INFLUENCE OF HALIDE ANIONS AND CERTAIN ORGANIC COMPOUNDS ON THE ELECTROCHEMICAL BEHAVIOR OF NICKEL IN ACID SOLUTION

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The influence of additives to a solution of 1 N H_2SO_4 on electrochemical reactions that take place on a nickel electrode was investigated. Halide ions increase the overvoltage of the discharging of H_3O^+ ions, as well as the anodic process of ionization nickel. Tetrabutylammonium cations inhibit the cathodic and anodic reactions, while anions of sulfonic acids accelerate the cathodic and decelerate the anodic reactions.

Halide anions, being adsorbed on the surface of cathodes, produce a change in the overvoltage η of the discharging of H_3O^+. There is a decrease in η on Hg and Zn [1-2] and an increase on Fe and Co [3-7]. Metal exist which occupy an intermediate position, for example, Pt, Ag, Cu, Cd, and Pb, the effect of halide ions on which is more complex [8-11]. The indicated difference in the action of halide anions is due to the fact that in the case of Ag, being specifically adsorbed, they are arranged in the outer shell of the double layer and shift the ψ_1-potential in the direction of negative values, while in the case of Fe and Co they are firmly bonded to the surface metal atoms by chemical bonds, frequently become part of the metallic shell of the double layer, and shift the ψ_1-potential toward positive potentials [3, 5, 7].

In the case of nickel, the effects of halide anions have received little study. According to [12], halide ions produce a decrease in the rate of solution of nickel and can be arrange in the series: $Br^- < F^- < Cl^- < I^-$. In [13,14], it was found that the Tafel' functions for the liberation of hydrogen in solutions of H_2SO_4, HCl, and HBr practically coincide, and it is concluded that there is no specific adsorption of Cl^- and Br^- ions on a nickel cathode. The influence of the adsorption of organic compounds on the electrochemical behavior of nickel was investigated in [15].

In this communication we cite the results of experiments on the study of the influence of the adsorption of halide ions, as well as certain organic compounds, on the kinetics of the discharging of H_2O^+ and the reaction of anodic ionization of nickel in H_2SO_4 solution.

As the electrodes we used spectrally pure nickel in the form of plates (containing Cu–0.00003%, Fe–0.00005%). Before the experiment, the plates were polished with fine glass powder, and then after thorough washing, were placed in a cell of the usual type for the polarization measurements, in which the electrode was subjected to cathodic polarization for 10 min before the measurement, at a current density of $2 \cdot 10^{-2}$ A/cm^2, to reduce the oxide film. The measurements were conducted in an atmosphere of hydrogen. Preliminary calcining of the electrode was not performed in most of the experiments, since this did not lead to any significant change in the polarization curve. The curves obtained for electrodes without preliminary calcining coincided well with the data of other authors [16, 17,18]. The solution obtained from double-distilled water and twice redistilled H_2SO_4 was preliminarily purified by cathodic polarization for 24 h on a platinized platinum grid. The potential of the nickel electrode was measured by the usual compensation method according to the hydrogen electrode in 1 N H_2SO_4 at t = 20 ± 1°C. To obtain steady-state conditions of the systems of reactions, the electrode was exposed for 2 min at each value of the current density to take the cathode curves and for 0.5 min to take the anode curves.

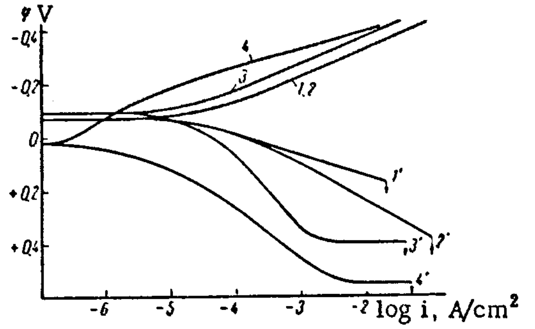

Fig. 1. Curves of the cathodic and anodic polarization of nickel in 1 N H_2SO_4 with additives (0.1 N): 1, 1') Without additives; 2, 2') KCl; 3, 3') KBr; 4, 4') KI.

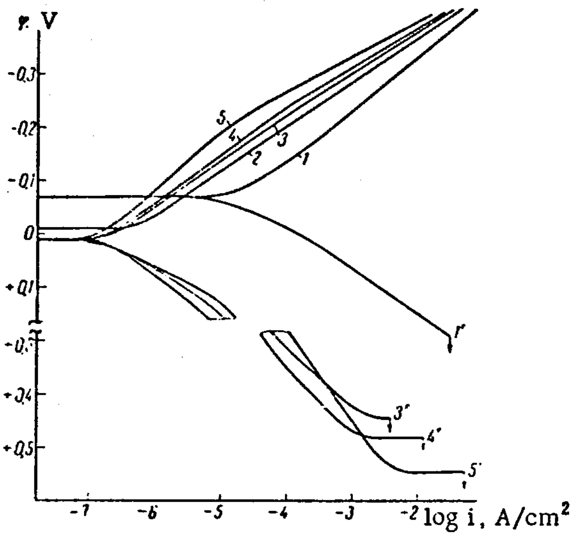

Fig. 2. Curves of the cathodic and anodic polarization of nickel in 1 N H_2SO_4, with an addition of KI: 1, 1') Without additive; 2) 10^{-4}; 3, 3') 10^{-3}; 4, 4') 10^{-2}; 5, 5') 10^{-1}.

