THE CONCENTRATION DEPENDENCE OF SODIUM AND CESIUM ION ADSORPTION ON THE PLATINUM ELECTRODE IN ACID SOLUTIONS

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The joint adsorption of alkali metal cations and hydrogen ions on the platinum electrode was discussed in [1-4]. It has been shown that the alkali metal cations are adsorbed preferentially before the hydrogen ions (although the difference in adsorbability between H^+ and Li^+ is small), and that their adsorbability rises when going from Li^+ to Cs^+. It was not clear, however, whether the ratio of the adsorbabilities of alkali metal cations, Me^+, and hydrogen ions remains constant at different concentrations of the latter in the solution. In order to solve this problem we determined the adsorption of the cations Na^+ and Cs^+ as a function of their concentration in sulfuric acid solutions at different pH.

The measurements were carried out on platinized platinum electrodes at the reversible hydrogen potential with the techniques of radiotracers [5] and of determining the change in hydrogen ion concentration in the solution during double-layer formation [6].

Standard methods were used to prepare the electrodes in both cases. The platinum sheet or net was lightly etched in boiling aqua regia and polarized anodically in 0.1 N HCl, then cathodically in 0.1 N H_2SO_4 at a current density of 15 mA/cm^2. Platinization was done from 2% H_2PtCl_6 ("pure") at a current density of 4 mA/cm^2 and a duration of 4 h. After the platinizing the electrode was polarized cathodically in 0.1 N H_2SO_4 (15 mA/cm^2). Electrode preparation for the experiments included anodic and cathodic polarization in 0.1 N H_2SO_4 (15 min duration, current density 15 mA/cm^2) and electrolyte exchange when the direction of polarization was changed. The true surface area of the electrodes was determined from the length of the hydrogen region on the charging curve in 1 N H_2SO_4 [7]. For the measurements with the radiotracer technique an electrode was used that had an apparent surface area of 2 cm^2 and a true surface area of 0.7-0.5 m^2. When determining the change in hydrogen ion concentration caused by the formation of the double layer, the apparent surface area of the electrode was 60 cm^2, the true surface area was between 8 and 4 m^2. All experiments were carried out at room temperature (22 ±2°C). The solutions were prepared with twice distilled water from reagents that had been subjected to careful purification.

The radiotracer measurements were carried out with the isotopes Na-22 and Cs-134 in a cell similar to that described in [5], and in two ways. Following the first way, the adsorption was found from the radioactivity of the electrode which was lowered to the bottom of the cell, after correcting for the radioactivity background of the solution and the radioactivity of the liquid layer between the electrode and the membrane. In order to define this correction the electrode was polarized anodically to the potentials of oxygen evolution in 0.1 N H_2SO_4, and then immersed into a solution of 1 N H_2SO_4 + 0.01 N Na_2SO_4 (or Cs_2SO_4) containing labelled Na^+ or Cs^+. Under these conditions one can neglect the adsorption of alkali metal cations on the platinum. The technique described can be applied to relatively dilute solutions (up to about 10^{-2} N). Therefore, an important part of the results was obtained in the following way. The electrode was kept for 15 min in the solution studied while hydrogen was passed. It had been established that this time is sufficient for adsorption equilibrium to be established. The solution was then drained and the system washed with several quantities of twice distilled water which was saturated with hydrogen. The electrode was washed by immersing it three times into twice distilled water, and its radioactivity was measured. In this case the activity was due to the adsorption of cations and to the natural radioactive background. In special experiments it

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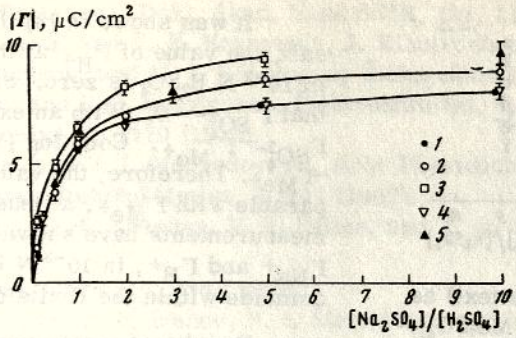

Fig. 1. The quantities Γ_{Na^+} (1-3) and Γ_{H^+} (4, 5) as functions of the ratio of concentrations $[Na_2SO_4]/[H_2SO_4]$ in the solutions: 1, 4) 10^{-3} N H_2SO_4 + x N Na_2SO_4; 2, 5) 10^{-2} N H_2SO_4 + x N Na_2SO_4; 3) 5×10^{-2} N H_2SO_4 + x N Na_2SO_4.

