Study of the peculiarities of the electrochemical process on the gauze platinum anode in the solution of sulfuric acid

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The mathematical description of electrochemical evolving of oxygen on a platinum anode in the solution of sulfuric acid and the criteria for the mechanism of the process were offered [1]. Electrochemical evolving of oxygen takes place in the region of the anodic potential from 1.2 V to 2.2 V. If the main role in this process plays adsorption of water molecules the criterion of adsorption estimation can be the following dependence: $\frac{i}{2F} = f\left(C_{\mathrm{H_2O}}\right)$, where i – the anode current density; $C_{\mathrm{H_2O}}$ - the concentration of water molecules in the solution of sulphuric acid. The experimentally obtained dependence on the gauze platinum anode at the anode potential 1.8 V is complicated. Therefore, to describe the dependence the mathematical modelling was used. It was shown, that the adsorption isotherms of Langmuir, Temkin, Frumkin, Kisarov, BET do not describe the obtained dependence. However, the dependence (fig. 1) is described by the Dubinin-Astahov equation which consists of two addends, one of them is described electrostatic interaction of water molecules with a surface of the gauze platinum anode and another one is described the dispersing interaction [2]:

$$\mathrm{a} = \mathrm{a}_{01}\exp\left[-(\mathrm{A}/E_d)^p\right] + \mathrm{a}_{02}\exp\left[-(\mathrm{A}/E_e)^q\right],$$ where

$$\mathrm{a}_\mathrm{o} = \frac{\mathrm{W_o}}{\mathrm{V}^*}; \quad \mathrm{A} = RT\ln(C_\mathrm{S}/C)$$

a_{01} and a_{02} – the limiting adsorption of water molecules as a result of filling pores with small and large diameter correspondingly; C – the equilibrium concentration of H_2O in H_2SO_4; C_s – the limiting concentration of H_2O in H_2SO_4; Wo – the limiting volume of the adsorption area or the volume of micropores; V* - the molar volume of adsorbate; E – the characteristic energy of adsorption, indexes d and e belong to dispersing and electrostatic forces correspondingly; p, q – the parameters characterising ordering of molecules and ions in the adsorbed state.

To determine the parameters p, q, E, a_o the Rosenbrock method of unconditional optimisation was chosen.

The following equation was calculated:

$$\mathrm{a} = 1.43\cdot 10^{-8}\cdot\exp\left[-\left(\frac{\mathrm{A}}{82}\right)^{0.45}\right] + 4.84\cdot 10^{-9}\cdot\exp\left[-\left(\frac{\mathrm{A}}{6738}\right)^{3.56}\right]$$

According to this model dispersing interaction of water molecules with the adsorbate in micropores composes 75 % , and electrostatic interaction composes 25 %.

The similar equation was obtained for adsorption of $\mathrm{HSO_4^-}$ at the anode potential 2.3 V, when the main reaction on the anode is formation of $H_2S_2O_8$. The obtained dependence $\frac{i}{2F} = f\left(C_{\mathrm{HSO_4^-}}\right)$ on the gauze platinum anode is described by the Dubinin-Astahov equation with two addends also($C_{\mathrm{HSO_4^-}}$ - the concentration of $\mathrm{HSO_4^-}$ in the solution of sulphuric acid).

The obtained equation is the following:

$$\mathrm{a} = 7.23\cdot 10^{-8}\cdot\exp\left[-\left(\frac{\mathrm{A}}{1122}\right)^{3.58}\right] + 8.12\cdot 10^{-8}\cdot\exp\left[-\left(\frac{\mathrm{A}}{2310}\right)^{1.62}\right]$$

In this case the specific (donor-acceptor and dispersing) interaction of $\mathrm{HSO_4^-}$ with adsorbate in micropores composes 53%, and electostatic interaction composes 47%. The value of characteristic energy (E) allows to determine the size of micropores.

Thus, adsorption of water molecules or $\mathrm{HSO_4^-}$ on the gauze platinum anode can be describe with the help of theory of volume filling of micropores.

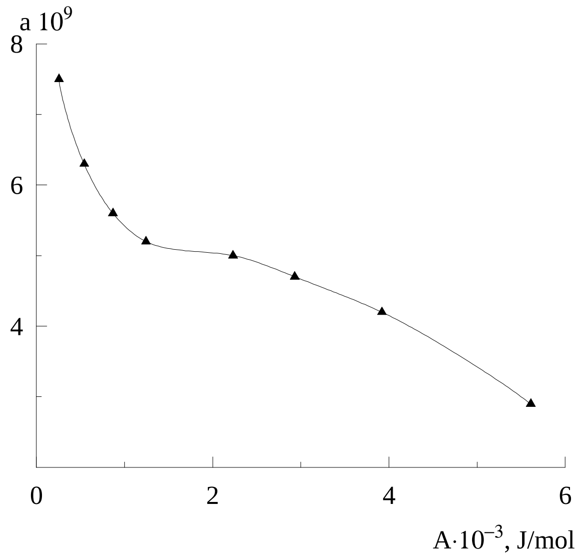

Fig. 1. The dependence of the limiting adsorption water molecules (a) on the differential molar work of adsorption (A)

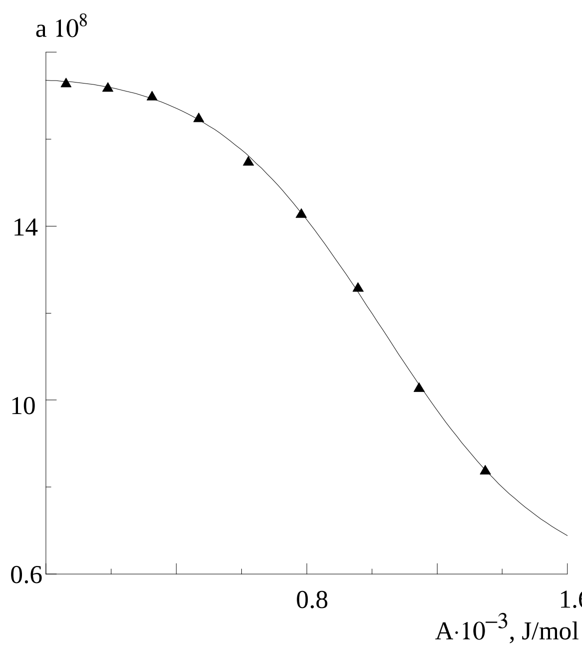

Fig. 2. The dependence of the limiting adsorption of $\mathrm{HSO_4^-}$ (a) on the differential molar work of adsorption (A)

References

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