Corrosion Inhibition of Iron in Sulphuric Acid Solutions by Antibacterial Cephalosporin

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Abstract: The inhibitive effects of some antibacterial cephalosporin (cefotaxime, cefalexin, cefradine and cefazolin) on the corrosion of iron in 0.5 M H_2SO_4 solution was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Results showed that the inhibition efficiency increased with an increase in concentration of inhibitor. Potentiodynamic studies proved that the inhibitors act as mixed type .The inhibitors are adsorbed on the iron surface according to Langmuir isotherm equation. All impedance spectra in EIS tests exhibit one capacitive loop which indicates that the corrosion reaction is controlled by charge transfer process. Inhibition efficiencies obtained from Tafel polarization, charge transfer resistance (R_{ct}) is consistent.

1.Introduction

Because iron is the back bone of industrial consideration, the inhibition of the iron corrosion in acid solutions of organic inhibitors has been studied in considerable detail. Acids are widely used in many industries. Some of the important areas of application are industrial acid cleaning, pickling, decaling and in acidization of oil wells [1]. It is reported that sulphur containing inhibitors such as sulphoxides [2, 3], sulphides[4], and thioureas [5] are found to be efficient in H_2SO_4 environment.

These investigated inhibitors are classified as the first generation of cephalosporin and were found to have good activity against gram-positive bacteria and relatively moderate activity against gram-negative microorganisms [6]. No data are recorded in the literature about the behavior of this investigated cephalosporin as inhibitors for metallic corrosion. Most of the data recorded in the literature were about the electro analytical behavior of this investigated cephalosporin. These inhibitors were selected as inhibitors because: They are nontoxic, relatively cheap, and easy to produce in purities with proportion of more than 99 % and they are rich in donating atoms such as -N, -O and –S atoms.

In the previous work the antibacterial cephalosporin compounds was used as corrosion inhibitors for dissolution of iron in 1.0MHCl solution [7]. The aim of this work is to study the effect of these cephalosporin compounds to inhibit the corrosion of iron in 0.5 M H_2SO_4 solution using potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental
2.1. Working electrode

An iron sample was served as working electrode. A 1 cm length of cylindrical iron ($\phi = 5$ mm) was fixed in at the end of a Teflon tube holder and covered with epoxy resin (Araldite) so as to leave only the surface exposed to the electrolyte. Before dipping in the cell, the electrode surface was polished with emery papers up to 600 grades, degreased with acetone and finally washed with second distilled water

2.2. Inhibitors

The following four cephalosporin antibiotics (Cefotaxime, cefalexin, cefradine and cefazolin) were kindly provided from Misr Company for Pharmaceuticals and Chemical Industries, Egypt and were used as received without further purification. Their structures are recorded in Table 1.

2.3. Solutions

Stock solutions (1000 ppm) of these inhibitors were prepared by dissolving the appropriate weight (1 gram) of each compound separately in bidistilled water in 100 ml measuring flask, then the required concentrations (10, 20, 30, 40,50 and 60 ppm) were prepared by dilution with doubly distilled water.. The aggressive solutions (H_2SO_4) used were made of analytical reagent grade. Stock solution of the acid (6 M) was prepared using bidistilled water and this concentration was checked

using standard solution of Na_2CO_3. From this stock concentrated solution, exactly 0.5M H_2SO_4 were prepared by dilution with bidistilled water, which

was used throughout experiments for the preparation of solutions.

