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Short Communication

Cephamycin; A Novel Corrosion Inhibitor for Mild Steel Corrosion in HCl Acid Solution

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The corrosion inhibition properties of cephamycin (CFC) for mild steel corrosion in HCl solution were analysed by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. Potentiodynamic polarization study clearly revealed that cephamycin acted as mixed type inhibitor. The experimental data showed a frequency distribution and therefore a modelling element with frequency dispersion behaviour, a constant phase element (CPE) has been used.

Keywords: EIS; Acid solutions; Mild steel; potentiodynamic polarization; acid inhibition

1. INTRODUCTION

Mild steel is widely applied as the constructional material in many industries due to its excellent mechanical properties and low cost. The main problem of applying mild steel is its dissolution in acidic solutions. Recently, the inhibition of mild steel corrosion in acid solutions by different types of organic inhibitors has been extensively studied [1-4].

The use of inhibitors is the most economical and practical methods of reducing corrosive attack on metals [5-7]. During the past decade, the inhibition of mild steel corrosion in acid solutions by various types of organic inhibitors has attracted much attention [8, 9]. There is a continuing effort to find a corrosion inhibitor that exhibits a greater effect with a smaller quantity in the corrosion medium. This is a challenging problem in the steel industry because corrosion over mild steel surfaces affects long term industrial projects. The performance of the corrosion inhibitors based on organic compounds containing nitrogen, sulphur and oxygen atoms shows promising results. The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process and thereby modify the metal dissolution in acids. The existing data show that most organic inhibitors act by adsorption on the metal surface. They change the structure of the electrical double layer by adsorption on the metal surface

This article reported our attempt to use electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization method to investigate the nature of adsorption of cephamycin on the mild steel surface. The structure of cephamycin is shown in Figure 1.

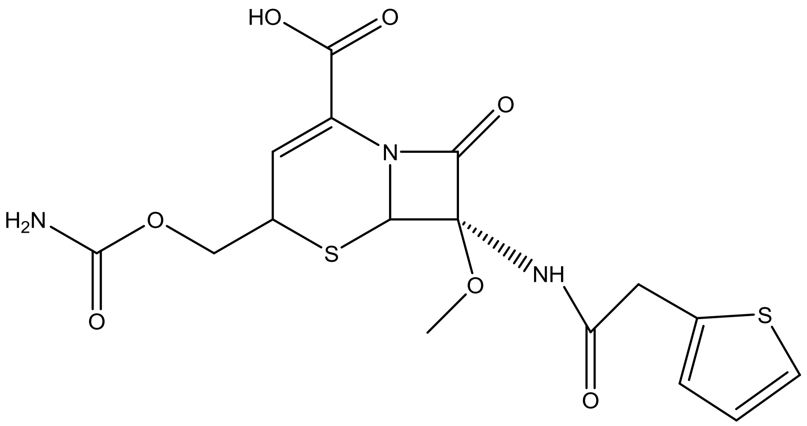

Figure 1. Structure of Cephamycin molecule

2. EXPERIMENTAL

2.1 Inhibitor

Stock solution of cephamycin was made in 10:1 ratio water: ethanol mixture to ensure solubility. This stock solution was used for all experimental purposes.

2.2 Corrosion measurements

Prior to all measurements, the mild steel specimens, having composition (wt %) C = 0.17, Mn= 0.46, Si = 0.26, S = 0.017, P = 0.019 and balance Fe, were abraded successively with emery papers from 600 to 1200 grade. The specimen were washed thoroughly with double distilled water, degreased with acetone and finally dried in hot air blower. After drying, the specimen were placed in desiccator and then used for experiment. The aggressive solution 1 M HCl was prepared by dilution of analytical grade HCl with double distilled water and all experiments were carried out in unstirred solutions. The rectangular specimens with dimension 2.5 × 2.0 × 0.025 cm were used in weight loss experiments and of size 1.0 cm × 1.0 cm (exposed) with a 7.5 cm long stem (isolated with commercially available lacquer) were used for electrochemical measurements.

2.3 Electrochemical impedance spectroscopy

The EIS tests were performed at 303 ±1 K in a three electrode assembly. A saturated calomel electrode was used as the reference; a 1 cm^2 platinum foil was used as counter electrode. All potentials are reported vs. SCE. Electrochemical impedance spectroscopy measurements (EIS) were performed using a Gamry instrument Potentiostat/Galvanostat with a Gamry framework system based on ESA 400 in a frequency range of 100000 Hz to 0.01 Hz under potentiodynamic conditions, with amplitude of 10 mV peak-to-peak, using AC signal at E_{corr}. Gamry applications include software DC105 for corrosion and EIS300 for EIS measurements, and Echem Analyst version 5.50 software packages for data fitting. The experiments were measured after 30 min. of immersion in the testing solution (no deaeration, no stirring). The working electrode was prepared from a square sheet of mild steel such that the area exposed to solution was 1 cm^2.

