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# Physical Chemistry

V. E. Kazarinov and N. A. Balashova

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**Abstract**

**Full Text**

## **Physical Chemistry**

**V. E. Kazarinov and N. A. Balashova**

### **Interaction of Oxygen and Solution Anions during Their Adsorption on Platinum**

*(Presented by Academician A. N. Frumkin, 15 II 1961)*

A number of studies have shown that the adsorption of surface-inactive sulfuric-acid anions on platinized platinum increases when the potential is changed from the reversible hydrogen potential to the potential corresponding to the onset of oxygen adsorption, which displaces into solution the anions adsorbed at a positive surface charge. This result was obtained by rapid measurement of adsorption from the change in the concentration of anions in solution as a function of potential. On oxidized platinum, at potentials of 1.1–1.2 V n.h.e., an increase in the adsorption of sulfuric-acid anions was observed, and with a further rise in potential a decrease in it was again observed (<sup>1</sup>, <sup>2</sup>). On smooth platinum oxidized at a potential of 2.0 V, the adsorption of sulfuric acid amounts to about 1% of the value obtained at a positive charge of unoxidized platinum (<sup>3</sup>).

In studying the dependence of the adsorption of surface-active iodine anions on platinum, work (<sup>4</sup>) likewise yielded a curve  $\Gamma - \varphi$  with a maximum. This result, however, was obtained by measuring adsorption from the radioactivity of an electrode kept in a sulfuric-acid solution at a given potential before adding the adsorbing iodine and removed into air after adsorption for its measurement.

The aim of the present work was to clarify the influence of preliminary oxidation of platinum on anion adsorption, using surface-active bromine anions as an example.

By the methods of labeled atoms (with Br<sup>82</sup>) and charging curves, the adsorption of bromine on platinum from acidic NaBr solutions was studied as a function of time and potential. Adsorption was measured from the change in the radioactivity of the solution and from the change in the radioactivity of an electrode washed with water in air. Special experiments on platinized platinum showed that, in the case of adsorption of bromine and iodine anions, which is very strong (<sup>3-5</sup>, <sup>7</sup>), the adsorption values measured from the radioactivity of the solution or of the electrode are practically identical, which indicates the applicability of the latter method of measurement in the presence of strong adsorption. The surface area of the platinized electrodes was measured from the hydrogen portion of the charging curves obtained in 1 N H<sub>2</sub>SO<sub>4</sub> (<sup>6</sup>).

Fig. 1. Dependence of bromine adsorption on potential.

Figure 1: Fig. 1. Dependence of bromine adsorption on potential.

Figure 1 presents the results for the dependence of bromine adsorption on the potential of platinized platinum. Curve 1 shows that, when the potential is shifted from the reversible hydrogen potential to more positive values, an increase in adsorption is observed up to the potential of bromine evolution, which is noticeable from the yellowing of the solution. When this curve is recorded in the reverse direction (curve 2), the magnitude of adsorption does not change in the interval from 1.0 to 0.2 V, which may be explained by the absence of reduction of chemisorbed bromine, beginning only at still less positive potentials, with subsequent desorption of the  $\text{Br}^-$  anions formed.

Simultaneously with the adsorption curves, charging curves were obtained, shown in Fig. 2. From a comparison of curves 1 and 2 it is seen that

the oxygen part in the presence of bromine begins at higher potentials than in its absence, as was noted earlier for iodine anions in work (5).

The results obtained show that in the case when bromine is initially strongly sorbed on unoxidized platinum, its rapid displacement by oxygen is not observed, and the  $\Gamma-\varphi$  curve does not pass through a maximum.

On an electrode on which oxygen had been adsorbed beforehand, an adsorption curve with a broadened maximum is obtained (Fig. 1, 3).

Fig. 1. Dependence of bromine adsorption on potential. 1 –upon shifting the potential by current in the anodic direction on a reduced electrode; 2 – upon shifting the potential by hydrogen in the cathodic direction (obtained immediately after curve 1); 3 –upon shifting the potential by current in the cathodic direction on an electrode preliminarily anodically oxidized (at 1.4 V vs. h.e.); solution  $1N H_2SO_4 + 1 \cdot 10^{-3}N NaBr$ ; 4 –upon shifting the potential by current in the anodic direction on a reduced electrode from a solution of  $1N H_2SO_4 + 5 \cdot 10^{-4}N NaBr$

In this case the platinum was first anodically oxidized in  $1N H_2SO_4$  at the potential of oxygen evolution (1.4 V) for 1 hour. After polarization, the dissolved oxygen was removed with nitrogen. At the established potential of 1.22 V, NaBr was added to the solution and the increase in adsorption was observed over time; its value after 1 hour reached only  $4 \cdot 10^{-11}$  g-ion/cm<sup>2</sup>. Then, at a constant density of cathodic current, changes in bromine adsorption were measured until the reversible hydrogen potential was reached (210 min.). A comparison of curves 3 and 4 in Fig. 2 and curve 3 in Fig. 1 in the potential interval from 1.2 to 0.9 V shows that bromine adsorption is practically not observed as a consequence of the removal of a very small amount of oxygen that is strongly sorbed at high anodic potentials. In the interval 0.9-0.7 V, apparently, complete desorption of oxygen occurs, and bromine adsorption reaches its maximum value.

