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ANTICORROSIVE PROTECTION OF CARBON STEEL BY ELECTROSYNTHESIS OF POLYANILINE

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ABSTRACT. The corrosion of carbon steel in 0.5 M H_2SO_4 and its inhibition in presence of electrosynthesized film of polyaniline (PAN) were investigated by using Tafel polarization (TP) and electrochemical impedance spectroscopy. The surface morphology of the carbon steel before and after aniline electropolymerization was also investigated. TP showed a significant shift of the corrosion potential towards more negative values at the same time with the decrease of the corrosion current density. This fact suggests that the polymeric film behaves as a mixed inhibitor, acting predominantly on the cathodic process. Microscopic images showed a clear modification of the surfaces morphology when the carbon steel was corroded in presence of the inhibitor.

Keywords: *carbon steel; anticorrosive protection; electropolymerization*

INTRODUCTION

Quite recently in electrochemistry is a growing interest in conducting polymers, particularly polyaniline, polypyrrole, polytiophen or mixed polymers of these ones, for the fabrication of anticorrosive protective coatings [1-10].

The polyaniline (PAN) can be easily obtained electrochemically on electrodes in the iron group, without any pretreatment, because the passive layer is a conducting one. From the other hand, the aniline (ANi) polymerization on metallic electrodes covered with insulating passive layers does not take place or only some cristalizing centres are formed. Under particular conditions, the mechanism of nucleation and growth for conducting polymers was found to be a three dimensional (3-D) instantaneous one [11-15].

The polymerization reaction of ANi, carried out by chemical or electrochemical methods, gives several products such as: leucoemeraldine (the completely reduced form), protoemeraldine, emeraldine (the neuter form), nigraniline, pernigraniline (the completely oxidated form). These forms of PAN are differentiated through the number of protons associated with the nitrogen atom, a number which also determines the degree of polyaniline oxidation. It has been observed that the electrochemical properties of PAN are directly

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influenced by many parameters such as: the nature of the anion associated to the protoning agent; the nature of the sublayer; the molecular mass; the solvent nature; the current density; the applied potential; the agitation; the temperature; the electronegativity and the solvation degree [16-20].

DeBerry [21] found that a decrease in the corrosion rate occurred for a prepassivated steel coated with an electrochemically generated PAN film. In this case, the polymer acts as a redox catalyst and a more noble metal with respect to iron.

Wessling [22] has established a general reaction mechanism, according to which PAN intervenes in the reaction between oxidizable metal and oxygen/water to form a passivating oxide layer.

RESULTS AND DISCUSSION

Tafel polarization

Tafel polarizations curves were recorded with a carbon steel electrode (surface area was 2 cm^2) immersed in 0.5 M H_2SO_4 and 0.5 M H_2SO_4 solutions containing different concentrations of ANi, at room temperature and scan rate of 10 mV/sec. The extrapolation of anodic and cathodic Tafel lines, corresponding to the corrosion domain controlled by charge transfer, gives the corrosion current density, i_{corr} and the corrosion potential, E_{corr} (Figure 1).

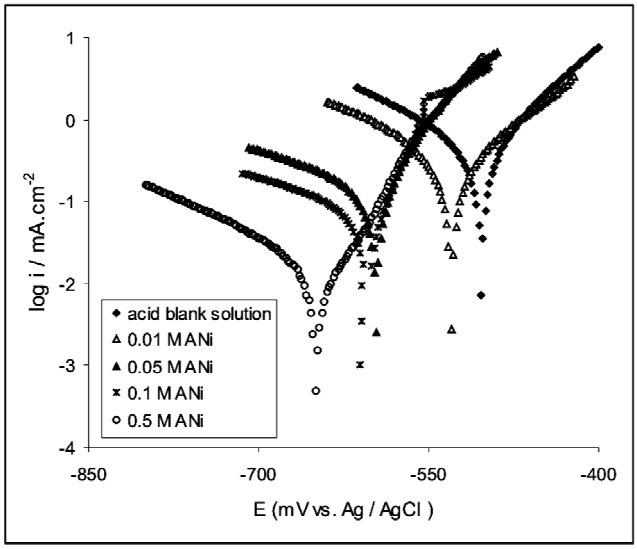

Figure 1. Tafel diagram of carbon steel corroded in 0.5 M H_2SO_4 solutions in absence and in presence of ANi inhibitor.

