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Analytical Aspects of Selenium(+4)-Rhodium(+3) Interactions under Voltammetric Conditions

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Voltammetry of selenium(+4)-rhodium(+3) system was studied in different electrolyte solutions with special attention paid to possible application of the observed effects in selenite determination at trace levels. Although the signals obtained from such mixtures can be more than 200 times higher than those resulting from simple selenium(+4) solutions without rhodium(+3) added, it remains questionable how such results could be applied in practice. The main problem is data treatment because (generally) current – concentration plot is not a straight line with zero intercept. Additionally, its shape changes with the selenite concentration range. The problem is illustrated taking as an example selenium(+4) determination in solutions of selenium(+6). At present, results obtained in the system of interest seem to be important as phenomena and possible indicators of some catalytic processes. Before their application in trace analysis the answers to some general questions should be found.

INTRODUCTION

Since the classical paper by Lingane and Niedrach,[1] published in 1949, the scheme of selenium(+4) reduction on mercury electrodes (from acidic medium) has been generally accepted, although some different statements[2] could be found from time to time. Selenite is reduced at relatively positive potentials giving selenium(–2), *i.e.* hydrogen selenide as a primary product. The latter reacts with the electrode material, producing HgSe that stays attached to the mercury surface. In a negative scan, reductive dissolution of the accumulated product, *i.e.* the reduction of Hg(+2) from the deposit, takes place, giving a well-known voltammetric signal which is often used for indirect determination of selenium(+4) initially present in the solution. Formation of HgSe in the accumulation step was really confirmed[3] by X-ray diffraction and X-ray fluorescence spectroscopy, applied to the solid products deposited during potentiostatic electrolysis on a large mercury surface (44 cm^2) under different conditions.

If copper(+2) is present in the aqueous phase at a relatively high concentration (10^{-5}–10^{-4} mol dm^{-3}), Cu_2Se accumulates instead of HgSe,[4] whereas the dissolution signal has somewhat better properties than in the absence of foreign ions.[5] For the latter, addition of copper(+2) became a usual step in voltammetric determination of selenium(+4) at trace levels.[6,7] When rhodium(+3) (at a nanomolar level) is used instead of copper(+2), results become quite different.[8–10] Although Wang and Lu[8] proposed the scheme with accumulation and reductive dissolution of Rh_2Se_3, the system does not behave in such a way.[11] Selenium(+4) enhances the signals that are already

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known from the study of simple rhodium(+3)-electrolyte systems and usually ascribed to the catalytic hydrogen reduction[12,13] on islets of Rh°. It is possible that selenite or its reduction products can modify the size and/or properties of rhodium clusters on the mercury drop. The effect is in agreement with the fact that selenium(+6), which always contains some selenium(+4) as an impurity, is a well-known additive in the production of good quality rhodium deposits on metal surfaces.[13,14]

The signal that reflects reductive dissolution of HgSe decreases under the influence of dissolved rhodium.[10,11] This could be a consequence of different processes, one of which is the competition of Rh° and mercury selenide for places on the electrode surface whereas other possibilities include the formation of presently unknown species that contain both selenium and rhodium.

In this article voltammetric properties of rhodium(+3)-selenium(+4) system will be further treated, especially the influence of rhodium(+3) on selenite response in different electrolytes. This is important because determination of selenium(+4) in the presence of dissolved rhodium seems to be more sensitive than any other voltammetric procedure previously used for the same purpose (detection limit:[8,9] 2.4–6 pmol dm^{-3}). Unfortunately, the complete explanation of the observed effects is still lacking whereas their practical application seems difficult.[10] The problem will be illustrated using selenium(+4) determination in a real sample (with and without rhodium(+3) added) as an example.

EXPERIMENTAL

Electrolyte solutions were prepared from 96 % H_2SO_4, 36.5 % HCl or 71–72 % $HClO_4$ (all of analytical reagent grade) and deionized water obtained in a Millipore Milli-Q system. For preparation of selenium(+4) stock solution (0.01 mol dm^{-3} in 0.1 mol dm^{-3} $HClO_4$), 99.999 % Na_2SeO_3 (Aldrich) was used. Rhodium atomic spectroscopy standard (Fluka) with 1.000 g dm^{-3} of Rh (from $RhCl_3$) in 1 mol dm^{-3} HCl served as a source of Rh(+3). Diluted solutions of both types were prepared daily.

