

**EVALUATION OF THE INHIBITOR EFFECT OF L-ASCORBIC  
ACID ON THE CORROSION OF MILD STEEL**

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**6° COTEQ Conferencia sobre Tecnologia de Materias  
22° CONBRASCORR – Congresso Brasileiro de Corrosão  
Salvador – Bahia  
19 a 21 de agosto de 2002**

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## ABSTRACT

The corrosion of mild steel in pH = 2.0 to 6.0 solutions in the presence of L-ascorbic acid (AA) was investigated by electrochemical and weight loss measurements. The maximum inhibitor efficiency obtained was 69.0% in pH = 4.0 solutions with  $10^{-3}$  mol.dm<sup>-3</sup> AA. In these conditions, AA acts as a mixed inhibitor. Activation energies of 49.4 and 65.7 kJ.mol<sup>-1</sup> for the corrosion processes were obtained in the absence and presence of AA, respectively. The inhibition mechanism was interpreted as being due to the adsorption on the metallic surface of the L-dehydroascorbic acid, a derived product of L-ascorbic acid.

## SINOPSE

Foi investigada a corrosão do aço-carbono, em soluções com pH = 2,0 a 6,0, na presença de -ácido L-ascórbico (AA) por medidas eletroquímicas e gravimétricas. A máxima eficiência do inibidor obtida foi de 69.0% em pH = 4.0, nas soluções contendo  $10^{-3}$  mol.dm<sup>-3</sup> AA. Nestas condições, AA atua como um inibidor misto. As energias de ativação obtidas para os processos corrosivos, na ausência e na presença de AA, foram 49.4 e 65.7 kJ.mol<sup>-1</sup>, respectivamente. O mecanismo de inibição foi interpretado como sendo a adsorção, na superfície metálica, do ácido L-dehidroascórbico, um derivado do ácido L-ascórbico.

*Keywords:* Mild steel; Weight loss; Polarization; Acid inhibition; L-ascorbic acid

## 1. INTRODUCTION

The main strategy to prevent electrochemical corrosion is to insulate the metal from the corrosive agents in the most effective possible way. Among the different methods available [1-3], the use of corrosion inhibitors is usually the most appropriate way to achieve this objective. Inorganic substances such as phosphate, chromate, dichromate, nitrite, nitrate and sulfide of alkaline metals, salts of cadmium and arsenic, which are extensively used as corrosion inhibitors in several media and for different metals and alloys [3], decrease considerably the generalized oxidation of metals. On the other hand, it is known that some of those products and their compounds are toxic or pollute the environment [4], which limits their application. Therefore, the development of new, non-toxic type of corrosion inhibitors is essential to overcome this problem. Among these alternative corrosion inhibitors, organic products containing one or more polar functions (with atoms of N, O and S) have showed to be quite efficient to prevent corrosion [5], as well as heterocyclic compounds containing polar groups and pair electrons [6]. The inhibiting action of those organic compounds is usually attributed to interactions with the metallic surface by adsorption. The polar function is usually regarded as the reaction center for the establishment of the adsorption process [7], the adsorption bond strength being determined by the electron density on the atom acting as the reaction center and by the polarizability of the function [8].

The present work is devoted to study the inhibitor effect of L-ascorbic acid on the corrosion of mild steel with 2.34% Cr in acid medium using measurements of weight loss and potentiodynamic polarization curves. L-ascorbic acid (vitamin C) is an easy to obtain, water-soluble compound whose molecule has characteristics desirable in a corrosion inhibitor (Fig. 1). Nevertheless, a review of the literature revealed that over the last two decades only a few works have studied corrosion in media containing L-ascorbic acid [9-15].

## 2. EXPERIMENTAL

### 2.1. Materials

The chemical composition of mild steel used in the corrosion experiments is shown in Table 1. The content of chromium of the mild steel used in this work is uncommon. The main plate from where the test coupons and disks used for our experiments were extracted was bought from a small local foundry where varying amounts of Cr are added to salvage metal pieces during the melting process in order to increase the resistance to corrosion of the final product.