The cathodic and anodic polarization curves exhibit a typical Tafel behavior. The addition of ANi increased both the cathodic and anodic overvoltages and caused mainly parallel displacement to the more negative and positive values, respectively. The corrosion current density ($i_{corr.}$) decreased with the increase of ANi concentration, indicating that this compound acts as an inhibitor, and the degree of inhibition depends on the inhibitor concentration. The degree of coverage (θ) of the surface of carbon steel was calculated using the following relation:

$$\theta = \frac{i'_{corr} - i_{corr}}{i'_{corr}} \quad (1)$$

where i'_{corr} and i_{corr} are the corrosion current densities in absence and in presence of inhibitor, respectively. These values were obtained by the extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. The degree of coverage increases with the inhibitor concentration, while the density of corrosion current decreases with the inhibitor concentration (Figure 2).

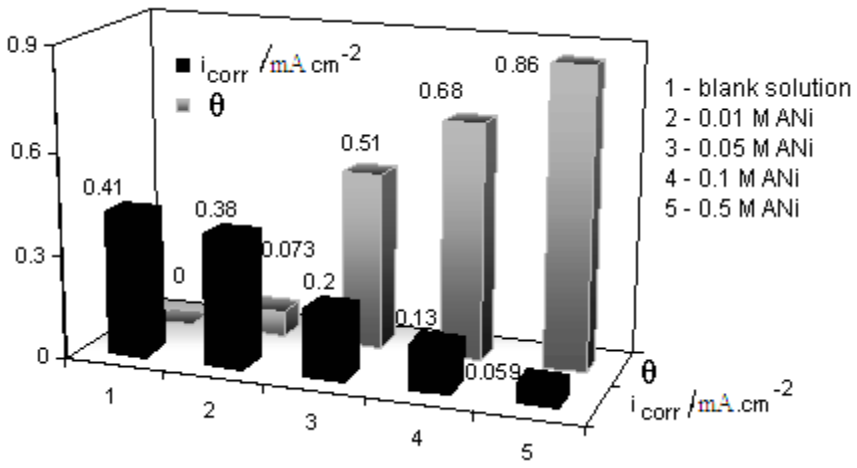

Figure 2. Variation of the corrosion current and the degree of coverage with the concentration of aniline for the carbon steel corroded in 0.5 M H_2SO_4, at room temperature.

The presence of inhibitor molecules can change the texture of carbon steel by electro-polymerization of aniline, which consequently results in the formation of impermeable layer. This layer restrains faradic processes such as electrode oxidation and the exchange of electrons between the electrode and solution. The behavior of this blocking film is attributed to its compactly packed structure, which obstructs the approach of solution SO_4^{2-} ions to the electrode surface. This behaviour shows that the addition of ANi reduces

anodic dissolution and also retards the hydrogen evolution reaction. This suggests that although inhibition is of mixed type, it is predominantly cathodic. The inhibition efficiency (IE %) was calculated using the relation:

$$IE = \theta \cdot 100 \quad (2)$$

The corrosion current densities decreases from a high value of 0.41 mA/cm^2, corresponding to unprotected carbon steel, to 0.059 mA/cm^2 for PAN protected carbon steel in presence of 0.5 M aniline and 0.5 M H_2SO_4. This behaviour proves the inhibition of the corrosion process by the polymer coating. The magnitude of this protective effect is proportional to aniline concentration.

As it can be observed from figure 3, the decrease of the corrosion current densities is associated with a shift of the corrosion potential towards more negative values. This fact suggests that polyaniline is a mixed inhibitor which acts predominantly cathodically.

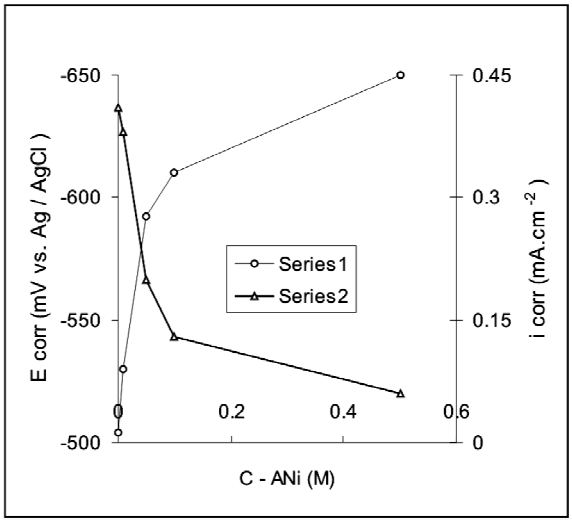

Figure 3. Variation of the corrosion potential and the corrosion current with the concentration of aniline for the carbon steel corroded in 0.5 M H_2SO_4, at room temperature.

