Influence of Tryptophan on the Corrosion Process of Carbon Steel in Aqueous Weak Acid Solutions

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Electrochemical behaviour of tryptophan as inhibitor in the corrosion process of carbon steel in acetic acid / acetate solution has been investigated by linear polarization, cyclic voltammetry and scanning electron microscopy. Tafel polarization method was used in order to investigate the influence of tryptophan as corrosion inhibitor at room temperature. The corrosion potential, resistance and corrosion rate have been determined by extrapolating Tafel slopes. These diagrams show that the tryptophan is a good corrosion inhibitor for carbon steel in weak acid media, and its inhibition efficiency increases with the increase of concentration in the range of 10^{-4} *-* 10^{-2} *mol* L^{-1}*. Scanning electron micrographs of the carbon steel surface revealed that tryptophan inhibits the corrosion process, due to his ability to adsorb on the metal surface. Also, the corrosion rate of carbon steel in the studied media has been determined by gravimetric method.*

Keywords: tryptophan, corrosion inhibitor, Tafel polarization, scanning electron microscopy

Corrosion of metals and alloys, especially in acid media, has become an important industrial problem and an academic subject. The use of corrosion inhibitors in order to diminish the dissolution process of metals and alloys is one of the most economic and practical method applied in anticorosive protection. In the last years, the decrease of corrosion rate using inhibitors for mild steel in hydrochloric and sulfuric acid, was intensively studied [1-6]. Also, the interest in the investigation of the behaviour of steels in organic acid solutions such as acetic acid and formic acid has been increased [7, 8]. The most used corrosion inhibitors are organic compounds containing nitrogen, oxygen, sulphur, phosphorus heteroatoms, aromatic rings or triple bounds in the molecules that facilitate their adsorption on the metal surface [9-12].

Organic compounds from amino acids class were used as effective corrosion inhibitors for steel [13-15], iron [16], cooper [17], nickel [18] and alloys [19, 20] in different corrosive solutions. The inhibitory effect of amino acids is generally owed to their adsorption on metal surface where they form a protective film. Adsorption of inhibitor molecules on the metal surface can occur due to electrostatic interaction between metallic surface and the inhibitor (a), interaction of unshared electron pairs from the inhibitor molecules with the metal (b), interaction of π-electron with the metal (c) or a combination of the (a-c) types (d) [21].

The availability of natural compounds, non toxic and environmental friendly, so called “green” corrosion inhibitors appears to be very attractive, because of their biodegradability and zero impact on the environment [22]. The amino acids and derivatives belong to this category.

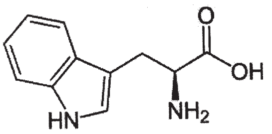

Fig. 1. Chemical structure and IUPAC name of tryptophan [(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid]

The present study was elaborated in solutions containing sodium acetate, used as deicing solutions [23], in order to investigate the inhibition properties of tryptophan (Trp) with the chemical structure presented in figure 1. To enlarge the aggressiveness of media and assurance of a constant value of *p*H during the experiments, a buffer acetic acid/ sodium acetate solution has been used.

The study was performed by weight loss measurements, linear polarization and cyclic voltammetry methods. Surface analysis of the samples after corrosive attack of the media has been performed using a scanning electron microscope and dispersive energy X-ray spectroscopy. The adsorption mechanism of the inhibitor has been also discussed.

Experimental part

Materials

The working electrode was a cylindrical disc cut from a carbon steel sample with the elemental composition presented in table 1.

Amino acid tested as corrosion inhibitor was tryptophan (Merck, ≥ 99.5% purity). The concentration range of inhibitor was $10^{-4} \div 10^{-2}$ mol L^{-1}. The test solution (CH_3COOH 0.5 mol L^{-1}/CH_3COONa 0.25 mol L^{-1}) was prepared starting from analytical grade reagents glacial acetic acid p.a. (Fluka, 99.8%) and sodium acetate p.a. (Fluka, 99%).

