ADSORPTION OF PERCHLORATE IONS ON PLATINUM AND RHODIUM ELECTRODES

S. Ya. Vasina and O. A. Petrii

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Although a great number of electrochemical investigations (see, e.g., [1-4]) were devoted to the behavior of platinum in solutions of perchloric acid, no direct data are available as to the adsorption of ClO_4^- anions on such an electrode. We studied the adsorption of perchloric acid on Pt/Pt and rhodium-plated electrodes.

The measurements were carried out with the help of the methods of charging curves, adsorption curves [5], isoelectric potential shifts [6], and the potentiostatic method, at 20 ± 1°C. In our investigations we used a P-5611 potentiostat. The potentials φ_r were referred to a reversible hydrogen electrode in the same solution. The preparation of the electrodes is described in [7, 8]. The true surface of the Pt/Pt electrode was 8.4-9.1 m^2, that of the rhodium electrode was 0.75 and 3.9-4.1 m^2; the solution and the operating parts of the cell had a volume of 20 cm^3. Before the experiment the electrodes were subject to anodic and cathodic polishing in 0.1 N H_2SO_4 and then washed with bidistillate.

The "chemically pure" perchloric acid was carefully purified. It was either distilled twice in vacuo or frozen out three times (in some cases the acid was distilled and then frozen out). For this purpose, in a special vessel a portion of $HClO_4$ was frozen out to one half in a mixture of dry ice and acetone. The nonfrozen acid was poured off, the residue was melted and the process was repeated. In addition to this, in special experiments we used $HClO_4$ solutions purified by means of activated carbon which had been kept for a long time in contact with hydrogen-saturated Pt/Pt grids or subject to cathodic purification on a mercury electrode.* The method used to purify $HClO_4$ could not be observed to exert great influence on the results obtained; most of the experiments were made with $HClO_4$ purified by freezing. A qualitative analysis showed that the acid used did not contain any other chlorine compounds other than ClO_4^-.

Figure 1 shows the charging curves for platinum and rhodium in 0.1 N $HClO_4$ and H_2SO_4. The anodic branch of the rhodium charging curve in $HClO_4$ is shorter than the anodic branch in H_2SO_4; the cathodic branch of this curve, however, shows a particularly strong distortion. Considering the drop of the electrode potential to $\varphi_r = 0$ in the solution, we could prove the presence of Cl^- ions using the reaction with $AgNO_3$. This indicates the reduction of the ClO_4^- ions to Cl^- on rhodium during the measurements of the slow charging curves. In order to determine the φ_r value at which the reduction of ClO_4^- sets in, a rhodium electrode washed with bidistillate on air was submerged in a $HClO_4$ solution (blown through by argon) and with the help of the potentiostat a potential of $\varphi_r = 0.6$ V was set. Apart from ClO_4^- no other chlorine compounds could be detected in the solution. After the stabilization of the potential we measured the cathodic charging curve. This curve is longer than that obtained under similar conditions in 0.1 N H_2SO_4 ($\Delta Q = 0.95$ C).

After the cathodic charging curve in 0.1 N $HClO_4$ was recorded, we applied a method of argentometric amperometric titration [9] to determine the Cl^- ion concentration; we obtained a value of $0.7 \cdot 10^{-4}$ g-eq./liter†. The formation of this quantity of Cl^- ions consumes about 1.07 C of electricity so that the difference in the quantity of electricity calculated from curves 4 and 5 of Fig. 1 is entirely due to the reduction of ClO_4^- to Cl^-. From curve 5 we can conclude that the reduction of ClO_4^- on Rh begins at $\varphi_r \leqslant 0.55$ V. With these φ_r values no hydro-

*We learned from I. A. Bagotskaya that the latter procedure permits the obtaining of reproducible values for the hydrogen overvoltage on gallium in perchloric acid solutions.

†With this method the Cl^- ion concentration in a solution can be determined with an accuracy of $\pm 1 \cdot 10^{-5}$ g-eq./liter.

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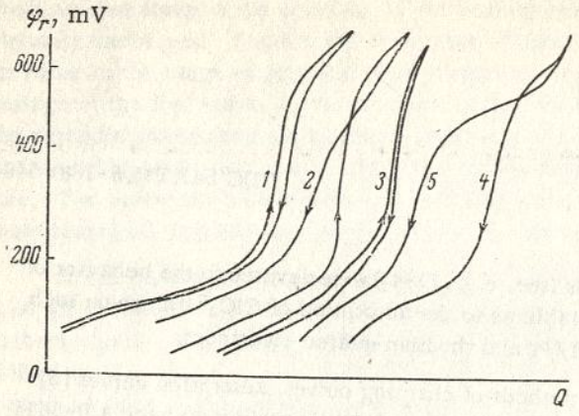

Fig. 1. Charging curves for rhodium-plated (1, 2, 4, 5) and Pt/Pt (3) electrodes in 0.1 N $HClO_4$ (2, 3, 5) and 0.1 N H_2SO_4 (1, 4); i = 0.1 $\mu A/cm^2$ of true surface. The arrows indicate the direction of recording.

gen is adsorbed. The reduction process can be assumed to take place according to an electrochemical mechanism.

