Short Communication

The Anodic Dissolution of Iron. IX. Strong, Selective Inhibition Caused by Acetylene

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Dedicated to Jannik Bjerrum on the occasion of
his 70th birthday

It has been shown that the anodic dissolution of iron takes place *via* two different reactions.^{1–5} A transition region separates the I_1 reaction at lower potentials and the I_2 reaction at higher potentials. These experimental observations have been interpreted by two kinetic models,^{2,4} both of which assume a stepwise formation of adsorbed intermediates containing Fe(I) or Fe(II) species and OH^- -groups. According to the author's model the oxidation of Fe(I) during the I_1 reaction can only take place at a defect site in the surface. The precise characteristics of the transition between the I_1 and the I_2 reactions are explained by adsorption of an Fe(II) intermediate of the I_2 reaction starting at defect sites and thereby blocking the I_1 reaction. As a consequence of this idea it has recently been predicted⁵ that a particular type of inhibition should be expected, if the only function of a given inhibitor molecule is to adsorb strongly at defect sites, yet less strongly than the Fe(II) intermediate of the I_2 reaction. We should then expect complete inhibition of the I_1 reaction and rather little influence on the I_2 reaction.

Acetylene was selected for use in the experiments. Earlier reports ascribe the inhibition due to this molecule to strong adsorption at the metal surface,⁷ but also secondary products formed by hydrogenation and polymerization are assumed to contribute to the observed effects.⁶ In order to avoid formation of secondary products we used the following procedure: A polarization diagram was recorded with an iron electrode in a given electrolyte solution, through which pure nitrogen was being bubbled.

Nitrogen was quickly replaced by acetylene, and the polarization diagram for the acetylene saturated solution was recorded. Acetylene was then replaced by nitrogen, and the final polarization diagram was recorded. The changes between the first and the last diagrams were found to be very small. We also found no difference between diagrams obtained with the iron electrode at anodic or cathodic potentials during the introduction of acetylene. These observations indicate a reversible adsorption of acetylene, and the observed short-term effects can be attributed to the simple molecule.

Experimental procedures have been described previously.¹ The acetylene was 99 % pure, the major contaminant being acetone. Two samples were used for rotating disk electrodes, pure iron (Johnson Matthey Chemicals Ltd., metallic impurities <15 ppm) and a 0.12 % carbon steel (annealed at 1350 °C). The disk surface was finished by diamond-polishing or by electro-polishing. Irrespective of the purity of the metal and the method of polishing the results for a given solution were similar.

The diagrams for acetate-perchlorate mixtures and for a 0.5 M $(\text{NH}_4)_2\text{SO}_4$ solution are well represented by Fig. 1. The agreement with the expectations is good, but in order to verify that the I_1 reaction is completely inhibited at potentials, where the I_2 reaction is unaffected, an additional analysis was performed. In the absence of inhibition the current density (cd) in the transition region is given by:^{1,3–5}

$$i = I_1(1 - \theta_1) + I_2\theta_1 \quad (1)$$

where i is the measured cd at a given potential, I_1 and I_2 are extrapolated values according to the two Tafel lines, and θ_1 is a fraction developing according to a Langmuir adsorption isotherm. Plots of $\log [\theta_1/(1 - \theta_1)]$ vs. potential are linear at not too low values of θ_1 and have slopes close to 0.03 V. Hence inspection of the plots shown in Fig. 2 allows the conclusion that the observed anodic current in the presence of acetylene is a pure I_2 -contribution, since plot b (constructed exclusively on the basis of the second term on the rhs of (1)) has very closely the same form as plot a.

Fig. 1 indicates a definite decrease in the cathodic current level in the presence of acetylene. However,

Fig. 1. Polarization diagram for a 0.12 % C-steel electrode in 0.99 M NaClO₄, 0.01 M Na-acetate, ca. 1 M acetic acid, pH = 2.44, 27 °C, 3000 rpm. Rate of potential sweeps: 5×10^{-4} V/s. The recordings were made going from anodic to cathodic potentials. a: Without acetylene, b: With acetylene saturated solution (1 atm). Extrapolated anodic and cathodic Tafel lines intersect at the corrosion potentials and indicate the magnitudes of the corrosion cd's in the two situations. A decrease in corrosion cd by 87 % is noted in passing from a to b.

Note: The highly increased slope at the low end of the I₁ region is a genuine feature presently being investigated.

Fig. 2. Diagram of $\log [\theta_1(1 - \theta_1)]$ vs. potential calculated for the curves shown in Fig. 1, where a and b refer to the experiments without and with acetylene, respectively. The two straight lines are close to parallel, and they have a slope near 0.036 V.

recording of the cathodic current at a fixed potential during the introduction of acetylene showed a considerable increase in current prior to the decrease. This observation obviously explains earlier reports of a short-term increase in corrosion rate prior to the establishment of efficient inhibition.⁶

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