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Article

Assessment of Caffeine Adsorption onto Mild Steel Surface as an Eco-Friendly Corrosion Inhibitor

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As propriedades de adsorção e de eficiência de inibição da cafeína como inibidor de corrosão "amigo do meio ambiente" para o aço-carbono em meio ácido foram avaliadas usando técnicas eletroquímicas e espectroscópicas. Experiências de polarização indicaram que a cafeína atua como um inibidor do tipo catódico. Dados de impedância mostraram que o recobrimento da superfície aumenta com o aumento da concentração da cafeína de 1,0 a 10,0 mmol L^{-1}. A eficiência de inibição máxima obtida foi de 92,4%. A adsorção do inibidor de corrosão ocorreu de acordo com a isoterma de Frumkin, com energia livre de adsorção de –66,1 kJ mol^{-1}. Medições de ângulo de contato revelaram a formação de um filme protetor com caráter hidrofóbico, enquanto que a microscopia eletrônica de varredura, a espectroscopia de energia dispersiva e experiências de fluorescência comprovaram a presença de cafeína na superfície do aço.

The adsorption and corrosion-inhibition properties of caffeine as an eco-friendly corrosion inhibitor for mild steel in acid medium were investigated by electrochemical and spectroscopic techniques. Polarization experiments indicated that caffeine behaves as a cathodic-type inhibitor. Impedance data showed that surface coverage increased with caffeine concentration in the range of 1.0 to 10.0 mmol L^{-1}. The maximum inhibition efficiency obtained was 92.4%. The adsorption of the corrosion inhibitor was consistent with the Frumkin adsorption isotherm with a free energy of adsorption of –66.1 kJ mol^{-1}. Contact angle measurements revealed the formation of a hydrophobic protective film, while scanning electron microscopy, energy dispersive spectroscopy and fluorescence experiments clearly verified the presence of caffeine on the surface.

Keywords: mild steel, caffeine, adsorption, electrochemical techniques, surface analysis

Introduction

The corrosion of low-carbon steel is an important academic and industrial topic, especially in acid media. This is due to the increasing industrial applications of aqueous acid solutions. The most important fields of application are acid pickling, industrial cleaning, acid descaling and in the petrochemical processes. As acidic solutions are among the most corrosive media, organic corrosion inhibitors are used to decrease the corrosion rate of low-carbon steels.

Organic compounds containing mainly nitrogen, oxygen and sulfur, with or without heterocyclics, have for a long time been studied as potential corrosion inhibitors for metals and their alloys.[1-17] In addition, some other compounds containing π electrons[5,18-21] are expected to act as corrosion inhibitors for industrial applications. The main characteristic of the organic corrosion inhibitors is their ability to adsorb onto metal surfaces. Most of them are so-called mixed corrosion inhibitors because they adsorb at cathodic as well as anodic sites,[22] providing corrosion inhibition for both reactions: the reduction of oxygen or protons at cathodic sites and the metal oxidation at anodic sites. The corrosion inhibition is achieved by modifying the activation energy of the cathodic and/or anodic reactions occurring at the electrode surface, or by decreasing the available reaction area via a geometric blocking effect.[23] In general, the active site in the organic molecule responsible for the adsorption process is a polar group and therefore the presence of heteroatoms

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in the chemical structure is fundamental for a corrosion inhibitor. As is well-known, the first step in adsorption, when the thermodynamic equilibrium is favorable, is the replacement of water or other polar or ionic compounds originally adsorbed onto the metallic surface by the corrosion inhibitor.

A problem commonly associated with inorganic corrosion inhibitors, such as chromates and nitrates, and organic corrosion inhibitors, such as azoles[10,12,13,17] or thiourea derivatives[11,14,24] is their toxicity. Fortunately, good results have been obtained using the so-called environmentally-friendly or eco-friendly corrosion inhibitors, which are employed as single compounds, dimmers, polymers and co-polymers, natural oils or extracts.[25-33] For instance, in aqueous solutions, caffeic,[3] L-ascorbic,[4] and succinic[6-8] acids have been recommended as potential corrosion inhibitors for mild steel.

Caffeine (1,3,7-trimethylxanthine) is a naturally occurring compound largely found in foods which is not associated with toxicity.

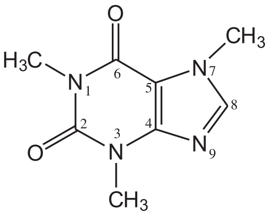

Figure 1. Chemical structure of caffeine (1,3,7-trimethylxanthine).

As can be seen from its chemical structure shown in Figure 1, caffeine presents the expected characteristics for a potential corrosion inhibitor. In addition caffeine is able to bind to a metal ion via the free oxygens located at positions 2 and 6.[34] Nevertheless, caffeine has been rarely exploited as a corrosion inhibitor.[9,35-37]

The aim of this study was to investigate the adsorption properties of caffeine as well as its potential for application as an eco-friendly corrosion inhibitor for mild steel in acidic solutions. To achieve this goal, the corrosion of mild steel in 0.1 mol L^{-1} H_2SO_4 was studied in the absence and presence of different concentrations of caffeine by potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) techniques. The data obtained were used to analyze the adsorption isotherms from which thermodynamic parameters were determined. The adsorption of caffeine onto the steel surface was also verified through water static contact angle measurements (SCA), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) experiments. The molecular-level characterization was performed by fluorescence emission spectroscopy (FES).

