ADSORPTION AND OXIDATION OF THIOSULFATE ON THE PLATINUM ELECTRODE IN A SLIGHTLY ALKALINE MEDIUM

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The aim of this research was to study the oxidation and reduction of the adsorbed thiosulfate on the platinum electrode in a slightly alkaline medium. The adsorption was performed at the open circuit conditions. The reduction of the adsorbed layer in the hydrogen region is slower in a slightly alkaline medium than in acid. The mechanism of reduction and oxidation of adsorbed molecules is probably the same. The nonstationary currents measured in presence of thiosulfates showed that the change in the oxidation number does not take place during the adsorption in the double layer region. In the hydrogen region, thiosulfate replaces the adsorbed hydrogen while beeing reduced. Nonstationary currents at higher concentrations of thiosulfate indicate the presence of more layers on the electrode. Upon reaching higher concentrations of thiosulfate the oxidation reaction takes place between thiosulfate in solution and adsorbed product of its reduction. The open circuit potential of the platinum electrode measured in a thiosulfate solution was 0.780 and 0.783 V against the hydrogen electrode in the same solution.
Key words: Nonstationary currents; Thiosulfate; Adsorbed dithionate; Adsorbed sulfur; Adsorbed multilayers; Electrooxidations; Electrochemistry.

In the preceding article[1] the adsorption of thiosulfate was studied on the platinum electrode in the acid medium. The adsorption was measured along with the charge required for the oxidation of the product adsorbed while the electric circuit was disconnected. At lower concentrations of thiosulfate a monolayer of the adsorbed product was reduced in the hydrogen region, while the formation of adsorbed sulfur and dithionate can be expected. In subsequent oxidation an increase of the oxidation number by four was found. This value does not correspond to the complete oxidation to sulfate (hydrogensulfate). At higher concentrations of thiosulfate ($>10^{-2}$ mol dm^{-3}), multilayers, mostly consisted of adsorbed sulfur were formed. Experiments with thiosulfate in acid medium were limited to lower concentrations since at concentrations exceeding value 10^{-3} mol dm^{-3} (in 0.5 M H$_2$SO$_4$) thiosulfate decomposed to colloidal sulfur and sulfites.

To expand knowledge about the adsorption and oxidation of thiosulfates on the platinum electrode, similar experiments were performed in a slightly alkaline medium in which the decomposition of thiosulfate does not occur. Nonstationary currents were measured while introducing thiosulfate into the solution. Also, the redox reaction of the adsorbed product was studied in a slightly alkaline medium. The potential of the platinum electrode in thiosulfate solution was measured at the open-circuit conditions.

EXPERIMENTAL

The measurements were performed in a solution of 0.05 M $Na_2B_4O_7$ (pH 9.2) prepared from solid $Na_2B_4O_7 \cdot 10\ H_2O$ (analytical grade, Lachema Brno) and double distilled water.

Details about the electrode, instruments and other chemicals are described in preceding articles[1,2]. Prior to each measurement, the electrode was activated by applying potential sweeps between 1.5 and 0 V at the rate of 0.5 V s^{-1} for a period of 20 min. Before each measurement, the electrode activity was assessed according to the charge Q_H consumed by oxidation of the adsorbed hydrogen. Changes in Q_H during all measurements did not exceed 10%. All reported potentials refer to the hydrogen electrode in the same solution. The experiments were performed at 20 ± 2 °C.

RESULTS AND DISCUSSION

Voltammetric Curve

Figure 1 shows the voltammetric curve obtained on the platinum electrode in solution of 10^{-3} M $Na_2S_2O_3$ and 0.05 M $Na_2B_4O_7$. Curve *1* corresponds to the unstirred solution, while for curve *2* the solution was stirred by bubbling of nitrogen.
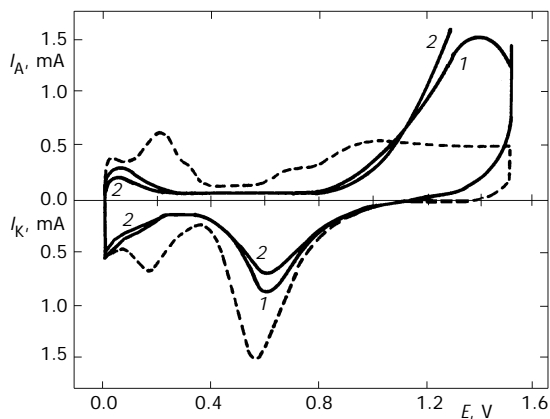

FIG. 1
Dependence of current on the potential of platinum electrode in solution of 10^{-3} M $Na_2S_2O_3$ in 0.05 M $Na_2B_4O_7$, scan rate 0.2 V s^{-1}. *2* Solution stirred by bubbling nitrogen, *1* the unstirred solution. The dashed line shows the platinum electrode in 0.05 M $Na_2B_4O_7$

The following facts can be obtained:

The suppression (or desorption) of hydrogen adsorption due to the co-adsorption of thiosulfate occurs in a slightly alkaline medium.

