MUTUAL INFLUENCE OF HYDROGEN IONS AND SODIUM AND CESIUM CATIONS DURING THEIR ADSORPTION ON PLATINIZED PLATINUM

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UDC 541.135.52.92-183 : 546.128

In the adsorption of metal cations from acid solutions on metallic electrodes, at the same time there may also be an adsorption of hydrogen ions. The ratios between the adsorbed amounts of metal and hydrogen cations on the surface of the electrode will depend on the ratio of their concentrations in solution, the charge and specific adsorbability. The predominant adsorbability of Cs^+ cations over H^+ ions on platinized platinum was first demonstrated in [1]. However, these data were qualitative.

In this work we investigated the influence of the hydrogen ion concentration on the adsorption of Cs^+ and Na^+ cations on platinized platinum at the reversible hydrogen potential for the case of dilute solutions of sodium and cesium sulfates. Under these conditions, the competition between the H^+ ions and metal cations during the adsorption process should be expressed most clearly, since the value of the adsorption at this potential is close to the maximum, while the influence of the adsorption of anions on the adsorption of cations can be neglected [1]. The adsorption of Na^+ and Cs^+ was measured from solutions with concentrations 10^{-3} and 10^{-2} N in the interval of pH from 0 to 4.

The amount of adsorbed cations at a set pH of the solution was determined by the radioactive tracer method according to the radioactivity of the electrode remaining in solution during the measurement [2] or removed from it, with a correction for the wetting layer of solution [3], and with other necessary corrections. The radioactive isotopes Na-22 and Cs-134 were used as tracers. The solutions were prepared from twice-recrystallized salts in double-distilled water and sulfuric acid. Preliminary preparation of the platinized electrodes and determination of their true surface were performed in the same way as in our earlier studies, for example, in [1]. The results obtained using various methods of measuring adsorption were in satisfactory agreement.

Figure 1 presents the pH dependence of the values of the adsorption (Γ) of Na^+ and Cs^+ cations. The presence of a pronounced dependence of the adsorption of both cations on the hydrogen ion concentration in solution is evidence of their mutual influence during the formation of an electrical double layer on platinum. From the figure it is evident that in the adsorption of Na^+ and Cs^+ cations from 10^{-3} and 10^{-2} N solutions within some pH interval, the amount of adsorbed cations is a linear function of the pH. For millinormal solutions at pH > 3, and for centinormal solutions at pH > 2, the slope of the curves of Γ versus pH decreases. The decrease in the slope is due to the fact that under these conditions there is an excess of metal cations in comparison with the concentration of hydrogen ions, the fraction of participation of which in the formation of the double layer drops. For the case of Na^+ ions at pH > 3, the measured values of the adsorption become poorly reproducible. The causes of this phenomenon, not associated with the procedure used, will require further elucidation.

It is interesting to note that when the metal ion concentration is varied by an order of magnitude, the Γ versus pH curves are displaced parallel to one another, and the value of this displacement corresponds to the change in the hydrogen ion concentration, also by an order of magnitude. The slope of the curves in this case remains constant up to pH 3.0-3.4 for the case of 10^{-3} N solutions and up to pH 2.0-2.4 for the case of 10^{-2} N solutions of sodium and cesium sulfates. Such a pattern is characteristic of ion-exchange processes.

From Fig. 2, on which the results obtained are presented in the form of a dependence of the amount of adsorbed Na^+ and Cs^+ cations on the ratio of their concentrations to the concentration of H^+ ions in solution, it is

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 6, No. 3, pp. 398-399, March, 1970. Original article submitted July 10, 1969.

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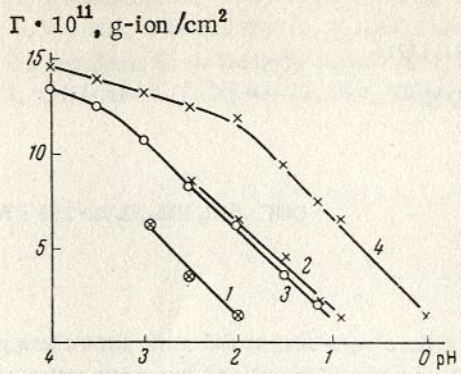


Fig. 1

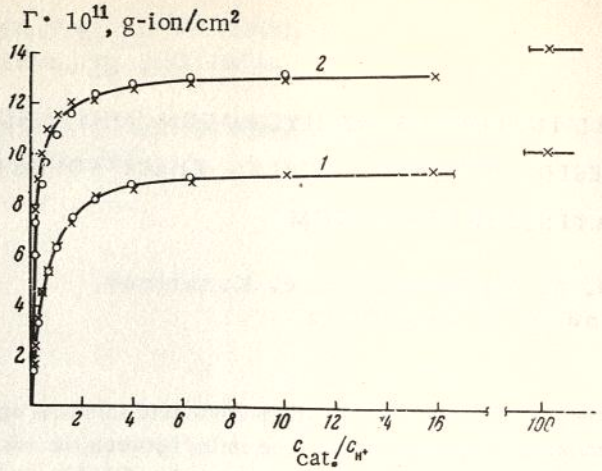


Fig. 2

Fig. 1. Dependence of the adsorption of Na^+ cations from 0.001 (1) and 0.01 N (2) Na_2SO_4 and Cs^+ cations from 0.001 (3) and 0.01 N (4) Cs_2SO_4.

Fig. 2. Dependence of the adsorption of Na^+ (1) and Cs^+ (2) cations on the ratio of their concentrations to the H^+ ion concentration in solution.

evident that the almost complete displacement of H^+ ions from the outer shell of the double layer on a hydrogen platinum electrode by Na^+ or Cs^+ cations occurs in the presence of a 5-6-fold excess of the latter in solution. In this case, no dependence on the initial concentration of the solution is manifested within the limits of the experimental error. Under these conditions the charge density of the electrode surface with the opposite sign can be assumed equal to the adsorption of metal cations. For the case of Na^+ cations, in the presence of a small excess of them, it comprises 10.5 $\mu C/cm^2$, while for the case of Cs^+ cations it is 14.5 $\mu C/cm^2$. The large value of the charge in the latter case is associated with the presence of appreciable specific adsorbability for the Cs^+ cations. It is manifested both in the large value of the adsorption (Fig. 1) and in the closeness of the values of their adsorption and that of Na^+ ions in the interval of pH 1-2.in the case when the Na^+ concentration is ten times as great as the Cs^+ concentration in solution. This also follows from the sharper rise of the Γ versus c_{cat}/c_{H^+} (Fig. 2), evidencing a more rapid displacement of H^+ ions from the double layer.

From the difference of the values of the adsorption of Cs^+ and Na^+ cations at various ratios c_{Cs^+}/c_{H^+} and c_{Na^+}/c_{H^+}, according to the data of Fig. 2, we can calculate the specific adsorption of Cs^+ with respect to Na^+. Thus, at values of these ratios from one to ten, the Cs^+ cations are adsorbed 1.5 ± 0.2 times more than the Na^+ cations. Such a method of determining the relative adsorbability can also be used in other cases.

The authors would like to thank A. N. Frumkin for his valuable suggestions in the discussion of the results of this work.

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