Experimental

Chemicals and solutions

Caffeine ($C_8H_{10}N_4O_2$) and sulfuric acid (H_2SO_4) of analytical grade were acquired from Vetec. They were used without prior purification. Filtered, distilled and deionized water was used to prepare all solutions. A stock solution of 0.1 mol L^{-1} H_2SO_4 was employed as the blank. To prepare the solutions containing caffeine, an appropriate weighed mass of the organic compound was added to a blank solution to give the desired final concentration. Solutions of 1.0, 3.0, 5.0, 10.0 or 50.0 mmol L^{-1} were used to test the adsorption onto mild steel and the inhibition capacity of caffeine. The mass of caffeine used to prepare the solutions was weighed on a Shimadzu Libror AEX 200G analytical balance. Except for the construction of the Arrhenius plots, all experiments were carried out at room temperature in naturally aerated solutions.

Corrosion tests

A double-walled one-compartment glass cell with a three-electrode configuration was used to carry out the corrosion tests. Disc-shaped working electrodes (WE) with a geometric area of 0.63 cm^2 were cut from a mild steel sheet (C: 0.049, Mn: 0.227, Cr: 2.34, S: 0.0005, Fe: balance wt.%) and subsequently mounted in a glass tube with Araldite® epoxy, without thermal treatment. Prior to each corrosion experiment, the electrode surface was abraded with 1200 emery paper, cleaned ultrasonically, degreased with ethanol and rinsed with deionized water. A graphite rod and a saturated calomel electrode (SCE) connected to the cell by a bridge and a Luggin-Haber capillary were used as auxiliary (AE) and reference electrodes (RE), respectively. All potentials in the text are quoted *versus* SCE. A Voltalab 10 potentiostat/galvanostat, model PGZ 100 Radiometer Copenhagen, computer controlled using the VoltaMaster 4.0 software, was used for the corrosion and impedance experiments. The open-circuit potential (OCP) was measured for 1.0 h before starting the PDP experiments. Potentiodynamic polarization curves were recorded in agreement with the ASTM G5 norm.[38] The initial potential sweep was always in the positive direction from –250 mV of the previously measured OCP, while the final potential was –100 mV *vs.* SCE. For other corrosion tests, the initial and final potentials were fixed according to the technique employed (Tafel, polarization resistance (R_p), etc.). The Arrhenius plots were obtained by measuring the corrosion current density (j_{corr}) at the corrosion potential (E_{corr}) determined from PDP experiments carried out at 20, 30, 40, 50 and 60 °C. The temperature of the solutions was controlled with a Microquímica MQBTC 99-20 thermostat. EIS was carried out at the open-circuit potential in the frequency range of 100 kHz to 100 mHz with a sine wave of 10 mV amplitude. Nyquist plots were used to calculate the double-layer capacitance (C_{dl}) and the inhibition efficiency (IE).

Surface analysis

Mild steel plates of 1.0 cm^2 were abraded with 1200 emery paper, cleaned ultrasonically, degreased with ethanol and rinsed with deionized water. They were then immersed for 24 h in 0.1 mol L^{-1} H_2SO_4 solutions in the absence and presence of 1.0, 3.0, 5.0, 10.0 or 50.0 mmol L^{-1} of caffeine at room temperature. Samples were then rinsed with distilled water and dried under vacuum for 24 h for subsequent surface analysis through water SCA, SEM, EDS and FES. The wetting characteristics of the steel surfaces before and after adsorption of caffeine molecules were evaluated through water contact angle measurements using a Dataphysics OCA 20 goniometer and the static sessile drop method. In this method, the profile of a water droplet in contact with a solid surface was measured with a high resolution camera. The contact angle results are an average of five replicate measurements. The morphology and composition of the caffeine-modified steel surfaces were determined using, respectively, a JEOL JSM 6390-LV scanning electron microscope and a Thermo Scientific spectrometer controlled by Noran System 6 software. The molecular-level characterization was performed by obtaining fluorescence emission spectra on a Hitachi F4500 spectrofluorimeter equipped with a thermostated cell holder set at 25.0 ± 0.1 °C. A solution of 10 mmol L^{-1} caffeine in 0.1 mol L^{-1} H_2SO_4 was used to obtain a reference spectrum. Slit width settings for both excitation and emission monochromators were adjusted to 5.0 nm. The samples were excited at 320 nm and the emission spectra were recorded at 335 to 440 nm.

Results and Discussion

Polarization measurements

Figure 2 shows representative potentiodynamic polarization curves for mild steel in 0.1 mol L^{-1} H_2SO_4 solutions with increasing concentrations of caffeine after 1.0 h of exposure. The values of the electrochemical parameters listed in Table 1 were obtained from them and from other techniques, as described in the Experimental section.

