

EFFECT OF SULFACETAMIDE ON THE COMPOSITION OF CORROSION PRODUCTS FORMED ONTO CARBON STEEL SURFACE IN HYDROCHLORIC ACID

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Effect of an antibacterial drug, sulfacetamide, IUPAC name *N*-[(4-aminophenyl) sulfonyl] acetamide (APSA) on the corrosion of carbon steel in 1.0 M HCl solution has been investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and XPS analysis. The electrochemical measurements indicated that the presence of APSA in 1.0 M HCl solution decreases the corrosion current (i_{corr}) and increases the polarization resistance (R_p). XPS surface analysis showed at this stage, in the absence of APSA, that the main product of corrosion is a non-stoichiometric Fe^{3+} oxide/oxide-hydroxide, consisting of a mixture of Fe_2O_3 and $\text{FeO}(\text{OH})$, where $\text{FeO}(\text{OH})$ is the main phase. Moreover, in presence of inhibitor the surface layer consists of $\text{FeO}(\text{OH})$ rather than pure oxide, adsorbed molecules of sulfacetamide and inorganic compounds such as: sulfides, carbonates, sulphates, nitrates, which were obtained by electrochemical degradation of APSA. UV-Vis spectrophotometry and HPLC technique were performed to determine the medium composition before and after corrosion. The results showed a decrease of the inhibitor concentration in 1.0 M HCl solution after carbon steel corrosion, indicating an adsorption process between organic compound molecules from aqueous phase and the electrode surface and/or the electrochemical degradation of APSA.

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1. Introduction

Treatments with organic compounds have been proposed in order to improve anticorrosion protection [1-6]. In fact, much attention should be given when selecting inhibitors for investigation or application to ensure the environmental regulations. The inhibitor must be environmentally friendly to replace the older, which is more toxic and harmful to the environment. When applying the ideas of green chemistry to the area of corrosion inhibitors, the major improvement is in the area of eliminating environmentally toxic compounds. Several organic molecules containing sulfur, oxygen, and nitrogen hetero-atoms were suggested as inhibitors for steel in acidic medium [7, 8]. Many investigators have been reported on the use of antibacterial drugs as corrosion inhibitors [9-13]. Sulfa drugs have been reported also as corrosion inhibitors by several authors [14]. The inhibition mechanism for this class of inhibitors is mainly based on adsorption [15, 16].

The objective of the present study is to investigate the effect of sulfacetamide, IUPAC name *N*-[(4-aminophenyl) sulfonyl] acetamide (APSA) on the corrosion of carbon steel in 1.0 M HCl solution. The choice of this drug as corrosion inhibitor is based on: it is healthy reportedly very important in biological reactions (environmentally friendly); APSA acts as antimicrobial

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agents by inhibiting bacterial growth; easily soluble in water; his molecules have O, N atoms as active centers.

2. Experimental

Materials

The experiments were performed with carbon steel, type C38, in the form of plates with the following composition: C = 0.1%, Mn = 0.5%, P = 0.025%, S = 0.025%, Fe remainder. The aggressive solutions used were made of HCl AR grade. Appropriate concentrations of acid were prepared using distilled water. The following antibacterial drug *N*-[(4-aminophenyl) sulfonyl] acetamide (APSA) was used as inhibitor for the corrosion of carbon steel in 1.0 M HCl. The tested inhibitor was obtained from Fluka. The molecular structure is presented in Fig. 1. All the tests were performed in 1.0 M HCl solution without and with various concentration of the inhibitor: 4 mM; 6 mM; 8 mM; 10 mM.

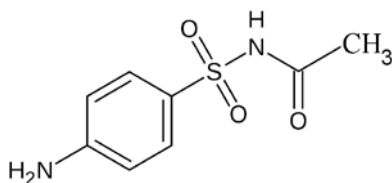


Fig. 1. Chemical molecular structure of Sulfacetamide (APSA).

Electrochemical measurements

Electrochemical measurements were conducted using an electrochemical system, VoltaLab 40, with a personal computer and VoltaMaster 4 software. A standard corrosion cell with a working electrode made of carbon steel with an active surface area of 1 cm² was used. A platinum plate (1 cm²) and a saturated Ag / AgCl electrode were used as auxiliary and reference electrodes, respectively. All the tests were performed in 1.0 M HCl solution without and with various concentration of the inhibitor: 4 mM; 6 mM; 8 mM; 10 mM. All reagents were obtained from Fluka. The immersion time of the plates in the respective media was 4 minutes in open circuit, at room temperature. Potentiodynamic polarization curves were obtained with the scan rate of 1 mV.s⁻¹, in a potential range from -700mV to -100mV.

Electrochemical impedance spectroscopy (EIS) was measured in a frequency range from 100 kHz to 10 mHz by a parturition signal of 10mV amplitude peak to peak at room temperature, after the immersion time of 4 minutes in open circuit. Potentiodynamic polarization and EIS data were analyzed by means of *Excel* and *Zview*, respectively.

