ADSORPTION PROPERTIES OF A PLATINUM ELECTRODE IN TETRAFLUOROBORIC ACID SOLUTIONS

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Measurements on mercury and cadmium electrodes have revealed [1-3] that BF_4^- and PF_6^- anions belong to the class of ions with minimal surface activity. It is of interest to investigate the adsorption properties of a platinum electrode in the presence of these ions.

This communication gives the results of an investigation of the behavior of a platinized platinum electrode in solutions of tetrafluoroboric acid HBF_4. This acid is used as the electrolyte for electrodeposition of a number of metals [4].

We used various methods for these measurements: charging curve, potentiodynamic, isoelectric potential shifts [5], and electrical conductivity [6].

The isoelectric potential shifts were measured on platinized platinum mesh with a visible surface of 15 cm^2 and a true surface of 1.2-1.4 m^2. The true surface was determined from the length of the hydrogen region of the charging curve in 1 N H_2SO_4 [7]. Measurement of the electrical conductivity and determination of the Gibbs adsorption of hydrogen ions, G_{H^+}, by direct titration were performed on a platinized platinum electrode with visible and true surfaces of 100 cm^2 and 12.5-14.0 m^2 respectively.

The working solutions were prepared from 40% tetrafluoroboric acid of "ch.d.a." ["analytical"] grade. This acid was diluted to 1 N and purified by cathodic polarization with a current of 1.0-1.5 mA/cm^2 of visible

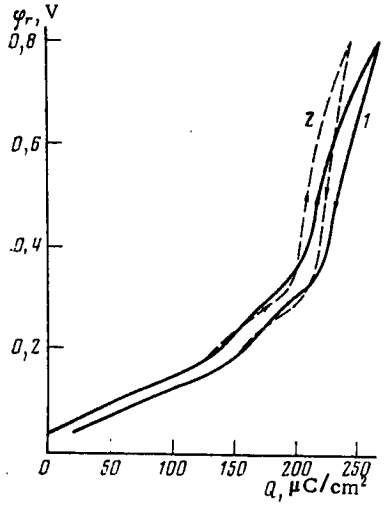

Fig. 1

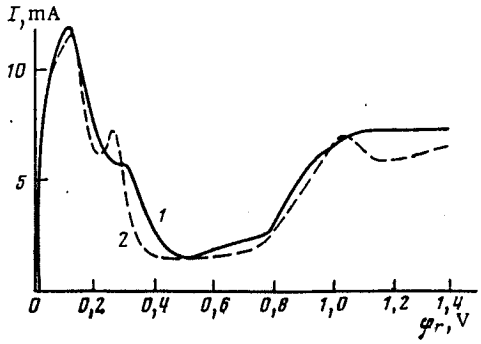

Fig. 2

Fig. 1. Charging curves of a Pt/Pt electrode in 0.6 N HBF_4 (1) and 0.5 N H_2SO_4 (2).

Fig. 2. Anodic potentiodynamic curves of a Pt/Pt electrode in solutions: 1) 0.6 N HBF_4; 2) 0.5 N H_2SO_4.

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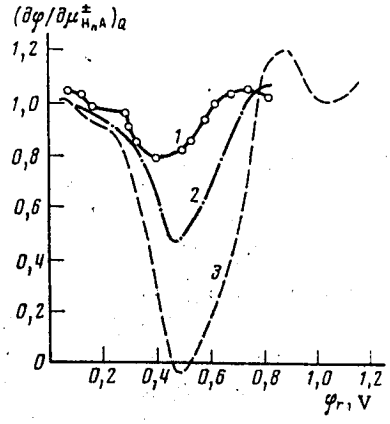

Fig. 3

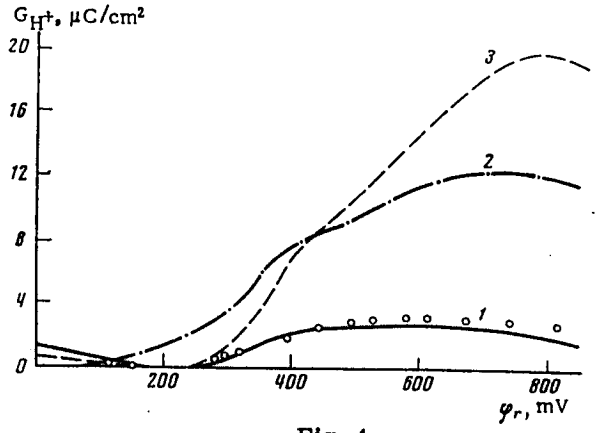

Fig. 4

Fig. 3. Isoelectric potential shifts vs potential of Pt/Pt electrode in solutions: 1) 0.01 N HBF_4; 2) 0.14 N HF (2); 3) 0.01 N H_2SO_4.

Fig. 4. Gibbs adsorption of hydrogen ions, equal to Gibbs adsorption of anions, vs potential of a Pt/Pt electrode in solutions: 1) $6 \cdot 10^{-3}$ N HBF_4; 2) 0.14 N HF (2); 3) $5 \cdot 10^{-3}$ N H_2SO_4. The points denote the G_{H^+} values calculated from the isoelectric potential shifts for 0.01 N HBF_4.

surface on platinized platinum mesh (true surface 6 m^2) for 14-16 h. The solution was then diluted to the required concentration. The reversibility of the charging curves after this treatment was no worse than in sulfuric acid solutions.

