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Expired streptomycin as corrosion inhibitor for carbon steel in acetic acid - sodium acetate buffer solution

MARIAN BOBINA, VALENTIN ORDODI, ANDREA KELLENBERGER, NICOLAE VASZILCSIN*

University Politehnica Timisoara, Piata Victoriei 2, 300006 Timisoara, Romania

Abstract. Corrosion inhibition of carbon steel in buffer acid solutions by expired streptomycin was studied by weight loss method, linear polarization, electrochemical impedance spectroscopy, as well as scanning electron microscopy. It was found that streptomycin reduces the metal corrosion rate, and the inhibition efficiency increases proportionally with the drug content. A high efficiency has been obtained for 10^{-3} M amount of inhibitor. Tafel polarization results indicate that the drug is active especially on the cathodic side and less on the anodic dissolution of iron reaction, acting as a mixed type corrosion inhibitor. The double layer capacitance of the metal - buffer solution interface, polarization resistance and film formation on the carbon steel surface have been emphasized by electrochemical impedance measurements. The scanning electron micrographs of the carbon steel samples in blank solutions have revealed a severe corrosion on the samples surface, while in the presence of the expired drug, the surface has remained almost unaffected. Electrochemical behavior of streptomycin has been also investigated by cyclic voltammetry.

Keywords: corrosion inhibitor, expired drug, streptomycin, electrochemical impedance spectroscopy.

1. Introduction

Corrosion of metals and alloys remains a delicate industrial and economic problem as well as a scientific subject. The ionization of iron from carbon steel is the most widespread form of a practical corrosion [1], and consequently it has been deeply studied because it is widely encountered in different industries such as chemical and electrochemical, medicine, nuclear plants, store tanks, petroleum refineries, pipeline fabrication and also in a daily life [2-6]. Among several methods used in

*Correspondence address: nicolae.vaszilcsin@upt.ro

the preventing of the metal corrosion the use of inhibitors is still the most cost effective and practical method.

A type of inhibitor is represented by organic compounds, which acts by adsorption on the iron surface due to the presence of multiple bonds, heteroatoms like nitrogen, oxygen and sulphur, or π electrons in the organic molecules [7-10]. By adsorption, a protective layer is realized on the metal surface that prevents the diffusion of the corrosion active species. In the last years, several drugs have been identified that fulfill the above conditions and can be used as corrosion inhibitors for metals and alloys with good performance [11-14]. Gece has found 17 classes of drugs having anticorrosive features for steel, stainless steel, Al and Al alloys, Cu, Zn and Ti in different aggressive solutions [15]. Five antibacterial drugs, namely ampicillin, cloxacillin, flucloxacillin, amoxicillin and streptomycin were approached as inhibitors for the corrosion of aluminum [11] and mild steel [16]. These compounds suppress the corrosion process by blocking the metal surface via formation of insoluble complexes or via adsorption of organic molecules [11, 16]. The active substances of medicines formulations, even they possess very good inhibitory properties, are expensive, and consequently they are rarely used as inhibitors, reason why our attention was focused toward the use of expired drugs or unused ones because of patient's non-compliance. R. S. Abdel Hameed started in 2009 his studies on unused drugs as corrosion inhibitor, reporting the effect of expired ranitidine on the corrosion rate of aluminum in hydrochloric acid solutions [17, 18]. Further, the inhibitory effect of expired carbamazepine and paracetamol has been reported [19]. F. H. Ali et al. [20] have studied the corrosion inhibition properties of Carbocisteine, Citicoline and Paracetamol in 1 M hydrochloric acid, and expired Declophen has been studied by R. S. Abdel Hameed as "friendly" inhibitor for carbon steel in a strong acid solutions [21]. In 1 M HCl medium, promising results was reported by N. K. Gupta et al. using expired Nifedipine and Atenolol for the protection of carbon steel [22]. Similar inhibitory efficiencies were obtained using expired Cefdinir and Tramadol [23,24]. Recently, the anticorrosive action of expired Etoricoxib on carbon steel in phosphoric acid solution has been studied [25]. There is a current review on the inhibitory effect of the expired drugs on the electrochemical processes [26].

Since, in most cases, the drugs contain besides active substances as well as some excipients, we have chosen streptomycin as potential inhibitor, taking into consideration that the active substance is pure and isolation process of excipients is not necessary.

The aim of the present paper is to study the streptomycin properties in order to be used as corrosion inhibitor for carbon steel in acetic acid - sodium acetate buffer solution. Sodium acetate is the main ingredient used in deicing solutions because it is active at low temperature in ice and deep snow [27]. It is often used on some winter roadways as alternative to chloride salts, since it is less corrosive and more sustainable than chloride salts [28]. An improved deicing mixture called "Ice Shear" consists of equimolar amounts of sodium acetate and sodium formate, having the ability to lower the freezing point of water, penetrate ice, and lower the

strength of bonding between the ice and pavement [29]. In our work, a more aggressive solution and constant pH was obtained by adding acetic acid, which presents industrial importance due to the reactive carboxyl group [30, 31].

2. Experimental

The inhibition efficiency of streptomycin has been determined by electrochemical methods like linear polarization and electrochemical impedance spectroscopy (EIS), as well as by weight loss. The electrochemical behavior of streptomycin has been investigated by cyclic voltammetry. The surface morphology of the carbon steel samples, after corrosive attack, has been studied by scanning electron microscopy (SEM). The nature of interactions between streptomycin molecules and metal has been studied and discussed based on adsorption isotherms.

