

ADSORPTION AND OXIDATION OF THIOSULFATE ON A PLATINUM ELECTRODE IN ACID SOLUTION

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The adsorption of thiosulfate on a platinum electrode was measured at the open circuit potential. A monolayer of the adsorption products covers the electrode at lower thiosulfate concentrations. The charge used up during the reduction of the monolayer roughly corresponds to 0.5 electron per surface site (e.p.s.), the charge used up during the oxidation of the monolayer after reduction corresponds approximately to 4 e.p.s. Multiple adsorbed layers, which are presumably constituted mainly by adsorbed sulfur, build up at higher thiosulfate concentrations. The amount of the adsorbed substance increases with increasing thiosulfate concentration and time of adsorption. Desorption from the surface coated by multiple layers can take place in supporting electrolyte solution. The build-up of multiple adsorbed sulfur layers also takes place during adsorption from solutions of colloidal sulfur.

Key words: Electrochemistry; Multilayers of adsorbed sulfur; Colloidal sulfur; Reduction to dithionite; Oxidation to dithionate.

The adsorption and electrochemical oxidation of sulfur compounds on platinum electrodes has been attracting interest, attention being mainly centered on sulfur dioxide¹⁻⁵, sulfane⁶⁻¹³, thiourea¹⁴⁻¹⁶, and cystine or cysteine¹⁷⁻²⁰. Few papers have dealt with the electrochemical oxidation of thiosulfate at platinum electrodes.

Konopik and Holzinger^{21,22} investigated the reduction of thiosulfate in a 0.1 M NaOH solution at a platinum electrode and observed the formation of identical quantities of S^{2-} and SO_3^{2-} ions. Glasstone and Hickling^{23,24} examined the anodic oxidation of thiosulfate to tetrathionate and sulfate, and obtained tetrathionate in the highest yield at a platinum electrode in slightly acid or neutral solutions at a relatively high current density. Voltammetric curves using a rotary platinum wire electrode were recorded by Kuzmina and Songina²⁵, who assume that in a weakly acid solution, thiosulfate is oxidized to elementary sulfur, whereas sulfur converts to sulfate. In neutral solutions, thiosulfate is oxidized to tetrathionate and dithionate. Klemenc²⁶ suggested that $S_2O_3^{2-}$ is oxidized to $S_4O_6^{2-}$ by free hydroxyl radicals created at the anode during the discharge of the OH^- ions. Previously it was supposed that thiosulfate is oxidized by oxygen^{25,26} or hydrogen peroxide^{23,24} forming at the anode.

No very recent papers dealing with the adsorption and electrochemical oxidation of thiosulfate on a platinum electrode can be found in the literature, and data of the structure of adsorbed thiosulfate as examined by non-electrochemical methods are also lacking. From among related substances, only the structure of sulfur dioxide adsorbed from an acid solution on a platinum electrode has been investigated by *in situ* infrared spectroscopy⁴. The authors of that paper suggest that the oxidation of sulfur dioxide is accompanied by formation of $S_2O_6^{2-}$ as the intermediate product; the formation of adsorbed sulfur at cathodic potentials is assumed.

Although the anodic oxidation of thiosulfate at platinum electrodes has been examined and various mechanisms have been suggested²¹⁻²⁷, the studies were not based on a deep insight into the adsorption of the substance on platinum. Gaining such insight was the aim of the present work.

EXPERIMENTAL

The measurements were performed in 0.5 M H_2SO_4 , prepared from the concentrated acid of reagent grade purity and redistilled water. Thiosulfate and sulfite solutions were obtained by dissolving solid $Na_2S_2O_3$ or Na_2SO_3 of reagent grade purity in redistilled water or in 0.5 M H_2SO_4 . Oxygen was removed from the solutions by nitrogen purging.

Details of the electrodes and instrumentation used have been given previously²⁸.

Prior to each measurement, the electrode was activated by applying cathodic and anodic cycles between $E = 1.5$ and 0 V at a rate of 0.5 V s⁻¹ for 20 min. The electrode activity was assessed based on the charge used up for the oxidation of adsorbed hydrogen before and after the measurement. During the measurement, the activity so assessed never deviated from the average value more than by 5%.

