ADSORPTION OF LITHIUM AND CESIUM CATIONS ON PLATINUM

O. A. Petrii, A. N. Frumkin, and I. G. Shchigorev

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As is well known, alkali metal cations possess a certain specific adsorbability on a mercury electrode, which increases with increasing radius of the cation [1, 2]. A number of data indicate that an analogous pattern is also observed on a platinum electrode [2, 3]. Thus, it was indicated in [3] that Cs^+ ions displace a larger portion of H^+ ions from the ionic portion of the double layer even at $[H^+] : [Cs^+] = 1 : 1$. In this work we made a detailed study of the adsorption of Li^+ and Cs^+ cations on a Pt/Pt electrode.

The measurements were performed by the method of adsorption curves, charging curves, and by a potentiodynamic method. In the latter case a P-5611 potentiostat was used 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 electrode and determination of the true surface were performed in the same way as in [4]. Methods of determining the adsorption of H^+ and Br^- ions on platinum are also indicated there and in [5]. These solutions were prepared in doubly-distilled water from twice-redistilled sulfuric and hydrobromic acids and alkali, obtained by cautious decomposition of amalgams of the corresponding metals, followed by prolonged purification of the solutions on Pt/Pt grids.

Figure 1 gives 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 background cations in 0.01 N H_2SO_4. For the determination of Γ_{H^+}, the working electrode, thoroughly washed with doubly-distilled water, and dried in a stream of hydrogen in the measuring cell, was brought into contact with a solution purged with hydrogen under atmospheric pressure. Then the change in the concentration of H^+ ions in solution, caused by the formation of the double layer, was determined [4, 6]. In general, $\Gamma_{H^+} = \varepsilon + \Gamma^i_{H^+}$, where ε is the free charge of the surface, $\Gamma^i_{H^+}$ is the surface density of hydrogen ions found within the ionic portion of the double layer [6, 7]. According to the experimental data, in 0.01 N H_2SO_4, at $\varphi_r = 0$, $\Gamma_{H^+} \simeq 0$, which is apparently due to the comparatively small negative value of ε and its compensation on account of $\Gamma^i_{H^+}$. When the background is added, two effects are observed, leading to an increase in Γ_{H^+}: 1) H^+ ions arising in the formation of the double layer in 0.01 N H_2SO_4 on account of the reaction $H_{ads} \rightarrow H^+ + e$, are displaced by the background cations into the solution; 2) the value of ε increases as a result of an increase in the concentration of the electrolyte. The basic factor, at least for small additions of the background, is apparently the first effect. This follows from a comparison of the experimentally found dependence of $\Gamma_{H^+} = \varepsilon + \Gamma^i_{H^+}$ on the background concentration with the dependence for the value of $\varepsilon + \Gamma^i_{H^+}$ that was calculated on the assumption that the structure of the electrical double layer on platinum is the same as on mercury and that H^+, Li^+, and Cs^+ ions are not specifically adsorbed (Fig. 1, curves 3 and 4). Taking into consideration the fact that the nature of the anion has little effect on the distribution of charges in the double layer in the case of sufficiently negative charges of the surface, we used the table values of ε on mercury [8] at various NaF for the latter calculation, at potentials that were selected in such a way that the values of ε coincided with the experimental values obtained on Pt when a 1 N concentration of the background was reached.*

From Fig. 1 it is evident that at a ratio $[H^+] : [Cs^+]$ (or Li^+) $\simeq$ (1/5) to (1/10), evidently the limiting value of Γ_{H^+} is practically reached. The limiting $[\Gamma_{H^+}]$ are 30% higher in the case of Cs^+ than in the case of Li^+. This fact

* To refine the model calculation it had to be considered that in our experiments we used a 1,2-charge electrolyte, and a certain specific adsorption of Cs^+ ions on mercury also had to be taken into account.