Table. 1. Chemical structures, names and molecular weights of cephalosporin

Inh.	Structure	Name	Molecular Weight
1		Cefotaxime (6R,7R,Z)-3-(acetoxymethyl)-7-(2-(2-aminothiazol-4-yl)-2-(methoxyimino)acetamido)-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid	347.39
2		Cefalexin (6R,7R)-7-{[(2R)-2-amino-2-phenylacetyl]amino}- 3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene- 2-carboxylic acid	454.51
3		Cefradine (6R,7R)-7-{[(2R)-2-amino-2-(1-cyclohexa-1,4-dienyl)acetyl]amino}-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid	455.47
4		Cefazolin 3-[(5-methyl-1,3,4-thiadiazol-2-yl)sulfanylmethyl]-8-oxo-7-([2-(tetrazol-1-yl)acetyl]amino)- 5-thia-1-azabicyclo[4.2.0] oct-2-ene-2-carboxyla	349.41
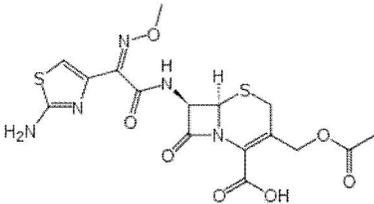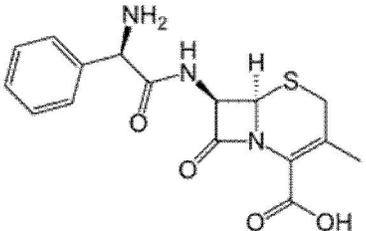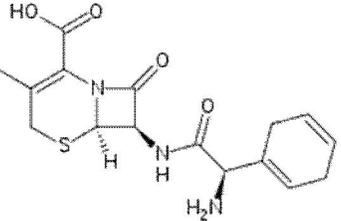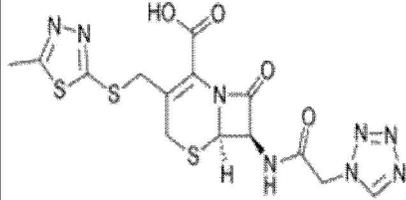
2.4. Electrochemical techniques [potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques].

The working electrode was prepared from aluminum rod, inserted in a Teflon tube and isolated with Araldite so that a circular cross-section (0.985 cm^2)only was exposed. Prior to every experiment, the electrode was polished with successive different grades of emery paper, degreased with alkaline solution and rinsed by bidistilled water.

Measurements were carried out in a three-compartment electrochemical cell. The counter electrode was a platinum sheet of large surface area.

The reference electrode was a saturated calomel electrode (SCE) to which all potentials are referred. The SCE was connected to the main compartment via a Luggin capillary. The cell was water-jacketed and was connected to an ultra thermostat at 25 $^{\circ}$C. The electrode potential was allowed to stabilize for 60 min before starting the measurements. For potentiodynamic polarization measurements the corrosion current density (j_{corr}) is determined, which is a measure of corrosion rate. Stern-Geary method [8] used for the determination of corrosion current is performed by extrapolation of anodic and cathodicTafel lines. Then j_{corr} was used for

calculation of inhibition efficiency and surface coverage (θ) as follows [8]:

$$\% \, IE = [1 - (j_{corr\,(inh)}/\, j_{corr\,(free)})] \times 100 \qquad (1)$$

$$\theta = [1 - (\, j_{corr\,(inh)}/\, j_{corr\,(free)})] \qquad (2)$$

Where, $j_{corr\,(free)}$ and $j_{corr\,(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -500 to 500 mV with scanning rate 5mVs^{-1}. All measurements were conduced using an electrochemical measurement system (VoltaLab 21) comprised of a PGZ 100 potentiostat, a PC and Voltamaster 4 version 7.08 software for calculations. All the experiments were carried out at 25 ± 1 $^{\circ}$C by using ultracirculating thermostat and solutions were not deaerated to make the conditions identcial to weight loss measurements. The procedure adopted for the polarization measurements was the same as described elsewhere [9]· Each polarization was run three times and corrosion potentials and corrosion currents were reproducible within ± 5 mV and ± 1 μA cm^{-2} respectively. The AC impedance measurements were carried out in the frequency range $10^5 - 5 \times 10^{-1}$ Hz with amplitude 10 mV peak-to-peak using ac signals at the open potential circuit. All measurements were carried out using potentiostat/galvanostat Gamry PCI 300/4 connected to computer. A corrosion software model EIS 300 was employed. The experimental impedance were analyzed and interpreted on the basis of the equivalent circuit.