Adsorption isotherm

Different adsorption isotherms were found to describe the adsorption of the inhibitors on steel. In the case of our results, it was found that the experimental data fitted well to the thermodynamic-kinetic model of El-Awady *et al*. [23] (figure 4), which is a modification of the Flory-Huggins adsorption isotherm. The model may be formulated as equations 3:

$$\log \theta /1 - \theta = \log K' + 1/n \log c \quad (3)$$

where *c* is the concentration of the adsorbate, *θ* is the coverage degree and *n* is the number of inhibitor molecules occupying one active site. The binding constant *K* is given by:

$$K^{(1/n)} = K' \quad (4)$$

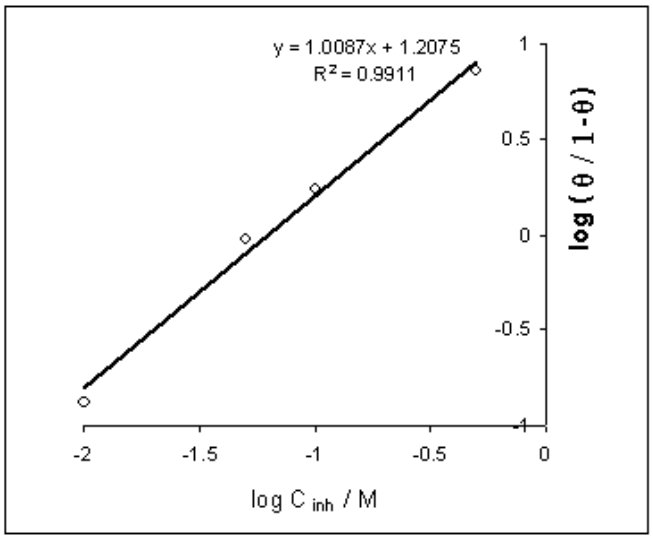

Figure 4. El-Awady *et al.* thermodynamic-kinetic model for mild steel in 0.5 M H2SO4 solution containing aniline.

The efficiency of a given inhibitor is a function of both the magnitude of its binding constant *K* and the number of active sites (n) which it is able to block, the first parameter being the most important [23]. Large values of *K* mean better and strong interaction, while small values of *K* mean that the interaction between the inhibitor molecules and the metal is weaker [24, 25]. Hence, according to the obtained numerical value of *K* (1.2), weak surface interactions occur between the inhibitor molecules and the carbon steel. The value of *n* obtained was practically one, suggesting that an inhibitor molecule will occupy one active site on the surface of carbon steel [23].

Electrochemical impedance spectroscopy (EIS)

In order to investigate the polyaniline coated carbon steel surface, measurements using electrochemical impedance spectroscopy were performed too (figure 5).

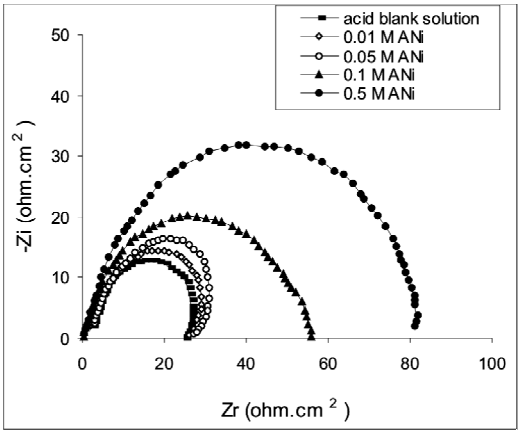

Figure 5. The electrochemical impedance spectra of carbon steel corroded in corroded in 0.5 M H_2SO_4 solutions in absence and in presence of ANi inhibitor.

