ADSORPTION OF ANIONS ON PLATINUM AT ANODE POTENTIALS

V. E. Kazarinov

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The author has used the method of radioactive indicators to study the effect of halide ions on adsorption of sulfate ions on smooth platinum in the potential range 1.5-2.0 V (n.h.e.). The effect of halide ions increases in the following order: $F^- > Cl^- > Br^- > I^-$. From data obtained by methods based on charging curves and labeled atoms, it is concluded that I^- and Br^- anions are desorbed in the anodic potential range owing to oxidation to oxygen-containing compounds.

The authors of [1-10] have shown that in acid and alkaline solutions anions occur in the following order with respect to adsorbability on unoxidized or slightly oxidized platinum: $F^- \leq SO_4^{2-} < Cl^- < Br^- < I^-$. It was noted that pre-adsorbed oxygen retards the adsorption of anions [7-12].

However, a number of facts indicate that these laws do not always hold true in the oxygen overvoltage potential range. For example, in the presence of fluorine anions the oxygen liberation overvoltage increases markedly; an earlier report [13] attributed this to marked adsorption of fluorine anions and their inclusion in the composition of the oxide film. It was recently shown [14-16] that there is a marked increase in adsorption of SO_4^{2-} anions when the oxygen liberation potential is reached. Other experimental data [17-19] indicate a change in the surface properties of platinum in the potential range above 1.5 V (n.h.e.).

The aim of the present work was to obtain data on the structure of the surface layer of platinum in the presence of SO_4^{2-}, F^-, Cl^-, Br^-, and I^- anions in the anode potential range. Owing to the practical difficulty of direct measurements of total adsorption at oxygen overvoltage potentials, we measured the relative adsorbabilities of these anions.

First, we plotted stable adsorption of SO_4^{2-} anions versus platinum potential in 0.1 N H_2SO_4, and then determined the effect of additions of F^-, Cl^-, Br^- and I^- anions on the adsorption of SO_4^{2-} anions.

The measurement procedure was as follows: before the adsorption experiments smooth platinum electrodes (20×20 mm^2) were heated in the flame of a gas burner with an air blast, then subjected to alternate anode–cathode polarization in unlabeled H_2SO_4, rinsed in double-distilled water and left in the latter until the experiments began ($\sim$1 h). The electrodes were then placed in labeled 0.1 N H_2SO_4, polarized for 5 min by a cathode current (1 mA/cm^2), and then kept in the same solution for 15 min at the prescribed anode potential (a longer residence time did not give an appreciable increase in adsorption). The electrodes were removed from the solution and rinsed in three portions of double-distilled water (30 sec each time). Adhering water was removed by drying. The adsorption was calculated from the electrode's radioactivity, measured in a 4π counter [20,21]. Some of the experiments involving use of F^- were performed in Teflon flasks. The results of these experiments were virtually the same as those obtained with glass cells.

The experimental data are given in Fig. 1; it will be seen that in the presence of fluorine and chlorine anions the adsorption of SO_4^{2-} anions decreases markedly. A similar but less pronounced effect is produced by addition of NaI or NaBr (10^{-2}N). It is most pronounced at $\simeq$1.9-2.0 V. The decrease in SO_4^{2-} adsorption at these potentials is more marked in the case of NaBr than NaI (26% and 8% respectively). However, the experimental conditions were not quite the same as in the case of H_2SO_4 + NaF because in the presence of iodide or bromide ions in this potential range they are oxidized to molecular halides and oxygen-containing anions. Assuming that the decrease in adsorption of SO_4^{2-} anions in the anode potential range in the presence of F^-, Cl^-, Br^-, or I^- is due to adsorption of these anions, it may be inferred that the effects exerted by halide ions on an electrode at $\varphi > 1.5$ V are in the following order: $I^- < Br^- < Cl^- < F^-$.

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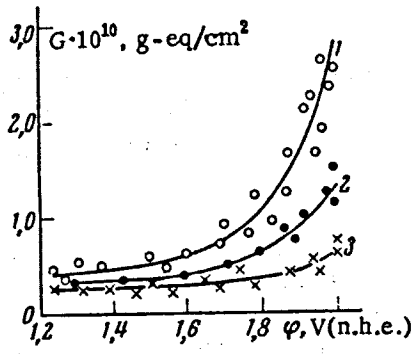


Fig. 1. Adsorption of SO_4^{2-} anions versus potential of smooth platinum: 1) in 0.1 N H_2SO_4 + 0.01 N Na_2SO_4; 2) in 0.1 N H_2SO_4 + 0.01 N NaCl; 3) in 0.1 N H_2SO_4 + 0.01 N NaF.

