Cephalosporin antibiotics as new corrosion inhibitors for nickel in HCl solution

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Abstract Inhibition of nickel corrosion in 1 M HCl solution in the absence and presence of some Cephalosporin antibiotics derivatives was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM) techniques. The results obtained show that the inhibition efficiency of these compounds depends on their concentrations and chemical structures. The inhibitive action of these compounds was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in their structures following the Langmuir adsorption isotherm. The polarization measurement showed that these inhibitors are acting as mixed inhibitors for both anodic and cathodic reactions. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also studied. The efficiencies obtained from the potentiodynamic polarization technique were in good agreement with those obtained from EIS and EFM techniques. This proves the validity of these tools in the measurements of the investigated inhibitors.

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Introduction

Nickel is used in many industrial processes because of its advantages, and in consumer products, including stainless steel, magnets, coinage, rechargeable batteries, electric guitar strings, and special alloys. It is also used for plating and as a green tint in glass. Nickel is pre-eminently an alloy metal, and its chief use is in nickel steels and nickel cast irons, of which there are many varieties. It is also widely used in many other alloys, such as nickel brasses, bronzes, and alloys with copper, chromium, aluminum, lead, cobalt, silver, and gold. Hydrochloric acid solutions are used for pickling, and chemical and electrochemical etching of nickel alloys. It is very important to add inhibitors to decrease the corrosion rate of nickel in such solutions. Compounds with functional groups containing hetero-atoms, which can donate lone pairs of electrons, are found to be particularly useful as inhibitors for metal corrosion [1–6]. Also, organic substances containing polar functions with nitrogen, oxygen, and or sulfur atoms in a conjugated system and compounds with π-bonds have been reported to show good inhibiting properties [7–12]. Both features obviously can be combined within the same molecule such as drugs. Recently, the use of antibiotics and other drugs have been investigated [13–18] and their inhibition efficiencies have been linked with their heterocyclic nature. Ciprofloxacin was investigated [19] as a corrosion inhibitor for the corrosion of mild steel in acidic medium. Also, the drug amoxycillin [20] was used as a corrosion inhibitor for mild steel in 1 N hydrochloric acid solution. Generally, it has been assumed that the first stage in the action mechanism of the inhibitors in aggressive acid media is the adsorption of the inhibitors onto the metal surface. The processes of adsorption of inhibitors are influenced by the nature and distribution of charge in the molecule, the type of aggressive electrolyte, the type of interaction between organic molecules, and the principal types of interaction between organic inhibitors and the metal surface.

The investigated pharmaceutical compounds, which are used in the treatment of hypertension diseases, are non-toxic, cheap, and environmentally friendly. They contain reactive centers like N atoms and aromatic rings with delocalize π-electron systems, which can aid their adsorption onto metal surfaces. Furthermore, they have high molecular weights and are likely to effectively cover more surface area (due to adsorption) of the metal, thus preventing corrosion from taking place.

The objective of the present investigation is to study the corrosion inhibition of nickel in acidic medium using some cephalosporin antibiotics derivatives and to propose a suitable mechanism for the inhibition using the potentiodynamic polarization and ac impedance spectroscopy methods. The names, chemical and molecular structures of the investigated compounds are shown in Table 1.

Experimental details

Materials and solutions

The chemical composition of nickel was 99.9 % BDH grade. For polarization measurements, nickel electrodes were cut from Ni wire (diameter 0.5 mm). The

Table 1 The names, chemical and molecular structures of the investigated compounds

Cpd. No.	Name	Structure	Molecular weight and chemical formula
1	(6R, 7R)-7-[[(2E)-2-(2-amino-1, 3-thiazol-4-yl)-2-methoxyiminoacetyl] amino]-3-[[2-methyl-5,6-dioxo-1H-1,2,4-triazin-3-yl)sulfanylmethyl]-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid (Ceftriaxone)		554.58, $C_{18}H_{18}N_8O_7S_3$
2	(7R)-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-carboxylic acid (Cefazolin)		454.507, $C_{14}H_{14}N_8O_4S_3$
3	(6R,7R)-7-[[(2Z)-2-(2-amino-1,3-thiazol-4-yl)-2-(1-hydroxy-2-methyl-1-oxopropan-2-yl) oxyiminoacetyl]amino]-8-oxo-3-(pyridin-1-ium-1-ylmethyl)-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylate (Ceftazidime)		546.58, $C_{22}H_{22}N_6O_7S_2$

Table 1 continued

Cpd. No.	Name	Structure	Molecular weight and chemical formula
4	(6R,7R)-3-(acetyloxymethyl)-7-[[2-(2-amino-1,3-thiazol-4-yl)-2-methoxyiminoacetyl]amino]-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid (Cefotaxime)		455.47, $C_{16}H_{17}N_5O_7S_2$

electrodes were of 1 cm in length. The samples were embedded in a glass tube. Epoxy resin was used to stick the sample to the glass tube. The electrode was abraded with different grades of emery papers, degreased with acetone and rinsed by bidistilled water. All chemicals and reagents used were of analytical grade. Cephalosporin antibiotics were supplied by Egyptian Pharmaceutical Industries. Stock solutions (1,000 ppm) of investigated compounds were prepared by dissolving 1 g of each material in 1 L of bidistilled water. The measurements were carried out at 25 and 40 °C using a thermostatic water bath controlled to ± 1 °C.