All chemicals used were of analytical reagent grade. Acid aqueous solutions with pH = 2.0, 3.0, 4.0, 5.0 and 6.0 were used as blanks. The blank solutions were prepared with 98% H<sub>2</sub>SO<sub>4</sub> and distilled water. The pH was adjusted with 0.1, 0.01 and 0.001 mol.dm<sup>-3</sup> NaOH solutions. The solutions with the inhibitor were prepared just before performing the experiments adding the L-ascorbic acid (solid or diluted) to the blank solution to reach the final concentrations of 10<sup>-3</sup>, 10<sup>-4</sup>, 10<sup>-5</sup>, 10<sup>-6</sup> and 10<sup>-7</sup>

$\text{mol}\cdot\text{dm}^{-3}$ . All experiments were carried out at room temperature in not-deaerated solutions.

## 2.2. Electrochemical measurements

A three-electrode cell was used to carry out the electrochemical measurements. Disks of mild steel (apparent surface area =  $0.502 \text{ cm}^2$ ) were employed as working electrodes. A graphite rod was used as auxiliary electrode and a saturated calomel electrode (SCE) as reference. All potentials are reported in relation to this reference electrode. Prior to carrying out the experiments, the working electrode was abraded with 1200 grit emery paper, cleaned with distilled water in ultrasonic bath, acetone, and dried with jets of hot air. An EG&G PARC model 263A potentiostat/galvanostat linked to a personal computer running an EG&G-PARC "SoftCorr II Model 252/352" software was used for data collection. The potentiodynamic polarization curves were shaped in agreement with the ASTM G5-78 norm [16], but the polarization of electrode for 120 s at potential 400 mV more negative than  $E_{\text{corr}}$  was performed prior to start the polarization curves in order to eliminate possible oxides formed during  $E_{\text{corr}}$  x time experiments. The results are the average of three parallel runs.

## 2.3. Weight loss measurements

The weight loss experiments were carried out using 20x20x1 mm mild steel coupons. The samples were treated before the immersion tests following the same procedure described for the electrochemical tests and weighed. After the immersion tests the corrosion products were carefully removed with the aid of a brush. The coupons were cleaned with distilled water in ultrasonic bath, acetone, dried with jets of hot air and reweighed. The experiments were carried out in triplicate and the corrosion rates were calculated based on the apparent surface area. The immersion periods applied were 2, 6, 12, 24, 72 and 168 hours. The accuracy of corrosion weight loss was 10%.

# 3. RESULTS AND DISCUSSION

## 3.1. Electrochemical results

Fig. 2 shows the  $E_{\text{corr}}$  x time curves obtained for mild steel in  $\text{pH} = 4.0$  solutions with different concentrations of AA ( $10^{-3}$ – $10^{-7} \text{ mol}\cdot\text{dm}^{-3}$ ). An accentuated displacement of  $E_{\text{corr}}$  to more negative values in the first instants of the experiment in solutions with and without the inhibitor was observed. After approximately 20 minutes, the  $E_{\text{corr}}$  measured in all solutions remained constant up to the end of the experiment, except when the concentration of AA in the solution was  $10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ . In this case, a gradual displacement of  $E_{\text{corr}}$  towards more positive potentials was observed, indicating the possible formation a film on the working electrode surface.

Table 2 shows the measured  $E_{\text{corr}}$  after a 1.0 hour immersion test in  $\text{pH} = 2.0$  to 6.0 solutions with different AA concentrations. The influence of the concentration of AA on the  $E_{\text{corr}}$  is not very clear. It was observed, however, that the  $E_{\text{corr}}$  value measured for practically all solutions with AA was more negative than the  $E_{\text{corr}}$  value measured for the blank solution, except for the  $\text{pH} = 5.0$  solution. This effect should

be related with the adsorption of AA or a derived product on the metallic surface, blocking the water adsorption reaction that is implicated in the corrosion process. In all cases, however, the displacement of the corrosion potential ( $E_{\text{corr}}$ ) at different AA concentrations was very small. According to Riggs Jr. [6], the classification of a substance as an anodic or cathodic inhibitor is possible when the  $E_{\text{corr}}$  displacement is at least 85 mV in relation to the  $E_{\text{corr}}$  measured for the blank solution. Sekine *et al.* [10] concluded from the electrochemical and gravimetric studies carried out using pH = 6.0 NaCl solutions (0.3 and 0.03%) that AA is an anodic inhibitor of mild steel corrosion, although they didn't carry out any  $E_{\text{corr}}$  x time experiments. Our experiments also showed a significant positive  $E_{\text{corr}}$  displacement in pH = 6.0 solutions, but only for relatively high inhibitor concentration. Gonçalves *et al.* [17] recently also observed positive shifts in the corrosion potential of steel in 0.5 mol.dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> with 10 mmol.dm<sup>-3</sup> AA deaerated solutions. We classify AA as a mixed inhibitor, acting simultaneously on anodic and cathodic reactions. This type of inhibitors does not produce displacements of  $E_{\text{corr}}$  in relation to the blank solution, or only very small ones [5].