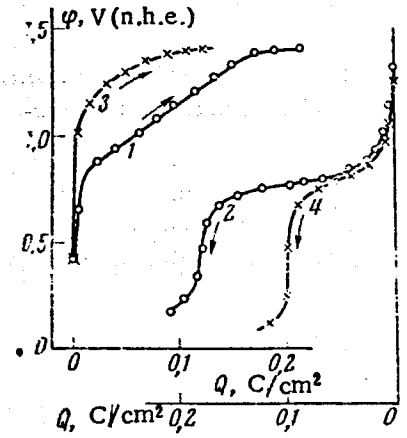


Fig. 2. Oxygen sectors of the charging curves obtained in 1 N H_2SO_4 (1,2); (3)(4) the same curves obtained in the presence of pre-adsorbed Br^- ions ($6 \cdot 10^{-10}$ g-ion/cm²).

SO_4^{2-} anions adsorbed at potentials in the range 1.5-2.0 V adhere firmly to the platinum surface. They are removed very slowly in water, acid* and alkali at the potentials acquired by platinum in air, but can be readily desorbed during cathode polarization in these solutions. This indicates that SO_4^{2-} anions are included in the composition of the oxide film formed on platinum at oxygen overvoltage potentials. F^- and Cl^- anions are probably also included in the oxide film because in the presence of F^- or Cl^- anions the adsorption properties of smooth platinum (with respect to SO_4^{2-} anions in pure H_2SO_4) can be restored after anode polarization of the electrodes only by cathode polarization.

It is of interest to note that within the experimental error the shape of the (G, φ) curve obtained during measurement of SO_4^{2-} adsorption in pure H_2SO_4 is independent of electrode pre-treatment (cathode polarization, heating in the flame of a gas burner, washing in hot nitric acid). This means that, regardless of the electrode's previous history, the electrochemical properties of platinum electrodes should differ little in the anode potential range. This was found to be true: under steady conditions the oxygen overvoltage potential is independent of the method by which the electrode surface is prepared [22].

These data, which indicate the adsorbability of chlorine anions at anode potentials agree with data obtained by other methods. For example, Obrucheva [23] observed a decrease in the amount of adsorbed oxygen in the oxide film formed on platinum in sulfuric acid in the presence of chloride containing anions [24] also indicates that chloride ions are adsorbed in the anode potential range.

The present results confirm the hypothetical oxygen overvoltage mechanism, involving participation of acid anions in the formation of the chemisorbed layer [25].

As already noted, in the presence of I^- or Br^- anions the adsorption of SO_4^{2-} anions at $\varphi \sim 1.9$ V hardly decreases at all, owing to the low adsorbabilities of I^- and Br^- anions (or their oxidation products) in this potential range.

This is also indicated by data in [7,12,26,27], which show that in acid solutions at potentials > 1.2-1.4 V the adsorption of I^- and Br^- ions decreases. Some authors [12,26] attribute this phenomenon to oxidation of the adsorbed ions to iodate ions, other authors [7] to oxidation to molecular halides. To solve this problem, I studied the behavior of adsorbed iodine and bromine anions at potentials more positive than the liberation potentials of the corresponding molecular halide by plotting charging curves and using radioactive indicators.

First, I obtained the charging curves of a platinized platinum electrode in 1 N H_2SO_4, from $\varphi = +0.4$ V to the liberation potential of oxygen and back again. Then, in the same cell the electrodes were kept at the reversible hydroden potential, labeled NaI* (NaBr*) free from dissolved oxygen was added to the solution, and the electrode potential was shifted to + 0.4 V for several hours. Liberation of molecular halides was not observed during this process. From the change in the solution's radioactivity [20,21] it was established that adsorption of iodide ions was $11 \cdot 10^{-10}$, that of bromine anions $6.2 \cdot 10^{-9}$ g-ion/cm² of the true surface, which was determined from the hydrogen part of the charging curve [15]. The solution in the cell was then replaced by pure 1 N H_2SO_4, through which nitrogen had been blown beforehand. Virtually complete removal of the NaI (NaBr) solution from the cell was

*In 0.1 N H_2SO_4 less than 10% of the SO_4^{2-} anions left after a 2-minute rinse are desorbed in 1 h. However, this does not mean that our measured value of adsorption is close to the equilibrium value, because the rate of desorption may decrease rapidly with time.