Surface characterization

The surfaces of the samples before and after corrosion were examined using a metallographic microscope Euromex with Canon camera and included software.

XPS spectra were recorded in a SPECS Multimethod spectrometer, Phoibos Analyzer 150 with a Mg K_α X-ray source (1486.4 eV photons energy) operated at 300 W (accelerating voltage 12.5 kV, emission current 24 mA). The pressure in the analysis chamber has not exceed the value of 2-3·10⁻⁸ torr during the all period of spectra acquisition. In order to perform the surface charge compensation, a FG40 flood gun device (Specs GmbH – Germany), has been used, with a 0.1 mA electronic current at 2 eV energy. The samples have been measured in an “as received” condition with no other surface cleaning treatment (chemical etching or Ar⁺ ion beam bombardment). Extended spectra were recorded with a window of 1250 eV and 100 eV pass energy. All spectra have been deconvoluted with SDP 2.3 XPS-International software, using Gaussian profile lines for peaks fitting.

UV-Vis spectrophotometry

In the UV-Vis spectrophotometry a spectrophotometer - type Varian-Cary 50 was used. Procedure: The solutions were placed in the UV-VIS beam and a graph of absorbance versus the wavelength was obtained; samples analysis reports were obtained using the CARY-WIN UV software.

HPLC technique

HPLC technique was performed to determine the electrolyte composition before and after electrochemical corrosion. Following chromatographic conditions were applied:

column - BDS HYPERSIL C18, 5 μm (250 mm \times 4.6 mm); mobile phase - Water - 1% glacial acetic acid (A); methanol (B) 95:5; flow rate - 1mL/min; Detection - UV-Vis; $\lambda=254$ nm; Injection volume - 5 μL .

3. Results and discussion

Potentiodynamic polarization

Potentiodynamic anodic and cathodic polarization scans were carried out at room temperature in 1.0 M HCl with different concentrations of APSA (Fig. 2a).

From Fig. 2a it can be seen that, in the presence of the inhibitor, the curves are shifted to lower current regions, showing the inhibition tendency of APSA. The presence of APSA in the corrosive medium increases the anodic and cathodic over-potentials and shifts the corrosion potential, E_{corr} , to higher values (see Table 1). This shows that APSA addition reduces anodic dissolution and also delays the hydrogen evolution reaction. The presence of this inhibitor in 1.0 M HCl solution does not disturb significantly cathodic reaction, but reduces the anodic reaction in a considerable manner. APSA acts as a corrosion inhibitor in 1.0 M HCl solution by suppressing simultaneously the cathodic and anodic processes, but predominantly anodic.

The corrosion current was calculated at intercept of the anodic and cathodic Tafel lines to corrosion potential, using VoltaMaster 4 software (see Table 1).

Table 1. The effect of APSA concentration on the corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (b_a & b_c), percentage inhibition efficiency (IE) of carbon steel corroded in 1.0 M HCl solution, at room temperature.

C-APSA (mM)	E_{corr} (mV vs. Ag/AgCl)	i_{corr} ($\mu\text{A} \cdot \text{cm}^{-2}$)	b_a (mV .dec ⁻¹)	b_c (mV .dec ⁻¹)	IE (%)
0	-476	258.7	81.4	-109.3	0
4	-471	115.6	80.9	-102.9	55.3
6	-465	87.4	78.3	-98.3	66.2
8	-455	60.5	78.1	-99.2	76.6
10	-447	39.6	77.5	-98.8	84.7

The results showed that the corrosion current density, i_{corr} , decreased with increasing APSA concentration, which indicates that this compound acts as inhibitor, and the inhibition degree depends on the APSA concentration. The slopes of the anodic and cathodic Tafel lines (b_a & b_c) were slightly changed by increasing the tested compound concentration (see Table 1). The small change may be due to the surface blockage. This could be attributed to the fact that the anodic carbon steel dissolution and cathodic hydrogen evolution reaction were both inhibited by the inhibitor through merely blocking the reaction sites of carbon steel surface.