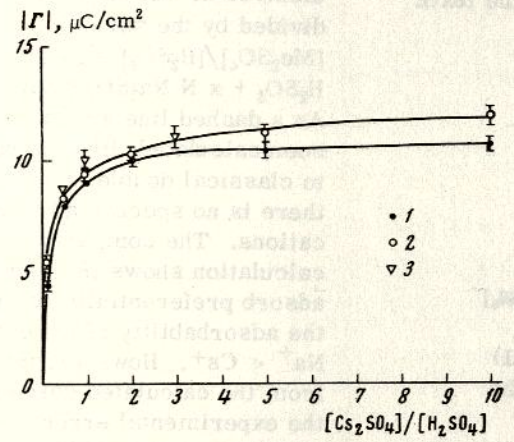

Fig. 2. The quantities Γ_{Cs^+} (1, 2) and Γ_{H^+} (3) (according to the data of [4]) as functions of the ratio of concentrations Cs_2SO_4/H_2SO_4 in the solutions: 1) 10^{-3} N H_2SO_4 + x N Cs_2SO_4; 2, 3) 10^{-2} N H_2SO_4 + x N Cs_2SO_4.

was shown that in this way results are obtained which agree with the results of measurements following the first way, i.e., without washing the electrode. A substantial washing-away of adsorbed cations, about 10-15%, was only observed after keeping the electrode for 15 min in the twice distilled water. The reasons for such a slow desorption of the cations in twice distilled water will be discussed in a separate communication. The application of washing made it possible to extend the limit of solution concentrations accessible in the measurements to 5×10^{-1} N. The specific activity of the solutions was here chosen so that the fraction of radioactive ions involved in the adsorption process remained approximately constant.

When determining the change in hydrogen ion concentration during double layer formation the electrode was washed, after the pretreatment described above, in boiling twice distilled water and then transferred into a cell. The system was then dried in a stream of hydrogen while heating it with the aid of a strong lamp, and seeing to it that the temperature within the cell did not rise above 50-60°C. At higher temperatures the surface area of the electrode shrinks substantially due to recrystallization. After the drying a portion of the test solution was introduced into the cell. The change in hydrogen ion concentration in the

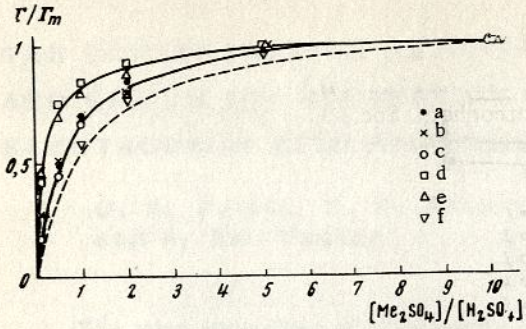

Fig. 3. The quantity Γ/Γ_m (cf. the text) as function of the concentration ratio $[Me_2SO_4]/[H_2SO_4]$ in the solutions: a) 10^{-3} N H_2SO_4 + x N Na_2SO_4; b) 10^{-2} N H_2SO_4 + xN Na_2SO_4; c) 5×10^{-2} N H_2SO_4 + x N Na_2SO_4; d) 10^{-3} N H_2SO_4 + x N Cs_2SO_4; e) 10^{-2} N H_2SO_4 + x N Cs_2SO_4; f) 10^{-2} N H_2SO_4 + x N Li_2SO_4 (according to the data of [4]). The dashed curve has been obtained as the result of a model calculation (explanations in the text).

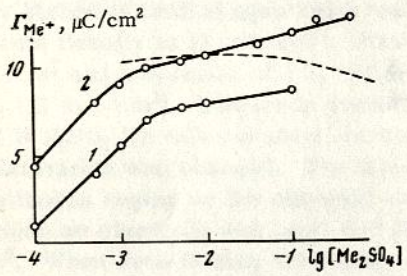

Fig. 4. The quantities Γ_{Na^+} (1) and Γ_{Cs^+} (2) as functions of the concentration of sodium and cesium sulfate, respectively, in a 10^{-3} N H_2SO_4 solution. The dashed line is the concentration dependence of electrostatic cation adsorption as calculated from the classical theory of the electric double layer.

solution was determined by titration with phenol red as an indicator. From this the adsorption of hydrogen ions, Γ_{H^+}, was calculated.