Absorbance measurements were accomplished on a Spekol 11 spectrophotometer (Zeiss, Jena).

All potentials reported here refer to the hydrogen electrode in 0.5 M H_2SO_4 at 25 °C.

The adsorption and oxidation of thiosulfate was examined by evaluating voltammetric curves or by measuring the charge used up during the oxidation of the adsorbed product in the supporting electrolyte solution.

Voltammetric Curves

Following electrode activation in 0.5 M H_2SO_4 supporting electrolyte solution, the concentration was adjusted by adding a fresh solution of thiosulfate or sulfite. Oxygen was removed by nitrogen purging, nitrogen feed was discontinued, and the solution was allowed to stand. The voltammetric curve was recorded between potentials of 0 and 1.5 V.

Adsorbed Product Oxidation and Reduction

The procedure was as shown schematically in Fig. 1. The electrode was first activated as described above. When changing the potential in the positive direction, the potential was stopped at a preselected value E_A , the electrode was removed from the vessel, rinsed thoroughly with oxygen-free redistilled water, and submerged in the solution examined, which had also been freed from oxygen. In this solution the electrode was left for the adsorption time t_A , during which the system was nitrogen purged vigorously. Subsequently, the electrode was rinsed thoroughly with approximately 20 ml of

oxygen-free redistilled water and engaged in the electric circuit at the potential E_A , at which it was kept for the desorption time t_D . During this desorption the solution was stirred continuously except for the last 15 s. Subsequently, the electrode potential was changed to 0 V at a rate of 0.2 V s^{-1} (cycle 0) and further cycled periodically between 0 and 1.5 V (cycles 1, 2, 3,...) at the same rate.

RESULTS AND DISCUSSION

Figure 2 shows the current vs potential plot for potential cycles between 0 and 1.5 V at 0.2 V s^{-1} . The dashed line was obtained in the supporting electrolyte solution ($0.5 \text{ M H}_2\text{SO}_4$), curves 1 and 2 correspond to the supporting electrolyte to which $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_3 , respectively, had been added to reach a final concentration of $1 \cdot 10^{-3} \text{ mol l}^{-1}$. The curves were recorded after attaining the steady state.

The voltammetric curve for sodium sulfite (curve 2) exhibits oxidation peaks at 0.6 and 1.2 V, a not very marked reduction peak at 0.15 V, and a pronounced reduction peak at 0.07 V. All of the peaks grow in intensity if the solution is stirred. Similar

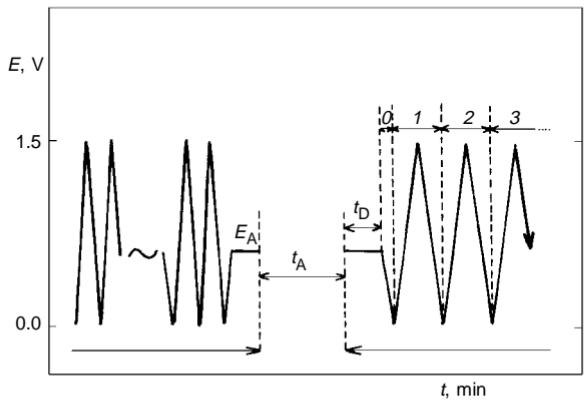


FIG. 1
Schematic of the time behaviour of the electrode potential for monitoring the oxidation of the adsorption products; t_A time of adsorption, t_D time of desorption, numbers denote cycles

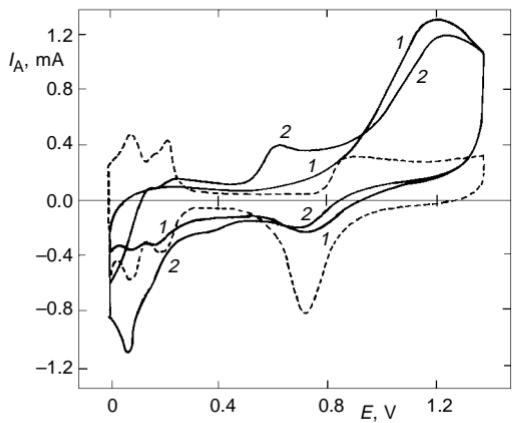


FIG. 2
Steady-state current curves in dependence on time for $\text{Na}_2\text{S}_2\text{O}_3$ (1) and Na_2SO_3 (2) at a concentration of $1 \cdot 10^{-3} \text{ mol l}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4$. Periodic potential cycle rate 0.1 V s^{-1} , unstirred solution; dashed line $0.5 \text{ M H}_2\text{SO}_4$