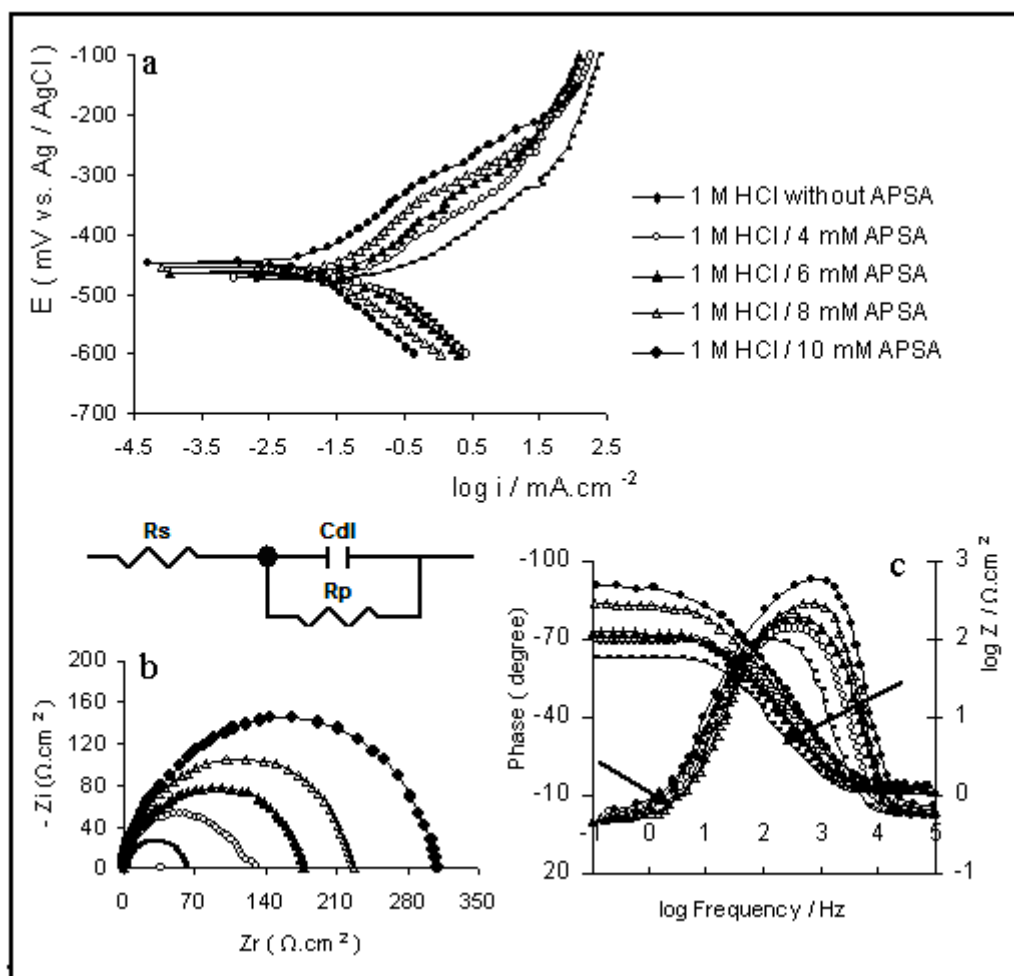


Fig. 2. Electrochemical measurements for carbon steel corroded in 1.0 M HCl solution without and with various concentrations of APSA: a – Potentiodynamic curves; b – Nyquist diagram and equivalent circuit; c- Bode diagram

The percentage inhibition efficiency, IE , of APSA was also determined from the polarization measurements according to the following equation:

$$IE = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities of carbon steel in 1.0 M HCl solution without and with APSA, respectively. IE increased with the increase of APSA concentration reaching a maximum value of 84.7 %, for the solution containing 10 mM APSA (Table 1).

Electrochemical impedance spectroscopy

Figs. 2b and 2c show the Nyquist and Bode plots for carbon steel in 1.0 M HCl solution without and with APSA; it can be seen that the impedance response of carbon steel in 1.0 M HCl solution shows a significantly change after APSA addition.

This indicates that the carbon steel impedance increases with increasing the inhibitor concentration and consequently the inhibition efficiency increases (Fig. 2c and Table 2). It is also apparent from these plots that Nyquist curves (Fig. 2b) are consisted in one capacitive loop (one phase angle maximum in Bode format – Fig. 2c).

Table 2. Impedance parameters for carbon steel in 1.0 M HCl solution in the absence and in presence of different concentrations of APSA, at room temperature.

C-APSA (%)	R_s ($m\Omega.cm^2$)	C_{dl} ($\mu F.cm^{-2}$)	R_p ($\Omega.cm^2$)	IE (%)
0	385.1	96.3	78.2	0
4	346.3	95.1	194.5	59.7
6	327.8	71.1	258.7	69.7
8	321.6	52.3	362.8	78.4
10	319.3	22.7	566.9	86.2

More pronounced frequency arcs were obtained for the samples which were immersed in 1.0 M HCl containing various concentrations of APSA. This behavior is usually assigned to changes in density and composition of substrate layer. It is clear that APSA presence produced a higher polarization resistance (R_p) which is interpreted in terms of the formation of an effective protective layer that diminishes the corrosion processes. For the description of EIS measurements an equivalent circuit is suggested [17] in Fig. 2b, where (R_s) is the solution resistance of the bulk electrolyte and (C_{dl}) represents the double layer capacitance of the electrolyte at the metal surface. (R_p) is the polarization resistance of the metal. The impedance parameters derived from EIS measurements are given in Table 2. EIS results show that R_s and C_{dl} decrease and R_p increases suggesting that the composition of substrate layer was changed. This decrease in C_{dl} could be attributed to the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. The R_p was used to calculate the inhibition efficiency from equation 2.

$$IE = \frac{R_p - R_p^0}{R_p} \times 100 \quad (2)$$

where R_p and R_p^0 represents the polarization resistances in the presence and in absence of inhibitor, respectively. The presence of APSA leads to an approx. 86.2% inhibition efficiency, a closer value to that obtained from potentiodynamic curves (see Tables 1 and 2).