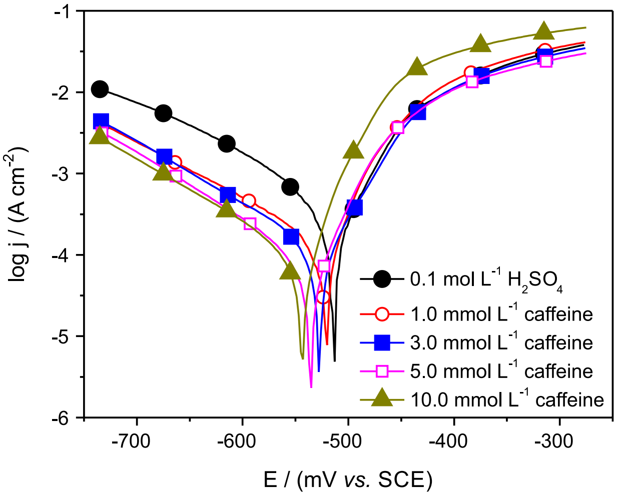

Figure 2. Potentiodynamic polarization curves for mild steel in 0.1 mol L^{-1} H_2SO_4 and solutions containing 1.0 to 10.0 mmol L^{-1} of caffeine.

The PDP curves show the typical behavior of mild steel in acid solutions with well-defined cathodic and anodic curves.[3,13,32] It can be clearly observed that the presence of caffeine shifted the E_{corr} values to more negative potentials in comparison to those obtained in the absence of the organic compound. This behavior indicates an effective interaction between the caffeine and the steel surface resulting in adsorption of the organic compound. In addition, as will be demonstrated below (Thermodynamic considerations), caffeine–Fe^{2+} or caffeine–Fe^{3+} complexes can be formed

Table 1. Electrochemical parameters for mild steel in 0.1 mol L^{-1} H_2SO_4 solutions in the absence and presence of caffeine

[Caffeine] / (mmol L^{-1})	OCP / mV	E_{corr} / mV	j_{corr} / (µA cm^{-2})	R_p / (Ω cm^2)	β_c / (mV dec^{-1})	β_a / (mV dec^{-1})	IE^a / %	IE^b / %
Blank	–515	–512	231	70	–153	49	-	-
1.0	–516	–517	208	75	–147	39	9.8	7.1
3.0	–519	–526	150	113	–145	33	34.9	38.2
5.0	–522	–535	88	136	–127	35	62.0	48.7
10.0	–525	–539	18	604	–112	31	92.4	88.5

[a]according to equation (1); [b]according to equation (2).

and to adsorb on the electrode surface, decreasing the corrosion rate of the low-carbon steel. The OCP values also shifted to more negative potentials, but a more pronounced effect was observed for the E_{corr} values, indicating that the adsorption could be a potential-dependent process. Indeed, to demonstrate indubitably such dependence with the potential, further experiments would be needed. Besides, the differences between OCP and E_{corr} values were not so high, suggesting that the observed difference can also be due to the different techniques used, since OCP measurements were determined at I = 0 (zero) while E_{corr} values were calculated from Tafel experiments, which is a quasi-steady state technique. There was a substantial decrease in the corrosion rate, as indicated by the decrease in the j_{corr} values from 231 μA cm^{-2} in the blank solution to 18 μA cm^{-2} in the presence of 10 mmol L^{-1} of caffeine. Under the same conditions, the R_p increased from 70 Ω cm^2 to 604 Ω cm^2, confirming the presence of a protective layer on the electrode surface. In the presence of caffeine, it is clear that the cathodic reduction reaction was inhibited and this inhibition became more pronounced with increasing caffeine concentration. The cathodic polarization curves give rise to parallel lines. The constant cathodic Tafel slope (βc) changed around 41 mV dec^{-1}, from –152 mV dec^{-1} (blank) to –131 mV dec^{-1} (10.0 mmol L^{-1} caffeine). This behavior confirms the strong interaction between caffeine and the steel surface, suggesting also that the mechanism for the proton reduction reaction was affected. On the other hand, the anodic metal dissolution was not affected by the presence of the organic compound. The anodic Tafel slope (β_a) changed just 18 mV dec^{-1}. Besides, the current densities remained almost the same for the blank solution and the solutions containing 1.0 to 5.0 mmol L^{-1} of caffeine, as can be observed in the anodic polarization curves shown in Figure 2. For 10.0 mmol L^{-1} of caffeine, a slight increase in the currents is observed at lower potentials. The performance of caffeine as a corrosion inhibitor was evaluated according to the equations given below:

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

$$IE(\%) = \left(1 - \frac{R^0_p}{R_p}\right) \times 100 \qquad (2)$$

where j^0_{corr} and R^0_p are the values for the corrosion current density and polarization resistance, respectively, obtained in the absence of caffeine, and j_{corr} and R_p are the same parameters obtained in the presence of the inhibitor. The IE(%) values (Table 1) for caffeine concentrations of 1.0 to 10.0 mmol L^{-1} remained at between 9.8% and 92.4%, as calculated using equation (1) and between 7.1% and 88.5% using equation (2). These findings are in agreement with those previously published for the corrosion inhibition of different metals by caffeine in various environments.[35-37,39]

EIS experiments

Figure 3 shows the Nyquist plots for mild steel in 0.1 mol L^{-1} H_2SO_4 and in the presence of 1.0 to 10 mmol L^{-1} caffeine.

