ADSORPTION OF ALKALI-METAL IONS ON THE PLATINUM ELECTRODE IN ALKALINE SOLUTIONS

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The structure of the electric double layer at the platinized platinum (Pt/Pt) electrode in alkaline solutions has been studied in [1-6]. It was found in [1, 5] that in the absence of specifically adsorbing anions, the Gibbs adsorption of hydrogen ions Γ_{H^+} to a first approximation is independent of the potential φ_r* over the range from 0 to 0.8 V. Correspondingly, according to the data of [4], the adsorption of the cations $Na^+(\Gamma_{Na^+})$ and $Cs^+(\Gamma_{Cs^+})$ in 0.01 N NaOH and CsOH is practically independent of φ_r up to 1.4 V, and $\Gamma_{Cs^+} > \Gamma_{Na^+}$. However, in [2]† an increase of Γ_{Na^+} was noted in the oxygen region when φ_r values corresponding to the evolution of molecular oxygen were approached, as well as appreciable hysteresis in the Γ_{Na^+} values when φ_r was varied in the anodic and cathodic direction. According to the data of [3], $\Gamma_{Na^+} > \Gamma_{Cs^+}$ at $\varphi_r > 0.9$ V, while a decrease of Γ_{Na^+} and Γ_{Cs^+} was detected in [6] at $\varphi_r > 0.4$ to 0.5 V in alkaline sodium and cesium sulfate solutions when φ_r was shifted anodically. The discrepancies in the data make it necessary to carry out further studies of the adsorption of alkali-metal ions on platinum in alkaline solutions, the more so as radiotracer measurements previously had been made with a technique involving removal of the electrode from the solution. The interest into this problem was further stimulated by the papers of Matsuda and Notoya [7], according to whom on platinum the alkali-metal ions can be deposited in atomic form, and do so already near $\varphi_r = 0$; alkali-metal adsorption increases with increasing cation concentration in the solution, especially strongly so when φ_r is displaced into the cathodic direction.

In the present work, the adsorption of alkali-metal ions was studied on the Pt/Pt electrode in alkaline solutions as a function of electrode potential, pH, and solution composition. The measurements were performed by the methods of adsorption curves [1], isoelectric potential shifts [8, 9], and radiotracers by the technique of [10]. The adsorption curves were obtained on an electrode having an apparent surface area of $S_{app} = 60$ cm^2, and a true surface area of S_{tr} = 10-5 m^2, the isoelectric shifts on an electrode with S_{app} = 20 cm^2 and S_{tr} = 1.0-1.5 m^2. In the radiotracer measurements, an electrode was used which had S_{app} = 2 cm^2 and S_{tr} = 0.7-0.5 m^2. The conditions of electrode preparation and the determination of their true surface areas have been described in [11, 12]. The alkali solutions, which were prepared from especially pure or "chemically pure" reagents, were subjected to two days of cathodic purification at mercury. Amalgams of the alkali metals were then obtained by using these solutions. By incomplete decomposition of the amalgams, alkali solutions were prepared, which were purified for one day at a large Pt/Pt net while the solution was agitated with nitrogen. The last step was prolonged adsorptive purification at a Pt/Pt net while passing hydrogen through the solution. A Cs_2CO_3 solution purified at a mercury cathode was used in preparing the cesium amalgam. Teflon vessels were used to decompose the amalgams and subsequently purify the solutions. The salts used in the work were twice recrystallized and calcined. The experiments were done at 22 ± 2°C.

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* The symbol φ_r denotes potentials referred to a reversible hydrogen electrode in the same solution.
† There is a misprint in this paper: the caption under Fig. 3 corresponds to Fig. 6, and that under Fig. 6 corresponds to Fig. 3.

