ADSORPTION OF CATIONS OF THE ALKALINE EARTH METALS ON PLATINUM

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The adsorption of cations of the alkaline earth metals on platinum was first studied in [1], according to which Ca^{2+}, Sr^{2+}, and Ba^{2+} ions do not produce any significant shifts of the potential of platinum under isoelectric conditions in a solution of 1 N $HClO_4$. According to the data of [2], in less acid solutions the shifts of the potential in the presence of Ca^{2+} and Ba^{2+} are comparable with the shifts induced by the cations Cd^{2+} and Tl^+ [1, 3], although the values of the adsorption of Ca^{2+} and Ba^{2+} ions in this case are relatively small and comparable with the values of the adsorption of Na^+ and Cs^+ [4]. Moreover, according to the data of [2, 5], in the presence of Ca^{2+} and Ba^{2+} the adsorption of atomic hydrogen on platinum is substantially reduced.

Measurements of the adsorption of Ca^{2+} and Ba^{2+} ions were conducted in perchloric acid solutions, in which, as we have recently discovered [6], there is a reduction of ClO_4^- ions, which might distort the result.

In this work we studied the adsorption of Ca^{2+}, Sr^{2+}, and Ba^{2+} ions on a platinized platinum electrode, considering this circumstance.

The measurements were performed by methods of determining the change in the hydrogen ion concentration in solution in the formation of an electrical double layer [7], the adsorption shifts of the potential [1], the charging curves, and by a potentiodynamic method. In the work we used a P-5611 potentiostat with electronic development of the potential. The experiments were conducted at 20 ± 1°C. The potentials φ_r were related to the reversible hydrogen electrode in the same solution.

The preparation of the Pt/Pt electrode and determination of its true surface were indicated in [6, 9]. Solutions of calcium, strontium, and barium perchlorates were prepared as follows: first the carbonates of the alkaline earth metals were precipitated from solutions of the twice-recrystallized chlorides with the aid of sodium carbonate. The precipitate was washed thoroughly with hot double-distilled water until complete removal of chloride ions (test with silver nitrate). The carbonates were decomposed with perchloric acid, frozen out three times [6], and the carbonates were again precipitated from the solutions of the perchlorates obtained. These carbonates, after thorough washing, were dried at 120-150°C and then used to prepare the solutions of perchlorates. Magnesium sulfate was recrystallized twice from double-distilled water and calcined at 500°C.

Figure 1 presents the results of a determination of the adsorption of hydrogen ions Γ_{H^+} at $\varphi_r = 0$ as a function of the nature and concentration of the background cations in solutions of 0.001 N $HClO_4$ or 0.001 N H_2SO_4 (in the case of Mg^{2+} ions). The details of the determination of Γ_{H^+} were described in detail earlier [8, 9]. According to [6], ClO_4^- ions are not reduced at $\varphi_r = 0$; therefore, the results obtained could not be distorted by the reaction of their reduction.

Since when $\varphi_r = 0$, $\Gamma_{SO_4^{2-}} \cong 0$ and $\Gamma_{ClO_4^-} \cong 0$ [6, 8], the results obtained in sulfuric and perchloric acid solutions are directly comparable and Γ_{H^+} can be set approximately equal to the adsorption of the cor-

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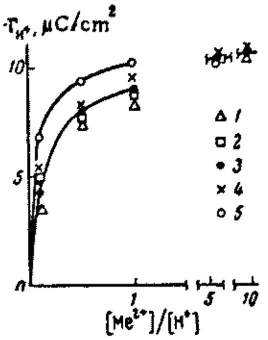

Fig. 1

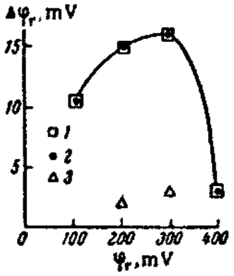

Fig. 2

Fig. 1. Dependence of the adsorption of Mg^{2+} (1), Ca^{2+} (2), Cs^+ (3), Sr^{2+} (4), and Ba^{2+} (5) on the ratio of their concentration to the hydrogen ion concentration in solutions of $1\cdot10^{-3}$ N $HClO_4$ (2, 4, 5) or $1\cdot10^{-3}$ N H_2SO_4 (1, 3) at φ_r=0 V.

Fig. 2. Dependence of the values of the adsorption potential shift in solutions of $1\cdot10^{-1}$ N $Ca(ClO_4)_2$+ $1\cdot10^{-2}$ N $HClO_4$ (1), $1\cdot10^{-1}$ N $Ba(ClO_4)_2$+ $1\cdot10^{-2}$ N $HClO_4$ (2), and $1\cdot10^{-1}$ N $MgSO_4$+$1\cdot10^{-2}$ N H_2SO_4 (3), on the initial potential in a solution of $1\cdot10^{-2}$ N $HClO_4$ (1, 2) or $1\cdot10^{-2}$ N H_2SO_4 (3).