Measurements

Polarization measurements

In this method, the working electrode was immersed in the test solution for 30 min until the open potential circuit potential was reached. After that, the working electrode was polarized in both cathodic and anodic directions. The values of corrosion current density (i_{corr}) were calculated from the extrapolation of Tafel lines to the pre-determined open circuit potential. A standard ASTM glass electrochemical cell was used. Platinum electrode was used as auxiliary electrode. All potentials were measured against saturated calomel electrode (SCE) as a reference electrode. Polarization measurements were carried from $-1,200$ to $+200$ mV with respect to corrosion potential (E_{corr}) at a scanning rate of 1 mV s^{-1}, and % IE was determined as:

$$\%\mathrm{IE} = \left[1 - \left(i_{corr}/i_{corr}^{\circ}\right)\right] \times 100 \qquad (1)$$

where i_{corr} and i°_{corr} are the current densities in the absence and presence of inhibitors, respectively.

Electrochemical impedance spectroscopy measurements (EIS)

Electrochemical impedance spectroscopy measurements were carried out at 25 ± 1 °C with the software program EIS 300. The measurements were carried out using AC signal 10 mV peak to peak at the open circuit potential in the frequency range of 100 kHz–0.5 Hz.

Electrochemical frequency modulation (EFM)

Electrochemical frequency modulation is a non-destructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small signal ac technique. Unlike EIS, however, two sine waves (at different frequencies) are applied to the cell simultaneously. Because current is a non-linear function of potential, the system responds in a non-linear way to the potential excitation.

The current response contains not only the input frequencies but also the frequency components which are the sum, difference, and multiples of the two input

frequencies. The two frequencies may not be chosen at random. They must both be small, integer multiples of a base frequency that determines the length of the experiment. Each spectrum is a current response as a function of frequency. The two large peaks, with amplitudes of about 100 A, are the response to the 2- and 5-Hz excitation frequencies. Those peaks between 1 and 20 A are the harmonics, sums, and differences of the two excitation frequencies. These peaks are used by the EFM140 software package to calculate the corrosion current and the Tafel constants. It is important to note that between the peaks the current response is very small. There is nearly no response (<100 nA) at 4.5 Hz, for example, while the frequencies and amplitudes of the peaks are not coincidences, but are the direct consequences of the EFM theory.

All electrochemical measurements were performed using a Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA 400. Gamry applications include DC105 for corrosion measurements, EIS300 software for EIS, and EFM140 software for EFM along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing, and fitting data.

Results and discussion

Potentiodynamic polarization technique

Figure 1 shows typical anodic and cathodic Tafel polarization curves for nickel in 1 M HCl in the absence and presence of varying concentrations of compound **4** at 25 °C. Similar curves were obtained for the other compounds (not shown). As reflected from the graph, the additive exhibits a significant effect on the corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) values. Table 2 shows the effect of the inhibitor concentration on the corrosion kinetics parameters, such as Tafel slopes (β_a, β_c), corrosion potential (E_{corr}), corrosion current density (i_{corr}), and inhibition efficiency (% IE). The results of Table 1 indicate that the Tafel lines are shifted to more negative and more positive potentials for the cathodic and the anodic processes, respectively, relative to the uninhibited (blank) curve. This means that these additives influence both the cathodic and the anodic processes, and that the process of inhibition is believed to be a mixed inhibition process, i.e., the inhibitors are of mixed type. It is also observed that the presence of these additives does not shift E_{corr} remarkably, and therefore these additives could be regarded as mixed-type inhibitors and their inhibition occurred by blocking effect mechanism [21]. The slopes of the cathodic and anodic Tafel lines are approximately constant and independent of the inhibitor concentration. This behavior suggests that the inhibitor molecules have no effect on the metal dissolution mechanism. A decrease in the corrosion current density (i_{corr}) was observed by increasing the concentration of the inhibitor used. The order of % IE obtained from polarization measurements is as follows: 1 > 2 > 3 > 4.
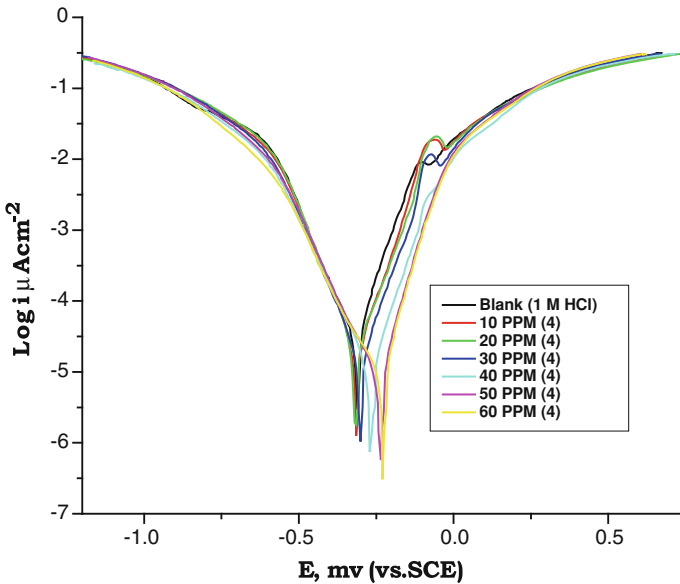
Fig. 1 Potentiodynamic polarization curves for nickel in 1 M HCl in the absence and presence of different concentrations of compound **4** at 25 °C

