

Electrochemical Evidences of Linalyl Acetate (LA) Adsorption on Low-Carbon Steel in Aqueous and Ethanol Medium

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O comportamento eletroquímico do aço-carbono em soluções aquosas contendo KNO_3 0,10 mol L^{-1} e soluções etanólicas contendo cloreto de tetraetilamônio 0,10 mol L^{-1} foi estudado na ausência e presença de diferentes concentrações de acetato de linalila. Técnicas eletroquímicas como a potenciometria, voltametria cíclica, cronoamperometria, curvas de Tafel e espectroscopia de impedância eletroquímica foram utilizadas a fim de compreender a interação entre o composto orgânico e a superfície do eletrodo. Medidas de perda de massa foram realizadas. O acetato de linalila adsorve na superfície do aço-carbono mesmo na presença de grande quantidade de água ou etanol. A energia de adsorção para este processo vale $-25,98 \text{ kJ mol}^{-1}$ em soluções aquosas e $-26,71 \text{ kJ mol}^{-1}$ em soluções etanólicas. Foi detectado que as espécies adsorvidas na superfície do metal diminuíram os valores das densidades de corrente anódicas, bem como a perda de massa do metal. Estes efeitos permitem-nos classificar o acetato de linalila como um inibidor de corrosão verde para o aço-carbono em soluções aquosas e etanólicas.

The electrochemical behavior of low-carbon steel in 0.10 mol L^{-1} KNO_3 aqueous solutions and 0.10 mol L^{-1} tetraethyl ammonium chloride ethanolic solutions was studied in absence and with different concentrations of linalyl acetate (LA). Electrochemical techniques such as potentiometry, cyclic voltammetry, chronoamperometry, Tafel polarization and electrochemical impedance spectroscopy were used in order to comprehend the interaction between the organic compound and electrode surface. Experiments involving weight loss measurements were performed. LA adsorbs on the low-carbon steel surface even in the presence of a large amount of water or ethanol. The adsorption energy for this process was $-25.98 \text{ kJ mol}^{-1}$ for aqueous solutions and $-26.71 \text{ kJ mol}^{-1}$ for ethanolic solutions. It was also detected that the adsorbed species on metal surface decreases the anodic current density values as well as the weight loss of the metal species. This effect allows us to classify the linalyl acetate as a green corrosion inhibitor of low-carbon steel in aqueous and ethanol medium.

Keywords: low-carbon steel, adsorption, corrosion, linalyl acetate, polarization

Introduction

The ability of an organic compound to interact with metal surface is closely associated with the chemical adsorption.¹⁻⁵ The efficiency of this interaction is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and π -electrons.⁶ Such compounds can adsorb onto the metal surface and block the active surface sites, thus reducing the electrochemical reactions involved in charge transfer processes.

The use of natural products in chemical industry has become extremely important because they are viewed as an

incredibly rich source of naturally chemical compounds that are biodegradable in nature and can be extracted by simple procedures with low cost.⁷⁻¹⁰ It was reported that natural extracts can be an excellent source of cheap, eco-friendly and non-toxic compounds for different purposes.¹¹⁻¹³ Our laboratory has previously carried out studies confirming the adsorption of caffeine onto zinc and low-carbon steel surfaces in ethanolic solutions.^{14,15} Studies involving natural products of plant origin, describes good interactions with metal surface.¹⁶⁻²⁴

This paper reports an evidence of the ability of the linalyl acetate (LA) to interact with low-carbon steel in aqueous and ethanol medium. The metallic alloy tested, as well as the mediums, were chosen with practical purposes

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in order to apply the data obtained in industry.²⁵ LA was studied because it is a natural product found in many flowers and spice plants like a kind of mint (*Mentha x gentilis L.*), it is non-toxic from environmental point of view and economically feasible. The adsorption capability of LA on steel surface was confirmed by means of potentiometric studies, cyclic voltammetry, chronoamperometry, polarization curves and electrochemical impedance spectroscopy (EIS). Weight loss measurements were performed in order to confirm the corrosion inhibitory ability of the compound. Since the compound is insoluble in water, it was first solubilized in ethanol and further in water. In ethanol medium, the addition of LA was made directly. The chemical structure of LA is presented in Figure 1.

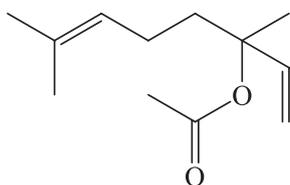


Figure 1. Linalyl acetate (3,7-dimethyl-1,6-octadien-3-yl acetate)(LA).