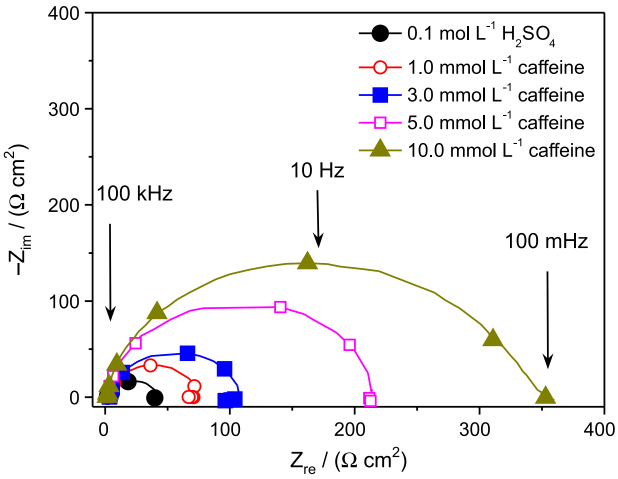

Figure 3. Nyquist plots for mild steel in 0.1 mol L^{-1} H_2SO_4 and solutions containing 1.0 to 10.0 mmol L^{-1} of caffeine.

The profile of the Nyquist diagrams is the same in the absence and presence of the organic compound. This behavior is in agreement with those reported in the literature for the corrosion of mild steel in solutions without[6-8,40,41] and with[18,42] corrosion inhibitors. As can be seen, a deviation from the ideal semicircle is observed in the Nyquist plots, which is generally attributed to the frequency dispersion[43] and roughness of the surface.[44] In addition, a simple charge transfer mechanism can be assigned to the mild steel corrosion in 0.1 mol L^{-1} H_2SO_4 and in caffeine-containing solutions, since the Nyquist plots show a single semi-circle not associated with the diffusion process.

The difference in the real impedance at lower and higher frequencies provides the charge transfer resistance (R_{ct}), but in this study the polarization resistance (R_p) was used instead of R_{ct}, based on discussions published elsewhere.[45] The solution resistance-R_s shown in Table 2 was used to obtain the R_p values. As can be seen, the R_p values increased as the caffeine concentration increased, indicating the formation of a protective layer on the surface.

In parallel, the C_{dl} values shown in Table 2, calculated according to equation (3), decreases due to the action of caffeine molecules, which displace water molecules

Table 2. Data obtained from EIS experiments on mild steel in 0.1 mol L^{-1} H_2SO_4 solutions in the absence and presence of caffeine

[Caffeine] / (mmol L^{-1})	R_s / (Ω cm^2)	R_p / (Ω cm^2)	C_{dl} / (μF cm^{-2})	Θ
0	3.2	38.3	249.2	-
1.0	2.5	72.3	66.5	0.73
3.0	2.2	105.3	32.4	0.87
5.0	1.7	220.2	10.5	0.96
10.0	1.4	350.4	3.2	0.98

originally adsorbed onto the mild steel surface. The fraction of the surface covered (θ) by adsorbed caffeine was calculated according to equation (4), considering that C_{dl} is proportional to the surface not covered by the corrosion inhibitor.

$$C_{dl} = 1/2\ \pi f_{\max} R_p \qquad (3)$$

$$\theta = 1 - \frac{C_d}{C_{dl}^0} \qquad (4)$$

where $f_{\max}$ is the frequency value at which the imaginary component of the impedance is maximal, R_p is the polarization resistance and C_{dl}^0 and C_{dl} are the double layer capacitance in the absence and presence of caffeine, respectively. The data summarized in Table 2 show a progressive increase in the θ value as a function of the caffeine concentration. The IE(%) value using R_p values obtained from the EIS experiments was also calculated according to equation (2). For caffeine concentrations ranging from 1.0 to 10.0 mmol L^{-1} the IE(%) value remained at between 47.0% and 89.1%. The data obtained from impedance experiments are in agreement with the data obtained from the polarization experiments. All experiments show the increase of IE(%) as a function of the caffeine concentration. Once more, these findings confirm that caffeine adsorbed onto the mild steel surface, modifying the properties of the interface and acting as a good corrosion inhibitor under acidic conditions.

Thermodynamic considerations

Thermodynamic data were obtained from the experiments on the effect of temperature and from the adsorption isotherms. These data can provide basic information on the interaction between caffeine and the mild steel surface.

The effect of temperature on the corrosion rate of mild steel was investigated by PDP experiments in 0.1 mol L^{-1} H_2SO_4 solutions alone and in the presence of 10.0 mmol L^{-1} caffeine. Experiments were carried out at 20, 30, 40, 50 and 60 °C. The Arrhenius plots shown in Figure 4 were obtained in order to gain some insight into the effect of temperature on the corrosion rate.

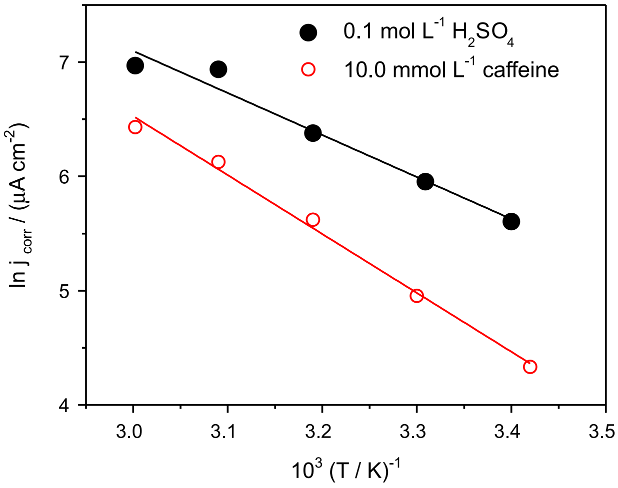

Figure 4. Arrhenius plot for mild steel in 0.1 mol L^{-1} H_2SO_4 and solutions containing 10.0 mmol L^{-1} of caffeine.