3. Results and Discussion
3.1. Potentiodynamic measurements

Fig.1represents the potentiodynamic polarization curves of iron electrode in 0.5 M H$_2$SO$_4$ with and without the addition of compound 4 as an example of the studied compounds as an example .Similar curves were obtained (not shown).The corrosion kinetic parameters such as corrosion current density (j_{corr}), corrosion potential (E_{corr}), and Tafel slopes β_a and β_c of different inhibitors derived from these Figures are given in Table (2). In all investigated compounds the inhibition efficiencies increase with increasing the concentration of these compounds.

Addition of all compounds shifts the corrosion potential slightly in the positive direction without an appreciable change in β$_a$ andβ$_c$ values. This suggests that the added compounds do not change the mechanism of iron dissolution and hydrogen evaluation reactions and the inhibitors decrease both reactions by surface coverage. The polarization resistance (Table 2) values showed an increase in the presence of inhibitors and also increases with increasing the concentration.

On the basis of the experimental data, it is not difficult to deduce that in 0.5 M H$_2$SO$_4$ these compounds act as mixed-type inhibitors. The order of decreased inhibition efficiency of all inhibitors at different concentrations is: 4 > 2 > 3 > 1
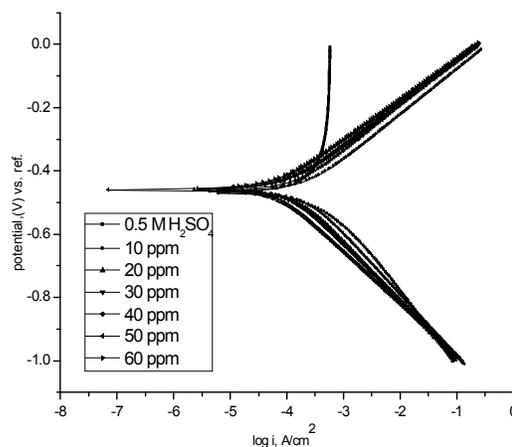
Fig. (1) Potentiodynamic curves for iron in 0.5 M H$_2$SO$_4$ in the absence and presence of different concentrations of inhibitor (4) at 25 ^{o}C.

3.2. Adsorption isotherm

Basic information on the interaction between the inhibitors and the iron surface can be explained by the adsorption of these compounds on the iron surface. Adsorption of the organic molecules occurs as the interaction energy between molecule and the metal surface is higher than that between the water molecules and surface [10]. The interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm [11]. In order to find out the adsorption isotherm, attempts were made to fit various isotherms viz., Frumkin, Freundlich, Langmuir and Temkin. However, the best fit was obtained only with Langmuir adsorption isotherm

Table 2: The effect of concentration of compounds (1-4) on the free corrosion potential (E$_{corr}$), corrosion current density (j$_{corr}$), Tafel slopes (β$_a$, β$_c$), inhibition efficiency (% IE), degree of surface coverage (θ) and polarization resistance (R$_p$) for the corrosion of iron in 0.5 M H$_2$SO$_4$ at 25 ^{o}C.

Comp.	Conc. ppm	-E$_{corr}$, mV	j$_{corr}$, μA cm^{-2}	β$_c$, mV dec^{-1}	β$_a$, mV dec^{-1}	R$_p$ Ω cm^2	θ$_{jcorr}$	%IE j$_{corr}$	%IE R$_p$
Blank	0	468	589	247	160	58.0	0.00	00.0	00.0