Table 1
ELEMENTAL COMPOSITION OF THE SAMPLES

Element	Fe	C	Si	Mn	P	S	Cr	Ni
%	96.98	0.4184	0.2510	0.7920	0.0132	0.0335	1.162	0.029
Element	Mo	Cu	Al	Ti	V	Co	Nb	W
%	0.2123	0.0234	0.0229	<0.004	0.0124	0.0222	<0.001	<0.010

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Weight loss measurements

Weight loss (*WL*) experiments were carried out with disc samples having the dimensions Φ15 mm x 5 mm. Before each experiment the samples were polished with different grade emery papers, washed with distilled water, rinsed with acetone and finally dried at room temperature. The samples were immersed in 100 mL of 0.5 mol L^{-1} acetic acid and 0.25 mol L^{-1} sodium acetate solutions, without and with different concentrations of the inhibitor. After 240 h exposure at room temperature, the specimens were taken out, brushed under running water to remove corrosion products, washed with distilled water, rinsed with acetone and dried. The steel was tested for a long time to get accurate results. Before and after corrosive attack of the media the samples have been weighed using an analytical balance (precision ± 0.1 mg). The weight loss (*WL*) in mg cm^{-2} h^{-1} has been calculated with the following equation (1) [24]:

$$WL = \frac{W_1 - W_2}{S \times t} \qquad (1)$$

where W_1 [mg] is the initial mass of the samples, W_2 [mg] the final mass of the samples, S [cm^2] is the total surface area of the specimens, t [h] is the exposure time.

Electrochemical measurements

The electrochemical experiments were carried out in a 100 mL cell with three electrode assembly (Princeton Applied Research) at room temperature. Carbon steel specimens with 1 cm^2 exposed area were used for electrochemical measurements as working electrode, a Ag/AgCl as reference electrode and two graphite rods as counter electrodes. The working electrode was prepared similar to samples used in gravimetric method. Electrochemical measurements were carried out with an AUTOLAB Potentiostat/Galvanostat model PGSTAT302N. All potentials were referred to the saturated Ag/AgCl reference electrode. Before each experiment the test solutions were deaerated by bubbling high purity nitrogen. Potentio-dynamic polarization curves were obtained with a scan rate of 1 mV s^{-1} in the potential range of - 230 to + 270 mV relative to the open circuit potential. Preliminary tests at different scan rates showed that a 1 mV s^{-1} scan rate ensures stationary conditions. Corrosion current density values were obtained by Tafel extrapolation method. Electrochemical behaviour of Trp was studied using Pt and carbon steel electrodes by cyclic voltammetry. Several runs were performed for each set of experiments in order to obtain reproducible data.

Surface analysis

Carbon steel surface was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using a FEI INSPECT S microscope. Images and EDX spectra of the samples, the same used in weight loss measurements, were recorded after 240 h exposure time in 0.5 mol L^{-1} CH_3COOH/0.25 mol L^{-1} CH_3COONa solutions, at room temperature, without and with different concentrations of Trp. During the experiment, the glasses with samples were covered against oxygen intrusion using a PARAFILM foil.

Results and discussions

Weight loss measurements

The *WL* of carbon steel specimens after exposure for 240 h in test solutions with and without addition of different amounts of Trp was calculated in mg cm^{-2} h^{-1} and the data obtained were given in table 2. The results show that if the concentration of Trp increases, the carbon steel corrosion rate decreases, indicating that Trp molecules act on the corrosion process. From the calculated *WL* the inhibition

Trp conc. [mol L^{-1}]	Δ*m* [mg]	*WL* x 10^2 [mg cm^{-2} h^{-1}]	(*θ*) Surface coverage	*IE* [%]
-	112.5	8.89	-	-
1x10^{-4}	68.7	5.66	0.36	36.3
1x10^{-3}	38.6	3.05	0.65	65.7
1x10^{-2}	11.7	0.98	0.89	89.0

Table 2
PARAMETERS OBTAINED FROM WEIGHT LOSS MEASUREMENTS AFTER 240 h EXPOSURE TIME IN THE TEST SOLUTIONS

Trp conc. [mol L^{-1}]	i_{corr} [μA cm^{-2}]	$-E_{corr}$ [mV]	b_c [mV dec^{-1}]	b_a [mV dec^{-1}]	R_p [Ω]	Corrosion rate x 10^2 [mg cm^{-2} h^{-1}]	*θ*	*IE* [%]
-	143	584	132	125	45	14.96	-	-
1×10^{-4}	99	609	120	124	58	12.02	0.31	31
5×10^{-4}	74	624	105	121	76	7.76	0.48	48.3
1×10^{-3}	51	638	99	112	95	5.33	0.64	64.3
5×10^{-3}	37	627	98	110	124	3.95	0.74	74.1
1×10^{-2}	21	597	104	78	171	2.24	0.85	85.3

