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Iron dissolution in aqueous AOT solution

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Abstract

The effects of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) on the electrochemical behavior of iron were studied by potentiodynamic and potentiostatic techniques and open-circuit potential measurements. Experiments were made in both neutral and alkaline AOT solutions (pH 7 and pH 12). It was found that AOT-assisted dissolution is initiated on a passivated iron surface and that the oxidation current leads to the formation of a gel-like film on the electrode surface. This dissolution process was investigated as a function of pH, potential, and electrode rotation rate and the corrosion products were characterized by polarizing microscopy, SEM/EDX, and IR spectroscopy. The gel-like material is a mixed NaAOT–$Fe(AOT)_3$ lamellar mesophase and a structure for this mesophase is proposed.

Keywords: Iron; AOT; Dissolution; Electrochemistry; Lamellar mesophase

1. Introduction

There are several uses of surfactants in the field of electrochemistry, principally because these molecules modify the electrode surface. One of the most important applications is related to the protection of metallic materials against corrosion [1]. The surfactant adsorption onto the metal surface normally inhibits the corrosion of the substrate. While many papers have been devoted to the study of interaction between the metal and the surfactant, which was obviously analyzed in the presence of an aggressive agent such as the chloride ion [2,3], little is known of this interaction in solutions containing only the surfactant.

It has been also demonstrated that surfactants are effective electrolytes for chemical or electrochemical synthesis of conducting polymers [4–7]. The surfactant molecules not only alter the electrode surface, facilitating the electropolymerization process, but also act as a dopant conditioning the properties of the polymer matrix. One of the motivations of this work originates from the fact that when polypyrrole was electrosynthesized onto iron electrodes in the presence of AOT, a gel-like product surrounding the polymer film was observed [8].

On the other hand, a widely employed method for obtaining size-controlled nanoparticles is based on the use of water-in-oil microemulsions, which are usually stabilized by AOT [9,10]. The produced materials are often metals. Thus, it is also of interest to study the interactions between AOT and the metal surface.

In this work we studied the electrochemical behavior of iron in aqueous AOT solutions. For this purpose, techniques including cyclic voltammetry, potential step methods, and measurements of the open-circuit potential (OCP) were used to clarify the role of the surfactant. The characterization of the electrode surface was done using polarizing microscopy, SEM/EDX, and IR spectroscopy.

2. Experimental

Disc electrodes made from pure iron rods embedded in a Teflon holder with an exposed area of 0.07 cm^2 were used as working electrodes. Before each experiment, the electrodes were polished with successively finer grades of SiC emery paper up to 1000 and then degreased with acetone and washed with triply distilled water. The auxiliary electrode was a large Pt

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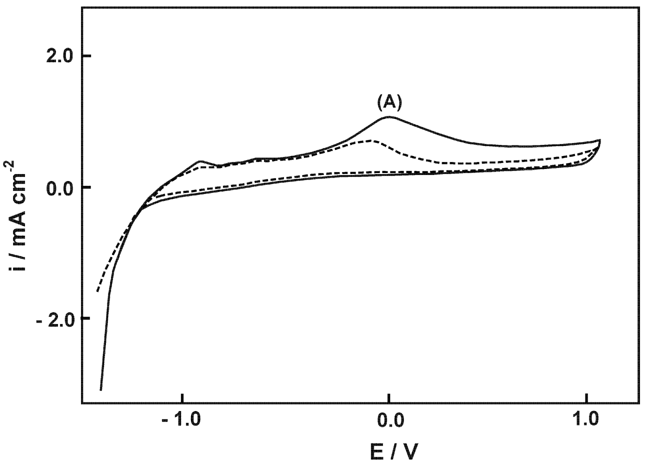

Fig. 1. Potentiodynamic polarization at 0.05 V s^{-1} in 0.05 M AOT, pH 7 solution. Scans 1 (full line) and 5 (discontinuous line) are displayed.