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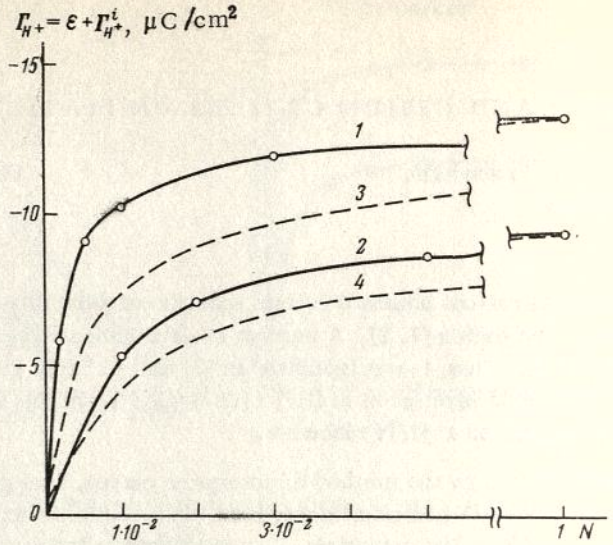

Fig. 1. Adsorption of hydrogen ions at $\varphi_r = 0$ on a Pt/Pt electrode in 0.01 N H_2SO_4 in the presence of Cs_2SO_4 (1) and Li_2SO_4 (2) in various concentrations and dependences of $\varepsilon + \Gamma^i_{H^+}$ on the concentration of the background, obtained on the basis of a model calculation (see text) (3 and 4).

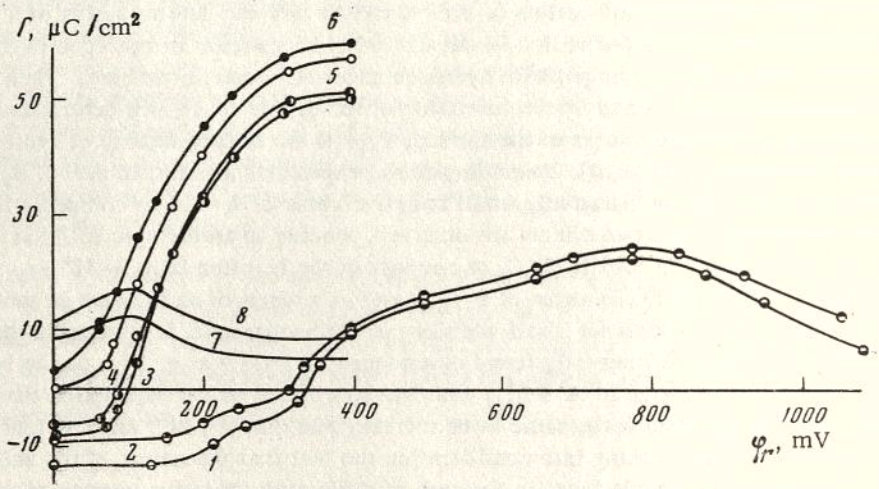

Fig. 2. Dependence of the adsorption of hydrogen ions (1-4), bromide ions (5, 6), and Li^+ (7) and Cs^+ (8) cations on the potential of a Pt/Pt electrode in solutions: 0.01 N H_2SO_4 + 0.2 N Cs_2SO_4 (1); 0.01 N H_2SO_4 + 0.3 N Li_2SO_4 (2); 0.005 N HBr + 0.05 N LiBr (3, 5, 7) and 0.005 N HBr + 0.05 N CsBr (4, 6, 8).

and the substantially larger difference in the values of Γ_{H^+} in the presence of Li^+ and Cs^+ at lower background concentrations, are evidence of the greater specific adsorption of Cs^+ on Pt.

Our experiments, in addition to demonstrating the specific adsorption of Cs^+, also show the correctness and limits of applicability of the double-layer model on platinum metals, proposed in [9] and subsequently used in [3, 10, 11]. In this model it is assumed that H^+ ions in the presence of an excess of background ions are entirely displaced from the surface layer. In such a case Γ_{H^+} is equivalent to the charge of the metallic lining of the double layer. This hypothesis is approximately fulfilled in the presence of a 5-10 fold excess of alkali metal cations in comparison with H^+ ions.