As can be seen, straight lines showed a good correlation, verifying the dependence of the corrosion rate on the temperature. As occurs for other reactions, the mild steel corrosion rate increased with increasing temperature. In addition, the temperature increase led to a decrease in the IE(%) value, which is a clear indication of the formation of a film by physical adsorption. The steeper slope of the Arrhenius plot for the caffeine-containing solution resulted in a higher value for the apparent activation energy (E_a), as demonstrated below. In corrosion inhibitor studies, the Arrhenius equation can be expressed via the corrosion rate (j_{corr}), as shown in equation (5),

$$\ln j_{corr} = K - \frac{E_a}{RT} \qquad (5)$$

where K is a constant, E_a is the apparent activation energy of the metal dissolution reaction, R is the gas constant and T is the thermodynamic temperature.

E_a values of 29.5 kJ mol^{-1} and 43.9 kJ mol^{-1} were calculated for the systems without and with corrosion inhibitor, respectively, in agreement with a general rule which states that the apparent activation energy is higher in a system in the presence of corrosion inhibitors.[8] According to some authors,[4,8,11,17] the increase in the apparent activation energy in the presence of an inhibitor indicates that electrostatic forces predominate at higher temperatures and therefore physical adsorption occurs in the first stage. Lower values for E_a in the presence of the inhibitor are associated with chemical adsorption.[3,14,32] Higher values of E_a for the inhibited system indicate that the inhibitor is more effective at lower temperatures.[46]

The adsorption of caffeine onto the mild steel surface was also characterized using surface coverage data obtained from the EIS experiments according to equation (4). The data were fitted to Langmuir, Temkin and Frumkin adsorption isotherms using the equations below:[3]

$$\text{Langmuir: } \frac{\theta}{1-\theta} = KC \tag{6}$$

$$\text{Temkin: } \log\left(\frac{\theta}{C}\right) = \log K - g\theta \tag{7}$$

$$\text{Frumkin: } \log\left(\frac{\theta}{(1-\theta)C}\right) = \log K + g\theta \tag{8}$$

where θ is the surface coverage, *K* is the adsorption-desorption equilibrium constant, *C* is the inhibitor concentration, and *g* is the adsorbate interaction parameter. All three isotherms shown in Figure 5 provided good fits with the experimental data.

In studies on corrosion inhibitors, acceptable correlation coefficients generally lie between 0.99 and 0.60.[3,8,32,42] A correlation coefficient of 0.88 was achieved for the Langmuir (Figure 5A), 0.82 for the Temkin (Figure 5B) and 0.93 for the Frumkin (Figure 5C) isotherms. These findings verify that the caffeine adsorption is best described by the Frumkin isotherm. A deviation of the correlation coefficient from 1.0 indicates that the adsorption process is controlled by the formation of a ligand-metal complex,[8] in this case caffeine–Fe^{2+} or caffeine–Fe^{3+}. The standard free-energy of adsorption (ΔG^0_{ads}) can be calculated considering the adsorption-desorption equilibrium constant (K) of the Frumkin isotherm graph and using the following relation:

$$K = \frac{1}{55.5} e^{-\frac{\Delta G^0_{ads}}{RT}} \tag{9}$$

where 55.5 is the water concentration, R is the universal gas constant and T is the thermodynamic temperature. The value obtained for the adsorption-desorption equilibrium constant was 6.8×10^9, which provides a ΔG°_{ads} value of –66.1 kJ mol^{-1}. The adsorption process is assumed to be spontaneous because the value for the standard free-energy of adsorption is negative. The spontaneous adsorption process commonly occurs in the case of organic corrosion

