INVESTIGATION OF THE ADSORPTION OF IONS AND THE STRUCTURE OF THE ELECTRIC DOUBLE LAYER ON RUTHENIUM—TITANIUM OXIDE ANODES. MUTUAL EFFECT OF PERCHLORATE, SULFATE, CHLORIDE, AND PHOSPHATE ANIONS

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In the previous report [1] it was shown that the anions of sulfuric, hydrochloric, and phosphoric acids are adsorbed specifically on ruthenium—titanium oxide anodes (RTOA). The present work was devoted to investigation of the mutual effect of these ions during simultaneous adsorption.

The method of preparation of the RTOA electrodes (30 mole % RuO_2 and 70 mole % TiO_2), the radioisotope procedure, and the radioactive preparations were the same as in [1]. The experiments were realized at 22 ± 2°C.

To determine the effect of chloride and sulfate ions on the adsorption of each other we studied their adsorption from mixtures of the acids. The relations between the adsorption of the anions of sulfuric acid and their concentration in the solution with various constant concentrations of hydrochloric acid and the analogous relations for the anions of hydrochloric acid with various constant concentrations of sulfuric acid are given in Figs. 1 and 2. The experiments were carried out at a potential of 0.7V. [The data which we obtained at a different potential in the region of 0.0-0.7 V coincided within the experimental error limits (± 5 %) with the results given in Figs. 1 and 2.] The relations between the adsorption of the anions and their concentration in the solution (Figs. 1 and 2) obtained with increase in the concentration of the anions coincide with those obtained with decrease in the concentration, and this demonstrates the equilibrium character of the processes of joint adsorption of these anions.

As indifferent electrolyte in all the experiments we used 0.1 M perchloric acid, since it followed from [1] that its anions have the greatest adsorption capacity compared with the anions of hydrochloric, sulfuric, and phosphoric acids. This conclusion is also confirmed by the following experiments. If after the attainment of a steady value for the adsorption of the hydrochloric acid anions at any potential in the range of 0.0-0.7 V from a solution of 10^{-3} M NaCl + 0.01 M $HClO_4$ the $HClO_4$ concentration is increased to 1 M, it is not possible to observe a decrease in the amount of anions previously adsorbed on the RTOA. Analogous data were obtained in experiments on the adsorption of the anions of sulfuric and phosphoric acids. Consequently, the anions of perchloric acid cannot displace the above-mentioned anions from the surface, and this agrees well with published data [1]. Determination of the adsorption of the anions of perchloric acid from a 10^{-3} M solution of perchloric acid by titration of the solution of the adsorbate with sodium hydroxide solution before and after adsorption of the perchloric acid anions on the RTOA showed that it is not greater than 10^{-11} mole/cm^2 of true surface.

From Fig. 1 it is seen that the presence of Cl^- ions in the solution has practically no effect on the adsorption of the sulfuric acid anions at Cl^- ion concentrations* of $\leqslant 10^{-1}$ M, while at Cl^- concentrations of 1 M they begin to displace the sulfuric acid anions partly from the surface of the RTOA (Fig. 1, curve 4). The presence of sulfuric acid anions in the solutions to the extent of 10^{-4} M (Fig. 2) fully suppresses the adsorption of Cl^- ions in the concentration range of 10^{-4}-$5\cdot10^{-3}$ M and substantially reduces that in the concentration

*Since our experiments were carried out in relatively dilute solutions, and the ionic strength varied little, the activities of the ions could be replaced by the concentrations.

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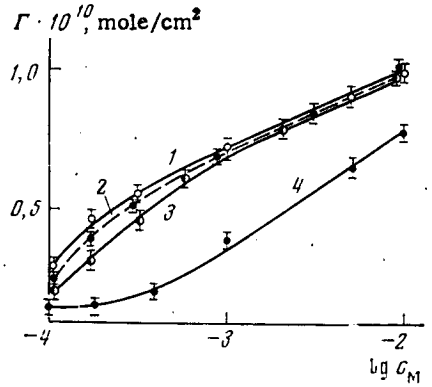

Fig. 1

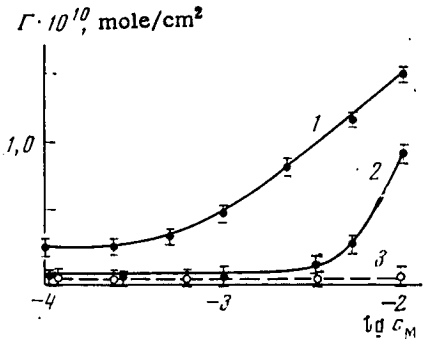

Fig. 2

Fig. 1. Dependence of the adsorption of sulfuric acid anions on the RTOA on their concentration in the solution at a potential of 0.7 V in the absence (1) and in the presence (2-4) of hydrochloric acid anions for solutions with the following compositions: 1) xM H_2SO_4 + 0.1 M $HClO_4$ without additions; 2)-4) the same with 10^{-2} (2), 10^{-1} (3), and 1 M (4) HCl.