A comparison of the experimental data and the results of the model calculation show that the adsorbability of Li^+ ions on platinum is somewhat higher than the adsorbability of H^+ ions. The data obtained agree with the

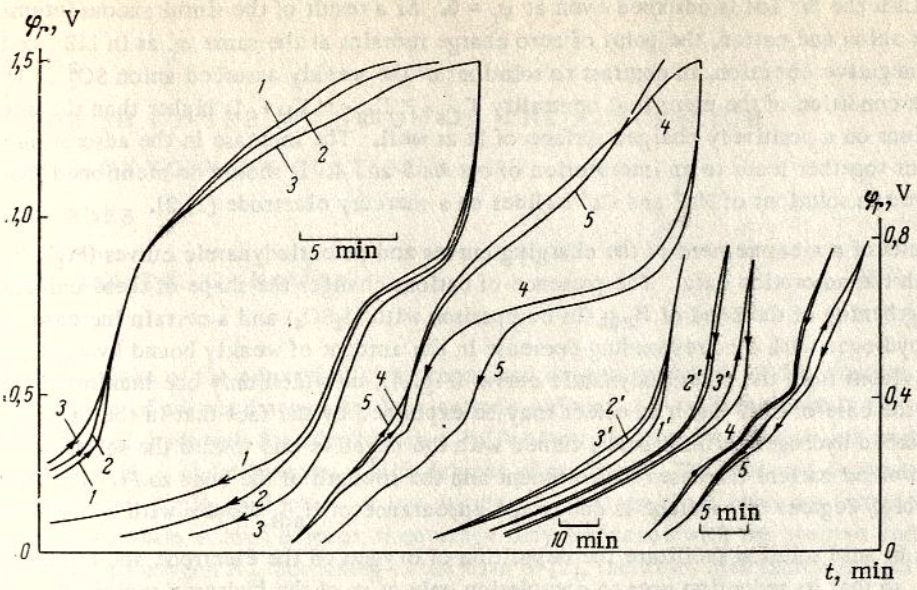

Fig. 3. Charging curves of a Pt/Pt electrode in 0.1 N H_2SO_4 (1,1') and in the presence of 0.7 N Li_2SO_4 (2,2') and Cs_2SO_4 (3,3'), and in 0.5 N LiOH (4) and CsOH (5). The arrows indicate the direction of recording of the curve. The current density was $2 \cdot 10^{-7}$ A/cm^2 in the measurement of curves 1-3, $5.4 \cdot 10^{-8}$ A/cm^2 for curves 1'-3', and $1.9 \cdot 10^{-7}$ A/cm^2 of the true surface for curves 4 and 5.

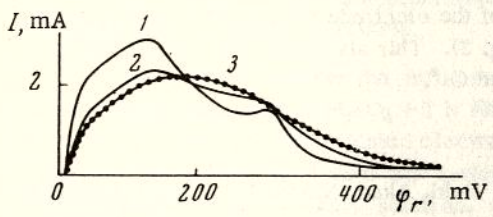

Fig. 4. Potentiodynamic curve of a Pt/Pt electrode in 0.1 N H_2SO_4 (1) and in the presence of 0.7 N Li_2SO_4 (2) and 0.7 N Cs_2SO_4 (3). Rate of development of the potential 15 mV/min.

results of measurements with the aid of radioactive tracers [12]. Thus, with respect to their adsorbability on a platinum electrode, the cations are arranged in the same series as on mercury [13]: $H^+ < Li^+ < Cs^+$.

The reaching of a limiting value of Γ_{H^+} with increasing background concentration and the fact that the coverage of the P surface by adsorbed hydrogen remains practically constant in this case means that it is possible to distinguish between adsorbed ions and atoms of hydrogen.

Figure 2 presents the dependence of the charge of the surface on φ_r in 0.01 N H_2SO_4 with additions of $3 \cdot 10^{-1}$ N Li_2SO_4 and $2 \cdot 10^{-1}$ N Cs_2SO_4. The Γ_{H^+} versus φ_r curves in solutions of cesium sulfite are lower than the curves in solutions of lithium sulfate in the entire potential region, which also indicates the greater adsorbability of Cs^+, but the difference between the curves depends upon φ_r. As we go from Li^+ to Cs^+, a shift of the point of zero charge by ~ 20 mV in the positive direction is observed, which is greater than that on mercury [1]. Thus, the difference in the adsorbability of alkali metal cations is more pronounced on platinum than on mercury.

