DEPENDENCE OF THE PLATINUM ZERO-CHARGE POTENTIAL ON THE pH OF SODIUM AND CESIUM SULFATE SOLUTIONS

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The dependence of the platinum zero-charge position on the solution pH is currently under discussion becuase data obtained in diffferent studies are not in agreement. Kheifets and Krasikov [1] have presented data based on measurement of the differential capacitance which shows a shift of the platinum zero-charge potential from 0.5 to -0.35 V (n.h.e.) as the pH of a Na_2SO_4 solution is changed from 2 to 12. The authors explained this effect by the presence of adsorbed and absorbed hydrogen in an amount which changes with pH. A linear dependence between the zero-charge potential and the charge expended to saturate the electrode with hydrogen was presented. According to Kabanov and Birintseva [2], however, the observed minimum [1] in the differential capacitance corresponds not to a maximum diffusiveness of the electrical double layer, but to a minimum adsorption of hydrogen. It was suggested in [2] that the zero-charge potential does not depend on the solution pH. An effect of adsorbed oxygen on the platinum zero-charge potential was observed in [3]. According to the data of this study, which was based on an electrokinetic method, there are two zero-charge points in the solution $2 \cdot 10^{-5}$ N H_2SO_4, at 0.15 and 0.50 (n.h.e.). The latter value refers to platinum on whose surface there is adsorbed oxygen.

Bockris and coworkers, in measurements of the differential capacitance and the adsorption of uncharged organic molecules on platinum in perchloric acid solutions, found a pH dependence of the zero-charge point given by the equation $V_c = 0.56 - 2.3\,RT/F \cdot pH$ [4, 5]. Frumkin [6, 7] showed, however, that such a large dependence of the zero-charge point on the pH could not be explained by the theory of the platinum electrode, and that the value of the platinum zero-charge point near 0.5 V* (at a pH 0f 2) was apparently incorrect, for it did not agree with data obtained by several other methods. In addition, the theory did not exclude some dependence of the zero-charge point on the pH, for metals which adsorb hydrogen and oxygen, due to the appearance of a polar bond between these latter and the metals. During a change in the pH of the solution at constant potential, the partial surface coverage of the metal by adsorbed gas atoms changes, causing a redistribution of the separate components of the total potential discontinuity at the metal/electrolyte interface.

The goal of the present study was to further clarify the dependence of platinum zero-charge point on the solution pH by direct measurements, with the aid of radioactive tracers, of the potential dependence of the adsorption of Na^{*+} and Cs^{*+} cations and $S^*O_4^{2-}$ anions on platinized platinum. The zero-charge potential is found from the intersection of the adsorption curves so obtained [8, 9].

The magnitude of ionic adsorption was determined from the radioactivity of the electrode when withdrawn from the solution at a given time. There was a correction for the radioactivity of the solution wetting it. The experimental procedure was as follows. A platinized platinum electrode with a known true surface area†, and which had been previously cathodically reduced in sulfuric acid and washed in a bidistillate saturated with hydrogen, was introduced into the solution, and the reversible hydrogen potential was obtained in a hydrogen atmosphere. Then the hydrogen was displaced by purified nitrogen, and some predetermined potential was put on the electrode by reducing the anodic current. After the attaining of adsorption equilibrium, the radioactivity of this electrode was measured. The electrode was then cleaned by cathodic and anodic polarization in sulfuric acid, and was used for the next adsorption experiment, which followed the same procedure.

* All potentials given are versus the normal hydrogen electrode.

† The actual surface area was determined from the length of the hydrogen part of charge curves taken in sulfuric acid.

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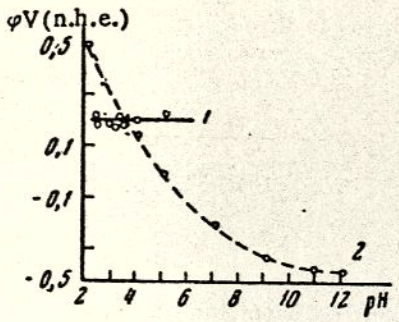


Fig. 1. Dependence of the platinum zero-charge potential on solution pH: 1) Na_2SO_4 10^{-3}-10^{-2} N; 2) Na_2SO_4 10^{-2} N according to [1].