Experimental

Working electrodes for potentiometric, potentiodynamic voltammetry, chronoamperometry and electrochemical impedance spectroscopy measurements were cut into a rectangular shape ($1.0 \times 0.5 \times 0.1$ cm) while the pieces for weight losses were cut into a square shape ($1.0 \times 1.0 \times 0.1$ cm) from a low-carbon steel sheet (C, 0.06; Mn, 0.31; P, 0.0104; S, 0.0114; Cr, < 0.001; Ni, 0.0051; Al, 0.0332 wt. %). The metal was used without thermal treatment. The metallic pieces were abraded with 600 and 1200 emery papers, rinsed with deionized water, and degreased with a PA grade acetone:chloroform mixture (1:1) prior to each experiment. The LA was supplied by ACRÓS-ORGANICS. Deionized water was used to prepare 0.10 mol L^{-1} KNO_3 aqueous solutions. Ethanol PA grade was used to prepare 0.10 mol L^{-1} tetraethyl ammonium chloride solutions. These salts were necessary in order to increase the conductivity of the water and ethanol, respectively. A platinum wire was employed as the auxiliary electrode and an Ag/AgCl (KCl saturated) as reference electrode.

The weight loss experiments were carried out using a Sartorius analytical balance (model B210S) while the electrochemical tests were performed with an Autolab potentiostat (model PGSTAT30) coupled to a personal computer. Open-circuit potential (OCP) measurements were taken with a digital voltmeter MINIPA (model ET1000). All experiments were repeated at least three times in order to get a good reproducibility of the data.

Results and Discussion

Potentiometry studies

The purpose of these studies was to determine the rate of interaction between the organic compound and the electrode surface by comparing the open-circuit potential changes in absence and in the presence of LA. In these experiments, a single glass cell equipped with working and reference electrodes was used. The OCP was read directly from digital voltmeter against different immersion times in the absence and in the presence of LA. The working electrode was immersed in tested solutions in the absence and presence of LA under constant stirring. Two organic compound concentrations 5.0 mmol L^{-1} and 10.0 mmol L^{-1} were studied. Figures 2A and 2B show the potential \times time curves in the absence and with two LA different concentrations.

The OCP \times time curves in absence of LA depend on the mechanism involving the metal oxide formation in

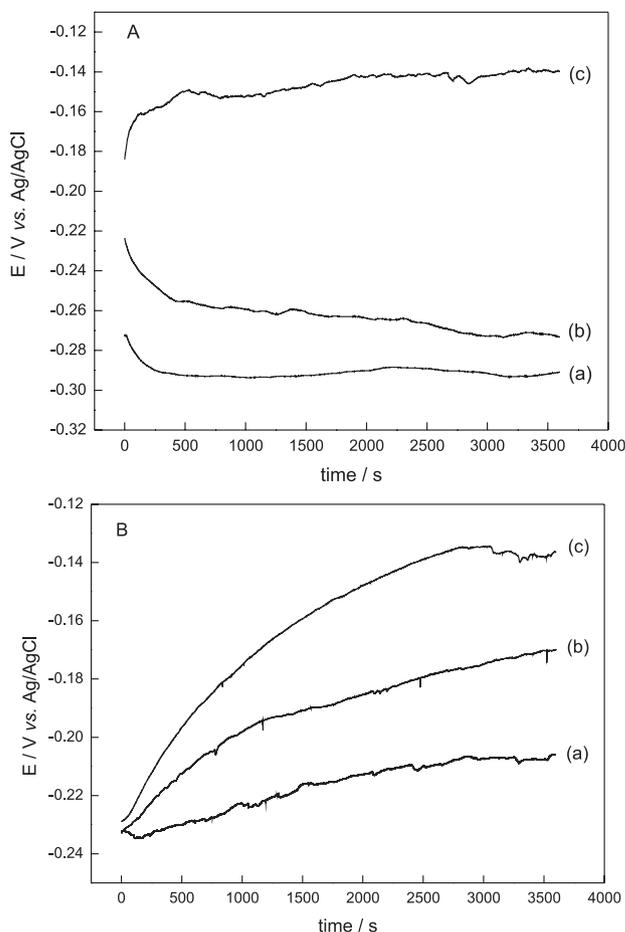


Figure 2. Open-circuit potential at different times of low-carbon steel in KNO_3 0.10 mol L^{-1} (A) and in 0.10 mol L^{-1} tetraethyl ammonium chloride in ethanol (B), in absence (a) and in the presence of inhibitor (b) 5.0 mmol L^{-1} and (c) 10.0 mmol L^{-1} .

