ADSORPTION OF IONS ON BRIGHT NICKEL FROM ACIDIFIED SOLUTIONS OF SODIUM SULFATE

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The adsorption of the ions of sulfuric acid and sodium sulfate on nickel has been little investigated. In the literature until recently it had been assumed that the anions of sulfuric acid are surface-inactive in relation to nickel. In [1] their adsorption was investigated by a radioactive tracer method on nickel sheet and single crystals. The effect of the pretreatment of the surface, adsorbed oxygen, and polarization on the adsorption kinetics and adsorbed quantities was established. The adsorbed quantities were in the order of 10^{-10} g-eq/cm^2. In [2] the dependence of the adsorption of SO_4^{2-} on time and potential was investigated by the same method in solutions of sulfuric acid and sodium sulfate, and the suggestion that the adsorption of SO_4^{2-} anions is nonelectrostatic in character was first put forward. There is hardly any information on the adsorption of Na^+ cations from acidic solutions. In [2] it was indicated that their adsorption on nickel powder is relatively small and reversible. In [3] a bilogarithmic relationship was obtained for the adsorption of Na^+ from sodium sulfate with pH 3 on bright nickel.

The available data cannot be explained on the basis of the usual ideas about the mechanism of the adsorption of Na^+ and SO_4^{2-} ions used for cases of their adsorption on mercury and platinum metals and require further refinement.

In the present work the effect of the method of pretreatment of the bright nickel surface on its adsorption characteristics in respect to the ions of sodium sulfate was investigated.

The kinetics of adsorption, desorption, and exchange of SO_4^{2-} anions and Na^+ cations and the dependence of their adsorption on the concentration and pH of the solution were investigated by the method of radioactive tracers with S-35 and Na-22 on bright nickel.

The adsorption values (Γ) were calculated from the radioactivity of the electrode without interruption of the process or removal of the electrode by the method described in [4] or with removal of the electrode according to the method in [5]. The results obtained from both methods agreed with an accuracy of 5-10%. The electrodes, in the form of disks 1.7 cm in diameter and 3 mm thick, were made from nickel of 99.998% purity. Before each experiment the electrode was degreased with alcohol, cleaned manually with glass powder (the fraction which did not settle in water in 15 sec) to a uniform light-gray color in air (approximately 15-20 min), washed with twice-distilled water, and placed in the electrochemical cell, where cathodic reduction of the surface was realized at high current densities (5-10 mA/cm^2 apparent surface) or at current densities securing $\varphi_r = -0.25$ to -0.30 V * in solutions of $5 \cdot 10^{-2}$ N sulfuric acid or 10^{-2} N sodium hydroxide for 3 h. After reduction the electrode was washed in an atmosphere of hydrogen with twice-distilled water, which was then replaced by the working solution. All the solutions were prepared from chemically pure twice-recrystallized salts with twice-distilled water and sulfuric acid. Before the experiments the solutions were further purified electrochemically with a large platinum electrode for two days.

The kinetics and adsorption values for the anions of sulfuric acid and the strength of the bond between the adsorbed particles and the nickel surface were found to depend strongly on the conditions of its preliminary reduction. On electrodes which had been subjected to cathodic treatment in labeled (S-35) sulfuric

*The potentials are referred to a reversible hydrogen electrode in the same solution (φ_r).

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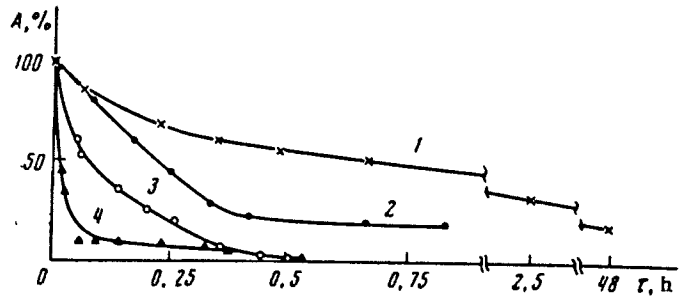


Fig. 1. Kinetics of desorption in water and air (1,3) and exchange at $\varphi_r = 0.0$ V with SO_4^{2-} anions (2,4) for sulfur-containing anions adsorbed after strong cathodic polarization (1,2) and after preparation of the electrode at $\varphi_r = -0.25$ V (3,4). Solution during adsorption and exchange: 10^{-2} N Na_2SO_4 + 10^{-3} N H_2SO_4. A is the amount of unexchanged ions, %.

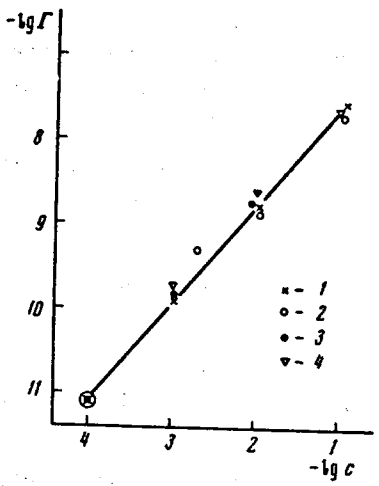


Fig. 2. Dependence of adsorption values for Na^+ from xN Na_2SO_4 + 10^{-3} N H_2SO_4 (1) and for SO_4^{-2} from $NaSO_4$ (pH 3) (2) and H_2SO_4 (3,4) on their concentration. The nickel was washed with water after preliminary strong cathodic polarization. The same relation for SO_4^{2-} anions adsorbed on nickel after reduction at $\varphi_r = -0.25$ V (4).