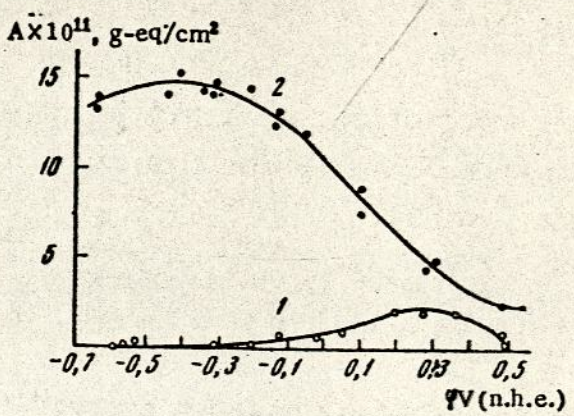


Fig. 2. Dependence of the extent of SO_4^{2-} anion (1) and Cs^+ cation (2) adsorption on the potential of platinum in a $1 \cdot 10^{-2}$ Cs_2SO_4 solution with a pH = 10.3.

Before and during the adsorption experiments, the solution pH was measured; its fluctuations were not allowed to be greater than 0.1.

The adsorption curves obtained in the present study, for the adsorption of cations and anions in Na_2SO_4 and Cs_2SO_4 solutions in the pH range from 2 to 5, agree well in both shape and magnitude with those published earlier [10, 11]. The zero-charge potential for platinum in this pH range is 0.18 ± 0.025 V, and is independent of pH within the experimental accuracy (curve 1, Fig. 1). This zero-charge potential is in good agreement with several earlier ones obtained by the same as well as by different methods, [3, 10-12] but it differs greatly from values obtained by the minimum capacitance method (curve 2, Fig. 1). It should be emphasized that the absence here of a dependence of the platinum equilibrium potential on the pH of sodium or cesium sulfate solutions in the range from 3 to 5 refers to rather dilute solutions (10^{-3} -10^{-2} N) in which specific adsorption of sulfuric acid anions still appears weakly.

No intersection of the adsorption curves for the cation and anion was observed (Fig. 2) for the basic cesium sulfate solution. Thus, zero-charged platinum surface is not realized in this case in the potential range studied. This result is in agreement with the data of [12], obtained from the change in hydrogen ion concentration.

The curve showing the dependence of the magnitude of SO_4^{2-} anion adsorption on the potential (curve 1) passes through a slight maximum in the potential range 0.2−0.4 V. Under the same conditions, at low pH values (2-3), the SO_4^{2-} adsorption maximum lies at a potential near 0.6 V [10, 11] due to the displacement of these anions by adsorbed oxygen. In basic sulfate solutions there may be adsorbed oxygen or OH^- groups over the whole range of potentials starting from the reversible hydrogen potential, and their amounts may grow with a positive shift of potential. One can apparently associate with this the smaller (than in acidic solutions) values of SO_4^{2-} adsorption under identical conditions. It could assumed that at a potential of 0.4 V the amount of adsorbed oxygen is sufficiently great, in the case of the basic solution, to displace the adsorbed anions in the solution.

An examination of the dependence of the amounts of Cs+ adsorption on the potential (curve 2) shows that there is an adsorption maximum near the reversible hydrogen potential analogous to that in acidic solutions, while with a change in the potential toward more positive values, there is a decrease in the amount of adsorption. The appearance of a maximum cation adsorption is predicted by the theory of the hydrogen platinum electrode [13, 14], and is associated with a change in the partial surface coverage by adsorbed hydrogen.

A similar curve for the dependence of cation adsorption on the potential was observed for the case of adsorption of Na+ from a basic solution of sodium sulfate.

The magnitude of the adsorption of Na+ and Cs^+ cations from NaOH and CsOH solutions is practically independent of the potential of the platinum electrode [12, 15]. The presence of a drop in the amount of adsorption of these cations with potential in basic sulfate solutions shows that the structure of the electrical double layer is different in this case. The absence of a dependence of cation adsorption on the potential in NaOH and CsOH solutions has been explained by the effect on the potential discontinuity at the platinum/solution interface of the changes in the amounts of adsorbed hydrogen or oxygen atoms, and in the magnitudes of the dipole moments of their bonds with the surface, when the potential changes [12]. On the basis of the results of this study, it can be proposed that there is a partial displacement of adsorbed OH^- ions by SO_4^{2-} ions from a platinum surface in basic sodium and cesium

sulfate solutions, as a result of which the state of the surface at potentials between the reversible hydrogen potential and 0.4 V approximates its state in acidic solutions. In the latter solutions there is a decrease in the adsorption of cations when the potential changes from 0.0 to 0.2 V, associated with a decrease in the negative charge of the surface. Since there is preferential adsorption of cations in a basic solution of cesium sulfate (Fig. 2) up to these potentials, the decrease in the negative charge of the surface could be considered the reason for the fall in the magnitude of cation adsorption.

The results of this study do not permit a definite fixing of the platinum equilibrium potential in basic sodium and cesium sulfate solutions, but they do demonstrate the impossibility of its being more negative than 0.0 V, and thus show the conclusions of [1, 4, 5] to be invalid.

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