Adsorption isotherm

The adsorption of the inhibitors is influenced by the nature and charge of the metal, the chemical structure of the inhibitors, the distribution of the charge in the molecule, and the type of electrolyte [22–24]. Important information about the interaction between the inhibitor and Ni surface can be obtained from the adsorption isotherm.

The values of surface coverage, θ, increase with the inhibitor concentration, this is attributed to more adsorption of inhibitors onto the Ni surface. The adsorption of organic adsorbate on the surface of nickel electrode is regarded as a substitutional adsorption process between the organic compound in the aqueous phase (Org$_{aq}$) and the H$_2$O molecules adsorbed on the nickel surface (H$_2$O)$_{ads}$ [25].

$$\text{Org}_{(sol)} + x\,(\text{H}_2\text{O})_{ads} \rightarrow \text{Org}_{(ads)} + x\,\text{H}_2\text{O}_{(sol)} \qquad (2)$$
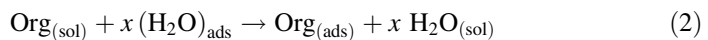
where x is the size ratio, that is, the number of H$_2$O molecules replaced by one organic molecule.

Attempts were made to fit θ values to various isotherms including Frumkin, Langmuir, Temkin, and Freundlich. The results were best fitted by far by the Langmuir adsorption isotherm which has the following equation:

$$C/\theta = 1/K + C \qquad (3)$$

where C is the inhibitor concentration in the electrolyte and K is the equilibrium constant for the adsorption/desorption process. The value of K is related to the free energy of adsorption, $\Delta G°_{ads}$, by the equation:

Table 2 The effect of inhibitor concentration on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a and β_c), inhibition efficiency (% IE), degree of surface coverage (θ), and polarization resistance (R_p) for the corrosion of nickel in 1 M HCl at 25 °C

Comp.	Conc. (ppm)	$-E_{corr}$ (mV) vs. SCE	i_{corr} (μA cm^{-2})	β_c, (mV dec^{-1})	β_a (mV dec^{-1})	$R_p \times 10^{-2}$ (Ω cm^2)	θ	% IE
1	0.0	311	15.91	265	282	3.726	–	–
	10	234	5.116	226	276	10.56	0.679	67.9
	20	330	4.284	221	220	11.20	0.731	73.1
	30	329	4.066	224	224	11.99	0.744	74.4
	40	317	3.619	290	210	12.56	0.773	77.3
	50	330	3.356	209	214	13.70	0.789	78.9
	60	325	1.236	192	204	34.79	0.922	92.2
2	10	240	4.120	248	250	13.13	0.741	74.1
	20	263	3.848	234	242	26.48	0.758	75.8
	30	288	3.480	215	232	13.95	0.781	78.1
	40	297	2.061	204	235	23.08	0.871	87.1
	50	252	1.787	202	189	23.81	0.888	88.8
	60	273	1.397	201	172	32.14	0.912	91.2
3	10	295	3.915	212	219	12.00	40.75	75.4
	20	236	3.481	223	231	14.18	0.781	78.1
	30	285	2.971	208	207	15.19	0.813	81.3
	40	182	2.471	232	242	20.83	50.84	84.5
	50	280	2.239	189	189	18.40	0.859	85.9
	60	271	1.925	197	186	21.63	0.879	87.9
4	10	315	9.890	250	250	57.58	0.378	37.8
	20	317	9.443	246	246	60.35	0.406	40.6
	30	302	6.812	231	231	77.46	0.572	57.2
	40	269	3.644	218	218	13.69	0.771	77.1
	50	237	2.624	219	219	17.55	0.835	83.5
	60	229	2.524	218	218	18.12	0.841	84.1