curves have been obtained previously^{1,2}. The voltammetric curve for thiosulfate (curve 1) displays a single oxidation peak at 1.2 V, nearly identical with that of sulfite. The reduction peaks of thiosulfate are considerably lower than those of sulfite.

The charge used up to oxidize adsorbed hydrogen gives evidence that a kind of adsorption which eliminates completely that of hydrogen takes place in the solutions of both thiosulfate and sulfite. In the two voltammetric curves the surface platinum oxide reduction peak is substantially lower than as obtained in the supporting electrolyte solution.

Decomposition to elementary sulfur and sulfite is characteristic of thiosulfate solutions. No haze due to the presence of colloidal sulfur in the solution was observed when recording the voltammetric curve in a 10^{-3} M solution of $\text{Na}_2\text{S}_2\text{O}_3$ in 0.5 M H_2SO_4 . To test the decomposition of thiosulfate, the concentration dependence of absorbance of its solutions in 0.5 M H_2SO_4 was investigated. The absorbance at 530 nm was measured 10 min after mixing the thiosulfate solution with sulfuric acid. The dependence, which is shown in Fig. 3, gives evidence that the decomposition does not take place at low concentrations (about 10^{-3} mol l^{-1}). The fact that the voltammetric curve for the $1 \cdot 10^{-3}$ M solution of thiosulfate in 0.5 M H_2SO_4 does not exhibit any oxidation peak at 0.6 V also indicates that no appreciable decomposition to elementary sulfur and sulfite ions occurs in this solution. Haze due to colloidal sulfur starts to be apparent at a thiosulfate concentration of $3 \cdot 10^{-3}$ mol l^{-1} .

In line with these results, Kuzmina and Songina²⁵ report the decomposition of thiosulfate in 1 M H_2SO_4 at concentrations exceeding 10^{-3} mol l^{-1} .

Oxidation of Adsorbed Product in Supporting Electrolyte Solution

Oxidation of the adsorbed product was examined as described in Experimental. The gradual oxidation of the product adsorbed from a $3 \cdot 10^{-3}$ M solution of thiosulfate in

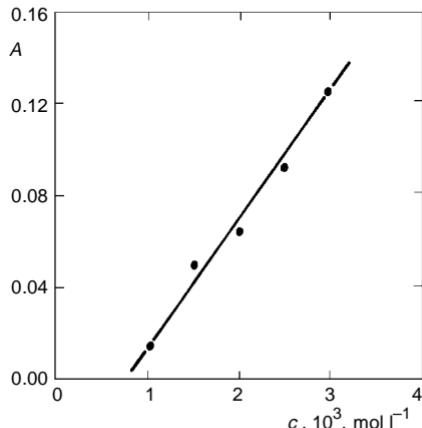


FIG. 3
Dependence of absorbance at 530 nm on sodium thiosulfate concentration in 0.5 M H_2SO_4 , measured 10 min after solution preparation

redistilled water is shown in Fig. 4. The adsorption and desorption periods t_A and t_D were 20 min and 1 min, respectively, the potential was $E_A = 0.4$ V. Seven cycles were required for a complete oxidation of the adsorbed product; only in the eighth cycle the voltammetric curve was identical with that of the platinum electrode in supporting electrolyte.

When varying the potential from 0.4 to 0 V (curve 0), a cathodic peak appeared at 0.155 V. There are two feasible explanations of this phenomenon:

In addition to sulfur atoms, the adsorbed product also contains oxygen atoms. The product undergoes reduction in the hydrogen region and the oxidation state of sulfur is reduced from the initial value of II.

The other explanation is based on the reduction of the difficult-to-reduce oxygen (for explanation of this term see ref.⁷). A similar cathodic peak has been observed⁶ for sulfur adsorbed on platinum at approximately 0.07 V (30 V s⁻¹ rate).