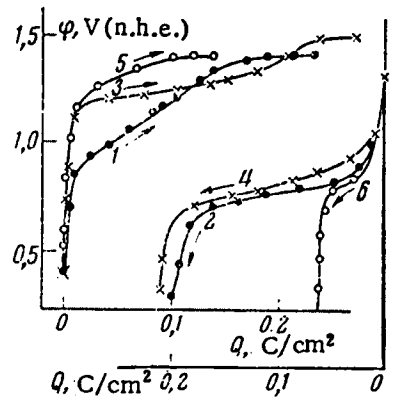


Fig. 3. Oxygen sectors of the charging curves obtained in 1N H_2SO_4 (1,2); the same curves obtained in the presence of pre-adsorbed I^- ions (3,4—$1.1 \cdot 10^{-9}$ g-ion/cm²; 5—$0.3 \cdot 10^{-9}$ g-ion/cm²).

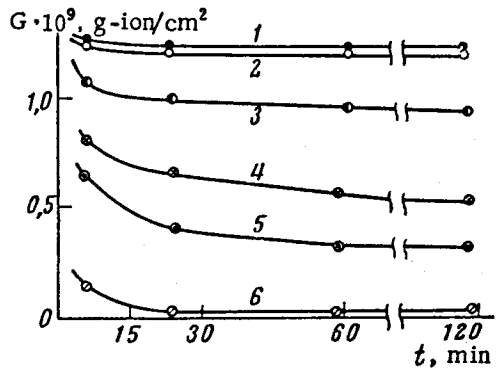


Fig. 4. Desorption of Br^- ions from smooth platinum in 1 N H_2SO_4 versus time at different potentials: 1) 0.76; 2) 1.15; 3) 1.40; 4) 1.60; 5) 1.70; 6) 1.95 V (n.h.e.).

achieved by replacing the acid five times. Separate determinations of the electrode's radioactivity showed that during this process less than 5% of the anions present are disorbed from the electrode.

During replacement of the solution the eletrode's potential was kept at 0.4 ± 0.02 V. Then, on electrodes with adsorbed labeled $I^-(Br^-)$ anions, I obtained charging curves from +0.4 V in the same way as on the clean electrodes. The solution's radioactivity was determined at the same time. The charging curves are given in Figs. 2 and 3.

It will be seen from Fig. 2 that, in accordance with [11], in the presence of adsorbed Br^- ions the amount of adsorbed oxygen decreases. Measurement of the solution's radioactivity shows that during curve determination all the bromine remains in the adsorbed state. Therefore, although the standard Br^-/Br_2 potential is exceeded by nearly 0.3 V, desorption of bromine does not occur. As seen from Fig. 3, the same phenomenon is observed in the presence of small amounts of adsorbed I^- ions ($\sim 0.3 \cdot 10^{-9}$ g-ion/cm²), although in this case the steady I^-/I_2 potential is exceeded by nearly 1 V. However, at sufficiently high coverages of the platinum surface by I^- ions ($> 0.8 \cdot 10^{-9}$ g-ion/cm²) a plateau appears on the anode charging curve at potential 1.2 V. At the same time, radioactivity is observed in the solution. At potential 1.4 V about 25% of the iodine present on the electrode at $\varphi \approx 0.4$ V ($1.1 \cdot 10^{-9}$ g-ion/cm²) is desorbed. Chemical analysis of the solution showed that all the desorbed iodine is quantitatively determined in the solution as the IO_3^- anion. The absence of Br^- ion desorption under these conditions may be due to the fact that on platinized platinum the potentials necessary for oxidizing the adsorbed Br^- ions to bromate ions are not attained. To verify this hypothesis, I studied the kinetics of I^- and Br^- anion desorption from smooth platinum at anode potentials. Anion adsorption was performed on pre-reduced electrodes in air from labeled solutions of 10^{-3} N NaI* (NaBr*) + 1 N H_2SO_4. The results are given in Figs. 4 and 5. From a comparison of these, it will be seen at similar desorption potential, coverage of the surface by the remaining Br^- anions was greater than in the case of iodine. This agrees with data of Schwabe and Schwenke [7] who plotted the adsorption of I^- ions versus the platinum potential under similar conditions but by a different method.