Figure 5 shows the impedance measurements of a carbon steel electrode in 0.5 M H_2SO_4 solution and in 0.5 M H_2SO_4 containing ANi in different concentrations vs. Ag/AgCl reference electrode, in the frequency range from 10^5 to 10^{-1} Hz with a value of 10 mV for the amplitude. In the case of the inhibitor film, the impedance spectrum is represented like a Nyquist diagram with a capacitive arc of circle more or less leveled, which presents a phase shift comparative with the real axe. This phase shift is due to the density variations or to the composition of the film or of the electrode surface coating. The size of the capacitive arcs of circles phase differed comparative with the axes is increasing in the case of solution containing the inhibitor. The formed film is not tridimensional; the impedance diagram would be more complex. For an enough thick film (some μm), the impedance spectrum from the Nyquist plot is formed from two capacity arcs of circles more or less uncoupled at certain frequencies. As shown in the Figure 5 a typical Nyquist diagram is obtained. As shown in Figure 5 when polyaniline film is deposited from 0.5 M H_2SO_4 solution on the carbon steel electrode a semicircle with a different diameter is obtained, in higher frequency region related to charge transfer process. This region is electrically described by a resistance in parallel with a capacitor related to the double-layer. In this region the reaction is purely kinetically controlled. For the description of EIS measurements an equivalent circuit is suggested in figure 6, where (R_s) is the solution resistance of the bulk electrolyte, (C_{dl}) represents the double layer capacitance of the electrolyte at the metal surface and (R_p) is the polarization resistance of the metal. The impedance parameters derived from EIS measurements and respective fitting results (e.g. C-steel / 0.5 M H_2SO_4 solution / 0.5 M ANi) are given in Table 1 and figure 6. The fitting results show that R_s, and C_{dl} decrease and R_p increases, suggesting that the amount of inhibitor molecules absorbed increases.

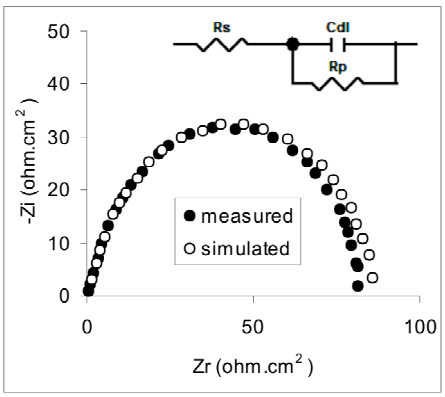

Figure 6. Equivalent circuit model for the studied inhibitor and the fit results for C-steel in 0.5 M H_2SO_4 solution containing 0.5 M ANi.

According to the data obtained from Nyquist plot it can observed that R_p increases with increasing ANi concentration. It is clear that the presence of PAN film produced a higher R_p value, which is an indication of the formation of an effective protective layer that hindered corrosion, which indicates that this film is formed by aniline polymerization. The electrode coverage (θ) is a key factor, which can be used to estimate the surface state of the electrode and it is related to the charge transfer resistance. According to this assumption, the following equation for the apparent fractional coverage of the electrode can be used:

$$\theta = 1 - \frac{R_p^0}{R_p} \tag{5}$$

where R_p^0 is the polarization resistance of carbon steel corroded in acidic medium in absence of the inhibitor and R_p is the polarization resistance of carbon steel corroded in acidic medium in presence of the inhibitor. The variation of R_p, the degree of coverage *(θ)* and EI(%) with the concentration of ANi for the carbon steel electrode in 0.5 M H_2SO_4 is presented in Table 1. These results are consistent with those obtained by Tafel polarization.

Table 1. Electrochemical parameters obtained from impedance measurements for C- steel in 0.5 M H_2SO_4 solution containing ANi.

c-ANi (M)	R_s *(Ω cm^2)*	C_{dl} *(μF cm^{-2})*	R_p *(Ω cm^2)*	*θ*	*IE (%)*
0	2.897	478.4	39.4	0	0
0.01	2.627	459.1	46.47	0.15	15
0.05	2.468	443.5	70.6	0.44	44
0.1	1.959	339.2	161.82	0.75	75
0.5	1.798	259.7	264.3	0.85	85

Surface characterization

The morphology of carbon steel surface after corrosion in 0.5 M H_2SO_4 solution (Figure 7a), and in 0.5 M H_2SO_4 solutions containing aniline was examined with a metallographic microscope. Figure 7 shows the evidence of formation of a thick film on the surface of carbon steel. In ”b”, ”c”, ”d”, ”e” cases the formation of specific layers of electrodepositions are observed; it is difficult to assess that they would be characteristic of a PAN or PAN/ANi. The corrosion spots are reduced in intensity in the case of carbon steel corroded in 0.5 M H_2SO_4 containing ANi (Figure 7b, 7c, 7d, 7e).

