The Effect of Atomic Hydrogen on the Dissolution of Iron in the presence of tetraethylammonium cations
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The investigation of the corrosion and electrochemical behavior of iron in acid solutions showed that one the basic problems is demarcation between the effects of adsorbed and absorbed hydrogen on the rate of the process under study.

Addition of some surface-active compounds in solution can change the ratio of the hydrogen surface coverage ($\theta$) to the hydrogen concentration in the metal ($C$). Then, having obtained the dependences of the iron dissolution rate on $\theta$ (or on C) at different $\theta/C$ ratios, one can try to demarcate the effects of the two forms of atomic hydrogen on the metal dissolution rate.

The goal of this study to investigate the effect of the adsorbed and absorbed hydrogen on the iron dissolution rate in the presence of tetraethylammonium (TEA) cations, which are known as inhibitor of hydrogen absorption into metal.

The experiments were carried out with a rotating disc electrode made of iron (0.005% C) with a surface area of 0.56 cm$^2$. The cyclic rectangular potential pulses (frequency 5x10$^{-2}$ to 2.5x10$^{-5}$ s$^{-1}$, amplitude 0.05 to 0.25 V) were set with a potentiostat PI-50. The driving time of potential accurately to 5 mV is no more than $1.5 \times 10^{-6}$ s. The amount of dissolved iron was determined using the photocolorimetric analyses of electrolyte.

The rate of hydrogen penetration through the 100 or 150-µm think iron (0.009% C) membrane was measured in a Devanathan-Stahurski cell. For studying the effect of absorbed hydrogen on the iron dissolution rate, the modified cell (bipolar electrode) was used.

The experiments were carried out at room temperature in an argon-deaerated 0.5 M Na$_2$SO$_4$ + 0.25 M H$_2$SO$_4$ solution (pH 1.3). An admixture of 10 mM tetraethylammonium bromide was additionally introduced.

The rate constants of hydrogen evolution and permeation into iron were determined using IPZ analyses with taking into account the surface coverage of TEA cations. The hydrogen surface coverage of iron was calculated according expressions given in 4.

The cyclic stepwise-pulse potential variation was used to obtain the dependences of iron dissolution rate on hydrogen surface coverage. The dissolution rate was found to decrease with an increase in the frequency and amplitude of potential pulse. The dependences of iron dissolution rate on hydrogen surface coverage in solutions with and without TEA cations were compared. It was shown that TEA cations inhibit the iron dissolution because they increase the amount of adsorbed hydrogen.

The effect of the absorbed hydrogen on the Fe dissolution rate was studied by the bipolar electrode method. The anodic current density ($i_a$) was measured at the working side of a membrane while varying the cathodic current density at other side of membrane and, correspondingly, the hydrogen permeation rate in metal. The $i_a$ values obtained were compared with the rate of anodic iron dissolution without cathodic polarization of the other membrane side ($i_{a,oc}$). A sharp bend in the curves of $i_a/i_{a,oc}$ vs. C recorded in the blank and inhibited solutions is observed at the same hydrogen concentration in iron near working side ($C \approx 3x10^{-2}$ mol m$^{-3}$) and different permeation rate of hydrogen through the membrane. One can assume that at $C \geq 3x10^{-2}$ g-at. m$^{-3}$ the metal undergoes plastic deformation at the working membrane side. As a result, the number of dislocations in its crystal lattice increases and, accordingly, the possible centers or iron dissolution become more numerous.

At the same time, with an increase in C, the absorbed H atoms reach the metal surface more rapidly, thus increasing $\theta$. In this case, a large number of possible sites of iron dissolution are occupied by hydrogen atoms. A weak dependence of $i_a$ on C (at $C \geq 3x10^{-2}$ g-at. m$^{-3}$) is due to a reciprocal compensation of these two factors. The iron dissolution rate becomes dependent on the ratio between the amounts of adsorbed and absorbed hydrogen ($\theta/C$). The iron dissolution rate decreases with an increase in the $\theta/C$ ratio, which in turn depends on the composition of electrolyte.

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REFERENCES

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