Table 3
POLARIZATION PARAMETERS AND CORRESPONDING INHIBITION EFFICIENCY FOR THE CORROSION OF CARBON STEEL IN TEST SOLUTIONS WITHOUT AND WITH VARIOUS CONCENTRATIONS OF TRP AT 25 °C

efficiency (*IE*) of the Trp was obtained using equation (2) [25]:

$$IE(\%) = \left(1 - \frac{W_{corr}}{W^0_{corr}}\right) \times 100 \qquad (2)$$

where W_{corr} and W^o_{corr} are the weight loss in the presence and the absence of inhibitor, respectively.

In order to study the adsorption isotherm of Trp on the metal surface, the surface coverage (θ) was computed based on weight loss data. The surface coverage is given by the formula (3) [25]:

$$\theta = 1 - \frac{W_{corr}}{W^0_{corr}} \qquad (3)$$

The data presented in table 2 show that inhibitor efficiency reaches to appreciable values for reduced concentrations of Trp.

Tafel polarization method

The manner in which Trp acts as a corrosion inhibitor and its effect on the corrosion rate can be estimated by different procedures, one of the most used being Tafel polarization method.

The potentiodynamic polarization curves of carbon steel in 0.5 M CH_3COOH/0.25 M CH_3COONa solutions without and with various concentrations of Trp are shown in figure 2. The values of associated electrochemical parameters, corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes and inhibition efficiency (*IE* %) calculated from these curves are given in table 3. The inhibition efficiency *IE* % was calculated from polarization measurements according to equation (4) [26]:

$$IE(\%) = \left(\frac{i_{corr} - i'_{corr}}{i_{corr}}\right) \times 100 \qquad (4)$$

where i_{corr} and i'_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

The values of the current densities were obtained by extrapolation of the current – potential curves to the corresponding corrosion potentials. Further the surface coverage grade can be calculated using equation (5) [26]:

$$\theta = \frac{i_{corr} - i'_{corr}}{i_{corr}} \qquad (5)$$

As it can be seen from table 2 and 3, the results obtained from weight loss measurements are similar to those obtained from Tafel polarization method, the inhibitor efficiency and surface coverage degree increase with increase of Trp concentration. It is observed that the addition of Trp has an inhibitive effect in the cathodic part (b_c) of the polarization curves while the anodic part (b_a) decreases less. At 10^{-2} M concentration of inhibitor the anodic Tafel slope significantly drops probably because of the presence of complexes between Fe^{2+} ions and Trp molecules as ligand. Moreover, transfer resistance associated with the ionization process $Fe \rightarrow Fe^{2+} + 2e^-$ increases with Trp concentration.

Inhibiting efficiency values of Trp on the carbon steel corrosion process in buffer acetic acid/acetate solution obtained by Tafel and weight loss methods are in good agreement.

The results clearly indicated that the inhibition mechanism involves blockage of carbon steel surface by the inhibitor molecules via adsorption, process that is influenced by the nature and surface charge of the metal and by the chemical structure of the inhibitor. Trp molecules can be adsorbed on the metal surface through the heterocyclic atoms and also the imidazole and indole ring, respectively [14].

The Tafel curves presented in figure 2 show that Trp significantly influences the cathodic process of hydrogen evolution reaction, and less the anodic process of dissolution/passivation of the metal. As the concentration of inhibitor is higher the diminution of the cathodic current is more pronounced, suggesting that Trp acts by adsorption on steel surface. It should be noted that in acid solutions Trp exists as a protonated species that adsorbs on the cathodic active sites of the carbon steel, similarly with other amino acids [16, 17].