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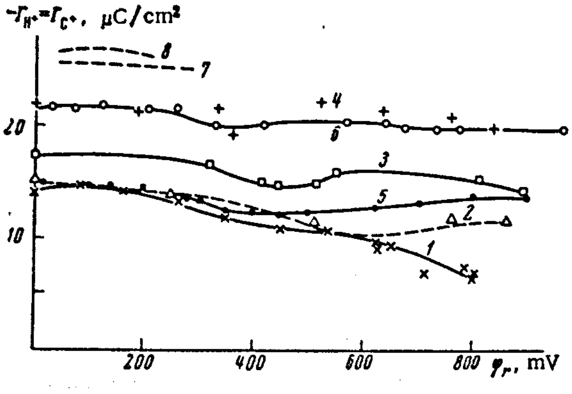

Fig. 1

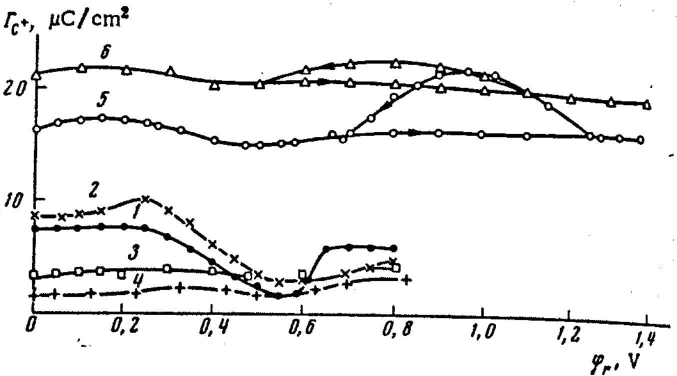

Fig. 2

Fig. 1. The adsorption of hydrogen ions (1–4, 7, 8) and of Na^+ (5) and Cs^+ (6) ions as function of the potential of a Pt/Pt electrode in the solutions: 1) 10^{-2} N LiOH, 2, 5) 10^{-2} N NaOH, 3) 10^{-2} N KOH, 4, 6) 10^{-2} N CsOH, 7) 1 N NaOH, 8) 3 N NaOH. Curves calculated from Eq. (1) are plotted as dashed lines. The position of curves 7 and 8 relative to the ordinate axis was arbitrarily chosen.

Fig. 2. Potential dependence of the adsorption of Na^+ (1–5) and Cs^+ (6) ions in the solutions: 1) $5 \cdot 10^{-3}$ N NaOH + $5 \cdot 10^{-3}$ N Na_2SO_4; 2) $5 \cdot 10^{-3}$ N NaOH + $5 \cdot 10^{-3}$ N Li_2SO_4; 3) $5 \cdot 10^{-3}$ N NaOH + $5 \cdot 10^{-3}$ N K_2SO_4; 4) $5 \cdot 10^{-3}$ N NaOH + $5 \cdot 10^{-3}$ N Cs_2SO_4; 5) 10^{-2} N NaOH; 6) 10^{-2} N CsOH. Arrows indicate the direction of potential change.

The adsorption of hydrogen ions, $-\Gamma_{H^+}$,* at the Pt/Pt electrode is shown in Fig. 1 as a function of φ_r. It can be seen there that in 0.01 N NaOH, KOH, and CsOH (curves 2–4), the values of $-\Gamma_{H^+}$ vary little with potential, in harmony with the data of [1, 4, 5]. According to [5, 14], such a shape of the $(-\Gamma_{H^+}) - \varphi_r$ curves can be explained as being due to the compensation of two effects: the adsorption of cations, which is attended by an ionization of adsorbed hydrogen atoms and decreases with increasing φ_r, and the adsorption of cations by oxide surface groups, which increases over a certain range of φ_r. However, a compensation of these effects is not observed in 0.01 N LiOH. It is possible that owing to their high energy of hydration, the interaction of the Li^+ ions with the surface oxides is hampered; this will also cause them to have a lower adsorbability in the oxygen region of φ_r.

We have used the radiotracer method to obtain the adsorption of Na^+ and Cs^+ ions as functions of φ_r. The $(\Gamma_{C^+}) - \varphi_r$ curves obtained coincide satisfactorily with the corresponding $(\Gamma_{H^+}) - \varphi_r$ curves found by titration (cp. curve 2 with curve 5, and curve 4 with curve 6 in Fig. 1); this lends support to the correctness of the equality $-\Gamma_{H^+} = \Gamma_{C^+}$ [5] (Γ_{C^+} is the adsorption of the cation). It can be seen from Fig. 1 that the adsorbability of the cations increases in the series $Na^+ < K^+ < Cs^+$, just as in acidic solutions [12, 15, 16, 17]. At φ_r between 0 and 0.4 V, the differences in the adsorbabilities of Na^+ and Li^+ are small, even though the adsorption of Li^+ is still somewhat lower. At $\varphi_r > 0.6$ V, $\Gamma_{Na^+} > \Gamma_{Li^+}$. In order to make further comparison between the adsorbabilities of the various cations, we have determined the adsorption of Na^+ in a solution of $5 \cdot 10^{-3}$ N NaOH where the Na^+ was labelled, and to which stable solutions of $5 \cdot 10^{-3}$ N Li_2SO_4, Na_2SO_4, K_2SO_4, and Cs_2SO_4 were added.† The experimental curves obtained are shown, without accounting for the effect of isotopic dilution upon addition of the stable salts, by curves 1–4 in Fig. 2. Inspection of these curves confirms that the adsorbability increases in the series $Li^+ < Na^+ < K^+ < Cs^+$ at φ_r between 0 and 0.45 V. Additional studies are required to explain the mutual disposition of the $(\Gamma_{C^+}) - \varphi_r$ values at $\varphi_r > 0.5$ V.