$$K = 1/55.5\exp\left(\Delta G_{ads}^{\circ}/RT\right) \tag{4}$$

where R is the universal gas constant, T is the absolute temperature, and 55.5 is the concentration of water in bulk solution in M^{-1}. The high value of K (Table 3) reflects the high adsorption ability of these compounds on the Ni surface. The value of K was found to be in the order: $1 > 2 > 3 > 4$ which runs parallel to the inhibition efficiency.

Plotting C/θ against C gives a straight line with an approximate unit slope value (Fig. 2), indicating that the adsorption of drug compounds **1–4** on the nickel surface follows the Langmuir adsorption isotherm and, hence, there is no interaction between the adsorbed species. This deviation from unity is due to the Langmuir isotherm, originally derived for the adsorption of gas molecules on solid surfaces, which was modified to fit the adsorption isotherm of solutes onto solid surfaces in

Table 3 Inhibitor binding constant (K), free energy of binding ($\Delta G°_{ads}$), of the investigated compounds for the corrosion of nickel in 1 M HCl at 25 °C

Inhibitors	Langmuir adsorption isotherm	
	$K \times 10^{-4}$ (M^{-1})	$-\Delta G_{ads}°$ (kJ mol^{-1})
1	9.2	9.8
2	3.1	7.0
3	2.1	6.1
4	1.0	4.2

solution. A modified Langmuir adsorption isotherm [26] could be applied to this phenomenon, which is given by the corrected equation:

$$C/\theta = n/K + nC \qquad (5)$$

where n is the value of slopes obtained from the plot in Fig. 2. The aim of modification was based on the fact that direct application of the Langmuir isotherm to solution systems often leads to poor data fitting [27]. The negative value of $\Delta G°_{ads}$ (Table 3) indicates spontaneous adsorption of investigated compounds on the Ni surface and also the strong interaction between inhibitor molecules and the metal surface [28]. Generally, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and the charged metal surface (physical adsorption), those of -40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [29]. The calculated standard free energy of adsorption values is <10 kJ mol^{-1}. Therefore, it can be concluded that these compounds are physically adsorbed on the Ni surface [30].
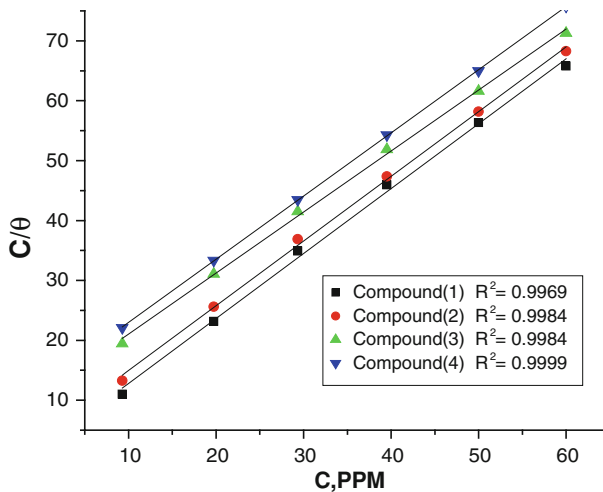

Fig. 2 Curve fitting of corrosion data obtained from potentiodynamic polarization method for nickel in 1 M HCl in the presence of different concentrations of investigated compounds to the Langmuir adsorption isotherm at 25 °C

Effect of temperature

The importance of temperature variation in corrosion studies involving the use of inhibitors is to determine the mode of inhibitor adsorption on the metal surface. Recently, the use of two temperatures to establish the mode of inhibitor adsorption on a metal surface has been reported and has been found to be adequate [31, 32]. Thus, the influence of temperature on the corrosion behavior of Ni in 1 M HCl in the absence and presence of cephalosporin antibiotics of varying concentrations were investigated by the potentiodynamic method at 25 and 40 °C. Therefore, in examining the effect of temperature on the corrosion process, the apparent activation energies (E_a*) were calculated from the Arrhenius equation [33]:

$$\text{Log} \left(\rho_{2/\rho_1} \right) = \left(E_a^* / 2.303R \right) [1/T_2 - 1/T_1] \tag{6}$$

where ρ_2 and ρ_1 are the corrosion rates at temperature T_2 and T_1, respectively, and R is the universal gas constant.