The potentiodynamic polarization curves for mild steel in pH = 4.0 solutions with different AA concentrations (10<sup>-3</sup>–10<sup>-7</sup> mol.dm<sup>-3</sup>) are shown in Fig. 3. The presence of AA alters significantly the profiles of the curves. This effect should be related with the adsorption of the organic compound onto the surface of the metallic electrode and the inhibition of the corrosion process. However, the polarization curves show a random order with the inhibitor concentration. It is well known that the adsorption process from solution on metallic surfaces is a replacement reaction of the water molecules by the adsorbent ones. This effect is potential dependent, even if the adsorption does not involve Faradaic charge transfer [18]. To trace the potentiodynamic polarization curves, after obtaining the  $E_{\text{corr}}$  x time curves, the electrode was kept 120 s in a potential 400 mV more negative than  $E_{\text{corr}}$ , in order to eliminate possible oxides formed during  $E_{\text{corr}}$  x time measurements. This polarization probably is also influencing the adsorption of AA onto the metallic surface and interfering in the order of polarization curves with the AA concentration, once the applied potential is not the same, because it depends on  $E_{\text{corr}}$ . This behavior, therefore, confirms that there is an adsorption process of AA on the electrode surface, as observed by other authors [17].

As can be seen in Fig. 3, there is no evidence of the formation of passivation film on the electrode surface either in the presence or in the absence of the inhibitor. Visual inspection of the samples after running the polarization curves revealed that there was uniform attack and small amounts of easily removable rust were deposited on the surface. In any experiments some type of localized corrosion was observed.

The inhibition efficiency (IE) was calculated using the classical formula  $IE = (i_{\text{corr}} - i_{\text{corr}}^{\text{inh}}/i_{\text{corr}}) \times 100$ , where  $i_{\text{corr}}^{\text{inh}}$  is the corrosion current density measured in the presence of AA. The IE of AA for mild steel was very low, rarely surpassing 30.0%, even for high concentrations of AA. The only conditions in which the organic reagent showed a reasonable efficiency at inhibiting the corrosion process was in pH = 4.0 solutions when the AA concentration was 10<sup>-3</sup> mol.dm<sup>-3</sup>. The inhibition

efficiency of 69.0% achieved in those conditions was attributed to the adsorption on the mild steel surface of AA.

The Arrhenius plot for the corrosion of the mild steel samples is shown in Fig. 4 (corrosion rates are expressed in mdd – milligrams per square decimeter per day). The data were obtained in pH = 4.0 solutions in the absence and presence of  $10^{-3}$  mol.dm<sup>-3</sup> AA. The activation energy determined from the slope of the Arrhenius plot corresponds to 49.4 kJ.mol<sup>-1</sup> (in the absence of AA) and 65.7 kJ.mol<sup>-1</sup> (in the presence of AA). The activation energy value obtained in the absence of AA is similar to that obtained by other authors in the same conditions [19-21]. The higher activation energy in the presence of AA can be interpreted as being due to the decrease of the degree of surface coverage with increasing temperature, since the corrosion process occurs essentially in the part of the surface free from adsorbed molecules [22]. A similar behavior had been previously observed in a study of the inhibition of low carbon steel corrosion by propargyl alcohol [23].

As expected, the corrosion rate increased proportionally to increases in temperature (20-60 °C) in pH = 4.0 solutions with or without  $10^{-3}$  mol.dm<sup>-3</sup> AA (Table 3). The increase in the corrosion rate with increasing temperatures was smaller in the solutions with AA and the inhibition efficiency fell drastically above 40 °C. This should be due to the reduction in surface coverage and corroborates the activation energy data obtained.