Voltammetric measurements were performed using μAutolab (Eco Chemie, Utrecht), connected to a 663 VA Stand (Metrohm) and a computer with the corresponding software installed (GPES, version 4.9). Glassy carbon rod served as a counter electrode whereas all potentials were defined with respect to Ag/AgCl (3 mol dm^{-3} KCl) reference electrode with the same solution in the electrolyte bridge. For measurements in 0.1 mol dm^{-3} perchloric acid, the bridge was filled with 3 mol dm^{-3} NaCl instead, to prevent the formation of poorly soluble $KClO_4$ in the frit. The other two electrolytes applied were 0.1 mol dm^{-3} H_2SO_4 and 0.3 mol dm^{-3} HCl, in accordance with the literature.[8–10]

At the start of each new experiment high purity nitrogen (99.999 %) was forced to pass through the solution in the polarographic cell for 15 minutes. All voltammetric measurements were performed on large mercury drops (0.52 mm^2) after accumulation from the solutions stirred at a rate of 1500 rotations per minute.

The room temperature was maintained at 25 °C.

RESULTS AND DISCUSSION

Selenium(+4)-rhodium(+3)-electrolyte System

In addition to the dissolution peak of accumulated HgSe (at nearly –0.47 V) and the signal that reflects catalytic reduction of hydrogen ions (at nearly –1.1 V), which are both known from different studies of simple selenium(+4)[3,5] and rhodium(+3) electrolyte solutions,[11,13] respectively, an additional signal (at nearly –0.7 V) is generally obtained from their mixtures. In other words, voltammogram with three peaks is usually recorded when selenium(+4) and rhodium(+3) are both present in the aqueous phase (Figure 1). In such a presentation the most positive peak is the lowest (*i.e.* an order of magnitude or more lower, when compared to the other two signals) and can even disappear at a high enough rhodium(+3) concentration.[10] Irrespective of the solution composition, it reflects a reversible reduction of the deposited material as follows from its forward and backward currents in square-wave voltammetry (SWV)[15] and linear dependence of the net peak height on the frequency. With increasing rhodium(+3) concentration this signal gradually decreases whereas the other two signals increase. In other words, the lowest selenite concentration that gives a measurable peak at –0.47 V depends (under otherwise identical conditions) on rhodium(+3) level in the electrolyte solution. Additionally, such a value is highly dependent on the deposition potential (E_d) applied. In 0.3 mol dm^{-3}

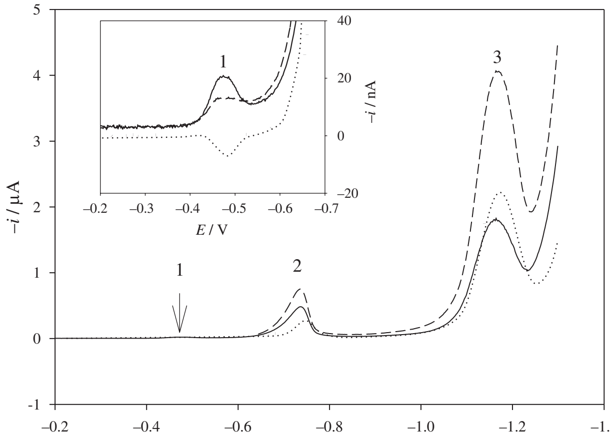

Figure 1. Square-wave voltammogram, together with its components. Inset: a part of the same plot on a different scale. Accumulation: 180 s at –0.2 V in 0.1 mol dm^{-3} H_2SO_4 containing 14 nmol dm^{-3} of selenium(+4) and 13.6 nmol dm^{-3} of Rh(+3); frequency (f): 100 s^{-1}; amplitude (E_{SW}): 25 mV; step potential (E_S): 2 mV. Solid line gives net current, short dash its forward component, whereas dotted line corresponds to backward current.

HCl, at a rhodium(+3) concentration of 3 μg dm^{-3} (*i.e.* 29 nmol dm^{-3}), it is 7 nmol dm^{-3} for E_d = – 0.3 V, and even 16 nmol dm^{-3} for E_d = – 0.1 V, *i.e.* much higher than in the corresponding selenite solution without rhodium(+3) added. In the latter case, the difference in the peak heights obtained after accumulation at the two potentials is not so pronounced, whereas the detection limit is only 0.98 nmol dm^{-3}. On the other hand, when the results obtained in rhodium(+3) solutions without selenite are compared it follows that the only peak (at –1.1 V) is well developed after accumulation at –0.1 V, but much less when E_d of –0.3 V is applied. The »opposite« dependence in selenite–rhodium mixtures could be explained in terms of quantities or properties of the rhodium deposit formed at the two accumulation potentials and its interference with the formation of HgSe, although possible role of chloride ions should not be ignored.

The main problem is the origin of a signal located at –0.7 V. A similar peak that reflects totally irreversible reduction, sometimes appears even in the absence of rhodium(+3), especially when a longer accumulation from a not too dilute selenium(+4) solution is applied.[3,5] Although the whole process is not clear, the reduction of elemental selenium, accumulated on the electrode surface (already covered by several layers of HgSe) was proposed as a possible explanation.[16] If so, the role of rhodium(+3) could be found in the »promotion« of such a form instead of HgSe, by preventing the dissolution of the electrode material which is necessary for the formation of the poorly soluble mercury selenide[17] (log $K_{sp} < -56$). In selenite-rhodium mixtures, however, the properties of the signal at –0.7 V,[11] cannot be ascribed to the reductive dissolution of some previously accumulated material. In fact, they cannot be ascribed to any simple and theoretically well-described process.