Increased activation energy (E_a*) in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface, while either unchanged or lower E_a in the presence of inhibitor suggest chemisorptions [34]. It is seen from Table 4 that E_a values were higher in the presence of the additives compared to those in their absence, hence leading to a reduction in the corrosion rates. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [35]. The E_a* values support the earlier proposed physisorption mechanism. Hence, corrosion inhibition is assumed to occur primarily through physical adsorption on the nickel surface, giving rise to the deactivation of these surfaces to hydrogen atom recombination. Similar results have been reported in earlier publications [36].

AC impedance technique

The corrosion behavior of nickel in 1 M HCl solution in the absence and presence of different concentrations of the investigated compounds was investigated by the EIS method at the open circuit potential conditions at 30 °C. Figure 3 shows the Nyquist plots for nickel in 1 M HCl solution in the absence and presence of different concentrations of compound 4 at 25 °C, respectively. Similar curves were obtained

Table 4 Activation energy of the corrosion of nickel in 1 M HCl at 60 ppm investigated compounds	Inhibitor	E_a* (kJ mol^{-1})
	Free acid	10.9
	1	65.6
	2	60.4
	3	58.0
	4	51.9

for other inhibitors (not shown). The Nyquist diagram obtained with 1 M HCl shows only one capacitive loop, both in uninhibited and inhibited solutions, and the diameter of the semicircle increases on increasing the inhibitor concentration suggesting that the formed inhibitive film was strengthened by the addition of inhibitors. The corresponding Bode plots are shown in Fig. 4 and all the main parameters deduced from the impedance technique are given in Table 5. The impedance data of nickel in 1 M HCl are analyzed in terms of an equivalent circuit model Fig. 5 which includes the solution resistance R_s or R_Ω and the double layer capacitance C_{dl} which is placed in parallel to the charge transfer resistance R_{ct} [37] due to the charge transfer reaction.

$$C_{dl} = (1/2\pi f_{max} R_{ct}) \tag{7}$$

where f_{max} is the maximum frequency. The inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements are defined by the following relations:

$$\%IE = \left[1 - \left(R_{ct}^\circ/R_{ct}\right)\right] \times 100 \tag{8}$$

$$\theta = \left[1 - \left(R_{ct}^\circ/R_{ct}\right)\right] \tag{9}$$

where $R_{ct}{}^\circ$ and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively. From the impedance data given in Table 5, we conclude that the value of R_{ct} increases with increasing the concentration of the inhibitors, indicating the decreased corrosion rate (i.e. increased corrosion inhibition) in acidic solution. As the impedance diagram obtained has a semicircle appearance, it shows that the corrosion of nickel is mainly controlled by a charge transfer process. The value of double layer capacitance (C_{dl}) decreases by increasing the inhibitor concentration, indicating the reduction of charges accumulated in the double layer due to the formation of adsorbed inhibitor layer [38], and its lower values indicate the inhomogeneity of surface of the metal has been roughened due to corrosion. The
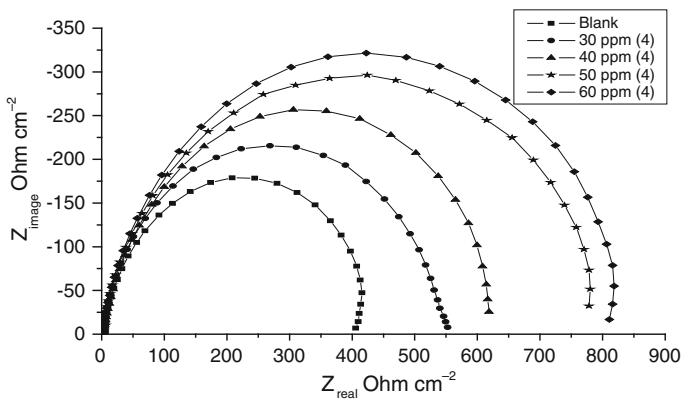

Fig. 3 The Nyquist plots for nickel in 1 M HCl solution in the absence and presence of different concentrations of compound **4** at 25 °C
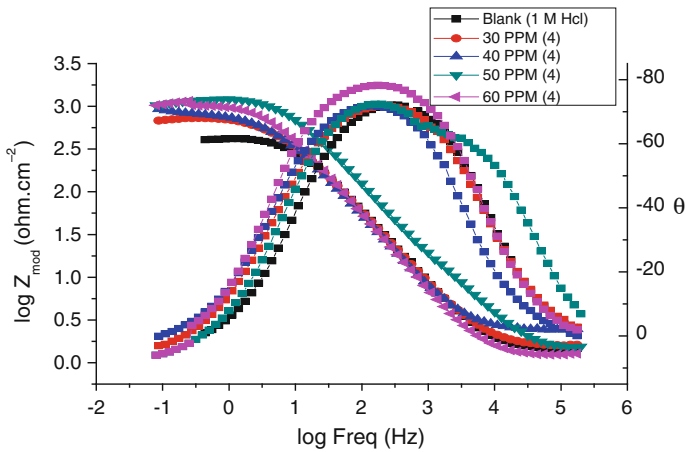
Fig. 4 The Bode plots for nickel in 1 M HCl solution in the absence and presence of different concentrations of compound **4** at 25 °C