aqueous (Figure 2A) and ethanol mediums (Figure 2B). As observed, the presence of a small amount of the organic compound shifts the electrode potential to less negatives values in both mediums. This effect was dependent on LA concentration. During the experiment time, it was not observed potential displacement that could indicate desorption of the compound. This behavior suggests a stable interaction between LA and the electrode surface. This fact may be associated with the inhibitory effect on the anodic reactions occurring on the electrode surface involving adsorbed solvent molecules. Despite of the great concentration difference between LA and water, the organic compound should adsorb preferentially on the active sites, confirming a stable interaction between LA and the metal surface. The same results were observed in ethanol medium.

Cyclic voltammetry

Cyclic voltammetric experiments were performed in order to observe the charge transfer processes on the metal surface during the potential sweeps in absence and in the presence of LA as well as to obtain the best conditions for the interaction between the organic compound and the electrode surface. The potential program was selected in order to get cathodic as well as anodic current involved in both processes. Figures 3A and 3B show the voltammograms of low-carbon steel in the absence and in the presence of two different concentrations of LA in both mediums. The curves were recorded at 10.0 mV s^{-1} after maintaining the electrode polarized for 45 s at the initial potential. This polarization time was necessary in order to guarantee a good surface coverage with the adsorbed species formed during the experiments in the presence of the organic.

In the absence of LA, redox processes were observed from -0.90 V to 0.00 V in both mediums. In aqueous medium, two peaks were observed during positive potential sweep, at -0.40 V and -0.05 V . Clearly, both peaks are related with metal electrooxidation. During negative potential sweep, only one cathodic peak was remarkable at -0.55 V . This peak should be related with electroreduction of an oxide film formed on the electrode surface. In ethanol, however, anodic currents were visible at -0.35 V . During negative potential sweep, cathodic currents corresponding to the electroreduction of the metal oxide formed, were visible after around -0.30 V . In the presence of LA, the anodic peaks decrease as LA concentration increases in both mediums. In the last addition of LA, the anodic processes almost disappear. Anodic charge transfer processes are being blocked by the presence of LA. Adsorbed LA clearly inhibits the

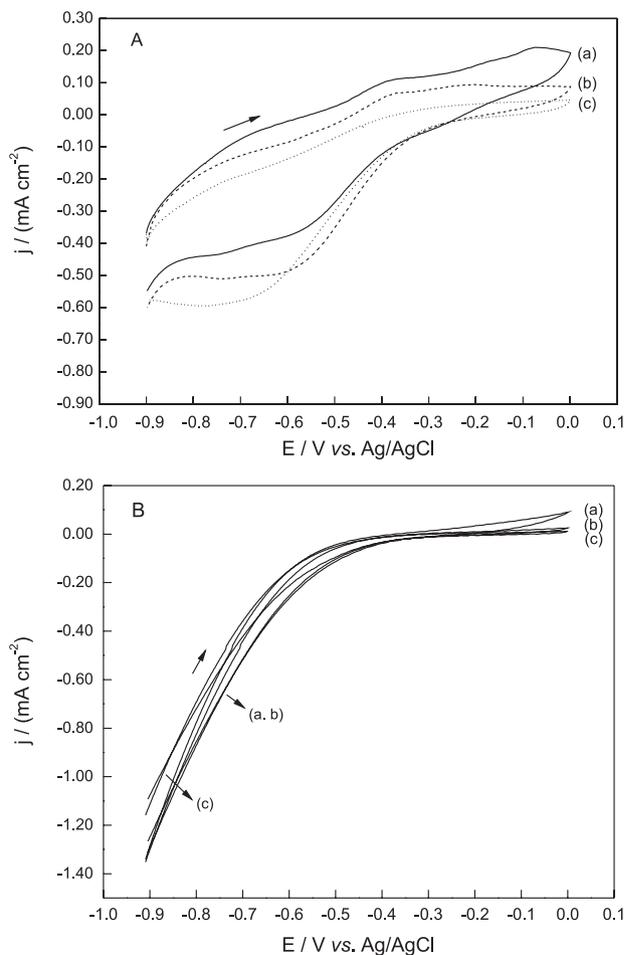


Figure 3. Cyclic voltammograms of low-carbon steel in aqueous $0.10 \text{ mol L}^{-1} \text{ KNO}_3$ (A) and in 0.10 mol L^{-1} tetraethyl ammonium chloride in ethanol (B), recorded at 0.10 V s^{-1} in absence (a) and in the presence of LA (b) 1.0 mmol L^{-1} and (c) 20.0 mmol L^{-1} .

electrooxidation of the metal. On the other hand, the cathodic process increases in the presence of LA during negative potential sweep in aqueous medium, suggesting that an electroreduction reaction of LA on the electrode surface is occurring at this potential range and decreases in ethanol medium, suggesting that LA adsorption can inhibit the reaction regarding to the metal oxide formation.