Surface morphology

The corroded carbon steel samples obtained after electrochemical corrosion in 1.0 M HCl solution without APSA and in 1.0 M HCl solution containing various concentrations of APSA were also examined using optical images. The optical images of carbon steel surface before corrosion (Fig. 3a) and after occurrence of the corrosive processes in 1.0 M HCl solution blank (Fig.3b) and in 1.0 M HCl solution containing 6 mM APSA; 8 mM APSA; 10 mM APSA; (Fig. 3c-e) are presented.

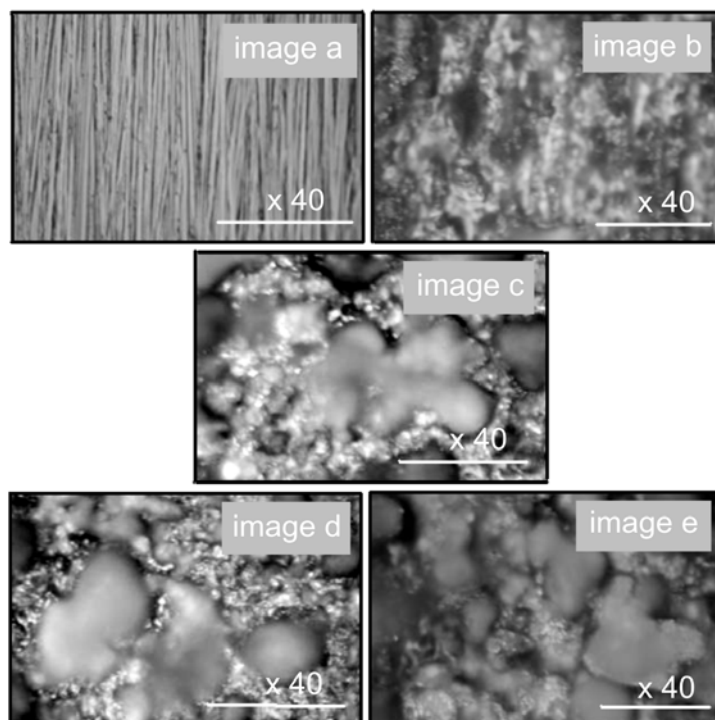


Fig. 3. Optical images of carbon steel: a- before corrosion; after corrosion in: b- 1.0 M HCl solution without APSA; c- 1.0 M HCl solution containing 6 mM APSA; d- 1.0 M HCl solution containing 8 mM APSA; e- 1.0 M HCl solution containing 10 mM APSA

In the case of carbon steel corroded in 1.0 M HCl solution without inhibitor random spread corrosion spots can be noticed (Fig. 3b). When APSA inhibitor was used the texture is modified and the corrosion spots have a low intensity. It can be observed that the surface morphology shown in the case of 1.0 M HCl solution containing 6 mM APSA; 8 mM APSA; 10 mM APSA; (Fig. 3c-e) is significantly different and denser than that obtained in 1.0 M HCl solution without APSA (Fig. 3b). In the presence of APSA the corrosion process is slowed, which is interpreted in terms of the formation a protective layer consisting of organic film and an amount of iron compounds. It can be considered that the APSA inhibitor acts as an incipient “rust transformer” (a compound which, through an electrochemical process, transforms rust into a substance which strongly adheres on the metal surface, preventing corrosion) and favors the formation of a “superficial closed layer” [4, 6].

XPS analysis

Fe $2p_{3/2}$ energy levels were monitored by XPS on the surface of carbon steel sample electrochemically corroded in 1.0 M HCl blank solution and 1.0 M HCl solution containing 4 mM APSA. The spectra are displayed in Figs. 4a and 4b. In Fig. 4a, the positions and energy are close to that observed for FeO(OH) or for Fe₂O₃ structures [18].