Table 5 Electrochemical kinetic parameters obtained by EIS technique for corrosion of nickel in 1 M HCl at different concentrations of investigated compounds at 25 ˙ C

Compound	Conc. (ppm)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	θ	% IE
Free acid	0	372.6	39.86	–	–
1	30	1,146	27.56	0.675	67.5
	40	1,181	20.02	0.685	68.5
	50	1,518	18.6	0.755	75.5
	60	2,833	16.49	0.869	86.9
2	30	880.1	33.99	0.577	57.7
	40	1,053	29.57	0.646	64.6
	50	1,329	23.67	0.732	73.2
	60	1,534	19.02	0.757	75.7
3	30	610.4	37.59	0.389	38.9
	40	713.5	31.42	0.478	47.8
	50	920.0	28.20	0.595	59.5
	60	1,067	31.42	0.651	65.1
4	30	487.4	34.26	0.236	23.6
	40	537.2	32.57	0.306	30.6
	50	655.1	32.88	0.431	43.1
	60	706.3	31.78	0.472	47.2

inhibition efficiencies calculated according to the impedance results are in the order: $1 > 2 > 3 > 4$, and these results follow the same trend as the polarization results. The % IE obtained from EIS measurements are close to those deduced from potentiodynamic polarization method.

Fig. 5 Equivalent circuit model
fits the impedance data
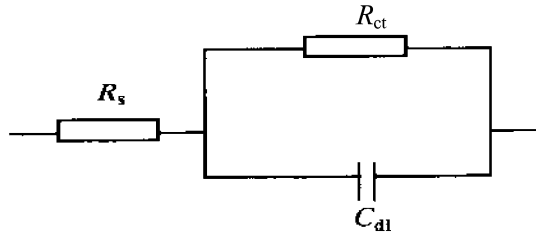
Electrochemical frequency modulation (EFM) technique

The EFM technique is used to calculate the anodic and cathodic Tafel slopes as well as corrosion current densities for the system Ni/HCl without and with various concentrations of compound **4** at 25 °C. Figures 6, 7, 8, 9, and 10 are examples representing the EFM intermodulation spectra (spectra of current response as a function of frequency) of nickel in aerated 1 M HCl solutions. Similar results were recorded for the other concentrations. The inhibition efficiency, % IE, of compound **4** was calculated at different concentrations using equation presented elsewhere [39].

$$\%IE_{EFM} = [1 - (i_{corr}/i^{\circ}{}_{corr})] \times 100 \tag{10}$$

where i_{corr} and $i^{\circ}{}_{corr}$ are the current densities in absence and presence of inhibitors, respectively.

The calculated electrochemical parameters i_{corr}, CF2, CF3, and % IE are given in Table 6. Inspections of these data infer that the values of causality factors obtained under different experimental conditions are approximately equal the theoretical values (2) and (3) indicating that the measured data are of high quality [40]. In the absence of the inhibitors (blank), the value of corrosion current density (i_{corr}) can be seen, and hence the rate of corrosion. Addition of increasing concentrations of compound **4** to the HCl solution decreases the corrosion current density (i_{corr}) at a given temperature, indicating that compound **4** inhibits the acid corrosion of nickel through adsorption. However, at a given inhibitor concentration, the corrosion current density (i_{corr}) still increases with increasing the temperature as a result of
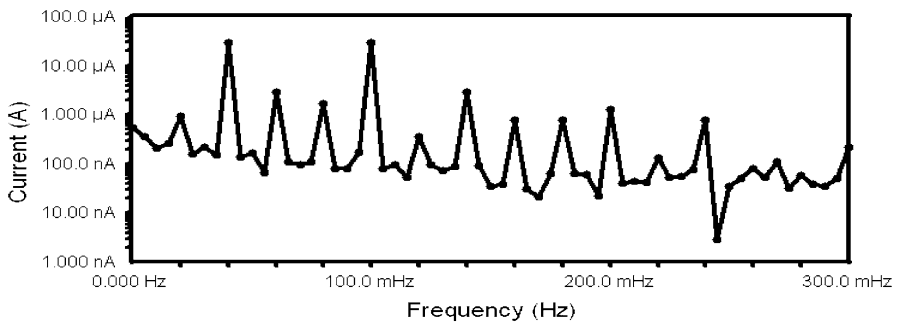