Figure 4 also documents that the charge used up in the hydrogen adsorption range in the individual cycles is higher than that used up during the oxidation of the adsorbed hydrogen. This effect, referred to as the reduction effect, has been observed previously⁶ and can again be ascribed to the reduction of species arising from the oxidation or reduction of the difficult-to-reduce oxygen.

The charges used up during the following processes were measured for each (n -th) cycle: oxidation of adsorbed hydrogen between potentials of 0 and 0.4 V (Q_1^n); oxidation of the adsorbed product and formation of surface platinum oxide between potentials of 0.4 and 1.5 V (Q_2^n); reduction of the surface oxide between potentials of 1.5 and 0.4 V (Q_3^n); and adsorption of hydrogen and the above cathodic process between potentials of 0.4 and 0 V (Q_4^n).

In the Coulomb balance, the charge was calculated as

$$Q_{\text{ox}} = \sum_{n=1}^k [(Q_2^n - Q_3^n) - (Q_4^n - Q_1^n)] \quad (1)$$

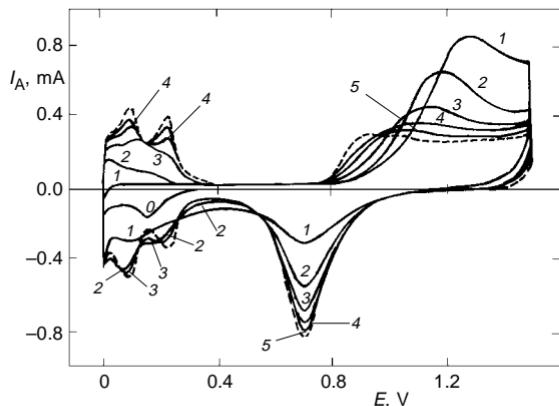


FIG. 4

Current vs potential plot for platinum electrode coated with the product of adsorption from a $3 \cdot 10^{-3}$ M solution of $\text{Na}_2\text{S}_2\text{O}_3$ in 0.5 M H_2SO_4 ; $t_A = 20$ min, $t_D = 1$ min, $E_A = 0.4$ V, potential cycle rate 0.2 V s⁻¹, numbers denote cycles

The charge Q_{ox} does not include the cathodic process in cathodic cycle 0 and corresponds to the charge required to oxidize the adsorbed species after cathodic cycle 0. Measured in mC, this charge is given relative to the charge used up during the adsorption of hydrogen on the uncoated surface of the platinum electrode and corresponds to the number of electrons per hydrogen-adsorbing surface site (e.p.s., ref.²⁹).

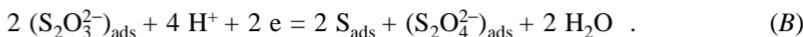
Based on a series of measurements, the Q_{ox} and $(Q_4^0 - Q_1^0)$ values were found to be 3.90 ± 0.21 e.p.s. and 0.44 ± 0.04 e.p.s., respectively. The charges remain virtually unchanged if the measurement is performed at $E_A = 0.7$ V. The values can be explained in two ways:

In the first concept, the $(Q_4^0 - Q_1^0)$ charge corresponds to the reduction of the difficult-to-reduce oxygen: the value obtained in ref.⁷ for the electrode completely covered with sulfur was 0.35 e.p.s., which approaches the above value of 0.44 e.p.s. The subsequent oxidation of the adsorbed product then proceeds as described by the following equation:



If one adsorbed particle blocks two platinum surface sites, then $Q_{\text{ox}} = 4$ e.p.s. This concept is based on the assumptions that (i) difficult-to-reduce oxygen was present in the subsurface platinum layers before the adsorption of thiosulfate, (ii) adsorption of thiosulfate brings about changes in the surface properties of the platinum electrode enabling the difficult-to-reduce oxygen to reduce within the hydrogen region, and (iii) the oxidation of the species arising from the adsorption of thiosulfate is not associated with a restoration of the difficult-to-reduce oxygen.