Fig. 2. Charging curves on platinized platinum. 1—*anodic in pure 1 N H<sub>2</sub>SO<sub>4</sub>*; 2—*anodic in 1 N H<sub>2</sub>SO<sub>4</sub> + 3 · 10<sup>-3</sup> N NaBr*; 3—*cathodic, obtained simultaneously with adsorption curve 3 in Fig. 1*; 4—*cathodic in 1 N H<sub>2</sub>SO<sub>4</sub> on a clean electrode*; 5—*cathodic in 1 N H<sub>2</sub>SO<sub>4</sub> after adsorption of bromine on the electrode*

Figure 2: Fig. 2. Charging curves on platinized platinum. 1—*anodic in pure 1 N H<sub>2</sub>SO<sub>4</sub>*; 2—*anodic in 1 N H<sub>2</sub>SO<sub>4</sub> + 3 · 10<sup>-3</sup> N NaBr*; 3—*cathodic, obtained simultaneously with adsorption curve 3 in Fig. 1*; 4—*cathodic in 1 N H<sub>2</sub>SO<sub>4</sub> on a clean electrode*; 5—*cathodic in 1 N H<sub>2</sub>SO<sub>4</sub> after adsorption of bromine on the electrode*

In the interval corresponding to the double-layer part of the charging curve, the values of bromine adsorption do not change with potential. This shows that the adsorbed bromine does not manage to react to changes in the potential in the double layer because of the great strength of its bond with platinum, which agrees with the data of work (8) on measurement of the capacitance of the double layer on platinum in bromide solutions.

The decrease in adsorption observed at the potentials of the hydrogen part of the charging curve is explained in the same way as for curve 2 in Fig. 1.

The slowness of the displacement of initially adsorbed oxygen by bromine can apparently explain the adsorption curve with a maximum obtained in work (4).

In the study of the exchange of bromine adsorbed on platinized platinum with bromine ions in solution, a dependence of the rate of exchange on potential is manifested. Exchange at a potential of 0.1 V proceeds comparatively rapidly (by 60% in 1 hour), whereas at a potential of 0.8 V during the same time, with the same degree of filling, exchange practically does not occur at all. This indicates a change in the strength of the bond of sorbed bromine with platinum.

A comparison of the cathodic charging curves 4 and 5 in Fig. 2 shows that on an electrode whose oxidation was carried out after bromine adsorption

(curve 5), oxygen with a large binding energy is absent. The total quantity of electricity required to take the complete charging curve, however, is the same in both cases. Desorption of bromine takes place at potentials corresponding to the hydrogen portion of the curve. For this reason this portion of charging curve 5 is longer than that of curve 4.

At potentials corresponding to the hydrogen portion of the charging curve, in a NaBr solution of low concentration ( $5 \cdot 10^{-4} N$ ), practically 100% adsorption of bromine from the solution can be observed, despite the presence in it of a more than 1000-fold excess of sulfate anions (Figs. 1, 4). When the electrode is held at the oxygen-evolution potential, very slow desorption of bromine with time is observed in this case (5% in 2 hours).

**Fig. 2.** Charging curves on platinized platinum. 1—*anodic in pure 1N H<sub>2</sub>SO<sub>4</sub>*;

Fig. 3

Figure 3: Fig. 3

**2**—anodic in  $1N$   $H_2SO_4 + 3 \cdot 10^{-3}N$   $NaBr$ ; **3**—cathodic, obtained simultaneously with adsorption curve **3** in Fig. 1; **4**—cathodic in  $1N$   $H_2SO_4$  on a clean electrode; **5**—cathodic in  $1N$   $H_2SO_4$  after adsorption of bromine on the electrode.

In studying the kinetics of bromine adsorption on air-oxidized platinized platinum, it was shown that the magnitude of adsorption varies linearly with the logarithm of time in the region of intermediate surface coverages from  $0.5 \cdot 10^{-10}$  to  $2 \cdot 10^{-10}$  g-ion/cm<sup>2</sup>, when the time is varied from  $2 \cdot 10^3$  to  $2 \cdot 10^5$  sec.