Measurements in 0.1 mol dm^{-3} H_2SO_4. – According to the literature data it is not quite clear how to choose the »best« electrolyte. Wang and Lu[8] applied sulfuric acid (0.1–0.2 mol dm^{-3}) but mentioned that other acids such as HCl, $HClO_4$ and HNO_3 could be used as well. Lange and van den Berg[9] chose 0.3 mol dm^{-3} hydrochloric acid instead, pointing to the possible role of chloride ions in the electrode process, but stressed that perchloric or nitric acid could not be applied for the same purpose. Our own results[10,11] indicate that 0.1 mol dm^{-3} $HClO_4$ is an acceptable electrolyte for the measurements of interest, although the sensitivity is not as high as in the literature examples. Therefore, it is of prime importance to test several electrolytes again under otherwise identical conditions.

Traces of rhodium(+3) and/or selenium(+4) usually do not give any voltammetric response without accumulation. The proper choice of the deposition potential is highly important, not only because the peak height depends on it but also because the form of current – concentration plot is affected by the chosen E_d. The phenomenon was described in our previous article[11] for rhodium(+3)-selenium(+4) system in 0.3 mol dm^{-3} HCl. Similar holds when 0.1 mol dm^{-3} H_2SO_4 is used as a basic electrolyte. In Figure 2 it is clearly seen that the peak height at –1.1 V changes differently, at increasing rhodium(+3) concentration and a constant selenite level, when the deposition potentials of –0.2 and –0.3 V are applied. The results obtained from the same solutions indicate that a lower rhodium(+3) concentration is needed for the appearance of the signal at –1.1 V than for the signal at –0.7 V if the accumulation potential of –0.3 V is chosen, whereas the opposite is true if E_d = –0.2 V. Peak current at –0.7 V is higher after accumulation at the more positive potential whereas the signal at –1.1 V becomes more pronounced when the more negative E_d

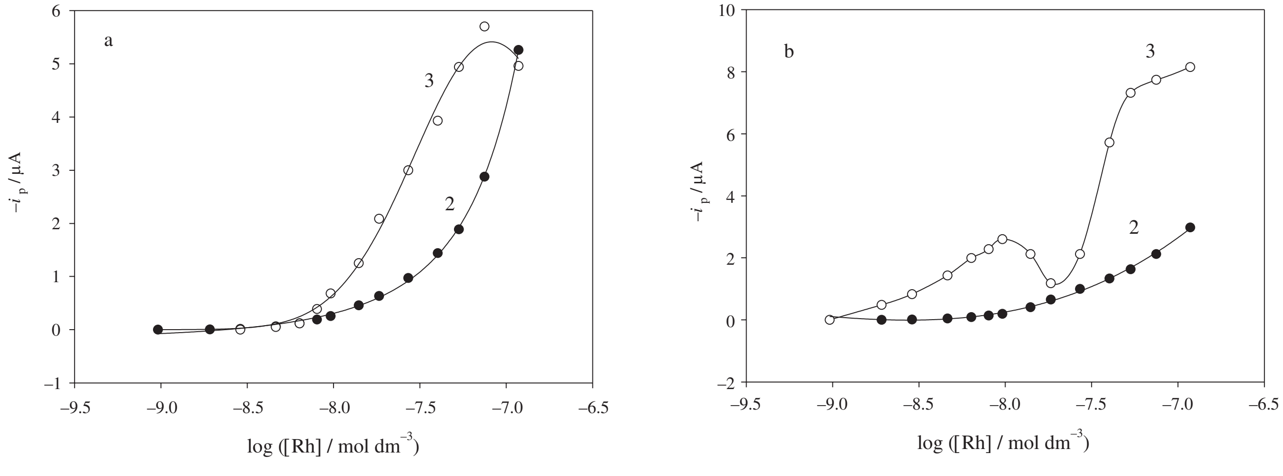

Figure 2. Dependence of square-wave peak height on the logarithm of rhodium(+3) concentration for the signals located at –0.7 and –1.1 V, after the deposition at –0.2 (a) and –0.3 V (b) from 0.1 mol dm^{-3} H_2SO_4. Selenite concentration: 14 nmol dm^{-3}, t_d = 180 s, f = 100 s^{-1}, E_{SW} = 25 mV, E_S = 2 mV. Numbers on the curves correspond to individual signals in accordance with Figure 1.