2.1. Materials and methods

All tests were carried out on discs samples of carbon steel having the following mass composition: C - 0.16; Mn - 0.73; Si - 0.29; S - 0.03; P - 0.08; Cr - 0.05; Ni - 0.08; Cu - 0.12; Al - 0.45; Mo - 0.01; V - 0.002; Ti - 0.007; Fe - balance.
As corrosion inhibitor streptomycin (MacLeods Pharmaceuticals), with the chemical structure formula presented in figure 1, has been used. Streptomycin is commercialized in bottles as streptomycin sulfate with 1 g substance. It is a white to slightly pink or pale brownish powder or granules, slightly soluble in water and hardly soluble in alcohol acetone, chloroform, ether and petroleum ether [32]. The drug was used directly without further purification.

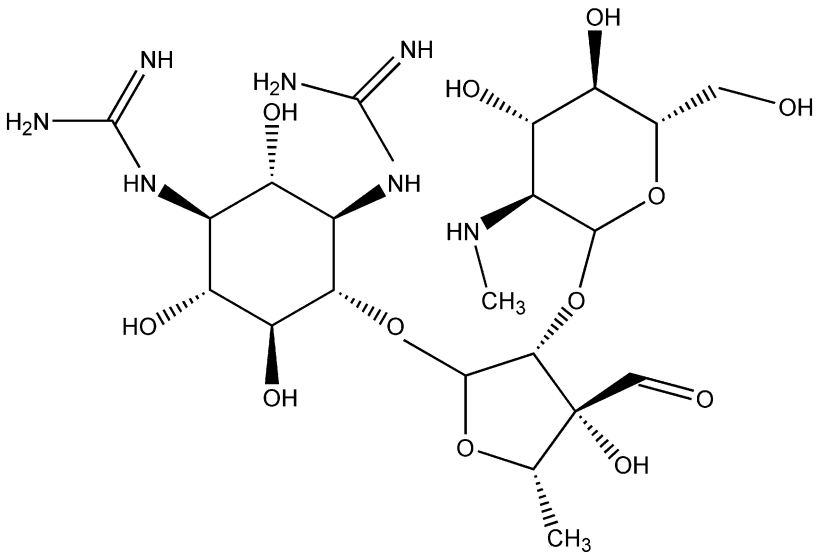


Fig. 1. Chemical structure of streptomycin.

The active substance content in the expired drug has been determinated by colorimetric method, with Mohr salt at 570 nm wavelength, using Microplate Reader Biorad 680 spectrophotometer and streptomycin solution (Fluka) as etalon. The obtained results have shown that the expired streptomycin used as corrosion inhibitor it is not degraded in the test solution in the limit of the method sensitivity. Likewise, applying the same method it has been found that the drug is not hydrolyzed even at 55°C.
Concentrations between 10^{-6} - 10^{-3} M of drug have been studied in order to find the inhibitory effect on the corrosion process of carbon steel in 0.5 M CH_3COOH - 0.25 M CH_3COONa weak acid solutions. Corrosive media has been prepared using acetic acid (Fluka reagent ≥99.7%) and sodium acetate (Fluka reagent ≥ 99.0%).

2.2. Weight loss method

Disc carbon steel samples *Φ*15 mm x 3 mm have been used in order to determine the weight loss in 100 mL test solutions at 25°C. Before immersion, the surface of the samples was grinded with SiC paper up to 2400, thoroughly washed with deionized water, treated in an ultrasound bath, rinsed using acetone and finally dried. After an exposure during 144 hours in 0.5 M CH_3COOH - 0.25 M CH_3COONa in the absence/presence of different concentrations of streptomycin, the samples were brushed and washed in order to remove the corrosion products, then washed with deionized water and acetone and dried. Before and after exposure, the samples have been weighted with a precision of ± 0.1 mg. To obtain more relevant results, longer exposure time then usual one has been used for the buffer solution, because the media is less corrosive and the weight loss is reduced.

2.3. Electrochemical techniques

The electrochemical experiments have been carried out with an Autolab 302 N potentiostat/galvanostat, in a 100 mL cell equipped with three electrodes as follow: steel samples as working electrode, Pt wire as counter electrode and, as reference, a saturated calomel electrode (SCE) provided with a Luggin capillary. The surface of specimens was prepared similarly as describe above. Thereafter the specimen was mounted in a Teflon holder leaving an exposed surface area of 1 cm^2 and it was immediately immersed in the test solutions. Before each experiment, pure nitrogen was bubbled in the test solutions for 30 minutes to avoid any reaction with dissolved oxygen. Fresh solutions and electrodes have been used for each measurement.
Linear polarization curves were recorded using the General Purpose Electrochemical System (GPES) software, after 1 hour immersion of the steel samples in the studied solution, in the potential range of ± 250 mV versus corrosion potential E_{corr}, using a scan rate of 0.5 mV s^{-1}.
Electrochemical impedance spectroscopy experiments have been realized with the Frequency Response Analyzer (FRA) module, at E_{corr} after the stationary state was

achieved (1 h equilibration time) in the frequency range of 100 mHz - 100 kHz and alternative voltage amplitude of 10 mV. The experimental impedance data have been modeled by a complex non-linear least squares (CNLS) method based on ZView 3.0 from Scribner Associates Inc. Software.
The electrochemical behavior of streptomycin was studied on Pt electrode in 0.5 M CH_3COOH - 0.25 M CH_3COONa solution by cyclic voltammetry at 100 mV s^{-1} scan rate.
All measurements were realized in thermostatic conditions, in the temperature range between 25 and 55°C (± 1°C) and repeated at least twice in order to obtain reproducible data.

2.4. Surface morphology

The surface morphology of the samples obtained after the weight loss investigations and removing of the corrosion products was examined with a FEI INSPECT S scanning electron microscope.