The adsorption of thiosulfate is affected by its diffusion. In the stirred solution, the suppression of hydrogen adsorption is much stronger than in unstirred solution.

Peaks of the surface oxide reduction on the platinum electrode are significantly reduced.

Peaks of thiosulfate oxidation at 1.4 V are shifted positively by about 200 mV compared to acid medium.

Measurement of the Open Circuit Potential

The open circuit potential (OCP) of the platinum electrode was measured in 0.05 M $Na_2B_4O_7$ to which, after disconnecting the electric circuit, a solution of thiosulfate was added to the final concentration of 0.01 mol dm^{-3}. During the first measurement the electric circuit was disconnected at the potential of 0.05 V (in the hydrogen region), while during the second measurements, the circuit was disconnected at 0.5 V (the double-layer region). After introducing the thiosulfate solution OCP stabilized in a few seconds. In the first case OCP was 0.783 V, in the second case 0.780 V which corresponds to start of the thiosulfate oxidation (see Fig. 1 for comparison).

Charge Required for Reduction of the Adsorbed Product

Adsorption experiments from ref.[1] were repeated in a solution of thiosulfate in double distilled water at the open-circuit conditions. The electrode was left in a solution of thiosulfate of selected concentration for a period of time referred to as t_A (adsorption time) then washed and transferred into a measuring cell with a solution of clean supporting electrolyte and exposed to the potential E_A for time t_D (time of desorption). Subsequently, by using periodic potential cycles, we measured the charge consumed for the reduction of adsorbed layer (Q_{red}) in the hydrogen region together with the charge required for the oxidation of the reduced adsorbed layer (Q_{ox}). Details concerning the methodology of these measurements can be found in the preceding article[1].

Figure 2 shows the reduction of the adsorbed product in the hydrogen region in acid medium (0.5 M H_2SO_4 – curve *2*) and in the slightly alkaline medium (0.05 M $Na_2B_4O_7$ – curve *1*). In both cases, the adsorbed product was obtained in the same way. The current of the reduced adsorbed product

shows a very significant peak at 0.13 V in acid medium, while in the slightly alkaline medium the peak does not appear. The Q_{red} charge is constant at concentrations ranging from 0.003 to 0.3 M $Na_2S_2O_3$ with the average value of 0.127 ± 0.006 mC (*i.e.* 0.37 ± 0.02 electron per surface site – e.p.s.). For the recalculation of the charge to the number of electrons pertaining to one surface site adsorbing hydrogen (e.p.s.) we used the charge value required for the hydrogen adsorbed on the uncovered surface of the platinum electrode in 0.5 M H_2SO_4, *i.e.* 0.3461 mC. For the reduction in acid medium[1] 0.44 ± 0.07 e.p.s. was found. The reaction scheme proposed for the reduction of adsorbed layer[1]

$$2\left(S_2O_3^-\right)_{ads} + 4\,H^+ + 2\,e\ =\ 2\,S_{ads} + \left(S_2O_4^{2-}\right)_{ads} + 2\,H_2O\,, \tag{1}$$
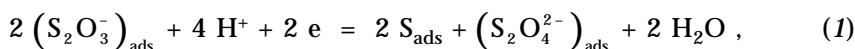
with the decreasing concentration of H^+ ions, the rate of reduction decreases. It may also explain the higher value of Q_{red} in acid than in slightly alkaline medium. Provided that the cathodic reduction in 0.05 M $Na_2B_4O_7$ in the hydrogen region was repeated with different setting of positive potential limit, it is possible to change Q_{red} even though it is significantly smaller than in the first cycle.

With the concentration of $Na_2S_2O_3$ raised to 1 mol dm^{-3}, the value of Q_{red} increased up to 0.184 mC (0.53 e.p.s.).

The possibility that the adsorbed sulfur can be formed during the reduction of thiosulfate is shown by Konopik and Holzinger[3,4] who found the same amount of S^{2-} and SO_3^{2-} formed during the reduction. The occurrence
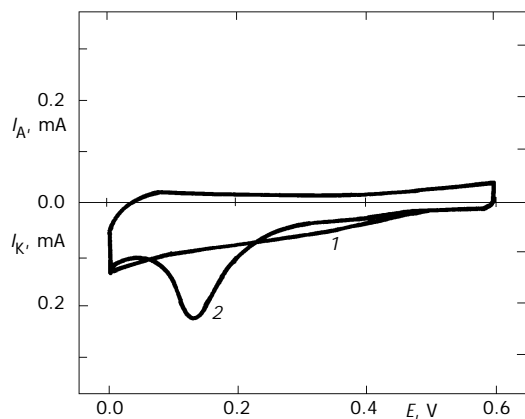

FIG. 2
Dependence of current on the potential of platinum electrode covered with the adsorbed product. Adsorption from $3 \cdot 10^{-3}$ M $Na_2S_2O_3$, time of adsorption t_A = 20 min, time of desorption t_D = 1 min, E_A = 0.6 V. *1* In 0.05 M $Na_2B_4O_7$, *2* in 0.5 M H_2SO_4; scan rate 0.2 V s^{-1}

of sulfur on the surface of the platinum electrode in the hydrogen region is possible[5,6] even during the reduction of sulfur dioxide which is close to thiosulfate.