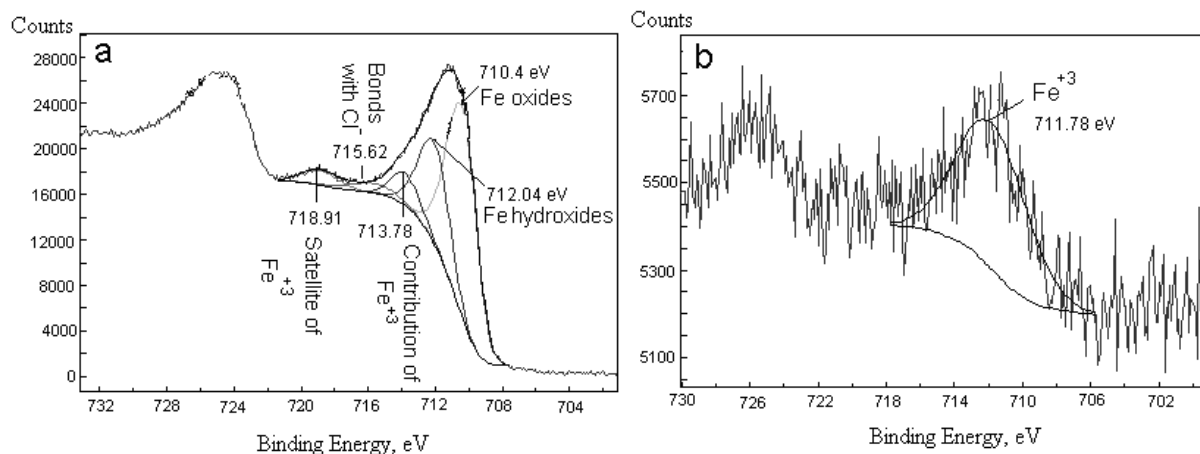


Fig. 4. Fe $2p_{3/2}$ XPS spectra of carbon steel corroded in 1.0 M HCl solution: a – without APSA; b – containing 4 mM APSA

For the sample corroded in 1.0 M HCl solution containing APSA the Fe $2p_{3/2}$ peak position at 711.8 eV related to metal oxides and/or oxide-hydroxides and /or a corrosion product consisting of a mixture of FeO(OH) and iron oxides. Oxide-hydroxides of iron may occur in anhydrous (FeO(OH)) or hydrated FeO(OH)· n H₂O forms.

The monohydrate (FeO(OH)·H₂O) might otherwise be described as iron(III) hydroxide (Fe(OH)₃), and is also known as hydrated iron oxide or yellow iron oxide.

The whole set of comparable binding energies obtained for the O 1s peak (Figs. 5a and 5b) deserves some comment. On the high binding energy side, precise assignments are difficult in relation to the existence of ionizations associated with adsorbed species [19]. The analyses have shown: from 530.5 to 531.1 eV, ionization characteristics of oxygen species integrated in the material as O²⁻ and OH⁻; from 531.1 to 532 eV, ionization of oxygen species that could allow compensation for some deficiencies in the subsurface of metal oxides. Formally, these oxide ions could be described as O⁻ species - indeed, owing to a higher covalence of the M-O bonds these low coordinated oxygen ions would be characterized by a lower electron density than the classical O²⁻ ions [19].

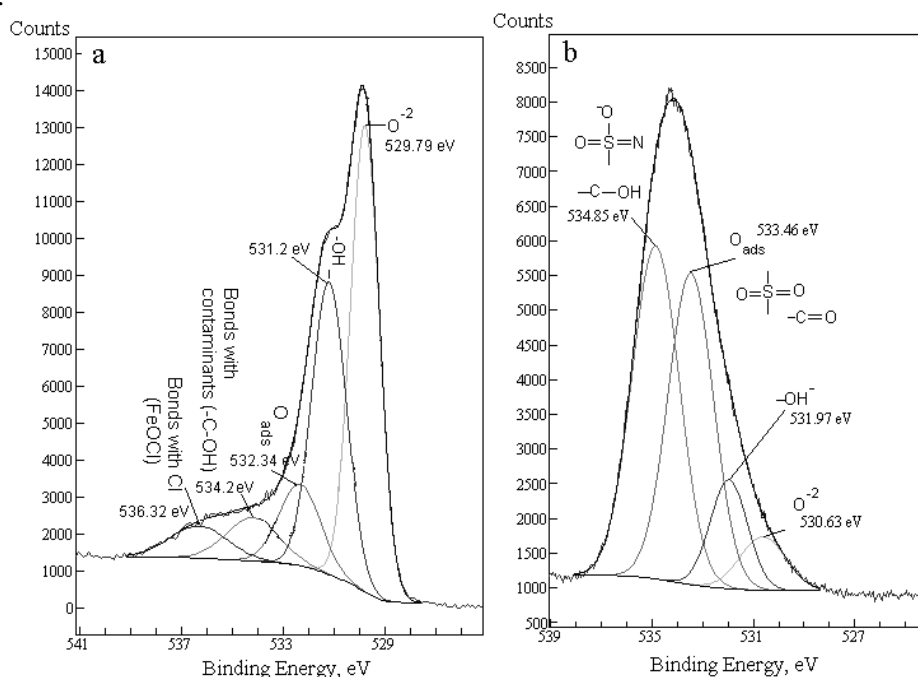


Fig. 5. Oxygen XPS spectra of carbon steel corroded in 1.0 M HCl solution: a – without APSA; b – containing 4 mM APSA