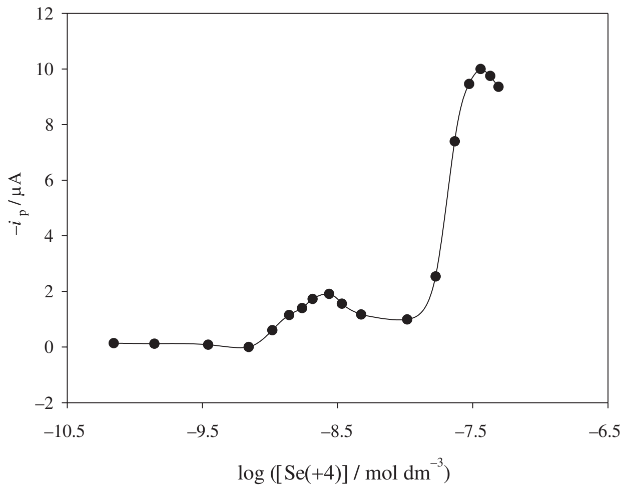

Figure 3. Dependence of the square-wave peak height at –1.1 V in 0.1 mol dm^{-3} H_2SO_4 on the logarithm of selenium(+4) concentration. Rhodium concentration: 29 nmol dm^{-3}; deposition potential: –0.3 V. Other conditions as for Figure 1.

value is applied. If the deposition at –0.3 V is chosen for experiments at a fixed rhodium(+3) level and gradually increasing selenium(+4) concentration, the dependence of i_p on log [Se] for the signal at –1.1 V is a curve with two maxima (Figure 3). In the system of interest such a dependence is not an exception because it was obtained for the same peak in some other cases as well (as described in the subsequent paragraphs). All this indicates that current – concentration linearity with zero intercept is extremely hard to reach.

Another problem which appeared during the measurements in 0.1 mol dm^{-3} H_2SO_4 was an unknown signal or a hump (located at the potentials that correspond to the reduction of HgSe) obtained, after accumulation, from the simple solution of sulfuric acid without selenium(+4) or rhodium(+3) added. The effect became more pronounced after the introduction of high frequencies and/or other changes that generally increase the peak height. Taking into account that some form of selenium appears in many, if not all sulfur compounds, it is possible that traces of selenite exist even in the reagent grade H_2SO_4. The concentration of such an impurity is so low that it can be detected only by extremely sensitive methods (with accumulation) whereas, for other purposes, such chemicals most probably can be used without problem. (While using the acid taken from different bottles of the same origin we found that only in some cases the mentioned signal appeared, whereas in other cases, measurements could be performed without difficulties.)

Measurements in 0.3 mol dm^{-3} HCl. – Similar experiments (as the above described) performed in 0.3 mol dm^{-3} HCl, indicate that the influence of the deposition potential on the i_p *vs.* log [Rh] plot is rather simple. Irrespective of the signal studied (at –0.7 or –1.1 V) a sigmoidal curve is obtained (Figure 6 in Ref. 11). However, when selenite concentration is gradually increased at a constant rhodium level (29 nmol dm^{-3}), the plot of the peak current (at –0.7 V) *vs.* log [Se(+4)] is a curve with more or less sharp maximum, depending on the accumulation potential applied (Figure 4a). The signal at –1.1 V, however, behaves in a somewhat different way (Figure 4b). After accumulation at –0.3 V, an S-shaped curve is obtained again (such as the one for the dependence of the peak height on the logarithm of rhodium(+3) concentration). If, however, E_d = –0.1 V is applied instead, Z – curve results, *i.e.* there is a range in which the signal decreases as the selenite concentration increases (Figure 4b). It is well-known that in chloride solutions selenium(+4) gives somewhat different voltammetric response when compared to the responses obtained in other acids, especially at relatively positive potentials.[18] The effect was