Fig. 6 Intermodulation spectrum recorded for nickel electrode in presence of 1 M HCl at 25 °C
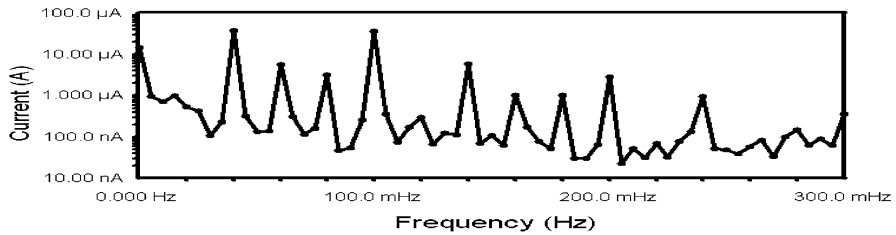
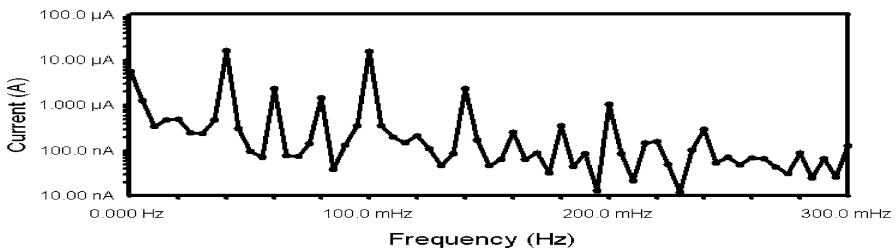**Fig. 7** Intermodulation spectrum recorded for nickel electrode in 1 M HCl solution in presence of 30 ppm of compound **4** at 25 °C

Fig. 8 Intermodulation spectrum recorded for nickel electrode in 1 M HCl solution in presence of 40 ppm of compound **4** 25 °C
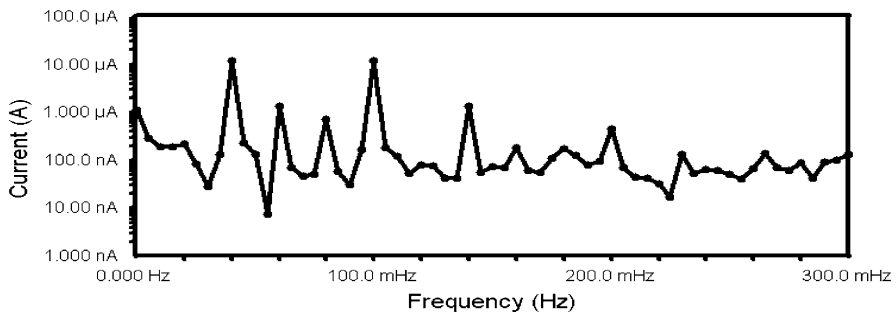

Fig. 9 Intermodulation spectrum recorded for nickel electrode in 1 M HCl solution in presence of 50 ppm of compound **4** 25 °C

increasing the rate of corrosion and partial adsorption of inhibitor species on the nickel surface. The calculated inhibition efficiency, % IE enhances with compound **4** concentration. The inhibition efficiencies calculated according to the EFM results are in the order: $1 > 2 > 3 > 4$, and these results follow the same trend as the polarization and impedance results.

Mechanism of corrosion inhibition

It is generally assumed that adsorption at the metal/solution interface is the first step in the inhibition mechanism in aggressive acidic media, which as most organic
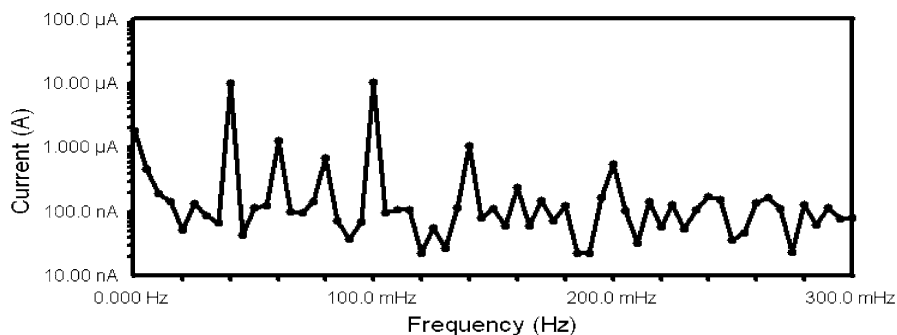
Fig. 10 Intermodulation spectrum recorded for nickel electrode in 1 M HCl solution in presence of 60 ppm of compound **4** 25 °C