For the sample corroded in 1.0 M HCl blank solution the oxygen peak could be deconvoluted to five components with peak positions at 529.8 eV, 531.2 eV, 532.3 eV, 534.2 eV and 536.3 eV related to metal oxides, oxide-hydroxides, O_{ads} , (adsorbed species such as oxygen from the water) [19], bonds with contaminants and bonds with Cl, respectively [20, 21]. For FeO(OH) two well resolved peaks were observed at 529.8 eV (O^{2-}) and 531.2 eV (HO^{\cdot}). The O 1s for Fe_2O_3 was found at 529.8 eV. Taking these data into account, we may conclude that the surface layer consists of FeO(OH) rather than pure oxide. For the sample corroded in HCl solution containing 4 mM APSA the oxygen peak could be deconvoluted to four components with peak positions at 530.6 eV, 531.9 eV, 533.4 eV and 534.8 eV related to metal oxides, oxide-hydroxides, O_{ads} , or other bond such as: $O=S=O/C=O$, respectively and/ or other adsorbed species (inorganic compounds). The adsorbed species amount, in this case, is appreciable in regard to the amount of species which were resulted from the corrosion of carbon steel in 1.0 M HCl solution without APSA. XPS analysis shows that in the presence of APSA, the corrosion process is slowed; at this stage, the main product of corrosion is a non-stoichiometric Fe^{3+} oxide/oxide-hydroxide, consisting of a mixture of Fe_2O_3 and FeO(OH) where FeO(OH) is the main phase.

Further relevant information about the chemical composition of surface corroded in 1.0 M HCl solution containing APSA is obtained from the XPS spectral analysis of N 1s and S 2p photo-peaks (Figs. 6c and 6b).

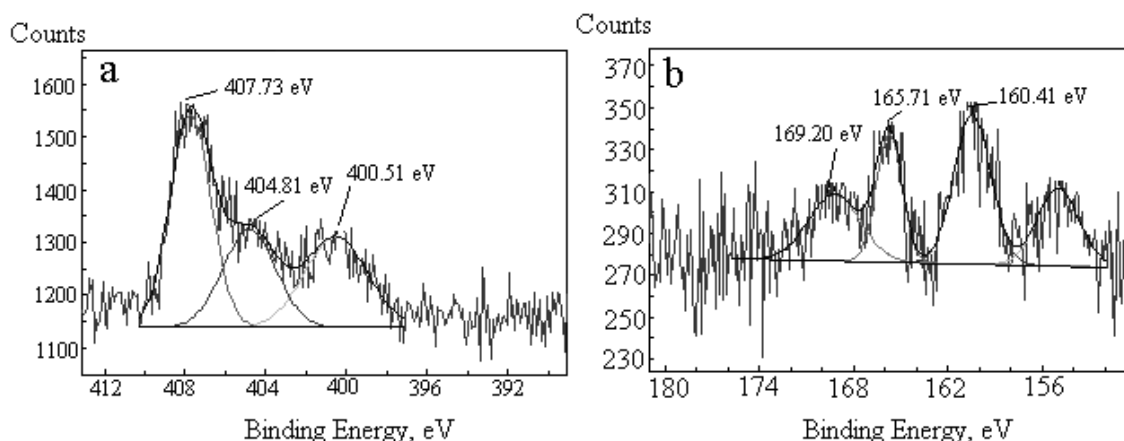
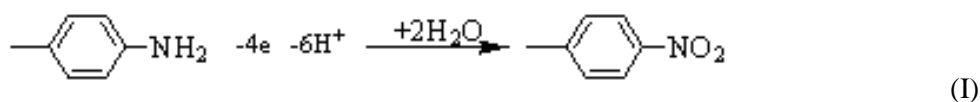


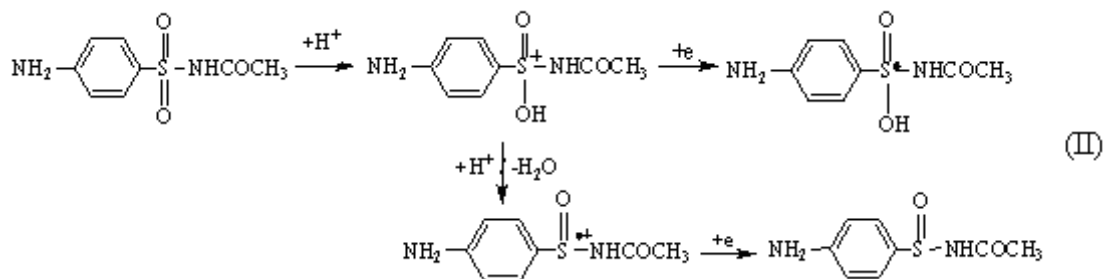
Fig. 6. XPS spectra of N 1s (a) and S 2p (b) for carbon steel corroded in 1.0 M HCl solution containing 4 mM APSA