The work was performed in freshly prepared solutions of tetrafluoroboric acid, because in dilute solutions HBF_4 is slowly hydrolyzed with formation of $HBF_3(OH)$ and HF as initial products [8].

In the measurement of the electrical conductivity, the charging curves, and the potentiostatic curves the HBF_4 concentration was the same, so that the hydrogen-ion activities in the HBF_4 solution and the H_2SO_4 solution used for comparison were the same. The hydrogen-ion activity was determined from the potential of a platinized hydrogen electrode in the test solution with respect to a saturated calomel electrode. Monitoring was performed by measuring the acid concentration by direct titration. However, direct titration of HBF_4 entails a serious error owing to hydrolysis, and the results of such titration greatly depend on the dilution and temperature [8].

The experiments were performed at 20 ± 1°C. The potentials φ_r were related to a reversible hydrogen electrode in the same solution, and the potentials φ to a constant reference electrode.

For the measurements we used a cell of ordinary glass No. 23. Our relatively dilute HBF_4 solutions did not display any phenomena indicating reaction of the solutions with the glass of the cell, and the measurement results were satisfactorily reproducible. However, when thin sections wetted with HBF_4 solutions were dried, we noted that the ground surfaces had suffered some damage.

Figure 1 compares the charging curves of a platinum electrode in 0.5 N H_2SO_4 and 0.6 N HBF_4 solutions. It will be seen that the bond energy of adsorbed hydrogen in HBF_4 solutions is higher than in sulfuric acid solutions. The slope of the curve in the "two-layer" region is flatter in a HBF_4 solution; this is due to the fact that oxygen is chemisorbed sooner on the electrode surface. Similar conclusions follow from the potentiodynamic curves measured in these solutions (Fig. 2). In HBF_4 solutions the second hydrogen maximum is less distinct. Similar changes in the charging and potentiodynamic curves were observed [9] in going from H_2SO_4 solutions to hydrofluoric acid solutions. The data suggest the lower adsorbability of tetrafluoroboric anions in comparison with sulfuric acid anions.

Figure 3 shows the isoelectric potential shifts for 0.01 N HBF_4. To measure these shifts, we replaced 10^{-3} N HBF_4 by 0.1 N HBF_4. At potentials φ_r close to 0, with retention of a complete surface charge Q, the electrode in a HBF_4 solution behaves approximately like a reversible hydrogen electrode, as shown by the fact that the values of $(\partial\varphi/\partial\mu_{HA^{\pm}})_Q$ are close to 1 ($\mu_{HA^{\pm}}$ is the mean chemical potential of the acid ions HA). At potentials $\varphi_r > 0.6$ V, the value of the derivative $(\partial\varphi/\partial\mu_{HA^{\pm}})_Q$ is greater than 1, owing to displacement of the BF_4^- anions from the electrode surface by chemisorbed oxygen. Over the φ_r range from 0.1 to 0.6 V the value of $(\partial\varphi/\partial\mu_{HA^{\pm}})_Q$ deviates negligibly from 1: The minimum value of the derivative is observed at $\varphi_r \sim 0.4$ V and

is 0.79, i.e., much greater than in 0.01 N H_2SO_4 and 0.14 N HF. This indicates greater overlapping of the region of adsorption of hydrogen and oxygen in HBF_4 solutions than in H_2SO_4 and HF solutions, owing to the weaker specific adsorbability of BF_4^- in comparison with SO_4^{2-} and F^- anions.

For direct determination of adsorption of BF_4^- anions on platinum we measured the electrical conductivity. The results are given in Fig. 4. To standardize the data for HBF_4 we directly measured G_{H^+} at φ_r = 550 mV by titration. For comparison Fig. 4 plots G_{H^+} vs φ_r, measured in a $5 \cdot 10^{-3}$ N H_2SO_4 solution, and gives the curve for a 0.14 N HF solution, taken from [10, 11]. In acid solutions without foreign substances G_{H^+} is equal to the Gibbs adsorption of anions on the electrode surface [12].

As we see from Fig. 4, the value of G_{H^+} in a HBF_4 solution is much less than in H_2SO_4, owing to the very low adsorbability of the BF_4^- anion on a platinum electrode. The value of G_{H^+} in HBF_4 solutions is less than in HF, but it is difficult to make a direct comparison of the adsorbabilities of BF_4^- and F^- owing to the differences in the concentrations and pH values of the solutions (the hydrogen-ion activity in 0.14 N HF is equal to that in 0.01 N H_2SO_4). The values of G_{H^+} in HBF_4 slowly increase with time, probably owing to hydrolysis of BF_4^- and to the appearance of anions with a higher surface activity than the latter.

Note a certain increase in G_{H^+} near the hydrogen zero in H_2SO_4 and, in particular, in HBF_4. The nature of this phenomenon remains obscure.

The points in Fig. 4 denote the G_{H^+} values calculated from the measured isoelectric potential shifts [5] for 0.01 N HBF_4. The calculated values are close to the values obtained experimentally in $6 \cdot 10^{-3}$ N HBF_4. In plotting the calculated results in Fig. 4 we assumed that $G_{H^+}=0$ at $\varphi_r=200$ mV.

Our results show that in HBF_4 solutions the principal contribution to the change in the potential jump at the platinum/solution interface is made by the change in the amount and polarity of the bonds of adsorbed hydrogen and oxygen with platinum. We must also take into account the effect of hydrogen and oxygen on the electric double layer capacitance.

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