POTENTIALS OF ZERO-FREE CHARGE OF A PLATINUM ELECTRODE IN THE PRESENCE OF THE STRONGLY ADSORBED IODIDE AND THALLIUM IONS

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At present a large amount of experimental data has been accumulated which show that during the adsorption of halide ions on a number of solid metals (Fe, Pb, Tl, Cd, Pt), strong chemisorption bonds arise between the adsorbed anions and the surface of the metal electrodes [1-4]. In the limiting case of such an interaction the adsorbed ions become part of the metal side of the double layer, their charge is part of the charge of the metal surface, and they approach an atomic state. The delay of exchange with ions in the bulk solution, high degrees of surface coverage [4], the peculiarities of the superequivalent adsorption of cations [5], a value of the Esin-Markov coefficient which is unity [6], and the analysis of the adsorption isotherms of the anions [7] provide evidence for the above in the case of platinum–metal electrodes. Similar conclusions are valid for the cations which become specifically adsorbed at platinum metals [4, 8].

It has been stressed in [6, 9, 10] that in the presence of charge transfer the concept of a potential of zero free charge (p.z.c.) becomes conditional, and this potential can only be determined within some model of the electric double layer. It is usually assumed that the charge of the ions adsorbed on solid metals will belong to the ionic side of the double layer, as in the case of mercury [6, 9-11]. It follows from such an assumption that the p.z.c. is displaced toward the negative side when there are specifically adsorbing anions and toward the positive side when there are cations [4, 9, 12]. However, when it is assumed that the charge of the chemisorbed ions is transferred to the metal surface, then the p.z.c. must be displaced to the positive side when there is chemisorption of anions and to the negative side when there is chemisorption of cations. Such a conclusion was first drawn in discussing the adsorption of oxygen on platinum. Were the anions of oxygen, e.g., OH^- ions, to retain their charge during adsorption, then their specific adsorption would cause the potential of zero free charge to shift toward the negative side. However, the adsorptive and electrokinetic properties of a platinum electrode having a layer of chemisorbed oxygen at its surface fully conform to the proposition according to which the p.z.c. during oxygen chemisorption shifts to the positive side [11, 13]. From this it follows that the charge of the oxygen atoms forming the negative ends of the Pt–O dipoles, which are turned toward the solution, must be included in the charge of the metal side rather than the ionic side of the double layer. This result is in complete harmony with the increase in electron work function of platinum when oxygen becomes chemisorbed at its surface. The proposition that the p.z.c. shifts toward the positive side in the presence of chemisorbed halide ions was made by Frumkin [3] and by Iofa and coworkers [1] and used to explain the effect of various surface active additives on the corrosion behavior of the iron electrode [1]. However, direct experimental evidence for this proposition has been lacking.

It is the aim of the present work to study the structure of the electric double layer on platinized platinum in the presence of the strongly adsorbed iodide and thallium ions. The work was done with the radiotracer method using the isotopes I-131, Tl-204, Na-22, and S-32 and following the technique developed in [14]. The Pt/Pt electrode was held at the reversible hydrogen potential in a 10^{-3} N H_2SO_4+x N KI (or Tl_2SO_4) solution and washed with twice-distilled water when a certain I^- or Tl^+ ion adsorption had been reached.

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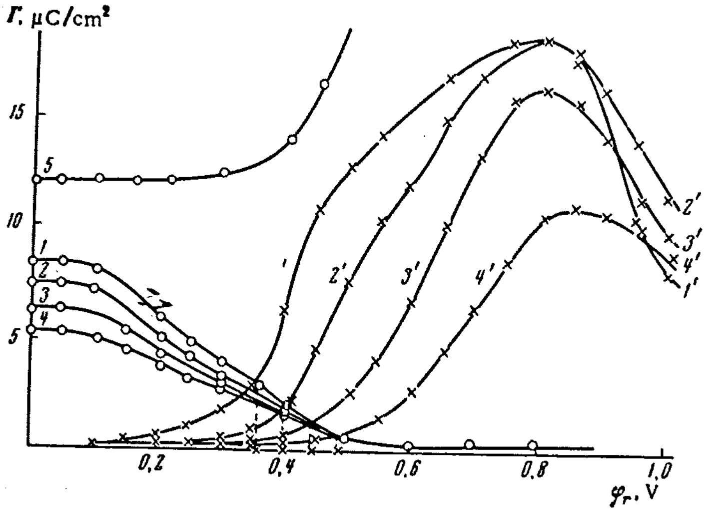

Fig. 1. Potential dependence of the adsorption of Na^+ ions (1-4) and SO_4^{2-} ions (1'-4') in $3 \cdot 10^{-3}$ N $Na_2SO_4 + 10^{-3}$ N H_2SO_4 solution at a Pt/Pt electrode when the adsorption of I^- ions is 0 (1, 1'); 12 (2, 2'); 26 (3, 3'); 38 (4, 4') μC/cm². Curve 5 is the φ_r dependence of the adsorption $\Gamma_{SO_4^{2-}} + \Gamma_{I^-}$ when the adsorption $\Gamma_{I^-} = 12$ μC/cm².