Charge Required for Oxidation of the Adsorbed Product

The dependence of Q_{ox} on the concentration of thiosulfate was measured for t_A = 20 min, t_D = 1 min and E_A = 0.4 V. The shape of the dependence is identical with the shape obtained for oxidation of the adsorbed product in acid medium. At thiosulfate concentrations ranging from 10^{-1} to 10^{-3} mol dm^{-3}, Q_{ox} is constant, *i.e.* 1.387 ± 0.093 mC (4.01 ± 0.26 e.p.s.), in acid medium Q_{ox} = 1.350 ± 0.073 mC (3.90 ± 0.21 e.p.s). From a comparison of Q_{ox} in acid and slightly alkaline media it is evident that the adsorbed product is oxidized to the same oxidation state in both acid and slightly alkaline media.

At higher concentrations of thiosulfate (10^{-2} mol dm^{-3}) we can observe an increase of Q_{ox} probably due to the formation of more adsorbed layers. Also Lamy-Pitara *et al.*[7] observed a formation of multilayers of sulfur species on platinum electrode using combination of cyclic voltammetry and UV-VIS reflectance spectroscopy. The Q_{ox} charge for 1 M $Na_2S_2O_3$ reaches the value corresponding to approximately 11 e.p.s. Under the same conditions the oxidation in acid medium reached the value of approximately 23 e.p.s. The above stated difference seems to be caused by a substantially faster desorption in alkaline medium (the time of desorption is 1 min in both cases).

If the oxidation number of sulfur in adsorbed product after its reduction in the hydrogen region is 1.5, it is changed during oxidation to 5.5. This value corresponds to *e.g.* oxidation to hydrogensulfate anions (oxidation No. 6) concurrently with the formation of dithionate anions (oxidation No. 5). The occurrence of dithionates during oxidation was proved by Korzeniewski *et al.*[8] using in situ FTIR spectroscopy. The aforementioned authors monitored the oxidation of sulfur dioxide. They found that the oxidation product is dithionate adsorbed at a lower potential than that corresponding to formation of platinum oxides. At such potentials adsorbed sulfates were formed.

Measuring Nonstationary Currents

The currents passing through the platinum electrode at a constant potential were measured while a solution of thiosulfate was introduced into the elec-

trolyte of 0.05 M $Na_2B_4O_7$. At potentials ranging from 0.0 to 0.25 V anodic nonstationary currents felt within few seconds to negligible values. At potentials positive from 0.25 V no currents passed while introducing thiosulfate solution. By integrating nonstationary currents measured at a constant potential, it was possible to determine Q_n.

The dependence of Q_n on the potential is shown in Fig. 3. The dashed curve in Fig. 3 shows the dependence of the charge consumed by the oxidation of adsorbed hydrogen (Q_H) on the electrode potential in 0.05 M $Na_2B_4O_7$.

The curve was obtained by integration of voltammetric curve in 0.05 M $Na_2B_4O_7$ (the dashed curve in Fig. 1). The full line in Fig. 3 shows values of Q_n at different potentials. It is evident that Q_n is slightly lower than Q_H and depends on the selected potential.

The obtained results can be explained as follows:

The anodic current passes through the platinum electrode only if hydrogen is adsorbed on the electrode surface; its amount depends on the potential. Thiosulfate replaces the adsorbed hydrogen in the reaction

$$Pt–H_{ads} + S_2O_3^{2-} = Pt–\left(S_2O_3^{2-}\right)_{ads} + H^+ + e \ . \tag{2}$$
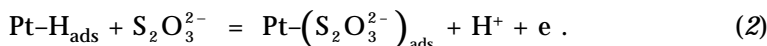
Assuming only this reaction, Q_n is equal to the charge required for the oxidation of adsorbed hydrogen at used potential.