3. Results and discussion

3.1. Weight loss data

The mass loss of the samples after corrosive attack in the absence/presence of streptomycin has been calculated in mg cm^{-2} h^{-1} using Eq. (1), obtained results been given in Table 1.

$$W = \frac{W_1 - W_2}{S \cdot t} \quad (1)$$

where W_1, W_2 are the initial, respectively final mass of the samples in mg, S - total area of specimens in cm^2 and t – corrosion test time in h.
From the weight loss of specimens the inhibition efficiency (η) and surface coverage (θ) have been evaluated by Eqs. (2) and (3):

$$\eta\,(\%) = \left(1 - \frac{W_{corr}}{W^o_{corr}}\right) \cdot 100 \quad (2)$$

$$\eta = 1 - \frac{W_{corr}}{W^o_{corr}} \quad (3)$$

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

Table 1. The weight loss, inhibition efficiency and surface coverage obtained for carbon steel in 0.5 M CH_3COOH - 0.25 M CH_3COONa after 144 h exposure time at 25°C.

Inhib. conc. [M]	W [mg cm^{-2} h^{-1}] $\times 10^2$	η [%]	θ
-	3.47	-	-
10^{-6}	2.38	31.4	0.314
10^{-5}	1.76	49.3	0.493
10^{-4}	1.31	62.2	0.622
10^{-3}	0.62	82.1	0.821

Analyzing the data from Table 1 it can be concluded that streptomycin reduces the ionization process of carbon steel in the test solutions, and its efficiency increases with the concentration, reaching a reasonable value for 10^{-3} M concentration of drug.

3.2. Linear polarization

Figure 2 shows Tafel polarization curves drawn at 25°C for steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa at different concentrations of streptomycin. The values of the parameters associated with the corrosion process, i.e. corrosion potential (E_{corr}), corrosion current densities (i_{corr}), anodic and cathodic Tafel slopes (b_a, b_c) and corrosion rate have been determined by extrapolating the linear polarization curves using GPES software. The efficiency and surface coverage degree have been calculated using Eqs. (4) and (5), and the results are presented in Table 2.

$$\eta(\%) = \left(\frac{i^o_{corr} - i_{corr}}{i^o_{corr}}\right) \cdot 100 \quad (4)$$

$$\theta = \frac{i^o_{corr} - i_{corr}}{i^o_{corr}} \quad (5)$$

where i^o_{corr} and i_{corr} are the uninhibited and inhibited corrosion current densities.

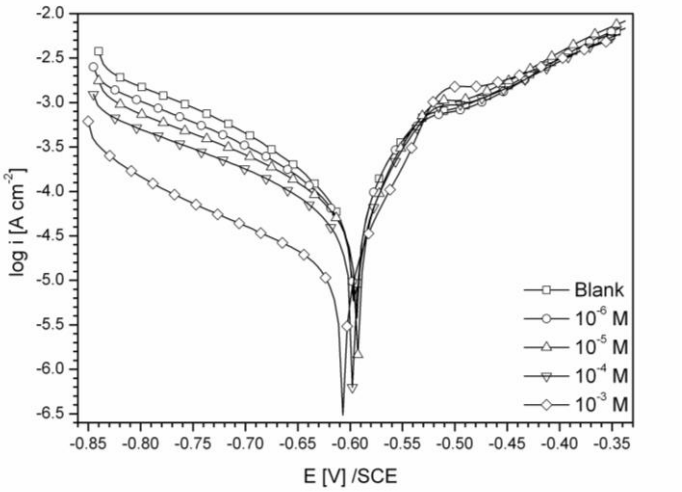


Fig. 2. Linear polarization curves drawn for steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa at 25°C in the absence and presence of streptomycin at different concentration.

Table 2. Linear voltammetric parameters and anticorrosive efficiency for carbon steel in 0.5 M CH_3COOH - 0.25 M CH_3COONa without and with various concentrations of streptomycin.

Inhib. conc. [M]	$i_{corr}\cdot10^5$ [A/cm^2]	$-E_{corr}$ [V]	$-b_c$ [V/dec]	b_a [V/dec]	R_p [Ω]	v_{corr} [mm/year]	η [%]	θ
–	8.81	0.595	0.155	0.064	50.7	1.03	–	–
10^{-6}	5.77	0.594	0.147	0.055	69.7	0.68	34.5	0.345
10^{-5}	4.22	0.592	0.147	0.048	99.7	0.49	52.1	0.521
10^{-4}	3.10	0.597	0.145	0.045	123.5	0.36	64.8	0.648
10^{-3}	1.11	0.606	0.174	0.042	292.8	0.13	87.4	0.874

From figure 2 and table 2 it can be seen that the corrosion rate of carbon steel decreases obviously after streptomycin addition. As it is expected, this effect is more pronounced at higher inhibitor concentrations and E_{corr} is slightly shifted to more negative values. The shape of the polarization curves indicates that the addition of the drug in the test solution does not modify the corrosion mechanism, acting preferentially on the cathodic hydrogen evolution reaction by blocking the active sites, but also slightly suppresses the anodic process of the metal ionization. Furthermore, at increased inhibitor concentration, the polarization resistance R_p becomes higher, and corrosion rate v_{corr} decreases.

3.3. EIS measurements

Electrochemical impedance spectra recorded for the carbon steel samples in the blank CH_3COOH - CH_3COONa buffer solution, as well as in the presence of different amounts of streptomycin, are given in figure 3.

