STUDY OF THE INTERRELATIONSHIP BETWEEN THE ADSORPTION OF CATIONS AND ANIONS ON PLATINUM FROM ACID SOLUTIONS AT DIFFERENT POTENTIALS

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Adsorption methods were used to study the dependence of Na^+ cations and F^-, SO_4^{2-}, Cl^-, Br^-, and I^- anions in acidified salt solutions on the potential of platinized platinum. We determined the zero charge potential of platinum in these solutions. It was demonstrated that it shifted in a negative direction when going from fluoride (sulfate) solutions to the iodide solution. At the zero charge point, ion adsorption increases in the same sequence. In the iodide solution at potentials more negative than the zero charge potential in the sodium sulfate solution, we observe recharging of the platinum surface by adsorbed iodine anions. A conclusion is drawn regarding the mechanism by which a binary electric layer forms on the platinum in the presence of surface-active anions.

Study of the interrelationship between anion and cation adsorption at different potentials is important in principle for establishing the structure of the surface layer forming on the metal-electrolyte boundary, for ascertaining the ion adsorption mechanism on the surface of metals and for determining the zero charge potential. Studies in this field were first begun by Frumkin and his co-workers [1], who used titration to determine variation in the hydrogen ion concentration in the electrolyte during the adsorption of ions on a polarized, platinized platinum electrode. To ascertain the detailed structure of the surface layer, we must have information on the dependence of the adsorption of cations and anions on the electrode potential. Data of this kind were first obtained on platinized platinum in a cesium sulfate solution, when the dependence of cation and anion adsorption on potential was measured by the radiochemical method during the same experiment. If identical conditions are carefully maintained, the same results can be obtained as well for measurement of cation and anion adsorption in separate experiments, as was done in [2]. Furthermore, it is possible to use the direct method to measure anion (or cation) adsorption and variation in the hydrogen ion content during adsorption in the same experiment, i.e., the difference between anion and cation adsorption. In this paper, we use the two latter methods to study adsorption of sodium cations and various anions SO_4^{2-}, F^-, Cl^-, Br^-, and I^- on platinum.

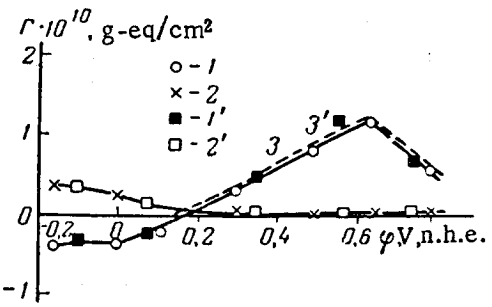


Fig. 1. Dependence of Γ_{H^+}, Γ_{Na^+}, and Γ_{A^-} on potential. 1) Γ_{H^+}; 2) Γ_{Na^+}; 3) (broken line) $\Gamma_{SO_4^{2-}}$ in 10^{-3} N N $_2SO_4$ + 10^{-3} N H_2SO_4; 1') Γ_{H^+}; 2') Γ_{Na^+}; 3') (broken line) $\Gamma_{F^-+SO_4^{2-}}$ in 10^{-3} N NaF + 10^{-3} N H_2SO_4.

In our research, we used the radioactive isotopes Na-22 and I-131 to determine the number of adsorbed sodium cations and iodine anions. Furthermore, the platinized platinum electrodes, for which the pretreatment conditions and method of measuring the true surface were the same as in [2], were deoxidized before the experiment by cathodic polarization in an H_2SO_4 solution (10^{-3} N) in a hydrogen atmosphere, soaked for a short time at the reversible hydrogen potential and then rinsed in the same cell with hydrogen-saturated doubly distilled water. Next, using a device enabling the electrode to be shifted in a vertical direction without