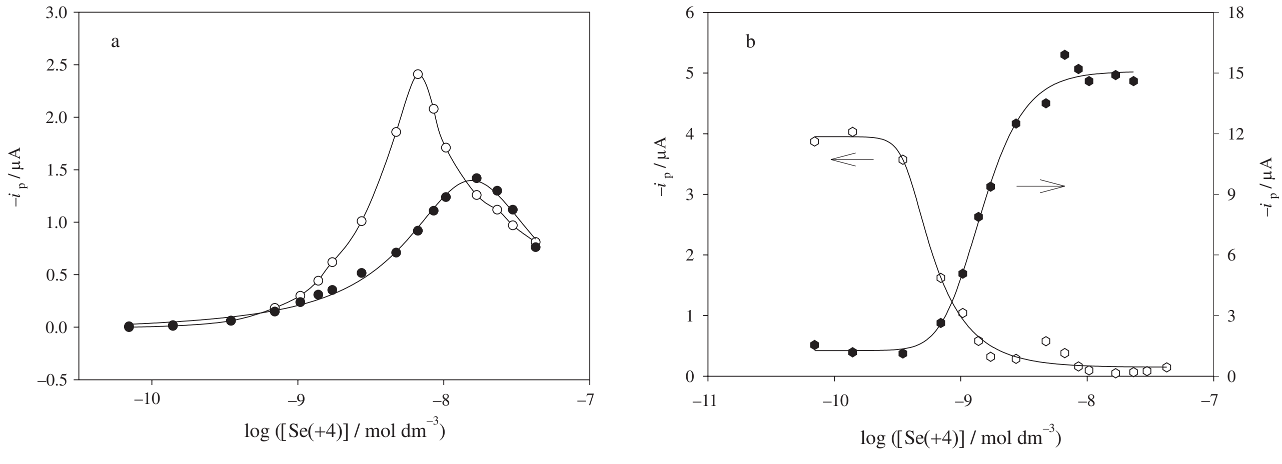

Figure 4. Dependence of square-wave peak height at –0.7 (a) and –1.1 V (b) in 0.3 mol dm^{-3} HCl on the logarithm of selenium(+4) concentration in solutions containing 29 nmol dm^{-3} of rhodium(+3). Deposition potential: –0.1 (empty circles) and –0.3 V (full circles). Other conditions as for Figure 1.

interpreted in terms of mercury / chloride interaction and its influence on the deposition processes of interest. As already mentioned, i_p *vs*. log [Se(+4)] plot for the peak at –1.1 V is usually a curve with two maxima. Therefore, the appearance of its descending part is not surprising although the entire curve in Figure 4b seems significantly different in comparison with those obtained from the other two electrolytes. The phenomenon that the signal at –1.1 V increases with increasing selenium(+4) concentration at a constant rhodium(+3) level as well as with increasing rhodium(+3) concentration at a constant selenium(+4) level, which was observed in sulfate solutions[11] and in 0.3 mol dm^{-3} HCl after accumulation at –0.3 V, obviously does not exist if the deposition at –0.1 V is applied. This could be of some practical importance when selenite determination at trace levels or formation of metal deposits is concerned.

For the appearance of a measurable peak at –0.73 V, rhodium(+3) level should be at least 1 nmol dm^{-3} if E_d = –0.1 V, and nearly 2 nmol dm^{-3} when the deposition at –0.3 V is performed. The signal at –1.1 V is (after deposition at –0.3 V) recognized by GPES, if rhodium concentration is 1 nmol dm^{-3} or more. This minimum concentration becomes twenty times higher when accumulation at –0.1 V is applied instead.

Measurements in 0.1 mol dm^{-3} HClO$_4$. – Some properties of selenium(+4)-rhodium(+3)-HClO$_4$ system have already been described.[10] All conclusions, however, were based on the experiments performed with a different measuring system and another kind of rhodium(+3) solution. Therefore, we repeated some of the experiments in order to obtain the results that can be compared with those described in the previous paragraphs.

The main impression is that with 0.1 mol dm^{-3} HClO$_4$ all results are more regular than with the other two electrolytes although higher rhodium(+3) level is needed for similar effects. The latter is in accordance with the previously described fact[11] that, in rhodium solutions without selenite, the lowest signal at –1.1 V is obtained in perchloric acid. Taking into account that the peak of interest reflects catalytic reduction of hydrogen ions on the islets of the deposited rhodium, it seems that the formation of such clusters is less efficient in perchlorate than in chloride and sulfate solutions or perhaps, some other metal modification is formed.

When the influence of selenite concentration on both peak heights (at –0.7 and –1.1 V) is followed at a constant rhodium level (58 nmol dm^{-3}), the previously mentioned i_p *vs*. log [Se(+4)] dependence with two maxima arises for the peak at –1.1 V after the deposition at –0.1 V (Figure 5). Taking into account the origin of this signal, the result can be explained in terms of two different rhodium modifications deposited on the electrode surface. Under the same conditions, the other signal (at –0.7 V) appears at about two orders of magnitude higher selenite concentration, whereas its i_p *vs*. log [Se(+4)] dependence can be described by a curve that passes through only one maximum in the concentration range studied (Figure 5). Some other effects point to the difference in the character of the processes that correspond to the signals 2 and 3 in Figure 1, in accordance with our previous results.[11] One of them is the influence of the applied voltammetric technique on the electrode response, obtained after accumulation at –0.1 V (Figure 6). When recorded from the same solution, square-wave and linear-scan voltammograms differ significantly. The latter consists of a relatively low signal at –0.7 V and about five times higher peak at –1.1 V. In comparison with it, the fourfold increase of the more positive and significant decrease of the more negative signal can be observed on the former.

