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The effect of pyridine on the electrochemical parameters of the hydroxonium discharge at the copper cathode

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Abstract

In this work, we studied the electrochemical reduction of hydrogen (hydroxonium ion) from acidic aqueous solutions in the presence of a surface active substance – pyridine. H_2SO_4 (r.h.) was used as a reagent to study the discharge of hydroxonium cations. The effect of pyridine on the reduction of hydrogen cations was carried out in solutions of sulfuric acid (0.09; 0.18; 0.36 M) with pyridine additives from $1.4 \cdot 10^{-3}$ to $8.4 \cdot 10^{-3}$ M.

Potentiostatic studies were performed on a *Potentiostat P-30Jcom Elins* using a three-electrode cell. The working electrode (cathode) was made of M1 grade copper with an area of 0.09 cm^2; auxiliary (anode) – from a platinum plate with an area of 0.20 cm^2, the reference electrode is silver chloride (AgCl/Ag). The results are presented according to the average data obtained during 30 s of electrolysis in the potential region (-950-1100 mV for AgCl/Ag), with potentiometric measurements. The results are presented by the average data obtained in the initial 5 s of the process, in studies in the galvanostatic mode at current densities from 0 to 110 mV/cm^2. An increase in the constant current of load almost to a small extent influenced the change in overvoltage with time, as shown by galvanostatic studies. Overvoltage, on average, decreased from 3-6 to 1-2 mV in the first 5 seconds of the beginning of the process, during the study with or without pyridine. Overvoltage ceased to depend after 10-15 s on the time of galvanostation.

The effect of the addition of pyridine to the electrolyte was studied and it was shown that the negative effect of pyridine on the discharge of the hydroxonium ion increases with increasing acidity of the electrolyte. An increase in the density of exchange currents with a decrease in the content of sulfuric acid in the electrolyte is noted, which is associated with the approach of the electrode system to the equilibrium state. The decrease in the transfer coefficients of the hydrogen discharge reaction with an increase in the acid of content in the electrolyte and pyridine additives was explained by the distant position of the transition state localization from the electrode surface. The calculations of the reaction order for the hydroxonium ion in the presence and absence of pyridine in the electrolyte are presented. The obtained value of the reaction order, taking into account standard errors close to unity, allows us to conclude that at the initial stage, the hydroxonium of molecule is discharged, the products of which are atomic hydrogen, the HSO_4 anion and water. In the kinetics of the process of the discharge of hydrogen cations, the stages can further play an important role: surface diffusion of hydrogen ad-atoms, formation of gas bubbles and their desorption, adsorption of hydrogen by metal.

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