Hydrogen Overvoltage on Iron in the Ethylene Glycol and Aqueous HCl Solutions with Constant Ionic Strength Containing Thiocyanate-ions.

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Corrosion damage of metals, first of all, various steels is often caused by their hydrogenation with following considerable change for the worse of their mechanical properties. It is often supposed a direct connection between an efficiency of the hydrogenation and a reduction rate of the various proton donors (H$_2$O$^-$ in the acidic media, H$_2$S (HS$^-$) and H$_2$CO$_3$, HCO$_3^-$ in the conditions of the hydrogen sulphide corrosion and the carbonic-acid one respectively). The hydrogenation rate and the absorbed hydrogen volume can essentially increase in the presence of the process stimulators, one of them is thiocyanate-ion. At the same time a stimulation of the hydrogenation is often in the complicated dependence from the stimulator concentration[1,2], its the various anion composition and pH.

Therefore the influence of the KCNS concentration (1 – 10 mM) on the hydrogen overvoltage on iron has been studied in the nonaqueous ethylene glycol and aqueous solutions of the electrolyte composition X M HCl + (1-X) M LiCl. Taking into account the different physicochemical properties of the solutions on a base of the mixed solvents, the media with a large alcohol concentrations (2–20 wt.% H$_2$O) and the large water ones (80–90 wt.%H$_2$O) has been studied too. By use of the aqueous saturated silver/silver-chloride electrode and the equilibrium hydrogen electrode in the investigated solution, the kinetic parameters of the hydrogen evolution reaction (HER) $d\ln i\ln i$ at a constant potential (E) and a constant hydrogen overvoltage (\eta) have been estimated in the investigated solutions and other ones: $dE/d\ln i$, $dE/d\ln i$, $d\eta/d\ln i$, $d\ln i/d\ln i$, where $i$ is the HER rate. It has been confirmed that the every mixed solvent composition must be considered as an independent solvent determining an adsorption ability for its components and co-adsorption of the surface active anions (Cl, CNS). The solvent molecules solvating the electrode surface or being present in the solution volume are not indifferent to the HER kinetics and the rate-determining step[3]. Even being present only in the solution volume, the water molecules interact with the adsorbate particles causing a differentiation of the active centers on iron surface responsible for the HER proceeding in the conditions of the slow discharge or the slow chemical recombination.

References