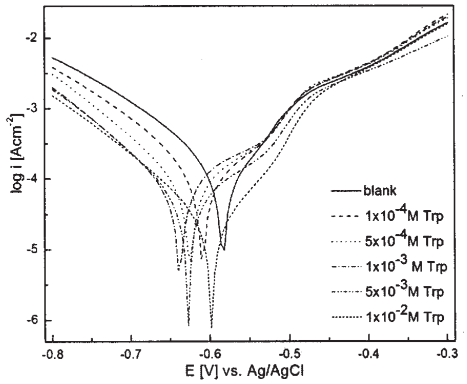

Fig. 2. Tafel polarization curves obtained for carbon steel at 25 °C in 0.5 mol L^{-1} CH_3COOH/0.25 mol L^{-1} CH_3COONa solutions with various concentrations of Trp

Cyclic voltammetry method

Information about how Trp can influence the corrosion process are pointed by its electrochemical behaviour in the studied media. One of the most used methods to investigate the electrochemical properties of various compounds is cyclic voltammetry.

In order to obtain information on Trp oxidation resistance, and its influence on the cathodic process of hydrogen evolution reaction, the voltammetry tests were performed first on a Pt working electrode, then on carbon steel electrode, considering that on Pt electrode the potential window for drawing the voltammograms is wider especially in the anodic domain.

Figure 3 shows the cyclic voltammograms drawn on Pt as working electrode, in 0.5 mol L^{-1} CH_3COOH / 0.25 mol L^{-1} CH_3COONa solutions without and with various concentrations of Trp. The base curve obtained in the absence of the inhibitor presents the characteristics of polarization curves drawn in acid media. There are distinct anodic branch of the voltammogram corresponding to oxygen release (curve 1) and the cathodic one for hydrogen evolution reaction (curve 2). Peaks 3 and 4, less obvious due to low sensitivity on current axis, associated with the formation and reduction of superficial oxide layer respectively, are observed. The cathodic peak 5 corresponds to the oxidation of adsorbed hydrogen on electrode surface. Addition of Trp in a test solutions leads to a more visible oxidation peak, which can be attributed to the oxidation process of the amino acid at a potential value around +0.9 V/(Ag/AgCl).

In order to identify how Trp influences the electrode processes, polarization curves where drawn separately at higher sensitivity, in cathodic domain as well as in anodic one. According to figure 4, the hydrogen evolution reaction in acetic acid/acetate solution in the presence of Trp is inhibited due to adsorption on carbon steel surface of amino acid molecules or, more exactly amphionic molecules. The effect is more obvious as the Trp concentration in corrosive media increases.

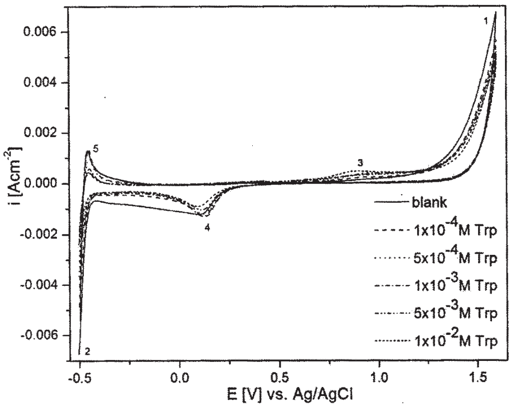

Fig. 3. Cyclic voltammograms on Pt electrode in test solutions without and with addition of Trp; scan rate 1 mV s^{-1}

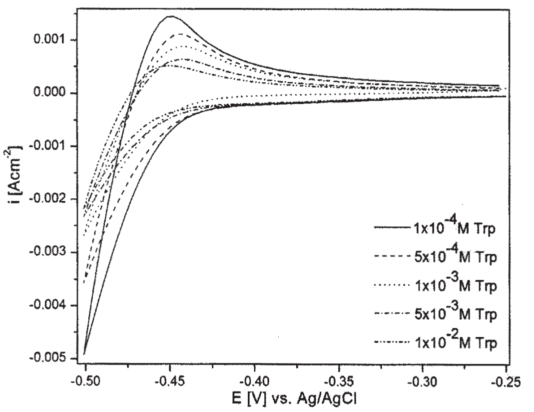

Fig. 4. Cyclic voltammograms on Pt electrode in test solutions with different concentrations of Trp; scan rate 1 mV s^{-1}

The pronounced peak from figure 5 , whose height is proportional to the concentration of inhibitor, can be assigned to irreversible oxidation of the amino acid. The value of *p*H for the buffer acetic acid/sodium acetate solution has been calculated using Henderson-Hasselbalch equation written as:

$$[H^+] = K_a \cdot \frac{c_{CH_3COOH}}{c_{CH\ COONa}} \qquad (6)$$

where K_a is the acidity constant for acetic acid/acetate ($1.75 \cdot 10^{-5}$) [27].