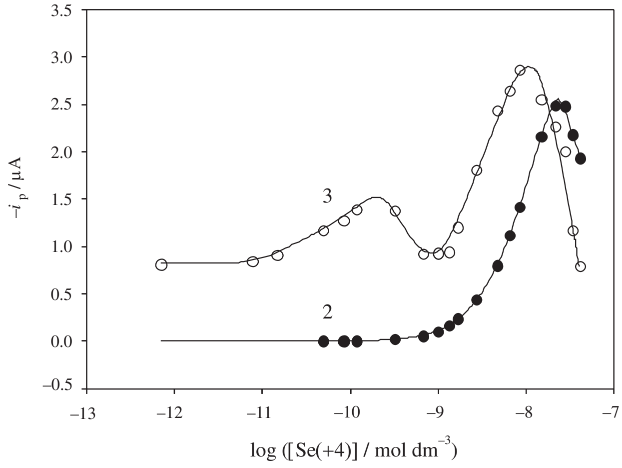

Figure 5. Peak height dependence on the logarithm of selenium(+4) concentration in 0.1 mol dm^{-3} HClO$_4$ containing 58.3 nmol dm^{-3} of rhodium(+3). Deposition potential: –0.1 V, deposition time: 180 s, f = 100 s^{-1}, E_{SW} = 25 mV, E_S = 2 mV. Numbers on the curves correspond to individual signals in accordance with Figure 1.

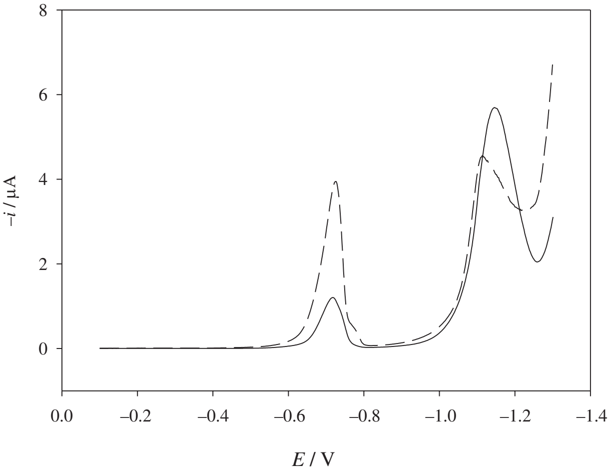

Figure 6. Reduction signals obtained by square wave voltammetry (dashed line) and linear scan voltammetry (solid line) from 0.1 mol dm^{-3} HClO$_4$ at selenium(+4) and rhodium(+3) concentrations of 18.2 and 58.3 nmol dm^{-3}, respectively. E_{SW} = 50 mV while other conditions are the same as for Figure 5. Scan rate in LSV: 50 mV/s.

Taking into account that both electrode processes are totally irreversible such result can be explained only in terms of presently unknown differences in their nature.

From the above paragraphs it follows that the results obtained in the three electrolytes differ in some detail. Table I gives the influence of rhodium(+3) on the selenite response as a ratio of the peak currents at –0.7 V and –0.4 V, the latter being measured in the absence of additive. It can be seen that in all cases the signals increase more than hundred times, although the exact values are highly dependent on the measuring conditions. The peak located at –1.1 V was not treated in the same way because it became poorly shaped under the influence of high rhodium(+3) concentrations. In fact, changing of parameters that cause peak height enhancement generally leads to poorly shaped signals. That is the reason why the extreme conditions, such as long deposition times, high SW frequencies and fast stirring were not applied in the present measurements.

Determination of an Unknown Selenite Concentration. – From the fact that after the addition of rhodium(+3) to selenite solution, much higher (although differently located) signals are obtained than in the absence of such an additive, possible application of the entire effect in trace analysis is expected. In two previously published papers such measurements were described[8,9] without mentioning any special problems. From our own experience[10,11] and results given in this article, current – concentration plot is generally not a straight line with zero intercept, irrespective of the electrolyte applied. In such a case, standard addition method cannot be applied in the usual way or, in other words, it is questionable in which way the experimental data should be treated. As some influence of the rhodium(+3) form on the voltammograms recorded in the presence of dissolved selenite was found,[10] we expected that the application of the same standard solution as used in the literature examples[8,9] could perhaps give better results. Unfortunately this was not the case.