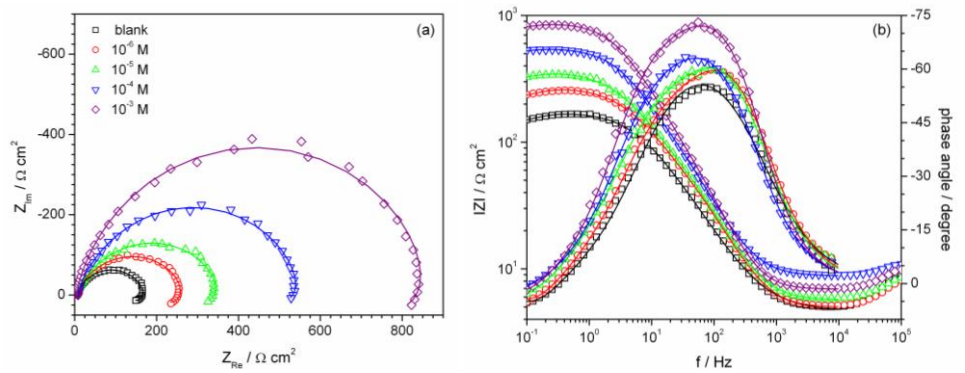


Fig. 3. Nyquist and Bode plots obtained on steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa with and without different amount of streptomycin. Open symbols are experimental data and continuous lines are the results of modeling to the electrical equivalent circuits EECs.

The Nyquist plots show the presence of one flattened capacitive loop at high to intermediate frequencies corresponding to the charge transfer resistance, followed by an inductive loop at low frequencies. It have to mention that the semicircle diameter increases proportionally with the drug concentration, providing a general view on the inhibition performances. The existence of an inductive loop is usually related to relaxation processes of adsorbed species such as H^+_{ads} or inhibitor [33-35], but it may be due to the dissolution of the passive layer at low frequencies [35].

The Bode plots reveal an increase of the impedance in the presence of streptomycin and positive phase angle values at frequencies lower that 0.3 Hz. Furthermore, the increase of streptomycin concentration leads to more negative phase angle values at intermediate frequencies, indicating a more capacitive behavior in the presence of the drug. Also, the phase angle plots have a wider shape than for the solution without streptomycin, which may suggest the appearance of a second time constant related to the formation of an inhibitor layer on the steel surface [36]. The two time constants in the Bode plots are not very well-resolved, probably due to similar time constants of charge transfer and film formation.

The parameters associated to the corrosion process were obtained by modeling the impedance data using the electrical equivalent circuits (EEC) presented in Fig. 4.

The electrical circuit consists of a parallel connection of a double layer capacitance C_{dl} and a charge transfer resistance R_{ct} in series with a parallel connection of the inductive elements L and R_L. In the case of streptomycin, to account for the second time constant, a parallel connection of film resistance R_f and capacitance C_f has been also introduced.

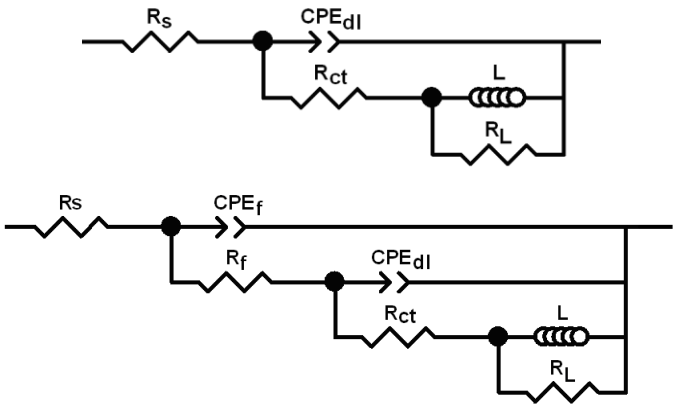


Fig. 4. Electrical equivalent circuits modelling the impedance data obtained for the blank solution (a) and for the solution containing streptomycin (b).

Due to the deviations from the ideal behavior the capacitance is usually replaced by a constant phase element (CPE), whose impedance is given by Eq. (6):

$$Z_{CPE} = \frac{1}{T}(j\omega)^n \tag{6}$$

where T is an amount related to the C_{dl} and n is an exponent between 0 and 1, describing the constant phase angle of the CPE. The double layer capacitance is given by the Eq. (7):

$$C_{dl} = (T_{dl} \cdot R_{ct}^{1-n})^{1/n} \tag{7}$$

The values of the electrochemical impedance parameters obtained by CNLS fitting in the test solutions are listed in Table 4. The experimental data are very well fitted by the proposed models, as indicated by the low chi-square (χ^2) and relative error values. The relative errors are less than 10%. The inhibition efficiencies have been calculated according to Eq. (8):

$$\vartheta\ (\%) = \left(\frac{R_p - R_p^o}{R_p}\right) \cdot 100 \tag{8}$$

where R_p and R_p^o are polarization resistances in the test solutions. For the blank solution R_p is equivalent to the charge transfer resistance R_{ct}, but for the case of two capacitive loops in the presence of streptomycin, R_p consists of charge transfer R_{ct} and film resistance R_f values [36].

Table 3. EIS parameters for carbon steel corrosion in 0.5 M CH_3COOH - 0.25 M CH_3COONa in the absence and presence of streptomycin (25°C).