Until the moment, the inhibition of the corrosion process was only attributed to the adsorption of AA on the electrodes surface. However, the chemical stability of AA is dependent of the pH of the solution. The ionization of AA generates the formation of the L-monoascorbate and ascorbate anions, which are also able to adsorb in the metallic surface or to originate other products that can act in the same way. The changes in composition that occur when a solution of a weak acid or a weak base is altered are sometimes of interest and can be visualized by plotting the relative concentration of the weak acid as well as the relative concentration of the conjugate base as a function of pH. These relative concentrations are called alpha values [24]. The alpha values of the species L-ascorbic acid and L-monoascorbate and ascorbate anions as a function of pH are shown in Fig. 5.

The mathematical expressions for alpha values were obtained in agreement with described in the literature [24]. In pH = 4.0 solutions, where the highest protection efficiency was obtained, there were about 60% L-ascorbic acid and 40% L-monoascorbate anion. The L-monoascorbate anion is a very reactive species, which can be easily oxidized to L-dehydroascorbic acid (DHA) [25-27], as shown in Fig. 6.

In the conditions in which the experiments were carried out, the concentration of DHA in the solution was certainly higher than that of L-monoascorbate anion. For

this reason, we believe that DHA is the main species involved in the inhibition process, although we don't have experimental evidence of the presence of DHA in the solution. The very low inhibition efficiency of solutions with  $\text{pH} < 4.0$  may be associated to the higher concentration of AA, a complexing agent for many metals [28]. Taking this aspect into consideration and being aware of the composition of the mild steel used (2.34% Cr), we believe that the complexation of chromium and iron ions by AA, which generates products with high stability constants, significantly diminishes the inhibition action of AA. The increase of the corrosion rate of alloys due to the action of complexing agents was also reported by Dean Jr. *et al* [5]. In  $\text{pH} > 4.0$  solutions, where the L-monoascorbate anion concentration was higher an increase in the protection efficiency was not observed. This can be taking place due to a competition for the sites of adsorption between DHA (derived of the L-monoascorbate anion) and the sulphate ions. It is known that sulphate ions can to adsorb on metals and to take part in the corrosion mechanism. Increasing sulphate concentration leads to an increase of the corrosion [29].

### 3.2. Weight loss measurements

Fig. 7 shows the graph of the corrosion rate obtained for different period of immersion tests as a function of pH when the AA concentration in the solution was  $10^{-3} \text{ mol.dm}^{-3}$ . It is obvious to hope (as it is seen in the Fig. 7) that an increase in the solution's pH causes a reduction of the mild steel corrosion rate values. Note, even so, that the longer the immersion periods, the lower the corrosion rates were. This is also in certain way waited in neutral or slightly acid solutions where the oxide film formation is possible. We observed this, however, in very acid solutions too, where the deposit of oxide films is more difficult. We attributed this behavior to the action of AA, indicating that the adsorption of the inhibitor in conditions of open circuit potential is time dependent.

Fig. 8 shows the corrosion rates as a function of pH in solutions with  $10^{-3} \text{ mol.dm}^{-3}$  AA obtained from the electrochemical and weight loss (time of immersion = 2 hours) experiments. Although there is a certain discrepancy in the data, the observed profile of the curves is quite similar, indicating that the AA inhibition mechanism is analogous in conditions of electrode polarization and in open circuit potential conditions. Corrosion rates obtained from electrochemical data are generally higher than those obtained from immersion tests due to the effects of electrode polarization [1].

## 4. CONCLUSIONS

The data obtained from potentiodynamic polarization curves and weight loss measurements show that AA is just a reasonable corrosion inhibitor for mild steel (with 2.34% Cr). The maximum inhibition efficiency achieved was 69.0% in  $\text{pH} = 4.0$  solutions with relatively high concentrations of AA ( $10^{-3} \text{ mol.dm}^{-3}$ ), and depended on the time of immersion. The results obtained are not sufficiently conclusive to characterize AA clearly as a cathodic, anodic or mixed inhibitor.

Nevertheless, the fact that in most of the experiments carried out the displacement of the corrosion potential at different AA concentrations was not significant would characterize it as a mixed inhibitor. Experiments at different temperatures showed that the protection efficiency decreases as temperature increases. The corrosion process is inhibited by the adsorption on the mild steel surface of the L-dehydroascorbic acid, with activation energies of 49.4 and 65.7 kJ.mol<sup>-1</sup> in the absence and in the presence of ascorbic acid, respectively.