The adsorbed layer of thiosulfate in the hydrogen region is subject to the reduction described by Eq. (*1*). That is why the anodic charge Q_n corresponds to oxidation of adsorbed hydrogen reduced according to Eq. (*1*). At
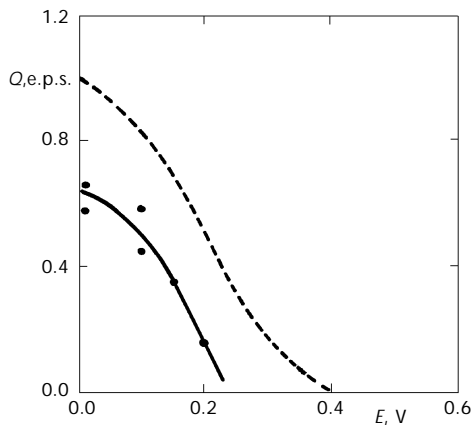

FIG. 3
Dependence of the charge Q_n (——) and Q_H (– –) on the potential in 0.05 M $Na_2B_4O_7$. The charge Q_H corresponds to the oxidation of adsorbed hydrogen, Q_n corresponds to the oxidation of thiosulfate in 0.05 M $Na_2B_4O_7$. The resulting concentration of $Na_2S_2O_3$ is 0.5 mol dm^{-3}

0 V, Q_n should be identical with the charge used for the oxidation of the hydrogen monolayer (1 e.p.s.) decreased by the charge value consumed for the reduction of adsorbed thiosulfate in the potential range from 0.4 to 0.0 V (Q_{red} corresponds to 0.37 e.p.s.). The measured values are in agreement with this assumption.

The dependence of Q_n on the concentration of the thiosulfate is shown in Fig. 4. Nonstationary currents were measured at the potential of 0.1 V. At lower thiosulfate concentrations, Q_n was closer to the constant value which may correspond to the adsorbed monolayer of product. At higher concentrations, the anodic charge grows, probably due to the appearance of another layer. If nonstationary currents are measured at higher concentrations than 10^{-1} mol dm^{-3} at potential of double layer (0.5 V), no anodic current passes through the electrode. The thiosulfate adsorption at higher concentrations and in the potential region of hydrogen adsorption seems to correspond not only to the oxidation of adsorbed hydrogen but also to the oxidation reaction between thiosulfate in solution and the reduced adsorbed product.

In the preceding work[1] it was shown that at higher concentrations of thiosulfate and at times sufficient for desorption, the Q_{ox} decreased to the value corresponding to 6 e.p.s. This indicates monolayer of adsorbed sulfur, providing its oxidation to sulfates or hydrogensulfates. Another layer of molecules containing sulfur and oxygen can be formed on the top of adsorbed sulfur. Due to its weak bounding it can desorb in basic solution. It is therefore possible to assume that such arrangement of layers also results from the oxidation reaction between thiosulfate in solution and adsorbed product of its reduction. The above mentioned results do not allow a more precise determination of the composition of adsorbed layer.
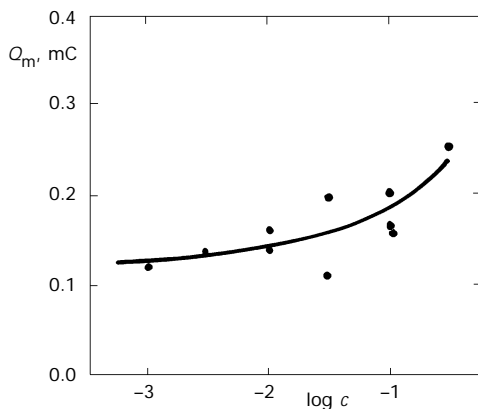

FIG. 4
Dependence of Q_{ox} on the concentration of $Na_2S_2O_3$ in 0.05 M $Na_2B_4O_7$ (Q_{ox} is the charge required for the oxidation of the adsorbed product after its reduction in the hydrogen region). Adsorption conditions: t_A = 20 min, t_D = 1 min, E_A = 0.6 V

CONCLUSION

At lower concentrations of thiosulfate, the number of adsorbed layers seems to be limited to monolayer. From measurements of nonstationary currents it is evident that the thiosulfate adsorption in the double-layer region occurs without any change in the oxidation number of sulfur. During the adsorption in the hydrogen region, thiosulfate replaces the adsorbed hydrogen. The adsorbed thiosulfate in the hydrogen region is concurrently reduced to adsorbed sulfur (oxidation No. 0) and dithionate (oxidation No. 3). The reduction of adsorbed thiosulfate in the hydrogen region is faster in acid medium than in slightly alkaline medium. The adsorbed product after reduction in the hydrogen region can be oxidized in both acid and slightly alkaline media probably to sulfates and dithionates.

At higher thiosulfate concentrations, there is no change in the oxidation number in the double-layer region. However, the presence of more layers on the electrode surface is indicated. The adsorption in the hydrogen region results in the reduced monolayer (probably of adsorbed sulfur and dithionate). At first, a thin layer of the adsorbed sulfur is formed to which a layer of molecules containing both sulfur and oxygen is weakly bound.

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