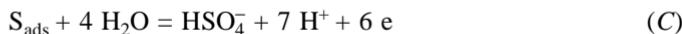
In the other concept, the adsorption of thiosulfate takes place at the open circuit potential without any change in the oxidation state. The adsorbed thiosulfate ion particle blocks two surface sites, and in cycle 0 the sulfur in the thiosulfate is reduced from the oxidation state II to 1.5. The charge corresponding to this reduction is $(Q_4^0 - Q_1^0) = 0.5$ e.p.s., approaching the observed value of 0.44 e.p.s. This reaction can be, for instance,



Within this reaction, sulfur transforms from the oxidation state II to the oxidation states 0 (adsorbed sulfur) and III (adsorbed dithionate anion). The average oxidation state after the reduction then is 1.5.

The formation of adsorbed sulfur on a platinum electrode has also been observed by infrared spectroscopy at cathodic potentials in sulfur dioxide solutions⁴.

The oxidation of the adsorbed species during the subsequent cycles follows the patterns:



and



The two reactions are associated with a charge $Q_{\text{ox}} = 4 \text{ e.p.s.}$, which approaches the observed value of 3.90 e.p.s.

Oxidation to dithionate anions is also assumed by Korzenienski and coworkers⁴ for sulfur dioxide adsorbed on a platinum electrode.

The adsorption of thiosulfate can be associated with a splitting of the ion, giving rise to adsorbed sulfur (blocking one surface site) and adsorbed sulfite ion or sulfur dioxide (also blocking one surface site). The experimental results, however, do not allow us to make an unambiguous conclusion concerning the structure of the adsorbed species.

Many substances are adsorbed in such a manner that the electrode surface sites capable of adsorbing hydrogen are blocked. As the amount of adsorbed substance increases, the charge used up for the oxidation of hydrogen decreases while the charge used up for the oxidation of the adsorbed product increases. The adsorption process takes place until all surface sites are blocked. The adsorption of hydrogen is then nearly completely suppressed and the charge used up for the oxidation of the adsorbed product reaches its limiting value. In thiosulfate solutions the adsorption follows different patterns. Although the platinum electrode surface is coated by the adsorbed product so that the adsorption of hydrogen is nearly completely suppressed, the charge used up for the oxidation of the adsorbed product continues to grow with extending time of adsorption t_A .

The dependence of the charge Q_{ox} of the time of adsorption t_A is shown in Fig. 5 for thiosulfate solutions in redistilled water at concentrations of 0.1 mol l^{-1} , 0.3 mol l^{-1} , and 1 mol l^{-1} (curves 3, 2, and 1, respectively). The desorption time t_D was 1 min, potential E_A (Fig. 1) was 0.4 V. Hydrogen adsorption was completely suppressed. The magnitude of the charge Q_{ox} suggests that multiple adsorbed layers were formed. No changes in the $(Q_4^0 - Q_1^0)$ charge were observed when examining the Q_{ox} vs t_A dependence: the average value for all measurements shown in Fig. 5 was $0.58 \pm 0.08 \text{ e.p.s.}$ Increasing Q_{ox} charge is associated with a growing number of cycles necessary for a complete oxidation of the adsorbed product. The highest Q_{ox} value reached was 21.6 e.p.s., in which case 25 cycles were required to completely oxidize the adsorbed product.

Figure 5 documents that the Q_{ox} charge is strongly dependent on the thiosulfate concentration in solution.

This dependence is shown in Fig. 6. At lower concentrations the charge was virtually constant, approaching 4 e.p.s., but increased appreciably at higher concentrations. The $(Q_4^0 - Q_1^0)$ charge was virtually unaffected by the thiosulfate concentration and its average value was 0.44 ± 0.07 e.p.s.

The amount of the adsorbed substance, as expressed *via* the charge Q_{ox} , also depends on the time of desorption t_D , as shown in Fig. 7 for thiosulfate solutions in redistilled water at concentrations of 1 mol l^{-1} , 0.5 mol l^{-1} , and 0.3 mol l^{-1} (curves 1, 2, and 3, respectively); the time of adsorption was 20 min, potential $E_A = 0.4 \text{ V}$. The amount of the adsorbed substance decreased first very rapidly to approach asymptotically a constant, steady-state value of approximately 6 e.p.s., which seems to be identical for all curves.