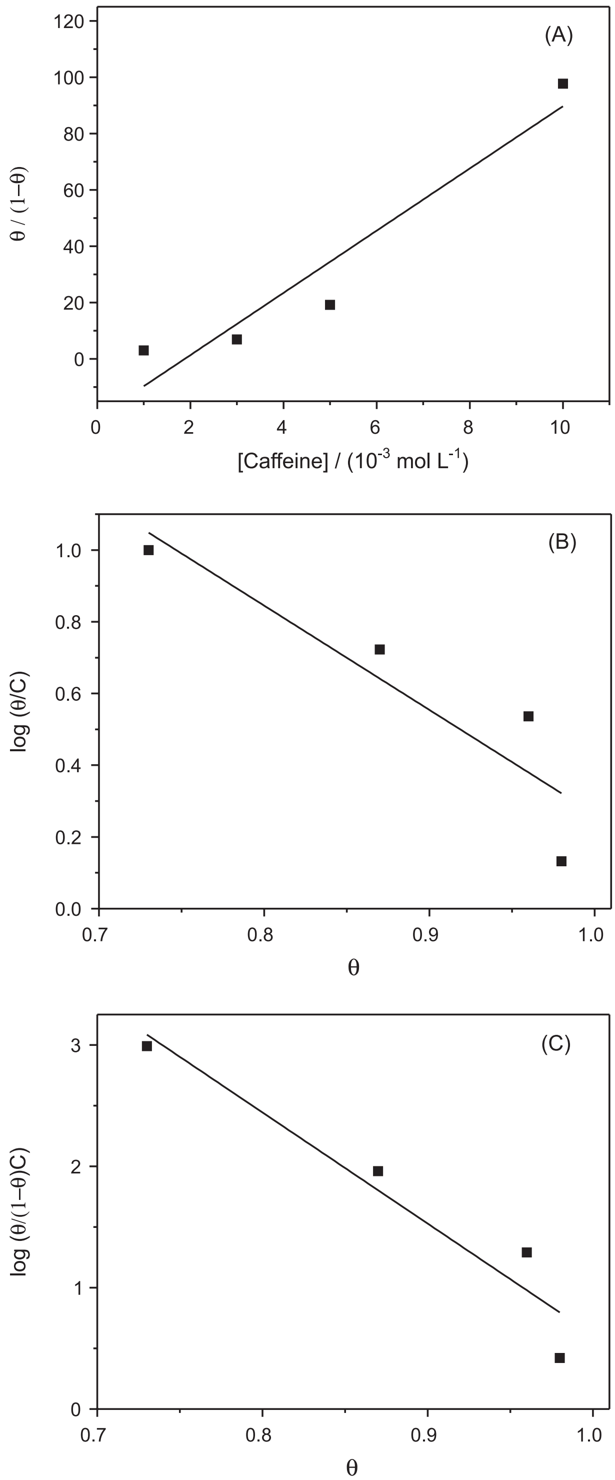

Figure 5. (A) Langmuir, (B) Temkin and (C) Frumkin isotherms for the adsorption of caffeine onto the mild steel surface in 0.1 mol L^{-1} H_2SO_4 solutions.

inhibitors, but the high value for ΔG°_{ads} demonstrates that the caffeine adsorption onto the mild steel surface is highly favored in acidic medium. ΔG°_{ads} values of around 50.0 kJ mol^{-1} or higher are associated with charge sharing or charge transfer from the inhibitor molecules to the metal[8] and indicate that chemisorption is the typical mechanism operating in the system. From the slope of the Frumkin isotherm was also possible to calculate the lateral parameter interaction (g). A value of –9.2 was obtained for this interaction parameter, indicating repulsive interaction between the adsorbed caffeine molecules.

The assignment of an inhibition mechanism based on purely thermodynamic data may be misleading. In addition, the phenomenon of the adsorption of organic molecules onto metal surfaces cannot be considered simply as an individual physical or chemical process. A variety of experimental conditions and parameters control the predominance of one process over the other.[47] Based on these considerations and on the thermodynamic data obtained, it is understandable that the adsorption of caffeine onto the surface of the carbon steel occurs primarily via electrostatic interaction (physical adsorption), as indicated by the results of the Arrhenius experiments, with the inhibitor displacing adsorbed water molecules. The adsorbed caffeine then reacts with the metal (iron) at the mild steel surface with charge sharing or charge transfer, according to a chemisorption process predicted by the Frumkin isotherm. Some chemical interactions can originate a caffeine–Fe^{2+} or caffeine–Fe^{3+} complex, as indicated by the Temkin isotherm. Nevertheless, the data clearly show a strong interaction between the caffeine and the mild steel surface, preventing the oxidation of iron and the deterioration of the metal alloy.

Surface analysis

The analysis of the mild steel surface corroded in 0.1 mol L^{-1} H_2SO_4 in the absence and presence of different concentrations of caffeine was carried out by SCA measurements, SEM, EDS and FES in order to verify the adsorption and corrosion inhibition properties of the organic compound.

The wetting characteristics of the mild steel surface were analyzed after 24 h of exposure of the mild steel to solutions with and without the corrosion inhibitor. Figure 6 shows the contact angle between a water droplet and the mild steel surface measured under different conditions.

Figure 6A shows, for instance, a water droplet on the freshly polished mild steel surface, which served as a reference. The contact angle of 105° characterizes a water repellent surface, typical of mirror-like areas. The contact angle for a water droplet on the mild steel surface after immersion for 24 h in 0.1 mol L^{-1} H_2SO_4 (caffeine-free) was found to decrease to 17° (Figure 6B), indicating an increase in the wettability. This hydrophilic characteristic is due to the formation of polar inorganic corrosion products, which modify the composition and properties of the surface. In the presence of 10.0 mmol L^{-1} caffeine, the water droplet contact angle was found to increase to 31° (Figure 6C) leading to a less hydrophilic surface. On the other hand, when 50.0 mmol L^{-1} of caffeine was present in the solution (Figure 6D), the contact angle increased considerably to 96°, characterizing a hydrophobic surface, attributed to the formation of a water-repellent film containing caffeine adsorbed on the mild steel surface. The presence of this hydrophobic film and caffeine on the mild steel surface was further confirmed by SEM imaging and EDS composition analysis, respectively.