Analysis of the cyclic voltammograms data

The decrease in the anodic current density values suggests that the anodic processes were inhibited in the presence of LA. At 0.00 V , the anodic current values were 76.0% lower in the presence of 20.0 mmol L^{-1} in aqueous solutions. This effect is notable considering the LA concentration. The interaction between the electrode surface and LA increases with compound concentration. This interaction was found to be potential-dependent. The anodic current values were lower when the electrode was polarized

at -0.90 V during 45 s before starting the potential sweep. This potential value (-0.90 V) was the best one in order to improve the interaction between LA and the electrode surface and was selected based on the anodic currents decrease observed directly from the voltammograms. The strategy used to determine the adsorption potential was to use different potential program starting at different potential values. This effect was observed by comparing the anodic current values recorded at 0.00 V in the absence and presence of LA. This dependence indicates an adsorption process involving LA and the low-carbon steel surface. Assuming this adsorption step, the fraction of the surface covered by adsorbed molecules of the inhibitor (θ) can be determined by the equation:¹⁴

$$\theta = \left(1 - \frac{I_{\text{inh}}}{I_o} \right) \quad (1)$$

where I_o and I_{inh} are the uninhibited and inhibited currents, respectively, taken at 0.00 V Ag/AgCl.

The plot of C/θ against the inhibitor concentration C yields a straight line, as shown in Figures 4A and 4B, for both mediums.

The strong correlation ($R = 0.9946$ in water and $R = 0.9999$ in ethanol) suggests that LA was adsorbed onto the low-carbon steel surface electrode according to the Langmuir isotherm:²⁶⁻²⁹

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (2)$$

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln (55.5 K_{\text{ads}}) \quad (3)$$

where 55.5 is the concentration of water in the solution in mol L^{-1} .

The adsorption free energy ($-\Delta G_{\text{ads}}^{\circ}$) reflects a spontaneous capacity of the inhibitor molecule adsorbed on the surface of the metal, which is less than -20.0 kJ mol^{-1} for spontaneous physical adsorption and is more than -40.0 kJ mol^{-1} for the chemical adsorption, in module. Between these values the interaction between the organic compound and metal surface should be a mix of chemical and physical adsorption.³⁰ The calculated equilibrium constant K of the adsorption reaction is 645.16 L mol^{-1} which gives a $\Delta G_{\text{ads}}^{\circ} = -25.98$ kJ mol^{-1} . The negative value suggests that LA spontaneously adsorbs onto the low-carbon steel surface and this value indicates that this adsorption is chemical and physical.

The same strategy was applied in ethanol medium; a linear Langmuir isotherm was observed as presented in Figure 4B. The adsorption energy calculated gives a $\Delta G_{\text{ads}}^{\circ} = -26.71$ kJ mol^{-1} . The negative value also suggests