Table 6 Electrochemical kinetic parameters obtained by EFM technique recorded for nickel electrode in 1 M HCl with additives of various concentrations at 25 ˙C

Compound	Conc. (ppm)	i_{corr} ($\mu A\ cm^{-2}$)	Causality factor (2)	Causality factor (3)	θ	% IE
Free acid	0.0	54.25	1.916	2.745	–	–
1	30	17.96	1.967	3.053	0.669	66.9
	40	13.02	2.026	3.282	0.760	76.0
	50	10.56	1.891	3.324	0.805	80.5
	60	7.94	2.003	2.881	0.854	85.4
2	30	24.28	1.871	2.797	0.552	55.2
	40	18.27	1.880	3.053	0.663	66.3
	50	16.30	1.948	3.151	0.700	70.0
	60	12.08	1.786	2.853	0.777	77.7
3	30	33.75	1.957	2.797	0.378	37.8
	40	24.28	1.871	3.053	0.552	55.2
	50	22.36	2.290	3.151	0.588	58.8
	60	18.60	1.902	2.853	0.657	65.7
4	30	40.52	1.918	3.240	0.253	25.3
	40	36.21	1.804	2.883	0.333	33.3
	50	33.56	1.942	3.372	0.381	38.1
	60	29.74	1.957	3.352	0.452	45.2

compounds contain at least one polar group with an atom of nitrogen, sulfur or oxygen, each might be a chemisorptions center. The inhibitive action depends on the electron densities around the adsorption center; the higher the electron density at the center, the more efficient is the inhibitor. Inhibition efficiency depends on several factors such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface, and extent of the formation of metallic complexes [41]. The order of inhibition efficiency obtained from electrochemical measurements is as follows: 1 > 2 > 3 > 4.

The adsorption of these inhibitors at the Ni surface can take place through their active centers, N, O and S atoms, in addition to a π electron interaction of the benzene ring nucleus with unshared d electrons of Ni atoms [42–45]. The adsorption and the inhibition effect of investigated inhibitors in 1 M HCl solution can be explained as follows: inhibitor molecules might be protonated in the acid solution (compound **1** as example) as:

$$[C_{17}H_{19}N_3O_3S] + xH^+ \rightarrow [C_{17}H_{19+x}N_3O_3S]^{x+} \tag{11}$$
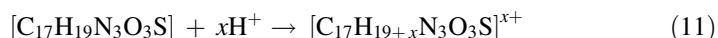
In aqueous acidic solutions, these inhibitors exist either as neutral molecules or as protonated molecules (cations). These inhibitors may adsorb on the metal/acid solution interface [46] by one and/or more of the following ways: (1) electrostatic attraction between charged molecules and charged metal, (2) interaction of unshared electron pairs in the molecule with the metal, (3) interaction of π electrons with the metal, and (4) a combination of the previous three.

In general, two modes of adsorption are considered on the metal surface in acid media. In one mode, the neutral molecules may be adsorbed on the surface of the Ni via a chemisorption mechanism, involving the displacement of water molecules from the nickel surface and the sharing of electrons between the hetero-atoms and the nickel. The inhibitor molecules can also adsorb on the Ni surface on the basis of donor–acceptor interactions between π-electrons of the aromatic ring and vacant d-orbitals of surface nickel atom. In the second mode, since it is well known that the nickel surface bears a positive charge in acid solution [47], it is difficult for the protonated molecules to approach the positively charged nickel surface due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, so they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, with the protonated inhibitors adsorbing via electrostatic interactions between the positively charged molecules and negatively charged metal surface. Thus, there is a synergism between adsorbed Cl^- ions and protonated inhibitors, and we can also conclude that inhibition of nickel corrosion in 1 M HCl is mainly due to electrostatic interaction. The decrease in inhibition efficiency with a rise in temperature supports electrostatic interaction.

In organic compounds differing in the functional donor atom (other factors being equal), the order of corrosion inhibition is usually: S > N > O, which is the reverse order of electronegativity. Sulfur compounds are better corrosion inhibitors than their nitrogen analogues because the S-atom, being less electronegative than N, draws fewer electrons to itself, and is thus the more efficient electron donor in forming the chemisorptive bond.

Compound **1** is the most efficient one, which is due to the presence of 3 S, 8 N, and 7 O atoms in its structure, but compound **2** comes after compound **1** in inhibition efficiency. This is due to the smaller number of oxygen atoms (4 O atoms) in its structure. Compound **3** comes after compound **2** in inhibition efficiency. This is due to the smaller number of nitrogen atoms (6 N atoms) and sulfur atoms (2 S atoms) in its structure. Compound **4** is the least effective inhibitor. This is due to the smaller number of nitrogen atoms (5 N atoms) in its structure.

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