## ACKNOWLEDGEMENTS

The authors wish to express their gratitude to CNPq for financial support of this work.

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FIGURE CAPTIONS

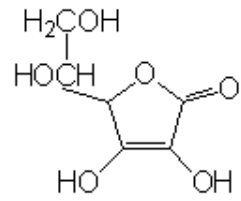


Fig. 1. Molecule of L-ascorbic acid

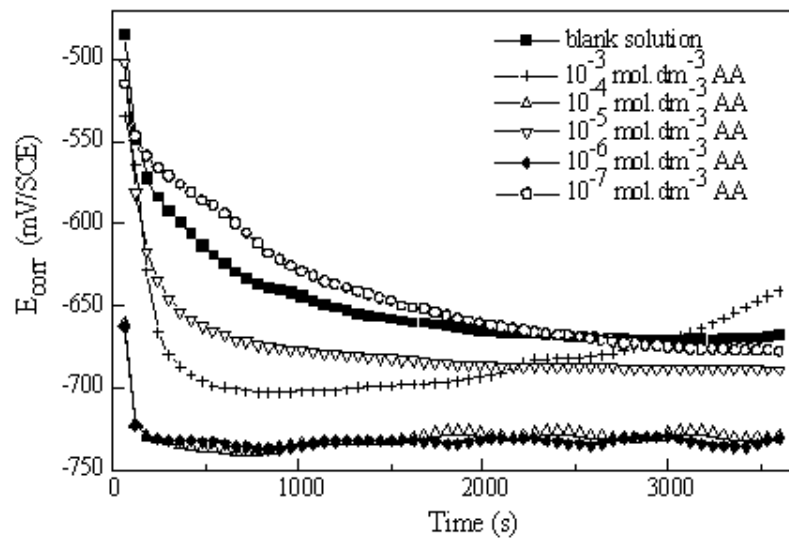


Fig. 2.  $E_{\text{corr}}$  x time curves for mild steel in pH = 4.0 solutions with  $10^{-3}$  to  $10^{-7}$  mol.dm<sup>3</sup> AA

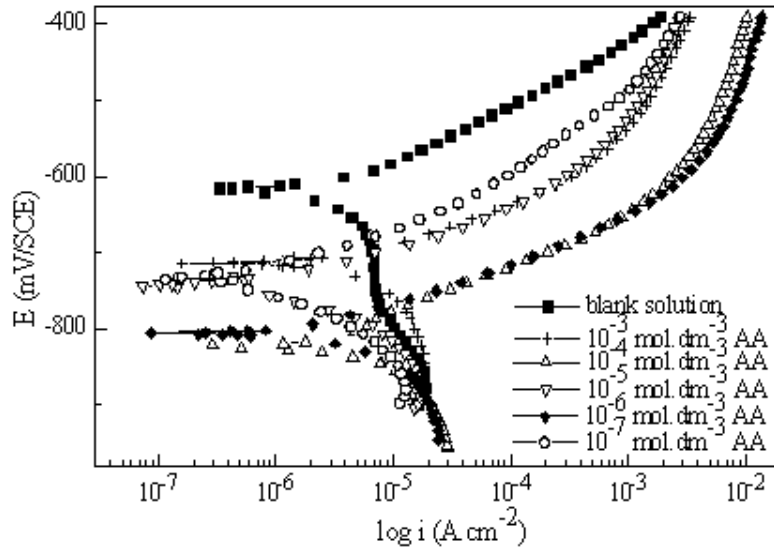


Fig. 3. Potentiodynamic polarization curves for mild steel in pH = 4.0 with  $10^{-3}$  to  $10^{-7}$  mol.dm<sup>-3</sup> AA at 1mV.s<sup>-1</sup> scan rate