During the desorption measurements, the $(Q_4^0 - Q_1^0)$ charge was found to decrease with increasing time of desorption t_D .

The results can be interpreted so that at lower thiosulfate concentrations the adsorption is associated with no change in the oxidation state (which is II), and a single layer is formed. Each adsorbed particle blocks two surface sites, and reduction by one-half

FIG. 5
Dependence of charge Q_{ox} used up during the oxidation of the adsorption product on time of adsorption t_A . Adsorption without external polarization, time of desorption $t_D = 1 \text{ min}$, $E_A = 0.4 \text{ V}$. Sodium thiosulfate concentration (mol l^{-1}): 1 1, 2 0.3, 3 0.1. Charge corresponding to one electron per surface site: 0.3461 mC

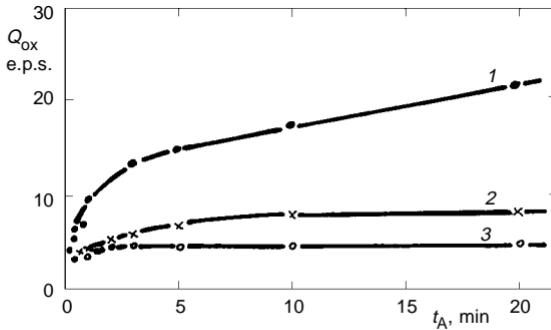
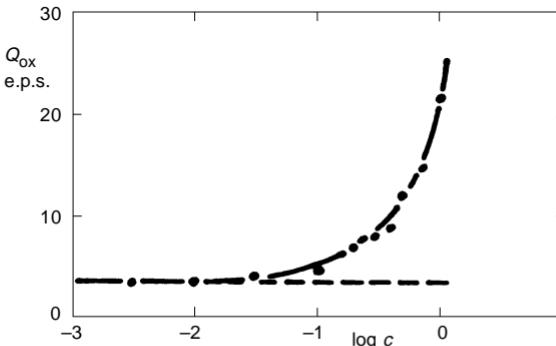


FIG. 6
Dependence of charge Q_{ox} used up during the oxidation of the adsorption product on the sodium thiosulfate concentration c (in mol l^{-1}). Adsorption without external polarization, $t_A = 20 \text{ min}$, $t_D = 1 \text{ min}$, $E_A = 0.4$. Charge corresponding to one electron per surface site: 0.3461 mC



oxidation degree (0.5 e.p.s.) occurs in the hydrogen region during cycle 0; this is consistent, *e.g.*, with Eq. (B). Oxidation of the monolayer requires a charge of 4 e.p.s. according to Eqs (C) and (D).

During the adsorption at the open circuit potential at higher concentrations, reactions occur within which additional layers build up on the initial monolayer. The deepest lying layer(s) are presumably formed by adsorbed sulfur, the last layer at the electrode–electrolyte interface also contains species involving oxygen atoms and thus can probably be reduced in the hydrogen region.

The additional adsorbed layers do not seem to be bonded so strongly as the first and can be desorbed. If the desorption period is long enough, only the monolayer of strongly adsorbed sulfur remains on the electrode. A charge of 6 e.p.s. is required to oxidize this monolayer according to Eq. (C). The results obtained do not allow any more detailed description of the composition of the layers and their mutual reactions.

An experiment examining the adsorption from a solution of colloidal sulfur was carried out to test the possibility of adsorption of sulfur in multiple layers. The solution was prepared by combining a sodium thiosulfate solution and a sulfuric acid solution (both were oxygen-free) so that the resulting concentration of thiosulfate was 0.1 mol l^{-1} in $0.5 \text{ M H}_2\text{SO}_4$. The adsorption was measured 30 min after mixing the solutions, using the procedure shown in Fig. 1. The parameters were as follows: $t_A = 5 \text{ min}$, $t_D = 1 \text{ min}$, $E_A = 0.4 \text{ V}$; the solution was allowed to stand without stirring during the adsorption. The voltammetric curves describing the oxidation of the adsorption products indicate that the adsorption of hydrogen was suppressed completely and no cathodic current was recorded in the hydrogen region during cycle 0. The voltammetric curve became constant after 35 cycles. This steady-state curve is shown as a dashed line in Fig. 8, in which the solid line is the voltammetric curve of the initial platinum electrode in the supporting electrolyte. The charge used up during the oxidation of the adsorbed hydrogen for curve 2 corresponds to 69% of the initial electrode surface (curve 3), hence, only 69% of the surface was freed from the adsorption products. However, the charge used up during the adsorption of hydrogen and the discussed cathodic process in the