Inh. conc. [M]	R_{ct} [Ω cm^2]	$T_{dl}\cdot10^4$ [F cm^{-2} s^{n-1}]	n_{dl}	C_{dl} [μF cm^{-2}]	R_f [Ω cm^2]	$T_f\cdot10^5$ [F cm^{-2} s^{n-1}]	n_f	C_f [μF cm^{-2}]	L [H cm^2]	R_L [Ω cm^2]	$\chi^2\cdot10^{-4}$	η [%]
–	133.1	2.99	0.80	134	–	–	–		40.4	37.4	24	–
10^{-6}	132.0	3.26	0.72	96	80.4	9.37	0.92	61	60.5	56.1	4.6	37.3
10^{-5}	205.2	2.79	0.72	92	97.2	9.32	0.92	62	70.0	59.4	6.5	56.0
10^{-4}	267.1	1.35	0.79	56	224.1	8.61	0.91	58	95.0	59.2	6.5	73.0
10^{-3}	511.8	0.876	0.77	35	235.6	4.80	0.99	46	196.0	125.7	9.2	82.2

Data presented in Table 3 show the increase of R_{ct} and decrease of C_{dl} values in the presence of streptomycin. The diminution of C_{dl} indicates that the streptomycin molecules adsorb on the inner Helmholtz plane blocking the active sites on the steel surface. The inhibitor film capacitance C_f is almost concentration independent, while the film resistance R_f increases with streptomycin concentration. Since R_f is directly related to the film thickness, its increase is a result of increased thickness of the protective layer. The inhibitory effect of streptomycin increases with the drug amount and the highest value of 82.2% has been obtained for 10^{-3} M streptomycin concentration.
Inhibitory effect obtained by mass loss, linear voltammetric curves and impedance data are in a good agreement.

3.4. Kinetic and thermodynamic considerations

Temperature influence of the carbon steel corrosion process has been studied as a function of temperature between 25 and 55°C in 0.5 M CH_3COOH - 0.25 M CH_3COONa by linear polarization and EIS measurements without inhibitor and with 10^{-3} M concentration of streptomycin. Figure 5 reveals the logarithmic dependence of current densities vs. potential at different temperatures and the results obtained by fitting these curves are given in Table 4.
In acetic acid - sodium acetate buffer solution, with and without of streptomycin, the corrosion resistance of carbon steel samples decreases with temperature, as it is expected. At higher values of temperature the corrosion potential is more negative because the hydrogen overpotential is significantly reduced. As well, the shape of Tafel curves remains unchanged with the increase of temperature, suggesting that the corrosion process mechanism is unaffected. A correlation between the corrosion current density and temperature is described by Arrhenius Eq. (9) [37, 38]:

$$logi_{corr} = \frac{-E_a}{2.303RT} + \log A \qquad (9)$$

On the other hand, the change of activation enthalpy and entropy for the transition state can be obtained from the Eq. (10) [30]:

$$log\frac{i_{corr}}{T} = log\frac{R}{Nh} + \frac{\Delta S^*}{2.303RT} - \frac{\Delta H^*}{2.303RT} \quad (10)$$

where E_a is the activation energy, A - pre-exponential factor, ΔH^* - activation enthalpy, ΔS^* - activation entropy, N - Avogadro's number and h - Plank constant. The activation energy can be evaluated using the linear dependence log i_{corr} as a function of $1/T$ (figure 7a) and log i_{corr}/T as a function of $1/T$. The last function is as well a linear dependency as shown in figure 7b. Activation enthalpy ΔH^* and entropy ΔS^* have been determined from the slope value of ($-\Delta H^*/R$) and from the intercept of ($\log R/Nh + \Delta S^*/2.303R$).

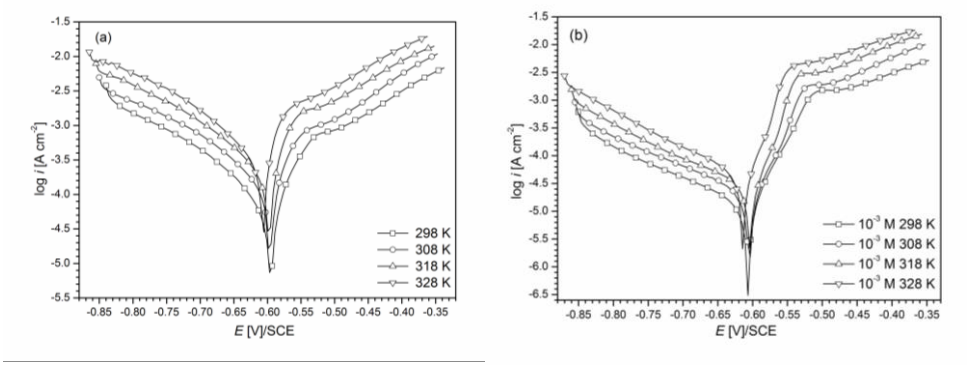


Fig. 5. Linear polarization curves obtained in 0.5 M CH_3COOH - 0.25 M CH_3COONa at different temperatures in the blank solution (a) and in the same solution having 10^{-3} M streptomycin (b).

Table 4. Linear voltammetric parameters and anticorrosive efficiency for carbon steel in 0.5 M CH_3COOH - 0.25 M CH_3COONa without and with 10^{-3} M streptomycin at various temperatures.