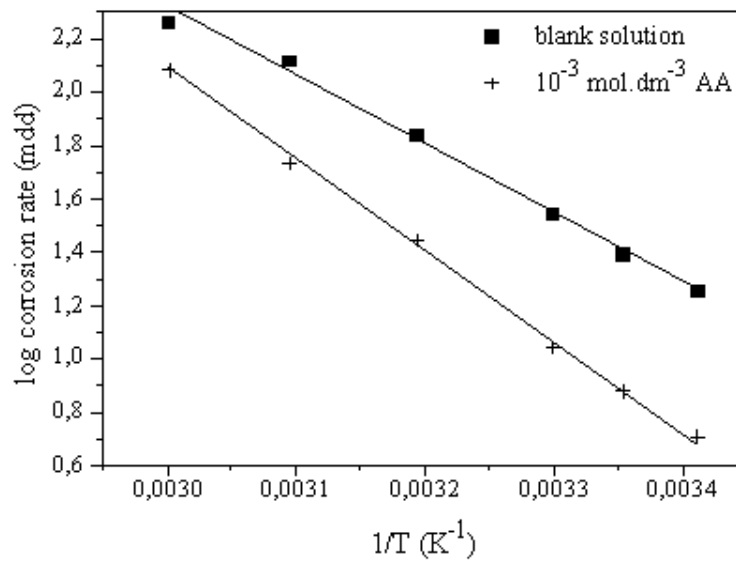


Fig. 4. Arrhenius plot for mild steel in pH = 4.0 solution with  $10^{-3}$  mol.dm<sup>-3</sup> AA