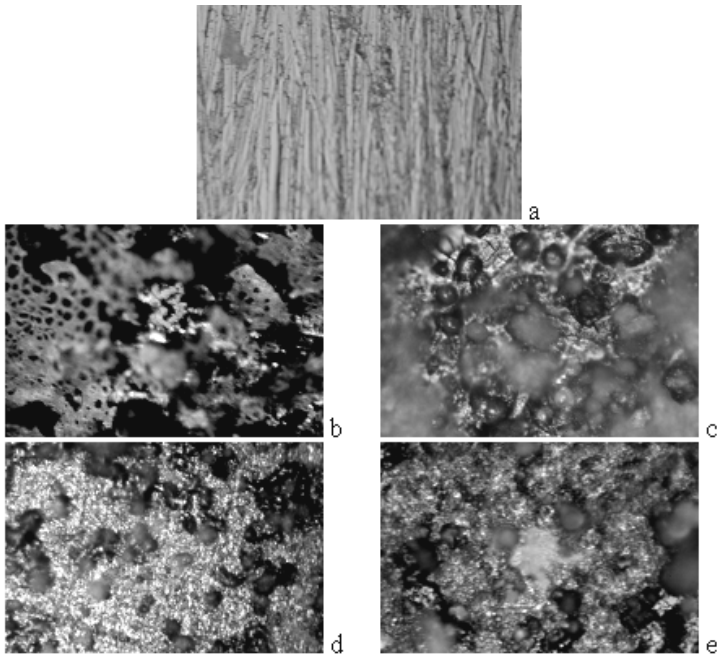

Figure 7. Microscopic images of unprotected carbon steel (a) and protected carbon steel with PAN or PAN/ANi coatings for different aniline concentrations: 0.01 M (b), 0.05 M (c), 0.1 M (d) and 0.5 M (e).

CONCLUSIONS

The corrosion and inhibition of carbon steel in 0.5 M H_2SO_4 in absence and presence of PAN electrosynthesized film was investigated using electrochemical measurements such as, Tafel polarization and electrochemical impedance spectroscopy. The cathodic and anodic curves obtained exhibit

a Tafel type behavior. Addition of ANi increased both the cathodic and anodic overvoltages and caused mainly parallel displacement to the more negative and positive values, respectively. The corrosion current density ($i_{corr.}$) decreased with increasing the concentration of ANi, which indicates that this compound acts as inhibitor. This behavior shows that the addition of ANi reduces anodic dissolution and also retards the hydrogen evolution reaction. This suggests that although inhibition is of mixed type, it is predominantly cathodic.

According to the data obtained from Nyquist plot it can observed that R_p increases with increasing ANi concentration. It is clear that the presence of PAN film produced a higher R_p value, which is an indication of the formation of an effective protective layer that hindered corrosion, which indicates that this film is formed by aniline polymerization.

The values of R_p, degree of coverage (θ) and EI (%) obtained from Nyquist diagram are consistent with those obtained by Tafel polarization.

Microscopic images show the evidence of formation of a thick film on the surface of carbon steel and the specific electrodeposited layers were observed too. It was difficult to assess that they are characteristic to PAN or PAN/ANi system.

EXPERIMENTAL SECTION

The present study aims to determine the role of aniline in providing the protection film in the case of generalized corrosion of carbon steel in sulphuric acid.

For electrochemical measurements a standard cell has been used with a plate working electrode (surface 2 cm^2) made of carbon steel, a platinum auxiliary electrode (surface 1 cm^2) and a Ag/AgCl reference electrode. The electrode made of carbon steel (wt %: C 0.13; Mn 0.35; Si 0.03; P 0.04; S 0.04; Al 0.0045; Fe balance) was polished with metalographic paper, washed in distilled water, degreased in acetone and dried in warm air. For each determination the samples were introduced for 4 minutes, at room temperature, in the following media: 0.5 M H_2SO_4 solution blank and 0.5 M H_2SO_4 solutions containing different concentrations of ANi (Fluka): 0.01 M; 0.05 M; 0.1 M; 0.5 M, at room temperature. A potentiostat VoltaLab 40 connected to a Computer with VoltaMaster 4 software was used in the measurements. Five determinations were made for each solution, taking into consideration the most reproductible responses for the same conditions, at room temperature.

The surface morphology of the substrate and polymer film was examined using Euromex microscope, having a Canon camera and the specific software included.

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