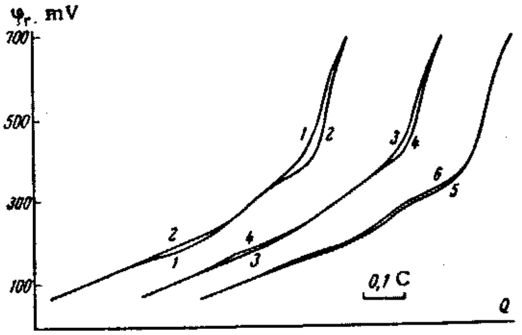

Fig. 3

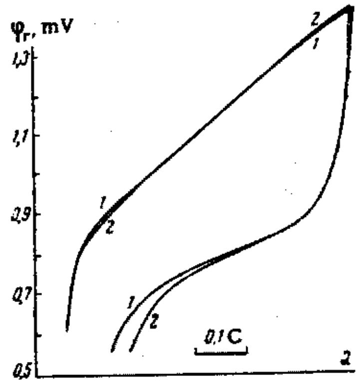

Fig. 4

Fig. 3. Influence of Ba^{2+}, Ca^{2+}, and Mg^{2+} cations on the anodic charging curves of a Pt–Pt electrode in solutions: 1, 3) $1\cdot10^{-1}$ N $HClO_4$; 2) $1\cdot10^{-1}$ N $HClO_4$+1 N $Ba(ClO_4(_2$; 4) $1\cdot10^{-1}$ N $HClO_4$+1 N $Ca(ClO_4(_2$; 5) $1\cdot10^{-1}$ N H_2SO_4; 6) $1\cdot10^{-1}$+1 N $MgSO_4$.

Fig. 4. Oxygen regions of the charging curves of a Pt–Pt electrode in solutions: 1) $1\cdot10^{-1}$ N $HClO_4$; 2) $1\cdot10^{-1}$ N $HClO_4$+1 N $Ba(ClO_4)_2$.

responding cations on the electrode [9]. From the figure it follows that at low concentrations the adsorption of the cations increases in the series: $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, that is, in order of increasing radius of the ions of the alkaline earth metals. The same order of increasing adsorbability of the cations of the alkaline earth metals follows from the results of kinetic measurements on a mercury electrode [10].

From Fig. 1 it can be concluded that the cations of the alkaline earth metals are adsorbed primarily before the hydrogen ions, since in the presence of a 2-5-fold excess of alkaline earth cations in solution, practically the limiting displacement of hydrogen ions from the electrical double layer is reached. The limiting values of the adsorption of the alkaline earth cations differ comparatively little.

For comparison, Fig. 1 presents the curves of the dependence of the adsorption of cesium ions on the potential from solutions of 0.001 N $H_2SO_4+Cs_2SO_4$. It is evident that cesium and calcium ions in equal concentrations displace hydrogen ions from the double layer approximately to the same degree, which probably means an approximate equal adsorbability of these cations. Thus, the cations can be arranged in the following series according to adsorbability: $Mg^{2+} < Ca^{2+} \approx Cs^{+} < Sr^{2+} < Ba^{2+}$.

Figure 2 presents the results of a measurement of the adsorption shifts of the potential of the Pt–Pt electrode in the presence of cations of the alkaline earth metals. In the determination of the shifts, the solution of 0.01 N $HClO_4$ was replaced by a solution of 0.01 N $HClO_4$ + 0.1 N $Ba(ClO_4)_2$ [or $Ca(ClO_4)_2$], while the solution of 0.01 N H_2SO_4 was replaced by a solution of 0.01 N H_2SO_4 + 1 N $MgSO_4$. In the presence of cations of the alkaline earth metals, the potential of platinum is shifted in the positive direction. However, according to our data the shifts are considerably smaller than according to the data of [2]. Thus, the maximum shift of the potential in our experiments in the case of Ba^{2+} and Ca^{2+} was only ~16 mV (~0.5 V according to [2]), and part of this shift was probably due to the reduction of ClO_4^- ions, the concentration of which increases when $Ba(ClO_4)_2$ or $Ca(ClO_4)_2$ is added. Magnesium ions cause a potential shift of ~3 mV, which is less than the adsorption shift of the potential in the presence of Cs^+ ion [11]. The relatively small shifts of the potential of platinum that we found in the case of adsorption of cations of the alkaline earth metals should have been expected, on the basis of the values of the adsorption of these cations.

The results of measurements of the charging curves in solutions of $Ca(ClO_4)_2$ and $Ba(ClO_4)_2$ are shown in Fig. 3. In the presence of Ca^{2+} and Ba^{2+}, the shape of the charging curves is somewhat changed. Since it is difficult to judge what changes in the shape of the curves are associated with the adsorption of cations, and what changes are related to the reduction of ClO_4^- ions, it is impossible to conduct a detailed consideration of the charging curves. However, apparently the indicated cations do not significantly change the amounts of adsorbed hydrogen on platinum. Magnesium ions produce a small strengthening of the bond of hydrogen to the surface of platinum in the case of low degrees of coverage and a weakening of it in the case of high degrees of coverage. The same conclusion was obtained from measurements of the potentiodynamic curves. The observable effects are comparable with those induced by the lithium ions [8] and can be explained on the basis of the concept of the polarity of the bond of platinum to hydrogen [8].

To determine the influence of cations of the alkaline earth metals on the adsorption of oxygen, the electrode was preliminarily adjusted to $\varphi_r = 0.6$ V in a solution of 0.1 N H_2SO_4 and washed with the investigated solution, maintaining the potential equal to 0.6 V. This made it possible to avoid the reduction of ClO_4^- ions [6]. Then the anodic and cathodic charging curves were measured in the interval φ_r 0.6–1.42 V. As can be seen from Fig. 4, the effects are small in a solution of 0.1 N $HClO_4$ + 1 N $Ba(ClO_4)_2$. Analogous phenomena were detected when the charging curves were measured in solutions of 0.1 N $HClO_4$ + 1 N $Ca(ClO_4)_2$ and 0.1 N H_2SO_4 + 1 N $MgSO_4$. The treatment of the observed effects was complicated by the fact that in the change from 0.1 N $HClO_4$ to 0.1 N $HClO_4$ + 1 N $Ba(ClO_4)_2$ (or $Ca(ClO_4)_2$], the concentration of ClO_4^- anions increases.

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