As can be seen from Fig. 1, the cathodic curve of η_k versus log i_K in pure 1 N H_2SO_4 represents a Tafel' straight line with constants a = 0.525 V and b = 0.100 V. The anodic curve is also linear (b = 0.800 V). The steady-state potential was equal to $\varphi_s = -0.070$ V. The addition of 0.1 N KCl does not change η_K and b_K. However, for the anodic reaction, thanks to the increase in the adsorption of Cl ions on account of the increase in the positive charge of the nickel surface, b_A is observed to increase to 0.140 V, and a certain increase in η_A is also observed upon an increase in i_A. In this respect, nickel differs from the other metals of the iron group, the adsorption of Cl^- ions on which substantially increases η_K and η_A [3, 4, 6].

The ions Br^- and Cl^- increase η_K and η_A. In the presence of I^- ions, b_K (0.065 V) is smaller than in the case of the addition of Br^- ions (b_K = 0.095 V). This indicates that the I^- ions are more readily desorbed when the negative charge of the nickel surface is increased than are Br^- ions. An analogous effect is also observed in the case of Fe and cobalt cathodes [4, 6]. In the presence of Br^- ions, φ_s is shifted toward negative potentials ($\varphi_s = -0.095$ V), on account of the stronger suppression of the rate of the cathodic reaction in comparison with the rate of the anodic reaction, while in the case of I^- ions it is displaced toward positive potentials ($\varphi_s = +0.020$ V), on account of the opposite character of the influences on the indicated reaction. The anodic polarization curves on nickel in the case of additions of KBr and KI lose their linear course: when $i_A = 10^{-5}$-10^{-3} A/cm², there is a sharp increase in φ_A, which is probably related to an increase in the adsorption of halide ions and a strengthening of their bond to the surfaces of the nickel atoms. When the current is further increased, $i_A > 10^{-3}$ A/cm², φ_A becomes almost independent of i_A until complete passivation of the anode. The independence of φ_A from i_A at high values of i has been explained in the case of other anodes [19, 6] by insufficient rate of adsorption of Br^- (I^-) ions in comparison with the rate of removal of the inhibitor, together with the ionized surface atoms of the metal.

From Fig. 2 it is evident that at a concentration of 10^{-4} N KI, there is already a considerable increase in η_K and η_A. The shape of the anodic curves changes little with increasing concentration of the additive, but it differs substantially from the anodic curve for pure 1 N H_2SO_4. An analogous picture is also observed in the case of additions of KBr.

The table presents the characteristics of the polarization curves, obtained for nickel electrode in 1 N H_2SO_4 with an addition of organic compounds. The peculiarity of these curves, in contrast to the action of halide ions, lies in the fact that the Tafel' dependence is preserved both for the cathodic reaction and for the anodic reaction (until the moment of passivation of the anode $i \approx 10^{-2}$ A/cm²). In the table, all the values are cited in mV; φ_K and φ_A are given for the current density $i = 10^{-3}$ A/cm². TBAS represents tetrabutylammonium sulfate, SSA—sulfosalicylic acid; BSA—benzenesulfonic acid.

As can be seen from the table, the cations of tetrabutylammonium sulfate (TBAS) increase the overvoltage of the cathodic and anodic reactions, which agrees with the theory predicting that the specific and electrostatic adsorption of cations should lead to a displacement of the ψ_1-potential in the direction of positive values and should slow down the electrochemical reactions in acid solutions. Although $\Delta\eta_K$ is small, however, it is greater than in the case of electrodes of Fe and Co under analogous conditions. Nickel also differs from the metals just enumerated in that hexanol is adsorbed on its surface and gives a small increase in η_K and η_A. Organic ions of sulfosalicylic acid (SSA)

Additive	φ_K	$\Delta\eta_K$	φ_A	$\Delta\eta_A$	b_K	b_A
Without additive	−225	–	+60	–	100	80
TBAS 10^{-3}	−240	15	+95	35	120	80
TBAS 10^{-2}	−260	35	+120	60	125	85
Hexanol, sat.	−240	15	+110	50	120	80
SSA 0.01 M	−170	−55	+120	60	115	80
BSA 0.01 M	−180	−45	+120	60	115	75

and benzenesulfonic acid (BSA), in accord with the negative ψ_1-potential that arises during adsorption, lower the overvoltage of the discharging of hydrogen ions; however, they increase the overvoltage of the anodic reaction of ionization of nickel. On an iron cathode, SSA lowers η_K to a greater extent; however, it exerts no influence on the anodic reaction [20].

When halide anions and TBAS cations are present together, the shape of the polarization curves remains analogous to the curves in the presence of halide anions (without TBAS). The addition of KCl and KBr to a solution of H_2SO_4, where there is already an addition of TBAS, does not lead to any supplementary effect above the summary action of 0.001 N TBAS and KCl or KBr. However, the addition of TBAS (0.001 N) to a solution of 0.1 N KI in 1 N H_2SO_4 gives a supplementary effect exceeding the sum of the action of each additive individually ($\Delta\eta_K$ = 170 mV, as against the summary 115 mV). A small supplementary action of the summary additive of KI and TBAS is also observed on the anodic reaction.

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