	10	465	247	197	157	121.6	0.581	58.1	52.3
	20	455	218	196	156	172.3	0.620	62.00	66.3
1	30	458	191	196	153	201.1	0.676	67.6	71.2
	40	461	175	187	147	201.8	0.703	70.3	71.3
	50	463	169	189	148	210.1	0.713	71.3	72.4
	60	454	160	187	147	214.1	0.728	72.8	72.9
	10	460	310	214	163	128.0	0.474	47.4	54.7
	20	460	255	203	159	178.0	0.567	56.7	67.4
2	30	454	192	198	155	192.3	0.674	67.4	69.8
	40	457	184	194	154	202.5	0.687	68.7	71.4
	50	457	178	197	154	248.7	0.698	69.8	67.7
	60	455	104	181	145	307.0	0.823	82.3	81.1
	10	452	310	210	162	153.1	0.474	47.4	62.1
	20	464	209	193	154	172.0	0.645	64.5	66.3
3	30	464	191	193	152	194.7	0.676	67.6	70.2
	40	459	181	192	151	203.2	0.693	69.3	71.5
	50	459	145	190	149	213.2	0.754	75.4	72.8
	60	458	112	179	142	222.8	0.810	81.0	74.0
	10	464	207	194	144	172.2	0.649	64.9	66.3
	20	461	141	190	155	253.3	0.761	76.1	77.1
4	30	456	103	177	134	320.0	0.825	82.5	81.9
	40	454.6	99	177	134.7	334.9	0.832	83.2	82.7
	50	459.6	62	163.9	128.6	506.0	0.895	89.5	88.5
	60	453.8	61	165.7	127.7	510.8	0.896	89.6	88.6
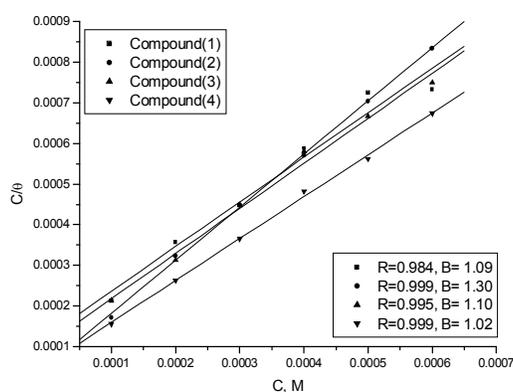
Fig. (2) Langmuir adsorption isotherm plotted as (C/Ө) versus C of compounds (1-4) for corrosion of iron in0.5 M H$_2$SO$_4$ solution at 25 ^{o}C.
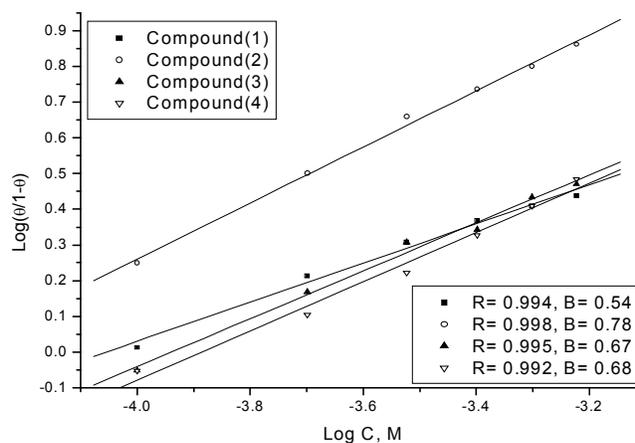
Fig.(3): El-Awady *et al.* model plotted as log(Ө/1-Ө) versuslog C of compounds (1-4) for corrosion of ironin 0.5 M H$_2$SO$_4$ solution at 25 ^{o}

Plotting C/θ versus concentration (C) gave a straight line with unit slope value (Fig.2) indicating the adsorption **of** antibacterial cephalosporin on the iron surface follows Langmuir isotherm. From these results one can postulates that there is no interaction between the adsorbed species

he equilibrium constant of the adsorption process, β, which is related to the standard free energy of adsorption (ΔG^o_{ads}) [12,13].

$$C/\theta = 1/\beta + C \qquad (3)$$
$$\beta = (1/55.5) \exp[-\Delta G^o_{ads}/RT] \qquad (4)$$

where R is the universal gas constant and T is the absolute temperature, C is inhibitor concentration and β is equilibrium constant of adsorption.