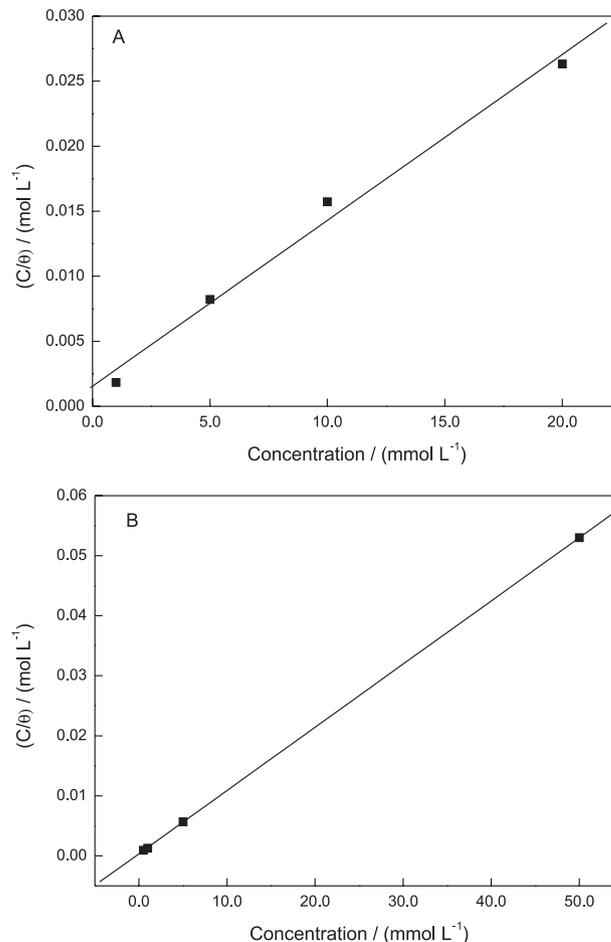


Figure 4. The Langmuir adsorption isotherm determined from four LA concentrations (1.0; 5.0; 10.0 and 20.0 mmol L^{-1}) for water containing KNO_3 0.10 mol L^{-1} (A) and (0.5; 1.0; 5.0; 50.0 mmol L^{-1}) for 0.10 mol L^{-1} tetraethyl ammonium chloride in ethanol (B).

that LA spontaneously adsorbs onto the low-carbon steel surface and this value indicates that this adsorption is a mix of chemical and physical interactions.

Chronoamperometric studies

The chronoamperometric experiments were performed in order to verify the ability of the LA to inhibit the anodic processes of the low-carbon steel during anodic potential polarization in both medium. Once again, the electrode was polarized for 45 s at the initial potential in order to increase the surface coverage with the adsorbed species formed and after the electrode potential was shift to 0.00 V (Ag/AgCl) during 600 s. The current density values associated with the electrooxidation of low-carbon steel in both mediums were recorded in the absence and in the presence of different concentrations of LA, as shown in Figures 5A and 5B.

As observed, the anodic current density values were stable during the experiments, suggesting that the oxide

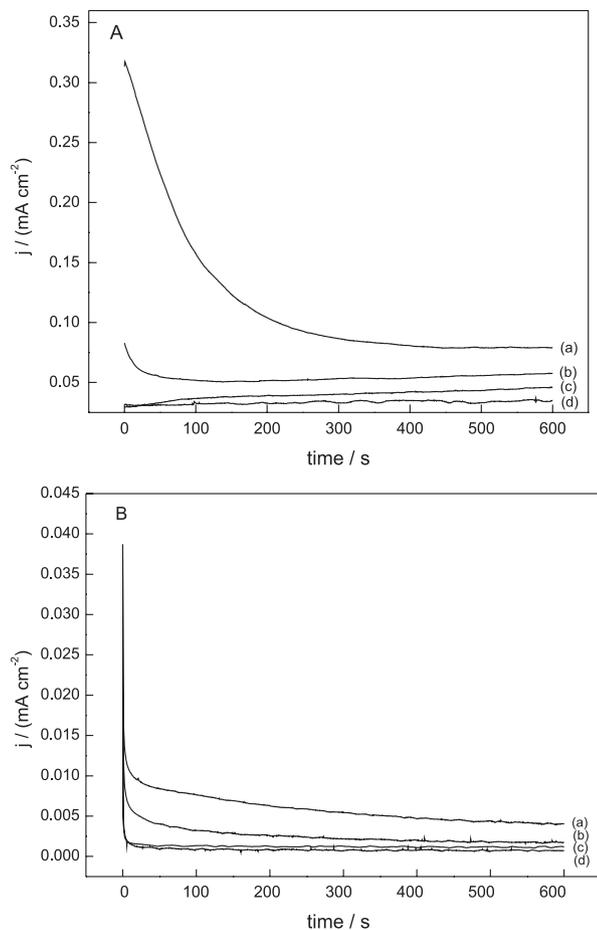


Figure 5. Chronoamperometric curves of low-carbon steel in KNO_3 0.10 mol L^{-1} (A) and in 0.10 mol L^{-1} tetraethyl ammonium chloride in ethanol (B), recorded at 0.00 V (Ag/AgCl) for 600 s in absence (a) and in the presence of LA (b) 1.0 mmol L^{-1} , (c) 5.0 mmol L^{-1} and (d) 10.0 mmol L^{-1} .

