selena(+4) u kiselim otopinama perklorata. U tu svrhu izvedena su različita polarografska i voltametrijska mjerenja koristeći kapajuću živinu elektrodu i viseću živinu kap. Eksperimentalni rad obuhvatio je i potenciostatsku elektrolizu na živinoj elektrodi.

Talozi stvoreni na elektrodnoj površini identificirani su difrakcijom i fluorescencijom x-zraka. Na površini živine elektrode, ovisno o koncentraciji selena(+4) u otopini, nakupljao se živin selenid ili elementarni selen. Na rezultate je jako utjecala prisutnost Hg^{2+} u perkloratnom mediju. Opaženo je da potencijal redukcijskog vrha ovisi o pH otopine. Površinski aktivne tvari smanjuju visinu tog vrha, a Cu^{2+} ioni znatno je povećavaju.