Also, it is found that the kinetic– thermodynamic model [14] are appreciable (Fig .3) which has the formula.

$$\log(\theta/1-\theta) = \log K' + Y \log C \qquad (5)$$

is valid to operate the present adsorption data. $\beta = \beta^o$ (1/y), β^o is constant, and 1/y is the number of the surface active sitesoccupied by one inhibitor molecule.

The values of ΔG°_{ads} were calculated and are listed in Table 3, It is clear that the value of ΔG°_{ads} decreases in the following order: 4 > 2 > 3 > 1 which is parallel to inhibition efficiency. The negative values of ΔG°_{ads} obtained here indicate that the adsorption process of these compounds on the iron surface is spontaneous one. The higher values of β suggested strong interaction of the inhibitors and the iron surface [15]. The increasing of β (4 > 2 > 3 > 1) reflects the increasing adsorption capability, due to structural formation on the metal surface [16].

Table (3) Number of active sites (1/Y), Slopes of Longmuir isotherm lines, equilibrium constant of the adsorption reaction (K) and free energy of adsorption (ΔG^o_{ads}) of inhibitors (1-4) on iron surface in 0.5 M H_2SO_4 at 25 ^{o}C.

Inhibitor	Kinetic Model			Langmuir isotherm	
	1/Y	log K	$-\Delta G^o_{ads}$ k J mol^{-1}	K L mol^{-1}	$-\Delta G^o_{ads}$ kJ mol^{-1}
1	1.851	2.22	22.618	793.65	26.496
2	1.470	2.67	25.186	1760.56	28.470
3	1.492	2.64	25.014	934.57	26.901
4	1.282	3.39	29.294	1945.52	28.718

3.3. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of iron in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of the investigated compounds is also investigated by the EIS method at E_{corr} at 25 ^{o}C after 30 min of immersion. The R_{ct} values were calculated from the difference in impedance at lower and higher frequencies from Nyquistplot . Fig.4 represents of iron electrode in 0.5 M H_2SO_4 with and without the addition of compound 4 as an example of the studied compounds as an example .Similar curves were obtained (not shown)Using R_{ct} values, C_{dl} values were computed from the Bode plot. Fig 5 represents the Bode plot of iron electrode in 0.5 M H_2SO_4 with and without the addition of compound 4 as an example of the studied compounds as an example .Similar curves were obtained (not shown) using the following equation:

$$C_{dl} = 1/2\pi f_{max} R_{ct} \qquad (6)$$

Where, f_{max} is the frequency at which the imaginary component of the impedance ($-Z_{max}$) is maximal. The impedance parameters derived from investigations

are given in Table 4. It is worth noting that the presence of inhibitor does not alter the profile of impedance diagrams which are almost semi-circle, indicating that a charge transfer process mainly controls the corrosion of iron. Deviations of perfect circular shape are often preferred to the frequency dispersion of interfacial impedance. This anomalous phenomenon is interpreted by the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [17]. In fact, the presence of investigated inhibitors enhances the values of R_{ct} in the acidic solution. Values of double layer capacitance decreased in the presence of inhibitors revealing the adsorption of the inhibitor on the metal surface in the acidic solution.