film is being formed on the electrode surface. However, the current values decrease significantly even in the presence of small quantities of LA, showing a stable interaction between the metal surface and the adsorbed compound. The charge below the curve $\text{current} \times \text{time}$ was used to calculate the protection efficiency of LA regarding the electrooxidation of the metal. The protection efficiency was calculated to be 52.8% for 1.0 mmol L^{-1} , 65.4% for 5.0 mmol L^{-1} and 71.0% for 10.0 mmol L^{-1} and this protection was determined taking into account the charge in absence and in the presence of LA in aqueous medium and 56.3% for 1.0 mmol L^{-1} , 71.3% for 5.0 mmol L^{-1} and 82.5% for 10.0 mmol L^{-1} in ethanol. This effect may be considered remarkable given that the potential imposed at the working electrode was not ideal for the adsorption of the organic compound.

Polarization measurements (Tafel plots)

These experiments were performed using the same procedure described for the cyclic voltammetry studies. Prior

to the linear potential sweep, the electrode was polarized during 45 s at the best adsorption potential (-0.90 V). The potential sweep was linearly scanned at 1.0 mV s^{-1} from -0.90 V to 0.00 V . The Tafel measurements in the absence and in the presence of two different concentrations of LA are presented in Figures 6A and 6B, in both mediums.

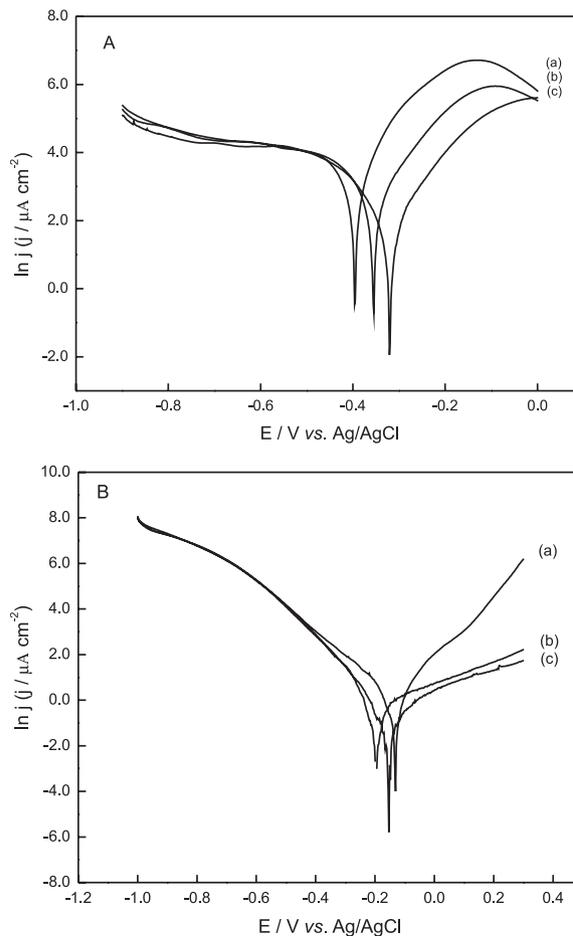


Figure 6. Tafel curves of low-carbon steel in aqueous KNO_3 0.10 mol L^{-1} (A) and in 0.10 mol L^{-1} tetraethyl ammonium chloride in ethanol (B), recorded in absence (a) and in the presence of LA (b) 1.0 mmol L^{-1} and (c) 5.0 mmol L^{-1} .

Similarly to cyclic voltammetry, redox processes were observed on the electrode surface. It is remarkable that a small amount of LA clearly decreases the anodic currents, probably due to the adsorption of the organic compound at the active sites of the electrode surface, retarding metal dissolution and consequently slowing the electrooxidation process. Following the same theory that the inhibitive action could be attributed to the adsorption of LA onto the low-carbon steel surface, the fraction of the surface covered by the adsorbed molecules (θ) was determined from:

$$\theta = \left(1 - \frac{I_{\text{corr}}^{\text{inh}}}{I_{\text{corr}}^{\text{o}}} \right) \quad (4)$$

where I_{corr}° and $I_{\text{corr}}^{\text{inh}}$ are the uninhibited and inhibited corrosion currents, respectively, obtained from the Tafel parameters. The inhibition efficiency (*I.E.*) was calculated from the equation

$$I.E. = \theta \times 100 \quad (5)$$

From the data, *I.E.* was calculated to be 65.6% in the presence of 1.0 mmol L⁻¹ and 86.9% for LA 5.0 mmol L⁻¹ in aqueous medium; *I.E.* = 19.4% and *I.E.* = 51.5% for the same concentrations in ethanol. These results are in agreement with those observed in the cyclic voltammetry.