In aqueous solutions, Trp presents two steps of deprotonation and forms the following species:

$$\underset{\alpha_2}{H_3N^+\text{–R–COOH}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\alpha_1}{H_3N^+\text{–R–COO}^-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\alpha_0}{H_2N\text{–R–COO}^-}$$

where α_i represents the relative proportion of chemical species in equilibrium.

The calculated value of *p*H, according to equation (6), for the buffer solution is 4.46, and at this value the value of the relative proportion α_1 is almost 1 taking into account that for Trp $pK_1 = 2.35$ and $pK_2 = 9.33$ [27].

From the analysis of voltammograms presented above following conclusions result:

- Trp acts as inhibitor of hydrogen evolution process;
- it is possible that Trp undergoes an oxidation process on platinum but at advanced anodic polarizations, which does not occur in corrosion process of iron in aqueous electrolyte solutions.

Cyclic voltammograms drawn on carbon steel as working electrode in the same electrolyte solutions with and without addition of inhibitor are given in figure 6. In the absence of Trp, starting from open circuit potential (OCP), in anodic sense a critical current (peak 1) is observed, at -0.27 V/ (Ag/AgCl), followed by achieving the passivity state due to the formation of an oxide layer on the metal surface. At potential values of over +1.5 V/ (Ag/AgCl) the oxygen evolution reaction takes place (curve 2). Shifting the potential in cathodic sense the appearance of peak 3 corresponding to the reduction of passivation film is observed. Thereby, the electrode surface becomes active again and anodic dissolution of metal can occur (peak 4, potential value about -0.32 V/(Ag/AgCl)). The current plateau 5 corresponding to the reduction of iron ions to metallic iron is recorded only at high speed polarization after anodic sweep because metal ions have not enough time to diffuse in mass solution. The process does not take place or is not recorded during the cathodic linear polarization because there are no iron ions at the interface. Further, hydrogen evolution reaction takes place (curve 6). In anodic sense, peak 7, corresponding to the oxidation of adsorbed hydrogen on metal surface, is observed.

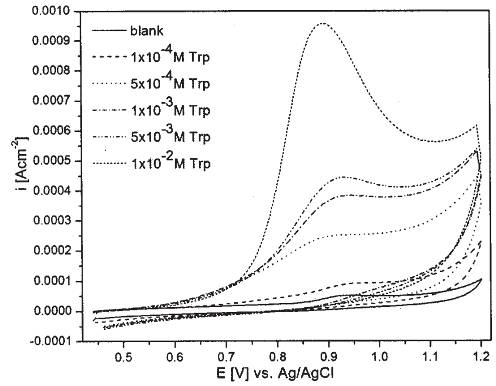

Fig. 5. Electrochemical behaviour of Trp on Pt electrode in test solutions; scan rate 1 mV s^{-1}

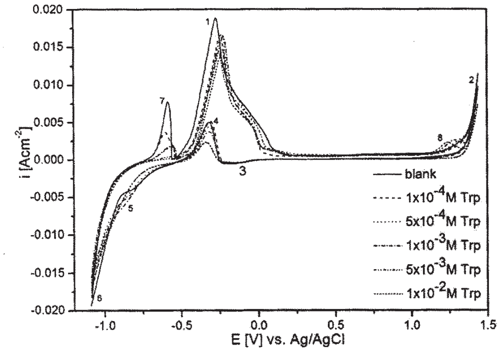

Fig. 6. Cyclic voltammograms on carbon steel electrode in test solutions without and with addition of Trp; scan rate 1 mV s^{-1}

In the presence of Trp in test solution, the passivation state occurs more easily, critical current of passivation being reduced. At higher positive potential values, over +1.25 V/ (Ag/AgCl), for 10^{-2}M Trp, an oxidation process takes place (peak 8), which can be assigned to amino acid oxidation.