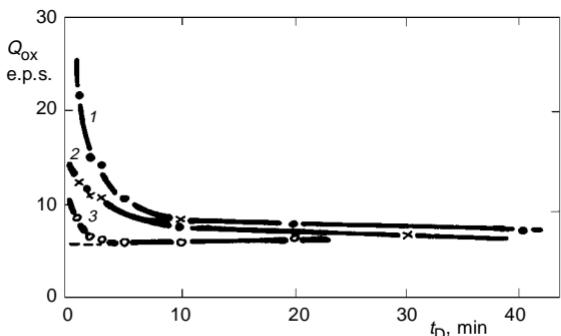


FIG. 7

Dependence of charge Q_{ox} used up during the oxidation of the adsorption product on the time of desorption t_D . Adsorption without external polarization, $t_A = 20 \text{ min}$, $E_A = 0.4$. Sodium thiosulfate concentration (mol l^{-1}): 1 1, 2 0.5, 3 0.3. Charge corresponding to one electron per surface site: 0.3461 mC

hydrogen region, Q_4^{35} , corresponds with the charge used up during the adsorption of hydrogen on the electrode surface free from the adsorbed substance. The shape of the voltammetric curve remained intact on a short-time (10 min) action of a mixture of $K_2Cr_2O_7$ and concentrated sulfuric acid followed by activation. The initial curve shape, corresponding to the completely free electrode surface, was only restored if the cleaning mixture was allowed to act for a longer period of time (24 h).

The Q_{ox} balance was only performed for the starting five cycles because subsequently the shape of the voltammetric curves changed only slightly and the balance for all of the 35 cycles would involve too large an error. The Q_{ox} charge for the starting 5 cycles was 13.32 e.p.s.

CONCLUSIONS

The results obtained lead to the following conclusions:

The amount of hydrogen adsorbed on the platinum electrode decreases due to the adsorption of thiosulfate.

There is an analogy between the oxidation of the thiosulfate adsorption product, adsorbed sulfur, and adsorbed sulfur dioxide.

A monolayer of the adsorbed product forms at lower concentrations (10^{-3} mol l^{-1}) and the product reduces within the hydrogen region. The charge used up during the reduction is approximately 0.5 e.p.s., whereas the charge used up during the oxidation of the reduced layer is roughly 4 e.p.s.

Multiple adsorption layers build up at higher thiosulfate concentrations. The first layer on the electrode surface probably contains adsorbed sulfur, the additional layers seem to involve species containing oxygen atoms, reducible in the hydrogen region. The adsorption layers are partly desorbed in the supporting electrolyte solution.

Adsorption from a colloidal sulfur solution results in the formation of multiple layers of adsorbed sulfur, which can be very difficult to remove from the electrode surface.

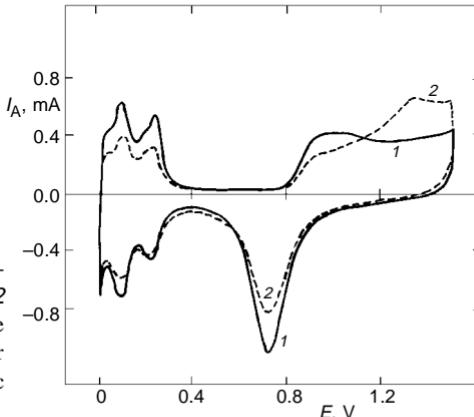


FIG. 8
Steady-state current *vs* potential plot; 1 baseline of the activated platinum electrode, 2 voltammetric curve of the platinum electrode coated with adsorbed colloidal sulfur after 35 cycles. Electrolyte: 0.5 M H_2SO_4 , periodic potential cycle rate 0.2 V s^{-1}

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