The inhibition efficiency and the surface coverage (θ) obtained from the impedance measurements are defined by the following relations:

$$\%IE = [1-(R^o_{ct}/R_{ct})] \times 100 \qquad (7)$$
$$\theta = [1-(R^o_{ct}/R_{ct})] \qquad (8)$$

Where, R^o_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively.
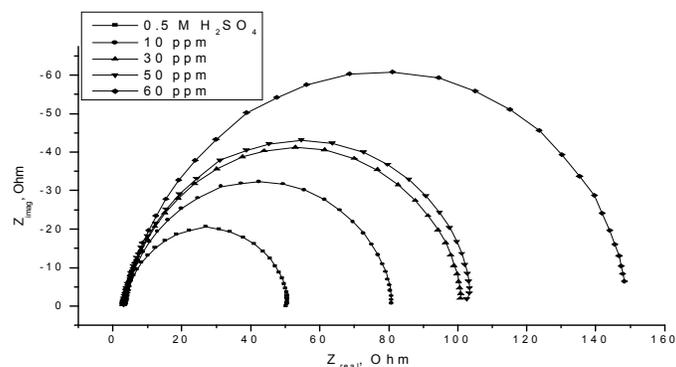
Fig. (4) The Nyquist plots for iron in 0.5 M H$_2$SO$_4$ solution in the absence and presence of different concentrations of compound (4) at 25 ^{o}C.
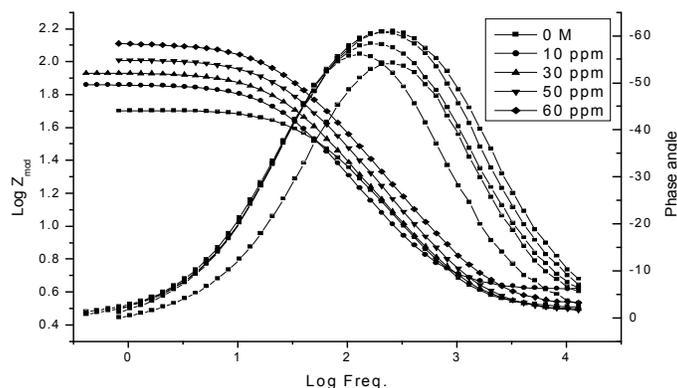
Fig.(5) The Bode plots for corrosion of iron in0.5 M H$_2$SO$_4$ in the absence and presence of different concentrations of compound (4) at 25 ^{o}C.

The %IE obtained from EIS measurements are close to those deduced from polarization. The order of inhibition efficiency obtained from EIS measurements is as follows: 4 > 2 > 3 > 1

Table (4): Electrochemical kinetic parameters obtained by EIS technique for corrosion of iron in 0.5 M H$_2$SO$_4$ at different concentration of compounds (1-4) at 25 ^{o}C.

Comp.	Conc., ppm	C$_{dl}$ μFcm^{-2}	R$_{ct}$ ohm	θ	IE%
Blank	0.0	58.09	44.66	0.00	0.00
1	10	55.70	50.11	0.1087	10.87
	20	49.95	58.08	0.2310	23.10
	30	44.03	72.53	0.3842	38.42
	60	40.84	88.52	0.4954	49.54
2	10	50.80	64.57	0.3083	30.83
	20	45.83	76.25	0.4142	41.42
	30	43.15	91.06	0.5095	50.95
	60	38.21	112.1	0.6016	60.16
3	10	53.10	58.05	0.2306	23.06
	20	48.57	67.67	0.3400	34.00
	30	46.67	77.53	0.4239	42.39
	60	37.43	97.51	0.5419	54.19
4	10	49.88	71.42	0.3746	37.46
	20	45.46	89.77	0.5025	50.25
	30	42.61	93.13	0.5204	52.04
	60	37.36	131.5	0.6603	66.03

4. Conclusions

1. Antibacterial cephalosporin acts as an inhibitors for iron corrosion in 0.5 M H_2SO_4 solution.
2. The inhibition efficiency increases with increase in the concentration of these compounds
3. The inhibitive action of cephalosporin molecules due to the adsorption on to the iron surface.
4. The adsorption of these compound the iron surface ds follows Langmuir adsorption isotherm.
5. Antibacterial cephalosporins act as mixed-type inhibitors.
6. EIS measurements indicate the single charge transfer process controlling the corrosion of iron.

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