Electrochemical impedance spectroscopy (EIS)

EIS is a well-established and powerful tool in the study of electrocatalysis. This study was carried out at OCP after 30 min of immersion in solution. The sine wave voltage (10 mV), peak-to-peak, was applied to the electrode at frequencies between 100 kHz and 10 mHz. The impedance diagrams are given in the Nyquist representation in the absence and in the presence of LA 5.0×10^{-3} mol L⁻¹, as show in Figures 7A and 7B, for both mediums.

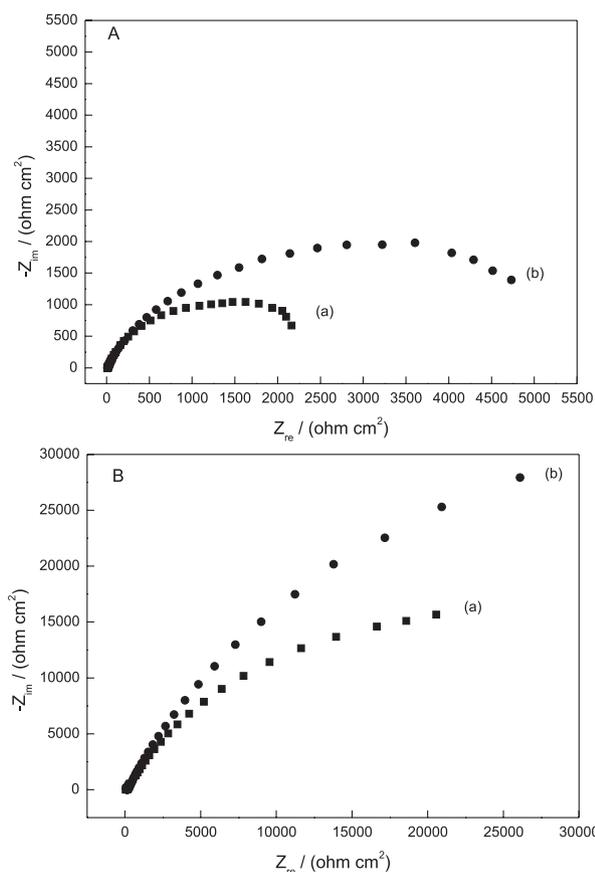


Figure 7. Nyquist plots of low-carbon steel in aqueous 0.10 mol L⁻¹ KNO₃ (A) and in 0.10 mol L⁻¹ tetraethyl ammonium chloride in ethanol (B), in absence (a) and in the presence (b) of LA 5.0 mmol L⁻¹.

The impedance diagrams obtained have almost a semicircular appearance for aqueous medium and a depressed capacitive loop in ethanol. This difference may be attributed to the use of the same frequency range for both mediums. However, the Nyquist appearances suggest that the electrooxidation of low-carbon steel in water and ethanol is mainly controlled by a charge transfer process.

Results obtained from EIS measurements show that with the addition of only 5.0 mmol L⁻¹ of LA, the charge transfer resistance (R_{ct}) increased. This effect suggests an increase in the corrosion resistance, attributable to the compounds adsorbed on the electrode surface, in agreement with the results obtained from others electrochemical measurements. From charge transfer resistance, it was possible to determine the double-layer capacitance by the equation:

$$C_{\text{dl}} = \frac{1}{2\pi f_{\text{max}} R_{\text{ct}}} \quad (6)$$

In addition, it was possible to notice that the values of the double-layer capacitance (C_{dl}) decrease in the presence of inhibitor. This decrease in C_{dl} values and the increase in R_{ct} values may be due to the gradual replacement of water molecules with LA molecules adsorbed on the metal surface.

Weight loss experiments

Electrochemical experiments were conclusive regarding to the interaction between the metal surface and LA and more remarkable regarding to the metal electrooxidation inhibition. Weight loss experiments were performed with the purpose to confirm the inhibition efficiency of LA as corrosion inhibitor of low-carbon steel in aqueous and ethanol medium. The strategy implemented uses square-shaped pieces of low-carbon steel ($1.0 \times 1.0 \times 0.1$ cm) totally immersed in 50 mL of water solutions, with and without the addition of LA. The same treatments described in the experimental section were also applied to these metal pieces. The immersion time for these experiments was 24 h at room temperature. The weight loss values were used to calculate the protection efficiency (η) as follows:

$$\eta\% = (1 - \Delta m / \Delta m^{\circ}) \times 100 \quad (7)$$

where Δm and Δm° are the weight loss difference of the steel samples with and without inhibitor, respectively. Figures 8A and 8B show the weight loss variation (Δm) and the protection efficiency for different concentrations of LA on the corrosion inhibition of low-carbon steel.