Direct chemical analysis of the solution after desorption of iodine from smooth platinum at 1.7 V in 1 N H_2SO_4 showed that practically all the iodine is present as iodate ions. In these experiments I used smooth platinum electrodes with visible surface 120 cm². After desorption of bromine at 2.0 V in H_2SO_4, bromate ions were detected qualitatively in the solution.

These results show that desorption of Br^- and I^- ions from platinum at anode potentials is due to their oxidation to iodate and bromate ions.

It will be seen from Fig. 3 that the oxygen sector of the charging curve determined in the presence of adsorbed iodine (curve 4) is somewhat longer than the reference curve. This may be due to partial reduction of the iodate ions, because replacement of the acid at the oxygen liberation potential removes this effect and leads only to a reduction in charging curve length (curve 6). In contrast to smooth platinum [28,29], reduction of IO_3^- ions on platinized platinum begins at more positive potentials. The present work also allows us to draw certain conclusions regarding the mechanism by which I^- ions are oxidized to IO_3^- ions on a platinum electrode. It is known [28,29] that on smooth platinum this process is reversible. In the determination of volt-ampere curves on a preoxidized electrode the wave corresponding to oxidation of I^- to IO_3^- is not observed at all. Adsorption data

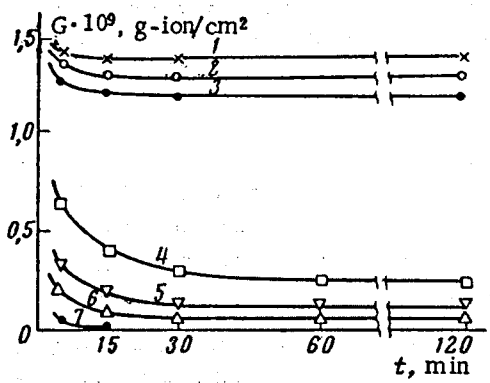


Fig. 5. Desorption of I^- ions from smooth platinum in 1N H_2SO_4 versus time at different potentials: 1) 0.78; 2) 1.0; 3) 1.25; 4) 1.35; 5) 1.45; 6) 1.55; 7) 1.75 V.

[7,11,12] show that under these conditions I^- ions are not adsorption on the platinum surface. It follows that a necessary stage for electrochemical oxidation of iodide ions to iodate ions is adsorption of the former on the electrode surface free from adsorbed oxygen. If we bear this in mind we can give a more precise meaning to the term "state of the surface," on which the rate of oxidation of I^- to IO_3^- greatly depends. This state is determined primarily by the ratio between the amounts of oxygen and I^- ions adsorbed on platinum. A change in this ratio towards the oxygen side retards the reaction.

The present results do not indicate participation of adsorbed oxygen in the oxidation of iodide ions to iodate ions by the reaction $PtO\,[O]_n + I^- \rightarrow IO_3^- + PtO\,[O]_{n-3}$, in contrast to statements in [29]. It would be more correct to infer that such a mechanism is absent, because, in the first place, formation of iodate at a high rate also takes place at potentials more negative than 1.5 V, when the amount of adsorbed oxygen is less than a monolayer; in the second place, in presence of large amounts of adsorbed oxygen the reaction is retarded [29], not accelerated as it would be if the above mechanism were correct.

A comparison of the graphs plotting adsorption of iodide and bromide ions versus potential in acid and alkaline solutions shows that in the latter case anion desorption takes place at lower anode potentials. As in the case of acid solutions, the cause of I^- anion desorption in alkaline solutions is their oxidation to IO_3^-, whereas in the case of Br^- anions desorption is due to their displacement by the adsorbed oxygen [9]. Another characteristic of the adsorption of iodide and bromine ions in alkaline solutions is the marked increase in adsorption of these anions when the oxygen liberation potentials (> 1.0 V) on smooth platinum [7,11] are reached. However, the chemical structure of the anions adsorbed under these conditions, and the cause of the marked increase in adsorption, remain uncertain. In the present case the anions are evidently included in the composition of the oxide film.

The results of the present work show that the relative adsorbabilities of anions on platinum change markedly with the solution potential and pH.

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