The spectral simulation of the N 1s photo-peak (Fig. 6a) for carbon steel corroded in presence of APSA shows organic nitrogen species at 400.5 eV such as amine, amide, imine, etc [22]. Indeed, this binding energy corresponds to amine group from APSA molecule and/or C-N bonds. Consequently, an accurate assignment with XPS is quite difficult with such specimens. The peak positions at 404.8 eV and 407.7 eV indicate $-NO_2$ group or nitrogen oxides. These compounds can be resulted from the electrochemical oxidation (such as reaction I) and electrochemical decomposition of APSA (see scheme III).

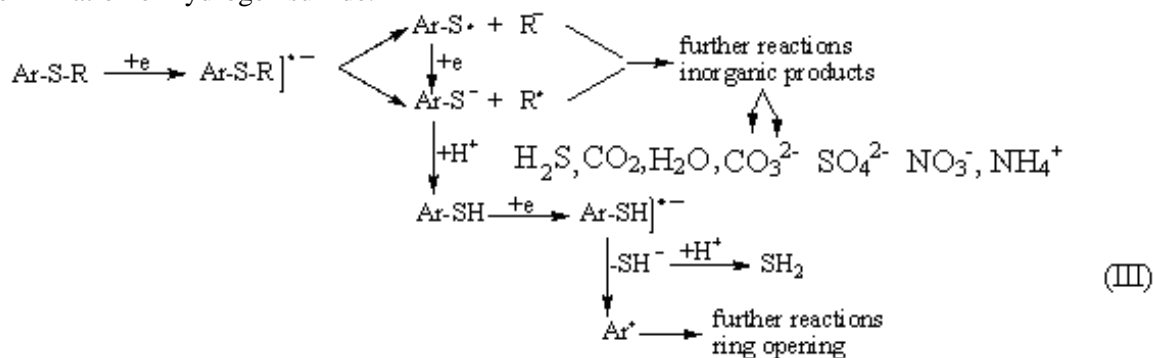


The S 2p levels spectrum consists of three sets of peaks: (i) at low binding energies (160.4 eV); (ii) at intermediate binding energies (165.7 eV) and (iii) at higher binding energy (169.2 eV). Photo-peak at high binding energies (169.2 eV) corresponds to highly oxidized (+VI) sulfur such as sulfone [22] from the APSA molecule or inorganic group SO_4^{2-} . Photo-peak at intermediate binding energies (165.7 eV) is due to less oxidized sulfur such as sulfoxides. Photo-peaks at low

binding energies (160.4 eV) are attributed to organic sulfur entities which are close to neutral sulfur and inorganic sulfides. Corresponding organic species may be thiophenes and disulfides [22]. More or less hypothetical species (sulfoxide, C-S bond or S^{2-}) with a binding energy of about 165.7 eV and 160.4 eV, respectively can be resulted by electrochemical decomposition of APSA (scheme of reactions is presented below).



Scheme (III) shows the electrochemical decomposition mechanism of APSA with elimination of hydrogen sulfide.



Taking these data into account, we may conclude that the surface layer consists of $FeO(OH)$ rather than pure oxide, adsorbed molecules of APSA and inorganic compounds such as: sulfides, carbonates, sulphates, nitrates which were obtained by electrochemical decomposition of APSA.

UV-Vis spectrophotometry and HPLC technique

1.0 M HCl solution containing 4 mM APSA, before and after carbon steel corrosion, was investigated by UV-VIS spectrophotometry and HPLC technique. Before injection, the solution at 0.4 mM was diluted.

Graph inserted in Fig. 7 shows the UV-Vis spectra of HCl solutions containing 0.4 mM APSA, before and after carbon steel corrosion in this medium (spectrophotometric scan of sulfacetamide at 254 nm). It was observed that concentration of APSA decreases after corrosion of carbon steel. This indicates APSA electrochemical degradation and an adsorption process between APSA molecules from aqueous phase and the electrode surface.

HPLC chromatograms of 1.0 M HCl solution containing APSA, before and after carbon steel corrosion are given in Fig.7. In the HPLC chromatogram of 1.0 M HCl solution containing APSA, before corrosion one peak was observed. This was identified as sulfacetamide (see Fig. 7). After corrosion of carbon steel in HCl solution containing inhibitor four peaks were identified such as: sulfanilamide and sulfanilic acid [23]; other two peaks could not be identified. The chromatograms and analysis reports showed that the sulfacetamide concentration decreased with 34.6%.