An attempt to determine selenite concentration in a real sample, with and without rhodium(+3) addition, is presented in Figures 7 and 8. As already mentioned, even selenium(+6) of the highest purity, always contains some selenium(+4), which can be a problem as in our study of uranyl-selenate interactions.[19] In that case, the impurity was eliminated by potentiostatic electrolysis on a large mercury surface. After being kept for seven years in the dark, at room temperature, one of such electrolyzed solutions (0.03 mol dm^{-3} Na_2SeO_4 in 0.001 mol dm^{-3} $HClO_4$) was analyzed again, in an attempt to determine newly formed selenite. Determination was performed with and without rhodium(+3) in each of the previously mentioned electrolytes to which an aliquot of the studied solution was added. The results that reflect measurements performed in the rhodium-free systems (after addition of 0.2 cm^3 of the test solution to 20 cm^3 of the electrolyte in the polarographic cell) are presented in Figure 7 for 0.3 mol dm^{-3} HCl and 0.1 mol dm^{-3} $HClO_4$. With 0.1 mol dm^{-3} H_2SO_4 the previously mentioned unknown peak was obtained before addition of the selenate aliquot. Therefore the analysis could not be performed in a satisfactory way.

TABLE I. Ratio of the peak heights at –0.7 V, measured in the presence of rhodium(+3)[(a)], and at –0.4 V, measured in rhodium-free solutions

Electrolyte	[Rh(+3)]/ nmol dm^{-3}	E_d/V	[Se(+4)]/ nmol dm^{-3}	$i_{p(0.7)}/i_{p(0.4)}$
$HClO_4$ 0.1 mol dm^{-3}	12.40	–0.1	14	126
HCl 0.3 mol dm^{-3}	9.98	–0.1	14	240
H_2SO_4 0.1 mol dm^{-3}	12.10	–0.2	14	176

[(a)] Results obtained at increasing rhodium(+3) concentration and a constant selenite level

It can be seen that current – concentration plot is a straight line with the slope which does not depend significantly on the electrolyte applied. The selenite concentration in the (initial) selenate medium before dilution is 0.30 ± 0.01 and 0.28 ± 0.02 μmol dm^{-3}, as measured in 0.1 mol dm^{-3} $HClO_4$ and 0.3 mol dm^{-3} HCl, respectively.

Measurements in the presence of dissolved rhodium were performed starting from a lower selenite level (*i.e.* 10 mm^3 of the test solution added to 20 cm^3 of the electrolyte in the polarographic cell). Results obtained in both

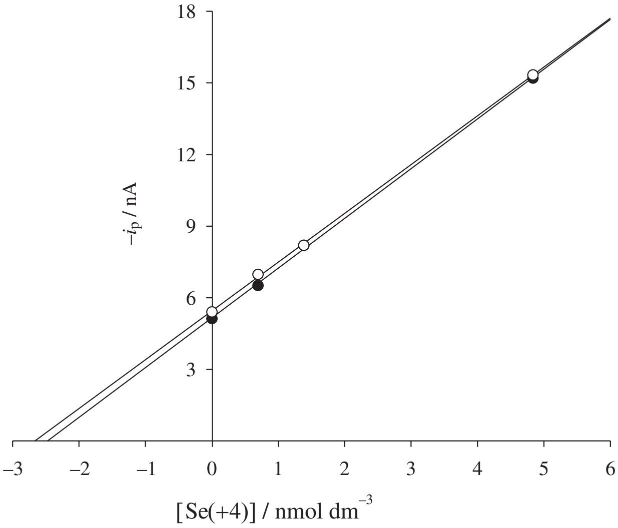

Figure 7. Determination of selenium(+4) present in selenium(+6) by following the peak height at –0.45 V. Measurements performed in 0.1 mol dm^{-3} $HClO_4$ (empty circles) and 0.3 mol dm^{-3} HCl (full circles) after the addition of 0.2 cm^3 of the initial 0.033 mol dm^{-3} selenate solution to 20 cm^3 of the electrolyte. Accumulation potential: –0.3 V. Other potential and timing parameters as for Figure 5.

TABLE II. Concentration of selenium(+4) in 0.033 mol dm^{-3} selenium(+6) solution, determined in the presence and in the absence of rhodium(+3)[(a)]

Electrolyte	[Rh(+3)]/ nmol dm^{-3}	E_p/mV	[Se(+4)]/ μmol dm^{-3}
$HClO_4$ 0.1 mol dm^{-3}	0	–475	0.30 ± 0.01
HCl 0.3 mol dm^{-3}	0	–443	0.28 ± 0.02
$HClO_4$ 0.1 mol dm^{-3}	58.3	–701 to –727	0.118
HCl 0.3 mol dm^{-3}	29.2	–739	0.174
HCl 0.3 mol dm^{-3}	29.2	–1068	0.600 ± 0.08

[(a)] Measurements performed by SWV after 180 s accumulation at –0.3 V (frequency: 100 s^{-1}; amplitude: 25 mV; step potential: 2 mV)

electrolytes of interest are presented in Figure 8a for the peak located at –0.7 V. Obviously, it is not possible to calculate selenium(+4) concentration from such a plot. The main problem is not a nonlinear current – concentration relationship, but the fact that the intercept of such a curve with *x*-axis points to the concentration that is far too low (Table II). With the signal at –1.1 V, current – concentration linearity can be achieved in a relatively wide range (Figure 8b), but standard addition method gives the concentration which is too high because the contribution of pure rhodium(+3) to the electrode response cannot be eliminated.