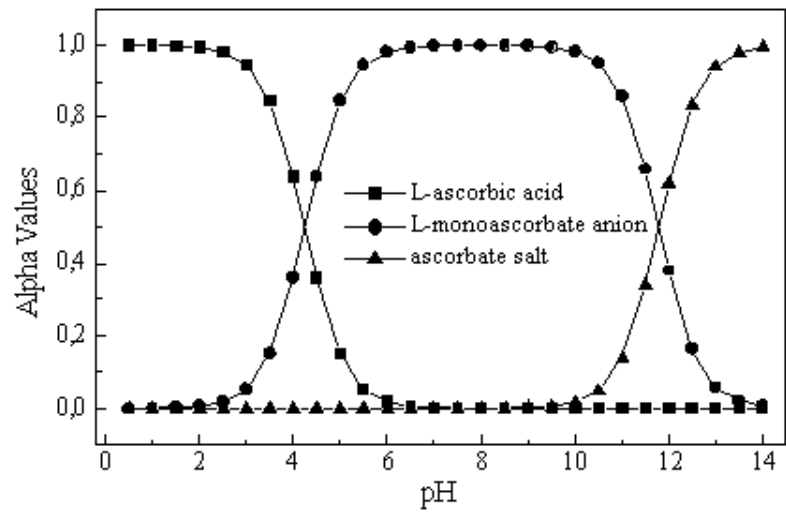


Fig. 5. Composition of AA solution as a function of pH

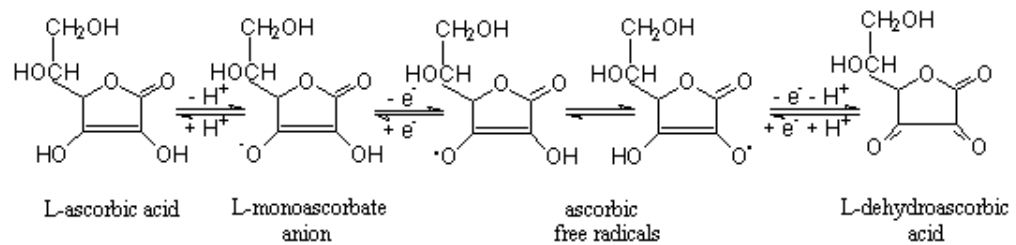


Fig. 6. Oxidation of L-monoascorbate anion to L-dehydroascorbic acid

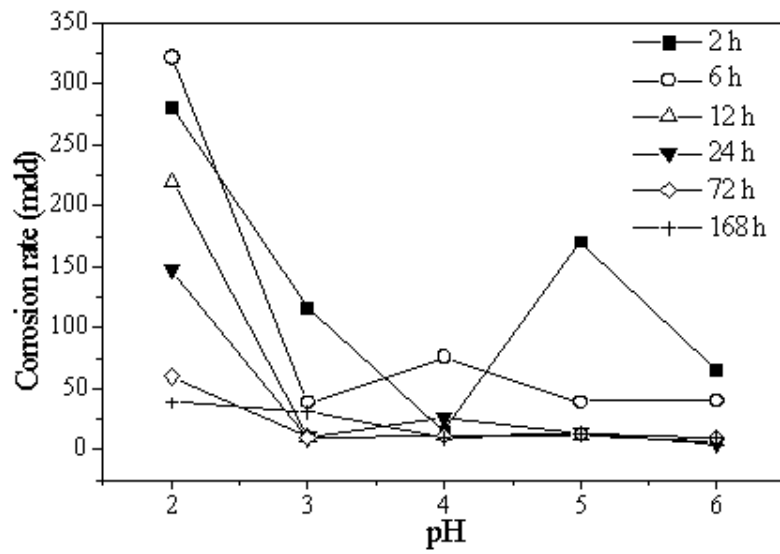


Fig. 7. Corrosion rates obtained from weight loss experiments for mild steel in pH = 2.0 to 6.0 solutions with  $10^{-3}$  mol.dm<sup>3</sup> AA

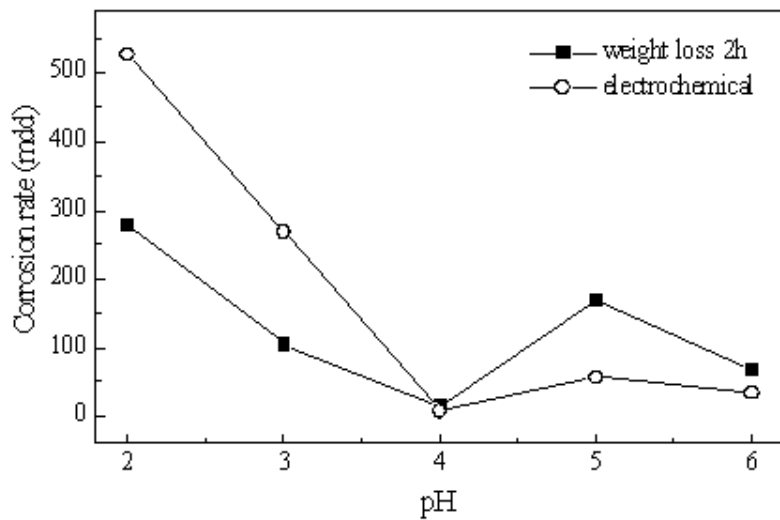


Fig. 8. Corrosion rates obtained from weight loss and electrochemical experiments for mild steel in pH = 2.0 to 6.0 solutions with  $10^{-3}$  mol.dm<sup>3</sup> AA

TABLE CAPTIONS

Table 1 - Chemical composition of mild steel

	C	Mn	Cr	S
wt %	0.049	0.227	2.34	0.0005

Table 2 -  $E_{\text{corr}}$  values for mild steel after 1.0 hour of immersion tests

[AA] mol.dm <sup>3</sup>	pH = 2.0		pH = 3.0		pH = 4.0		pH = 5.0		pH = 6.0	
	$E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{a}}$	$E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{a}}$	$E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{a}}$	$E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{a}}$	$E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{a}}$
Blank	-597		-711		-668		-736		-668	
10 <sup>-3</sup>	-605	-8	-727	-16	-641	+27	-732	+4	-484	+184
10 <sup>-4</sup>	-655	-58	-727	-16	-729	-61	-712	+24	-711	-43
10 <sup>-5</sup>	-628	-61	-734	-23	-689	-21	-726	+10	-675	-7
10 <sup>-6</sup>	-667	-70	-727	-16	-731	-63	-716	+20	-676	-8
10 <sup>-7</sup>	-631	-34	-715	-4	-678	-10	-727	+9	-583	+85

<sup>a</sup> $\Delta E_{\text{corr}} = E_{\text{corr}}(\text{inhibitor}) - E_{\text{corr}}(\text{blank})$  – expressed in mV

Table 3 - Effect of the temperature on the inhibition efficiency (IE) of 10<sup>-3</sup> mol.dm<sup>-3</sup> AA for mild steel in pH = 4.0 solution

Temperature (°C)	Corrosion rate (mdd)		IE (%)
	Blank solution	10 <sup>-3</sup> mol. dm <sup>-3</sup> AA	
20.0	17.9	5.1	71.5
25.0	24.5	7.6	69.0
30.0	25.2	8.1	67.8
40.0	127.9	42.2	67.0
50.0	130.5	76.6	41.8
60.0	152.6	92.5	39.4