The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following Eqn.

$$E\% = \frac{R_{\mathrm{ct}}^{\mathrm{i}} - R_{\mathrm{ct}}^{0}}{R_{\mathrm{ct}}^{\mathrm{i}}} \times 100 \qquad (1)$$

where R_{ct}^{0} and $R_{\mathrm{ct}}^{\mathrm{i}}$ are the charge transfer resistance in absence and in presence of inhibitor, respectively.

2.4 Potentiodynamic polarization

The electrochemical behaviour of mild steel sample in inhibited and non-inhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1 M HCl solution containing different concentrations of the tested inhibitors by changing the electrode potential automatically from -250 to +250 mV vs. corrosion potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}).

The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$E\% = \frac{I_{\mathrm{corr}}^{0} - I_{\mathrm{corr}}^{\mathrm{i}}}{I_{\mathrm{corr}}^{0}} \times 100 \qquad (2)$$

where, I_{corr}^{0} and $I_{\mathrm{corr}}^{\mathrm{i}}$ are the corrosion current density in absence and presence of inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1Electrochemical impedance spectroscopy

The corrosion behaviour of mild steel in 1 M HCl in absence and presence of pcephamycin were investigated by EIS after immersion for 30 min at 303 ± 1 K. Nyquist plots of mild steel in uninhibited and inhibited acid solutions containing different concentrations of cephamycin are presented in Fig 2a. EIS spectra obtained consists of one depressed capacitive loop (one time constant in Bode-phase plot). The increased diameter of capacitive loop obtained in 1 M HCl in presence of cephamycin indicated the inhibition of corrosion of mild steel. The high frequency capacitive loop may be attributed to the charge transfer reaction.

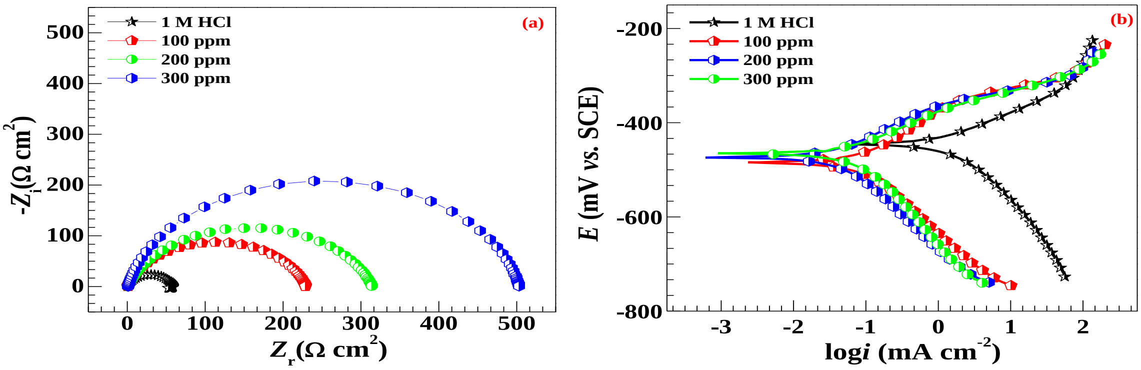

Figure 2. (a) Nyquist plots in absence and presence of different concentration of Cephamycin and (b) potentiodynamic polarization curves in absence and presence of Cephamycin

Corrosion kinetic parameters derived from EIS measurements and inhibition efficiencies are given in Table 1. Double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were obtained from EIS measurements as described elsewhere [10]. It is apparent from Table 1 that the impedance of the inhibited system amplified with the inhibitor the C_{dl} values decreased with inhibitor. This decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the iron corrosion by adsorption at the metal/acid interface [11]. The depression in Nyquist semicircles is a feature for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogenities of the solid electrode [12]. In this behaviour of solid electrodes, the parallel network: charge transfer resistance-double layer capacitance is established where an inhibitor is present. For the description of a frequency independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as in Eqn. (6)

$$Z_{\text{CPE}} = Y_0^{-1}(i\omega)^{-n} \qquad (6)$$

where, Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $i^2 = -1$ is the imaginary number and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [13]. Depending on the value of n, CPE can represent resistance ($n = 0$, $Y_0 = R$), capacitance ($n = 1$, $Y_0 = C$), inductance ($n = -1$, $Y_0 = L$) or Warburg impedance ($n = 0.5$, $Y_0 = W$).

Fig 3 showed the electrical equivalent circuit employed to analyse the impedance spectra. Excellent fit with this model was obtained for all experimental data.