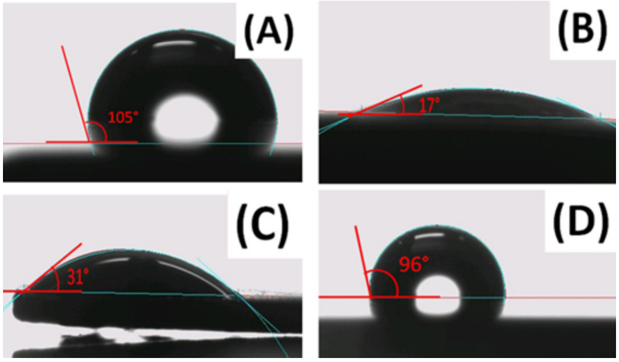

Figure 6. Water droplet contact angles on mild steel surfaces: (A) reference, and after 24 h in 0.1 mol L^{-1} H_2SO_4 in (B) the absence and presence of (C) 10 mmol L^{-1} and (D) 50 mmol L^{-1} of caffeine.

Figure 7 shows a selection of SEM images recorded for mild steel coupons before and after immersion in a 0.1 mol L^{-1} H_2SO_4 solution for 24 h in the absence and presence of different caffeine concentrations (1.0-10.0 mmol L^{-1}).

The morphology of the steel surface exhibited in Figure 7A reveals only marks remaining from the polishing. When the steel samples were immersed in the acid solution (Figure 7B) the surface morphology changed considerably. As a result of the action of the acid, the surface was highly corroded, generating an irregular porous surface. However, in the presence of caffeine (Figure 7C to 7F) the corrosion was suppressed and an increase in the surface coverage of a caffeine-based protective layer is clearly perceived. This protective layer overlaid the entire surface of the steel when it was obtained from a solution containing 10 mmol L^{-1} of caffeine (Figure 7F). This film, however, seems to be brittle, as shown by the cracks that appeared on the surface. The SEM micrographs corroborate the results obtained in the EIS experiments, which evidenced an increasing in the surface coverage with increasing caffeine concentration.

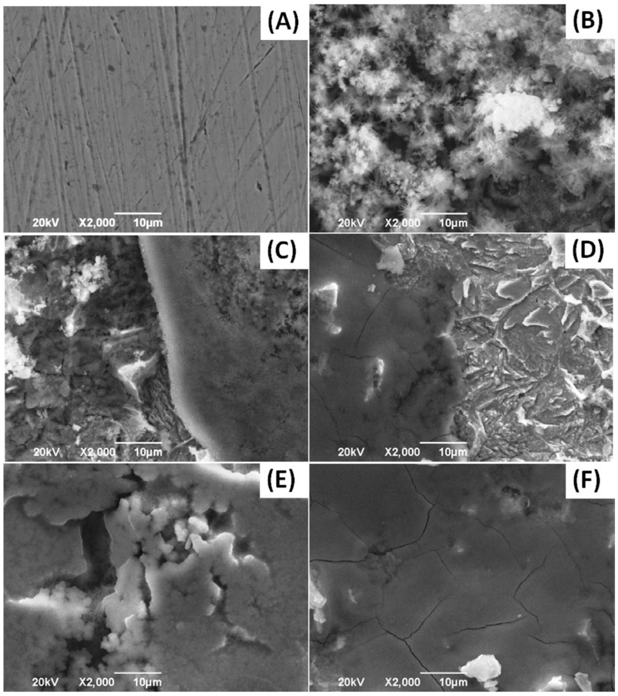

Figure 7. SEM images of mild steel surface for (A) reference coupon and after 24 of immersion in (B) 0.1 mol L^{-1} H_2SO_4 and solutions containing (C) 1.0, (D) 3.0, (E) 5.0 and (F) 10.0 mmol L^{-1} of caffeine.

The amount of caffeine species in the hydrophobic layer after immersion was found to increase with the concentration of inhibitor, as characterized by EDS.

The EDS spectrum for the reference sample (Figure 8A) shows the main elements present in the mild steel used and oxygen, the latter being due to the spontaneous formation of an oxide layer. After immersion in the 0.1 mol L^{-1} H_2SO_4 solution, the EDS spectrum of the surface featured an additional signal attributed to the presence of S atoms from the corrosive medium (Figure 8B). The presence of caffeine adsorbed on the surface is supported by the peaks related to carbon and oxygen atoms, the integrated areas of which increased proportionally to the caffeine content added to the corrosive solution (Figures 8C-8F). This enhancement in the carbon and oxygen signals is due to the carbon and oxygen atoms of the adsorbed caffeine.

The SEM and EDS data show that a carbonaceous material containing oxygen atoms covered the steel surface. This protective layer is attributed to the inhibitor. Therefore, surface analysis by SEM and EDS support the results obtained by different techniques and discussed in the preceded paragraphs.

As a final point, to characterize the molecular-level interaction between the steel surface and caffeine, fluorescence emission experiments were carried out at an excitation wavelength of 320 nm.[48] Figure 9 shows the fluorescence emission spectra obtained.