Solution	T [K]	$i_{corr}\cdot 10^5$ [A cm^{-2}]	$-E_{corr}$ [V]	$-b_c$ [V dec^{-1}]	b_a [V dec^{-1}]	R_p [Ω]	v_{corr} [mm year^{-1}]	η [%]	θ
Blank	298	8.81	0.595	0.155	0.074	50.7	1.03	–	–
	308	15.3	0.595	0.166	0.068	31.8	1.81	–	–
	318	25.9	0.597	0.163	0.067	18.2	3.01	–	–
	328	39.8	0.607	0.161	0.066	11.6	4.70	–	–
10^{-3} M	298	1.11	0.606	0.174	0.042	292.8	0.13	87.4	0.874
	308	1.81	0.605	0.175	0.040	174.7	0.22	88.2	0.882
	318	2.54	0.604	0.172	0.039	107.7	0.30	90.2	0.902
	328	4.04	0.614	0.158	0.040	63.4	0.47	89.8	0.898

Analyzing Table 4 it can be observed that with the increase of the temperature the inhibition efficiency increase too, and consequently the activation energy becomes lower for inhibited solution. As it is suggested by some authors [39, 40], the improvement of inhibitory activity with the increase of the temperature is due to

some chemical effects in the organic molecules, that cause an elevated electron density at the adsorption centers of molecules.
Other authors assign this phenomenon to the increase of the inhibitor surface coverage having as a consequence a significant obstruction of the active chemical species through the surface layer, composed of inhibitor molecules and corrosion products. In these circumstances, the diffusion process becomes the rate determining step, whereby metal dissolution is diminished [41].
Further, the influence of temperature on the corrosion of the steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa buffer solution has been also investigated by EIS method. The impedance spectra recorded at several temperatures for both blank and 10^{-3} M streptomycin solution and are given in Fig. 6.

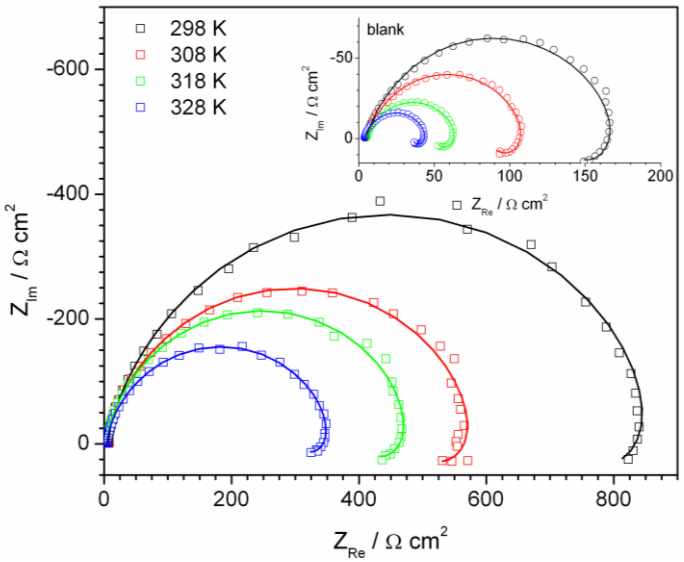


Fig. 6. Nyquist plots for steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa and 10^{-3} M streptomycin at different temperatures. Inset: Nyquist plots for the blank solution at same temperatures.

The temperature raising accelerates the corrosion process, as it can be observed from the decrease of the diameter of capacitive semicircle for both blank and 10^{-3} M streptomycin solutions. Impedance results have been fitted to the equivalent circuit from figure 4a for the blank, respectively figure 4b for the solution with inhibitor, and the results are presented as continuous lines in figure 6. The obtained parameter values are given in Table 5 as a function of temperature.

Table 5. Electrochemical impedance parameters for steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa and 10^{-3} M streptomycin at different temperatures.

Solution	t°C	R_{ct} [Ω cm^2]	$T_{dl} \cdot 10^4$ [F cm^{-2} s^{n-1}]	n_{dl}	C_{dl} [μF cm^{-2}]	R_f [Ω cm^2]	$T_f \cdot 10^5$ [F cm^{-2} s^{n-1}]	n_f	C_f [μF cm^{-2}]	η [%]
blank	25	133.1	3.0	0.80	134	–	–	–	–	–
	35	83.0	2.8	0.81	116	–	–	–	–	–
	45	46.4	4.7	0.80	180	–	–	–	–	–
	55	32.5	5.4	0.82	222	–	–	–	–	–
10^{-3} M	25	511.8	8.76	0.77	35	235.6	4.80	0.99	46	82.2
	35	312.2	0.976	0.78	36	181.3	4.08	1.00	41	83.2
	45	207.6	1.15	0.82	50	201.4	6.17	0.99	59	88.6
	55	80.0	2.04	0.81	78	226.4	11.1	0.95	91	89.4

It is interesting to note that, even though temperature increase enhances the charge transfer reaction, and the R_{ct} values decrease for both solutions (blank and 10^{-3} M streptomycin), the film resistance values are however almost temperature independent. This is the explanation for the increased inhibition efficiency at higher temperatures.

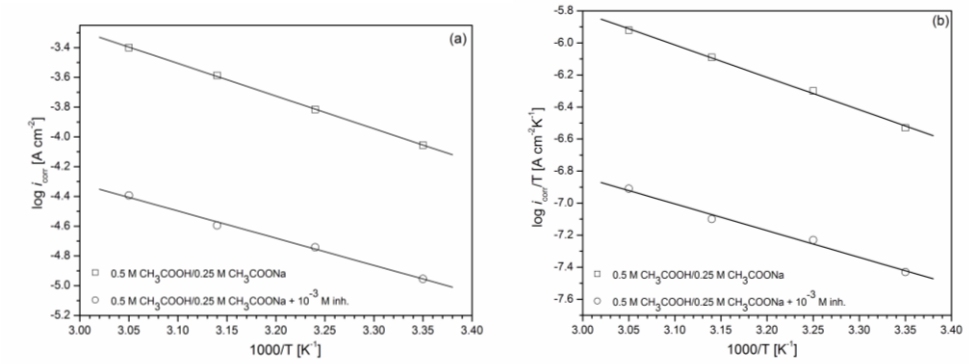


Fig. 7. Arrhenius plots of (a) log i_{corr} vs. 1/T and (b) log i_{corr}/T vs. 1/T without and with 10^{-3} M streptomycin.