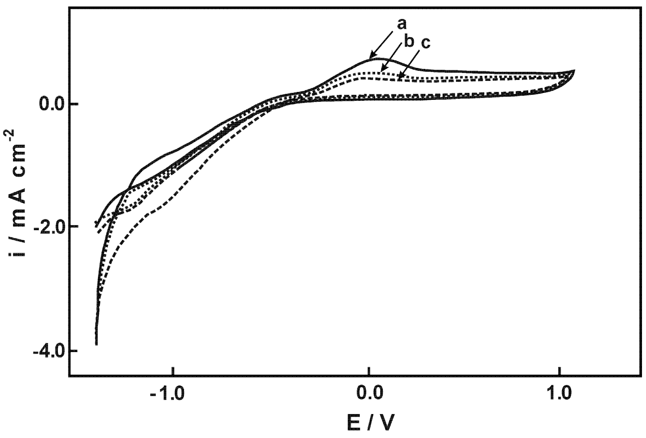

Fig. 2. Potentiodynamic polarization at 0.05 V s^{-1} in 0.05 M AOT, pH 7 solution at different rotation rates: (a) 200, (b) 500, and (c) 800 rpm. The first cycle is displayed.

sheet. Potentials were measured against a SCE reference electrode connected through a Luggin–Haber capillary tip and are given so throughout this work. Electrolyte solutions were prepared from analytical grade chemicals. The pH was adjusted by NaOH addition. Potentiodynamic and potentiostatic measurements were performed with a PAR Model 273A potentiostat–galvanostat. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive X-ray analyzer were used to examine the electrode surface characteristics. Microscopic observations were carried out in an Ernst–Leitz Wetzlar crystallographic microscope. Infrared spectra were made with a Nicolet FT-IR Model Nexus 470 infrared spectrophotometer. Iron and sulfur were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

3. Results and discussion

3.1. Electrochemical results

The voltammograms for the first and fifth cycles of iron in 0.05 M AOT, pH 7 solution are shown in Fig. 1. The first anodic scan presents anodic peaks in the potential range between −0.80 and −0.50 V. Active dissolution peaks have been observed for iron in different electrolytes at neutral pH [11,12]. Basically, the formation of a complex mixture of Fe(II)-containing oxide and Fe(II)-containing salts on the electrode surface in this potential range has been postulated. It was reported that passivation conferred by Fe(III)-containing oxide occurs at more positive potentials followed by oxygen evolution. In the presence of AOT a significant anodic peak at 0.05 V can be seen (peak A). As the AOT concentration decreases, the anodic process associated with this peak is initiated at higher potentials, presenting smaller currents. These results support the occurrence of AOT-based dissolution on the electrode surface.

The potentiodynamic runs presented in Fig. 1 indicate that the total anodic charge cycled decreases progressively until a stabilized response is achieved. After one complete voltammetric cycle the total cathodic charge is smaller than the anodic one and there are no distinguishable cathodic peaks in the reverse scan, indicating that the products of the oxidation process are not completely reduced. No reduction peaks were observed even when the potential limit was extended to −2.0 V. Visual observation of the sample submitted to the potentiodynamic runs showed a gel-like product on the electrode surface. Thus, it is reasonable to suppose that the gel-like product is a compound containing AOT and oxidized iron that thickens at each new potential cycle.

The electrodissolution process was also analyzed on a rotating iron disk electrode. The first potentiodynamic cycles obtained at different rotation speeds are presented in Fig. 2. The peak associated with the AOT-assisted dissolution practically disappears at the second anodic scan (not shown in the figure). The more significant feature of the curves is that the current peak decreases as the rotation rate increases. This behavior can be explained by assuming increased oxygen transport from the solution to the electrode surface, stabilizing the passive oxide film [13].

Different potentiodynamic behavior was obtained when a 0.05 M AOT pH 12 solution was employed, sweeping the potential between −1.40 and 1.10 V (Fig. 3). During the positive scan, anodic waves are observed in the potential range between −1.2 and −0.4 V, which were attributed to the formation of iron oxides with different stoichiometry [14,15]. An anodic peak at very positive potentials is observed in the presence of AOT (peak A). This current peak does not appear in pure 0.01 M NaOH solution. The more positive potentials needed to initiate AOT-assisted dissolution in alkaline solution can be explained by assuming that more protective oxide film is formed onto iron electrodes as the pH is increased. Although in smaller amounts, the gelatinous film was also obtained after cycling in the alkaline AOT-containing solution. Peak A is initiated at a potential very close to that corresponding to oxygen evolution in 0.01 M NaOH solution. Oxygen evolution occurs on top of the passive layer at potentials more positive than 0.6 V, shifting the pH to more acid values. As a result, the destabilization of the passive layer allows the formation of a product containing AOT and Fe(III). The anodic peak disappears under rotation, which re-