The influence of inhibitor on the anodic process of metal dissolution $Fe \rightarrow Fe^{2+} + 2e^-$ is slight and can be attributed to the formation of complex iron-Trp compounds on metal surface or to the adsorption Trp molecules which block the active sites of metal surface. For more information about how Trp can influence the corrosion rate of carbon steel in test solutions, the voltammograms were separately investigated on specific potential domains. As one can see from figure 7 and figure 4, the hydrogen evolution reaction is inhibited in the presence of Trp; the cathodic curves are moved to more negative potentials. The inhibition efficiency of the amino acid increases proportionally with the increase of Trp concentration. The voltammograms presented in figures 6 and 7 highlight that addition of Trp in

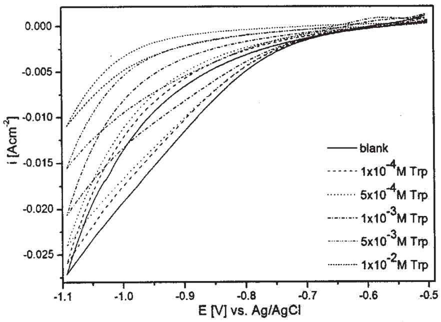

Fig. 7. Cyclic voltammograms on carbon steel electrode in test solutions without and with different concentrations of Trp; scan rate 1 mV s^{-1}

the studied media has more pronounced influence on hydrogen evolution reaction than on metal ionization.

Adsorption isotherms

Useful information about the inhibition mechanism can be gained from adsorption isotherm [14, 15]. The parameter which characterizes the type of interactions between inhibitor and metal is the adsorption Gibbs energy, calculated using equation (7) [28].

$$\Delta G_{ads} = -RT\ln(55.5k_{ads}) \qquad (7)$$

where R is the universal gas constant, T the thermodynamic temperature, k_{ads} the equilibrium constant for the adsorption process and value 55.5 is the concentration of water in the solution [28, 29].

In the case of amino acids adsorption on metals or alloys, the most suitable isotherm was found to be Langmuir isotherm, written in the linear form (8) [15, 28].

$$\frac{c_{inh}}{\theta} = \frac{1}{k_{ads}} + c_{inh} \qquad (8)$$

The value of adsorption constant was calculated starting from the linear dependence $c_{inh}/\theta = f(c_{inh})$ (fig. 8) drawn on the basis of the experimental parameters computed from weight loss data and Tafel slopes.

The regression coefficient R^2 for both methods was very close to 1, proving that the adsorption process of Trp on the metal surface takes place according to the Langmuir isotherm.

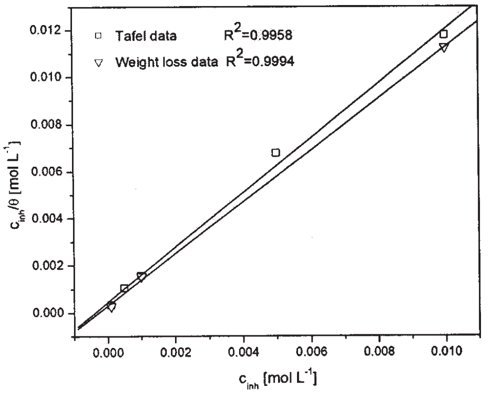

Fig. 8. Langmuir adsorption isotherms for different Trp concentrations in test solutions, obtained from weight loss and Tafel data

The negative values of the Gibbs energy ΔG_{ads} = -30.1 kJ mol^{-1} calculated from weight loss data and ΔG_{ads} = -29.1 kJ mol^{-1} from Tafel slopes show that the process of adsorption on metal surface of Trp molecules is a spontaneous one due to electrostatic interactions between amino acid molecules and metal surface. Generally, values of the free energy less negative than -40 kJ mol^{-1} are associated with processes that occur by physical adsorption of the inhibitor on metal surface [29].

SEM images and EDX spectra

In the absence of the inhibitor, from figure 9 (a) a severe damage of carbon steel surface due to metal ionization is observed. The image reveals clear pits and cavities with roughness. The EDX spectra for carbon steel are presented in figure 9 (b) and (d). In the absence of the inhibitor the spectra shows the characteristic peaks of the elements constituting carbon steel sample. At addition of the inhibitor in test solution, figure 9 (c), there are fewer cracks observed in the micrographs, reaching to a uniform surface of carbon steel in the presence of 10^{-2} mol L^{-1} of Trp. Also, the EDX spectrum shows an additional line of oxygen due to oxide layer formed. The results of EDX analysis are listed in table 4.