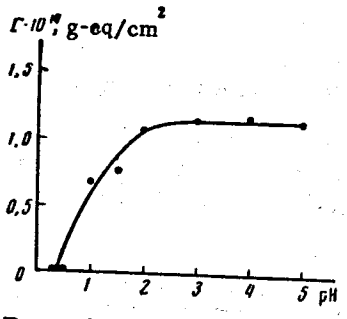


Fig. 3. Dependence of adsorption values for Na^+ cations at nickel on pH of 10^{-3} N solution of sodium sulfate. The nickel was reduced with strong cathodic polarization and washed with water.

acid at high current densities there was in the first 30-60 min at first a sharp and then a slower increase in the radioactivity of the electrode during polarization and after the polarization had been disconnected. The steady radioactivity values were not very reproducible but in all experiments amounted to several tens of thousands of counts per minute, whereas all the necessary corrections amounted to about 1000 counts per minute in value. Calculated on the SO_4^{2-} ions for 10^{-2} N sulfuric acid solution the adsorbed quantities corresponded to values in the order of 10^{-8} g-eq/cm² of true electrode surface. The roughness factor was ~28. Assuming that one adsorbed particle is required for one nickel atom, the number of which in 1 cm² amounts to $1.48 \cdot 10^{15}$, we obtain a surface coverage corresponding to 4-5 monolayers. Even larger values were obtained in some experiments. When the electrodes were washed with water after such treatment (in air) a very slow decrease in their radioactivity was observed (Fig. 1, curve 1). Exchange of the adsorbed sulfur-containing particles by the anions of sulfuric acid or sodium sulfate, at $\varphi_r = 0.0$ V, takes place more quickly than desorption in water (curve 2). However, the adsorbed quantity remaining after exchange for 30-50 min amounted to about a monolayer.

The observed sharp increase in the amount of adsorbed sulfur-containing particles to extremely high surface coverages can be explained by adsorption of HS^- or S^{2-} anions, formed by cathodic reduction of SO_4^{2-} anions, with the formation of nickel complexes. Reduction of SO_4^{2-} can take place both directly and with participation of atomic hydrogen adsorbed on the nickel surface. In [6] it was suggested that sulfuric acid could be reduced and HS^- anions could form under the influence of atomic hydrogen, which in the opinion of Kesten and Feller [6] is formed during dissolution of nickel.

Electron-microscopic data show that after strong cathodic polarization the surface of nickel disintegrates,

and individual inclusions are found on it.* The latter may be due to the formation of chemical compounds in the form of a phase.

Phenomena like those described above were not observed after treatment of nickel in sulfuric acid at $\varphi_r = -0.25$ V. However, the adsorption values in this case amounted to about 0.4 monolayer. Such values cannot be wholly attributed to forces of electrostatic adsorption of the anions.

To eliminate the effect of previously adsorbed sulfur-containing particles, obtained by reduction of sulfuric acid with strong cathodic polarization, on the adsorption of the SO_4^{2-} anions the nickel was first treated in sodium hydroxide at the same high cathodic current densities as for the treatment in sulfuric acid. After this the electrode was washed in twice-distilled water saturated with hydrogen and then placed in sulfuric acid or sodium sulfate solution. The adsorption values for SO_4^{2-} and the adsorption kinetics in these cases were similar to those obtained after treatment at $\varphi_r = -0.25$ V in sulfuric acid. The kinetics of desorption in water and the exchange kinetics (Fig. 1, curves 3 and 4) differ significantly from those for treatment with high cathodic polarization in acid.

The adsorption of Na^+ cations on nickel from sodium sulfate solutions with pH 3, their desorption in water, and their exchange with the same cations of the solution after all forms of pretreatment take place very quickly (less than 1 min). The adsorption values for Na^+, however, are very large under all conditions and particularly after previous strong cathodic polarization in sulfuric acid or sodium sulfate and sulfuric acid. In the last case, even after the electrode had been washed for a long time in twice-distilled water saturated with hydrogen after cathodic preparation, the adsorption of Na^+ cations on it from 10^{-3} N Na_2SO_4 + 10^{-3} N H_2SO_4 solution at $\varphi_r = 0.0$ V amounted to about 0.08 monolayer.

The adsorption values for Na^+ cations almost coincide with the values for the adsorption of SO_4^{2-} from 10^{-4} to 10^{-1} N solutions of H_2SO_4 and $Na_2SO_4 + H_2SO_4$ (Fig. 2).

From the data in Fig. 2 it also follows that the dependence of the adsorption values for Na^+ and SO_4^{2-} on the concentration of sodium sulfate solution corresponds to the Freundlich isotherm, which is characteristic for a nonuniformly inhomogeneous surface. In addition, from these results it follows that H^+ cations have no effect on the adsorption of Na^+ both with equal concentrations and with a tenfold excess of the former. This was also shown by direct measurements of the dependence of the adsorption values for Na^+ on the pH of a sodium sulfate solution (10^{-3} N) (Fig. 3). Consequently, considerable preferential adsorbability of Na^+ cations appears under these conditions. With further increase in the acidity of the solution the adsorption of Na^+ drops, and with a c_{H^+}/c_{Na^+} ratio of 500 it becomes equal to zero.

The obtained results make it possible to consider that the adsorption of the anions of sulfuric acid or its reduction products takes place jointly with Na^+ or H^+ cations. The slowness of the adsorption of the anions, the large coverages of the surface with them, and the slowness of the desorption and exchange with SO_4^{2-} in solution demonstrates the chemisorption character of their adsorption on nickel. It can be supposed that the anions are adsorbed specifically and, possibly, with the formation of complicated complexes of the anionic type with nickel. The cations are attracted by the charge of the anions and do not form strong bonds with the nickel. A certain part of the sulfur-containing particles evidently form chemical compounds with nickel.

The results from the present work are of interest for investigations into the mechanism of the adsorption of sulfur-containing anions and their inclusion in the composition of electrolytic deposits of nickel.

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