As expected, the freshly-polished mild steel sample exhibits only reflective behavior. On the other hand, after immersion for 24 h in 0.1 mol L^{-1} H_2SO_4 in the presence of 10 mmol L^{-1} of caffeine, the same coupon shows a maximum emission peak at 369 nm, which was attributed to the caffeine adsorbed onto the surface. This spectrum was obtained from the difference between the fluorescence

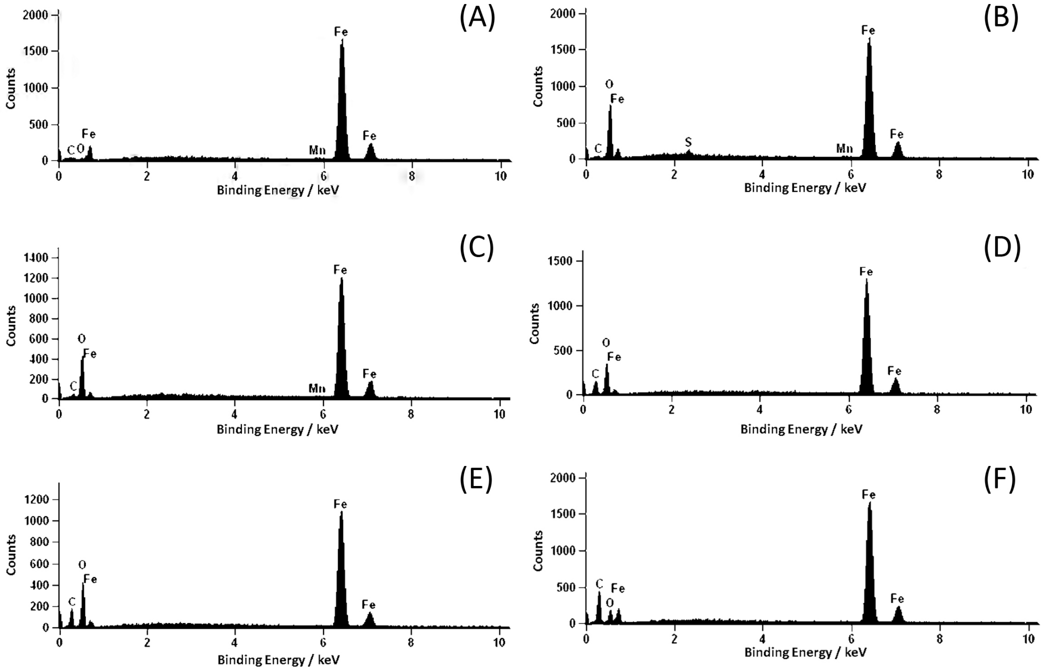

Figure 8. EDS spectra for the mild steel surface of (A) the reference coupon, and after 24 h of immersion in (B) 0.1 mol L^{-1} H_2SO_4 and solutions containing (C) 1.0, (D) 3.0, (E) 5.0 and (F) 10.0 mmol L^{-1} of caffeine.

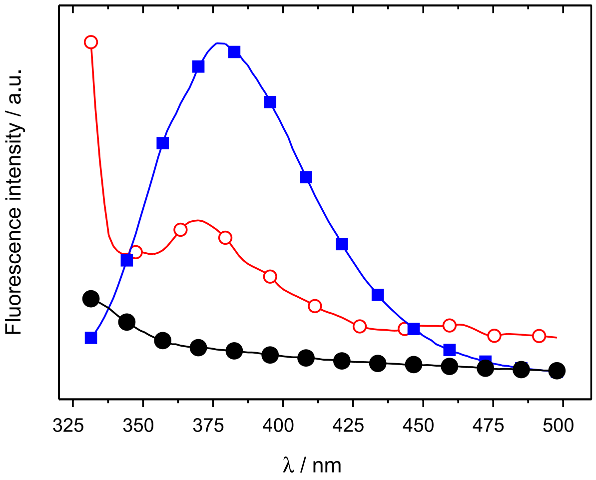

Figure 9. Fluorescence emission spectra for (●) the mild steel surface, (○) the mild steel surface after 24 h of immersion in 0.1 mol L^{-1} H_2SO_4 in the presence of 10 mmol L^{-1} caffeine and (■) 10 mmol L^{-1} caffeine in 0.1 mol L^{-1} H_2SO_4 aqueous solution.

emission intensities of the caffeine-modified steel surface and the unmodified steel surface. The spectrum for 10.0 mmol L^{-1} of caffeine in 0.1 mol L^{-1} H_2SO_4 aqueous solution presents a maximum emission peak at 377 nm, in good agreement with the fluorescence emission spectrum for caffeine published in the literature.[48] The shift in the maximum emission wavelength observed for caffeine adsorbed on the surface compared to that of caffeine in solution is due to the suppression effect caused by the binding between the steel and the caffeine, which alters the degree of freedom of the π-electrons.[49] These findings confirm that caffeine is indeed bound to the mild steel surface and that an inhibitory effect is promoted by this organic compound, corroborating all results presented and discussed above.

Conclusions

The adsorption properties and corrosion inhibition efficiency of caffeine was evaluated for a corrosion system comprising a mild steel and an acid medium. The inhibition efficiency was more pronounced with increasing caffeine concentration. The inhibitor acts by decreasing the rate of the cathodic proton reduction reaction. The inhibition efficiency was also related to the adsorption of caffeine on the steel surface and the formation of a protective film with hydrophobic characteristics. According to the results presented, caffeine is strongly adsorbed onto the mild steel surface; the adsorption occurring through a spontaneous process involving a chemisorption mechanism. Surface micrographs showed an increase in the surface coverage with increasing caffeine concentration, in agreement with the data provided by impedance experiments. The presence of caffeine adsorbed on the mild steel was verified by spectroscopic measurements of the surface after corrosion tests in the presence of the corrosion inhibitor. Thus, as a general conclusion, caffeine shows good potential as an eco-friendly corrosion inhibitor for mild steel in acid solutions.

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