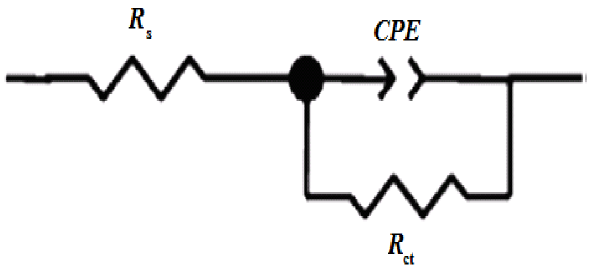

Figure 3. electrochemical equivalent circuit used to fit the impedance measurements that include a solution resistance (R_s), a constant phase element (*CPE*) and a polarization resistance or charge transfer (R_{ct})

The electrochemical parameters, including R_s, R_{ct}, Y_0 and n, obtained from fitting the recorded EIS data using the electrochemical circuit of Figure 3 are listed in Table 1. C_{dl} values derived from CPE parameters according to Eqn. (7) are listed in Table 1.

$$C_{dl} = (Y_0 . R_{ct}^{1-n})^{1/n} \qquad (7)$$

Table 1. Impedance parameters and inhibition efficiency values for mild steel after 30 min immersion period in 1 M HCl in absence and presence of different concentrations of cephamycin

Name of Inhibitor	Conc. Of Inhibitor (ppm)	R_s (□ cm^2)	R_{ct} (□ cm^2)	Y_0 (□F cm^{-2})	n	C_{dl} (□F cm^{-2})	E_{EIS}%
-	-	1.13	50.24	172.0	0.809	56.02	-
CMC	100	1.09	230.5	113.9	0.820	55.33	78.2
	200	1.03	312.6	101.9	0.821	51.31	83.9
	300	1.06	504.8	86.9	0.822	46.60	90.0

3.2 Potentiodynamic polarization measurements

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Fig 2b presented the results of the effect of CFC on the cathodic and anodic polarization curves of mild steel in 1 M HCl, respectively. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of cephamycin, which suggested that the cephamycin reduced anodic dissolution and also retarded the hydrogen evolution reaction. Electrochemical corrosion kinetics parameters, i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a, b_c) and corrosion current density (I_{corr}) obtained from the extrapolation of the polarization curves, were given in Table 2.

Table 2. Potentiodynamic polarization parameters for mild steel in absence and presence of 200 ppm cephamycin in 1 M HCl

Name of Inhibitor	Conc. Of Inhibitor (ppm)	$-E_{corr}$ (mV *vs.* SCE)	i_{corr} (□A cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	E_{PDP}%
-	-	448	1400.0	83	120	-
CMC	100	484	326.2	77	171	76.7
	200	465	236.6	70	155	83.1
	300	475	158.2	78	162	88.7

The parallel cathodic Tafel curves in Fig 2b suggested that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of the inhibitor. The region between linear part of cathodic and anodic branch of polarization curves becomes wider as the inhibitor is added to the acid solution. Similar results were found in the literature [14]. The values of b_c changed with increasing inhibitor concentration, indicated the influence of the compounds on the kinetics of hydrogen evolution.

Due to the presence of some active sites, such as aromatic rings, hetero-atoms in the studied compound for making adsorption, they may act as adsorption inhibitors. Being absorbed on the metal surface, these compounds controlled the anodic and cathodic reactions during corrosion process, and then their corrosion inhibition efficiencies are directly proportional to the amount of adsorbed inhibitor. The functional groups and structure of the inhibitor play important roles during the adsorption process. On the other hand, an electron transfer takes place during adsorption of the neutral organic compounds at metal surface [15]. As it can be seen from Table 2, the studied inhibitor reduced both anodic and cathodic currents with a slight shift in corrosion potential (3 mV). According to Ferreira and others [16, 17], if the displacement in corrosion potential is more than 85mV with respect to corrosion potential of the blank solution, the inhibitor can be seen as a cathodic or anodic type. In the present study, the displacement was 3 mV which indicated that the studied inhibitor is mixed-type inhibitor. The results obtained from Tafel polarization showed good agreement with the results obtained from EIS.

4. MECHANISM OF INHIBITION

The inhibition efficiency of CFC against the corrosion of mild steel in 1 M HCl can be explained on the basis of the number of adsorption sites, molecular size and mode of interaction with the metal surface [18, 19]. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair electrons. The CFC molecule exists as cation in equilibrium with the corresponding molecular form

$$\text{CFC} + x\text{H}^+ \leftrightarrow [\text{CFC}_x]^{x+} \qquad (14)$$

The protonated cephamycin, however, could be attached to the mild steel surface by means of electrostatic interaction between Cl^- and protonated CFC since the mild steel surface has positive charge in the HCl medium [5, 20-21]. This could further be explained based on the assumption that in the presence of Cl^-, the negatively charged Cl^- would attach to positively charged surface. When cephamycin adsorbs on the mild steel surface, electrostatic interaction takes place by partial transference of electrons from the polar atom (N atom and delocalized π-electrons of the aromatic ring) of cephamycin to the metal surface.

5. CONCLUSIONS

The following main conclusions are drawn from the present study:

1. Cephamycin was found to be a good inhibitor for mild steel corrosion in acid medium.
2. Potentiodynamic polarization curves revealed that cephamycin is a mixed-type inhibitor

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