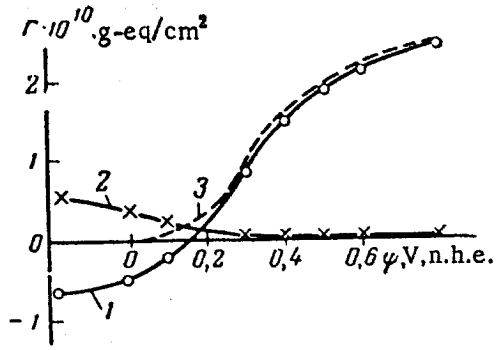


Fig. 2. Dependence of Γ_{H^+} (1), Γ_{Na^+} (2), and Γ_{Cl^-} (3) on potential in 10^{-3} N NaCl + 10^{-3} N HCl.

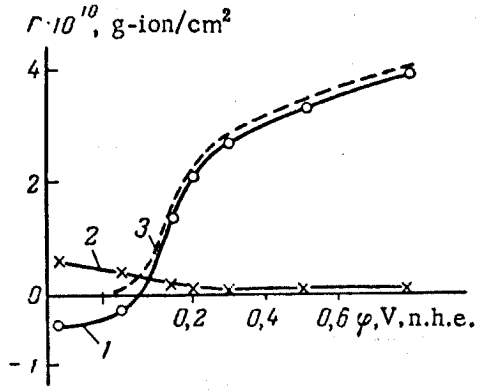


Fig. 3. Dependence of potential Γ_{H^+} (1), Γ_{Na^+} (2), and Γ_{Br^-} (3) in 10^{-3} N NaBr + 10^{-3} N H_2SO_4.

contact with the outside atmosphere, the electrode was raised to the top of the electrochemical cell and the hydrogen-saturated working solution was poured in. The electrode was then immersed in the solution, kept in it at a reversible hydrogen potential for 1 hour and subjected to anodic polarization in a nitrogen atmosphere. By means of a decreasing current density, the electrode was brought up to the prescribed potential and was kept there for 1 hour without current. From the radioactivity of the dry electrode, with correction for the tagged sodium atoms brought out together with it, we determined the adsorption of sodium ions [3, 4]. The solution left in the cell was analyzed for its hydrogen-ion content. To prevent variation in the composition of the solution through ionic transfer by the current, the auxiliary electrode used for polarization, which took the form of a smooth platinum wire, was placed in the same volume as the electrode under study. The quantity Γ_{H^+} was calculated from the accurately known volume of solution, the variation in hydrogen-ion concentration and the true surface of the electrode. A negative value corresponds to predominant adsorption of cations and a positive value to predominant adsorption of anions. The sodium salt solutions were acidified with sulfuric acid in the case of the fluorides, bromides, and iodides, and hydrochloric acid in the case of chlorides. In the case of the bromide and iodide, this was permissible because sulfuric acid has no special effect on the adsorbability of the anions studied [5, 6].

The results of the experiments are shown in Figs. 1-4. The broken line shows the dependence of anion adsorption on potential calculated as the difference between Γ_{H^+} and Γ_{Na^+}. The captions to the figures give the initial concentrations. The final concentration varied as a result of ion adsorption most often in the case of iodine anions, but this fact could not have any great effect on the dependence of I^- adsorption on potential (logarithmic isotherm) [5, 7, 8]. It should be noted that the adsorption values given in Figs. 1-3 are close to equilibrium since an increase in adsorption time (up to 6 h) did not result in any further increase in it beyond the experimental error limits.

It is clear from Figs. 1-3 that equality between cation and anion adsorption in sulfate and fluoride solutions occurs at a potential of 0.18 V, in the chloride solution at 0.14 V, and in the bromide solution at 0.04 V. These potentials correspond to the position of the zero charge point for platinum in these solutions. Thus, the zero point for platinum shifts in this series toward less positive potentials; this accords with the results of [1]. But the absolute zero charge potentials in chloride and bromide solutions are more positive (by a factor of 90 and 60 mV, respectively). This difference is evidently due to the smaller concentration (three orders) of the electrolytes used in our work. Comparison of ion adsorption values at the zero charge potential shows that they increase as we go from sulfate and fluoride anions to chloride and bromide anions. This, together with the shift of the zero charge potential to the negative side, accords with an increase in the surface activity of the anions in this series.