The cell was then filled with an inactive solution of $3 \cdot 10^{-3}$ N $Na_2SO_4 + 10^{-3}$ N H_2SO_4, and the electrode polarized in the φ_r range between 0 and 1.0 V (φ_r are potentials measured relative to a reversible hydrogen electrode in the same solution). Changes in the radioactivity of the electrode were not observed when it was polarized, with the surface coverages θ by I^- and Tl^+ ions used by us (up to $\theta \simeq 0.3$ for I^- and $\theta \simeq 0.5$ for Tl^+); it can be assumed, therefore, that the adsorption of these ions remained constant during the entire experiment. In defining the surface coverage by I^- and Tl^+ ions it was assumed that full coverage corresponds to an I^- adsorption of about 140 and a Tl^+ adsorption of about 100 μC/cm² [4, 7]. The adsorption of the weakly surface-active Na^+ ions (Γ_{Na^+}) and SO_4^{2-} ions ($\Gamma_{SO_4^{2-}}$) was recorded as a function of potential φ_r between 0.1 and 1.0 V on electrodes prepared as described above. We have assumed that in the adsorption of Na^+ and SO_4^{2-} ions, charge transfer need not be taken into account to a first approximation, and that in the range of potentials where the p.z.c. is located, the degree of charge transfer in the Pt-I (Pt-Tl) dipoles does not change. The experiments were carried out at a temperature of 22 ± 2°C. The electrodes were prepared and their true surface area determined as in [15]. The radioactive solutions were purified by cathodic polarization at a Pt/Pt net and diluted to the required concentration with the corresponding stable solutions. The adsorption was measured from $3 \cdot 10^{-3}$ N $Na_2SO_4 + 10^{-3}$ N H_2SO_4 solution labeled by radioactive sodium or sulfur, depending on the ion whose adsorption was determined.

The results of the measurements in presence of strongly adsorbed iodide ions are presented in Fig. 1. It can be seen from this figure that with increasing coverage of the electrode surface by iodide ions, the adsorption of Na^+ ions decreases although the shape of the Γ_{Na^+}, φ_r curve remains practically unchanged. At $\varphi_r < 0.85$ V the adsorption of SO_4^{2-} decreases to a large extent in the presence of I^- while the shape of the $\Gamma_{SO_4^{2-}}, \varphi_r$ curve changes somewhat. Conversely, at $\varphi_r > 0.85$ V the adsorption of SO_4^{2-} increases rather than being lowered. This is probably due to the inhibition of oxygen adsorption in the presence of I^- ions. However, further investigation is required for a more detailed explanation of this last effect.

When the p.z.c. is determined from the condition $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}}$, i.e., when the charge of the chemisorbed ion is included in the charge of the metal side of the double layer, it follows from the data obtained that in the presence of adsorbed iodide ions the p.z.c. shifts to the positive side. Such a result corresponds to the hypothesis that at the surface iodine exists in a state close to the atomic but forms dipoles with the platinum which are oriented with their negative end to the solution side. If it is assumed, however, that the p.z.c. corresponds to the condition $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}} + \Gamma_{I^-}$, i.e., that the I^- at the surface is part of the ionic side of the double layer, then it can be concluded from the same data that the p.z.c. is shifted to the negative side in the presence of adsorbed I^- ions; this follows from a comparison of curves 2 and 5 of Fig. 1. Curve 5 shows the φ_r dependence of $\Gamma_{SO_4^{2-}} + \Gamma_{I^-}$ for an electrode on which 12 μC/cm² of I^- ions are adsorbed. Curves 2 and 5 do not intersect in the φ_r range under consideration. The intersection corresponding to attainment of the p.z.c. could only happen at $\varphi_r < 0$, after desorption of part of the I^- from the surface.