Calculated E_a, $\Delta H^*$and ΔS^* for the corrosion process of steel samples in the corrosive media without and with 10^{-3} M streptomycin are given in Table 6.

Table 6. Thermodynamic parameters for steel samples in 0.5 M CH_3COOH - 0.25 M CH_3COONa without and with 10^{-3} M inhibitor.

Solution	E_a [kJ mol^{-1}]	ΔH^* [kJ mol^{-1}]	ΔS^* [J mol^{-1} K^{-1}]
0.5 M CH_3COOH - 0.25 M CH_3COONa	42.0	38.7	–58.7
0.5 M CH_3COOH - 0.25 M CH_3COONa with 10^{-3} M streptomycin	35.1	32.0	–98.6

A considerable drop of the activation energy E_a, versus to the uninhibited solution indicates a chemisorption surface process [42, 43]. Changes in the nature of adsorption manner occur with the raising of the temperature: at lower temperatures the inhibitor is physically adsorbed, while chemisorption is favored at higher ones [44]. The positive sign of ΔH^* shows that the iron ionization process is endothermic, meaning that the dissolution of metal is the slow step of the corrosion. The more negative value of ΔS^* obtained for the buffer acetic acid - sodium acetate solution with inhibitor emphasizes that the activated complex in the rate determining step represents an association rather than a dissociation, indicating that a decrease in disorder takes place [45].

3.5. Adsorption isotherms

To obtain information about the corrosion inhibition mechanism the adsorption isotherms was used to compute the adsorption standard free energy (ΔG^o_{ads}) based on Eq. (11):

$$\Delta G^o_{ads} = -RTln(55.5K_{ads}) \quad (11)$$

where R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), T - thermodynamic temperature, K, K_{ads} – adsorption equilibrium constant.

Generally, values of standard free energy up to -20 kJ mol^{-1} were consistent with the electrostatic interaction between the drug molecules and metal (physical adsorption) [46]. Instead, values about -40 kJ mol^{-1} means that electrons sharing or transfer from the streptomycin molecules to steel surface take place in order to form coordinative bonds (chemisorption) [47]. In our case, the Langmuir adsorption isotherm, written in simplified form (12), and plots c_{inh}/θ vs c_{inh} were used to obtain the values of adsorption constant.

$$\frac{c_{inh}}{\theta} = \frac{1}{K_{ads}} + c_{inh} \quad (12)$$

Eq. 12 is proper for all results obtained by weight loss, linear voltammetry and EIS as it is shown in figure 8. The graphs yielded a good fitting, regression coefficient been very close to unit, suggesting that the adsorption of studied drug meets the Langmuir isotherm.

The obtained data emphasized that addition of streptomycin has as a result the negative ΔG^o_{ads} values which show that the adsorption of streptomycin on the steel occurs spontaneously. The calculated values for standard free energy are slightly

less negative than -40 kJ mol^{-1} (-37 kJ mol^{-1}), revealing that the adsorption of streptomycin molecules takes places due to a combined physical and chemical adsorption [37, 38, 48, 49].

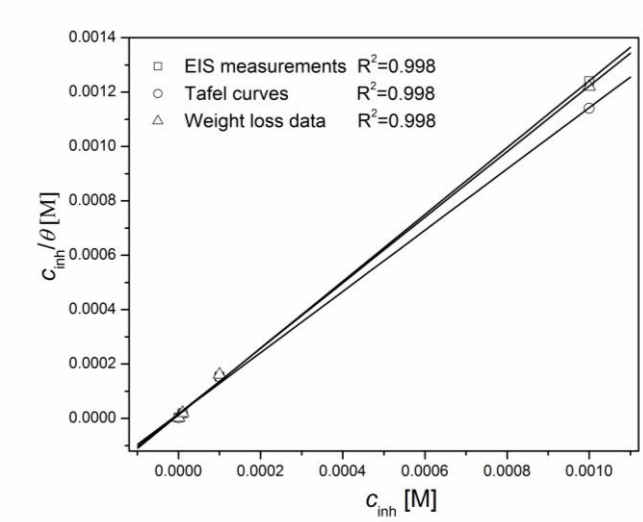


Fig. 8. Langmuir adsorption isotherms for streptomycin on carbon steel obtained by weight loss, EIS and Tafel data.

3.6. Inhibition mechanism

Inhibition of carbon steel corrosion in weak acid solutions consists in the adsorption of streptomycin on the metal surface. It has been shown that the adsorption of the organic molecules on the metal surface is the first stage of the inhibition mechanism in a such solution. The adsorption of the inhibitor may occur in four ways: **a** - electrostatic interaction between organic molecules and metal atoms, **b** - interaction of unshared electron pairs of streptomycin with the electrons from the Fermi level of the iron atom, **c** - interaction of π electrons of the organic substrate with the metal, and d - a mixture of **a**, **b** and **c** [50].
In acid media, streptomycin consists in a protonated molecules which adsorb on the cathodic sites and suppress the cathodic process of hydrogen evolution reaction. The effect is more pronounced with the rise of the concentration, because the number of streptomycin molecules on the metal - solution interface increases, and accordingly, the corrosion rate of the metal decreases. Instead, on the anodic active sites the adsorption of inhibitor molecules takes place due to π electrons of aromatic ring or unshared electron pairs of nitrogen atoms, which realize a metastable layer on the steel surface.

3.7. Cyclic voltammetry

In order to reveal the chemical stability of streptomycin in redox processes, the electrochemical behavior of this organic compound has been studied by cyclic voltammetry. To avoid interferences with the corrosion process taking place at the solution–carbon steel interface the curves were recorded on a Pt electrode. Figure 9 illustrates the cyclic voltammograms obtained in 0.5 M CH_3COOH - 0.25 M CH_3COONa without and with of 10^{-3} M concentration of streptomycin.