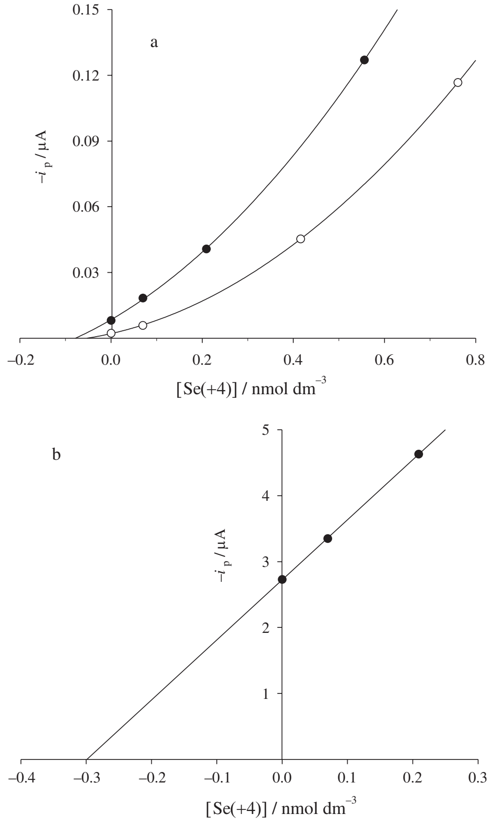

Figure 8. Determination of selenium(+4) present in selenium(+6) by following the peak height at –0.7 V (a) and –1.1 V (b). Measurements performed in 0.1 mol dm^{-3} $HClO_4$ (empty circles) and 0.3 mol dm^{-3} HCl (full circles) after the addition of 10 mm^3 of the initial 0.033 mol dm^{-3} selenate solution to 20 cm^3 of the electrolyte. Accumulation potential: –0.1 V. Other potential and timing parameters as for Figure 5. Rhodium(+3) concentration: 29 nmol dm^{-3} in hydrochloric and 58 nmol dm^{-3} in perchloric acid.

CONCLUDING REMARKS

Although the addition of rhodium(+3) produces much higher (but differently located) signals compared to the peaks obtained from simple selenite solutions without additives, the practical application of such a phenomenon is not simple at all. Electrode processes of interest are not fully understood but another, yet more pronounced problem comes from the fact that current – concentration plot is generally not a straight line with zero intercept. Because of the latter, it is not possible to use standard addition method. Moreover, some limited selenite concentration range can be found in which the peak current at –1.1 V decreases with increasing concentration of the analyte, especially if rhodium level is not high. When the results obtained in three different acids (*i.e.* HCl, H_2SO_4 and $HClO_4$, at the concentrations of 0.3, 0.1 and 0.1 mol dm^{-3}, respectively) are compared, it follows that they are similar but not identical. Taking into account that hydrogen ions play an important role in the processes of interest, it would be useful to perform additional experiments at a constant acidity. In such a way, possible role of individual anions would become more obvious.

Examples of irregular current – concentration dependences with non-zero intercepts (as described here for the signal at –0.7 V) could be found in the literature, mainly connected with catalytic processes. In other words, the problem of data treatment in such a situation is not specific for the studied system, but appears relatively often. Consequently, its solution would be of prime importance. On the other hand, curves of the similar type could, perhaps, be used for diagnostic purposes during the studies of unknown electrode processes.

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SAŽETAK

Analitički aspekti interakcije selenija(+4) s rodijem(+3) pod voltametrijskim uvjetima

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Ispitivana su voltametrijska svojstva sustava selenij(+4) – rodij(+3) u različitim elektrolitnim otopina s posebnom pažnjom usmjerenom prema mogućoj primjeni opaženih pojava u određivanju tragova selenita. Iako signali, dobiveni u takvim smjesama, mogu biti i preko dvije stotine puta viši od onih snimljenih u jednostavnim otopinama selenija(+4) bez dodatka rodija(+3), ostaje upitno kako bi se ovi rezultati mogli primijeniti u praksi. Glavni problem je obrada podataka jer (općenito) prikaz ovisnosti struje o koncentraciji nije pravac koji prolazi ishodištem. Osim toga, tip ovisnosti mijenja se s koncentracijskim područjem selenita. Problem je prikazan na primjeru određivanja selenija(+4) u otopinama selenija(+6). Čini se, da su ovog momenta rezultati dobiveni u ispitivanom sustavu, važni kao pojave i kao mogući pokazatelji nekih katalitičkih procesa. Prije njihove primjene u analizi tragova treba naći odgovore na neka opća pitanja.