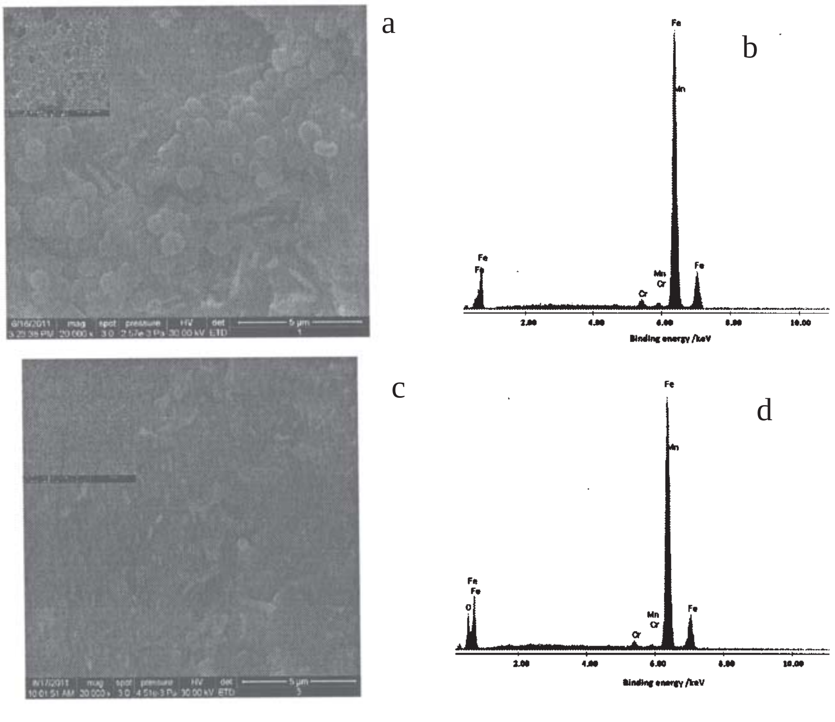

Fig. 9. SEM images and corresponding EDX spectra of carbon steel samples after immersion for 240 h in test solutions, with and without inhibitor addition

Table 4
RESULTS OF EDX ANALYSIS OF THE
CARBON STEEL SAMPLES
AFTER EXPOSURE IN TEST SOLUTIONS

Inhibitor	Fe %	Mn %	Cr %	O %
Blank	97.59	1.08	1.33	-
Trp $1x10^{-2}$ mol L^{-1}	70.13	0.72	1.06	28.09

The metal surface was protected by adsorption of inhibitor molecules that form a protective film, or due to complex compounds between iron and Trp molecules. The micrographs suggest that corrosion process of carbon steel is inhibited which is supported as well by the weight loss measurement, cyclic voltammetry and polarization results.

Conclusions

Tryptophan was found to be a good corrosion inhibitor for carbon steel in 0.5 mol L^{-1} CH_3COOH/0.25 mol L^{-1} CH_3COONa solutions at room temperature. The inhibition efficiency of the amino acid proportionally increases with the increasing concentration, efficiency exceeding 80% for 10^{-2} M concentration of Trp. Tafel diagrams emphasized that Trp is a cathodic type corrosion inhibitor, acting on hydrogen evolution reaction, process associated with metal dissolution. This is confirmed by the cathodic polarization curves drawn on carbon steel in studied media. Tryptophan also acts on the anodic process of metal ionization but with a small contribution.

Adsorption process of the inhibitor on metal surface is developed according to Langmuir isotherm, the regression coefficient being almost 1. The negative values of adsorption energy reveal that adsorption of Trp is a spontaneous process. Since the adsorption Gibbs energy values are smaller in absolute value than 40 kJ mol^{-1}, the adsorption of Trp occurs preferentially through physical interactions.

Taking into account the experimental results, finally one can conclude that Trp is a good corrosion inhibitor at low concentration for carbon steel in weak acid solutions.

Acknowledgment: "This work was partially supported by the strategic grant POSDRU 107/1.5/S/77265 and POSDRU/21/1.5/G/13798, inside POSDRU Romania 2007-2013 co-financed by the European Social Fund – Investing in People."

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Manuscript received: 6.04.2012