It was shown in [8] that in the absence of foreign salt, the value of Γ_{H^+} at the reversible hydrogen potential in 10^{-2} N H_2SO_4 is zero. Since $\Gamma_{H^+} = \Gamma_{SO_4^{2-}}$, this means that $\Gamma_{SO_4^{2-}} = 0$. With an excess of foreign salt, $\Gamma_{H^+} = \Gamma_{SO_4^{2-}} - \Gamma_{Me^+}$. Counting $\Gamma_{SO_4^{2-}} = 0$ one can write $\Gamma_{H^+} = -\Gamma_{Me^+}$. Therefore, the values of Γ_{H^+} are directly comparable with Γ_{Me^+}, at least in dilute solutions. In fact, measurements have shown that the amounts adsorbed, Γ_{Na^+} and Γ_{H^+}, in 10^{-3} N H_2SO_4 + 10^{-2} N Na_2SO_4 solution coincide within the limits of experimental error (±5%).

Results of measuring Γ_{Na^+}, Γ_{Cs^+}, and Γ_{H^+} are shown in Figs. 1 and 2. The measuring accuracy of the adsorption values is indicated by the length of the vertical lines. The data obtained with different methods are seen to coincide sufficiently well. For a discussion it is more appropriate to represent the experimental data in a plot where on the ordinate are shown, not the quantities Γ themselves but the values of Γ at a given concentration divided by the value Γ_m at a ratio of concentrations $[Me_2SO_4]/[H_2SO_4] = 10$ (or 5 in the case of 5×10^{-2} N H_2SO_4 + x N Na_2SO_4 solutions). This is realized in Fig. 3. As a dashed line a relation is given in this figure which has been calculated, like the relation for Γ_{H^+} in [4], according to classical double layer theory under the assumption that there is no specific adsorption of hydrogen ions or metal cations. The comparison between experimental data and calculation shows that the cations of the alkali metals adsorb preferentially before the hydrogen ions and that the adsorbability of the cations rise in the order $Li^+ < Na^+ < Cs^+$. However, the deviation of the data for Li^+ from the calculated curve is only insignificantly outside the experimental error. The coincidence of the curves referring to the same cation but different acid concentrations signifies that at constant concentration ratios $[Me_2SO_4]/[H_2SO_4]$ the relative adsorbabilities of the cations Na^+ and Cs^+ and of the hydrogen ions remains constant. Regardless of their concentration the hydrogen ions are fully displaced from within the electric double layer when there is a five- to ten-fold excess of cations.

Results of measurements of the adsorption of cations, Γ_{Na^+} and Γ_{Cs^+}, over a wide range of concentrations are plotted semilogarithmically in Fig. 4. The slopes of Γ_{Na^+} and Γ_{Cs^+} as functions of cation concentration differ between low and high salt concentrations. At low concentrations the shape of the curve is determined by the process of expulsion of hydrogen ions from the double layer, but at high concentrations by the increase in electrolyte concentration. At salt concentrations larger than about 10^{-2} N, Γ_{Cs^+}, is 30% larger than Γ_{Na^+}. This result and the substantially larger difference between Γ_{Cs^+} and Γ_{Na^+} at low solution concentrations are caused by the higher specific adsorbability of the Cs^+ ions. Accordingly complete expulsion of hydrogen ions from the double layer is reached at somewhat lower concentrations of Cs^+ ions in the solution. The dashed line in Fig. 4 shows the concentration dependence of the Gibbs adsorption of the cation as calculated according to classical double-layer theory with the use of tabulated data given in [9]. It is seen that the electrostatic adsorption only rises up to a concentration of about 10^{-2} N but then begins to fall. The increase in Γ_{Me^+} on platinum up to high solution concentrations is a consequence of specific adsorption of the cations Cs^+ and Na^+ which seems to indicate that during their adsorption these cations are at least partly dehydrated [10]. The results obtained in the present work are in harmony with the data of [1-4].

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