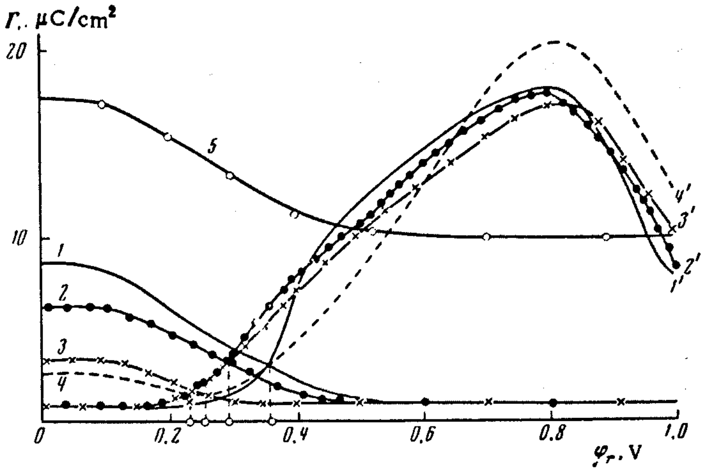

Fig. 2. Potential dependence of the adsorption of Na^+ ions (1-4) and SO_4^{2-} ions (1'-4') in $3 \cdot 10^{-3}$ N $Na_2SO_4 + 10^{-3}$ N H_2SO_4 solution at a Pt/Pt electrode when the adsorption of Tl^+ ions is 0 (1, 1'), 10 (2, 2'), 26 (3, 3'), and 53 (4, 4') μC/cm². Curve 5 is the φ_r dependence of $\Gamma_{Na^+} + \Gamma_{Tl^+}$ on the electrode when $\Gamma_{Tl^+} = 10$ μC/cm².

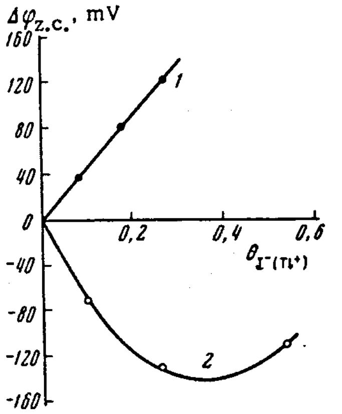

Fig. 3. The shift of the potential of zero free charge of the Pt/Pt electrode ($\Gamma_{Na^+} = \Gamma_{SO_4^{2-}}$) as a function of surface coverage by strongly adsorbed iodide (1) and thallium (2) ions.

Figure 2 gives the results of measurements of the adsorption of Na^+ and SO_4^{2-} on a Pt/Pt electrode on which various amounts of thallium ions were preadsorbed. Sodium ion adsorption decreases monotonically when the surface becomes covered with thallium ions. Coverage of the surface with Tl^+ ions exerts a more complicated influence on the adsorption of SO_4^{2-}. At φ_r between 0.2 and 0.4 V the first amounts of Tl^+ produce an increase in $\Gamma_{SO_4^{2-}}$, but subsequent amounts produce a decrease. A decrease in SO_4^{2-} adsorption at φ_r between 0.3 and 0.7 V when Tl^+ ions are present in solution was observed in [16] for the system 1 N $HClO_4$ + 10^{-4} N $H_2SO_4 + 2 \cdot 10^{-4}$ N $TlClO_4$. The p.z.c. as determined from the condition $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}}$ shifts to the negative side in the presence of Tl^+. A similar effect was observed in [17] when a Pt/Pt electrode was poisoned with mercury ions. Since the equilibrium potential of the system Hg/Hg^{2+} is larger than zero, the mercury was present on the surface in an atomic form, and the p.z.c. was determined from the condition $\Gamma_{Na^+} = \Gamma_{Cl^-}$.

The φ_r dependence of $\Gamma_{Na^+} + \Gamma_{Tl^+}$ is shown in Fig. 2 (curve 5) for an electrode where 10 μC/cm² of Tl^+ had been adsorbed. This curve intersects with curve 2' at $\varphi_r = 0.5$ V. Thus, the p.z.c. as determined from the condition $\Gamma_{Na^+} + \Gamma_{Tl^+} = \Gamma_{SO_4^{2-}}$ is shifted to the positive side in the presence of Tl^+ ions, in harmony with results that were previously obtained [4].

Figure 3 shows the shift of p.z.c. ($\Gamma_{Na^+} = \Gamma_{SO_4^{2-}}$) $\Delta\varphi_{z.c.}$ as a function of surface coverage by I^- or Tl^+. In the first case $\Delta\varphi_{z.c.}$ increases approximately linearly with θ_{I^-} over the θ_{I^-} range studied. In the second case the magnitude of the shift goes through a maximum. One reason for such a θ_{Tl^+} dependence of the p.z.c. may be that in the presence of Tl^+ the p.z.c. shifts into the region of hydrogen adsorption. The hydrogen dipoles contribute to the potential drop at the Pt electrode [9, 18, 19]. The expulsion of adsorbed hydrogen by Tl^+ ions [20], by altering the contribution of H_{ads} to the potential drop, leads to a more complicated θ_{Tl^+} dependence of $\Delta\varphi_{z.c.}$.

The experiments performed clearly demonstrate the conditionality of the concept of a potential of zero free charge when there is strong chemisorption of ions at the electrode. It must be stressed that in our experiments the p.z.c. values corresponding to the condition $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}}$ appear to correspond more closely to the real structure of the electrode/solution interface than those corresponding to condition $\Gamma_{Na^+} + \Gamma_{Tl^+} = \Gamma_{SO_4^{2-}}$ or $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}} + \Gamma_{I^-}$. It should be interesting to check this conclusion with the position of the capacity minimum of the electric double layer in the dilute solution of an inactive electrolyte.

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