Similar measurements were also made with a Pt/Pt electrode. In this case it was not possible to conclude the reduction of ClO_4^- ions immediately from the charging curve measurements (Fig. 1); this is due to the considerably lower rate of this process on Pt. In fact, if a Pt/Pt electrode in a $HClO_4$ solution is kept at φ_r = 0.3-0.4 V for 30 min and φ_r is then reduced to zero (by cathodic polarization or blowing through of hydrogen), Cl^- ions can be detected in the solution.

To study the process of ClO_4^- reduction in detail we carried out the following measurements. The electrode was kept at a chosen value of φ_r in a $HClO_4$ solution. After stabilization of the potential, part of the solution was poured off and analyzed for possible reduction products of ClO_4^-. In the whole interval of φ_r investigated it was not possible to detect any trace of ClO_4^- reduction products in the solution. Then hydrogen was blown through the solution and after having reached φ_r = 0 the solution was again analyzed. In the solution we only discovered ClO_4^- and Cl^- ions.* At the same time we determined the variation of the hydrogen ion concentration in the solution. The ClO_4^- ion reduction

$$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$$

can be represented in the form

$$ClO_4^- + 4H_2 \rightarrow Cl^- + 4H_2O.$$

Consequently, the pH variation of the solution arising when hydrogen is blown through can only be due to the difference in the quantity of $HClO_4$ adsorbed with the initial φ_r and φ_r = 0, i.e., in spite of the reduction reaction the adsorption of $HClO_4$ on the electrode can be determined. These experiments permit a direct comparison between the $HClO_4$ adsorption and the quantity of Cl^- ions formed in its reduction. In the presence of excessive indifferent electrolyte the electrode surface charge can be determined from the variation of the H^+ ion concentration during the formation of the double layer [11].

Figure 2 illustrates the results of the experiments described above. On Rh the quantity of Cl^- ions obtained in the reduction of $HClO_4$ is virtually equal to the adsorption of acid up to $\varphi_r \approx 0.5$ V. With higher anodic potentials (φ_r) the acid adsorption decreases owing to the adsorption of oxygen on the electrode, the Cl^- ions, however, are found in the same quantity as with the initial value of φ_r = 0.3-0.4 V. This result is due to the fact that, when hydrogen is blown through the solution, the electrode potential passes through the values of 0.3-0.4 V and the ClO_4^- ions then adsorbed are reduced to Cl^-. At φ_r = 0 the adsorption of $HClO_4$ drops to zero and no Cl^- ions are discovered in the solution. A comparison of the adsorption of H_2SO_4† and $HClO_4$ (Fig. 2) permit the conclusion that the adsorbabilities of ClO_4^- and SO_4^{2-} are almost equal. It is, however, necessary to take into account that the SO_4^{2-} ions adsorbed are in equilibrium with the ions of the solution, while in the case of ClO_4^- adsorption there is no such equilibrium. Other experiments showed that ClO_4^- is adsorbed less strongly. Thus, if the electrode potential is reduced to φ_r = 0.6 V in 0.01 N H_2SO_4 and the solution is then replaced by 1 N $HClO_4$ and blown through by hydrogen, the quantity of Cl^- ions discovered in the solution will be lower by an order of magnitude compared with that obtained in the experiments shown in Fig. 2.

This indicates that even small quantities of SO_4^{2-} ions in the solution hinder the adsorption and reduction of ClO_4^-. The reduction of ClO_4^- virtually cannot be observed in a solution of 1 N $HClO_4$ + 10^{-4} N HCl. Thus we see that foreign anions reduce the rate of reduction of ClO_4^- anions by removing them from the surface layer. On the basis of these results we can reveal an analogy between the processes of reduction of ClO_4^- anions on Rh and Pt and and of $S_2O_3^{2-}$ anions on Hg [12]: in both cases the reaction rate decreases when we pass over to negative surface

*The fact that the solution did not contain chlorine compounds of an intermediate valence agrees with data from [10] according to which these compounds are rapidly reduced at these potentials.

†Data on the adsorption of sulfuric acid on rhodium were obtained by V. V. Topolev.

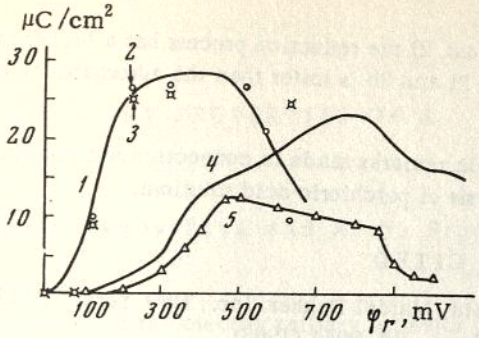

Fig. 2

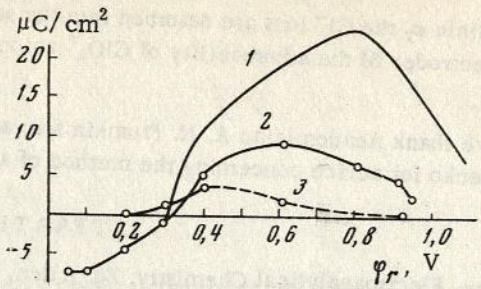

Fig. 3

Fig. 2. Dependence of hydrogen ion adsorption (1, 2, 4, 5) and the quantity of chlorine ions (3) formed in the reduction of ClO_4^- on the potential of the rhodium (1-3) and the platinum electrode (4, 5) in the following solutions: 1,4) 0.01 N H_2SO_4; 2,3,5) 0.01 N $HClO_4$.