The minimum difference in Γ_{H^+} in the presence of different cations is observed at φ_r of the "double-layer" region, at which the surface is positively charged. The difference itself is probably due to a certain superequivalent adsorption of the SO_4^{2-} ion on Pt [10]. When salts are added to a solution of acid at these φ_r, there is a displacement of H^+ ions, attracted by the superequivalent adsorbed SO_4^{2-} ions. Since the amount of such ions is small [10], in the presence of cations there is little effect on Γ_{H^+}. The decrease in Γ_{H^+} in the presence of Cs^+ agrees with the conclusion of specific adsorption of this cation, since the increase in the adsorbability of the background cation at positive ε leads to a decrease in Γ_{H^+}.

When φ_r is further shifted in the anodic direction, the curves again begin to diverge. This is due to the appearance of adsorbed oxygen and adsorption of cations on the sites of the surface occupied by oxygen. Apparently, this process is promoted by the formation of dipoles of oxygen, turned with the negative end toward the solution [14].

The conclusion on the specific adsorption of Cs^+ is confirmed by experiments in acidified solutions of $5 \cdot 10^{-2}$ N CsBr and LiBr (Fig. 2). In the presence of Cs^+, the adsorption of Br^- (Γ_{Br^-}) is higher than in the presence of Li^+;

moreover, in CsBr the Br^- ion is adsorbed even at $\varphi_r = 0$. As a result of the simultaneous intensification of the adsorption of the anion and cation, the point of zero charge remains at the same φ_r as in LiBr, or is even somewhat shifted in the negative direction, in contrast to solutions of the weakly adsorbed anion SO_4^{2-}. The adsorption of Cs^+, found from the condition of the electrical neutrality $\Gamma_{Cs^+} = \Gamma_{Br^-} - \Gamma_{H^+}$, is higher than the adsorption of Li^+ in bromide solutions on a positively charged surface of Pt as well. The increase in the adsorption of Br^- and Cs^+ when they are present together leads to an intersection of curves 3 and 4. It should be mentioned that analogous phenomena are observed in solutions of Na^+ and Cs^+ halides on a mercury electrode [1, 2].

The results of a measurement of the charging curves and potentiodynamic curves (Figs. 3 and 4) are in full agreement with the adsorption data. The presence of cations changes the shape of these curves. In solutions of Cs_2SO_4 a strengthening of the bond of H_{ads} (in comparison with Li_2SO_4) and a certain increase in the amount of firmly bound hydrogen with a corresponding decrease in the amount of weakly bound hydrogen are observed. This is especially evident from the potentiodynamic curves (Fig. 4), on which only one maximum in the hydrogen region is observed in the case of Cs^+. Such an effect may be explained by the fact that in the case of low degrees of coverage, the adsorbed hydrogen forms dipoles, turned with the negative end toward the solution, and the presence of specifically adsorbed cations increases their amount and the strength of the bond to Pt. The inversion of the effect in the case of high degrees of coverage is due to the appearance of H_{ads} dipoles with opposite orientation [12].

Cs^+ ions in acid solution facilitate the deposition of oxygen on the electrode and hinder the reduction of adsorbed oxygen, so that its reduction goes to completion only at φ_r of the hydrogen region (Fig. 3).

In alkaline solutions Cs^+ exerts the same influence on the charging curves as in acid solutions (Fig. 3), so that the possibility of separating the curve into hydrogen, double-layer, and oxygen regions is hindered in comparison with solutions of LiOH. The only exception is the region of $\varphi_r \geq 1.3$ V, at which Cs^+ somewhat weakens the bond of the adsorbed oxygen to platinum.

Simultaneously with the increase in the specific adsorbability, as we go from Li^+ to Cs^+, a deterioration of the reversibility of the charging curves is observed during polarization of the electrode to $\varphi_r \simeq 0.8$-0.9 V, while within the hydrogen region the curves remain practically reversible (Fig. 3). This also indicates a difference in the strength of the bond of oxygen to platinum in the presence of Li^+ and Cs^+.

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