Measurements with radiotracers were carried out in the φ_r range between 0 and 1.4 V (Fig. 2). It was found, in harmony with [4], that the independence of Γ_{Na^+} and Γ_{Cs^+} on φ_r during the anodic scan of the curves is retained up to φ_r values corresponding to the evolution of molecular oxygen. This means that over the entire φ_r range studied, the potential drop is chiefly due to the polarity of the bond between Pt and the hydrogen or oxygen, and to the variation in the effective dipole moment of these bonds. When

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* The quantity $-\Gamma_{H^+} = \Gamma_{OH^-}$, where Γ_{OH^-} is the Gibbs adsorption of OH^- ions [5, 13].

† V. N. Andreev took part in these experiments.

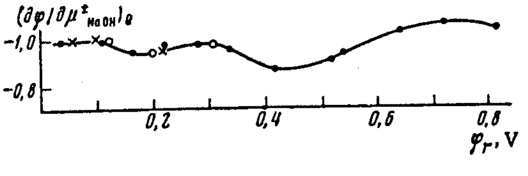

Fig. 3

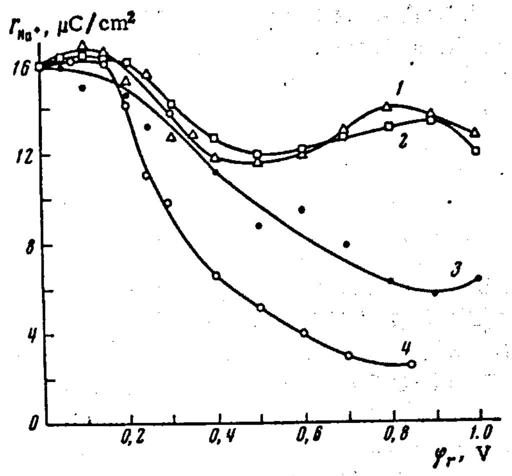

Fig. 4

Fig. 3. The isoelectric potential shifts of a Pt/Pt electrode in solutions of 0.01 N (full circles), 1 N (open circles), and 3 N (crosses) NaOH.

Fig. 4. Potential dependence of the adsorption of Na^+ ions in the solutions: 1) 10^{-3} N NaOH + 10^{-2} N Na_2SO_4; 2) 10^{-3} N NaOH + 10^{-2} N NaCl; 3) 10^{-3} N NaOH + 10^{-2} N NaBr; 4) 10^{-3} N NaOH + 10^{-2} N NaI.

the curves are recorded in the cathodic direction, hysteresis is found which is due to the irreversibility of oxygen adsorption. A conspicuous feature is the increase in the adsorption Γ_{Na^+} over a certain range of φ_r during the cathodic scan, where values close to Γ_{Cs^+} or even somewhat higher than Γ_{Cs^+} are attained. The differences between the adsorption values obtained during the anodic and cathodic potential scan depend on the anodic φ_r value attained while the curve was recorded in the anodic direction; they increase when this value becomes higher, or when the electrode is kept for a longer time at this and subsequent values of φ_r. The $(\Gamma_{C^+})-\varphi_r$ curves recorded with anodic and cathodic potential scan coincide for $\varphi_r < 0.7$ V in NaOH solutions and for $\varphi_r < 0.5$ V in CsOH solutions.