Consideration of the structure of the surface layer in the case of the iodine-anion adsorption is of particular interest. Figure 4 shows the adsorption curves for Na^+ and I^- obtained under the same conditions as for the other anions (curves 1, 2, and 3). It can be seen that in the iodide solution the zero charge point lies on the negative side of the reversible hydrogen potential. These curves, however, do not correspond to equilibrium values of I^- adsorption, which increases with time over a large number of hours. In view of this, we obtained data on the dependence of I^- adsorption (curve 4) and Na^+ adsorption (curve 5) in equilibrium conditions. In this case, the ion adsorption was determined by measuring the radioactivity of the electrode. Extrapolation of the adsorption curves

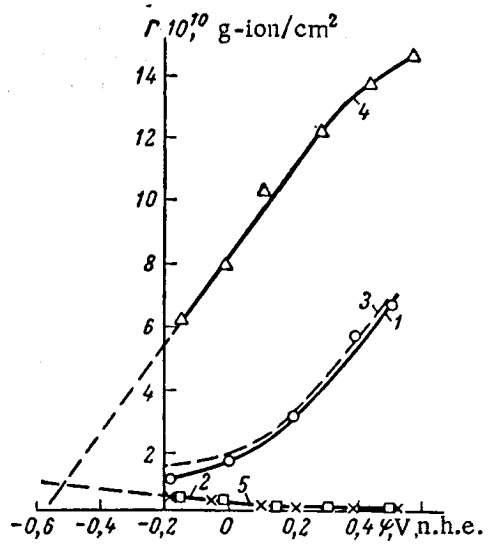


Fig. 4. Dependence of potential Γ_{H^+} (1), Γ_{Na^+} (2), and Γ_{I^-} (3) in 10^{-3} N NaI + 10^{-3} N H_2SO_4 (soaking at each potential for 1 hour); Γ_{I^-} (4) and Γ_{Na^+} (5) (in equilibrium conditions) in $5 \cdot 10^{-3}$ N NaI + $5 \cdot 10^{-3}$ N H_2SO_4.

for anions and cations in the negative potential region shows that the zero charge point for platinum in an acid sodium-iodide solution lies at the potential ~ −0.5 V, i.e., it is almost 0.7 V more negative than in an acid sodium sulfate solution. The position of the zero charge point is close to its position in an alkaline sodium-iodide solution (10^{-2} N) [9]. Thus, variation in the pH value of the iodide solution by 10 units has no appreciable effect on the position of the zero charge potential in the case of platinum.

Comparison of the position of the zero points in acid and alkaline bromide solutions shows that they are different, that is to say, in the alkaline solution the zero charge potential is more negative than in the acid solution. The difference, according to [1], is ~330 mV, and according to our data [9], ~420 mV. This discrepancy may be explained by the difference in the adsorbed anion concentration, which in the first case was two orders higher than in the second. In accordance with the increased surface activity of the anions, anion and cation adsorption at the zero charge point in the iodide solution is considerably higher.

At the reversible hydrogen potential (Fig. 4), the iodide solution does not show an increase in the hydrogen-ion concentration, but a decrease with respect to the initial solution. In the other solutions studied (Figs. 1, 2, and 3), the opposite is true. Consequently, it is only in the iodide solution close to the reversible hydrogen potential that there is predominant adsorption of the anions; this is connected with the occurrence of positive charges through recharging of the platinum surface by adsorbed I^- anions. The jump in potential in this case is created by a positive jump in potential in the denser part of the binary layer and by a negative jump in the diffuse part. The iodide anions attracted superequivalently to the charge ensure adsorption of the sodium cations in this potential region. According to the binary electric layer theory, an increase in cation adsorption with the increase in superequivalent adsorption might be expected, but the opposite is true in the case of platinum.