Fig. 3. Dependence of the surface charge of the Pt/Pt electrode on the potential in 0.01 N H_2SO_4 + 1 N Na_2SO_4 (1) (after data from [14]) and in 0.01 N $HClO_4$ + 1 N $NaClO_4$ (2); dependence of the quantity of chlorine ions (3) formed in the reduction of ClO_4^- on the initial potential.

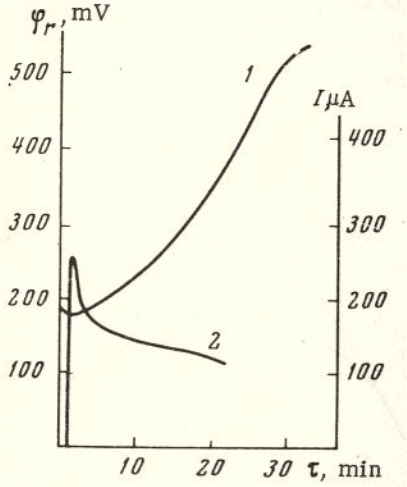

Fig. 4. Potential shift (1) with open circuit and time dependence of current (2) at $\varphi_r = 0.198$ V after replacement of the 0.01 N $HClO_4$ by 1 N $HClO_4$ on a rhodium electrode.

charges, and in the presence of anions adsorbed in a specific way. In our case, however, the reduction process can only be influenced by adsorbed ClO_4^- anions.

With all potentials the adsorption of $HClO_4$ on platinum was less intense than the adsorption of H_2SO_4 (Fig. 2), in particular with $\varphi_r > 0.4$ V. The decrease of $HClO_4$ adsorption with $\varphi_r > 0.4$ V indicates that at these potentials adsorbed oxygen is present on the Pt surface in $HClO_4$ solutions. In agreement with the lower adsorbability of ClO_4^-, the surface charges with anodic φ_r are lower than the surface charges in a sodium sulfate solution. According to Fig. 3, only part of the ClO_4^- ions adsorbed on Pt are reduced down to Cl^-. The decrease of the quantity of Cl^- ions with an initial potential of $\varphi_r > 0.4$ V is caused by the fact that the ClO_4^- reduction rate is lower for Pt than for Rh so that, when hydrogen is blown through, not all the adsorbed ClO_4^- ions can be reduced. If we assume that, in spite of the reduction process taking place, we can speak of a point of zero charge in the $HClO_4$ solutions, in an acidified solution of sodium perchlorate the latter will be close to the point of zero charge in acidified sulfate (Fig. 3) [13].

We also measured the isoelectric potential shifts caused by a variation of the solution's pH on Rh and Pt electrodes. In the case of H_2SO_4 solutions the inceasing H^+ ion concentration shifts φ_r toward the cathodic side. In $HClO_4$ solutions in Rh φ_r is initially also shifted to the cathodic side, then it begins slowly to grow; this is caused by the reduction of ClO_4^-. Under potentiostatic conditions the appearance of a cathodic current corresponds to this process (Fig. 4). The shift of φ_r on Pt accompanying the increase in $HClO_4$ concentration in the hydrogen range of φ_r takes place toward the cathodic side, however, the amount of the shift is hardly reproducible and with $\varphi_r > 0.2$ V it is considerably smaller than in H_2SO_4 solutions.

The measurements also show that the quantity of Cl^- ions increases (by 10-15%) with the $HClO_4$ concentration in the solution (from 0.01 N to 1 N), with the holding time of the electrode at $\varphi_r = 0.3$-0.4 V, and also with a slow periodic variation of φ_r of the electrode in the interval between 0 and 0.4 V with simultaneous blowing through of argon. When the electrode is kept at $\varphi_r = 0.4$ V, the quantity of Cl^- ions then detected does not depend on whether the solution is stirred or not.

From the total of results achieved in our investigations we can draw the following conclusions: 1) The ClO_4^- anions adsorbed on Pt at $\varphi_r \simeq 200 \div 550$ mV and on Rh at $\varphi_r = 100 \div 550$ mV are reduced to Cl^-; at higher

cathodic potentials φ_r the Cl^- ions are desorbed into the solution; 2) the reduction process has a higher rate in the case of a Rh electrode; 3) the adsorbability of ClO_4^- anions on Pt and Rh is lower than the adsorbability of SO_4^{2-} anions.

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