The kinetics of bromine adsorption from acidic solutions of  $0.005N$   $NaBr + 0.005N$   $Br_2$  or  $0.01N$   $NaBr$  are identical. Consequently, the rate of bromine adsorption is determined not by the process of oxidation of  $Br^-$  followed by adsorption of bromine on the electrode, but by the rate of displacement of oxygen previously adsorbed on the surface. Direct experiments on air-oxidized platinum in a nitrogen atmosphere showed that, during adsorption of bromine from a  $NaBr + H_2SO_4$  solution, there is a decrease in  $H^+$  cations equivalent to the amount of adsorbed bromine, with an accuracy of up to 10%.

The kinetics of bromine adsorption were studied as a function of the degree of oxidation of smooth platinum. After the corresponding preliminary treatment, the samples were placed in a solution of  $1N$   $H_2SO_4 + 2 \cdot 10^{-3}N$   $NaBr$  for a specified time. After rinsing with water (20 sec), their radioactivity was measured. The samples were then again immersed in the same solution and all operations were repeated, which made it possible to study the adsorption kinetics on one and the same surface.

On the unreduced sample (Fig. 3, 1) bromine is adsorbed rapidly, which agrees with the data of work (9) for the case of  $I^-$ ,  $CN^-$ ,  $CNS^-$  on unreduced platinum deposited in vacuum. With time, however, the value of bromine adsorption decreases somewhat, which we explain by its displacement by oxygen before the equilibrium state is reached. From a comparison of curves 1-5 it is evident that the longer the platinum was oxidized in air, the smaller the initial values of bromine adsorption. With time they increase owing to the slow displacement of adsorbed oxygen by bromine, tending toward an equilibrium state. On anodically oxidized platinum (curve 6), bromine adsorption at first proceeds very slowly, and after 500-600 sec a jump-like increase in adsorption is observed, rapidly reaching its limiting value. It may be assumed that here there is a phenomenon of destruction of the passivating oxide layer on platinum, analogous to the phenomenon of "breakdown" in corrosion.

**Fig. 3.** Kinetics of bromine adsorption on smooth platinum. Samples, after activation by alternating anodic and cathodic polarization in  $1N$   $H_2SO_4$ , were kept in air for: 1 —several seconds, 2 —1 min, 3 —2 h, 4 —2 days; 5 —after heating in the flame of a gas burner; 6 —after anodic oxidation at a current of

10 mA/cm<sup>2</sup> for 2 h.

Desorption of bromine from platinized platinum in water in air practically does not occur, but proceeds comparatively rapidly in electrolyte solutions at potentials more negative than the normal hydrogen potential (>90% in several tens of minutes).

From smooth platinum under anodic polarization in 1 N H<sub>2</sub>SO<sub>4</sub>, almost complete desorption of bromine is observed within several minutes; we explain this by attainment of a high potential (1.9 V), at which BrO<sub>3</sub><sup>-</sup> anions are formed, which are not adsorbed on anodically oxidized platinum (10). Desorption of bromine can also be carried out in water in air, but much more slowly. In this case the dependence

$$\Gamma = a \lg(t + t_0)$$

is observed, indicating that the processes of adsorption and desorption on oxidized platinum occur with an activation energy that varies linearly with surface coverage, which should correspond to adsorption on a heterogeneous surface obeying the Temkin isotherm (11).

The totality of the results obtained proves the chemical nature of bromine adsorption on platinum and the mutual displacement of bromine and oxygen.

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Institute of Electrochemistry  
Academy of Sciences of the USSR

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## REFERENCES

1. A. Schlygin, A. Frumkin, W. Medwedowski, *Acta physicochim. URSS*, **4**, 911 (1936).
2. N. A. Balashova, *DAN*, **103**, 639 (1955).
3. N. A. Balashova, N. S. Merkulova, *Proceedings of the IV Conference on Electrochemistry*, Publ. House of the USSR Academy of Sciences, 1959, p. 48.
4. N. A. Balashova, *ZhFKh*, **32**, issue 10, 2267 (1958).
5. A. D. Obrucheve, *ZhFKh*, **32**, issue 10, 2155 (1958).

6. B. Ershler, *Acta physicochim. URSS*, **7**, No. 3, 327 (1937).
7. V. I. Nesterova, A. N. Frumkin, *ZhFKh*, **26**, No. 8, 1178 (1952).
8. T. P. Brintseva, B. N. Kabanov, *ZhFKh*, **33**, 844 (1959).
9. Ch. Weissmantel, Dissertation, Technische Hochschule, Dresden, 1958.
10. V. E. Kazarinov, N. A. Balashova, *DAN*, **134**, No. 4, 864 (1960).
11. S. Z. Roginskii, *Adsorption and Catalysis on Heterogeneous Surfaces*, Publ. House of the USSR Academy of Sciences, 1948.

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