Fig. 2. Dependence of the adsorption of hydrochloric acid anions on the RTOA on their concentration in the solution at a potential of 0.7 V in the absence (1) and in the presence (2, 3) of sulfuric acid anions in the solution for solutions with the following compositions: 1) xM HCl + 0.1 M $HClO_4$ without additions; 2) and 3) the same with 10^{-4} (2) and 10^{-3} M (3) H_2SO_4.

range of $5 \cdot 10^{-3}$-10^{-2} M. The presence of sulfuric acid anions in the solution to the extent of 10^{-3} M fully suppresses the adsorption of Cl^- ions in the NaCl concentration range of 10^{-4}-10^{-2} M.

By means of the formal thermodynamics employed in the description of adsorption on ion exchangers we calculated the adsorption selectivity constants from the data of curve 2 in Fig. 2, as was done in [2].

This calculation showed that the adsorption capacity of the sulfuric acid anions is more than 10 times greater than the adsorption capacity of the hydrochloric acid anions.

The relations between the adsorption of the anions and their concentrations in the solution (Figs. 1 and 2) give good straight lines against the coordinates Γ and log c. From this it follows that the model of a uniformly inhomogeneous surface can be used to describe the adsorption processes in these systems. However, in order to obtain ideas about the energy structure of the surface of the RTOA it is necessary to use differential isotope methods, which can provide valuable information about the inhomogeneity of the surface, as in the case of platinum [4].

From the combination of experimental data described above it follows that the relationships presented in Figs. 1 and 2 can be regarded as true isotherms. This is consistent with data [1] from investigation of the individual adsorption of hydrochloric and sulfuric acid anions, in which it was shown that systems with these ions are close to equilibrium systems. Unfortunately, the production of experimental data required for theoretical calculation of the relationships governing the joint adsorption of two anions (or cations) by the methods used in [2, 3] for equilibrium systems is complicated in the case of mixtures of the sulfuric and hydrochloric acid anions by too large differences in the adsorption capacity of these anions, which do not make it possible to study their joint adsorption in a sufficiently wide range of concentrations.

A similar calculation cannot be made for mixtures of sulfuric and phosphoric acid anions on account of the deviations of the characteristics of these systems from equilibrium, due to the high strength of the bond between the adsorbed anions of phosphoric acid and the surface of the RTOA [1], which (as will be shown below) plays a determining role in the joint adsorption of these anions.

In connection with the foregoing the processes of displacement of previously adsorbed anions by the anions of the solution in solutions with various compositions were investigated in order to compare the adsorption capacities of the anions on the RTOA. The experimental procedure was as follows: After the attainment of a steady value for the adsorption of the sulfuric acid anions from a solution of $5\cdot10^{-4}$ M H_2SO_4 + 0.1 M $HClO_4$ at a potential of 0.2 V (or any other potential in the range of 0.0-0.7 V) phosphoric acid was added to the solution so that its concentration in the solution was 10^{-6} M. After 10 min the amount of adsorbed sulfuric acid anions remaining on the RTOA was measured. The phosphoric acid concentration was then increased to 10^{-5} M, and after 10 min the adsorption of the sulfuric acid anions was measured again. In these experiments the phosphoric acid concentration was increased to 10^{-3} M, and the sulfuric acid concentration was kept constant. These measurements showed that the phosphoric acid anions are capable of displacing previously adsorbed sulfuric acid anions from the surface of the RTOA. The rate of these displacement processes is determined by the ratio of the concentrations of the sulfuric and phosphoric acid anions in the solution. Thus, if the concentration of sulfuric acid in the solution is $5\cdot10^{-4}$ M, with a phosphoric acid concentration of $3\cdot10^{-5}$ M $\sim$ 50% of the previously adsorbed sulfuric acid anions will be displaced from the surface of the RTOA after 10 min, and with a phosphoric acid concentration of 10^{-3} M the sulfuric acid anions will be displaced almost completely from the RTOA after the same time.

Similar measurements in order to establish the possibility of displacement of phosphoric acid anions, previously adsorbed on the RTOA from a solution of $5\cdot10^{-4}$ M H_3PO_4 + 0.1 M $HClO_4$ at a potential of 0.2 V, by the sulfuric acid anions showed that sulfuric acid anions are not capable of displacing phosphoric acid anions from the solution with variation of the sulfuric acid concentration of the solution between 10^{-3} and 10^{-1} M.

Thus, the obtained experimental data make it possible to place the anions in the following order according to their adsorbability on the RTOA: $ClO_4^- << Cl^- < HSO_4^- < H_2PO_4^-$. This order does not change in the region of potentials of 0.0-0.7 V. At more anodic potentials changes in the relative adsorption capacity of the anions on the RTOA can be expected on account of the interaction of the adsorbed anions and oxygen with large degrees of surface coverage by the latter.

LITERATURE CITED

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