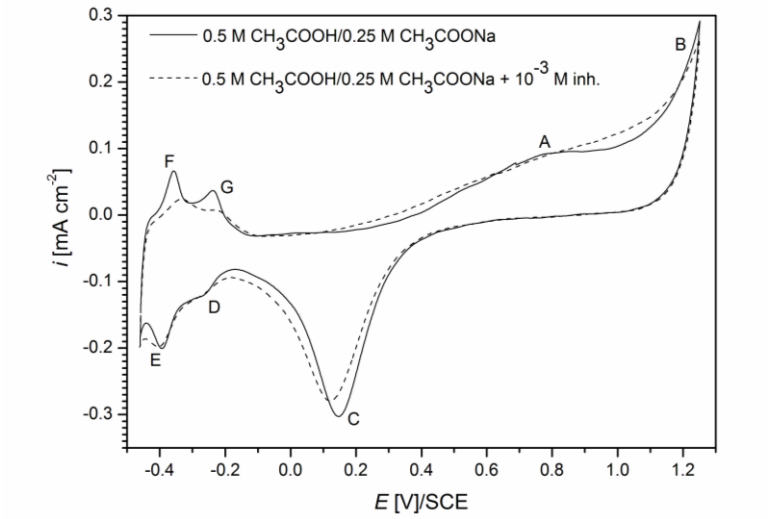
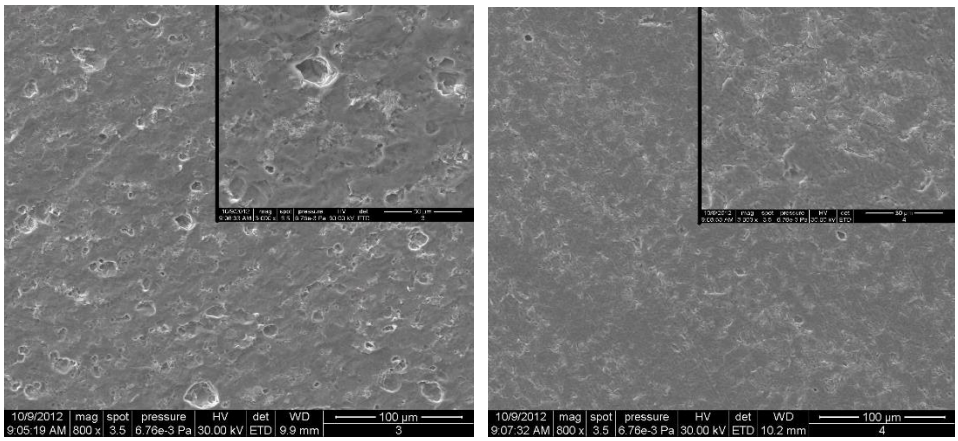


Fig. 9. Cyclic voltammograms drawn on Pt electrode.

On the base curve, drawn in anodic sense in blank solution, starting from equilibrium potential, the appearance of peak (A), assigned to the oxides formation on Pt surface, and the anodic branch corresponding to the oxygen evolution (curve B) are distinctive. Further, on the reverse part of the voltammogram it can be observed the reduction peak (C) of the oxides layer previously formed. The potential sweep in cathodic way has as a result the apparition of (D) and (E) areas associated with adsorption of hydrogen atoms and hydrogen molecules at electrode surface followed by hydrogen evolution reaction. They are also distinguishing peaks (F and G) corresponding to the oxidation of adsorbed atomic and molecular hydrogen. The addition of the streptomycin in test solution, as depicted from the graph, does not undergo to major changes. Consequently, in the corrosion potential frame of –0.85 to – 0.35 V/SCE with relevance for carbon steel, streptomycin remains stable in test solution and does not suffer major transformations.

3.8. SEM analysis

The morphology of the carbon steel surface was investigated on samples used at weight loss experiments. It is observed, in blank solution, a severe damage with clear pits and cavities with roughness due to metal dissolution. In the presence of streptomycin, there are fewer cracks and corrosion marks observed over the samples, which means that the steel surface is screened via the formation of inhibitor film by streptomycin molecules.



(a) (b)

Fig. 10. SEM images recorded on carbon steel samples after 144 h immersion in 0.5 M CH_3COOH - 0.25 M CH_3COONa: (a) without inhibitor; (b) with 10^{-3} M streptomycin.

4. Conclusions

Streptomycin proved as a good corrosion inhibitor for carbon steel in buffer acetic acid - sodium acetate solutions. Inhibition properties of the drug were tested by three different methods, all giving comparable results. Tafel polarization curves indicate that streptomycin decrease the corrosion rate of carbon steel by suppressing preferentially the cathodic process and less the anodic one of the metal ionization. Inhibition effect of drug increases with the amount of inhibitor and the value of about 90% has been obtained for 10^{-3} M concentration of inhibitor. Also, the efficiency of streptomycin is temperature dependent and his addition in test solution leads to a significant drop of the activation corrosion energy. The EIS diagrams emphasize that streptomycin reduces the metal dissolution due to a protective film on carbon steel, phenomenon argued by apparition of a new constant phase element in EEC. The adsorption of streptomycin obeys Langmuir adsorption isotherm, and the standard free energy (very close to - 40 kJ mol^{-1}) indicates that the nature of the interactions are a conjunction of physical adsorption and chemisorption. From surface morphology examination it can be observed that in the presence of the inhibitor the surface of carbon steel was protected against

corrosion by a inhibitor film formed by streptomycin molecules which prevents penetration of corrosive solution.

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