A detailed inspection of the $(\Gamma_{Na^+})-\varphi_r$ and $(\Gamma_{Cs^+})-\varphi_r$ curves show that there is a small maximum in Γ_{C^+} at φ_r corresponding to the hydrogen region, and a minimum at φ_r between 0.4 and 0.6 V. These features of the curves cannot be reproduced sufficiently well, and it was noted in addition that the depth of the minimum decreases as the electrode becomes older. The maximum is more clearly developed on an electrode that was prereduced cathodically in acid and is not observed when the $(\Gamma_{C^+})-\varphi_r$ curve is recorded after measuring curves where the potential was varied anodically and cathodically over a φ_r range between 0 and 1.4 V. During the measurements in the region of $\varphi_r > 0.9$ V, it is observed that the Γ_{C^+} values decrease at first and then increase, when φ_r is rapidly raised (by 50–100 mV). This effect seems to be due to properties of the adsorbed oxygen which change with time [18], and requires further investigation.

The isoelectric potential shifts of a Pt/Pt electrode obtained upon replacing a 0.001 N NaOH solution by a 0.1 N, a 0.5 N by a 2 N, and a 1 N by a 9 N NaOH solution are shown in Fig. 3. The $(\partial\varphi/\partial\mu^{\pm}_{NaOH})_Q$ values (φ is the potential referred to a constant reference electrode) are close to −1 over the entire range of φ_r studied; in harmony with [5], this is evidence for a small φ_r dependence of Γ_{H^+}, i.e., for strong overlap of the hydrogen and oxygen adsorption regions. The magnitude of the isoelectric potential shifts is practically independent of alkali concentration.

The isoelectric potential shifts and the charging curves (measured at a current density of 0.01 μA · cm^{-2} of true surface area) were used to calculate the φ_r dependence of Γ_{H^+} by Eq. (1) [5, 13]

$$(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu^{\pm}_{NaOH}} = {}^1/_2\,(\partial\varphi/\partial\mu^{\pm}_{NaOH})_Q\,(\partial Q/\partial\varphi_r)_{\mu^{\pm}_{NaOH}}, \tag{1}$$

where Q is the total surface charge density, and $\mu^{\pm}_{NaOH}$ is the mean chemical potential of the alkali. The $(\Gamma_{H^+})-\varphi_r$ curve calculated for 0.01 N NaOH is compared in Fig. 1 with the curve found by experiment. The experimental value of Γ_{H^+} at $\varphi_r = 0.3$ V was used as the integration constant. The satisfactory agreement between the calculated and experimental results means that the system is reversible over the φ_r range studied. The calculated $(\Gamma_{H^+})-\varphi_r$ curves for 1 and 3 N NaOH (curves 7 and 8 of Fig. 1) have been arbitrarily shifted along the ordinate axis, because for these conditions the integration constants are unknown. In the hydrogen region of φ_r, the $(\Gamma_{H^+})-\varphi_r$ curves are practically unchanged in character when the alkali concentration is varied, as can be seen by comparing curves 2, 7, and 8 of Fig. 1. Thus, in the potential range which we have studied, the effects described in [7] for smooth platinum and for Pt films evaporated in vacuo have not been found for the Pt/Pt electrode. During the radiotracer measurements in 0.01 and 0.1 N NaOH, the Pt/Pt electrode was cathodically polarized (up to 50 mA/cm² of apparent surface area), and under current flow dropped to the bottom of the cell in order to measure the radioactivity. However, an increase in Γ_{Na^+} was not detected under these conditions.

We have determined the φ_r dependence of Γ_{Na^+} in solutions having the composition 10^{-3} N NaOH + 10^{-2} N Na_2SO_4 and 10^{-3} N NaOH + 10^{-2} N NaA where A = Cl, Br, or I (Fig. 4). In the presence of Na_2SO_4 and NaCl, one observes similar values for Γ_{Na^+} over the entire range of φ_r values, because the adsorption of Cl^- and SO_4^{2-} ions in alkaline solutions is insignificant [1, 3, 4, 5]. A drop in the adsorption of the Na^+ ion is observed at $\varphi_r > 0.2$ V, where Br^- and I^- are adsorbed at platinum in alkaline solutions [1,3,5]. This is probably due to the fact that at these φ_r the Na^+ ions are adsorbed through oxygen bridges, e.g., in the form of ONa^- [3-5, 14]. The Br^- ions, and even more so the I^- ions, displace the ONa^- ions from the electrode surface, which leads to the decrease in Γ_{Na^+}.

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