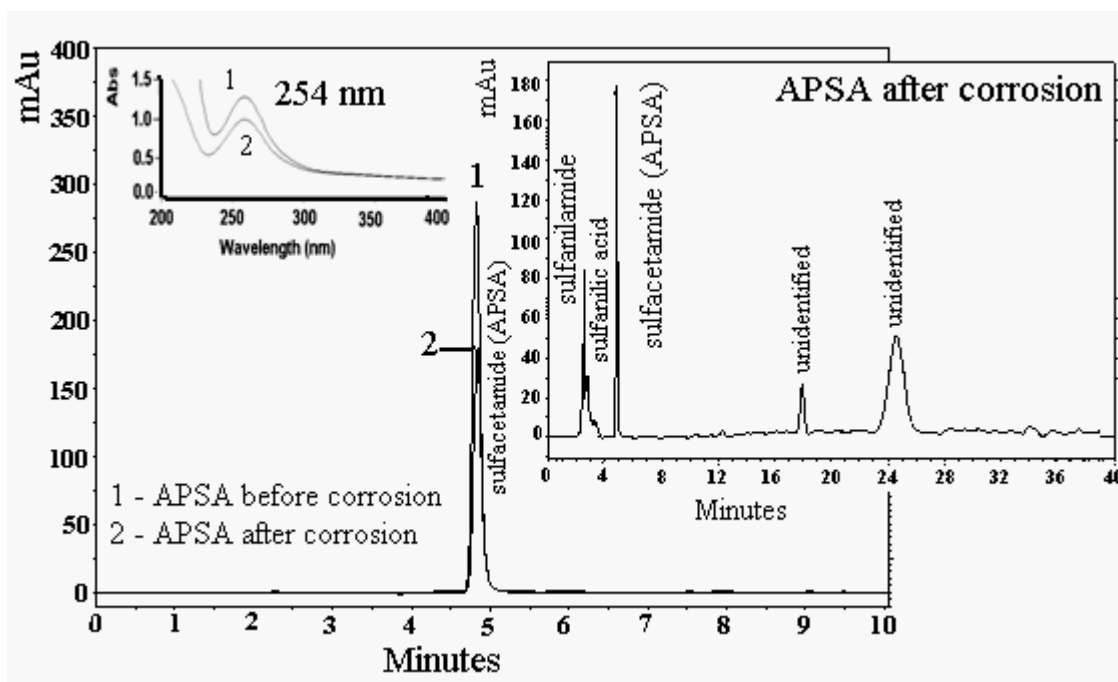


Fig. 7. UV-Vis spectra and HPLC chromatograms of HCl solution containing 0.4 mM sulfacetamide, before and after carbon steel corrosion

The electrochemical decomposition products are in small amount, regarding to sulfacetamide which was degraded. Moreover, the difference between peak 1 and peak 2 may be given by APSA degradation to inorganic compounds and APSA adsorption on the carbon steel surface.

4. Conclusions

APSA is an inhibitor of carbon steel corrosion in 1.0 M HCl solution; it has an efficiency of 84.7 % obtained from potentiodynamic curves and 86.2% from EIS, respectively; the results are in good agreement.

Optical images indicate that the surface morphology shown in the case of 1.0 M HCl solution containing different concentrations of APSA is significantly different and denser than that obtained in 1.0 M HCl solution without APSA; also, the corrosion spots have a low intensity. Optical images show that APSA inhibitor modified the surface texture and the corrosion spots have a low intensity.

XPS analysis shows that in the presence of APSA the corrosion process is slowed; at this stage, the main product of corrosion is a non-stoichiometric Fe^{3+} oxide/oxide-hydroxide, consisting of a mixture of Fe_2O_3 and $\text{FeO}(\text{OH})$ where $\text{FeO}(\text{OH})$ is the main phase. Oxide-hydroxides of iron may occur in anhydrous ($\text{FeO}(\text{OH})$) or hydrated $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$ forms. The monohydrate ($\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$) might otherwise be described as iron(III) hydroxide ($\text{Fe}(\text{OH})_3$), and is also known as hydrated iron oxide or yellow iron oxide. Moreover, in the presence of APSA, the surface layer consists of $\text{FeO}(\text{OH})$ rather than pure oxide, adsorbed molecules of APSA and inorganic compounds such as: sulfides, carbonates, sulphates, nitrates which were obtained by electrochemical decomposition of APSA. It can be considered that the APSA inhibitor acts as an incipient "rust transformer" (a compound which, through an electrochemical process, transforms rust into a substance which strongly adheres on the metal surface, preventing corrosion) and favors the formation of a "superficial closed layer".

UV-Vis spectrophotometry and HPLC confirm the electrochemical degradation of sulfacetamide and an adsorption process between APSA molecules from aqueous phase and electrode surface.

Acknowledgements

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