Study of the kinetics of the adsorption of iodine anions and sodium cations at the reversible hydrogen potential shows that with time there is a decrease in the cation adsorption concurrently with an increase in anion adsorption. For example, when the adsorption time is changed from 30 min to 15.5 h, the I^- adsorption varies between $2.3 = 10^{-10}$ and $6.1 \cdot 10^{-10}$ g-ion/cm² and Na^+ between $5.3 \cdot 10^{-11}$ and $3.8 \cdot 10^{-11}$ g-ion/cm². This interrelated variation with time in cation and anion adsorption shows that although the over-all jump in potential on the metal/solution interface remains unchanged, there is redistribution of the potential jumps in the dense and diffuse areas of the surface layer. This may be due to the fact that as the anion adsorption increases, there is strengthening of their bonds with the surface (through coming nearer to it), on account of which the positive potential jump in the dense area may retain its former value, or even be reduced, despite the increased number of anions. In our case it is this that occurs.

The experiments show that the slowness in anion adsorption at the reversible hydrogen potential cannot be associated with diffusional difficulties in the solution and therefore reflects the kinetics of the chemisorption process. The chemisorptional nature of iodine anion adsorption on platinum has been proved on a number of occasions both by us and other investigators [5, 8, 10, 11]. In this paper it can be shown, in particular, by the high capacitance retaining a constant value throughout the potential region, right up to the formation of a monolayer coating on the platinum surface. As calculated from the data in Fig. 4, curve 4, it amounts to 130 μF/cm². The capacitance for sodium cations under these conditions is considerably smaller. This shows that during I^- adsorption there is considerable predominance of the potential jump component related to the ψ'-potential.

The above mentioned redistribution of the components of the total potential jump during anion adsorption should alter the rate of the electrochemical reactions taking place on the platinum electrode close to the hydrogen potential. It might be expected that, at first, the effect of the ψ'-potential would predominate, but that it would increase with time and that the effect of the second component, determined by chemisorption, would produce an increased effect. This was actually observed in [12] during study of the ionization rate of hydrogen adsorbed on platinum in bromide solutions. In this way, when interpreting the results from electrochemical kinetics, we must take into account the structural peculiarities of the binary electric layer on the platinum, as compared with the same for mercury, as was first pointed out by Frumkin [13].

As was described earlier, the increase in anion adsorption with potential only occurs in the case of poorly surface-active anions until oxygen adsorption begins, and in the case of anions possessing marked surface activity until their oxidation potential. The results given in Fig. 1 for fluorine anions, which are close to those for sulfate anions, suggest that these anions differ little from each other as regards adsorption activity. This accords with the results of [11, 14], in which other methods were used.

In the region of positive potentials, where we observe an increase in anion adsorption, there is a reduction in the adsorption of cations. Between potentials 0.3 and 0.8 V, the adsorption of sodium cations hardly depends on the potential and is very small (as compared with the anion adsorption) $-1.2 \cdot 10^{-12}$ g-ion/cm^2. This residual adsorption is marked by great strength. Its nature is not yet clear.

All these facts taken together suggest that under equilibrium conditions, after the adsorption act, there is a transition by the anions from the ionic to an intermediate state, and the greater the adsorption time and higher the positive potential, so the closer it is to the atomic state. The positive jump in potential on the solution boundary is due to the dipolar nature of the platinum–halogen bond in the same way as occurs during oxygen adsorption. Variation in the potential jump in this case is not only due to variation in the coverage of the surface, but also to variation in the dipolar moment of the platinum-adsorbed halogen bond. This shows up in the increased strength of the bond as the potential rises. If the potential varies toward the negative side, the bond weakens, i.e., becomes ionic.

On the basis of data obtained in our work, it can be stated that in the region of potentials more positive than the zero charge point for platinum in halogen solutions (excluding fluorine), the potential jump is basically found in the denser area of the surface layer formed by chemisorbed anions.

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