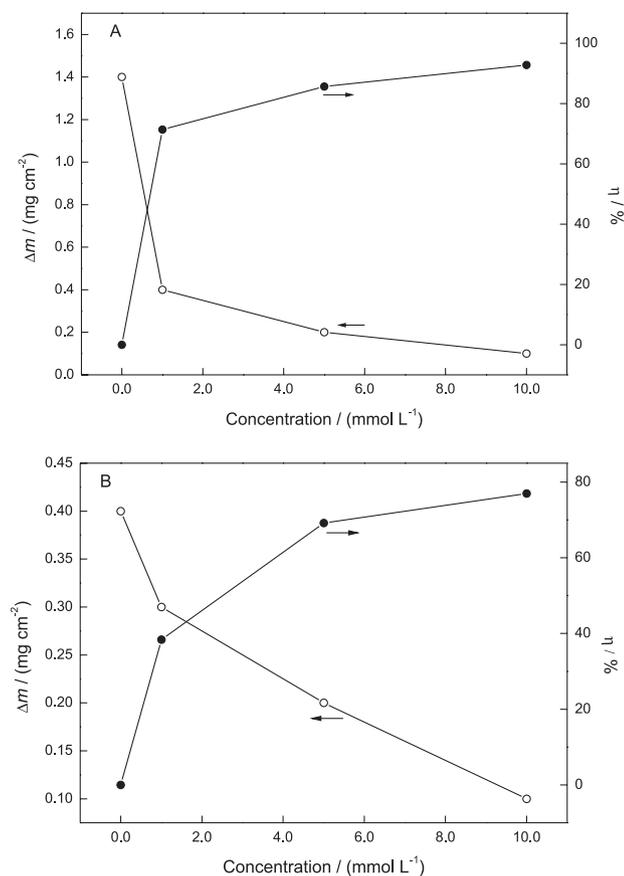


Figure 8. Protection efficiency $\eta\%$ (●) and weight loss difference (○) of LA in relation to the corrosion of low-carbon steel after 24 h of immersion in KNO_3 0.10 mol L^{-1} (A) and in 0.10 mol L^{-1} tetraethyl ammonium chloride in ethanol (B) at room temperature.

As observed, the protection efficiency was 71.4% in the presence of 1.0 mmol L^{-1} , 85.7% for 5.0 mmol L^{-1} and 92.8% for 10.0 mmol L^{-1} in aqueous medium and 38.4% in the presence of 1.0 mmol L^{-1} , 69.2% for 5.0 mmol L^{-1} and 76.9% for 10.0 mmol L^{-1} in ethanol. These results reveal that LA acts as a good corrosion inhibitor for low-carbon steel in both mediums.

Conclusions

Different electrochemical methods were employed in order to confirm the ability of LA to adsorb on low-carbon steel surface in aerated aqueous and ethanol solutions. Potentiometric measurements confirm that the OCP shifts to more positive values in the presence of LA. Cyclic voltammetry showed that both anodic and cathodic processes were affected by the presence of LA in the medium. The current values associated with anodic process decreased in the presence of the organic compound. The interaction between LA and the electrode surface was dependent on the electrode potential. The maximum interaction was observed when the electrode remained polarized at

$-0.90 \text{ V (Ag/AgCl)}$ for 45 s. At this potential, the anodic current value, taken at 0.00 V , decreases 76.0% in the presence of 20.0 mmol L^{-1} LA in aqueous and in ethanol medium. The surface area covered by the inhibitor was dependent of LA concentrations. Langmuir adsorption isotherm was assumed to calculate the standard free energy of adsorption of the organic compound ($\Delta G_{ads}^0 = -25.98 \text{ kJ mol}^{-1}$ in aqueous medium and $-26.71 \text{ kJ mol}^{-1}$ for ethanolic solutions). Chronoamperometric experiments confirmed the capability of LA to decrease the electrooxidation processes of low-carbon steel under anodic polarization. Tafel plots showed that I_{corr} decreases in the presence of LA. Finally, weight loss experiments were conclusive regarding the ability of LA to inhibit the corrosion processes of low-carbon steel in aqueous and ethanol mediums.

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